

Surface properties of bolaamphiphiles in ethanol/water mixed solutions

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Abstract

The effect of ethanol on the surface properties of bolaamphiphiles and their mixed systems with oppositely charged conventional surfactants is studied and compared with the corresponding conventional surfactant systems. It is found that both the bolaamphiphile and the conventional surfactant have the similar variation tendency of γ_{cmc} and Γ_{∞} in the single surfactant system. However, in the cationic and anionic mixed surfactants system the γ_{cmc} decreases with the ethanol addition in the bolaamphiphile systems. This tendency is reverse to that in conventional surfactant system. Surface activity of the asymmetric bolaamphiphiles SHMC decreases greatly when ethanol is added into the system due to the existence of the hydroxyl group in the SHMC molecule. Adding opposite charged surfactant may greatly increase surface activity in the SHMC/C₁₂NEt₃Br/ethanol systems.

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1. Introduction

Bolaamphiphiles are molecules with two polar groups connected by one or two hydrophobic chains [1,2]. On the basis of design and synthesis of many kinds of bolaamphiphiles, the research on the bolaamphiphiles was greatly developed in the past two decades, especially on the area of monolayer membrane formation [1–7]. Recently, the researches on asymmetric bolaamphiphile, which usually had two different polar groups in its molecular structure, were carried out in this field [8–12].

Moreover, the properties of both symmetric and asymmetric bolaamphiphiles in air/water surface were also studied [13–15]. Compared to that in conventional surfactant system, usually, in bolaamphiphile system, the surface tension was higher and the adsorption amount was smaller due to their reverse U-shape conformation in the surface [15–17]. However, so far little work was focused on the surface properties of bolaamphiphiles in polar non-aqueous solvents and their mixture with water.

As to conventional surfactants, the study of surfactants in non-aqueous solvents was rather limited in comparison with the numerous works of surfactants in water. Among the researches in the non-aqueous solvents, the work in the polar solvent and their mixture with water was still less than the work done in the apolar solvents. Early efforts were made by Ray [18] and the concept ‘solvophobic effect’ was suggested after correlating the micelle formation for a kind of nonionic surfactant in about 20 kinds of solvents. Later the researches of micelle formation were carried on in many kinds of solvents including ethylene glycol [19], glycerol, formamide, various alcohols, diols, formic acid [18], amides, DMSO [20], hydrazine [21], and low-melting fused salts [22]. However, most of the works were concentrated on the cmc variation in these solvents, the tendency about the change of γ_{cmc} was still rare.

In 1999 [23], the surface properties of various kinds of conventional surfactants in mixed ethanol–water solvents were studied in our lab. It was found that the varying tendency of γ_{cmc} induced by ethanol amount may be predicted according to the saturation adsorption amount (Γ_{∞}) and γ_{cmc} values in water. For the surfactants with bigger Γ_{∞} and smaller γ_{cmc} values in water, the γ_{cmc} values increased

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with ethanol addition; for the surfactants with smaller Γ_{∞} and bigger γ_{cmc} values in water, the effect was opposite. Although some interesting results were found, more details and profound work were still needed to obtain more insight of the nature in this aspect.

Considering the specific molecular structure and conformation in the air/water interface, we studied the effect of ethanol on the surface properties of bolaamphiphiles and their mixed systems with oppositely charged conventional surfactants in this paper. Bolaamphiphiles with simple structure, flexible (sodium eicosanedioate [NaOOC(CH₂)₁₈COONa] (SED), 1,20-eicosamethylene dipyridinium dibromide [Br⁻C₅H₅N⁺(CH₂)₂₀N⁺C₅H₅Br⁻] (EMPB)) or with rigid group (phenyl-1,4-bis(oxyhexamethylene trimethyl ammonium bromide) [Br⁻(CH₃)₃N⁺(CH₂)₆OC₆H₄O(CH₂)₆N⁺(CH₃)₃Br⁻] (PHTAB)), and a kind of asymmetric bolaamphiphiles (sodium-4-(6-hexamethyleneoxy) cinnamate [HO(CH₂)₆OC₆H₄CH=CHCOONa] (SHMC)) were synthesized and studied. Their surface properties were compared with that in the conventional surfactant systems. This is the first report about the surface properties of bolaamphiphiles in the mixed solvents.

