

Chapter III

**Physico - chemical behaviour of dodecylbenzene
sulfonate micelles as influenced by counter ion
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3.1 Introduction and review of the previous work

The study of surface chemistry is not applicable for only academic interest but also for various technological applications in industry and our daily lives including different biological fields. Surfactants modify the surfaces or interfaces of the systems in which they are contained. Surfactants have the ability to locate at the surfaces, thereby altering significantly the physical properties of the interfaces [1]. Due to characteristics molecular structure of the surfactant molecules they can be adsorbed between two immiscible liquids or between the liquid-gas or between a solid and a liquid. A surfactant molecule must contain two different parts in their structures, a hydrophilic part which likes polar molecules and a hydrophobic part which does not likes polar molecules but likes non-polar molecules. So, they are often called amphiphiles. The non-polar part which generally consists of long chain hydrocarbon is also called a 'tail' whereas the polar part is termed as "head". Their composite character is described by a property known as "hydrophobic lipophilic balance" i.e., HLB. It is the HLB which primarily decides their micellization, dispersion and emulsification activities [2-8]. Usually the long chain hydrocarbon acts as the hydrophobic part with which the hydrophilic part is attached and the latter determines the general classification of the surfactant molecules. Generally, the hydrophilic part is of four types, viz., cationic, anionic, nonionic and zwitterionic [9].

As has already been mentioned, surfactant aggregates become popular to the researchers in recent years due to a huge benefit achieved in many industries producing detergents, cosmetics and pharmaceuticals which have surfactants as one of their constituents [10-12]. Surfactant molecules in aqueous media form micelles above their critical micelle concentration (cmc), accompanying striking changes in the

various physico-chemical properties [13-14]. With increasing surfactant concentration the micelles undergo a special set of structural transitions, transforming from spherical shape into cylindrical, rodlike or long threadlike, disk-like vesicles and other supramolecular shapes [15]. The shapes of the micelles depend upon the environments of the surfactants as well.

1. Spherical micelles are formed with the interior composed of hydrocarbon chains and a surface of polar head groups facing water. Spherical micelles are characterized by a low aggregation number (critical packing parameter) and the hydrocarbon core has a radius close to the length of the extended alkyl chain.
2. Cylindrical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups facing water. The cross section of the hydrocarbon core is similar to that of spherical micelles. The micellar length is highly variable to these micelles are polydisperse in nature.
3. Surfactant bilayers which build up lamellar liquid crystals for surfactant water systems having a hydrocarbon core with a thickness of about 80% of the length of two extended alkyl chains.
4. Reverse or inverted micelles having a water core surrounded by the surfactant polar head groups. The alkyl chains together with a non-polar solvent make up the continuous medium.
5. A bicontinuous structure with the surfactant molecules aggregated into a connected films characterized by two curvature of opposite sign. The mean curvature is small (zero for a minimal surface structure).
6. Vesicles are built from bilayers similar to those of the lamellar phase and are characterized by two distinct water components, with one forming the

core and the one the external medium. Vesicles may have different shapes and there are also reversed-type vesicles.

The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH and ionic strength [16-17]. In water, the hydrophilic "heads" of surfactant molecules are always in contact with the solvent, regardless of whether the surfactants exist as monomers or as part of a micelle formation. However, the lipophilic "tails" of surfactant molecules have less contact with water when they are part of a micelle – this being the basis for energetic drive for micelle formation. Those micelles which are composed of ionic surfactants have an electrostatic attraction to the ions that surround them in solution, the latter known as counterions. Although the closest counterions partially mask a charged micelle, the effects of micelle charge affect the structure of the surrounding solvent at appreciable distances from the micelle. Adding salts to a colloid containing ionic micelles can decrease the strength of electrostatic interactions and lead to the formation of larger ionic micelles [18]. This is more accurately seen from the point of view of an effective charge in hydration of the system. Since surfactant solutions can have certain aggregation structures which are responsible for giving the solution its physical properties, they are sometimes defined as complex fluids. However, Gruen has described a realistic model for micelle which involves a rather sharp interface between a dry hydrophobic hydrocarbon core and a region filled with surfactant head groups, part of the counterions and water, viz., the stern region [19].

Over a very small concentration range, the cmc value is usually determined from the abrupt change in physical properties. It is possible to distinguish between methods examining the behaviour of a bulk solution property such as surface tension, conductance, light scattering etc. and those using some spectroscopic property. Counterion binding and diffusion coefficient of a micelle, compared with that of a single surfactant molecule, together explain the sudden decrease in equivalent conductivity of a surfactant solutions beyond the cmc. Micelles only form when the concentration of surfactant is greater than the cmc, and the temperature of the system is greater than the critical micelle temperature or Krafft temperature. Micelles can form spontaneously because of a balance between entropy and enthalpy. In water, the hydrophobic effect is the driving force for a micelle formation, despite the fact that

assembling surfactant molecules together reduces their entropy. Above the cmc, the entropic penalty of assembling the surfactant molecules is less than the entropic penalty of caging the surfactant monomers with water molecules. Also important are enthalpic considerations, such as the electrostatic interactions that occur between charged parts of surfactants. The parameters that illustrates the temperature dependence of hydrophobic effect is the heat capacity of micellization ($\Delta_{mic}C_p^0$) which is generally highly negative and mainly reflects the amount of non-polar solvent accessible area buried on micellization [19].

Spherical micelles are formed by ionic surfactants since the electrostatic repulsion between adjacent head groups result in a large value for optimal head group area. Direct visualization was made by Bellare et al. in a cryo-TEM image of 10 mM solution of ditetradecyldimethyl-ammonium acetate with a micelle radius of 3.0 ± 0.3 nm [4]. The most precise dimension of spherical micelle has been established by small angle neutron scattering technique.

There are so many different studies of counterions on the aggregation behaviour of surfactants to understand the adsorption kinetics and surface rheology [20-21]. In these studies, it has been proved that various parameters, viz., Gibbs elasticity (E_G) etc., determined by theoretical and experimental way differs very much from each other which perhaps due to counterion bindings with the surfactant molecules. Further study proves that the effects are less important in case of non-ionic surfactants. The counterion binding alters the interactions in surfactant adsorption monolayer and the average surface charge density [20]. In the old literature, ionic micelle's counterion binding was not considered importantly [22-23]. In so many recent works, the importance of counterion bindings have been recognized as a important factor for the micellization process and the mole fraction scale have been used to evaluate the energetics of the process [24-26]. It has been shown by researchers that the counterion has also pronounced effects on the various properties of the micelles of anionic and cationic surfactants [27-29]. The study of the effect of counterions eliminates some of the complications by leaving the properties of the amphiphilic ion as a constant factor and thus simplifies some of the interpretation of the experimental results. But, it often leads to complications connected with limited stability and preparative difficulties of the surfactant containing different counterions. It has been shown that the shape of micelle of cetyltrimethyl ammonium bromide (CTAB) is spherical over a large concentration range and also in presence of additives

[30]. The most of the work for containing counterion has been carried out for the single tail anionic surfactants mainly on sodium dodecyl sulfate [31-33]. Though there is some amount of work done on the counterionic properties of double traileed surfactant, AOT [34].

Surfactant molecules show dramatic temperature dependability. For many ionic surfactants, the solubility is very low at low temperature but increases with increase in temperature by orders in a narrow temperature range. The phenomenon is generally known as Krafft Phenomenon and the temperature is known as the Krafft Temperature [13, 35]. The effects shown by the surfactant at Krafft temperature is best described as due to micellization of the surfactant molecules.

3.2. Effect of counter ion in aqueous medium

The aggregation number of ionic micelles depends on the counterions at a constant temperature in the aqueous phase. Surfactants having more tightly bound counterions with the hydrophobic part show more non-ionic nature than those surfactants with loosely bound counterions. As we know, the more non-ionic character, the less is the solubility in water and more non-spherical shape in aqueous solution. It was observed that most of the counterions interact with the surfactant by electrostatic interaction only; no chemical interactions are present in between surfactant molecules and counterions [24, 26-28, 36]. Zana et al. have reported that the degree of binding of counterion is related to the surface area per head group in the micelle in a number of experiments on cationic surfactants with varying counterions [14]. The surface area per head group decreases with degree of binding of counter ions. Ionic micelles grow in response to increase in the value of whether the counterions are provided by the added electrolytes or the surfactant alone [37]. Counterion binding also increases with the addition of electrolyte to the surfactant system and it will also increase with the increase of surfactant concentration because increasing concentration of the surfactants produces micellar growth in the solution [26, 28]. As stated above, the aggregation number of ionic micelle depends only upon the concentration of ionic surfactants in aqueous phase which can be defined below by the equation:

$$C_{aq} = F(S_t) [\alpha S_1 + (1 - \alpha) S_m] \quad (3.1)$$

where, S_t and S_m are the total concentration of the surfactant and monomeric concentration of the surfactant respectively. The factor $F(S_t) = \frac{1}{(1-\theta)}$, where θ is related to the volume fraction occupied by the micelle.

In this present work, a series of counterionic activity of DBS moiety was measured by preparing surfactants with respective counterions in the temperature range 283 K to 313 K with an interval of 5 K. The counterions investigated are monovalent alkali metals counterion, viz., Li^+ , Na^+ , K^+ and also ammonium and different tetraalkyl ammonium counterions, viz., tetramethyl ammonium, tetraethyl ammonium, tetrapropyl ammonium and tetrabutyl ammonium counterions. The objective of this present work is to determine the cmc of the surfactant as a function of counter ion size and hydrophobicity at various temperatures in aqueous medium and to find out the different thermodynamic parameters and surface parameters, viz., standard Gibb's free energy of micellization (ΔG_m^0), standard enthalpy of micellization (ΔH_m^0), standard entropy of micellization (ΔS_m^0), heat capacity of micellization ($\Delta_{mic} C_p^0$), minimum surface area per molecule (A_{min}) and maximum surface excess concentration (Γ_{max}) at the air / water interface. This is a part of the series of work done in our laboratory on the influence of counter ions of dodecyl sulfate, AOT and DBS moiety to understand the effect of different alkali metal ions and organic ions with hydrophobic chain length on the micelle formation. Since very little work of this type is reported in the literature [38], a comparative data for three surfactants with varying hydrophobic chain length is also presented to understand the effect.

3.3. Thermodynamics of micellization: The Mass-Action model

Among many theories proposed and reviewed by different researchers [39-42], mass action model has wide acceptance. In the mass-action model [34], the micelle formation is followed as a chemical equilibrium between free surfactant and micelle.

In solution, the formation of aggregates from free surfactant can be represented, as shown in equation (3.2).



where n is the number of free surfactant molecules (S), which form a micelle (S_n). Both micelles and free surfactants are treated as solutes in an aqueous solution. In the mass-action model, the thermodynamic formulations are slightly different for non-ionic and ionic surfactant solutions. Such thermodynamic formulations may be described as follows (Blandamer and et al.):

For non-ionic (neutral) surfactant solutions, at equilibrium, we have:

$$n_g \mu_{i,mon} = \mu_{i,micelle} \quad (3.3)$$

where $\mu_{i,mon}$ is the chemical potential of monomer (free) surfactant i , $\mu_{i,micelle}$ is the chemical potential of surfactant i in the micelle form, n_g is the aggregation number. The chemical potentials of monomeric surfactant and surfactant in micelle are given as:

$$\mu_{i,mon} = \mu_{i,mon}^0 + RT \ln x_{i,mon} \gamma_{i,mon} \quad (3.4)$$

$$\mu_{i,micelle} = \mu_{i,micelle}^0 + RT \ln x_{i,micelle} \gamma_{i,micelle} \quad (3.5)$$

Now, we have

$$\Delta G_{i,m}^0 = \frac{1}{n_g} \mu_{i,micelle}^0 - \mu_{i,mon}^0 = RT \ln x_{i,mon} \gamma_{i,mon} - \frac{1}{n_g} RT \ln x_{i,micelle} \gamma_{i,micelle} \quad (3.6)$$

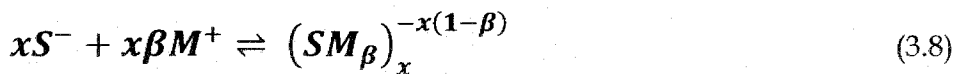
where $x_{i,mon}$ and $x_{i,micelle}$ are the mole fraction of monomeric surfactant and surfactant in micelle, respectively, where $\gamma_{i,mon}$ and $\gamma_{i,micelle}$ are the activity coefficients and $\mu_{i,mon}^0$ and $\mu_{i,micelle}^0$ are the standard state chemical potential of the same, $\Delta G_{i,m}^0$ is the standard Gibbs energy of micellization.

For a dilute solution, the activity coefficients of monomeric surfactant and surfactant in micelle are set equal to 1. Then, equation (3.6) becomes

$$\Delta G_{i,m}^0 = RT \ln x_{i,mon} - \frac{1}{n_g} RT \ln x_{i,micelle} \quad (3.7)$$

In surfactant solution, the total concentration of surfactant, x_{tot} , which is a sum of free surfactant, $x_{i,mon}$ and surfactants in micelles, $x_{i,micelle}$. Assuming a sufficiently high value for n_g , the second term in the above equation become very small and can be neglected. Then $x_{i,mon}$ can be approximated to cmc.

But for ionic surfactants the micellization equilibrium can be expressed as:



where $(SM_\beta)_x$ is the micelle composed of x surfactant monomers and $x\beta$ counterions bearing S^- and M^+ as the monomer and counterion of the surfactant forming micelles. The value of β may corresponds the fraction of bound counterion in the micelle. But for nonionic surfactants monomers and micelles are obviously uncharged and M^+ does not enter to the equation and the model approaches to a limiting case having $\beta = 0$. However, applying the mass action law to the monomer-micelle equilibrium for the ionic surfactant, and taking into account the charges of counterion along with the other parameters, the Standard Gibbs free energy, ΔG_m^0 can be expressed as [24, 39, 43]:

$$\Delta G_{i,m}^0 = (2 - \alpha) RT \ln x_{i,cmc} \quad (3.9)$$

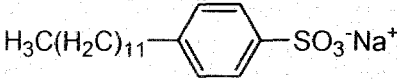
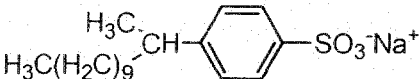
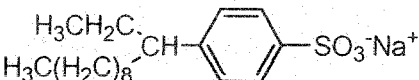
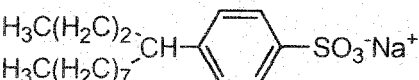
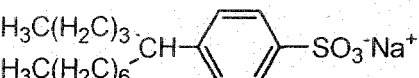
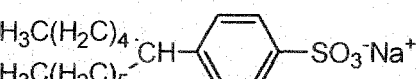
for an ionic uni-univalent surfactant. Here, x_{cmc} is the cmc expressed in mole fraction scale and $\alpha = 1 - \beta$.

The standard thermodynamic parameters, ΔG^0 , ΔH^0 and ΔS^0 indicate what is happening in a process. The standard free energy change upon micellization, ΔG_m^0 tells us whether the process is spontaneous ($\Delta G_m^0 < 0$) or not and the magnitude of the driving force. The standard enthalpy change upon micellization, ΔH_m^0 , on the other hand shows whether bond making ($\Delta H_m^0 < 0$) or bond breaking ($\Delta H_m^0 > 0$) predominates in the micellization process. The standard entropy change, ΔS_m^0 , indicates whether the system becomes more structured ($\Delta S_m^0 < 0$) or more random ($\Delta S_m^0 > 0$).

Because of the characteristics behaviour of surfactants to orient at surfaces and to form micelles, their applicability varies with the phase as foaming agents, emulsifiers, solubilization, suspension, wetting detergency and dispersants. The type of surfactant behaviour, whether acting as emulsifiers or dispersant or otherwise, depends on the structural groups on the molecule. So, the functions and properties of the surfactant systems depend on their structural type, concentration, and composition in addition to environmental conditions such as p^H , temperature, pressure and presence and absence of additives. It has been a long term goal of surfactant chemists to devise a quantitative way of correlating the chemical structure of surfactant molecules with their surface activity to facilitate the choice of material for a particular use.

Anionic surfactants, among which the alkyl benzene sulfonates form a major constituent of synthetic detergents, are widely used in various industrial process, such as in paper industries, electroplating, cosmetics, food processing, laundry, vehicle washing. Commercial alkyl benzene sulfonate (ABS) surfactants are generally produced by using a process that results in a mixture of alkyl chain homologues with a range of head group positional isomers. The positional isomers have a molecular structure where the benzene sulfonate head group is attached at different positions along the alkyl chain [44]. In Table 3.1 the structure of different SDBS positional isomer along with their cmc values in literature is given:

Table 3.1
Different positional isomers of SDBS with their cmc values at 298 K

Name	Structure	cmc	Reference
Na-1-DBS ^a (1φC ₁₂)		-	[45]
Na-2-DBS (2φC ₁₂)		1.04	[45]
Na-3-DBS (3φC ₁₂)		1.38	[45]
Na-4-DBS (4φC ₁₂)		1.65	[45]
Na-5-DBS (5φC ₁₂)		1.94	[45]
Na-6-DBS (6φC ₁₂)		2.78	[46]
		3.10	This work

^aThe cmc of Na-1-DBS could not be determined due to its very high Krafft temperature rendering it insoluble at 25°C even at very low surfactant concentrations.

Sodium dodecyl benzene sulfonates are known to form micelles in dilute solution and display an array of liquid crystalline phases at higher concentrations [47]. Also, this reagent is employed in floatation application (as collectors). In this process, these reagents have a high specificity for a given mineral surface and are utilized in

relatively low dosages [48]. In particular, it is already known that a micelle to vesicle aggregate transition can be induced by a change in ionic strength, resulting in a reduction of the air-aqueous solution interfacial tension [49-50]. The ability to control the self-assembly aggregate structure can also be a desirable from a formulation and consumer accessibility perspective. Very recent developments in nanotube research indicated that the SDBS is the substance used to stabilize Single-Walled Carbon nanotubes (SWNT) dispersions with varying effectiveness [51-58]. Alkyl benzene sulfonate contains fluorescing group as part of their molecular architecture which exhibit excimer-monomer emission [59]. The alkyl benzene sulfonate is also applied to a typical commercial petroleum sulfonate (TRS 10-80) which is one of a family of surfactants used in chemical flooding oil recovery and is obtained by direct sulfonation of a large variety of aromatic petroleum feed stocks [60]. The dodecyl benzene sulfonate moiety is an effective surface-active compound. It can also conveniently interact with neutral and cationic polymers forming solutions of different constituencies. It has antifungal properties and has a low cost of production. So far, the solution properties of this surfactant have not been critically examined although few reports are available in the literature [46,61-62]. These considerations prompted us to make elaborate and critical study of the micellization and interfacial properties of DBS moiety with varying counterions.

3. 4. Materials and methods

3. 4. 1. Materials and ion-exchange procedure

Surfactants with the desired counterions were prepared from a sample of purified sodium dodecyl benzene sulfonate (SDBS) (from Across Organics, 88%, USA) by the technique used by Eastoe and et al. [39] and the extended work of Temsamani and et al. [64] and Benrraou and et al. [65]. The procured sample produced no minima in surface tension vs. concentration plot indicates good purity of the sample. Surfactants with different counterions were prepared from purified SDBS by ion-exchange techniques using a strong ion-exchange resin (Amberlite IR-120, 20-50 mesh, Loba Cheme, India) using following process:

About 2 gm sample of SDBS was dissolved in 20 ml of a 1:1 (v/v) mixture of water and ethanol. The solution was passed through the column of 40 cm × 2 sq. cm size of a strong cationic ion exchanger in the H⁺ form very slowly. The resin was put in the acid form by using a large excess of a 0.20 M aqueous hydrochloric acid solution and washed with water until the complete removal of the excess acid takes place. The free sulphonic acid formed on passing the aqueous sodium dodecyl benzene sulfonate solution through the resin was then immediately neutralized with an aqueous solution of the hydroxides of desired counterions viz., Li⁺, K⁺, NH₄⁺, (CH₃)₄N⁺, (C₂H₅)₄N⁺, (C₃H₇)₄N⁺ and (C₄H₉)₄N⁺. All the hydroxides of high purity were procured from Fluka, Switzerland and Merck, India. The solvent water was then removed first by freeze drying and then keeping under vacuum (bath temperature 313 K) for several days and the waxy solid was finally dried in vacuum over P₂O₅. The residual water of the sample was finally removed by the action of P₂O₅ (from Loba Cheme, India) on a solution of surfactant in isooctane (≥ 99.5% from Merck, India). Controlling the flow rate of the solution through the ion exchange column had optimized the extent of Na⁺/H⁺ ion exchange and H⁺ content of the surfactant solution (acid form) was measured by titrating with standard NaOH to determine the extent of exchange. The extent of exchange was found to be more than 99%. Doubly distilled water having conductivity of 2 μS cm⁻¹ was used throughout experiment. Among all the ion-exchanged surfactants TBADBS did not crystallize at room temperature even after keeping at low temperature for several months. It appeared as a highly viscous, colourless semi-solid material.

