

Chapter 3

**Studies on Micellization of Anionic Surfactants in
Aqueous Media: Effect of Counterions and Alcohols**

3.1 Introduction and Review of the Previous Work

It is known that the science of surface active agents (Surfactants) is one of the important subtopics of the colloidal science. Surfactants have gained great interest in recent years due to a huge benefit achieved in many industries producing detergent, cosmetics and pharmaceuticals. Surfactants with lower concentration greatly reduce the surface tension between two or more incompatible phases. In some sense, the structural features of surfactants are responsible for the surface activity. The structural features of a surfactant are characterized by the existence of a polar head and a non-polar tail. The polar head of the surfactant may be charged or uncharged (but polar). A charged polar head may carry a positive or a negative charge or both, while the nonpolar (hydrophobic) tail is usually a flexible hydrocarbon chain (C_8 - C_{18}) which may contain an aromatic ring. Their composite character is described by a property known as 'hydrophilic lipophilic balance' i.e., HLB. It is the HLB which primarily decides their micellization, dispersion and emulsification activities. The four major types of surfactants are classified as anionic, cationic, amphoteric or zwitterionic and nonionic depending on the head group [1-5].

Surfactant molecules in aqueous media form micelles above their critical micelle concentration (cmc), accompanying striking changes in the various physical properties [6]. 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 shapes [7].

- (a) Spherical micelles are formed with an interior composed of hydrocarbon chains and a surface of polar head groups (pictured as spheres) 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.
- (b) 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 so these micelles are polydisperse in nature.

- (c) 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.
- (d) Reversed or inverted micelles having a water core surrounded by the surfactant polar head groups. The alkyl chains together with a nonpolar solvent make up the continuous medium.
- (e) A bicontinuous structure with the surfactant molecules aggregated into connected films characterized by two curvatures of opposite sign. The mean curvature is small (zero for a minimal surface structure).
- (f) Vesicles are built from bilayers similar to those of the lamellar phase and are characterized by two distinct water compartments, with one forming the core and one the external medium. Vesicles may have different shapes and there are also reversed-type vesicles.

The shape of a micelle depends on the concentration of surfactant and the presence of additives or hydrotrops for single systems, and is controlled by the spontaneous curvature of the micellar interface [8,9]. 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 [10] has described a realistic model for a micelle. This model involves a rather sharp interface between a dry hydrophobic hydrocarbon core and a region filled with surfactant head groups, part of the counter ions and water, viz. the Stern region.

Micelle formation from surfactant monomers has proved an excellent model process for studying the hydrophobic effect. The formation of an ionic micelle from monomeric ions results in a balance between hydrophobic interactions between the hydrophobic part of the micelle-forming ions, electrostatic interactions between their hydrophilic charged parts, as well as with and between the counterions. Hartley's model [4a] for micelles was that of a spherical aggregate of surfactant molecules whose alkyl groups formed a hydrocarbon core and the polar groups formed a charged surface. The hydrocarbon core is liquid-like and, since there is no void space inside this anhydrous region, the radius is not greater than the stretched-out length

of the surfactant molecule. As a result the aggregate comprises at most 50-100 molecules. The charge density on the micelle surface is less than that expected from the density of packing of charged head groups due to the binding of counter ions to the micelle surface. 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 surfactant solutions beyond the cmc; i.e. this description of a micelle of an anionic surfactant has not really been superseded and can be judged from a schematic drawing (Figure 3.1) of sodium dodecyl sulfate [9].

Spherical micelles are formed by anionic surfactants since the electrostatic repulsion between adjacent head groups result in a large value for optimal head group area. Despite this fact, direct visualization has been claimed by Bellare and et al. [2a] in a cryo-TEM image of a 10 mM solution of ditetradecyldimethyl-ammonium acetate. Measurements from the photograph suggest a micelle radius of 3.0 ± 0.3 nm. The dimension of a spherical micelle have been established using several techniques but the most precise has been small angle neutron scattering.

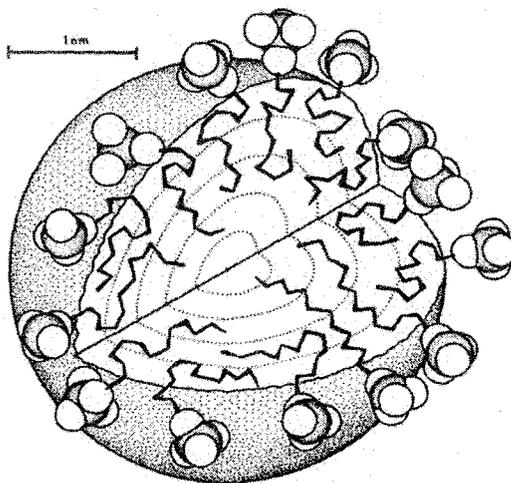


Figure 3.1 Schematic representation of a micelle

In addition, the changes in hydration energies and specific interactions with counterions may also be important [11-15]. The strength and importance of these various interactions depend upon externally controllable factors, such as temperature and ionic strength on the properties of the particular ions involved. Moreover, the structure of the resulting micelle, in particular, its aggregation number, n , its shape, and the compactness of its electrical double layer show some

kind of dependency [14]. Even the molecular conformation of some dimeric surfactants (known as Gemini surfactants) affects the micellization to a large extent [15]. The parameter that illustrates the temperature dependence of hydrophobic effect is the heat capacity of micellization ($\Delta_{\text{mic}} c_p^0$) which is highly negative and mainly reflects the amount of non-polar solvent accessible area buried on micellization [16]. Since the thermodynamic parameters of micellization are often obtained from the measurements of the critical micelle concentration (cmc), it is important to note that negative values of $\Delta_{\text{mic}} c_p^0$ causes a typical U-shaped temperature dependency of cmc. Its minimum occurs at a characteristic temperature (T^*) that is often close to room temperature [20]. The shallow minimum around room temperature can be compared with a similar minimum in the solubility of the hydrocarbons in water. Non-ionic surfactants of the polyoxyethylene type deviate from this behaviour and show typically a monotonic, and much more pronounced decrease in cmc with increasing temperature [1,4]. Pressure has little influence on the cmc, even up to high values.

Turning next to the effect of cosolutes, salt addition gives a dramatic lowering of the cmc, though the effect is moderate for short-chain surfactants but is much larger for long-chain ones.

Besides cmc there are many important and intriguing temperature effects in surfactant self-assembly. One, which is of great practical significance, is the dramatic temperature dependant solubility displayed by many ionic surfactants. The solubility may be very low at low temperature and then increases by orders of magnitude in a relatively narrow temperature range. The phenomenon generally denoted as the Krafft phenomenon with the temperature for the onset of the strongly increasing solubility being known as the Krafft temperature [6]. The Krafft phenomenon is best discussed from the interplay between the temperature dependence of the surfactant unimer solubility and the temperature dependence of the cmc.

For surfactants, water does not interact favourably with the hydrophobic groups and there is a driving force for expelling them from the aqueous environment. This may be achieved by a macroscopic phase separation or by 'hiding' the non-polar groups in some other way. For a hydrocarbon in water there is a strong driving force for transfer it to a hydrocarbon phase or some other non-polar

environment. When a polar group is attached to the hydrocarbon an opposing force is created, which counteracts the phase separation. If the opposing force is weak, phase separation will still result. If it is very strong compared to the hydrophobic effect, on the other hand, the amphiphile will occur as single molecules or as small aggregates, like dimmers. It is the common intermediate situation with a balance between hydrophobic and hydrophilic interactions that researchers are concerned within surfactant self-assemblies.

Besides the essential contribution of the hydrophobic effect, the micellization of ionic surfactants in aqueous solution is largely influenced by the electrostatic interactions between the ionized head-groups and their interactions with the surrounding counterions and water molecules. Therefore, the effective charge of the micelle and the nature of counterion have a significant effect on the values of the thermodynamic parameters of micellization. Obviously, the actually existing micelles correspond to the lowest free energy state of the system. Thus, the intense interest in determining the thermodynamic parameters of micelle formation in aqueous solutions, namely, the Gibbs free energy, ΔG_m^0 , the enthalpy, ΔH_m^0 , and the entropy, ΔS_m^0 , because they quantify the relative importance of hydrophobic interactions, surfactant-water contact and (for ionic surfactants) head-group repulsion. These parameters can be derived from the temperature dependence of the critical micelle concentration (cmc), though very highly accurate cmc's are required in order to give satisfactory ΔH_m^0 . Among available techniques for studying surfactant aggregation, calorimetry has a distinct advantage, for it is possible to calculate both the cmc and ΔH_m^0 directly from the experimental data. Additionally, the calculated enthalpy and entropy characterizes the balance of forces involved in micelle formation. For example, whereas the aggregation is entropy-driven at room temperature, it is enthalpy-driven at higher temperatures [17].

Since the properties of solutions of surface-active agents change markedly when micelle formation commences, many investigations have been concerned with determining values of the cmc in various systems, and a great deal of work has been done on elucidating the various factors that determine the cmc at which micelle formation becomes significant, especially in aqueous media. Among the factors known to affect cmc in aqueous solution are (i) the structure of the surfactant, (ii) the presence of added electrolyte in solution, (iii) the presence of various organic

compounds in solution, (iv) the presence of a second liquid phase and (v) temperature of the solution.

In aqueous medium, the cmc decreases as the number of carbon atoms in the hydrophobic groups increases. For ionic surfactants it was generally found that the cmc became halved by the addition of one methylene group to a straight chain hydrophobic part attached to a single terminal hydrophilic group [4]. Compared to non-ionic surfactants ionic surfactants have much higher cmc values containing equivalent hydrophobic groups. For 12-carbon straight-chain ionics have cmc of $\sim 1 \times 10^{-2}$ M, whereas nonionics with the same hydrophobic group have cmc values of $\sim 1 \times 10^{-4}$ M. Zwitterionics appear to have slightly smaller cmc value than ionics with the same number of carbon atoms in the hydrophobic groups.

It has also been found [18] that the cmc is higher when the charge on an ionic hydrophilic group is closer to the α -carbon atom of the alkyl hydrophobic group. This is explained as being due to an increase in electrostatic self-potential of the surfactant ion when the ionic head groups moves from the bulk water to the vicinity of the nonpolar micellar core during the process of micellization; work is required to move an electric charge closer to a medium of lower dielectric constant.

In the old literature, the counterion binding of the ionic micelles was not considered; the choice of the standard state was also not consistent [18,19]. In the current literature, the role of the counterion binding has been recognized and the mole fractional scale has been used in the evaluation of the energetics of the process [20,21]. Some cationic surfactants display dramatic effects associated with the nature of the counterion, such as micelle growth, viscoelasticity, shear-thickening, etc. [22,23]. It has been reported that the cetyltrimethylammonium chloride micelles remain nearly spherical over a large range of concentration, even in the presence of NaCl [24]. A substantial amount of work have already been carried out on the binding of monovalent counterions to micelle [13,25,26] for single tail anionic surfactant like dodecyl sulfate. 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. For cationic surfactants micelle growth is even more pronounced in the presence of lyotropic counterions

such as salicylate, chlorate and nitrate [27,28]. These differences in behaviour reflect differences in the extent of counterion binding to micelles. Thus, the degree of counterion binding to cationic micelles increases in the order $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{salicylate}^-$ [28-30]. However, the critical micellization concentration (cmc) varies only little in going from lithium to cesium dodecyl sulfate [32]. The variations are not dramatic even when replacing the monovalent alkali metal ions by divalent cations such as Mg^{2+} , Co^{2+} and Cd^{2+} . For instance in the case of the dodecyl sulfate surfactants, this substitution results in a decrease of the cmc (expressed in mole of surfactant ion per liter) by a factor of 2 and an increase of the micelle aggregation number from about 65 to 90 [33,34]. However, when compared with Na^+ counterions, polyvalent ions usually markedly reduces the cmc [31] by several order of magnitude and lead the formation of large micelles that may be confirmed from the increase in micellar aggregation number [32,33,41,42]. In aqueous solution the micelles are known to be charged due to a fraction, α , of their counterions dissociates into the aqueous pseudophase. The value of α for a given pure surfactant is important, because both the physical [35,36] and chemical [37] properties of the micelle are influenced by surface charges. The decrease of the surface potential of micelles with decreasing hydrated radius from Li^+ to Cs^+ is in agreement with the modification of the counterion binding [38]. Liu and et al. [39] showed that for a given counterion (Cs^+), the ions are more dissociated in micelles of surfactants with C_{10} chains than with C_{12} chains. From a structural point of view, the effect of counterions has been well documented by Missel et al. [40] for dodecyl sulfates in a salty solution of the same alkali-metal chloride by quasi-elastic light scattering. They proved the tendency of micelles to grow from spherical to long rodlike structures in the order $\text{Li}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$ with a significant change in the aggregation number with temperature.

One of the most interesting aspects of micelles is their ability to accommodate organic molecules [43,44]. An increased flexibility of the micellar membrane and thereby an improved ability to solubilize hydrophobic molecules can be achieved by adding neutral salt and a medium chain alcohol [47-50]. There fore, these elements make the basic components in most microemulsions. However, the intricate behaviour of these mixed micellar aggregates makes it difficult to predict any variation in the system upon variation in the composition of the solution. This

problem is caused by a delicate balance of attractive and repulsive forces among the amphiphilic molecules in the micelles.

The size and shape of micelle aggregates containing commonly used surfactants and co-surfactants have been thoroughly investigated during the past decades [51,52]. The commonly used sodium SDS micelles form spherically aggregates consisting of about 60 monomers in aqueous solutions at cmc [53,54]. Compounds with polar groups such as alcohol molecules can be expected to solubilize in the hydrophilic regions. Addition of alcohol can strongly influence the behaviour of the micelles and changes the micellar size depending on the hydrophilic/hydrophobic character of the alcohol [55,56]. The hydrophilic alcohols (methanol to propanol) mainly solubilize in the aqueous solution and affect the micellization process by modifying the solvent [57], whereas the hydrophobic alcohol molecules (pentanol and higher homologues) take part in the micellization process and become unique components of the micelle aggregates [58]. The degree of solubilization into this shell region depends on the amphiphilic character of the alcohol molecules [57]. The degree of counterion binding also decreases with solubilization of short-chain alcohols ($C_2 - C_6$) in the palisade layer of the micelle, whereas the solubilization of octane which occurs in the interior of the micelle, does not affect the degree of counterion binding [59]. This is presumably because solubilization in the palisade layer increases the surface area per ionic head group, whereas solubilization in the interior of the micelle does not. It is also decreased by the addition of urea, replacing water from the interface [60].

However, the roles of the amphiphilic alcohol molecules as co-surfactants are still unclear and a matter of discussion. This is especially true for the medium chain length alcohol molecules which are the most commonly used co-surfactants in microemulsions. Even though the influence of *n*-alcohols on the structure of SDS micelles has been extensively investigated, several conflicting results have been reported. Attwood and et al. [61] indicated that SDS micelles decrease progressively in size upon addition of butanol in aqueous salt solutions. Similar result was shown by Boström and et al. [62] in micellar SDS solutions without salt. On the other hand, McGreevy and Schechter [63] observed that the size of the SDS micelles is not influenced upon addition of 1-butanol. Stilbs [64] also reported that SDS micelles grow upon addition of small amounts of butanol and progressively break down

upon addition of butanol in the high concentration range. Førland and et al. [56] on the other hand showed that butanol influences SDS micelles by either increasing or decreasing the size of the micelles depending on the concentration range of the alcohol. However, one can conclude that alcohols affect micellization by extensively regulating the thermodynamics of the process.

Thermodynamics of Micellization: The Mass-action Model

Blandamer et al. [65], Blankschtein et al. [66], Hines, [67] and Zana [68] have reviewed the theories for surfactant solutions. These reviews include many different theories and models for surfactant solutions. However, only few of them have been applied in practice. Different thermodynamic treatments for micelle formation in surfactant solutions are known. Although many efforts have been made towards theoretical understanding of surfactant solutions, capturing the nature of such solutions is still considered rather difficult. In contrast to the rigorous universal thermodynamic treatment of fluid phase equilibrium, many thermodynamic formulations have been proposed for micelle formation. Between those theoretical approaches mass-action model shows its wide acceptance to a number of researchers.

In the mass-action model, the micelle formation is considered as a chemical equilibrium between free surfactant and micelle. At low concentrations, the micelle solution is the formation of aggregates from free surfactant, as shown in equation (3.1).



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 nonionic and ionic surfactant solutions. Such thermodynamic formulation may be described as follows (Blandamer and et al.) [65]:

For nonionic (neutral) surfactant solutions, at chemical equilibrium, we have:

$$n_g \mu_{i,mon} = \mu_{i,micelle} \quad (3.2)$$

where $\mu_{i,mon}$ is the chemical potential of monomeric (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:

$$\mu_{i,\text{mon}} = \mu_{i,\text{mon}}^0 + RT \ln x_{i,\text{mon}} \gamma_{i,\text{mon}} \quad (3.3)$$

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

Now, we have:

$$\Delta G_{i,m}^0 = \frac{1}{n_g} \mu_{i,\text{micelle}}^0 - \mu_{i,\text{mon}}^0 = RT \ln x_{i,\text{mon}} \gamma_{i,\text{mon}} - \frac{1}{n_g} RT \ln x_{i,\text{micelle}} \gamma_{i,\text{micelle}} \quad (3.5)$$

where $x_{i,\text{mon}}$ and $x_{i,\text{micelle}}$ are the mole fraction of monomeric surfactant and surfactant in micelle, respectively, where $\gamma_{i,\text{mon}}$ and $\gamma_{i,\text{micelle}}$ are the activity coefficients and $\mu_{i,\text{mon}}^0$ and $\mu_{i,\text{micelle}}^0$ 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 (3.5) becomes

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

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

But for ionic surfactants the micellization equilibrium for ionic surfactant 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 [21a,68,69]:

$$\Delta G_{i,m}^0 = (2 - \alpha)RT \ln x_{i,cmc} \quad (3.8)$$

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 characteristic behaviour of surfactants to orient at surfaces and to form micelles, their applicability varies with the phase as foaming agents, emulsifiers, and dispersants. The type of surfactant behaviour, whether acting as an emulsifier or dispersant or otherwise, depends on the structural groups on the molecule. 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.

Sodium lauryl sulfate (SLS) or sodium dodecyl sulfate (SDS), $C_{12}H_{25}SO_4Na$ is an anionic surfactant that is used in industrial products including engine degreasers, floor cleaners and car wash soaps; as well as in household products such as toothpastes, shampoos, shaving foams, some dissolvable aspirins, fiber therapy caplets, and bubble baths for its thickening effect and its ability to create a lather. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent. It is probably the most researched anionic surfactant compound

that attracted researchers from early decades [32,34] to present times [11-13] due to its simple single tail structure and the ability to form stable micelles. Besides micellization interaction with dyes [70], electrophoresis and electrokinetics [72] with SDS has also been reported. It has recently found application as a surfactant in gas hydrate or methane hydrate formation reactions, increasing the rate of formation as much as 700 times [71].

On the other hand Aerosol-OT (AOT, sodium bis-(2-ethyl-1-hexyl) sulfosuccinate), bears great myths in surfactant science [73,74] due to reach phase behaviour and its ability to form microemulsion. It is a nontoxic compound and can be used in pharmaceutical and medicinal preparations. Unlike most amphiphiles and like many phospholipids, it is a double tailed anionic surfactant which can conveniently used in solubilization and emulsification purposes. Its versatile surface chemical performance, wide use and nontoxic nature classify AOT with a distinction, and a comprehensive discussion on its physicochemical and surface chemical properties and uses is, therefore needed. This promoted us to select the above single and double tailed anionic surfactants (viz., SDS and AOT) for the present study. Figure 3.2 shows the molecular structures of SDS and AOT schematically.

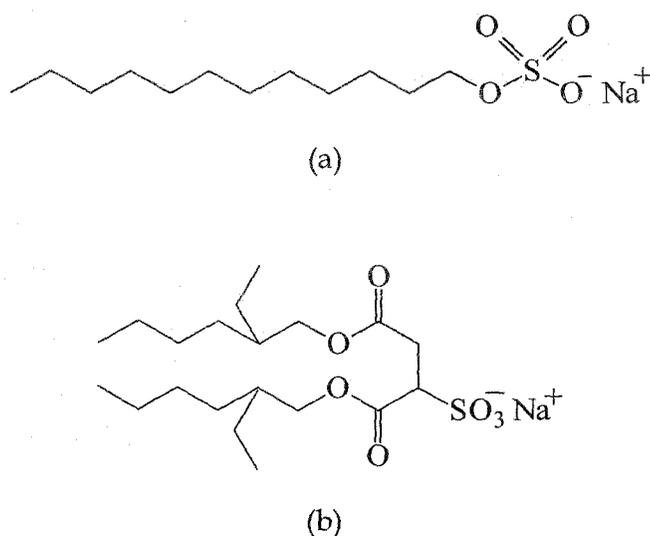


Figure 3.2 Schematical molecular structures of (a) SDS and (b) AOT surfactants.

3.2 Effect of Counter Ions on Temperature Dependant Micellization in Aqueous Medium

In a number of series of cationic surfactants, Zana [6b] has shown that the degree of binding is related to the surface area per head group in the micelle. It was observed that as the degree of binding increasing, the surface area per head group decreases (i.e., as the surface charge density increases). Counterion binding also increases with increase in the electrolyte content of the solution [21b] and may also increase when surfactant concentration increase produces micellar growth [22b], presumably because both of these are accompanied by a decrease in head group area. The ionic micelles that have more tightly bound counterions are more nonionic in character than those with a greater degree of ionization, have lower water solubility, and are more likely to have nonspherical micelles in aqueous solution.

In connection with micellization it is also evident that the aggregation number of ionic micelles, at a constant temperature, depends only on the concentration of counterions, C_{aq} in the aqueous phase [12]. Ionic micelles grow in response to increase in the value of whether the counterions are provided by the surfactant alone or by the surfactant plus any added electrolyte [12]. Thus C_{aq} can be written as [11]:

$$C_{aq} = F(S_t)[\alpha S_t + (1 - \alpha)S_m] \quad (3.9)$$

where S_m and S_t are the monomeric and the total concentration of the surfactant respectively. The factor $F(S_t) = 1/(1-\theta)$, where θ is related to the volume fraction occupied by the micelles. In this present work some studies with a series of surfactants derived from SDS and AOT (the sodium salt of the diester) by varying the counter ions. Thus a series of alkali metal ions, viz. Li^+ , Na^+ , K^+ along with the NH_4^+ and tetraalkylammonium ions, viz. $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$, $N^+(C_4H_9)_4$ are investigated. There are some evidences [21,22,32] that the counterions exhibit mainly electrostatic interaction or, no chemical interaction is to be expected on the structural grounds. Therefore, it is the system where the cmc differences are rather small and the effect of ionic size and of physical adsorption can be best investigated. The objective is, therefore, to determine the cmc with high accuracy within a temperature range of 283 - 313K of both SDS and AOT surfactants having different

counter cations in aqueous medium and to calculate different thermodynamic parameters of micellization, viz. changes in standard Gibbs free energy (ΔG_m^0), standard enthalpy (ΔH_m^0), standard entropy (ΔS_m^0), maximum surface excess concentration (Γ_{\max}), and the minimum areas per molecule (A_{\min}) at the surface in order to examine the effect of ionic sizes on the micellization.

3.2.1 Experimental section

Materials

Surfactants with the desired counterions were prepared by following the technique of Eastoe and et al. [75] and the extended work of Temsamani and et al. [76] and Benrraou and et al. [13]. A high grade purified sample of SDS and AOT from Fluka (Switzerland) were used for the present study. Both of them produced no minima in the surface tension vs concentration plots indicating good purity of the compounds. The samples are converted into the surfactants bearing different counterions by ion exchange technique using a strong ion exchange resin (Amberlite IR-120, 20-50 mesh, Loba Cheme, India). The process is described below:

A 10g sample of SDS or AOT was dissolved in 20mL of a 1:1 (v/v) mixture of water and ethanol. The solution was passed through a column (40cm x 2 sq. cm) of a strong ion exchanger in the H^+ form slowly. The resin was put in the acid form by using a large excess of a 0.20M aqueous hydrochloric acid solution and washed with water until the complete removal of the excess acid takes place. The free acid formed on passing the SDS or AOT through the resin was then immediately neutralized with an aqueous solution of the hydroxides of the desired counter ions (viz. Li^+ , K^+ , NH_4^+ , $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$ and $N^+(C_4H_9)_4$). All the hydroxides of high purity were procured from Across Chem., Belgium. The solvent water was then removed fast by freeze drying and then keeping under vacuum (bath temperature 313K) for several days and the waxy solid was finally dried in vacuum over P_2O_5 . These materials contain residual water, which were finally removed by the action of P_2O_5 (from Loba Cheme, India) on a solution of surfactant in isooctane ($\geq 99.5\%$ from Merck, India). The extent of Na^+/H^+ ion exchange was optimized by controlling the flow rate of the solution and finally H^+ content of the surfactant solution (acid form) was measured by titrating with standard NaOH. The extent of exchange was found

to be more than 99%. Among all the ion-exchanged surfactants TBADS and tetrabutylammonium-AOT 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. Doubly distilled water having conductivity $2 \mu\text{S cm}^{-1}$ was used throughout the experiment.

Methods

The cmc values were determined [77-80] from the surface tension as well as specific conductance data. It is customary to plot the (i) surface tension γ against the logarithmic value of the surfactant concentration C and the (ii) conductance Λ against the concentration of the surfactant, where the break indicates the cmc of a particular system. The surface tension experiments were done by platinum ring detachment method using a Tensiometer (K9, KRÜSS; Germany), at different temperatures. The accuracy of the measurement 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. 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 ranges 283 – 313K. Measurements were made at 5K intervals of temperature. In this connection it may be noted that for anionic surfactants of structure $\text{RC(O)N(R}^1\text{)CH}_2\text{CH}_2\text{COO}^-\text{Na}^+$, it has been found [81-83] that the break in the conductance-surfactant concentration plot may be smaller than expected or absent, yielding binding values (β) much smaller than those of comparable surfactants without the amide group. This may be due to the protonation of the carboxylate group and hydrogen bonded ring formation with the amido group, with simultaneous release of the Na^+ , upon micellization.

3.2.2 Results and Discussion

The cmc corresponds to a concentration at which a very small but often clearly detectable concentration of the micelles exists. Typical experimental curves of salt free systems are obtained in both surface tension and conductance measurements. The 'break point' or the point of intersection of the two surface

tension and conductivity lines was taken as the cmc at a particular temperature. The cmc values determined by two methods for both dodecyl sulfate and bis-(2-ethyl-1-hexyl) sulfosuccinate) with each counterion are in close agreement with one another. The cmc of SDS and AOT is also in good agreement with the literature value [13,16,75,76]. Figure 3.3 - 3.31 are the plots obtained in the surface tension and conductivity measurements.

In all instances, the change of cmc with temperature is small. 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 tetraalkylammonium counterions. It is found that at a concentration of 10 times the cmc, potassium dodecyl sulfate and potassium salt of AOT is not completely soluble in water at room temperature. The solution contains hydrated crystals dispersed in a micellar phase. Below 313K K-AOT (bis-(2-ethyl-1-hexyl) sulfosuccinate having K^+ as counter ion) forms clear solution. Thus the micellization of K-AOT has been investigated in the limited range within 283-308K. However, in the case of potassium dodecyl sulfate, which has a Krafft temperature of 307K at the cmc [84] it was impossible to investigate the micellization process since the temperature leading to a clear solution was too high (323K). Mukerjee and et al. [85] and Romsted et al. [86] also reported this solubility gap for potassium alkyl sulfates.