2. Materials and methods

2.1. Materials

Sodium eicosanedioate, 1,20-eicosamethylene dipyridinium dibromide and phenyl-1,4-bis(oxyhexamethylene trimethyl ammonium bromide) were synthesized according to the literatures [14,15]. Sodium 4-(6-hexamethyleneoxy) cinnamate was synthesized as followed steps: 1.64 g 4-hydroxycinnamic acid and 0.8 g sodium hydroxide was dissolved in 10 ml water, and 0.012 mol 6-bromo-1-hexanol was dissolved in 40 ml ethanol. These two solutions were mixed and the mixed solution was stirred for 24 h at 60 °C. The product was recrystallized from an ethanol–water mixture. ¹H NMR (200 MHz, D₂O): δ , ppm: 7.45 (d, 2H), 7.2 (d, 2H), 6.9 (d, 2H), 6.3 (d, 2H), 4.0 (t, 2H), 3.5 (t, 2H), 1.6–1.7 (t, 2H), 1.30–1.5 (t, 2H). Anal. Calc. for C₁₅H₁₉O₄Na: C, 62.93; H, 6.64; Found: C, 62.75; H, 6.37.

Decyl trimethyl ammonium bromide (C₁₀NMe₃Br) and sodium dodecanoate (C₁₁COONa) was synthesized according to the literatures [23]. Dodecyl triethyl ammonium bromide (C₁₂NEt₃Br) was synthesized from n-dodecyl bromide and triethyl amine. The product was recrystallized five times from an ethanol–acetone mixture. SDS (AR) was purchased from Sigma and used as received. The purities of all the surfactants were examined by the examination of surface tension, and no surface tension minimum was found in all the surface tension curves (γ –log c curves).

Ethanol was refluxed with magnesium scraps and iodine more than 2 h and distilled. Sodium bromide is of AR grade and has been baked at 500 °C for 6 h. Na₂B₄O₄·10H₂O (AR) was product of Beijing Chemical Co. Water was dis-

tilled from the KMnO₄-containing deionized water to remove traces of organic compounds.

2.2. Methods

The surface tension of surfactant solution was measured by the drop volume method [24]. The density of the ethanol–water mixture needed for calculating the surface tension was measured with a DMA45 densitometer (Anton Paar K.G.A-8054, GRAZ, Australia). The surfactants were mixed in molar ratios and the solvents (ethanol/water) were mixed in volume ratios. The temperature of the experiments was kept at 30 ± 0.5 °C.

The ionic strengths of all solutions were adjusted to 0.1 mol/kg with NaBr. The pH values were adjusted to 9.2 with Na₂B₄O₄·10H₂O in the systems containing carboxylate surfactants.

The values of critical micelle concentration (cmc), and the surface tension at cmc (γ_{cmc}) was determined from the inflection points in the γ –log c curve. The saturation adsorption amount of surfactants (Γ_{∞}) was calculated according to the Gibbs adsorption equation:

$$\Gamma_{\infty} = \left(-\frac{1}{2.303RT} \right) \frac{d\gamma}{\lg c}$$

Here γ was the surface tension in mN/m, c was the concentration of corresponding surfactant in single surfactant system, while it represented the total concentration in mixed system. Γ_{∞} was the saturate adsorption amount in mol/m², T was the absolute temperature, and $R = 8.314 \text{ J/mol K}$.

3. Results and discussion

3.1. The surface properties of single system of EMPB

The γ –log c curves and the values of cmc, γ_{cmc} and Γ_{∞} of EMPB in ethanol–water mixtures are shown in Fig. 1 and

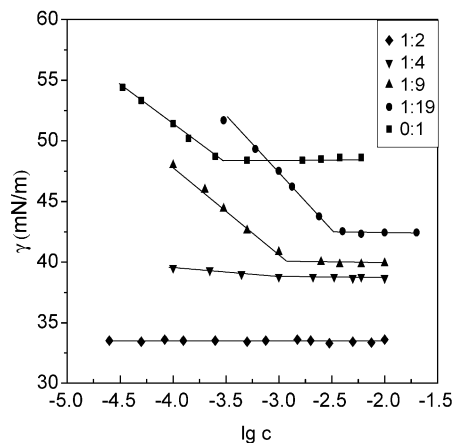


Fig. 1. Surface tension of EMPB system in ethanol/water mixture with various volume ratios.

