Analysis of Mixed Micellar and Interfacial Behavior of Cationic Gemini Hexanediyl-1,6-bis(dimethylcetylammonium bromide) with Conventional Ionic and Nonionic Surfactants in Aqueous Medium

Kabir-ud Din,*,[†] Mohmad Shafi Sheikh,[†] and Aijaz Ahmad Dar*,[‡]

Department of Chemistry, Aligarh Muslim University, Aligarh-202 002, India and Department of Chemistry, University of Kashmir, Srinagar-190 006, J&K, India

The interaction between cationic gemini hexanediyl-1,6-bis(dimethylcetylammonium bromide) (16-6-16, abbreviated as G6) with conventional cationic cetylpyridinium chloride (CPC), anionic sodium bis(2-ethyl hexyl)sulfosuccinate (AOT) and nonionic polyoxyethylene 10 cetyl ether (Brij56) in aqueous medium has been investigated at 25 °C. Different physicochemical properties such as critical micelle concentration (cmc), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), and interaction parameters (β^m, β^σ) as well as other thermodynamic and micellar properties have been determined. The interfacial and bulk behaviors were explored using theoretical models of Clint, Rubingh, Rosen, Motomura, and Maeda for justification and comparison of results of different binary combinations with the geminis of alkanediyl-α,ω-bis(dimethylcetylammonium bromide) series. Synergism was observed in all the binary combinations in the micelle and at interface with lowering of packing parameter due to slight expansion of A_{min}. The results of the present study could be of interest for selection of surfactant mixtures for surfactant-enhanced remediation (SER) of soils and aquifers contaminated by hydrophobic organic compounds (HOCs).

Introduction

Gemini surfactants or bisquaternary ammonium surfactants have attracted the attention of various research groups. The great majority of geminis have symmetrical structures with identical chains, connected at or near headgroup by rigid or flexible spacers.[1] The superiority of geminis is almost found in all fields of surfactant applications compared to their conventional counterparts, such as, low critical micelle concentration (cmc) values,[2] better efficiency in reducing surface tension,[2,3] better wetting properties,[4] unusual micellar structure,[5] better solubilizing power, better viscoelasticity and gelification,[6] low Kraft temperatures,[7,8] and some even showing antimicrobial activity.[9,10]

New surfactant molecules have been appearing at a relatively rapid pace with the emphasis on to increase the basic performance of surfactant formulations and provision of new surfactant technologies to a diverse range of disciplines. Performance limitations of conventional surfactants have initiated interest in alternate surfactant structures. The search in developing new amphiphiles waned as performance of the commercial products could be enhanced by the judicious selection of additives. Mixed micellar systems including geminis and conventional surfactants is one remedy and is receiving much attention. Also from environmental perspective, it is highly desirable to select the surfactants from existing ones. Most of the studies, however, are made from the perspective of synergism or blending effects in surfactant mixtures,[11,12] as mixing of different species of surfactants enhances the performance.[13,14]

Various theoretical models have been proposed to interpret the formulation of mixed micelles. The first model, given by Lange[15] and used by Clint,[16] assumes ideal mixing of the surfactants in the micellar phase, which is based on the phase separation model. Rubingh[17] proposed a model based on regular solution theory (RST) for nonideal mixed systems and extensively used by different workers.[18,19] Rosen et al.,[20,21] have extended the nonideal solution treatment of Rubingh[17] for mixed micelle formation by binary surfactant systems to estimate, from surface tension data, the surfactant molecular interaction and composition in adsorbed mixed monolayer at air/water interface. But both these models neglect the electrical contribution of surfactants toward micellization.[13,17] Apart from this, Maeda's[22] approach has been used to explain the stability of mixed ionic nonionic surfactant systems. Motomura[23] proposed their model to calculate excess thermodynamic properties. Blankschtein's group[24,25] proposed a molecular thermodynamic approach as a valuable tool to predict solution properties of mixed surfactant systems. The cause of nonideality among surfactant mixtures are electrostatic interactions among ionic and polar head groups as suggested by molecular thermodynamic approach.[24–27] Sugihara et al.[28] have proposed another thermodynamic quantity for evaluation of synergism upon mixing and introduced a quantity G_{min}^s, which is the minimum free energy of the given surface with the fully adsorbed surfactant molecules. The reasons for the nonideal behavior among surfactant molecules upon mixing are the various types of molecular interactions such as (1) electrostatic interactions between ionic hydrophilic groups, (2) ion−dipole interaction between ionic and nonionic groups, (3) steric interaction between bulky head groups, (4) van der Waals interactions between hydrophobic groups, and (5) hydrogen bonding among constituent surfactant molecules.
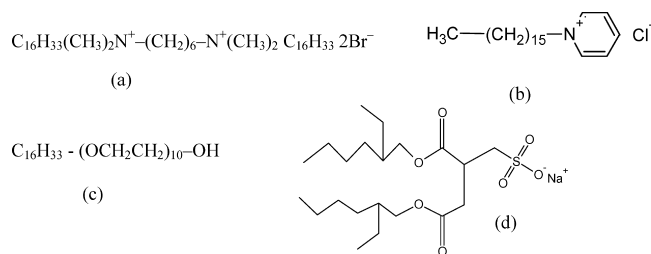
In view of the above-mentioned scenario, we have carried out studies on the mixed micellization of hexanediyl-α,ω-bis(dimethylcetylammonium bromide) (G6) with conventional cationic cetylpyridinium chloride (CPC), anionic sodium bis(2-

* To whom correspondence should be addressed. E-mail: (K.-u.D.) kabir7@rediffmail.com; (A.A.D.) aijaz_n5@yahoo.co.in. Tel.: (0571) - 2700920 ext. 3353.
[†] Aligarh Muslim University.
[‡] University of Kashmir.

