

Conductometric studies on micellar properties of dodecyldimethylammonium bromide in presence of additives at various temperature

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Abstract

Specific conductivity of aqueous solutions of dodecyldimethylammonium bromide has been determined in the temperature range of 25-45°C. The critical micelle concentration (cmc) and ionization degree of the micelles, β , were determined from the data. Thermodynamic functions, such as standard Gibbs free energy, ΔG_m^0 , enthalpy, ΔH_m^0 , and entropy, ΔS_m^0 , of micellization, were estimated by assuming that the system conforms to the mass action model, was estimated from the temperature dependence of ΔH_m^0 . An enthalpy-entropy compensation phenomenon for the studied system has been found.

Keywords: conductivity, critical micelle concentration, dodecyldimethylammonium bromide, enthalpy, entropy and standard Gibbs free energy, temperature dependence.

Introduction

Cationic surfactants became important because of their bacteriostatic properties. They have been introduced into several commercial products as antiseptic agents in cosmetics and as germicides [1]. Cationic surfactants have found also wide application in phase transfer catalysis [2] and, more recently, in the production of silica-based mesoporous catalysts [3]. Their performance in these fields is related to their self-association properties.

Interactions of cationic surfactants with polymers and vesicles were evaluated by applying the DSC technique [4, 5]. Knowledge of thermodynamic parameters of micellization of cationics in aqueous solution is thus essential. In a previous paper we used an approximate method to estimate the thermal parameters related with the self-association process of dodecylpyridinium salts [6]. In this paper we report our results of conductivity measurements of dodecyldimethylammonium bromide (C₁₂DABr) in aqueous solution at 25, 30, 35, 40 and 45°C. Although the micellar and thermodynamic properties of homologous alkyldimethylammonium halides have been studied extensively, little attention was devoted to the homologous group of alkyldimethylammonium halides even though one of the representatives of this series, the title compound, is available commercially. As far as we are aware, only three contributions to the knowledge of micellar properties of this salt have been reported as yet. One is due to Zana *et al.* [7], who studied conductometrically and potentiometrically the micellar behavior of C₁₂DABr, and the other two are due to

Peña *et al.* [8, 9] who studied the molecular encapsulation and micellization process of this surfactant in aqueous solution in the presence of non polar additives like urea and acetamide ..

Our conductometry results enabled us to determine the temperature dependence of cmc and β and hence to estimate the relevant thermodynamic parameters associated with the process of micellization of the studied surfactant. Surfactant molecules when dissolved in water above a certain concentration, referred to as critical micellar concentration (cmc), self-aggregate into supramolecular structure. The simplest aggregate of these surfactant molecules is called a micelle and the dispersion of these aggregates in aqueous solution is referred to as a micellar solution[10]The investigation of interfacial and thermodynamic properties of surfactants in solution, both in the presence and in the absence of additives, can provide extensive information about solute-solute and solute-solvent interaction of the surfactant in solution[11].The interfacial and micelle properties of surfactant solutions are governed by a delicate balance of solvophobic and solvophilic interaction.

Experimental

$C_{12}DABr$ was provided by Fluka with a purity of 99% and it was used without further purification. This salt is monohydrated according to potentiometric and thermo gravimetric analysis. All solutions were prepared by mass using distilled water with conductivity below 3 mS cm^{-1} at 25°C . The concentrations are expressed in molalities. The additives urea and acetamide was the product of Sigma Aldrich, USA, (urea mol.wt. 60.60 and acetamide mol.wt. 59.07 gm/mol). Both the additives are dialyzed to remove low molecular weight fractions and other associated electrolytic impurities before use. Water, with conductivity $1.05 \times 10^{-6} \text{ S.cm}^{-1}$ at 303.15 K was used for preparation of solutions and was obtained by distilling deionized water from alkaline KMnO_4 , to remove organic matter. If any stock solutions of $1 \text{ M (mol kg}^{-1})$ of each urea and acetamide in water were prepared and used as solvents to prepare solutions of 0.0, 0.2, 0.4, 0.8 and 1.2 m and 0.001 to 0.0095 M in order to cover the pre- and post – micellar concentration range of 0.001 to 0.0095 M. The weighings were done on a precise XB- 220A, Swiss make electronic balance with a precision of $\pm 0.0001 \text{ gm}$. All necessary precautions were taken to prepare solutions. The solutions were stored in special air tight bottles to minimize absorption of atmospheric moisture and carbon dioxide. Conductivities of the solution were measured by using digital conductivity meter (Model-306, Systronics) having cell constant 1.007 cm^{-1} . The conductivity meter was calibrated by measuring the conductivities of the solution of potassium chloride (Merck, purity >99%) of different concentrations, (0.01 and 0.1 N). The solution and the measuring cell were immersed in an electronically controlled thermostated water bath maintaining the temperature within $\pm 0.02 \text{ K}$.