Table 1
The surface physico-chemical properties of EMPB in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-3} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:4	0.95	38.9	0.12
1:9	1.17	40.0	1.26
1:19	3.31	42.5	1.60
0:1	0.30	48.3	1.10

Table 1. The Γ_{∞} and γ_{cmc} versus the ethanol content curves of EMPB and the conventional surfactant decyl trimethyl ammonium bromide ($\text{C}_{10}\text{NMe}_3\text{Br}$) [23] are shown in Fig. 2.

From Table 1 we can find that in aqueous solution Γ_{∞} is greatly lower in EMPB system (1.10×10^{-6} mol/m²) than that in $\text{C}_{10}\text{NMe}_3\text{Br}$ system (3.63×10^{-6} mol/m²) [23]. Combined the fact that EMPB molecules will take the reverse U-shape conformation in the air water system, which makes the outside group of the adsorption layer is $-\text{CH}_2$ not $-\text{CH}_3$, the γ_{cmc} of EMPB (48.3 mN/m) is bigger than that of $\text{C}_{10}\text{NMe}_3\text{Br}$ (39.8 mN/m) [23] in water. However, the difference of γ_{cmc} and Γ_{∞} between the two surfactant aqueous solutions does not influence the variation tendency of the ethanol addition, both the γ_{cmc} and Γ_{∞} decrease with the increase of ethanol concentration in EMPB and $\text{C}_{10}\text{NMe}_3\text{Br}$ systems.

With the addition of ethanol, the solvophobic effect [18] of the surfactants is reduced, which makes the Γ_{∞} decrease. In addition, as the ethanol concentration goes up, more ethanol molecules will participate in the surface layer which makes the Γ_{∞} of the system decrease due to the competition adsorption. With the decrease of the Γ_{∞} , the γ_{cmc} of the both surfactant solutions would increase with the addition of ethanol. However, the ethanol addition also changes the composition of the mixed solvents and the surface tension of the mixed solvents will be greatly lower since the surface tension of ethanol is much smaller than that of water, thus the surface tension of the solvents and the γ_{cmc} of the systems would decrease. It is obviously that the later effect has the greater contribution to γ_{cmc} in EMPB and $\text{C}_{10}\text{NMe}_3\text{Br}$ systems, which makes the γ_{cmc} decrease with the ethanol addition.

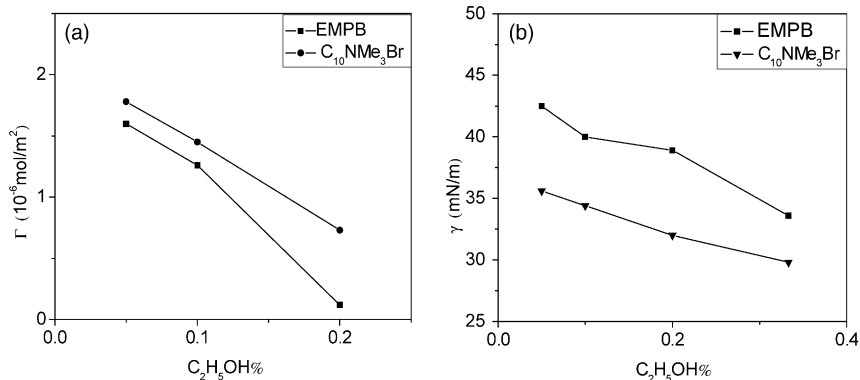


Fig. 2. Γ_{∞} (a) and γ_{cmc} (b) vs. the ethanol content curves of EMPB and $\text{C}_{10}\text{NMe}_3\text{Br}$.

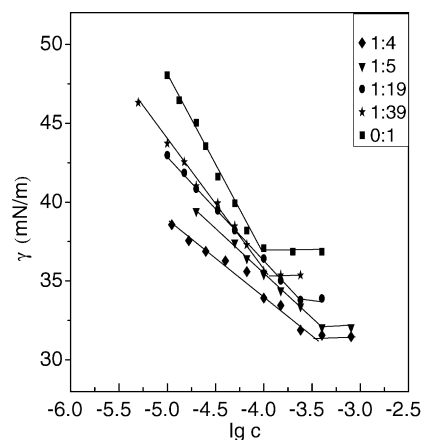


Fig. 3. Surface tension of 1:6 EMPB/SDS system in ethanol/water mixture with various volume ratios.

