

Note

Reverse time effect of surface tension in cationic bolaform surfactant/anionic surfactant mixed systems

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Abstract

The time effect in a series of flexible and rigid bolaform amphiphiles and their mixed systems with oppositely charged conventional surfactants was investigated. An increase of surface tension with time was found in these systems at surfactant concentrations below the cmc. This result can be attributed to large numbers of surfactant molecules being gradually adsorbed on the wall of the vessel, which causes great changes of concentration and composition in mixed surfactant solutions. Contact angle data and UV research supported our proposal. It was also found that this reverse time effect in single bolaform cationic surfactant systems is decided by the structure of the hydrocarbon chains and only happens in flexible cationic bolaform surfactant solutions.

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Keywords: Bolaform amphiphiles; Reverse time effect; Surface tension

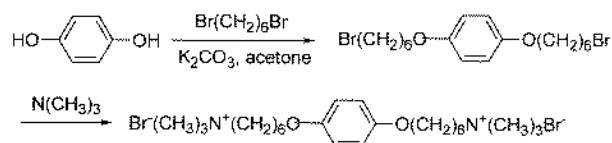
1. Introduction

Bolaform amphiphiles (bolaamphiphiles) are molecules with two polar head groups connected by one or two hydrophobic chains. These compounds have been the subject of much research [1–5] in the past two decades for their diverse interesting properties. Many efforts were made to design and synthesize bola molecules with different structures [6–8] and characterize the aggregation behaviors of their aqueous solutions [9–11]. The basic physical chemistry (such as the micellization and surface activity) of these compounds has also been studied. Usually the surface tension of bolaamphiphiles is higher and the aggregation number is smaller than for conventional surfactants [12–14]. Moreover, bolaamphiphiles tend to occupy large areas at the air/water interface compared to conventional surfactants, indicating that they adopt a looped conformation [15–17]. However, mixed systems of bolaamphiphiles with oppositely charged conventional surfactants are much less than enough. Based on the great significance of cationic surfactants with simple structures, we would like to extend the research to mixed aqueous systems of bolaamphiphiles with oppositely charged conventional surfactants.

In this study, bolaamphiphiles with simple structures, flexible ($[\text{NaOOC}(\text{CH}_2)_{18}\text{COONa}](\text{C}_{20}\text{Na}_2)$, $[\text{Br}^-(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{20}\text{N}^+(\text{CH}_3)_3\text{Br}^-(\text{C}_{20}\text{Me}_6)]$ and $[\text{Br}^-\text{C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{20}\text{N}^+\text{C}_5\text{H}_5\text{Br}^-(\text{C}_{20}\text{Py}_2)]$) or rigid ($[\text{Br}^-(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_6\text{OC}_6\text{H}_4\text{O}(\text{CH}_2)_6\text{N}^+(\text{CH}_3)_3\text{Br}^-(\text{C}_6\text{PhC}_6)]$ and $[\text{Br}^-(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_6\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_6\text{N}^+(\text{CH}_3)_3\text{Br}^-(\text{C}_6\text{BPhC}_6)]$), were synthesized, and a novel time effect of surface tension was observed in mixed systems of a cationic bolaform surfactant and a single-head anionic surfactant. A special adsorption mechanism for bolaform cationic amphiphiles in mixed systems on negatively charged glass walls was proposed.

2. Materials and methods

The bolaamphiphiles, C_{20}Na_2 , C_{20}Me_6 , and C_{20}Py_2 were synthesized according to the literature method [18–20] from eicosanedioic acid. C_6PhC_6 was synthesized according



Scheme 1. Synthesis of bolaamphiphiles, C_6PhC_6 .

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to Scheme 1. First, hydroquinone was allowed to react with excess 1-dibromohexane to get a dibromide with a phenyl group in the center. Then the dibromides were quaternized with trimethyl amine to get the final products. C_6BPhC_6 was prepared by the same procedure as C_6PhC_6 except that 2,2'-biphenol was used instead of hydroquinone. All the intermediates and the final products were determined to be pure by 1H NMR and TLC and gave satisfactory analytical results.

The surface tensions of different mixed systems of bolaform amphiphiles/oppositely charged conventional surfactants were measured by the drop volume method [21]. The concentration of $C_{20}Py_2$ in the $C_{20}Py_2/SDS$ system at various aging times was determined at Shimadzu UV-250. The contact angle was measured by JY-82 contact angle measurements.

3. Results and discussion

The γ - $\log C$ curves of different mixed systems of bolaform amphiphiles/oppositely charged conventional surfactant are shown in Fig. 1.