The cell constant was determined by calibration with several different concentrations of KCl solutions using the procedure suggested by Monk [10]. All measurements were carried out in a thermostat bath (Polyscience 9010) maintaining the temperature constant to within $\pm 0.05^\circ\text{C}$.

Results and discussion

Effect of temperature on CMC of DDMAB:

Conductance results were used to estimate the values of the CMC and β , at several temperatures. In Fig. 1, 2, 3 and 4, the conductivity Vs molality plots are presented for $C_{12}DABr$ in water and in presence of urea and acetamide in the range of 25 to 45°C at 5°C intervals. In this figure breaks in the specific conductivity vs. molality plots can be observed. These breaks are generally attributed to the beginning of formation of micelles, i.e., to critical micelle concentration (CMC). In order to estimate the values of critical micelle molality, we fit the linear fragments, above and below the breaks and we treat the molality at which intersection of these lines occurs as the *cmc*. Ionization degree of the micelles, β , has been calculated as the ratio of the slopes of the two intersecting lines. The values obtained for *cmc* and β for $C_{12}DABr$ at 25°C amount to 0.0513 mol kg⁻¹ and 0.46, respectively. These values are close to previous results of 0.05144 mol kg⁻¹ and 0.48, respectively reported by Junquera *et al.* [9] and 0.0514 mol kg⁻¹ and 0.48, respectively reported by Zana [7]. Taking into account the values of *cmc* and β reported for dodecyl dimethyl ammonium bromide [7, 11, 12] it appears that the introduction of a methylene group into the headgroup has an almost negligible effect on the hydrophobicity of the cation. It is well known that increase in the length of the main hydrocarbon chain by one methylene group leads to about a two-fold decrease in CMC [7]. Figure 5, 6, 7, and Figure 8, represents the temperature dependence of ΔG_m^0 and the ionization degree of the micelles (β) for $C_{12}DABr$.

Figure shows the typical U-shaped dependence of *cmc* on temperature. The minimum of this curve is close to 25°C. This result appears to conform to a general finding that the minimum, for ionic surfactants with a dodecyl alkyl chain is close to room temperature. Thus e.g. T_{mim} at 25°C was reported for sodium dodecyl sulfate by Goddard *et al.* [13] whereas the results of Zielinski *et al.* [14] for dodecyl dimethyl ammonium bromide shows a T_{mim} around 20°C. According to Chen *et al.* [15] the minimum which appears on the *cmc* vs. temperature plots is a consequence of two opposing effects: 1) the decrease in the hydration of the ionic head group (and presumably of the counterion) with temperature which leads to growth of hydrophobicity of the surfactant and hence to lowering of *cmc* the breakdown of the structure of water which leads to decrease of hydrophobic interactions and hence to growth of the *cmc* value.

The rate of change of the specific conductivity with molality in the region of the breaks appears to be lower the higher the temperature. Such behavior indicates that β grows with temperature. Figure 7 and 8, shows a linear dependence of β on the temperature. The relevant thermal parameters, such as ΔG_m^0 , ΔH_m^0 and S_m^0 , can be obtained assuming the mass action model [16]. According to this model the relations among thermal functions are as follows

$$\Delta G_m^0 = (2 - \beta)RT \ln cmc$$

Where the CMC is the molality of the surfactant solution at CMC. The temperature dependence of the thermal parameters ΔG_m^0 , ΔH_m^0 and ΔS_m^0 is shown in Table 1 and 2. The temperature dependence of $\ln cmc$ was fitted to a second order polynomial curve to derive relevant values. The micellization process is exothermic and ΔG_m^0 is negative in the whole temperature range studied as seen in Figure 5 and 6 for urea and acetamide.

On the other hand, the entropy of micellization is positive in the low temperature range, but decreases with temperature. The apparent change in heat capacity of the surfactant upon micellization can be estimated from data of ΔH_m^0 using the following relation the results yield a value of $-867 \text{ J mol}^{-1} \text{ K}^{-1}$. According to some authors [17,19] the values of $\Delta C_{p,m}^0$ estimated from show better agreement with calorimetric data when the ionization degree of the micelles is neglected. In our case such an approach leads to a $\Delta C_{p,m}^0$ value of $.471 \text{ J mol}^{-1} \text{ K}^{-1}$. Several chemical processes exhibit a linear relation between ΔH_m^0 and ΔS_m^0 . This phenomenon is known as enthalpy-entropy compensation [15, 19]. The enthalpy-entropy compensation are shown for the present compound in Figure 9 and 10. In general the compensation effect can be described by the relation

$$\Delta H_m^0 = H_m^* + T_c \Delta S_m^0$$

Where T_c is the so-called compensation temperature and ΔH_m^0 is the intercept. T_c for the present system amounts to $301 \pm 3 \text{ K}$ in satisfactory agreement with the value of $308 \pm 4 \text{ K}$ reported by Chen *et al.* [15] for homologous alkyltrimethylammonium bromides.

