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Mixing Behavior of Anionic Hydrotropes with Cationic Gemini Surfactants

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In this article, we report the results of the mixing behavior of alkanediyl-α,ω-bis(dimethylcetylammonium bromide) gemini surfactants with anionic hydrotropes (sodium salicyalte, sodium benzoate, and sodium tosylate) in aqueous solutions using conductivity measurements. The critical micelle concentration (cmc) for different mixing mole fractions at different temperatures, their ideal cmc values, and different interaction parameters have been estimated. The results show that the mixing behavior is nonideal and the interactions among the surfactants and the hydrotropes are synergistic in nature.

Introduction

In aqueous solution, surfactant monomers associate themselves to form different types of morphologies above the critical micelle concentration (cmc). Because of this unique capability to form self-organized structures in solution, surfactants find applications in almost every chemical industry, such as in detergents, paints, dyestuffs, paper coatings, inks, plastics, fibers, personal care and cosmetics, agrochemicals, pharmaceuticals, food processing, and so forth. They also play a vital role in the oil industry, for example, in enhanced and tertiary oil recovery and oil slick dispersion for environmental protection, among others.[1,2] Because of such widespread applications, the search for new surface active materials with new property profiles had always been a topic of pursuit for academics and industrialists. A new class of surfactants known as gemini surfactants, having two hydrophobic tails and two hydrophilic groups connected at the level of head groups by a spacer, is attracting a lot of interest. This class of surfactants shows much lower cmc values (10 to 100 times) and high efficiency to reduce the surface tension of water than the corresponding conventional surfactants.[3]

In almost all practical applications, surfactants are mixed with different additives (such as, surfactants, organics, polymers, salts, etc.) to improve their performance, as these mixtures often show better performance (synergism) than the individual surfactants.[2,4−8] In recent years, binary mixtures with different surfactant systems have been studied,[4−24] and relevant theories have been proposed and used to analyze and compare the experimental results to reveal the synergistic (and, at times, antagonistic) behaviors of the binary combinations.

Some organic salts, also often called hydrotropes, are surface-active and highly water-soluble, which can increase the solubility of sparingly soluble solutes in water. Hydrotropes have structures somewhat similar to surfactants in that they have hydrophilic and hydrophobic groups. However, they differ from surfactants in that the hydrophobic group is generally short, cyclic, and/or branched. Hydrotropes inhibit the formation of surfactant liquid crystalline phases by forming mixed micellar structures with surfactants. Since the hydrotropes' hydrophilic heads are large and their hydrophobic groups are small, they tend to form spherical rather than lamellar or liquid−crystalline structures, thus inhibiting the formation of the latter. This destruction or inhibition of the liquid crystalline phase increases the solubility of the surfactant in the aqueous phase and the capacity of its micellar solution to solubilize material. The increase in solubility in water is presumably through a self-aggregation process of hydrotrope molecules because of their amphiphilic nature and varies with the nature of the compound.[25,26]

In this paper, we report a systematic study of mixing behavior of cationic gemini surfactants bis(quaternary ammonium bromides) with anionic hydrotropes. The conductivity method has been used to find the cmc at different temperatures, and different thermodynamic parameters were calculated from the obtained results. Although there are many reports on the mixing behavior of different binary surfactant systems, less attention has been paid to the surfactant and hydrotrope systems.[27,28]

Materials and Methods

The gemini surfactants, butanediyl-1,4-bis(dimethylcetylammonium bromide), pentanediyl-1,5-bis(dimethylcetylammonium bromide), and hexanediyl-1,6-bis(dimethylcetylammonium bromide) (in this paper referred to as 16-4-16, 16-5-16, and 16-6-16, Scheme 1), were synthesized in the laboratory by following the literature method.[29] The purity of gemini surfactants (more than 0.99 in mass fraction) was checked via C, H, and N analysis. Other chemicals, such as sodium salicylate, NaSal (0.995 in mass fraction), sodium benzoate, NaBen (0.995 in mass fraction), and sodium tosylate, NaTos (0.70 to 0.8 in mass fraction) (Scheme 1), were the same as those used earlier.[30] The water used to prepare the solutions was demineralized and double-distilled in an all-glass distillation apparatus. The conductivity of the water was in the range of $(1 \text{ to } 2) \cdot 10^{-6}$ $\text{S} \cdot \text{cm}^{-1}$.

