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ORIGINAL ARTICLE

Mixed Micellization of Cationic Gemini Surfactants with Primary Linear Alkylamines

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Abstract Due to the potential use of amines as co-surfactants in microemulsions, the effect of adding alkylamines (C_4–C_8NH_2) on the aggregation properties of cationic gemini surfactants [pentanediyl-1, 5-bis(dimethylcetylammonium bromide) and hexanediyl-1, 6-bis(dimethylcetylammonium bromide), referred to as 16-5-16 and 16-6-16 compounds] has been studied using tensiometry at 303 K. Data on critical micelle concentration (CMC), the surface properties C_{20} (the surfactant concentration required to reduce the surface tension by 20 mN/m), Γ_{max} (maximum surface excess), A_{min} (minimum surface area per molecule) evaluated from the surface tension versus surfactant concentration plot, the interaction parameters β^{σ} (for mixed monolayer formation at the aqueous solution/air interface), and β^{m} (for mixed micelle formation in aqueous medium) are reported. A synergistic interaction was observed both in the micelle as well as at interface, as evident from interaction parameters. Theoretical models of Clint, Rubingh and Rosen were used to explain and compare the results. More synergistic interaction was observed in 16-5-16 as compared to 16-6-16. The CMC values of 16-*s*-16 ($s = 5, 6$) decreased with increasing amine concentrations and the extent of the effect followed the sequence: octylamine > heptylamine > hexylamine > pentylamine > butylamine.

Keywords Gemini surfactants · Alkyl amines · Mixed micelles · Synergism

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Introduction

New types of surfactants, known as gemini (or dimeric) surfactants, have been reported in the scientific literature in the past decade [1–9]. Such surfactants consist of two hydrophobic chains and two hydrophilic head groups covalently attached through a spacer. Their surface properties were first described by Okahara and his colleagues [10]. Recently, the study of gemini surfactants is being investigated very actively. A considerable number of investigations have reported their remarkable physicochemical properties, including their high surface activity [2, 4, 8, 11–13], unusual viscosity changes with an increase in surfactant concentration [14, 15], unusual micelle structure [3, 5, 16], aberrant aggregation behavior [17], and stronger interaction with oppositely charged surfactants [18]. The greater efficiency and effectiveness of geminis over comparable conventional surfactants [2–9] make them cost–effective as well as environmentally desirable.

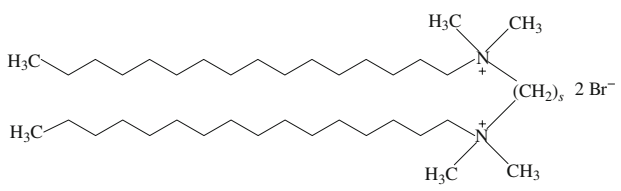
In aqueous media, surfactants in pure and mixed states self-assemble to form micelles [1]. To improve the surface or interfacial properties of a surfactant, one of the best ways is to add to it another surfactant with which it can interact to produce synergy between them. Synergy [1] is defined here as the condition in which the properties of the mixture are better than those attainable with the individual components by themselves and can be predicted from molecular interactions between the two surfactants and relevant properties of the individual surfactants by themselves [1]. Recently, the molecular interactions in mixed systems involving conventional surfactants [18, 19] and gemini surfactants [20–23] have been of academic and industrial interest.

We have investigated the effect of alkanols on the micellization of gemini surfactant [24]. As the interactions

between conventional cationic surfactants and alkylamines produce stable mixed micellar aggregates [25–28], the work has been extended to investigate the molecular interactions in the micellization of the cationic gemini surfactants pentanediyl-1, 5-bis(dimethylcetylammonium bromide) and hexanediyl-1, 6-bis(dimethylcetylammonium bromide) (referred to as 16-*s*-16 where $s = 5$, 6, see Scheme 1) and linear primary alkylamines (C_nNH_2, $n = 4$–8) at 303 K, using tensiometry. The mixtures are characterized by their CMC. The different surface properties of the gemini surfactants in aqueous solutions are evaluated using the surface tension (γ) versus logC_t plots in absence as well as presence of additives (alkylamines). The standard Gibbs energies of adsorption (ΔG^0_{ads}) of the gemini surfactants are also evaluated. The work has relevance as regards the use of alkylamines as co-surfactants for microemulsion formulations with surfactant + oil systems [29, 30]. Further, microemulsions are considered to be good drug carriers and the presence of amines in such combinations may show their specific effects [31] as blood and saliva are known to contain various amines and polyamines [32].

Experimental Section

The additives butylamine (C_4NH_2, >98%, Fluka, Switzerland), pentylamine (C_5NH_2, ≥98.5%, Fluka, Switzerland), hexylamine (C_6NH_2 >98%, Merck, Germany), heptylamine (C_7NH_2, ≥98%, Fluka, Switzerland) and octylamine (C_8NH_2, >98%, Fluka, Switzerland) were used as received. The gemini surfactants were synthesized by refluxing the corresponding α,ω-dibromoalkane ($Br(CH_2)_sBr$, $s = 5$, 6) with *n*,*n*-hexadecyl-*N*,*N*-dimethylamine in dry ethanol for 48 h. The solvent was removed under vacuum and the solids thus obtained were recrystallized three times from hexane/ethyl acetate mixtures to obtain pure surfactants. Both the geminis gave satisfactory ^{1}H-NMR analysis which well matched the literature data [33–35]. Doubly distilled and deionized water (sp. conductivity = 1–2 × 10^{-6} S cm^{-1}) was used throughout. Stock solutions of surfactants were prepared by dissolving the surfactant in aqueous + additive (alkylamine) solutions. The alkylamine concentrations which were used for the preparation of different mole fractions were 0.25, 0.7, 1.5, 4.0 mM.



