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

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Abstract

Surface properties of three cationic bolaamphiphile eicosanediyl 1,20-bis(pyridinium bromide) $[Py^+(CH_2)_{20}Py^+]2Br^-$, phenyl 1,4-bis(oxyhexyl trimethyl ammonium bromide) (C_6PhC_6), phenyl 1,4-bis(oxydecyl trimethyl ammonium bromide) ($C_{10}PhC_{10}$), 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 C_6PhC_6/SDS and $C_{20}Py_2$/SDS mixed systems were constructed based on the regular solution theory. It was found that the structural difference between the two bolaamphileles 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) ($C_{22}Me_6$) are mostly folded in surfactant aggregates [7]. But some studies of ^{13}C-, ^{14}N-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 amhiphiles 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_6PhC_6, $C_{10}PhC_{10}$) were synthesized, their surface physicochemical properties and those of the mixed systems with oppositely charged conventional surfactant sodium dodecyl sulfite (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
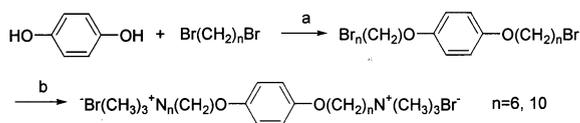
method [17] from eicosanedioic acid (TCI, Japan). 1,6-dibromohexane and 1,10-dibromodecane were prepared from the corresponding diol and hydrogen bromide acid (Beijing Chemical Co.).

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): δ, ppm: 6.82 (4H, s), 3.90 (4H, t, $-CH_2O-$), 3.4 (4H, t, $-CH_2Br$), 1.6–1.9 (8H, m, $-CH_2-CH_2Br$, $-CH_2CH_2O-$), 1.46 (8H, m, $-(CH_2)_2-$).

2.1.2. Phenyl 1,4-bis(oxyhexyltrimethylammonium bromide) (C_6PhC_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 ethanol. Yield: 75%. M.p.: above 200 °C. ^{1}H-NMR (200 MHz, D$_2$O, HDO): δ, ppm: 6.82 (4H, s), 3.90 (4H, t, $-CH_2O-$), 3.20 (4H, t, $-CH_2-N-$), 2.97 (18H, s, $-N(CH_3)_3$), 1.60 (8H, m, $-CH_2CH_2-N-$, $-CH_2CH_2O-$) 1.35 (8H, m, $-(CH_2)_2-$); Anal. Calc. for $C_{24}H_{46}N_2O_2Br_2 \cdot H_2O$: C, 50.35; H, 8.39; N, 4.90. Found: C, 50.87; H, 8.26; N, 4.71%.

2.1.3. Phenyl 1,4-bis(oxydecyltrimethylammonium bromide) ($C_{10}PhC_{10}$)

Phenyl 1,4-bis(oxydecyltrimethylammonium bromide) ($C_{10}PhC_{10}$) was prepared by the same procedure as that for C_6PhC_6 except that 1,10-dibromodecane was used instead of 1,6-dibromohexane. ^{1}H-NMR (200 MHz, D$_2$O, HDO): δ, ppm: 6.87 (4H, s), 3.93 (4H, t, $-CH_2O-$), 3.18 (4H, t, $-CH_2-N-$), 2.98(18H, s, $-N(CH_3)_3$), 1.60

(a) anhydrous K_2CO_3, acetone, reflux; (b) trimethylamine, EtOH.

Scheme 1. Synthesis of C_nPh_n ($n = 6, 10$).

