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Micellar Properties of Benzyl Dimethyl Dodecyl Ammonium Bromide in Aqueous Non Polar Organic Additives

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ABSTRACT

The micellar properties of benzyl dimethyl dodecyl ammonium bromide have been studied by conductivity method. The micellization process of cationic surfactant BDDAB in aqueous medium by conductivity method in the presence of additives such as urea and acetamide at different temperatures ranging from 303.15 to 318.15 K has been investigated. From the conductivity data the critical micelle concentration (CMC) and the effective degree of counter-ion binding (β), were obtained at various temperatures using a simple non-linear function obtained by direct integration of a Boltzmann-type sigmoidal function. The thermodynamics of micellization i.e. Gibbs free energy (ΔG^0_m), enthalpy (ΔH^0_m) and entropy (ΔS^0_m) have also been determined. The thermodynamic parameters were estimated from the temperature dependence of the equilibrium constants for the micellization of surfactant using the phase separation model. The stability of the micellization process for this surfactant is both enthalpy and entropy controlled. The resulting ΔH^0_m Vs $T\Delta S^0_m$ plots showed significant correlation, an indication of enthalpy-entropy compensation in the micellization process. The increase of critical micelle concentration of BDDAB with additives has been discussed on the basis of water structure, solvent properties and hydrophobic interaction. In the present studies, micellization behavior of benzyl dimethyl dodecyl ammonium bromide, BDDAB has been studied in the aqueous solution, containing 0.2, 0.4 and 0.6M urea and acetamide as a solvent, using specific conductance's (κ), in the temperature range 30–45°C at an interval of 5°C. The CMC of BDDAB was determined from the plots of specific conductance (κ) of BDDAB in aqueous and in non-polar organic additive solution. The CMC values of surfactant increase with increase in temperature but they decrease linearly with increase in the concentration of the additives. By using CMC data various thermodynamic parameters have also been evaluated.

Keywords: Micellization, electrical conductivity, BDDAB, urea, acetamide.

INTRODUCTION

Benzyl dimethyl dodecyl ammonium bromide is a versatile and important cationic surfactant. In micellar enzymology, use of different cationic surfactants has been found to be of great significance and several studies in this area have been reported in the literature [1-5]. In non-aqueous micellar enzymatic catalysis, solvent selection is a very important factor for the successful application of enzymes. The use of organic solvents in such reactions increases the solubility of organic substrates [6-8], which are insoluble or poorly soluble in water. Also, low solubility of enzymes of facilitates the enzyme and product recovery. Therefore, the knowledge of the physical properties and thermodynamics of micellization of surfactant in binary solvent mixtures organic mixed systems has been extensively investigated [8-13]. Micellar properties of cationic surfactants in bulk aqueous system have been extensively studied [14, 15]. These studies are justified from both theoretical interest and the large number of their industrial applications. The quaternary ammonium salts are known for their germicidal and antifungal properties [16, 17]; there is also the possibility of employing cationic amphiphiles as vectors in gene delivery [18, 19].

Majority of fundamental studies on cationic surfactants were on those with quaternary ammonium and pyridinium head groups [20-25]. Studies on the Benzyl dimethyl dodecyl ammonium bromides are rather scanty. The present work is of interest because this surfactant possesses a bulky and highly hydrophobic Benzyl dimethyl dodecyl head group which is expected to play a significant role in their micellar properties. The critical micelle concentration CMC appears to be the most important property in the study of the micellization of surfactants and the two models commonly employed in the theoretical thermodynamic treatment of micelles, namely the mass action and the phase separation models both required the knowledge of the CMC which is often obtained from the abrupt change in the physical property-concentration curve.

The synthesis and the micellar properties of dodecyltriphenylphosphonium bromide (C_{12}TPPBr) have been studied by Jiang et al [26]. The thermodynamics of the micellization of decyl-(C_{10}), dodecyl- (C_{12}), tetradecyl-(C_{14}) and hexadecyl-(C_{16}) –triphenyl phosphonium bromides by the method of isothermal titration Calorimetry had been reported [27]. Their micellar properties in binary water-glycols mixtures [28] as well as study on their mixed surfactants systems have also been reported [29]. In most of these studies, Conductometric method was employed and the CMC determined from the break point in the conductance-concentration plots. A frequent problem arising from the conductivity method is that it is usually difficult to determine the CMC for systems in which the conductance-concentration plot does not show a sharp transition from the pre-micellar to the post-micellar region, but rather exhibits a curvature. Consequently, the CMC and the degree of counter-ion binding (α) obtained will be affected to a greater uncertainty.

