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# Studies on Binary and Ternary Amphiphile Combinations of Tetradecyltrimethylammonium Bromide (C<sub>14</sub>TAB), Tetradecyltriphenylphosphonium Bromide (C<sub>14</sub>TPB), and Tetradecylpyridinium Bromide (C<sub>14</sub>PB). A Critical Analysis of Their Interfacial and Bulk Behaviors

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Mixed surfactants play a promising role in surface chemical applications. In this study, interfacial and bulk behaviors of binary and ternary combinations of tetradecyltrimethylammonium bromide (C<sub>14</sub>TAB), tetradecyltriphenylphosphonium bromide (C<sub>14</sub>TPB), and tetradecylpyridinium bromide (C<sub>14</sub>PB) have been examined in detail using the methods of tensiometry, conductometry, fluorimetry, and microcalorimetry. The state of micellar aggregation, amphiphile composition in the micelle, extent of counterion binding by the micelle, and interaction among the surfactant monomers in the binary and ternary combinations have been quantitatively assessed in the light of the regular solution theories of Rubingh and that of Rubingh and Holland. The monomer packing in the micelles and their expected shapes have also been estimated from topological considerations. Conceptual rationalization of results has been presented together with associated energetics of the interfacial adsorption and self-aggregation in the bulk.

## Introduction

By virtue of their better performances in solubilization, suspension, dispersion, transportation, etc., mixed surfactants have gained importance in industrial, pharmaceutical, and biological fields.<sup>1,2</sup> Binary combinations of different types of surfactants such as cationic/nonionic,<sup>3–8</sup> anionic/nonionic,<sup>3,9–13</sup> cationic/cationic,<sup>14–18</sup> and anionic/anionic<sup>19–20</sup> have been studied, and the nature of mutual interaction of monomers in the mixed micelles has been quantitatively analyzed in the light of the theories of Motomura,<sup>21</sup> Rosen,<sup>22,23</sup> Blankschtein,<sup>24</sup> Rubingh,<sup>25</sup> and Maeda.<sup>26</sup> Of these theories, that of Blankschtein is more quantitative but complex; Rubingh's formalism is much simpler in terms of mathematical manipulation to extract physicochemical information. The other theories are less quantitative and are not frequently used. A comparative assessment of the aforementioned theories and their comprehensive adoption can be found in the literature.<sup>7,27,28</sup> Although a good number of accounts on binary surfactant mixtures are reported, detailed fundamental studies on multicomponent surfactant mixtures (say ternary combinations) are limited.<sup>29,30</sup>

A useful theory on mixed ternary surfactant systems was proposed by Rubingh and Holland.<sup>31</sup> However, its use in practice has been very limited.<sup>8,32</sup> Conversion of ternary combinations into pseudobinary forms (by treating two of the three components as one) has been considered in the past<sup>28</sup> as an alternative to the proposition of Rubingh and Holland.<sup>31</sup> This adopted treatment was basically that of Rubingh done in a manipulative

form. Consequently, the results on micellar composition and component interaction became dependent on the selection of surfactants' pairing. The treatment offered a simplified approach to the complex problem. Whatever might be the importance of the above approach, the ternary mixed surfactant systems have remained minimally explored and further research with pragmatic analysis of data is wanted. This has been the impetus behind the present study. In a recent paper,<sup>33</sup> an elaborate physicochemical investigation on decylalkyl chains containing surfactants with four different cationic head groups (ammonium, trimethylammonium, triphenylphosphonium, and pyridinium) has been made. In the present investigation, the alkyl chains of the surfactants were all tetradecyl and the heads were trimethylammonium, triphenylphosphonium, and pyridinium with bromide as the counterion. Several binary and ternary combinations of the surfactant mixtures were selected, and their interfacial and bulk behaviors were critically studied. A detailed understanding of the thermodynamics of micellization and interfacial adsorption of the combinations, counterion binding, aggregation number, micellar composition, nature and magnitude of monomer interaction in micelles, and nature of amphiphile packing was contemplated. Such an elaborate study with identical surfactant tails and different bulky head groups in mixed states was not done in the past.

The study has revealed that the components in the micelles of the studied combinations were moderately to fairly nonideal, showing considerably high activity coefficients of one of the components in the binaries and all three components in the ternaries. The self-aggregation processes were exothermic and fairly entropy controlled, and compared to the binaries, the ternary micelles were all conclusively spherical.

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## Materials

The tetradecyltrimethylammonium bromide (C<sub>14</sub>TAB) was an AR grade product from Fluka (Switzerland). The tetradecyltriphenylphosphonium bromide (C<sub>14</sub>TPB) and tetradecylpyridinium bromide (C<sub>14</sub>PB) were synthesized and purified by us as described elsewhere.<sup>15,16</sup> Doubly distilled conductivity water (specific conductance 2–4  $\mu\text{S cm}^{-1}$ , 298 K) was used for all sample preparations.

## Methods

**Tensiometry.** A calibrated Krüss (Germany) tensiometer, based on the du Noüy ring detachment method, was used to measure the surface tension ( $\gamma$ ) at the air/solution interface of the surfactant solutions. A concentrated solution of a surfactant was progressively added in steps, with the help of a Hamilton microsyringe, in water (taken in a container) maintained at a constant temperature with an accuracy of  $\pm 0.1$  K. The surface tensions were measured allowing  $\sim 20$  min for equilibration after each addition. The experiments were duplicated to check reproducibility, and the mean values were used for data acquisition and treatment. The  $\gamma$  values were accurate within  $\pm 0.1$  mN m<sup>-1</sup>.

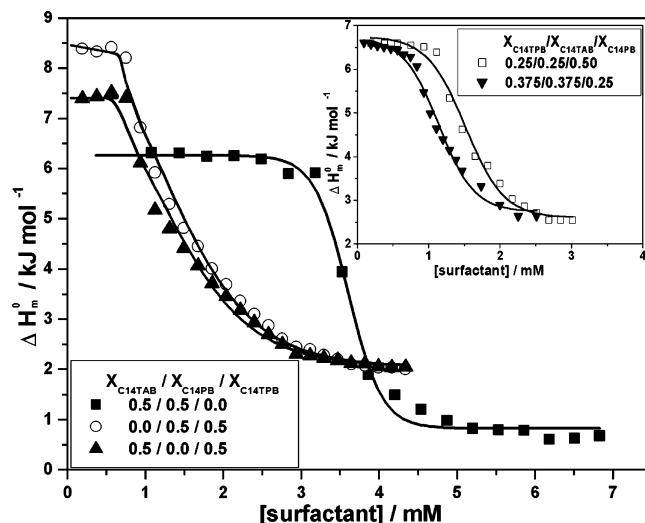
**Conductometry.** The specific conductance of a surfactant solution was measured using a Jenway conductance bridge (U.K.) with a cell of unit cell constant. The concentration of the surfactant solution was increased progressively following the same protocol as that in tensiometry. Measurements were taken after thorough mixing and allowing time for thermal equilibration. The experiments were duplicated, and mean values of the results were considered for analysis. The uncertainties in measurements were within  $\pm 2\%$ .

**Microcalorimetry.** An Omega ITC microcalorimeter of Microcal (Northampton, MA) was used for thermometric measurements. The calorimetric cell was calibrated following the instructions given in the manual, and the error in the heat of dilution measurements was checked by titrating water against water in the cell. The observed error was within  $\pm 1.5\%$  and was neglected in the enthalpy calculation. In the actual experiments, concentrated degassed surfactant solution ( $\sim 20$  times its critical micelle concentration (CMC)) was taken in the microsyringe and added in steps to 1.325 mL of degassed water taken in the calorimeter cell under constant stirring (300 rpm) conditions. The calorimeter was set to 293 K with a Neslab RTE 100 bath and scanned to the studied temperature of 298 K which fluctuated within the limit of  $\pm 0.01$  K. The heat released or absorbed at each step of dilution of the surfactant solution was recorded in the instrument, and the enthalpy change per mole of injectant was calculated by the ITC software. Each run was duplicated to check reproducibility. Further details of the experimental protocol can be found in our earlier reports.<sup>34,35</sup>

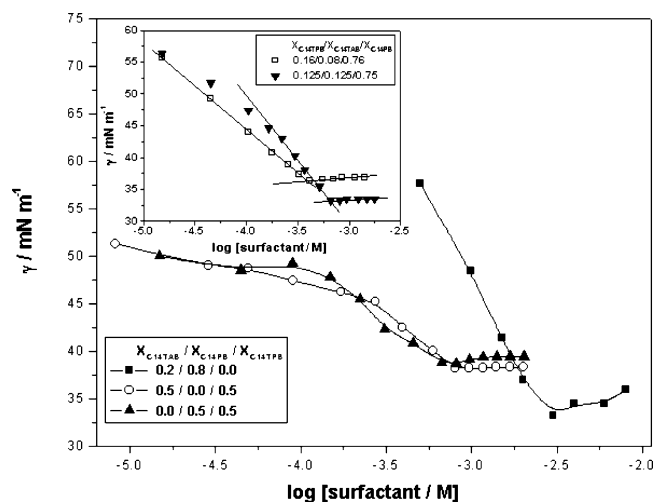
**Fluorimetry.** The fluorescence spectra of Crystal Violet were measured as a function of surfactant mixture concentration using a JY Horiba Spex Fluoromax-3 fluorometer (Japan), using a 1 cm quartz cuvette. The dye was excited at 590 nm, and the emission range 600–700 nm was scanned. The excitation and emission band widths were 7.00 and 9.00 nm, respectively. The concentration of the dye was kept at  $1 \times 10^{-5}$  M to prevent dye dimerization.

