Surface properties of cationic bolaamphiphiles and their mixed systems with oppositely charged conventional surfactant

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Abstract

Surface properties of three cationic bolaamphiphilie eicosanediyl 1,20-bis(pyridinium bromide) \([\text{Py}^+\text{(CH}_2\text{)}_{20}\text{Py}^-\text{]}\text{2Br}^-\), phenyl 1,4-bis(oxyhexyl trimethyl ammonium bromide) \((\text{C}_6\text{PhC}_6)\), phenyl 1,4-bis(oxydecyl trimethyl ammonium bromide) \((\text{C}_{10}\text{PhC}_{10})\), and their mixed systems with oppositely charged conventional surfactant sodium dodecyl sulfite (SDS) were studied. The results showed that bolaamphiphiles with rigid group also adopted reverse U-shape conformation at the air/water interface as those with flexible skeleton. Micellization in these bolaamphiphile systems is easier than those of the comparable conventional surfactants. Micellization thermodynamic parameters were calculated according to the phase separation model and entropy was found to be the main driving force in the process of micellization. Diagrams for the \((\text{C}_6\text{PhC}_6)/\text{SDS}\) and \((\text{C}_{20}\text{Py}_2)/\text{SDS}\) mixed systems were constructed based on the regular solution theory. It was found that the structural difference between the two bolaamphiphiles affects the interaction between the two components in each mixed systems greatly.

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1. Introduction

Bolaamphiphiles are molecules with two hydrophilic heads connected by one or two hydrophobic chains. In recent years, this kind of compound has drawn more and more attention [1,2] in both fundamental investigations and applications. Most of the works were concentrated in methylene-skeletoned bolaamphiphile (flexible bolaamphiphile). These bolaamphiphiles are of special characteristics from the conventional surfactants (with unipolar group). Usually the critical micellization concentrations are larger [3–5], and the sizes of the micelles are smaller [4,5] than those of unipolar surfactants of the same carbon number. Bolaamphiphiles have also been shown to adopt a folded, reverse U-shape conformation at the air/water interface [5,6]. However, conformation of the hydrophobic chain in bolaamphiphiles seemed to be complicated in aqueous solution. Zana et al. concluded that the alkyl chains of \(N,N'-1-22\)-docosanediyl bis(trimethyl ammonium bromide) \((\text{C}_{22}\text{Me}_6)\) are mostly folded in surfactant aggregates [7]. But some studies of \(^{13}\text{C},^{14}\text{N}-\text{NMR spin-}

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lattice relaxation and $^{13}$C nuclear Overhauser effect techniques probed that the surfactant chains can adopt a predominantly stretched conformation in micelles [8].

In contrast to the works in ‘flexible’ bolaamphiphiles, bola compounds with more complex structure, such as those containing rigid group [9,10], were also synthesized. Compared with the many researches on the aggregation behaviors [11–14] of bolaamphiphiles, the systematical works on surface physicochemical properties are scarce. It is well known that the mixtures of different amphiphiles are of great theoretical and industrial interest, since the mixed systems can have superior properties to those of respective surfactant components involved. However, to the best of our knowledge, the research on the mixtures of bolaform molecules and conventional surfactants is still rare [15,16]. In this study, the cationic bolaamphiphiles with flexible hydrocarbon chain (C$_{20}$Py$_2$), or with rigid phenylene group in the center of the molecules (C$_6$PhC$_6$, C$_{10}$PhC$_{10}$) were synthesized, their surface physicochemical properties and those of the mixed systems with oppositely charged conventional surfactant sodium dodecyl sulfate (SDS) were studied.

2. Materials and methods

2.1. Materials

Water was distilled from the KMnO$_4$-containing deionized water. Sodium bromide is of AR grade and has been baked for 6 h to remove traces of organic compounds.

SDS was from Sigma Co. and used as received. The bolaamphiphiles C$_{20}$Py$_2$ were synthesized as shown in Scheme 1 according to the literature method [17] from eicosanedioic acid (TCI, Japan). 1,6-dibromohexane and 1,10-dibromodecane were prepared from the corresponding diol and hydrogen bromide acid (Beijing Chemical Co.).

