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ORIGINAL ARTICLE

Micellization Behavior of Cationic Gemini Surfactants in Aqueous-Ethylene Glycol Solution

Deepti Tikariha · Birendra Kumar · Namrata Singh · Kallol K. Ghosh · Pierluigi Quagliotto

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Abstract The micellization behavior of gemini surfactants i.e. alkanediyl-α,ω-bis(cetyldimethylammonium bromide) (C_{16}-s-C_{16},$2Br^-$ where $s = 3, 4, 10$) in 10% (v/v) ethylene glycol solution was investigated by surface tension and conductometric measurements at 300 K. The critical micelle concentration, degree of micellar ionization, surface excess concentration, minimum surface area per molecule of surfactant, surface pressure at the CMC and Gibbs energy of adsorption of the dimeric surfactants have also been determined in the presence of different salts (NaCl, NaBr and NaI). The critical micelle concentration and degree of micellar ionization values decrease significantly in the presence of sodium halides and follows the sequence NaCl < NaBr < NaI. The free energy, enthalpy and entropy of micellization of dimeric surfactants in 10% (v/v) ethylene glycol solution were determined using the temperature dependence of the critical micelle concentration. The standard free energy of micellization was found to be negative in all the cases.

Keywords Gemini surfactant · Micellization · Effect of salt · CMC · Thermodynamics of micellization

Introduction

Dimeric or gemini surfactants consist of two hydrophobic and two hydrophilic groups connected by a flexible or rigid spacer chain in a molecule, revealing unique physicochemical properties such as low critical micelle concentration (CMC), high efficiency in lowering the surface tension, and excellent wetting ability superior to the conventional monomeric surfactants [1–9].

It is well known that inorganic salt affects the adsorption of ionic surfactants at air/water interfaces and the aggregation of them in aqueous solutions since the salt screens the charge of ionic head groups and results in the reduction of the electrostatic repulsion between the head groups within the adsorption film and the micelle [10–13].

The effect of inorganic electrolytes on the micellar rates of various substrates and the micellar properties have been known for a long-time, the subject of extensive investigation [14–18]. The study gives an idea about the adsorption behavior of gemini surfactants as a hydrophobic surface in the presence of electrolytes. The study may be useful in some applications such as wetting, colloid stability and dispersion of polymers, etc., where surfactant adsorption is an important parameter. Moreover, the surfactant consumption can also be reduced by adding small amounts of electrolytes to the surfactant solvations. The aggregation and surface properties of surfactants in solution depends on the types and amounts of additive used. The presence of a third component in the surfactant water system may often have a dramatic effect on the physical characteristics of the solution. Such a substance can act through two different mechanisms [19]. First, micellar properties are affected by surfactant-solvent interactions. Compounds in this category include electrolytes, urea and co-solvents. It is well known that additives can influence the micellization of surfactants.

D. Tikariha · B. Kumar · N. Singh · K. K. Ghosh (✉)
School of Studies in Chemistry, Pt. Ravishankar Shukla
University, Raipur (C.G.) 492010, India
e-mail: kallolkghosh@yahoo.com

P. Quagliotto
Dipartimento di Chimica Generale ed Organica Applicata e
Centro di Eccellenza NIS, Università degli Studi di Torino,
Corso Massimo D'Azeglio 48, 10125 Torino, Italy

Secondly, micellar properties are affected by incorporation of the additives into the micelles. Some gemini surfactants are not soluble in water. Therefore, 10% (v/v) ethylene glycol medium was chosen for the CMC measurements. Ethylene glycol (EG) is one of the most commonly used solvents for micellization, as it possesses a high cohesive energy, a fairly high dielectric constant and has many characteristics similar to water. EG has the ability to form hydrogen bonded networks similar to water, although differing in the details of the structure [20–24].

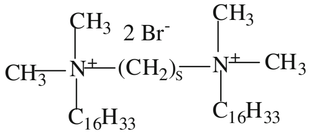
You et al. [10] have discussed the strong effect of NaBr on self-assembly of quaternary ammonium gemini surfactants at air/water interface and in aqueous solution by surface tension and fluorescence technique. Lu et al. [25] have studied the salt effect on microstructures in cationic gemini surfactant solutions as studied by dynamic light scattering. Micellization behavior of sodium dodecyl sulfate in different electrolyte media was investigated by Umlong [26].