The adsorption amount of surfactants (Γ_∞) was calculated according to the Gibbs adsorption equation since the ionic strength was kept constant:

$$\Gamma_\infty = -d\gamma/2.303RT d \log C.$$

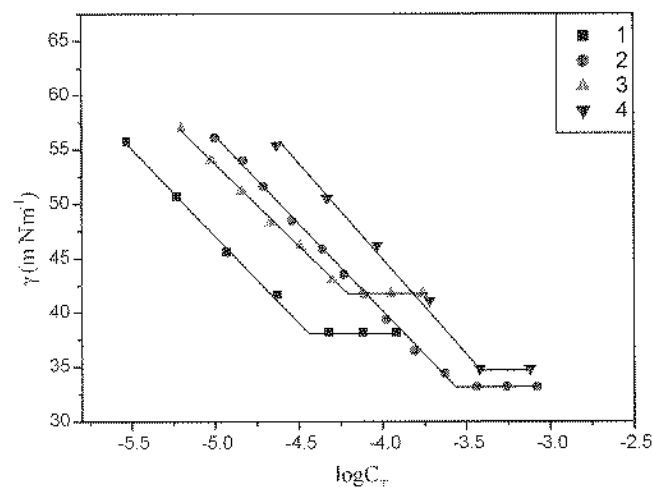


Fig. 1. γ - $\log C$ curves of mixed systems of bolaform amphiphiles/oppositely charged conventional surfactants (30 °C, $X_{bola} = 0.33$): (1) $C_{20}Py_2/SDS$; (2) C_6PhC_6/SDS ; (3) C_6PhPhC_6/SDS ; (4) $C_{20}Na_2/C_{12}Et_3$.

Table 1
Surface physicochemical properties of bolaform amphiphile/oppositely charged conventional surfactant systems ($X_{bola} = 0.33$, 30 °C)

	$10^4 c_{cmc}$ (mol/l)	γ_{cmc} (mN/m)	$10^6 \Gamma_{max}$ (mol/m ²)	A_{min} (nm ²)
$C_{20}Py_2/SDS$	0.33	38.6	2.72	0.61
C_6PhC_6/SDS	2.8	33.19	2.82	0.59
C_6BPhC_6/SDS	0.61	41.8	2.65	0.63
$C_{20}Na_2/C_{12}Et_3$	3.76	34.8	2.68	0.62

Here γ is the surface tension in mN/m. C is the concentration of the corresponding surfactant in a single system, while it represents the total concentration in a mixed bola/SDS system. Γ_∞ is the saturate adsorption amount in mol/m². $d\gamma/d \log C$ is the maximal slope in each case. T is absolute temperature. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Then the minimum average area per surfactant molecule (A_{min}) is obtained from the saturated adsorption by

$$A_{min} = 10^{18}/N_A \Gamma_\infty.$$

Here N_A is the Avogadro constant.

The surface tension of concentration at the cmc (γ_{cmc}), the saturated adsorption (Γ_{max}), and the minimum average molecular area (A_{min}) in mixed surfactant systems are listed in Table 1, as well as the cmc. It is seen that all the cmc values of these cationic systems are small, but the γ_{cmc} 's are higher than those of conventional [22–24] cationic systems and gemini-containing mixed systems [25].

The time effect of surface tension for various cationic bola/oppositely charged conventional surfactant [sodium dodecylsulfate (SDS) or $C_{11}H_{23}COONa$] systems at total concentrations of surfactants (C_T) below the cmc is shown in Fig. 2. It is very interesting to note that the surface tension of all these systems increased apparently within 24 h. This

