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ORIGINAL CONTRIBUTION

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Formation and coexistence of the micelles and vesicles in mixed solution of cationic and anionic surfactant

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Abstract In the aqueous mixtures of sodium alkylcarboxylate and alkyltrimethylammonium bromide, large unilamelar vesicles can be formed spontaneously or by sonication as the total carbon number in the HC chains is 19 (or larger). Vesicle formation can be influenced by changes of pH, molar ratio of the two surfactant components, and the polar head group of cationic surfactant. Micelles may coexist with the vesicles in these mixed systems. The larger hydrodynamic radius (~ 200 nm) and aggregation number (~ 800) illustrate that the shape of the micelle in 1:1 $C_9H_{19}COONa$–$C_{10}H_{21}N(CH_3)_3Br$ is rod-like. In some mixed systems, the micelles can be transformed into stable vesicles by sonication – a phenomenon revealed for the first time. The surface-chemical properties of these catanionic surfactant solutions and the stabilities of vesicle have been studied systematically.

Key words Vesicle formation – cationic-anionic surfactant mixture – shape of mixed micelle – micelle-vesicle transformation – vesicle stability

1. Introduction

Vesicle formation from natural surfactants (mainly the phospholipids) and from the synthetic surfactants was investigated rather fully [1] [2]. Now, synthetic bilayer vesicles have become very attractive models for the study of trans-membrane process. However, the nature of vesicle formation and many peculiar properties of the vesicle systems still remain unclear, particularly for the mixed surfactant system. It was shown that the simple single-tailed surfactant could not form vesicles, probably due to the relatively large hydrophilio head effect of the surfactant [3]. Early studies revealed that in the mixed cationic-anionic surfactant systems, the mean ionic head size in an organized assembly (e.g., the surface adsorption layer) would become rather small [4] [5]. This is due to the strong molecular interaction between the two oppositely charged surfactant ions in the adsorption layer, which is omni-present is many mixed catanionic surfactant systems [6–9]. Then, according to the geometrical rule [3], the value of V/Al (V: HC chain volume, A; area occupied by the ionic head: 1: HC chain length) is about 0.8 for C_{8-14} alkyl chain, which shows the possibility of vesicle formation in the aqueous mixture of cationic-anonic surfactants. In reality, it has been found that in the mixed catanionic surfactant systems, even a spontaneous vesicle formation could occur [10, 11].

In the present paper, we report that micelle and vesicle formations in the aqueous mixtures of sodium alkylcarboxylate (C*n*COONa) and quaternary-ammonium bromide (C*m*NR_3Br, R = CH_3, C_2H_5, C_3H_7 , C_4H_9). Some factors influencing the vesicle formation and the physicochemical properties of the vesicle systems have been investigated.

2. Experimental

Materials

Sodium alkylcarboxylate (*Cn*COONa, $n = 7, 9, 11$) was prepared from the neutralization of the corresponding carboxylic acid(*Cn*COOH) and NaOH at equimolar ratio in ethanol, then the solvent was removed and *Cn*COONa was vacuum dried. C_7COOH and C_9COOH were double distilled, and $C_{11}COOH$ was recrystallized five times in ethanol-water mixture (m.p. 43–44 °C). Quaternary ammonium bromide was synthesized from n-alkylbromide and tri-methyl (or-ethyl, -propyl and -butyl) amine. Alkyltrimethylammonium bromide (*Cm*NMBr, $m = 8, 10, 12$) was recrystallized five times in acetones -ethanol mixture. Alkyltriethylammonium bromide (*Cm*NEBr, $m = 8, 12$) was recrystallized five times in methanol-acetone, ethyl acetate-ather mixed solvents, respectively. Dodecyltripropylammonium bromide ($C_{12}NPBr$) and dodecyltributylammonium bromide ($C_{12}NBBr$) were recrystallized five times in methanol-ether mixture. Water was deionized water treated with $KMnO_4$ and distilled. Other reagents and solvents were products of Beijing Chemical Co., A.R. Grade.

Methods

Vesicle preparation

The mixed surfactant vesicles were prepared by simply mixing the cationic and anionic surfactant solution at room temperature (~ 25 °C) or by sonicating the mixed surfactant solution for 0.5–1.5 hr. (usually 30 min) at 50 °C (Sonicator: Haitung CQ-250). Vesicle image was observed with electron microscope (JEM-100CXII) by the negative-staining technique (with uranyl acetate) or by the freeze-fracture technique.

Surface-chemical properties measurement

Surface tension (γ) of the mixed surfactant solution was measured with drop volume method [12] at 30 °C (± 0.1 °C). CMC and γ_{cmc} (surface tension at CMC) were determined from the inflection point of the $\gamma \sim \log c$ (c: molar concentration of total surfactnat solution) curve. Γ_T^∞ (total saturated adsorption capacity) and A_m (the average molecular area at saturated adsoption) were also calculated from the $\gamma \sim \log c$ curve [13].

Micelle aggregation number measurement

When a fluorescent probe is added to micellar solutions, the probe distributes itself statistically among the micelles. The aggregation number of the micelle (N) can be related to the average number of probe per micelle (*n*), CMC, molar concentration of the probe (*Cp*) and molar concentration of surfactant (C) by the expression [14]: $N = n(C - CMC)/Cp$, where *n* can be obtained from the equation $\ln(I_t/I_0) = -n - kt$ at $t \rightarrow 0$

pH adjustment: The pH values of the mixed surfactant solutions were controlled at 9.2 and 13 by $Na_2B_4O_7 \cdot 10H_2O$(~ 0.01 mol dm^{-3}) and NaOH, respectively; The pH value of unbuffered solution is about 5–6.