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SCHEME 1: Structure of Surfactant Molecules Used in This Study: (A) Dimeric Gemini (G6), (b) Cetylpyridinium Chloride (CPC), (c) Polyoxyethylene 10 Cetyl Ether (Brij 56), and (d) Sodium bis(2-ethylhexyl)sulfosuccinate (AOT)

$C_{16}H_{33}(CH_3)_2N^+–(CH_2)_6–N^+(CH_3)_2\ C_{16}H_{33}\ 2Br^-$

(a)

$H_3C\!\!-\!\!(CH_2)_{15}\!\!-\!\!N^{+\cdot}$ ⬡ Cl^-

(b)

$C_{16}H_{33} - (OCH_2CH_2)_{10}–OH$

(c)

(d)

SCHEME 2: Protocol for the Synthesis of 16-s-16 Compounds (s = 4, 5, 6)

Reflux, dry ethanol

$Br\,(CH_2)_S\,Br + 2\ CH_3–(CH_2)_{15}–N(CH_3)_2$ ⟶ 48h, 80 °C

$C_{16}H_{33}\,(CH_3)_2N^+–\,(CH_2)_S–\,N^+(CH_3)_2C_{16}H_{33}.\ 2Br^-$

(s = 4, 5, 6)

ethyl hexyl)sulfosuccinate (AOT) and nonionic polyoxyethylene 10 cetyl ether (Brij56) surfactants (see Scheme 1) in an aqueous medium and studied their micellization and related behaviors (counterion binding, interfacial adsorption, thermodynamics of the self-aggregation process, mutual interaction, and micellar composition). Also, the comparison of the results with the butanediyl-α,ω-bis(dimethylcetylammonium bromide) (G4) and pentanediyl-α,ω-bis(dimethylcetylammonium bromide) (G5) has been presented. In addition, some experimental results of G6–SDS system have been incorporated to find effect of branching near headgroup in the case of G6–AOT system on micellization and adsorption properties of such mixed surfactant systems.

The analysis of the data has been made in the light of various theoretical models, like those of Rubingh, Rosen, Clint, Motomura, and Maeda to reveal the comparative performance of these models. Such a detailed study with dissimilar headgroups of surfactants in binary combinations has been assessed in the light of existing theories of the mixed micelle formation. This paper thus presents a systematic study of surface and micellar properties of the above-mentioned surfactants using conductometric and tensiometric techniques.

The experimental results of the present study may be of prolific use to understand and predict mixing effect on the solubilization capabilities, and for judicious selection of surfactant mixtures for surfactant-enhanced remediation (SER) of soils and aquifers. We have already started working on this aspect and our results of synergism on the solubilization of polycyclic aromatic hydrocarbons (PAHs) in binary combinations of gemini–conventional systems vis-à-vis single surfactants may be taken as a case in hand.[29]

Experimental Section

Materials. The surfactants (nonionic Brij56, cationic cetylpyridiniumchloride, CPC, and anionics sodium bis(2-ethylhexyl)-sulfosuccinate, AOT, and sodium dodecyl suphate, SDS) were all Aldrich products and used as received.

Synthesis of Gemini Surfactants. The dimeric geminis alkanediyl-α,ω-bis(dimethylcetylammonium bromides) $C_{16}H_{33}(CH_3)_2–N^+(CH_2)_S–N^+(CH_3)_2C_{16}H_{33},2Br^-$, (16-s-16, s = 4, 5, 6) (G), were synthesized by refluxing corresponding α,ω-dibromoalkane with *N,N*-dimethylcetylamine (molar ratio 2.1:1) in dry ethanol with continuous stirring at 80 °C for 48 h to ensure as much as possible a complete bisquaternization. The progress of the reaction was monitored by using TLC technique (see Scheme 2).

The solvent was removed under vacuum after the completion of the reaction.
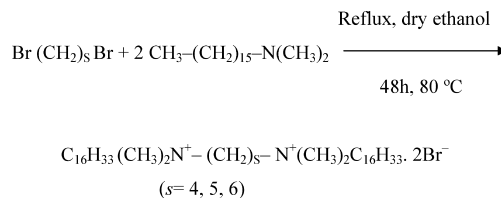
After recrystallizations, the three surfactants were characterized by ^{1}H NMR and FT-IR.[30] All of the values obtained were satisfying, which indicated that the surfactants were well purified. The purity of the gemini surfactants was further ensured by the absence of minimum in surface tension γ versus log [gemini] plots (Figure 1).

Surface Tension Measurements. The tensiometric experiments were performed using a platinum ring by the ring detachment method with a Krüss (Germany) Model K9 tensiometer. Surfactant concentration was varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing and temperature equilibration. The measured surface tension values were corrected according to the procedure of Harkins and Jordan in-built in the instrument software. Temperature was maintained at 25 ± 0.3 °C by circulating water from a HAAKE GH thermostat. The accuracy of γ measurements was within ±0.1 mN m^{-1}. The cmc values were determined by noting inflections in the γ versus logarithm of surfactant concentration isotherms.

Conductivity Measurements. The conductivity of solutions was recorded at 25 °C by a digital microprocessor based conductivity meter (CyberScan CON500) from Eutech Instruments (Singapore) having a sensitivity of 0.1 μS cm^{-1} and an accuracy of 0.5%. Temperature was maintained constant within ±0.3 °C using a constant temperature bath. The dip type conductivity probe (EC- CONSEN 21B) provided with the instrument has an inbuilt temperature probe.

All the solutions were prepared in deionized double distilled water on weight basis by dissolving appropriate amount of surfactant in appropriate volume of water (pH around 7) having conductivity in the range of 2–3 μS. The concentrations of individual surfactants were kept higher than cmc values and then mixed by appropriate volumes to obtain different bulk mole fraction binary surfactant systems. These solutions were used as stocks in both surface tension and conductivity measurements.

Results and Discussion

Surfactant–Surfactant Interactions in Mixed Micelles. Mixed surfactant systems in water undergo several physicochemical changes due to interaction between amphiphiles and invariably yield enhanced interfacial as well micellar properties. The average cmc values, determined by tensiometric and conductimetric methods (plots of G6–CPC as a prototype are shown in Figure 2 and others in Supporting Information), of pure and binary mixtures of geminis with conventional surfactants are presented in Table 1 along with the ideal cmc values. The experimental cmc values are less than ideal cmc values obtained by the use of Clint eq 1[16]

