



**Faculty of Graduate Studies
Chemistry Department**

**Effects of Temperature and Addition of Sodium Chloride and Calcium Chloride on the
Surface Tension of Benzyl-dimethyl-hexadecyl-ammonium Chloride and its Mixture
with Sodium Dodecyl Benzene Sulfonate**

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Committee Decision

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Abstract

In this work the surface tension of the cationic surfactant Benzyltrimethylhexadecyl ammonium chloride (BAC) as a function of its concentration was measured. The effect of addition of sodium chloride and Calcium chloride, at concentrations between 0.1 M - 0.3 M and temperatures in the range of 10 °C – 50 °C was investigated. In addition the surface tension of a mixtures of BAC with different concentrations and a fixed amount of the anionic surfactant of sodium dodecyl benzene sulfonate (SDBS) was measured. According to the result obtained it was found that: the surface tension of BAC decreases with increasing its concentration in solution and increasing the temperature. The critical micelle concentration (CMC) of pure BAC was found to be 0.50 mM and decreases with increasing temperature in the temperature range studied. The change of CMC with temperature is a consequence of the decrease of hydrophilicity of the surfactant molecule. The addition of salts was found to decrease the CMC of BAC. This could be due to the reduction of the migration of the surfactant caused salt ions. In addition, interfacial packing of the adsorbed molecules particularly of the ionic type can be increased by the presence of salt and this is due to the reduction in the electrostatic repulsive forces. Charge valence of the cation has little effect of the CMC of BAC. Regarding the BAC mixture with SDBS, a synergetic effect was observed as a significant decrease in the surface tension of the mixture was observed. This synergetic effect was found in the entire mixture range studied. A peak in the behavior of the surface tension as a function of BAC concentration with added SDBS was observed. Such a behavior may originate from the fact that, at the beginning we start with a mixture of the two surfactants with low amount of BAC and the synergism is at maximum where the surface tension of the mixture is minimum. As we add more BAC and since the BAC hydrophobic tail is longer there will be less synergism due to surface adsorption competition of the two surfactant and the surface tension increases until the CMC of BAC is reached and the addition of more BAC will strengthen the synergism again where the surface tension decreases again.

الملخص

تم في هذا البحث قياس التوتر السطحي لمحاليل مائية للمركب الكاتيوني النشط سطحيا المسمى بنزين ثنائي ميثيل سداسي ديسيل كلوريد الامونيوم (BAC) عند تراكيز مختلفة ودرجات حرارة مختلفة ، كما تم دراسة تأثير اضافة كلوريد الصوديوم وكلوريد الكالسيوم بتراكيز تتراوح بين 0.3- 0.1مول/لتر الى المحاليل السابقة وعند درجات حرارة مختلفة في المدى بين 10 الى 50 درجة مئوية ، بالاضافة الى ذلك تم قياس التوترالسطحيلمزيج من BAC بتراكيز مختلفة عند اضافة كمية ثابتة من المركب الأنيوني النشط سطحيا والمسمى بنزين دوديسيلسلفونات الصوديوم (SDBS) ، وطبقا للنتائج التي تم الحصول عليها فقد وجد ان هناك تناقص في قيم التوتر السطحي لمحاليل BAC مع زيادة تركيزه في المحلول وكذلك مع زيادة درجة الحرارة ، كما تم قياس قيمة تركيز المذيلات الحرج (CMC) لمركب BAC ووجد انها تساوي 0.50 مول/لتر ، وتنخفض هذه القيمة مع زيادة درجة الحرارة في المدى الذي تم دراسته ، ويمكن ان يعزى هذا الانخفاض الى زيادة صد جزيئات مركب BAC للماء كما ان اضافة الاملاح الى المحاليل السابقة كان لها ذات التأثير على قيم CMC ويمكن تفسير ذلك الى تناقص في الميول الى انتقال جزيئات المركب النشط سطحيا نحو الطبقة العليا من المحلول، كما ان وجود ايونات الاملاح يعمل على زياد اصطفاف جزيئات BAC المتواجدة على السطح من خلال التقليل من قوى التنافر بينها ، علما ان تغيير ارقام التكافؤ للأيونات الموجبة للأملاح المضافة لم يكن له أثر ملموس على التغيرات السابقة .

أما النتائج المتعلقة بإضافة مركب SDBS على المحاليل المائية لمركب BAC فقد لوحظ حدوث اثر تآزري بين المركبين السابقين من خلال النقصان الكبير في قيم التوتر السطحي ، كما لوحظ انه مع الازدياد في تراكيز مركب BAC وثبات كمية SDBS حصل زيادة في قيم التوتر السطحي للمزيج وصولا الى قيمة عليا تقترب من قيمة CMC لمركب BAC التي تم الاشارة لها سابقا ، وقد تم اقتراح التفسير التالي لهذا السلوك غير المتوقع : وهو ان عدد جزيئات كلا المركبات النشطة سطحيا ذات الشحنات السالبة والموجبة تكون متقاربة وبالتالي فان حصول الاثر التآزري يكون في اعلى قيمه المتوقعة وبالتالي فان قيم التوتر السطحي للمزيج السابق وصلت الى قيم متدنية ومع زيادة كمية مركب BAC مع ثبات كمية SDBS فتكون هناك فرصة لجزيئات الماء الموجودة على السطح لإعادة تموضعها واصطفافها بما يعزز قوى الروابط الهيدوجينية بين جزيئات الماء الموجودة على السطح والتي تم اضعافها بفعل وجود جزيئات المركبات النشطة سطحيا .

Chapter 1

Introduction

Background

1.1 Surface and Interfacial Phenomena

In a liquid, each molecule in the bulk is surrounded by a certain number of similar molecules in its close proximity where it makes attractive and repulsive forces with these molecules from all directions. Attractive forces dominate because of their longer range than repulsive forces. The latter have much shorter range and become important at high pressures [1-2]. Because of the existing symmetry of interatomic or intermolecular forces around this molecule, the resultant force averaged over time will be zero. Therefore, the potential energy of this molecule will be reduced because of this force symmetry [1-2]. These forces are responsible for the cohesion between similar molecules (a molecule in the liquid and its neighbours of the same kind) and responsible for the adhesion between dissimilar molecules (a molecule in the liquid with other molecules of different type). At the surface region of a liquid, the number of molecules surrounding any surface molecule of the same kind is less and there is a broken symmetry in the interatomic or intermolecular interactions. This is because the density of the adjacent phase (gas or vapour) is much smaller than that of the liquid. This causes the potential energy of a surface molecule to be higher than that of a bulk molecule [2].

A surface molecule of a liquid experience weaker forces from the vapour or the gas phase than it would experience if the gas or vapour was replaced by a liquid. The surface molecule therefore will suffer an inward force pulling him down to the bulk. This force will be normal to the liquid surface. If a bulk molecule to be transferred to the surface, work has to be done against this pulling down force. This makes a surface molecule having a greater energy than a bulk molecule. The mentioned pulling down force is what is called the surface of tension or simply surface tension.

The potential energy of the surface per unit area is the surface tension of a liquid. Therefore, the unit of the surface tension is joule per square meter or J/m^2 or Newton per meter N/m since the pulling down force will act on the length of the surface. Figure 1.1 shows bulk and surface molecules and the bonds each makes with the surrounding molecules.

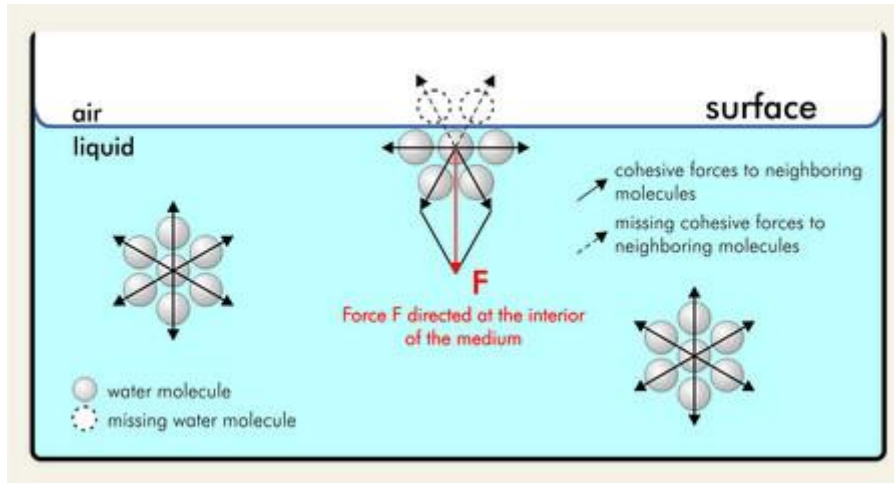


Figure 1.1. Surface and bulk molecules and the bonds they are making with neighboring molecules.

The phenomenon of surface and interfacial tension finds its importance in many technological process and applications. It finds application and existence in detergency and detergents formulation. In coatings and oil recovery. Measurements of the surface tension are important for the evaluation of the quality of a new made detergent or is made when formulation of a new coating is synthesised [2].

1.2 Measuring Surface and Interfacial Tensions

There are several methods of surface tension measurements including [3]:

1. Stallagmometer method – drop weight method
2. Capillary rise method
3. Maximum bulk pressure method.
4. Wilhelmy plate or Du Nouy ring method
5. Methods analyzing the shape of the hanging liquid drop or gas bubble.
6. Dynamic methods.

The main method used in this work is the Wilhelmy plate method and therefore will be described in details.

1.3 The Wilhelmy Plate Method

In this method, a probe made of platinum is utilised. This probe is made in a form of plate of certain thickness. The technique is based on the calculation made on the perimeter of the plate being wetted by the liquid. The plate has to be completely wetted by the liquid. It is of utmost

importance to precisely know the plate position in relation to the surface position. By making notice of the exact moment of contact, the instrument will monitor any changes in force on the plate. This happens when the surface is brought close to the plate. This position is labelled the “zero depth of immersion”. Immersion of the plate to a known depth by the apparatus is made. The depth of immersion is in the range of few mm below the liquid surface. Recording of the force is made when the probe or plate is brought back to the zero depth. Direct measurement of the adhesion tension is made by this method (Figure 1.2). This adhesion tension is when the liquid acts on the perimeter of a plate. Certain accessories of this method are able to record the advancing and receding angle of contact [4]. A change in force F will be recorded as the probe is moved in and out of the liquid and this force is given by:

$$F = dw\gamma\cos\theta \quad (1-1)$$

where θ is the contact angle the plate makes with liquid surface, d is the thickness of the plate and w is the width of the plate and γ is the surface tension of the liquid.

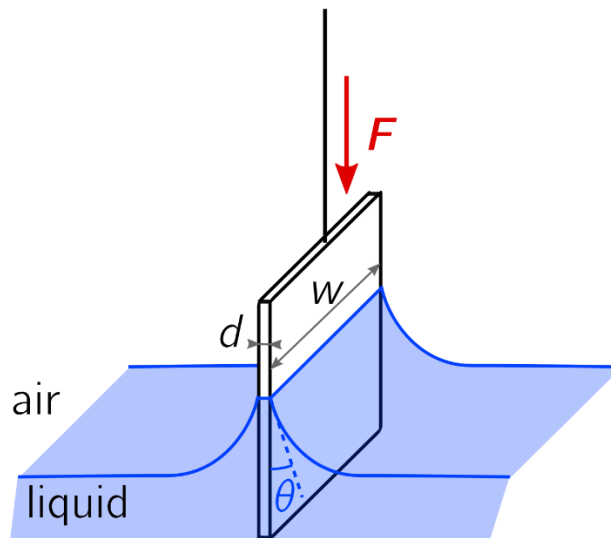


Figure 1.2. Wilhelmy plate method for measurement of surface tension of liquids.

1.4 Adsorption at Liquid Surfaces and Interfaces

We encounter adsorption phenomena in our daily life. An example is the condensation of water vapor on the surface of glass bottle in hot climate. If a solute is added to pure water or to any other liquid, the physical properties of that liquid or water will be influenced without changing the chemical nature of water. Adsorption depends on the type and nature of the solute added. Of the physical properties of the liquid that will be changed by addition of solute is its surface tension. Some solutes such as electrolytes, acids and bases and salts will increase the surfacetension of water. Other kinds of solutes will decrease the surface tension of water. Increasing the surface tension of water means that the added substance does not like to migrate to the surface and prefer to stay in the bulk. In this case, we will have negative adsorption. On the other hand, when the added solute lowers the surface tension of water, it means that the solute prefers to migrate to the surface. In this case, we will have positive adsorption. Examples of solutes that lower the surface tension of water are alcohols and surfactants [5].

In order to understand adsorption phenomenon at liquid surfaces and interfaces, it is inevitable to deal with the thermodynamics of adsorption based on Gibbs's formulation.

1.5 Gibbs Adsorption Isotherm and Equation

Consider a system that is open to consist of two bulk phases separated by an interface that are brought into contact with each other. The internal energy according to Gibbs treatment, when the interface is subject to a hydrostatic pressure p , given by [6]:

$$dU = TdS - pdV + FdZ + \sum \mu_i dn_i \quad (1-2)$$

where U is the internal energy of the system, T is the temperature, S is the entropy, p is the pressure, F is a force experienced by a molecule, V is the volume, Z is the surface area, μ_i is the chemical potential of i component, and n_i is the amount of i component. Let an extra interfacial term be represented by FdZ , with F as the intensive and Z the coupled extensive variable. Equ. (1-2) is related to the characteristic energy function by:

$$dU = TdS - pdV + zdF + \sum d\mu_i n_i \quad (1-3)$$

Then the Gibbs-Duhem type equations given as:

$$dU = TdS - Vdp + ZdF + \sum n_i d\mu_i \quad (1-4)$$

This formulation is valid for the displacement of the system along the multi-dimensional equilibrium surface. For liquid-liquid and liquid-gas interfaces, which are considered to be planar, the interfacial tension γ is represented by F and the surface area is represented by Z . Both of these quantities can be measured. Based on this fact and if the term FdZ is represented by γdA an extension of the surface work acts on the system can be made possible.

More specific equations to describe certain aspects of the system can be derived from these generalized equations given by equations (2-4). Since we are concerns with the interface between a liquid and a gas, focus will be on this type of interface and derivation of Gibbs adsorption equation will be provided below.

Under constant temperature and constant pressures, the term TdS and the term Vdp in equation (1-4) will be zero since the differential of a constant is zero. The assumption of the latter condition is for the solid-liquid interfaces. This is because variations of the pressure do not affect the thermodynamic properties of the adjoining condensed phases. It has to be mentioned that the pressure is due to variation of the vapour pressure caused by changes of the composition of the condensed phase. When one of the condensed phases is replaced by a gas (liquid-gas or solid-gas), then the assumption of zero variation in pressure will be false. This is because at constant temperature conditions when there are changes in concentration then there will be certainly changes in pressure. When we have mixture of gases then it is possible to envisage a series of varying relative compositions under constant pressure. When one uses the advantage of general thermodynamic framework, then it is reasonable useful convention to select the reference system so that the surface excess volume equals to zero. This is given by equation (1-5) below:

$$V^\sigma = V = n^\sigma V_m^\sigma - n^\beta V_m^\beta \quad (1-5)$$

Equation 1-5 is the famous Guggenheim and Adam [6] equation. It has been derived from the original equation of Gibbs. In his formulation Gibbs used an imaginary surface which was named after his name. This surface or interface is called Gibbs dividing surface and is parallel to the interface. The bulk phase considered here is to be homogeneous up to the interface and this homogeneity start to break at the interface. In the previous formulation, the bulk phase properties stay the same throughout the bulk. Smooth surface can be considered as Gibbs dividing surfaces but it is not reasonable to regard porous adsorbents surfaces as Gibbs dividing surfaces. Based on the mentioned discussion, the generalized differential Gibbs adsorption isotherm equation is given by:

$$dF = - \sum \frac{n_i^\sigma}{Z} d\mu_i \quad (dT, V^\sigma dp = 0) \quad (1-6)$$

we can now specify equation (1-6) for liquid-gas interface.

