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Surface Properties and Mixed Micellization of Cationic Gemini Surfactants with Ethyleneamines

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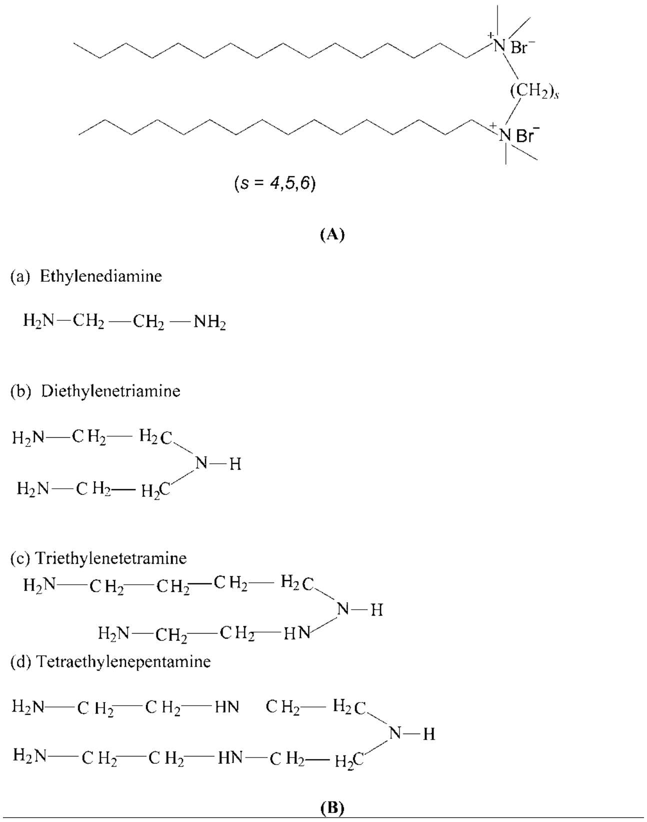
Herein, we report the surface properties and mixed micellization of cationic gemini surfactants (butanediyl-1,4-bis(dimethylcetylammonium bromide), pentanediyl-1,5-bis(dimethylcetylammonium bromide), and hexanediyl-1,6-bis(dimethylcetylammonium bromide), respectively referred to as 16-4-16, 16-5-16, and 16-6-16) in the presence of different mole fractions of ethyleneamines (ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine) at 303 K. The surface properties (critical micelle concentration (CMC), C_{20} (surfactant concentration required to reduce the surface tension of the solvent by 20 $\text{mN}\cdot\text{m}^{-1}$), $\Gamma_{\max}$ (maximum surface excess), $A_{\min}$ (minimum surface area per molecule), and interaction parameter β (for mixed monolayer formation at the aqueous solution/air interface (β^{σ}) and for mixed micelle formation in aqueous medium (β^{m})) are reported. A synergistic effect has been observed in all instances that were found to be correlated with the chain length of ethyleneamines. The CMC values of 16-*s*-16 decreased with increasing amine concentrations, and the extent of the effect followed the sequence: tetraethylenepentamine > triethylenetetramine > diethylenetriamine > ethylenediamine and 16-6-16 > 16-5-16 > 16-4-16. The standard Gibbs energies of adsorption ($\Delta G^{0}_{\text{ads}}$) and the excess free energies of micellization (ΔG_{ex}) of 16-*s*-16 with the amines were also evaluated.

Introduction

Surfactants have received wide attention because of their efficient solubilization, suspension, dispersion, and transportation properties.[1] In the present era, the rising demand for newer materials with improved and novel properties has given emphasis to the studies of surfactant–additive systems. Most of the studies are made from the perspective of synergism in mixtures.[2,3] This synergistic phenomenon can also be highly beneficial for the environment as it allows lesser amounts of surfactants to be released and their impact to be substantially reduced.[4] Despite a vast literature available on conventional surfactants, the studies on the effect of additives on gemini surfactants (having two hydrophilic (mainly ionic) groups and two tails per surfactant molecule linked by a spacer group) are still scant. Gemini surfactants possess a number of superior properties compared to conventional single-headed, single-tailed surfactants.[5] So far the most investigated geminis have been the alkanediyl-α,*ω*-bis(dimethylcetylammonium bromide) (so-called m-*s*-m type). Studies of solubilization of organic compounds in gemini micellar solutions are still scarce.[6,7] The addition of KBr to a solution of gemini surfactant causes the formation of a lamellar phase followed by phase separations.[8] Studies by Kabir-ud-Din et al.[9−15] on the influence of a variety of additives (organic/inorganic compounds, nonelectrolytes, surfactants, etc., using viscometry, tensiometry, DLS, and ^{1}H NMR techniques) have yielded important results including structural transitions and growth of micelles in gemini solutions. The results on the effect of aromatic acids/salts added to 16-*s*-16 (s = 4, 5, 6) need special mention as the site of solubilization has been located on the basis of ^{1}H NMR studies.[14,15] Further,

Scheme 1. Molecular Structure of (A) Gemini Surfactants (Butanediyl-1,4-bis(dimethylcetylammonium Bromide), 16-4-16; Penanediyl-1,5-bis(dimethylcetylammonium Bromide), 16-5-16; Hexanediyl-1,6-bis(dimethylcetylammonium Bromide), 16-6-16) and (B) Ethyleneamines



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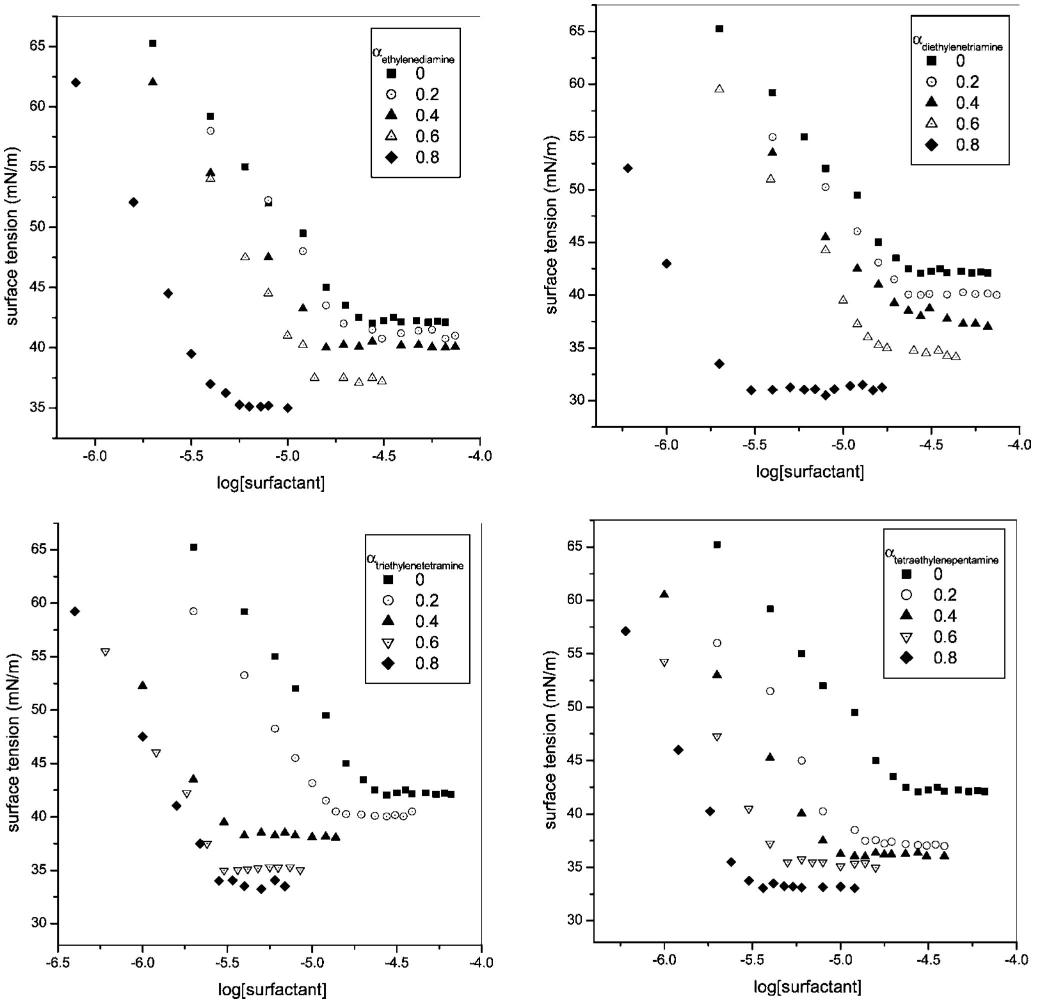