## Results and Discussion

**Critical Micellar Concentration.** The methods of calorimetry, tensiometry, conductometry, and fluorimetry were em-



**Figure 1.** Differential enthalpy of dilution vs [surfactant] profiles for the 1:1 binary mixtures of C<sub>14</sub>TAB, C<sub>14</sub>TPB, and C<sub>14</sub>PB at 298 K. The binary compositions are represented by symbols, as shown in the graph. The points are experimental, and the curves are SBE fitted. Inset: Similar enthalpograms for two ternary compositions.



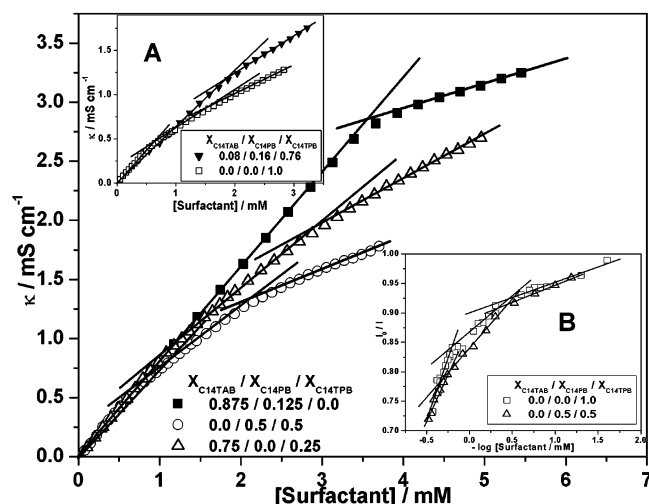
**Figure 2.** Surface tension ( $\gamma$ ) vs  $\log[\text{surfactant}]$  profiles for the binary combinations C<sub>14</sub>TAB–C<sub>14</sub>TPB, C<sub>14</sub>TAB–C<sub>14</sub>PB, and C<sub>14</sub>TPB–C<sub>14</sub>PB at 298 K. Inset: Tensiometric profiles for two ternary mixtures at 298 K.

ployed to investigate the CMCs of the studied pure and mixed surfactant systems.

Considering that readers are conversant with the nature of plots of results by the methods herein used, the graphical presentations for pure systems are not presented. A few representative plots for the binary and ternary mixtures are only illustrated. Figure 1 represents the ITC enthalpograms for binary and ternary mixtures (inset). The experimental points were subjected to fit the sigmoidal Boltzmann equation (SBE) to estimate the CMCs.<sup>34,35</sup>

Figure 2 illustrates the tensiometric plots  $\gamma$  versus  $\log C$  for binary and ternary mixtures (inset). The break point in each corresponded to the CMC.

The conductometric plots of specific conductance ( $\kappa$ ) versus [surfactant] shown in Figure 3 (main diagram) exhibited clear breaks, i.e., the CMCs. C<sub>14</sub>TPB alone showed two CMCs in the pure state (Figure 3, inset A); the binary mixtures of C<sub>14</sub>TPB with either C<sub>14</sub>TAB or C<sub>14</sub>PB also showed two CMCs (main diagram). Double CMCs were also evidenced from fluorimetry (Figure 3, inset B); they fairly agreed with the results



**Figure 3.** Specific conductance ( $\kappa$ ) vs [surfactant] profiles for the binary combinations  $C_{14}TAB-C_{14}TPB$ ,  $C_{14}TAB-C_{14}PB$ , and  $C_{14}TPB-C_{14}PB$  at 298 K. Inset A: Similar profiles for pure  $C_{14}TPB$  and one ternary mixture. Inset B: Fluorimetric plots demonstrating two CMCs for pure  $C_{14}TPB$  and its 1:1 binary mixture with  $C_{14}PB$ .

from conductometry. The formation of two CMCs by fluorimetry was also reported in the past.<sup>17,36</sup> The ternary mixtures indicated only one type of micelle formation (conductometry results shown in inset A of Figure 3).

The CMCs of the binary combinations were also determined following the method of Junquera et al.<sup>37</sup> A premicellar solution of surfactant 1 was titrated with a concentrated solution of surfactant 2. The measured conductance of the solution plotted against [surfactant 2] produced a break. The sum of the final [surfactant 1] ( $C_1$ ) and [surfactant 2] ( $C_2$ ) at the break point, i.e., ( $C_1 + C_2$ ), was the CMC\* of the mixed micelle.

The CMCs obtained by different methods were quite close. The average CMC values were reported in Table 1 and were used for all calculations.

The binary systems  $C_{14}TAB-C_{14}TPB$  and  $C_{14}TPB-C_{14}PB$  produced two CMCs, whereas the  $C_{14}TAB-C_{14}PB$  system produced only a single CMC. The ternary combinations also yielded a single CMC. There are reports on the formation of two CMCs for long chain cationic surfactants both in pure as well as in their binary mixtures.<sup>14,16,17</sup> In Figure 4, the observed CMCs of the binaries by method I (using stoichiometric mixtures) and method II (Junquera et al.) have been compared. In the main diagram,  $[C_{14}TAB]_{\text{Break}} = C_1$  and  $[C_{14}PB]_{\text{Break}} = C_2$ ; similar are representations in the inset. The CMC values of method I were split according to stoichiometric compositions and plotted in the diagram. Good correlations between the two methods were realized. Operationally, method I is better in the sense that measurements can be done at the choice of compositions of the experimenter, whereas, in the second, the composition is known only after experimentation.

In Figure 5, a comparison of the CMC<sub>1</sub> values of the binaries observed and those obtained from Clint's equation (given below) has been illustrated:

$$\frac{1}{(\text{CMC}_1)_{\text{mix}}} = \sum_i \frac{x_i}{\text{CMC}_i} \quad (1)$$

where  $\text{CMC}_i$  and  $(\text{CMC}_1)_{\text{mix}}$  stand for the  $i$ th species and the mixture, respectively, and  $x_i$  is the stoichiometric mole fraction of the  $i$ th component in the solution. The depictions in parts a (main diagram and inset) and b (main diagram) of Figure 5

suggested synergism for all three studied compositions following the order  $C_{14}TPB-C_{14}PB \geq C_{14}TAB-C_{14}TPB \gg C_{14}TAB-C_{14}PB$ . This feature will be further discussed in a subsequent section.

The  $(\text{CMC}_2)_{\text{mix}}$  values have been depicted against the stoichiometric mole fraction of one of the components in the inset of Figure 5b. The patterns are exponential in nature. For the absence of the second CMC for both  $C_{14}TAB$  and  $C_{14}PB$ , estimation of CMC<sub>2</sub> by Clint's method was not possible.

The  $\text{CMC}_{\text{mix}}$  values found by Clint's method for the ternary systems are presented in Table 5. Fair synergism was observed in the results.

