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Micellar Properties and Related Thermodynamic Parameters of the 14-6-14, 2Br$^-$ Gemini Surfactant in Water + Organic Solvent Mixed Media[†]

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Micellar parameters such as critical micelle concentration (cmc), degree of counterion dissociation (α), and aggregation number (N_{agg}) of the cationic gemini surfactant hexamethylene-1,6-bis(tetradecyldimethylammonium bromide) (14-6-14, 2Br$^-$) have been determined in aqueous binary mixtures of dioxane (DO), dimethylformamide (DMF), and ethylene glycol (EG) by employing conductivity and fluorescence methods. An increase in the cmc and α values and a decrease in the N_{agg} were observed when volume fractions (ϕ) of the studied organic solvents were varied (0 to 0.80 for conductivity and 0 to 0.50 for fluorescence studies) at 303.15 K. The temperature dependence of the cmc values provided information about various thermodynamic parameters and its effect on the selected compositions ($\phi = 0$, 0.10, 0.20, 0.30, and 0.50) of the mixed media on varying the nature of the medium. The Gibbs energy of micellization (ΔG^0_{m}) increased with the increase in the ϕ of the studied organic solvents. It was also observed that the increase in the cmc with the rise in temperature was more in the media containing a higher ϕ of the organic solvents.

Introduction

Surfactants form micelles in aqueous solution because of their amphiphilic nature (the presence of both hydrophilic and hydrophobic groups within the molecule) to minimize unfavorable interaction with water. The concentration at which the above phenomenon takes place is termed the critical micelle concentration (cmc). Besides having relevance in usual household and industrial applications, the most important significance of micellization from the pharmaceutical point of view is that micelles are capable of solubilizing drugs of limited water solubility. The inclusion of different types of additives is well-known to influence the micellar properties of surfactant solutions by making modifications to the solvent structure and surfactant aggregates.[1−4] The micellar properties may also be affected by the nature of the hydrophobic group, hydrophilic group, counterion, temperature, and so forth.

Micellization of the various conventional (anionic, cationic, nonionic, and zwitterionic) and gemini surfactants in aqueous medium have been studied in detail under various physicochemical conditions,[5−20] and now the colloidal scientists are more interested in investigating how the change from aqueous solutions to organic solvents affects the micellization and related properties; this is due to the increasing use of these materials for applications which require water-free or water-poor media, such as lubrication or cleaning operations.[21,22] Thus, for such studies, an obvious and general method is the gradual replacement of water by other organic solvents (as this will provide a wide range of polarities), and this strategy has been followed by different research groups.[23−32] The hydrophobic or solvophobic effect, in which the tails of the surfactant molecules reduce their contact with water or solvent (bulk phase) and cause micellization, can be changed not only by the nature of the surfactant but also by that of the bulk phase, and as a result, various micellization parameters, such as the cmc, degree of counterion dissociation (α), aggregation number (N_{agg}), polarity, and so forth, are expected to be altered by the presence of organic solvent in the system.

Gemini surfactants, which are composed of two hydrophilic head groups and two hydrocarbon chains covalently attached through a spacer, are an important class of amphiphilic molecules which are being researched by both industrial and academic groups because of their wide applicability and increased commercial uses. The gemini surfactants are superior in their properties in comparison with conventional single tail−single head surfactants. In many instances, their unusual behavior makes the study of the solution and interfacial properties of this class of amphiphiles more interesting.[33] They possess very low cmc, are more efficient in lowering the surface tension of water, and have better wetting properties.[34−37] In addition, some gemini surfactants have shown interesting antimicrobial or antibacterial activities.[38,39]

Despite the gemini surfactants being more effective to meet various practical applications, their micellization behavior in water + organic solvent mixed media has attracted scant attention.[40−44] On the contrary, studies of conventional surfactants in various water + organic solvent mixed media have widely been reported.[23−32] Further, as can be seen, the studies on the micellization behavior of gemini surfactants in mixed media (water + organic solvent mixtures) were carried out only at a few selected compositions of the organic solvents, and therefore, a systematic study in which the compositions of the mixed medium are varied gradually by the addition of organic solvent is needed. As mentioned earlier, the micellization process is sensitive to temperature, and knowledge about various thermodynamic parameters in the presence of different organic solvents will give an insight into the proper understanding of the behavior of the amphiphiles in the mixed media.

Herein, we report the various micellar properties of the hexamethylene-1,6-bis(tetradecyldimethylammonium bromide) gemini surfactant (14-6-14, 2Br$^-$) in water (WR) and in different water + organic solvent mixed media studied through conduc-

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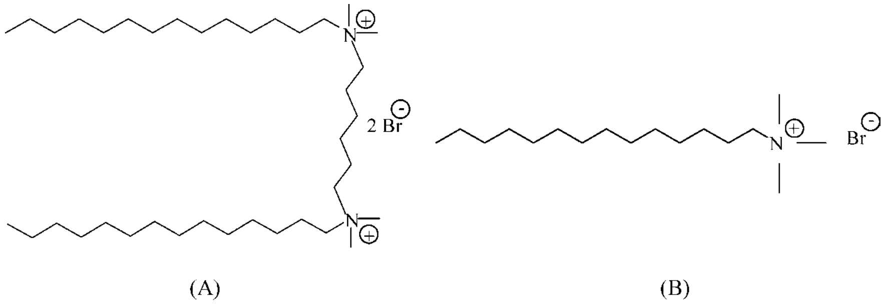
Scheme 1. Structures of Hexamethylene-1,6-bis(tetradecyldimethylammonium bromide), 14-6-14, 2Br$^-$ (A), and Its Monomeric Counter Part, Tetradecyltrimethylammonium Bromide, TTAB (B)



