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Micellization and Thermodynamic Parameters of Butanediyl-1,4-bis(tetradecyldimethylammonium Bromide) Gemini Surfactant at Different Temperatures: Effect of the Addition of 2-Methoxyethanol

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Abstract The effect of the addition of 2-methoxyethanol on the critical micelle concentration (*cmc*) and on the degree of counterion dissociation (α) of butanediyl-1,4-bis(tetradecyldimethylammonium bromide) gemini surfactant, $[C_{14}H_{29}N^{+}(CH_3)_2–(CH_2)_4–N^{+}(CH_3)_2C_{14}H_{29}, 2Br^{-}]$ (referred as 14–4–14,2Br$^-$), has been studied by varying the compositions of the 2-methoxyethanol + water mixed solvent media (0 to 50 %). To determine various thermodynamic parameters of micellization, on the basis of the mass–action model for micelle formation, the experiments were performed at selected compositions of the mixed solvent at four temperatures ranging between 25 °C and 50 °C. Furthermore, the air/bulk surface tensions of the pure and mixed media were determined, and a successful attempt was made to correlate the cohesive energy density described through the Gordon parameter with the values of Gibbs energy of micellization.

Keywords Self-association · Degree of counterion dissociation · Thermodynamics of micellization · 2-Methoxyethanol–water mixed solvent

1 Introduction

Aqueous solutions of surfactants and their mixtures with additives are of interest for their chemical, pharmaceutical, cosmetic, mineral processing and petroleum engineering applications [1–3]. In a suitable solvent (usually an aqueous medium), the surfactant molecules are initially adsorbed at the interfaces. Upon exceeding a certain minimum concentration, called the critical micelle concentration (*cmc*), their molecules aggregate to form various

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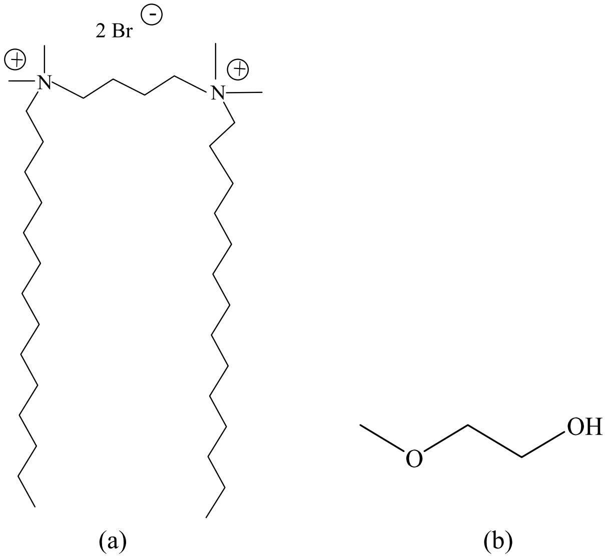


Fig. 1 Structures of the gemini surfactant, butanediyl-1,4-bis(tetradecyldimethylammonium bromide) (14–4–14,2Br$^-$) (**a**), and the organic solvent, 2-methoxyethanol (**b**), used in this study

structures including micelles, vesicles, membranes, bilayers, etc., and these microstructures have a strong influence on the rheological properties of the resulting solutions [4–7].

Gemini surfactants are an emerging class of surfactants that have drawn considerable attention both from academic and industrial scientists due to their superior performance such as strong aggregation ability at relatively low surfactant concentration, better efficiency to reduce the interfacial tension, interesting rheological properties, etc. [8–11]. These surfactants are made from two amphiphilic moieties covalently linked with spacers of different lengths at the level of their head groups, and are more cost-effective as well as environmentally preferable.