**Aggregation Number.** The fluorescence quenching (FQ) method is convenient for the determination of the aggregation number of micelles. We have earlier found<sup>36</sup> that surfactants with pyridinium and triphenylphosphonium head groups themselves can significantly quench the fluorescence of pyrene, 2-anthracene sulfonate, safranin-T, tryptophan, etc. Thus, the FQ method was not suitable in the present study. A procedure to simulate ITC enthalpograms was, therefore, tried to determine the aggregation number ( $n$ ) of the micelles using the software SCIENTIST as reported earlier.<sup>33,35,39,40</sup> Illustrations are not presented.<sup>41</sup> The  $n$  values determined for the pure micelles of  $C_{14}TAB$ ,  $C_{14}TPB$ , and  $C_{14}PB$  at the CMC points were 24, 9, and 15, respectively. They were much lower than that determined by the FQ method for  $C_{14}TAB$  (70)<sup>7</sup> and by light scattering for  $C_{14}PB$  (77).<sup>42,43</sup> Hansson et al.<sup>44</sup> have considered that  $n$  essentially depends on the alkyl chain length and not on the type of the head group. We, therefore, considered that the  $n$  values for  $C_{14}TAB$ ,  $C_{14}TPB$ , and  $C_{14}PB$  were all equal. However, with reference to the report of Jiang et al.,<sup>45</sup>  $n$  for  $C_{16}TPB$  is 15 which corroborated with our results of low values of  $n$  by the ITC simulation. Until more reports are available on  $n$  at CMC, we have considered  $n$  for the tetradecylalkyl chain comprising amphiphiles and their mixtures to be 70 in the data treatment.

**Counterion Binding to the Micelles ( $\beta = m/n$ ).** The fraction of counterion bound to a micelle was conductometrically determined as done in the past by us<sup>7,8,17,20</sup> and others.<sup>46,47</sup> In this method, the ratio of the pre- and post-micellar slopes ( $S_1$  and  $S_2$ , respectively) of the specific conductance versus concentration plots are considered. The ratio  $S_2/S_1$  is considered as the fraction of counterion dissociated from the micelle so that the fraction bound,  $\beta = (1 - S_2/S_1)$ . This is the simplest method to get a fairly quantitative estimation of an important micellar parameter. The  $\beta$  values determined are shown in Table 1.

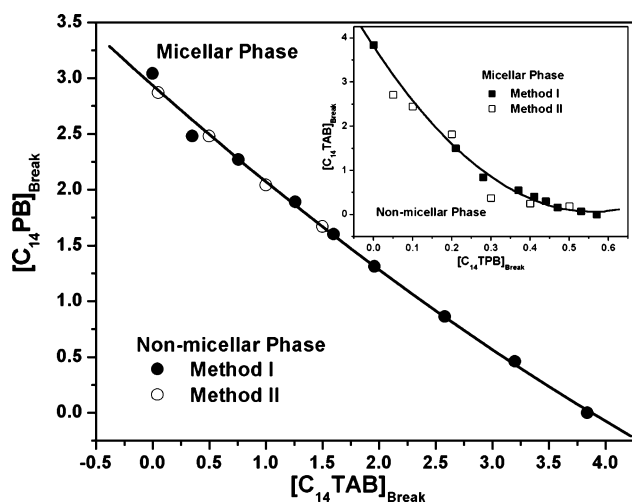
The surface charge density of the formed mixed micelles depended on the head groups of the components, since their tails were all identical. The fraction of counterion ( $\text{Br}^-$ ) bound ( $\beta$ ) can be determined by different methods. Counterion-selective membrane electrodes can be used to ascertain the ion activity to estimate the fraction bound to the micelle.<sup>48</sup> Dai et al.<sup>49</sup> have suggested a procedure based on ITC enthalpograms. However, the validity of the method has been found to be system specific.<sup>20,50</sup> The simpler technique to obtain  $\beta$  from conductivity results by the slope ratio method is most often used.<sup>46,47</sup> Buckingham et al.<sup>51</sup> have shown that  $\beta$  values obtained by the electrometric (ion-selective electrode) and conductometric (slope ratio) methods were in good agreement. Although the conductivity method neglects the mobility of the charged micelles, due to simplicity of experimentation, calculation, and understanding, it is the most frequently used method. Hoffman and Ulbright<sup>52</sup> have reported a  $\beta$  value close to our result on  $C_{14}PB$  (at 25 °C)



TABLE 1: First and Second CMCs and  $\beta$  Values of the Studied Binary and Ternary Mixtures at 298 K

C <sub>14</sub> TAB–C <sub>14</sub> TPB System										
$X_{C_{14}TAB}$	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
CMC <sub>1</sub> (CMC <sub>2</sub> ) (mM)	0.69 (2.06)	0.72 (1.44)	0.79 (1.53)	0.83 (1.92)	0.90 (2.33)	1.09 (2.09)	1.26 (2.77)	1.84 (3.60)	3.86 (-)	
$\beta_1$ ( $\beta_2$ )	0.46 (0.58)	0.44 (0.53)	0.41 (0.52)	0.44 (0.55)	0.38 (0.61)	0.31 (0.48)	0.32 (0.54)	0.37 (0.52)	0.75 (-)	
C <sub>14</sub> TPB–C <sub>14</sub> PB System										
$X_{C_{14}TPB}$	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
CMC <sub>1</sub> (CMC <sub>2</sub> ) (mM)	3.11 (-)	1.43 (3.74)	1.22 (2.89)	0.90 (2.22)	0.83 (2.45)	0.74 (1.90)	0.78 (2.26)	0.57 (2.58)	0.69 (2.06)	
$\beta_1$ ( $\beta_2$ )	0.73 (-)	0.39 (0.69)	0.38 (0.59)	0.39 (0.56)	0.42 (0.68)	0.41 (0.55)	0.42 (0.58)	0.45 (0.58)	0.46 (0.58)	
C <sub>14</sub> TAB–C <sub>14</sub> PB System										
$X_{C_{14}TAB}$	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
CMC <sub>1</sub> (CMC <sub>2</sub> ) (mM)	3.11 (-)	3.02 (-)	3.08 (-)	3.19 (-)	3.18 (-)	3.28 (-)	3.34 (-)	3.55 (-)	3.86 (-)	
$\beta_1$ ( $\beta_2$ )	0.73 (-)	0.72 (-)	0.73 (-)	0.73 (-)	0.73 (-)	0.73 (-)	0.73 (-)	0.74 (-)	0.75 (-)	
C <sub>14</sub> TAB–C <sub>14</sub> PB–C <sub>14</sub> TPB System										
ternary mixtures <sup>a</sup>	1	2	3	4	5	6	7	8	9	10
CMC (mM)	1.77	1.36	1.47	1.04	1.19	1.60	1.12	1.14	0.85	0.77
$\beta$	0.38	0.48	0.44	0.40	0.37	0.46	0.42	0.32	0.38	0.39

<sup>a</sup>  $X_{C_{14}TPB}/X_{C_{14}TAB}/X_{C_{14}PB}$ : **1**, 0.08/0.16/0.76; **2**, 0.125/0.125/0.75; **3**, 0.16/0.08/0.76; **4**, 0.333/0.167/0.50; **5**, 0.25/0.25/0.50; **6**, 0.167/0.333/0.50; **7**, 0.333/0.333/0.333; **8**, 0.25/0.50/0.25; **9**, 0.375/0.375/0.25; **10**, 0.50/0.25/0.25.



**Figure 4.** Correlation between the binary compositions of surfactants at their mixed micellar CMC observed by methods I and II (described in the text) at 298 K. Main diagram: C<sub>14</sub>TAB–C<sub>14</sub>PB system. Inset: C<sub>14</sub>TAB–C<sub>14</sub>TPB system.

by the above procedure. Other relevant literature reports can be found in refs 53–55.

The  $\beta$  values herein obtained have been tabulated in Table 1. The values for C<sub>14</sub>TAB–C<sub>14</sub>TPB and C<sub>14</sub>TPB–C<sub>14</sub>PB were on the whole comparable. Those for C<sub>14</sub>TAB–C<sub>14</sub>PB were appreciably higher. This system had a higher surface charge density. Cationic surfactants with  $C_n = 16^{15}$  produced similar results. The pyridinium group is structurally smaller than the other two head groups, and the facile delocalization of the electron cloud over the sp<sup>2</sup>-hybridized carbon atoms and the nitrogen atom of the pyridinium ring caused the C<sub>14</sub>PB micelles to have a higher surface charge density and hence increased  $\beta$ . The less electronegative phosphorus with three bulky phenyl groups in the periphery ended up with a lower surface charge density for the C<sub>14</sub>TPB micelles. This was corroborated by the following features. The  $A_{\min}$  values for the pure amphiphiles followed the order C<sub>14</sub>TPB > C<sub>14</sub>TAB > C<sub>14</sub>PB. The surface charge density of their micelles and hence the associated  $\beta$  should follow a reverse order. The observed order was C<sub>14</sub>PB  $\approx$  C<sub>14</sub>TAB > C<sub>14</sub>TPB, which grossly tallied with expectation.