Conductivity measurements were carried out on Systronics conductivity meter 306, using a dip cell (cell constant $0.1 \text{ cm}^{-1}/1.026 \text{ cm}^{-1}$). The conductivity experiments were carried out at desired temperatures maintained within ± 0.5 K. Temperature control was maintained by placing the solution to be studied into a temperature-controlled water bath. Equimolar stock solutions of the hydrotropes and gemini surfactants were

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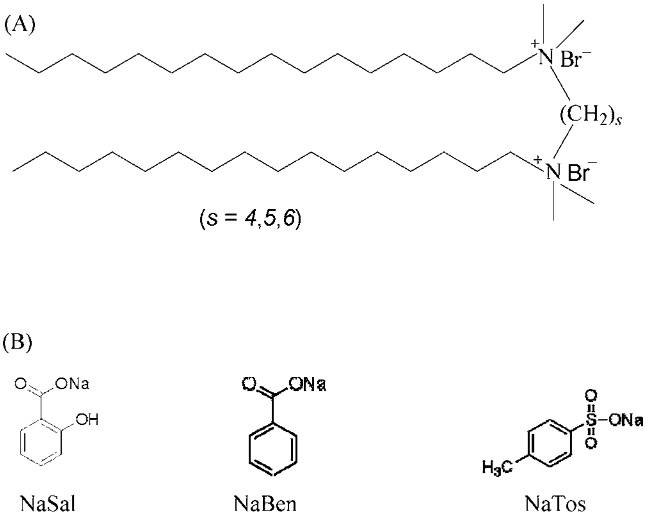
Scheme 1. Molecular Structure of (A) Gemini Surfactants (Butanediyl-1,4-bis(dimethylcetylammonium bromide), 16-4-16; Pentanediyl-1,5-bis(dimethylcetylammonium bromide), 16-5-16; Hexanediyl-1,6-bis(dimethylcetylammonium bromide), 16-6-16) and (B) Hydrotropes (Sodium Salicylate, NaSal; Sodium Benzoate, NaBen; Sodium Tosylate, NaTos)



prepared in doubly distilled water, and then the desired mole fractions were obtained by mixing precalculated volumes of the stock solutions. The conductivity at each concentration was measured by successive addition of concentrated solutions of specified mole fractions in pure water. The measurements were performed three times (sometimes five times), and the average value was taken. The intersection of two linear segments, corresponding to the pre- and postmicellar forms, obtained from the plots of specific conductance (κ) versus the concentration of surfactant, was taken as the cmc.

Results and Discussion

a. Critical Micelle Concentration. The cmc values obtained from the conductivity measurements are recorded in Tables 1 to 3. The values for gemini surfactants in pure water are in fair agreement with the published data.[29,31] Micellar aggregates are also formed in an aqueous solution containing surfactant−hydrotrope mixtures. However, the tendency of aggregation is different from that of the pure surfactants. In general, the cmc values were found to decrease with the increase in mole fraction of the hydrotropes (Tables 1 to 3 and Tables S1 to S6 of the Supporting Information, SI). The results indicate that the added hydrotropes are assisting in the micelle formation of the gemini surfactants, and they partition between the monomers of the surfactants.

For ideal conditions, the cmc of the mixed system (cmc*) and pure components can be related by the Clint equation[32]

$$\frac{1}{\text{cmc*}} = \frac{\alpha_1}{c_{c,1}^{\text{mic}}} + \frac{\alpha_2}{c_{c,2}^{\text{mic}}} \tag{1}$$

where α_1 and α_2 are the stoichiometric mole fractions of components (hydrotrope, 1, and surfactant, 2) in binary mixtures and $c_{c,1}^{\text{mic}}$ and $c_{c,2}^{\text{mic}}$ are the cmc's of hydrotrope (also known as mhc, minimum hydrotrope concentration) and surfactant, respectively.

