Chapter IV

Aggregation behaviour of dodecyl benzene sulfonate in presence of symmetrical bromide salts and ethylene glycol

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4.1. Dodecyl Benzene Sulfonate in presence of Symmetrical Bromide Salts

4.1.1. Introduction and Review of Previous Works

The self-assembly of surfactants in water into micelles is a widely studied phenomenon. These micellar systems have immense technological applications such as flow field regulators, solubilising and emulsifying agents, membrane mimetic media, nanoreactors, to name a few [1-4]. Altering or modifying important physicochemical properties of aqueous surfactant solutions is highly desirable as far as potential applications of such systems are concerned. One way to alter/modify the physicochemical properties of a given aqueous surfactant solution is to use of the external means, such as changes in temperature/pressure and/or addition of a variety of modifiers like cosolvents, cosurfactants, electrolytes and polar organics [1-12].

Added electrolytes are known to affect the aggregation behaviour of ionic surfactants. Micellization, which is a manifestation of both hydrophobic and hydrophilic effects, is likely to undergo a significant change in the presence of such additives. It has been generally observed that the addition of electrolytes, with both organic and inorganic counterions, to aqueous ionic micellar solutions increases the solubilization power of surfactant micelles [7,13]. It is thus not surprising that the effect of different kinds of electrolytes, with either organic or inorganic counterions, on the cmc, aggregation number, micellar shape and the solubilization power of aqueous aggregates have been examined in detail. The cmc value can serve as a measure of micelle stability in a given state and the thermodynamics of micellization can be determined from the study of the temperature dependence of the cmc of a surfactant system. In addition, the changes in hydration energies and specific interactions with counterions may also be important [14-18]. 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, its shape, and the compactness of its electrical double layer show some kind of dependency [17]. Even the molecular conformation of some dimeric surfactants (known as Gemini surfactants) affects the micellization to a large extent [18]. 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^0_{mic}, the enthalpy, ΔH^0_{mic}, and the entropy, ΔS^0_{mic}, is generated 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 achieve satisfactory values of ΔH^0_{mic}.

Among available techniques for studying surfactant aggregation, for example, conductivity, surface tension, NMR and calorimetry has a distinct advantage, for it is possible to calculate both the cmc and ΔH^0_{mic} directly from the experimental data. Additionally, the calculated enthalpy and entropy characterize 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 [19]. 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 as has already been mentioned [20]. Also phase separation on heating is a general phenomenon that has been investigated in great detail in the context of non-ionic surfactants which is not included in our present study [21-23]. Ionic surfactant solutions are complex in nature. Since the micelles are charged, there must be an electrostatic repulsion between the micelles in addition to the van der Waals attraction force.

Over the years a considerable amount of literature on anionic surfactant-electrolyte system has been compiled, majority of which involved sodium dodecyl sulfate (SDS) as the surfactant and NaCl as the electrolyte. However, in recent years, attention has been focused on the interactions of other surfactants with hydrophobic counterions and to this effect in many studies [7,16,24-32]. The alkali metal ions are heavily hydrated in aqueous solution and hence cannot approach to close proximity of the highly charged micellar surface [33,34]. These ions are, therefore, less effective in screening the charge on the micellar heads. Unlike the alkali metal halides the tetramethyl ammonium ion (TAA^+) ions are weakly hydrated in aqueous solution as the positive charge is supposed to be wrapped in the paraffin shell and are thus hydrophobic in nature [24]. Therefore, the TAA^+ ions, in addition to the electrostatic interaction, can interact hydrophobically with the anionic head groups of the micelle as well. This is clearly evident from the previous study where it has been shown that micelles of sodium dodecylbenzene sulfonate interact more strongly with the TAA^+ ions than with the alkali metal ions [35].

In the present study, the surfactant chosen is again dodecyl benzene sulfonate (DBS) with different counterions, viz., Na^+, Li^+, K^+, NH_4^+, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$ and $(C_4H_9)_4N^+$ and the electrolytes are the symmetrical bromides and tetra alkyl bromides. The NH_4^+ ion, in terms of size, is in fact an ion that stands between the largest common alkali metal ion Cs^+ and the smallest tetraalkyl ammonium ion, viz., TMA^+ [36]. All the TAA^+ ions are fairly surface active, while TPA^+ and TBA^+ show signs of self-aggregation in aqueous solution [37]. TBA^+ is one of the most effective additives for the occurrence of clouding in anionic surfactants. Hence the DBS with different counterions and the corresponding bromide salt systems seem to be an interesting combination in this respect as well. Present study is, therefore, undertaken on the micellization of DBS with different counter ions in aqueous bromide salt solutions mainly by surface tension measurements and also by electrical conductivity measurements. The dependence of the thermodynamic parameters of micellization of DBS with different counterions on the corresponding bromide ions has been studied. In many applications, the stability of micellar solutions at elevated temperatures is of practical importance [38,39]. Therefore, the occurrence of temperature dependent thermodynamic study has also been reported.

4.1.2. Materials and Methods

Materials

A high grade purified sample of SDBS from Across Organics (New Jersey, USA) was 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). Surfactants with the desired counterions were prepared by following the technique of Eastoe and et al. [40] and the extended work of Temsamani and et al. [41] and Benrraou and et al. [42]. The process is same as discussed in the chapter III. Sodium bromide is of AR grade (LOBA-CHEMIE INDOAUSTRANAL CO., India). Potassium bromide is of AR grade (Sigma-Aldrich Co., St. Louis, USA). Lithium bromide and the other tetraalkyl ammonium bromides were of puriss grade (Fluka, Switzerland) and were purified by standard procedures. The recrystallised salts were dried in vacuum for 12 hours before use.

Methods

Electrical conductivity measurements: The cmc values were determined from the surface tension as well as specific conductance data as discussed in chapter III, section 3.4.2.

4.1.3. Results and discussions

4.1.3.1. Critical micellization concentration (cmc)

The critical micellization concentrations of DBS with different counter ions in presence of corresponding aqueous bromide salt solutions in the concentration range of (5-0.5) mM were determined mainly by surface tension and partly also by the electrical conductivity method. (Conductivity measurement in the whole salt concentration range was not done to avoid the chance of merging surfactant conductivity data by the salt conductance at high concentration.) Figure 4.1-4.48 shows the plot of surface tension value (γ) with logarithm of the concentration of the surfactant solution in presence of varying concentrations of same bromide salt as that of the counter ion and figure 4.49 - 4.56 also shows the plot of experimental values of conductivity (κ) as a function of DBS concentration with different counter ions. From these figures, a substantial decrease in the cmc of DBS with all counterions with increasing concentration of bromide salt is apparent.

Increasing the concentration of a particular electrolyte causes a substantial decrease in the cmc. This can be accounted for by the fact that in solutions of high ionic strength, the forces of electrostatic repulsion between head groups in a micelle are considerably reduced due to charge screening. The charge screening increases the attractive force between the micellar head and the positive counterion of the electrolyte making the so-called Stern layer more densely packed, thus promoting micelle formation to be more facile. Such reduction in the cmc values of anionic surfactants is also observed in presence of all systems with corresponding bromide electrolytes. However, as has already been mentioned, due to the greater hydration in aqueous solutions, these ions cannot approach the oppositely charged micellar heads to a great extent. For example, it has been reported that the cmc of SDS is decreased from 7.8mM to 2.3mM on the addition of 0.05M of NaCl [9], while the identical concentration of TBAB could lower the cmc to as low as 0.23mM at 298K [7]. In the present study, e.g., the cmc of ADBS in water is 2.41mM at 293.15K and is lowered to 1.82mM, 1.66mM, 1.59mM, 1.49mM, 1.40mM and 1.33mM in presence of 0.0005M, 0.001M, 0.002M, 0.003M, 0.004M and 0.005M Ammonium Bromide solution respectively at the same temperature. The cmc values of all the DBS moiety with different counterions in the presence of symmetrical bromide salts are given in Table 4.1.1 - 4.1.4. From these results one may be able to examine the role of the positive ions in modifying the aggregation properties of aqueous DBS moiety. This large decrease in cmc value probably indicates the existence of strong hydrophobic interaction between the alkyl groups of the corresponding positive ions with the hydrocarbon tails of surfactant molecules along with the strong electrostatic interaction (due to weak hydration) with the surfactant head groups.

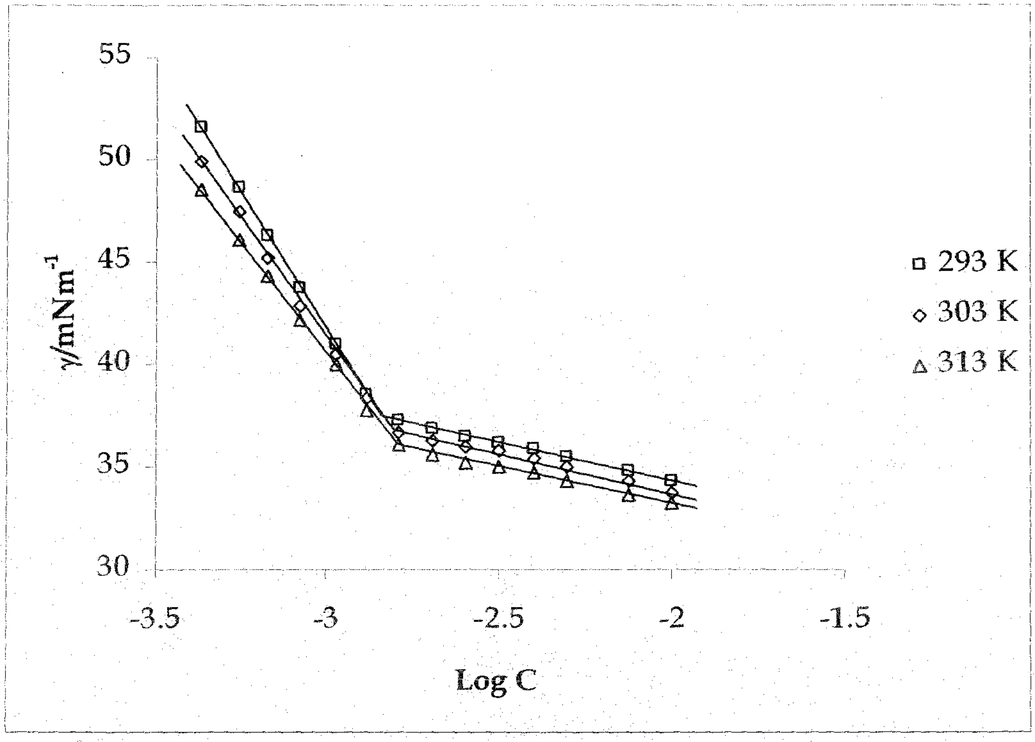

Figure 4.1: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.0005 M.

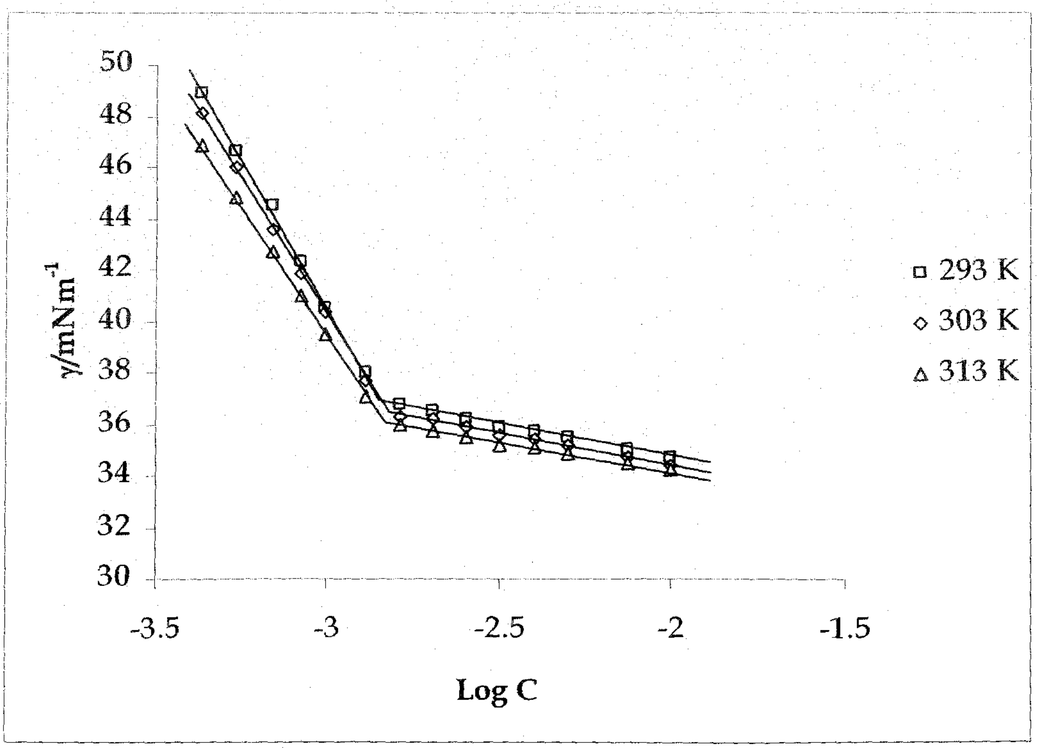

Figure 4.2: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.001 M.

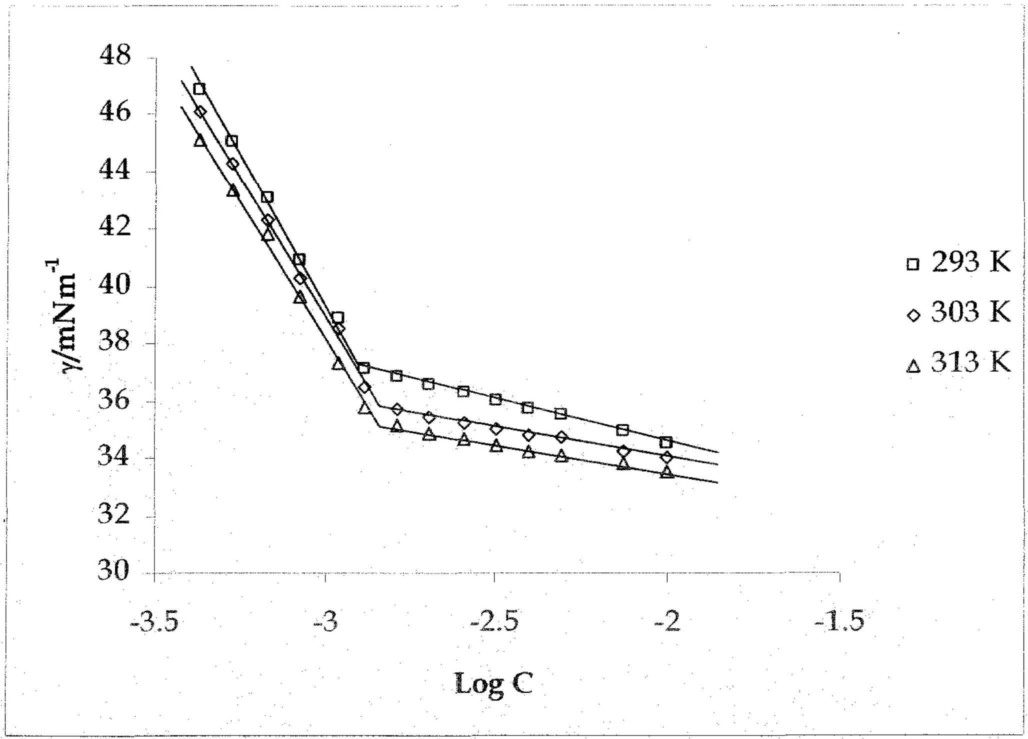

Figure 4.3: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.002 M.

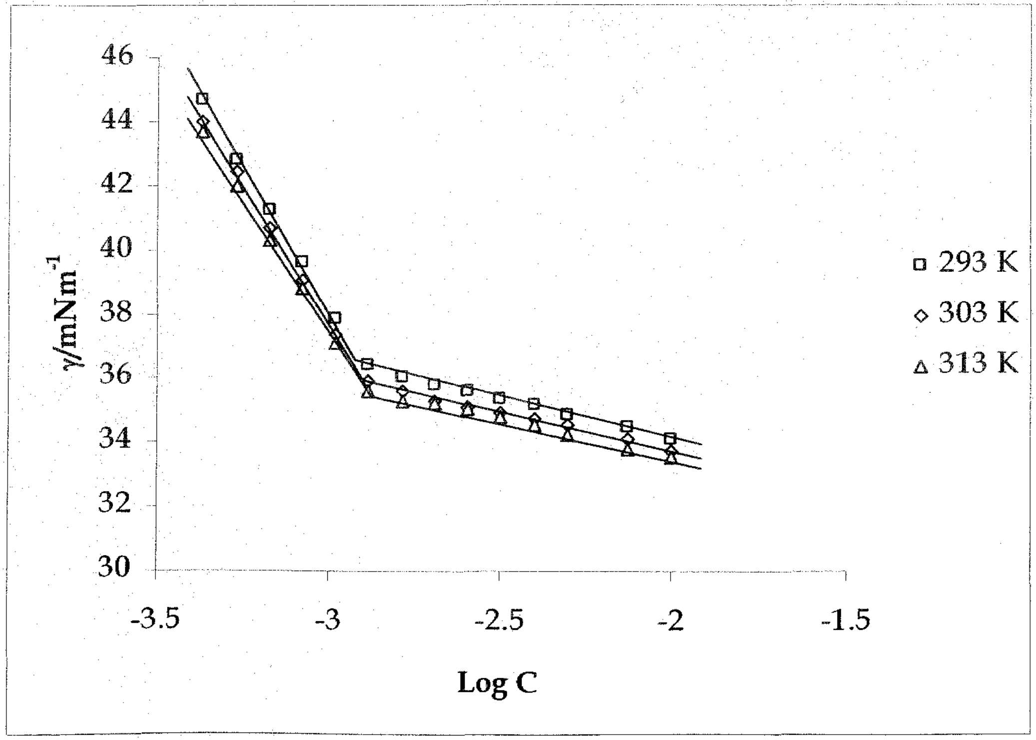

Figure 4.4: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.003 M.

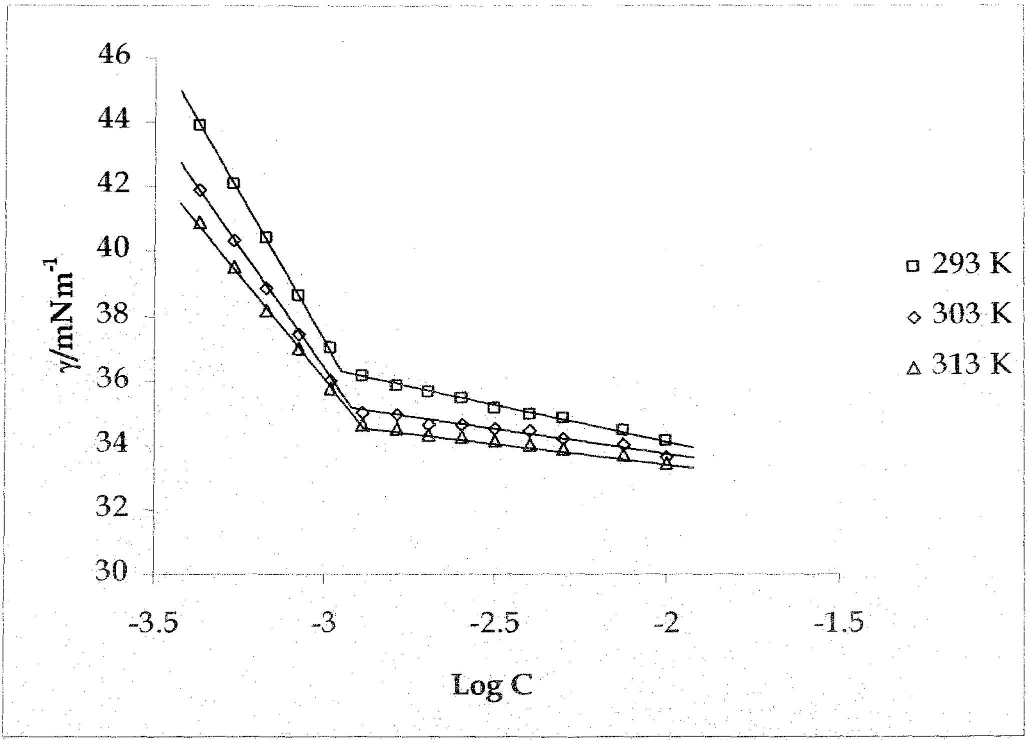

Figure 4.5: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.004 M.

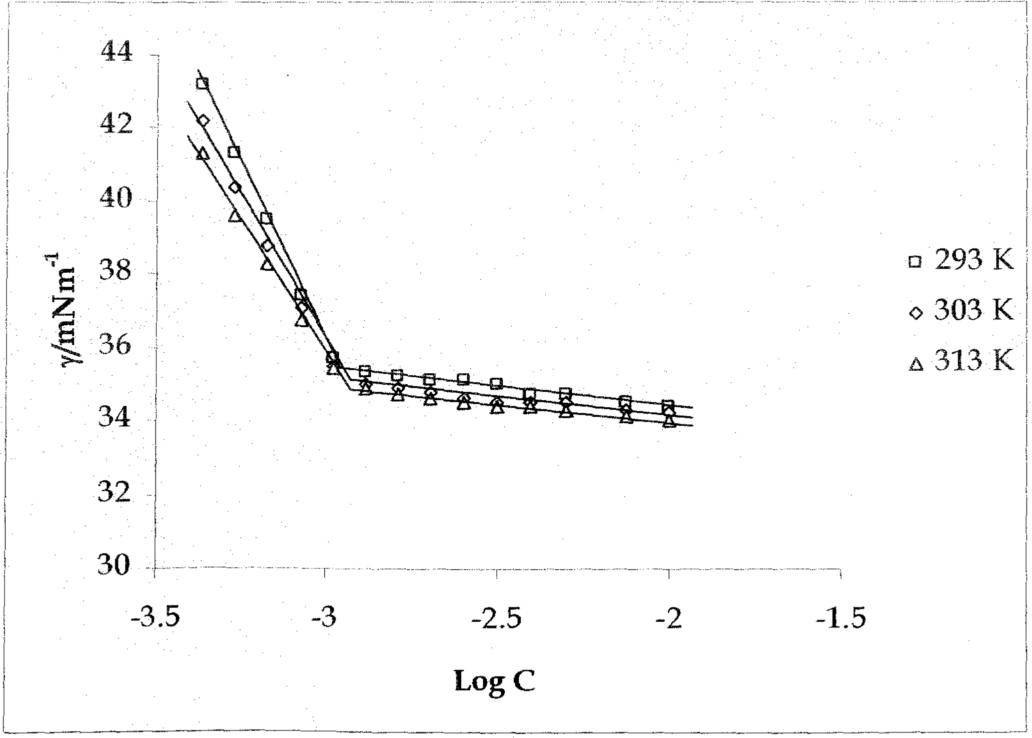

Figure 4.6: Surface Tension, γ, vs. Log C (mM) plot of SDBS in temperature range 293 – 313 K at 10 K intervals in the NaBr concentration 0.005 M.

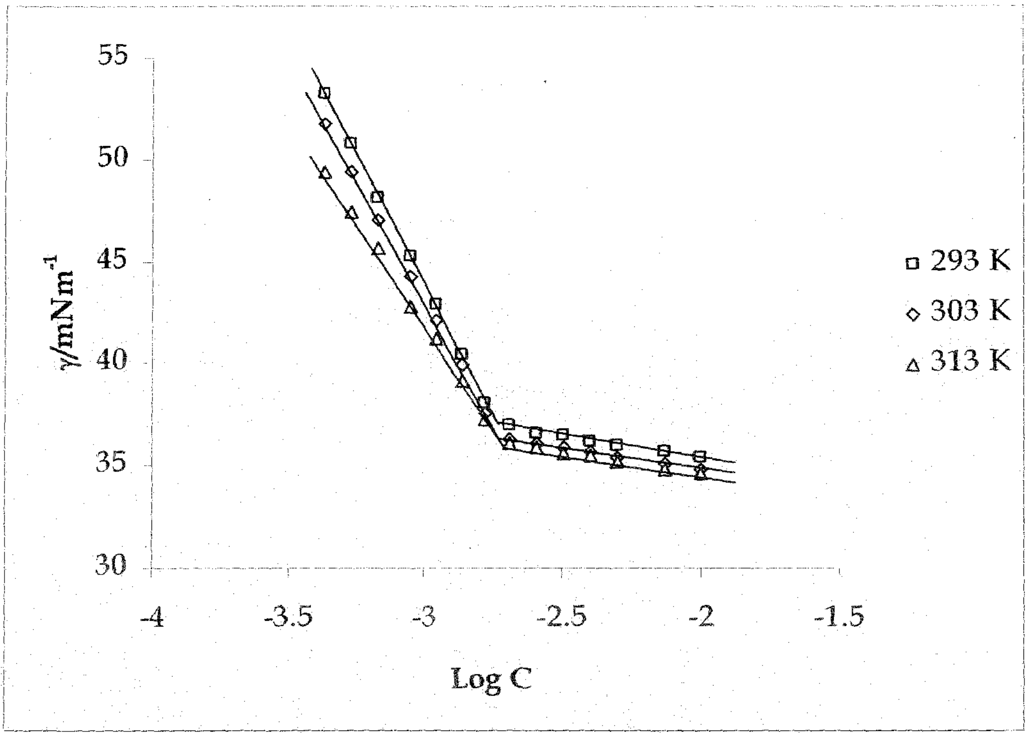

Figure 4.7: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.0005 M.

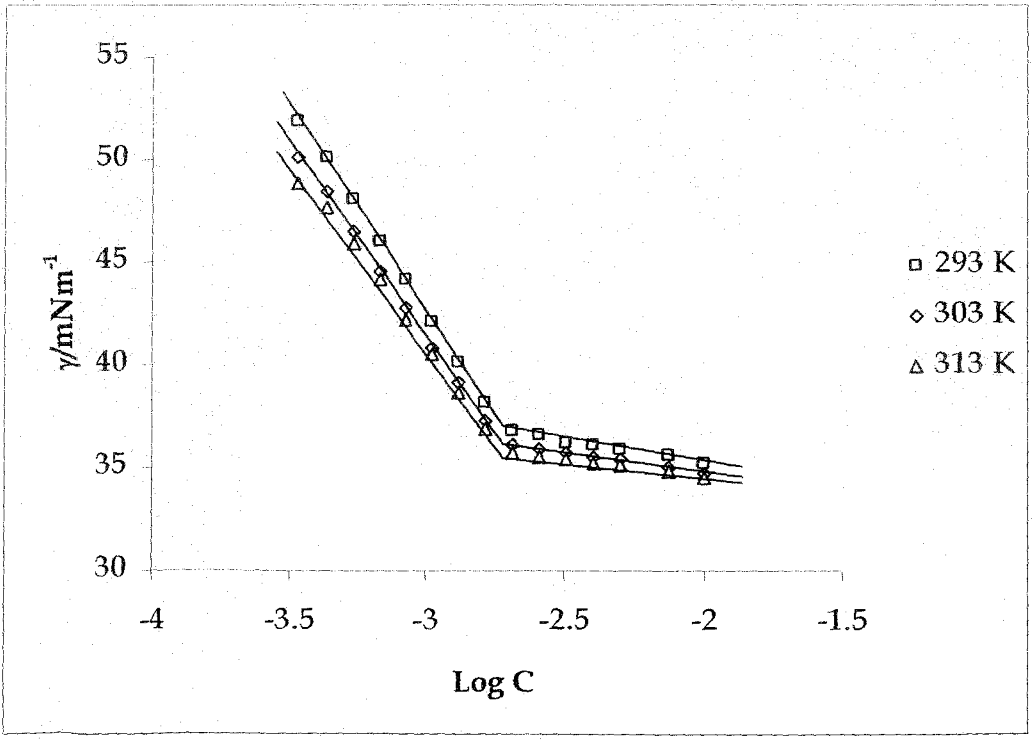

Figure 4.8: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.001 M.

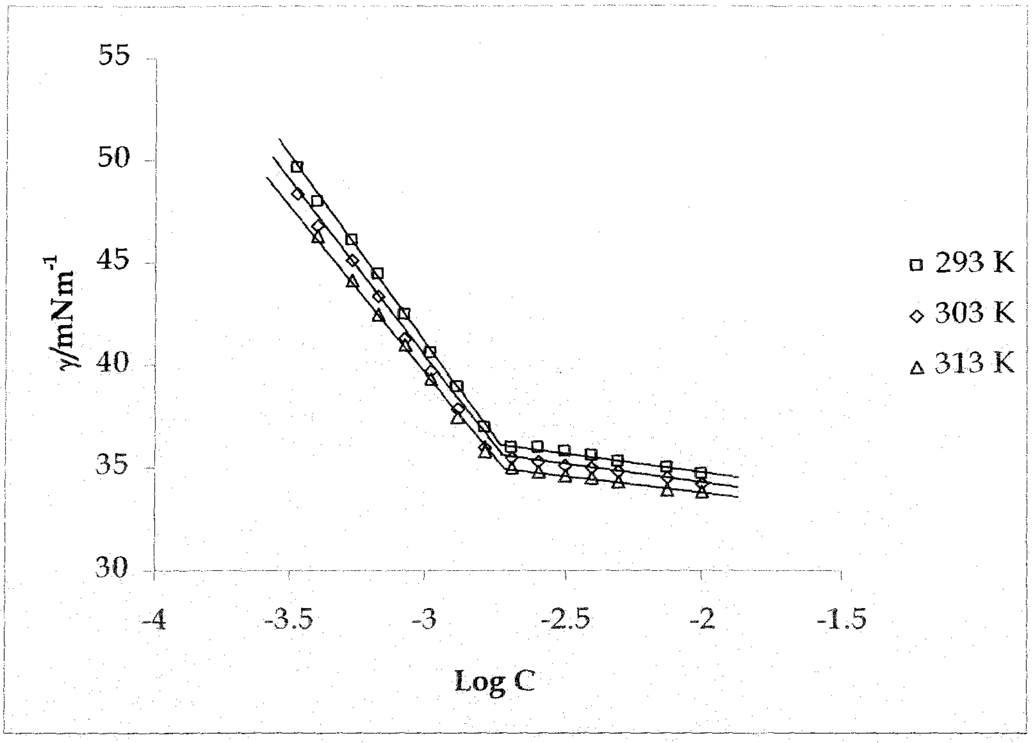

Figure 4.9: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.002 M.