### 2.1.1. Phenyl 1,4-bis(oxyhexyl bromide)

According to a general method, a mixture of hydroquinone (2.2 g, 0.02 mol), 1,6-dibromohexane (29 g, 0.12 mol) and freshly fused and finely powered potassium carbonate (12 g, 0.087 mol) in 100 ml of dry acetone were refluxed under nitrogen atmosphere for 24 h. Then the reaction mixture was filtered off the insoluble residue. White solid was obtained after the solution being cooled. The solid was further purified by recrystallization from acetone and silica gel chromatography with ether to give 3.5 g (Yield: 58%) white solid product: melting point (m.p.) 96–98°C; $^1$H-NMR (200 MHz, CDCl$_3$, TMS): $\delta$, ppm: 6.82 (4H, s), 3.90 (4H, t, $CH_2O$), 3.4 (4H, t, $CH_2Br$), 1.6–1.9 (8H, m, $CH_2CH_2Br$, $CH_2CH_2O$), 1.46 (8H, m, $CH_2_2$).

### 2.1.2. Phenyl 1,4-bis(oxyhexyltrimethylammonium bromide) (C$_6$PhC$_6$)

The above product (phenyl 1,4-bis(oxyhexyl bromide)) was quaternized by trimethylamine in ethanol in a sealed ampoule at 70°C for 3 days. White precipitates crystallized after the solution was cooled. The solid was purified by recrystallization from acetone and silica gel chromatography with ether and with water to give 2.5 g (Yield: 58%) white solid product: melting point (m.p.) 180–182°C; $^1$H-NMR (200 MHz, D$_2$O, HDO): $\delta$, ppm: 6.82 (4H, s), 3.90 (4H, t, $CH_2O$), 3.18 (4H, t, $CH_2_2$), 2.97 (18H, s, $N(CH_3)_3$), 2.98 (8H, m, $CH_2CH_2N$), 1.60 (8H, m, $CH_2CH_2N$), 1.35 (8H, m, $CH_2_2$); Anal. Calc. for C$_{24}$H$_{46}$N$_2$O$_2$Br$_2$: C, 50.35; H, 7.89; N, 4.90. Found: C, 50.87; H, 7.30; N, 4.71%.

### 2.1.3. Phenyl 1,4-bis(oxydecytrimethylammonium bromide) (C$_{10}$PhC$_{10}$)

Phenyl 1,4-bis(oxydecytrimethylammonium bromide) (C$_{10}$PhC$_{10}$) was prepared by the same procedure as that for C$_6$PhC$_6$ except that 1,10-dibromodecane was used instead of 1,6-dibromohexane. $^1$H-NMR (200 MHz, D$_2$O, HDO): $\delta$, ppm: 6.87 (4H, s), 3.93 (4H, t, $CH_2O$), 2.98 (18H, s, $N(CH_3)_3$), 1.60

Scheme 1. Synthesis of C$_n$Ph$_n$ ($n=6, 10$).

(a) anhydrous K$_2$CO$_3$, acetone, reflux; (b) trimethylamine, EtOH.
(8H, m, \(-CH_2CH_2N\)–, \(-CH_2CH_2O\)–) 1.35
(24H, m, \(-(CH_2)_2\)–); Anal. Calc. for
C_{32}H_{62}N_2O_2Br_2\cdot2H_2O: C, 54.70; H, 9.40; N, 3.99. Found: C, 55.31; H, 9.09; N, 3.87%.

2.2. Methods

The surface tension of aqueous surfactant solutions was measured by the drop volume method [18]. As the cationic bolaamphiphiles will adsorb onto negatively charged glass surfaces, all glassware was thoroughly soaked with the solution to be measured; soaking solutions were then discarded and replaced with fresh solution. The fresh solution was aged for several hours before surface tension measurement. Values were taken until the drop volume was constant for certain time intervals. Reproducibility of the surface tension measurements is less than 0.2 mN m\(^{-1}\). In order to provide constant ionic strength, all solutions were adjusted to 0.1 or 0.3 mol kg\(^{-1}\) with NaBr.

The adsorption amount of surfactants (\(\Gamma_\infty\)) was calculated according to the Gibbs adsorption equation since the ionic strength was much higher than CMC of each surfactant and [19] kept constant:

\[
\Gamma_\infty = \frac{-d\gamma}{2.303RTd \log C}
\]

(1)

Here \(\gamma\) is the surface tension in mN m\(^{-1}\), \(C\), the concentration of corresponding surfactant in single system, while it represents the total concentration in mixed bola/SDS system. \(\Gamma_\infty\) is the saturate adsorption amount in mol m\(^{-2}\), \(d\gamma/d \log C\) is the maximal slope in each case, \(T\) is absolute temperature, \(R = 8.314\) J mol\(^{-1}\) K\(^{-1}\). Then the minimum area per surfactant molecule (\(A_{\text{min}}\)) is obtained from the saturate adsorption by:

\[
A_{\text{min}} = \frac{10^{18}}{N_A \Gamma_\infty}
\]

(2)

Here \(N_A\) is the Avogadro’s constant.