In the present investigation, the micellar properties of gemini surfactants (Scheme 1) in the presence of sodium salts (NaCl, NaBr and NaI) were studied by surface tension and conductivity measurements. These measurements were performed in 10% (v/v) ethylene glycol solution. The thermodynamic parameters of micellization (free energy ΔG°_{m}, enthalpy ΔH°_{m} and entropy ΔS°_{m}) have also been studied.

Experimental

Materials

All the gemini surfactants were synthesized by refluxing the corresponding α,ω-dibromoalkane ($Br(CH_2)_sBr$, $s = 3, 4, 10$) with *N*-hexadecyl-*N*,*N*-dimethyl amine in dry ethanol for 48 h and were recrystallized from hexane/ethyl acetate mixtures [27, 28]. The solvent ethylene glycol (EG) was obtained from Merck Fine Chemicals (Mumbai, India). All the solutions were prepared in 10% (v/v) ethylene glycol aqueous binary solution. All sodium halides (NaCl, NaBr, and NaI) were obtained from Merck and S.D. Fine Chemicals and used as received. All chemicals were of high purity (99.0%) and were used without further purification.



$$CH_3-\overset{CH_3}{\underset{C_{16}H_{33}}{N^{+}}}-(CH_2)_s-\overset{CH_3}{\underset{C_{16}H_{33}}{N^{+}}}-CH_3 \quad 2\,Br^{-}$$

(s = 3, 4, 10)

Scheme 1 Alkanediyl-α,ω-bis(cetyldimethylammonium bromide) (16-s-16,2Br- where $s = 3, 4, 10$)

Methods

Electrical Conductivity Measurements

The critical micelle concentration and the degree of micellar ionization of the gemini surfactants were determined, conductance measurements using a Systronics direct reading digital conductivity meter (Type 304 and 306) were carried out. The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. A concentrated surfactant solution [$\sim$10–20 times the CMC] was progressively added to 20 mL of water-organic solvent medium in a thermostated container (having a temperature accuracy of ±0.01°C) using a micropipette. After ensuring thorough mixing and temperature equilibration at 300–320 K, the specific conductance (κ) was measured.

Surface Tension Measurement

The surface tensions of aqueous solutions of surfactants at various concentrations were determined with a surface tensiometer (Jencon, India) using a platinum ring by the ring detachment technique. The tensiometer was calibrated against distilled water. The platinum ring was thoroughly cleaned and dried before each measurement. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension. It was then pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension. Each experiment was repeated several times until good reproducibility was achieved. The results were accurate within $\pm 0.1\ mNm^{-1}$.

Results and Discussion

Effect of Salts on Critical Micelle Concentration (CMC)

The CMC is generally used to characterize the ability of micelle formation [29]. Representative plots of κ versus concentration for gemini surfactants in presence of salts are shown in Figs.1 and 2. Figure 1 shows the conductivity plot for the gemini surfactant at 300 K in mixed solvent (10% aqueous ethylene glycol) and in the presence of 1 mM NaCl. The CMC values of cationic gemini surfactants in absence and presence of salts are given in Table 1.

The classical method for obtaining the CMC requires the determination of two lines in the pre- and post-micellar

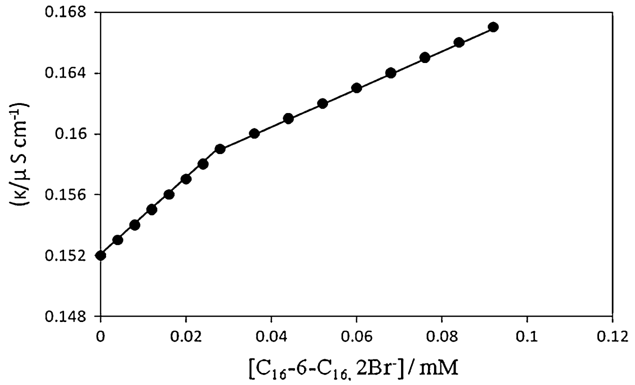


Fig. 1 Specific conductivity (κ) versus concentration plot for C_{16}-6-C_{16}, $2Br^-$ in 10% (v/v) EG in 1 mM NaCl at 300 K