Commercial SDBS may contain five different isomers viz. 2 φC₁₂, 3 φC₁₂, 4 φC₁₂, 5 φC₁₂ and 6 φC₁₂ depending upon the number of carbon atoms in the branched chain [46] as stated earlier. However the supplier of the product which was used in the present study (sodium dodecyl benzene sulfonate, 88%; Acros, USA, Product Code 325912500) did not mentioned the isomeric identification of their product. While the separation of isomers from their mixtures and their identification are difficult, the cmc and other parameters indicate the presence of 6 φC₁₂ as the major component of the present surfactant system. Further, the recrystallised product of SDBS was subjected to ion exchange treatment in order to prepare surfactant with different counterions, followed by repeated recrystallization to ensure adequate purification. Therefore, it may be argued that the major component of each of SDBS, LDBS, PDBS, ADBS,

TMADBS, TEADBS, TPADBS and TBADBS was essentially $6\phi C_{12}$ isomers as shown in Figure 3.1 [66].

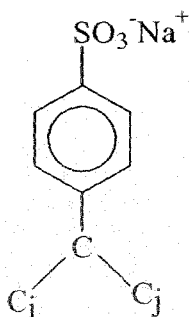


Figure 3.1. Schematical general molecular structure of DBS ($6\phi C_{12}$ isomer) where $i = 5$, $j = 6$.

3. 4. 2. Methods of measurement

The cmc and other thermodynamic parameters were determined from the surface tension as well as specific conductance data. The surface tension measurements were done by a calibrated Tensiometer (K9, KRÜSS; Germany), to measure the surface tension at the air / water interface of the solution by the platinum ring detachment methods at different temperatures. The ring was cleaned by washing with doubly distilled water followed by burning in an alcohol flame. Solutions of known concentration were progressively diluted in water solutions. The accuracy of the measurements was within $\pm 0.1 \text{ mNm}^{-1}$. Temperature of the system was maintained by circulating auto-thermostated water through a double-wall glass vessel containing the solution to keep the temperature constant within $\pm 0.1 \text{ K}$. similar studies were also done conductometrically by using an electrical conductivity bridge (METTLER TOLEDO, Switzerland). The conductance values were uncertain within the limit of $\pm 1\%$. Each measurement was repeated several times at each temperature in the range of 283 to 313 K. Measurements were made at 5 K intervals of temperature.

3. 5. Results and discussions

3. 5. 1. Critical micelle concentrations (cmc)

Since, the cmc data are not available in the literature (except sodium dodecyl benzene sulfonate, SDBS) for the present system and also to maintain the adequate accuracy of the results for this systems, cmc values were determined in both surface tension as well as in specific conductance methods for each surfactant with varying counter ions throughout the temperature range of 283 - 313 K at 5 K intervals (Figure 3.2 - 3.17). The value of cmc was determined from these figures at the break points of premicellar and post micellar region in the usual manner. At the intersection of almost each plot, nonlinearity in a very small range is present which may be due to traces of surface-active impurities or some small aggregation of surfactant molecules [67-68]. Ignoring this nonlinearity, the cmc values are determined by drawing two straight lines through the two straight portions of the plot. In table 3.2 and table 3.3, we present the cmc values of all the surfactant systems at various temperatures with varying counterions along with different surface parameters and degree of binding of counterions, α . The changes of cmc values with varying temperatures of different surfactants are very small but clearly detectable. At a specific temperature, the cmc values of the surfactants follow the order $\text{Na}^+ > \text{Li}^+ > \text{NH}_4^+ > \text{K}^+ > \text{N}^+(\text{CH}_3)_4 > \text{N}^+(\text{C}_2\text{H}_5)_4 > \text{N}^+(\text{C}_3\text{H}_7)_4 > \text{N}^+(\text{C}_4\text{H}_9)_4$. So, it can be said from the results that the cmc values of the DBS moiety depends on the counterions with the above order. For the present purpose the surfactants having different counterions have been classified into two categories: one containing different alkali metal counterions along with NH_4^+ and the other having various tetraalkyl ammonium counterions. It is apparent that the hydrodynamic radii along with the accessibility of the counterion towards the head group play an important role in micellization. For the tetraalkyl ammonium counterions, the binding ability of the counterions with the head group of the micelle can explain the relative cmc values of the surfactants. Among tetraalkyl ammonium cations along with ammonium cations, the binding ability is highest for $\text{N}^+(\text{C}_4\text{H}_9)_4$ and decreases in the following order $\text{N}^+(\text{C}_4\text{H}_9)_4 > \text{N}^+(\text{C}_3\text{H}_7)_4 > \text{N}^+(\text{C}_2\text{H}_5)_4 > \text{N}^+(\text{CH}_3)_4 > \text{NH}_4^+$. As a result, the reduction of the electrostatic intermicellar repulsive force occurs which leads to the formation of the micelle in the lower concentration range which is shown in the figure 3.18.

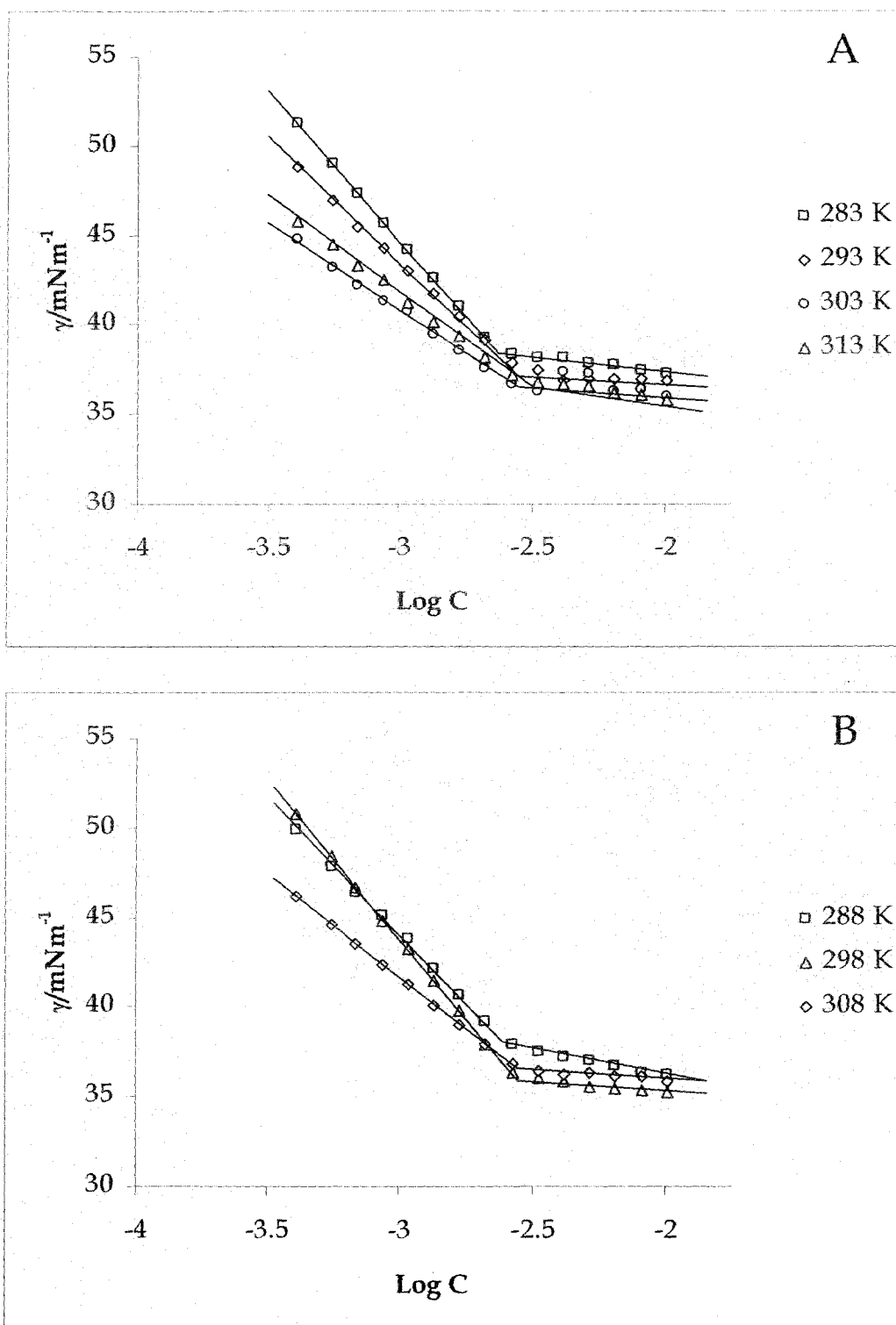


Figure 3.2: Surface tension, γ , of Lithium dodecyl benzene sulfonate (LDBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

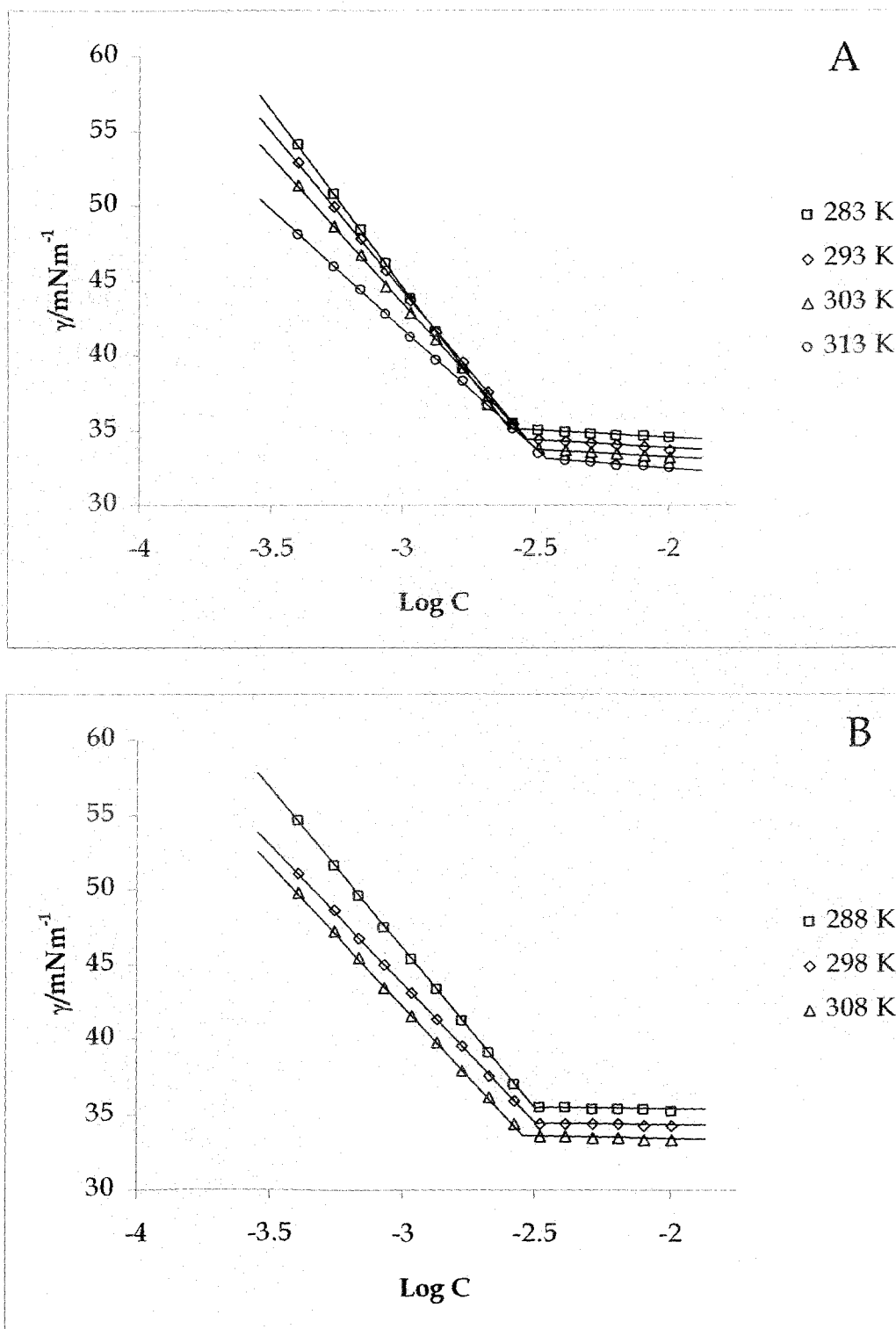


Figure 3.3: Surface tension, γ , of Sodium dodecyl benzene sulfonate (SDBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

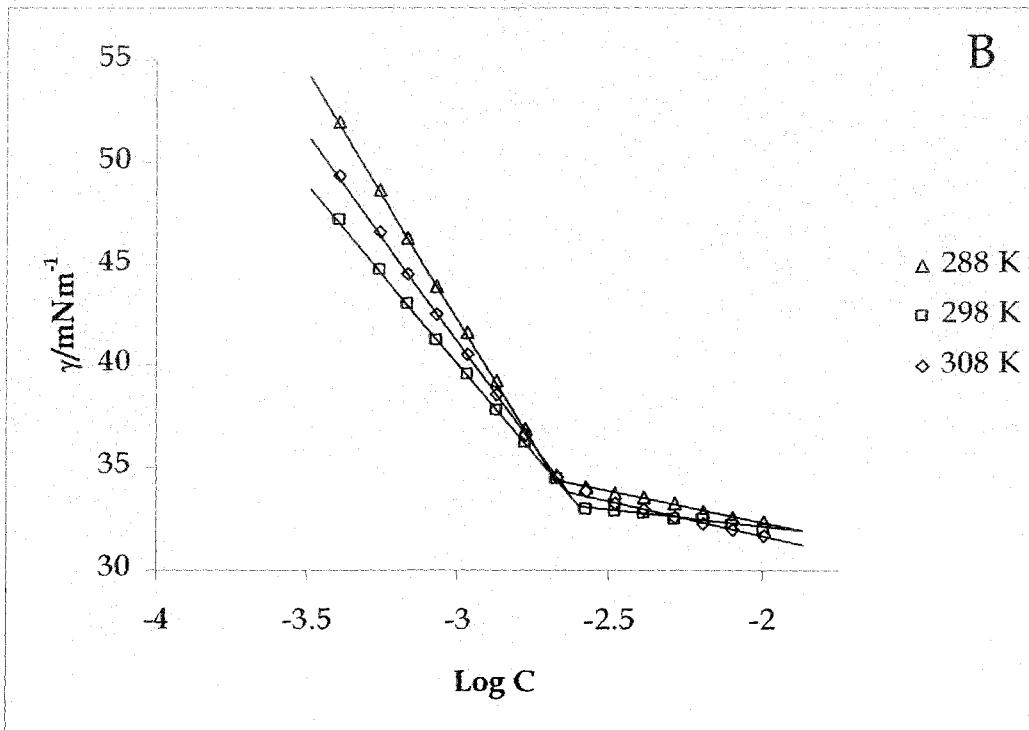
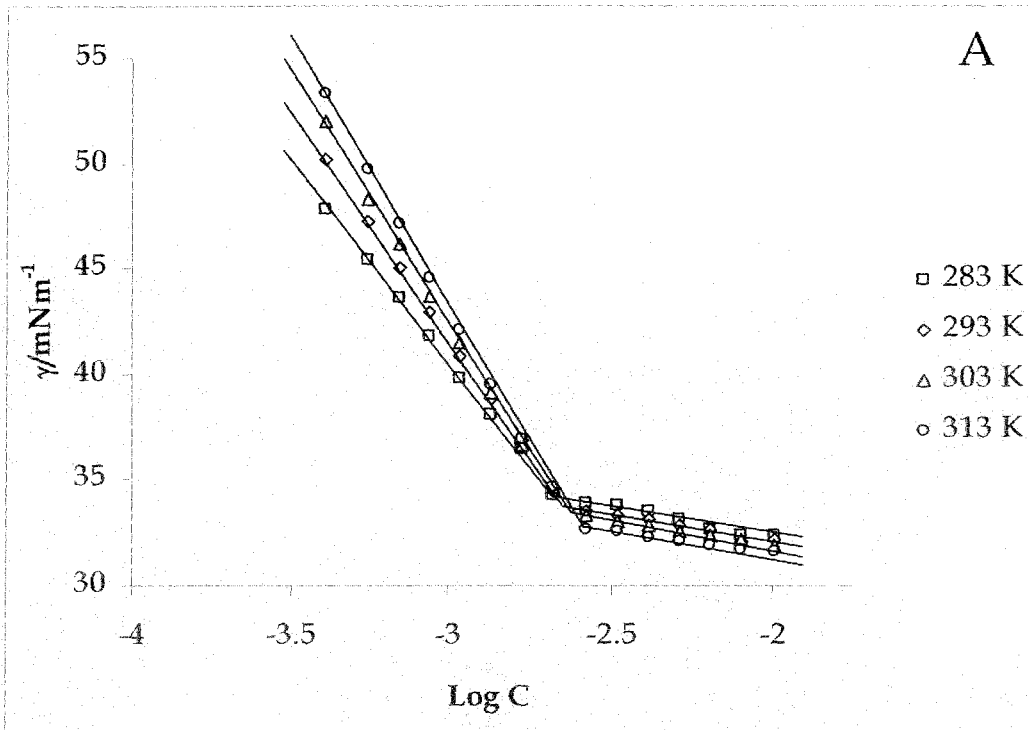


Figure 3.4: Surface tension, γ , of Potassium dodecyl benzene sulfonate (PDBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

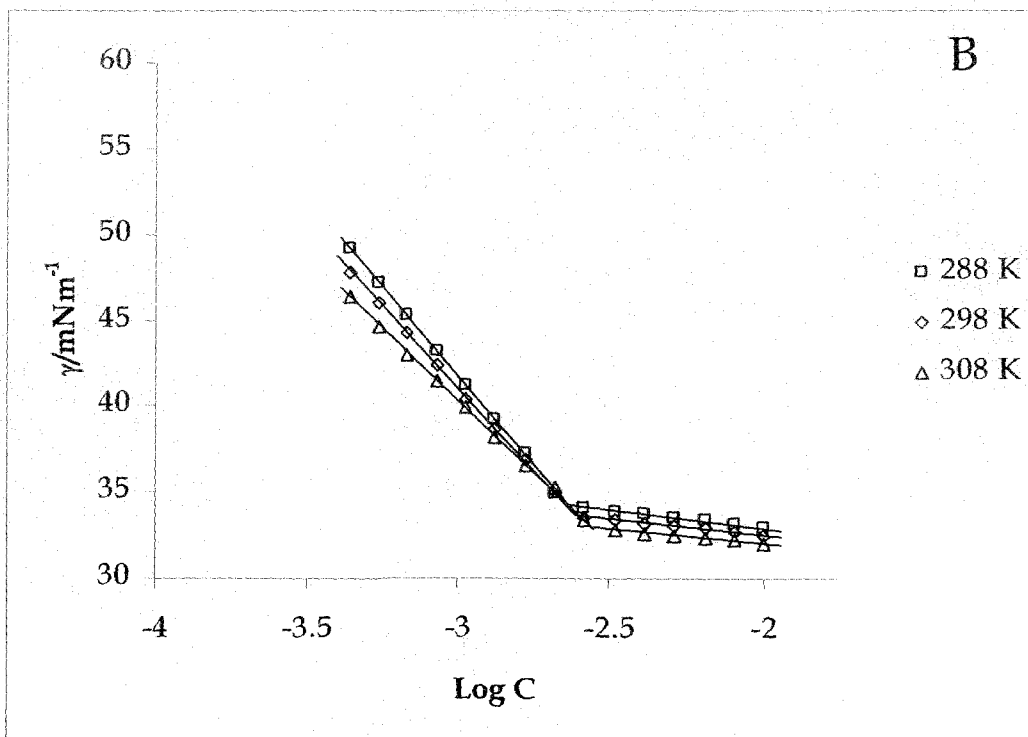
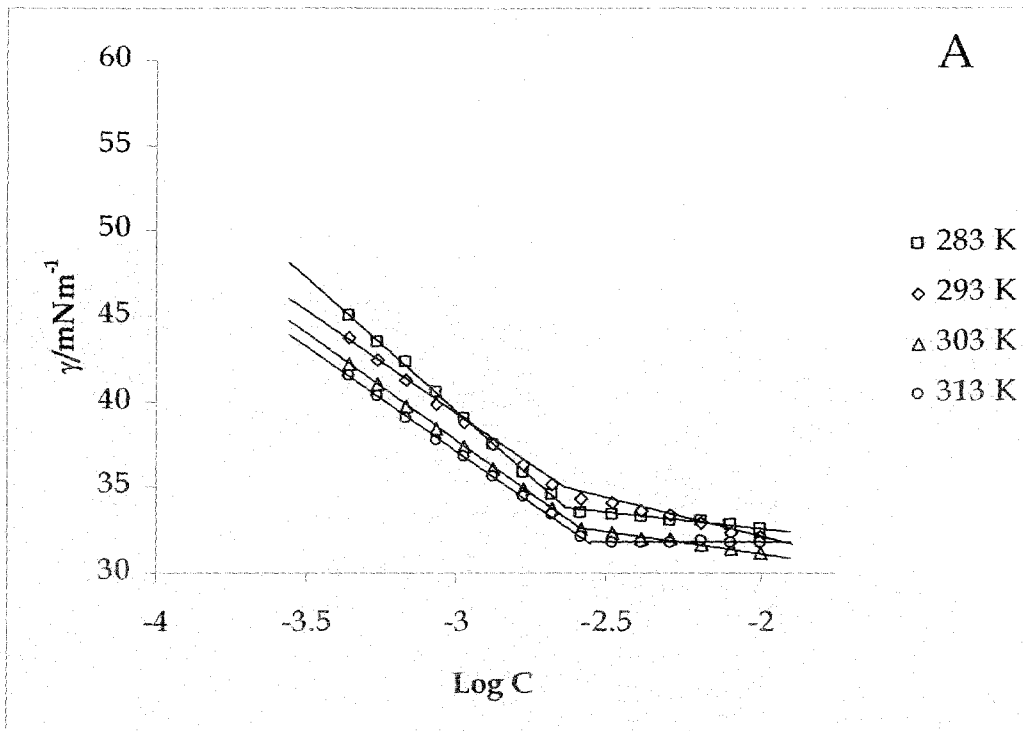


