



Faculty of Graduate Studies
Chemistry Department

**Effect of Temperature and Added Salts on the Critical Micelle
Concentration (CMC) and Some Thermodynamic Variables of
Sodium Dodecyl Benzene Sulphonate Solutions**

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Degree of Master of Chemistry, College of Graduate Studies and Academic
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Abstract

In this work the state-of-art Kruss K11 tensiometer was employed to study the effect of temperature in the range of 283-333 K, and added salts on the critical micelle concentration (CMC) of sodium dodecyl benzene sulfonate (SDBS). The temperature range studied exceeded that of the temperature range used in previous studies. The salts were sodium chloride, calcium chloride and 1 – Ethyl – 3 – Methylimidazolium Bromide (EMIB). To the best of my knowledge this is the first time that the effect of an organic salt (molten salt) on the CMC of surfactant has been investigated. It is found that the CMC decreases with increasing temperature up to 305 K and then increases up to the highest temperature studied (333 K). The addition of salt decreases the onset of CMC regardless of the identity of the salt and the effect of divalent salt is more pronounced than that of the monovalent salt. The effect of the molten salt is that the decrease of the surface tension is sharper than in the case of inorganic salt while the surface tension values are comparable to those of the monovalent salt but higher than those of the divalent salt. The surface excess concentration was calculated and shown to vary with both temperatures and concentrations of added salts. The onset of micellization is enhanced by increasing temperature and by the presence of the salt regardless of the identity of the salt. The Gibbs free energy of micellization is negative and becomes more negative with temperature and with the addition of salt. The enthalpy of micellization is also negative and exhibits a behavior similar to that of Gibbs free energy micellization. The calculated entropy of micellization is positive indicating that micellization is accompanied by an increase in the disorder of the system. The findings of this study are of benefit to the practical applications of ionic surfactants.

Chapter 1

Introduction

I Background

1.1 Surface and Interfacial Tensions

A boundary or surface is defined as the termination of the bulk state (a solid or liquid) where the equations based on three-dimensionality are not sufficient to describe the complete physical state of the system [1]. At the surface region, bulk symmetry is perturbed and gives rise to altered interaction forces. This broken symmetry, sketched in Fig. 1.1, is responsible for the peculiar behavior of surfaces and interfaces which leads to different types of phenomena e.g. surface tension, the existence of capillary waves at liquid surfaces etc. In the figure, atoms or molecules in the bulk experience bonding from all directions and thus the resultant force is zero. These atoms or molecules are thus in a state of low energy. On the contrary, atoms or molecule at the surface experience bonding or forces from atoms or molecules in the same plane and from underneath. From the side of the other phase they experience no bonding. Lack of symmetry of bonding leads these atoms or molecules of being in a state of high energy. Atoms or molecule at the surface feel an inward force from other atoms or molecules below it and this force is defined as the force of tension. For liquid state, this force can be measured but for solid state it cannot be measured directly. In the literature this force is referred to as surface tension for liquid state and surface energy for solid state.

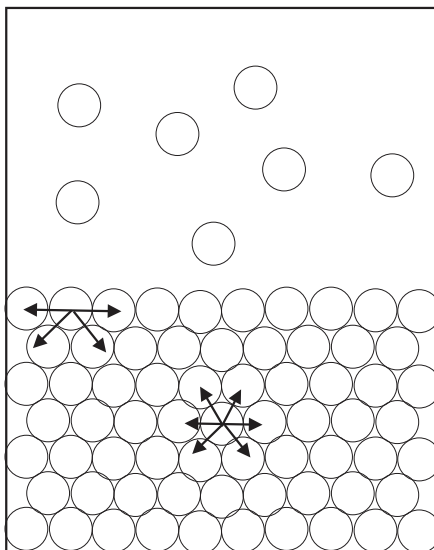


Fig. 1.1 Schematic sketch of atomic or molecular bonding at the surface and in the bulk

1.2 Introduction to Surfactant

Surfactants are among the most versatile products of chemical industry, appearing in such diverse products as motor oils used in automobiles, pharmaceuticals taken to cure illness, detergents used in cleaning laundry and homes, drilling muds used in prospecting for petroleum, and flotation agents used in beneficiations of ores. Applications of surfactants were extended in the last decades to high standard areas of research [2].

A surfactant or surface – active – agent is any substance that will significantly reduce the surface tension of a liquid when present at low concentration [3-4]. A surfactant must have at least one lyophilic (solvent – loving) part and one lyophobic (solvent – hating) part. If water is used as a solvent, the two parts of the surfactant are described as hydrophilic (polar or ionic) and hydrophobic (nonpolar) groups as shown in Fig. 1.2. The presence of these opposing forces within the same molecule leads to two phenomena: adsorption and aggregation.

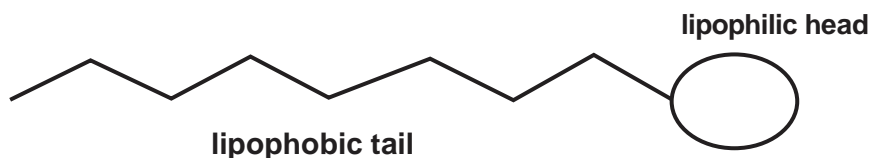


Fig. 1.2 Schematic diagram of surface active agent or surfactant molecules

In aqueous media the dual preference for water by the two groups of the surfactant molecule presents a problem. On one hand, the hydrophobic groups (hydrocarbon tails) do not mix well in the aqueous phase so they have strong tendency to minimize their contacts with water. On the other hand, formation of surfactant phase is also unfavorable as the hydrophilic groups of the surfactant (polar or ionic groups) prefer the contact with water. The opposing forces lead to migration of small parts of molecules to air-water interface and arrange as a monolayer and this process is referred to as adsorption. The majority of molecules find an

alternative way to minimize their unfavorable contact with the medium by aggregation in the bulk solution. This can take place by orientation of hydrophilic groups toward the aqueous phase and the hydrophobic groups away from it. This process is called micellization or micelle formation or self – association. The process is very important since the behavior of this assembled structure composed of many surfactant molecules is qualitatively different from that of free unassociated molecules [5].

1.2.1 Types of Surfactants

A common method of classification of surfactants is based on the type of head – groups they possess. The elementary classification is made into four types: anionic, cationic, zwitterionic and nonionic. The main features of these surfactants will be given in the following sections.

1.2.1.1 Anionic Surfactants

The head of anionic surfactant is negatively charged and this head is commonly neutralized by an alkali metal cation. The members of this group have the highest cleansing power, good wetting properties but moderate disinfectant properties. Soaps (RCOO^-Na^+), alkyl sulphates ($\text{RSO}_4^-\text{Na}^+$) and alkyl benzene sulphonates ($\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$) are some of the well – known examples of this type of surfactants. Anionic surfactants are the most widely used in industrial practices due to their excellent cleaning properties and moderate cost and they include laundering detergent, dishwashing liquids and shampoos.

1.2.1.2 Cationic Surfactant

The head-group of cationic surfactant has positive charge. Most of these surfactants are stable in a wide range of pH. Due to poor detergency and higher cost, cationic surfactants are not widely used in industry. Some of well-known cationic surfactants are salts of long chain amines (RNH_3^+X^-), quaternary ammonium salts $[\text{RN}(\text{CH}_3)_3^+\text{X}^-]$ and quaternary salts of polyethylene oxide – amine derivatives $[\text{RN}(\text{CH}_3)\{(\text{C}_2\text{H}_4\text{O})_x\text{H}\}_2^+\text{Cl}^-]$. Common uses of cationic surfactants are in ore floatation, textile industries, pesticides applications, adhesion, corrosion inhibition and preparation of cosmetics [6].

1.2.1.3 Non-ionic Surfactant

These surfactants are second most widely used surfactants in industry. They do not have any electrical charges so they may have very little or no electrical interaction between the head groups. Most of non-ionic surfactants are available as viscous liquids. They are lower foaming and less affected by water hardness ions [7]. The most commonly used non-ionic surfactants are alkyl ethoxylate $[\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$ acting as excellent emulsifier and used as greasy stain removal. The polyoxopropylene glycols are used as dispersing agents for pigments and paints, foam-control agents and for removing scales of boilers. Poloxyethylene mercaptans $[\text{RS}(\text{C}_2\text{H}_4\text{O})_n\text{H}]$ are used in textile detergents, metal cleaning and wetting agents. As foams in wastewater streams are a significant problem in some industrial cleaning processes, mercaptan surfactants can be used for these applications as they can be converted to non-foaming sulfones using bleach and base before disposing them [8]. Sorbitan esters as nonionic surfactants are edible and used as emulsifying agents in the preparation of emulsions, ice creams, beverages, desserts, confectionary products in addition to pharmaceutical and cosmetic products.

1.2.1.4 Zwitterion Surfactant

Zwitterion surfactants are characterized by a molecular structure containing two different functional groups, with anionic and cationic characters respectively. The long chain amino acids $(\text{RNH}_2^+\text{CH}_2\text{COO}^-)$ and phospholipids are examples of natural zwitterion substances while betaines $(\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-)$ or sulfobetaines $(\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-)$ are examples of synthetic surfactants. Most of these surfactants are able to behave as cationic or anionic surfactants depending on the pH of the medium. They are extensively used in liquid cleansers, moisturizing body wash, shower gel, shaving products, shampoo, toothpastes, detergent for contact lenses. The wide utilization of these surfactants is related to their good cleansing power, low toxicity, antibacterial properties, excellent resistance to hard water, and excellent compatibility with various kinds of surfactants at different pH values [9]. Some representative surfactants along with their chemical formulae are listed in Table 1.1.

Table 1.1 Some representative examples of different types of surfactants

| Class | Examples | Molecular structure |
|--------------|-------------------------------------|---------------------------------------------------------------------------------|
| Anionic | Sodium stearate | $\text{CH}_3(\text{CH}_2)_{16}\text{-COO}^-\text{Na}^+$ |
| | Sodium dodecyl sulfate | $\text{CH}_3(\text{CH}_2)_{11}\text{-SO}_4^-\text{Na}^+$ |
| | Sodium dodecyl benzene sulphonate | $\text{CH}_3(\text{CH}_2)_{10}\text{C}_6\text{H}_4\text{-SO}_3^-\text{Na}^+$ |
| Cationic | Laurylamine hydrochloride | $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3^+\text{Cl}^-$ |
| | Hexadecyltrimethylammonium bromide | $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ |
| | Tetradecyltrimethylammonium bromide | $\text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ |
| Non-ionic | Polyoxyethylene(4)dodecanol | $\text{CH}_3(\text{CH}_2)_{11}\text{-O-(CH}_2\text{CH}_2\text{O)}_4\text{H}$ |
| | Polyoxyethylene(9)hexadecanol | $\text{CH}_3(\text{CH}_2)_{15}\text{-O-(CH}_2\text{CH}_2\text{O)}_9\text{H}$ |
| Zwitterionic | Dodecyl betaine | $\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ |
| | Dodecyldimethylammonium acetate | $\text{CH}_3(\text{CH}_2)_{11}(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{COO}^-$ |

1.3 Adsorption of Surfactant at Surfaces and Interfaces

A fundamental characteristic of surfactants is their tendency to adsorb at interfaces in an oriented fashion as mentioned previously. This adsorption has been studied to determine the following:

- The concentration of surfactant at the interface, since this is a measure of how much of the interface has been covered (and thus changed) by the surfactant.
- The performance of the surfactant in many interfacial processes as foaming, detergency and emulsification depends on its concentration at the interface.
- The orientation and packing of the surfactant at the interface. Surfactants molecules that adsorbed at the interface between two immiscible liquids as oil and water will orient themselves in a way so their hydrophilic group is located in water and their

hydrophobic group is in oil. This orientation and packing at the interface determines how the interface will be affected by the adsorption i.e. whether it will become more hydrophilic or more hydrophobic.

- The rate at which adsorption at the interface occurs and this determines the performance in phenomena such as the speed of wetting or spreading.
- The changes in Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) that accompanied adsorption process. These quantities provide information on the type and mechanism of any interactions involving the surfactant at the interface and the efficiency and effectiveness of its operation as a surface-active material.

1.4 Measuring Adsorption at Interfaces

The direct determination of the amount of surfactant adsorbed per unit area of liquid–gas (L/G) or liquid–liquid (L/L) interface, although possible, is not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large [10]. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from the surface or interfacial tension measurements. The amount of surfactant adsorbed at the interface which is called excess surface concentration (Γ) can be obtained by plotting values of surface tension versus equilibrium concentrations of surfactant using Gibbs adsorption equation [11].

1.5 The Gibbs Adsorption Isotherm

Gibbs derived an equation for the thermodynamic relationship between surface or interfacial tension with concentration to find the value of excess surface concentration in moles per unit area. At equilibrium the Gibbs free energy $\Delta G^\sigma = 0$. Then Gibbs – Deuhem equation can be written as:

$$\Delta G^\sigma = -S^\sigma dT + A d\gamma + \sum n_i^\sigma d\mu_i \quad (1 - 1)$$

Where

S^σ : entropy at the interface

dT : change in temperature

A : area of the interface

$d\gamma$: change in surface or interfacial tension

n_i^σ : change in the amounts of component i

$d\mu_i$: change in chemical potential of component i

If a surfactant (component 2) is adsorbed at the surface of a solvent (component 1) then:

$$A d\gamma = - \sum n_i^\sigma d\mu_i \quad (1 - 2)$$

If the excess surface concentration is defined as:

$$\Gamma_i^\sigma = \frac{n_i^\sigma}{A} \quad (1 - 3)$$

and

$$d\gamma = - \sum \frac{n_i^\sigma}{A} d\mu_i$$

then equation (1-3) is rearranged to:

$$d\gamma = - \sum \Gamma_i^\sigma d\mu_i \quad (1 - 4)$$

Where

$d\gamma$: change in the surface tension

Γ_i^σ : surface excess concentration of i – th component

$d\mu_i$: change in chemical potential of i – th component

The surface excess concentration is defined as the difference between surfactant concentration in the surface region and the surfactant concentration in the bulk phase at equilibrium with the surface region [11]. At equilibrium between interfacial and bulk phase concentration, another form of Gibbs adsorption equation was derived:

$$\Gamma_i^\sigma = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln c} \right) \quad (1-5)$$

where, γ is the surface tension in mJ/m² or equivalently in mN/m, c is the concentration, T is the absolute temperature and R is the gas constant.

In the discussion of performance of a surfactant in lowering the surface tension of solution it is necessary to consider two aspects:

- The concentration of surfactant in the bulk phase required to give a certain reduction in surface tension.
- The maximum reduction in surface tension that can be obtained regardless of the concentration of the surfactant in the bulk.

An illustration of the change of surface tension of an aqueous solution of ionic surfactant with concentration is shown in Fig. 1.3. At low surfactant concentrations, a decrease in surface tension values is observed with increase in the concentration of surfactant up to a certain value indicating the CMC point. After reaching CMC point surface tension values become almost constant as these values represent the maximum reduction in surface tension. From the linear part of the figure before reaching the CMC point it is possible to find the value of the surface excess (Γ_i^σ). The surface area occupied by each surfactant molecule at the interface (A) can be estimated by the following relation:

$$A = \frac{1}{\Gamma_i^\sigma N_A} \quad (1-6)$$

Where

A : area occupied by each surfactant molecule (nm²)

N_A : Avogadro's number

The calculated area is a useful value as it gives information about the orientation of surfactant molecules at interface.

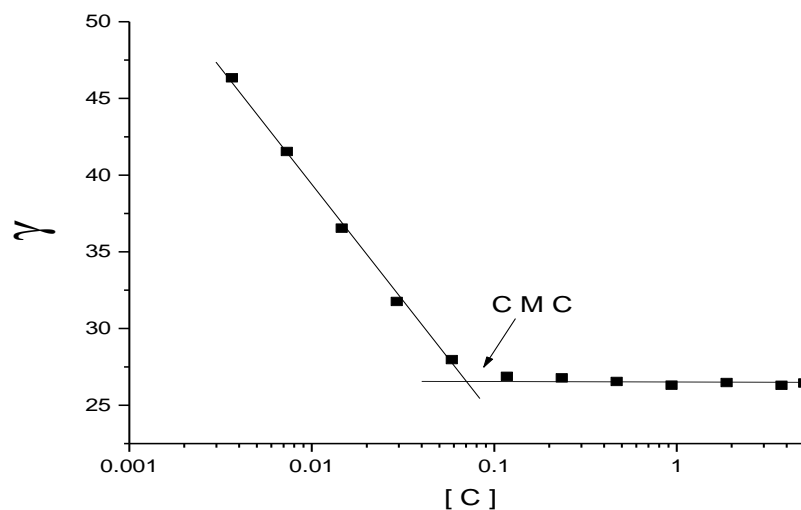


Fig. 1.3 Schematic plot of surface tension (γ) vs. logarithm of surfactant concentration (c)

1.6 Thermodynamic Parameters of Adsorption and Micellization

A clear understanding of adsorption and micellization processes of surfactants in their solutions is necessary for rational explanation of the effects of structural and environmental factors of surfactants on the value of CMC and for predicting the effects on it of new structural and environmental variation. Determination of the thermodynamic parameters: Gibbs energy (ΔG), enthalpy (ΔH) and entropy (ΔS) played an important role in developing such understanding as they are related to the tendency of surfactant molecules towards adsorption at the interface or micellization in the bulk of their solutions. The adsorption free energy (ΔG_{ads}) is the energy loss due to the ordered adsorption of one mole of surfactants at the air – solution interface. The standard free energy of micellization (ΔG_{mic}) is the energy loss in the system due to the transfer of one mole of surfactant molecule from the adsorbed monolayer at the air – solution interface to solution bulk to form the micelles. Negative values of ΔG_{ads} and ΔG_{mic} indicate spontaneous adsorption and micellization processes. The standard enthalpy of adsorption and micellization (ΔH_{ads} and ΔH_{mic}) are related to bonds breaking and

bond forming while the standard entropy changes (ΔS_{ads} and ΔS_{mic}) indicate whether the system become more structured or more random [12].

The determination of thermodynamic parameters depends on the value of critical micelle concentration (CMC) according to the mass action model as will be given in the following section [13]. The standard Gibbs free energy of micellization ΔG_{mic} for ionic and nonionic surfactants solutions can be calculated by using the equations (1 – 7, 1 – 8):

$$\Delta G_{mic}^o = (2 - B) R T \ln X_{CMC} \quad (1 - 7)$$

$$\Delta G_{mic}^o = R T \ln X_{CMC} \quad (1 - 8)$$

where

B : counter ion dissociation constant. For a completely ionized micelle $B=1$ and for neutral molecules $B = 0$

X_{CMC} : surfactant mole fraction at CMC

The corresponding entropy and enthalpy of micellization are determined by the following expression respectively:

$$\Delta S_{mic}^o = - \frac{d (G_{mic}^o)}{\Delta T} \quad (1 - 9)$$

$$\Delta H_{mic}^o = \Delta G_{mic}^o + T \Delta S_{mic}^o \quad (1 - 10)$$

The standard free energy value of adsorption ΔG_{ads} at air – liquid interface (a measure of free energy of transfer per mole of surfactant at unit concentration from bulk to surface at unit pressure) can be determined by using the equation (1 – 11):

$$\Delta G_{ads}^o = \Delta G_{mic}^o - 6.023 \times 10^{-1} \pi_{cmc} \cdot A \quad (1 - 11)$$

where, π_{cmc} is the effectiveness and is defined as the difference between the surface tension of pure water and the surface tension of the surfactant solution in (mN/m) and A is area per surfactant molecule (nm^2). The values of ΔS_{ads}^o , ΔH_{ads}^o can be obtained by using the corresponding equation:

$$\Delta S_{ads}^o = - \frac{d(G_{ads}^o)}{\Delta T} \quad (1 - 12)$$

$$\Delta H_{ads}^o = \Delta G_{ads}^o + T\Delta S_{ads}^o \quad (1 - 13)$$

1.7 Micelle Formation by Surfactants

Surfactants have fundamental and important property as they are adsorbed at interfaces. This property called micelle formation or micellization in which a surfactant forms a colloidal-sized cluster in solution. The micellization is an important interfacial phenomenon due to its relation to a number of phenomena such as detergency, solubilization and surface or interfacial tension reduction that depends on the existence of micelles in solutions [14].

