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ORIGINAL CONTRIBUTION

Mixed micellization of an anionic gemini surfactant (GA) with conventional polyethoxylated nonionic surfactants in brine solution at pH 5 and 298 K

Tanushree Chakraborty · Soumen Ghosh

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Abstract The micellization behavior of an anionic gemini surfactant, GA with nonionic surfactants $C_{12}E_8$ and $C_{12}E_5$ in presence of 0.1 M NaCl at 298 K temperature, has been studied tensiometrically in pure and mixed states, and the related physicochemical parameters (cmc, γ_{cmc}, pC_{20}, Γ_{max}, and A_{min}) have been evaluated. Tensiometric profile (γ vs log [surfactant]), for conventional surfactants, generally consists of a single point of intersection; a gradually decreasing line (normally linear, or with slight curvature) ultimately saturates in γ at a particular [surfactant], corresponding to complete monolayer saturation. The gemini, in this report, led to two unequivocal breaks in the tensiometric isotherm. An attempt to the interpretation of the two breaks from molecular point of view is provided, depending solely on the chemical structure of the surfactant. The gemini, even in mixed state with the conventional nonionic surfactants $C_{12}E_5$ and $C_{12}E_8$, manifested the dual breaks; of course, the dominance of the feature decreases with increasing mole fraction of the nonionics in the mixture. Theories of Clint, Rosen, Rubingh, Motomura, Georgiev, Maeda, and Nagarajan have been used to determine the interaction between surfactants at the interface and micellar state of aggregation, the composition of the aggregates, the theoretical cmc in pure and mixed states, and the structural parameters according to Tanford and Israelachvili. Several thermodynamic parameters have also been predicted from those theories.

Keywords Gemini surfactant · POE · Surface tension · Regular solution theory

T. Chakraborty · S. Ghosh (✉)
Centre for Surface Science, Department of Chemistry,
Jadavpur University,
Kolkata 700 032, India
e-mail: gsoumen70@hotmail.com

Introduction

Geminis are a special class of surfactants containing two hydrophobic tails and two hydrophilic heads interspaced by a spacer, whose affinity toward water can be tuned by judicial choice [1–3]. The geminis, being much surface active compared to the conventional surfactants [4–9], are of most interest in the field of surface chemical studies in recent days. Du et al. [10] has worked on anionic gemini surfactant with conventional nonionic surfactant in aqueous medium, phase behavior, and microstructures of the gemini–SDS–H_2O ternary system was studied by Shang et al. [11]; thermodynamics and aggregation properties of gemini surfactants designed for gene delivery was focused by Wettig et al. [12]; cationic ester-containing Gemini surfactants were synthesized, and their properties were investigated by Tehrani-Bagha et al. [13]; the effect of the spacer group on the association behavior of gemini surfactants in aqueous solution was studied by Zana [14]; supramolecular expression of chirality in assemblies of gemini surfactants was viewed by Sommerdijk et al. [15]; double helical silica fibrils by sol–gel transcription of chiral aggregates of gemini surfactants was studied by Sugiyasu et al. [16]. Earlier, we have reported the mixed micellization of an anionic gemini (212) with the two conventional polyethoxylated nonionic surfactants $C_{12}E_8$ and $C_{12}E_5$ (POE) in brine solution at pH 11 [17].

In this paper, we are reporting a surface chemical study of mixed micellization of another anionic gemini, GA ($((CH_2)_2[N(COC_{11}H_{23})CH(COOH)CH_2(COOH)]_2.2NaOH$) in pure and mixed states with the nonionic surfactants $C_{12}E_8$ and $C_{12}E_5$ in 0.1 M NaCl at pH=5 and 298 K. In contrast to the commonly reported tensiometric profiles, we observed two distinct breaks for GA, which is also prominent in its mixed state with the conventional nonionic

surfactants, although with decreasing dominance with increasing mole fraction of the nonionics in the solution. The first break in the profile corresponds to the onset of interfacial adsorption of the gemini. This additional feature originates from the increased hydrophilicity of the surfactant monomer in solution owing to the presence of two carboxylic acid groups (compared to a reported similar gemini, 212) in the head group of the surfactant, which can be efficiently solvated in aqueous solution. This enhanced solubility of the molecule increases its distribution coefficient among the bulk and the interfacial solution, and is manifested in a very slight lowering in interfacial tension of the solution in low [GA] regime. After reaching the threshold at c_m, it distributes itself between the bulk and interface as usual surfactant, and results in a concomitant decrease in γ, and ultimately saturates at cmc. Similar feature is also prominent for the nonionic $C_{12}E_8$ under the experimental condition, whereas it is absent in case of $C_{12}E_5$. This is rationalized on the basis of the presence of more polyoxyethylene moiety in the head group of $C_{12}E_8$, compared to $C_{12}E_5$, and the resultant solvation of the former. The established theories of Clint [18, 19], Rosen [20, 21], Rubingh [22], Motomura [23, 24], Georgiev [25], Maeda [26, 27], and Nagarajan [28–31] have been used to quantify the interaction parameters, composition, packing parameter, and theoretical cmc. Regular solution theory and pseudo-phase model of micellization has been applied to determine various thermodynamic functions.