Lets define $V^\sigma = 0$, $F = \gamma$ and $Z = A$ and introduce further surface excess concentrations:

$$\Gamma_i = \frac{n_i^\sigma}{A_s} \quad (1-7)$$

where now A_s refers to area of the surface. Then equation (1-6) becomes:

$$d\gamma = - \sum \Gamma_i d\mu_i \quad (1-8)$$

From the respective isothermal Gibbs-Duhem equations, each referred to unit amounts of the two equilibrium bulk phases, there follows (with superscripts l and g instead of a and β , respectively):

$$dP = \frac{1}{v_m^l} \sum x_i^l d\mu_i = \sum c_i^l d\mu_i = \frac{1}{v_m^g} \sum x_i^g d\mu_i = \sum c_i^g d\mu_i \quad (1-9)$$

where x_i^l is the mole fraction of the liquid component, and x_i^g is the mole fraction of the gas component, c_i^l is the mout of the liquid phase and c_i^g is the amount of the gas phase.

and thus:

$$d\mu_i = - \frac{\sum_{i=2}^k (c_i^l - c_i^g) d\mu_i}{c_1^l - c_1^g} \quad (1-10)$$

where k is the number of components. Now, introducing this into equation. (8), yields:

$$d\gamma = \sum_{i=2}^k \left(\Gamma_1 \frac{c_i^l - c_i^g}{c_1^l - c_1^g} \Gamma_i \right) d\mu_i \quad (1-11)$$

Equation. (1-11) can be simply written as:

$$d\gamma = - \sum_{i=2}^k \Gamma_i^1 d\mu_i \quad (1-12)$$

From the above argument and equation. (1-12), the classical Gibbs adsorption equation can be defined as:

$$\Gamma_i = - \left(\frac{\partial \gamma}{\partial \mu_i} \right) = - \left(\frac{\partial \gamma}{\partial a_i} \right) \quad (1-13)$$

Using equation (1-13), one can calculate the surface excess concentration from the concentration dependence of the surface tension. This is made possible if the activity

coefficient data are available. If it is difficult to obtain the activity coefficient data then it can be approximated by the concentration.

1.6 Surfactants

Surfactants are chemical compounds that are surface active. These substances consists of hydrophilic (water-loving) moiety (head group) and a hydrophobic (water-hating) moiety (tail) as is illustrated in figure 1.3 [7].

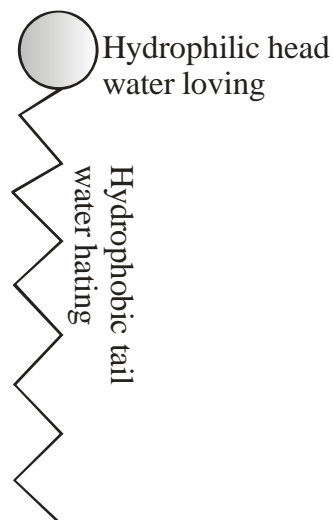


Figure 1.3. Schematic sketch of a surfactant structure showing the main structure moieties.

Surfactants have dual affinity [8] and this is the reason they are called amphiphiles. In 1929 the Swiss scientist Kurt Von Neergaard discovered the first surfactant. Based on his studies in the laboratory he suspected that there is pulmonary surfactant. Because of the surfactant dual affinity, it does not fully like to be 100% in water which polar liquid nor likes to be 100% in a non-polar solvent. Because of their dual character, these substances prefer to migrate to the surface of the liquid to which they are added and accumulate there. They will orient themselves in such a way that the solvent hating part will be close to air while the solvent loving part will be into the surface of the liquid. This is illustrated for water in figure 1.4 below:

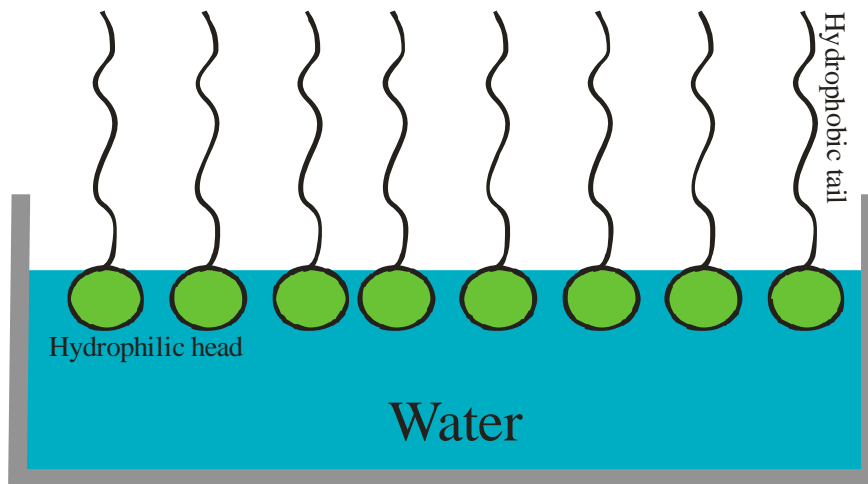


Figure 1.4. Orientation of surfactant molecule at the water/air interface.

If the amount of added surfactant is sufficient to fill the surface and the surface is saturated then they will go to the bulk and aggregate and form a sort of spherical giant particles called micelle [7-9]. These micelles usually consist of 50 or more surfactant molecules. In water the water loving part of the micelle will be toward the water while the water hating part will gather away from it. The hydrophilic head will be in the water and the hydrophobic tail will be away from the water. This is illustrated in figure 1.5.

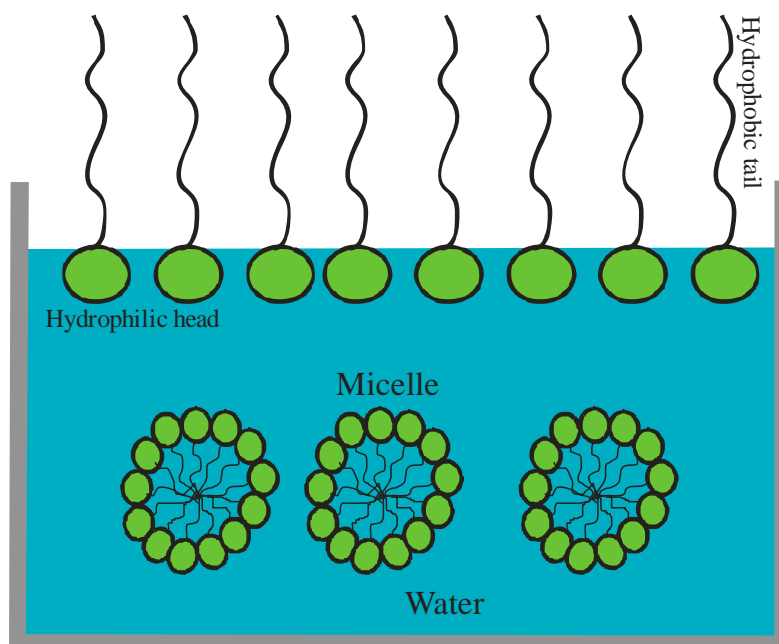


Figure 1.5. Formation of micelles in water when the surface is covered with surfactant molecules and sufficient amount of surfactant present.

If on the other hand the solvent is oil, the hydrophobic tail will be in the oil while the hydrophilic head will be away from it. The presence of surfactant molecules at the water/air interface will decrease the surface tension of water depending on the concentration of the surfactant.

There are different types of surfactants, anionic, cationic and non-ionic:

1.6.1 Ionic Surfactants

These substances have charged hydrophilic head and in industry they are used the most [10]. When added to water they will dissociate to form surfactant anion and a metal ion generally alkali metal ion (Na^+ , K^+). Example of these are alkylbenzenesulfonates (detergents), (fatty acid) soaps, laurylsulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants). The world production consists of 50% of anionic surfactants. Example of ionic surfactants is Sodium Dodecylsulphate which is shown in figure 1.6 with other examples [10]:

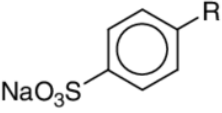
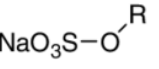
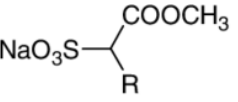
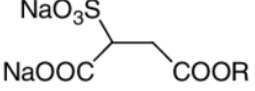
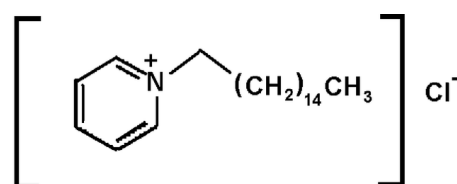
Type	Formula	Formula
Linear alkylbenzene sulfonates (LAS)		$\text{R} = \text{C}_{10}-\text{C}_{13}$
Alkylsulfonates	$\text{NaO}_3\text{S}-\text{R}$	$\text{R} = \text{C}_{11}-\text{C}_{17}$
α -Olefine sulfonates	$\text{NaO}_3\text{S}-(\text{CH}_2)_m\text{HC}=\text{CH}(\text{CH}_2)_n\text{CH}_3$	$m + n = 9-15$
Alkylsulfates		$\text{R} = \text{C}_{11}-\text{C}_{17}$
Fatty alcohol ether sulfates	$\text{NaO}_3\text{S}-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{R}$	$\text{R} = \text{C}_{12}-\text{C}_{14}; n = 1-4$
α -Sulfo fatty acid methyl esters		$\text{R} = \text{C}_{14}-\text{C}_{16}$
Sulfo succinate esters		$\text{R} = \text{C}_{12}$
Soaps	$\text{NaOOC}-\text{R}$	$\text{R} = \text{C}_{10}-\text{C}_{16}$

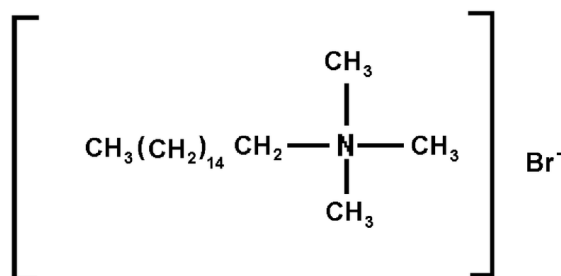
Figure 1.6. Examples of ionic surfactant and their chemical structures.

1.6.2 Cationic Surfactants

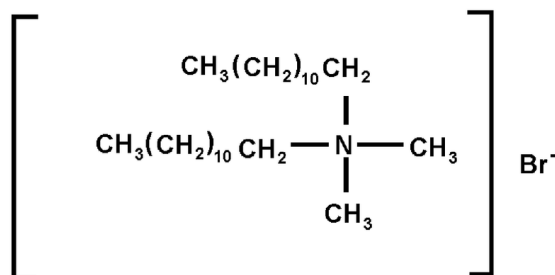
These substances when in water dissociated into an amphiphilic cation and an anion, most often of the halogen type [11]. Nitrogen compounds form the major class of these compounds. These nitrogen compounds are fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. Cationic surfactants are more expensive than their counter part anionic surfactants because of the way they are produced. They are usually produced or synthesised by high-pressure hydrogenation reaction. Sometimes they are produced because there are no cheap alternative and especially are made as bactericide and positively charged substance, which can be adsorbed on negatively charged substrates to produce antistatic and hydrophobant effect. This is of great commercial importance for corrosion inhibition. Examples of cationic surfactants are shown in figure 1.7.



Cetylpyridinium chloride (CPC)



Cetyltrimethylammonium bromide (CTAB)



Dimethyldidodecylammonium bromide (DDAB)

Figure 1.7 Chemical structures of some cationic surfactants.

1.6.3 Nonionic Surfactants

These chemical substances do not dissociate in water solutions because they do not consist of ionisable groups. Their hydrophilic parts usually contain an alcohol, phenol, ether, ester, or amide group [12-13]. A widely used non-ionic surfactant is polyethylene glycol obtained by polycondensation of ethylene oxide. They are called polyethoxylated non-ionics. Recently, glucoside (sugar based) head groups have been introduced in the market. This is because they are less toxic. Alkyl-benzene type groups are the most lipophilic group in these types of surfactants. They usually come from fatty acids of natural origin. Examples of non-ionic surfactants are shown in figure 1.8.

Poly (alkylene-oxide) block copolymers	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	Pluronic PEO-PPO-PEO
	$\text{HO}(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n\text{H}$	Pluronic R PPO-PEO-PPO
	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	PEO-PBO-PEO
	$\text{HO}(\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	PBO-PEO
	$\text{H}(\text{O}(\text{CH}_2\text{CH}_2\text{O})_n(\text{O}(\text{CH}(\text{CH}_3)\text{CH}_2)_m\text{N}(\text{CH}_2\text{CH}_2)_m\text{N}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H})_2$	Tetronic
Oligomeric alkyl-ethylene oxides	$\text{CH}_3(\text{CH}_2)_n(\text{O}-\text{CH}_2\text{CH}_2)_m\text{OH}$	Brij
	$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)-(\text{O}-\text{CH}_2\text{CH}_2)_x\text{OH}$	Tergitol
Alkyl-phenol poly-ethylenes	$\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}=\text{CH})_2-\text{C}(\text{CH}=\text{CH})_2-\text{C}(\text{O}-\text{CH}_2\text{CH}_2)_x\text{OH}$	Triton
Sorbitan esters	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_w(\text{C}_6\text{H}_4\text{O})_z(\text{O}-\text{CH}_2\text{CH}_2)_x\text{OH}$ <p>$x + y + z + w = 20$</p> $\text{CH}_2-\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{C}(\text{O})-\text{R}$	Tween
	$\text{HO}(\text{C}_6\text{H}_4\text{O})_z\text{CH}_2\text{O}-\text{C}(\text{O})-(\text{CH}_2)_n\text{CH}_3$	Span

Figure 1.8. Examples of non-ionic surfactants and their chemical structures.

1.6.4 Zwitterionic

There are certain surfactants that have both positive and negative groups. These are called Zwitterionic or amphoteric surfactants. They usually have long chain and they are neutral molecules. The length of their hydrocarbon hydrophobic chain determines their properties in addition to their methylene segment number and their positive and negative charged groups. Examples of these zwitterionic neutral surfactants are provided in figure 1.9.

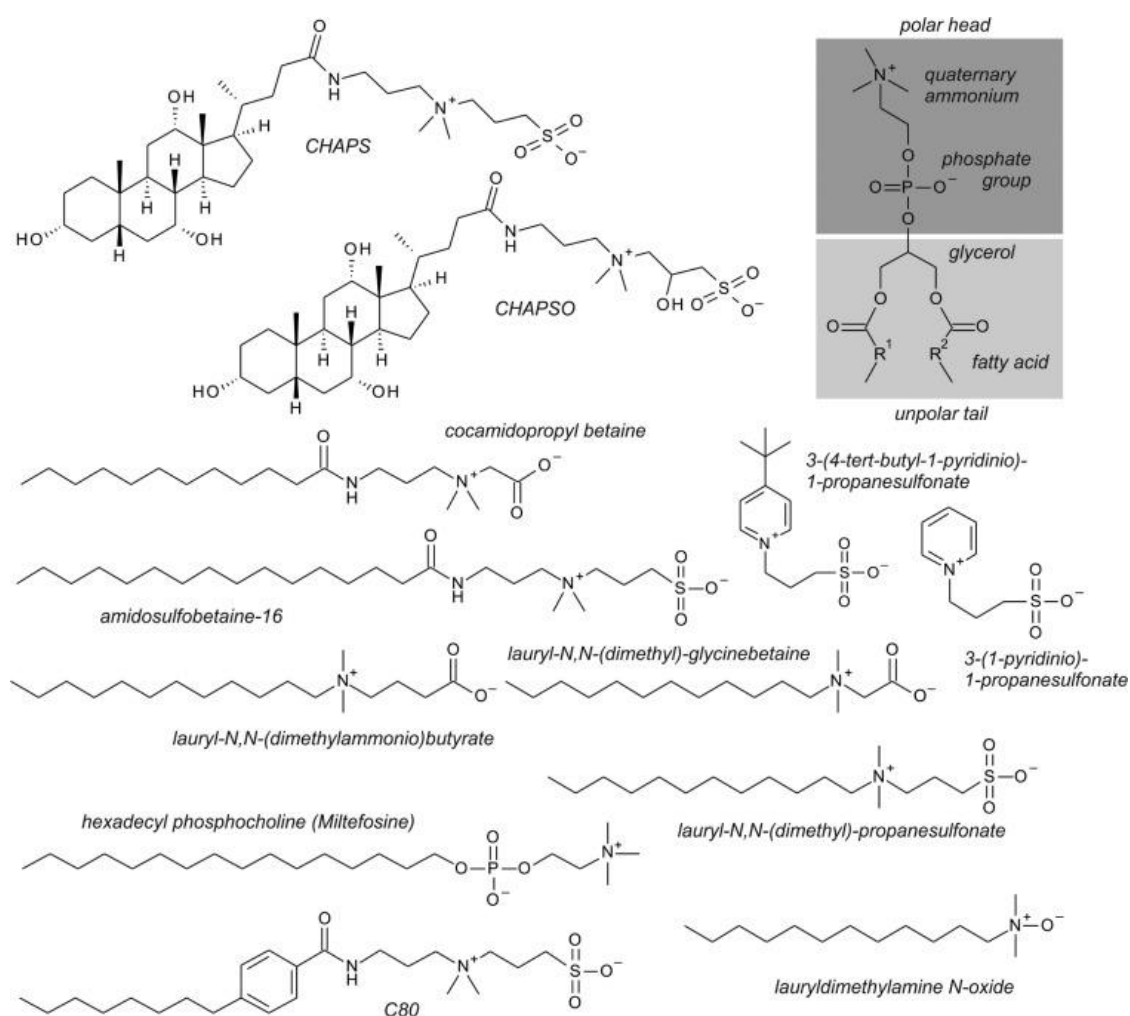


Figure 1.9. Examples of zwitterionic and their chemical structures.