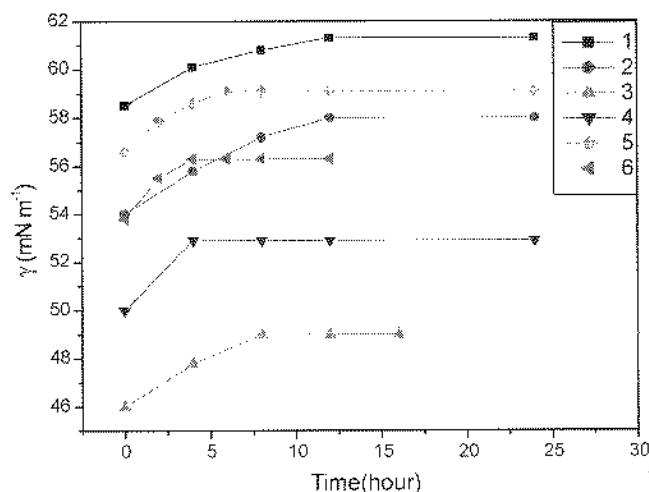


Fig. 2. Time-dependent surface tension changes of cationic bolaform amphiphiles and mixed surfactants (30 °C): (1) $C_{20}Py_2$, $2.5 \times 10^{-5} \text{ M}$, $[NaBr] = 0.1 \text{ M}$; (2) $C_{20}Py_2/SDS$, $C_T = 6.25 \times 10^{-6} \text{ M}$, $X_{bola} = 0.33$, $[NaBr] = 0.1 \text{ M}$; (3) $C_{20}Py_2/SDS$, $C_T = 2.25 \times 10^{-5} \text{ M}$, $X_{bola} = 0.33$, $[NaBr] = 0.1 \text{ M}$; (4) $C_{20}Py_2/C_{11}H_{23}COONa$, $C_T = 4 \times 10^{-5} \text{ M}$, $X_{bola} = 0.33$, $[NaBr] = 0.1 \text{ M}$, $[Na_2B_4O_7 \cdot 10H_2O] = 0.01 \text{ M}$; (5) C_6PhC_6/SDS , $C_T = 7.84 \times 10^{-5} \text{ M}$, $[NaBr] = 0.1 \text{ M}$; (6) C_6BPhC_6/SDS , $C_T = 9.53 \times 10^{-6} \text{ M}$, $[NaBr] = 0.1 \text{ M}$.

Table 2

The changes of absorbance and surface tension of C₂₀Py₂/SDS system with time

<i>t</i> (h)	0	4	8	12	16
Absorbance	0.141	0.120	0.110	0.107	0.106
10 ⁶ <i>c</i> (mol dm ⁻³)	5.63	4.31	3.63	3.44	3.38
γ _{calc} (mN m ⁻¹)	46.0	47.7	48.7	49.0	49.1
γ (mN m ⁻¹)	46.0	48.1	49.2	49.5	49.5

$X_{\text{bola}} = 0.33$; $C_T = 2.25 \times 10^{-5}$ M; γ_{calc} was calculated from the concentration detected by UV-vis spectra; γ was the examined surface tension of the solution by experiment.

phenomenon is obviously different from the normal *dynamic surface tension*, which usually *decreases* with time and for most aqueous surfactant solution reaches equilibrium within an hour. Moreover, this a fascinating phenomenon is observed in mixed cationic bola surfactant/anionic single-head-group surfactant systems, but not in mixed anionic bolaform surfactant/cationic single-head-group surfactant systems or conventional cationic–anionic surfactant mixed systems. In a mixed C₂₀Na₂/decyltriethylammonium bromide (C₁₂Et₃) or C_{*n*}H_{2*n*+1}(NMe₃Br⁻/C_{*m*}H_{2*m*+1})COONa (*n* = 8, 10, 12, *m* = 8, 10, 12) solution, the surface tension will reach equilibrium in 30 min. Thus the slow increase of surface tension in these systems cannot be attributed to the adsorption of surfactants onto the air/water interface.

It is well known that the surface tension is determined by the surface composition, and hence by the composition of the bulk solution; therefore the most possible cause for this phenomenon may be to the decrease of surfactant concentration in bulk solution. In order to prove this, we determined the C₂₀Py₂ concentration in the C₂₀Py₂/SDS system at various aging times by UV-vis spectrum. The results (Table 2) showed that the concentration of C₂₀Py₂ decreased with time. According to these measured concentrations, corresponding surface tension values of the solution can be read from the equilibrate surface tension curve and listed in Table 2 as calculated surface tensions (γ_{calc}). Interestingly, these calculated surface tension values coincide with the original measured results very well, thus providing strong support to our assumption.

A further question is the mechanism of the very slow variation of surfactant concentration. It is well known that glass surfaces are usually negatively charged and tend to absorb the cationic surfactants. As an evidence, when a C₂₀Py₂/sodium dodecylsulfate (SDS) mixed solution ($X_{\text{bola}} = 0.33$, $C_T = 4 \times 10^{-5}$ M) was put into a glass vessel, the surface tension of the solution was found to increase gradually with time. After about 24 h the surface tension value did not change any more. Then the solution was removed from the vessel and the same vessel was refilled with a fresh C₂₀Py₂/SDS solution at the same concentration. The surface tension of this fresh solution was measured again and no change with aging time was detected. Similarly, we examined the concentration change of C₂₀Py₂ in the refilled vessel by UV-vis spectra. It was found that the surfactant con-