This is well known that hydrophobic property of the tail and the hydrophilic property of the head group of a surfactant molecule are together responsible in forming micelles in water. It is, therefore, not surprising that as the hydrocarbon chain length is increased; micelles are formed at lower concentrations due to increased hydrophobicity of the hydrocarbon tail [92]. Similarly it is quite obvious that as the hydrated ionic size is increased from NH_4^+ to Na^+ , cmc value is decreased due to increasing hydrophilicity. The counterionic activity in micellization is not completely similar in dodecyl sulfate and AOT. At a particular temperature (below 303K), cmc depends upon the nature of the counterion following the order $\text{NH}_4^+ > \text{Li}^+ > \text{Na}^+$ in dodecyl sulfate, whereas for AOT cmc decreases in the order $\text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{K}^+$. But at high temperature (above 323K) AOT micelles are rather insensitive to temperature variation. This decrease was explained by considering the binding of counterions to micelles. The determination of partial volumes and

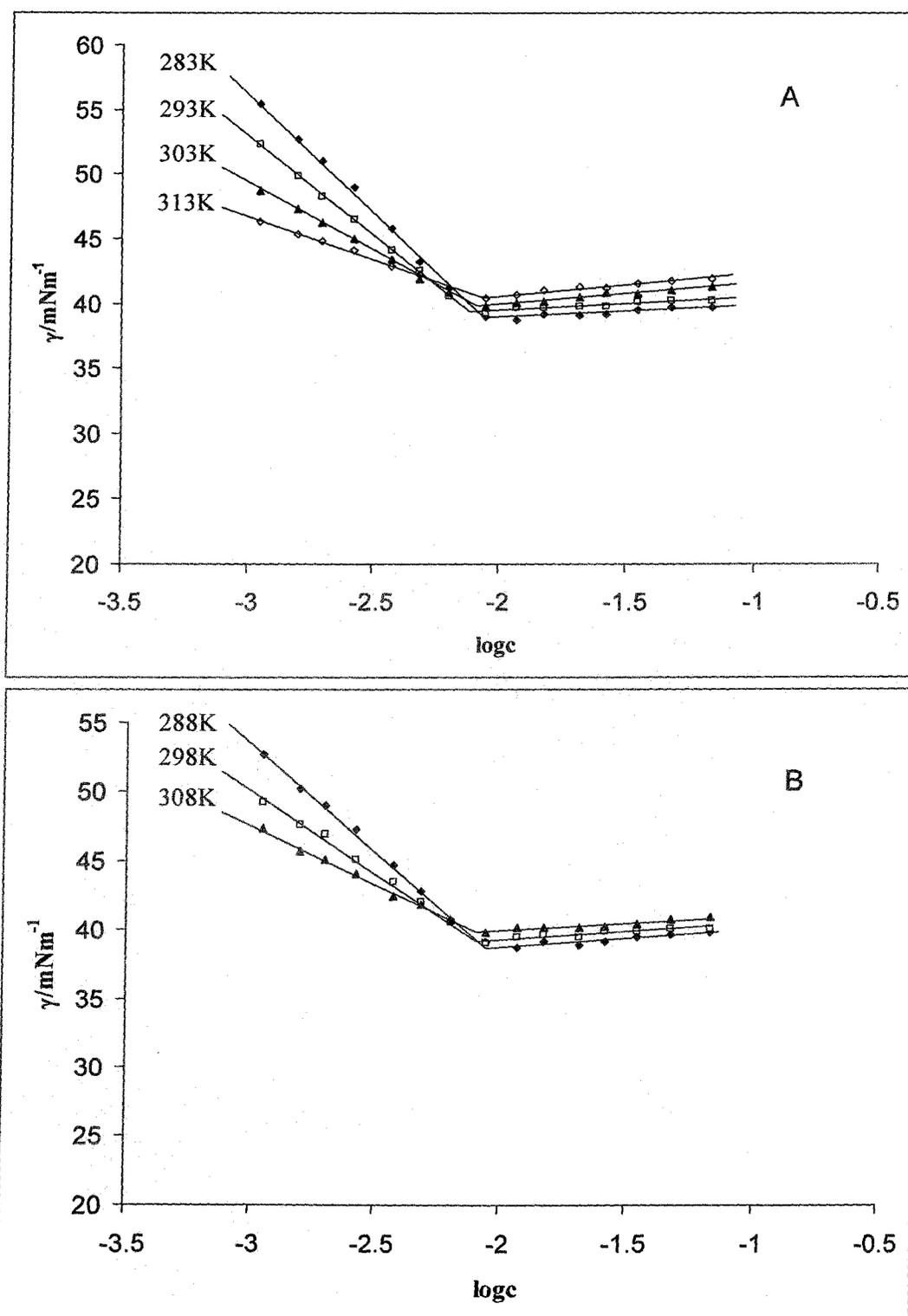


Figure 3.3: Surface tension, γ , of lithium dodecyl sulfate (LDS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

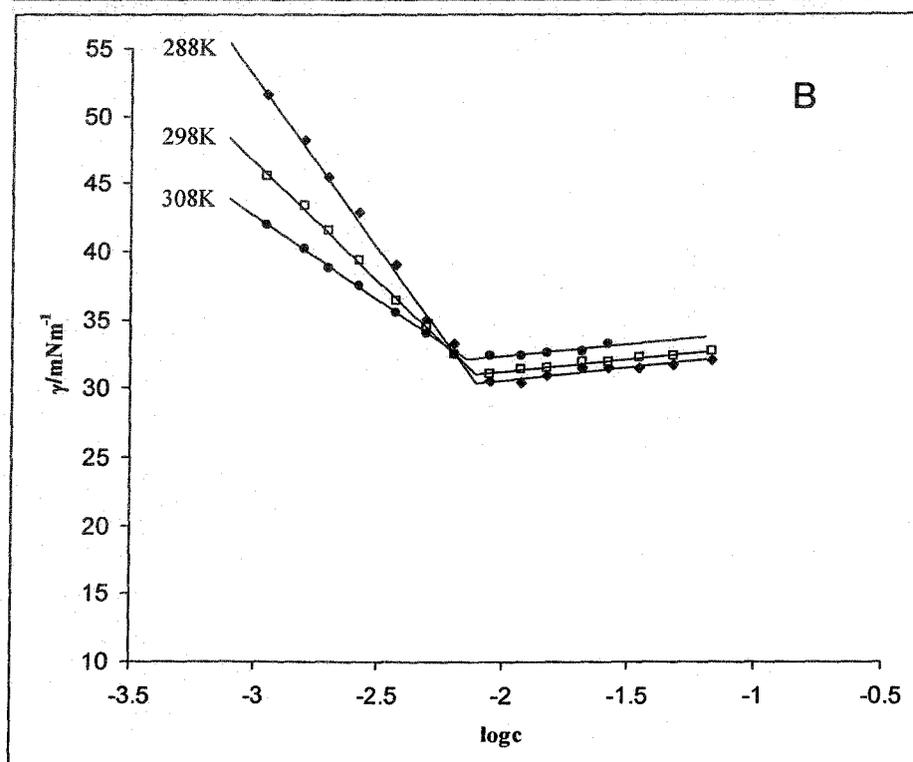
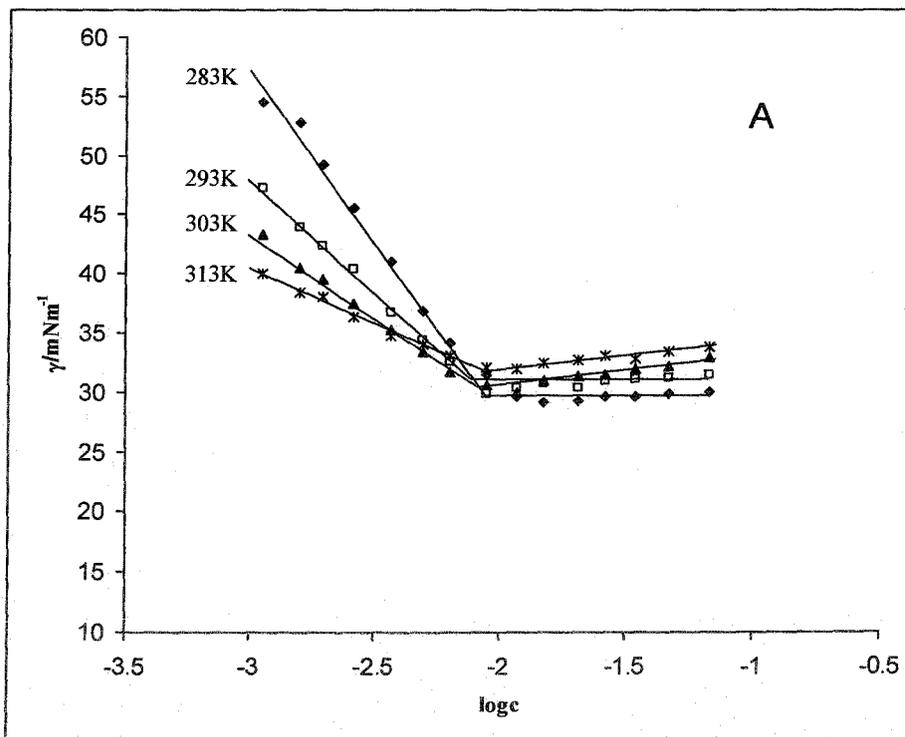


Figure 3.4: Surface tension, γ , of SDS in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

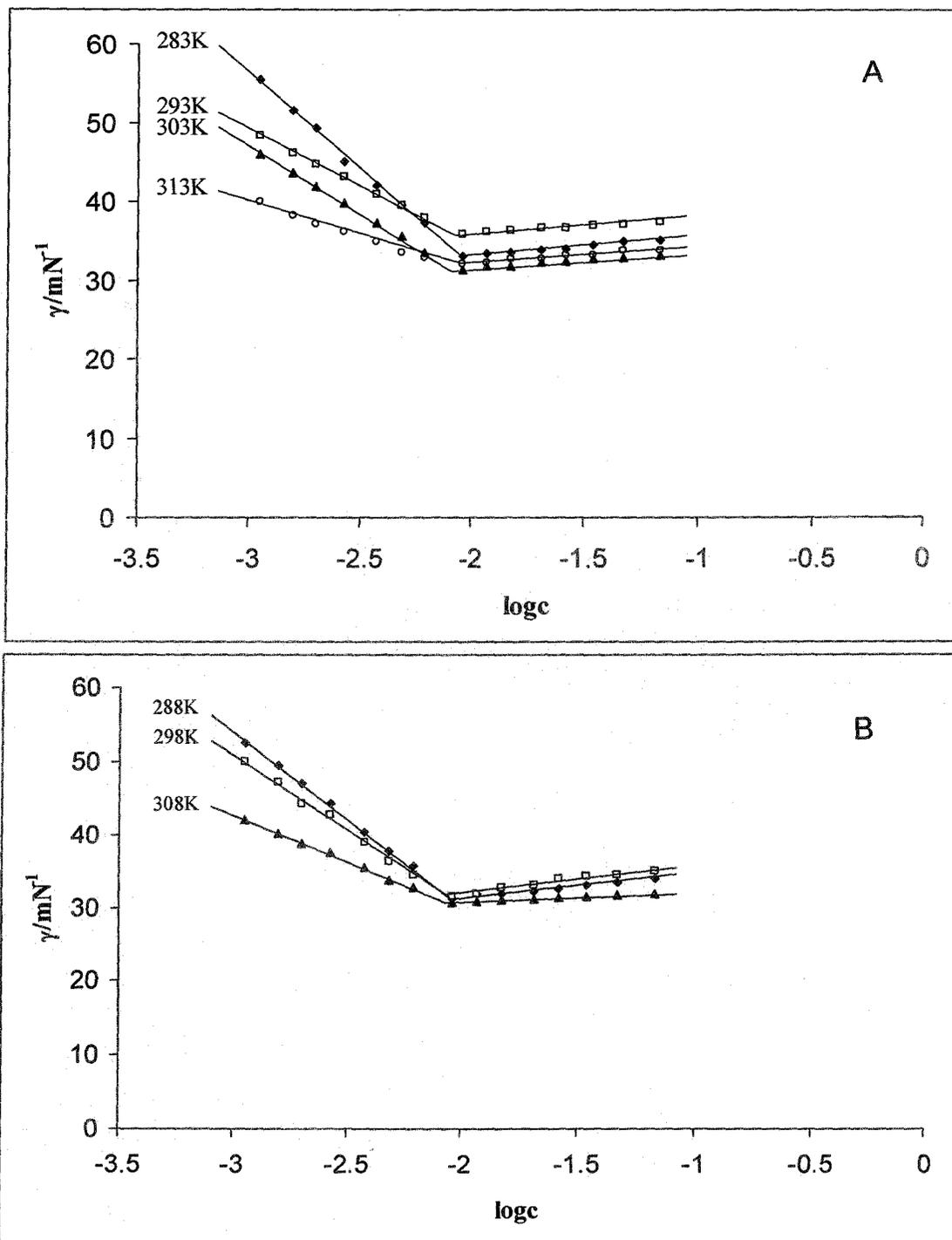


Figure 3.5: Surface tension, γ , of ammonium dodecyl sulfate (ADS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

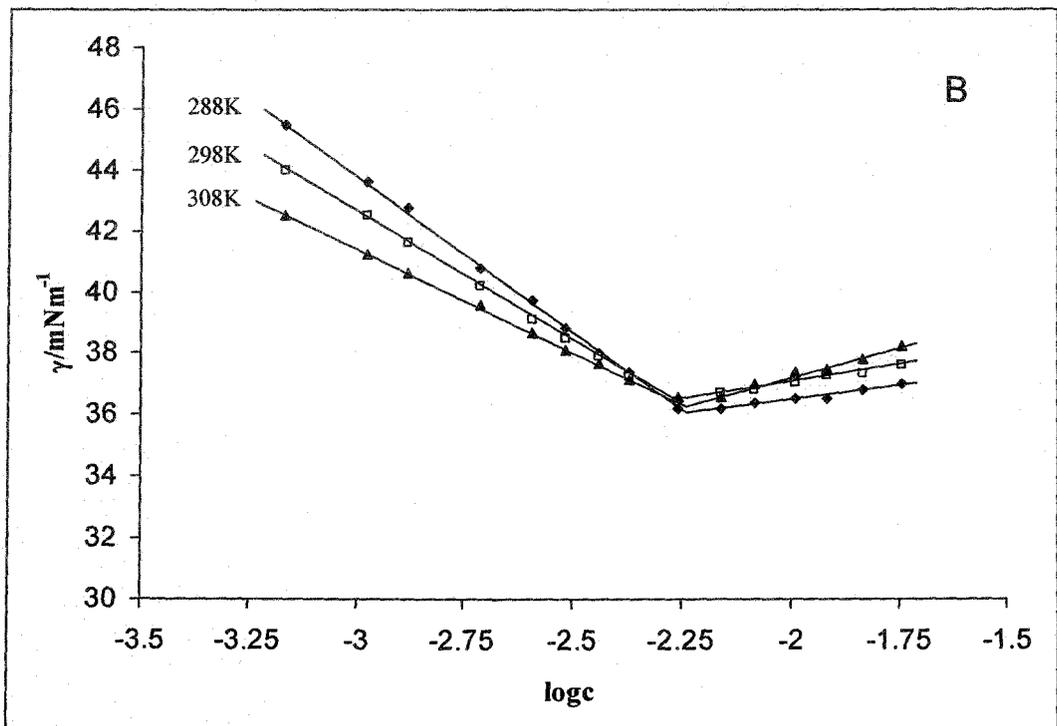
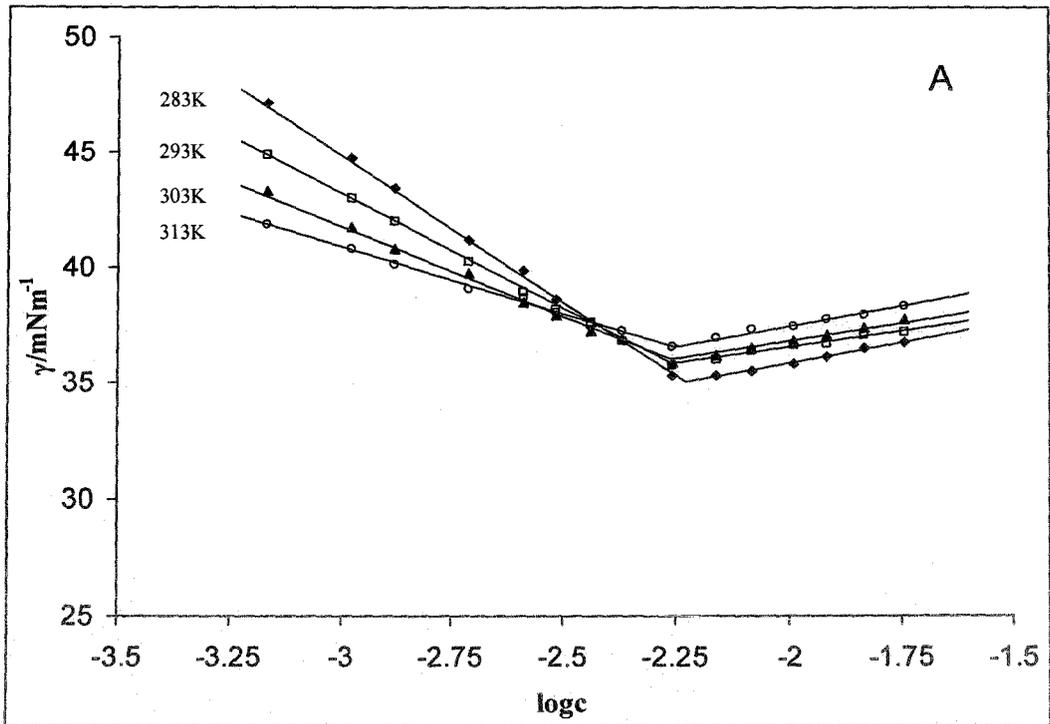


Figure 3.6: Surface tension, γ , of tetramethylammonium dodecyl sulfate (TMADS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

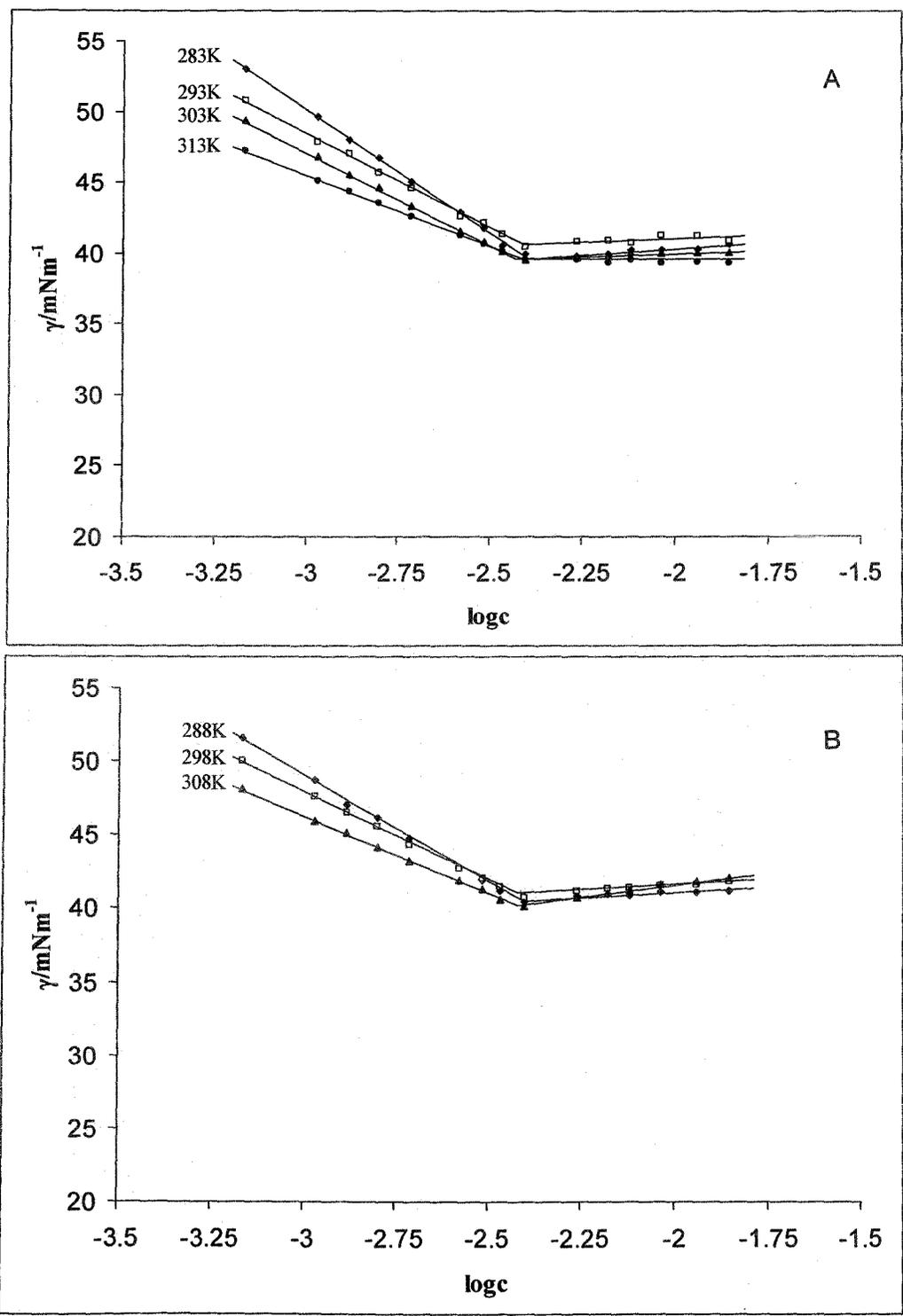


Figure 3.7: Surface tension, γ , of tetraethylammonium dodecyl sulfate (TEADS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

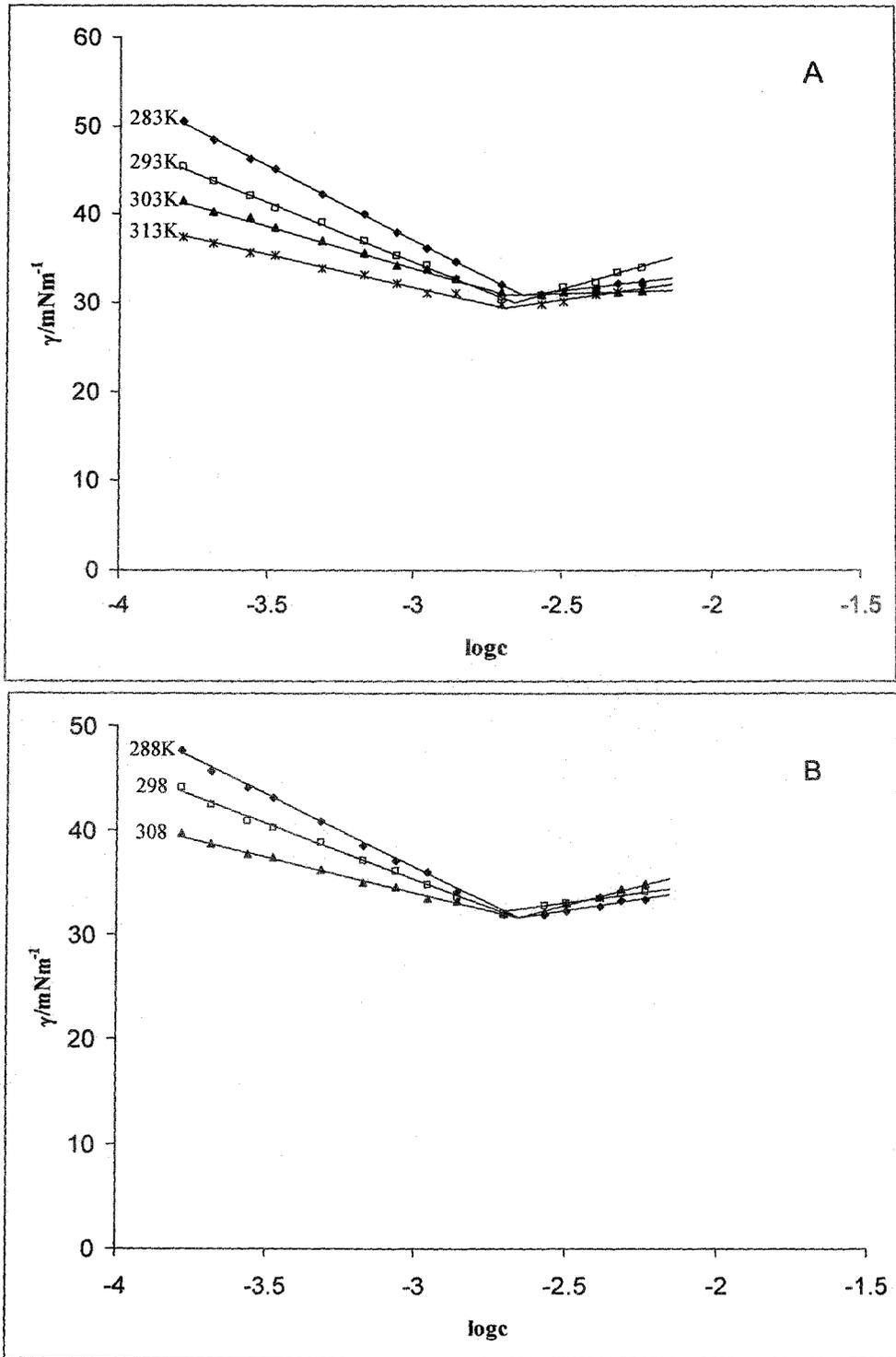


Figure 3.8: Surface tension, γ , of tetrapropylammonium dodecyl sulfate (TPADS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

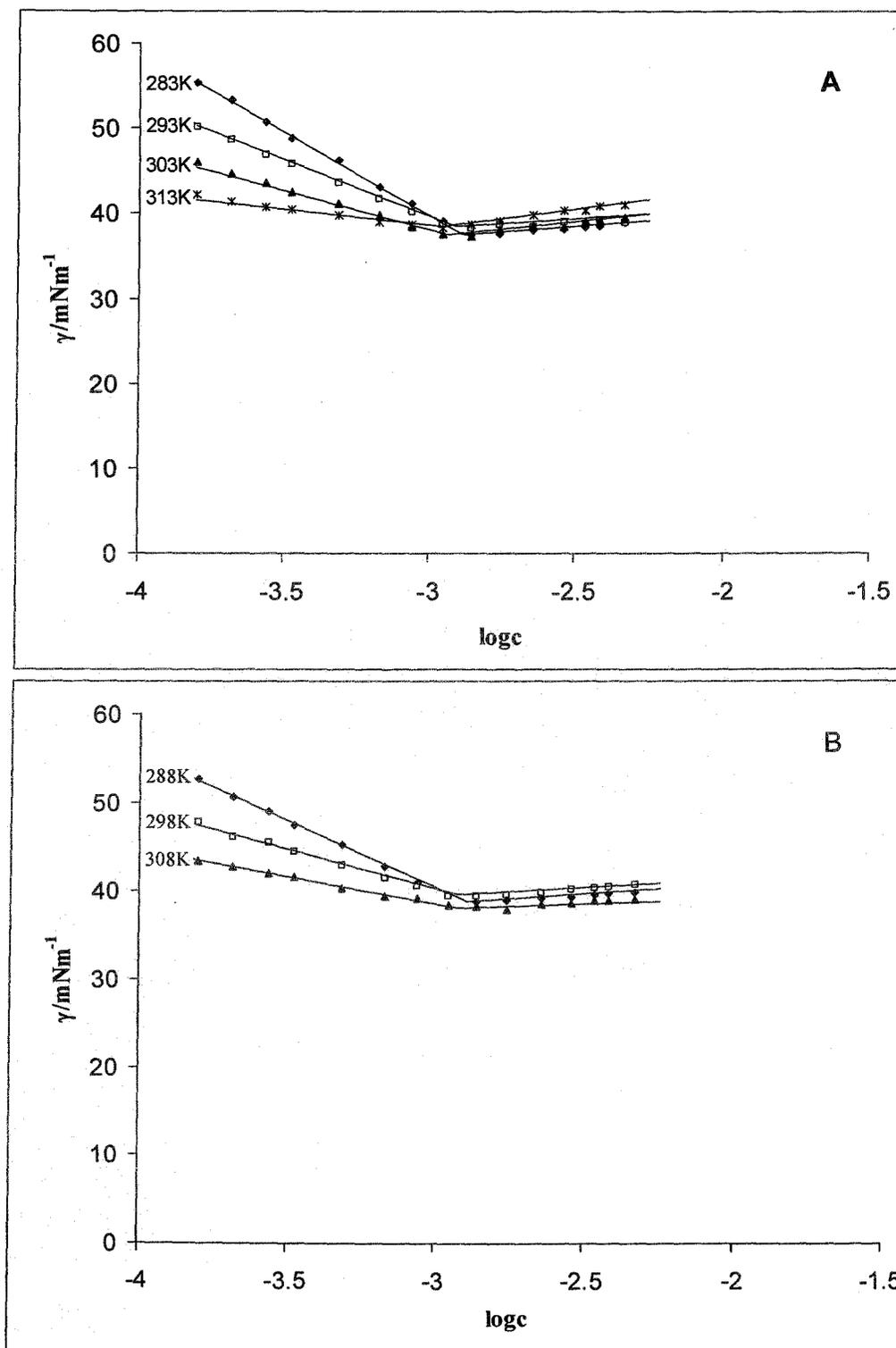


Figure 3.9: Surface tension, γ , of tetrabutylammonium dodecyl sulfate (TBADS) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

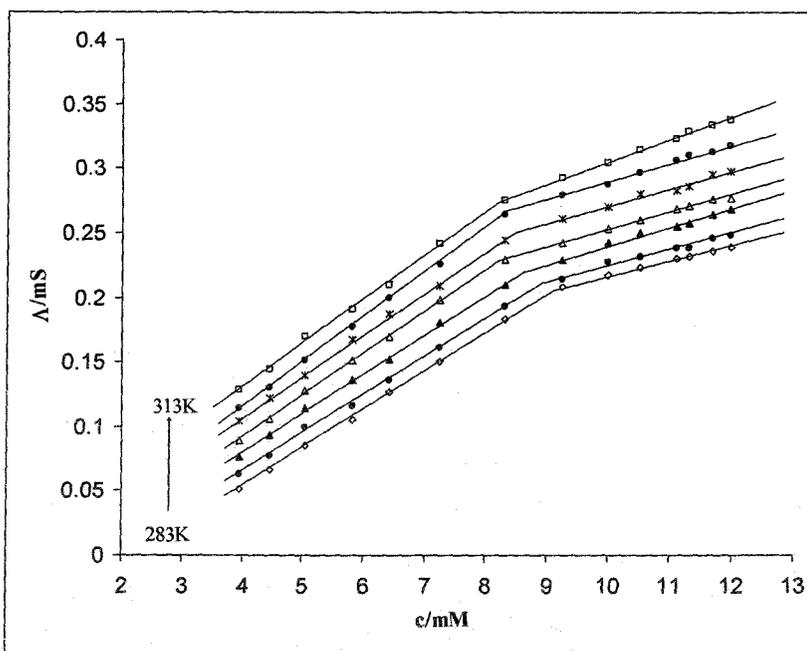


Figure 3.10: Conductance, Λ , of Lithium dodecyl sulfate (LDS) in aqueous solution as a function of the surfactant concentration at temperatures ranging 283K to 313K with 5K interval.