Experimental

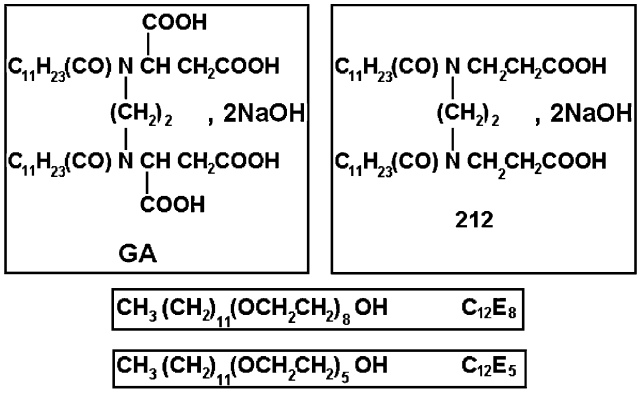
Materials

The anionic gemini surfactant GA was gifted by K. Tsubone, Wakamiya 13-104, Kanagawa, 254-0911, Japan. The procedures for its (GA) synthesis and purification have been reported elsewhere [32]. The nonionic amphiphiles, $C_{12}E_5$ and $C_{12}E_8$ were the products of Nikkol Chemical Co. (Tokyo, Japan). The schematic representations of all the surfactants used are shown in Scheme 1.

All solutions were prepared in double-distilled water at pH=5 in the presence of 0.1 M NaCl, and experiments were done under thermostated conditions at 298 K with an accuracy of ±0.01 K.

Method

The tensiometric experiments were performed using a platinum ring by the ring detachment method in a calibrated du Noüy Tensiometer (Krüss, Germany) at a constant temperature of 298 K. Detailed procedure has been reported earlier [33–38]. Each experiment was repeated several times to achieve good reproducibility. The γ values were accurate within ±0.1 mN m^{-1}.



Scheme 1 Structures of GA, 212, $C_{12}E_8$, and $C_{12}E_5$

Results and discussion

The tensiometric profile of anionic gemini surfactant, GA, is documented in Fig. 1a. The inset in Fig. 1a shows the tensiometric profile for another anionic gemini, 212 in 0.1 M NaCl at pH 11. Using 212, we have experienced a single break in the γ vs log C profile, whereas for GA, under the experimental condition, there are two distinct breaks. The surface tension of GA in 0.1 M NaCl at pH 5 decreases slowly up to a certain surfactant concentration, and then decreases steeply till the air/solution interface is completely saturated with GA; whereafter, the surface tension remains almost unaffected. It is assumed that up to a certain [GA] corresponding to the first break, the GA molecules populate the bulk phase preferentially; afterwards, the monomers start populating the interface, and on increasing [GA], surface population increases resulting in a decrease in the γ values. The surfactant concentration corresponding to the first break is called the critical monolayer concentration [39] (c_m), and at cmc (the second break), the interface is saturated with the surfactant monomers.

In case of 212, c_m was not observed [9, 17]. Tsubone and Ghosh [40] reported the first break of GA in 0.1 M NaCl at 1×10^{-6} M using fluorescence method. The presence of c_m in the profile of GA is probably due to the presence of two additional carboxylic acid groups in the head group per GA molecule compared to 212 ($(CH_2)_2[N(COC_{11}H_{23})CH_2CH_2COONa]_2$), and hence, enhanced solubilization in aqueous solution through hydration. Actually, weakly ionizable surfactants like 212 and GA are very sensitive to changes in pH of the solution and exist as different chemical species following the pH values of the solutions [40]. In the presence of a large amount of NaCl at pH 11, the molecule 212 dissociates completely and exists as one chemical species, whereas for GA at pH 5, the acids, the