Thermodynamics of micellization

The thermodynamics of micellization, viz, Gibbs free energy ΔH_m^0 and entropy ΔS_m^0 can be derived from the temperature dependence of the CMC. The availability of these parameters (Table 1 and 2) at various temperatures in all the solvents can give valuable insight into the principles which govern the formation of micelles.

The Gibbs free energy of micellization ΔG_m^0 was calculated using the equation, $\Delta G_m^0 = (2-\alpha) RT \ln X_{CMC}$

Where α is the degree of counter ion dissociation, which was calculated from the relation, $\alpha = S_2/S_1$, where S_1 and S_2 are the slopes in the pre- and post-micellar regions determined from conductivity plots. Where, X_{CMC} is the CMC value expressed in the mole fraction scale.

The standard enthalpies of micellization were obtained by employing the equation,

$$\Delta H_m^0 = - (2-\alpha) RT^2 (d \ln X_{CMC} / dT)$$

($d \ln X_{CMC} / dT$) value was calculated from slope of the plot of $\ln X_{CMC}$ versus temperature.

The entropy values of micelle formation were evaluated from the well-known relationship,

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

The formation of micellization was always found to be connected with a large, negative change in (ΔG_m^0) i.e. the aggregation process is thermodynamically favored and spontaneous. In the temperature range studied (Table 1, 2 and Figure 5, 6), small differences in (ΔG_m^0) are observed in the case of urea and acetamide can be noted from the given data that both in aqueous and in additives, the (ΔG_m^0) values become less negative with increase in temperature. No definite trends have been observed in case of urea and acetamide. The effect of Urea and acetamide on free energy of micellization of DDAB (ΔG_m^0) with temperature (Figure 5 and Figure 6) shows that, (ΔG_m^0) values obtained are less negative for DDAB in water than in additives.

The result also shows that the (ΔH_m^0) values calculated for all additives are negative. The negative (ΔH_m^0) values can be taken as evidence that London dispersion interactions represent the major attraction force for micellization [20]. The overall micellization process was found to be exothermic.

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Table1: Standard thermodynamic parameters of micellization of DDAB in presence and absence of Urea and acetamide at different temperatures T (K).

T (K)	ΔG_m° kJ mol ⁻¹	ΔH_m° kJ mol ⁻¹	ΔS_m° JK ⁻¹ mol ⁻¹
DDAB + Water			
298.15	-45.07	-11.72	0.190
303.15	-45.42	-11.79	0.188
308.15	-45.78	-11.86	0.187
313.15	-46.13	-11.94	0.185
318.15	-46.48	-12.08	0.184
DDAB + 0.2M Urea			
298.15	-45.98	-11.91	0.194
303.15	-46.33	-11.99	0.192
308.15	-46.69	-12.07	0.190
313.15	-47.05	-12.14	0.189
318.15	-47.41	-12.22	0.187
DDAB + 0.4M Urea			
298.15	-47.12	-12.44	0.199
303.15	-47.51	-12.52	0.198
308.15	-47.90	-12.60	0.196
313.15	-48.29	-12.69	0.194
318.15	-48.68	-12.77	0.193
DDAB +0.8 M Urea			
298.15	-48.54	-12.56	0.204
303.15	-49.02	-12.65	0.203
308.15	-49.50	-12.74	0.201
313.15	-49.98	-12.83	0.200
318.15	-50.46	-12.92	0.199

Table 2: Standard thermodynamic parameters of micellization of DDAB in acetamide at different temperatures T (K).

T (K)	ΔG_m° kJ mol ⁻¹	ΔH_m° kJ mol ⁻¹	ΔS_m° JK ⁻¹ mol ⁻¹
DDAB+0.2M Acetamide			
298.15	-46.93	-11.99	0.196
303.15	-47.44	-12.36	0.195
308.15	-47.95	-12.73	0.194
313.15	-48.46	-13.10	0.193
318.15	-48.97	-13.47	0.192
DDAB+0.4M Acetamide			
298.15	-47.42	-12.29	0.200
303.15	-48.05	-12.67	0.199
308.15	-48.66	-13.05	0.198
313.15	-49.27	-13.43	0.197
318.15	-49.88	-13.80	0.196
DDAB+0.8M Acetamide			
298.15	-48.16	-12.63	0.204
303.15	-48.87	-13.02	0.203
308.15	-49.58	-13.41	0.202
313.15	-50.29	-13.80	0.201
318.15	-51.00	-14.19	0.200

Table 3: Values of Critical micelle concentration (CMC) and degree of ionization (β) of DDAB in water and in 0.2, 0.4, and 0.8 M Urea at different temperatures.

