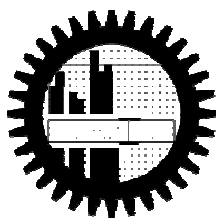


Micellization Behaviors of Surfactants and the Study of the
Location of Solubilized Species within the Micellar System by
Complexation with Metals

by

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ABSTRACT

Knowledge of Micellar behavior of a surfactant is essential for its wide range of applications. In the present work a comprehensive study of micellization, adsorption and thermodynamic behavior of TTAB, CTAB and OTAB (in pure water and also in presence of NaCl) has been conducted by conductivity and surface tension methods. From the CMC studies it is observed that increase of temperature causes increase of CMC of TTAB and CTAB which is due to thermal solubility of the surfactant monomers. Then slight decreases of the CMC were observed with further increase of temperature (above 313 K) which is due to dehydration of the head groups. These CMC studies have been utilized to evaluate the Stauff- Klevens empirical relation of $\log \text{CMC} = A - Bn$, where n is the number of carbon atom in the alkyl chain of the surfactant and A is constant for a particular ionic head at a given temperature. This empirical relation was found to become insignificant in presence of NaCl. The surface excess concentration (Γ_m) and the counter ion binding (β) values of the surfactants were found to be greater in presence of NaCl than in pure water. From the thermodynamic calculations it was found that both the adsorption and micellization processes are enthalpy and entropy controlled. ΔG_m° and ΔH_m° values were found to be negative whereas ΔS_m° values were positive. For each of the surfactants ΔG_m° and ΔH_m° values were found to increase, whereas ΔS_m° values decrease, with increase of temperature. Greater ΔG_m° and ΔS_m° values were obtained for the surfactant with larger alkyl chain. The CMC measurement and the thermodynamic studies were not possible, for OTAB below temperature of 313 K since the Krafft temperature of OTAB

is higher than this temperature (the T_K is 309.5 K). Experimental results show that T_K of TTAB, CTAB and OTAB are 12.4°C, 24.7 °C and 36.5 °C respectively. The Krafft temperature (T_K) the surfactants were found to decrease in presence of NaCl, NaF, Na_2SO_4 where as the T_K values increase in presence of NaBr and NaI . NMR studies and the metal (zinc, cadmium and mercury) – ligand complexation studies were carried out to identify solubilization site the ligand (DiphenylCarbazide). The experimental results show that

(a) The solubilization site for DPC in TTAB is in between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise of outer core of the micelle interior.

(b) The solubilization site for DPC in CTAB is more deeply seated in the palisade layer of the micelle.

(c) The solubilization site for DPC in OTAB is even more deeply seated than the palisade layer, almost near about the inner core of the micelle.

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ABBREVIATIONS

Tetradecyl Trimethyl Ammonium Bromide: **TTAB**

Hexadecyl Trimethyl Ammonium Bromide: **CTAB**

Octadecyl Trimethyl Ammonium Bromide: **OTAB**

Diphenyl Carbazide: **DPC**

Sodium Dodecyl Sulphate : **SDS**

Krafft Temperature : T_k

CANDIDATES 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

.....

Name of the candidate

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MOHAMMAD REZAUR RAHMAN

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ABBREVIATIONS

Tetradecyl Trimethyl Ammonium Bromide: **TTAB**

Hexadecyl Trimethyl Ammonium Bromide: **CTAB**

Octadecyl Trimethyl Ammonium Bromide: **OTAB**

Diphenyl Carbazide: **DPC**

Sodium Dodecyl Sulphate : **SDS**

Krafft Temperature : T_k

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INTRODUCTION

1.1 Surfactants

Surface active agents (surfactants) are amphipathic molecules consisting of a nonpolar hydrophobic portion (usually a straight or branched hydrocarbon containing a chain of 8-18 carbon atoms) attached to a polar (hydrophilic) ionic portion. This typical structure causes significant changes on a larger number of physical properties of surfactant's solutions such as conductivity, molecular fluorescence, surface tension etc, which determine their extensive use in many industrial fields such as detergents, paints, cosmetics, pharmaceuticals, adhesives, inks, agrochemicals and food industries. The polar head groups of ionic surfactants want to interact with water molecules and at the same times their hydrocarbon chains want to separate the water molecules, which cause an increase in energy of the system. So the surfactant molecules present in the system arrange themselves in such a way so that the hydrocarbon portions can be exposed at the surface [1]. Thus a surfactant molecule dissolves in water by a balance interaction of the attractive tendency of water molecules with the polar head group and the expelling tendency of water with the nonpolar group. [2]. As a result, due to the presence of both hydrophilic and hydrophobic parts, in aqueous solution they frequently assemble and self- associate in an attempt to sequester their polar regions from the contact with the aqueous phase. When present at low concentration in a system, the surfactants have the property of adsorbing on to the surface or interface of the system and thereby alter to a marked degree (of surface or interfacial) free energies of the surfaces[3]. When dissolved in a solvent, the surfactants distort the solvent structure and thereby increase the free energy of the system. As a result to minimize the free energy, the surfactants are concentrated at the surface.

Generally surfactants lower surface tension. Naturally occurring surfactants are playing some important functions in our body, specially controlling the surface tension in our lungs. The solubility of many hydrophobic molecules can be greatly increased by using surfactants, micelles [4-7]. Surfactants are widely used for coating, oil recovery from mud, extraction of oil, ore extraction, cosmetics, food industry, automobiles, textile, pharmaceutical and agrochemical industries.

1.2 CLASSIFICATION OF SURFACTANTS

Surfactants may be classified according to their applications (as emulsifiers, foaming agents, wetting agents, dispersants, etc), or for some physical characteristics (e.g. water or oil solubility) or for their difference in structure (type of linking group between the hydrophile and hydrophobe e.g. oxygen, nitrogen, amide, sulphamide etc).

The most useful chemical classification of the surface- active agents is based on the nature of hydrophile. Depending on the nature of the hydrophilic groups, surfactants are classified into four groups. These are anionic, cationic, zwitterionic and nonionic surfactants.

(A) ANIONIC SURFACTANTS:

The surface active portions of these surfactant molecules bear a negative charge e.g. RCOO^- (Soap) and $\text{RC}_6\text{H}_4\text{SO}_3^-$ (alkyl benzene sulfonates). These are used as the textile treating agents in preparation of raw material and for dyeing purposes.

(B) CATIONIC SURFACTANTS:

The surface active portions of these surfactant molecules bear a positive charge e.g. $RN^+H_3Cl^-$ or $RN^+H_3Br^-$ (Salts of long chain amines) and $RN^+(CH_3)_3Cl^-$ (quarternary ammonium chlorides) or $RN^+(CH_3)_3Br^-$ (quarternary ammonium bromides). These surfactants are excellent fungicides, germicides, softening and leveling agents. They are widely used in agrochemical and pharmaceutical industries.

(C) ZWITTERIONIC SURFACTANTS:

These surfactants' molecules contain, or can potentially contain, both a negative and positive charge.. e.g. $RN^+H_2CH_2COO^-$ (long chain amino acid) and $RN^+(CH_3)_2CH_2SO_3^-$ (sulfobetains).

(D) NONIONIC SURFACTANTS:

The surface active portions of these surfactants have no charge but due to highly polar groups they are soluble in water. e.g. $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acids) and $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkyl phenols). These surfactants are efficient in removing grease and oils from metal surfaces and fabrics. These are mainly used in the fields of oil extraction, oil recovery and degreasing agents.

1.3 PROPERTIES OF SURFCATANTS

Surfactants distort water structure and raise free energy of solution. The system, however, has natural tendency to minimize its free energy. To satisfy this natural desire the system may undergo.

(A) Adsorption

(B) Micellization

(A) ADSORPTION OF SURFACTANTS

At low surfactant concentration free energy of solution may be lessened by expelling their hydrophobic parts out of water in such a way that their hydrophilic parts remain attached to the solution surface [3]. Usually, the adsorption is studied to determine:

- The concentration of surfactant at interface (The performance of surfactant in many interfacial processes, i.e. foaming, detergency, emulsification etc, depends on interfacial concentration of surfactants)
- The orientation of surfactants at interface
- The free energy change in system (ΔG), enthalpy change (ΔH) and entropy change (ΔS) during adsorption. One of the most commonly measured properties of surfactant related to their adsorption at air/solution interface is reduction in surface tension.

Surface Tension

It is the minimum amount of work required to expand the interface by unit area. It is the measure of interfacial free energy per unit area of boundary between liquid and the air above it [2]. Reduction in surface tension depends directly on the replacement of solvent molecules at interface by those of surfactant. It is one of the most fundamental interfacial phenomena. The surface molecules of liquid have greater magnitude of potential energy than those in the interior and the work required to bring molecules at surface is equal to difference in potential energy of surface and bulk molecules and is the measure of surface free energy per unit area, or surface tension [2, 3].

(B) MICELLIZATION

Interfacial adsorption is a way to diminish free energy of solution but there is a limit of concentration to which adsorption may occur. After having reached this limit, no more adsorption is possible and energetically unfavorable contact between hydrophobic part and water may be further avoided by self aggregation of surfactant molecules within bulk of solution. These aggregates are called micelles, the simplest form of associated colloid. The most important property of the amphiphatic molecules or ions, characterized by their polar head group and a non polar hydrocarbon tail, is their tendency to form large aggregates which is possible above a certain concentration of each type of surfactants. Above the certain concentration of the surfactant in the system micellization appears by a delicate balance between the hydrophobic interactions with in the alkyl chains and the opposing repulsive interactions between the ionic head groups of an ionic surfactant [3, 8-9]. The opposing repulsive interactions between the ionic head groups are greatly influenced (minimized) by the associated counter ions of the surfactants as well as the presence of added electrolytes. [9-11]. These aggregates are known as micelle which is typical colloidal particles with its surrounding stabilizing agents [12-17]. In aqueous solutions the amphiphilic molecules frequently assemble at the interfaces and self associate in an attempt to sequester their polar regions from contact with the aqueous phase. This self association is not limited just to the aqueous solutions, it is sometimes observed in non aqueous polar solvents such as ethylene glycols and non-polar solvents such as hexane [18-19].

1.4 REASONS FOR SELF- AGGREGATION OF SURFACTANT MOLECULES

(A) Hydrophobic Interaction

One of the important features that make water unique as a solvent is its response to a-polar solutes. 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. From a thermodynamic point of view, surfactant self-assembly is an entropy driven process [20]. 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 that 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 [21].

(B) Hydration

As a solvent, water displays a very complex behavior because of its highly structured nature. So not only the direct ion-molecule interactions but also the effect of a solute on the hydrogen bonded network is important. As a result the non-polar solutes also exert great influences on water structure. So it is found that the hydrophobic chains (alkyl groups) have important effect on reduction of the rotational and the translational mobility of the water molecules. 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. Crystalline hydrates [22] 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 amphiphile monomer in water is surrounded by a hydrogen-bonded organized structure. The polar heads of the monomer interact with water in a way similar to simple polar solutes and electrolytes through hydrogen-bond, dipole-dipole and ion-dipole interactions. But when the amphiphiles are in micelle these hydration features get affected. The nature and the extent of this effect are interesting for many of the researchers. Very few studies have been done on the hydration of non-ionic surfactants because of the sensitive effects of temperature and concentration on their micellar size and shape [23-24]. There are 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 octanoate are appreciably oriented [14].

(C)Counter-ion Binding

A counterion is the ion that accompanies an ionic species in order to maintain electric neutrality. In table salt (NaCl), the sodium cation is the counterion for the chlorine anion and vice versa. In a charged transition metal complex, a (i.e. non-coordinated) ion accompanying the complex is termed the counterion. In the older literature, the term gegenion is sometimes used. Counterions are generally vaguely defined in biological systems. Depending on their charge, proteins are associated with a variety of smaller anions and cations. In plant cells, the anion malate is often accumulated in the vacuole to decrease water potential and drive cell expansion. To maintain neutrality, K^+ ions are often accumulated as the counterion. Ion permeation through hydrophobic cell walls is mediated by ion transport channels. Nucleic acids are anionic, the corresponding cations are often protonated polyamines. Compared to the ionic surfactants, the non ionic surfactants have greater tendency to aggregate and as a result for the nonionic amphiphiles the micelles form at much lower concentrations. The micellization of non ionic surfactants, in most of the cases, are not affected by the smaller concentrations of electrolyte but for the ionic amphiphiles the micellization process and the micellar size is greatly influenced by the added electrolyte concentrations. The changes of CMC and the micellar size of the ionic surfactants, for

the added electrolyte concentrations, are mainly due to the counter ion binding which effectively reduce the surface charge of the ionic surfactant units. 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 [25-26]. The trends in counter-ion binding with ionic radius are successfully reproduced by most experimental approaches. It has been reported [3] 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 $\text{NO}_3^- < \text{Br}^- < \text{Cl}^-$ and this sequence persists in the presence

of added sodium salt of the anion [3]. Likewise the CMC of N-alkyltrimethyl ammonium bromides is considerably lower than of the corresponding N-alkyltrimethyl ammonium chlorides.

1.5 Surfactant micelles packing parameter

(i) Differences in shape

The shape of a surfactant molecule can be described by its surfactant packing parameter, N_s [8]. The packing parameter takes into account the volume of the hydrophobic chain (V_c), the cross sectional area of the hydrophilic core of the aggregate expressed per molecule in the aggregate (a), and the length of the hydrophobic chain (L_c). [27]

$$N_s = V_c / a \times L_c$$

It should also be noted that the packing parameter for a specific surfactant is not a constant. It is dependent on various conditions which affect each the volume of the hydrophobic chain, the cross sectional area of the hydrophilic head group, and the length of the hydrophobic chain. Things that can affect these include, but are not limited to, the properties of the solvent, the solvent temperature, and the ionic strength of the solvent.

(ii) Cone, wedge, and cylinder shaped micelles

The shape of a micelle is directly dependent on the packing parameter of the surfactant. Surfactants with a packing parameter of $N_s \leq 1/3$ appear to have a cone-like shape which

will pack together to form spherical micelles when in an aqueous environment [28-29]. Surfactants with a packing parameter of $1/3 < N_s \leq 1/2$ appear to have a wedge-like shape and will aggregate together in an aqueous environment to form cylindrical micelles (bottom in figure). Surfactants with a packing parameter of $N_s > 1/2$ appear to have a cylindrical shape and pack together to form a bilayer in an aqueous environment [28-29].

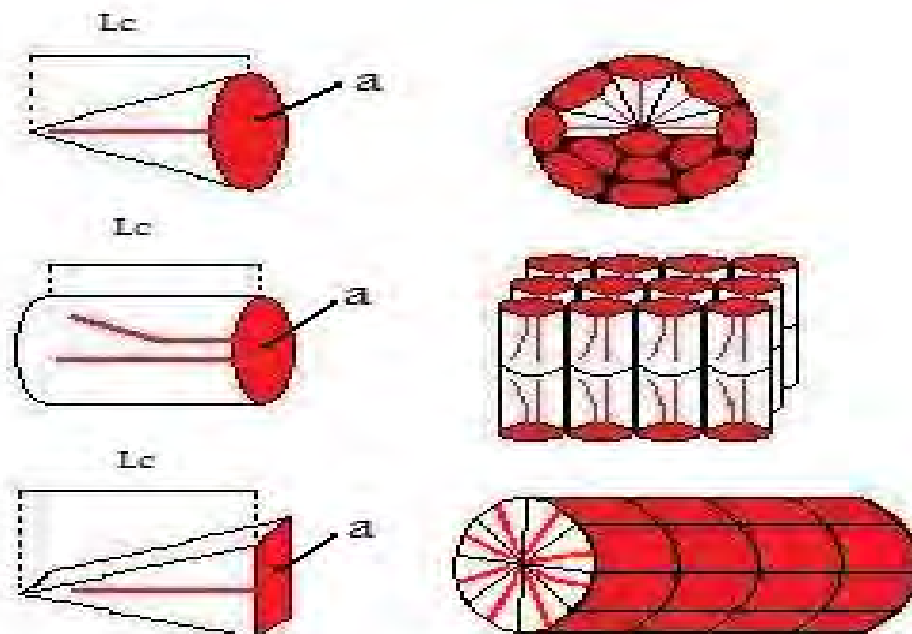


Figure 1.1. The packing Parameter and Shape of micelle

1.6 FACTORS AFFECTING CMC IN AQUEOUS SOLUTION

The common factors known to affect the CMC markedly in aqueous solutions are:

- (a) Structure of the surfactant
- (b) Presence of added electrolytes
- (c) Presence of organic additives
- (d) Temperature of the solution

1.6. a. STRUCTURE OF THE SURFACTANT

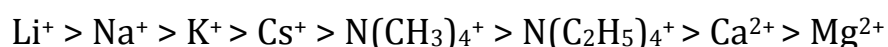
In aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophilic chain increases to about 16. A general rule for ionic surfactants is that the CMC is halved by the addition of one ethylene group to a straight-chain hydrophobic group stanchied to a single terminal hydrophilic group. this rule no longer holds possibly due to coiling of chains in solutions when the number of carbon atoms in a straight chain exceeds 16 [34]. The CMC no longer decreases so rapidly with increase in the length of the chain above this number of carbons i.e. it may remain substantially unchanged with further increase in the chain length. [2]. Mukerjee also [30] has explained this phenomenon by the coiling effect of the chains in water. For non ionics the decrease with increase in the hydrophilic group is larger, an increase by two ethylene units reducing the CMC to about one-tenth (compared to one quarter in ionics). A phenyl group being a part of a hydrophobic group with terminal hydrophilic group plays a role equivalent to about three and one-half methylene group , in CMC reduction. The branched carbon atoms appear to have about one-half the effect of carbon atoms on a straight chain [2], The presence of sp² hybridized carbon (for C=C bond) causes CMC to

increase [34]. The instauration in hydrophobic chain, generally causes increment in CMC than that of the corresponding saturated compound, where the cis isomer generally have a higher CMC than the trans [2]. The replacement of a hydrocarbon-based hydrophobic group by a fluorocarbon-based one (with the same number of carbon atoms) appears to cause a decrease in the CMC [31]. For homologous straight chain surfactants in aqueous medium, an empirical equation relating to CMC and the number of carbon atoms, N in the hydrophobic chain, was found as [3].

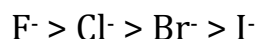
$$\log \text{CMC} = A - Bn \text{ -----(1.1)}$$

Where A is a constant for a particular ionic head at given temperature and n is the number of carbon atom in the alkyl chain [3,32]. In aqueous medium, ionic surfactants have higher CMCs than nonionic surfactants containing equivalent hydrophobic groups. Zwitter ionics have about the same increases as the hydrophilic group is moved from a terminal position to a more critical position. Keeping the hydrophobic groups same, the ionic surfactants reflect high values of CMC as compared to nonionic surfactants. Molecules having more than one hydrophilic group show larger CMCs than those having one hydrophilic group and equivalent hydrophobic group. Substitution of hydrogen atoms on an element of the hydrophilic group causes to increase the groups in size, results in CMC depression.

Increased binding of the counter ion, in aqueous system, causes a decrease in the CMC of the surfactant. The binding extents of the counter ions increase with their polarizability and valency, whereas decrease with the increase in their hydrated radii. Thus, in aqueous medium, for the anionic lauryl sulfates, the CMC decreases in the order [3]:



For the cationic dodecyltrimethylanmonium and dodecyl pyridinium salts, the order of decreasing CMC in aqueous medium [2] is:



The surfactants having same hydrophobic but different hydrophilic groups have pronounced difference between their CMC values [34]. The aqueous solution of nonionic surfactants has much lower CMC than that of ionics with same number of carbon atoms. The CMC of zwitterionics and ionics is almost the same provided they have the same number of carbon atoms. The CMC will increase if hydrophilic group is shifted from terminal to more critical position. In this case hydrophobic group act as if it had become branched at the position of hydrophilic group, with carbon atoms at shorter end of chain having half of their usual effect on CMC. The CMC is higher if charge on hydrophilic group is closer to α -carbon of hydrophobic group or when more than one hydrophilic groups are attached to hydrophobic group [3, 34].

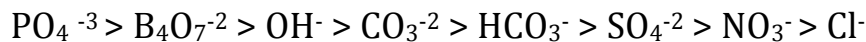
1.6 b. PRESENCE OF ELECTROLYTES IN SOLUTION

In aqueous solution the presence of an electrolyte causes a decrease in CMC. The effect is more pronounced for anionic and cationic than zwitterionic surfactants and more pronounced for zwitterionic than for nonionics. The effect of the concentration of electrolyte for the anionic and cationic surfactants is given by the equation:

$$\text{Log CMC} = -a \log C_1 + b \text{ ----- (1.2)}$$

Here a and b are constants for a given logic head at a particular temperature and C_1 is the (monovalent) counter ion concentration in moles per liter [3, 35]. This depression is mainly due to the decrease in the thickness of the ionic atmosphere surrounding the head groups in the presence of an additional electrolyte and consequently decreased

electrical repulsion between them in the micelle. As for sodium laurite and sodium naphthenate, the order of decreasing effect of the anion in depressing CMC is [3,35-37].



Equation 1.2 does not hold for nonionics and zwitterionics. The effect of concentration of electrolyte for zwitter ionic and nonionics is given [38, 39] as:

$$\text{Log CMC} = -KC_s + \text{Constant} \quad C_s < 1 \quad \text{-----} \quad (1.3)$$

Here K is a constant for a particular surfactant, electrolyte and temperature where C, is the concentration of electrolyte in moles per liter. The changes in the CMC of nonionics and zwitter ionics on the addition of electrolytes has been attributed mainly to the “salting in” or “salting out” of the hydrophobic groups in aqueous solvent by the electrolytes [38].

For anionic surfactants, the following relationship has been found to account for the effect of monovalent electrolytes.

$$\log \text{CMC} = A'' - B'' \log S \quad \text{.....} \quad (1.4)$$

Where S is the solubility; A'' and B'' are constants which depend upon the surfactant and the type of the electrolyte. The effect is even stronger with polyvalent cations (Ca⁺⁺, Mg⁺⁺), a consequence of their action on the electrical double layer which surrounds the micelle. For nonionic and amphoteric surfactants the effect is qualitatively the same, but much lower in magnitude. It has been represented by a relationship with a linear solubility contribution.

$$\log \text{CMC} = A^* - B^* S \quad \text{.....} \quad (1.5)$$

In this case the CMC decrease is attributed to the dehydration of the hydrophilic group, as well as an increase of interaction between some hydrophobe (polypropylene oxide) and the aqueous phase. Furthermore, the presence of electrolyte can turn spherical micelles in cigar or rod-like ones. [2,40,41].

1.6. c. ORGANIC ADDITIVES

Small amount of organic material may produce marked changes in the CMC in aqueous media. Organic additives have been classified in two major categories depending upon the way in which they affect the CMC. Class I materials effect CMC by being incorporated into the micelles, and class II materials that change the CMC by modifying solvent-micelle or solvent-surfactant interaction. Materials in the first class are generally polar organic compounds, such as alcohols and amides. They affect the CMC at much lower liquid phase concentration than those in the second class. Hydrogen bonding between polar groups of the additive and water molecules helps counterbalance lateral pressure tending to push the additive into the interior of micelle, so that they remain in the outer core between the surfactant molecules. Therefore, the additive having more than one group capable of forming hydrogen bonds with water in a polar group causes more depression in CMC compared to that with only one group capable of hydrogen bonding to water [2]. Members of class I reduce the CMC and members of class II compounds change the CMC, but the bulk phase concentrations usually are considerably higher than those at which class II members are effective. The members of this class change the CMC by modifying the interaction of water with the surfactant molecule or with the micelle, doing this by modifying the structure of water, its dielectric constant or its solubility parameters. It was observed that urea and guanidinium salt cause to increase the CMC

due to their disruption of the water structure. This may increase the degree of hydration of the hydrophilic group and since hydration of the hydrophilic group oppose micellization [35, 41-44], materials that promote water structure, such as fructose for similar reason, decrease the CMC of the surfactant [35].

1.6. d. EFFECT OF TEMPERATURE

The effect of temperature on the CMC of the surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Temperature increase causes decreased hydration of the hydrophilic group, which favors micellization. However, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range. Counter ions play an important role in this case as in bivalent metal alkyl sulfates. [44]. For TTAB and CTAB it was found that the CMC, in pure water, gradually increases with increase of temperature up to a certain range and then the CMC values slightly decrease with further increase of temperature. The initial increase in CMC for increased temperature is due to the thermal solubility of the surfactant monomers and a slight decrease of the CMC with further increase of temperature is due to dehydration of the head group resulting an increase in the hydrophobic character, which dominates over the solubility effect [32, 45]

1.7 KRAFFT POINT OF SURFACTANTS

Although the typical (amphipathic) structure of surfactants causes significant changes on a large number of physical properties of the solutions such as conductivity, viscosity, molecular fluorescence, surface tension etc. which is the basis of application of the surfactants in many purposes but these applications for surfactant become limited below a certain temperature. Because below a certain temperature solubility of the ionic surfactant becomes very limited and the surfactant loses its activities such as dispersing, emulsifying and micelle forming properties. [47-48]. This certain temperature for a specific (ionic) surfactant is known as the Kraft temperature (T_K) which is generally considered to be the melting temperature of a hydrated solid surfactant [49-51]. If the CMC exceeds the solubility of the surfactant at a particular temperature, then the minimum surface tension will be achieved at the point of maximum solubility, rather than at CMC. At the Krafft point the solubility of an ionic surfactant becomes equal to the CMC. For surfactants being used below T_K , then, the maximum reduction in surface tension will be determined by the concentration of surfactant at solution saturation and these materials may show lower effectiveness in reducing surface tension than similar materials that are being used above their Krafft points. For many industrial purposes certain amount of salts are dissolved in the surfactant solutions, in addition to the surfactant ions and their counter ions, since salts can lower the critical micelle concentration (CMC) or increase the viscosity and surface activity of the surfactants [52-55]. But unfortunately (some type of) added salts elevate the T_K of surfactants which limits their industrial applications [55-57]. The effect of alkyl chain length, head group size and different additives on the T_K and the CMC of ionic surfactants have been

investigated extensively [56-58] which reveal that the CMC decreases while the T_K increases with increasing the concentration of the electrolytes. T. Gu et. al. found that the Krafft point increases with increase in the number of carbon atoms in the hydrophobic group and decrease with branching or unsaturation in that group in a homologous series of ionic surfactant [59] . The Krafft point also depends upon the nature of counterion, increasing in the order of $Li^+ > NH_4^+ > Na^+ > K^+$ for anionics [3]. Oxyethylenation of alkyl sulfates decreases their Krafft point; oxypropylenation decreases them even further. The alkyl sulfonates have higher krafft point than their corresponding alkyl sulfates [3]. Davey et. al. found that the substitution of triethyl for trimethyl in the head groups of cationic alkyl bromides leads to significant reduction in their Krafft points [56].

1.8 SOLUBILIZATION PROCESS

Solubilization is the process of incorporating the solubilize (the component that undergoes solubilization) into or onto the micelles. Solubilization may occur in a system consisting of a solvent, an association colloid (a colloid that forms micelles), and at least one other solubilize. One of the most important properties of aqueous micelle solution that is directly related to micelle formation is solubilization. Solubilization may be defined as the spontaneous dissolving of a substance by the reversible interaction with the micelle of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. Solvent-insoluble materials may be dissolved by the solubilization mechanism; the importance of the phenomenon from the practical point of view is that it makes possible the

dissolving of substances in solvents in which they are normally insoluble. In solubilization, the solubilized material is in the same phase as the solubilizing solution, and the system is consequently thermodynamically stable. According to McBain, solubilization is a spontaneous passage of solute molecules of a substance insoluble in water into an aqueous solution of a surfactant in which a thermodynamically stable solution is formed which is distinguished from hydrotropic, blending and emulsification [60]

If we plot the solubility of a poorly soluble compound as a function of the concentration of surfactant, as shown in figure 1.2, usually what happens is that the solubility is very low until the surfactant concentration reaches the *CMC*. At surfactant concentrations above the *CMC* the solubility increases linearly with the concentration of surfactant, indicating that solubilization is related to micellization. Micelles have particular significance in pharmacy because of their ability to increase the solubility of sparingly soluble substances in water [61]. Micelles are known to have a certain distribution pattern of water within their structure where the water concentration decreases from the surface towards the core of the micelle. Consequently, the spatial position of a solubilized drug in a micelle will depend on its polarity: nonpolar molecules will be solubilized in the micellar core, and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions.

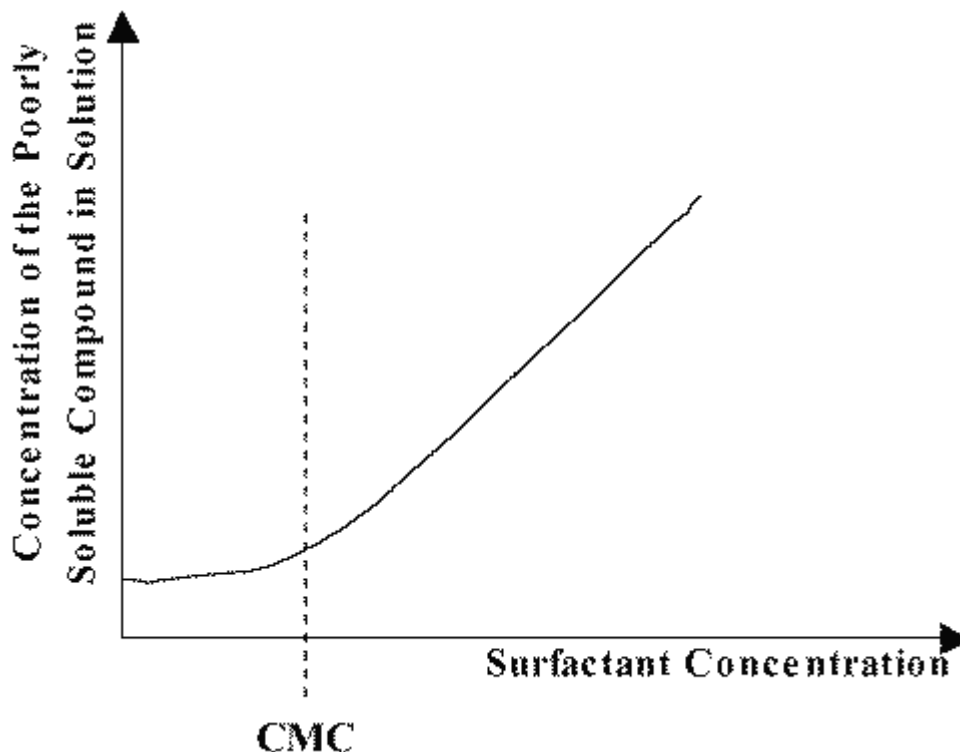


Figure 1.2: Schematic plot of the concentration of a poorly soluble compound as a function of the surfactant concentration in aqueous solution.

Many investigators have used various physical methods to study the solubility of polar and non polar organic substances in toxic and nontoxic surfactant micelles [38,62]. Studies of solubilization of organic solutes have been made to determine the effect of micellar structure and changes in the environment at the site of solubilization. Solubilization within surfactant micelles is probably the most important mechanism for the removal of small amounts of oily soil from substrates. Removal of oily soil becomes significant only above the CMC for nonionic and even for the anionic surfactants having low CMC, and reaches its maximum only at several times than concentration. Since the adsorption of surfactants at interfaces involves the monomeric, rather than micellar form of the surfactant, whereas solubilization involves only the micellar form, this

appears to indicate that in these cases solubilization is a more important factor in the cleaning process than mechanism dependent on adsorption (e.g. wetting, soil rollback). The extent of the material to be solubilized depends on the chemical structure of the surfactant, its concentration and the temperature. At low concentrations, the micelles are more or less spherical in shape and only a relative amount of material can be solubilized. Whereas at high surfactant concentrations (10-100 times the CMC), solubilization is more similar to micro emulsion formation, and the high surfactant concentration can accommodate a much large amount of matter. Many investigations have been done on the solubilization of drugs and antibiotics for their efficiency in terms of the bioavailability [64-67]

1.9 THERMODYNAMICS FOR SOLUBILIZATION

From the thermodynamic point of view, the solubilization can be considered as a normal partitioning of the drug between two phases, micelle and aqueous, and the standard free energy of solubilization (ΔG_s°) can be represented by the following expression (1.17):

$$\Delta G_s^{\circ} = -RT \ln P \dots\dots\dots(1.19)$$

where R is the universal constant of the gases, T is the absolute temperature, and P is the partition coefficient between the micelle and the aqueous phase.

Usually, the solubilization of a molecule by a surfactant can be evaluated based on two descriptors that are the molar solubilization capacity, χ , and the micelle-water partition coefficient, P [66]. The χ value is defined as the number of moles of the solute (drug) that can be solubilized by one mol of micellar surfactant, and characterizes the ability of the

surfactant to solubilize the drug. It can be calculated based on the general equation for micellar solubilization:

$$\chi = (S_{tot} - S_w) / (C_{surf} - CMC) \dots\dots\dots(1.20)$$

where S_{tot} is the total drug solubility, S_w is the water drug solubility, C_{surf} is the molar concentration of surfactant in solution, and cmc is the critical micelle concentration [68]. Since above the cmc the surfactant monomer concentration is approximately equal to the cmc , the term $(C_{surf} - CMC)$ is approximately equal to the surfactant concentration in the micellar form and, therefore, χ is equal to the ratio of drug concentration in the micelles to the surfactant concentration in the micellar form.

On the other hand, the micelle-water partition coefficient is the ratio of drug concentration in the micelle to the drug concentration in water for a particular surfactant concentration, as follows:

$$P = (S_{tot} - S_w) / S_w \dots\dots\dots(1.21)$$

Combining Equations (1.18) and (1.19), we can relate the two solubility descriptors. Accordingly, for a given surfactant concentration:

$$P = \chi (C_{surf} - CMC) / S_w \dots\dots\dots(1.22)$$

As can be seen, P is related to the water solubility of the compound, in contrary to χ [68]. In order to eliminate the dependence of P on the surfactant concentration, a molar micelle-water partition coefficient (P_M), corresponding to the partition coefficient when $C_{surf} = 1$ M, can be defined as follows:

$$P_M = \chi (1 - CMC) / S_w \dots\dots\dots(1.23)$$

The lower is the CMC value of a given surfactant, the more stable are the micelles. This is especially important from the pharmacological point of view, since upon dilution with a large volume of the blood, considering intravenous administration, only micelles of surfactants with low CMC value still exist, while micelles from surfactants with high cmc value may dissociate into monomers and their content may precipitate in the blood [69].

1.10 FACTORS AFFECTING SOLUBILIZATION

1.10. a. EFFECT OF STRUCTURE OF SOLUBILIZER

There are a number of factors regarding the structure of solubilizer such as chain length, substitutions in the chain, and position of hydrophilic group which effect the solubilization. The amount of material solubilized generally increases with increase in the size of the micelles. The factors that cause an increase in either the diameter of the micelle or its aggregation number can be expected to produce increased solubilization. Increase in dissimilarity between solvent and surfactant causes increase in aggregation number, where an increase in the chain length of the hydrophobic portion of the surfactant generally results in increased solubilization of hydrocarbons in the interior of the micelle in aqueous medium. Bivalent counter ions cause greater solubilizing power

than corresponding univalent which is due to greater micellar aggregation [55]. Because of low critical micelle concentrations, nonionic surfactants are better solubilizing agents than ionic surfactants in very dilute solutions. In general, the order of solubilizing power for hydrocarbons and polar compounds having same hydrophobic chain length, solubilized in the inner core is as follows: [35,38].

Nonionics > cationics > anionics

The introduction of the second ionic head group into the surfactant molecule cause decreases of solubilization of non polar compound whereas increase of polar compounds. This is because of increased hydrophilic character of the surfactant molecule and consequently decreases the aggregation number of micelles. The decreased aggregation member in the micelles causes reduced solubilization of nonpolar substance, whereas the increased repulsion between the head groups causes an increase in the space for solubilization between the surfactant molecules' in the palisade layer which consequently results in increased solubilizaion of polar molecules .

1.10. b. EFFECT OF STRUCTURE OF THE SOLUBILIZATE

In the polar solubilizates, the structure of solubilizate shows variation in the depth of penetration into the palisade layer of the micelle. In case of more or less spherical micelle, the polar compounds are solubilized close to the micelle-water interface. The polar compounds that are solublized more deeply in the palisade layer would be less soluble than those whose locus of solubilization is closer to the micelle-water interface. Usually the molecules having longer alkyl chain length and less polarity in nature show the smaller degree of solubilization due to its weaker interaction with either the polar head group of the surfactant molecules in micelle or the water molecules at the water-

micelle interact [38]. For condensed aromatic hydrocarbons the extent of solubilization appears to decrease with increase in the molecular size [38]. The latent heat of fusion of solid compounds opposes the change of state from crystalline solid to solubilized compound. Therefore, the case of solubilization of a solid compound is less than that of the same compound existing as a super cooled liquid or of a closely related liquid compound.

1.10. c. EFFECT OF ELECTROLYTES

The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC and increasing the aggregation number and volume of micelles, the increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. The decrease in mutual repulsion of the ionic head groups causes closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available therefore solubilization of polar compounds. As the chain length of the polar compound increases, this reduction of solubility by electrolytes appears to decrease.

1.10. d. EFFECT OF ORGANIC ADDITIVES

The presence of solubilized hydrocarbon in the surfactant micelles generally increases the solubility of polar compounds in these micelles. The solubilized hydrocarbon causes the micelle to swell, which make it possible for the micelles to incorporate more polar material in the palisade layer. On the other hand, the solubilization of polar compounds

such as long chain alcohols, amines and fatty acids etc into the micelles of the surfactant appears to increase the solubilization of hydrocarbons. The long chain polar compounds which are less capable of forming hydrogen bonding show the greater power to increase the solubilization of hydrocarbons. Macromolecular compounds including synthetic polymers, proteins, starches and cellulose derivatives, interact with surfactant molecules are absorbed onto the macromolecules, mainly by electrical and hydrophobic interactions. At higher concentration of the surfactant, polymer surfactant complexes show greater solubilizing power than that of the surfactant alone [38, 66,69].

1.10. e. EFFECT OF TEMPERATURE

The increase in temperature of ionic surfactant results in an increase in the solubilization of both polar and non polar solubilize, because the increased thermal agitation increases the space available for solubilization in the micelle [70]. For nonionic surfactants, the effect of temperature increase depends on the nature of the solubilize, Nonpolar materials which are solubilized in the inner core of the micelle, show increased solubility as the temperature is raised. However, the solubility behavior of polar materials, whose locus of solubilization is the palisade layer of the micelle, behaves very differently passing through the maximum as the temperature is raised to the cloud point. Increase in temperature above 10°C causes the increase in thermal agitating of the surfactant molecules in micelle which results in increased solubilization. Further increase in temperature decreases the amount of material solubilized due to increased dehydration and tighter coiling of the chains, decreasing the space available in the palisade layer. This decreased solubility becomes prominent as the cloud point is

approached particularly for short-chain polar compounds which are solubilized close to the surface of the micelle.

1.11 LOCUS OF SOLUBILIZATION

One of the most significant applications of the surfactants is their micelle enhanced solubilization. The solubilization capacity increases rapidly if the surfactant concentration reaches to CMC [3] which provides the basis of the application for detergency, micellar catalysis, extraction, oil recovery, micro emulsion polymerization [71] and a wide range of pharmaceutical purposes since low solubility in water appears to be an intrinsic property of many drugs [72-73]. Micelle are chosen for the pharmaceutical purposes because they can increase the bioavailability of drugs by staying long enough in body and by providing the gradual accumulation of the drugs in the required area [74]. But the drugs may be solubilized at different locations of the micelle depending on the drug (or the solubilizate) nature. [3, 74]. So the bioavailability of the drugs dissolved in the micelle may be affected by the micellar environment such as micellar surface charge or hydrophobic nature of the micellar core. The metal-ligand complexation and their solubility constant values are exploited in wide variety of applications. Treatment of various metal related illnesses is based on the binding of an ideal ligand to the target metal ion and not to others. But this degree of selectivity is very hard to achieve due to lack of bio availability of the ligands or the metal chelators [75]. Micellar environment which is used to dissolve the poorly soluble ligands may affect these ligand metal bindings and the bioavailability of the ligands.

The exact location of solubilization in the micelle varies with the nature of the material and it reflects the type of interaction occurring between surfactant and solubilization. Based on different studies [38], solubilization is believed to occur at a number of different sites in the micelles as: (1) One is the surface of the micelle at the micelle solvent interface, (2) Between the hydrophilic head groups. (3) In the so called palisade layer of the micelle between the hydrophilic ground and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micelle interior (4) More deeply in the palisade layer (5) In the inner core of the micelle. Generally ionic micelles have an extensive hydrophobic core region, which can interact strongly with the hydrocarbon and the halogenated hydrocarbon groups of the solutes. Although the hydrophobic effects are often been considered to be dominant in the determination of locus of solubilization [38], but the effect of electrostatic interactions are also considered in relation to the solubilization of organic solutes in the ionic micelles. The surfactant micelles can be pictured as having a highly non polar interior and a relatively polar interfacial region, Therefore, the nonpolarized or easily polarizable compounds are solubilized, in aqueous medium, in the inner core of the micelle, between the ends of the hydrophobic groups of the surfactant molecules. Polarizable hydrocarbons are solubilized by absorption at the micelle-water interface, replacing water molecules that may have penetrate into the outer core of the micelle close to the polar heads, but solubilization of additional material is either deep in the palisade layer as located in the inner core of the micelle [76]. The polarizability of the π -electron cloud of the aromatic nucleus and its consequent ability to interact with the positively charged groups at the

micelle-water interface may account for the initial adsorption of these hydrocarbons in that location (78).

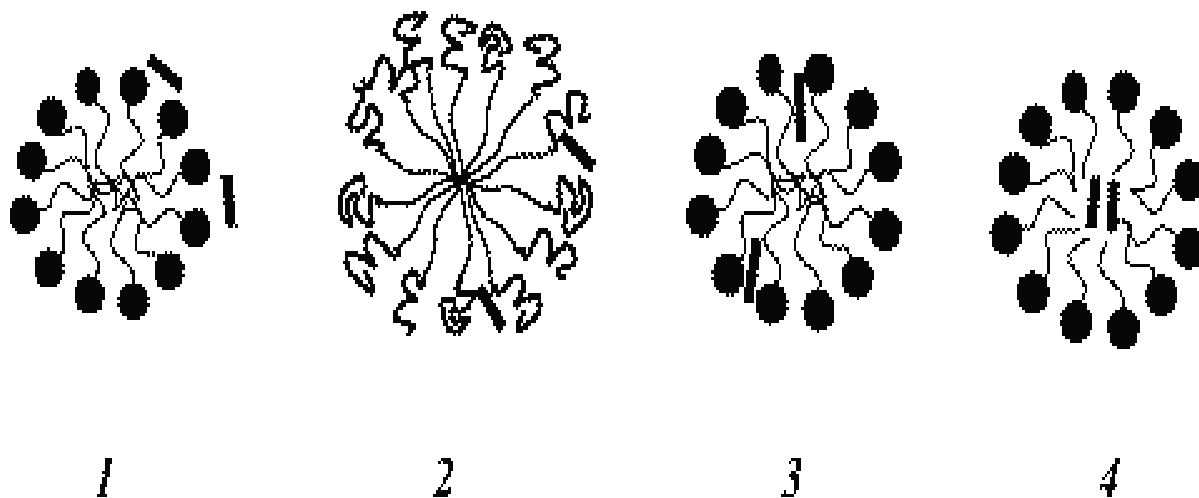


Figure 1.3: Possible loci of solubilization of drugs in surfactant micelles, depending on the drug hydrophobicity. The black bold lines (-) represent the drug at different sites in the micelle. The black circles represent the surfactant head, and the light black curved lines represent the surfactant tails.

Solubilize molecules of relatively high polarity such as long chain alcohols or polar dye stuffs are believed to be solubilized in the interfacial region of the micelles. so that their polar functional groups could retain their contact with water, Here the interaction is presumably by H-bonding or dipole-dipole attraction between the polar groups of solubilize and surfactant. Depth of penetration in the palisade layer depends on the ratio of polar to non polar structures in the solubilize structure [38].

1.12 SOLUBILIZATION IN DRUG DELIVERY

In physicochemical systems molecules added to biological systems find their way into membrane structures. The interactions of these molecules with lipid bilayers and other organized lipid assemblies are of great importance for both endogenous and exogenous substances. Among the latter, drugs and toxicants are of particular interest in terms of their binding and uptake, transport, chemical and metabolic activities. Since the forces which stabilize micelles are similar, in principle, to the forces which are responsible for the formation of bilayers and the biological membranes, micellar model systems are used to provide useful insight into such phenomena. The solubilization of water-insoluble drugs by micelles has been investigated as a means of improving solubility for drug delivery, in parental or oral administration, but also for ophthalmic topical, rectal, and nasal delivery [78- 79], The protection of labile drugs from the environment through solubilization has also been examined. Owing to their labile nature, micelles can only be used as drug carriers and not as drug targeting systems which alter the bio distribution of a drug by administering it in a micelle solution [38]. This alteration has however, been attributed to a direct effect of the surfactant on bio membranes permeability. Two types of approaches of hydrophobic drug solubilization are being followed in drug delivery systems [80-81]. The first one includes the chemical bonding , the hydrophobic drugs can be covalent coupled to polymers to form micelle structures. Within the context of the micelle structures, high quantities of drugs could be bound and shielded from the external environment by a palisade layer of hydrophobic portion of the micelle. In another approach, hydrophobic drugs can also be physically incorporated within the hydrophobic cores of polymeric micelles .In this way the

hydrophobic drugs do not need to have appropriate chemical functional groups for covalent attachments to the polymers for incorporation within the micelles.

1.13 SURFACTANTS FOR CHELATION THERAPY

Now a day's micelles are being used to develop the drug carriers containing metal ion cores. These carriers comprise a metal (including transition metals) at the center (i.e., metal core), which interacts with the polymer (including block copolymers) possessing chelating ligands to form the coordinate bonds. Drugs that can donate a lone pair of electrons (including drugs possessing functional groups, such as carboxylic acids, alcohols, ketones, furans, amines, anilines, pyrroles, thiols, esters, amides, imines, pyridines, pyrimidines, imidazoles, pyrazols, sulfonamides, phosphonic acids, etc.) can also bind to metal center through coordinate bonds, which then form a complex, or chelating complex micelles (CCM) with the polymer containing chelating ligands. The coordinate bond (also known as dipolar bond) is a special kind of covalent bond in which the two electrons derive from the same atom. The formation of coordinate bond requires two conditions: first, the metal ion must have an incomplete octet of electrons; and second, the ligand donates a lone pair of electrons. Typically, a coordinate bond is formed when a Lewis base donates a pair of electrons to a Lewis acid. The Chelating Complex Micelles (CCM), is much easier than the physical encapsulation and chemical bonding of drugs. Physical encapsulation that requires large quantities of organic solvents is limited to encapsulate hydrophobic drugs due to the intrinsic property of block copolymer. On the other hand, drugs loaded via chemical bonding exhibit the

shortcoming of insufficient loading capacity. For developing the chelating complex micelles, the only requirement for the drug is to have a functional group that can donate a lone pair of electrons. The chelating complex micelles are formed when drugs and polydentate ligands bind to metal center at the same time. These micelles can carry not only hydrophobic but also hydrophilic drugs; thus, can be used extensively in the drug delivery systems. The metal in the core is selected mainly from the following list, including any combinations, or combinations of its derivatives thereof: Fe, Cu, Ni, In, Ca, Co, Cr, Gd, Al, Sn, Zn, W, Sc, Ti, Mn, Mg, Be, La, Au, Ag, Cd, Hg, Pd, Re, Tc, Cs, Ra, Ir or Ga. The ligand is selected from the compound possessing functional groups in following list, including any combinations, or combinations of its derivatives thereof: carboxylic acids, alcohols, ketones, furans, amines, anilines, pyrroles, thiols, esters, amides, imines, pyridines, pyrimidines, imidazoles, pyrazols, sulfonamides, and phosphonic acids [82-84]. Metals are an integral part of many structural and functional components in the body, and the critical role of metals in physiological and pathological processes has always been of interest to researchers. chelation therapy which is an important concept and tool for modifying metal concentrations in the body. Chelation has its origin in the Greek word *chele* that means claw of a lobster, thus depicting the concept of clinging or holding with a strong grip. The term *chelate* was first applied by Sir Gilbert T. Morgan and H. D. K. Drew in 1920. They suggested the term for the caliper-like groups which function as two associating units and fasten to a central atom so as to produce heterocyclic rings [85]. Metal toxicity may occur due to essential metal overload or exposure to heavy metals from various sources. Most metals are capable of forming

covalent bonds with carbon, resulting in metal-organic compounds. Metals and metal compounds interfere with functions of various organ systems like the central nervous system (CNS), the haematopoietic system, liver, kidneys, *etc.* Diagnostic testing for the presence of heavy metals, and subsequently decreasing the body's burden of these substances, should be an integral part of the overall treatment regimen for individuals with a metal poisoning symptomatology or a known exposure to these substances. Although the concept of chelation is based on simple coordination chemistry, evolution of an ideal chelator and chelation therapy that completely removes specific toxic metal from desired site in the body involves an integrated drug design approach. Chelating agents are organic or inorganic compounds capable of binding metal ions to form complex ring-like structure called 'chelates'. Chelating agents possess "ligand" binding atoms that form either two covalent linkages or one covalent and one co-ordinate or two co-ordinate linkages in the case of bidentate chelates. Mainly atoms like S, N and O function as ligand atoms in the form of chemical groups like -SH, -S-S, -NH₂, =NH, -OH, -OPO₃H, or >C=O. Bidentate or multidentate ligands form ring structures that include the metal ion and the two-ligand atoms attached to the metal [86]. For inter cellular toxic metal removal and toxic metal poisoning chelating agents are wide used [87-90]. At present days uses of micelles for these purposes have attracted much attention of the scientists.

1.14. AIMS AND OBJECTIVES

Surfactants micelles are extensively used in many industrial fields such as detergents, paints, cosmetics, pharmaceuticals, adhesives, inks, agrochemicals and food industries. It is essential to know the thermodynamic and adsorption properties of a surfactant for its wide range of applications. The micellization process of the surfactants is affected by temperature, concentrations of different salts and additives and other properties of the solution medium. The location of solubilization in the micellar system is also important for the activity and applications of the solubilized substances (such as drugs and the chelating agents). The applications of each surfactant may be limited below the krafft temperature, which depends on concentrations of different salts. Keeping all these in mind the main objectives of the present work is to study the micellization (and adsorption) behavior and related properties of a series of cationic surfactants, N-alkyltrimethylammoniumbromide, in pure water and also in presence of 0.01M aqueous NaCl solution. In the present work conductometric, UV and NMR studies are carried out to identify the solubilization site of an insoluble ligand (Dipheny Carbazide) within the TTAB, CTAB and OTAB micelle.

The specific objectives are:

- i. Study of the micellization and adsorption behavior of TTAB, CTAB and OTAB in pure water at different temperatures and investigation of empirical relation of the related properties of these surfactants.
- ii. Study of micellization and adsorption behavior of TTAB, CTAB and OTAB in

0.01M aq. NaCl at different temperatures and investigation of empirical relation of the related properties of these surfactants.

- iii. Study of correlation between counter ion binding and surface excess concentration of each of the surfactants at different temperatures in pure water and also in presence of 0.01M aq. NaCl solution.
- iv. Study of Krafft temperature of each of the surfactants in presence of different salts' concentrations.
- v. Conductometric study to understand the role of these surfactants to dissolve an insoluble ligand, Diphenyl Carbazide, and the micellar properties of these surfactants in presence of this insoluble ligand.
- vi. Complexation studies of Diphenyl Carbazide with Zn, Cd and Hg in the presence of each of these surfactants to understand the solubilization site and efficiency of this ligand, within these micelles.
- vii. NMR studies for clear understanding of the solubilization site of the ligand within each of these surfactants micelles.

EXPERIMENTALS

2.1 CHEMICALS

The surfactants Tetradecyl trimethylammoniumbromide (TTAB), Hexadecyl trimethylammoniumbromide (CTAB), Octadecyl trimethylammoniumbromide (OTAB) and Sodium dodecylsulfate (SDS) with purity 99% were purchased from Sigma - Aldrich and were used as received.

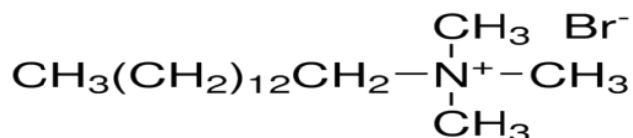


Figure 2.1 Structure of Tetradecyl trimethylammoniumbromide (TTAB)

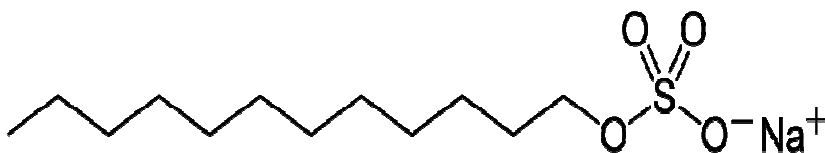


Figure 2.2 Structure of Sodium dodecylsulfate (SDS)

Analytical grade NaCl, Zinc nitrate, Cadmium nitrate, Mercury nitrate and Diphenyl Carbazide (DPC) obtained from E. Merck, Germany was used as received. For all solution preparation double distilled water was used.

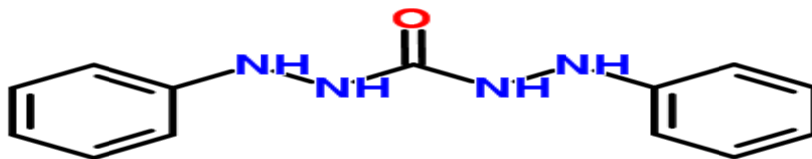


Figure 2.3 Structure of Diphenyl Carbazide (DPC)

2.2 CONDUCTIVITY MEASUREMENT

2.2 a. Critical micelle concentration measurement of surfactants in pure water

Conductivity was measured with a Eutech –Cyber Scan –Con – 510 conductivity meter equipped with a temperature compensated cell (the cell constant provided by the manufacturer is 1.0 cm^{-1}). Temperature of the solution was controlled by using a circulating water bath (Haake B 3, Germany) with a precision of $\pm 0.1 \text{ K}$. The conductivity cell was calibrated with KCl solutions of appropriate concentration range. For the CMC measurements of the surfactants in pure water, 50 cm^3 double distilled water was put into a thermostated vessel with in $\pm 0.1 \text{ K}$, and successive injections, from a micellar stock solution of the surfactant, were made. The conductivity value was

acquired after sufficient stirring and then after 5 min to ensure the attainment of equilibrium in the system.

2.2 b. Critical micelle concentration measurement of surfactants in aqueous NaCl solutions

For the CMC measurements of the surfactants in 0.01M NaCl solutions, a 50 cm³ of 0.01M NaCl solution was put into a thermostated cell, with in ± 0.1 K , and successive injections, from a micellar stock solution of the surfactant at 0.01 M NaCl, were made. The conductivity value was acquired after sufficient stirring and then after 5 min to ensure the attainment of equilibrium in the system.

2.2 C. CMC measurement of surfactants in presence of DPC

Fixed mass of Diphenyl carbazide (DPC) were added to the micellar surfactant solutions in 100 cm³ reagent bottles. The solutions were kept under rotation for 48 h. Then the solutions were kept undisturbed in a thermostat at the experimental temperature to settle down any insoluble ligand. Then the decanted solutions were centrifuged for 15 min at 3000 rpm by a centrifuge machine (Hettich Universal 16A). 10 cm³ portion of each of the supernatant solutions were treated for conductivity measurements. Thus for the conductivity measurements of the surfactants in presence of DPC, a known volume of a micellar stock solution of the surfactant, with the fixed amount of dissolved DPC, was put into a thermostated cell, with in ± 0.1 K , and successive injections of double distilled water were made. The conductivity values were acquired after sufficient stirring and then after 5 min to ensure the attainment of equilibrium in the system [74]

2.3 SURFACE TENSION MEASUREMENTS

A surface tensiometer (Kruss K9) equipped with a platinum plate was used to measure the surface tension of the aqueous surfactant solutions of different concentrations. The tensiometer was connected to a water flow thermostat maintained at ± 0.1 K of the desired temperature. Prior to each measurement the plate was heated by holding above a Bunsen burner until glowing. The vessel was cleaned by using dichromic sulfuric acid, boiled in distilled water, and then dried in oven for several hours. The precision in the measurements was ± 1 mN/ m. For surface tension measurement 50cm³ water was put into a thermostated vassel with the help of a JSRC -13C refrigerated bath circulator, with in ± 0.1 K, and successive injections of the micellar solution were made. The surface tension value was recorded 20 min after injection to ensure the attainment of equilibrium in the system. The CMC was evaluated from the break point of the surface tension (mN/m) vs. log C curve.

2.4 KRAFFT TEMPERATURE MEASUREMENTS

For Krafft temperature measurements 7.5×10^{-3} M TTAB, 4.0×10^{-3} M CTAB and 2.5×10^{-3} M OTAB solutions were prepared in pure water (or in the specific salt concentration). These solutions are cooled in a refrigerator for 24 h at about 3°C to get precipitate of the hydrated surfactants. The conductivity of this solution is measured with gradual increase of the temperature at a rate of about 1°C interval/ 10 min with constant stirring. For each temperature the conductivity of the solution was checked for about 3 min until it reached a steady value. The T_K value was obtained at the sharp break point of the conductivity vs. temperature plot.

2.5 UV - Vis SPECTROSCOPIC MEASUREMENTS

The ultraviolet-visible (UV-Vis) spectrophotometer is an instrument commonly used in the laboratory that analyzes compounds in the ultraviolet (UV) and visible (Vis) regions of the electromagnetic spectrum. Unlike infrared spectroscopy (which looks at vibrational motions), ultraviolet-visible spectroscopy looks at electronic transitions. It allows one to determine the wavelength and maximum absorbance of compounds. From the absorbance information and using a relationship known as Beer's Law ($A = \epsilon bc$, where A = absorbance, ϵ = molar absorption coefficient, b = path length, and c = concentration), one is able to determine either the concentration of a sample if the molar extinction coefficient is known. Molar extinction coefficients are specific to particular compounds; therefore UV-Vis spectroscopy helps one in determining an unknown compound's identity. Furthermore, the energy of a compound can be ascertained from this method by using the equation $E = hc/\lambda$ where E = energy, h = Planck's constant, c = speed of light, and λ = wavelength.

Preparation of Diphenyl carbazide solutions: 0.012g of Diphenyl carbazide (DPC) was added to each 50 cm³ aqueous TTAB solutions of different concentrations in 100 cm³ reagent bottles. The solutions were kept under shaking for 48 h. Then the solutions were kept undisturbed in a thermostat at the experimental temperature to settle down any insoluble ligand. Then the solution is decanted and then it is centrifuged for 15 min at 3000 rpm by a centrifuge machine (Hettich Universal 16A). 10 cm³ of each of the supernatant solutions were treated with equal volume of 1.98×10^{-3} M freshly prepared aqueous Zn(NO₃)₂ solutions and the resulting solutions were analyzed by a UV-visible spectrometer (Simadzu UV Spectrophotometer model UV-

1601 PCS). The cells used for the visible spectroscopy were cuvettes of quartz, 1 cm thick (internal distance between parallel walls). For analyzing the solutions of Diphenyl carbazide – metal complexes at each concentrations of the surfactant, we used the Diphenyl carbazide solutions (without the metal ion) at the respective concentrations of the same surfactant as the blank solutions.

2.6 NMR analysis

The ^1H chemical shifts of various protons in each of the three surfactant units were monitored as a function of the surfactant concentration below and above its CMC. The micellar solutions of each surfactant were also studied in the presence of constant concentration of DPC to quantify the influence of DPC on the protons of the alkyl chain. The NMR spectra were recorded on a Bruker spectrometer operating at 400.172 MHz. Deuterium frequency-field lock (also known as deuterium lock or field lock) is used to offset the effect of the natural drift of the NMR's magnetic field.

RESULTS AND DISCUSSION

3.1 CMC OF SURFACTANTS AND THEIR BULK BEHAVIORS IN PURE WATER

The CMC of TTAB, CTAB and OTAB at different temperatures, ranging from 293 K to 328 K, were measured by the conductometric method. These values were found to be in good agreement with some of the reference values [3]. The experimental conductivities (κ) for TTAB, CTAB and OTAB in pure water at different temperatures are shown in fig3.1 to 3.4. It is observed that the specific conductivity (κ) values of the solution shows a linear increase with gradual increase of concentration of the surfactant which is due to the increase of surfactant monomers.

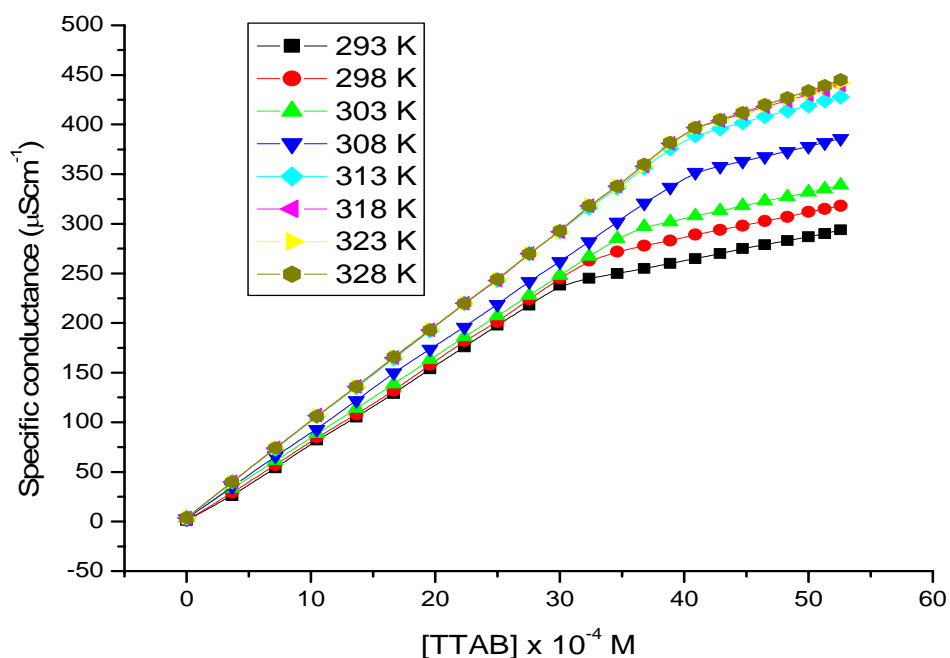


Figure 3.1 Specific conductances (κ) vs. concentration of TTAB at different temperatures

The break in the plot (micelle formation) is due to the binding of some counter ions of the ionic surfactant which favors the micellization process by decreasing and screening the surface charges. The degree of ionization, α was determined by the ratio, S_2/S_1 of the slopes above and below the break point (i.e. post and pre micellization) [91]. The

fraction of counter ion binding (β) was obtained from the relation $\beta = (1 - S_2/S_1)$. CMC measurements for CTAB and OTAB were not possible below 298 K and 313 K because the Krafft Temperature of these two surfactants were found to be 24.7 °C and 36.5 °C respectively.

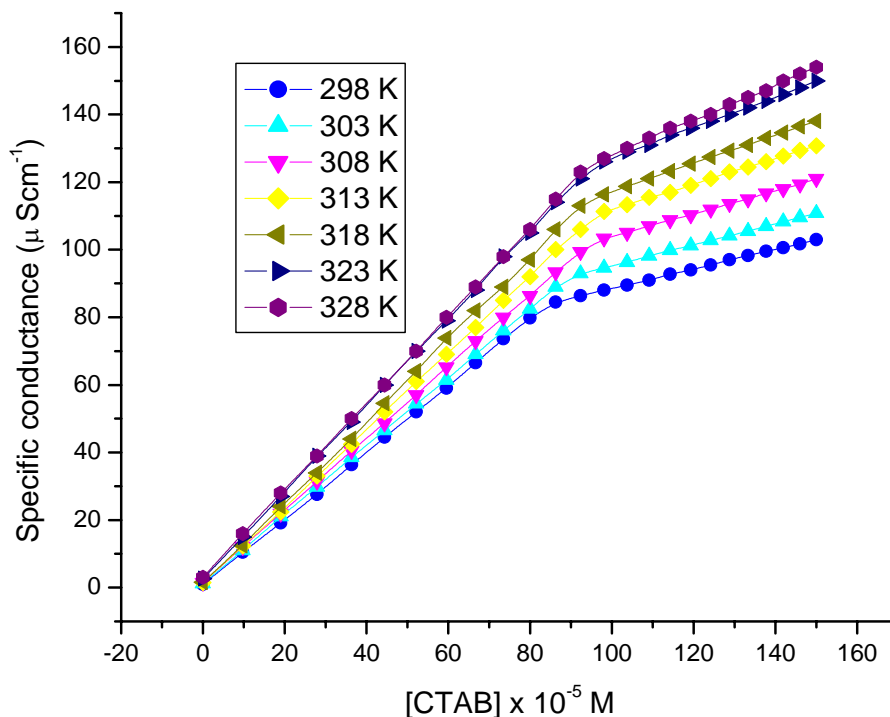


Figure 3.2 Specific conductances (κ) vs. concentration of CTAB at different temperatures

For TTAB and CTAB it was found that the CMC, in pure water, gradually increases with increase of temperature up to a certain range and then the CMC values slightly decrease with further increase of temperature. The initial increase in CMC for increased temperature is due to the thermal solubility of the surfactant monomers and a slight decrease of the CMC with further increase of temperature is due to dehydration of the head group which dominates over the solubility effect [45].

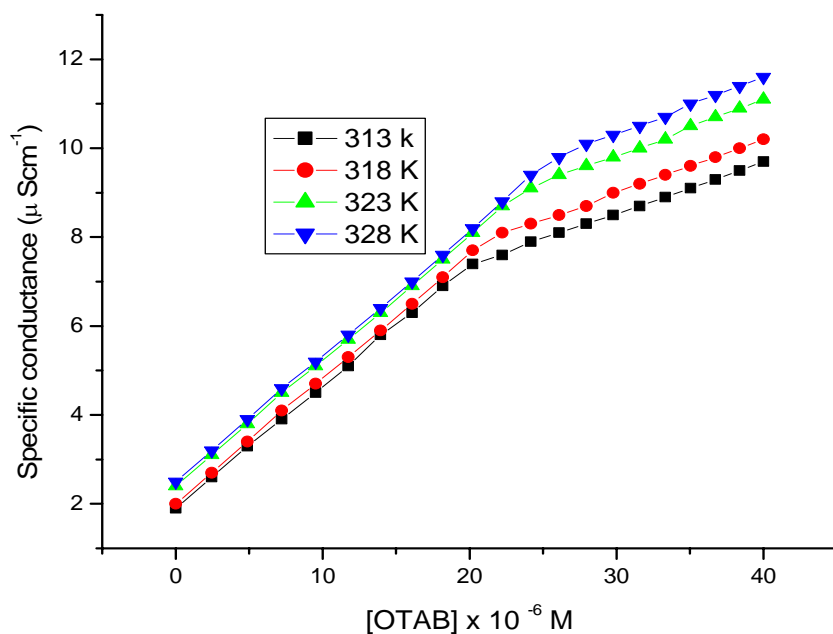


Figure 3.3 Specific conductances (κ) vs. concentration of OTAB at different temperatures for first micellization (CMC_1)

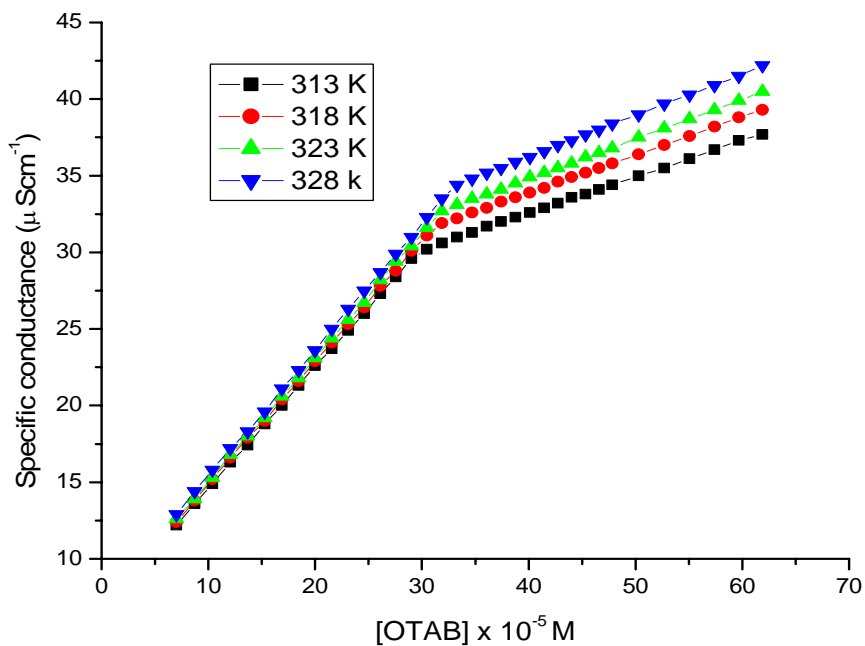


Figure 3.4 Specific conductances (κ) vs. concentration of OTAB at different temperatures for second micellization (CMC_2)

OTAB was found to produce two CMCs; the first has low aggregation, while the second one is higher. The second CMC value is in agreement with the reported values [3]. Both the CMC_1 and CMC_2 values for OTAB were found to increase with increase of temperature. Figure 3.5 to 3.6 shows the variation of cmc of TTAB and CTAB at different temperatures.