Figure 1. Plots of surface tension (γ) with the logarithm of the gemini surfactant 16-4-16 concentration (log C_t) at different fixed concentrations of ethyleneamines.

tensiometric, conductometric, and fluorescence studies with amines,[16,17] alkanols,[16,18] and conventional surfactants[19−22] have shown formation of gemini-additive mixed micelles with synergism.

Among various additives, amines are potential candidates as cosurfactants in microemulsions. As evident from above, reports pertaining to the effect of amine additives on the micellization of gemini surfactants are rare.[16,17] Polyamines are distributed in living tissues and are of great importance in a number of cellular functions, including protein synthesis.[23] Blood and saliva contain various amines and polyamines.[24,25] The purpose of selecting the present systems is to find out the effect of various amine additives on the gemini surfactants, which can further be used for drug encapsulation and delivery. Thus, the experimental results of this study may be useful in understanding and predicting the surfactant selection for controlled drug release and targeted delivery.

Here, we report a detailed tensiometric study of the mixed micellization and interfacial behavior of gemini surfactants with different mole fractions of ethyleneamines at 303 K. The chemical structure of gemini surfactants and ethyleneamines are presented in Scheme 1. To the best of our knowledge, this is the first report on gemini/ethyleneamine systems.

Materials and Methods

The additives ethylenediamine (≥ 99 %, Fluka, Switzerland), diethylenetriamine (≥ 97 %, Fluka, Switzerland), triethylenetetramine (99 %, Loba Chemie, India), and tetraethylenepentamine (85 %, Fluka, Switzerland) were used as received. The gemini surfactants alkanediyl-α,ω-bis(dimethylcetylammonium bromides), $C_{16}H_{33}(CH_3)_2N^+-(CH_2)_S-N^+-(CH_3)_2C_{16}H_{33}\cdot 2Br^-$, (16-*s*-16, $s = 4, 5, 6$) 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 biquaternization. The reactions were completed in single batch. The progress of the reaction was monitored by using the thin-layer chromatography (TLC) technique. The solvent was removed under vacuum after completion of the reaction. An ethanol/ethylacetate mixture was used for recrystallization (at least three times).

After recrystallizations, all of the three surfactants were characterized by ^{1}H NMR and Fourier transform infrared chromatography (FT-IR). All of the values obtained were in agreement with the literature values.[14,26] The purity of the gemini surfactants was further ensured by the absence of a minimum in surface tension versus log[surfactant] plots (Figure 1). Pertinent details are given below:

16-4-16. ^{1}H NMR (solvent $CDCl_3$): δ 0.88 (t, 6H, alkyl chain $2\cdot 1CH_3$), 1.25−1.40 (br m, 44H, alkyl chain $2\cdot 11CH_2$), 1.70−2.00 (m, 12H, alkyl chain $2\cdot 3CH_2$), 2.20 (br s, 4H, spacer chain $1\cdot 2CH_2CH_2N^+$), 3.30 (s, 12H, $2\cdot 2N^+CH_3$), 3.40−3.50 (m, 4H, alkyl chain $2\cdot 1CH_2N^+$), 4.00 (br s, 4H, spacer chain $2\cdot 1CH\ _2N^+$). IR ν_{max} (KBr): C-*N* = 1043.08 cm^{-1}.

Table 1. Effect of Additive (Ethyleneamines) Concentrations on the CMC (Determined by Surface Tension Measurements), C_{20}, CMC/C_{20}, Π_{CMC}, $A_{\min}$, $\Gamma_{\max}$, $\Delta G^0_{\mathrm{ads}}$, and $G^{(s)}_{\min}$ Values of Cationic Gemini Surfactants, 16-4-16, 16-5-16, and 16-6-16, in Aqueous Solutions at 303 K

α_{amine}	$\mathrm{CMC}\cdot 10^5$ / $\mathrm{mol}\cdot\mathrm{dm}^{-3}$	$C_{20}\cdot 10^5$ / $\mathrm{mol}\cdot\mathrm{dm}^{-3}$	CMC/C_{20}	Π_{CMC} / $\mathrm{mN}\cdot\mathrm{m}^{-1}$	$\Gamma_{\max}\cdot 10^6$ / $\mathrm{mol}\cdot\mathrm{m}^{-2}$	$A_{\min}$ / Å^2	$-\Delta G^0_{\mathrm{ads}}$ / $\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	$G^{(s)}_{\min}$ / $\mathrm{kJ}\cdot\mathrm{mol}^{-1}$
(A) 16-4-16								
Ethylenediamine								
0	2.72	0.83	3.27	30.00	1.66	100.0	44.554	25.297
0.2	2.34	1.09	2.15	30.76	2.15	77.2	41.168	19.176
0.4	1.54	0.60	2.61	31.69	2.26	73.5	41.937	17.835
0.6	1.38	0.63	2.18	34.24	2.87	57.9	40.121	13.157
0.8	0.46	0.24	1.91	36.62	2.91	57.1	43.543	12.157
Diethylenetriamine								
0.2	2.19	0.91	2.40	31.94	1.88	88.3	44.017	21.305
0.4	1.90	0.63	3.01	33.76	2.01	82.6	44.181	19.024
0.6	1.58	0.30	5.23	36.77	2.27	73.1	44.048	15.511
0.8	0.29	0.17	1.73	41.06	2.73	60.8	47.161	11.330
Triethylenetetramine								
0.2	1.44	0.48	3.01	31.84	1.87	88.8	45.110	21.497
0.4	0.35	0.14	2.41	33.75	2.30	72.2	46.321	16.633
0.6	0.30	0.13	2.26	36.95	2.36	70.3	47.692	14.814
0.8	0.28	0.12	2.32	37.95	2.51	66.1	47.329	13.556
Tetraethylenepentamine								
0.2	1.38	0.38	3.63	34.55	1.94	85.6	46.000	19.308
0.4	0.91	0.25	3.63	35.75	2.15	77.2	45.868	16.855
0.6	0.50	0.14	3.60	36.57	2.34	70.9	46.377	15.130
0.8	0.30	0.12	2.49	38.77	2.91	57.0	45.358	11.408
(B) 16-5-16								
Ethylenediamine								
0	3.80	0.87	4.36	27.00	1.62	102.7	42.306	27.835
0.2	3.63	1.81	2.00	27.84	2.05	81.0	39.335	21.544
0.4	3.10	1.32	2.35	30.58	2.26	73.5	39.683	18.336
0.6	1.51	0.72	2.08	34.38	2.63	63.1	41.036	14.298
0.8	0.36	0.27	1.32	36.86	2.69	61.7	45.279	13.059
Diethylenetriamine								
0.2	3.31	1.00	3.31	29.05	1.76	94.3	42.493	24.394
0.4	2.91	0.87	3.34	30.88	1.94	85.6	42.229	21.200
0.6	0.79	0.40	1.99	33.96	2.06	80.6	46.081	18.467
0.8	0.29	0.14	2.00	36.47	2.87	57.8	44.828	12.369
Triethylenetetramine								
0.2	2.29	0.83	2.75	28.59	2.03	81.8	40.999	21.387
0.4	0.48	0.32	1.52	30.70	2.39	69.5	43.696	17.288
0.6	0.14	0.06	2.19	33.79	2.48	66.9	47.580	15.396
0.8	0.04	0.03	1.38	36.61	2.58	64.3	51.301	13.706
Tetraethylenepentamine								
0.2	1.96	0.50	3.91	29.53	1.67	99.4	44.990	25.426
0.4	0.53	0.29	1.83	32.71	2.62	63.4	43.086	15.003
0.6	0.36	0.17	2.16	33.74	2.87	57.8	43.332	13.319
0.8	0.30	0.19	1.57	37.42	3.08	53.9	44.185	11.226
(C) 16-6-16								
Ethylenediamine								
0	4.57	1.00	4.19	22.00	1.22	136.1	43.207	40.983
0.2	2.40	0.83	2.88	25.65	1.32	125.8	46.229	35.114
0.4	1.17	0.55	2.13	28.76	1.70	97.7	45.524	25.434
0.6	0.99	0.33	2.99	32.95	1.95	85.1	45.925	20.024
0.8	0.60	0.15	3.95	38.84	2.22	74.8	47.785	14.937
Diethylenetriamine								
0.2	2.57	0.72	3.55	27.76	1.42	116.9	46.174	31.154
0.4	1.58	0.32	5.00	34.64	1.62	102.5	49.233	23.026
0.6	0.59	0.23	2.57	37.56	1.76	94.3	51.672	19.569
0.8	0.36	0.12	2.96	39.34	1.85	89.8	52.841	17.654
Triethylenetetramine								
0.2	1.26	0.52	2.40	27.15	1.56	106.4	45.824	28.754
0.4	0.72	0.13	5.75	33.25	1.66	100.0	49.860	23.343
0.6	0.40	0.12	3.16	35.06	1.94	85.5	49.383	19.022
0.8	0.23	0.06	3.71	36.71	2.32	71.6	48.528	15.210
Tetraethylenepentamine								
0.2	0.79	0.36	2.19	27.02	1.47	112.9	47.977	30.599
0.4	0.55	0.19	2.88	31.98	1.94	85.6	46.993	20.628
0.6	0.28	0.07	4.08	35.34	2.08	79.8	49.199	17.624
0.8	0.20	0.05	3.99	38.67	2.41	68.9	49.102	13.829

