

The mixing behavior of *n*-alkylpyridinium bromide–NP-9 mixed surfactant systems

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Abstract

The interaction between *n*-alkylpyridinium bromide (C_m PB, $m = 16, 14, 12,$ and 10) cationic surfactants and nonylphenyl ethoxylates ($4-C_9H_{19}C_6H_4(OCH_2CH_2)_9OH$, NP-9) nonionic surfactant are investigated using surface tension method. The mixed critical micellar concentration (CMC) values determined from the experimental data are used to calculate the interaction parameter (β_{12}) using regular solution theory (RST) of the mixed surfactant systems. Four different alkylpyridinium bromide surfactants show almost ideal behavior when mixed with NP-9, the interaction parameter values calculated using RST is close to zero. The micellar mole fraction of the cationic surfactant decreases in the mixed micelle with decreasing the alkyl chain length of the cationic surfactant.

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1. Introduction

Mixed surfactant systems are used in many applications due to their better performance and less consumption than the pure surfactants [1–4]. The mixed surfactant systems always show synergistic behavior, resulting reduces the total amount of surfactant used in a particular application, which in turn thus reduces both cost and environmental impact. Due to the synergistic behavior, the physical properties of mixed surfactant systems such as CMC and interfacial tensions are often substantially lower than would be expected based on the properties of pure components. In general, for practical applications the mixtures of dissimilar surfactants are used. The mixtures of dissimilar surfactants show more nonideal behavior is of both theoretical interest and practical importance.

The CMCs of mixtures of similarly structured ionic surfactants [5–7] or nonionic surfactants [8–11] can be predicted by assuming that the ideal solution theory is obeyed in micellar phase. However, for mixtures of ionic and nonionic surfactant solutions the CMC values obtained are much lower than those predicted by ideal solution theory. Rubingh [12] suc-

cessfully explained the nonideal behavior and the interaction between the two surfactants by using the pseudo-phase separation model and regular solution approximation. The regular solution theory is most widely used to explain the nonideal behavior of binary mixtures of cationic–nonionic [7,13–20], anionic–nonionic [7,17,18] and anionic–cationic [7,17,21]. However, Blankschtein and co-workers [22–27] and Nagara-jan [28,29] used molecular–thermodynamic theory to predict the interactions and other properties of different mixed surfactant systems.

In this paper the mixed CMC and interaction parameter of *n*-alkylpyridinium bromide–NP-9 systems are determined experimentally. The effect of chain length of the cationic surfactant on the interaction parameter and the micellar compositions of the cationic–nonionic mixed systems have been studied. Most of the reported study on the cationic–nonionic surfactants mixture show nonideal behavior, because of the synergistic effects. This study shows the ideal behavior in the mixed system, which is attributed in terms of the structural similarity present in the surfactant molecules.

2. Materials and method

The cationic surfactants cetylpyridinium bromide (C_{16} PB) was obtained from Aldrich Chemicals and was used as received.

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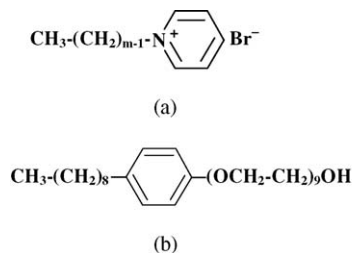


Fig. 1. Chemical structures of (a) *n*-alkylpyridinium bromide and (b) NP-9 surfactants.

Tetradecylpyridinium bromide (C_{14}PB), dodecylpyridinium bromide (C_{12}PB), decylpyridinium bromide (C_{10}PB) was synthesized in our laboratory and was recrystallized five times from acetone before use. A nonionic surfactant, nonylphenyl ethoxylates (4- $\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_9\text{OH}$), NP-9 (Igepal CO 630) was obtained from Aldrich Chemicals and was used as received. The structures of surfactants used in this study are shown in Fig. 1. The critical micelle concentrations (CMC) of single and mixed surfactants were determined by surface tension measurement at 25 °C. Surface tension was measured by Wilhelmy plate method using Kruss K100 tensiometer. Ultra pure water of 18.2 MΩ resistivity (Barnstead International) was used for all experiments. The pure surfactants solutions were prepared by diluting the concentrated stock solutions. The mixed solutions were prepared by mixing two pure solutions and were kept for at least 30 min. for equilibration before measuring the surface tension.