Table 3

The variations in concentration of C₂₀Py₂ in the fresh C₂₀Py₂/SDS system

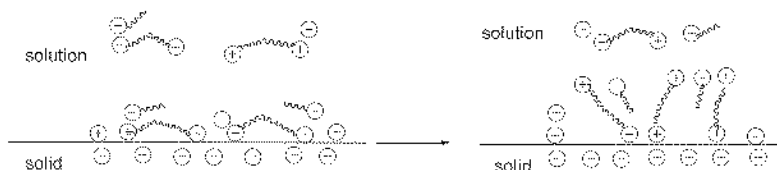
<i>t</i> (h)	0	1	5	12	24
Absorbance	0.150	0.151	0.151	0.151	0.151
10 ⁶ <i>c</i> (mol dm ⁻³)	5.90	5.91	5.91	5.91	5.91

$X_{\text{bola}} = 0.33$; $C_T = 2.25 \times 10^{-5}$ M. The data were recorded after the original C₂₀Py₂/SDS solution was removed from the vessel, and then the vessel was refilled with fresh C₂₀Py₂/SDS solution.

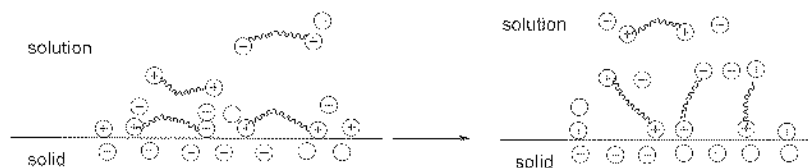
centration of this fresh solution did not vary within 24 h. The result is listed in Table 3. Obviously, after the adsorption on the vessel wall was saturated, no more surfactant molecules would be adsorbed. Hence the concentration of the solution would not decrease and the surface tension of the solution would not change.

A possible explanation for the phenomena mentioned above is that cationic bolaform amphiphiles will be adsorbed onto the solid/liquid interface through a special process. We supposed, first, that the cationic bola surfactant molecules would be adsorbed onto the negatively charged glass surface by electrostatic attraction, with two head groups tightly tied to the surface. By this time, the adsorption amount is small and the area taken by each molecule in the solid/liquid interface is large. After this fast process, the glass surface is covered by lying down bolaform cationic surfactants and it becomes somewhat hydrophobic for the exposure of the hydrocarbon chain to the aqueous media, which is not beneficial to the energy decrease of the whole system. The surfactant molecules in the solutions still have a strong tendency to "escape" to the solid/liquid interface due to the hydrophobic effect. Afterwards, one of the polar heads of the bolaform cationic molecule gradually leaves the surface of the vessel, making the cationic bolaamphiphilic molecules stand up (Scheme 2) and leave area for other surfactant molecules in the solutions. This causes an increase of the adsorption amount and a decrease of the area per molecule taken in the solid/liquid interface. Since both the vessel wall and the anionic molecules, especially the anionic surfactant molecules in solution, may attract the polar heads of cationic bolaamphiphiles, it takes a long time for the bolaform molecules to stand up.

Since the concentrations of the systems studied were considerably low, the change of concentration caused by adsorption could not be ignored and the change of solution surface tension can be easily observed. If the explanation above is true, a change of the glass surface from hydrophobic to hydrophilic should be observed. To determine this, the contact angles of several mixed surfactant solutions on the glass surface were measured (Fig. 3). It was found that the contact angles of these systems decreased gradually with time (the total decrease of contact angle was large), which was in accordance with the results of surface tension measurement and the supposed adsorption process. On the other hand, the contact angles of conventional cationic surfactants and anionic bolaform surfactants hardly changed



Scheme 2. Proposed mechanism for adsorption of bolaform cationic amphiphiles in mixed systems on the surface of glass.



Scheme 3. Proposed mechanism for adsorption of single flexible bolaform cationic amphiphiles systems on the surface of glass.