1.7.1 Critical Micelle Concentration CMC

Critical micelle concentration (CMC) is defined as the concentration of surface active compounds above which micelle forms and all the additional surfactant added to the system will be transformed into micelles spontaneously. Formation of micelles is the most fascinating behavior of many surfactants molecule in solutions. In aqueous solutions the major interactions between surfactant molecules and water are summarized as follows [15]:

- The interaction force between the hydrophobic groups of surfactant and water.
- The attractive force between the hydrophobic groups to adjacent surfactant molecule.
- The solvation of the hydrophilic group of surfactants by water.
- The interaction between solvated hydrophilic groups to adjacent surfactant molecule.
- The interaction between the ionic groups of surfactant and co-ion.
- The geometric and packing constraints originating from the molecular structure of surfactant.

In diluted solution, the surfactant acts as a normal solute. An ionic surfactant is dissolved in the aqueous phase and adsorbed on the water – air interface and in the interior wall of the container. As the concentration of the surfactant is increased, the surfactant molecules adsorbed at the water – air interface become more and more crowded until a critical surfactant concentration is reached. At this point which is called critical micelle concentration or CMC, water – air interface becomes saturated with adsorbed surfactant molecules and these molecules start to aggregate to form the micelles as a result of the complex interactions mentioned above. In these micelles the surfactant hydrophobic hydrocarbon chains are oriented towards the core of the micelle to decrease the contact between the hydrophobic parts of the surfactants with water while the hydrophilic groups are oriented toward the surrounding aqueous medium. Ideally, upon reaching CMC, any further addition of surfactants will just increase the number of micelles only. Micelles could be spherical, cylindrical, ellipsoidal or disc-like in shape. The formation of micelles from an ionic surfactant in aqueous phase at the critical micelle concentration is depicted in Fig. 1.4. Many experimental methods were used to determine the critical micelle concentration for aqueous solutions including osmotic pressure, turbidity, electrical conductance, and surface tension. Fig. 1.5 shows the changes in several physical properties around the CMC.

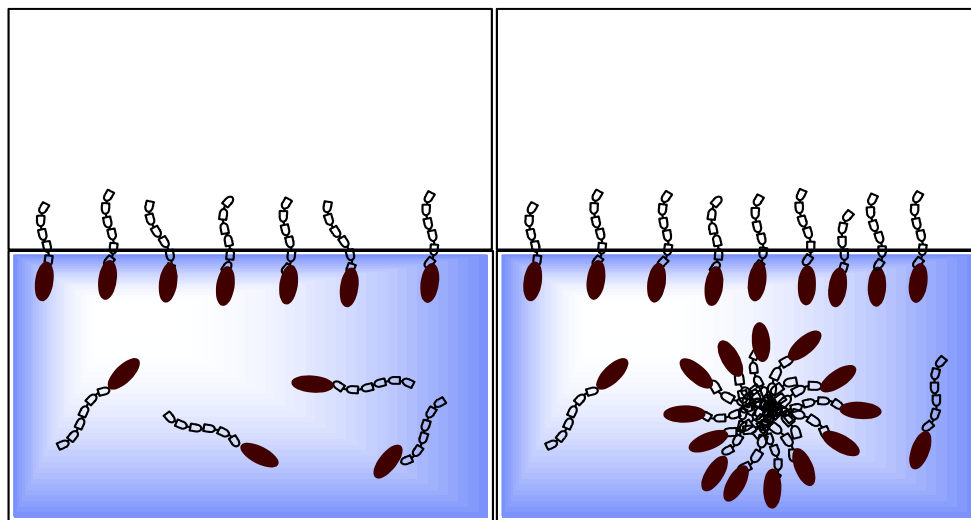


Fig. 1.4 Formation of micelles from surfactants in an aqueous solution at the critical micelle concentration.

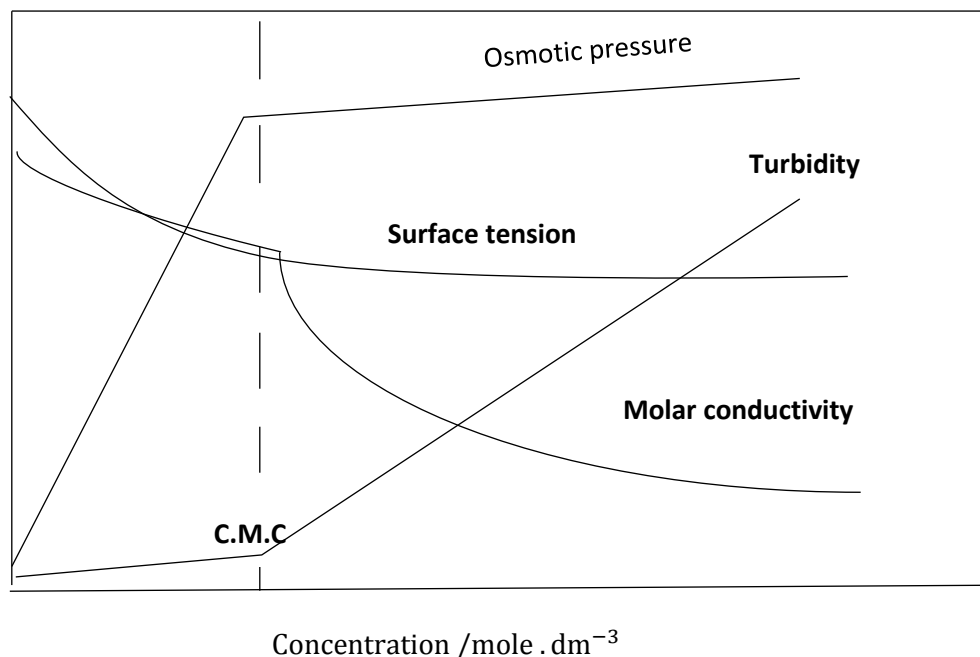


Fig. 1.5 Changes in some physical properties of aqueous solution of a surfactant in the neighborhood of the CMC.

As the values of CMC obtained from different physical properties are not quite identical, the method used for CMC determination must be clearly stated. Surface tension measurement is the classical method for CMC determination. The change in surface tension as a function of surfactant concentration is measured and by plotting the surface tension versus the logarithm of surfactant concentration as shown in Fig. 1.6, the value of CMC can be easily determined [16].

Many important structural factors of a surfactant effect CMC values. These factors can be summarized as follows:

- Many C_{12} ionic surfactants have a CMC value of approximately 10^{-2} mole/L, and the addition of two CH_2 groups reduced the CMC value to one-quarter its previous value.
- Nonionic surfactants having the same length exhibit a much lower CMC.
- A phenyl group present in the hydrophobic tail has the same impact on the CMC as 3.5 CH_2 groups.

- The branching in hydrocarbon chains at a constant number of carbon atoms raises the CMC value, and moving the hydrophilic group from an end position to more central position has the same effect [17].
- The CMC declines with increasing valency of the counter ion.

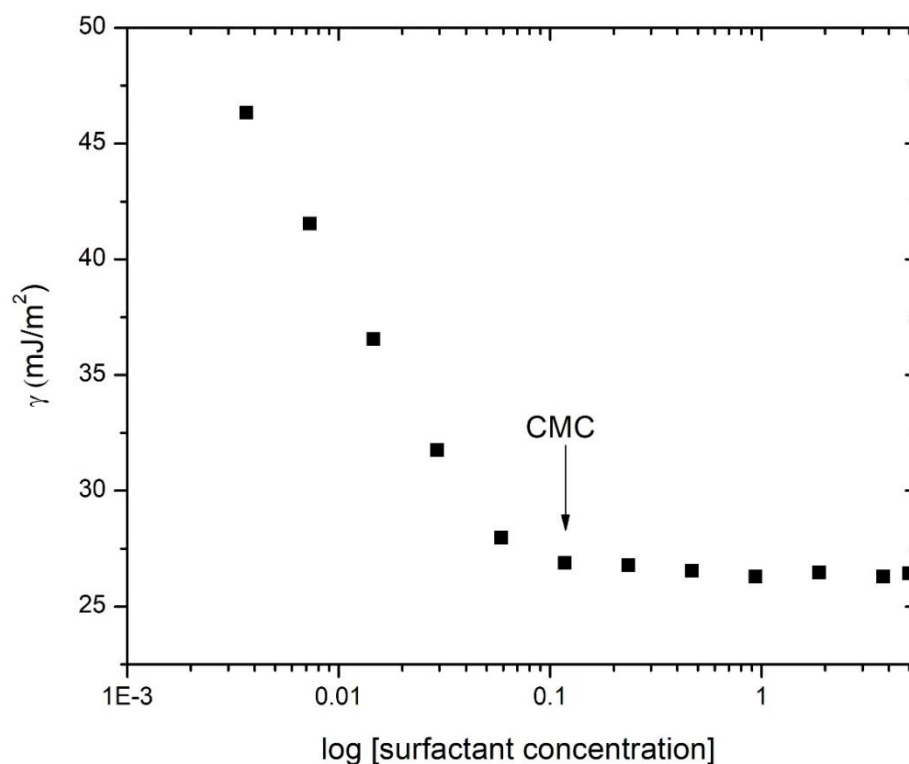


Fig. 1.6 Surface tension as a function of surfactant concentration. The point at which the surface tension starts to saturate is taken as the CMC of aqueous surfactant solutions as indicated by the arrow.

1.7.2 Factors Affecting the Value of CMC in Aqueous Solutions

The CMC is affected by factors that change its value. The impact of these factors on CMC may be summarized as:

- Structure of the hydrophobic group: increase in length of the hydrocarbon chain results in a decrease in CMC, which for compounds with identical polar head groups is expressed by the linear equation:

$$\log [\text{CMC}] = A - B m \quad (1 - 14)$$

where m is the number of carbon atoms in the chain and A and B are constants for a homologous series.

- Nature of the hydrophilic group: non – ionic surfactants generally have very much lower CMC values and higher aggregation numbers than their ionic counterparts with similar hydrocarbon chains.
- An increase in the ethylene oxide chain length of a non-ionic surfactant makes the molecule more hydrophilic and the CMC increases [18].
- Increase of concentration of a surfactant solution frequently causes a transition from the typical spherical micellar structure to a more elongated or rod – like micelle.
- Further increase in concentration may cause the orientation and close packing of the elongated micelles into hexagonal arrays; this is a liquid crystalline state termed the middle phase or hexagonal phase.
- With some surfactants, further increase of concentration results in the separation of a second liquid crystalline state – the neat phase or lamellar phase.
- In some surfactant systems another liquid crystalline state, the cubic phase, occurs between the middle and neat phases.
- Type of counter ion: micellar size increases for a particular cationic surfactant as the counter ion is changed according to the series $\text{Cl}^- < \text{Br}^- < \text{I}^-$, and for a particular anionic surfactant according to $\text{Na}^+ < \text{K}^+ < \text{Cs}^+$.
- Ionic surfactants with organic counter ions (e.g. maleates) have lower CMCs and higher aggregation numbers than those with inorganic counter ions.
- Effect of salt concentration: addition of salt in surfactant solution is another way of reducing CMC of surfactant. In general, repulsive forces between the head groups of

ionic surfactants are fighting against the aggregation. In the presence of salt, the repulsive forces of head group of anionic surfactant monomer decrease due to the electrostatic shielding effect resulting in the formation of micelle at lower CMC [19]. They further explained that electrical double layer was compressed due to the increased electrolyte concentration resulting in the reduced electrostatic attraction between ions and the micelles.

- Effect of temperature: for ionic and amphoteric surfactants, micellization is affected by temperature as the hydrophobic and head group interactions change with temperature. Accordingly, CMC versus temperature studies have been performed to obtain information on these interactions. For ionic surfactants in an aqueous solution, the CMC first monotonically decreases to a certain minimum around 25 °C while temperature is increasing temperature and then increases with further increase in temperature displaying a U-shaped behavior. In nonionic surfactants, CMC decreases as the temperature is increased. This is due to an increasing in the destruction of hydrogen bonds between water molecules and surfactants hydrophilic groups. The log CMC versus $1/T$ plot is nearly linear.

1.8 Measurement of Surface and Interfacial Tension

There are several techniques to measure the surface and interfacial tensions of liquids. The main techniques will be discussed briefly in the following sections.

1.8.1 Capillary Rise Method

Capillary rise is a fundamental phenomenon existing in many natural processes and human activities. Experimental method based on capillary rise is widely used for porous media characterization (i.e. pore radius, contact angle, free surface energy) and an illustration of this method is given in Fig. 1.7.

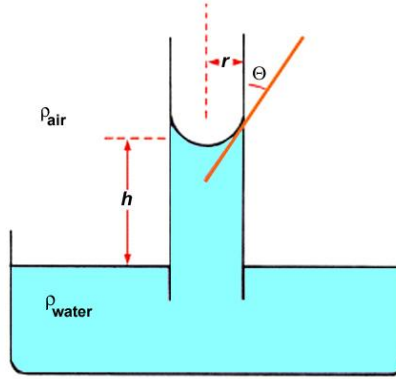


Fig. 1.7 Rise of water meniscus in a glass capillary

In capillary rise method a glass capillary is cleaned and immersed into a liquid or solution. In the case of water or aqueous solutions as the force of adhesion between the liquid molecules and the capillary wall is greater than the cohesion forces between liquid molecules, the liquid will rise up in the capillary. The height at which the liquid raised inside the capillary is related to the surface tension by the equation:

$$\gamma = \frac{\rho g h r}{2 \cos \theta} \quad (1 - 15)$$

If the contact angle θ is very small ($\theta \approx 0$) then $\cos \theta \approx 1$ is cosine will be 1 and the surface tension can be easily calculated from equation (1 – 16) below.

$$\gamma = \frac{1}{2} \rho g h r \quad (1 - 16)$$

1.8.2 Du Noüy Ring Method

A sketch of the method is shown in Fig.1.8. In this method a platinum-iridium ring is immersed in the liquid so that the ring will be under the surface of the liquid. The ring will be pulled carefully until it reaches the surface of the liquid. The force necessary to detach a platinum iridium ring is measured and is proportional to the surface or interfacial tension as:

$$\gamma = \frac{F}{L \cos \theta} \quad (1 - 17)$$

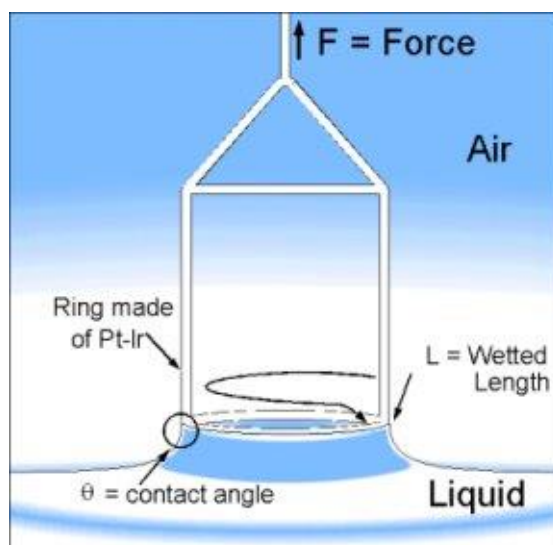


Fig. 1.8 A schematic sketch of Du Noüy ring method used for measuring the surface and interfacial tension of liquids

Du Noüy ring method is convenient and has the advantage of obtaining a fair degree of accuracy even with simple experimental procedure although it becomes much more complicated when a higher degree of accuracy is sought. The essential of the procedure are a ring, capable of being wetted by the liquid whose surface tension is to be measured, suspended horizontally in the flat surface of the liquid, and some device to measure the force necessary to separate ring and liquid.

1.8.3 Wilhelmy Plate Method

Consists of plate (glass or platinum) attached to a suitable balance. The plate is immersed in liquid, and the liquid container is gradually lowered. A sketch of the method is shown in Fig. 1.9. The reading on the balance immediately prior to detachment is noted.

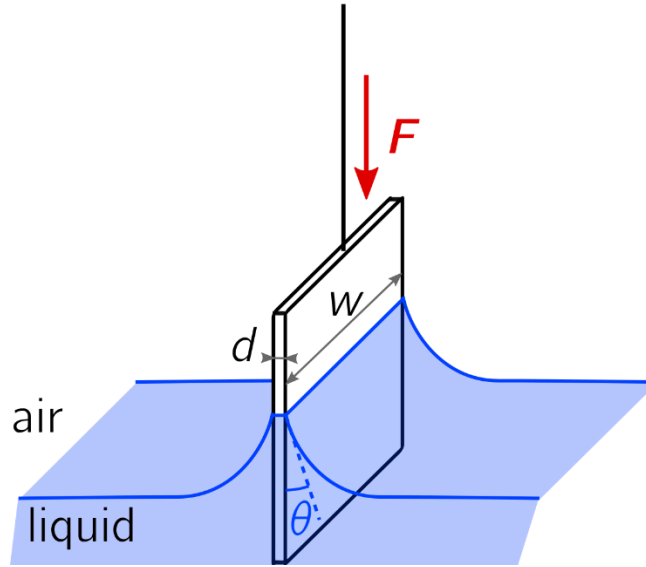


Fig. 1.9 A schematic sketch of Wilhelmy plate method used for measuring the surface and interfacial tension of liquids

One major difference between ring and plate methods is the way in which the measurement is carried out. The ring moves through the interface whereas the plate is static at the interface. Therefore, there is no ‘artificial’ disturbance of the interface and no increase in the time to reach equilibrium when using the plate method. Any time dependent effects are true effects hence the plate is the recommended geometry for studying time dependent characteristics[20].

1.8.4 The Spinning Drop Method

This technique is used to measure an ultralow interfacial tension of surfactant solutions. A drop of the surfactant solution in question is injected into a glass cylinder and is forced to rotate rapidly as shown in Fig.1.10. The drop will naturally spread sideways and take the shape of the glass cylinder. The spinning drop will have an elliptical shape with a radius R that depends on the interfacial tension γ , the difference in density $\Delta\rho$ and the angular velocity ω . Thus:

$$\gamma = \frac{1}{4} \Delta\rho \omega^2 R^3 \quad (1 - 18)$$

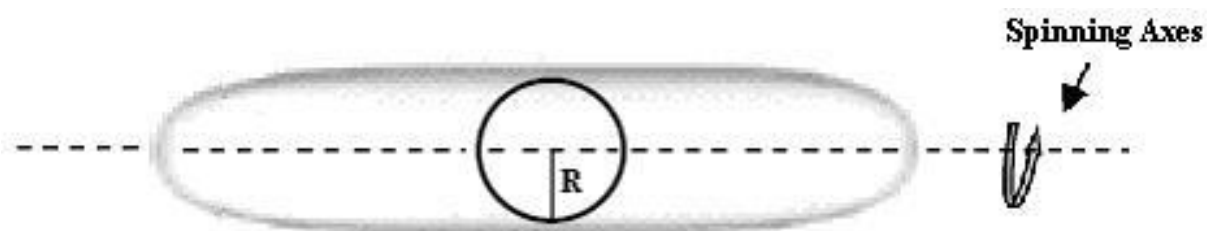


Fig. 1.10 A schematic sketch of the spinning drop in a cylindrical glass capillary

One advantage of spinning drop technique is that measurement of the contact angle between the liquid drop and the solid glass cylinder is not required.

1.9 Applications of Surface Active Agents

In all processes that take place at interfaces, surfactants can become effective. By application of surfactants, work processes may be simplified, accelerated, or economized. Also, the quality, as well as the efficiency of much differing products, may be optimized. An overview of the manifold application areas is given below.

1.9.1 Consumer Products

An important field of application for surfactants is consumer products. These products are detergents, dishwashing agents, cleaning agents and personal products.

1.9.1.1 Detergents and Dishwashing

The primary traditional application for surfactants is their use as soaps and detergents for a wide variety of cleaning processes. Soap has been used in personal hygiene for well over 2000 years with little change in the basic chemistry of their production and use. New products with pleasant colors, odors, and deodorant and antiperspirant activity have crept in to the market since the early twentieth century. The soaps and detergents are used mainly in washing our clothes, dishes, houses, and so on to remove unwanted dirt, oils, and other pollutants from the substrate[21].