Survey of the available literature reveals that no serious attempt has been made to study the micellization phenomenon of benzyldimethyldodecylammonium bromide ((BDDAB) surfactant in non-polar aqueous solvents. Herein, we report preliminary study on the micellar properties, CMC and degree of counter ion dissociation (α), and thermodynamic parameters ($\Delta G^0_{m,}$ $\Delta H^0_{m,}$ and ΔS^0_{m}**)** of the Benzyldimethylammonium bromide (BDDAB) in presence and absence of additives such as urea and acetamide water mixtures. In the present work, we have investigated the thermodynamics of aggregation of these surfactants by Conductometric methods in aqueous medium, and over a temperature range between 30 to 45^{o}C.To solve the problem mentioned above, we have adopted the procedure proposed by Carpena et al [30] for the accurate determination of the CMC and α which are necessary for calculating the thermodynamic parameters of aggregation.

MATERIALS AND METHODS

Benzyldimethyldodecylammoniumbromide was the product from Sigma Aldrich, the additives; viz. urea and acetamide of highly purity were obtained from Qualigens and were used without further purification. Triply distilled water prepared in laboratory, was used for the preparation of all solution. Conductance was measured with a Systronics microprocessor based conductivity meter (Systronics -306). Conductance was measured at different temperature ranging from 303.15 to 318.15 K in various non polar additives. A concentrated surfactant solution progressively added to 20mL thermostated container (temperature accuracy ±0.1) using a Qualigens variable volume pipette. After ensuring thorough mixing and temperature equilibration, the specific conductance was measured. The break point concentration and that point were assumed to be CMC of BDDAB. 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^{-1}). Both the additives are dialyzed to remove low molecular weight fractions and other associated electrolytic impurities before use. Water, with conductivity 1.05 X 10^{-6} 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 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, 0.6 M and 0.0005 M BDDAB in order to cover the pre- and post- micellar concentration range of BDDAB. The weighing was done on a precise CA-123, CONTECH electronic balance with a precision of ± 0.0001 g. 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 solutions were measured by using digital conductivity meter (Model-306, Systronics) having cell constant 1.007cm^{-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 ± 0.02 K.

RESULTS AND DISCUSSION

Effect of Temperature on CMC of BDDAB: From the conductivity data, the CMC was evaluated. Representative plots of specific conductance's versus surfactant concentration are presented in Fig.1 the intersection point between the two straight lines gave the CMC. It was also possible to compare the degree of counter ion dissociation (α) from the ratio between the slopes of the post-micellar region and pre-micellar region. The values of CMC and α for Benzyl dimethyl dodecyl ammonium bromide (BDDAB) are given in Table 1. As temperature increases specific conductance also increases and hence CMC also increases from 0.0057 to 0.0066 as temperature was increased from 308.15 to 318.15 K.

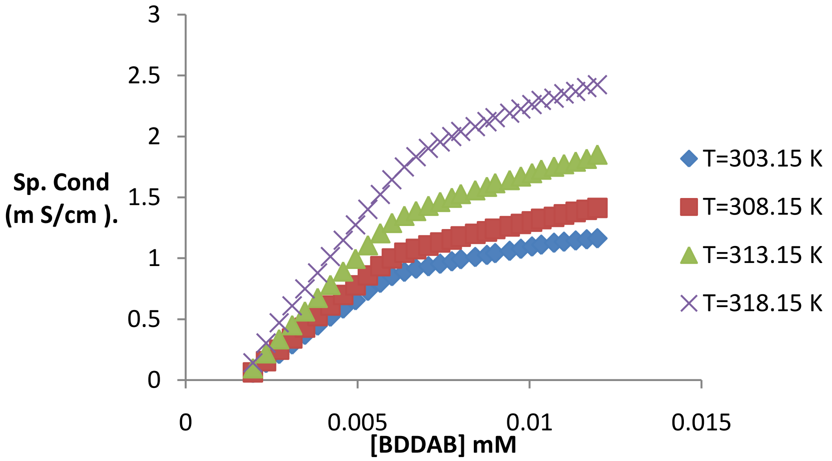

Fig 1. Specific conductivity vs. [BDDAB] at different temperatures in aqueous medium.