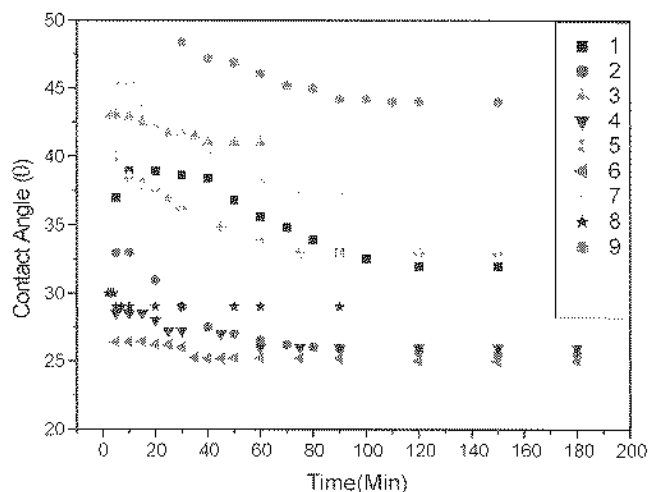


Fig. 3. Change of contact angles of different systems on the surface of glass: (1) $C_{20}Py_2$, $C_T = 2.5 \times 10^{-5}$ M; (2) $C_{20}Py_2/SDS$, $C_T = 2 \times 10^{-4}$ M; (3) $C_{10}Py$, $C_T = 1.0 \times 10^{-3}$ M; (4) C_6PhC_6 , $C_T = 0.01$ M; (5) C_6PhC_6/SDS , $C_T = 7.84 \times 10^{-5}$ M; (6) C_6BPhC_6 , $C_T = 8.0 \times 10^{-4}$ M; (7) C_6BPhC_6/SDS , $C_T = 9.6 \times 10^{-6}$ M; (8) $C_{20}Na_2$, $C_T = 2.6 \times 10^{-5}$ M; (9) $C_{20}Me_6$, $C_T = 2.5 \times 10^{-4}$ M.

with time (Fig. 3). The above measurement fully supports our assumption about the surface adsorption.

However, for the single-cationic-bolaamphiphile systems, the situation is a little different. The reverse time effect is found only in flexible-chained cationic bolaamphiphiles (Fig. 2), such as $C_{20}Py_2$ and $C_{20}Me_6$, but not in rigid C_6PhC_6 and C_6BPhC_6 systems. This may be attributed to the different flexibility of the hydrocarbon chain in these cationic surfactants. For $C_{20}Py_2$ and $C_{20}Me_6$, the flexible hydrocarbon chain stands up easily under electrostatic interaction with reverse ions and hydrophobic interaction with other bolas in the solution (Scheme 3). But for the rigid bola molecules, this process becomes a little difficult. On one hand, the interface energy of water/benzene is 35 mN/m (20 °C), while that of water/alkyl is as high as 50 mN/m [26] under the same conditions. Thus the phenyl group is somewhat hydrophilic when compared with the alkyl chain; therefore it is a little more comfortable for the rigid bolas to ex-

pose their hydrocarbon skeleton to water than for flexible-chained molecules to do so. On the other hand, the rigidity of the phenyl group restricts the free movement of the hydrocarbon skeleton. Both factors make it difficult for the rigid bola molecules to stand up. The time-dependent contact angle experiments (Fig. 3) support this proposal very well.

4. Summary

In summary, the surface tension will increase in cationic bolaform amphiphile/anionic surfactant mixed solutions, due to large amounts of surfactant molecules are gradually adsorbed on wall of vessel, which cause great change of concentration and composition in mixed surfactant solutions. This effect will be obvious at surfactant concentrations below the cmc, since the relative influence of solid/liquid adsorption on concentration and composition in mixed surfactant solutions will be far greater. But the reverse time effect in single bolaform cationic surfactant systems is up to the structure of the hydrocarbon chains, which can be observed only in flexible cationic bolaform surfactant solutions.

Acknowledgment

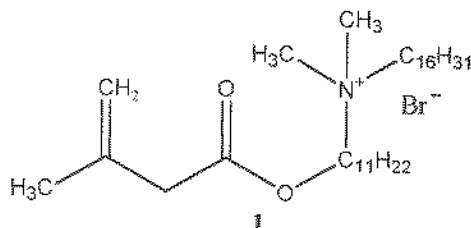
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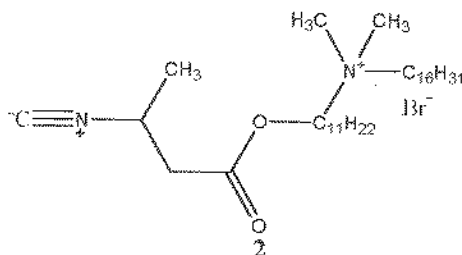
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分子 1(结构式见下图)聚合形成的聚合物囊泡,在体系中存在 25%(体积分数,下同)的乙醇时仍未被



破坏.1983年 Poks 等^[21]报道疏水链中含有异氰基的分子 2(结构式见下图)形成的聚合物囊泡在 30% 的乙醇溶液中仍保持稳定.1997年, Komatsu 等^[22]制成的聚合物囊泡可在 95% 的乙醇中保持稳定.2001年, Stanish 等^[23]对磷脂类聚合物囊泡的稳定性作了详尽的研究,它们的聚合物囊泡在约 30% 的乙醇溶液中的大小与在水中相同.



