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SHORT COMMUNICATION

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From precipitation to vesicles: a study on self-organized assemblies by alkylammonium and its mixtures in polar solvents

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Abstract The formation of self-organized assemblies by $C_nH_{2n+1}NH_2 \cdot HCl$ and $C_{12}H_{25}SO_4Na$ in polar solvents was studied. By adding 1-propanol or 2-propanol, the precipitation formed in aqueous solution was resolved and a bilayer structure was discovered. Furthermore, multilamellar vesicle formation could be observed by methods of adjusting the molar ratio of $C_nH_{2n+1}NH_2 \cdot HCl$ to $C_{12}H_{25}SO_4Na$, changing the length of the hydrocarbon chain of $C_nH_{2n+1}NH_2 \cdot HCl$, or adding 1-octanol to the mixed surfactant systems.

Key words Cationic and anionic surfactant mixtures · Self-organized assemblies · Vesicle · Alkylprimary-ammonium chlorides · Polar solvents

Introduction

Since Kaler et al. [1] gave the first example of vesicle formation from mixed cationic and anionic surfactants using cetyltrimethylammonium tosylate and sodium dodecylbenzene sulfonate, 1:1 mixed cationic–anionic surfactants have showed outstanding vesicle-forming capability, even better than double-chained surfactants [2, 3]. In contrast to the numerous research work on vesicle formation in aqueous systems [1, 4–7], fewer reports on vesicle formation in nonaqueous solutions have been published and they mainly focused on the systems of double-chained fluorocarbon surfactants [8–11] and natural phospholipids [12–14]. Compared with phospholipids and other double-chained amphiphiles, the cationic–anionic surfactants have the characteristics of simple structure, excellent stability, and convenience in production; thus the investigation of vesicle formation by such systems is of great significance. However, mixed cationic–anionic surfactant systems, especially 1:1 mixtures, usually precipitate in aqueous solutions, which greatly limited their advances in both theory and application. In our previous work [15, 16], we reported the vesicle formation of 1:1 cationic and anionic surfactant mixtures in different nonaqueous polar solvents, and the effect of the medium dielectric constant [15] could explain the results very well. In this work, we deal with mixed cationic–anionic surfactant systems that precipitate easily in aqueous solutions, which is quite different from the systems we investigated before; nonaqueous polar solvents were used to improve the solubility of the system and a bilayer structure could also be observed by this way. Moreover, multilamellar vesicles were observed after further adjustments were applied.

Experimental

Material

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 were 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 measuring the surface tensions of aqueous solutions using the drop-volume method [17] and no surface tension minimum was found in their surface tension curves (γ-log$c$). 1-Propanol and 2-propanol were treated with 4-Å molecular sieves to remove traces of water and were then distilled. 1-Octanol was distilled before use.

Deionized water was treated with $KMnO_4$ and was distilled before use.

Methods

The mixed surfactant self-organized assemblies were prepared by simple mixing of the cationic and anionic surfactants in the solvent at room temperature (around 25 °C) or by heating to about 70 °C.

Micrographs were obtained with an electron microscope (JEM-100CXΠ) using the negative-staining technique for sample preparation: a few drops of the sample solution were applied to carbon-coated Cu grids and dried, then a drop of uranyl acetate–ethanol solution was added as the staining agent. The staining process was 1–2 min depending on the different systems.

The phase-transition temperature, T_c, of the vesicle in the mixed cationic and anionic surfactant systems was measured by use of a differential scanning calorimeter (DSC) (Dupont 1090; with a heating rate of 2 or 5 °C/min). The endothermic peak was determined to be the T_c value of the system.

Results and discussion

In aqueous solutions, the strong electrostatic attraction between $C_nH_{2n+1}NH_2{\cdot}HCl$ and $C_{12}H_{25}SO_4Na$ makes their 1:1 mixture precipitate easily, like the 1:1 $C_nH_{2n+1}N(CH_3)_3Cl$ and $C_{12}H_{25}SO_4Na$ mixed system. The latter could be resolved when the molar ratio of $C_nH_{2n+1}N(CH_3)_3Cl$ to $C_{12}H_{25}SO_4Na$ was far from 1, but the former, however, still could not form stable homogeneous solutions even when the molar ratio of $C_nH_{2n+1}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4Na$ varied from 100 to 0.01, and the electron microscopy (EM) results showed no sign of self-organized assembly formation in such systems.