(8H, m, $-CH_2CH_2-N-$, $-CH_2CH_2O-$) 1.35
(24H, m, $-(CH_2)_2-$); Anal. Calc. for
$C_{32}H_{62}N_2O_2Br_2 \cdot 2H_2O$: 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 (Γ_∞) was calculated according to the Gibbs adsorption equation since the ionic strength was much higher than CMC of each surfactant and [19]kept constant:

$$\Gamma_\infty = \frac{-\mathrm{d}\gamma}{2.303RT\mathrm{d}\log C} \qquad (1)$$

Here γ 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. Γ_∞ is the saturate adsorption amount in mol m^{-2}, dγ/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 ($A_{\min}$) is obtained from the saturate adsorption by:

$$A_{\min} = \frac{10^{18}}{N_A\Gamma_\infty} \qquad (2)$$

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_6PhC_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. γ log C curves of $C_{20}Py_2$, C_6PhC_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_{min} and molecular conformation

$A_{\min}$ is an important parameter to judge the conformation of molecules in the surface adsorption layer. Table 1 shows that the $A_{\min}$ 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 $A_{\min}$ in the C_6PhC_6 and $C_{10}PhC_{10}$ systems are almost the same value of
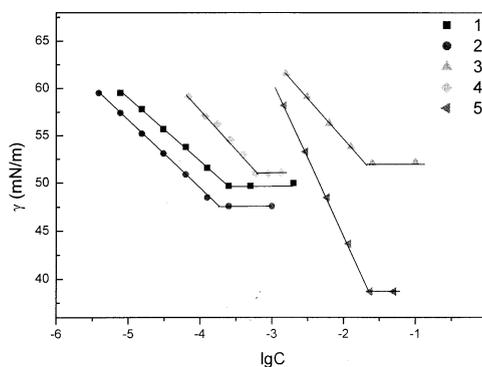

Fig. 1. Surface tension curves of bolaamphiphiles and $C_{10}Py$ ([NaBr] = 0.1 M). (1) $C_{20}Py_2$, 30 °C; (2) $C_{20}Py_2$, 40 °C; (3) C_6PhC_6, 30 °C; (4) $C_{10}PhC_{10}$, 40 °C; (5) $C_{10}Py$, 30 °C.

Table 1
Surface properties of $C_{20}Py_2$, C_6PhC_6, and $C_{10}PhC_{10}$ and $C_{10}Py$ ([NaBr] = 0.1 M)

	t (°C)	CMC (mol dm^{-3})	γ_{CMC} (mN m^{-1})	Γ_∞ (mol m^{-2})	A_{min} (nm^2)
$C_{20}Py_2$	30	2.50×10^{-4}	49.7	1.2×10^{-6}	1.38
	40	1.75×10^{-4}	47.6	1.2×10^{-6}	1.38
$C_{10}Py$	30	2.34×10^{-2}	38.7	2.8×10^{-6}	0.59
C_6PhC_6	30	4.90×10^{-2}	51.3	1.5×10^{-6}	1.11
$C_{10}PhC_{10}$	40	5.60×10^{-4}	51.5	1.5×10^{-6}	1.11

1.11 nm^2. Since the area of –N(CH$_3$)$_3$ group [21,22] is about 0.40 nm^2 and that of the rigid –O–ph–O– group in the two molecules is about 0.3 nm^2, it indicates that the C_6PhC_6 and $C_{10}PhC_{10}$ 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 ^{2}H-NMR technique [23].

3.1.2. γ_{CMC}

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 $C_{10}Py$ is about twice that of $C_{20}Py_2$. 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 $C_{20}Py_2$ system is similar to that in $C_{10}Py$ system. Therefore, the higher γ_{CMC} value of $C_{20}Py_2$ system should be caused by the outmost groups in the adsorption layer. For conventional surfactant $C_{10}Py$, the outmost group in the adsorption layer is –CH$_3$. Correspondingly, due to the reverse U-shape conformation of bolaamphiphiles at the air/water interface, the –CH$_2$– group in $C_{20}Py_2$ becomes the outmost one instead of –CH$_3$ in the adsorption layer. Since the ability of the –CH$_2$– group to reduce the surface tension of the water is weaker than that of –CH$_3$ [24,25], the γ_{CMC} value

of $C_{20}Py_2$ solution is higher (49.7 mN m^{-1}) than that of $C_{10}Py$ (38.7 mN m^{-1}, Table 1). However, in the cases of C_6PhC_6 and $C_{10}PhC_{10}$, the outmost group is phenylene, which is also weaker [26] than methyl group in decreasing surface tension of water. Therefore, the γ_{CMC} values of the two systems are higher than that of $C_{20}Py_2$ system.