3. Results and discussion

3.1. Individual surfactants

At 25 °C, the solubility of C\(_{20}\)Py\(_2\) and C\(_6\)PhC\(_6\) is good. Clear and homogeneous solution of the two compounds can be obtained at the concentration of 0.02 and 0.25 mol dm\(^{-3}\), respectively. The Krafft point of C\(_{10}\)PhC\(_{10}\) is about 38 °C. \(\gamma \log C\) curves of C\(_{20}\)Py\(_2\), C\(_6\)PhC\(_6\), C\(_{10}\)PhC\(_{10}\) and a conventional surfactant decylpyridinium bromide (C\(_{10}\)Py) at different temperatures are shown in Fig. 1. Some results are listed in Table 1.

3.1.1. \(A_{\text{min}}\) and molecular conformation

\(A_{\text{min}}\) is an important parameter to judge the conformation of molecules in the surface adsorption layer. Table 1 shows that the \(A_{\text{min}}\) of C\(_{20}\)Py\(_2\) (1.38 nm\(^2\)) is close to twice that of C\(_{10}\)Py (0.59 nm\(^2\)). This result can be attributed to the reverse U-shape conformation of bolaamphiphiles at the air/water interface [5,6]. Menger et al. [6] have proved that a vertical loop would form at the air/water interface when the number of \(-CH_2-\) group is equal or larger than 12. Recently, Minghua Liu et al. have proved that the minimum \(-CH_2-\) number could be 6 to permit a bolaamphiphile to anchor at the air/water interface [20]. Therefore, it is understandable that the flexible C\(_{20}\)Py\(_2\) molecules bend at the air/water interface. It is interesting to find that the \(A_{\text{min}}\) in the C\(_6\)PhC\(_6\) and C\(_{10}\)PhC\(_{10}\) systems are almost the same value of
1.11 nm². Since the area of −N(CH₃)₃ group [21,22] is about 0.40 nm² and that of the rigid −O–PH−O− group in the two molecules is about 0.3 nm², it indicates that the C₆PhC₆ and C₁₀PhC₁₀ molecules also adopt reverse U-shape conformation at the air/water interface. In fact, bolaamphiphiles with rigid diacetylene group adopt ‘loop’ conformation in the lipid membrane has been observed by Cuccia et al. using the ²H-NMR technique [23].

3.1.2. γCMC

It is well known that the surface tension of surfactant solution is decided both by the adsorption amount and the outmost groups in the adsorption layer. When the adsorption amount is similar, the outmost groups will become the decisive factor of the surface tension. Table 1 shows that the saturate adsorption amount of C₁₀Py is about twice that of C₂₀Py₂. However, considering the reverse U-shape conformation of bola molecules, the area per bolaamphiphile takes at the air/water interface is usually as twice as or more than that of conventional surfactant molecule. Thus, the area taken by per head in the C₂₀Py₂ system is similar to that in C₁₀Py system. Therefore, the higher γCMC value of C₂₀Py₂ system should be caused by the outmost groups in the adsorption layer. For conventional surfactant C₁₀Py, the outmost group in the adsorption layer is −CH₃. Correspondingly, due to the reverse U-shape conformation of bolaamphiphiles at the air/water interface, the −CH₂– group in C₂₀Py₂ becomes the outmost one instead of −CH₃ in the adsorption layer. Since the ability of the −CH₂– group to reduce the surface tension of the water is weaker than that of −CH₃ [24,25], the γCMC value of C₂₀Py₂ solution is higher (49.7 mN m⁻¹) than that of C₁₀Py (38.7 mN m⁻¹, Table 1). However, in the cases of C₆PhC₆ and C₁₀PhC₁₀, the outmost group is phenylene, which is also weaker [26] than methyl group in decreasing surface tension of water. Therefore, the γCMC values of the two systems are higher than that of C₂₀Py₂ system.

