

Structure and physico-chemical properties in mixed aqueous solution of sodium alkylcarboxylate-alkyltrimethylammonium bromide

HUANG, Jian-Bin*(黄建滨) ZHAO, Guo-Xi(赵国玺) HE, Xu(何煦) ZHU, Bu-Yao(朱步瑶)
FU, Hong-Lan(付宏兰)

Institute of Physical Chemistry, Peking University, Beijing 100871, China

The physico-chemical properties of organized assemblies (micelle or vesicle) from sodium alkylcarboxylate - alkyltrimethylammonium bromide mixture have been investigated systematically. In different mixed cationic-anionic surfactant systems, micelles and vesicles can coexist or be transformed into each other on different conditions. The experimental results are explained preliminarily from the viewpoint of molecular packing geometry. The solubilization of organic compound in the mixed surfactant system was also studied in detail.

Keyword Cationic-anionic surfactant mixture, micelle-vesicle transformation, solubilization of organic compounds in micelles

Introduction

In the last two decades, synthetic vesicles have attracted more and more attention because they have been very useful in understanding the nature of biomembrane and in developing new technique by biomimesis.^{1,2} Up to ten years ago, amphiphiles used to form vesicles were mainly the double chained compounds including natural and synthesized amphiphiles. In 1989, Kaler *et al.*³ first reported the vesicle formation in cationic and anionic surfactant system. Similar work also started in our group in 1990.⁴ However, the nature of vesicle formation and many peculiar properties of the mixed cationic-anionic surfactants remain unclear. Unfortunately most of the mixed solutions of cationics and anionics are opalescent at 1:1 mixing ratio while the surfactant concentration is greater than the critical micellar concentration (cmc), which makes it difficult to investigate its physi-

co-chemical properties at proper concentration. However, the 1:1 sodium alkylcarboxylate - alkyltrimethylammonium bromide systems have a good solubility, especially for the solution of decanate-decyltrimethylammonium bromide which is very clear at any mixing ratio even if the concentration is far beyond cmc, providing a suitable model system for studying the characteristics of this kind of system.

In the present work, the aqueous mixtures of sodium alkylcarboxylate-alkyltrimethylammonium bromide have been investigated. Results on the formation of various organized assemblies, transformation between them, the solubilization of organic compounds in the cationic-anionic micelles were provided.

Experimental

Materials

Sodium alkylcarboxylate (C_nCOONa , $n = 9, 11$) was prepared from the neutralization of the corresponding carboxylic acid (C_nCOOH) and NaOH at equimolar ratio in ethanol, then the solvent was removed and C_nCOONa was dried under vacuum. C_9COOH was doubly distilled and $C_{11}COOH$, recrystallized five times in ethanol-water mixture (m. p. 43—44 °C). Alkyltrimethylammonium bromides (C_mNMBr , $m = 8, 10$) were synthesized from n -alkyl bromide and tri-methyl amine. The crude products were recrystallized five times from an ethanol-acetone mixture. The purities of all the surfactants were ex-

aminated by surface tension measurement using drop volume method and no surface tension minimum was found in their surface tension curves. *p-N*, *N*-Dimethylaminostyrylphenylmalononitrile is the product of Fluka, A. R. grade. Pyrene was recrystallized twice before use. Water was deionized and treated with KMnO_4 and distilled. Other reagents and solvents were products of Beijing Chemical Co., A. R. grade.

Methods

The mixed surfactant vesicles were prepared by simply mixing the cationic and anionic surfactant solution at room temperature ($\sim 25^\circ\text{C}$) or by sonicating the mixed surfactant solution for 0.5 h at 50°C (Sonicator: Haitung CQ-250). The pH value was adjusted to 9.2 (by $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $0.01 \text{ mol} \cdot \text{dm}^{-3}$). Vesicle image was observed with transmission electronic microscope (JEM-100CXII) by the freeze-fracture and negative-staining technique (with uranyl acetate). Pyrene and *p-N*, *N*-dimethylaminostyrylphenylmalononitrile were used as the fluorescence probes to measure the aggregation number of cationic-anionic micelle⁴ and micro viscosity of organized assemblies.⁵ The phase transition temperature (T_c) of organized assemblies was determined by differential scanning calorimeter (DSC, Dupont 1090B) with the heating rate of $5^\circ\text{C}/\text{min}$. Polar or non-polar organic compounds were added into the surfactant micellar solution until the solution is cloudy. The solubility of organic compounds was used as the parameter of solubilization in micelles for the further investigation. The viscosities were measured using Oswald Viscometer.