CMC of BDDAB - Urea system: Table 1 Summarizes the values of CMC and α for BDDAB in urea. The plots of specific conductance versus BDDAB + 0.2 M Urea and 0.6 M Urea concentration and temperatures are presented in fig.2 and 3 respectively. The values of CMC and α for BDDAB+ Urea are given in table 1. As temperature increases specific conductance also increases and hence CMC also increases from 0.0060 to 0.0068 as Urea concentration was increased from 0.2 to 0.6 M and temperature was increased from 308.15 to 318.15 K.

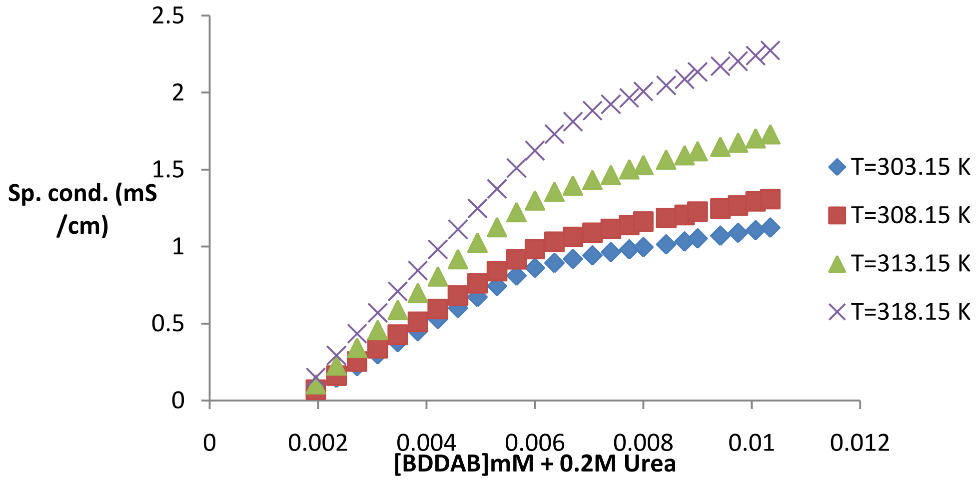

Fig 2. Specific conductivities versus [BDDAB] at different temperatures in 0.2 M Urea.

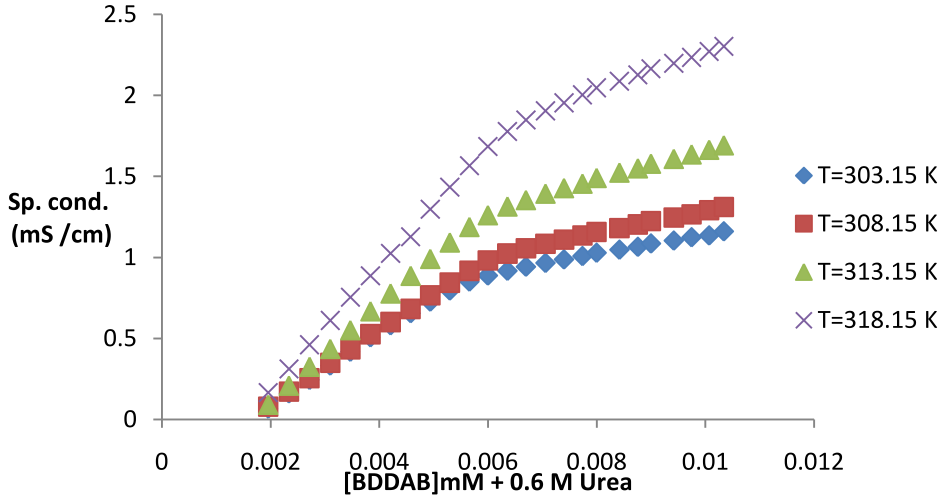

Fig 3. Specific conductivity versus [BDDAB] at different temperatures in 0.6 M Urea.

Table 1: Values of Critical micelle concentration (CMC) and degree of ionization (α) of BDDAB in water and in 0.2, 0.4 and 0.6 M Urea at different temperatures.