Figure 3.5: Surface tension, γ , of Ammonium dodecyl benzene sulfonate (ADDBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

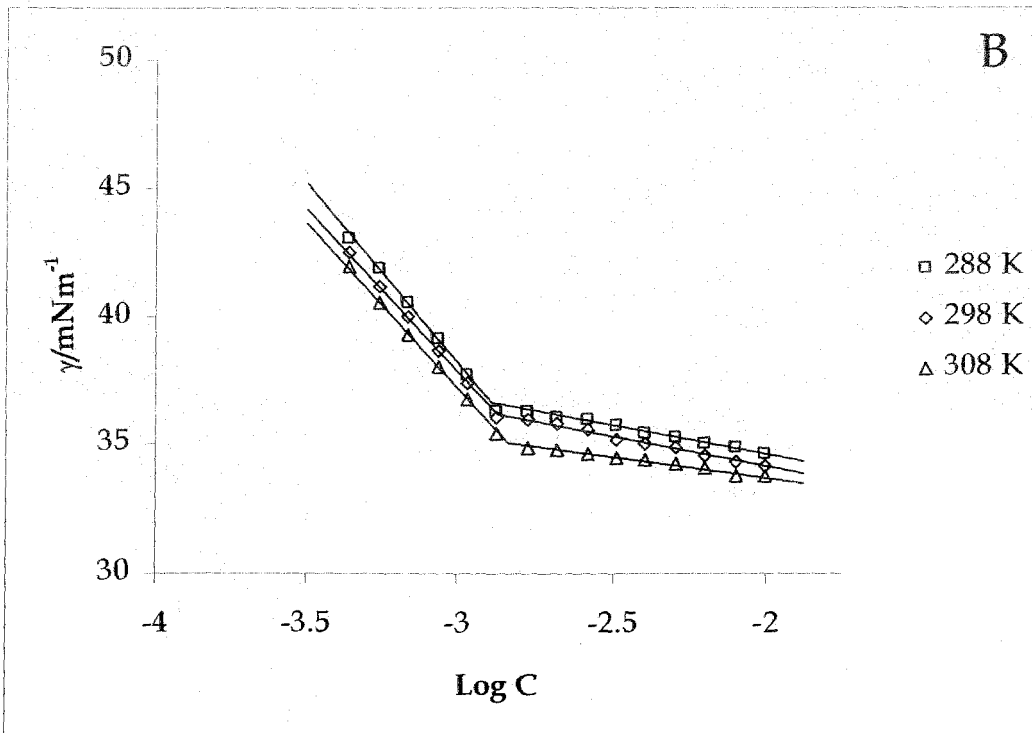
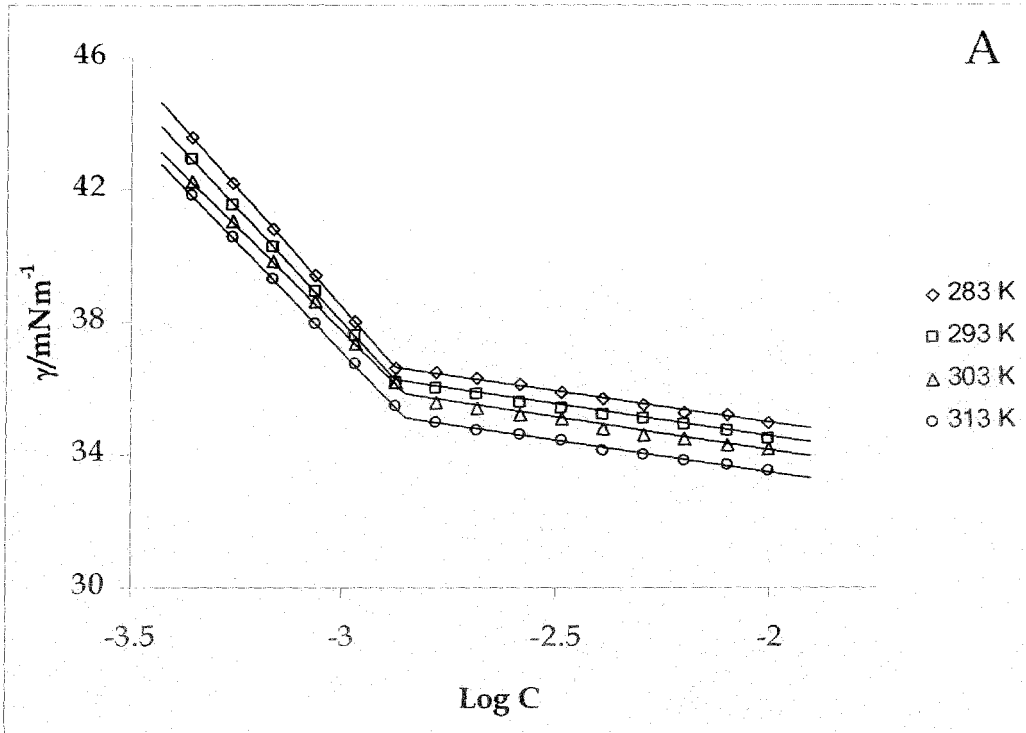


Figure 3.6: Surface tension, γ , of Tetramethylammonium dodecyl benzene sulfonate (TMADBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

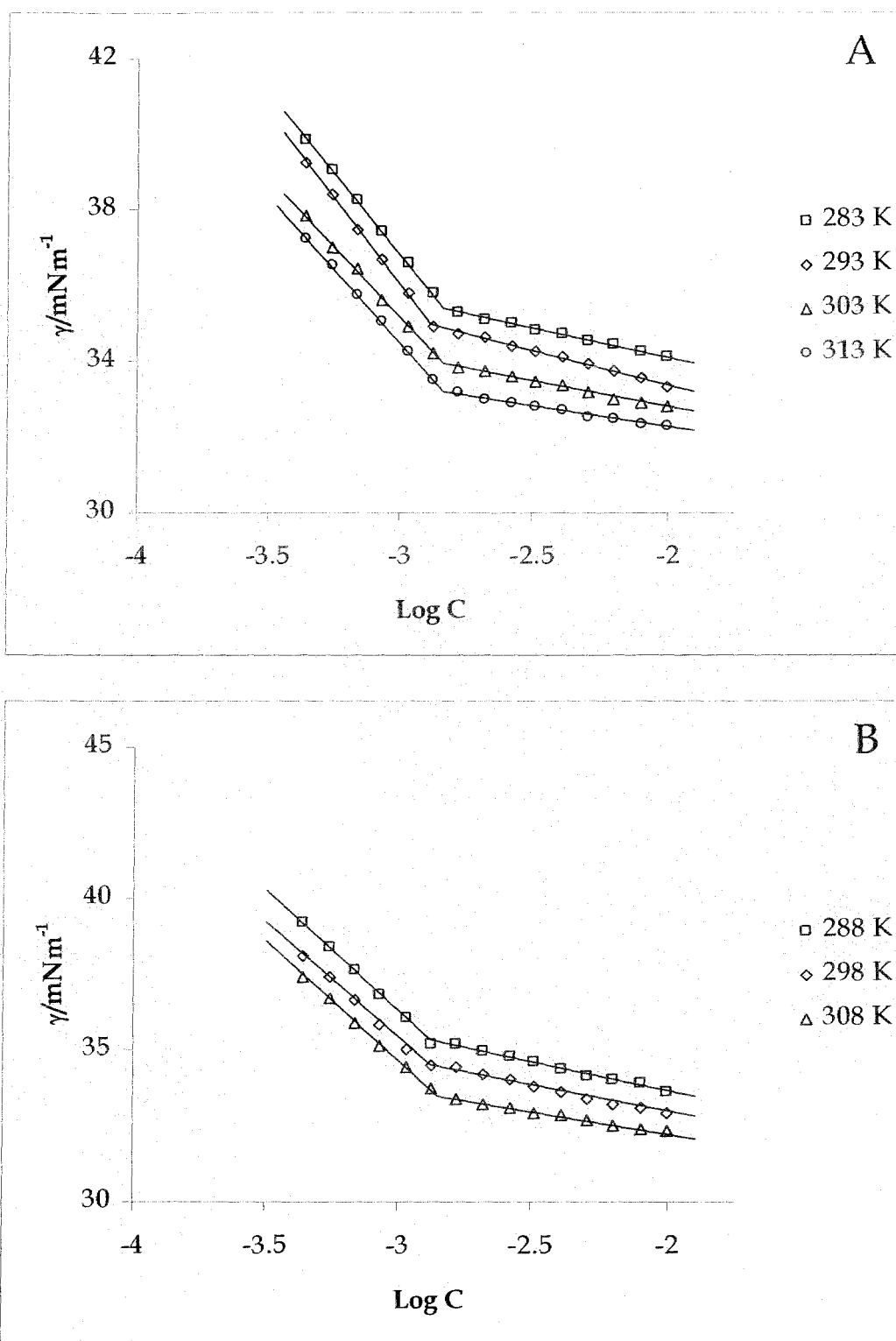


Figure 3.7: Surface tension, γ , of Tetraethylammonium dodecyl benzene sulfonate (TEADBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

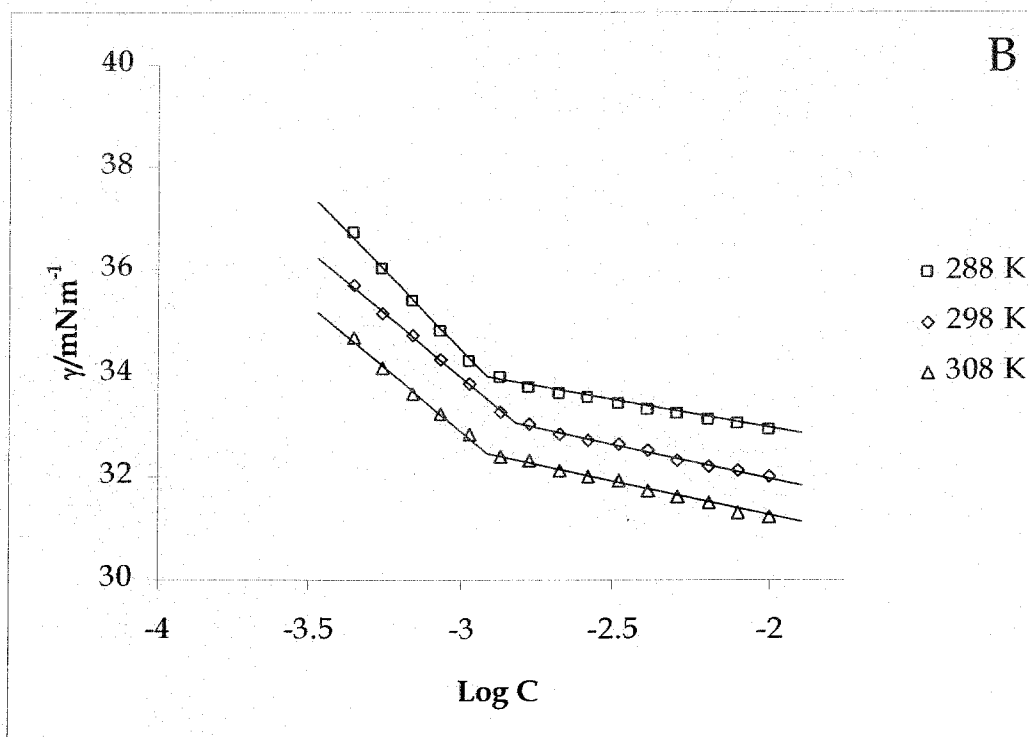
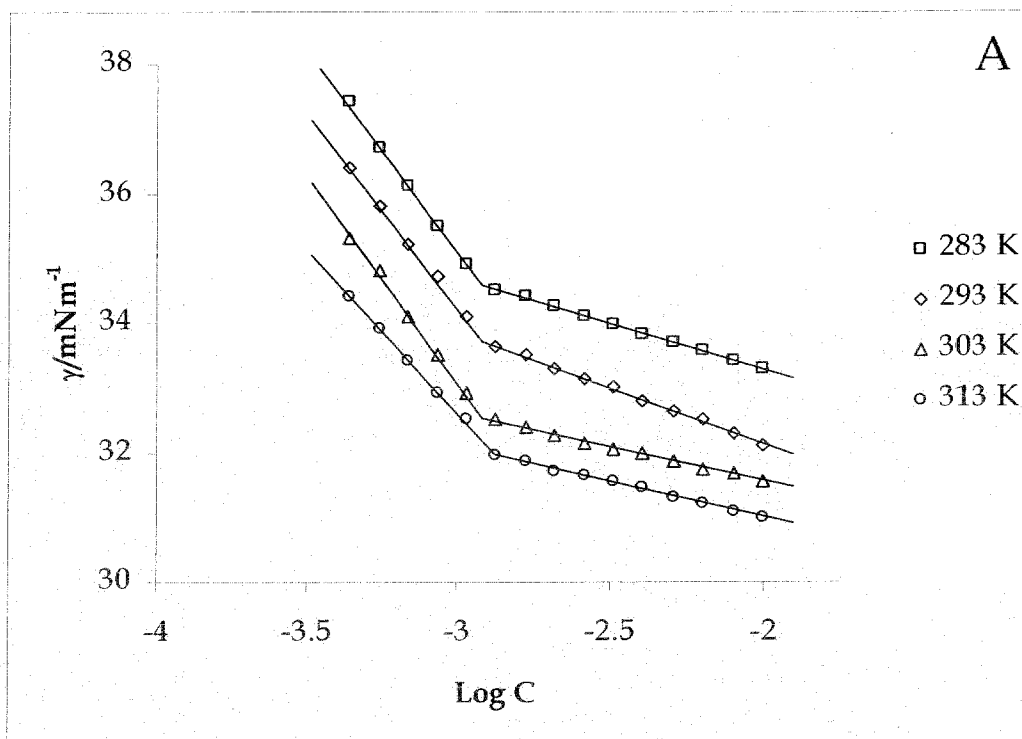


Figure 3.8: Surface tension, γ , of Tetrapropylammonium dodecyl benzene sulfonate (TPADBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

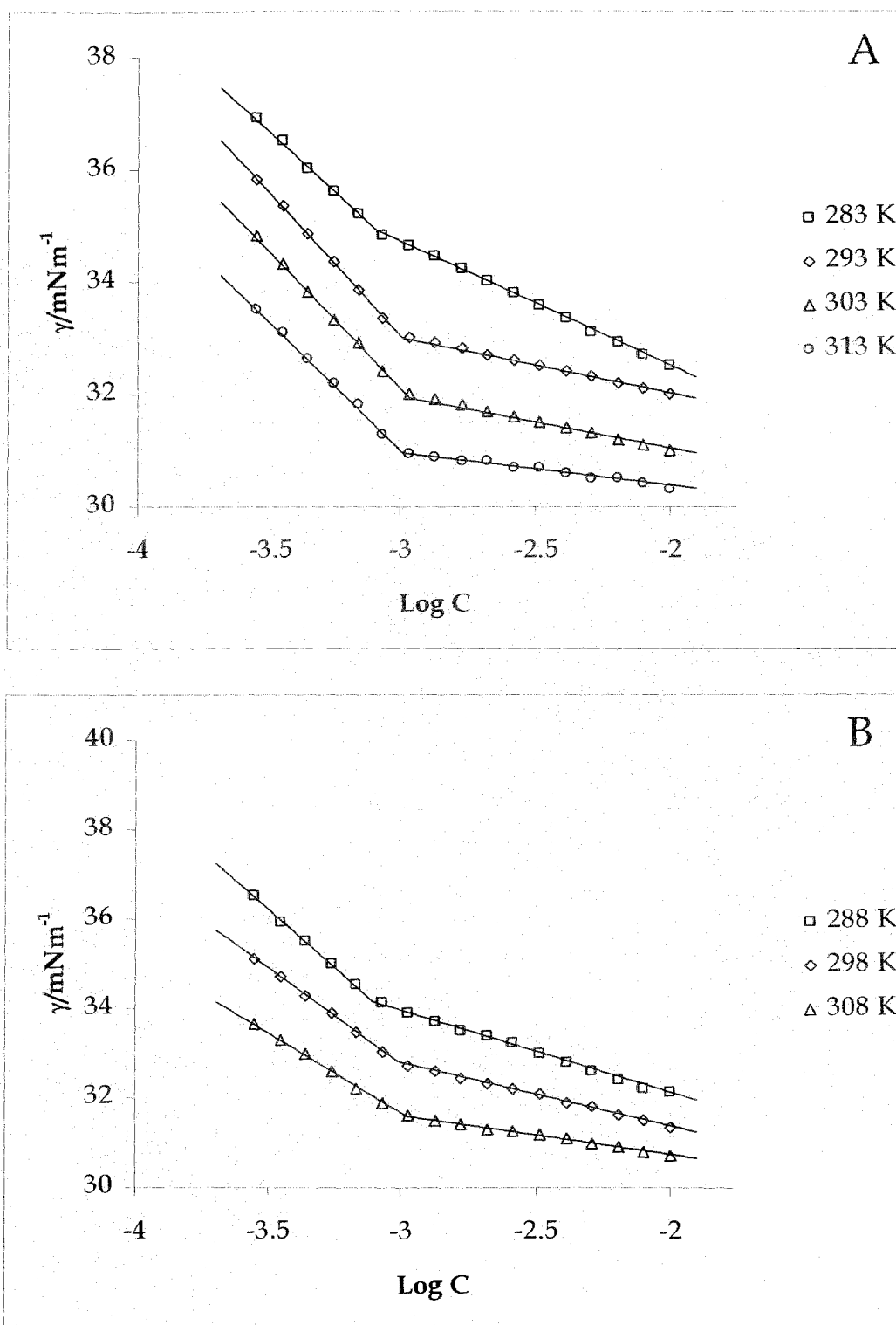


Figure 3.9: Surface tension, γ , of Tetrabutylammonium dodecyl benzene sulfonate (TBADBS) in aqueous solution as a function of the logarithm of the surfactant concentration (mM) at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