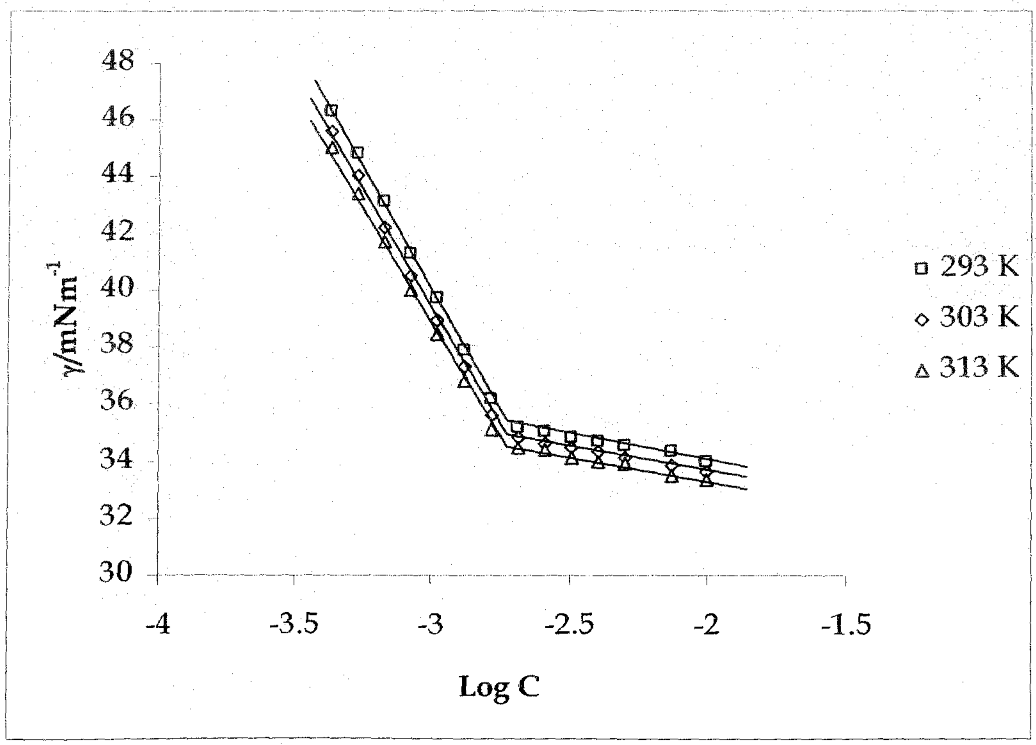

Figure 4.10: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.003 M.

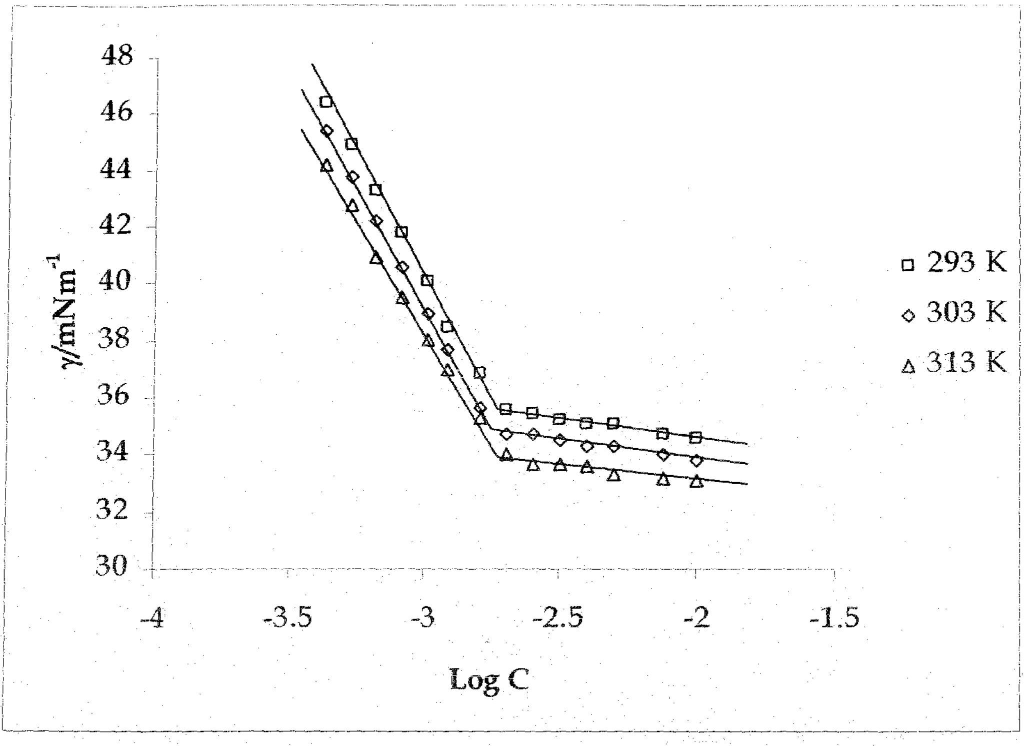

Figure 4.11: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.004 M.

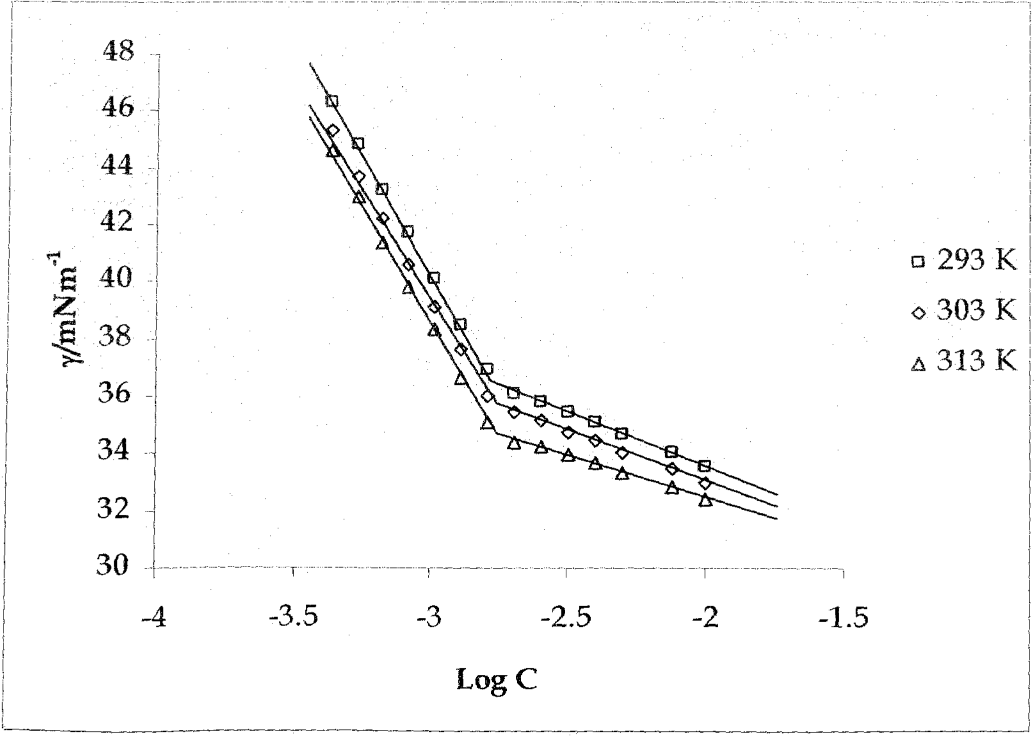

Figure 4.12: Surface Tension, γ, vs. Log C (mM) plot of LDBS in temperature range 293 – 313 K at 10 K intervals in the LiBr concentration 0.005 M.

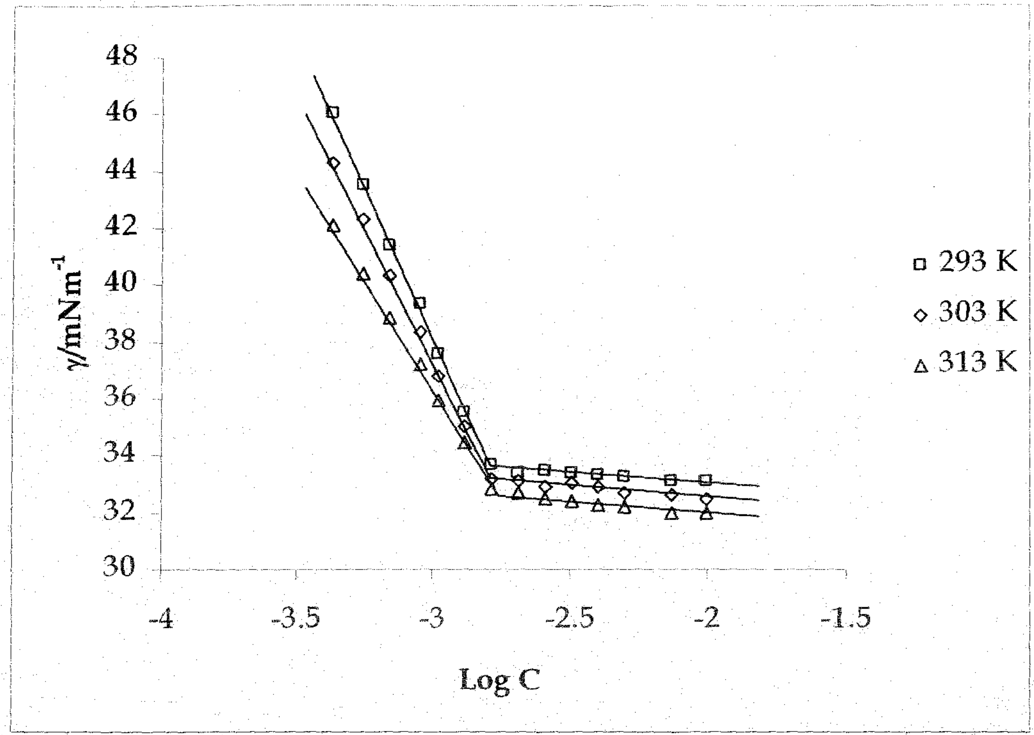

Figure 4.13: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.0005 M.

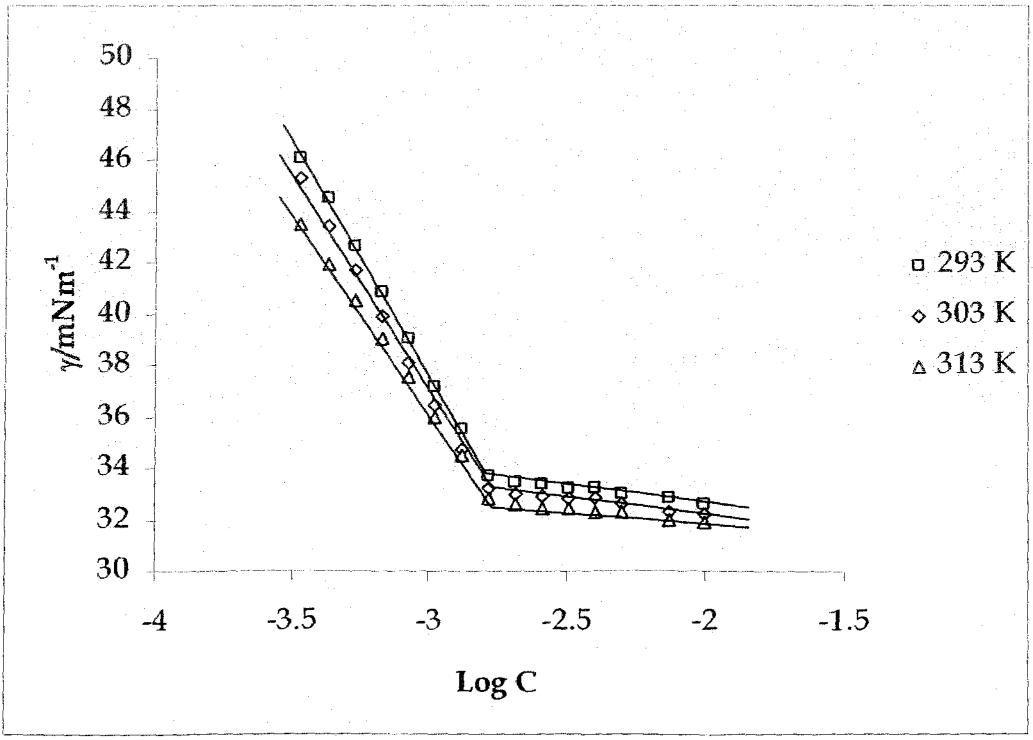

Figure 4.14: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.001 M.

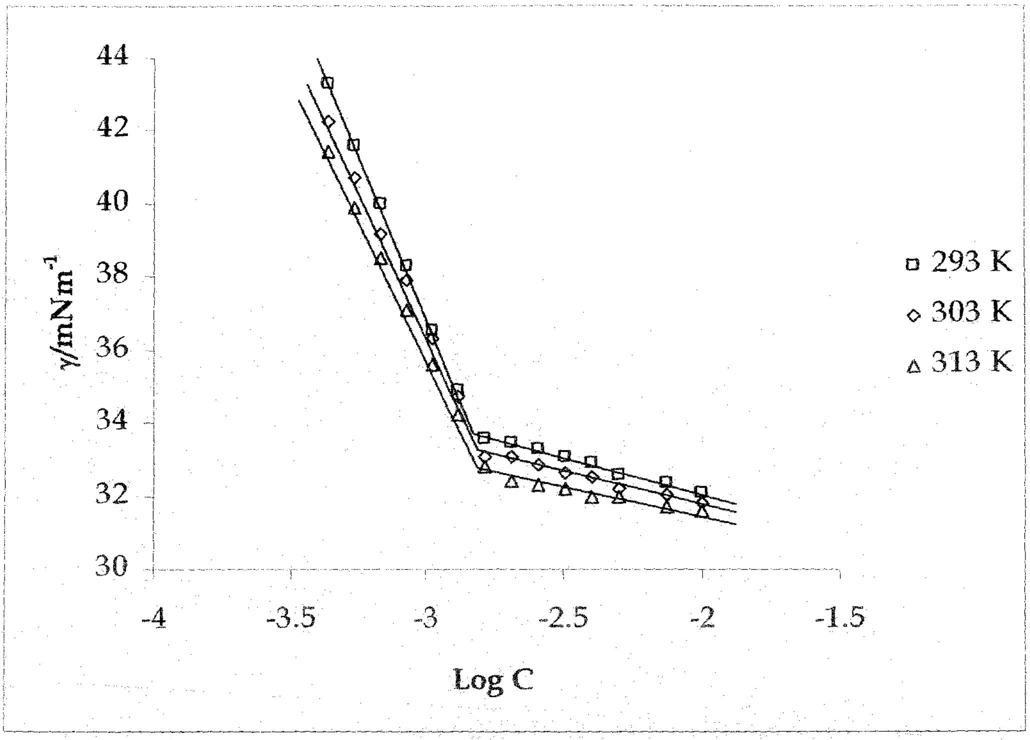

Figure 4.15: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.002 M.

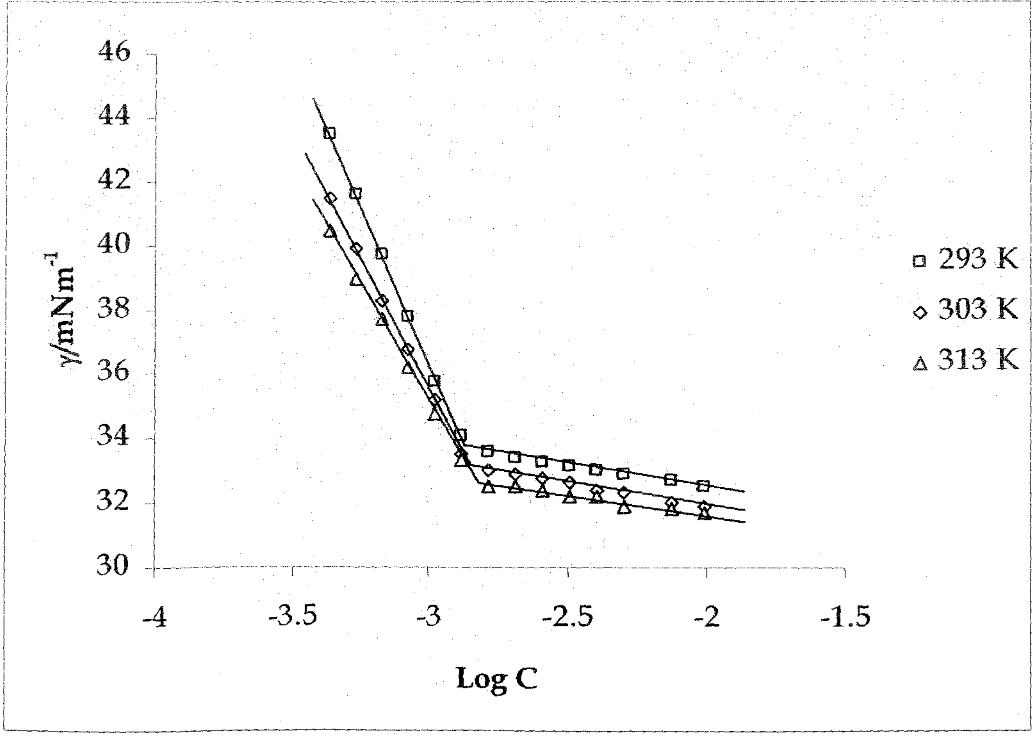

Figure 4.16: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.003 M.

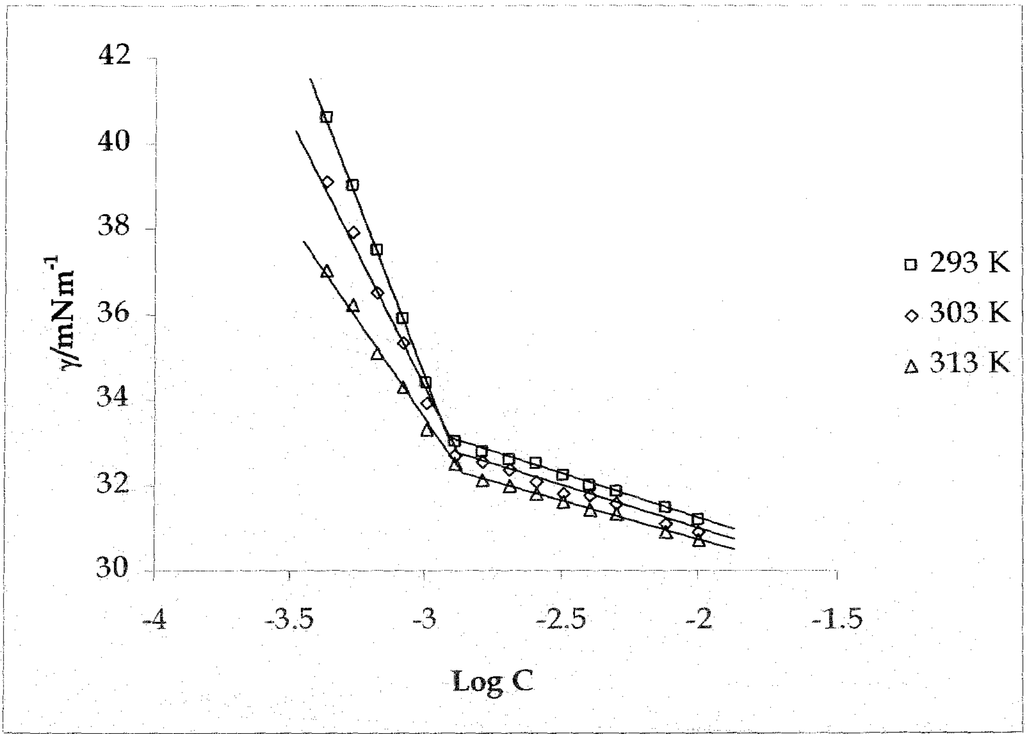

Figure 4.17: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.004 M.

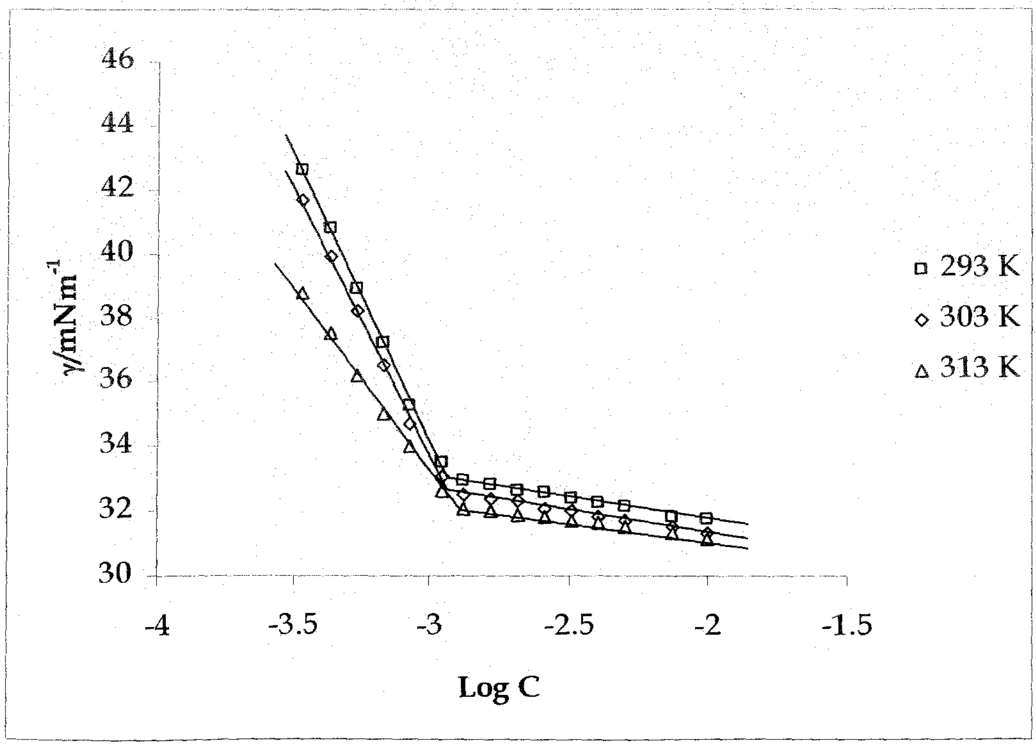

Figure 4.18: Surface Tension, γ, vs. Log C (mM) plot of PDBS in temperature range 293 – 313 K at 10 K intervals in the KBr concentration 0.005 M.

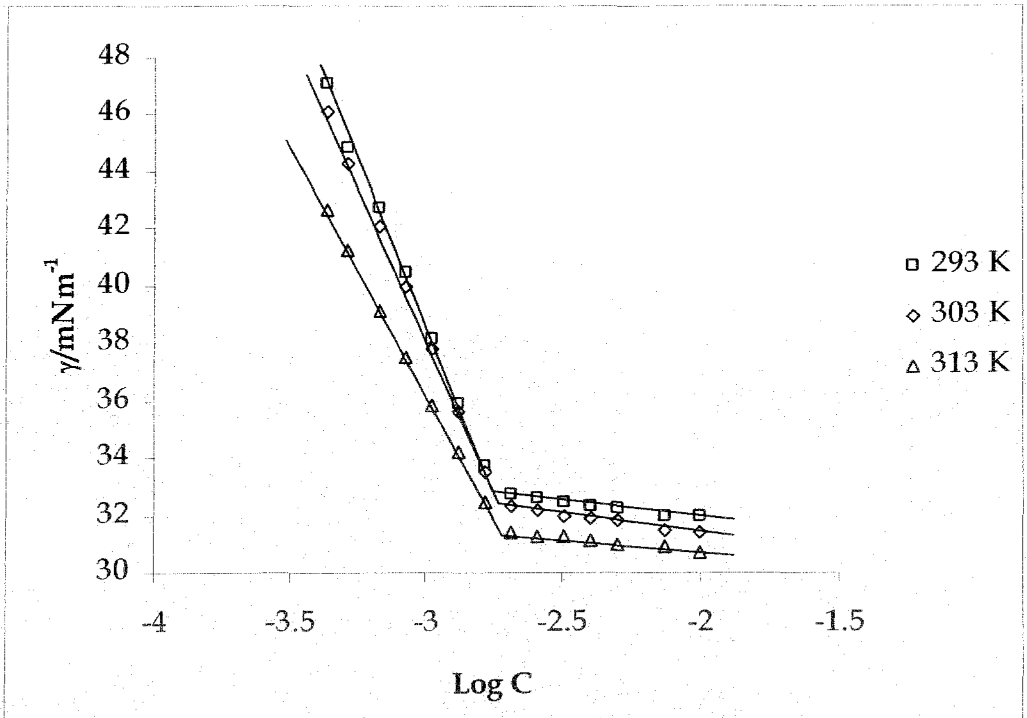

Figure 4.19: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.0005 M.

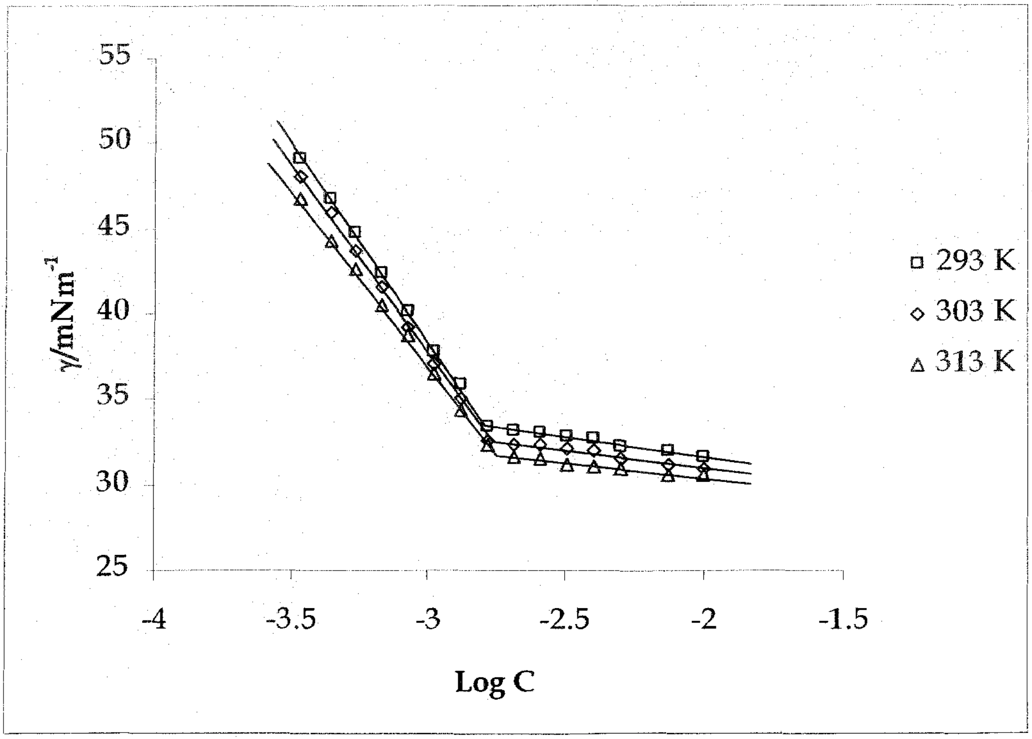

Figure 4.20: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.001 M.

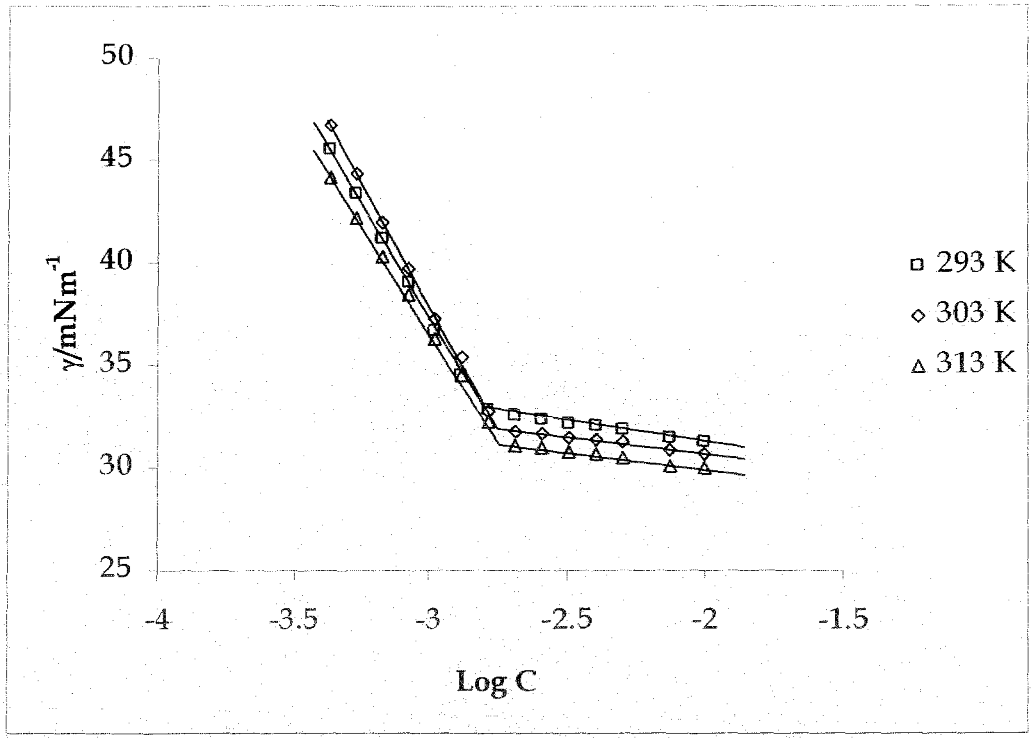

Figure 4.21: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.002 M.

