

## Binary mixtures of cationic surfactants with triton X-100 and the studies of physicochemical parameters of the mixed micelles

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**Abstract**—The mixtures of alkylpyridinium chloride ( $C_nPC$ ,  $n=14, 16$ ) and Triton X-100 were studied over the entire mole fractions at 298.15 K. For each mixture, CMC was obtained from surface tension measurements. To estimate the interaction parameter values ( $\beta$ ), the calculation of the monomer concentrations and the mole fractions of the individual surfactants in the mixed micelles, the CMC data were used by applying the regular solution theory. The obtained results showed that the increase of the chain length of  $C_nPC$  led to the stronger preferential incorporation of cationic surfactant in mixed micelle. The large values of  $|\Delta G^o|$  confirmed that mixed micelle of  $C_{16}PC$  and Triton X-100 was significantly favorable.

Keywords: Surface Tension, CMC, Synergism, Interaction, Regular Solution

### INTRODUCTION

The physico-chemical properties (hydrophobicity, cloud point, Kraft point, etc.) of mixed surfactants are completely different from those of pure surfactants of individual components. In some cases, this is involuntary, since the commercial detergents used, even when designated by the name of an individual surfactant, e.g., sodium lauryl sulfate, are mixtures of surface active materials as a result of the nonhomogeneous raw materials used in their manufacture and/or the presence of unreacted raw materials and manufactured co-products. From the application point of view, surfactant mixtures are of great importance in technological, biological, pharmaceutical and medicinal formulation, enhanced oil recovery process for the purpose of solubilization, dispersion, suspension, etc [1-3].

Synergism (or antagonism) has been observed in mixed surfactant solutions: the surfactant concentration required for achieving the set interaction energy in the mixed solutions was lower (higher) than in the solutions of the individual components. Synergism here is defined in an aqueous solution containing two surfactants when a given surface tension can be attained at a total mixed surfactant concentration lower than that required of either surfactant by itself. Synergistic effects in mixtures of surfactants have been extensively studied and different theoretical approaches have been proposed [4-6]. The critical micelle concentration, *cmc*, is the property that has been used in the development of these theories, and synergistic effects have been attributed to deviations from ideal behavior of surfactant mixtures [7,8].

Alkyl pyridinium chlorides (particularly cetyl pyridinium chlorides) are a cationic quaternary ammonium compound in some types of mouthwashes, toothpastes, lozenges, throat sprays, breath

sprays, and nasal sprays. They are an antiseptic that kills bacteria and other microorganisms, and have been shown to be effective in preventing dental plaque and reducing gingivitis [9]. Also, alkyl pyridinium chlorides are especially useful as an electrolyte for primary and secondary batteries.

Triton X-100 (TX-100) is a nonionic surfactant with a hydrophobic group and a hydrophilic polyethylene oxide group (on average it has 9.5 oxyethylene groups (OE)). TX-100 differs from conventional nonionic surfactants, having hydrophilic part longer than the hydrophobic region of the molecule [10].

In the present study, the interaction between a set of two cationic surfactants (tetradecyl pyridinium chloride ( $C_{14}PC$ ) and hexadecyl pyridinium chloride ( $C_{16}PC$ )) with TX-100, was investigated by using the surface tension method.

A surface tension study of surfactant mixtures was carried out to determine the cmc of the surfactant mixtures at various ratios. In addition, surface tension measurements were used to gain an insight into the corresponding micelle compositions ( $X_1$ ) and the monomer concentration ( $m_1$ ) of the surfactant mixtures. To complete the experimental results the interaction parameter ( $\beta$ ) between the surfactant molecules in the mixed micelles using regular solution approach was calculated. Finally, the total surfactant adsorption ( $\Gamma_{tot}$ ) and the micellization free energy change ( $\Delta G_m^o$ ) of the mixed systems were determined by the Gibbs adsorption equation and Maeda approach, respectively [11-13]. In this research, the calculation of the surfactant free monomer concentration in equilibrium with micelle was improved in comparison to the previous studies.

### EXPERIMENTAL SECTION

#### 1. Materials

Tetradecylpyridinium chloride ( $C_{14}PC$ ) and hexadecylpyridinium chloride ( $C_{16}PC$ ) were obtained from Aldrich and used with-

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out further purification. Triton X-100(TX-100) (>99%) was obtained from Merck and used as received. All solutions were prepared with doubly distilled water.

$C_n$ PC/TX-100 mixtures at a range of mole fractions of ionic surfactant per nonionic surfactant, as well as pure  $C_n$ PC and TX-100 solutions, were prepared as the initial solutions. The initial solutions were injected by a micropipet into a glass cell containing a known volume of aqueous solution and progressively diluted in such a way that for a given surfactant mixture, the mole ratio of surfactants remained constant throughout the experiment. All experiments were performed at  $25 \pm 0.01$  °C.

## 2. Apparatus and Procedure

Surface tension was measured with a PC controlled KSV Sigma 701 tension balance that employs the Du Noüy ring-detachment method. The platinum/iridium ring was thoroughly cleaned and flamed before each measurement. Each measurement was repeated up to seven times for reproducibility. The uncertainty of the surface tension measurement is  $\pm 0.04$  mN·m<sup>-1</sup> of the final value of surface tension, and the corresponding reproducibility is  $\pm 0.01$  mN·m<sup>-1</sup>.

The sample under measurement was kept thermostated in a double-jacketed glass cell by means of a water bath, using a LAUDA circulator (model ECO RE415) equipped with a Pt100 probe, immersed in solution, and able to control the temperature within  $\pm 0.01$  K. The binary mixtures were prepared by mass using a Sartorius analytical balance (model BP 121S, accurate to  $\pm 0.1$  mg). The uncertainty of the mole fractions was estimated to be within  $\pm 1 \cdot 10^{-4}$ .

## RESULTS AND DISCUSSION

### 1. Determination of Interaction Parameter and Micellar Composition

In the absence of any significant net interaction between surfactant types, the ideal solution theory predicts the cmc of mixture as follows (Clint's theory):

$$\frac{1}{\text{cmc}_{\text{mix}}^{\text{id}}} = \frac{y_1}{\text{cmc}_1} + \frac{y_2}{\text{cmc}_2} \quad (1)$$

where  $\text{cmc}_i$  and  $y_i$  are the cmc of the pure surfactant and the mole fraction of surfactant in the mixture, respectively [14,15].