1.9.1.2 Cosmetics and Personal Care Products

Cosmetics and personal care products make up a vast multi-billion-dollar market worldwide, continues to grow as a result of improved overall living standard. Such products are formulated mainly from surfactants and other amphiphilic materials.

1.9.2 Industrial Applications

1.9.2.1 Food Products

The food industry utilizes surfactants as cleaners and emulsifiers. Through application of natural or synthetic emulsifiers, O/W emulsions (milk substitutes, ice cream, mayonnaise, sauces, etc.) and W/O emulsions (e.g., margarine) food products can be improved in their consistency.

1.9.2.2 Pharmaceutical Industry

The primary application of surfactants in the pharmaceutical industry is as emulsifiers for creams and salves, but they are also used as dispersing agents in tablets or as synergists for active ingredients. The most important criterion for a specific application is the pharmacological or toxicological product safety.

1.9.2.3 Insecticides and Herbicides

Active substances for the protection of growing plants are offered as powder or liquid concentrates, which are diluted to so-called spray liquors for application. Surfactants are used here as aids for preparing satisfactorily dispersed spray liquors for adequate wetting of the target, as well as for promoting penetration of active substances into the plant.

1.9.2.4 Agriculture

In agriculture, surface active polymeric carboxylic acids or short chain alkane sulfonates effect hydrophilizing of heavy soils. To prevent caking of fertilizers in mixers and to achieve uniform distribution of fertilizers in the soil, dilute solutions of fatty alcohol polyglycol ethers, alkyl benzene sulfonates or cationic surfactants are advantageous.

1.9.2.5 Textiles and Fibers

In the manufacture and further processing of textiles, surfactants have a role as auxiliaries in a number of process steps. In pretreating of textile material, natural fibers are freed of accompanying substances (waxes, fats, pectines, seed hulls and other impurities). The detergents and wetting agents needed for this are primarily mixtures of different surfactant

types. In the manufacture of textiles, surfactants are applied to optimize individual processing steps (drawing, spinning, twisting, texturizing, coning, weaving, knitting, etc.).

1.9.2.6 Chemical Industry

The wetting and dispersing power of surfactants is being utilized in chemical processes to aid processing. In systems containing immiscible components, the reaction speed may be increased by the emulsification effect of surfactants, e.g., in splitting of fats by the Twitchell process, in hydrolytic splitting of wool wax and in hydrolysis of polyvinyl acetate. Also, worth mentioning is phenol manufacture by the cumene process, the preparation of ethylene carbamates, as well as chlorination reactions. Surfactants may also be applied to increase the yield in extraction processes.

1.9.2.7 Plastics Industry

The application of surfactants in the plastics industry is in the preparation of plastics dispersions (emulsion polymerization), pearl polymerization, polyurethane foams, as mold release agents and in micro encapsulation processes.

1.9.2.8 Paints and Lacquers

Surfactants are of great importance in the manufacture of coating materials, paints, varnishes, lacquers, dyestuff pigments, binding materials, and binders. Paints are basically a suspension of pigments in the form of finely ground solids dissolved in volatile liquid. Polymeric or resinous materials are added to act as binder. Surfactants are added to the previous mixture to speed up the preparation of dispersions and improve the dispersion degree and stability [22].

II Literature Review

As mentioned earlier, micelle is a thermodynamic aggregate that exists in equilibrium with monomeric surfactant species in aqueous phase. This equilibrium is affected by various factors including surfactant nature (chain length, hydrophobic volume, and head group area) and depends on relevant thermodynamic parameters such as temperature, concentration and pressure. A principal driving force behind surfactant adsorption and aggregation is the hydrophobic–hydrophilic interactions of the surfactant with the medium. Controlling over the aggregation and adsorption states may be achieved by appropriate adjustments of these

interactions. This may be achieved by addition of new species as the addition of electrolytes to ionic surfactant or modifying the pH of zwitterionic surfactants solutions.

A deep knowledge on CMC behavior as a function of temperature is of great importance in order to understand the thermodynamics of micellization. Many experimental studies suggest that CMC is temperature dependent and in the case of ionic surfactant system it presents a U-shape that has minimum at about room temperature. The decrease in CMC values with increasing temperatures was observed to occur up to about 298 K followed by a dramatic increase and this behavior was explained by the effect of two opposing factors. At one hand the increase of the temperature causes decrease in the hydration of the hydrophilic groups which favors the micellization. On the other hand such increase in temperature causes disruption of structured water surrounding the hydrophobic group, an effect that disfavors micellization. These two opposing effects determine whether CMC increases or decreases over temperature rang. Nonionic and zwitterionic materials are not quite predictable. While studies reported a general tendency of decreasing in CMC values as a temperature is increased some nonionic surfactants showed a U-shape behavior with minimum about 50°C [23]. This is due to an increasing in the destruction of hydrogen bonds between water molecules and surfactant hydrophilic groups. On the other hand, the presence of indifferent electrolyte causes a decrease in CMC of most surfactants and the greatest effect is found for ionic materials. This behavior was explained by the partial screening of the electrostatic repulsion between the head groups which leads to lowering of CMC.

This work focuses on studying the effect of temperature and salts on the CMC values of the anionic surfactant sodium dodecyl benzene sulfonate (SDBS). This surfactant which belongs to alkyl aryl sulfonate family has received a considerable attention in recent years due to its importance in tertiary oil recovery and many other applications [24]. The related literature is thoroughly reviewed and reported in the following sections.

Light scattering was used to examine the size and the shape of SDBS micelle in aqueous solutions. Measurements were made as a function of temperature at constant concentration of sodium chloride NaCl (0.2 M) and SDBS concentrations. The data indicates that the micelles have spherocylinders shapes with an aggregation number; $N_{agg} = 28$, and the length of micelles decreases with temperature and increases strongly with salt concentration [25].

In another study, conductivity measurement were used to investigate the effect of temperature and added amino acids on the CMC values of the two surfactants SDBS and dodecyltrimethylammonium bromide (DTAB) [26]. According to this study, aqueous solutions of both surfactants showed decrease in CMC values with increasing temperatures in the range 293 K to 313 K. In case of SDBS values of CMC were 1.20, 1.28 and 1.51 mM at the temperatures 293, 298 and 313 K respectively. In the presence of amino acids the two surfactants behave differently in response to changes in temperature. While SDBS showed a linear increase of CMC values with rising temperature, the DTAB showed first a decrease then values pass through a broad minimum at around $T = 298$ to 308 K then rising again at 313 K.

The interaction between water-soluble polymers polyacrylamide (PAA) and xanthan gum and the anionic surfactants SDS and SDBS have been studied by surface tension and conductivity measurements. The behavior of surfactant – polymer interaction was found to be dependent on both surfactant and polymer concentrations. It was found that addition of NaOH, NaCl and Na_2CO_3 had a significant influence on the surfactant – polymer interactions. The reported CMC value of SDBS aqueous solution at 298 K was equal to 2.3mM [27].

The effect of adding KCl salt to aqueous solutions of sodium dodecyl sulphate (SDS) and SDBS on CMC values was investigated in another study [28]. Measurements were based on conductivity-concentration data and carried out at 298 K. The CMC of SDBS showed a decrease from 1.87mM for a solution in absence of added salt to 1.4 and 1.03 mM when KCl was added at concentration of 1.0 and 5.0 mM respectively.

The value of CMC of SDBS was determined by spectrophotometers and found to have a value of 1.6 mM at 298 K. The study indicates that non-transition electrolytes lower the critical micelle concentration of this surfactant [28].

The interfacial and thermodynamic properties of SDBS in the presence of the additives poly ethylene glycol (PEG), sucrose, and urea have been investigated and CMC was determined by both surface tension and conductivity measurements. The maximum surface excess (Γ_i^σ), the minimum area per molecule (A_{min}) and the thermodynamic parameters of micellization and adsorption were determined from surface tension data. According to this work the CMC value of SDBS decreases in low – temperature region, shows a minimum and then increases with increasing in temperature [29]. In the presence of different concentrations of PEG, sucrose, and urea a similar effect was also observed and the overall micellization process was exothermic and entropy of micellization was positive.

From these previous studies, one finds that there is a discrepancy of the CMC values of the anionic surfactant SDBS in aqueous medium at 298 K and this may be the result of variations in the analytical methods used to determine the CMC values. Moreover, the effects of added electrolytes on CMC values were studied only for limited number of added salts and measurements were usually carried by varying electrolyte concentrations and fixing temperature or vice versa. The thermodynamic parameters of adsorption and micellization of SDBS in presence of added electrolytes were reported in limited number of studies.

III Objectives

In this work, experiments were designed with the aim of obtaining more comprehensive study related to the effect of temperature and added salts on the surface tension of the anionic surfactant SDBS. The fulfillment the objectives of the study will be achieved by:

- Measurement of the surface tension of aqueous solutions of different concentrations of the anionic surfactant SDBS as a function of temperature in the range (283 K – 328 K).
- Determination of the critical micelle concentration (CMC) of SDBS solutions at the wide temperature range (283 K – 328 K).

- Determination of the effect of adding the monovalent salt NaCl and divalent salt CaCl_2 at different concentrations and 4 different temperatures in the range (283 K – 328 K) on surface tension and CMC values of SDBS aqueous solutions.
- Determination of the effect of adding the molten salt $\text{C}_6\text{H}_{11}\text{BrN}_2$ at two different temperatures on surface tension and CMC values of SDBS aqueous solutions.
- Determination of the surface parameters of SDBS solutions in the absence and presence of added salts. These parameters are effectiveness π_{cmc} , surface excess Γ_i^σ , and minimum surface area A_{min} .
- Determination of the thermodynamic parameters: Gibbs energy, enthalpy and entropy of micellization of SDBS solutions.

Chapter 2

Materials and Experimental Techniques

2.1 Materials

2.1.1 Surfactant

Sodium dodecyl benzene sulfonate (SDBS) was obtained from Sigma – Aldrich (purity = 99.8%). It is an organic compound with the molecular formula $C_{12}H_{25}C_6H_4SO_3Na$ and has a molar mass of $348.48 \text{ g mole}^{-1}$. The surfactant is a white to light yellow sand – like solid with solubility in water of 20% at 298 K. The structural formula of SDBS is shown in Fig. 2.1.

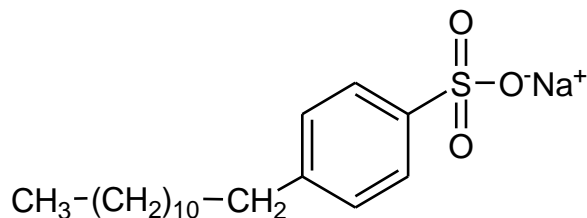


Fig.2.1 Structural formula of sodium dodecyl benzene sulfonate (SDBS)

2.1.2 Salts

1. Sodium chloride ($NaCl$) from Sigma – Aldrich with purity 99.99% by mass and molar mass of $58.44 \text{ g mole}^{-1}$.
2. Calcium chloride ($CaCl_2$) from Sigma – Aldrich with purity 99.99% by mass and molar mass of $110.98 \text{ g mole}^{-1}$.
3. 1 – Ethyl – 3 – methylimidazolium bromide (EMIB) from Fluka with purity 97%, and molecular weight $191.07 \text{ g mole}^{-1}$. The structural formula of this molten salt is shown in Fig. 2.2.

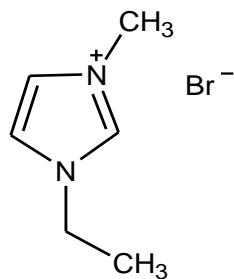


Fig. 2.2 Chemical structure of 1 – ethyl – 3 – methylimidazolium bromide (EMIB)

2.2 Equipment and Tools

2.2.1 Tensiometer

Surface tension was measured with the state – of – the – art K11 – MK3 tensiometer (Krüss, Germany) shown in Fig. 2.3. The tensiometer is fully automatic, with high resolution (0.01 mN/m) and constant position force measurement with overload protection. It is equipped with high precision force sensor that does not have to be recalibrated and with thermostat jacket for temperature-controlled measurements between –10 and 130 °C.

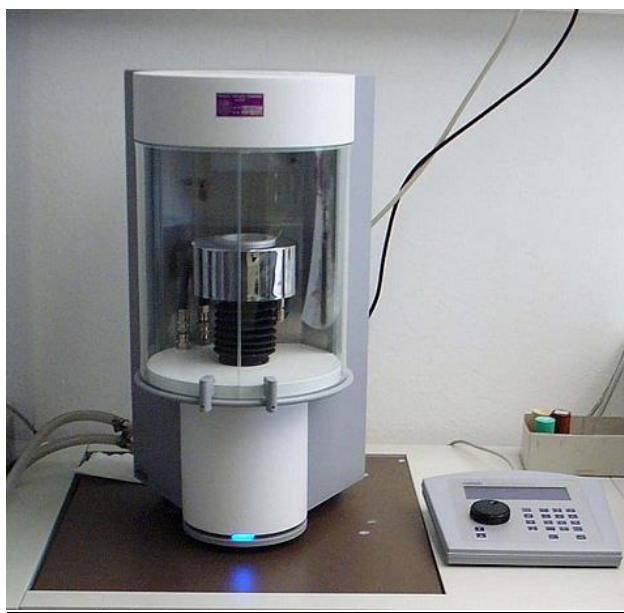


Fig. 2.3 Force Tensiometer – K11 (Krüss -Germany)

2.2.2 Temperature Control

A refrigerated circulating water bath connected to the tensiometer was used to control temperature. It has accuracy of ± 0.1 °C. The temperature controller shown in Fig. 2.4 was connected to the tensiometer and has the ability to supply cooling and heating. An effective system to thermostat and control temperature was very important during this work as surface tension is temperature dependent.



Fig. 2.4 A refrigerated circulating water bath with temperature controller that has accuracy of ± 0.1 °C

2.2.3 Furnace

A Lab furnace manufactured by CM Furnaces and has a maximum operating temperature up to 2000 K was used for drying salts. The furnace shown in Fig. 2.5 has sealed designs that support atmosphere control necessary for advanced processes including heat treating, sintering, annealing, glass or ceramic firing



Fig. 2.5 A Lab furnace by CM Furnaces with heating temperature up to 2000 K

2.3 Methods

2.3.1 Preparation of Tools and Measuring Procedure

All glassware (beakers, volumetric flasks, pipets, burets, funnels) were carefully cleaned by filling them with hot distilled water for several hours and then rinsed them thoroughly. Freshly prepared distilled water that was used to prepare solutions throughout this work was tested repeatedly for the values of surface tension and conductivity to ensure its purity.

The procedure that was followed for all surface tension measurements was as follows: before the onset of each measurement, the tensiometer was switched on for two hours to get the magnet inside the measuring chamber to the right temperature. This was recommended by the manufacturer. The surface tension of the freshly prepared distilled water was measured repeatedly to ensure that:

- The quality of water purity is accepted to prepare surfactant solutions.
- The tensiometer is working properly.

The accepted values of surface tension of distilled water at room temperature was in range between 71 – 72 mN/m. For each reading of surface tension measurement the ring was heated to redness using propane torch to get rid of surface impurities according to manufacturer instructions. The temperature of the solution vessel was brought to the desired value and kept for about half an hour to reach thermal equilibrium. Measurement of surface

tension of each sample was repeated five times and the average value was tabulated. The temperature of the sample was measured at the surface as it is known that bulk and surface temperatures are not the same. This surface temperature was measured with an accurate thermocouple that was supplied with the tensiometer.

Preparation of different concentrations of surfactant was carried out either by direct weighing or by successive dilution. Using serial dilution from stock solution was the preferred procedure as the working concentrations needed to determine the CMC at certain conditions were very low to be prepared by direct weighing. A 250 mL of the highest concentration was prepared and divided to two parts. Half of the solution was used for surface tension measurements and the other half was diluted by added distilled water in the 250 mL volumetric flask to the mark and thoroughly mixed. The process was repeated until the lowest desired concentration was achieved. The critical micelle concentrations of SDBS alone or in the presence of added salts at different temperatures were determined by plotting the needed data using the powerful plotting and fitting program Origin 8.

Chapter 3

Results and Discussion

3.1 Surface tension of water at different temperatures

The surface tension of pure distilled water was measured using the K11 – tensiometer in the temperature range of 273 – 343 K. The measurements were carried out using both Wilhelmy plate (platinum) and Du Noüy ring (platinum – iridium) methods. These measurements were performed as preliminary training and testing the precision of these two methods and checking the reproducibility and validity of the data obtained from the tensiometer with the heating system integrated to it. As shown in Table 3.1, the measured surface tension values are in a good agreement with the reported values according to Vargaftik et. al. [30]. The linear decrease of surface tension of water with temperature is shown in Fig. 3.1. This decrease is expected because increasing temperature means molecules are moving faster and the intermolecular forces (hydrogen bonds in case of water) between molecules become weaker and less effective. As the measured and reported values of surface tension at different temperatures are very close with no significant difference between them, this was a solid indication that the tensiometer and the heating system were functioning properly.

Table 3.1 Measured and reported values surface tension of pure water at different temperatures in the range 273 – 343 K

| T (K) | 273 | 283 | 293 | 303 | 313 | 323 | 333 | 343 |
|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\gamma_{\text{meas.}} (\text{mN/m})$ | 75.12 | 73.95 | 72.78 | 71.13 | 69.61 | 67.63 | 66.18 | 64.98 |
| $\gamma_{\text{rep.}} (\text{mN/m})$ | 75.64 | 74.23 | 72.75 | 71.20 | 69.60 | 67.94 | 66.24 | 64.47 |

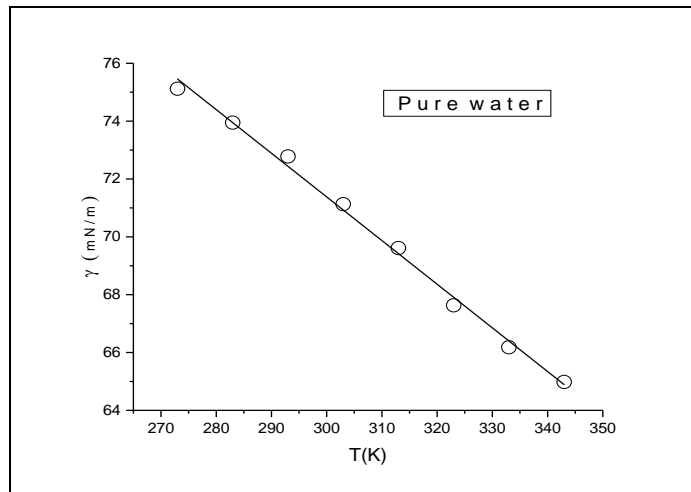


Fig. 3.1 Change of surface tension of pure water with temperatures in the range 273 – 343 K

3.2 Surface Tension of Sodium Chloride Solutions

Surface tension of aqueous solutions of sodium chloride (NaCl) in the range of 0.1 – 1.901 mol /L were measured at 298 K. Prior to preparation of solutions, the solid salt was annealed in the furnace at 823 K for several hours to get rid of impurities or traces of humidity that may present in the salt. All solutions were prepared by direct weighing of appropriate mass and the values of concentrations and surface tensions are shown in Table 3.2.

Table 3.2 Values of measured surface tension of different concentrations of aqueous solutions of NaCl at 298 K

| Mass of NaCl (g) | Molarity of NaCl (mol/L) | Density of solution (g/mL) | γ (mN/m) |
|-----------------------------|-------------------------------------|-------------------------------------------|---------------------------------------|
| 0.581 | 0.099 | 1.00 | 71.24 |
| 1.731 | 0.296 | 1.01 | 71.71 |
| 2.933 | 0.501 | 1.01 | 72.03 |
| 4.095 | 0.700 | 1.02 | 72.42 |
| 5.265 | 0.901 | 1.03 | 72.61 |
| 6.436 | 1.101 | 1.04 | 72.97 |
| 7.588 | 1.298 | 1.04 | 73.24 |
| 8.765 | 1.499 | 1.05 | 73.65 |
| 9.937 | 1.700 | 1.06 | 73.86 |
| 11.108 | 1.901 | 1.07 | 74.04 |

Figure 3.2 shows the surface tension of sodium chloride solutions as a function of salt concentration up to 2 molars. The surface tension increases with increasing the concentration NaCl solution. This behavior is expected for electrolytes and inorganic acids as they usually have a negative surface excess values. Ions dissolved in water do not like to accumulate at the surface to avoid contact with air but they prefer to stay in bulk so they will be surrounded with water from all directions. The results obtained are in accord with that of Norihiro et al [31].

