

Chuanzhong Wang
Shihua Tang
Jianbin Huang
Xinran Zhang
Honglan Fu

Transformation from precipitates to vesicles in mixed cationic and anionic surfactant systems

Received: 7 November 2001
Accepted: 24 January 2002
Published online: 26 April 2002
© Springer-Verlag 2002

C. Wang · S. Tang · J. Huang (✉)
X. Zhang · H. Fu
Institute of Physical Chemistry,
Peking University, Beijing 100871,
China
E-mail: jbhuang@chem.pku.edu.cn
Tel.: +86-10-62753557
Fax: +86-10-62751708

Abstract Self-organized assemblies in easily precipitated mixed surfactant systems [$C_mH_{2m+1}N(CH_3)_3Br-C_{12}H_{25}SO_4Na$ $m=8, 12$, $C_nH_{2n+1}NH_2 \cdot HCl-C_{12}H_{25}SO_4Na$ $n=8, 12$] were investigated. Short-chained alcohols effectively improved the solubility of such systems and led to the dissolution of precipitation. Organized structures, such as bilayers or vesicles, could be observed under the transmission electron microscope when the volume

ratio of alcohol was appropriate. Sonication could be used as a simple method to promote the formation of vesicles. Adjusting the molar ratio of cationic and anionic surfactants resulted in the construction of multilamellar vesicular structures.

Keywords Surfactants · Transformation · Precipitate · Vesicle

Introduction

Since Kaler [1] reported vesicle formation in the cetyltrimethylammonium tosylate and sodium dodecylbenzene sulfonate system, mixed cationic–anionic surfactants have attracted great attention owing to their outstanding vesicle-forming capability, various kinds of organized assemblies, and peculiar phase behavior [2, 3]. Compared with phospholipids and other double-chained amphiphiles [4, 5], cationic–anionic surfactants have the characteristics of simple structure, excellent stability, and convenience in production; thus, the investigation of vesicle formation in such systems is of great significance. However, mixed cationic–anionic surfactant systems, especially 1:1 mixtures, usually precipitate in aqueous solutions, which greatly limit their advances in both theory and application. In contrast to the many recent works focusing on the transition between micelles and vesicles in aqueous catanionic mixtures [6, 7, 8], fewer reports on the transformation from precipitates to vesicles have been published [9]. Using the development of vesicle formation in nonaqueous media as a base [10], in this work we try to find effective ways to transform

precipitates to vesicles by introducing nonaqueous polar solvents into the mixed cationic–anionic surfactant systems which prefer to precipitate in aqueous solution. As a result, bilayer structures or multilamellar vesicles can be observed in a such case. Moreover, it was found that sonication was a simple and effective way to promote the formation of vesicles.

Experimental

Materials

Quaternary ammonium bromide was synthesized from *n*-alkyl bromide and trimethyl amine. Alkyltrimethylammonium bromide [$C_mH_{2m+1}N(CH_3)_3Br$ $m=8, 12$] was recrystallized five times in an ethanol–acetone mixture. Alkylprimaryammonium chlorides ($C_nH_{2n+1}NH_2 \cdot HCl$ $n=8, 12$) were prepared by neutralizing the corresponding alkyl primary amides ($C_nH_{2n+1}NH_2$) with HCl in ethanol, and then recrystallized 3–7 times from ethanol. Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) was of AR grade and was recrystallized four times from ethanol. The purities of all the surfactants were examined by the drop-volume method and no surface tension minimum was found on the curves of the surface tension versus the logarithm of the surfactant concentration. Ethanol, 1-propanol and 2-propanol were distilled after being treated with 4-A molecular

sieves for 48 h. 1-Octanol was distilled before use. Deionized water was treated with KMnO_4 and distilled before use.

Methods

The self-organized assemblies were prepared either by simply mixing the cationic and anionic surfactants in the solvent selected at 30 °C or by sonicating the mixtures at 50 °C. Micrographs were obtained with a transmission electron microscope (JEM-100CX II) using the freeze fracture or negative-staining technique for sample preparation.