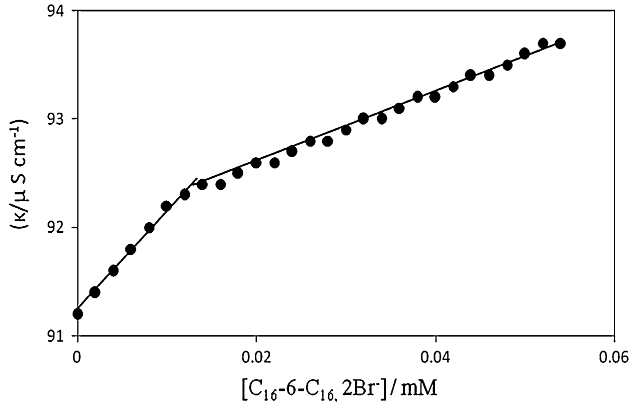


Fig. 2 Specific conductivity (κ) versus concentration plot for C_{16}-6-C_{16}, $2Br^-$ in 10% (v/v) EG in 1 mM NaI at 300 K

regions, respectively [30, 31]. Since the determination of the CMC for a gemini surfactant is sometimes difficult due to smoothness of the κ versus concentration plot, in the last years the use of a non-linear fitting method was proposed as a general method [32] and successfully applied to gemini surfactants [33, 34]. In the case of gemini surfactants, the aggregation is promoted by the two alkyl chains to be transferred to the micellar phase but also made difficult by the steric requirements connected to put the two chains in the restricted micellar core environment [35, 36]. Thus a method that avoids the researcher's personal taste about the determination of the two lines should be preferred. This method relies on the equation:

$$F(x) = F(0) + A_1 x + \Delta x (A_2 - A_1) \ln\left(\frac{1 + e^{(x - x_0)/\Delta x}}{1 + e^{-x_0/\Delta x}}\right) \tag{1}$$

where $F(0)$ is the initial conductivity of water, A_1 and A_2 are the limiting slopes for low and high concentration respectively, x_0 is the central point of the transition, i.e. the CMC and Δx is the width of the transition. The α value, representing the degree of micellar ionization can be deduced from the ratio A_2/A_1.

This equation can carefully represent the conductivity versus C data set, since it is the integral of the Boltzmann sigmoid. The data were fitted to this non linear equation and the resulting CMC of surfactants in pure water and with added sodium halides are given in Table 1, along with the proper degree α of micellar ionization.

The CMC values obtained from the conductance are given in Table 1 and are found to be in agreement with these determined from the surface tension. As indicated in this Table, the CMC value decreases with the addition of salts in the order NaCl > NaBr > NaI. The surface tension of surfactants was measured for a range of concentrations above and below the critical micelle concentration. As shown in the Fig. 3, a linear decrease in surface tension was observed with an increase in surfactant concentrations for all of the surfactants up to the CMC, beyond which no considerable change was noticed. This is a common behavior shown by surfactants in solution and is used to determine their CMC.

The absence of a minimum near the CMC is normally taken as a confirmation of substantial surfactant purity [37]. The problem of assessing the surfactant purity and how the impurities could affect the surface tension versus Log C plots was thoroughly addressed in the last decades [38–40]. Exceptionally pure surfactant solutions gave insight on

Table 1 CMC (mM), α, ΔG^{o}_{m}, and ΔG^{o}_{ads} values of cationic surfactants in absence and presence of sodium salts at 300 K by conductivity and the surface tensiometer method

Salts	C_{16}-3-C_{16}, $2Br^-$					C_{16}-4-C_{16}, $2Br^-$					C_{16}-10-C_{16}, $2Br^-$				
	CMC (mM)		α	ΔG^{o}_{m} kJ/mol	ΔG^{o}_{ads} kJ/mol	CMC (mM)		α	ΔG^{o}_{m} kJ/mol	ΔG^{o}_{ads} kJ/mol	CMC (mM)		α	ΔG^{o}_{m} kJ/mol	ΔG^{o}_{ads} kJ/mol
	Cond.	ST.				Cond.	ST.				Cond.	ST.			
EG	0.045	0.047	0.52	−68.6	−101.2	0.048	0.044	0.56	−65.5	−93.5	0.055	0.052	0.54	−66.2	−88.9
NaCl	0.026	0.022	0.50	−72.7	−96.0	0.024	0.024	0.50	−73.1	−91.1	0.031	0.033	0.51	−71.1	−85.8
NaBr	0.016	0.016	0.47	−77.4	−95.2	0.018	0.020	0.49	−75.3	−88.4	0.023	0.018	0.48	−74.8	−87.4
NaI	0.010	0.012	0.44	−82.2	−96.3	0.010	0.008	0.47	−79.8	−91.4	0.012	0.014	0.46	−79.6	−93.7

