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ORIGINAL ARTICLE

The Effect of Methanol on the Micellar Properties of Dodecyltrimethylammonium Bromide (DTAB) in Aqueous Medium at Different Temperatures

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Abstract The micellar properties of dodecyltrimethylammonium bromide (DTAB) in water and methanol water mixtures at different temperatures have been studied by conductivity and surface tension measurements. The critical micelle concentrations (CMC), degree of ionization (α), standard Gibbs free energy of micellization (ΔG_m^o), standard enthalpy of micellization (ΔH_m^o), standard entropy of micellization (ΔS_m^o) and free energy of transfer (ΔG_{trans}^o) were evaluated from conductivity data. The CMC, maximum excess surface concentration (Γ_{max}), area occupied per surfactant molecule (A_{min}), surface pressure at the CMC (π_{cmc}), packing parameter (P) and standard free energy interfacial adsorption (ΔG_{ads}^o) were estimated from surface tension measurements. The CMC of DTAB was found to increase with increasing volume fraction of methanol and increasing temperature. Thermodynamic parameters and surface properties revealed that the addition of methanol changes the relevant physicochemical properties which affect the process of micellization.

Keywords Cationic surfactant · Methanol · Surface tension · Micelle · Conductivity · Surface properties

Introduction

Surfactant molecules are characterized by the presence of polar and non-polar parts. Under certain conditions they form aggregates called micelles in solution [1]. The concentration at which micelle are formed is called the critical micelle concentration (CMC). Micelle formation is an important characteristic property of surfactants which is caused by hydrophobic interaction of hydrocarbon tails with water balanced by electrostatic repulsions between the surfactant head groups [2]. Physicochemical properties such as CMC, degree of ionization and thermodynamics of micellization depend on the nature of the hydrophobic tail, the hydrophilic head group and the counter ion species [3].

Organic additives can significantly affect micelle formation. This has prompted investigations concerning the effect of organic additives on the micellization of individual surfactants [4]. The effect of alcohol on micellization has been extensively studied in the preparation of microemulsions [5]. The investigations show that alcohol interacts with the micelle in the surface region resulting in: (a) insertion of alcohol molecules between the ionic head groups of the micelle [6]; (b) a decrease in the dielectric constant at the micellar interface [7]; and (c) a change in the molecular order of the interfacial region of the micelle [5].

In this paper, we investigated the effect of methanol addition and temperature change on the micellization of dodecyltrimethylammonium bromide (DTAB) by conductivity and surface tension measurements.

Experimental Section

Materials

Dodecyltrimethylammonium bromide was purchased from Loba Chemie Private Limited (Mumbai, India). Methanol (E. Merck, India, 99 % pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g cm^{-3} and a

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co-efficient of viscosity of 0.4742 mPa s at 308.15 K which matches that in the literature [8].

DTAB was dried for 1 h and solutions were prepared using triply distilled water. The purity of DTAB was verified by CMC measurement using conductivity and surface tension at 298.15 K. The measured values are in close agreement with those in the literature [9]. Triply distilled water with a specific conductance of less than 10^{-6} S cm^{-1} at 308.15 K was used for the preparation of methanol–water mixed solvent media as well as the DTAB solutions.

Electrical Conductivity Measurements

The conductivity of freshly prepared DTAB solutions was measured using a digital conductivity meter (Systronics, India) with a dip type conductivity cell having a cell constant of 1.002 cm^{-1} and an uncertainty of 0.01 %. The cell was calibrated using aqueous potassium chloride solution [10].

Surface Tension

The surface tension of freshly prepared DTAB solutions was measured using a Borosil Mansingh Survismeter (calibration no. 06070582/1.01/c-0395, NPL, New Delhi) [11] by pendant drop number (PDN) as explained in the literature [12]. The temperature inside the Survismeter was controlled by a thermostat [13].

Solution densities required for the calculation of surface tension were determined using a thermostated 25 cm^3 Sprengel-Ostwald pycnometer. The temperature control had an accuracy of ± 0.1 °C and the reproducibility was $\pm 5 \times 10^{-5}$ g/cm^3 [14].

Results and Discussion

Critical Micelle Concentration (CMC) and Degree of Ionization (α)

Cationic surfactants are generally tertiary ammonium salts of long-chain paraffins which act as strong electrolytes in dilute solution [1]. The critical micelle concentration (CMC) of DTAB was determined by conductometric and tensiometric methods. In the conductometric method, the CMC was obtained from the intersection of the two straight lines of the conductivity-concentration plots [13]. The ratio of the slopes of the linear fragments above and below the break gives an estimate of the degree of micelle ionization, α.