Summary of surfactant types including examples on each and briefly their uses is given in table 1.1

Surfactant type	Example	Use
Anionic	Alkyl sulfates, soaps, Calsoft®, Texapon®	50 % of overall industrial production, laundry detergent, dishwashing liquids, shampoos
Cationic	Quaternary ammonium salts	Used together with nonionic surfactants but not with anionic, softeners in textiles, anti-static additives
Nonionic	Ethoxylated aliphatic alcohol, polyoxyethylene surfactants, Triton™ X-100, Span®, Tergitol™	45 % of overall industrial production, a wetting agent in coatings, food ingredient
Zwitterionic	Betaines, amphotacetates	Expensive, special use e.g. cosmetics

Table 1.1. Summary of the different types of surfactants providing examples on each and their general uses.

1.7. Importance of Surfactants

Because of their peculiar properties and their possible industrial application, scientist around the world have been attracted to conduct research to understand surfactants behaviour in solution and their possible modifications. This has led to a wide range of published research articles. Books have been written to provide basic information such as e.g Rosen [14] Myers [15] and Mittal [16]. Alkylbenzenesulfonates, ethersulfates and alcohol ethoxylates have dominated the technological application of these surfactants. These substances account for the major portion of surfactants used in industry. They are mostly used in laundry detergents, personal care products and household products. Research on their mixtures in order to enhance their properties and performance in industry have been conducted. Commercially, and during the oil crisis in 1970s, micro-emulsions have been formulated to enhance the production of oil. These newly formulated micro-emulsion had been largely investigated. New formulations have been made by organizing surfactant molecules into new shapes and structures. These newly created shapes and structures have been heavily studied and manipulated in laboratories. Not only that but the origin of life was suspected to be involved with such surfactant substances. Boundary membranes which are assemblies of lipid-like compounds may be an interstellar prebiotic earth source of cell-membrane material. New surfactants have been synthesised in the past

decade in such a rapid manner. This growth in surfactant synthesis has been paralleled the emphasis on increasing the basic performance of surfactant formulations and the provision of new surfactant technologies to a diverse range of disciplines. Despite all this progress there is still issues that can be developed such as new surfactant formulation and new research to deepen our understanding on surfactant properties in different types of solutions. For example, new formulation in nanotechnology can be made. These new materials have spurred on the quest for improved molecular models, computer simulations, and improved structure–activity relationships [11,13].

1.8. Surface Activity of Surfactants

The surface activity of surfactants can be determined by measuring the surface tension of surfactant solutions [16]. Figure 1.10 illustrate a general behaviour of the surface tension of surfactant solution as function of logarithm of surfactant concentration.

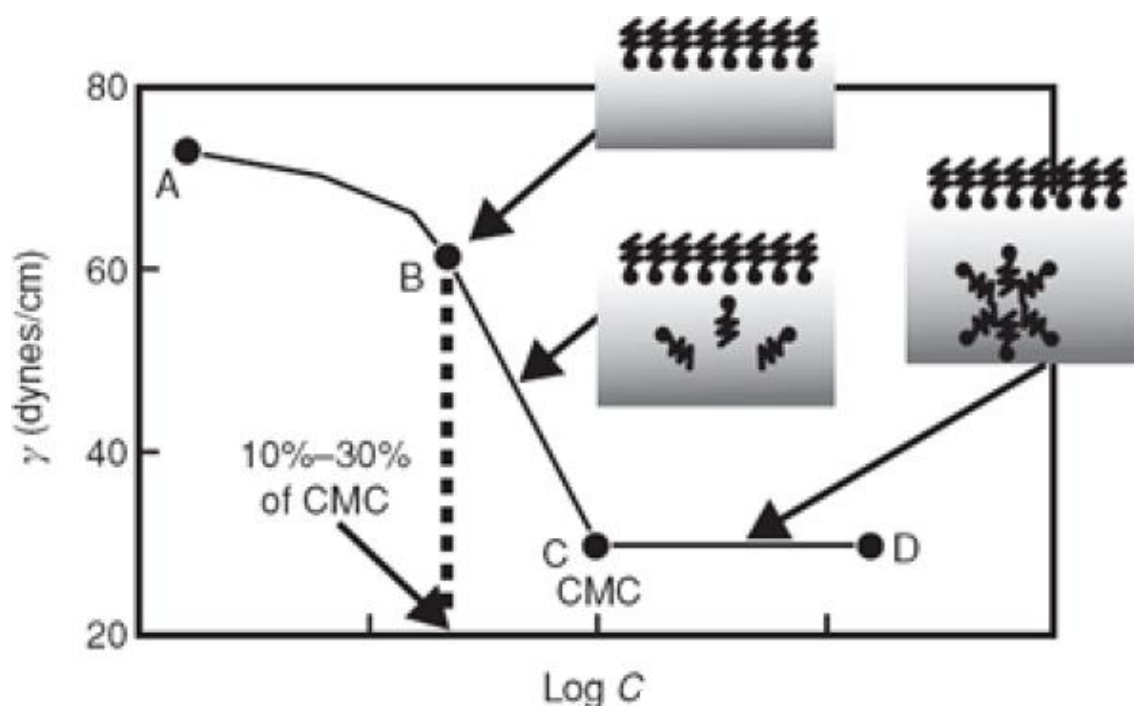


Figure 1.10. Behaviour of the surface tension of surfactant solution with surfactant concentration.

When the concentration of the surfactant is low (segment A-B in figure 1.10), the surfactant molecules will migrate to surface of the solution and align themselves in such a way to keep the hydrophobic tail outside the surfactant solution and the hydrophilic part immersed in the surfactant solution. When more surfactant is added (segment B-C), The surface

tension of the solution starts to decrease rapidly until the critical micelle concentration (CMC) is reached. This is marked by the point C. At the CMC of a surfactants two things start to happen. First, the surface tension starts to be constant and the micelle in the bulk of the liquid or solution start to form. This means that above the CMC, where the line becomes horizontal in the figure any further additions of surfactant are no longer being accompanied by a decrease in surface tension. Each surfactant has its own CMC value. The value of the CMC is affected by temperature; addition of simple salts such as sodium chloride and any other additions such as alcohol substances. A low CMC is favoured by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte.

1.9 Surfactant Mixtures

Mixed surfactant systems, including their mixed micelles exhibit changes in their physical properties as compared to single-component surfactants and hence are of great theoretical and practical interest [17]. These systems are encountered in numerous applications for the purpose of separation foam, generation, dispersion, and detergency [18-19]. On the basis of the type of head groups in surfactants, various combinations of non-ionic/cationic/anionic surfactants have been studied by a number of workers [20-21] and several models have been proposed to rationalize their behaviour [22-26]. Among them, two widely used models are those of Clint [22] and Rubingh [23]. The former describes ideal surfactant mixtures, and the latter uses regular solution theory to describe non-ideal surfactant mixtures. Among all of the possibilities, binary mixtures of oppositely charged surfactants (i.e., cationic and anionic) are of special interest because of their strong electrostatic interaction in water and thus enhanced surface activity.

Research on surfactant mixtures is of considerable interest for numerous technical applications, because surfactant mixtures enhance the performance of applications when compared to the use of neat surfactants. When mixing surfactants, one is allowed to combine properties that are of interest. In some cases even new properties are found, such as in the case of mixing cationic and anionic surfactants.

There are many examples of surfactant mixtures in the household market. Since it is a well-established idea that cationic and anionic surfactants cannot be present in the same formulation, mixtures are generally between anionic/anionic, cationic/cationic, non-ionic/non-ionic, amphoteric/amphoteric, anionic/nonionic, cationic/nonionic or amphoteric/nonionic.

However, synergism increases with the degree of charge difference [27-28] meaning that synergism between anionic/anionic or nonionic/nonionic is less than that between anionic/nonionic or cationic/nonionic, which, in turn, is less than that between cationic/anionic. Consequently, the higher synergism is obtained by mixing anionic and cationic surfactants, and therefore, a better understanding of that system may broaden the horizon for household formulations [28].

1.9.1. Anionic/Cationic Complexes

When small amounts of either anionic or cationic surfactants are added to an aqueous solution, they exist only as monomers in solution. When the concentration is increased and reaches the CMC, micelles start to form. If, however, the concentrations of both the anionic and cationic monomers exceed the solubility product, precipitation will occur. As precipitation generally renders the surfactant ineffective in solution, it is important to understand that system. Precipitation of anionic surfactants [29-31] and mixtures of anionic/nonionic surfactants [32] has been previously successfully modelled, and the behaviour and physicochemical properties of mixtures of a highly branched cationic and sodium alkyl sulfate have been widely studied by Zhi-Jian Yu and co-workers [33-35]. Stellner and co-workers studied mixtures of anionic and cationic surfactants [36] over a wide range of concentrations in order to develop a model that could provide complete phase boundaries for that system. Figure 1.11 shows a schematic diagram of the equilibrium proposed by Stellner [36].

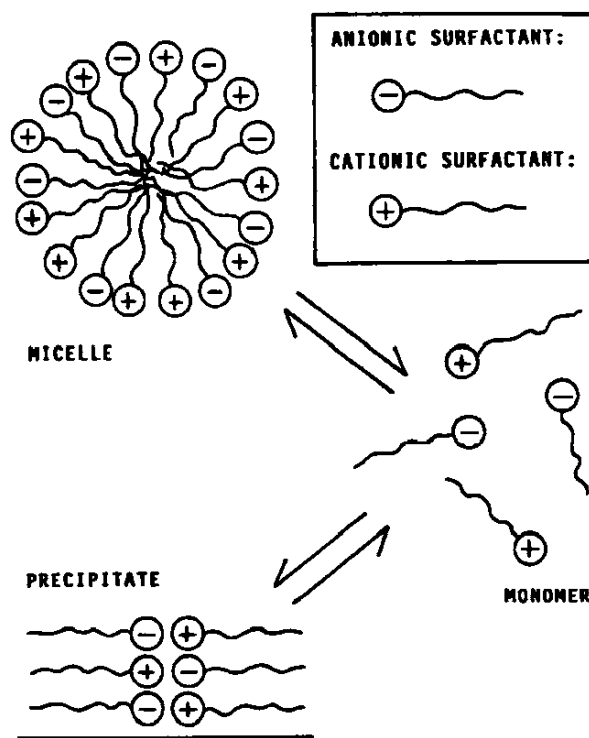


Figure 1.11. Schematic diagram of basic equilibrium in a cationic/anionic system.

1.9.2. Mixed Surfactants at Interfaces

When surfactants of different types and charges are mixed the surface activity will be different from the surface activity of the individual surfactants. The surface tension of the mixed surfactants will be lower than the surface tension of the individual surfactant. The presence for example of cationic surfactant with an anionic surfactant in the same solution will cause synergistic effects. This synergism is of technological importance for wide industrial applications. This is important in applications such as foaming, emulsification, detergency [37]. Generally, synergistic effects seem to be negligible for mixtures of non-ionic surfactants [38-41]. Ionic/nonionic mixtures, on the other hand, do show appreciable synergism, which in some cases can be described in terms of a regular solution model for the surface mixture (42, 43). Maximum synergistic effects were found in cationic/anionic mixtures. There is a physically simple explanation for the enhanced synergism in such mixed charge systems. The basic idea is that only adsorption of electroneutral combinations of ions can take place.

Because surfactants mixtures show more surface tension lowering and lower critical micelle concentration than individual surfactants [44-48], mixed surfactants are widely

used rather than individual surfactants for industrial applications. Recently, many studies about different combinations of mixed surfactant systems have been reported, including cationic/anionic [49-55], cationic/ cationic [56], cationic/nonionic [57], anionic/nonionic [58] and zwitterionic/anionic [59] surfactant systems. It has been well known for a long time that mixtures of anionic and cationic surfactants exhibit the largest synergistic effects, as evidenced by the ultralow surface tension and CMC produced by these systems. Such synergetic effects originate from the strong interactions between two surfactant molecules with oppositely charged head groups [60-62]. They are important for a wide range of applications in industries such as enhanced oil recovery and pharmaceutical applications, wastewater treatment, textile wetting, detergency, froth flotation, paper manufacturing and pharmaceutical production [63–65].

1.10 Effect of Temperature and Salt Addition

Changing the temperature and/or adding simple salt will change the critical micelle concentration of a surfactant or surfactant mixture. Chen et al [66] investigated the temperature effect on the CMC of n-dodecyl polyoxyethylenemonoether by Wilhelmy plate technique in the range of 10-80 °C. They also evaluated the effects of enthalpy and entropy on micelle formation. Their results indicated that the temperature of 321 K was excellent for their experiments. Noll et al. [67] studied the effect of temperature, salinity, and alcohol on the CMC of a series of surfactants and showed that the CMC of the studied surfactants increased with a rise in temperature, and the presence of electrolyte at a fixed temperature lowered the CMC but increased the sharpness of the onset of micellization. Maeda et al. [68] determined the CMC of dodecyl dimethyl amine oxide (DDAO) at 25 °C as a function of NaCl concentration for both nonionic and cationic species by measuring the surface tension. Their research showed that the CMC of the cationic species was lower than that of the nonionic species in the range of NaCl concentration higher than about 0.2 M, which strongly suggested an attractive interaction between the head groups of two cationic species in micelles, most probably the hydrogen bonding (Maeda et al., [68]). Parak et al. [69] evaluated the synergistic effect in micelle formation of surfactant mixtures at different mass ratios of various surfactants by the surface tension measurement method; a mixture consisted of anionic (alpha olefin sulfonate [AOS]) and nonionic (Triton X-100) surfactants at ratios of 1:2, 1:1, and 2:1. They concluded that the CMC of the mixed surfactants decreased by raising the mole fraction of TX100 in the system, which reduces the electrostatic repulsion of the charged head group of the anionic

surfactant, thereby causing the mixture to reach CMC more easily. However, the CMC of the mixed surfactants was not intimately linked to the mole fraction of Triton X-100 in the mixture after equilibrium [69]. Sammalkorpi et al. studied the properties of sodium dodecyl sulfate (SDS) aggregates in saline solutions of excess sodium chloride (NaCl) or calcium chloride (CaCl₂) ions through extensive molecular dynamics simulations. They observed that significantly more stable salt bridges between the charged SDS head groups were mediated by Ca²⁺ than Na⁺. The presence of these salt bridges helps stabilize the more densely packed micelles [70]. Karnanda *et al.* [71] investigated the effects of surfactant type, salt type, temperature, and pressure on the CMC of Triton X-405 and Zonyl FSE. They reported that temperature and pressure had no effect on the CMC of Triton X-405; however, the CMC of Zonyl FSE solutions decreased by increasing pressure but leveled out by raising temperature except at temperatures higher than 80 °C, where CMC increased [71]. Khanamiri *et al.* [72] studied the effect of brine composition on the rock and injected fluid properties. They observed that the CMC of their surfactant (SDBS) in the pure sodium chloride solution and Ca²⁺/Na⁺ ratio of 0.022 were nearly 105 mg/L and 65 mg/L respectively. The CMC of the surfactant without any salt was 500 mg/L. Their experiments showed that increased ionic strength in the presence of sodium chloride and the combination of sodium chloride and calcium chloride led to a reduction in CMC [72]. Javadian *et al.* [73] evaluated the micellization characteristics of mixtures of CTAB and TritonX-100 in aqueous media containing different concentrations of NaBr by surface tension (ST) method. They showed that decreasing the electrostatic interactions by raising the ionic strength of the solution had a better influence on the planar air/solution interface than on the convex micellar surface in the solution [73]. Miyagishi *et al.* [74] investigated the effect of a series of salts on the CMC of nonionic surfactants (N-acyl-N-methylglucamides). Their experiments illustrated that salt can lower the CMC value, and a decline in CMC was observed in the order of Ca > Na > K > Cs > Li for cations and in the order of SO₄⁻ > CO₃⁻ > SO₃⁻ > HPO₄⁻ > F > Cl > Br > NO₃⁻ > I > SCN for anions (Miyagishi et al., [74]).

Recently, in our lab. at the University of Hebron, department of chemistry, Irziqat and Takrori [75] studied the effect of temperature and salt addition on the critical micelle concentration of SDBS and found a similar trends as those found by Khanamiri et al. [72]. Their study however was an extended one with much wider temperature range and salt combinations. Owiwi [76] studied the effect of salt addition on the behaviour of the cationic surfactant benzyldimethylhexadecylammonium chloride (BAC) and found the CMC of the surfactant indeed decreases with the addition of salt.

In this work I studied the effect of temperature and salt addition on the surface tension of benzyl-dimethyl-hexadecyl-ammonium chloride alone and its mixture with sodium dodecyl benzene sulfonate. Measuring the surface tension was carried out by the state-of-the-art KRÜSSK-100 force tensiometer. The effect of added salts and changing temperature on the surface tension of the cationic/anionic mixture was investigated. To the best of our knowledge, this cationic/anionic mixture has never been studied before neither in pure water nor as a function of salt addition at different temperatures.

Chapter 2

Material and Experimental Techniques

2.1 Material

2.1.1 Surfactants:

The main material used was benzyldimethylhexadecyl ammonium chloride (16-BAC) which was obtained from Sigma –Aldrich with purity of 99.7%. It is an organic compound with the molecular formula $C_{23}H_{42}ClN$ and has a molar mass of $396.09 \text{ g mol}^{-1}$. This cationic surfactant is white powder. Its structural formula is shown in figure 2.1



Figure 2.1. Structural formula of Benzyldimethylhexadecyl ammonium chloride (16-BAC).

