

Micellization of Dodecyltrimethyl Ammonium Bromide in Pure and Binary Solvent System of Water and Ethylene Glycol: A Thermodynamic Approach

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Abstract; Despite extensive studies made on surfactant since its potential for wide variety of applications, exploring the micellization of DTAB in pure solvent and in binary solvent systems of various compositions of water and ethylene glycol at different temperatures have been studied via thermodynamic approach due to the industrial applications which are largely depend on it. From conductivity measurements, the critical micelle concentration and degree of ionization were determined and a phase separation model which gives quantitative theoretical interpretation of thermodynamic parameters of micellization to evaluate the free energy, enthalpy and entropy of micellization for ionic surfactant. On the basis of results, increase of CMC and degree of counter ion dissociation with temperature and solvent composition has been discussed from thermodynamic analysis that the process is spontaneous and exothermic but micellization is less favourable in binary solvent system compared to pure water. The ΔS_m° values for aqueous solution of DTAB are higher than that of binary solvent systems that micellization is favoured by entropy gain in aqueous solution.

Keywords: Binary solvent system, dodecyltrimethyl ammonium bromide [DTAB], ethylene glycol, micellization, thermodynamic parameters.

INTRODUCTION

Tremendous application potential and economical consideration of surfactants to make an extensive contribution in the field of academic and commercial. The behavior of surfactant is of considerable interest from both fundamental and practical point of view in the case of systems containing lesser amount of water or poor water medium. The intrinsic duality of the molecular characteristic of surfactant is the key to form micelles at specific concentration range [cmc] and a temperature known as krafft temperature. The critical micelle concentration is affected by various factors such as surfactant architecture, temperature, nature of head group, pH, etc. Among the other factors that influence the cmc, co-solvent play an important role in controlling the micellization of surfactant [1,2]. Co solvents such as glycol, glycerol ethanol, etc. are used in pharmaceutical formulation, in cosmetics production, etc. to increase the solubility of the active compound. Micellization process of ionic and nonionic surfactants in presence of co solvent has been studied by many investigators [3-7]. The investigation of self-association phenomenon in the presence of co solvent may be useful to select appropriate surfactant systems of specific utility, so the present work is the systematic study of micellization of DTAB in water, in EG as well as in binary solvent systems of water and ethylene glycol

EXPERIMENTAL WORK

Material and Method: Dodecyltrimethyl ammonium bromide [DTAB] is cationic surfactant purchased from Spectrochem Pvt. Ltd. [Mumbai]. Ethylene Glycol was obtained from Merck Pvt. Ltd. and used without further purification. Conductivity water was used for preparing all solutions. Conductance measurement: Concentrated stock solutions of DTAB were prepared individually in pure solvent [H₂O and EG] and in different compositions of binary solvent of EG with water.

Initially 25 ml. of solvent [water or EG] or desired binary mixture of solvent was taken in a thermostate container and a known concentration of DTAB solution progressively added from a micropipette .After mixing and attaining temperature equilibrium at a specific temperature, the specific conductance was measured by using digital systronics conductivity meter [306] equipped with a dip cell of cell constant 1.00cm⁻¹The procedure was repeated at different temperatures from 298-318 K.

RESULTS AND DISCUSSIONS

Effect of temperature on CMC and degree of ionization: The values of specific conductance and molar concentration of DTAB in aqueous and in binary solvent system of EG at different temperature are listed in table [1-4].

Table 1, 2, 3 and 4: Shows specific conductance and molar concentration of DTAB surfactant in water, 5% , 15% and 25% of binary solvent system of EG, respectively at different temperature