1.2 乙醇等极性溶剂中正负离子表面活性剂混合体系形成的囊泡

对乙醇中表面活性剂囊泡研究的突破是发现正负离子表面活性剂混合体系在乙醇中形成的囊泡.1995年,我们^[24]报道了烷基羧酸盐与溴化季铵盐混合体系形成的囊泡在 50% 的乙醇溶液中仍保持稳定.1997年,又报道了上述体系可在纯乙醇中形成囊泡^[25],扩展了非水溶剂中囊泡的研究.

对于非水及混合溶剂中囊泡的形成,我们认为,乙醇等极性溶剂的加入有两方面的影响:第一,使混合溶剂的极性变小,表面活性剂的疏溶剂效应降低,不利于囊泡的形成;第二,使体系中溶剂的介电常数发生改变,导致表面活性剂极性基团之间的相互作用变化.根据 Coulomb 公式:

$$F = Q_1 Q_2 / \epsilon_0 \epsilon r^2$$

式中 Q_1 、 Q_2 为两质点所带电荷, ϵ_0 为真空介电常数, ϵ 为体系的相对介电常数, r 为两质点距离,极性基团之间的静电相互作用与介质的介电常数有关.由于乙醇的介电常数(24.3)小于水的介电常数(78.5),在表面活性剂溶液中加入乙醇后,表面活性剂极性基团之间的作用力将增强.对于阳离子表面

活性剂或阴离子表面活性剂单体系溶液,极性基团之间的作用力为斥力,作用力增强导致囊泡解离,与疏溶剂效应减弱的作用相同.但对于正负离子表面活性剂混合体系,极性基团之间的作用力为引力,作用力增强会使表面活性剂排列更加紧密,与疏溶剂效应引起的作用相反.一般认为,静电作用强于疏溶剂相互作用,故静电作用的增强有可能抵消疏溶剂效应减弱带来的囊泡解离效应,从而使得体系可以在低介电常数溶剂中形成囊泡,甚至在特殊情况时有可能使体系形成囊泡的能力提高^[25].

基于上述理论,我们对一系列正负离子表面活性剂混合体系进行了研究.发现对于相对介电常数小于水的溶剂,如乙醇、正丙醇、异丙醇、二甲亚砜、*N,N*-二甲基甲酰胺、四氢呋喃(相对介电常数分别为 24.3、20.3、18.3、46.6、26.7、7.6)正负离子表面活性剂混合体系都可能形成囊泡.我们^[25]于 1997 年报道了烷基羧酸盐与溴化季铵盐的混合体系可在纯乙醇中形成囊泡,1999 年^[26]报道了上述体系可在纯正丙醇、异丙醇以及 90%(体积比)的 DMSO 中形成囊泡,于 2000 年^[27]报道了上述混合体系可在 *N,N*-二甲基甲酰胺、四氢呋喃中形成囊泡.

对于烷基羧酸盐与溴化季铵盐的混合体系在上述非水溶剂中形成囊泡的情况在表 1 中给出(表中, $C_n\text{COONa}$ 代表 $n+1$ 酸钠, $C_m\text{NMBr}$ 代表溴化 m 烷基三甲铵).从表中可以看出,在各种介电常数小于水的体系中都可以形成囊泡.

图 1、图 2 分别为摩尔比为 1:1 的 $C_{11}\text{COONa}-C_{12}\text{NMBr}$ 体系在正丙醇、异丙醇中形成囊泡的透射电镜(TEM)照片(冰冻复型(freeze fracture)制样技术).特别值得注意的是,癸酸钠与溴化癸基三甲铵摩尔比为 1:1 的混合体系,在水溶液中不超声时不能形成囊泡,而在乙醇溶液中不必超声,就可以自发形成囊泡.也就是说,该体系在乙醇中比在水中更容易形成聚集体,这显然是介电常数改变引起的增强效应大于疏溶剂效应减弱的一个实例^[25].

另外,我们发现除烷基羧酸盐与溴化季铵盐混合体系外,烷基硫酸盐与溴化季铵盐混合体系、烷基磺酸盐与溴化季铵盐混合体系在乙醇等溶剂中都可形成稳定的囊泡.