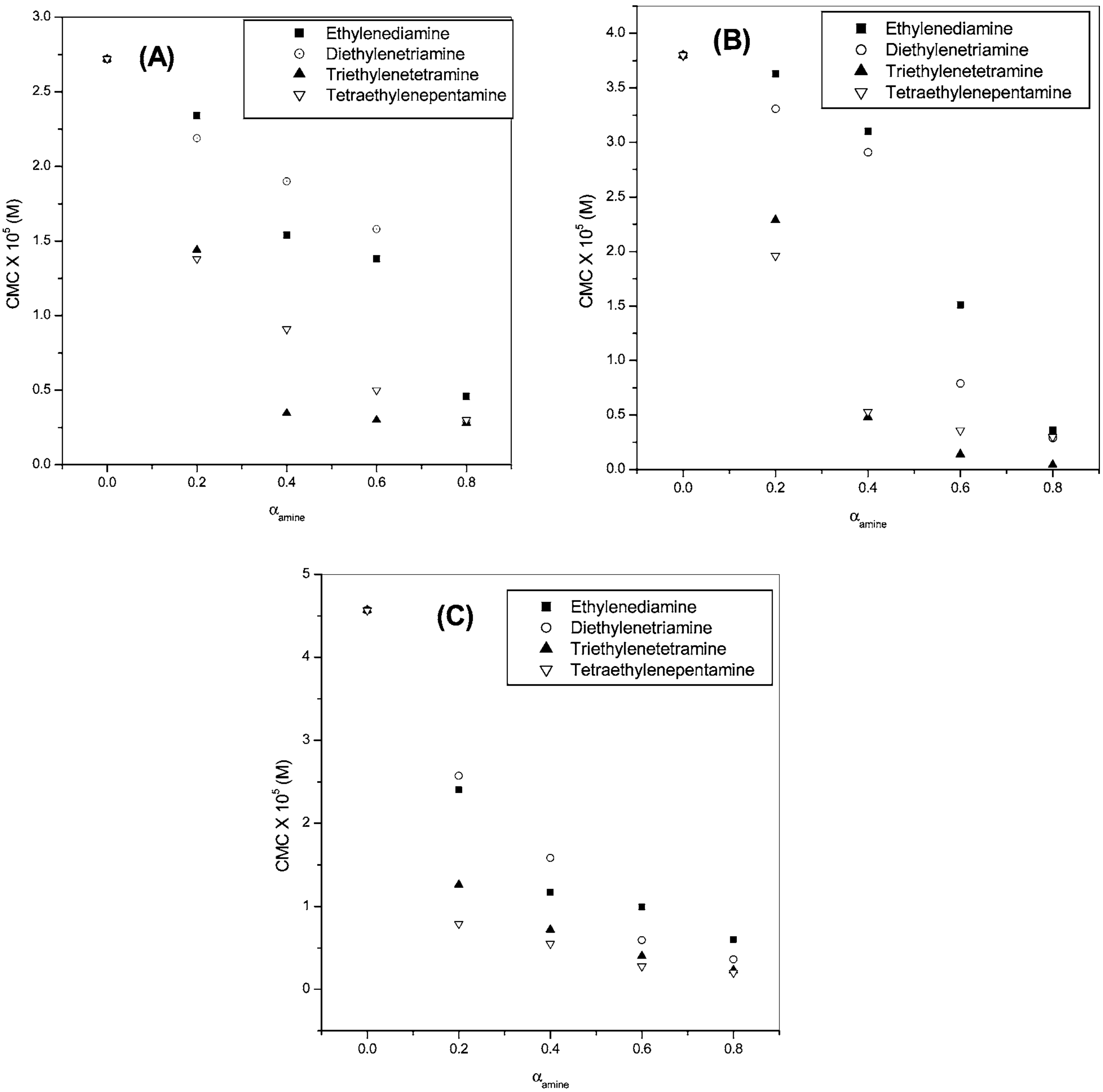

Figure 2. Values of CMC of the gemini surfactants (16-4-16 (A), 16-5-16 (B), and 16-6-16 (C)) at different mole fractions of ethyleneamines.

16-5-16. ^{1}H NMR (solvent $CDCl_3$): δ 0.88 (t, 6H, alkyl chain $2\cdot 1CH_3$), 1.25−1.35 (br m, 42H, alkyl chain $2\cdot 10CH_2$, spacer chain 1 CH_2), 1.60 (crude t, 16H, alkyl chain $2\cdot 4$ CH_2), 2.04−2.08 (br m, 4H, spacer chain $1\cdot 2CH_2CH_2N^+$), 3.38 (s, 12H, $2\cdot 2N^+CH_3$), 3.54 (crude, 4H, alkyl chain $2\cdot 1CH_2N^+$), 3.82−3.86 (crude t, 4H, spacer chain $1\cdot 2CH_2N^+$). IR ν_{max} (KBr): C-N = (1227.1 to 1047.4) cm^{-1}.