3. Results and discussion

3.1 Mixed surfactnat vesicle formation

3.1.1 Vesicle formation in 1:1 aqueous solution of surfactant mixture

Electron microscopic (EM) observation of the mixed solutions by the negative-staining technique (e.g., see Fig. 1 and Fig. 3) and the freeze-fracture technique (see Fig. 2) demonstrated the existence of vesicles in the 1:1 mixed *Cn*COONa–*Cm*NMBr solution. The results are shown in Table 1. From the results, we can see that the vesicle formation occurs as the total number of carbon in the HC chains is 19 (or larger). In general, the unilamellar vesicles were formed only by ultrasonication. However, Table 1 shows that unilamellar vesicles were formed either by sonication or spontaneously (without sonication) in some systems. The electron micrograph of vesicles spontaneously formed in $C_{11}COONa$–C_8NMBr solution (pH = 9.2) is shown in Fig. 3. Perhaps Fig. 3(b) is the clearest micrograph of this type ever seen. The bimolecular layer of the vesicle is clearly shown and its thickness can be measured with certainty (~ 4 nm). These results obviously demonstrate the superior vesicle-forming capability of the catanionic surfactants (especially the spontaneity of vesicle formation) at pH = 9.2.

However, with the change of pH of the mixed surfactant solutions (to pH 5 ~ 6 or pH 13), the vesicle-forming capability of the catanionic surfactants obviously decreases. We find that there is no vesicle formation in almost all the mixed surfactant systems (except for $C_{11}COONa$–C_8NMBr system at pH = 5 ~ 6). Thus, we can consider that pH = 9.2 is the better condition for vesicle formation in these mixed surfactant systems.

The pH effect is mainly caused by the free carboxylic acid(*Cn*COOH) produced by the hydrolysis. From the

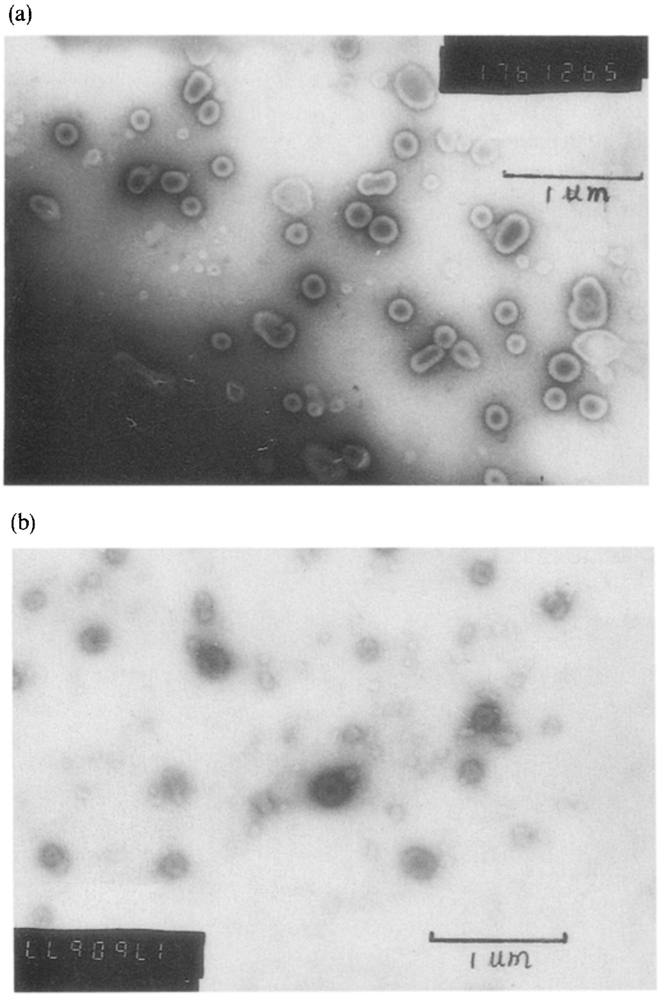


Fig. 1 Vesicles formed (by sonication) in the 1:1 mixed solution (pH = 9.2) of C_9COONa–$C_{12}NMBr$ (a) and C_9COONa–$C_{10}NMBr$ (b)

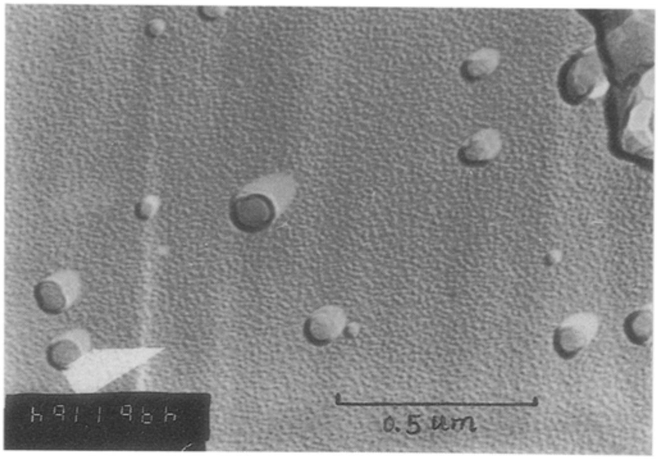


Fig. 2 Vesicles formed (by sonication) in the 1:1 mixed C_9COONa–$C_{10}NMBr$ solution (pH = 9.2, EM observed by freeze-fracture technique)