The micellar mole fractions of one surfactant in the ideal mixed micelle ( $X_1^{\text{id}}$ ) calculated according to Motomura's theory [16,17]:

$$X_1^{\text{id}} = \frac{y_1 \text{cmc}_{\text{mix}}^{\text{id}}}{\text{cmc}_1} = \frac{y_1 \text{cmc}_2}{y_1 \text{cmc}_1 + y_2 \text{cmc}_2} \quad (2)$$

The ideal mixing theory has been successful in explaining the properties of mixtures composed of surfactants with similar chemical structures; however, for mixtures of dissimilar surfactants, as in the present study with mixtures of cationic and nonionic surfactants, the ideal behavior modeled by Eqs. (1), (2) fails. A better representation for the real mixed micelle has been found by using Rubingh's theory (based on regular solution theory) [4,11,12].

For mixtures of different surfactants, under the condition of micellization equilibrium ( $\mu_1^{\text{M}} = \mu_1^{\text{B}}$  and  $\mu_2^{\text{M}} = \mu_2^{\text{B}}$  where  $\mu_i^{\text{M}}$  and  $\mu_i^{\text{B}}$  are the chemical potentials of a component in the micelle and bulk phases respectively) the monomer concentrations,  $m_i$ , of each surfactant may be represented as follows:

$$m_1 = X_1 f_1 \text{cmc}_1 \quad \text{and} \quad m_2 = X_2 f_2 \text{cmc}_2 \quad (3)$$

where  $X_1$  and  $X_2$  are the mole fraction of the surfactant 1 and 2 in the mixed micelle, and  $f_1$  and  $f_2$  represent the activity coefficients of the surfactant monomers. Eq. (3) at the cmc of the mixture ( $\text{cmc}_{\text{mix}}$ ), become:

$$y_1 \text{cmc}_{\text{mix}} = X_1 f_1 \text{cmc}_1 \quad (4)$$

$$(1 - y_1) \text{cmc}_{\text{mix}} = (1 - X_1) f_2 \text{cmc}_2 \quad (5)$$

In the regular solution approximation where the excess entropy of mixing is defined to be zero ( $S^{\text{E}} = 0$ ), the interaction parameter ( $\beta$ ) can be formally interpreted as a logarithm of the activity coefficients are expressed in terms of a single empirical parameter,  $\beta$  parameter representing an excess heat ( $H^{\text{E}}$ ) of mixing [18,19]. The natural

$$f_1 = \exp \beta (1 - X_1)^2 \quad (6)$$

$$f_2 = \exp \beta (1 - X_2)^2 \quad (7)$$

where  $\beta$  is the molecular interaction parameter. From Eqs. (4)-(7),

$$\beta = \frac{1}{(1 - X_1)^2} \ln \frac{y_1 \text{cmc}_{\text{mix}}}{X_1 \text{cmc}_1} \quad (8)$$

or

$$\beta = \frac{1}{(X_1)^2} \ln \frac{(1 - y_1) \text{cmc}_{\text{mix}}}{(1 - X_1) \text{cmc}_2} \quad (9)$$

$$(X_1)^2 \ln \left( \frac{\text{cmc}_{\text{mix}} y_1}{\text{cmc}_1 X_1} \right) = (1 - X_1)^2 \ln \left( \frac{\text{cmc}_{\text{mix}} (1 - y_1)}{\text{cmc}_2 (1 - X_1)} \right) \quad (10)$$

Thus, the interaction parameter can be calculated from surface tension-concentration curves of aqueous mixtures at a particular value of  $y_1$  and aqueous solutions of pure surfactants. From these curves  $\text{cmc}_{\text{mix}}$ ,  $\text{cmc}_1$ , and  $\text{cmc}_2$  are obtained for a given value of surface tension. With these values Eq. (10) is solved iteratively for  $X_1$ , and this is finally used to calculate  $\beta$  from Eq. (8) [11,12,17,20-25].

For attractive interaction, the sign of  $\beta$  is negative; for repulsive interaction, it is positive. Thus, a negative  $\beta$  value indicates that, upon mixing, the two surfactants experience either greater attraction or less repulsion than before mixing; a positive  $\beta$  value, less attraction or greater repulsion upon mixing than before mixing. A value close to zero indicates little or no change in interactions upon mixing. Since in ionic surfactant-containing mixtures there is always repulsive interaction between the ionic surfactant molecules before mixing, the  $\beta$  parameter is almost always negative, if only because of the dilution effect upon mixing with a second surfactant, except for anionic-anionic mixtures. Steric effects contribute to the value of the  $\beta$  parameter when there are variations in the size of the hydrophilic head group or in the branching of the hydrophobic groups of the two surfactants [26].

In all cases the critical micelle concentrations (cmc's) of binary mixtures containing different mole fractions of the surfactants ( $y_1 = 0.1-0.9$ ) were measured using surface tension measurement. Fig. 1(a), (b) shows surface tension ( $\sigma$ ) as a function of the  $\log[C]_i$  at different mole fractions of  $C_n$ PC.

The cmc values acquired in the surface tension measurements were obtained from the intersection of the straight lines created above and below the cmc. The straight line above the cmc value