The ‘hydrophobic interaction’, which is the main driving force behind aggregation, is not water specific and, therefore, a more general term ‘solvophobic interaction’ is used to describe the adsorption and aggregation properties of amphiphilic solutes [12]. In the last decade, as evidenced from published research papers, many researchers have turned their attention towards the aggregation process of surfactants in non-aqueous or organic solvent–aqueous mixed solvent media [13–27]. Addition of organic solvents to aqueous solutions of surfactants alters the ability of the surfactant molecules to avoid contact with the bulk phase, and thereby changes various micellization parameters. The importance of studying aggregation processes in the presence of organic solvents is driven both by fundamental and practical conditions; for example, recently Sreejith et al. [7] reported a micelle-to-vesicle transition of the cetyltrimethylammonium bromide/KBr system caused simply by the addition of octanol.

In the present paper, through a conductometric study, we investigated the micellization and related thermodynamic parameters of a cationic gemini surfactant butanediyl-1,4-bis(tetradecyldimethylammonium bromide) (14–4–14,2Br$^-$) in the presence of 2-methoxyethanol (the structures of 14–4–14,2Br$^-$ and 2-methoxyethanol are given in Fig. 1). 2-Methoxyethanol (Me) belongs to a class of solvents known as ‘glycol ethers’ which are notable for their ability to dissolve a variety of different types of chemical compounds and also for their miscibility with water and other solvents. The study described herein should be of interest as organic solvents are often used with surfactants in order to control certain properties such as viscosity or volatility of the resulting solutions. This study has been performed with two approaches. First, at a particular temperature (30 °C), the compositions of the mixed solvent media were varied in between 0 and 50 % (v/v) (at nine different compositions) to understand how and to what extent the added solvent affects the micellization parameters such as the critical micelle concentration (*cmc*) and degree of counterion dissociation (α). Second, to determine the effect of temperature on the above parameters and also to calculate various thermodynamic parameters of micellization, the studies (in pure water and in selected compositions of the mixed solvent media (10 %, 20 % and 30 %)) were performed at four temperatures (25, 30, 40 and 50 °C). Further, the Gordon parameters [28] of the mixed solvent systems were evaluated and correlated with the Gibbs energies of micellization of the studied gemini surfactant.

2 Experimental

2.1 Materials

The gemini surfactant butanediyl-1,4-bis(tetradecyldimethylammonium bromide) (14–4–14,2Br$^-$) was synthesized by refluxing N,N-dimethyltetradecylamine ($\geq$95 %, Fluka, Germany) with 1,4-dibromobutane ($\geq$98 %, Fluka, Germany) in dry ethanol for 48 h at 80 °C. The product was re-crystallized from ethanol/ethyl acetate mixtures at least five times, and then characterized by ^{1}H- and ^{13}C-NMR. For ^{1}H-NMR in $CDCl_3$ (ppm), the following peaks were obtained: (0.88, CH_3, t, 6H), (1.25, CH_2, m, 52H), (1.7, CH_2, m, 4H), (2.1, CH_3, s, 12H), (3.4, CH_2, t, 4H). The ^{13}C spectra showed the characteristic peaks of aliphatic carbons ranging from 14.7 to 63.4 ppm in $CDCl_3$. 2-Methoxyethanol (Me) ($\geq$99 %, S.D. Fine-chem., India) was mixed thoroughly with appropriate volumes of doubly-distilled water (distilled once over alkaline $KMnO_4$) at a controlled temperature (25 °C) to obtain the various compositions of 2-methoxyethanol–water mixed solvents.

2.2 Methods

2.2.1 Conductivity Measurements

The conductance measurements were performed on an ELICO CM 82 T type Conductivity Bridge equipped with a dip cell of cell constant 1.02 cm^{-1}. All of the experiments were done in a thermostatted water bath holding the solution under study. The solvent was equilibrated at the desired temperature for at least 30 minutes before addition of the suitably prepared concentrated stock solution of 14–4–14,2Br$^-$. After each addition, the solution was mixed carefully without the formation of foam.

2.2.2 Surface Tension Measurements

The solvent (water or 2-methoxyethanol–water mixed solvent medium) surface tensions were measured by the ring detachment method using a S.D. Hardson tensiometer (India) at 30 °C. For each system, the platinum ring was cleaned well and heated briefly in an alcoholic flame until it glowed. The precision in the surface tensions is ±0.1 mN·m^{-1}.