hydrolysis equilibrium

$$CnCOO^- + H_2O = CnCOOH + OH^- \ , \tag{1}$$

we have

$$[CnCOOH]/[CnCOO^-] = [H^+]/Ka \ , \tag{2}$$

where $[CnCOO^-]$, $[CnCOOH]$ and $[H^+]$ are the concentrations of $CnCOO^-$, $CnCOOH$ and H^+, respectively; Ka is the dissociation constant. Suppose pKa = 4.89 [15], at pH = 13, $[CnCOOH]/[CnCOO^-] = 7.8 \times 10^{-9}$, [CnCOOH] is so low as to be neglected; at pH = 5 ~ 6, $[CnCOOH]/CnCOO^-] = 0.78 \sim 7.8 \times 10^{-2}$, [CnCOOH] is so high that it can be influence the stability of surfactant solution (precipitate may occur). At pH = 9.2, $[CnCOOH]/[CnCOO^-] = 4.9 \times 10^{-5}$. According to our results [16], as a polar organic compond, CnCOOH can reduce the electrostatic repulsion of an ionic surfactant at the surface and make the molecular packing closer. Therefore, on the basis of geometrical rule, V/Al will increase as A goes down. From the view-point of Tanford [17] and Isrealachivili [18], micelle forms at $0 < V/Al < 1/2$ and vesicle forms at $1/2 < V/Al < 1$. The increase of V/Al will be beneficial to vesicle formation. Therefore, we can conclude that it is CnCOOH that makes these catanionic surfactant systems have superior vesicle-forming capability at pH = 9.2. The results that vesicles formed in 1:1 mixed $C_{11}COONa$–C_8NMBr (pH = 13) system with octanol (Fig. 4) gives evidence, of what we conclude.

3.1.2 Effect of the molar ratio of mixed surfactant and size of cationic surfactant headgroup on the vesicle-forming capability

At pH = 9.2. we studied the vesicle formation of CnCOONa- CmNMBr systems at different mixed surfactant molar ratio. Some results of the EM observation are listed in Table 2. From Table 2, we find that with α_1 (anionic surfactant molar fraction in the mixed surfactant) leaving 0.5, the vesicle-forming capability decreases and disappears --- indicating $\alpha_1 = 0.5$ is the better mixed ratio for vesicle formation in these mixed surfactant systems.

We may take the 1:1 ($\alpha_1 = 0.5$) mixture as a simple (catanionic) surfactnat [19]; then the mixture of α_1 other than 0.5 is the mixed system of a catanionic surfactant and an ionic (cationic or anionic) surfactant. Just like the system of a phospholipid with added surfactant [20], the formed vesicles would be converted into mixed micelles with added ionic surfactant.

Table 3 shows (from EM observation) the vesicle-forming capability in the 1:1 mixed surfactant systems of CnCOONa–CmNEBr, CnCOONa–CmNPBr,

Table 1 Vesicle formation in mixed surfactant systems (pH = 9.2)

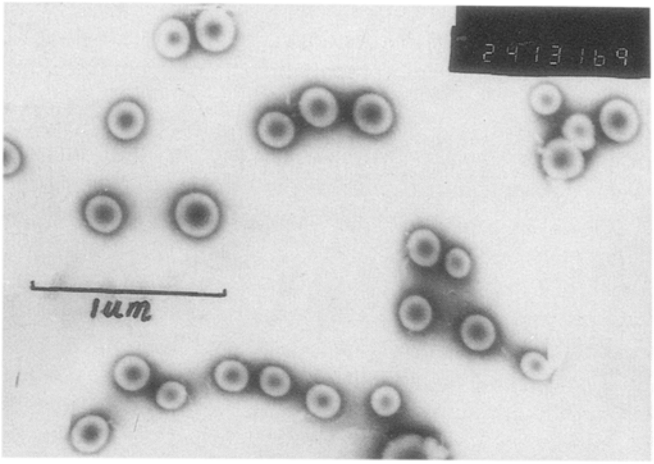
1:1 Mixed systems	Concentration c/mol dm^{-3}	Solution appearance[a])	EM observation[b]) S.	N.S.
$C_{11}COONa$–$C_{12}NMBr$	5.0×10^{-3}	T.S.	+	+
$C_{11}COONa$–$C_{10}NMBr$	2.1×10^{-2}	T.S.	+	+
$C_{11}COONa$–C_8NMBr	8.3×10^{-2}	T.S.	+	+
C_9COONa–$C_{12}NMBr$	7.5×10^{-3}	T.S.	+	–
C_9COONa–$C_{10}NMBr$	2.4×10^{-2}	C.S.	+	–
C_7COONa–$C_{12}NMBr$	1.0×10^{-1}	C.S.	–	–
C_9COONa–C_8NMBr	1.0×10^{-1}	C.S.	–	–
C_7COONa–$C_{10}NMBr$	1.0×10^{-1}	T.S.	–	–
C_7COONa–C_8NMBr	2.0×10^{-1}	T.S.	–	–