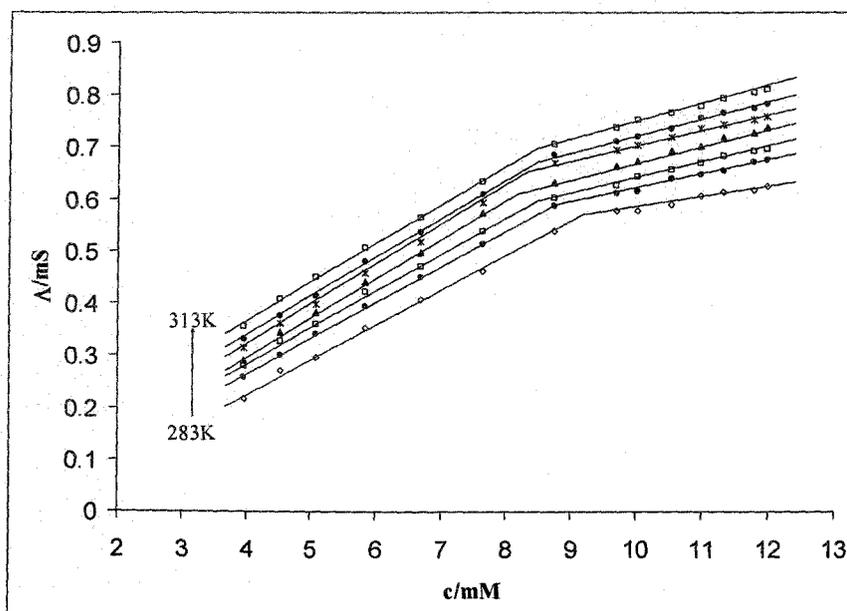


Figure 3.11: Conductance, Λ , of SDS in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

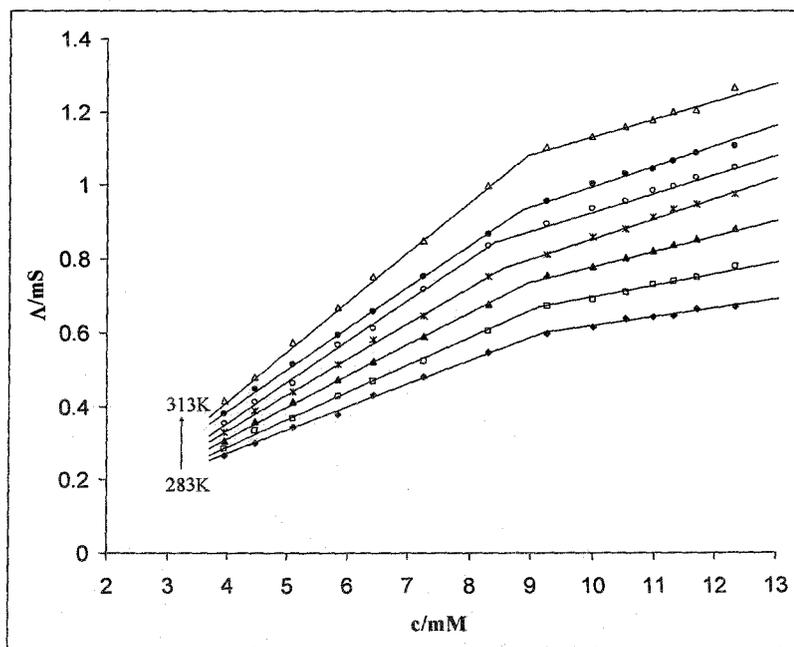


Figure 3.12: Conductance, Λ , of Ammonium dodecyl sulfate (ADS) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

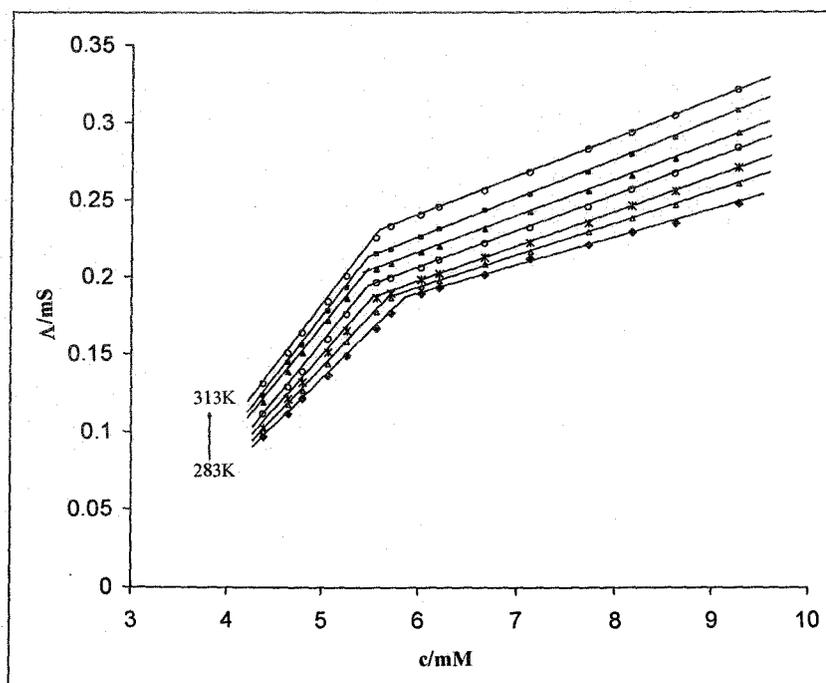


Figure 3.13: Conductance, Λ , of Tetramethylammonium dodecyl sulfate (TMADS) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

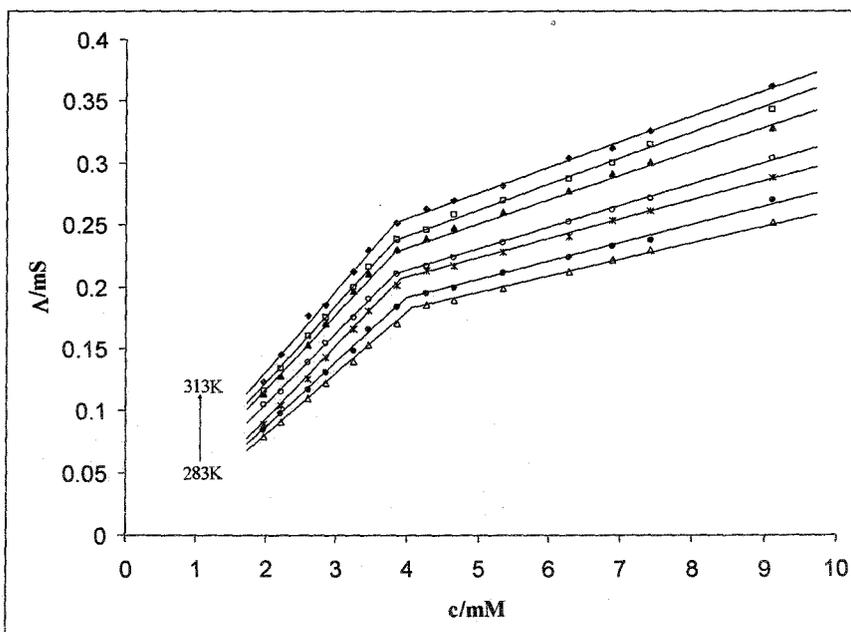


Figure 3.14: Conductance, Λ , of tetraethylammonium dodecyl sulfate (TEADS) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

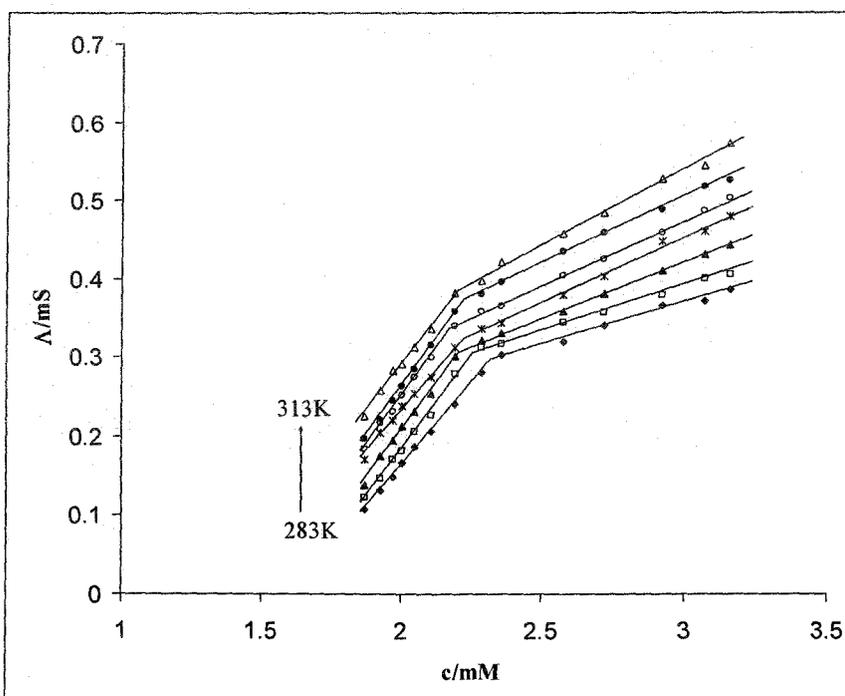
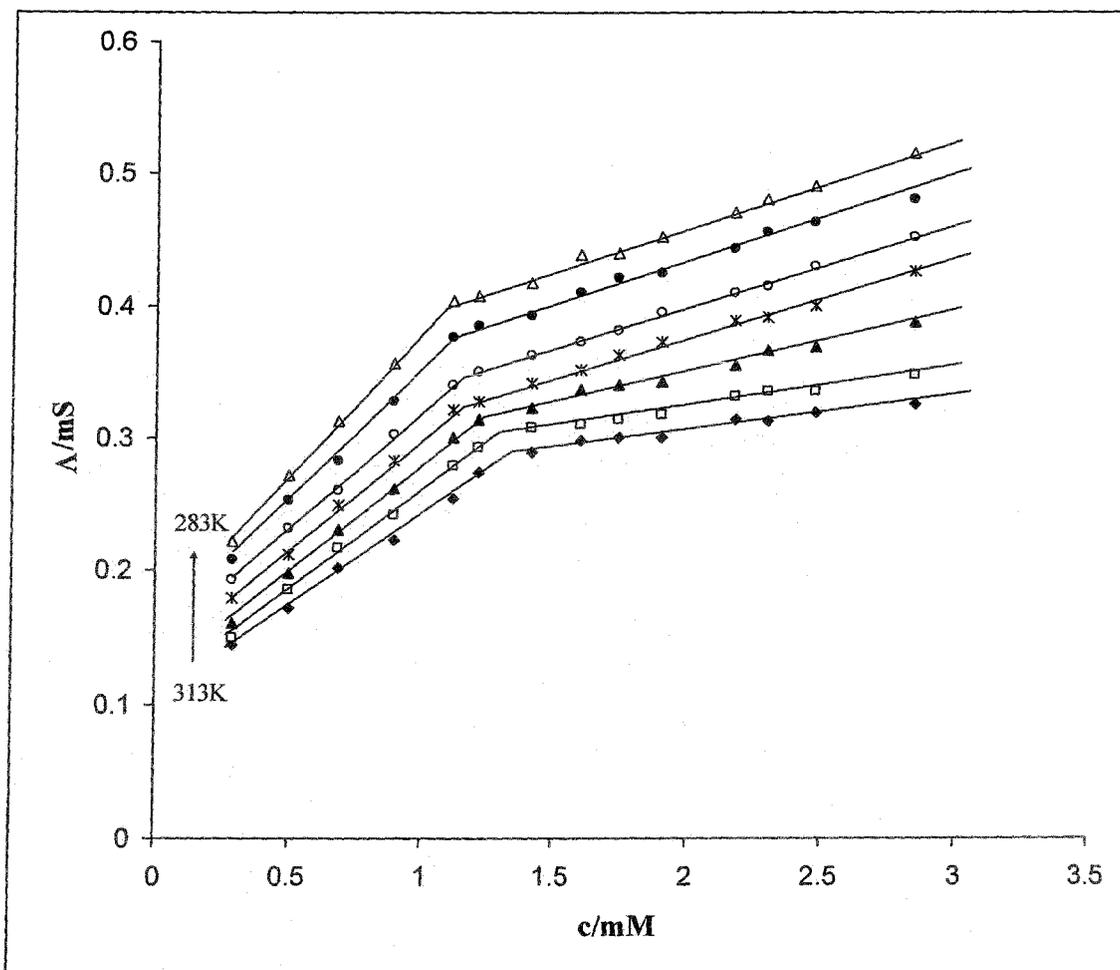


Figure 3.15: Conductance, Λ , of tetrapropylammonium dodecyl sulfate (TPADS) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.



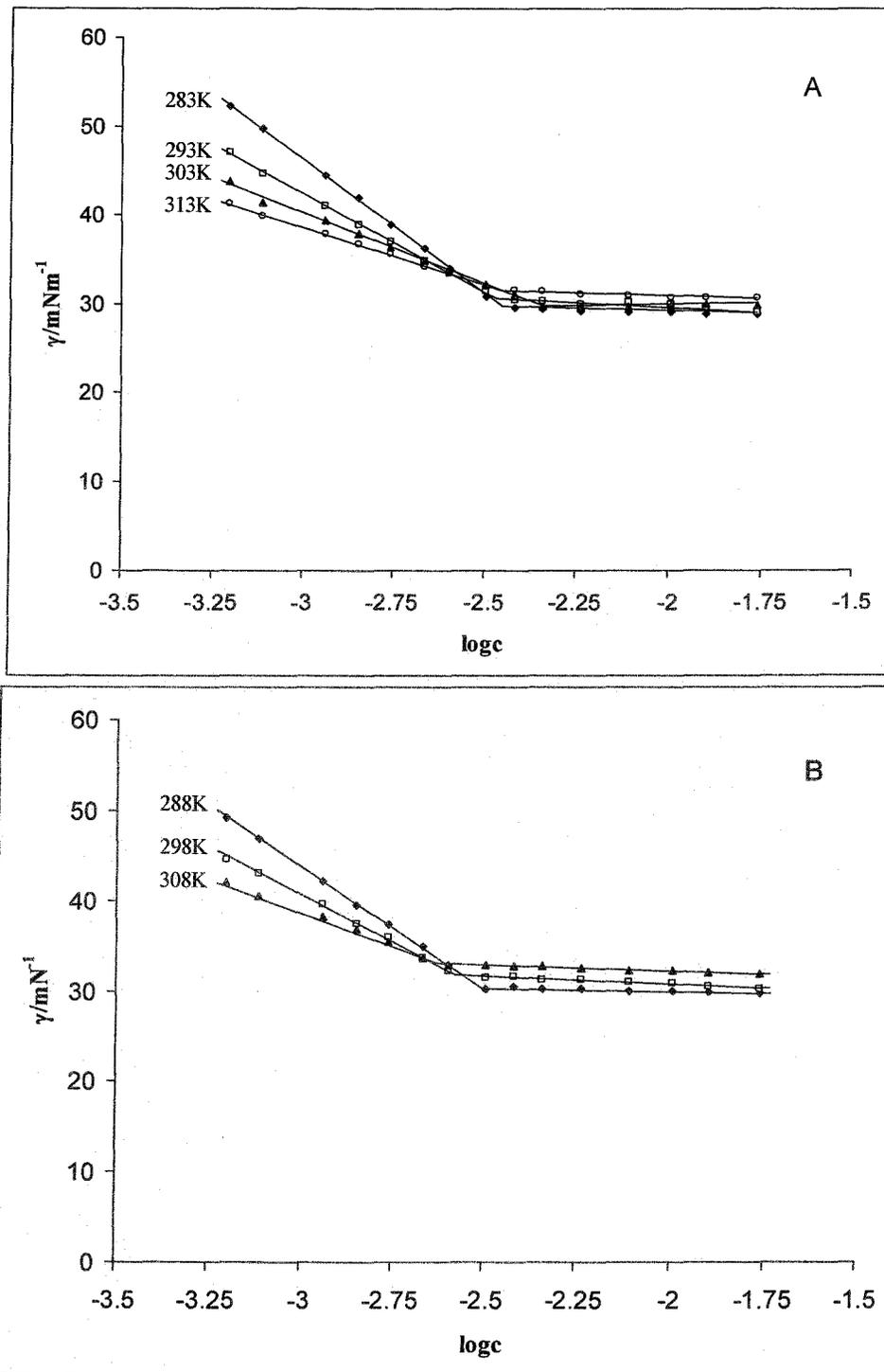


Figure 3.17: Surface tension, γ , of AOT (sodium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

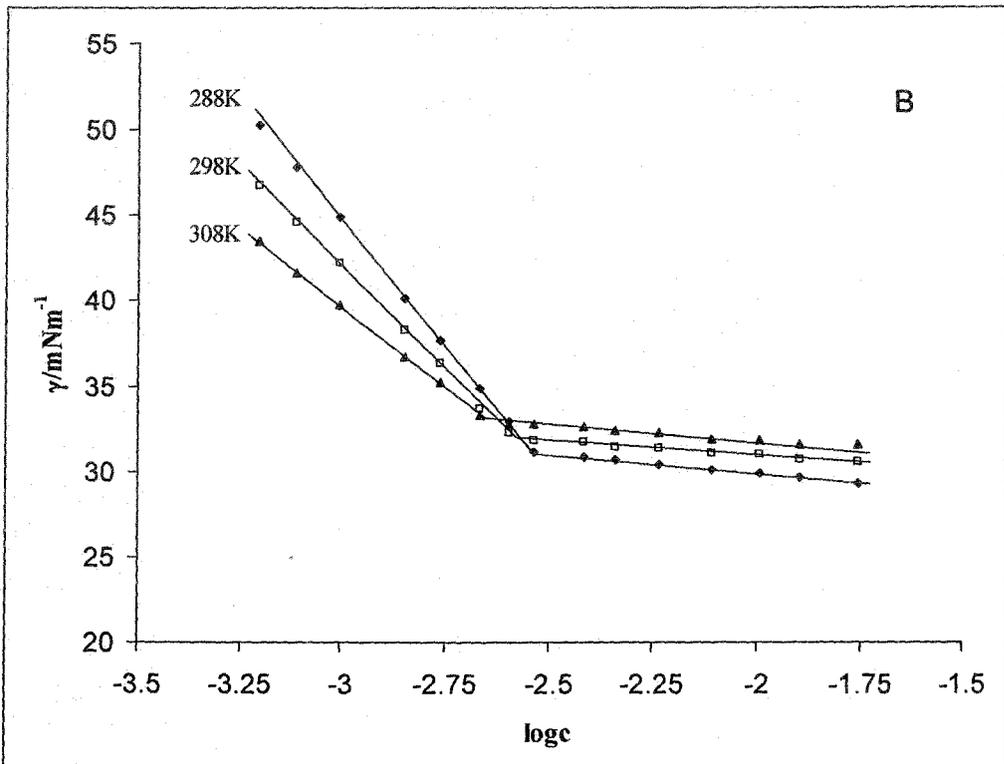
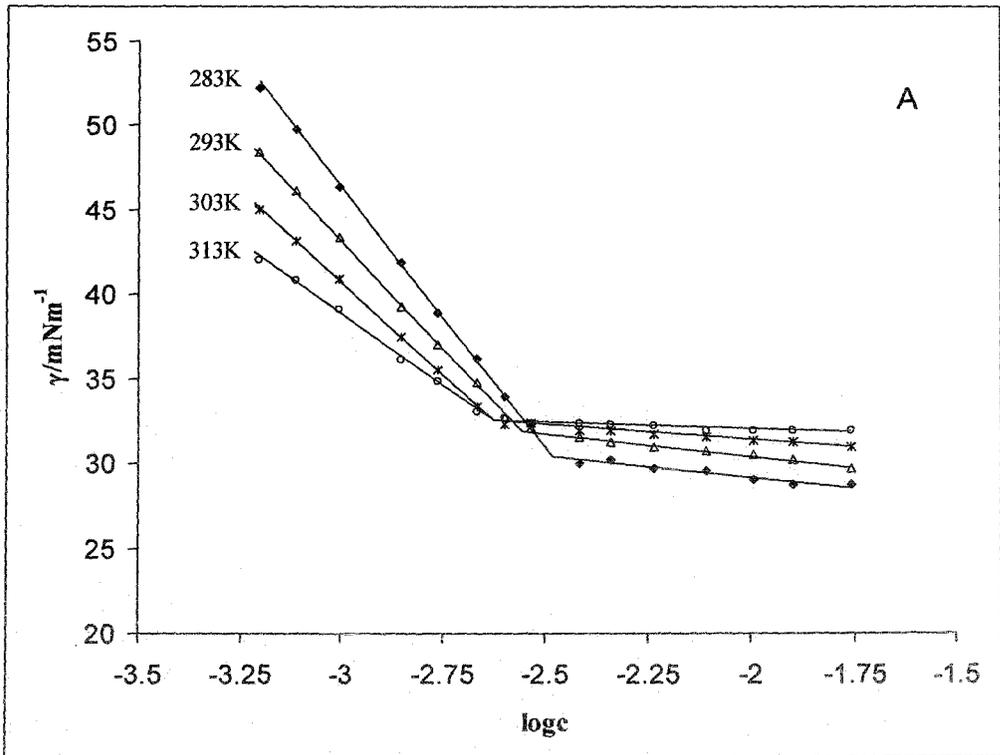


Figure 3.18: Surface tension, γ , of AOT (lithium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

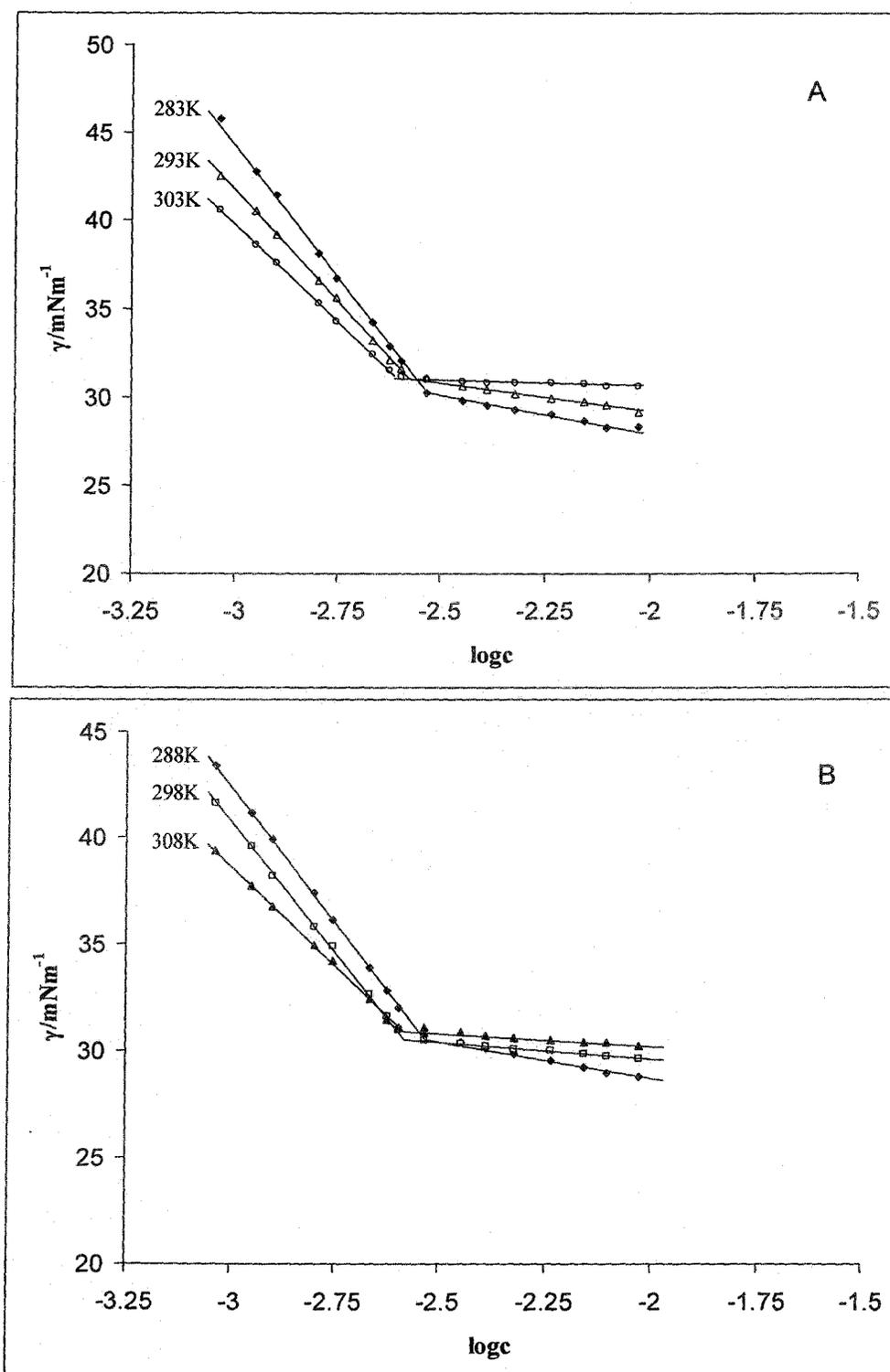


Figure 3.19: Surface tension, γ , of AOT (potassium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