	CMC			
Temperature (K)	**BDDAB**	**BDDAB + 0.2 M Urea**	**BDDAB + 0.4 M Urea**	**BDDAB + 0.6 M Urea**
303.15	0.0057	0.0060	0.0062	0.0063
308.15	0.0060	0.0062	0.0063	0.0064
313.15	0.0063	0.0064	0.0065	0.0066
318.15	0.0066	0.0067	0.00675	0.0068
	α			
303.15	0.270	0.273	0.274	0.278
308.15	0.280	0.288	0.284	0.298
313.15	0.303	0.289	0.294	0.307
318.15	0.320	0.336	0.313	0.312

CMC of BDDAB - Acetamide system: The plots of specific conductance versus BDDAB + 0.2 M acetamide and 0.6 M acetamide concentration and temperatures are presented in fig. 4 and 5 respectively. Values of CMC and α for BDDAB + acetamide are given in table 2. As temperature increases specific conductance also increases and hence CMC also increases from 0.0063 to 0.0068 as acetamide concentration was increased from 0.2 to 0.6 M and temperature was increased from 308.15 to 318.15 K. It has been observed that the CMC values of BDDAB are higher in presence of acetamide than in urea.

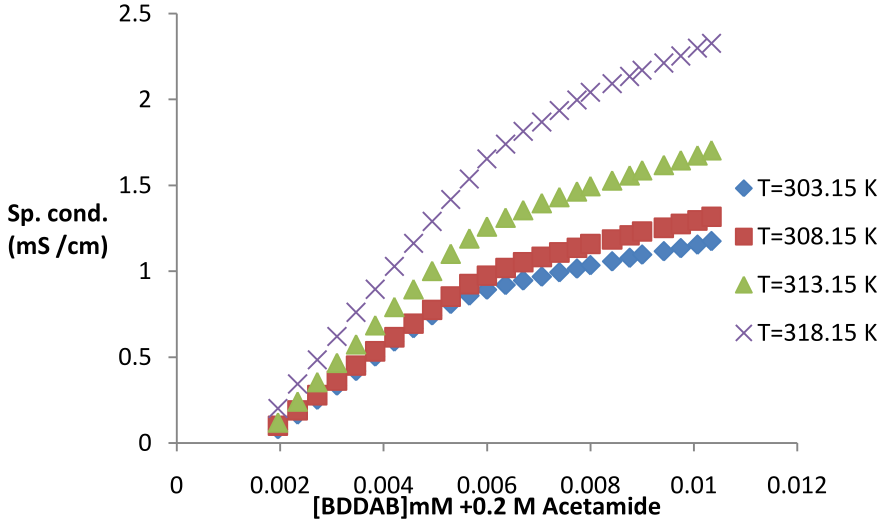

Fig 4. Specific conductivities versus [BDDAB] at different temperatures in 0.2 M Acetamide.

Table 2: Values of Critical micelle concentration (CMC) and degree of ionization (α) of BDDAB in 0.2, 0.4 and 0.6 M Acetamide at different temperatures

	CMC		
Temperature (K)	**BDDAB + 0.2 M Acetamide**	**BDDAB + 0.4 M Acetamide**	**BDDAB + 0.6 M Acetamide**
303.15	0.0063	0.0064	0.0066
308.15	0.0064	0.0065	0.0067
313.15	0.0065	0.0066	0.00675
318.15	0.0066	0.0067	0.0068
	α		
303.15	0.278	0.302	0.299
308.15	0.320	0.314	0.334
313.15	0.328	0.333	0.342
318.15	0.366	0.358	0.347

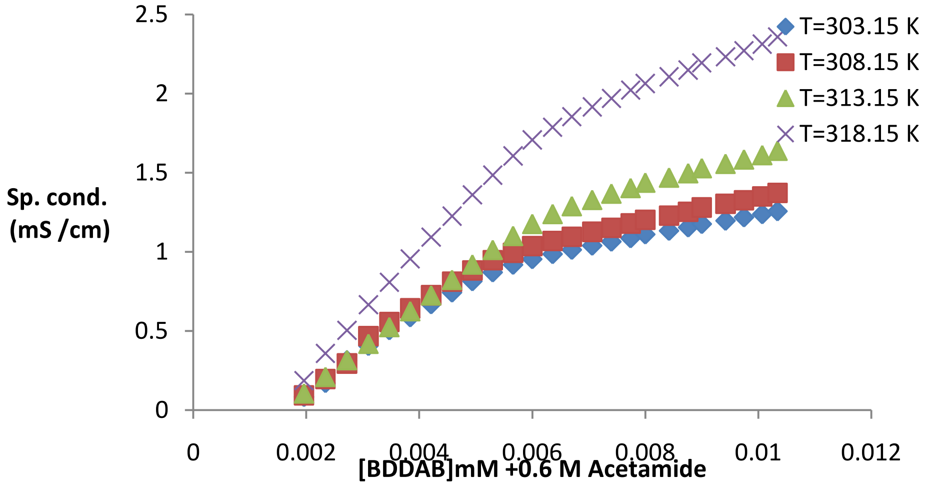

Fig 5. Specific conductivities versus [BDDAB] in 0.6 M Acetamide at different temperatures.