[a]) T.S. = translucent solution, C.S. = clear solution

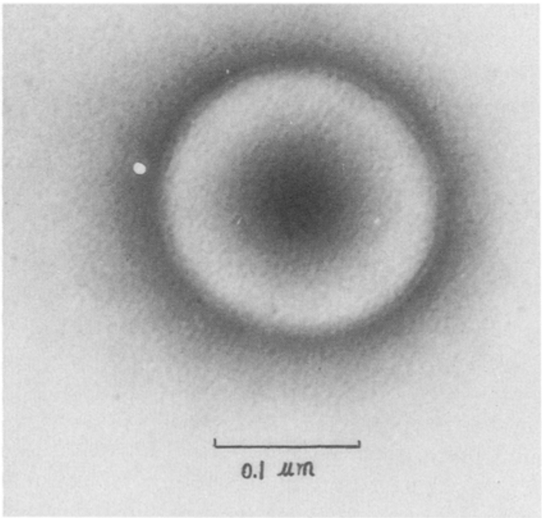
[b]) S. = sonication, N.S. = no sonication
+ = unilamellar vesicle formed,
– = no vesicle

Fig. 3 Vesicles spontaneously formed in the 1:1 mixed $C_{11}COONa$–$C_{10}NMBr$ solution (pH = 9.2). a) × 24000 times b) × 172800 times

a)



b)



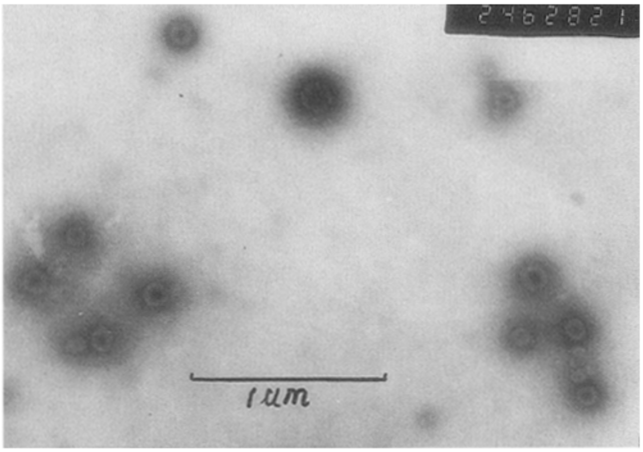


Fig. 4 Vesicles formed in 1:1 mixed $C_{11}COONa$–C_8NMBr (pH = 13) system with octanol (6.0×10^{-3} mol dm^{-3})

Fig. 5 Vesicles spontaneously formed in the 1:1 mixed $C_{11}COONa$–C_8NEBr solution (pH = 9.2)

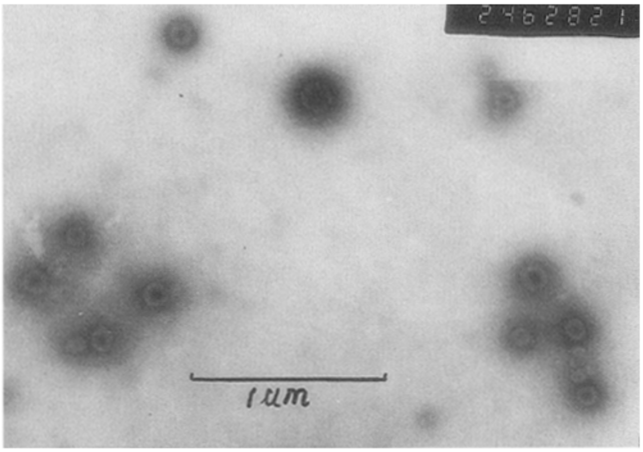


Table 2 Effect of mixed surfactant ratio on vesicle formation[a])

1:Mixed systems	Concentration c/mol dm^{-3}	α_1 0.90	0.75	0.50	0.25	0.10
$C_{11}COONa–C_{12}NMBr$	5.0×10^{-3}	–	–	+	–	–
$C_{11}COONa–C_{10}NMBr$	2.1×10^{-2}	–	–	+	+ –	–
$C_{11}COONa–C_8NMBr$	8.3×10^{-2}	–	–	+	+ –	–
$C_9COONa–C_{12}NMBr$	7.5×10^{-3}	–	–	+	–	–
$C_9COONa–C_{10}NMBr$	2.4×10^{-2}	–	–	+	–	–

[a]) + – = organized assemblies, but not certain if it is vesicle by EM observation
[b]) All systems were sonicated.

