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Micellization of monomeric and dimeric (gemini) surfactants in polar nonaqueous-water-mixed solvents

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Abstract Dimeric or gemini surfactants are novel surfactants that are finding a great deal of discussion in the academic and industrial arena. They consist of two hydrophobic chains and two polar head groups covalently linked by a spacer. Data on critical micelle concentration (cmc) and degree of counterion dissociation (α) are reported on bis-cationic $C_{16}H_{33}N^+(CH_3)_2-(CH_2)_s-N^+(CH_3)_2C_{16}H_{33}$, $2Br^-$, referred to as 16-*s*-16, for spacer lengths *s*=4, 5, 6 in aqueous and in polar nonaqueous (1-propanol, 2-methoxyethanol or methyl cellosolve, dimethyl sulfoxide, acetonitrile)-water-mixed solvents. The behavior is compared with conventional monomeric surfactant cetyltrimethylammonium bromide (CTAB). Thermodynamic parameters are ob-

tained from the temperature dependence of the cmc values. It is observed that micellization tendency of the surfactants decreases in the presence of polar nonaqueous solvents. However, detailed studies with dimethyl sulfoxide (DMSO) show that the geminis nearly outclass the micellization-arresting property of this solvent. Also, within geminis, higher spacer length is found suitable for showing micellization even with high DMSO content (50% v/v). The implications of these results of gemini micellization may be useful in micellar catalysis in polar nonaqueous solvents.

Keywords Gemini surfactant · CTAB · Micellization · Critical micelle concentration · Conductivity · Mixed solvents

Introduction

Micelle formation in nonaqueous polar solvents has attracted less attention as compared to the extensive investigations that have been reported in the literature dealing with the formation of micelles in aqueous surfactant solutions. The term “solvophobic interaction” has been coined to describe the micellization in nonaqueous polar solvents, in analogy with “hydrophobic interactions” [1], responsible for aggregation in water. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process [2]. The micelles formed in nonaqueous solvents are similar in many respects to the micelles that are formed in water, although, micelle formation is not as favored in such solvents as in water for a given surfactant [3, 4].

A new class of surfactants has been introduced in the scientific literature during the last decade [5]. Such surfactants are made of two hydrophobic chains and two hydrophilic head groups covalently attached through a spacer. These surfactants are known as gemini surfactants and few of them possess intriguing properties such as a very low critical micelle concentration (cmc) and a high efficiency in reducing the surface/interfacial tension [6]. Because the polar head groups are connected by a spacer in geminis, the distance between the polar heads within a dimeric unit depends both on the nature and the spacer length [5d]. The conformational arrangement in gemini micelles arises at the expense of interfacial contacts of the hydrocarbon spacer with background water. The force that drives the aggregation is entropic in origin and facilitates the release of “structured” water molecules [7].

It is widely recognized that the cmc is the most important parameter in studies dealing with micellization of surfactants. The cmc of ionic surfactants is usually determined as the intersection point of the two straight lines in conductivity–concentration plots above and below the cmc, whereas the degree of counterion dissociation of micelles, α , is determined as the ratio between the slopes of postmicellar region to that of premicellar region [8, 9]. In such an analysis, the interionic interactions are ignored and conductivity is assumed to be linearly related to surfactant concentration. In addition, this procedure presents difficulties when conductivity–concentration plots exhibit weak curvature especially observed for ionic surfactants in mixed organic solvent systems [10], in the presence of organic additives like urea [11], and in mixed state with the nonionic surfactants [12, 13].

Many approaches based on the differentiation of conductivity data against the surfactant concentration have been proposed [14, 15] to obtain more precise cmc and α values. Such first derivative plots behave as sigmoid; the fitting of which allows evaluation of “width” of transition (the central point of transition width corresponds to the cmc value) and α . Because this procedure involves finding of numerical derivative of the experimental data as first step, it introduces numerical errors which get amplified when joined with experimental errors, and hence lead to unavoidable errors in determination of fitted parameters. This way, the sigmoidal-like derivative shows noisy behavior (instead of a perfect and regular one).