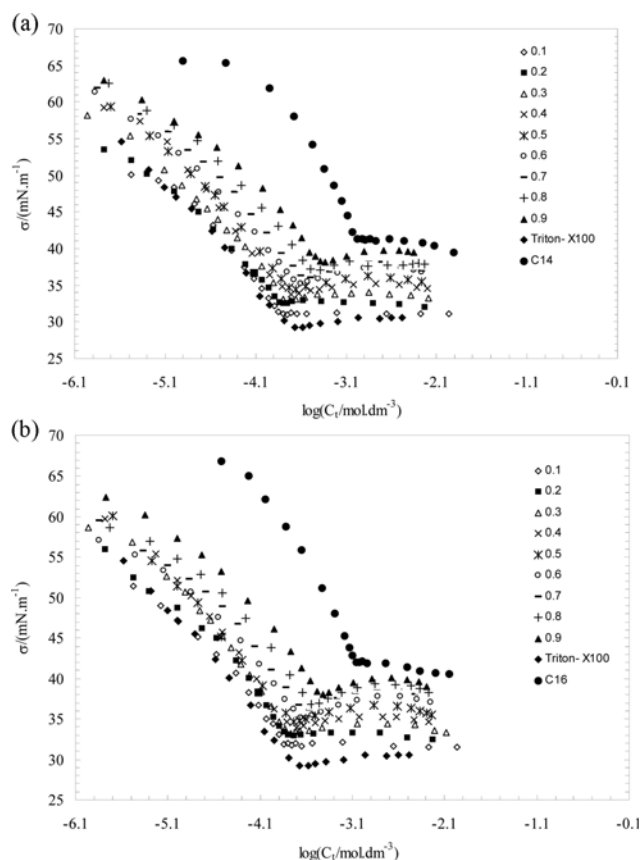


Fig. 1. (a) Plot of the surface tension vs. the total surfactant concentration of the system  $C_{14}PC/TX-100$  at different mole fractions of  $C_{14}PC$  in solution, (b) plot of the surface tension vs. the total surfactant concentration of the system  $C_{16}PC/TX-100$  at different mole fractions of  $C_{16}PC$  in solution.

was determined by linear regression starting at the highest concentration, while the straight line below the cmc value was obtained by linear regression beginning at the lowest concentration of investigated binary mixtures. The regression diagnostic was constantly

Table 1.  $cmc_{min}$  and  $cmc_{mix}^{id}$  values obtained from surface tension for  $C_nPC/TX-100$  mixtures at different mole fractions of ionic surfactant in solution

$y_1$	$C_{14}PC$		$C_{16}PC$	
	$cmc_{mix}$ (mM)	$cmc_{mix}^{id}$ (mM)	$cmc_{mix}$ (mM)	$cmc_{mix}^{id}$ (mM)
0	0.167		0.167	
0.1	0.173	0.184	0.170	0.182
0.2	0.162	0.205	0.151	0.200
0.3	0.153	0.232	0.138	0.222
0.4	0.142	0.267	0.128	0.249
0.5	0.149	0.313	0.126	0.282
0.6	0.159	0.399	0.146	0.339
0.7	0.196	0.495	0.154	0.397
0.8	0.286	0.660	0.201	0.482
0.9	0.340	0.985	0.272	0.612
1	2.50		0.909	

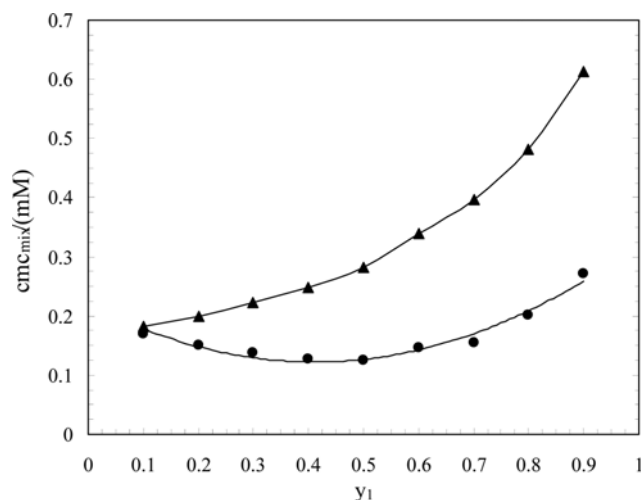


Fig. 2. Comparison of experimental  $cmc_{mix}$  values for the  $C_{16}PC/TX-100$  mixtures with those calculated by assuming ideal mixing of the components ( $cmc_{mix}^{id}$  according to Clint's theory) vs. total mole fraction of  $C_{16}PC$ : (●) experimental, (▲) ideal mixing. The solid lines are guide to the eyes.

performed after addition of each subsequent experimental point. If an experimental point was identified as an outlier, by measuring Cook's distance, the regression would be stopped and the straight line would be formed using previously added experimental points [10,27].

The cmc values for mixed and pure solutions obtained from surface tension for  $C_nPC/TX-100$  systems in water are in Table 1, where the results show deviation of the  $cmc_{mix}$  values from those calculated according Eq. (1) ( $cmc_{mix}^{id}$ ) indicating non-ideal behavior of examined mixtures and existence of mutual interactions of the micelles.

Fig. 2 shows the  $cmc_{mix}$  values obtained from surface tension experiments for the  $C_{16}PC/TX-100$  system estimated as a function of the mole fraction of ionic surfactant ( $y_1$ ). It can be observed that  $cmc_{mix}$  experimental values in  $C_{16}PC/TX-100$  mixture are lower than those obtained by assuming ideal behavior according to Clint theory ( $cmc_{mix}^{id}$ ). This behavior was observed for  $C_{14}PC/TX-100$  system.

The physico-chemical parameters for the  $C_nPC/TX-100$  mixed micelles were calculated according to Eqs. (6)–(10). The obtained values of  $X_1$ ,  $f_1$ ,  $f_2$  and  $\beta$  are presented in Table 2, where values of the  $\beta$  parameter come out to be negative at all mole fractions of the mixtures. The more negative value of the  $\beta$  interaction parameter indicates stronger synergistic interactions between the components (for  $C_{14}PC/TX-100$  mixture). These values correspond to the deviation between the experimentally obtained ( $cmc_{mix}$ ) and ideal cmc values ( $cmc_{mix}^{id}$ ) and indicate synergism in all investigated  $C_nPC/TX-100$  mixtures. The results in Table 2 show that there is a trend towards decreasing interaction with TX-100 as the length of the hydrocarbon tail of the cationic surfactant increases from 14 to 16 carbons.