Sodium dodecyl benzene sulfonate (SDBS) was obtained from Sigma – Aldrich with purity of 99.8%. It is an organic compound with molecular formula $C_{18}H_{29}NaO_3S$ and molar mass of $348.48 \text{ g mol}^{-1}$. The anionic surfactant is a white to light yellow sand like–solid. The structure of SDBS surfactant used is shown in figure 2.2:

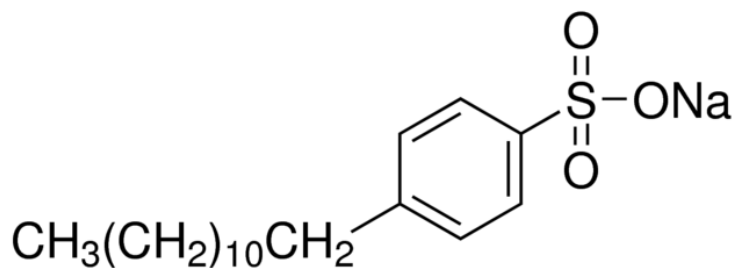


Figure 2.2. Structural formula of sodium dodecyl benzene sulfonate (SDBS).

2.1.2 Salts

Sodium chloride (NaCl) from Sigma Aldrich with purity of 99.99% by mass and molar mass of 58.44 g mol⁻¹. Calcium chloride (CaCl₂) from Sigma Aldrich with purity of 99.99% by mass and molar mass was of 110.98 g mol⁻¹.

2.2 Equipment and Tools.

2.2.1 Tensiometer

The state of the art K100-MK3 tensiometer (Kruss, Germany) was used to measure surface tension. A photo of the apparatus is shown in figure 2.3. The tensiometer is fully automatic, with high resolution (0.01mN/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 measurement between – 10 and 130°C.

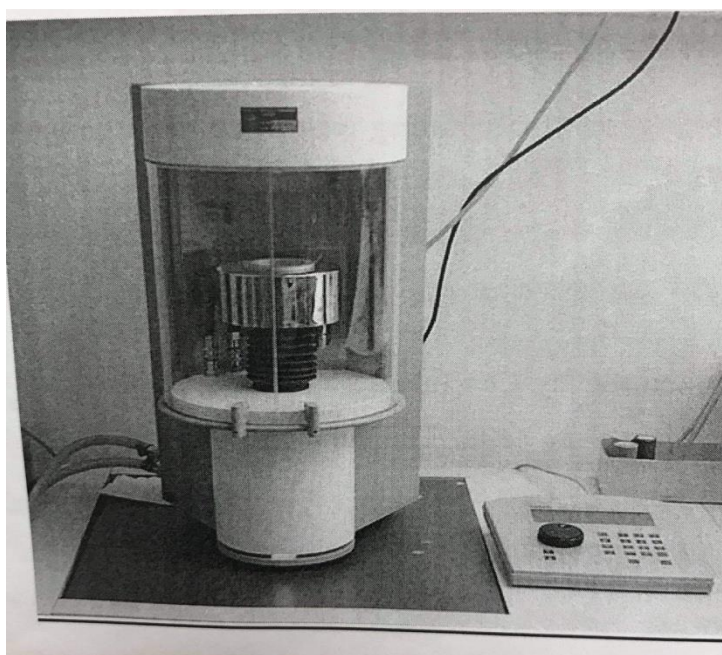


Figure 2.3. Force Tensiometer – K100 (Kruss- Germany)

2.2.2 Temperature Control

A refrigerated circulating water bath connected to the tensiometer was used to control the temperature. It has accuracy of $\pm 0.1^\circ\text{C}$. The temperature controller is shown in Figure 2.4. This circulating water bath was used for cooling and heating.



Figure 2.4. Refrigerated circulating water bath with temperature controller that has accuracy of $\pm 0.1^\circ\text{C}$.

2.2.3 Furnace

For drying the salts used in this work, a lab furnace manufactured by CM Furnaces was used. It has a maximum operating temperature of up to 2000 K. The salts were dried below their melting point. The furnace has sealed designs that support atmosphere control necessary for advanced processes including heat treating, sintering, annealing, glass or ceramic firing.

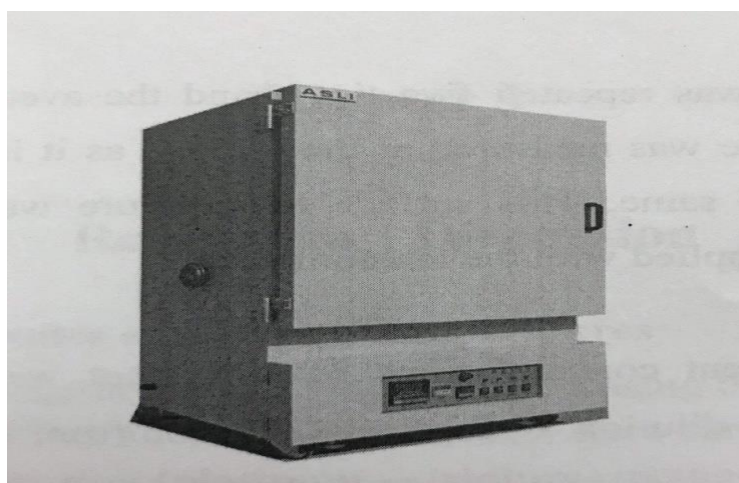


Figure 2.5. Furnace with heating temperature up to 2000.

2.3 Methods

2.3.1 Preparation of Tools and Measuring Procedure

Throughout this work freshly prepared distilled water was used to prepare solution, and to clean the tools. Distilled water was tested all the times repeatedly for the values of surface tension and conductivity to ensure its purity. All glassware (breakers, volumetric flasks, pipets, burets, funnel, spatulas) were carefully cleaned by filling them with distilled water and boiling them for several hours and then rinsed them thoroughly with distilled water again.

The procedure that was followed for all surface tension measurements was as follows: before the beginning of any measurement, the tensiometer was switched on for two hours to get the magnet inside the measuring chamber to the right temperature as this was recommended by the manufacturer. The surface tension of the freshly prepared distilled water was measured repeatedly to ensure that the tensiometer is working properly and the quality of water purity is accepted.

2.3.2 Surfactant Solution Preparation

The accepted values of surface tension of distilled water at room temperature (25°C) was in range between 71-72 mN/m. Before any reading of surface tension measurement, the plate 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 required value and kept for about half an hour to reach thermal equilibrium. Measurement of surface tension of each sample was repeated three times and the average value was tabulated. The temperature of the sample was measured at the surface. This surface temperature was measured with an accurate thermocouple that was supplied with the tensiometer.

Preparation of different concentrations of surfactant was carried out by successive dilution using serial dilution from stock solution to determine the CMC. It was done as follows: a 200 ml of the highest concentration was prepared and divided to two parts. Half of the solution used for surface tension measurement and the other half was diluted by adding distilled water in the 200 ml volumetric flask to the mark and thoroughly mixed. The process was repeated until the lowest desired concentration was achieved. The solution in question were prepared 24 hours in advanced to ensure that they reached

equilibrium. The CMC values of 16-BAC alone or in the presence of added salts and SDBS at different temperature were determined by plotting the data using the powerful plotting and fitting program Origin 8.

Chapter 3

Results and Discussion

3.1 Surface Tension of BAC Aqueous Solution

Figure 3.1 shows the surface tension of BAC surfactant in pure water as a function of BAC concentration and temperature from 10 °C to 50 °C in steps of 10 degrees. From figure 1, one can see that the surface tension decreases with increasing surfactant concentration and then saturates at the critical micelle concentration of 0.50 mM at 20 °C and 0.474 mM at 30 °C.

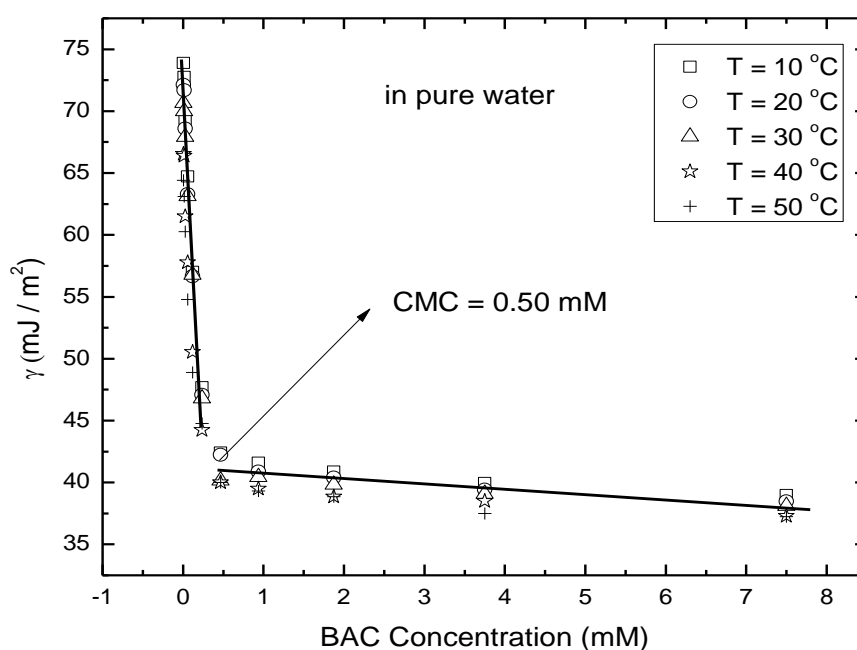


Figure 3.1 Surface tension of BAC aqueous solution as a function of BAC concentration and temperature. The CMC of BAC was determined to be 0.5mM at 20°C.

Nazrul et al [77] determined the critical micelle concentration of BAC and reported a value of 0.6 mM at 35 °C. Within experimental errors our value is close to their value and in the same order of magnitude. The behaviour of the CMC of BAC as a function of temperature is shown in figure 3.2. The CMC decreases with increasing temperature. This can be explained by multiple factors. First of all, as temperature increases there will be a decrease in the hydrophilicity of the surfactant molecules. At higher temperatures there will a reduction in the hydration of hydrophilic group. Second of all, as the temperature increases the micellization

onset occurs at lower concentrations. On the other hand, dissolving the surfactant molecules in distilled water makes the hydrophobic group distort the water structure. Additionally increase in temperature also causes an increase in the breakdown of the structured water surrounding the hydrophobic groups, which disfavours micellization.

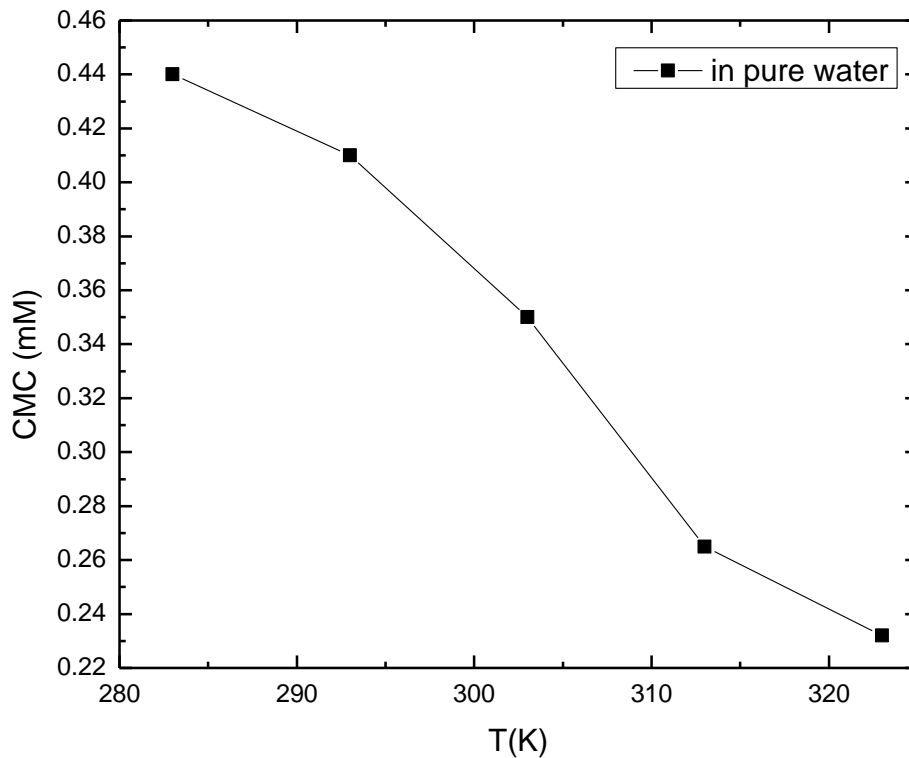


Figure 3.2 Critical micelle concentration of BAC as a function of temperature. The solid squares are the experimental points and the solid line is just to guide the eye.

3.2 The Surface Excess Concentration of BAC :

The surface excess concentration Γ of BAC in pure water was calculated according to the Gibbs's adsorption equation:

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln(C)} \quad (3-1)$$

where R is the gas constant, T is the temperature and C is the concentration of the surfactant. So as was mentioned before, from the plot of the surface tension with logarithm of the

surfactant concentration, the surface excess concentration can be determined. Figure 3 shows the surface excess concentration as a function of temperature. As can be seen, the surface excess concentration decreases with increasing temperature, which can be explained by better solubility of the surfactant at higher temperature. When temperature increases the solubility of the surfactant increases which in turn will decrease the surface excess concentration.

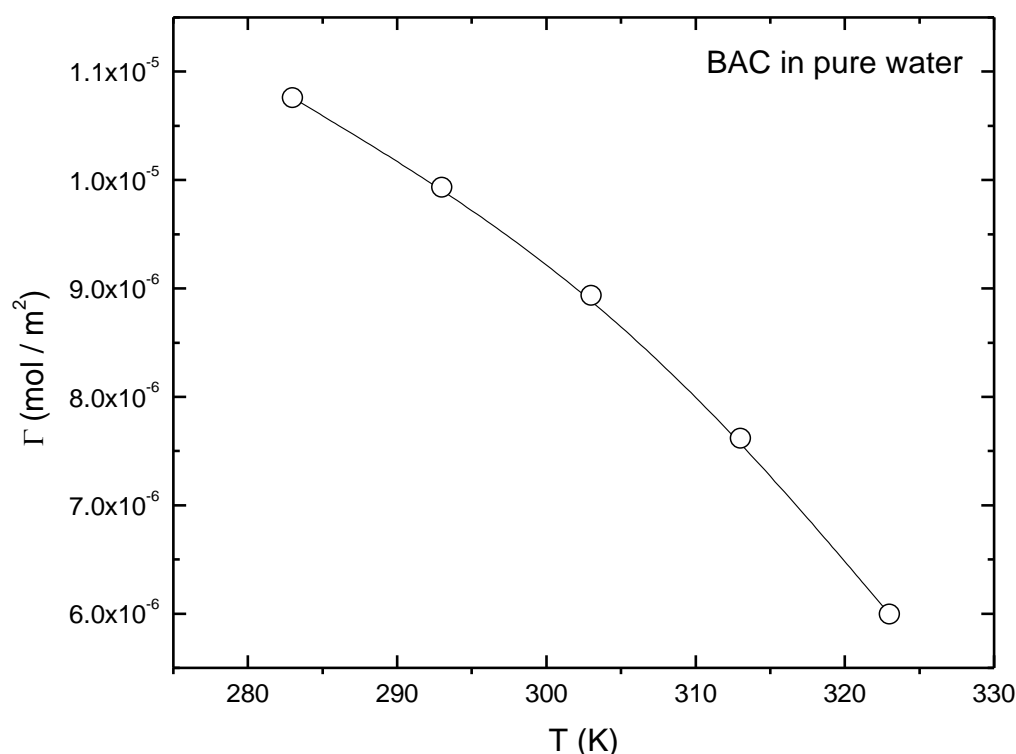


Figure 3.3 The surface excess concentration of BAC as a function temperature. The open circles are the experimental points and the solid line is just to guide the eye.

3.3 Surface Tension of BAC Solutions, Temperature and Salt Effects

Figures 3.4-3.6 show the surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.1 M, 0.2 M and 0.3 M NaCl, respectively. As can be seen, the surface tension decreases with increasing both the BAC concentration and temperature. The micellization of ionic surfactant is a delicate balance between the favourable interaction between the hydrophobic alkyl chains and the opposing repulsive interaction between the charged head group along with the extent of screening of the micelle surface charge by the

associated counterions. From figures 3.4-3.6, it is extracted that the CMC decreases significantly in the presence of the added electrolytes, favouring aggregation of the surfactant molecules in the bulk of the aqueous solution. The counterions adsorb at the micelle surface and thereby screen the charge of the surfactant head group. As a result, electrostatic repulsion between the surfactant molecules is substantially reduced. The screening of the micelle surface charge reduces the electrostatic repulsion between the charged head groups and promotes growth of micelles.