Results and discussion

Transformation from precipitates to organized structures in 1:1 mixed systems

Two kinds of mixed cationic–anionic surfactant systems $\text{C}_m\text{H}_{2m+1}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ ($m=8, 12$) and $\text{C}_n\text{H}_{2n+1}\text{NH}_2\cdot\text{HCl}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ ($n=8, 12$) were used to study the transformation from precipitates to vesicles in catanionic surfactant mixtures. For the $\text{C}_m\text{H}_{2m+1}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ aqueous system, precipitates were easily formed when the molar ratio of cationic and anionic surfactant, C/A , was 1:1. Transition electron microscopy (TEM) results showed no sign of self-organized assemblies in such systems. Homogeneous solutions could be obtained when C/A was far from 1 ($0.25 < C/A < 4$). On the other hand, the solubility of the $\text{C}_n\text{H}_{2n+1}\text{NH}_2\cdot\text{HCl}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ system was poorer. A homogeneous solution could not be obtained even through C/A varied from 100 to 0.01. Considering the

size of the headgroup in the cationic surfactant, the molecules in the $\text{C}_n\text{H}_{2n+1}\text{NH}_2\cdot\text{HCl}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ system will be packed more densely than that in $\text{C}_m\text{H}_{2m+1}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$. As a result, the solubility of the latter is a little better.

The addition of a short-chained alcohol, such as ethanol, propanol, or butanol, will improve the solubility. For the 1:1 $\text{C}_m\text{H}_{2m+1}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ system, with the increase in the amount of alcohol added, a clear two-phase aqueous solution appeared. Double refraction phenomenon was found in the upper phase, and a vesicular structure still existed in the lower phase. When the volume ratio of alcohol was more than about 20%, a clear homogeneous solution was obtained. TEM results showed that a vesicular structure existed in the system. (Table 1, Fig. 1) It was found that with the increase in the chain length of the alcohol, the polarity of the solvent decreases, and less alcohol is needed to dissolve the precipitate in mixed systems.

For 1:1 $\text{C}_n\text{H}_{2n+1}\text{NH}_2\cdot\text{HCl}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ systems, more alcohol is needed to dissolve the precipitate. A homogeneous solution appeared at $V_{1\text{-propanol}}/V_{\text{total}} > 30\%$. The addition of 2-propanol had the same effect, but $V_{2\text{-propanol}}/V_{\text{total}}$ should be more than 50%. It is worth noting that the bilayer structures could be observed when the amount of 1-propanol or 2-propanol was appropriate (Table 2, Fig. 2).

It is well known that the kind of aggregate formed in a system depends on the value of the molecular packing parameter $P = V_c/A_0l_c$ [11], where V_c and l_c are the volume and chain length of the hydrophobic group, respectively,

Table 1. Microstructure of the 1:1 $\text{C}_m\text{H}_{2m+1}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ /short-chain alcohol/water system (30 °C)

System	Solvent	$V_{\text{alcohol}}/V_{\text{total}}$	Appearance of solution	Transmission electron microscope observation
$\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	Ethanol/water	0.10–0.21	Two phases	Vesicles
	Ethanol/water	0.25	Homogeneous	Vesicles
	1-Propanol/water	0.07–0.14	Two phases	Vesicles
	1-Propanol/water	0.20	Homogeneous	Vesicles
	1-Butanol/water	≥ 0.05	Two phases	Vesicles
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	1-Propanol/water	0.15–0.21	Two phases	Vesicles
	1-Propanol/water	0.25	Homogeneous	Vesicles

Fig. 1. Electron microscope image of the 1:1 $\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3\text{Br}-\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ system in 10% propanol solution ($V_{\text{alcohol}}/V_{\text{total}}$) by **a** negative-staining **b** freeze–fracture techniques

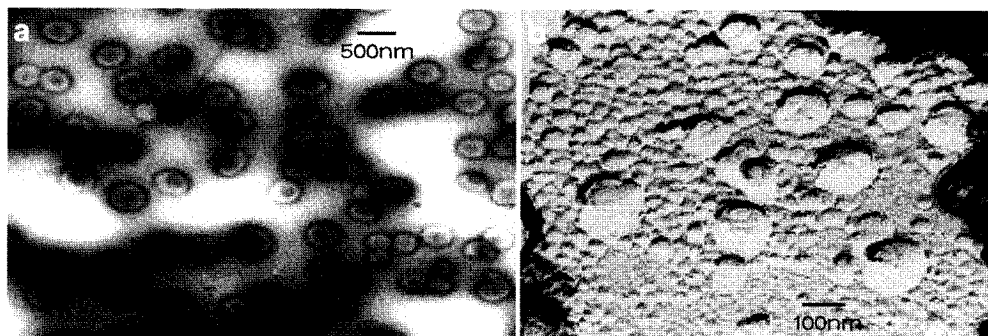


Table 2. Formation of self-organized assemblies in $C_{12}H_{25}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$ systems (total surfactant concentration of 0.010 mol l^{-1}) in mixed solvents