Table 1 Critical micelle concentration (*cmc*), degree of counterion dissociation (α), Gibbs energy of micelle formation (ΔG^0_{m}) and Gibbs energy of transfer ($\Delta G^0_{\mathrm{trans}}$) values of butanediyl-1,4-bis-(tetradecyldimethylammonium bromide) (14–4–14,2Br$^-$) in various compositions of 2-methoxyethanol–water (Me–Wr) mixed media at 30 °C

Me, %-v/v	*cmc*, mmol·dm^{-3}	α	ΔG^0_{m}, kJ·mol^{-1}	$\Delta G^0_{\mathrm{trans}}$, kJ·mol^{-1}
0	0.15	0.29	−78.1	0
5	0.17	0.30	−76.6	1.5
10	0.29	0.31	−72.6	5.5
15	0.34	0.32	−70.6	7.5
20	0.43	0.40	−64.3	13.8
25	0.65	0.35	−64.3	13.8
30	0.97	0.34	−62.7	15.4
40	1.21	0.36	−59.6	18.5
50	1.53	0.50	−50.5	27.6

3 Results and Discussion

3.1 Effect of 2-Methoxyethanol on the Critical Micelle Concentration (cmc) and the Degree of Counterion Dissociation (α)

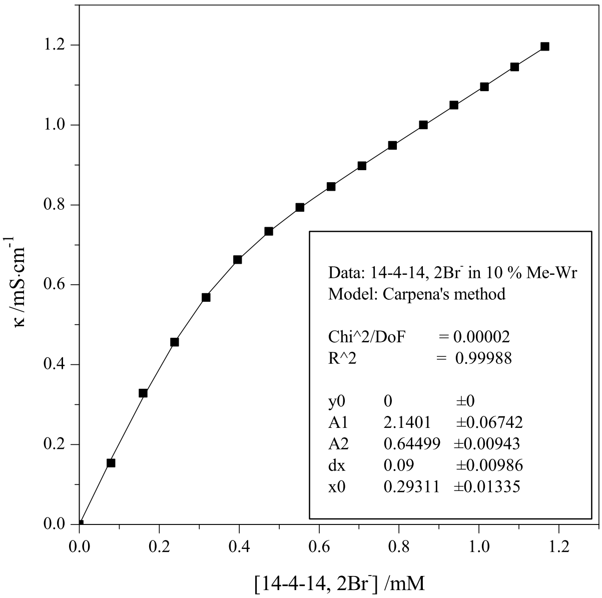
The critical micelle concentration (*cmc*) and the degree of counterion dissociation (α) values of 14–4–14,2Br$^-$ in various compositions (0 %, 5 %, 10 %, 15 %, 20 %, 25 %, 30 %, 40 % and 50 %) of 2-methoxyethanol–water mixtures were estimated through conductometric experiments at 30 °C. In this technique, *cmc* values are usually determined from the inflection/discontinuity in the plots of specific conductance (κ) versus surfactant concentration (c) (Williams's method [29]). In the present study, with the increase in the compositions of 2-methoxyethanol in the mixed solvent medium, a less abrupt change in κ was obtained at the transition region of the plots. As this may introduce greater uncertainties in the values, to get more precise values we have applied Carpena's [30] method to determine the *cmc* and α values. This method is based on the fitting of the κ as a function of c to the integral of a Boltzmann-type sigmoidal equation:

$$\kappa_{(c)} = \kappa_{(0)} + A_1 c + \Delta c(A_2 - A_1)\ln\left(\frac{1 + e^{(c - c_0/\Delta c)}}{1 + e^{-c_0/\Delta c}}\right) \tag{1}$$

In the above equation, κ_0, A_1, A_2 and Δc are the conductivity of the solution at zero concentration of the surfactant, the pre-micellar slope, the post-micellar slope, and width of the transition, respectively. A detailed description of the fitting procedure has been provided in our earlier paper [16]. In this method, the central point on the width of the transition (c_0) corresponds to the *cmc* and the degree of counterion dissociation (α) is determined from the ratios of the post-micellar slopes to pre-micellar slopes, $\alpha = A_2/A_1$. A representative plot (κ versus [14–4–14,2Br$^-$]) of fitting using Carpena's method, for the studied gemini surfactant in 10 % 2-methoxyethanol–water mixed solvent, is shown in Fig. 2. The *cmc* and α values obtained by applying the aforementioned method are listed in Table 1.