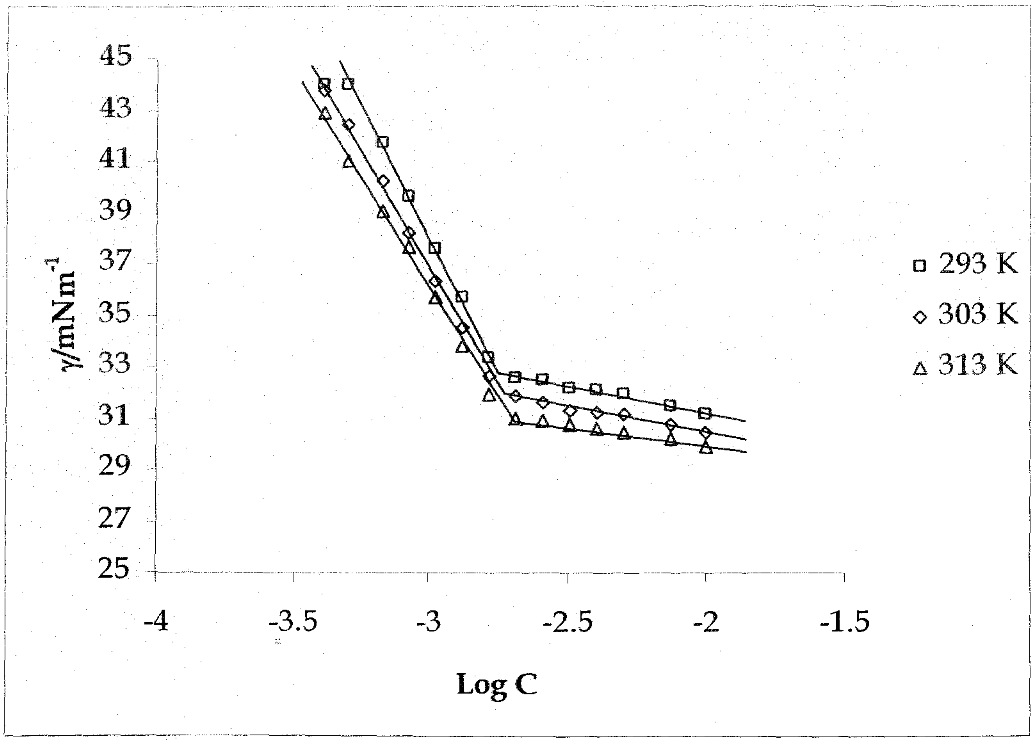

Figure 4.22: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.003 M.

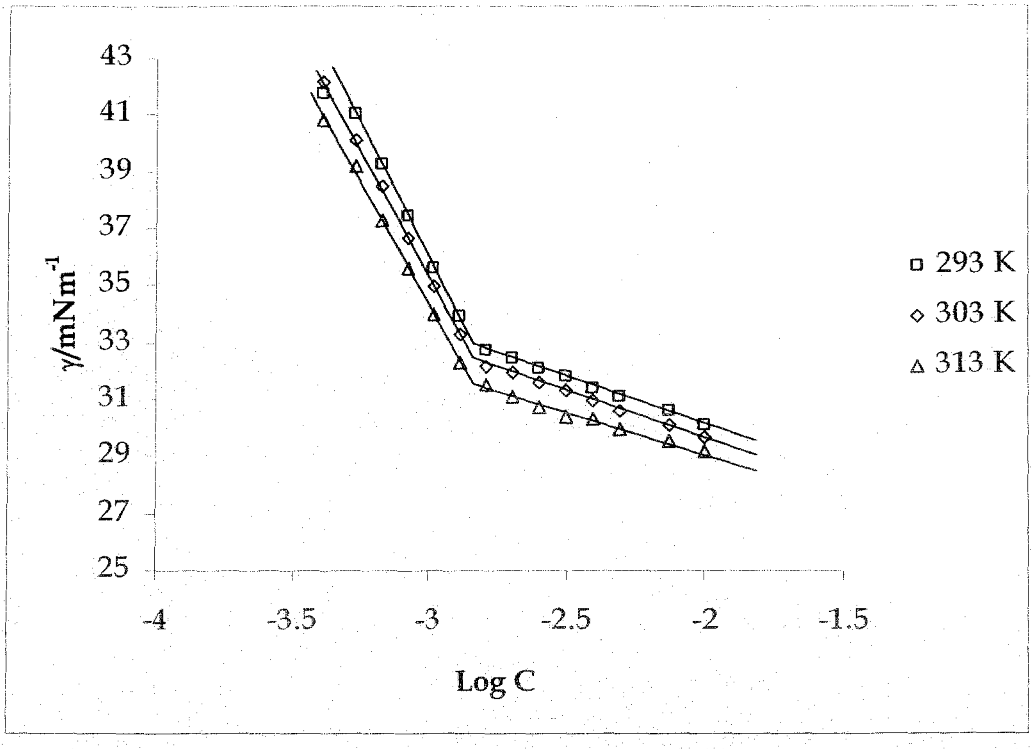

Figure 4.23: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.004 M.

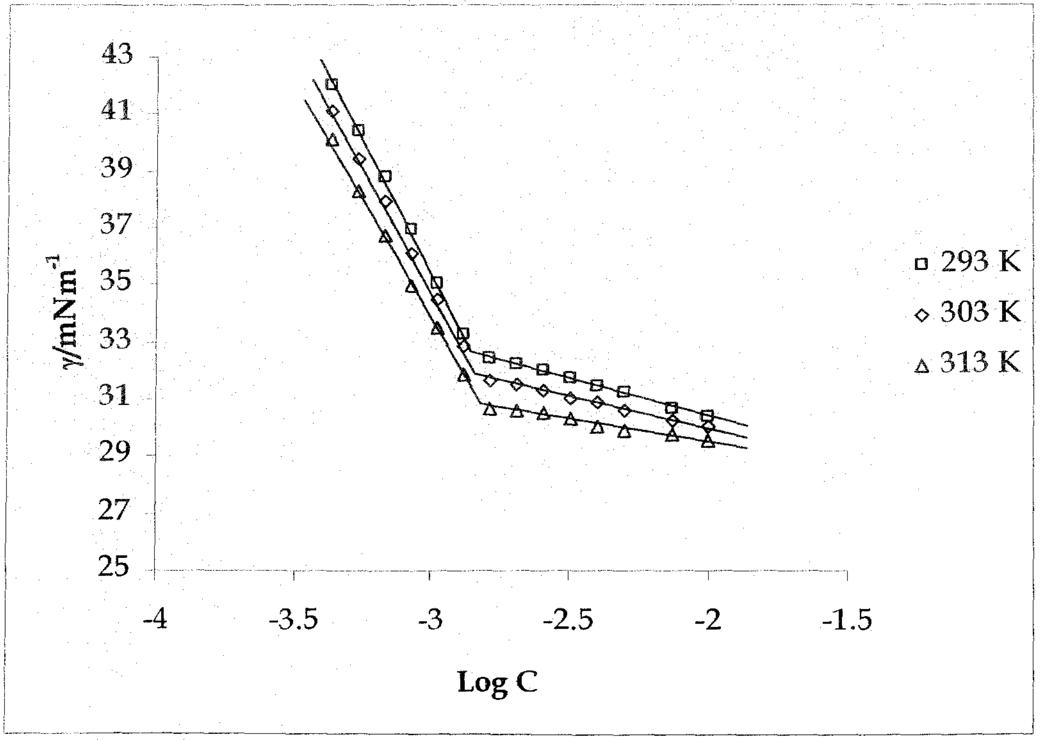

Figure 4.24: Surface Tension, γ, vs. Log C (mM) plot of ADBS in temperature range 293 – 313 K at 10 K intervals in the NH_4Br concentration 0.005 M.

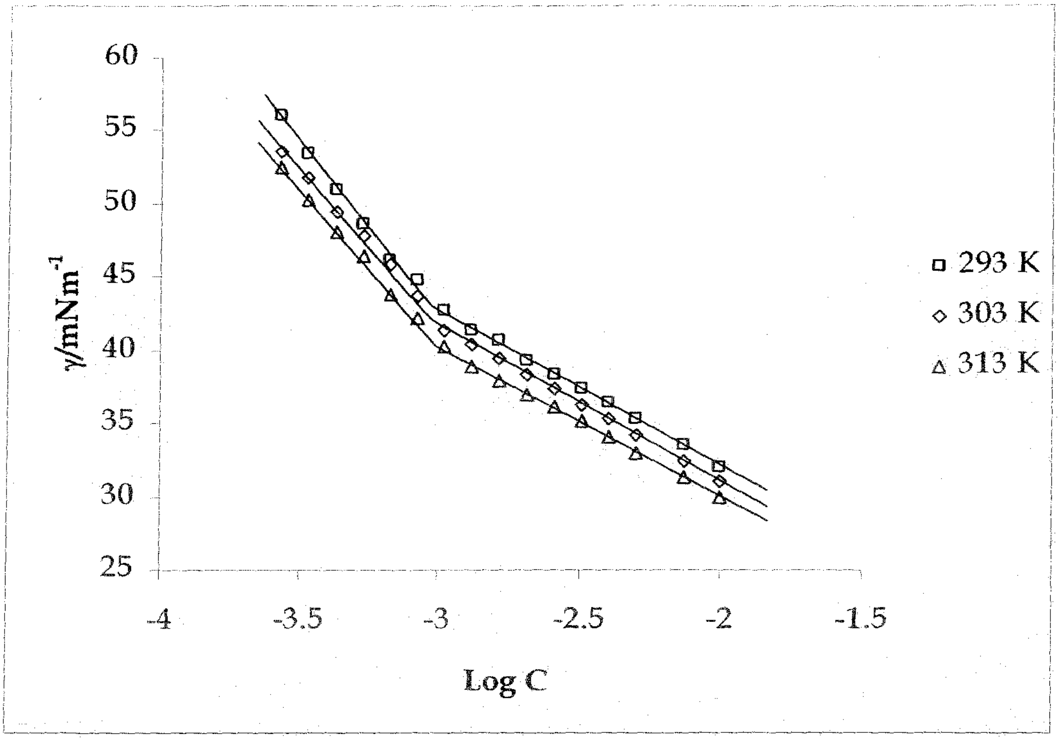

Figure 4.25: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.0005 M.

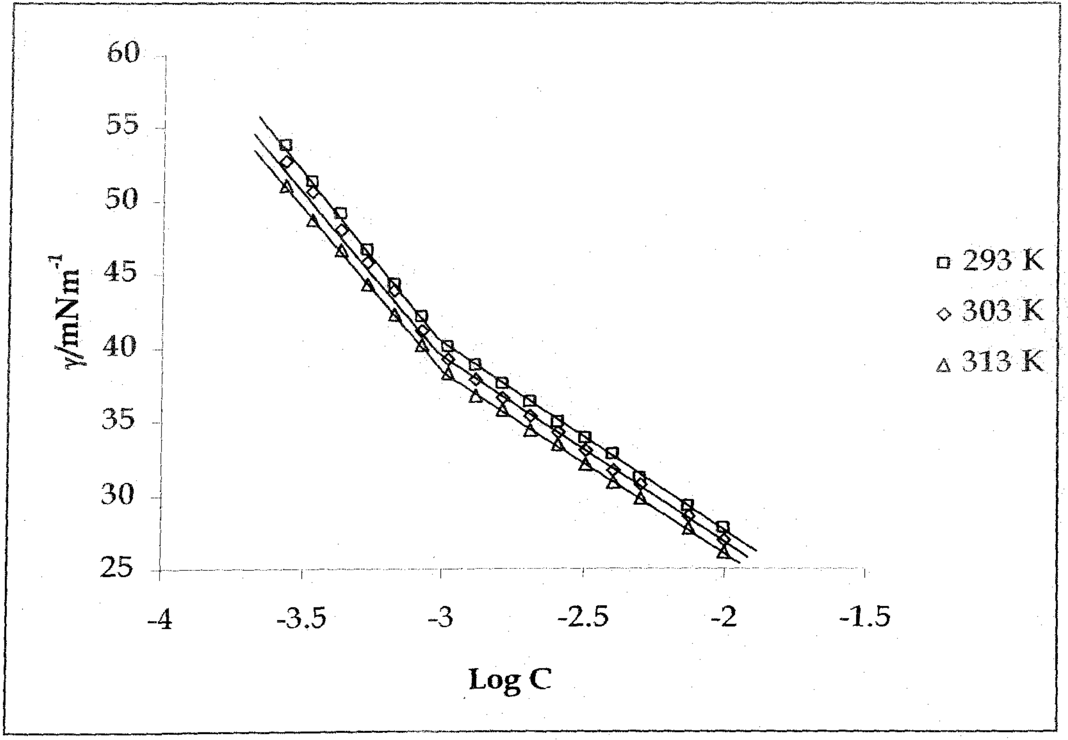

Figure 4.26: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.001 M.

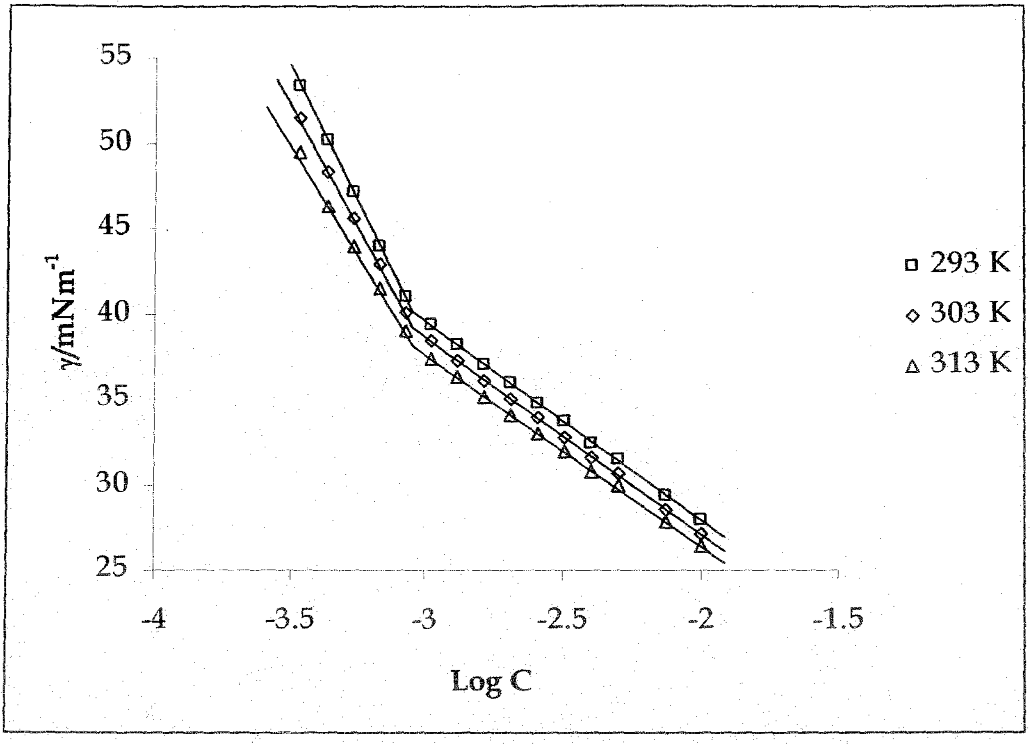

Figure 4.27: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.002 M.

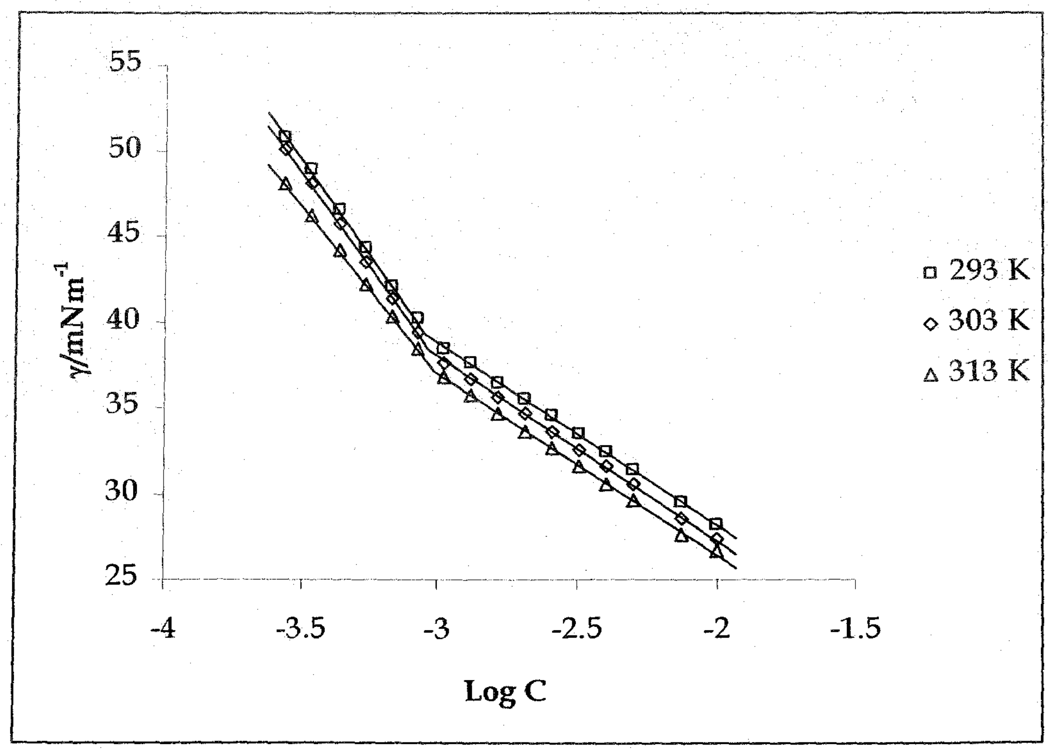

Figure 4.28: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.003 M.

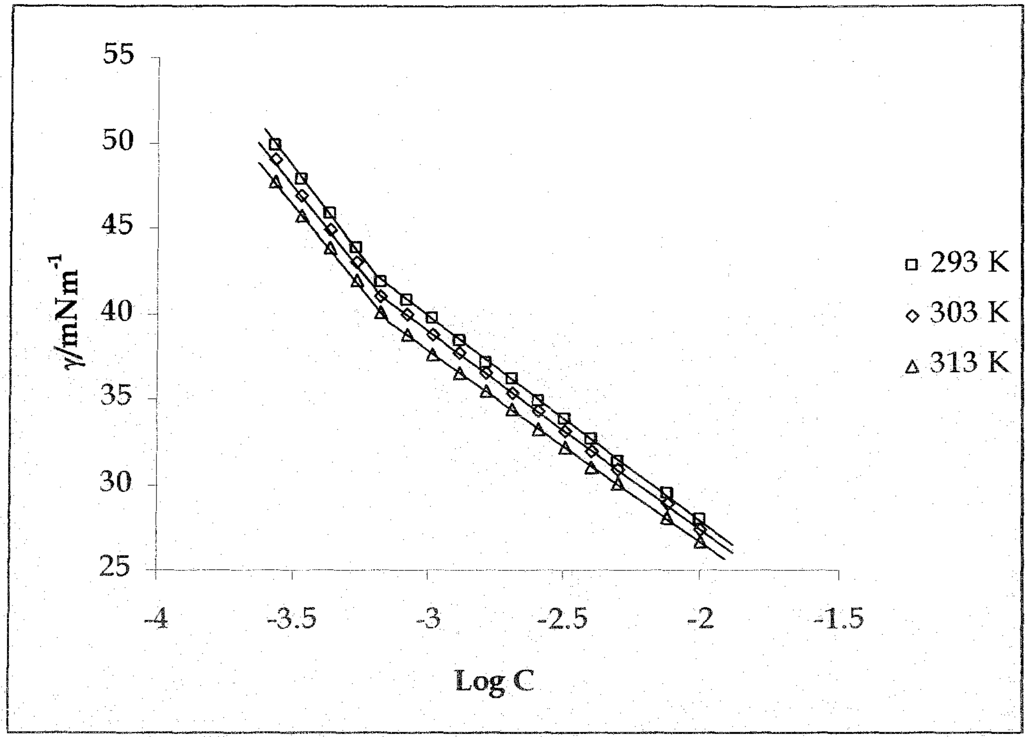

Figure 4.29: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.004 M.

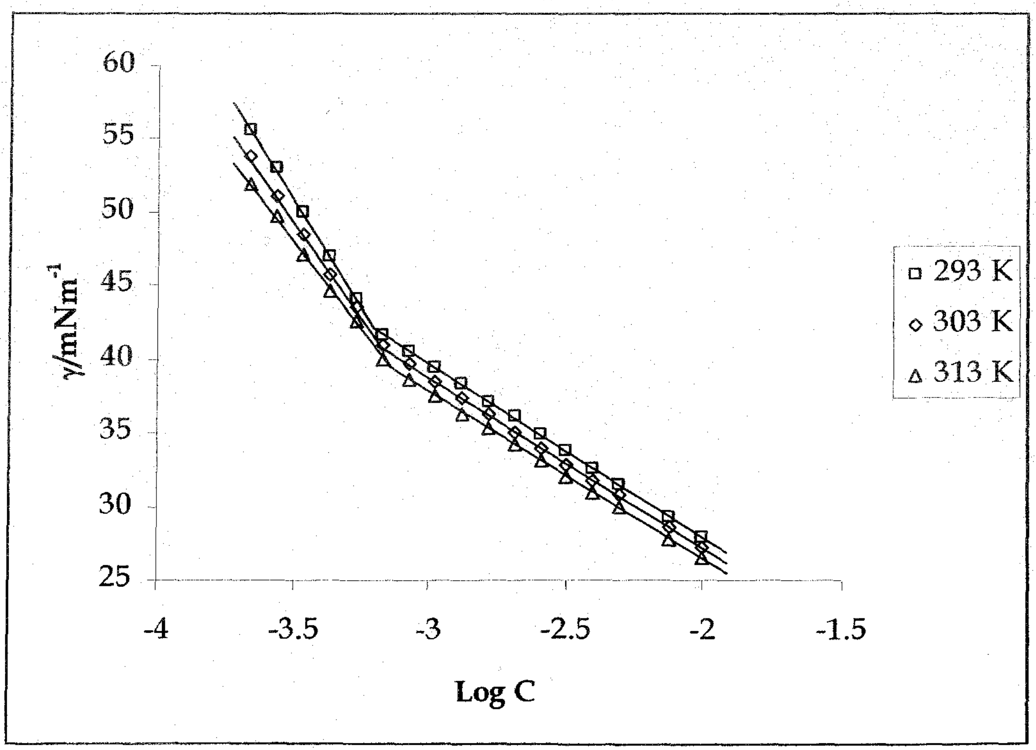

Figure 4.30: Surface Tension, γ, vs. Log C (mM) plot of TMADBS in temperature range 293 – 313 K at 10 K intervals in the TMABr concentration 0.005 M.

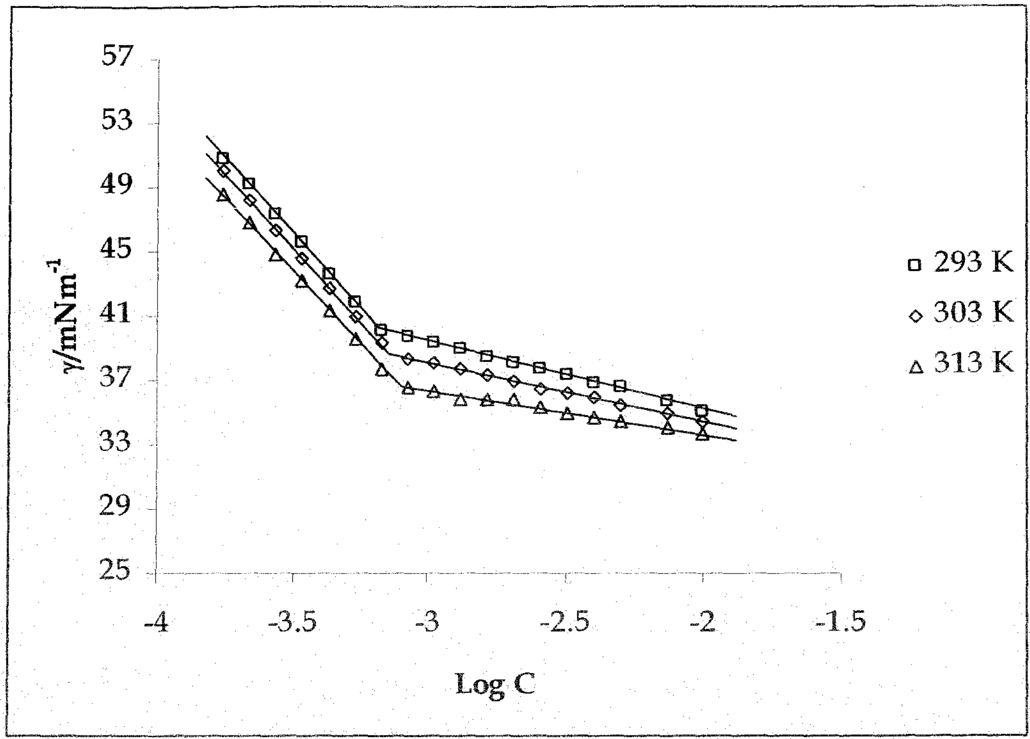

Figure 4.31: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.0005 M.

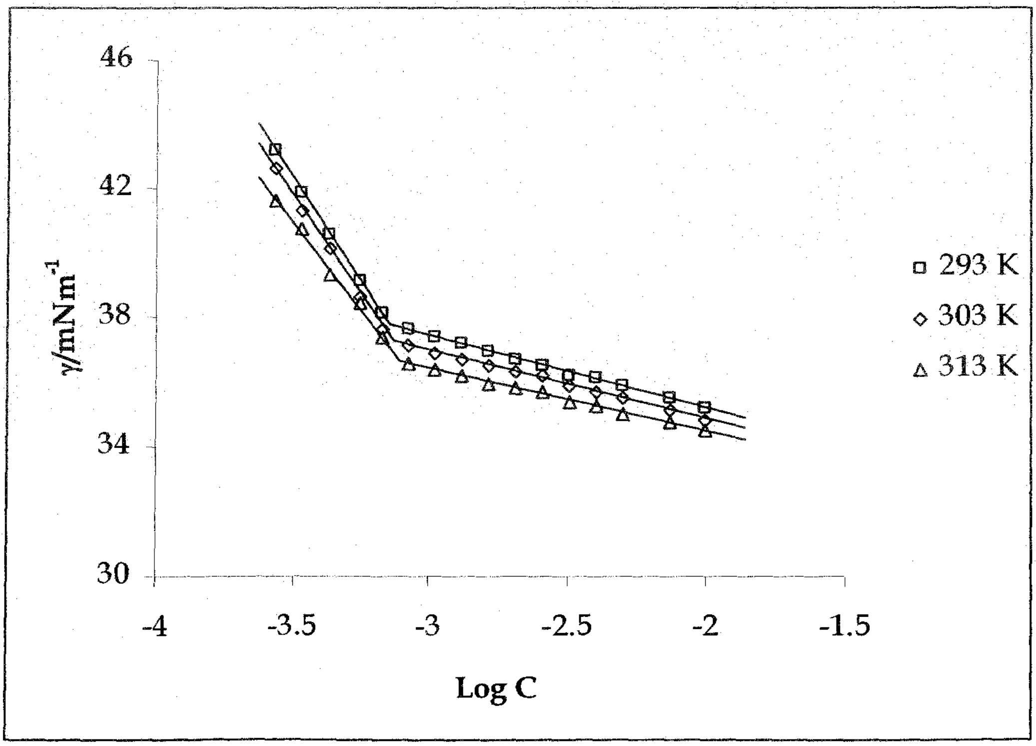

Figure 4.32: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.001 M.

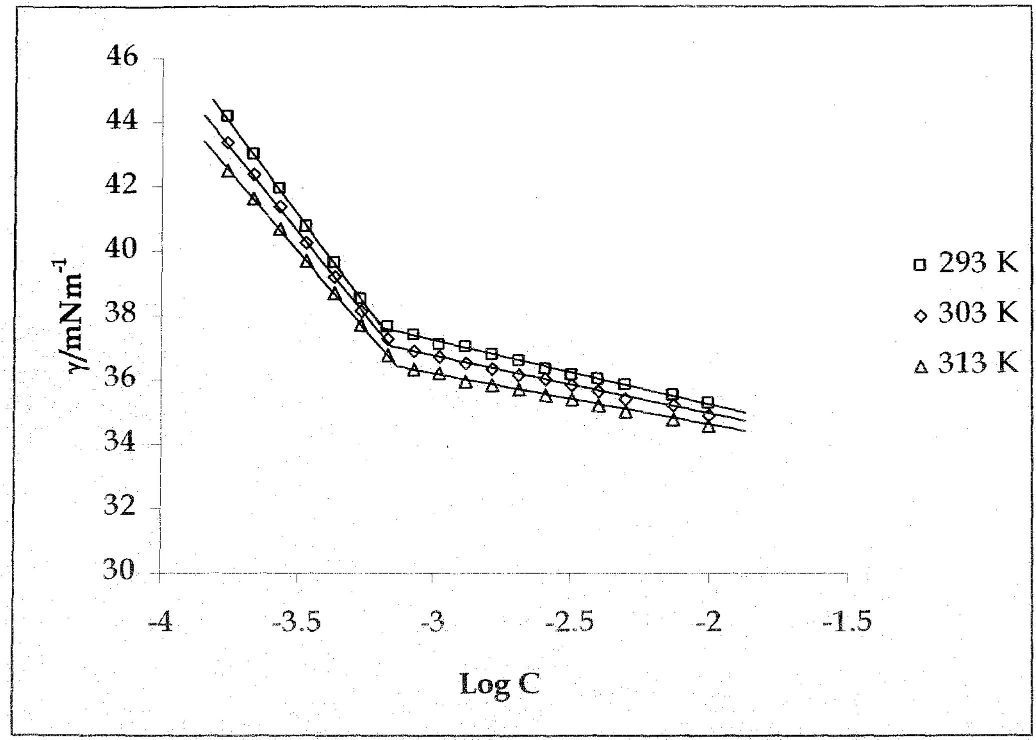

Figure 4.33: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.002 M.