T (K)	Water	0.2M Urea	0.4M Urea	0.8M Urea
298.15	0.00513	0.00530	0.00553	0.00566
303.15	0.00530	0.00553	0.00566	0.00584
308.15	0.00553	0.00566	0.00584	0.0060
313.15	0.00566	0.00584	0.0060	0.00621
318.15	0.00584	0.0060	0.00621	0.00636
β				
298.15	0.462	0.487	0.507	0.529
303.15	0.474	0.498	0.518	0.538
308.15	0.486	0.506	0.526	0.547
313.15	0.498	0.515	0.537	0.556
318.15	0.507	0.526	0.549	0.565

Table 4: Values of Critical micelle concentration (CMC) and degree of ionization (β) of DDAB in 0.2, 0.4, and 0.8 M Acetamide at different temperatures

T (K)	0.2M Acetamide	0.4M Acetamide	0.8M Acetamide
298.15	0.00553	0.00584	0.00636
303.15	0.00566	0.0060	0.00648
308.15	0.00584	0.00621	0.00655
313.15	0.0060	0.00636	0.00669
318.15	0.00621	0.00648	0.00670
β			
298.15	0.492	0.521	0.542
303.15	0.503	0.534	0.553
308.15	0.514	0.544	0.564
313.15	0.524	0.553	0.572
318.15	0.534	0.566	0.582

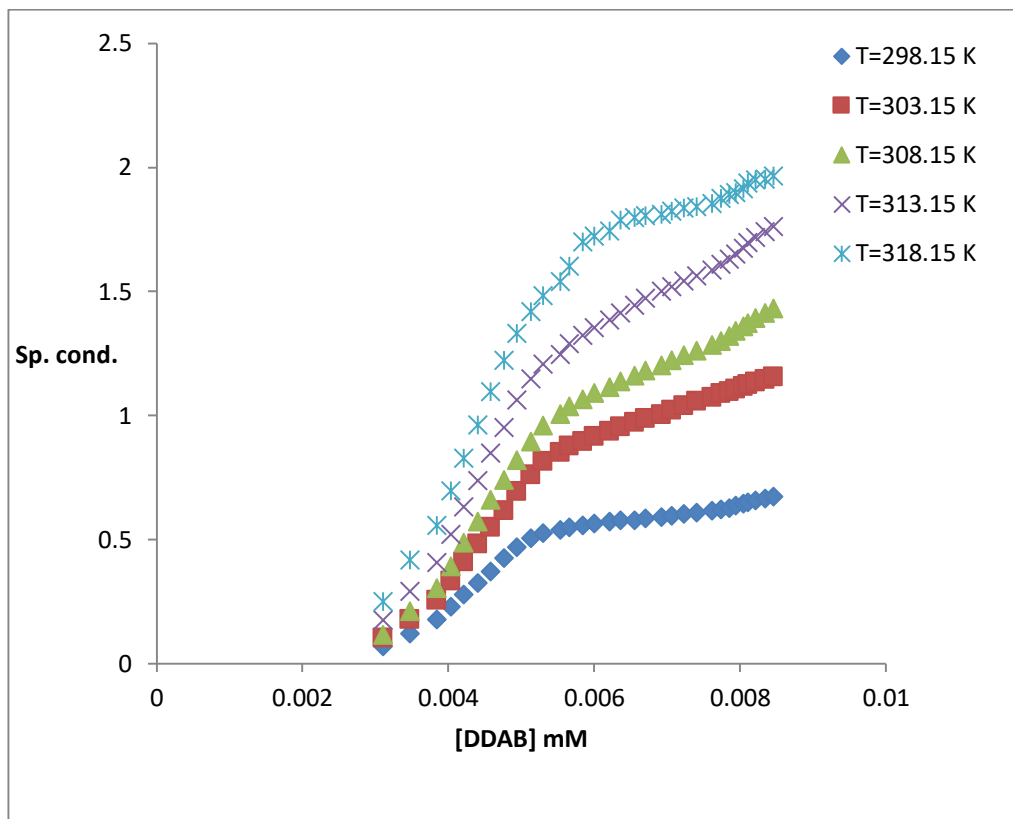


Fig 1.Plots between specific conductivities versus [DDAB] at different temperatures in aqueous medium.