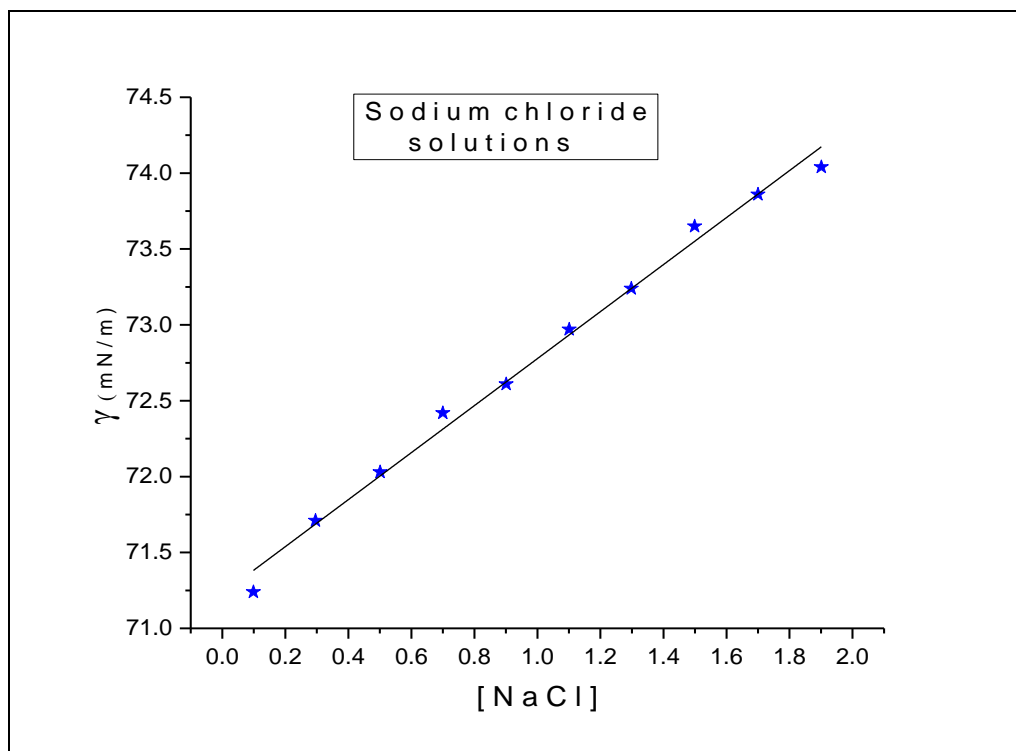


Fig. 3.2 Surface tension of sodium chloride solutions as a function of salt concentration at 298 K

3.3 Surface Tension of SDBS Solutions as a Function of Time

A 3.4 mg of sodium dodecyl benzene sulfonate (SDBS) was dissolved in 100 ml distilled water and the solution was left for 24 hours. After pouring the solution in the tensiometer sample vessel the surface tension values were monitored for 50 minutes at 5 minutes intervals at room temperature. The same procedure was-repeated with 11.4 mg of SDBS. The change in surface tension values with time are shown in Table 3.3 and Figs. 3.3 and 3.4. From these results it is clear that there is a decrease in the values of surface tension of the solutions for the two selected concentrations. However after the elapsed of about 30 minutes, surface tension values became almost constant. Based on these findings and for all subsequent surface tension measurements, readings were started after about 30 min. of transferring solution to sample vessel to obtain steady values. Very recently, Wen et .al. found that agitation of electrolytes solutions caused an increase in measured surface tension values of these solutions and they recommended that measurement of surface tension have to be conducted carefully to make sure that the steady surface tension can be measured accurately [32].

Table 3.3 Surface tension of SDBS as a function of time for two different concentrations

| Time (min.) | [SDBS] = 0.1 mM γ (mN/m) | [SDBS] = 0.3 mM γ (mN/m) |
|-------------|------------------------------------|------------------------------------|
| 0 | 50.29 | 33.30 |
| 5 | 49.98 | 32.32 |
| 10 | 49.48 | 31.96 |
| 15 | 49.21 | 31.68 |
| 20 | 49.23 | 31.36 |
| 25 | 49.11 | 31.27 |
| 30 | 48.98 | 31.19 |
| 35 | 48.81 | 31.19 |
| 40 | 48.82 | 31.21 |
| 45 | 48.73 | 31.18 |
| 50 | 48.80 | 31.19 |

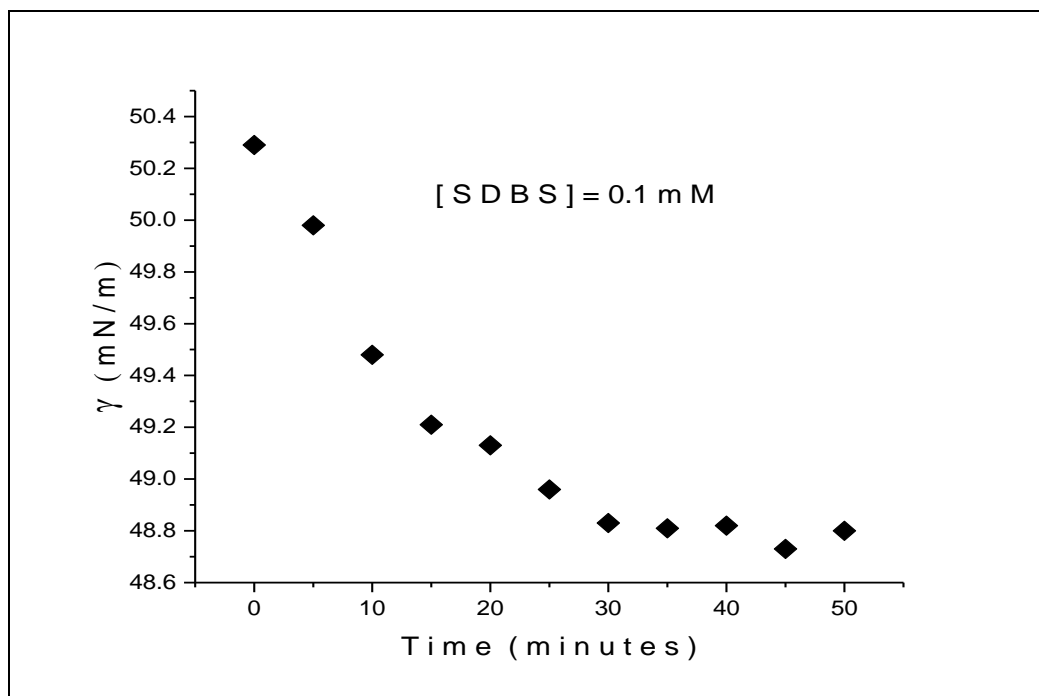


Fig. 3.3 Surface tension of 0.1 mM SDBS as a function of time

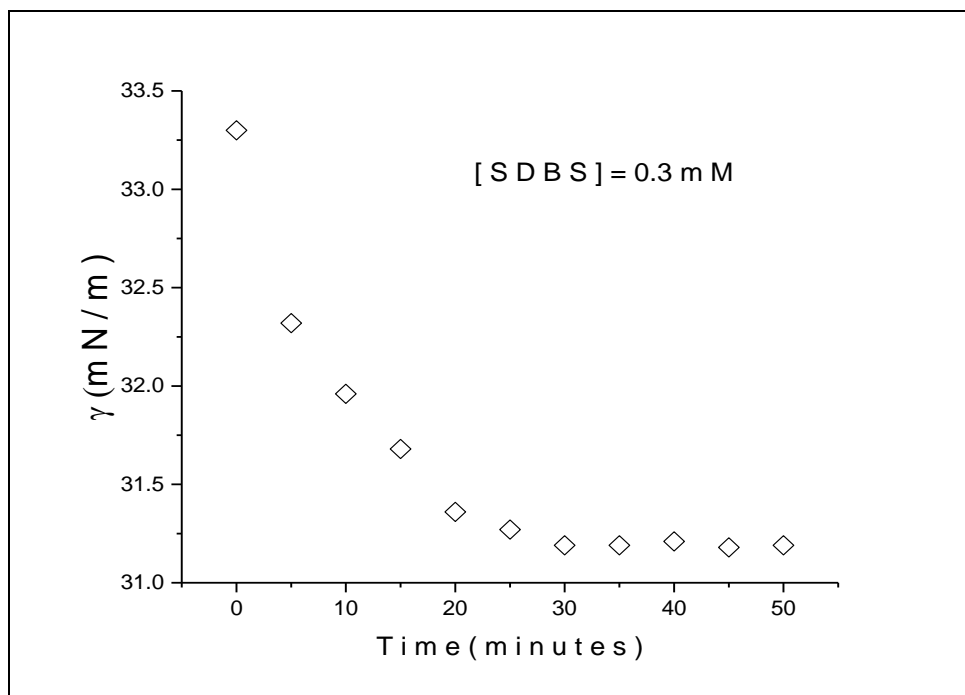


Fig. 3.4 Surface tension of 0.3 mM SDBS as a function of time

3.4 Concentration Dependence of the Surface Tension of SDBS

Surface tensions of SDBS solutions in the concentration range of 0.1 – 10 mM were measured and all experiments were carried out at 283 K . The solutions were prepared by direct weighing of the required masses and left 24 hours to reach equilibrium. Table 3.4 shows the outcome of these measurements and the amount of SDBS required for the preparation of each concentration.

Table 3.4 Surface tension of SDBS solutions in pure water as a function of SDBS concentrations at 283 K. Direct weighing was used to prepare solutions

| Mass of SDBS (g) | Molarity of SDBS (mM) | γ (mN/m) |
|-----------------------------|----------------------------------|---------------------------------------|
| 0.0032 | 0.0918 | 51.63 |
| 0.0097 | 0.0278 | 46.06 |
| 0.0184 | 0.5280 | 42.86 |
| 0.0241 | 0.6400 | 40.85 |
| 0.0345 | 0.9900 | 38.95 |
| 0.0672 | 1.920 | 35.04 |
| 0.1040 | 2.984 | 34.49 |
| 0.1396 | 4.001 | 34.03 |
| 0.1736 | 4.980 | 33.31 |
| 0.2125 | 6.100 | 33.65 |
| 0.2407 | 6.910 | 33.46 |
| 0.2778 | 7.970 | 33.27 |
| 0.3138 | 9.000 | 33.10 |
| 0.3502 | 10.100 | 32.98 |

Surface tension values of series of SDBS solutions were measured at the temperatures 288 K, 293 K, 298 K, 303 K, 308 K, 313 K, 318 K, 323 K, 328 K, 333 K. The data obtained are tabulated in tables 3.5, 3.6, 3.7 and plotted in Fig. 3.5, 3.6, 3.7 .

Table 3.5 Surface tension of SDBS solutions at the temperatures 288 , 293 and 298K

| Molarity of SDBS (mM) | γ (mN/m) At 288 K | Molarity of SDBS (mM) | γ (mN/m) At 293 K | Molarity of SDBS (mM) | γ (mN/m) At 298 K |
|--------------------------------------|----------------------------------------------------|--------------------------------------|----------------------------------------------------|--------------------------------------|----------------------------------------------------|
| 0.186 | 49.54 | 0.106 | 50.99 | 0.119 | 53.9 |
| 0.289 | 46.62 | 0.331 | 44.81 | 0.333 | 46.8 |
| 0.528 | 42.32 | 0.500 | 42.45 | 0.499 | 44.15 |
| 0.761 | 40.81 | 0.685 | 41.91 | 0.697 | 42.12 |
| 0.987 | 39.29 | 1.124 | 38.09 | 1.07 | 38.86 |
| 1.968 | 35.16 | 1.986 | 35.17 | 2.08 | 35.12 |
| 2.964 | 34.54 | 3.00 | 34.39 | 2.94 | 34.62 |
| 4.066 | 34.22 | 4.01 | 34.01 | 4.27 | 34.25 |
| 4.941 | 34.06 | 5.06 | 33.79 | 4.94 | 34.04 |
| 5.945 | 33.70 | 6.01 | 33.52 | 5.97 | 33.71 |
| 7.047 | 33.44 | 7.04 | 33.14 | 6.95 | 33.47 |
| 7.756 | 33.40 | 7.81 | 33.16 | 7.92 | 33.22 |
| 9.065 | 32.81 | 9.02 | 32.99 | 9.17 | 33.06 |
| 9.932 | 32.86 | 9.72 | 32.92 | 10.00 | 32.8 |

Table 3.6 Surface tension of SDBS solutions at the temperatures 303 , 308 and 313K

| Molarity of SDBS (mM) | γ (mN/m) At 303 K | Molarity of SDBS (mM) | γ (mN/m) At 308 K | Molarity of SDBS (mM) | γ (mN/m) At 313 K |
|------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|
| 0.10 | 40.08 | 0.126 | 38.09 | 0.141 | 36.79 |
| 0.29 | 31.65 | 0.293 | 31.65 | 0.320 | 31.23 |
| 0.52 | 29.56 | 0.660 | 28.04 | 0.534 | 27.88 |
| 0.69 | 29.49 | 0.701 | 27.93 | 0.694 | 27.36 |
| 1.05 | 29.43 | 1.071 | 28.07 | 0.998 | 27.61 |
| 1.98 | 30.99 | 2.040 | 30.25 | 2.040 | 29.52 |
| 3.13 | 32.13 | 3.058 | 31.73 | 3.290 | 31.49 |
| 3.99 | 32.67 | 3.950 | 31.96 | 4.150 | 32.03 |
| 4.97 | 32.88 | 4.940 | 32.26 | 5.020 | 32.25 |
| 5.86 | 32.93 | 6.061 | 32.41 | 6.590 | 32.25 |
| 6.77 | 32.69 | 6.875 | 32.39 | 6.980 | 32.32 |
| 7.85 | 32.67 | 7.830 | 32.31 | 7.850 | 32.13 |
| 8.95 | 32.50 | 8.970 | 32.28 | 9.001 | 32.12 |
| 9.85 | 32.37 | 10.064 | 32.12 | 10.03 | 31.93 |

Table 3.7 Surface tension of SDBS solutions at the temperatures 318 , 323, 328 and 333 K

| Molarity of SDBS (mM) | γ (mN/m) At 318 K | Molarity of SDBS (mM) | γ (mN/m) At 323 K | Molarity of SDBS (mM) | γ (mN/m) At 328 K | Molarity of SDBS (mM) | γ (mN/m) At 333 K |
|------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|------------------------------|--------------------------------------------|
| 0.149 | 36.00 | 0.169 | 42.70 | 0.223 | 38.08 | 0.166 | 42.07 |
| 0.373 | 30.13 | 0.333 | 35.93 | 0.275 | 36.26 | 0.318 | 41.02 |
| 0.545 | 28.08 | 0.514 | 34.19 | 0.533 | 33.80 | 0.519 | 38.99 |
| 0.743 | 28.21 | 0.77 | 33.12 | 0.806 | 32.54 | 0.78 | 38.43 |
| 0.935 | 28.17 | 1.02 | 32.66 | 0.990 | 32.10 | 1.00 | 36.93 |
| 1.95 | 29.40 | 1.96 | 31.46 | 2.040 | 31.05 | 2.06 | 33.36 |
| 3.01 | 31.39 | 2.89 | 32.43 | 3.047 | 32.98 | 2.99 | 33.31 |
| 3.92 | 31.99 | 4.13 | 32.80 | 4.020 | 32.88 | 4.04 | 33.16 |
| 5.00 | 32.36 | 4.91 | 32.69 | 4.990 | 32.80 | 4.97 | 32.80 |
| 5.78 | 32.26 | 5.82 | 32.54 | 5.960 | 32.50 | 5.97 | 32.60 |
| 6.89 | 32.33 | 7.15 | 32.34 | 6.980 | 32.30 | 7.01 | 31.94 |
| 7.77 | 32.27 | 7.84 | 32.21 | 7.840 | 31.70 | 7.97 | 32.11 |
| 9.05 | 32.00 | 9.14 | 32.04 | 9.340 | 31.84 | 9.12 | 31.90 |
| 10.03 | 31.82 | 10.12 | 31.84 | 10.11 | 31.77 | 10.18 | 31.70 |

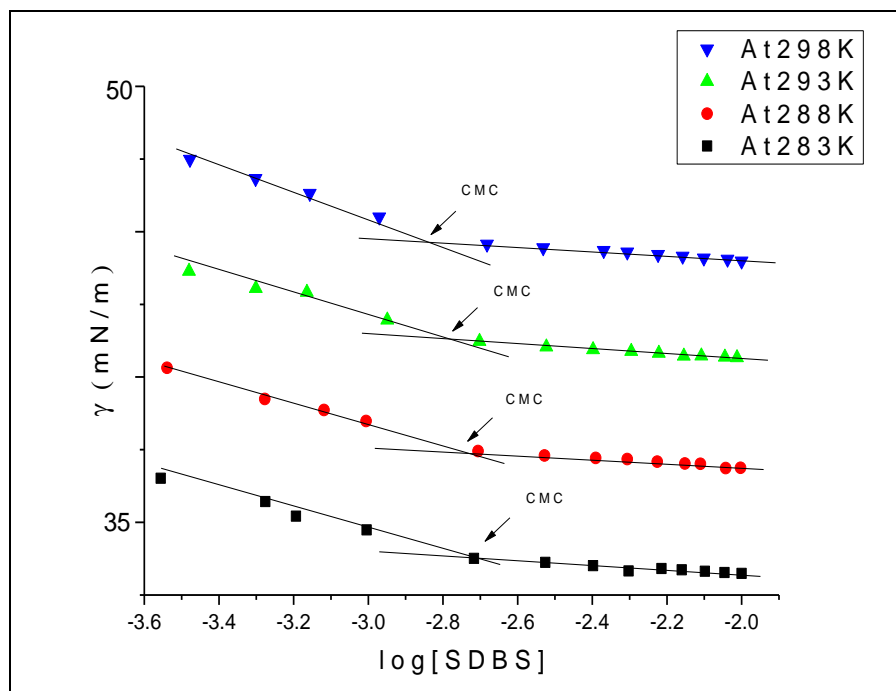


Fig. 3.5 Surface tension of SDBS solutions as a function of the logarithm of SDBS concentration at 283, 288, 293 and 298 K

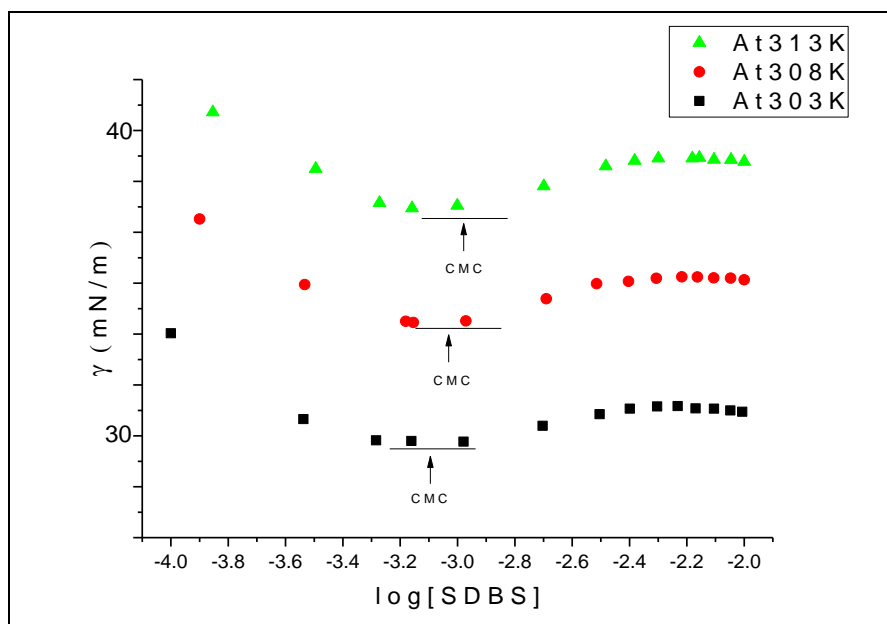


Fig. 3.6 Surface tension of SDBS solutions as a function of the logarithm of SDBS concentration at 303, 308 and 313 K

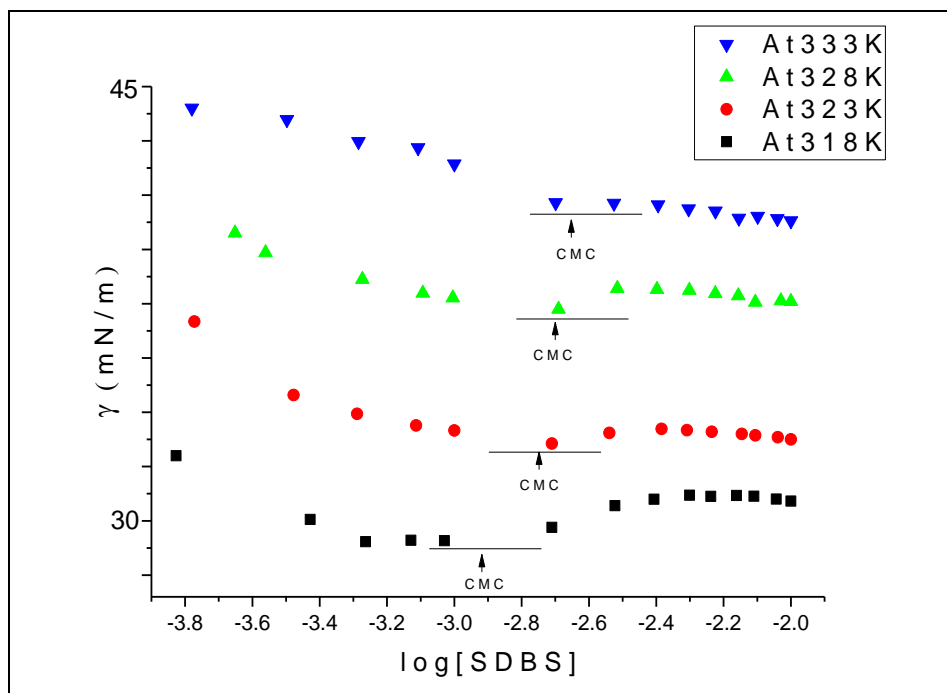


Fig. 3.7 Surface tension of SDBS solutions as a function of the logarithm of SDBS concentration at 318, 323, 328 and 333 K

As can be seen from the previous figures, surface tension of SDBS decreases with increasing surfactant concentration and such effect is expected as more and more surfactants molecules present at the surface. The decrease will cease and surface tension comes to be almost constant when the CMC point is reached. This is an indication that the surface is saturated with the surfactant and the addition of more and more surfactants will not decrease the surface tension any further. At this point a self-organization of the surfactant molecules takes place as micelles inside the aqueous phase. The formation of these micelles means that surfactant molecules shield their non-polar chains from the surrounding aqueous phase with their polar head groups.