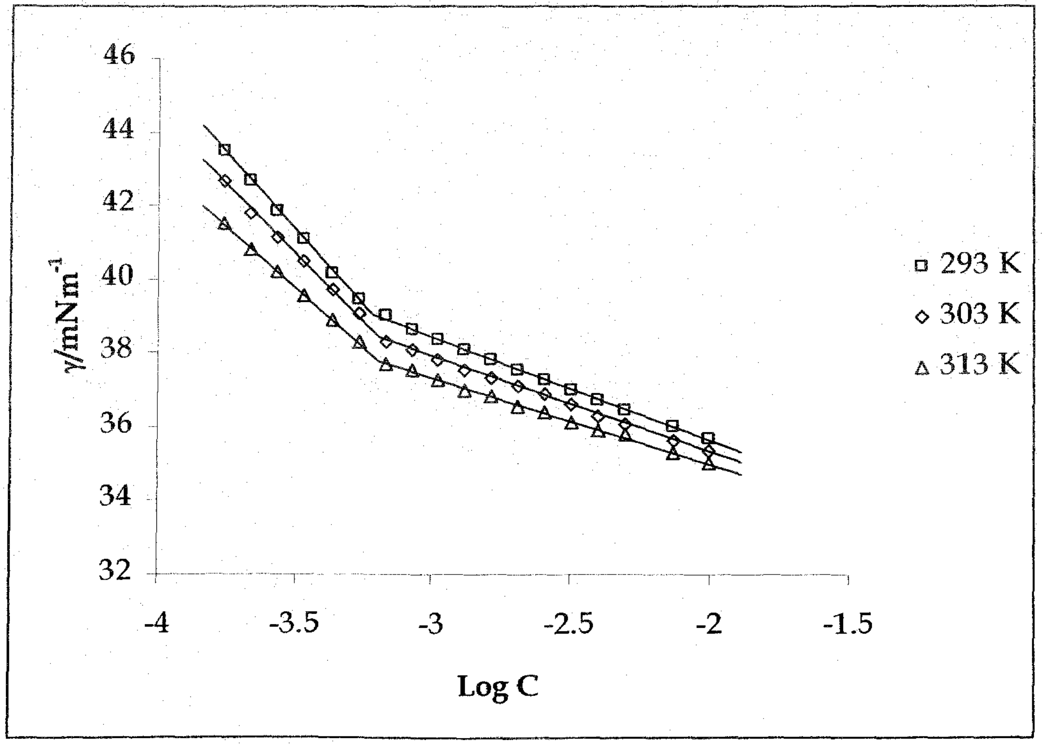

Figure 4.34: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.003 M.

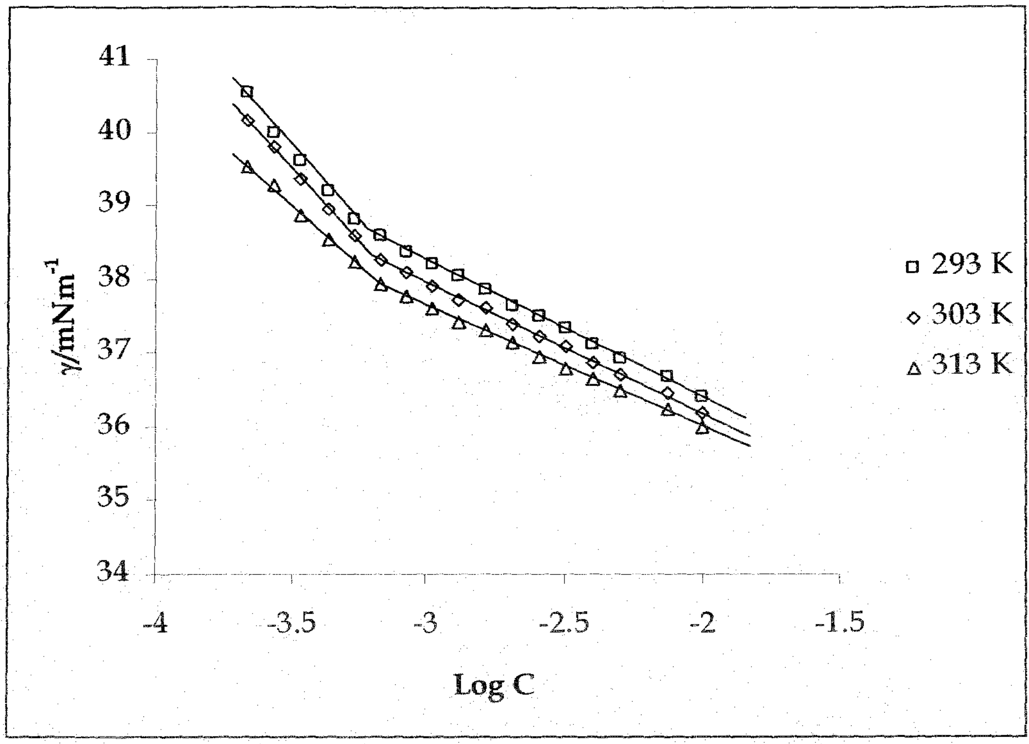

Figure 4.35: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.004 M.

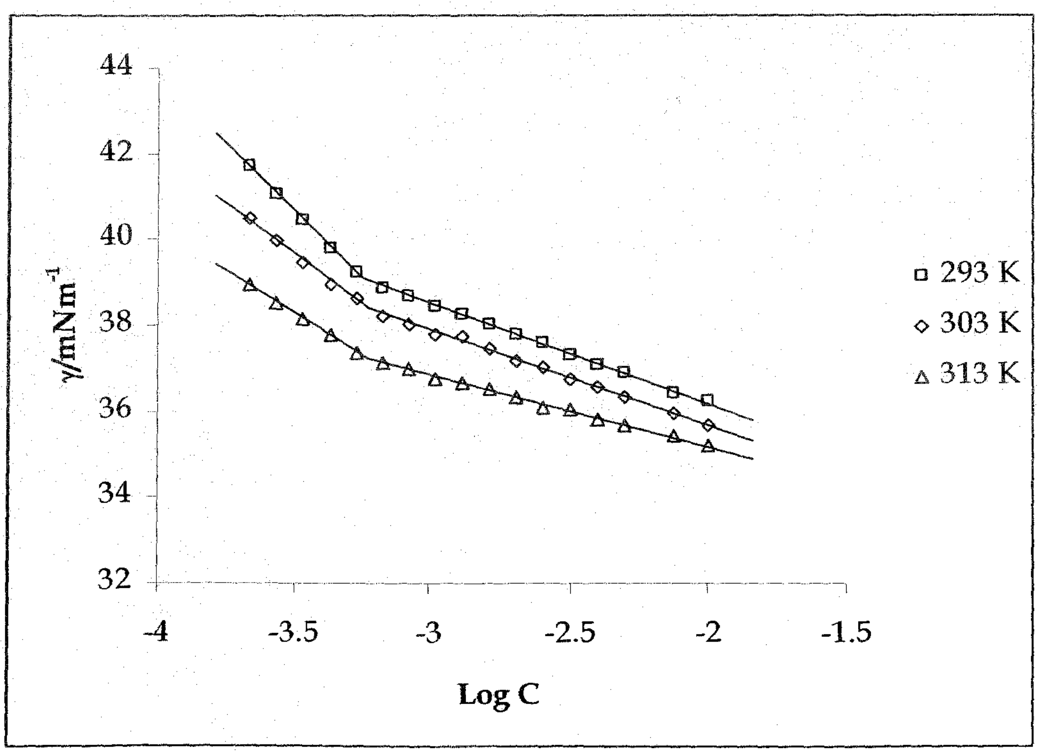

Figure 4.36: Surface Tension, γ, vs. Log C (mM) plot of TEADBS in temperature range 293 – 313 K at 10 K intervals in the TEABr concentration 0.005 M.

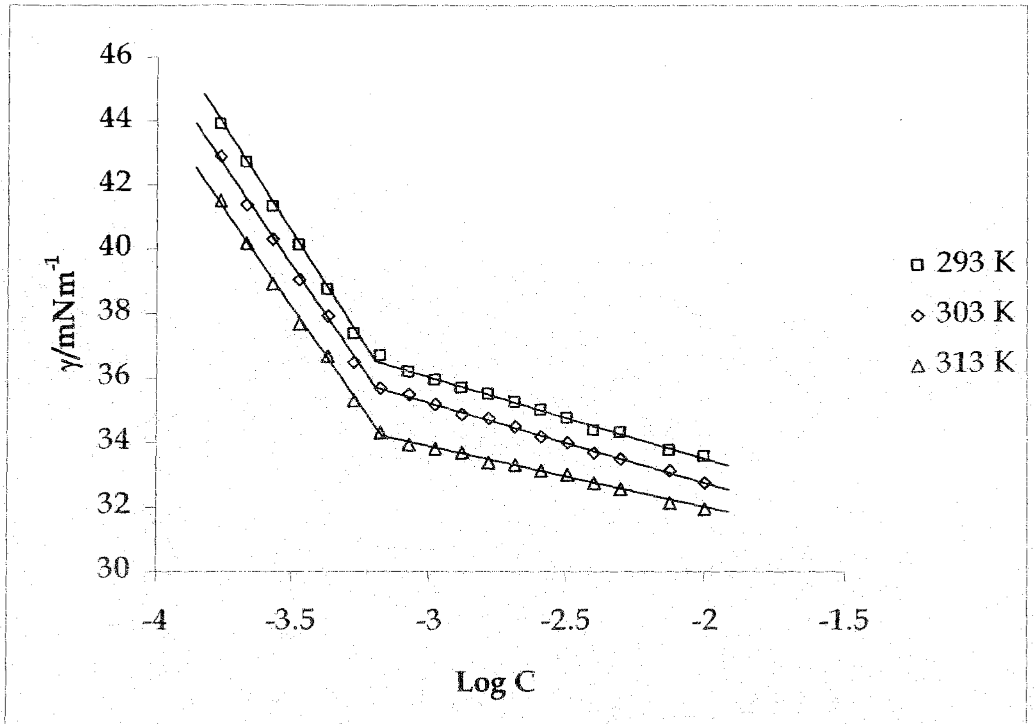

Figure 4.37: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.0005 M.

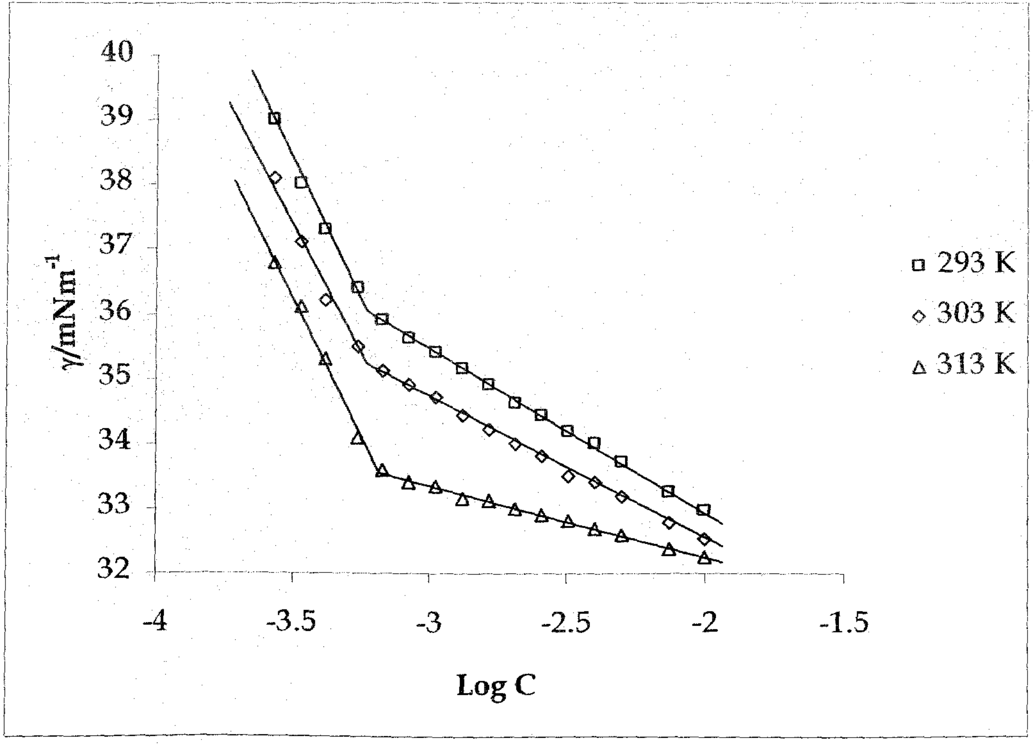

Figure 4.38: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.001 M.

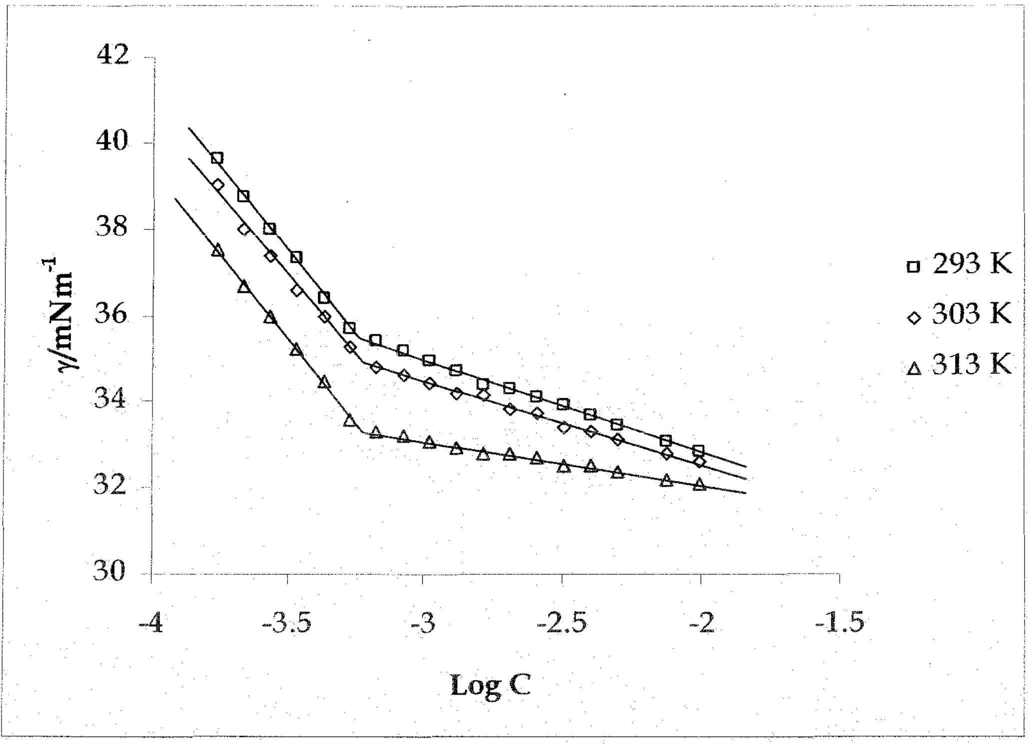

Figure 4.39: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.002 M.

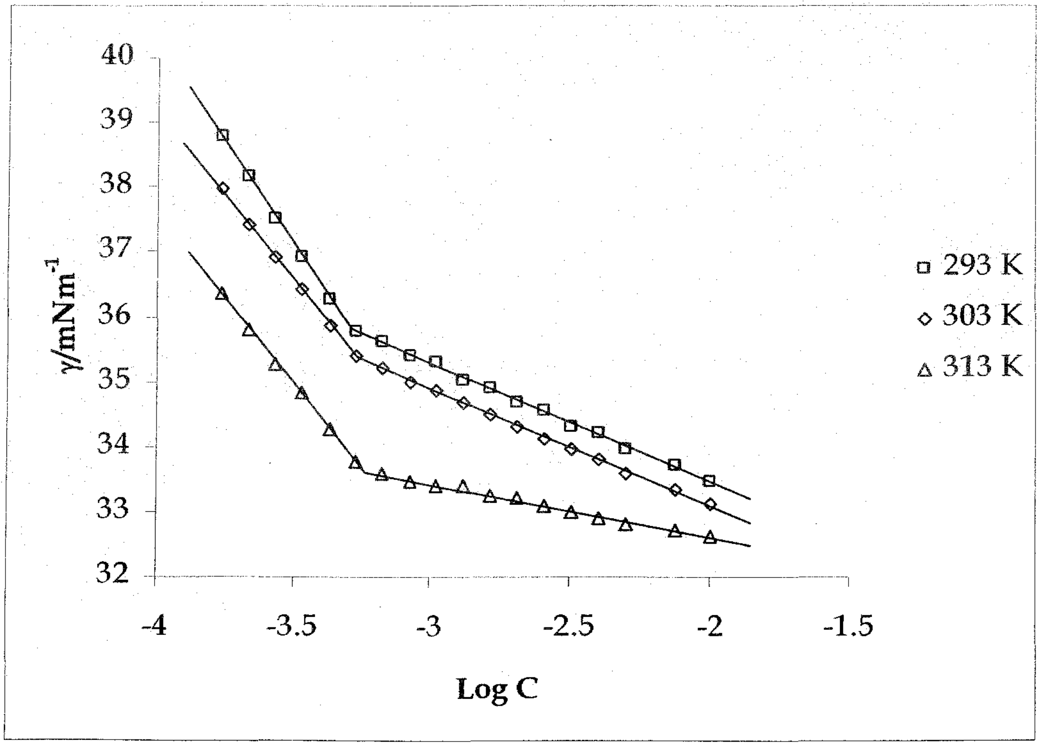

Figure 4.40: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.003 M.

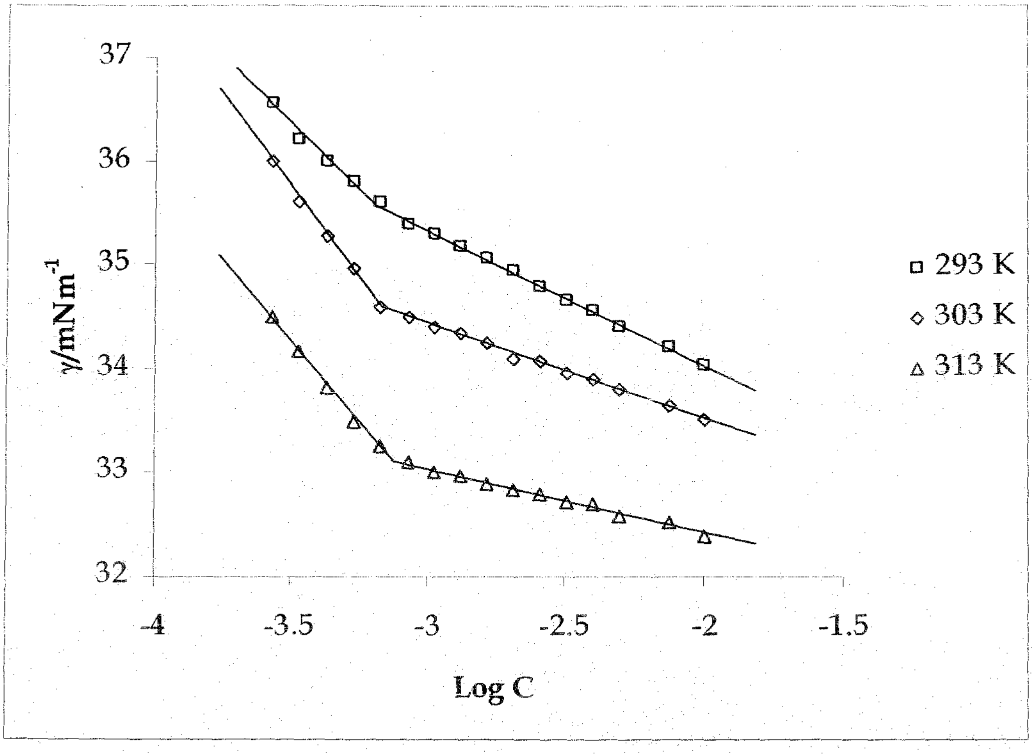

Figure 4.41: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.004 M.

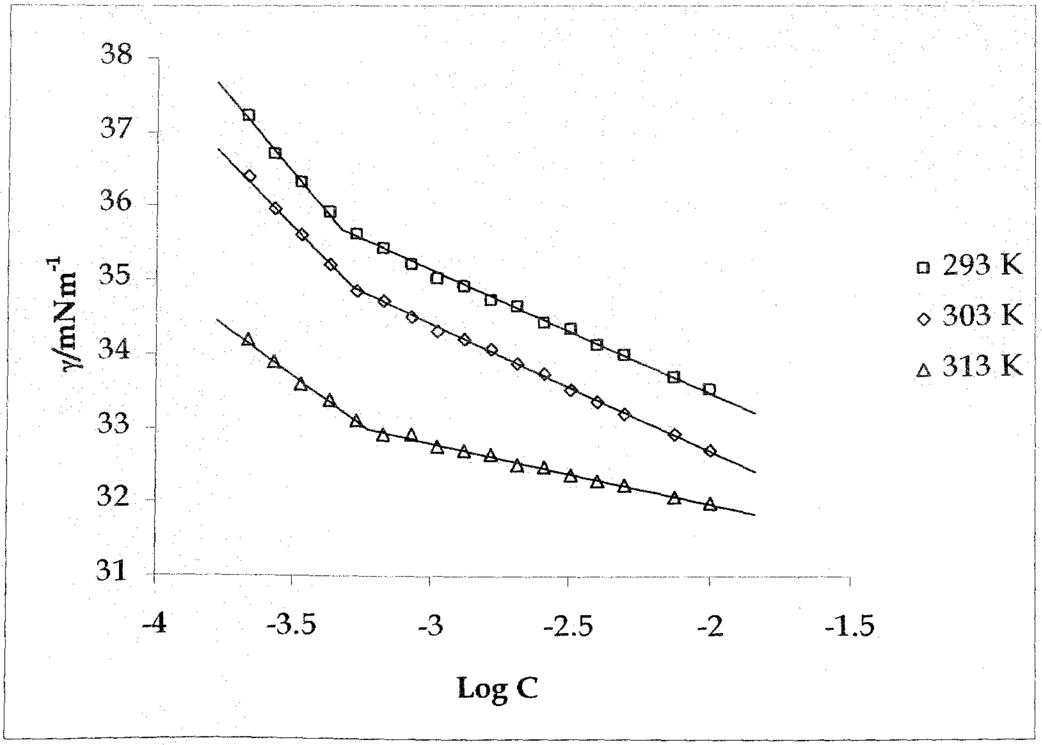

Figure 4.42: Surface Tension, γ, vs. Log C (mM) plot of TPADBS in temperature range 293 – 313 K at 10 K intervals in the TPABr concentration 0.005 M.

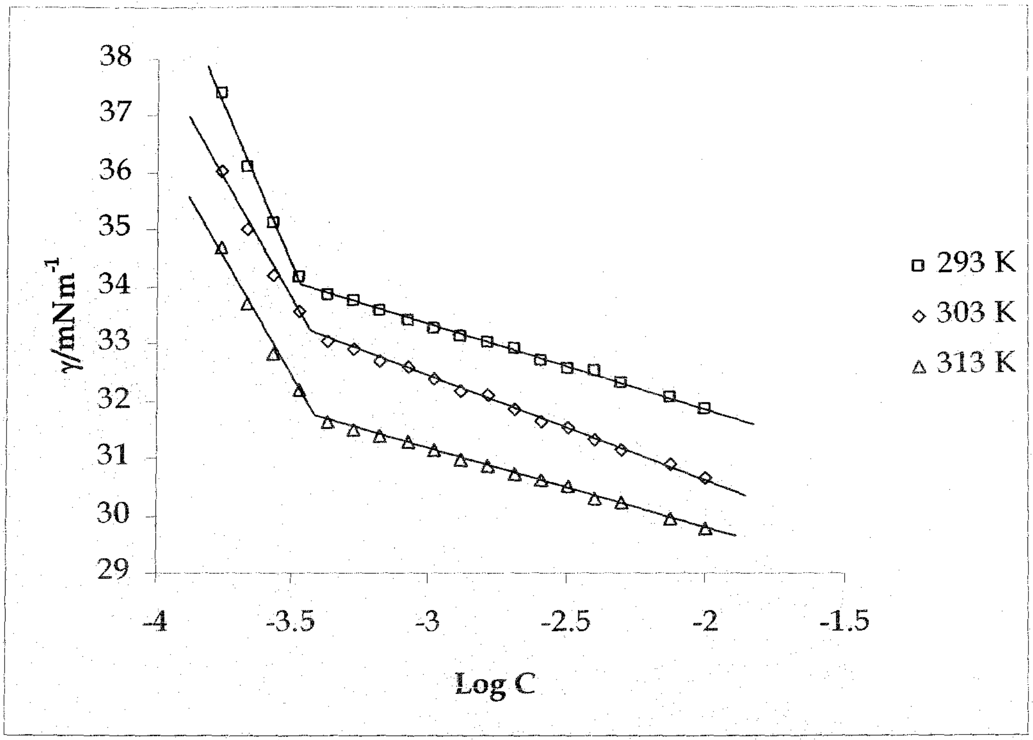

Figure 4.43: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.0005 M.

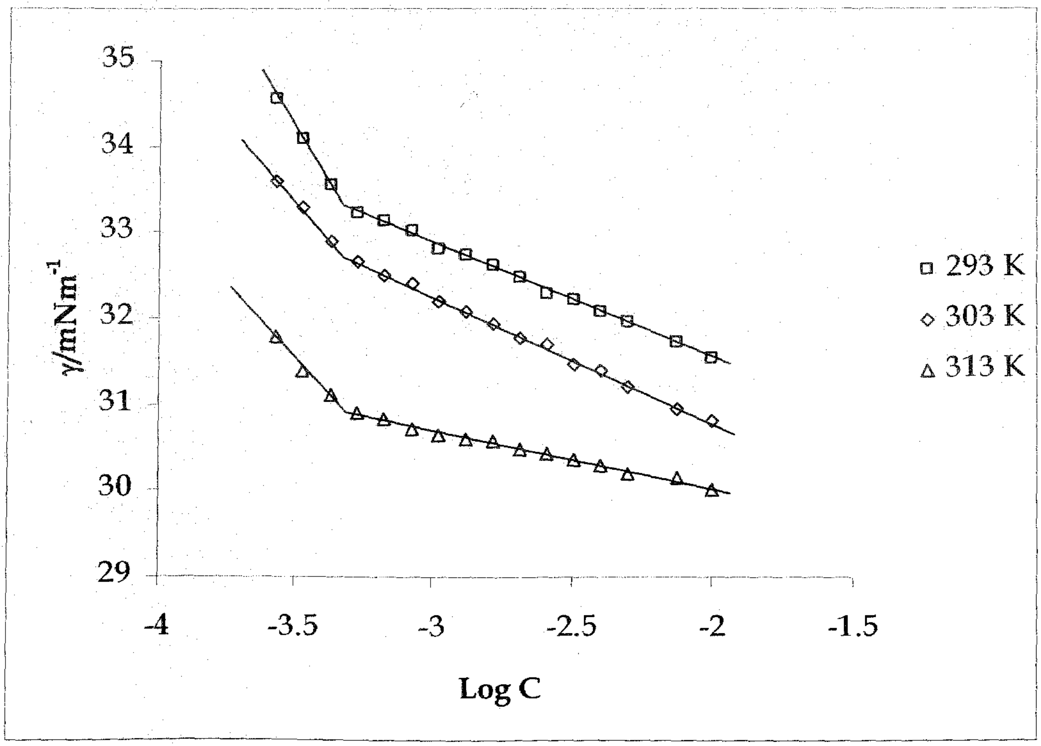

Figure 4.44: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.001 M.

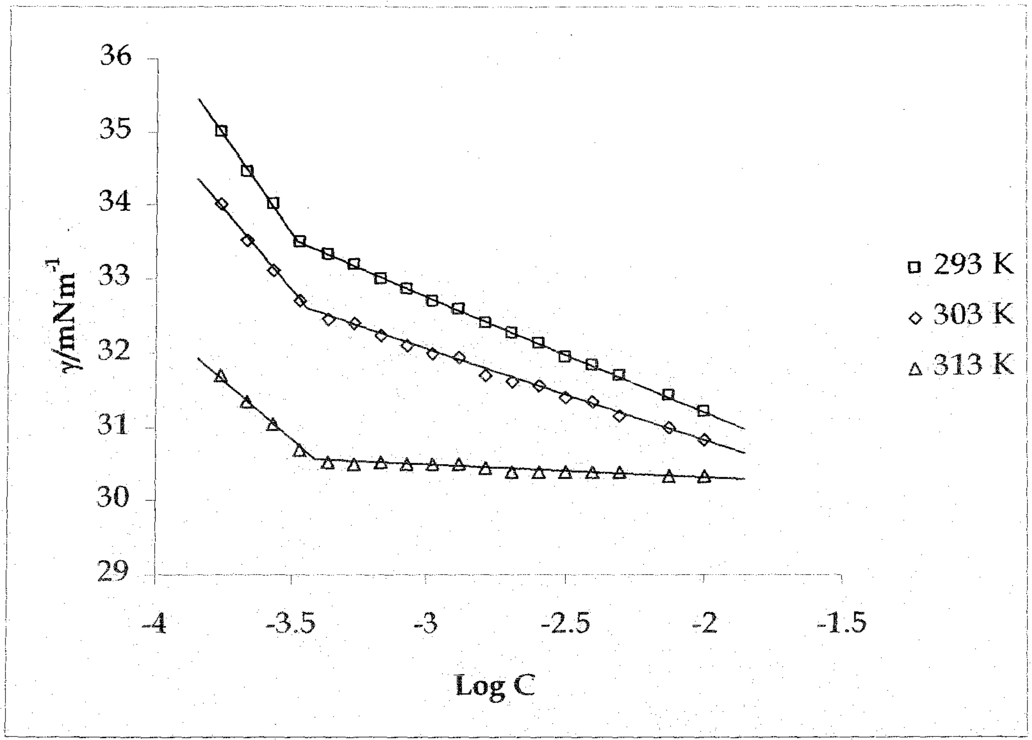

Figure 4.45: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.002 M.