16-6-16. ^{1}H NMR (solvent $CDCl_3$): δ 0.87 (t, 6H, alkyl chain $2\cdot 1CH_3$), 1.25−1.35 (s + br m, 48H, alkyl chain $2\cdot 12CH_2$), 1.55−1.72 (br m, 12H, spacer chain $1\cdot 2$ $CH_2CH_2N^+$, alkyl chain $2\cdot 1CH_2CH_2CH_2N^+$),1.97 (br s, 4H, spacer chain $1\cdot 2$ $CH_2CH_2N^+$), 3.39 (br s, 16H, $2\cdot 2$ N^+CH_3, alkyl chain $2\cdot 1CH_2N^+$), 3.82−3.86 (m, 4H, spacer chain $1\cdot 2CH_2N^+$). IR ν_{max} (KBr): C-N = 1246.4 cm^{-1}.

The surface tension values were measured by the ring detachment method using an S.D. Hardson tensiometer (Kolkata, India). The surface tension of doubly distilled water, 71.2 mN·m^{-1} at 30 °C, was used in the calibration.[27] To avoid adsorption kinetics effects, the measurements were performed (15 to 20) minutes after the addition of surfactants. The CMC values were obtained from surface tension (γ) vs log C_t (C_t is the total surfactant concentration) plots. The respective uncertainties on the CMC and C_{20} were estimated to be less than ± (0.1 to 0.3)·10^{-5} and ± (0.15 to 0.61)·10^{-5}.

Results and Discussion

As shown in Scheme 1, the 16-*s*-16 gemini surfactants possess two hydrophobic chains of 16 carbons and two ionic head groups with a flexible spacer and chain length of four to six carbons. The general molecular formula of this type of surfactant is $C_mH_{2m+1}(CH_3)_2N^+-(X)_S-N^+(CH_3)C_mH_{2m+1}\cdot 2Br^-$. The hydrophobic/hydrophilic nature of the spacer X can dramatically affect the physicochemical properties of the gemini surfactants presumably because of the modification of the mobility and packing of surfactant monomers within the aggregate (see Scheme 1).

The CMC values of different combinations of the gemini surfactant (16-*s*-16, where *s* = 4, 5, 6) and ethyleneamine (ethylenediamine, diethylenetriamine, triethylenetetramine,

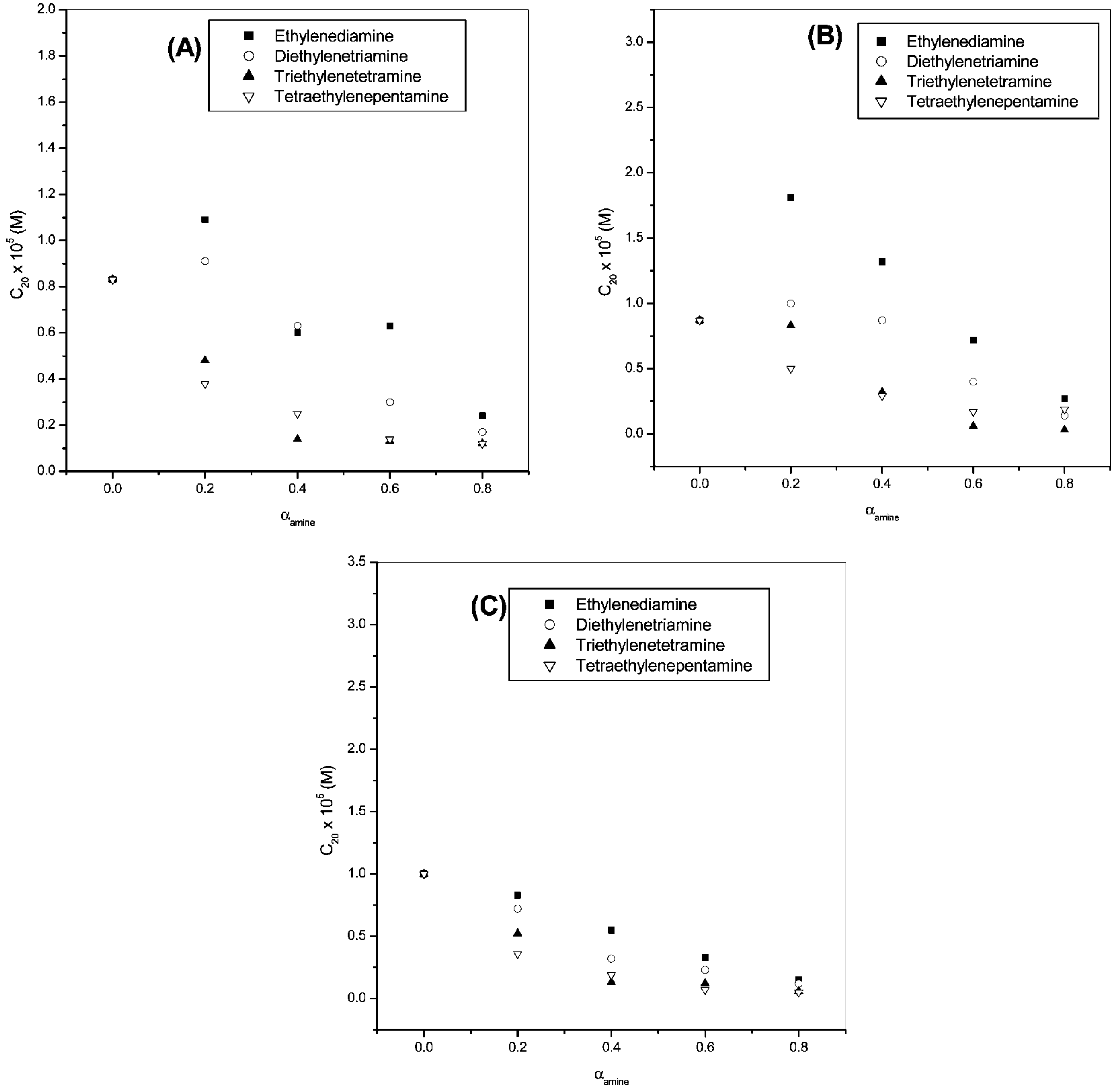

Figure 3. Values of C_{20} of the gemini surfactants (16-*s*-16, $s = 4$ (A), 5 (B), and 6 (C)) at different mole fractions of ethyleneamines.

and tetraethylenepentamine) mixtures, evaluated from the surface tension (γ) versus the logarithm of the total gemini surfactant concentration in solution (log C_t) profiles (Figure 1, where representative plots are shown for 16-4-16), are presented in Table 1. The CMC values decrease with increasing concentration as well as the number of ethylene groups of the additives, whereas an increase in the spacer chain length of the gemini surfactant produces the opposite effect (Table 1). The trend is shown in Figure 2A−C wherein we find the order to be the following: tetraethylenepentamine > triethylenetetramine > diethylenetriamine > ethylenediamine and 16-6-16 > 16-5-16 > 16-4-16. The CMC values of the gemini surfactants in water are in good agreement with the literature values (Table 1).[26,28]

The values of different surface properties (viz., C_{20} (the efficiency of surfactant in reducing the surface tension of water is the surfactant concentration required to reduce the surface tension by 20 mN·m^{-1}), the CMC/C_{20} ratio, Π_{CMC} (the surface pressure at the CMC), Γ_{max} (the maximum surface excess), and A_{min} (the minimum surface area per molecule)) and thermodynamic parameters (ΔG^0_{ads} (the standard Gibbs energy of adsorption) and $G^{(s)}_{min}$ (the free energy at the air/water interface)) obtained at different mole fractions of the added ethyleneamines in 16-*s*-16 solutions are collected in Table 1. In all cases, the C_{20} values decrease with additive concentration and follow a similar trend for all of the amines (Figure 3A−C). The magnitude of the negative log of the C_{20} value is two or three orders smaller than that of comparable conventional cationic surfactants[29] and also in good agreement with previous work.[30] The greater surface activity may be due to the presence of two hydrophobic groups in the gemini surfactant molecules. As expected, the C_{20} value increases with increasing spacer chain length of the gemini surfactants (see Table 1). The CMC/C_{20} ratio is a measure of surfactant preference for adsorption relative to micelle formation. The CMC/C_{20} ratio also measures how far the surface tension of water can be reduced by the presence of the surfactant.