Cond conductivity, *ST* surface tensiometer

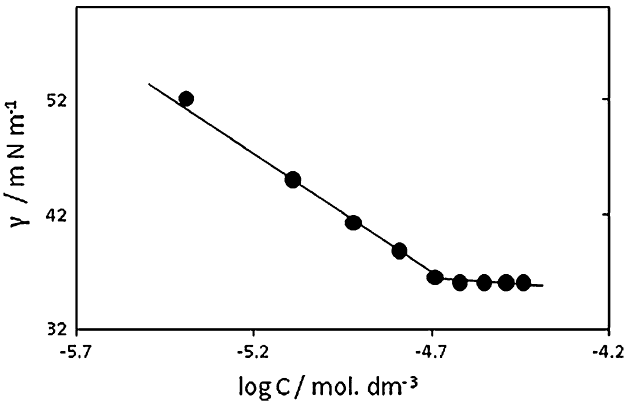


Fig. 3 Plot of surface tension versus log conc. of C_{16}-10-C_{16}, $2Br^-$ in the presence of 1 mM NaBr

particular behavior of surfactants that in general are hardly seen [40]. This kind of purity of surfactant solutions is normally not attained, but at least the absence of a minimum in the γ versus Log C plot is highly advisable and required to be sure to rely on a reasonable purity of the surfactant solutions and to give the opportunity to perform careful studies and to obtain repeatable results. Even when the minimum is not present, very small quantities of impurities can affect the portion of the plot in which the surface tension is steeply decreasing, giving a too linear decrease. If the decrease was really linear, the slope and thus the surface excess concentration (Γ_{max}) would be constant with the change of concentration, in a wide range. On the basis of the Gibbs adsorption theory this would be impossible, since the minimum area would be constant over that concentration range and the surfactants would be not be adsorbed anymore. A question would be raised at this point: if the surfactant adsorption does not occur in this concentration range, why the surface tension is decreasing? This is normally know as the Gibbs paradox. Even if modifications of the original Gibbs interpretation where proposed in those last years [41–44], it was already shown that a careful purification can evidence that the γ versus Log C plot is not completely linear but shows a small but perceptible curvature towards the Log C axis [40, 45]. This accounts for the Γ_{max} and the minimum surface area per surfactant molecule A_{min} always increasing, in agreement with the Gibbs theory. Very recently, we were able to demonstrate that even almost cheap and easily applied methods already proposed by Rosen [39] for the surfactant purification could be enough to obtain a sufficient surfactant solution purity that can enable us to detect that the surface tension decrease is not really linear but that it shows a small curvature towards the Log C axis [37]. In the present case, the experimental constraint would make the framework almost problematic, since the organic solvent could also contain small quantities of highly hydrophobic impurities that would affect the final result. Luckily, the sufficient purity of the surfactants and a substantial pure organic solvent and water made the surface tension measurements possible and reliable. In general, the surface tension decrease is linear enough to permit to accurately extrapolate the CMC, but a careful inspection (Fig. 3) reveals that a small curvature is present. This enabled us to have a reasonable confidence on the reliability and accuracy of the surface tension measurements.

The observed decrease in the CMC value, connected with the salt addition, is primarily due to a reduction in the electrostatic repulsion between head groups in the presence of the excess counter ions from the electrolyte [46]. The repulsion between head groups of surfactants is one of the main factors opposing micellization [47].

The effect of electrolytes is interestingly quite different. This provided the easiest way for practical applications to control the properties of the micellar solutions by the addition of the electrolytes. Micelles are formed by the delicate balance of opposing forces: the attractive tail–tail hydrophobic interaction provided for the aggregation of surfactant molecules, while the electrostatic repulsion between the polar head groups limits the size that a micelle can attain [48].