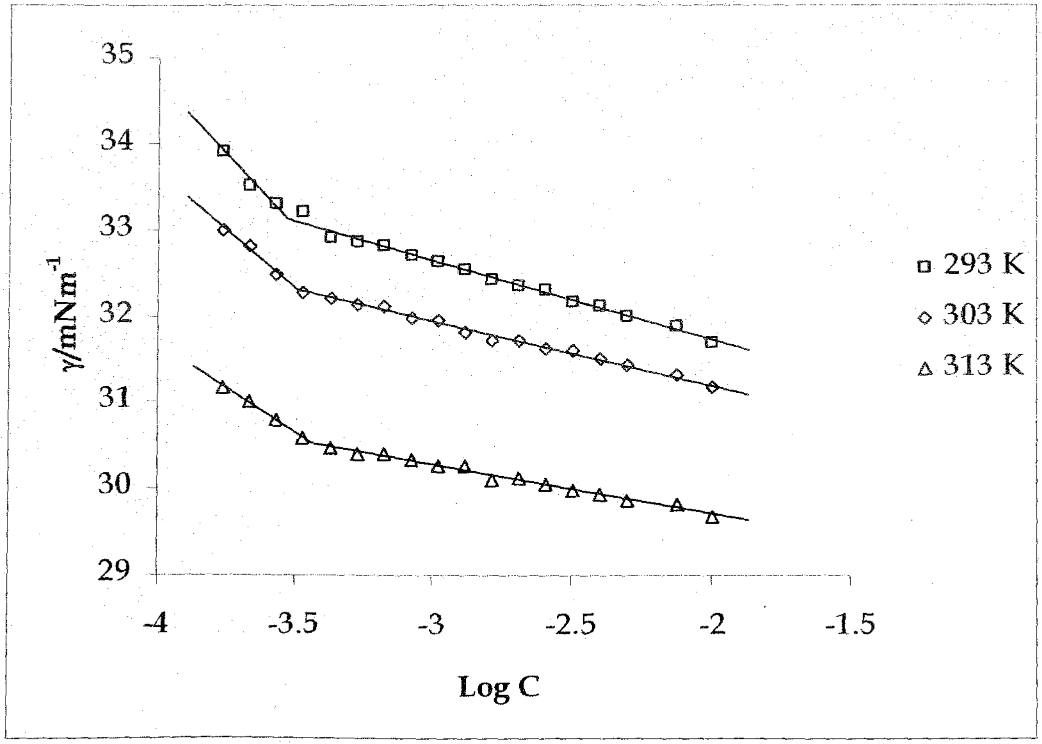

Figure 4.46: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.003 M.

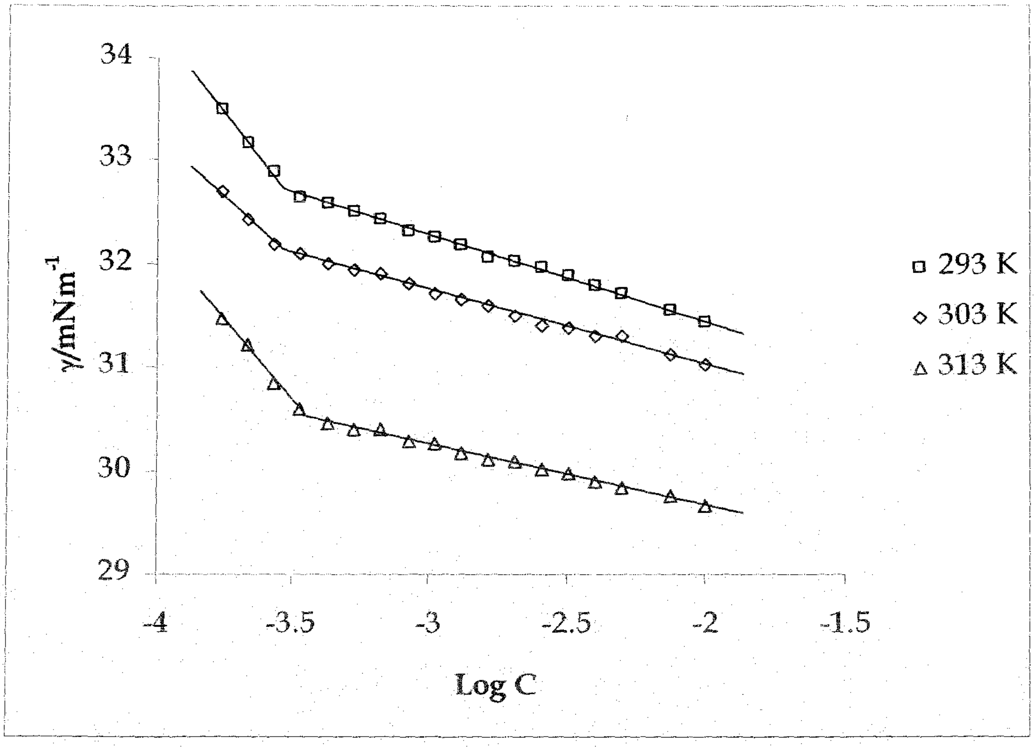

Figure 4.47: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.004 M.

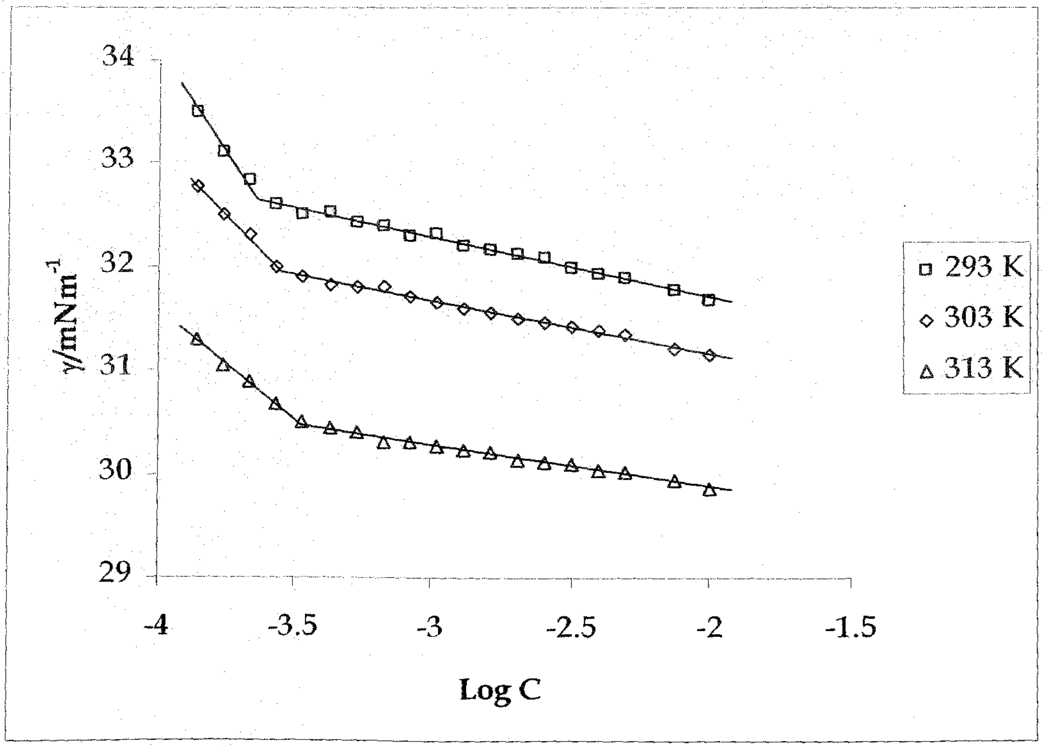

Figure 4.48: Surface Tension, γ, vs. Log C (mM) plot of TBADBS in temperature range 293 – 313 K at 10 K intervals in the TBABr concentration 0.005 M.

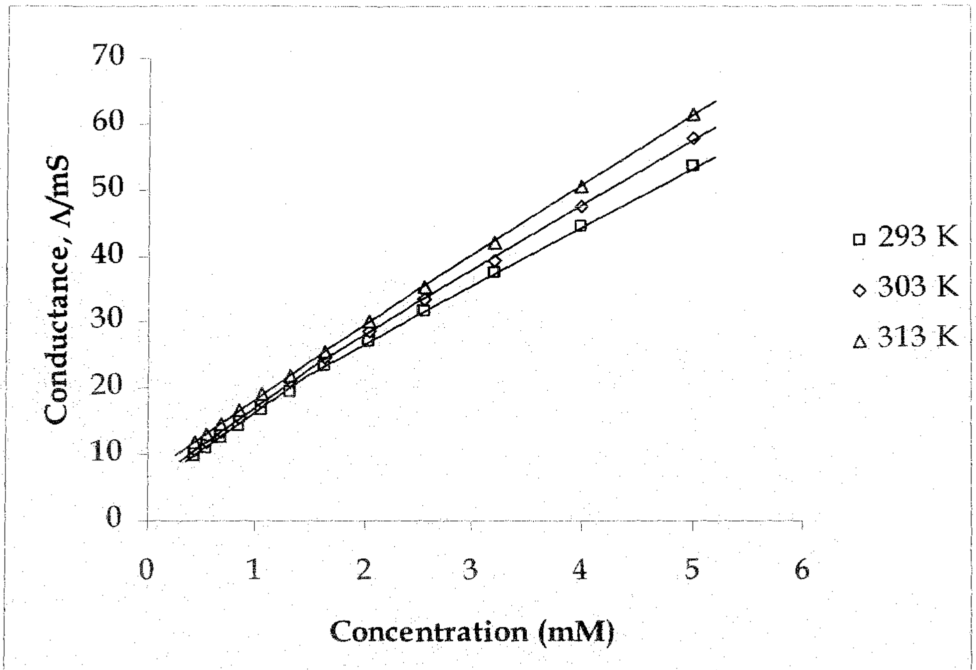

Figure 4.49: Conductance, Λ, of Sodium dodecyl benzene sulfonate (SDBS) in aqueous NaBr solution [NaBr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

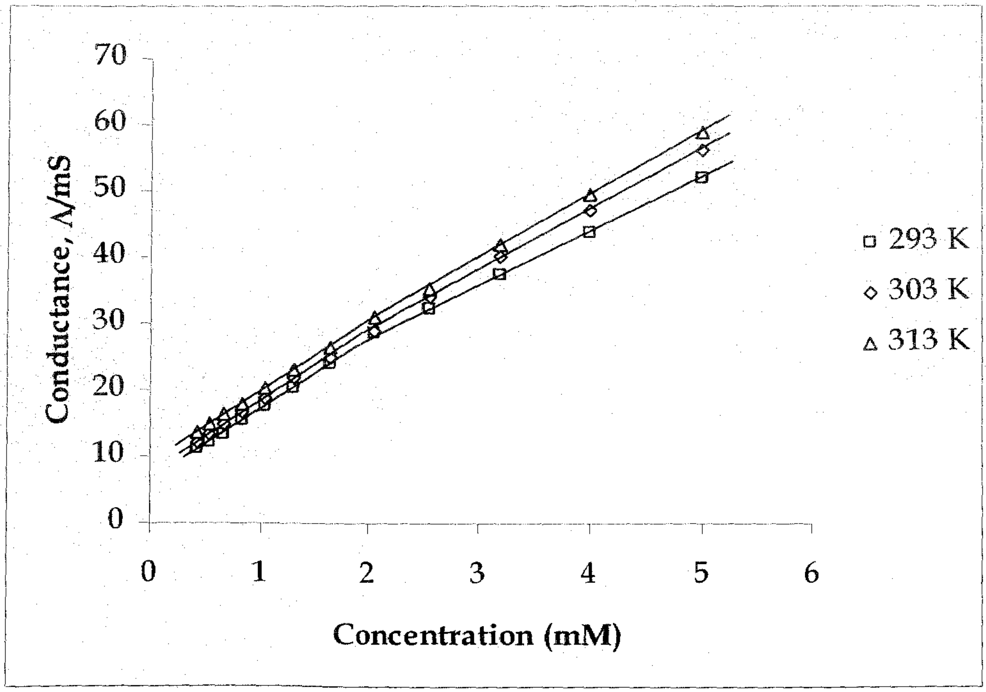

Figure 4.50: Conductance, Λ, of Lithium dodecyl benzene sulfonate (LDBS) in aqueous LiBr solution [LiBr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

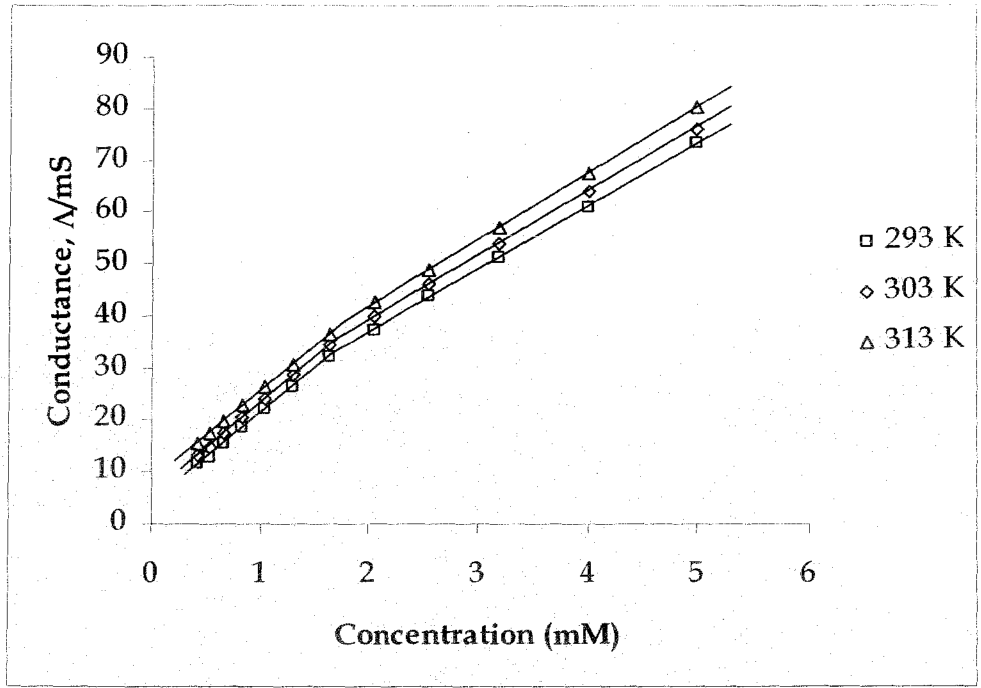

Figure 4.51: Conductance, Λ, of Potassium dodecyl benzene sulfonate (PDBS) in aqueous KBr solution [KBr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

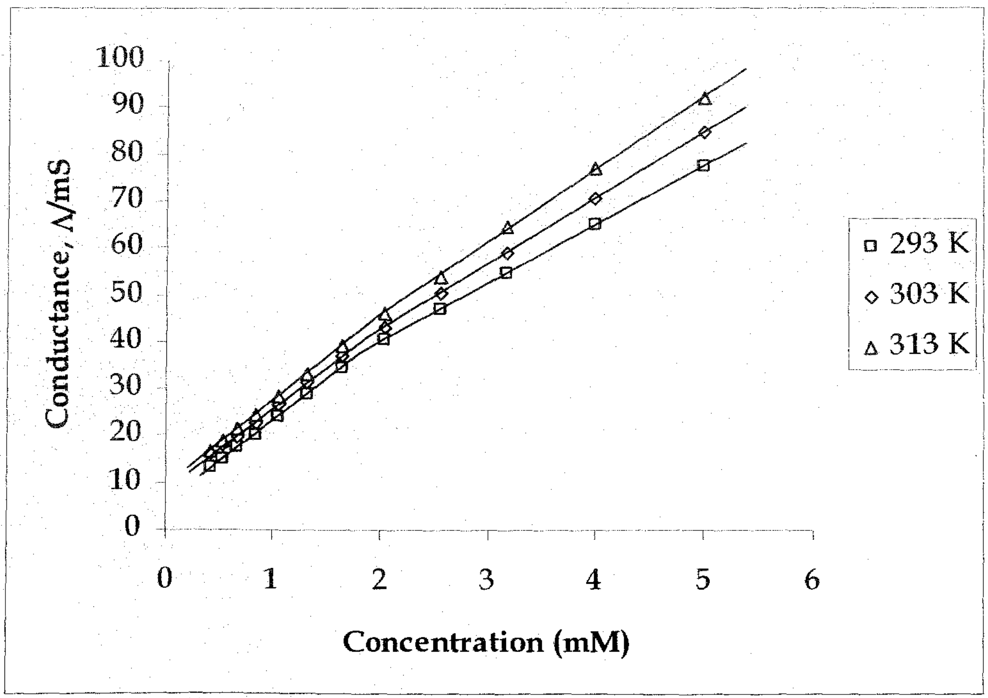

Figure 4.52: Conductance, Λ, of Ammonium dodecyl benzene sulfonate (ADBS) in aqueous NH_4Br solution $[NH_4Br]$ = 0.0005(M) as a function of the surfactant concentration at different temperatures.

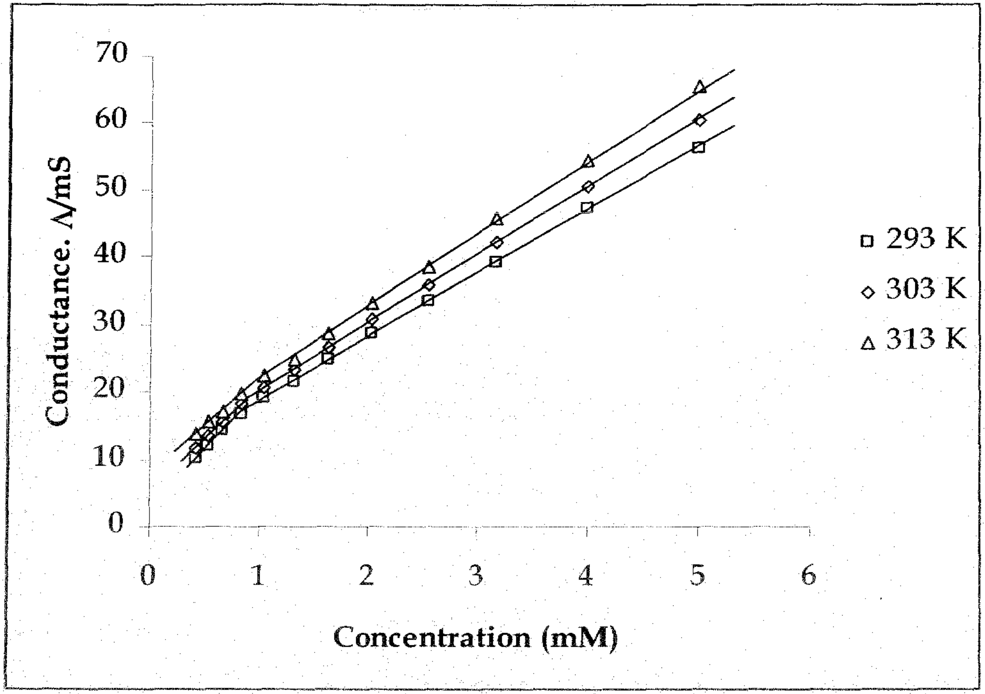

Figure 4.53: Conductance, Λ, of Tetramethylammonium dodecyl benzene sulfonate (TMADBS) in aqueous KBr solution [TMABr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

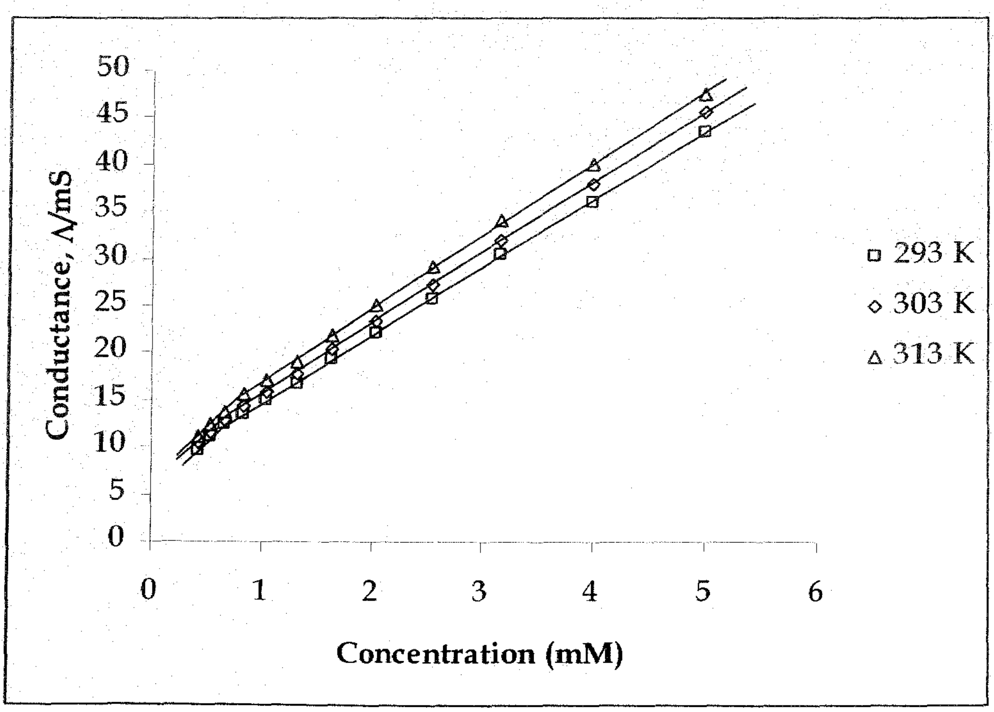

Figure 4.54: Conductance, Λ, of Tetraethylammonium dodecyl benzene sulfonate (TEADBS) in aqueous TEABr solution [TEABr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

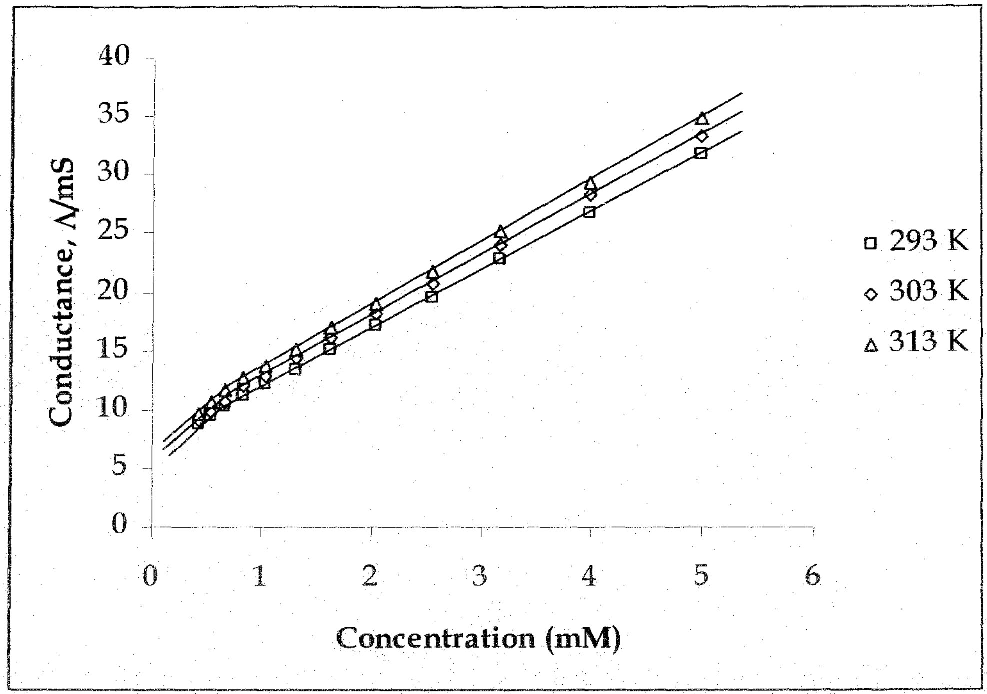

Figure 4.55: Conductance, Λ, of Tetrapropylammonium dodecyl benzene sulfonate (TPADBS) in aqueous TPABr solution [TPABr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

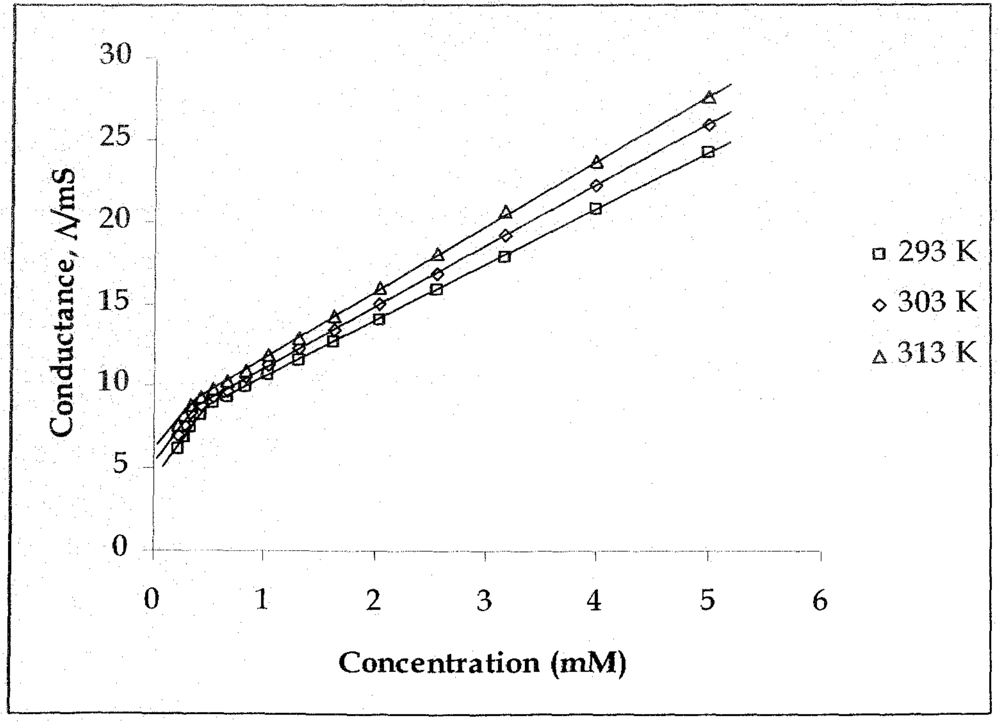

Figure 4.56: Conductance, Λ, of Tetrabutylammonium dodecyl benzene sulfonate (TBADBS) in aqueous TBABr solution [TBABr] = 0.0005(M) as a function of the surfactant concentration at different temperatures.

TMA^+ ions with smallest ionic size are the most hydrated in aqueous solution compared to that of the others in the group, viz., TEA^+, TPA^+ and TBA^+. Therefore, the hydration shell of TMA^+ ions limits the distance of closest approach to the micellar heads of DBS, thereby causing a small reduction in cmc as compared to TEA^+, TPA^+ or TBA^+ ions. In other words it appears that this salt behaves as the common non-hydrophobic electrolytes, interacting only with the TMADBS micelle surface and screening the ionic charge around that location. The higher homologues of the series, TPA^+ and TBA^+, have long hydrocarbon chains and some of these chains are supposed to penetrate in the micellar core due to hydrophobic interaction. These ions are weakly hydrated in aqueous solution because the positive charge is wrapped in the paraffin shell and are thus more hydrophobic. Therefore, the ions, in addition to the electrostatic interaction, can interact hydrophobically as well with the anionic head groups of the micelle. Hence, at a given temperature, the formation of micelles of DBS in these electrolyte media favours a cmc lowering in the order TMAB > TEAB > TPAB >TBAB. Interestingly this is also the order of their effectiveness in water structure breaking [3].

Table 4.1.1.

Micellization and surface parameters of SDBS and LDBS with symmetrical bromide salts at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Surfactant	Salt	Temp./K	Conc. of Salt/ M	Cmc^a/ mol dm^{-3} $\times 10^3$	Γ_{max}/ mol cm^{-2} $\times 10^6$	$A_{min} \times 10^{19}$	β
Sodium Dodecyl Benzene Sulfonate (SDBS)	NaBr	293	0.0005	1.45	2.92	0.57	0.288
			0.001	1.41	3.12	0.53	
			0.002	1.26	3.73	0.44	
			0.003	1.19	3.09	0.54	
			0.004	1.13	3.16	0.53	
			0.005	1.08	3.22	0.52	
		303	0.0005	1.55	3.14	0.53	0.310
			0.001	1.51	3.18	0.52	
			0.002	1.40	3.21	0.52	
			0.003	1.30	3.29	0.50	
			0.004	1.23	3.40	0.49	
			0.005	1.15	3.44	0.48	
		313	0.0005	1.63	3.40	0.49	0.352
			0.001	1.53	3.43	0.48	
			0.002	1.47	3.50	0.47	
			0.003	1.36	3.52	0.47	
			0.004	1.29	3.63	0.46	
			0.005	1.17	3.68	0.45	
Lithium dodecyl benzene sulfonate (LDBS)	LiBr	293	0.0005	1.91	2.66	0.63	0.145
			0.001	1.89	2.78	0.60	
			0.002	1.82	2.91	0.57	
			0.003	1.76	3.14	0.53	
			0.004	1.71	3.18	0.52	
			0.005	1.67	3.38	0.49	
		303	0.0005	1.94	3.30	0.50	0.115
			0.001	1.91	3.34	0.50	
			0.002	1.86	3.41	0.49	
			0.003	1.82	3.51	0.47	
			0.004	1.77	3.56	0.47	
			0.005	1.74	3.59	0.46	
		313	0.0005	1.98	3.51	0.47	0.113
			0.001	1.96	3.56	0.47	
			0.002	1.91	3.65	0.45	
			0.003	1.86	3.60	0.46	
			0.004	1.82	3.66	0.45	
			0.005	1.78	3.69	0.45	

[a] The cmc values determined by surface tension method.

Table 4.1.2.