Alkanediyl-α,ω- bis(dimethylcetylammonium bromide) (16-*s*-16, s = 4,5,6)

Scheme 1 Molecular structure of gemini surfactants

The CMCs of gemini surfactants (with and without additives) in aqueous media were determined by measuring the surface tension of the pure gemini as well as of 16-*s*-16/additive (C_4NH_2–C_8NH_2) solutions of various mole fractions at 303 K. The surface tension values were measured by the ring detachment method using an S. D. Hardson tensiometer (Kolkata, India). For each set of experiments, the ring was cleaned by heating it in an alcohol flame. The CMC values were obtained by plotting surface tension (γ) versus logC_t. The surface tension values decrease continuously and then become constant along a wide concentration range (Fig. 1). The break point, where the constancy of surface tension begins, was taken as the CMC of the system.

Results and Discussion

Surface tension (γ) versus the logarithm of total surfactant concentration (logC_t) profiles for different constant composition mixtures of 16-*s*-16 and alkylamines (C_4NH_2–C_8NH_2) in aqueous solutions are shown in Fig. 1. The break point concentrations corresponding to the CMCs are presented in Table 1. The CMC values decrease with increasing concentration as well as the alkyl chain length of the additives whereas an increase in spacer chain length of the gemini surfactant produces an opposite effect (Table 1). The trend is illustrated in Fig. 2 wherein we find the order to be: $C_8NH_2 > C_7NH_2 > C_6NH_2 > C_5NH_2 > C_4NH_2$ and 16-6-16 > 16-5-16 > 16-4-16 [36]. The CMC values of the gemini surfactants in water are in good agreement with the literature values [33–35] (Table 1).

Like our earlier findings with CTAB [26], which can be considered as the conventional counterpart of 16-*s*-16, we see, once again, that the amines are less effective than the corresponding alkanols in reducing the CMC values of all the gemini surfactants [36]. The amines are weak bases and, due to feeble hydrolysis ($-NH_2 + H_2O \leftrightarrow NH_3^+ + OH^-$), the protonated amine species get repelled by the cationic geminis. This specific interaction between the surfactant head groups and amines is responsible for the latter to be less effective.

The variation of C_{20} (the efficiency of the surfactant in reducing the surface tension of water is the surfactant concentration required to reduce the surface tension by 20 mN/m), the CMC/C_{20} ratio, and Π_{CMC} (the surface pressure at the CMC), Γ_{max} (the maximum surface excess), A_{min} (the minimum surface area per molecule) and ΔG^0_{ads} (the standard Gibbs energy of adsorption) values, obtained