The dependence of specific conductivity and surface tension with DTAB concentration in pure water and in different volume fractions (0.1, 0.2, 0.3 and 0.4) of

methanol–water mixtures at 298.15 K are shown in Figs. 1 and 2 respectively. Figure 1 shows that the conductivity of DTAB solutions decreases both in the pre- and post-micellar regions with an increasing volume fraction of methanol. This behavior is caused by two effects of the solvent-medium properties. Alcohol is known to have structure breaking effects on water and the increase in viscosity of the medium with increasing the methanol content [15, 16].

The data from conductivity and surface tension measurements are summarized in Table 1. The CMC as well as α of DTAB in water are in close resemblance to literature data at 298.15 K [3, 9]. Both the CMC and α increase with increasing volume fraction of methanol at all temperatures.

Increase in α with increasing volume fraction of methanol can be explained by two effects. Intercalation of methanol molecules between the DTAB ions in the micelle causes the average distance between ionic head groups to increase and the micellar surface charge density and ionization decreases [17]. The second effect concerns the dielectric constant of the palisade layer. Methanol probably replaces the water molecules from the palisade layer of the micelle which would decrease the dielectric constant [18]. The measurements done by Zana et al. [19], have shown that addition of alcohol to micellar solutions of tetradecyltrimethylammonium bromide (TTAB) brings about a decrease in polarity which increases the repulsion between ionic head groups and decreases micelle stability. Hence the corresponding charge density decreases and results in an increase of degree of ionization (α).

Increasing temperature may increase the steric volume of the N-atom-head in the micelle and hence degree of
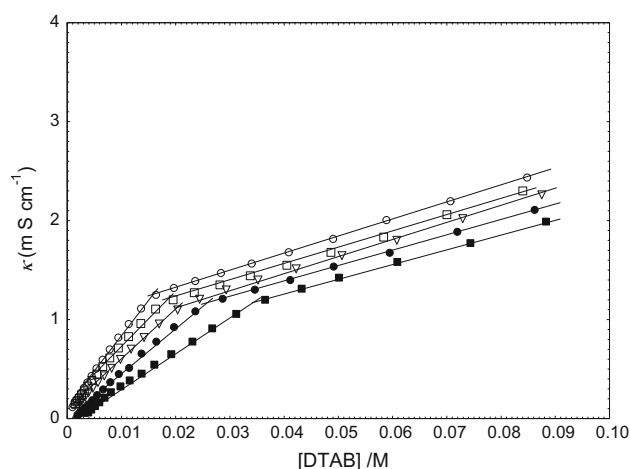

Fig. 1 Plot of specific conductivity *versus* concentration of DTAB solution at 298.15 K, in pure water (*open circles*) different volume fractions of methanol–water mixtures (*open squares*, 0.10 methanol; *open inverted triangles*, 0.20 methanol; *closed circles*, 0.3 methanol; *closed squares*, 0.40 methanol)
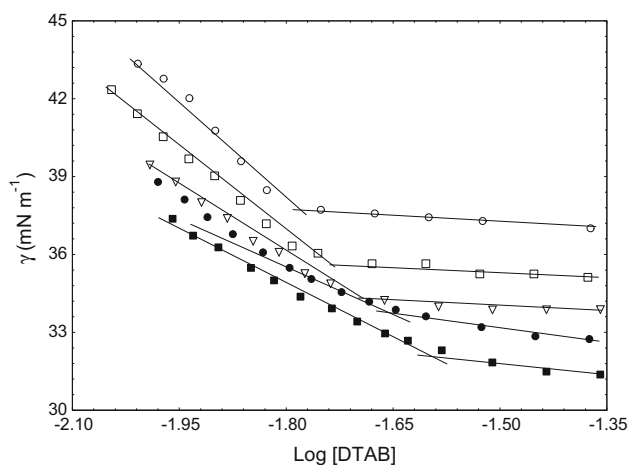
Fig. 2 Plot of surface tension concentration of DTAB solution at 298.15 K, in pure water (*open circles*) different volume fractions of methanol–water mixtures (*open squares*, 0.10 methanol; *open inverted triangles*, 0.20 methanol; *closed circles*, 0.3 methanol; *closed squares*, 0.40 methanol)

ionization (α) is affected [20]. Similar types of variations are found in this investigation in all volume fractions of methanol–water. According to Kabir-Ud-Din et al. [21], two forces, coulombic and thermal, are responsible for the increase in α. The former force is attributed to the attraction of the counter ions to the polar head and the second force is dependent on the temperature. When temperature is increased, the thermal force predominates over the coulombic force and the value of α increases.