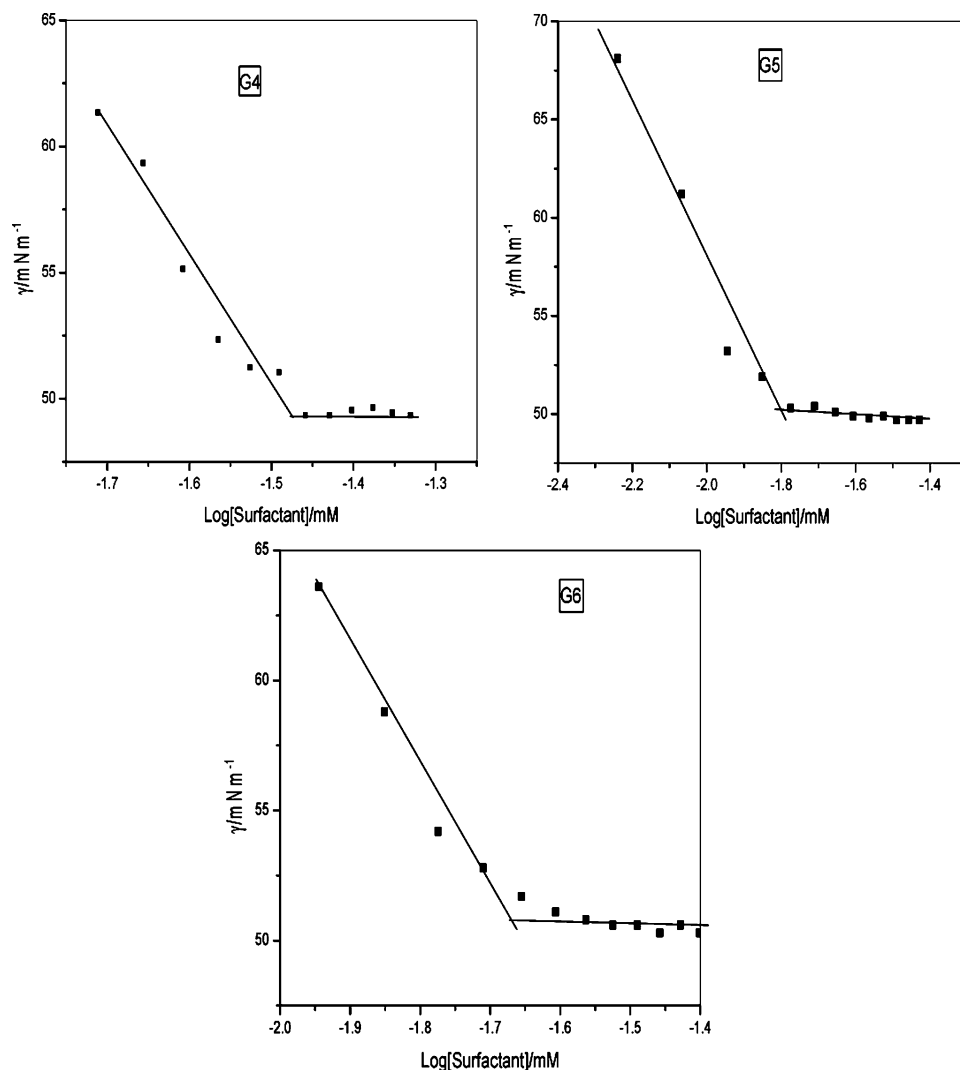$$1/cmc_{ideal} = \sum_{i=1}^{i} \alpha_i/cmc_i \qquad (1)$$

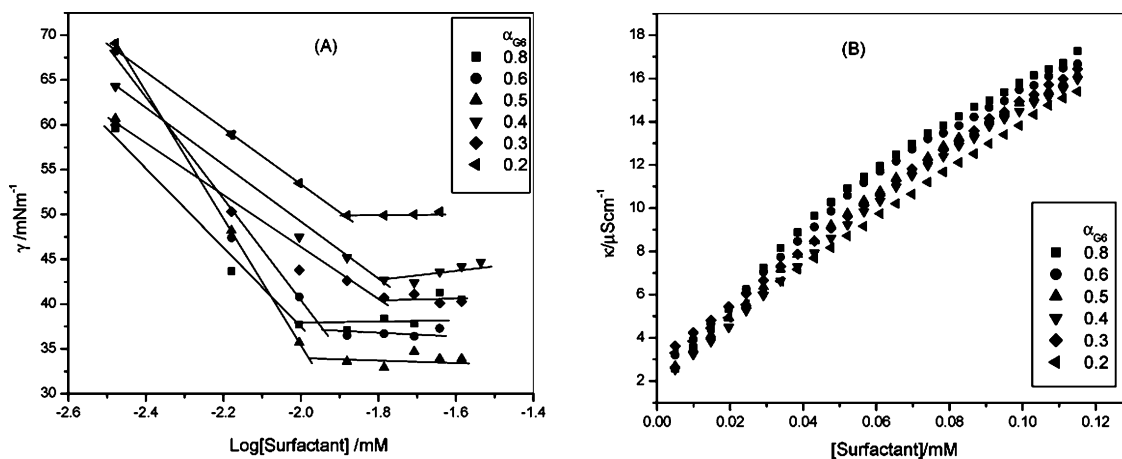**Figure 1.** Surface tension plots of gemini surfactants G4, G5, and G6 at 25 °C.

Figure 2. Surface tension (A) and specific conductivity (B) plots of Gemini G6−CPC, binary mixtures at 25 °C.

where α_i is the bulk mole fraction of the ith component in mixed surfactant solution and cmc_i is its critical micelle concentration in pure form. The Clint equation makes difference between the ideal and nonideal behaviors of surfactants in their mixtures. The obtained cmc values are lower than both the ideal as well as the component cmcs, indicating synergistic interaction. The cmc values of pure surfactants agree well with the literature values.[31−34]

The micellar mole fraction in the ideal state (X_1^{ideal}) has been computed from Motomura equation.[35] Micellar mole fraction X_1^m (calculated from Rubingh's equation discussed ahead) is less than the X_1^{ideal} in the case of binary mixtures, but little difference is observed in the case of gemini and Brij56 in all the geminis (G4, G5, G6), indicating more propensity of nonionic surfactants toward micellization. Thus we can safely conclude that the gemini surfactants partition easily into mixed micelles as compared to

TABLE 1: Micellar Parameters (Ideal and Experimental Average cmc (cmc$_{ideal}$ and cmc$_{exp}$) Interaction Parameter (β), Activity Coefficients (f_i) and Counterion Binding (g)) of Gemini G6 with Conventional Surfactants in Binary Mixtures at 25 °C