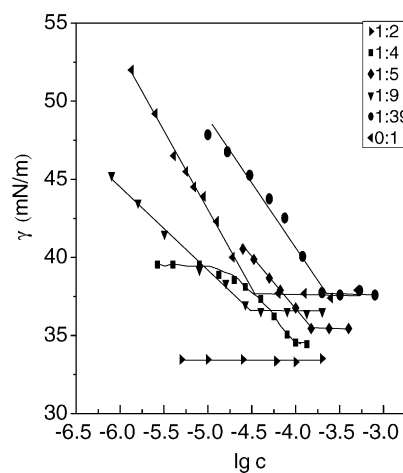


Fig. 4. Surface tension of 1:2 EMPB/SDS system in ethanol/water mixture with various volume ratios.

3.2. The surface properties of the mixed systems of symmetric bolaamphiphiles and their oppositely charged conventional surfactants

The mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants were also

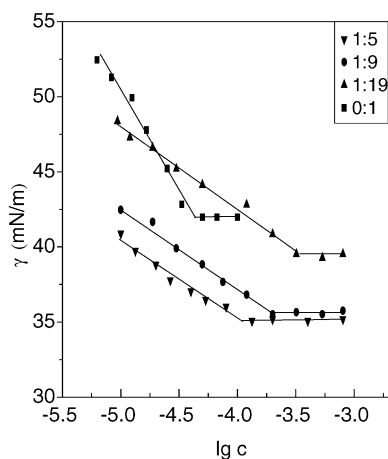


Fig. 5. Surface tension of 3:2 EMPB/SDS system in ethanol/water mixture with various volume ratios.

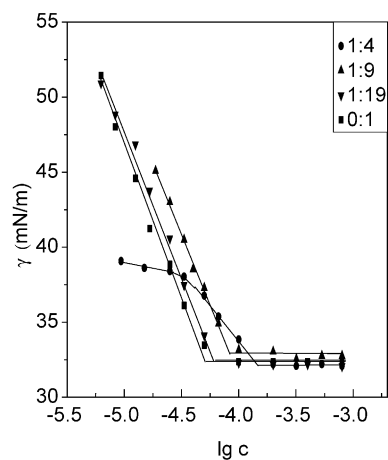


Fig. 6. Surface tension of 1:6 PHTAB/SDS system in ethanol/water mixture with various volume ratios.

investigated. The γ - $\log c$ curves and the results are shown in Figs. 3–8 and Tables 2–7. The curves of Γ_{∞} and γ_{cmc} versus the content of ethanol in these mixed systems and conventional mixed system ($C_{11}COONa/C_{12}NET_3Br$) are shown in Fig. 9.

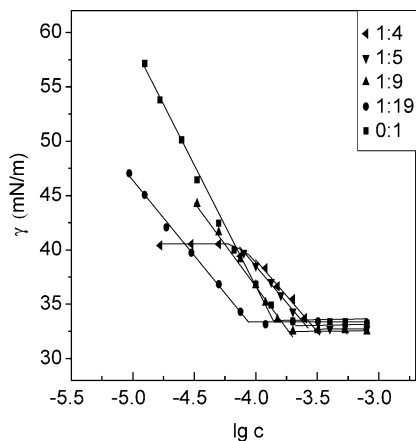


Fig. 7. Surface tension of 1:2 PHTAB/SDS system in ethanol/water mixture with various ethanol/water mixture volume ratios.

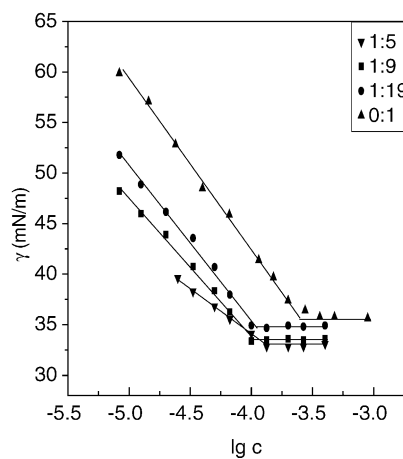


Fig. 8. Surface tension of 1:2 SED/ $C_{12}NET_3Br$ system (pH = 9.2) in with various volume ratios.