The mean values of the interaction parameter ( $\bar{\beta}$ ) and the respective standard deviations of the fittings for analyzed binary mixtures are presented in order in Table 2 to make the results easily comparable. The mean interaction parameter values ( $\bar{\beta}$ ) show that

**Table 2.**  $y_1$ ,  $\beta$ ,  $X_1$ ,  $f_1$  and  $f_2$  values calculated for  $C_n$ PC/TX-100 system at cmc (obtained from surface tension measurements) in different mole fractions of  $C_n$ PC in solution

Component	$y_1$	$X_1$	$\beta$	$f_1$	$f_2$
$C_{14}$ PC	0.1	0.060	-2.44	0.12	0.99
	0.2	0.155	-3.48	0.08	0.92
	0.3	0.221	-4.08	0.08	0.82
	0.4	0.273	-4.71	0.08	0.70
	0.5	0.305	-4.81	0.10	0.64
	0.6	0.335	-4.92	0.11	0.58
	0.7	0.363	-4.64	0.15	0.54
	0.8	0.388	-3.86	0.24	0.56
	0.9	0.462	-4.59	0.27	0.38
$\bar{\beta}$			$-4.17 \pm 0.80$		
$C_{16}$ PC	0.1	0.075	-1.63	0.25	0.99
	0.2	0.195	-2.73	0.17	0.90
	0.3	0.269	-3.32	0.17	0.79
	0.4	0.322	-3.77	0.18	0.68
	0.5	0.361	-4.05	0.19	0.59
	0.6	0.397	-3.79	0.25	0.55
	0.7	0.434	-4.00	0.28	0.47
	0.8	0.472	-3.52	0.38	0.46
	0.9	0.538	-3.29	0.50	0.39
$\bar{\beta}$			$-3.34 \pm 0.76$		

TX-100 generates stronger synergistic interactions with investigated  $C_{14}$ PC than  $C_{16}$ PC.

In general, the considerably negative  $\bar{\beta}$  values indicate a strong attractive interaction between  $C_n$ PC and TX-100 in the mixed micelle, which can be attributed to the decrease in surface charge density of the micelles due to the presence of the non-ionic surfactant. Thus, the mixed micelles of  $C_n$ PC and TX-100 are more stable than micelles containing only  $C_n$ PC. So, the main reason for synergism when an ionic surfactant is involved comes from the reduction of electrostatic repulsion between charged heads when a nonionic surfactant is intercalated in the micelle [15,28].

In statistics, a confidence interval is a type of interval estimate of a population parameter and is used to indicate the reliability of an estimate. The confidence interval was computed using either the  $t$  distribution (by using  $t$ -table) for the confidence level and the standard deviation of the point estimate. The use of  $t$  again depends on whether the sample sizes are large or small (in this work:  $n_1 \leq 30$  and  $n_2 \leq 30$ ) [29]:

$$(\bar{\beta}_{C_{14}} - \bar{\beta}_{C_{16}}) \pm t \sqrt{\frac{S_{C_{14}}^2}{n_{C_{14}}} + \frac{S_{C_{16}}^2}{n_{C_{16}}}} \quad (11)$$

where  $\bar{\beta}_i$  is the mean interaction parameter of component  $i$ , and  $S_i$  is the standard deviation of  $\beta_i$ ;  $t$  is statistical  $t$ -value which depends on degrees of freedom (DF) and significant level. We considered 90% confidence interval for the difference in the mean interaction parameter ( $\bar{\beta}$ ) between  $C_{14}$ PC/TX-100 and  $C_{16}$ PC/TX-100 systems and DF=16. The confidence interval of the  $\beta$ 's is -1.29 to -

0.36. The confidence intervals for the difference in means provide a range of likely values for  $(\mu_1 - \mu_2)$ . Note that all values in the confidence interval are equally likely estimates of the true value of  $(\mu_1 - \mu_2)$ . If there is no difference between the population means (the mean interaction parameter), then the difference will be zero (i.e.,  $\mu_1 - \mu_2 = 0$ ). Zero is the *null value* of the parameter (in this case the difference in means). If a 90% confidence interval includes the null value, then there is no statistically meaningful or statistically significant difference between the mixtures. If the confidence interval does not include the null value, then we conclude that there is a statistically significant difference between the mixtures [29].

Since, in this work, the confidence interval does not contain zero, there is a statistically significant difference between the mixtures.

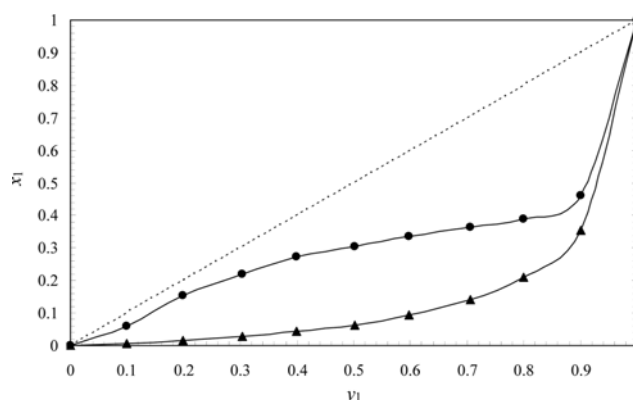
As the chain length of  $C_n$ PC increases, the preferential incorporation of ionic surfactant becomes stronger because the presence of  $C_n$ PC in the micelles gives rise and, consequently, a larger number of  $C_n$ PC molecules are incorporated into the mixed micelles ( $X_{C_{16}PC} > X_{C_{14}PC}$ ) [30].

For the two mixed systems,  $C_{14}$ PC/TX-100 and  $C_{16}$ PC/TX-100, the change of mole fraction of  $C_n$ PC in the micelle ( $X_1$ ) versus total mole fraction ( $y_1$ ) according three model (the simple model of  $X_1 = y_1$ , Motomura's and Rubingh theories) is shown in Fig. 3 (for  $C_{16}$ PC/TX-100 system see to supplementary information). It can be seen that  $X_1$  (from Eq. (10)) in two system is greater than (from Eq. (2)) and the difference between  $X_1$  (Rubingh's theory) and  $X_1^{id}$  (Motomura's theory) indicates non-ideal behavior of the two mixtures.

It is evident from Table 2 that the mole fraction of  $C_n$ PC in the mixed micelle ( $X_1$ ) is much lower compared to the mole fraction of  $C_n$ PC in the bulk ( $y_1$ ), indicating that TX-100 is the dominant component in the mixed micelles at all mixing ratios. The above results corroborate that TX-100 is more surface-active than  $C_n$ PC, which is in line with the slightly lower cmc of pure TX-100 compared to pure  $C_n$ PC.

## 2. Evaluation of Free Monomer Concentration in Surfactant Mixture

Fewer experimental measurements of free monomer concentrations and micelle composition have been carried out in mixed micellar systems. If either of these is known at a given surfactant



**Fig. 3.** Mole fraction of  $C_{14}$ PC in the micelle vs. total mole fraction of  $C_{14}$ PC at various model: (---)  $y=x$ , (●) Rubingh's theory, (▲) Motomura's theory. The solid lines are guide to the eyes.

concentration, the other can be calculated using the critical micelle concentrations.