In the mixed states,  $\beta_{(C_{14}TAB-C_{14}PB)} > \beta_{(C_{14}TPB-C_{14}PB)} > \beta_{(C_{14}TAB-C_{14}TPB)}$ , which was in line with head group negativity. The first two binary systems in Table 1 produced two CMCs. Changes in aggregation and in the shape of the micelles at the higher concentrations were envisaged.<sup>16,17</sup> The  $\beta$  value for the secondary micelle was obtained from the relation  $\beta_2 = 1 - S_3/S_1$ , where  $S_3$  is the post-micellar slope corresponding to the second break. The  $A_{\min}$  and  $\beta$  values in Table 1 are the manifestations of the activities of the individuals in isolation and in mixtures. A gross difference in this respect was found for the C<sub>14</sub>TAB–C<sub>14</sub>PB combinations. Their micellar packing parameters ( $P$ , discussed in section 5) were also moderately higher than 0.333. The micelles were to some extent nonspherical; their higher surface charge density yielded higher  $\beta$  values.

**Interfacial Properties.** The adsorption efficacy of the studied surfactants and their mixtures at the air/solution interface was assessed in the light of the Gibbs adsorption equation:<sup>7,8,18,20</sup>

$$\Gamma_{\max} = -\frac{1}{2.303iRT} \lim_{C \rightarrow \text{CMC}} \frac{d\gamma}{d \log C} \text{ mol m}^{-2} \quad (2)$$

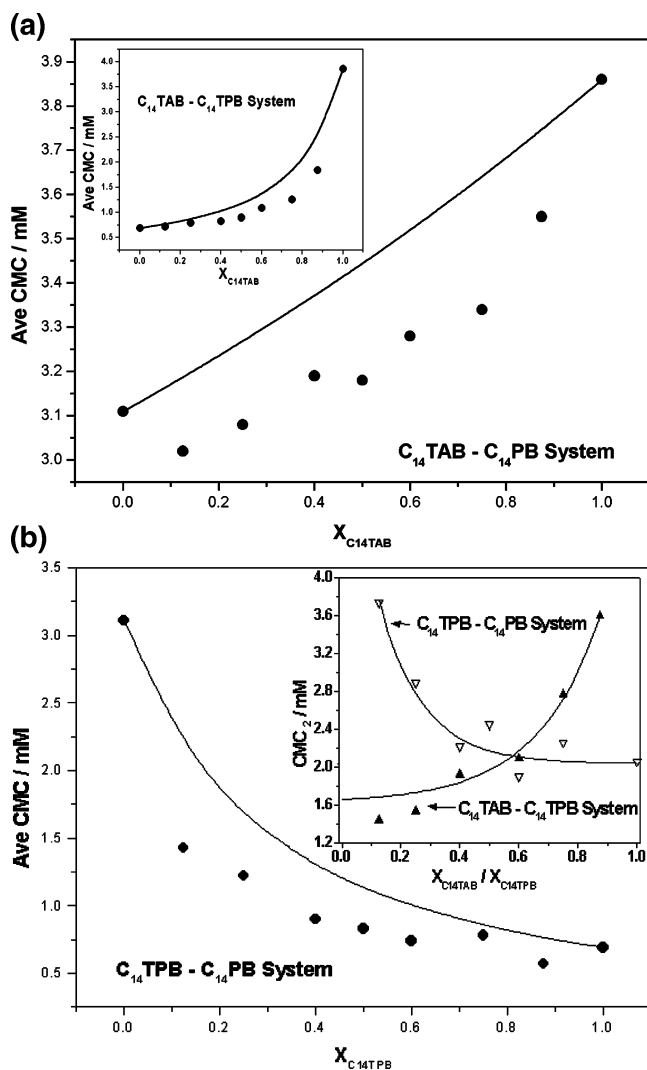
where  $\Gamma_{\max}$ ,  $i$ ,  $R$ ,  $T$ , and  $C$  are the maximum surface excess at CMC, the number of species formed by way of dissociation of surfactant monomer, the gas constant, the absolute temperature, and the concentration of surfactant, respectively. With increasing surfactant concentration,  $\gamma$  decreased due to increased accumulation of the amphiphile at the interface. The CMC corresponded to the saturation of this monolayer; further addition of surfactants to this system resulted in micelle formation. The minimum head group area of a monomer molecule in the saturated monolayer was obtained from the relation

$$A_{\min} = \frac{10^{18}}{N\Gamma_{\max}} \text{ nm}^2 \text{ molecule}^{-1} \quad (3)$$

where  $N$  is the Avogadro number.

The standard Gibbs free energy of adsorption was obtained from the relation

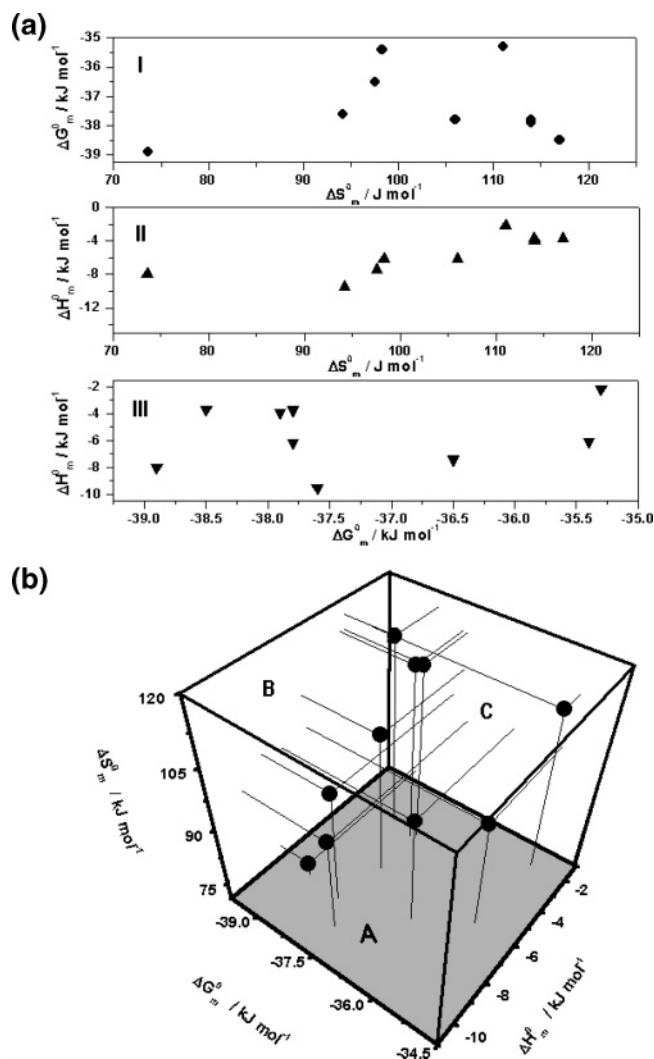
$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{m}}^{\circ} - \frac{\Pi_{\text{CMC}}}{\Gamma_{\max}} \quad (4)$$



**Figure 5.** (a) Dependence of average CMCs of binary C<sub>14</sub>TAB-C<sub>14</sub>PB systems on  $X_{C_{14}TAB}$  at 298 K. Points are experimental; curves are according to Clint. Inset: Similar profile for the C<sub>14</sub>TAB-C<sub>14</sub>TPB system. (b) Dependence of average CMCs of binary C<sub>14</sub>TPB-C<sub>14</sub>PB systems on  $X_{C_{14}TPB}$  at 298 K. Points are experimental; curves are according to Clint. Inset: Dependence of the second CMC of the two binary systems C<sub>14</sub>TAB-C<sub>14</sub>TPB and C<sub>14</sub>TPB-C<sub>14</sub>PB on  $X_{C_{14}TAB}$  and  $X_{C_{14}TPB}$ , respectively. The systems are identified in the figure by symbols.

where  $\Delta G_m^\circ$  is the standard Gibbs free energy of micellization (to be discussed later) and  $\Pi_{CMC}$  is the surface pressure ( $\gamma_{water} - \gamma_{soln}$ ) at CMC. The results are presented in Table 2. The  $\Delta G_{ads}^\circ$  values (calculated from eq 4) for the tetradecyls in pure, binary, and ternary mixtures were all higher than  $\Delta G_m^\circ$  ( $\Delta G_{ads}^\circ / \Delta G_m^\circ \approx 1.4$ ). The process of interfacial adsorption of the amphiphiles was nearly 1.4 times more favorable than micellization.