Table 1

DTAB Concentration (mM)	specific conductance(mScm ⁻¹)				
	298K	303K	308K	313K	318K
0	0	0	0	0	0
1.58	0.16	0.18	0.20	0.22	0.24
2.37	0.22	0.25	0.27	0.30	0.33
3.14	0.28	0.32	0.35	0.39	0.42
3.92	0.33	0.38	0.42	0.47	0.51
4.68	0.39	0.44	0.49	0.55	0.61
5.44	0.46	0.52	0.56	0.63	0.69
6.20	0.53	0.59	0.65	0.71	0.78
6.95	0.58	0.64	0.72	0.80	0.86
7.69	0.64	0.70	0.79	0.87	0.94
8.43	0.70	0.77	0.86	0.94	1.02
9.16	0.75	0.84	0.93	1.02	1.11
9.88	0.81	0.90	1.00	1.10	1.20
10.60	0.86	0.97	1.07	1.18	1.29
11.32	0.92	1.03	1.14	1.27	1.38
12.00	0.98	1.10	1.22	1.34	1.46
12.70	1.02	1.16	1.28	1.41	1.54
13.40	1.06	1.21	1.35	1.49	1.62
14.10	1.09	1.25	1.40	1.54	1.70
14.80	1.12	1.29	1.44	1.59	1.75
15.50	1.15	1.31	1.48	1.63	1.80
16.17	1.17	1.34	1.52	1.67	1.85
16.80	1.19	1.36	1.56	1.71	1.90
17.50	1.22	1.38	1.60	1.75	1.95
18.20	1.25	1.40	1.63	1.78	2.00
18.80	1.27	1.42	1.66	1.82	2.01
19.50	1.29	1.45	1.68	1.85	--
20.10	1.31	1.47	1.70	1.88	--
20.70	1.33	1.48	1.72	--	--
21.40	1.35	1.50	1.74	--	

Table 2

DTAB Concentration (mM)	specific conductance(mScm ⁻¹)				
	298K	303K	308K	313K	318K
0	0	0	0	0	0
1.58	0.11	0.12	0.13	0.15	0.17
2.37	0.15	0.18	0.19	0.21	0.24
3.14	0.20	0.23	0.26	0.28	0.31
3.92	0.25	0.28	0.32	0.35	0.38
4.68	0.29	0.33	0.37	0.42	0.46
5.44	0.33	0.38	0.43	0.48	0.53
6.2	0.38	0.44	0.49	0.54	0.60
6.95	0.42	0.49	0.55	0.60	0.67
7.69	0.46	0.53	0.60	0.67	0.74
8.43	0.51	0.59	0.66	0.73	0.80
9.16	0.57	0.63	0.72	0.79	0.87
9.88	0.61	0.68	0.77	0.84	0.93
10.6	0.65	0.72	0.82	0.90	1.00
11.32	0.70	0.76	0.86	0.95	1.06
12	0.74	0.80	0.90	1.01	1.12
12.7	0.77	0.85	0.95	1.07	1.19
13.4	0.80	0.90	1.00	1.13	1.26
14.1	0.85	0.95	1.05	1.19	1.33
14.8	0.90	1.01	1.10	1.26	1.40
15.5	0.92	1.04	1.15	1.31	1.46
16.17	0.95	1.08	1.20	1.36	1.51
16.8	0.98	1.11	1.25	1.41	1.58
17.5	1.00	1.14	1.30	1.46	1.63
18.2	1.02	1.16	1.32	1.49	1.66
18.8	1.04	1.18	1.33	1.52	1.70
19.5	1.05	1.19	1.35	1.54	1.73
20.1	1.07	1.21	1.37	1.56	1.76
20.7	1.09	1.23	1.38	1.58	1.79
21.4	1.10	1.25	1.40	1.61	1.82

Table 3

DTAB Concentration (mM)	specific conductance(mScm ⁻¹)				
	298K	303K	308K	313K	318K
0	0	0	0	0	0
1.58	0.08	0.1	0.11	0.13	0.14
2.37	0.13	0.14	0.16	0.18	0.2
3.14	0.17	0.19	0.21	0.23	0.26
3.92	0.21	0.23	0.26	0.28	0.32
4.68	0.24	0.28	0.31	0.35	0.39
5.44	0.28	0.33	0.37	0.41	0.46
6.20	0.32	0.38	0.42	0.47	0.53
6.95	0.36	0.42	0.47	0.52	0.58
7.69	0.4	0.46	0.52	0.58	0.64
8.43	0.44	0.51	0.57	0.64	0.71
9.16	0.48	0.56	0.63	0.69	0.78
9.88	0.52	0.6	0.68	0.75	0.83
10.60	0.55	0.64	0.73	0.81	0.89
11.32	0.59	0.69	0.78	0.86	0.95
12.00	0.64	0.74	0.83	0.92	1.01
12.70	0.68	0.78	0.88	0.97	1.07
13.40	0.72	0.81	0.92	1.01	1.14
14.10	0.75	0.85	0.96	1.06	1.19
14.80	0.77	0.88	1	1.11	1.25
15.50	0.79	0.91	1.03	1.16	1.3
16.17	0.81	0.94	1.06	1.21	1.35
16.80	0.83	0.97	1.1	1.27	1.4
17.50	0.85	1	1.13	1.32	1.45
18.20	0.87	1.02	1.15	1.35	1.49
18.80	0.88	1.04	1.18	1.37	1.53
19.50	0.89	1.06	1.21	1.4	1.57
20.10	0.9	1.08	1.24	1.42	1.61
20.70	0.91	1.1	1.26	1.45	1.65
21.40	0.93	1.13	1.28	1.47	1.69