Table 3 Effect of polar head size of surfactant on vesicle formation

1:1 Mixed systems	Concentration c/mol dm^{-3}	Solution appearance	Time of sonication	EM observation S.	N.S.
$C_{11}COONa–C_{12}NMBr$	5.0×10^{-3}	T.S	0.5 hr.	+	+
$C_{11}COONa–C_{12}NEBr$	1.0×10^{-2}	C.S	1.0 hr.	+	–
$C_{11}COONa–C_{12}NPBr$	2.1×10^{-2}	C.S	1.5 hr.	+	–
$C_{11}COONa–C_{12}NBBr$	2.2×10^{-2}	C.S.	1.5 hr.	+ –	–
$C_9COONa–C_{12}NMBr$	7.5×10^{-3}	T.S	0.5 hr.	+	–
$C_9COONa–C_{12}NEBr$	1.7×10^{-2}	C.S	1.0 hr.	+	–
$C_9COONa–C_{12}NPBr$	2.0×10^{-2}	C.S	1.5 hr.	+	–
$C_{11}COONa–C_8NMBr$	8.3×10^{-2}	T.S	0.5 hr.	+	+
$C_{11}COONa–C_8NEBr$	8.3×10^{-2}	T.S	0.5 hr.	+	+

*Cn*COONa–*Cm*NBBr; and *Cn*COONa–*Cm*NMBr together. From Table 3, we can see that in the mixed $C_{11}COONa–C_8NEBr$ system, the vesicles can also form spontaneously (see Fig. 5), as in the mixed $C_{11}COONa–C_8NMBr$ system. Furthermore, in general, the larger the size of the headgroup of the cationic surfactant, the more difficult the vesicle formation and the longer the time of sonication and greater concentration necessary.

The effect of the headgroup size of cationic surfactant can also be explained by the influence of V/Al on vesicle formation, such as the pH effect. Because of the steric hindrance, the catanionic surfactant molecules pack more sparsely while the size of cationic surfactant headgroup enlarges. Thus, the vesicle-forming capability decreases with increasing A.

3.2 Simultaneous existence of micelle and vesicle in the mixed catanionic surfactant system

3.2.1 Critical micellar concentration (CMC) measurement

In the mixed catanionic surfactant systems we discussed in Section 3.1, there are two types of systems in which vesicles can form. The mixed solutions of type A, such as $C_{11}COONa–C_{12}NMBr$, $C_{11}COONa–C_{10}NMBr$, $C_9COONa-C_{12}NMBr$, $C_{11}COONa–C_8NMBr$ and $C_{11}COONa–C_8NEBr$, are translucent; and those of type B, such as $C_9COONa–C_{10}NMBr$, are clear. While the solutions of type A are diluted, they become clear. At pH = 9.2, we measured the surface tension (γ) at different molar concentrations (c) in all the systems of type A and B (the mixed surfactant solution is always clear in our experimental range). The surface tension (γ-log c) curves are shown in Figs. 6 and 7. CMC and other surface chemical properties were determined or approximately calculated from the curves. Some results are listed in Table 4.

From Table 4, we can see that, like in many other catanionic surfactant systems [19], the surface chemical properties in these systems are influenced very much by the total carbon number of the HC chains and the size of the catanionic headgroup. With enlarging of the size of the catanionic surfactant, the γ_{cmc}, A_m and Γ_T^∞ increase, which shows that the catanionic surfactant molecular packing is more sparse due to steric hindrance. However, the CMC in little influenced by the size of the catanionic surfactant; it is mainly controlled by the total carbon number of the HC chains.

3.2.2 Co-existence of micelle and vesicle and micelle-to-vesicle transformation in the mixed surfactant solution

Comparing the results of Table 1 with Table 4, we find that in all the mixed systems the concentration at which vesicle formed is always greater than CMC. The results of EM observation were supported by the results obtained by quasi-elastic light scattering method (QELS): with those below CMC no particles were found. Therefore, we think that there may be a simultaneous existence of micelles and

Table 4 Surface chemical properties in 1:1 mixed surfactant solution (30 °C, pH = 9.2, I⟨Ioninic strength⟩ ≈ 0.03 mol kg^{-1})

1:1 Mixed systems	CMC (mol dm^{-3})	γ_{cmc} (mM m^{-1})	Γ_T^∞ [a] (10^{10} mol cm^{-2})	A_m (nm^2)
C_9COONa–$C_{12}NMBr$	9.8×10^{-3}	23.5	3.8	0.43
$C_{11}COONa$–$C_{10}NMBr$	2.1×10^{-3}	24.4	4.7	0.36
$C_{11}COONa$–$C_{12}NMBr$	6.9×10^{-4}	22.4	5.1	0.32
C_9COONa–$C_{12}NMBr$	1.5×10^{-3}	23.4	4.7	0.36
$C_{11}COONa$–C_8NMBr	6.3×10^{-3}	25.0	4.6	0.35
$C_{11}COONa$–C_8NEBr	6.9×10^{-3}	27.8	4.6	0.35
$C_{11}COONa$–$C_{12}NEBr$	6.6×10^{-4}	25.6	4.2	0.40
$C_{11}COONa$–$C_{12}NPBr$	6.8×10^{-4}	27.2	3.2	0.52
$C_{11}COONa$–$C_{12}NBBr$	3.4×10^{-4}	27.2	2.9	0.58
C_9COONa–$C_{12}NEBr$	2.5×10^{-3}	27.2	4.1	0.41