Alcohols have lower dielectric constants than pure water and the dielectric constant of the medium decreases when alcohol is added to water. Lower dielectric constant decreases the hydrophobic interaction and increases the CMC [22]. This effect is seen with other hydrogen bonded organic solvents in aqueous medium. The presence of glycols in aqueous medium reveals water structure breaking properties which decreases the relative permittivity of the medium and stabilizes surfactant monomers [23]. In addition, hydrogen bonded organic solvents like alkoxyethanols

Table 1 Critical micelle concentration (CMC), degree of ionization (α) values and thermodynamic parameters of the micellization of DTAB[a] in water and 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol at 298.15 to 323.15 K

Volume fraction of methanol	CMC (mM)		Degree of ionization (α)	ΔG_m^o (kJmol^{-1})	ΔH_m^o (kJmol^{-1})	ΔS_m^o (kJmol^{-1})	ΔG_{trans}^o (kJmol^{-1})
	Conductometry	Tensiometry					
298.15 K							
0.0	14.5 ± 0.10	14.6 ± 0.11	0.21 ± 0.001	−36.58	−9.42	91.11	–
0.1	17.5 ± 0.12	17.1 ± 0.10	0.24 ± 0.002	−34.90	−8.74	87.73	1.68
0.2	20.5 ± 0.12	19.2 ± 0.13	0.28 ± 0.001	−33.17	−7.75	85.25	3.41
0.3	25.1 ± 0.10	25.3 ± 0.14	0.36 ± 0.003	−30.54	−5.88	82.73	6.04
0.4	34.5 ± 0.13	34.1 ± 0.12	0.48 ± 0.004	−26.85	−4.57	74.73	9.73
308.15 K							
0.0	15.4 ± 0.14	15.1 ± 0.15	0.22 ± 0.002	−36.1	−10.00	84.67	–
0.1	18.1 ± 0.13	17.8 ± 0.16	0.25 ± 0.001	−34.54	−9.28	81.96	1.56
0.2	21.7 ± 0.15	21.5 ± 0.14	0.29 ± 0.003	−32.72	−8.23	79.46	3.38
0.3	26.4 ± 0.16	26.7 ± 0.17	0.37 ± 0.002	−30.14	−6.24	77.54	5.96
0.4	35.6 ± 0.14	35.7 ± 0.16	0.49 ± 0.003	−26.54	−4.85	70.38	9.56
318.15 K							
0.0	16.3 ± 0.17	16.4 ± 0.18	0.24 ± 0.001	−35.43	−10.5	78.21	–
0.1	19.5 ± 0.16	19.3 ± 0.19	0.25 ± 0.002	−34.2	−9.90	76.38	1.23
0.2	22.8 ± 0.18	23.1 ± 0.17	0.31 ± 0.003	−32.11	−8.68	73.67	3.32
0.3	27.3 ± 0.20	28.1 ± 0.16	0.39 ± 0.004	−29.61	−6.57	72.42	5.82
0.4	36.7 ± 0.19	37.4 ± 0.20	0.51 ± 0.002	−26.05	−5.10	65.85	9.38
323.15 K							
0.0	17.3 ± 0.29	17.2 ± 0.31	0.25 ± 0.001	−34.96	−10.8	74.70	–
0.1	20.5 ± 0.30	20.8 ± 0.33	0.27 ± 0.002	−33.58	−10.1	72.69	1.38
0.2	23.7 ± 0.31	23.4 ± 0.34	0.32 ± 0.003	−31.75	−8.90	70.72	3.21
0.3	28.1 ± 0.36	28.2 ± 0.30	0.40 ± 0.001	−29.30	−6.74	69.83	5.66
0.4	37.8 ± 0.39	37.6 ± 0.40	0.52 ± 0.003	−25.76	−5.23	63.53	9.20

[a] Errors in ΔG_m^o, ΔH_m^o, ΔS_m^o and ΔG_{trans}^o are within ±2, ±4, ±5 and ±7 % respectively

in aqueous medium makes the medium less hydrophilic and increases surfactant monomer solubility [24]. Increasing temperature disrupts the water structured around the surfactant molecules and increases the CMC.