而对于相对介电常数大于水的溶剂,如甲酰胺(相对介电常数为 111.0),其对正负离子表面活性剂囊泡有着较为显著的破坏作用.我们曾发现在

表 1 烷基羧酸盐与溴化季铵盐 1:1 混合体系在非水溶剂中的囊泡形成

Table 1 Vesicle formation of 1:1 (molar ratio) alkylcarboxylate and quaternary ammonium bromide in nonaqueous solvents

solvent		C ₆ COONa/C ₁₆ NMBr	C ₁₁ COONa/C ₁₂ NMBr	C ₁₁ COONa/C ₁₆ NMBr
water	NS	-	+	+
	S	+	+	+
ethanol	NS	+	+	+
	S	+	+	+
1-propanol	NS	+	+	+
	S	+	+	+
iso-propanol	NS	+	+	+
	S	+	+	+
DMSO(90%)	NS	+	+	+
	S	+	+	+
DMF	NS	+	+	+
	S	+	+	+
THF(95%)	NS	+	+	+
	S	+	+	+

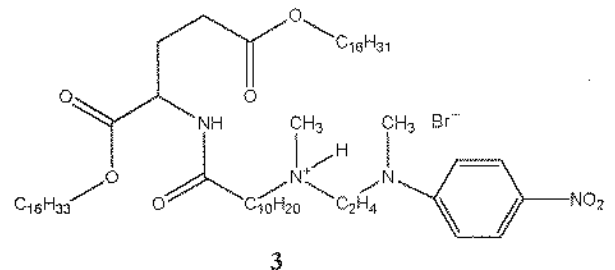
NS: without sonication; S: sonication; +: vesicle formed; -: no vesicle formed; *The content of DMSO is 75% (volume fraction).

烷基羧酸盐与溴化季铵盐 1:1 混合体系的水溶液中加入约 5% (体积分数) 的甲酰胺后, 囊泡即被破坏^[26, 28]. 这些实验事实都证实了我们的观点.

由于介电常数减小而引起的极性基团之间的静电引力增强, 进而使囊泡稳定性增加的效应只限于正负离子表面活性剂混合体系, 因为其它离子型表面活性剂体系极性基团之间的静电作用表现为斥力, 而斥力的增大反而破坏囊泡. 这是正负离子表面活性剂混合体系形成的囊泡特殊的优点, 这一结果对于非水溶剂中表面活性剂聚集体的研究有着重要意义.

1.3 乙醇中囊泡形成的其它研究工作

1996 年 Kimizuka 等^[29]曾报道了双链表面活性剂 3 (结构式见右图) 在水中形成囊泡. 在 40% ~



60% 的乙醇溶液中, 双分子层仍然存在. 囊泡亦可存在于 40% 的异丙醇、乙腈溶液中. 他们的成功在于选取疏水部分较大的表面活性剂, 使表面活性剂分子本身具有强烈的疏溶剂效应. 加入乙醇后, 疏溶剂效应虽有降低, 但仍未降低到可以破坏囊泡的程度, 故囊泡仍然稳定存在. 1997 年, 他们^[30]又将

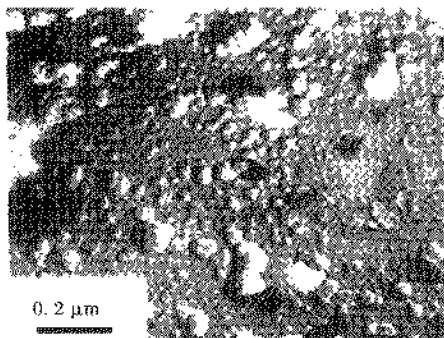


图 1 1:1C₁₁COONa/C₁₂NMBr 体系在正丙醇中形成囊泡的 TEM 照片

Fig. 1 TEM image of 1-propanol of 1:1 (molar ratio) C₁₁COONa/C₁₂NMBr system

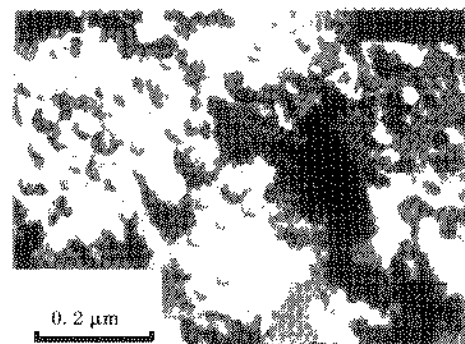
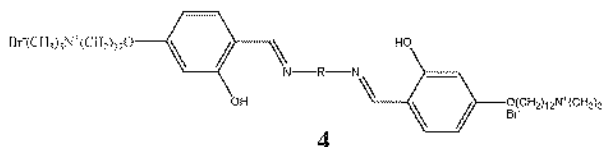


