

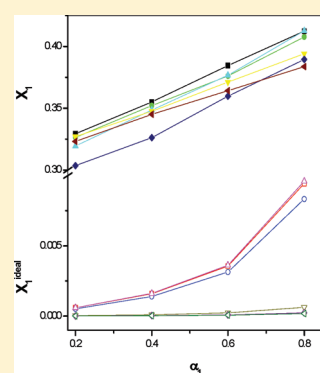
Analysis of Mixed Micellar Behavior of Cationic Gemini Alkanediyl- α,ω -bis(dimethylcetylammmonium bromide) Series with Ionic and Nonionic Hydrotropes in Aqueous Medium at Different Temperatures

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S Supporting Information

ABSTRACT: The interaction between cationic symmetrical gemini alkanediyl- α,ω -bis(dimethylcetylammmonium bromide) series (16-s-16, $s = 5, 6$, abbreviated as G5 and G6) with hydrotropes (cationic: aniline hydrochloride, *para*-toluidine hydrochloride, and *ortho*-toluidine hydrochloride; nonionic: phenol, resorcinol, and pyrogallol) in aqueous medium has been investigated at four different temperatures ranging from 298.15 to 313.15 K. Different physico-chemical parameters such as critical micelle concentration (cmc), interaction parameter (β^m , an energetic parameter that represents the excess Gibbs free energy of mixing), activity coefficients (f_i), mole fraction of hydrotrope in mixed micelles at ideal mixing conditions (X_1^{ideal}), excess free energy of mixing ($\Delta_{\text{mix}}G^E$), standard enthalpy ($\Delta_{\text{mic}}H^\circ$), entropy ($\Delta_{\text{mic}}S^\circ$), and Gibbs free energy ($\Delta_{\text{mic}}G^\circ$) of micellization were evaluated and then intracompared. For further understanding, similar studies were carried out with their conventional counterpart cetyltrimethyl ammonium bromide (CTAB) and then compared. The bulk behaviors were explored using different theoretical models of Clint, Rubingh, and Motomura for justification and comparison of results of different binary combinations of hydrotropes with the gemini series and CTAB. Synergistic interaction was observed in all binary combinations at all temperatures in the micelles which decreases slightly with increasing temperature. This study will give insight into the selection of surfactants in different applications as their properties get modified by interaction with hydrotropes, thus influencing their solution behavior which, in turn, modifying the phase-forming behavior, microemulsion, liquid crystal forming systems, clouding phenomenon, cleaning, and laundry processes besides solubilization. The ability of hydrotropes to dramatically alter the solubility of other molecules in a medium can be exploited for the purpose of selective encapsulation and release.



INTRODUCTION

Surfactants are amphiphathic molecules that consist of a non-polar hydrophobic portion attached to a polar or ionic portion (hydrophilic). The surfactants aggregate in water above a certain concentration known as critical micelle concentration (cmc)¹ which (i.e., micellization) results due to reduction of contact between the hydrophobic portion and water, thereby reducing the free energy of the system. The cmc values of surfactants depend upon hydrocarbon chain length, chain structure, valence and nature of counterions, temperature, and often the presence of nonelectrolytes/electrolytes. Due to widespread use and application of surfactants as well as of their micellar aggregates in chemical, biochemical, pharmaceutical, and industrial fields, detailed investigations on the fundamentals of aggregation of existing and newer amphiphiles are continuing since long.

Interest in increasing the performance of conventional surfactants (one head and one tail) has led to research into the development of bis-surfactants, termed as Gemini surfactants. All the geminis possess at least two ionic or polar headgroups and two hydrophobic chains connected at the headgroup level with spacers of different nature.^{2,3} Though some unsymmetrical geminis and geminis with more polar groups or tails have been

reported,^{4–7} the great majority have symmetrical structures with two identical polar/ionic headgroups and two identical chains. The general formula of ionic bis-quaternary surfactants is $H_{2n+1}C_n(CH_3)_2N^+(Y)_s-N^+(CH_3)_2C_nH_{2n+1} \cdot 2X^-$ and are referred to as m-s-m type.² Because of their unique solution properties such as low cmc, high detergency, high solubilization power, etc., the geminis find a wide range of applications in diverse areas such as petroleum/pharmaceutical/biochemical research,⁸ as catalyst,^{9,10} anticorrosive,¹¹ antimicrobial agents,^{12,13} etc.

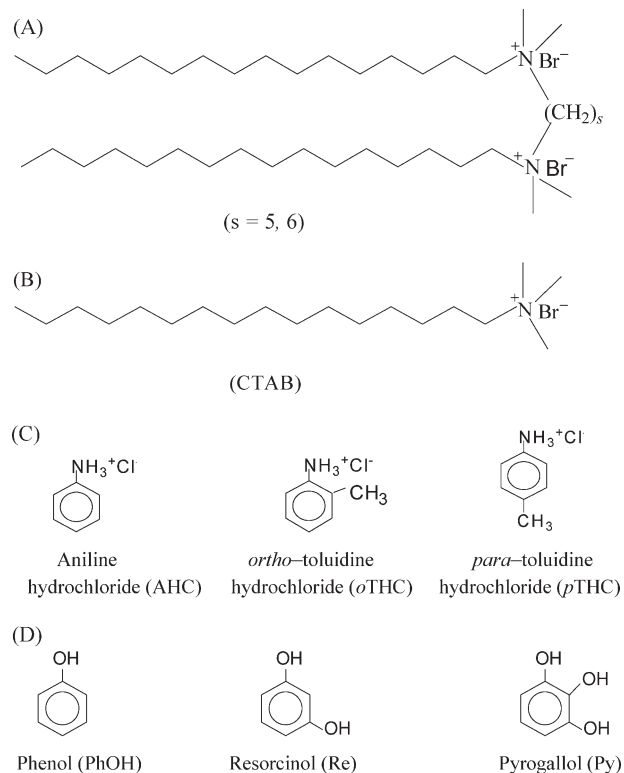
Despite their significant use in a myriad of applications (e.g., soil/water remediation, oil recovery, detergency, etc.), their performance could be further enhanced to meet the growing demands by the judicious selection of additives, giving a favorable cost/performance ratio. Mixed micellar systems including geminis and hydrotropes is one remedy and is receiving wide attention. Also, from an environmental perspective, it is desirable to select surfactants from existing ones rather than to hunt for newer ones. Interest in mixed micelles has largely been driven by industry in

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Scheme 1. Molecular Structure of (A) Gemini Surfactants (Alkanediyl- α,ω -bis(dimethylcetylammmonium Bromide), 16-s-16), (B) Cetyltrimethylammmonium Bromide (CTAB), (C) Cationic Hydrotropes (Aniline Hydrochloride, *ortho*-Toluidine Hydrochloride, and *para*-Toluidine Hydrochloride), and (D) Nonionic Hydrotropes (Phenol, Resorcinol, and Pyrogallol)



search of properties that lie beyond that defined by each surfactant component. Hines' review¹⁴ describes some recent advances in the theoretical evaluation of micellization in mixed surfactant systems.

Geometry of micelles is a result of a delicate balance of two opposing forces: attractive tail–tail hydrophobic interactions and electrostatic repulsions between headgroups which limits the size of micelles. The geometry of the micelles can be tuned by the addition of various excipients of organic and inorganic in nature. One such additive is hydrotropes, which are an essential ingredient of cleaning and laundry products.

The hydrotropes refer to short chain amphiphiles showing three common features:

- They do not aggregate in ordered structures such as micelles but rather form dimers, trimers, etc.
- Above a given concentration in water, hydrotropes enable the solubilization of large quantities of hydrophobic compounds in water, the solubilization vs hydrotrope concentration curves follow power series.
- Hydrotropes break ordered lyotropic phases formed by surfactants at high concentration.