The decrease in the CMC values caused by the salt addition may be interpreted as follows. The cationic surfactant forms ionic monolayer at the air/solution interface, the addition of electrolyte anions leads to the reduction of the thickness and potential of the electric double layer at the interface because of the electrostatic interaction between opposite charges. Consequently, it induces the screening of the electrostatic repulsion among the polar head groups and leads to remarkably lower CMC. Once the sodium halides have been added, the electrostatic repulsion can be screened immediately due to the electrostatic interaction between the opposite charges, and this effect is more remarkable for the surfactants with shorter spacer length which would exhibit the stronger salt effect.

Effect of Sodium Salts on Interfacial Properties

From the surface tension measurements, several parameters referring to interface properties were determined: (1) CMC, taken as the concentration at the point of intersection of the two linear portions of the γ versus log C plots, (2) maximum surface excess concentration (Γ_{max} [mol cm^{-2}]) calculated using the Gibbs adsorption Equation (1), [12] (3) area per molecule at the interface (A_{min} [Å^2]) calculated using Equation (2), (4) efficiency in surface tension reduction, measured by C_{20} (or pC_{20}), which is the molar surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m, (5) effectiveness of the surface tension reduction, measured by the surface tension

Table 2 Surface pressure at the CMC (π_{cmc}), the maximum surface excess (Γ_{max}), and the minimum surface area per molecule (A_{min}), values of cationic gemini surfactants in presence and absence of salt at 300 K

Salts	Conc. of salt (mM)	C_{16}-3-C_{16}, $2Br^-$			C_{16}-4-C_{16}, $2Br^-$			C_{16}-10-C_{16}, $2Br^-$		
		π_{cmc} m Nm^{-1}	Γ_{max} 10^6 mol m^{-2}	A_{min} 10^{20} m^2mol^{-1}	π_{cmc} m Nm^{-1}	Γ_{max} 10^6 mol m^{-2}	A_{min} 10^{20} m^2 mol^{-1}	π_{cmc} m Nm^{-1}	Γ_{max} 10^6 mol m^{-2}	A_{min} 10^{20} m^2 mol^{-1}
EG	0.0	30	0.92	180	28	1.00	166	25	1.10	150
NaCl	1.0	24	1.03	161	20	1.11	149	18.8	1.28	129
NaBr	1.0	22	1.24	134	18	1.38	120	19	1.51	110
NaI	1.0	20	1.42	117	19	1.64	101	20	1.42	117

at the CMC (γ_{cmc}) and (6) the CMC/C_{20} ratio, which is the measure of the tendency to form micelles relative to the tendency to adsorb at the air/water interface.

The values of surface excess, for gemini surfactant at air/solution interface near its CMC in the presence of the electrolytes were calculated from the respective surface tension data using the Gibbs adsorption equation [49–52]

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left[\frac{d\gamma}{d\log C}\right]_{T,P} \tag{2}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, C is the surfactant concentration, and $d\gamma/d(\log C)$ is the slope of the γ versus Log C plot taken at the CMC (Fig. 3). The number of species whose concentration at the interface varies with the surfactant bulk phase concentration (n) was taken as 3. Surface excess is a measure of effectiveness of the surfactant adsorption, the increase of which has substantial effect in applications e.g., floatation, improved oil recovery, in situ and ex situ soil remediation, detergency, setting, surfactant based separation process, since coherently packed interfacial films have different properties from that of non-coherent loosely packed films [53].

Γ_{max} values were used to calculate the minimum area of the per surfactant molecule (A_{min}) at the air/solvent interface using the relationship

$$A_{min} = 1/N\,\Gamma_{max} \tag{3}$$

where N is Avogadro's number. The trend in the variation of A_{min} with electrolyte concentration is just opposite to that of Γ_{max}.

The values of the surface pressure at the CMC (π_{cmc}) were obtained from Eq. 4, where γ_o is the surface tension of the solvent and γ_{cmc} is the surface tension at the CMC.