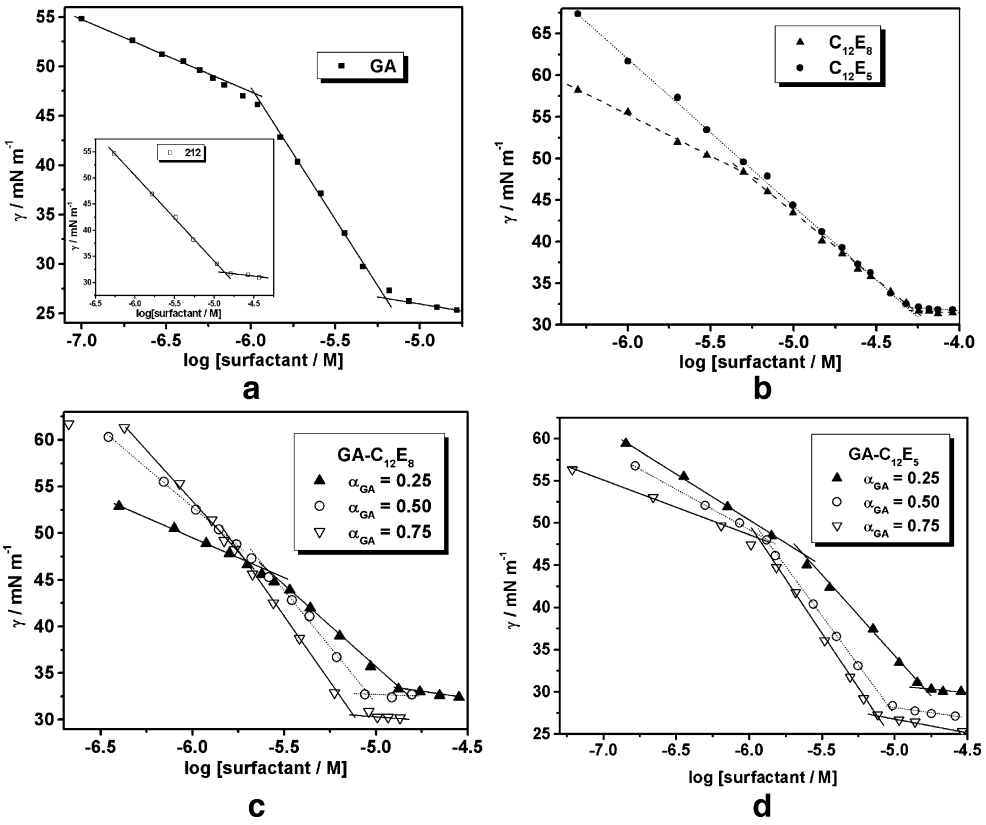


Fig. 1 Tensiometric plots showing the variation of surface tension (γ) with log [surfactant] at 0.1 M NaCl, pH 5 and 298 K; **a** pure GA (*inset* pure 212); **b** pure $C_{12}E_8$ and $C_{12}E_5$; **c** mixed GA–$C_{12}E_8$; and **d** mixed GA–$C_{12}E_5$

anions, and the so-called acid soaps all co-exist [40]. Two molar equivalents of NaOH are used to neutralize two carboxylate groups in a GA molecule having four carboxylate groups, and based on this, the values of micelle ionization degree have been evaluated (0.75 for c_m and 0.97 for cmc), whereas that value of 212 is 0.96 [40].

Figure 1b,c and d represent the tensiometric profiles of two pure nonionic surfactants ($C_{12}E_8$ and $C_{12}E_5$) and the mixed micellization of GA-$C_{12}E_8$ and GA-$C_{12}E_5$, respectively. The c_m and cmc values for GA, $C_{12}E_8$, and $C_{12}E_5$ in pure state are reported in Tables 1 and 2. GA is more surface active compared to the conventional nonionic surfactants as evidenced from the lower cmc and γ_{cmc} values compared to the nonionics. Between $C_{12}E_8$ and $C_{12}E_5$, the latter has the lower cmc (c_m is not observed) as expected from the lower degree of solvation at the polyethoxylated head group and, hence, less tendency to populate the bulk phase in monomeric form. Both the nonionics have greater cmc at pH 11 in 0.1 M NaCl solutions as observed in our earlier study [17]. This is probably due to the enhanced solubilization in bulk water of the protonated POE head groups in alkaline pH (11).

The Gibbs surface excess (Γ_{max}) was calculated from the slope of the γ vs log C profile near the cmc point [33–38] using the relation

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\underset{c\sim cmc}{Lt}\frac{d\gamma}{d\log C} \quad (1)$$

where n is the number of species in solution [17] and n is taken as unity for both the pure ionic and the nonionic surfactants due to the presence of swamping amount of Na^+ in solution [7, 17], R is the universal gas constant and T is the temperature in absolute scale. For the mixtures, n is considered to be 2. The higher the Γ_{max}, steeper is the

Table 1 Surface chemical properties of pure GA, $C_{12}E_8$, and $C_{12}E_5$ in 0.1 M NaCl at pH 5 and 298 K

Surfactants	$c_m \times 10^6$/M	cmc$\times 10^6$/M	$\Gamma_{max} \times 10^6$	A_{min}	pC_{20}	γ_{cmc}	$-\Delta G^0_m$	$-\Delta G^0_{ad}$
GA	1.05	6.30	4.64	0.36	6.61	26.4	39.6	48.9
$C_{12}E_8$	4.97	53.9	2.84	0.59	5.71	31.6	34.3	48.0
$C_{12}E_5$	–	48.3	3.07	0.54	5.44	32.0	34.6	46.8

Γ_{max} in mol m^{-2}, A_{min} in nm^2 $molecule^{-1}$, γ_{cmc} in mN m^{-1}, and ΔG^0 in kJ $mole^{-1}$ units

Table 2 Surface chemical properties of binary mixed micelles of GA-$C_{12}E_8$ and GA-$C_{12}E_5$ in 0.1 M NaCl at pH 5 and 298 K

α_{GA}	$c_m\times10^6$/ M	cmc$\times10^6$/ M	$\Gamma_{max}\times10^6$	A_{min}	pC_{20}	γ_{cmc}	$-\Delta G_m^0$	$-\Delta G_{ad}^0$	cmc$^C\times10^6$/ M
GA–$C_{12}E_8$									
0.25	2.64	13.6	1.55	1.08	6.37	33.3	37.7	50.0	18.6
0.50	2.65	9.21	2.12	0.78	5.98	32.7	38.7	47.4	11.3
0.75	1.84	7.54	2.46	0.68	5.94	30.4	39.1	47.7	8.08
GA–$C_{12}E_5$									
0.25	2.42	16.2	1.68	0.98	6.07	30.4	37.3	49.9	18.1
0.50	1.28	9.23	1.97	0.86	6.21	28.1	38.6	49.7	11.1
0.75	1.10	7.63	2.26	0.74	6.45	27.1	39.1	48.8	8.05

Γ_{max} in mol m^{-2}, A_{min} in nm^2 molecule^{-1}, γ_{cmc} in mN m^{-1}, and ΔG^0 in kJ mole^{-1} units

approach to cmc and higher is the surface activity. So, GA is the most surface active, following $C_{12}E_5$ and $C_{12}E_8$. Similar trend was also observed in our earlier study at pH 11 and 0.1 M NaCl solution [17].