3. Theoretical background

The chemical potential of the *i*th surfactant monomer in the bulk of a mixed micellar solution can be written as [12]

$$\mu_i = \mu_i^0 + RT \ln C_i^m \quad (1)$$

where μ_i^0 is the standard chemical potential and C_i^m is the concentration of monomeric surfactant *i* in the bulk. In the mixed micelle, the chemical potential of the component *i* can be written as

$$\mu_i^M = \mu_i^0 + RT \ln C_i + RT \ln f_i x_i \quad (2)$$

where C_i , f_i , and x_i are the CMC of pure surfactant *i*, the activity coefficient, and the mole fraction of the surfactant *i* in the mixed micelles, respectively. In the case of ideal behavior, the value of activity coefficient is 1. Since at equilibrium $\mu_i = \mu_i^M$, the monomer concentration can be written as

$$C_i^m = x_i f_i C_i = \alpha_i C^* \quad (3)$$

where C^* is the mixed CMC and α_i is the mole fraction of the surfactant *i* in the bulk. Now, for a binary surfactant system mixed CMC can be represented as

$$\frac{1}{C^*} = \sum_{i=1}^2 \frac{\alpha_i}{f_i C_i} \quad (4)$$

In the case of binary nonideal mixtures, the activity coefficients of the components can be expressed as [12]

$$f_1 = \exp \beta_{12} (1 - x_1)^2 \quad (5a)$$

$$f_2 = \exp \beta_{12} x_1^2 \quad (5b)$$

where β_{12} is an interaction parameter which indicates the interaction between two surfactant molecules in the mixed micelle and is a measure of deviation from the ideal behavior. The micellar mole fraction x_1 can be calculated by solving iteratively the following equation

$$\frac{x_1^2 \ln(\alpha_1 C^*/x_1 C_1)}{(1 - x_1)^2 \ln((1 - \alpha_1)C^*/(1 - x_1)C_2)} = 1 \quad (6)$$

β_{12} can be now calculated by substituting the value of x_1 in the equation below

$$\beta_{12} = \frac{\ln(\alpha_1 C^*/x_1 C_1)}{(1 - x_1)^2} \quad (7)$$

The β parameter quantitatively captures the extent of nonideality for a mixed surfactant system. The negative value of β indicates synergism in mixed micelle formation, a positive value indicates antagonism, and if $\beta = 0$, then mixed micelle formation is ideal. The larger the absolute value of β , stronger the mixing nonideality.

4. Results and discussion

4.1. Mixed CMC, interaction parameter, and micellar composition

The variation of mixed CMC values of *n*-alkylpyridinium bromide (C_mPB , $m = 16, 14, 12, 10$) + NP-9 systems as a function of mole fraction of pyridinium bromide are given in Figs. 2–5. Figs. 2–5 also show comparisons between the experimental and the calculated mixed CMC values of the systems using equation [4] for the ideal behavior ($f = 1$) against the mole fraction of pyridinium bromide. It is observed from the figures that

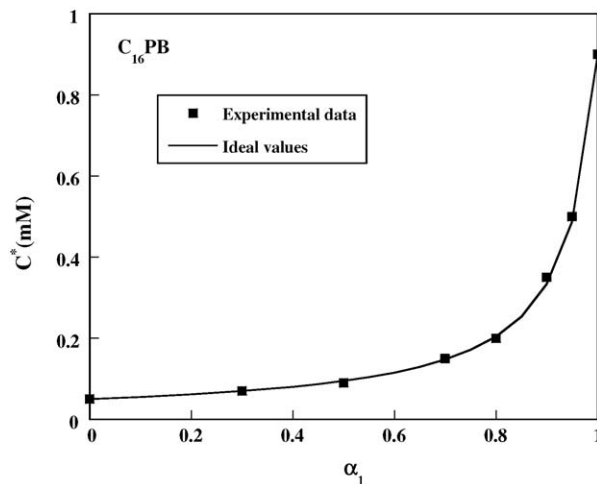


Fig. 2. Experimental and predicted critical micellar concentration of C_{16}PB –NP-9 mixtures as a function of mole fraction of C_{16}PB at 25 °C.