tometric and fluorimetric experiments at 303.15 K. The organic solvents used were dioxane (DO), dimethylformamide (DMF), and ethylene glycol (EG) (at their different volume fractions (ϕ), ranging from 0 to 0.80 for conductivity and 0 to 0.50 for fluorescence measurements). The conductivity measurements at different temperatures from (298.15 to 323.15) K were also performed at selected compositions of the binary mixtures and in pure water. The objectives of this work are (i) to investigate the phenomenon of micellization under the gradual variation in the polarity of the bulk phase by the addition of different organic solvents which may simultaneously provide information about the dependence of the properties of the organic solvents, if any, on the said process, and (ii) to analyze various thermodynamic parameters of the micellization of 14-6-14, 2Br$^-$ with respect to the compositions of the different mixed media in the studied temperature range. The results have been compared with those of the conventional monomeric counterpart tetradecyltrimethylammonium bromide (TTAB, Scheme 1). The work described herein is of interest since the knowledge about the interfacial and thermodynamic properties of the surfactants in both the presence and the absence of additives can provide information about solute−solute and solute−solvent interactions of the surfactants in solution.

Materials and Methods

The organic solvents, namely, DO (≥ 99 %, Merck), DMF (≥ 99.5 %, Merck), EG (≥ 98 %, Qualigens Fine Chemicals), and the quencher (cetylpyridinium chloride, CPC) for the steady-state fluorescence measurements were used as received. Pyrene (≥ 98 %, Acros Organics) was recrystallized several times from *n*-hexane. The gemini surfactant hexamethylene-1,6-bis(tetradecyldimethylammonium bromide) (14-6-14, 2Br$^-$), whose chemical structure is shown in Scheme 1, was synthesized by refluxing 1,6-dibromohexane ($(CH_2)_6Br_2$) with *N*,*N*-dimethyltetradecylamine (≥ 95 %, Fluka) in dry ethanol (≥ 99.9 %, Merck) for 48 h. To ensure the purity, the product obtained was recrystallized in ethanol−ethyl acetate (≥ 99.7 %, Merck) at least four times, and it gave satisfactory NMR data. Demineralized doubly distilled water was used throughout the study.

The conductance measurements were carried out using an Elico CM 82 T conductivity bridge equipped with a dip cell (cell constant = 1.02 cm^{-1}). The uncertainty in specific conductance (κ) was found to be less than ± 1 %. An appropriate concentration of the stock solution of 14-6-14, 2Br$^-$ was made in the desired solvent medium. From this, measured volumes ($\pm 5\cdot10^{-7}$ dm^{-3}, using a Hamilton microliter syringe) were added to a certain volume [$(30 \pm 0.05)\cdot10^{-3}$ dm^{-3}] of the same solvent (water or water + organic solvent mixture) and kept in a water bath (maintained within ± 0.1 K of the desired temperature), and the conductance of the solution was recorded on successive additions. The solvent (water or water + organic solvent mixture) was equilibrated at the desired temperature for at least 30 min before the addition of the suitably prepared concentrated stock solution of surfactant.

The fluorescence measurements were made on a Hitachi F-2500 fluorescence spectrophotometer at 303.15 ± 0.1 K. Excitation was done at 337 nm, and emission spectra were recorded in the range of (350 to 450) nm at a scan speed of 60 nm·min^{-1}. The width of the excitation and emission slits was 2.5 nm. Pyrene ($3\cdot10^{-6}$ mol·dm^{-3}) in water + organic solvent containing surfactant micellar solutions was prepared as described elsewhere.[20] A measured volume ($\pm 5\cdot10^{-7}$ dm^{-3}) of the quencher (CPC) was added to the surfactant solution containing pyrene, confirming full solubilization of the probe in the micelles and Poisson distribution for quencher. It was ensured that the fluorescence lifetime of pyrene was longer than the residence lifetime of the quencher in the micelle.

Results and Discussion

a. Effect of Organic Solvent Addition on the Micellization Parameters. In this study, the volume fractions (ϕ) of the organic solvents in the binary mixed media were varied from 0 to 0.80, to see how the solvent media affect the cmc and degree of counterion dissociation (α) of 14-6-14, 2Br$^-$ gemini surfactant. Conductivity data of 14-6-14, 2Br$^-$ in WR−DO, WR−DMF, and WR−EG mixed media containing different volume fractions (ϕ) of organic solvents at 303.15 K are given in Table S1 (Supporting Information, SI). Usually the cmc is determined from the break point in the conductivity (κ) versus [surfactant] plots assuming the conductivity to be linearly related to the surfactant concentration, and more often the interionic interactions are ignored. Such a determination creates the difficulty to choose the exact break point in the κ-concentration profiles when there is a weak curvature (as observed for ionic surfactants in mixed solvent systems[45] and in the presence of organic additives like urea[46]).

We have, therefore, used Carpena's method[47] to obtain cmc and α values from the conductivity data. The procedure involves fitting of the experimental data (κ) as a function of surfactant concentration (c) to the integral of Boltzmann-type sigmoidal equation

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

Here κ_0, A_1, A_2, and Δc are the conductivity of the solution at zero concentration of the surfactant, the premicellar slope, the postmicellar slope, and the width of the transition, respectively. The details of the fitting procedure have been explained in our

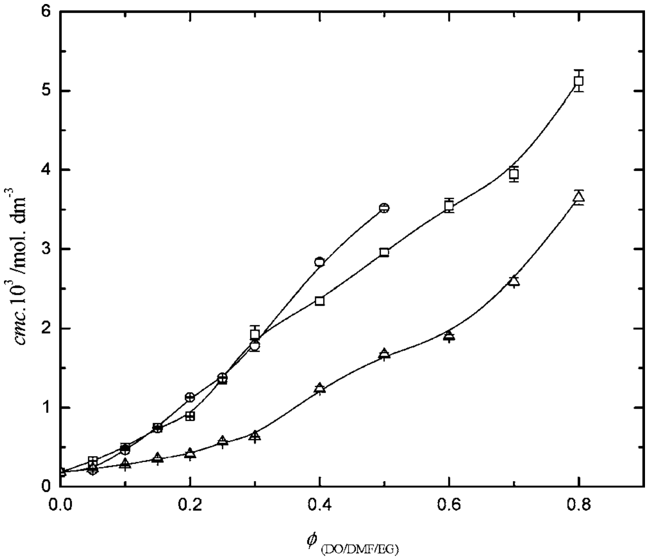


Figure 1. Plots of cmc values versus volume fractions (ϕ) of different organic solvents for the 14-6-14, $2Br^-$ gemini surfactant at 303.15 K: □, DO; ○, DMF; △, EG. Solid lines are for visual purposes. The uncertainty limit of cmc is ± 3 %.