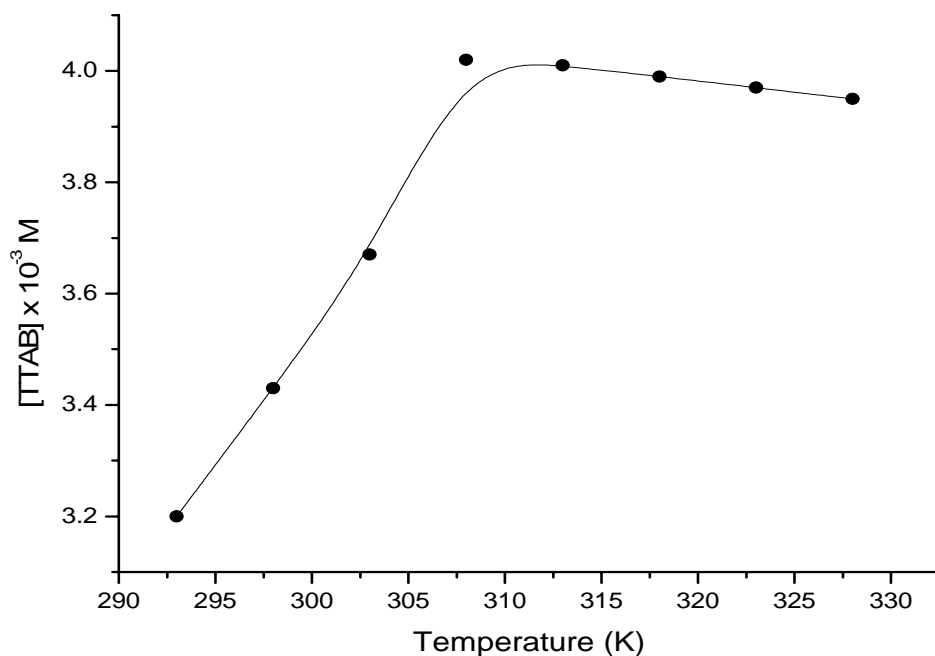


Figure 3.5 Variation of CMC of TTAB in pure water with temperatures.

At each temperature the CMC values were found to decrease with gradual increase of alkyl chain length of the N-alkyl Trimethylammonium Bromide Surfactants which is due to the increased hydrophobicity. The β values were found to decrease gradually with increase of temperature. This gradual decrease of β with increase of temperature indicates that the degree of dissociation of the micelle increase with increase of temperature which is caused by the decrease of aggregation number [92]. After a certain range (i.e. above 308 K), further increase of temperature causes a much greater

decrease of β for TTAB compared to the other two surfactants, which indicates that the surface charge density of TTAB aggregates decreased with increasing temperature by the way of enhanced counter ion dissociation.[93]. At every certain temperature, it was found that the surfactant with larger alkyl chain length has greater counter ion binding (β) value. For OTAB, the counter ion binding (β) of second micelle was found to be greater than the first, suggesting more charge density of the later.

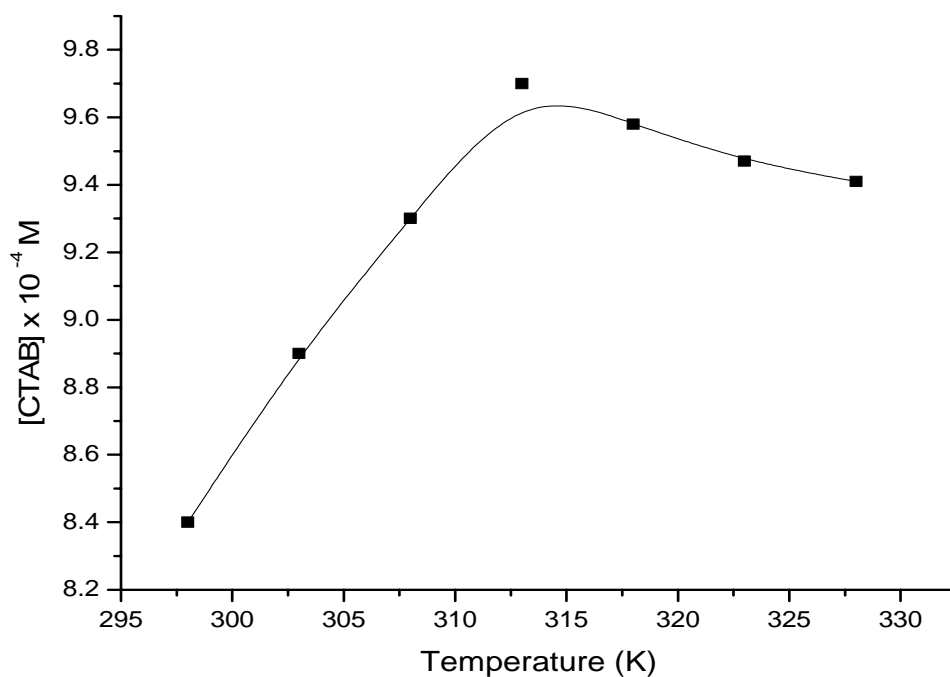


Figure 3.6 Variation of CMC of CTAB in pure water with temperatures.

Table 3.1 shows variation of the CMC and the counter- ion Binding (β) for TTAB, CTAB and OTAB in pure water at different temperatures.

Table 3.1 CMC and the fraction of counter ion binding (β) for TTAB, CTAB and OTAB in pure water at different temperatures. (Subscripts 1 and 2 to the column title refer to the micellization process 1 and 2 respectively for OTAB)

T/K	TTAB		CTAB		OTAB	
	10^3CMC/M	β	10^3C/MC/M	β	$10^5 \text{CMC}_1/\text{M}$ ($10^4 \text{CMC}_2/\text{M}$)	β_1 (β_2)
293	3.2	0.70	--	--	--	--
298	3.43	0.69	0.84	0.70	--	--
303	3.67	0.68	0.89	0.69	--	--
308	4.02	0.67	0.93	0.68	--	--
313	4.01	0.64	0.97	0.67	2.02 (2.96)	0.58 (0.70)
318	3.99	0.62	0.96	0.66	2.22 (3.08)	0.57 (0.69)
323	3.97	0.60	0.95	0.65	2.30 (3.19)	0.56 (0.68)
328	3.95	0.58	0.94	0.60	2.41 (3.27)	0.55 (0.67)

3.2 THERMODYNAMIC PARAMETERS FOR MICELLIZATIONS OF THE SURFACTANTS

The free energy (ΔG_m°), the enthalpy (ΔH_m°) and the entropy (ΔS_m°) changes of micellization have been calculated from the following expressions [8, 91]:

$$\Delta G_m^\circ = (1 + \beta) RT \ln X_{\text{cmc}} \dots\dots\dots(2)$$

$$\Delta S_m^\circ = - \{ \delta \Delta G_m^\circ / \delta T \}_P \dots\dots\dots(3)$$

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \dots\dots\dots(4)$$

Here X_{cmc} is the mole fraction of the surfactant at the CMC. Table 3.2 shows thermodynamic parameters of TTAB, CTAB and OTAB, in pure water. In the present experiment the ΔG_m° values for micellization of the surfactants in the given temperature range were found to be negative which indicates the spontaneity of the process. The ΔG_m° values for TTAB, CTAB and OTAB (ΔG_{m2}° for OTAB), in pure water at different temperatures, as a function of number of carbon atoms in the alkyl chain of the surfactants are shown in figure 3.7. The negative ΔG_m° values show a linear increase with gradual increase of alkyl chain length of the surfactants, which indicates that micellization becomes more spontaneous with increase of the alkyl chain length of the cationic surfactants. This trend is attributed to greater hydrophobic nature of the larger alkyl chain. For OTAB, ΔG_m° values of first micelle were found to be more negative than the second, suggesting increased spontaneity of the first micellization with low aggregation number.

Table 3.2 Values of the free energy of micellization, ΔG_m° , Enthalpy of micellization, ΔH_m° and Entropy of micellization, ΔS_m° for TTAB, CTAB and OTAB at various temperatures.

T/K	TTAB			CTAB			OTAB		
	ΔG_m°	ΔS_m°	ΔH_m°	ΔG_m°	ΔS_m°	ΔH_m°	ΔG_{m1}° (ΔG_{m2}°)	ΔS_{m1}° (ΔS_{m2}°)	ΔH_{m1}° (ΔH_{m2}°)
293	-40.37	20.72	-34.30						
298	-40.51	20.37	-34.44	-47.02	34.45	-36.75			
303	-40.62	20.02	-34.55	-47.20	33.83	-36.95			
308	-40.70	19.67	-34.65	-47.35	33.21	-37.12			
313	-40.78	19.32	-34.73	-47.52	32.59	-37.32	-60.96 (-53.72)	69.23 (77.40)	-39.29 (-29.49)
318	-40.87	18.97	-34.84	-47.69	31.97	-37.52	-61.30 (-54.08)	68.53 (77.00)	-39.51 (-29.60)
323	-40.98	18.62	-34.97	-47.84	31.35	-37.71	-61.65 (-54.50)	67.83 (76.60)	-39.74 (-29.76)
328	-41.09	18.27	-35.10	-48.00	30.73	-37.92	-61.98 (-54.86)	67.13 (76.20)	-39.96 (-29.87)

Here the Energetic Parameters are expressed in kJ mol^{-1} for ΔG_m° and ΔH_m° and $\text{J K}^{-1} \text{mol}^{-1}$ for ΔS_m° . Subscript 1 and 2 in case of OTA are for first and second micellization respectively.

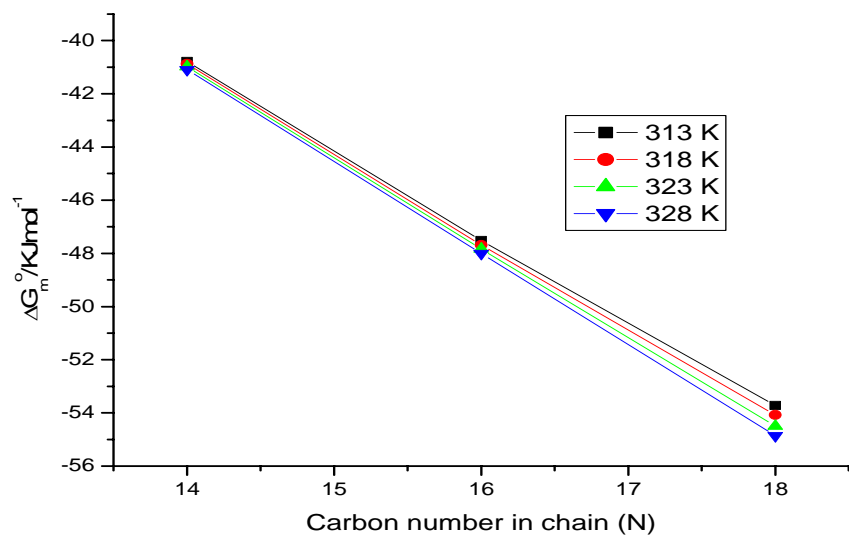


Figure 3.7 Effect of chain length on ΔG_m^0 of TTAB, CTAB and OTAB (ΔG_{m2}^0 of OTAB is used here)

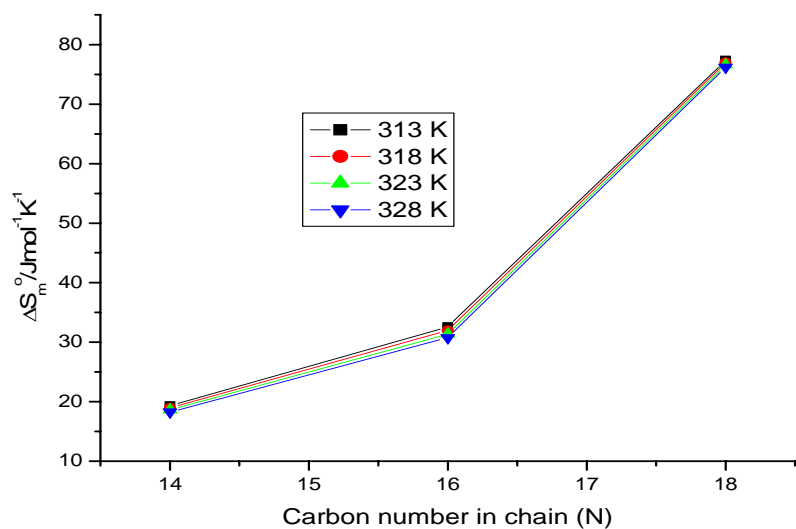


Figure 3.8 Effect of chain length on ΔS_m^0 of TTAB, CTAB and OTAB (ΔS_{m2}^0 of OTAB is used here)

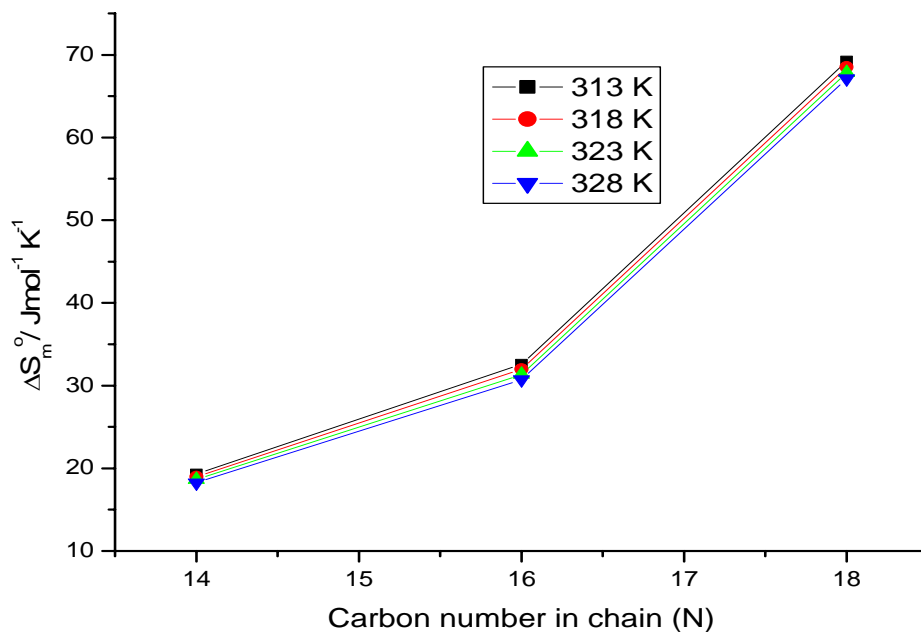


Figure 3.9 Effect of chain length on ΔS_m^0 of TTAB, CTAB and OTAB (ΔS_{m1}^0 of OTAB is used here)

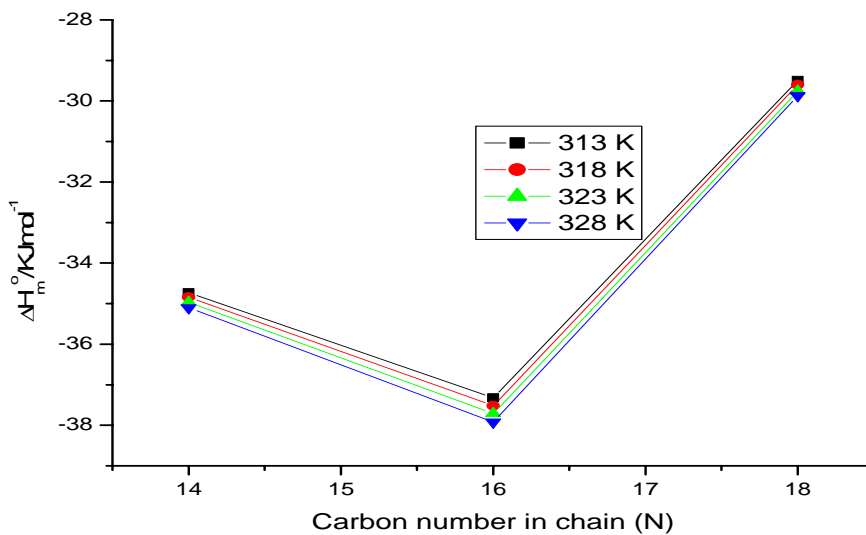


Figure 3.10 Effect of chain length on ΔH_m^0 of TTAB, CTAB and OTAB (ΔH_{m2}^0 of OTAB is used here)

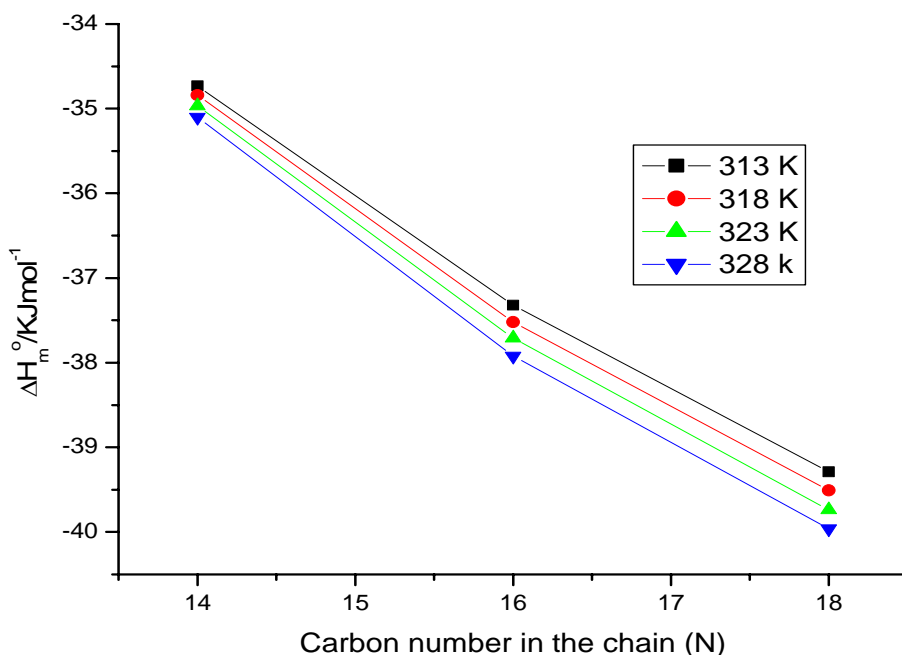


Figure 3.11 Effect of chain length on ΔH_m° of TTAB, CTAB and OTAB (ΔH_{m1}° of OTAB is used here)

Micellization is associated with the destruction of the highly ordered H-bonded water molecules or iceberg around the alkyl chains which gives a positive enthalpy change [8, 94, and 95]. Yet the ΔH_m° is found to be negative and becomes further negative with increase of temperature. The negative ΔH_m° is associated by the way of (i) disruption of the hydrophobic hydration (or melting of the “iceberg”) surrounding the hydrophobic tails of the monomers, and (ii) increased degree of freedom of the tails in the interior of the micelle [93] where the London dispersion force is the major attractive force and which is greater for a larger hydrocarbon chain [91, 41]. Figure 3.11 shows that the surfactant with larger the alkyl chain length shows more negative ΔH_m° value. But

figure 3.10 shows different trend of ΔH_m° , which shows that the ΔH_m° value for second micellization of OTAB is less negative than the ΔH_m° value of CTAB. This is due to greater aggregation for the second micellization of OTAB. For 2nd micellization additional number of surfactant monomers has to disrupt more hydrophobic hydration. This required energy is not sufficiently compensated by the increased degree of freedom of the new hydrophobic tails in the micelle. As a result ΔH_m° value becomes less exothermic. In the present study the ΔH_m° values are found to be increasing with increase of temperature which is attributed to the disruption of greater number of hydrogen bonding between the water molecules at higher temperature [96, 97]. So less energy is required to break the iceberg structure around the hydrophobic alkyl chains.

On the other hand, although temperature is raised the ΔS_m° on micelle formation is positive and its value decreases with increase of temperature. This arises because the “structured water layer” around the hydrophobic moiety of a monomer surfactant becomes thinner as temperature increases or alternatively the degree of structure in the water layer decrease. Therefore the extent of randomness increased (producing a free energy gain) upon micelle formation becomes less and less with increasing temperature. Greater entropy values are obtained for the surfactants with larger alkyl chain (figure 3.8 and 3.9). Greater entropy of the system is obtained when the larger hydrocarbon chains are removed from aqueous medium to the interior of the micelle which is because of greater degree of disruption of structured water layer by the larger chain.

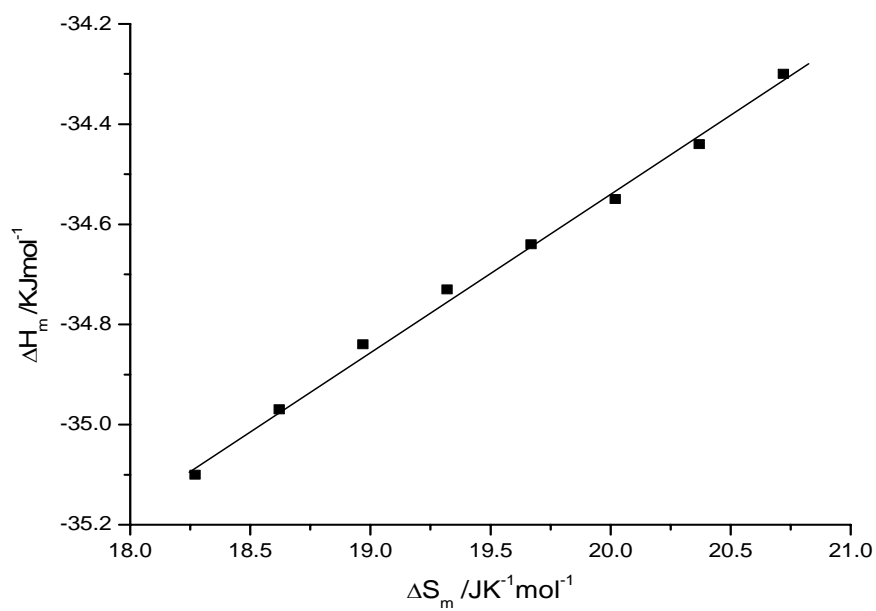


Figure 3.12 Enthalpy-Entropy compensation plots for micellization of TTAB in pure water

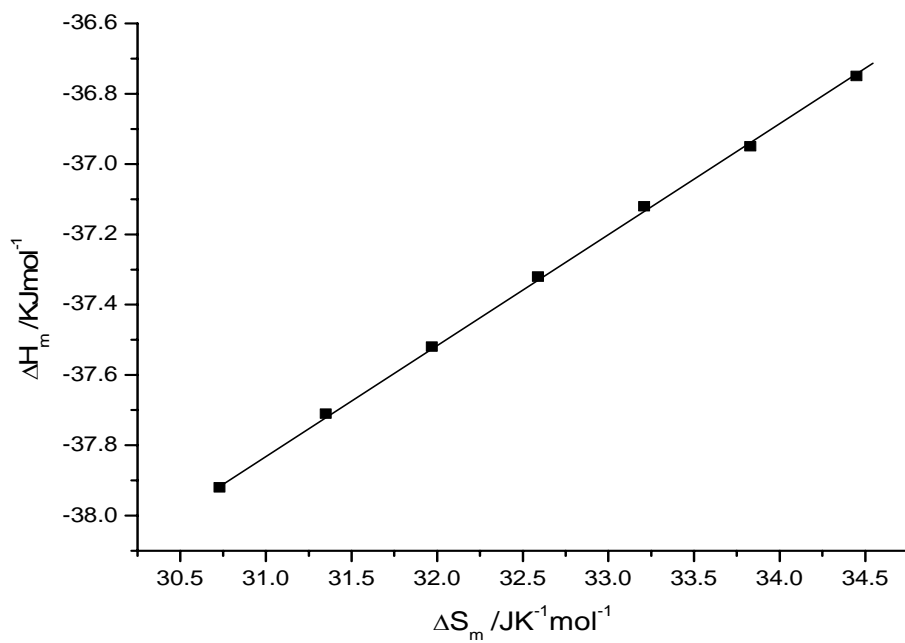


Figure 3.13 Enthalpy-Entropy compensation plots for micellization of CTAB in pure water

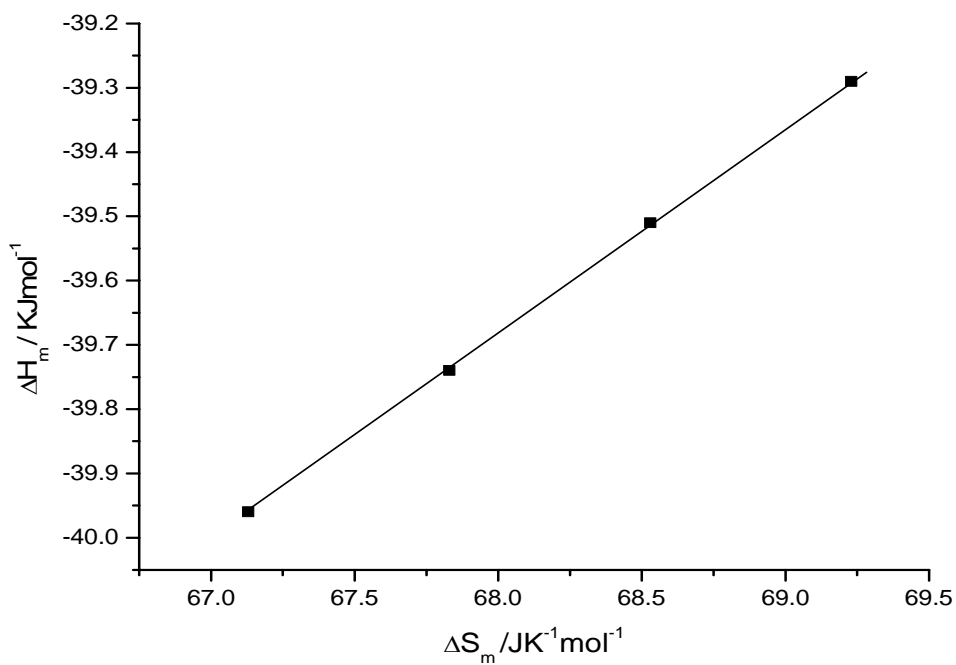


Figure 3.14 Enthalpy-Entropy compensation plots for CMC_1 of OTAB in pure water

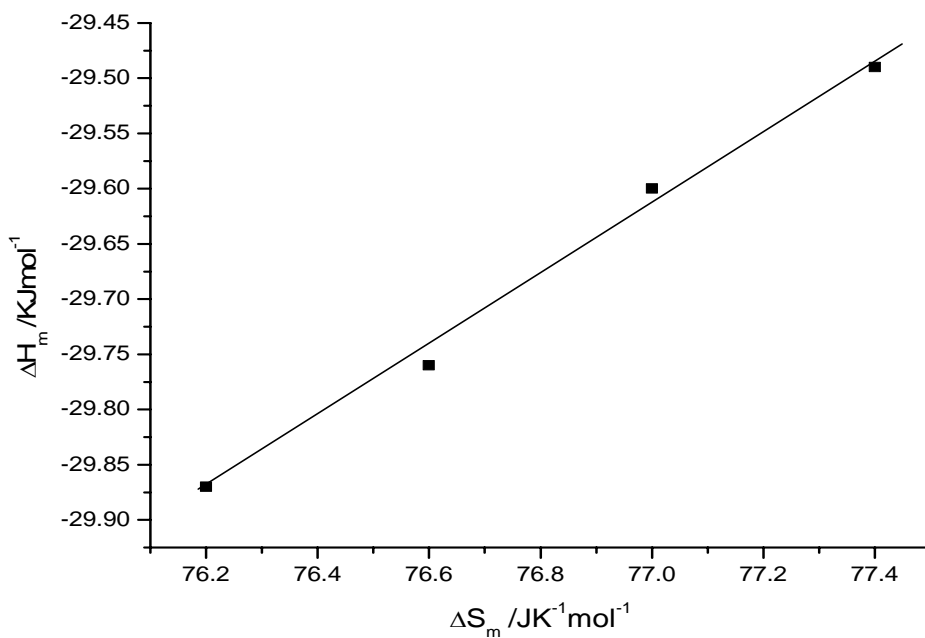


Figure 3.15 Enthalpy-Entropy compensation plots for CMC_2 of OTAB in pure water

The enthalpy –entropy compensation plots for bulk micellization of TTAB, CTAB and OTAB are shown in figure 3.12 to 3.15. Linear relationships obtained for micelle formation of these surfactants. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy nearly constant. Such behaviors were shown for aqueous solutions of ionic surfactants and smaller molecules, in some of the previous studies [91, 98-100].

3.3 EMPIRICAL REATION FOR CRITICAL MICELLE CONCENTRATION OF THE SURFACTANTS

Figure 3.16 shows the Log CMC vs n (number of carbon in the alkyl chain of the surfactants) plots at 313 K- 328K temperature. Linear relationship between the log CMC and n were obtained, as predicted from the Stauff-Klevens empirical rule for the cationic surfactants which is: $\log \text{CMC} = A - Bn$. The values for A and B of these plots are also in good agreement with few the reference values [3]. It was observed that both of the A and B values decrease with increase of temperature.

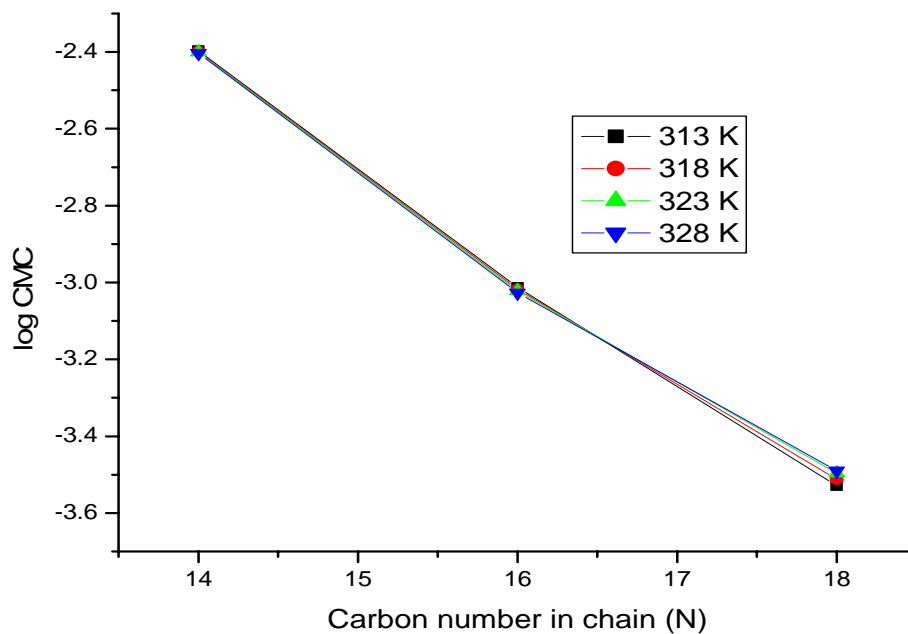


Figure 3.16 Effect of chain length on the CMC of alkyltrimethylammoniumbromide surfactants (CMC₂ of OTAB is used).

Table -3.3 Constants for the Relation $\text{Log CMC} = A - BN$ of N-Alkyl Trimethylammonium Bromides at Different temperatures

Temperature/K	A	B
313	1.55	0.283
318	1.48	0.278
323	1.41	0.274
328	1.36	0.271

3.4 ADSORPTION BEHAVIOR OF THE SURFACTANTS IN PURE WATER

Figure 3.17 to 3.20 shows the surface tension (γ) as a function of logarithmic concentration ($\log_{10}C$) of TTAB, CTAB and OTAB in pure water at different temperatures. A gradual decrease in the surface tension with increasing the surfactant concentration is observed due to spontaneous adsorption of the surfactant molecules from the bulk to the air-water interface. After a certain concentration a sharp break point followed by a plateau region of constant γ values are obtained because of the saturation of the solution surface by the adsorbed molecules. The surface tension data for figure 3.17 to 3.20 shows a constant surface tension (γ) at the micellar concentrations and no minimum γ values were obtained for further increase of the surfactant concentration. This indicates that the surfactants are free from impurity [101]. At a certain temperature CMC is determined from the intersection point of this type of γ versus $\log_{10}C$ plot.

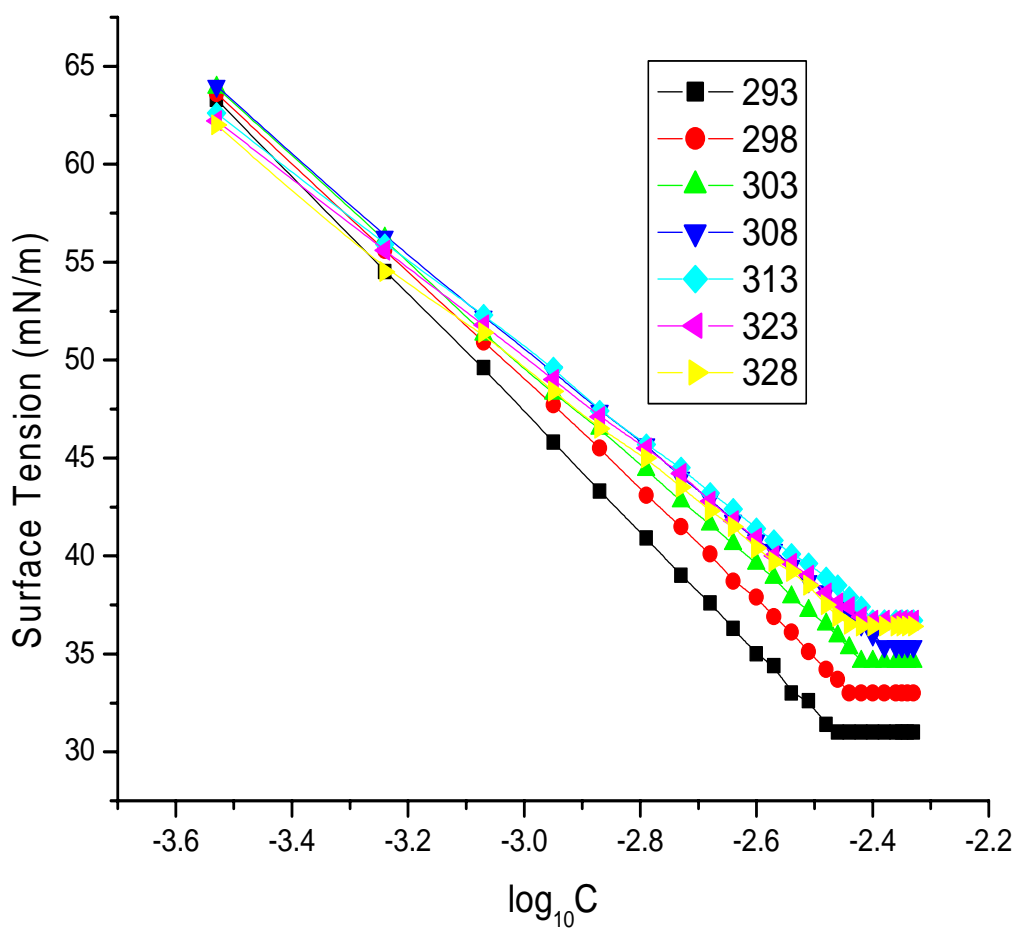


Figure 3.17 Surface Tension (γ) vs. logarithmic concentration ($\log_{10}C$) of TTAB in pure water at different temperatures

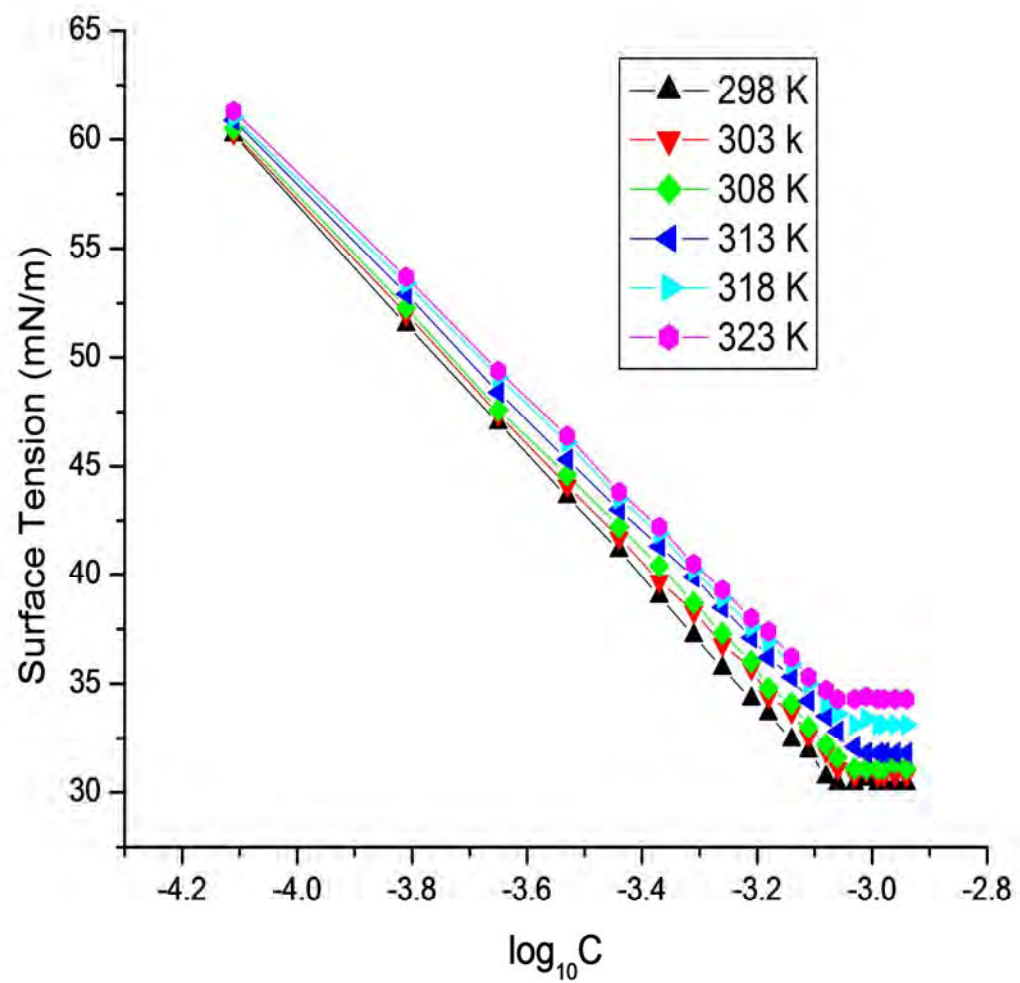


Figure 3.18 Surface Tension (γ) vs. logarithmic concentration ($\log_{10}C$) of CTAB in pure water at different temperatures

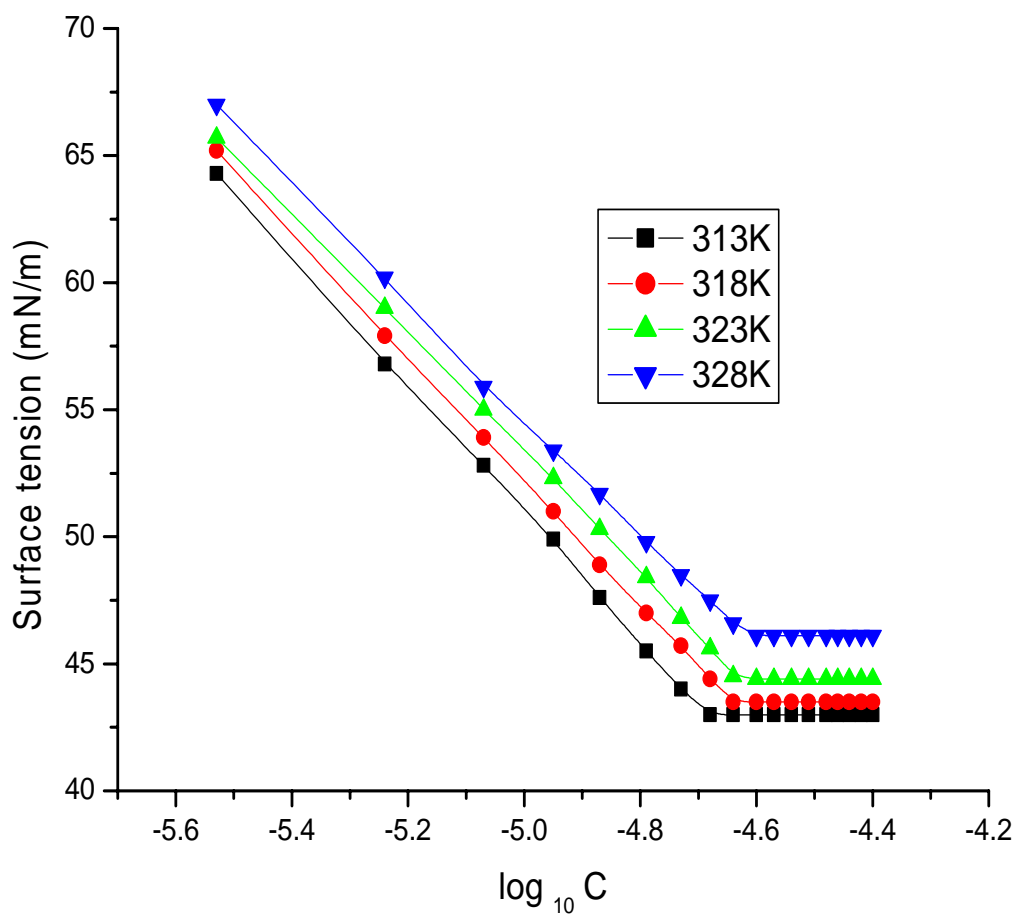


Figure 3.19 Surface Tension (γ) vs. logarithmic concentration ($\log_{10}C$) of OTAB in pure water at different temperatures (for 1st CMC)

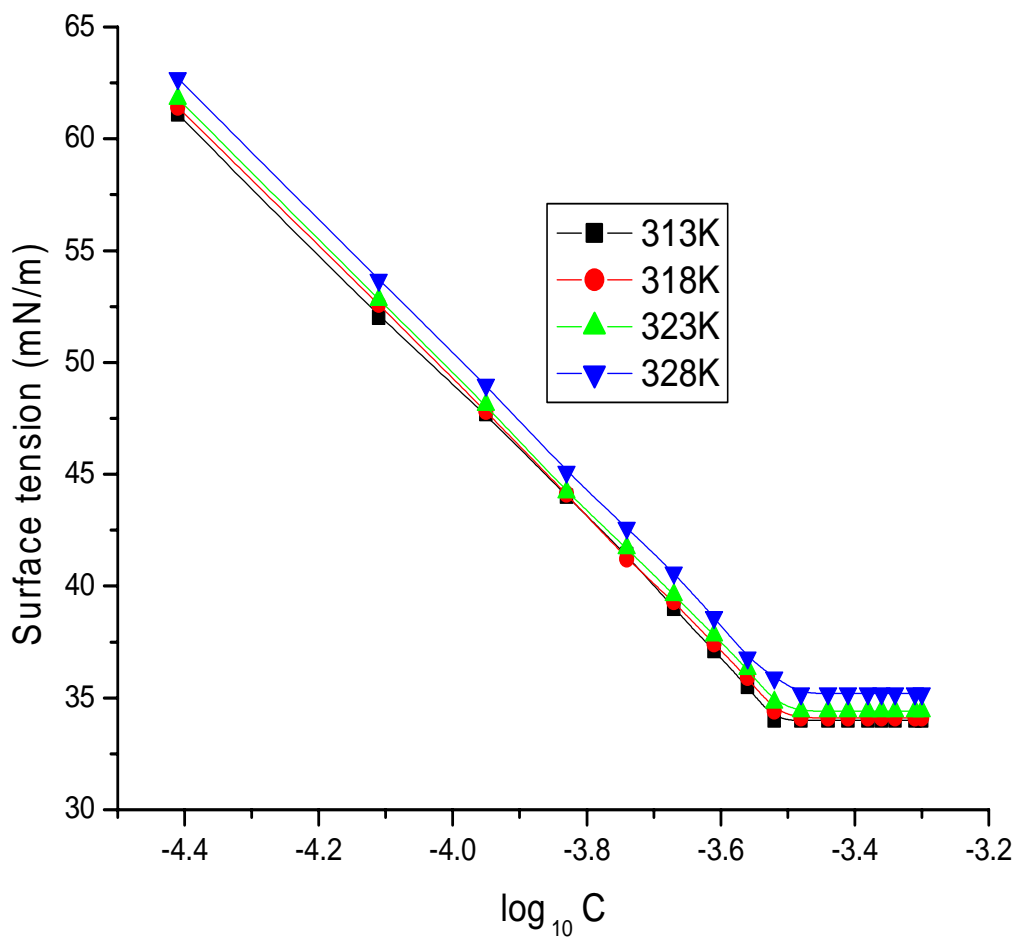


Figure 3.20 Surface Tension (γ) vs. logarithmic concentration ($\log_{10}C$) of OTAB in pure water at different temperatures (for 2nd CMC).

The slope of the straight line of this surface tension (γ) versus $\log_{10}C$ plot, before the CMC, is used to calculate the surface excess concentration (Γ_m) of TTAB at different temperatures by the following equation:

$$\Gamma_m = - 1/RT (\delta\gamma/ \delta \ln C)_{T,P} \dots\dots\dots(1)$$

Here R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, C is the surfactant concentration in the bulk. Figure 3.21 shows the Γ_{\max} of TTAB, CTAB and OTAB at different temperatures in pure water which reveals that the Γ value decreases gradually with increasing temperature.

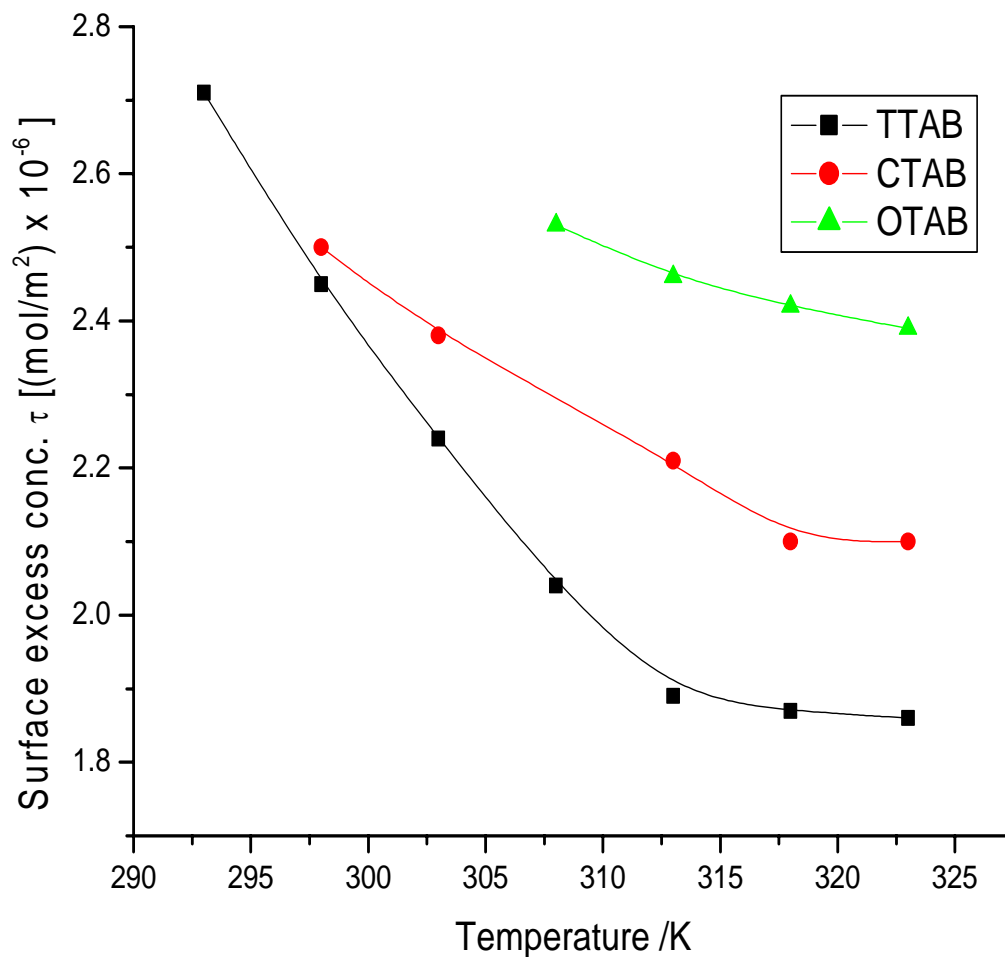


Figure 3.21 Surface excess concentration, Γ_m of TTAB, CTAB and OTAB at different temperatures

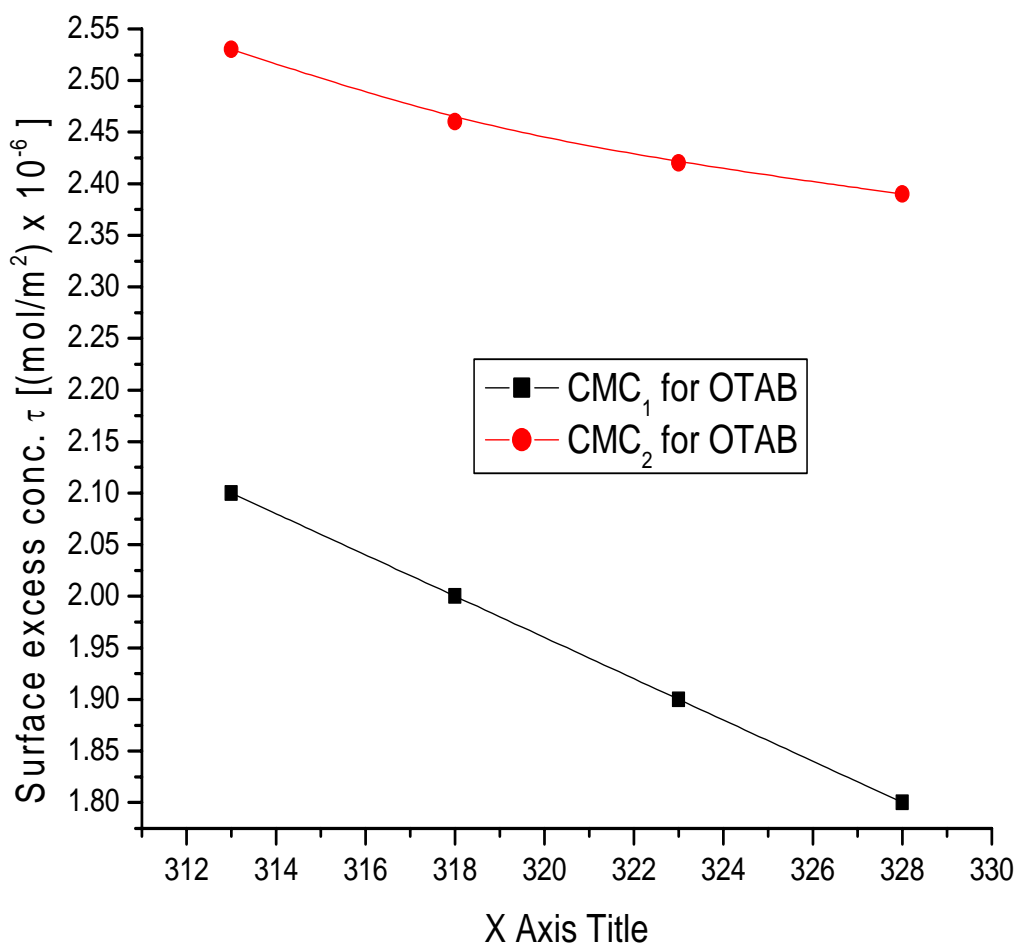


Figure 3.22 Surface excess concentrations, Γ_m of OTAB (for CMC_1 and CMC_2) at different temperatures.

The higher Γ value at the lower temperature is due to higher degree of vander Waals interaction between the hydrophobic alkyl chains. As a result a closer molecular packing occurs in the adsorbed monolayer [102]. But increase in temperature causes an increase in the kinetic energy, thermal motion and chain flexibility that consequence disorganization of the adsorbed molecules at the air-water interface [94, 98]. Increase in temperature makes the vander Waals interaction between the alkyl chains more unfavorable. Thus the closer molecular packing of the monolayer at the air-water

interface is hindered by the perturbation of the adsorbed molecules. Due to increase of temperature this factor dominates over the dehydration effect and consequently the Γ decreases gradually.

From figure 3.21 it has been observed that at a certain temperature the surfactant with larger chain length shows greater surface excess concentration, Γ value, which may be due to greater degree of counterion binding by the surfactant molecules with longer chain [3]. Higher surface excess concentration, Γ value, were also observed for the second micellization of OTAB compared to its first micellization process since second micellization involves greater concentration of the surfactant which causes greater number of counter ion binding (β). Figure 3.23 to 3.26 shows the relation between the counter ion binding and Γ value of TTAB, CTAB and OTAB.

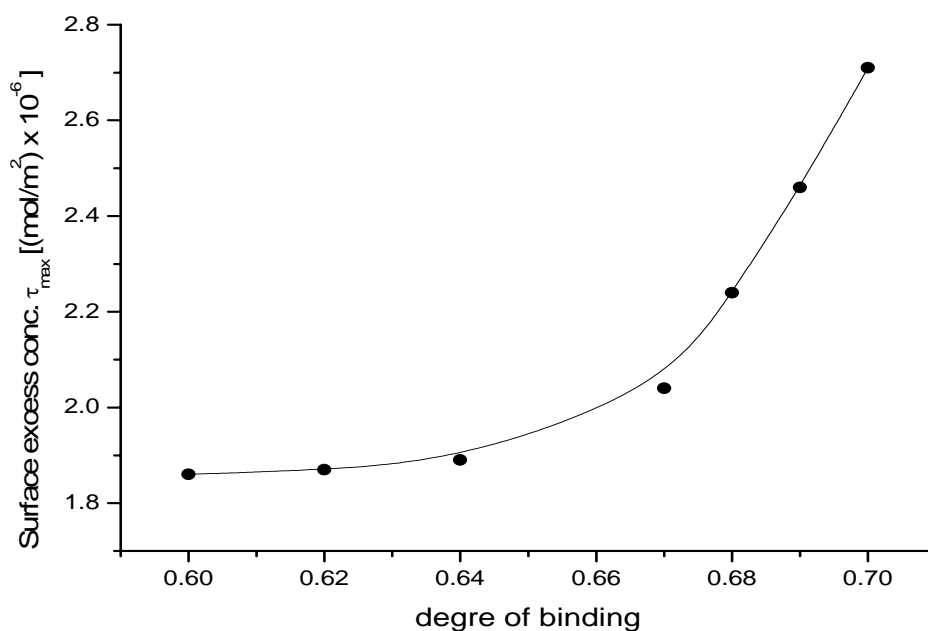


Figure 3.23 Relation between the counter ion binding and Γ value of TTAB

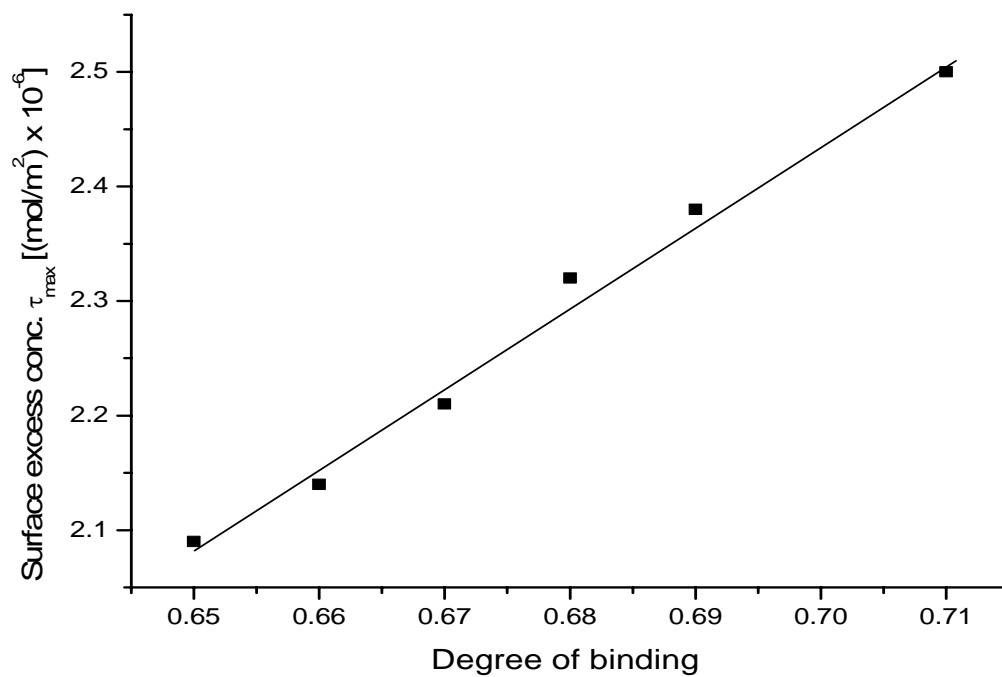


Figure 3.24 Relation between the counter ion binding and Γ value of CTAB

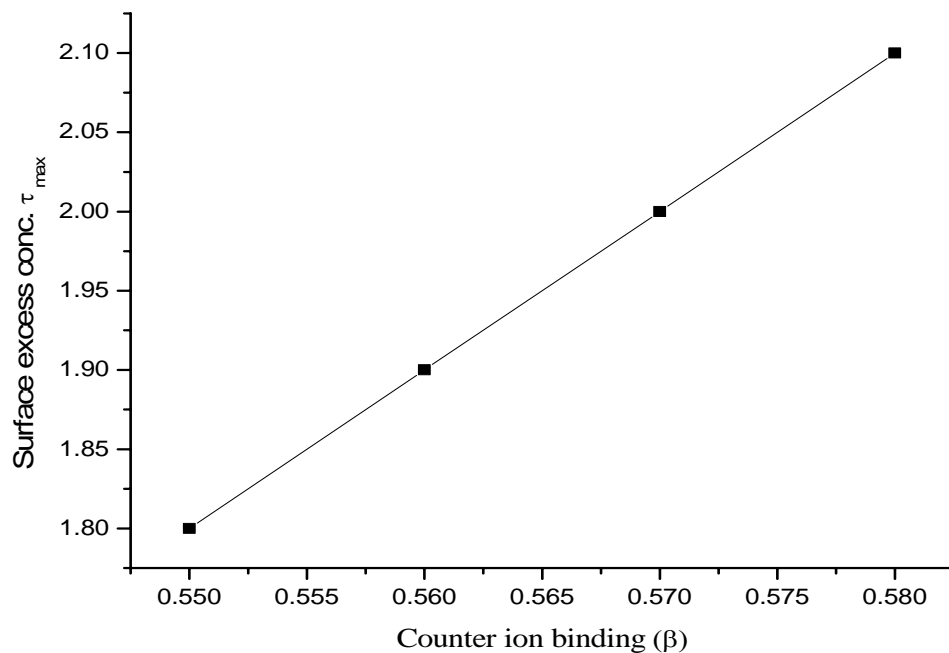


Figure 3.25 Relation between the counter ion binding and Γ value of OTAB (for 1st micellization)

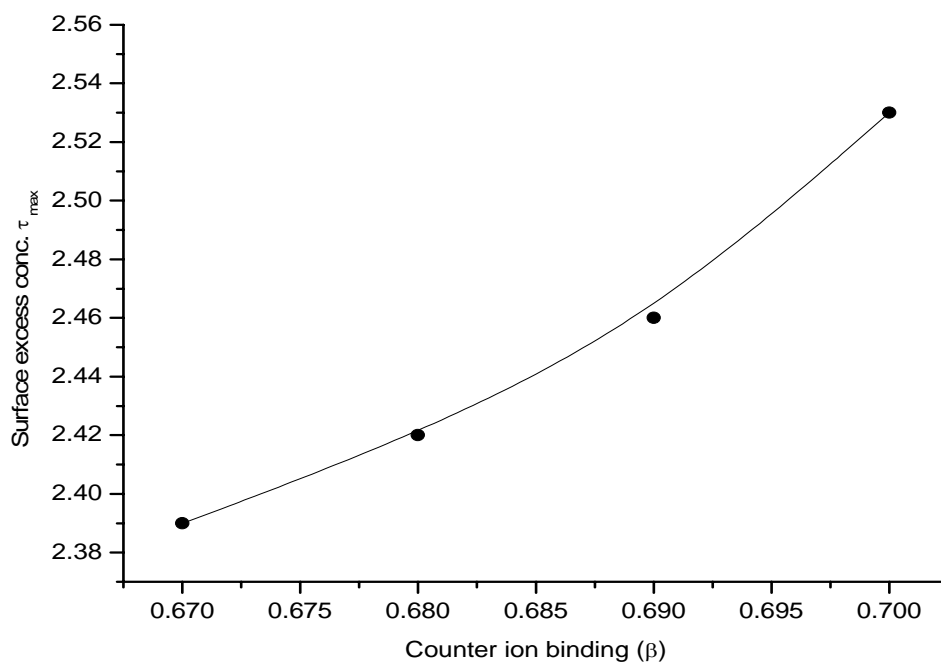


Figure 3.26 Relation between the counter ion binding and Γ value of OTAB (for 2nd micellization).

3.5 EMPIRICAL REATION OF CRITICAL MICELLE CONCENTRATION FOR ADSORPTION OF THE SURFACTANTS

Figure 3.27 shows the log CMC vs n (number of carbon in the alkyl chain of the surfactants) plots at 313 K- 323K temperature. Linear relationship between the log CMC and n were obtained, as predicted from the Stauff-Klevens empirical rule for the cationic surfactants which is: $\log \text{CMC} = A - Bn$ [3].

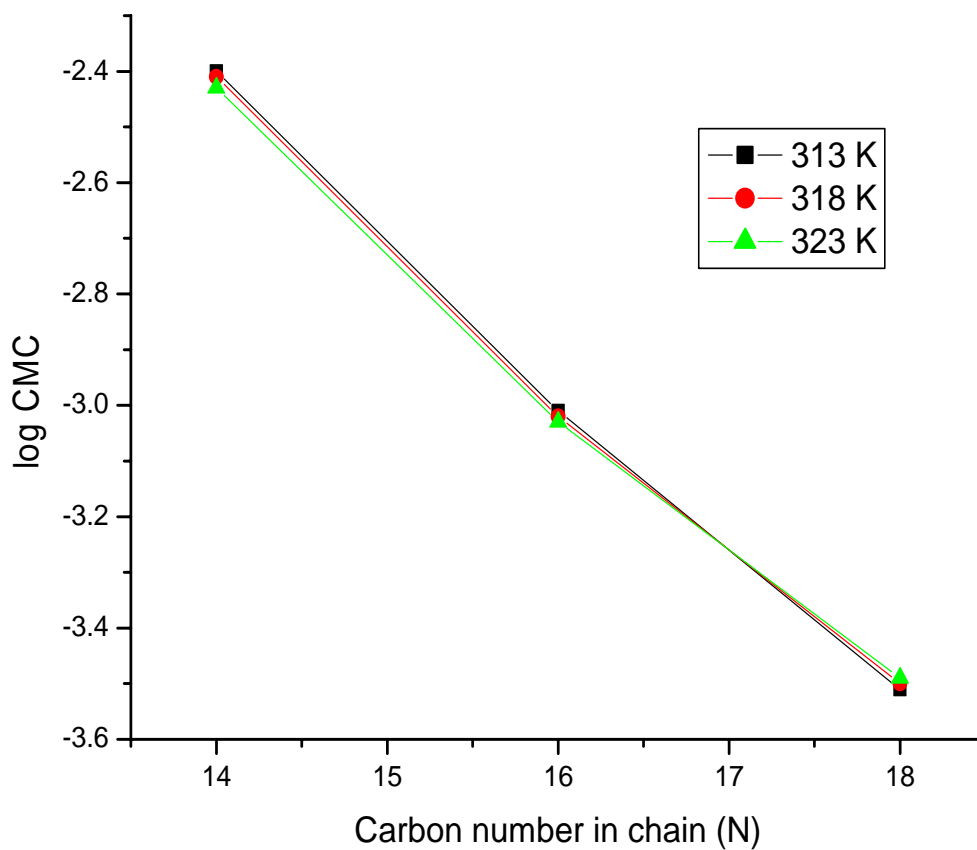


Figure 3.27 Effect of chain length on CMC for adsorption of N-alkyl trimethyl ammonium bromide surfactants (CMC₂ of OTAB is used).

The values for A and B of these plots are also in good agreement with the literature values, reported for the micellization processes [3]. It was observed that both of the A and B values decrease with increase of temperature. Both A and B values for adsorption are found to be less compared to the bulk micellization.

Temperature/K	A	B
313	1.47	0.278
318	1.38	0.273
323	1.26	0.265

Table 3.4 Constants for the Relation $\text{Log CMC} = A - Bn$ of *N*-alkyltrimethylammonium bromides for adsorption at Different temperatures

3.6 THERMODYNAMIC PARAMETERS FOR ADSORPTION OF THE SURFACTANTS

Table 3.4 shows the thermodynamic parameters for the adsorption of TTAB, CTAB and OTAB at the air-water interface (for pure water). The free energy changes of adsorption $\Delta G_{\text{ad}}^{\circ}$ at different temperatures were calculated from the following expressions [3, 8]

$$\Delta G_{\text{ad}}^{\circ} = \Delta G_{\text{m}}^{\circ} - (\pi_{\text{cmc}} / \Gamma_{\text{max}}) \dots\dots\dots(5)$$

Here π_{cmc} and the Γ_{max} are the equilibrium surface pressure and the surface concentration of the adsorbed molecules, respectively at above the CMC. $\Delta S_{\text{ad}}^{\circ}$ and $\Delta H_{\text{ad}}^{\circ}$ were calculated from the relationship as in equation:

$$\Delta S_{\text{m}}^{\circ} = - \{ \delta \Delta G_{\text{m}}^{\circ} / \delta T \}_{\text{P}} \dots\dots\dots(3)$$

$$\Delta G_{\text{m}}^{\circ} = \Delta H_{\text{m}}^{\circ} - T \Delta S_{\text{m}}^{\circ} \dots\dots\dots(4)$$

The $\Delta G_{\text{ad}}^{\circ}$ values were negative over the studied temperature range which shows that adsorption is a spontaneous process. As the temperature increased the $\Delta G_{\text{ad}}^{\circ}$ becomes

slightly more negative, suggesting the adsorption driving force increases. This result is consistent with the fact that the dehydration of the head group causes an increase in hydrophobicity of the surfactant molecules with increasing temperature. ΔG_{ad}° values of the surfactants were found to be more negative compared to their respective ΔG_m° values at each certain temperature which reveals that the adsorption of the surfactant monomers at the air-water interface is more spontaneous than micelle formation in the bulk. The hydrophobicity of the amphiphiles primarily leads them towards the air-water interface and then the micelle formation occurs above the CMC; the later process is secondary and less spontaneous [8]. The ΔH_{ad}° is negative over the studied temperature range which is a general phenomenon for the adsorption of most of the surfactant molecules [96]. The ΔH_{ad}° value becomes more negative with further increase of temperature. This behavior is due to the decrease of hydration at the increased temperatures which lowers the required energy for the surfactant molecules to be adsorbed at the air-water interface. The ΔS_{ad}° values were found to be positive within the experimental temperature range as expected for all the micellization process. At each temperature ΔS_{ad}° values were found to be more positive than the ΔS_m° . These greater ΔS_{ad}° values can arise from the destruction of the ice berg structure around the hydrophobic alkyl chain and the subsequent dangling of the alkyl chain of the adsorbed surfactant molecules at the air-water interface [103]. Water molecules at the air-water interface have a preferential orientation, with oxygen atoms outermost [104-105] which results an electric double layer with a negative outermost surface and a positive inner end, directed to the solvent side [104]. The gradual adsorption of the hydrophobic chain, with charge, is associated with effective interactions with this layer which may attribute to higher ΔS_{ad}° value compared to the ΔS_m° value at certain temperature.

Table .3.5 Thermodynamic parameters for adsorption of the surfactants .

T/K	TTAB			CTAB			OTAB		
	ΔG_{ad}°	ΔS_{ad}°	ΔH_{ad}°	ΔG_{ad}°	ΔS_{ad}°	ΔH_{ad}°	$\Delta G_{ad 1}^{\circ}$	$\Delta S_{ad 1}^{\circ}$	$\Delta H_{ad 1}^{\circ}$
							$(\Delta G_{ad 2}^{\circ})$	$(\Delta S_{ad 2}^{\circ})$	$(\Delta H_{ad 2}^{\circ})$
293	-53.92	36.96	-43.09						
298	-54.11	36.27	-43.30	-61.88	50.08	-46.96			
303	-54.28	35.58	-43.50	-62.17	49.20	-47.26			
308	-54.43	34.89	-43.68	-62.40	48.32	-47.51			
313	-54.67	34.20	-43.96	-62.62	47.44	-47.77	-74.05 (-68.15)	71.22 (79.16)	-51.76 (-43.37)
318	-54.81	33.51	-44.15	-62.84	46.57	-48.03	-74.40 (-68.54)	68.92 (78.26)	-52.48 (-43.65)
323	-54.96	32.82	-44.36	-63.11	45.69	-48.35	-74.75 (-68.93)	66.62 (77.36)	-53.23 (-43.94)
328	----	----	----	----	----	----	-75.07 (-69.31)	64.32 (76.46)	-53.97 (-44.23)

Here the Energetic Parameters are expressed in $KJ mol^{-1}$ for ΔG_{ad}° and ΔH_{ad}° and $J K^{-1} mol^{-1}$ for ΔS_{ad}° . Subscript 1 and 2 to the column title refer to micellization processes 1 and 2 respectively for OTAB.