Solvents	$V_{\text{alcohol}}/V_{\text{total}}$	Transmission electron microscope observation
1-Propanol/water	0.30	Bilayer structures
	0.50	Bilayer structures
	0.75	Bilayer structures
	0.90	No self-organized assembly
2-Propanol/water	0.50	Bilayer structures
	0.75	Bilayer structures
	1.00	No self-organized assembly

and A_0 is the optimum area per polar group. For vesicle formation, the proper value of P falls in the range of 0.5–1, while for bilayers or even precipitates, P is more than 1. The transition from precipitates to vesicles in these systems could be attributed to the decrease in P . In aqueous solution of single cationic or anionic surfactants, no vesicles are formed, micelles are formed instead, suggesting that P is smaller than 0.5. In the mixed systems, there are strong electrostatic interactions between the headgroups of the cationic and anionic surfactants, so the mixed cationic–anionic surfactant molecules pack very tightly, indicating that the P is very large and may be larger than 1 in this case. Since the polar group of $C_nH_{2n+1}NH_2 \cdot HCl$ is smaller than that of $C_mH_{2m+1}N(CH_3)_3Br$, the of $C_nH_{2n+1}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$ molecules will be packed more densely than those of $C_mH_{2m+1}N(CH_3)_3Br$ – $C_{12}H_{25}SO_4Na$; therefore P of the former is much larger than that of the latter.

Since alcohol molecules may participate in the formation of the assemblies, the addition of a short-chained alcohol would lead to molecules packing loosely in the organized assemblies. Consequently the average area of the polar group would increase and P may drop in the range of 0.5–1. Therefore, the formation of the vesicular structure would be induced by the addition of the short-chained alcohol.

It is seen from Table 3 that no self-organized assembly was observed in the $C_{12}H_{25}NH_2 \cdot HCl$ –

Table 3. Formation of self-organized assemblies of 1:1 cationic surfactant systems in 1-propanol

System	c (mol l^{-1})	Transmission electron microscope observation
$C_{12}H_{25}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$	0.010	No self-organized assembly
$C_8H_{17}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$	0.010	Bilayer structures

$C_{12}H_{25}SO_4Na$ –1-propanol system. The situation was different when $C_{12}H_{25}NH_2 \cdot HCl$ was replaced by $C_8H_{17}NH_2 \cdot HCl$ (Table 3). Bilayers and vesicles were found to coexist in this system. It seemed that self-organized assemblies could be constructed more easily when the “tails” of the two surfactants were asymmetric. P could be effectively reduced, which finally resulted in the formation of self-organized assemblies.

In the mixtures of $C_mH_{2m+1}N(CH_3)_3Br$ – $C_{12}H_{25}SO_4Na$, no organized assemblies were found, precipitates were found instead. However, a great number of vesicles were observed after sonication for 1 h. It seemed that sonication could break the dense structure of the precipitates and lead to the formation of a vesicular structure. However, in the $C_nH_{2n+1}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$ system, sonication did not have any effect on the formation of self-organized assemblies. These facts may be attributed to the difference in the P factors in such systems. As mentioned earlier, P of the $C_mH_{2m+1}N(CH_3)_3Br$ – $C_{12}H_{25}SO_4Na$ system is much closer to 1 than that of the $C_nH_{2n+1}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$ system; therefore, the formation of vesicles will be much easier in the former system than in the latter. In addition, sonication will promote the transition of precipitates to vesicles in $C_mH_{2m+1}N(CH_3)_3Br$ – $C_{12}H_{25}SO_4Na$ systems. Thus, sonication can be used as a simple method to transform precipitates to vesicles in some systems.

It is noteworthy that the vesicles formed by sonication in $C_mH_{2m+1}N(CH_3)_3Br$ – $C_{12}H_{25}SO_4Na$ disappear after 3 weeks, indicating that the vesicles formed by sonication just have short-term stability. After enough time they will return to their equilibrium state:

Fig. 2. Electron microscope image of the 1:1 $C_{12}H_{25}NH_2 \cdot HCl$ – $C_{12}H_{25}SO_4Na$ system in **a** 1-propanol/water ($V_{1\text{-propanol}}/V_{\text{total}}=0.50$, $c=0.010 \text{ mol l}^{-1}$) and **b** 2-propanol/water ($V_{2\text{-propanol}}/V_{\text{total}}=0.50$, $c=0.010 \text{ mol l}^{-1}$) by the negative-staining technique