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \tag{4}$$

where γ_o and γ_{cmc} refers to the surface tension of solvent and the surfactant solution at the CMC, respectively. This parameter indicates the maximum reduction of surface tension caused by the dissolution of surfactant molecules; hence, it becomes a measure of effectiveness of the surface tension reduction [54], and the greater the π_{cmc} values, the higher the effectiveness of the surfactants. π_{cmc} values are listed in Table 2. It can be seen that the π_{cmc} values increase in order [C_{16}-3-C_{16}. $2Br^-$] > [C_{16}-4-C_{16}. $2Br^-$] > [C_{16}-10-C_{16}. $2Br^-$], which indicates that [C_{16}-3-C_{16}. $2Br^-$], having the highest π_{cmc}, is superior to the two surfactants in the effectiveness of surface tension reduction (π_{cmc}).

Thermodynamics of Micellization

The study of CMC versus temperature is often undertaken to obtain information on hydrophobic and headgroup interactions. This involves driving various thermodynamic parameters of micelle formation. The Gibbs energy of micelle formation is calculated from the pseudo-phase model for ionic surfactants according to the equation (5)

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

where R is the gas constant, T is temperature, and X_{cmc} is the CMC value on the mole fraction scale, α is the degree of micellar ionization. The above expression, proposed by Zana [19] accounts for the presence of two alkyl chains (and two polar head groups) in the surfactant. The standard free energy of adsorption (ΔG^{o}_{ads}) at the air/water interface was calculated by using the expression.

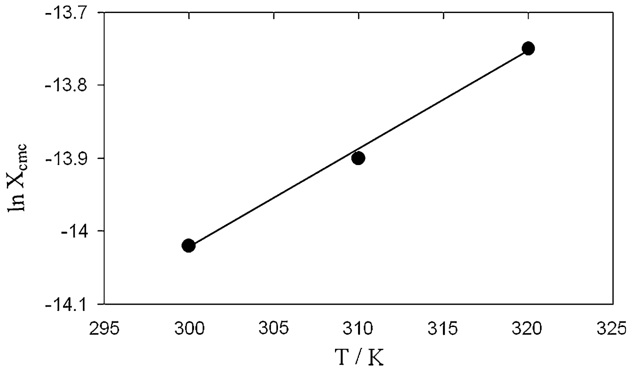


Fig. 4 ln X_{cmc} versus temperature plot of C_{16}-3-C_{16}, $2Br^-$ in 10% (v/v) Ethylene–Glycol solution

Table 3 Thermodynamic parameters of micellization of gemini surfactants in 10% (v/v) EG solution

Surfactants	Temp. (K)	CMC (mM)	α	ΔG^{o}_{m} kJ/mol	ΔH^{o}_{m} kJ/mol	ΔS^{o}_{m} JK^{-1} mol^{-1}
C_{16}-3-C_{16}, $2Br^{-}$	300	0.045	0.52	−68.6	−19.8	162
	310	0.051	0.56	−67.3	−20.3	152
	320	0.059	0.59	−66.3	−20.9	142
C_{16}-4-C_{16}, $2Br^{-}$	300	0.048	0.56	−65.5	−18.9	155
	310	0.062	0.57	−65.7	−20.1	147
	320	0.063	0.59	−66.3	−20.9	141
C_{16}-10-C_{16}, $2Br^{-}$	300	0.055	0.54	−66.2	−15.1	170
	310	0.066	0.59	−61.9	−15.3	150
	320	0.068	0.64	−62.3	−15.4	146

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{m} - \pi_{cmc}/\Gamma_{max} \tag{6}$$

From Table 1 it can be observed that the ΔG^{o}_{m} and ΔG^{o}_{ads} values were all found to be negative in both the presence and absence of salts for gemini surfactants, indicating a spontaneous micellization process due to hydrophobicity of amphiphiles, which leads them toward air/water interface. The ΔG^{o}_{ad} is greater than that of ΔG^{o}_{m} for all the systems. Their difference is a measure of the spontaneity difference of the two processes; the adsorption process is fairly stronger than the bulk process of micellization. Thus, the head group architecture of the surfactants play a decisive role in the surface chemical behaviors of the surfactants.

The enthalpy of micelle formation, ΔH^{o}_{m} can be obtained from the temperature variation of CMC by applying the Gibbs–Helmholtz equation (7 & 8):

$$\frac{\partial(\Delta G^{\circ}_{m}/T)}{\partial(1/T)} = \Delta H^{\circ}_{m} \tag{7}$$

$$\Delta H^{\circ}_{m} = -2(1.5-\alpha)RT^{2}\left[\frac{\partial \ln X_{cmc}}{\partial T}\right] \tag{8}$$

Therefore, if the dependence of the CMC values on temperature is known, a plot of ln X_{cmc} versus temperature can be constructed [Fig. 4]. The slope can be found at each temperature.