Results and discussion

Formation of organized assemblies in 1:1 mixed aqueous solution of sodium alkylcarboxylate - alkyltrimethylammonium bromide

The cmc of 1:1 $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$ system is $9.8 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ determined by surface tension method. For this system at the total concentration of $5.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, the aggregation number is ~ 798 obtained by fluorescence probe method⁵ and no vesicle has been found in the solution by transmission electronic microscope (TEM) observation. The hydrodynamic radius of the micelle obtained by quasi-elastic light scattering

method is about 20 nm. It is too large for a spherical micelle, indicating that micelles in this cationic-anionic surfactant solution should be of rod-like shape.⁶ The cmc value of 1:1 $\text{C}_{11}\text{COONa}-\text{C}_8\text{NMBr}$ system ($6.3 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) is smaller than that in 1:1 $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$ system, showing that the micelle formation is easier in 1:1 $\text{C}_{11}\text{COONa}-\text{C}_8\text{NMBr}$ system than that in 1:1 $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$ system.

After sonicated, no visible change in the micellar solution of 1:1 $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$ system has been found. However, TEM observation shows the existence of unilamellar vesicles in the mixed system (Fig. 1). The vesicles disappeared after a week at room temperature ($\sim 20^\circ\text{C}$), albeit the solution appearance still keeps unchanging. Sonicating this solution, we find that vesicles can form again and then disappear after about a week. This process of sonication-vesicle formation-aging-vesicle disappearance can be repeated many times in this system. It reveals that vesicle formation in this system is not a spontaneous process, but a process occurring in the condition of sonication; and when left there, transformation from vesicle to micelle occurs spontaneously. The transforming velocity is influenced by temperature. It is found that at lower temperature ($\sim 2^\circ\text{C}$) the vesicles can stand for a longer time (more than three weeks) than at room temperature, indicating that the transformation from vesicle to micelle is slower or the vesicle is more stable at lower temperature.

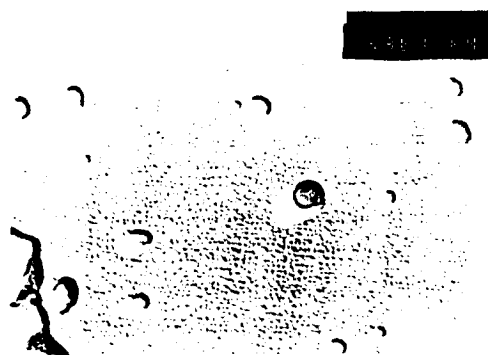


Fig. 1 Vesicle formation in 1:1 mixed $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$ system ($\times 49,000$ times, with sonication, TEM observation by freeze-fracture technique, $C = 2.4 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$).

However, situation is different in 1:1 mixed C_{11} -

COONa-C₈NMBr system. Vesicles formed either by sonication or spontaneously (without sonication), which could be stable in 4 weeks (Fig. 2). But the solution became cloudy and precipitates formed while vesicles disappeared after more than one month. Only few vesicles were found when re-sonicating the cloudy system. However, it is interesting to find that a small amount of ethanol added to the solution can make the precipitates dissolve and the solution clear. TEM observation demonstrates that vesicles formed again in C₁₁COONa-C₈NMBr system after adding small amount of ethanol.

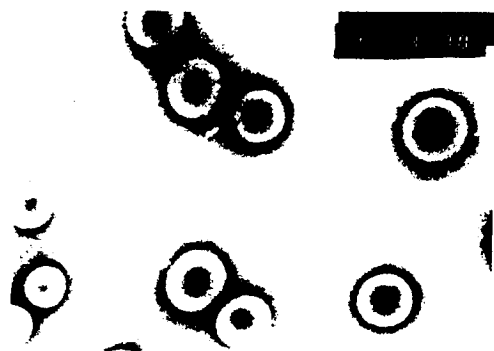


Fig. 2 Vesicle formation in 1:1 mixed C₁₁COONa-C₈NMBr system ($\times 49,000$ times, without sonication, $8.3 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, aging 4 weeks).