The hydrotrope refers to water-soluble organic compounds whose addition in water leads to an increased solubilization of hydrophobic compounds.¹⁵ Hydrotropes have been extensively studied, and they are found to have numerous applications.¹⁶ A term minimum hydrotrope concentration (MHC) has been used in consonant with cmc.^{17,18}

Typical binding counterions for cationic micelles include salicylate,¹⁹ *para*-toluene sulfonate,²⁰ chlorobenzoate,²¹ hydroxyl naphthalene carboxylate,²² and alkyl sulfates.²³ These counterions belong to the family of hydrotropes. They interact with the micelle-forming surfactants electrostatically as well as hydrophobically, and the orientation of hydrotrope at the micellar surface is important. NMR measurements show that the salicylate ion is strongly adsorbed to CTAB micelles in a configuration that allows the carboxylic and hydroxyl groups to protrude from the micelles,²⁴ in which *ortho*-salicylate isomer is more effective than the hydroxybenzoates in deriving micellar growth.²⁵ One of the most extensively studied systems is the mixture of CTAB with sodium salicylate which forms long thread like micelles and behaves like a living polymer. The interfacial position of sodium salicylate on CTAB micelles has been discussed by Manohar et al.²⁴ Therefore, surfactant-organic counterion mixed systems have attracted considerable interest from both academic and industrial researchers. Worm-like micelles are used as drag reducing agents in recirculation systems and in fracturing fluids in oil production.²⁶

Reports on mixtures of ionic gemini surfactants and organic counterions are rare so far.^{27–34} As most of the counterion effects have been focused on inorganic ions, systematic studies on organic counterions are limited. No general picture can be derived from these singular studies concerning the effect of hydrotropes on the solution properties of gemini surfactants. We have, therefore, performed conductivity measurements on various transparent mixtures of the cationic gemini surfactants and hydrotropes (cationic and nonionic; Scheme 1) in water to learn about the influence of these on the micellization behavior of the geminis. These studies are aimed to elucidate the effects of the surfactant composition and the spacer length on the aggregation properties of mixed micelles of gemini surfactants with different kinds of hydrotropes. In order to obtain satisfactory results for the thermodynamic quantities related to the micellization process, high accuracy in the cmc determination and a large number of experimental points were obtained in the selected temperature range. Thermodynamic properties of surfactant solutions are discussed in terms of the temperature dependence of the free energy, enthalpy and entropy of micellization which provides further insight into the role of temperature, headgroup size and counterion specificity on the micellization of cationic gemini surfactants in aqueous solutions. In addition, some experimental results of CTAB (conventional counterpart of alkanediyl- α,ω -bis-(dimethylcetylammmonium bromide) series) with some of the above-mentioned hydrotropes have also been incorporated to find out their effect on the micellization behavior of CTAB which showed different trend in some micellar parameters. These studies gave some preliminary and important results about the aggregation behavior of mixtures of cationic gemini surfactants and hydrotropes.

EXPERIMENTAL SECTION

Materials. The cationic hydrotropes [aniline hydrochloride (AHC, 99.0%, Fluka, Switzerland), *para*-toluidine hydrochloride (pTHC, 99.0%, Fluka, Switzerland), and *ortho*-toluidine hydrochloride (oTHC, 99.0%, Fluka, Switzerland)], nonionic hydrotropes [phenol (PhOH, 99.5%, Merck, Germany), resorcinol (Re, 99.0%, Merck, Germany), and pyrogallol (Py, 99.0%, Merck, Germany)], and cetyltrimethylammmonium bromide (CTAB, 99.0%, Merck, Germany) were used as received. The dimeric geminis alkanediyl- α,ω -bis(dimethylcetylammmonium bromides),

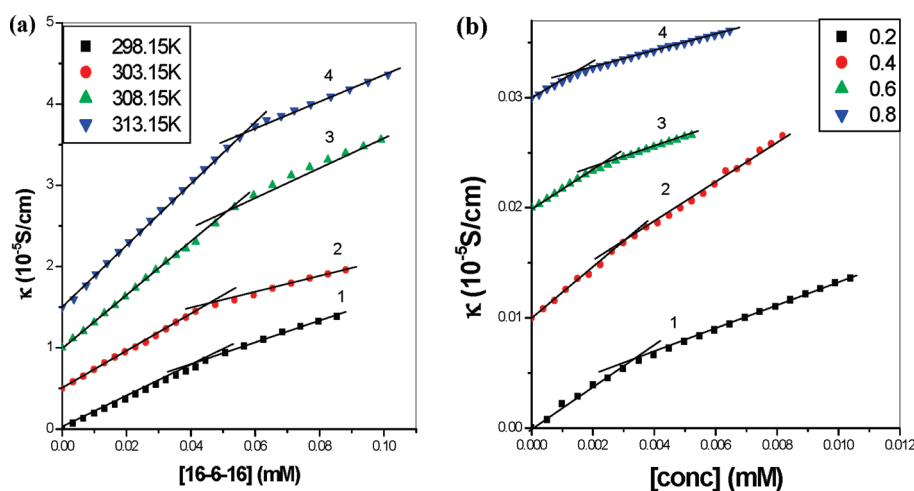


Figure 1. (a) Conductivity plots of G6 in pure water at different temperatures. Curves 2, 3, and 4 have been shifted vertically by 0.5, 1.0, and 1.5 scale units ($1 \times 10^{-5} \text{ S/cm}$). (b) Conductivity plots of binary mixtures of oTHC-G6 of different bulk mole fractions at 298.15 K. Curves 2, 3, and 4 have been shifted vertically by 0.01, 0.02, and 0.03 scale units ($1 \times 10^{-5} \text{ S/cm}$).

(16-s-16) were synthesized by refluxing α,ω -dibromoalkane (pentane and hexane) with a slight excess of *N,N*-dimethylcetylamine in dry ethanol at $\sim 80^\circ \text{C}$ for 48 h. The product formed was recrystallized in ethanol/ethyl acetate at least 4 times and the purity of gemini surfactants was (more than 99.0%) checked via C, H, and N analysis and ^1H NMR.^{32,35}

Conductivity Measurements. The conductance measurements were taken on a Systronic conductivity meter 306, using a dip cell (cell constant 0.1 cm^{-1}). The experiments were performed at constant temperature by circulating water through a jacketed cell holding the solution under study. Equimolar stock solutions of the hydrotropes and gemini were prepared in double distilled water and then desired mole fractions were obtained by mixing precalculated volumes of the stock solutions. The conductivity at each mole fraction was measured by successive addition of concentrated solution in pure water. The intersection of two linear segments, corresponding to the pre- and post-micellar forms, obtained from the plots of specific conductance (κ) versus the [surfactant], was taken as cmc.

Surface Tension Measurements. The tensiometric measurements were performed using a platinum ring by the ring detachment method with a Kruss tensiometer model K11 MK3. Pure nonionic hydrotrope concentration was varied by adding concentrated hydrotrope solution in water, and the readings were noted after thorough mixing and temperature equilibration. Temperature was maintained by circulating water from an Orbit RS10S thermostat. The MHC values were determined by noting inflections in the γ vs logarithm of hydrotrope concentration isotherms.