α_1	cmc$_{ideal}$ (mM)	cmc$_{exp}$ (mM)	X_1^m	β^m	f_1^m	f_2^m	g
			G6(1)−Brij56(2)				
1.0		0.0338					0.59
0.8	0.0362	0.0241	0.7018	−2.3320	0.812	0.317	0.351
0.7	0.0376	0.0242	0.6496	−2.1460	0.768	0.404	0.294
0.6	0.0391	0.0246	0.6013	−2.0043	0.727	0.485	0.286
0.4	0.0423	0.0265	0.5008	−1.8778	0.626	0.624	0.199
0.3	0.0442	0.0277	0.444	−1.9190	0.553	0.684	0.092
0.0		0.051					
			G6(1)−AOT(2)				
0.8	0.0417	0.0064	0.653	−12.206	0.2314	0.0054	0.353
0.7	0.0472	0.0073	0.643	−11.395	0.2341	0.0089	0.115
0.6	0.0540	0.0093	0.637	−10.307	0.2585	0.0152	0.064
0.5	0.0640	0.0091	0.619	−10.528	0.2178	0.0176	0.259
0.4	0.0780	0.0094	0.602	−10.694	0.18396	0.0207	0.157
0.3	0.0100	0.0107	0.585	−10.595	0.1619	0.0265	
0.0		0.68					
			G6(1)−CPC(2)				
0.8	0.0419	0.0307	0.832	−4.8140	0.873	0.0355	0.558
0.6	0.0550	0.0377	0.796	−4.1530	0.841	0.0719	0.474
0.5	0.0650	0.0368	0.744	−4.8005	0.731	0.0698	0.478
0.4	0.0800	0.0442	0.727	−4.4650	0.717	0.0942	0.388
0.3	0.0100	0.0492	0.689	−4.6740	0.637	0.1084	0.321
0.2	0.0140	0.0513	0.634	−5.5105	0.478	0.1089	0.298
0.0		1.03					0.542
			G6(1)−SDS(2)				
0.8	0.0423	0.0097	0.714	−13.8370	0.323	0.0008	0.289
0.6	0.0561	0.0138	0.702	−12.3910	0.334	0.0022	0.771
0.5	0.0673	0.0148	0.692	−12.1620	0.314	0.0097	0.822
0.4	0.0839	0.0251	0.707	−10.0940	0.420	0.0064	
0.0		8.00					0.663

conventional surfactants; this strengthens the hydrophobic environment in the mixed state resulting in onset of micellization at lower concentrations in comparison to pure state.

The estimate of negative deviation of experimental cmc from the ideal cmc and hence nonideality of mixed micellar systems can be quantified in the light of Rubingh's eq 2[17]

$$\frac{(X^m)^2 \ln(\text{cmc}_{12}\alpha_1/\text{cmc}_1 X_1^m)}{(1 - X_1^m)^2 \ln\{\text{cmc}_{12}(1 - \alpha_1)/\text{cmc}_2(1 - X_1^m)\}} = 1 \tag{2}$$

Here cmc$_1$, cmc$_2$, and cmc$_{12}$ denote the experimental cmc values of the surfactants 1, 2, and their binary mixture, respectively, X_1^m being the micellar mole fraction of surfactant 1 (G6) in the mixed micelle and α_i is the bulk mole fraction of component 1, that is, gemini. The attractive interaction between the two surfactants in the mixed micelle is accompanied by the decrease of free energy, which is measured in terms of interaction parameter β^m, given by

$$\beta^m = \frac{\ln(\text{cmc}_{12}\alpha_1/\text{cmc}_1 X_1^m)}{(1 - X_1^m)^2} = \frac{\ln(\text{cmc}_{12}\alpha_2/\text{cmc}_2 X_2^m)}{(1 - X_2^m)^2} \tag{3}$$

β^m is an indicator of degree of interaction between two surfactants in mixed micelles relative to the self-interaction of two surfactants under similar conditions before mixing and accounts for deviation from ideality. The β^m is negative (Table 1), which can be ascribed to the interaction between the head

groups leading to electrostatic stabilization. The larger the negative value of β^m, the stronger is the attractive interaction between two surfactant molecules. The β^m is an energetic parameter that represents excess Gibbs free energy of mixing and reflects two main contributions toward mixed micellization, (1) free energy contribution associated with interactions between hydrophobic groups of surfactants 1 and 2 in the micelle core, which in the case of two hydrocarbon-based (or fluorocarbon-based) surfactants are zero; and (2) electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2. The activity coefficients, f_i^m, of the two surfactants within the mixed micelle are related to the interaction parameter through equations

$$f_1^m = \exp\{\beta^m(1 - X_1^m)^2\} \tag{4a}$$

$$f_2^m = \exp\{\beta^m(X_1^{m^2})\} \tag{4b}$$

The values of β^m for all the binary combinations are negative indicating that interaction between the two surfactants after mixing are more attractive (or less repulsive) than before mixing (i.e., synergistic interaction). The β^m values, although not constant for all the binary combinations throughout the concentration ranges, are all negative with average values of (β^m_{av}) being −2.05, −5.51, −10.95, −12.12 for G6−Brij56, G6−CPC, G6−AOT, and G6−SDS, respectively, suggesting strong synergism in the mixed micelle formation. Least synergism is observed in G6−Brij56 and highest in G6−SDS and G6−AOT. Cationic geminis should bind tightly, via electrostatic and hydrophobic forces, to an anionic surfactant AOT and hence

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TABLE 2: (A) Comparison Between the Average Interaction Parameters (β_{av}) for Various Gemini-Conventional Surfactant Mixtures Obtained Using Rubingh, Rosen, and Maeda's Methods; (B) Micellar Composition (X_1^m), Excess Free Energy (g^{ex}), Activities of ionic (Gemini) and Nonionic (Brij56) (a_1, a_2), and Interaction Parameter (β^{Maeda}) from Maeda's Model[45]

(Part A)			
system	β^m_{av}	β^σ_{av}	β^{Maeda}_{av} (ref 43)
G4–CPC	−6.51	−2.45	
G4–Brij56	−2.34	−3.86	−0.283
G4–AOT	−10.23	−5.44	
G5–CPC	−9.87	−7.72	
G5–Brij56	−6.90	−9.68	−0.708
G5–AOT	−11.86	−3.98	
G6–CPC	−5.51	−3.69	
G6–Brij56	−2.05	−4.98	−0.528
G6–AOT	−10.95	−2.11	

(Part B)					
α_1	X_1^m	g^{ex}	a_1	a_2	β^{Maeda}
		G4(1)-Brij56(2)			
0.8	0.844	−0.459	0.466	0.005	−0.084
0.7	0.765	−0.424	0.451	0.009	−0.131
0.6	0.649	−0.506	0.404	0.012	−0.273
0.5	0.571	−0.582	0.322	0.015	−0.437
0.4	0.491	−0.474	0.306	0.022	−0.491
		G5(1)-Brij56(2)			
0.8	0.856	−1.027	0.281	0.003	−0.172
0.6	0.667	−1.109	0.237	0.007	−0.553
0.5	0.571	−1.157	0.198	0.009	−0.867
0.4	0.481	−1.153	0.163	0.012	−1.241
0.2			0.083	0.016	
		G6(1)-Brij56(2)			
0.8	0.842	−0.356	0.596	0.007	−0.066
0.7	0.663	−0.481	0.443	0.011	−0.244
0.6	0.562	−0.495	0.377	0.014	−0.385
0.4	0.382	−0.471	0.254	0.024	−0.761
0.3	0.278	−0.439			−1.136

the highest attraction leading to the formation of nonmicellar aggregates (such as lamella or bilayers) called "ion paired amphiphiles" or catanionic systems.[36–40] Such a strong synergistic interaction was also observed between G6 and SDS with molecular interaction parameter ($\beta^m = -12.13$) greater in magnitude that of G6–AOT binary systems well supported by low-activity coefficients of gemini ($f_1^m = 0.29$) indicating high degree of nonideality. The larger value of β^m in G6–SDS than that of G6–AOT is obviously due to steric hindrance by branching close to headgroup in AOT. This synergistic interaction and hence nonideality leads to polymorphism by complex interplay between geometric packing and electrostatic interaction. The existence of synergism in mixtures containing surfactants depends not only on the strength of interaction but also on the relevant properties of individual surfactants of the mixture.[41]