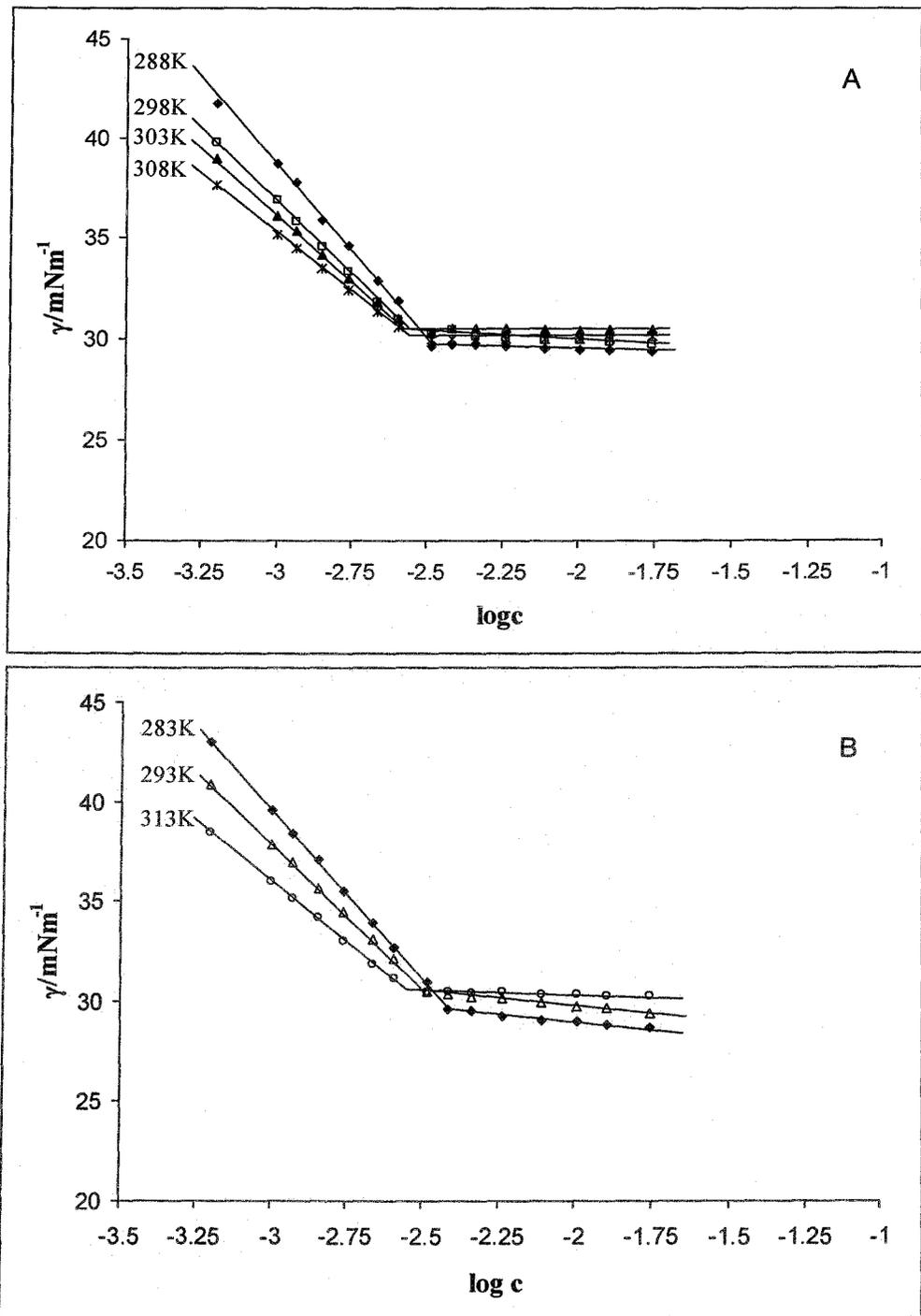


Figure 3.20: Surface tension, γ , of AOT (ammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

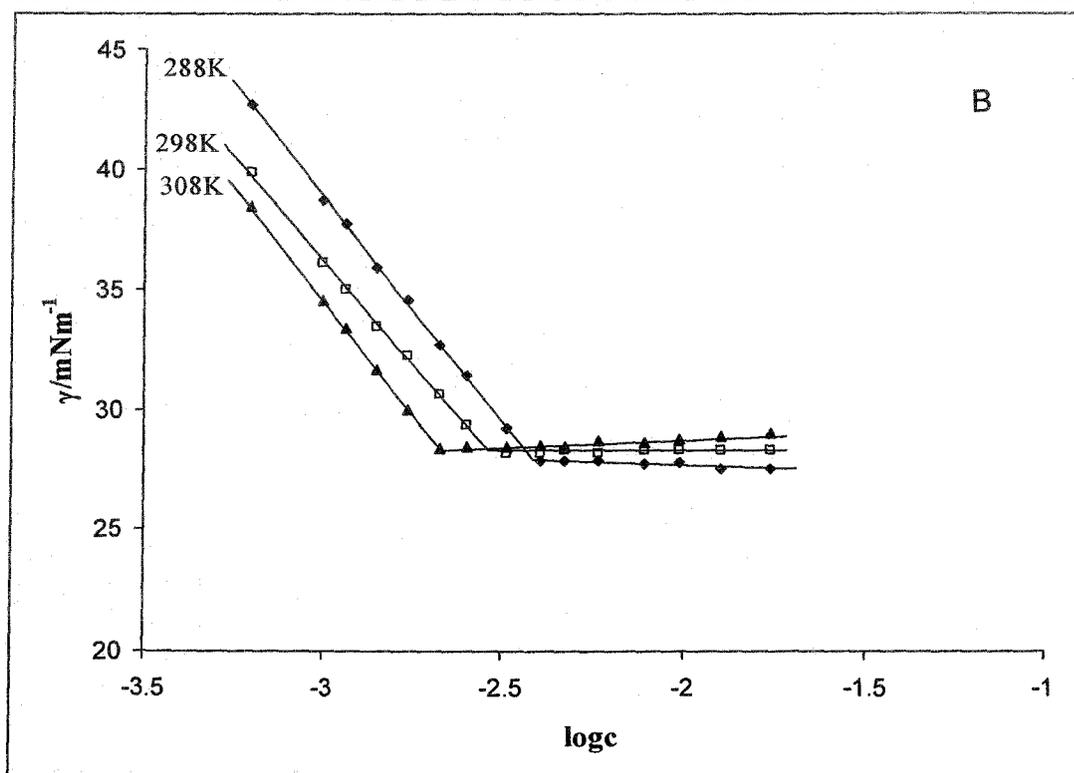
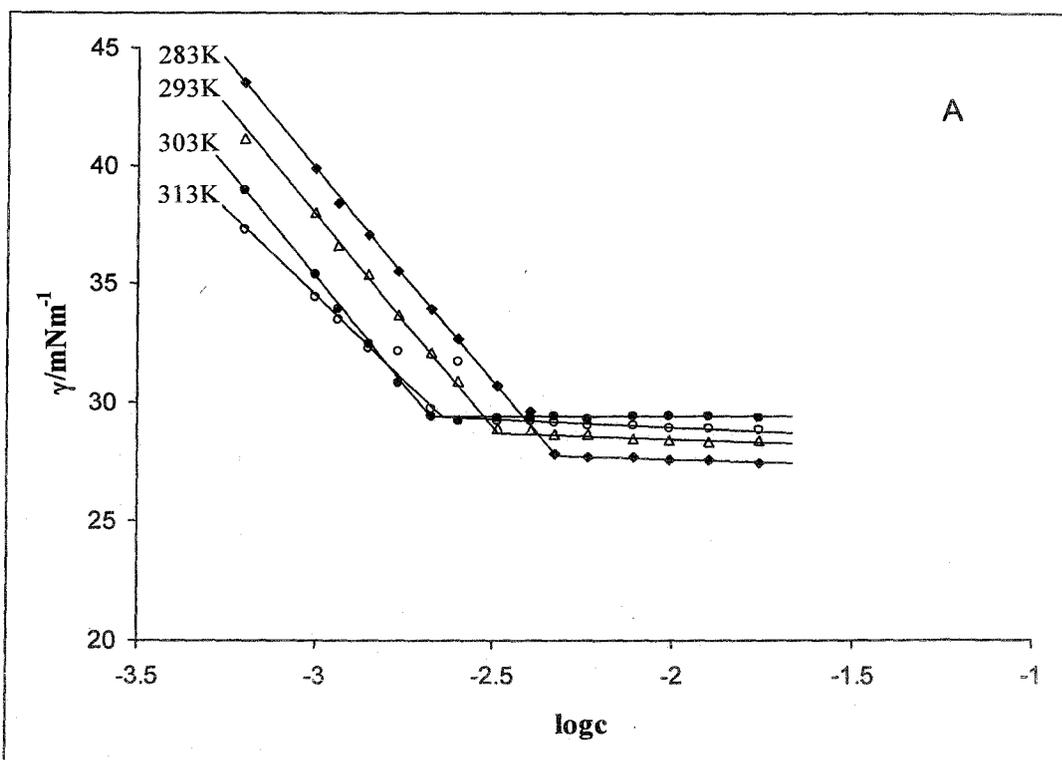


Figure 3.21: Surface tension, γ , of AOT (tetramethylammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K).

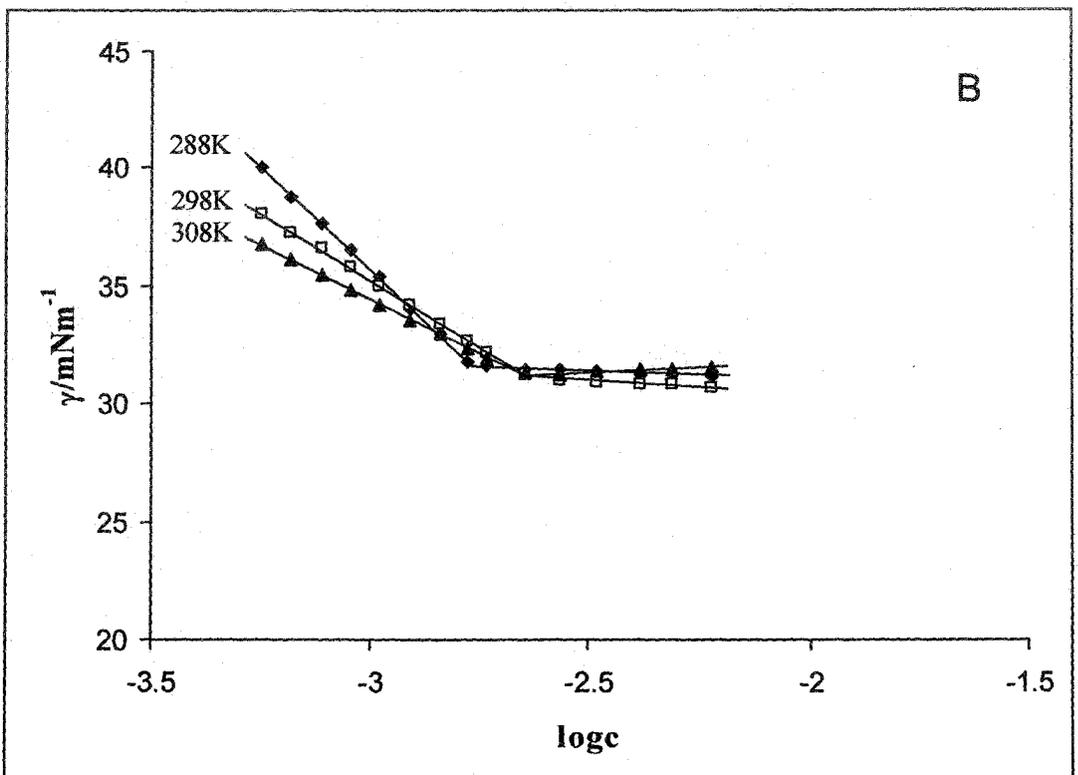
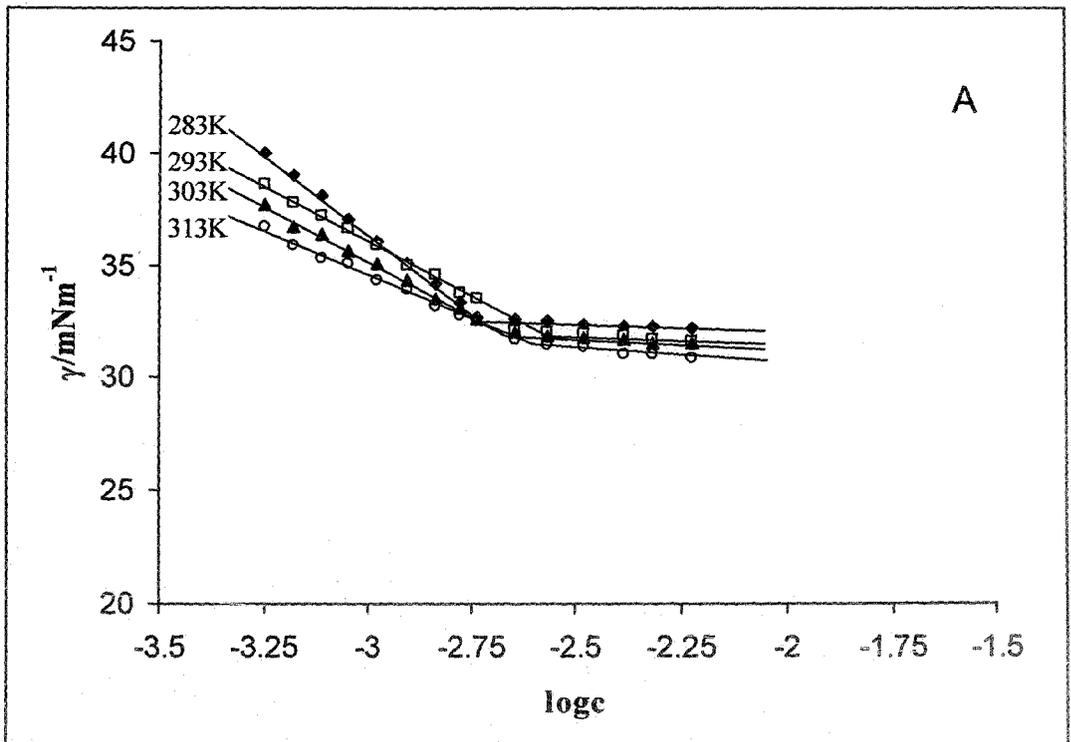


Figure 3.22: Surface tension, γ , of AOT (tetraethylammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K)

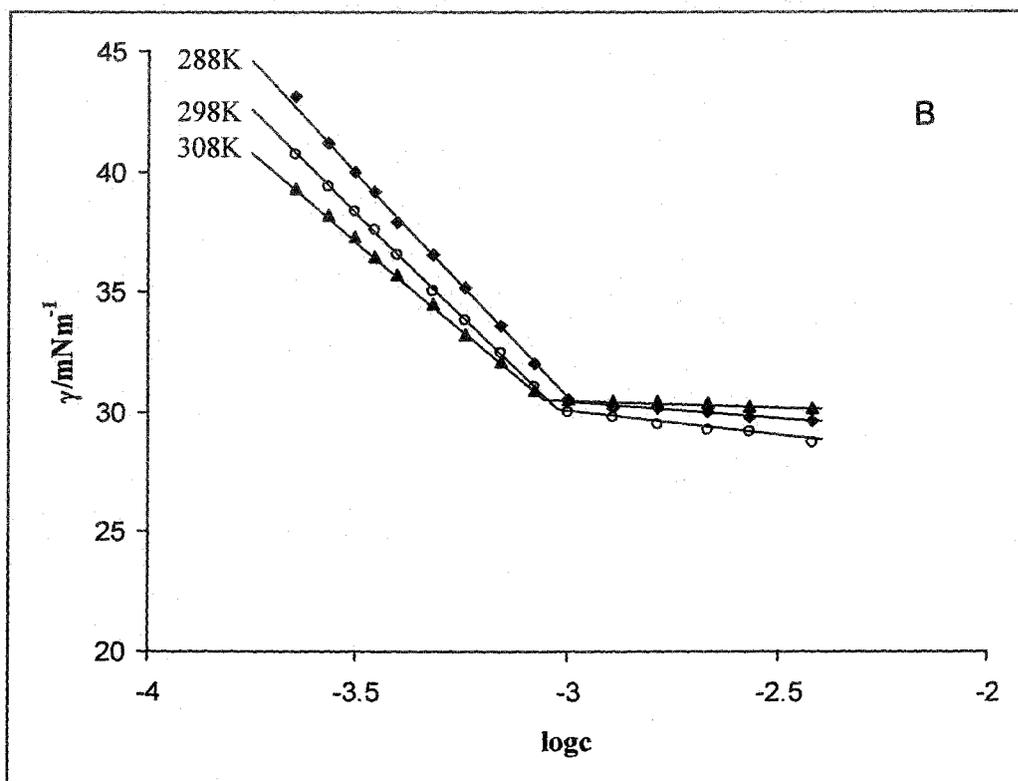
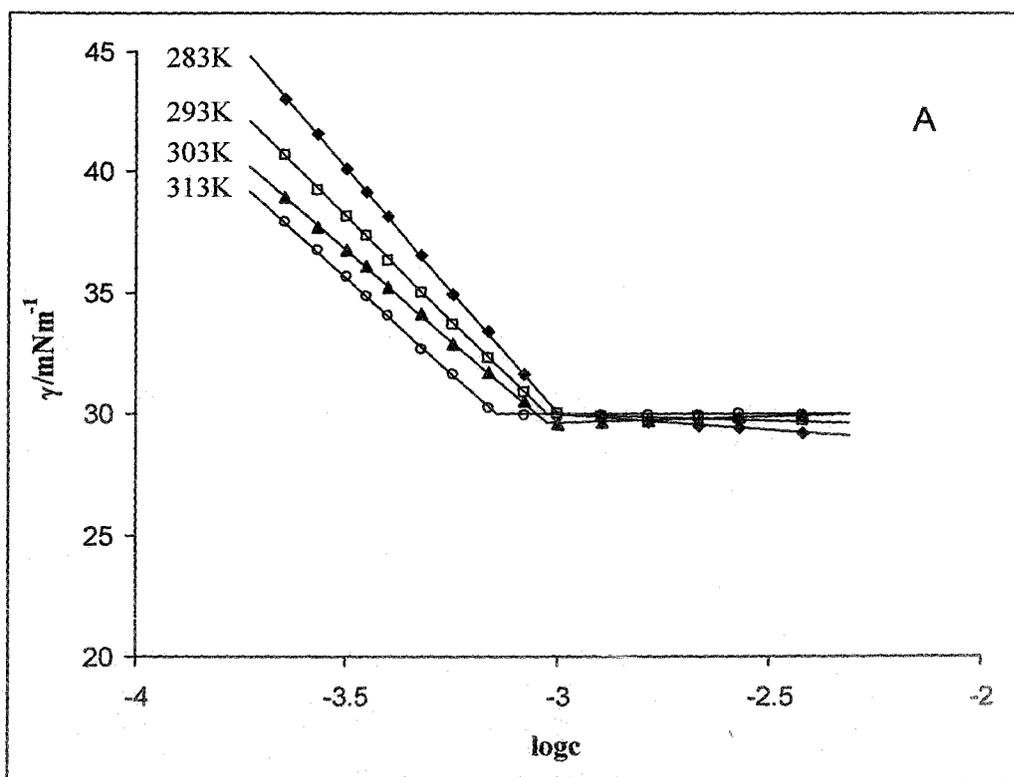


Figure 3.23: Surface tension, γ , of AOT (tetrapropylammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures (A: temperature 283K, 293K, 303K, 313K), B: temperature 288K, 298K, 308K)

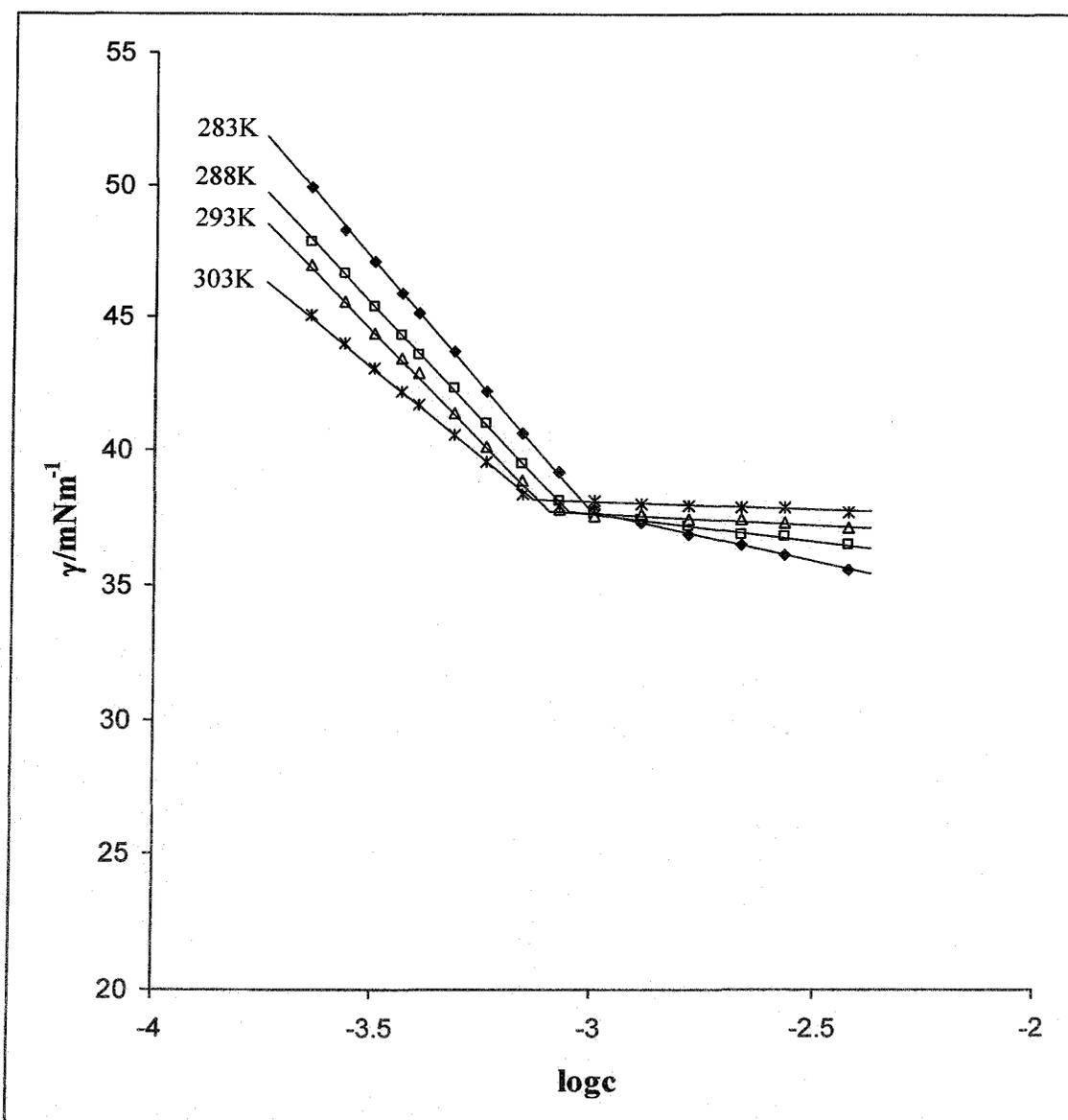


Figure 3.24: Surface tension, γ , of AOT (tetrabutylammonium salt) in aqueous solution as a function of the logarithm of the surfactant concentration at different temperatures

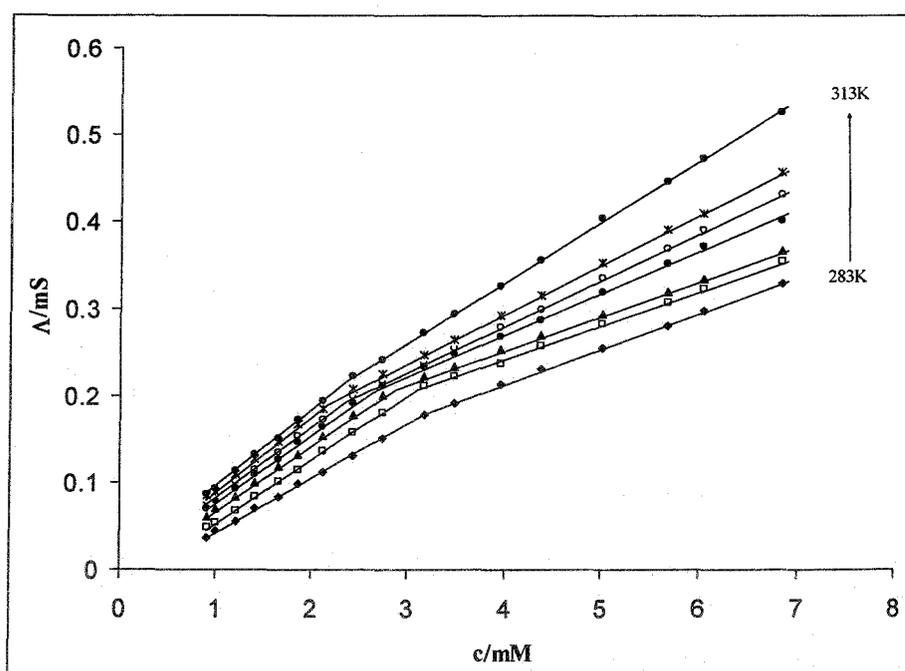


Figure 3.25: Conductance, Λ , of AOT (lithium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

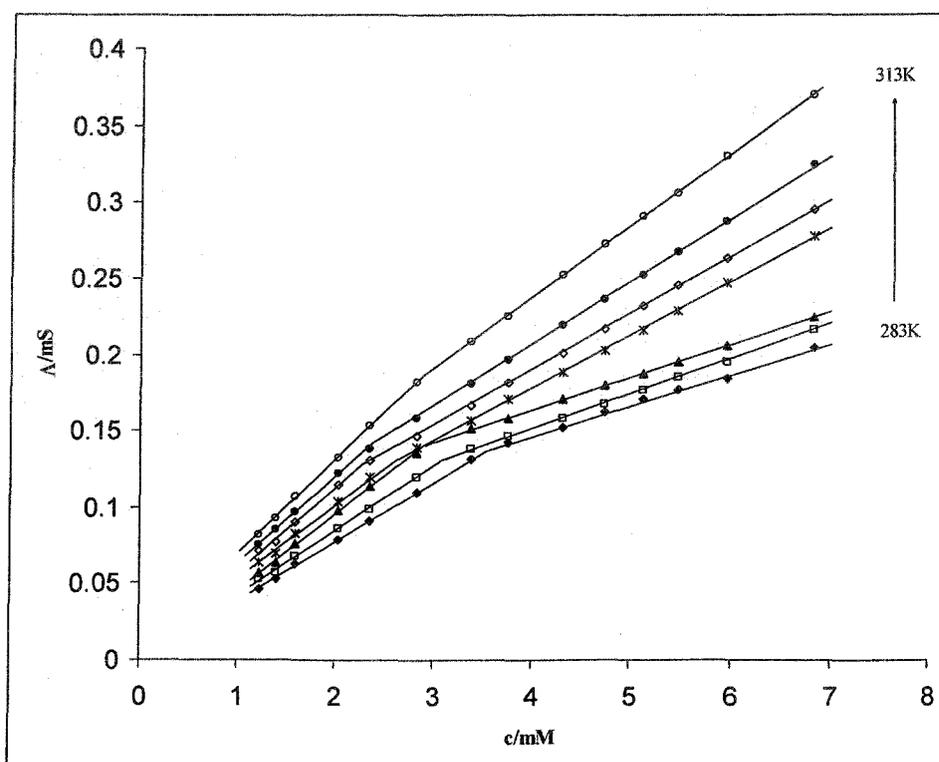


Figure 3.26: Conductance, Λ , of of AOT (sodium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