The values of Π_{CMC} were obtained by using the equation

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \qquad (1)$$

where γ_0 and γ_{CMC} are the surface tension of the solvent and of the mixture at the CMC, respectively. With increasing amine

Table 2. Micellar Compositions (X_1^m, X_1^σ), Interaction Parameters (β^m, β^σ), and Activity Coefficients (f_1^m, f_2^m, f_1^σ, f_2^σ) of Binary Mixtures of Gemini Surfactants (16-4-16, 16-5-16, 16-6-16) and Ethyleneamines at Different Mole Fractions (α_{amine})

α_{amine}	X_1^m	β^m	f_1^m	f_2^m	ΔG_{ex} / kJ·mol^{-1}	X_1^σ	β^σ	f_1^σ	f_2^σ
(A) 16-4-16									
Ethylenediamine									
0.2	0.158	−8.130	0.00314	0.816	−2.725	0.106	−8.345	0.00127	0.910
0.4	0.263	−11.009	0.00253	0.467	−5.375	0.133	−7.971	0.00250	0.868
0.6	0.313	−12.453	0.00280	0.295	−6.747	0.241	−11.130	0.00164	0.524
0.8	0.393	−18.788	0.00098	0.055	−11.293	0.353	−18.062	0.00052	0.105
Diethylenetriamine									
0.2	0.176	−8.059	0.00420	0.779	−2.944	0.057	−3.475	0.04547	0.989
0.4	0.250	−9.372	0.00513	0.557	−4.426	0.093	−5.277	0.01302	0.955
0.6	0.313	−11.177	0.00512	0.334	−6.056	0.295	−11.914	0.00268	0.354
0.8	0.410	−19.994	0.00095	0.035	−12.170	0.394	−20.512	0.00053	0.041
Triethylenetetramine									
0.2	0.243	−9.946	0.00335	0.556	−4.608	0.063	−5.347	0.00915	0.979
0.4	0.359	−16.597	0.00109	0.118	−9.620	0.322	−15.862	0.00068	0.193
0.6	0.387	−17.665	0.00131	0.078	−10.411	0.356	−17.289	0.00079	0.112
0.8	0.418	−19.180	0.00151	0.035	−11.755	0.391	−19.061	0.00085	0.054
Tetraethylenepentamine									
0.2	0.251	−9.763	0.00418	0.540	−4.626	0.191	−9.148	0.00251	0.716
0.4	0.321	−11.809	0.00432	0.296	−6.485	0.277	−11.549	0.00239	0.412
0.6	0.378	−15.016	0.0030	0.117	−8.893	0.350	−15.621	0.00136	0.147
0.8	0.422	−18.378	0.00215	0.038	−11.291	0.389	−17.439	0.00148	0.071
(B) 16-5-16									
Ethylenediamine									
0.2	0.135	−6.907	0.00570	0.882	−2.031	0.056	−5.796	0.005711	0.982
0.4	0.229	−8.682	0.00574	0.634	−3.862	0.101	−6.020	0.007706	0.940
0.6	0.332	−13.101	0.00289	0.236	−7.320	0.304	−13.619	0.00136	0.284
0.8	0.409	−20.592	0.00075	0.032	−12.538	0.395	−22.611	0.00025	0.029
Diethylenetriamine									
0.2	0.162	−7.086	0.00690	0.830	−2.424	0.106	−5.944	0.00865	0.935
0.4	0.244	−8.435	0.00806	0.605	−3.920	0.171	−6.467	0.01174	0.828
0.6	0.366	−15.225	0.00220	0.130	−8.900	0.375	−18.009	0.00088	0.079
0.8	0.421	−20.840	0.00092	0.025	−12.795	0.411	−20.643	0.00078	0.030
Triethylenetetramine									
0.2	0.231	−8.768	0.00560	0.626	−3.924	0.217	−9.448	0.00305	0.641
0.4	0.364	−16.097	0.00149	0.118	−9.392	0.346	−16.237	0.00096	0.143
0.6	0.413	−21.698	0.00057	0.025	−13.266	0.400	−22.162	0.00034	0.029
0.8	0.448	−28.006	0.00020	0.004	−17.290	0.431	−25.839	0.00023	0.008
Tetraethylenepentamine									
0.2	0.254	−9.233	0.00587	0.551	−4.408	0.252	−10.621	0.00263	0.509
0.4	0.366	−15.245	0.00218	0.130	−8.909	0.355	−16.428	0.00108	0.126
0.6	0.401	−17.262	0.00204	0.062	−10.454	0.419	−26.085	0.00015	0.010
0.8	0.433	−19.178	0.0021	0.027	−11.885	0.414	−18.735	0.00161	0.040
(C) 16-6-16									
Ethylenediamine									
0.2	0.238	−10.589	0.00214	0.549	−4.836	0.275	−14.670	0.00045	0.330
0.4	0.324	−14.185	0.00153	0.226	−7.824	0.330	−17.320	0.00042	0.152
0.6	0.360	−15.501	0.00175	0.134	−8.997	0.350	−17.201	0.00070	0.122
0.8	0.407	−19.030	0.00124	0.043	−11.562	0.403	−22.759	0.00030	0.025
Diethylenetriamine									
0.2	0.236	−9.603	0.00368	0.586	−4.361	0.305	−12.599	0.00227	0.310
0.4	0.315	−12.120	0.00339	0.300	−6.590	0.375	−16.927	0.00134	0.093
0.6	0.383	−16.980	0.00156	0.083	−10.104	0.413	−20.562	0.00084	0.030
0.8	0.423	−20.370	0.00113	0.026	−12.536	0.442	−23.311	0.00070	0.011
Triethylenetetramine									
0.2	0.304	−12.504	0.00234	0.315	−6.664	0.324	−15.622	0.00079	0.194
0.4	0.360	−14.861	0.00227	0.146	−8.623	0.387	−21.238	0.00034	0.042
0.6	0.401	−17.803	0.00168	0.057	−10.777	0.395	−19.115	0.00092	0.051
0.8	0.436	−21.109	0.00121	0.018	−13.086	0.431	−22.916	0.00060	0.014
Tetraethylenepentamine									
0.2	0.333	−14.189	0.00181	0.207	−7.943	0.340	−17.276	0.00054	0.136
0.4	0.374	−15.573	0.00224	0.113	−9.187	0.363	−16.955	0.00103	0.107
0.6	0.412	−18.690	0.00156	0.042	−11.404	0.413	−23.105	0.00035	0.019
0.8	0.443	−21.243	0.00137	0.015	−13.250	0.434	−23.674	0.00051	0.012

concentration, the value of Π_{CMC} increases, indicating that the efficiency of the system increases (Table 1). Also, the values of Π_{CMC} decrease with increasing spacer length of the gemini surfactants.