Table 1. Micellar Parameters (Experimental and Ideal Critical Micelle Concentrations (c_c^{mic} and cmc*), Micellar Mole Fractions of Hydrotrope (x_1), Mole Fractions of Hydrotrope in Ideal State (x_1^{ideal}), Interaction Parameter (β^{m}), Activity Cofficients (f_1, f_2), and Excess Free Energy, ($\Delta_{\text{mix}}G^{\text{E}}$)) for Hexanediyl-1,6-bis (dimethylcetylammonium bromide)/Sodium Salicylate Mixed Systems at Different Temperatures Evaluated on the Basis of Conductivity Measurements

	c_c^{mic}	cmc*						$\Delta_{\text{mix}}G^{\text{E}}$
α_{NaSal}	mmol·dm^{-3}	mmol·dm^{-3}	x_1	$10^4 \cdot x_1^{\text{ideal}}$	β^{m}	$10^4 \cdot f_1$	f_2	kJ·mol^{-1}
				$T = 298$ K				
0.0	0.042							
0.2	0.004	0.053	0.297	0.219	−24.3	0.061	0.117	−11.5
0.4	0.003	0.071	0.323	0.583	−25.4	0.086	0.070	−12.9
0.6	0.003	0.106	0.346	1.310	−26.9	0.100	0.040	−14.7
0.8	0.002	0.212	0.374	3.500	−29.5	0.097	0.016	−17.2
1.0	484.8							
				$T = 303$ K				
0.0	0.046							
0.2	0.012	0.058	0.257	0.226	−19.8	0.177	0.270	−8.9
0.4	0.010	0.077	0.287	0.603	−20.7	0.276	0.182	−10.6
0.6	0.007	0.115	0.325	1.360	−23.3	0.241	0.085	−12.9
0.8	0.006	0.231	0.357	3.620	−25.6	0.248	0.038	−14.8
1.0	510.8							
				$T = 308$ K				
0.0	0.051							
0.2	0.023	0.064	0.218	0.229	−16.7	0.371	0.452	−6.6
0.4	0.019	0.085	0.259	0.610	−17.9	0.526	0.300	−8.4
0.6	0.014	0.128	0.302	1.370	−20.3	0.503	0.156	−10.6
0.8	0.007	0.256	0.354	3.660	−25.0	0.294	0.044	−14.4
1.0	560.9							
				$T = 313$ K				
0.0	0.057							
0.2	0.026	0.072	0.218	0.238	−16.6	0.389	0.454	−6.6
0.4	0.022	0.095	0.258	0.636	−17.8	0.568	0.307	−8.4
0.6	0.017	0.143	0.299	1.430	−19.9	0.578	0.169	−10.4
0.8	0.012	0.286	0.344	3.810	−23.1	0.472	0.065	−13.3
1.0	600.9							

Table 2. Micellar Parameters (Experimental and Ideal Critical Micelle Concentrations (c_c^{mic} and cmc*), Micellar Mole Fractions of Hydrotrope (x_1), Mole Fractions of Hydrotrope in Ideal State (x_1^{ideal}), Interaction Parameter (β^{m}), Activity Cofficients (f_1, f_2), and Excess Free Energy, ($\Delta_{\text{mix}}G^{\text{E}}$)) for Pentanediyl-1,5-bis(dimethylcetylammonium bromide)/Sodium Salicylate Mixed Systems at Different Temperatures Evaluated on the Basis of Conductivity Measurements