Table 2

The surface physico-chemical properties of 1:6 EMPB/SDS in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:4	3.24	31.6	0.94
1:5	3.98	32.1	0.98
1:19	2.35	33.9	1.14
1:39	1.12	35.3	1.42
0:1	0.96	37.0	1.94

Table 3

The surface physico-chemical properties of 1:2 EMPB/SDS in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:4	1.00	34.5	1.20
1:5	1.51	35.5	1.14
1:9	0.31	36.6	0.92
1:39	2.29	37.7	1.44
0:1	0.30	38.1	1.80

Table 4

The surface physico-chemical properties of 3:2 EMPB/SDS in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:5	1.10	35.1	0.86
1:9	2.04	35.6	0.96
1:19	3.31	39.5	0.95
0:1	0.44	42.0	2.32

Table 5

The surface physico-chemical properties of 1:6 PHTAB/SDS in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:4	1.45	32.2	1.64
1:9	0.85	32.9	3.22
1:19	0.63	32.5	3.38
0:1	0.51	32.4	3.46

Table 6

The surface physico-chemical properties of 1:2 PHTAB/SDS in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:4	3.02	32.7	2.26
1:5	2.63	32.9	2.32
1:9	1.91	32.5	2.68
1:19	0.87	33.3	2.70
0:1	1.38	33.5	3.80

From Fig. 9a we can find that Γ_{∞} usually decreases with the increase of ethanol content in the two series of mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants, which is same to the tendency of Γ_{∞} variation in conventional cationic and anionic mixed surfactant system. Similarly to the case of the single bolaamphiphile system, it may be attribute to the decrease of solvophobic effect, as we said above.

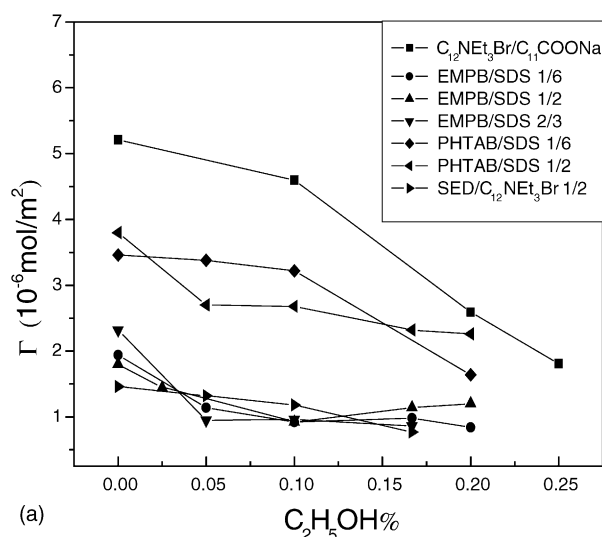
On the other hand, from Fig. 9b we can see the tendency of the γ_{cmc} variation in the mixed solutions of bolaamphiphiles and their oppositely charged conventional surfactants is completely different to the case in the conventional cationic surfactant mixed systems. In the system of $\text{C}_{11}\text{COONa}/\text{C}_{12}\text{NET}_3\text{Br}$, the γ_{cmc} increases with ethanol addition, while in the mixed systems of symmetric bolaamphiphiles and their oppositely charged conventional surfactants, the γ_{cmc} values usually decrease (in EMPB/SDS systems) or nearly keep constant (in PHTAB/SDS and SED/ $\text{C}_{12}\text{NET}_3\text{Br}$ systems) with the increase of ethanol concentration.