The head group areas of the binary mixtures were in between those of pure components. Larger values of  $A_{min}$  than the individual components of binaries were also reported in the literature.<sup>17,20</sup> The values for C<sub>14</sub>TAB-C<sub>14</sub>TPB mixtures were in accordance with their stoichiometric compositions, whereas, for C<sub>14</sub>TPB-C<sub>14</sub>PB, the  $A_{min}$  values were close to that of C<sub>14</sub>-TPB excepting that at  $X_{C_{14}PB} = 0.2$ . In the ternary mixtures, the exclusion volumes were greater than those for the binary mixtures due to the stronger repulsion among the three cationic head groups. Dissimilar packing of the components might also produce higher  $A_{min}$  values. Similar was our finding on cetylpyridinium chloride, cetyltrimethylammonium bromide, and



**Figure 6.** (a) Pairwise interdependence of energetic parameters for the ternary systems at 298 K. I,  $\Delta G_m^\circ - \Delta S_m^\circ$ ; II,  $\Delta H_m^\circ - \Delta S_m^\circ$ ; III,  $\Delta H_m^\circ - \Delta G_m^\circ$ . (b) Three-dimensional representation of interdependence among  $\Delta G_m^\circ$ ,  $\Delta H_m^\circ$ , and  $\Delta S_m^\circ$  for the ternary systems at 298 K. Their links in different planes are  $\Delta G_m^\circ - \Delta H_m^\circ$  (A),  $\Delta H_m^\circ - \Delta S_m^\circ$  (B), and  $\Delta G_m^\circ - \Delta S_m^\circ$  (C).

Brij 56 (polyoxyethylene cetyether) mixed systems.<sup>8</sup> The report of Fujio<sup>42</sup> on pure C<sub>14</sub>PB ( $A_{min} = 0.41 \text{ nm}^2$ ) was lower than our finding ( $0.55 \text{ nm}^2$ ).

**Energetics of the Micellization Process.** The thermodynamic state functions, the standard Gibbs free energy change ( $\Delta G_m^\circ$ ), the enthalpy change ( $\Delta H_m^\circ$ ), and the entropy change ( $\Delta S_m^\circ$ ) during the process of micellization were important parameters for the basic understanding of the feasibility of the process and its inherent constraints, etc.  $\Delta G_m^\circ$  was calculated according to the pseudophase model (PM) by the relation<sup>56</sup>

$$\Delta G_m^\circ = (1 + \beta)RT \ln X_{CMC} \quad (5)$$

The enthalpy changes for the process  $\Delta H_m^\circ$  were obtained directly from ITC measurements.<sup>7,17,20</sup>

The entropy changes ( $\Delta S_m^\circ$ ) then followed from the relation

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ - \Delta G_m^\circ}{T} \quad (6)$$

The thermodynamic parameters herein reported were based on calorimetric measurements. The results are presented in Table 3. Among the binaries, the C<sub>14</sub>TAB-C<sub>14</sub>PB system was more

**TABLE 2: Interfacial Parameters of the Studied Binary and Ternary Mixtures at 298 K**

C <sub>14</sub> TAB–C <sub>14</sub> TPB System									
$X_{C_{14}TAB}$	0.0	0.2	0.4	0.6	0.8	1.0			
$\Gamma_{\max} \times 10^6$ <sup>a</sup>	1.88	2.09	2.17	2.29	2.47	2.66			
$A_{\min}$ <sup>b</sup>	0.88	0.80	0.77	0.72	0.67	0.62			
$\Delta G_{\text{ads}}^{\circ}$ <sup>c</sup>	−56.0	−53.4	−53.5	−49.1	−48.0	−54.7			
$P$	0.24	0.26	0.27	0.29	0.31	0.34			
C <sub>14</sub> TPB–C <sub>14</sub> PB System									
$X_{C_{14}TPB}$	0.0	0.2	0.4	0.6	0.8	1.0			
$\Gamma_{\max} \times 10^6$ <sup>a</sup>	2.99	1.96	1.91	1.92	1.57	1.88			
$A_{\min}$ <sup>b</sup>	0.55	0.85	0.87	0.86	1.05	0.88			
$\Delta G_{\text{ads}}^{\circ}$ <sup>c</sup>	−53.4	−52.7	−53.7	−54.5	−58.3	−56.0			
$P$	0.38	0.25	0.24	0.24	0.20	0.24			
C <sub>14</sub> TAB–C <sub>14</sub> PB System									
$X_{C_{14}TAB}$	0.0	0.2	0.4	0.6	0.8	1.0			
$\Gamma_{\max} \times 10^6$ <sup>a</sup>	2.99	3.02	2.91	3.18	3.00	2.66			
$A_{\min}$ <sup>b</sup>	0.55	0.55	0.57	0.52	0.55	0.62			
$\Delta G_{\text{ads}}^{\circ}$ <sup>c</sup>	−53.4	−53.2	−53.9	−52.7	−53.6	−54.7			
$P$	0.38	0.38	0.37	0.40	0.38	0.34			
C <sub>14</sub> TAB–C <sub>14</sub> PB–C <sub>14</sub> TPB System									
ternary mixtures <sup>d</sup>	1	2	3	4	5	6	8	9	10
$\Gamma_{\max} \times 10^7$ <sup>a</sup>	5.15	7.95	4.35	5.79	3.52	5.32	7.03	5.19	5.22
$A_{\min}$ <sup>b</sup>	3.22	2.09	3.82	2.87	4.72	3.12	2.36	3.20	3.18
$\Delta G_{\text{ads}}^{\circ}$ <sup>c</sup>	−43	−44	−47	−45	−48	−46	−41	−46	−46
$P$	0.07	0.10	0.06	0.07	0.04	0.07	0.09	0.07	0.07

<sup>a</sup> Units of mol m<sup>−2</sup>. <sup>b</sup> Units of nm<sup>2</sup> molecule<sup>−1</sup>. <sup>c</sup> Units of kJ mol<sup>−1</sup>. <sup>d</sup>  $X_{C_{14}TPB}/X_{C_{14}TAB}/X_{C_{14}PB}$ : **1**, 0.08/0.16/0.76; **2**, 0.125/0.125/0.75; **3**, 0.16/0.08/0.76; **4**, 0.333/0.167/0.50; **5**, 0.25/0.25/0.50; **6**, 0.167/0.333/0.50; **7**, 0.333/0.333/0.333; **8**, 0.25/0.50/0.25; **9**, 0.375/0.375/0.25; **10**, 0.50/0.25/0.25.

spontaneous for self-association in comparison with the other two. The ternary systems were a little less spontaneous than the binaries.

$\Delta G_m^{\circ}$  was also calculated according to the mass action model (MM):<sup>56</sup>

$$\Delta G_m^{\circ} = (1 + \beta)RT \ln X_{\text{CMC}} + \left(\frac{RT}{n}\right) \ln[2n^2(1 + \beta)] \quad (7)$$

Equations 5 and 7 were developed for the micellization of pure surfactants and were extended to use on mixed amphiphile systems.<sup>7,8,15,20</sup> The equations require  $\beta$  and CMC, which are experimentally determined quantities. For large values of  $n$ , eq 7 becomes identical to eq 5, making PM and MM equivalent. The  $\Delta G_m^{\circ}$  (MM) values are also included in Table 3, in parentheses. The PM values were minorly lower than the MM values; the differences between the two models were not appreciable because the magnitude of  $n$  was not small.

The micellization processes of the tetradecyls were all exothermic of which C<sub>14</sub>TPB and C<sub>14</sub>TAB produced comparable and high negative  $\Delta H_m^{\circ}$  values, whereas C<sub>14</sub>PB showed very low negative enthalpies. In our earlier work, a similar head group dependence of thermodynamic parameters involving cationics with  $C_n = 16$  was reported.<sup>15</sup> There, C<sub>16</sub>PC showed minimum exothermicity among all other C<sub>16</sub> representatives. This similarity in observation led us to propose that the small pyridinium head group has a low heat evolution characteristic. The  $\Delta S_m^{\circ}$  values of the representatives were positive and large, of which that for C<sub>14</sub>PB was the largest and the other two were comparable. The process  $\Delta G_m^{\circ}$  for C<sub>14</sub>PB was more entropy controlled than C<sub>14</sub>TAB and C<sub>14</sub>TPB. The energetic parameters of the mixed systems were comparable, with minor variations between the binaries and ternaries. The processes were all fairly exothermic with large entropy values.