[a] Γ_T^∞ and A_m are calculated approximately

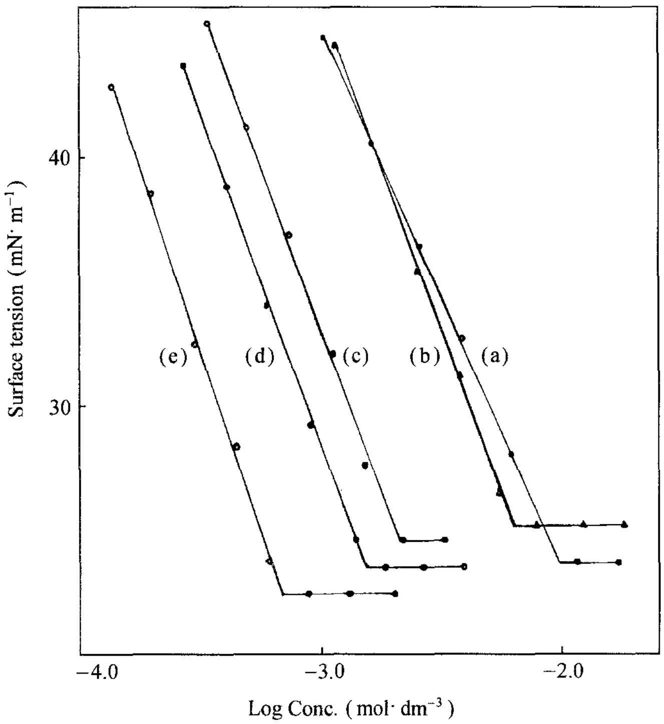


Fig. 6 Surface tension curves in the 1:1 mixed system (pH = 9.2) of (a) C_9COONa–$C_{10}NMBr$ (b) $C_{11}COONa$–C_8NMBr (c) $C_{11}COONa$–$C_{10}NMBr$ (d) C_9COONa–$C_{12}NMBr$ (e) $C_{11}COONa$–$C_{12}NMBr$

vesicles in mixed systems if the concentration is great enough (~ 5–10 CMC). The experimental results of type A mixed systems give evidence of this view. The 1:1 mixed $C_{11}COONa$–$C_{12}NMBr$ solution (5.0×10^{-3} mol dm^{-3}) would become two layers after high-speed-centrifugation (12000 r.p.m.). The top layer is cloudy and the vesicles in it were found by EM observation. On the contrary, the bottom layer is clear and no vesicle was found in it. The hydrodynamic diameter of the micelles (Dm) in the bottom layer was determined to be larger than 100 nm by QELS (detailed results are shown in Table 5).

On the other hand, for type B system, we have clear solutions after centrifugation at the same speed. The hydrodynamic diameters of the particle (Dp) measured by QELS in C_9COONa– $C_{10}NMBr$ system before and after sonication are shown in Tables 6 and 8. It is worth noting that no vesicle formed in the clear aqueous solution of 1:1 C_9COONa-$C_{10}NMBr$ (thus the data in Table 7 are Dm values), whereas the stable vesicles of medium size (~ 20-80 nm determined from EM observation by freeze-fracture technique) (cf. Fig. 2) formed after sonication, indicating that the surfactant micelle can be transformed into a stable vesicle by sonication – a phenomenon revealed for the first time (similar results were also obtained in other type B systems). Table 7 shows that after sonication, Dp changed very little (compared with that before sonication) though vesicles have formed. Maybe it is because a) only a few micelles can be transformed into vesicles and b) the size of the vesicles is close to the Dm in 1:1 mixed C_9COONa–$C_{10}NMBr$ systems.

3.2.3 The shape of catanionic surfactant micelle and the stability of mixed surfactant solution

While *Cp* (the concentration of pyrene) = 4.59×10^{-5} mol cm^{-3}, for the 1:1 mixed C_9COONa–$C_{10}NMBr$ solution at the total concentration of 5.2×10^{-2} mol dm^{-3}, n (the average number of probe per micelle) = 0.867. Thus, the aggregation number of the C_9COONa-$C_{10}NMBr$ micelle was calculated to be ~ 798 which is too large a value for a spherical micelle. In connection with the result that the Dm obtained by QELS is about 37 nm, being also too large for a spherical micelle (see Table 6), it therefore may be concluded that this catanionic surfactant micelle should be of rod-like shape [8] (in many other catanionic surfactant systems, the micelles are of long rod-like shape). Because the Dm values are close (in other type-B systems; see Table 8) to or larger (in type A systems; see Table 1) than that of

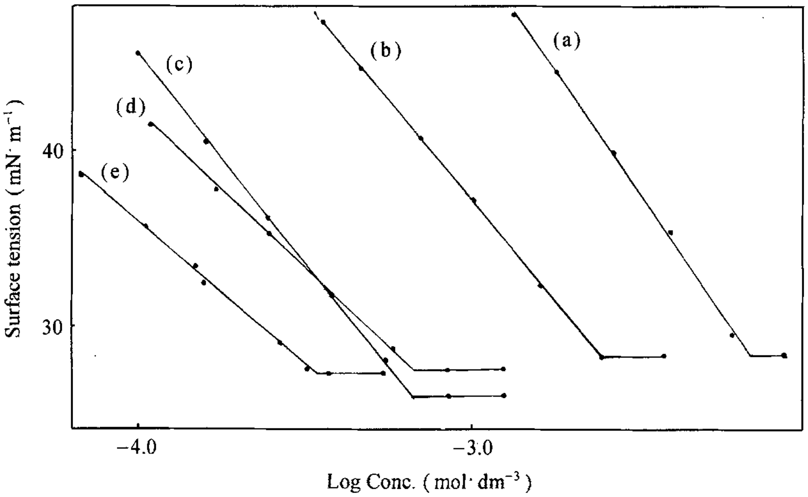


Fig. 7 Surface tension curves in the 1:1 mixed systems (pH = 9.2) of
(a) $C_{11}COONa$-C_8NEBr
(b) C_9COONa-$C_{12}NEBr$
(c) $C_{11}COONa$-$C_{12}NEBr$
(d) $C_{11}COONa$-$C_{12}NPBr$
(e) $C_{11}COONa$-$C_{12}NBBr$

C_9COONa-$C_{10}NMBr$, it should be considered that in all type A and B systems the catanionic surfactant micelles are of rod-like shape.