The γ_{cmc} of solution is usually determined by the surface tension of the solvent, and adsorption amount of the solutes. Compared with that in the single surfactant system, Γ_{∞} of the mixed conventional cationic surfactant system is usually very big. Thus the surfactant molecules in the surface are more and the solvent molecules are less. So the surface tension of the solution is affected more by the surfactants in the surface layer than by the solvent. In fact the γ_{cmc} of the aqueous cationic surfactant system is very low (~ 22 – 25 mN/m [23], near the surface tension of ethanol, 22 mN/m) and the solvent effect to the γ_{cmc} is very tiny. Thus with the addition of ethanol, the Γ_{∞} of the surfactants decreases, and the γ_{cmc} increases. In addition, according to the previous work [23], surface tension of liquid is also determined by the atoms and atomic groups forming

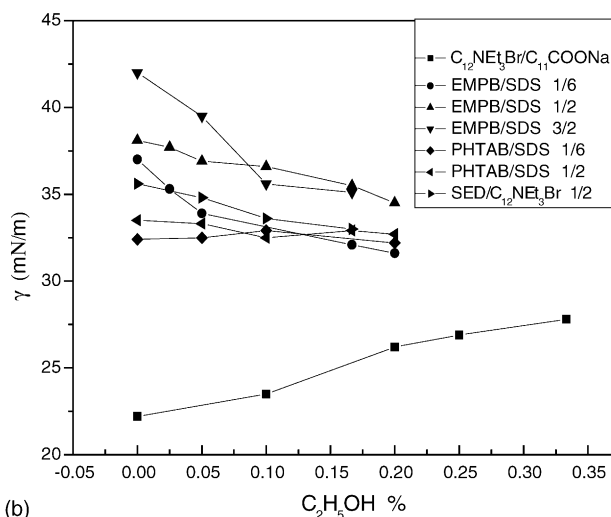
Table 7

The surface physico-chemical properties of 1:2 SED/ $\text{C}_{12}\text{NET}_3\text{Br}$ (pH = 9.2) in ethanol–water mixtures

Ethanol–water ratio	cmc (10^{-4} mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10^{-6} mol/m ²)
1:5	1.32	33.0	1.54
1:9	1.05	33.6	2.36
1:19	1.07	34.8	2.64
0:1	2.51	35.6	2.92



(a)



(b)

Fig. 9. Γ_{∞} (a) and γ_{cmc} (b) vs. the ethanol content curves of conventional cationic and anionic surfactants and bolaamphiphiles and their oppositely charged conventional surfactants.

the outmost layer of surface [25]. The contribution of CH_3 to surface energy is less than that of CH_2 and much less than that of water [26]. With the addition of ethanol, the Γ_{∞} of the system decreases, then some surfactant molecules would change the conformation from upstanding to bending and the groups forming the outmost layer are partly replaced from methyl to methylene. Therefore, the area ratio occupied by methylene in the outmost layer will gradually increase (see Fig. 10a and b), which also makes the γ_{cmc} of the system increases. This fact is prevalent in the mixed systems of conventional cationic and anionic surfactants [23].

However, it is completely different in the mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants. According to the previous work [15], EMPB, SED and PHTAB molecules will adopt reverse U-shape conformation in the surface. Thus methylene group is the outmost group of the bolaamphiphiles adsorption

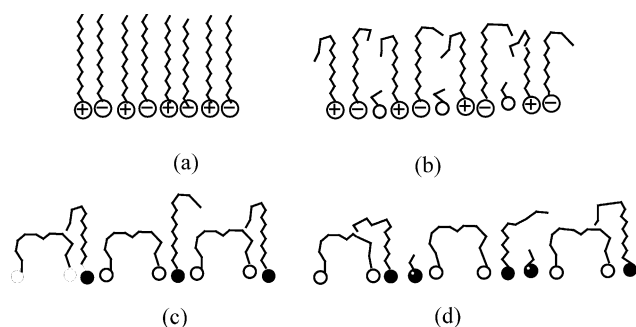


Fig. 10. Schematic diagram for the structure of surface phase of system: (a) conventional cationic and anionic surfactants without participation of ethanol molecules; (b) conventional cationic and anionic surfactants with participation of ethanol molecules; (c) the reverse U-shape conformation of bolaamphiphiles in the surface without participation of ethanol molecules; (d) the reverse U-shape conformation of bolaamphiphiles in the surface with participation of ethanol molecules.