It can be seen that the addition of 2-methoxyethanol decreases the aggregation tendency of the 14–4–14,2Br$^-$ gemini surfactant and thereby increases its *cmc*. The plot of *cmc* of 14–4–14,2Br$^-$ against the volume-% of 2-methoxyethanol is shown in Fig. 3. It is clear

Fig. 2 Representative fitting plot of specific conductance κ versus [14–4–14,2Br$^-$] in 10 % 2-methoxyethanol–water mixed solvent medium at 30 °C



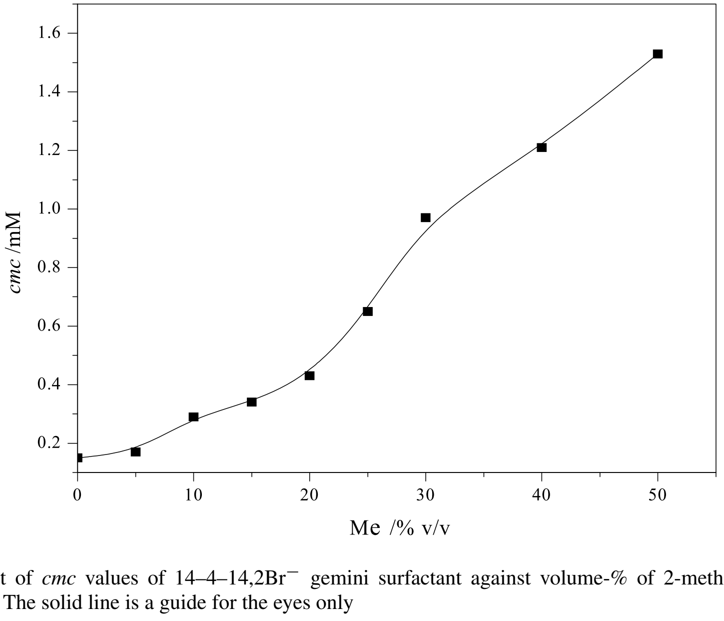


Fig. 3 Plot of *cmc* values of 14–4–14,2Br$^-$ gemini surfactant against volume-% of 2-methoxyethanol, $T = 30$ °C. The solid line is a guide for the eyes only

from this figure that the increase in *cmc* is comparatively less below 20 volume-% of 2-methoxyethanol, which shows the predominance of aqueous character in the bulk phase. A steep increase was observed, however, on increasing the 2-methoxyethanol beyond 20 % in the binary mixed solvent. The increase can be explained on the basis of hydrophobic/solvophobic interactions of the gemini tails. That is, the addition of 2-methoxyethanol decreases this driving force and, as a result, the transfer of surfactant monomers from the

Table 2 Surface tension (γ), average molar volume ($\overline{V_\mathrm{m}}$) and Gordon parameter (G) data of 2-methoxyethanol–water mixed medium at 30 °C

Me[a], %-v/v	γ, mN·m^{-1}	$\overline{V_\mathrm{m}}$, cm^3·mol^{-1}	G, J·m^{-3}
0	71.35	18.07	2.72
10	58.50	19.58	2.17
20	52.10	21.37	1.88
30	48.65	23.52	1.70
50	42.90	29.43	1.39

[a] Me denotes 2-methoxyethanol

bulk phase to the micellar region becomes progressively less favorable with the increase of the amount of 2-methoxyethanol in the mixed solvent medium.