In addition to the effect of changing surfactant concentration, experiments were repeated for series of surfactant concentrations at different temperatures. From Figs 3.5 – 3.7 it is clear that surface tension decreases with increasing temperature. Two factors are usually related to the effect of temperature on surface tension values of solutions of ionic surfactants. The first is related to the decrease in the value of surface tension of the solvent (water) and such effect

was shown in Fig.3.1 in this work. The second factor is related to the effect of raising temperature on the solubility of surfactants in water. Increasing solubility means part of surfactant molecules leave the surface and in this case the surface tension is expected to increase as the temperature is increased. Results of previous works showed that for low concentrated solutions of ionic surfactants, increasing temperature leads to decrease in surface tension and the effect on the solvent predominate and causes such decrease. In the range of medium ionic surfactant concentrations, almost no temperature dependence was observed while for concentrations that are close to CMC the most common trend was an increase in surface tension with raising temperatures [33].

A decrease in CMC values with temperatures was also observed. Such a decrease is a consequence of the decrease in hydrophilicity of the surfactant molecules. Increasing temperature is weakening hydrogen bonding between surfactant molecules and water. In other words, the increase in temperature causes the decrease in hydration of the hydrophilic group, which favors micellization. Consequently, the onset of micellization occurs at lower concentrations as the temperature increases. The CMC value also decreases with increasing temperature. The decrease of the CMC with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules, owing to the smaller probability of hydrogen bond formation at higher temperatures. In other words, the increase in temperature causes the decrease in hydration of the hydrophilic group, which favors micellization. Consequently, the onset of micellization occurs at lower concentrations as the temperature increases.

Figure 3.8 shows the temperature dependence of the surface tensions of SDBS solutions for different surfactant concentrations. The decreasing effect can be explained as in the previous paragraph for Figs. 3.5 – 3.7.

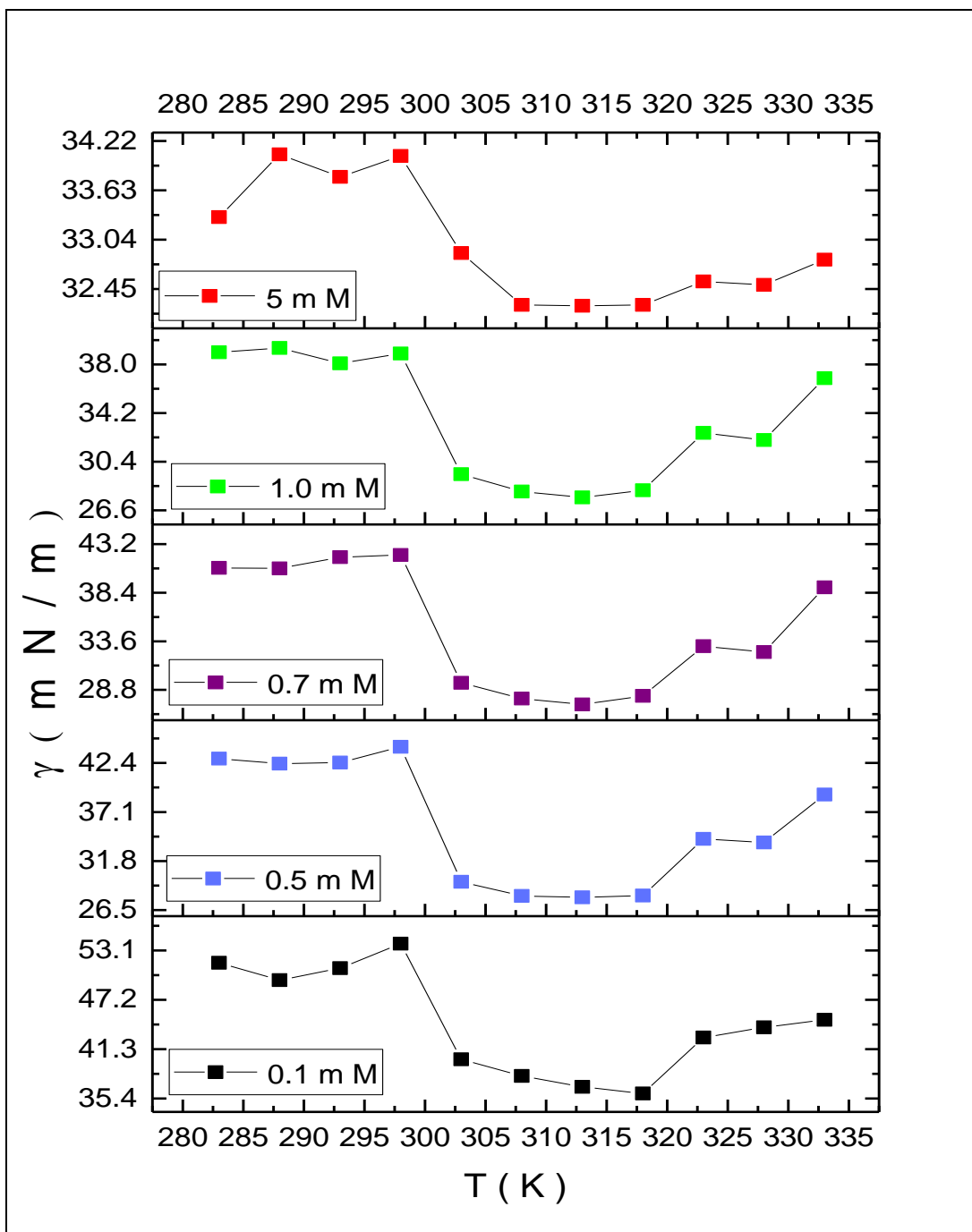


Fig. 3.8 Surface tension as a function of temperature for 0.1 mM, 0.5 mM, 0.7 mM, 1.0 mM and 5.0 mM of SDBS

3.5 Surface Tension of SDBS Solutions in Presence of Electrolytes at Different Temperatures

In the previous section the effect of changing the concentration of SDBS in pure water on the measured surface tension of these solutions was investigated. In other sets of experiments the effect of changing temperature was also examined. In the following sections, the effect of adding different salts to surfactant solutions will be investigated by changing the type and concentration of added salts and the temperature.

3.5.1 Surface Tension of SDBS Solutions in Presence of Sodium Chloride at Different Temperatures

Surface tensions of SDBS solutions in the concentration range of 0.003 to 10 mM and in the presence of sodium chloride (NaCl) were measured at different temperatures. The salt concentrations were in the range of 0.1 to 0.3 M. Solutions of SDBS were prepared by dilution of stock solution of the surfactant at concentration of 10 mM, and the subsequent concentrations were prepared by successive dilution. Prior to solutions preparation, sodium chloride salt was annealed in a laboratory furnace at 823 K for several hours to get rid of impurities. The SDBS – electrolyte solutions were left 24 hours to attain equilibrium. Surface tensions of these solutions were measured at planned temperatures. Prior to each measurement, solutions were left for about 30 minutes at the measuring temperature to reach equilibrium. Measurements were carried out as a function of:

- 1- SDBS concentration
- 2- Sodium chloride concentration
- 3- Solution temperature

The results of these experiments are shown in Tables 3.8 – 3.11, and Figs. 3.9 – 3.12.

Table 3.8 Surface tension of SDBS solutions in the presence of 0.1 M of NaCl at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 0.07 | 34.50 | 33.40 | 33.10 | 32.80 |
| 0.1 | 32.23 | 31.49 | 30.12 | 30.42 |
| 0.3 | 29.73 | 29.59 | 28.48 | 28.09 |
| 0.5 | 29.47 | 29.22 | 28.45 | 27.78 |
| 0.7 | 29.29 | 28.97 | 28.25 | 27.65 |
| 1.0 | 29.26 | 29.22 | 28.13 | 27.72 |
| 2.0 | 29.30 | 29.28 | 28.29 | 27.61 |
| 3.0 | 29.05 | 28.56 | 28.01 | 27.69 |
| 4.0 | 29.04 | 28.53 | 28.07 | 27.61 |
| 5.0 | 29.10 | 28.83 | 27.94 | 27.55 |
| 6.0 | 29.16 | 28.98 | 27.94 | 27.65 |
| 7.0 | 29.08 | 28.70 | 27.89 | 27.62 |
| 8.0 | 29.08 | 28.90 | 27.98 | 27.56 |
| 9.0 | 29.08 | 28.39 | 27.85 | 27.66 |
| 10.0 | 29.12 | 28.32 | 27.73 | 27.13 |

Table 3.9 Surface tension of SDBS solutions in the presence of 0.2 M of NaCl at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | [SDBS] (mM) | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|----------------|--------------------------------|--------------------------------|----------------|--------------------------------|--------------------------------|
| 0.025 | 39.61 | 36.04 | 0.0146 | 48.63 | 45.15 |
| 0.05 | 35.23 | 33.59 | 0.0292 | 42.59 | 39.41 |
| 0.07 | 32.10 | 30.29 | 0.0585 | 36.41 | 33.46 |
| 0.10 | 30.69 | 29.64 | 0.1172 | 30.15 | 27.81 |
| 0.30 | 28.80 | 27.95 | 0.2343 | 27.84 | 26.69 |
| 0.50 | 29.00 | 27.95 | 0.4687 | 27.15 | 26.44 |
| 0.70 | 29.10 | 27.91 | 0.9375 | 27.09 | 26.48 |
| 1.00 | 28.67 | 27.98 | 1.875 | 27.00 | 26.47 |
| 2.00 | 28.62 | 27.79 | 3.750 | 26.98 | 26.32 |
| 3.00 | 28.52 | 28.04 | ⊖ | ⊖ | ⊖ |
| 4.00 | 28.69 | 27.94 | ⊖ | ⊖ | ⊖ |
| 5.00 | 28.62 | 27.92 | ⊖ | ⊖ | ⊖ |

Table 3.10 Surface tension of SDBS solutions in the presence of 0.3 M of NaCl at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.0073 | 48.45 | 45.54 | 39.45 | 47.70 |
| 0.0146 | 42.31 | 35.84 | 36.87 | 42.51 |
| 0.0292 | 34.75 | 33.63 | 30.14 | 36.35 |
| 0.0585 | 30.12 | 28.97 | 28.69 | 29.72 |
| 0.1172 | 29.75 | 27.91 | 27.12 | 26.38 |
| 0.2343 | 29.41 | 27.86 | 26.76 | 25.89 |
| 0.4687 | 29.20 | 27.47 | 26.85 | 25.79 |
| 0.9375 | 29.18 | 27.43 | 26.74 | 25.86 |
| 1.8750 | 29.29 | 27.57 | 26.74 | 25.80 |
| 3.750 | 28.90 | 27.41 | 26.94 | 25.27 |
| 5.00 | 28.74 | 27.67 | 26.81 | 25.87 |

Table 3.11 Surface tension of SDBS solutions in the presence of 0.4 M of NaCl at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.00365 | 49.16 | 49.23 | 46.34 | 44.61 |
| 0.0073 | 47.1 | 47.64 | 41.54 | 41.32 |
| 0.0146 | 42.15 | 41.87 | 36.54 | 39.61 |
| 0.0292 | 35.03 | 31.12 | 31.76 | 36.36 |
| 0.0585 | 32.9 | 28.46 | 27.97 | 32.91 |
| 0.1172 | 31.08 | 28.24 | 26.88 | 25.41 |
| 0.2343 | 29.81 | 27.71 | 26.78 | 25.43 |
| 0.4687 | 29.77 | 27.68 | 26.55 | 25.41 |
| 0.9375 | 29.43 | 27.72 | 26.31 | 25.48 |
| 1.875 | 29.27 | 27.48 | 26.48 | 25.41 |
| 3.75 | 28.83 | 27.75 | 26.3 | 25.27 |

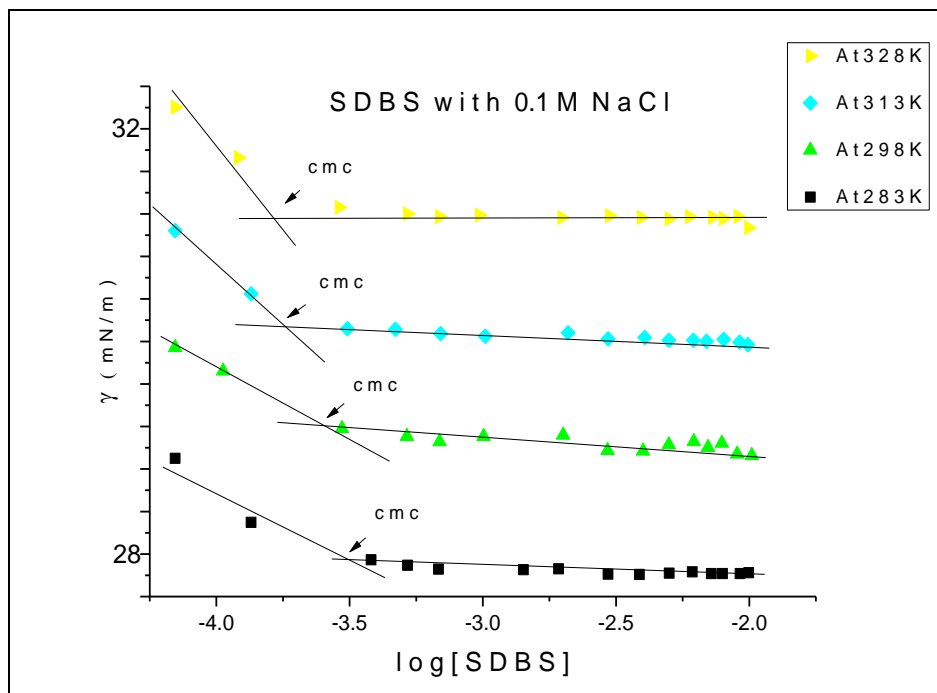


Fig. 3.9 Surface tension of SDBS in the presence of 0.1 M NaCl at 283, 298, 313 and 328K

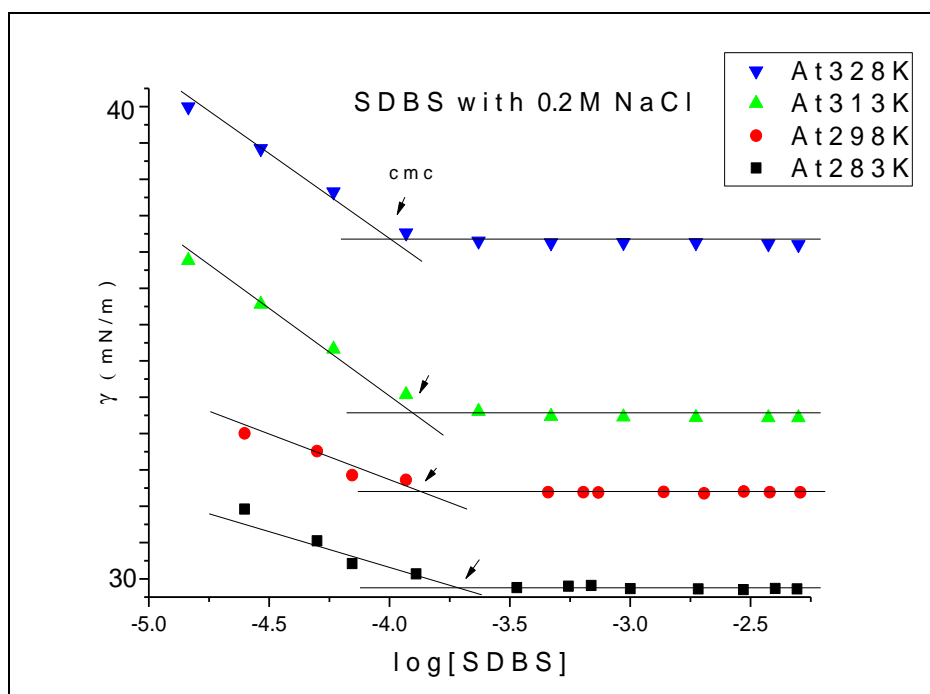


Fig. 3.10 Surface tension of SDBS in the presence of 0.2 M NaCl at 283, 298, 313 and 328K

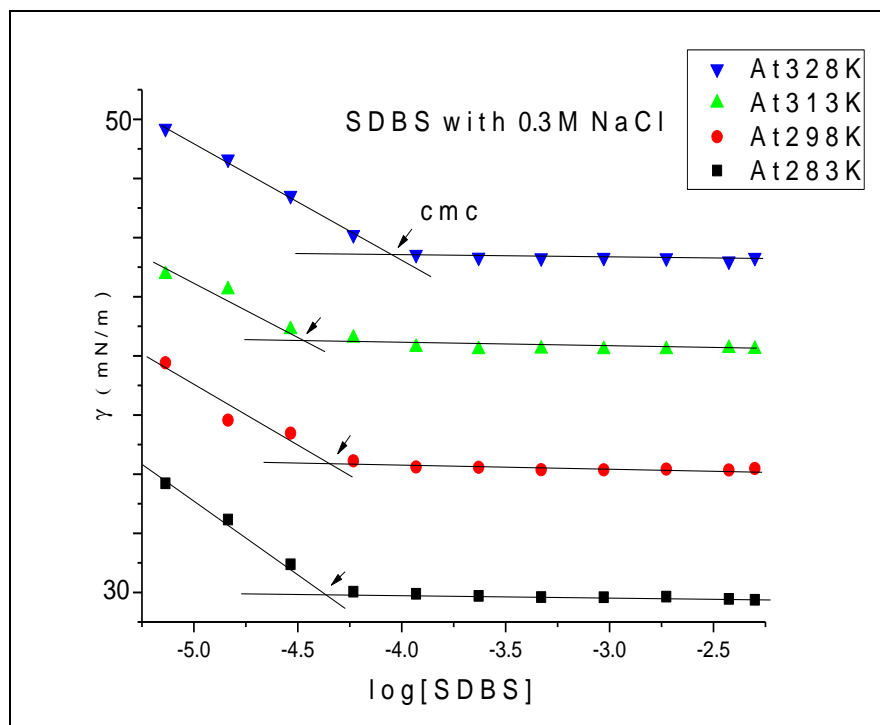


Fig. 3.11 Surface tension of SDBS in the presence of 0.3 M NaCl at 283, 298, 313 and 328K