Comparison of average values reveals that β^m_{av} is highest for G5–conventional surfactants among G4, G5, and G6 in all the three cases (Table 2 part A), while it is least for gemini–nonionic combinations. The gemini monomers in solution exist such that the two hexadecyl chains are on the same side to allow for the intramolecular interaction between two alkyl chains of the molecule. This arrangement of alkyl chains in gemini G5 presents least conformational strain, which allows for maximum interaction among G5–conventional binary systems and hence highest synergism.[31] The bimodal distribution

of distances between the head groups, one from electrostatic repulsions between head groups (the thermodynamic distance) and another from the distance that corresponds to the length of the spacer, are known to affect the properties of gemini surfactant micelles significantly.

In aqueous solutions, strong coulombic repulsions between the two positively charged headgroups within a surfactant unit makes the spacer chain fully stretched, however, the unfavorable contact with water makes it shrink toward the hydrophobic nucleus. Therefore, a critical distance between the two head groups will result to balance these two opposing tendencies for gemini with spacer 5, that is, G5. The micellar mole fraction of the gemini surfactant (X_1^m) is higher in the mixed micelle even in the poor region of the geminis thus indicating their higher propensity toward micellization. Among binary combinations, least attractive interaction is observed in the gemini–nonionic and highest in the gemini–anionic. For gemini–anionic, opposite charges usually exhibit highest electrostatic interaction whereas in gemini–cationic, interaction of N$^+$ with π-electron cloud of pyridine ring exists, besides hydrophobic interactions. The nonionic surfactant Brij56 with poly(oxyethylene) has a large number of oxygen atoms with lone pair of electrons and will have a tendency to interact Coulombically with the cationic gemini surfactants. However, because of the presence of long oxyethylene headgroup in nonionic surfactant, thermal vibrations might be imposing some steric constraints restricting the effective headgroup interactions between gemini and nonionic surfactant and hence lead to the lesser value of interaction parameter.

The micellar mole fraction of the G6 is higher than the conventional surfactants (Table 1), which is well supported by their activity coefficients calculated from eq 4a. The activity coefficients (f_1^m) of the G6 is reasonably higher than the conventional surfactant (f_2^m), though both are less than unity, indicating nonideal behavior and attractive interaction between surfactants in the micelle. The highest deviation in f_1^m and f_2^m is found in gemini–AOT and G6–SDS whereas least deviation is found in the gemini–Brij56 binary systems, which is also supported by the values of X_1^m, in conformity with the earlier findings of Errico et al.[42] The lowest interaction is found in the gemini–Brij56, which shows that long-range electrical interactions are absent. According to Maeda[43] and Ruiz and Aguair,[44] both chain–chain and headgroup–headgroup interactions may operate in the mixed system. Maeda[22,43] suggested another parameter B_1, the chain–chain interaction parameter, which contributes to the stability of mixed micelles; this parameter is neglected by β^m, which encompasses only head–head interactions.

The free energy of micellization (ΔG°_{Maeda}), as a function of ionic component in the mixed micelle X_i^m, is given by

$$\Delta G^\circ_{Maeda} = RT[B_0 + B_1 X_1^m + B_2 (X_1^m)^2] \quad (5)$$

where

$$B_0 = \ln C_2 \quad (C_2 \text{ is the cmc of nonionic surfactant})$$
$$B_1 + B_2 = \ln(C_1/C_2) \quad (C_1 \text{ is the cmc of ionic surfactant})$$
$$B_2 = -\beta^m$$

The parameter B_1, as per Maeda's model, is related to the standard free energy change associated with the introduction of ionic species into nonionic micelle coupled with the release of one nonionic species from the micelle. Thus it consists of

two different contributions, the interaction between head groups and between hydrocarbon chains. In the case of G4, G5, and G6 chain lengths are comparable with Brij56, then negative value of B_1 is determined primarily by the interaction between head groups (chain−chain interactions are negligible). This explains the negative values of B_1 found throughout the bulk mole fraction range [in systems containing nonionic Brij56] (G4−Brij56, −3.53, −2.81,−2.79,−2.94,−2.45; G5−Brij56, −6.11, −5.21, −5.18, −5.11,−15.34, and G6−Brij56, −2.74, −2.56, −2.42, −2.29, −2.33) The highest negative values of B_1 for G5−Brij56 confirm its stability in comparison to G4 and G6 counterparts.

Another theoretical model of Maeda[45] is based on the Gibbs−Duhem equation to predict the excess free energy (g^{ex}) of the ionic-nonionic mixed micelles. This model relates g^{ex} with X_1^m (micellar mole fraction of ionic surfactant) as

$$g^{ex} = X_1^m(\ln f_1) + (1 - X_1^m)\ln f_2 \quad (6a)$$

$$X_1^m = \frac{\alpha_1\left[1 - (1 - \alpha_1)\left(\dfrac{d \ln cmc_{mix}}{d\alpha_1}\right)\right]}{\left[1 + g(1 - \alpha_1)\left\{\alpha_1\left(\dfrac{d \ln cmc_{mix}}{d\alpha_1}\right) + 1\right\}\right]} \quad (6b)$$

The activities of ionic (a_1) and nonionic (a_2) components are calculated from

$$a_1 = (\alpha_1 cmc_{mix}/C_1) \quad (6c)$$

$$a_2 = (1 - \alpha_1)cmc_{mix}/C_2 \quad (6d)$$

and then β^{Maeda} from

$$\beta^{Maeda} = g^{ex}/X_1^m(1 - X_1^m) \quad (6e)$$

Here C_1, C_2, and cmc_{mix} are the cmc's of ionic (gemini), nonionic (Brij56) surfactants, and their mixtures, respectively, and g is counterion binding constant (details ahead).