Average area of exclusion at the saturated air/solution interface per surfactant molecule was calculated using

$$A_{\min}\left(nm^2 molecule^{-1}\right) = \frac{10^{18}}{N_A \Gamma_{\max}} \tag{2}$$

where N_A is the Avogadro number. Tables 1 and 2 shows that $C_{12}E_8$ and $C_{12}E_5$ have more or less similar A_{min}, whereas it is much less for GA, implying greater number density of GA monomer at the interface. The lower γ_{cmc} value for GA also indicates its enhanced surface activity.

For the mixtures, c_m and cmc decrease with increasing stoichiometric composition of GA for either of the mixtures. The enhancement in Γ_{max} with increasing stoichiometric mole fraction of GA (α_{GA}), also indicates increased surface activity of the mixture. Similar results have been observed from the decreasing value of γ_{cmc} and A_{min} of the mixture.

Another physical quantity pC_{20} is defined as pC_{20}= −logC_{20}, where C_{20} is the surfactant molar concentration required to decrease the surface tension of pure water by 20 mN m^{-1} and also dictates the surface activity of a surfactant [20, 36]. The higher the pC_{20} value, the higher is the efficacy of the surfactant to adsorb at the interface and, thus, lowering the surface tension values of the solution [20]. In Tables 1 and 2, the pC_{20} value increases with increasing stoichiometric mole fraction of GA in GA–$C_{12}E_5$ mixture, but the reverse trend is observed in case of GA–$C_{12}E_8$ mixture.

The standard free energy of micellization (ΔG_m^0) is calculated in accordance with the pseudophase model using

$$\Delta G_m^0 = (1+\nu)\, RT\, ln\, X_{cmc} \tag{3}$$

where X_{cmc} is the cmc of the surfactant in mole fraction unit and ν is the degree of counter ion binding of the aggregates. Here, we have neglected ν in calculating ΔG_m^0 because of the presence of the swamping amount of NaCl in the solution [17]. The ΔG_m^0 values are reported in Table 1 and 2. The negative values of ΔG_m^0 signify spontaneity of aggregate formation and slightly decrease with increasing values of α_{GA}.

The standard free energy of interfacial adsorption at the air/solution interface is calculated using the relation [33–38]

$$\Delta G_{ad}^0 = \Delta G_m^0 - \left(\frac{\pi_{cmc}}{\Gamma_{\max}}\right) \tag{4}$$

where π_{cmc} is the surface pressure at cmc and is calculated as $\pi_{cmc} = \gamma_0 - \gamma_{cmc}$, γ_0 being the surface tension value of 0.1 M NaCl solution at pH 5. From Tables 1 and 2, it is observed that the values of ΔG_{ad}^0 are almost constant with the change of α_{GA}.

Application of theories of micellization

1. *Clint model*. For ideal mixtures, where the individual components are noninteracting, cmc of a mixture can be predicted using the Clint model [18, 19], where the cmc of a mixed surfactant solution (cmc_{mix}^C) is given by

$$\frac{1}{cmc_{mix}^C} = \sum_{i=1}^{n}\left(\frac{\alpha_i}{cmc_i}\right) \tag{5}$$

where α_i is the stoichiometric mole fraction of the *i*th component in the mixture and cmc$_i$ is the critical micellar concentration of the pure *i*th component under the similar experimental condition. The model is useful for comparison between ideal and nonideal mixtures. A lower value of observed cmc for the mixture ($cmc_{mix} < cmc_{mix}^C$) as reported in Tables 1 and 2 signifies synergistic interaction among the components in the mixture.

2. *Rosen model.* It considers the interaction between the amphiphiles in a mixed surfactant solution at the air/

solution interface. In this model, the effects of counterion condensation are neglected; consequently, solutions containing any ionic surfactants should have the same total ionic strength with a swamping excess of any counterions [20]. The interfacial mole fraction of the surfactant 1 (X^{σ}) at the mixed adsorbed film can be calculated iteratively from the Rosen model [20, 21] solving the equation

$$\frac{(X^{\sigma})^2 \ln\left(\alpha_1 \, C_{mix}/X^{\sigma}C_1^0\right)}{(1-X^{\sigma})^2 \ln\left[(1-\alpha_1)C_{mix}/(1-X^{\sigma})C_2^0\right]} = 1 \qquad (6)$$

where C_{mix}, C_1^0 and C_2^0 are the concentrations of the mixture, pure surfactants 1 and 2, respectively, at a fixed γ value, α_1 is the stoichiometric mole fraction of surfactant 1 in solution. The X^{σ} value was then used to evaluate the interaction parameter (β^{σ}) at the air/solution interface using

$$\beta^{\sigma} = \frac{\ln\left(\alpha_1 C_{mix}/X^{\sigma}C_1^0\right)}{(1-X^{\sigma})^2} \qquad (7)$$

According to Rosen [20, 21], the surfactant mixtures are generally used above their cmc, and β^{σ} should be determined using C_1^0, C_2^0, and C_{mix} values taken from the γ-log$C$ plots at such a lowest possible value of γ that the slopes are almost linear. The β^{σ} and X^{σ} values of the GA–$C_{12}E_8$ and GA–$C_{12}E_5$ mixtures are presented in Table 3. The negative value of β^{σ} indicates synergistic interaction. The interaction parameter decreases on increasing α_{GA}. Higher value of X^{σ} compared to α_{GA} indicates propensity of GA to preferentially populate the interface as compared to the nonionics.