3.1.3. CMC

It can be seen from Table 1 that the CMC values of C₂₀Py₂ and C₁₀PhC₁₀ solutions are very small (in the order of 10⁻⁴ mol dm⁻³) and the CMC of C₂₀Py₂ solution is lower than that of C₁₀Py by nearly two orders. In fact, the CMC of bolaamphiphiles is usually smaller than those of conventional ionic surfactants with a half number of carbon atoms in the hydrophobic chain [27]. This indicates that the micellization ability of bolaamphiphiles is far greater than that of the comparable classical surfactants while the nature of the hydrocarbon chain remains the same. Although the carbon number in the hydrocarbon chain of the C₆PhC₆ is similar to that of C₂₀Py₂, the phenylene group and the hydrophilic ether oxygen atom in the former decreases its hydrophobicity. Therefore, the CMC of C₆PhC₆ system is higher than that of C₂₀Py₂. For the difference of CMC between C₆PhC₆ and C₁₀PhC₁₀ systems, it can be attributed to the different hydrocarbon chain length. In addition, it seems that the rigid group has no obvious effect on the CMC value.

3.1.4. Thermodynamics of micellezation

The thermodynamic parameters of micellization of amphiphiles can be calculated from the phase separation model. Assumed that n bola cation Bola²⁺ and 2β⁻ counter ion A⁻ formed micelle
M in NaBr solution:

\[ n \text{Bola}^{2+} + 2\beta n\text{A}^- \rightarrow M \]

Then the standard Gibbs energy change \( \Delta G_m^o \) should be:

\[ \Delta G_m^o = RT \ln \text{CMC} + 2\beta RT \ln a_A. \]  

(3)

Here, \( \beta \) is the degree of counter ion binding and \( a_A \) is the activity of the counter ion. The \( \beta \) values for the bolaamphiphiles in our study are proved to be approximately 1 (not shown here) from the plot log CMC versus log[NaBr] [28]. Thus the change of entropy \( \Delta S_m^o \) is determined by the following equation:

\[ \Delta S_m^o = -\frac{d\Delta G_m^o}{dT} \]  

(4)

and enthalpy \( \Delta H_m^o \) is obtained from the Van’t Hoff plot (\( \Delta G_m^o/T \) vs. \( 1/T \)).

It is seen that \( \Delta G_m^o \) in Table 2 are all big negative values which means these bolaamphiphiles have strong ability to form micelle. The positive \( \Delta H_m^o \) values indicates that the change of entropy (\( \Delta S_m^o \)) is the main driving force in this process. It is clear that the \( \Delta S_m^o \) of C\(_6\)PhC\(_6\) is lower than that of C\(_{20}\)Py\(_2\). This maybe because the free motion of C\(_6\)PhC\(_6\) is restricted by the rigid group in it’s skeleton. However, to the conventional surfactants, such as dodecyl pyridinium bromide (C\(_{12}\)Py), the \( \Delta H_m^o \) and \( \Delta S_m^o \) are approximately -5 J·mol\(^{-1}\) and 40–60 kJ·mol\(^{-1}\) (25–40 °C) [29]. The higher \( \Delta S_m^o \) of bolaamphiphiles in micelleization can be attributed to their longer hydrocarbon chains.

3.2. Mixed surfactant

The mixed C\(_{20}\)Py\(_2\)/SDS and C\(_6\)PhC\(_6\)/SDS solutions are prepared in 0.1 mol l\(^{-1}\) NaBr. The addition of NaBr in the mixed systems prohibited the precipitation of insoluble surfactant ion-pairs. \( \gamma \log C \) curves for C\(_{20}\)Py\(_2\)/SDS, and C\(_6\)PhC\(_6\)/SDS (30 °C) systems are shown in Fig. 2(a and b), respectively, and some of the results are listed in Table 3.

For all the mixed systems above, the CMC values are lower than those of the two single surfactant systems. This is similar to the case in usual mixed cationic and anionic systems [30], but the situation of \( \gamma_{\text{CMC}} \) is different. Usually in the mixed cationic and anionic systems, the values of \( \gamma_{\text{CMC}} \) are far lower than those of the two single surfactants. But the \( \gamma_{\text{CMC}} \) in C\(_{20}\)Py\(_2\)/SDS and C\(_{10}\)PhC\(_{10}\)/SDS mixed systems fell between the two single surfactant systems while \( \gamma_{\text{CMC}} \) in C\(_6\)PhC\(_6\)/SDS mixed systems are close to that of SDS. These abnormal behaviors may be attributed to the special arrangement of bolaamphiphiles and SDS molecules at the air/water interface. As stated before, bola molecules would adopt reverse U-shape conformation at the air/water interface, which will restrict the close packing of bolaamphiphiles and SDS due to the electrostatic attraction between the oppositely charged head groups. This is meaning that the electrostatic attraction between the oppositely charged head groups and the reverse U-shaped conformation of bola molecules will affect the packing of surfactant molecules in the mixed systems from opposite sides. The combination of the two factors finally made the \( \gamma_{\text{CMC}} \) values in the these mixed systems do not increase as much as that in the usual mixed systems.