Micellization and surface parameters of PDBS and ADBS with symmetrical bromide salts at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Surfactant	Salt	Temp./K	Conc. of Salt/ M	Cmc[a]/ mol dm^{-3} ×10^{3}	Γ_{max}/ mol cm^{-2} ×10^{6}	$A_{min}\times10^{19}$	β
Potassium dodecyl benzene sulfonate (PDBS)	KBr	293	0.0005	1.70	2.68	0.62	0.420
			0.001	1.66	2.82	0.59	
			0.002	1.50	2.88	0.58	
			0.003	1.34	2.94	0.56	
			0.004	1.24	2.98	0.56	
			0.005	1.17	3.03	0.55	
		303	0.0005	1.74	2.98	0.56	0.397
			0.001	1.69	3.03	0.55	
			0.002	1.54	3.10	0.54	
			0.003	1.40	3.15	0.53	
			0.004	1.30	3.24	0.51	
			0.005	1.22	3.33	0.50	
		313	0.0005	1.79	3.32	0.50	0.368
			0.001	1.73	3.39	0.49	
			0.002	1.58	3.47	0.48	
			0.003	1.47	3.55	0.47	
			0.004	1.43	3.62	0.46	
			0.005	1.27	3.67	0.45	
Ammonium dodecyl benzene sulfonate (ADBS)	NH_4Br	293	0.0005	1.82	2.73	0.61	0.306
			0.001	1.66	2.81	0.59	
			0.002	1.59	2.90	0.57	
			0.003	1.49	2.95	0.56	
			0.004	1.40	2.99	0.55	
			0.005	1.33	3.04	0.55	
		303	0.0005	1.85	2.97	0.56	0.262
			0.001	1.77	3.05	0.54	
			0.002	1.63	3.09	0.54	
			0.003	1.54	3.15	0.53	
			0.004	1.47	3.19	0.52	
			0.005	1.42	3.23	0.51	
		313	0.0005	1.89	3.18	0.52	0.254
			0.001	1.85	3.23	0.51	
			0.002	1.70	3.28	0.51	
			0.003	1.60	3.35	0.50	
			0.004	1.52	3.42	0.49	
			0.005	1.48	3.49	0.48	

[a] The cmc values determined by surface tension method.

Table 4.1.3.

Micellization and surface parameters of TMADBS and TEADBS with symmetrical bromide salts at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Surfactant	Salt	Temp./K	Conc. of Salt/ M	Cmc[a]/ mol dm^{-3} $\times 10^3$	Γ_{max}/ mol cm^{-2} $\times 10^6$	$A_{min} \times 10^{19}$	β
Tetra methyl ammonium dodecyl benzene sulfonate (TMADBS)	$(CH_3)_4NBr$	293	0.0005	0.93	2.66	0.62	0.326
			0.001	0.87	2.72	0.61	
			0.002	0.76	2.76	0.60	
			0.003	0.69	2.80	0.59	
			0.004	0.64	2.85	0.58	
			0.005	0.61	2.91	0.57	
		303	0.0005	0.95	2.90	0.57	0.302
			0.001	0.89	3.01	0.55	
			0.002	0.79	3.22	0.52	
			0.003	0.72	3.35	0.50	
			0.004	0.67	3.40	0.49	
			0.005	0.64	3.46	0.48	
		313	0.0005	0.98	2.83	0.59	0.306
			0.001	0.93	3.02	0.55	
			0.002	0.84	3.15	0.53	
			0.003	0.76	3.50	0.47	
			0.004	0.71	3.44	0.48	
			0.005	0.67	3.57	0.46	
Tetra ethyl ammonium dodecyl benzene sulfonate (TEADBS)	$(C_2H_5)_4NBr$	293	0.0005	0.71	2.67	0.62	0.163
			0.001	0.68	2.71	0.61	
			0.002	0.64	2.75	0.60	
			0.003	0.60	2.83	0.59	
			0.004	0.58	2.86	0.58	
			0.005	0.56	2.93	0.57	
		303	0.0005	0.75	2.91	0.57	0.169
			0.001	0.72	3.02	0.55	
			0.002	0.67	3.25	0.51	
			0.003	0.63	3.36	0.49	
			0.004	0.61	3.42	0.49	
			0.005	0.59	3.47	0.48	
		313	0.0005	0.79	2.86	0.58	0.204
			0.001	0.76	3.03	0.55	
			0.002	0.74	3.17	0.52	
			0.003	0.66	3.45	0.48	
			0.004	0.67	3.53	0.47	
			0.005	0.60	3.59	0.46	

[a] The cmc values determined by surface tension method.

Table 4.1.4.
Micellization and surface parameters of TPADBS and TBADBS with symmetrical bromide salts at various temperatures (T/K): cmc, maximum surface excess concentration, minimum areas per molecule and ionization degree.

Surfactant	Salt	Temp./K	Conc. of Salt/ M	cmc[a]/ mol dm^{-3} $\times 10^3$	Γ_{max}/ mol cm^{-2} $\times 10^6$	$A_{min} \times 10^{19}$	β
Tetrapropyl ammonium dodecyl sulfonate (TPADBS)	$(C_3H_7)_4NBr$	293	0.0005	0.63	2.69	0.62	0.167
			0.001	0.60	2.74	0.61	
			0.002	0.56	2.77	0.60	
			0.003	0.52	2.83	0.59	
			0.004	0.50	2.87	0.58	
			0.005	0.49	2.96	0.56	
		303	0.0005	0.65	2.92	0.57	0.147
			0.001	0.62	3.07	0.54	
			0.002	0.58	3.20	0.52	
			0.003	0.55	3.37	0.49	
			0.004	0.53	3.45	0.48	
			0.005	0.52	3.49	0.48	
		313	0.0005	0.68	2.87	0.58	0.119
			0.001	0.66	3.06	0.54	
			0.002	0.62	3.20	0.52	
			0.003	0.60	3.46	0.48	
			0.004	0.58	3.54	0.47	
			0.005	0.57	3.61	0.46	
Tetrabutyl ammonium dodecyl sulfonate (TBADBS)	$(C_4H_9)_4NBr$	293	0.0005	0.37	2.70	0.61	0.280
			0.001	0.36	2.75	0.60	
			0.002	0.33	2.79	0.60	
			0.003	0.30	2.84	0.58	
			0.004	0.27	2.89	0.57	
			0.005	0.24	2.97	0.56	
		303	0.0005	0.35	3.00	0.55	0.258
			0.001	0.39	3.09	0.54	
			0.002	0.36	3.21	0.52	
			0.003	0.33	3.38	0.49	
			0.004	0.30	3.52	0.47	
			0.005	0.27	3.70	0.45	
		313	0.0005	0.39	2.96	0.56	0.142
			0.001	0.39	3.07	0.54	
			0.002	0.38	3.21	0.52	
			0.003	0.36	3.55	0.47	
			0.004	0.34	3.60	0.46	
			0.005	0.32	3.65	0.46	

[a] The cmc values determined by surface tension method.

4.1.3.2. Degree of counter ion binding (β)

In aqueous solution, the presence of electrolyte causes a change in the cmc, the effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionic than for nonionics [3]. Experimental data indicate that for the first two classes of surfactants, the effect of the concentration of electrolyte, according to the mass action model, is given by Corrin-Harkins equation [43],

$$Log\,(cmc) = k - \beta \log C \tag{4.1}$$

where k is a constant, β is the counterion binding constant and C stands for the total counterion concentration. The decrease in the cmc values is mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and the consequent decrease of electrostatic repulsion between the headgroups. The Corrin-Harkins plot gives an overall value for β in a chosen range of electrolyte concentration. The aggregation number is known to vary with electrolyte concentration; β is expected to vary with cmc resulting in the nonlinearity of the above plot. However, in the study of the micellization of different dodecylbenzene sulfonate with symmetrical cations, it is observed that the plot of $log\ cmc\ vs.\ log\ C$ is almost linear which envisages that both the aggregation number and the counterion binding to the DBS micelle vary in such a way that β remains constant. Such a rationale has also been put forward by Chatterjee et. al. for the micellization of three typical ionic surfactants, Sodium dodecyl sulphate (SDS), Cetylpyridinium chloride (CPC) and Aerosol OT (AOT) in NaCl environment [19]. Similar results were also reported by Bales et. al. for the micellization of SDS and quaternary ammonium (chloride and bromide) surfactants [44,45]. The parallel slopes of the lines corresponding to different salt concentrations also indicate that the nature of the micelles is similar within the concentration range studied. A continuous increase in the β values with the increase in the size of the alkyl chain length of the TAA^+ ions is observed from TEA^+ to TBA^+. The largest ion, TBA^+, is the most strongly bound to DBS micelle with β value of 0.280 at 293 K (Table 4.1.1 - 4.1.4). As discussed earlier, a different order is observed for the TMA^+ ion which may be due to the smallest size among all the TAA^+ ions. Therefore, the hydration shell of TMA^+ ions limits the distance of closest approach to the micellar heads of DBS, thereby causing a small increase in β values as compared to TEA^+, TPA^+ or TBA^+ ions. A high degree of counterion binding reduces the repulsive forces between the surfactant head groups of the ionic micelles to a great extent. As has been already mentioned, for the higher homologues of tetraalkyl ammonium ions, the increasing hydrophobic interactions between the alkyl parts of the electrolytes and the DBS micellar core results in greater charge screening of the head groups and this leads to lower cmc as well as higher β values. The increase in the β values on moving from TEA^+ to TBA^+ is due mainly to the increased hydrophobic interaction between the alkyl parts of both the surfactant and the added electrolyte. For inorganic ions including ammonium ions, similar result is observed due to the increase in size of the cations. The cation with largest size show highest β values ensures most strongly bound to DBS moiety. Here, the order of β values is $K^+ > Na^+ > NH_4^+ > Li^+$. The hydration of the inorganic ions also has a definite role in determine the counter ion binding constant values. The ions with higher degree of hydration, lesser will be the interaction with the micelle. This explains the anomalies between Li^+ and NH_4^+ ions in respect of the above. Γ_{max} is a useful measure of the effectiveness of adsorption of the surfactant at air-solution interface, since it is the maximum value that adsorption can attain. It is well known that the air-solution interface of a surfactant solution is well populated by the adsorbed molecules. The general trend of Γ_{max} with increase of temperature is a slight decrease in its value for both nonionic and anionic surfactants but there is some other cases are also reported where opposite trend is observed [46-49]. In the present case, slight increase in the values of Γ_{max} is observed which may be due to the effectiveness of adsorption. For dodecyl benzene moiety with varying counterions and in presence of symmetrical salts, a slight increase is observed which may be due to the lower hydration effect of the dodecyl benzene sulfonate part of surfactants at higher temperature and hence increasing tendency to move to the air-liquid interface. The benzene ring in the surfactants may also be partially responsible for this result causing steric inhibition during adsorption as has already been mentioned previously. The area per molecule at the air / water interface gives the information on the packing and orientation of the adsorbed surfactant molecules when compared with the dimensions of the molecule obtained from the molecular model data. The minimum area per molecule (A_{min}) is obtained following the same procedure as described in chapter III. With increase in temperature, the A_{min} value shows the inverse trend as that of Γ_{max}.

4.1.3.3. Thermodynamics of micellization in presence of salts

Theory

General trend of the plot of cmc against temperature has the parabolic shape typical for ionic surfactants. The cmc decreases, reaches a shallow minimum (cmc*) and then increases as the temperature is raised. But other trend of cmc is also observed for surfactant systems like sodium dodecyl benzene sulfonate where the cmc increases with increase in temperature, as also reported in the literature [50]. For ionic surfactants, the cmc is related to the standard Gibbs free energy change, ΔG^0_{mic}, by the expression

$$\Delta G^0_{mic} = (1 + \beta)RT\, ln\, X_{cmc} \tag{4.2}$$

where X_{cmc} is the mole fraction of the surfactant in the liquid phase at the cmc and β is the fraction of the counterions bound to the micelles. The standard state is a hypothetical system with a unit mole fraction of the surfactant at cmc. From the knowledge of the temperature dependence of cmc, the enthalpy of micellization, ΔH^0_{mic}, can be evaluated from the Gibbs-Helmholtz relation,

$$\Delta H^0_{mic} = -(1 + \beta)RT^2 \left(\frac{\partial lnX_{cmc}}{\partial T}\right)_p \tag{4.3}$$

Equation 4.3 assumes that β does not vary much with temperature. However, β is not strictly temperature independent and the more appropriate form of equation 4.3 should be,

$$\frac{-\Delta H^0_{mic}}{T^2} = (1 + \beta)R \left(\frac{\partial lnX_{cmc}}{\partial T}\right)_p + R \ln X_{cmc} \left[\frac{\partial(1+\beta)}{\partial T}\right] \tag{4.4}$$

Because the variation of β with temperature is not well defined and is devoid of any general trend, the quantity $\left[\frac{\partial(1+\beta)}{\partial T}\right]$ is difficult to determine experimentally [54]. Therefore, at least to gain qualitative information regarding the thermodynamics of the present system, equation 4.3 has been applied at the appropriate β. Moreover, equation 4.3 has been widely used as an indirect method for the determination of ΔH^0_{mic} as the values so calculated agree well with those obtained from the direct calorimetric measurement [51,52]. The term $\left(\frac{\partial ln X_{cmc}}{\partial T}\right)$ is calculated by fitting a second-order polynomial to plots of $\partial ln X_{cmc}$ vs temperature and taking the corresponding temperature derivative. Thus,

$$\frac{dlnX_{cmc}}{dT} = b + 2aT \qquad (4.5)$$

The entropies of micelle formation, ΔS^0_{mic}, are determined from the equation

$$\Delta S^0_{mic} = \frac{\Delta H^0_{mic} - \Delta G^0_{mic}}{T} \qquad (4.6)$$

Table 4.5

Thermodynamic parameters of micellization for DBS with different counterions in presence of symmetrical bromide salts at various temperatures: cmc, Standard Gibb's free energy, Enthalpy and Entropy.

Surfactant	**Salt**	**Conc/ M**	**T/K**	**cmc[b]/ mol dm^{-3} $\times 10^3$**	**α**	**$-\Delta G_m^0$ /(kJmol^{-1})**	**$-\Delta H_m^0$ /(kJmol^{-1})**	**ΔS_m^0 /(JK^{-1}mol^{-1})**
Sodium dodecyl benzene sulfonate	NaBr	0.0005	293	1.53	0.7922	31.1	22.4	29.67
			303	1.60	0.8378	30.7	23.7	23.06
			313	1.64	0.8795	30.4	25.1	16.94
Lithium dodecyl benzene sulfonate	LiBr	0.0005	293	1.89	0.8442	28.9	20.1	30.14
			303	1.94	0.9077	28.2	20.8	24.48
			313	1.97	0.7945	32.1	25.1	22.42
Potassium dodecyl benzene sulfonate	KBr	0.0005	293	1.69	0.6913	33.1	29.0	14.16
			303	1.70	0.9233	28.1	26.2	6.50
			313	1.76	0.7770	32.9	32.5	1.31
Ammonium dodecyl benzene sulfonate	NH_4Br	0.0005	293	1.64	0.8420	29.1	18.8	35.18
			303	1.67	0.8571	29.7	20.4	30.67
			313	1.62	0.8572	30.6	22.3	26.46
Tetra methyl ammonium dodecyl benzene sulfonate	$(CH_3)_4NBr$	0.0005	293	0.91	0.8612	30.5	21.0	32.46
			303	0.94	0.8832	30.9	22.7	26.99
			313	0.98	0.9047	31.2	24.5	21.48
Tetra ethyl ammonium dodecyl benzene sulfonate	$(C_2H_5)_4NBr$	0.0005	293	0.73	0.8075	32.7	13.0	67.52
			303	0.74	0.8027	33.8	14.3	64.52
			313	0.79	0.7973	34.9	15.7	61.48
Tetra propyl ammonium dodecyl benzene sulfonate	$(C_3H_7)_4NBr$	0.0005	293	0.60	0.8260	32.6	9.0	80.39
			303	0.65	0.8183	33.8	9.9	78.96
			313	0.69	0.8347	34.3	10.6	75.76
Tetrabutyl ammonium dodecyl benzene sulfonate	$(C_3H_7)_4NBr$	0.0005	293	0.29	0.6913	38.0	22.3	56.58
			303	0.27	0.7278	38.4	23.8	48.23
			313	0.31	0.8023	37.7	24.5	40.02

[b] The cmc values determined by conductivity method.

This theory is very much applicable for surfactant with high cmc value where the temperature dependence of cmc shows the parabolic nature. But in the present study, the surfactant with different counterions does not show this type of parabolic nature as a function of temperature. Furthermore, the cmc of the dodecyl benzene sulfonate is very low (for sodium-DBS ~ 3.0 mM) and it further decreases with the addition of electrolyte and So, the determination of cmc in high salt concentration with the help of conductivity is very difficult as because the conductivity due to the electrolyte may merge that of the surfactant. In this chapter, we are mainly concerned with the surface activity of the surfactant at the air/water interface only in presence of the electrolyte and also presented a general view of the different thermodynamic parameters with the help of mass-action model as described in the previous chapter only due to the fact that these are the systems which are not available in the literature except sodium dodecyl benzene sulfonate. At the time of calculating by the previous model, the concentration of the electrolyte is kept very low, viz., 0.0005 (M) so that the effect of conductivity of electrolyte is very small and we can get the general overview of the parameters of micellization of the surfactant. The values of ΔG_{mic}^{0}, $\Delta H_{mic}^{0}$and ΔS_{mic}^{0} in the presence of 0.0005 M corresponding bromide salts have been presented in table 4.1.5.

The temperature dependence of micellization of DBS with different counterions in presence of bromide salts (0.0005 M) has been studied to determine the thermodynamic parameters of micellization. The change in cmc of DBS with different counterions in pure aqueous solution as a function of temperature is small. Such weak temperature dependence of cmc in aqueous solution has been observed for all the dodecyl benzene sulfonate surfactant and already mentioned in the previous chapter. Recently it has been shown that the double tailed anionic surfactant, AOT, also display similar characteristics in presence of electrolytes [29]. The dependence of cmc on temperature further weakens in solutions of symmetrical ions suggesting the solubilization of the additives in the hydrocarbon environment of the surfactant micelle.

Addition of bromide salts to the corresponding surfactant show substantial decrease in the critical micellar concentration. The variation of $\Delta G_{mic}^{0}$with temperature is small for all the systems investigated. According to the pseudo-phase model the minimum in the cmc in the ln X_{cmc} vs. T plot should correspond to a minimum in the $(\Delta G_{mic}^{0}/T)$ curve. However, the absence of such a minima for the present dodecyl benzene sulfonate system may be due to the dominance of the RT term over ln X_{cmc} in equation 4.3 [53].

The value of ΔH_{mic}^{0} increases with the increase in temperature in all the case. The enthalpy of micellization shows negative values in all the cases indicating that the formation of micelles is an exothermic process. The higher negative values of enthalpy at higher temperatures probably suggest the importance of London-dispersion interactions as an attractive force contribution for micellization.

The entropy of micellization for different systems are all large and positive except potassium dodecyl benzene sulfonate, indicating that the micellization process is entropy dominated. The large positive values of ΔS^0_{mic}, which increases with the increase in the size of the added electrolyte, suggests that the micellization process in these salty solutions are governed primarily by the entropy gain and the driving force for the process is the tendency of the hydrophobic groups of dodecyl benzene sulfonate to transfer from the TAA^+ rich solvent to the interior of the micelle. Studies on the effect of counterions on clouding of charged surfactants are rare in the literature the present study gives a brief introduction in this direction.

4.1.3.4. Thermodynamic properties

A critical examination of the Table 4.1.1 - Table 4.1.4 in dodecyl benzene sulfonate moiety, it is observed that the headgroups ($-SO_3^-$) are hydrated due to their polar nature. Water molecules can form stable hydrogen bonds with the head group of the surfactants, and the counterions are distributed close to the air/water interphase. Presence of salt may screen electrostatic repulsion between headgroups and decrease the thickness of the interfacial water layer. The counterions may penetrate into the hydration shell of the surfactant headgroups and restrict the mobility of the water molecules situated in this area. It is known that the inorganic ions and also the ammonium ions interact very strongly with an anionic surfactant. Therefore, it is meaningful to investigate the interaction between an anionic surfactant and inorganic salt and also ammonium salts. It is observed by theoretical measurements of sodiumdodecylbenzene sulfonate that the counter ions are distributed close to the air/water interface, near the oppositely charged sulfonate headgroups on the addition of salts to the surfactant systems. The headgroups are hydrated and localized in the water layer, whereas the tail groups (carbon chain) are excluded from the interface. In dodecylbenzene sulfonate, most of the sulfonate group is hydrated due to its polar nature. Only a small fraction of water molecules penetrate into the hydrocarbon tail part of the surfactants, suggesting that headgroups and benzene ring groups help water molecules penetrate into the monolayer film. In the bulk phase, water is a highly structured liquid due to an extensive network of hydrogen bonds, whereas water molecules at the interface region undergo volume expansion and a decrease of its density. The thickness of the interfacial layer is decreased when salts are added into surfactant systems. The reason is that the positive ions of the salt can enter into the interfacial region and destroy the hydrated layer. Water molecules in the interfacial layer are displaced into the bulk phase. The volume effect is also important on the addition of salt to surfactant systems. Smaller positive ions may enter easily more into the region of headgroups as compared with larger ones.

4.2. Dodecyl Benzene Sulfonate in presence of Ethylene glycol in aqueous medium

4.2.1 Introduction and review of the previous work

The most interesting aspects of these microheterogeneous entities are their ability to accommodate organic molecules [54-57]. As we know, the London dispersion forces are the main attractive forces in the formation of the micelle and the micelle formation is supposed to be the result of hydrophobic interaction. So, it is understood that the ionic surfactants form micelle by self-association due to the hydrophobic and electrostatic forces. Alcohols have the ability to solubilize hydrophobic molecules very easily due to the increased flexibility of the micellar membrane [58]. Several works on the effect of alcohols on the surfactant micellization have been carried out by different researchers with different types of alcohols. Also, the size and shape of micelle formed by a number of commonly used surfactants and co-surfactants have been investigated earlier [59,60].

The structural changes in presence of different alcohols are very interesting and are performed by many researchers for the surfactant sodium dodecyl sulfate. Førland et al. reported that propanol successively breaks down the micelles while pentanol brings about a structural change towards large worm like aggregates of sodium dodecyl sulfate. Butanol shows a highly complex behaviour on the structure of the micelles and can decrease and increase the size of the aggregates, depending on the added alcohol concentration [61]. Many researchers became interested in mixed alcohol-water systems particularly due to their importance in the preparation of microemulsions [62,63]. Reports of Onori et at. [64-66] 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 benzene sulfonate (SDS) and Triton X-100 micelles in the presence of alcohol was investigated by previous workers [67-72] but the works on the behaviour of sodium dodecyl benzene sulfonate with ethylene glycol are rare. Micellization studies with diols having the same number of carbons but different molecular structure have also been carried out [73,74]. Carnero Ruiz [75] 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 mixture 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 in recent studies [76]. Similar reports are available for middle and short chain alcohols also [77-79]. It was suggested that for ionic surfactants, the cmc is related by the following equation [80]:

$$\log(cmc) = Z(1-\beta)\left[log\frac{2000\pi\sigma^2}{\varepsilon_r RT} - log c_i\right] + \left[\frac{\Delta G_{(-CH_2-)}}{2.303RT}\right]n + B \qquad (4.7)$$

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 4.7 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 cmc is lowered. But due to the presence of alcohol the dielectric constant of the solvent decreases considerably, which predicts 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 parameters of micellization process in water-alcohol binary mixtures. In this respect ethylene glycol (EG) showed the reverse effect compared to the other alcohols and this may be explained by its higher dielectric constant, small hydrophobic surface and greater capability of hydrogen bond formation. Sjöberg [79] 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. Recently, there has been a considerable amount of research dealing with the effects of nonaqueous polar solvents on the micellization process [81,82]. 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.

It has been proposed that the ability of a solvent to form hydrogen bonds is a necessary condition for the formation of micelles. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process [83]. Ethylene glycol (EG) is of particular interest in that it has many characteristics similar to those of water. The molecule is small and can form hydrogen-bonded networks similar in nature to those of water but considerably different in the details of the structure. Ethylene glycol also possesses a high cohesive energy and a fairly high dielectric constant. Because of the similarities between water and ethylene glycol, the study of the latter is important from the point that it provides a better understanding of the structure of liquids on the micellization process [84]. In this connection the influence of very common short chain alcohols, viz. ethylene glycol on the micellization of DBS with different counterions in aqueous medium are studied in the present investigation within the temperature range of 293-313K. Though it is said that the highly water-soluble alcohols such as ethylene glycol dissolve mainly in the aqueous bulk solution [85-86], there are number of reports [87-88] 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 [89]. In recent times, some surface active drugs are in use. The understanding of the thermodynamic aspects of the surface active drug is important from both fundamental as well as practical standpoints because the thermodynamic parameters governing the aggregate formation are the key to effective physical processing [90]. To elucidate the effects of ethylene glycol on the micellization process, it is useful to study the behaviour of the molecule as a cosolvent on model compounds. Most of the investigation in recent times using ethylene glycol as a cosolvent or as a pure solvent were carried out with ionic surfactants [84,91-103]. Micellization of nonionic surfactants in non-aqueous polar solvents, and in particular ethylene glycol, has been less frequently investigated [104-108]. Sometimes, the size is also increased due to mixing of cosolvents which is due to decrease hydration of the polar head groups for the interaction between water and cosolvents resulting in a reduction of the curvature of the aggregate [108].

4.2.2. Materials and Methods

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 293K to 313K. The temperature was maintained in a thermostated double-glass water jacket by the flow of constant temperature with in ±0.01K. The alcohol (Merck) associated in the experiments are used after necessary distillation as described elsewhere [109]. To check the reproducibility of the results, SDBS with different proportion of the alcohols are performed in spectro-photometrically by an UV-visible Spectrophotometer. Absorption spectra were recorded on a double beam Jasco V-530 uv/vis spectrophotometer (Japan). The spectra were recorded with a quartz cell having 1mm optical path length. The temperature of the whole experiment was maintained at 20^0C with a thermostatic arrangement coupled with the spectrophotometer.

4.2.3. Results and discussion

Similar to the previous measurements the cmc values of the DBS with different counterions in the presence of ethylene glycol, a hydrophilic alcohol, were determined by the 'break points' of the conductance vs. concentration plots (figure 4.57 - 4.80). The cmc and the other related thermodynamic parameters of DBS with different counter ions are given in Table 4.2.1 and Table 4.2.2 respectively. All the thermodynamic parameters including cmc are determined by similar procedure as described in the previous section (chapter III). As expected, the cmc values increase considerably upon addition of ethylene glycol. The larger cmc at higher ethylene glycol content is a result of the presence of a structure-breaking solute. Structure breaking solutes in the aqueous phase may disturb the hydrophobic group causing a decrease in hydrophobic effect. Ethylene glycol in the present study is acting as a cosolvent and a structure-breaking solute, decreases the hydrophobic effect and possibly that is the driving force for micellization. The increase in cmc values with temperature at a given concentration of ethylene glycol is attributed to the disruption of the solvent structure with the increase in temperature. For SDBS-ethylene glycol-water system [10%, 20% and 30% ethylene glycol (w/w)], the cmc was determined conductometrically. At alcohol concentrations lower than 0.1mM, the change in conductivity is less pronounced. As presented out 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 the cases the process of micelle formation is energetically favoured and this is supported by effective negative value of ΔG_m^0. With increase in temperature, the ΔG_m^0 value becomes more negative, which is a general trend as found in Table 4.2.1 and Table 4.2.2. This indicates that the micellization process is more favourable with increase in temperatures. With increase in temperature the cmc values increases with the present additives. This indicates that the change in the magnitude of the logarithm of the cmc term is more than compensated by the change in the values of the RT term. The other two thermodynamic parameters viz. ΔH_m^0 and ΔS_m^0 also show their necessary contribution in favour of micellization process. The entropy of micellization is positive in water and becomes less positive in the presence of increasing amounts of ethylene glycol. In a prewater medium, the presence of hydrated ionic groups of the surfactant introduces structure in the liquid water phase. Removal of the surfactant monomers due to micellization results in an overall increase in randomness and high entropy values. In the presence of the additive, the entropy changes are not as pure water indicating that the additives lowers the energy of the three-dimensional water structure due to its structure breaking ability. Based on the relation between cmc and the thermodynamic functions the effect of alcohols on micellization can also be well explained. Table 4.2.1 and Table 4.2.2 suggests that in aqueous-alcohol medium comparatively greater negative values of ΔH^0_m contributes to the negative ΔG^0_m for the micellization of DBS moiety with different counterions when compared with aqueous medium (Table 4.2.3). But this phenomenon is somehow comparatively less pronounced than other anionic surfactants due to its more hydrophobic benzene moiety [109].