Determination of Degree of ionization (α): It is observed from table 1 and 2, that, there is an increase in CMC and α value with increasing concentration of urea and acetamide (Fig 6, 7). Hydrophobic interaction of electrostatic repulsions is two important factors for micellization. The dielectric constant of medium decreases in the presence of additives. This decrease in the dielectric constant is expected to cause an increase in the electrostatic repulsions between the cationic head group at the micellar surface and also decrease hydrophobic interactions between the hydrocarbon tails. As a result, the CMC and α values increase with additives.

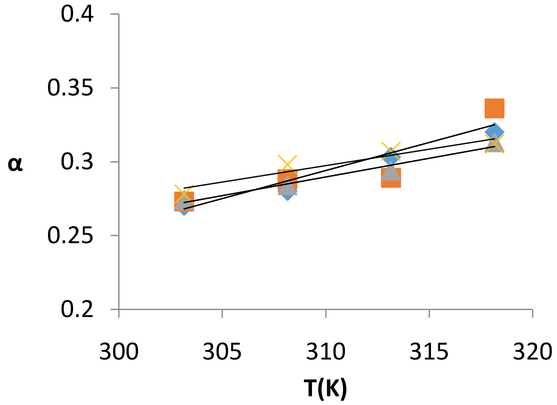

Fig. 6. Variation of degree of ionization (α) of BDDAB with temperature in presence of 0.2, 0.4 and 0.6 M Urea.

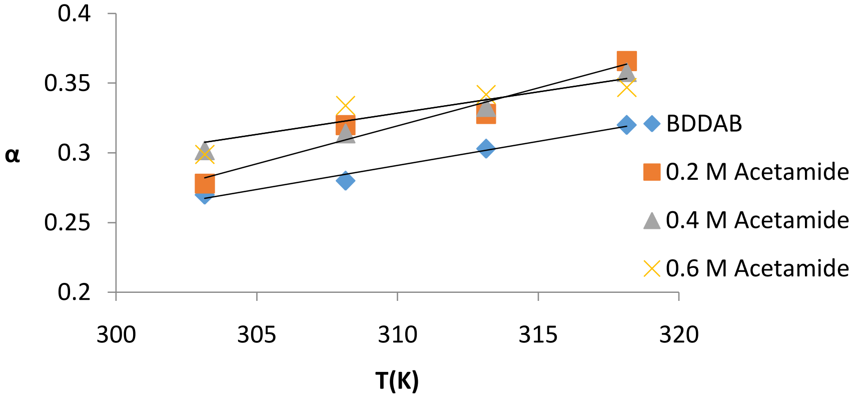

Fig 7. Variation of degree of ionization (α) of BDDAB with temperature in presence of 0.2, 0.4 and 0.6 M Acetamide.

The polarity of the medium alone cannot be a primary guide for this effect. The delay in micellization in the presence of urea and acetamide can be explained in terms of the formation of hydrogen bonds between solvent and water molecules. The inhibitory effect of BDDAB can be understood by taking of the H_2O-BDDAB system, known to form stoichiometric hydrates with water of the type BDDAB, $2H_2O$. The Hydrate formation substantially restricts the motion of the surfactants molecules and reduces hydrophobic interaction with a concomitant increase in CMC. Dielectric constant of urea is very low, which decrease polarity of the medium. As a result the hydrophobic interaction micellization occurs only at a higher [surfactant]. Compounds that penetrate into the micelles a delay micellization by missed micelle formation do not allow multiple hydrogen bonding and have inhibitory effect upon micellization. Destruction of the original 3D structure of water and formation of new H-bonds between water and the alcohols play a significant role. Alcohol-water mixture is a better solvent for surfactants than pure water and thus micelles are formed at higher [surfactant]. Urea and acetamide acts as a structure breakers and decreases the hydrophobic effect due to the increase of cohesive energy and dielectric constant. Therefore, addition of additives mainly produces an increase in CMC. The interaction of the surfactant hydrophilic group also control micellization process and can form 3D cage-like structure as can water, in binary mixture.