RESULTS AND DISCUSSION

Surfactant-Hydrotrope Interactions in Mixed Micelles. A complex balance of intermolecular forces is responsible for the formation of mixed micelles when hydrotropes and surfactants are in the same solution. To obtain the cmc, conductivity measurements were carried out. At all temperatures break in the conductance vs concentration plots, characteristic of micelle formation, was observed. The typical plots of specific conductivity vs [surfactant] are presented in Figure 1a as a prototype of pure and binary mixtures of oTHC-G6 (see Figure 1b). It is

observed that even at the highest temperature studied, the change of slope is clearly noticeable. Our results show that the cmc of pure surfactants agree well with the literature^{32,35–37} values and also the MHC values of pure hydrotropes.^{17,38,39}

The ideal cmc values ($\text{cmc}_{\text{ideal}}$) were obtained by the use of Clint eq 1⁴⁰

$$1/\text{cmc}_{\text{ideal}} = \sum \alpha_i/\text{cmc}_i \quad (1)$$

where α_i is the bulk mole fraction of the *i*th component in mixed surfactant solution and cmc_i its critical micelle concentration in pure form. α_1 is the bulk mole fraction of hydrotrope and α_2 that of the surfactant, so, cmc_1 is that of hydrotrope. The experimental cmc values of both the CTAB-hydrotrope and gemini-hydrotrope systems are lower than the ideal as well as that of component cmc's indicating nonideal synergistic interactions. The hydrotropes influence the self-aggregation (micellization) behavior of surfactants in solution by decreasing the cmc of gemini/conventional surfactants by reducing the effective headgroup area. The cmc values of the mixed systems decrease with the increasing α_1 [Figures 2 and S1–S3 (Supporting Information)]. The decrease in cmc is a consequence of efficient charge neutralization/screening. On the other hand, a hydrotrope of large size and having substitution is detrimental to close packing by way of interaction with the amphiphile molecules producing enhanced solubilizing effect, but inhibiting micelle formation.⁴¹ For dimeric surfactants, the spacer group affects the interaction upon the addition of hydrotropes, the maximum reduction in the cmc is observed in G4,^{37,42} followed by G5 and G6 (present work), whereas in the CTAB-hydrotrope mixed systems, maximum reduction in cmc is observed in the order of CTAB-anionic > CTAB-nonionic > CTAB-cationic in tune with their interaction parameters in both gemini-hydrotrope and CTAB-hydrotrope binary systems (Figure S1). From the results it can be concluded that the mixed micellization is favored by strengthening of the hydrophobic interactions allowing micellization to take place at lower concentrations (lower cmc) in both the gemini-hydrotrope and CTAB-hydrotrope mixtures. The difference between the experimental cmc and ideal cmc is less in CTAB-hydrotrope systems compared to gemini-hydrotropes proving stronger interaction in geminis with the hydrotropes due to two charge sites

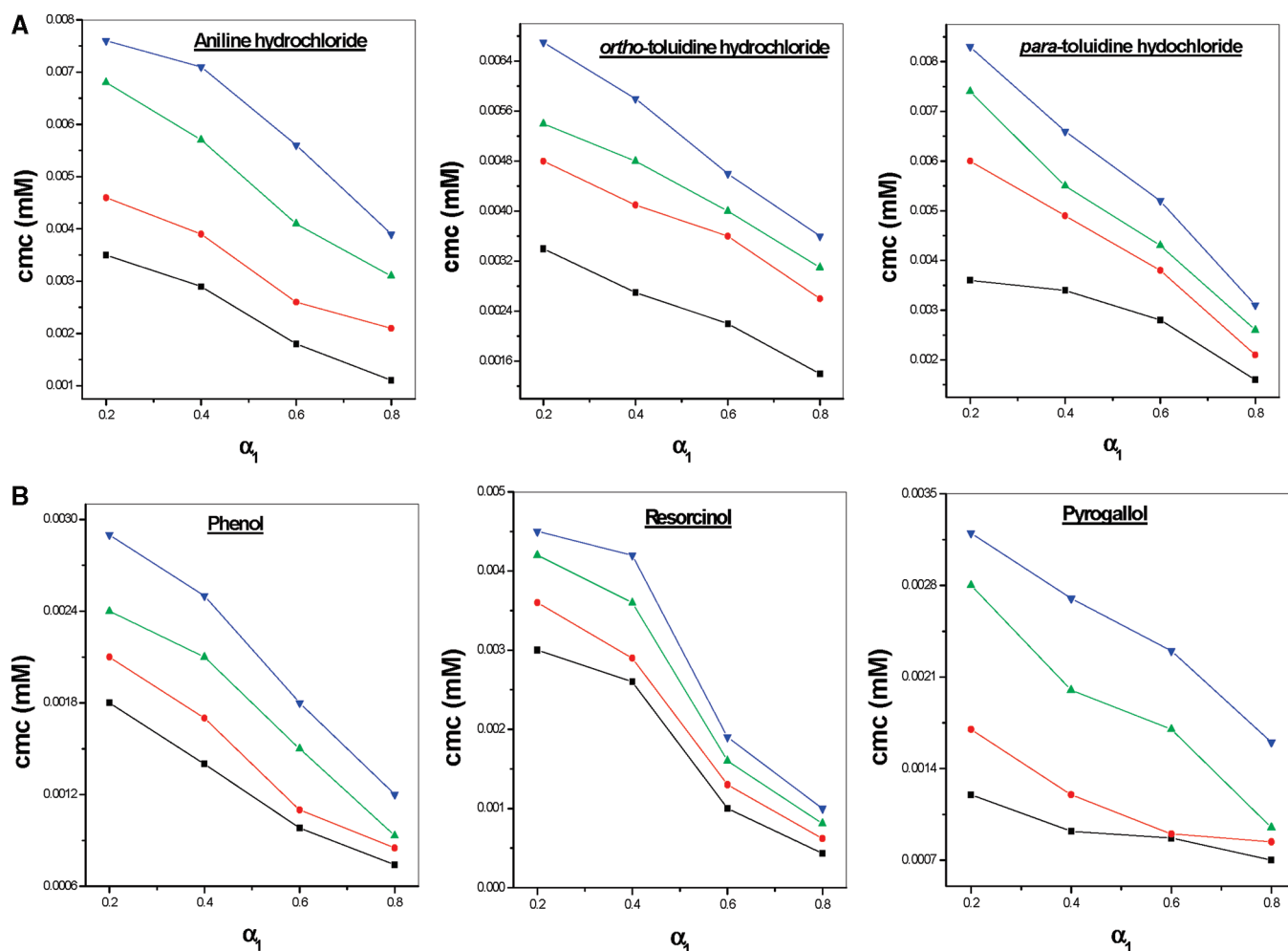


Figure 2. (A) Critical micelle concentration (cmc) vs mole fraction of hydrotropes (α_1) in cationic hydrotrope-surfactant (G6) mixtures at different temperatures: 298.15 (■), 303.15 (●), 308.15 (▲), and 313.15 K (▲). (B) Critical micelle concentration (cmc) vs mole fraction of hydrotropes (α_1) in nonionic hydrotrope-surfactant (G6) mixtures at different temperatures: 298.15 (■), 303.15 (●), 308.15 (▲), and 313.15 K (▲).