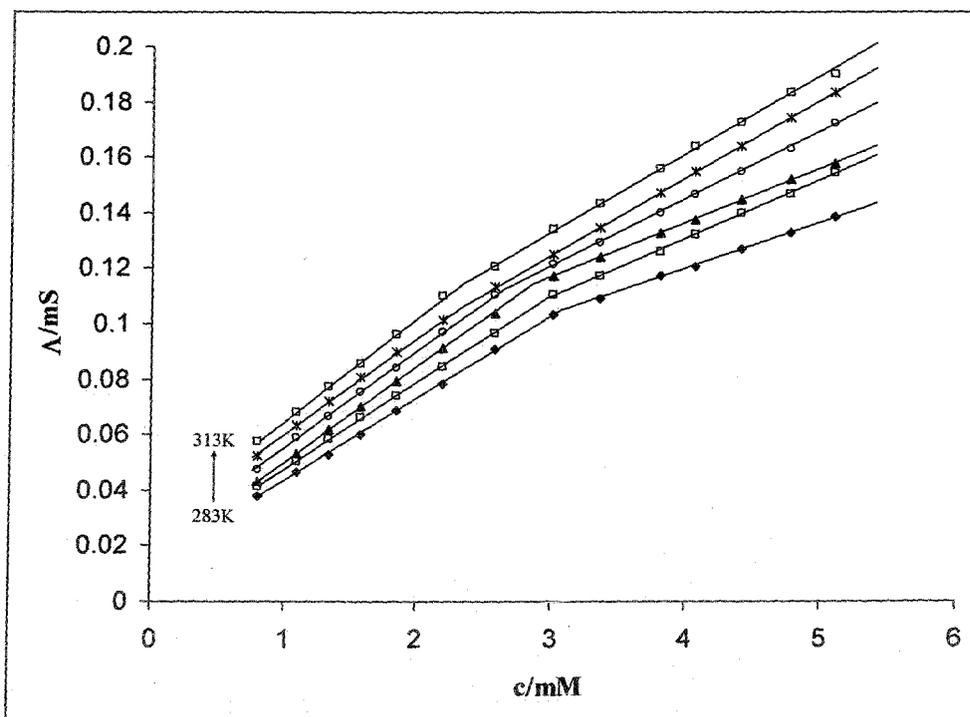


Figure 3.27: Conductance, Λ , of AOT (potassium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

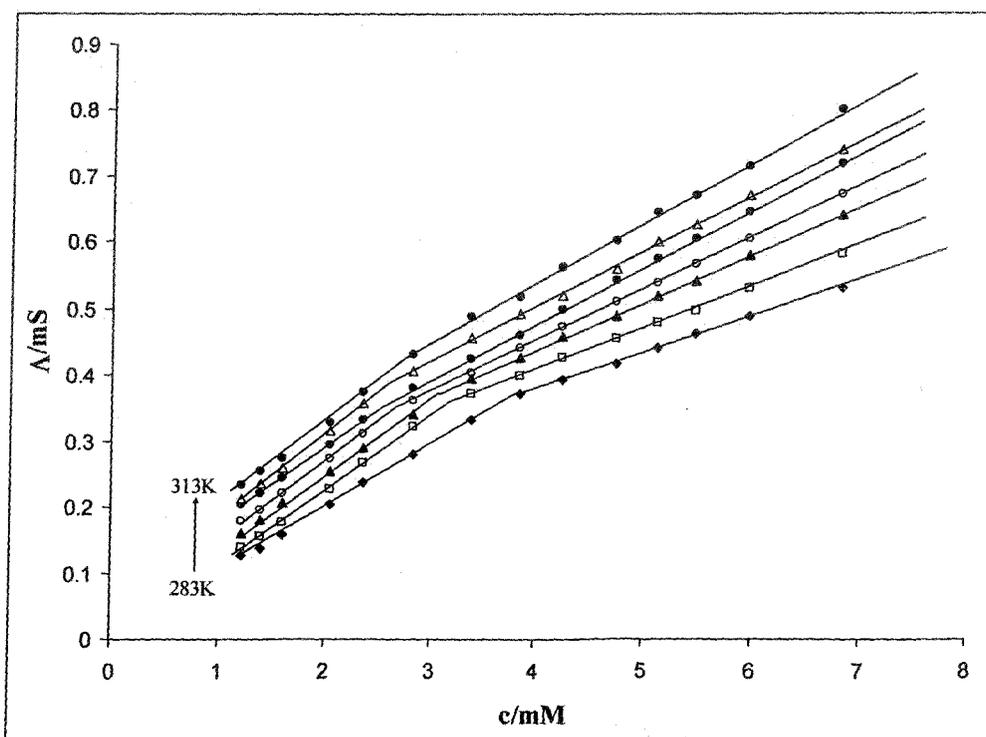


Figure 3.28: Conductance, Λ , of AOT (ammonium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

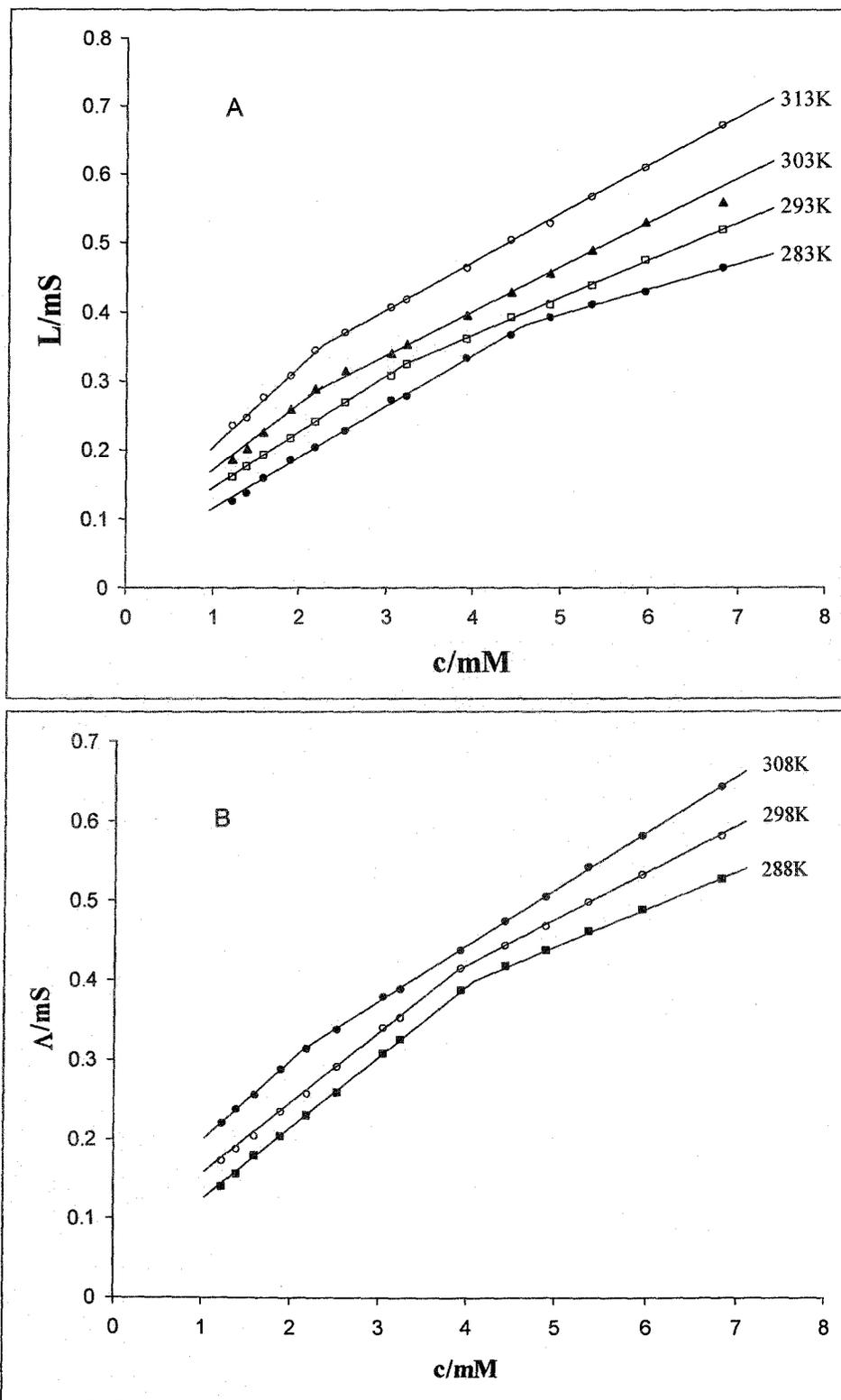


Figure 3.29: Conductance, Λ , of AOT (trramethylammonium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval

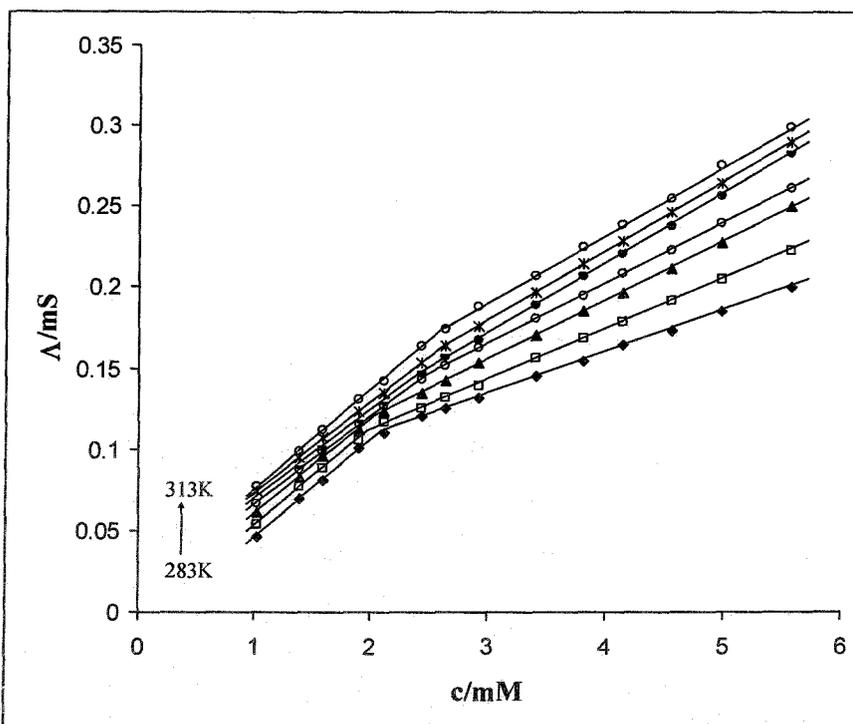


Figure 3.30: Conductance, Λ , of AOT (tetraethylammonium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval.

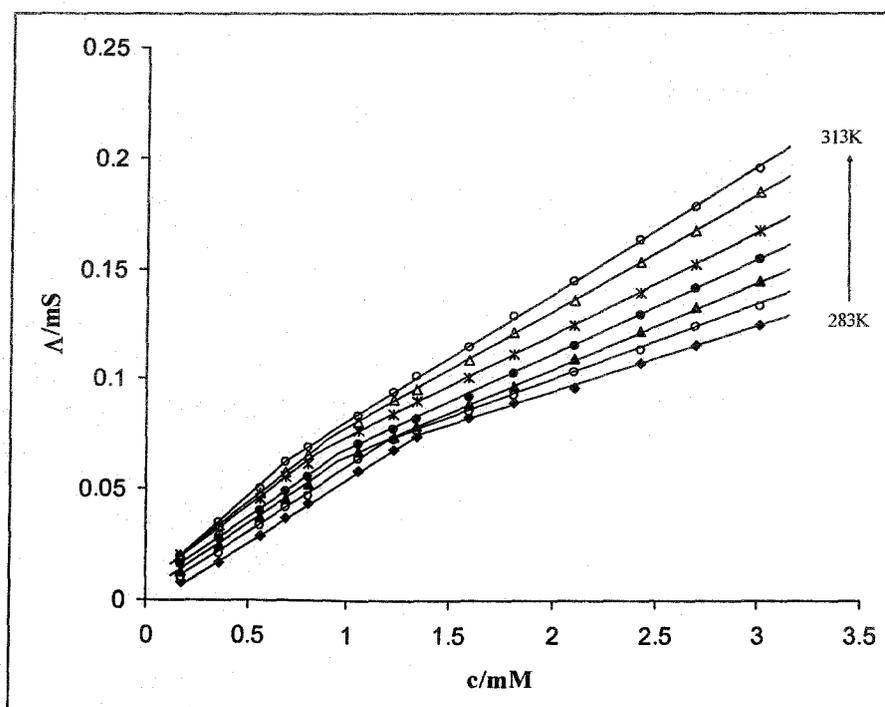


Figure 3.31: Conductance, Λ , of AOT (tetrapropylammonium salt) in aqueous solution as a function of the surfactant concentration at different temperatures ranging 283K to 313K with 5K interval

calculations of the hydration of micelles indicated a very small change in hydration during micellization [84]. This means that the hydration shell of cations limits the distance of closest approach. It seems apparent that the size of hydrated counter ion is important; bigger the size of counter ion i.e., low is its accessibility towards the head group, greater is the chance for micellization at lower concentration. The hydration number derived from the corrected ionic radii [87] along with the ionic and hydrated radius [88-90] of the above four ions are shown in the Table 3.9.

The larger the hydrated radius, the further the ion is located from the surface of the negatively charged surfactant head groups. Thus, NH_4^+ having the large ionic and hydrated radius cannot approach the highly charged surface of the micelle as close as smaller ions. Therefore, it can neither screen the charge at the surface of micelles nor reduce the surface potential as effectively as the smaller ions [91]. Dodecyl sulfate and AOT behaves differently towards micellization when Na^+ and Li^+ are present as counterion. Li^+ ion with its largest hydrated radius may modify slightly the internal structure of the double tailed AOT micelle which interacts with the hydrated Li^+ ion resulting lower cmc value. The K^+ , however, gives anomalous result due to its strong tendency for ion pair formation in K-AOT.

It has been observed that in case of dodecyl sulfate and AOT having tetraalkylammonium counterions the cmc values follow the order $\text{N}^+(\text{CH}_3)_4 > \text{N}^+(\text{C}_2\text{H}_5)_4 > \text{N}^+(\text{C}_3\text{H}_7)_4 > \text{N}^+(\text{C}_4\text{H}_9)_4$ (at temperature range $< 298\text{K}$). It seems that the hydrodynamic size of the counterion plays an important role along with the hydrophobicity of tetraalkylammonium ions. Measurement of partial molar volumes [93,94] and calculation of hydration of micelles [95] by previous workers indicated that there was little loss of hydration water in this system during micellization. Therefore, the tightly bound hydration shell would limit the distance of closest approach. It is well known that the increase of the number of carbon atoms of hydrocarbon tail of a surfactant allows micellization to occur at a lower concentration due to increased hydrophobicity of the hydrocarbon tail [92]. But the increased ionic size from $\text{N}^+(\text{CH}_3)_4$ to $\text{N}^+(\text{C}_4\text{H}_9)_4$ enhances the micellization tendency and eventually reduces the cmc.

Table - 3.1
Surface properties of dodecyl sulfate having different alkyl 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)	$\Gamma_{\text{max}}/$ mol cm ⁻² ×10 ¹⁰	$A_{\text{min}}/$ 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 3.2
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)	$\Gamma_{\max}/$ mol cm ⁻² × 10 ¹⁰	$A_{\min}/$ 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 3.3
Thermodynamic parameters of micellisation for Dodecyl sulfate with different alkyl counterions along with NH_4^+ at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp./°C	$-\Delta G_m^\circ$ / (kJ mol ⁻¹)	ΔH_m° / (kJ mol ⁻¹)	ΔS_m° / (J mol ⁻¹)
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 3.4
Thermodynamic parameters of micellisation for Dodecyl sulfate with different tetraalkylammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp./°C	$-\Delta G_m^\circ /$ (kJ mol ⁻¹)	$\Delta H_m^\circ /$ (kJ mol ⁻¹)	$\Delta S_m^\circ /$ (J mol ⁻¹)
(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 3.5
Micellization and surface parameters of AOT surfactants having different alkyl 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)	$\Gamma_{\text{max}}/$ mol cm ⁻² ×10 ⁸	$A_{\text{min}}/$ 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 3.6
**Micellization and surface parameters of AOT surfactants having different tetraalkyl-
 ammonium 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)	$\Gamma_{\max}/$ mol cm ⁻² ×10 ⁸	$A_{\min}/$ 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

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

Table 3.7
Thermodynamic parameters of micellization for AOT surfactants with different alkyl counterions at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	Temp./°C	$-\Delta G_m^\circ$ / (kJ mol ⁻¹)	$-\Delta H_m^\circ$ / (kJ mol ⁻¹)	ΔS_m° / (J mol ⁻¹)
Li ⁺	283	29.0	09.9	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 3.8
Thermodynamic parameters of micellization for AOT surfactants with different tetraalkyl-ammonium counterions at various temperatures: Standard Gibb's free energy, Enthalpy and Entropy.

Counterion	T/C	$-\Delta G_m^\circ /$ (kJ mol ⁻¹)	$-\Delta H_m^\circ /$ (kJ mol ⁻¹)	$\Delta S_m^\circ /$ (J K ⁻¹ mol ⁻¹)
(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

Table 3.9
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

Here the hydrocarbon exterior of the tetraalkyl ions undergoes hydrophobic interactions with the exposed hydrocarbon of the micelle surface and overcome steric hindrance. However, such a phenomenon is little or absent in the set of counterions viz., N⁺(CH₃)₄, NH₄⁺ and Na⁺. In the absence of any appreciable hydrophobic interaction, NH₄⁺ and Na⁺ ions interact with the micellar head groups more strongly than N⁺(CH₃)₄ ions due to their smaller sizes. Eventually they lead to form micelle more readily via efficient charge screening than that of N⁺(CH₃)₄ ions and the systems yield low cmc values. But in case of other tetraalkylammonium ions as the bulkiness of the ion increases due to the presence of large alkyl groups the hydrophobicity plays important role causing increasingly micellization to occur at lower concentrations as has already been mentioned.

The cmc in aqueous solution for a particular surfactant reflects the degree of binding of the counterion to the micelle. Increased binding of the counterion, in the aqueous system causes a decrease in the cmc of the surfactant. The extent of binding of the counterion increases also with increase in the polarizability and charge of the counterion and decreases with increase in its hydrated radius. Thus in aqueous medium, for anionic lauryl sulfates, the cmc decreases in the order Li⁺ > Na⁺ > K⁺ > Cs⁺ > N⁺(CH₃)₄ > N⁺(C₂H₅)₄ > Ca⁺, Mg⁺, which is same order as the increase in the degree of binding of the cation [78]. The depression of cmc from Li⁺ to K⁺ is small, but for other counter ions it is quite substantial. When the counterion is a cation of a primary amine, RNH₃⁺, the cmc decreases with increase in the chain length of the amine [79].

On the other hand, when comparing surfactants of different structural types, the value of cmc does not always increase with decrease in degree of binding of the counterion. Thus although in the series $RN^+(CH_3)_3$ the degree of binding increases and the cmc decreases with increase in length of R, the decrease in cmc is due mainly to the increased hydrophobicity of the surfactant as a result of increase in alkyl chain length, and only to a minor extent due to the smaller area per head group.

It has been reported that in case of dodecyl sulfate (DS) cmc shows very little temperature dependency when a counter ion varies within different alkali metals viz. from lithium to cesium ion [96] and tetraalkylammonium ion [13]. Similar result is observed when the counterion is changed from Li^+ to tetrabutylammonium ion (TBA^+) for the present study of dodecyl sulfate (Table 3.1 and 3.2). It is observed that when Li^+ , Na^+ and NH_4^+ are present as counterion the cmc of dodecyl sulfate show pronounced temperature dependency and passes through a shallow minimum at the temperature range 298 – 308K (Figure 3.32). But when tetraalkylammonium ion is present as counterion, the cmc of dodecyl sulfate show a little temperature sensitivity. On the other hand, in AOT the cmc values give more pronounced temperature dependency even when the counterion is tetraalkylammonium ion. Figure 3.33 represents the temperature dependency in cmc of AOT as a function of different counterions. The decrease in the cmc with temperature (at lower temperatures) is possibly due to the hydration of the monomers, whilst further temperature increase causes a disruption of the structured water around the hydrophobic groups that opposes micellization. In the case of K-AOT the cmc can't be determined at 40°C due to the very low solubility of the particular surfactant at that temperature which may be hardly sufficient to make micelle. The variation of cmc with temperature shows good agreement with the empirical equation given by La Mesa [100]:

$$(cmc - cmc^*) = \left[\frac{(T - T^*)}{T^*} \right]^{\gamma'} \quad (3.10)$$

where cmc^* is the minimum value of cmc and T^* the temperature at the minimum with $\gamma' = 1.74 \pm 0.03$. It should be mentioned that the exponent γ' has no obvious physical meaning, but, both cmc^* and the related temperature in case of a particular surfactant are the measure of the hydrophobic-hydrophilic balance of micelle [46].

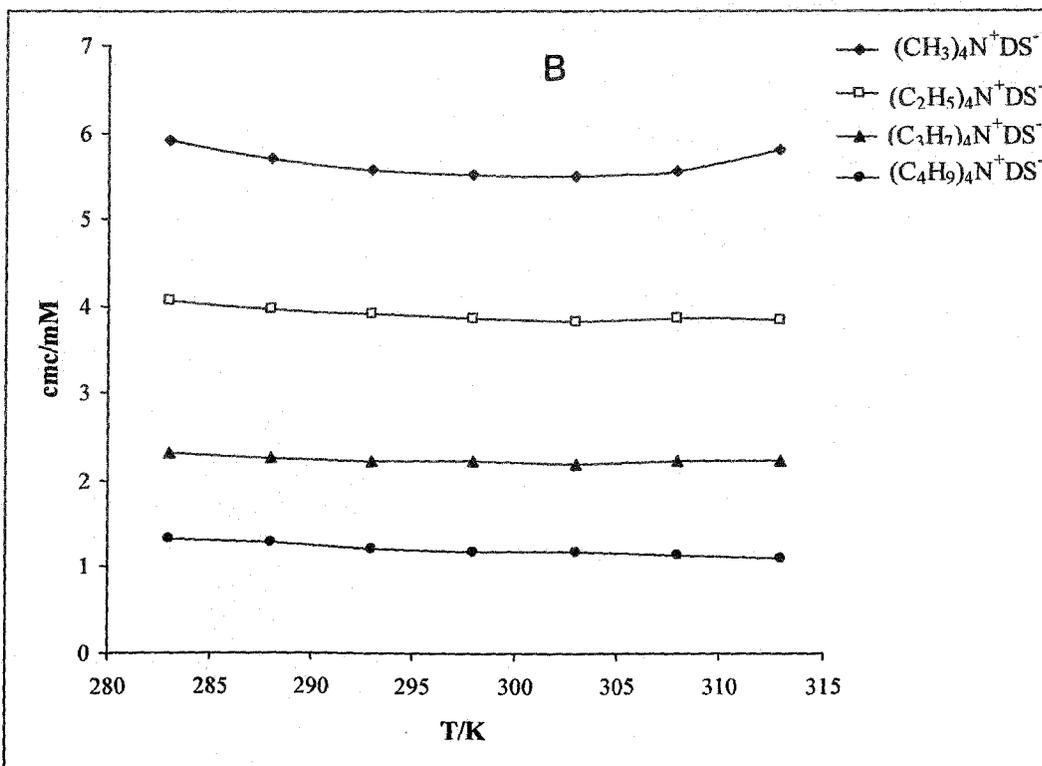
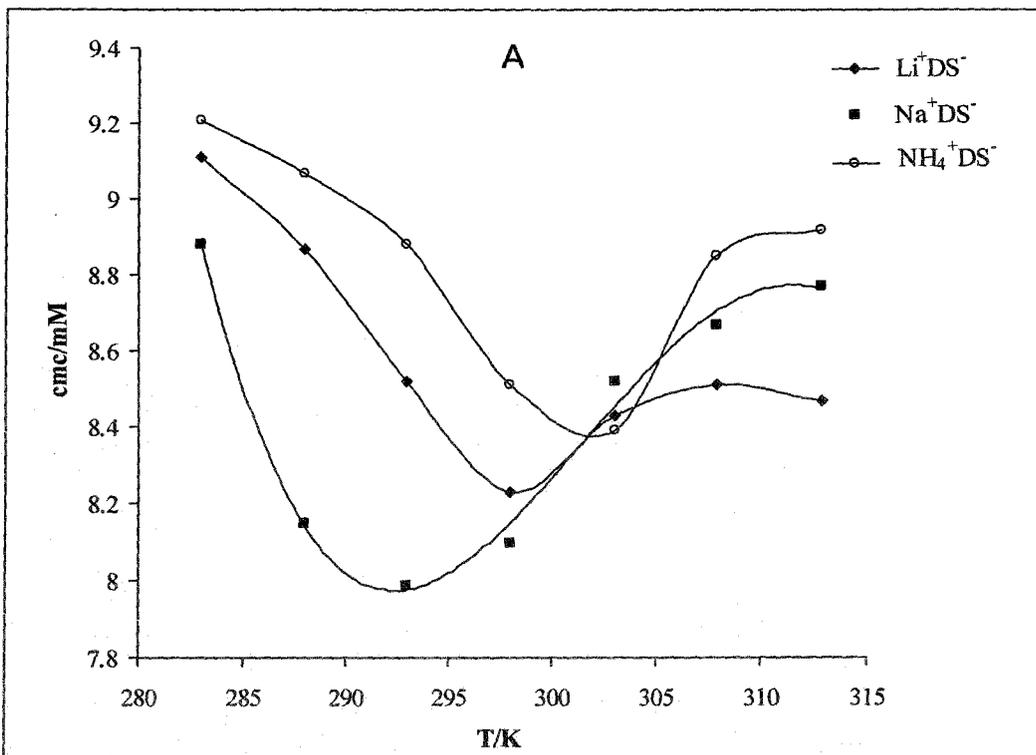


Figure 3.32: Variation of cmc with temperature (K) of dodecyl sulfate having different counterion.

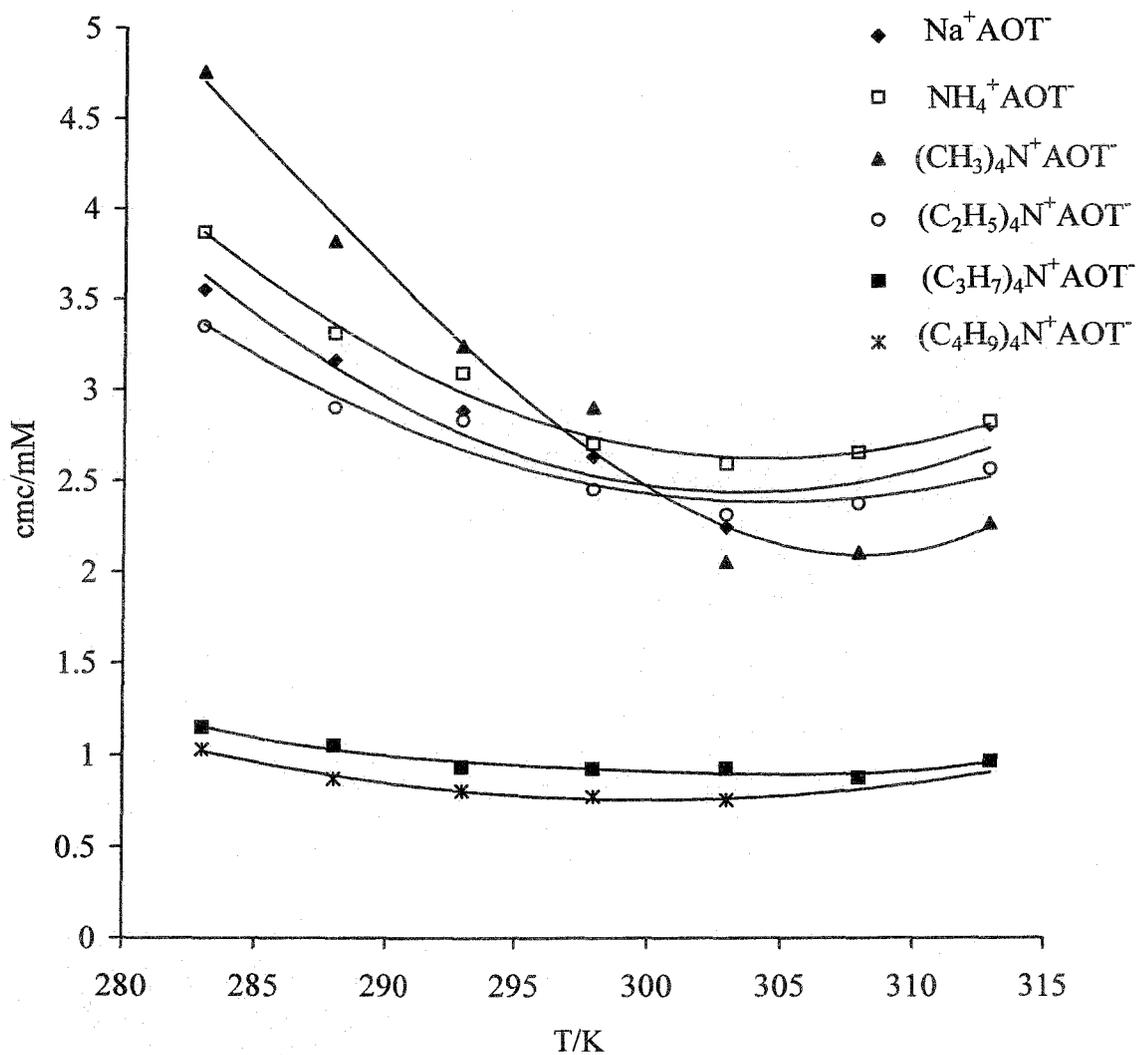


Figure 3.33: Variation of cmc with temperature (K) of AOT having different counter cation

The position of the minimum has thermodynamic significance also. The minimum in cmc represents minimum in free energy of micellization.