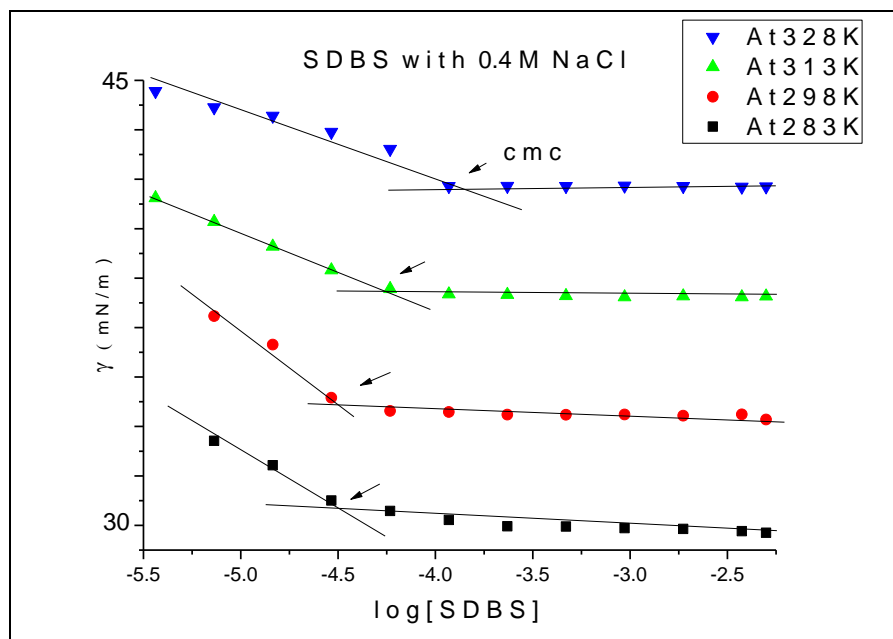


Fig. 3.12 Surface tension of SDBS in the presence of 0.4 M NaCl at 283, 298, 313 and 328K

The onset of surface tension saturation indicated by CMC at each salt concentration and temperature conditions are shown in Figs. 3.9 – 3.12. From these figures it is possible to conclude that values of surface tension of SDBS solutions at each concentration of added salt decrease with increasing temperature and such behavior was explained in previous sections. However, the effect of changing temperatures on CMC values of the ionic surfactants in the presence of added electrolyte salts is more complicated and not straight forward. While number of works reported decrease in CMC values when the temperature is increased others showed that CMC first decreases, then undergoes through a minimum, and finally increases [34]. Similar pattern was observed with nonionic surfactant solutions [35]. The ups and downs variations were attributed to two competing opposite effects. On one hand, an increase in temperature can bring a reduction in the hydration of the surfactant hydrophilic group. This effect tends to drive the surfactant out of the aqueous solution and thus it favors the formation of micelles, i.e., it decreases the CMC. On the other hand, an increase in temperature results in an increasing disorder in the structure of water phase, in particular the molecules which are located next to the surfactant hydrophobic tail. The higher in disorder, the less defined the direction of the unfavorable polar/apolar contact, and as a consequence it becomes the weaker. This means that the hydrophobic effect which drives the surfactant molecule "tail" out of the water phase is reduced as the temperature is increased. While the reduction in surface tension is proportional to the adsorbed amount of surfactant according to Gibbs' adsorption isotherm, the presence of salt reduces the electrostatic repulsion between the surfactant's ionized head-groups which means that they can pack together closer at the interface. Therefore, more surfactant molecules are adsorbed at the surface and the reduction of the surface tension is greater.

3.5.2 Surface Tension of SDBS Solutions in Presence of Calcium Chloride at Different Temperatures

Surface tension values of SDBS solutions in the range of 0.003 – 5 mM in the presence of calcium chloride (CaCl_2) having molarity in the range of 0.1 – 0.4 M were measured at different temperatures. The SDBS solutions were prepared using a stock solution of concentration 5 mM using successive dilution method. The calcium chloride salt was annealed

in the furnace at 403 K for several hours to get rid of impurities. The mixture was left for 24 hours and then, surface tension was measured at the specified temperature after 30 min to get steady measurements and thermal equilibrium. The results of these measurements are shown tables 3.12 – 3.15 and figures 3.13-3.16, respectively.

Table 3.12 Surface tension of SDBS solutions in the presence of 0.1 M of CaCl_2 at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.00365 | 58.70 | 56.22 | 54.18 | 51.26 |
| 0.0073 | 49.28 | 41.28 | 41.27 | 39.98 |
| 0.0146 | 38.78 | 35.04 | 34.46 | 27.92 |
| 0.0292 | 31.22 | 30.92 | 27.94 | 27.14 |
| 0.0585 | 30.79 | 30.08 | 27.26 | 26.17 |
| 0.1172 | 30.26 | 29.32 | 27.39 | 26.03 |
| 0.2343 | 30.57 | 29.27 | 27.55 | 25.93 |
| 0.4687 | 29.95 | 29.17 | 27.15 | 25.83 |
| 0.9375 | 30.05 | 29.14 | 27.48 | 25.92 |
| 1.875 | 30.73 | 29.18 | 27.92 | 25.92 |
| 3.75 | 31.11 | 29.27 | 27.37 | 25.71 |
| 5.00 | 30.57 | 29.13 | 27.18 | 25.62 |

Table 3.13 Surface tension of SDBS solutions in the presence of 0.2 M of CaCl_2 at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.00365 | 50.91 | 49.06 | 46.88 | 46.13 |
| 0.0073 | 40.87 | 48.87 | 41.27 | 38.14 |
| 0.0146 | 36.11 | 37.72 | 28.86 | 26.26 |
| 0.0292 | 33.12 | 29.07 | 28.08 | 26.92 |
| 0.0585 | 30.04 | 28.97 | 27.42 | 26.47 |
| 0.1172 | 30.48 | 28.71 | 27.22 | 26.13 |
| 0.2343 | 29.72 | 28.62 | 27.30 | 26.30 |
| 0.4687 | 30.12 | 28.50 | 27.16 | 26.15 |
| 0.9375 | 30.22 | 28.49 | 27.22 | 26.29 |
| 1.875 | 30.46 | 28.60 | 27.35 | 26.15 |
| 3.75 | 30.65 | 28.72 | 27.48 | 26.31 |
| 5.00 | 29.78 | 29.44 | 27.20 | 25.82 |

Table 3.14 Surface tension of SDBS solutions in the presence of 0.3M of CaCl_2 at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.00365 | 53.37 | 69.11 | 66.26 | 45.48 |
| 0.0073 | 48.84 | 47.65 | 45.41 | 37.31 |
| 0.0146 | 38.29 | 37.12 | 34.94 | 31.92 |
| 0.0292 | 32.40 | 28.91 | 33.45 | 26.58 |
| 0.0585 | 30.02 | 28.52 | 27.44 | 26.26 |
| 0.1172 | 30.62 | 28.58 | 27.31 | 26.30 |
| 0.2343 | 30.17 | 28.65 | 27.21 | 26.23 |
| 0.4687 | 30.61 | 28.55 | 27.35 | 26.26 |
| 0.9375 | 30.53 | 28.73 | 27.25 | 26.46 |
| 1.875 | 29.90 | 29.08 | 27.75 | 26.51 |
| 3.75 | 29.65 | 28.91 | 27.82 | 26.90 |
| 5.00 | 29.62 | 28.83 | 28.04 | 27.32 |

Table 3.15 Surface tension of SDBS solutions in the presence of 0.4 M of CaCl_2 at 283, 298, 313 and 328 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K | γ (mN/m) at 313 K | γ (mN/m) at 328 K |
|------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 0.00365 | 55.06 | 46.68 | 42.64 | 45.09 |
| 0.0073 | 40.54 | 43.01 | 32.16 | 40.45 |
| 0.0146 | 34.98 | 32.58 | 30.13 | 34.81 |
| 0.0292 | 30.19 | 29.29 | 29.37 | 27.57 |
| 0.0585 | 30.31 | 29.08 | 29.17 | 26.49 |
| 0.1172 | 30.29 | 28.85 | 29.02 | 26.50 |
| 0.2343 | 30.05 | 28.57 | 28.42 | 26.41 |
| 0.4687 | 29.58 | 28.90 | 28.17 | 26.58 |
| 0.9375 | 29.77 | 28.71 | 28.07 | 26.75 |
| 1.875 | 29.77 | 28.84 | 28.09 | 27.24 |
| 3.75 | 29.87 | 28.75 | 28.13 | 27.04 |
| 5.00 | 29.43 | 28.73 | 28.03 | 27.43 |

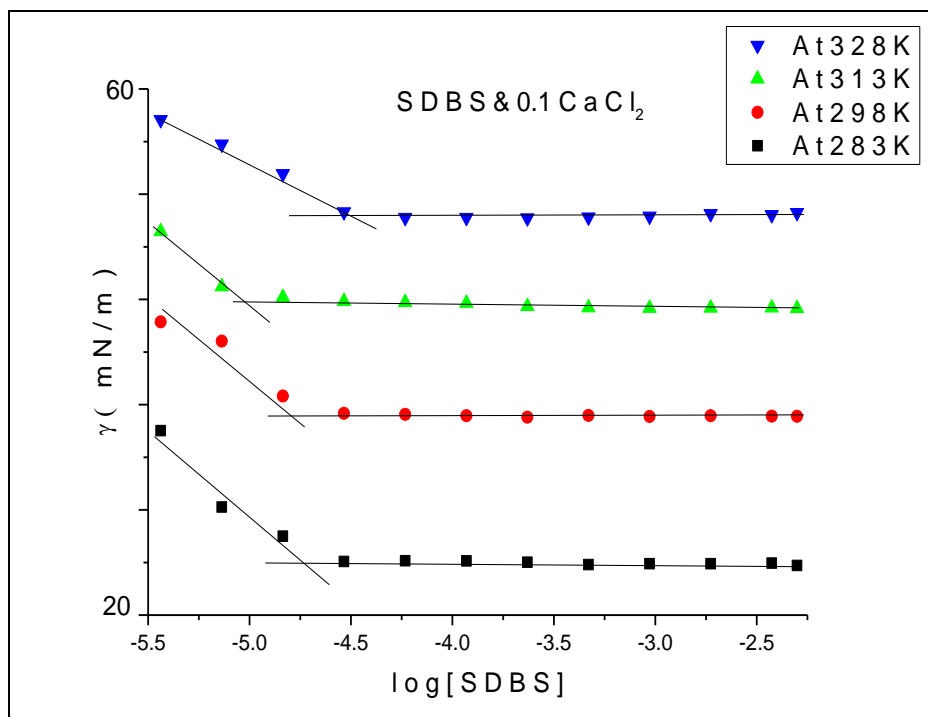


Fig. 3.13 Surface tension of SDBS in the presence of 0.1 M CaCl_2 at 283, 298, 313 and 328K

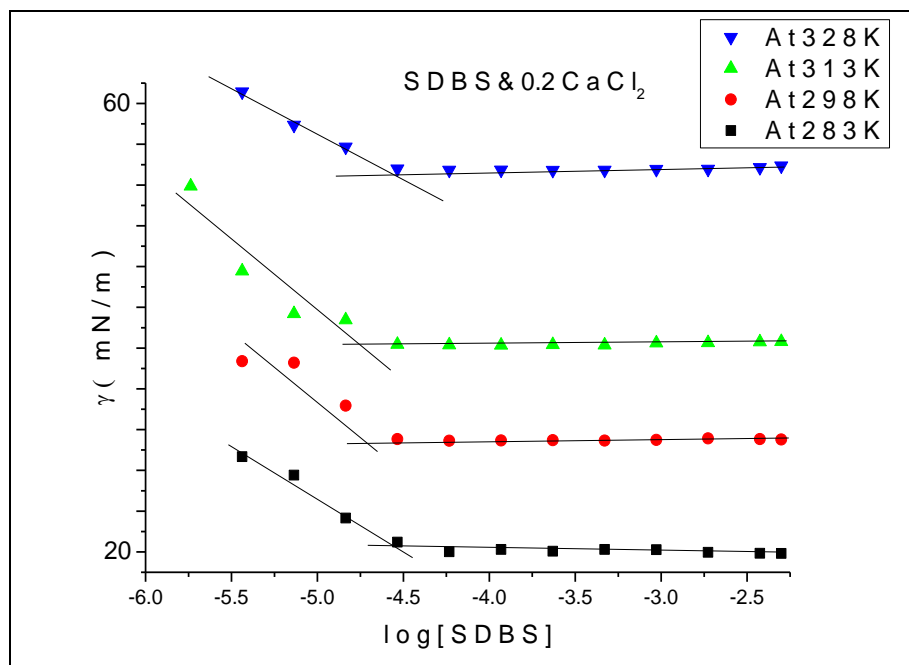


Fig. 3.14 Surface tension of SDBS in the presence of 0.2 M CaCl_2 at 283, 298, 313 and 328K

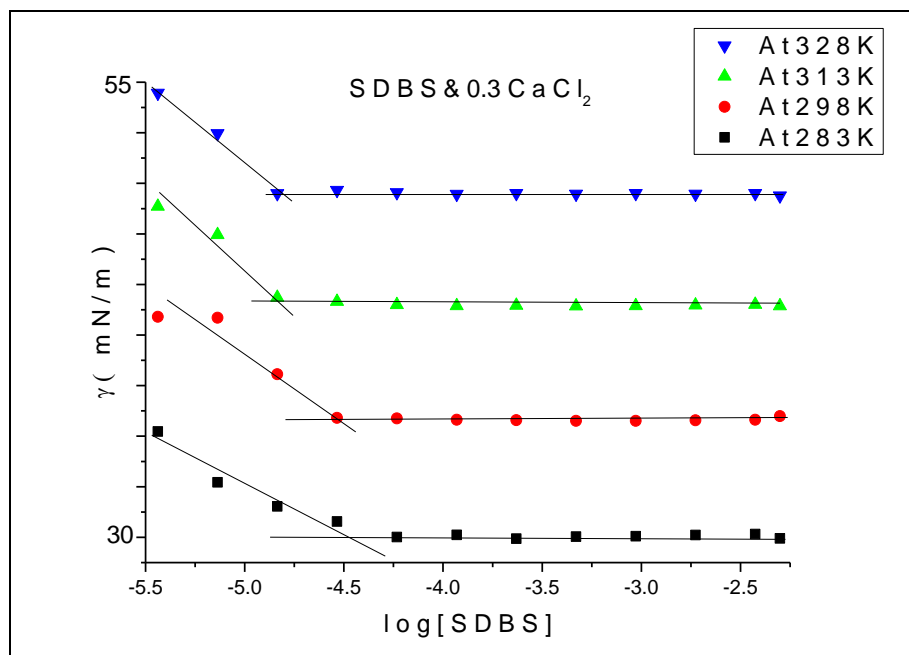


Fig. 3.15 Surface tension of SDBS in the presence of 0.3 M CaCl_2 at 283, 298, 313 and 328K

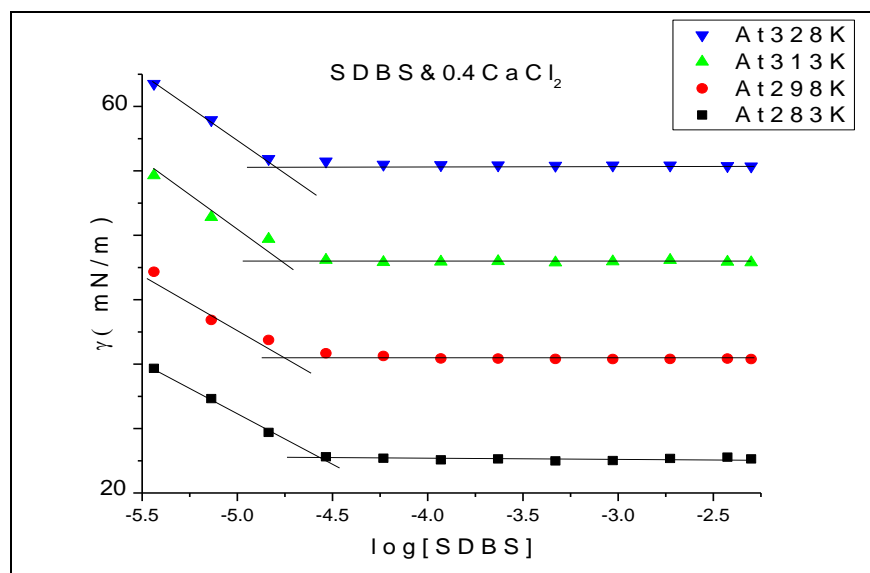


Fig. 3.16 Surface tension of SDBS in the presence of 0.4 M CaCl_2 at 283, 298, 313 and 328K

From Tables 3.12 – 3.15 and Figs. 3.13 – 3.16, it is possible to see the same tendency of decreasing of the surface tension values of SDBS solutions that contain the added electrolyte salt with increasing SDBS concentration and temperature. Changing the valency of the cation from monovalent to divalent (Na^+ to Ca^{2+}) leads to further decrease in surface tension values. This may be related to the fact that screening of the surfactant head groups is more influential in the presence of Ca^{2+} compared to that of Na^+ . This implies that the calcium cation makes stronger interaction with the surfactant head groups than the sodium cation.

3.5.3 Surface Tension of SDBS Solutions in Presence of the Molten Salt EMIB at Different Temperatures

The surface tension of SDBS solutions in the range of 0.003 – 5 mM and in the presence of 1 – ethyl – 3 – methylimidazolium bromide (EMIB) was measured at 283 K and 298 K. This molten salt was chosen for it being an organic salt different from inorganic salts. Molten salts are of growing interest in recent years from the academic and industrial chemical communities due to interest in using these liquids as alternative media for green chemical synthesis, liquid-liquid separations and other important applications [36]. The salt was used directly after preparing the SDBS solutions by successive dilution. The surface tension measurements of SDBS solutions in presence of 1.911 g of this molten salt at 283 K, 298 K are shown in Table 3.16.

Table 3.16 Surface tension of SDBS solutions in the presence of 0.1 M EMIB at 283 and 298 K

| [SDBS] (mM) | γ (mN/m) at 283 K | γ (mN/m) at 298 K |
|----------------|--------------------------------|--------------------------------|
| 0.00365 | 51.52 | 47.44 |
| 0.0073 | 48.56 | 44.46 |
| 0.0146 | 41.67 | 40.23 |
| 0.0292 | 36.00 | 35.66 |
| 0.0585 | 34.23 | 34.82 |
| 0.1172 | 33.01 | 31.64 |
| 0.2343 | 32.24 | 30.32 |
| 0.4687 | 31.81 | 30.38 |
| 0.9375 | 31.76 | 30.26 |
| 1.875 | 31.82 | 30.32 |
| 3.75 | 31.95 | 30.26 |
| 5.00 | 31.81 | 30.14 |

Figure 3.17 shows the surface tension of SDBS solutions as a function of SDBS concentration in the presence of 0.1 M EMIB. To the best of our knowledge, the effects of these types of organic salts on the surface tension of surfactant solution have not been studied before. Addition of EMIB salt has less effect on the surface tension of SDBS compared with the effect of calcium chloride. This conclusion can be reached by looking at the values of surface tension at 283 K for SDBS solution that has a concentration of 0.0585 mM in the presence of 0.1 M of the molten salt which is equal to 34.23 mN/m whereas in the presence of calcium chloride the value is 30.79 mN/m. Such behavior was unexpected due to the fact that EMIB has an organic portion with many carbon atoms, so it was estimated that the hydrophobic part of the molten salt will act in a similar way as a tail in surfactant molecules.

