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Micellization behavior of $[C_{16-4-C_{16}}]_2Br^-$ gemini surfactant in binary aqueous-solvent mixtures

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The micellization behavior of a bis cationic gemini surfactant, $C_{16}H_{33}N^+(CH_3)_2-(CH_2)_4-N^+(CH_3)_2C_{16}H_{33}$, $2Br^-$, has been studied in binary aqueous mixtures of dimethyl sulfoxide, methanol, 1, 4-dioxane, dimethyl formamide and ethylene glycol by conductivity measurements at 300-320 K. The critical micelle concentration, degree of micellar ionization and thermodynamic parameters, i.e., Gibbs free energy, enthalpy, and entropy of micellization of the gemini surfactant have also been determined. The cmc increases whereas Gibbs free energy decreases with increasing volume percentage of organic solvents in the organic solvent-water binary mixture. The negative value of enthalpy of micellization indicates that the micellization process is exothermic.

Keywords: Thermodynamics, Surfactants, Gemini surfactants, Micellization, Solvent effect

The gemini surfactants are special type of surfactants¹⁻³, comprising two hydrophobic chains and two polar head groups covalently connected through a spacer group. The most widely investigated gemini surfactants are made up of hydrocarbon side chains and hydrocarbon spacer^{4,5}. These surfactants have lower critical micelle concentration (cmc), higher efficiency in reducing the oil/water interfacial tension, unusual aggregation morphologies and are better wetting, solubilizing and foaming agents as compared to conventional surfactants⁶⁻¹⁰. In addition, some dimeric surfactants have interesting rheological properties at relatively low concentration¹¹⁻¹³.

The micellization of surfactants can be controlled by the solvent. The micellization in non-aqueous polar solvents is described by "solvophobic

interaction" by analogy with hydrophobic interactions in water¹⁴. However, the ability of water to form unique hydrogen-bonded networks is not a necessary condition for the aggregation process. The micelles formed in non-aqueous solvents are similar in many aspects to the micelles that are formed in water, although micelle formation is not as favored in such non-aqueous solvents for a given surfactant^{15,16}.

Recently, Rodriguez *et al.*¹⁷ have studied the effects of ethylene glycol on the micellization process of gemini surfactants (12-s-12, $2Br^-$, s = 3, 4, 5) and the effects of different organic solvent-water mixtures on the micellization of 12-3-12, $2Br^-$ and monomeric surfactants^{18,19}. Similarly the micellar properties and thermodynamic parameters of the gemini surfactants (16-s-16, $2Br^-$ s = 4, 5, 6) in water and various polar non-aqueous solvents have been studied by Kabir-uddin *et al.*²⁰. They found that the gemini surfactants with a hydrophilic flexible spacer formed a more closely packed micelle structure than the one with a hydrophobic rigid spacer.

In the present study the micellar behavior of $C_{16-4-C_{16}}$, $2Br^-$ (**I**) in binary aqueous mixtures of ethylene glycol, 1,4 dioxane, dimethyl sulphoxide, methanol and dimethyl formamide (20 and 40% v/v) has been studied by conductivity measurements. Thermodynamic parameters of micellization (ΔG_m° , ΔH_m° , ΔS_m°) in the presence of solvents (20% v/v) have also been determined.

Experimental

The gemini surfactant was synthesized by refluxing the corresponding α , ω -dibromoalkane ($Br(CH_2)_sBr$, s = 4), hexadecyl-N, N-dimethyl amine in dry ethanol for 48 hours and recrystallized from hexane/ethyl acetate mixtures^{21,22}. The solvents dimethyl sulfoxide (DMSO), 1,4 dioxane and dimethyl formamide (DMF) were obtained from Qualigens Fine Chemicals (Mumbai, India) while other solvents, like methanol and ethylene glycol (EG) were obtained from Merck (Mumbai, India). All the solutions were prepared in triply distilled water.

Conductometric measurements were carried out using a Systronics direct reading conductivity meter (Type 304 and 306). The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. A concentrated surfactant

solution (~10-20 times the critical micelle concentration (cmc)) was progressively added to 25 mL of water-organic solvent medium in a thermostat container (having a temperature accuracy of $\pm 0.01^\circ\text{C}$) using a micropipette. After ensuring thorough mixing and temperature equilibration of 300-320 K, the specific conductance (κ) was measured.