This is explained by noting that the addition of 2-methoxyethanol decreases the cohesive energy of the solution, which increases the solubility of the monomeric 14–4–14,2Br$^-$ gemini molecules. Here it is useful to consider the values of Gordon parameter (G) [28], as the cohesive energy density related to solubility behavior is similar to that of solvation. The values, which can be used to characterize the solvent's ability to induce association of the amphiphilic molecules, along with the average molar volumes ($\overline{V_\mathrm{m}}$) of the mixed media, are given in Table 2. The G values were calculated from the relation:

$$G = \gamma / \overline{V_\mathrm{m}}^{1/3} \tag{2}$$

where γ is the surface tension of the pure or mixed solvent media and $\overline{V_\mathrm{m}}$ the molar volumes (the values of γ are also given in Table 2). The molar volumes of the various compositions of the mixed solvent media were calculated by the summation of the $\overline{V_\mathrm{m}}$ values of water and 2-methoxyethanol corresponding to their mole fractions, $\overline{V_\mathrm{m}} = \sum_{i=1}^{2} x_i \overline{V_i}$, where x_i and $\overline{V_i}$ are the mole fraction and molar volume of the ith component, respectively. The plot of Gordon parameters, G, against the values of Gibbs energy of micellization (ΔG^0_m, details are provided below) are shown in Fig. 4.

It can be seen that a reduction in the G value corresponds to a decrease in the spontaneity of the aggregation in all the cases and this trend yields a straight line with a correlation coefficient $r \approx 0.96$. This shows a linear dependence of the bulk phase with ΔG^0_m for the studied gemini surfactant in 2-methoxyethanol–water solvent media at 30 °C. From these results, it can be concluded that the cohesive energy density of the bulk phase plays a major role in the solvophobic effect of 14–4–14,2Br$^-$ in the studied mixed solvent. In addition to this, an increase in the volume-% of 2-methoxyethanol also decreases the dielectric constant (polarity) of the bulk phase. This will increase the repulsion among the head groups of the individual gemini molecules and cause the *cmc* values to increase.

The values of the degree of counterion dissociation (α) give an idea about the fractions of the counterions associated with the micelles ($\beta = 1 - \alpha$). At 30 °C, although their values do not show a regular trend, a rough increase can be seen with the volume-% of 2-methoxyethanol. This behavior is not anticipated since the addition of 2-methoxyethanol ($\varepsilon = 16.94$ at 25 °C [31]) to pure water ($\varepsilon = 78.39$ at 25 °C [32]) decreases the dielectric constant (polarity) of the bulk phase, and, thereby, in order to diminish the repulsion among the ionic head groups, a larger fraction of the Br$^-$ ions are expected to remain at the micellar surface. However, at the same time, it is known that an increase in the organic solvent content decreases the aggregation number of the micelles, which then causes a reduction

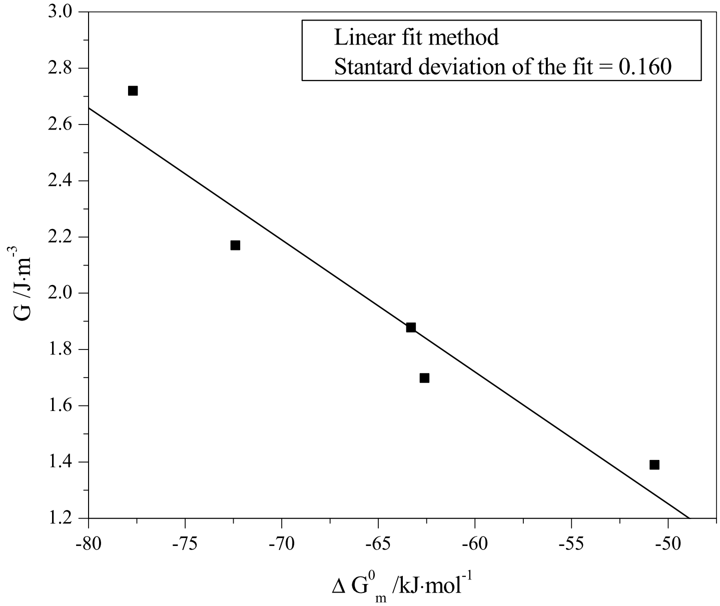


Fig. 4 Plot of Gibbs energy of micellization $\Delta G_{\mathrm{m}}^{0}$ versus the Gordon parameter G of the 2-methoxy-ethanol–water on bulk phase, $t = 30$ °C