Mass balance considerations combined with Eq. (3) for two surfactants lead to Eq. (12) [4,19,30]:

$$X_1 + X_2 = 1 \quad \text{or} \quad \frac{y_1 C_1}{C_1 + f_1 \text{cmc}_1 - m} + \frac{y_2 C_2}{C_1 + f_1 \text{cmc}_1 - m} = 1 \quad (12)$$

If  $C_t$  is the total concentration of the mixture, and  $m$  is the sum of the monomer concentrations:

$$m = m_1 + m_2 \quad (13)$$

Solving Eqs. (3), (12) and (13) for the total monomer concentration is straightforward for any number of components once the activity coefficients have been calculated, and the following expressions can be used to obtain individual monomer concentrations of ionic surfactant ( $m_1$ ) (see the supplementary information):

$$m_1 = \frac{-(C_t - f_2 \text{cmc}_2 + f_1 \text{cmc}_1) \pm \sqrt{(C_t - f_2 \text{cmc}_2 + f_1 \text{cmc}_1)^2 + 4 \left( \frac{f_2 \text{cmc}_2}{f_1 \text{cmc}_1} - 1 \right) y_1 f_1 \text{cmc}_1 C_t}}{2 \left( \frac{f_2 \text{cmc}_2}{f_1 \text{cmc}_1} - 1 \right)} \quad (14)$$

and since,  $m_2 = f_2(1 - X_1)\text{cmc}_2 = f_2 \left( 1 - \frac{m_1}{f_1 \text{cmc}_1} \right) \text{cmc}_2$ , the monomer

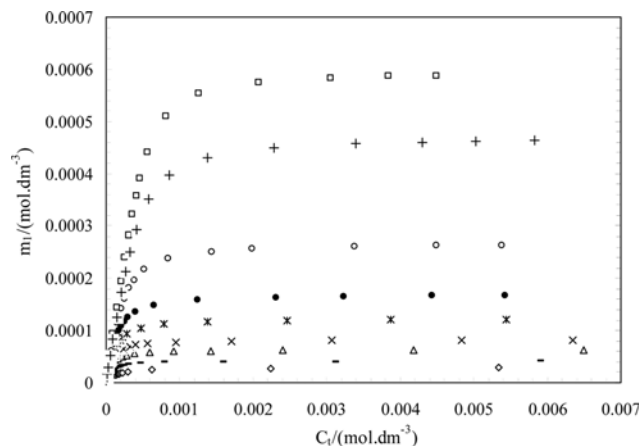


Fig. 4. Variation of the free monomer concentration of  $C_{14}\text{PC}$  ( $m_1$ ) vs the total surfactant concentration at different bulk mole fractions of  $C_{14}\text{PC}$  in  $C_{14}\text{PC}/\text{TX-100}$  mixtures: ( $\diamond$ ) 0.1, ( $-$ ) 0.2, ( $\triangle$ ) 0.3, ( $\times$ ) 0.4, ( $*$ ) 0.5, ( $\bullet$ ) 0.6, ( $\circ$ ) 0.7, ( $+$ ) 0.8, ( $\square$ ) 0.9.

concentrations of non-ionic surfactant ( $m_2$ ) can be given as:

$$m_2 = \left( 1 - \frac{m_1}{f_1 \text{cmc}_1} \right) f_2 \text{cmc}_2 \quad (15)$$