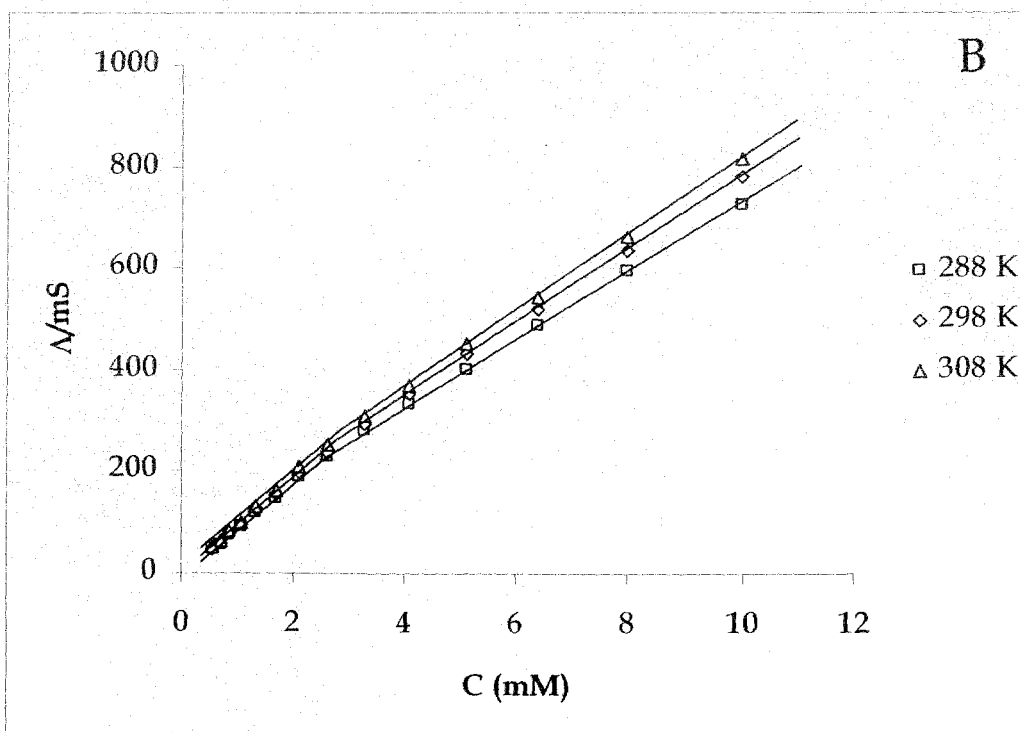
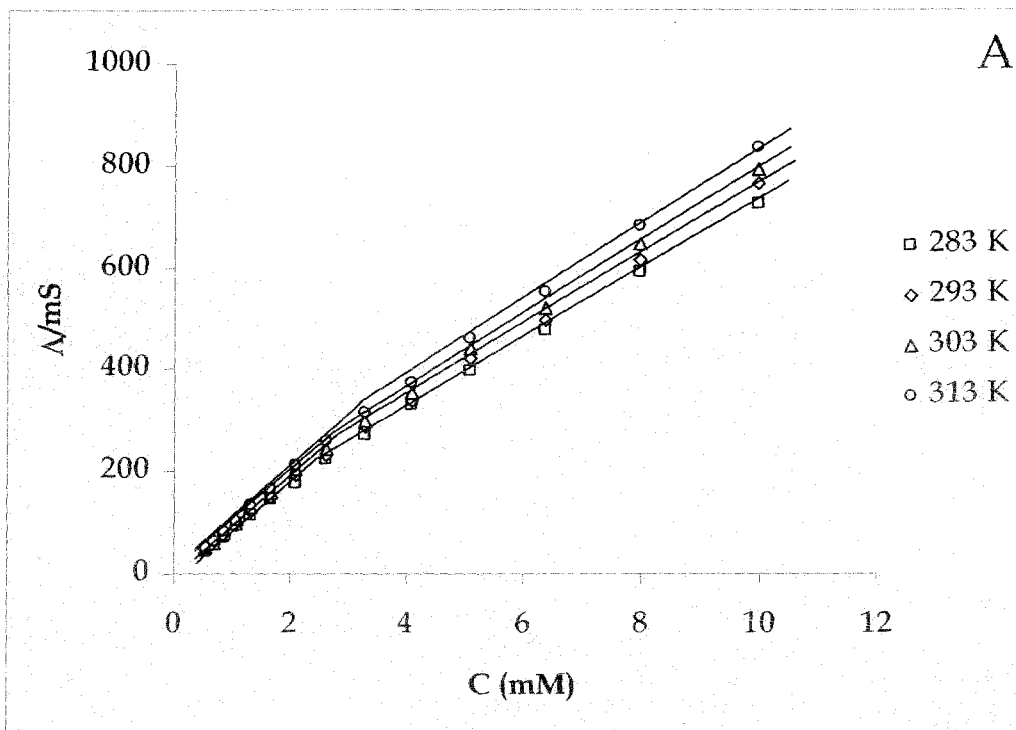


Figure 3.10: Conductance, Λ , of Lithium dodecyl benzene sulfonate (LDBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

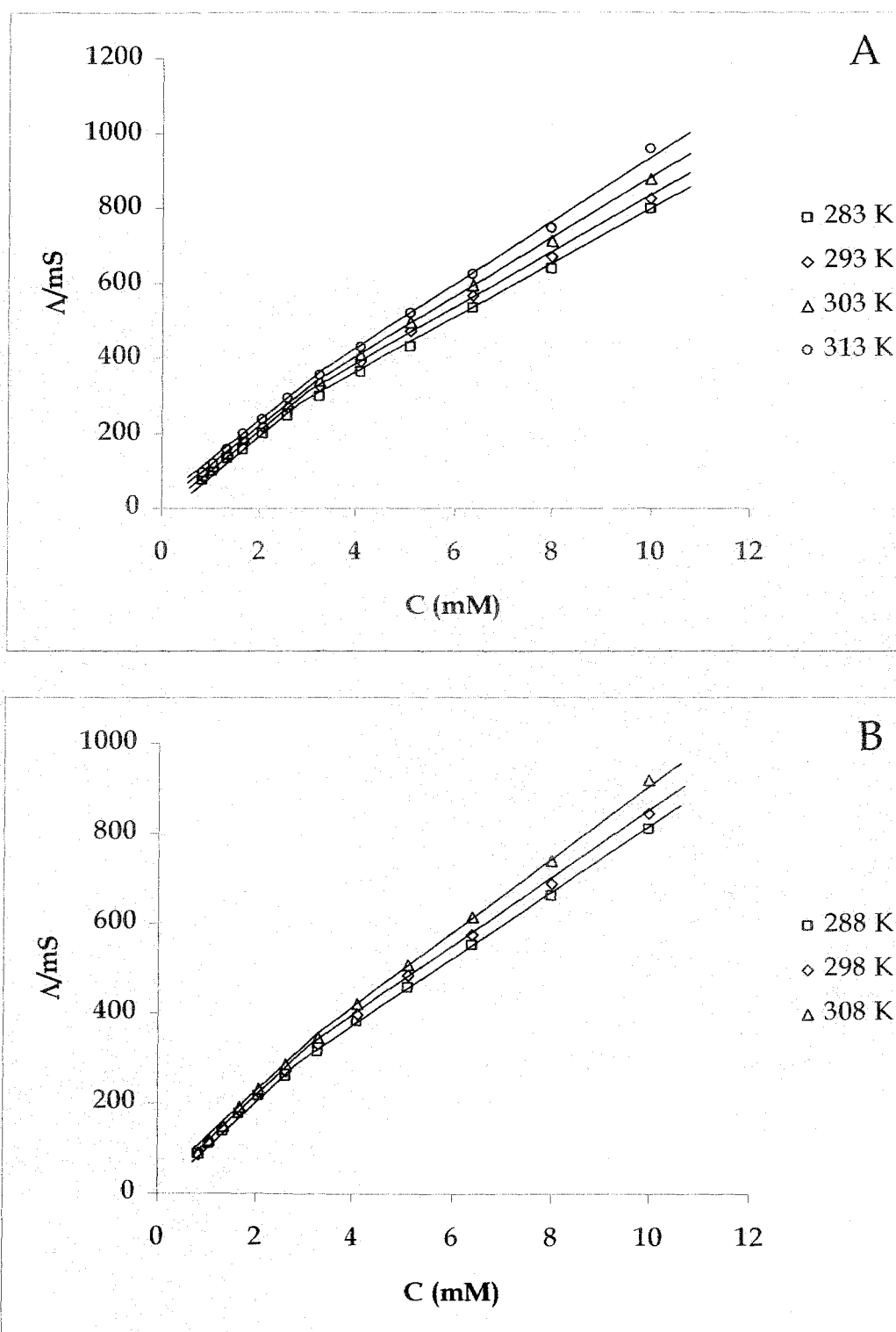


Figure 3.11: Conductance, Δ , of Sodium dodecyl benzene sulfonate (SDBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

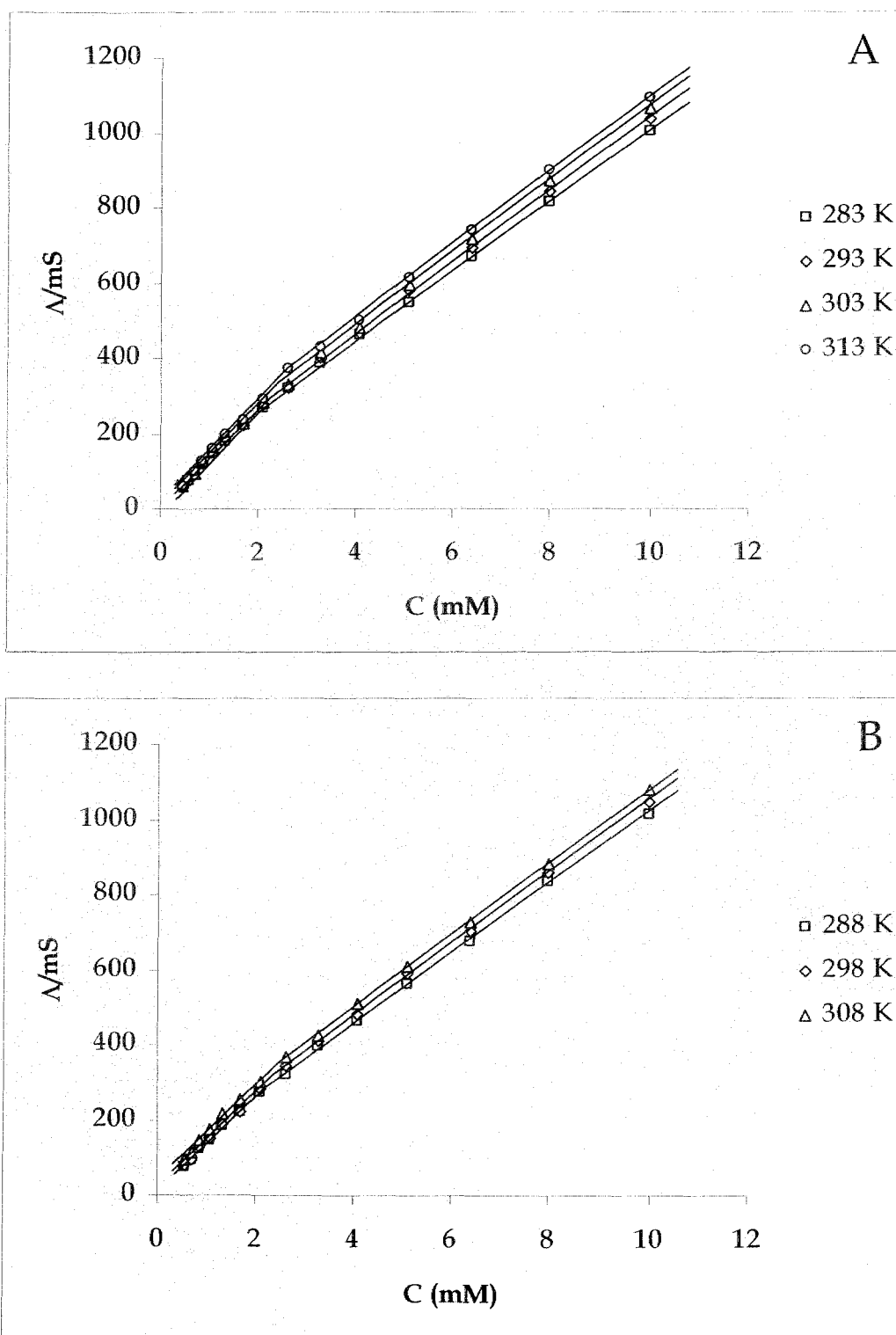


Figure 3.12: Conductance, Λ , of Potassium dodecyl benzene sulfonate (PDBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

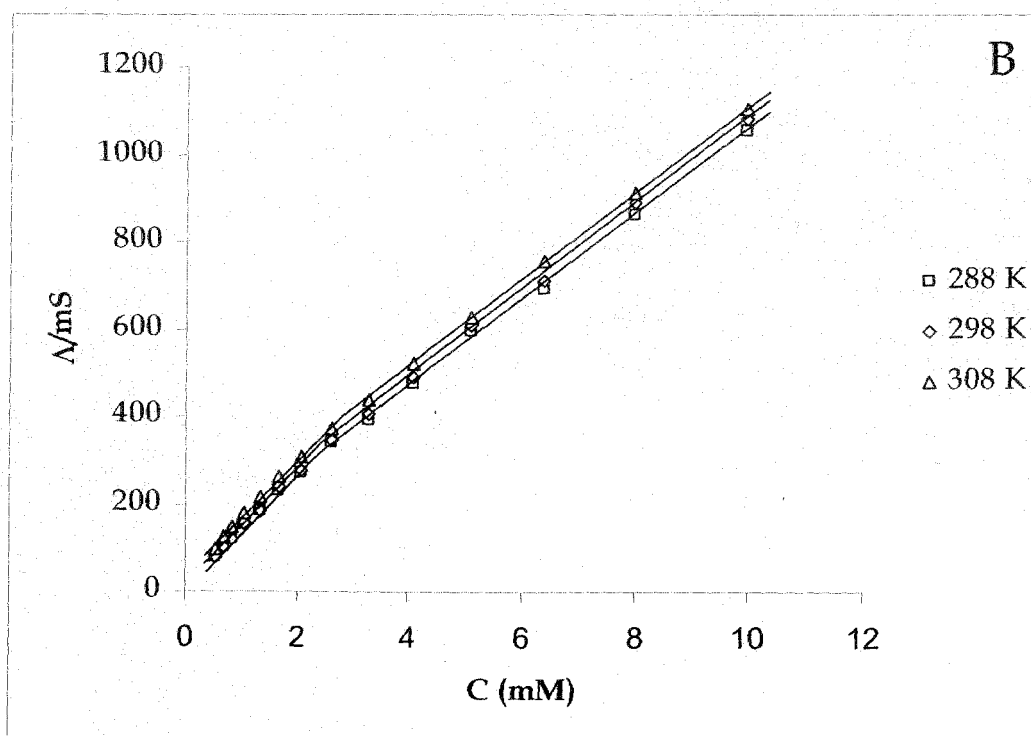
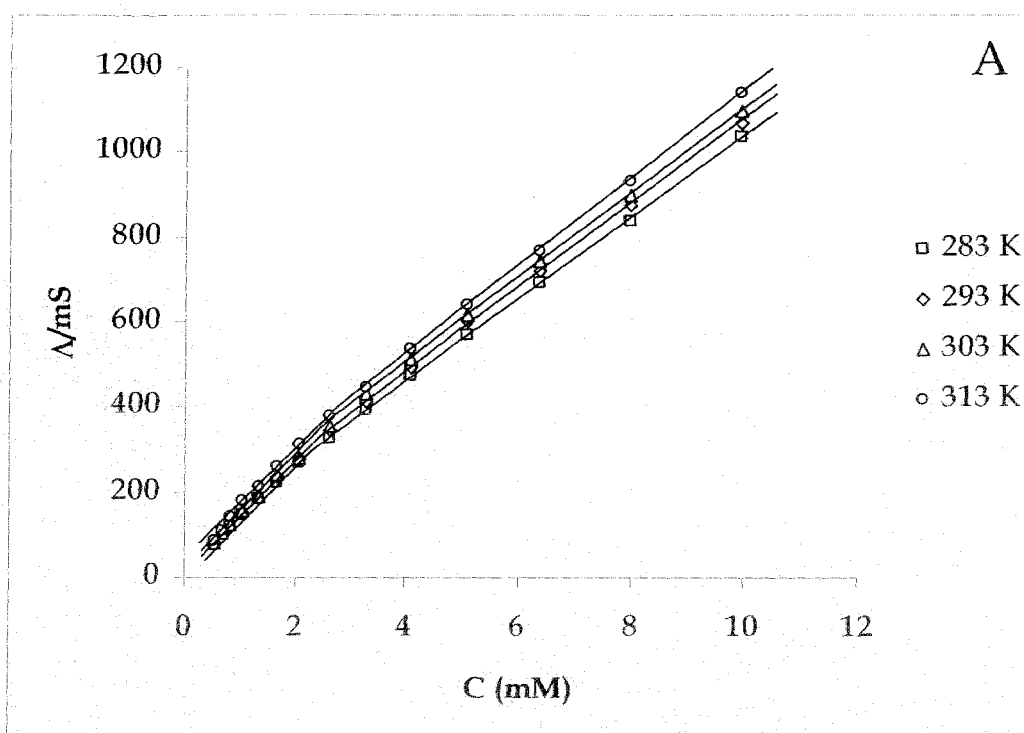


Figure 3.13: Conductance, Λ , of Ammonium dodecyl benzene sulfonate (ADBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

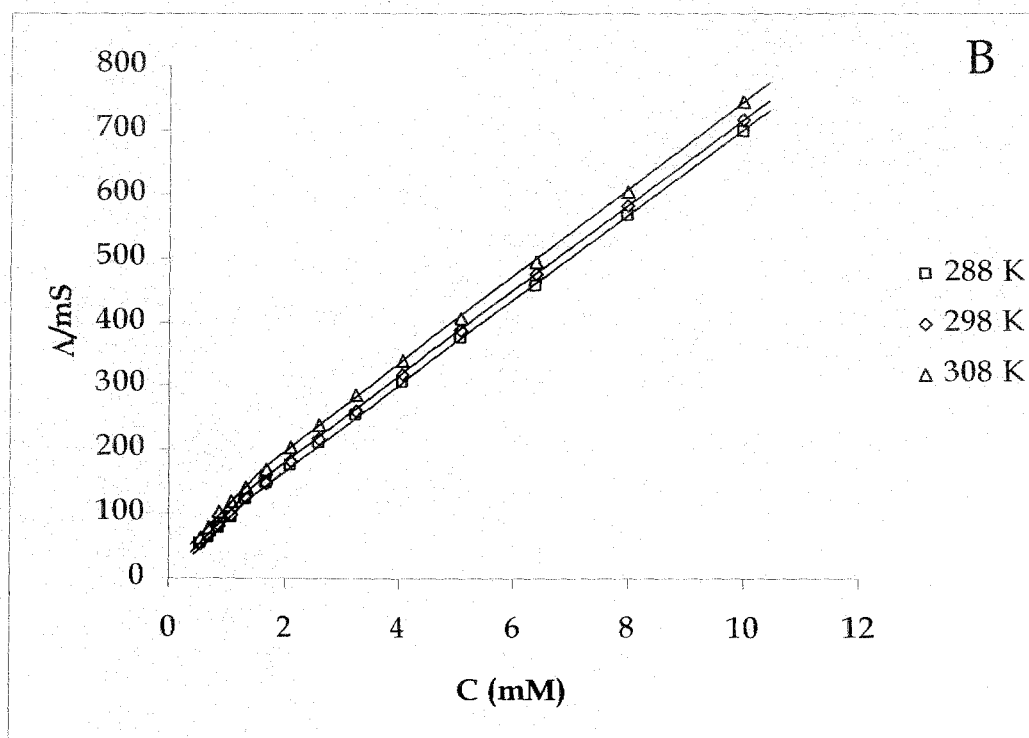
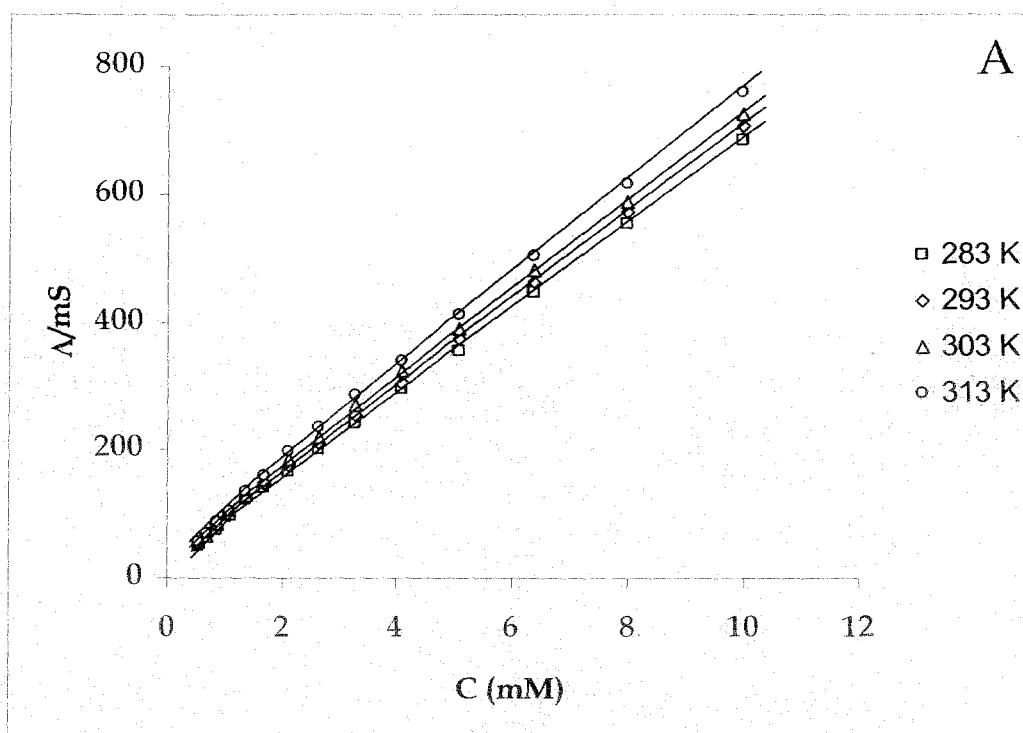