Thermodynamics of Micellization

On the basis of a pseudo-phase separation model [25, 26] the standard Gibbs free energy of micellization, ΔG_m^o, is calculated from Eq. 1:

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

where X_{cmc} is the mole fraction of surfactant at the CMC, R is the universal gas constant and T is the temperature. Standard enthalpies of micelle formation, ΔH_m^o, can be calculated from Gibbs–Helmholtz equation [25, 26]

$$\Delta H_m^o = -RT^2(2 - \alpha)\left[\partial \ln X_{cmc}/\partial T\right]_P \tag{2}$$

The term $\left[\partial \ln X_{cmc}/\partial T\right]_P$ is calculated by fitting the plot of $\ln X_{cmc}$ *versus* temperature and taking the corresponding temperature derivative. From the values of ΔG_m^o and ΔH_m^o, the standard entropy of micellization, ΔS_m^o can be calculated using Eq. 3.

$$T\Delta S_m^o = \Delta H_m^o - \Delta G_m^o \tag{3}$$

In addition, the effect of additives on the micellization process can be studied by means of free energy of surfactant tail transfer, ΔG_{trans}^o, which is defined by [26]

$$\Delta G_{trans}^o = (\Delta G_m^o)_{methanol + water} - (\Delta G_m^o)_{water} \tag{4}$$

Thermodynamic properties of micellization such as standard free energy of micellization (ΔG_m^o), standard enthalpy of micellization (ΔH_m^o), the standard entropy of micellization (ΔS_m^o) and standard free energy of transfer ΔG_{trans}^o are calculated from Eqs. 1 to 4 respectively and the values are displayed in Table 1 in pure water, 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol at 298.15, 308.15, 318.15 and 323.15 K. The free energy of micellization signifies the spontaneity of the micellization process. The more negative the standard free energy change the greater the spontaneity of micellization. It is seen from the data of Table 1 that the standard free energy of micellization is negative in water as well as in methanol–water mixed solvent media at all investigated temperatures. Moreover, the ΔG_m^o values become less negative with increasing volume fraction of methanol–water at constant temperature indicating that addition of methanol makes the micellization less favorable. It can also be observed that with the increase in temperature ΔG_m^o values become less negative indicating less spontaneity of micellization at higher temperature. This phenomenon can be attributed to agitation of the micelle due to thermal forces at higher temperature [27].

According to the theory of surfactant self-assembly [28], the major contribution to the standard free energy of micellization is associated with transfer of the surfactant tail from solvent into the micelle ΔG_{trans}^o. The ΔG_{trans}^o values in Table 1 are all positive and increase with the increasing volume fraction of methanol in water indicating the transfer of the surfactant tail from the bulk into the micelle is less favorable. It is also seen that ΔG_{trans}^o values decrease with increasing temperature. The organic solvent–water mixed solvent media is a better solvent for the surfactant molecules [29]. This makes the hydrophobic tail transfer from the bulk phase into the micelle less favorable. It can also be understood on the basis of a reduction in the solvophobic interactions which leads to an increase in the solubility of hydrocarbon tails in the presence of methanol, and consequently to an increase in the CMC.

The values of ΔH_m^o of DTAB in aqueous as well as in methanol–water are also negative. The values become more negative with increasing temperature, suggesting that the micellization of the surfactant is exothermic. The observed decrease of ΔH_m^o with increasing temperature is probably due to destruction of the ordered aqueous region diminishing hydrogen bonding between water molecules surrounding the hydrocarbon chain of the surfactant [30]. The negative ΔH_m^o values can be taken as evidence that London-Dispersion interactions play a more predominant role as the temperature increases [27].

The ΔS_m^o values are positive and decrease with an increasing volume fraction of methanol. The positive entropy change indicates that the micellization process is favored by entropy gain, associated with the destruction of the iceberg structure around the hydrophobic alkyl chain, a pre-requisite condition for micelle formation [31]. The ΔS_m^o values shows a decreasing trend with increasing temperature. This implies that disordering of water molecules becomes less pronounced due to the destruction of the iceberg water structure around the alkyl group with increasing temperature [25, 26].