Thermodynamics of micellization: The thermodynamics of micellization, viz, Gibbs free energy of micellization (ΔG^0_m), enthalpy (ΔH^0_m) and entropy (ΔS^0_m) of micellization can be derived from the temperature dependence of the CMC. The availability of these parameters (Table. 4) 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^0_m was calculated using the equation,

$$\Delta G^0_m = (2-\alpha)\, RT \ln X_{CMC}$$

Where X_{CMC} is the CMC value expressed in the mole fraction scale.

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

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

($d\ln X_{CMC}/dT$) 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,

$$\Delta S^0_m = (\Delta H^0_m - \Delta G^0_m)/T.$$

Thermodynamic parameters for BDDAB in different aqueous solutions of urea and acetamide at different temperatures are given in tables 3 and 4. The values (ΔH^0_m) decrease at all urea and acetamide concentrations with temperature although the (ΔH^0_m) < 0, at all concentrations revealing the exothermic behavior of surfactant in aqueous BDDAB + urea and BDDAB + acetamide system. The positive (ΔS^0_m)

value is probably due to the destruction of iceberg structure of water because of decrease in hydrogen bond interaction as concentration of urea and acetamide is increased.

Further, the observed drop in the magnitude (ΔS^0_m) of values of BDDAB with rise in temperature and at all concentrations of urea and acetamide can be suggested to indicate the contribution due to the presence of –NH_2 group. The negative value of (ΔG^0_m) of micelle formation is mainly due to positive value of (ΔS^0_m) and therefore, micellization seems to be entropy driven process. The estimated uncertainties are ±0.2 $kJmol^{-1}$ in case of (ΔH^0_m), ±2 $Jmol^{-1}$ in (ΔS^0_m) and ±0.1 $kJmol^{-1}$ in case of (ΔG^0_m). Urea and acetamide are hydrogen bonding aprotic solvents.

Table 3: Standard thermodynamic parameters of micellization of BDDAB in presence and absence of Urea at different temperatures T (K).

Temperature (K)	**$-\Delta G^o_m$ kJ mol^{-1}**	**$-\Delta H^o_m$ kJ mol^{-1}**	**ΔS^o_m JK^{-1} mol^{-1}**
BDDAB			
303.15	37.80	9.31	93.9
308.15	36.64	10.01	86.4
313.15	35.49	10.23	80.66
318.15	34.52	10.53	75.40
BDDAB + 0.2M Urea			
303.15	45.07	9.34	126.31
308.15	45.35	9.74	124.34
313.15	47.00	9.98	123.38
318.15	46.60	10.14	119.73
BDDAB + 0.4M Urea			
303.15	47.26	9.21	127.72
308.15	47.51	9.42	127.68
313.15	47.41	9.71	124.14
318.15	47.04	9.88	121.86
BDDAB +0.6 M Urea			
303.15	47.43	11.72	119.60
308.15	47.35	12.03	116.72
313.15	46.67	12.34	115.04
318.15	47.89	12.71	113.31

Table 4: Standard thermodynamic parameters of micellization of BDDAB in acetamide at different temperatures T (K).

Temperature (K)	**$-\Delta G^o_m$ kJ mol^{-1}**	**$-\Delta H^o_m$ kJ mol^{-1}**	**ΔS^o_m JK^{-1} mol^{-1}**
BDDAB + 0.2 M Acetamide			
303.15	47.49	14.58	110.20
308.15	47.01	15.03	106.09
313.15	47.21	15.17	104.01
318.15	46.61	15.43	100.0

BDDAB + 0.4 M Acetamide			
303.15	47.03	15.41	106.02
308.15	47.24	16.02	103.24
313.15	47.10	16.21	100.41
318.15	46.91	16.53	97.32
BDDAB + 0.6 M Acetamide			
303.15	47.29	18.11	98.14
308.15	46.79	18.44	94.04
313.15	46.93	18.97	91.14
318.15	47.33	19.56	89.31

The formation of micellization was always found to be connected with a large, negative change in ΔG^0_m i.e. the aggregation process is thermodynamically favored and spontaneous. In the temperature range studied (Table 3), small differences in ΔG^0_m 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^0_m values become less negative with increase in temperature (Fig 8, 9). No definite trends have been observed.

