

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

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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.<sup>1,2</sup> 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.*<sup>3</sup> first reported the vesicle formation in cationic and anionic surfactant system. Similar work also started in our group in 1990.<sup>4</sup> 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-

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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  $\text{KMnO}_4$  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  $50^\circ\text{C}$  (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 micelle<sup>4</sup> and micro viscosity of organized assemblies.<sup>5</sup> 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  $\sim 798$  obtained by fluorescence probe method<sup>5</sup> 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.<sup>6</sup> 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.

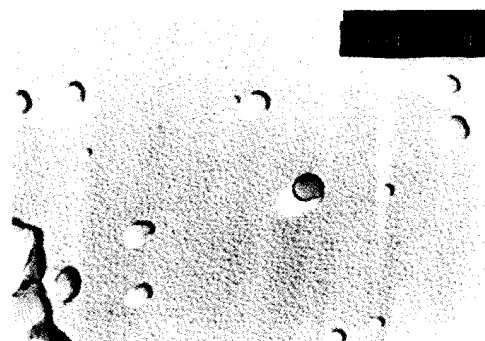


Fig. 1 Vesicle formation in 1:1 mixed  $\text{C}_9\text{COONa}-\text{C}_{10}\text{NMBr}$  system ( $\times 49,000$  times, with sonication, TEM observation by freeze-fracture technique,  $C = 2.4 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ).

However, situation is different in 1:1 mixed  $\text{C}_{11}$ -

COONa-C<sub>8</sub>NMBr 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 C<sub>11</sub>COONa-C<sub>8</sub>NMBr system after adding small amount of ethanol.



**Fig. 2** Vesicle formation in 1:1 mixed C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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 C<sub>9</sub>COONa-C<sub>10</sub>NMBr system were different from those of C<sub>11</sub>COONa-C<sub>8</sub>NMBr system, which might be explained as follows:

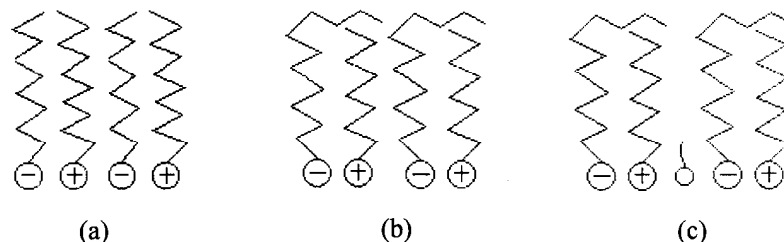
It is well known, surfactant aggregates have a wide variety of structures including micelles, vesicles and bilayers. In a system, what kind of aggregate forming will depend on the value of molecular packing parameter  $P = V_c/A_0l_c$ , where  $V_c$  and  $l_c$  are the volume and chain length of the 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.<sup>7</sup> 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 C<sub>9</sub>COONa-C<sub>10</sub>NMBr system, the hydrocarbon chains of the two organic ionic surfactants are near the same length, while in C<sub>11</sub>-

COONa-C<sub>8</sub>NMBr 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 C<sub>8</sub>NMBr 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 C<sub>11</sub>COONa-C<sub>8</sub>NMBr system, which increase the possibility to form the vesicles. Thus it is understandable to see that vesicles can form spontaneously in C<sub>11</sub>COONa-C<sub>8</sub>NMBr system but just form after sonication in C<sub>9</sub>COONa-C<sub>10</sub>NMBr system. Similar results are also obtained in the 1:1 mixed systems of C<sub>*m*</sub>NMBr and sodium alkylsulphate (C<sub>*n*</sub>SO<sub>4</sub>Na). Vesicles form in 1:1 C<sub>12</sub>SO<sub>4</sub>Na-C<sub>8</sub>NMBr system after sonication, but no vesicles are found in 1:1 C<sub>10</sub>SO<sub>4</sub>Na-C<sub>10</sub>NMBr system whether with or without sonication. The unsymmetric cationic-anionic surfactant system (C<sub>12</sub>-SO<sub>4</sub>Na-C<sub>8</sub>NMBr) still shows stronger vesicle forming capability than C<sub>10</sub>SO<sub>4</sub>Na-C<sub>10</sub>NMBr 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 C<sub>9</sub>COONa-C<sub>10</sub>NMBr system; while a system with a quite large value of  $P$  tends to form vesicle, bilayer or even precipitate, as the situation of C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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 C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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 C<sub>11</sub>COONa-C<sub>8</sub>NMBr solution changed its appearance to clear after small amount of ethanol addition in it, indicating that the  $P$  value of C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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 ethanol<sup>8</sup> (especially in 1:1 cationic-anionic surfactant mixed systems<sup>9</sup>), thus,

it is understandable that vesicles can form again in the C<sub>11</sub>COONa-C<sub>8</sub>NMBr systems after the addition of small amount of ethanol.