Γ_{max} of the gemini surfactant molecules at the air/solution interface was calculated by using Gibbs equation[31]

$$\Gamma_{max} = -\frac{1}{2.303 \cdot n \cdot RT}(d\gamma/d \log C_t)_T \qquad (2)$$

where γ, R, and T are the surface tension, gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$), and temperature, respectively. The correct prefactor n is the number of species at the air/solution interface. For calculating Γ_{max} $n = 2$.[32] The slope of the tangent at the given concentration of the γ versus log C_t plot (Figure 1A−C) was used to calculate Γ_{max} which increases with an increase in the concentration of the additives (amines) (Table 1). The gemini surfactant solutions with amines, compared to a pure gemini surfactant solution, have greater preference to be adsorbed at the air/water interface. The repulsion among the head groups decreases in the presence of ethyleneamines and causes adsorption of more gemini surfactant molecules at the interface. This is confirmed by the low values of A_{min} which were evaluated by using the relation

$$A_{min} = 10^{20}/(N_A \cdot \Gamma_{max})(\AA^2) \qquad (3)$$

where N_A is Avogadro's number. A_{min} decreases with increasing additive concentration. The progressive charge shielding and closer packing of the gemini surfactant ions in the surface causes a decrease in the area with increasing additive concentration (Table 1). This result suggests that the orientation of the gemini surfactant molecules at the interface is thus almost perpendicular to the interface.[33] The Γ_{max} values decrease with increasing spacer length both in the absence and the presence of amines and are in the following order: 16-4-16 < 16-5-16 < 16-6-16; however, the A_{min} followed the reverse order, that is, 16-6-16 > 16-5-16 > 16-4-16. This may be due to intramolecular headgroup distances. In this case, the spacer chain could be in contact with water. With the addition of amines, the values of Γ_{max} increase, and the values of A_{min} decrease; the same trend is followed by all of the systems.

Sugihara et al.[27,34] have proposed a thermodynamic quantity for the evaluation of synergism in mixing, which is the free energy of the given air/water interface, $G_{min}^{(s)}$, defined as

$$G_{min}^{(s)} = A_{min} \cdot \gamma_{CMC} \cdot N_A \qquad (4)$$

The $G_{min}^{(s)}$ values listed in Table 1 are found to decrease with increasing additive (amines) mole fraction. $G_{min}^{(s)}$ is regarded as the work needed to make an interface per mole or the free energy change accompanied by the transition from the bulk phase to the surface phase of the solution components. In other words, the lower the value of $G_{min}^{(s)}$, the more thermodynamically stable surface is formed.

To quantify the effect of ethyleneamines in the mixture on the micellization process, the standard Gibbs energy of micellization,[35] ΔG_m^0, and the standard Gibbs energy of adsorption,[36] ΔG_{ads}^0, were calculated by using eqs 5 and 6,

$$\Delta G_m^0 = RT \cdot \ln C_{12}^m \qquad (5)$$

C_{12}^m is the CMC of the mixture of the two components at a given mole fraction.

$$\Delta G_{ads}^0 = \Delta G_m^0 - \Pi_{CMC}/\Gamma_{max} \qquad (6)$$

ΔG_{ads}^0 decreases with increasing ethyleneamine concentrations. The standard state for the adsorbed surfactant is a hypothetical monolayer at its minimum surface area per molecule, but at zero surface pressure. The last term in eq 6 expresses the work involved in transferring the surfactant molecule from a monolayer at a zero surface pressure to the micelle. In the present case, the last term of eq 6 is very small as compared to ΔG_m^0, which indicates that the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle is negligible. All of the ΔG_{ads}^0 values are negative (Table 1), implying that the adsorption of the surfactants at the air/mixture interface takes place spontaneously and are in the following order: 16-4-16 > 16-5-16 > 16-6-16.

Molecular interactions between two compounds (amphiphiles) at an interface or in micelles are commonly measured by the so-called β parameters,[36−40] which are conveniently obtained from surface (or interfacial) tension or from CMC data by using eqs 7, 8, 11, and 12. Equations 7 and 8 are used to calculate the interaction in the micelle (β^m) from critical micelle concentration data,[40] whereas eqs 11 and 12 are used to calculate interactions at the air/aqueous solution interface (β^σ) from surface tension data.[39]

By calculating the values of the β (interaction) parameters, the nature and strength of the interaction between two components can be ascertained. From Rubingh's theory[40] for mixed micelles the mole fraction of component 1, $X_1{}^m$, in the mixed micelles is related to α_1 (the mole fraction of the indicated component) as

$$\frac{[(X_1^m)^2 \cdot \ln(C_{12}^m \cdot \alpha_1/C_1^m \cdot X_1^m)]}{[(1 - X_1^m)^2 \cdot \ln\{(C_{12}^m \cdot (1 - \alpha_1)/C_2^m \cdot (1 - X_1^m)]} = 1 \qquad (7)$$

and

$$\beta^m = \frac{\ln(C_{12}^m \cdot \alpha_1/C_1^m \cdot X_1^m)}{(1 - X_1^m)^2} \qquad (8)$$

where C_1^m and C_2^m are the CMCs for component 1 and component 2, respectively.

The activity coefficients $f_1{}^m$ and $f_2{}^m$ are related to β^m as

$$f_1^m = \exp\{\beta^m \cdot (1 - X_1^m)^2\} \qquad (9)$$

$$f_2^m = \exp\{\beta^m \cdot (X_1^m)^2\} \qquad (10)$$

Using Rosen's approach,[39] the composition of the adsorbed mixed monolayer of binary component systems in equilibrium with the singly dispersed components can be evaluated using equations

$$\frac{[(X_1^\sigma)^2 \cdot \ln(C_{12}^S \cdot \alpha_1/C_1^S \cdot X_1^\sigma)]}{[(1 - X_1^\sigma)^2 \cdot \ln\{C_{12}^S \cdot (1 - \alpha_1)/C_2^S \cdot (1 - X_1^\sigma)\}]} = 1 \qquad (11)$$

and

$$\beta^\sigma = \frac{\ln(C_{12}^S \cdot \alpha_1/C_1^S \cdot X_1^\sigma)}{(1 - X_1^\sigma)^2} \qquad (12)$$

where C_1^S, C_2^S, and C_{12}^S are the molar concentrations of components 1, 2, and their mixture at α_1, required to produce a given surface tension reduction (corresponding to $\gamma = 55$