Results and discussion

Critical micelle concentration (cmc) and micellar ionization degree (α) were obtained from conductivity measurements. The cmc values have been determined from the break points in the specific conductivity (κ) versus surfactant concentration plots. The degree of micellar ionization (α) was taken as the ratio of the slopes of the lines above and below the cmc in the plots of κ versus C (Figs 1-3). Figure 1 indicates that the cmc value increases with increasing concentration of EG. Figure 2 depicts the effect of temperature on the cmc values for $\text{C}_{16}\text{-4-C}_{16}$, 2Br^- in 20% (v/v) MeOH, while Fig. 3 shows the temperature dependence of cmc of gemini surfactant in 20% (v/v) 1,4 dioxane. Both, Figs 2 and 3, indicate that there is an increase in cmc value with rise in temperature.

The critical micelle concentration and α values for the $\text{C}_{16}\text{-4-C}_{16}$, 2Br^- surfactant in aqueous organic solvents of two compositions (20 and 40% v/v) are summarized in Table 1. Data presented in this table show that the cmc values increase with increasing volume percent of the binary aqueous solution. The cmc values are also found to increase with increasing temperature (Table 1). At higher temperature, the

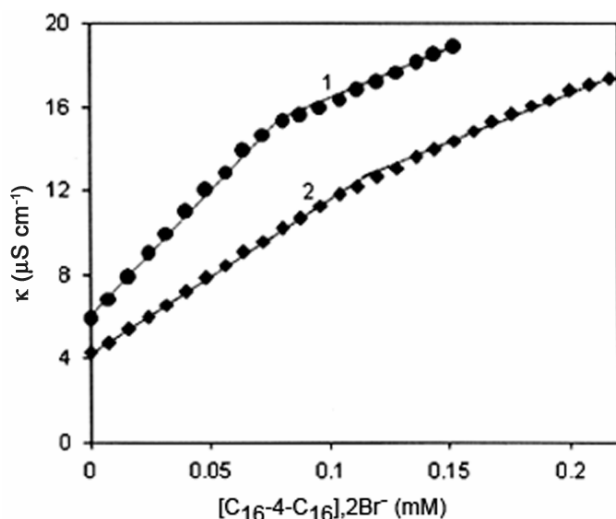


Fig. 1 — Specific conductivity versus concentration plots for $[\text{C}_{16}\text{-4-C}_{16}]$, 2Br^- in different % (v/v) of EG at 300 K. [1, 20%; 2, 40% v/v].

dielectric constant of the solution decreases resulting in greater repulsion between the ionic head groups of the surfactant molecules, which leads to increased cmc values. The cmc value is higher in 1, 4-dioxane- H_2O binary solvents than in other binary solvent systems. This is attributed to the larger hydrophobic surface area coupled with the fluxional nature of the dioxane molecule (since dioxane molecule can exist in either boat or chair form)²³. Ethylene glycol is a structure breaker. It breaks up the structure of the water molecules around the hydrophobic chains, thereby decreasing the hydrophobic effect and increasing the cmc values. As temperature increases, the increase in thermal motion of the water molecules

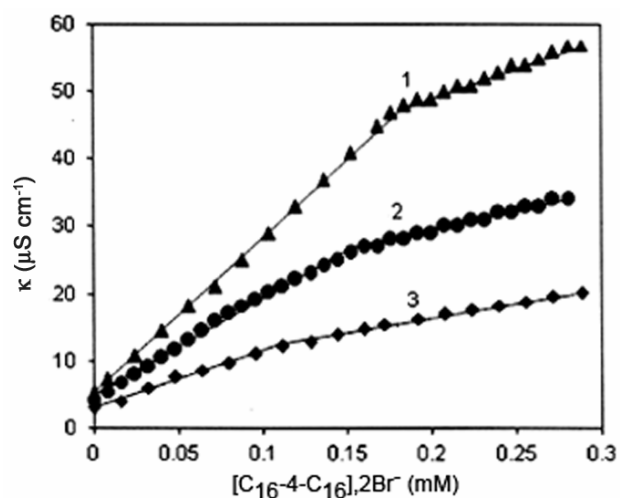


Fig. 2 — Specific conductivity versus concentration plots for $[\text{C}_{16}\text{-4-C}_{16}]$, 2Br^- in presence of 20% (v/v) methanol at different temperatures. [1, 320K; 2, 310K; 3, 300K].