Table 4

DTAB Concentration (mM)	specific conductance(mScm ⁻¹)				
	298K	303K	308K	313K	318K
0	0	0	0	0	0
1.58	0.06	0.07	0.08	0.09	0.1
2.37	0.09	0.1	0.12	0.13	0.14
3.14	0.11	0.13	0.15	0.17	0.19
3.92	0.13	0.16	0.22	0.21	0.23
4.68	0.16	0.19	0.26	0.25	0.28
5.44	0.19	0.22	0.3	0.3	0.33
6.2	0.22	0.26	0.34	0.34	0.38
6.95	0.25	0.29	0.37	0.36	0.43
7.69	0.27	0.32	0.41	0.4	0.47
8.43	0.3	0.35	0.45	0.45	0.52
9.16	0.33	0.38	0.48	0.49	0.56
9.88	0.36	0.41	0.51	0.52	0.6
10.6	0.38	0.45	0.54	0.54	0.64
11.32	0.41	0.48	0.57	0.58	0.69
12	0.43	0.5	0.6	0.62	0.73
12.7	0.46	0.53	0.63	0.67	0.78
13.4	0.48	0.56	0.67	0.71	0.82
14.1	0.51	0.6	0.71	0.75	0.86
14.8	0.54	0.63	0.75	0.8	0.9
15.5	0.57	0.65	0.78	0.84	0.94
16.17	0.59	0.67	0.81	0.88	0.99
16.8	0.61	0.7	0.84	0.91	1.03
17.5	0.63	0.74	0.88	0.94	1.07
18.2	0.66	0.77	0.91	0.98	1.12
18.8	0.68	0.79	0.94	1.02	1.16
19.5	0.7	0.81	0.97	1.06	1.2
20.1	0.73	0.83	1	1.1	1.25
20.7	0.74	0.85	1.03	1.14	1.3
21.4	0.75	0.87	1.06	1.18	1.36

The variation of specific conductance values of micellar aqueous solution of DTAB as a function of its molar concentration gave two straight lines with different slopes for aqueous, various compositions of ethylene glycol, and pure EG at different temperatures.[Figure1-5]. These plots exhibits change of slope at a specific point and it is used to determine the CMC and the ratio of the slopes of post micellar region to pre micellar region determine degree of ionization [8]. The CMC and degree of ionization of DTAB in water and in binary solvent systems increased with increase in temperature as shown in table[5] ,this could be explained that at elevated temperature disruption of water molecules around the polar head groups and hence the repulsive forces of head groups increases which decrease the micellization [9]. From Table 5, it is clear that the degree of ionization value [α] increase with temperature [Figure 6]. This behavior could be attributed to the fact that thermal forces increases the separation between the ionic head groups and counter ions [10].