Figure 3.14: Conductance, Λ , of Tetramethylammonium dodecyl benzene sulfonate (TMADBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

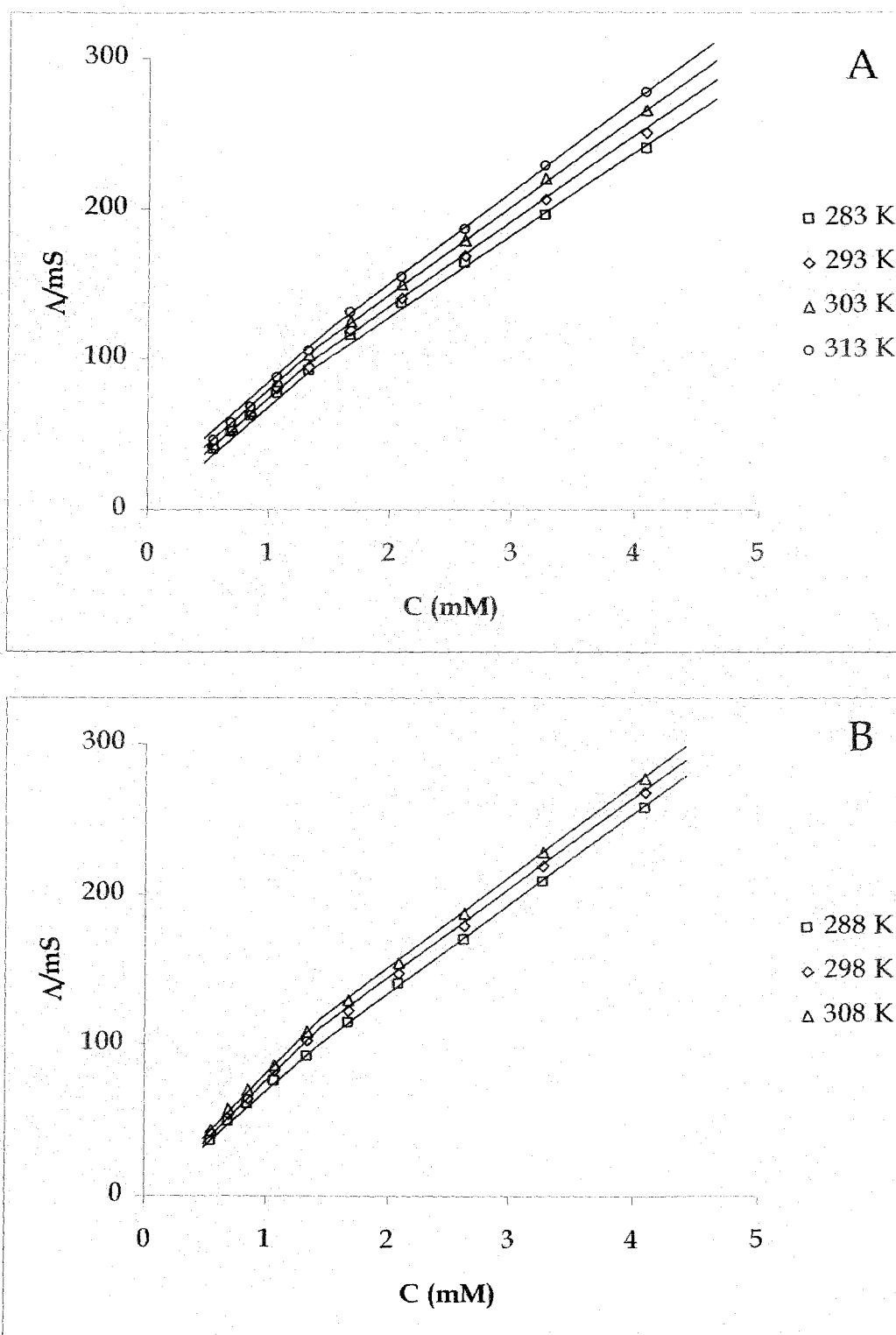


Figure 3.15: Conductance, Λ , of Tetraethylammonium dodecyl benzene sulfonate (TEADBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

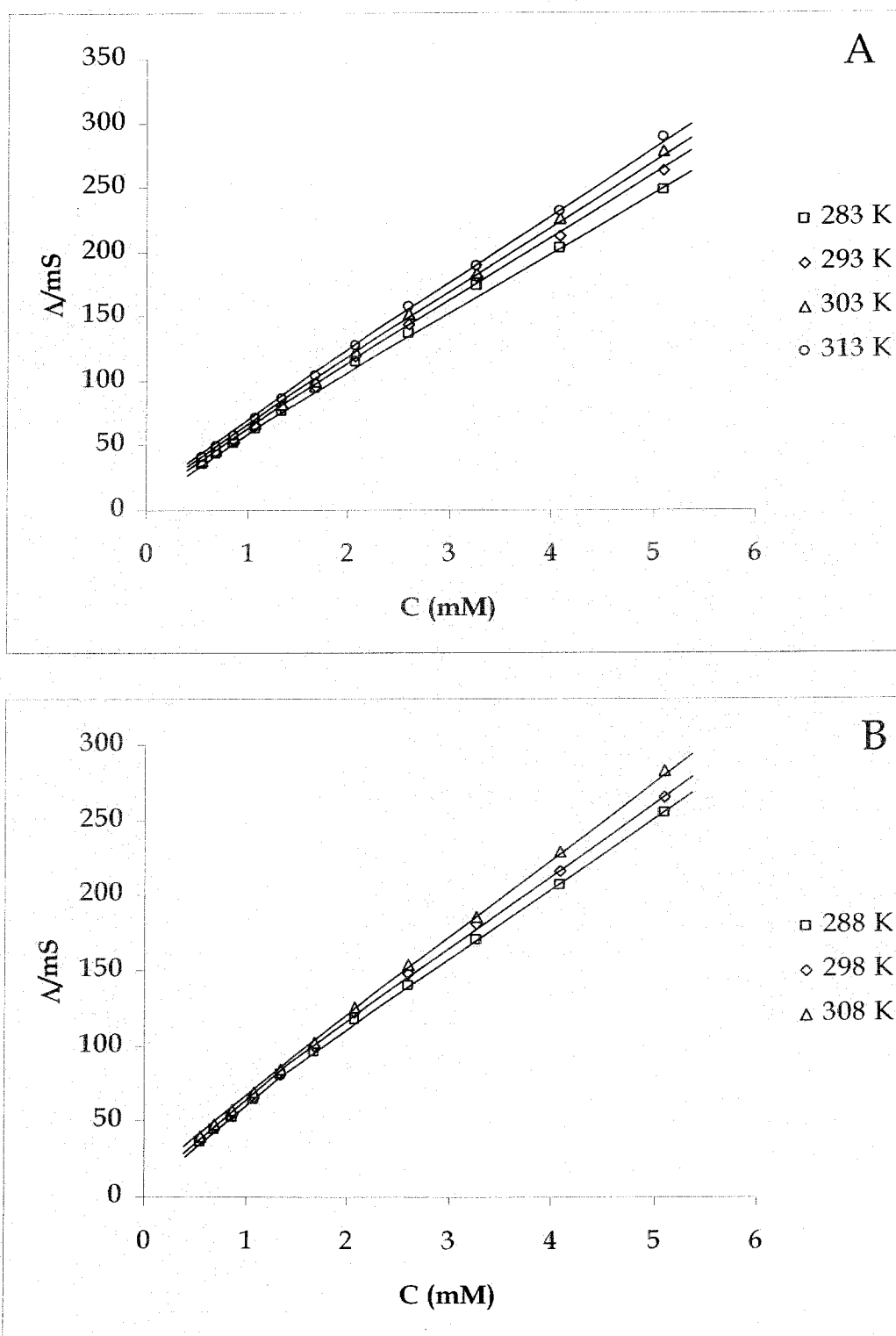


Figure 3.16: Conductance, Δ , of Tetrapropylammonium dodecyl benzene sulfonate (TPADBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

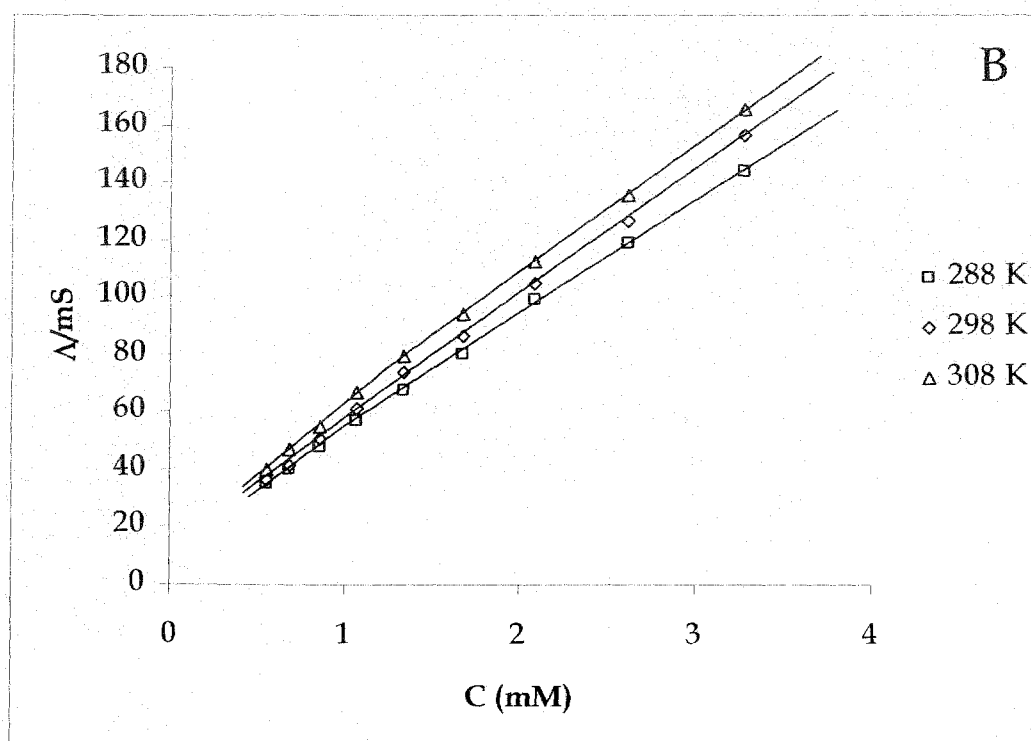
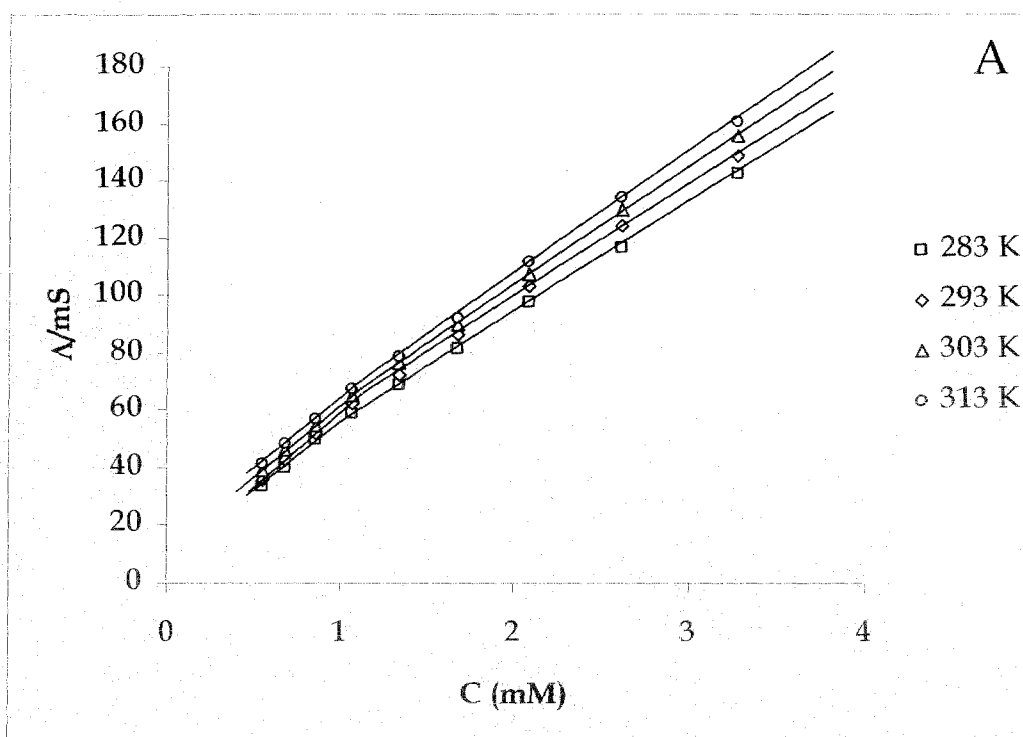


Figure 3.17: Conductance, Λ , of Tetrabutylammonium dodecyl benzene sulfonate (TBADBS) in aqueous solution as a function of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), (B: temperature 288K, 298K, 308K).

It has been also reported that the NH_4^+ binds more strongly to the dodecyl head group compared to Na^+ thus a lower value in cmc observed [69]. The observed cmc values are also in good agreement with the literature values [38,45-46,70-73]. The hydrated radius along with hydration number of alkali metal ions with NH_4^+ ion derived from corrected ionic radii is given in the table 3.4. In the present case of dodecyl benzene sulfonate, there is a branched carbon chain in the molecular structure of the anion. Though the actual nature of dependency of hydrophobic tail on the interaction of the hydrated counterions is not still well understood, it can be said that , "branched chain molecular structure" of DBS makes the environment around more hydrophobic in nature, where Li^+ along with its large hydrated volume binds more readily than that of Na^+ with the hydrophobic head. But NH_4^+ , which has the lowest hydration number shows anomalous behaviour towards its accessibility to the head group [74].

Table 3.2

Micellization and Surface parameters of Dodecyl benzene sulfonate having different alkali counterions along with NH_4^+ ion at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	$\Gamma_{\text{max}}/ \text{mol cm}^{-2} \times 10^6$	$A_{\text{min}}/\text{nm}^2 \times 10^2$	α
Li ⁺	283	2.50 (2.41)	3.10	0.54	0.75
	288	2.60 (2.54)	2.98	0.57	0.71
	293	2.83 (2.76)	3.18	0.52	0.72
	298	2.82 (2.80)	3.22	0.52	0.72
	303	2.79 (2.84)	3.22	0.51	0.72
	308	2.91 (2.90)	3.27	0.51	0.71
	313	3.21 (3.17)	3.29	0.50	0.71
Na ⁺	283	2.82 (2.77)	2.99	0.56	0.76
	288	2.91 (2.86)	3.16	0.53	0.70
	293	2.98 (2.95)	3.21	0.52	0.71
	298	3.10 (3.13)	3.25	0.51	0.72
	303	3.21 (3.20)	3.27	0.51	0.74
	308	3.27 (3.31)	3.27	0.50	0.76
	313	3.33 (3.36)	3.32	0.48	0.77
K ⁺	283	2.11 (2.14)	3.40	0.49	0.70
	288	2.18 (2.19)	3.46	0.48	0.70
	293	2.25 (2.24)	3.52	0.47	0.69
	298	2.38 (2.32)	3.55	0.47	0.71
	303	2.42 (2.41)	3.54	0.47	0.70
	308	2.50 (2.52)	3.58	0.46	0.71
	313	2.61 (2.60)	3.61	0.46	0.70
NH ₄ ⁺	283	2.28 (2.23)	3.12	0.53	0.74
	288	2.39 (2.36)	3.17	0.52	0.74
	293	2.41 (2.40)	3.23	0.51	0.73
	298	2.52 (2.48)	3.28	0.51	0.74
	303	2.68 (2.62)	3.38	0.49	0.78
	308	2.81 (2.82)	3.41	0.49	0.74
	313	2.80 (2.82)	3.49	0.47	0.74

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.3

Micellization and Surface parameters of Dodecyl benzene sulfonate having different tetraalkylammonium counterions at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	Γ _{max} / cm ⁻² × 10 ⁶	mol	A _{min} /nm ² × 10 ²	α
(CH ₃) ₄ N ⁺	283	1.31 (1.28)	3.11		0.53	0.71
	288	1.34 (1.29)	3.14		0.53	0.73
	293	1.34 (1.30)	3.17		0.52	0.74
	298	1.37 (1.31)	3.20		0.52	0.73
	303	1.39 (1.34)	3.28		0.51	0.74
	308	1.45 (1.37)	3.30		0.50	0.75
	313	1.49 (1.45)	3.36		0.49	0.73
(C ₂ H ₅) ₄ N ⁺	283	1.27 (1.27)	3.05		0.55	0.76
	288	1.28 (1.32)	3.03		0.55	0.77
	293	1.27 (1.22)	3.02		0.55	0.79
	298	1.30 (1.24)	3.10		0.54	0.79
	303	1.32 (1.25)	3.14		0.53	0.80
	308	1.32 (1.27)	3.19		0.52	0.79
	313	1.37 (1.29)	3.26		0.51	0.81
(C ₃ H ₇) ₄ N ⁺	283	1.08 (1.10)	3.02		0.55	0.79
	288	1.17 (1.15)	3.04		0.55	0.81
	293	1.18 (1.17)	3.07		0.54	0.81
	298	1.22 (1.19)	3.08		0.54	0.82
	303	1.23 (1.20)	3.11		0.53	0.82
	308	1.25 (1.23)	3.16		0.53	0.82
	313	1.31 (1.25)	3.19		0.52	0.82
(C ₄ H ₉) ₄ N ⁺	283	0.79 (0.75)	2.93		0.57	0.87
	288	0.84 (0.81)	2.96		0.56	0.84
	293	0.99 (0.96)	2.99		0.55	0.84
	298	1.05 (1.02)	2.99		0.56	0.83
	303	1.05 (1.03)	3.00		0.55	0.83
	308	1.10 (1.05)	3.01		0.55	0.82
	313	1.01 (0.82)	3.05		0.54	0.83

^aThe values in the parenthesis represent cmc determined by conductivity method.