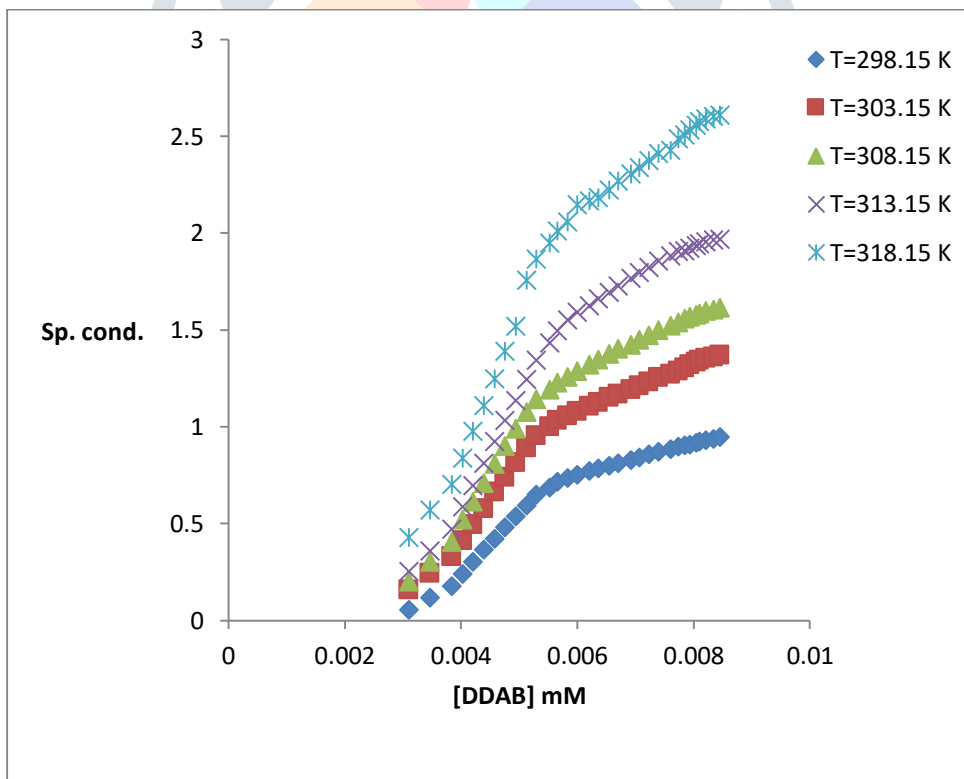


Fig 2.Variation of specific conductivities versus [DDAB] at different temperatures in 0.2 M Urea.

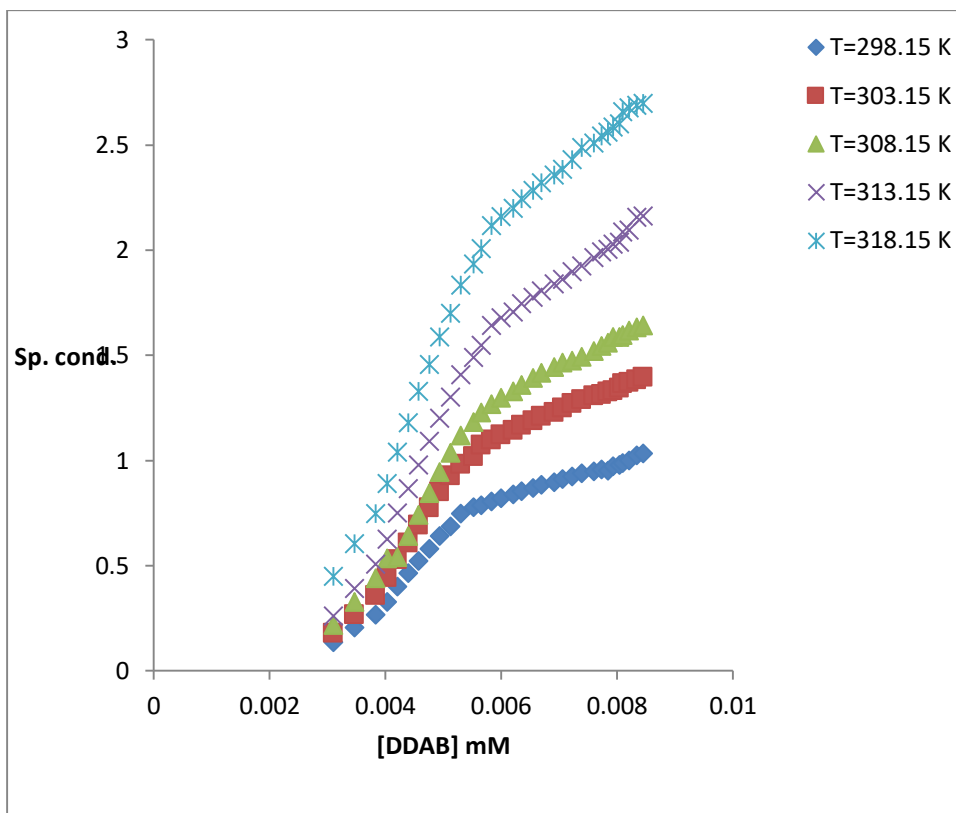


Fig 3. Variation of specific conductivities versus [DDAB] at different temperatures in 0.6 M Urea.