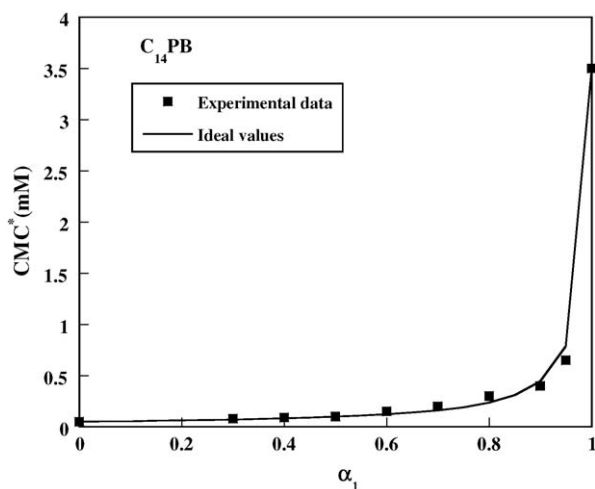


Fig. 3. Experimental and predicted critical micellar concentration of $C_{14}PB$ –NP-9 mixtures as a function of mole fraction of $C_{14}PB$ at 25 °C.

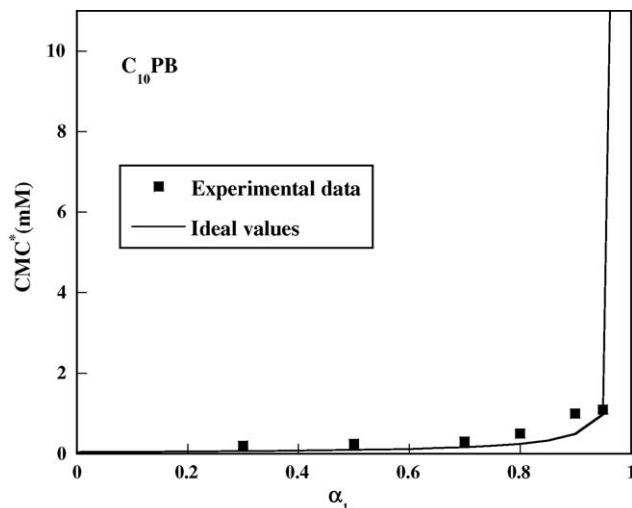


Fig. 5. Experimental and predicted critical micellar concentration of $C_{10}PB$ –NP-9 mixtures as a function of mole fraction of $C_{10}PB$ at 25 °C.

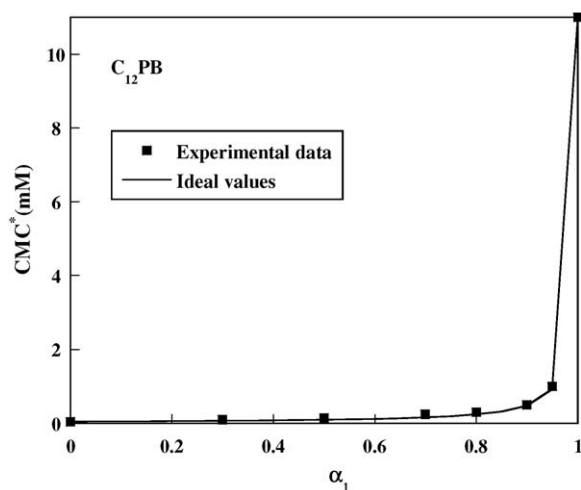


Fig. 4. Experimental and predicted critical micellar concentration of $C_{12}PB$ –NP-9 mixtures as a function of mole fraction of $C_{12}PB$ at 25 °C.

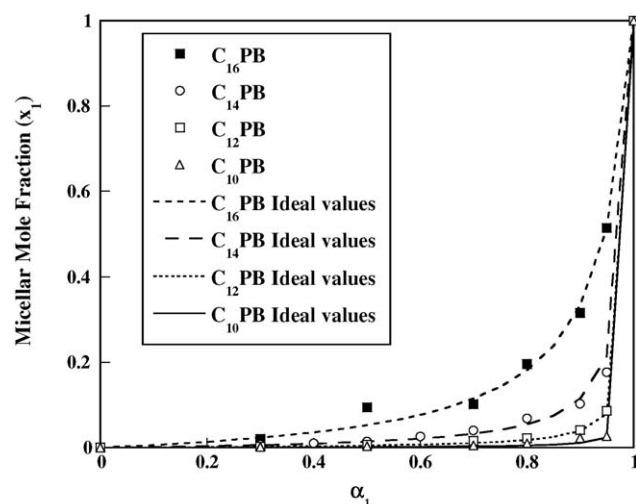


Fig. 6. Plots of micellar mole fraction of n -alkylpyridinium bromide as a function of mole fraction in solution. The points are calculated for different β_{12} values evaluated at respective α_1 values of different mixed systems at 25 °C.