The vesicle forming-ability and stability of C₉COONa-C₁₀NMBr system were different from those of C₁₁COONa-C₈NMBr system, which might be explained as follows:

It is well known, surfactant aggregates have a wide variety of structures including micelles, vesicles and bilayers. In a system, what kind of aggregate forming 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, A_0 is the optimum area per polar group. For vesicle formation, the proper value of P falls in the range of $1/2$ to 1 and for rod-like micelle, $1/3$ to $1/2$.⁷ Albeit there are the same hydrophilic headgroups and the same total hydrocarbon chain carbon numbers in the two mixed systems, the situations of hydrophobic part of individual surfactants for the two systems are different. For the C₉COONa-C₁₀NMBr system, the hydrocarbon chains of the two organic ionic surfactants are near the same length, while in C₁₁-

COONa-C₈NMBr system the hydrophobic chain length of anionic surfactant is much longer than that of cationic surfactant. In the former case, all the hydrocarbon chains would be stretching and packing parally (Fig. 3a). On the other hand, in the latter case, *i. e.*, in the unsymmetric cationic-anionic surfactant system, the anionic surfactant molecules would tend to shrink themselves and make their length of hydrophobic part close to that of C₈NMBr molecules for the benefit of the hydrophobic effect and lowering the energy level of the system (Fig. 3b). This effect will increase the value of V_c/l_c and the value of P in C₁₁COONa-C₈NMBr system, which increase the possibility to form the vesicles. Thus it is understandable to see that vesicles can form spontaneously in C₁₁COONa-C₈NMBr system but just form after sonication in C₉COONa-C₁₀NMBr system. Similar results are also obtained in the 1:1 mixed systems of C_{*m*}NMBr and sodium alkylsulphate (C_{*n*}SO₄Na). Vesicles form in 1:1 C₁₂SO₄Na-C₈NMBr system after sonication, but no vesicles are found in 1:1 C₁₀SO₄Na-C₁₀NMBr system whether with or without sonication. The unsymmetric cationic-anionic surfactant system (C₁₂-SO₄Na-C₈NMBr) still shows stronger vesicle forming capability than C₁₀SO₄Na-C₁₀NMBr system.

The phase behaviours in these two systems are also consistent with the conclusion we mentioned above. Generally, a system with a small value of P tends to form a micelle solution, which is clear and thermodynamically stable just like the situation in C₉COONa-C₁₀NMBr system; while a system with a quite large value of P tends to form vesicle, bilayer or even precipitate, as the situation of C₁₁COONa-C₈NMBr system. According to this view point, it is also understandable that the addition of a small amount of ethanol would promote the transformation from precipitate to vesicles in C₁₁COONa-C₈NMBr system since the small amount of ethanol would enter the assemblies and reside in the polar group layer (Fig. 3c), resulting in expanding the polar layer and decreasing the P value of the system. In fact the C₁₁COONa-C₈NMBr solution changed its appearance to clear after small amount of ethanol addition in it, indicating that the P value of C₁₁COONa-C₈NMBr system may be decreased and smaller than original one, which maybe too large for vesicle formation and brings about precipitation. With the precipitation dissolved, the effective surfactant concentration also increased. Consider-

ing the fact that vesicles can be formed in some surfactant systems with large amount of ethanol⁸ (especially in 1:1 cationic-anionic surfactant mixed systems⁹), thus,

it is understandable that vesicles can form again in the $C_{11}COONa-C_8NMBr$ systems after the addition of small amount of ethanol.