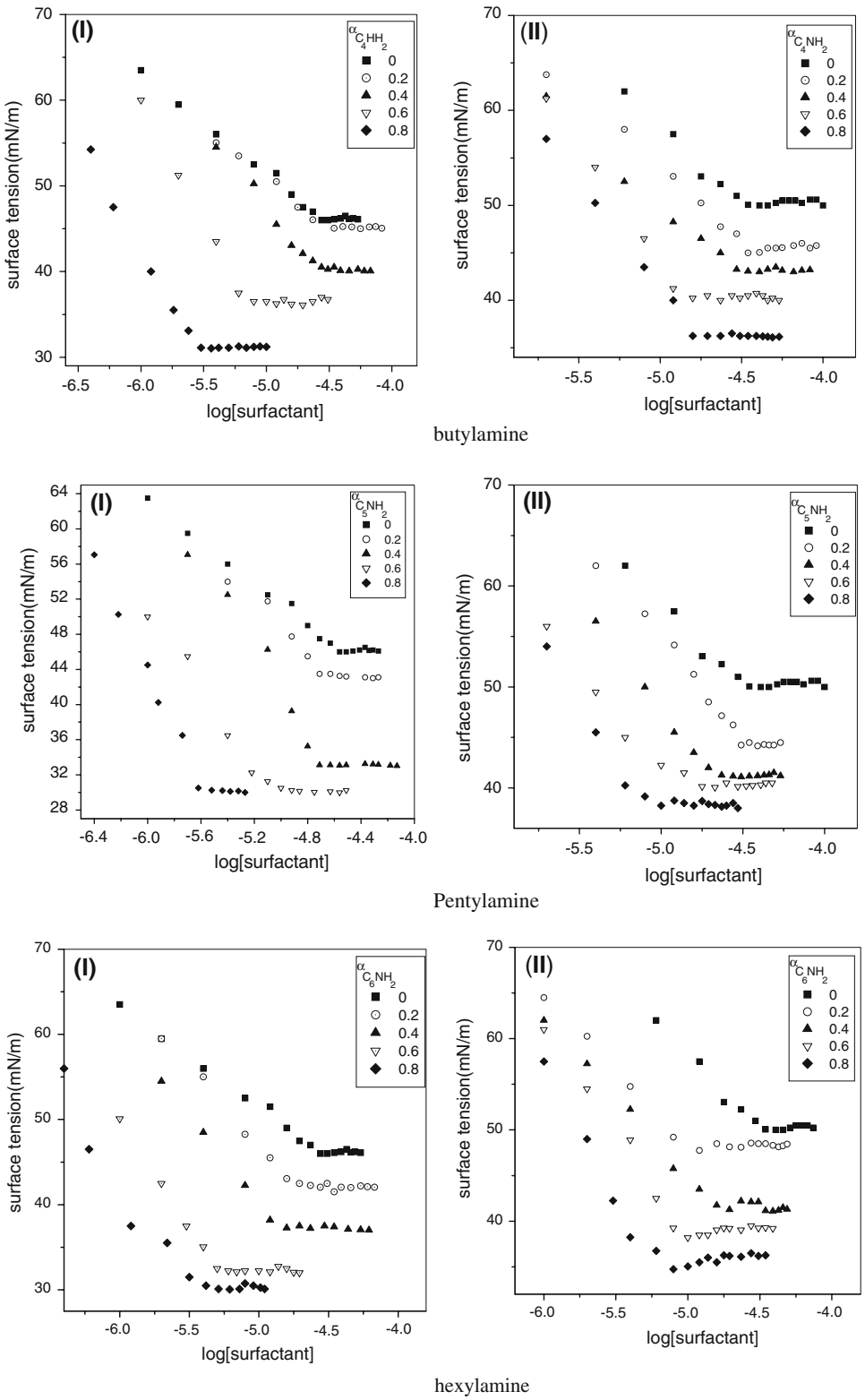
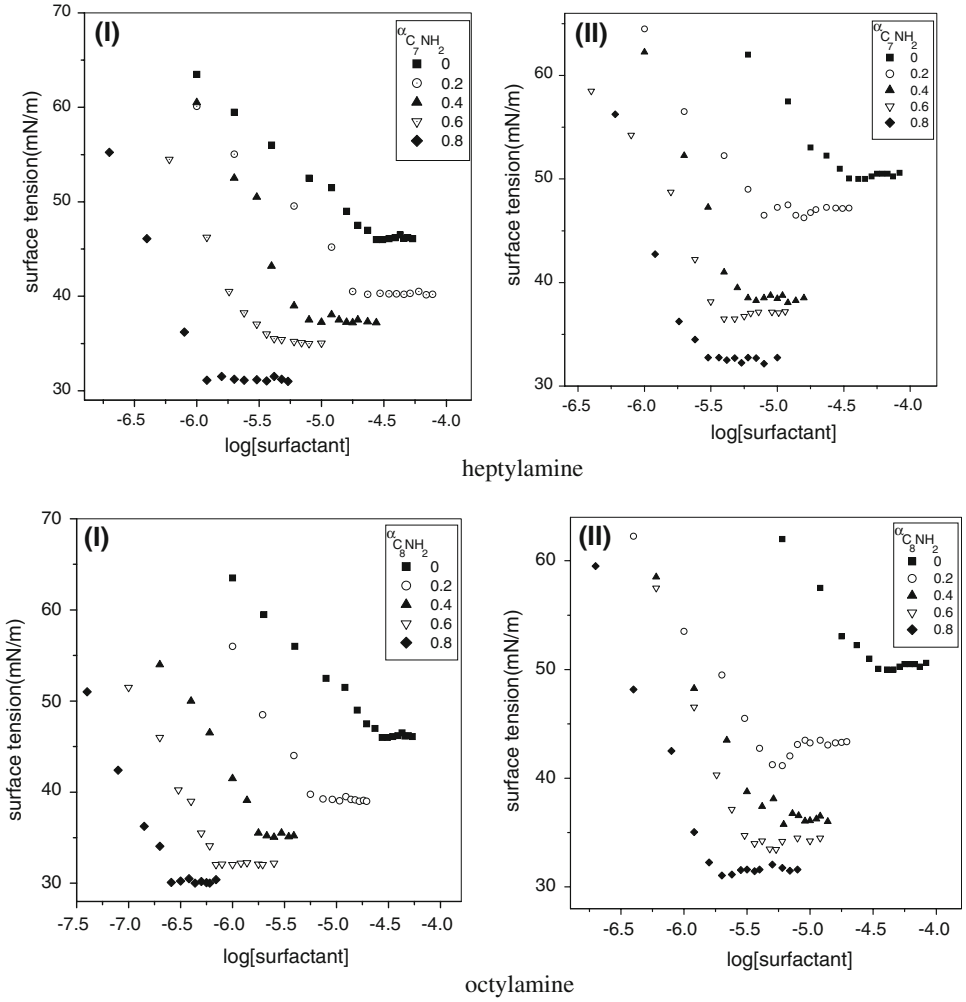


Fig. 1 Plots of surface tension (γ) with logC_t of pure gemini surfactants and alkylamine-16-*s*-16 mixtures [$s = 5$ (I), 6 (II)] at different mole fractions of alkylamines (C_4NH_2–C_8NH_2)

at different mole fractions of the added primary alkylamines in 16-*s*-16 solutions, are also collected in Table 1. In all cases, the C_{20} values decrease with additive concentration and follow similar trend for all the amines. The magnitude of the negative log of the C_{20} value is 2 or 3 orders smaller than those of comparable conventional cationic surfactants. This is in good agreement with previous work [18] showing that the presence of two hydrophobic groups in the gemini molecule results in greater surface activity. The C_{20} value increases with increasing the spacer

Fig. 2 continued



chain length of the gemini surfactants. The CMC/C_{20} ratio is a measure of tendency of the surfactant to adsorb at the air/water interface, relative to its tendency to form micelles. The CMC/C_{20} ratio also measures how far the surface tension of water can be reduced by the presence of the surfactant. The CMC/C_{20} effectiveness is in the order: 16-6-16 > 16-5-16 > 16-4-16 [36], which supports the tendency of the 16-6-16 to adsorb at the air/water interface more than 16-5-16. In our previous study we found a similar trend of decreasing CMC with increasing amine concentrations [36].

Values of the Π_{CMC} were obtained by using the equation

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

where γ_0 and γ_{CMC} are the surface tension of the solvent and the surface tension of the mixture at the CMC, respectively. On increasing the amine concentration, the values of Π_{CMC} increase, indicating that the efficiency increases (Table 1). The values of Π_{CMC} decrease with increasing the spacer length of the gemini surfactants.