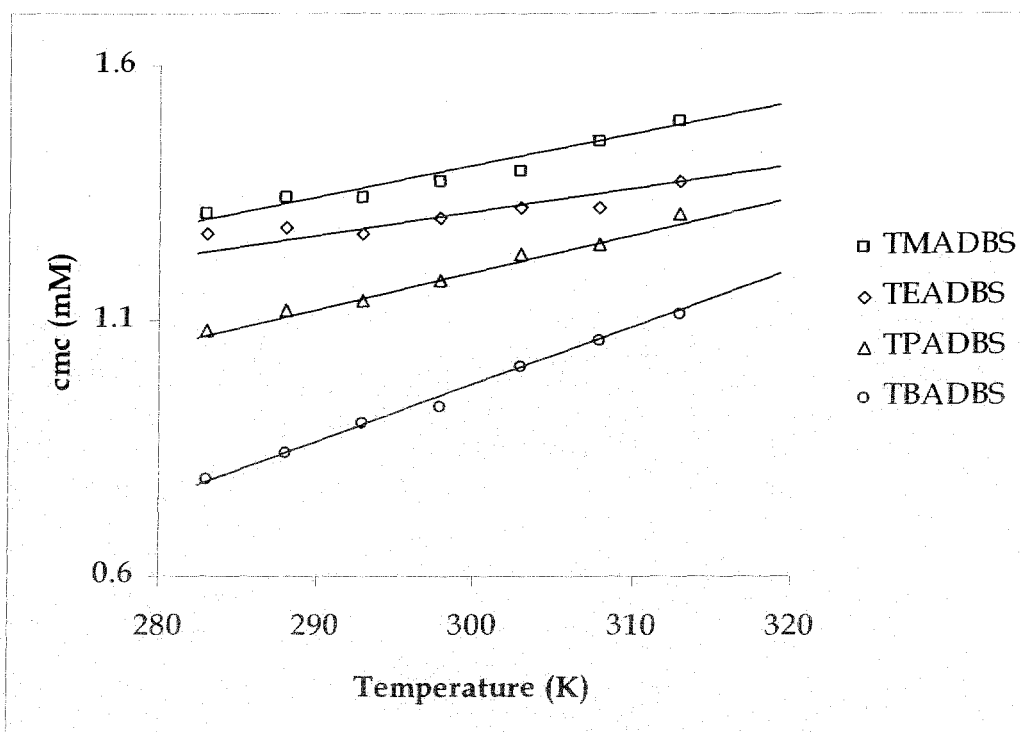


Figure 3.18. Variation of cmc with temperature of DBS having different tetra alkyl ammonium counterions.

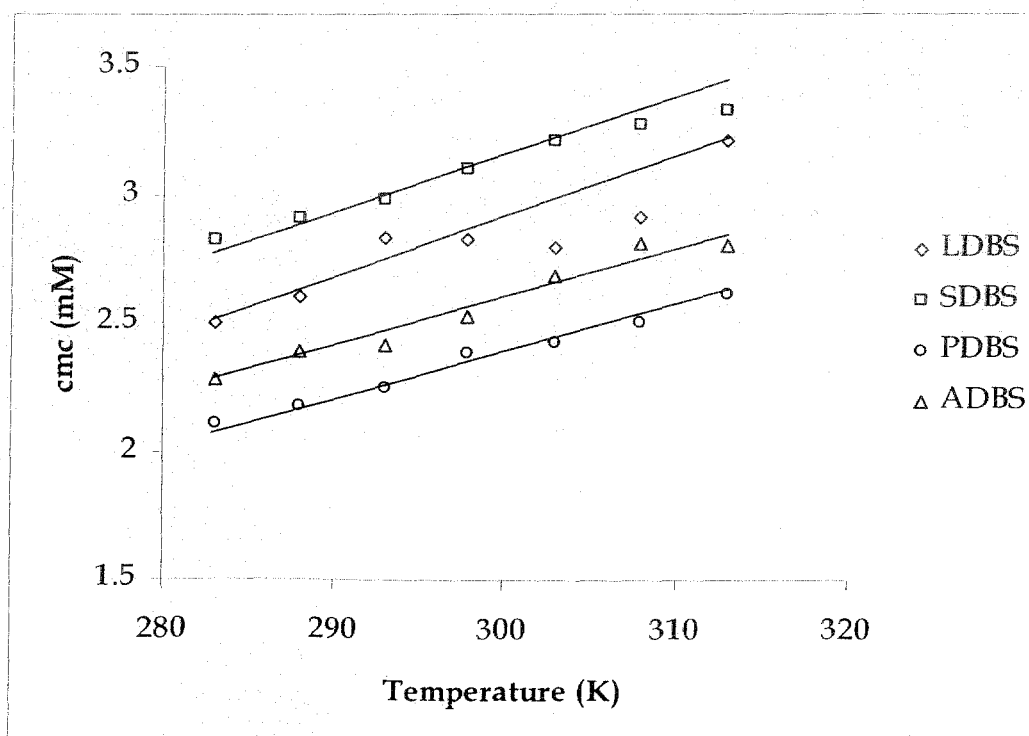


Figure 3.19. Variation of cmc with temperature of DBS having different alkali metal counterions along with NH_4^+ .

Table 3.4
Ionic and Hydrated radius along with Hydration number of ions derived from corrected ionic radii

Ion	Hydration number	Ionic Radius (Å)	Hydrated Radius (Å)
NH ₄ ⁺	4.6	1.48	3.31
K ⁺	5.1	1.37	2.23
Na ⁺	6.5	0.99	2.76
Li ⁺	7.4	0.59	3.40

It has been also reported [75] that the binding tendency of alkali metal cations to polyethylene oxide (PEO) follows the order $K^+ > Cs^+ > Na^+$. However, among all the alkali ions under investigation in the present study, K^+ binds most strongly to DBS resulting in the lowest cmc at a particular temperature. Figure 3.19 represents the variation of cmc with temperature for DBS containing different alkali metal counterions along with NH_4^+ .

3.5.2. Surface parameters

The maximum surface excess concentrations (Γ_{max}) in the aqueous-air interface are calculated by using Gibb's adsorption equation since the Γ_{max} is a useful measure of the effectiveness of adsorption of the surfactant at air-solution interface, since it is the maximum value that adsorption can attain. It is well known that the air-solution interface of a surfactant solution is well populated by the adsorbed molecules. The general trend of Γ_{max} with increase of temperature is a slight decrease in its value for both nonionic and anionic surfactants but there is some other cases where opposite trend is also observed [76-78]. For 1:1 ionic surfactant in the absence of any additives, Γ_{max} has the following expression [76-77,79]:

$$\Gamma_{max} = \left(\frac{1}{2.303n'RT} \right) \left(- \frac{\partial \gamma}{\partial \log C} \right) \quad (3.10)$$

where γ , C and n' are the surface tension, molar concentration and number of particles per molecule of surfactant respectively. γ vs. $\log C$ plot was fitted to a second order

polynomial to measure the Γ_{\max} value and also all the surfactants behave like a univalent electrolyte for which n' value is taken equal to 2.

The area per molecule at the air / water interface gives us the information on the packing degree and also the adsorbed surfactant molecules orientation when compared with the dimensions of the molecule as obtained by the use of molecular models. The minimum area per molecule (A_{\min}) can be easily obtained from the expression of surface excess concentration by using the following relations:

$$A_{\min} = \frac{10^{14}}{(N\Gamma_{\max})} \quad (3.11)$$

where Γ_{\max} is in mol/cm² and N is the Avogadro's number. So, with increase in temperature, the A_{\min} value generally shows the inverse trend as that of Γ_{\max} .

A closer look at the table 3.2 and table 3.3 show that the Γ_{\max} values of all the counterions change in the opposite way from general trend. However, the result can be explained in the following way. The Γ_{\max} values generally decrease due to the increased thermal motion with a consequent decrease in the effective adsorption process. But for dodecyl benzene moiety with varying counterions, a slight increase may be due to the lower hydration effect of the dodecyl benzene sulfonate surfactants at higher temperature and hence increasing tendency to move the molecules to the air-liquid interface [80-84]. The benzene ring in the surfactants may also be partially responsible for this result via steric inhibition during adsorption process. Similar type of result is also reported in the literature [81]. At a particular temperature, with changes in counterions, the Γ_{\max} value shows some irregularities due to the enhanced hydrophobicity of the anionic part of the surfactant molecules depending upon the accessibility of their corresponding counterions. Some part of the tetraalkyl ammonium counterion in the dodecyl benzene sulfonate layer may be responsible for the gradual decrease Γ_{\max} value. This type of penetration is found in the literature [83] also. With increase in temperature, amphiphilic molecule tend to form a closely packed monolayer film of the hydrocarbon chain at the air / solution interface owing to the decreased repulsion between the oriented head groups indicated by the value of A_{\min} .

3. 5. 3. Thermodynamic parameters

The temperature dependency of DBS micelles having different counterions also enables one to determine the thermodynamic parameters of micellization. According to the pseudo-phase separation model the standard Gibbs free energy of micellization, ΔG_m^0 for ionic uni-univalent surfactant can be expressed as [21,24,85]:

$$\Delta G_m^0 = (2 - \alpha) RT \ln x_{cmc} \quad (3.12)$$

Here, x_{cmc} is the cmc expressed in mole fraction scale and α , the ionization degree or counterionic ionization constant of the micelle, can be expressed by $\alpha = \frac{p}{n}$, where p and n are the effective charge and the aggregation number of the micelle respectively. It is well known that the value of α can be determined from the ratio of the slope of the two linear fragments of conductivity-concentration plot above and below cmc [85-86].

The standard enthalpy change ΔH_m^0 can be obtained from Gibb's-Helmholtz equation [25]:

$$\Delta H_m^0 = -RT^2 \left[(2 - \alpha) \left(\frac{\partial \ln x_{cmc}}{\partial T} \right)_p - \ln x_{cmc} \left(\frac{\partial (2 - \alpha)}{\partial T} \right)_p \right] \quad (3.13)$$

However, as the variation of α with temperature is not well defined due to polydispersity of micelle and does not follow any general trend, it is difficult to estimate the second term in the parenthesis experimentally [87-88]. The term, however, is small in comparison with the first one, and therefore, to gain quantitative information regarding the thermodynamics we neglect the second term of the equation (3.13), and the expression now becomes:

$$\Delta H_m^0 = -(2 - \alpha)RT^2 \left(\frac{\partial \ln x_{cmc}}{\partial T} \right)_p \quad (3.14)$$

The enthalpy of micellization may be obtained if the dependency of the cmc on the temperature is known. The ΔS_m^0 and $\Delta_{mic}C_p^0$ are also determined as essential thermodynamic parameters from the common expressions:

$$\Delta S_m^0 = \frac{(\Delta H_m^0 - \Delta G_m^0)}{T} \quad (3.15)$$

$$\Delta_{mic}C_p^0 = \left(\frac{\partial \Delta H_m^0}{\partial T} \right)_p \quad (3.16)$$

In table 3.5 and table 3.6, the various thermodynamic data associated with micellization are presented. These parameters are found to vary with temperature and also with the nature of the associated counterions. Negative sign of ΔH_m^0 suggests that surfactant aggregation is an endothermic process. The variation of the standard thermodynamic parameters with different counterions at a particular temperature can also be explained by the size and the hydration of the counterion. In the figure 3.20, the variation of enthalpy with the variation of counterion of alkali metals along with ammonium ion is given. From the plot, it is clear that the enthalpy first increases from LDBS to SDBS and then decreases to a very low value in all the temperatures for PDBS and after that it will further increases to the higher values close to LDBS. Similar plot of enthalpy with tetraalkyl ammonium counterions are presented in the Figure 3.21. From these two tables it is clear that the counterionic activity is more pronounced in the case of alkali metal ions. The tetraalkyl ammonium surfactants have their enthalpy of micellization relatively close to each other. The enthalpy value first decreases with increase in chain length, reaches a shallow minimum for tetrapropyl ammonium counterions and then increases.

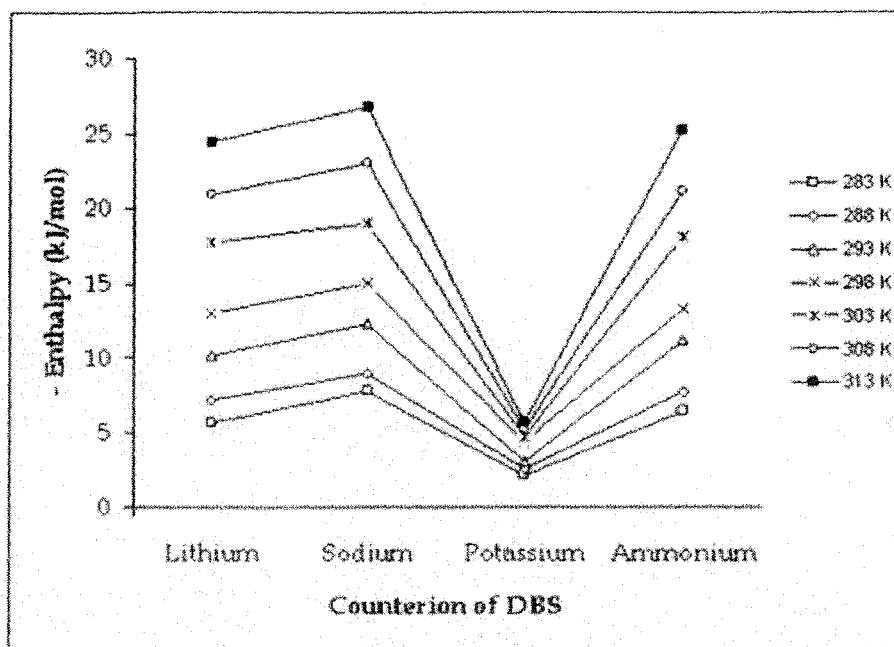


Figure 3.20. Enthalpy Change with the change in alkali metal counterions along with NH_4^+ ion.

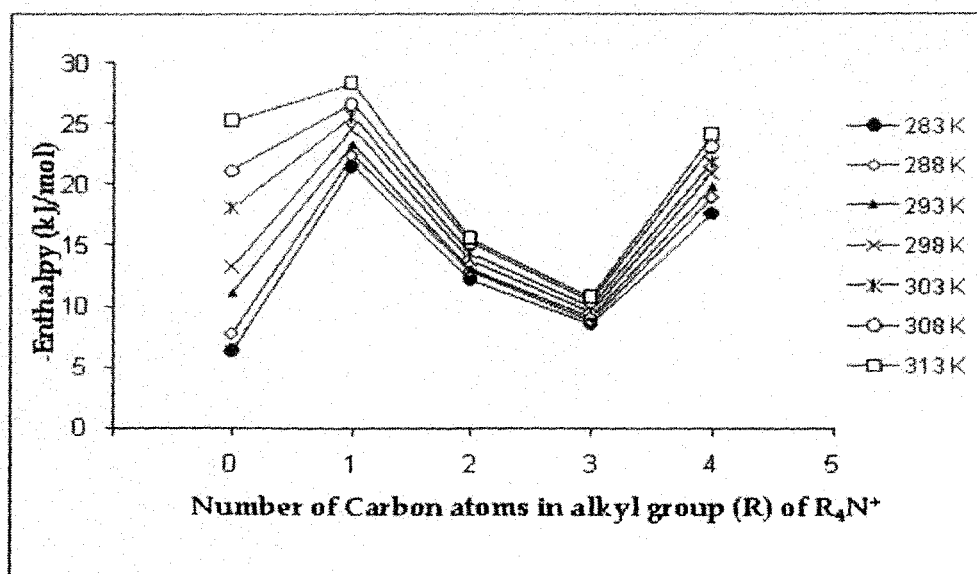


Figure 3.21. Enthalpy Change with the change in Alkyl Chain Length of R in R_4N^+ counterion.

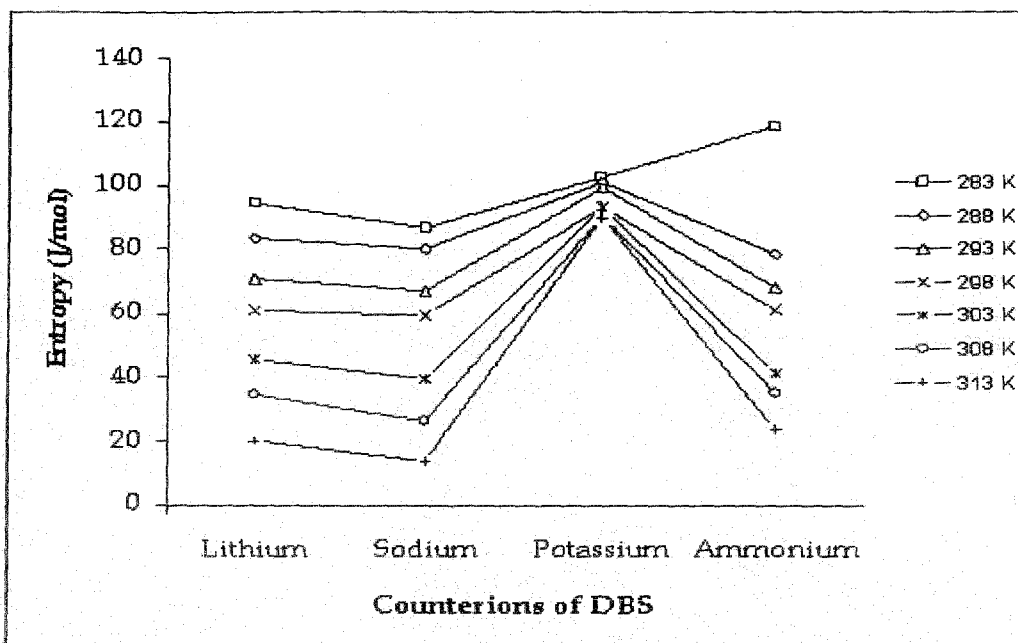


Figure 3.22. Entropy Change with the change in alkali metal counterions along with NH_4^+ ion.

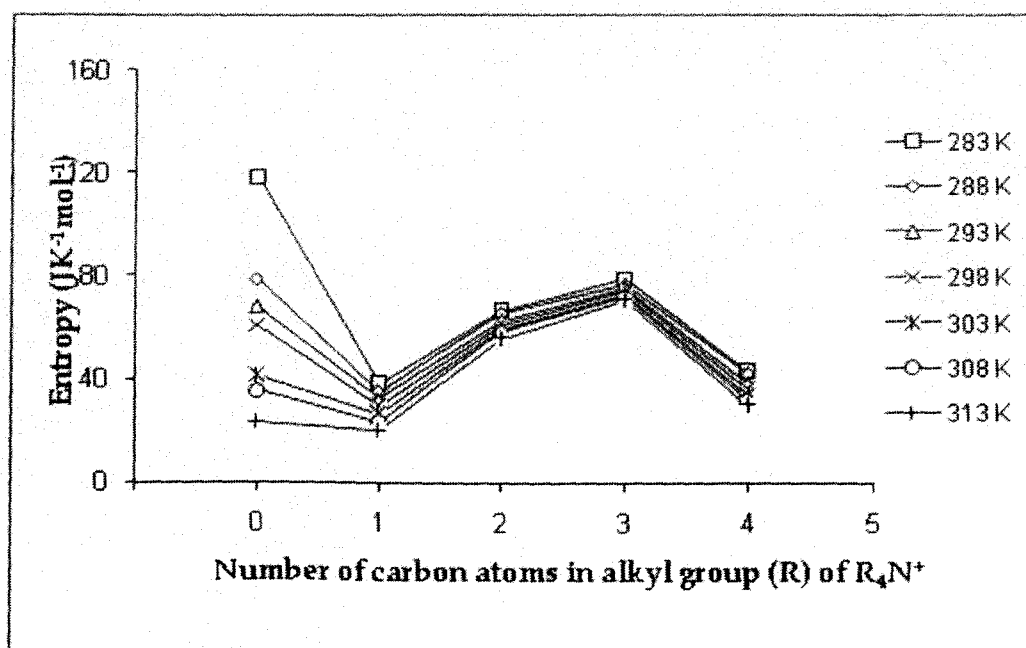


Figure 3.23. Entropy Change with the change in Alkyl Chain Length of R in R_4N^+ counterion.

In figure 3.22 and 3.23, the entropy changes as a function of counterions are given. The opposite trend of what is observed in enthalpy changes is attributed to the fact that in a normal micellization process the contribution of both entropy and enthalpy ultimately makes the process spontaneous according to the Gibbs-Helmholtz equation.

Different researchers often attempted to represent the thermodynamic variables of micellization into additive contribution of two factors: (1) interactions between hydrocarbon chains with water and (2) interactions between head groups, counterions and surfaces [89-90]. It is, therefore, logical to suppose that the second factor is important for the present work. A close look on the thermodynamic parameters support the view that in order to form micelle the gain in entropy is the major factor leading to negative change in Gibb's free energy [91-92]. But for the alkali metals counterions, the fact that though the free energy changes are not very different, the entropy change is significantly higher and the enthalpy changes are much lower for K^+ counterion containing DBS compared to all other systems. This suggests that the entropy contributes as a major driving force in micellization. Less hydration and higher binding capacity of K^+ ion may cause higher contribution of ΔS_m^0 in aggregation process. With increasing temperature, ΔS_m^0 decreases systematically for a particular type of counterion, suggesting a disruption of ordered arrangement of water dipoles around the amphiphilic part of the surfactant molecules [5,7,44]. Conceptually, ΔG_m^0 may be imagined to be divided into an electric contribution, F_{el}^0 arising from the ionic head groups and a hydrocarbon contribution, F_{hc}^0 .

$$\Delta G_m^0 = F_{el}^0 + F_{hc}^0 \quad (3.17)$$

Where F_{el}^0 is positive and its contribution to the total ΔG_m^0 value is generally small (about 3 ~ 4%). The F_{hc}^0 value may be divided into the free energy components $\Delta G_{-CH_2-}^0$ (contribution of $-CH_2-$ groups) and $\Delta G_{-CH_3}^0$ (contribution of terminal $-CH_3$ groups). $\Delta G_{-CH_3}^0$ is constant, however, $\Delta G_{-CH_2-}^0$ depends upon the chain length. The reported value for ionic surfactants is approximately $2.93 \sim 3 \text{ kJ mol}^{-1}$ [5,7,44]. Though the free energy change is not very different for all the systems, the enthalpy change is relatively higher.