It is well known that there is enthalpy-entropy compensation for micellization of surfactants [26]. The enthalpy-entropy compensation plot is displayed in Fig. 3. It shows a linear co-relation between enthalpy and entropy over all the volume fractions studied. It is seen that as the volume fraction of methanol increases the enthalpic contribution becomes lower indicating a less favorable condition for micellization process.

Surface Properties

The maximum surface excess concentration at the air/methanol–water interface (Γ_{max}), has been calculated by applying the Gibbs adsorption isotherm [32]:

$$(\Gamma_{max}) = -\frac{1}{2.303nRT}\left[\frac{d\gamma}{d\log C}\right]_{T,P} \tag{5}$$

where γ denotes the surface tension, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, C is the surfactant concentration, $(\frac{d\gamma}{d\log C})$ is the slope of the γ versus $\log C$ plot taken at the CMC. For conventional univalent ionic surfactants the constant n takes a value of 2. The area occupied per surfactant molecule (A_{min}) at the air/methanol–water interface [33] has been obtained by,

$$(A_{min}) = 1/NT_{max} \tag{6}$$

where N is Avogadro's number. Low values of A_{min} suggest that the orientation of the surfactant molecule at the interface is almost perpendicular to the interface [34]. The value of the surface pressure at the CMC (π_{cmc}) is obtained as:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \tag{7}$$

where γ_o and γ_{cmc} are the values of surface tension of water and the surfactant solution at the CMC respectively. The surface excess concentration (Γ_{max}) is an effective measure of adsorption at air/solution interface. It measures how much the air/solution interface has been changed by surfactant adsorption and depends on the molecular structures of surfactants. The standard free energy interfacial adsorption at the air/saturated monolayer interface can be evaluated from the relation [34].

$$\Delta G_{ads}^{o} = \Delta G_{m}^{o} - \pi_{cmc}/\Gamma_{max} \tag{8}$$

Israelachvili et al. [34] proposed that the micellar shape is mainly governed by the geometry of the surfactant and its packing. The surface area of amphiphiles in mixed micelles

Fig. 3 Plot of variation of $T\Delta S_m^o$ with ΔH_m^o for DTAB in pure water (*open circles*) different volume fractions of methanol–water mixtures (*open squares*, 0.10 methanol; *open inverted triangles*, 0.20 methanol; *closed circles*, 0.3 methanol; *closed squares*, 0.40 methanol)

and micellar growth (spherical–nonspherical) can be used to calculate the packing parameters (P):

$$P = \frac{V_o}{A_{min}l_c} \tag{9}$$

where V_o is the volume of exclusion per monomer in the micelle, given by Tanford's formula [2]. $V_o = [27.4 + 26.9(n_c - 1)]2\text{Å}^3$, $l_c = [1.54 + 1.26(n_c - 1)]\text{Å}$, is the maximum chain length and n_c is the number of carbon atoms in the hydrocarbon chain. The packing parameter (P) gives information about the geometry of micelles and indicates minimum size of aggregates in solution, due to which the Gibbs free energy of micellization (ΔG_m^o) is minimized.

The maximum surface excess concentration at the air/methanol–water interface (Γ_{max}), area occupied per surfactant molecule (A_{min}, surface pressure at the CMC (π_{cmc}), standard free energy interfacial adsorption (ΔG_{ads}^o) and the packing parameters (P) calculated by Eqs. 5 to 9 are displayed in Table 2. The data shows that Γ_{max} as well as π_{cmc} values decrease with increase in volume fraction of methanol at a constant temperature indicating a reduced population of surfactant molecules at the interface as the volume fraction of methanol is increased. However, A_{min} values increase with increasing volume fraction of methanol which indicates that the surfactant molecule occupies more area as the methanol content is increased. Negative values of ΔG_{ads}^o indicate that the adsorption of surfactant molecules on the surface is spontaneous and is more spontaneous that micellization. The ΔG_{ads}^o values become less negative with increasing volume fraction of methanol at constant temperature which indicates less spontaneity of adsorption of surfactant molecules on the surface. Similar types of investigations are found in the literature [9, 16].

Data from Table 2 suggests that the surface properties of DTAB in water and in the presence of methanol are highly dependent on temperature. As a general rule, when the temperature of a system increases, thermal expansion changes several properties of the system. In our case, there is a decrease in Γ_{max}, an increase in A_{min}, a decrease in π_{cmc} and decrease in P with increasing temperature. These variations can be understood on the basis of thermal expansion of the solution with increase in temperature. Similar variations are observed by others in the literature [9].