It can be seen from Fig. 2(a and b) and Table 3 that the surface physico-chemical properties in the C\(_6\)PhC\(_6\)/SDS and C\(_{20}\)Py\(_2\)/SDS mixed systems are different. We conclude that the structure difference between the two bolaamphiphiles may be responsible for this variance. To interpret the structure effect of bolaamphiphiles on the surface physico-chemical properties for the mixed systems, we next discuss the interaction between the oppositely charged head groups in C\(_6\)PhC\(_6\)/SDS and C\(_{20}\)Py\(_2\)/SDS mixed systems and the composition both in their micelles and adsorbed films based on theory of regular solution.

3.2.1. The interaction parameter and the composition of mixed micelle

The composition of mixed C\(_6\)PhC\(_6\)/SDS, C\(_{20}\)Py\(_2\)/SDS micelles in our study was analyzed on the basis of Rubingh’s equation [31]:

\[ \omega_R = \frac{\ln(Y_2^{\gamma \text{CMC}}/Y_1^{\gamma \text{CMC}}) \gamma_2^{\gamma \text{CMC}}}{(1 - Y_2)^2} \]  

(5)
Table 2
Micellization thermodynamic parameters of C_{20}Py_{2} and C_{6}PhC_{6}.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>C_{20}Py_{2} [NaBr] = 0.1 mol dm^{-3}</th>
<th>C_{6}PhC_{6} [NaBr] = 0.3 mol dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10^{-4} CMC (mol dm^{-3})</td>
<td>$\Delta G_m$ (kJ mol^{-1})</td>
</tr>
<tr>
<td>298</td>
<td>2.75</td>
<td>-31.7</td>
</tr>
<tr>
<td>303</td>
<td>2.50</td>
<td>-32.5</td>
</tr>
<tr>
<td>308</td>
<td>1.95</td>
<td>-33.7</td>
</tr>
<tr>
<td>313</td>
<td>1.75</td>
<td>-34.5</td>
</tr>
</tbody>
</table>
\[ (1 - Y_2) \ln[(1 - X_2)\text{CMC}/(1 - Y_2)\text{CMC}] \]
\[ Y_2 \ln(X_2\text{CMC} / Y_2\text{CMC}) \]
\[ = 1 \]

where, \(X_1\) is the composition of component 1 in the bulk solution, \(Y_2\) is that in the mixed micelle. CMC, \(\text{CMC}_1\), \(\text{CMC}_2\) are the critical micelle concentration of the mixed solution, the single surfactant solution of component 1 and 2, respectively. In this study, bolaamphiphiles are assigned as component 2. \(\omega_R\) is the interaction parameter of the two surfactants in the mixed solutions. The results are listed in Table 3.

It is seen that for both mixed systems the interaction parameter are negative values, indicating the negative deviation from those of ideal mixing. The more negative average \(\omega_R\) value (−11.0) in the \(C_6\text{PhC}_6/\text{SDS}\) systems than that in the \(C_{20}\text{Py}_2/\text{SDS}\) (−7.5) indicates the stronger interaction in the former. In addition, the \(\omega_R\) values for the \(C_6\text{PhC}_6/\text{SDS}\) systems are similar to those of alkyl quarter ammonium/alkyl sulfate mixtures (−13.2–10.4 [32,33]), suggesting that the electrostatic attractive interaction between the cationic and anionic head groups is much superior to the hydrophobic interaction between the hydrocarbon chains in determination of the interaction in the mixtures.

Data in Table 3 show that the composition in micelles is different from that in the bulk solution and changes with it. The CMC–composition curves for the two mixed systems are constructed as shown in Fig. 3(a and b). It is obviously seen that each mixed systems has an azotropic point, which is at \(X_{C_6\text{PhC}_6} \approx 0.33\) in the \(C_6\text{PhC}_6/\text{SDS}\) while at \(X_{C_{20}\text{Py}_2} \approx 0.58\) in the \(C_{20}\text{Py}_2/\text{SDS}\) mixed systems. The azotropic point for both systems is expected at the electroneutral mixing ratio which has the smallest CMC due to the strong interaction between the oppositely charge head groups. However, it is hard to explain that the azotropic point deviates from the electroneutral mixing ratio and appears at \(X_{C_{20}\text{Py}_2} \approx 0.58\) in the \(C_{20}\text{Py}_2/\text{SDS}\) mixed systems. It seems that the rigid group in the center of \(C_6\text{PhC}_6\) makes it easier for the interaction between oppositely charged head groups.