experimental CMC values are very close to those calculated by assuming the ideal behavior. The interaction parameter (β_{12}) and the micellar mole fraction of pyridinium bromide (x_1) for different compositions are calculated using equation [6,7] are given in Table 1. The data presented in Table 1 shows the values of interaction parameter, β_{12} , is almost zero for different composition of four different alkyl chain length pyridinium bro-

mid and NP-9 mixed surfactant systems. Many researchers have reported the nonideal synergistic behavior (negative value of interaction parameter) of cationic–nonionic mixed surfactant systems [7,13–20], where as, for this cationic–nonionic surfactant systems are found almost ideal behavior. Fig. 6 shows the

Table 1

The values of mixed CMC (C^*), micellar mole fraction (x_1), and interaction parameter (β_{12}) of four mixed surfactant systems at 25 °C

α_1	$C_{16}PB$			$C_{14}PB$			$C_{12}PB$			$C_{10}PB$		
	C^* (mM)	x_1	β_{12}	C^* (mM)	x_1	β_{12}	C^* (mM)	x_1	β_{12}	C^* (mM)	x_1	β_{12}
1	0.9	1	–	3.5	1	–	11	1	–	40	1	–
0.95	0.5	0.514	0.11	0.65	0.176	–0.001	1	0.086	–0.001	1.1	0.026	–0.003
0.9	0.35	0.315	0.222	0.4	0.103	0.0	0.5	0.41	–0.001	1	0.023	–0.002
0.8	0.2	0.195	–0.147	0.3	0.68	–0.001	0.3	0.022	0.001	0.5	0.01	0.0
0.7	0.15	0.102	0.171	0.2	0.04	0.0	0.25	0.016	–0.006	0.3	0.005	0.01
0.5	0.09	0.094	–0.768	0.1	0.014	–0.001	0.15	0.007	0.003	0.25	0.003	0.002
0.3	0.07	0.020	0.157	0.08	0.007	0.001	0.1	0.003	–0.008	0.2	0.002	0.0

variation of micellar mole fraction of cationic surfactant (x_1) obtained from equation [6] with bulk composition. The micellar mole fraction of the cationic surfactants decreases as the mole fraction of NP-9 in bulk increases. Which indicate at low mole fraction of the cationic surfactants the mixed micelle is predominately formed by NP-9. Even, at the same composition, with decreasing the chain length of cationic surfactants the mole fraction of cationic surfactants in micellar phase decreases or the micelle is predominately formed by NP-9. There is also a difference in x_1 between C₁₆PB and C₁₄PB but the difference is less between C₁₂PB and C₁₀PB, where the micelle is predominately form with NP-9 as discussed above. Fig. 6 also shows the comparisons of micellar mole fractions calculated from equation [6] and that of ideal (using $\beta_{12}=0$). In this figure, it is observed that there is a good agreement between the micellar mole fractions calculated from the experimental data and that for the ideal solution.

The main reason for showing the ideal behavior of this type of binary surfactant mixtures is not very clear. The probable explanation is due to the presence of similar ‘benzene type’ structure in the head group of the both surfactant molecules and also the presence of similar straight chain hydrocarbon tail.