More recently, Carpena et al. [16] have proposed an efficient method to analyze the conductivity–concentration data of ionic surfactant solutions in the context of the determination of micellization parameters viz cmc and α . Their method is based on the fit of the experimental raw data to a simple, nonlinear function obtained by the direct integration of Boltzmann-type sigmoidal function. The method shows much better performance than the conventional [8, 9] and differential conductivity methods [14, 15] for the real systems that present a very gradual transition from the premicellar to postmicellar region and in which the break in conductivity–concentration plots is hard to determine. They have shown by means of Monte Carlo simulations that the errors in the estimation of micellization parameters is smaller than by using derivative of original data in which processing of data introduces spurious errors through numerical differentiation. In addition, the effect of experimental errors on evaluation of the micellization parameters has been shown to be minimal by using this procedure.

Recently, there has been a distinct progress in research dealing with the effects of nonaqueous polar solvents on the micellization process [4, 17]. Geminis have already shown promise in skin care, antibacterial regimens, construction of high-porosity material, analytical separations, and solubilization processes [6]. Scores of patents dealing with geminis have appeared in the last few years [5e]. Because all practical applications of surfactants involve the

presence of other species [18] such as glycols and alcohols, it is important to establish the effects of such and related compounds on micellization to explore their fundamental behavior. Survey of available literature [5e and f, 6] reveals that no serious attempt has been made to study the micellization phenomenon of gemini surfactants in polar nonaqueous solvents. In this communication, we report a preliminary study on the micellar properties [cmc, degree of counter ion dissociation (α), and thermodynamic parameters (ΔG_m^o , ΔH_m^o , and ΔS_m^o)] of the gemini surfactants, $C_{16}H_{33}N^+(CH_3)_2-(CH_2)_s-N^+(CH_3)_2C_{16}H_{33}$, $2Br^-$ ($s=4, 5$, or 6 ; $16-s-16$) in water and polar nonaqueous solvent (1-propanol, PrOH; 2-methoxyethanol or methyl cellosolve, MC; dimethylsulfoxide, DMSO; and acetonitrile, AN)–water mixtures.

Experimental section

Cetyltrimethylammonium bromide (CTAB, 99%), *n,n*-hexadecyl-*N,N*-dimethylamine ($\geq 95\%$), 1,4-dibromobutane ($\geq 98\%$), 1,5-dibromopentane ($\geq 98\%$), and 1,6-dibromohexane ($\geq 97\%$) were purchased from Fluka. All the reagents and solvents (1-PrOH, MC, DMSO, and AN) were of highest purity grade available commercially and were used as received. Demineralized double-distilled water was used throughout.

The gemini surfactants were synthesized by refluxing the corresponding α,ω -dibromoalkane ($Br(CH_2)_sBr$, $s=4, 5$ or 6) with *n,n*-hexadecyl-*N,N*-dimethylamine in dry ethanol for 48 h. The solvent was removed under vacuum and the solids thus obtained were recrystallized thrice from hexane/ethylacetate mixture to obtain pure surfactants. All the three gemini surfactants gave satisfactory 1H NMR analysis well matched with the literature data [19].

Conductometry was used to determine the cmc and α values. The measurements were performed on an ELICO (type CM 82T) bridge equipped with platinized electrodes (cell constant = 1.02 cm^{-1}). The conductivity runs were carried out by adding progressively concentrated surfactant stock solution into the thermostated solvent.

The procedure of cmc determination involves fitting of experimental conductivity data, κ , as a function of surfactant concentration, x , to the equation [16]

$$\kappa(x) = \kappa_0 + A_1x + \Delta x(A_2 - A_1) \ln \left(\frac{1 + e^{(x-x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}} \right) \quad (1)$$

which is integral of Boltzmann-type sigmoid equation [16]. Here, κ_0 represents the conductivity of solution when $x=0$; A_1 and A_2 represent the pre- and postmicellar slopes, respectively; and Δx , the width of transition whose central point, x_0 , corresponds to the cmc. A smaller value of Δx

means abrupt transition (micellization is highly cooperative), while its higher value shows a gradual transition (micellization process is less cooperative). In the analysis, κ_0 was set equal to zero because conductivity of water was subtracted corresponding to each data point.