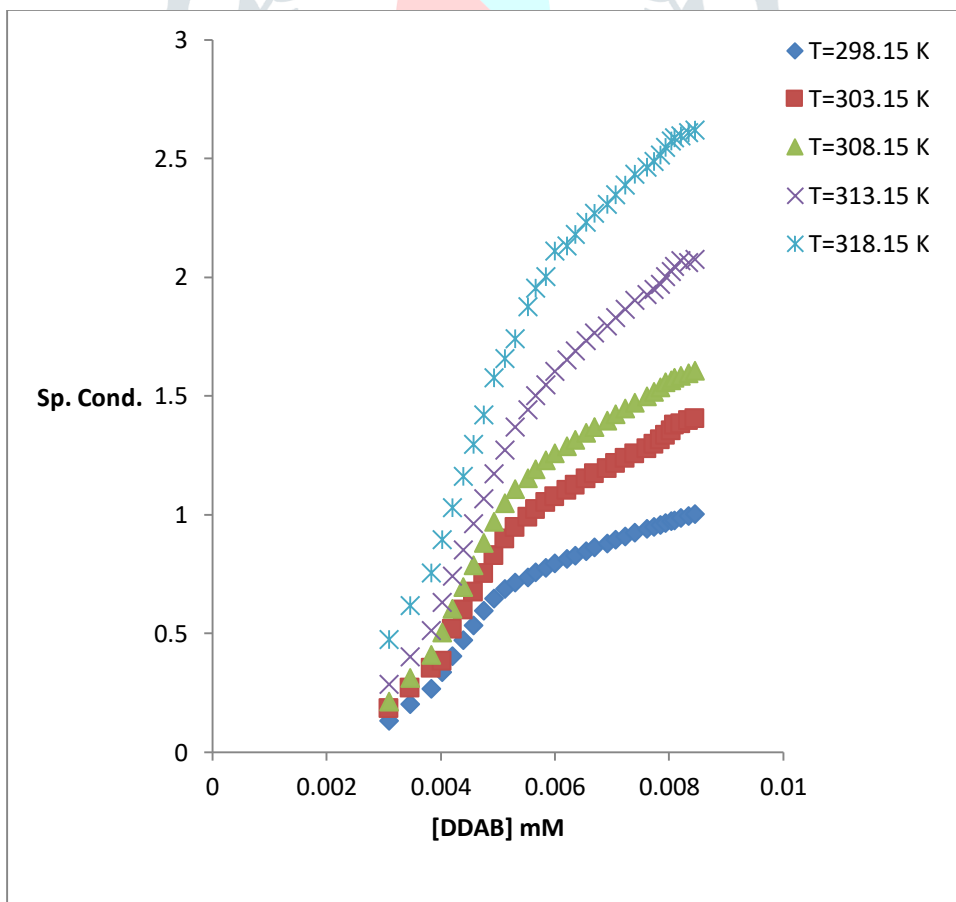


Fig 4. Variation of specific conductivities versus [DDAB] at different temperatures in 0.2 M Acetamide.

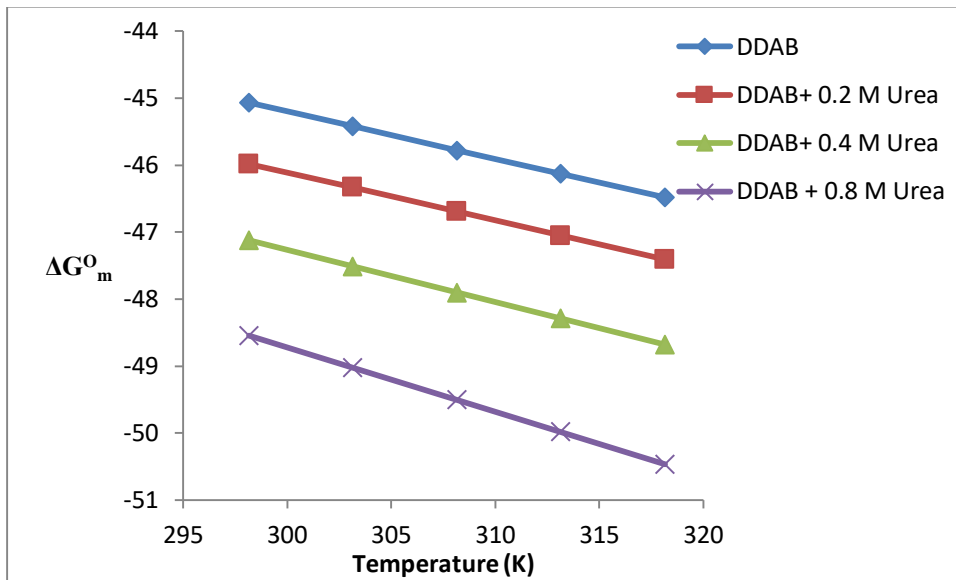


Fig 5.Effect of Urea on free energy of micellization of DDAB (ΔG^0_m) with Temperature.