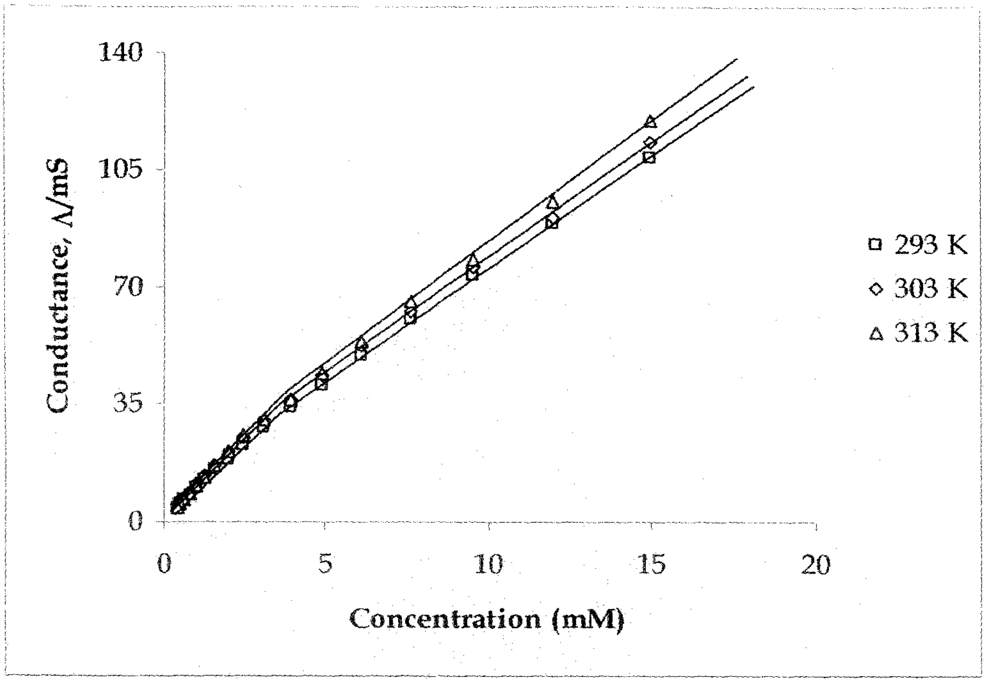

Figure 4.57: Conductance, Λ of SDBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

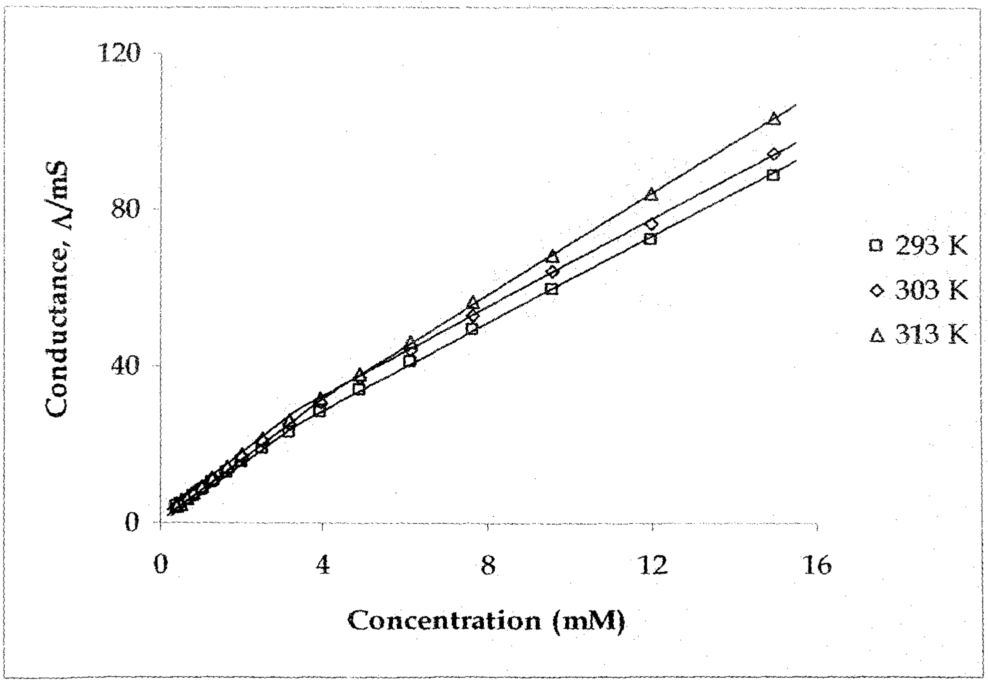

Figure 4.58: Conductance, Λ of SDBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

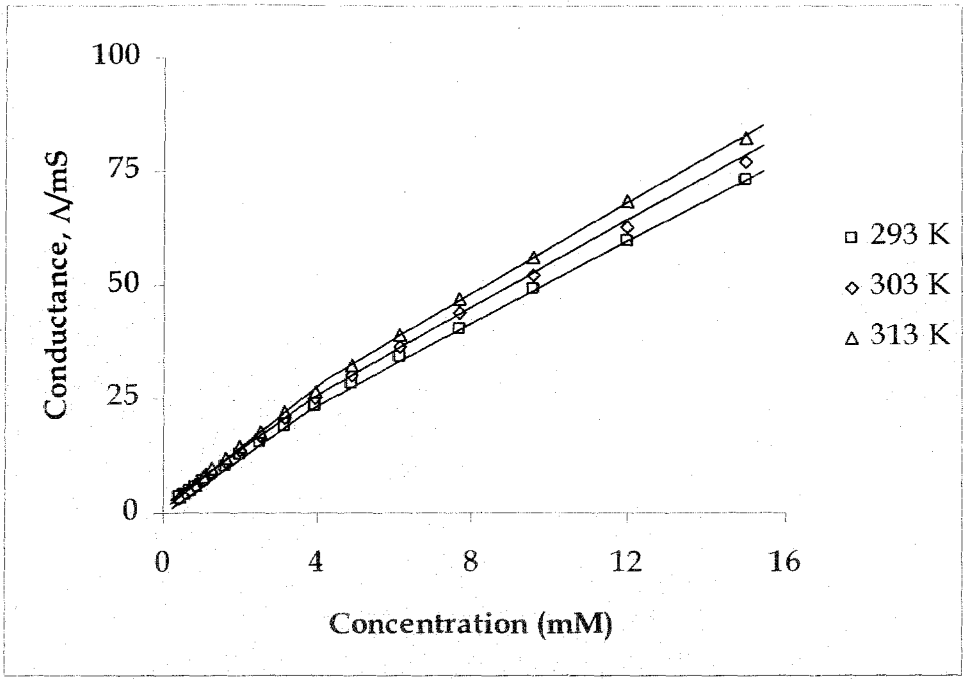

Figure 4.59: Conductance, Λ of SDBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

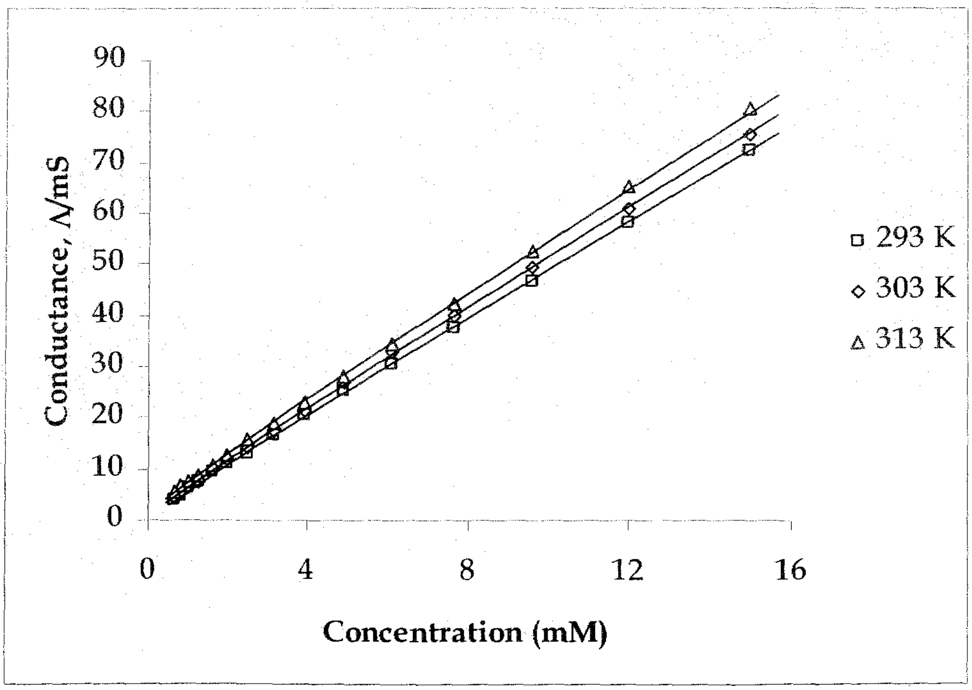

Figure 4.60: Conductance, Λ of LDBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

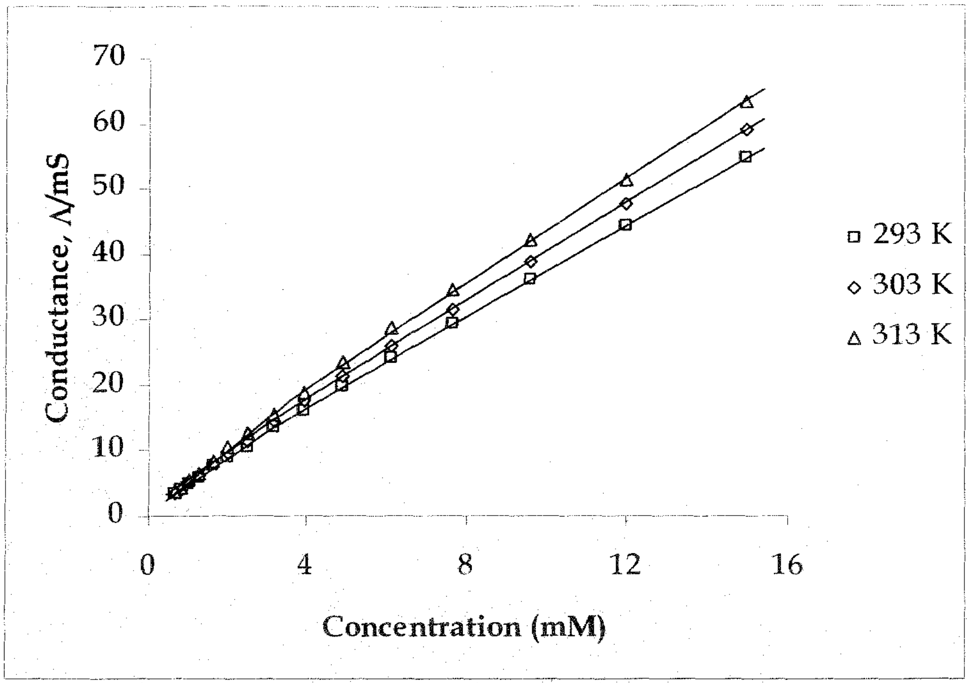

Figure 4.61: Conductance, Λ of LDBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

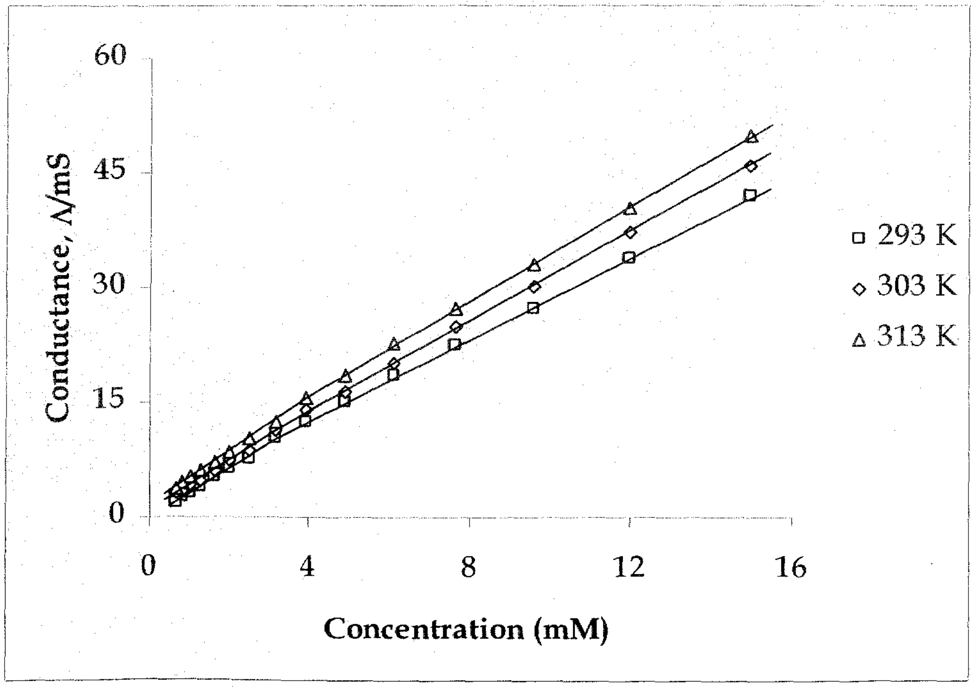

Figure 4.62: Conductance, Λ of LDBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

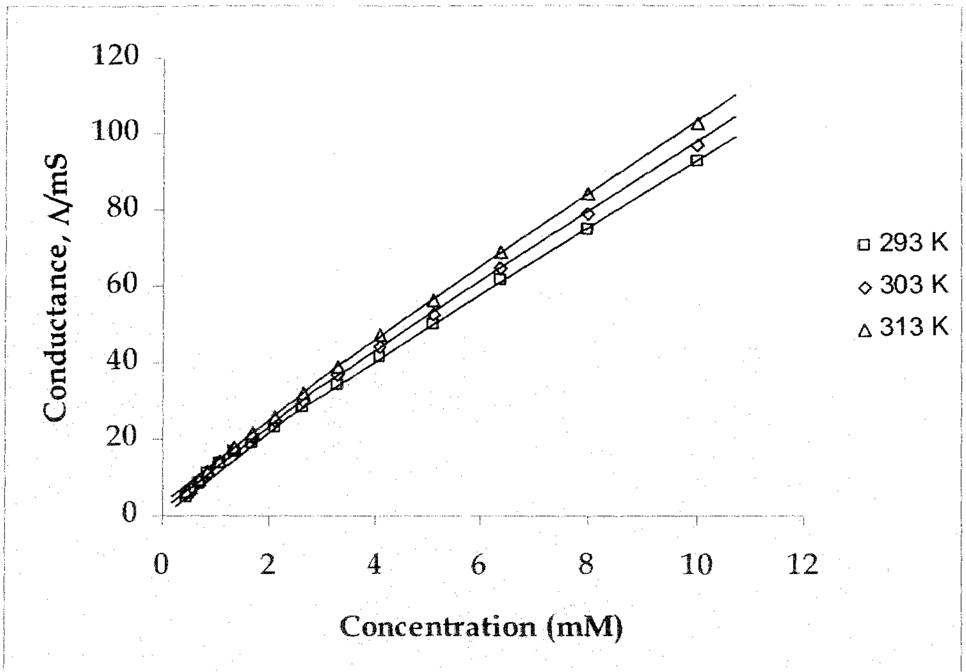

Figure 4.63: Conductance, Λ of PDBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

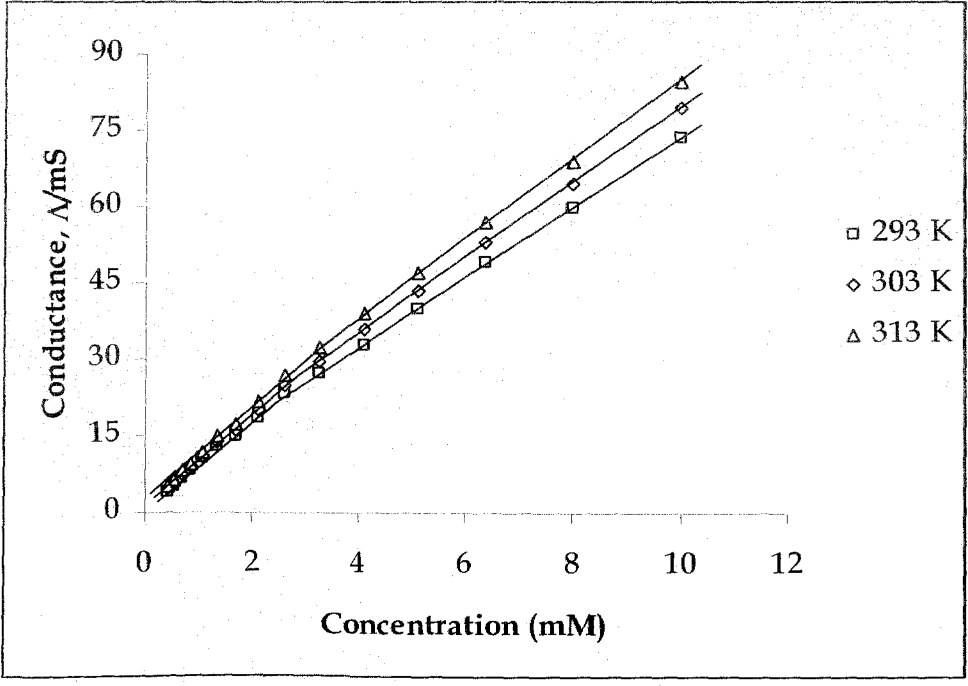

Figure 4.64: Conductance, Λ of PDBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

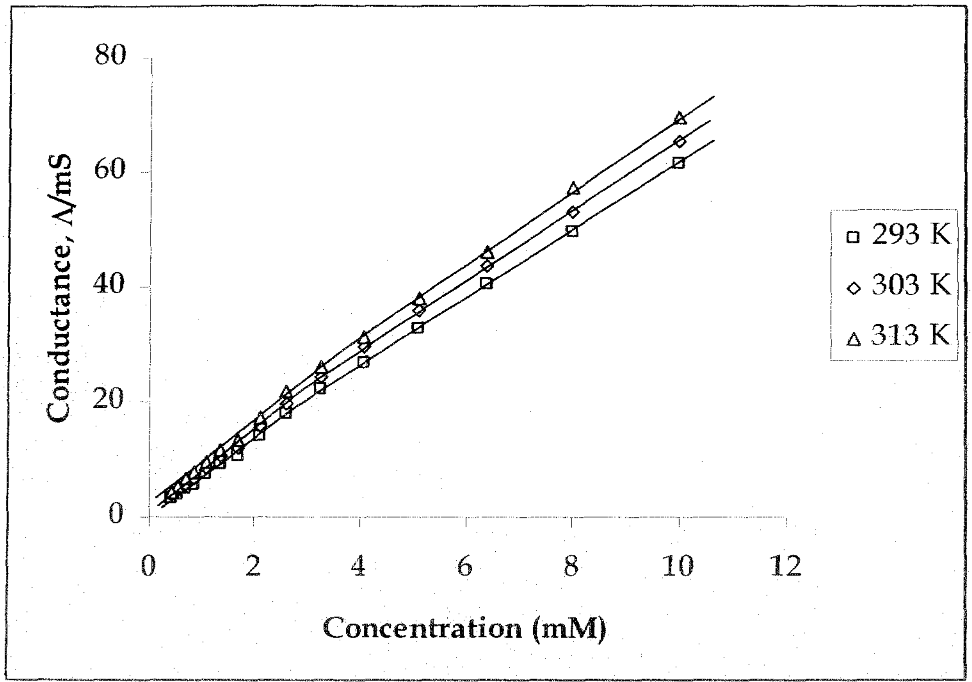

Figure 4.65: Conductance, Λ of PDBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

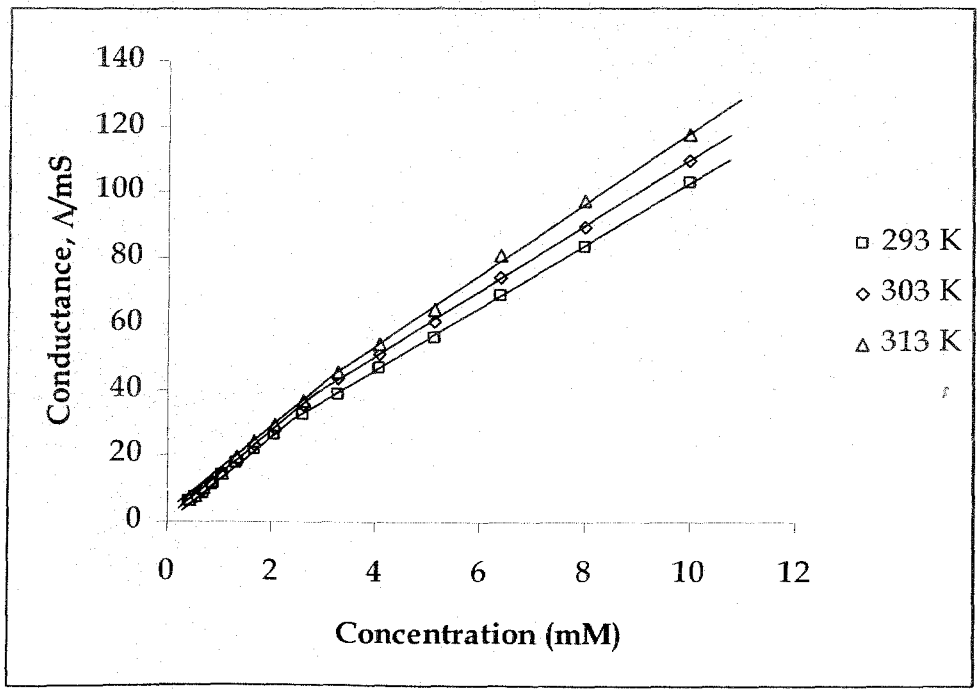

Figure 4.66: Conductance, Λ of ADBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

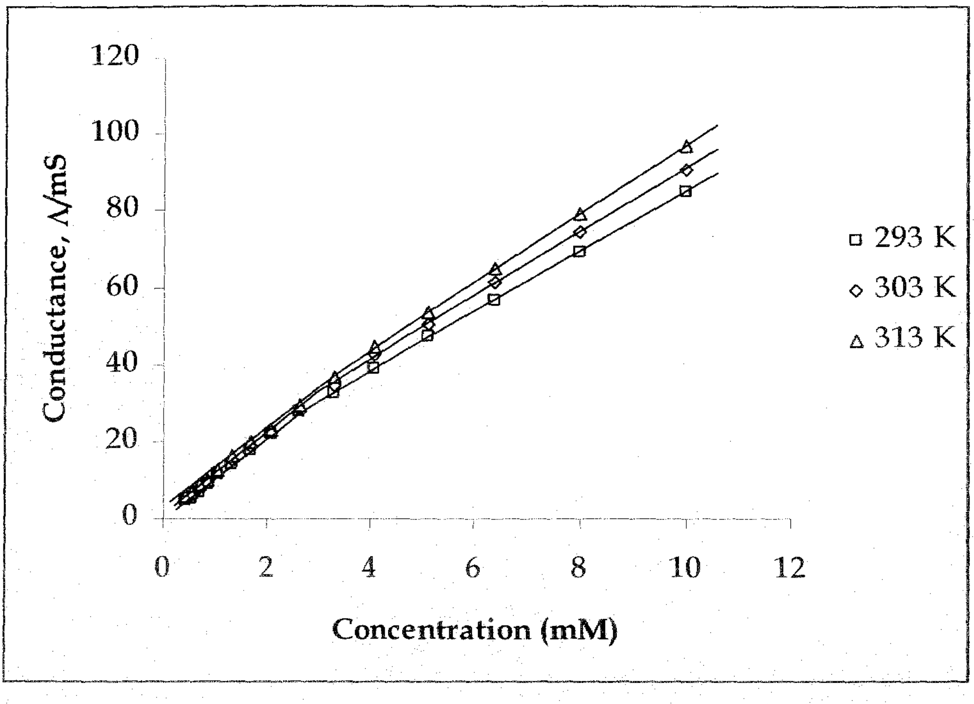

Figure 4.67: Conductance, Λ of ADBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

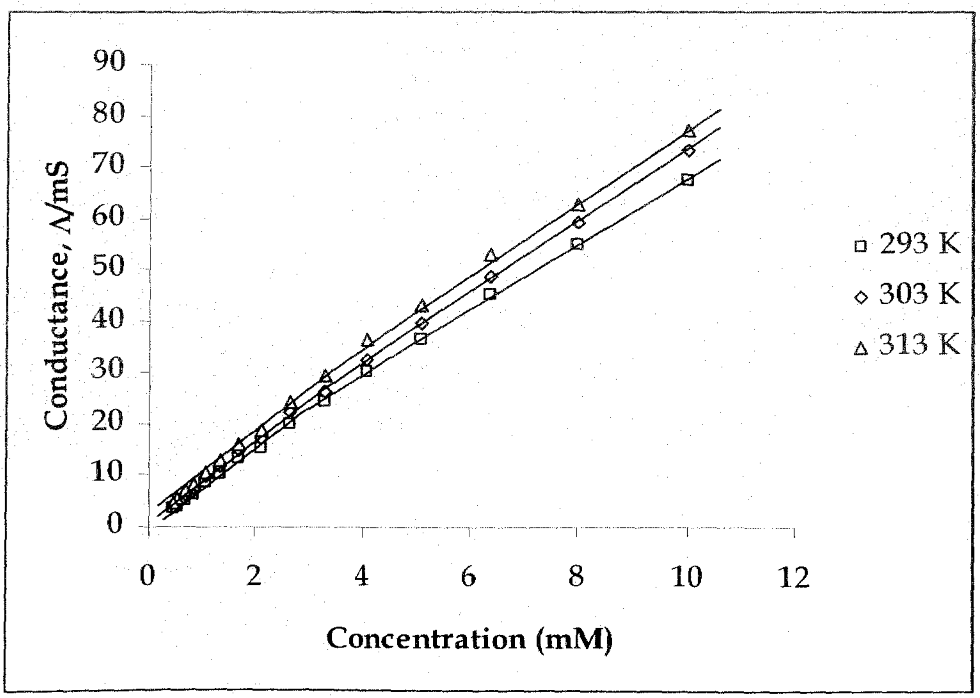

Figure 4.68: Conductance, Λ of ADBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

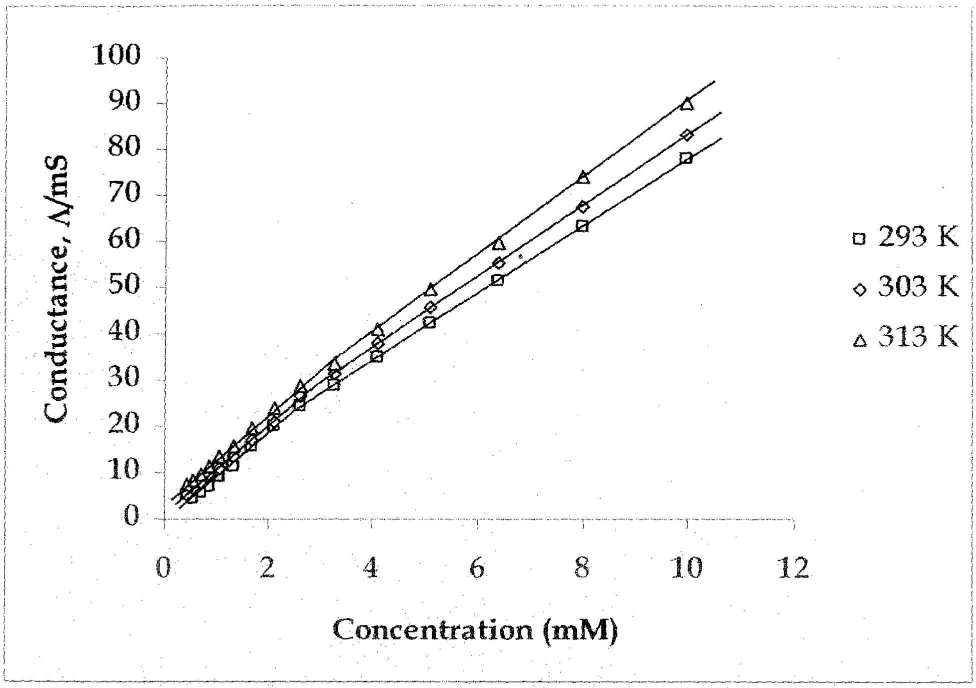

Figure 4.69: Conductance, Λ of TMADBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

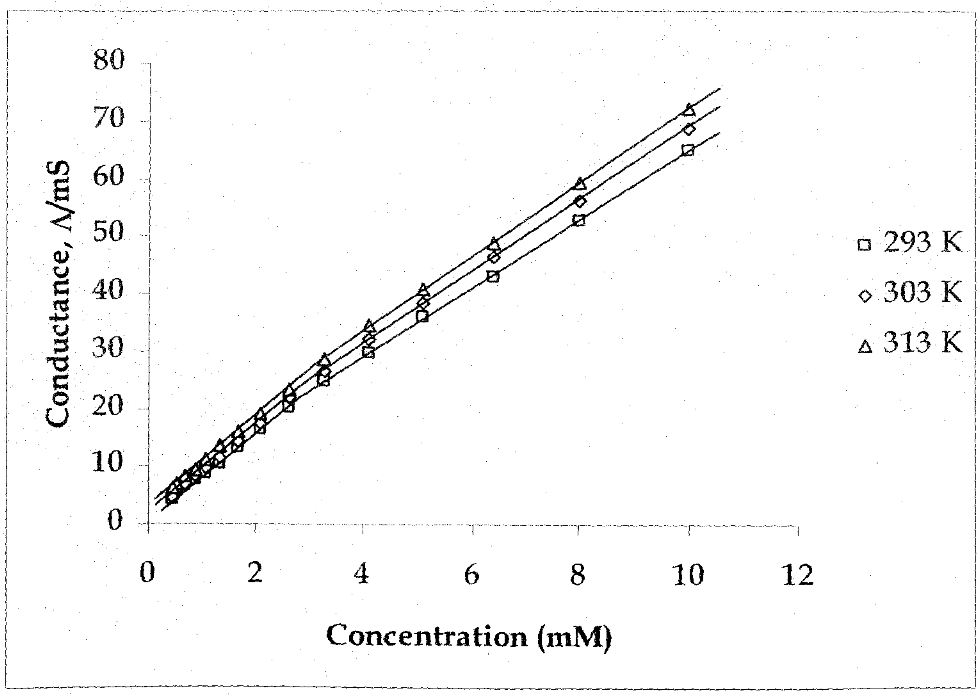

Figure 4.70: Conductance, Λ of TMADBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

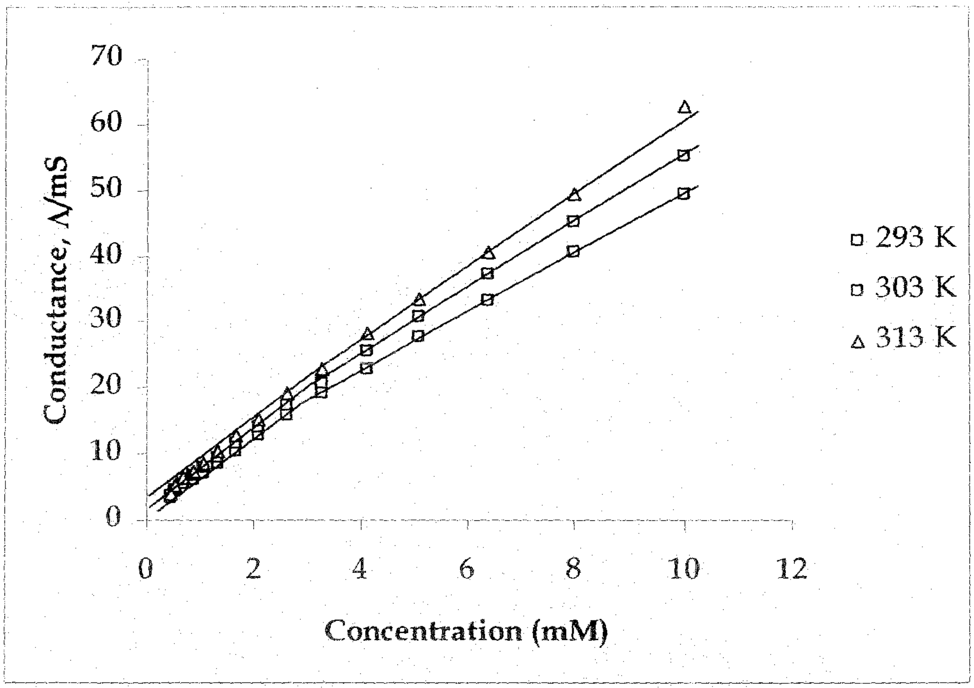

Figure 4.71: Conductance, Λ of TMADBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