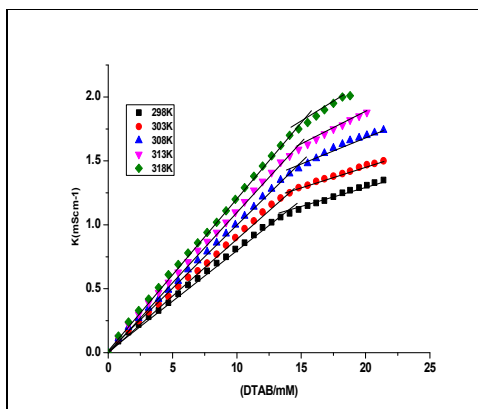


Figure 1

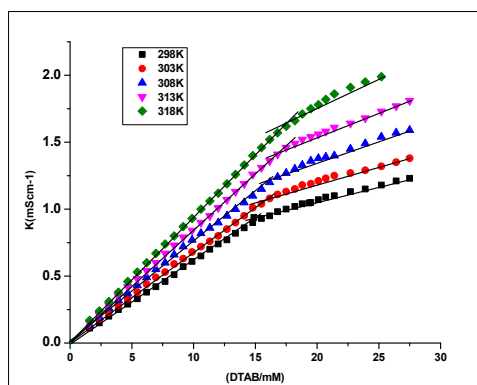


Figure 2

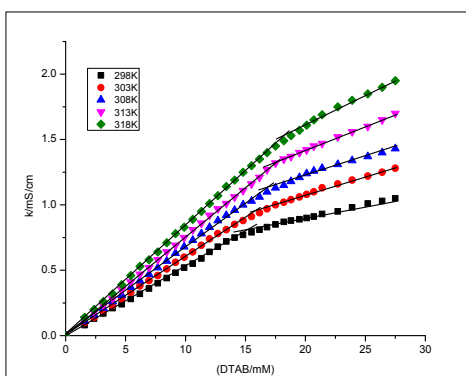


Figure 3

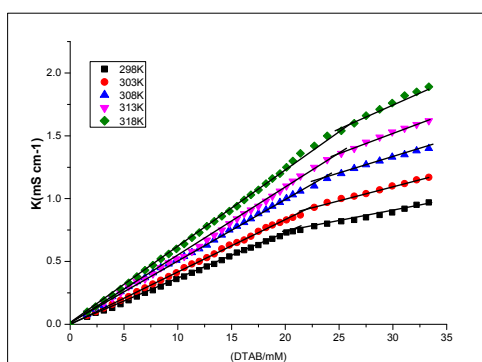


Figure 4

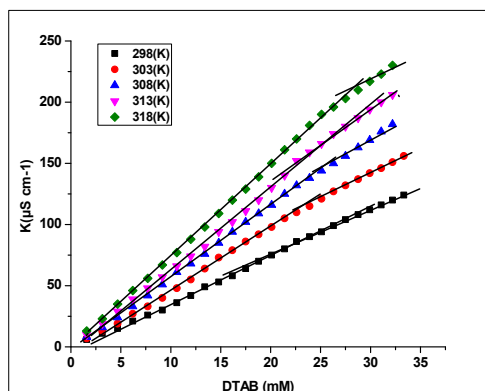


Figure 5

Figure 1, 2, 3, 4 and 5: Plot of specific conductance and molar concentration of DTAB surfactant in water, 5%, 15%, 25% of binary solvent system of EG and in pure EG, respectively at different temperatures

Table -5: CMC and degree of counter ion dissociation value[α] of DTAB in aqueous and in binary solvent system of [EG+water] at different temperatures and also cmc values of DTAB in pure EG solvent system

Co-solvent (%)	Temperature(K)									
	298		303		308		313		318	
	cmc(mM)	α	cmc(mM)	α	cmc(mM)	α	cmc(mM)	α	cmc(mM)	α
Water	14.06	0.32	14.34	0.37	14.57	0.41	14.9	0.45	15.23	0.49
5%EG	14.95	0.40	15.85	0.44	16.28	0.47	16.86	0.50	17.54	0.54
15%EG	15.4	0.47	15.93	0.5	16.9	0.54	17.48	0.58	18.32	0.61
25%EG	21.01	0.52	22.18	0.56	23.57	0.59	24.56	0.64	25.78	0.68
Pure EG	22.63	-	23.13	-	25.10	-	26.37	-	28.56	-