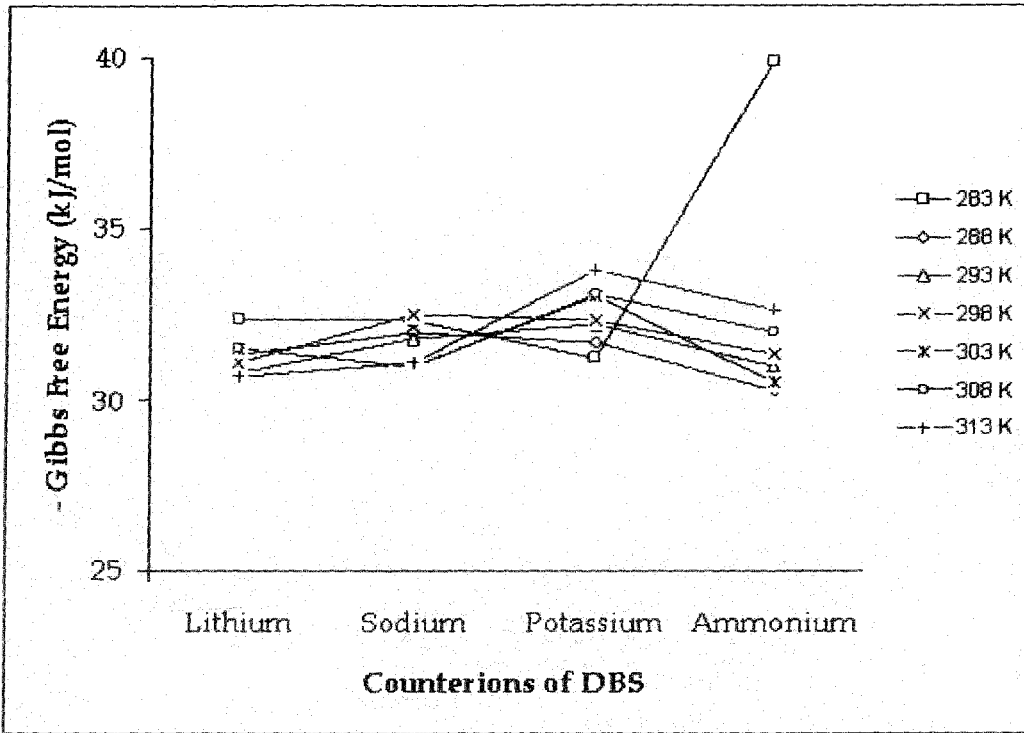


Figure 3.24. Gibbs Free Energy Change with the change in alkali metal counterions along with NH_4^+ ion.

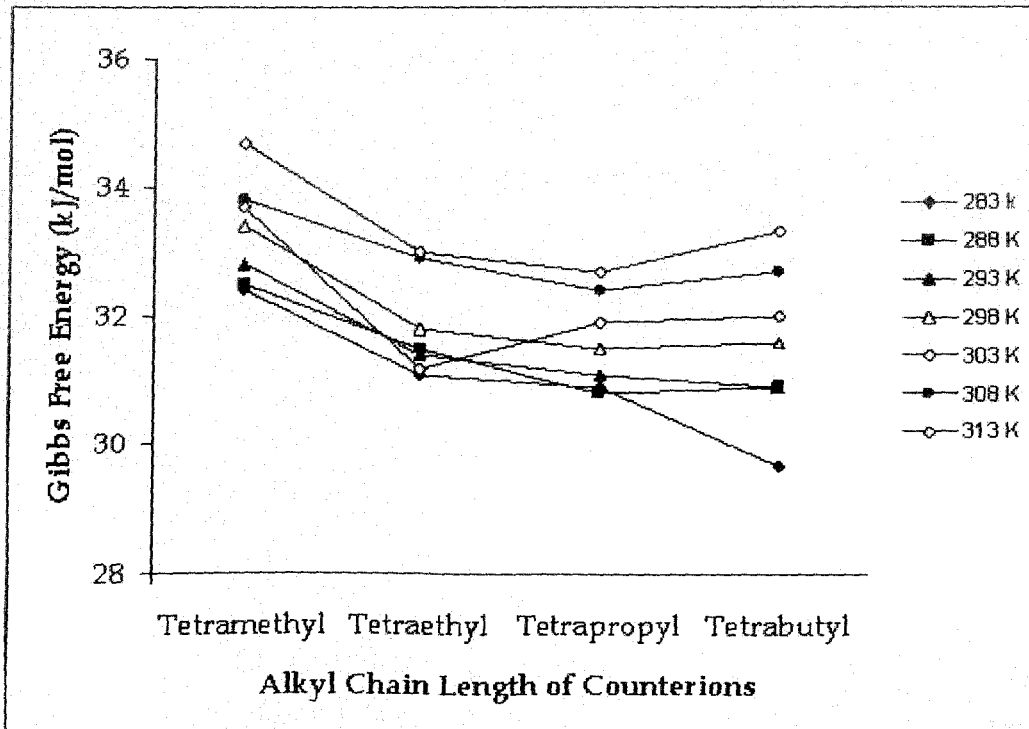


Figure 3.25. Entropy Change with the change in Alkyl Chain Length of R in R_4N^+ counterion.

Table 3.5

Thermodynamic parameters of micellization for Dodecyl benzene sulfonate with different alkali counterions along with NH_4^+ at various temperatures: Standard Gibb's free energy, Enthalpy, Entropy and standard heat capacity.

Counterion	T/K	$-\Delta G_m^\circ$ (kJ mol ⁻¹)	$-\Delta H_m^\circ$ (kJ mol ⁻¹)	ΔS_m° (J mol ⁻¹)	$-\Delta C_{pm}^\circ$ (J mol ⁻¹ K ⁻¹)
Li ⁺	283	32.4	5.7	94.3	409
	288	31.3	7.2	83.7	480
	293	30.8	10.1	70.6	551
	298	31.1	12.9	61.1	622
	303	31.5	17.7	45.5	693
	308	31.5	20.8	34.7	764
	313	30.7	24.3	20.4	835
Na ⁺	283	32.3	7.8	86.6	382
	288	32.0	9.0	79.9	474
	293	31.8	12.2	66.9	566
	298	32.5	14.9	59.1	658
	303	31.0	19.0	39.6	750
	308	31.0	22.9	26.3	842
	313	31.1	26.7	14.0	934
K ⁺	283	31.2	2.1	102.8	127
	288	31.7	2.6	101.0	117
	293	32.2	3.1	99.3	107
	298	32.3	4.4	93.6	97
	303	33.0	4.7	93.4	87
	308	33.1	5.2	90.6	77
	313	33.8	5.7	89.8	67
NH ₄ ⁺	283	39.9	6.3	118.7	405
	288	30.3	7.7	78.5	488
	293	31.0	11.1	67.9	571
	298	31.3	13.2	60.7	654
	303	30.5	18.0	41.2	737
	308	32.0	21.1	35.4	820
313	32.6	25.2	23.6	903	

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.6

Thermodynamic parameters of micellization for Dodecyl benzene sulfonate with different tetraalkyl ammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy, Entropy and standard heat capacity.

Counterion	T/K	$-\Delta G_m^\circ$ (kJ mol ⁻¹)	$-\Delta H_m^\circ$ (kJ mol ⁻¹)	ΔS_m° (J mol ⁻¹)	$-\Delta C_{pm}^\circ$ (J mol ⁻¹ K ⁻¹)
(CH ₃) ₄ N ⁺	283	32.4	21.5	38.34	141
	288	32.5	22.4	35.05	159
	293	32.8	23.3	32.21	177
	298	33.4	24.6	29.46	195
	303	33.7	25.6	26.47	213
	308	33.8	26.6	23.17	231
	313	34.7	28.3	20.41	249
(C ₂ H ₅) ₄ N ⁺	283	31.1	12.2	66.68	108
	288	31.5	12.8	65.09	116
	293	31.4	13.1	62.50	124
	298	31.8	13.8	60.81	132
	303	31.2	14.3	59.08	140
	308	32.9	15.1	58.02	148
	313	33.0	15.6	55.53	156
(C ₃ H ₇) ₄ N ⁺	283	30.9	8.5	79.05	81
	288	30.8	8.7	76.50	87
	293	31.1	9.1	75.00	93
	298	31.5	9.5	73.71	99
	303	31.9	9.9	72.76	105
	308	32.4	10.3	71.64	111
	313	32.7	10.7	70.26	117
(C ₄ H ₉) ₄ N ⁺	283	29.7	17.6	43.07	245
	288	30.9	18.9	41.71	241
	293	30.9	19.8	38.01	237
	298	31.6	20.9	35.79	233
	303	32.0	21.8	33.60	229
	308	32.7	23.1	31.38	225
	313	33.3	24.0	29.90	221

^aThe values in the parenthesis represent cmc determined by conductivity method.

for tetramethyl ammonium ion compared to the other counter ions. It can, therefore, be concluded that for the present system, enthalpy contribution is the major factor for micellization. Loosely bound water dipole with the $N^+(CH_3)_4$ ion may cause lower contribution of ΔS_m^0 in aggregation process.

The effective interactions associated with hydrocarbon chains may be expressed by standard heat capacity of micelle formation, $\Delta_{mic}C_p^0$. In all the surfactant systems, the standard heat capacity changes linearly with temperature, as shown in figure 3.26.

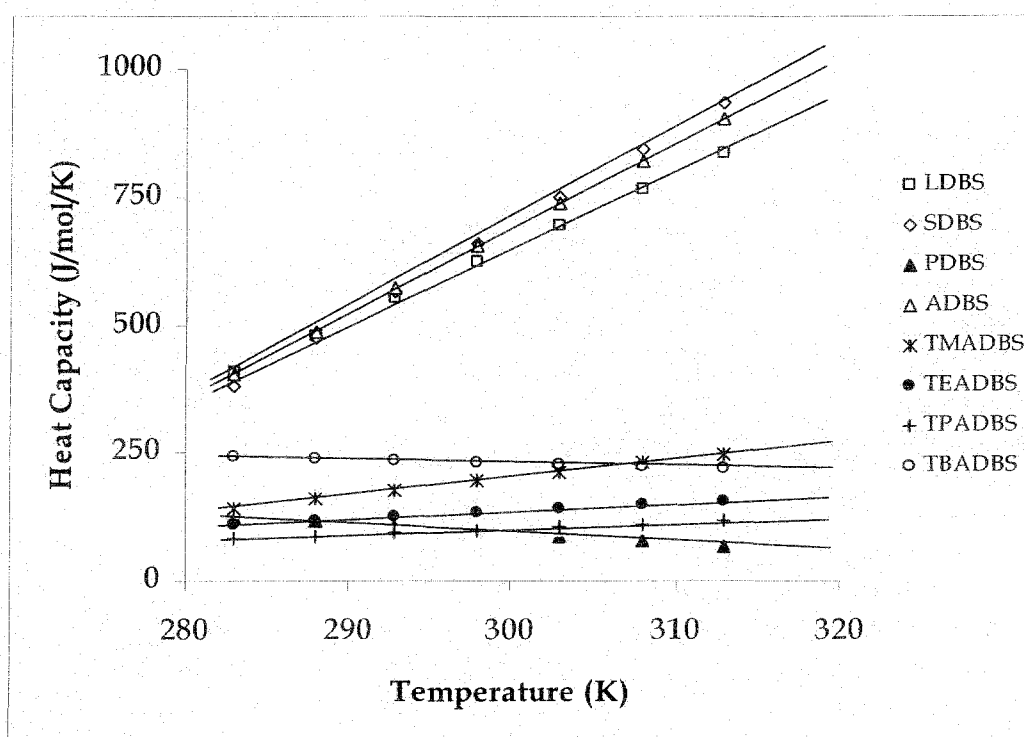


Figure 3.26. Variation of Heat capacity of the surfactants as a function of temperature.

The calculated values of $\Delta_{mic}C_p^0$ for DBS with varying counterions fall between a wide range of value viz., -67 to -934 J mol⁻¹ K⁻¹, for the variation of temperature between 283 K and 313 K. For all the counterions except K⁺, $\Delta_{mic}C_p^0$'s do not change significantly at lower temperatures (<25°C); but at higher temperatures, $\Delta_{mic}C_p^0$ values follow the order Na⁺ > NH₄⁺ > Li⁺ > K⁺. Potassium ion, however, shows anomalous behaviour, which may be due to its strong tendency of ion-pair formation. For the tetraalkyl ammonium counterions, the order of $\Delta_{mic}C_p^0$ values at a particular temperature is as follows: (CH₃)₄N⁺ > (C₄H₉)₄N⁺ > (C₂H₅)₄N⁺ > (C₃H₇)₄N⁺. This irregularity in behaviour

may also be explained by the tendency to form ion pair with the DBS moiety. Counterion binding also reduces the number of water molecules in the solvation shell of the counterion as well as the negatively charged head groups of DBS. At high temperatures, $\Delta_{mic}C_p^{0'}$'s give large negative values due to solvation of ions upon demicellization, and this is quite reasonable because as the temperature is increased cmc value also increases in all the present systems.

Enthalpy and entropy change in the micellization process show a linear relationship for all the surfactant systems at a particular temperature and this is known as the enthalpy-entropy compensation and it is true for any other following processes, viz., oxidation-reduction, hydrolysis, protein unfolding etc. The entropy-enthalpy compensation plot is given in the figure 3.27 for different surfactant system at 298 K [25,77-78].

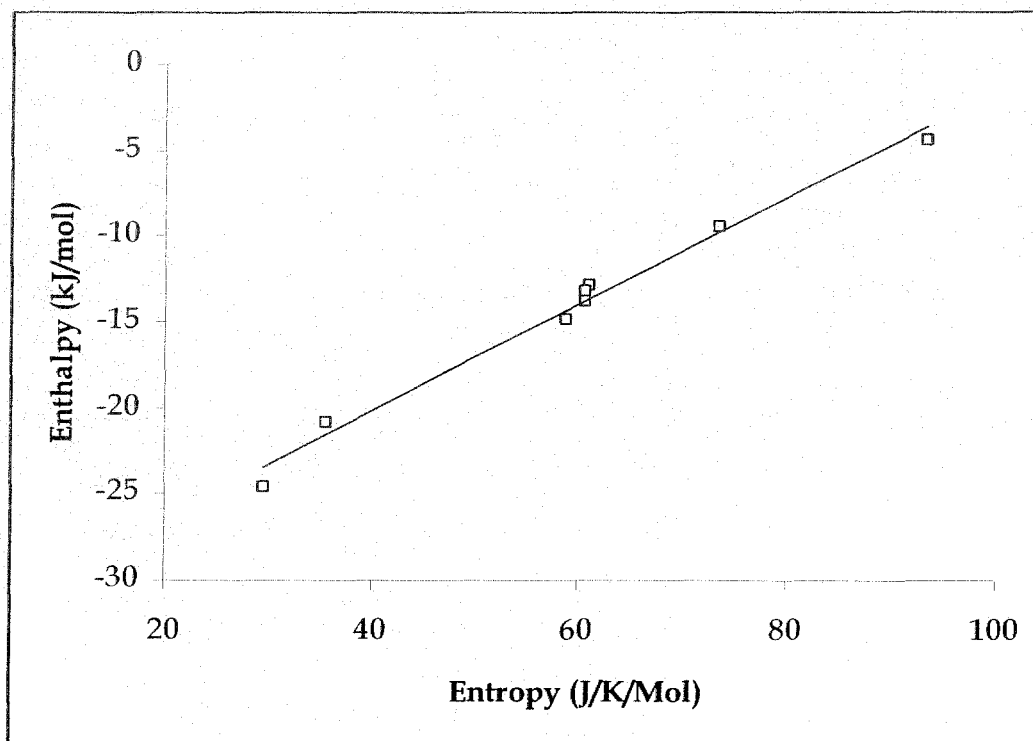


Figure 3.27. Entropy-enthalpy compensation plot of surfactant with different counterions at 298 K temperature.

The importance of this value lies in the fact with hydrophobicity of surfactant which leads to stable micelle formation. The compensation phenomenon between the enthalpy change, ΔH_m^0 , and the entropy change, ΔS_m^0 , in various processes can be described in the form of [83-84]

$$\Delta H_m^0 = \Delta H_m^* + T_c \Delta S_m^0 \quad (3.18)$$

The compensation temperature can be calculated from the slope of the enthalpy-entropy compensation plot, which is a straight line. The slope and intercept of the straight line has different meanings, slope interprets a measure of desolvation part of micellization which means a characteristic of solute-solute and solute-solvent interaction whereas the intercepts interprets solute-solute interactions. From the figure 3.27, the intercepts (ΔH_m^*) has been found to be $-32.6 \text{ kJ mol}^{-1}$ for DBS which correspond to the driving force of micellization where the entropy does not contribute the process at that particular temperature.

3.6. Effects of counterions on the micellization of dodecyl benzene sulfonate, dodecyl sulfate and bis-(2-ethyl-1-hexyl) sulfosuccinate: A brief comparison

Present work constitutes a part of the series of research performed in our laboratory on the effect of counterions and temperature on the micellization of various anionic surfactants; some of them are already published [80 - 82]. The work has been carried out mainly on the three anionic surfactants viz., dodecyl benzene sulfonates, dodecyl sulfate and bis-(2-ethyl-1-hexyl) sulfosuccinate with varying counterions. The reason for selecting these surfactants stems from their structural differences at the hydrophobic ends. The general structure of dodecyl benzene sulfonate with sodium ion is given in figure 3.1. As discussed earlier, the DBS moiety contains a benzene ring attached with the sulfonate group and also the C_{12} -hydrocarbon tail is branched in the present system of the study. Furthermore, the literature concerning DBS surfactant is not so huge as compared to SDS or AOT. This may be due to the presence of several

isomeric forms of DBS moiety. Sodium dodecyl sulfate is probably the most researched anionic surfactants possibly due to its simple structure [36-37,74,93-94]. It shows many other properties like interactions with dyes, electrophoresis and electrokinetics or methane hydrate formation reactions [95-97]. The schematic molecular structure of SDS is in Figure 3.28.

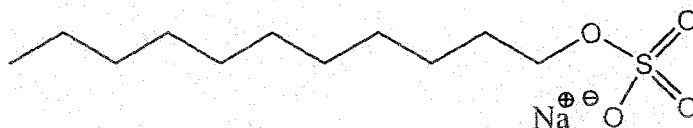


Figure 3.28: Schematic molecular structure of SDS

AOT (Aerosol-OT, sodium bis-(2-ethyl-1-hexyl) sulfosuccinate), a double tailed anionic surfactant, used mainly in medicinal and pharmaceutical purposes due to its non-toxic property, It can form microemulsion and has the rich phase behaviour in solution [98-99]. Figure 3.29 shows the schematic molecular structure of AOT.

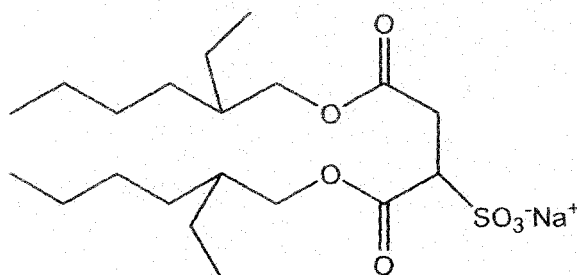


Figure 3.29: Schematic molecular structure of AOT

In tables 3.7, 3.8, 3.11 and 3.12, the cmc values were determined by surface tension and conductivity measurements, are given. The range of cmc values of the following three surfactants with varying counterions are 3.33 mM to 0.79 mM, 9.21 mM to 1.10 mM and 3.55 mM to 0.75 mM for DBS, DS and AOT respectively. The insertion of a phenyl ring and the branching of hydrophobic tail lowered the cmc values of DBS and AOT compared to DS. On the other hand, benzene ring with branching hydrocarbon chain brings more hydrophobicity to the surfactant than double strand structure of AOT and as a result, the cmc values are less than as compared to AOT.