### Table 3

<table>
<thead>
<tr>
<th>C(_6\text{PhC}_6/\text{SDS}) systems</th>
<th>(10^4) CMC (mol dm(^{-3}))</th>
<th>(Y_2)</th>
<th>(\omega_R)</th>
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<tr>
<td>0</td>
<td>17</td>
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</tr>
<tr>
<td>0.05</td>
<td>4.5</td>
<td>0.24</td>
<td>−10.7</td>
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<td>0.14</td>
<td>3.8</td>
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<td>0.90</td>
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<tr>
<td>Average (\omega_R)</td>
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<table>
<thead>
<tr>
<th>(C_{20}\text{Py}_2/\text{SDS}) systems</th>
<th>(10^4) CMC (mol dm(^{-3}))</th>
<th>(Y_2)</th>
<th>(\omega_R)</th>
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<tbody>
<tr>
<td>0</td>
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<td>2.3</td>
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<tr>
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<td>1</td>
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</tr>
<tr>
<td>Average (\omega_R)</td>
<td></td>
<td>−7.5</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2. The interaction parameter and composition of mixed adsorbed film

Similarly, the composition of the mixed surface adsorption film was analyzed by using the following extensively accepted equation [34]:
\[ \omega_A = \frac{\ln(X_2 C_1/Z_2 C_2)}{(1 - Z_2)^2} \]
\[ (1 - Z_2)^2 \ln[(1 - X_2) C_1/(1 - Z_2) C_1] \]
\[ Z_2^2 \ln(X_2 C_1/Z_2 C_2) \]

where, \( X_2 \) is the composition of component 2 in the bulk solution, \( Z_2 \) is that in the mixed adsorbed film. \( C_1, C_1^0, C_2^0 \) are the concentration of the mixed solution, the single surfactant solution of component 1 and 2 under the same surface tension, respectively. Here, bolaamphiphiles are assigned as component 2 and \( \omega_A \) is then the interaction parameter of the two surfactants in the mixed adsorbed films. The results are listed in Table 4.

Seen from Table 4 that the average interaction parameter in the adsorbed films for the C6PhC6/SDS is more negative than that in the C20Py2/SDS mixtures although the latter is examined under higher surface pressure (the surface pressure for C6PhC6/SDS is 72.0/57.5/14.5 mN m\(^{-1}\) and it is 72.0–52.5 = 19.5 mN m\(^{-1}\) for the C20Py2/SDS mixtures), indicating the interaction between the two components in the former systems are far more stronger than that in the latter. As stated in the pretext, this may be attribute to the different special arrangement of molecules at the air/water interface, and it seems that the rigid group in the center of C6PhC6 favoring the orientation of molecules when interaction occurs.

Comparing the negative \( \omega_R \) and \( \omega_A \) value in Tables 3 and 4, it is found that in both systems the average \( \omega \) values for the adsorbed films are more negative than that in the mixed micelles, indicating a stronger interaction between the two components in the former. In regard to the comparison of the mixed adsorbed films, it is notable that at most mixing ratios of both systems, the composition in the former is closer to the electroneutral mixing than that in the latter, which is believed to the reason why the interaction in the adsorbed film is usually stronger than that in the mixed micelle.

Fig. 4(a and b) show the phase diagrams of monomers in bulk solution \((C_t - X)\) and adsorbed film at the air/water interface \((C_t - Z_2)\). Similarly, both systems have an azeotrope point at \( Z_2 \approx 0.33 \) and 0.52 for the C6PhC6/SDS and C20Py2/SDS, respectively, indicating surfactants ion-pair formation at the air/water interface [35]. The azeotropic points in Fig. 3(a), Fig. 4(a) correspond well with each other for the C6PhC6/SDS mixtures, while a variance of 0.06 (0.58–0.52 = 0.06) for that of C20Py2/SDS mixed systems which may be caused by the experiment error.