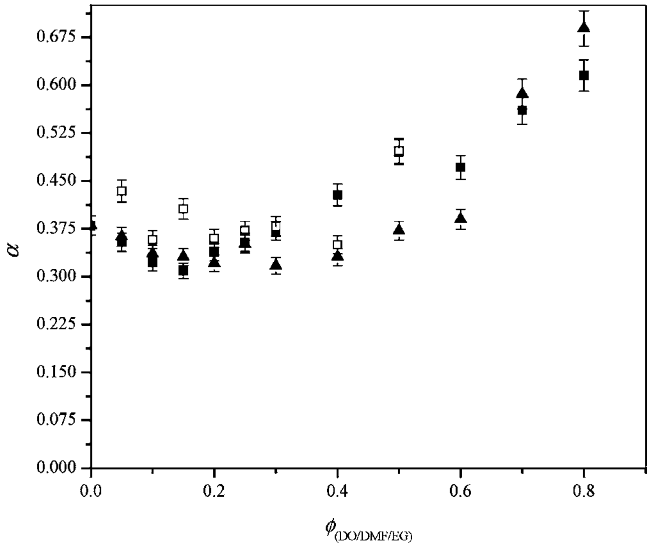


Figure 2. Plots of counterion dissociation values (α) versus volume fractions (ϕ) of different organic solvents for the 14-6-14, $2Br^-$ gemini surfactant at $T = 303.15$ K: ■, DO; □, DMF; ▲, EG. The uncertainty limit of α is ± 4 %.

earlier paper.[40] The central point on the width of the transition (c_0) corresponds to the cmc, and the degree of counterion dissociation (α) was determined from the ratio of postmicellar slope to premicellar slope as $\alpha = A_2/A_1$.

The values of cmc and α of 14-6-14, $2Br^-$ in different water + organic solvent mixed media are given in the Table S2 (SI), and their plots against the ϕ of the organic solvents are shown in Figures 1 and 2. Clearly, the presence of organic solvents delays the micellization process of the gemini surfactant (Figure 1). The cmc values increased to about 28 and 20 times than that in the pure water as the ϕ of DO and EG in the mixed media varied to 0.80, whereas the inclusion of 0.50 ϕ of DMF augmented the value 19 times. It is obvious from the increased cmc values that the studied mixed solvents provide a better medium than pure water for surfactant molecules, and as a result, the transfer of hydrocarbon tails of the surfactant into the micellar core and that of the methylene group in the spacer and methyl groups in the head part to the micellar surface become progressively less favorable with the increase in the ϕ of the organic solvent in the mixed medium. This increase in the cmc could be due to possible modifications (mentioned below) caused by the presence of organic solvents. Their inclusion to aqueous micellar solution decreases both the solvophobicity of the surfactant tails in the medium and the polarity of the bulk phase. The two effects, respectively, enhance the solubility and repulsion between the ionic head groups of the surfactant monomers which, in turn, causes the gemini to micellize at a higher concentration. The values show that the different amounts of the organic solvents are able to make a specific delay in the micellization. For example, it could be possible to increase the cmc of 14-6-14, $2Br^-$ to a value around 3.5 mM by the addition of 0.60, 0.50, and 0.80 ϕ of DO, DMF, and EG to the WR-14-6-14, $2Br^-$ micellar solutions, respectively.

According to the theory of surfactant aggregation proposed by Nagarajan and Ruckenstien,[48] there are several Gibbs energy contributions to the ΔG^0_m value of a surfactant in solution. One among them is that associated with the electrostatic repulsion between the charged head groups at the micellar surface which is dependent on factors such as size, shape, orientation of the charged headgroup, dielectric constant (ε) of the medium, discrete charge effects, and so forth. For the micellization of a given surfactant in different media, the polarity of the bulk phase described through its ε has to be taken into account. The diminution of the polarity of a particular medium by the addition of an organic solvent leads to an increased repulsion between charged head groups. To balance this enhancement, some more fractions of the counterions may get moved to the micellar surface from their dissociated state, and a decline in the values of α may be expected, at least for the lower volume fractions of the organic solvent, as observed mainly for DO and EG (Figure 2). However, at the same time, the increase in the amount of organic solvent in the bulk phase is also associated with a decrease in aggregation number (N_{agg}) (see next section), causing a reduction in the net charge on the micellar surface and favoring the dissociation of counterions. The experimental data show that the net effect of these two factors determines the value of α at a particular composition of the mixed media.

It can be seen that the increase in the cmc values of 14-6-14, $2Br^-$ is comparatively less below the 0.20 volume fraction of the organic solvents showing the predominance of water character in the bulk phase, and it is also dependent on the characteristic properties of the solvents. Comparatively lesser cmc values in the WR−EG mixed medium than that in the WR−DO and WR−DMF mixed media show that, though micellization is not favored as in pure water, it is favored in the WR−EG mixed medium rather than in the other two media, that is, the postponement of the micellization is due to different reasons (although each solvent delays that). EG is a polar protic solvent which has many properties similar to water (e.g., cohesive energy, relatively higher ε, and considerable H-bonding capability), and it is expected to favor the micellization up to some extent. However, the delay in the micellization may be due to its structure-breaking property[49] (such solutes reduce the hydrophobicity of the surfactant monomers and cause an increase in the cmc).