Γ_{max} of the gemini surfactant molecules at the air/water interface was calculated by using the Gibb's equation

$$\Gamma_{max} = -\frac{1}{2.303nRT}(d\gamma/d\log C_t)_T \quad (2)$$

where R and T are the universal gas constant (8.314 J mol^{-1} K^{-1}) and temperature, respectively. The prefactor n is the number of species at the air/aqueous interface. For calculating Γ_{max} of gemini surfactants, there is an ongoing dispute about the value of n. In this case, for calculating Γ_{max}, we used a value of 2 for n. The slope of the tangent at the given concentration of the γ versus log C_t plot was used to calculate Γ_{max}. The value of Γ_{max} increases with an increase in the additive (amine) concentrations (Table 1). This indicates that the gemini surfactant solutions in presence of amines have a greater tendency to be adsorbed at the air/water interface, compared to a pure gemini surfactant solution. The presence of alkylamines decreases the repulsion among head groups and more gemini surfactant molecules can be adsorbed at the interface.

Table 1 The effect of additive concentrations on the CMC (determined by surface tension measurements), C_{20}, CMC/C_{20}, Π_{cmc}, A_{min}, Γ_{max} and ΔG^0_{ads} values of cationic gemini surfactants in aqueous solutions at 303 K

α_{amine}	16-5-16							16-6-16						
	10^5CMC moldm^{-3}	10^5C_{20}mol dm^{-3}	CMC/C_{20}	$\prod_{cmc}$ mN/m	$10^6\Gamma_{max}$ mol/m^2	A_{min} Å^2	$-\Delta G^0_{ads}$ kJ/mol	10^5CMC moldm^{-3}	10^5C_{20} mol dm^{-3}	CMC/C_{20}	$\prod_{cmc}$ mN/m	$10^6\Gamma_{max}$ mol/m^2	A_{min} Å^2	$-\Delta G^0_{ads}$ kJ/mol
C_4NH_2														
0	3.8(3.6)[29–31]	0.87	4.36	26.5	1.03	161.2	64.8	4.6(4.7)[29–31]	1.00	4.19	26.5	0.88	188.7	72.9
0.2	3.16	0.83	3.79	27.0	1.13	146.9	67.9	3.63	0.95	3.80	27.0	1.32	125.78	65.8
0.4	2.51	0.76	3.31	32.0	1.88	88.3	66.5	3.02	0.83	3.63	28.7	1.50	110.69	53.7
0.6	0.79	0.40	1.99	35.5	2.77	73.1	54.3	1.86	0.63	2.95	31.8	1.88	88.31	56.9
0.8	0.28	0.11	2.52	41.0	2.37	70.0	79.8	1.66	0.60	2.76	35.5	2.07	80.21	64.8
C_5NH_2														
0.2	2.34	0.81	2.56	27.5	1.85	89.7	63.2	2.88	0.94	3.02	27.7	1.84	90.2	56.1
0.4	1.96	0.66	2.96	34.0	2.29	72.5	62.9	2.29	0.91	2.51	30.7	1.94	85.6	73.9
0.6	0.72	0.30	2.40	37.0	2.66	62.4	56.3	1.07	0.55	1.95	32.0	2.05	80.9	62.3
0.8	0.24	0.12	1.99	39.0	2.78	59.7	94.9	0.80	0.50	1.58	33.8	2.15	77.2	78.9
C_6NH_2														
0.2	1.96	0.76	2.58	30.0	1.83	90.7	73.2	1.29	0.69	1.86	24.5	1.45	114.50	52.1
0.4	1.26	0.60	2.09	34.5	1.93	86.0	75.9	1.23	0.63	1.95	30.7	1.53	97.05	77.6
0.6	0.55	0.17	3.15	40.0	2.15	77.2	75.4	1.00	0.44	2.29	33.8	2.10	79.06	70.6
0.8	0.21	0.08	2.51	42.0	2.51	66.1	73.4	0.62	0.35	1.77	37.3	2.53	65.62	69.7
C_7NH_2														
0.2	1.77	0.83	2.13	31.5	1.76	94.3	74.2	0.91	0.72	1.26	25.5	1.61	103.12	79.6
0.4	0.79	0.30	2.63	33.5	2.46	67.5	69.8	0.60	0.36	1.66	33.5	2.40	69.18	79.4
0.6	0.28	0.15	1.82	36.0	2.56	64.8	92.7	0.40	0.29	1.71	35.5	2.58	64.35	63.2
0.8	0.12	0.05	2.18	41.0	2.87	57.8	97.4	0.27	0.17	1.62	39.4	2.69	61.72	84.4
C_8NH_2														
0.2	0.72	0.04	1.66	33.0	1.67	99.4	70.7	0.50	0.19	2.50	30.7	1.61	103.12	73.2
0.4	0.22	0.09	2.30	37.0	1.70	97.6	102.2	0.40	0.13	2.88	36.2	1.88	88.31	85.6
0.6	0.08	0.03	2.63	40.0	1.95	85.1	98.5	0.35	0.12	2.82	38.2	2.10	79.06	80.8
0.8	0.03	0.01	2.62	42.0	2.15	77.2	92.6	0.18	0.07	2.63	41.0	2.69	61.72	65.2