(in geminis). It was earlier found by De et al.³⁵ that gemini surfactants control the morphology and micellar growth in water in mixed gemini-CTAB micelles. It was also found that an increase in the spacer length generally suppressed the tendencies of mixed micelles toward micellar growth.^{37,43,44}

Molecules that are most effective in reducing cmc are solubilized in the outer portion of the micelle core where they are under lateral pressure tending to force them into the inner portion of micellar core. These hydrotropes bind strongly to the positively charged surfactant ions confirmed by large negative values of the interaction parameters (discussed ahead) and reduce the headgroup area because of the neutralization/screening effect. As a result, micelles are formed at much lower concentration, thus the decrease in cmc being dependent upon the concentration of hydrotropes. This pressure increases cross-sectional area thus producing swollen micelles.^{45–47} Mukerjee⁴⁸ proposed that an additive which is active to hydrocarbon/water interface will be mainly solubilized at the micellar surface and will promote micellar growth. Phenol, being a polar organic additive and more water-soluble, is known to get partitioned between aqueous and palisade layers of the micellar phase.^{49,50} With an increase in concentration of hydrotropes, cmc decreases due to partitioning

and preferential adsorption on the ionic headgroup of surfactants and into the palisade layer of surfactant micelles, thereby reducing the headgroup repulsions between the hydrophilic groups, thus favoring early micellization. This penetration results in charge neutralization/screening in headgroup region of the micelle along with simultaneous increase in hydrophobic interactions between the surfactant tail and the hydrophobic portion of the additive. This is also reflected by the increase in the magnitude of β^m which otherwise should have become less negative had only electrical effects been significant. Some of these additives being salts will also exert a salting-out effect which will decrease the water content in the headgroup region of micelles, thereby allowing the headgroups to come closer and hence reduce cmc. When oppositely charged surfactants are mixed, new properties appear. Aqueous catanionic mixtures exhibit a wide range of unique properties that arise from strong electrostatic interactions between oppositely charged heads and, as a result, exhibit low cmc values. An increase in temperature increases cmc in both pure and mixed systems indicating weakened tendency for micelles to grow. This indicates the thermal impediment of micellar growth, for which temperature, therefore, plays an important role.

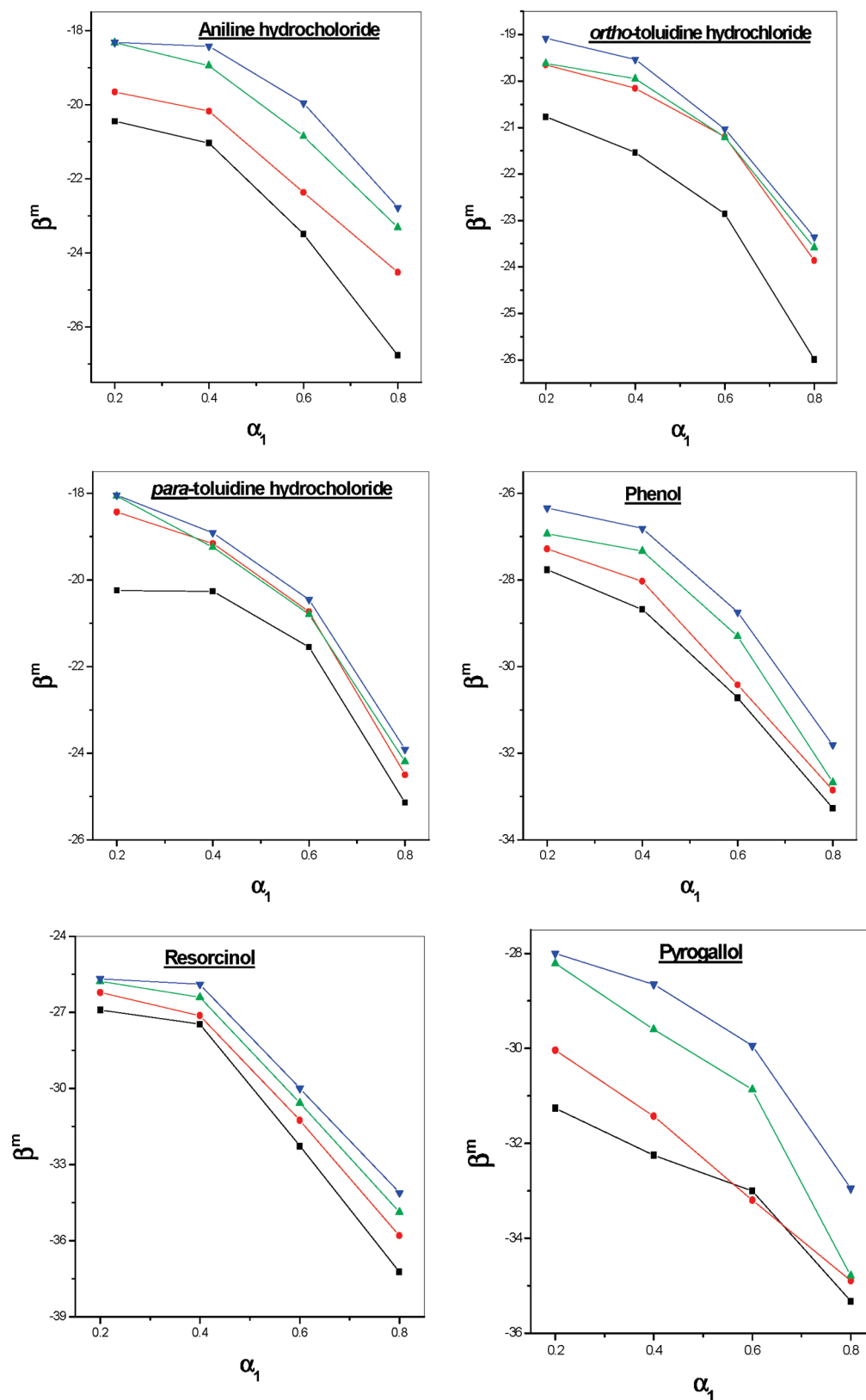


Figure 3. Variations of β^m vs mole fraction of hydrotropes (α_1) in hydrotrope–surfactant (G6) mixtures at different temperatures: 298.15 (■), 303.15 (●), 308.15 (▲), and 313.15 K (▲).

A mixture of hydrotropes with a gemini/conventional surfactant should lead to the formation of a mixed aggregate because of

surface active nature of both components, albeit in different manner. Mixed micelles formed in the solutions of such

Table 1. Comparison Between the Average Interaction Parameters (β_{av}^m) for Various CTAB/Gemini–Hydrotrope Mixed Systems at Different Temperatures (Evaluated on the Basis of Conductance Measurements)

	β_{av}^m									
T/K	CTAB		G6		G5			G4 (ref 42)		
	Cationic Hydrotropes									
	AHC	AHC	<i>o</i> THC	<i>p</i> THC	AHC	<i>o</i> THC	<i>p</i> THC	AHC	<i>o</i> THC	<i>p</i> THC
298.15	−7.02	−22.94	−22.79	−21.80	−23.37	−20.61	−22.38	−24.42	−24.60	−24.42
303.15	−6.83	−21.68	−21.36	−20.70	−19.43	−20.14	−21.38	−23.58	−23.52	−23.22
308.15	−6.55	−20.36	−21.09	−20.57	−21.62	−20.13	−21.56	−22.32	−22.63	−22.73
313.15	−6.45	−19.87	−20.75	−20.53	−20.89	−19.63	−20.82	−21.51	−21.57	−21.79
	Nonionic Hydrotropes									
	Re	PhOH	Re	Py	PhOH	Re	Py	PhOH	Re	Py
298.15	−24.45	−30.11	−30.96	−32.96	−31.32	−28.98	−32.88	−34.99	−37.00	−38.24
303.15	−24.25	−29.65	−30.10	−32.39	−30.79	−28.51	−32.74	−34.45	−35.31	−36.92
308.15	−23.94	−20.06	−29.40	−30.87	−29.90	−28.10	−30.74	−34.00	−33.96	−34.95
313.15	−23.40	−28.42	−28.91	−29.88	−29.21	−27.27	−29.94	−32.18	−33.07	−33.47
	Anionic Hydrotropes (ref 37)									
	NaSal	NaSal	NaBen	NaTos	NaSal	NaBen	NaTos	NaSal	NaBen	NaTos
298.15	−32.13	−26.52	−14.70	−21.65	−22.73	−17.28	−19.55	−22.03	−19.80	−16.83
303.15	−31.08	−22.35	−13.37	−19.00	−22.43	−17.20	−17.55	−20.63	−15.50	−16.08
308.15	−30.64	−19.97	−12.70	−14.73	−22.20	−15.80	−15.75	−19.83	−13.75	−16.47
313.15	−30.22	−19.35	−13.40	−16.20	−19.85	−15.15	−14.55	−18.53	−11.85	−14.10