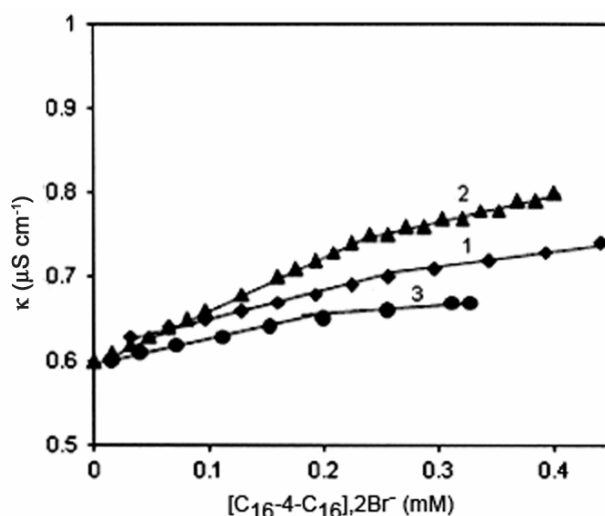


Fig. 3 — Specific conductivity versus concentration plots for $[\text{C}_{16}\text{-4-C}_{16}]$, 2Br^- in presence of 20% (v/v) 1, 4 dioxane at different temperatures. [1, 320; 2, 310K; 3, 300K].

Table 1 — The cmc, α and thermodynamic parameters for the micellization of $[C_{16-4-C_{16}}]_2Br^-$ in 20% (v/v) solvent and at different temperatures

Solvent	Temp. (K)	cmc ^a (mM)	α^a	ΔG_m° (kJ/mol ⁻¹)	$\Delta G_{m\text{tail}}^\circ$ (kJ/mol ⁻¹)	ΔH_m° (kJ/mol ⁻¹)	ΔS_m° (JK ⁻¹ mol ⁻¹)
DMSO	300	0.092 (0.099)	0.67 (0.69)	-55.0 (-53.4)	-27.5 (-26.7)	-34.7	68.0
	310	0.136	0.64	-57.2		-38.4	60.6
	320	0.160	0.60	-61.0		-42.9	56.5
MeOH	300	0.100 (0.120)	0.72 (0.70)	-51.4 (-52.0)	-25.7 (-26.0)	-35.6	52.6
	310	0.160	0.46	-68.3		-50.6	57.0
	320	0.184	0.36	-76.5		-59.2	53.7
1,4-Dioxane	300	0.200 (0.255)	0.65 (0.72)	-53.1 (-47.8)	-26.5 (-23.9)	-19.7	111.3
	310	0.240	0.51	-63.0		-24.5	124.1
	320	0.272	0.66	-54.6		-22.1	101.5
EG	300	0.078 (0.096)	0.42 (0.50)	-72.5 (-66.1)	-36.2 (-33.0)	-39.5	110.0
	310	0.112	0.38	-75.6		-43.8	102.5
	320	0.128	0.34	-80.1		-48.3	99.0
DMF	300	0.092 (0.102)	0.65 (0.67)	-56.4 (-54.6)	-27.9 (-27.3)	-38.7	59.0
	310	0.152	0.61	-58.7		-43.3	49.6
	320	0.192	0.60	-60.1		-46.7	41.8

^aValues in brackets are in 40% (v/v) solvent.

further decreases in hydrophobic effect resulting in increase in cmc values²⁴⁻²⁶.

The presence of alcohol within the micellar interface makes water less polar, which increases Coulombic interactions between head groups and counterions with decrease in the hydrophobic effect²⁷ and concomitant increase in cmc values of surfactant. Figure 1 shows that an increase in the percentage by volume of organic solvent results in a less abrupt change in conductivity in going from the pre-micellar surfactant concentration range to the post-micellar surfactant concentration range. The degree of micellar ionization (α) increases regularly with increasing organic solvent content. 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.2H₂O²⁸. The hydrate formation substantially restricts the motion of the surfactant molecules and reduces hydrophobic interactions with a concomitant increase in cmc. The dielectric constant of DMF is much smaller than that of water. However, with arise in volume percentage of DMF the dielectric constant decreases. Due to this decrease in the dielectric constant²⁹, the ionic interactions at the micellar surface increases. Also, these interactions decrease with an increase in volume