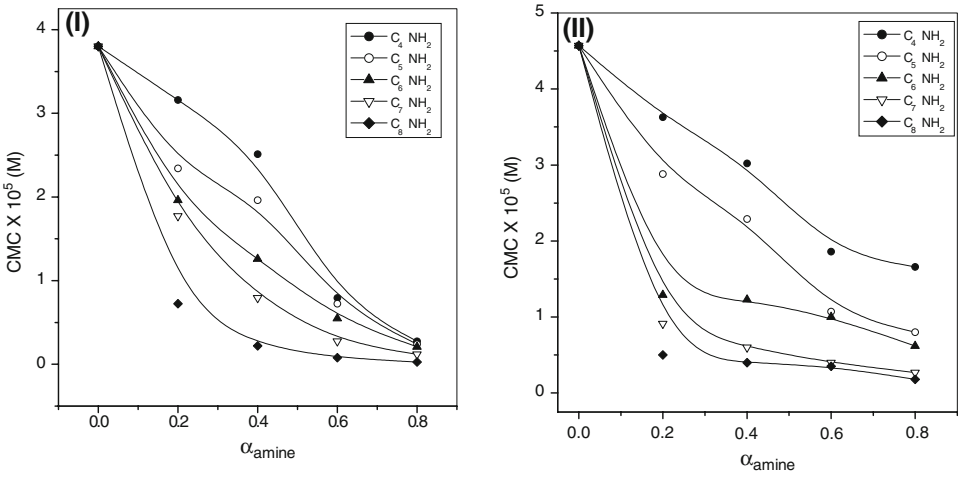


Fig. 2 Values of CMC of the gemini surfactants [16-5-16 (I) and 16-6-16 (II)] at different mole fractions of alkylamines (C_4NH_2–C_8NH_2)

A_{min} was evaluated by using the relation

$$A_{\min} = 10^{20}/N_A\Gamma_{\max}\left(\text{Å}^2\right) \quad (3)$$

where N_A is Avogadro's number. The A_{min} area decrease with increasing additive concentration (Table 1) takes place due to progressive charge shielding and closer packing of the gemini surfactant ions at the surface. This result suggests that the orientation of the gemini surfactant molecules at the interface is almost perpendicular to the interface [37]. Whereas Γ_{max} decreases with increasing the spacer length, both in the absence and presence of amines, the A_{min} followed a reverse order, i.e., 16-6-16 > 16-5-16 > 16-4-16 [36]. This may be due to intramolecular head group distances. In this case, the spacer chain could be in contact with water. With addition of amines, the values of Γ_{max} increase and the values of A_{min} decrease and the trend is followed by all the systems.

To quantify the effect of alkylamines in the mixture on the micellization process, the standard Gibbs energy of micellization, ΔG^0_m, and the standard Gibbs energy of adsorption, ΔG^0_{ads}, were evaluated using Eqs. 4 and 5,

$$\Delta G^0_m = (3 - 2g)RT \ln C^m_{12} \quad (4)$$

(C^m_{12} is the CMC of the mixture of the two components at a given mole fraction and g is the degree of counterion dissociation to the micelles)

$$\Delta G^0_{ads} = \Delta G^0_m - \Pi_{CMC}/\Gamma_{max}. \quad (5)$$

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. 5 expresses 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. 5 is very small compared to the ΔG^0_m, which indicates that the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle is negligible. All the ΔG^0_{ads} values are negative (Table 1), which implies that the adsorption of the surfactants at the air/mixture interface takes place spontaneously and are in the order: 16-4-16 [36] > 16-5-16 > 16-6-16. The average values of ΔG^0_{ads} for amines follow the order: C_8NH_2 > C_7NH_2 > C_6NH_2 > C_5NH_2 > C_4NH_2 in the case of both gemini surfactants (16-5-16 and 16-6-16) (Table 1), which is in accordance with their hydrophobicity order. The hydrophobicity is the main cause of adsorption.

Molecular interactions between two compounds (amphiphiles) at an interface or in micelles are commonly measured by the so-called β parameters [1, 4, 11, 13], which are conveniently obtained from surface (or interfacial) tension or from CMC data by using well-known equations [11, 38]. By calculating the value of β (interaction) parameters, the nature and strength of the interaction between two components can be determined (β^m is the interaction parameter for mixed micelle formation in an aqueous medium and β^σ is the interaction parameter for mixed monolayer formation at an aqueous solution/air interface). The following alkylamine concentrations were used to calculate the values of β – for β^m: C_4NH_2, $C^m_1 = 8.28 \times 10^{-3}$ M; C_5NH_2, $C^m_1 = 4.17 \times 10^{-3}$ M; C_6NH_2, $C^m_1 = 3.98 \times 10^{-3}$ M; C_7NH_2, $C^m_1 = 3.48 \times 10^{-3}$M; C_8NH_2, $C^m_1 = 1.18 \times 10^{-3}$M; for β^σ: C_4NH_2, $C^\sigma_1 = 3.02 \times 10^{-3}$ M; C_5NH_2, $C^\sigma_1 = 6.31 \times 10^{-3}$ M; C_6NH_2, $C^\sigma_1 = 7.58 \times 10^{-4}$ M; C_7NH_2, $C^\sigma_1 = 1.58 \times 10^{-3}$M; C_8NH_2, $C^\sigma_1 = 1.99 \times 10^{-4}$M). The corresponding activity coefficients (f^σ_1 and f^σ_2, f^m_1 and f^m_2) were calculated using the relevant Eqs. 6 and 7

$$f_1 = \exp\left\{\beta(1 - X_1)^2\right\} \quad (6)$$

$$f_2 = \exp\left\{\beta(X_1)^2\right\} \quad (7)$$

β indicates the degree of interaction between the two components and also accounts for the deviation from

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 16-*s*-16 and primary linear alkylamines at different mole fractions of alkylamines (α_{amine})