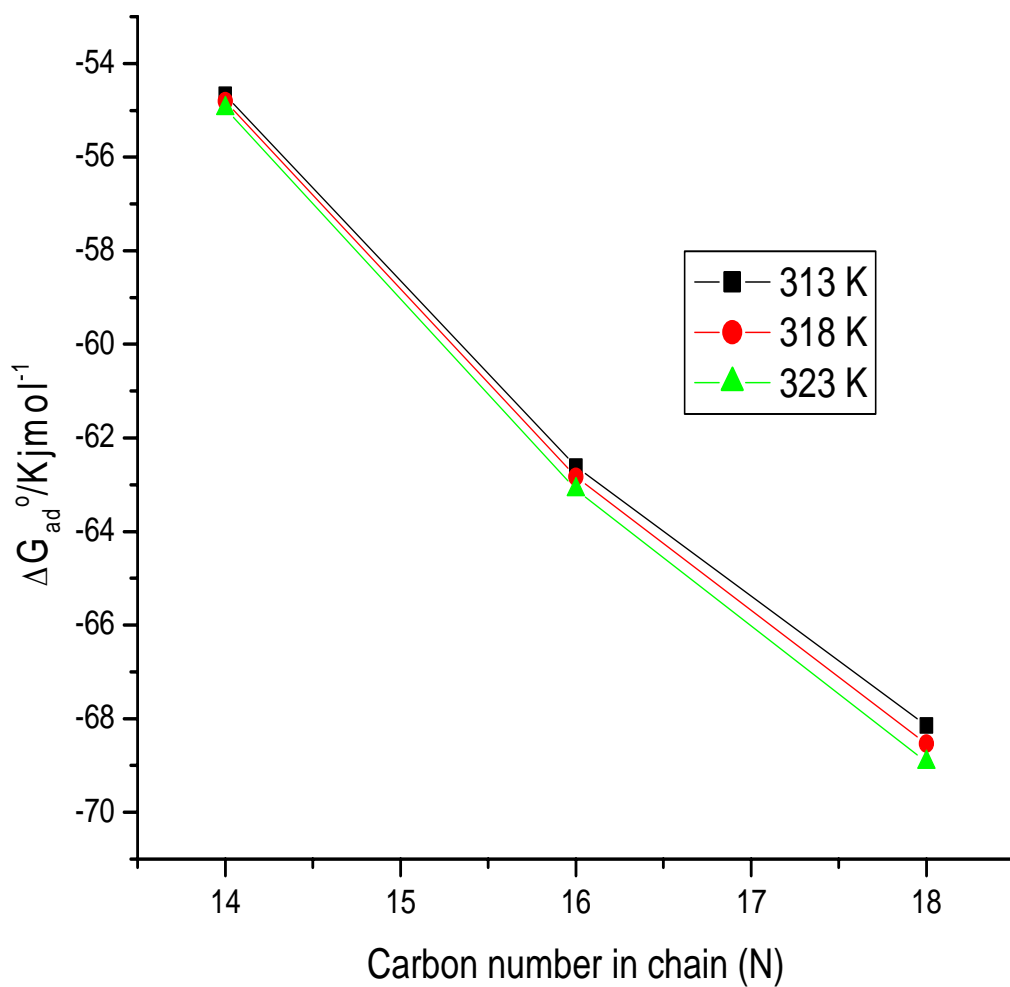


Figure 3.28 Effect of chain length on $\Delta G_{\text{ad}}^{\circ}$ of TTAB, CTAB and OTAB ($\Delta G_{\text{ad}2}^{\circ}$ of OTAB is used here).

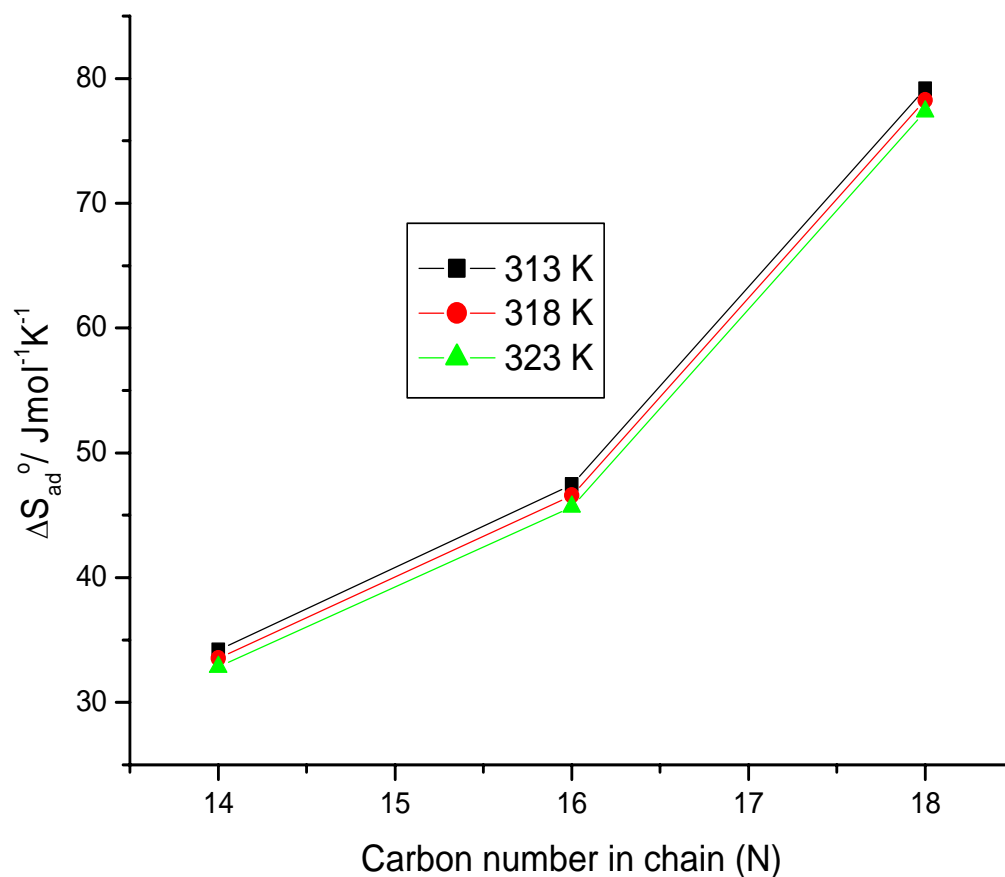


Figure 3.29 Effect of chain length on $\Delta S_{\text{ad}}^{\circ}$ of TTAB, CTAB and OTAB ($\Delta S_{\text{ad}2}^{\circ}$ of OTAB is used here)

The enthalpy -entropy compensation plots for both surface adsorption and bulk micellization of the surfactants are shown in figure 3.30-3.33. For each case a linear relationship was observed. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy nearly constant. Previous studies have shown such behaviors for aqueous solutions of ionic surfactants and smaller molecules [91, 98-100]

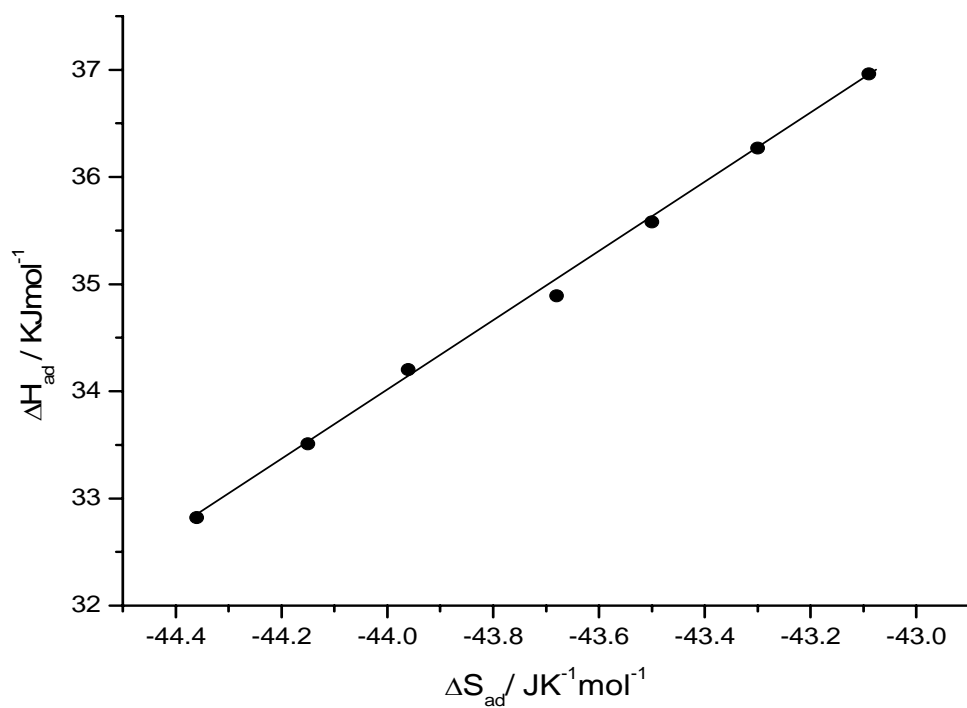


Figure 3.30 Enthalpy-Entropy compensation plots for adsorption of TTAB in pure water.

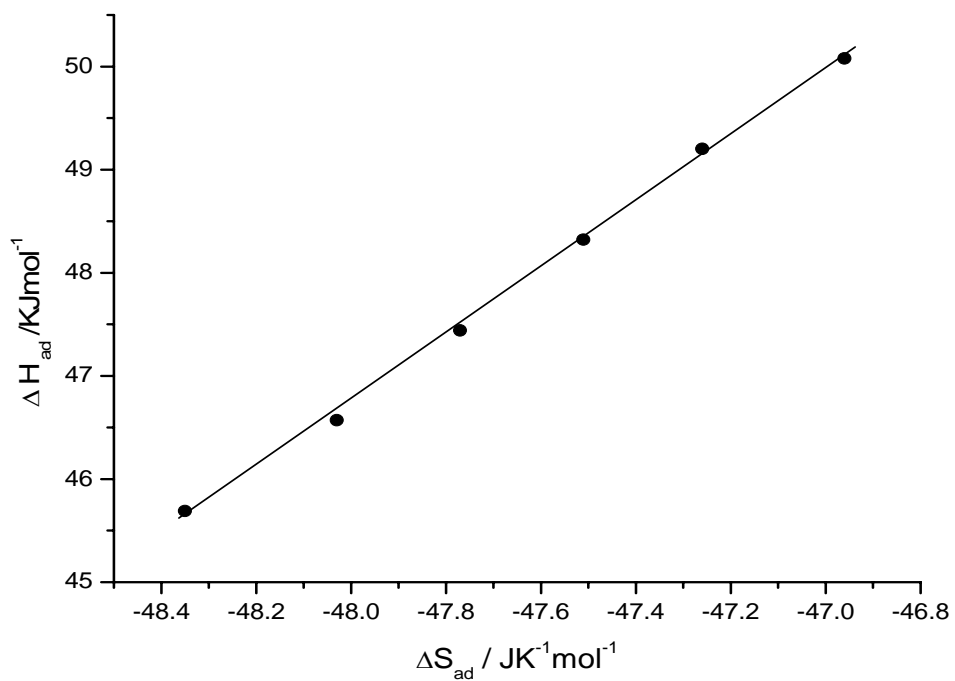


Figure 3.31 Enthalpy-Entropy compensation plots for adsorption of CTAB in pure water.

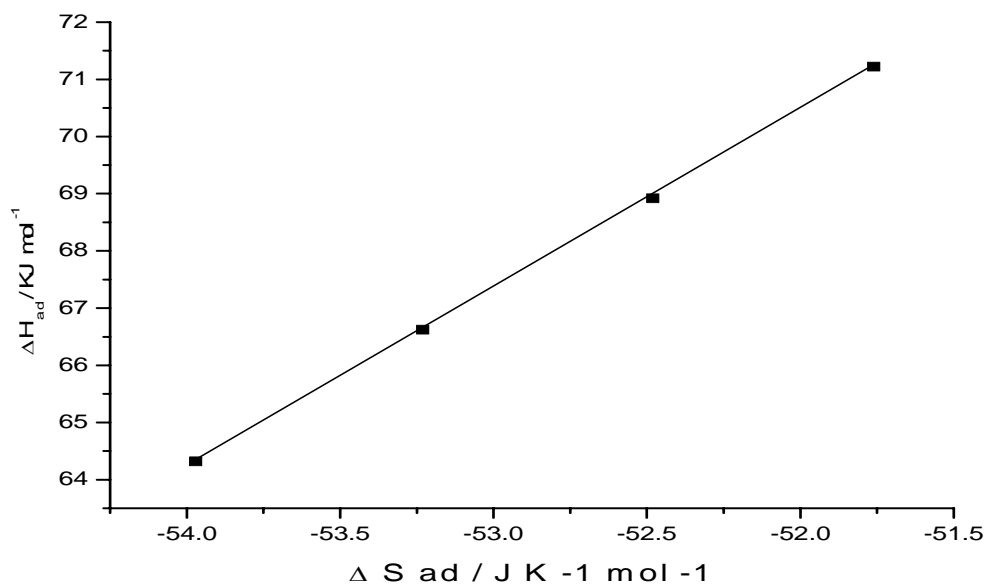


Figure 3.32 Enthalpy-Entropy compensation plots for adsorption of OTAB in pure water (for CMC_1)

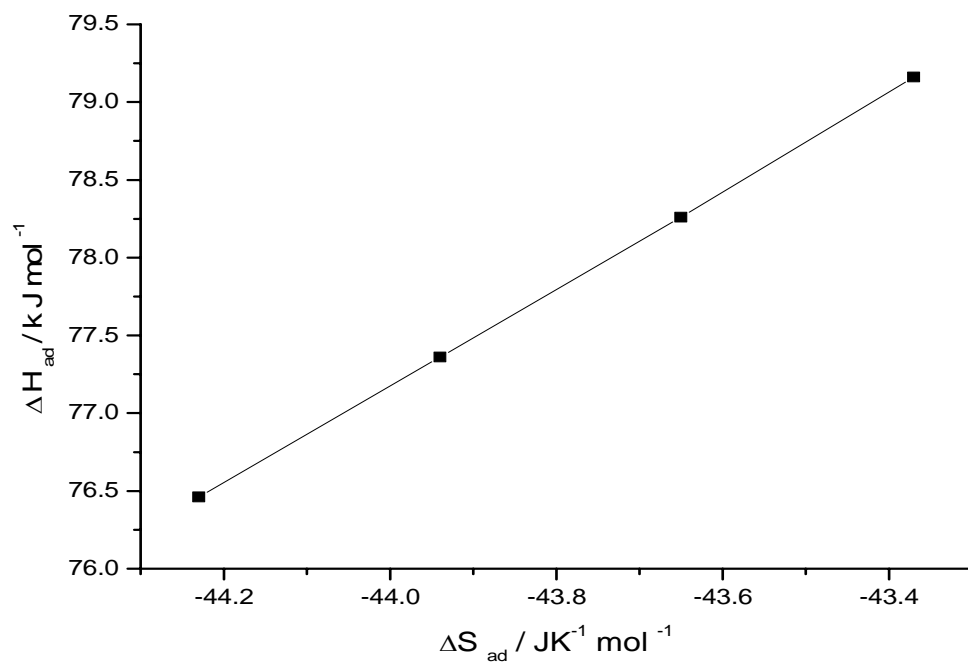


Figure 3.33 Enthalpy-Entropy compensation plots for adsorption of OTAB in pure water (for CMC_2)

3.7 CMC OF SURFACTANTS AND THEIR BULK BEHAVIORS IN 0.01 M AQUEOUS NaCl SOLUTION

Some of the previous studies showed that the increase of the concentration of an electrolyte, with a common ion to the ionic surfactant, causes decrease of the CMC [102-106]. This is attributed due to screening of surface charge by the excess counter ion. Similar reason is for the CMC of TTAB, CTAB and OTAB in presence of NaCl which is significantly lower than the CMC of the respective surfactants in pure water. Because the excess counter ions neutralize the charge of micelle and reduce the repulsive force between the head groups. But in presence of NaCl the CMC of TTAB and CTAB increases and then gradually decreases with increasing temperature, showing a bell shaped curve. This initial increase is due to the thermal solubility of the surfactant monomers which disfavors micellization and then after a certain temperature the decrease of CMC is because of dehydration of the head groups which dominate over the solubility effect and thus favors the micellization. In fact these two effects oppose each other depending on a number of factors [41] and their relative dominating ability determines whether an increase of temperature will cause increase or decrease of CMC. For OTAB increases of CMC were observed for increase of temperature, for the stated experimental range, and we could not study its CMC above the stated temperature range due to chance of solvent evaporation.

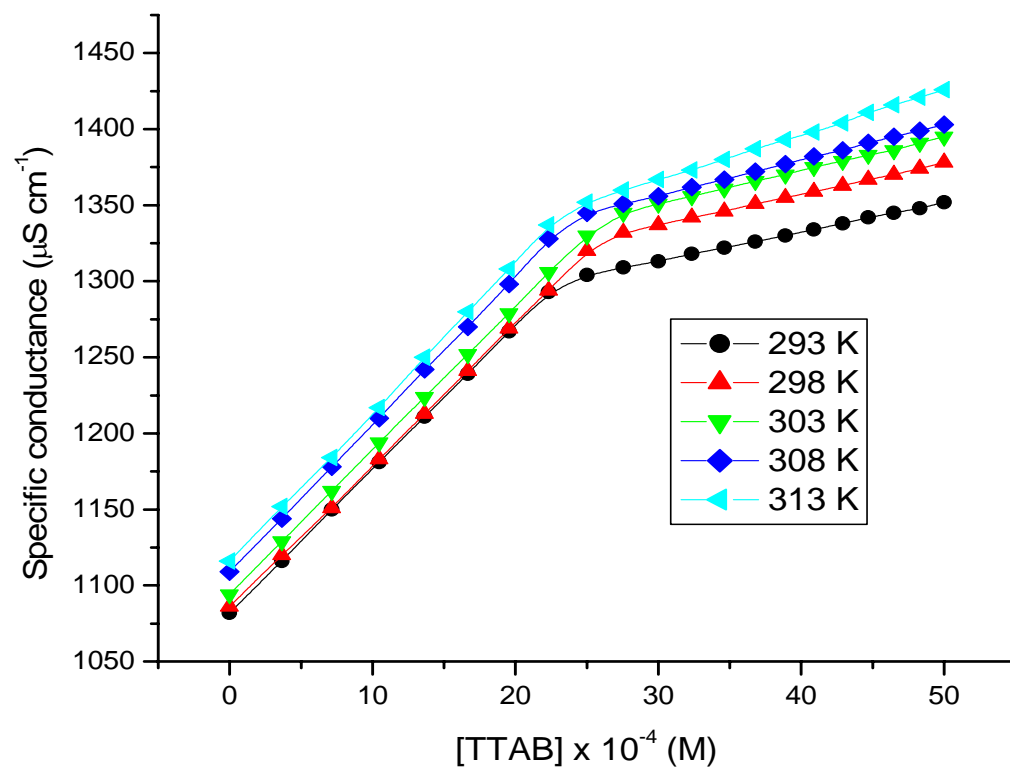


Figure 3.34 Specific conductances (κ) vs. concentration of TTAB at different temperatures in 0.01M aqueous NaCl solution

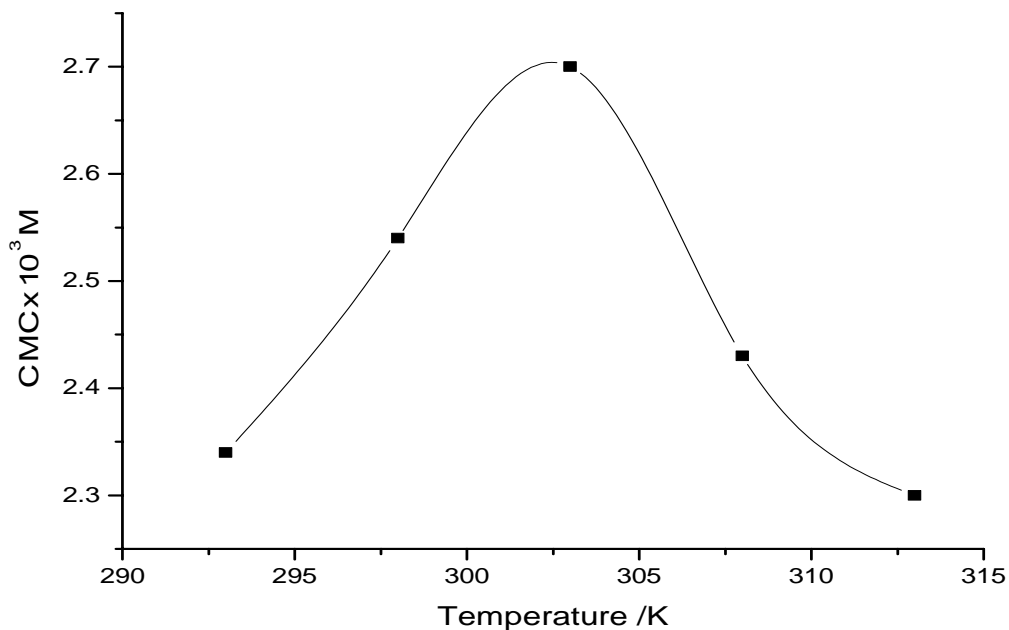


Figure 3.35 Variation of CMC of TTAB in presence of 0.01M NaCl at different temperatures.

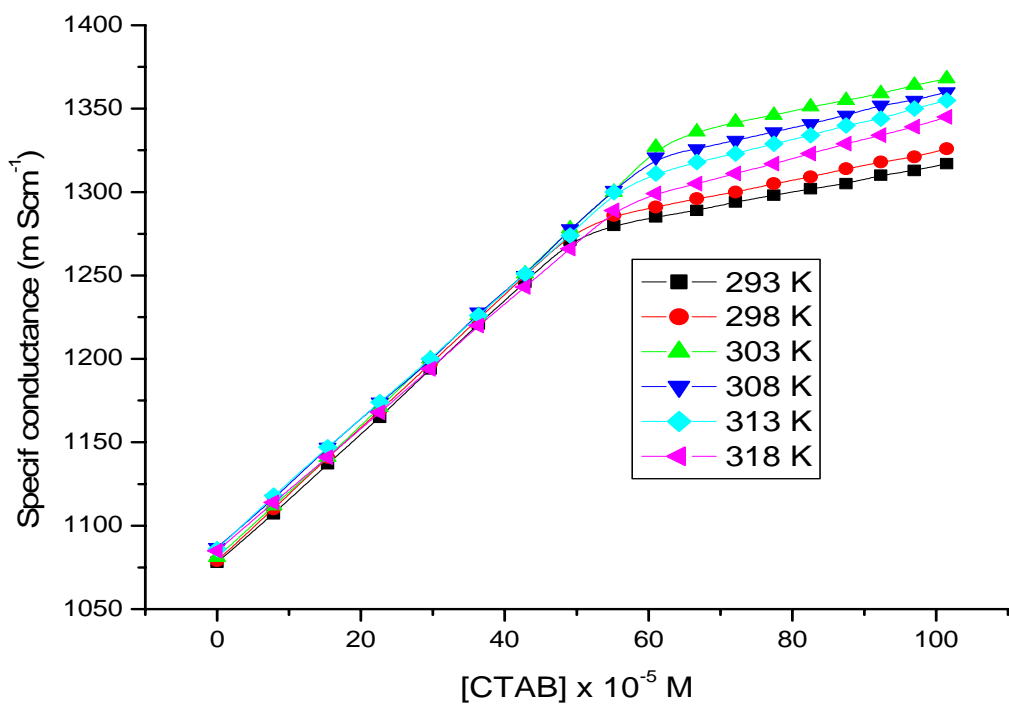


Figure 3.36 Specific conductances (κ) vs. concentration of CTAB at different temperatures in 0.01M aqueous NaCl solution.

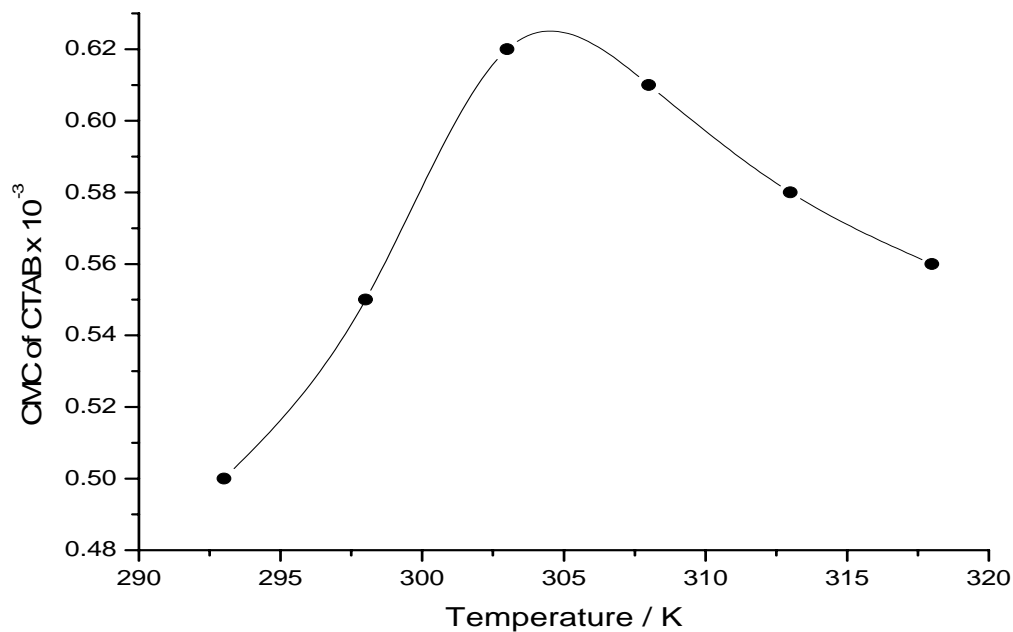


Figure 3.37 Variation of CMC of TTAB in presence of 0.01M NaCl at different temperatures.

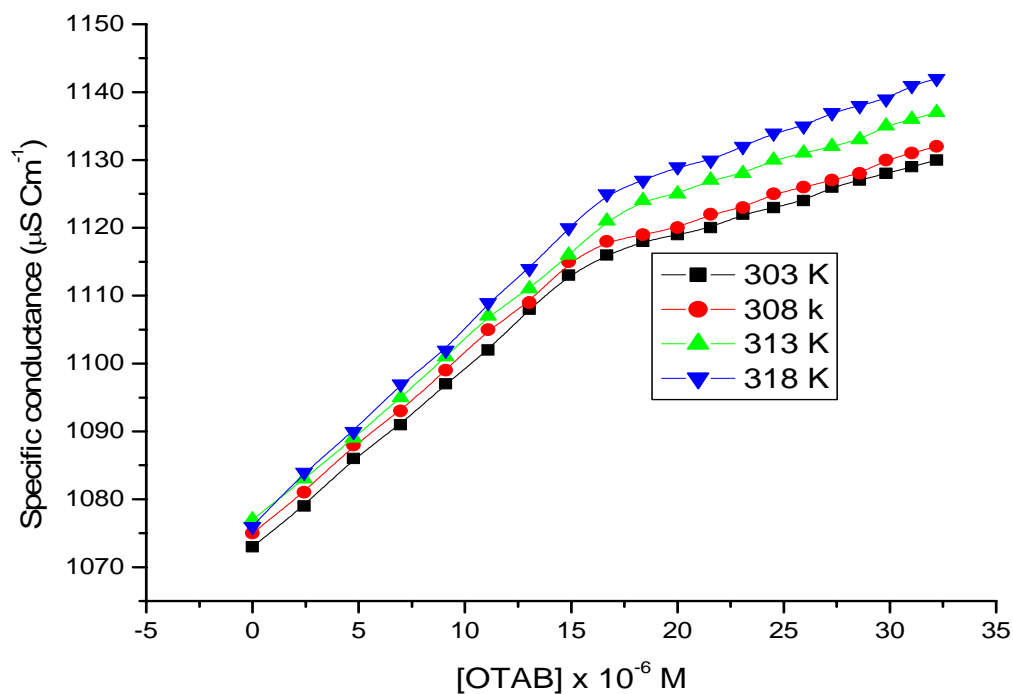


Figure 3.38 Specific conductances (κ) vs. concentration of OTAB at different temperatures in 0.01M aqueous NaCl solution (for CMC₁)

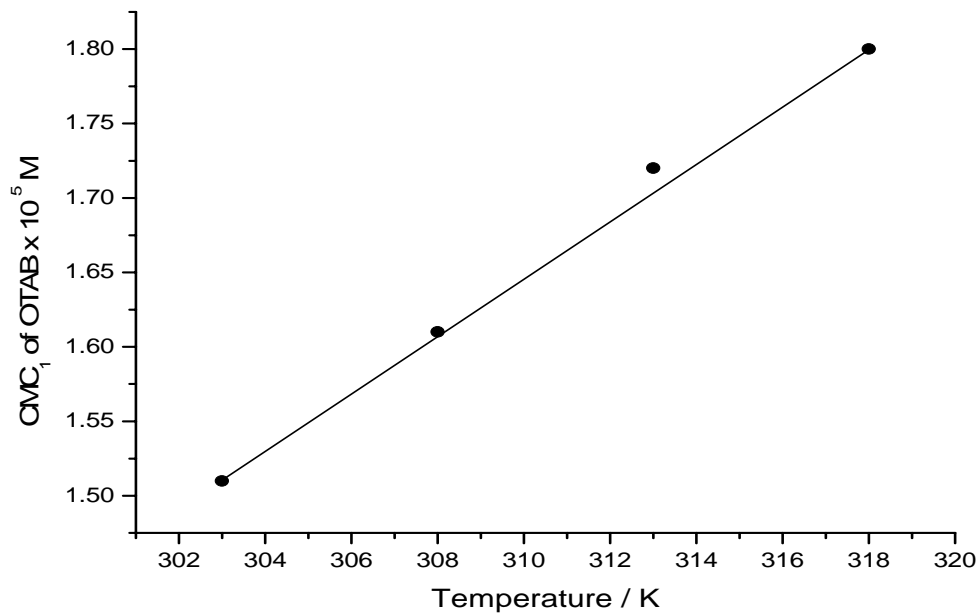


Figure 3.39 Variation of CMC of OTAB in presence of 0.01M NaCl at different temperatures (for CMC₁).

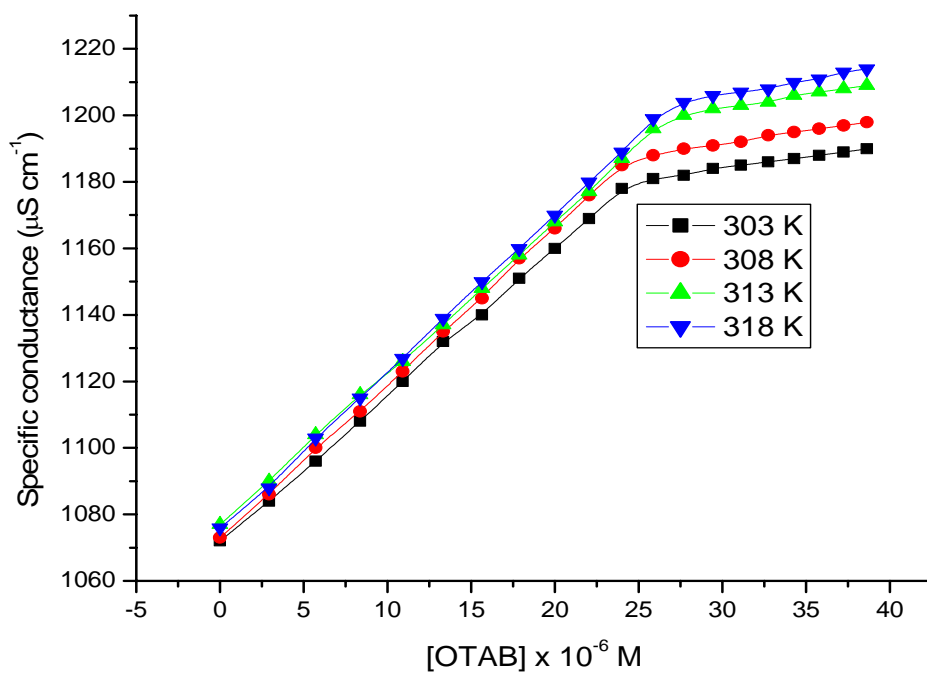


Figure 3.40 Specific conductances (κ) vs. concentration of OTAB at different temperatures in 0.01M aqueous NaCl solution (for CMC₁)

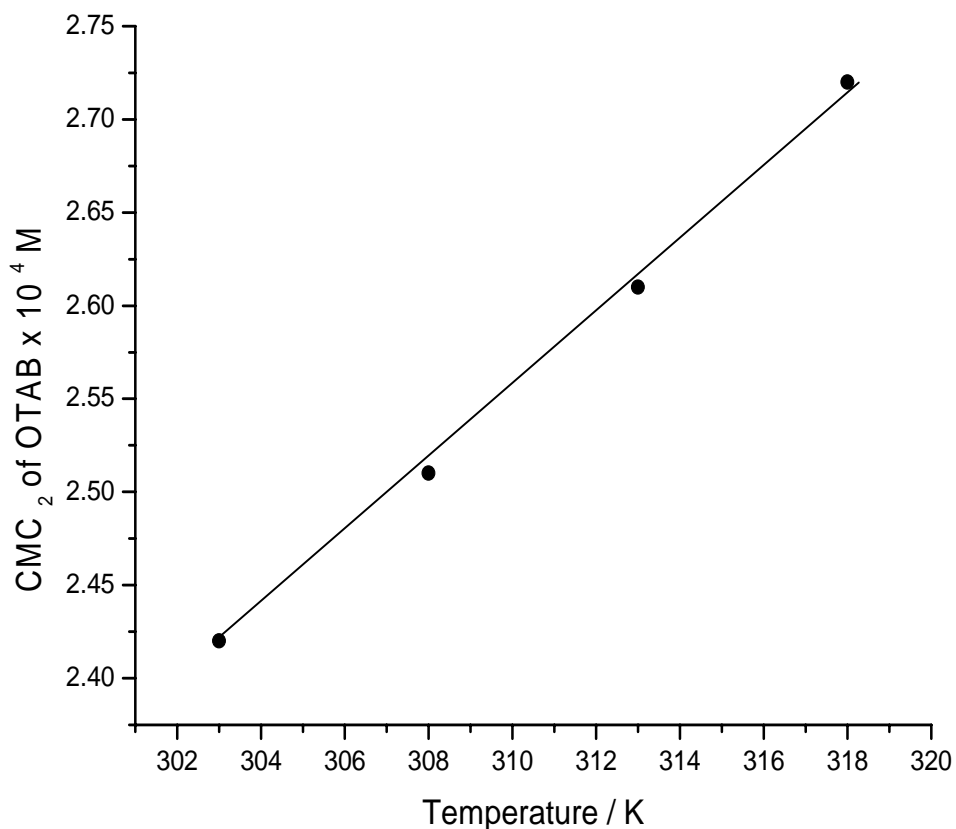


Figure 3.41 Variation of CMC of OTAB in presence of 0.01M NaCl at different temperatures (for CMC₂).

It has been reported that the presence of electrolytes increases the aggregation number which favors micellization [45]. This increase of aggregation number increases the charge density which causes an increase in the degree of dissociation of the micelles. So presence of NaCl gives a higher β value compared to the β value in pure water. After a certain temperature a sharp decrease in the β value is due to the dehydration of the head group as we know that normally the micellar head group region is associated with a certain number of water of hydration [107].

Table 3.6 CMC and the fraction of Counter Ion Binding (β) for TTAB, CTAB and OTAB at Different Temperatures, in presence of 0.01M NaCl .

T/K	TTAB		CTAB		OTAB	
	$10^3 \text{ CMC} / \text{M}$	β	$10^3 \text{ CMC} / \text{M}$	β	$10^5 \text{ CMC}_1 / \text{M}$ ($10^4 \text{ CMC}_2 / \text{M}$)	β_1 (β_2)
293	2.34	0.80	0.50	0.80	--	--
298	2.54	0.78	0.55	0.79	--	--
303	2.70	0.77	0.62	0.78	1.51 (2.42)	0.66 (0.84)
308	2.43	0.76	0.60	0.75	1.61 (2.51)	0.65 (0.83)
313	2.30	0.70	0.58	0.72	1.72 (2.61)	.64 (0.82)
318	--	--	0.56	0.69	1.80 (2.72)	0.63 (0.81)

3.8 EMPIRICAL REATION FOR CRITICAL MICELLE CONCENTRATION OF THE SURFACTANTS, IN PRESENCE OF 0.01 M NaCl.

Figure 3.42 shows the Log CMC vs n (number of carbon in the alkyl chain of the surfactants) plots at 303 K- 313K temperature. No linear relationship between the log CMC and n were obtained, as predicted from the Stauff-Klevens empirical rule for the cationic surfactants which is: $\log \text{ CMC} = A - Bn$ [3]. It shows that, in the presence of neutral salts, cationic surfactants' micellization process does not follow any empirical relation, which is attributed to the enhanced thermal solubility of the longer chain surfactants. Because Cl^- ion has a preferential tendency to be negatively adsorbed at air water interface and its presence increase the concentration of free water molecules in

the bulk [108], which facilitates enhanced solubility of less soluble, larger chain, surfactants. As a result counter ion effect is less on reduction of the CMC the larger chain surfactant and it needs higher number of counter ion bindings for the micellization.

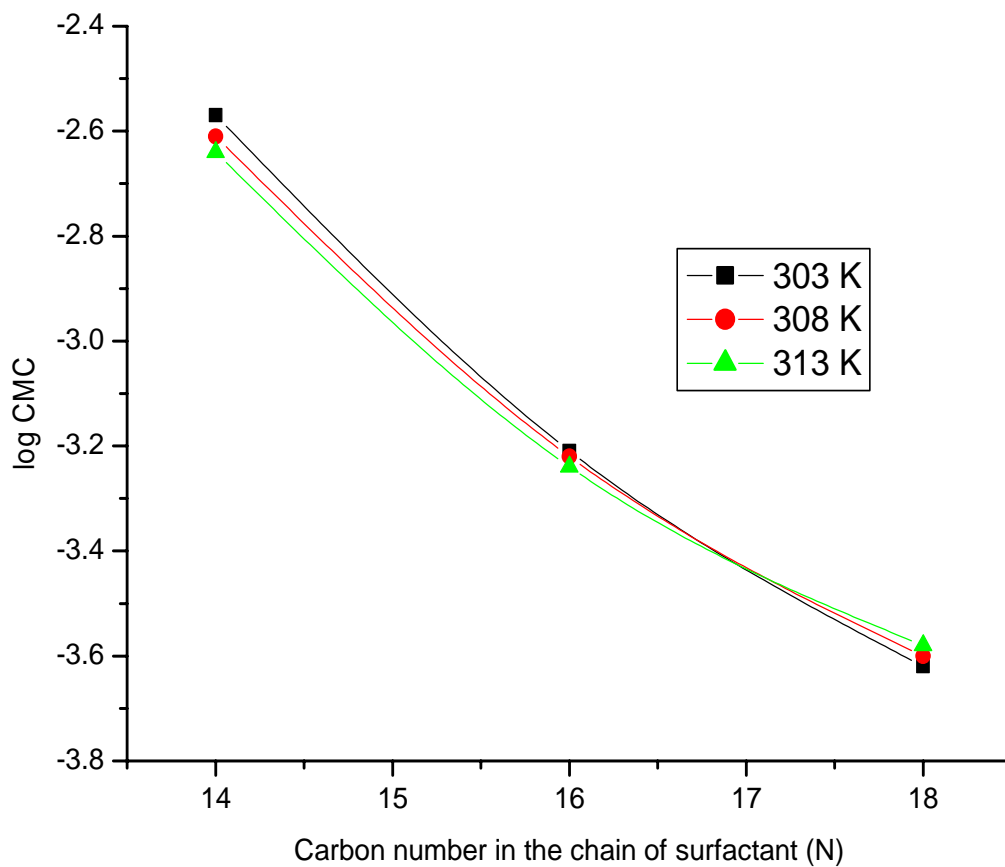


Figure 3.42 Effect of chain length on CMC of *N*-alkyltrimethylammoniumbromide surfactants (CMC_2 is used)

3.9 THERMODYNAMIC PARAMETRS FOR MICELLIZATIONS OF THE SURFACTANTS IN 0.01M aq. NaCl SOLUTION.

The free energy changes (ΔG_m°) of the surfactants were calculated from the following expression:

$$\Delta G_m^\circ = RT [\ln X_{cmc} + (1-\alpha) \ln (X_{cmc} + X_S)] \dots\dots\dots(7)$$

Here X_{cmc} is mole fraction of the surfactant whereas X_S is the mole fraction of NaCl. At a certain temperature the ΔG_m° values of each of the surfactants in NaCl solution were found to be more negative than the ΔG_m° values of the respective surfactants in pure water which indicates greater spontaneity of their micellization process, favored by greater number of counter ions. The changes of ΔG_m° values of each of the surfactants in NaCl, at the experimental temperature ranges, were found to follow the same pattern as for their changes of ΔG_m° values in pure water.

The ΔG_m° values for micellization of each of the surfactants in NaCl solution were found to be less negative than their ΔH_m° values in pure water, at the respective temperatures. This can be attributed to the hydration (weakly chaotropic) effect of the counter ion Cl^- . The hydration of Cl^- causes destruction of structure of free water which causes greater hydration of the surfactants [45] and causes greater iceberg (associated water molecules around the hydrophobic tail). As a result more kinetic energy is needed to break this iceberg. The ΔS_m° values in presence of NaCl were found to be greater than the ΔS_m° value in pure water which may be also attributed to the greater destruction of structure of free water, caused by the hydration of Cl^- ions. Nuclear magnetic resonance

studies show that water molecules adjacent to a chaotropic ion trip up more readily than those in the bulk solution [109].

Initially, at 293K, $\Delta G_{\text{ad}}^{\circ}$ value in NaCl solution was found to be more negative than the $\Delta G_{\text{ad}}^{\circ}$ value in NaCl solution but at higher temperatures the $\Delta G_{\text{ad}}^{\circ}$ values are found to be less negative than the $\Delta G_{\text{ad}}^{\circ}$ value in pure water which indicates that at higher temperature the adsorption of TTAB in presence of NaCl solution becomes less spontaneous than its adsorption in pure water. Less values of $\Delta H_{\text{ad}}^{\circ}$ in NaCl solution compared to the $\Delta H_{\text{ad}}^{\circ}$ values in pure water is also attributed to the greater hydration of TTAB in presence of NaCl solution. The changing pattern of $\Delta G_{\text{m}}^{\circ}$, $\Delta H_{\text{m}}^{\circ}$, $\Delta S_{\text{m}}^{\circ}$, G_{ad}° , $\Delta H_{\text{ad}}^{\circ}$ and $\Delta S_{\text{ad}}^{\circ}$ with increase of temperature is same as the changing pattern of these parameters in pure water. The $\Delta S_{\text{ad}}^{\circ}$ value is more positive in NaCl solution compared to water is for the destruction of iceberg (highly ordered H-bonded water molecules around the hydrophobic tail).

Table 3.7 Thermodynamic parameters of micellization for TTAB, CTAB and OTAB at various temperatures, in presence of 0.01M NaCl.

T/K	TTAB			CTAB			OTAB		
	ΔG_m^o	ΔS_m^o	ΔH_m^o	ΔG_m^o	ΔS_m^o	ΔH_m^o	ΔG_{m1}^o	ΔS_{m1}^o	ΔH_{m1}^o
							(ΔG_{m2}^o)	(ΔS_{m2}^o)	(ΔH_{m2}^o)
293	-40.86	39.66	-29.24	-45.02	45.43	-31.71	---	---	---
298	-41.05	38.69	-29.52	-45.26	44.98	-31.85	---	---	---
303	-41.24	37.72	-29.81	-45.47	44.53	-31.98	-52.49 (-49.34)	87.77 (93.86)	-25.90 (-20.90)
308	-41.43	36.75	-30.11	-45.69	44.08	-32.11	-52.95 (-49.81)	87.67 (93.46)	-25.93 (-21.02)
313	-41.61	35.78	-30.41	-45.92	43.63	-32.26	-53.36 (-50.27)	87.57 (93.06)	-25.96 (-21.15)
318	---	---	---	-46.12	43.18	-32.40	-53.82 (-50.74)	87.47 (92.66)	-25.99 (-21.27)

Here the Energetic Parameters are expressed in KJ mol⁻¹ for ΔG_m^o and ΔH_m^o and J K⁻¹ mol⁻¹ for ΔS_m^o . Subscript 1 and 2 to the column title refer to micellization processes 1 and 2 respectively for OTAB.

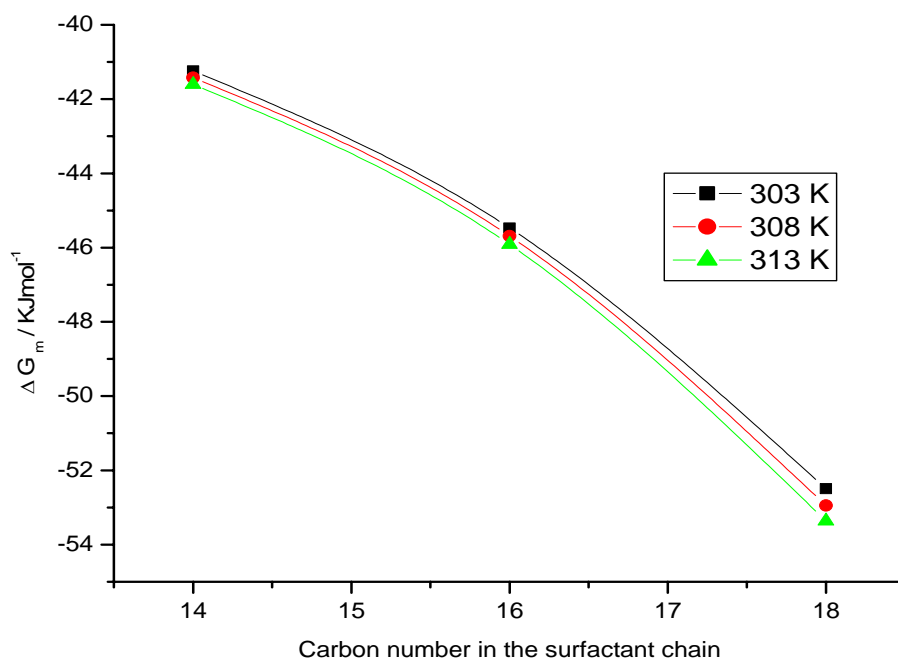


Figure 3.43 Effect of chain length on ΔG_m^0 of TTAB, CTAB and OTAB (ΔG_{m1}^0 of OTAB is used here).

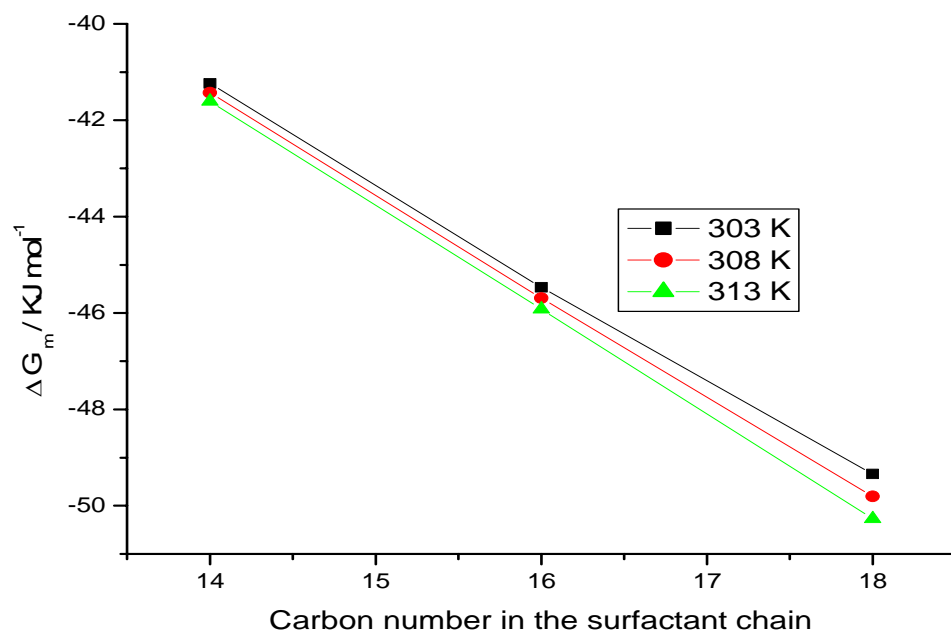


Figure 3.44 Effect of chain length on ΔG_m° of TTAB, CTAB and OTAB (ΔG_{m2}° of OTAB is used here).

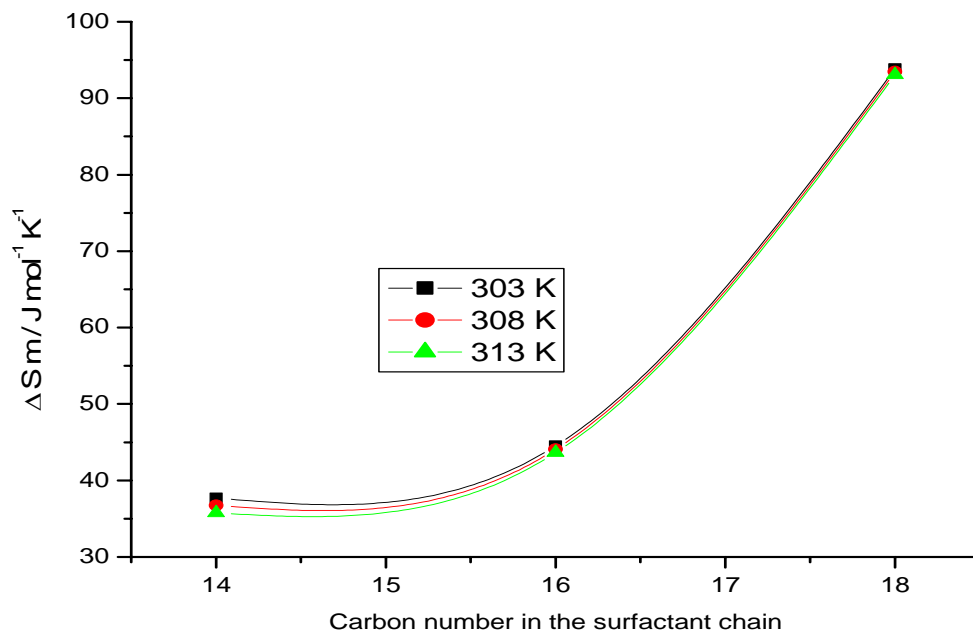


Figure 3.45 Effect of chain length on ΔS_m° of TTAB, CTAB and OTAB (ΔS_{m2}° of OTAB is used here).

In presence of NaCl, ΔS_m° is found to be more positive and ΔH_m° is found to be less negative compared to the respective parameters in pure water. These result in more negative ΔG_m° values in aq. NaCl compared to the ΔG_m° values in pure water which is attributed to change in degree of non polarity of the interior of the micelle with change in the polarity of the hydrophilic head because of penetration of water, surrounding the counter ion, in to the micelle, at least in the vicinity of the first five or six carbon atoms adjacent to the hydrophilic head [4, 38-39, 70]. Fig 3.44 shows that linear increase of ΔG_m° value (more negative) with the number of carbon atoms in the alkyl chain. Similar trend is also observed in fig 3.43. But here no linear relation is obtained because although the first micellization of OTAB is by smaller aggregation number yet the

micellization is feasible by the more negative ΔG_m° values. In fig 3.45 more positive ΔS_m° values were observed for the larger alkyl chain length which is due to greater degree of disruption of the structured water layer around the larger chain. The enthalpy –entropy compensation plots for bulk micellization of TTAB in presence of 0.01M NaCl solutions are shown in figures 3.46-3.48. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy nearly constant.

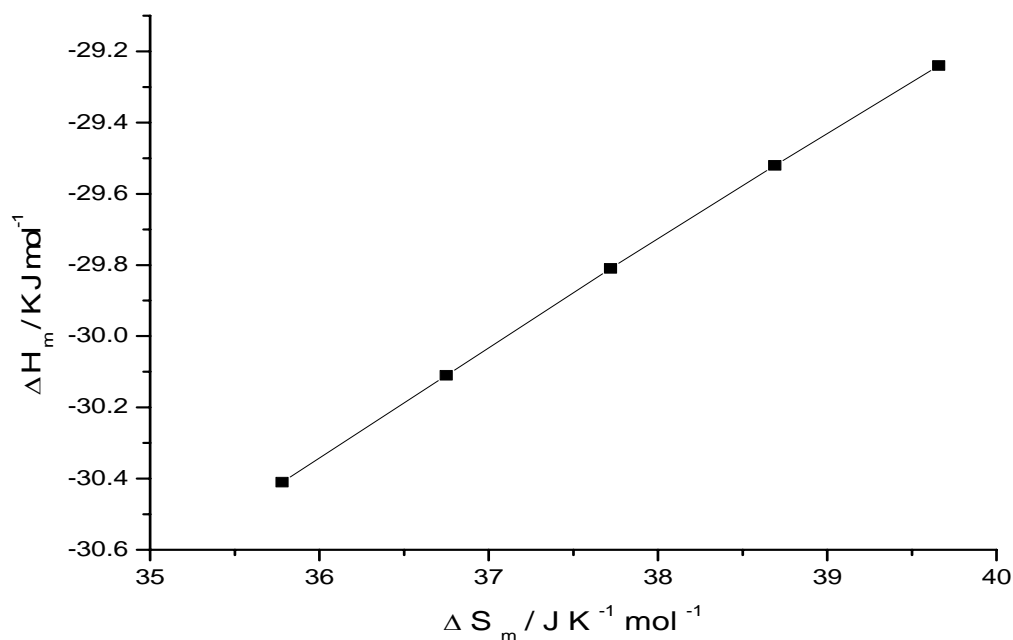


Figure 3.46 Enthalpy-Entropy compensation plots for micellization of TTAB in 0.01 M NaCl.

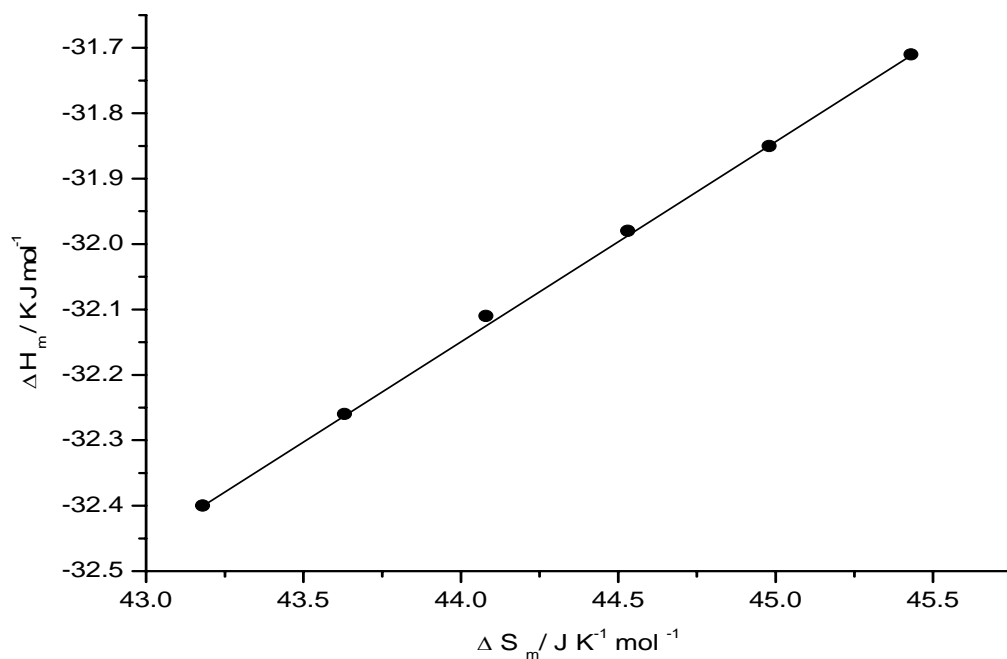


Figure 3.47 Enthalpy-Entropy compensation plots for micellization of CTAB in 0.01 M NaCl.

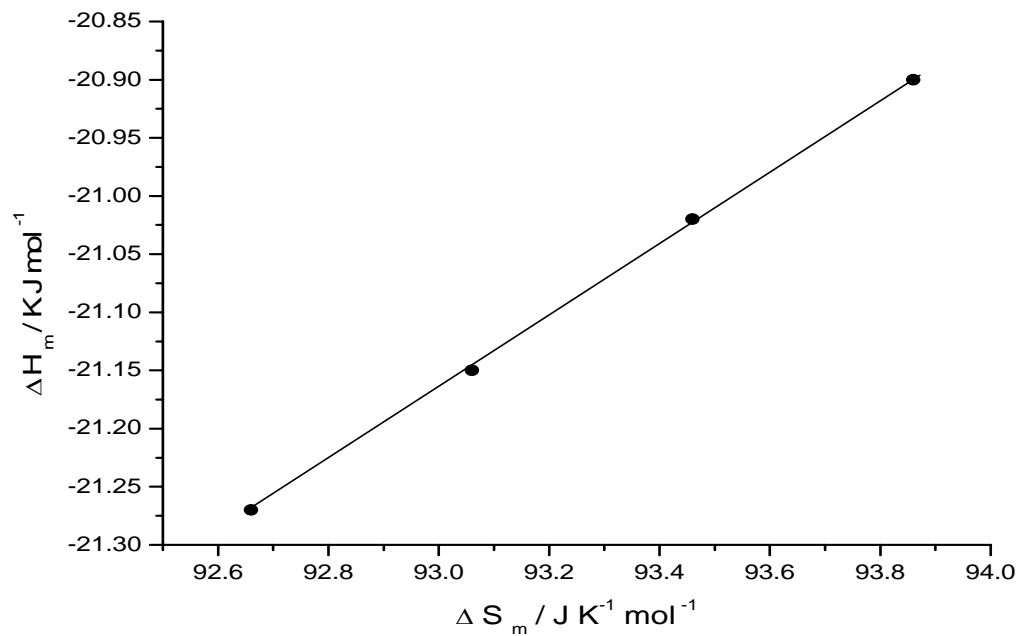


Figure 3.48 Enthalpy-Entropy compensation plots for micellization of OTAB in 0.01 M NaCl (for CMC₂).

3.10 ADSORPTION BEHAVIOR OF THE SURFACTANTS IN 0.01 M NaCl SOLUTION

Figures 3.49 to 3.52 show the surface tension (γ) as a function of logarithmic concentration ($\log_{10}C$) of TTAB, CTAB and OTAB in 0.01 M NaCl solution at different temperatures. A gradual decrease in the surface tension with increasing the surfactant concentration is observed due to spontaneous adsorption of the surfactant molecules from the bulk to the air-water interface. After a certain concentration a sharp break point followed by a plateau region of constant γ values are obtained because of the saturation of the solution surface by the adsorbed molecules. At a certain temperature CMC is determined from the intersection point of this type of γ versus $\log_{10}C$ plot.

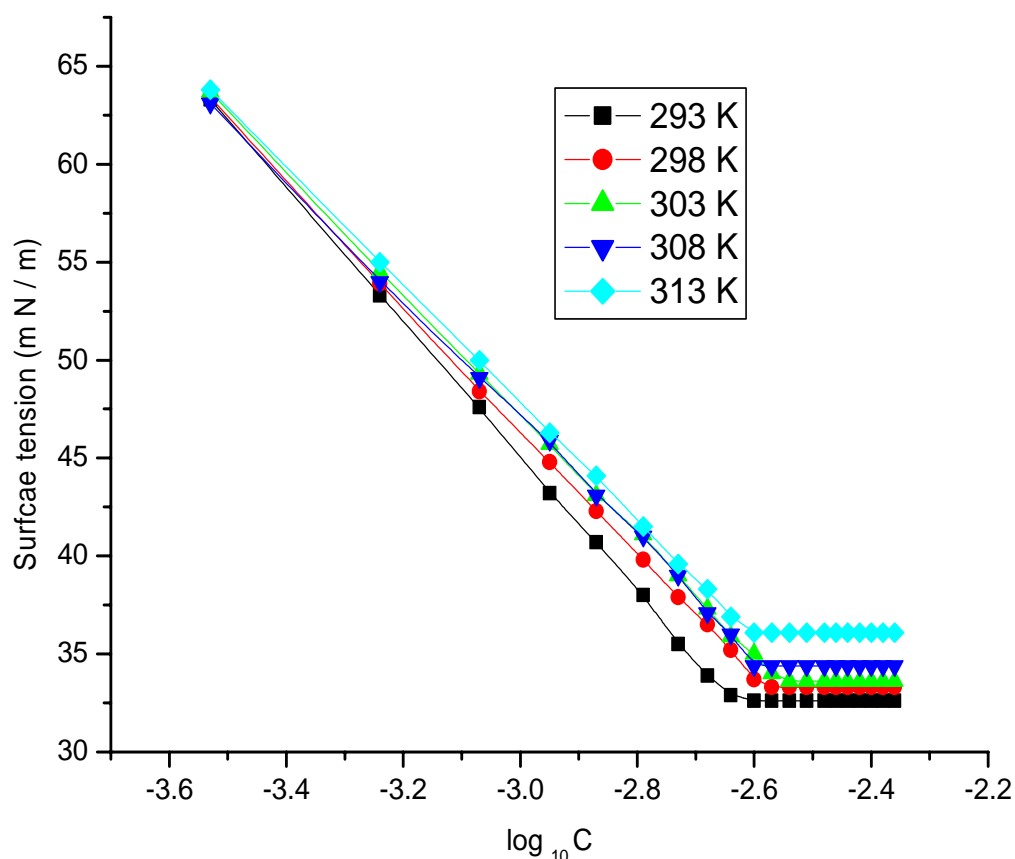


Figure 3.49 Surface tension vs. conc. of TTAB plots in 0.01 M aq. NaCl solution, at different temperatures.

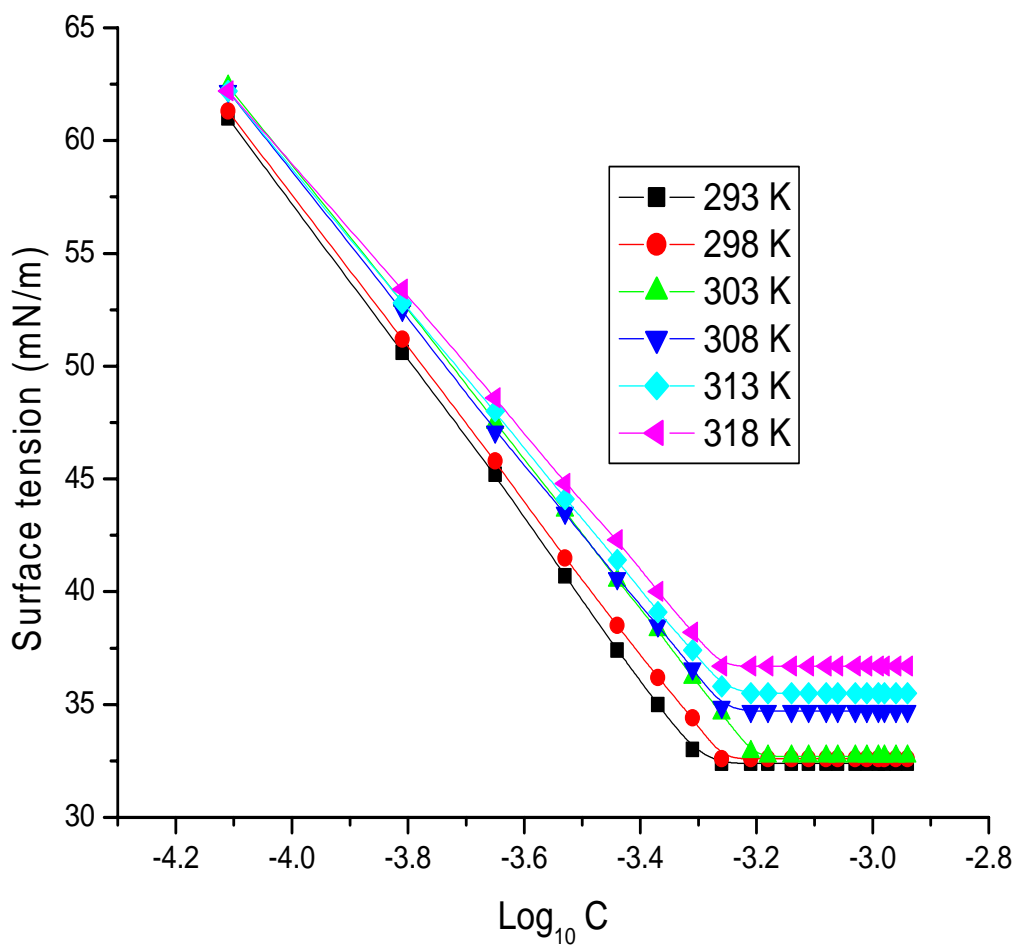


Figure 3.50 Surface tension vs. conc. of CTAB plots in 0.01 M aq. NaCl solution, at different temperature.

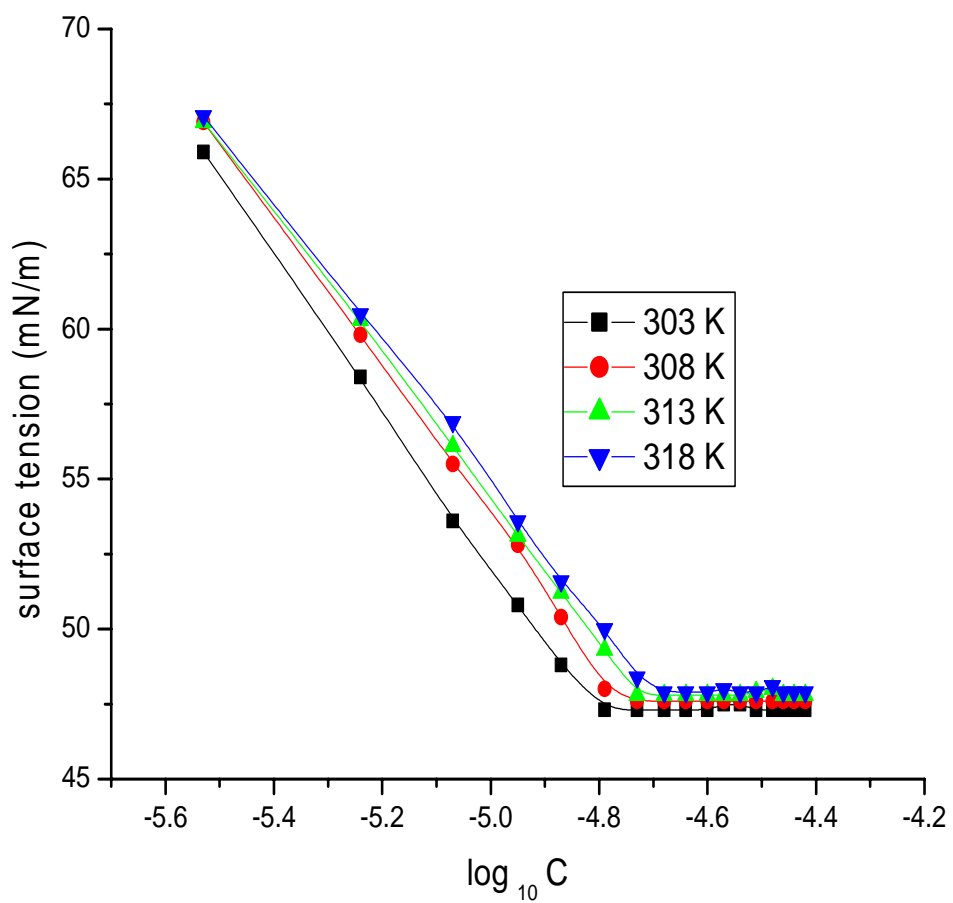


Figure 3.51 Surface tension vs. conc. of OTAB plots in 0.01 M aq. NaCl solution, at different temperature (CMC_1).

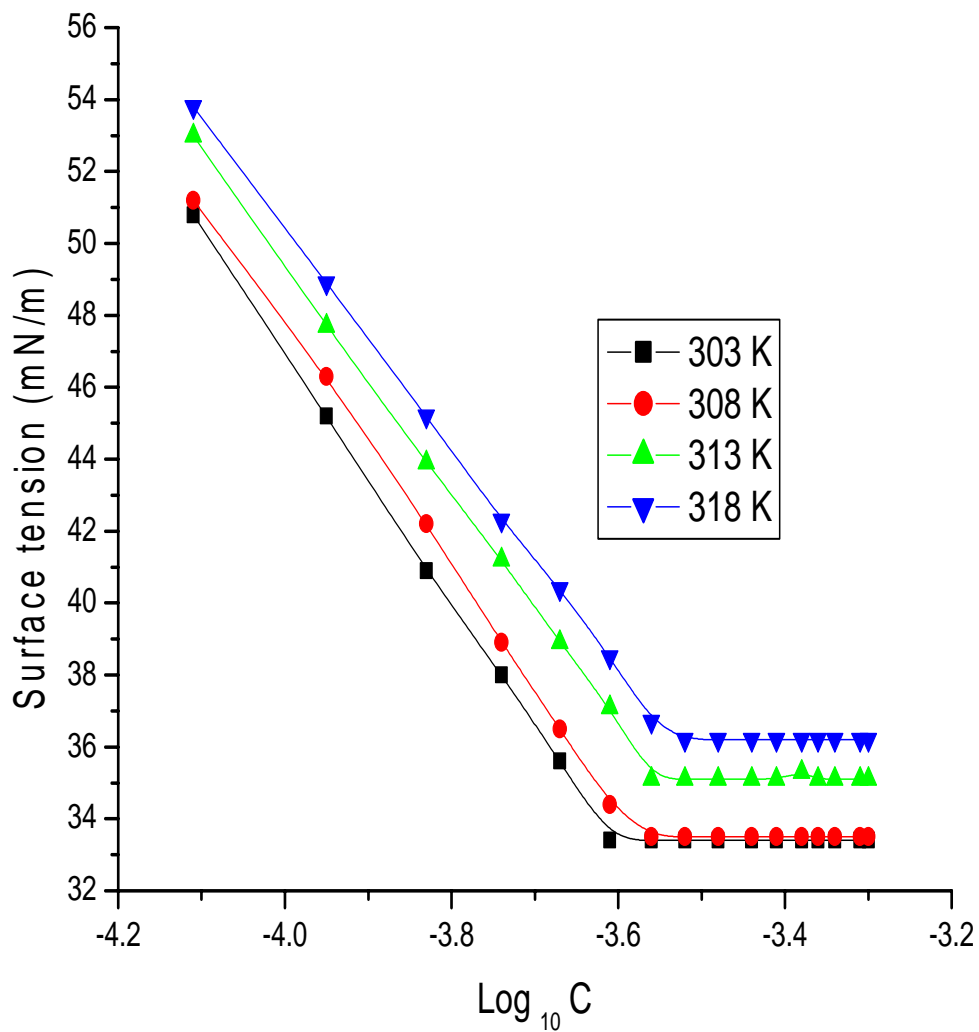


Figure 3.52 Surface tension vs. conc. of OTAB plots in 0.01 M aq. NaCl solution, at different temperature (CMC₂).