3. *Rubingh model.* The model [22] is based on regular solution theory approximation and is a modification of the Moroi approach [41] to the Lange–Shinoda model [42]. The model was reported to be applicable for ionic–nonionic mixtures [22]. The mole fraction of component 1 (X_{R}) and the interaction parameter (β_{R}) in this model are iteratively calculated, solving a similar type of equation as in Rosen model, only replacing mole fraction of surfactant 1 at the air/solution interface, X^{σ} by micellar mole fraction of the same component, X_{R}, as

$$\frac{(X_R)^2 \ln\left(\alpha_1 \, C_{12}/X_R C_1\right)}{(1-X_R)^2 \ln\left[(1-\alpha_1)\, C_{12}/(1-X_R)C_2\right]} = 1 \qquad (8)$$

and

$$\beta_R = \frac{\ln\left(\alpha_1 \, C_{mix}/X_R C_1\right)}{(1-X_R)^2} \qquad (9)$$

where X_{R} is the mole fraction of a surfactant in the total surfactant mixture in the mixed micellar phase, and C_1, C_2, and C_{12} are the critical micellar concentrations for surfactants 1 and 2 and their mixture, respectively, at a mole fraction α_1.

The interaction parameters in the mixed micelles, and micellar mole fraction of GA, are reported in Table 3. Negative β_{R} values for all the mixtures indicate synergistic interaction in the micellar phase. The micellar phase is again majorly populated by the gemini as observed from $X_{\mathrm{R}} > \alpha_{\mathrm{GA}}$ values. The Rubingh model suffers from the limitation that it is not uniquely applied to dictate the interaction features of any types of mixed micelles.

4. *Motomura model.* Thermodynamically, Motomura et al. [23, 24] considered mixed micelles as a macroscopic bulk phase, and the related energetic parameters can be found out from the excess thermodynamic quantities. The fundamental equation follows:

$$X_2^{Mo} = \widehat{X}_2 - \left(\widehat{X}_1 \, \widehat{X}_2 \Big/ \widehat{cmc}\right)\left(\partial \widehat{cmc} \Big/ \partial \widehat{X}_2\right)_{T,P} \qquad (10)$$

where

$$\widehat{X}_2 = \frac{\nu_2 X_2}{\nu_1 X_1 + \nu_2 X_2}$$

and

$$\widehat{cmc} = (\nu_1 X_1 + \nu_2 X_2) cmc$$

The subscripts 1 and 2 represent surfactant POE and GA, respectively; X represents the mole fraction in solution, and ν represents the number of ions dissociated from the surfactant in solution. The mole fractions of a surfactant in the mixed micelle (X^{Mo}, simple form of X_2^{Mo}) determined by the Motomura equation are presented in Table 3. The X^{Mo} values are very close to that predicted by Rubingh model, ensuring viability of either model in our system under the experimental condition. Motomura's model is

Table 3 Molecular interaction parameters and interfacial and micellar compositions of the mixed micelles obtained using Rosen, Rubingh, Georgiev, and Motomura's models in 0.1 M NaCl at pH 5 and 298 K

α_{GA}	β^{σ}	X^{σ}	β^{R}	X^{R}	X^{Mo}	X^{G}
GA–$C_{12}E_8$						
0.25	−0.51	0.81	−1.47	0.65	0.59	0.50
0.50	−1.04	0.89	−1.48	0.79	0.75	0.68
0.75	−1.46	0.94	−0.42	0.95	0.89	0.82
GA–$C_{12}E_5$						
0.25	−0.39	0.81	−0.47	0.68	0.71	0.48
0.50	−0.73	0.90	−1.07	0.80	0.85	0.68
0.75	−1.14	0.95	−0.61	0.93	0.89	0.82

independent of the nature of surfactants and their counterions and is suitable in the prediction of micellar compositions when the cmc of the mixed micelle is measured as a function of temperature and pressure.

5. *Georgiev model.* This model is based on Markov's chain model for polymerization process of mixed micelles [25]. Using this model, micellar composition, X^{G}, is determined from the values of mole fraction of surfactants in solution (α_i) and two parameters, G_1 and G_2 as follows:

$$\frac{X_1^G}{X_2^G} = \frac{\alpha_1}{\alpha_2}\left(\frac{G_1\alpha_1 + \alpha_2}{G_2\alpha_2 + \alpha_1}\right) \tag{11}$$

where G_i represents the ratio between the equilibrium constants for the formation of micelles constructed by the same type of surfactants (K_{ii}) and different types of surfactants (K_{ij}). The advantage of this new model is that it introduces only two molecular interaction parameters (G_1 and G_2) instead of one (β) as in the regular solution theory (RST). Another advantage of this model over RST is that G_i (i=1, 2) parameters account for the change of the free energy arising out of surfactant self-aggregation and not only of the aggregation enthalpy. The parameter, X^{G} calculated from this model is presented in Table 3. The values of micellar mole fractions of surfactant GA (X^{G}) are concurrent and follow the same trend as the X values obtained from other methods.