4.2. Thermodynamic parameters of micellization

The regular solution theory (RST) assumes that the excess entropy of mixing (S^E) is zero, so, the entropy of mixing will be same as the ideal behavior ($\Delta S_M = \Delta S^{\text{ideal}}$). According to RST, as both S^E and ΔH^{ideal} are zero, the relationship between the excess free energy, G^E , the excess enthalpy, H^E , and the

enthalpy of micellization, ΔH_M can be written as [20]

$$G^E = H^E = \Delta H_M = RT \sum_{i=1}^2 x_i \ln f_i \quad (8)$$

The excess free energy of micellization represents the deviation from the ideal behavior ($G^E = \Delta G_M - \Delta G_M^{\text{ideal}}$). The free energy of micellization can be given by

$$\Delta G_M = RT \sum_{i=1}^2 x_i \ln x_i f_i \quad (9)$$

Using the values of enthalpy and free energy of micellization the entropy of micellization can be calculated as

$$\Delta S_M = \frac{\Delta H_M - \Delta G_M}{T} \quad (10)$$

The values of different thermodynamic functions at 25 °C are calculated from the experimental data are given in Table 2. It can be observed from the table, for a certain alkyl chain length of PB if the mole fraction of PB increases the free energy of micellization is more negative, which indicate that the formation of mixed micelle is more favorable. For the same composition, with different chain length of PB the micellization is less favorable when chain length is shorter. Which also indicate that the hydrophobic effect in the surfactant molecules is the major driving force for the micellization. The excess free energy or the enthalpy of micellization is almost zero for all the cases, since, the mixed system behave almost ideally. The higher change in entropy at higher ionic surfactant mole fraction can be in terms of micellar hydration stability [14,15]. The hydration of mixed micelle

Table 2
The values of ΔG_M , ΔH_M , and ΔS_M of four mixed surfactant systems at 25 °C

C _n PB	α_1	x_1	ΔG_M (kJ mol ⁻¹)	ΔH_M (kJ mol ⁻¹)	ΔS_M (JK ⁻¹ mol ⁻¹)
C ₁₆ PB	0.95	0.514	-1.669	0.047	5.757
	0.9	0.315	-1.387	0.156	5.180
	0.8	0.195	-1.235	-0.012	4.106
	0.7	0.102	-0.733	0.081	2.730
	0.5	0.094	-0.257	0.514	2.588
	0.3	0.02	-0.218	0.026	0.817
C ₁₄ PB	0.95	0.176	-1.154	0.0	3.872
	0.9	0.103	-0.820	0.0	2.753
	0.8	0.068	-0.619	0.0	2.078
	0.7	0.04	-0.416	0.0	1.396
	0.5	0.014	-0.186	0.0	0.623
	0.3	0.007	-0.102	0.0	0.340
C ₁₂ PB	0.95	0.086	-0.728	0.0	2.444
	0.9	0.041	-0.423	0.0	1.420
	0.8	0.022	-0.260	0.0	0.872
	0.7	0.016	-0.203	0.0	0.682
	0.5	0.007	-0.101	0.0	0.338
	0.3	0.003	-0.047	0.0	0.158
C ₁₀ PB	0.95	0.026	-0.301	0.0	1.008
	0.9	0.022	-0.267	0.0	0.896
	0.8	0.01	-0.139	0.0	0.465
	0.7	0.005	-0.080	0.0	0.270
	0.5	0.003	-0.052	0.0	0.175
	0.3	0.002	-0.028	0.0	0.094

Table 3
The values of B_1 of four mixed surfactant systems at 25 °C

Surfactant system	B_1 (average)
C ₁₆ PB–NP-9	2.85
C ₁₄ PB–NP-9	4.25
C ₁₂ PB–NP-9	5.39
C ₁₀ PB–NP-9	6.69

increases with increasing the ionic component in the micelle, as more hydrated structure formed the stability of mixed micelle increases, on the other hand, entropic contribution increases. As the micellar mole fraction of the ionic component decreases with decreasing the alkyl chain length, the hydration also will decrease with decreasing the alkyl chain length, which in turn, decreases the entropic contribution.