In all the three surfactants, the change of cmc values with temperature is small but it is in detectable range. In potassium salts of DS and AOT, it was found that at a concentration of 10 times the cmc, they are immiscible in water at room temperature. The solution contains hydrated crystals dispersed in a micellar phase. So, the micellization property can be studied for K-AOT in the temperature lower than 313 K and we have studied the cmc within the temperature range 283-308 K. Potassium dodecyl sulfate has the Krafft temperature of 307 K [100-102] at the cmc. So, it is impossible to investigate the micellization process in our temperature range for KDS since the temperature leading to a clear solution was too high. But for DBS moiety, no such problem arises in the temperature range 283 - 308 K.

For all the surfactant systems with tetraalkyl ammonium counterions, cmc decreases with increase in tetraalkyl ammonium chain length. The order of alkali metal cations and ammonium ion is not same for the three surfactants. The orders are: $\text{NH}_4^+ > \text{Li}^+ > \text{Na}^+$ for dodecyl sulfate, $\text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{K}^+$ for AOT and $\text{Na}^+ > \text{Li}^+ > \text{NH}_4^+ > \text{K}^+$ for DBS. This trend can be explained by the counterion binding to micelles. K^+ gives anomalous results owing to its tendency towards ion-pair formation in K-AOT. Li^+ has the highest hydrated radius can modify the internal structure of double trailed structure of AOT micelle resulting a lower cmc values. The general tendency of cmc change with temperature is parabolic in nature [103-106]. These are true to the micelles of surfactants viz., LDS, SDS, ADS, Na-AOT, NH_4 -AOT, TMA-AOT, TEA-AOT. Other surfactants of DS and AOT have very low temperature dependency. However, the present DBS with different counterions show linear types of temperature dependency.

Table 3.7*

Surface properties of dodecyl sulfate having different alkali counterions along with NH_4^+ ion at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule at the surface.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	Γ_{max} / mol cm ⁻² × 10 ¹⁰	A_{min} /nm ² × 10 ²	α
Li ⁺	283	9.11 (9.06)	3.22	0.52	0.30
	288	8.87 (8.92)	3.10	0.54	0.29
	293	8.52 (8.55)	2.98	0.55	0.31
	298	8.23 (8.18)	3.08	0.54	0.33
	303	8.43 (8.42)	2.94	0.56	0.34
	308	8.51 (8.52)	2.90	0.57	0.32
	313	8.47 (8.45)	2.91	0.57	0.33
Na ⁺	283	8.88 (8.96)	3.12	0.53	0.28
	288	8.15 (8.17)	3.01	0.55	0.30
	293	8.05 (8.01)	3.11	0.54	0.30
	298	7.96 (7.94)	2.90	0.57	0.32
	303	8.58 (8.62)	2.88	0.58	0.35
	308	8.65 (8.67)	2.78	0.60	0.32
	313	8.77 (8.80)	2.73	0.61	0.34
NH ₄ ⁺	283	9.21 (9.16)	3.21	0.52	0.27
	288	9.07 (9.10)	3.18	0.52	0.29
	293	8.88 (8.90)	3.11	0.53	0.28
	298	8.51 (8.62)	3.02	0.55	0.32
	303	8.39 (8.38)	2.93	0.57	0.30
	308	8.85 (8.76)	2.87	0.58	0.31
	313	8.92 (8.88)	2.88	0.58	0.28

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.8*

Surface properties of dodecyl sulfate having different tetraalkylammonium counterions at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule at the surface.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	Γ _{max} / cm ⁻² × 10 ¹⁰	mol	A _{min} /nm ² × 10 ²	α
(CH ₃) ₄ N ⁺	283	5.92 (6.01)	3.34		0.50	0.21
	288	5.70 (5.66)	3.24		0.51	0.21
	293	5.58 (5.55)	3.18		0.52	0.23
	298	5.51 (5.52)	3.15		0.53	0.25
	303	5.49 (5.47)	3.20		0.52	0.22
	308	5.56 (5.60)	3.14		0.53	0.24
	313	5.80 (5.72)	3.08		0.54	0.23
(C ₂ H ₅) ₄ N ⁺	283	4.08 (4.10)	3.28		0.51	0.20
	288	3.98 (3.97)	3.25		0.51	0.21
	293	3.92 (3.91)	3.19		0.52	0.23
	298	3.86 (3.86)	3.11		0.53	0.24
	303	3.82 (3.85)	3.18		0.52	0.24
	308	3.87 (3.88)	3.09		0.54	0.22
	313	3.85 (3.85)	2.99		0.56	0.23
(C ₃ H ₇) ₄ N ⁺	283	2.32 (2.36)	3.35		0.49	0.20
	288	2.26 (2.30)	3.30		0.50	0.19
	293	2.22 (2.23)	3.22		0.51	0.20
	298	2.23 (2.24)	3.19		0.52	0.21
	303	2.18 (2.21)	3.20		0.52	0.21
	308	2.23 (2.20)	3.17		0.52	0.19
	313	2.22 (2.21)	3.11		0.53	0.19
(C ₄ H ₉) ₄ N ⁺	283	1.34 (1.32)	3.33		0.50	0.19
	288	1.29 (1.28)	3.28		0.50	0.18
	293	1.22 (1.24)	3.20		0.52	0.20
	298	1.17 (1.15)	3.14		0.53	0.20
	303	1.18 (1.21)	3.09		0.54	0.18
	308	1.15 (1.17)	2.91		0.57	0.18
	313	1.10 (1.11)	3.01		0.55	0.17

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.9*

Thermodynamic parameters of micellization for Dodecyl sulfate with different alkali counterions along with NH_4^+ at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp/K	$-\Delta G_m^\circ$	ΔH_m°	ΔS_m°
Li ⁺	283	34.9	27.2	219.2
	288	35.8	25.9	214.4
	293	36.2	24.1	205.7
	298	36.5	22.2	196.9
	303	36.8	20.3	188.3
	308	37.8	18.6	182.9
	313	38.2	16.3	174.2
Na ⁺	283	35.4	-9.4	91.8
	288	35.9	-14.3	75.1
	293	36.6	-19.6	57.8
	298	36.8	-25.0	39.5
	303	36.5	-30.4	19.8
	308	37.7	-37.4	1.2
	313	37.8	-43.5	-18.3
NH ₄ ⁺	283	35.4	-15.7	69.8
	288	35.7	-19.6	56.0
	293	36.6	-24.1	42.9
	298	36.6	-28.0	28.6
	303	37.7	-33.2	14.7
	308	37.8	-38.1	-0.9
	313	39.1	-44.3	-16.5

Table 3.10*

Thermodynamic parameters of micellization for Dodecyl sulfate with different tetraalkylammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp/K	$-\Delta G_m^\circ$	ΔH_m°	ΔS_m°
(CH ₃) ₄ N ⁺	283	38.5	-2.3	128.1
	288	39.4	-6.1	115.7
	293	39.7	-10.0	101.4
	298	40.0	-14.0	86.9
	303	41.4	-18.9	74.2
	308	41.5	-23.4	58.6
	313	42.2	-28.7	43.2
(C ₂ H ₅) ₄ N ⁺	283	40.3	19.0	209.8
	288	40.9	18.4	205.9
	293	41.2	17.6	200.6
	298	41.7	16.8	196.4
	303	42.5	16.0	193.0
	308	43.6	15.3	191.3
	313	44.1	14.3	186.5
(C ₃ H ₇) ₄ N ⁺	283	42.7	21.1	225.4
	288	43.8	20.7	224.1
	293	44.4	20.0	220.0
	298	44.9	20.0	215.4
	303	45.8	18.6	212.3
	308	46.9	18.0	210.7
	313	47.7	17.1	207.1
(C ₄ H ₉) ₄ N ⁺	283	45.3	14.0	209.4
	288	46.5	13.3	207.7
	293	47.0	12.3	202.6
	298	48.0	11.4	199.5
	303	49.3	10.6	197.7
	308	50.3	9.5	194.0
	313	51.6	8.3	191.4

Table 3.11*

Micellization and Surface parameters of AOT surfactants having different alkali counterions along with NH_4^+ ion at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	Γ_{max} / cm ⁻² × 10 ¹⁰	mol	A _{min} /nm ² × 10 ²	α
Li ⁺	283	3.35 (3.40)	1.63		1.02	0.73
	288	2.98 (3.15)	1.60		1.04	0.51
	293	2.82 (2.90)	1.59		1.04	0.49
	298	2.66 (2.63)	1.59		1.44	0.58
	303	2.40 (2.37)	1.56		1.06	0.70
	308	2.24 (2.19)	1.61		1.03	0.68
	313	2.39 (2.23)	1.60		1.05	0.77
Na ⁺	283	3.55 (3.53)	1.42		1.17	0.61
	288	3.16 (3.20)	1.45		1.14	0.51
	293	2.88 (2.77)	1.49		1.11	0.46
	298	2.63 (2.40)	1.57		1.06	0.70
	303	2.24 (2.20)	1.76		0.94	0.69
	308	2.37 (2.26)	1.70		0.98	0.70
	313	2.80 (2.69)	1.71		0.97	0.67
K ⁺	283	2.97 (3.11)	1.84		0.90	0.74
	288	2.90 (3.01)	2.01		0.83	0.63
	293	2.82 (2.90)	2.22		0.75	0.58
	298	2.70 (2.62)	2.25		0.74	0.73
	303	2.44 (2.35)	2.30		0.72	0.85
	308	2.42 (2.32)	2.44		0.68	0.75
	313	-	-		-	-
NH ₄ ⁺	283	3.87 (3.85)	1.56		1.06	0.45
	288	3.31 (3.20)	1.58		1.05	0.58
	293	3.09 (3.12)	1.45		1.14	0.66
	298	2.70 (2.65)	1.55		1.07	0.68
	303	2.59 (2.52)	1.80		0.92	0.77
	308	2.65 (2.60)	1.72		0.96	0.66
	313	2.82 (2.75)	1.76		0.94	0.71

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.12*

Micellization and Surface parameters of AOT surfactants having different tetraalkylammonium counterions at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Counterion	T/K	cmc ^a / (mol dm ⁻³ × 10 ⁻³)	Γ _{max} / mol cm ⁻² × 10 ¹⁰	A _{min} /nm ² × 10 ²	α
(CH ₃) ₄ N ⁺	283	4.76 (4.61)	1.68	0.99	0.50
	288	3.82 (4.10)	1.65	1.01	0.51
	293	3.24 (3.40)	1.53	1.08	0.67
	298	2.90 (2.90)	1.60	1.04	0.74
	303	2.05 (2.35)	1.80	0.92	0.72
	308	2.10 (2.20)	1.72	0.96	0.76
	313	2.26 (2.31)	1.67	0.99	0.74
(C ₂ H ₅) ₄ N ⁺	283	1.88 (2.10)	1.44	1.15	0.42
	288	1.78 (2.00)	1.33	1.25	0.56
	293	2.95 (1.85)	1.46	1.14	0.65
	298	2.45 (2.50)	1.43	1.16	0.67
	303	2.31 (2.43)	1.76	0.94	0.80
	308	2.37 (2.50)	1.31	1.27	0.69
	313	2.56 (2.63)	1.41	1.12	0.66
(C ₃ H ₇) ₄ N ⁺	283	1.18 (1.34)	1.67	0.99	0.56
	288	1.05 (1.20)	1.71	0.97	0.69
	293	0.93 (0.98)	1.85	0.89	0.66
	298	0.97 (0.95)	1.71	0.97	0.65
	303	0.92 (0.85)	1.77	0.94	0.68
	308	0.87 (0.90)	1.69	0.98	0.75
	313	0.74 (0.80)	1.93	0.86	0.74
(C ₄ H ₉) ₄ N ⁺	283	1.04 (1.11)	1.32	1.26	0.57
	288	0.87 (0.91)	1.40	1.18	0.58
	293	0.80 (0.83)	1.42	1.17	0.59
	298	0.77 (0.80)	1.63	1.02	0.76
	303	0.75 (0.78)	1.82	0.91	0.67
	308	-	-	-	-
	313	-	-	-	-

^aThe values in the parenthesis represent cmc determined by conductivity method.

Table 3.13*

Thermodynamic parameters of micellization for AOT surfactants with different alkali counterions along with NH_4^+ at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp/K	$-\Delta G_m^\circ$	ΔH_m°	ΔS_m°
Li ⁺	283	29.0	9.9	63.4
	288	35.1	12.1	80.0
	293	36.3	12.6	80.9
	298	34.9	12.3	76.0
	303	32.8	11.6	69.9
	308	34.3	12.3	71.5
	313	32.1	12.0	73.3
Na ⁺	283	44.4	23.5	73.8
	288	37.2	25.3	41.3
	293	37.0	25.4	39.7
	298	32.1	22.1	33.3
	303	33.5	23.1	34.1
	308	33.6	23.8	32.0
	313	34.2	24.3	34.4
K ⁺	283	29.2	5.7	83.4
	288	32.4	6.4	90.5
	293	34.1	6.8	93.2
	298	31.3	6.3	84.0
	303	29.2	5.9	76.8
	308	32.3	6.7	83.3
	313	-	-	-
NH ₄ ⁺	283	35.0	16.5	61.3
	288	33.0	15.6	56.9
	293	32.0	14.3	50.2
	298	32.5	15.9	56.6
	303	30.9	15.8	52.0
	308	34.1	16.0	50.0
	313	33.2	16.3	53.5

Table 3.14*

Thermodynamic parameters of micellization for AOT surfactants with different tetraalkylammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp/K	$-\Delta G_m^\circ$	ΔH_m°	ΔS_m°
(CH ₃) ₄ N ⁺	283	33.0	29.1	13.7
	288	34.2	30.0	14.6
	293	31.7	27.9	13.3
	298	30.8	27.2	12.1
	303	33.0	28.6	14.5
	308	32.3	28.5	12.2
	313	33.1	29.0	12.8
(C ₂ H ₅) ₄ N ⁺	283	35.0	12.2	80.6
	288	33.0	11.7	74.0
	293	32.0	12.2	67.6
	298	32.5	12.3	67.8
	303	30.9	11.9	62.7
	308	34.1	13.3	67.5
	313	35.2	13.7	67.7
(C ₃ H ₇) ₄ N ⁺	283	36.4	8.5	98.7
	288	34.7	8.1	92.3
	293	35.8	8.5	93.3
	298	36.6	8.8	93.1
	303	36.6	8.9	91.2
	308	35.4	8.7	86.5
	313	36.8	8.8	90.6
(C ₄ H ₉) ₄ N ⁺	283	36.6	14.4	78.4
	288	37.6	14.9	78.8
	293	38.2	15.3	78.2
	298	34.4	15.2	64.4
	303	37.7	15.5	73.3
	308	-	-	-
	313	-	-	-

* Data are collected from our previous work [34,80-81].

Surface parameters are also listed in the table as mentioned above for cmc values. Among the Γ_{max} values of DS, DBS and AOT, only the DS follows the general trend with temperature. The order of Γ_{max} values is lower in the case of DBS as compared to DS and AOT suggesting weaker adsorption of this surfactant at air-solution interface is low. The lower A_{min} values for DS and AOT suggest that these amphiphiles tend to form a more closely packed monolayer film of the hydrocarbon chain at air / liquid interface as compared to DBS with same counterions.

The thermodynamic parameters have been reported in the tables 3.9, 3.10, 3.13, 3.14. From the tables, it is clear that the micellization process is spontaneous as indicated by large negative values of ΔG_m^0 for all the surfactant systems. A close look in all the systems in the table shows that at low temperature, the entropy gain is the main factor for the formation of micelle leading to the negative Gibb's free energy change. Therefore, the magnitude and the signs of ΔG_m^0 and ΔS_m^0 suggest the stability of the micelle. The ΔG_m^0 values of the three systems are almost in the same range and with increase in temperatures the ΔG_m^0 value generally increases for DS and DBS systems whereas for AOT some reverse trend is observed. The reverse trend may be due to the double traileed structure of AOT which facilitates more disruption of water structures at higher temperatures. In between the DS and DBS systems, the ΔG_m^0 value is higher for DS systems, particularly more pronounced for the alkyl ammonium counterions. The enthalpy of micellization is negative for all the counterions in case of AOT and DBS. But for DS, there are both positive and negative value of enthalpy change of micellization suggests that both exothermic and endothermic process to occur at the micellization process. The lower enthalpy values are shown by potassium counterions for both AOT and DBS surfactants with higher enthalpy values.

The effective interaction associated with hydrocarbon chains may be expressed by standard heat capacity of micelle formation, $\Delta_{mic}C_p^0$. The $\Delta_{mic}C_p^0$ values for comparison are calculated for only SDBS and SDS systems due to their very similar molecular formula and also for the presence of a dodecyl moiety in hydrocarbon chains. In both the systems, the standard heat capacity changes with temperature are shown in figure 3.30.

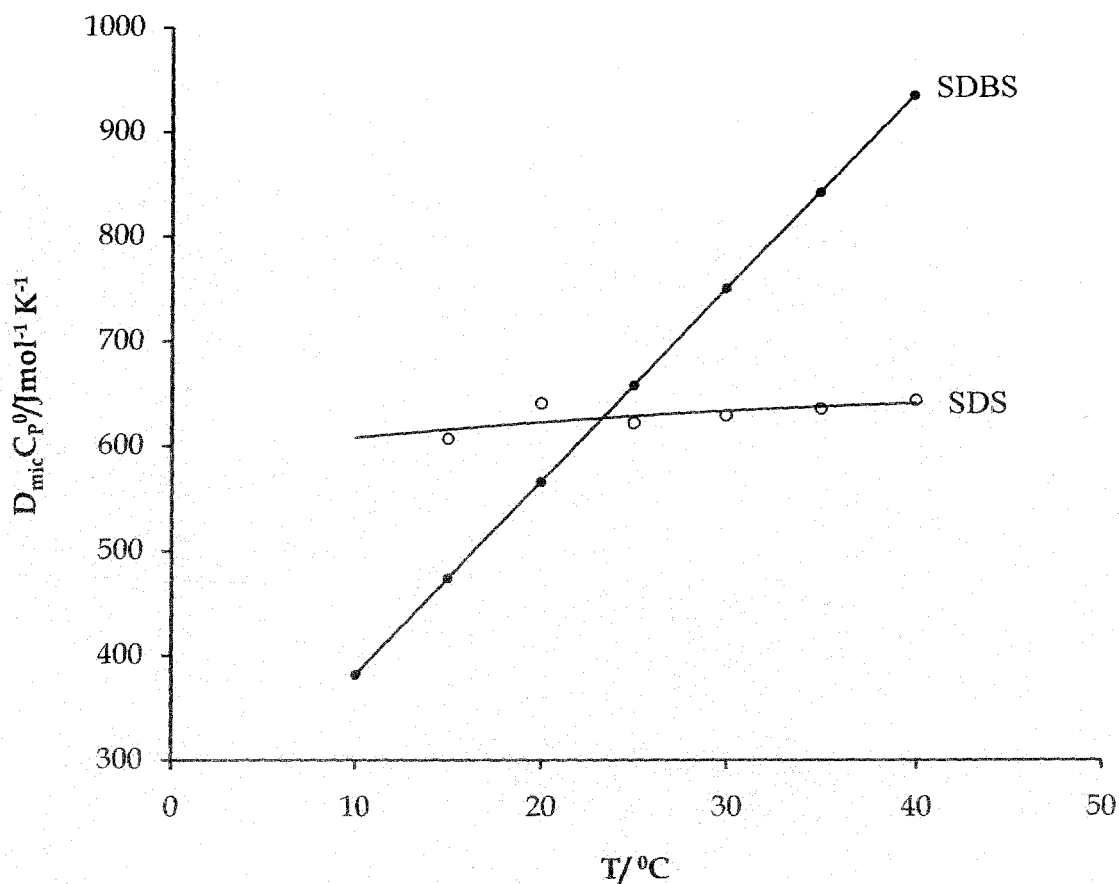


Figure 3.30: Variation of standard heat capacity of micelle formation, $\Delta_{mic}C_p^0$ as a function of temperature for SDBS and SDS.

The calculated values of $\Delta_{mic}C_p^0$ for SDBS fall between a wide range of value viz., -381.8 to -933.8 J mol⁻¹ K⁻¹ for the temperature range 283-293 K. On the other hand, SDS which also yields $\Delta_{mic}C_p^0$ values between -607 and -644 J mol⁻¹ K⁻¹.

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