Thermodynamic Parameters:

The temperature dependency of dodecyl sulfate (DS) and AOT micelles having different counterions also enables to determine the corresponding thermodynamic parameters of micellization. According to mass action or phase separation model the standard free energy of micelle formation per mole of monomer of ionic uni-univalent surfactants is expressed by well-known equation [21a,69]:

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} \quad (3.11)$$

Here X_{cmc} is the cmc expressed in mole fraction scale and $\alpha = 1 - \beta = p/n$, is the ionization degree or counter ionic ionization constant of the micelle, where p and n are the effective charge and the aggregation number of the micelle respectively. 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 [32,97]. The values of ΔG_m^0 determined for each surfactant-counterion pair at different temperatures eventually give the standard enthalpy (ΔH_m^0) and entropy (ΔS_m^0) of micellization from the simple thermodynamic relations:

$$\Delta H_m^0 = - (2 - \alpha) RT^2 \left(\frac{\partial \ln X_{cmc}}{\partial T} \right)_P \quad (3.12)$$

The equation 3.12 is obtained from the well known Gibbs-Helmholtz relation and equation 3.11 assumes that α does not vary much with temperature. However, α is not strictly temperature independent and the more appropriate form of equation 3.12 should be

$$-\Delta H_m^0/T^2 = (2 - \alpha) R \left(\frac{\partial \ln X_{cmc}}{\partial T} \right)_P + R \ln X_{cmc} \left(\frac{\partial (2 - \alpha)}{\partial T} \right) \quad (3.13)$$

Since the variation of α with temperature is not well defined and is devoid of any general trend, the quantity $\partial(2 - \alpha)/\partial T$ is difficult to find out experimentally [98]. Therefore, at least to gain qualitative information regarding the thermodynamics, equation 3.12 has been applied at the appropriate α .

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T \quad (3.14)$$

The $\ln X_{cmc}$ vs T plot is not linear. To evaluate ΔH_m^0 , following polynomial form of variation of $\ln X_{cmc}$ with temperature has been considered.

$$\ln X_{cmc} = a + bT + cT^2 \quad (3.15)$$

where a , b , c are respective polynomial constants.

Thus,

$$\left(\frac{\partial \ln X_{cmc}}{\partial T}\right) = b + 2cT \quad (3.16)$$

The polynomial constants b and c were evaluated from the fitting of experimental data. For all DS and AOT surfactants with different counterions the calculated thermodynamic parameters of micellization are listed in Table 3.2 and 3.4. Spontaneity of the micellization process is well explanatory from the large negative values of ΔG_m^0 . Micelles containing the same amphiphile but different counterions show different values of thermodynamic parameters because of the different counterions could bind to an amphiphile to a different extent and with different energy. Micellization in aqueous medium usually leads to a positive entropy change, which is mainly due to the melting of the "flickering cluster" that arises out of the hydrophobic effect of amphiphilic part of the surfactant molecules [99]. During formation of a micelle, the endothermic melting of the ordered polar solvent molecules around the nonpolar tail of amphiphile is greater than the subsequent exothermic association of the molecules. The resulting disordered state is actually reflected in the positive entropy change. The variation of the standard thermodynamic parameters with different counter ions at a certain temperature can also be explained by the size and the hydration of the counter ion as has been already discussed. Like cmc , the ΔG_m^0 and ΔH_m^0 also show temperature dependency for all the surfactant-counterion systems.

A close look on the thermodynamic parameters (Table 3.3, 3.4, 3.7 and 3.8) support the view that in order to form micelle the gain in entropy is the major factor leading to negative change in Gibbs free energy [101-103] if the temperature is not very high. 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. For ionic surfactants in aqueous solution, the reported [4,103] value of $\Delta G_{-CH_2-}^0$ is approximately 2.93~3 kJ.mol⁻¹. However, the fact that though the free energy changes are not very different, the enthalpy change is significantly higher and the entropy changes are much lower for $N^+(CH_3)_4$ counterion containing AOT compared to all other systems. This leads one to interpret that the enthalpy contributes major driving force in micellization. Loosely bound water dipole with the $N^+(CH_3)_4$ ion may cause lower contribution of ΔS_m^0 in aggregation process. Similarly, for other counterions in both DS and AOT systems ΔH_m^0 and ΔS_m^0 contribute differently to get similar ΔG_m^0 . However, like a variety of processes such as oxidation-reduction, hydrolysis, protein unfolding, etc., micellization process also exhibit a linear relationship between the enthalpy and entropy change which is known as enthalpy-entropy compensation [20,104,105]. This is important in connection with the hydrophobicity of surfactant which leads to stable micelle formation. In general, 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 [106]

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

In a plot of ΔH_m^0 vs ΔS_m^0 , the slope T_c has a dimension of temperature and is known as compensation temperature. This can be interpreted as a measure of desolvation part of micellization, that means a characteristic of solute-solute and solute-solvent interaction, and the intercept characterizes the solute-solute interaction. Present experimental results also show a good agreement with the enthalpy-entropy compensation linearity for all AOT surfactants having different

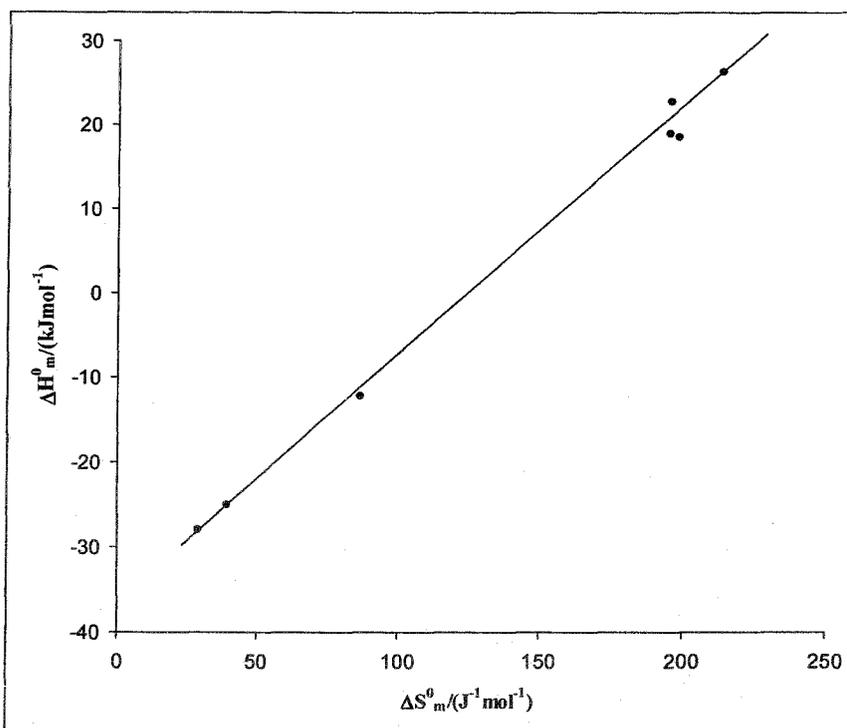


Figure 3.34: Enthalpy–entropy compensation plots for dodecyl sulfate having different counterions at 298 K

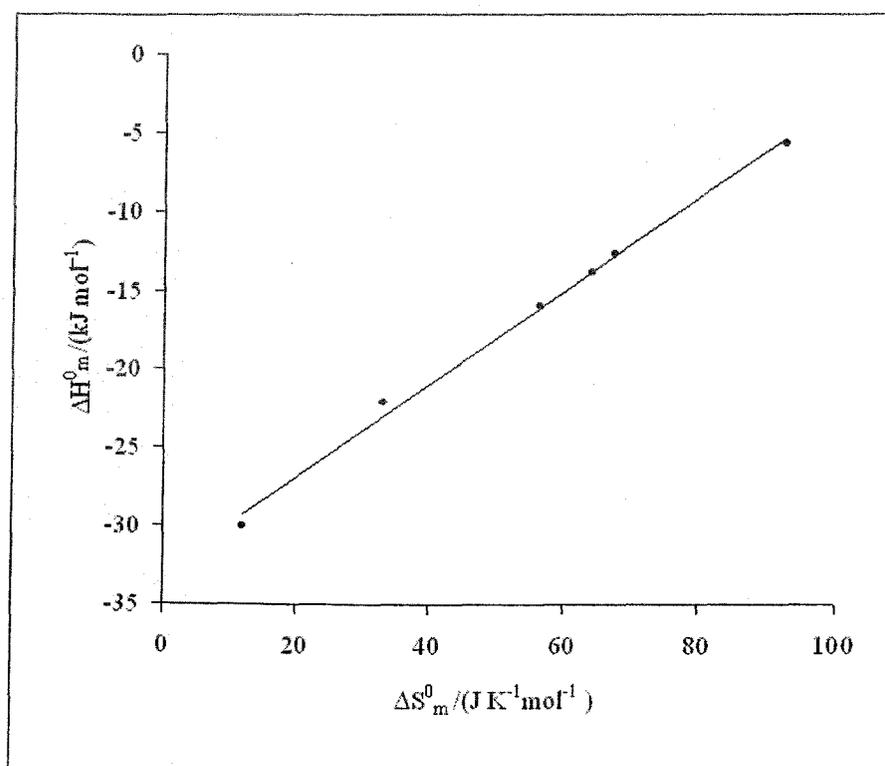


Figure 3.35: Enthalpy–entropy compensation plots AOT surfactants having different counterions at 298 K

counterions. Figure 3.34 and Figure 3.35 represent the enthalpy-entropy compensation plots at 298K for DS and AOT. The calculated compensation temperature value of 303.2 K for DS and 295.6 K for AOT satisfactorily follows the characteristic range of other ionic surfactants [20,78,105]. The intercept, ΔH_{mv}^* has been calculated as -37.8 kJmol^{-1} and -32.8 kJmol^{-1} for DS and AOT respectively which correspond to the driving force of micellization where the entropy does not contribute the process at that particular temperature.

It is well known that the air-solution interface of a surfactant solution is well populated by the adsorbed molecules. The maximum surface excess concentrations (Γ_{\max}) in the aqueous-air interface are calculated by using common Gibbs adsorption equation. For 1:1 ionic surfactant in the absence of any other solutes, Γ_{\max} may be expressed by the following relation [107-109]:

$$\Gamma_{\max} = (1/2.303n'RT) \left(-\partial\gamma/\partial \log C \right) \quad (3.19)$$

where γ expresses the surface tension, C and n' are the molar concentration and number of particles per molecule of the surfactant respectively. Since in aqueous solution at concentrations less than cmc, both dodecyl sulfate and AOT behave like a uni-univalent electrolyte, the thermodynamic treatment requires $n' = 2$, states an equimolar ratio of surfactant anion and counterion in the interface. Similar to analysis of $\ln X_{\text{cmc}}$ vs T plot, γ vs $\ln C$ plot was also fitted to a second order polynomial to measure Γ_{\max} . The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by the use of molecular models. From the surface excess concentration the minimum area per molecule (A_{\min}) at the interface in square nanometer is calculated from the relation:

$$A_{\min} = 10^{14}/(N\Gamma_{\max}) \quad (3.20)$$

where N is the Avogadro's number and Γ_{\max} is in mol/cm^2 .

The surface excess concentration at surface saturation 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 for

both nonionic [108] and anionic [109] surfactants, Γ_{\max} values slightly decreases with temperature while in some other cases an increase of the surface excess quantity has been reported [110] in presence of additives. With increasing temperature Γ_{\max} for dodecyl sulfate follow more or less general trend as expected, which presumably due to increased thermal motion with a consequent decrease in the effectiveness of adsorption. But in the case of AOT surfactant with six different counter ions, the change of Γ_{\max} does not follow a regular trend. A critical examination of Table 3.5 and 3.6 show a slight increment in Γ_{\max} with temperature for all the counter ions, which may be due to the effect of lower hydration of the sulfosuccinate part of AOT at higher temperature and hence an increasing tendency to move to the air-liquid interface [45,46]. While in case of dodecyl sulfate Γ_{\max} decreases with temperature (Table 3.1 and 3.2), and this suggests greater salvation of the amphiphilic molecules at higher temperature, where salvation energy overcome the so called dehydration process. It is quite obvious that the standard state for the adsorbed surfactant is a hypothetical monolayer at its minimum surface area per molecule, but at zero surface pressure. The typical double chain of the amphiphile may also partially be responsible for this result causing 'steric inhibition' during adsorption. The moderate increase in the effectiveness of adsorption at the air-water interface with temperature is due to increased thermal motion, and therefore, A_{\min} display an inverse trend with temperature, as expected. With increasing bulkiness of the counterions of the amphiphiles the increase of Γ_{\max} are quite noticeable. At a particular temperature, Γ_{\max} shows anomalous behaviour as the counter ion of the surfactant changes. It may be attributed to the enhanced hydrophobicity of the anionic part of the surfactant molecules depending upon accessibility of their corresponding counter ions. A study of the behaviour of tetramethylammoniumdodecyl sulfate at the air-solution interface indicated to a penetration of a part of the $N^+(CH_3)_4$ ions in the dodecyl sulfate layer [111]. A similar phenomenon may also partially be responsible for the observed surface behaviour in the present systems.

3.3 Effect of Alcohols on the Aggregation Properties of Micellar systems in Aqueous Medium

The hydrophobic and electrostatic forces among ionic surfactant molecules play an essential role for the self-association and formation of micelles. One of the

most interesting aspects of these heterogeneous micelles is their ability to accommodate organic molecules [112-115]. An increased flexibility of the micellar membrane and thereby an improved ability to solubilize hydrophobic molecules can be achieved by adding alcohols [116]. The size and shape of micelle aggregates containing commonly used surfactants and co-surfactants have been investigated earlier [117,118]. Many researchers are interested in mixed alcohol-water systems particularly due to their importance in the preparation of microemulsions [119,120]. Reports of Onori et al. [121-123] showed that the effects due to alcohols on two very different systems and processes, the thermal denaturation of t-RNA (transfer ribonucleic acid) and the micellization of several surfactant molecules were strikingly similar and were closely paralleled in simpler properties of alcohol-water mixtures themselves. These results support the hypothesis that the dominant mechanism by which an alcohol affects this process is through its effect on structure of water. At higher concentrations some other effects like the alteration in the dielectric constants of the solvent or the partition of the alcohol molecules between bulk and the micellar phase may be more important. The behaviour of sodium dodecyl sulfate (SDS) micelles in the presence of *n*-alcohols was extensively investigated by many researchers [45,56,57,124,125]. Micellization studies with hydrophilic alcohols and diols with the same number of carbons but different molecular structure have also been carried out [126, 127]. Carnero Ruiz [141] reported the thermodynamics of micellization in tetradecyltrimethylammonium bromide in a dihydric alcohol, ethylene glycol-water binary mixtures, and showed that with increasing the percentage of alcohol in the solvent both the cmc and counter ion dissociation constant (α) increased to a considerable extent. But in case of other progressively long chain alcohols, (e.g. *n*-heptanol to *n*-decanol) opposite observations were reported recently [115]. Similar reports are available for middle and short chain alcohols also [45,50,142]. It was suggested that for ionic surfactants, the cmc is related by the following equation [103]:

$$\log(\text{cmc}) = Z(1 - \beta) \left[\log \frac{2000\pi\sigma^2}{\epsilon_r RT} - \log c_i \right] + \left[\frac{\Delta G_{(-\text{CH}_2-)}}{2.303RT} \right] n + B \quad (3.21)$$

where Z is the charge of the surfactant ion, β is the fraction of counter ions bound by the micelle in the case of ionic surfactants, σ is the surfactants charge

density on the micelle, ϵ_r is the dielectric constant of the solvent, c_i is the concentration of counter ions in the polar solution, n is the carbon number of the surfactant and B is an arbitrary constant depending upon the system.

Equation 3.21 suggests that it is difficult to predict the effect of temperature on the cmc. But an increase in temperature may also decrease β , so the overall effect for an increase in temperature is to increase the cmc. When the β parameter of the system increases with an increment in carbon number of alcohol, it also indicates that the cmc of surfactant will also decrease.

But when the fraction of long-chain alcohol increases, the extent of counterion binding to the micelle also increases and as a result lowering of cmc will be observed. But due to the presence of alcohol the dielectric constant of the solvent decreases considerably, which suggest an easier denaturation of micelles and the cmc of the surfactant should be increased. In general all the factors mentioned above are reflected in the resulting cmc and related thermodynamic values of micellization in water-alcohol binary mixtures. As mentioned earlier ethylene glycol (EG) showed the reverse effect than the other alcohols which may be explained by its higher dielectric constant, small hydrophobic surface and greater capability of hydrogen bond formation. Sjöberg [133] also observed that in strong polar solvents, such as formamide and EG, micelles are found with qualitatively the same features as in water. It was found that the cmc of hexadecyl -trimethylammonium bromide (C_{16} TAB) is much higher in formamide (100 mM) than water (1mM) at 333K temperature. It is a general feature, also exemplified by smaller micelle radii and aggregation numbers, that self-assembly is much less co-operative in alternative polar solvents.

In this connection the influence of very common short chain alcohols, viz. ethanol, 1-propanol and 2-propanol on the micellization of SDS and AOT in aqueous medium are studied in the present investigation within the temperature range of 298-313K. Though it is said that the highly water-soluble alcohols such as methanol, ethanol and propanol dissolve mainly in the aqueous bulk solution [57,128], there are number of reports [129-130] supporting the influence of these short chain alcohols on micellization. The results of the investigation are relevant to several applied topics in colloids where micelles and microemulsions in alcohol-water mixtures have been used as an elution medium in micellar liquid chromatography [134]. 2-propanol is

also used in studies of photohydrogen abstraction by ketones in both homogeneous and micellar solutions [135].

3.3.1 Experimental Section

As discussed earlier, to investigate the micellization properties conductivity measurements of the solutions containing different proportion of alcohols and surfactants are performed within the temperature range of 298K to 313K. The temperature was maintained in a thermostated double-glass water jacket by the flow of constant temperature within ± 0.01 K. All the alcohols (Merck) associated in the experiments are used after necessary distillation as described elsewhere [136].

3.3.2 Results and Discussion

Similar to the previous measurements the cmc values of the SDS and AOT solutions in the presence of hydrophilic alcohols were determined by the 'break points' of the concentration versus conductance plots. The cmc and the other related thermodynamic parameters of SDS and AOT are given in Table 3.10 and 3.11 respectively. All the thermodynamic parameters including cmc are determined by similar procedure as described in the previous section (section 3.2.2). As expected, the cmc decreases upon addition of short chain alcohols, but the decrease is less than in case of a medium chain alcohol such as *n*-butanol [114,127]. For SDS-propanol systems the calculated cmc and α values are well similar to the reported [50] values determined spectroscopically. At alcohol concentrations higher than 1M, the determination of the cmc becomes more difficult because the change in conductivity is less pronounced. As mentioned above to explain the deviations observed in the micellization parameters two factors, viz., lowering of dielectric constant with addition of alcohol and the effective hydrophobic area of the alcohol molecule must be considered. In all cases the process of micelle formation is energetically favoured which can be supported by effective negative value of ΔG_m^0 . The other two thermodynamic parameters viz. ΔH_m^0 and ΔS_m^0 also show their necessary contribution in favour of micellization process.

Based on the relation between cmc and the thermodynamic functions the effect of alcohols on micellization can also be well explained. Table 3.10 suggests that in aqueous-alcohol medium relatively greater negative values of ΔH_m^0 (-22.1 ~ -38.2

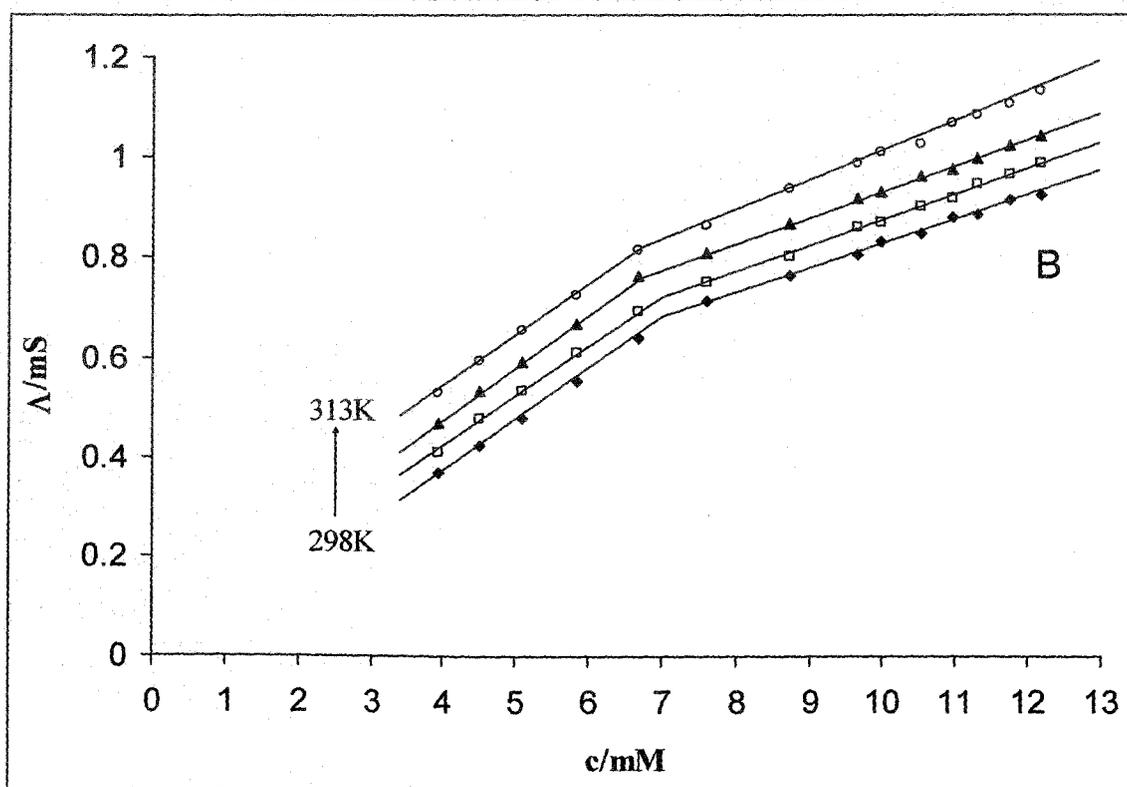
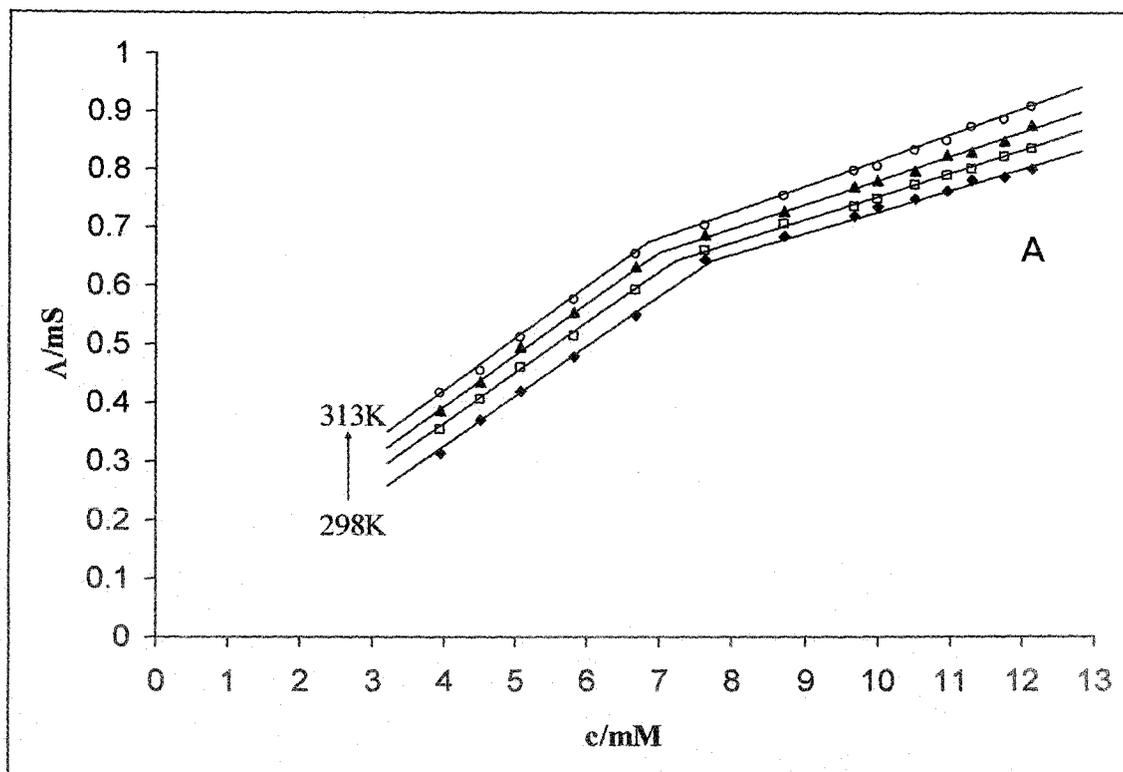


Figure 3.36 : Variation of conductance, Δ , with concentration of SDS having different proportion of ethanol (A: 0.4M ethanol; B: 0.7M ethanol)