The pairwise interdependence of the energetic parameters for the ternary systems is presented in Figure 6a (I–III). On the

whole, the points offered linear trends of which the  $\Delta H_m^{\circ} - \Delta S_m^{\circ}$  dependence was the best among the three. It revealed a kind of enthalpy–entropy compensation observed in different equilibrium and kinetic processes.<sup>15,57</sup>

Displayed in three dimensions is the interdependence of  $\Delta G_m^{\circ}$ ,  $\Delta H_m^{\circ}$ , and  $\Delta S_m^{\circ}$  (top view) in Figure 6b. The points are distributed at different depths in space. The projections of the points on plane A manifest the correlation between  $\Delta G_m^{\circ}$  and  $\Delta H_m^{\circ}$ . Those on plane B represent correlation between  $\Delta H_m^{\circ}$  and  $\Delta S_m^{\circ}$ , whereas that between  $\Delta G_m^{\circ}$  and  $\Delta S_m^{\circ}$  is profiled in plane C.

The free energy contributions of different groups  $\Delta G_m^{\circ}$  (H), i.e., the head group,  $\Delta G_m^{\circ}$  (CH<sub>2</sub>), and  $\Delta G_m^{\circ}$  (CH<sub>3</sub>) toward the total free energy of transfer of 1 mol of monomer from the bulk (aqueous environment) into the micelle (oil environment) was estimated for C<sub>14</sub>TAB, C<sub>14</sub>TPB, and C<sub>14</sub>PB following the additivity rationale,<sup>58</sup> as shown below:

$$\Delta G_m^{\circ} = \Delta G_m^{\circ}(\text{H}) + \Delta G_m^{\circ}(\text{CH}_2) C_{n-1} + \Delta G_m^{\circ}(\text{CH}_3) \quad (8)$$

Taking  $\Delta G_m^{\circ}(\text{CH}_3) = -8.40$  kJ mol<sup>−1</sup><sup>57</sup> and  $\Delta G_m^{\circ}(\text{CH}_2) = -2.63$  kJ mol<sup>−1</sup> (average of reports in refs 15 and 17), the  $\Delta G_m^{\circ}(\text{H})$  values for C<sub>14</sub>TAB, C<sub>14</sub>TPB, and C<sub>14</sub>PB were found to be 1.08, 1.73, and 0.63 kJ mol<sup>−1</sup>, respectively. Thus, head groups adversely contributed to the free energy of the self-aggregation process following the order triphenylphosphonium > trimethylammonium > pyridinium. The head group contributions on  $\Delta G_m^{\circ}$  of the mixed systems were also estimated following a similar procedure. The results are shown in Table 3 under the head  $\Delta G_m^{\circ}(\text{H})$ . Among the binaries, the combination of C<sub>14</sub>TAB–C<sub>14</sub>PB made weak nonspontaneous head group contribution to  $\Delta G_m^{\circ}$ . The head groups of the ternary systems on the whole imparted larger nonspontaneity than the binaries.



TABLE 3: Thermodynamic Parameters  $\Delta G_{\text{mic}}^{\circ}$ ,  $\Delta H_{\text{mic}}^{\circ}$ , and  $\Delta S_{\text{mic}}^{\circ}$  for the Studied Binary and Ternary Mixtures at 298 K

C <sub>14</sub> TAB–C <sub>14</sub> TPB System										
<i>X</i> <sub>C<sub>14</sub>TAB</sub>	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
$\Delta G_{\text{m}}^{\circ a}$ PM (MM)	−40.9 (−40.6)	−40.1 (−39.8)	−39.0 (−38.7)	−39.6 (−39.3)	−37.7 (−37.4)	−35.2 (−34.9)	−35.0 (−34.7)	−35.0 (−34.7)	−41.5 (−41.2)	
$\Delta G_{\text{m}}^{\circ}$ (H) <sup><i>a</i></sup>	1.73	2.44	3.60	2.95	4.88	7.41	7.62	7.58	1.08	
$\Delta H_{\text{m}}^{\circ b}$	−5.82	−6.18	−5.16	−4.56	−3.35	−3.52	−3.43	−3.35	−5.05	
$\Delta S_{\text{m}}^{\circ c}$	119	116	116	119	117	108	107	109	123	
C <sub>14</sub> TPB–C <sub>14</sub> PB System										
<i>X</i> <sub>C<sub>14</sub>TPB</sub>	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
$\Delta G_{\text{m}}^{\circ a}$ PM (MM)	−42.0 (−41.7)	−36.4 (−36.1)	−36.7 (−36.4)	−38.0 (−37.7)	−39.1 (−38.8)	−39.2 (−38.9)	−39.3 (−39.0)	−41.3 (−41.0)	−40.9 (−40.6)	
$\Delta G_{\text{m}}^{\circ}$ (H) <sup><i>a</i></sup>	0.63	6.20	5.92	4.60	3.50	3.37	3.38	1.32	1.73	
$\Delta H_{\text{m}}^{\circ b}$	−0.007	−2.95	−5.95	−4.20	−5.32	−4.13	−6.68	−8.31	−5.82	
$\Delta S_{\text{m}}^{\circ c}$	141	112	103	113	113	118	111	112	119	
C <sub>14</sub> TAB–C <sub>14</sub> PB System										
<i>X</i> <sub>C<sub>14</sub>TAB</sub>	0.0	0.125	0.25	0.40	0.50	0.60	0.75	0.875	1.0	
$\Delta G_{\text{m}}^{\circ a}$ PM (MM)	−42.0 (−41.7)	−41.8 (−41.5)	−42.0 (−41.7)	−41.9 (−41.6)	−41.9 (−41.6)	−41.7 (−41.4)	−41.7 (−41.4)	−41.6 (−41.3)	−41.5 (−41.4)	
$\Delta G_{\text{m}}^{\circ}$ (H) <sup><i>a</i></sup>	0.63	0.74	0.58	0.74	0.72	0.85	0.93	0.95	1.08	
$\Delta H_{\text{m}}^{\circ b}$	−0.007	−5.33	−5.92	−5.78	−5.13	−	−5.13	−6.10	−5.05	
$\Delta S_{\text{m}}^{\circ c}$	141	122	121	121	123	−	128	119	123	
C <sub>14</sub> TAB–C <sub>14</sub> PB–C <sub>14</sub> TPB System										
ternary mixtures <sup><i>d</i></sup>	1	2	3	4	5	6	7	8	9	10
$\Delta G_{\text{m}}^{\circ a}$ PM (MM)	−35.4 (−35.1)	−38.9 (−38.6)	−37.6 (−37.3)	−37.8 (−37.5)	−36.5 (−36.2)	−37.8 (−37.5)	−38.0 (−37.7)	−35.3 (−35.0)	−37.9 (−37.6)	−38.5 (−38.2)
$\Delta G_{\text{m}}^{\circ}$ (H) <sup><i>a</i></sup>	7.19	3.66	4.99	4.83	6.10	4.77	4.55	7.29	4.68	4.07
$\Delta H_{\text{m}}^{\circ b}$	−6.11	−	−9.53	−3.74	−7.43	−6.18	−8.43	−2.16	−3.96	−3.68
$\Delta S_{\text{m}}^{\circ c}$	98.3	73.6	94.2	114	97.6	106	99.2	111	114	117

<sup>a</sup> Units of kJ mol<sup>−1</sup>. <sup>b</sup> Units of kJ mol<sup>−1</sup>. <sup>c</sup> Units of J mol<sup>−1</sup>. The errors in  $\Delta G_{\text{m}}^{\circ}$ ,  $\Delta H_{\text{m}}^{\circ}$ , and  $\Delta S_{\text{m}}^{\circ}$  are  $\pm 3$ ,  $\pm 5$ , and  $\pm 8\%$ , respectively. <sup>d</sup>  $X_{\text{C}_{14}\text{TPB}}/X_{\text{C}_{14}\text{TAB}}/X_{\text{C}_{14}\text{PB}}$ : **1**, 0.08/0.16/0.76; **2**, 0.125/0.125/0.75; **3**, 0.16/0.08/0.76; **4**, 0.333/0.167/0.50; **5**, 0.25/0.25/0.50; **6**, 0.167/0.333/0.50; **7**, 0.333/0.333/0.333; **8**, 0.25/0.50/0.25; **9**, 0.375/0.375/0.25; **10**, 0.50/0.25/0.25.