From Tables 6 and 8, we can see that the Dm of type B systems can change reversibly with temperature, demonstrating that the micellar solution of type B systems is thermodynamically stable. In contrast with type B, the Dm of type A systems changes irreversibly with temperature. For example, while the temperature of 1:1 mixed $C_{11}COONa$-$C_{12}NMBr$ solution (5.0×10^{-3} mol dm^{-3}) varies from 30 °C to 40 °C and back to 30 °C, the Dm changes from 167 nm to 249 nm (measured by QELS). Table 5 also shows that the Dm of type A increase one-way with time. All these facts mean that the micellar solutions of type A are not thermodynamically stable although they are sometimes clear when observed by the naked eye.

3.3 The stability of the vesicles formed in the catanionic surfactant solution

3.3.1 The influences of aging time

At pH = 9.2 and room temperature (~ 20 °C), we continuously observed vesicles formed in CnCOONa-CmNMBr systems. The results of EM observation are listed in Table 9. From Table 9, we can see that all the vesicles formed in the mixed systems are rather stable in

Table 5 Dm (nm) in the bottom layer of the 1:1 $C_{11}COONa$-$C_{12}NMBr$ solution (pH = 9.2, 30 °C)

Time[a]/hr.	C[b] = 5.0×10^{-3}	C = 1.0×10^{-2}
6	167.0	169.1
24	171.4	183.7
48	175.0	195.9
96		207.5

a) Time is counted from the mix of cationic and anionic solution
b) C is the total concentration of catanionic surfactant (mol dm^{-3})

Table 6 Dm (nm) in 1:1 mixed C_9COONa-$C_{10}NMBr$ system (pH = 9.2)

Temperature °C	C[b] = 2.1×10^{-2}	C = 5.2×10^{-2}
30	24.1	37.2
40	17.2	27.6
30[a]	24.0	38.0

a) Measurement was done after heating at 40 °C
b) C is the total concentration of the surfactant mixture (mol dm^{-3})

Table 7 Dp in 1:1 mixed C_9COONa-$C_{10}NMBr$ system (sonicated, pH = 9.2, 30 °C)

C/mol dm^{-3}	Dp/nm
2.1×10^{-2}	24.2
5.2×10^{-2}	37.1

C is the total concentration of the surfactant mixture

Table 8 Dm[a]) (nm) in type B systems (pH = 9.2)

1:1 Mixed systems	Concentration c/mol dm^{-3}	Dm 30 °C	40 °C	30 °C[b])
$C_{11}COONa$-$C_{12}NEBr$	1.0×10^{-2}	28.7	24.4	28.6
$C_{11}COONa$-$C_{12}NPBr$	1.0×10^{-2}	14.3	13.1	14.3
$C_{11}COONa$-$C_{12}NBBr$	1.0×10^{-2}	20.0	23.6	20.0
C_9COONa-$C_{12}NEBr$	1.7×10^{-2}	13.7	12.4	13.8

[a]) Dm was measured by QELS.
[b]) Measurement was done after heating to 40 °C.

Table 9 The influences of aging time

1:1 Mixed systems	Concentration c/mol dm^{-3}	Aging time/days 2–3	7	14	21	28
$C_{11}COONa–C_8NMBr$ (N.S.)	8.3×10^{-2}	+	+	+	+	+
$C_{11}COONa–C_8NMBr$ (S.)	8.3×10^{-2}	+	+	+	+	+
$C_{11}COONa–C_{10}NMBr$ (N.S.)	2.1×10^{-2}	+	+	+	+	+
$C_{11}COONa–C_{10}NMBr$ (S.)	2.1×10^{-2}	+	+	+	+	+
$C_{11}COONa–C_{12}NMBr$ (N.S.)	5.0×10^{-3}	+	+	+	+ –	–
$C_{11}COONa–C_{12}NMBr$ (S.)	5.0×10^{-3}	+	+	+	+ –	–
$C_9COONa–C_{12}NMBr$ (S.)	7.5×10^{-3}	+	+	+	+ –	–
$C_9COONa–C_{10}NMBr$ (S.)	2.4×10^{-2}	+	–	–		
$C_9COONa–C_{10}NMBr$ (S.)[a]	2.4×10^{-2}	+	+	+	+	–

[a]) This surfactant solution was kept in 2 °C environment

Table 10 The influences of temperature

1:1 Mixed system	Concentration c/mol dm^{-3}	50 °C		85 °C		2 °C		– 17 °C	
		N.S.	S.	N.S.	S.	N.S.	S.	N.S.	S.
$C_{11}COONa–C_8NMBr$	8.3×10^{-2}	+	+	+	+	+	+	+	+
$C_{11}COONa–C_{10}NMBr$	2.1×10^{-2}	+	+	+	+	+	+	+	+
$C_{11}COONa–C_{12}NMBr$	5.0×10^{-3}	+	+	+	+	+	+	+	+
$C_9COONa–C_{12}NMBr$	7.5×10^{-3}		+		+		–		–
$C_9COONa–C_{10}NMBr$	2.4×10^{-2}		+		+		+		–

3 weeks or even more, except for C_9COONa-$C_{10}NMBr$ system. The vesicles in C_9COONa-$C_{10}NMBr$ vanished after 1 week, while the surfactant solutions were still clear. Sonicating this solution, we find that vesicles can form and vanish (after several days) again. This process (sonication – vesicle formation–aging–vesicle vanish) can be repeated many times in this system, indicating that vesicle and micelle can be transformed into each other at different conditions (sonicating or aging). At lower temperature (2 °C), the vesicles formed in C_9COONa-$C_{10}NMBr$ system can remain for a longer time than that at room temperature.