Figure 3.53 shows the Γ_{\max} of TTAB, CTAB and OTAB at different temperatures in pure water which reveals that the Γ value decreases gradually with increasing temperature.

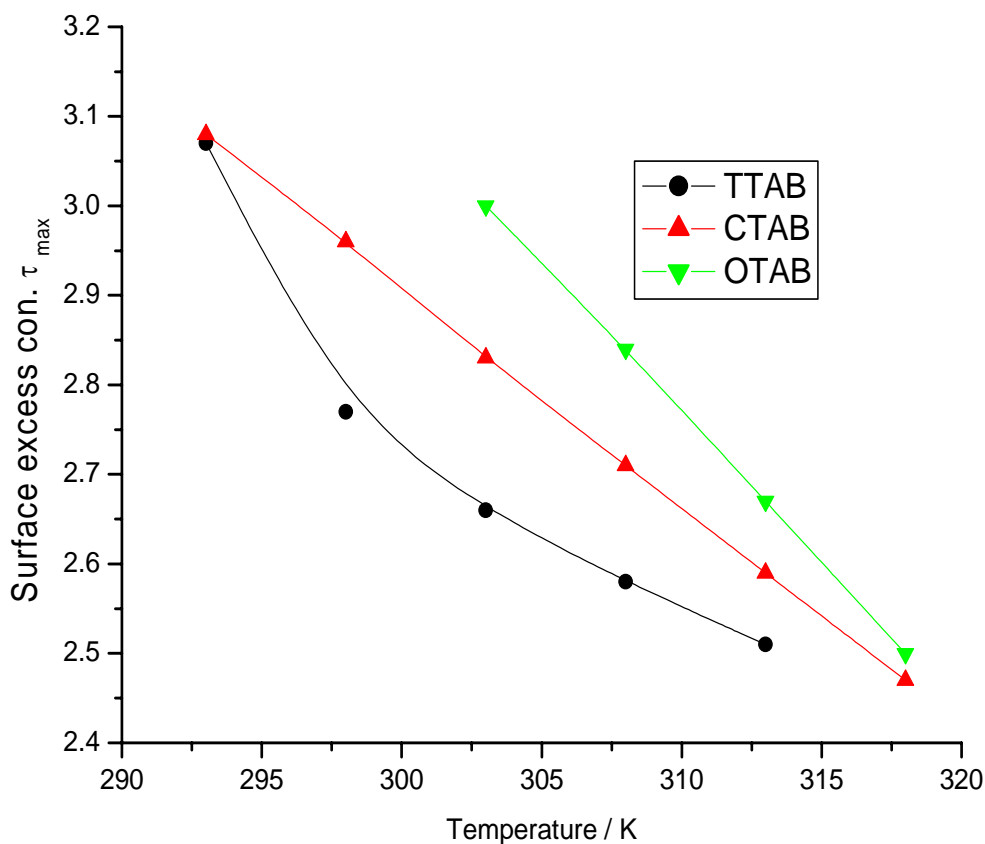


Figure 3.53 Surface excess concentration (Γ_m) of TTAB, CTAB and OTAB at different temperatures, in 0.01 M aq. NaCl solution. (For OTAB CMC₂ used).

The higher Γ value at the initial temperature is due to dehydration of the hydrophilic head group since the size of the head group is reduced upon dehydration. As a result a closer molecular packing occurs in the adsorbed monolayer [102]. But increase in temperature causes an increase in the kinetic energy, thermal motion and chain flexibility that consequence disorganization of the adsorbed molecules at the air-water interface [94, 96]. Increase in temperature makes the Vander Waals interaction between the alkyl chains more unfavorable. Thus the closer molecular packing of the monolayer at the air-water interface is hindered by the perturbation of the adsorbed

molecules. Due to increase of temperature this factor dominates over the dehydration effect and consequently the Γ decreases gradually.

From figure 3.53 it has been observed that at a certain temperature the surfactant with larger chain length shows greater surface excess concentration, Γ value, which may be due to greater degree of binding by the surfactant molecules with larger chain length [3]. Greater surface excess concentration, Γ value, were also observed for the second micellization of OTAB compared to its first micellization process since second micellization involves greater concentration of the surfactant which causes greater number of counter ion binding (β). For solutions of the ionic surfactants, an electrostatic surface potential is progressively created during the adsorption process which acts as a barrier to the adsorption of additional molecules as they migrate from the bulk of the solution to the air- water interface. Due to addition of electrolyte to the surfactant solution electrostatic screening for the surface potential occurs at the air-water interface [110] which causes substantial reduction of the obstruction for further adsorption of the surfactant molecules. As a result each Γ values at a definite temperature of the adsorbed molecules in presence of NaCl in found to be greater than the corresponding Γ value in pure water.

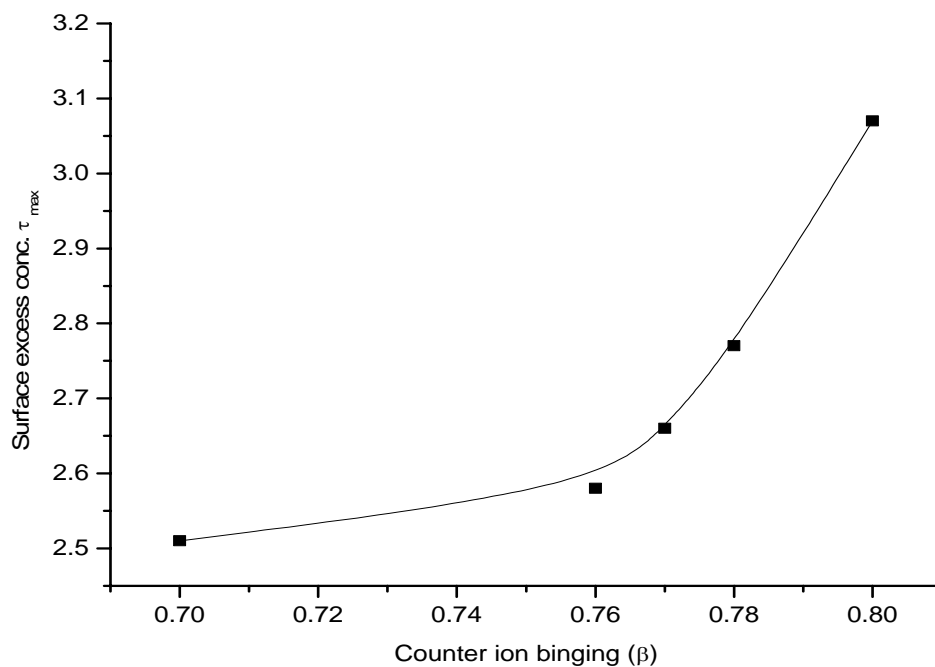


Figure 3.54 Relation between the counter ion binding and Γ value of TTAB in 0.01 M aq. NaCl solution.

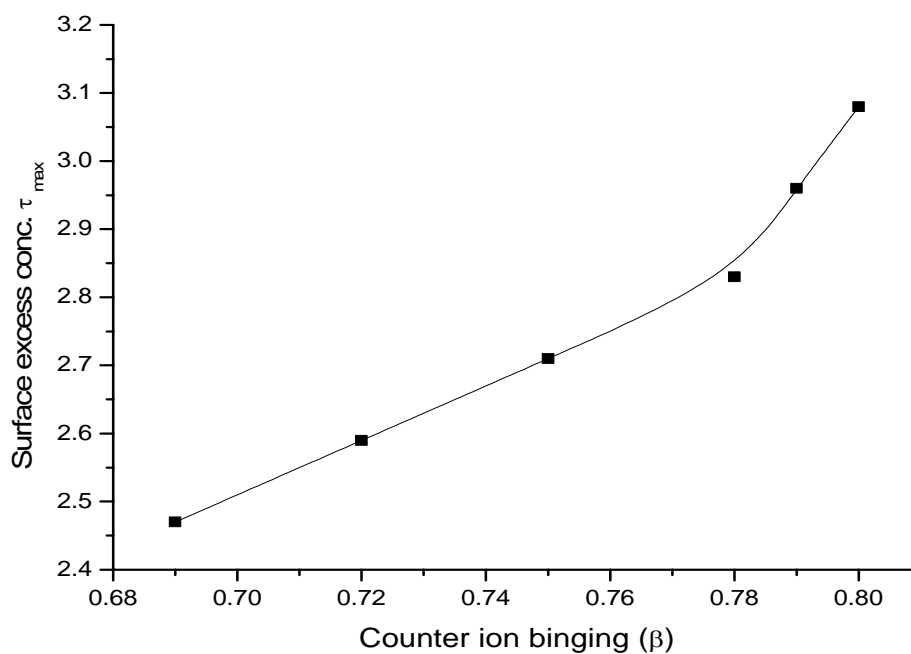


Figure 3.55 Relation between the counter ion binding and Γ value of CTAB in 0.01 M aq. NaCl solution.

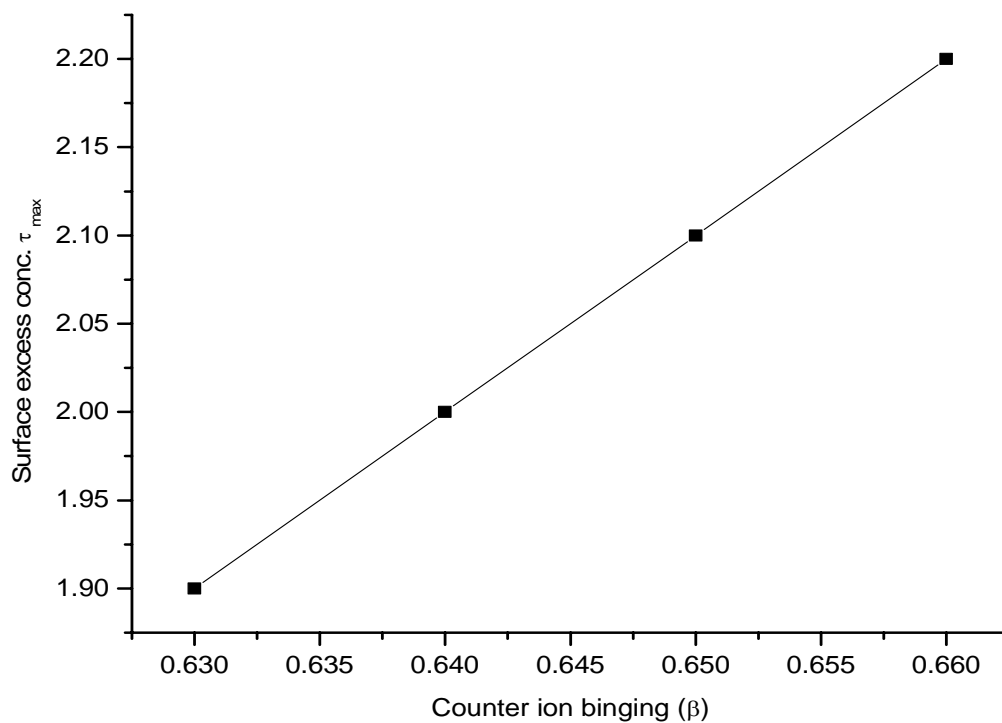


Figure 3.56 Relation between the counter ion binding and Γ value of OTAB in 0.01 M aq. NaCl solution (for CMC_1)

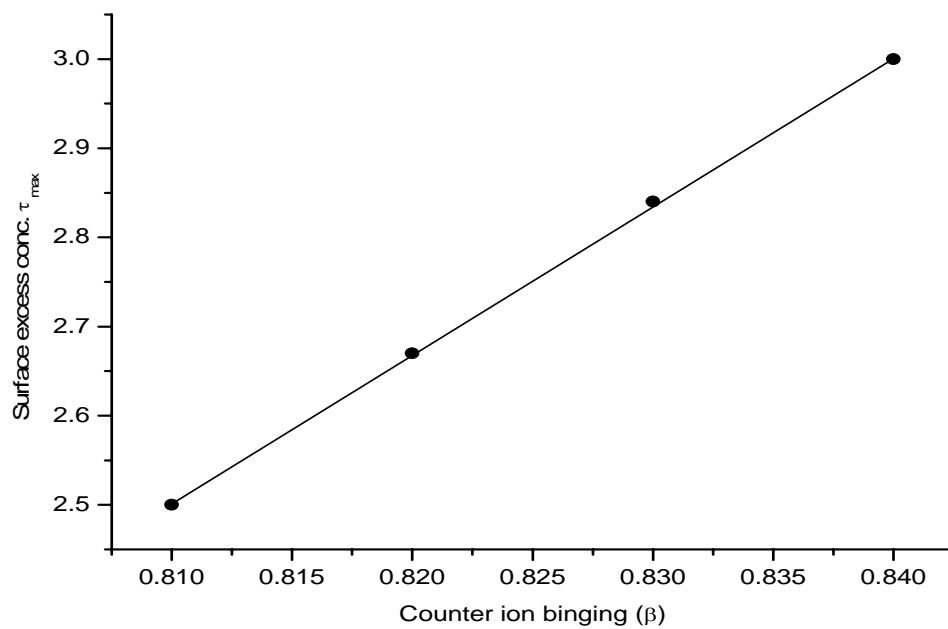


Figure 3.57 Relation between the counter ion binding and Γ value of OTAB in 0.01 M aq. NaCl solution (for CMC_2).

Table 3.8 Surface excess concentration, Γ_{max} , of TTAB, CTAB and OTAB in pure water and in 0.01 M aq. NaCl solution.

T/K	TTAB		CTAB		OTAB	
	water	NaCl	water	NaCl	water _{m1} (water _{m2})	NaCl _{m1} (NaCl _{m2})
293	2.71	3.07	2.50	3.08	----	----
298	2.46	2.77	2.38	2.96	----	----
303	2.24	2.66	2.32	2.83	2.1 (2.53)	2.2 (3.0)
308	2.04	2.58	2.21	2.71	2.0 (2.46)	2.1 (2.84)
313	1.89	2.51	2.14	2.59	1.9 (2.42)	2.0 (2.67)
318	1.87	----	2.09	2.47	1.8 (2.39)	1.9 (2.50)
323	1.86	----	----	----	----	----

Here the surface excess concentration, Γ_{max} , is in $(\text{mol}/\text{m}^2) \times 10^{-6}$. The subscript 1 and 2 to the column title refer to micellization processes 1 and 2 respectively for OTAB.

From figure 3.54-3.61 it is observed that increase of counter ion binding causes increase of surface excess concentration. The surfactant with smaller chain length has less ability of counter ion binding. So at higher temperature due to greater degree of ionization (of

the micelle of the surfactant of smaller alkyl chain) more decrease of counter ion binding is observed by the TTAB and CTAB. So from Fig 3.54 -3.55 no linear relation is observed. But for OTAB a linear relation between counter ion binding and surface excess concentration is observed, since OTAB has higher ability of counter ion binding and less degree of ionization, even at the higher temperature.

3.11 THERMODYNAMIC PARAMETERS FOR ADSORPTION OF THE SURFACTANTS

Table 3.8 shows the thermodynamic parameters for the adsorption of TTAB, CTAB and OTAB at the air-water interface, in 0.01 M aq. NaCl solution. The free energy changes of adsorption ΔG_{ad}° at different temperatures were calculated from the following expressions [3, 91]

$$\Delta G_{ad}^{\circ} = \Delta G_m^{\circ} - (\pi_{cmc} / \Gamma_m) \dots\dots\dots(5)$$

Here π_{cmc} and the Γ_{max} are the equilibrium surface pressure and the surface concentration of the adsorbed molecules, respectively at above the CMC. ΔS_{ad}° and ΔH_{ad}° were calculated from the relationship as in equation:

$$\Delta S_m^{\circ} = - \{ \delta \Delta G_m^{\circ} / \delta T \}_P \dots\dots\dots(3)$$

$$\Delta G_m^{\circ} = \Delta H_m^{\circ} - T\Delta S_m^{\circ} \dots\dots\dots(4)$$

Table .3.9 Thermodynamic parameters for adsorption of the surfactants in 0.01 M aq. NaCl solution.

T/K	TTAB			CTAB			OTAB		
	ΔG_{ad}°	ΔS_{ad}°	ΔH_{ad}°	ΔG_{ad}°	ΔS_{ad}°	ΔH_{ad}°	ΔG_{ad1}°	ΔS_{ad1}°	ΔH_{ad1}°
							(ΔG_{ad2}°)	(ΔS_{ad2}°)	(ΔH_{ad2}°)
293	-54.22	45.14	-41.00	-58.17	45.84	-44.74			
298	-54.45	42.40	-41.81	-58.41	45.08	-44.98			
303	-54.64	39.66	-42.62	-58.62	44.32	-45.19	-63.99	90.17	-36.67
							(-63.80)	(94.5)	(-35.16)
308	-54.85	36.92	-43.48	-58.84	43.56	-45.43	-64.45	90.07	-36.70
							(-64.26)	(93.5)	(-35.47)
313	-55.01	34.18	-44.31	-59.05	42.80	-45.66	-64.90	89.97	-36.74
							(-64.73)	(92.5)	(-35.78)
318	----	----	----	-59.27	42.04	-45.90	-65.35	89.87	-36.77
							(-65.19)	(91.5)	(-36.09)

Here the Energetic Parameters are expressed in $KJ mol^{-1}$ for ΔG_{ad}° and ΔH_{ad}° and $J K^{-1} mol^{-1}$ for ΔS_{ad}° . Subscript 1 and 2 to the column title refer to micellization processes 1 and 2 respectively for OTAB.

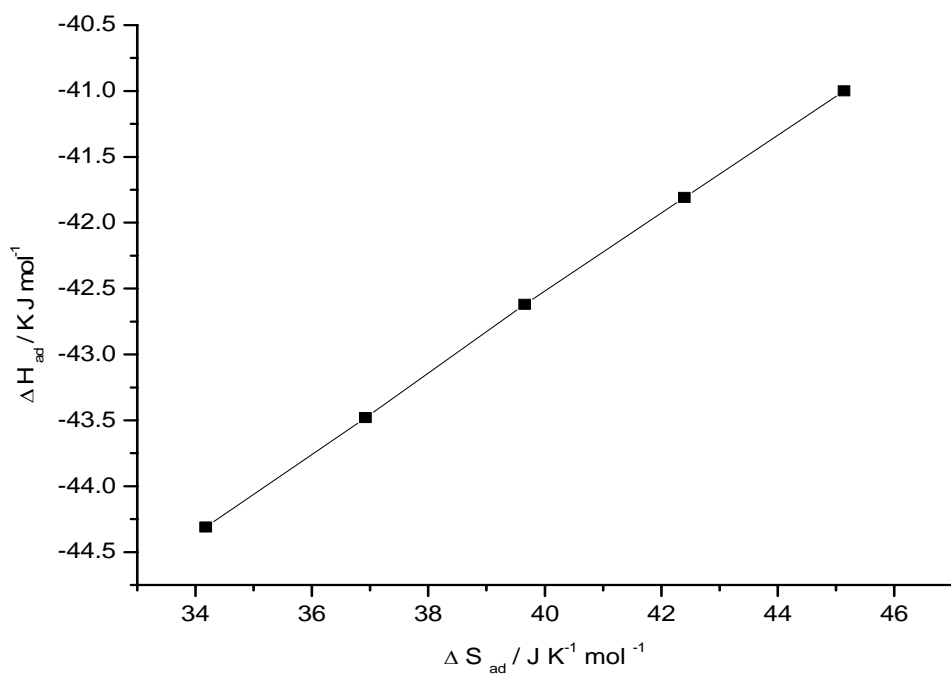


Figure 3.58 Enthalpy-Entropy compensation plots for adsorption of TTAB in 0.01 M NaCl.

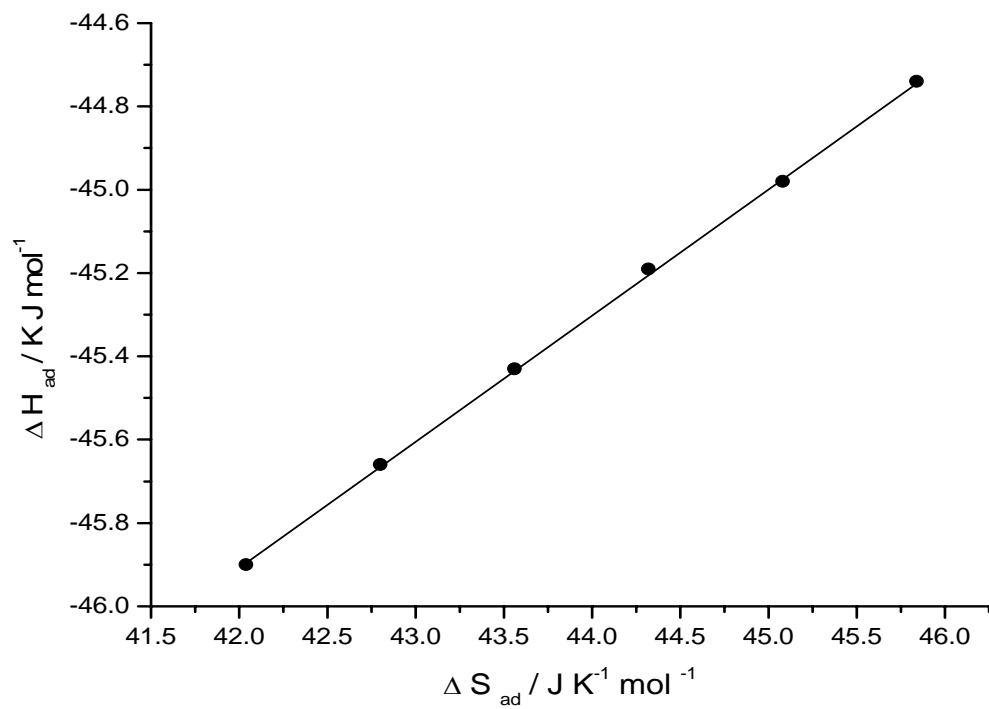


Figure 3.59 Enthalpy-Entropy compensation plots for adsorption of CTAB in 0.01 M NaCl.

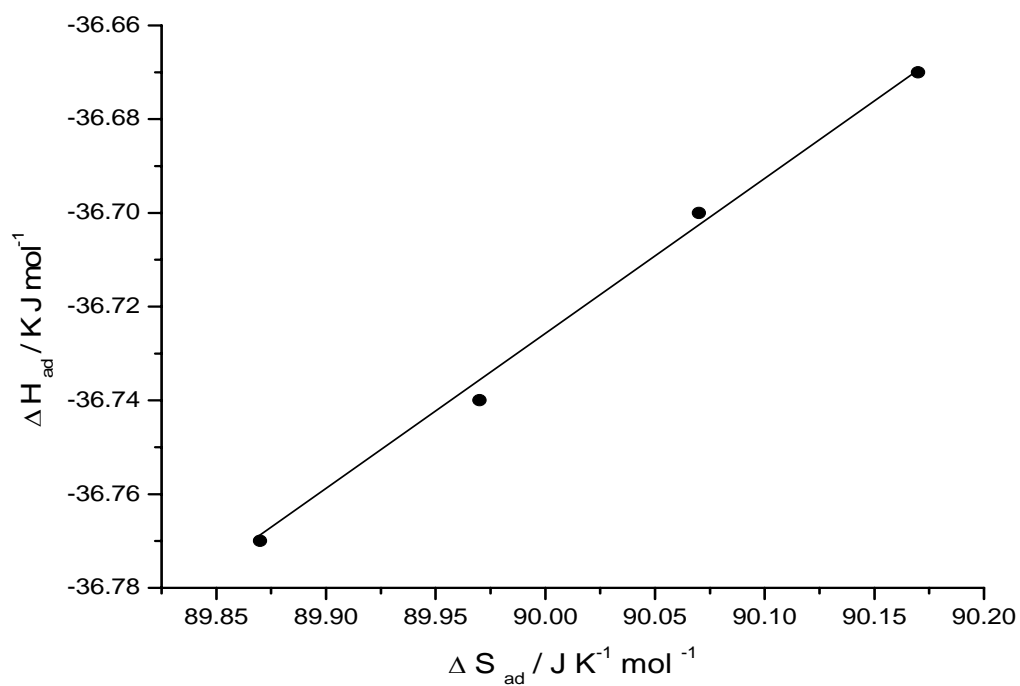


Figure 3.60 Enthalpy-Entropy compensation plots for adsorption of OTAB in 0.01 M NaCl (CMC_1).

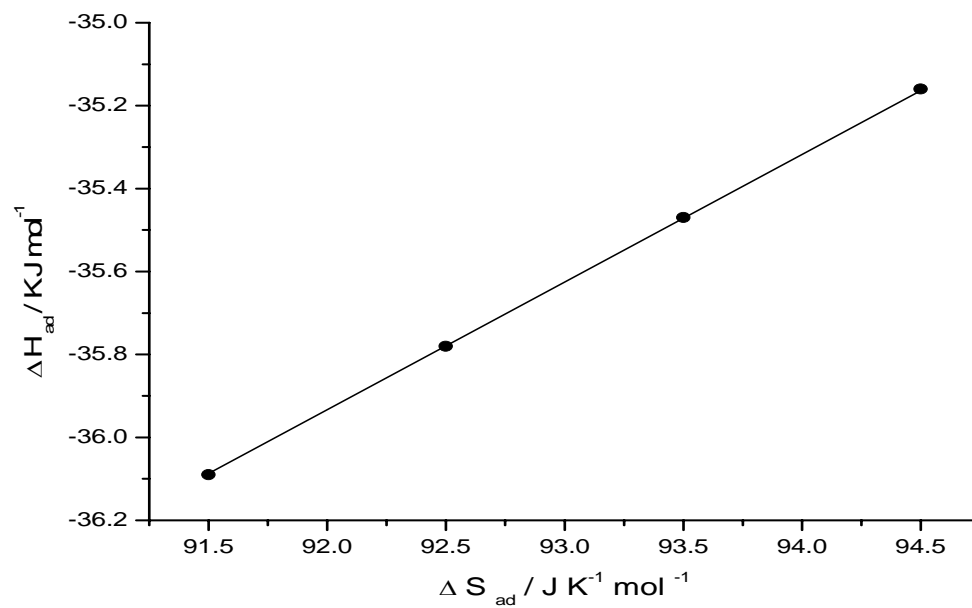


Figure 3.61 Enthalpy-Entropy compensation plots for adsorption of OTAB in 0.01 M NaCl (CMC_2).

The enthalpy –entropy compensation plots for adsorption of TTAB, CTAB and OTAB are shown in figure 3.58 to 3.61. Linear relationships obtained for micelle formation of these surfactants. When the entropy term contributes less to the free energy, its counterpart, the enthalpy term contributes more to keep the negative free energy nearly constant. The adsorption process of the surfactants in aqueous NaCl solution of both entropy and enthalpy controlled.

3.12 KRAFFT TEMPERATURE OF THE SURFACTANTS

Although the typical (amphipathic) structure of surfactants causes significant changes on a large number of physical properties (such as conductivity, viscosity, surface tension etc) of the solutions which is the basis of the applications of the surfactants in many purposes but these applications for a surfactant becomes insignificant below a certain temperature. This is because of very solubility of an ionic surfactant below the certain temperature. This certain temperature for a specific surfactant is known as the Krafft temperature (T_k) which is generally considered to be the melting temperature for hydrated solid surfactant [49, 50, 51]. Figure 3.62-3.64 shows Krafft temperature (T_k) of TTAB, CTAB and OTAB respectively. It is clear from the figure that initially the κ values of the surfactant solutions remain almost steady and then increases sharply when a certain temperature is reached. The T_k was taken from the sharp break in the κ versus temperature plot. The T_k of TTAB, CTAB and OTAB in pure water were found to be 12.4 °C, 24.7 °C and 36.5 °C respectively. The surfactant with larger chain length has greater T_k value which is due to increased hydrophobic nature of larger alkyl chain.

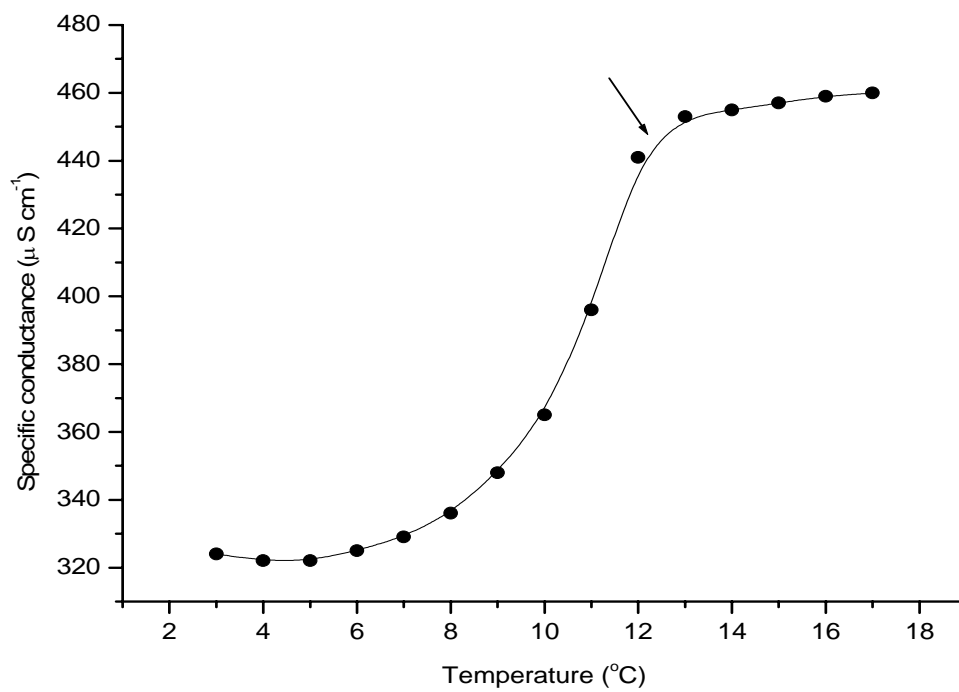


Figure 3.62 Krafft temperature (T_k) of TTAB in pure water.

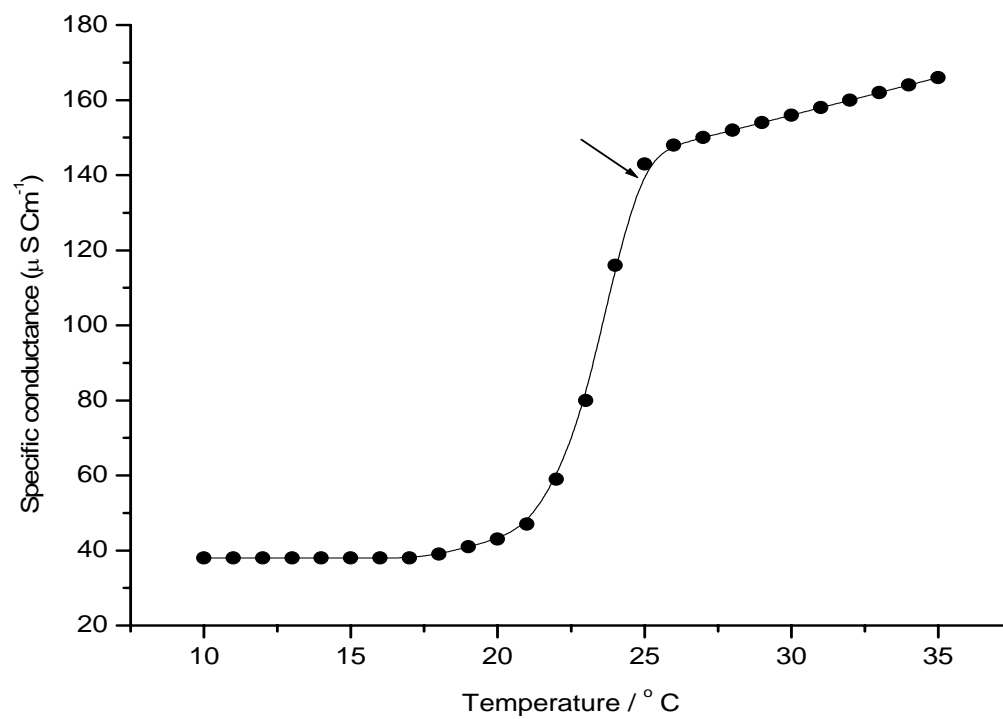


Figure 3.63 Krafft temperature (T_k) of CTAB in pure water.

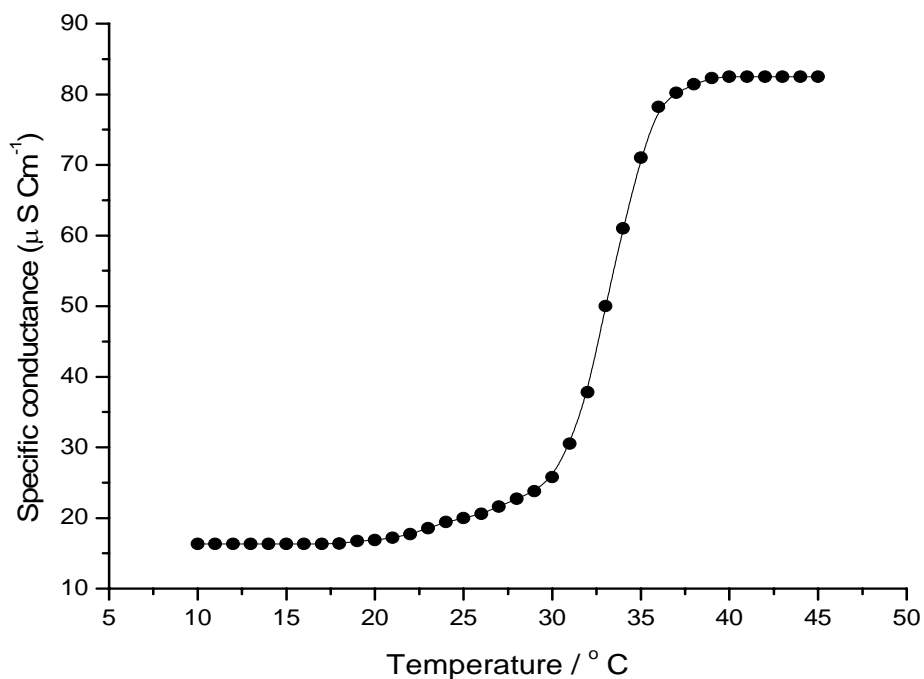


Figure 3.64 Krafft temperature (T_K) of OTAB in pure water.

3.13 EFFECT OF ELECTROLYTES ON THE KRAFFT TEMPERATURE OF TTAB

The kraft temperature of ionic surfactants may be increased or decreased due to the nature and concentrations of the added electrolytes. The T_K of a number of ionic surfactants has been measured in presence of added electrolytes containing an ion common to that of the surfactants. [55, 57, 58 , 108]. These studies have revealed that the T_K increase with increasing concentration of added electrolyte. It was shown that T_K of hexadecyltrimethylammoniumbromide (CTAB) increase due to NaBr [95]. Similarly the T_K of hexadecylpyridinium surfactants increase in the presence of electrolytes having anions common to the anionic part of the surfactant [57]. In the present study the T_K of TTAB is measured in presence of different concentration (0.001 M, 0.003 M, 0.005 M, 0.0075 M and 0.01 M) of aqueous NaF, NaCl , NaBr , NaI, NaNO₃ and NaSO₄

solutions. From these experiments it was found that the T_K of TTAB decreases due to increased concentration of F^- , Cl^- , NO_3^- and SO_4^{2-} where as the T_K of TTAB increase due to Br^- and I^- concentrations. Curves for I^- are not shown in the following figures because I^- causes much higher increase of T_K and at these high temperatures conductance readings were not possible due to solvent evaporation

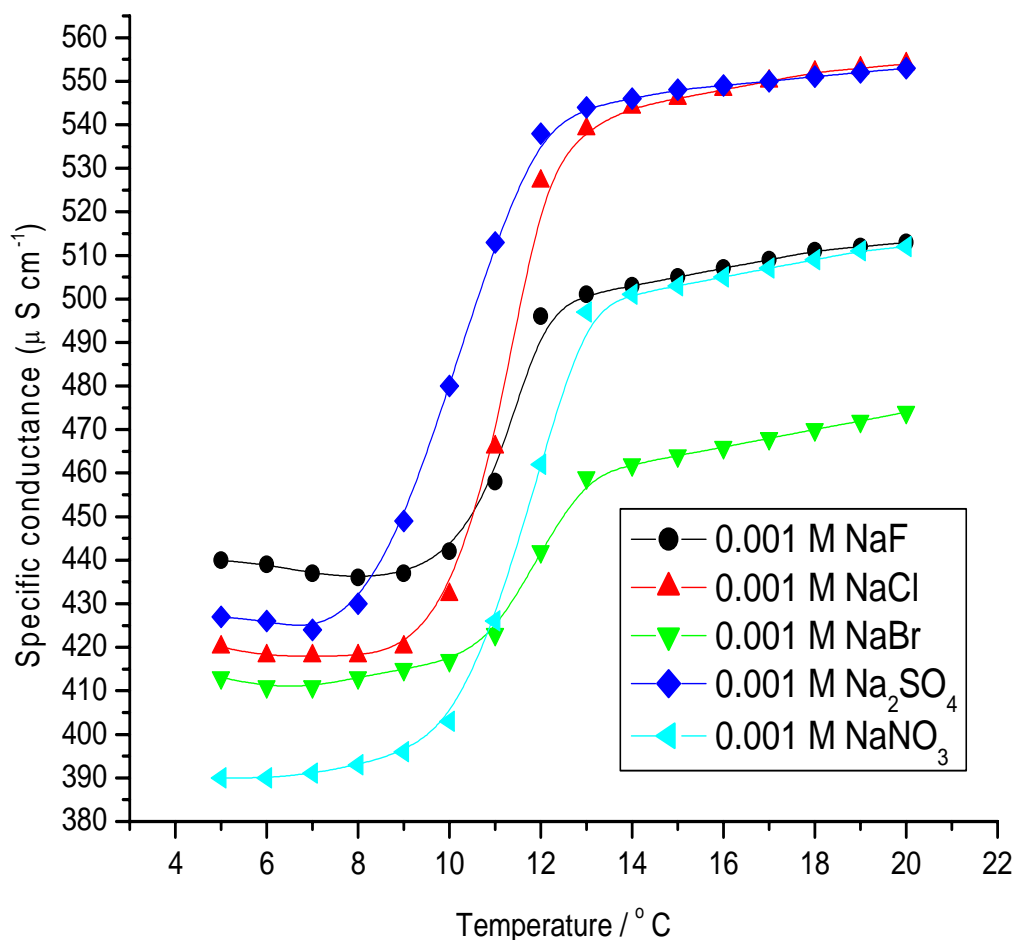


Figure 3.65 Krafft temperature (T_K) of TTAB in 0.001 M aqueous NaF, NaCl, NaBr, $NaNO_3$ and Na_2SO_4 solutions. For Na_2SO_4 ionic strength (μ) is used.

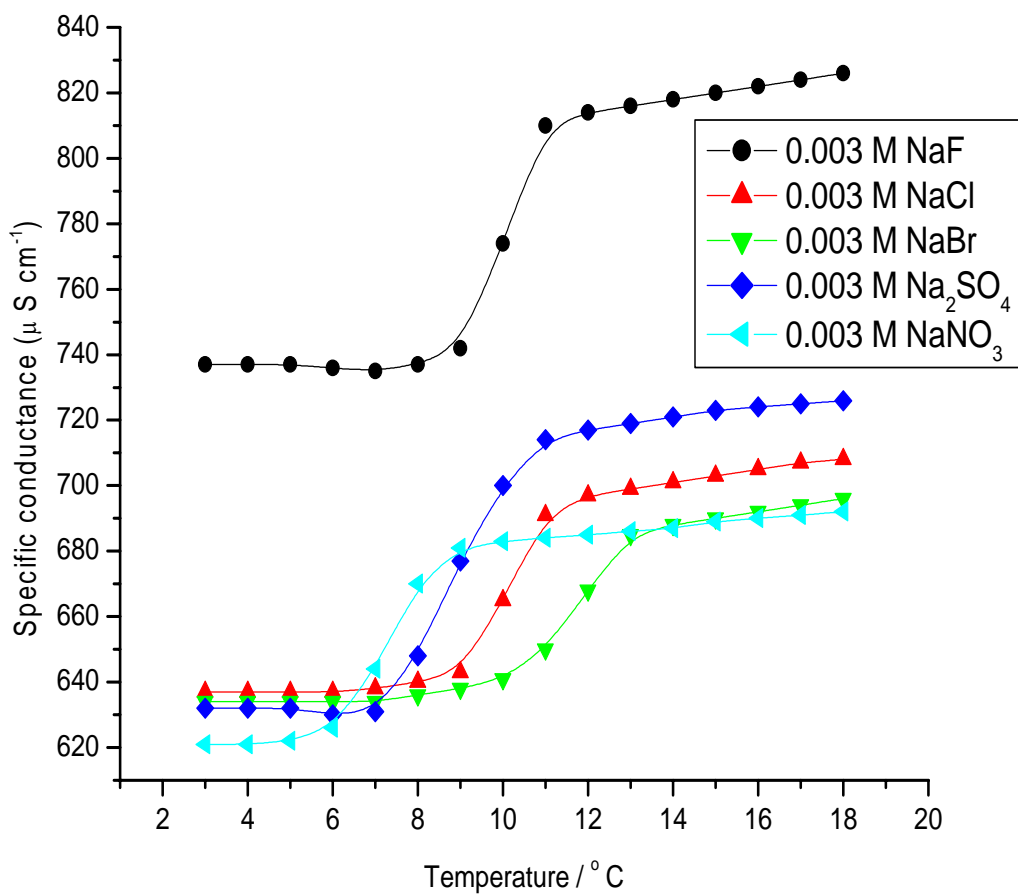


Figure 3.66 Krafft temperature (T_k) of TTAB in 0.003 M aqueous NaF, NaCl, NaBr, NaNO_3 and Na_2SO_4 solutions. For Na_2SO_4 ionic strength (μ) is used.

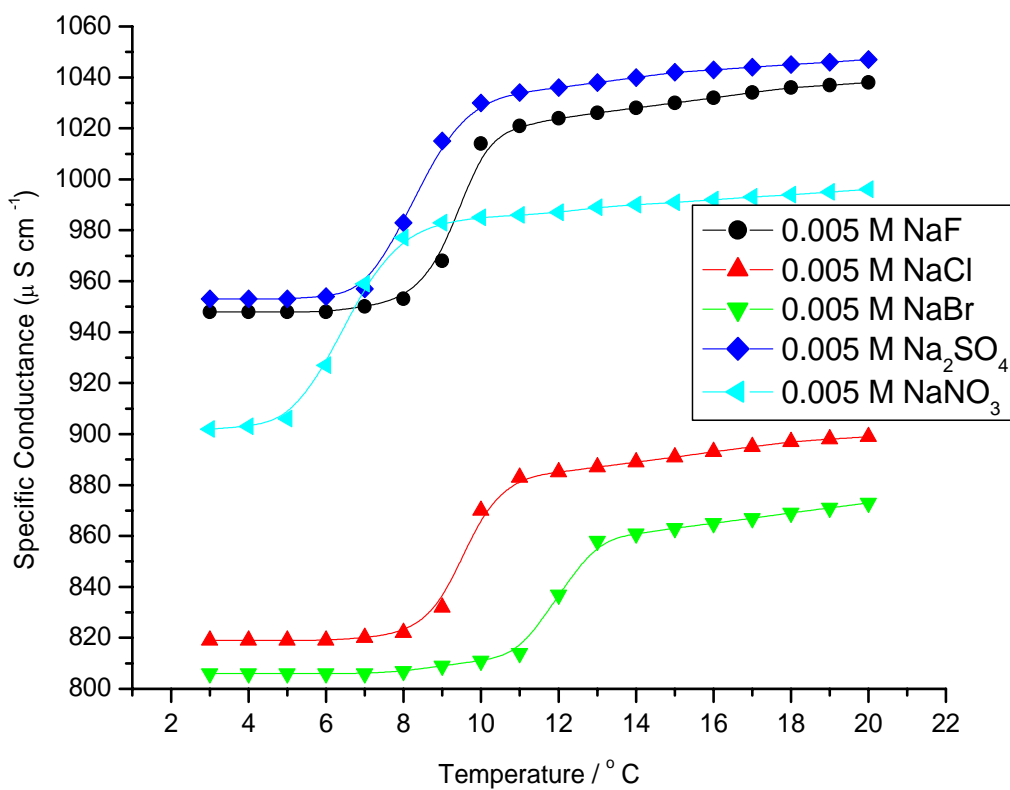


Figure 3.67 Krafft temperature (T_k) of TTAB in 0.005 M aqueous NaF, NaCl, NaBr, NaNO_3 and Na_2SO_4 solutions. For Na_2SO_4 ionic strength (μ) is used.

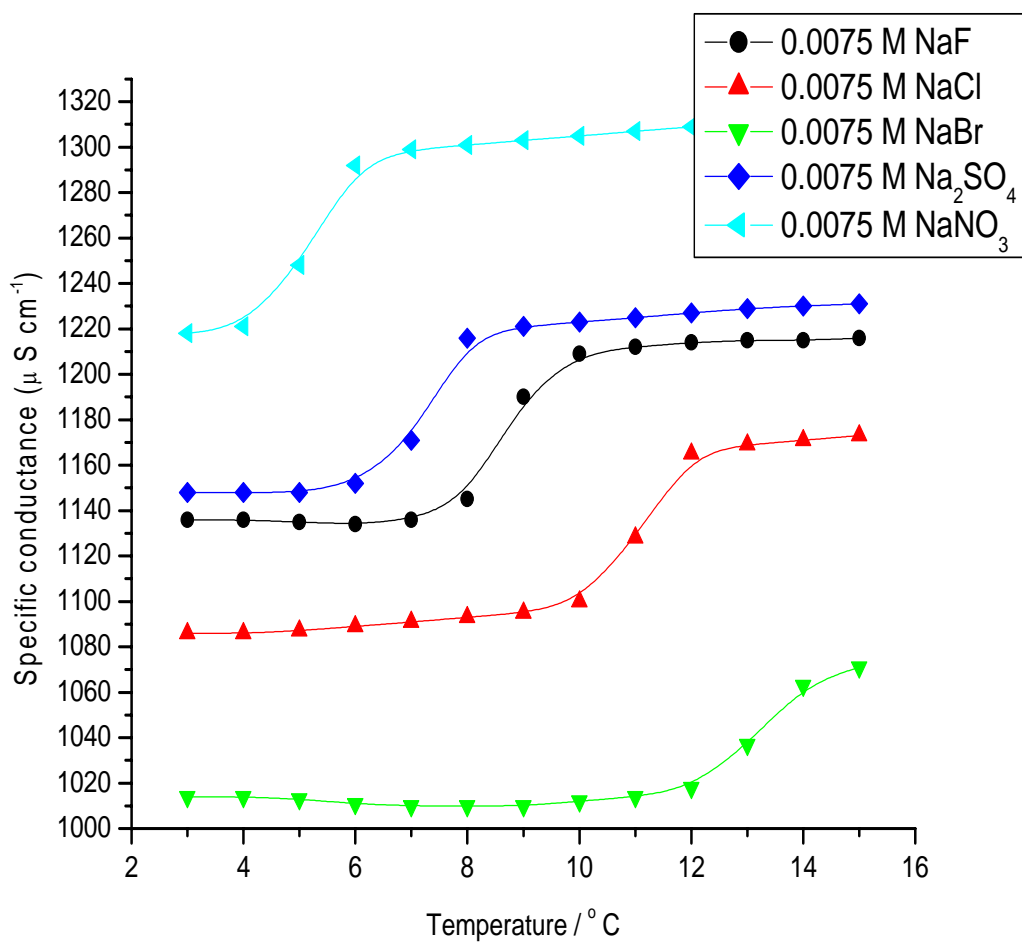


Figure 3.68 Krafft temperature (T_k) of TTAB in 0.0075 M aqueous NaF, NaCl, NaBr, NaNO₃ and Na₂SO₄ solutions. For Na₂SO₄ ionic strength (μ) is used.

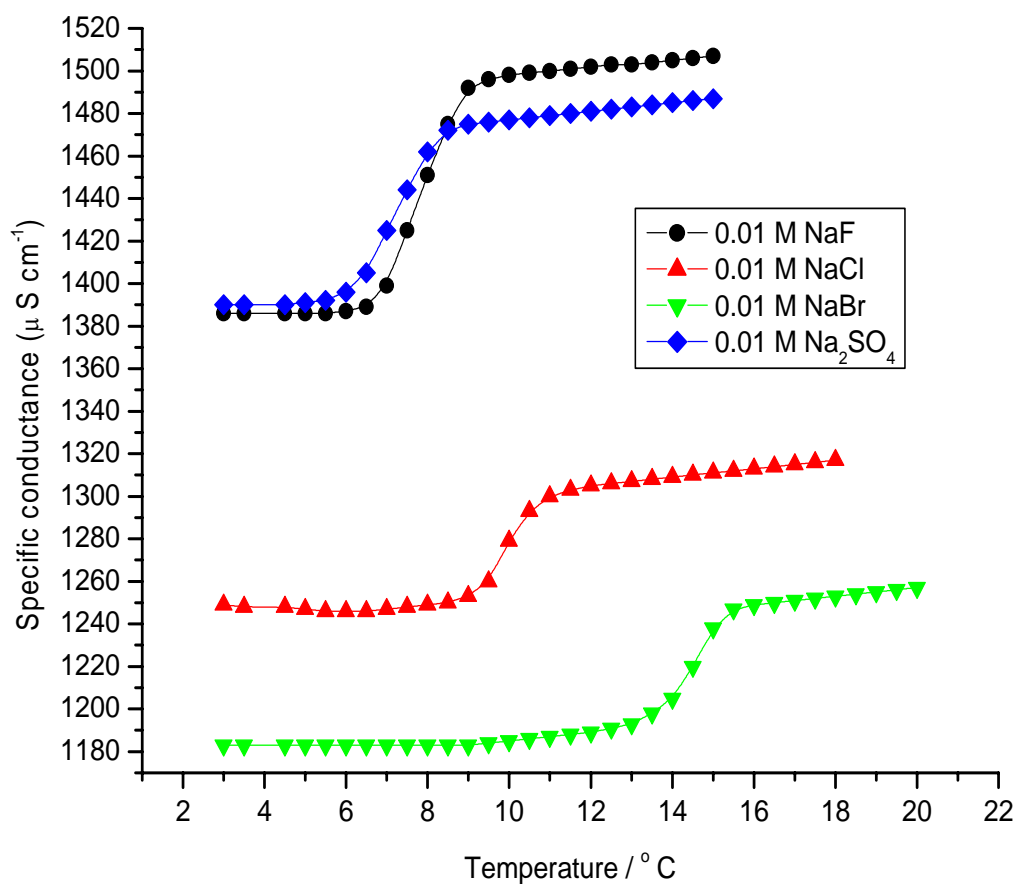


Figure 3.69 Krafft temperature (T_K) of TTAB in 0.01 M aqueous NaF, NaCl, NaBr and Na_2SO_4 solutions. For Na_2SO_4 ionic strength (μ) is used.

In the present study it was found that the T_K of TTAB is increased very little due to 0.01 M NaBr (up to 15.5°C) whereas T_K of TTAB is much more increased due to 0.01 M NaI (up to 50°C). Cl^- , Br^- are termed as chaotropes or structure breaking because of their low charge to radius ratio. So their hydration causes destruction of the structure of free water, surrounding them, to a considerable extent. According to the law of matching water affinities [111], chaotropes can form contact ion pair with other chaotropes. Thus a larger anion with low charge density has a tendency to pair with a larger cation when their affinities are similar. These pairs with similar water affinities will be less hydrated

and hence they are less soluble than the separate ions. In some previous studies it has been reported that the T_K of hexadecyltrimethyl ammonium bromide (CTAB) increase up to a significant range due to presence of Br^- [55, 45]. But in the present experiment it was found that lower concentration of Br^- has very little effect on the T_K of TTAB since TTAB has a cation with smaller chain compared to CTAB and hence the TTAB is less Chaotropic. But after a certain concentration of Br^- the T_K raises significantly. This may be explained in terms of the solubility product. It is well known that when a solution contains a poorly soluble salt in equilibrium with its ions, it is expected that an increase in 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 solution. As a result the solubility of TTAB in presence of Br^- decreases to maintain the constant value of solubility product. Thus higher concentration of Br^- causes significant increase of T_K value of TTAB. Due to common ion effect $[\text{Br}^-]$ causes an increase of T_K of TTAB. Similar trend is observed for the T_K values of cetylpyridinium nitrate in presence of NO_3^- [57]. Compared to Br^- , I^- shows more Chaotropic effect and it is weakly hydrated because of its lower charge density. So, according to the concept of matching water affinities [45], it can form direct ion pair with other chaotropes. Thus it can pair with tetradecyltrimethylammonium ion, which is also a chaotrop. So these will form contact ion pair with low solubility.

The T_K of TTAB gradually decreases from 12.7°C to 9°C with increasing of $[\text{Cl}^-]$ up to 0.01M. Like Br^- , we know that Cl^- is also a chaotrope or structure breaker. But unlike Br^- , the Cl^- concentration is causing decrease of T_K of TTAB. Cl^- has greater charge to radius ratio compared to Br^- . So Cl^- is less chaotropic than Br^- . So Cl^- shows greater hydration tendency than Br^- [112]. It has been reported that when an ion is more strongly

hydrated than its oppositely charged partner, dehydrating the more strongly hydrated ion costs more its energy than it can gain by forming a contact pair with more weakly hydrated ion [111]. Therefore the tetradecylammonium ion, being weakly hydrated compared to Cl^- , will not be able to make a contact pair and consequently they will tend to stay apart. As a result T_K of TTAB decreases. NO_3^- is less chaotropic and it exhibits a higher tendency for hydration, compared to I^- . But due weakly chaotropic nature, the presence of $[\text{NO}_3^-]$ increases the concentration of free water molecules which increases the hydration of the surfactant. As a result solubility of the surfactant increase in presence of NO_3^- , resulting a decrease in the Krafft point of TTAB.

F^- and SO_4^{2-} are kosmotropes or structure making since they have high charge to radius ratio. So their presence induces a more organized structure of water around the hydrated sphere. So their presence causes more solubility of the surfactant, leading to a decrease of the T_K value of the surfactant. The principle of salting – in effect suggests that an added salt having no common ion should increase the solubility of a sparingly soluble salt when the activity coefficient is less than 1[113]. Here the addition of salt causes an increase of ionic strength of the medium and thus the activity coefficient decreases. As a result for maintaining a constant the thermodynamic solubility product, the solubility of the surfactant increases. In the present study, the concentrations (ionic strength, μ) of SO_4^{2-} were up to 0.01 μ the activity coefficient of the salt solution is below unity. So solubility of the surfactant increases with gradual increase of the salt concentration. It is also expected that the kosmotropes are strongly hydrated and they have a higher affinity of hydration and they have greater tendency to remain in the bulk of the solution. So dehydrating the more strongly hydrated ion costs more energy to form a contact pair with more weakly hydrated tetradecyl trimethyl ammonium ion

[111], which is unfavorable. So presence of kosmotropes cause decrease in the T_K values of the surfactant.

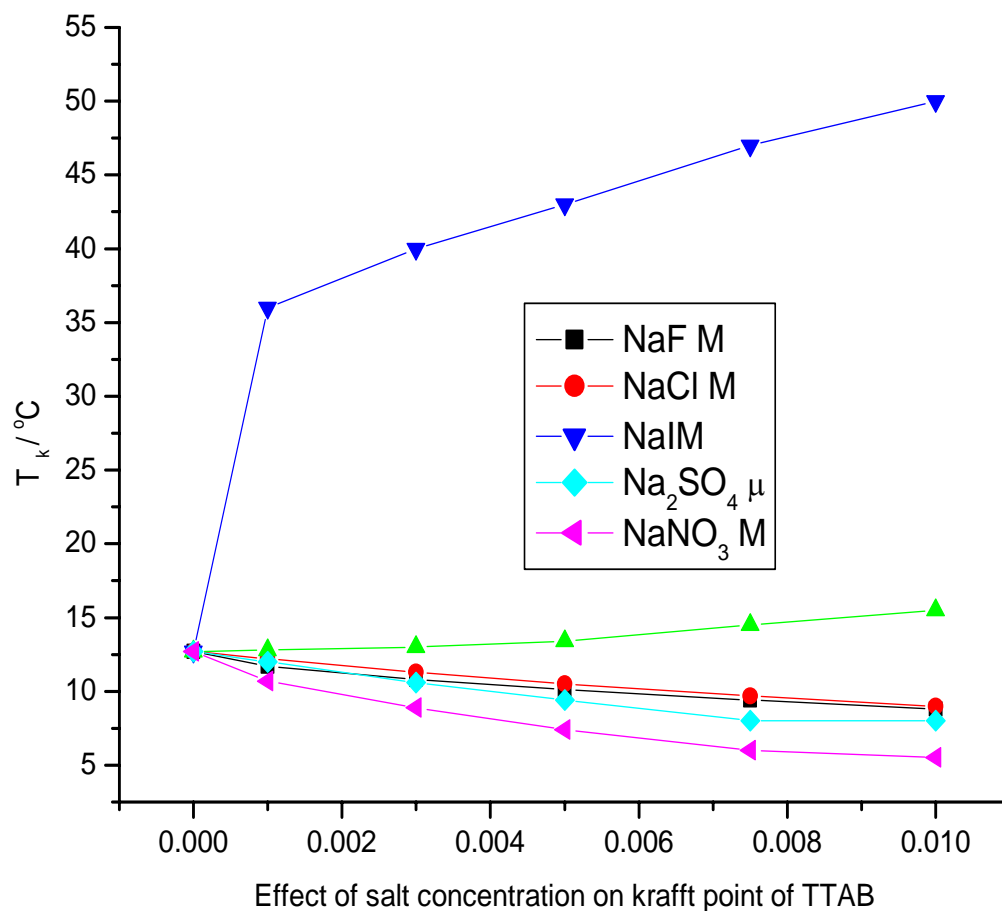


Figure 3.70 Effect of salt concentration on the Krafft point of TTAB. For Na_2SO_4 ionic strength (μ) is used.

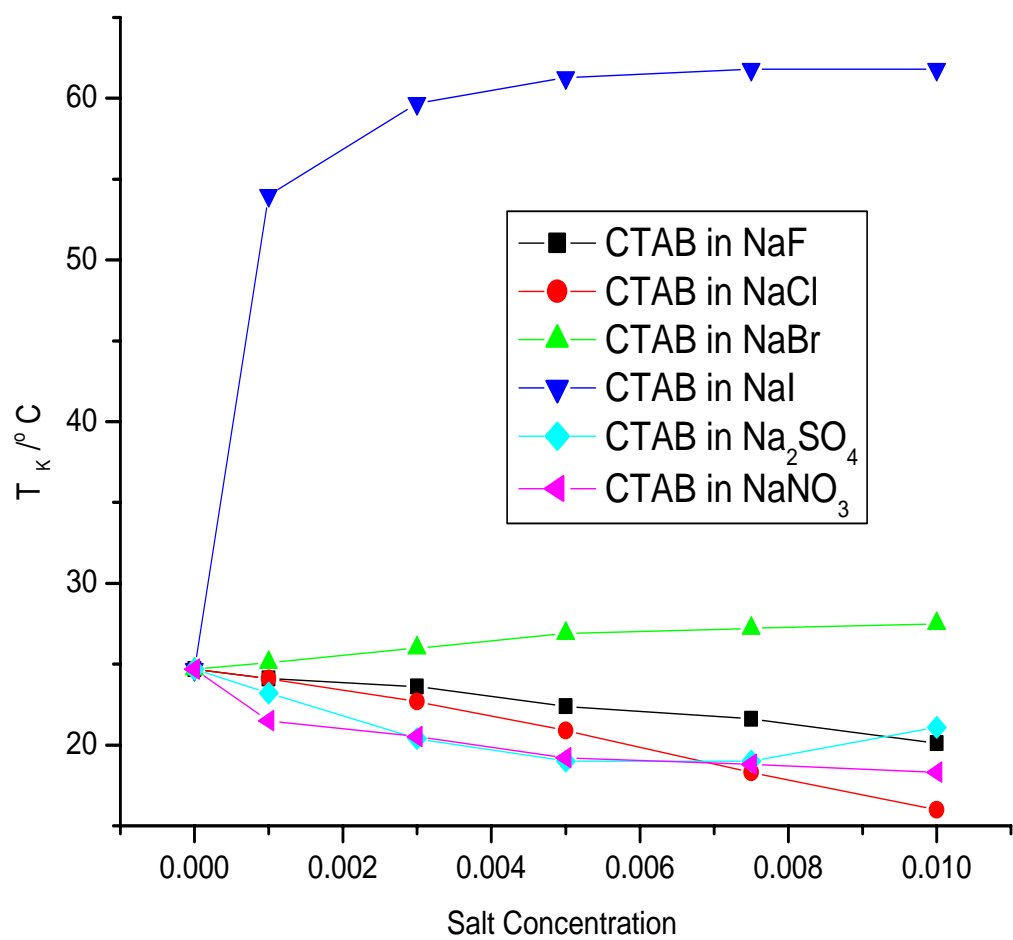


Figure 3.71 Effect of salt concentration on the Krafft point of CTAB. For Na₂SO₄ ionic strength (μ) is used.

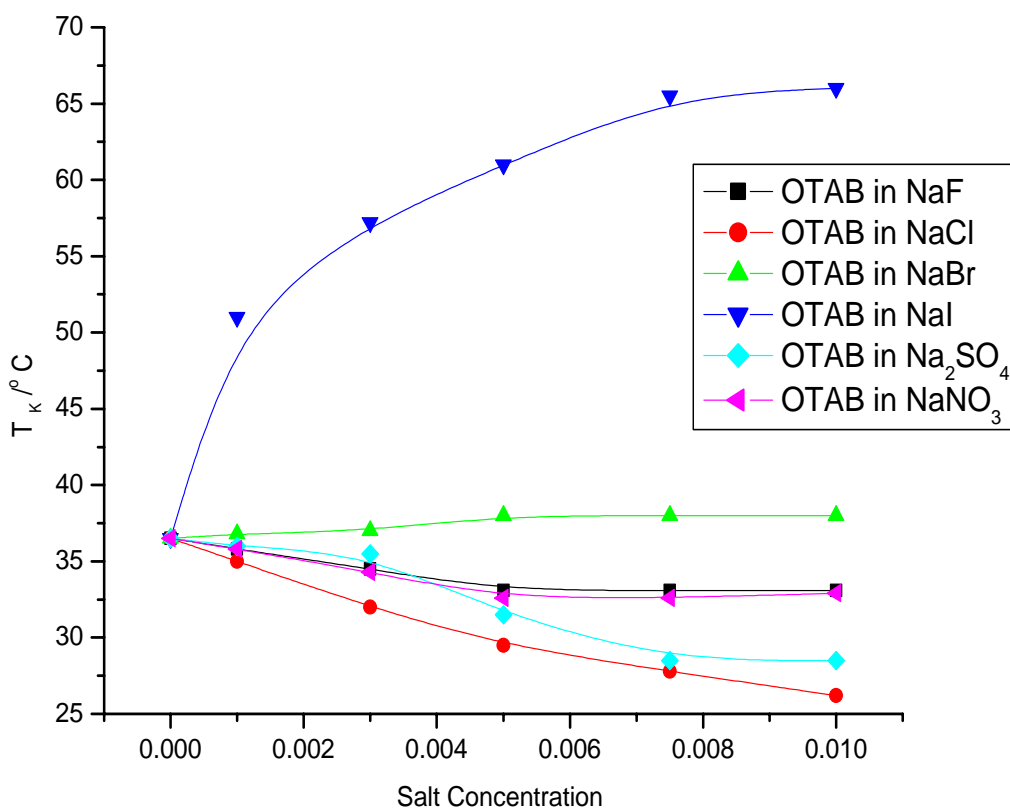


Figure 3.72 Effect of salt concentration on the Krafft point of OTAB. For Na_2SO_4 ionic strength (μ) is used.

3.14 MICELLIZATION OF THE SURFACTANTS IN PRESENCE OF DIPHENYL CARBAZID (DPC)

Effect of Diphenyl carbazide on the micellization of TTAB, CTAB and OTAB is studied by the conductivity measurement. The experimental conductivities (κ) for TTAB and CTAB in presence of DPC, of different concentrations, at 25°C temperature are shown in fig3.73 to 3.74.

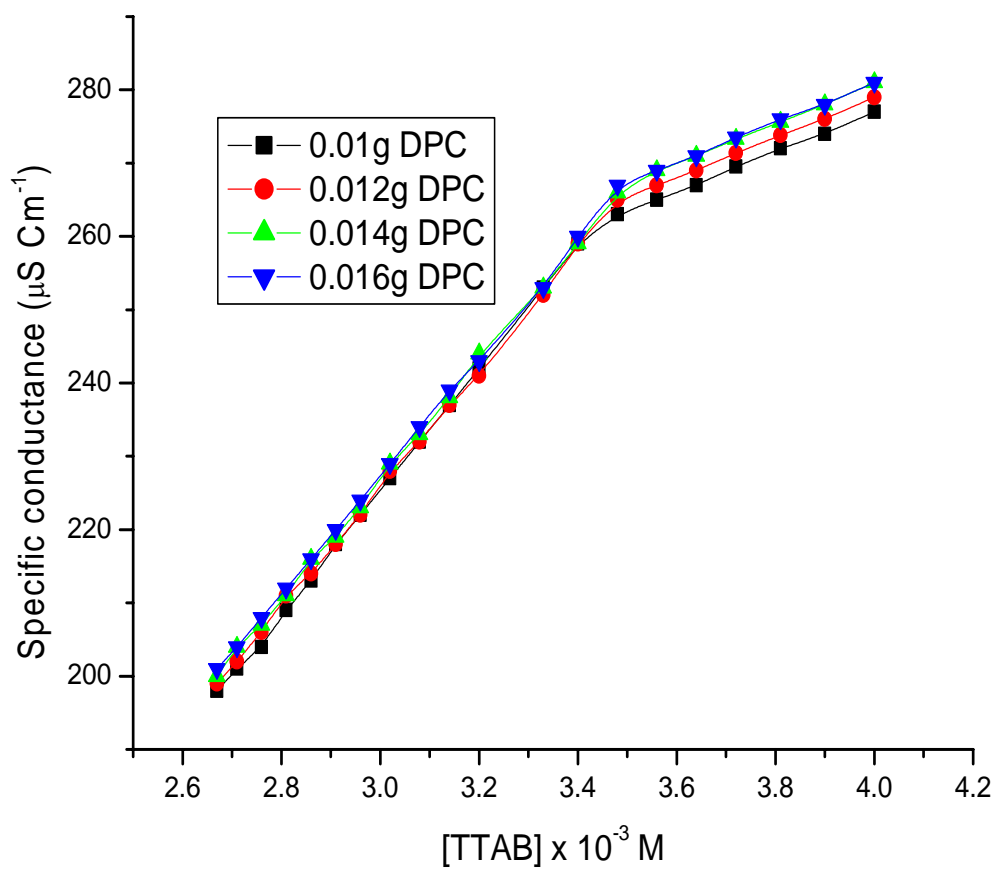


Figure 3.73 Specific conductances (κ) vs. concentration of TTAB at each fixed amount of DPC.

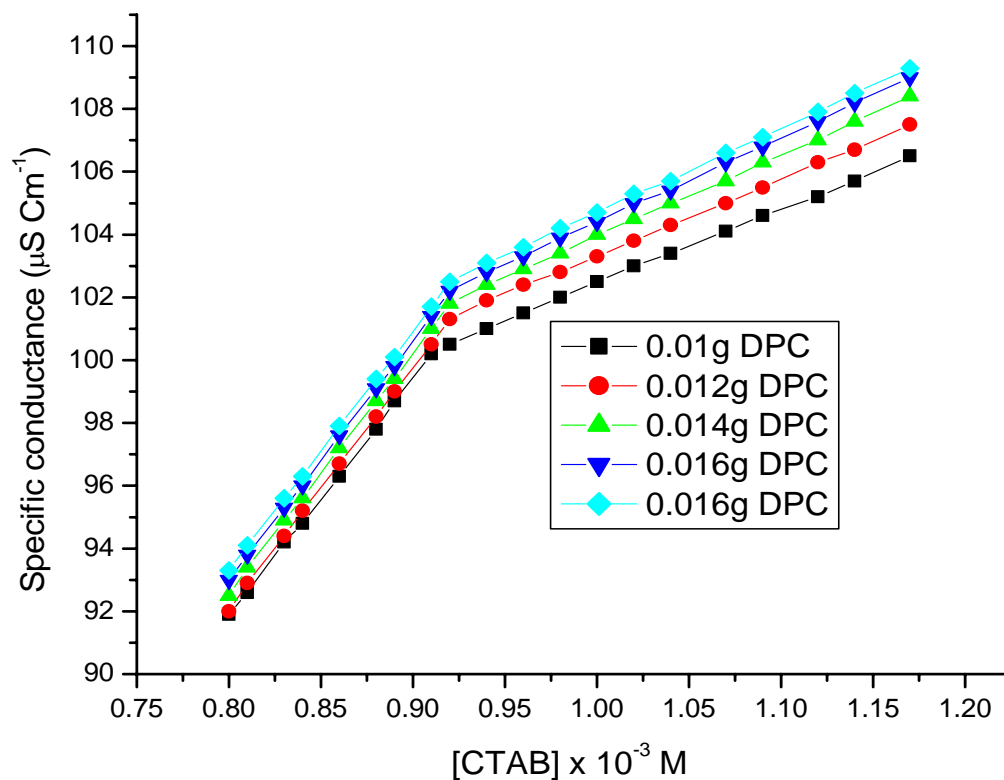


Figure 3.74 Specific conductances (κ) vs. concentration of CTAB at each fixed amount of DPC.