Data fitting was carried out by making use of initial guess values of A_1 , A_2 , x_0 , and Δx in Eq. 1 to calculate an approximate value of conductivity, κ_x^{approx} , corresponding to each surfactant concentration. Chi-square, χ^2 , the sum of the squares of the deviations of approximate conductivity from the experimental values, defined as

$$\chi^2 = \sum_{i=1}^N [\kappa_i - \kappa_i^{\text{approx}}]^2 \quad (2)$$

(where N is the number of data points, and κ_i and κ_i^{approx} the experimental conductivity and approximate conductivity at a given total surfactant concentration, respectively) was minimized with respect to these parameters and their values corresponding to the minimum were then used as the new set of guess values in an iterative procedure till χ^2 effectively stopped decreasing, indicating convergence of input and output parameters. The minimized value of χ^2 gives maximum likelihood estimate of model parameters. Equation 1 being nonlinear in the parameters, a computer programme for nonlinear least squares fitting of data, as described by Press et al. [20] and making use of Levenberg–Marquardt algorithm, was written with necessary modification to perform the iterative procedure for optimization of parameters. The final set of values of A_1 , A_2 , x_0 , and Δx , when χ^2 effectively stopped decreasing, was taken as their best-fit parameters. From the ratio A_2/A_1 , the degree of counterion dissociation (α) of micelles was determined following Evan's procedure [21]. Uncertainties in the values of cmc and α are not more than $\pm 0.03 \times 10^{-5} \text{ mol dm}^{-3}$ and ± 0.01 , respectively.

Results and discussion

In this study, representatives of three different classes of solvents were chosen which mainly affect the properties of background solvent medium: (1) alcohols (PrOH and MC) which mainly enhance micellization at very low mole fractions and inhibit it at higher concentrations, (2) compound that forms relatively strong hydrogen bond with water (AN), and (3) compound that is known for hydrate formation with water (DMSO) [22].

A representative plot of the conductivity vs the bulk phase (surfactant) in aqueous solution is shown in Fig. 1. Similar type of plots was obtained in other cases. The cmc values of CTAB and geminis in water (Table 1) are in fair agreement with the published data in the literature [19, 23, 24]. Also, the α values obtained in aqueous solutions for all the geminis and the α values reported by Zana et al. [24]

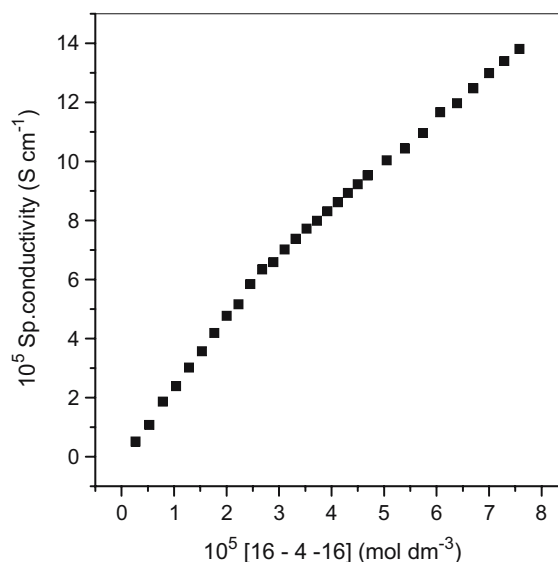


Fig. 1 Specific conductivities of 16-4-16 solutions as a function of surfactant concentration at 30°C

using the solution conductivities appear to be in good agreement.