The counter-ions that remain bound to the micelle surface are distributed among the ionic surfactant heads, causing a lowering of the net micelle surface charge. As a result, the electrostatic repulsion between the head groups is significantly reduced, favouring a closer packing of the molecules, which facilitates micellar aggregation at a much lower BAC concentration in the presence of added electrolytes. As mentioned above, because of steric hindrance, tetraalkylammonium derivatives suffer from spatial distribution of water and therefore behave like a chaotrope (a molecule that disrupt the hydrogen bonding between water molecules).

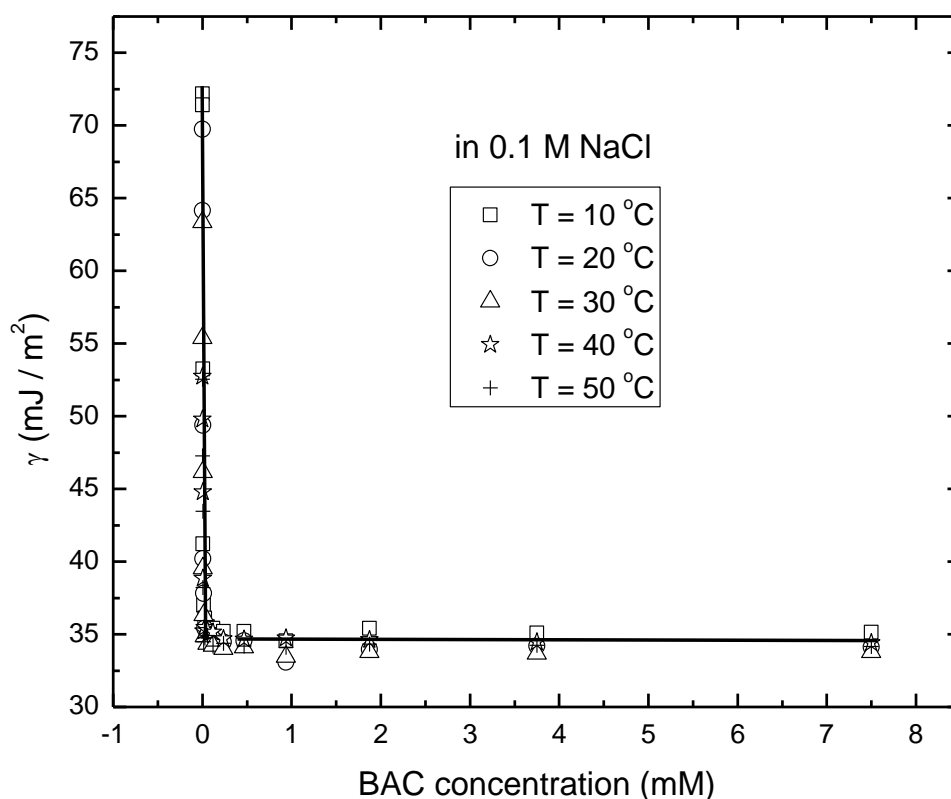


Figure 3.4 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.1 M NaCl. Open symbols are the experimental points and the solid line is just to guide the eye.

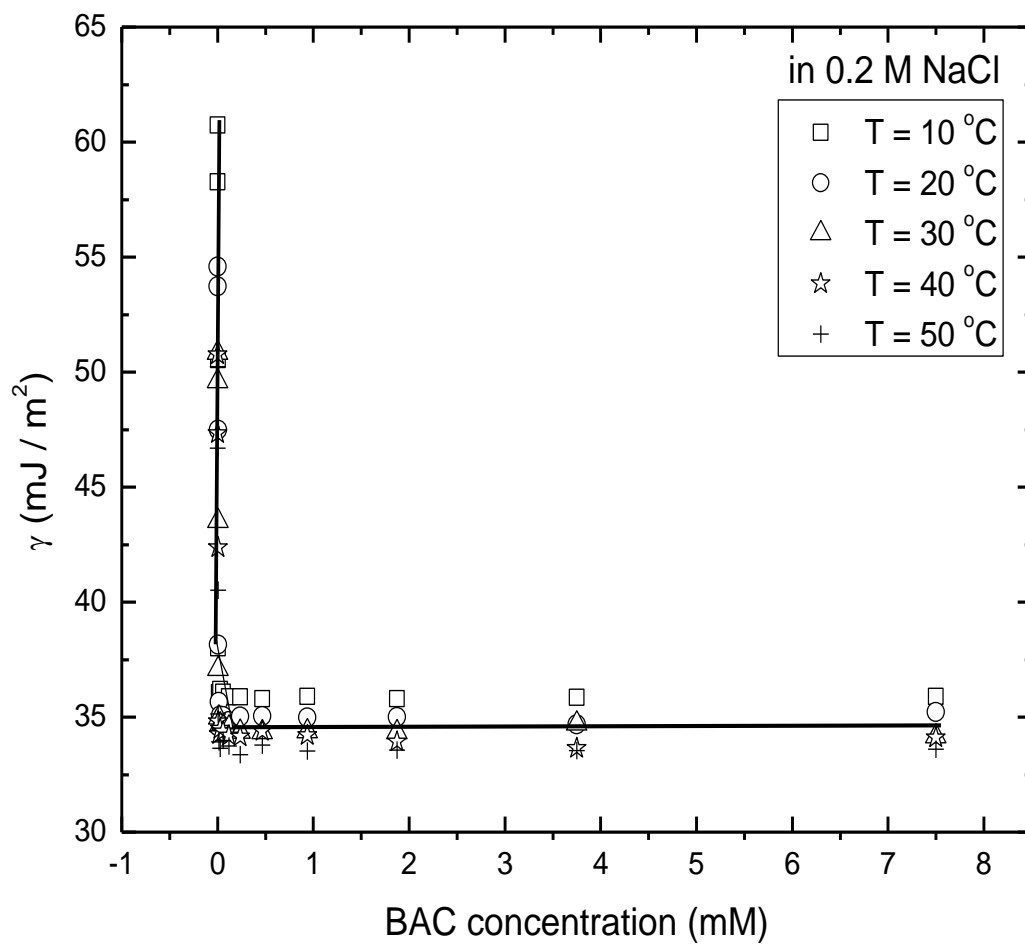


Figure 3.5 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.2 M NaCl. Open symbols are the experimental points and the solid line is just to guide the eye.

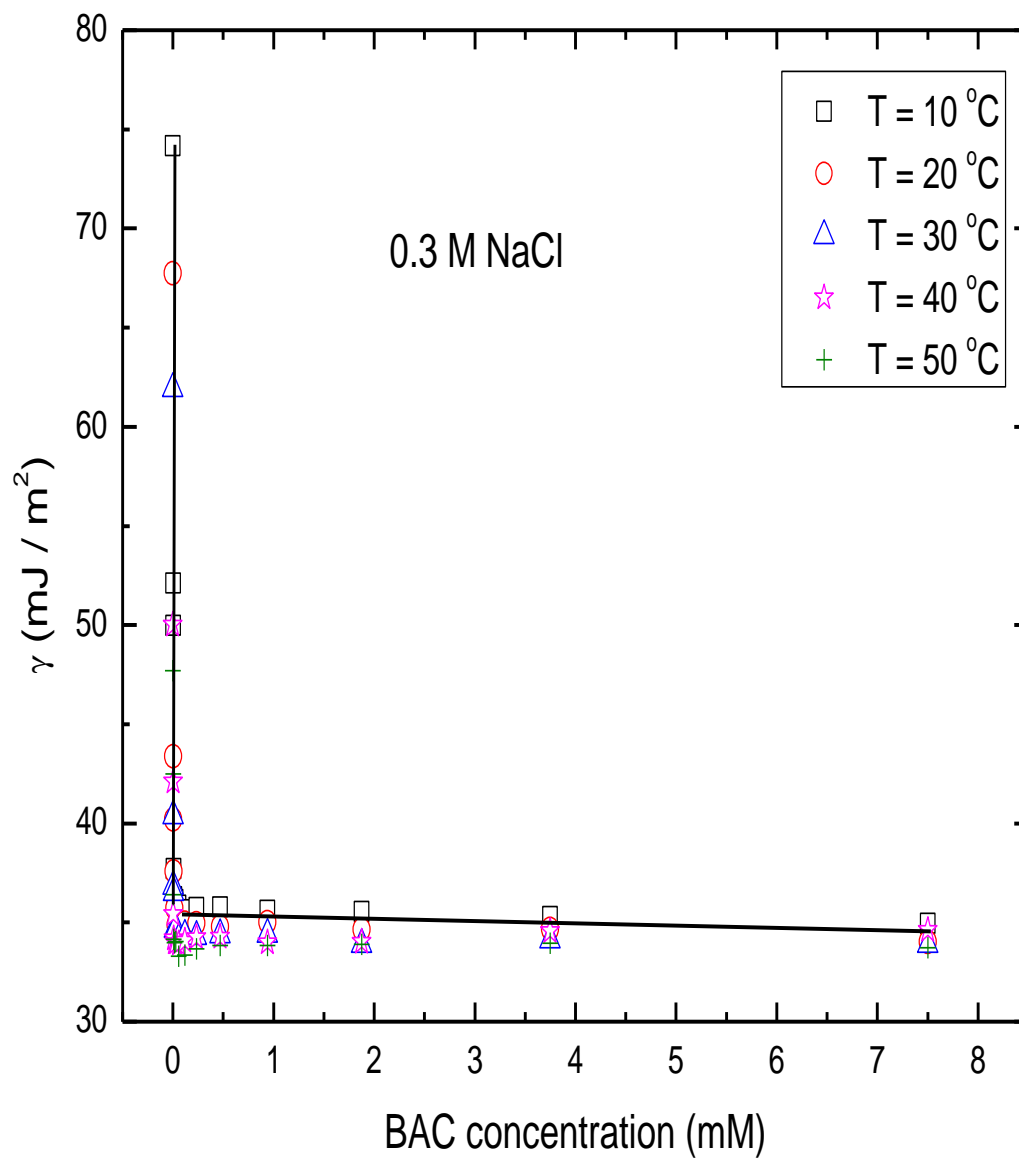


Figure 3.6 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.3 M NaCl. Open symbols are the experimental points and the solid line is just to guide the eye.

Figure 3.7 shows the critical micelle concentration as a function of temperature of BAC in pure water in comparison with that of BAC at different concentrations of NaCl solutions.

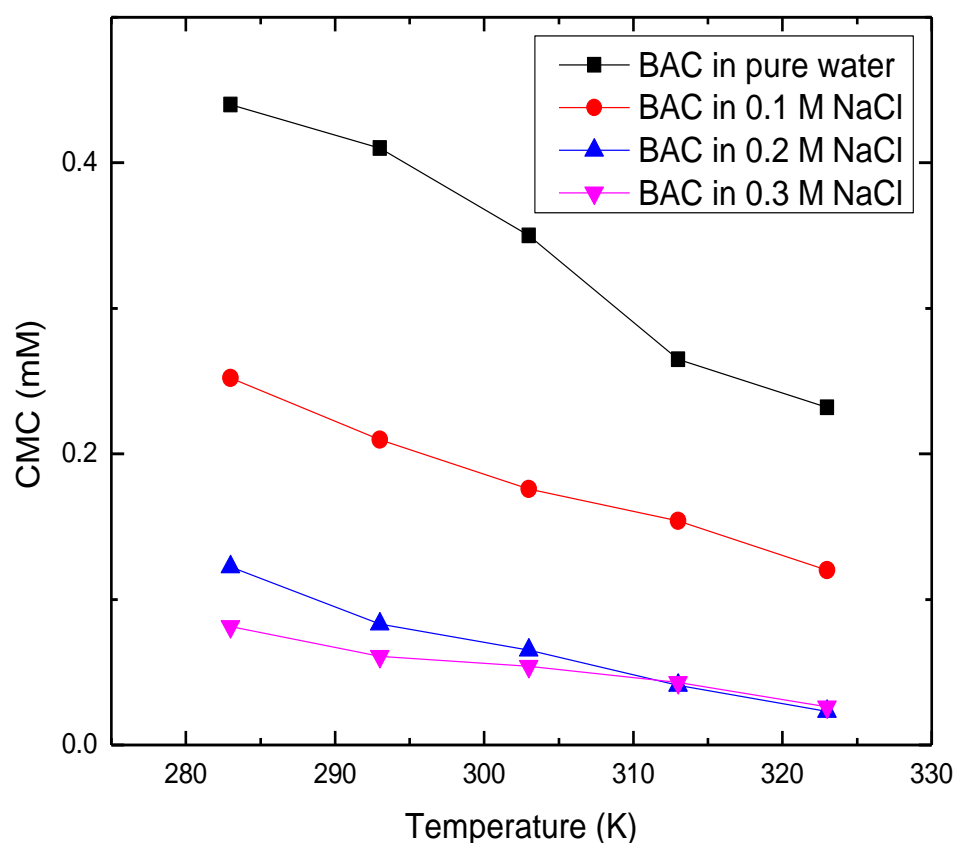


Figure 3.7 Critical micelle concentration as a function of temperature of BAC in pure water in comparison with that of BAC in different NaCl concentration of 0.1 M, 0.2 M and 0.3 M NaCl. The solid line is drawn to guide the eye.

From figure 3.7 it is possible to note the following:

1. There is a decrease in CMC with increasing temperature. Due to the smaller probability of hydrogen bond formation at higher temperatures, the decrease of the CMC with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules. In other words, the increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favour micellization.
2. There is a significant decrease in CMC in NaCl solutions in comparison to that in pure water. The magnitude of the reduction depended on the salt concentration. The higher

the NaCl concentration the higher the decrease in CMC. The factors which operate in ionic surfactant solutions tending to retard surface molecules migration are likely to be:

- a. The electrokinetic potential in the electrical double layer surrounding an ionic species that is developed when the compound dissociates.
- b. The hydrophobic bonding between the non polar hydrocarbon portions of the surfactant and “iceberg” water. These factors may also govern the degree of micellization of the surfactant at high concentration. With a nonionic surfactant, account must be taken of the hydration forces due to the presence of hydroxyl groups and ether linkages which can make hydrogen bond with water molecules. The observed reduction in interfacial tension and the lowering of the CMC by salts may be due to a reduction of the factors retarding migration by the salts. In addition, interfacial packing of the adsorbed monomers, particularly of the ionic type, can be increased by the presence of salts as a result of the reduction in electrostatic repulsive forces between the charged heads in the aqueous phase adjacent to the interface.

3.4 Effects of CaCl₂ Addition

The surface tension as a function of BAC concentration at different CaCl₂ concentration of 0.1 M, 0.2 M and 0.3 M are shown in figures 3.8-3.10. As can be seen, the surface tension decreases with increasing BAC concentration up to its critical micelle concentration. The surface tension decreases with increasing temperature. Figure 11 shows the critical micelle concentration, extracted from figures 8-10, as a function of temperature and different CaCl₂ concentrations. The CMC decreases with increasing temperature and increasing CaCl₂ concentration. As the system temperature increases, the CMC decreases owing to the smaller probability of hydrogen bond formation at higher temperatures while the decrease of the CMC with temperature is a consequence of the decreased hydrophilicity of the surfactant molecules. As was mentioned before, the increase in temperature causes the reduction in hydration of the hydrophilic oxyethylene group, which favour micellization. Consequently, an increase in temperature causes micellization onset to occur at lower concentrations. On the other hand, dissolving the surfactant molecules in distilled water makes the hydrophobic group distorts the water structure. Additionally increase in temperature also causes an increase in the breakdown of the structured water surrounding the hydrophobic groups, which disfavours micellization.