Table 3.10 shows the CMC, degree of ionization (α) and the standard free energy of micellization (ΔG_m°) for TTAB and CTAB in presence of different amount of DPC. It was observed that the CMC and degree of ionization (α) values increase where as standard free energy of micellization (ΔG_m°) values become less negative, due presence of DPC .

Table 3.10 micellization of surfactants in presence of DPC

[DPC] x 10 ⁻⁴ / M	TTAB			CTAB		
	CMC (mM)	α	ΔG_m°	CMC 10 ⁻³ /M	α	ΔG_m°
8.26 x 10 ⁻⁴	3.45	0.319	-40.32	0.911x 10 ⁻³	0.313	-46.05
9.91 x 10 ⁻⁴	3.48	0.331	-40.02	0.921 x 10 ⁻³	0.317	-45.90
11.56 x 10 ⁻⁴	3.50	0.335	-39.90	0.929 x 10 ⁻³	0.338	-45.29
13.21 x 10 ⁻⁴	3.51	0.336	-39.86	0.940 x 10 ⁻³	0.350	-44.92
14.86x 10 ⁻⁴	-----	-----	-----	0.942 x 10 ⁻³	0.353	-44.83

Here the Concentration is expressed in moldm⁻³ and standard free energy of micellization (ΔG_m°) is expressed in KJ mol⁻¹.

The presence of some organic substances in aqueous solution can affect the micellization process, thereby modifying such parameters as the CMC, α and standard free energy of micellization (ΔG_m°) [19, 114-117]. Our present study also shows that [DPC] has noticeable effect on these parameters. The CMC and α value increase with increase of DPC concentration. Simultaneously, the phenomenon of micellization becomes less spontaneous on DPC addition, as indicated by less and less negative value of ΔG_m° . These observations suggest that DPC is solubilized within the TTAB and CTAB

micelle. But below the CMC the DPC interacts with the surfactant units stabilizing the monomeric state. T. Farias et al [74] found no significant change in the CMC, α and ΔG_m° of dodecyldimethylammonium chloride (BC12), tetradecyldimethylammonium chloride (BC14) and hexadecyldimethylammonium chloride (BC16) in presence of metronidazole since there is no interaction of the drug with the surfactants, rather the drug solubilizes by the weak interaction with the head groups. But sulfomethoxazole causes a significant change in the CMC, α and ΔG_m° of these surfactants which is because of solubilization of the drug by interaction with the micelle, mainly near the surfactant head groups.

3.15 INTERACTION OF DPC WITH THE SURFACTANTS UV STUDIES

To understand the interaction of DPC with the surfactants UV and NMR studies are done, in this experiment. DPC is insoluble in water so it is solubilized by using the surfactant micelle. This solubilization is possible by its interaction with a number of different sites [3] of the micelle: (1) on the surface of the micelle, at the micelle – solvent interface; (2) between the hydrophilic head groups ; (3) between the so-called palisade layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise of outer core of the micelle interior; (4) more deeply in the palisade layer ; and (5) the inner core of the micelle. Figure 3.75 shows the possible loci of the micelle where the insoluble surfactant interacts to be dissolved.

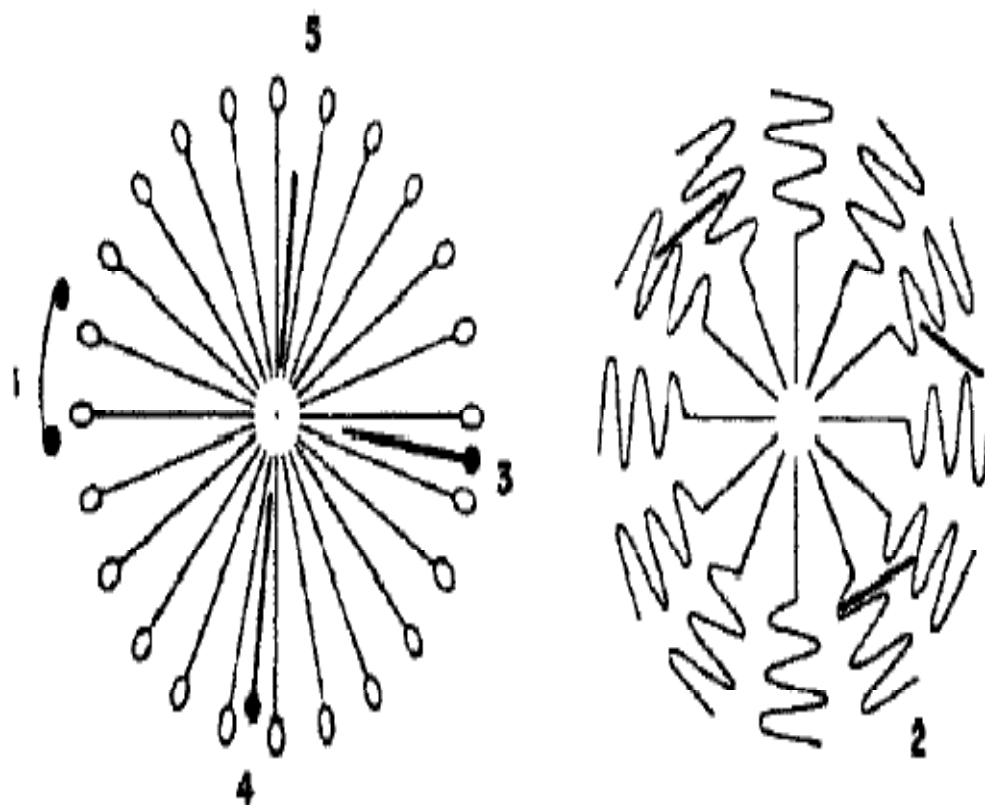


Figure 3.75 Loci of solubilization of material in a surfactant.

It is expected that the interaction of the solubilize with the micelle may affect the chemical behavior of the dissolved substance, which in some specific cases may influence its activity and coordination capability. But specific research work is still lacking in this field. The aim of the present section is to study the effect of surfactants micelles on the coordinating efficiency of diphenyl carbazide (DPC) which will give important information on its solubilization site in the micelle.

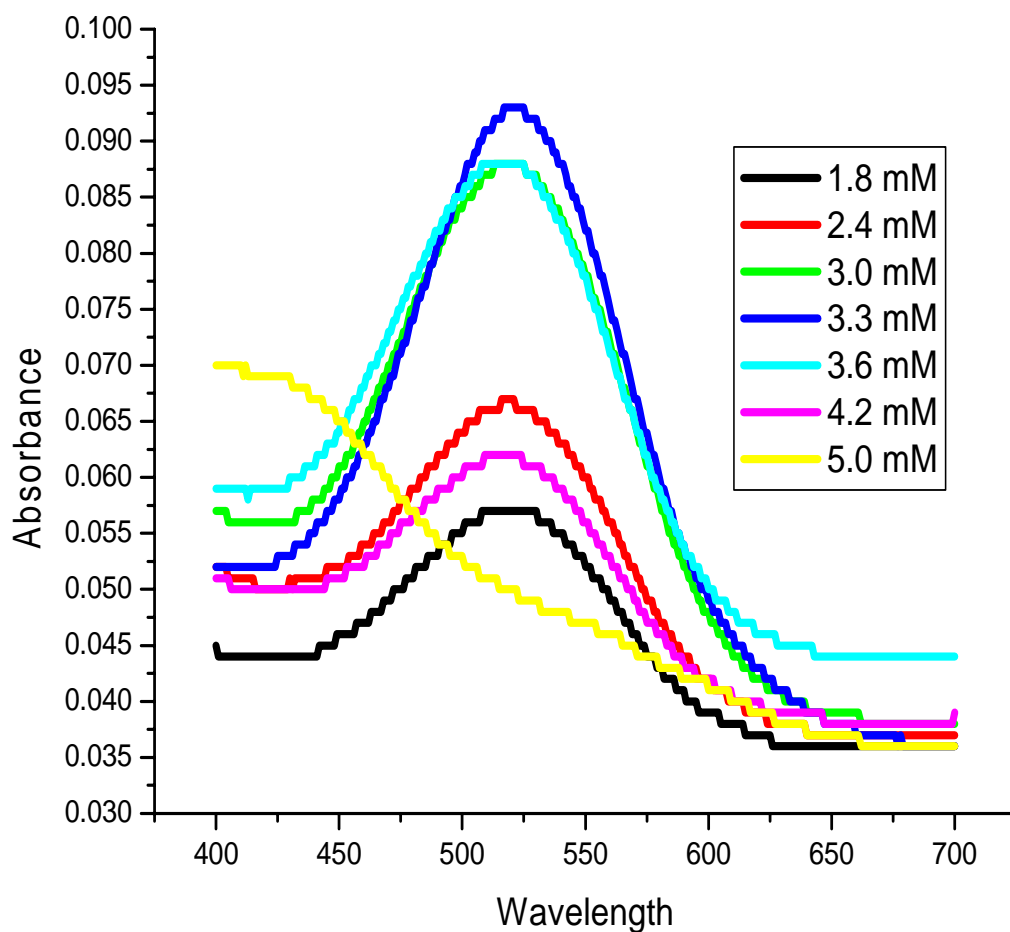


Figure 3.76 Effect of TTAB concentrations on absorption spectra of Zn- DPC complex.

Figure 3.76 shows the visible spectra for a Zn(II) diphenyl carbazide (DPC) complexes in different concentrations of aqueous solutions of TTAB ranging from 1.8 mM to 5.0 mM concentration at 25°C. It reveals that an increase of concentration of TTAB causes an increase of absorbance with gradual increase of the maximum wave length (λ_{\max}) from 515.5 to 518.5 for Zn (II) DPC complexes which indicates the interaction of DPC with the TTAB molecules in the bulk. The increase of absorbance of the complexes is attributed

to the increase of amount of dissolved ligand (concentration of DPC) in the bulk due to increase of the concentration of TTAB. Since greater concentration of TTAB provides greater dispersion facility for the insoluble DPC molecules which help more DPC to be dissolved. After 3.3 mM concentration of TTAB, further increase of concentration of the surfactant, the absorbance of the complexes starts decreasing. Slight displacement, towards a decreasing order, of the maximum wave length (λ_{\max}) values was also observed for the further increase of the concentration of TTAB from 3.6 mM to 5.0 mM. Displacement of the λ_{\max} values for Zn-Dithizone complexes in micellar media were also reported in some previous experiments [118]. This sudden decrease of absorbance is due to the micelle formation which consists of positively charged outer surface with hydrated counter ions along with any bound water molecules [119].

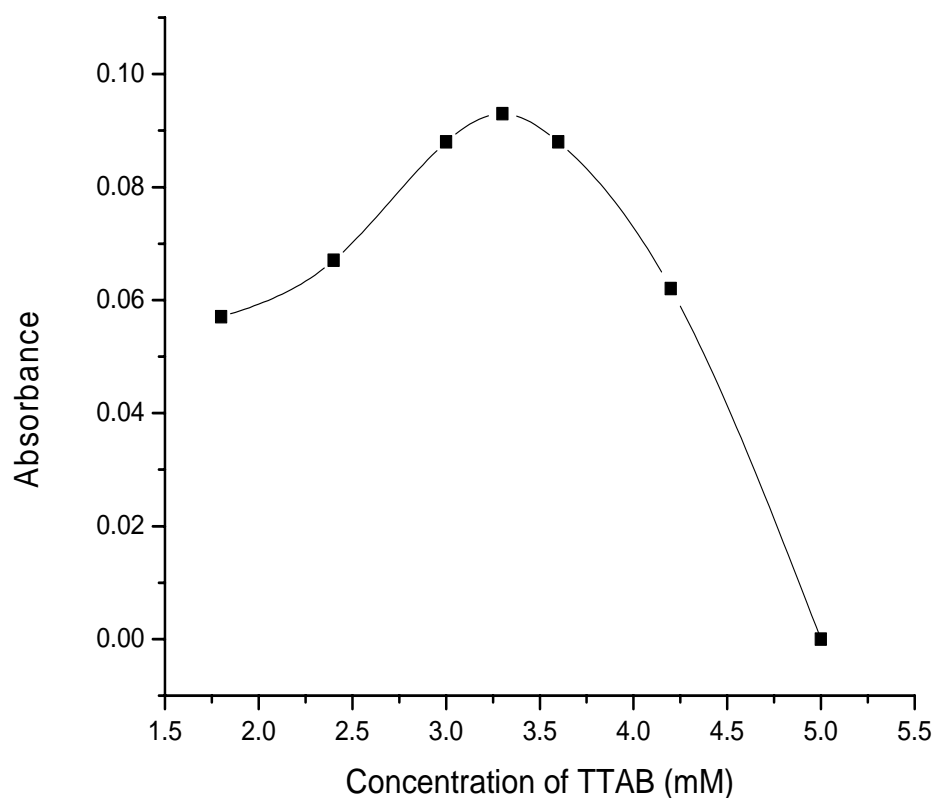


Figure 3.77 Absorbance of Zn- DPC complexes at different concentration of TTAB

From figure 3.77 it is found that the concentration of TTAB at which the highest absorbance is obtained represents the concentration which is just before the CMC. This figure represents that the CMC of TTAB in presence of DPC at 25°C is 3.45mM (i.e. more than 3.3mM) which is slightly higher than the CMC value for TTAB (3.43 mM) in pure water. The presence of some organic substances in aqueous solution can affect the micellization process and thus can modify some thermodynamic parameters [74]. If a low soluble drug (sulfamethoxazole) is dissolved with in micelle the CMC value increases and makes the micellization less spontaneous whereas below CMC the low soluble substance interacts with the surfactant units stabilizing the monomer state [74]. Similar trend is observed for the solubilization of DPC with TTAB solutions. Below CMC, an increase of concentration of TTAB causes gradual increased interaction between DPC and the surfactant units. As a result solubility of DPC gradually increase. Thus the extent of Zn (II)-DPC complexation increases with gradual increase of TTAB concentration which results increase of the absorbance. But after the CMC appeared, DPC is solubilized with in the micelle by the hydrophobic interaction. Although a sharp increase of solubilization occurs due to the CMC [119] but the interesting observation of the present experiment of a gradual decrease of the absorbance is attributed to the micellar surface charge which (i) favors the binding of the counter ions (Cl^- from ZnCl_2) and some water molecules [12-17, 119] and (ii) disfavors the entrance of the metal ion (Zn^{2+} aq.) through the positively charged surface in to the inner region, where DPC is dissolved. A competitive environment of these two factors brings the limitations for the metal ion to be coordinated with DPC, dissolved within the micelle, and consequently the absorbance decreases. Further increase of the concentration of TTAB, even after the CMC, causes a consistent decrease of the absorbance which is due to increase of the micellar aggregation number. The micellar aggregation number is a function of the

surfactant concentration, the solution temperature and the concentration of the electrolyte in solution [120]. Swollen micelle and micellar growth is a consequence of certain range of salt and additive concentrations [37]. Thus due to increased concentration of TTAB up to a certain range causes more aggregation number which results greater surface charge and there by creates greater steric hindrance and greater repulsive environment for the incoming metal ions. As a result there is greater limitation for the metal-ligand binding and causes lower absorbance. After a certain range of concentration the micellar surface charge gets a saturation limit, with a specific micellar shape [119], and does not allow any metal ion to enter into the micelle. As a result the metal-ligand coordination is not possible anymore and shows no absorbance within the visible range. It has been reported that the electronic absorption spectra of solutions of many dyes are affected by the surfactant concentration and the CMC [121].

Figure 3.78 shows visible spectra for a Zn(II) diphenyl carbazide (DPC) complexes in different concentrations of aqueous solutions of SDS ranging from 2 mM to 12mM concentration at 25°C. It reveals that an increase of concentration of SDS causes an increase of absorbance with gradual increase of the maximum wave length (λ_{\max}) from 515.5 to 525.5 for Zn (II) DPC complexes which indicates the interaction of DPC with the SDS molecules in the bulk. The increase of absorbance of the complexes is attributed to the increase of amount of dissolved ligand (concentration of DPC) in the bulk due to increase of the concentration of SDS. Since greater concentration of SDS provides greater dispersion facility for the insoluble DPC molecules which help more DPC to be dissolved. Maximum absorbance was obtained at 9.0mM concentration of SDS, further increase of concentration of the surfactant show the same level of absorbance for the Zn- DPC complexes. The maximum absorbance is attributed to the maximum amount of

the surfactant dissolved within the micelle since at the surfactant concentrations above the *CMC* the solubilization capacity of a surfactant becomes maximum which may depend on the miceller shape [122]. The absorbance of Zn – DPC complexes are not decreased even after appearance of the CMC of SDS (at 25 °C CMC of SDS in pure water is 8.2×10^{-3} M). The charge density of this anionic surfactant's micelle does not provide any repulsive environment for the incoming metal ions; rather it should facilitate entrance of the metal ion. As a result the absorbance for Zn – DPC complexes is found to be greater in the micellar concentration of SDS.

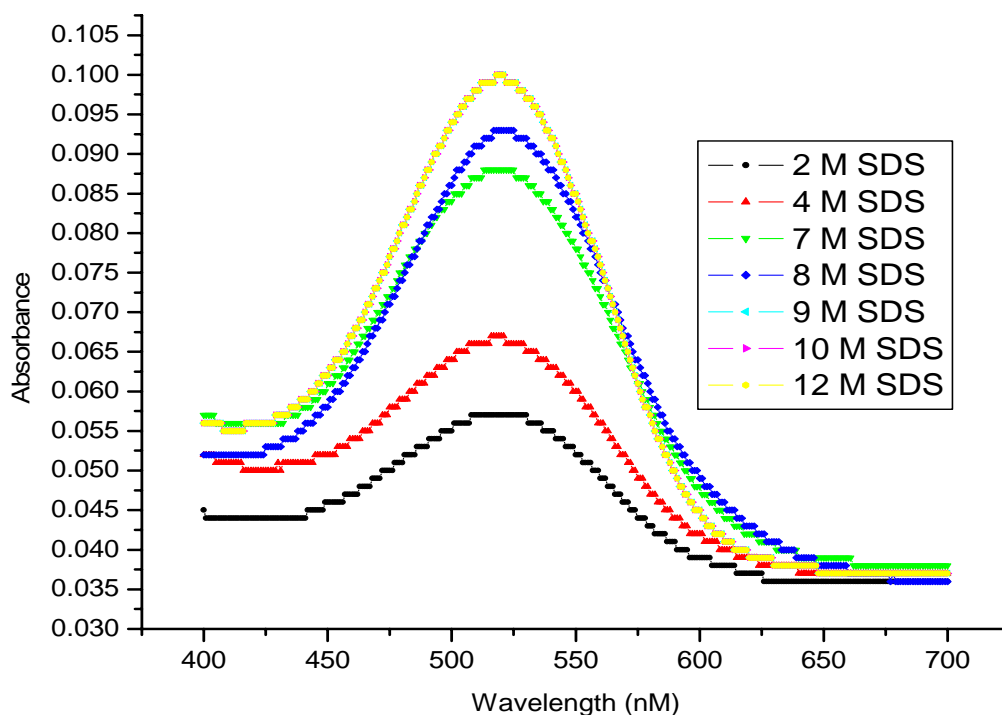


Figure 3.78 Effect of SDS concentrations on absorption spectra of Zn- DPC complex.

Table 3.11 Absorbance of Zn - DPC complexes at different concentrations of SDS

concentration (mM)	absorbance
2	0.057
4	0.067
7	0.088
8	0.093
9	0.1
10	0.1
12	0.1

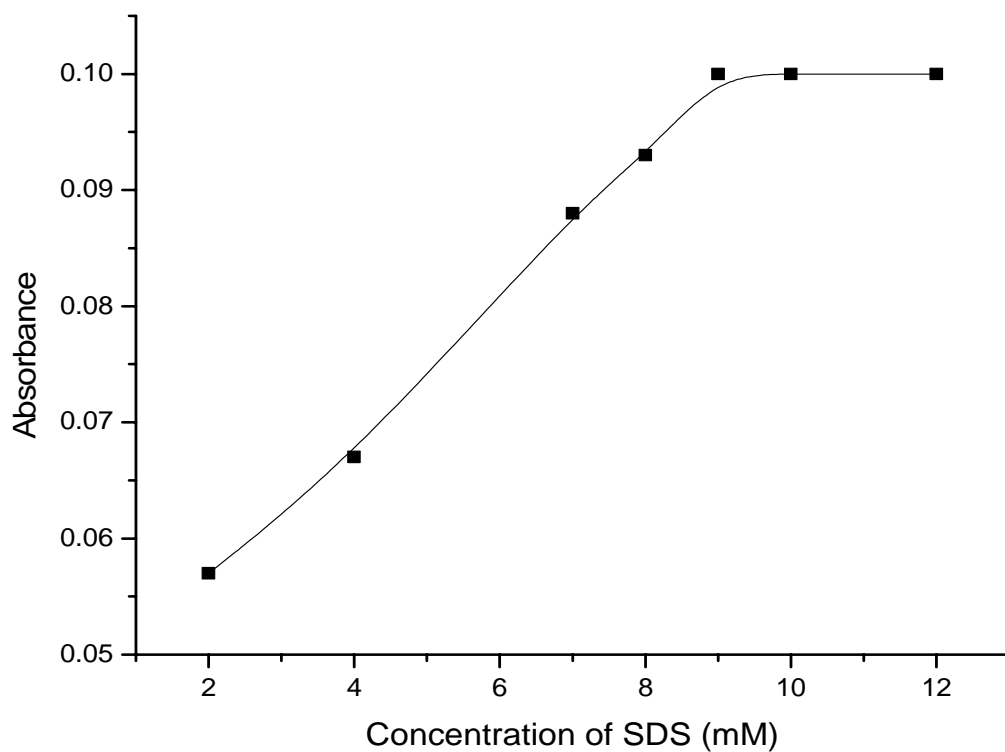


Figure 3.79 Absorbance of Zn- DPC complexes at different concentration of SDS.

Figure 3.80 show the Cd-DPC absorbance in presence of different concentrations of TTAB. Similar trend for change of absorbance, as for Zn – DPC complexes, were obtained. But in this case although the absorbance decreases at a concentration of the surfactant above CMC but unlike the Zn – DPC complexes the absorbance of Cd- DPC complexes did not reach zero even above the CMC. This is because of less charge density of Cd, compared to Zn.

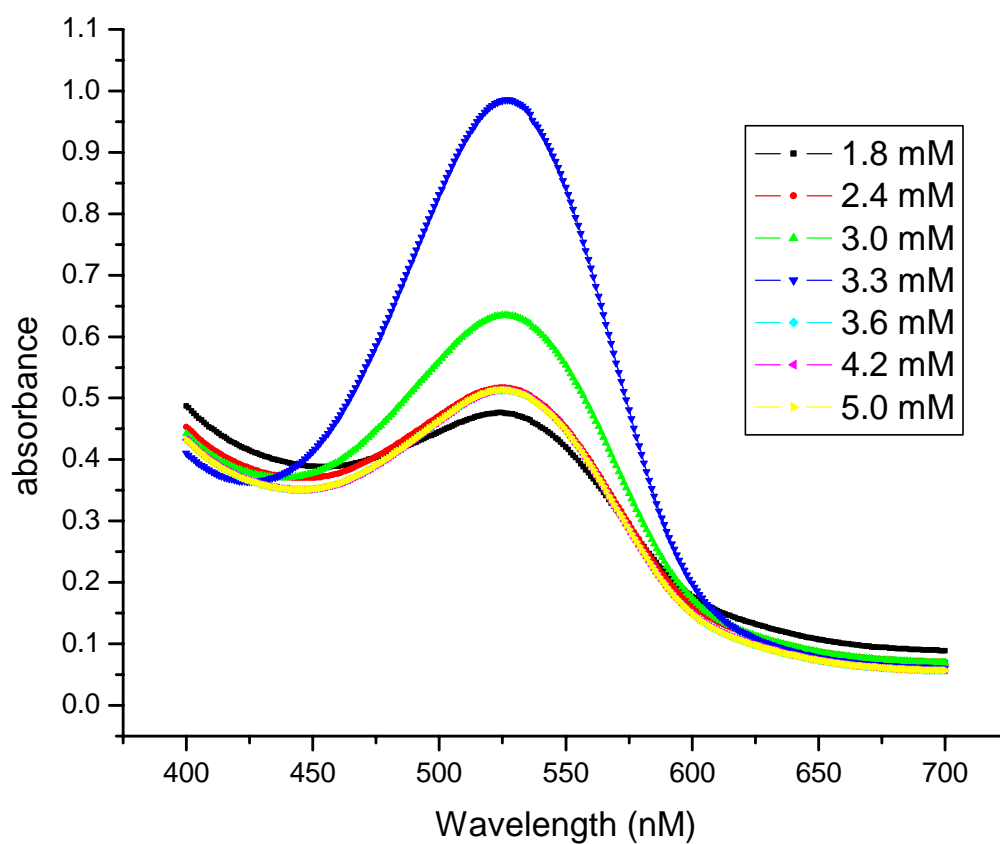


Figure 3.80 Effect of TTAB concentrations on absorption spectra of Cd- DPC complex.

But Cd is weakly hydrated due to larger ionic radius, compared to Zn. So the presence of $[Cd^{2+}]$ increases the concentration of free water molecules which causes the micellar surface charge to be less intense. As a result the entrance of cadmium ions into the micellar surface, to coordinate with the ligand, experiences less electrostatic repulsion. Similar trend of change of absorption was observed for Hg - DPC complexes in different concentrations of TTAB

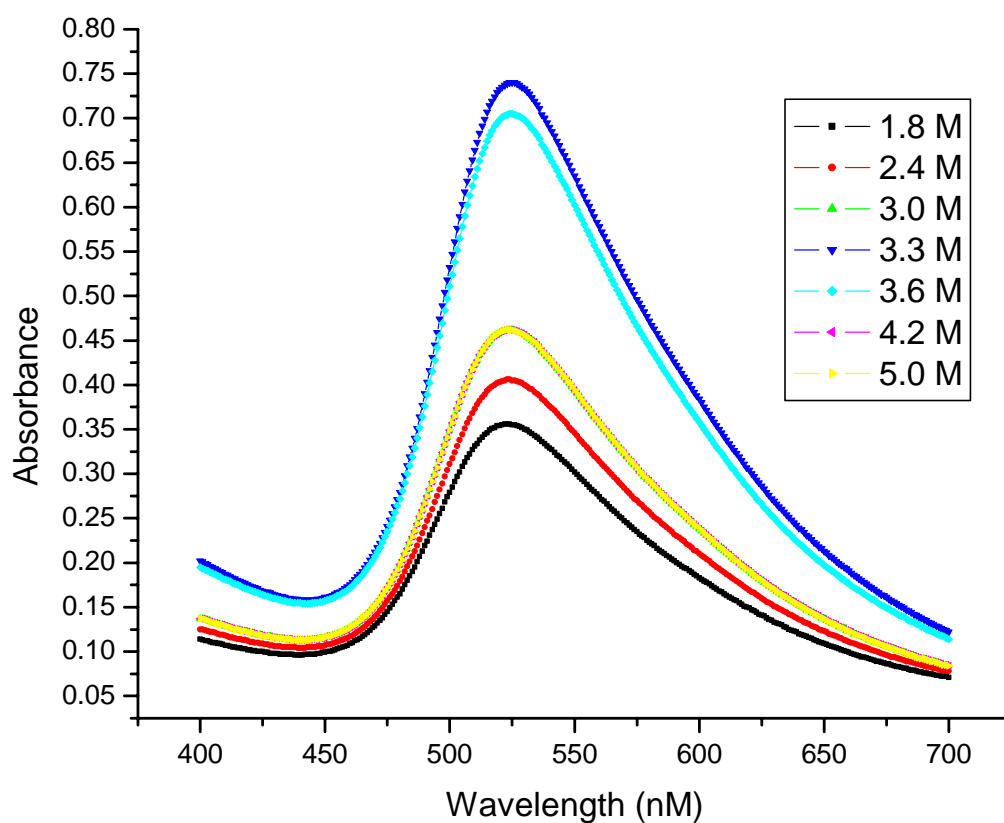


Figure 3.81 Effect of TTAB concentrations on absorption spectra of Hg- DPC complex.

Table 3.12 Absorbance of Hg – DPC complexes at different concentrations of TTAB

concentration (mM)	absorbance
1.8	0.356
2.4	0.406
3.0	0.462
3.3	0.740
3.6	0.705
4.2	0.462
5.0	0.462

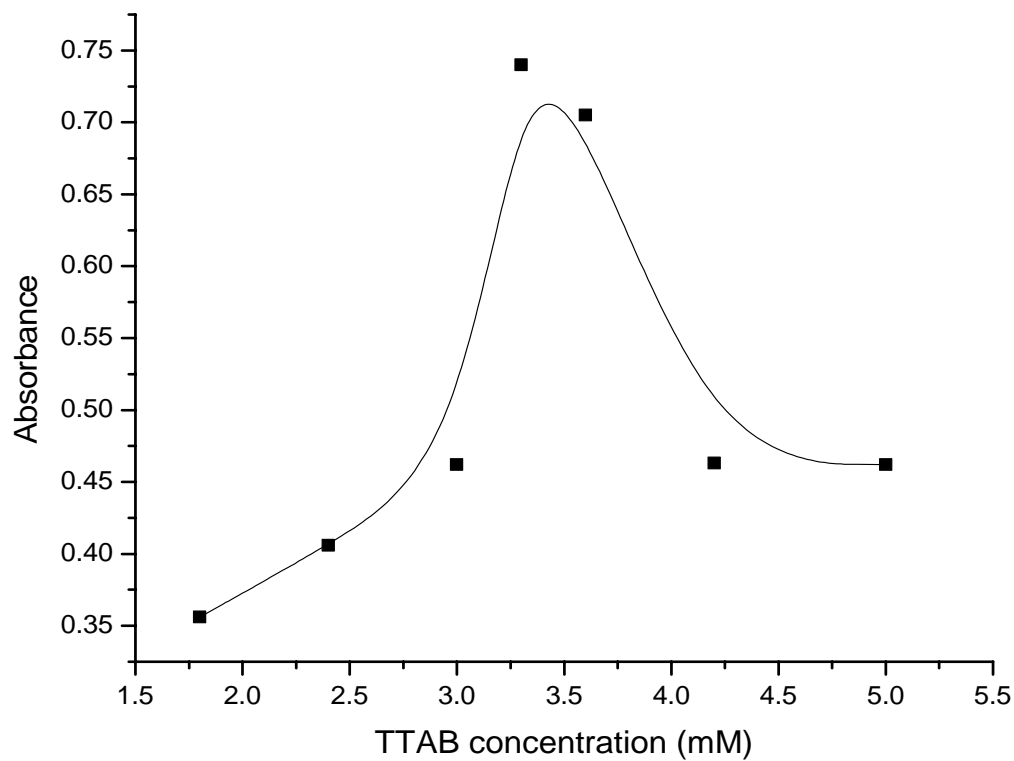


Figure 3.82 Absorbance of Hg- DPC complexes at different concentration of TTAB.

Figure 3.83 shows spectra for a Zn(II) DiPhenylCarbazid (DPC) complexes in different concentrations of aqueous solutions of CTAB ranging from 0.3mM to 1.5 mM concentration at 25°C. It reveals that an increase of concentration of CTAB (below the CMC) causes an increase of absorbance.

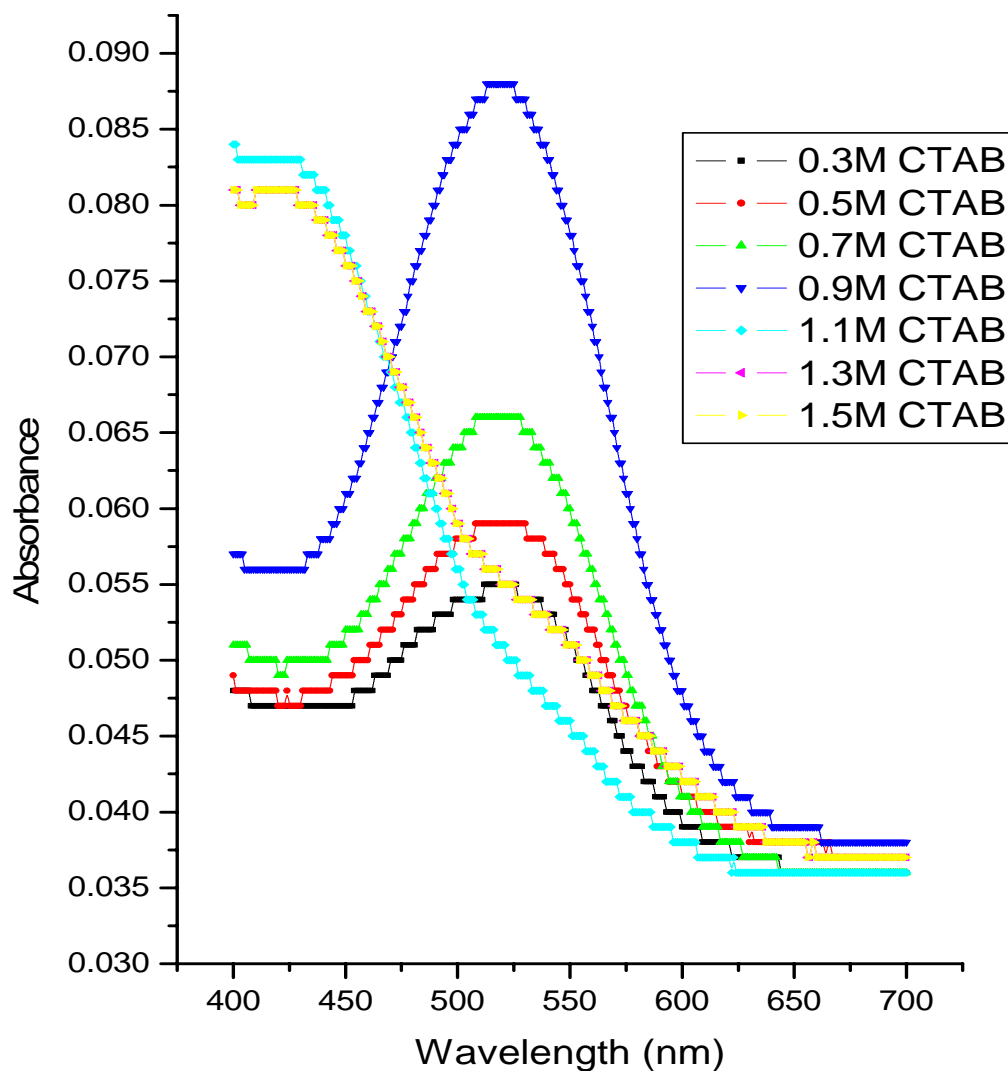


Figure 3.83 Effect of CTAB concentrations on absorption spectra of Zn- DPC complex.

But at concentrations of CTAB above the CMC (the CMC of CTAB at 25°C in presence of 8.26×10^{-4} M DPC was found to be 0.9×10^{-3} M) no absorption peaks are obtained. This shows that Zn - DPC complexation was not possible at the micellar concentrations of

CTAB. These restrictions of complexation in the CTAB micelles are attributed to the larger chain length of the CTAB aggregates since an increase in the chain length of the hydrophobic portion of the surfactant generally results in increase of solubilization capacity in the hydrocarbons in the interior of the micelle in aqueous media [3]. Another possible reason for this is due to greater surface charge density of CTAB, compared to that of TTAB (table 3.1). As a result in the micellar solution of CTAB no absorbance was found (figure 3.84).

Table 3.13 Absorbance of Zn – DPC complexes at different concentrations of CTAB

Concentration of CTAB (mM)	Absorbance
0.3	0.054
0.5	0.059
0.7	0.073
0.9	0.089
1.1	0
1.3	0
1.5	0

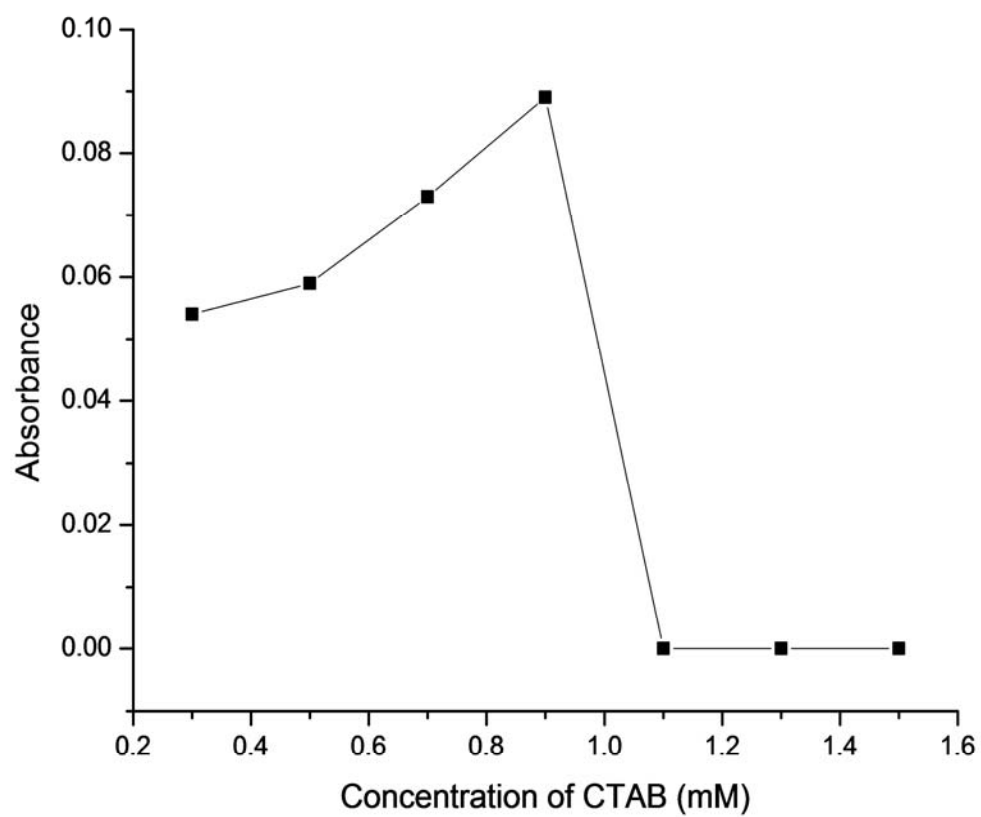


Figure 3.84 Absorbance of Zn- DPC complexes at different concentration of CTAB.

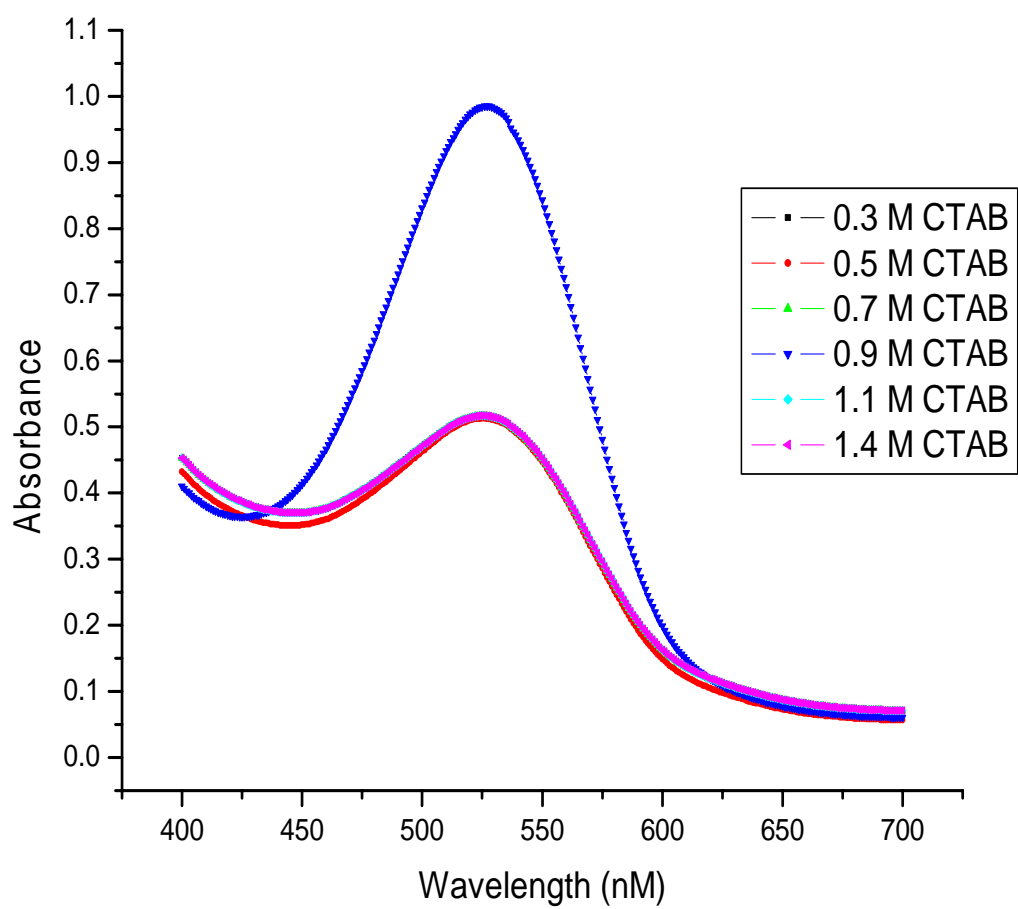


Figure 3.85 Absorption spectra of Cd- DPC complexes at different concentration of CTAB.

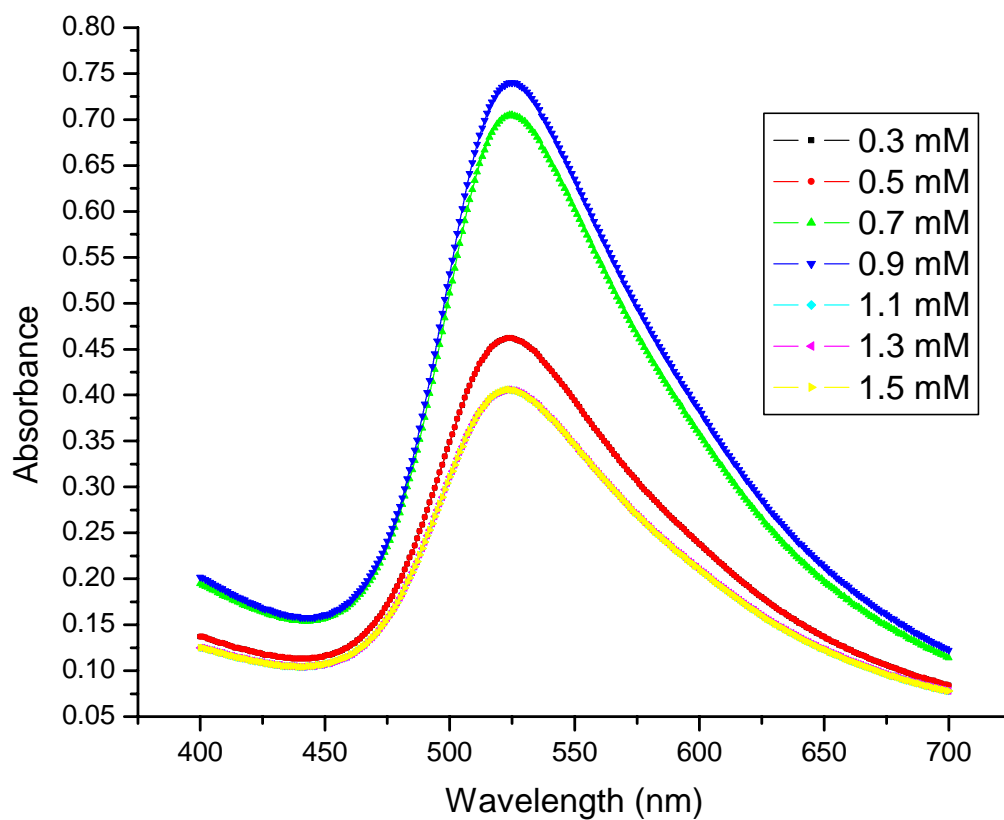


Figure 3.86 Absorption spectra of Hg- DPC complexes at different concentration of CTAB.

Similar trend of change of absorption for Zn- DPC complexes are obtained in cases of different concentrations of OTAB (fig 3.87). At a concentration above the CMC of OTAB, the metal- ligand complexation was not possible as a result no absorbance at the visible range was obtained. This suggests that the interaction site for DPC within the OTAB micelle is at the inner core, compared to the interaction site for the CTAB with the micelle.

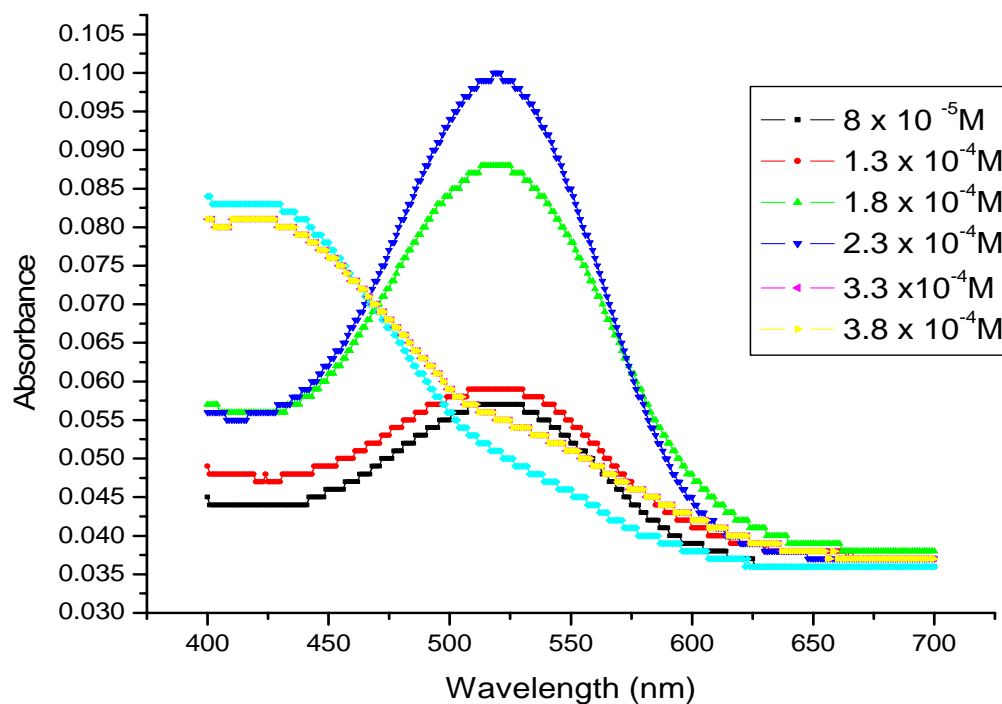


Figure 3.87 Absorption spectra of Zn- DPC complexes at different concentration of OTAB.

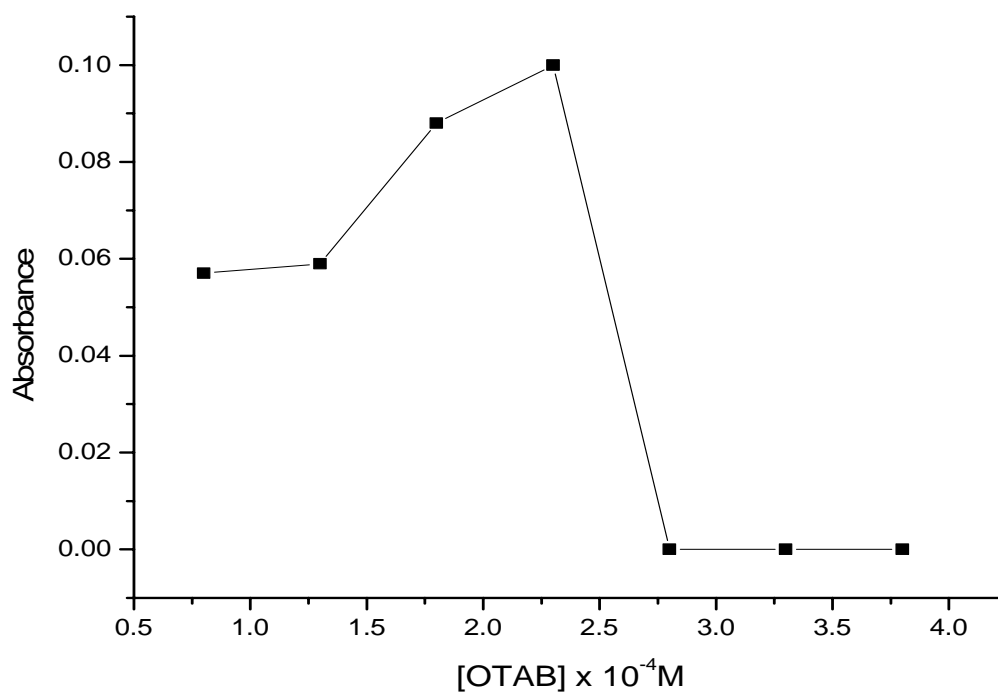


Figure 3.88 Absorbance of Zn- DPC complexes at different concentration of OTAB.

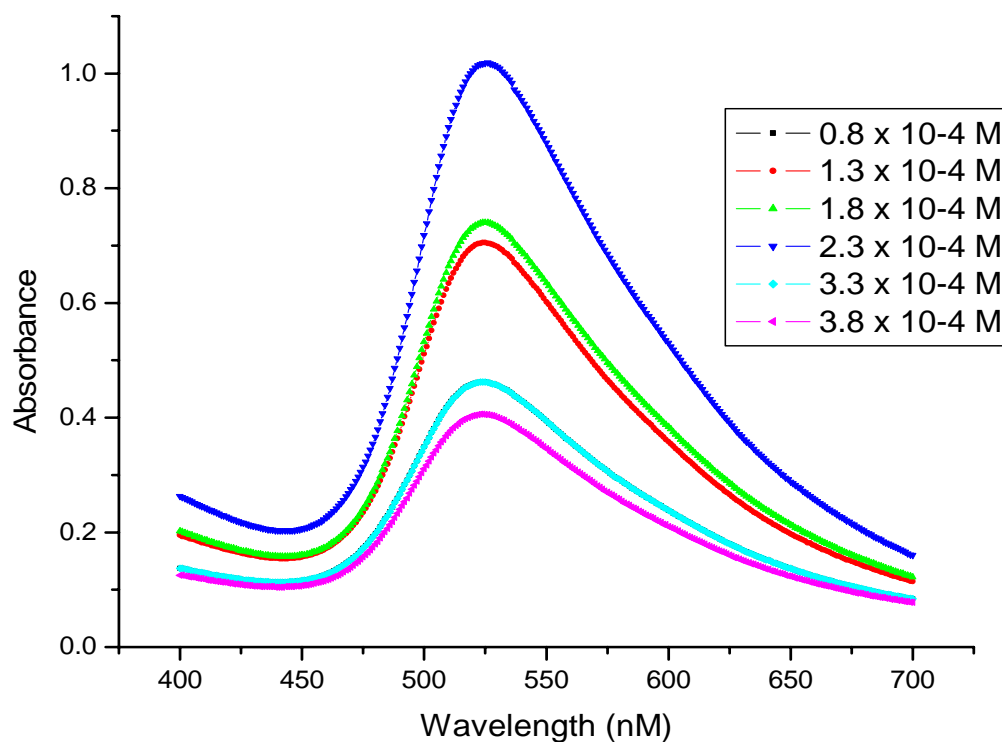


Figure 3.89 Absorption spectra of Hg- DPC complexes at different concentration of OTAB.

Hg –DPC complexation was found to be possible event at the micellar concentrations of OTAB (fig 3.89). It is due to the larger ionic radius Hg. Hg is weakly hydrated, compared to Zn. So the presence of [Hg] increases the concentration of free water molecules which causes the micellar surface charge to be less intense. As a result the entrance of Hg^{2+} ions into the micellar surface, to coordinate with the ligand, experiences less electrostatic repulsion. Similar results were obtained for Hg complexation in the micellar solution of TTAB (fig 3.81) and CTAB (fig 3.86)

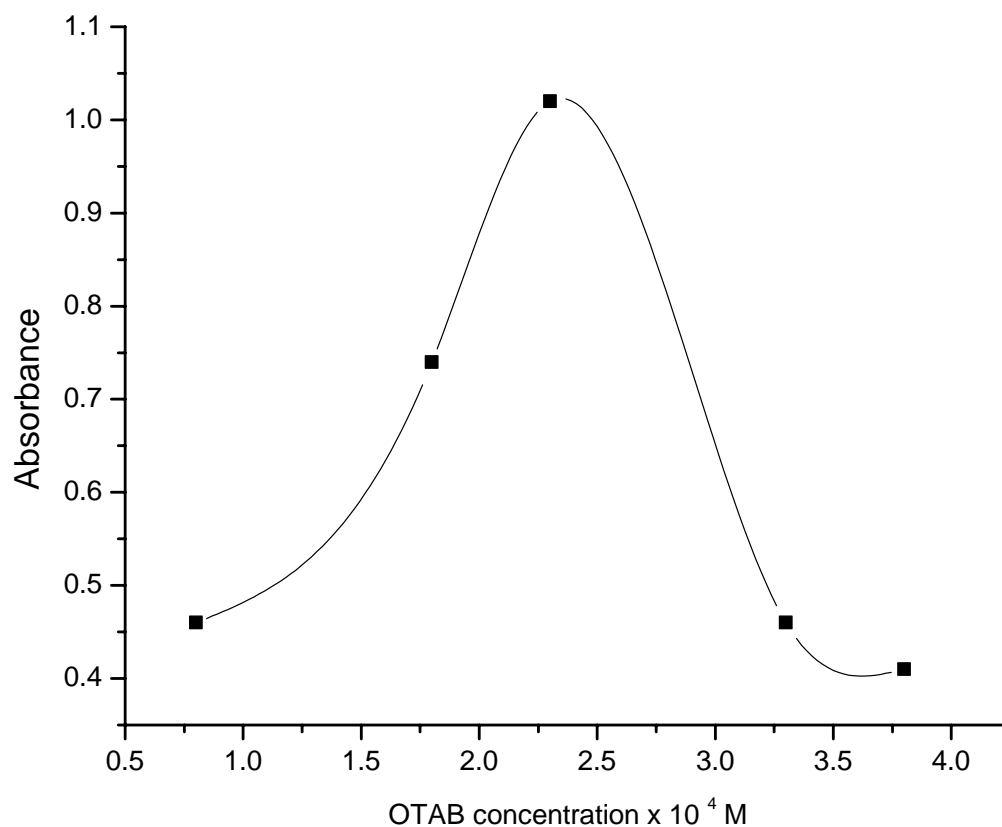


Figure 3.90 Absorbance of Hg- DPC complexes at different concentrations of OTAB.

3.16 NMR EXPERIMENTS FOR MICELLIZATION OF THE SURFACTANTS AND THE INTERACTIONS OF DPC WITH THESE SURFACTANTS' MICELLES.

In some previous experiments NMR parameters as the chemical shift and relaxation time have been successfully utilized to study the formation of micelle and the relevant properties [123-125]. The ¹H chemical shifts appear very sensitive to nonbonding interactions and subtle changes in the total environment of surfactant units and additive molecules. Below the CMC the average environment of various protons in the surfactant tail is aqueous. But above the CMC, the hydrocarbon chain mostly resides in

the molecular interior surrounded by an amphipathic environment which may account for some changes in the chemical shifts [126]. To obtain essential information about the micellar effect on the chemical shifts ^1H NMR experiments were carried out for the solutions of TTAB, CTAB and OTAB at concentrations below and above CMC. In order to obtain essential information about the solubilization sites provided by the surfactants' micelles for the dissolved DPC few ^1H NMR experiments were carried out for the micellar solutions of TTAB, CTAB and OTAB with $8.26 \times 10^{-4}\text{M}$ dissolved DPC.

Figure 3.92 and 3.93 show the ^1H NMR spectra of TTAB solutions at concentrations below and above CMC (i.e. 3.0 mM and 3.75 mM). Molecular structure of this surfactant together with the peak assignments are attached with these figures.

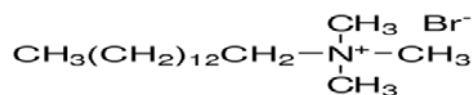


Figure 3.91 molecular structure of TTAB

Conclusion

Micellar solutions of surfactants are extensively used in a wide range of practical applications. So the thermodynamic properties for adsorption and micellization of a series of cationic surfactants along with the temperature effect and salt's (NaCl) effect on their CMC are studied. Counter ion binding and Surface Excess Concentration (Γ) studies were carried out to understand the interaction of the surfactant ion with counter ions, the surface charge density and the relative tendency of the surfactant towards bulk and the air water interface which is relevant to the surfactant's efficiency. We were interested to find out the location of the solubilized substance (DPC) within the micelle. Since the solubilization site may affect the efficiency of the Solubilized substances, which is important in the field of the treatment of various metal related illnesses and Chelation Therapy. To accomplish this Conductimetric, Surface tension, UV and NMR studies have been carried out. The Specific outcomes of the present studies are:

- i. CMC of TTAB and CTAB were found to increase with increase of temperature (up to 313K) which is due to thermal solubility of the surfactant monomers. But further increase in temperature, above that range, there has been decrease of the CMC values which may be due to their dehydration effect.
- ii. Two CMC values were obtained in case of OTAB. The CMC values were found to increase with increase of our selected range of temperature.
- iii. Increase of chain length, in the studied series of surfactants, causes decrease of CMC. Stauff- Klevens equation was applied in this case to observe the change in CMC values with the number of carbon atoms present in the alkyl chains. It

shows that, in pure water, change in CMC values of cationic surfactants follow the Stauff- Klevens equation. But it was not followed in presence of electrolyte (NaCl). It shows that the hydrophobic interaction among the alkyl chains has been favored in pure water whereas in presence of electrolyte the interaction between the hydrophilic (charged) portion and the counterions becomes more significant in micelle formation.

- iv. ΔG° and ΔH° values were found to be negative whereas ΔS° values were positive which shows the spontaneity of the adsorption and micellization of these surfactants. ΔG_{ad}° values were found to be more negative than the ΔG_m° values which shows that adsorption is more spontaneous (and prior) process than their micellization.
- v. A linear relationship of ΔG_m° and number of carbon atoms (n) in the alkyl chain of the surfactant in pure water has been observed. Thus higher negative ΔG_{ad}° and ΔG_m° value for a longer chain makes its adsorption and micellization more spontaneous. Both ΔG_{ad}° and ΔG_m° values were found to be more negative where as ΔS_m° and ΔS_{ad}° values were found to be more positive in presence of the electrolyte than those in pure water.
- vi. The surfactant with longer alkyl chain length has the ability of higher degree of Counterion binding. So greater Surface Excess Concentration (Γ) values were obtained for the surfactant with longer alkyl chain. For CTAB and OTAB's first micellization a linear relationship is observed between surface excess

concentration and the counter ion binding, which is due to greater degree of binding by a surfactant of larger chain. For the second micellization of OTAB this linear relationship becomes insignificant which shows that the second micellization of OTAB was possible with gradual replacement of the bound counter ion by the new surfactant monomers.

- vii. Both counter ion binding (β) and the surface excess concentration (Γ) values were found to decrease gradually with increase of temperature which shows that the surfactants' effectiveness of adsorption decrease with increase of temperature. The electrolytes concentration causes an increase of this effectiveness.
- viii. Experimental results show that the Krafft point (T_K) of TTAB, CTAB and OTAB are 12.4°C, 24.7 °C and 36.5 °C respectively. It was not possible to carry out the experiments above 323K because of greater chance of solvent evaporation.
- ix. Increase of the surfactant's concentrations raises the amount of solubilized DPC which favors more Metal- DPC complexation. So the absorbance for the metal-ligand complexes was found to increase with increase of surfactants' concentration. But at the micellar concentration the availability of the ligand for the metals to make complexes becomes restricted due to the micellar surface charge. As a result lower absorbance values were obtained for the metal – DPC complexes at the micellar concentrations (or at above the micellar concentrations) of the surfactants. This restriction is not found for micellar concentration of SDS since it is an anionic surfactant and it's negatively charged micellar surface favors the binding of Metal to the solubilized ligand.

- x. The restriction of Hg – DPC binding was minimized by the associated water molecules, since it has larger ionic radius and lower charge density (compared to Zn).
- xi. The locations of solubilized DPC in the surfactants micelles were confirmed by the NMR studies which reveal that:
 - (a) The solubilization site for DPC in TTAB is in between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise of outer core of the micelle interior.
 - (b) The solubilization site for DPC in CTAB is more deeply seated in the palisade layer of the micelle.
 - (c) The solubilization site for DPC in OTAB is even more deeply seated than the palisade layer, almost near about the inner core of the micelle.

Scope of Further Work

- (1) Research work may be carried out to observe the effect of different electrolytes on the adsorption, micellization and the relevant thermodynamic properties these surfactants.
- (2) Works may be carried out with different types of surfactants and ligands to understand the effect of surfactants and ligands structure on the solubilization sites of these ligands within the surfactants micelles.
- (3) There is a scope of doing works to understand the effect of micellar environment on the coordination ability and related behavior of the solubilized ligands. These studies will give much important and effective information for the field of Chelation therapy and the treatment of metal related illness.

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APPENDIX

4.1. CALCULATIONS RELATED FOR CONDUCTIVITY MEASUREMENTS

(a). Calculations for Degree of ionization (α) and Counter ion binding (β):

$\alpha = \text{Slope of post micellar zone} / \text{Slope of post micellar zone}$

Then, $\beta = 1 - \alpha$ 2.1

(b) Thermodynamic parameters (ΔG_m° , ΔS_m° and ΔH_m°) calculations for TTAB in Pure water:

For ΔG_m° calculation (in pure water) we used the following equation:

$\Delta G_m^\circ = (1 + \beta) RT \ln X_{CMC}$ 2.2

Here, X_{CMC} is the mole fraction of the surfactant at the CMC.

Example: it was found that at 293 K the Degree of ionization (α) of TTAB in pure water is 0.302 and the volume of TTAB (of concentration 1.5×10^{-2} M) added to 50 cm³ pure water in order to reach the CMC is 13.56 cm³.

So, mole of TTAB needed for CMC = $(13.56 \times 1.5 \times 10^{-2}) / 1000$

$= 2.034 \times 10^{-4}$ mol

Mole water = $50 / 18 = 2.778$ mol

Total mole in the system = $(2.034 \times 10^{-4}) + 2.778 = 2.778$

Mole fraction of TTAB at CMC = $(2.034 \times 10^{-4}) / 2.778$

$= 7.32 \times 10^{-5}$

So $\ln X_{CMC} = -9.762$

So, $\Delta G_m^\circ = (1 + \beta) RT \ln X_{CMC}$
 $= (1 + 0.698) \times 8.314 \times 293 \times (-9.762)$
 $= -40.378 \text{ KJ mol}^{-1}$.

For ΔS_m° calculation we followed the following equation:

$\Delta S_m^\circ = - \{ \delta (\Delta G_m^\circ) / \delta T \}$ 2.3

For this calculation if we plot ΔG_m° vs. T in excel sheet we get a polynomial equation of order 2, as:

$\Delta G_m^\circ = 0.035 T^2 - 41.228 T - 31318$

Thus at 293 K we get $\Delta S_m^\circ = - \{ \delta (\Delta G_m^\circ) / \delta T \} = 20.718 \text{ JK}^{-1} \text{ mol}^{-1}$.

For ΔH_m° calculation we followed the following equation:

$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ$ 2.4

By using the values of T, ΔS_m° and ΔG_m° we can calculate the ΔH_m° values.

(C) Thermodynamic parameters (ΔG_m° , ΔS_m° and ΔH_m°) calculations for TTAB in presence of 0.01 M aqueous NaCl solution:

For ΔG_m° calculation (in presence of 0.01 M aqueous NaCl) we used the following equation:

$\Delta G_m^\circ = RT [\ln X_{CMC} + (1-\alpha) \ln (X_{CMC} + X_s)]$ 2.5

Here X_{CMC} is the mole fraction of the surfactant and X_s is the mole fraction of NaCl at the CMC.

Example: it was found that at 293 K the Degree of ionization (α) of TTAB in pure water is 0.204 and the volume of TTAB (of concentration 1.5×10^{-2} M) added to 40 cm^3 0.01M NaCl solution in order to reach the CMC is 7.39 cm^3 .

So, mole of TTAB needed for CMC = $(7.39 \times 1.5 \times 10^{-2}) / 1000$

$$= 1.1085 \times 10^{-4} \text{ mol}$$

Mole water = $47.39 / 18 = 2.6327 \text{ mol}$

Mole of NaCl = $(47.39 \times 0.01) / 1000 = 4.739 \times 10^{-4} \text{ mol}$

Total mole in the system = $(1.1085 \times 10^{-4}) + (4.739 \times 10^{-4}) + 2.6327 = 2.6333$

The mole fraction of the surfactant (X_{CMC}): $1.1085 \times 10^{-4} / 2.6333 = 4.2095 \times 10^{-5}$.

The mole fraction of the salt (X_s): $4.739 \times 10^{-4} / 2.6333 = 1.7996 \times 10^{-4}$.

Thus from equation 2.5 we get the ΔG_m° value at 293 K = $-40.856 \text{ KJ mol}^{-1}$.

Then the ΔS_m° and ΔH_m° values are calculated by using equation 2.3 and equation 2.4 respectively.

4. 2. CALCULATIONS RELATED TO SURFACE TENSION MEASUREMENT

2.5a. Calculation of surface excess concentration (Γ):

Following equation was used to calculate the surface excess concentration in pure water or in presence of NaCl solutions:

$$\Gamma = -1/RT (\delta\gamma / \delta \ln C)_{T,P} \dots\dots\dots 2.6$$

At 293 K the $\delta\gamma / \delta \ln C$ value (from the slope of the surface tension data) was found to be -34.418.

So the Γ value is:

$$\Gamma = 1/ 4.606 \times 1/ 8.314 \times 1/ 293 \times (-34.418/1000)$$
$$= 3.067$$

2.3 b. Thermodynamic parameters (ΔG_{ad}° , ΔS_{ad}° and ΔH_{ad}°) of adsorption calculations (for TTAB) in pure water or in presence of NaCl:

For ΔG_{ad}° calculation (in pure water or in presence of 0.01 M aqueous NaCl) we used the following equation:

$$\Delta G_{ad}^{\circ} = \Delta G_m^{\circ} - (\pi_{CMC} / \Gamma) \dots\dots\dots 2.7$$

Here π is the surface pressure (the reduction in surface tension). The value of π was found to be 41 for TTAB in 0.01 M NaCl solution at 293 K. so the we get the ΔG_{ad}° value as :

$$\Delta G_{ad}^{\circ} = -40.856 - (41/3.067) = - 54.224 \text{ KJ mol}^{-1}.$$

The ΔS_{ad}° and ΔH_{ad}° were calculated by the same way as for ΔS_m° and ΔH_m° calculations.

Table 4.1 Data for Specific conductance ($\mu\text{S cm}^{-1}$) of aqueous TTAB solutions in pure water at different temperatures.

[TTAB] x 10 ⁻⁴ M	293K	298K	303K	308K	313K	318K	323K	328 K
0	1	1.03	3.59	2.9	3.4	3.6	3.8	3.8
3.66	25.8	29.2	33.5	35	40	40	40	40
7.14	54	57	61	66.2	73	74	74	74
10.47	82	85	88.5	93	106	107	107	106
13.64	105	108	114	122	135	136	136	136
16.67	129	132	138.5	150	164	165	166	166
19.57	154	158	163	174	192	193	194	193
22.34	176	182	186	196	220	220	220	220
25	198	201	207	219	243	243	244	244
27.55	218	224	228	242	270	270	270	270
30	238	245	248	262	292	292	292	293
32.35	245	263	267	282	316	318	319	318
34.62	250	272	285	302	336	338	338	338
36.79	255	278	297	321	356	358	358	360
38.89	260	283	302	337	376	381	381	382
40.9	265	289	308	352	389	397	397	397
42.9	270	294	313	358	396	404	405	405
44.7	275	298	318	363	402	411	412	412
46.5	279	303	323	368	408	418	419	420
48.3	283	307	327	373	414	424	426	427
50	287	312	332	378	419	430	432	434
51.31	290	315	335	382	424	435	438	439
52.6	294	318	339	386	428	440	442	445

Table 4.2 Data for Surface tension (mN/m) of TTAB in pure water at different temperatures.

Log ₁₀ C	298K	303K	308K	313K	318K	323	328
-3.53	63.3	63.6	63.9	64	62.6	62.2	62
-3.24	54.5	55.6	56.2	56.3	55.9	55.6	54.5
-3.07	49.6	50.9	51.3	52.2	52.3	51.8	51.4
-2.95	45.8	47.7	48.3	49.4	49.6	49	48.4
-2.87	43.3	45.5	46.5	47.4	47.4	47.1	46.5
-2.79	40.9	43.1	44.4	45.7	45.7	45.5	45
-2.73	39	41.5	42.8	44	44.5	44.2	43.5
-2.68	37.6	40.1	41.6	42.9	43.2	42.8	42.3
-2.64	36.3	38.7	40.6	41.8	42.4	41.8	41.5
-2.6	35	37.9	39.6	40.8	41.4	40.9	40.4
-2.57	34.4	36.9	38.9	40.3	40.8	40	39.7
-2.54	33	36.1	37.9	39.5	40.1	39.6	39.2
-2.51	32.6	35.1	37.2	38.7	39.6	39	38.5
-2.48	31.4	34.2	36.5	38.2	38.9	38.1	37.5
-2.46	31	33.7	35.9	37.5	38.5	37.6	36.9
-2.44	31	33	35.3	36.9	37.9	37.4	36.5
-2.42	31	33	34.6	36.5	37.4	36.9	36.4
-2.4	31	33	34.6	36	36.7	36.7	36.4
-2.38	31	33	34.6	35.4	36.7	36.7	36.4
-2.36	31	33	34.6	35.4	36.7	36.7	36.4
-2.35	31	33	34.6	35.4	36.7	36.7	36.4
-2.34	31	33	34.6	35.4	36.7	36.7	36.4
-2.33	31	33	34.6	35.4	36.7	36.7	36.4

Table4.3 Data for Specific conductance (μSCm^{-1}) at of aqueous TTAB solutions in 0.01M NaCl different temperatures.