The addition of 1-propanol improved the solubility of these systems. In the 1:1 $C_nH_{2n+1}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed system, the precipitation was resolved as the volume ratio of 1-propanol in total solvents was more than 30%. The addition of 2-propanol had the same effect, but the volume ratio of 2-propanol in total solvents should be more than 50%. It is worth noting that a bilayer structure could be observed when the amount of 1-propanol or 2-propanol was appropriate (Table 1, Fig. 1).

Table 1 Self-organized assembly formation of 1:1 $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4$ systems (with a concentration of 0.010 mol l^{-1} mixed surfactants) in mixed and pure solvents. α_0 is the volume ratio of 1-propanol or 2-propanol in total solvents, + represents bilayer structures, and − represents no self-organized assembly

Solvents	α_0 (%)	Electron microscopy results
1-Propanol/water	30	+
	50	+
	75	+
	90	−
	100	−
2-Propanol/water	50	+
	75	+
	100	−

In aqueous solution, the 1:1 $C_nH_{2n+1}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed system could be illustrated as molecules packing parallelly and densely (Fig. 2a), and it seemed that 1-propanol could enter the assemblies and reside in the polar group layer (Fig. 2b), making surfactant molecules pack loosely and they were thus soluble.

It is well known that the kind of aggregate forming in a system will depend on the value of molecular packing parameter, $P = V_c/A_0l_c$, where V_c and l_c are the volume and chain length of the hydrophobic group, respectively, and A_0 is the optimum area per polar group. For vesicle formation, the proper value of P is between 0.5 and 1, and for bilayer and precipitation, the P value will be more than 1 [18]. Most probably, the P value of the 1:1 $C_nH_{2n+1}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed system in aqueous solution is more than 1; thus, precipitation occurs easily. The addition of 1-propanol or 2-propanol not only improved the solubility of such a system, but

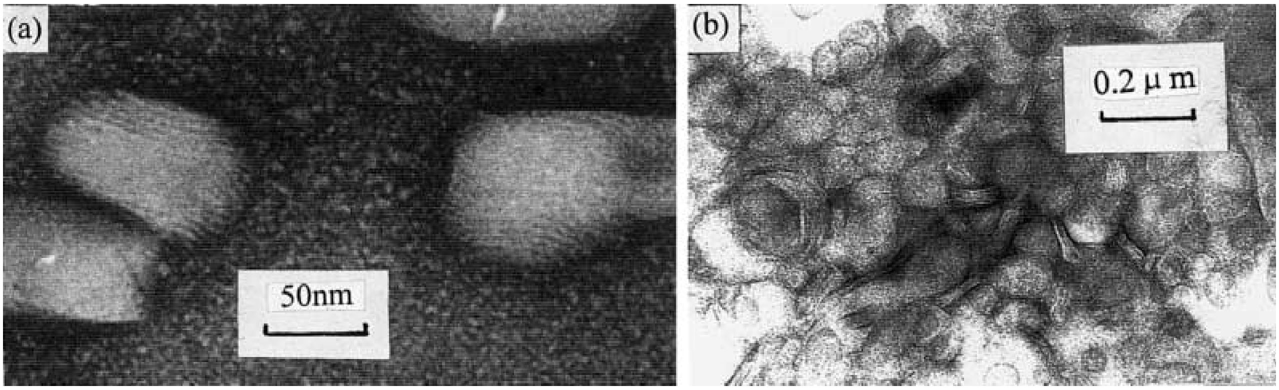


Fig. 1 Electron microscopic image from the 1:1 $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed systems in **a** 1-propanol/water ($\alpha_0 = 50\%$, $c = 0.010$ mol l^{-1}) and **b** 2-propanol/water ($\alpha_0 = 50\%$, $c = 0.010$ mol l^{-1}), observed by the negative-staining technique