α_{amine}	X_1^m	β^m	f_1^m	f_2^m	X_1^σ	β^σ	f_1^σ	f_2^σ
16-5-16								
C_4NH_2								
0.2	0.169	−7.820	0.00452	0.799	0.172	−9.049	0.00202	0.765
0.4	0.256	−9.670	0.00474	0.531	0.220	−9.389	0.00331	0.635
0.6	0.360	−15.720	0.00159	0.130	0.346	−16.484	0.00087	0.139
0.8	0.415	−18.402	0.00184	0.042	0.410	−24.140	0.00022	0.017
C_5NH_2								
0.2	0.221	−9.388	0.00336	0.632	0.032	−5.761	0.00453	0.994
0.4	0.283	−10.559	0.00439	0.429	0.232	−12.350	0.00069	0.514
0.6	0.368	−15.726	0.00187	0.119	0.326	−18.024	0.00028	0.147
0.8	0.422	−21.668	0.00072	0.021	0.383	−23.592	0.00013	0.031
C_6NH_2								
0.2	0.248	−9.776	0.00397	0.548	0.223	−8.798	0.00493	0.646
0.4	0.321	−12.006	0.00394	0.290	0.319	−12.119	0.00362	0.291
0.6	0.384	−16.181	0.00215	0.092	0.393	−18.225	0.00121	0.059
0.8	0.431	−21.415	0.00097	0.019	0.431	−22.268	0.00074	0.016
C_7NH_2								
0.2	0.261	−10.158	0.00390	0.500	0.220	−9.992	0.00229	0.616
0.4	0.346	−13.883	0.00264	0.190	0.325	−14.705	0.00123	0.211
0.6	0.402	−18.855	0.00118	0.047	0.382	−19.431	0.00060	0.059
0.8	0.439	−23.425	0.00063	0.011	0.425	−25.098	0.00025	0.011
C_8NH_2								
0.2	0.339	−12.866	0.00362	0.228	0.339	−14.376	0.00187	0.192
0.4	0.403	−17.667	0.00184	0.057	0.407	−21.140	0.00059	0.030
0.6	0.438	−22.129	0.00092	0.014	0.437	−25.731	0.00029	0.007
0.8	0.466	−23.919	0.00109	0.005	0.462	−30.880	0.000131	0.001
16-6-16								
C_4NH_2								
0.2	0.180	−7.918	0.00487	0.774	0.151	−7.724	0.00382	0.838
0.4	0.259	−9.432	0.00563	0.531	0.260	−10.608	0.00300	0.488
0.6	0.336	−12.517	0.00401	0.243	0.339	−14.451	0.00181	0.190
0.8	0.385	−14.491	0.00417	0.117	0.383	−16.457	0.00190	0.089
C_5NH_2								
0.2	0.221	−9.046	0.00413	0.643	0.125	−7.326	0.00366	0.892
0.4	0.288	−10.436	0.00504	0.421	0.274	−12.125	0.00168	0.402
0.6	0.364	−14.536	0.00279	0.146	0.343	−15.884	0.00105	0.154
0.8	0.408	−17.133	0.00247	0.057	0.396	−20.290	0.00061	0.041
C_6NH_2								
0.2	0.301	−12.568	0.00215	0.320	0.297	−11.980	0.00268	0.347
0.4	0.335	−12.668	0.00369	0.241	0.335	−12.305	0.00433	0.251
0.6	0.374	−14.070	0.00403	0.140	0.379	−14.218	0.00417	0.130
0.8	0.421	−17.387	0.00294	0.046	0.424	−17.375	0.00314	0.044
C_7NH_2								
0.2	0.322	−13.967	0.00163	0.235	0.320	−15.848	0.00066	0.197
0.4	0.366	−15.601	0.00189	0.124	0.355	−16.744	0.00090	0.124
0.6	0.401	−17.755	0.00171	0.057	0.388	−18.746	0.00089	0.059
0.8	0.435	−20.537	0.00142	0.020	0.425	−22.454	0.00060	0.017
C_8NH_2								
0.2	0.365	−15.057	0.00231	0.134	0.374	−15.399	0.00239	0.116
0.4	0.397	−15.633	0.00340	0.085	0.408	−16.543	0.00303	0.064
0.6	0.423	−16.390	0.00427	0.053	0.434	−17.739	0.00340	0.035
0.8	0.458	−20.141	0.00269	0.015	0.465	−21.020	0.00244	0.011

Table 3 Comparison table for synergism of the mixed systems of gemini surfactants and alkyl amines

α_{amine}	System	$\ln(C_1^{\sigma}/C_2^{\sigma})$	$\ln(C_1^{m}/C_2^{m})$	β^{σ}	β^{m}	$\beta^{\sigma} - \beta^{m}$
16-5-16						
0.2	C_4NH_2/16-5-16	6.12	5.34	−9.049	−7.820	−1.229
0.4				−9.389	−9.670	+0.281
0.6				−16.484	−15.720	−0.764
0.8				−24.140	−18.402	−5.738
0.2	C_5NH_2/16-5-16	7.41	5.11	−5.761	−9.388	+3.627
0.4				−12.350	−10.559	−1.791
0.6				−18.024	−15.726	−2.298
0.8				−23.592	−21.668	−1.924
0.2	C_6NH_2/16-5-16	4.74	4.65	−8.798	−9.776	+0.978
0.4				−12.119	−12.006	−0.113
0.6				−18.225	−16.181	−2.044
0.8				−22.268	−21.415	−0.853
0.2	C_7NH_2/16-5-16	5.48	4.52	−9.992	−10.158	+0.166
0.4				−14.705	−13.883	−0.822
0.6				−19.431	−18.855	−0.576
0.8				−25.098	−23.425	−1.673
0.2	C_8NH_2/16-5-16	3.91	3.43	−14.376	−12.866	−1.510
0.4				−21.140	−17.667	−3.473
0.6				-25.731	−22.129	−3.602
0.8				−30.880	−23.919	−6.961
16-6-16						
0.2	C_4NH_2/16-6-16	5.73	5.20	−7.724	−7.918	+0.194
0.4				−10.608	−9.432	−1.176
0.6				−14.451	−12.517	−1.934
0.8				−16.457	−14.491	−1.966
0.2	C_5NH_2/16-6-16	6.05	4.93	−7.326	−9.046	−1.720
0.4				−12.125	−10.436	−1.689
0.6				−15.884	−14.536	−1.348
0.8				−20.288	−17.133	−3.155
0.2	C_6NH_2/16-6-16	4.35	4.46	−11.980	−12.568	+0.588
0.4				−12.305	−12.668	+0.363
0.6				−14.218	−14.070	−0.148
0.8				−17.375	−17.387	+0.012
0.2	C_7NH_2/16-6-16	5.08	4.33	−15.848	−13.967	−1.881
0.4				−16.744	−15.601	−1.143
0.6				−18.746	−17.755	−0.991
0.8				−22.454	−20.537	−1.917
0.2	C_8NH_2/16-6-16	3.01	3.25	−15.399	−15.057	−0.342
0.4				−16.543	−15.633	−0.910
0.6				−17.739	−16.390	−1.349
0.8				−21.020	−20.141	−0.879