nonhomogenous surface active materials are expected to be nonideal. This nonideal mixing was quantified in the light of Rubingh's eq 2.⁵¹ To investigate the nature of the interactions among the components of the present investigations, we calculated various other parameters using the said model.⁵¹ This model is based on regular solution theory for nonideal mixed systems. The micellar mole fraction of component 1 in the mixed micelle (X_1) and the micellar interaction parameter (β^m) are the optimization parameters, which can be calculated iteratively using eqs 2 and 3

$$\frac{[X_1^2 \ln(\text{cmc}\alpha_1/\text{cmc}_1X_1)]}{(1 - X_1)^2 \ln[\text{cmc}(1 - \alpha_1)/\text{cmc}_2(1 - X_1)]} = 1 \quad (2)$$

Here cmc_1 , cmc_2 , and cmc denote, respectively, the experimental cmc values of hydrotrope, surfactant, and their binary mixture and X_1 is the micellar mole fraction of hydrotrope in the mixed micelle.

The interaction between hydrotropes–surfactants in the mixed micelles is measured in terms of interaction parameter β^m

$$\beta^m = [\ln(\text{cmc}\alpha_1/\text{cmc}_1X_1)]/(1 - X_1)^2 \quad (3)$$

The intercomponent interaction parameter, β^m , is an energetic parameter that represents the excess Gibbs free energy of mixing. It measures the interaction between two different amphiphiles after mixing relative to their self-interaction before mixing under the same conditions. In the mixed micelle it accounts for deviation from ideality. The structural differences in the headgroup region affect the interaction between surfactants and hydrotropes as shown by the cmc in two cases. To know how structural differences affect the extent of interaction, we studied a range of ionic and nonionic hydrotropes with varied structures in each case. The β^m values are negative [Figures 3 and S4 (Supporting Information)] which can be ascribed to the interaction between

the headgroups leading to electrostatic stabilization. The large negative values of β^m reflect stronger attractive interaction between the two components. In case of the three gemini surfactants (G6, G5, and G4), the β^m values represent the following trend: nonionic hydrotrope > cationic hydrotrope > anionic hydrotrope, which is different from the conventional surfactant (CTAB), viz., anionic hydrotrope > nonionic hydrotrope > cationic hydrotrope.

The β^m values, although not constant for all binary combinations throughout the concentration range [Figures 3 and S4 (Supporting Information)], are all negative at different temperatures, suggesting strong synergism in the mixed micelle formation. The synergistic interaction decreases with increase in temperature in all the systems due to increased thermal vibrations (Table 1). In the case of gemini–cationic hydrotropes, little effect is observed on the synergistic interaction upon introduction of the CH_3 group at ortho and para positions, whereas in the case of nonionic hydrotropes, an increase in the number of OH groups increases the synergistic interaction. A careful examination (Figure 3) reveals that at higher bulk mole fraction of hydrotropes ($\alpha_1 = 0.8$), the synergistic interaction is highest in almost all cases (barring a few cases of G4) and the reduction in cmc is observed to be the lowest.^{37,42} In case of anionic hydrotropes, highest synergistic interaction is observed with G6–NaSal³⁷ which decreases on moving to NaTos and also with decrease in spacer length of the gemini. The combined hydrophobic and electrostatic forces of these hydrotropes are NaSal > NaTos > NaBen. Hence, the interaction with NaSal is greater than the other two hydrotropes.³⁸ Ion–specificity has often been found as one of the important factors in micellar transition. A carboxylate headgroup is “hard”, whereas 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. The variation in synergism (negative deviation) is observed in all the

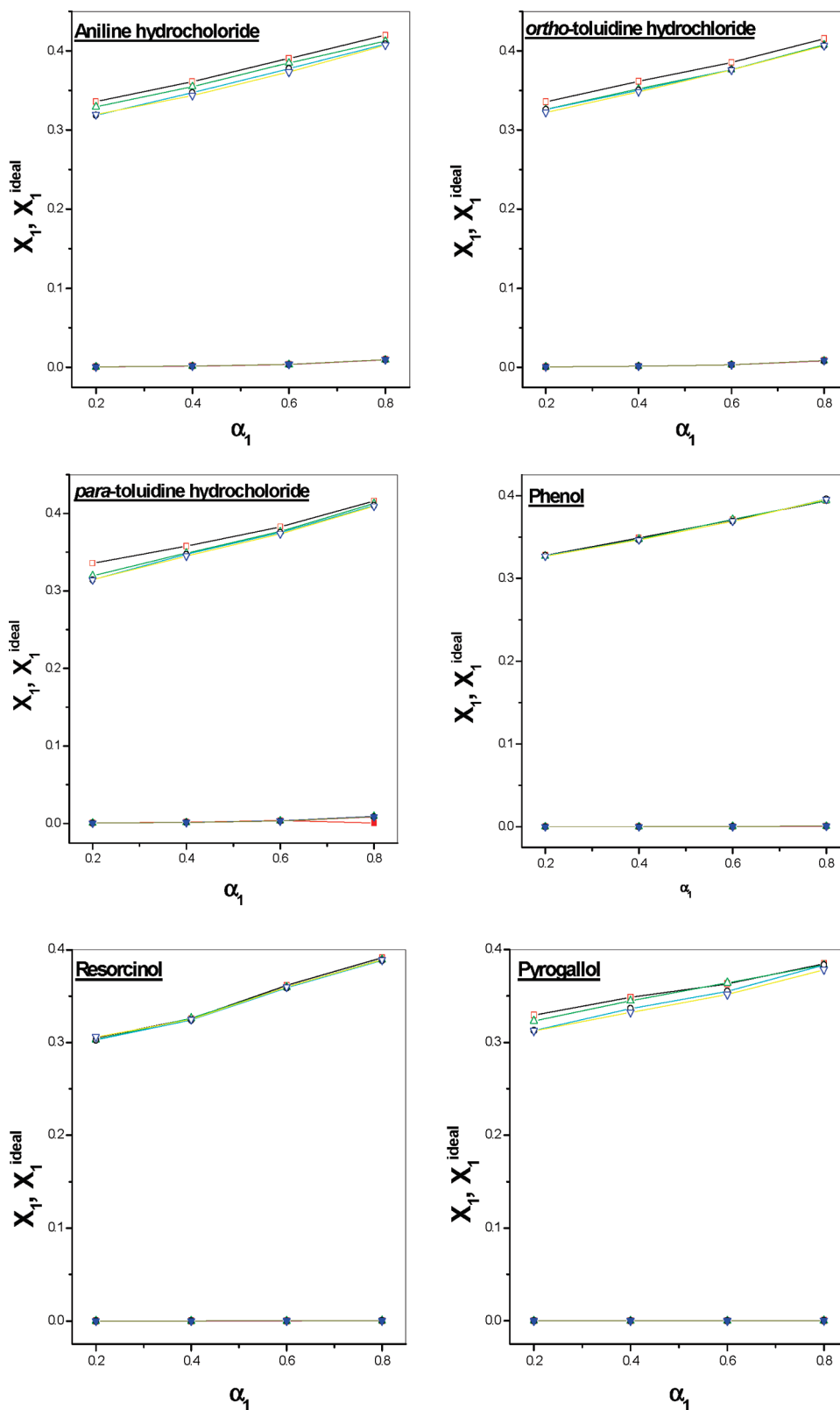


Figure 4. Variation of X_1 and X_1^{ideal} vs mole fraction of hydrotropes (α_1) in hydrotrope–surfactant (G6) mixtures at different temperatures: 298.15 (red \square, \blacksquare), 303.15 (green $\triangle, \blacktriangle$), 308.15 (\circ, \bullet), and 313.15 K (blue $\nabla, \blacktriangledown$). Open symbols are for Rubingham's and filled symbols are for Motomura's model.