Concentration of TTAB x 10 ⁻⁴ M	293K	298K	303K	308K	313K
0	1082	1086	1094	1109	1116
3.66	1116	1120	1129	1144	1152
7.14	1150	1151	1162	1178	1184
10.47	1181	1183	1194	1210	1217
13.64	1211	1213	1224	1242	1250
16.67	1239	1241	1252	1270	1280
19.57	1267	1269	1279	1298	1308
22.34	1293	1294	1306	1328	1337
25	1304	1320	1330	1345	1352
27.55	1309	1332	1345	1351	1360
30	1313	1337	1351	1356	1367
32.35	1318	1342	1356	1362	1373
34.62	1322	1346	1361	1367	1380
36.79	1326	1351	1366	1372	1387
38.89	1330	1355	1370	1377	1393
40.9	1334	1359	1375	1382	1398
42.9	1338	1363	1379	1386	1404
44.7	1342	1367	1383	1391	1411
46.5	1345	1370	1386	1395	1416
48.3	1348	1374	1391	1399	1421
50	1352	1378	1395	1403	1426

Table 4.4 Data for Surface tension(mN/m) of TTAB in 0.01M NaCl at different temperatures.

Log ₁₀ C	Surface tension (mN/m) at 293K	Surface tension (mN/m) at 298K	Surface tension (mN/m) at 303K	Surface tension (mN/m) at 308K	Surface tension (mN/m) at 313K
-3.53	63.3	63.4	63.7	63.1	63.8
-3.24	53.3	53.9	54.5	54	55
-3.07	47.6	48.4	49.3	49.1	50
-2.95	43.2	44.8	45.7	45.9	46.3
-2.87	40.7	42.3	43.1	43.1	44.1
-2.79	38	39.8	41.1	41	41.5
-2.73	35.5	37.9	39	39	39.6
-2.68	33.9	36.5	37.3	37.1	38.3
-2.64	32.9	35.2	35.9	36	36.9
-2.6	32.6	33.7	35	34.4	36.1
-2.57	32.6	33.3	34	34.4	36.1
-2.54	32.6	33.3	33.6	34.4	36.1
-2.51	32.6	33.3	33.6	34.4	36.1
-2.48	32.6	33.3	33.6	34.4	36.1
-2.46	32.6	33.3	33.6	34.4	36.1
-2.44	32.6	33.3	33.6	34.4	36.1
-2.42	32.6	33.3	33.6	34.4	36.1
-2.4	32.6	33.3	33.6	34.4	36.1
-2.38	32.6	33.3	33.6	34.4	36.1
-2.36	32.6	33.3	33.6	34.4	36.1

Table 4.5 Counter ion binding and surface excess concentration of TTAB at different temperatures

Temperature /K	Counter ion binding of TTAB	Surface excess concentration of TTAB
293	0.7	2.71
298	0.69	2.46
303	0.68	2.24
308	0.67	2.04
313	0.64	1.89
318	0.62	1.87
323	0.6	1.86

Table 4.6 Data for Specific conductance (μScm^{-1}) of aqueous CTAB solutions in pure water at different temperatures.

[CTAB] x 10^{-5}M	298K	303K	308K	313K	318K	323K	328K
0	0.96	1.2	1.48	1.52	1.6	2.6	3
9.76	10.5	11	12.1	12.3	12.5	15	16
19.05	19.1	21	22	22.4	24	27	28
27.91	27.6	29.8	31.5	33	34	39	39
36.36	36.4	38.5	40.5	42.4	44	49	50
44.44	44.5	46.5	48.7	52	54.5	60	60
52.17	52	54.4	57	61	64	70	70
59.57	59	61.4	65.3	69	73.8	79	80
66.67	66.5	69	73	77	82	88	89
73.47	73.6	76	80	85	89	98	98
80	79.8	82.5	86.4	92	97	105	106
86.27	84.5	89	93.4	100	106	114	115
92.31	86.4	92.9	99.4	106	113	121	123
98.11	88	94.6	103.4	111.3	116.3	126	127
103.7	89.5	96.3	105.1	113.3	118.7	129	130
109.1	91	98.2	107	115.5	121	131	133
114.29	92.7	99.8	108.8	117	123.2	134	136
119.3	94	101.2	110.3	119	125.4	136	138
124.14	95.5	102.8	112	121	127.4	138	140
128.81	97	104.1	113.6	123	129.3	140	143
133.33	98.3	105.5	115	124.5	131	142	145
137.7	99.5	106.9	116.7	126	133	144	147
141.94	100.6	108.3	118	127.7	134.6	146	150
146.03	101.7	109.5	119.4	129.4	136.5	148	152
150	103	110.8	121	130.7	138	150	154

Table 4.7 Data for Surface tension (mN/m) of aqueous CTAB solutions in pure water at different temperatures.

Log 10 C	298 oC	303	308	313	318	323
-4.11	60.2	60.3	60.5	60.9	61	61.3
-3.81	51.5	52	52.3	52.9	53.4	53.7
-3.65	47	47.4	47.6	48.4	49.1	49.4
-3.53	43.6	44.1	44.6	45.3	46.1	46.4
-3.44	41.1	41.7	42.2	43	43.5	43.8
-3.37	39	39.7	40.4	41.3	41.9	42.2
-3.31	37.2	38.3	38.7	39.9	40.2	40.5
-3.26	35.7	36.8	37.3	38.5	38.9	39.3
-3.21	34.3	35.7	36	37.1	37.6	38
-3.18	33.6	34.4	34.8	36.2	36.9	37.4
-3.14	32.4	33.7	34.1	35.3	35.9	36.2
-3.11	31.9	32.6	33	34.2	35	35.3
-3.08	30.7	31.9	32.2	33.5	34.1	34.7
-3.06	30.4	31.1	31.6	32.8	33.6	34.3
-3.03	30.4	30.8	31.1	32.1	33.1	34.3
-3.01	30.6	31	31.1	31.8	33.4	34.4
-2.99	30.4	30.8	31.1	31.8	33.1	34.3
-2.98	30.4	30.8	31.1	31.8	33.1	34.3
-2.96	30.4	30.8	31.4	31.8	33.1	34.3
-2.94	30.4	30.8	31.1	31.8	33.1	34.3

4.8 Data for Surface tension (mN/m) of aqueous CTAB solutions in 0.01M NaCl at different temperatures.

Log ₁₀ C	293K	298K	303K	308K	313K	318K
-4.11	61	61.3	62.4	62.2	62.2	62.2
-3.81	50.6	51.2	52.9	52.5	52.8	53.4
-3.65	45.2	45.8	47.5	47.1	48	48.6
-3.53	40.7	41.5	43.6	43.5	44.1	44.8
-3.44	37.4	38.5	40.5	40.6	41.4	42.3
-3.37	35	36.2	38.3	38.5	39.1	40
-3.31	33	34.4	36.2	36.6	37.4	38.2
-3.26	32.4	32.6	34.6	34.9	35.8	36.7

-3.21	32.4	32.6	32.9	34.7	35.5	36.7
-3.18	32.4	32.6	32.7	34.7	35.5	36.7
-3.14	32.4	32.6	32.7	34.7	35.5	36.7
-3.11	32.4	32.6	32.7	34.7	35.5	36.7
-3.08	32.4	32.6	32.7	34.7	35.5	36.7
-3.06	32.4	32.6	32.7	34.7	35.5	36.7
-3.03	32.4	32.6	32.7	34.7	35.5	36.7
-3.01	32.4	32.6	32.7	34.7	35.5	36.7
-2.99	32.4	32.6	32.7	34.7	35.5	36.7
-2.98	32.4	32.6	32.7	34.7	35.5	36.7
-2.96	32.4	32.6	32.7	34.7	35.5	36.7
-2.94	32.4	32.6	32.7	34.7	35.5	36.7

4.9 Data for Specific conductance (μScm^{-1}) at of aqueous CTAB solutions in 0.01M NaCl at different temperatures.

[CTAB] x 10^{-5}M	293 K	298 K	303 K	308 K	313 K	318K
0	1078	1079	1081	1087	1086	1085
7.84	1107	1110	1112	1116	1118	1114
15.38	1137	1141	1141	1147	1147	1141
22.64	1165	1169	1171	1174	1174	1168
29.63	1194	1197	1200	1198	1200	1194
36.36	1221	1224	1226	1228	1226	1220
42.86	1246	1250	1251	1250	1251	1243
49.12	1271	1275	1278	1278	1274	1266
55.17	1280	1286	1300	1301	1300	1289
61.02	1285	1291	1327	1321	1311	1299
66.7	1289	1296	1336	1326	1318	1305
72.13	1294	1300	1342	1331	1323	1311
77.42	1298	1305	1346	1336	1329	1317
82.54	1302	1309	1351	1341	1334	1323
87.5	1305	1314	1355	1346	1340	1329
92.31	1310	1318	1359	1352	1344	1334
96.97	1313	1321	1364	1355	1350	1339
101.49	1317	1326	1368	1360	1355	1345

Table 4.10 Counter ion binding and surface excess concentration of CTAB at different temperatures

Temperature /K	Counter ion binding of CTAB	Surface excess concentration of CTAB
298	0.71	2.5
303	0.69	2.38
308	0.68	2.32
313	0.67	2.21
318	0.66	2.14
323	0.65	2.09

Table 4.11 Specific conductance ($\mu\text{S cm}^{-1}$) of TTAB in presence of 0.001 M aqueous NaF, NaCl, NaBr, NaNO₃ and NaSO₄ solutions.

Temperature / ^o C	0.001 M NaF,	0.001 M NaCl	0.001 M NaBr	0.001 M NaSO ₄	0.001 M NaNO ₃
5	440	420	413	427	390
6	439	418	411	426	390
7	437	418	411	424	391
8	436	418	413	430	393
9	437	420	415	449	396
10	442	432	417	480	403
11	458	466	423	513	426
12	496	527	442	538	462
13	501	539	459	544	497
14	503	544	462	546	501
15	505	546	464	548	503
16	507	548	466	549	505
17	509	550	468	550	507
18	511	552	470	551	509
19	512	553	472	552	511
20	513	554	474	553	512

Table 4.12 Specific conductance (μScm^{-1}) of TTAB in presence of 0.003 M aqueous NaF, NaCl , NaBr , NaNO₃ and NaSO₄ solutions.

Temperature /° C	0.003 M NaF,	0.003 M NaCl	0.003 M NaBr	0.003 M NaSO ₄	0.003 M NaNO ₃
3	737	637	634	632	621
4	737	637	634	632	621
5	737	637	634	632	622
6	736	637	634	630	626
7	735	638	634	631	644
8	737	640	636	648	670
9	742	643	638	677	681
10	774	665	641	700	683
11	810	691	650	714	684
12	814	697	668	717	685
13	816	699	685	719	686
14	818	701	688	721	687
15	820	703	690	723	689
16	822	705	692	724	690
17	824	707	694	725	691
18	826	708	696	726	692

Table 4.13 Specific conductance (μScm^{-1}) of TTAB in presence of 0.0075 M aqueous NaF, NaCl , NaBr , NaNO₃ and NaSO₄ solutions.

Temperature /° C	0.0075 M NaF,	0.0075 M NaCl	0.0075 M NaBr	0.0075 M Na ₂ SO ₄	0.0075 M NaNO ₃
3	1136	1086	1014	1148	1218
4	1136	1086	1014	1148	1221
5	1135	1087	1013	1148	1248
6	1134	1089	1011	1152	1292
7	1136	1091	1010	1171	1299
8	1145	1093	1010	1216	1301
9	1190	1095	1010	1221	1303
10	1209	1100	1012	1223	1305
11	1212	1128	1014	1225	1307
12	1214	1165	1018	1227	1309
13	1215	1169	1037	1229	1311
14	1215	1171	1063	1230	1312
15	1216	1173	1071	1231	1313

Table 4.14 Specific conductance ($\mu\text{S cm}^{-1}$) of TTAB in presence of 0.01 M aqueous NaF, NaCl, NaBr and Na_2SO_4 solutions.

Temperature / $^{\circ}\text{C}$	0.01 M NaF,	0.01 M NaCl	0.01 M NaBr	0.01 M Na_2SO_4
3	1386	1249	1183	1390
3.5	1386	1248	1183	1390
4.5	1386	1248	1183	1390
5	1386	1247	1183	1391
5.5	1386	1246	1183	1392
6	1387	1246	1183	1396
6.5	1389	1246	1183	1405
7	1399	1247	1183	1425
7.5	1425	1248	1183	1444
8	1451	1249	1183	1462
8.5	1475	1250	1183	1472
9	1492	1253	1183	1475
9.5	1496	1260	1184	1476
10	1498	1279	1185	1477
10.5	1499	1293	1186	1478
11	1500	1300	1187	1479
11.5	1501	1303	1188	1480
12	1502	1305	1189	1481
12.5	1503	1306	1191	1482
13	1503	1307	1193	1483
13.5	1504	1308	1198	1484
14	1505	1309	1205	1485
14.5	1506	1310	1220	1486
15	1507	1311	1238	1487
15.5		1312	1247	
16		1313	1249	
16.5		1314	1250	
17		1315	1251	
17.5		1316	1252	
18		1317	1253	
18.5			1254	
19			1255	
19.5			1256	
20			1257	

Table 4.15 Krafft Temperature of CTAB at different concentrations of NaF, NaCl , NaBr, NaI, NaNO₃ and NaSO₄ solutions.

[Salt]/M	T _k (⁰ C) of CTAB in NaF	T _k (⁰ C) of CTAB in NaCl	T _k (⁰ C) of CTAB in NaBr	T _k (⁰ C) of CTAB in NaI	T _k (⁰ C) of CTAB in Na ₂ SO ₄	T _k (⁰ C) of CTAB in NaNO ₃
0	24.7	24.7	24.7	24.7	24.7	24.7
0.001	24.1	24.1	25.1	54	23.2	21.5
0.003	23.6	22.7	26	59.7	20.4	20.5
0.005	22.4	20.9	26.9	61.3	19	19.2
0.0075	21.6	18.3	27.2	61.8	19	18.8
0.01	20.1	16	27.5	61.8	21.1	18.3
0	24.7	24.7	24.7	24.7	24.7	24.7

Table 4.16 Krafft Temperature of OTAB at different concentrations of NaF, NaCl , NaBr, NaI, NaNO₃ and NaSO₄ solutions.

[Salt]/M	T _k (⁰ C) of OTAB in NaF	T _k (⁰ C) of OTAB in NaCl	T _k (⁰ C) of OTAB in NaBr	T _k (⁰ C) of OTAB in NaI	T _k (⁰ C) of OTAB in Na ₂ SO ₄	T _k (⁰ C) of OTAB in NaNO ₃
0	36.5	36.5	36.5	36.5	36.5	36.5
0.001	35.8	35	36.8	51	36	35.8
0.003	34.5	32	37	57.2	35.5	34.3
0.005	33.1	29.5	38	61	31.5	32.6
0.0075	33.1	27.8	38	65.5	28.5	32.6
0.01	33.1	26.2	38	66	28.5	32.9
0	36.5	36.5	36.5	36.5	36.5	36.5

Table4.17 Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) data for OTAB at 313K to 333 K temperatures (2nd CMC)

[OTAB]x 10 ⁻⁵ M	Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) at 313 K	Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) at 318 K	Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) at 323 K	Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) at 328 K	Specific conductance ($\mu\text{S}\text{Cm}^{-1}$) at 333 K
7	12.2	12.4	12.6	12.9	13.5
8.7	13.6	13.8	13.9	14.4	15
10.37	14.9	15.2	15.3	15.8	16.3
12.03	16.3	16.6	16.8	17.2	17.8
13.67	17.4	17.9	18	18.3	19
15.28	18.8	19	19.2	19.6	20.5
16.88	20	20.4	20.6	21.1	22
18.46	21.3	21.6	21.8	22.3	23.1
20	22.6	22.9	23.1	23.6	24.6
21.57	23.7	24.1	24.4	25	26
23.1	24.9	25.3	25.6	26.3	27.2

24.6	26	26.4	26.7	27.5	28.3
26.1	27.3	27.8	28.2	28.7	29.5
27.56	28.4	28.8	29.4	29.9	30.8
29.02	29.6	30.1	30.4	31	32.2
30.46	30.2	31.1	31.6	32.3	33.3
31.89	30.6	31.9	32.7	33.5	34.6
33.3	31	32.2	33.1	34.4	35.4
34.69	31.3	32.6	33.5	34.8	35.8
36.07	31.7	32.9	33.8	35.2	36.2
37.43	32	33.3	34.1	35.5	36.6
38.78	32.3	33.6	34.5	35.9	37
40.12	32.6	33.9	34.9	36.2	37.4
41.44	32.9	34.2	35.2	36.6	37.8
42.74	33.2	34.6	35.5	37	38.2
44.03	33.6	34.9	35.8	37.3	38.6
45.32	33.8	35.2	36.2	37.7	39
46.58	34.1	35.5	36.5	38	39.3
47.83	34.4	35.8	36.8	38.4	39.7
50.3	35	36.4	37.5	39	40.4
52.71	35.5	37	38.1	39.7	41.2
55.08	36.1	37.6	38.7	40.3	41.8
57.4	36.7	38.2	39.3	40.9	42.5
59.67	37.3	38.8	39.9	41.5	43.2
61.9	37.7	39.3	40.5	42.2	43.9

Table 4.18 Specific conductance (μScm^{-1}) for OTAB (first CMC)

[OTAB] $\times 10^{-6}$ M	Specific conductance at 313 K	Specific conductance at 318 K	Specific conductance at 323 K	Specific conductance at 328 K
0	1.9	2	2.4	2.5
2.47	2.6	2.7	3.1	3.2
4.88	3.3	3.4	3.8	3.9
7.23	3.9	4.1	4.5	4.6
9.52	4.5	4.7	5.1	5.2
11.76	5.1	5.3	5.7	5.8
13.95	5.8	5.9	6.3	6.4
16.09	6.3	6.5	6.9	7
18.18	6.9	7.1	7.5	7.6
20.22	7.4	7.7	8.1	8.2
22.22	7.6	8.1	8.7	8.8
24.18	7.9	8.3	9.1	9.4
26.09	8.1	8.5	9.4	9.8
27.96	8.3	8.7	9.6	10.1
29.78	8.5	9	9.8	10.3

31.58	8.7	9.2	10	10.5
33.33	8.9	9.4	10.2	10.7
35.05	9.1	9.6	10.5	11
36.73	9.3	9.8	10.7	11.2
38.38	9.5	10	10.9	11.4
40	9.7	10.2	11.1	11.6

Table 4.19 Surface tension (mN/m) data for second micellization of OTAB

Log C	313K	318 K	323K	328 K
-4.41	61.1	61.4	61.8	62.7
-4.11	52	52.6	52.8	53.7
-3.95	47.7	47.8	48.1	49
-3.83	44	44.1	44.2	45.1
-3.74	41.4	41.2	41.7	42.6
-3.67	39	39.3	39.6	40.6
-3.61	37.1	37.4	37.8	38.6
-3.56	35.5	35.9	36.3	36.8
-3.52	34	34.4	34.8	35.9
-3.48	34	34.1	34.4	35.2
-3.44	34	34.1	34.4	35.2
-3.41	34	34.1	34.4	35.2
-3.38	34	34.1	34.4	35.2
-3.36	34	34.1	34.4	35.2
-3.34	34	34.1	34.4	35.2
-3.31	34	34.1	34.4	35.2
-3.3	34	34.1	34.4	35.2

Table 4.20 Surface tension (mN/m) data for 1st micellization of OTAB

Log C	313K	318K	323K	328K
-5.53	64.3	65.2	65.7	67
-5.24	56.8	57.9	59	60.2
-5.07	52.8	53.9	55	55.9
-4.95	49.9	51	52.3	53.4
-4.87	47.6	48.9	50.3	51.7
-4.79	45.5	47	48.4	49.8
-4.73	44	45.7	46.8	48.5
-4.68	43	44.4	45.6	47.5
-4.64	43	43.5	44.5	46.6
-4.6	43	43.5	44.4	46.1
-4.57	43	43.5	44.4	46.1
-4.54	43	43.5	44.4	46.1
-4.51	43	43.5	44.4	46.1
-4.48	43	43.5	44.4	46.1
-4.46	43	43.5	44.4	46.1
-4.44	43	43.5	44.4	46.1
-4.42	43	43.5	44.4	46.1
-4.4	43	43.5	44.4	46.1

Table 4.21 Adsorption (mN/m) of of OTAB (2nd micellization) in presence of 0.01M NaCl

-log C	303 K	308 K	313 K	318 K
-4.41	61.3	61.6	62.5	62.9
-4.11	50.8	51.2	53	53.8
-3.95	45.2	46.3	47.7	48.9
-3.83	40.9	42.2	43.9	45.2
-3.74	38	38.9	41.2	42.3
-3.67	35.6	36.5	38.9	40.4
-3.61	33.4	34.4	37.1	38.5
-3.56	33.4	33.5	35.1	36.7
-3.52	33.4	33.5	35.1	36.2
-3.48	33.4	33.5	35.1	36.2
-3.44	33.4	33.5	35.1	36.2
-3.41	33.4	33.5	35.1	36.2
-3.38	33.4	33.5	35.3	36.2
-3.36	33.4	33.5	35.1	36.2
-3.34	33.4	33.5	35.1	36.2
-3.31	33.4	33.5	35.1	36.2
-3.3	33.4	33.5	35.1	36.2

Table 4.22 Adsorption (mN/m) of OTAB (for 1st CMC) in presence of 0.01M NaCl

-log C	303 K	308 K	313 K	318 K
-5.53	65.9	66.9	66.9	67.1
-5.24	58.4	59.8	60.3	60.5
-5.07	53.6	55.5	56.1	56.9
-4.95	50.8	52.8	53.1	53.6
-4.87	48.8	50.4	51.2	51.6
-4.79	47.3	48	49.3	50
-4.73	47.3	47.6	47.8	48.4
-4.68	47.3	47.6	47.8	47.9
-4.64	47.3	47.6	47.8	47.9
-4.6	47.3	47.6	47.8	47.9
-4.57	47.5	47.6	47.8	48
-4.54	47.5	47.6	47.8	47.9
-4.51	47.3	47.6	47.9	47.9
-4.48	47.3	47.6	48	48.1
-4.46	47.3	47.6	47.8	47.9
-4.44	47.3	47.6	47.8	47.9
-4.42	47.3	47.6	47.8	47.9
-4.4	47.3	47.6	47.8	47.9

Table 4.23 Specific conductance ($\mu\text{S cm}^{-1}$) of OTAB in 0.01 M NaCl at different temperatures (for 1st CMC)

[OTAB] x 10 ⁻⁶ M	303 K	308 K	313 K	318 K
0	1073	1075	1077	1076
2.44	1079	1081	1083	1084
4.76	1086	1088	1089	1090
6.98	1091	1093	1095	1097
9.09	1097	1099	1101	1102
11.1	1102	1105	1107	1109
13.04	1108	1109	1111	1114
14.89	1113	1115	1116	1120
16.67	1116	1118	1121	1125
18.38	1118	1119	1124	1127
20	1119	1120	1125	1129
21.57	1120	1122	1127	1130
23.08	1122	1123	1128	1132
24.53	1123	1125	1130	1134
25.93	1124	1126	1131	1135
27.27	1126	1127	1132	1137
28.57	1127	1128	1133	1138
29.82	1128	1130	1135	1139
31.03	1129	1131	1136	1141
32.2	1130	1132	1137	1142

Table 4.24 Specific conductance (μSCm^{-1}) of OTAB in 0.01 M NaCl at different temperatures (for 2nd CMC)

[OTAB] x 10 ⁻⁶ M	303 K	308 K	313 K	318 K
0	1072	1073	1077	1076
2.93	1084	1086	1090	1088
5.71	1096	1100	1104	1103
8.37	1108	1111	1116	1115
10.91	1120	1123	1126	1127
13.33	1132	1135	1137	1139
15.65	1140	1145	1148	1150
17.87	1151	1157	1158	1160
20	1160	1166	1168	1170
22.04	1169	1176	1177	1180
24	1178	1185	1187	1189
25.88	1181	1188	1196	1199
27.69	1182	1190	1200	1204
29.43	1184	1191	1202	1206
31.11	1185	1192	1203	1207
32.73	1186	1194	1204	1208
34.29	1187	1195	1206	1210
35.79	1188	1196	1207	1211
37.24	1189	1197	1208	1213
38.64	1190	1198	1209	1214

Table 4.25 UV Data for Zn – DPC complexes in presence of TTAB

400	0.045	0.052	0.057	0.052	0.059	0.051	0.07
401	0.044	0.052	0.057	0.052	0.059	0.051	0.07
402	0.044	0.052	0.057	0.052	0.059	0.051	0.07
403	0.044	0.052	0.057	0.052	0.059	0.051	0.07
404	0.044	0.052	0.057	0.052	0.059	0.051	0.07
405	0.044	0.051	0.056	0.052	0.059	0.051	0.07
406	0.044	0.051	0.056	0.052	0.059	0.05	0.07
407	0.044	0.051	0.056	0.052	0.059	0.05	0.07
408	0.044	0.051	0.056	0.052	0.059	0.05	0.07
409	0.044	0.051	0.056	0.052	0.059	0.05	0.07
410	0.044	0.051	0.056	0.052	0.059	0.05	0.07
411	0.044	0.051	0.056	0.052	0.059	0.05	0.069
412	0.044	0.051	0.056	0.052	0.059	0.05	0.07
413	0.044	0.051	0.056	0.052	0.058	0.05	0.069
414	0.044	0.051	0.056	0.052	0.059	0.05	0.069
415	0.044	0.051	0.056	0.052	0.059	0.05	0.069
416	0.044	0.05	0.056	0.052	0.059	0.05	0.069
417	0.044	0.05	0.056	0.052	0.059	0.05	0.069
418	0.044	0.05	0.056	0.052	0.059	0.05	0.069
419	0.044	0.05	0.056	0.052	0.059	0.05	0.069
420	0.044	0.05	0.056	0.052	0.059	0.05	0.069
421	0.044	0.05	0.056	0.052	0.059	0.05	0.069
422	0.044	0.05	0.056	0.052	0.059	0.05	0.069
423	0.044	0.05	0.056	0.052	0.059	0.05	0.069
424	0.044	0.05	0.056	0.052	0.059	0.05	0.069
425	0.044	0.05	0.056	0.053	0.059	0.05	0.069
426	0.044	0.05	0.056	0.053	0.059	0.05	0.069
427	0.044	0.05	0.056	0.053	0.059	0.05	0.069
428	0.044	0.05	0.056	0.053	0.059	0.05	0.069
429	0.044	0.05	0.056	0.053	0.059	0.05	0.069
430	0.044	0.051	0.056	0.053	0.06	0.05	0.069
431	0.044	0.05	0.056	0.053	0.06	0.05	0.068
432	0.044	0.051	0.056	0.054	0.06	0.05	0.068
433	0.044	0.051	0.057	0.054	0.06	0.05	0.068
434	0.044	0.051	0.057	0.054	0.06	0.05	0.068
435	0.044	0.051	0.057	0.054	0.06	0.05	0.068
436	0.044	0.051	0.057	0.054	0.061	0.05	0.068
437	0.044	0.051	0.057	0.054	0.061	0.05	0.068
438	0.044	0.051	0.057	0.055	0.061	0.05	0.067
439	0.044	0.051	0.058	0.055	0.061	0.05	0.067
440	0.044	0.051	0.058	0.055	0.061	0.05	0.067

441	0.044	0.051	0.058	0.056	0.062	0.05	0.067
442	0.045	0.051	0.058	0.056	0.062	0.05	0.067
443	0.045	0.051	0.058	0.056	0.062	0.05	0.067
444	0.045	0.051	0.059	0.056	0.062	0.05	0.066
445	0.045	0.052	0.059	0.057	0.063	0.051	0.066
446	0.045	0.052	0.059	0.057	0.063	0.051	0.066
447	0.045	0.052	0.06	0.057	0.063	0.051	0.066
448	0.045	0.052	0.06	0.058	0.063	0.051	0.066
449	0.046	0.052	0.06	0.058	0.064	0.051	0.065
450	0.046	0.052	0.061	0.058	0.064	0.051	0.065
451	0.046	0.052	0.061	0.059	0.065	0.051	0.065
452	0.046	0.052	0.061	0.059	0.065	0.051	0.065
453	0.046	0.052	0.062	0.06	0.065	0.052	0.064
454	0.046	0.053	0.062	0.06	0.066	0.052	0.064
455	0.046	0.053	0.062	0.06	0.066	0.052	0.064
456	0.046	0.053	0.063	0.061	0.067	0.052	0.063
457	0.047	0.053	0.063	0.061	0.067	0.052	0.063
458	0.047	0.053	0.064	0.062	0.067	0.052	0.063
459	0.047	0.054	0.064	0.062	0.068	0.052	0.063
460	0.047	0.054	0.065	0.063	0.068	0.052	0.062
461	0.047	0.054	0.065	0.063	0.069	0.053	0.062
462	0.047	0.054	0.066	0.064	0.069	0.053	0.062
463	0.048	0.054	0.066	0.064	0.07	0.053	0.062
464	0.048	0.055	0.067	0.065	0.07	0.053	0.061
465	0.048	0.055	0.067	0.065	0.07	0.053	0.061
466	0.048	0.055	0.068	0.066	0.071	0.054	0.061
467	0.048	0.055	0.068	0.067	0.071	0.054	0.061
468	0.049	0.056	0.069	0.067	0.072	0.054	0.06
469	0.049	0.056	0.069	0.068	0.072	0.054	0.06
470	0.049	0.056	0.07	0.068	0.073	0.054	0.06
471	0.049	0.056	0.07	0.069	0.073	0.055	0.059
472	0.05	0.057	0.071	0.069	0.074	0.055	0.059
473	0.05	0.057	0.071	0.07	0.074	0.055	0.059
474	0.05	0.057	0.072	0.071	0.075	0.055	0.058
475	0.05	0.058	0.072	0.071	0.075	0.056	0.058
476	0.05	0.058	0.073	0.072	0.076	0.056	0.058
477	0.051	0.058	0.073	0.072	0.076	0.056	0.058
478	0.051	0.058	0.074	0.073	0.077	0.056	0.057
479	0.051	0.059	0.075	0.074	0.077	0.056	0.057
480	0.051	0.059	0.075	0.074	0.078	0.057	0.057
481	0.052	0.059	0.076	0.075	0.078	0.057	0.057
482	0.052	0.059	0.076	0.076	0.078	0.057	0.056
483	0.052	0.06	0.077	0.076	0.079	0.057	0.056
484	0.052	0.06	0.077	0.077	0.079	0.057	0.056
485	0.052	0.06	0.078	0.077	0.08	0.058	0.056
486	0.053	0.061	0.078	0.078	0.08	0.058	0.055

487	0.053	0.061	0.079	0.079	0.081	0.058	0.055
488	0.053	0.061	0.079	0.079	0.081	0.058	0.055
489	0.053	0.061	0.08	0.08	0.082	0.058	0.055
490	0.053	0.062	0.08	0.081	0.082	0.059	0.054
491	0.054	0.062	0.081	0.081	0.082	0.059	0.054
492	0.054	0.062	0.081	0.082	0.083	0.059	0.054
493	0.054	0.062	0.082	0.082	0.083	0.059	0.054
494	0.054	0.063	0.082	0.083	0.084	0.059	0.054
495	0.054	0.063	0.083	0.083	0.084	0.059	0.053
496	0.055	0.063	0.083	0.084	0.084	0.06	0.053
497	0.055	0.063	0.083	0.085	0.085	0.06	0.053
498	0.055	0.064	0.084	0.085	0.085	0.06	0.053
499	0.055	0.064	0.084	0.086	0.085	0.06	0.053
500	0.055	0.064	0.084	0.086	0.085	0.06	0.053
501	0.056	0.064	0.085	0.087	0.086	0.061	0.052
502	0.056	0.065	0.085	0.088	0.086	0.061	0.052
503	0.056	0.065	0.085	0.088	0.086	0.061	0.052
504	0.056	0.065	0.085	0.088	0.087	0.061	0.052
505	0.056	0.065	0.086	0.089	0.087	0.061	0.052
506	0.056	0.065	0.086	0.089	0.087	0.061	0.052
507	0.056	0.066	0.086	0.09	0.087	0.061	0.051
508	0.057	0.066	0.087	0.09	0.088	0.061	0.051
509	0.057	0.066	0.087	0.091	0.088	0.062	0.051
510	0.057	0.066	0.087	0.091	0.088	0.062	0.051
511	0.057	0.066	0.087	0.091	0.088	0.062	0.051
512	0.057	0.066	0.087	0.091	0.088	0.062	0.051
513	0.057	0.066	0.088	0.092	0.088	0.062	0.051
514	0.057	0.066	0.088	0.092	0.088	0.062	0.051
515	0.057	0.066	0.088	0.092	0.088	0.062	0.05
516	0.057	0.067	0.088	0.092	0.088	0.062	0.05
517	0.057	0.067	0.088	0.093	0.088	0.062	0.05
518	0.057	0.067	0.088	0.093	0.088	0.062	0.05
519	0.057	0.067	0.088	0.093	0.088	0.062	0.05
520	0.057	0.067	0.088	0.093	0.088	0.062	0.05
521	0.057	0.067	0.088	0.093	0.088	0.062	0.05
522	0.057	0.066	0.088	0.093	0.088	0.062	0.05
523	0.057	0.066	0.088	0.093	0.088	0.062	0.049
524	0.057	0.066	0.088	0.093	0.088	0.062	0.049
525	0.057	0.066	0.088	0.093	0.088	0.061	0.049
526	0.057	0.066	0.087	0.092	0.087	0.061	0.049
527	0.057	0.066	0.087	0.092	0.087	0.061	0.049
528	0.057	0.066	0.087	0.092	0.087	0.061	0.049
529	0.057	0.066	0.087	0.092	0.087	0.061	0.049
530	0.057	0.065	0.087	0.092	0.086	0.061	0.049
531	0.056	0.065	0.086	0.091	0.086	0.061	0.049
532	0.056	0.065	0.086	0.091	0.086	0.061	0.048

533	0.056	0.065	0.086	0.091	0.085	0.06	0.048
534	0.056	0.065	0.085	0.09	0.085	0.06	0.048
535	0.056	0.064	0.085	0.09	0.085	0.06	0.048
536	0.056	0.064	0.085	0.09	0.084	0.06	0.048
537	0.055	0.064	0.084	0.089	0.084	0.06	0.048
538	0.055	0.064	0.084	0.089	0.083	0.059	0.048
539	0.055	0.063	0.084	0.088	0.083	0.059	0.048
540	0.055	0.063	0.083	0.088	0.083	0.059	0.048
541	0.055	0.063	0.083	0.088	0.082	0.059	0.048
542	0.054	0.063	0.082	0.087	0.082	0.058	0.048
543	0.054	0.062	0.082	0.086	0.081	0.058	0.048
544	0.054	0.062	0.081	0.086	0.081	0.058	0.047
545	0.054	0.062	0.081	0.085	0.08	0.058	0.047
546	0.053	0.061	0.08	0.085	0.08	0.057	0.047
547	0.053	0.061	0.08	0.084	0.079	0.057	0.047
548	0.053	0.061	0.079	0.084	0.079	0.057	0.047
549	0.053	0.06	0.079	0.083	0.078	0.056	0.047
550	0.052	0.06	0.078	0.082	0.078	0.056	0.047
551	0.052	0.06	0.078	0.082	0.077	0.056	0.047
552	0.052	0.059	0.077	0.081	0.076	0.055	0.047
553	0.051	0.059	0.076	0.08	0.076	0.055	0.047
554	0.051	0.058	0.076	0.08	0.075	0.055	0.047
555	0.051	0.058	0.075	0.079	0.075	0.054	0.046
556	0.051	0.058	0.075	0.078	0.074	0.054	0.046
557	0.05	0.057	0.074	0.078	0.073	0.054	0.046
558	0.05	0.057	0.073	0.077	0.073	0.053	0.046
559	0.05	0.056	0.073	0.076	0.072	0.053	0.046
560	0.049	0.056	0.072	0.075	0.071	0.053	0.046
561	0.049	0.056	0.071	0.074	0.071	0.052	0.046
562	0.049	0.055	0.071	0.074	0.07	0.052	0.046
563	0.048	0.055	0.07	0.073	0.069	0.052	0.046
564	0.048	0.054	0.069	0.072	0.069	0.051	0.046
565	0.048	0.054	0.068	0.071	0.068	0.051	0.045
566	0.047	0.053	0.068	0.071	0.067	0.051	0.045
567	0.047	0.053	0.067	0.07	0.067	0.05	0.045
568	0.047	0.052	0.066	0.069	0.066	0.05	0.045
569	0.046	0.052	0.066	0.068	0.066	0.05	0.045
570	0.046	0.052	0.065	0.067	0.065	0.049	0.045
571	0.046	0.051	0.064	0.067	0.064	0.049	0.044
572	0.045	0.051	0.063	0.066	0.064	0.048	0.044
573	0.045	0.05	0.063	0.065	0.063	0.048	0.044
574	0.045	0.05	0.062	0.064	0.062	0.048	0.044
575	0.044	0.049	0.061	0.064	0.062	0.047	0.044
576	0.044	0.049	0.061	0.063	0.061	0.047	0.044
577	0.044	0.049	0.06	0.062	0.06	0.047	0.044
578	0.044	0.048	0.059	0.062	0.06	0.047	0.044

579	0.043	0.048	0.059	0.061	0.059	0.046	0.044
580	0.043	0.047	0.058	0.06	0.059	0.046	0.043
581	0.043	0.047	0.057	0.059	0.058	0.046	0.043
582	0.042	0.047	0.057	0.059	0.058	0.046	0.043
583	0.042	0.046	0.056	0.058	0.057	0.045	0.043
584	0.042	0.046	0.055	0.057	0.057	0.045	0.043
585	0.042	0.046	0.055	0.057	0.056	0.045	0.043
586	0.042	0.045	0.054	0.056	0.056	0.044	0.043
587	0.041	0.045	0.054	0.055	0.055	0.044	0.043
588	0.041	0.045	0.053	0.055	0.055	0.044	0.043
589	0.041	0.044	0.053	0.054	0.054	0.044	0.042
590	0.041	0.044	0.052	0.054	0.054	0.043	0.042
591	0.04	0.044	0.052	0.053	0.053	0.043	0.042
592	0.04	0.044	0.051	0.053	0.053	0.043	0.042
593	0.04	0.043	0.051	0.052	0.053	0.043	0.042
594	0.04	0.043	0.05	0.052	0.052	0.043	0.042
595	0.04	0.043	0.05	0.051	0.052	0.042	0.042
596	0.039	0.042	0.049	0.051	0.052	0.042	0.042
597	0.039	0.042	0.049	0.05	0.051	0.042	0.042
598	0.039	0.042	0.048	0.05	0.051	0.042	0.042
599	0.039	0.042	0.048	0.05	0.051	0.042	0.042
600	0.039	0.042	0.048	0.049	0.05	0.042	0.041
601	0.039	0.042	0.047	0.049	0.05	0.042	0.041
602	0.039	0.041	0.047	0.048	0.05	0.042	0.041
603	0.039	0.041	0.047	0.048	0.049	0.041	0.041
604	0.039	0.041	0.046	0.048	0.049	0.041	0.041
605	0.038	0.041	0.046	0.047	0.049	0.041	0.041
606	0.038	0.041	0.046	0.047	0.049	0.041	0.041
607	0.038	0.041	0.045	0.047	0.049	0.041	0.041
608	0.038	0.04	0.045	0.046	0.048	0.041	0.041
609	0.038	0.04	0.045	0.046	0.048	0.041	0.04
610	0.038	0.04	0.044	0.046	0.048	0.04	0.04
611	0.038	0.04	0.044	0.045	0.048	0.04	0.04
612	0.038	0.04	0.044	0.045	0.047	0.04	0.04
613	0.038	0.04	0.044	0.045	0.047	0.04	0.04
614	0.038	0.04	0.043	0.045	0.047	0.04	0.04
615	0.037	0.039	0.043	0.044	0.047	0.04	0.04
616	0.037	0.039	0.043	0.044	0.047	0.04	0.04
617	0.037	0.039	0.043	0.044	0.047	0.04	0.039
618	0.037	0.039	0.042	0.043	0.047	0.04	0.039
619	0.037	0.039	0.042	0.043	0.046	0.04	0.039
620	0.037	0.039	0.042	0.043	0.046	0.04	0.039
621	0.037	0.039	0.042	0.043	0.046	0.04	0.039
622	0.037	0.039	0.042	0.043	0.046	0.039	0.039
623	0.037	0.039	0.042	0.042	0.046	0.039	0.039
624	0.037	0.038	0.041	0.042	0.046	0.039	0.039

625	0.037	0.038	0.041	0.042	0.046	0.039	0.039
626	0.036	0.038	0.041	0.042	0.046	0.039	0.039
627	0.036	0.038	0.041	0.041	0.046	0.039	0.038
628	0.036	0.038	0.041	0.041	0.045	0.039	0.038
629	0.036	0.038	0.041	0.041	0.045	0.039	0.038
630	0.036	0.038	0.041	0.041	0.045	0.039	0.038
631	0.036	0.038	0.04	0.041	0.045	0.039	0.038
632	0.036	0.038	0.04	0.041	0.045	0.039	0.038
633	0.036	0.038	0.04	0.04	0.045	0.039	0.038
634	0.036	0.038	0.04	0.04	0.045	0.039	0.038
635	0.036	0.038	0.04	0.04	0.045	0.039	0.038
636	0.036	0.038	0.04	0.04	0.045	0.039	0.038
637	0.036	0.038	0.04	0.04	0.045	0.039	0.038
638	0.036	0.038	0.04	0.04	0.045	0.039	0.038
639	0.036	0.038	0.04	0.039	0.045	0.039	0.038
640	0.036	0.037	0.039	0.039	0.045	0.039	0.037
641	0.036	0.037	0.039	0.039	0.045	0.039	0.037
642	0.036	0.037	0.039	0.039	0.045	0.039	0.037
643	0.036	0.037	0.039	0.039	0.044	0.039	0.037
644	0.036	0.037	0.039	0.039	0.044	0.039	0.037
645	0.036	0.037	0.039	0.039	0.044	0.039	0.037
646	0.036	0.037	0.039	0.039	0.044	0.039	0.037
647	0.036	0.037	0.039	0.038	0.044	0.038	0.037
648	0.036	0.037	0.039	0.038	0.044	0.038	0.037
649	0.036	0.037	0.039	0.038	0.044	0.038	0.037
650	0.036	0.037	0.039	0.038	0.044	0.038	0.037
651	0.036	0.037	0.039	0.038	0.044	0.038	0.037
652	0.036	0.037	0.039	0.038	0.044	0.038	0.037
653	0.036	0.037	0.039	0.038	0.044	0.038	0.037
654	0.036	0.037	0.039	0.038	0.044	0.038	0.037
655	0.036	0.037	0.039	0.038	0.044	0.038	0.037
656	0.036	0.037	0.039	0.038	0.044	0.038	0.037
657	0.036	0.037	0.039	0.038	0.044	0.038	0.037
658	0.036	0.037	0.039	0.038	0.044	0.038	0.037
659	0.036	0.037	0.039	0.038	0.044	0.038	0.037
660	0.036	0.037	0.039	0.037	0.044	0.038	0.037
661	0.036	0.037	0.039	0.037	0.044	0.038	0.037
662	0.036	0.037	0.038	0.037	0.044	0.038	0.036
663	0.036	0.037	0.038	0.037	0.044	0.038	0.036
664	0.036	0.037	0.038	0.037	0.044	0.038	0.036
665	0.036	0.037	0.038	0.037	0.044	0.038	0.036
666	0.036	0.037	0.038	0.037	0.044	0.038	0.036
667	0.036	0.037	0.038	0.037	0.044	0.038	0.036
668	0.036	0.037	0.038	0.037	0.044	0.038	0.036
669	0.036	0.037	0.038	0.037	0.044	0.038	0.036
670	0.036	0.037	0.038	0.037	0.044	0.038	0.036

671	0.036	0.037	0.038	0.037	0.044	0.038	0.036
672	0.036	0.037	0.038	0.037	0.044	0.038	0.036
673	0.036	0.037	0.038	0.037	0.044	0.038	0.036
674	0.036	0.037	0.038	0.037	0.044	0.038	0.036
675	0.036	0.037	0.038	0.037	0.044	0.038	0.036
676	0.036	0.037	0.038	0.037	0.044	0.038	0.036
677	0.036	0.037	0.038	0.036	0.044	0.038	0.036
678	0.036	0.037	0.038	0.037	0.044	0.038	0.036
679	0.036	0.037	0.038	0.036	0.044	0.038	0.036
680	0.036	0.037	0.038	0.036	0.044	0.038	0.036
681	0.036	0.037	0.038	0.036	0.044	0.038	0.036
682	0.036	0.037	0.038	0.036	0.044	0.038	0.036
683	0.036	0.037	0.038	0.036	0.044	0.038	0.036
684	0.036	0.037	0.038	0.036	0.044	0.038	0.036
685	0.036	0.037	0.038	0.036	0.044	0.038	0.036
686	0.036	0.037	0.038	0.036	0.044	0.038	0.036
687	0.036	0.037	0.038	0.036	0.044	0.038	0.036
688	0.036	0.037	0.038	0.036	0.044	0.038	0.036
689	0.036	0.037	0.038	0.036	0.044	0.038	0.036
690	0.036	0.037	0.038	0.036	0.044	0.038	0.036
691	0.036	0.037	0.038	0.036	0.044	0.038	0.036
692	0.036	0.037	0.038	0.036	0.044	0.038	0.036
693	0.036	0.037	0.038	0.036	0.044	0.038	0.036
694	0.036	0.037	0.038	0.036	0.044	0.038	0.036
695	0.036	0.037	0.038	0.036	0.044	0.038	0.036
696	0.036	0.037	0.038	0.036	0.044	0.038	0.036
697	0.036	0.037	0.038	0.036	0.044	0.038	0.036
698	0.036	0.037	0.038	0.036	0.044	0.038	0.036
699	0.036	0.037	0.038	0.036	0.044	0.038	0.036
700	0.036	0.037	0.038	0.036	0.044	0.039	0.036

Table 4.26 Data for Zn – DPC complexes in SDS

Wavelength	2mM SDS	4mM SDS	7mM SDS	8mM SDS	9mM SDS	10mM SDS	12mM SDS
400	0.045	0.052	0.057	0.052	0.056	0.056	0.056
401	0.044	0.052	0.057	0.052	0.056	0.056	0.056
402	0.044	0.052	0.057	0.052	0.056	0.056	0.056
403	0.044	0.052	0.057	0.052	0.056	0.056	0.056
404	0.044	0.052	0.057	0.052	0.056	0.056	0.056
405	0.044	0.051	0.056	0.052	0.056	0.056	0.056
406	0.044	0.051	0.056	0.052	0.056	0.056	0.056
407	0.044	0.051	0.056	0.052	0.056	0.056	0.056
408	0.044	0.051	0.056	0.052	0.055	0.055	0.055
409	0.044	0.051	0.056	0.052	0.055	0.055	0.055

410	0.044	0.051	0.056	0.052	0.055	0.055	0.055
411	0.044	0.051	0.056	0.052	0.055	0.055	0.055
412	0.044	0.051	0.056	0.052	0.055	0.055	0.055
413	0.044	0.051	0.056	0.052	0.055	0.055	0.055
414	0.044	0.051	0.056	0.052	0.055	0.055	0.055
415	0.044	0.051	0.056	0.052	0.055	0.055	0.055
416	0.044	0.05	0.056	0.052	0.055	0.055	0.055
417	0.044	0.05	0.056	0.052	0.056	0.056	0.056
418	0.044	0.05	0.056	0.052	0.056	0.056	0.056
419	0.044	0.05	0.056	0.052	0.056	0.056	0.056
420	0.044	0.05	0.056	0.052	0.056	0.056	0.056
421	0.044	0.05	0.056	0.052	0.056	0.056	0.056
422	0.044	0.05	0.056	0.052	0.056	0.056	0.056
423	0.044	0.05	0.056	0.052	0.056	0.056	0.056
424	0.044	0.05	0.056	0.052	0.056	0.056	0.056
425	0.044	0.05	0.056	0.053	0.056	0.056	0.056
426	0.044	0.05	0.056	0.053	0.056	0.056	0.056
427	0.044	0.05	0.056	0.053	0.056	0.056	0.056
428	0.044	0.05	0.056	0.053	0.056	0.056	0.056
429	0.044	0.05	0.056	0.053	0.057	0.057	0.057
430	0.044	0.051	0.056	0.053	0.057	0.057	0.057
431	0.044	0.05	0.056	0.053	0.057	0.057	0.057
432	0.044	0.051	0.056	0.054	0.057	0.057	0.057
433	0.044	0.051	0.057	0.054	0.057	0.057	0.057
434	0.044	0.051	0.057	0.054	0.057	0.057	0.057
435	0.044	0.051	0.057	0.054	0.058	0.058	0.058
436	0.044	0.051	0.057	0.054	0.058	0.058	0.058
437	0.044	0.051	0.057	0.054	0.058	0.058	0.058
438	0.044	0.051	0.057	0.055	0.058	0.058	0.058
439	0.044	0.051	0.058	0.055	0.059	0.059	0.059
440	0.044	0.051	0.058	0.055	0.059	0.059	0.059
441	0.044	0.051	0.058	0.056	0.059	0.059	0.059
442	0.045	0.051	0.058	0.056	0.059	0.059	0.059
443	0.045	0.051	0.058	0.056	0.06	0.06	0.06
444	0.045	0.051	0.059	0.056	0.06	0.06	0.06
445	0.045	0.052	0.059	0.057	0.06	0.06	0.06
446	0.045	0.052	0.059	0.057	0.061	0.061	0.061
447	0.045	0.052	0.06	0.057	0.061	0.061	0.061
448	0.045	0.052	0.06	0.058	0.062	0.062	0.062
449	0.046	0.052	0.06	0.058	0.062	0.062	0.062
450	0.046	0.052	0.061	0.058	0.062	0.062	0.062
451	0.046	0.052	0.061	0.059	0.063	0.063	0.063
452	0.046	0.052	0.061	0.059	0.063	0.063	0.063
453	0.046	0.052	0.062	0.06	0.064	0.064	0.064
454	0.046	0.053	0.062	0.06	0.064	0.064	0.064
455	0.046	0.053	0.062	0.06	0.064	0.064	0.064

456	0.046	0.053	0.063	0.061	0.065	0.065	0.065
457	0.047	0.053	0.063	0.061	0.065	0.065	0.065
458	0.047	0.053	0.064	0.062	0.066	0.066	0.066
459	0.047	0.054	0.064	0.062	0.067	0.067	0.067
460	0.047	0.054	0.065	0.063	0.067	0.067	0.067
461	0.047	0.054	0.065	0.063	0.068	0.068	0.068
462	0.047	0.054	0.066	0.064	0.068	0.068	0.068
463	0.048	0.054	0.066	0.064	0.069	0.069	0.069
464	0.048	0.055	0.067	0.065	0.069	0.069	0.069
465	0.048	0.055	0.067	0.065	0.07	0.07	0.07
466	0.048	0.055	0.068	0.066	0.071	0.071	0.071
467	0.048	0.055	0.068	0.067	0.071	0.071	0.071
468	0.049	0.056	0.069	0.067	0.072	0.072	0.072
469	0.049	0.056	0.069	0.068	0.073	0.073	0.073
470	0.049	0.056	0.07	0.068	0.073	0.073	0.073
471	0.049	0.056	0.07	0.069	0.074	0.074	0.074
472	0.05	0.057	0.071	0.069	0.075	0.075	0.075
473	0.05	0.057	0.071	0.07	0.075	0.075	0.075
474	0.05	0.057	0.072	0.071	0.076	0.076	0.076
475	0.05	0.058	0.072	0.071	0.077	0.077	0.077
476	0.05	0.058	0.073	0.072	0.078	0.078	0.078
477	0.051	0.058	0.073	0.072	0.078	0.078	0.078
478	0.051	0.058	0.074	0.073	0.079	0.079	0.079
479	0.051	0.059	0.075	0.074	0.08	0.08	0.08
480	0.051	0.059	0.075	0.074	0.081	0.081	0.081
481	0.052	0.059	0.076	0.075	0.081	0.081	0.081
482	0.052	0.059	0.076	0.076	0.082	0.082	0.082
483	0.052	0.06	0.077	0.076	0.083	0.083	0.083
484	0.052	0.06	0.077	0.077	0.083	0.083	0.083
485	0.052	0.06	0.078	0.077	0.084	0.084	0.084
486	0.053	0.061	0.078	0.078	0.085	0.085	0.085
487	0.053	0.061	0.079	0.079	0.086	0.086	0.086
488	0.053	0.061	0.079	0.079	0.086	0.086	0.086
489	0.053	0.061	0.08	0.08	0.087	0.087	0.087
490	0.053	0.062	0.08	0.081	0.088	0.088	0.088
491	0.054	0.062	0.081	0.081	0.088	0.088	0.088
492	0.054	0.062	0.081	0.082	0.089	0.089	0.089
493	0.054	0.062	0.082	0.082	0.09	0.09	0.09
494	0.054	0.063	0.082	0.083	0.09	0.09	0.09
495	0.054	0.063	0.083	0.083	0.091	0.091	0.091
496	0.055	0.063	0.083	0.084	0.091	0.091	0.091
497	0.055	0.063	0.083	0.085	0.092	0.092	0.092
498	0.055	0.064	0.084	0.085	0.093	0.093	0.093
499	0.055	0.064	0.084	0.086	0.093	0.093	0.093
500	0.055	0.064	0.084	0.086	0.094	0.094	0.094
501	0.056	0.064	0.085	0.087	0.094	0.094	0.094

502	0.056	0.065	0.085	0.088	0.095	0.095	0.095
503	0.056	0.065	0.085	0.088	0.095	0.095	0.095
504	0.056	0.065	0.085	0.088	0.096	0.096	0.096
505	0.056	0.065	0.086	0.089	0.096	0.096	0.096
506	0.056	0.065	0.086	0.089	0.097	0.097	0.097
507	0.056	0.066	0.086	0.09	0.097	0.097	0.097
508	0.057	0.066	0.087	0.09	0.097	0.097	0.097
509	0.057	0.066	0.087	0.091	0.098	0.098	0.098
510	0.057	0.066	0.087	0.091	0.098	0.098	0.098
511	0.057	0.066	0.087	0.091	0.098	0.098	0.098
512	0.057	0.066	0.087	0.091	0.099	0.099	0.099
513	0.057	0.066	0.088	0.092	0.099	0.099	0.099
514	0.057	0.066	0.088	0.092	0.099	0.099	0.099
515	0.057	0.066	0.088	0.092	0.099	0.099	0.099
516	0.057	0.067	0.088	0.092	0.099	0.099	0.099
517	0.057	0.067	0.088	0.093	0.099	0.099	0.099
518	0.057	0.067	0.088	0.093	0.1	0.1	0.1
519	0.057	0.067	0.088	0.093	0.1	0.1	0.1
520	0.057	0.067	0.088	0.093	0.1	0.1	0.1
521	0.057	0.067	0.088	0.093	0.1	0.1	0.1
522	0.057	0.066	0.088	0.093	0.099	0.099	0.099
523	0.057	0.066	0.088	0.093	0.099	0.099	0.099
524	0.057	0.066	0.088	0.093	0.099	0.099	0.099
525	0.057	0.066	0.088	0.093	0.099	0.099	0.099
526	0.057	0.066	0.087	0.092	0.099	0.099	0.099
527	0.057	0.066	0.087	0.092	0.098	0.098	0.098
528	0.057	0.066	0.087	0.092	0.098	0.098	0.098
529	0.057	0.066	0.087	0.092	0.098	0.098	0.098
530	0.057	0.065	0.087	0.092	0.097	0.097	0.097
531	0.056	0.065	0.086	0.091	0.097	0.097	0.097
532	0.056	0.065	0.086	0.091	0.097	0.097	0.097
533	0.056	0.065	0.086	0.091	0.096	0.096	0.096
534	0.056	0.065	0.085	0.09	0.096	0.096	0.096
535	0.056	0.064	0.085	0.09	0.095	0.095	0.095
536	0.056	0.064	0.085	0.09	0.095	0.095	0.095
537	0.055	0.064	0.084	0.089	0.094	0.094	0.094
538	0.055	0.064	0.084	0.089	0.093	0.093	0.093
539	0.055	0.063	0.084	0.088	0.093	0.093	0.093
540	0.055	0.063	0.083	0.088	0.092	0.092	0.092
541	0.055	0.063	0.083	0.088	0.092	0.092	0.092
542	0.054	0.063	0.082	0.087	0.091	0.091	0.091
543	0.054	0.062	0.082	0.086	0.09	0.09	0.09
544	0.054	0.062	0.081	0.086	0.089	0.089	0.089
545	0.054	0.062	0.081	0.085	0.089	0.089	0.089
546	0.053	0.061	0.08	0.085	0.088	0.088	0.088
547	0.053	0.061	0.08	0.084	0.087	0.087	0.087

548	0.053	0.061	0.079	0.084	0.086	0.086	0.086
549	0.053	0.06	0.079	0.083	0.085	0.085	0.085
550	0.052	0.06	0.078	0.082	0.085	0.085	0.085
551	0.052	0.06	0.078	0.082	0.084	0.084	0.084
552	0.052	0.059	0.077	0.081	0.083	0.083	0.083
553	0.051	0.059	0.076	0.08	0.082	0.082	0.082
554	0.051	0.058	0.076	0.08	0.081	0.081	0.081
555	0.051	0.058	0.075	0.079	0.08	0.08	0.08
556	0.051	0.058	0.075	0.078	0.079	0.079	0.079
557	0.05	0.057	0.074	0.078	0.079	0.079	0.079
558	0.05	0.057	0.073	0.077	0.078	0.078	0.078
559	0.05	0.056	0.073	0.076	0.077	0.077	0.077
560	0.049	0.056	0.072	0.075	0.076	0.076	0.076
561	0.049	0.056	0.071	0.074	0.075	0.075	0.075
562	0.049	0.055	0.071	0.074	0.074	0.074	0.074
563	0.048	0.055	0.07	0.073	0.073	0.073	0.073
564	0.048	0.054	0.069	0.072	0.072	0.072	0.072
565	0.048	0.054	0.068	0.071	0.071	0.071	0.071
566	0.047	0.053	0.068	0.071	0.07	0.07	0.07
567	0.047	0.053	0.067	0.07	0.069	0.069	0.069
568	0.047	0.052	0.066	0.069	0.068	0.068	0.068
569	0.046	0.052	0.066	0.068	0.067	0.067	0.067
570	0.046	0.052	0.065	0.067	0.066	0.066	0.066
571	0.046	0.051	0.064	0.067	0.065	0.065	0.065
572	0.045	0.051	0.063	0.066	0.064	0.064	0.064
573	0.045	0.05	0.063	0.065	0.063	0.063	0.063
574	0.045	0.05	0.062	0.064	0.062	0.062	0.062
575	0.044	0.049	0.061	0.064	0.061	0.061	0.061
576	0.044	0.049	0.061	0.063	0.06	0.06	0.06
577	0.044	0.049	0.06	0.062	0.059	0.059	0.059
578	0.044	0.048	0.059	0.062	0.058	0.058	0.058
579	0.043	0.048	0.059	0.061	0.058	0.058	0.058
580	0.043	0.047	0.058	0.06	0.057	0.057	0.057
581	0.043	0.047	0.057	0.059	0.056	0.056	0.056
582	0.042	0.047	0.057	0.059	0.055	0.055	0.055
583	0.042	0.046	0.056	0.058	0.054	0.054	0.054
584	0.042	0.046	0.055	0.057	0.054	0.054	0.054
585	0.042	0.046	0.055	0.057	0.053	0.053	0.053
586	0.042	0.045	0.054	0.056	0.052	0.052	0.052
587	0.041	0.045	0.054	0.055	0.052	0.052	0.052
588	0.041	0.045	0.053	0.055	0.051	0.051	0.051
589	0.041	0.044	0.053	0.054	0.05	0.05	0.05
590	0.041	0.044	0.052	0.054	0.05	0.05	0.05
591	0.04	0.044	0.052	0.053	0.049	0.049	0.049
592	0.04	0.044	0.051	0.053	0.048	0.048	0.048
593	0.04	0.043	0.051	0.052	0.048	0.048	0.048

594	0.04	0.043	0.05	0.052	0.047	0.047	0.047
595	0.04	0.043	0.05	0.051	0.047	0.047	0.047
596	0.039	0.042	0.049	0.051	0.046	0.046	0.046
597	0.039	0.042	0.049	0.05	0.046	0.046	0.046
598	0.039	0.042	0.048	0.05	0.045	0.045	0.045
599	0.039	0.042	0.048	0.05	0.045	0.045	0.045
600	0.039	0.042	0.048	0.049	0.045	0.045	0.045
601	0.039	0.042	0.047	0.049	0.044	0.044	0.044
602	0.039	0.041	0.047	0.048	0.044	0.044	0.044
603	0.039	0.041	0.047	0.048	0.043	0.043	0.043
604	0.039	0.041	0.046	0.048	0.043	0.043	0.043
605	0.038	0.041	0.046	0.047	0.043	0.043	0.043
606	0.038	0.041	0.046	0.047	0.042	0.042	0.042
607	0.038	0.041	0.045	0.047	0.042	0.042	0.042
608	0.038	0.04	0.045	0.046	0.042	0.042	0.042
609	0.038	0.04	0.045	0.046	0.042	0.042	0.042
610	0.038	0.04	0.044	0.046	0.041	0.041	0.041
611	0.038	0.04	0.044	0.045	0.041	0.041	0.041
612	0.038	0.04	0.044	0.045	0.041	0.041	0.041
613	0.038	0.04	0.044	0.045	0.041	0.041	0.041
614	0.038	0.04	0.043	0.045	0.04	0.04	0.04
615	0.037	0.039	0.043	0.044	0.04	0.04	0.04
616	0.037	0.039	0.043	0.044	0.04	0.04	0.04
617	0.037	0.039	0.043	0.044	0.04	0.04	0.04
618	0.037	0.039	0.042	0.043	0.04	0.04	0.04
619	0.037	0.039	0.042	0.043	0.04	0.04	0.04
620	0.037	0.039	0.042	0.043	0.039	0.039	0.039
621	0.037	0.039	0.042	0.043	0.039	0.039	0.039
622	0.037	0.039	0.042	0.043	0.039	0.039	0.039
623	0.037	0.039	0.042	0.042	0.039	0.039	0.039
624	0.037	0.038	0.041	0.042	0.039	0.039	0.039
625	0.037	0.038	0.041	0.042	0.039	0.039	0.039
626	0.036	0.038	0.041	0.042	0.039	0.039	0.039
627	0.036	0.038	0.041	0.041	0.039	0.039	0.039
628	0.036	0.038	0.041	0.041	0.039	0.039	0.039
629	0.036	0.038	0.041	0.041	0.039	0.039	0.039
630	0.036	0.038	0.041	0.041	0.038	0.038	0.038
631	0.036	0.038	0.04	0.041	0.038	0.038	0.038
632	0.036	0.038	0.04	0.041	0.038	0.038	0.038
633	0.036	0.038	0.04	0.04	0.038	0.038	0.038
634	0.036	0.038	0.04	0.04	0.038	0.038	0.038
635	0.036	0.038	0.04	0.04	0.038	0.038	0.038
636	0.036	0.038	0.04	0.04	0.038	0.038	0.038
637	0.036	0.038	0.04	0.04	0.038	0.038	0.038
638	0.036	0.038	0.04	0.04	0.038	0.038	0.038
639	0.036	0.038	0.04	0.039	0.038	0.038	0.038

686	0.036	0.037	0.038	0.036	0.037	0.037	0.037
687	0.036	0.037	0.038	0.036	0.037	0.037	0.037
688	0.036	0.037	0.038	0.036	0.037	0.037	0.037
689	0.036	0.037	0.038	0.036	0.037	0.037	0.037
690	0.036	0.037	0.038	0.036	0.037	0.037	0.037
691	0.036	0.037	0.038	0.036	0.037	0.037	0.037
692	0.036	0.037	0.038	0.036	0.037	0.037	0.037
693	0.036	0.037	0.038	0.036	0.037	0.037	0.037
694	0.036	0.037	0.038	0.036	0.037	0.037	0.037
695	0.036	0.037	0.038	0.036	0.037	0.037	0.037
696	0.036	0.037	0.038	0.036	0.037	0.037	0.037
697	0.036	0.037	0.038	0.036	0.037	0.037	0.037
698	0.036	0.037	0.038	0.036	0.037	0.037	0.037
699	0.036	0.037	0.038	0.036	0.037	0.037	0.037
700	0.036	0.037	0.038	0.036	0.037	0.037	0.037

Table 4.27 Cd-DPC complex in TTAB

400	0.487	0.453	0.442	0.41	0.432	0.432	0.432
401	0.484	0.45	0.438	0.407	0.429	0.429	0.429
402	0.479	0.446	0.434	0.403	0.425	0.425	0.425
403	0.475	0.442	0.43	0.4	0.421	0.421	0.421
404	0.471	0.438	0.426	0.396	0.417	0.417	0.417
405	0.467	0.434	0.423	0.393	0.413	0.413	0.413
406	0.464	0.431	0.419	0.39	0.41	0.41	0.41
407	0.46	0.427	0.416	0.388	0.406	0.406	0.406
408	0.457	0.424	0.413	0.385	0.403	0.403	0.403
409	0.453	0.421	0.41	0.383	0.4	0.4	0.4
410	0.451	0.418	0.407	0.38	0.397	0.397	0.397
411	0.448	0.415	0.404	0.378	0.395	0.395	0.395
412	0.445	0.413	0.402	0.376	0.392	0.392	0.392
413	0.442	0.41	0.399	0.374	0.389	0.389	0.389
414	0.439	0.408	0.397	0.373	0.387	0.387	0.387
415	0.437	0.405	0.395	0.371	0.384	0.384	0.384
416	0.434	0.403	0.393	0.37	0.382	0.382	0.382
417	0.431	0.401	0.391	0.369	0.38	0.38	0.38
418	0.429	0.399	0.389	0.368	0.378	0.378	0.378
419	0.427	0.397	0.387	0.367	0.376	0.376	0.376
420	0.425	0.394	0.385	0.366	0.374	0.374	0.374
421	0.422	0.393	0.384	0.365	0.372	0.372	0.372
422	0.42	0.391	0.382	0.365	0.37	0.37	0.37
423	0.418	0.389	0.381	0.365	0.369	0.369	0.369
424	0.417	0.388	0.38	0.364	0.367	0.367	0.367
425	0.415	0.386	0.378	0.364	0.366	0.366	0.366
426	0.413	0.385	0.377	0.364	0.364	0.364	0.364

427	0.411	0.383	0.376	0.365	0.363	0.363	0.363
428	0.41	0.382	0.375	0.365	0.362	0.362	0.362
429	0.408	0.38	0.374	0.365	0.36	0.36	0.36
430	0.407	0.379	0.374	0.366	0.359	0.359	0.359
431	0.405	0.378	0.373	0.367	0.358	0.358	0.358
432	0.404	0.377	0.372	0.367	0.357	0.357	0.357
433	0.403	0.376	0.372	0.369	0.356	0.356	0.356
434	0.401	0.375	0.371	0.37	0.355	0.355	0.355
435	0.4	0.375	0.371	0.371	0.355	0.355	0.355
436	0.399	0.374	0.371	0.372	0.354	0.354	0.354
437	0.398	0.373	0.371	0.374	0.353	0.353	0.353
438	0.397	0.372	0.37	0.376	0.353	0.353	0.353
439	0.396	0.372	0.37	0.378	0.352	0.352	0.352
440	0.395	0.371	0.371	0.38	0.352	0.352	0.352
441	0.394	0.371	0.371	0.382	0.351	0.351	0.351
442	0.393	0.37	0.371	0.385	0.351	0.351	0.351
443	0.392	0.37	0.372	0.388	0.351	0.351	0.351
444	0.392	0.37	0.372	0.391	0.351	0.351	0.351
445	0.391	0.37	0.373	0.394	0.351	0.351	0.351
446	0.39	0.37	0.374	0.397	0.351	0.351	0.351
447	0.39	0.37	0.375	0.401	0.351	0.351	0.351
448	0.389	0.37	0.376	0.405	0.351	0.351	0.351
449	0.389	0.37	0.377	0.409	0.351	0.351	0.351
450	0.389	0.37	0.378	0.413	0.352	0.352	0.352
451	0.389	0.37	0.379	0.417	0.352	0.352	0.352
452	0.388	0.371	0.381	0.422	0.353	0.353	0.353
453	0.388	0.371	0.382	0.427	0.353	0.353	0.353
454	0.388	0.372	0.384	0.432	0.354	0.354	0.354
455	0.388	0.373	0.386	0.437	0.355	0.355	0.355
456	0.388	0.373	0.388	0.442	0.356	0.356	0.356
457	0.388	0.374	0.39	0.448	0.357	0.357	0.357
458	0.389	0.375	0.392	0.454	0.358	0.358	0.358
459	0.389	0.376	0.394	0.46	0.359	0.359	0.359
460	0.389	0.377	0.396	0.466	0.36	0.36	0.36
461	0.39	0.378	0.399	0.473	0.361	0.361	0.361
462	0.39	0.38	0.402	0.48	0.363	0.363	0.363
463	0.391	0.381	0.405	0.487	0.365	0.365	0.365
464	0.391	0.383	0.408	0.494	0.366	0.366	0.366
465	0.392	0.384	0.411	0.502	0.368	0.368	0.368
466	0.393	0.386	0.414	0.509	0.37	0.37	0.37
467	0.394	0.388	0.417	0.517	0.372	0.372	0.372
468	0.395	0.39	0.421	0.526	0.374	0.374	0.374
469	0.396	0.392	0.425	0.534	0.376	0.376	0.376
470	0.397	0.394	0.428	0.542	0.378	0.378	0.378
471	0.398	0.396	0.432	0.551	0.381	0.381	0.381
472	0.4	0.398	0.436	0.559	0.383	0.383	0.383