Along with the cmc and α values in pure aqueous medium, Table 1 also contains the values in polar non-aqueous solvent + water mixtures (10% solvent + 90% water). The presence of 10% of the solvent in binary mixtures (with water) causes increase in cmc of all the surfactants. The inhibitory effect of the solvents (10%) for each surfactant depends upon the nature of the solvent. The behavior can be interpreted in terms of solvent interaction with water and its possible influence on solvophobic forces operating for micellization. Although each solvent postpones micellization, the reasons are quite different. In the case of PrOH or MC, the interaction consists of the destruction of the original water's 3D structure and the formation of new H-bonds between water and the alcohols [25]. These alcohol–water mixtures are better solvents for surfactants than pure water and micelles thus form at higher [surfactant]. The α values reflect the electrostatic interactions between charged micelle surfaces and counterions and, to a first approximation, is a measure of the fraction of counterions located very close to the micellar surface which is mainly affected by the surface solubilization of the alcohol. The alcohol solubilization at the micellar surface reduces the surface charge density. This effect in itself is sufficient to explain the increase of α [25]. However, such alcohol effect is not studied in literature for gemini micelles and a decrease in α (Table 1) in the presence of PrOH or MC demands clarification. The presence of alcohol within the micellar interface makes water less polar that increases Coulombic interactions between headgroups and counterions with a concomitant decrease in α . However, a higher α value for 16-6-16 (Table 1) on the addition of PrOH or MC needs further clarification. As the spacer chain length in-

Table 1 Cmc and α values of surfactants in polar nonaqueous-water-mixed solvents (10:90% v/v) at 30°C

Surfactant	H ₂ O		PrOH		MC		DMSO		AN	
	cmc $\times 10^5$ (mol dm ⁻³)	α	cmc $\times 10^5$ (mol dm ⁻³)	α	cmc $\times 10^5$ (mol dm ⁻³)	α	cmc $\times 10^5$ (mol dm ⁻³)	α	cmc $\times 10^5$ (mol dm ⁻³)	α
16-4-16	2.83	0.64	10.62	0.44	9.92	0.43	6.5	0.63	18.42	0.41
16-5-16	3.63	0.67	8.39	0.49	7.08	0.35	5.67	0.36	11.32	0.62
16-6-16	4.37	0.47	10.75	0.62	7.38	0.55	5.49	0.65	17.10	0.58
CTAB	100.54	0.29	205.38	0.52	152.80	0.36	154.42	0.27	218.04	0.34

Uncertainties on cmc and α are estimated to be less than or equal to $\pm 0.03 \times 10^{-5}$ mol dm⁻³ and ± 0.01 , respectively

creases, the surfactant head group area is reported to increase [19, 26, 27] with the concomitant increase in the hydration of the micelle. In case the spacer chain length is sufficiently larger, looping towards the micellar core may take place [19, 24]. In either case, an increased hydration of the micelle will consequently take place. Due to this increased hydration, one can expect that the PrOH/MC may get solubilized into the head group region of 16-6-16 micelles (instead of being present in the interfacial region). If it is so, the solubilization effect will predominate, reducing the surface charge density and increasing α . Probably the latter effect dominates with the surfactant of higher spacer length (e.g., 16-6-16). However, this explanation needs an independent verification. The postponement of micellization in the presence of AN can also be understood in terms of the formation of hydrogen bonds between water and AN molecules. The inhibitory effect of DMSO can be explained by taking into consideration the increased structuring of the H₂O–DMSO liquid system. DMSO is known to form stoichiometric hydrates with water of the type DMSO·2H₂O [28]. The hydrate formation substantially restricts the motion of the surfactant molecules and reduces hydrophobic interactions with a concomitant increase in cmc (Table 1). However, the cmc increase is lower with DMSO in comparison to other solvents. The α values for gemini + DMSO systems follow the same trend as observed for PrOH. The presence of DMSO may cause a decrease in the overall polarity of the solvent and of α . However, an increase of α in the case of 16-6-16 + DMSO system may again be due to the solubilization effect as discussed in the case of 16-6-16 + PrOH system. Because not much data are available on gemini + nonaqueous solvent systems, further discussion on α is restricted in this study.