hydrotrope–gemini binary systems. This is explained by the lower hydrophilicity of the sulfonate compared to the carboxylate moiety⁵² or by a stronger interaction of the cationic surfactant head groups

with sulfonate anions compared to carboxylates as per their relative positions in the Hofmeister series.⁵³ Ions with high charge density and high polarizing power are hard while those with low charge

Table 2. Physicochemical Parameters for Hydrotrope – G6 Gemini Surfactant Mixed Systems at Various Temperatures (Evaluated on the Basis of Conductance Measurements)

α_1	$10^4 \cdot f_1$	f_2	$\Delta_{\text{mix}} G^E$ (kJ mol ⁻¹)	g	$10^4 \cdot f_1$	f_2	$\Delta_{\text{mix}} G^E$ (kJ mol ⁻¹)	g	$10^4 \cdot f_1$	f_2	$\Delta_{\text{mix}} G^E$ (kJ mol ⁻¹)	g
G6												
AHC				σ THC				p THC				
$T = 298.15$ K				$T = 298.15$ K				$T = 298.15$ K				
0.2	1.2	0.099	-11.3	0.265	1.0	0.096	-11.5	0.424	1.3	0.102	-11.1	0.113
0.4	1.9	0.064	-12.0	0.512	1.5	0.060	-12.3	0.227	2.3	0.075	-11.5	0.239
0.6	1.6	0.028	-13.9	0.190	1.8	0.034	-13.4	0.487	2.7	0.043	-12.6	0.301
0.8	1.2	0.009	-16.2	0.548	1.4	0.011	-15.6	0.461	1.9	0.013	-15.1	0.379
$T = 303.15$ K				$T = 303.15$ K				$T = 303.15$ K				
0.2	1.4	0.119	-10.9	0.382	1.3	0.012	-10.9	0.284	2.0	0.152	-10.1	0.308
0.4	2.3	0.078	-11.6	0.321	2.1	0.082	-11.6	0.340	2.9	0.097	-11.0	0.367
0.6	2.1	0.037	-13.3	0.367	2.6	0.050	-12.5	0.341	3.2	0.053	-12.3	0.296
0.8	2.1	0.015	-15.0	0.327	2.3	0.019	-14.5	0.334	2.1	0.015	-15.0	0.450
$T = 308.15$ K				$T = 308.15$ K				$T = 308.15$ K				
0.2	2.0	0.155	-10.2	0.427	1.3	0.125	-11.0	0.279	2.0	0.168	-10.0	0.201
0.4	3.1	0.102	-11.0	0.264	2.2	0.086	-11.6	0.332	2.7	0.098	-11.1	0.388
0.6	3.1	0.051	-12.5	0.506	2.6	0.050	-12.7	0.164	3.0	0.054	-12.5	0.440
0.8	2.9	0.020	-14.4	0.468	2.5	0.020	-14.6	0.320	2.2	0.017	-15.0	0.447
$T = 313.15$ K				$T = 313.15$ K				$T = 313.15$ K				
0.2	2.1	0.154	-10.3	0.278	1.6	0.138	-10.8	0.223	2.1	0.169	-10.1	0.219
0.4	3.6	0.113	-10.8	0.319	2.5	0.093	-11.5	0.140	3.0	0.105	-11.1	0.222
0.6	3.9	0.062	-12.1	0.313	2.8	0.051	-12.8	0.556	3.3	0.058	-12.5	0.217
0.8	3.3	0.023	-14.3	0.548	2.7	0.021	-14.7	0.294	2.4	0.018	-15.0	0.279
PhOH				Re				Py				
$T = 298.15$ K				$T = 298.15$ K				$T = 298.15$ K				
0.2	0.04	0.050	-15.2	0.498	0.02	0.081	-14.1	0.331	0.008	0.034	-17.1	0.769
0.4	0.05	0.030	-16.1	0.419	0.04	0.055	-14.9	0.511	0.011	0.020	-18.1	0.386
0.6	0.05	0.015	-17.8	0.321	0.01	0.015	-18.5	0.644	0.015	0.013	-18.9	0.216
0.8	0.05	0.006	-20.0	0.592	0.01	0.003	-22.0	0.618	0.016	0.005	-20.7	0.236
$T = 303.15$ K				$T = 303.15$ K				$T = 303.15$ K				
0.2	0.04	0.054	-15.1	0.103	0.03	0.089	-14.0	0.274	0.011	0.043	-16.6	0.292
0.4	0.06	0.034	-16.0	0.290	0.05	0.056	-15.0	0.405	0.014	0.024	-17.9	0.489
0.6	0.06	0.015	-17.9	0.352	0.03	0.018	-18.1	0.781	0.015	0.012	-19.4	0.733
0.8	0.06	0.006	-19.8	0.580	0.02	0.004	-21.4	0.514	0.018	0.006	-20.8	0.576
$T = 308.15$ K				$T = 308.15$ K				$T = 308.15$ K				
0.2	0.05	0.056	-15.2	0.325	0.04	0.094	-13.9	0.290	0.016	0.063	-15.5	0.769
0.4	0.08	0.038	-15.8	0.172	0.06	0.062	-14.8	0.455	0.022	0.035	-16.9	0.426
0.6	0.09	0.019	-17.5	0.664	0.04	0.019	-18.0	0.466	0.026	0.021	-18.1	0.357
0.8	0.07	0.006	-20.0	0.504	0.02	0.005	-21.2	0.513	0.018	0.006	-21.0	0.388
$T = 313.15$ K				$T = 313.15$ K				$T = 313.15$ K				
0.2	0.07	0.060	-15.1	0.507	0.04	0.091	-14.2	0.319	0.018	0.065	-15.7	0.226
0.4	0.11	0.040	-15.8	0.635	0.08	0.065	-14.8	0.455	0.028	0.042	-16.5	0.264
0.6	0.11	0.020	-17.4	0.299	0.05	0.021	-18.0	0.534	0.034	0.025	-17.8	0.431
0.8	0.09	0.007	-19.8	0.731	0.03	0.006	-21.1	0.234	0.029	0.009	-20.2	0.329

density and low polarizing power are soft. According to Collins “matching water affinity” concept,⁵⁴ soft ions come close to soft ions while hard ions with hard ones. However, if hard ions come in contact with soft ions, they do not approach each other very closely and their hydration spheres remain intact, hence the interaction between them would be weak. Therefore, such mixtures are attractive in view of a potential performance enhancement of a given gemini surfactant (quaternary ammonium ions forming

the headgroups of the present geminis behave like soft ions). The relative importance of the synergistic effects depends on the gemini and aromatic anion which must be individually optimized for a given property.