In the case of nonpolar aprotic cyclic ether DO, the observed delay may be due to its larger hydrophobic surface area[50] which can cause the solvation of more surfactant monomers. Though the addition of all three studied organic solvents decreases the polarity of the bulk phase, the decrease would be relatively more in the case of DO than for the others as the ε of DO, DMF,

Table 1. Various Micellization (cmc, α, and N_{agg}) and Thermodynamic Parameters (ΔG^0_m, $\Delta G^0_{m,tail}$, $\Delta G^0_{m,trans}$, ΔH^0_m, and ΔS^0_m) of 14-6-14, 2Br$^-$ in Water + DO Mixed Media at Different Temperatures [T = (298.15 to 323.15) K][a]

ϕ_{DO}	T / K	cmc·10^3 / mol·dm^{-3}	α	N_{agg}	ΔG^0_m / kJ·mol^{-1}	$\Delta G^0_{m,tail}$ / kJ·mol^{-1}	$\Delta G^0_{m,trans}$ / kJ·mol^{-1}	ΔH^0_m / kJ·mol^{-1}	ΔS^0_m / kJ·K^{-1}·mol^{-1}
0.00	298.15	0.158	0.369		−71.62	−35.81	0.00	−26.75	0.150
0.00	303.15	0.182	0.380	32	−71.27	−35.64	0.00	−27.38	0.145
0.00	313.15	0.215	0.391		−71.98	−35.99	0.00	−28.94	0.137
0.00	323.15	0.252	0.397		−72.90	−36.45	0.00	−30.63	0.131
0.10	298.15	0.387	0.281		−71.25	−35.62	0.37	−34.23	0.124
0.10	303.15	0.499	0.322	59	−68.51	−34.25	2.76	−34.20	0.113
0.10	313.15	0.523	0.332		−69.89	−34.95	2.09	−36.19	0.108
0.10	323.15	0.634	0.356		−69.45	−34.72	3.45	−37.74	0.098
0.20	298.15	0.763	0.330		−63.97	−31.98	7.65	−38.06	0.087
0.20	303.15	0.892	0.338	46	−63.64	−31.82	7.63	−39.06	0.081
0.20	313.15	1.128	0.352		−63.54	−31.77	8.44	−41.17	0.071
0.20	323.15	1.395	0.366		−63.47	−31.73	9.43	−43.30	0.062
0.30	298.15	1.730	0.362		−57.03	−28.51	14.59	−25.23	0.107
0.30	303.15	1.922	0.372	37	−56.88	−28.44	14.39	−25.86	0.102
0.30	313.15	2.193	0.396		−56.76	−28.38	15.22	−27.01	0.095
0.30	323.15	2.314	0.397		−58.17	−29.09	14.72	−28.73	0.091
0.50	298.15	1.988	0.411		−52.55	−26.28	19.07	−45.06	0.025
0.50	303.15	2.958	0.495	24	−47.32	−23.66	23.95	−43.01	0.014
0.50	313.15	3.226	0.563		−45.13	−22.57	26.85	−42.77	0.008
0.50	323.15	3.971	0.596		−43.92	−21.96	28.98	−43.94	0.000

[a] The uncertainty limits of cmc, α, and N_{agg} are ± 3 %, ± 4 %, and ± 3, and those of ΔG^0_m, $\Delta G^0_{m,tail}$, $\Delta G^0_{m,trans}$, ΔH^0_m, and ΔS^0_m are (± 3, ± 3, ± 3, ± 5, and ± 5) %, respectively.

EG, and WR are, respectively, 2.2, 36.7, 37.7, and 78.5 at 298.15 K. The WR−DO mixed medium becomes a better solvent for hydrocarbon tails, and a higher surfactant concentration is required to start the aggregation. The higher dipole moment (μ = 3.82 D at 298.15 K) of the polar aprotic solvent DMF may be increasing the solvating ability of the bulk phase to solvate the hexamethylene-1,6-bis(tetradecyldimethylammonium) ion via its negative dipole, making a delay in the micellization in the WR−DMF mixed system. An increase in the values of cmc and α with an increase in the amount of the organic solvent in WR−DMF and WR−EG mixed media have been reported for the TTAB (TTAB in WR−DMF[51] and TTAB in WR−EG[45,51−53]), which is the monomer of the studied gemini 14-6-14, 2Br$^-$, and the values are recorded in Tables 2 and 3.

b. Aggregation Number of 14-6-14, 2Br$^-$ Gemini Surfactant. The aggregation number (N_{agg}), the number of monomers that come together to form micelles, was measured by the steady-state fluorescence quenching (SSFQ) method, and the interpretations are made as follows.[54] It is well-known that the fluorescence intensity in the absence of quencher [I_0], that in the presence of the quencher [I] and concentration of the quencher [Q], and that of surfactant [S] are related as