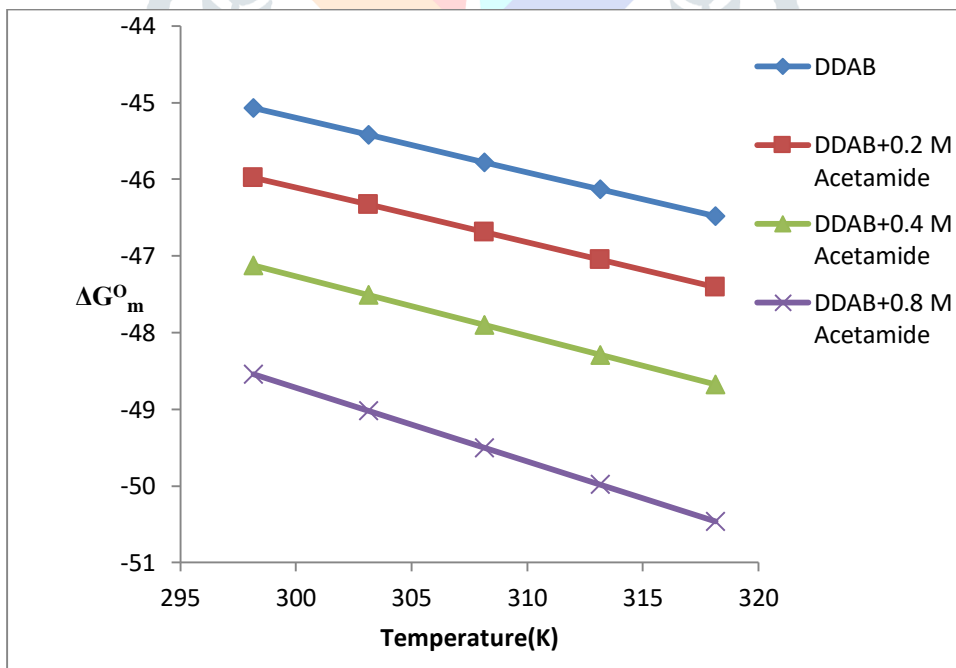


Fig 6.Effect of Acetamide on free energy of micellization of DDAB (ΔG^0_m) with Temperature.

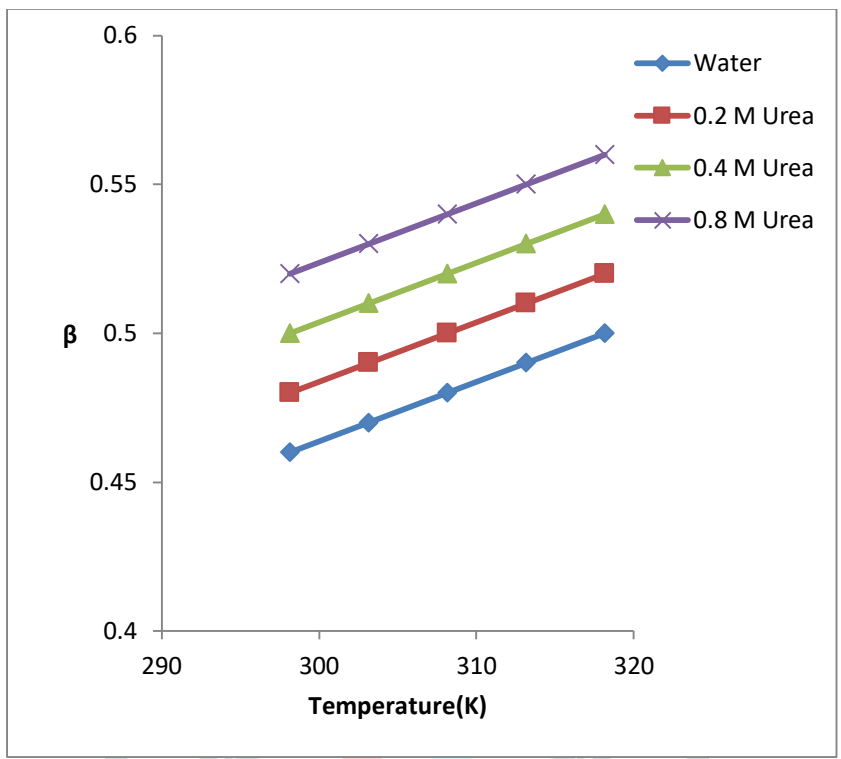


Fig. 7. Variation of degree of ionization (β) of DDAB with temperature in presence of 0.2, 0.4 and 0.8 m Urea.