At higher concentrations of hydrotropes, besides interaction of delocalized π -electrons of the aromatic ring with the N^+ of the gemini/CTAB, additional π - π aromatic interactions between the headgroups of hydrotropes are observed, this being the reason

for the higher interaction.^{55,56} The large negative value of β^m (Table 1) can be ascribed to the interaction between the headgroups leading to electrostatic stabilization since hydrophobic interactions are very small. Cationic geminis bind with anionic hydrotropes via electrostatic forces, leading to the formation of nonmicellar aggregates called “ion paired amphiphiles” or cationic systems such as lamellae or bilayers,⁵⁷ while in gemini–nonionics it is polar headgroup of the nonionics which stabilizes positive charge of ionic surfactants. β^m values become less negative as the concentration of geminis decreases (Figures 3 and S4). According to Maeda,⁵⁸ as the chain lengths differ, there should be chain–chain interactions helping the stability of mixed micelles.

At low concentrations, “salting-in” effect is ruled out, but at higher salt concentrations “salting-out” effect may be observed which decreases the surfactant solubility.

The micelle mole fraction in the ideal state (X_1^{ideal}) has been calculated by the Motomura eq⁵⁹

$$X_1^{\text{ideal}} = [(\alpha_1 \text{cmc}_2)/(\alpha_1 \text{cmc}_2 + (1 - \alpha_1) \text{cmc}_1)] \quad (4)$$

No doubt, this theory has certain limitations (because of the rigid structures of hydrotropes). Also, it does not consider the difference in sizes of the mixed micelle forming components such as hydrotropes. Though $X_1 > X_1^{\text{ideal}}$ in case of all the binary mixtures, less difference in multiplicands is observed in the case of nonionic hydrotropes (PhOH, Re, and Py) in comparison to X_1^{ideal} , indicating more propensity of nonionic hydrotropes toward the micellization (but overall micellar mole fraction of hydrotropes is very low compared to surfactant even in poor surfactant region, showing lesser tendency of micellization of hydrotropes). No doubt, in case of cationic (AHC, *o*THC, and *p*THC) and anionic hydrotropes (NaSal, NaBen, and NaTos) the difference is quite large,³⁸ but, in all the three cases, the difference is observed in their multiplicands [see Figures 4 and S5 (Supporting Information)]. This difference can be attributed to screening of repulsions between headgroups of the cationic gemini surfactants. In all the cases the micellar mole fraction (X_1) decreases with increase of temperature, indicating the thermal impediment of micellar growth. We can then conclude that the hydrotropes partition into micelles of gemini surfactants, thus strengthening the hydrophobic environment in the mixed state and resulting in onset of micellization at lower concentration (in comparison to pure state).

The activity coefficients (f_i) of the hydrotropes–surfactants within the mixed micelles are related to the interaction parameter through eqs

$$f_1 = \exp\{\beta^m(1 - X_1)^2\} \quad (5a)$$

$$f_2 = \exp\{\beta^m X_1^2\} \quad (5b)$$

The activity coefficients of gemini surfactants are higher than of the hydrotropes [Tables 2 and TS1 (Supporting Information); though both are less than unity], indicating nonideal behavior and synergistic interaction between two components in the mixed micelles. The activity coefficients in case of cationic hydrotrope AHC are higher at 0.4 bulk mole fraction and in *o*THC and *p*THC at 0.6. Whereas nonionic PhOH and Re follow the trend of AHC, Py shows maximum at 0.8 bulk mole fraction. The activity coefficients of hydrotropes (f_1) are very much low even in the poor region of surfactants. The micellar mole fractions in the ideal state calculated from Motomura equation are much less than the experimental micellar mole fraction

calculated from the Rubingh equation. With increase of temperature, the value of activity coefficient of gemini surfactant (f_2) increases. Thus, we can conclude that hydrotropes have less propensity of micellization even in poor region of the geminis.

As evident from data (Tables 2 and TS1), the activity coefficients of the gemini/CTAB surfactants within their respective mixed micelles are in consonance with their interaction parameters (Figures 3 and S4 and Table 1). The greater the value of the interaction parameter, the greater the extent of nonideality in the system will be and hence the smaller the value of activity coefficients will be. The activity coefficients, obtained from eq 5, are less than unity, indicating nonideal behavior with synergistic interaction between components in the micelle. The low hydrophobicity and high cmc values, besides other factors, such as structure and chain length, also affect the surfactant interaction within micelles. Interactions between the surfactants in binary mixtures are the result of mainly two contributions, one associated with interactions between hydrophobic moieties of the two mixing components in the micellar core and the other with electrostatic interactions between the headgroups of both surfactants at the interface. Besides, possibility of hydrogen bonding cannot be ruled out.

Variation of Counterion Binding. The variation of counterion binding “*g*” to micelles in various systems are presented in Tables 2 and TS1 (Supporting Information). The counterion association properties of the pure and mixed micelles have been evaluated from the degree of dissociation (obtained from ratio of post- to pre-micellar slopes using the specific conductance isotherms). Higher counterion association (with cationic hydrotropes) is due to increased charge density while much lower association (with anionic hydrotropes) may be due to complex formation with reduction in the charge density. In cationic hydrotropes, Cl^- and Br^- ions compete with the headgroups for water and consequently headgroups are less hydrated. Cl^- and Br^- ions are weakly hydrated chaotropes (water structure breaker) and hence soft, so they prefer to interact with soft ammonium group of the gemini, while Na^+ ion is a kosmotrope (water structure maker), hence hard. An ion’s position in the lyotropic series can be correlated with its charge density and hydrated radius. Depending on the charge density of the anion, it can interact more or less with the cationic headgroups of micellar surface. Such a binding decreases the electrostatic repulsion between the surfactant headgroups and hence favors aggregation.

Thermodynamics of Micellization. The relationship between the cmc and free energy of micellization for gemini surfactants was derived by Zana⁶⁰ and used by other authors.⁶¹ We adopted analogous approach for the calculation of thermodynamic parameters and the excess free energy for mixed micelle formation ($\Delta_{\text{mix}}G^E$) in the studied range of temperatures has been evaluated from eq 6

$$\Delta_{\text{mix}}G^E = RT[X_1 \ln f_1 + (1 - X_1) \ln f_2] \quad (6)$$

where R and T are the solution constant and absolute temperature, respectively. The $\Delta_{\text{mix}}G^E$ increases with increase of hydrotrope mole fraction in mixed systems, but decreases with increase of temperature [Tables 2 and TS1 (Supporting Information)]. In all the cases of gemini–nonionic systems, introduction of higher concentration of hydrotropes makes the micelles more stable; which is supported by their interaction parameters (Table 1 and Figures 3 and S4). The negative $\Delta_{\text{mix}}G^E$ values suggest that mixed micelles are more stable than the micelles of pure surfactants.