3.2.3. The surface excess and partial molecular area

The surface excess \( \Gamma \) versus the composition of bolaamphiphiles in the bulk phase \( X_n \) and adsorbed film \( Z_n \) for the two mixed systems are shown as Fig. 5(a and b). In Fig. 5(a) the surface excess for C6PhC6/SDS system is lower than that for each single surfactant system and the maximum is attained at \( X_{C_pH_{C_6}} = 0.33 \), at which the mixed adsorbed film shows an azeotropic point. Although the maximum \( \Gamma \) value for the mixed systems is only higher than that of the single SDS by a factor of 1.1 (3.8/3.4 ≈ 1.1, see Table 4), it higher by a factor of 2.6 (3.9/1.5 = 2.6, see Table 4)
Table 4
Values of $C_t$, $Z_2$, $\omega_\Lambda$, for the C$_6$PhC$_6$/SDS and C$_{20}$Py$_2$/SDS mixed adsorbed films at 30 °C, [NaBr] = 0.1 mol dm$^{-3}$

$$
\begin{array}{cccccc}
X_{C_6PhC_6} & 10^5 C_t \text{ (mol dm}^{-3}\text{)} & Z_2 & 10^6 \Gamma \text{ (mol m}^{-2}\text{)} & A_m \text{ (nm}^2\text{)} & X_{C_{20}Py_2} \\
0 & 170 & 0 & 3.4 & 0.49 & 0 \text{.} 18.6 \text{.} 0 \text{.} 3.4 \text{.} 0.49 \\
0.05 & 3.26 & 0.26 & -14.2 & 3.8 & 0.44 & 0.05 \text{.} 3.56 \text{.} 0.38 \text{.} -8.1 \text{.} 2.1 \text{.} 0.78 \\
0.14 & 2.77 & 0.29 & -14.0 & 3.8 & 0.44 & 0.14 \text{.} 4.88 \text{.} 0.41 \text{.} -8.0 \text{.} 2.4 \text{.} 0.69 \\
0.33 & 2.69 & 0.32 & -13.5 & 3.9 & 0.43 & 0.33 \text{.} 0.47 \text{.} 0.49 \text{.} -13.4 \text{.} 2.6 \text{.} 0.63 \\
0.60 & 3.33 & 0.35 & -13.2 & 3.8 & 0.44 & 0.60 \text{.} 0.74 \text{.} 0.54 \text{.} -12.0 \text{.} 2.4 \text{.} 0.69 \\
0.82 & 5.47 & 0.37 & -12.0 & 3.8 & 0.44 & 0.82 \text{.} 3.44 \text{.} 0.63 \text{.} -6.2 \text{.} 2.1 \text{.} 0.78 \\
0.90 & 6.13 & 0.42 & -13.4 & 3.8 & 0.44 & 1 \text{.} 10.5 \text{.} 1.00 \text{.} 1.2 \text{.} 1.38 \\
1 & 1000 & 1 & 1.5 & 1.11 & & \\
\hline
\text{Average } \omega_\Lambda & -13.4 & & & & -9.5
\end{array}
$$
than the single C6PhC6, indicating more molecules in the mixed adsorbed films than in the single films. However, the situation in the C20Py2/SDS is different from that in the C6PhC6/SDS mixed

![Fig. 4. Phase diagrams of monomers in bulk solution and adsorbed film at air/water interface for (a) C6PhC6/SDS (at 57.5 mN m⁻¹) and (b) C20Py2/SDS (at 57.5 mN m⁻¹) systems (30 °C, [NaBr] = 0.1 M).]

![Fig. 5. The surfaces excess Γ curves as function of X₂ and Z₂ for (a) C6PhC6/SDS (at 57.5 mN m⁻¹) and (b) C20Py2/SDS (at 57.5 mN m⁻¹) systems (30 °C, [NaBr] = 0.1 M).]
system except for the existence of an azeotropic point (at ca. $X_{C_{20}Py_2} = 0.52$). At different mixing ratios, the surface excess for the $C_{20}Py_2/SDS$ mixed system, including the azeotropic point, all fell between the two single surfactant systems. But compared with the $C_{20}Py_2$ single system, the surface excess of the mixed systems at the azeotropic point is higher by a factor of 2.2 (2.6/1.2 ≈ 2.2, Table 4) than the single $C_{20}Py_2$, also indicating more molecules in the mixed adsorbed films than in the single films. The variance of surface excess in the two systems is probably caused by the different arrangement of SDS/$C_{20}Py_2$ and SDS/$C_6PhC_6$ at the air/water interface. In regard to the azeotropic point in the two systems, it maybe reflect strong interaction between the oppositely charge head groups. This interaction is also reflected on the partial molecular surface area in the adsorbed film.