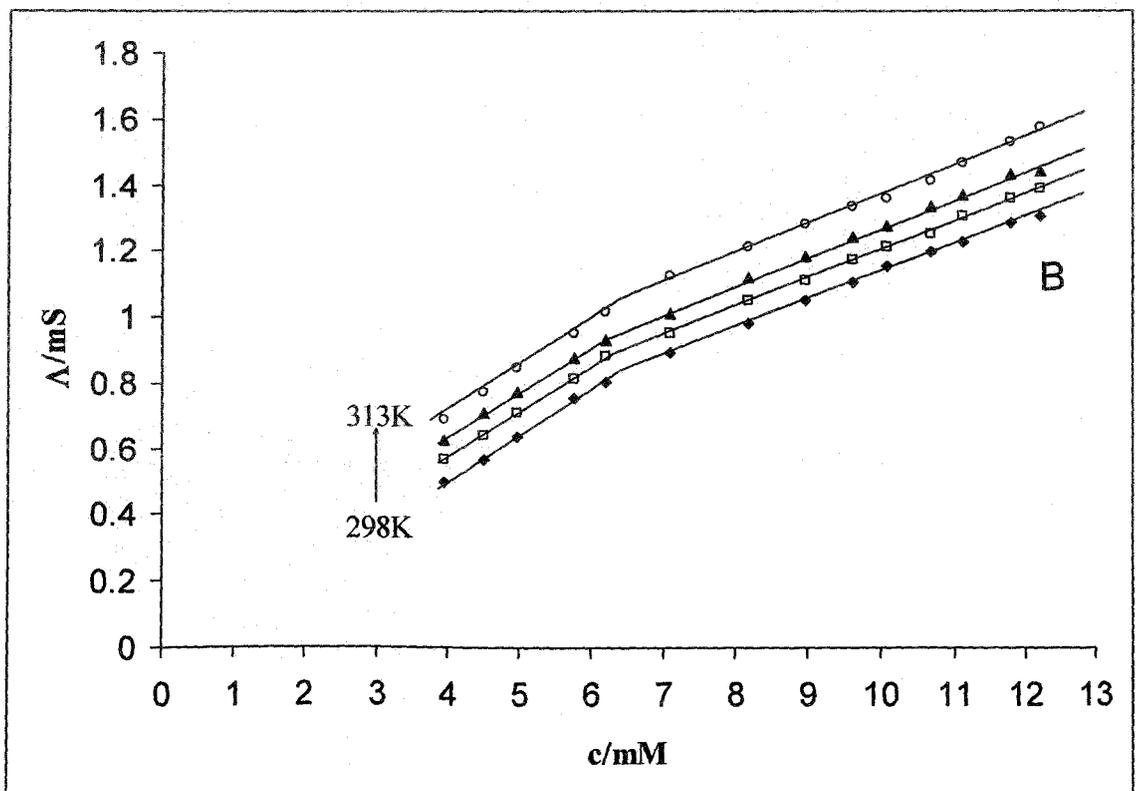
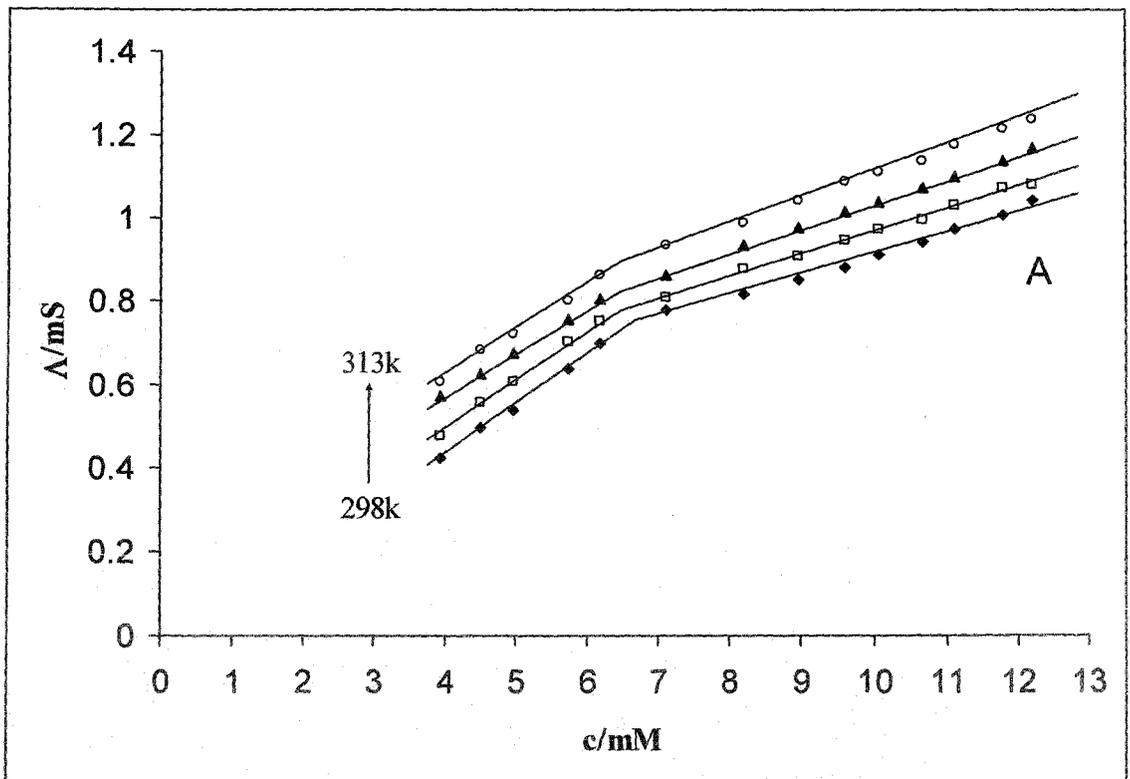


Figure 3.37: Variation of conductance, Λ , with concentration of SDS having different proportion of ethanol (A: 1.0M ethanol; B: 1.4M ethanol)

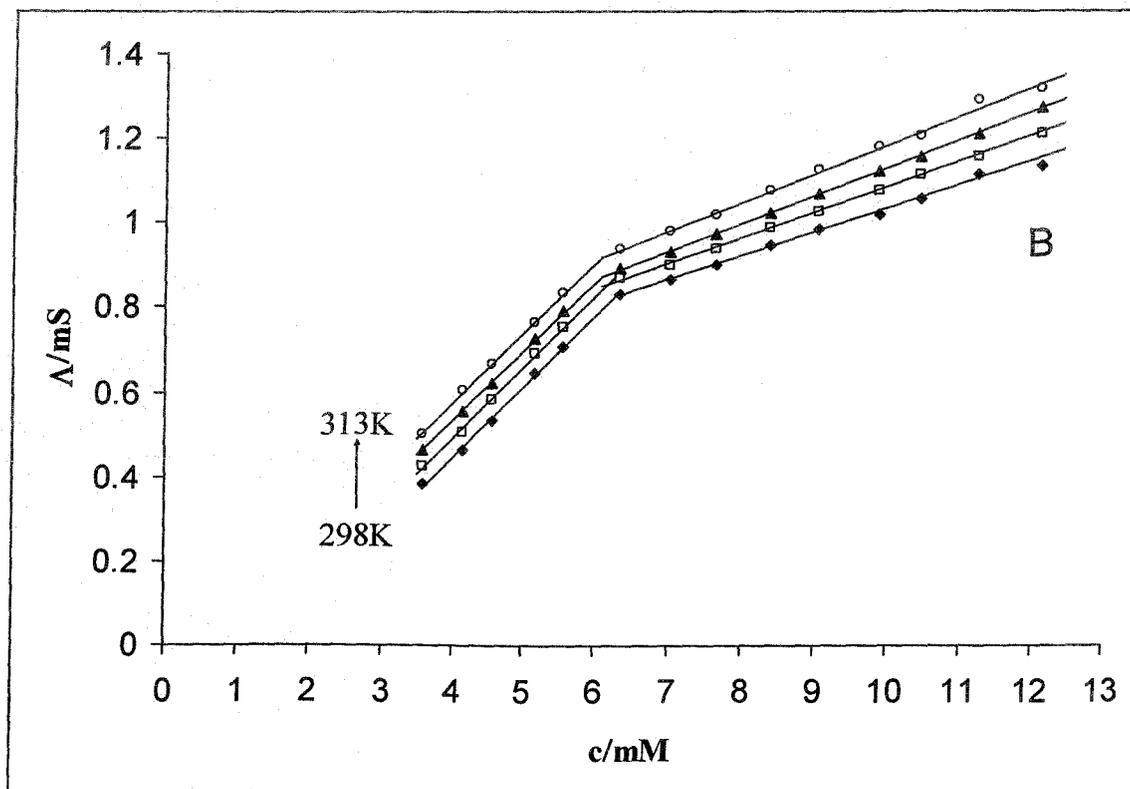
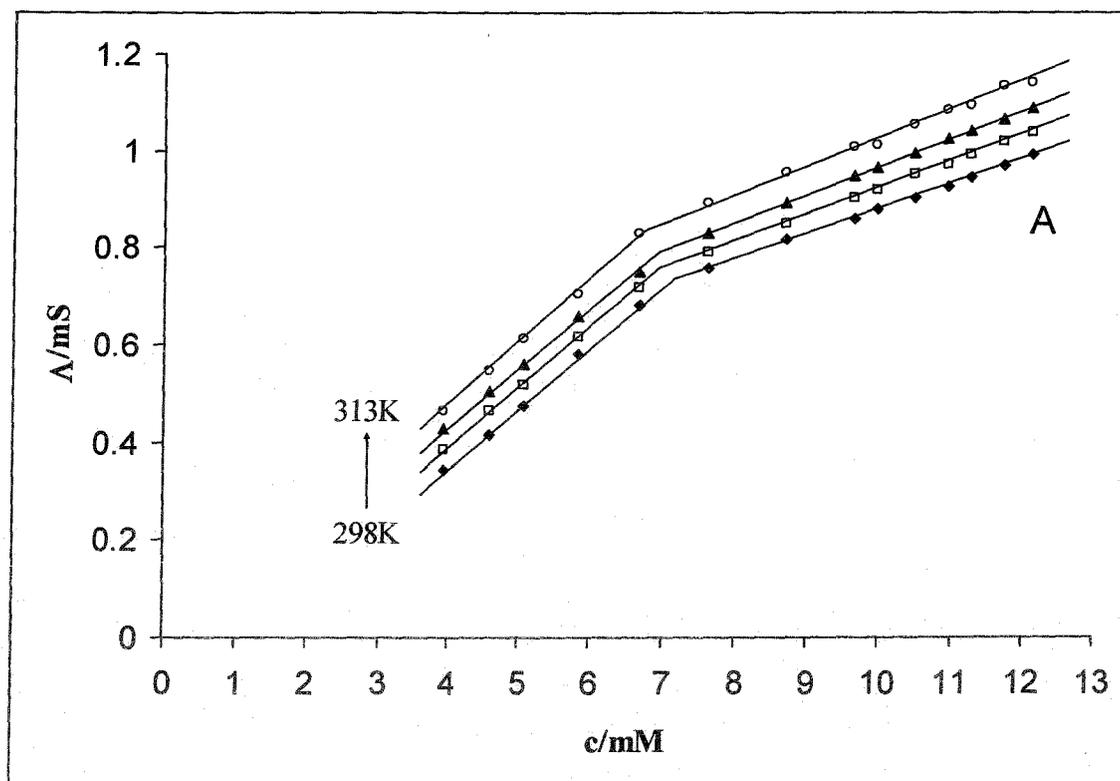


Figure 3.38: Variation of conductance, Δ , with concentration of SDS having different proportion of 1-propanol (A: 0.2M 1-propanol; B: 0.4M 1-propanol)

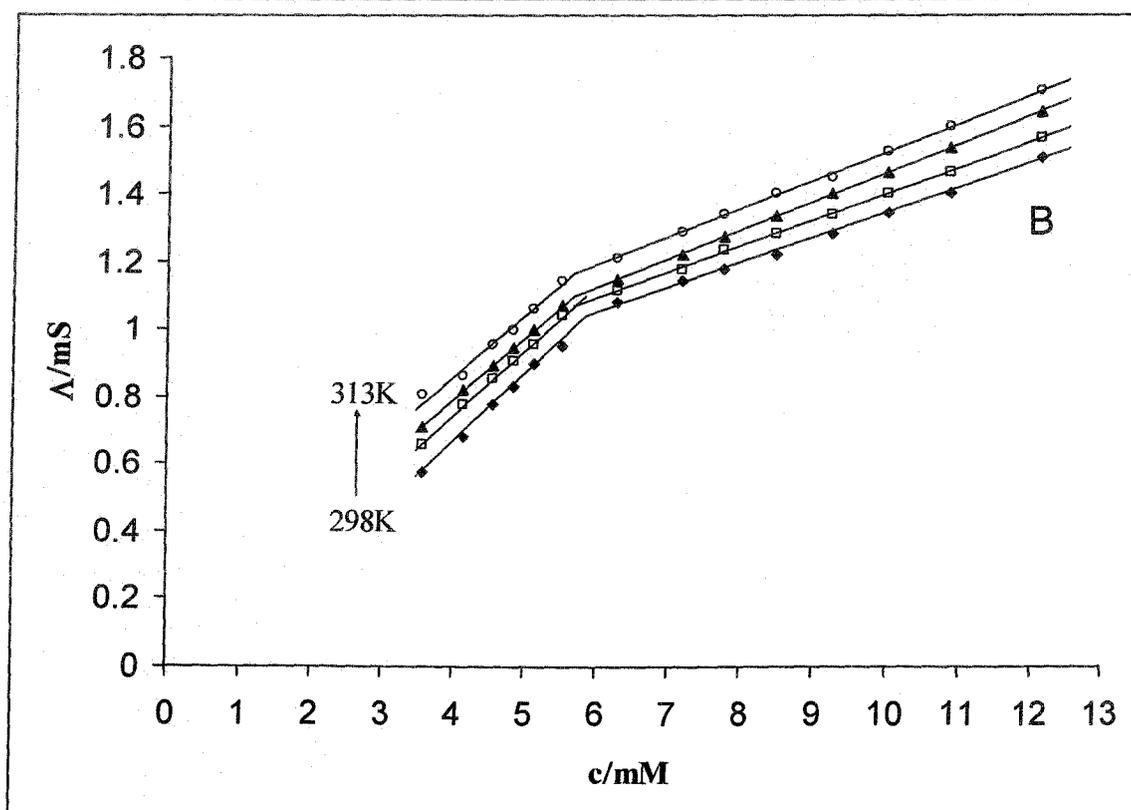
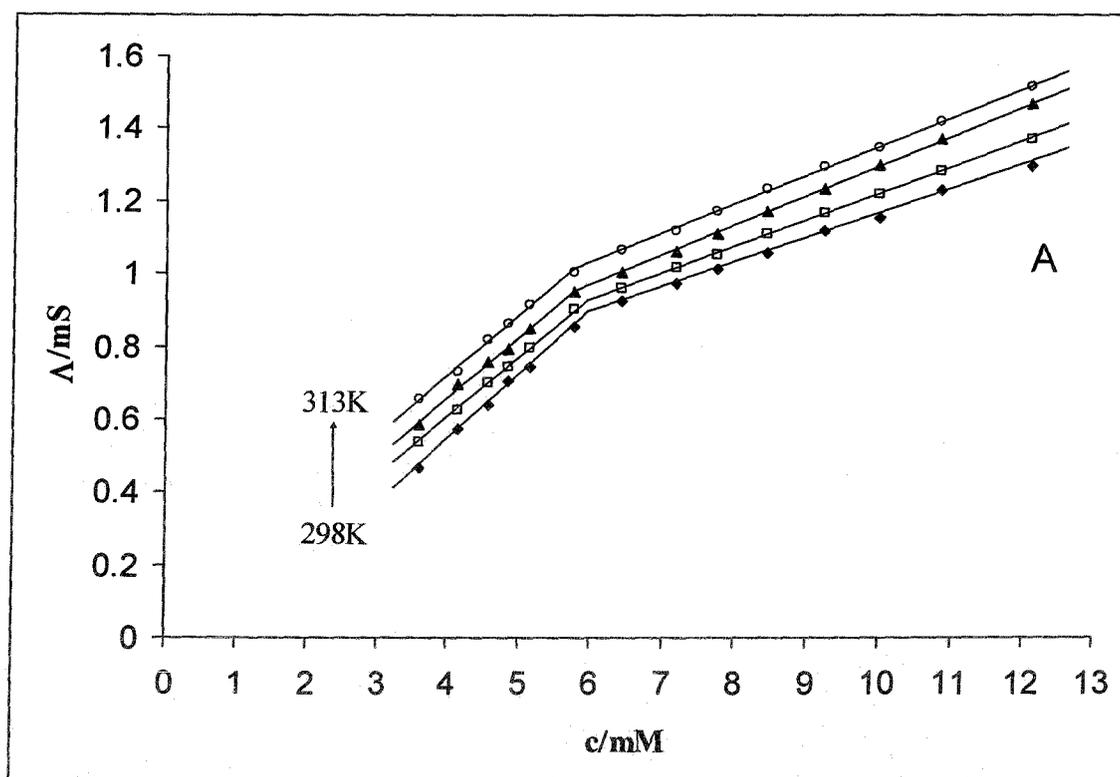


Figure 3.39: Variation of conductance, Δ , with concentration of SDS having different proportion of 1-propanol (A: 0.6M 1-propanol; B: 0.8M 1-propanol)

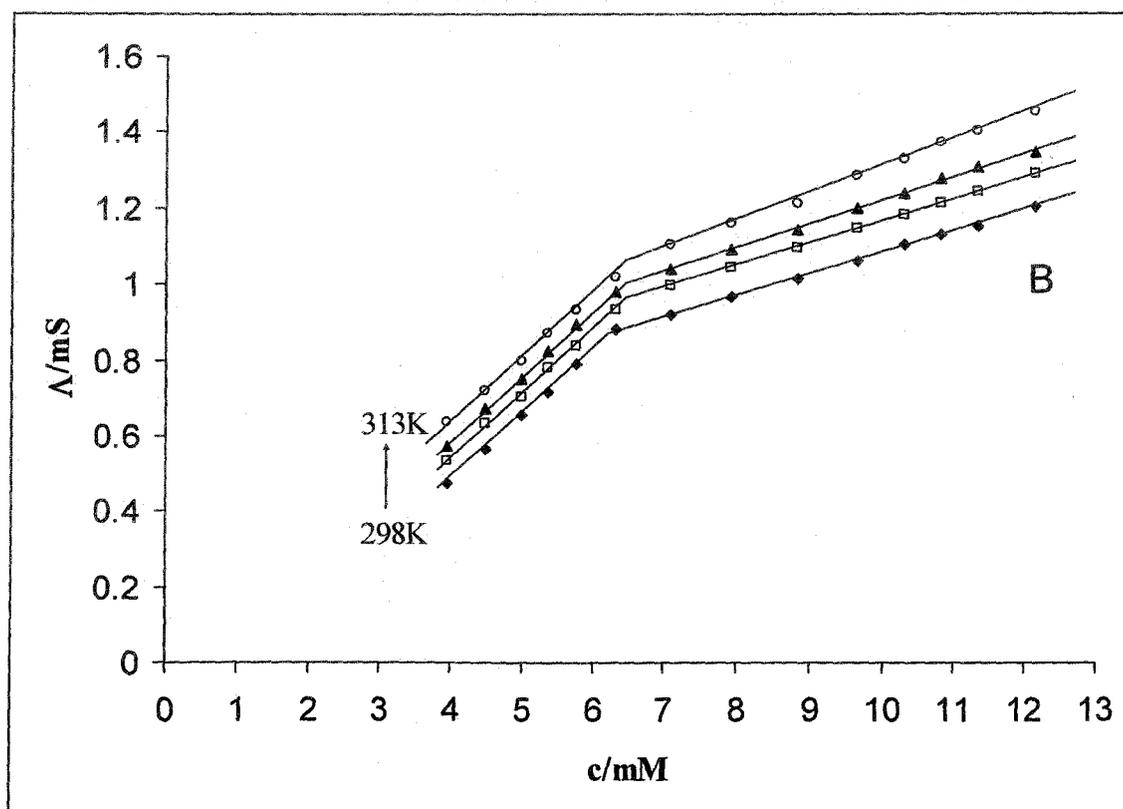
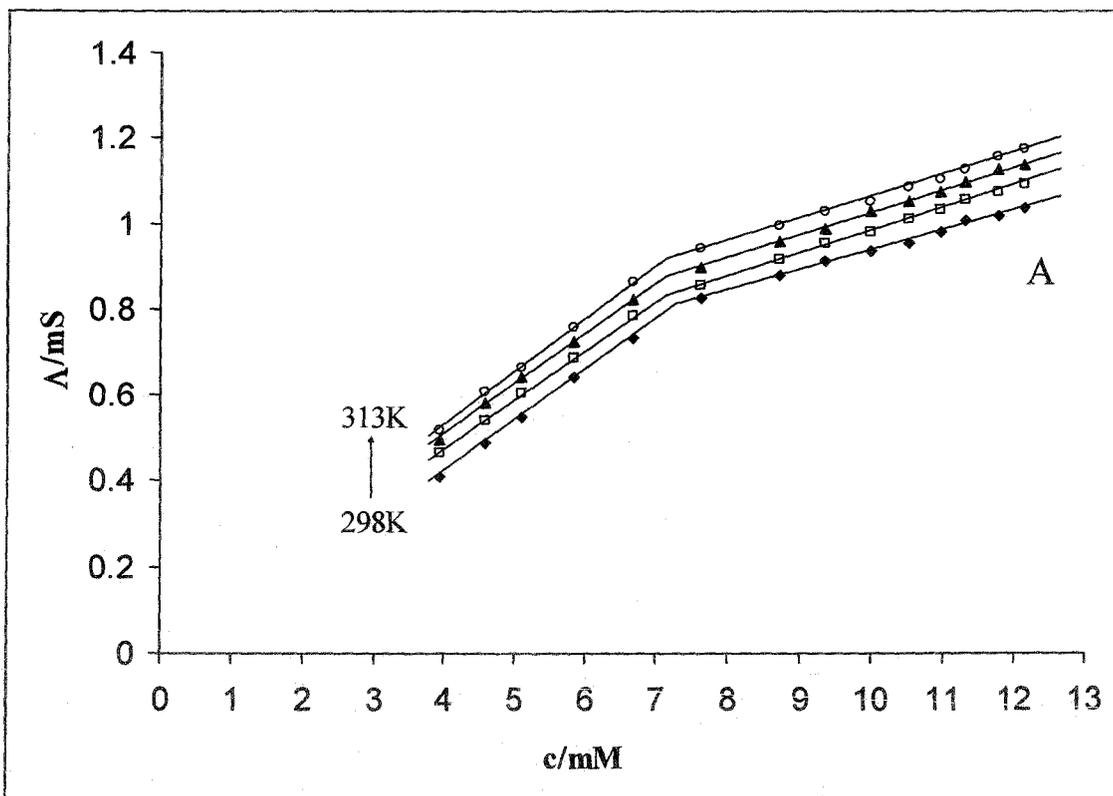


Figure 3.40: Variation of conductance, Λ , with concentration of SDS having different proportion of 2-propanol (A: 0.2M 2-Propanol; B: 0.4M 2-Propanol)

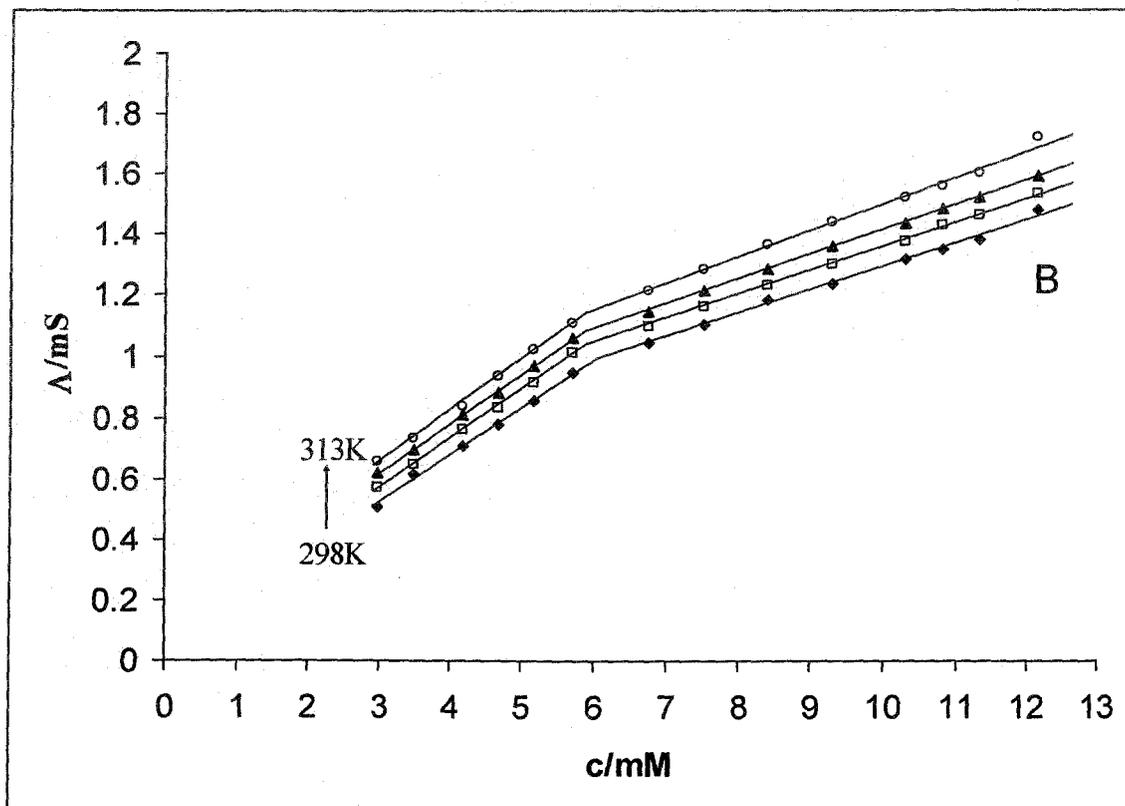
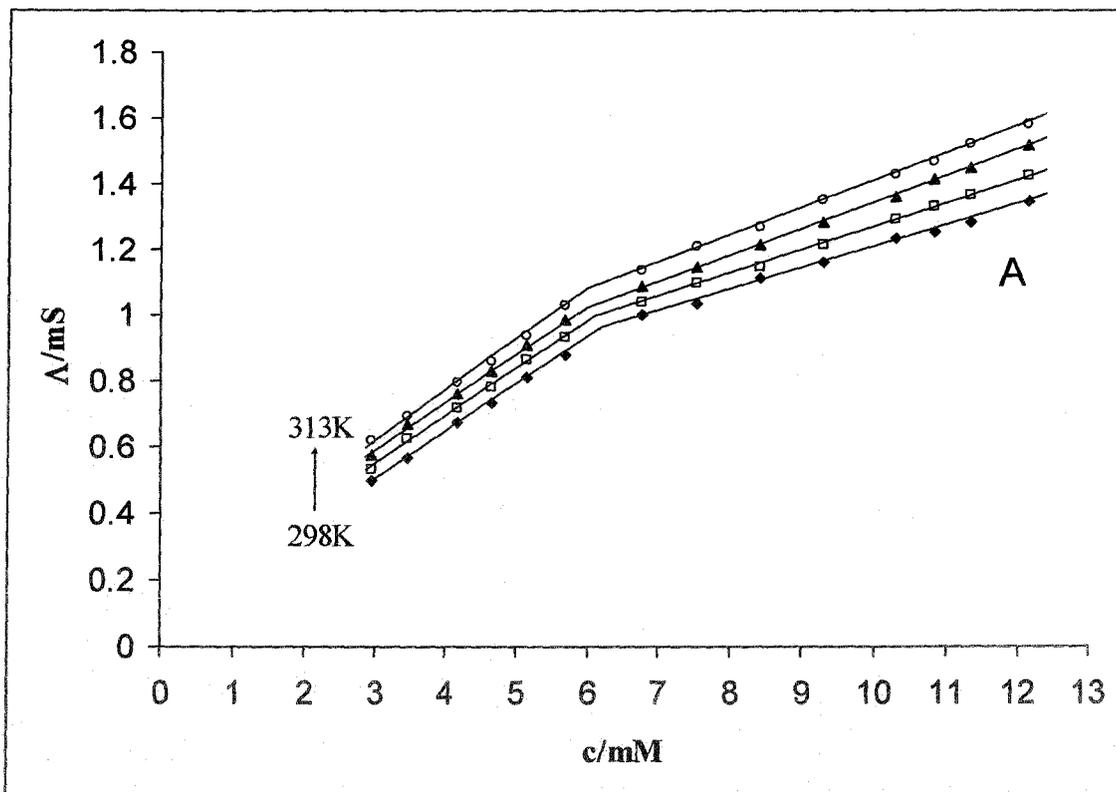


Figure 3.41: Variation of conductance, Λ , with concentration of SDS having different proportion of 2-propanol (A: 0.6M 2-Propanol; B: 0.8M 2-Propanol)