473	0.401	0.4	0.44	0.568	0.385	0.385	0.385
474	0.402	0.402	0.444	0.576	0.388	0.388	0.388
475	0.403	0.405	0.448	0.585	0.39	0.39	0.39
476	0.405	0.407	0.452	0.594	0.393	0.393	0.393
477	0.406	0.409	0.455	0.603	0.395	0.395	0.395
478	0.408	0.411	0.46	0.613	0.398	0.398	0.398
479	0.409	0.414	0.464	0.622	0.4	0.4	0.4
480	0.41	0.416	0.469	0.631	0.403	0.403	0.403
481	0.412	0.419	0.473	0.641	0.406	0.406	0.406
482	0.414	0.421	0.477	0.651	0.409	0.409	0.409
483	0.415	0.424	0.482	0.662	0.412	0.412	0.412
484	0.417	0.427	0.487	0.671	0.414	0.414	0.414
485	0.418	0.429	0.491	0.681	0.417	0.417	0.417
486	0.42	0.432	0.496	0.691	0.42	0.42	0.42
487	0.422	0.435	0.5	0.701	0.423	0.423	0.423
488	0.423	0.438	0.505	0.711	0.426	0.426	0.426
489	0.425	0.44	0.51	0.721	0.429	0.429	0.429
490	0.427	0.443	0.514	0.731	0.432	0.432	0.432
491	0.428	0.446	0.519	0.741	0.435	0.435	0.435
492	0.43	0.448	0.524	0.751	0.438	0.438	0.438
493	0.432	0.451	0.529	0.762	0.441	0.441	0.441
494	0.434	0.454	0.533	0.772	0.444	0.444	0.444
495	0.436	0.457	0.538	0.782	0.447	0.447	0.447
496	0.438	0.46	0.542	0.792	0.451	0.451	0.451
497	0.439	0.463	0.547	0.802	0.453	0.453	0.453
498	0.441	0.465	0.552	0.812	0.457	0.457	0.457
499	0.443	0.468	0.556	0.821	0.459	0.459	0.459
500	0.445	0.471	0.56	0.831	0.463	0.463	0.463
501	0.447	0.474	0.565	0.84	0.465	0.465	0.465
502	0.449	0.476	0.57	0.85	0.469	0.469	0.469
503	0.451	0.479	0.574	0.859	0.471	0.471	0.471
504	0.452	0.482	0.578	0.867	0.474	0.474	0.474
505	0.454	0.485	0.583	0.877	0.477	0.477	0.477
506	0.456	0.487	0.587	0.886	0.48	0.48	0.48
507	0.458	0.49	0.591	0.894	0.483	0.483	0.483
508	0.46	0.492	0.595	0.902	0.486	0.486	0.486
509	0.461	0.495	0.599	0.91	0.489	0.489	0.489
510	0.463	0.497	0.603	0.918	0.491	0.491	0.491
511	0.464	0.5	0.606	0.924	0.494	0.494	0.494
512	0.466	0.502	0.609	0.931	0.496	0.496	0.496
513	0.467	0.504	0.613	0.937	0.498	0.498	0.498
514	0.469	0.506	0.616	0.943	0.5	0.5	0.5
515	0.47	0.508	0.619	0.95	0.502	0.502	0.502
516	0.471	0.509	0.621	0.955	0.504	0.504	0.504
517	0.472	0.511	0.624	0.96	0.506	0.506	0.506
518	0.473	0.512	0.626	0.965	0.507	0.507	0.507

519	0.474	0.513	0.628	0.969	0.509	0.509	0.509
520	0.474	0.514	0.63	0.973	0.51	0.51	0.51
521	0.475	0.515	0.631	0.976	0.511	0.511	0.511
522	0.475	0.516	0.633	0.979	0.512	0.512	0.512
523	0.476	0.516	0.634	0.981	0.512	0.512	0.512
524	0.476	0.517	0.634	0.983	0.512	0.512	0.512
525	0.476	0.517	0.635	0.984	0.513	0.513	0.513
526	0.475	0.517	0.635	0.985	0.513	0.513	0.513
527	0.475	0.516	0.635	0.985	0.512	0.512	0.512
528	0.474	0.516	0.634	0.985	0.512	0.512	0.512
529	0.474	0.515	0.634	0.984	0.511	0.511	0.511
530	0.473	0.514	0.633	0.982	0.51	0.51	0.51
531	0.471	0.513	0.631	0.98	0.509	0.509	0.509
532	0.47	0.512	0.63	0.978	0.508	0.508	0.508
533	0.469	0.51	0.628	0.975	0.506	0.506	0.506
534	0.467	0.508	0.626	0.971	0.505	0.505	0.505
535	0.466	0.506	0.624	0.967	0.503	0.503	0.503
536	0.464	0.504	0.621	0.962	0.5	0.5	0.5
537	0.46	0.5	0.616	0.952	0.497	0.497	0.497
538	0.458	0.498	0.613	0.946	0.494	0.494	0.494
539	0.456	0.495	0.61	0.941	0.491	0.491	0.491
540	0.453	0.492	0.606	0.934	0.488	0.488	0.488
541	0.451	0.489	0.602	0.927	0.485	0.485	0.485
542	0.448	0.486	0.597	0.919	0.481	0.481	0.481
543	0.445	0.482	0.593	0.911	0.478	0.478	0.478
544	0.442	0.478	0.588	0.903	0.474	0.474	0.474
545	0.439	0.474	0.583	0.894	0.47	0.47	0.47
546	0.435	0.47	0.577	0.885	0.465	0.465	0.465
547	0.432	0.466	0.572	0.875	0.461	0.461	0.461
548	0.428	0.462	0.566	0.865	0.457	0.457	0.457
549	0.424	0.457	0.56	0.854	0.452	0.452	0.452
550	0.42	0.452	0.554	0.843	0.447	0.447	0.447
551	0.416	0.447	0.547	0.831	0.442	0.442	0.442
552	0.411	0.442	0.54	0.819	0.436	0.436	0.436
553	0.407	0.437	0.533	0.807	0.431	0.431	0.431
554	0.403	0.431	0.526	0.794	0.425	0.425	0.425
555	0.398	0.425	0.519	0.781	0.42	0.42	0.42
556	0.393	0.42	0.511	0.768	0.414	0.414	0.414
557	0.388	0.414	0.504	0.754	0.408	0.408	0.408
558	0.383	0.408	0.495	0.74	0.401	0.401	0.401
559	0.378	0.402	0.487	0.726	0.395	0.395	0.395
560	0.373	0.396	0.479	0.712	0.389	0.389	0.389
561	0.368	0.389	0.471	0.697	0.383	0.383	0.383
562	0.363	0.383	0.462	0.682	0.376	0.376	0.376
563	0.357	0.376	0.454	0.666	0.369	0.369	0.369
564	0.352	0.37	0.445	0.651	0.363	0.363	0.363

565	0.346	0.363	0.436	0.636	0.356	0.356	0.356
566	0.341	0.356	0.427	0.62	0.349	0.349	0.349
567	0.335	0.349	0.417	0.604	0.341	0.341	0.341
568	0.329	0.343	0.408	0.589	0.334	0.334	0.334
569	0.324	0.336	0.398	0.573	0.327	0.327	0.327
570	0.318	0.329	0.39	0.557	0.32	0.32	0.32
571	0.312	0.322	0.38	0.542	0.313	0.313	0.313
572	0.307	0.316	0.372	0.527	0.307	0.307	0.307
573	0.301	0.309	0.363	0.511	0.3	0.3	0.3
574	0.296	0.302	0.354	0.497	0.293	0.293	0.293
575	0.29	0.296	0.345	0.481	0.286	0.286	0.286
576	0.285	0.289	0.336	0.466	0.279	0.279	0.279
577	0.279	0.282	0.328	0.451	0.272	0.272	0.272
578	0.274	0.276	0.319	0.437	0.266	0.266	0.266
579	0.268	0.27	0.311	0.422	0.259	0.259	0.259
580	0.263	0.263	0.302	0.408	0.252	0.252	0.252
581	0.258	0.257	0.294	0.394	0.246	0.246	0.246
582	0.252	0.251	0.286	0.38	0.24	0.24	0.24
583	0.247	0.245	0.278	0.366	0.233	0.233	0.233
584	0.242	0.238	0.27	0.353	0.227	0.227	0.227
585	0.237	0.232	0.263	0.34	0.221	0.221	0.221
586	0.232	0.226	0.255	0.328	0.215	0.215	0.215
587	0.227	0.221	0.248	0.316	0.209	0.209	0.209
588	0.223	0.215	0.241	0.305	0.203	0.203	0.203
589	0.218	0.21	0.234	0.294	0.198	0.198	0.198
590	0.214	0.205	0.227	0.283	0.192	0.192	0.192
591	0.209	0.2	0.221	0.273	0.187	0.187	0.187
592	0.205	0.195	0.215	0.263	0.182	0.182	0.182
593	0.201	0.191	0.209	0.254	0.177	0.177	0.177
594	0.198	0.186	0.203	0.245	0.173	0.173	0.173
595	0.194	0.182	0.198	0.236	0.169	0.169	0.169
596	0.19	0.178	0.193	0.228	0.164	0.164	0.164
597	0.187	0.174	0.188	0.22	0.16	0.16	0.16
598	0.183	0.17	0.183	0.212	0.156	0.156	0.156
599	0.181	0.166	0.179	0.205	0.153	0.153	0.153
600	0.177	0.163	0.174	0.199	0.149	0.149	0.149
601	0.175	0.16	0.17	0.192	0.146	0.146	0.146
602	0.172	0.156	0.166	0.186	0.143	0.143	0.143
603	0.169	0.153	0.162	0.18	0.139	0.139	0.139
604	0.167	0.151	0.158	0.175	0.136	0.136	0.136
605	0.164	0.148	0.155	0.169	0.134	0.134	0.134
606	0.162	0.145	0.152	0.164	0.131	0.131	0.131
607	0.16	0.143	0.149	0.16	0.129	0.129	0.129
608	0.158	0.141	0.146	0.156	0.126	0.126	0.126
609	0.156	0.138	0.143	0.152	0.124	0.124	0.124
610	0.154	0.136	0.141	0.148	0.122	0.122	0.122

611	0.152	0.134	0.139	0.144	0.12	0.12	0.12
612	0.15	0.132	0.136	0.141	0.118	0.118	0.118
613	0.149	0.13	0.134	0.137	0.116	0.116	0.116
614	0.147	0.129	0.132	0.134	0.114	0.114	0.114
615	0.146	0.127	0.13	0.131	0.112	0.112	0.112
616	0.144	0.125	0.128	0.129	0.111	0.111	0.111
617	0.143	0.124	0.126	0.126	0.109	0.109	0.109
618	0.141	0.122	0.124	0.123	0.108	0.108	0.108
619	0.14	0.12	0.122	0.121	0.106	0.106	0.106
620	0.139	0.119	0.121	0.119	0.105	0.105	0.105
621	0.137	0.118	0.119	0.117	0.103	0.103	0.103
622	0.136	0.117	0.118	0.115	0.102	0.102	0.102
623	0.135	0.115	0.116	0.113	0.101	0.101	0.101
624	0.134	0.114	0.115	0.111	0.099	0.099	0.099
625	0.132	0.113	0.113	0.109	0.098	0.098	0.098
626	0.131	0.111	0.112	0.107	0.097	0.097	0.097
627	0.13	0.11	0.111	0.105	0.096	0.096	0.096
628	0.129	0.109	0.109	0.104	0.094	0.094	0.094
629	0.128	0.108	0.108	0.102	0.093	0.093	0.093
630	0.126	0.106	0.107	0.101	0.092	0.092	0.092
631	0.125	0.105	0.105	0.099	0.091	0.091	0.091
632	0.124	0.104	0.104	0.098	0.09	0.09	0.09
633	0.123	0.103	0.103	0.096	0.089	0.089	0.089
634	0.122	0.102	0.102	0.095	0.088	0.088	0.088
635	0.121	0.101	0.101	0.094	0.086	0.086	0.086
636	0.12	0.1	0.1	0.092	0.085	0.085	0.085
637	0.119	0.099	0.099	0.091	0.084	0.084	0.084
638	0.118	0.098	0.098	0.09	0.083	0.083	0.083
639	0.117	0.097	0.097	0.089	0.082	0.082	0.082
640	0.116	0.096	0.096	0.088	0.082	0.082	0.082
641	0.115	0.095	0.095	0.087	0.081	0.081	0.081
642	0.114	0.094	0.094	0.086	0.08	0.08	0.08
643	0.113	0.093	0.093	0.084	0.079	0.079	0.079
644	0.112	0.092	0.092	0.083	0.078	0.078	0.078
645	0.111	0.091	0.091	0.083	0.077	0.077	0.077
646	0.11	0.09	0.09	0.082	0.076	0.076	0.076
647	0.11	0.09	0.089	0.081	0.075	0.075	0.075
648	0.109	0.089	0.089	0.08	0.075	0.075	0.075
649	0.108	0.088	0.088	0.079	0.074	0.074	0.074
650	0.107	0.087	0.087	0.078	0.073	0.073	0.073
651	0.107	0.087	0.086	0.077	0.072	0.072	0.072
652	0.106	0.086	0.085	0.077	0.072	0.072	0.072
653	0.105	0.085	0.085	0.076	0.071	0.071	0.071
654	0.104	0.085	0.084	0.075	0.07	0.07	0.07
655	0.104	0.084	0.083	0.075	0.07	0.07	0.07
656	0.103	0.083	0.083	0.074	0.069	0.069	0.069

657	0.103	0.083	0.082	0.073	0.068	0.068	0.068
658	0.102	0.082	0.082	0.073	0.068	0.068	0.068
659	0.101	0.082	0.081	0.072	0.067	0.067	0.067
660	0.101	0.081	0.081	0.072	0.067	0.067	0.067
661	0.1	0.081	0.08	0.071	0.066	0.066	0.066
662	0.1	0.08	0.08	0.071	0.066	0.066	0.066
663	0.099	0.079	0.079	0.07	0.065	0.065	0.065
664	0.099	0.079	0.079	0.07	0.065	0.065	0.065
665	0.098	0.078	0.078	0.069	0.064	0.064	0.064
666	0.098	0.078	0.078	0.069	0.064	0.064	0.064
667	0.097	0.078	0.077	0.068	0.064	0.064	0.064
668	0.097	0.077	0.077	0.068	0.063	0.063	0.063
669	0.096	0.077	0.076	0.068	0.063	0.063	0.063
670	0.096	0.076	0.076	0.067	0.063	0.063	0.063
671	0.095	0.076	0.076	0.067	0.062	0.062	0.062
672	0.095	0.076	0.075	0.066	0.062	0.062	0.062
673	0.095	0.075	0.075	0.066	0.062	0.062	0.062
674	0.094	0.075	0.075	0.066	0.061	0.061	0.061
675	0.094	0.075	0.074	0.065	0.061	0.061	0.061
676	0.094	0.075	0.074	0.065	0.061	0.061	0.061
677	0.094	0.074	0.074	0.065	0.06	0.06	0.06
678	0.093	0.074	0.074	0.064	0.06	0.06	0.06
679	0.093	0.074	0.073	0.064	0.06	0.06	0.06
680	0.093	0.074	0.073	0.064	0.059	0.059	0.059
681	0.092	0.073	0.073	0.064	0.059	0.059	0.059
682	0.092	0.073	0.073	0.063	0.059	0.059	0.059
683	0.092	0.073	0.072	0.063	0.059	0.059	0.059
684	0.092	0.073	0.072	0.063	0.059	0.059	0.059
685	0.092	0.072	0.072	0.063	0.058	0.058	0.058
686	0.091	0.072	0.072	0.063	0.058	0.058	0.058
687	0.091	0.072	0.071	0.063	0.058	0.058	0.058
688	0.091	0.072	0.071	0.062	0.058	0.058	0.058
689	0.091	0.072	0.071	0.062	0.058	0.058	0.058
690	0.091	0.072	0.071	0.062	0.058	0.058	0.058
691	0.09	0.072	0.071	0.062	0.057	0.057	0.057
692	0.09	0.071	0.071	0.062	0.057	0.057	0.057
693	0.09	0.071	0.07	0.062	0.057	0.057	0.057
694	0.09	0.071	0.07	0.062	0.057	0.057	0.057
695	0.09	0.071	0.07	0.061	0.057	0.057	0.057
696	0.09	0.071	0.07	0.061	0.057	0.057	0.057
697	0.09	0.071	0.07	0.061	0.057	0.057	0.057
698	0.089	0.071	0.07	0.061	0.057	0.057	0.057
699	0.089	0.071	0.07	0.061	0.057	0.057	0.057
700	0.089	0.071	0.07	0.061	0.057	0.057	0.057

Table 4.28 Data for Hg – DPC complexes in TTAB.

Wavelength	1.8mM TTAB	2.4mM TTAB	3.0mM TTAB	3.3mM TTAB	3.6mM TTAB	4.2mM TTAB	5.0mM TTAB
400	0.114	0.125	0.137	0.202	0.195	0.137	0.137
401	0.113	0.125	0.137	0.201	0.193	0.137	0.137
402	0.112	0.124	0.136	0.199	0.192	0.136	0.136
403	0.112	0.123	0.135	0.198	0.191	0.135	0.135
404	0.111	0.122	0.134	0.196	0.189	0.134	0.134
405	0.11	0.122	0.133	0.195	0.188	0.133	0.133
406	0.11	0.121	0.132	0.193	0.187	0.132	0.132
407	0.109	0.12	0.131	0.192	0.185	0.131	0.131
408	0.109	0.119	0.13	0.19	0.184	0.13	0.13
409	0.108	0.119	0.13	0.189	0.182	0.13	0.13
410	0.107	0.118	0.129	0.187	0.181	0.129	0.129
411	0.107	0.117	0.128	0.186	0.18	0.128	0.128
412	0.106	0.116	0.127	0.184	0.179	0.127	0.127
413	0.105	0.116	0.126	0.183	0.177	0.126	0.126
414	0.105	0.115	0.125	0.182	0.176	0.125	0.125
415	0.104	0.114	0.125	0.18	0.175	0.125	0.125
416	0.104	0.114	0.124	0.179	0.174	0.124	0.124
417	0.103	0.113	0.123	0.178	0.172	0.123	0.123
418	0.103	0.113	0.123	0.177	0.171	0.123	0.123
419	0.102	0.112	0.122	0.175	0.17	0.122	0.122
420	0.102	0.111	0.121	0.174	0.169	0.121	0.121
421	0.101	0.111	0.121	0.173	0.168	0.121	0.121
422	0.101	0.11	0.12	0.172	0.167	0.12	0.12
423	0.1	0.11	0.119	0.171	0.166	0.119	0.119
424	0.1	0.109	0.119	0.169	0.165	0.119	0.119
425	0.1	0.109	0.118	0.168	0.164	0.118	0.118
426	0.099	0.108	0.117	0.167	0.163	0.117	0.117
427	0.099	0.108	0.117	0.167	0.162	0.117	0.117
428	0.098	0.107	0.117	0.166	0.161	0.117	0.117
429	0.098	0.107	0.116	0.165	0.16	0.116	0.116
430	0.098	0.106	0.116	0.164	0.16	0.116	0.116
431	0.098	0.106	0.115	0.163	0.159	0.115	0.115
432	0.097	0.106	0.115	0.162	0.158	0.115	0.115
433	0.097	0.105	0.115	0.162	0.157	0.115	0.115
434	0.097	0.105	0.114	0.161	0.157	0.114	0.114
435	0.097	0.105	0.114	0.16	0.156	0.114	0.114
436	0.097	0.105	0.114	0.16	0.156	0.114	0.114
437	0.097	0.105	0.113	0.159	0.155	0.113	0.113
438	0.096	0.105	0.113	0.159	0.155	0.113	0.113
439	0.096	0.104	0.113	0.159	0.155	0.113	0.113

440	0.096	0.104	0.113	0.158	0.155	0.113	0.113
441	0.096	0.104	0.113	0.158	0.154	0.113	0.113
442	0.097	0.104	0.113	0.158	0.154	0.113	0.113
443	0.097	0.105	0.113	0.158	0.154	0.113	0.113
444	0.097	0.105	0.113	0.158	0.154	0.113	0.113
445	0.097	0.105	0.114	0.158	0.155	0.114	0.114
446	0.097	0.105	0.114	0.158	0.155	0.114	0.114
447	0.098	0.106	0.114	0.159	0.155	0.114	0.114
448	0.098	0.106	0.115	0.159	0.156	0.115	0.115
449	0.099	0.106	0.115	0.16	0.156	0.115	0.115
450	0.099	0.107	0.116	0.161	0.157	0.116	0.116
451	0.1	0.108	0.117	0.161	0.158	0.117	0.117
452	0.1	0.108	0.117	0.162	0.159	0.117	0.117
453	0.101	0.109	0.118	0.163	0.16	0.118	0.118
454	0.102	0.11	0.119	0.165	0.161	0.119	0.119
455	0.103	0.111	0.12	0.166	0.163	0.12	0.12
456	0.104	0.112	0.121	0.167	0.164	0.121	0.121
457	0.105	0.113	0.122	0.169	0.166	0.122	0.122
458	0.106	0.114	0.124	0.171	0.167	0.124	0.124
459	0.107	0.115	0.125	0.173	0.169	0.125	0.125
460	0.109	0.117	0.127	0.175	0.172	0.127	0.127
461	0.11	0.118	0.129	0.178	0.174	0.129	0.129
462	0.112	0.12	0.13	0.181	0.177	0.13	0.13
463	0.113	0.122	0.133	0.184	0.18	0.133	0.133
464	0.115	0.124	0.135	0.187	0.183	0.135	0.135
465	0.117	0.126	0.138	0.19	0.186	0.138	0.138
466	0.119	0.128	0.14	0.194	0.19	0.14	0.14
467	0.121	0.131	0.143	0.198	0.194	0.143	0.143
468	0.124	0.134	0.146	0.203	0.198	0.146	0.146
469	0.127	0.136	0.149	0.207	0.202	0.149	0.149
470	0.129	0.139	0.152	0.212	0.207	0.152	0.152
471	0.132	0.142	0.156	0.217	0.212	0.156	0.156
472	0.135	0.146	0.159	0.222	0.217	0.159	0.159
473	0.138	0.149	0.163	0.228	0.223	0.163	0.163
474	0.142	0.153	0.168	0.234	0.229	0.168	0.168
475	0.145	0.157	0.172	0.241	0.235	0.172	0.172
476	0.149	0.161	0.177	0.248	0.242	0.177	0.177
477	0.153	0.165	0.181	0.255	0.249	0.181	0.181
478	0.157	0.169	0.187	0.263	0.256	0.187	0.187
479	0.161	0.174	0.192	0.271	0.264	0.192	0.192
480	0.165	0.179	0.198	0.279	0.272	0.198	0.198
481	0.17	0.184	0.203	0.288	0.281	0.203	0.203
482	0.175	0.19	0.21	0.298	0.29	0.21	0.21
483	0.18	0.196	0.216	0.309	0.3	0.216	0.216
484	0.185	0.201	0.223	0.319	0.309	0.223	0.223
485	0.19	0.207	0.229	0.329	0.319	0.229	0.229

486	0.195	0.213	0.236	0.34	0.329	0.236	0.236
487	0.201	0.219	0.244	0.351	0.34	0.244	0.244
488	0.207	0.226	0.252	0.364	0.352	0.252	0.252
489	0.213	0.233	0.259	0.377	0.364	0.259	0.259
490	0.219	0.24	0.267	0.39	0.376	0.267	0.267
491	0.224	0.247	0.275	0.403	0.389	0.275	0.275
492	0.231	0.253	0.283	0.416	0.402	0.283	0.283
493	0.237	0.26	0.291	0.431	0.415	0.291	0.291
494	0.243	0.268	0.299	0.445	0.428	0.299	0.299
495	0.249	0.275	0.307	0.459	0.442	0.307	0.307
496	0.255	0.282	0.316	0.474	0.455	0.316	0.316
497	0.261	0.289	0.324	0.489	0.469	0.324	0.324
498	0.268	0.297	0.333	0.504	0.484	0.333	0.333
499	0.274	0.304	0.341	0.518	0.497	0.341	0.341
500	0.279	0.311	0.349	0.532	0.511	0.349	0.349
501	0.285	0.317	0.357	0.547	0.524	0.357	0.357
502	0.291	0.324	0.365	0.561	0.538	0.365	0.365
503	0.297	0.331	0.374	0.576	0.552	0.374	0.374
504	0.302	0.338	0.381	0.589	0.565	0.381	0.381
505	0.308	0.344	0.389	0.603	0.578	0.389	0.389
506	0.313	0.351	0.397	0.617	0.59	0.397	0.397
507	0.318	0.357	0.404	0.629	0.602	0.404	0.404
508	0.322	0.362	0.41	0.641	0.613	0.41	0.41
509	0.327	0.368	0.417	0.653	0.624	0.417	0.417
510	0.331	0.373	0.423	0.664	0.634	0.423	0.423
511	0.334	0.378	0.428	0.673	0.643	0.428	0.428
512	0.338	0.382	0.434	0.683	0.652	0.434	0.434
513	0.341	0.386	0.438	0.691	0.66	0.438	0.438
514	0.344	0.389	0.442	0.699	0.667	0.442	0.442
515	0.346	0.393	0.446	0.707	0.674	0.446	0.446
516	0.349	0.396	0.45	0.714	0.681	0.45	0.45
517	0.351	0.398	0.453	0.719	0.686	0.453	0.453
518	0.352	0.4	0.455	0.724	0.691	0.455	0.455
519	0.354	0.402	0.457	0.729	0.695	0.457	0.457
520	0.354	0.403	0.459	0.732	0.698	0.459	0.459
521	0.355	0.404	0.46	0.735	0.701	0.46	0.46
522	0.356	0.405	0.461	0.737	0.703	0.461	0.461
523	0.356	0.406	0.462	0.739	0.704	0.462	0.462
524	0.356	0.406	0.462	0.74	0.705	0.462	0.462
525	0.355	0.405	0.462	0.74	0.705	0.462	0.462
526	0.355	0.405	0.461	0.74	0.704	0.461	0.461
527	0.354	0.404	0.46	0.739	0.703	0.46	0.46
528	0.353	0.403	0.459	0.737	0.702	0.459	0.459
529	0.352	0.402	0.458	0.735	0.7	0.458	0.458
530	0.35	0.4	0.456	0.733	0.698	0.456	0.456
531	0.349	0.398	0.454	0.73	0.695	0.454	0.454

532	0.347	0.396	0.452	0.727	0.692	0.452	0.452
533	0.345	0.395	0.45	0.723	0.688	0.45	0.45
534	0.343	0.392	0.448	0.719	0.685	0.448	0.448
535	0.341	0.39	0.445	0.715	0.681	0.445	0.445
536	0.339	0.388	0.442	0.711	0.677	0.442	0.442
537	0.336	0.384	0.438	0.704	0.67	0.438	0.438
538	0.334	0.382	0.435	0.7	0.666	0.435	0.435
539	0.331	0.379	0.432	0.695	0.661	0.432	0.432
540	0.329	0.376	0.429	0.69	0.656	0.429	0.429
541	0.327	0.374	0.426	0.685	0.651	0.426	0.426
542	0.324	0.371	0.422	0.68	0.646	0.422	0.422
543	0.321	0.368	0.419	0.674	0.641	0.419	0.419
544	0.319	0.365	0.416	0.669	0.635	0.416	0.416
545	0.316	0.362	0.412	0.663	0.63	0.412	0.412
546	0.313	0.359	0.409	0.658	0.625	0.409	0.409
547	0.311	0.356	0.405	0.652	0.62	0.405	0.405
548	0.308	0.352	0.402	0.647	0.614	0.402	0.402
549	0.305	0.349	0.398	0.641	0.608	0.398	0.398
550	0.302	0.346	0.394	0.635	0.602	0.394	0.394
551	0.299	0.343	0.39	0.63	0.597	0.39	0.39
552	0.296	0.339	0.387	0.623	0.591	0.387	0.387
553	0.294	0.336	0.383	0.618	0.586	0.383	0.383
554	0.291	0.333	0.379	0.612	0.58	0.379	0.379
555	0.288	0.33	0.375	0.606	0.574	0.375	0.375
556	0.285	0.327	0.372	0.601	0.569	0.372	0.372
557	0.282	0.323	0.368	0.595	0.563	0.368	0.368
558	0.28	0.32	0.364	0.589	0.557	0.364	0.364
559	0.277	0.317	0.361	0.583	0.551	0.361	0.361
560	0.274	0.314	0.357	0.578	0.546	0.357	0.357
561	0.271	0.311	0.354	0.572	0.541	0.354	0.354
562	0.269	0.308	0.35	0.567	0.535	0.35	0.35
563	0.266	0.305	0.347	0.561	0.529	0.347	0.347
564	0.263	0.302	0.343	0.555	0.524	0.343	0.343
565	0.26	0.299	0.34	0.55	0.518	0.34	0.34
566	0.258	0.296	0.336	0.544	0.513	0.336	0.336
567	0.255	0.293	0.333	0.539	0.507	0.333	0.333
568	0.252	0.29	0.329	0.533	0.502	0.329	0.329
569	0.25	0.287	0.326	0.528	0.497	0.326	0.326
570	0.247	0.284	0.323	0.522	0.491	0.323	0.323
571	0.245	0.281	0.319	0.517	0.486	0.319	0.319
572	0.242	0.278	0.316	0.512	0.481	0.316	0.316
573	0.24	0.275	0.313	0.507	0.476	0.313	0.313
574	0.237	0.272	0.31	0.502	0.471	0.31	0.31
575	0.235	0.27	0.307	0.496	0.466	0.307	0.307
576	0.232	0.267	0.303	0.492	0.461	0.303	0.303
577	0.23	0.265	0.3	0.487	0.457	0.3	0.3

578	0.228	0.262	0.297	0.482	0.452	0.297	0.297
579	0.225	0.259	0.294	0.477	0.447	0.294	0.294
580	0.223	0.257	0.292	0.472	0.443	0.292	0.292
581	0.221	0.254	0.289	0.467	0.438	0.289	0.289
582	0.219	0.251	0.286	0.463	0.434	0.286	0.286
583	0.216	0.249	0.283	0.458	0.429	0.283	0.283
584	0.214	0.247	0.28	0.453	0.425	0.28	0.28
585	0.212	0.244	0.277	0.449	0.42	0.277	0.277
586	0.21	0.242	0.275	0.444	0.416	0.275	0.275
587	0.208	0.24	0.272	0.44	0.412	0.272	0.272
588	0.206	0.237	0.269	0.435	0.407	0.269	0.269
589	0.204	0.235	0.266	0.431	0.403	0.266	0.266
590	0.202	0.232	0.264	0.426	0.399	0.264	0.264
591	0.2	0.23	0.261	0.422	0.395	0.261	0.261
592	0.198	0.228	0.259	0.418	0.391	0.259	0.259
593	0.196	0.226	0.256	0.413	0.387	0.256	0.256
594	0.194	0.224	0.254	0.409	0.382	0.254	0.254
595	0.193	0.221	0.251	0.405	0.378	0.251	0.251
596	0.191	0.219	0.248	0.401	0.374	0.248	0.248
597	0.189	0.217	0.246	0.396	0.37	0.246	0.246
598	0.187	0.214	0.243	0.392	0.366	0.243	0.243
599	0.185	0.213	0.241	0.388	0.362	0.241	0.241
600	0.183	0.21	0.238	0.384	0.358	0.238	0.238
601	0.181	0.208	0.236	0.38	0.354	0.236	0.236
602	0.179	0.206	0.233	0.375	0.35	0.233	0.233
603	0.178	0.204	0.231	0.371	0.346	0.231	0.231
604	0.176	0.202	0.228	0.367	0.342	0.228	0.228
605	0.174	0.199	0.226	0.362	0.338	0.226	0.226
606	0.172	0.197	0.223	0.358	0.334	0.223	0.223
607	0.17	0.195	0.221	0.354	0.33	0.221	0.221
608	0.168	0.193	0.218	0.35	0.326	0.218	0.218
609	0.167	0.191	0.216	0.346	0.323	0.216	0.216
610	0.165	0.189	0.214	0.342	0.319	0.214	0.214
611	0.163	0.187	0.211	0.338	0.315	0.211	0.211
612	0.161	0.185	0.209	0.334	0.311	0.209	0.209
613	0.16	0.183	0.206	0.33	0.307	0.206	0.206
614	0.158	0.181	0.204	0.326	0.304	0.204	0.204
615	0.157	0.179	0.202	0.323	0.3	0.202	0.202
616	0.155	0.177	0.199	0.319	0.296	0.199	0.199
617	0.153	0.175	0.197	0.315	0.293	0.197	0.197
618	0.151	0.173	0.195	0.311	0.289	0.195	0.195
619	0.15	0.171	0.193	0.307	0.286	0.193	0.193
620	0.149	0.169	0.191	0.304	0.282	0.191	0.191
621	0.147	0.167	0.188	0.3	0.279	0.188	0.188
622	0.146	0.166	0.186	0.297	0.276	0.186	0.186
623	0.144	0.164	0.184	0.293	0.272	0.184	0.184

624	0.142	0.162	0.182	0.29	0.269	0.182	0.182
625	0.141	0.16	0.18	0.286	0.266	0.18	0.18
626	0.14	0.158	0.178	0.283	0.262	0.178	0.178
627	0.138	0.156	0.176	0.279	0.259	0.176	0.176
628	0.136	0.155	0.174	0.276	0.256	0.174	0.174
629	0.135	0.153	0.172	0.272	0.253	0.172	0.172
630	0.133	0.151	0.17	0.269	0.25	0.17	0.17
631	0.132	0.15	0.168	0.266	0.247	0.168	0.168
632	0.131	0.148	0.166	0.263	0.244	0.166	0.166
633	0.13	0.147	0.164	0.26	0.241	0.164	0.164
634	0.128	0.145	0.163	0.257	0.238	0.163	0.163
635	0.127	0.144	0.161	0.254	0.235	0.161	0.161
636	0.125	0.142	0.159	0.251	0.233	0.159	0.159
637	0.124	0.141	0.157	0.248	0.23	0.157	0.157
638	0.123	0.139	0.156	0.245	0.227	0.156	0.156
639	0.122	0.138	0.154	0.242	0.224	0.154	0.154
640	0.12	0.136	0.152	0.239	0.222	0.152	0.152
641	0.119	0.135	0.151	0.237	0.219	0.151	0.151
642	0.118	0.133	0.149	0.234	0.217	0.149	0.149
643	0.117	0.132	0.147	0.231	0.214	0.147	0.147
644	0.116	0.131	0.146	0.229	0.212	0.146	0.146
645	0.115	0.129	0.144	0.226	0.209	0.144	0.144
646	0.113	0.128	0.143	0.223	0.207	0.143	0.143
647	0.112	0.127	0.141	0.221	0.204	0.141	0.141
648	0.111	0.125	0.14	0.218	0.202	0.14	0.14
649	0.11	0.124	0.138	0.216	0.2	0.138	0.138
650	0.109	0.123	0.137	0.213	0.197	0.137	0.137
651	0.108	0.122	0.135	0.211	0.195	0.135	0.135
652	0.107	0.12	0.134	0.208	0.193	0.134	0.134
653	0.106	0.119	0.132	0.206	0.191	0.132	0.132
654	0.105	0.118	0.131	0.204	0.189	0.131	0.131
655	0.104	0.117	0.13	0.201	0.187	0.13	0.13
656	0.103	0.116	0.128	0.199	0.185	0.128	0.128
657	0.102	0.115	0.127	0.197	0.182	0.127	0.127
658	0.101	0.113	0.126	0.195	0.181	0.126	0.126
659	0.1	0.112	0.124	0.193	0.178	0.124	0.124
660	0.099	0.111	0.123	0.191	0.177	0.123	0.123
661	0.098	0.11	0.122	0.188	0.174	0.122	0.122
662	0.097	0.109	0.12	0.186	0.172	0.12	0.12
663	0.096	0.108	0.119	0.184	0.17	0.119	0.119
664	0.095	0.107	0.118	0.182	0.169	0.118	0.118
665	0.094	0.106	0.117	0.18	0.167	0.117	0.117
666	0.094	0.105	0.116	0.178	0.165	0.116	0.116
667	0.093	0.104	0.115	0.176	0.163	0.115	0.115
668	0.092	0.103	0.113	0.174	0.161	0.113	0.113
669	0.091	0.102	0.112	0.172	0.159	0.112	0.112

670	0.09	0.101	0.111	0.17	0.158	0.111	0.111
671	0.089	0.1	0.11	0.168	0.156	0.11	0.11
672	0.089	0.099	0.109	0.166	0.154	0.109	0.109
673	0.088	0.098	0.108	0.164	0.152	0.108	0.108
674	0.087	0.097	0.107	0.163	0.151	0.107	0.107
675	0.086	0.096	0.106	0.161	0.149	0.106	0.106
676	0.086	0.095	0.105	0.159	0.148	0.105	0.105
677	0.085	0.094	0.104	0.157	0.146	0.104	0.104
678	0.084	0.094	0.103	0.156	0.145	0.103	0.103
679	0.083	0.093	0.102	0.154	0.143	0.102	0.102
680	0.083	0.092	0.101	0.152	0.141	0.101	0.101
681	0.082	0.091	0.1	0.151	0.14	0.1	0.1
682	0.081	0.09	0.099	0.149	0.139	0.099	0.099
683	0.081	0.089	0.098	0.147	0.137	0.098	0.098
684	0.08	0.089	0.097	0.146	0.135	0.097	0.097
685	0.079	0.088	0.096	0.144	0.134	0.096	0.096
686	0.079	0.087	0.095	0.142	0.133	0.095	0.095
687	0.078	0.086	0.094	0.141	0.131	0.094	0.094
688	0.077	0.086	0.093	0.139	0.13	0.093	0.093
689	0.077	0.085	0.092	0.138	0.128	0.092	0.092
690	0.076	0.084	0.092	0.136	0.127	0.092	0.092
691	0.076	0.083	0.091	0.135	0.125	0.091	0.091
692	0.075	0.083	0.09	0.133	0.124	0.09	0.09
693	0.075	0.082	0.089	0.132	0.123	0.089	0.089
694	0.074	0.081	0.089	0.13	0.122	0.089	0.089
695	0.073	0.081	0.088	0.129	0.12	0.088	0.088
696	0.073	0.08	0.087	0.128	0.119	0.087	0.087
697	0.072	0.079	0.086	0.126	0.118	0.086	0.086
698	0.072	0.079	0.085	0.125	0.117	0.085	0.085
699	0.072	0.078	0.085	0.124	0.115	0.085	0.085
700	0.071	0.078	0.084	0.122	0.114	0.084	0.084

Table 4.29 Cd– DPC complex in CTAB

Wavelength	0.3mM CTAB	0.5mM CTAB	0.7mM CTAB	0.9mM CTAB	1.1mM CTAB	1.4mM CTAB
400	0.453	0.432	0.453	0.41	0.453	0.453
401	0.45	0.429	0.45	0.407	0.45	0.45
402	0.446	0.425	0.446	0.403	0.446	0.446
403	0.442	0.421	0.442	0.4	0.442	0.442
404	0.438	0.417	0.438	0.396	0.438	0.438
405	0.434	0.413	0.434	0.393	0.434	0.434
406	0.431	0.41	0.431	0.39	0.431	0.431
407	0.427	0.406	0.427	0.388	0.427	0.427
408	0.424	0.403	0.424	0.385	0.424	0.424

409	0.421	0.4	0.421	0.383	0.421	0.421
410	0.418	0.397	0.418	0.38	0.418	0.418
411	0.415	0.395	0.415	0.378	0.415	0.415
412	0.413	0.392	0.413	0.376	0.413	0.413
413	0.41	0.389	0.41	0.374	0.41	0.41
414	0.408	0.387	0.408	0.373	0.408	0.408
415	0.405	0.384	0.405	0.371	0.405	0.405
416	0.403	0.382	0.403	0.37	0.403	0.403
417	0.401	0.38	0.401	0.369	0.401	0.401
418	0.399	0.378	0.399	0.368	0.399	0.399
419	0.397	0.376	0.397	0.367	0.397	0.397
420	0.394	0.374	0.394	0.366	0.394	0.394
421	0.393	0.372	0.393	0.365	0.393	0.393
422	0.391	0.37	0.391	0.365	0.391	0.391
423	0.389	0.369	0.389	0.365	0.389	0.389
424	0.388	0.367	0.388	0.364	0.388	0.388
425	0.386	0.366	0.386	0.364	0.386	0.386
426	0.385	0.364	0.385	0.364	0.385	0.385
427	0.383	0.363	0.383	0.365	0.383	0.383
428	0.382	0.362	0.382	0.365	0.382	0.382
429	0.38	0.36	0.38	0.365	0.38	0.38
430	0.379	0.359	0.379	0.366	0.379	0.379
431	0.378	0.358	0.378	0.367	0.378	0.378
432	0.377	0.357	0.377	0.367	0.377	0.377
433	0.376	0.356	0.376	0.369	0.376	0.376
434	0.375	0.355	0.375	0.37	0.375	0.375
435	0.375	0.355	0.375	0.371	0.375	0.375
436	0.374	0.354	0.374	0.372	0.374	0.374
437	0.373	0.353	0.373	0.374	0.373	0.373
438	0.372	0.353	0.372	0.376	0.372	0.372
439	0.372	0.352	0.372	0.378	0.372	0.372
440	0.371	0.352	0.371	0.38	0.371	0.371
441	0.371	0.351	0.371	0.382	0.371	0.371
442	0.37	0.351	0.37	0.385	0.37	0.37
443	0.37	0.351	0.37	0.388	0.37	0.37
444	0.37	0.351	0.37	0.391	0.37	0.37
445	0.37	0.351	0.37	0.394	0.37	0.37
446	0.37	0.351	0.37	0.397	0.37	0.37
447	0.37	0.351	0.37	0.401	0.37	0.37
448	0.37	0.351	0.37	0.405	0.37	0.37
449	0.37	0.351	0.37	0.409	0.37	0.37
450	0.37	0.352	0.37	0.413	0.37	0.37
451	0.37	0.352	0.37	0.417	0.37	0.37
452	0.371	0.353	0.371	0.422	0.371	0.371
453	0.371	0.353	0.371	0.427	0.371	0.371
454	0.372	0.354	0.372	0.432	0.372	0.372

455	0.373	0.355	0.373	0.437	0.373	0.373
456	0.373	0.356	0.373	0.442	0.373	0.373
457	0.374	0.357	0.374	0.448	0.374	0.374
458	0.375	0.358	0.375	0.454	0.375	0.375
459	0.376	0.359	0.376	0.46	0.376	0.376
460	0.377	0.36	0.377	0.466	0.377	0.377
461	0.378	0.361	0.378	0.473	0.378	0.378
462	0.38	0.363	0.38	0.48	0.38	0.38
463	0.381	0.365	0.381	0.487	0.381	0.381
464	0.383	0.366	0.383	0.494	0.383	0.383
465	0.384	0.368	0.384	0.502	0.384	0.384
466	0.386	0.37	0.386	0.509	0.386	0.386
467	0.388	0.372	0.388	0.517	0.388	0.388
468	0.39	0.374	0.39	0.526	0.39	0.39
469	0.392	0.376	0.392	0.534	0.392	0.392
470	0.394	0.378	0.394	0.542	0.394	0.394
471	0.396	0.381	0.396	0.551	0.396	0.396
472	0.398	0.383	0.398	0.559	0.398	0.398
473	0.4	0.385	0.4	0.568	0.4	0.4
474	0.402	0.388	0.402	0.576	0.402	0.402
475	0.405	0.39	0.405	0.585	0.405	0.405
476	0.407	0.393	0.407	0.594	0.407	0.407
477	0.409	0.395	0.409	0.603	0.409	0.409
478	0.411	0.398	0.411	0.613	0.411	0.411
479	0.414	0.4	0.414	0.622	0.414	0.414
480	0.416	0.403	0.416	0.631	0.416	0.416
481	0.419	0.406	0.419	0.641	0.419	0.419
482	0.421	0.409	0.421	0.651	0.421	0.421
483	0.424	0.412	0.424	0.662	0.424	0.424
484	0.427	0.414	0.427	0.671	0.427	0.427
485	0.429	0.417	0.429	0.681	0.429	0.429
486	0.432	0.42	0.432	0.691	0.432	0.432
487	0.435	0.423	0.435	0.701	0.435	0.435
488	0.438	0.426	0.438	0.711	0.438	0.438
489	0.44	0.429	0.44	0.721	0.44	0.44
490	0.443	0.432	0.443	0.731	0.443	0.443
491	0.446	0.435	0.446	0.741	0.446	0.446
492	0.448	0.438	0.448	0.751	0.448	0.448
493	0.451	0.441	0.451	0.762	0.451	0.451
494	0.454	0.444	0.454	0.772	0.454	0.454
495	0.457	0.447	0.457	0.782	0.457	0.457
496	0.46	0.451	0.46	0.792	0.46	0.46
497	0.463	0.453	0.463	0.802	0.463	0.463
498	0.465	0.457	0.465	0.812	0.465	0.465
499	0.468	0.459	0.468	0.821	0.468	0.468
500	0.471	0.463	0.471	0.831	0.471	0.471

501	0.474	0.465	0.474	0.84	0.474	0.474
502	0.476	0.469	0.476	0.85	0.476	0.476
503	0.479	0.471	0.479	0.859	0.479	0.479
504	0.482	0.474	0.482	0.867	0.482	0.482
505	0.485	0.477	0.485	0.877	0.485	0.485
506	0.487	0.48	0.487	0.886	0.487	0.487
507	0.49	0.483	0.49	0.894	0.49	0.49
508	0.492	0.486	0.492	0.902	0.492	0.492
509	0.495	0.489	0.495	0.91	0.495	0.495
510	0.497	0.491	0.497	0.918	0.497	0.497
511	0.5	0.494	0.5	0.924	0.5	0.5
512	0.502	0.496	0.502	0.931	0.502	0.502
513	0.504	0.498	0.504	0.937	0.504	0.504
514	0.506	0.5	0.506	0.943	0.506	0.506
515	0.508	0.502	0.508	0.95	0.508	0.508
516	0.509	0.504	0.509	0.955	0.509	0.509
517	0.511	0.506	0.511	0.96	0.511	0.511
518	0.512	0.507	0.512	0.965	0.512	0.512
519	0.513	0.509	0.513	0.969	0.513	0.513
520	0.514	0.51	0.514	0.973	0.514	0.514
521	0.515	0.511	0.515	0.976	0.515	0.515
522	0.516	0.512	0.516	0.979	0.516	0.516
523	0.516	0.512	0.516	0.981	0.516	0.516
524	0.517	0.512	0.517	0.983	0.517	0.517
525	0.517	0.513	0.517	0.984	0.517	0.517
526	0.517	0.513	0.517	0.985	0.517	0.517
527	0.516	0.512	0.516	0.985	0.516	0.516
528	0.516	0.512	0.516	0.985	0.516	0.516
529	0.515	0.511	0.515	0.984	0.515	0.515
530	0.514	0.51	0.514	0.982	0.514	0.514
531	0.513	0.509	0.513	0.98	0.513	0.513
532	0.512	0.508	0.512	0.978	0.512	0.512
533	0.51	0.506	0.51	0.975	0.51	0.51
534	0.508	0.505	0.508	0.971	0.508	0.508
535	0.506	0.503	0.506	0.967	0.506	0.506
536	0.504	0.5	0.504	0.962	0.504	0.504
537	0.5	0.497	0.5	0.952	0.5	0.5
538	0.498	0.494	0.498	0.946	0.498	0.498
539	0.495	0.491	0.495	0.941	0.495	0.495
540	0.492	0.488	0.492	0.934	0.492	0.492
541	0.489	0.485	0.489	0.927	0.489	0.489
542	0.486	0.481	0.486	0.919	0.486	0.486
543	0.482	0.478	0.482	0.911	0.482	0.482
544	0.478	0.474	0.478	0.903	0.478	0.478
545	0.474	0.47	0.474	0.894	0.474	0.474
546	0.47	0.465	0.47	0.885	0.47	0.47

547	0.466	0.461	0.466	0.875	0.466	0.466
548	0.462	0.457	0.462	0.865	0.462	0.462
549	0.457	0.452	0.457	0.854	0.457	0.457
550	0.452	0.447	0.452	0.843	0.452	0.452
551	0.447	0.442	0.447	0.831	0.447	0.447
552	0.442	0.436	0.442	0.819	0.442	0.442
553	0.437	0.431	0.437	0.807	0.437	0.437
554	0.431	0.425	0.431	0.794	0.431	0.431
555	0.425	0.42	0.425	0.781	0.425	0.425
556	0.42	0.414	0.42	0.768	0.42	0.42
557	0.414	0.408	0.414	0.754	0.414	0.414
558	0.408	0.401	0.408	0.74	0.408	0.408
559	0.402	0.395	0.402	0.726	0.402	0.402
560	0.396	0.389	0.396	0.712	0.396	0.396
561	0.389	0.383	0.389	0.697	0.389	0.389
562	0.383	0.376	0.383	0.682	0.383	0.383
563	0.376	0.369	0.376	0.666	0.376	0.376
564	0.37	0.363	0.37	0.651	0.37	0.37
565	0.363	0.356	0.363	0.636	0.363	0.363
566	0.356	0.349	0.356	0.62	0.356	0.356
567	0.349	0.341	0.349	0.604	0.349	0.349
568	0.343	0.334	0.343	0.589	0.343	0.343
569	0.336	0.327	0.336	0.573	0.336	0.336
570	0.329	0.32	0.329	0.557	0.329	0.329
571	0.322	0.313	0.322	0.542	0.322	0.322
572	0.316	0.307	0.316	0.527	0.316	0.316
573	0.309	0.3	0.309	0.511	0.309	0.309
574	0.302	0.293	0.302	0.497	0.302	0.302
575	0.296	0.286	0.296	0.481	0.296	0.296
576	0.289	0.279	0.289	0.466	0.289	0.289
577	0.282	0.272	0.282	0.451	0.282	0.282
578	0.276	0.266	0.276	0.437	0.276	0.276
579	0.27	0.259	0.27	0.422	0.27	0.27
580	0.263	0.252	0.263	0.408	0.263	0.263
581	0.257	0.246	0.257	0.394	0.257	0.257
582	0.251	0.24	0.251	0.38	0.251	0.251
583	0.245	0.233	0.245	0.366	0.245	0.245
584	0.238	0.227	0.238	0.353	0.238	0.238
585	0.232	0.221	0.232	0.34	0.232	0.232
586	0.226	0.215	0.226	0.328	0.226	0.226
587	0.221	0.209	0.221	0.316	0.221	0.221
588	0.215	0.203	0.215	0.305	0.215	0.215
589	0.21	0.198	0.21	0.294	0.21	0.21
590	0.205	0.192	0.205	0.283	0.205	0.205
591	0.2	0.187	0.2	0.273	0.2	0.2
592	0.195	0.182	0.195	0.263	0.195	0.195

593	0.191	0.177	0.191	0.254	0.191	0.191
594	0.186	0.173	0.186	0.245	0.186	0.186
595	0.182	0.169	0.182	0.236	0.182	0.182
596	0.178	0.164	0.178	0.228	0.178	0.178
597	0.174	0.16	0.174	0.22	0.174	0.174
598	0.17	0.156	0.17	0.212	0.17	0.17
599	0.166	0.153	0.166	0.205	0.166	0.166
600	0.163	0.149	0.163	0.199	0.163	0.163
601	0.16	0.146	0.16	0.192	0.16	0.16
602	0.156	0.143	0.156	0.186	0.156	0.156
603	0.153	0.139	0.153	0.18	0.153	0.153
604	0.151	0.136	0.151	0.175	0.151	0.151
605	0.148	0.134	0.148	0.169	0.148	0.148
606	0.145	0.131	0.145	0.164	0.145	0.145
607	0.143	0.129	0.143	0.16	0.143	0.143
608	0.141	0.126	0.141	0.156	0.141	0.141
609	0.138	0.124	0.138	0.152	0.138	0.138
610	0.136	0.122	0.136	0.148	0.136	0.136
611	0.134	0.12	0.134	0.144	0.134	0.134
612	0.132	0.118	0.132	0.141	0.132	0.132
613	0.13	0.116	0.13	0.137	0.13	0.13
614	0.129	0.114	0.129	0.134	0.129	0.129
615	0.127	0.112	0.127	0.131	0.127	0.127
616	0.125	0.111	0.125	0.129	0.125	0.125
617	0.124	0.109	0.124	0.126	0.124	0.124
618	0.122	0.108	0.122	0.123	0.122	0.122
619	0.12	0.106	0.12	0.121	0.12	0.12
620	0.119	0.105	0.119	0.119	0.119	0.119
621	0.118	0.103	0.118	0.117	0.118	0.118
622	0.117	0.102	0.117	0.115	0.117	0.117
623	0.115	0.101	0.115	0.113	0.115	0.115
624	0.114	0.099	0.114	0.111	0.114	0.114
625	0.113	0.098	0.113	0.109	0.113	0.113
626	0.111	0.097	0.111	0.107	0.111	0.111
627	0.11	0.096	0.11	0.105	0.11	0.11
628	0.109	0.094	0.109	0.104	0.109	0.109
629	0.108	0.093	0.108	0.102	0.108	0.108
630	0.106	0.092	0.106	0.101	0.106	0.106
631	0.105	0.091	0.105	0.099	0.105	0.105
632	0.104	0.09	0.104	0.098	0.104	0.104
633	0.103	0.089	0.103	0.096	0.103	0.103
634	0.102	0.088	0.102	0.095	0.102	0.102
635	0.101	0.086	0.101	0.094	0.101	0.101
636	0.1	0.085	0.1	0.092	0.1	0.1
637	0.099	0.084	0.099	0.091	0.099	0.099
638	0.098	0.083	0.098	0.09	0.098	0.098

639	0.097	0.082	0.097	0.089	0.097	0.097
640	0.096	0.082	0.096	0.088	0.096	0.096
641	0.095	0.081	0.095	0.087	0.095	0.095
642	0.094	0.08	0.094	0.086	0.094	0.094
643	0.093	0.079	0.093	0.084	0.093	0.093
644	0.092	0.078	0.092	0.083	0.092	0.092
645	0.091	0.077	0.091	0.083	0.091	0.091
646	0.09	0.076	0.09	0.082	0.09	0.09
647	0.09	0.075	0.09	0.081	0.09	0.09
648	0.089	0.075	0.089	0.08	0.089	0.089
649	0.088	0.074	0.088	0.079	0.088	0.088
650	0.087	0.073	0.087	0.078	0.087	0.087
651	0.087	0.072	0.087	0.077	0.087	0.087
652	0.086	0.072	0.086	0.077	0.086	0.086
653	0.085	0.071	0.085	0.076	0.085	0.085
654	0.085	0.07	0.085	0.075	0.085	0.085
655	0.084	0.07	0.084	0.075	0.084	0.084
656	0.083	0.069	0.083	0.074	0.083	0.083
657	0.083	0.068	0.083	0.073	0.083	0.083
658	0.082	0.068	0.082	0.073	0.082	0.082
659	0.082	0.067	0.082	0.072	0.082	0.082
660	0.081	0.067	0.081	0.072	0.081	0.081
661	0.081	0.066	0.081	0.071	0.081	0.081
662	0.08	0.066	0.08	0.071	0.08	0.08
663	0.079	0.065	0.079	0.07	0.079	0.079
664	0.079	0.065	0.079	0.07	0.079	0.079
665	0.078	0.064	0.078	0.069	0.078	0.078
666	0.078	0.064	0.078	0.069	0.078	0.078
667	0.078	0.064	0.078	0.068	0.078	0.078
668	0.077	0.063	0.077	0.068	0.077	0.077
669	0.077	0.063	0.077	0.068	0.077	0.077
670	0.076	0.063	0.076	0.067	0.076	0.076
671	0.076	0.062	0.076	0.067	0.076	0.076
672	0.076	0.062	0.076	0.066	0.076	0.076
673	0.075	0.062	0.075	0.066	0.075	0.075
674	0.075	0.061	0.075	0.066	0.075	0.075
675	0.075	0.061	0.075	0.065	0.075	0.075
676	0.075	0.061	0.075	0.065	0.075	0.075
677	0.074	0.06	0.074	0.065	0.074	0.074
678	0.074	0.06	0.074	0.064	0.074	0.074
679	0.074	0.06	0.074	0.064	0.074	0.074
680	0.074	0.059	0.074	0.064	0.074	0.074
681	0.073	0.059	0.073	0.064	0.073	0.073
682	0.073	0.059	0.073	0.063	0.073	0.073
683	0.073	0.059	0.073	0.063	0.073	0.073
684	0.073	0.059	0.073	0.063	0.073	0.073

685	0.072	0.058	0.072	0.063	0.072	0.072
686	0.072	0.058	0.072	0.063	0.072	0.072
687	0.072	0.058	0.072	0.063	0.072	0.072
688	0.072	0.058	0.072	0.062	0.072	0.072
689	0.072	0.058	0.072	0.062	0.072	0.072
690	0.072	0.058	0.072	0.062	0.072	0.072
691	0.072	0.057	0.072	0.062	0.072	0.072
692	0.071	0.057	0.071	0.062	0.071	0.071
693	0.071	0.057	0.071	0.062	0.071	0.071
694	0.071	0.057	0.071	0.062	0.071	0.071
695	0.071	0.057	0.071	0.061	0.071	0.071
696	0.071	0.057	0.071	0.061	0.071	0.071
697	0.071	0.057	0.071	0.061	0.071	0.071
698	0.071	0.057	0.071	0.061	0.071	0.071
699	0.071	0.057	0.071	0.061	0.071	0.071
700	0.071	0.057	0.071	0.061	0.071	0.071

Table 4.30 Absorbance for Hg- DPC in CTAB

400	0.137	0.137	0.195	0.202	0.125	0.125	0.125
401	0.137	0.137	0.193	0.201	0.125	0.125	0.125
402	0.136	0.136	0.192	0.199	0.124	0.124	0.124
403	0.135	0.135	0.191	0.198	0.123	0.123	0.123
404	0.134	0.134	0.189	0.196	0.122	0.122	0.122
405	0.133	0.133	0.188	0.195	0.122	0.122	0.122
406	0.132	0.132	0.187	0.193	0.121	0.121	0.121
407	0.131	0.131	0.185	0.192	0.12	0.12	0.12
408	0.13	0.13	0.184	0.19	0.119	0.119	0.119
409	0.13	0.13	0.182	0.189	0.119	0.119	0.119
410	0.129	0.129	0.181	0.187	0.118	0.118	0.118
411	0.128	0.128	0.18	0.186	0.117	0.117	0.117
412	0.127	0.127	0.179	0.184	0.116	0.116	0.116
413	0.126	0.126	0.177	0.183	0.116	0.116	0.116
414	0.125	0.125	0.176	0.182	0.115	0.115	0.115
415	0.125	0.125	0.175	0.18	0.114	0.114	0.114
416	0.124	0.124	0.174	0.179	0.114	0.114	0.114
417	0.123	0.123	0.172	0.178	0.113	0.113	0.113
418	0.123	0.123	0.171	0.177	0.113	0.113	0.113
419	0.122	0.122	0.17	0.175	0.112	0.112	0.112
420	0.121	0.121	0.169	0.174	0.111	0.111	0.111
421	0.121	0.121	0.168	0.173	0.111	0.111	0.111
422	0.12	0.12	0.167	0.172	0.11	0.11	0.11
423	0.119	0.119	0.166	0.171	0.11	0.11	0.11
424	0.119	0.119	0.165	0.169	0.109	0.109	0.109
425	0.118	0.118	0.164	0.168	0.109	0.109	0.109

426	0.117	0.117	0.163	0.167	0.108	0.108	0.108
427	0.117	0.117	0.162	0.167	0.108	0.108	0.108
428	0.117	0.117	0.161	0.166	0.107	0.107	0.107
429	0.116	0.116	0.16	0.165	0.107	0.107	0.107
430	0.116	0.116	0.16	0.164	0.106	0.106	0.106
431	0.115	0.115	0.159	0.163	0.106	0.106	0.106
432	0.115	0.115	0.158	0.162	0.106	0.106	0.106
433	0.115	0.115	0.157	0.162	0.105	0.105	0.105
434	0.114	0.114	0.157	0.161	0.105	0.105	0.105
435	0.114	0.114	0.156	0.16	0.105	0.105	0.105
436	0.114	0.114	0.156	0.16	0.105	0.105	0.105
437	0.113	0.113	0.155	0.159	0.105	0.105	0.105
438	0.113	0.113	0.155	0.159	0.105	0.105	0.105
439	0.113	0.113	0.155	0.159	0.104	0.104	0.104
440	0.113	0.113	0.155	0.158	0.104	0.104	0.104
441	0.113	0.113	0.154	0.158	0.104	0.104	0.104
442	0.113	0.113	0.154	0.158	0.104	0.104	0.104
443	0.113	0.113	0.154	0.158	0.105	0.105	0.105
444	0.113	0.113	0.154	0.158	0.105	0.105	0.105
445	0.114	0.114	0.155	0.158	0.105	0.105	0.105
446	0.114	0.114	0.155	0.158	0.105	0.105	0.105
447	0.114	0.114	0.155	0.159	0.106	0.106	0.106
448	0.115	0.115	0.156	0.159	0.106	0.106	0.106
449	0.115	0.115	0.156	0.16	0.106	0.106	0.106
450	0.116	0.116	0.157	0.161	0.107	0.107	0.107
451	0.117	0.117	0.158	0.161	0.108	0.108	0.108
452	0.117	0.117	0.159	0.162	0.108	0.108	0.108
453	0.118	0.118	0.16	0.163	0.109	0.109	0.109
454	0.119	0.119	0.161	0.165	0.11	0.11	0.11
455	0.12	0.12	0.163	0.166	0.111	0.111	0.111
456	0.121	0.121	0.164	0.167	0.112	0.112	0.112
457	0.122	0.122	0.166	0.169	0.113	0.113	0.113
458	0.124	0.124	0.167	0.171	0.114	0.114	0.114
459	0.125	0.125	0.169	0.173	0.115	0.115	0.115
460	0.127	0.127	0.172	0.175	0.117	0.117	0.117
461	0.129	0.129	0.174	0.178	0.118	0.118	0.118
462	0.13	0.13	0.177	0.181	0.12	0.12	0.12
463	0.133	0.133	0.18	0.184	0.122	0.122	0.122
464	0.135	0.135	0.183	0.187	0.124	0.124	0.124
465	0.138	0.138	0.186	0.19	0.126	0.126	0.126
466	0.14	0.14	0.19	0.194	0.128	0.128	0.128
467	0.143	0.143	0.194	0.198	0.131	0.131	0.131
468	0.146	0.146	0.198	0.203	0.134	0.134	0.134
469	0.149	0.149	0.202	0.207	0.136	0.136	0.136
470	0.152	0.152	0.207	0.212	0.139	0.139	0.139
471	0.156	0.156	0.212	0.217	0.142	0.142	0.142

472	0.159	0.159	0.217	0.222	0.146	0.146	0.146
473	0.163	0.163	0.223	0.228	0.149	0.149	0.149
474	0.168	0.168	0.229	0.234	0.153	0.153	0.153
475	0.172	0.172	0.235	0.241	0.157	0.157	0.157
476	0.177	0.177	0.242	0.248	0.161	0.161	0.161
477	0.181	0.181	0.249	0.255	0.165	0.165	0.165
478	0.187	0.187	0.256	0.263	0.169	0.169	0.169
479	0.192	0.192	0.264	0.271	0.174	0.174	0.174
480	0.198	0.198	0.272	0.279	0.179	0.179	0.179
481	0.203	0.203	0.281	0.288	0.184	0.184	0.184
482	0.21	0.21	0.29	0.298	0.19	0.19	0.19
483	0.216	0.216	0.3	0.309	0.196	0.196	0.196
484	0.223	0.223	0.309	0.319	0.201	0.201	0.201
485	0.229	0.229	0.319	0.329	0.207	0.207	0.207
486	0.236	0.236	0.329	0.34	0.213	0.213	0.213
487	0.244	0.244	0.34	0.351	0.219	0.219	0.219
488	0.252	0.252	0.352	0.364	0.226	0.226	0.226
489	0.259	0.259	0.364	0.377	0.233	0.233	0.233
490	0.267	0.267	0.376	0.39	0.24	0.24	0.24
491	0.275	0.275	0.389	0.403	0.247	0.247	0.247
492	0.283	0.283	0.402	0.416	0.253	0.253	0.253
493	0.291	0.291	0.415	0.431	0.26	0.26	0.26
494	0.299	0.299	0.428	0.445	0.268	0.268	0.268
495	0.307	0.307	0.442	0.459	0.275	0.275	0.275
496	0.316	0.316	0.455	0.474	0.282	0.282	0.282
497	0.324	0.324	0.469	0.489	0.289	0.289	0.289
498	0.333	0.333	0.484	0.504	0.297	0.297	0.297
499	0.341	0.341	0.497	0.518	0.304	0.304	0.304
500	0.349	0.349	0.511	0.532	0.311	0.311	0.311
501	0.357	0.357	0.524	0.547	0.317	0.317	0.317
502	0.365	0.365	0.538	0.561	0.324	0.324	0.324
503	0.374	0.374	0.552	0.576	0.331	0.331	0.331
504	0.381	0.381	0.565	0.589	0.338	0.338	0.338
505	0.389	0.389	0.578	0.603	0.344	0.344	0.344
506	0.397	0.397	0.59	0.617	0.351	0.351	0.351
507	0.404	0.404	0.602	0.629	0.357	0.357	0.357
508	0.41	0.41	0.613	0.641	0.362	0.362	0.362
509	0.417	0.417	0.624	0.653	0.368	0.368	0.368
510	0.423	0.423	0.634	0.664	0.373	0.373	0.373
511	0.428	0.428	0.643	0.673	0.378	0.378	0.378
512	0.434	0.434	0.652	0.683	0.382	0.382	0.382
513	0.438	0.438	0.66	0.691	0.386	0.386	0.386
514	0.442	0.442	0.667	0.699	0.389	0.389	0.389
515	0.446	0.446	0.674	0.707	0.393	0.393	0.393
516	0.45	0.45	0.681	0.714	0.396	0.396	0.396
517	0.453	0.453	0.686	0.719	0.398	0.398	0.398

518	0.455	0.455	0.691	0.724	0.4	0.4	0.4
519	0.457	0.457	0.695	0.729	0.402	0.402	0.402
520	0.459	0.459	0.698	0.732	0.403	0.403	0.403
521	0.46	0.46	0.701	0.735	0.404	0.404	0.404
522	0.461	0.461	0.703	0.737	0.405	0.405	0.405
523	0.462	0.462	0.704	0.739	0.406	0.406	0.406
524	0.462	0.462	0.705	0.74	0.406	0.406	0.406
525	0.462	0.462	0.705	0.74	0.405	0.405	0.405
526	0.461	0.461	0.704	0.74	0.405	0.405	0.405
527	0.46	0.46	0.703	0.739	0.404	0.404	0.404
528	0.459	0.459	0.702	0.737	0.403	0.403	0.403
529	0.458	0.458	0.7	0.735	0.402	0.402	0.402
530	0.456	0.456	0.698	0.733	0.4	0.4	0.4
531	0.454	0.454	0.695	0.73	0.398	0.398	0.398
532	0.452	0.452	0.692	0.727	0.396	0.396	0.396
533	0.45	0.45	0.688	0.723	0.395	0.395	0.395
534	0.448	0.448	0.685	0.719	0.392	0.392	0.392
535	0.445	0.445	0.681	0.715	0.39	0.39	0.39
536	0.442	0.442	0.677	0.711	0.388	0.388	0.388
537	0.438	0.438	0.67	0.704	0.384	0.384	0.384
538	0.435	0.435	0.666	0.7	0.382	0.382	0.382
539	0.432	0.432	0.661	0.695	0.379	0.379	0.379
540	0.429	0.429	0.656	0.69	0.376	0.376	0.376
541	0.426	0.426	0.651	0.685	0.374	0.374	0.374
542	0.422	0.422	0.646	0.68	0.371	0.371	0.371
543	0.419	0.419	0.641	0.674	0.368	0.368	0.368
544	0.416	0.416	0.635	0.669	0.365	0.365	0.365
545	0.412	0.412	0.63	0.663	0.362	0.362	0.362
546	0.409	0.409	0.625	0.658	0.359	0.359	0.359
547	0.405	0.405	0.62	0.652	0.356	0.356	0.356
548	0.402	0.402	0.614	0.647	0.352	0.352	0.352
549	0.398	0.398	0.608	0.641	0.349	0.349	0.349
550	0.394	0.394	0.602	0.635	0.346	0.346	0.346
551	0.39	0.39	0.597	0.63	0.343	0.343	0.343
552	0.387	0.387	0.591	0.623	0.339	0.339	0.339
553	0.383	0.383	0.586	0.618	0.336	0.336	0.336
554	0.379	0.379	0.58	0.612	0.333	0.333	0.333
555	0.375	0.375	0.574	0.606	0.33	0.33	0.33
556	0.372	0.372	0.569	0.601	0.327	0.327	0.327
557	0.368	0.368	0.563	0.595	0.323	0.323	0.323
558	0.364	0.364	0.557	0.589	0.32	0.32	0.32
559	0.361	0.361	0.551	0.583	0.317	0.317	0.317
560	0.357	0.357	0.546	0.578	0.314	0.314	0.314
561	0.354	0.354	0.541	0.572	0.311	0.311	0.311
562	0.35	0.35	0.535	0.567	0.308	0.308	0.308
563	0.347	0.347	0.529	0.561	0.305	0.305	0.305