From a comparison of the mole fraction of GA at the air/solution interface (X^{σ}), that in the micelles (X^{R}, X^{Mo}, and X^{G}), it is evident that the interface is richer in GA compared to the micellar phase.

6. *Maeda model.* The model [26] is applicable for ionic/nonionic mixed systems with moderately high ionic strength where the short-range electric interaction is no longer negligible. There lies a difference of this model from the RST where only the long-range electric interaction plays an important role in the mixed system. The model assumes the decrease in repulsion among the ionic head groups in an ionic/nonionic mixed micelle due to the presence of nonionic surfactant molecules in the micellar phase. The proposed equation for free-energy change due to the micellization process as a polynomial function of X_2 (the mole fraction of ionic component, GA, in the micellar phase) as

$$\Delta G_{Ma}^{0} = RT\left(B_0 + B_1X_2 + B_2X_2^2\right) \tag{12}$$

where

$$B_0 = \ln X_{cmc.1} \tag{13}$$

$X_{cmc.1}$ is the cmc of the nonionic surfactant in mole fraction scale, and B_2 is the interaction parameter in the micellar phase. Again,

$$B_1 + B_2 = \ln\left(\frac{X_{cmc.2}}{X_{cmc.1}}\right) \tag{14}$$

($X_{cmc.2}$ is the cmc of the ionic surfactant in mole fraction scale),

$$B_2 = -\beta_R \tag{15}$$

(β_R being the interaction parameter in the micellar phase obtained from Eq. 9).

The limitation of this model is that several contributions affecting the stability of the mixed micelles, such as (a) deviation of the mixing free energy from the assumed ideal behavior and (b) direct and/or cooperative interactions among the head groups, are neglected in the present treatment, as they have X_2 dependence.

The ΔG_{Ma}^{0}, B_0, B_1, and B_2 values are presented in Table 4. For a binary system, the B_0 value is constant for all compositions. For GA/$C_{12}E_8$ system, both B_1 and B_2 values decrease with increasing value of α_{GA}, whereas both are independent with the variation of α_{GA} in case of GA/$C_{12}E_5$ system. The negative values of B_1 of GA/POE systems indicate a major role of the tail–tail interaction in the stability of the mixed micelles. Here, GA has two chains of 12 carbons. From Tables 2, and 4, the close resemblance of ΔG_m^0 and ΔG_{Ma}^0 for the GA/POE systems also reflects negligible counterion dissociation of the gemini as described earlier [17].

Very recently, Maeda [27] proposed another theoretical model based on the Gibbs–Duhem equation considered by Hall [43] to predict the excess free energy (g_{ex}) of the ionic–nonionic mixed micelle, which is even applicable to low ionic strength regime. The model relates g_{ex} and the micellar mole fraction of the ionic species x as

$$g^{ex} = x\ln f_I + (1-x)\ln f_N \tag{16}$$

Table 4 Free energy and interaction parameters of binary mixtures obtained from Maeda's models in 0.1 M NaCl at pH 5 and 298 K

α_{GA}	Maeda model [26]				Maeda model [27]		
	$-B_0$	$-B_1$	B_2	$-\Delta G_{Ma}^0$	X^{Ma}	$-g^{ex}$	β^{Ma}
GA–$C_{12}E_8$							
0.25	13.85	3.62	1.47	36.3	0.54	0.41	−1.65
0.50		3.62	1.48	37.9	0.77	0.26	−1.49
0.75		2.56	0.42	39.1	0.86	0.10	−0.85
GA–$C_{12}E_5$							
0.25	13.96	2.50	0.47	36.1	0.65	0.11	−0.48
0.50		3.11	1.07	37.8	0.87	0.14	−1.28
0.75		2.64	0.61	38.7	0.91	0.05	−0.65

ΔG_{Ma}^0 in kJ mole^{-1} unit

where f_I and f_N are the activity coefficients of the ionic (GA) and the non-ionic (POE) species, respectively, and x can be calculated from the ln cmc vs stoichiometric mole fraction of the ionic species (x_1) plot using the equation

$$x = \frac{x_1\left[1-(1-x_1)d\ln cmc/dx_1\right]}{\left[1+\nu(1-x_1)\left\{x_1\left(d\ln cmc/dx_1\right)+1\right\}\right]} \quad (17)$$

The degree of counter ion binding (ν) is negligible in our case due to the presence of swamping amount of salt in the medium and the equation becomes

$$x_{\nu=0} = x_1\left[1-(1-x_1)\left(d\ln cmc/dx_1\right)\right] \quad (18)$$

The activities of the ionic (α_I) and the non-ionic (α_N) components are given by

$$a_I = xf_I = x_1\frac{cmc_{mix}}{cmc_I}$$

and

$$a_N = (1-x)f_N = (1-x_1)\frac{cmc_{mix}}{cmc_N}$$

where cmc_I, cmc_N, and cmc_{mix} are the cmc of the pure ionic, non-ionic component and the mixtures, respectively, under the identical environmental condition.