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

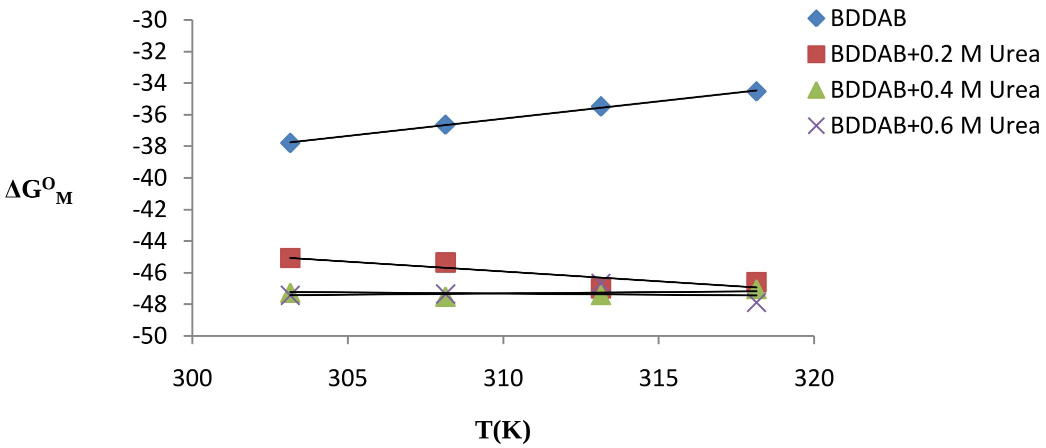

Fig 8. Effect of Urea on free energy of micellization of BDDAB ($\Delta G^0{}_m$) with Temperature.

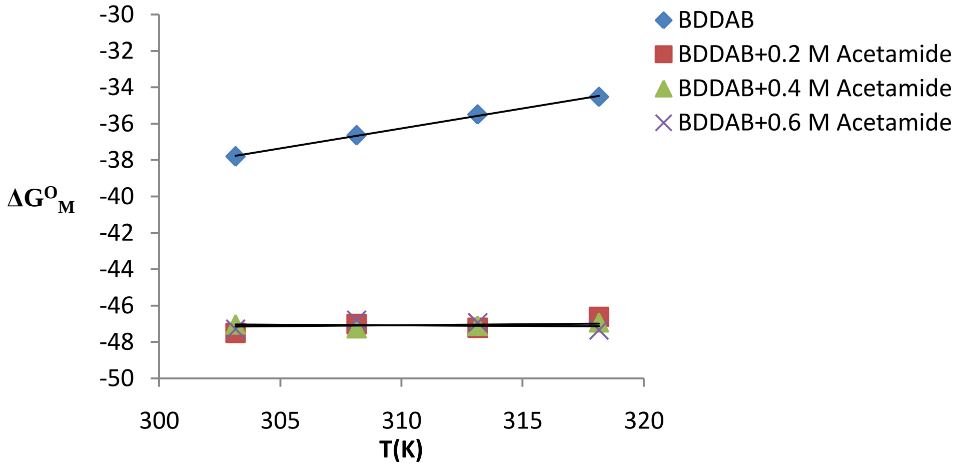

Fig 9.Effect of Acetamide on free energy of micellization of BDDAB ($\Delta G^0{}_m$) with Temperature.