	c_c^{mic}	cmc*						$\Delta_{\text{mix}}G^{\text{E}}$
α_{NaSal}	mmol·dm^{-3}	mmol·dm^{-3}	x_1	$10^4 \cdot x_1^{\text{ideal}}$	β^{m}	$10^4 \cdot f_1$	f_2	kJ·mol^{-1}
				$T = 298$ K				
0.0	0.032							
0.2	0.019	0.040	0.188	0.166	−15.3	0.417	0.582	−5.8
0.4	0.014	0.053	0.249	0.441	−17.8	0.447	0.332	−8.4
0.6	0.003	0.080	0.332	0.993	−25.3	0.124	0.061	−14.4
0.8	0.001	0.160	0.381	2.650	−32.5	0.388	0.009	−17.7
1.0	484.8							
				$T = 303$ K				
0.0	0.036							
0.2	0.025	0.045	0.171	0.177	−14.2	0.566	0.659	−5.0
0.4	0.016	0.060	0.248	0.471	−17.6	0.489	0.339	−8.2
0.6	0.004	0.090	0.333	1.060	−25.2	0.133	0.061	−14.3
0.8	0.001	0.180	0.382	2.830	−32.7	0.386	0.008	−17.8
1.0	510.8							
				$T = 308$ K				
0.0	0.042							
0.2	0.034	0.052	0.144	0.186	−12.8	0.852	0.767	−3.9
0.4	0.017	0.069	0.252	0.496	−17.8	0.481	0.323	−8.4
0.6	0.004	0.104	0.334	1.120	−25.3	0.133	0.059	−14.4
0.8	0.001	0.208	0.384	2.970	−32.9	0.375	0.008	−18.0
1.0	560.9							
				$T = 313$ K				
0.0	0.045							
0.2	0.044	0.056	0.111	0.188	−14.2	0.131	0.839	−3.5
0.4	0.023	0.075	0.236	0.500	−16.5	0.652	0.398	−7.5
0.6	0.008	0.113	0.316	1.130	−22.6	0.257	0.105	−12.5
0.8	0.005	0.225	0.356	3.000	−26.1	0.200	0.037	−15.6
1.0	600.9							

The cmc* values obtained from the above equation are given in Tables 1 to 3 for all of the mixtures. The differences in cmc and cmc* values show the deviation from the ideality. It is clear that the cmc values are much lower than the cmc* values, which

Table 3. Micellar Parameters (Experimental and Ideal Critical Micellar Concentrations (c_c^{mic} and cmc*) Micellar Mole Fractions of Hydrotrope (x_1), Mole Fractions of Hydrotrope in Ideal State (x_1^{ideal}), Interaction Parameter (β^m), Activity Cofficients (f_1, f_2), and Excess Free Energy ($\Delta_{mix}G^E$)) for Butanediyl-1,4-bis(dimethylcetylammonium bromide)/Sodium Salicylate Mixed Systems at Different Temperatures Evaluated on the Basis of Conductivity Measurements

	c_c^{mic}	cmc*						$\Delta_{mix}G^E$
α_{NaSal}	mmol·dm^{-3}	mmol·dm^{-3}	x_1	$10^4 \cdot x_1^{ideal}$	β^m	$10^4 \cdot f_1$	f_2	kJ·mol^{-1}
$T = 298$ K								
0.0	0.028							
0.2	0.015	0.035	0.200	0.144	−16.3	0.303	0.522	−6.6
0.4	0.009	0.046	0.265	0.385	−19.5	0.273	0.255	−9.5
0.6	0.006	0.070	0.305	0.866	−21.9	0.261	0.131	−11.7
0.8	0.001	0.140	0.371	2.310	−30.4	0.605	0.015	−13.5
1.0	484.8							
$T = 303$ K								
0.0	0.034							
0.2	0.023	0.042	0.172	0.165	−14.4	0.521	0.653	−5.2
0.4	0.016	0.056	0.241	0.441	−17.1	0.520	0.369	−7.9
0.6	0.008	0.084	0.305	0.992	−21.5	0.306	0.135	−11.5
0.8	0.002	0.169	0.370	2.650	−29.5	0.081	0.017	−13.0
1.0	510.8							
$T = 308$ K								
0.0	0.037							
0.2	0.028	0.046	0.157	0.165	−13.6	0.636	0.715	−4.5
0.4	0.025	0.062	0.210	0.441	−15.0	0.863	0.516	−6.3
0.6	0.009	0.093	0.303	0.992	−21.2	0.331	0.142	−11.3
0.8	0.002	0.185	0.370	2.650	−29.5	0.082	0.017	−13.0
1.0	560.9							
$T = 313$ K								
0.0	0.040							
0.2	0.054	0.050		0.167				
0.4	0.041	0.067	0.162	0.445	−12.4	1.660	0.722	−4.2
0.6	0.017	0.100	0.281	1.000	−18.8	0.586	0.226	−9.6
0.8	0.007	0.200	0.345	2.670	−24.4	0.279	0.054	−13.9
1.0	600.9							

indicate the formation of mixed micelles between the hydrotropes and the surfactants. A synergism occurs, that is, an attractive interaction is operating between the two components of the mixtures. The charge neutralization between the head groups of the two components and the intercalation of hydrophobic part of the hydrotrope into the gemini micelles[33] improve the hydrophobic environment in the mixed state in comparison to that in the pure state. As a result, the cmc values are lower than the cmc* values.