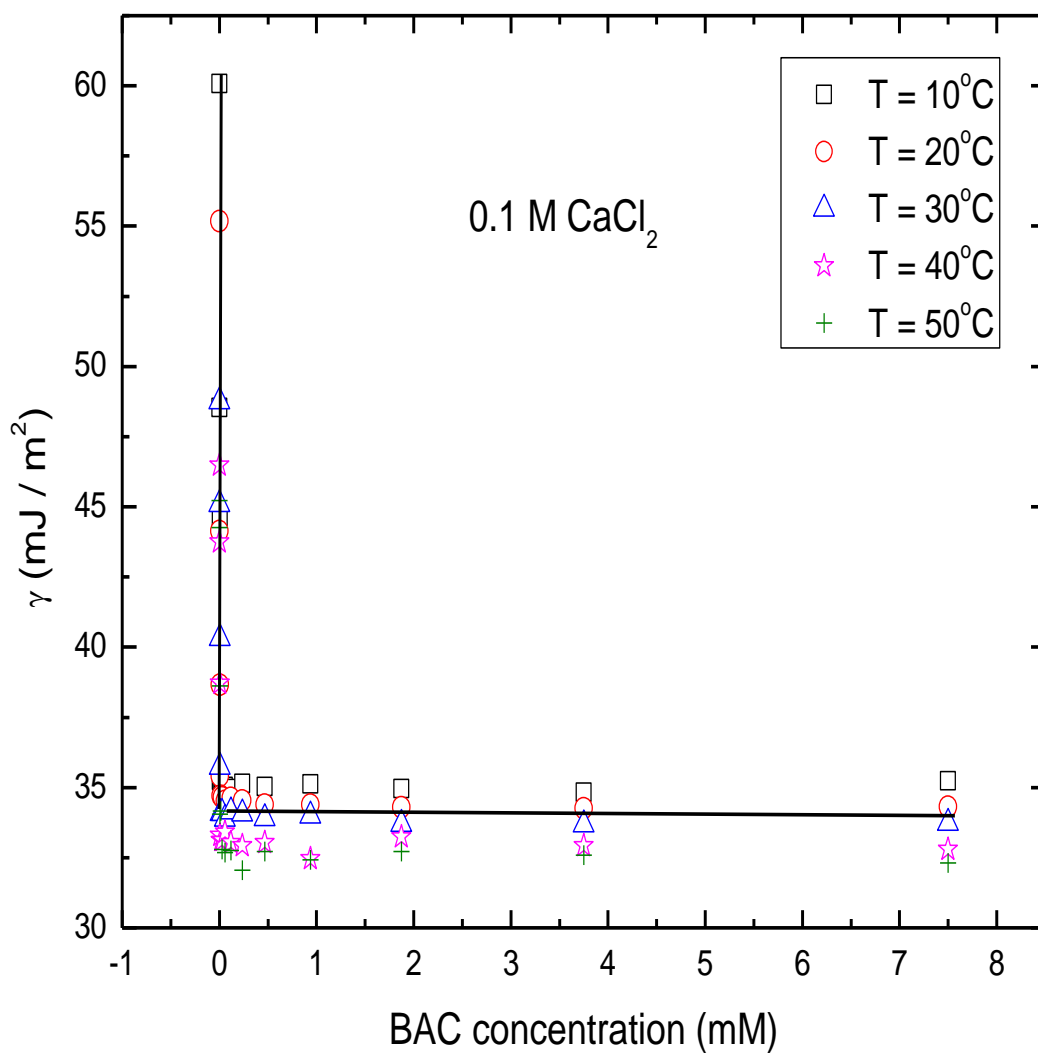


Figure 3.8 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.1 M CaCl₂. Open symbols are the experimental points and the solid line is just to guide the eye.

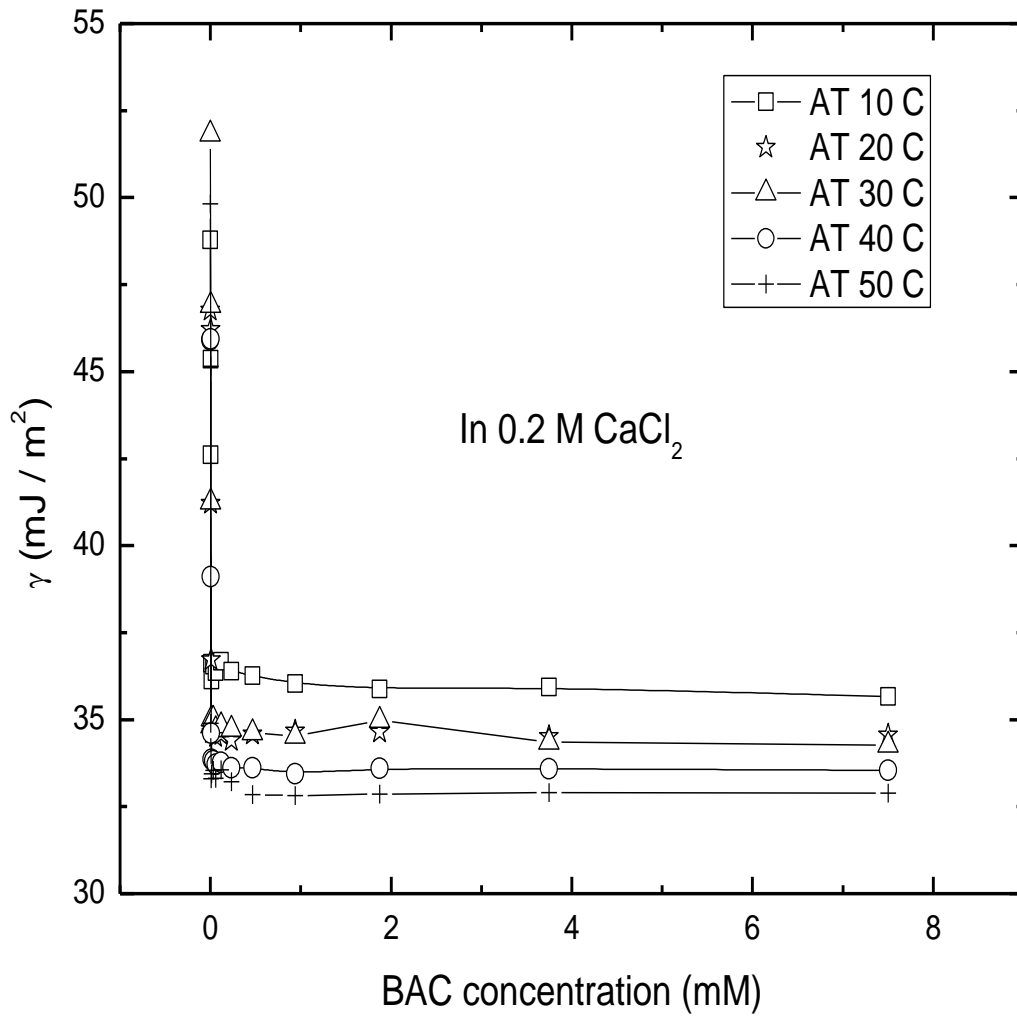


Figure 3.9 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.2 M CaCl₂. Open symbols are the experimental points and the solid line is just to guide the eye.

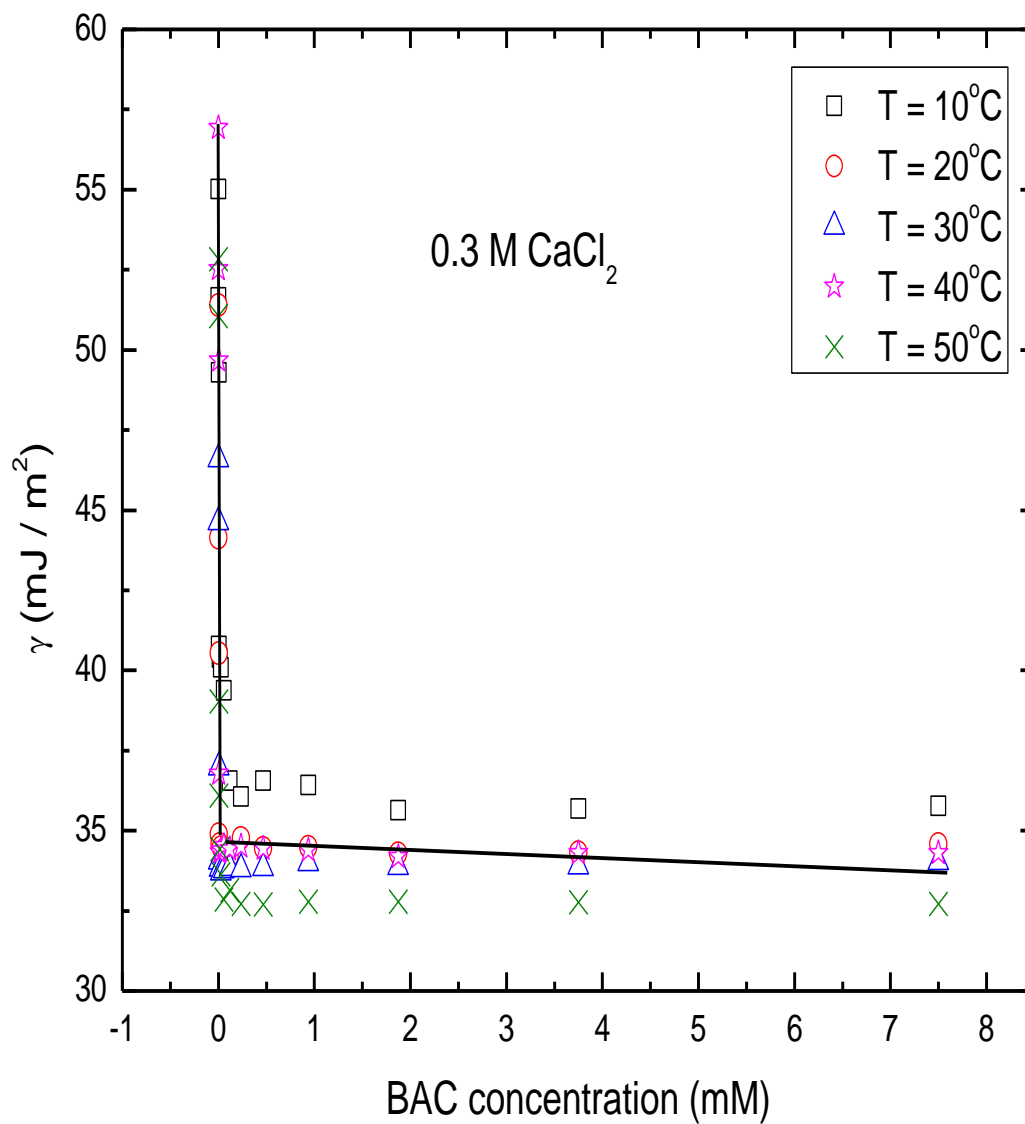


Figure 3.10 Surface tension of BAC aqueous solutions as a function of BAC concentration and temperature in 0.3 M CaCl₂. Open symbols are the experimental points and the solid line is just to guide the eye.

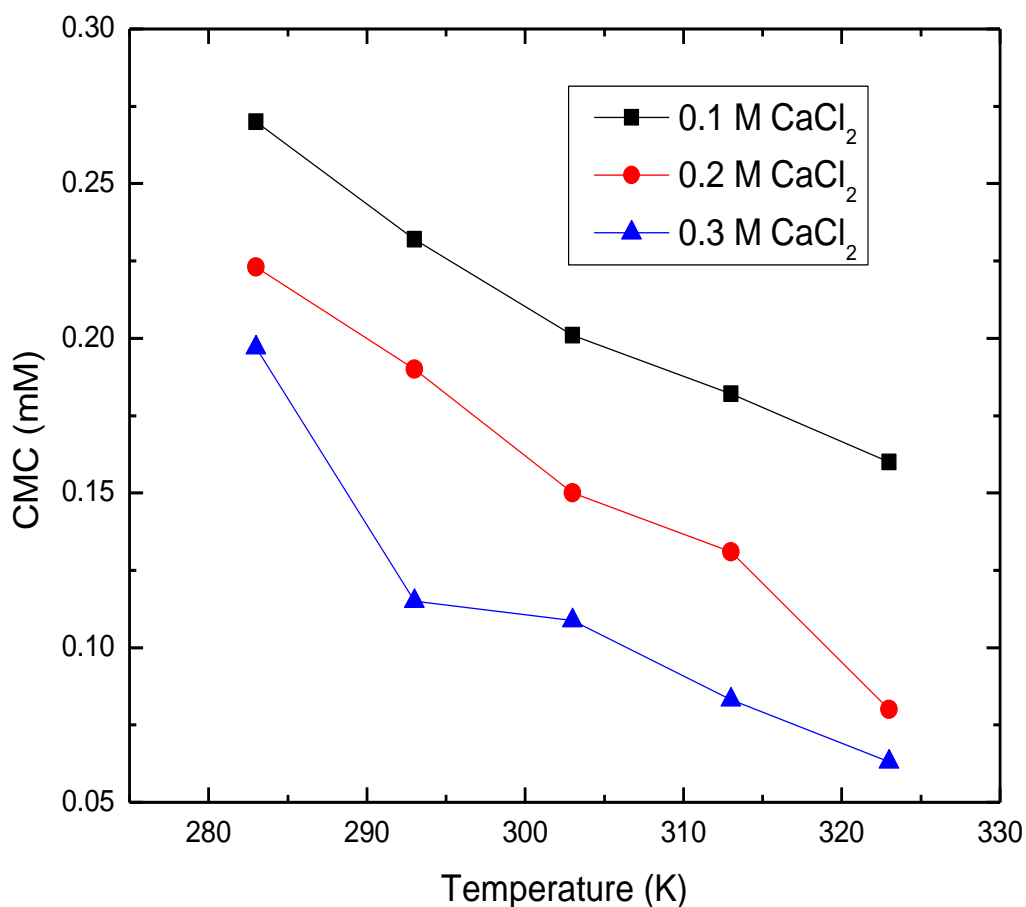


Figure 3.11 Critical micelle concentration of BAC as a function of temperature and at different CaCl₂ concentration as indicated in the figure. The solid lines are just to guide the eye.

3.5. Mixed Surfactant System

The optimization of mixtures of surfactants in aqueous solution is an important part of the formulation of many commercial cleaning products. There are many examples in the literature showing that binary mixtures of different types of surfactants are non-ideal in such a way that important properties of the mixture are quite different from those of the individual species [78-85]. One of the keys to the successful use of mixtures in commercial formulations is to take advantage of this synergy, but the prediction of the properties of such strongly interacting systems is not trivial.

The surface tension of Benzyl-dimethyl-hexadecyl-ammonium chloride/Sodium dodecyl benzene Sulfonate mixture have been measured in this work. Figure 3.12 shows the surface tension of BAC/SDBS mixture as a function of BAC concentration at a fixed amount of SDBS of 0.0184 g at 25 °C.

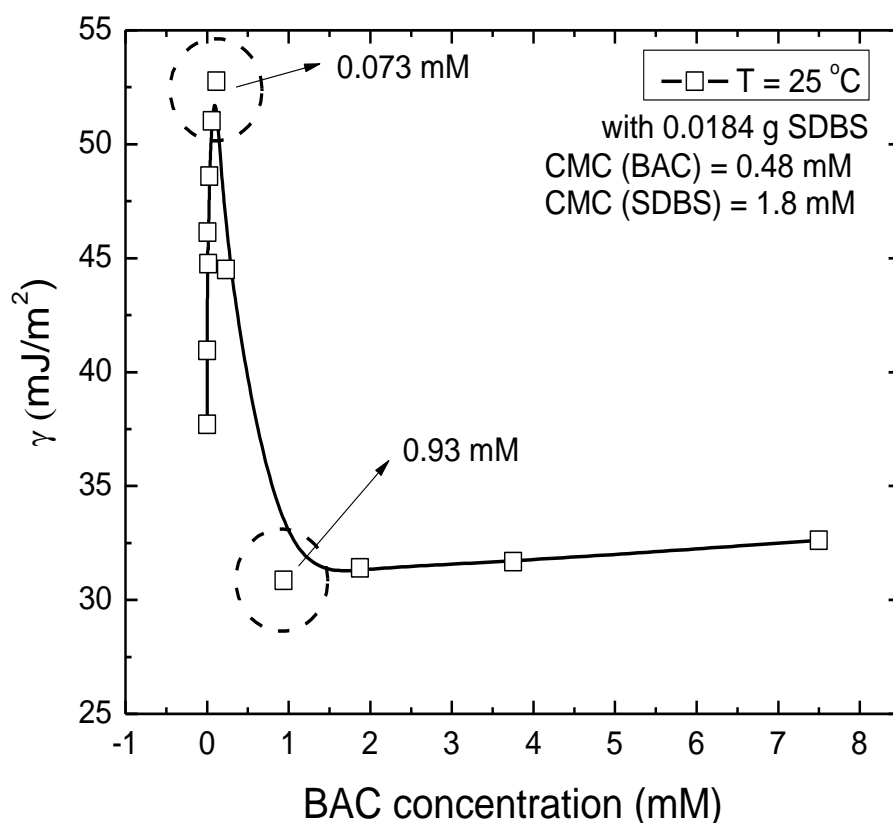


Figure 3.12 Surface tension of BAC/SDBS as a function of BAC concentration at a fixed amount of SDBS of 0.0184 g. The solid line is drawn to guide the eye.

As can be seen from figure 3.12, the surface tension first increases from a value of 38 mJ/m², reaches a maximum of 53 mJ/m² and then decrease to value of 31 mJ/m². The BAC concentration at the maximum is 0.073mM, which is much lower than its CMC of ~ 0.6 mM and also much lower than the CMC of SDBS of 2.7 mM. The amount of SDBS (molar mass 288.3 g/mol) added (0.0184 g) corresponds to 0.063 mM of SDBS. The maximum of the peak occurs at 0.114 mM BAC which is far from–equimolar value of both surfactants. Such a behaviour may be explained as following: at the beginning of the peak (at $\gamma = 38$ mJ/m²) and at very low BAC concentration, the water surface is partially covered with BAC and SDBS.

Since the amount of SDBS is more than that of BAC then there is more SDBS than BAC and the synergetic effect is maximum and the surface tension is low. As more BAC is added this synergetic effect is disturbed as one approaches the 1:1 molar ratio and the surface tension starts to increase. Far from the 1:1 molar ration, there is no charge neutrality and the surface tension is maximum. As more and more BAC is added beyond the 1:1 molar ration and since the CMC of BAC is approached the surface tension starts to decrease again.