The interaction parameter (β^{Ma}) in the micellar phase is given by

$$\beta^{Ma} = \frac{g^{ex}}{x(1-x)} \quad (19)$$

All these values are presented in Table 4. It shows that micellar mole fractions of GA/POE systems are higher than the corresponding stoichiometric mole fractions.

7. *Nagarajan model.* It is the first molecular model in the literature [28–31] that needs only the molecular information for the pure surfactants instead of any experimental data. Using the equilibrium of a monomeric surfactant in the bulk solution and in the micellar aggregate, according to Tanford [44],

$$\ln X_{cmc} = \frac{\Delta\mu_g^0}{kT} \quad (20)$$

where g is the aggregation number of the aggregate, X_{cmc} is the critical micellar concentration of the pure surfactant in the mole fraction unit and $\Delta\mu_g^0$ is the difference in the standard state chemical potential between a surfactant monomer present in an aggregate of aggregation number g and in singly dispersed state in solution.

In the phenomenological model of Nagarajan [28–31], there are four different contributions for $\left(\Delta\mu_g^0/kT\right)$, viz., (1) $\left(\Delta\mu_g^0/kT\right)_T$, which is a negative free-energy contribution arising out of transfer of surfactant tail from solution to more favorable hydrocarbon-like environment of the aggregate core; −1.4841 and −3.6031 (at 298 K) contribution per $-CH_2-$ and $-CH_3$ groups is considered; (2) $\left(\Delta\mu_g^0/kT\right)_I$ is a positive contribution that accounts for the allowance of penetration of water molecules to the aggregate core; (3) $\left(\Delta\mu_g^0/kT\right)_H$ is another positive contribution arising out of the repulsive (steric or electrostatic) interaction between the head groups crowding at the aggregate surface; and (4) $\left(\Delta\mu_g^0/kT\right)_P$ is the contribution of packing of a monomer within the core of the aggregate. Thus,

$$\frac{\Delta\mu_g^0}{kT} = \left(\frac{\Delta\mu_g^0}{kT}\right)_T + \left(\frac{\Delta\mu_g^0}{kT}\right)_I + \left(\frac{\Delta\mu_g^0}{kT}\right)_H + \left(\frac{\Delta\mu_g^0}{kT}\right)_P \quad (21)$$

following Tanford's rationale, the interfacial $\left(\Delta\mu_g^0/kT\right)_I$ and head $\left(\Delta\mu_g^0/kT\right)_H$ contributions is calculated from

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_I = \left(\frac{\sigma}{kT}\right)a_e$$

and

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_H = \left(\frac{\alpha}{kT}\right)\frac{1}{a_e}$$

where α is the head-group repulsion parameter ($\alpha = \sigma a_e^2$), and α_e is the area per surfactant monomer at the interface of the aggregate core and was evaluated using

$$a_e = \left[\frac{2\pi e^2 d}{\varepsilon\sigma}\left(\frac{1}{1+\kappa l_0}\right)\right]^{1/2}$$

where e is the electronic charge, d is the capacitor thickness in the double-layer model, ε is the permittivity or dielectric constant of bulk solution (80 for water), σ is the surface tension value calculated from the Nagarajan model, κ^{-1} is the Debye length depending on the ionic strength, and l_0 is the extended tail length per surfactant monomer and is obtained from Tanford's equation:

$$l_C \le l_{\max} \approx (0.154 + 0.1265 n_C)\ \text{nm}$$

where n_C is the number of carbon atoms in the surfactant tail (12 in our case).

According to the Israelachvili model [45], the packing parameter (P) dictating the shape of the aggregates is given as

$$P = \frac{v_0}{l_0\, a_e}$$

where ν_0 is the volume of exclusion per monomer in the aggregate and is given by the Tanford equation as

$$v_0 = (0.0274 + 0.0269 n_C)\,\mathrm{nm}^3$$

The micelles will be spherical ($P<1/3$), non-spherical ($1/3<P<1/2$), vesicles or bilayers ($1/2<P<1$), or inverted ($P>1$), depending on the value of packing parameter.

The radius of the aggregate R is calculated from

$$R = \frac{3v}{a_e}$$

Assuming the tail to deform nonuniformly [46], the packing free energy can be calculated from

$$\left(\frac{\Delta\mu_g^0}{kT}\right)_P = \frac{Q}{a_e^{/}}$$

with $Q_{sph} = \left(\frac{27}{8}\right)v_0 L$, $Q_{cyl} = \left(\frac{20}{8}\right)v_0 L$, $Q_{bilayer} = \left(\frac{10}{8}\right)v_0 L$, and $a_e^{/}$ is given by $a_e^{/} = \left(\frac{a}{\sigma} + \frac{2Q/a_e}{\sigma/kT}\right)$ and L is the length per unit segment $4.6A^0$

For the gemini, because the number of $-CH_2-$ units in the spacer (2 in GA) is less than $a_e^{1/2}/l_{CH_2}$, the contribution of the spacer to the $\left(\Delta\mu_g^0/kT\right)_T$ was not considered [47]. The contribution of the spacer toward the packing free energy was also neglected as $\lfloor (S+1)l_{CH_2} \rfloor > a_{eff}$ with $a_{eff} = \frac{v_0}{\eta\pi R}$ where η is shape-dependent constant (=1 for bilayer).