**Fig. 3** Scheme illustration for the structures of (a) C<sub>9</sub>COONa-C<sub>10</sub>NMBr system and (b) C<sub>11</sub>COONa-C<sub>8</sub>NMBr system in aqueous solution and (c) C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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<sub>9</sub>COONa-C<sub>10</sub>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

( $60 \times 10^{-3}$  mpa·s) is obviously higher than that before sonication ( $47 \times 10^{-3}$  mpa·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<sub>11</sub>COONa-C<sub>8</sub>NMBr 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 <sup>a</sup>	$C^b$ (mol·dm <sup>-3</sup> )	Organized assemblies <sup>c</sup>	Viscosity (mpa·s)	$T_c$ (°C)
C <sub>9</sub> COONa-C <sub>10</sub> NMBr <sup>ns</sup>	0.052	M & V	60	33.1
C <sub>9</sub> COONa-C <sub>10</sub> NMBr <sup>s</sup>	0.052	M	47	28.5
C <sub>11</sub> COONa-C <sub>8</sub> NMBr <sup>ns</sup>	0.083	M & V	55	25.6
C <sub>11</sub> COONa-C <sub>8</sub> NMBr <sup>s</sup>	0.083	M & V	55	25.6

<sup>a</sup> pH = 9.2, <sup>s</sup> sonication; <sup>ns</sup> no sonication. <sup>b</sup>  $C$  is the total surfactant concentration. <sup>c</sup> 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<sub>11</sub>COONa-C<sub>8</sub>NMBr 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<sub>9</sub>COONa-C<sub>10</sub>NMBr vesicular dispersion (33.1°C) is higher than that in C<sub>11</sub>COONa-C<sub>8</sub>NMBr system, implying the molecular packing is more compact in C<sub>9</sub>COONa-C<sub>10</sub>NMBr vesicles than that in C<sub>11</sub>COONa-C<sub>8</sub>NMBr 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<sub>9</sub>COONa-C<sub>10</sub>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<sub>9</sub>COONa-C<sub>10</sub>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<sup>a</sup>

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

<sup>a</sup>  $pH = 9.2$ , the total surfactant concentration is  $0.2 \text{ mol} \cdot \text{dm}^{-3}$ .  $\alpha_a$  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  $\alpha_a$ . There is a maximum solubility for *n*-octane at  $\alpha_a = 0.75$ , while a minimum for *n*-octanol at the same  $\alpha_a$  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.<sup>10</sup> 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 shape<sup>4</sup> 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,<sup>11</sup> 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<sup>a</sup>

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

<sup>a</sup>  $\alpha_a = 0.75$ ,  $pH = 9.2$ , the total surfactant concentration is  $0.20 \text{ mol} \cdot \text{dm}^{-3}$ .  $C_2$  is the solubility of *n*-octane,  $\eta$  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,<sup>11</sup> which was also attributed to the reason mentioned above.

**Table 4** Solubility ( $\text{mol} \cdot \text{dm}^{-3}$ ) of organic compounds in  $\text{C}_9\text{-COONa-C}_{10}\text{NMBr}$  system<sup>a</sup> ( $I = 0.13 \text{ mol} \cdot \text{kg}^{-1}$ )

$\alpha_a$	<i>n</i> -Octanol	<i>n</i> -Octane
0.10	$6.9 \times 10^{-2}$	$3.2 \times 10^{-2}$
0.20	$5.3 \times 10^{-2}$	$5.1 \times 10^{-2}$
0.50	$7.4 \times 10^{-3}$	$9.4 \times 10^{-2}$
0.75	$3.5 \times 10^{-2}$	$5.2 \times 10^{-2}$
0.90	$4.0 \times 10^{-2}$	$2.0 \times 10^{-2}$