3.1.3. CMC

It can be seen from Table 1 that the CMC values of $C_{20}Py_2$ and $C_{10}PhC_{10}$ solutions are very small (in the order of 10^{-4} mol dm^{-3}) and the CMC of $C_{20}Py_2$ solution is lower than that of $C_{10}Py$ 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 C_6PhC_6 is similar to that of $C_{20}Py_2$, the phenylene group and the hydrophilic ether oxygen atom in the former decreases its hydrophobicity. Therefore, the CMC of C_6PhC_6 system is higher than that of $C_{20}Py_2$. For the difference of CMC between C_6PhC_6 and $C_{10}PhC_{10}$ 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 micellization

The thermodynamic parameters of micellization of amphiphiles can be calculated from the phase separation model. Assumed that n bola cation Bola^{2+} and $2\beta n$ counter ion A$^-$ formed micelle

M in NaBr solution:

$$nBola^{2+} + 2\beta nA^- \rightarrow M$$
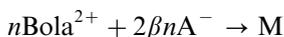
Then the standard Gibbs energy change ΔG_m° should be:

$$\Delta G_m^\circ = RT \ln CMC + 2\beta RT \ln a_{A^-} \quad (3)$$

Here, β is the degree of counter ion binding and a_{A^-} is the activity of the counter ion. The β 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 ΔS_m° is determined by the following equation:

$$\Delta S_m^\circ = \frac{-d\Delta G_m^\circ}{dT} \quad (4)$$

and enthalpy ΔH_m° is obtained from the Van't Hoff plot ($\Delta G_m^\circ/T$ vs. $1/T$).

It is seen that ΔG_m° in Table 2 are all big negative values which means these bolaamphiphiles have strong ability to form micelle. The positive ΔH_m° values indicates that the change of entropy (ΔS_m°) is the main driving force in this process. It is clear that the ΔS_m° of C_6PhC_6 is lower than that of $C_{20}Py_2$. This maybe because the free motion of C_6PhC_6 is restricted by the rigid group in it's skeleton. However, to the conventional surfactants, such as dodeceyl pyridinium bromide ($C_{12}Py$), the ΔH_m° and ΔS_m° are approximately -5 J·mol^{-1} and $40–60$ kJ·mol^{-1} ($25–40$ °C) [29]. The higher ΔS_m° 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_6PhC_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. γ log C curves for $C_{20}Py_2$/SDS, and C_6PhC_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 γ_{CMC} is different. Usually in the mixed cationic and anionic systems, the values of γ_{CMC} are far lower than those of the two single surfactants. But the γ_{CMC} in $C_{20}Py_2$/SDS and $C_{10}PhC_{10}$/SDS mixed systems fell between the two single surfactant systems while γ_{CMC} in C_6PhC_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 γ_{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_6PhC_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_6PhC_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_6PhC_6/SDS, $C_{20}Py_2$/SDS micelles in our study was analyzed on the basis of Rubingh's equation [31]:

$$\omega_R = \frac{\ln(X_2 CMC / Y_2 CMC_2^\circ)}{(1 - Y_2)^2} \quad (5)$$

Table 2
Micellization thermodynamic parameters of $C_{20}Py_2$ and C_6PhC_6

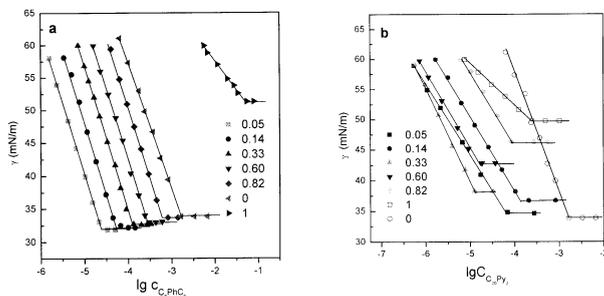| T (K)	$C_{20}Py_2$, [NaBr] = 0.1 mol dm^{-3}				C_6PhC_6, [NaBr] = 0.3 mol dm^{-3}			
	10^4 CMC (mol dm^{-3})	ΔG_m° (kJ mol^{-1})	ΔS_m° (J K^{-1} mol^{-1})	ΔH_m° (kJ mol^{-1})	10^2 CMC (mol dm^{-3})	ΔG_m° (kJ mol^{-1})	ΔS_m° (J K^{-1} mol^{-1})	ΔH_m° (kJ mol^{-1})
298	2.75	−31.7	192	24.8	2.04	−15.6	80	8.2
303	2.50	−32.5	192	24.8	1.97	−16.0	80	8.2
308	1.95	−33.7	192	24.8	1.86	−16.4	80	8.2
313	1.75	−34.5	192	24.8	1.78	−16.8	80	8.2

Fig. 2. Surface tension curves of (a) C_6PhC_6/SDS and (b) $C_{20}Py_2$/SDS systems (30 °C, [NaBr] = 0.1 M).

$$\frac{(1 - Y_2)^2 \ln[(1 - X_2)CMC/(1 - Y_2)CMC_1^\circ]}{Y_2^2 \ln(X_2 CMC/Y_2 CMC_2^\circ)}$$
$$= 1 \qquad (6)$$

where, X_1 is the composition of component 1 in the bulk solution, Y_2 is that in the mixed micelle. CMC, CMC_1°, 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. ω_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 ω_R value (−11.0) in the C_6PhC_6/SDS systems than that in the $C_{20}Py_2$/SDS (−7.5) indicates the stronger interaction in the former. In addition, The ω_R values for

the C_6PhC_6/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 azeotropic point, which is at $X_{C_6PhC_6} \approx 0.33$ in the C_6PhC_6/SDS while at $X_{C_{20}Py_2} \approx 0.58$ in the $C_{20}Py_2$/SDS mixed systems. The azeotropic 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 azeotropic point deviates from the electroneutral mixing ratio and appears at $X_{C_{20}Py_2} \approx 0.58$ in the $C_{20}Py_2$/SDS mixed systems. It seems that the rigid group in the center of C_6PhC_6 makes it easier for the interaction between oppositely charged head groups.

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]:

Table 3
Values of CMC, Y_2, ω_R, for the $C_{20}Py_2$/SDS, C_6PhC_6/SDS mixed micelles at 30 °C, [NaBr] = 0.1 mol dm^{-3}

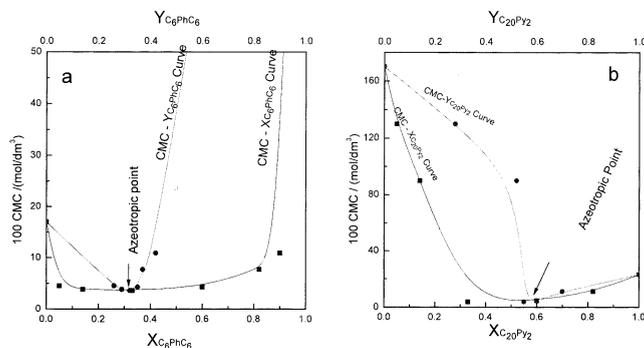| C_6PhC_6/SDS systems				$C_{20}Py_2$/SDS systems			
$X_{C_6PhC_6}$	10^4 CMC (mol dm^{-3})	Y_2	ω_R	$X_{C_{20}Py_2}$	10^4 CMC (mol dm^{-3})	Y_2	ω_R
0	17	0		0	17	0	
0.05	4.5	0.24	−10.7	0.05	13	0.28	−9.2
0.14	3.8	0.32	−12.2	0.14	9	0.52	−0.14
0.33	3.6	0.35	−11.7	0.33	0.38	0.55	−11.4
0.60	4.3	0.39	−11.6	0.60	0.45	0.60	−10.2
0.82	7.7	0.43	−10.8	0.82	1.1	0.70	−6.4
0.90	10.9	0.49	−8.8	1	2.3	1	
1	97	1					
Average ω_R			−11.0				−7.5