$$\ln\left(\frac{I_0}{I}\right) = \frac{N_{agg}[Q]}{[S] - \text{cmc}} \tag{2}$$

In all of the cases a surfactant concentration higher than the cmc was taken, and linear plots were obtained between ln I_0/I versus [Q] with a slope equal to $N_{agg}/\{[S] - \text{cmc}\}$ (representative fluorescence (emission) spectra of 3.10^{-6} mol·dm^{-3} pyrene in 0.10 ϕ of DMF micellar solution of 14-6-14, 2Br$^-$ at different quencher concentrations and a quenching plot of the same in 0.50 ϕ of EG are shown, respectively, in Figures S1 and S2, SI). The values of N_{agg} were calculated from such slopes which are recorded in Tables 1 to 3 for WR−DO, WR−DMF, and WR−EG, respectively, along with the values of the monomeric counterpart (TTAB). A decrease in the aggregation number was observed for the micellization of 14-6-14, 2Br$^-$ in all of the water + organic solvent mixed media with the increase in the ϕ of the DO, DMF, and EG (as obtained for the TTAB in different media[51,52]). This decrease in the aggregation number could be due to the decrease in the water−hydrocarbon interfacial tension caused by the presence of the studied organic solvents. However, although N_{agg} decreases with volume fraction in all three mixed media, the value obtained in pure water for 14-6-14, 2Br$^-$ is lower (except in WR-DMF medium) than that of the 0.10, 0.20, and 0.30 volume fractions of WR-DO and in all volume fractions of WR−EG mixed media, whereas that of the TTAB was always higher. In addition, a smaller decrease in the values of α in the lower ϕ of organic solvents (especially for DO and EG), than that in the pure water, may be due to this increase in the N_{agg}, causing a little higher charge on the micellar surface. Moreover, it should be noted that, as the water + organic solvent systems are more complicated than pure water (to favor aggregation), the values reported herein should be viewed as approximate and care should be given to the effect of solvent on N_{agg}.

c. Effect of Temperature on cmc and α. To investigate the effect of temperature on the micellization of 14-6-14, 2Br$^-$ in water and in the presence of different organic solvents, conductivity measurements were carried out at four temperatures ranging from (298.15 to 323.15) K. The conductivity data of all of these systems are given in Table S3 (SI). Representative κ-concentration profiles in WR−DMF mixed media, depicted in Figure 3, show the effect of temperature on the micellization. An increase in the temperature makes the transition from the premicellar region to the postmicellar region gradually and alters the slopes of the plots, mainly that in the postmicellar region. Tables 1 to 3 list the cmc and α values of 14-6-14, 2Br$^-$ both in pure water and in the studied mixed media at different temperatures. A similar trend in the increase of cmc and α values were observed for both TTAB and 14-6-14, 2Br$^-$ surfactants in different mixed media.

It is seen that, at a particular ϕ of the organic solvent (DO, DMF, EG), the cmc and α values increase with the rise in temperature. In a surfactant solution, an increase in the temperature can favor or disfavor the aggregation of the surfactant monomers, as it causes a decrease in the degree of hydration of the hydrophilic groups or disruption of the water structure surrounding the surfactant tails (hydrophobic group), and the predominance of one over another would make the resultant decrease or increase in the cmc. In the case of micellization of 14-6-14, $2Br^-$, an increase in the cmc with respect to temperature shows that the disruption of water structure around the surfactant tails is more pronounced than the change in the degree of hydration of the hydrophilic groups.

It can be seen from Figure S3 (SI) that the increase in the cmc with respect to temperature becomes more pronounced as the ϕ of the organic solvent in the medium increases. Here, the parameter given on the Y-axis, cmc_{diff}, is the difference in the cmc at higher and lower temperatures for a particular system (in this study, $cmc_{diff} = cmc_{323.15K} - cmc_{298.15K}$). The cmc_{diff} value is less in pure water (0.094 mM) compared to that in mixed media. Clearly (see Figure S3, SI), the magnitude of the cmc_{diff} is less in the case of WR−EG mixed medium than the other two mixed media (WR−DO, WR−DMF) for the micellization of 14-6-14, $2Br^-$ gemini surfactant. For ionic surfactants, an increase in the temperature decreases the aggregation number (N_{agg}), with the result that the surface charge density on the micelles decreases and a larger fraction of the gemini and counterions stays in dissociated form. This could be the reason for the gradual increase in the α values with the rise in temperature at a particular composition of the mixed media. It can be observed that the α values of 14-6-14, $2Br^-$ are comparatively higher at all of the temperatures in the 0.50ϕ of WR−DO and WR−DMF mixed media than in the WR−EG mixed medium.

d. Thermodynamics of Micellization. As the micellization process is sensitive to temperature, various thermodynamic parameters were calculated from the temperature dependence of cmc values. According to the equilibrium model for micelle formation, the micellization of the gemini surfactant 14-6-14, $2Br^-$ can be written as (since one gemini monomer can give three ions in solution, one gemini cation, and two counterions)

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

where G^{2+} represents the gemini cation, Br^- the counterion of the 14-6-14, and M^{p+} the aggregate of n monomers with an effective charge of p. The Gibbs energy of micelle formation per mole of the gemini surfactant, ΔG^0_m, is given by

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

where R, T, and a are the gas constant, temperature, and activities, respectively. For a micelle formed with an adequate number of monomer units, the first term in the parentheses would be small and can be neglected. Under this condition, the activities of the corresponding ions can be replaced by that at the cmc expressed in mole fraction scale, x_{cmc}, of the surfactant. By the above approximation, for the gemini surfactants, ΔG^0_m can be written as[55]

$$\Delta G^0_m = (3 - 2\alpha)RT \ln x_{cmc} \tag{5}$$

The corresponding enthalpy change, ΔH^0_m, can be calculated by the expression

$$\Delta H^0_m = -RT^2(3 - 2\alpha)\left(\frac{d \ln x_{cmc}}{dT}\right)_P - \ln x_{cmc}\left(\frac{d\alpha}{dT}\right)_P \tag{6}$$

It can be seen from Tables 1 to 3 that, at a particular composition of the water + organic solvent mixed media, the variation of α with temperature is small and, therefore, the second term in eq 6 can be neglected. The above equation then becomes

$$\Delta H^0_m = -RT^2(3 - 2\alpha)\left(\frac{d \ln x_{cmc}}{dT}\right)_P \tag{7}$$

The values of ln x_{cmc} at a particular composition in all of the water + organic solvent mixed media were plotted against the

Table 2. Various Micellization (cmc, α, and N_{agg}) and Thermodynamic Parameters (ΔG^0_m, $\Delta G^0_{m,tail}$, $\Delta G^0_{m,trans}$, ΔH^0_m, and ΔS^0_m) of 14-6-14, $2Br^-$ (A) and TTAB (B) in Water + Dimethylformamide Mixed Media at Different Temperatures [T = (298.15 to 323.15) K][a]