b. Interaction Parameters. Interaction parameters for mixed micellar systems were calculated by applying the Rubingh's model.[34] According to this model, α_1, cmc (c_c^{mic}) and x_1 (mole fraction of component 1, i.e., hydrotrope) in mixed micelles are related according to the following equation

$$\frac{[x_1^2 \ln(c_c^{mic}\alpha_1/c_{c,1}^{mic}x_1)]}{(1 - x_1)^2 \ln[c_c^{mic}(1 - \alpha_1)/c_{c,2}^{mic}(1 - x_1)]} = 1 \qquad (2)$$

The values of x_1 were obtained by solving eq 2 iteratively.

The micelle mole fraction in the ideal state (x_1^{ideal}) has been computed using

$$x_1^{ideal} = [(\alpha_1 c_{c,2}^{mic})/(\alpha_1 c_{c,2}^{mic} + (1 - \alpha_1)c_{c,1}^{mic})] \qquad (3)$$

From the data of Tables 1 to 3 (and Tables S1 to S6 of the SI), it is clear that x_1 values are always much more than x_1^{ideal}; that is, the mixed systems are rich in hydrotrope in comparison to that in the ideal mixing state.

The micellar molecular interaction parameter (β^m) is given by the equation:

$$\beta^m = [\ln(c_c^{mic}\alpha_1/c_{c,1}^{mic}x_1)]/(1 - x_1)^2 \qquad (4)$$

The β^m values may vary from negative to positive through zero. This demonstrates the extent of interaction between the two components which leads to the deviation from ideality. Various theoretical models are available to interpret the formulation of mixed micelles. The first model given by Lange, and used by Clint, is based on the phase separation model and assumes ideal mixing of the surfactants in the micellar phase. Rubingh proposed a treatment based on regular solution theory (RST) for nonideal mixed systems which have been extensively used. The reason for the nonideal behavior among surfactant molecules upon mixing are the various types of molecular interactions. These interactions (either synergistic or antagonistic) can be analyzed by RST which allows the evaluation of micelle mole fraction (x_1) and interaction parameter (β^m). According to RST, the molecules of mixing components should be of comparable size, completely interchangeable, and the interaction energy could be expressed as sum of pairwise neighbor interactions. As the value of β^m is proportional to the free energy of mixing, a negative β^m value means synergism in the system. It indicates that the attractive interactions between the two component molecules are stronger than the interaction among molecules of same components. Positive β^m values have been ascribed to antagonistic behavior. It means that the repulsive forces between two mixing components are stronger than the repulsions among similar molecules. A β^m value close to zero indicates almost ideal mixing.

In our case, β^m is negative throughout the concentration range (Tables 1 to 3, and Tables S1 to S6 of the SI). With an increase in the α_1 value, β^m becomes more negative, indicating a greater attraction among the two components in mixed systems.

From the values it can also be seen that with the increase in temperature, the values of x_1 decrease and β^m have less negative values, that is, less interaction among the components. This is due to the increase in the thermal motion of the monomers of the components, which disfavor micellization. This is also supported from the fact that cmc increases with the rise in temperature (see Tables 1 to 3 and Tables S1 to S6 of the SI).

The β^m is related to the activity coefficients (f_1 and f_2) in the mixed systems by the following equations

$$f_1 = \exp\{\beta^m(1 - x_1)^2\} \qquad (5)$$

$$f_2 = \exp\{\beta^m {x_1}^2\} \qquad (6)$$

The activity coefficients are found to be less than 1 (Tables 1 to 3 and Tables S1 to S6 of the SI), which show the nonideality of the systems.