Fig. 3. Phase diagrams of (a) C_6PhC_6/SDS and (b) $C_{20}Py_2$/SDS systems (30 °C, [NaBr] = 0.1 M).

$$\omega_A = \frac{\ln(X_2 C_t / Z_2 C_2^{\circ})}{(1 - Z_2)^2} \qquad (7)$$

$$\frac{(1 - Z_2)^2 \ln[(1 - X_2)C_t / (1 - Z_2)C_1^{\circ}]}{Z_2^2 \ln(X_2 C_t / Z_2 C_2^{\circ})} = 1 \qquad (8)$$

where, X_2 is the composition of component 2 in the bulk solution, Z_2 is that in the mixed adsorbed film. C_t, 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 ω_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 C_6PhC_6/SDS is more negative that that in the $C_{20}Py_2$/SDS mixtures although the latter is examined under higher surface pressure (the surface pressure for C_6PhC_6/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 $C_{20}Py_2$/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 C_6PhC_6 favoring the orientation of molecules when interaction occurs.

Comparing the negative ω_R and ω_A value in Tables 3 and 4, it is found that in both systems the average ω values for the adsorbed films are more negative than that in the mixed micelles, indicating a stronger interaction between the two compo-

nents 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 C_6PhC_6/SDS and $C_{20}Py_2$/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 C_6PhC_6/SDS mixtures, while a variance of 0.06 (0.58–0.52 = 0.06) for that of $C_{20}Py_2$/SDS mixed systems which may be caused by the experiment error.

3.2.3. The surface excess and partial molecular area

The surface excess Γ 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 C_6PhC_6/SDS system is lower than that for each single surfactant system and the maximum is attained at $X_{C_6PhC_6} = 0.33$, at which the mixed adsorbed film shows an azeotropic point. Although the maximum Γ 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, ω_A, for the C_6PhC_6/SDS and $C_{20}Py_2$/SDS mixed adsorbed filsms at 30 °C, [NaBr] = 0.1 mol dm^{-3}

C_6PhC_6/SDS $\gamma = 57.5$ mN m^{-1}						$C_{20}Py_2$/SDS $\gamma = 52.5$ mN m^{-1}					
$X_{C_6PhC_6}$	$10^5 C_t$ (mol dm^{-3})	Z_2	ω_A	$10^6 \Gamma$ (mol m^{-2})	A_m (nm^2)	$X_{C_{20}Py_2}$	$10^5 C_t$ (mol dm^{-3})	Z_2	ω_A	$10^6 \Gamma$ (mol m^{-2})	A_m (nm^2)
0	170	0		3.4	0.49	0	18.6	0		3.4	0.49
0.05	3.26	0.26	−14.2	3.8	0.44	0.05	3.56	0.38	−8.1	2.1	0.78
0.14	2.77	0.29	−14.0	3.8	0.44	0.14	4.88	0.41	−8.0	2.4	0.69
0.33	2.69	0.32	−13.5	3.9	0.43	0.33	0.47	0.49	−13.4	2.6	0.63
0.60	3.33	0.35	−13.2	3.8	0.44	0.60	0.74	0.54	−12.0	2.4	0.69
0.82	5.47	0.37	−12.0	3.8	0.44	0.82	3.44	0.63	−6.2	2.1	0.78
0.90	6.13	0.42	−13.4	3.8	0.44	1	10.5	1.00		1.2	1.38
1	1000	1		1.5	1.11						
Average ω_A			−13.4						−9.5		