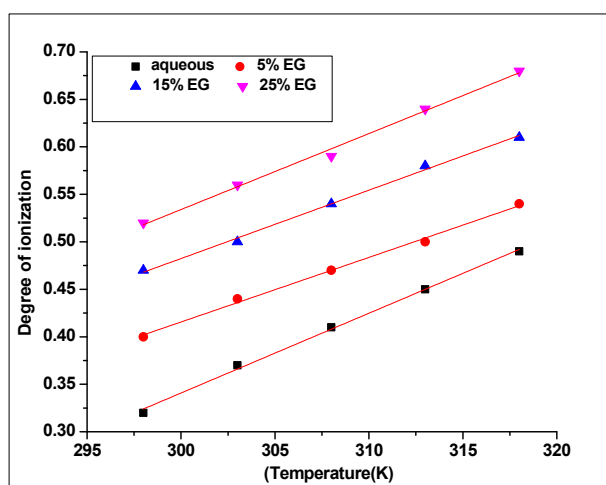


Figure 6: Variation of degree of ionization value with temperature

Effect of Ethylene glycol on cmc and degree of ionization: On addition of polar solvent [ethylene glycol] to an aqueous solution of surfactant, an increase in CMC and degree of ionization values are observed([table 5]) due to change in the bulk phase properties [e.g. dielectric constant, dipole moment, viscosity, etc.] of the solvent system [11]. An increase in EG solvent content in aqueous solution causes decrease of the dielectric constant of solvent mixture because EG dielectric constant[$\epsilon=37.7$] is lower than water[$\epsilon=78.54$],so lowering of dielectric constant would result in an increase in the repulsion between the ionic head groups leading to delayed micellization [12]. Another fact that water structure breaker property of ethylene glycol would facilitate the interaction between the hydrocarbon part of organic solvent and hydrophobic tail of the surfactant molecule, which made it difficult for the hydrocarbon chain of surfactant to aggregate due to solvation of them and so the lesser number of monomer to form micelles and hence increase cmc of surfactant [13]. An increase in degree of ionization with respect to solvent percentage is expected due to decrease charge density on the micellar surface caused by a reduction of the micellar aggregation number [14]. The high viscous nature of the EG than water and also the solubility of the hydrophobic part of surfactant increases in pure EG solvent as well as the temperature increases and hence association of surfactant monomer become difficult and increases the value of cmc in pure EG system [table5].

Thermodynamics of micellization: All physico-chemical processes are energetically controlled. Two thermodynamic models [a] phase separation model and [b] mass action model are used to interpret energetics of micellization. Variation of CMC values with temperature are used to evaluate thermodynamic parameters which are further analyzed in terms of the phase separation model for micelle formation [15]. According to this model for ionic surfactant the standard Gibb's free energy of micellization are calculated from the following equation

$$\Delta G_m^o = (2 - \alpha)RT \ln X_{cmc} \quad [1]$$

Where, R, T and X_{cmc} are ideal gas constant, absolute temperature and cmc expressed in mole fraction unit respectively.

The effect of EG on micellization process may be studied by means of free energy of surfactant tail transfer ΔG_{trans}^o , which is defined by the expression [16].

$$\Delta G_{trans}^o = \Delta G_{m(EG+H_2O)}^o - \Delta G_{m(H_2O)}^o \quad [2]$$

The corresponding enthalpy of micellization may be obtained from the following equation

$$\Delta H_m^o = -(2-\alpha)RT^2(d \ln X_{cmc}/dT) \quad [3]$$

The values of ΔH_m^o can be calculated by substituting the value of slope of the curve between $\ln X_{cmc}$ versus temperature [Figure7]. Further the entropy of micelle formation can be calculated using the equation