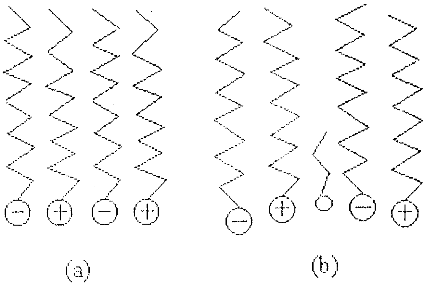


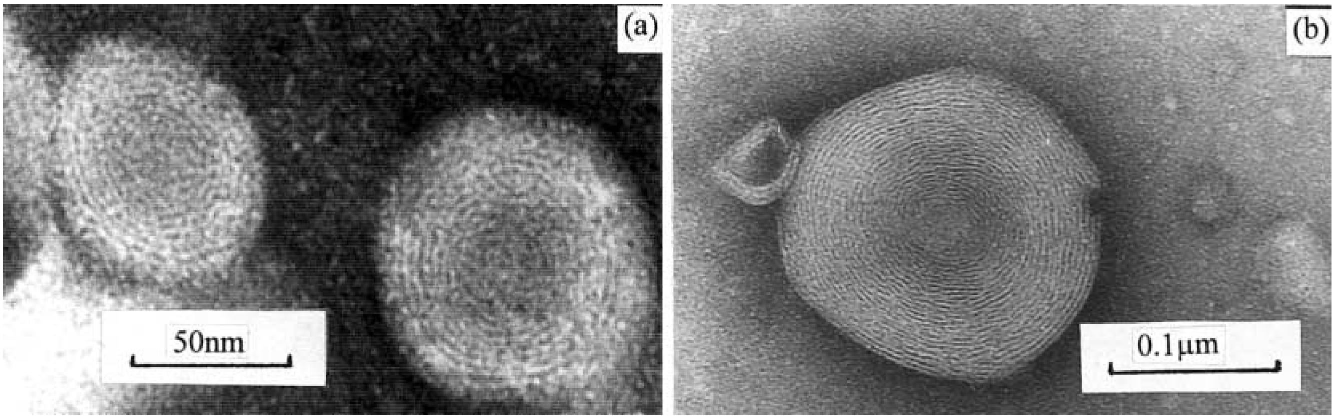
Fig. 2 Scheme illustration for the structures of **a** the $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ system in aqueous solution and **b** the $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ system with addition of 1-propanol

Table 2 Self-organized assembly formation of $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4$ systems when the molar ratio of $C_{12}H_{25}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4$ (*N*/*S*) was adjusted. *c* is the total concentration of mixed surfactants; + + represents vesicles

N/*S*	*c* (mol l^{-1})	Solvents	Electron microscopy results
1	0.010	1-Propanol	–
0.5	0.0138	1-Propanol	–
2	0.015	1-Propanol	+ +
3	0.016	1-Propanol	+ +
5	0.015	1-Propanol	+ +
10	0.0165	1-Propanol	+
0.5	0.015	1-Propanol	–
1	0.010	2-Propanol	–
0.5	0.015	2-Propanol	–
0.5	0.015	50% 2-Propanol	–
2	0.015	2-Propanol	+
2	0.015	50% 2-Propanol	–

also enlarged the value of A_0, which resulted in a smaller value of *P* and thus promoted the transformation from precipitation to a bilayer structure.

Fig. 3 Electron microscopic image from $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed systems in pure 1-propanol observed by the negative-staining technique: **a** *N*/*S* = 2, *c* = 0.015 mol l^{-1}; **b** *N*/*S* = 5, *c* = 0.015 mol l^{-1}