Fig. 6(a and b) show the $A_m-Z_2$ curves for the two mixed systems. Both the two figures deviated negatively from the ideal mixing (dotted lines). It is interesting that the average areas in the $C_6PhC_6/SDS$ mixtures (Fig. 6(a)) at different mixing ratios are nearly the same values with that at $X_{C_6PhC_6} = 0.33$, maybe indicating ion pair formation due to strong interaction between the two oppositely charged surfactants at these the mixing ratios. However, the average areas in the $C_{20}Py_2/SDS$ mixtures change with mixing ratio while show an obvious minimum at approximately $X_{C_{20}Py_2} = 0.52$. Though it is hard to explain why the area minimum does not appear at the electroneutral mixing ($X_{C_{20}Py_2} = 0.33$), it is clear that the interaction between the oppositely charged head groups in the $C_{20}Py_2/SDS$ mixtures is weaker than that of $C_6PhC_6/SDS$.

The partial molecular areas (PMA) were obtained by using the following equation developed by Sugihara et al. [36]:

$$A_m = A_1 + Z_2 \left( \frac{\delta A_m}{\delta Z_2} \right)_{T,V,p_1}$$  \hspace{1cm} (9)

Here, $A_1$ is the PMA of component 1. At constant temperature, volume or pressure and fixed surface tension, $A_1$ and $A_2$ at any $Z_2$ can be determined from the respective intercepts on $A_m$-axis at $Z_2 = 0$ and $Z_2 = 1$ by making a tangent through the point corresponding to the $Z_2$ in the the $A_m-Z_2$ curves. It is clear that two intercepts would be obtained and the one on $A_m$-axis at $Z_2 = 0$ corresponds to $A_1$, then the other at $Z_2 = 1$ corresponds to $A_2$ [35]. The PMA is plotted against $Z_2$ for each component of the two mixed

![Fig. 6](https://example.com/figure6.png)

**Fig. 6.** The changes in mean molecular area ($A_m$) with mole fraction for (a) $C_6PhC_6/SDS$ and (b) $C_{20}Py_2/SDS$ mixed systems (30 °C, $[NaBr] = 0.1$ M).
systems (see Fig. 7). For the C₆PhC₆/SDS mixtures shown in Fig. 7(a), the PMA–Z₆₈Curves demonstrate that the PMA of each surfactant in the mixing range near Z₆₈ = 0.33 increases suddenly while the increasing trend becomes slow in the range away from 0.33, but no process ‘via maximum then suddenly decreases’ was observed as Sugihara et al. [35] in their systems. The PMA curves of the two surfactants meet each other at Z₆₈ ≈ 0.33, meaning that the two surfactants have the same PMA value at this time. The PMA curves for each component in C₂₀Py₂/SDS mixed system also have a meeting point at approximately Z₆₈ ≈ 0.5. It seems that the PMA of SDS in the C₂₀Py₂/SDS mixtures slightly increases after a maximum then decrease suddenly as Z₆₈ approaches 0.5. The case for C₂₀Py₂ is hard to say yet for the inconvenience determination of its PMA at the mixing ration far from Z₆₈ ≈ 0.5. However, the minor component (less than 0.33 in mole fraction) in any case for the two mixed systems has a less PMA, indicating the molecules of the minor component shrinks more than that of the major one. This observation is in agreement with the results of Sugihara et al.

4. Conclusions

Surface properties of flexible (C₂₀Py₂) and rigid-group-containing (C₆PhC₆ and C₁₀PhC₁₀) cationic bolaamphiphiles, and their mixed systems with oppositely charged conventional surfactant SDS were studied. Both flexible and rigid-group-containing bolaamphiphiles adopt reverse U-shape conformation at the air/water interface. Compared with conventional surfactants, bolaamphiphiles show stronger micellization ability. The main driving force in the process of micellization was found to be entropy according the phase separation model. It was found that the interaction between the oppositely charged head groups in the C₆PhC₆/SDS is stronger than that in the C₂₀Py₂/SDS mixtures both in the micelles and in the adsorbed films. This may be attributed to the rigid group in the center of C₆PhC₆ favoring the orientation of molecules when interaction occurs. Azeotropic point was found in the CMC–X₂ Curve, CMC–Y₂, C₁–X₂/C₁–Z₂ and T–Y₂/Z₂ curves for both mixed systems, indicating surfactant ion-pairs were formed due to strong interaction in these mixtures. The azeotropic point in the...
C_{6}PhC_{6}/SDS systems appearing at X (or Y or Z) C_{6}PhC_{6}: 0.33 suggested the strong interaction at the electroneutral mixing. While it is hard to explain that the azeotropic point in the C_{20}Py_{2}/SDS systems appears at X (or Y or Z) C_{20}Py_{2} being 0.5—0.6. Anyway, the structure difference between C_{6}PhC_{6} and C_{20}Py_{2} affects the properties of micelle and adsorbed films apparently.

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References