For other mixed systems, the surfactant solutions are cloudy and precipitates (or crystal) were found while vesicles vanished. Only few vesicles were found after sonicating the solution. Adding very small amount of ethanol to the solution, we found that the vesicles in $C_{11}COONa$-C_8NMBr system formed again while the precipitates dissolved and the solution became clear, which shows that the disappearance of vesicle in these systems is caused by instability of catanionic solution.

3.3.2 The influences of temperature, organic solvent and ionic strength

The influences of temperature on the vesicle-stability were studied by leaving the *Cn*COONa–*Cm*NMBr solutions at a particular temperature for 0.5–1.5 hr. The EM observation was done after the solutions returned to room temperature (~ 20 °C). The results are shown in Table 10. From it, we can see that the vesicles can maintain their stability through a rather large temperature variation (heating to 85 °C or cooling to 2 °C). At – 17 °C, the samples are frozen. We think, that the vesicles in the mixed systems have been already destroyed at this time. Because the EM observation was done after the temperature of solution returned to ~ 20 °C, the systems which can form vesicles spontaneously at room temperature formed vesicles again. On the other hand, for C_9COONa–$C_{12}NMBr$ and C_9COONa–$C_{10}NMBr$ systems in which vesicles cannot form without sonication, the results of EM observation must be different.

For studying the influences of organic solvents and ionic strength, we added ethanol or NaBr to the surfactant solution before sonication (if sonication is necessary for vesicle formation). The results are shown in Tables 11 and 12, respectively. It is interesting to note that all the mixed solutions are clear and the vesicles are still stable with such a large amount of ethanol in the solutions. The influences of ionic strength are similar to previous reports [1, 2] that vesicles are destroyed in high concentration of salts, but the concentrations of electrolytes which make the vesicles vanish in the catanionic surfactant systems are a little higher than the usually reported value (0.1 mol dm^{-3}).

Table 11 The influences of ethanol addition

1:1 Mixed system	Concentration c/mol dm^{-3}	Ve/Vt* = 0.30		Ve/Vt = 0.50	
		N.S.	S.	N.S.	S.
$C_{11}COONa-C_8NMBr$	8.3×10^{-2}	+	+	+	+
$C_{11}COONa-C_{10}NMBr$	2.1×10^{-2}	+	+	+	+
$C_{11}COONa-C_{12}NMBr$	5.0×10^{-3}	+	+	+	+
$C_9COONa-C_{12}NMBr$	7.5×10^{-3}		+		−
$C_9COONa-C_{10}NMBr$	2.4×10^{-2}		+		+

* Ve and Vt are the volume of adding ethanol and the total volume of solution, respectively.

Table 12 The influences of NaBr addition

1:1 Mixed system	Concentration c/mol dm^{-3}	$C_b = 0.1$		$C_b = 0.2$		$C_b = 0.5$	
		N.S.	S.	N.S.	S.	N.S.	S.
$C_{11}COONa-C_8NMBr$	8.3×10^{-2}	+	+	+	+	−	−
$C_{11}COONa-C_{10}NMBr$	2.1×10^{-2}	+	+	+	+	−	−
$C_{11}COONa-C_{12}NMBr$	5.0×10^{-3}	+	+	+	+	−	−
$C_9COONa-C_{12}NMBr$	7.5×10^{-3}		+		+		+ −
$C_9COONa-C_{10}NMBr$	2.4×10^{-2}		+		+		−

C_b is the concentration of NaBr (mol dm^{-3})

4. Conclusions

Unilamellar vesicles can be formed spontaneously or by sonication in the aqueous solution of the CnCOONa-CmNMBr mixture as the total carbon number $(n + m) \geq 19$. The influences of pH, mixed surfactant ratio and size of headgroup of the catanionic surfactant, on the vesicle -forming capability were studied. The factors which can make the area occupied by the catanionic surfactant headground smaller are beneficial to the vesicle formation such as pH = 9.2, 1:1 mixed ratio and small size of catanionic surfactant headgroup. Rod-like micelles simultaneously exist with the vesicles in the mixed surfactant systems. Moreover, the transformation between micelle and vesicle can occur at special conditions (sonicating or aging the catanionic surfactant solution) in type B systems in which the micelle solutions are clear and thermodynamically stable. It is interesting to note that all the vesicles formed in the mixed systems are rather stable, i.e., they can exist more than 3 weeks and maintain their stability through a rather large temperature variation of with the addition of a large amount of ethanol. The unusual vesicle stability may be attributed to the strong attraction between the surface active anions and cations in the mixed bilayer of the vesicle.

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