In Eqs. (4) and (15) the values of  $f_1$  and  $f_2$  can be estimated by the

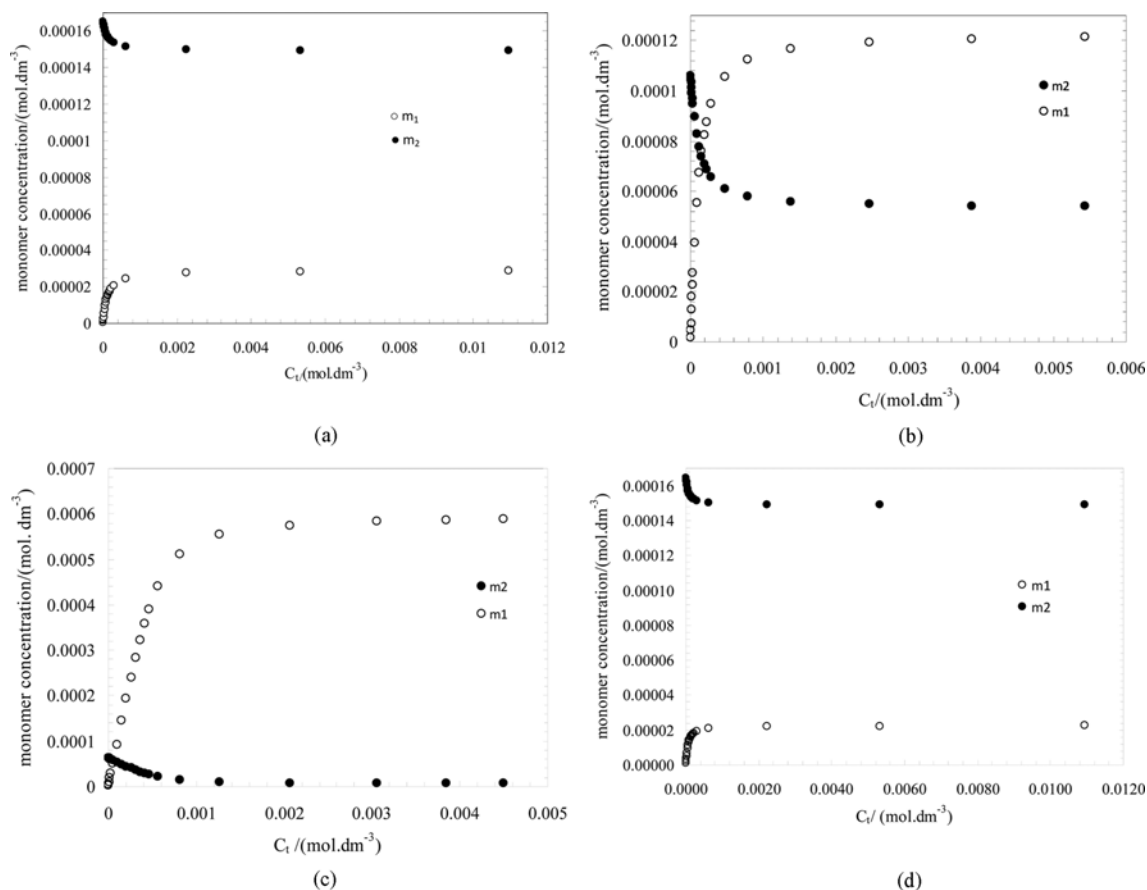


Fig. 5. Monomer concentration of cationic ( $m_1$ ) and nonionic ( $m_2$ ) surfactants vs total concentration of mixed surfactants for the  $C_n\text{PC}/\text{TX-100}$  mixtures: (a)  $C_{14}\text{PC}$  (at  $y_1=0.1$ ), (b)  $C_{14}\text{PC}$  (at  $y_1=0.5$ ), (c)  $C_{14}\text{PC}$  (at  $y_1=0.9$ ), (d)  $C_{16}\text{PC}$  (at  $y_1=0.1$ ).

regular solution model (by Eqs. (6) and (7)) and the quantities  $\text{cmc}_1$ ,  $\text{cmc}_2$  and  $C_i$  are all experimentally available.

The changes in  $m_1$  and  $m_2$  with increasing total concentration ( $C_t$ ) of the mixed surfactants are shown in Figs. 4-5(a), (b), (c) and (d) (for other figures refer to the supplementary information).

Fig. 4 shows the variation of  $m_1$  as a function of total surfactant concentration,  $C_p$ , at different bulk mole fractions of  $C_{14}\text{PC}$  ( $y_1$ ).

As observed in Figs. 5(a), (b), (c) and (d), the variation of the  $m_1$  and  $m_2$  with total surfactant concentration ( $C_t$ ) follows distinctively similar patterns.

In the low concentrations of surfactant, there is no measurable interaction between the ionic and nonionic surfactant (in the form of free monomers).

The ionic surfactant in comparison with non-ionic surfactant will tend to prefer the bulk rather than the interface. Therefore, in all the plots, the  $m_1$  value increases with increasing the total surfactant concentration ( $C_t$ ) and finally reaches a maximum value of the monomer concentration ( $m_1^{\text{max}}$ ). When  $m_1$  remains almost constant with increasing  $C_p$ , it signifies formation of mixed micelles saturated by cationic surfactant ( $C_n\text{PC}$ -rich-mixed micelles) [30,31].

### 3. The Calculation of the Total Surfactant Adsorption

In surfactant mixtures, the component with the lower cmc is usually dominant in mixed micelles and at the air-water interface due to its higher surface activity. The above results are in accordance with the fact that TX-100 is much more surface active than  $C_n\text{PC}$ . The total adsorbed amount of the mixture ( $\Gamma$ ) at the air-water surface can be calculated using the Gibbs adsorption equation:

$$\Gamma_{\text{tot}} = -\frac{1}{RT} \left( \frac{d\sigma}{d \ln C_{\text{tot}}} \right)_{C_n\text{PC}/\text{TX-100}} \quad (16)$$

Measuring the surface tension ( $\sigma$ ) as a function of the total surfactant concentration ( $C_{\text{tot}}$ ) for binary surfactant mixture enables the calculation of the total surfactant adsorption at the surface ( $\Gamma_{\text{tot}}$ ).

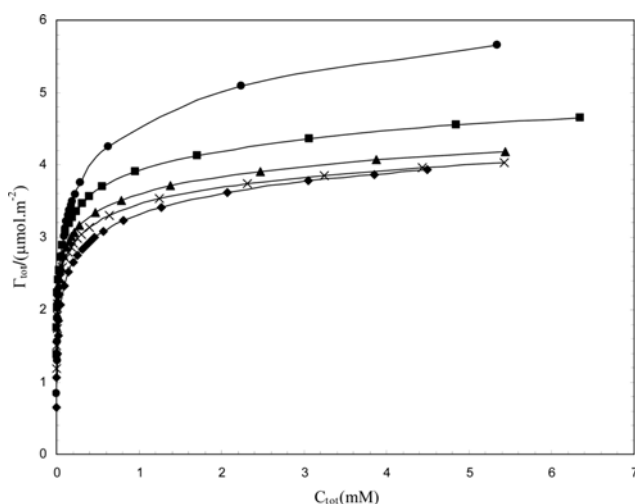


Fig. 6. A typical plot of the values of the total surfactant adsorption against the total surfactant concentration in the bulk solution for the  $C_{14}\text{PC}/\text{TX-100}$  mixture at different bulk mole fractions: (●)  $y_1=0.1$ , (■)  $y_1=0.4$ , (▲)  $y_1=0.5$ , (×)  $y_1=0.6$ , (◆)  $y_1=0.9$ . The solid lines are guide to the eyes.

Fig. 6 shows typical plots of the total surfactant adsorption,  $\Gamma_{\text{tot}} = \Gamma_{C_{14}\text{PC}} + \Gamma_{\text{TX-100}}$ , vs. the total surfactant concentration in the bulk solution ( $C_{\text{tot}}$ ).

As observed the variation of the total surfactant adsorption with composition follows distinctively same patterns at various mole fractions. Fig. 6 also shows a linear relation between  $\Gamma_{\text{tot}}$  and  $C_{\text{tot}}$  at low concentrations of surfactant at different mole fractions (in the Henry law region).

The  $\Gamma_{\text{tot}}$  value increases gradually with increasing concentration of total surfactant and finally reaches a maximum value of the saturated surface adsorption.

According to what we have observed from the surface activity behavior of surfactants, it is obvious that at low total surfactant concentrations in two mixtures TX-100 dominates the interface (due to its higher surface activity), while at high total surfactant concentrations both surfactants (TX-100 and  $C_n\text{PC}$ ) are equally represented at the interface.

Only at concentrations close to the cmc of this surfactant mixture is the total amount of surfactant constant and equivalent amounts of both surfactants are adsorbed at the air-water interface. These observations are in accordance with the fact that much valuable and precise information on the adsorption behavior of surfactants can be gained if rigorous and meticulous analysis of the surface tension curves is carried out [32,33].