Table 2B shows that micellar mole fractions are higher than the corresponding stoichiometric mole fractions. For all the systems, β^{Maeda} and g^{ex} values are negative throughout (Table 2B), which increase with the mole fraction of nonionic surfactant, indicating synergism. The average β^{Maeda} values also confirm least conformational strain with highest interaction from G5−Brij56 compared to G4−Brij56 and G6−Brij56. The difference in β values (obtained from Rubingh's and Maeda's models) is ascribed to counterion binding that has been neglected while using Rubingh eq 3. The excess free energy is highest for G5−Brij56, which shows the maximum deviation for this system. The comparison between the interaction parameters using theoretical models of Rubingh and Maeda have been presented in the Table 2A.

Counterion Binding (g). In ionic micelles, the layer just adjacent to the surface of the micelles is known as Stern layer to which counterions are bound strongly and migrate with micelles in an electrical field, as influence of thermal agitation is negligible on it. Following the procedure of Evans,[46] the counterion association (g) properties of the pure and mixed micelles have been evaluated from the degree of dissociation

(obtained from the ratio of post- to premicellar slopes using the specific conductance (κ) isotherms). Although conductivity method neglects the mobility of charged micelles due to simplicity of experimentation, calculation, and understanding, it is the most frequently used method. In case of G6−AOT, much lower counterion association (Table 1) may be attributed to the complex formation, which reduces charge density. Among G4, G5, and G6, G5−AOT shows slightly higher counterion association, again showing the least conformational strain in G5. The surface charge density of formed mixed micelles is dependent on the head groups of the components, since their tails in the two binary systems are identical. In systems with unequal chain lengths, however, surface charge density is also dependent on the tail length. Decreased surface charge density of the micelles with increased molecular heterogeneity of mixed surfactant systems may occur due to increased micellar size by interamphiphile repulsive interactions. The pyridinium group is structurally smaller than the other two head groups, and the facile delocalization of the π-electron cloud over the sp²-hybridized carbon atoms and the nitrogen atom of the pyridinium ring causes the gemini−CPC micelles to have a higher surface charge density and hence increased g values. The increased counterion association reduces cmc.

Properties of Surfactant Mixtures at Air/Water Interface. Because of the presence of hydrophobic effect, surfactant molecules adsorb at interfaces, even at low surfactant concentrations, hence decrease the surface tension of water. Dynamic equilibrium exists between the adsorption and desorption (due to thermal motions). Surfactant adsorption may occur due to electrostatic interaction, van der Waals interaction, hydrogen bonding, and/or solvation and desolvation of adsorbate and adsorbent species. The concentration of surfactant is always more at the surfaces than that in the bulk. The amount of surfactant adsorbed per unit area of the surface can be calculated with the help of Gibbs adsorption equation.

For surfactant mixtures in water, the Gibbs surface excess is related to surface pressure [$\pi = \gamma_o - \gamma_s$] (where γ_o and γ_s are surface tensions of pure solvent and solution respectively) by the relation $d\pi = \Sigma \Gamma_i RT \, d \ln a_i$ (Γ_i is surface excess, a_i is activity of the ith component at temperature T). The surface excess Γ_{max} (mol m⁻²) is an effective measure of adsorption at air /water interface. The values of surface excess and minimum area per molecule A_{min} (Å²) were calculated using eqs 7 and 8[21]

$$\Gamma_{max} = -(1/nRT)d\gamma/d \ln c \quad (7)$$

$$A_{min} = 10^{20}/N_A\Gamma_{max} \quad (\text{Å}) \quad (8)$$

where $d\gamma/d \ln c$ is the maximum slope and R, T, c, and N_A are gas constant, temperature, concentration, and Avogadro's number, respectively. The slope of the tangent near the cmc of γ versus $\ln c$ has been used for the calculation. The number of species whose concentration at the interface vary with the surfactant bulk phase concentration (n) were taken as 3.[7] Surface excess is a measure of effectiveness of the surfactant adsorption and has number of applications such as ore floatation, improved oil recovery, in situ and ex situ soil remediation, detergency, wetting, surfactant-based separation processes, as coherently packed interfacial films have different properties from that of noncoherent loosely packed films.

The minimum area per molecule is higher in mixed surfactant systems than the conventional surfactants but lower

than the pure gemini surfactants except in few cases (Table 3) and is also lower than the ideal one. The low A_{min} values (Table 3) suggest that surfactant molecules are close packed at air/water interface so that their orientation is almost perpendicular to the interface. In case of G6–CPC, with decrease in G6 mole fraction the A_{min} values generally decrease and Γ_{max} increase possibly due to (a) bigger size of G6, (b) increase in delocalized π-electron interaction with the gemini with increase in CPC mole fraction, and (c) additional π–π electron interactions between CPC head groups.[47] In the case of G6–Brij56, insertion of Brij56 monomers will increase A_{min}, but at the same time reduce the self-repulsion of cationic and nonionic surfactants upon mixing due to dilution effects and some ion–dipole interaction after mixing; while in the case of G6–AOT, larger A_{min} than other two systems is due to bulky AOT molecules having branching close to hydrophilic group, though having electrostatic attraction between the head groups (see Scheme 1). In the case of G6–SDS system, the A_{min} values are lowest of all the three systems due to strong electrostatic interactions and less steric factor between G6 and single chain anionic surfactant SDS (Table 1S in Supporting Information).

Surfactant–Surfactant Interactions at Air/Water Interface. The interfacial compositions (X_1^σ) and interaction parameters (β^σ) between two surfactant molecules at the Langmurian monolayer formation were determined (Table 3) using Rosen's approach.[20,21] For an ideal monolayer, amphiphile–amphiphile interaction parameter β^σ is zero while as, negative and positive for synergistic and antagonistic interactions, respectively. This can be obtained from the surface tension isotherms of aqueous solutions of the individual surfactants and their mixtures. From the analogy with the derivation of Rubingh's equation, the mole fraction of surfactant 1, α_1, in solution is related to its mole fraction in mixed monolayer, X_1^σ, by the equation

$$\frac{\left[(X_1^\sigma)^2 \ln\left(\frac{C_{12}^s \alpha_1}{C_1^s X_1^\sigma} \right) \right]}{\left[(1 - X_1^\sigma)^2 \ln\left(\frac{C_{12}^s (1 - \alpha_1)}{C_1^s (1 - X_1^\sigma)} \right) \right]} = 1 \quad (9)$$

where C_1^s, C_2^s and C_{12}^s are the molar concentrations of component 1, 2 and mixed surfactants in the bulk solution at a given surface tension reduction. The interaction parameter β^σ in the mixed monolayer at the air/aqueous solution interface is given by

$$\beta^\sigma = \ln(C_{12}^s \alpha_1 / C_1^s X_1^\sigma)/(1 - X_1^\sigma)^2 \quad (10)$$