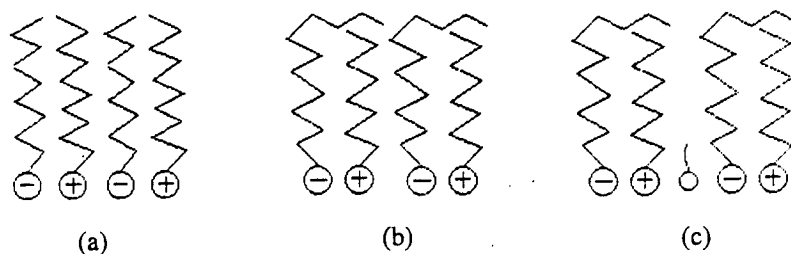


Fig. 3 Scheme illustration for the structures of (a) $C_9COONa-C_{10}NMBr$ system and (b) $C_{11}COONa-C_8NMBr$ system in aqueous solution and (c) $C_{11}COONa-C_8NMBr$ system with small amount ethanol addition.

Microviscosity and phase transition temperature of organized assemblies in the 1:1 cationic-anionic surfactant systems

The microenvironment of organized assemblies (micelle and vesicle) is studied using of fluorescence probe. It is seen from Table 1 that in $C_9COONa-C_{10}NMBr$ system the values of microviscosity in various forms of organized assemblies are different. The microviscosity value of the assemblies in the system after sonication

($60 \times 10^{-3} \text{ mpa} \cdot \text{s}$) is obviously higher than that before sonication ($47 \times 10^{-3} \text{ mpa} \cdot \text{s}$). This result is reasonable, since it is well known that the packing of amphiphiles in vesicles is more compact than that in micelles. On the other hand, in $C_{11}COONa-C_8NMBr$ system, whether before or after sonication the microviscosities are of the same value. This phenomenon is also coincident with the results by EM observation—vesicles formed in both cases.

Table 1 Microviscosity (20°C) and T_c in cationic-anionic surfactant system

Surfactant systems ^a	C^b ($\text{mol} \cdot \text{dm}^{-3}$)	Organized assemblies ^c	Viscosity ($\text{mpa} \cdot \text{s}$)	T_c (°C)
$C_9COONa-C_{10}NMBr^{ns}$	0.052	M & V	60	33.1
$C_9COONa-C_{10}NMBr^s$	0.052	M	47	28.5
$C_{11}COONa-C_8NMBr^{ns}$	0.083	M & V	55	25.6
$C_{11}COONa-C_8NMBr^s$	0.083	M & V	55	25.6

^a pH = 9.2, ^s sonication; ^{ns} no sonication. ^b C is the total surfactant concentration. ^c M - micell; V - vesicle.

The T_c results in 1:1 mixed cationic-anionic surfactant system are also listed in Table 1. The phase transition in $C_{11}COONa-C_8NMBr$ system occurs at 25.6°C, whether the system is sonicated or not, indicating the assemblies existing in both cases are all the same once again. The phase transition temperature in the $C_9COONa-C_{10}NMBr$ vesicular dispersion (33.1°C) is higher than that in $C_{11}COONa-C_8NMBr$ system, implying the molecular packing is more compact in $C_9COONa-C_{10}NMBr$ vesicles than that in $C_{11}COONa-C_8NMBr$ system. These results support our inference about the conformation of hydrocarbon chains in assemblies (Fig. 3) and the ex-

planation on the regularity of vesicle formation very well. It is noteworthy that the DSC measurement also shows a jump for $C_9COONa-C_{10}NMBr$ system without sonication, although no vesicle has been found by EM observation in that case. It may indicate that there also exist change of chain conformation in large rod-like micelle. T_c value of vesicular system is higher than that for micellar solution of $C_9COONa-C_{10}NMBr$ mixture, demonstrating that the packing of the mixed cationic-anionic surfactant molecules in the vesicles is more compact than that in micelles, which is in accord with the result of microviscosity measurement.

Solubilization of organic compounds in cationic-anionic surfactant micelle

In contrast to most aqueous cationic-anionic surfactant systems, the solution of $C_9COONa-C_{10}NMBr$ is very clear at any ratio even if the total surfactant concentration is far beyond the cmc. Thus, it is possible to make research on solubilization of organic compounds in this cationic-anionic surfactant micelle. *n*-Octanol and *n*-octane were used as typical polar and non-polar solubilizes. The results of solubilization in $C_9COONa-C_{10}NMBr$ system (pH = 9.2, $C = 0.20 \text{ mol} \cdot \text{dm}^{-3}$) are shown in Table 2.