564	0.343	0.343	0.524	0.555	0.302	0.302	0.302
565	0.34	0.34	0.518	0.55	0.299	0.299	0.299
566	0.336	0.336	0.513	0.544	0.296	0.296	0.296
567	0.333	0.333	0.507	0.539	0.293	0.293	0.293
568	0.329	0.329	0.502	0.533	0.29	0.29	0.29
569	0.326	0.326	0.497	0.528	0.287	0.287	0.287
570	0.323	0.323	0.491	0.522	0.284	0.284	0.284
571	0.319	0.319	0.486	0.517	0.281	0.281	0.281
572	0.316	0.316	0.481	0.512	0.278	0.278	0.278
573	0.313	0.313	0.476	0.507	0.275	0.275	0.275
574	0.31	0.31	0.471	0.502	0.272	0.272	0.272
575	0.307	0.307	0.466	0.496	0.27	0.27	0.27
576	0.303	0.303	0.461	0.492	0.267	0.267	0.267
577	0.3	0.3	0.457	0.487	0.265	0.265	0.265
578	0.297	0.297	0.452	0.482	0.262	0.262	0.262
579	0.294	0.294	0.447	0.477	0.259	0.259	0.259
580	0.292	0.292	0.443	0.472	0.257	0.257	0.257
581	0.289	0.289	0.438	0.467	0.254	0.254	0.254
582	0.286	0.286	0.434	0.463	0.251	0.251	0.251
583	0.283	0.283	0.429	0.458	0.249	0.249	0.249
584	0.28	0.28	0.425	0.453	0.247	0.247	0.247
585	0.277	0.277	0.42	0.449	0.244	0.244	0.244
586	0.275	0.275	0.416	0.444	0.242	0.242	0.242
587	0.272	0.272	0.412	0.44	0.24	0.24	0.24
588	0.269	0.269	0.407	0.435	0.237	0.237	0.237
589	0.266	0.266	0.403	0.431	0.235	0.235	0.235
590	0.264	0.264	0.399	0.426	0.232	0.232	0.232
591	0.261	0.261	0.395	0.422	0.23	0.23	0.23
592	0.259	0.259	0.391	0.418	0.228	0.228	0.228
593	0.256	0.256	0.387	0.413	0.226	0.226	0.226
594	0.254	0.254	0.382	0.409	0.224	0.224	0.224
595	0.251	0.251	0.378	0.405	0.221	0.221	0.221
596	0.248	0.248	0.374	0.401	0.219	0.219	0.219
597	0.246	0.246	0.37	0.396	0.217	0.217	0.217
598	0.243	0.243	0.366	0.392	0.214	0.214	0.214
599	0.241	0.241	0.362	0.388	0.213	0.213	0.213
600	0.238	0.238	0.358	0.384	0.21	0.21	0.21
601	0.236	0.236	0.354	0.38	0.208	0.208	0.208
602	0.233	0.233	0.35	0.375	0.206	0.206	0.206
603	0.231	0.231	0.346	0.371	0.204	0.204	0.204
604	0.228	0.228	0.342	0.367	0.202	0.202	0.202
605	0.226	0.226	0.338	0.362	0.199	0.199	0.199
606	0.223	0.223	0.334	0.358	0.197	0.197	0.197
607	0.221	0.221	0.33	0.354	0.195	0.195	0.195
608	0.218	0.218	0.326	0.35	0.193	0.193	0.193
609	0.216	0.216	0.323	0.346	0.191	0.191	0.191

610	0.214	0.214	0.319	0.342	0.189	0.189	0.189
611	0.211	0.211	0.315	0.338	0.187	0.187	0.187
612	0.209	0.209	0.311	0.334	0.185	0.185	0.185
613	0.206	0.206	0.307	0.33	0.183	0.183	0.183
614	0.204	0.204	0.304	0.326	0.181	0.181	0.181
615	0.202	0.202	0.3	0.323	0.179	0.179	0.179
616	0.199	0.199	0.296	0.319	0.177	0.177	0.177
617	0.197	0.197	0.293	0.315	0.175	0.175	0.175
618	0.195	0.195	0.289	0.311	0.173	0.173	0.173
619	0.193	0.193	0.286	0.307	0.171	0.171	0.171
620	0.191	0.191	0.282	0.304	0.169	0.169	0.169
621	0.188	0.188	0.279	0.3	0.167	0.167	0.167
622	0.186	0.186	0.276	0.297	0.166	0.166	0.166
623	0.184	0.184	0.272	0.293	0.164	0.164	0.164
624	0.182	0.182	0.269	0.29	0.162	0.162	0.162
625	0.18	0.18	0.266	0.286	0.16	0.16	0.16
626	0.178	0.178	0.262	0.283	0.158	0.158	0.158
627	0.176	0.176	0.259	0.279	0.156	0.156	0.156
628	0.174	0.174	0.256	0.276	0.155	0.155	0.155
629	0.172	0.172	0.253	0.272	0.153	0.153	0.153
630	0.17	0.17	0.25	0.269	0.151	0.151	0.151
631	0.168	0.168	0.247	0.266	0.15	0.15	0.15
632	0.166	0.166	0.244	0.263	0.148	0.148	0.148
633	0.164	0.164	0.241	0.26	0.147	0.147	0.147
634	0.163	0.163	0.238	0.257	0.145	0.145	0.145
635	0.161	0.161	0.235	0.254	0.144	0.144	0.144
636	0.159	0.159	0.233	0.251	0.142	0.142	0.142
637	0.157	0.157	0.23	0.248	0.141	0.141	0.141
638	0.156	0.156	0.227	0.245	0.139	0.139	0.139
639	0.154	0.154	0.224	0.242	0.138	0.138	0.138
640	0.152	0.152	0.222	0.239	0.136	0.136	0.136
641	0.151	0.151	0.219	0.237	0.135	0.135	0.135
642	0.149	0.149	0.217	0.234	0.133	0.133	0.133
643	0.147	0.147	0.214	0.231	0.132	0.132	0.132
644	0.146	0.146	0.212	0.229	0.131	0.131	0.131
645	0.144	0.144	0.209	0.226	0.129	0.129	0.129
646	0.143	0.143	0.207	0.223	0.128	0.128	0.128
647	0.141	0.141	0.204	0.221	0.127	0.127	0.127
648	0.14	0.14	0.202	0.218	0.125	0.125	0.125
649	0.138	0.138	0.2	0.216	0.124	0.124	0.124
650	0.137	0.137	0.197	0.213	0.123	0.123	0.123
651	0.135	0.135	0.195	0.211	0.122	0.122	0.122
652	0.134	0.134	0.193	0.208	0.12	0.12	0.12
653	0.132	0.132	0.191	0.206	0.119	0.119	0.119
654	0.131	0.131	0.189	0.204	0.118	0.118	0.118
655	0.13	0.13	0.187	0.201	0.117	0.117	0.117

656	0.128	0.128	0.185	0.199	0.116	0.116	0.116
657	0.127	0.127	0.182	0.197	0.115	0.115	0.115
658	0.126	0.126	0.181	0.195	0.113	0.113	0.113
659	0.124	0.124	0.178	0.193	0.112	0.112	0.112
660	0.123	0.123	0.177	0.191	0.111	0.111	0.111
661	0.122	0.122	0.174	0.188	0.11	0.11	0.11
662	0.12	0.12	0.172	0.186	0.109	0.109	0.109
663	0.119	0.119	0.17	0.184	0.108	0.108	0.108
664	0.118	0.118	0.169	0.182	0.107	0.107	0.107
665	0.117	0.117	0.167	0.18	0.106	0.106	0.106
666	0.116	0.116	0.165	0.178	0.105	0.105	0.105
667	0.115	0.115	0.163	0.176	0.104	0.104	0.104
668	0.113	0.113	0.161	0.174	0.103	0.103	0.103
669	0.112	0.112	0.159	0.172	0.102	0.102	0.102
670	0.111	0.111	0.158	0.17	0.101	0.101	0.101
671	0.11	0.11	0.156	0.168	0.1	0.1	0.1
672	0.109	0.109	0.154	0.166	0.099	0.099	0.099
673	0.108	0.108	0.152	0.164	0.098	0.098	0.098
674	0.107	0.107	0.151	0.163	0.097	0.097	0.097
675	0.106	0.106	0.149	0.161	0.096	0.096	0.096
676	0.105	0.105	0.148	0.159	0.095	0.095	0.095
677	0.104	0.104	0.146	0.157	0.094	0.094	0.094
678	0.103	0.103	0.145	0.156	0.094	0.094	0.094
679	0.102	0.102	0.143	0.154	0.093	0.093	0.093
680	0.101	0.101	0.141	0.152	0.092	0.092	0.092
681	0.1	0.1	0.14	0.151	0.091	0.091	0.091
682	0.099	0.099	0.139	0.149	0.09	0.09	0.09
683	0.098	0.098	0.137	0.147	0.089	0.089	0.089
684	0.097	0.097	0.135	0.146	0.089	0.089	0.089
685	0.096	0.096	0.134	0.144	0.088	0.088	0.088
686	0.095	0.095	0.133	0.142	0.087	0.087	0.087
687	0.094	0.094	0.131	0.141	0.086	0.086	0.086
688	0.093	0.093	0.13	0.139	0.086	0.086	0.086
689	0.092	0.092	0.128	0.138	0.085	0.085	0.085
690	0.092	0.092	0.127	0.136	0.084	0.084	0.084
691	0.091	0.091	0.125	0.135	0.083	0.083	0.083
692	0.09	0.09	0.124	0.133	0.083	0.083	0.083
693	0.089	0.089	0.123	0.132	0.082	0.082	0.082
694	0.089	0.089	0.122	0.13	0.081	0.081	0.081
695	0.088	0.088	0.12	0.129	0.081	0.081	0.081
696	0.087	0.087	0.119	0.128	0.08	0.08	0.08
697	0.086	0.086	0.118	0.126	0.079	0.079	0.079
698	0.085	0.085	0.117	0.125	0.079	0.079	0.079
699	0.085	0.085	0.115	0.124	0.078	0.078	0.078
700	0.084	0.084	0.114	0.122	0.078	0.078	0.078

Table 4.31 Absorbance for Zn-DPC in CTAB

400	0.048	0.049	0.051	0.057	0.084	0.081	0.081
401	0.048	0.048	0.051	0.057	0.084	0.081	0.081
402	0.048	0.048	0.051	0.057	0.083	0.081	0.081
403	0.048	0.048	0.051	0.057	0.083	0.08	0.08
404	0.048	0.048	0.051	0.057	0.083	0.08	0.08
405	0.048	0.048	0.051	0.056	0.083	0.08	0.08
406	0.048	0.048	0.051	0.056	0.083	0.08	0.08
407	0.048	0.048	0.05	0.056	0.083	0.08	0.08
408	0.047	0.048	0.05	0.056	0.083	0.08	0.08
409	0.047	0.048	0.05	0.056	0.083	0.08	0.08
410	0.047	0.048	0.05	0.056	0.083	0.081	0.081
411	0.047	0.048	0.05	0.056	0.083	0.081	0.081
412	0.047	0.048	0.05	0.056	0.083	0.081	0.081
413	0.047	0.048	0.05	0.056	0.083	0.081	0.081
414	0.047	0.048	0.05	0.056	0.083	0.081	0.081
415	0.047	0.048	0.05	0.056	0.083	0.081	0.081
416	0.047	0.048	0.05	0.056	0.083	0.081	0.081
417	0.047	0.048	0.05	0.056	0.083	0.081	0.081
418	0.047	0.048	0.05	0.056	0.083	0.081	0.081
419	0.047	0.048	0.05	0.056	0.083	0.081	0.081
420	0.047	0.047	0.049	0.056	0.083	0.081	0.081
421	0.047	0.047	0.049	0.056	0.083	0.081	0.081
422	0.047	0.047	0.049	0.056	0.083	0.081	0.081
423	0.047	0.047	0.049	0.056	0.083	0.081	0.081
424	0.047	0.048	0.05	0.056	0.083	0.081	0.081
425	0.047	0.047	0.05	0.056	0.083	0.081	0.081
426	0.047	0.047	0.05	0.056	0.083	0.081	0.081
427	0.047	0.047	0.05	0.056	0.083	0.081	0.081
428	0.047	0.047	0.05	0.056	0.083	0.081	0.081
429	0.047	0.047	0.05	0.056	0.083	0.08	0.08
430	0.047	0.047	0.05	0.056	0.083	0.08	0.08
431	0.047	0.048	0.05	0.056	0.082	0.08	0.08
432	0.047	0.048	0.05	0.056	0.082	0.08	0.08
433	0.047	0.048	0.05	0.057	0.082	0.08	0.08
434	0.047	0.048	0.05	0.057	0.082	0.08	0.08
435	0.047	0.048	0.05	0.057	0.082	0.08	0.08
436	0.047	0.048	0.05	0.057	0.082	0.08	0.08
437	0.047	0.048	0.05	0.057	0.081	0.079	0.079
438	0.047	0.048	0.05	0.057	0.081	0.079	0.079
439	0.047	0.048	0.05	0.058	0.081	0.079	0.079
440	0.047	0.048	0.05	0.058	0.081	0.079	0.079
441	0.047	0.048	0.05	0.058	0.081	0.079	0.079
442	0.047	0.048	0.05	0.058	0.08	0.078	0.078
443	0.047	0.048	0.051	0.058	0.08	0.078	0.078

444	0.047	0.049	0.051	0.059	0.079	0.078	0.078
445	0.047	0.049	0.051	0.059	0.079	0.078	0.078
446	0.047	0.049	0.051	0.059	0.079	0.077	0.077
447	0.047	0.049	0.051	0.06	0.079	0.077	0.077
448	0.047	0.049	0.051	0.06	0.078	0.077	0.077
449	0.047	0.049	0.051	0.06	0.078	0.077	0.077
450	0.047	0.049	0.052	0.061	0.078	0.076	0.076
451	0.047	0.049	0.052	0.061	0.077	0.076	0.076
452	0.047	0.049	0.052	0.061	0.077	0.076	0.076
453	0.047	0.049	0.052	0.062	0.076	0.076	0.076
454	0.048	0.05	0.052	0.062	0.076	0.075	0.075
455	0.048	0.05	0.052	0.062	0.076	0.075	0.075
456	0.048	0.05	0.052	0.063	0.075	0.075	0.075
457	0.048	0.05	0.053	0.063	0.075	0.074	0.074
458	0.048	0.05	0.053	0.064	0.074	0.074	0.074
459	0.048	0.05	0.053	0.064	0.074	0.073	0.073
460	0.048	0.05	0.053	0.065	0.073	0.073	0.073
461	0.048	0.051	0.054	0.065	0.073	0.073	0.073
462	0.048	0.051	0.054	0.066	0.073	0.073	0.073
463	0.049	0.051	0.054	0.066	0.072	0.072	0.072
464	0.049	0.051	0.054	0.067	0.072	0.072	0.072
465	0.049	0.051	0.055	0.067	0.071	0.072	0.072
466	0.049	0.052	0.055	0.068	0.071	0.071	0.071
467	0.049	0.052	0.055	0.068	0.07	0.071	0.071
468	0.049	0.052	0.055	0.069	0.07	0.07	0.07
469	0.049	0.052	0.056	0.069	0.07	0.07	0.07
470	0.05	0.052	0.056	0.07	0.069	0.07	0.07
471	0.05	0.052	0.056	0.07	0.069	0.069	0.069
472	0.05	0.053	0.057	0.071	0.068	0.069	0.069
473	0.05	0.053	0.057	0.071	0.068	0.069	0.069
474	0.05	0.053	0.057	0.072	0.067	0.068	0.068
475	0.05	0.053	0.057	0.072	0.067	0.068	0.068
476	0.051	0.054	0.058	0.073	0.067	0.068	0.068
477	0.051	0.054	0.058	0.073	0.066	0.067	0.067
478	0.051	0.054	0.058	0.074	0.066	0.067	0.067
479	0.051	0.054	0.058	0.075	0.065	0.067	0.067
480	0.051	0.054	0.059	0.075	0.065	0.066	0.066
481	0.051	0.055	0.059	0.076	0.064	0.066	0.066
482	0.052	0.055	0.059	0.076	0.064	0.066	0.066
483	0.052	0.055	0.06	0.077	0.063	0.065	0.065
484	0.052	0.055	0.06	0.077	0.063	0.065	0.065
485	0.052	0.055	0.06	0.078	0.062	0.064	0.064
486	0.052	0.056	0.061	0.078	0.062	0.064	0.064
487	0.052	0.056	0.061	0.079	0.061	0.064	0.064
488	0.052	0.056	0.061	0.079	0.061	0.063	0.063
489	0.052	0.056	0.061	0.08	0.061	0.063	0.063

490	0.053	0.056	0.062	0.08	0.06	0.063	0.063
491	0.053	0.057	0.062	0.081	0.06	0.062	0.062
492	0.053	0.057	0.062	0.081	0.059	0.062	0.062
493	0.053	0.057	0.062	0.082	0.059	0.062	0.062
494	0.053	0.057	0.063	0.082	0.058	0.061	0.061
495	0.053	0.057	0.063	0.083	0.058	0.061	0.061
496	0.053	0.057	0.063	0.083	0.058	0.061	0.061
497	0.053	0.057	0.063	0.083	0.057	0.06	0.06
498	0.054	0.057	0.064	0.084	0.057	0.06	0.06
499	0.054	0.058	0.064	0.084	0.056	0.059	0.059
500	0.054	0.058	0.064	0.084	0.056	0.059	0.059
501	0.054	0.058	0.064	0.085	0.056	0.059	0.059
502	0.054	0.058	0.064	0.085	0.055	0.058	0.058
503	0.054	0.058	0.065	0.085	0.055	0.058	0.058
504	0.054	0.058	0.065	0.085	0.054	0.058	0.058
505	0.054	0.058	0.065	0.086	0.054	0.058	0.058
506	0.054	0.058	0.065	0.086	0.054	0.057	0.057
507	0.054	0.058	0.065	0.086	0.054	0.057	0.057
508	0.054	0.059	0.066	0.087	0.053	0.057	0.057
509	0.054	0.059	0.066	0.087	0.053	0.057	0.057
510	0.054	0.059	0.066	0.087	0.053	0.057	0.057
511	0.054	0.059	0.066	0.087	0.053	0.057	0.057
512	0.055	0.059	0.066	0.087	0.052	0.056	0.056
513	0.055	0.059	0.066	0.088	0.052	0.056	0.056
514	0.055	0.059	0.066	0.088	0.052	0.056	0.056
515	0.055	0.059	0.066	0.088	0.052	0.056	0.056
516	0.055	0.059	0.066	0.088	0.052	0.056	0.056
517	0.055	0.059	0.066	0.088	0.051	0.056	0.056
518	0.055	0.059	0.066	0.088	0.051	0.056	0.056
519	0.055	0.059	0.066	0.088	0.051	0.055	0.055
520	0.055	0.059	0.066	0.088	0.051	0.055	0.055
521	0.055	0.059	0.066	0.088	0.051	0.055	0.055
522	0.055	0.059	0.066	0.088	0.05	0.055	0.055
523	0.055	0.059	0.066	0.088	0.05	0.055	0.055
524	0.055	0.059	0.066	0.088	0.05	0.055	0.055
525	0.055	0.059	0.066	0.088	0.05	0.055	0.055
526	0.055	0.059	0.066	0.087	0.05	0.054	0.054
527	0.054	0.059	0.066	0.087	0.049	0.054	0.054
528	0.054	0.059	0.066	0.087	0.049	0.054	0.054
529	0.054	0.059	0.065	0.087	0.049	0.054	0.054
530	0.054	0.059	0.065	0.087	0.049	0.054	0.054
531	0.054	0.058	0.065	0.086	0.049	0.054	0.054
532	0.054	0.058	0.065	0.086	0.049	0.054	0.054
533	0.054	0.058	0.065	0.086	0.048	0.054	0.054
534	0.054	0.058	0.064	0.085	0.048	0.053	0.053
535	0.054	0.058	0.064	0.085	0.048	0.053	0.053

536	0.054	0.058	0.064	0.085	0.048	0.053	0.053
537	0.054	0.058	0.064	0.084	0.048	0.053	0.053
538	0.053	0.058	0.063	0.084	0.048	0.053	0.053
539	0.053	0.057	0.063	0.084	0.047	0.053	0.053
540	0.053	0.057	0.063	0.083	0.047	0.053	0.053
541	0.053	0.057	0.063	0.083	0.047	0.052	0.052
542	0.053	0.057	0.062	0.082	0.047	0.052	0.052
543	0.053	0.057	0.062	0.082	0.047	0.052	0.052
544	0.052	0.056	0.062	0.081	0.047	0.052	0.052
545	0.052	0.056	0.062	0.081	0.046	0.052	0.052
546	0.052	0.056	0.061	0.08	0.046	0.052	0.052
547	0.052	0.056	0.061	0.08	0.046	0.052	0.052
548	0.052	0.055	0.061	0.079	0.046	0.051	0.051
549	0.051	0.055	0.06	0.079	0.046	0.051	0.051
550	0.051	0.055	0.06	0.078	0.046	0.051	0.051
551	0.051	0.054	0.059	0.078	0.045	0.051	0.051
552	0.051	0.054	0.059	0.077	0.045	0.051	0.051
553	0.05	0.054	0.059	0.076	0.045	0.051	0.051
554	0.05	0.054	0.058	0.076	0.045	0.05	0.05
555	0.05	0.053	0.058	0.075	0.045	0.05	0.05
556	0.05	0.053	0.057	0.075	0.045	0.05	0.05
557	0.049	0.053	0.057	0.074	0.044	0.05	0.05
558	0.049	0.052	0.057	0.073	0.044	0.05	0.05
559	0.049	0.052	0.056	0.073	0.044	0.049	0.049
560	0.048	0.052	0.056	0.072	0.044	0.049	0.049
561	0.048	0.052	0.055	0.071	0.044	0.049	0.049
562	0.048	0.051	0.055	0.071	0.043	0.049	0.049
563	0.048	0.051	0.054	0.07	0.043	0.049	0.049
564	0.047	0.05	0.054	0.069	0.043	0.048	0.048
565	0.047	0.05	0.054	0.068	0.043	0.048	0.048
566	0.047	0.05	0.053	0.068	0.042	0.048	0.048
567	0.047	0.049	0.053	0.067	0.042	0.048	0.048
568	0.046	0.049	0.052	0.066	0.042	0.048	0.048
569	0.046	0.049	0.052	0.066	0.042	0.047	0.047
570	0.046	0.048	0.051	0.065	0.042	0.047	0.047
571	0.045	0.048	0.051	0.064	0.042	0.047	0.047
572	0.045	0.048	0.05	0.063	0.041	0.047	0.047
573	0.045	0.047	0.05	0.063	0.041	0.047	0.047
574	0.044	0.047	0.05	0.062	0.041	0.046	0.046
575	0.044	0.047	0.049	0.061	0.041	0.046	0.046
576	0.044	0.046	0.049	0.061	0.041	0.046	0.046
577	0.044	0.046	0.048	0.06	0.041	0.046	0.046
578	0.043	0.046	0.048	0.059	0.04	0.046	0.046
579	0.043	0.046	0.047	0.059	0.04	0.046	0.046
580	0.043	0.046	0.047	0.058	0.04	0.046	0.046
581	0.043	0.045	0.047	0.057	0.04	0.045	0.045

582	0.043	0.045	0.047	0.057	0.04	0.045	0.045
583	0.042	0.045	0.046	0.056	0.04	0.045	0.045
584	0.042	0.045	0.046	0.055	0.04	0.045	0.045
585	0.042	0.044	0.045	0.055	0.04	0.045	0.045
586	0.042	0.044	0.045	0.054	0.04	0.045	0.045
587	0.042	0.044	0.045	0.054	0.039	0.044	0.044
588	0.041	0.044	0.044	0.053	0.039	0.044	0.044
589	0.041	0.043	0.044	0.053	0.039	0.044	0.044
590	0.041	0.043	0.044	0.052	0.039	0.044	0.044
591	0.041	0.043	0.043	0.052	0.039	0.044	0.044
592	0.041	0.043	0.043	0.051	0.039	0.044	0.044
593	0.04	0.043	0.043	0.051	0.039	0.043	0.043
594	0.04	0.042	0.042	0.05	0.039	0.043	0.043
595	0.04	0.042	0.042	0.05	0.039	0.043	0.043
596	0.04	0.042	0.042	0.049	0.038	0.043	0.043
597	0.04	0.042	0.042	0.049	0.038	0.043	0.043
598	0.04	0.042	0.042	0.048	0.038	0.043	0.043
599	0.04	0.042	0.041	0.048	0.038	0.043	0.043
600	0.039	0.041	0.041	0.048	0.038	0.042	0.042
601	0.039	0.041	0.041	0.047	0.038	0.042	0.042
602	0.039	0.041	0.041	0.047	0.038	0.042	0.042
603	0.039	0.041	0.041	0.047	0.038	0.042	0.042
604	0.039	0.041	0.04	0.046	0.038	0.042	0.042
605	0.039	0.041	0.04	0.046	0.038	0.042	0.042
606	0.039	0.041	0.04	0.046	0.038	0.042	0.042
607	0.039	0.04	0.04	0.045	0.037	0.041	0.041
608	0.039	0.04	0.04	0.045	0.037	0.041	0.041
609	0.038	0.04	0.039	0.045	0.037	0.041	0.041
610	0.038	0.04	0.039	0.044	0.037	0.041	0.041
611	0.038	0.04	0.039	0.044	0.037	0.041	0.041
612	0.038	0.04	0.039	0.044	0.037	0.041	0.041
613	0.038	0.04	0.039	0.044	0.037	0.041	0.041
614	0.038	0.04	0.039	0.043	0.037	0.041	0.041
615	0.038	0.04	0.039	0.043	0.037	0.04	0.04
616	0.038	0.039	0.039	0.043	0.037	0.04	0.04
617	0.038	0.039	0.038	0.043	0.037	0.04	0.04
618	0.038	0.039	0.038	0.042	0.037	0.04	0.04
619	0.038	0.039	0.038	0.042	0.037	0.04	0.04
620	0.038	0.039	0.038	0.042	0.037	0.04	0.04
621	0.038	0.039	0.038	0.042	0.037	0.04	0.04
622	0.037	0.039	0.038	0.042	0.036	0.04	0.04
623	0.037	0.039	0.038	0.042	0.037	0.04	0.04
624	0.037	0.039	0.038	0.041	0.036	0.039	0.039
625	0.037	0.039	0.038	0.041	0.036	0.039	0.039
626	0.037	0.039	0.038	0.041	0.036	0.039	0.039
627	0.037	0.039	0.037	0.041	0.036	0.039	0.039

628	0.037	0.039	0.037	0.041	0.036	0.039	0.039
629	0.037	0.039	0.037	0.041	0.036	0.039	0.039
630	0.037	0.038	0.037	0.041	0.036	0.039	0.039
631	0.037	0.039	0.037	0.04	0.036	0.039	0.039
632	0.037	0.038	0.037	0.04	0.036	0.039	0.039
633	0.037	0.038	0.037	0.04	0.036	0.039	0.039
634	0.037	0.038	0.037	0.04	0.036	0.039	0.039
635	0.037	0.038	0.037	0.04	0.036	0.039	0.039
636	0.037	0.038	0.037	0.04	0.036	0.039	0.039
637	0.037	0.038	0.037	0.04	0.036	0.038	0.038
638	0.037	0.038	0.037	0.04	0.036	0.038	0.038
639	0.037	0.038	0.037	0.04	0.036	0.038	0.038
640	0.037	0.038	0.037	0.039	0.036	0.038	0.038
641	0.037	0.038	0.037	0.039	0.036	0.038	0.038
642	0.037	0.038	0.037	0.039	0.036	0.038	0.038
643	0.037	0.038	0.036	0.039	0.036	0.038	0.038
644	0.036	0.038	0.036	0.039	0.036	0.038	0.038
645	0.036	0.038	0.036	0.039	0.036	0.038	0.038
646	0.036	0.038	0.036	0.039	0.036	0.038	0.038
647	0.036	0.038	0.036	0.039	0.036	0.038	0.038
648	0.036	0.038	0.036	0.039	0.036	0.038	0.038
649	0.036	0.038	0.036	0.039	0.036	0.038	0.038
650	0.036	0.038	0.036	0.039	0.036	0.038	0.038
651	0.036	0.038	0.036	0.039	0.036	0.038	0.038
652	0.036	0.038	0.036	0.039	0.036	0.038	0.038
653	0.036	0.038	0.036	0.039	0.036	0.038	0.038
654	0.036	0.038	0.036	0.039	0.036	0.038	0.038
655	0.036	0.038	0.036	0.039	0.036	0.038	0.038
656	0.036	0.038	0.036	0.039	0.036	0.037	0.037
657	0.036	0.038	0.036	0.039	0.036	0.037	0.037
658	0.036	0.038	0.036	0.039	0.036	0.038	0.038
659	0.036	0.038	0.036	0.039	0.036	0.038	0.038
660	0.036	0.038	0.036	0.039	0.036	0.037	0.037
661	0.036	0.038	0.036	0.039	0.036	0.037	0.037
662	0.036	0.038	0.036	0.038	0.036	0.037	0.037
663	0.036	0.038	0.036	0.038	0.036	0.037	0.037
664	0.036	0.037	0.036	0.038	0.036	0.037	0.037
665	0.036	0.038	0.036	0.038	0.036	0.037	0.037
666	0.036	0.038	0.036	0.038	0.036	0.037	0.037
667	0.036	0.037	0.036	0.038	0.036	0.037	0.037
668	0.036	0.037	0.036	0.038	0.036	0.037	0.037
669	0.036	0.037	0.036	0.038	0.036	0.037	0.037
670	0.036	0.037	0.036	0.038	0.036	0.037	0.037
671	0.036	0.037	0.036	0.038	0.036	0.037	0.037
672	0.036	0.037	0.036	0.038	0.036	0.037	0.037
673	0.036	0.037	0.036	0.038	0.036	0.037	0.037

674	0.036	0.037	0.036	0.038	0.036	0.037	0.037
675	0.036	0.037	0.036	0.038	0.036	0.037	0.037
676	0.036	0.037	0.036	0.038	0.036	0.037	0.037
677	0.036	0.037	0.036	0.038	0.036	0.037	0.037
678	0.036	0.037	0.036	0.038	0.036	0.037	0.037
679	0.036	0.037	0.036	0.038	0.036	0.037	0.037
680	0.036	0.037	0.036	0.038	0.036	0.037	0.037
681	0.036	0.037	0.036	0.038	0.036	0.037	0.037
682	0.036	0.037	0.036	0.038	0.036	0.037	0.037
683	0.036	0.037	0.036	0.038	0.036	0.037	0.037
684	0.036	0.037	0.036	0.038	0.036	0.037	0.037
685	0.036	0.037	0.036	0.038	0.036	0.037	0.037
686	0.036	0.037	0.036	0.038	0.036	0.037	0.037
687	0.036	0.037	0.036	0.038	0.036	0.037	0.037
688	0.036	0.037	0.036	0.038	0.036	0.037	0.037
689	0.036	0.037	0.036	0.038	0.036	0.037	0.037
690	0.036	0.037	0.036	0.038	0.036	0.037	0.037
691	0.036	0.037	0.036	0.038	0.036	0.037	0.037
692	0.036	0.037	0.036	0.038	0.036	0.037	0.037
693	0.036	0.037	0.036	0.038	0.036	0.037	0.037
694	0.036	0.037	0.036	0.038	0.036	0.037	0.037
695	0.036	0.037	0.036	0.038	0.036	0.037	0.037
696	0.036	0.037	0.036	0.038	0.036	0.037	0.037
697	0.036	0.037	0.036	0.038	0.036	0.037	0.037
698	0.036	0.037	0.036	0.038	0.036	0.037	0.037
699	0.036	0.037	0.036	0.038	0.036	0.037	0.037
700	0.036	0.037	0.036	0.038	0.036	0.037	0.037

4.32 Absorbance for Hg- DPC complexes in OTAB

Wavelength	8×10^{-5} M OTAB	1.3×10^{-4} M OTAB	1.8×10^{-4} M OTAB	2.3×10^{-4} M OTAB	3.3×10^{-4} M OTAB	3.8×10^{-4} M OTAB
400	0.137	0.195	0.202	0.263	0.137	0.125
401	0.137	0.193	0.201	0.261	0.137	0.125
402	0.136	0.192	0.199	0.259	0.136	0.124
403	0.135	0.191	0.198	0.257	0.135	0.123
404	0.134	0.189	0.196	0.255	0.134	0.122
405	0.133	0.188	0.195	0.253	0.133	0.122
406	0.132	0.187	0.193	0.251	0.132	0.121
407	0.131	0.185	0.192	0.249	0.131	0.12
408	0.13	0.184	0.19	0.247	0.13	0.119
409	0.13	0.182	0.189	0.245	0.13	0.119
410	0.129	0.181	0.187	0.243	0.129	0.118
411	0.128	0.18	0.186	0.241	0.128	0.117
412	0.127	0.179	0.184	0.239	0.127	0.116

413	0.126	0.177	0.183	0.238	0.126	0.116
414	0.125	0.176	0.182	0.236	0.125	0.115
415	0.125	0.175	0.18	0.234	0.125	0.114
416	0.124	0.174	0.179	0.232	0.124	0.114
417	0.123	0.172	0.178	0.23	0.123	0.113
418	0.123	0.171	0.177	0.229	0.123	0.113
419	0.122	0.17	0.175	0.227	0.122	0.112
420	0.121	0.169	0.174	0.225	0.121	0.111
421	0.121	0.168	0.173	0.223	0.121	0.111
422	0.12	0.167	0.172	0.222	0.12	0.11
423	0.119	0.166	0.171	0.22	0.119	0.11
424	0.119	0.165	0.169	0.219	0.119	0.109
425	0.118	0.164	0.168	0.217	0.118	0.109
426	0.117	0.163	0.167	0.216	0.117	0.108
427	0.117	0.162	0.167	0.215	0.117	0.108
428	0.117	0.161	0.166	0.213	0.117	0.107
429	0.116	0.16	0.165	0.212	0.116	0.107
430	0.116	0.16	0.164	0.211	0.116	0.106
431	0.115	0.159	0.163	0.21	0.115	0.106
432	0.115	0.158	0.162	0.209	0.115	0.106
433	0.115	0.157	0.162	0.208	0.115	0.105
434	0.114	0.157	0.161	0.207	0.114	0.105
435	0.114	0.156	0.16	0.206	0.114	0.105
436	0.114	0.156	0.16	0.205	0.114	0.105
437	0.113	0.155	0.159	0.205	0.113	0.105
438	0.113	0.155	0.159	0.204	0.113	0.105
439	0.113	0.155	0.159	0.203	0.113	0.104
440	0.113	0.155	0.158	0.203	0.113	0.104
441	0.113	0.154	0.158	0.203	0.113	0.104
442	0.113	0.154	0.158	0.203	0.113	0.104
443	0.113	0.154	0.158	0.203	0.113	0.105
444	0.113	0.154	0.158	0.203	0.113	0.105
445	0.114	0.155	0.158	0.203	0.114	0.105
446	0.114	0.155	0.158	0.203	0.114	0.105
447	0.114	0.155	0.159	0.203	0.114	0.106
448	0.115	0.156	0.159	0.204	0.115	0.106
449	0.115	0.156	0.16	0.205	0.115	0.106
450	0.116	0.157	0.161	0.206	0.116	0.107
451	0.117	0.158	0.161	0.207	0.117	0.108
452	0.117	0.159	0.162	0.208	0.117	0.108
453	0.118	0.16	0.163	0.209	0.118	0.109
454	0.119	0.161	0.165	0.211	0.119	0.11
455	0.12	0.163	0.166	0.213	0.12	0.111
456	0.121	0.164	0.167	0.215	0.121	0.112
457	0.122	0.166	0.169	0.217	0.122	0.113
458	0.124	0.167	0.171	0.219	0.124	0.114

459	0.125	0.169	0.173	0.222	0.125	0.115
460	0.127	0.172	0.175	0.226	0.127	0.117
461	0.129	0.174	0.178	0.229	0.129	0.118
462	0.13	0.177	0.181	0.233	0.13	0.12
463	0.133	0.18	0.184	0.237	0.133	0.122
464	0.135	0.183	0.187	0.241	0.135	0.124
465	0.138	0.186	0.19	0.246	0.138	0.126
466	0.14	0.19	0.194	0.251	0.14	0.128
467	0.143	0.194	0.198	0.256	0.143	0.131
468	0.146	0.198	0.203	0.262	0.146	0.134
469	0.149	0.202	0.207	0.268	0.149	0.136
470	0.152	0.207	0.212	0.275	0.152	0.139
471	0.156	0.212	0.217	0.281	0.156	0.142
472	0.159	0.217	0.222	0.289	0.159	0.146
473	0.163	0.223	0.228	0.297	0.163	0.149
474	0.168	0.229	0.234	0.305	0.168	0.153
475	0.172	0.235	0.241	0.314	0.172	0.157
476	0.177	0.242	0.248	0.323	0.177	0.161
477	0.181	0.249	0.255	0.333	0.181	0.165
478	0.187	0.256	0.263	0.344	0.187	0.169
479	0.192	0.264	0.271	0.354	0.192	0.174
480	0.198	0.272	0.279	0.366	0.198	0.179
481	0.203	0.281	0.288	0.379	0.203	0.184
482	0.21	0.29	0.298	0.393	0.21	0.19
483	0.216	0.3	0.309	0.407	0.216	0.196
484	0.223	0.309	0.319	0.422	0.223	0.201
485	0.229	0.319	0.329	0.436	0.229	0.207
486	0.236	0.329	0.34	0.451	0.236	0.213
487	0.244	0.34	0.351	0.468	0.244	0.219
488	0.252	0.352	0.364	0.486	0.252	0.226
489	0.259	0.364	0.377	0.503	0.259	0.233
490	0.267	0.376	0.39	0.521	0.267	0.24
491	0.275	0.389	0.403	0.539	0.275	0.247
492	0.283	0.402	0.416	0.557	0.283	0.253
493	0.291	0.415	0.431	0.577	0.291	0.26
494	0.299	0.428	0.445	0.596	0.299	0.268
495	0.307	0.442	0.459	0.615	0.307	0.275
496	0.316	0.455	0.474	0.636	0.316	0.282
497	0.324	0.469	0.489	0.656	0.324	0.289
498	0.333	0.484	0.504	0.677	0.333	0.297
499	0.341	0.497	0.518	0.698	0.341	0.304
500	0.349	0.511	0.532	0.718	0.349	0.311
501	0.357	0.524	0.547	0.738	0.357	0.317
502	0.365	0.538	0.561	0.759	0.365	0.324
503	0.374	0.552	0.576	0.779	0.374	0.331
504	0.381	0.565	0.589	0.798	0.381	0.338

505	0.389	0.578	0.603	0.819	0.389	0.344
506	0.397	0.59	0.617	0.838	0.397	0.351
507	0.404	0.602	0.629	0.856	0.404	0.357
508	0.41	0.613	0.641	0.873	0.41	0.362
509	0.417	0.624	0.653	0.89	0.417	0.368
510	0.423	0.634	0.664	0.906	0.423	0.373
511	0.428	0.643	0.673	0.92	0.428	0.378
512	0.434	0.652	0.683	0.933	0.434	0.382
513	0.438	0.66	0.691	0.945	0.438	0.386
514	0.442	0.667	0.699	0.957	0.442	0.389
515	0.446	0.674	0.707	0.968	0.446	0.393
516	0.45	0.681	0.714	0.977	0.45	0.396
517	0.453	0.686	0.719	0.986	0.453	0.398
518	0.455	0.691	0.724	0.994	0.455	0.4
519	0.457	0.695	0.729	1	0.457	0.402
520	0.459	0.698	0.732	1.005	0.459	0.403
521	0.46	0.701	0.735	1.01	0.46	0.404
522	0.461	0.703	0.737	1.014	0.461	0.405
523	0.462	0.704	0.739	1.016	0.462	0.406
524	0.462	0.705	0.74	1.017	0.462	0.406
525	0.462	0.705	0.74	1.018	0.462	0.405
526	0.461	0.704	0.74	1.019	0.461	0.405
527	0.46	0.703	0.739	1.017	0.46	0.404
528	0.459	0.702	0.737	1.016	0.459	0.403
529	0.458	0.7	0.735	1.014	0.458	0.402
530	0.456	0.698	0.733	1.011	0.456	0.4
531	0.454	0.695	0.73	1.008	0.454	0.398
532	0.452	0.692	0.727	1.003	0.452	0.396
533	0.45	0.688	0.723	0.999	0.45	0.395
534	0.448	0.685	0.719	0.994	0.448	0.392
535	0.445	0.681	0.715	0.989	0.445	0.39
536	0.442	0.677	0.711	0.983	0.442	0.388
537	0.438	0.67	0.704	0.972	0.438	0.384
538	0.435	0.666	0.7	0.966	0.435	0.382
539	0.432	0.661	0.695	0.96	0.432	0.379
540	0.429	0.656	0.69	0.953	0.429	0.376
541	0.426	0.651	0.685	0.947	0.426	0.374
542	0.422	0.646	0.68	0.94	0.422	0.371
543	0.419	0.641	0.674	0.932	0.419	0.368
544	0.416	0.635	0.669	0.925	0.416	0.365
545	0.412	0.63	0.663	0.917	0.412	0.362
546	0.409	0.625	0.658	0.91	0.409	0.359
547	0.405	0.62	0.652	0.902	0.405	0.356
548	0.402	0.614	0.647	0.895	0.402	0.352
549	0.398	0.608	0.641	0.887	0.398	0.349
550	0.394	0.602	0.635	0.879	0.394	0.346

551	0.39	0.597	0.63	0.871	0.39	0.343
552	0.387	0.591	0.623	0.863	0.387	0.339
553	0.383	0.586	0.618	0.855	0.383	0.336
554	0.379	0.58	0.612	0.847	0.379	0.333
555	0.375	0.574	0.606	0.839	0.375	0.33
556	0.372	0.569	0.601	0.831	0.372	0.327
557	0.368	0.563	0.595	0.823	0.368	0.323
558	0.364	0.557	0.589	0.815	0.364	0.32
559	0.361	0.551	0.583	0.807	0.361	0.317
560	0.357	0.546	0.578	0.799	0.357	0.314
561	0.354	0.541	0.572	0.791	0.354	0.311
562	0.35	0.535	0.567	0.783	0.35	0.308
563	0.347	0.529	0.561	0.775	0.347	0.305
564	0.343	0.524	0.555	0.767	0.343	0.302
565	0.34	0.518	0.55	0.76	0.34	0.299
566	0.336	0.513	0.544	0.752	0.336	0.296
567	0.333	0.507	0.539	0.744	0.333	0.293
568	0.329	0.502	0.533	0.736	0.329	0.29
569	0.326	0.497	0.528	0.729	0.326	0.287
570	0.323	0.491	0.522	0.721	0.323	0.284
571	0.319	0.486	0.517	0.713	0.319	0.281
572	0.316	0.481	0.512	0.706	0.316	0.278
573	0.313	0.476	0.507	0.699	0.313	0.275
574	0.31	0.471	0.502	0.692	0.31	0.272
575	0.307	0.466	0.496	0.685	0.307	0.27
576	0.303	0.461	0.492	0.678	0.303	0.267
577	0.3	0.457	0.487	0.671	0.3	0.265
578	0.297	0.452	0.482	0.665	0.297	0.262
579	0.294	0.447	0.477	0.658	0.294	0.259
580	0.292	0.443	0.472	0.651	0.292	0.257
581	0.289	0.438	0.467	0.645	0.289	0.254
582	0.286	0.434	0.463	0.638	0.286	0.251
583	0.283	0.429	0.458	0.632	0.283	0.249
584	0.28	0.425	0.453	0.625	0.28	0.247
585	0.277	0.42	0.449	0.619	0.277	0.244
586	0.275	0.416	0.444	0.613	0.275	0.242
587	0.272	0.412	0.44	0.607	0.272	0.24
588	0.269	0.407	0.435	0.6	0.269	0.237
589	0.266	0.403	0.431	0.594	0.266	0.235
590	0.264	0.399	0.426	0.589	0.264	0.232
591	0.261	0.395	0.422	0.582	0.261	0.23
592	0.259	0.391	0.418	0.577	0.259	0.228
593	0.256	0.387	0.413	0.571	0.256	0.226
594	0.254	0.382	0.409	0.565	0.254	0.224
595	0.251	0.378	0.405	0.559	0.251	0.221
596	0.248	0.374	0.401	0.553	0.248	0.219

597	0.246	0.37	0.396	0.547	0.246	0.217
598	0.243	0.366	0.392	0.541	0.243	0.214
599	0.241	0.362	0.388	0.535	0.241	0.213
600	0.238	0.358	0.384	0.53	0.238	0.21
601	0.236	0.354	0.38	0.524	0.236	0.208
602	0.233	0.35	0.375	0.518	0.233	0.206
603	0.231	0.346	0.371	0.512	0.231	0.204
604	0.228	0.342	0.367	0.506	0.228	0.202
605	0.226	0.338	0.362	0.5	0.226	0.199
606	0.223	0.334	0.358	0.494	0.223	0.197
607	0.221	0.33	0.354	0.488	0.221	0.195
608	0.218	0.326	0.35	0.483	0.218	0.193
609	0.216	0.323	0.346	0.477	0.216	0.191
610	0.214	0.319	0.342	0.471	0.214	0.189
611	0.211	0.315	0.338	0.465	0.211	0.187
612	0.209	0.311	0.334	0.46	0.209	0.185
613	0.206	0.307	0.33	0.454	0.206	0.183
614	0.204	0.304	0.326	0.449	0.204	0.181
615	0.202	0.3	0.323	0.443	0.202	0.179
616	0.199	0.296	0.319	0.438	0.199	0.177
617	0.197	0.293	0.315	0.432	0.197	0.175
618	0.195	0.289	0.311	0.427	0.195	0.173
619	0.193	0.286	0.307	0.422	0.193	0.171
620	0.191	0.282	0.304	0.416	0.191	0.169
621	0.188	0.279	0.3	0.411	0.188	0.167
622	0.186	0.276	0.297	0.406	0.186	0.166
623	0.184	0.272	0.293	0.401	0.184	0.164
624	0.182	0.269	0.29	0.396	0.182	0.162
625	0.18	0.266	0.286	0.391	0.18	0.16
626	0.178	0.262	0.283	0.386	0.178	0.158
627	0.176	0.259	0.279	0.381	0.176	0.156
628	0.174	0.256	0.276	0.376	0.174	0.155
629	0.172	0.253	0.272	0.371	0.172	0.153
630	0.17	0.25	0.269	0.367	0.17	0.151
631	0.168	0.247	0.266	0.362	0.168	0.15
632	0.166	0.244	0.263	0.358	0.166	0.148
633	0.164	0.241	0.26	0.354	0.164	0.147
634	0.163	0.238	0.257	0.35	0.163	0.145
635	0.161	0.235	0.254	0.345	0.161	0.144
636	0.159	0.233	0.251	0.341	0.159	0.142
637	0.157	0.23	0.248	0.337	0.157	0.141
638	0.156	0.227	0.245	0.333	0.156	0.139
639	0.154	0.224	0.242	0.329	0.154	0.138
640	0.152	0.222	0.239	0.325	0.152	0.136
641	0.151	0.219	0.237	0.321	0.151	0.135
642	0.149	0.217	0.234	0.317	0.149	0.133

643	0.147	0.214	0.231	0.314	0.147	0.132
644	0.146	0.212	0.229	0.31	0.146	0.131
645	0.144	0.209	0.226	0.306	0.144	0.129
646	0.143	0.207	0.223	0.302	0.143	0.128
647	0.141	0.204	0.221	0.299	0.141	0.127
648	0.14	0.202	0.218	0.295	0.14	0.125
649	0.138	0.2	0.216	0.292	0.138	0.124
650	0.137	0.197	0.213	0.288	0.137	0.123
651	0.135	0.195	0.211	0.285	0.135	0.122
652	0.134	0.193	0.208	0.282	0.134	0.12
653	0.132	0.191	0.206	0.279	0.132	0.119
654	0.131	0.189	0.204	0.276	0.131	0.118
655	0.13	0.187	0.201	0.272	0.13	0.117
656	0.128	0.185	0.199	0.269	0.128	0.116
657	0.127	0.182	0.197	0.266	0.127	0.115
658	0.126	0.181	0.195	0.263	0.126	0.113
659	0.124	0.178	0.193	0.26	0.124	0.112
660	0.123	0.177	0.191	0.257	0.123	0.111
661	0.122	0.174	0.188	0.254	0.122	0.11
662	0.12	0.172	0.186	0.251	0.12	0.109
663	0.119	0.17	0.184	0.248	0.119	0.108
664	0.118	0.169	0.182	0.245	0.118	0.107
665	0.117	0.167	0.18	0.242	0.117	0.106
666	0.116	0.165	0.178	0.239	0.116	0.105
667	0.115	0.163	0.176	0.236	0.115	0.104
668	0.113	0.161	0.174	0.234	0.113	0.103
669	0.112	0.159	0.172	0.231	0.112	0.102
670	0.111	0.158	0.17	0.228	0.111	0.101
671	0.11	0.156	0.168	0.226	0.11	0.1
672	0.109	0.154	0.166	0.223	0.109	0.099
673	0.108	0.152	0.164	0.22	0.108	0.098
674	0.107	0.151	0.163	0.218	0.107	0.097
675	0.106	0.149	0.161	0.215	0.106	0.096
676	0.105	0.148	0.159	0.213	0.105	0.095
677	0.104	0.146	0.157	0.21	0.104	0.094
678	0.103	0.145	0.156	0.208	0.103	0.094
679	0.102	0.143	0.154	0.205	0.102	0.093
680	0.101	0.141	0.152	0.203	0.101	0.092
681	0.1	0.14	0.151	0.2	0.1	0.091
682	0.099	0.139	0.149	0.198	0.099	0.09
683	0.098	0.137	0.147	0.196	0.098	0.089
684	0.097	0.135	0.146	0.193	0.097	0.089
685	0.096	0.134	0.144	0.191	0.096	0.088
686	0.095	0.133	0.142	0.189	0.095	0.087
687	0.094	0.131	0.141	0.187	0.094	0.086
688	0.093	0.13	0.139	0.184	0.093	0.086

689	0.092	0.128	0.138	0.182	0.092	0.085
690	0.092	0.127	0.136	0.18	0.092	0.084
691	0.091	0.125	0.135	0.178	0.091	0.083
692	0.09	0.124	0.133	0.176	0.09	0.083
693	0.089	0.123	0.132	0.174	0.089	0.082
694	0.089	0.122	0.13	0.172	0.089	0.081
695	0.088	0.12	0.129	0.17	0.088	0.081
696	0.087	0.119	0.128	0.168	0.087	0.08
697	0.086	0.118	0.126	0.166	0.086	0.079
698	0.085	0.117	0.125	0.163	0.085	0.079
699	0.085	0.115	0.124	0.161	0.085	0.078
700	0.084	0.114	0.122	0.16	0.084	0.078

Table 4.33 Absorption for Zn- DPC complexation in OTAB

400	0.049	0.045	0.057	0.056	0.063	0.062	0.055
401	0.048	0.044	0.057	0.056	0.063	0.061	0.055
402	0.048	0.044	0.057	0.056	0.063	0.061	0.055
403	0.048	0.044	0.057	0.056	0.063	0.061	0.055
404	0.048	0.044	0.057	0.056	0.063	0.061	0.055
405	0.048	0.044	0.056	0.056	0.063	0.061	0.055
406	0.048	0.044	0.056	0.056	0.063	0.061	0.055
407	0.048	0.044	0.056	0.056	0.063	0.061	0.055
408	0.048	0.044	0.056	0.055	0.063	0.061	0.055
409	0.048	0.044	0.056	0.055	0.063	0.061	0.054
410	0.048	0.044	0.056	0.055	0.062	0.061	0.055
411	0.048	0.044	0.056	0.055	0.063	0.061	0.054
412	0.048	0.044	0.056	0.055	0.063	0.061	0.054
413	0.048	0.044	0.056	0.055	0.063	0.061	0.054
414	0.048	0.044	0.056	0.055	0.063	0.061	0.055
415	0.048	0.044	0.056	0.055	0.063	0.061	0.055
416	0.048	0.044	0.056	0.055	0.063	0.061	0.055
417	0.048	0.044	0.056	0.056	0.063	0.061	0.055
418	0.048	0.044	0.056	0.056	0.063	0.061	0.055
419	0.048	0.044	0.056	0.056	0.063	0.06	0.055
420	0.047	0.044	0.056	0.056	0.062	0.06	0.055
421	0.047	0.044	0.056	0.056	0.062	0.06	0.055
422	0.047	0.044	0.056	0.056	0.062	0.06	0.055
423	0.047	0.044	0.056	0.056	0.062	0.06	0.055
424	0.048	0.044	0.056	0.056	0.062	0.06	0.055
425	0.047	0.044	0.056	0.056	0.062	0.06	0.056
426	0.047	0.044	0.056	0.056	0.062	0.06	0.056
427	0.047	0.044	0.056	0.056	0.062	0.06	0.056
428	0.047	0.044	0.056	0.056	0.062	0.06	0.056
429	0.047	0.044	0.056	0.057	0.062	0.06	0.056

430	0.047	0.044	0.056	0.057	0.062	0.06	0.056
431	0.048	0.044	0.056	0.057	0.062	0.06	0.057
432	0.048	0.044	0.056	0.057	0.062	0.06	0.057
433	0.048	0.044	0.057	0.057	0.062	0.06	0.057
434	0.048	0.044	0.057	0.057	0.062	0.059	0.057
435	0.048	0.044	0.057	0.058	0.061	0.059	0.058
436	0.048	0.044	0.057	0.058	0.061	0.059	0.058
437	0.048	0.044	0.057	0.058	0.061	0.059	0.058
438	0.048	0.044	0.057	0.058	0.061	0.059	0.059
439	0.048	0.044	0.058	0.059	0.061	0.059	0.059
440	0.048	0.044	0.058	0.059	0.061	0.059	0.059
441	0.048	0.044	0.058	0.059	0.061	0.059	0.06
442	0.048	0.045	0.058	0.059	0.06	0.059	0.06
443	0.048	0.045	0.058	0.06	0.06	0.058	0.06
444	0.049	0.045	0.059	0.06	0.06	0.058	0.061
445	0.049	0.045	0.059	0.06	0.06	0.058	0.061
446	0.049	0.045	0.059	0.061	0.06	0.058	0.062
447	0.049	0.045	0.06	0.061	0.059	0.058	0.062
448	0.049	0.045	0.06	0.062	0.059	0.058	0.063
449	0.049	0.046	0.06	0.062	0.059	0.057	0.063
450	0.049	0.046	0.061	0.062	0.059	0.057	0.064
451	0.049	0.046	0.061	0.063	0.059	0.057	0.064
452	0.049	0.046	0.061	0.063	0.058	0.057	0.065
453	0.049	0.046	0.062	0.064	0.058	0.057	0.066
454	0.05	0.046	0.062	0.064	0.058	0.057	0.066
455	0.05	0.046	0.062	0.064	0.058	0.057	0.067
456	0.05	0.046	0.063	0.065	0.057	0.056	0.067
457	0.05	0.047	0.063	0.065	0.057	0.056	0.068
458	0.05	0.047	0.064	0.066	0.057	0.056	0.069
459	0.05	0.047	0.064	0.067	0.057	0.056	0.069
460	0.05	0.047	0.065	0.067	0.057	0.056	0.07
461	0.051	0.047	0.065	0.068	0.056	0.055	0.071
462	0.051	0.047	0.066	0.068	0.056	0.055	0.072
463	0.051	0.048	0.066	0.069	0.056	0.055	0.072
464	0.051	0.048	0.067	0.069	0.056	0.055	0.073
465	0.051	0.048	0.067	0.07	0.055	0.055	0.074
466	0.052	0.048	0.068	0.071	0.055	0.055	0.075
467	0.052	0.048	0.068	0.071	0.055	0.054	0.076
468	0.052	0.049	0.069	0.072	0.055	0.054	0.077
469	0.052	0.049	0.069	0.073	0.054	0.054	0.077
470	0.052	0.049	0.07	0.073	0.054	0.054	0.078
471	0.052	0.049	0.07	0.074	0.054	0.054	0.079
472	0.053	0.05	0.071	0.075	0.054	0.054	0.08
473	0.053	0.05	0.071	0.075	0.053	0.053	0.081
474	0.053	0.05	0.072	0.076	0.053	0.053	0.082
475	0.053	0.05	0.072	0.077	0.053	0.053	0.083

476	0.054	0.05	0.073	0.078	0.053	0.053	0.084
477	0.054	0.051	0.073	0.078	0.053	0.053	0.084
478	0.054	0.051	0.074	0.079	0.052	0.053	0.086
479	0.054	0.051	0.075	0.08	0.052	0.052	0.086
480	0.054	0.051	0.075	0.081	0.052	0.052	0.087
481	0.055	0.052	0.076	0.081	0.052	0.052	0.088
482	0.055	0.052	0.076	0.082	0.052	0.052	0.089
483	0.055	0.052	0.077	0.083	0.051	0.052	0.09
484	0.055	0.052	0.077	0.083	0.051	0.052	0.091
485	0.055	0.052	0.078	0.084	0.051	0.052	0.092
486	0.056	0.053	0.078	0.085	0.051	0.052	0.093
487	0.056	0.053	0.079	0.086	0.051	0.051	0.094
488	0.056	0.053	0.079	0.086	0.05	0.051	0.095
489	0.056	0.053	0.08	0.087	0.05	0.051	0.095
490	0.056	0.053	0.08	0.088	0.05	0.051	0.096
491	0.057	0.054	0.081	0.088	0.05	0.051	0.097
492	0.057	0.054	0.081	0.089	0.049	0.051	0.098
493	0.057	0.054	0.082	0.09	0.049	0.051	0.099
494	0.057	0.054	0.082	0.09	0.049	0.05	0.1
495	0.057	0.054	0.083	0.091	0.049	0.05	0.1
496	0.057	0.055	0.083	0.091	0.049	0.05	0.101
497	0.057	0.055	0.083	0.092	0.048	0.05	0.102
498	0.057	0.055	0.084	0.093	0.048	0.05	0.103
499	0.058	0.055	0.084	0.093	0.048	0.05	0.103
500	0.058	0.055	0.084	0.094	0.048	0.049	0.104
501	0.058	0.056	0.085	0.094	0.048	0.049	0.104
502	0.058	0.056	0.085	0.095	0.047	0.049	0.105
503	0.058	0.056	0.085	0.095	0.047	0.049	0.106
504	0.058	0.056	0.085	0.096	0.047	0.049	0.106
505	0.058	0.056	0.086	0.096	0.047	0.049	0.107
506	0.058	0.056	0.086	0.097	0.047	0.049	0.107
507	0.058	0.056	0.086	0.097	0.047	0.049	0.108
508	0.059	0.057	0.087	0.097	0.047	0.049	0.108
509	0.059	0.057	0.087	0.098	0.046	0.048	0.109
510	0.059	0.057	0.087	0.098	0.046	0.048	0.109
511	0.059	0.057	0.087	0.098	0.046	0.048	0.11
512	0.059	0.057	0.087	0.099	0.046	0.048	0.11
513	0.059	0.057	0.088	0.099	0.046	0.048	0.11
514	0.059	0.057	0.088	0.099	0.046	0.048	0.11
515	0.059	0.057	0.088	0.099	0.046	0.048	0.111
516	0.059	0.057	0.088	0.099	0.046	0.048	0.111
517	0.059	0.057	0.088	0.099	0.046	0.048	0.111
518	0.059	0.057	0.088	0.1	0.045	0.048	0.111
519	0.059	0.057	0.088	0.1	0.045	0.048	0.111
520	0.059	0.057	0.088	0.1	0.045	0.048	0.111
521	0.059	0.057	0.088	0.1	0.045	0.048	0.111

522	0.059	0.057	0.088	0.099	0.045	0.048	0.111
523	0.059	0.057	0.088	0.099	0.045	0.048	0.111
524	0.059	0.057	0.088	0.099	0.045	0.048	0.111
525	0.059	0.057	0.088	0.099	0.045	0.048	0.11
526	0.059	0.057	0.087	0.099	0.045	0.047	0.11
527	0.059	0.057	0.087	0.098	0.045	0.047	0.11
528	0.059	0.057	0.087	0.098	0.044	0.047	0.109
529	0.059	0.057	0.087	0.098	0.044	0.047	0.109
530	0.059	0.057	0.087	0.097	0.044	0.047	0.109
531	0.058	0.056	0.086	0.097	0.044	0.047	0.108
532	0.058	0.056	0.086	0.097	0.044	0.047	0.108
533	0.058	0.056	0.086	0.096	0.044	0.047	0.107
534	0.058	0.056	0.085	0.096	0.044	0.047	0.107
535	0.058	0.056	0.085	0.095	0.044	0.047	0.106
536	0.058	0.056	0.085	0.095	0.044	0.047	0.106
537	0.058	0.055	0.084	0.094	0.044	0.047	0.105
538	0.058	0.055	0.084	0.093	0.044	0.047	0.104
539	0.057	0.055	0.084	0.093	0.044	0.047	0.104
540	0.057	0.055	0.083	0.092	0.044	0.047	0.103
541	0.057	0.055	0.083	0.092	0.044	0.047	0.102
542	0.057	0.054	0.082	0.091	0.043	0.047	0.101
543	0.057	0.054	0.082	0.09	0.043	0.047	0.101
544	0.056	0.054	0.081	0.089	0.043	0.047	0.1
545	0.056	0.054	0.081	0.089	0.043	0.046	0.099
546	0.056	0.053	0.08	0.088	0.043	0.046	0.098
547	0.056	0.053	0.08	0.087	0.043	0.046	0.097
548	0.055	0.053	0.079	0.086	0.043	0.046	0.096
549	0.055	0.053	0.079	0.085	0.043	0.046	0.095
550	0.055	0.052	0.078	0.085	0.042	0.046	0.094
551	0.054	0.052	0.078	0.084	0.042	0.046	0.093
552	0.054	0.052	0.077	0.083	0.042	0.046	0.092
553	0.054	0.051	0.076	0.082	0.042	0.046	0.091
554	0.054	0.051	0.076	0.081	0.042	0.045	0.09
555	0.053	0.051	0.075	0.08	0.042	0.045	0.089
556	0.053	0.051	0.075	0.079	0.042	0.045	0.088
557	0.053	0.05	0.074	0.079	0.042	0.045	0.087
558	0.052	0.05	0.073	0.078	0.042	0.045	0.086
559	0.052	0.05	0.073	0.077	0.042	0.045	0.085
560	0.052	0.049	0.072	0.076	0.042	0.045	0.084
561	0.052	0.049	0.071	0.075	0.042	0.045	0.083
562	0.051	0.049	0.071	0.074	0.041	0.044	0.082
563	0.051	0.048	0.07	0.073	0.041	0.044	0.08
564	0.05	0.048	0.069	0.072	0.041	0.044	0.079
565	0.05	0.048	0.068	0.071	0.041	0.044	0.078
566	0.05	0.047	0.068	0.07	0.041	0.044	0.077
567	0.049	0.047	0.067	0.069	0.041	0.044	0.076

568	0.049	0.047	0.066	0.068	0.04	0.044	0.074
569	0.049	0.046	0.066	0.067	0.04	0.043	0.073
570	0.048	0.046	0.065	0.066	0.04	0.043	0.072
571	0.048	0.046	0.064	0.065	0.04	0.043	0.071
572	0.048	0.045	0.063	0.064	0.04	0.043	0.07
573	0.047	0.045	0.063	0.063	0.04	0.043	0.068
574	0.047	0.045	0.062	0.062	0.04	0.043	0.067
575	0.047	0.044	0.061	0.061	0.04	0.043	0.066
576	0.046	0.044	0.061	0.06	0.039	0.043	0.065
577	0.046	0.044	0.06	0.059	0.039	0.042	0.064
578	0.046	0.044	0.059	0.058	0.039	0.042	0.063
579	0.046	0.043	0.059	0.058	0.039	0.042	0.062
580	0.046	0.043	0.058	0.057	0.039	0.042	0.061
581	0.045	0.043	0.057	0.056	0.039	0.042	0.06
582	0.045	0.042	0.057	0.055	0.039	0.042	0.059
583	0.045	0.042	0.056	0.054	0.039	0.042	0.058
584	0.045	0.042	0.055	0.054	0.039	0.042	0.057
585	0.044	0.042	0.055	0.053	0.039	0.042	0.056
586	0.044	0.042	0.054	0.052	0.039	0.042	0.055
587	0.044	0.041	0.054	0.052	0.039	0.042	0.055
588	0.044	0.041	0.053	0.051	0.039	0.042	0.054
589	0.043	0.041	0.053	0.05	0.039	0.042	0.053
590	0.043	0.041	0.052	0.05	0.039	0.042	0.052
591	0.043	0.04	0.052	0.049	0.039	0.041	0.051
592	0.043	0.04	0.051	0.048	0.038	0.041	0.051
593	0.043	0.04	0.051	0.048	0.038	0.041	0.05
594	0.042	0.04	0.05	0.047	0.038	0.041	0.049
595	0.042	0.04	0.05	0.047	0.038	0.041	0.049
596	0.042	0.039	0.049	0.046	0.038	0.041	0.048
597	0.042	0.039	0.049	0.046	0.038	0.041	0.047
598	0.042	0.039	0.048	0.045	0.038	0.041	0.047
599	0.042	0.039	0.048	0.045	0.038	0.041	0.046
600	0.041	0.039	0.048	0.045	0.038	0.041	0.046
601	0.041	0.039	0.047	0.044	0.038	0.041	0.045
602	0.041	0.039	0.047	0.044	0.038	0.04	0.045
603	0.041	0.039	0.047	0.043	0.038	0.04	0.044
604	0.041	0.039	0.046	0.043	0.038	0.04	0.044
605	0.041	0.038	0.046	0.043	0.038	0.04	0.044
606	0.041	0.038	0.046	0.042	0.038	0.04	0.043
607	0.04	0.038	0.045	0.042	0.038	0.04	0.043
608	0.04	0.038	0.045	0.042	0.038	0.04	0.042
609	0.04	0.038	0.045	0.042	0.037	0.04	0.042
610	0.04	0.038	0.044	0.041	0.037	0.04	0.042
611	0.04	0.038	0.044	0.041	0.037	0.04	0.041
612	0.04	0.038	0.044	0.041	0.037	0.039	0.041
613	0.04	0.038	0.044	0.041	0.037	0.039	0.041

614	0.04	0.038	0.043	0.04	0.037	0.039	0.041
615	0.04	0.037	0.043	0.04	0.037	0.039	0.04
616	0.039	0.037	0.043	0.04	0.037	0.039	0.04
617	0.039	0.037	0.043	0.04	0.037	0.039	0.04
618	0.039	0.037	0.042	0.04	0.037	0.039	0.04
619	0.039	0.037	0.042	0.04	0.037	0.039	0.039
620	0.039	0.037	0.042	0.039	0.037	0.039	0.039
621	0.039	0.037	0.042	0.039	0.037	0.039	0.039
622	0.039	0.037	0.042	0.039	0.037	0.039	0.039
623	0.039	0.037	0.042	0.039	0.037	0.039	0.039
624	0.039	0.037	0.041	0.039	0.037	0.039	0.039
625	0.039	0.037	0.041	0.039	0.037	0.039	0.038
626	0.039	0.036	0.041	0.039	0.037	0.039	0.038
627	0.039	0.036	0.041	0.039	0.037	0.038	0.038
628	0.039	0.036	0.041	0.039	0.037	0.038	0.038
629	0.039	0.036	0.041	0.039	0.036	0.038	0.038
630	0.038	0.036	0.041	0.038	0.036	0.038	0.038
631	0.039	0.036	0.04	0.038	0.036	0.038	0.038
632	0.038	0.036	0.04	0.038	0.036	0.038	0.038
633	0.038	0.036	0.04	0.038	0.036	0.038	0.038
634	0.038	0.036	0.04	0.038	0.036	0.038	0.038
635	0.038	0.036	0.04	0.038	0.036	0.038	0.038
636	0.038	0.036	0.04	0.038	0.036	0.038	0.037
637	0.038	0.036	0.04	0.038	0.036	0.038	0.037
638	0.038	0.036	0.04	0.038	0.036	0.038	0.037
639	0.038	0.036	0.04	0.038	0.036	0.038	0.037
640	0.038	0.036	0.039	0.038	0.036	0.038	0.037
641	0.038	0.036	0.039	0.038	0.036	0.038	0.037
642	0.038	0.036	0.039	0.038	0.036	0.038	0.037
643	0.038	0.036	0.039	0.038	0.036	0.038	0.037
644	0.038	0.036	0.039	0.038	0.036	0.038	0.037
645	0.038	0.036	0.039	0.038	0.036	0.038	0.037
646	0.038	0.036	0.039	0.038	0.036	0.038	0.037
647	0.038	0.036	0.039	0.038	0.036	0.038	0.037
648	0.038	0.036	0.039	0.037	0.036	0.038	0.037
649	0.038	0.036	0.039	0.037	0.036	0.038	0.037
650	0.038	0.036	0.039	0.037	0.036	0.038	0.037
651	0.038	0.036	0.039	0.037	0.036	0.038	0.037
652	0.038	0.036	0.039	0.037	0.036	0.038	0.037
653	0.038	0.036	0.039	0.037	0.036	0.037	0.037
654	0.038	0.036	0.039	0.037	0.036	0.037	0.037
655	0.038	0.036	0.039	0.037	0.036	0.037	0.037
656	0.038	0.036	0.039	0.037	0.036	0.037	0.036
657	0.038	0.036	0.039	0.037	0.036	0.037	0.037
658	0.038	0.036	0.039	0.037	0.036	0.037	0.037
659	0.038	0.036	0.039	0.037	0.036	0.037	0.037