$$\Delta S_m^o = \Delta H_m^o - \Delta G_m^o/T \quad [4]$$

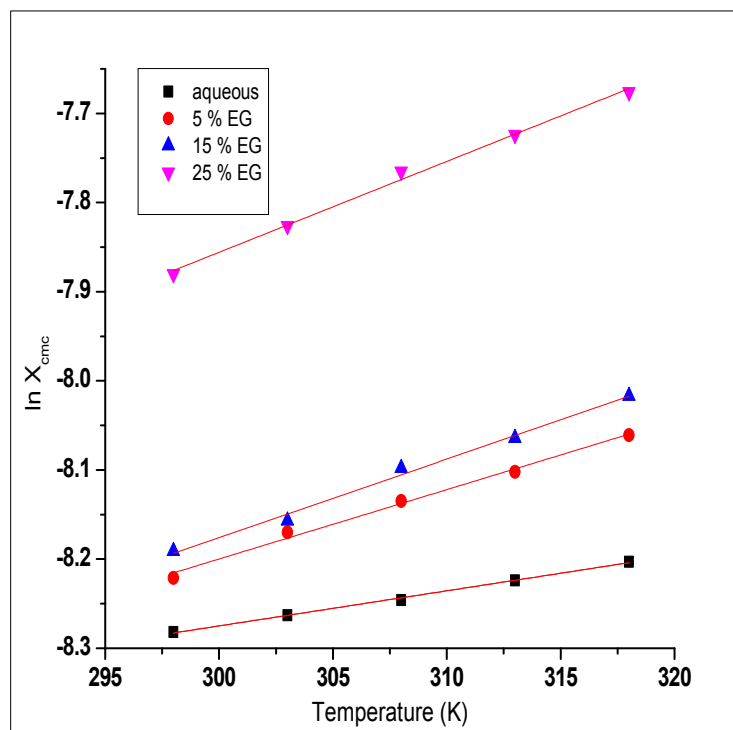


Figure 7: variation of $\ln X_{cmc}$ of DTAB with temperature

Table-6: Thermodynamic parameters of DTAB in aqueous and different compositions of [EG+water] binary solvent system at different temperatures

Co-solvent	Temperature(K)				
	298	303	308	313	318
	change in Gibbs free energy ΔG_m° (kJ mol ⁻¹)				
water	-34.47	-33.93	-33.57	-33.17	-32.75
5%EG	-32.58	-32.10	-31.87	-31.62	-31.11
15%EG	-31.05	-30.82	-30.27	-29.8	-29.46
25%EG	-28.89	-28.39	-28.03	-27.33	-26.78
	change in enthalpy of micellization ΔH_m° = (kJ mol ⁻¹)				
water	-4.83	-4.85	-4.89	-4.92	-4.95
5%EG	-9.09	-9.16	-9.29	-9.40	-9.45
15%EG	-9.94	-10.07	-10.13	-10.17	-10.28
25%EG	-11.14	-11.21	-11.26	-11.29	-11.32
	change in entropy of micellization ΔS_m° (K ⁻¹ J mol ⁻¹)				
water	99.43	95.96	93.11	90.25	87.41
5%EG	78.80	75.68	73.30	70.96	68.11
15%EG	70.83	68.46	65.39	62.69	60.31
25%EG	59.56	56.69	54.44	51.24	48.61
	change in Gibbs free energy of tail transfer ΔG_{trans}° (kJ mol ⁻¹)				
water	-	-	-	-	-
5%EG	2.15	1.85	1.71	1.54	1.21
15%EG	3.42	3.11	3.30	3.15	3.69
25%EG	5.58	5.54	5.53	5.62	5.31

The ΔG_m° values in all cases are negative, $\Delta G_m^{\circ} < 0$, over the entire temperature range in aqueous and in binary solvent systems, that thermodynamically stable micelles are formed spontaneously. Increase in temperature and in binary solvent system its become less negative suggesting that micellization is less favourable in binary solvent system. This can be explained according to the surfactant aggregation theory [17] that there may be different types of free energy associated with micellization process, one of them is the surfactant tail transfer Gibbs free energy which give rise to the effect of co solvent on the micellization process. From [table 6] values of ΔG_{trans}° are positive and increase with increase of EG[%] is due to reduction in solvophobic interaction. The transfer of surfactant tail from the bulk phase to the micellar region become less favourable and it is responsible for delayed micellization in binary solvent system.