layer in both aqueous system and in the mixture of water and ethanol (see Fig. 10c and d). So the effect of outmost groups in the bolaamphiphile systems on the change of γ_{cmc} is very tiny. Moreover, the Γ_{∞} in this kind of mixed systems is small. Hence the solvent molecules in the surface are more and the solvent effect is primary. Combined to the contribution of Γ_{∞} decrease to the γ_{cmc} , it is reasonable that the γ_{cmc} of the mixed systems of bolaamphiphiles and their oppositely charged conventional surfactants will decrease (EMPB/SDS systems) or nearly keep constant (PHTAB/SDS and SED/C₁₂NEt₃Br systems) with ethanol addition. This variation tendency is completely different from that of conventional system in despite of the same variation tendency of Γ_{∞} in the respective systems.

The cmc variation tendency of these systems was also studied. Usually the cmc values of the mixed systems will increase with the addition of ethanol, which may be attributed to the reduction of solvophobic effect. However, in the 1:2 PHTAB/SDS systems and 1:2 SED/C₁₂NEt₃Br systems, the cmc values decrease first and then increase with the ethanol addition, indicating that small amount of the ethanol addi-

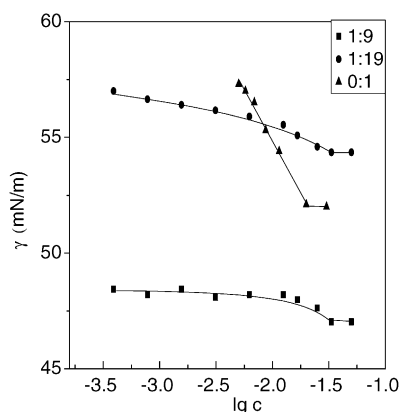


Fig. 11. Surface tension of SHMC system (pH = 9.2) in ethanol/water mixture with various volume ratios.

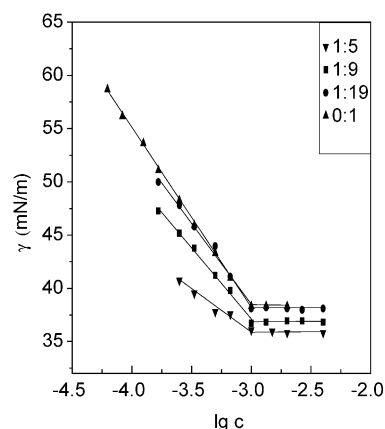


Fig. 12. Surface tension of 1:2 SHMC/C₁₂NEt₃Br system (pH = 9.2) in ethanol/water mixture with various volume ratios.

tion will be helpful to the micelle formation. The relative dielectric constant of solvent would decrease with the ethanol addition. According to Coulomb's law, the attractive force between the headgroups of bolaamphiphiles and their oppositely charged conventional surfactants will increase, which leads to low cmc in the system. However, this effect is overcome by the reduction of solvophobic effect at high ethanol content, which leads to the cmc increases with the ethanol addition.

However, the variation tendency of cmc in some systems, such as 1:2, 3:2 EMPB/SDS and single EMPB system is very complex. Based on the current data and research work it is difficult to explain the cmc variation tendency in these three systems. More work is needed to study the cmc tendency with the ethanol addition in this field.

3.3. The surface properties of asymmetric bolaamphiphile SHMC and its mixture with C₁₂NEt₃Br

The γ - $\log c$ curves of the SHMC and 1:2 SHMC/C₁₂NEt₃Br systems in various ethanol proportions are shown in Figs. 11 and 12, respectively. The surface-chemical properties of SHMC/C₁₂NEt₃Br are shown in Table 9.

From Fig. 11, it is interesting that the surface activity of SHMC decreases greatly when small amount of ethanol is added into the aqueous system. From the results of our previous work [23] and the work in 3.1 and 3.2, usually the surfactant will lose its surface activity when the mixed volume ratio of ethanol and water is equal to or bigger than 1:2. However, in the SHMC system, the variety of surface tension is very small (<3 mN/m) in a broad concentration range (from

Table 8

The values of γ_{cmc} of SHMC (pH = 9.2) in ethanol–water mixtures and the values of surface tension of mixed solvent (γ_{solvent})

Ethanol–water ratio	γ_{cmc} (mN/m)	γ_{solvent} (mN/m)
1:9	54.4	61.3
1:19	47.1	49.0