As the cmc increase in 16-4-16–DMSO is comparatively more with respect to water than the other gemini–DMSO combinations, to substantiate the effect, therefore, we have studied micellization phenomenon in different DMSO–water mixtures. Figure 2 shows the variation of the ratio (cmc/cmc₀) of the cmc in DMSO and water mixture (cmc)

to that in pure water (cmc₀) with the increasing volume percent of DMSO in DMSO–water mixtures. The data clearly demonstrate that the cmc increasing effect is much smaller in the case of 16-6-16 than the other geminis. This effect can be understood in light of the variation in the length of the spacer. The presence of a longer spacer in a gemini molecule produces greater hydrophobic interaction due to its folding towards micellar core, hence, aggregation in highly unfavorable situation (at high DMSO volume percent). Thus, the role of the spacer chain length in the overall aggregation in DMSO–water mixture is quite distinct. However, more work is needed with other spacer chains to substantiate the point.

The thermodynamic parameters of micellization were obtained from the temperature dependence of the cmc

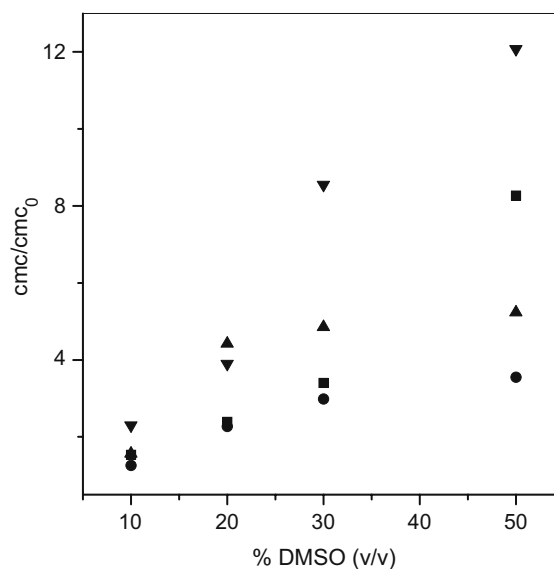


Fig. 2 Variation of cmc ratio (cmc/cmc₀) of different surfactants as a function of volume percent of DMSO in DMSO–water mixed solvent: CTAB (■), 16-4-16 (▼), 16-5-16 (▲), and 16-6-16 (●)

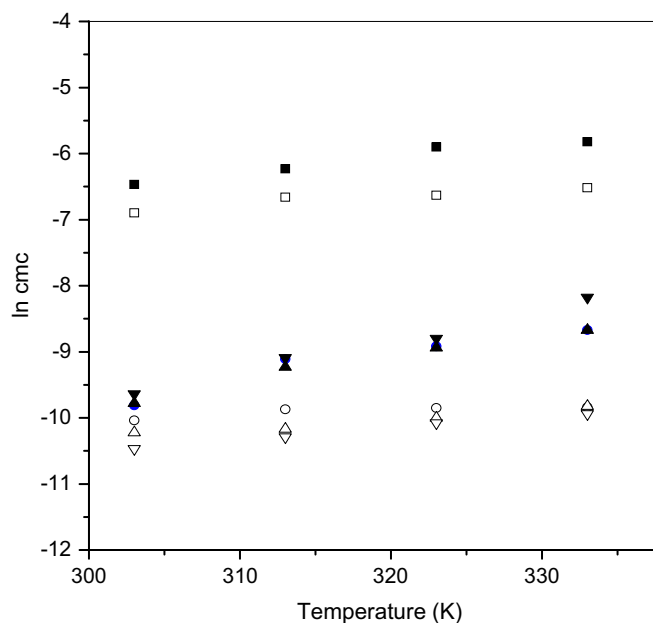


Fig. 3 Variation of $\ln \text{cmc}$ with temperature: CTAB ($\square$, $\blacksquare$), 16-4-16 (∇ , $\blacktriangledown$), 16-5-16 (Δ , $\blacktriangle$), and 16-6-16 ($\circ$, $\bullet$) (open symbols are for water while closed symbols are for 10% DMSO–water mixtures)

values (Fig. 3). For ionic monomeric and dimeric surfactants, the relationship between the free energy of micellization per alkyl chain, ΔG_m^o , the cmc in mole of

alkyl chain per cubic decimeter, and the α values are written, respectively [29], as:

$$\Delta G_m^o (\text{monomer}) = RT(2 - \alpha) \ln \text{cmc} \quad (3)$$

and

$$\Delta G_m^o (\text{dimer}) = RT(1.5 - \alpha) \ln \text{cmc} \quad (4)$$

In Eqs. 3 and 4, the cmc is expressed in mole per cubic decimeter. In the reported literature [26], the cmc is expressed in mole fraction unit. For surfactants with low cmc values (<10 mM), the values of ΔG_m^o would only differ by the constant term $\approx \ln 55.5$ when using one or the other unit [6]. The enthalpies of micellization were obtained by employing the equation

$$\Delta H_m^o = -RT^2 (d \ln \text{cmc} / dT)_P \quad (5)$$

The entropy values of micelle formation were evaluated from the calculated ΔH_m^o and ΔG_m^o values as follows:

$$\Delta S_m^o = (\Delta H_m^o - \Delta G_m^o) / T \quad (6)$$

The equation employed to calculate the ΔG_m^o applies normally when the mean aggregation number is large but

Table 2 Thermodynamic parameters of micellization of different surfactants in water and DMSO–water mixture

Percent of DMSO (v/v)	Temperature (°C)	16-6-16			16-5-16		
		ΔG_m^o (kJ mol ⁻¹)	ΔH_m^o (kJ mol ⁻¹)	ΔS_m^o (J K ⁻¹ mol ⁻¹)	ΔG_m^o (kJ mol ⁻¹)	ΔH_m^o (kJ mol ⁻¹)	ΔS_m^o (J K ⁻¹ mol ⁻¹)
0	30	-26.03	12.97	128.71	-21.36	12.21	110.79
	40	-21.56	13.84	113.10	-25.05	13.03	121.66
	50	-23.53	14.74	118.48	-25.41	13.87	121.61
	60	-18.79	15.67	103.48	-21.74	14.74	109.55
10	30	-20.99	27.47	159.95	-28.07	29.75	190.83
	40	-25.59	29.31	175.39	-26.41	31.75	185.81
	50	-23.46	31.21	169.26	-27.60	33.81	190.11
	60	-26.39	33.17	178.86	-26.15	35.94	186.46
		16-4-16			CTAB		
0	30	-22.67	14.50	122.67	-29.71	11.90	137.33
	40	-26.50	15.47	134.09	-28.41	12.70	131.34
	50	-27.06	16.47	134.77	-28.83	13.52	131.11
	60	-26.68	17.51	132.70	-27.24	14.38	124.98
10	30	-21.12	35.86	188.04	-28.18	20.60	160.99
	40	-25.30	38.26	203.06	-26.90	21.98	156.17
	50	-26.91	40.75	209.50	-28.82	23.41	161.70
	60	-24.66	43.31	204.11	-23.67	24.88	145.80

may not be accurate for higher concentrations of co-solvent [30, 31]. As indicated by the negative values of the ΔG_m^0 , it is evident that the micellization process is spontaneous in water as well as in 10% DMSO (Table 2). In the absence of DMSO, ΔG_m^0 is nearly equal for CTAB and geminis. The low cmc values of 16-s-16 arise mainly because more than one chain is transferred simultaneously from background solvent to the micelle [29, 32]. The ΔH_m^0 values in water or water–DMSO mixtures are positive and weakly dependent on temperature within the experimental error. The enthalpy values calculated from Eq. 5 may differ from the directly measured calorimetric values [33]; however, we were unable to locate any data for the systems for comparison. The value of ΔS_m^0 in water becomes more in the presence of DMSO. ΔS_m^0 changes are larger in comparison to water indicating that the DMSO enhances the energy of the 3D water structure due to the formation of DMSO-2H₂O. Because the thermodynamic parameters are dependent on

both cmc and α , their values do not show any trend, which is expected as α value has no clear-cut trend with the spacer chain length as well as with temperature. The α values were not following any trend in the earlier study also [24]. Therefore, much discussion on these parameters would not be appropriate.

In conclusion, we can say that the micellization of gemini surfactants occurs in many adverse situations, such as in the presence of nonaqueous solvents which are known to arrest the phenomenon of micellization. Therefore, these systems may be utilized for the organic reactions which are occurring in polar solvents or in the presence of binary solvents whose one component is water.

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