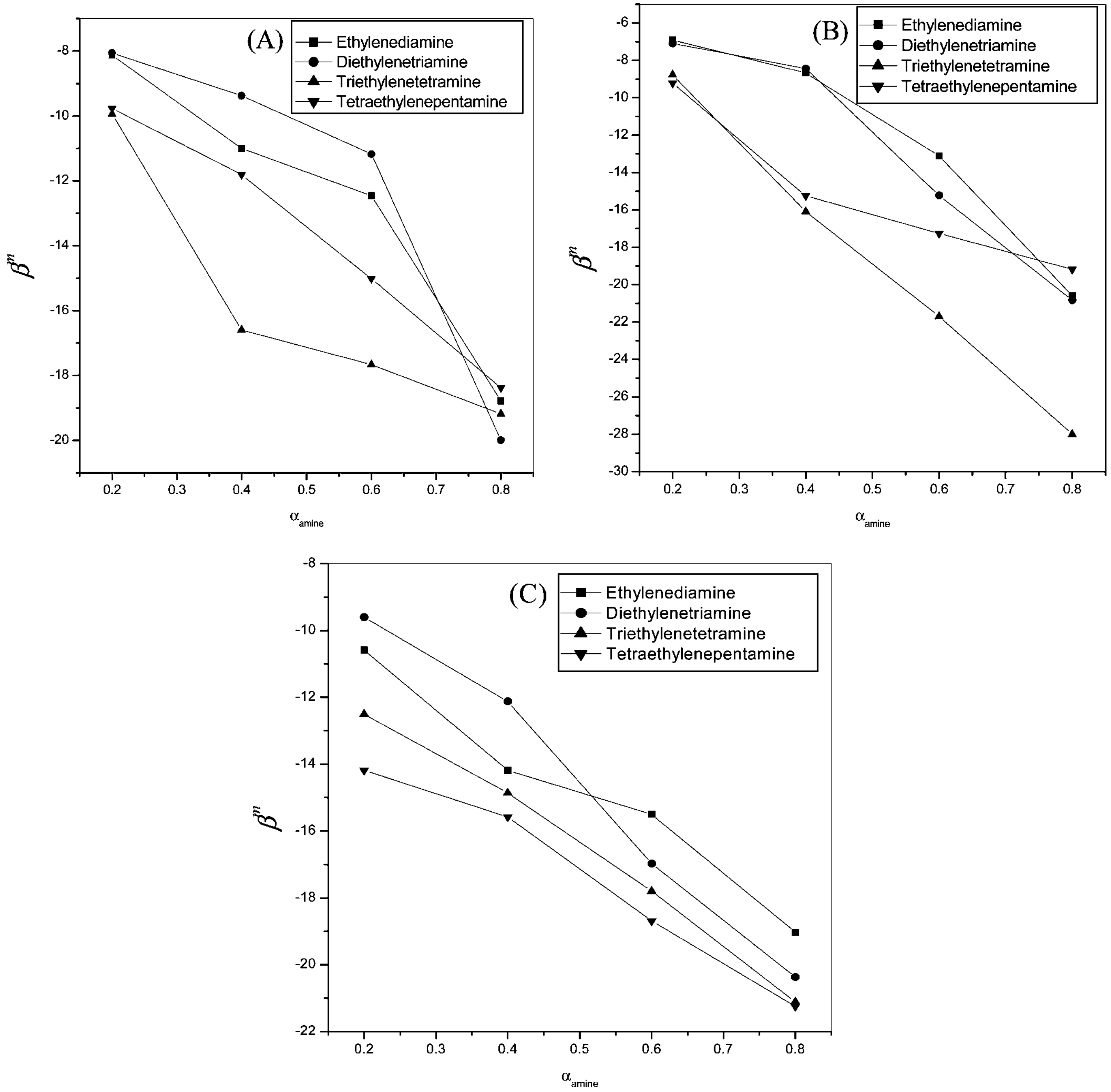

Figure 4. Values of β^m of the gemini surfactants (16-*s*-16, $s = 4$ (A), 5 (B), and 6 (C)) at different mole fractions of ethyleneamines.

mN·m^{-1} in the present work). The activity coefficients f_1^σ and f_2^σ of the surfactants in mixed monolayer are related to β^σ as

$$f_1^\sigma = \exp\{\beta^\sigma \cdot (1 - X_1^\sigma)^2\} \tag{13}$$

$$f_2^\sigma = \exp\{\beta^\sigma \cdot (X_1^\sigma)^2\} \tag{14}$$

Equations 7 and 11 are solved numerically for X_1 which are then substituted into eqs 8 and 12 to obtain the respective β values, which indicate the degree of interaction between the two components and also account for the deviation from ideality. For ideal mixing of two components, β assumes a value of zero. A positive β value means repulsive interaction among mixed species, whereas a negative β value implies an attractive interaction; the more negative its value, the greater the interaction. At all mole fractions of the mixed systems, the β^m values are negative (Table 2), suggesting that the interaction is more attractive in between the two components in the mixed micelles than the self-interaction of the two components before mixing. As the mole fraction of alkylamines increases, β^m values become more negative. This indicates an increase in the attractive interaction with an increase in amines due to the intercalation of amines in the micelles of the gemini surfactants which increases the hydrophobic interactions (also evident from the CMC values, Table 1), which decrease with increasing amines (see Figure 4).

The β^σ trend is similar (Table 2, Figure 5), that is, the mixtures of geminis/amines show stronger attractive interaction at the solution/air interface. The β^σ values are more negative than β^m, which implies that the interactions at the solution/air interface are stronger than in mixed micelles. This is due to the steric factor which is more important in micelle formation than in monolayer formation at a planar interface. Increased bulkiness in the hydrophobic group causes greater difficulty for incorporation into the curved mixed micelle

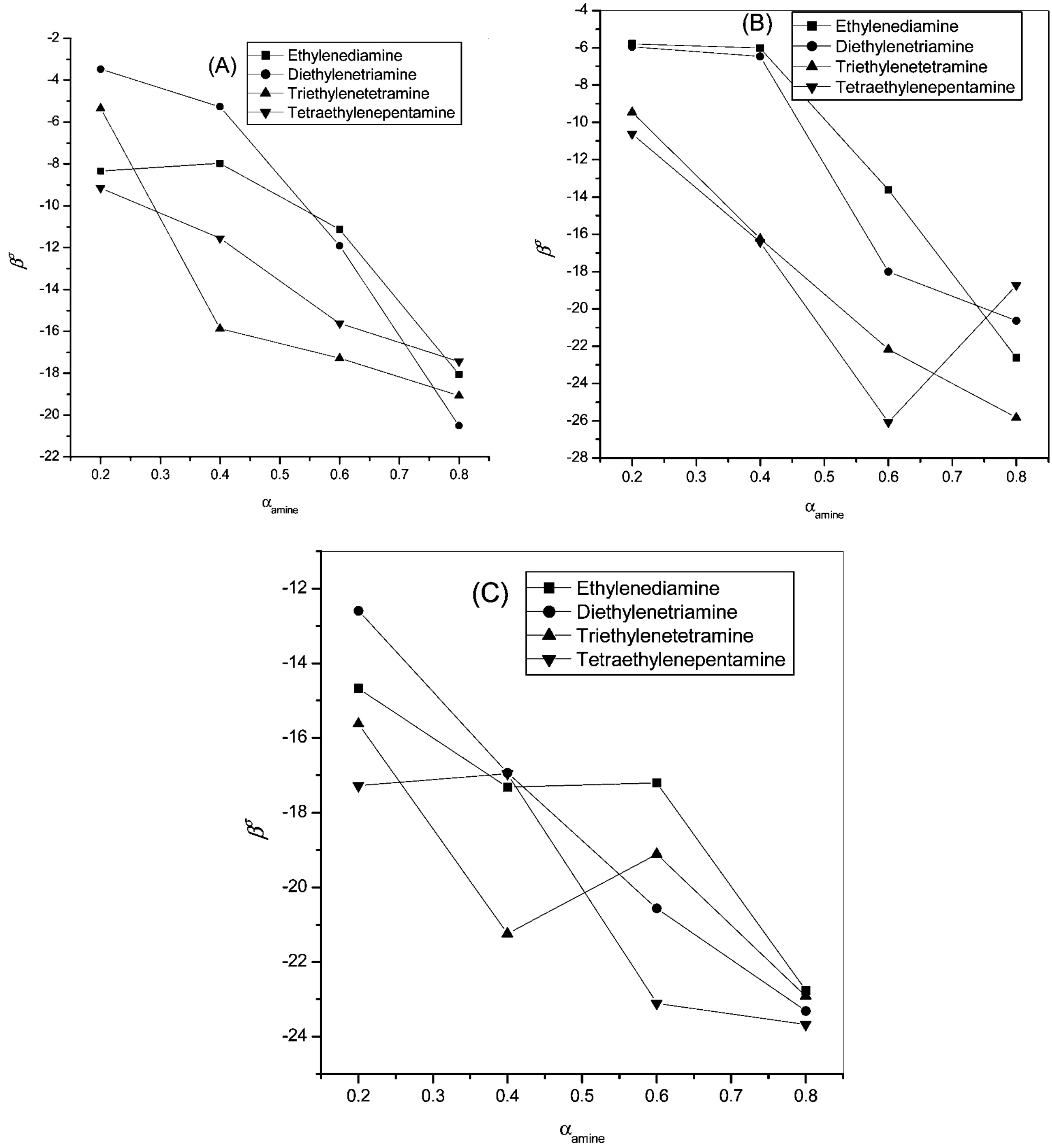

Figure 5. Values of β^σ of the gemini surfactants (16-*s*-16, $s = 4$ (A), 5 (B), and 6 (C)) at different mole fractions of ethyleneamines.

compared to that of accommodating at the planar interface. The average values of interaction parameters indicate that the attractive interaction of gemini/amines are more in case of longer spacer chain length than that of the smaller spacer chain length of the gemini (Table 2).