The activity coefficients f_1^σ and f_2^σ of the surfactants in the mixed monolayer are related to β^σ as

$$f_1^\sigma = \exp\{\beta^\sigma (1 - X_1^\sigma)^2\} \quad (11a)$$

$$f_2^\sigma = \exp\{\beta^\sigma (X_1^\sigma)^2\} \quad (11b)$$

In mixed micelles X_2^m values are less than X_1^m showing more propensity of the Gemini surfactants toward micellization whereas in monolayer X_2^σ is almost equal to or greater than X_1^σ (Table 3). From the use of Rosen's formulation, less mole fraction of gemini (compared to bulk mole fraction) is incorporated into the mixed monolayer, depicting its greater micellization tendency. The calculated values of surface interaction parameters (β^σ) are negative with the respective average values being -2.11, -4.92, and -3.69 for G6–AOT, G6–Brij56, and G6–CPC. The negative β^σ values, in the case of gemini–CPC, indicate an overall attractive interaction between the two

TABLE 3: Interfacial Composition (X_1^σ), Interaction Parameter at Interface (β^σ), Surface Excess (Γ_{max}), Minimum Area per Molecule (A_{min}), and Packing Parameters (p) of Gemini G6 with Conventional Surfactants at 25 °C

α_1	X_1^σ	β^σ	f_1^σ	f_2^σ	γ_{cmc}	$10^6\ \Gamma_{max}$ (mol m^{-2})	A_{min}/A^{ideal}_{min} (Å^2)	p
					G6(1)-AOT(2)			
1.0					52.0	2.40	200.12	0.21
0.8	0.57	−4.43	0.45	0.22	40.8	0.95	174.1/186.3	0.24
0.7	0.55	−2.67	0.58	0.44	49.3	1.30	127.2/179.5	0.33
0.6	0.50	−3.45	0.42	0.41	46.4	1.09	151.9/172.6	0.27
0.5	0.46	−2.96	0.42	0.53	52.7	1.32	125.7/165.8	0.33
0.4	0.34	−0.44	0.83	0.94	50.8	1.29	128.7/158.9	0.32
0.3	0.26	−0.38	0.81	0.97	54.4	1.25	132.8/152.1	0.31
0.2	0.18	−0.46	0.73	0.98				
0.0					40.2	1.26	131.06	0.32
					G6(1)-Brij56(2)			
0.8	0.62	−4.04	0.69	0.13	45.2	1.43	115.6/177.8	0.36
0.6	0.64	−4.58	0.55	0.14	39.2	1.42	116.4/155.5	0.36
0.5	0.62	−4.03	0.56	0.21	37.0	1.52	108.9/144.4	0.38
0.3	0.51	−5.81	0.25	0.21	37.2	1.47	112.4/133.3	0.37
0.2	0.47	−6.13	0.19	0.24	37.2	1.44	115.1/122.1	0.36
0.0					32.8	1.26	88.66	0.47
					G6(1)-CPC(2)			
0.8	0.57	−7.09	0.27	0.09	37.3	1.14	145.1/174.4	0.29
0.6	0.52	−5.63	0.27	0.21	36.1	0.95	173.8/148.6	0.24
0.5	0.49	−5.87	0.22	0.23	33.5	2.59	64.2/135.8	0.65
0.4	0.45	−3.69	0.33	0.45	42.3	1.31	126.9/122.9	0.33
0.3	0.43	−5.46	0.17	0.34	40.0	1.36	121.1/110.1	0.34
0.2	0.37	−3.65	0.23	0.60	49.4	1.75	94.6/97.2	0.44
0.0					31.3	2.32	71.5	0.58

TABLE 4: Thermodynamic Parameters (Free Energy of Micellization (ΔG°_m), Free Energy of Adsorption (ΔG°_{ad}), Surface Free Energy (G^s_{min}), Excess Free Energy (ΔG_{ex}), and Free Energy of Micellization from Maeda's approach (ΔG°_{Maeda})) of Gemini G6 and Conventional Surfactants at 25 °C

α_1	ΔG°_m (kJ mol^{-1})	ΔG°_{ad} (kJ mol^{-1})	G^s_{min} (kJ mol^{-1})	ΔG_{ex} (kJ mol^{-1})	ΔG°_{Maeda} (kJ mol^{-1})
			G6(1)-AOT(2)		
1.0	−71.74	−80.08	62.70		
0.8	−67.57	−100.28	42.79	−6.93	
0.7	−48.33	−65.66	37.84	−6.48	
0.6	−43.64	−73.75	54.61	−5.91	
0.5	−58.79	−73.38	39.91	−6.19	
0.4	−50.26	−67.25	39.45	−6.13	
0.0	−28.02	−53.81	31.85		
			G6(1)- CPC(2)		
0.8	−75.58	−105.88	32.60	−1.69	
0.6	−68.59	−106.13	37.83	−1.72	
0.5	−69.02	−83.89	12.97	−2.28	
0.4	−61.89	−85.19	32.35	−2.25	
0.3	−56.66	−80.57	29.22	−2.54	
0.2	−56.01	−69.33	28.18	−3.22	
0.0	−56.39	−56.39	13.5		
			G6(1)-Brij56(2)		
0.8	−61.82	−80.02	31.92	−1.21	−7.38
0.6	−57.68	−80.63	27.52	−1.25	−6.85
0.5	−57.01	−79.96	24.29	−1.21	−6.63
0.3	−50.46	−74.51	25.23	−1.18	−5.83
0.2	−42.61	−67.25	25.84	−1.19	−5.39
0.0	−34.43	−66.07	17.53		
			G6(1)-SDS(2)		
0.8	−64.87	−81.63	37.86	−7.05	
0.6	−96.05	−115.51	28.91	−6.43	
0.5	−99.08	−112.47	20.29	−5.53	
0.4			16.01	−5.15	

surfactants; the van der Waals interaction between hydrophobic tails is, therefore, the prevailing factor over electrostatic repulsion. These negative values of β^σ show synergism in mixed monolayer formation. Among all the three systems of G4−conventional, G5−conventional, and G6−conventional, only gemini−Brij56 combination showed greater negative value of β^σ_{av} than their β^m_{av} values (Table 2A), indicating more interactions between the surfactants in mixed monolayer than in mixed micelles. The rest of the combinations between gemini−conventional ionics showed more interactions in mixed micelles than in mixed monolayer. For ionic−nonionic surfactant systems, β^σ_{av} is more than β^m_{av} because reduction of electrostatic repulsion of the ionic groups is more effective at the planar air/aqueous solution interface than at the convex micelle surface.[21,48] The opposite trend in the gemini−conventional ionic surfactant systems might be due to following reasons: (a) similar charged headgroup of CPC, giving more contribution to head−head repulsions in gemini−CPC system without any effective compensation through hydrophobic interactions as prevalent inside the mixed micelles; (b) though electrostatic interactions are favorable in gemini−AOT systems, bulky headgroup nature of AOT molecules together with the branching in the vicinity of headgroup increases unfavorable steric contribution to form mixed monolayer where freedom of molecules is not as restricted as in the case of mixed micelles.