Figure 3.13 below shows the surface tension of BAC aqueous solutions as a function of BAC concentration with 0.0241 g SDBS added at 10, 20 ,30 ,40 and 50 °C. The surface tension as is well known decreases with increasing temperature. At all temperatures in figure 13 there is peak in the behaviour of the surface tension as a function of BAC concentration. Again in the beginning the surface tension is very low when the surface is partially covered with both BAC and SDBS and then as more BAC is added the surface tension starts to increase reaches a maximum and then starts decreasing again. However, what is very interesting is that the maximum of the peak shifts to lower BAC concentration as temperature increases and the value of the surface tension occurs at lower values as temperature increases. As temperature increases, the critical micelle concentration of both surfactant decreases and this explains the shift in cmc as temperature increases.

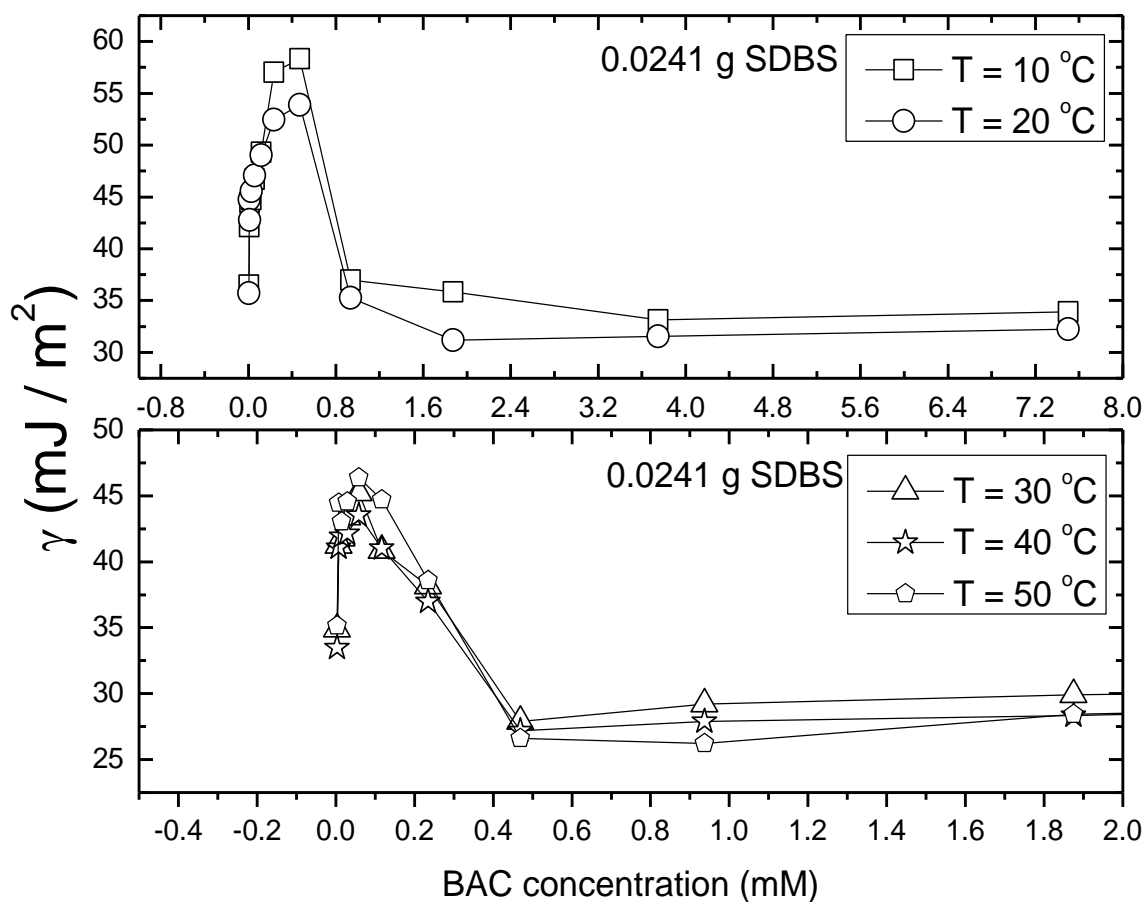


Figure 3.13 Surface tension of BAC aqueous solutions as a function of BAC concentration with 0.0241 g SDBS added at different temperatures. The solid lines are drawn just to guide the eye.

Figure 3.14 shows the surface tension of BAC aqueous solutions as a function of BAC concentration with added 0.0672 g of SDBS at different temperatures as indicated in the figure. This set of data was obtained in pure water. Here again there is peak in the surface tension behaviour as a function of BAC concentration with the addition of SDBS. It has to be mentioned that surfactant mixtures have shown synergetic effects in their surface activity and surface properties. Here again the surface tension decreases with increasing temperature as the maximum of the peak occurs at lower surface tension value. With the exception of the data at $10\text{ }^\circ\text{C}$, the maximum of the peak shifts to lower BAC concentration as temperature increases.

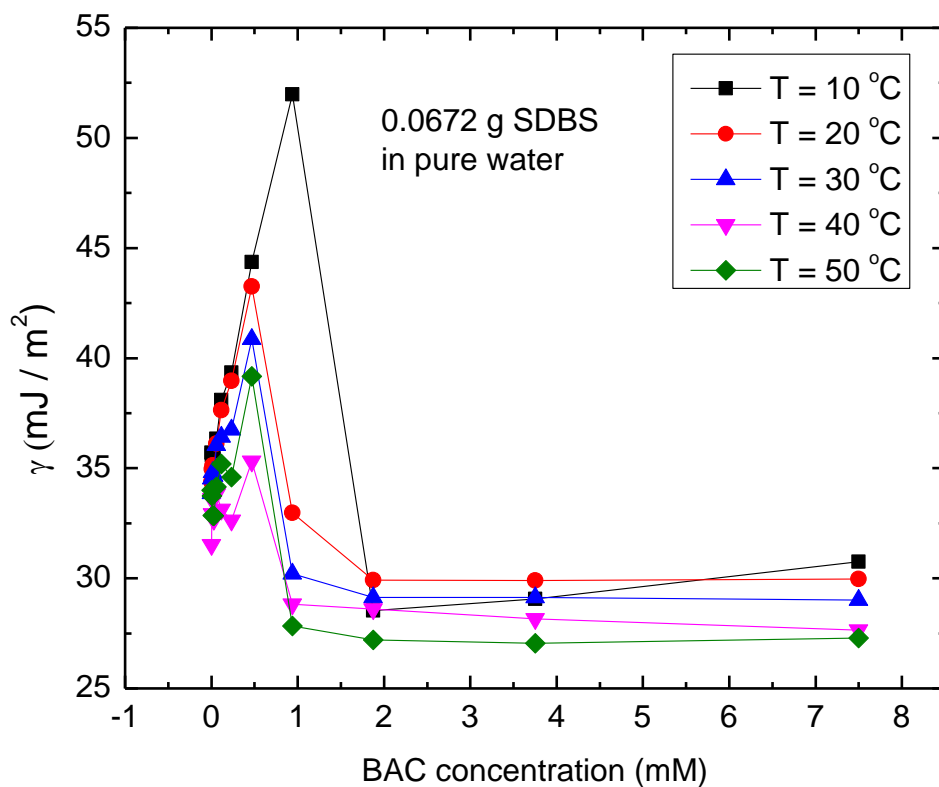


Figure 3.14 shows the surface tension of BAC aqueous solutions as a function of BAC concentration with added 0.0672 g of SDBS at different temperatures as indicated in the figure. This set of data was obtained in pure water.

Figure 3.15 shows the surface tension of BAC concentration as a function of BAC concentration with 0.0672 g of SDBS added at two different temperatures of 10 and 40 degree Celsius. As can be seen, the surface tension decreases with increasing temperature as the maximum of the peak occurs at lower values of the surface tension. In addition, salt addition decreases the value of the surface tension at which the peak maximum occurs. In pure water there is shift in the maximum of the peak to lower BAC concentration while in the presence of the salts there is little shift in the maximum of the peak. The presence of the salt, as was in the case of the individual surfactants is known to decrease the cmc of the surfactant. It seems that the salt screen similar charge repulsion and enhance the charge / charge attraction of dissimilar charges on the surfactants head groups. It seems that the salt enhances the synergetic effect of the mixed surfactant system.

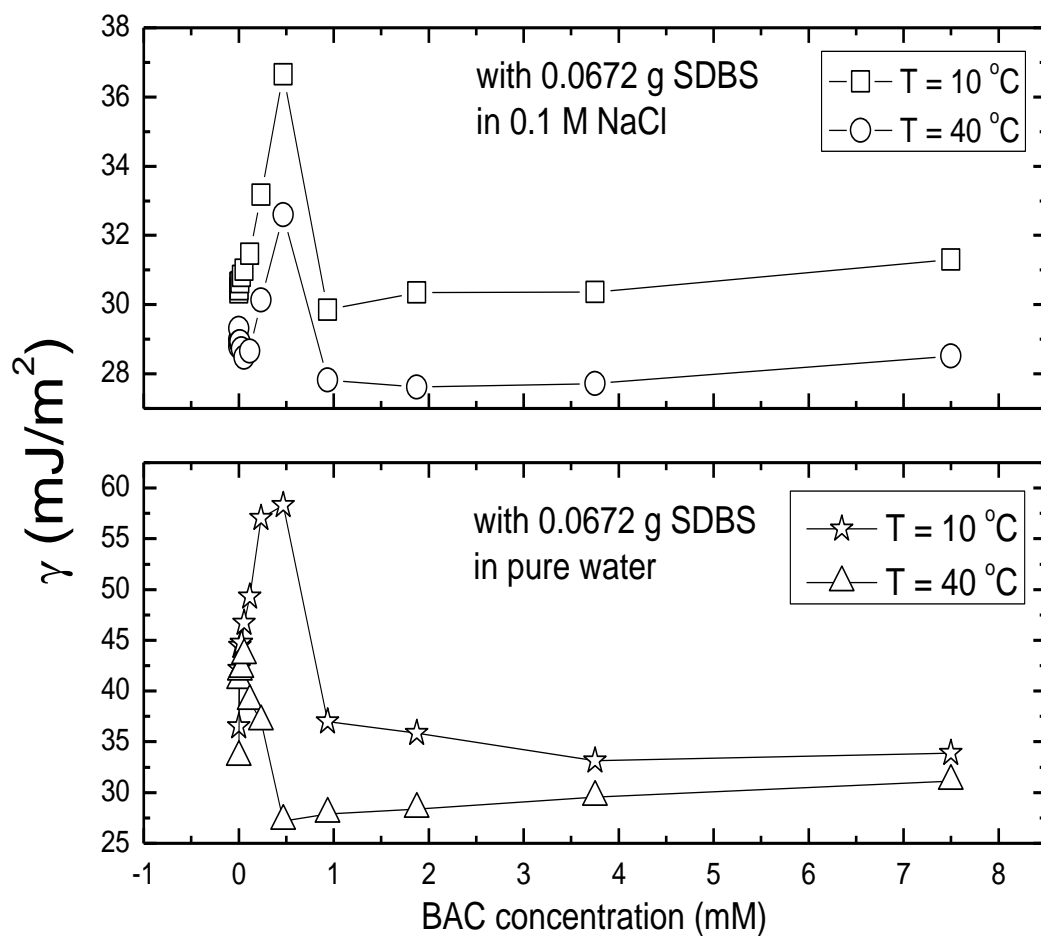


Figure 3.15 Surface tension of BAC aqueous solutions as a function of BAC concentration with 0.0672 g SDBS added at two different temperatures. The solid lines are drawn just to guide the eye.

The surface tension of BAC aqueous solutions as a function of BAC concentration at different temperatures is shown in figure 16. In the latter figure, the surface tension in the beginning is very **low** and as more BAC is added it starts to increase reaching a maximum value and then starts to decrease. This is almost the same behaviour as before. The maximum of the peak decreases with increasing temperature.

The surface tension at the maximum of the observed peak as a function of the amount of SDBS added is shown in figure 3.17. It can be seen that the surface tension at the maximum of the peak decreases with increasing the added SDBS amount. This effect indicates that the synergetic effect is more the higher the SDBS added amount.

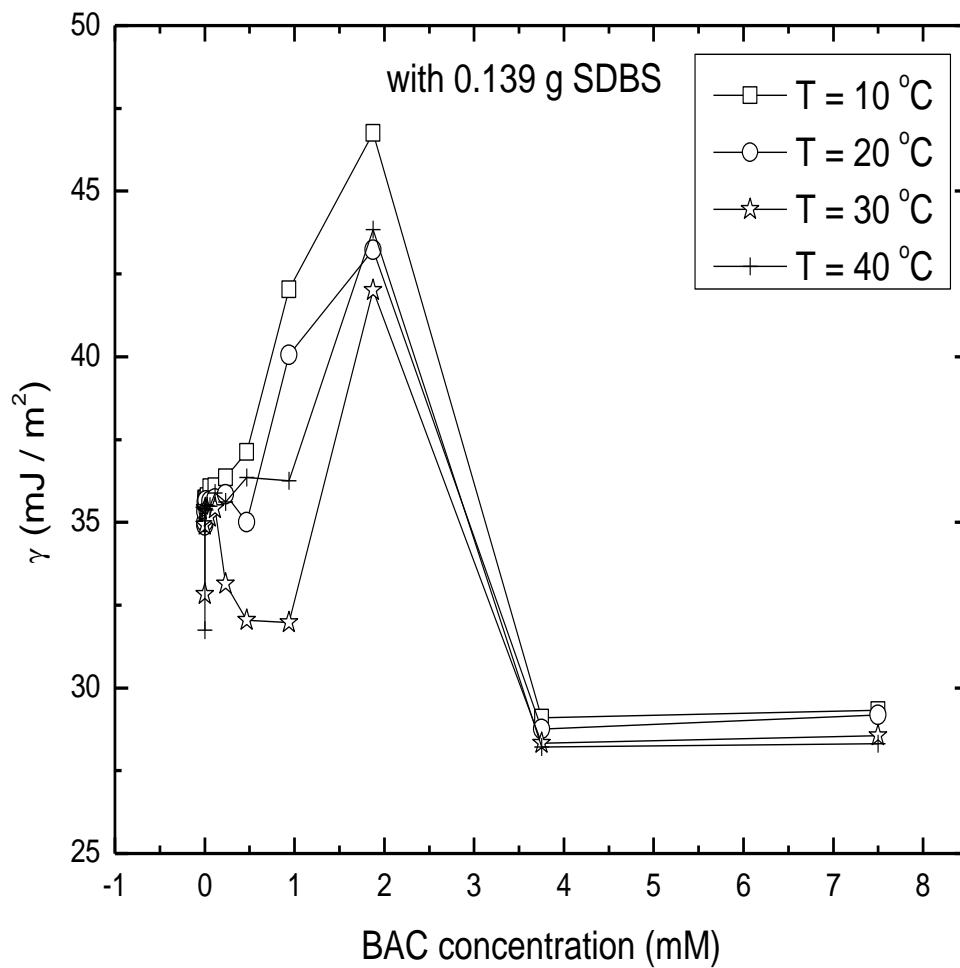


Figure 3.16 Surface tension of BAC aqueous solutions as a function of BAC concentration with 0.139 g SDBS added at two different temperatures.

The solid lines are drawn just to guide the eye.

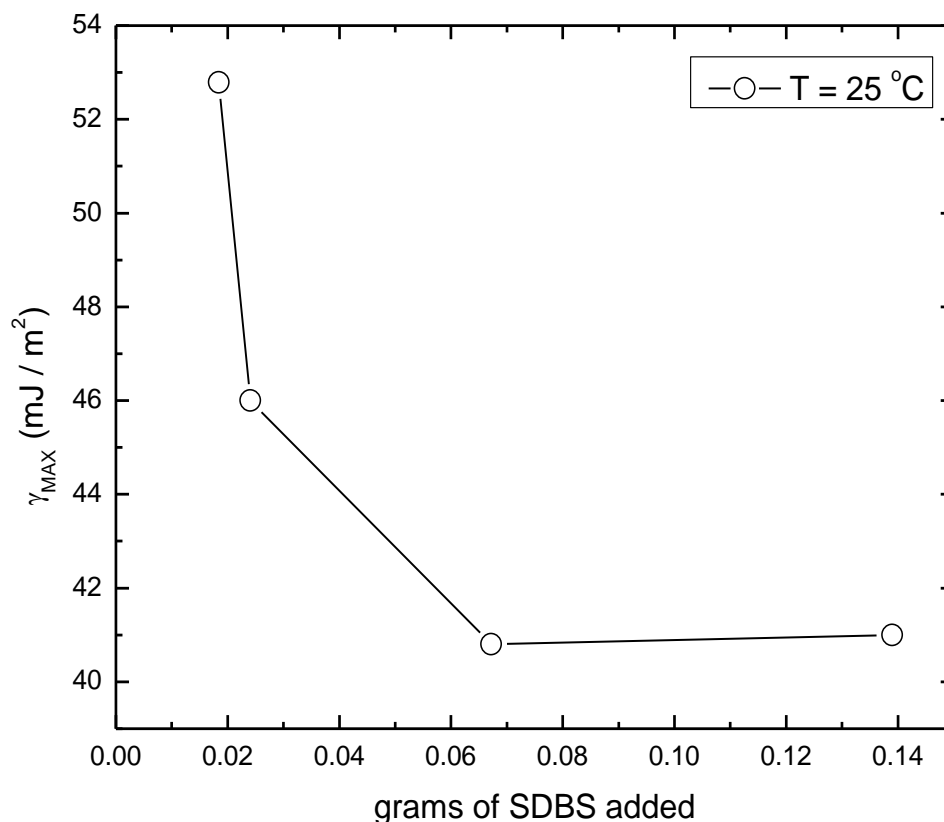


Figure 3.17 Surface tension at the peak maximum as a function of added amount of SDBS. The solid line is just drawn to guide the eye.