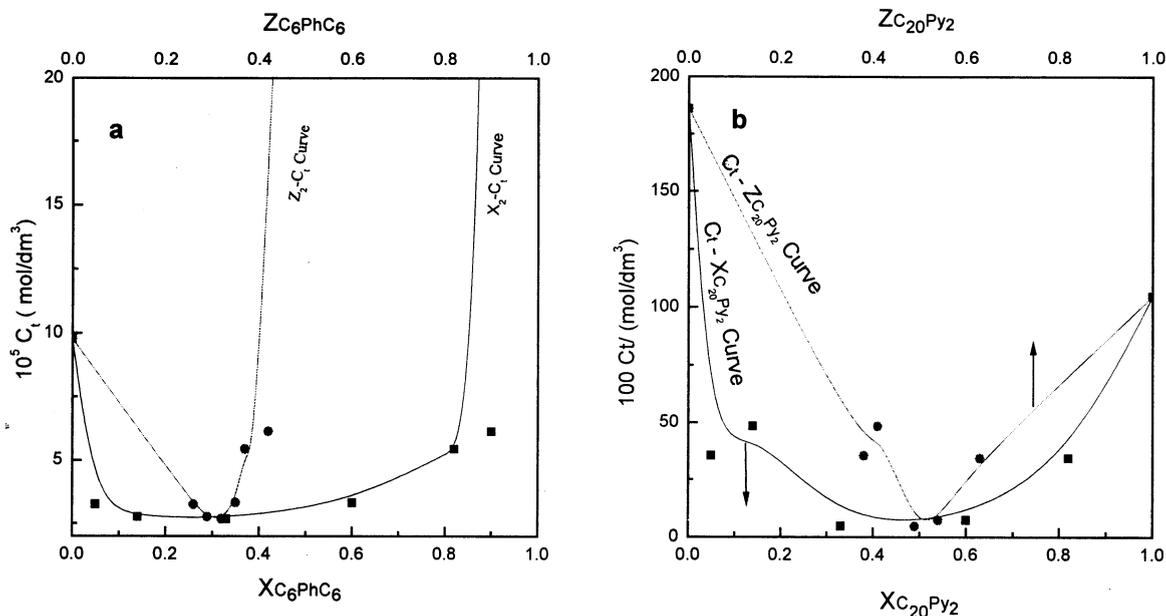Y. Yan et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 215 (2003) 263–275

271

Fig. 4. Phase diagrams of monomers in bulk solution and adsorbed film at air/water interface for (a) C_6PhC_6/SDS (at 57.5 mN m^{-1}) and (b) $C_{20}Py_2$/SDS (at 57.5 mN m^{-1}) systems (30 °C, [NaBr] = 0.1 M).

than the single C_6PhC_6, indicating more molecules in the mixed adsorbed films than in the single

films. However, the situation in the $C_{20}Py_2$/SDS is different from that in the C_6PhC_6/SDS mixed
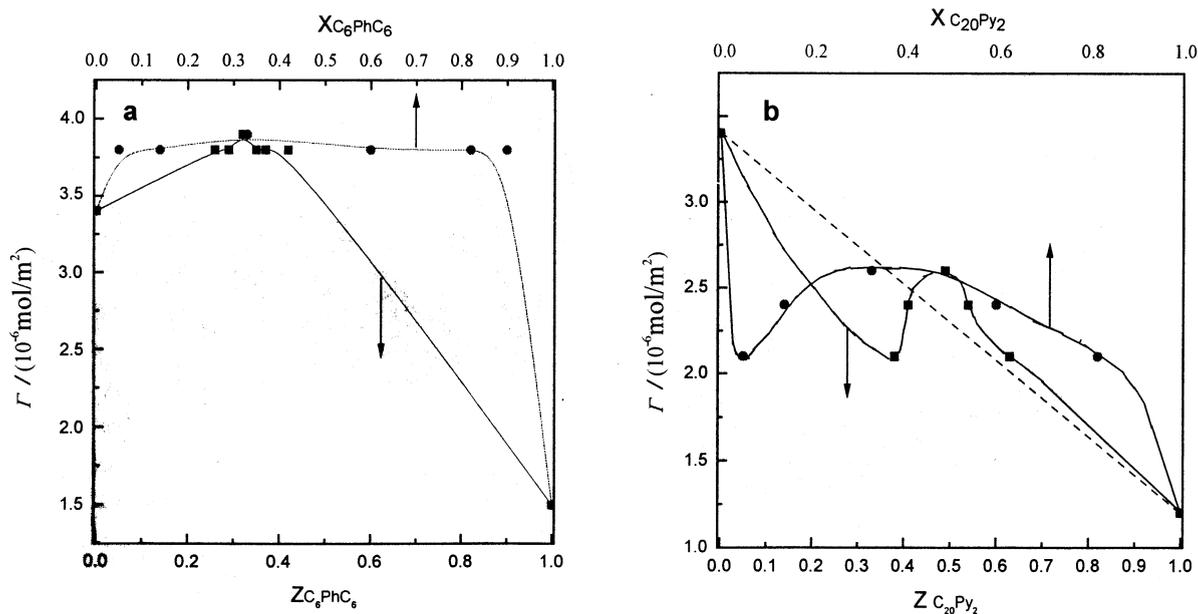