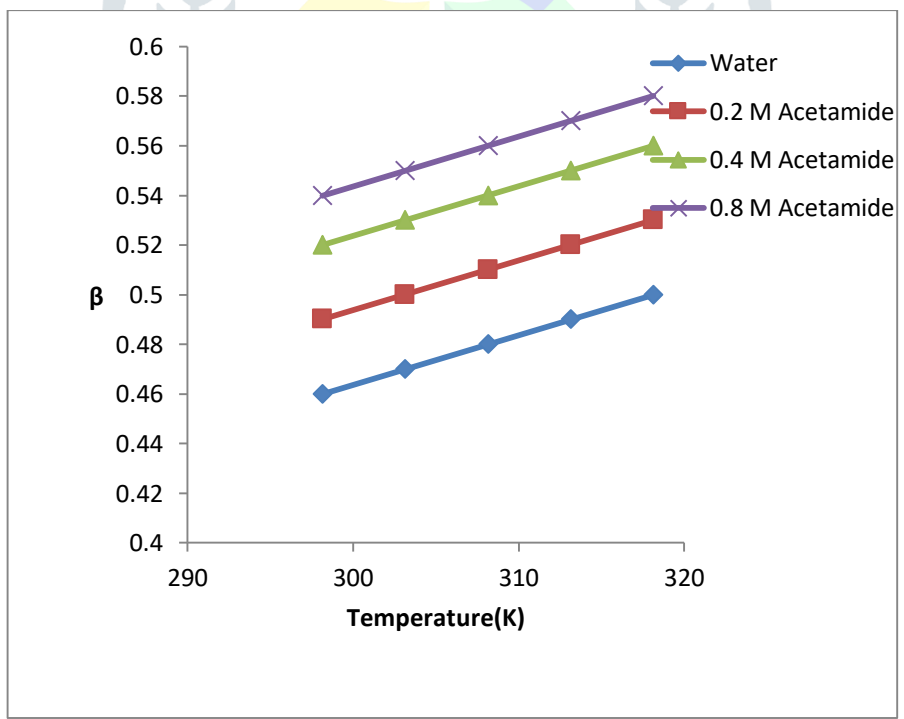


Fig. 8. Variation of degree of ionization (β) of DDAB with temperature in presence of 0.2, 0.4 and 0.8 m Acetamide.

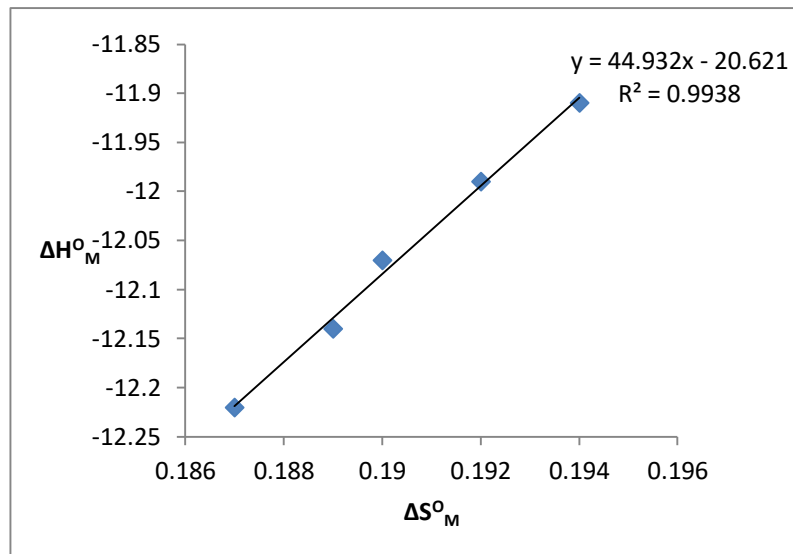


Fig 9: Enthalpy - entropy compensation plot of DDAB + 0.2M Urea.

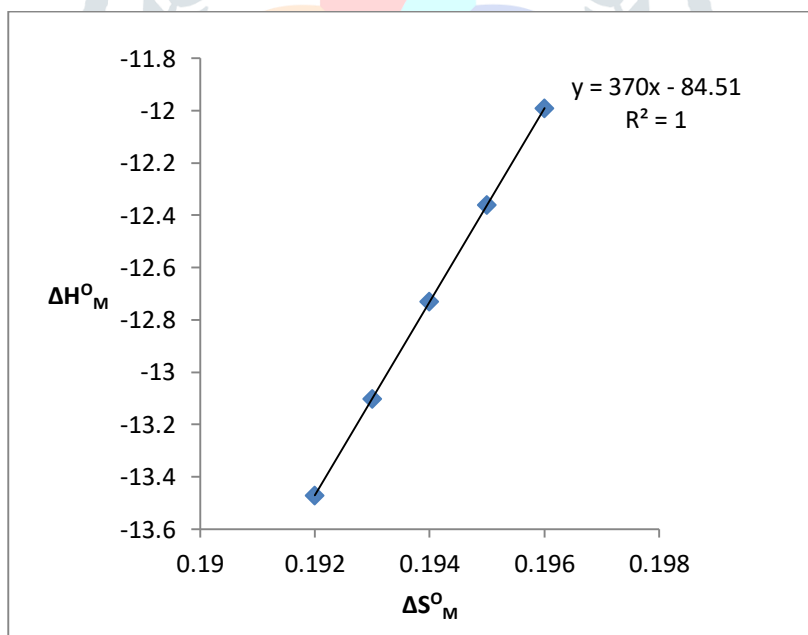


Fig 10: Enthalpy - entropy compensation plot of DDAB + 0.2M Acetamide.