Israelachvili et al. [34] have proposed that depending on the value of the packing parameter (P), surfactant aggregates acquire different shapes. They showed that, in general, micelles are spherical for $P < 1/3$. In our investigation, P is less than 1/3 in all the cases suggesting the presence of spherical micelles. The P values decrease with an increasing volume fraction of methanol at constant
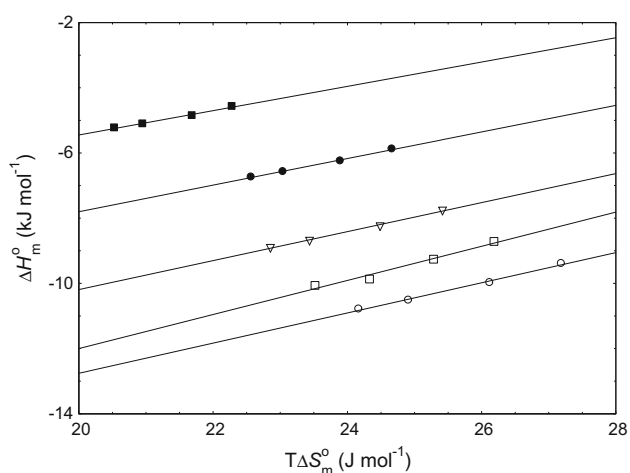
Table 2 Surface properties of DTAB[a] in water, 0.1, 0.2, 0.3 and 0.4 volume fractions of methanol from 298.15 to 323.15 K

Volume fractions of methanol	$\Gamma_{max} 10^6$ (mol m^{-2})	A_{min} (Å^2 mol^{-1})	π_{cmc} (m Nm^{-1})	P	ΔG^o_{ads} (kJmol^{-1})
298.15 K					
0	2.85	58.15	34.43	0.36	−48.63
0.1	2.18	76.14	19.99	0.27	−44.06
0.2	1.35	122.54	13.03	0.17	−42.78
0.3	0.82	200.97	7.87	0.10	−40.06
0.4	0.64	258.98	5.32	0.08	−35.14
308.15 K					
0	2.68	61.92	33.56	0.33	−48.61
0.1	2.00	82.72	18.59	0.25	−43.79
0.2	1.21	137.20	10.9	0.15	−41.72
0.3	0.61	271.67	5.55	0.07	−39.21
0.4	0.52	319.00	3.86	0.06	−33.95
318.15 K					
0	2.53	65.42	32.64	0.32	−48.28
0.1	1.86	89.10	19.32	0.23	−44.56
0.2	1.06	155.69	11.73	0.13	−43.11
0.3	0.46	355.22	7.03	0.05	−44.65
0.4	0.37	440.72	4.06	0.04	−36.82
323.15 K					
0	2.46	67.26	32.17	0.31	−47.99
0.1	1.79	92.55	20.25	0.22	−44.86
0.2	0.99	166.53	11.85	0.12	−43.63
0.3	0.39	417.16	6.99	0.05	−46.86
0.4	0.30	540.24	3.69	0.03	−37.76

[a] Errors in $\Gamma_{max} 10^6$, A_{min}, π_{cmc}, P and ΔG^o_{ads} are within ±3, ±3, ±5, ±4 and ±7 % respectively

temperature. Previous investigations have shown that the micelle aggregation number (N_{agg}) increases with increasing volume fraction of methanol [35]. The decrease in N_{agg} and P values suggest that micellar aggregates get smaller when methanol is added. Pan et al. [35] observed that there is no evidence of micelle formation when the volume fraction exceeds 50 %.

Conclusion

Thermodynamic and surface properties of DTAB in water and methanol–water mixtures at different temperatures were determined using conductometry and tensiometry. Methanol is miscible in water in all proportions and breaks down the three-dimensional H-bonded water structure and alters the micellization of DTAB. The CMC and degree of ionization (α) of DTAB increases with increasing volume fraction of methanol. Methanol decreases the cohesiveness of water making the medium more acceptable to the alkyl chain of DTAB making self-assembly more difficult.

Thermodynamic parameters suggest that the driving force for the hydrophobic effect, which is required for micelle formation is due to the cohesive force of the solvent. The change in cohesive force due to methanol addition slows down the aggregation of DTAB. Surface properties suggest that methanol acts as a surface active agent and alters the surface properties by competing with the surfactant molecules for interfacial adsorption. More importantly, the size of the micelle decreases with an increasing volume fraction of methanol.

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