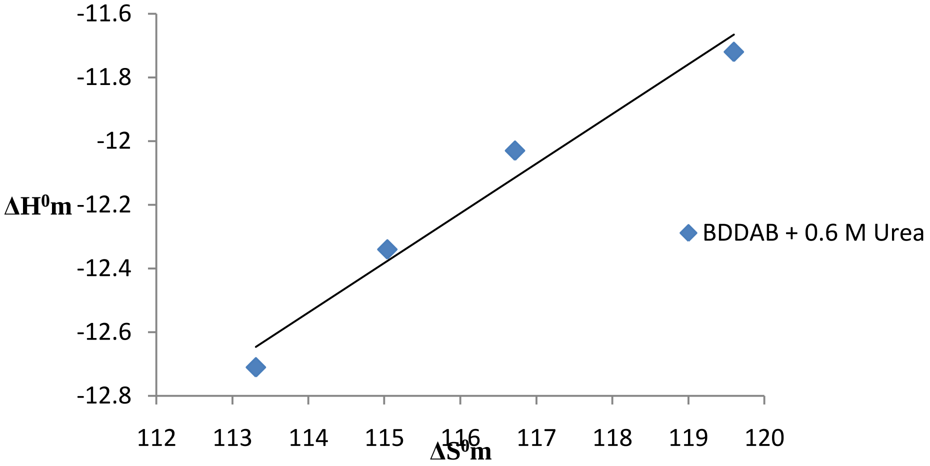

Fig 10: Enthalpy - entropy compensation plot of BDDAB + 0.6M Urea

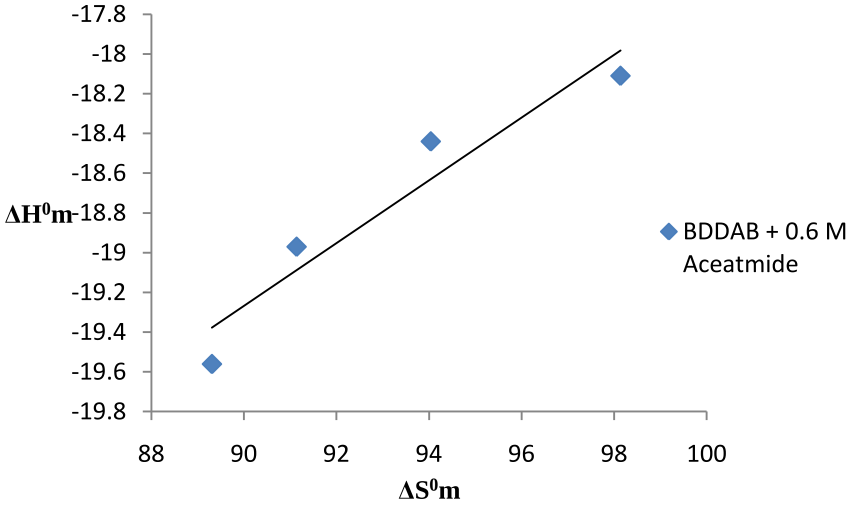

Fig 11: Enthalpy - entropy compensation plot of BDDAB + 0.6M Acetamide

The Enthalpy - entropy compensation plot of BDDAB + 0.6M Urea (Fig 10) and BDDAB + 0.6M Acetamide (Fig 11) indicates that as enthalpy change increases entropy also. The $\Delta S^0{}_m$ values for

BDDAB-additives system were positive, indicating that the micellization process is entropy dominated. As observed in Table 3 and 4, the magnitudes of ΔS^0_m are lower in the presence of additives relative to that in the absence of additives. This suggests that these additives still control the three-dimensional water matrix, indicating that the micellization process of the studied surfactant is exothermic. According to the large, positive values of ΔS^0_m for aqueous solutions of urea and acetamide, the system becomes more random after micellization. The positive values of ΔS^0_m clearly indicate that the micellization of the studied surfactant in aqueous as well as various additives is governed mainly by hydrophobic interaction between the surfactant cations resulting in the breakdown of the structural water surrounding the hydrophobic groups.

APPLICATIONS

These studies indicate that micellization of BDDAB affect in the presence of additives. In case of urea and acetamide with BDDAB, at lower concentration electrostatic interactions prevail and are more dominant but at higher concentration of surfactant, micellization seems to be the predominant process due to increase in hydrophobic forces. So the studies clearly substantiate the fact that CMC of BDDAB gets decreased in the presence of urea and acetamide additives.

CONCLUSIONS

The above study shows that the micellization of benzyl dimethyl dodecyl ammonium bromide occurs in the presence of non-polar mixed solvents which are known to slow down the micellization process. Therefore, these systems may be utilized for the organic reactions and enzymatic hydrolysis which occur in non-polar solvents or in presence of binary solvents, where one of the components is water. The micellization behavior of the cationic surfactant, the benzyl dimethyl dodecyl ammonium bromide as a function of temperature has been studied by electrical conductivity method. This has made the calculation of the thermodynamic functions of micellization possible. With the pseudo-phase separation model, we have been able to show that the variation of enthalpy and entropy of micellization compensates each other. The large changes in entropy (ΔTS^0_m) and enthalpy (ΔH^0_m) with increasing temperature result in moderate decrease in the Gibbs energy. The enthalpy change at all temperatures varied linearly with temperature. From the above studies, thus it is concluded that micellization of BDDAB was affected in the presence of additives. In case of urea and acetamide with BDDAB, at lower concentration electrostatic interactions prevail and are more dominant but at higher concentration of surfactant, micellization seems to be the predominant process due to increase in hydrophobic forces. The CMC values of surfactant obtained from conductance studies show significant temperature and concentration (urea and acetamide) dependence. The studies clearly substantiate the fact that CMC of BDDAB gets decreased in the presence of urea and acetamide additives.

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