### 4. Calculation of the Standard Free Energy of Micellization

Recently, Maeda proposed a simple thermodynamic analysis of ionic and non-ionic mixed micelles. In Maeda's approach, which is based on the pseudo-phase separation model, the thermodynamic stability is described by  $\Delta G_m^0$  (the standard free energy of micellization per mole of monomer unit), which is given as a function of the mole fraction of the ionic component in the mixed micelle [13,34]

$$\Delta G_m^0 = RT(B_0 + B_1 X_2 + B_2 X_2^2) \quad (17)$$

where  $B_0$  is an independent term related to the cmc of the non-ionic surfactant by

$$B_0 = \ln(\text{cmc}_2) \quad (18)$$

$B_1$  is related to the standard free energy of micellization associated with the introduction of one ionic species into a non-ionic micelle coupled with the release of one non-ionic species from the micelle. The final coefficient,  $B_2$ , is equivalent to  $-\beta$  in the regular solution theory.

The parameters  $B_1$  and  $B_2$  are related to the cmc values of pure systems by

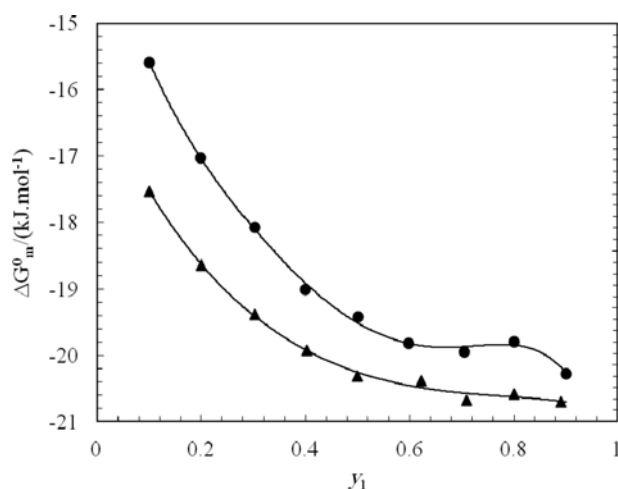
$$\ln \left( \frac{\text{cmc}_1}{\text{cmc}_2} \right) = B_1 + B_2 \quad (19)$$

When  $B_2$  is evaluated, one can obtain  $B_1$  from Eq. (19). Maeda's approach parameters obtained for our systems are in Table 3. Now, based on the description proposed by Maeda, we have estimated the stability of the mixed systems as a function of the micellar composition. Fig. 7 shows the dependence of  $\Delta G_m^0$  on micellar composition, where  $\Delta G_m^0$  is defined as the stability relative to that of TX-100 pure micelles.

As can be seen in Fig. 7, as the chain length of  $C_n\text{PC}$  increases, the stability of the mixed system increases due to the greater pres-

**Table 3. Interaction parameters according to Maeda's approach for binary mixtures of  $C_n$ PC(1)/TX-100(2) at various mole fractions**

Component	$y_1$	$B_0$	$B_1$	$B_2$
$C_{14}$ PC	0.1	-8.69	0.27	2.44
	0.2	-8.69	-0.78	3.48
	0.3	-8.69	-1.37	4.79
	0.4	-8.69	-2.01	4.71
	0.5	-8.69	-2.10	4.81
	0.6	-8.69	-2.21	4.92
	0.7	-8.69	-1.93	4.63
	0.8	-8.69	-1.15	3.86
	0.9	-8.69	-1.88	4.58
$C_{16}$ PC	0.1	-8.69	0.06	1.63
	0.2	-8.69	-1.40	2.73
	0.3	-8.69	-1.63	3.32
	0.4	-8.69	-2.07	3.77
	0.5	-8.69	-2.36	4.05
	0.6	-8.69	-2.11	3.79
	0.7	-8.69	-2.31	4.00
	0.8	-8.69	-1.83	3.52
	0.9	-8.69	-1.59	3.29



**Fig. 7. Plot of the standard free energy of micellization per mole of monomer unit,  $\Delta G_m^0$ , against the bulk mole fractions for the  $C_n$ PC/TX-100 mixtures: (●)  $C_{14}$ PC/TX-100, (▲)  $C_{16}$ PC/TX-100. The solid lines are guide to the eyes.**

ence of the ionic surfactant in mixed micelles. This behavior is reasonable; the more negative  $\Delta G_m^0$  values of  $C_{16}$ PC/TX-100 mixture indicate the incorporation of ionic monomers is associated with a decrease of the surface charge density, causing the electrostatic stabilization of the system.

## CONCLUSION

Binary mixtures of the two cationic surfactant alkyl pyridinium chlorides ( $C_{14}$ PC and  $C_{16}$ PC) with the non-ionic surfactant Triton X-100 (TX-100) were studied at different total mole fractions. Sur-

face tension measurements were used to determine the critical micelle concentration and the surfactant composition at the micelle.

From surface tension measurements both cationic surfactants ( $C_{14}$ PC and  $C_{16}$ PC) used in the study showed synergistic intermolecular interactions when mixed with the nonionic surfactant (Triton X-100). The synergistic effect was most pronounced for the mixture with  $C_{14}$ PC/TX-100, which has a larger deviation from the ideal behavior than the  $C_{16}$ PC/TX-100. The non-ionic TX-100 interacts with the cationic  $C_n$ PC and dominates in mixed micelles due to its much higher surface activity. The cmc of mixed surfactants almost was lower than either of the pure surfactants, which is highly beneficial as it reduces the total amount of surfactant used in industrial application (particular as antifoam and detergent), leading to reduction of cost and environmental effect. Hence micelle formed by mixing of two surfactants is more stable in comparison to micelle formed by an individual one. The analysis of the obtained results shows that  $|\Delta G_m^0|$  values increase with increasing the length of the  $C_n$ PC chain and increase the stability of the mixed micelle.