Table 9

The surface physico-chemical properties of 1:2 SHMC/C₁₂NEt₃Br (pH = 9.2) in ethanol–water mixtures

Ethanol–water ratio	cmc (10 ⁻³ mol/L)	γ_{cmc} (mN/m)	Γ_{∞} (10 ⁻⁶ mol/m ²)
1:5	0.99	35.9	1.40
1:9	1.04	36.9	2.32
1:19	1.06	38.2	2.60
0:1	0.96	38.5	2.92

3.9×10^{-4} to 5.0×10^{-2} mol/L), when the mixed volume ratio of ethanol and water is just 1:19. Furthermore, with ethanol addition, the value of γ_{cmc} of SHMC is close to the value of surface tension of mixed solvent (see Table 8). That is to say, the surface activity of SHMC is very sensitive to the ethanol addition. This may be attributed to the existence of the hydroxyl group in the SHMC molecule, which makes the solvophobic effect in SHMC system greatly reduces after the ethanol addition. Side support is that the solubility of SHMC in ethanol is much better than that in water.

However, when the opposite charged conventional surfactant C₁₂NEt₃Br is added into the SHMC system, the result is greatly changed. From Fig. 12 and Table 9, it can be found that the ethanol effect to the surface activity of the SHMC/C₁₂NEt₃Br system is not as strong as that in single SHMC system, but similar to that of other bolaamphiphiles. The mixed surfactants can obviously decrease the surface tension of the mixed solvents even at the mixed volume ratio of ethanol and water is 1:5. It is reasonable to think that the electrostatic attractive force between anionic and cationic head groups of SHMC and C₁₂NEt₃Br tends to make the headgroups close in the mixed systems which greatly reduces the effect of hydroxyl group. Thus a simple and effective way was found to promote the surface activity of SHMC in the ethanol/water mixtures. The Γ_{∞} , γ_{cmc} versus the content of ethanol curves in 1:2 SHMC/C₁₂NEt₃Br systems are shown in Fig. 13. The Γ_{∞} and γ_{cmc} both decrease with the addition of ethanol, which is similar to that of bolaamphiphiles we studied above.

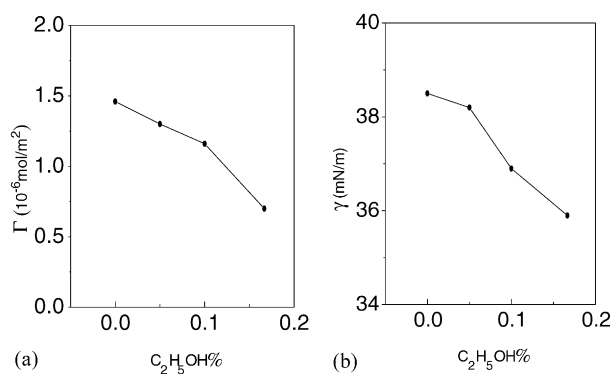


Fig. 13. Γ_{∞} (a) and γ_{cmc} (b) vs. the ethanol content curves of SHMC/C₁₂NEt₃Br system.

4. Conclusion

The effect of ethanol on the surface properties of bolaamphiphiles and their mixed systems with oppositely charged conventional surfactants are studied. In the single surfactant system, the Γ_{∞} and γ_{cmc} in bolaamphiphiles system change similarly to that in the conventional surfactant system. In the system of bolaamphiphiles and their oppositely charged conventional surfactants, the Γ_{∞} has the similar tendency while the γ_{cmc} has the reverse tendency to that of the conventional cationic and anionic surfactants. The different variation tendency of γ_{cmc} in bolaamphiphiles system comes from the low adsorption amount and the reverse U-shape conformation in the surface of bolaamphiphiles. Surface activity of SHMC greatly decreases after ethanol addition due to the hydroxyl group in the SHMC molecule. However, a simple and effective way is found to promote the surface activity of SHMC in the ethanol/water mixtures by adding the oppositely charged conventional surfactant. This is the first report about the surface properties of bolaamphiphiles in mixed solvents and we hope it would shed a light on the theoretical research and the application of bolaamphiphiles in non-aqueous systems.

Acknowledgements

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