in the electrostatic repulsion (that overcomes the effect of polarity changes) and leads to a diminution in the electrical charge density at the micellar surface. This may be the reason for the increase in values of α.

3.2 Effect of Temperature on the cmc and α

Conductivity measurements were performed in pure water and in the selected compositions of the 2-methoxyethanol–water mixed solvents (i.e., 10 %, 20 % and 30 % v/v) at 25, 30, 40 and 50 °C. The *cmc* and α values of 14–4–14,2Br$^-$ in the studied media at these four temperatures are given in Table 3. Increases in the *cmc* values with the increasing temperature, at all the compositions of the mixed solvent media, can be seen. This increase becomes pronounced at higher volume-% of 2-methoxyethanol in the binary mixed solvent. This trend becomes clearer if one calculates the *cmc* difference (cmc_{diff}, the difference in the *cmc* at highest and lowest temperatures for a particular system: i.e., $cmc_{\text{diff}} = cmc_{50\ ^\circ\text{C}} - cmc_{25\ ^\circ\text{C}}$). The value of cmc_{diff} is smaller in pure water (0.08) and is greater in 30 % 2-methoxyethanol–water mixed solvent (1.14). However, with the increase in temperature, the α values gradually increases for most of the systems.

The increase in the *cmc* with respect to temperature is usually analyzed in two ways. First, the degree of hydration of the hydrophilic head groups decreases (when the temperature increases), which favors micellization (and thereby decreases the *cmc*). Second, as the temperature increases, the water structure around the hydrophobic group is gradually destroyed, which is unfavorable for micellization (and hence an increase in the *cmc* happens). The gradual increase in α with respect to the temperature could be due to the decrease in the charge density on the micellar surface and, therefore, a larger fraction of the counterions is dissociated because the increase in the temperature reduces the aggregation number of the ionic surfactants [33, 34].

Table 3 Critical micelle concentration (*cmc*), degree of counterion dissociation (α) and estimated thermodynamic parameters of micellization of butanediyl-1,4-bis(tetradecyldimethylammonium bromide) (14–4–14, $2Br^-$) in various compositions of 2-methoxyethanol–water mixed media at different temperatures

Me[a], %-v/v	T, °C	*cmc*, $\text{mmol}\cdot\text{dm}^{-3}$	α	ΔG^0_m, $\text{kJ}\cdot\text{mol}^{-1}$	ΔG^0_trans, $\text{kJ}\cdot\text{mol}^{-1}$	ΔH^0_m, $\text{kJ}\cdot\text{mol}^{-1}$	ΔS^0_m, $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0	25	0.12	0.29	−78.4	–	−26.5	0.17
0	30	0.15	0.29	−78.1	–	−27.4	0.17
0	40	0.18	0.35	−75.5	–	−27.7	0.15
0	50	0.20	0.37	−76.1	–	−29.0	0.15
10	25	0.24	0.32	−71.8	6.7	−44.3	0.09
10	30	0.29	0.31	−72.5	5.6	−46.2	0.09
10	40	0.34	0.35	−71.5	4.0	−47.6	0.08
10	50	0.45	0.48	−63.7	12.4	−44.9	0.06
20	25	0.35	0.26	−72.4	6.0	−55.2	0.06
20	30	0.43	0.40	−64.3	13.8	−50.8	0.04
20	40	0.70	0.40	−63.7	11.8	−54.2	0.03
20	50	0.78	0.41	−64.5	11.6	−57.2	0.02
30	25	0.51	0.29	−68.0	10.4	−86.6	−0.06
30	30	0.97	0.34	−62.5	15.6	−85.8	−0.08
30	40	1.20	0.36	−62.3	13.2	−90.0	−0.09
30	50	1.65	0.47	−56.2	19.9	−86.6	−0.09