**TABLE 4: Micellar Mole Fractions ( $X^R$ ), the Interaction Parameter ( $g$ ), and the Activity Coefficients ( $f_1^R$  and  $f_2^R$ ) of the Studied Binary Mixtures at 298 K as Determined by Rubingh's Analysis**

C <sub>14</sub> TAB–C <sub>14</sub> TPB System							
$X_{C_{14}TAB}$	0.125	0.25	0.40	0.50	0.60	0.75	0.875
$X^R_{C_{14}TAB}$	0.08	0.13	0.23	0.27	0.30	0.42	0.54
$g$	–1.46	–1.23	–1.66	–1.58	–1.17	–1.60	–1.22
$f_1$	0.29	0.39	0.37	0.43	0.56	0.58	0.77
$f_2$	0.71	0.61	0.63	0.57	0.44	0.42	0.23
C <sub>14</sub> TPB–C <sub>14</sub> PB System							
$X_{C_{14}TPB}$	0.125	0.25	0.40	0.50	0.60	0.75	0.875
$X^R_{C_{14}TPB}$	0.45	0.57	0.65	0.70	0.74	0.87	0.82
$g$	–1.83	–1.38	–1.79	–1.69	–2.06	–1.53	–3.89
$f_1$	0.58	0.78	0.80	0.86	0.87	0.97	0.88
$f_2$	0.42	0.22	0.20	0.14	0.13	2.55	0.12
C <sub>14</sub> TAB–C <sub>14</sub> PB System							
$X_{C_{14}TAB}$	0.125	0.25	0.40	0.50	0.60	0.75	0.875
$X^R_{C_{14}TAB}$	0.15	0.25	0.38	0.47	0.56	0.70	0.85
$g$	–0.52	–0.31	–0.23	–0.29	–0.22	–0.28	–0.19
$f_1$	0.69	0.84	0.91	0.92	0.96	0.98	0.99
$f_2$	0.31	0.16	8.50	7.82	4.24	0.02	4.25

**Components Mutual Interaction in Binary and Ternary Mixtures.** The interaction of amphiphiles in the mixed micelles can be qualitatively assessed from Clint's formalism for ideal mixing,<sup>60</sup> eq 1.

If the experimental  $CMC_{mix}$  values are lower than that expected from Clint's equation, the system is nonideal with synergistic or attractive interaction between the two components, whereas higher experimental  $CMC_{mix}$  values means interaction with antagonism or repulsion. In this study, nonideal synergistic interaction was observed among all three binary pairs (Figure 5). By this rationale, the ternary mixtures were all synergistically more nonideal than the binaries (Table 5).

The extent of component interaction in binary mixed micelles can be assessed by theoretical treatments.<sup>21–25</sup> Among these, Rubingh's regular solution theory<sup>25</sup> has been very commonly used for its simplified approach. We have examined the mixed binary systems in the light of this theory to calculate the interaction parameter,  $g$ , from the relation

$$g = \frac{\ln\left(\frac{CMC_{mix}x_1^R}{CMC_1x_1^R}\right)}{(1 - x_1^R)^2} \quad (9)$$

where  $x_1^R$  is the micellar mole fraction; the other terms are already defined.  $x_1^R$  can be obtained by iteratively solving the following equation:

$$\frac{x_1^{R^2} \ln\left[\frac{CMC_{mix}x_1^R}{CMC_1x_1^R}\right]}{(1 - x_1^R)^2 \ln\left[\frac{CMC_{mix}(1 - x_1^R)}{CMC_2(1 - x_1^R)}\right]} = 1 \quad (10)$$

The activity coefficients of both components in the mixed micelles ( $f_1^R$  and  $f_2^R$ ) can be evaluated from the relations

$$\begin{aligned} f_1^R &= \exp[g(1 - x_1^R)^2] \\ f_2^R &= \exp[g(x_1^R)^2] \end{aligned} \quad (11)$$

The values of  $g$ ,  $x_1^R$ ,  $f_1^R$ , and  $f_2^R$  determined for the components of the studied systems are presented in Table 4.

For both the C<sub>14</sub>PB–C<sub>14</sub>TPB and C<sub>14</sub>TAB–C<sub>14</sub>TPB systems, C<sub>14</sub>TPB was the major constituent in the mixed micelles. However, for the C<sub>14</sub>PB–C<sub>14</sub>TAB system, the micellar mole fractions were only moderately different from the stoichiometric mole fractions. The  $g$  values in all three binary compositions were found to be negative. The average values of  $g$  ( $g_{ave}$ ) were –1.42, –1.71, and –0.29 for the C<sub>14</sub>TAB–C<sub>14</sub>TPB, C<sub>14</sub>TPB–C<sub>14</sub>PB, and C<sub>14</sub>TAB–C<sub>14</sub>PB systems, respectively; the synergism followed the order C<sub>14</sub>TPB–C<sub>14</sub>PB ≥ C<sub>14</sub>TAB–C<sub>14</sub>TPB >> C<sub>14</sub>TAB–C<sub>14</sub>PB. The closer CMC values of C<sub>14</sub>TAB and C<sub>14</sub>PB have resulted in a lower degree of synergism between the pair, whereas C<sub>14</sub>TPB, having a much lower CMC, showed high compatibility with both. The activity coefficients of the components in the mixtures of the C<sub>14</sub>TAB–C<sub>14</sub>TPB system were all below unity; for the pair C<sub>14</sub>PB–C<sub>14</sub>TPB at  $X_{C_{14}TPB} = 0.75$ ,  $f_{C_{14}PB}$  was greater than unity. For the other mixture (C<sub>14</sub>TAB–C<sub>14</sub>PB), the  $f_{C_{14}TAB}$  values were all high at  $X_{C_{14}TAB} > 0.40$ . Such high values of the activity coefficients were not quite uncommon for mixed binary ionic systems.<sup>27,61</sup> An explanation for such findings is not at hand.

Theoretical treatment of surfactant mixtures of more than two components is very limited.<sup>29,30</sup> The treatment of Holland and Rubingh<sup>31</sup> is the only rational treatment for ternary surfactant systems. For such a system, the activity coefficient of the  $i$ th species ( $f_i$ ) among the micelle-forming amphiphilic species  $i, j, k, \dots$ , can be expressed on a general basis in the form

$$\ln f_i = \sum_{j=1}^n g_{ij}x_j^{R^2} + \sum_{j=1}^n \sum_{k=1}^{j-1} (g_{ij} + g_{ik} - g_{jk})x_j^R x_k^R \quad (12)$$

where  $g_{ij}$  represents the net (pairwise) interaction between the components  $i$  and  $j$  as obtained from Rubingh's theory and  $x_j^R$  is the mole fraction of the  $j$ th component in the micelles;  $g_{ik}$ ,  $g_{jk}$ , and  $x_k^R$  have similar significance.

The following relation holds at CMC for the micellar mole fraction of the  $i$ th component ( $x_i^{RH}$ )

$$x_i^{RH} = \frac{x_i C_i f_i x_j^R}{(C_i x_j^R)} \quad (13)$$

where the new terms  $C_i$  and  $C_j$  represent the CMCs of the  $i$ th and  $j$ th components, respectively, and  $f_i$  and  $f_j$  are the respective activity coefficients.

The activity coefficients for the studied three-component system, i.e.,  $f_1$ ,  $f_2$ , and  $f_3$ , were calculated using the above equations following the method of "successive substitution".<sup>8,32</sup> Then, the mixed micellar  $CMC^{RH}$  was obtained by using these  $f$  values in the relation

$$\frac{1}{CMC^{RH}} = \sum_{i=1}^n \frac{x_i}{f_i CMC_i} \quad (14)$$

The values of  $x_i$ ,  $f_i$ , and  $CMC^{RH}$  along with the experimental values and those found by the Clint equation ( $CMC^{exp}$  and  $CMC^{Clint}$ , respectively) are tabulated in Table 5. The  $CMC^{RH}$  values were on the whole comparable with the average experimental CMCs (except at compositions three and five), and both were lower than the CMC by Clint, indicating a nonideal and synergistic nature of the mixed micellar systems. In the mixed micelles, at all compositions, the proportion of the components followed the order C<sub>14</sub>TPB > C<sub>14</sub>PB > C<sub>14</sub>TAB.