The negative values of ΔH_m° [table 6] indicate that the enthalpy change favor the process of micellization and proceed via an exothermic process that indicate the presence of London-dispersion interaction which is the major attractive force for micellization [18]. As the EG content increases the enthalpy of micellization find become more negative [Figure8] due to intermolecular hydrogen bonding of EG with water and negative value of ΔH_m° increase with temperature which may be attributed that disruption of large number of hydrogen bonding of three dimensional water structure around the hydrocarbon ends of surfactant monomer and at higher temperature it require less energy to break the bonds of water around the hydrophobic moiety of surfactant [19]. On the other hand ΔS_m° value [table 6] is positive in all systems that the micellization is favoured by entropy gain and it is reduced at higher temperature it may be due to the decreasing water layer around alkyl chain as temperature increases. Therefore the extent of randomness decrease with increasing temperature [20]. Hence it is less favourable for micellization. The positive value of entropy in binary solvent system is mainly by the hydrophobic interaction between the hydrocarbon part of both surfactant and solvent resulting in the total breakdown of water structure surrounding the hydrophobic part of surfactant.

Although the magnitude of ΔS_m^o is lower in the presence of co solvent than in the aqueous solution, the solvent still control the 3-dimensional water structure [21] and increase orderliness of water by intermolecular hydrogen bonding between water and ethylene glycol around the hydrocarbon chain of surfactant which result in a decrease in the entropy of the binary solvent systems.

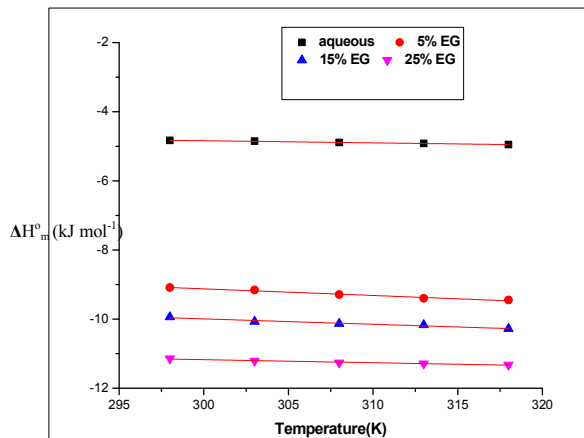


Figure 8: The change in enthalpy ΔH_m^o (kJ mol⁻¹) with temperature

Enthalpy-Entropy compensation for DTAB: In the micellization process exhibit a linear relation between ΔH_m^o and ΔS_m^o known as Enthalpy-Entropy compensation which represent [Figure 9]. that when the entropy contributes less to the free energy, the enthalpy contributes more to the free energy to compensate each other so the micellization process favoured by enthalpy gain at higher temperature and by entropy gain at lower temperature [22].

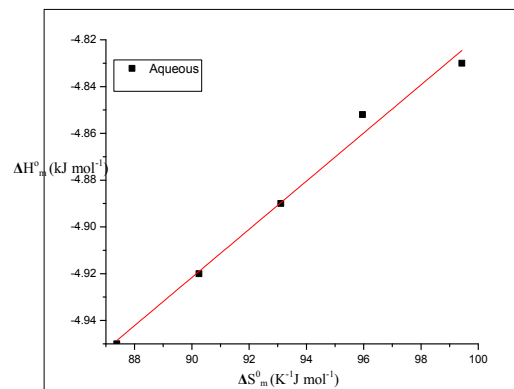


Figure 9: Enthalpy-entropy compensation plot for DTAB in aqueous solution

CONCLUSION

Surfactant-binary solvent system have received considerable attention due to their wide range of applications, where one solvent is other than water. Due to change in bulk phase properties [dielectric constant, viscosity etc.] and high solubility of hydrophobic part of the surfactant with hydrocarbon part of EG in mixed solvent system, in pure EG solvent system and thermal agitation of surfactant molecule are responsible for unfavourable micellization and hence increase in cmc and degree of ionization for DTAB surfactant. According to thermodynamics of micellization decrease in free energy of system suggesting micellization is spontaneous and favourable but increase in temperature and addition of EG decreases the spontaneity of micellization of DTAB surfactant.

Dominance of London-dispersion interaction which favour the micellization and therefore enthalpy values are found to increase and values of entropy decrease with increases of temperature and addition of ethylene glycol. Micellization is favoured by increase the enthalpy change at higher temperature and entropy gain at lower temperature and also they compensate each other. Knowledge of CMC and thermodynamics of the process are essential for characterization and comparison in terms of spontaneity and stability. So it would be beneficial for various types of applications like cleaning, lubrications, pharmaceutical, cosmetic, petroleum and mineral processing etc. which require lesser amount of water.

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