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## Supporting Information

### Binary mixtures of cationic surfactants with triton X-100 and the studies of physicochemical parameters of the mixed micelles

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#### Mathematical procedure to drive the monomer concentration of surfactants ( $m_1$ and $m_2$ ):

Mass balance considerations combined with Eqs. ( $m_1 = X_1 f_1 cmc_1$  and  $m_2 = X_2 f_2 cmc_2$ ) for two surfactant lead to Eq. (1) [1-3]:

$$X_1 + X_2 = 1 \quad \text{or} \quad \frac{y_1 C_t}{C_t + f_1 cmc_1 - m} + \frac{y_1 C_t}{C_t + f_1 cmc_1 - m} = 1 \quad (1)$$

If  $C_t$  is the total concentration of the mixture, and  $m$  is the sum of the monomer concentrations:

$$m = m_1 + m_2 \quad (2)$$

Solving Eqs. (1) for the total monomer concentration is straight forward for any number of components once the activity coefficients have been calculated, and the following expressions can be used to obtain individual monomer concentrations of ionic surfactant ( $m_1$ ):

$$m_1 = \frac{y_1 f_1 cmc_1 C_t}{C_t + f_1 cmc_1 - m} = \frac{y_1 f_1 cmc_1 C_t}{C_t + f_1 cmc_1 - m_1 - m_2} \quad (3)$$

by combining Eqs. ( $m_1 = X_1 f_1 cmc_1$  and  $m_2 = X_2 f_2 cmc_2$ ) and (2), can be derived as

$$m_1 = \frac{y_1 f_1 cmc_1 C_t}{C_t + f_1 cmc_1 - m_1 - f_2(1 - x_1) cmc_2} \quad (4)$$

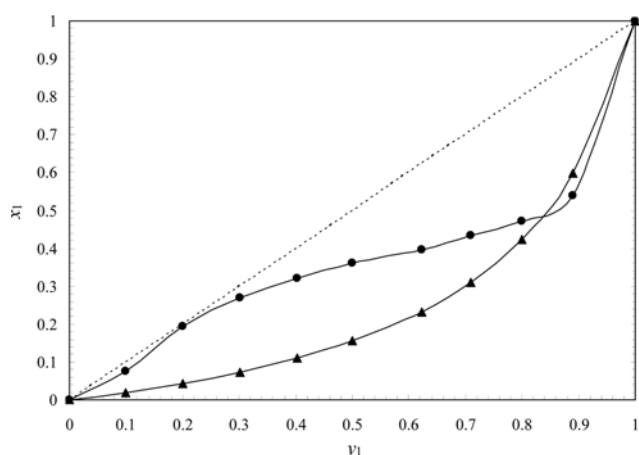


Fig. S1. Mole fraction of  $C_{16}PC$  in the micelle vs. total mole fraction of  $C_{16}PC$  at various model: (---)  $y=x$ , (●) Rubingh's theory, (▲) Motomura's theory. The solid lines are guide to the eyes.

$$m_1 = \frac{y_1 f_1 cmc_1 C_t}{(C_t - f_2 cmc_2 + f_1 cmc_1) - m_1 - f_2 x_1 cmc_2} \quad (5)$$

$$m_1 = \frac{y_1 f_1 cmc_1 C_t}{(C_t - f_2 cmc_2 + f_1 cmc_1) + \left(\frac{f_2 cmc_2}{f_1 cmc_1} - 1\right) m_1} \quad (6)$$

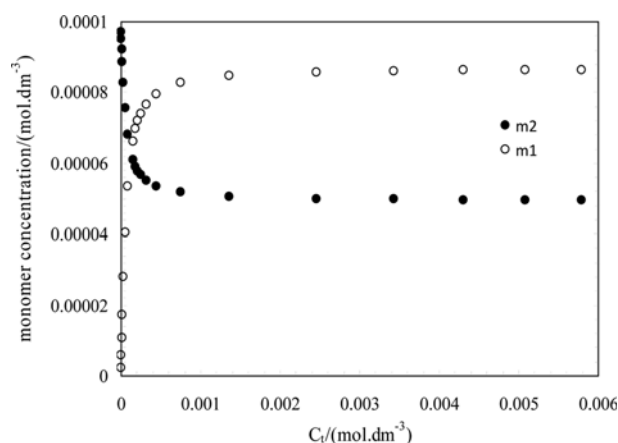


Fig. S2. Monomer concentration of cationic ( $m_1$ ) and nonionic ( $m_2$ ) surfactants vs total concentration of mixed surfactants for the  $C_{16}PC/TX-100$  mixtures at  $y_1=0.5$ .

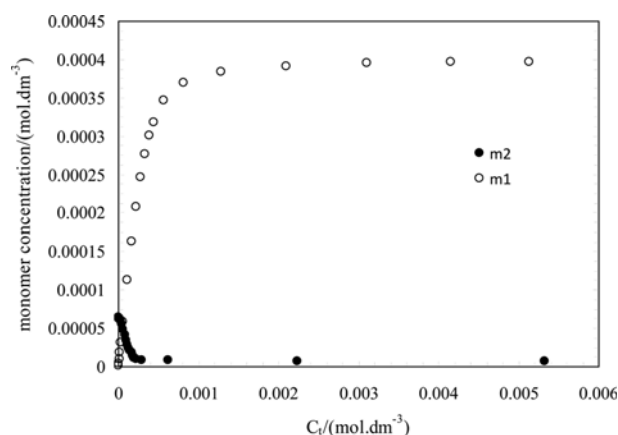


Fig. S3. Monomer concentration of cationic ( $m_1$ ) and nonionic ( $m_2$ ) surfactants vs total concentration of mixed surfactants for the  $C_{16}PC/TX-100$  mixtures at  $y_1=0.9$ .

by rearrangement of Eq. (6), we obtain:

$$\left(\frac{f_2 cmc_2}{f_1 cmc_1} - 1\right)m_1^2 + (C_t - f_2 cmc_2 + f_1 cmc_1)m_1 - \gamma_1 f_1 cmc_1 C_t = 0 \quad (7)$$

we can solve the above quadratic equation by the delta method:

$$m_1 = \frac{-(C_t - f_2 cmc_2 + f_1 cmc_1) \pm \sqrt{(C_t - f_2 cmc_2 + f_1 cmc_1)^2 + 4\left(\frac{f_2 cmc_2}{f_1 cmc_1} - 1\right)\gamma_1 f_1 cmc_1 C_t}}{2\left(\frac{f_2 cmc_2}{f_1 cmc_1} - 1\right)} \quad (8)$$

and since,  $m_2 = f_2(1 - X_1)cmc_2 = f_2\left(1 - \frac{m_1}{f_1 cmc_1}\right)cmc_2$ , the monomer con-

centrations of non-ionic surfactant ( $m_2$ ) can be given as:

$$m_2 = \left(1 - \frac{m_1}{f_1 cmc_1}\right)f_2 cmc_2 \quad (9)$$

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