The excess free energy of mixing ($\Delta_{mix}G^E$) has been calculated by using the following equation

$$\Delta_{mix}G^E = RT[x_1 \ln f_1 + (1 - x_1) \ln f_2] \qquad (7)$$

where R and T are the gas constant and absolute temperature, respectively. The calculated $\Delta_{mix}G^E$ values, recorded in Tables 1 to 3 and S1 to S6 of the SI, are found to be negative, indicating stable mixed systems. A comparison of $\Delta_{mix}G^E$ values of NaSal, NaBen, and NaTos show that the interaction of hydrotropes with the gemini surfactants is in the order of NaSal > NaTos > NaBen. This can be understood from the structure of these

Table 4. Thermodynamic Parameters ($\Delta_{\mathrm{mix}}G^\circ$, $\Delta_{\mathrm{mix}}H^\circ$, $T\Delta S^\circ_{\mathrm{mix}}$) of Micellization of 16-*s*-16 with Sodium Salicylate at Different Temperatures [$T = (298\ \mathrm{to}\ 313)$ K]

		16-6-16			16-5-16			16-4-16		
α_{NaSal}	T / K	$\Delta_{\mathrm{mix}}G^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{mix}}H^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$T\Delta_{\mathrm{mix}}S^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{mix}}G^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{mix}}H^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$T\Delta_{\mathrm{mix}}S^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{mix}}G^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{mix}}H^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$	$T\Delta_{\mathrm{mix}}S^\circ$ / $\mathrm{kJ \cdot mol^{-1}}$
0.2	298	−79.0	−238.7	−159.7	−61.5	−69.7	−8.2	−60.8	−104.0	−43.3
	303	−68.0	−222.0	−154.0	−56.7	−66.4	−9.8	−60.6	−108.6	−48.0
	308	−59.6	−207.1	−147.5	−53.0	−64.6	−11.6	−61.0	−112.7	−51.7
	313	−58.3	−207.4	−149.1	−54.4	−68.6	−14.2	−50.9	−100.2	−49.3
0.4	298	−80.3	−249.3	−169.1	−62.9	−44.8	18.1	−62.9	−120.9	−58.0
	303	−68.6	−231.9	−163.3	−58.5	−42.7	15.7	−62.1	−126.2	−64.2
	308	−60.4	−216.4	−156.0	−55.6	−41.6	14.0	−61.4	−130.9	−69.5
	313	−58.9	−216.7	−157.8	−56.9	−44.1	12.8	−52.0	−116.4	−64.4
0.6	298	−81.2	−233.8	−152.6	−60.7	−44.8	15.9	−64.1	−77.0	−12.9
	303	−70.4	−217.4	−147.0	−64.0	−25.9	38.0	−64.9	−80.4	−15.5
	308	−61.6	−202.9	−141.3	−60.8	−25.2	35.6	−65.6	−83.4	−17.8
	313	−59.9	−203.2	−143.3	−60.9	−26.8	34.1	−55.3	−74.2	−18.9
0.8	298	−82.3	−165.6	−83.2	−74.1	−14.9	59.2	−70.3	−136.7	−66.4
	303	−71.1	−154.0	−82.8	−69.3	−14.2	55.1	−70.8	−142.7	−71.9
	308	−64.3	−143.7	−79.4	−66.1	−13.8	52.3	−71.8	−148.0	−76.2
	313	−61.3	−143.9	−82.6	−62.5	−14.7	47.9	−58.3	−131.6	−73.3

hydrotropes (Scheme 1). The combined hydrophobic and electrostatic forces of these hydrotropes are: NaSal > NaTos > NaBen.[33] Hence, the interaction with NaSal is greater than the other two hydrotropes. Ion-specificity has often been found as one of the important factors in micellar transition. A carboxylate headgroup is "hard", and a sulfonate headgroup is "soft". As a result, their interactions with the soft ammonium headgroups are different, and the hydrotropes are in competition with bromide.[35,36]

c. Thermodynamic Analysis. The thermodynamic parameters of micellization for ionic surfactants in aqueous solution can be obtained by using a mass action model.[37]