Further, the standard entropy of micelle formation, ΔS^{o}_{m}, is obtained by using following relation;

$$\Delta S^{\circ}_{m} = \Delta H^{\circ}_{m} - \Delta G^{\circ}_{m}/T \tag{9}$$

All the thermodynamic parameters of micellization of gemini surfactants in 10% (v/v) ethylene glycol mixtures are given in Table 3. The values of ΔG^{o}_{m} becomes less negative with increasing temperature, that means, at higher temperature the water structure due to hydrogen bonding, is more released, making the hydrophobic effect less important and consequently the surfactants show a higher CMC. The standard enthalpy of micellization is negative. The negative value of ΔH^{o}_{m} indicates that the micellization process is exothermic. The entropy change is positive in all the cases. However, it decreases with increasing temperature. Ethylene glycol is acting as a co solvent and as a structure-breaking solute. In micellar solutions, structure-breaking solutes lower the hydrophobic effect, which is considered the driving force for micellization. The presence of structure breakers in the aqueous phase may disrupt the organization of the water produced by the dissolved hydrophobic group, thereby decreasing entropy increase on micellization. The magnitude and sign of the ΔH^{o}_{m} and ΔS^{o}_{m} values are in accord with the destruction of hydrophobic hydration in the process of micellization [55].

Conclusions

The micellar and surface properties were determined by conductivity and surface tension measurements. Addition of additives at very low concentration resulted into decrease in the CMC of the surfactants. The CMC and α value of gemini surfactants increased with increasing temperature. The CMC, π_{cmc} and Γ_{max} values decreased significantly in the presence of sodium halides and the values obtained in presence of NaCl were thus higher than that for NaBr and NaI respectively. The thermodynamic parameters of micellization (ΔG^{o}_{m}, ΔH^{o}_{m} and ΔS^{o}_{m}) were evaluated in 10% (v/v) EG solution. The ΔG^{o}_{ad} is greater than that of ΔG^{o}_{m} for all the systems. The overall micellization process was exothermic and entropy of micellization was positive.

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Author Biographies

Deepti Tikariha has completed her M. Phil. degree and is presently working as a senior research scholar under the supervision of Prof. Kallol K. Ghosh at the School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India. She is grateful to Pt. Ravishankar Shukla University, Raipur, India for giving her a university fellowship. Her research interest is to study the physicochemical properties of gemini and monomeric surfactants.

Birendra Kumar has completed his M. Phil. degree and is presently working as a Research Scholar (JRF) under the supervision of Prof. Kallol K. Ghosh at the School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India. He is grateful to the University Grant Commission, New Delhi for giving him the Rajiv Gandhi National Fellowship F. 14-2 (SC)/2009 (SA—III). His research interest is to study the physicochemical properties of gemini and monomeric surfactants and micellar catalysis.

Namrata Singh has completed her M.Sc. (Chemistry) and is presently working as a Research Scholar under the supervision of Prof. Kallol K. Ghosh at School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India. She is grateful to Pt. Ravishankar Shukla University, Raipur, India for giving her a university fellowship. Her research interest is to study the physicochemical properties of novel and functionalized surfactants and micellar catalysis.

Kallol K. Ghosh is a professor of physical chemistry at the School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India. He had been INSA/JSPS fellow at Seikei University, Tokyo, Japan and James Chair visiting fellow at St. Francis Xavier University, Antigonish, Canada. His research is focused on micellar catalysis, reaction mechanisms, hydroxamic acids, detoxifications, and enzyme kinetics.

Pierluigi Quagliotto is a faculty researcher in organic chemistry at Dipartimento di Chimica Generale e Chimica Organica, Università degli Studi di Torino, and NIS—Centre of Excellence "Nanostructured Surfaces and Interfaces", Università degli Studi di Torino, Torino, Italy. His research activity is focused on the synthesis, characterization and application of novel surfactants, and on the synthesis and photochemical characterization of functional dyes for application in dye-sensitized solar cells.