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 between the two components in the mixed micelle 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 the increase in [amines] (also evident from the CMC values (Table 1), which decrease with increasing [amines]).

The β^{σ} trend is similar (Table 2), i.e., the mixtures of alkylamines/gemini surfactants show stronger attractive interaction at the solution/air interface. The β^{σ} values are more negative than β^{m} values 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 compared to that of accommodating at the planar interface. Table 2 data indicate that the attractive interactions of geminis/amines are more in the case of a smaller spacer chain length than that of the long spacer chain length of the geminis.

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 [39]. 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
(b) $|\beta^{\sigma}| > |\ln (C_1^{\sigma}/C_2^{\sigma})|$

where C_1^{σ} and C_2^{σ} are the molar concentrations of amphiphile 1 and 2, respectively, required to achieve that same surface tension value. All mixtures of the cationic gemini surfactant with alkylamines exhibit synergism in surface tension reduction efficiency. The data also show that there is very good synergism in surface tension reduction efficiency for the gemini/alkylamine mixtures (Table 3).

Synergism in the mixed micelle formation exists when the CMC of the mixture is less than that of either amphiphile of the mixture. The conditions for this to exist in a mixture of two surfactants are the following [39]:

(a) β^{m} must be negative
(b) $|\beta^{m}| > |\ln (C_1^{m}/C_2^{m})|$
(c) $|\beta^{\sigma} - \beta^{m}| > [|\ln (C_1^{\sigma}/C_2^{\sigma})| - |\ln (C_1^{m}/C_2^{m})|]$

where C_1^{m} and C_2^{m} are the critical micelle concentrations of amphiphiles 1 and 2, respectively. Table 3 also shows that all the mixtures of cationic surfactants exhibit synergism in mixed micelle formation with the alkylamines.

Conclusions

The interaction of two cationic gemini surfactants [pentanediyl-1, 5-bis(dimethylcetylammonium bromide) and hexanediyl-1, 6-bis(dimethylcetylammonium bromide)] with primary linear alkylamines were investigated. The following conclusions were drawn:

(a) The trend of the increase of Γ_{max} and decrease of CMC and A_{min} are due to formation of mixed micelles with the gemini surfactants.
(b) Increasing the spacer chain length of the geminis increases the CMC, C_{20}, A_{min} values and decreases the Π_{CMC}, Γ_{max} values.
(c) The ΔG_{ads}^{0} values indicate that the adsorption of the surfactant at the air/solution interface takes place spontaneously.
(d) The β values (both β^{m} and β^{σ}) indicate the attractive interaction and the interaction is more in the case of a smaller spacer chain length because in the case of 16-5-16 we get more negative β values in comparison to 16-6-16 (Table 2).
(e) The gemini surfactant/alkylamine systems show an increase in synergism with the increase in amine concentration.
(f) From the values of interaction parameters, we can say that there is increased synergism in the mixed monolayer in comparison to the mixed micelle (as $\beta^{\sigma} > \beta^{m}$, Table 2).

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References

1. Rosen MJ (2004) Surfactants and interfacial phenomena, 3rd edn. Wiley-Interscience, New York
2. Menger FM, Littau CA (1991) Gemini surfactants: synthesis and properties. J Am Chem Soc 113:1451–1452
3. Zana R, Talmon Y (1993) Dependence of aggregation morphology on structure of dimeric surfactants. Nature 362:228–230
4. Rosen MJ (1993) Geminis: a new generation of surfactants. Chemtech 23:30–33
5. Karaborni S, Esselink K, Hilbers PAJ, Smit B, Karthauser J, van Os NM, Zana R (1994) Simulating the self-assembly of gemini (Dimeric) surfactants. Science 266:254–256
6. Rosen MJ, Tracy DJ (1998) Gemini surfactants. J Surfact Deterg 1:547–554
7. Menger FM, Keiper JS (2000) Gemini surfactants. Angew Chem Int Ed 39:1906–1920
8. Menger FM, Littau CA (1993) Gemini surfactants: a new class of self-assembling molecules. J Am Chem Soc 115:10083–10090
9. Zana R (1997) In: Esumi K, Ueno M (eds) Structure–performance relationship in surfactants, chap 6. Dekker, New York, pp 255–283
10. Okahara M, Masuyama A, Sumida Y, Zhu Y-P (1988) Surface active properties of new types of amphipathic compounds with