Table 3. Various Thermodynamic Parameters of Hydrotrope–G6 Gemini Surfactant Mixed Systems at Different Temperatures

α_1	T/K	$\Delta_{\text{mic}}G^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{mic}}H^\circ$ (kJ mol ⁻¹)	$T\Delta_{\text{mic}}S^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{mic}}G^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{mic}}H^\circ$ (kJ mol ⁻¹)	$T\Delta_{\text{mic}}S^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{mic}}G^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{mic}}H^\circ$ (kJ mol ⁻¹)	$T\Delta_{\text{mic}}S^\circ$ (kJ mol ⁻¹)
		AHC			<i>o</i> THC			<i>p</i> THC		
0.2	298.15	-72.22	-85.67	-13.45	-74.07	-59.80	14.2	-62.17	-35.82	26.35
	303.15	-69.75	-85.54	-15.79	-67.60	-56.68	10.93	-69.10	-41.77	27.33
	308.15	-74.66	-95.36	-20.70	-64.00	-54.94	9.06	-70.46	-43.86	26.59
	313.15	-71.07	-92.89	-21.82	-66.58	-58.86	7.71	-60.04	-38.26	21.78
0.4	298.15	-73.03	-79.18	-6.14	-74.78	-45.19	29.59	-62.38	-49.25	13.13
	303.15	-70.46	-79.06	-8.60	-68.26	-42.82	25.44	-69.97	-57.43	12.54
	308.15	-75.49	-88.14	-12.65	-64.47	-41.51	22.96	-71.78	-60.31	11.46
	313.15	-71.38	-85.86	-14.48	-67.18	-44.48	22.71	-60.92	-52.61	8.30
0.6	298.15	-75.11	-99.94	-24.83	-76.01	-31.90	44.12	-63.11	-34.70	28.41
	303.15	-72.19	-99.80	-27.61	-68.80	-30.23	38.57	-71.07	-40.46	30.61
	308.15	-77.04	-111.26	-34.22	-65.19	-29.30	35.89	-72.87	-42.49	30.38
	313.15	-72.44	-108.38	-35.93	-68.15	-31.39	36.76	-61.83	-37.07	24.76
0.8	298.15	-77.26	-133.69	-56.43	-78.03	-42.53	35.50	-65.21	-49.25	15.97
	303.15	-73.11	-133.50	-60.39	-70.15	-40.30	29.85	-73.62	-57.43	16.19
	308.15	-78.35	-148.82	-70.47	-66.20	-39.07	27.14	-75.11	-60.31	14.80
	313.15	-74.07	-144.97	-70.90	-69.17	-41.86	27.32	-63.80	-52.61	11.19
		PhOH			Re			Py		
0.2	298.15	-81.78	-43.81	37.97	-85.08	-50.00	35.08	-78.89	-86.58	-7.69
	303.15	-71.56	-39.33	32.23	-82.89	-50.08	32.82	-89.18	-101.51	-12.33
	308.15	-79.55	-44.79	34.76	-78.19	-48.46	29.72	-84.77	-100.99	-16.23
	313.15	-91.02	-52.67	38.35	-75.30	-47.63	27.67	-70.53	-86.09	-15.55
0.4	298.15	-82.97	-55.11	27.86	-85.80	-56.06	29.75	-80.08	-95.90	-15.82
	303.15	-72.44	-49.48	22.97	-83.98	-56.15	27.83	-90.97	-112.44	-21.47
	308.15	-80.18	-56.35	23.83	-78.92	-54.34	24.58	-86.46	-111.87	-25.41
	313.15	-91.83	-66.26	25.56	-75.61	-53.4	22.21	-71.25	-95.36	-24.10
0.6	298.15	-84.66	-56.53	28.13	-90.66	-63.63	27.03	-80.33	-86.58	-6.25
	303.15	-74.26	-50.74	23.52	-87.99	-63.73	24.26	-92.46	-101.51	-9.06
	308.15	-81.76	-57.80	23.96	-82.79	-61.68	21.11	-87.28	-100.99	-13.71
	313.15	-93.61	-67.96	25.65	-79.27	-60.62	18.65	-71.93	-86.09	-14.15
0.8	298.15	-85.99	-45.22	40.77	-94.95	-84.84	10.11	-81.30	-39.96	41.34
	303.15	-75.34	-40.60	34.75	-91.70	-84.98	6.72	-92.81	-46.85	45.96
	308.15	-84.00	-46.24	37.76	-86.03	-82.24	3.79	-90.22	-46.61	43.61
	313.15	-95.81	-54.37	41.44	-82.23	-80.83	1.41	-73.47	-39.73	33.74

The negative value corresponds to positive synergism as to the surface activity.

The standard free energy of micellization (calculated from pseudo phase separation model of ionic surfactants) per mole of monomer unit of ionic surfactants is related to counterion binding and cmc⁶⁰ (the expression accounts for the presence of two alkyl chains and two polar headgroups in the surfactant molecule).

The thermodynamic parameters of micellization (their evaluation procedure is described elsewhere³⁷) reveal that for all additives the $\Delta_{\text{mic}}G^\circ$ is negative [Tables 3 and TS2 (Supporting Information)]; however, $\Delta_{\text{mic}}H^\circ$ and $T\Delta_{\text{mic}}S^\circ$ values are negative or positive [Tables 3 and TS2 (Supporting Information)], depending upon the type and nature of the additive.

Negative Values of $\Delta_{\text{mic}}H^\circ$ and $T\Delta_{\text{mic}}S^\circ$. The value of $\Delta_{\text{mic}}H^\circ$ and $T\Delta_{\text{mic}}S^\circ$ were found to be negative for most of the systems including G4.^{37,42} The solubilization of these excipients into the micelles results into the formation of larger aggregates that end up with the release of heat with overall ordering in the system. But the spontaneity of these systems is decided by the

large negative values of $\Delta_{\text{mic}}H^\circ$. Negative values of enthalpy change ($\Delta_{\text{mic}}H^\circ$) for micellization indicate exothermic nature of micellization process. Nusselder and Engberts⁶² have suggested that for negative $\Delta_{\text{mic}}H^\circ$ the dispersion forces play a major role in the micelle formation. The $\Delta_{\text{mic}}H^\circ$ values do not vary significantly with temperature, indicating no significant variation in the environment surrounding the hydrocarbon chain of the surfactant molecule with temperature variation.

Positive Values of $\Delta_{\text{mic}}H^\circ$ and $T\Delta_{\text{mic}}S^\circ$. Nonionic and cationic hydrotropes form mixed micelles with surfactants, disturb the water structure near headgroup which increases overall entropy of the system. These hydrotropes weaken the hydrophilic interactions between the headgroups of surfactants by incorporation through preferential interaction which lowers chemical potential and enhances the solubility of amphiphile. The higher positive value of entropy compensates the enthalpic loss and makes the micellization spontaneous at higher temperature, besides the orientation and hydration. There are so many other factors which may influence the $T\Delta_{\text{mic}}S^\circ$ values like packing, microenvironment, etc.

CONCLUSIONS

The hydrotropic salt addition to gemini surfactant systems brings richer microstructure transitions. The interaction between gemini surfactants and hydrotropic salts is closely related to the charge of the salts and the structure of the gemini surfactants, including the polar headgroup and spacer. This work may advance further understanding of interaction between hydrotropic salts and gemini surfactants, and promote their applications in other fields.

The main conclusions of the present study are:

1. The experimental cmc values are lower than both the ideal as well as the component cmc's, indicating synergistic interaction. The cmc values were found to decrease with the increase in bulk mole fraction of hydrotropes.
2. The β^m values are all negative throughout the concentration range suggesting strong synergism in the mixed micelle formation. In all these systems, β^m values decrease with increase in temperature successively. The magnitude of synergistic interaction with the CTAB is less than the gemini surfactants except anionic hydrotropes.
3. Excess free energy ($\Delta_{\text{mix}}G^E$) values are negative, indicating stable mixed micellar systems which are well supported by their interaction parameters (β^m).
4. Negative values of enthalpy change for micellization ($\Delta_{\text{mix}}H^\circ$) indicate exothermic nature of micellization process. The entropy change for micellization ($T\Delta_{\text{mix}}S^\circ$) being more positive, in the systems under study, indicates micellization to be entropy driven.

ASSOCIATED CONTENT

S Supporting Information. Plots of cmc, β^m , X_1 , and X_1^{ideal} vs mole fractions of cationic/nonionic hydrotrope (α_1)-G5/CTAB mixtures at different temperatures (Figures S1–S5). The physicochemical parameters for hydrotrope–G5/CTAB at various temperatures (Table TS1). Various thermodynamic parameters for hydrotrope–G5/CTAB (Table TS1–TS3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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