The surface area of amphiphiles in mixed micelles can be used to find out the packing parameter, $p\ (= V_0/l_c A_{min}$, V_0 is the volume of exclusion per monomer in the aggregate, given by Tanford's formula[41] $V_0 = [27.4 + 26.9(n_c - 1)]2$ Å^3, $l_c = [1.54 + 1.26(n_c - 1)]$ Å is the maximum chain length, and n_c is the number of carbon atoms in the hydrocarbon chain).[49] The A_{min} refers to a property related to the surfactant monolayer at the air/water interface and in reality different from the required A value at the micellar surface. In the absence of exact estimation and also because the determination of the headgroup area on the micellar surface is comparatively difficult, we have used A_{min} values in our calculations. The packing parameter determines the geometry of micelles and indicates minimum sized aggregates in solution, which minimizes the Gibbs free energy of micellization. The low values of packing parameter ($p < 1/3$) in the case of G6−AOT and G6−Brij56 indicate spherical micelles formation whereas in the G6−CPC mostly nonspherical micelles are formed. In gemini−Brij56, the size of the mixed micelles in the solution is mainly determined by the repulsions between head groups due to steric origin for oxyethylene head groups and electrostatic origin for quaternary ammonium head groups and also by the packing parameters of the surfactants composing the mixture. The unique behavior in the packing parameter is observed at equal concentrations of the geminis (G4, G5, G6) and conventional surfactants. For these surfactants, the ratio V_0/l_c is constant and only the A_{min} makes the difference in their packing parameters. The A_{min} and g values are the manifestations of the activities of the individuals in isolation and in mixtures. A difference in this respect was found for the gemini−CPC combinations. Their micellar packing parameter p were also moderately higher. The micelles were to some extent nonspherical; their higher surface charge density yielded higher g values. A vesicle can form when the surfactant packing parameter p is in the range 0.5−1. When cationic and anionic surfactants are mixed, A_{min} is significantly reduced, increasing p to 0.5−1, leading to formation of vesicles. This is evident in the case of G6−SDS at higher mole fractions on SDS. However, values of p are lower than 0.5 in G6−AOT due to high A_{min} values as discussed earlier. Moreover, for a gemini molecule, the spacer group counteracts the strong electrostatic effect between head groups, which decreases A_{min}

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compared to what it would be for two conventional single chain surfactants. These effects might give a some explanation about the formation of vesicles in such systems.[39]

Thermodynamics of Micellization and Interfacial Adsorption Phenomena. The standard free energy of micellization per mole of monomer unit (ΔG°_m) for the binary combinations in the case of ionic gemini surfactants is related to cmc through the eq 12[50]

$$\Delta G^\circ_m = (3 - 2g_1)RT \ln X_{cmc} \qquad (12)$$

X_{cmc} is cmc in mole fraction units and g_1 is degree of dissociation. The ΔG°_m values (Table 4) reveal that all the binary systems have considerable spontaneity of micellization. The standard free energy of micellization (ΔG°_m) is translated into the standard free energy of adsorption (ΔG°_{ad}) at the air/water interface using eq 13[51]

$$(\Delta G^0_{ad}) = (\Delta G^0_m) - (\pi_{cmc}/\Gamma_{max}) \qquad (13)$$

where π_{cmc} is the surface pressure at cmc.

Both ΔG^0_m and ΔG^0_{ad} are negative and their magnitudes reveal the latter to be more spontaneous due to hydrophobicity of amphiphiles, which leads them toward air/water interface. From this it is concluded that micelle formation is secondary and less spontaneous compared to adsorption. The micellization and adsorption tendency of G6−SDS is higher than that of G6−AOT due to strong electrostatic interaction between opposite charges and absence of any steric hindrance.

The synergism in the mixed adsorbed monolayer formation can also be quantified in terms of another thermodynamic quantity, known as free energy $G^s_{min} = A_{min}\gamma_{cmc}N_A$ of a surface at equilibrium,[28] γ_{cmc} being the surface tension of the surfactant system at equilibrium. G^s_{min} not only contains contribution of A_{min} but also γ_{cmc}, which affects mixed monolayer formation, hence synergism. It may be defined as work needed to make a surface area per mole or free energy change accompanied by transition from the bulk phase to the surface phase of solution. The lower the value of free energy, the more thermodynamically a stable surface is formed or the more surface activity is attained, which is a measure of evaluation of synergism. Since the obtained values are lower in magnitude (Table 4), it can be inferred that thermodynamically stable surfaces are formed with synergistic interaction not only with the G6 but with G5 and G4 too.

The excess free energy of micellization, ΔG_{ex}

$$\Delta G_{ex} = [X_1 \ln f_1 + (1 - X_1)\ln f_2]RT \qquad (14)$$

in the case of G6−CPC and G6−Brij56 is lower compared to G6−SDS and G6−AOT, whereas in the case of G6−CPC, with increase in mole fraction of CPC, stability of micelles increases (Table 4) in accordance with their interaction parameters. The average values of ΔG_{ex} are −1.21, −2.28, −6.33, and ∼−6.33 (kJmol^{-1}) for G6−Brij56, G6−CPC, G6−AOT, and G6−SDS, respectively.

Conclusions

Mixing of gemini surfactants with conventional surfactants are important from industrial as well as research point of view, because their properties get blended with enhancement of micellar and surface properties. To gain further insight of the

mixing behavior, we have carried out studies on the mixed micellization and monolayer formation of gemini (G6) with CPC, AOT, and Brij56 in binary combinations.

The following are the main conclusions:

1. The cmc values of binary mixtures are less than the ideal cmc values obtained by the use of Clint equation.

2. The micellar mole fraction of the gemini surfactant is higher than the conventional surfactants, even in the poor region of gemini showing more propensity of gemini toward micellization.

3. Highest synergism in mixed micelle formation is observed in G6−AOT and lowest in G6−Brij56.

4. Among the three geminis (G4, G5, G6), the highest synergistic interaction is observed between G5−conventional surfactants rationalized in terms of cis conformation with the least conformational strain.

5. The interaction parameters in the micelle as well as at interface are negative, indicating synergistic interaction.

Supporting Information Available: Plots of binary mixtures of surface tension and conductivity of G6−Brij56 and G6−AOT. Also some interfacial parameters of G6−SDS. This material is available free of charge via the Internet at http://pubs.acs.org.

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