Maeda [30] has proposed an equation to calculate the thermodynamic stability of the ionic–nonionic mixed micelle (G_{mic}) based on phase separation mode as,

$$\frac{G_{mic}}{RT} = B_0 + B_1x_1 + B_2x_1^2 \quad (11)$$

where B_0 is an independent term related to CMC of nonionic surfactant ($B_0 = \ln C_2$). The parameter, B_1 is related to the standard free energy change due to replacement of a nonionic monomer in the nonionic pure micelle by an ionic monomer, and B_2 is same as interaction parameter in RST ($B_2 = -\beta_{12}$). The relation between B_1 and B_2 to CMC of pure surfactant is

$$\ln \frac{C_1}{C_2} = B_1 + B_2 \quad (12)$$

where C_1 is the CMC of ionic surfactant. The average values of B_1 for four compositions are given in Table 3. It is observed that B_1 values are positive and decrease as the length of alkyl chain of cationic surfactant increases, which is consistent with Ruiz and Aguiar [14,15]. Maeda [30] also mentioned that the value of B_1 can be both positive and negative. According to Maeda [30], the transfer process of an ionic surfactant monomer to the nonionic micelle consists of two different contributions: the interaction between the headgroups and the interaction between the hydrocarbon chains. When the hydrocarbon chains are of the same kind, the first contribution is predominant, however, when there is dissimilarity between the hydrocarbon tails the interactions between these tails become more significant, and as a consequence the value of the parameter B_1 increases. Since the head groups of the four ionic surfactants are same the difference in B_1 is due to the compatibility of the different chain length in the nonionic micelle. Lowest value of B_1 C₁₆PB–NP-9 system indicates less distortion in the nonionic micelle occurs when NP-9 molecule is replaced by C₁₆PB. In the original paper of Maeda [30] it is mentioned that the analysis can be applied to the systems in the media of moderately high ionic strengths, at least higher than CMC of the ionic surfactant. Recently, it is showed that the similar analysis can be used for the nonionic–ionic mixed surfactant systems in absence of electrolyte [14,15]. Although the present study is in absence of electrolyte, similar approach

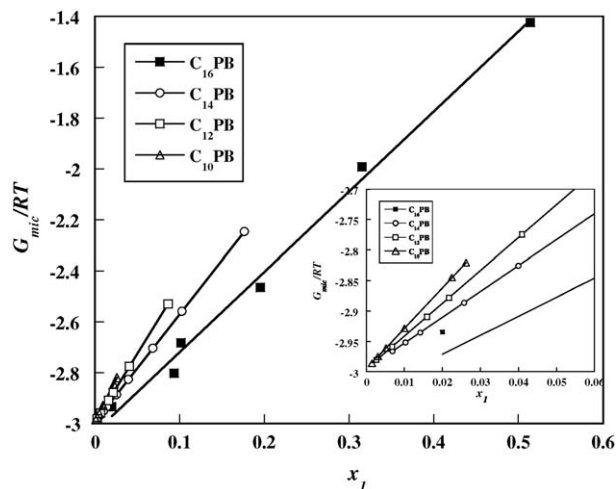


Fig. 7. Plots of G_{mic}/RT as a function of x_1 of different mixed systems at 25 °C. The inset shows at lower x_1 values.

has been used to calculate the parameter, B_1 . In Maeda's analysis electrostatic free energy (G_{el}) is assume to be a quadratic function of degree of ionization of micelles (γ): $G_{el} = a_2\gamma^2$. G_{el} for the medium of low ionic strength can be given as [14] $G_{el} = a_1\gamma + a_2\gamma^2$, then $B_1 = a_1 + B_1^*$. Where B_1^* refers to the contribution from the short range interactions. The positive values of B_1 are due to the positive a_1 term.

Fig. 7 shows the variation of micellar stability (G_{mic}/RT) relative to that of pure NP-9 micelles with the mole fraction of PB. It is observed from the figure that the micelle is more unstable (less negative value of G_{mic}/RT) when the mole fraction cationic surfactant increases, can be attributed to increasing electrostatic repulsion (destabilization of the system) in the micelle. In addition, it is also observed the change in micellar stability is linear with micellar mole fraction.

5. Conclusion

The results obtained from this study show the mixture of *n*-alkylpyridinium bromide–NP-9, cationic–anionic system behave almost ideally. The values of interaction parameters obtained using RST are almost zero. The micellar mole fraction of the cationic surfactant decreases in the mixed micelle with decreasing the alkyl chain length, showing the micelle is predominantly formed by the nonionic surfactant. For a particular alkyl chain length of PB if the mole fraction of PB increases the free energy of micellization is more negative, and for the same composition but different chain length the free energy of micellization is more negative with longer alkyl chain length. The micellar stability of the mixed micelle increases linearly with decreasing the mole fraction of the ionic surfactant in the mixed micelle.

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