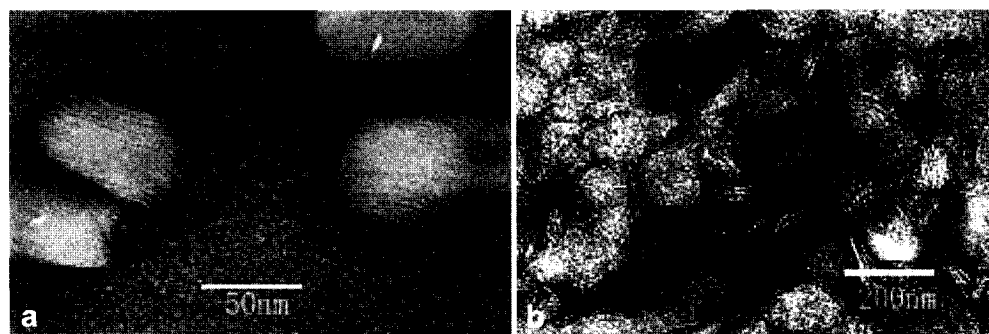


Table 4. Self-organized assembly formation of $C_{12}H_{25}NH_2 \cdot HCl-C_{12}H_{25}SO_4Na$ system with different mixed ratios. The total concentration of mixed surfactants is represented by c

C/A	c (mol l ⁻¹)	Solvent	Transmission electron microscope observation
0.5	0.015	1-Propanol	No self-organized assembly
1	0.010	1-Propanol	No self-organized assembly
1.5	0.014	1-Propanol	No self-organized assembly
2	0.015	1-Propanol	Vesicles
3	0.016	1-Propanol	Vesicles
5	0.015	1-Propanol	Vesicles
10	0.016	1-Propanol	Bilayer structures
0.5	0.015	2-Propanol	No self-organized assembly
1	0.010	2-Propanol	No self-organized assembly
2	0.015	2-Propanol	Bilayer structures

precipitates. As a comparison, the vesicles transformed by adding alcohol are more stable. The vesicles still existed after 10 weeks in $C_mH_{2m+1}N(CH_3)_3Br-C_{12}H_{25}SO_4Na$ systems.

Changing the molar ratio of cationic and anionic surfactants

The formation of self-organized assemblies in our systems was affected by the molar ratio of cationic and anionic surfactants (Table 4). In 1-propanol solutions, multilamellar vesicles (Fig. 3) could be found when C/A was between 2 and 5. In 2-propanol solution, similar results were also obtained. A bilayer structure was found when $C/A=2$. It seemed that a higher C/A ratio is beneficial to the formation of organized assemblies.

It was reported that double-chained surfactant [12, 13] can form ordered bilayer assemblies in nonaqueous media. In a previous article, we reported that a system of 1:1 cationic and anionic surfactant mixtures can also form vesicles in ethanol [10]. Our present work suggests that vesicles can be formed spontaneously in propanol by adjusting C/A . This provides a simple and effective method to obtain ordered bilayer assemblies in non-aqueous solvents.

The addition of cosurfactant also seemed to be an effective method for the transformation of self-organized assemblies in solution. In previous work, long-chained fatty alcohol was used to adjust the formation and transformation of various self-organized assemblies in a sodium alkylcarboxylate system [14]. After $0.0025 \text{ mol l}^{-1}$

1-octanol had been added to a 2:1 mixture of $C_{12}H_{25}NH_2 \cdot HCl$ and $C_{12}H_{25}SO_4Na$ (total concentration of $0.0150 \text{ mol l}^{-1}$), multilamellar vesicles were observed by TEM (Fig. 4).

Conclusion

In this work, the formation of self-organized assemblies by easily precipitated mixed surfactant systems [$C_mH_{2m+1}N(CH_3)_3Br-C_{12}H_{25}SO_4Na$, $C_nH_{2n+1}NH_2 \cdot HCl$ –