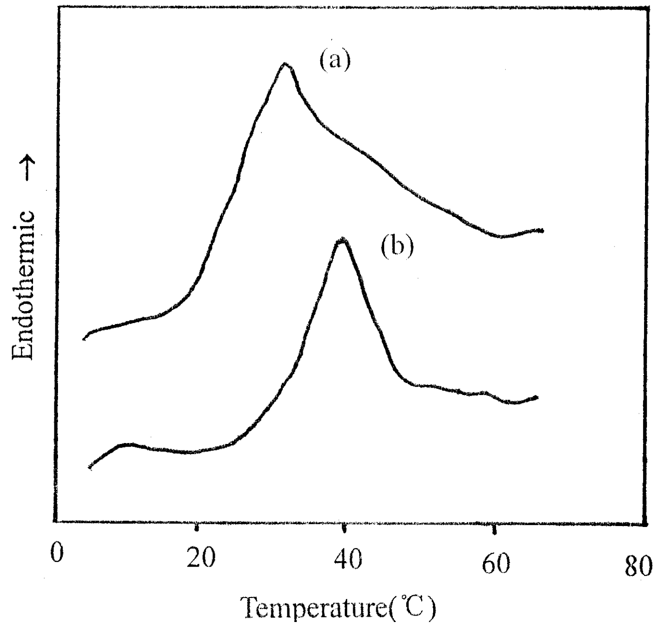


Fig. 4 Differential scanning calorimetry curves of $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ mixed systems in pure 1-propanol: **a** *N*/*S* = 2, *c* = 0.015 mol l^{-1}; **b** *N*/*S* = 5, *c* = 0.015 mol l^{-1}

Further adjustments were also applied in each case where we had observed the transformation of self-organized assemblies.

Formation of organized assemblies in our systems was affected largely by the molar ratio of $C_{12}H_{25}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4Na$ (Table 2). In 100% 1-propanol solutions, multilamellar vesicles (Fig. 3) could be observed when the molar ratio of $C_{12}H_{25}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4Na$ was between 2 and 5 (DSC curves confirmed the existence of bilayer structure formation, Fig. 4, Table 3) and no organized structure was observed under EM when the molar ratio of $C_{12}H_{25}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4Na$ was less than 1. In 2-propanol systems, the results were similar to 1-propanol systems. It is obvious that the electrostatic

Table 3 Differential scanning calorimetry results of some vesicle systems

Mixed systems	*N*/*S*	*c* (mol l^{-1})	Solvents	T_c (°C)
$C_{12}H_{25}NH_2 \cdot HCl + C_{12}H_{25}SO_4$	2	0.015	1-Propanol	30.6
	5	0.015	1-Propanol	39.1
$C_8H_{17}NH_2 \cdot HCl + C_{12}H_{25}SO_4$	1	0.010	1-Propanol	46.4
	2	0.015	1-Propanol	41.5
$C_{12}H_{25}NH_2 \cdot HCl + C_{12}H_{25}SO_4 + C_8H_{17}OH$	2	0.0175 (containing 0.0025 mol l^{-1} $C_8H_{17}OH$)	2-Propanol	66.5

attraction between $C_{12}H_{25}NH_2 \cdot HCl$ and $C_{12}H_{25}SO_4Na$ is strongest when they are mixed 1:1, so the $C_{12}H_{25}NH_2 \cdot HCl$–$C_{12}H_{25}SO_4Na$ systems mixed unequally could result in weaker electrostatic attraction, which might make the value of *P* smaller and fall in the range 0.5–1. This effect could explain the vesicle formation when the molar ratio of $C_{12}H_{25}NH_2 \cdot HCl$ to $C_{12}H_{25}SO_4Na$ was between 2 and 5, but it was not suitable for the situations when the amount of $C_{12}H_{25}NH_2 \cdot HCl$ was less than that of $C_{12}H_{25}SO_4Na$. Thus, we suggest that $C_{12}H_{25}NH_2 \cdot HCl$ played the main role in the processes of forming self-organized assemblies, and the adjustment of the $C_{12}H_{25}SO_4Na$ concentration might have two opposite results: promoting the transformation from bilayers to vesicles when the concentration was low and destroying organized assemblies when the concentration was too high. The following result was in agreement with our explanation: in a 100% 1-propanol solution with a concentration of 0.0145 mol l^{-1} $C_{12}H_{25}NH_2 \cdot HCl$, an obvious bilayer structure was observed.

As already mentioned, in 100% 1-propanol, no self-organized assembly was observed under EM from the system of the 1:1 $C_{12}H_{25}NH_2 \cdot HCl$–$C_{12}H_{25}SO_4Na$ mixture. However, the situation was quite different after $C_{12}H_{25}NH_2 \cdot HCl$ was changed for $C_8H_{17}NH_2 \cdot HCl$ (Table 4); we observed the coexistence of bilayers and vesicles. It seemed that when the "tails" of the two surfactants were asymmetric, the value of *P* could be

Table 4 Self-organized assembly formation of $C_8H_{17}NH_2 \cdot HCl$–$C_{12}H_{25}SO_4$ systems in mixed and pure solvents