The standard Gibbs energy of micelle formation, $\Delta_{\mathrm{mix}}G^\circ$, involving gemini as one of the components, is related to the following equation.[2,38]

$$\Delta_{\mathrm{mix}}G^\circ = (3 - 2g)RT \ln x_{\mathrm{C}} \tag{8}$$

where g is the degree of dissociation (obtained from the ratio of post- to premicellar slopes using the specific conductivity) and x_{C} is the experimental cmc in the mole fraction unit at each α value. That is, the values were calculated as $x_{\mathrm{C}} = c_{\mathrm{c}}^{\mathrm{mic}}/(c_{\mathrm{c}}^{\mathrm{mic}}$ + number of moles of the solvent). For the micellization in pure water, the number of moles of solvent is taken as 55.556 $\mathrm{mol \cdot dm^{-3}}$. R and T have their usual meanings. The $\Delta_{\mathrm{mix}}G^\circ$ values for the mixed systems, calculated according to eq 8, are listed in Table 4 and Tables S7 and S8 of the SI.

The standard enthalpy ($\Delta_{\mathrm{mix}}H^\circ$) and entropy ($\Delta_{\mathrm{mix}}S^\circ$) changes have been calculated from the equations

$$\Delta_{\mathrm{mix}}H^\circ = -RT^2(3 - 2g)(\mathrm{d} \ln x_{\mathrm{c}}/\mathrm{d}T) \tag{9}$$

and

$$\Delta_{\mathrm{mix}}S^\circ = \frac{\Delta_{\mathrm{mix}}H^\circ - \Delta_{\mathrm{mix}}G^\circ}{T} \tag{10}$$

For all of the systems the term d ln x_{C}/dT was evaluated from the linear ln x_{C} versus T plots.

The negative values of $\Delta_{\mathrm{mix}}G^\circ$ (Table 4) indicate that the micellization process is somewhat spontaneous in nature. The values of both $\Delta_{\mathrm{mix}}H^\circ$ and $T\Delta_{\mathrm{mix}}S^\circ$, provided in Table 4, are found to be negative. Although some $T\Delta_{\mathrm{mix}}S^\circ$ values were found to be positive, which decreased with the increase in temperature for a particular mole fraction, no trend was observed. This decrease in the entropy indicates that the tendency of micellization reduces at higher temperature, as the enthalpy of micellization is negative and becomes more negative with the rise in temperature. It is also clear that $\Delta_{\mathrm{mix}}H^\circ < T\,\Delta_{\mathrm{mix}}S^\circ$, which indicates that the whole mixed system is entropy-controlled.

On comparing Tables 1 to 4 (also Tables S1 to S8) data, we can see that, when we move from $s = 4$ to $s = 6$ (spacer chain length), the interaction between the hydrotropes with the gemini surfactants increases. This can be understood from the following discussion. The chain length and nature of spacer strongly affect the micellization and adsorption characteristics of cationic gemini surfactants.[39] In the case of gemini surfactants, for a given hydrophobic chain length, the surfactant headgroup area increases with the increase in the spacer chain length.[40] On the addition of hydrotropes with an opposite charge and with some hydrophobicity, the electrostatic repulsion between the headgroups is reduced, whereas the hydrophobic interaction increases, the extent being more with the surfactant having larger spacer chain length. Hence, more stable mixed systems with the higher spacer chain length are formed.

Conclusion

We can say that the gemini surfactants and hydrotrope systems form stable mixed micelles because of synergism. The cmc of the mixed systems lies between the cmc's of the pure components. The hydrotrope contribution is higher in the mixed systems. The whole process is enthalpy-controlled. With the longer spacer chain length, the interaction increases among the gemini surfactants and hydrotropes because of the combined electrostatic and hydrophobic interactions.

Supporting Information Available:

Condutivity data (at all of the studied temperatures) for all systems and different parameters ($c_{\mathrm{c}}^{\mathrm{mic}}$, cmc*, x_1, x_1^{ideal}, β^{m}, f_1, f_2, $\Delta_{\mathrm{mix}}G^{\mathrm{E}}$) for 16-*s*-16 + NaBen/NaTos mixed systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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