Table 2 Solubilization ($\text{mol} \cdot \text{dm}^{-3}$) of organic compounds in $C_9COONa-C_{10}NMBr$ system^a

α_a	<i>n</i> -Octanol	<i>n</i> -Octane
0.10	8.1×10^{-2}	3.1×10^{-2}
0.20	5.7×10^{-2}	3.8×10^{-2}
0.50	2.1×10^{-2}	5.1×10^{-2}
0.75	3.2×10^{-3}	6.2×10^{-2}
0.80	6.3×10^{-3}	5.4×10^{-2}
0.90	1.1×10^{-2}	2.4×10^{-2}

^a pH = 9.2, the total surfactant concentration is $0.2 \text{ mol} \cdot \text{dm}^{-3}$. α_a is the anionic surfactant molar fraction in the bulk of the mixed surfactant.

It is seen that the solubilization of these two organic compounds varied as α_a . There is a maximum solubility for *n*-octane at $\alpha_a = 0.75$, while a minimum for *n*-octanol at the same α_a value. These results are interesting and can be explained in terms of the characteristics of composition and structure of the micelle and the solubilities. It is well known, mechanisms of solubilization of the polar and non-polar organic compounds in micelles are different.¹⁰ The polar organic compound, particularly alkanols is solubilized in the palisades of the micelle, while the non-polar organic compounds like alkanes are usually solubilized in the inner cores of the micelles. Therefore, solubilization of polar and non-polar organic compounds will depend on the capacity of outside polar group layer and that of the inner nonpolar core of the micelles, respectively. Mixed cationic and anionic surfactants can form micelles with different charge depending on the mole fraction of the mixed surfactant in solution and micellization capability of the two components. When the mixed micelle is electrical neutral, there is

the largest attractive interaction between the polar groups in the micelle resulting in the largest volume of micelle and the closest polar group layer. As described above, rod-like would be a proper shape⁴ for the micelles in 1:1 $C_9COONa-C_{10}NMBr$ system. The closest polar layer determines the lowest solubilization amount of *n*-octanol. On the other hand, in condition of keeping surface area constant, a rod-like micelle can enlarge its volume by changing its shape to spheric,¹¹ implying that there is a large room for non-polar compound (*n*-octane) to be solubilized. This would make more *n*-octane solubilized in this kind of system than usual one.

Table 3 Influence of solubilizing *n*-octane to viscosity in 1:1 $C_9COONa-C_{10}NMBr$ system^a

C_2 ($\text{mol} \cdot \text{dm}^{-3}$)	η ($\text{mpa} \cdot \text{s}$)
0	2.312
7.75×10^{-3}	2.073
1.65×10^{-2}	1.326
2.48×10^{-2}	1.127
3.31×10^{-2}	1.059
4.44×10^{-2}	0.9767
5.47×10^{-2}	0.9567

^a $\alpha_a = 0.75$, pH = 9.2, the total surfactant concentration is $0.20 \text{ mol} \cdot \text{dm}^{-3}$. C_2 is the solubility of *n*-octane, η is viscosity.

The variation of the molecular solution viscosity also supports this explanation. At $30 \pm 0.2^\circ\text{C}$, for the system in which $1.60 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ *n*-octanol was solubilized in 1:1 $C_9COONa-C_{10}NMBr$ surfactant solution (pH = 9.2, $0.20 \text{ mol} \cdot \text{dm}^{-3}$), the viscosity increased from 2.312 to 2.689 ($\text{mpa} \cdot \text{s}$), which may be attributed to the increase in volume fraction of micelles in solution. On the other hand, the viscosity significantly decreased at $\alpha_a = 0.75$ with the addition of *n*-octane in surfactant solution (see Table 3). It is an unusual phenomenon that the viscosity decreased with the amount of adding material. However, it is understandable if it was considered that *n*-octanol addition changed the shape of the mixed micelle from long rod-like shape to symmetric spherical micelle since usually the surfactant system with long rod-like shape micelle would have the bigger viscosity value than spherical micelle system. In fact, similar results were also obtained in another kind of cationic-anionic surfactant system,¹¹ which was also attributed to the reason mentioned above.