ϕ_{DMF}	T / K	cmc·10^3 / mol·dm^{-3}	α	N_{agg}	ΔG^0_m / kJ·mol^{-1}	$\Delta G^0_{m,tail}$ / kJ·mol^{-1}	$\Delta G^0_{m,trans}$ / kJ·mol^{-1}	ΔH^0_m / kJ·mol^{-1}	ΔS^0_m / kJ·K^{-1}·mol^{-1}
				(A) 14-6-14, $2Br^-$					
0.00	298.15	0.158	0.369		−71.62	−35.81	0.00	−26.75	0.150
0.00	303.15	0.182	0.380	32	−71.27	−35.64	0.00	−27.38	0.145
0.00	313.15	0.215	0.391		−71.98	−35.99	0.00	−28.94	0.137
0.00	323.15	0.252	0.397		−72.90	−36.45	0.00	−30.63	0.131
0.10	298.15	0.418	0.329		−68.01	−34.00	3.61	−22.50	0.153
0.10	303.15	0.464	0.358	25	−66.86	−33.43	4.41	−22.69	0.146
0.10	313.15	0.510	0.362		−68.25	−34.13	3.73	−24.12	0.141
0.10	323.15	0.585	0.364		−69.47	−34.74	3.43	−25.64	0.136
0.20	298.15	0.737	0.329		−64.23	−32.11	7.39	−25.96	0.128
0.20	303.15	1.130	0.360	24	−61.12	−30.56	10.15	−26.13	0.115
0.20	313.15	1.360	0.377		−61.11	−30.56	10.87	−27.47	0.107
0.20	323.15	1.552	0.388		−61.64	−30.82	11.25	−28.96	0.101
0.30	298.15	1.362	0.346		−59.27	−29.63	12.35	−29.01	0.101
0.30	303.15	1.784	0.379	20	−57.00	−28.50	14.27	−29.13	0.092
0.30	313.15	2.135	0.407		−56.37	−28.18	15.61	−30.29	0.083
0.30	323.15	2.553	0.436		−55.58	−27.79	17.31	−31.39	0.075
0.50	298.15	2.394	0.488		−48.01	−24.01	23.61	−13.46	0.116
0.50	303.15	3.518	0.497	11	−46.41	−23.21	24.86	−13.79	0.108
0.50	313.15	3.836	0.547		−45.13	−22.57	26.85	−13.98	0.099
0.50	323.15	4.222	0.538		−46.52	−23.26	26.37	−15.03	0.097
				(B) TTAB[b]					
0.000	298.15	3.62	0.23	58	−24.60		0.00		
0.053	298.15	4.94	0.26	46	−22.90		1.70		
0.105	298.15	6.42	0.28	38	−21.50		3.10		
0.209	298.15	11.00	0.32	28	−18.80		5.80		

[a] The uncertainty limits of cmc, α, and N_{agg} are ± 3 %, ± 4 %, and ± 3, and those of ΔG^0_m, $\Delta G^0_{m,tail}$, $\Delta G^0_{m,trans}$, ΔH^0_m, and ΔS^0_m are (± 3, ± 3, ± 3, ± 5, and ± 5) %, respectively. [b] Data taken from ref 51.

temperature, T. A linear plot was obtained for each of the systems studied, and the slope of these plots was taken as the values of d ln x_{cmc}/dT. Accordingly, the entropy change, ΔS^0_{m}, was calculated by the expression

$$\Delta S^0_{\mathrm{m}} = \frac{\Delta H^0_{\mathrm{m}} - \Delta G^0_{\mathrm{m}}}{T} \tag{8}$$

Finally, to estimate the effect of second solvent (cosolvent) on the micellization process, the Gibbs energy of transfer values, $\Delta G^0_{\mathrm{m,trans}}$, were obtained through eq 9

$$\Delta G^0_{\mathrm{m,trans}} = \Delta G^0_{\mathrm{m(water-organic\,solvent\,mixed\,medium)}} - \Delta G^0_{\mathrm{m(pure\,water)}} \tag{9}$$

The Gibbs energy of micellization per alkyl tail of the gemini surfactant, $\Delta G^0_{\mathrm{m,tail}}$, was also calculated using

$$\Delta G^0_{\mathrm{m,tail}} = \frac{\Delta G^0_{\mathrm{m}}}{2} \tag{10}$$

Table S4 (SI) lists various Gibbs free energies of the 14-6-14, 2Br$^-$, both in pure water and in the three water + organic mixed solvent systems at 303.15 K. The ΔG^0_{m} values were found to be negative in all of the cases, and the positive values of $\Delta G^0_{\mathrm{m,trans}}$ augmented with the increase in the ϕ of the organic solvent. It can be seen from the Tables 1 to 3 and S4 (SI) that, although variations are there on the increment in the values of ΔG^0_{m} in the three different water + organic solvent mixed systems, the values become less negative with the increase in ϕ. This reveals that the micellization process, as the volume fraction of the studied organic solvent increases, becomes less spontaneous than that in pure water. In comparison to WR−DO and WR−DMF mixed solvent systems, the micellization process of 14-6-

Table 3. Various Micellization (cmc, α, and N_{agg}) and Thermodynamic Parameters (ΔG^0_{m}, $\Delta G^0_{\mathrm{m,tail}}$, $\Delta G^0_{\mathrm{m,trans}}$, ΔH^0_{m}, and ΔS^0_{m}) of 14-6-14, 2Br$^-$ (A) and TTAB (B) in Water + Ethylene Glycol Mixed Media at Different Temperatures [T = (298.15 to 323.15) K][a]