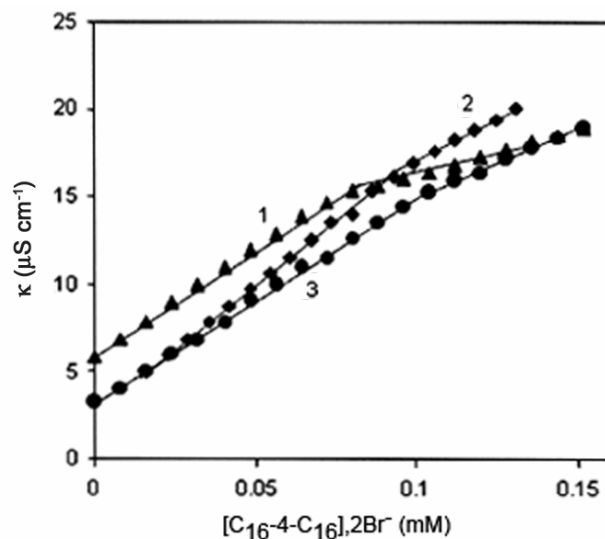


Fig. 4 — Specific conductivity versus concentration plots for $[C_{16-4-C_{16}}]_2Br^-$ in presence of 20% (v/v) different organic solvents at 300K. [1, EG; 2, DMSO; 3, DMF].

percent of DMF in the micellar medium and hence the cmc value increases. A comparative graph (Fig. 4) shows the influence of three solvents (20% v/v) on cmc.

The cmc values were determined at various temperatures and further used for evaluation of the thermodynamic parameters of micellization. The

Gibbs energy of micelle formation is calculated from the pseudo-phase separation model for ionic surfactants according to Eq. (1),

$$\Delta G_m^\circ = 2(1.5 - \alpha) RT \ln X_{\text{cmc}} \quad \dots (1)$$

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 and the other symbols have their usual meanings. The above expression, proposed by Zana^{30,12}, accounts for the presence of two alkyl chains (and two polar head groups) in the surfactant. In the case of dimeric surfactants an extra packing Gibbs energy term has to be considered, which accounts for the packing constraints on the tails. These are connected by the spacer and favor micellar growth since it decreases as micelle size increases. Gibbs free energy of micellization per alkyl tail¹⁸, is given by $\Delta G_{\text{m,tail}}^\circ = \Delta G_m^\circ/2$.

The standard enthalpy change for the micellization process, ΔH_m° , can be determined using the Gibbs-Helmholtz Eqs (2) and (3).

$$\Delta H_m^\circ = \{\delta (\Delta G_m^\circ)/T\}/\{\delta (1/T)\} \quad \dots (2)$$

$$\Delta H_m^\circ = -2(1.5 - \alpha) RT^2 [\delta \ln X_{\text{cmc}}/\delta T] \quad \dots (3)$$

Therefore, if the dependence of the cmc values on temperature is known, a linear plot of $\ln X_{\text{cmc}}$ versus temperature can be constructed and the slope can be found at each temperature.

Further, the standard entropy of micelle formation, ΔS_m° , is obtained by using Eq. (4).

$$\Delta S_m^\circ = \Delta H_m^\circ - \Delta G_m^\circ/T \quad \dots (4)$$

All the thermodynamic parameters of micellization in 20% (v/v) aqueous binary mixtures are given in Table 1. The values of ΔG_m° decrease with increasing temperature indicating that an increase in temperature tends to drive the equilibrium towards the hydrophobic bonding. The tail deformation Gibbs energy accounts for the stretching and deforming the surfactant tails so as to pack within the micelle core, meeting liquidlike density constraints. It also limits the micellar growth since its magnitude increases upon increasing micellar size and it is larger for cylindrical than for spherical micelles. In the case of dimeric surfactants an extra packing Gibbs energy term has to be considered. It accounts for the packing constraints on the tails as they are connected by the spacer and favors micellar growth since it decreases as micelle size increases. The standard enthalpy of micellization is negative, indicating that the micellization process is exothermic.

The entropy change is positive in all the cases³¹. The ΔS_m° of the gemini surfactant decreases with an increase in the temperature. The positive values of standard entropy of micelle formation, ΔS_m° , are due to the melting of “flickering cluster” around the hydrocarbon tails of the surfactant and the increased randomness of the hydrocarbon chains in the micellar core. Data indicate that the micellization is favored in general by both entropy and enthalpy at higher temperatures, whereas it is favored mainly by entropy at low temperatures.

The present study shows that the cmc and α value of C₁₆₋₄-C₁₆, 2Br⁻ increases with increasing temperature as well as increasing volume percentage (20 and 40% v/v) of binary-organic solvents. The cmc value is higher in 1, 4 dioxane-H₂O binary solvents than in other binary solvent system. Thermodynamic parameters of micellization have been calculated from temperature dependence of cmc. The Gibbs energy of micellization becomes more negative with increasing temperature in the presence of co-solvents for the C₁₆₋₄-C₁₆, 2Br⁻.

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