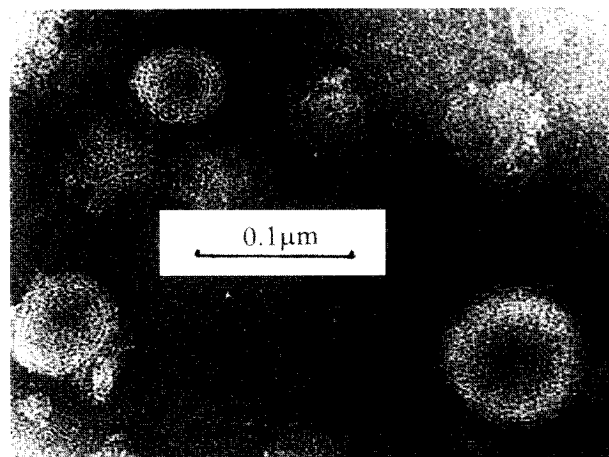
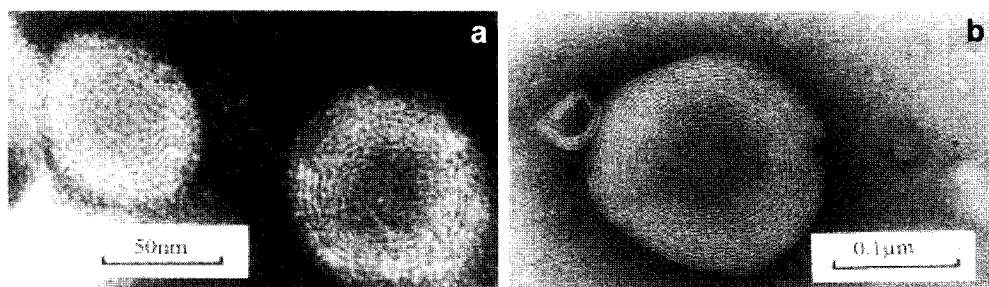


Fig. 4. Electron microscope image of the 2:1 $C_{12}H_{25}NH_2 \cdot HCl-C_{12}H_{25}SO_4Na$ system in pure 2-propanol ($c=0.0175 \text{ mol l}^{-1}$, containing $0.0025 \text{ mol l}^{-1}$ 1-octanol), observed by the negative-staining technique

Fig. 3. Electron microscope image of the $C_{12}H_{25}NH_2 \cdot HCl-C_{12}H_{25}SO_4Na$ system in pure 1-propanol with **a** $C/A=2$, $c=0.015 \text{ mol l}^{-1}$ and **b** $C/A=5$, $c=0.015 \text{ mol l}^{-1}$ by the negative-staining technique



$C_{12}H_{25}SO_4Na$] was investigated. The solubility of the system with the larger polar group [$C_mH_{2m+1}N(CH_3)_3Br-C_{12}H_{25}SO_4Na$] was better than that with the smaller one ($C_nH_{2n+1}NH_2\cdot HCl-C_{12}H_{25}SO_4Na$). The addition of a short-chained alcohol can transform the precipitates to a bilayer structure or vesicles. It seems that self-organized assemblies can be constructed more easily when the "tails" of the two surfactants are asymmetric. Sonication could be used as a simple method to promote the formation of vesicles, but these

just have short-term stability. Adjusting the molar ratio of cationic and anionic surfactants led to the construction multilamellar vesicular structures. This work provides an effective way of transforming precipitates to the desired organized microstructure and opens a vista of research on mixed cationic-anionic surfactant systems.

Acknowledgement The project was supported by the National Natural Science Foundation of China (20073002, 29992590-4).

References

1. Kaler EW, Murthy AK, Rodriguez BE, Zasadinski TAN (1989) *Science* 245:1371
2. Zhao GX, Huang JB (1992) *Acta Physicochim Sin* 8:583
3. Huang JB, Zhao GX (1995) *Colloid Polym Sci* 273:156
4. Isikawa Y, Kuwahara H, Kunitake T (1994) *J Am Chem Soc* 116:5579
5. Kimizuka N, Wakiyama T, Miyauchi H, Yoshimi T, Tokuhito M, Kunitake T (1996) *J Am Chem Soc* 118:5805
6. Bergstrom M, Pedersen JS, Schurt-enberger P, Egelhaaf SU (1999) *J Phys Chem B* 103:888
7. Villeneuve M, Kaneshina S, Imae T, Aratono M (1999) *Langmuir* 15:2529
8. Salkar RA, Mukesh D, Samant SD, Manohar C (1998) *Langmuir* 14:3778
9. Zhang XR, Huang JB, Mao M, Tang SH, Zhu BY (2001) *Colloid Polym Sci* 279:1245
10. Huang JB, Zhu BY, Zhao GX, Zhang ZY (1997) *Langmuir* 13:5759
11. Israelachvili JN (1985) *Intermolecular and surface forces: with applications to colloidal and biological systems*. Academic, London
12. Kimizuka N, Tokuhito M, Miyauchi H, Wakiyama T, Kunitake T (1997) *Chem Lett* 1049
13. Kuwahara H, Isikawa Y, Kunitake T (1993) *J Am Chem Soc* 115:3002
14. Mao M, Huang JB, Shi HT, He X, Zhu BY, Fu HL (2000) *Chin J Chem* 18:688