Fig. 5. The surfaces excess Γ curves as function of X_2 and Z_2 for (a) C_6PhC_6/SDS (at 57.5 mN m^{-1}) and (b) $C_{20}Py_2$/SDS (at 57.5 mN m^{-1}) systems (30 °C, [NaBr] = 0.1 M).

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 ($2.6/1.2 \approx$ 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]:

$$A_m = A_1 + Z_2 \left(\frac{\delta A_m}{\delta Z_2} \right)_{T,V,\gamma,n_1} \tag{9}$$

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
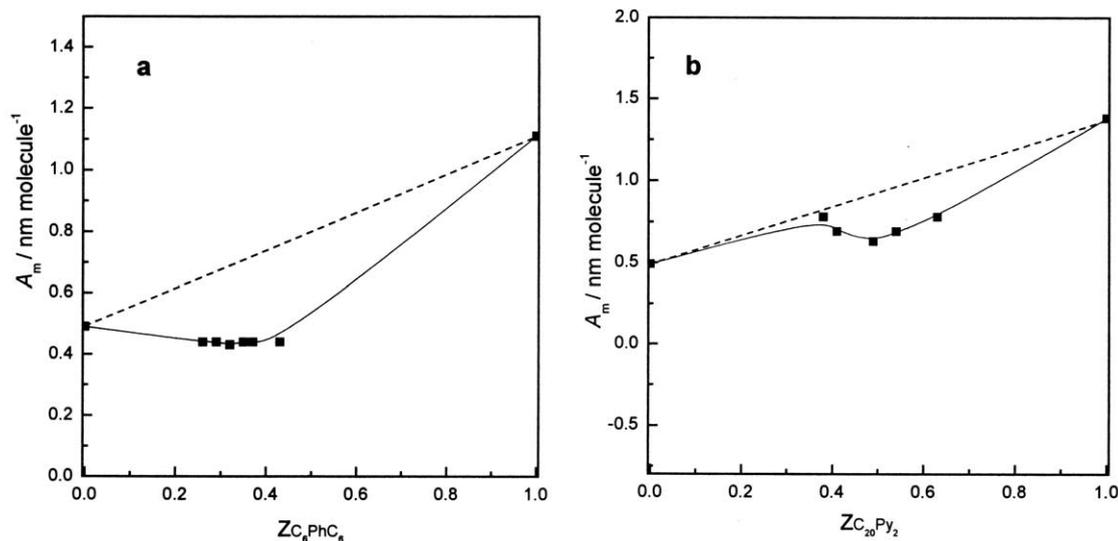

Fig. 6. The changes in mean molecular area (A_m) with mole fraction for (a) C_6PhC_6/SDS and (b) $C_{20}Py_2$/SDS mixed systems (30 °C, [NaBr] = 0.1 M).