two hydrophilic ionic groups and two lipophilic alkyl chains. Yukagaku 37:746–748
11. Rosen MJ, Zhu ZH, Hua XY (1992) Relationship of structure to properties of surfactants. 16. Linear decyldiphenylether sulfonates. J Am Oil Chem Soc 69:30–33
12. Song LD, Rosen MJ (1996) Surface properties, micellization, and premicellar aggregation of gemini surfactants with rigid and flexible spacers. Langmuir 12:1149–1153
13. Li F, Rosen MJ, Sulthana SB (2001) Surface properties of cationic gemini surfactants and their interaction with alkylglucoside or maltoside surfactants. Langmuir 17:1037–1042
14. Siddiqui US, Ghosh G, Kabir-ud-Din (2006) Dynamic light scattering studies of additive effect on the microstructure of aqueous gemini micelles. Langmuir 22:9874–9878
15. Kabir-ud-Din, Siddiqui US, Kumar S (2007) Viscometric studies on aqueous gemini micelles in the presence of additives. Colloids Surf A 301:209–213
16. Rodriguez A, Graciani MM, Mufioz M, Robina I, Moya ML (2006) Effects of ethylene glycol addition on the aggregation and micellar growth of gemini surfactants. Langmuir 22:9519–9525
17. Rosen MJ, Mathias JN, Davenport L (1999) Aberrant aggregation behavior in cationic gemini surfactants investigated by surface tension, interfacial tension, and fluorescence methods. Langmuir 15:7340–7346
18. Haque ME, Das AR, Rakshit AK, Moulik SP (1996) Properties of mixed micelles of binary surfactant combinations. Langmuir 12:4084–4089
19. Rosen MJ, Sulthana SB (2001) The interaction of alkylglucosides with other surfactants. J Colloid Interface Sci 239:528–534
20. Liu L, Rosen MJ (1996) The interaction of some novel diquaternary gemini surfactants with anionic surfactants. J Colloid Interface Sci 179:454–459
21. Ghosh S, Chakraborty T (2007) Mixed micelle formation among anionic gemini surfactant (212) and its monomer (SDMA) with conventional surfactants ($C_{12}E_5$ and $C_{12}E_8$) in brine solution at pH 11. J Phys Chem B 111:8080–8088
22. Azum N, Naqvi AZ, Akram M, Kabir-ud-Din (2008) Studies of mixed micelle formation between cationic gemini and cationic conventional surfactants. J Colloid Interface Sci 328:429–435
23. Kabir-ud-Din, Sheikh MS, Dar AA (2009) Interaction of a cationic gemini surfactant with conventional surfactants in the mixed micelle and monolayer formation in aqueous medium. J Colloid Interface Sci 333:605–612
24. Khan IA, Mohammad R, Alam MdS, Kabir-ud-Din (2009) The interaction of cationic gemini surfactant 1, 4-butanediyl- α, ω-bis(dimethylcetylammonium bromide) with primary linear alkanols. J Dispersion Sci Technol 30 (in press)
25. Kumar S, Aswal VK, Singh HN, Goyal PS, Kabir-ud-Din (1994) Growth of sodium dodecyl sulfate micelles in the presence of *n*-octylamine. Langmuir 10:4069–4072
26. Kabir-ud-Din, Kumar S, Kirti, Goyal PS (1996) Micellar growth in presence of alcohols and amines: a viscometric study. Langmuir 12:1490–1494
27. Kabir-ud-Din, Kumar S, Aswal VK, Goyal PS (1996) Effect of addition of *n*-alkylamines on the growth of sodium dodecyl sulfate micelles. J Chem Soc Faraday Trans 92:2413–2415
28. Garcia-Rio L, Leis JR, Mejuto JC, Mosquera V, Rodriguez-Dafonte P (2007) Stability of mixed micelles of cetylpyridinium chloride and linear primary alkylamines. Colloids Surf A 309:216–223
29. Wormuth KR, Kaler EW (1987) Amines as microemulsion cosurfactants. J Phys Chem 91:611–617
30. Singh HN, Prasad CD, Kumar S (1993) Water solubilization in microemulsions containing amines as cosurfactant. J Am Oil Chem Soc 70:69–73
31. Ahmad T, Khan ZA, Naqvi AZ, Kabir-ud-Din (2009) Study of the cloud point variation of amitriptyline hydrochloride solutions in presence of amines and amino acids. Colloid J (in press)
32. Kawase M, Yamanaka K, Yamanaka K, Yamanaka J, Fuchita N, Nakao H, Kamei Y (1985) In: Imahori K, Suzuki F, Suzuki O, Bachrach U (eds) Polyamines: basic and clinical aspects. VNU Science, Ultrecht, pp 447–454
33. Zana R, Benrraou M, Rueff R (1991) Alkanediyl-α, ω-bis(dimethylalkylammonium bromide) surfactants. 1. Effect of the spacer chain length on the critical micelle concentration and micelle ionization degree. Langmuir 7:1072–1075
34. De S, Aswal VK, Goyal PS, Bhattacharya S (1996) Role of spacer chain length in dimeric micellar organization. Small-angle neutron scattering and fluorescence studies. J Phys Chem 100:11664–11671
35. Kabir-ud-Din, Fatma W, Khan ZA, Dar AA (2007) ^{1}H NMR and viscometric studies on cationic gemini surfactants in presence of aromatic acids and salts. J Phys Chem B 111:8860–8867
36. Khan IA, Mohammad R, Alam Md S, Kabir-ud-Din (2009) Effect of alkylamine chain length on the critical micelle concentration of cationic gemini surfactant butanediyl-α, ω-bis(dimethylcetylammonium bromide) surfactant. J Dispersion Sci Technol 30 (in press)
37. Anand K, Yadav OP, Singh PP (1991) Studies on the surface and thermodynamic properties of some surfactants in aqueous and water + 1, 4-dioxane solutions. Colloids Surf 55:345–348
38. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry of surfactants, vol 1. Plenum, New York, pp 337–354
39. Rosen MJ (1998) Molecular interaction and the quantitative prediction of synergism in the mixtures of surfactants. Prog Colloid Polym Sci 109:35–41

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