For double-tailed surfactants, a unit contribution for one tail and 0.6 contribution for the other tail, and a total 1.6 contribution per monomer was accounted in $\left(\Delta\mu_g^0/kT\right)_T$, $\left(\Delta\mu_g^0/kT\right)_I$ and $\left(\Delta\mu_g^0/kT\right)_P$ was considered where contribution of the tail is important. Due to the presence of two head groups per gemini molecule, a correction for the nonuniformity effect in the $\left(\Delta\mu_g^0/kT\right)_H$ was done following Camesano and Nagarajan [47]. A comparative analysis of the magnitude and shape dependence of the individual contributions to the free energy shows that the nonuniform charge distribution at the aggregate surface and the additional packing constraints on the tails, both originating from the short range of the spacer, play a central role in determining the equilibrium shape of the aggregates.

For mixtures of nonionics with gemini, the weighted part in the $\left(\Delta\mu_g^0/kT\right)_I$ and $\left(\Delta\mu_g^0/kT\right)_H$, was corrected accordingly. The calculated free-energy contributions from each part, the total free-energy change of micellization $\left(\Delta G_{m,N}^0\right)$ and critical micellar concentrations (cmc_N) of the pure components and their mixtures are reported in Table 5, whereby good correlation with experimentally observed cmc was obtained. All the parameters obtained from Nagarajan's model for two nonionic surfactants are same because (a) all the pure components (GA, $C_{12}E_8$, and $C_{12}E_5$) have very much similar cmc and area of exclusion at the air/water interface under the experimental conditions; moreover, such a high salinity of the solution, the value of

Table 5 Parameters of pure and binary mixtures obtained from Nagarajan's model in 0.1 M NaCl at pH 5 and 298 K

Surfactant/α_{GA}	a_e/A^{02}	P value	R/A^0	κ^{-1}/A^0	$-\left(\Delta\mu_g^0/\mathrm{kT}\right)_T$	$-\left(\Delta\mu_g^0/\mathrm{kT}\right)_I$	$-\left(\Delta\mu_g^0/\mathrm{kT}\right)_H$	$-\left(\Delta\mu_g^0/\mathrm{kT}\right)_P$	$-\left(\Delta G_{m,N}^0/\mathrm{kJ\ mol^{-1}}\right)$	$cmc_N \times 10^6$/M
Pure components										
GA	69.29	0.58	9.71	9.60	31.88	13.66	2.01	0.09	39.94	5.54
$C_{12}E_8$	49.19	0.42	14.24	9.60	19.93	6.01	–	0.06	34.32	53.44
$C_{12}E_5$	49.19	0.42	14.24	9.60	19.93	6.01	–	0.06	34.32	53.44
GA–$C_{12}E_8$										
0.25	62.25	0.54	8.99	9.60	27.70	10.64	2.06	0.08	36.96	18.40
0.50	65.07	0.55	9.30	9.60	29.37	11.81	2.39	0.08	37.37	15.59
0.75	68.28	0.57	9.62	9.60	31.28	13.21	2.74	0.09	37.76	13.36
GA–$C_{12}E_5$										
0.25	62.86	0.54	9.06	9.60	28.06	10.89	2.13	0.08	37.06	17.67
0.50	65.27	0.56	9.32	9.60	29.49	11.89	2.41	0.10	37.35	15.73
0.75	67.88	0.57	9.58	9.60	31.05	13.03	2.70	0.12	37.66	13.87

the Debye length (κ) is the same for all of them. (b) $C_{12}E_8$ and $C_{12}E_5$ have got a 12-carbon decorated tail, both of them have the same $\left(\Delta\mu_g^0/kT\right)_T$ value, but due to the presence of a second tail in gemini surfactant, 0.6 factor is included in calculation of $\left(\Delta\mu_g^0/kT\right)_T$. (c) Due to the same molecular weight of the tail moiety ($C_{12}H_{25}$) of both nonionics, σ_S and, hence, σ_{agg}, have an equal value, but GA has different σ_{agg} value for double tail; κ is same for all, so a_e has the same value for the two nonionics, but different value for GA due to the presence of two head groups in a molecule.

Lastly, as all the free energies calculated from Nagarajan's model depend on a_e, hence, both nonionics have identical $\Delta G^0_{m,N}$ and cmc_N values.

Conclusions

Both GA and $C_{12}E_8$ evidenced two distinct breaks in the tensiometric profile at pH 5 and 0.1 M NaCl solution. For another gemini, 212, with slightly modified head group, we found only one break [17]. The two additional carboxylic acid groups in the head group of GA probably resulted for two breaks. Two breaks for $C_{12}E_8$ are probably due to increased degree of solvation of the polyether head group in acidic medium (pH 5). Only one break for $C_{12}E_5$ was probably due to the lesser number of oxygen centers in the head group and, hence, decreased degree of solvation.

For either of the mixtures, the interaction parameters increased with increasing stoichiometric mole fraction of GA. The interaction parameter at the interface obtained from Rosen model is self-explanatory. The interaction parameters in the micellar phase obtained from the Rubingh and Maeda model were close enough, establishing the concurrence of either of the theories. The micellar mole fraction of GA obtained from Rubingh, Georgiev, Motomura, and Maeda also resembled well. The cmc values observed from Nagarajan model were also in close resemblance with the experimentally observed value.

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