**TABLE 5: CMCs of the Ternary Systems as Predicted by Rubingh–Holland Theory**

$X_{C_{14}TPB}/X_{C_{14}TAB}/X_{C_{14}PB}$	$X_1 (X_2) X_3$	$f_1 (f_2) f_3$	CMC <sup>RH</sup> (CMC <sup>obsd</sup> ) CMC <sup>Clint</sup>
0.08/0.16/0.76	0.385 (0.111) 0.504	0.518 (0.619) 0.764	1.57 (1.77) 2.41
0.125/0.125/0.75	0.451 (0.082) 0.467	0.592 (0.557) 0.696	1.34 (1.36) 2.11
0.16/0.08/0.76	0.127 (0.004) 0.869	0.264 (0.715) 0.972	0.804 (1.47) 1.92
0.333/0.167/0.50	0.616 (0.098) 0.286	0.774 (0.419) 0.509	0.902 (1.04) 1.36
0.25/0.25/0.50	0.563 (0.146) 0.291	0.716 (0.476) 0.564	0.378 (1.19) 1.60
0.167/0.333/0.50	0.497 (0.198) 0.305	0.640 (0.550) 0.635	1.20 (1.60) 1.94
0.333/ 0.333/ 0.333	0.619 (0.188) 0.194	0.771 (0.437) 0.501	0.90 (1.12) 1.38
0.25/0.50/0.25	0.569 (0.279) 0.152	0.714 (0.500) 0.543	1.03 (1.14) 1.63
0.375/0.375/0.25	0.644 (0.210) 0.147	0.794 (0.419) 0.472	0.859 (0.850) 1.29
0.50/0.25/0.25	0.705 (0.147) 0.149	0.856 (0.353) 0.412	0.760 (0.770) 1.06

TAB. Their nonideality in the micelle decreased with their increased presence therein which was expected. The sums of their activity coefficients ( $f_1 + f_2 + f_3$ ) were close with an average value of 1.8. The average value of the sums ( $f_1 + f_2$ ) of the binaries was 1.0. In the binary micelles, the activities were in a way complimentary to each other, while, in the ternaries, the summed up activities of all three components were greater than unity.

**Nature of the Amphiphilic Packing in Micelles.** The nature of amphiphile packing in micelles and their structural geometry was predicted by Israelachvili<sup>62</sup> in terms of packing parameter ( $P$ ) defined by the relation

$$P = \frac{v}{Al_c} \quad (15)$$

where  $l_c$  is the maximum effective length of the hydrophobic chain of a monomer,  $A$  is the surface area of the head group, and  $v$  is the volume of the hydrophobic chain considered to be fluid and incompressible.

Both  $l_c$  and  $v$  for a saturated hydrocarbon chain with  $C_n$  number of carbon atoms can be obtained from the proposed formulas of Tanford.<sup>59</sup> Thus,

$$l_c \equiv (0.154 + 0.1265C_n) \text{ nm} \quad (16)$$

and

$$v = (0.0274 + 0.0269C_n) \text{ nm}^3 \quad (17)$$

In this study, we have dealt with three surfactants having the same  $C_n$ ; hence, the  $v$  and  $l_c$  values were the same. The other parameter required for calculating  $P$  was  $A$ . In earlier works,<sup>7,8,20</sup> the head group cross-sectional areas at CMC, i.e.,  $A_{\min}$ , obtained from tensiometry were used. Effectively, this  $A_{\min}$  refers to a property related to the surfactant monolayer at the air/water interface and in reality different from the required  $A$  value at the micellar surface. Fujio and Ikeda<sup>63</sup> have shown that, for the dodecylpyridinium bromide micelles, the area per monomer was 0.63 nm<sup>2</sup> on the surface of a spherical micelle and was 0.59 nm<sup>2</sup> on an aqueous surface at CMC; i.e., the values were fairly close. In the absence of an exact estimation and also because the determination of the head group area on the micellar surface is comparatively difficult, we have used the  $A_{\min}$  values in our calculation as done earlier.<sup>7,8,20</sup> For the mixed micelles, we used the equation of  $P_{\text{effect}}$  (effective packing fraction), as reported earlier,<sup>7,8</sup>

$$P_{\text{effect}} = \left( \frac{v}{Al_c} \right)_{\text{effect}} = \frac{\sum v_i x_i^{\text{mic}}}{(\sum A_i x_i^{\text{mic}}) l_c} \quad (18)$$

where  $x_i^{\text{mic}}$  and  $A_i$  are the micellar mole fraction and the  $A_{\min}$  value of the  $i$ th component in the mixed micelle, respectively.

The packing parameters for all three binary and ternary mixtures at all compositions are presented in Table 2. The micellar mole fraction obtained from the models of Rubingh and Rubingh and Holland were used as  $x_i^{\text{mic}}$  in the calculations. The shape and type of amphiphilic aggregates can be predicted from the magnitude of  $P$  or  $P_{\text{eff}}$ . For spherical assemblies,  $P \leq 0.333$ ; for nonspherical shape,  $0.333 < P < 0.5$ ; for vesicles and bilayers,  $0.5 < P < 1$ ; and for inverted structures,  $P > 1$ . According to the above rationale,  $C_{14}TPB$  produced spherical micelles, while  $C_{14}TAB$  and  $C_{14}PB$  showed a tendency to yield nonspherical (prolate or oblate) micelles. Usually, nonionic surfactants and their mixtures with the ionics tend to form nonspherical micelles, as reported for Brij 56,<sup>8</sup> Triton X 100,<sup>64</sup> and MEGA 10– $C_{16}TAB$ .<sup>7</sup> For the  $C_{14}TAB$ – $C_{14}TPB$  and  $C_{14}TPB$ – $C_{14}PB$  systems, spherical micelles were found to be formed, while, for the  $C_{14}PB$ – $C_{14}TAB$  system, the mixed micelles were toward nonspherical. The ternary mixtures, on the other hand, supported formation of spherical micelles. Their  $P$  values were strikingly much smaller than 0.333. Fairly lower  $P$  values have been reported by Basu Ray et al. on binary mixtures of MEGA 10 and ATABs.<sup>7</sup> SANS measurements<sup>65</sup> on the herein studied systems could lend further support to the above-realized structural features of the mixed micellar systems. The scope for further exploration thus remains open.

## Conclusion

Of the three surfactants used in this study,  $C_{14}TPB$  alone produced two types of micelles, whereas both  $C_{14}TAB$  and  $C_{14}PB$  produced one in aqueous solution. The mixed binary combinations  $C_{14}TAB$ – $C_{14}TPB$  and  $C_{14}TPB$ – $C_{14}PB$  in aqueous solution produced two kinds of micelles with two CMCs, whereas  $C_{14}TAB$ – $C_{14}PB$  produced one type of micelle. All of the ternary combinations have evidenced the formation of a single type of micelle. The binaries bound 40 and 60% counterions on average for the first and second micelles, respectively, except the  $C_{14}TAB$ – $C_{14}PB$  combination where the extent of binding was 73%. The FQ method was inapplicable to determine the micellar aggregation number, for the components themselves were efficient quenchers. The ITC simulation method produced appreciably low values of  $n$ . Until more reports become available for confirmation of such results, a value of 70 was used for  $C_{14}$  amphiphiles following the arguments of Hansson et al.<sup>44</sup> The  $A_{\min}$  values of the binary combinations were less than those of the ternaries. The three-component system produced greater exclusion among their components, resulting in loose association. The binary and ternary combinations were energetically comparable except for the  $C_{14}TAB$ – $C_{14}PB$  combinations which were more spontaneous than the others and were associated with higher entropy change. The system was associated with a difference in amphiphile packing in micelles than other binaries, evidencing tendencies of the formation of nonspherical assemblies. The low values of  $P$  for ternaries were rare findings; binary combinations

of MEGA 10 and ATABs have been observed by us<sup>7</sup> to yield fairly low  $P$ . For the binaries, the micellar compositions depended on the type of mixtures and their stoichiometry which for the ternaries have evidenced a lower proportion of C<sub>14</sub>TAB in the mixed micelles for a large number of compositions.

The head group differences among the three studied surfactants were responsible for their property differences. On the whole, the behaviors of C<sub>14</sub>TAB and C<sub>14</sub>PB were comparable but different from that of C<sub>14</sub>TPB. It produced two types of micelles, produced the lowest  $\beta$  value, yielded the maximum  $A_{\min}$  value, and demonstrated the lowest  $P$  value. Its  $\Delta G_{\text{mic}}^{\circ}$  (H) was maximum nonspontaneous, and consequently,  $\Delta G_{\text{ad}}^{\circ}$  was most spontaneous among the three. The head group activity differences arose from the electrostatic, steric, and solvation factors in which hydrophobic hydration of the triphenylphosphonium ion contributed a fair share along with steric restrictions.

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