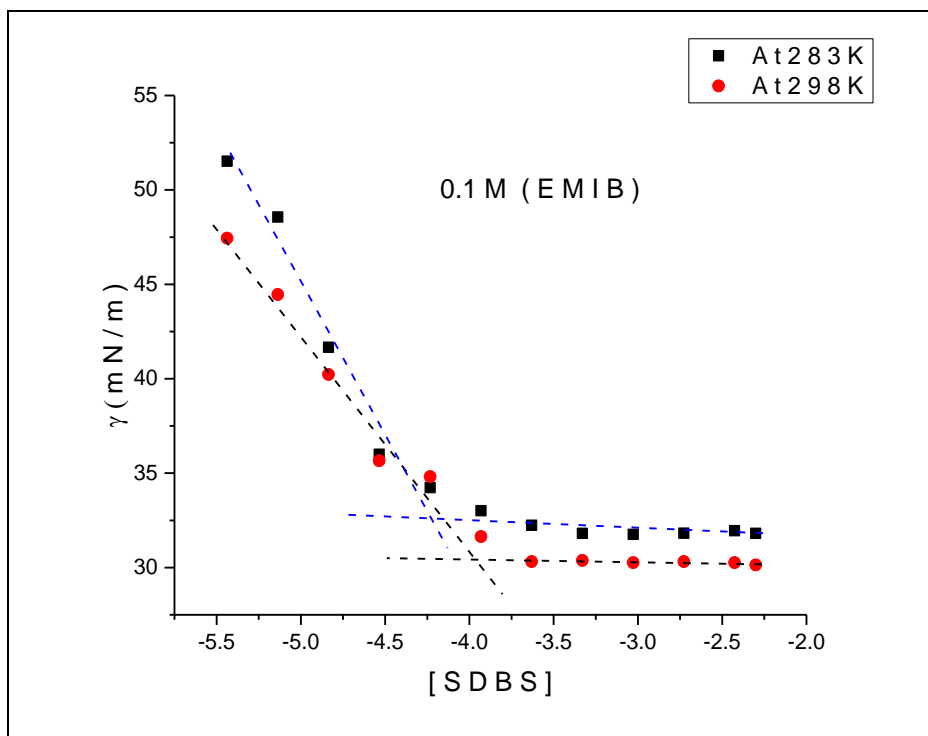


Fig. 3.17 Surface tension of SDBS in the presence of 0.1 M of EMIB at 283, 298 K

The fact that this molten salt did not reduce the surface tension further in comparison to the studied inorganic salts mean that, although it is an organic salt and has a carbon chain, there were a competition with the surfactant at the surface. The surfactant has a stronger tendency to be at the surface and therefore it leaves no space for the molten salt at the surface.

Moreover, it also means that there is negligible interaction between this molten salt and the head groups of the surfactant. This behavior is different from that of the cation of inorganic salts where it interacts by screening the repulsion between the surfactant head groups. The effect of this molten salt on the surface tension of SDBS resembles that of sodium chloride.

3.6 Effect of Temperature and Added Salt on the CMC of SDBS

3.6.1 CMC of SDBS in Pure Water

The extracted results of the temperature dependence of the critical micelle concentration of SDBS in aqueous phase are shown in Table 3.17 and Fig. 3.18. These CMC values show a decrease as the temperature is increased and reaches a minimum at about 303 K then started to increase again up to the maximum temperature under investigation. The existence of this U-shape from a plot of CMC versus temperature is a well reported phenomena for many ionic surfactants in aqueous solutions. This behavior was explained by assuming the existence of two types of hydration around the surfactant. The increase in temperature affects the water surrounding the hydrocarbon tail and this leads to gradual dehydration of the hydration shell around the hydrocarbon chain and hence promoting micelle formation. The increase in temperature has also an effect on the partial hydration of the hydrophilic head group. This effect leads to an increase in the repulsion between ionic head groups and hence acts against micellization and leading to higher CMC values. The U-shape form of the CMC versus temperature is the result of the combination of these two effects. At lower temperatures the disruption of the structural water surrounding the hydrocarbon tail is dominant so it acts in favor CMC formation. This means there is a decrease in CMC values. By raising temperature the dehydration of the charged head group dominants and this process goes against the micellization. This means that raising temperature leads to an increase on CMC values.

Table 3.17 CMC Values of SDBS in Pure Water at Different Temperatures

| T (K) | 283 | 288 | 293 | 298 | 303 | 308 | 313 | 318 | 323 | 328 | 333 |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CMC (mM) | 1.835 | 1.710 | 1.620 | 1.477 | 1.390 | 1.440 | 1.660 | 1.875 | 2.070 | 2.300 | 2.550 |

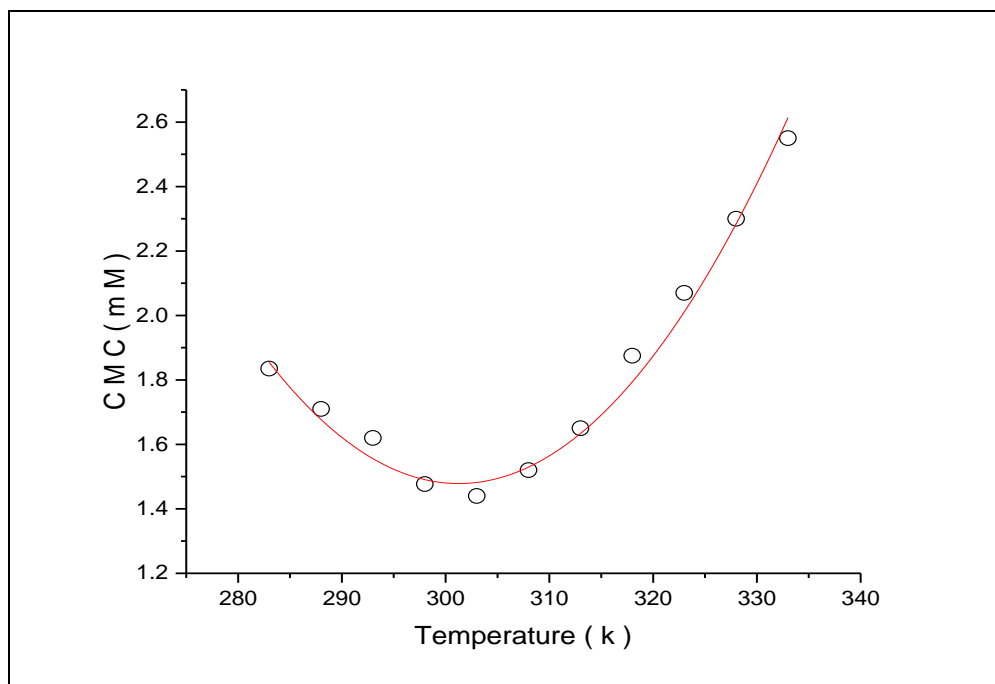


Fig. 3.18 Change of CMC values of SDBS in pure water with temperature. Open circles are experimental points and solid line is a polynomial fit to the data.

3.6.2 CMC in the Presence of Salts

Table 3.18 and Fig. 3.19 show the values of CMC as a function of temperature in the presence of sodium chloride salt at varying concentrations.

Table 3.18 Values of CMC as a function of temperature at different NaCl concentration

| Temp. (K) | Concentration of added NaCl (mol/L) | | | |
|-----------|-------------------------------------|-------|--------|--------|
| | 0.1 | 0.2 | 0.3 | 0.4 |
| 283 | 0.350 | 0.177 | 0.0826 | 0.032 |
| 298 | 0.280 | 0.141 | 0.0446 | 0.0313 |
| 313 | 0.180 | 0.117 | 0.0346 | 0.056 |
| 328 | 0.149 | 0.095 | 0.089 | 0.131 |

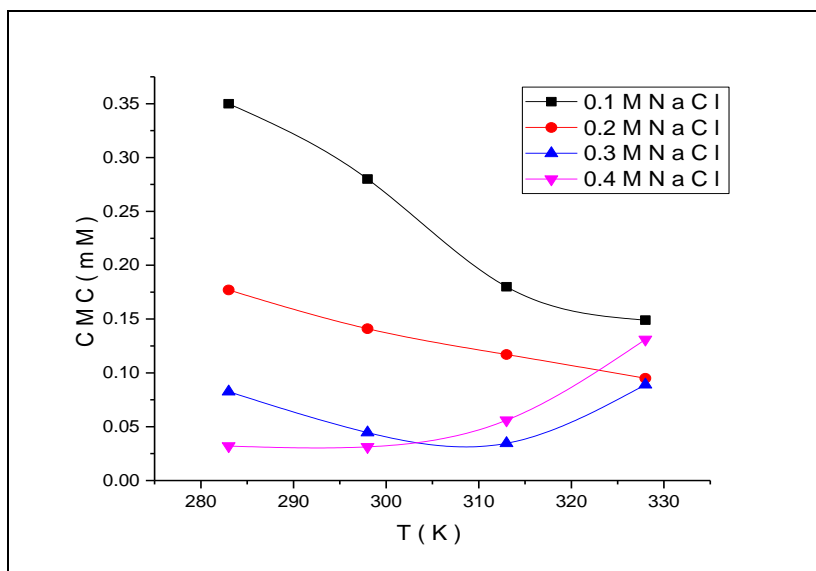


Fig. 3.19 CMC of SDBS as a function of temperature and NaCl concentration. Solid lines are drawn to guide the eye.

The reduction of CMC in the presence of salt relative to that in pure water is clearly seen in Table 3.18 and Fig. 3.19. For example, at 283 K (10 °C) the CMC value is 0.350 mM at NaCl concentration of 0.1 M while that of pure water at the same temperature is 1.835 mM. With increasing NaCl concentration, CMC decreases even further. This reduction is due to the fact that repulsive forces between the head groups of ionic surfactants are fighting against the aggregation. In the presence of salt, the repulsive forces of head group of SDBS monomer decreases due to the electrostatic shielding effect resulting in the formation of micelles at lower CMC.

Table 3.19 and figure 3.20 show the behavior of CMC as a function of temperature and CaCl_2 concentration. Changing the valency of the cation of the salt, from +1 to +2 leads to much more reduction on the values of CMC. This is due to the fact the Ca^{2+} makes much stronger interaction with the surfactant head groups and thus its screening effect is much more pronounced than that of Na^+ . By increasing the concentration of calcium chloride more decrease in CMC was observed. Concerning the change of temperature, the effect can be explained as previous sections.

Table 3.19 Values of CMC as a function of temperature at different CaCl_2 concentration

| Temp. (K) | Concentration of added CaCl_2 (mol/L) | | | |
|-----------|------------------------------------------------|--------|--------|--------|
| | 0.1 | 0.2 | 0.3 | 0.4 |
| 283 | 0.032 | 0.0335 | 0.0288 | 0.019 |
| 298 | 0.0313 | 0.0292 | 0.0180 | 0.0153 |
| 313 | 0.056 | 0.0193 | 0.0165 | 0.0123 |
| 328 | 0.131 | 0.0162 | 0.0162 | 0.0316 |

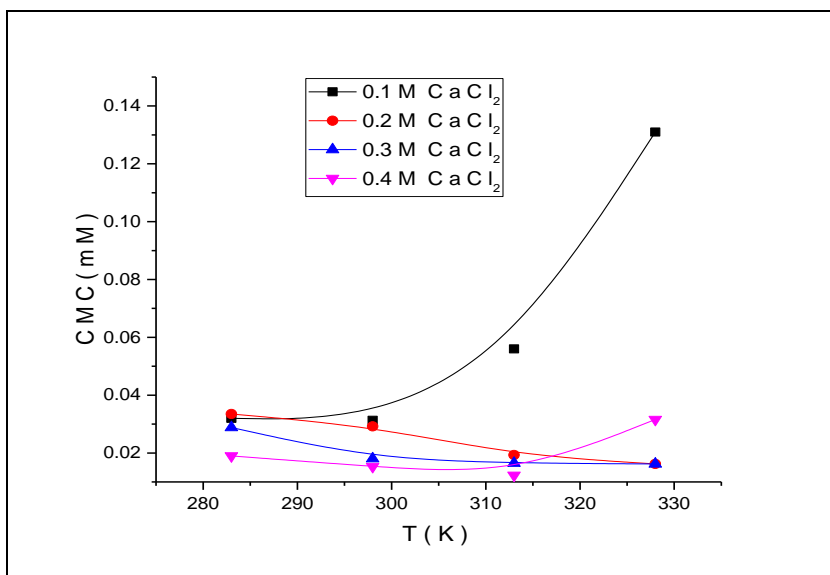


Fig. 3.20 CMC of SDBS as a function of temperature and CaCl_2 concentration. Solid lines are drawn to guide the eye.

Table 3.20 shows values of CMC as a function of temperature and at 0.1 M of the added molten salt $\text{C}_6\text{H}_{11}\text{BrN}_2$. Notice that the value of CMC is much higher than that of calcium chloride and slightly less than that of sodium chloride. The interesting thing is that this molten salt causes the CMC to increase with temperature. This may be attributed to the competition between the surfactant and this organic salt. It seems likely that as the temperature increase the presence of the surfactant chains diminish and the presence of the organic salt increases. It has to be said here that as the temperature increases the amount of surfactant present at the surface increases and the head group repulsion diminishes as well.

Table 3.20 Values of CMC as a function of temperature at 0.1 M of the molten salt $C_6 H_{11} Br N_2$.

| | | |
|-----------------|-------|-------|
| T (K) | 283 | 298 |
| CMC (mM) | 0.057 | 0.113 |

3.7 Surface Excess Concentration Thermodynamic Parameters

3.7.1 Surface Excess Concentration of SDBS in Pure water

Surface excess concentration (Γ) can be calculated from the famous Gibb's adsorption equation (1 – 5). The results of calculation of surface excess concentrations of SDBS in pure water are shown in Table 3.21 and Fig. 3.21.

Table 3.21 Surface excess concentration of SDBS in pure water as a function of temperature

| T (K) | Pearson's r of line | Slope of line $\times 10^{-3}$ | $\Gamma \times 10^{-6}$ (mol/m²) |
|--------------|----------------------------|--------------------------------------------------|---------------------------------------------------------------|
| 283 | 0.76 | -2.5 | 1.06 |
| 288 | 0.997 | -6.29 | 2.63 |
| 293 | 0.995 | -5.32 | 2.18 |
| 298 | 0.999 | -6.78 | 2.73 |
| 303 | 0.931 | -4.69 | 1.86 |
| 308 | 0.958 | -4.95 | 1.93 |
| 313 | 0.956 | -5.06 | 1.94 |
| 318 | 0.947 | -4.46 | 1.69 |
| 323 | 0.945 | -5.45 | 2.03 |
| 328 | 0.985 | -3.85 | 1.41 |
| 333 | 0.980 | -2.8 | 1.01 |

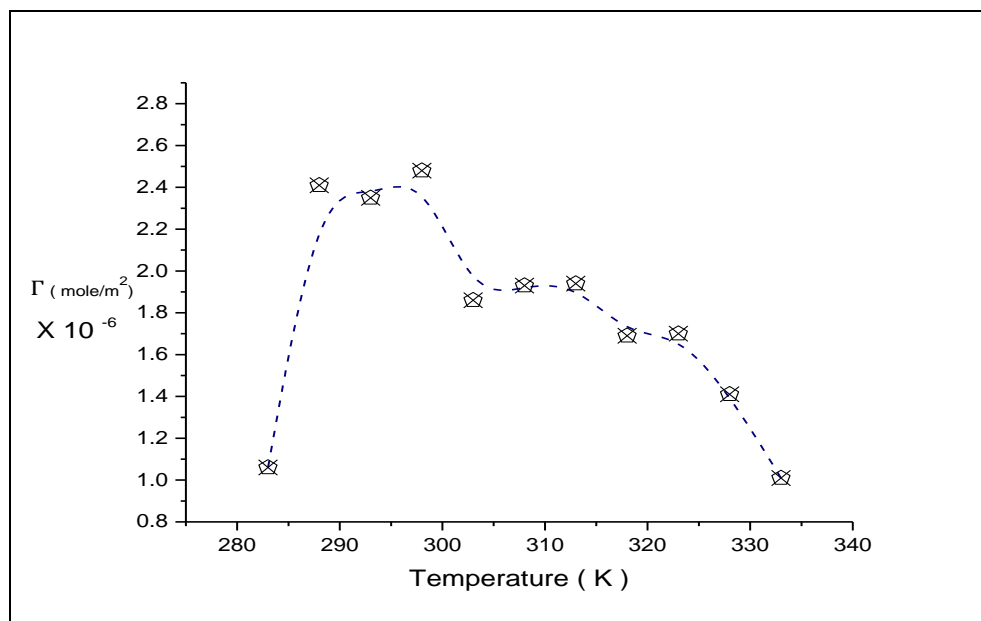


Fig. 3.21 Surface excess concentration of SDBS in pure water as a function of temperature

In Fig. 3.21, the surface excess concentration increases with increasing temperature up to 290 K and then gradually decreases and reaching a minimum value at the highest temperature under investigation. It is thus deduced that for SDBS surfactant the surface excess concentration displays nearly a peak shape with a maximum at about 295 K. Careful examination of Fig. 3.21 reflects the wide range of variation in Γ values with temperature. This may attributed to opposing effects of raising temperature on the amounts of surfactant molecules adsorbed at the surface. At one hand, the enhanced molecular motion of surfactant molecules at elevated temperature leads to fewer surfactant molecules being adsorbed at the air– water interface [37,38]. On the other hand increasing temperature leads to increase in the dehydration around the surfactant molecules upon increasing the temperature which leads more packing of surfactants at the interface and increase in surface excess concentration of surfactant present at the surface increases.

3.7.2 Surface Excess Concentration of SDBS in the Presence of NaCl

Table 3.22 shows the surface excess concentration values in the presence of 0.1 M, 0.2 M, 0.3 M and 0.4 M of NaCl respectively while Fig. 3.22 summarizes these results. As can be seen, for 0.1 M and for 0.3 M, the higher the temperature the lower is the surface excess while for 0.2 M and 0.4 M the surface excess concentration first increases and then slightly decreases. The general trend is that increasing the salt concentration increases the surface excess concentration. This can be safely said up to 0.3 M NaCl. For the 0.4 M however, the value of the surface excess is lower than that at 0.1 and 0.2 M. Comparing with the results in Table 3.20 for SDBS in pure water, the presence of salt causes more increase in the surface excess concentration of the surfactant and this may be attributed to the screening effect that was mentioned previously.