[a] Me denotes 2-methoxyethanol

3.3 Thermodynamics of Micellization of 14–4–14,$2Br^-$ in 2-Methoxyethanol–water Mixed Solvent

Phase-separation and mass–action approaches are two models that have received wide acceptance for the interpretation of the energetics of the micellization. For ionic surfactants, however, the mass–action approach is usually preferred [34] and various thermodynamic parameters may be deduced from the temperature dependence of the *cmc* values. According to this model, the micellization of 14–4–14,$2Br^-$ gemini surfactant can be written as:

$$nG^{2+} + 2(n-p)Br^- \rightleftarrows M^{2p+} \tag{3}$$

where G^{2+} represents the gemini cations, Br^- the counterions, and M^{2p+} the aggregate of n monomers with an effective charge of $2p$. The Gibbs energy of micelle formation per mole of the surfactant, ΔG^0_m , is given by:

$$\Delta G^0_\text{m} = RT\left[\left(\frac{-1}{n}\right)\ln a_{M^{2p+}} + \ln a_{G^{2+}} + 2\left(1-\frac{p}{n}\right)\ln a_{Br^-}\right] \tag{4}$$

where R and T have their usual meanings and the a_i are the respective activities. In general, for a micelle formed with an adequate number of monomer units, the first term in the parentheses will be small and can be neglected. In this situation, the activities of the corresponding ions can be replaced by their activities at the *cmc* and this value may be set equal to the *cmc* expressed on the mole fraction scale, x_{cmc}, of the surfactant.

By the above approximation, for the 14–4–14,2Br$^-$ gemini surfactant, the value of ΔG^0_{m} depends on both the *cmc* and α and can be written as [35]:

$$\Delta G^0_{\mathrm{m}} = 2RT(1.5-\alpha)\ln x_{cmc} \tag{5}$$

The ratio of the *cmc* of 14–4–14, 2Br$^-$ to the total concentration of all components in the system was calculated to get the x_{cmc} value (i.e., the values were calculated as $x_{cmc} = cmc/(cmc + \text{number of moles of the solvent}))$ (the solvent is either water alone or a 2-methoxyethanol–water mixed solvent). For micellization in pure water, the concentration of solvent is taken as 55.556 mol·dm^{-3}. It should be noted that the total number of moles of solvent decreases with the increase in the amount of 2-methoxyethanol in the mixed solvent. Furthermore, the Gibbs energy of transfer values ($\Delta G^0_{\mathrm{trans}}$), which can be accounted for by the effect of cosolvent on the micellization process, were estimated through the relation $\Delta G^0_{\mathrm{trans}} = \Delta G^0_{\mathrm{m(Me-water)}} - \Delta G^0_{\mathrm{m(water)}}$ where "Me" denotes 2-methoxyethanol. The values of ΔG^0_{m} and $\Delta G^0_{\mathrm{trans}}$ at 30 °C are listed in Table 3. The values of ΔG^0_{m} are found to be negative in all cases and the positive values of $\Delta G^0_{\mathrm{trans}}$ increase with increasing volume-% of 2-methoxyethanol. These values suggest that, although 14–4–14,Br$^-$ gemini forms micelles spontaneously, even in the presence of 50 % 2-methoxyethanol, the spontaneity of the process decreases as the volume-% of 2-methoxyethanol increases in the mixed solvent media.