Solvents	c (mol l^{-1})	N/S	α_0 (%)	Electron microscopy results
1-Propanol/water	0.010	1	50	+ +
	0.010	1	100	+ +
	0.015	2	100	+ +
2-Propanol/water	0.010	1	50	+

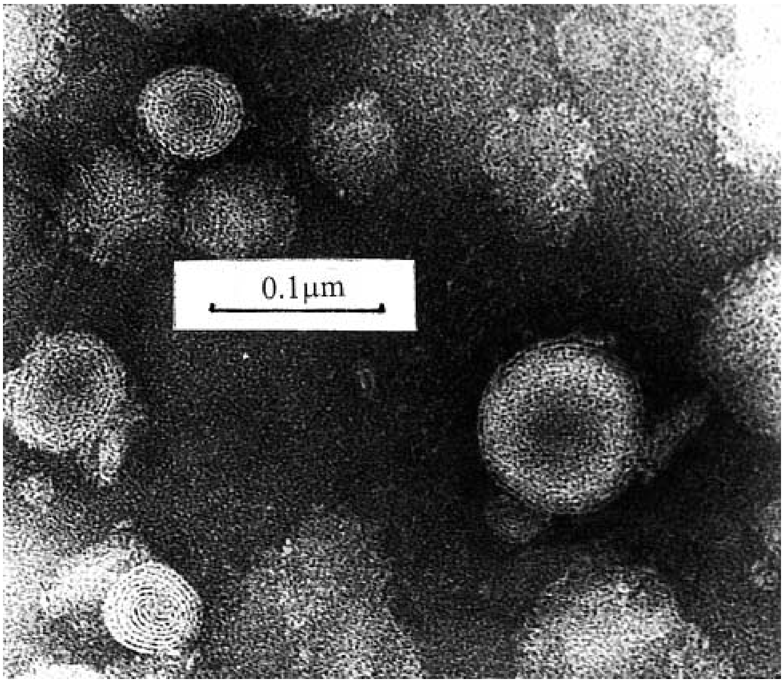


Fig. 5 Electron microscopic image from the 2:1 $C_{12}H_{25}NH_2 \cdot HCl$–$C_{12}H_{25}SO_4Na$ mixed system in pure 2-propanol ($c = 0.0175$ mol l^{-1}, containing 0.0025 mol l^{-1} 1-octanol), observed by the negative-staining technique

effectively decreased, which finally resulted in easier construction of organized assemblies.

The addition of cosurfactant also seemed to be an effective method for the transformation of self-organized assemblies in solution. In our previous report [19], fatty alcohol as cosurfactant added to the sodium alkylcarboxylate system was used to adjust the formation and transformation of various self-organized assemblies. For the systems discussed here, the addition of 1-octanol seemed to have no effect on the formation and transformation of self-organized assemblies, but for one exception: in 100% 2-propanol and the 2:1 $C_{12}H_{25}NH_2{\cdot}HCl$–$C_{12}H_{25}SO_4Na$ system (total concentration 0.0150 mol l^{-1}) with addition of 0.0025 mol l^{-1} 1-octanol. Multilamellar vesicles were observed in this system under EM (Fig. 5), compared with a bilayer structure before the addition of 1-octanol. It is reasonable that the T_c value of this system was quite high (Table 3), since the participation of 1-octanol in oriented bimolecular layers made the molecules pack more closely.

Conclusion

The formation of self-organized assemblies by mixed $C_nH_{2n+1}NH_2{\cdot}HCl$ and $C_{12}H_{25}SO_4Na$ systems in nonaqueous polar solvents (1-propanol and 2-propanol) was investigated. Nonaqueous polar solvents effectively improved the solubility of such systems, and bilayer structures could be observed at the appropriate volume ratio of 1-propanol/water or 2-propanol/water. Adjustments of the molar ratio of $C_nH_{2n+1}NH_2{\cdot}HCl$ to $C_{12}H_{25}SO_4Na$ and the length of hydrocarbon chain were both effective methods to construct multilamellar vesicle structures; the addition of 1-octanol sometimes also had an effect on vesicle formation. This work showed a simple way of transforming a precipitate to the desired organized microstructure and opened a vista of research on mixed cationic–anionic surfactant systems.

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