Table 3.22 Surface excess concentration of SDBS in presence of different concentrations of NaCl as a function of temperature

| [NaCl] mM | T (K) | Pearson's r of line | Slope of line $\times 10^{-3}$ | $\Gamma \times 10^{-6}$ (mol/m ²) |
|--------------|-------|------------------------|-----------------------------------|--------------------------------------------------|
| 0.1 | 283 | 0.967 | -3.03 | 1.29 |
| | 298 | 0.957 | -2.00 | 0.81 |
| | 313 | 0.885 | -2.10 | 0.81 |
| | 328 | 0.950 | -2.40 | 0.88 |
| 0.2 | 283 | 0.996 | -6.99 | 2.97 |
| | 298 | 0.975 | -5.02 | 2.03 |
| | 313 | 0.999 | -8.87 | 3.41 |
| | 328 | 0.999 | -8.34 | 3.06 |
| 0.3 | 283 | 0.996 | -9.05 | 3.84 |
| | 298 | 0.959 | -7.50 | 3.03 |
| | 313 | 0.975 | -5.50 | 2.11 |
| | 328 | 0.998 | -8.69 | 3.18 |
| 0.4 | 283 | 0.965 | -4.80 | 2.04 |
| | 298 | 0.935 | -6.06 | 2.44 |
| | 313 | 0.991 | -4.93 | 1.89 |
| | 328 | 0.966 | -2.63 | 0.96 |

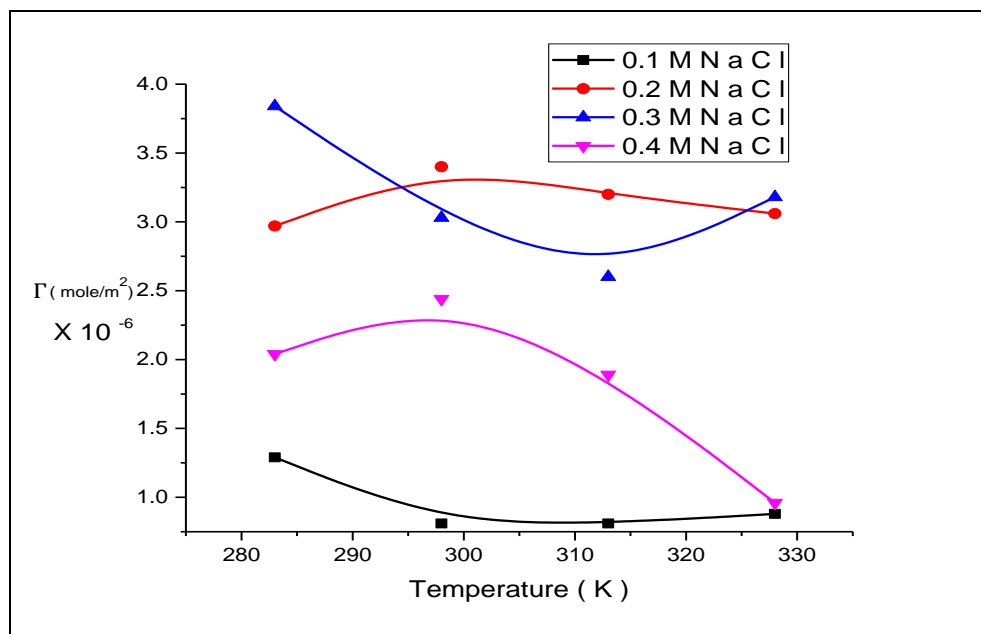


Fig. 3.22 Surface excess concentration of SDBS in presence of different concentrations of NaCl as a function of temperature

Table 3.23 Surface excess concentration of SDBS in presence of different concentrations of CaCl_2 as a function of temperature

| [CaCl_2] mM | T (K) | Pearson's r of line | Slope of line $\times 10^{-3}$ | $\Gamma \times 10^{-6}$ (mol/m^2) |
|---------------------------|-------|------------------------|-----------------------------------|-------------------------------------------------|
| 0.1 | 283 | 0.998 | -13.41 | 5.69 |
| | 298 | 0.955 | -11.84 | 4.77 |
| | 313 | 0.983 | -12.33 | 4.74 |
| | 328 | 0.953 | -12.16 | 4.46 |
| 0.2 | 283 | 0.963 | -8.38 | 3.55 |
| | 298 | 0.952 | -10.27 | 4.14 |
| | 313 | 0.954 | -9.92 | 3.81 |
| | 328 | 0.941 | -10.02 | 3.67 |
| 0.3 | 283 | 0.987 | -10.59 | 4.5 |
| | 298 | 0.972 | -18.91 | 7.63 |
| | 313 | 0.928 | -15.69 | 6.1 |
| | 328 | 0.994 | -8.95 | 3.2 |
| 0.4 | 283 | 0.959 | -11.56 | 4.91 |
| | 298 | 0.975 | -9.03 | 3.64 |
| | 313 | 0.876 | -6.03 | 2.32 |
| | 328 | 0.995 | -8.40 | 3.08 |

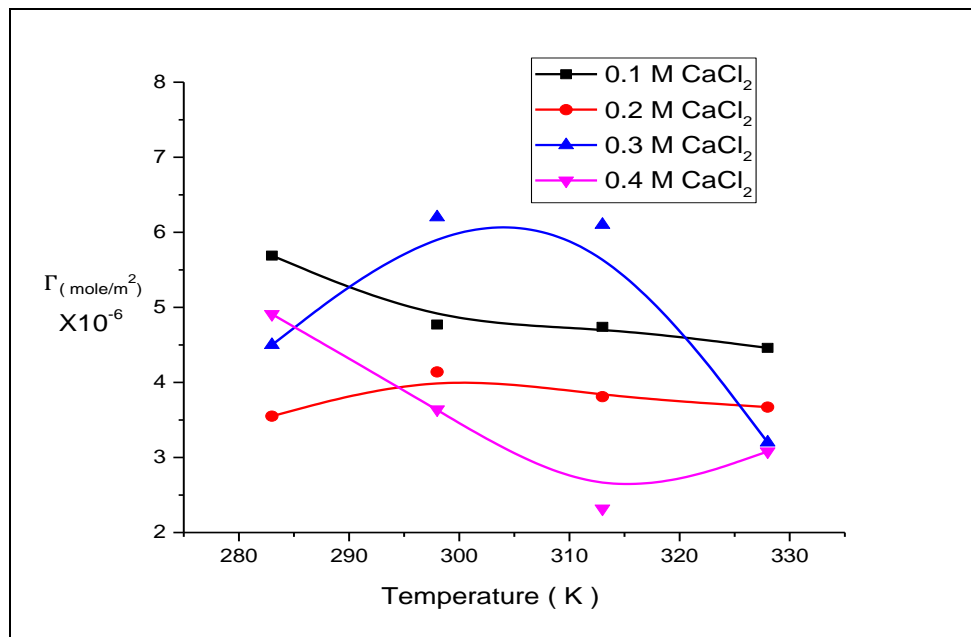


Fig. 3.23 Surface excess concentration of SDBS in presence of different concentrations of CaCl_2 as a function of temperature

Fig. 3.23 shows the surface excess concentrations of SDBS as a function of temperature at in the presence of CaCl_2 salt. The surface excess concentration first increases as temperature increases and then slightly decreases for 0.2 and 0.3 M of CaCl_2 . For 0.1 M and 0.4 M the surface excess decreases with increasing temperature. Comparing the effect of the monovalent salt NaCl with that of the divalent salt CaCl_2 on the surface excess, one can see that the presence of the divalent salt has the larger effect, where the value of the surface excess is more in the CaCl_2 than in the NaCl case.

3.7.3 Area Occupied by SDBS Molecule and the Surface Pressure at different temperatures and salt Molarity

Table 3.24 shows the vales of the area, A_{\min} , occupied by one SDBS molecule and the surface pressure π_{cmc} . The area was calculated from the surface excess values determined previously by the equation(1 – 6). Also included is the surface pressure π_{cmc} and is given by:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \quad (3 - 3)$$

where γ_o is the surface tension of water and γ_{cmc} is the surface tension at the CMC of the surfactant. The area occupied by a SDBS molecule shows an inverse variation with temperature compared to the behavior of the surface excess concentration. The surface pressure displays a slight variation with temperature.

Table 3.24 shows the vales of the area, A_{min} , occupied by one SDBS molecule and the surface pressure π_{cmc} .

| System | T(K) | A_{min} (\AA^2) | π_{cmc} (mN/m) |
|--------|------|---------------------------------|-----------------------|
| SDBS | 283 | 156.3 | 36.99 |
| | 288 | 63.2 | 37.46 |
| | 293 | 76.2 | 37.61 |
| | 298 | 60.8 | 37.75 |
| | 303 | 89.3 | 39.87 |
| | 308 | 86.1 | 40.87 |
| | 313 | 85.5 | 41.21 |
| | 318 | 98.47 | 42.6 |
| | 323 | 81.87 | 39.57 |
| | 328 | 117.6 | 39.12 |
| | 333 | 164.3 | 38.69 |

Tables 3.25 shows values of surface pressure and area occupied by SDBS molecules at different temperatures concentrations of added salts. Areas occupied by SDBS molecule were found to vary with temperature as in the case of SDBS in pure water. When going from NaCl to CaCl_2 , the area occupied becomes smaller. This is due to strong interaction between the calcium chloride and the surfactant head group. The presence of the divalent cation Ca^{2+} causes screening of the surfactant head group repulsion and the thus the area the molecule occupies become smaller. The surface pressures display a slight increase with temperature and values were almost comparable for different salts.

Tables 3.25 Values of area occupied by a SDBS and surface pressure π_{cmc} at different temperatures and concentrations of added salts

| System | T(K) | A_{min} (\AA^2) | π_{cmc} (mN/m) |
|---------------------------------------------------|------|---------------------------------|-----------------------|
| SDBS + 0.1 M NaCl | 283 | 129 | 42.27 |
| | 298 | 205 | 42.41 |
| | 313 | 205 | 43.52 |
| | 328 | 188 | 43.91 |
| SDBS + 0.2 M NaCl | 283 | 55.8 | 43.2 |
| | 298 | 82.0 | 44.05 |
| | 313 | 48.7 | 44.16 |
| | 328 | 54.2 | 45.31 |
| SDBS + 0.3 M NaCl | 283 | 43.3 | 42.25 |
| | 298 | 54.8 | 44.09 |
| | 313 | 78.7 | 44.88 |
| | 328 | 52.2 | 45.62 |
| SDBS + 0.4 M NaCl | 283 | 81.4 | 42.19 |
| | 298 | 68.1 | 44.29 |
| | 313 | 87.9 | 45.12 |
| | 328 | 172 | 46.59 |
| SDBS + 0.1 M CaCl₂ | 283 | 29.2 | 42.05 |
| | 298 | 34.8 | 42.68 |
| | 313 | 35.1 | 44.06 |
| | 328 | 37.3 | 44.86 |
| SDBS + 0.2 M CaCl₂ | 283 | 46.7 | 42.28 |
| | 298 | 40.1 | 42.93 |
| | 313 | 43.6 | 43.92 |
| | 328 | 45.2 | 45.74 |
| SDBS + 0.3 M CaCl₂ | 283 | 36.9 | 42.1 |
| | 298 | 21.76 | 43.09 |
| | 313 | 27.2 | 44.56 |
| | 328 | 51.9 | 45.42 |
| SDBS + 0.4 M CaCl₂ | 283 | 33.8 | 42.42 |
| | 298 | 45.6 | 42.71 |
| | 313 | 71.5 | 42.83 |
| | 328 | 53.9 | 44.43 |
| SDBS + 0.1 M EMIB | 283 | 50.8 | 38.99 |
| | 298 | 71.8 | 40.36 |

3.7.4 Thermodynamic Parameters of Micellization

Thermodynamic parameters of micellization were calculated using equations 1 – 8, 1 – 9 and 1 – 10. Equations were applied for SDBS solutions in the absence and presence of added salts and the results are tabulated in Table 3.26 and plotted in the above figures (3.24,3.25).

Table 3.26 Thermodynamic parameters of micellization of SDBS in presence of 0.1 M of NaCl, CaCl₂ and EMIB

| System | T (K) | CMC (mM) | X_{cmc} $\times 10^{-5}$ | $-\Delta G_{mic}^o$ (kJ/mol) | ΔS_{mic}^o (kJ/mol K) | $-\Delta H_{mic}^o$ (kJ/mol) |
|----------------------------------------------|----------|-------------|-------------------------------|---------------------------------|----------------------------------|---------------------------------|
| SDBS | 283 | 1.835 | 3.31 | 24.27 | 64.98 | 6.73 |
| | 298 | 1.477 | 2.64 | 26.12 | | 7.65 |
| | 313 | 1.660 | 2.98 | 27.12 | | 7.75 |
| | 328 | 2.300 | 4.13 | 27.52 | | 7.22 |
| SDBS 0.1 M NaCl | 283 | 0.35 | 0.629 | 28.18 | 64.7 | 10.06 |
| | 298 | 0.28 | 0.504 | 30.22 | | 11.15 |
| | 313 | 0.18 | 0.323 | 32.90 | | 12.86 |
| | 328 | 0.149 | 0.267 | 34.99 | | 13.99 |
| SDBS 0.1 M CaCl₂ | 283 | 0.032 | 0.058 | 30.49 | 55.4 | 14.81 |
| | 298 | 0.0313 | 0.056 | 35.65 | | 19.14 |
| | 313 | 0.056 | 0.101 | 35.92 | | 18.57 |
| | 328 | 0.131 | 0.235 | 35.34 | | 17.16 |
| SDBS 0.1 M EMIB | 283 | 0.057 | 0.103 | 32.45 | 74.9 | 11.25 |
| | 298 | 0.113 | 0.203 | 32.47 | | 10.15 |

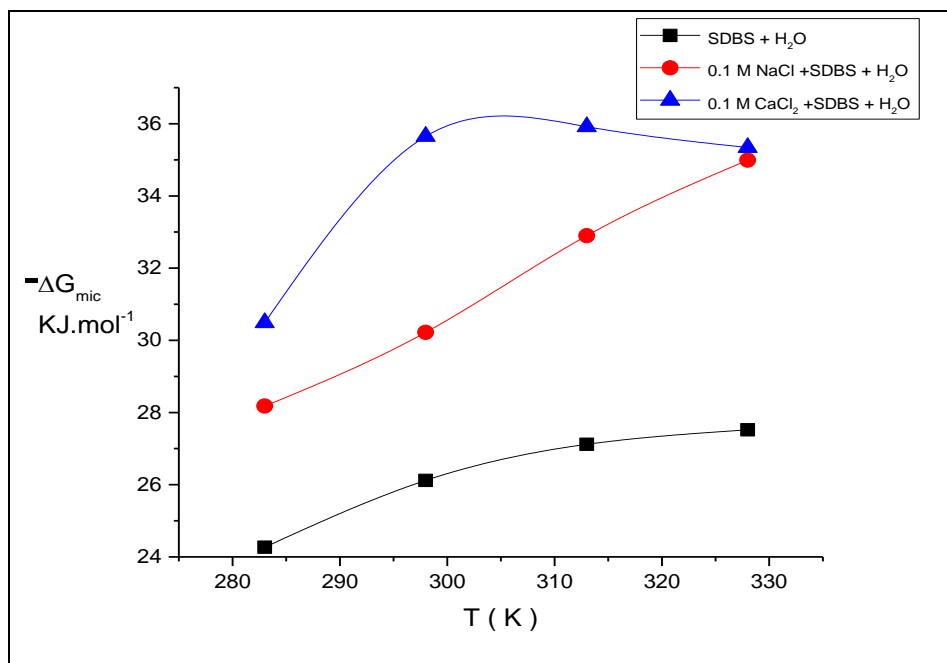


Fig. 3.24 Gibbs free energy of micellization for SDBS as a function of temperature in the absence and presence of added salt

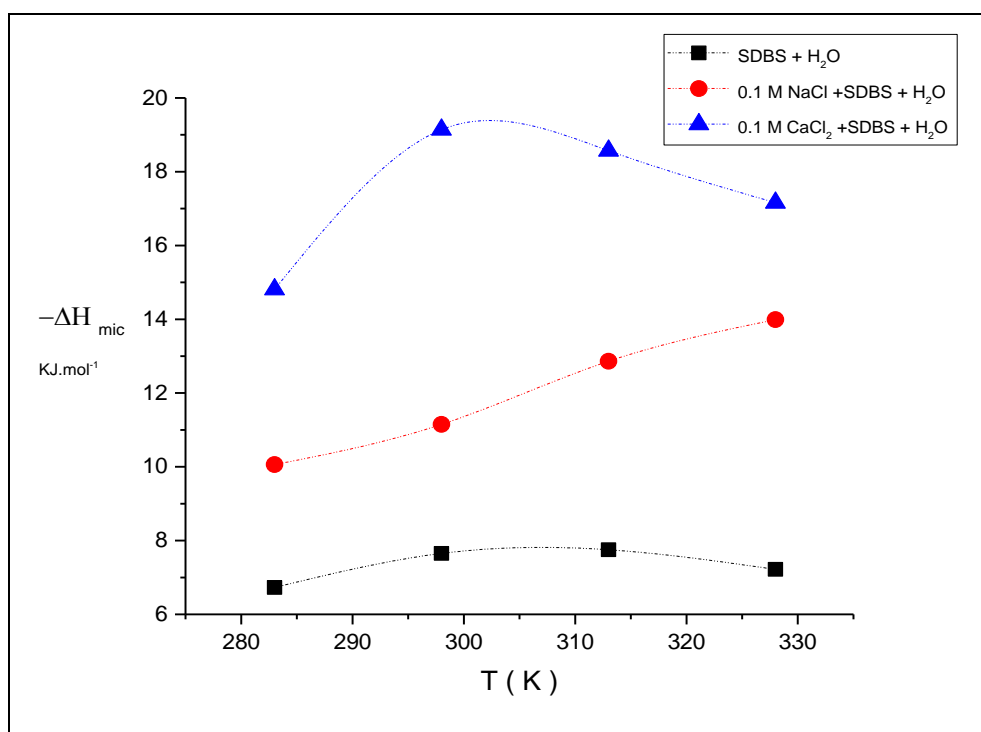


Fig. 3.25 Enthalpy of micellization for SDBS as a function of temperature in the absence and presence of added salt

The main reason for micelle formation is the attainment of a minimum free energy state. The main driving force for the formation of micelles is the increase of entropy that occurs when the hydrophobic regions of the surfactant are removed from water and the ordered structure of the water molecules around this region of the surfactant molecule is lost. Any process that leads to free energy decrease will occur spontaneously because it leads to the formation of a more stable system. Micelle formation is, therefore, a spontaneous process. The standard free energy change of micellization values for studied surfactant solutions with or without electrolytes are all negative suggesting the feasibility of the micellization. The free energy change of micellization becomes more negative on mixing the electrolytes (especially calcium chloride) and also with rising in temperature. Therefore, addition of electrolytes in a surfactant solution irrespective of the nature of added electrolyte as well as higher temperature both enhances the feasibility of micellization process. Though micellization process is generally opposed by endothermic enthalpy change, yet the driving force in micellization process is the entropy gain [39-40]. On mixing of electrolytes, ΔG_{mic}^o further decreases (become more negative) it shows that ionic salts in aqueous surfactant solution facilitates micellization

The positive entropy of micellization values are attributed to the disruption of water structure around the hydrocarbon part of surfactant molecule as it transfers from the aqueous bulk phase to non-aqueous micellar interior. Addition of electrolytes leads to increase in entropy of micellization. It is because the presence of electrolytes in the aqueous solution causes water molecules to get enhancement in arrangement so the entropy gain by transfer of surfactant hydrophobic chain from bulk to micelle involves more water structure disruption [38, 39].

Conclusions

In this master thesis work I used the state of the art Kruess K11 tension meter to study the effect of temperature and added salt on the CMC of SDBS. The findings of this work can be summarized as follows:

1. The CMC decreases with increasing temperature up to 305 K and then increases up to the highest temperature studied. It has to be mentioned here that in this work the temperature scale has been expanded comparing to previous studies on this particular subject.
2. The CMC decreases with the addition of electrolytes for the studied systems. Such decrease in CMC is more favored on increasing the valence of cation of the electrolyte.
3. The surface excess concentration decreases with increasing temperature for 0.1 and 0.3 M in the case of NaCl solution while for the same salt and at 0.2 and 0.4 M the surface excess increases first with increasing temperature and then decreases. Almost the same behavior is found for calcium chloride salt. The surface excess concentration values are in the right order of magnitude.
4. The area occupied by one SDBS molecule was calculated from the determined values of the surface excess concentrations. Its value exhibits variation with both temperature and added salt in a non-regular fashion.
5. The presence of electrolytes causes lowering of the CMC but increase the value of the excess surface concentration of surfactants. Hence addition of electrolyte in SDBS is more beneficial.
6. The surface pressure was also calculated at different temperature and for different salts used. It shows a slight increase with temperature and its value is comparable for different salts studied.
7. Standard Gibbs free energy change of micellization is negative for the studied system indicating the feasibility of micellization process. On addition electrolytes, the Gibbs free energy further decreases showing that the presence of these electrolytes in aqueous solution facilitates the process of micellization.

8. Enthalpy of micellization is exothermic in the case of the studied surfactant. The decrease of CMC on mixing electrolytes in surfactant solution suggests that the presence of salt would enhance detergency and solubilizing efficiency of surfactant.
9. This is the first time the effect of an organic salt (molten salt) on the CMC behavior of a surfactant has been studied. The findings in this work are considered as preliminary results and more experiments are needed in this part of work.

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