3.6 Conclusions :

In this work, the surface tension of the aqueous solution of pure Benzyl-dimethyl-hexadecyl-ammonium chloride and its mixture with Sodium dodecyl benzene Sulfonate and their mixture at different temperatures was studied. The following can be concluded;

1. For the surface tension of aqueous solutions of pure Benzyl-dimethyl-hexadecyl-ammonium chloride at different temperature and different salts concentration, the surface tension was found to decrease with increasing temperature.
2. For the same system in point a, the critical micelle concentration was found to decrease with increasing temperature and added salt.
3. Changing the valency of the cation of the added salt has no effect on the value of the critical micelle concentration of Benzyl-dimethyl-hexadecyl-ammonium chloride.

4. For the surface tension of a mixture of Benzyl-dimethyl-hexadecyl-ammonium chloride with the anionic surfactant SDBS, a peak was observed in the behaviour of the surface tension as a function of BAC concentration.
5. The maximum of the observed peak was found to decrease with increasing temperature and addition of NaCl salt.
6. The surface tension at the maximum of the peak is found to decrease with increasing the amount of added SDBS.
7. Synergetic effect was found in the entire mixture range studied.

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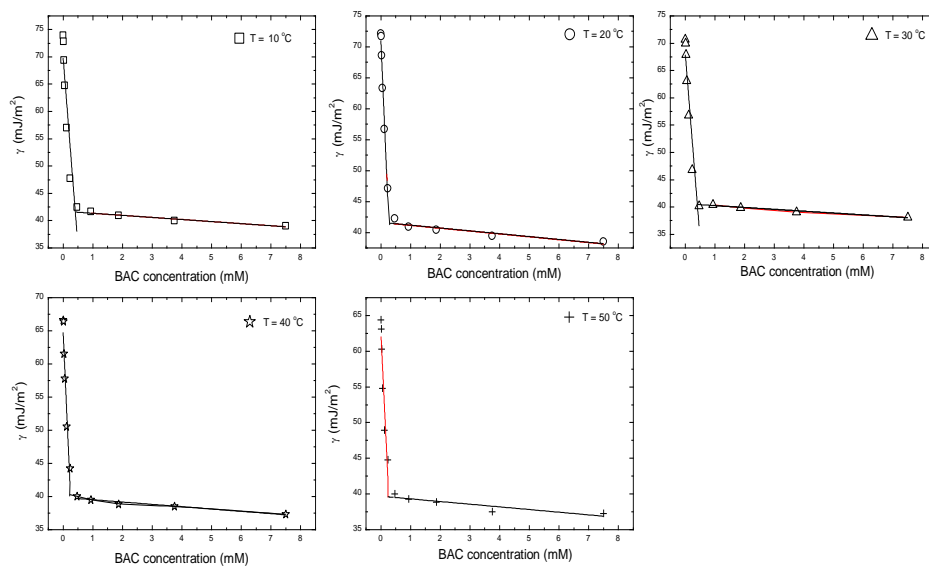
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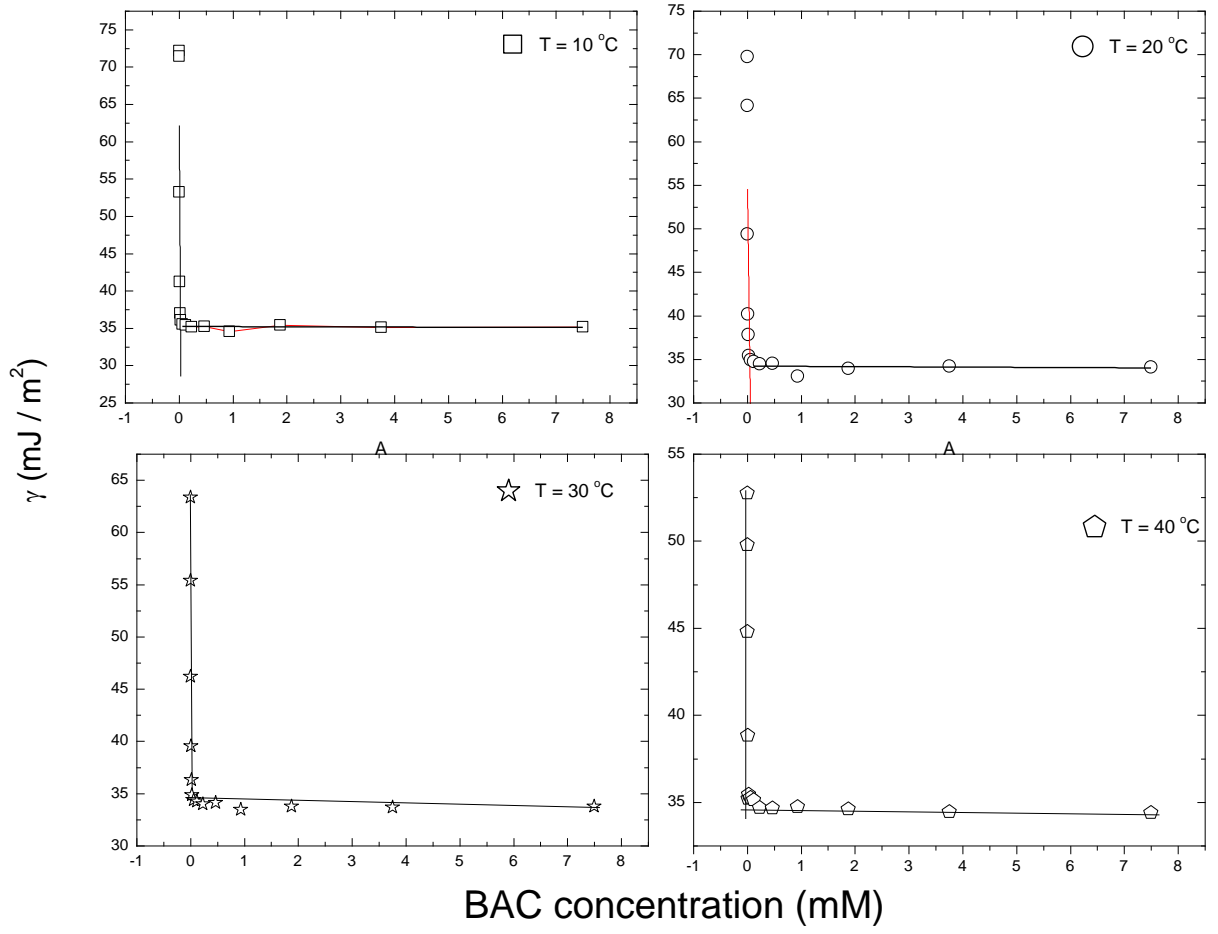
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Appendix

in pure water



in 0.1 M NaCl



16-BAC with 0.0241 gm SDBS and 0.1M NaCl

Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
28.11	28.05	28.55	28.89	29.77	0.00366
28.46	27.94	28.71	29.18	29.79	0.00732
28.41	27.7	28.46	29.09	29.98	0.01464
28.76	27.83	28.69	29.3	30.11	0.02929
28.94	28.44	28.92	29.61	30.82	0.05859
31.55	29.66	32.39	32.98	33.89	0.11719
35.36	31.98	35.8	37.34	37.91	0.23437
25.66	26.59	27.79	29.17	30.75	0.46875
25.89	26.28	27.61	28.9	29.35	0.9375
26.22	27.21	28.9	29.6	30.12	1.875
27.52	27.18	28.62	29.69	30.98	3.75
29.12	29.5	29.72	29.9	30.97	7.5

16-BAC with 0.1M NaCl

Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
52.55	52.74	63.36	69.74	72.17	9.15E-04
47.27	49.78	55.39	64.15	71.43	0.00183
43.46	44.78	46.18	49.38	53.26	0.00366
38.23	38.83	39.54	40.2	41.23	0.00732
34.48	35.21	36.32	37.81	37	0.01464
34.75	35.45	34.86	35.4	36.1	0.02929
34.92	35.25	34.36	34.94	35.52	0.05859
34.18	35.13	34.23	34.71	35.42	0.11719
34.38	34.68	34	34.45	35.18	0.23437
34.19	34.64	34.1	34.54	35.2	0.46875
34.11	34.74	33.45	33.07	34.55	0.9375
34.33	34.61	33.78	33.96	35.4	1.875
34.24	34.45	33.67	34.2	35.08	3.75
34.15	34.4	33.78	34.1	35.14	7.5

BAC with 0.2 M NaCl					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
50.24	50.76	50.83	54.59	60.74	9.15E-04
46.7	47.34	49.6	53.72	58.26	0.00183
40.51	42.38	43.53	47.49	50.53	0.00366
35.14	34.8	37.1	38.15	38.01	0.00732
33.92	34.24	34.98	35.65	36.05	0.01464
33.65	34.48	34.69	35.05	36.19	0.02929
33.98	34.36	34.56	35.03	36.08	0.05859
33.75	34.18	34.55	34.82	35.88	0.11719
33.37	34.14	34.36	35.02	35.87	0.23437
33.78	34.39	34.35	35.04	35.8	0.46875
33.52	34.2	34.39	34.98	35.89	0.9375
33.57	33.93	34.34	35	35.8	1.875
33.54	33.64	34.72	34.68	35.86	3.75
33.61	34.1	34.17	35.22	35.9	7.5

BAC with 0.3 M NaCl					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
47.7	50	61.92	67.73	74.18	9.15E-04
42.48	42.09	40.4	43.38	52.11	0.00183
36.39	35.42	36.83	40.18	49.99	0.00366
34.15	34.19	36.52	37.57	37.72	0.00732
33.97	33.99	34.68	35.72	36.29	0.01464
34.05	33.97	34.7	34.87	36.14	0.02929
33.31	33.93	34.16	34.85	35.86	0.05859
33.35	34.07	34.35	34.98	35.63	0.11719
33.67	34.23	34.31	34.95	35.75	0.23437
33.83	34.27	34.39	34.78	35.77	0.46875
33.84	33.97	34.4	35	35.62	0.9375
33.9	34	33.9	34.65	35.56	1.875
33.95	34.56	34.14	34.66	35.3	3.75
33.74	34.61	33.89	34	34.95	7.5

BAC with 0.1 M CaCl₂					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
45.23	46.48	48.76	55.17	60.07	9.15E-04
44.26	43.74	45.1	44.13	48.53	0.00183
38.62	38.72	40.32	38.66	44.65	0.00366
34.05	33.29	35.73	35.4	35.25	0.00732
34.16	33.1	34.09	34.69	34.94	0.01464
32.79	33.1	34.08	34.64	34.95	0.02929
32.68	33.4	33.89	34.51	35.03	0.05859
32.76	33.03	34.14	34.62	34.95	0.11719
32.05	32.92	34.07	34.54	35.15	0.23437
32.71	33.03	33.9	34.39	35.04	0.46875
32.42	32.46	34	34.38	35.13	0.9375
32.72	33.23	33.7	34.3	34.95	1.875
32.59	32.92	33.69	34.25	34.82	3.75
32.31	32.8	33.74	34.31	35.23	7.5

BAC with 0.3 M CaCl₂					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
52.83	56.93	46.6	51.4	55.01	9.15E-04
51.05	52.52	44.63	44.13	51.63	0.00183
39.03	49.67	36.98	40.54	49.3	0.00366
36.09	36.78	34.05	34.88	40.76	0.00732
34.43	34.32	33.82	34.57	40.4	0.01464
33.64	34.39	33.71	34.47	40.09	0.02929
32.85	34.52	33.78	34.38	39.38	0.05859
33.15	34.43	33.85	34.2	36.55	0.11719
32.71	34.5	33.81	34.76	36.07	0.23437
32.7	34.44	33.85	34.46	36.56	0.46875
32.79	34.39	34	34.49	36.42	0.9375
32.79	34.18	33.88	34.29	35.64	1.875
32.76	34.3	33.89	34.32	35.69	3.75
32.72	34.3	34.03	34.57	35.77	7.5

BAC with 0.0241 gm SDBS

Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
35.13	33.47	34.9	35.69	36.5	0.00366
44.45	41.07	41.25	44.73	42.14	0.00732
43.03	41.91	41.8	42.78	44.45	0.01464
44.54	42.15	43.38	45.54	44.72	0.02929
46.37	43.51	45.23	47.05	46.7	0.05859
44.72	35.92	40.87	49.04	49.29	0.11719
38.57	36.97	38.17	52.45	57.02	0.23437
26.62	27.17	27.88	53.88	58.32	0.46875
26.22	27.9	29.2	35.25	36.99	0.9375
28.43	28.35	29.9	31.19	35.85	1.875
29.6	29.56	30.6	31.53	33.13	3.75
31.25	31.13	30.3	32.23	33.9	7.5

BAC with 0.0672 SDBS

Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
33.99	31.52	33.87	34.38	35.7	0.00366
33.74	33.6	34.53	34.95	35.59	0.00732
32.86	32.92	34.82	35.12	35.52	0.01464
32.84	32.66	34.64	35.01	35.45	0.02929
34.15	33.82	36.05	36.12	36.34	0.05859
35.19	33.13	36.43	37.64	38.1	0.11719
34.6	32.63	36.75	38.97	39.35	0.23437
39.18	35.32	40.86	43.25	44.36	0.46875
27.84	28.83	30.2	32.98	51.97	0.9375
27.2	28.61	29.13	29.91	28.53	1.875
27.05	28.16	29.14	29.9	29.07	3.75
27.29	27.64	29.02	29.97	30.75	7.5

BAC without addition					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
64.41	66.55	70.67	72.11	73.9	0.00732
63.1	66.38	69.99	71.68	72.75	0.01464
60.27	61.49	67.91	68.59	69.35	0.02929
54.78	57.78	63.12	63.29	64.71	0.05859
48.9	50.54	56.78	56.66	57	0.11719
44.78	44.22	46.8	47.07	47.69	0.23437
37.52	37.84	40.16	42.22	42.42	0.46875
39.3	39.49	40.44	40.88	41.6	0.9375
38.84	38.84	39.82	40.39	40.88	1.875
37.5	38.49	39.09	39.42	39.96	3.75
37.24	37.3	38.1	38.46	38.99	7.5

BAC with 0.139 gm SDBS				
Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
31.75	32.82	34.91	35.72	9.15E-04
35.04	34.92	35	35.46	0.00183
35.42	35.35	35.32	35.57	0.00366
35.42	35.41	35.61	35.68	0.00732
35.37	35.35	35.66	35.72	0.01464
35.5	35.34	35.34	35.78	0.02929
35.48	35.16	35.64	36.06	0.05859
35.89	35.42	35.71	36.08	0.11719
35.62	33.14	35.84	36.36	0.23437
36.35	32.04	35	37.12	0.46875
36.26	31.97	40.05	42.03	0.9375
43.84	42	43.23	46.76	1.875
28.22	28.33	28.76	29.1	3.75
28.32	28.56	29.19	29.32	7.5

BAC WITH 0.2M CaCl₂					
Y(Mn/m) AT 50 C	Y(Mn/m) AT 40 C	Y(Mn/m)AT 30 C	Y(Mn/m)AT 20 C	Y(Mn/m) AT 10 C	Molarity of BAC(mM)
49.82	51.83	45.91	46.76	48.78	9.15E-04
45.16	46.91	45.94	46.2	45.35	0.00183
34.9	41.26	39.1	41.21	42.61	0.00366
33.3	34.82	34.61	36.71	36.61	0.00732
33.44	35.02	33.86	34.62	36.13	0.01464
33.54	35.01	33.82	34.61	36.56	0.02929
33.31	34.71	33.72	34.51	36.38	0.05859
33.56	34.82	33.77	34.57	36.67	0.11719
33.21	34.72	33.62	34.4	36.39	0.23437
32.85	34.62	33.61	34.58	36.26	0.46875
32.82	34.52	33.45	34.66	36.03	0.9375
32.86	34.98	33.6	34.64	35.88	1.875
32.9	34.35	33.59	34.51	35.94	3.75
32.89	34.27	33.54	34.55	35.67	7.5