ϕ_{EG}	T/K	cmc·10^3/mol·dm^{-3}	α	N_{agg}	ΔG^0_{m}/kJ·mol^{-1}	$\Delta G^0_{\mathrm{m,tail}}$/kJ·mol^{-1}	$\Delta G^0_{\mathrm{m,trans}}$/kJ·mol^{-1}	ΔH^0_{m}/kJ·mol^{-1}	ΔS^0_{m}/kJ·K^{-1}·mol^{-1}
					(A) 14-6-14, 2Br$^-$				
0.00	298.15	0.158	0.369		−71.62	−35.81	0.00	−26.75	0.150
0.00	303.15	0.182	0.380	32	−71.27	−35.64	0.00	−27.38	0.145
0.00	313.15	0.215	0.391		−71.98	−35.99	0.00	−28.94	0.137
0.00	323.15	0.252	0.397		−72.90	−36.45	0.00	−30.63	0.131
0.10	298.15	0.178	0.288		−75.62	−37.81	−4.00	−21.50	0.182
0.10	303.15	0.277	0.336	61	−71.25	−35.62	0.02	−21.35	0.165
0.10	313.15	0.314	0.340		−72.58	−36.29	−0.60	−22.70	0.159
0.10	323.15	0.356	0.347		−73.62	−36.81	−0.72	−24.01	0.154
0.20	298.15	0.244	0.293		−72.94	−36.47	−1.32	−33.90	0.131
0.20	303.15	0.409	0.321	60	−69.41	−34.71	1.86	−34.25	0.116
0.20	313.15	0.488	0.360		−68.24	−34.12	3.74	−35.32	0.105
0.20	323.15	0.607	0.365		−68.82	−34.41	4.08	−37.46	0.097
0.30	298.15	0.525	0.314		−66.70	−33.35	4.92	−21.04	0.153
0.30	303.15	0.633	0.317	43	−66.54	−33.27	4.73	−21.70	0.148
0.30	313.15	0.741	0.364		−65.04	−32.52	6.94	−22.22	0.137
0.30	323.15	0.804	0.392		−64.97	−32.49	7.93	−23.08	0.130
0.50	298.15	0.920	0.368		−59.46	−29.73	12.15	−25.10	0.115
0.50	303.15	1.670	0.337	36	−58.60	−29.30	12.67	−26.65	0.105
0.50	313.15	2.083	0.353		−58.41	−29.21	13.57	−28.06	0.097
0.50	323.15	2.287	0.362		−59.22	−29.61	13.67	−29.64	0.092
					(B) TTAB[b]				
0.000	298.15	3.6	0.24	75	−42.30		0.00		
0.091	298.15	4.0	0.24		−41.30		1.00		
0.183	298.15	4.6	0.25	60	−40.20		2.10		
0.278	298.15	5.3	0.25		−39.20		3.10		
0.375	298.15	7.8	0.27	43	−36.80		5.50		
0.473	298.15	12.9	0.30	35	−33.00		9.30		
					TTAB[c]				
0.000	298.15	3.74	0.250		−41.67		0.00		
0.090	298.15	4.13	0.255		−40.84		0.83		
0.183	298.15	4.80	0.268		−39.59		2.08		
0.278	298.15	5.77	0.285		−38.10		3.57		
0.375	298.15	8.14	0.327		−35.39		6.28		
0.473	298.15	11.94	0.378		−32.39		9.28		
0.278	298.15	5.77	0.285		−38.10		0.00	−25.57	0.042
0.278	303.15	6.22	0.299		−38.09		0.01	−26.21	0.039
0.278	318.15	6.88	0.308		−38.08		0.02	−26.94	0.036
0.278	313.15	7.68	0.315		−38.06		0.04	−27.71	0.033
0.278	318.15	8.46	0.326		−38.00		0.10	−28.41	0.030
0.278	323.15	9.51	0.333		−37.89		0.21	−29.19	0.027
					TTAB[d]				
0.000	303.15	3.93	0.250		−37.38		0.00	−7.51	0.099
0.183	303.15	5.18	0.278		−34.99		2.39	−15.53	0.064
0.375	303.15	9.00	0.329		−31.07		6.31	−28.55	0.008
0.574	303.15	24.25	0.385		−25.35		12.03	−22.72	0.009

[a] The uncertainty limits of cmc, α, and N_{agg} are ± 3 %, ± 4 %, and ± 3, and those of ΔG^0_{m}, $\Delta G^0_{\mathrm{m,tail}}$, $\Delta G^0_{\mathrm{m,trans}}$, ΔH^0_{m}, and ΔS^0_{m} are (± 3, ± 3, ± 3, ± 5, and ± 5) %, respectively. [b] Data taken from ref 53. [c] Data taken from ref 52. [d] Data taken from ref 45.

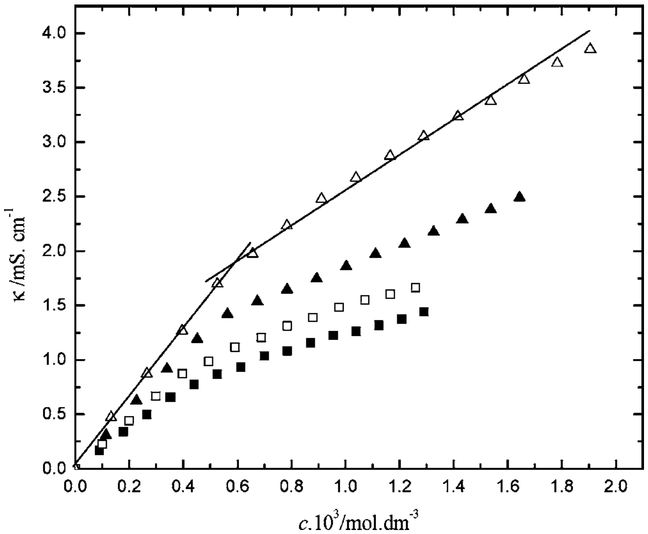


Figure 3. Conductivity (κ) versus concentration plots (c) in 0.10 ϕ of DMF micellar solution of 14-6-14, 2Br$^-$ at T = (298.15 to 323.15) K: ■, 298.15 K; □, 303.15 K; ▲, 313.15 K; △, 323.15 K. The uncertainty limit of κ is ± 1 %.