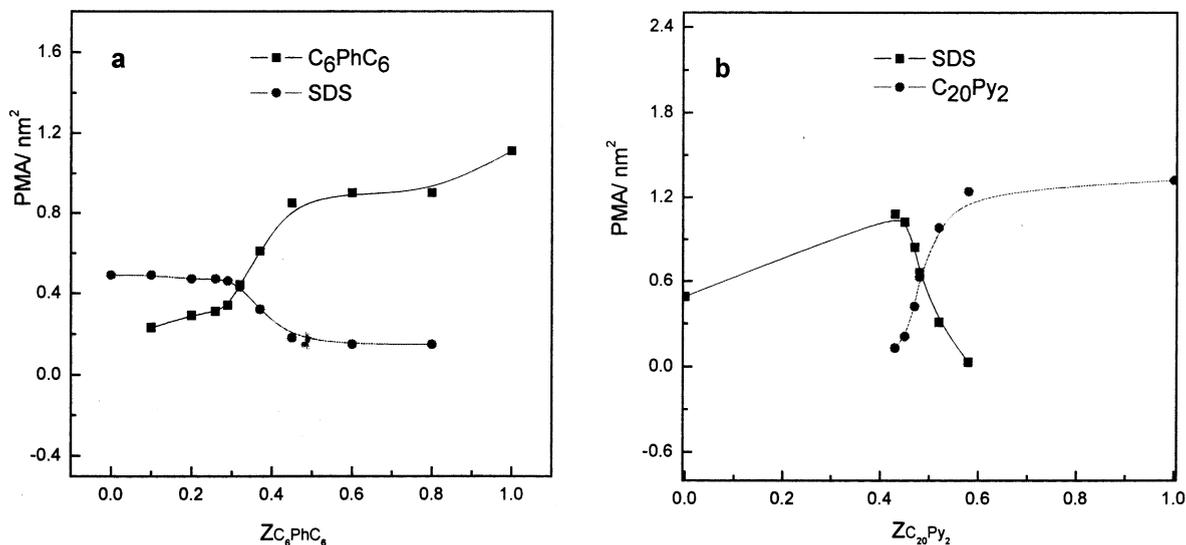Fig. 7. The changes in PMA for (a) C_6PhC_6/SDS and (b) $C_{20}Py_2$/SDS mixed systems (30 °C, [NaBr] = 0.1 M).

systems (see Fig. 7). For the C_6PhC_6/SDS mixtures shown in Fig. 7(a), the PMA–$Z_{C_6PhC_6}$ curves demonstrate that the PMA of each surfactant in the mixing range near $Z_{C_6PhC_6} = 0.33$ 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 $Z_{C_6PhC_6} \approx 0.33$, meaning that the two surfactants have the same PMA value at this time. The PMA curves for each component in $C_{20}Py_2$/SDS mixed system also have a meeting point at approximately $Z_{C_{20}Py_2} \approx 0.5$. It seems that the PMA of SDS in the $C_{20}Py_2$/SDS mixtures slightly increases after a maximum then decrease suddenly as $Z_{C_{20}Py_2}$ approaches 0.5. The case for $C_{20}Py_2$ is hard to say yet for the inconvenient determination of its PMA at the mixing ration far from $Z_{C_{20}Py_2} \approx 0.5$. 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 ($C_{20}Py_2$) and rigid-group-containing (C_6PhC_6 and $C_{10}PhC_{10}$) 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 charge head groups in the C_6PhC_6/SDS is stronger than that in the $C_{20}Py_2$/SDS mixtures both in the micelles and in the adsorbed films. This may be attributed to the rigid group in the center of C_6PhC_6 favoring the orientation of molecules when interaction occurs. Azeotropic point was found in the CMC–X_2/CMC–Y_2, C_t–X_2/C_t–Z_2 and Γ–Y_2/Z_2 curves for both mixed systems, indicating surfactant ion-pairs were formed due to strong interaction in these mixtures. The azeotropic point in the

C_6PhC_6/SDS systems appearing at X (or Y or $Z)_{C_6PhC_6} \approx 0.33$ 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_6PhC_6 and $C_{20}Py_2$ affects the properties of micelle and adsorbed films apparently.

Acknowledgements

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