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

As for why the maximum solubility for *n*-octane and the minimum for *n*-octanol occur at  $\alpha_a = 0.75$ , it can be attributed to the fact that the micellization capability of  $\text{C}_9\text{COONa}$  is weaker than that of  $\text{C}_{10}\text{NMBr}$  which can be revealed from their cmc values (determined by surface tension method),  $0.217 \text{ mol} \cdot \text{dm}^{-3}$  for  $\text{C}_9\text{COONa}$  and  $0.054 \text{ mol} \cdot \text{dm}^{-3}$  for  $\text{C}_{10}\text{NMBr}$ . In order to form the electronic neutral micelle, *i. e.* there are equal amount of  $\text{C}_9\text{COONa}$  and  $\text{C}_{10}\text{NMBr}$  molecules in the mixed micelle, the concentration of  $\text{C}_9\text{COONa}$  in solution must be higher than that of  $\text{C}_{10}\text{NMBr}$  in a proper amount. According to this view point, adjusting the conditions of the solution, such as pH or ion strength to make the cmcs of the two components almost the same, we can move the  $\alpha_a$  for maximum and minimum solubility of octane and octanol to  $\sim 0.5$ . Result presented in Table 4 is just the case, where the ion strength of the system is  $0.13 \text{ mol} \cdot \text{kg}^{-1}$  by adding NaBr and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and the cmcs are  $0.075 \text{ mol} \cdot \text{dm}^{-3}$  and  $0.048 \text{ mol} \cdot \text{dm}^{-3}$  for  $\text{C}_9\text{COONa}$  and  $\text{C}_{10}\text{NMBr}$ , respectively.

## Conclusion

Organized assemblies (micelle or vesicle) formation and transformation in two 1:1 alkylcarboxylate-alkyltrimethylammonium bromide aqueous systems have been investigated. Sonication is necessary for vesicle formation in  $\text{C}_9\text{COONa-C}_{10}\text{NMBr}$  system but not for  $\text{C}_{11}\text{-COONa-C}_8\text{NMBr}$  system. However, both vesicular dispersions are unstable, each transforms to different stable

state—micellar solution for  $\text{C}_9\text{COONa-C}_{10}\text{NMBr}$  system and dilute solution with precipitates for  $\text{C}_{11}\text{-COONa-C}_8\text{NMBr}$  system spontaneously. An explanation for these results was provided based on the consideration of packing in the assemblies. Physico-chemical properties of the organized assemblies have been also investigated. The microviscosity and phase-transition-temperature are higher in the vesicles of  $\text{C}_9\text{COONa-C}_{10}\text{NMBr}$  system than those of  $\text{C}_{11}\text{COONa-C}_8\text{NMBr}$  system. Organic compounds especially non-polar organic compounds show large solubilization amount in the cationic-anionic surfactant micelles, and at the same time make the shape of cationic-anionic surfactant micelle change from long rod-like to spherical. These results can be explained by the consideration of molecular packing and also support our inference on assembly structures very well.

## References

1. Fendler, J. H., *Membrane Mimetic Chemistry*, Chapter 6, Wiley, New York, 1982.
2. Kunitake, T., *Surfactants in Solution*, Eds., Mittal, K. L.; Bothorel, P., Vol. 5, Plenum, New York, 1986, p. 727.
3. Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. N., *Science*, **245**, 1371 (1989).
4. Zhao, G.-X.; Huang, J.-B., *Acta Physico-Chim. Sin.*, **8**, 583 (1992).
5. Huang, J.-B.; Zhao, G.-X., *Colloid Polym. Sci.*, **274**, 747 (1996).
6. Yu, Z.-J.; Zhao, G. X., *J. Colloid Interface Sci.*, **130**, 421 (1989).
7. Isrelachiveli, J. N., *Intermolecular and Surface Force*; Chapter 16, Academic Press, London, 1985.
8. Kimizuka, N.; Wakiyama, T.; Miyachi, H.; Yoshimi, T.; Tokuhira, M.; Kunitake, T., *J. Am. Chem. Soc.*, **118**, 5808 (1996).
9. Huang, J. B.; Zhu, B. Y.; Zhao, G. X.; Zhang, Z. Y.; *Langmuir*, **13**, 5759 (1997).
10. Zhao, G.-X., *Physical Chemistry of Surfactant* (in Chinese), Peking University, Press, Beijing, 1984, p. 184.
11. Zhao, G.-X.; Li, X.-G., *J. Colloid and Interface Sci.*, **144**, 185 (1991).