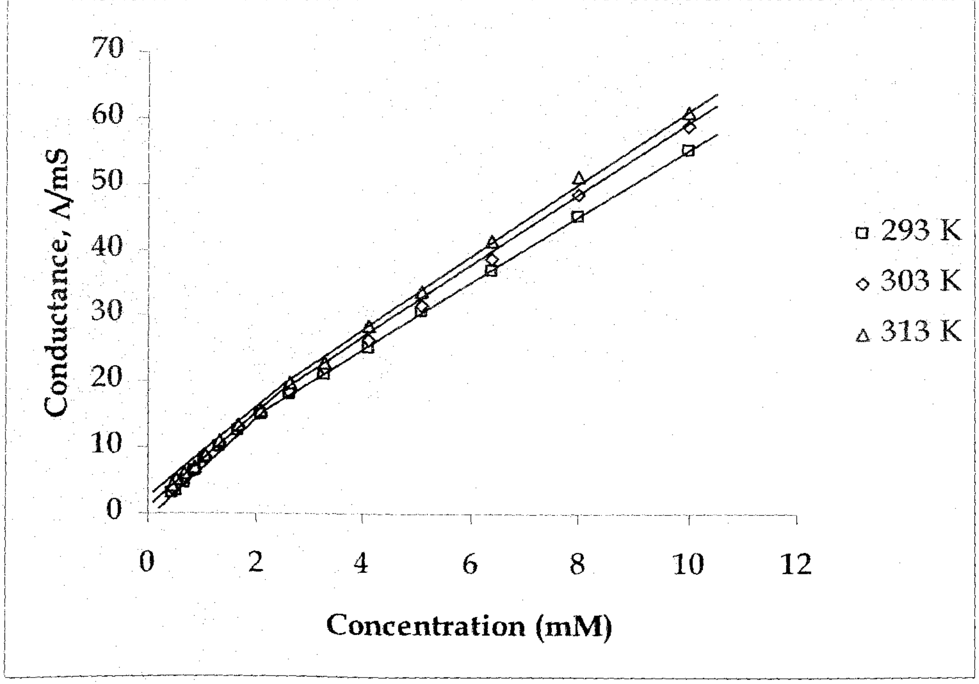

Figure 4.72: Conductance, Λ of TEADBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

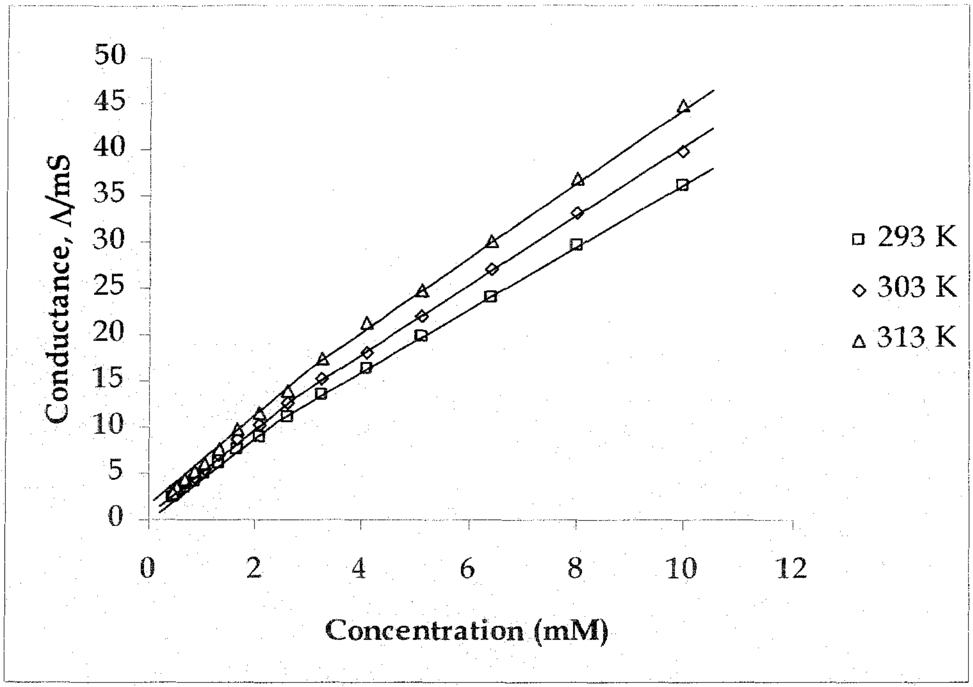

Figure 4.73: Conductance, Λ of TEADBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

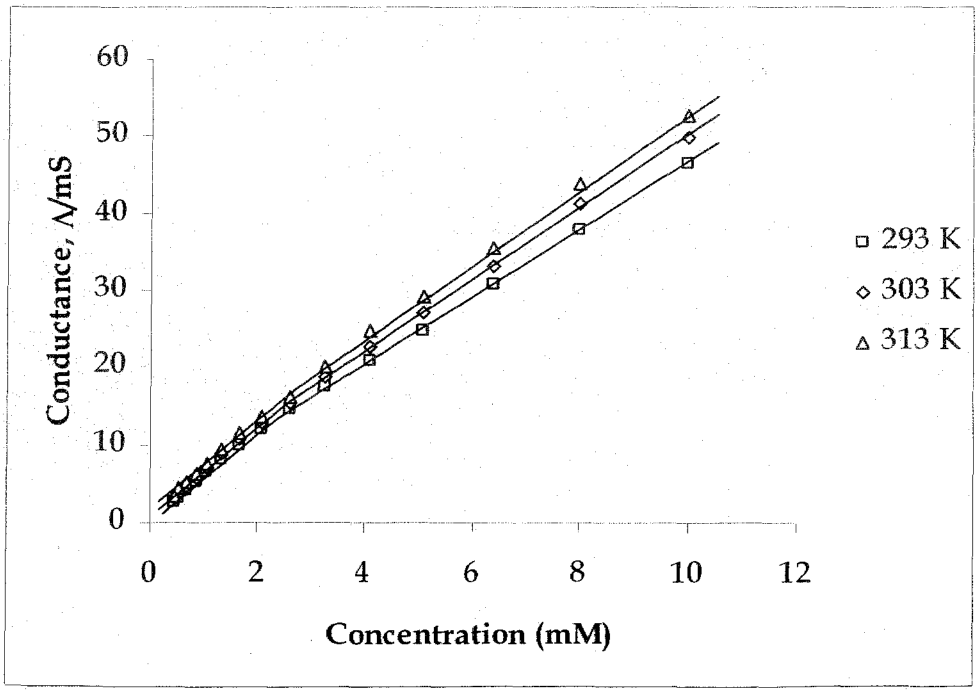

Figure 4.74: Conductance, Λ of TEADBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

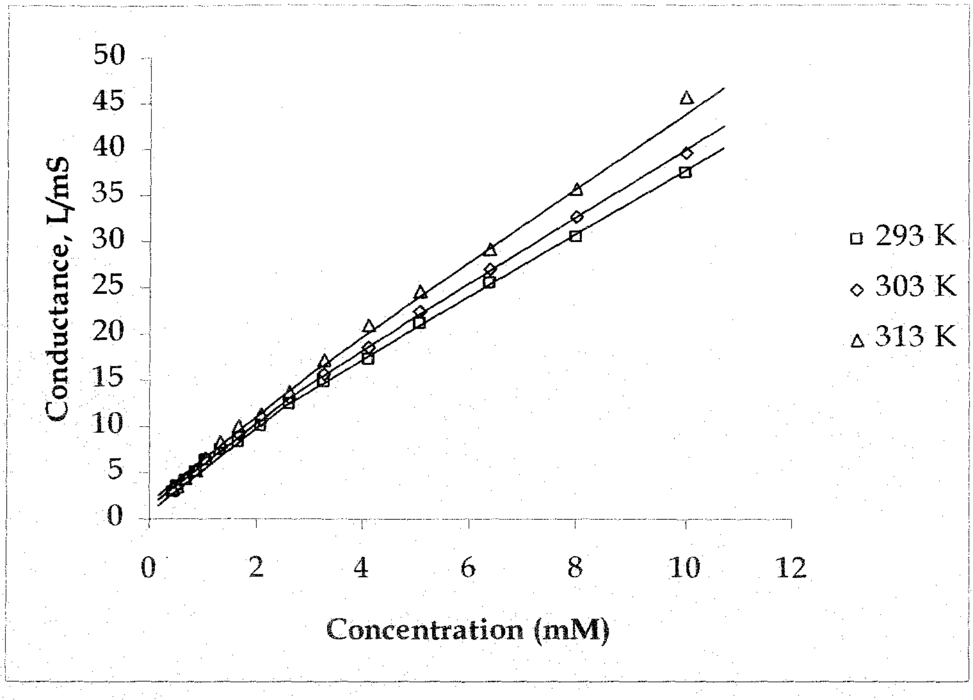

Figure 4.75: Conductance, Λ of TPADBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

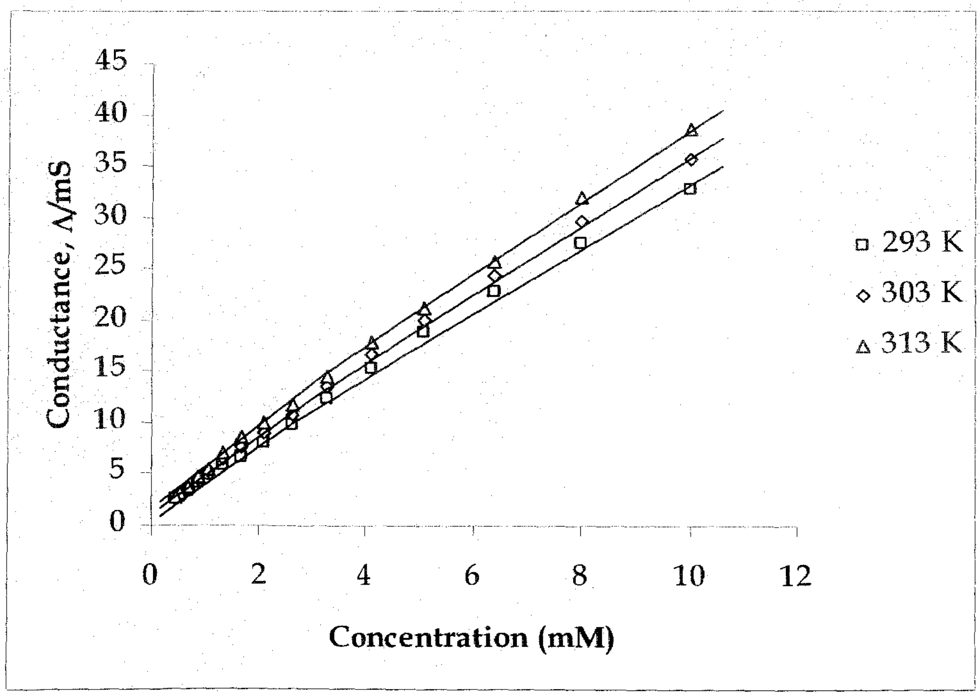

Figure 4.76: Conductance, Λ of TPADBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

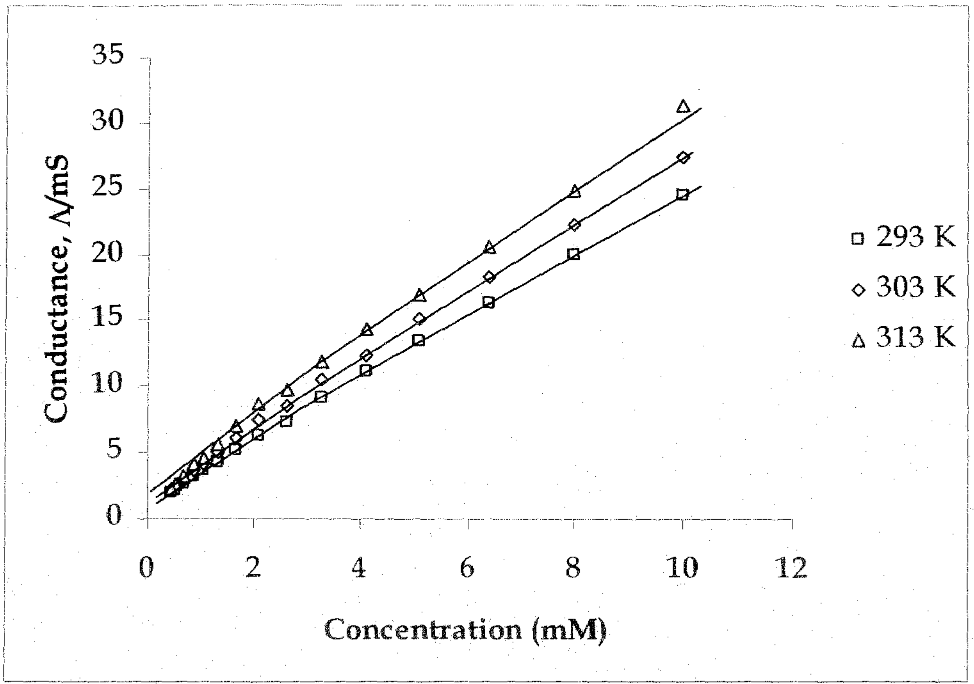

Figure 4.77: Conductance, Λ of TPADBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

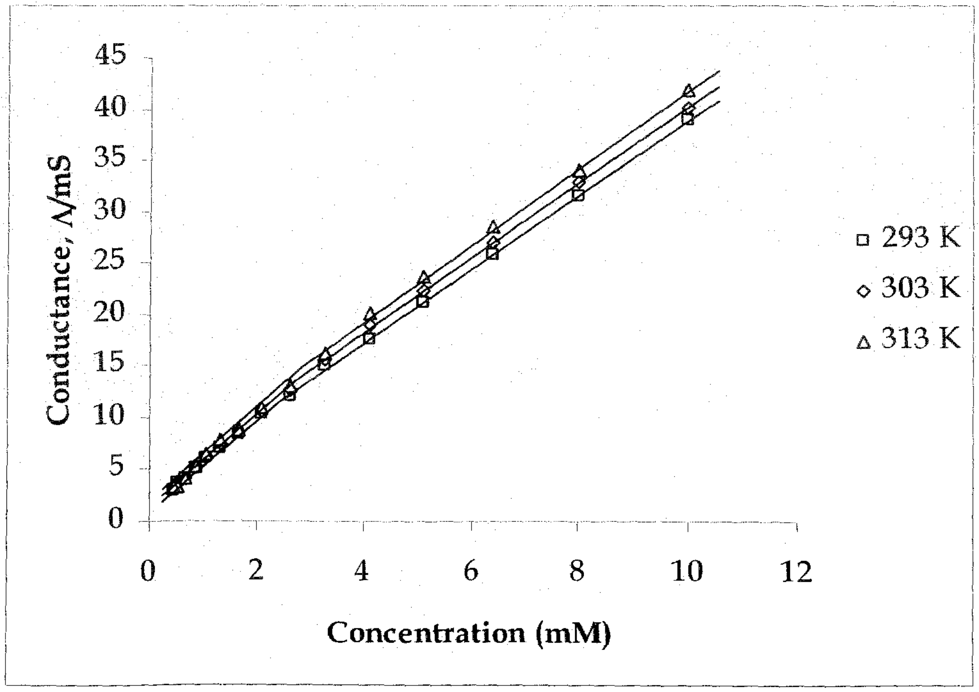

Figure 4.78: Conductance, Λ of TBADBS in 10% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

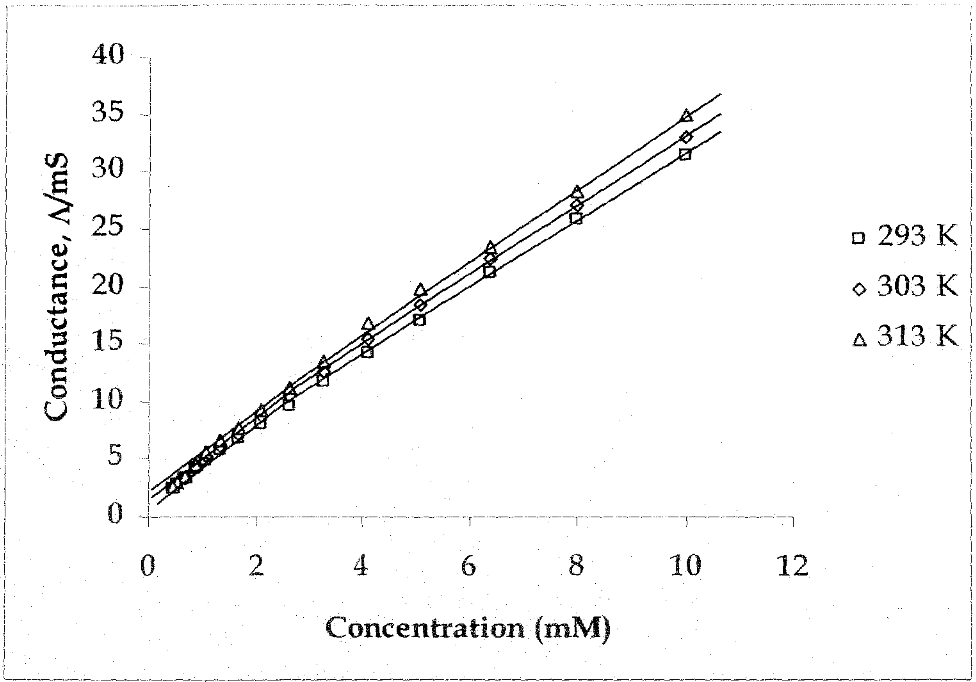

Figure 4.79: Conductance, Λ of TBADBS in 20% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

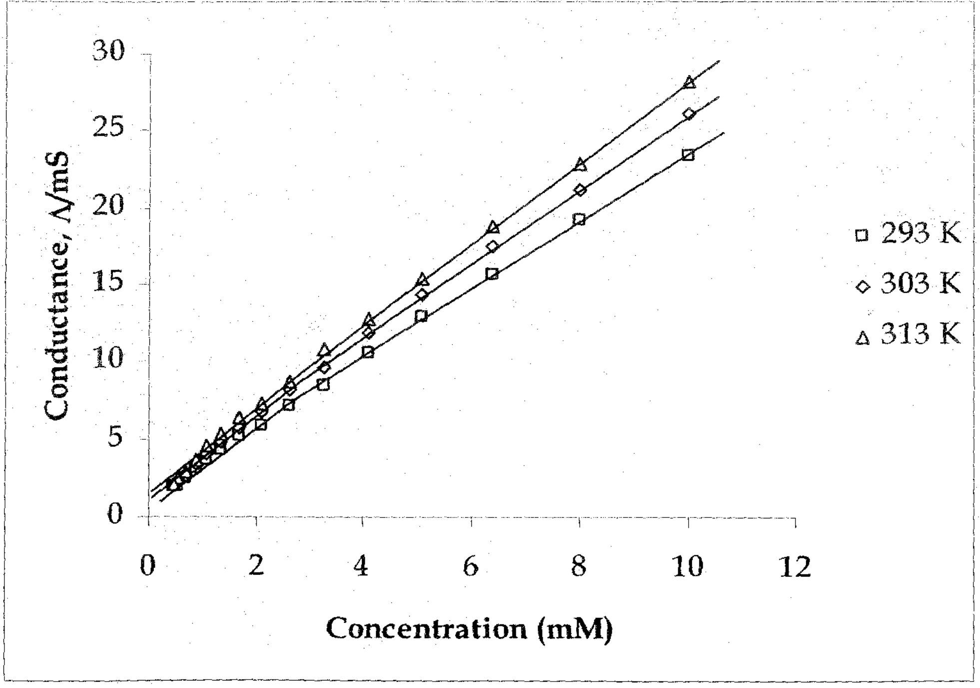

Figure 4.80: Conductance, Λ of TBADBS in 30% ethylene glycol-water (w/w) solution as a function of the surfactant concentration (mM) at different temperatures ranging 293 K to 313 K with 10 K intervals.

The effect of alcohol on the micellization process, given by ΔG^0_t, was calculated using the following equation:

$$\Delta G_t^0 = \Delta G^0_{m(alcohol-water)} - \Delta G^0_{m(water)} \tag{4.8}$$

It may be noted that, micellization process of DBS with different counterions are more favourable in water-alcohol binary mixture as compared to pure aqueous solvent, which is well supported by the positive values of ΔG_t^0,i.e., the positive values of ΔG_t^0 can be understood on the basis of a reduction of the hydrophobic interactions caused by improved salvation. The overall exothermicity of the present system indicates that both the structure-breaking ability of ethylene glycol and its interaction with the hydrophilic groups of the surfactants are dominating factors. Depending upon the temperature and the proportion of ethylene glycol present, small negative ΔG_t^0 as observed are there in different surfactants, may be due to a reduction of the micelle solvation in the mixed solvent. MacManus et. al. [110] 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 [110] 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 [111]:

$$D_A = (1 - a)D_A^{free} + aD_A^{mic} \tag{4.9}$$

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 4.2.1

Micellization parameters of DBS with different counterion in different proportions of ethylene glycol-water mixtures

Surfactant	Wt% EG	T/K	cmc^a /(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})
Sodium dodecyl benzene sulfonate (SDBS)	10%	293	3.43	0.7568	29.4	10.9	63.13
		303	3.62	0.7231	31.0	13.7	57.18
		313	3.81	0.7671	30.8	15.9	47.47
	20%	293	3.65	0.7563	29.2	10.9	62.51
		303	3.75	0.7154	31.1	13.8	57.15
		313	3.96	0.7353	31.4	16.3	48.29
	30%	293	3.85	0.7584	29.0	10.8	61.86
		303	3.95	0.7283	30.6	13.6	56.03
		313	4.12	0.7385	31.2	16.3	47.75
Lithium dodecyl benzene sulfonate (LDBS)	10%	293	2.65	0.8657	27.5	10.2	58.87
		303	3.19	0.8856	27.4	10.9	54.39
		313	3.55	0.8506	28.9	12.4	52.65
	20%	293	3.12	0.8466	27.5	10.4	58.30
		303	3.28	0.8656	27.8	11.1	55.10
		313	3.57	0.8289	29.4	12.6	53.59
	30%	293	3.15	0.8390	27.7	10.5	58.59
		303	3.44	0.8216	28.8	11.6	56.77
		313	3.76	0.8349	29.1	12.6	52.81
Potassium dodecyl benzene sulfonate (KDBS)	10%	293	2.42	0.8046	29.2	9.9	65.98
		303	2.83	0.7188	31.9	12.7	63.29
		313	3.25	0.9286	27.2	12.6	46.63
	20%	293	2.62	0.7596	30.1	10.3	67.64
		303	2.92	0.7711	30.5	12.2	60.39
		313	3.43	0.8883	28.0	13.1	47.89
	30%	293	2.79	0.8502	27.7	9.5	62.10
		303	2.96	0.8081	29.6	11.8	58.43
		313	3.71	0.8545	28.7	13.5	48.59
Ammonium dodecyl benzene sulfonate (ADBS)	10%	293	2.52	0.6940	31.8	13.7	61.72
		303	2.81	0.8955	27.5	13.9	44.83
		313	3.32	0.8282	29.7	17.5	38.84
	20%	293	2.75	0.7480	30.2	13.2	58.25
		303	3.01	0.7923	29.9	15.2	48.33
		313	3.33	0.8351	29.5	17.4	38.58
	30%	293	2.81	0.7626	29.8	13.0	57.35
		303	3.16	0.8088	29.3	15.0	47.19
		313	3.35	0.8681	28.6	16.9	37.43

[a] cmc values are calculated by conductivity method.

Table 4.2.2

Micellization parameters of DBS with different counterion in different proportions of ethylene glycol-water mixtures

Surfactant	Wt% EG	T/K	Cmc^a /(mol dm^{-3}×10^3)	α	$-\Delta G_m^o$/ (kJ mol^{-1})	$-\Delta H_m^o$/ (kJ mol^{-1})	ΔS_m^o/ (J K^{-1}mol^{-1})
Tetra methyl ammonium dodecyl benzene sulfonate (TMADBS)	10%	293	2.55	0.9241	26.2	19.8	21.75
		303	2.95	0.8992	27.3	22.4	16.34
		313	3.15	0.8550	29.1	25.6	11.45
	20%	293	2.80	0.8860	26.9	20.5	21.65
		303	3.01	0.9534	25.9	21.2	15.36
		313	3.20	0.9128	27.6	24.3	10.73
	30%	293	2.90	0.8729	27.1	20.8	21.58
		303	3.10	0.8695	27.9	23.0	16.31
		313	3.30	0.8914	28.1	24.7	10.66
Tetra ethyl ammonium dodecyl benzene sulfonate (TEADBS)	10%	293	2.20	0.7670	30.5	13.4	58.28
		303	2.45	0.7567	31.4	14.8	54.83
		313	2.65	0.7747	31.7	16.0	50.37
	20%	293	2.40	0.8051	29.3	13.0	55.61
		303	2.55	0.8254	29.6	14.0	51.41
		313	3.10	0.8308	29.8	15.2	46.54
	30%	293	2.42	0.7851	29.7	13.2	56.46
		303	2.62	0.6933	32.8	15.6	56.89
		313	3.20	0.9048	27.8	14.3	43.30
Tetra propyl ammonium dodecyl benzene sulfonate (TPADBS)	10%	293	2.58	0.8238	28.6	9.1	66.64
		303	2.82	0.8416	28.9	9.7	63.15
		313	2.94	0.7950	30.9	11.0	63.55
	20%	293	2.61	0.9023	26.7	8.5	62.09
		303	2.85	0.8591	28.4	9.58	62.10
		313	3.20	0.8125	30.2	10.8	61.79
	30%	293	2.80	0.8980	26.6	8.49	61.69
		303	2.93	0.7546	30.9	10.5	67.50
		313	3.26	0.9010	27.9	10.0	57.01
Tetra butyl ammonium dodecyl benzene sulfonate (TBADBS)	10%	293	2.47	0.9119	26.6	18.6	27.32
		303	2.71	0.8867	27.8	20.8	23.20
		313	2.82	0.7598	31.9	25.4	20.97
	20%	293	2.62	0.8721	27.4	19.2	27.77
		303	2.76	0.8248	29.3	22.0	24.31
		313	2.83	0.8096	30.6	24.3	20.09
	30%	293	2.71	0.8399	28.1	19.8	28.23
		303	2.79	0.8340	29.1	21.8	24.02
		313	2.85	0.7888	31.1	24.8	20.37

^{a} cmc values are calculated by conductivity method.

Table 4.2.3.

Effect of ethylene glycol and water mixtures on the micellization of DBS with different counterions

Surfactant	Wt% EG	T/K	ΔG^0_t (kJ mol^{-1})	Surfactant	Wt% EG	T/K	ΔG^0_t (kJ mol^{-1})
Sodium dodecyl benzene sulfonate (SDBS)	10%	293	2.44	**Tetra methyl ammonium dodecyl benzene sulfonate (TMADBS)**	10%	293	6.72
	20%	303	-0.01		20%	303	6.40
	30%	313	0.33		30%	313	5.56
	10%	293	2.62		10%	293	6.04
	20%	303	-0.08		20%	303	7.80
	30%	313	-0.33		30%	313	7.08
	10%	293	2.83		10%	293	5.82
	20%	303	0.40		20%	303	5.80
	30%	313	-0.12		30%	313	6.62
Lithium dodecyl benzene sulfonate (LDBS)	10%	293	3.30	**Tetra ethyl ammonium dodecyl benzene sulfonate (TEADBS)**	10%	293	0.85
	20%	303	4.08		20%	303	0.78
	30%	313	1.81		30%	313	1.27
	10%	293	3.30		10%	293	2.04
	20%	303	3.67		20%	303	2.64
	30%	313	1.28		30%	313	3.20
	10%	293	3.14		10%	293	1.58
	20%	303	2.73		20%	303	-0.60
	30%	313	1.59		30%	313	5.17
Potassium dodecyl benzene sulfonate (KDBS)	10%	293	2.95	**Tetra propyl ammonium dodecyl benzene sulfonate (TPADBS)**	10%	293	2.51
	20%	303	1.09		20%	303	3.04
	30%	313	6.62		30%	313	1.82
	10%	293	2.09		10%	293	4.45
	20%	303	2.49		20%	303	3.51
	30%	313	5.75		30%	313	2.53
	10%	293	4.47		10%	293	4.53
	20%	303	3.45		20%	303	0.99
	30%	313	5.14		30%	313	4.83
Ammonium dodecyl benzene sulfonate (ADBS)	10%	293	-0.82	**Tetra butyl ammonium dodecyl benzene sulfonate (TBADBS)**	10%	293	4.33
	20%	303	2.97		20%	303	4.15
	30%	313	2.94		30%	313	1.38
	10%	293	0.76		10%	293	3.52
	20%	303	0.61		20%	303	2.66
	30%	313	3.12		30%	313	2.67
	10%	293	1.18		10%	293	2.84
	20%	303	1.16		20%	303	2.92
	30%	313	3.98		30%	313	2.16

However, a close look at the table 4.2.1 and 4.2.2 also shows that at a fixed proportion of alcohol the cmc and other associated thermodynamic parameters except α progressively increases with temperature. This effect of temperature variation may also be explained by the dehydration of the hydrocarbon tail of the surfactant molecule at high temperature followed by the greater adherence of the alcohol molecules to the micellar pseudophase. This can also be explained by the fact that short chain alcohol like ethanol [111], ethylene glycol affects the surface properties of the surfactants to a great extent by the effective adsorption in air-aqueous interface. In general, the alcohols may be distributed among three energetically different sites. It can be dispersed in the aqueous bulk solution, oriented in the micellar surface, and located in the hydrocarbon core of the aggregates. In this respect it may be said that the alcohol content works quite similar to temperature change with respect to the effect on micelle formation at constant pressure. The structure breaking ability of ethylene glycol is a dominating factor in the micellization process. It was found that the surface activity of any surfactant decreases slightly with increasing concentration of ethylene glycol at a given temperature. It was also found previously that the change of surface area per head group of the surfactant suggested an alteration in the nature of its solvation layer, produced probably by a certain participation of cosolvent in the micellar solvation layer.

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