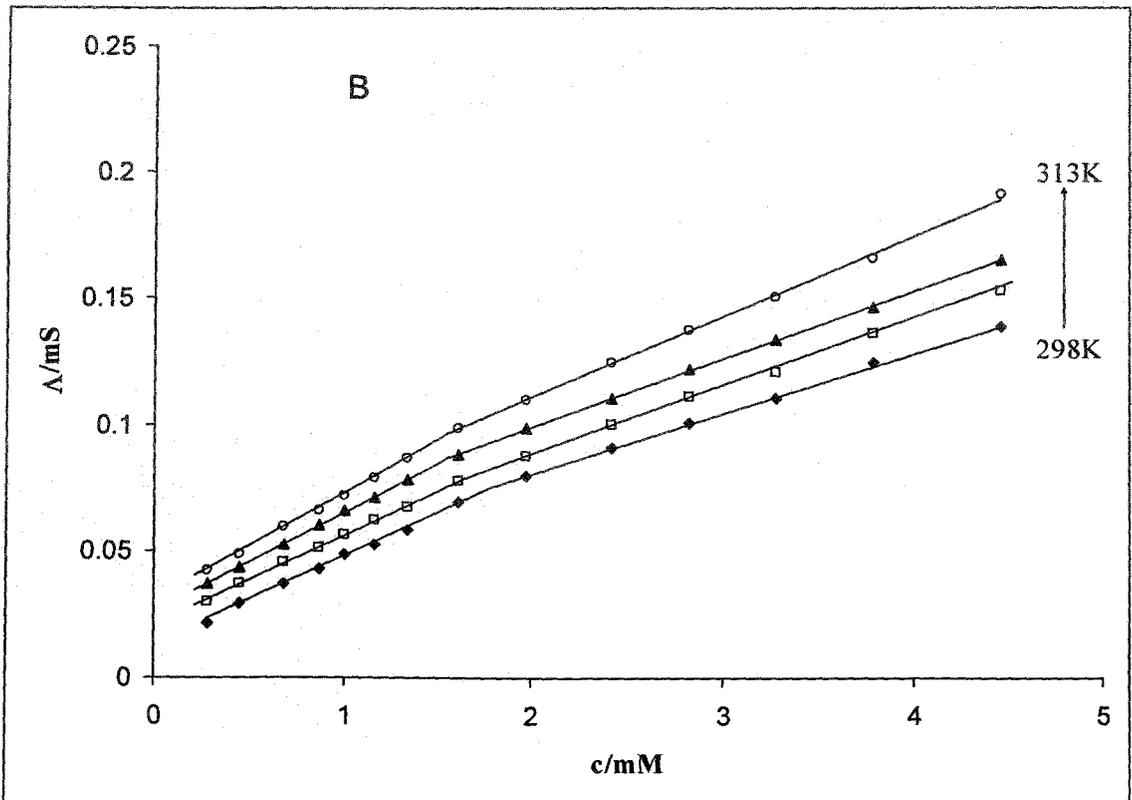
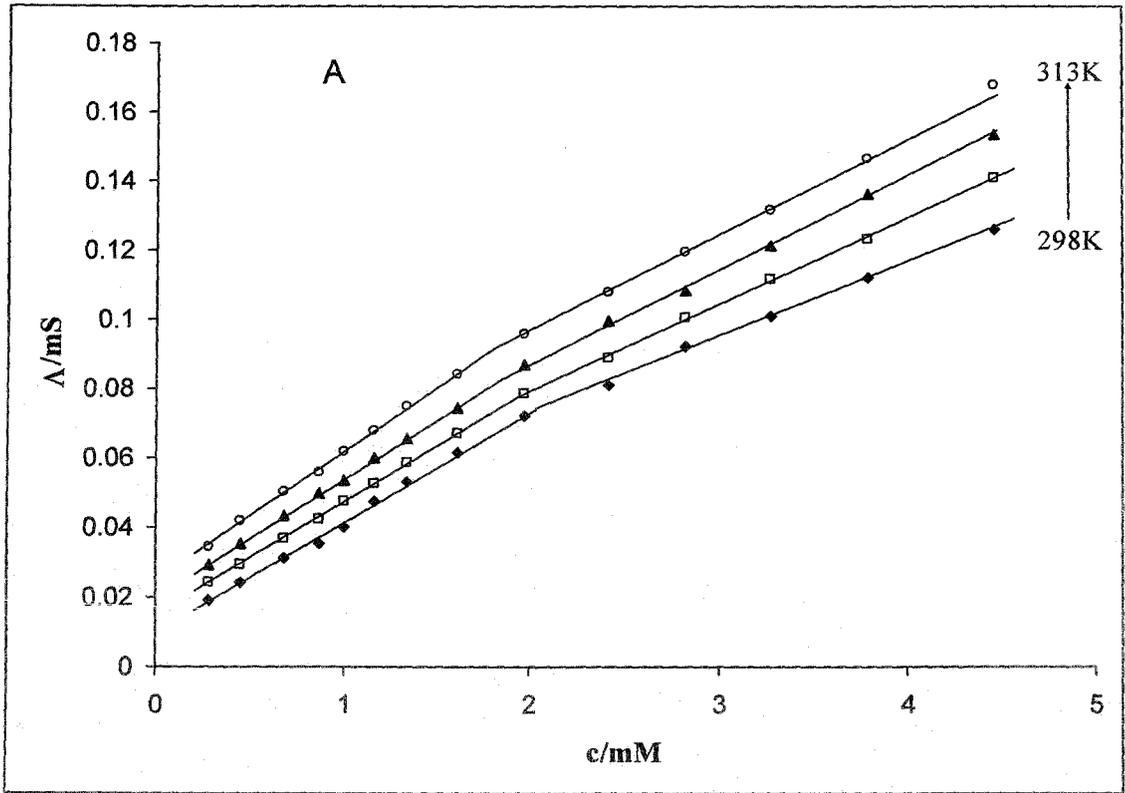


Figure 3.42: Variation of conductance, Λ , with concentration of AOT having different proportion of Ethanol (A: 0.4M Ethanol; B: 0.7M Ethanol).

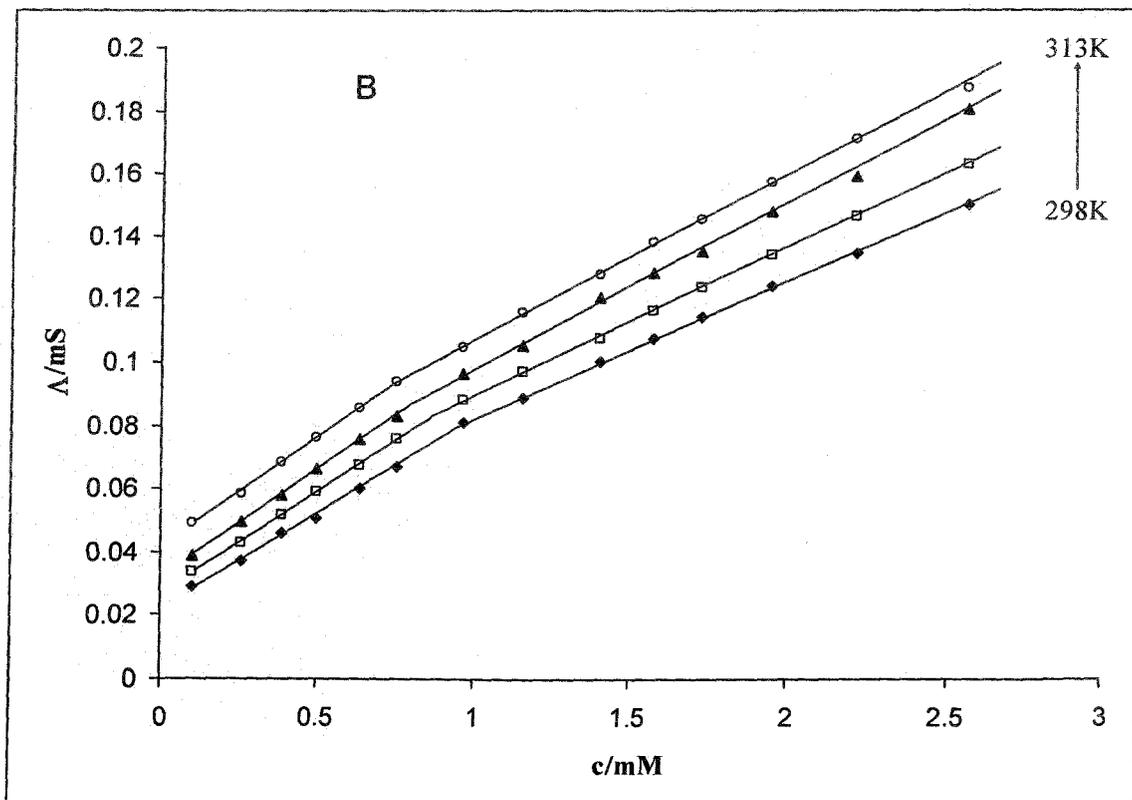
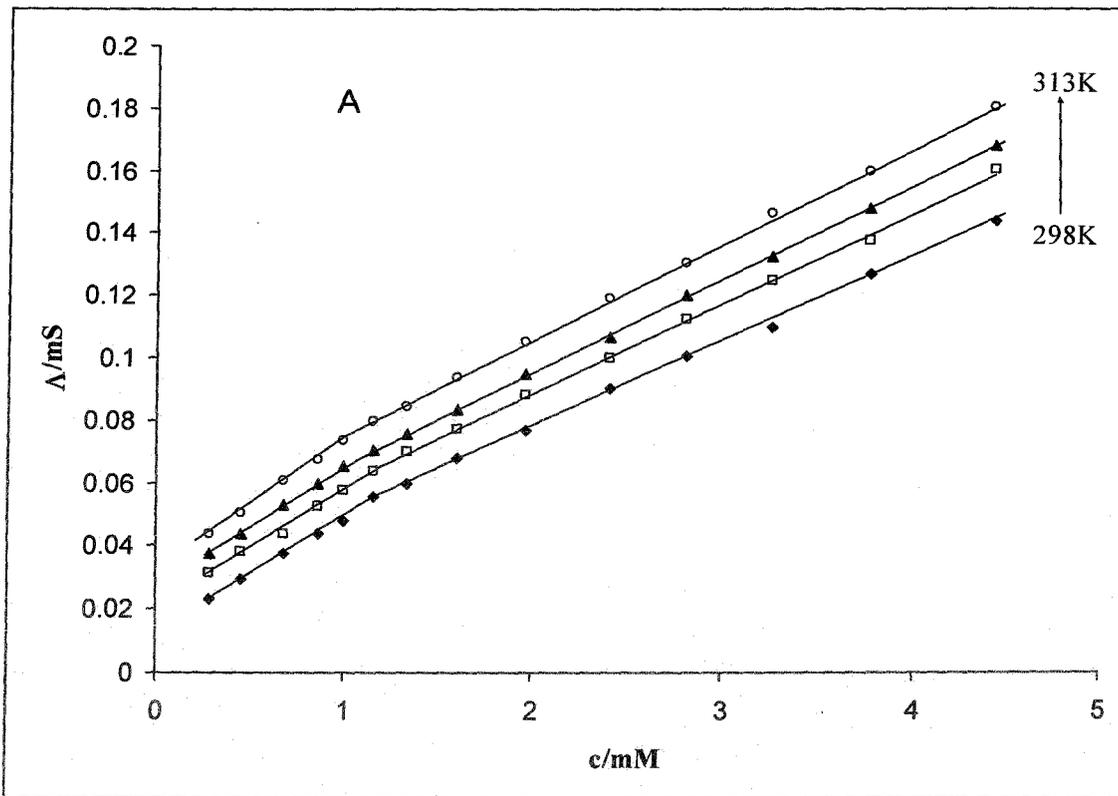


Figure 3.43: Variation of conductance, Δ , with concentration of AOT having different proportion of 1-Propanol (A: 0.6M 1-Propanol; B: 0.8M 1-Propanol).

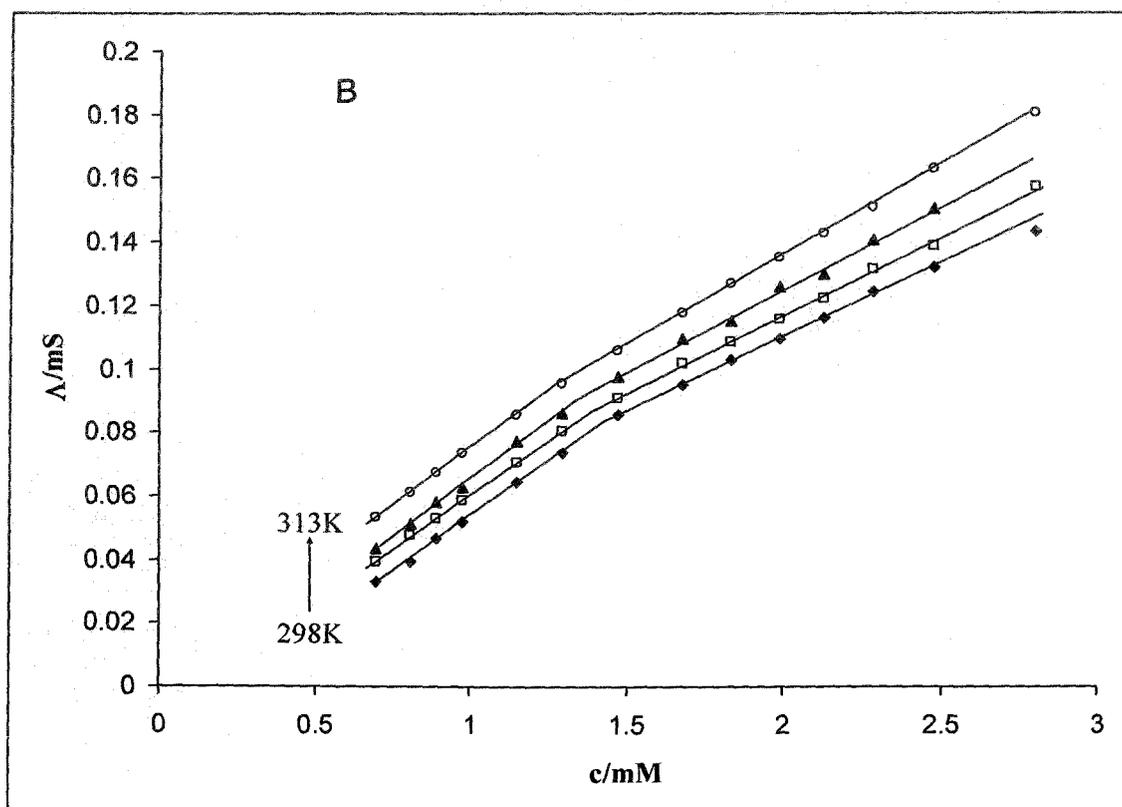
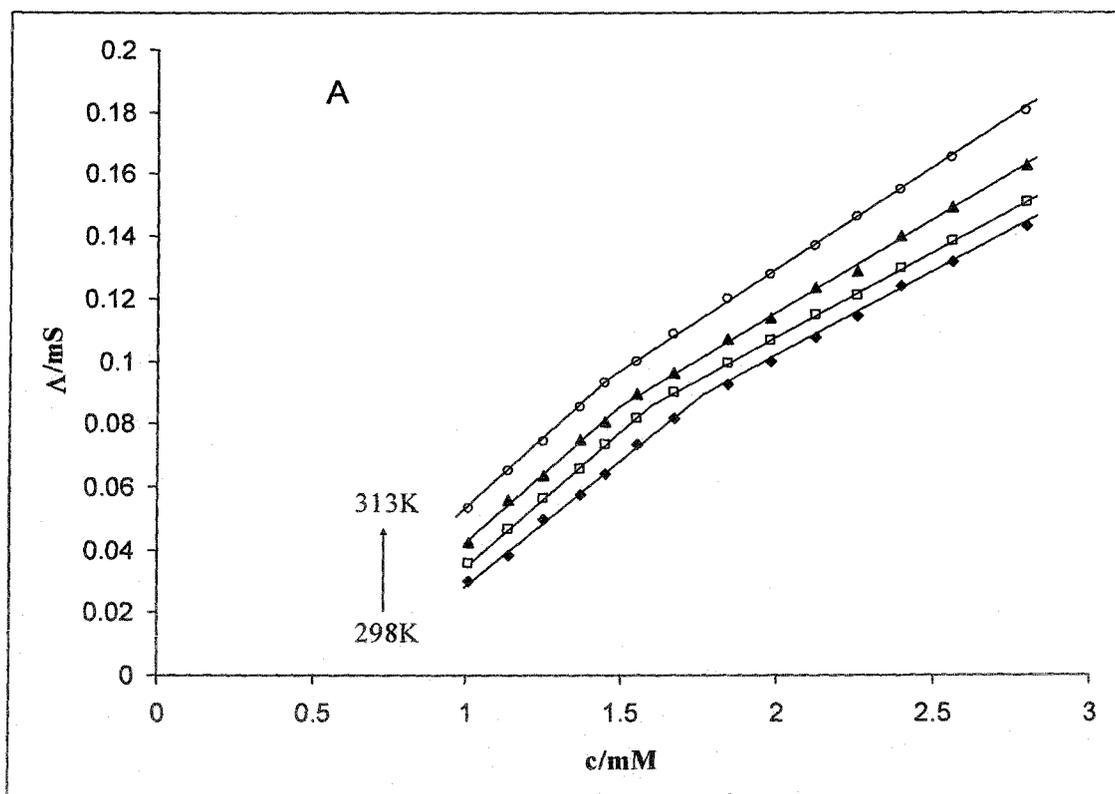


Figure 3.44: Variation of conductance, Δ , with concentration of AOT having different proportion of 2-Propanol (A: 0.2M 2-Propanol; B: 0.4M 2-Propanol).

kJmol^{-1}) contributes to the negative ΔG_m^0 ($-31.0 \sim -39.6 \text{kJmol}^{-1}$) for the micellization of SDS when compared with aqueous neat medium (Table 3.3). But for AOT this phenomenon is somehow less pronounced due to its more hydrophobic double strand molecular moiety. The effect of alcohol on the micellization process, given by ΔG_t^0 , is calculated using the following equation:

$$\Delta G_t^0 = \Delta G_{m(\text{alcohol-water})}^0 - \Delta G_{m(\text{water})}^0 \quad (3.20)$$

It may be noted that for AOT, micellization process is less favourable in water-alcohol binary mixture than SDS, which is well supported by the all positive values of ΔG_t^0 . For SDS, on the other hand, ΔG_t^0 gives both positive and negative values depending upon the temperature and the proportion of alcohols present in the solvent.

MacManus et. al. [137] showed that the position of the solubilized alcohol depends on the alkyl chain length. More hydrophobic alcohols seem to penetrate deeper into the hydrocarbon interior of the micelles than the hydrophilic ones. The solubilization of alcohol leads to a decrease in the electrostatic interaction between the surfactant head groups, and makes the surfactant molecules more energetically favorable for being a part of the micelles. Although the short-chain alcohols are highly hydrophilic, they undergo partitioning between the micellar pseudophase and the aqueous phase which can be supported by enhancement of the degree of ionization, α with addition of alcohols. The decrease of local polarity of the micelle was reported [138] upon addition of allyl alcohol may also favors micellization at the lower concentration of surfactants.

In order to quantify the solubilization or association of alcohol in the micelles, the fraction (a) of alcohol which is present in the micellar pseudophase may be expressed with self-diffusion coefficients [139]:

$$D_A = (1-a)D_A^{\text{free}} + aD_A^{\text{mic}} \quad (3.19)$$

where D_A is the measured self-diffusion coefficient of the alcohol, D_A^{free} is the self-diffusion coefficient of the free alcohol molecules, and D_A^{mic} is the self-diffusion coefficient of the alcohol molecules bound in the micelles. In solutions where the cmc is low and the concentration of the surfactant is large compared to the cmc, the D_A^{mic} may be considered equal to the measured self-diffusion coefficient of the surfactant.

Table 3.10
Micellization parameters of SDS having different proportion of alcohols

Alcohol /(mol dm ⁻³)	T/(K)	cmc /(mol dm ⁻³ ×10 ³)	α	$-\Delta G_m^\circ$ / (kJ mol ⁻¹)	$-\Delta H_m^\circ$ / (kJ mol ⁻¹)	ΔS_m° / (J K ⁻¹ mol ⁻¹)
Ethanol						
0.4	298	7.81	0.31	37.1	25.2	40.0
	303	7.21	0.32	37.9	31.0	22.8
	308	6.90	0.33	38.5	35.1	11.0
	313	6.85	0.32	39.4	32.1	23.3
0.7	298	7.03	0.43	34.9	23.4	38.6
	303	6.90	0.45	35.1	28.6	21.5
	308	6.82	0.44	36.0	34.7	0.4
	313	6.79	0.47	35.9	34.1	0.6
1.0	298	6.66	0.52	33.1	22.1	36.9
	303	6.56	0.55	33.0	26.8	20.5
	308	6.49	0.56	33.4	31.5	6.2
	313	6.48	0.60	33.0	31.8	3.8
1.4	298	6.40	0.62	31.0	20.6	34.9
	303	6.34	0.63	31.3	25.3	19.8
	308	6.29	0.62	32.1	30.7	4.5
	313	6.21	0.64	32.2	31.0	3.8
1-Propanol						
0.2	298	7.22	0.33	37.0	24.9	40.6
	303	7.02	0.35	37.3	30.5	22.4
	308	6.90	0.37	37.5	36.2	4.2
	313	6.78	0.36	38.5	37.4	3.5
0.4	298	6.34	0.37	36.7	23.4	44.6
	303	6.21	0.39	36.9	28.6	27.4
	308	6.17	0.41	37.1	34.7	7.8
	313	6.17	0.41	37.7	34.9	8.9
0.6	298	6.01	0.43	35.5	23.4	40.6
	303	5.95	0.45	35.7	28.6	23.4
	308	5.81	0.44	36.6	34.7	6.2
	313	5.80	0.47	36.5	35.0	4.8
0.8	298	5.88	0.48	34.5	22.7	39.6
	303	5.76	0.48	35.1	28.1	23.1
	308	5.68	0.51	35.1	33.1	6.5
	313	5.65	0.47	36.6	34.0	8.3
2-Propanol						
0.2	298	7.30	0.29	37.9	25.5	41.6
	303	7.22	0.31	38.1	31.2	22.8
	308	7.16	0.33	38.3	37.1	3.9
	313	7.16	0.30	39.6	38.2	4.5
0.4	298	6.62	0.33	37.3	24.9	41.6
	303	6.55	0.32	38.4	31.0	24.4
	308	6.50	0.34	38.5	36.9	5.2
	313	6.47	0.37	38.4	37.1	4.1
0.6	298	6.21	0.37	36.7	24.3	41.6
	303	6.17	0.38	37.2	29.9	24.1
	308	6.11	0.41	37.1	35.4	5.5
	313	6.05	0.40	38.0	37.0	3.2
0.8	298	6.03	0.41	36.0	23.7	41.3
	303	5.94	0.42	36.4	29.2	23.8
	308	5.92	0.45	36.3	34.5	5.8
	313	5.88	0.46	36.7	35.1	5.1

Table 3.11
Micellization parameters of AOT having different proportion of alcohols

Alcohol /(mol dm ⁻³)	T/(K)	cmc /(mol dm ⁻³ ×10 ³)	α	$-\Delta G_m^\circ$ / (kJ mol ⁻¹)	$-\Delta H_m^\circ$ / (kJ mol ⁻¹)	ΔS_m° / (J K ⁻¹ mol ⁻¹)
Ethanol						
0.4	298	2.03	0.67	33.7	19.8	46.4
	303	1.95	0.70	32.2	24.0	27.1
	308	1.83	0.72	32.4	28.5	12.8
	313	1.80	0.71	33.2	31.5	5.4
0.7	298	1.78	0.72	32.8	19.1	46.1
	303	1.63	0.72	33.7	23.6	33.0
	308	1.56	0.73	34.1	28.2	18.9
	313	1.56	0.74	34.4	33.0	4.2
1.0	298	1.41	0.75	32.8	18.6	47.4
	303	1.34	0.73	34.0	23.5	34.8
	308	1.30	0.75	34.1	27.8	20.5
	313	1.20	0.74	35.2	33.0	6.9
1.4	298	1.01	0.76	33.5	18.5	50.5
	303	1.00	0.79	33.3	22.3	36.1
	308	0.92	0.77	34.7	27.3	23.7
	313	0.88	0.80	34.5	31.5	9.7
1-Propanol						
0.2	298	1.78	0.70	33.3	19.4	46.8
	303	1.66	0.72	33.6	23.6	32.8
	308	1.53	0.72	34.4	28.5	19.3
	313	1.52	0.71	35.3	33.8	4.6
0.4	298	1.50	0.73	33.1	18.9	47.5
	303	1.51	0.73	33.6	23.4	33.6
	308	1.39	0.72	34.7	28.5	20.3
	313	1.35	0.74	34.8	33.0	5.7
0.6	298	1.23	0.74	33.5	18.8	49.2
	303	1.20	0.73	34.4	23.5	36.0
	308	1.09	0.75	34.7	27.8	22.4
	313	1.01	0.75	35.5	32.8	8.7
0.8	298	0.94	0.75	34.0	18.6	51.6
	303	0.88	0.75	34.8	23.1	38.7
	308	0.80	0.77	35.1	27.4	25.2
	313	0.73	0.77	36.0	32.2	11.9
2-Propanol						
0.2	298	1.77	0.69	33.6	19.5	47.2
	303	1.60	0.70	34.2	24.0	33.7
	308	1.50	0.72	34.5	28.5	19.5
	313	1.47	0.72	35.1	33.6	4.9
0.4	298	1.43	0.72	33.5	19.1	48.4
	303	1.38	0.73	33.9	23.5	34.5
	308	1.35	0.73	34.6	28.4	20.5
	313	1.25	0.74	35.1	33.0	6.5
0.6	298	1.15	0.73	33.9	18.9	50.3
	303	1.07	0.73	34.7	23.4	37.2
	308	0.99	0.75	35.0	27.8	23.4
	313	0.88	0.75	36.0	32.8	10.1
0.8	298	0.80	0.75	34.5	18.6	53.3
	303	0.77	0.77	34.7	22.7	39.4
	308	0.69	0.76	35.9	27.6	26.9
	313	0.70	0.77	36.1	32.2	12.3

Table 3.12
Effect of alcohol on micellization

SDS			AOT		
Alcohol /(mol dm ⁻³)	T/(K)	ΔG_t^0	Alcohol (mol dm ⁻³)	T/(K)	ΔG_t^0
Ethanol					
0.4	298	0.3	0.4	298	1.6
	303	1.4		303	-1.3
	308	0.8		308	-1.2
	313	1.6		313	-1.0
0.7	298	-1.9	0.7	298	0.7
	303	-1.4		303	0.2
	308	-1.7		308	0.5
	313	-1.9		313	0.2
1.0	298	-3.7	1.0	298	0.7
	303	-3.5		303	0.5
	308	-4.3		308	0.5
	313	-4.8		313	1.0
1.4	298	-5.8	1.4	298	1.4
	303	-5.2		303	-0.2
	308	-5.6		308	1.1
	313	-5.6		313	0.3
1-Propanol					
0.2	298	0.2	0.2	298	1.2
	303	0.8		303	0.1
	308	-0.2		308	0.8
	313	0.7		313	1.1
0.4	298	-0.1	0.4	298	1.0
	303	0.4		303	0.1
	308	-0.6		308	1.1
	313	-0.1		313	0.6
0.6	298	-1.3	0.6	298	1.4
	303	-0.8		303	0.9
	308	-1.1		308	1.1
	313	-1.3		313	1.3
0.8	298	-2.3	0.8	298	1.9
	303	-1.4		303	1.3
	308	-2.6		308	1.5
	313	-1.2		313	1.8
2-Propanol					
0.2	298	1.1	0.2	298	1.5
	303	1.6		303	0.7
	308	0.6		308	0.9
	313	1.8		313	0.9
0.4	298	0.5	0.4	298	1.4
	303	1.9		303	0.4
	308	0.8		308	1.0
	313	0.6		313	0.9
0.6	298	-0.1	0.6	298	1.8
	303	0.7		303	1.2
	308	-0.6		308	1.4
	313	0.2		313	1.8
0.8	298	-0.8	0.8	298	2.4
	303	-0.1		303	1.2
	308	-1.4		308	2.3
	313	-1.1		313	1.9

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