According to the theory of surfactant aggregation, proposed by Nagarajan and Wang [36], there may be various types of energy contribution to Gibbs energy of micellization. It is known that the $\Delta G^0_{\mathrm{trans}}$ (Gibbs energy contribution associated with the transfer of surfactant tails) is mainly responsible for the delay in the micellization of surfactants in mixed media [18, 37], and its value depends on the transfer Gibbs energies from pure water and the organic solvents in addition to their mutual interaction. As the addition of 2-methoxyethanol modifies the bulk phase, making it more favorable than pure water for surfactant molecules [32], the transfer of the hydrophobic tail from the bulk phase to the micellar region becomes less favorable, and hence the value of ΔG^0_{m} increases (becomes less negative). The corresponding enthalpy and entropy changes were calculated from the following expressions:

$$\Delta H^0_{\mathrm{m}} = -2RT^2(1.5-\alpha)(d\ln x_{cmc}/dT)_p \tag{6}$$

$$\Delta S^0_{\mathrm{m}} = \left(\Delta H^0_{\mathrm{m}} - \Delta G^0_{\mathrm{m}}\right)/T \tag{7}$$

The values of $\ln x_{cmc}$ at particular compositions of the mixed media were plotted against the temperature T. Linear plots were obtained for each of the systems and the slopes of these plots were taken as the values of $d\ln x_{cmc}/dT$ in Eq. 7. The various thermodynamic parameters for the selected compositions of the mixed solvent at different temperatures are listed in Table 3. The ΔG^0_{m}, ΔH^0_{m} and ΔS^0_{m} values in all the cases are, respectively, negative, negative and positive (except in 30 volume-% of the mixed solvent). The ΔS^0_{m} values decrease with the increase in volume-% of 2-methoxyethanol in the mixed solvent media (as 2-methoxyethanol replaces the water molecules surrounding the hydrophobic parts of the gemini), and in 30 volume-% of 2-methoxyethanol–water medium negative entropies were obtained. At a fixed solvent composition, the ΔG^0_{m} values become less negative with the rise in temperature, whereas the ΔH^0_{m} values varied only slightly. The decrease in ΔG^0_{m} and increase in $\Delta G^0_{\mathrm{trans}}$ with the rise in temperature show the disfavoring of the micellization process in 2-methoxyethanol–water solvent media. From their values, one can see that the values ΔH^0_{m} in pure water are much less than $T\Delta S^0_{\mathrm{m}}$ but are greater in 10 %, 20 % and 30 % 2-methoxyethanol–water mixed media, which suggest that the process is mainly entropically driven in water and enthalpically driven in the mixed solvent.

4 Conclusions

As a large number of organic solvents are used with surfactants to impart beneficial qualities to the formulations, an understanding of their micellization and related thermodynamic parameters in the presence of organic solvents at different temperatures is important. In this work, the micellization behavior of a cationic gemini surfactant, butanediyl-1,4-bis(tetradecyldimethylammonium bromide) (14–4–14,2Br$^-$), was systematically studied in various compositions of 2-methoxyethanol–water mixed solvents at four temperatures ranging between 25 °C and 50 °C.

From the results obtained, the following conclusions can be drawn. The inclusion of 2-methoxyethanol and an increase in temperature results in an increase in the critical micelle concentration (*cmc*) and degree of counterion dissociation (α) of 14–4–14,2Br$^-$ gemini micelles. The gradual variation in the amount of 2-methoxyethanol in the bulk phase reveals that the mixed solvent media containing up to approximately 20 volume-% of 2-methoxyethanol show predominantly aqueous character (here, the increase in *cmc* is comparatively less than others). For a fixed composition of the mixed solvent, the increase in *cmc* with increasing temperature (cmc_{diff}) was observed to be larger in the mixed solvent media containing a higher volume-% of 2-methoxyethanol. The bulk phase energy density, described through its Gordon parameter, shows a good linear relation (correlation coefficient, $r \approx 0.96$) with the ΔG^0_{m} values of 14–4–14,2Br$^-$ in various compositions of 2-methoxyethanol–water mixed solvents. Various thermodynamic parameters indicate that the micellization process is exothermic, but with the increase in the volume-% of 2-methoxyethanol in the mixed media, it becomes less favorable. The thermodynamic data illustrate that the process of micellization is driven entropically in pure water whereas it is enthalpically driven in 2-methoxyethanol–water mixed solvents.

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