The values of excess free energy of micellization, ΔG_{ex}, calculated by eq 15,

$$\Delta G_{ex} = [X_1 \cdot \ln f_1 + (1 - X_1) \cdot \ln f_2] \cdot RT \qquad (15)$$

are listed in Table 2, which are negative for all mole fractions of the amines, and the magnitude increases (ΔG_{ex} becomes more negative) with increasing amine mole fraction, indicating stability of the micelles.

Synergism. In mixtures containing two amphiphiles, the existence of synergism has been shown to depend not only on the strength of interaction between them (measured by the values of the β parameter) but also on the relevant properties of the individual amphiphile components of a mixture.[41] The conditions for synergism in surface tension reduction efficiency (when the total concentration of mixed surfactant required to reduce the surface tension of the solvent to a given value is less than that of individual amphiphile) are the following: (a) β^σ must be negative and (b) $|\beta^\sigma| > |\ln (C_1^S/C_2^S)|$, where C_1^S and C_2^S are the molar concentrations of amphiphile 1 and 2, respectively, required to achieve the same surface tension value. The data show that there is very good synergism in surface tension reduction efficiency for the gemini surfactant/ethylenelamine mixtures (Table 3).

Analogously, synergism in the mixed micelle formation exists when the CMC of the mixture is less than that of either

Table 3. Comparison Table for Synergism of the Mixed Systems of Gemini Surfactants (16-4-16, 16-5-16, 16-6-16) and Ethyleneamines

α_{amine}	system	$\ln(C_1^s/C_2^s)$	$\ln(C_1^m/C_2^m)$	β^σ	β^m	$\beta^\sigma - \beta^m$
	(A)16-4-16					
0.2	ethylenediamine/16-4-16	7.32	5.85	−8.345	−8.130	−0.215
0.4				−7.971	−11.009	+3.038
0.6				−11.130	−12.453	+1.323
0.8				−18.062	−18.788	+0.726
0.2	diethylenetriamine/16-4−16	5.48	5.38	−3.475	−8.059	+4.584
0.4				−5.277	−9.732	+4.455
0.6				−11.914	−11.177	−0.737
0.8				−20.512	−19.994	−0.518
0.2	triethylenetetramine/16-4-16	5.99	4.87	−5.347	−9.946	+4.599
0.4				−15.862	−16.597	+0.735
0.6				−17.289	−17.665	+0.378
0.8				−19.061	−19.180	+0.119
0.2	tetraethylenepentamine/16-4-16	5.94	4.57	−9.148	−9.763	+0.615
0.4				−11.549	−11.809	+0.260
0.6				−15.621	−15.016	−0.605
0.8				−17.439	−18.378	+0.939
	(B)16-5-16					
0.2	ethylenediamine/16-5-16	6.59	5.52	−5.796	−6.907	+1.111
0.4				−6.020	−8.682	+2.662
0.6				−13.619	−13.101	−0.518
0.8				−22.611	−20.592	−2.019
0.2	diethylenetriamine/16-5-16	4.74	5.05	−5.944	−7.086	+1.142
0.4				−6.467	−8.435	−2.784
0.6				−18.009	−15.225	+1.968
0.8				−20.643	−20.842	+0.199
0.2	triethylenetetramine/16-5-16	5.25	4.53	−9.448	−8.768	−0.680
0.4				−16.237	−16.097	−0.140
0.6				−22.162	−21.698	−0.464
0.8				−25.839	−20.006	−5.833
0.2	tetraethylenepentamine/16-5-16	5.20	4.24	−10.621	−9.233	−1.388
0.4				−16.428	−15.245	−1.183
0.6				−26.085	−17.262	−8.823
0.8				−18.735	−19.178	+0.443
	(C)16-6-16					
0.2	ethylenediamine/16-6-16	6.19	5.33	−14.670	−10.589	−4.081
0.4				−17.320	−14.185	−3.135
0.6				−17.201	−15.501	−1.700
0.8				−22.759	−19.030	−3.729
0.2	diethylenetriamine/16-6-16	4.35	4.86	−12.599	−9.603	−2.993
0.4				−16.927	−12.120	−4.807
0.6				−20.562	−16.980	−3.582
0.8				−23.311	−20.370	−2.941
0.2	triethylenetetramine/16-6-16	4.86	4.35	−15.622	−12.504	−3.118
0.4				−21.238	−14.681	−6.557
0.6				−19.115	−17.803	−1.312
0.8				−22.916	−21.109	−1.826
0.2	tetraethylenepentamine/16-6-16	4.81	4.05	−17.276	−14.189	−3.087
0.4				−16.955	−15.573	−1.382
0.6				−23.105	−18.690	−4.415
0.8				−23.674	−21.243	−2.431

amphiphile of the mixture. The conditions for this to exist in a mixture of two surfactants are the following:[41] (a) β^m must be negative, (b) $|\beta^m| > |\ln(C_1^m/C_2^m)|$, and (c) $|\beta^\sigma - \beta^m| > [|\ln(C_1^s/C_2^s)| - |\ln(C_1^m/C_2^m)|]$, where C_1^m and C_2^m are the critical micelle concentrations of amphiphiles 1 and 2, respectively. All of the mixtures are found to exhibit synergism in mixed micelle formation with the ethyleneamines (Table 3 and Figures 4−5).

Conclusions

Micellar and interfacial properties of gemini surfactants 16-*s*-16 ($s = 4, 5, 6$) in the presence of ethyleneamines have been studied by surface tension measurements. The results show mixed micellization. The CMC and headgroup area values (A_{min}) decrease while Γ_{max} increase with increasing additive concentrations. Increasing the spacer chain length of the gemini surfactants increases the CMC, C_{20}, and A_{min} values and decreases the Π_{CMC} and Γ_{max} values. $G_{\text{min}}^{(s)}$ values decrease with increasing ethyleneamine mole fraction, which indicates a thermodynamically stable surface, while ΔG_{ads}^0 values indicate that the adsorption of the surfactants at the air/solution interface takes place spontaneously. The values of the interaction parameter (β) for mixed monolayer formation in the aqueous solution/air interface (β^σ) and for mixed micelle formation in aqueous medium (β^m) indicate attractive interactions which increase as the spacer chain length of the gemini surfactants increases (i.e., 16-6-16 > 16-5-16 ≈ 16-4-16). All of the values of ΔG_{ex} are negative for all mole fractions of amines indicating the stability of the micelles. Rosen's approach reveals increased synergism in the mixed monolayer in comparison to the mixed micelles (i.e., $\beta^\sigma > \beta^m$; Table 2).

The experimental results obtained in the present study may be useful for the selection of mixed surfactant systems. Thus, the main purpose of our study is to utilize mixed surfactant systems for the development of controlled release and targeted delivery of drugs.

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