14, 2Br$^-$, is relatively more spontaneous in the WR−EG mixed solvent system (the decrease in the value of ΔG^0_m is less), and this may be due to the resemblance of EG to WR, as mentioned earlier. Obviously, the changes in the values of $\Delta G^0_{m,trans}$ also support the above discussion. If we compare the values of $\Delta G^0_{m,trans}$ up to 0.50 volume fraction of the organic solvents in all the three studied mixed systems, it is found to be less in WR−EG than that in the WR−DO or WR−DMF.

Tables 1 to 3 also list the other thermodynamic parameters of 14-6-14, 2Br$^-$ in pure water and in the WR−DO, WR−DMF, and WR−EG mixed solvent systems at the selected ϕ (0.10, 0.20, 0.30, and 0.50) of the organic solvents. At a particular composition of the water + organic solvent mixed system, the ΔG^0_m values were found to become slightly more or less negative with the rise in temperature, suggesting that the micellization of 14-6-14, 2Br$^-$ in these media depends only slightly on the studied temperature range. The enthalpy of micellization, ΔH^0_m, was negative, and the variation is not so significant with the rise in temperature for a particular composition of the mixed media. However, on plotting the variation of ΔH^0_m against the ϕ of the organic solvents at all of the temperatures, a maximum in the value of ΔH^0_m with respect to the composition of the medium was observed. The plots obtained at 298.15 K are shown in Figure S4 (SI).

It can be understood from Figure S4 (SI) and Tables 1 to 3 that the micellization of 14-6-14, 2Br$^-$ is exothermic in nature and the magnitude of which considerably varies with the composition of the medium rather than the temperature. The ΔH^0_m values were found to be higher when the ϕ of the organic solvents was 0.50 for WR−DO, 0.30 for WR−DMF, and 0.20 for WR−EG mixed media. This behavior indicates the dependency of the composition of the mixed medium on the micellization process of 14-6-14, 2Br$^-$ and can be explained on the basis of various interactions between the solute−solvent and the solvent−solvent. With the increase in the ϕ of the organic solvent in the mixed media, the micellization is energetically controlled by the balanced contributions from both the enthalpic and the entropic factors to ΔG^0_m, making the process less spontaneous. However, at the above-mentioned compositions of the mixed media, depending on the properties of the organic solvent, the process is mainly favored by the enthalpic contribution in the studied temperature range. During the micellization of 14-6-14, 2Br$^-$, there may be breaking of the some of the bonds between WR−WR and organic solvent−organic solvent (if any interaction exists there; an endothermic process), and they may be partially reformed at the end (an exothermic process). The overall magnitude of enthalpy would be depending on the overall energies of the two processes and which one exceeds over the other. Ruiz[45] has reported the thermodynamics of micellization of TTAB in WR−EG binary mixtures at four selected mass fractions (0, 0.20, 0.40, and 0.60). Here, if ΔH^0_m is plotted against the volume fractions (we converted the mass fractions into volume fractions for the sake of comparison) of EG at a particular temperature, a similar type of behavior can be seen (i.e., the magnitude of ΔH^0_m shows maximum at a particular composition). The values are more at around 0.37 and 0.18 volume fractions of the EG at a temperature in between (298.15 and 313.15) K and at 318.15 K, respectively. However, this comparison should be viewed only as approximate as the studied compositions in the two cases are different.

The values of ΔS^0_m were found to be positive, which decreased with the increase in temperature for a particular composition, but no particular trend was observed with the ϕ of the organic solvent at a particular temperature. However, a decrease in the values indicates that the ordering of the randomly oriented gemini cations from the solvated form into the micelle structure is more pronounced than the disruption of water structure with the increase in the temperature, causing an effective decrease in the degree of randomness of the system.

Conclusions

To study the effect of different organic solvents (DO, DMF, and EG) and temperature on the micellization and thermodynamic parameters of a cationic gemini surfactant hexamethylene-1,6-bis(tetradecyldimethylammonium bromide) (14-6-14, 2Br$^-$), conductivity and fluorescence measurements were carried out. The following conclusions were drawn from the study:

(1) Although the micellization of 14-6-14, 2Br$^-$ is not as favored in the presence of organic solvents as in water (solvophobic effect), a comparatively smaller increment in the cmc values in WR−EG mixed solvent indicates that it is more favored in this medium than in WR−DO or WR−DMF. For 0.5ϕ of the WR−DO, WR−DMF, and WR−EG mixed media at 303.15 K, the respective cmc values were found to be 16, 19, and 9 times higher than that in WR. For a particular application that requires the presence of water-poor micellar medium in a minimum surfactant concentration, the organic solvents which are similar to water in some properties, such as EG, may be preferred.

(2) The values of cmc$_{diff}$ were found to be different at different compositions of the water + organic solvent mixed media. The values are more at higher volume fractions of the organic solvents, and they are comparatively less in the WR−EG mixed medium.

(3) In all of the studied water + organic solvent mixed media, the aggregation number (N_{agg}) of the 14-6-14, 2Br$^-$ gemini surfactant decreased with the increase in the ϕ of the DO, DMF, and EG.

(4) As the ϕ of the organic solvent increased in the mixed media, the Gibbs energy of micellization (ΔG^0_m) values became less negative, showing the micellization process to be less favorable. The values of ΔH^0_m showed that the micellization of 14-6-14, 2Br$^-$ was exothermic at all of the studied combinations of the water and different organic solvents and its

magnitude depended on the nature (endothermicity/exothermicity) of various interactions between the solute−solvent and/or solvent−solvent.

Supporting Information Available:

Conductivity data (at all of the studied temperatures), values of cmc, α, and the different free energies (at 303.15 K) of 14-6-14, 2Br$^-$ gemini surfactant in studied mixed media and Figures S1 to S4 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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