图 2 1:1C₁₁COONa/C₁₂NMBr 体系在异丙醇中形成囊泡的 TEM 照片

Fig. 2 TEM image of iso-propanol of 1:1 (molar ratio) C₁₁COONa/C₁₂NMBr system

表面活性剂 **3** 的反离子由溴离子变为对甲基苯磺酸根离子, 使双层结构可在纯乙醇溶液中稳定存在. 这一工作是基于对甲基苯磺酸根离子与表面活性剂极性基团之间的静电作用、van der Waals 作用以及可能存在的偶极-偶极相互作用使极性基团紧密结合, 致使极性基团间的相互作用加强, 提高了囊泡的稳定性. 这同我们在正负离子表面活性剂体系中利用低介电常数溶剂加入的手段有异曲同工之妙.

Liang 等^[31]于 2001 年报道了季铵盐类 Bola 表面活性剂分子 **4** (结构式见下图) 在乙醇溶液中形成的单分子层囊泡结构. 他们认为, 是溶剂介电常数降低引起的表面活性剂极性基团之间的相互作用增强而使囊泡在乙醇中稳定, 同时, 氢键作用以及苯环之间的 π - π 相互作用也有助于囊泡稳定. 但我们认为, 他们所研究的分子是单一的正离子表面活性剂, 极性基团之间的库仑作用力为斥力, 溶剂介电常数降低会使斥力增大, 似乎不利于囊泡的稳定. 这一体系囊泡能够稳定存在, 可能更大程度上要归结为氢键作用以及苯环之间的 π - π 相互作用.



2 沉淀体系转化为囊泡体系

正负离子表面活性剂混合体系往往因正负离子间强烈的电性相互作用而形成沉淀, 极大地限制了这一类具有高表面活性和聚集能力体系的基础研究和实际应用. 因此我们在正负离子表面活性剂易沉淀体系中开展了极性溶剂对聚集体形成转化影响的研究, 并取得了一些有意义的结果. 我们在溴化季铵盐 ($C_mH_{2m+1}N(CH_3)_3Br$, $m=8, 12$)/十二烷基硫酸钠、氯化烷基伯铵 ($C_nH_{2n+1}NH_2 \cdot HCl$, $n=8, 12$)/十二烷基硫酸钠等一些正负离子表面活性剂沉淀体系中加入少量乙醇、正丙醇, 发现这些极性溶剂的加入可使得体系中表面活性剂分子由沉淀转化为囊泡. 另外, 还发现了这类体系在混合溶剂中形成的双水相和多水相的奇异现象^[32-35]. 我们认为, 表面活性剂沉淀体系中沉淀转化为囊泡的现象可归结为是环境因素对表面活性剂分子体系中临界排列参数 P 调节的结果 (P 由公式 $P = V/a_0 l_c$ 求出^[36], 式中 V 是表面活性剂疏水部分的体积, a_0 为表面活

性剂分子极性头基所占的平均面积, l_c 为疏水链的最大伸展长度). 一般认为: $P > 1$ 时, 表面活性剂分子形成沉淀; 而 $1 > P > 0.5$ 时, 则形成囊泡. 对沉淀体系加入乙醇等极性溶剂分子后, 乙醇等分子插入表面活性剂分子的极性区, 可能使极性区变得松散, 即 a_0 变大, 进而导致 P 变小, 落入 $1 > P > 0.5$ 区域, 从而实现沉淀到囊泡的转化^[35]. Barry 等^[37]曾用核磁共振方法确定了乙醇在磷脂酰胆碱、磷脂酰乙醇水溶液中存在双分子层的极性区. 认为乙醇和极性基团之间存在着强烈的相互作用, 改变了极性基周围水的结构. 这与我们的工作结果是吻合的.

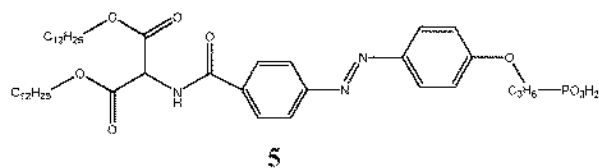
3 各种溶剂中的多种形式的分子有序组合体

与水溶液体系类似, 表面活性剂分子在非水溶剂中也不仅局限于胶束和囊泡, 还可以形成各式各样的分子聚集体. 溶剂也并不同于上面主要讨论的乙醇, 亦可以是各式各样的有机溶液. 这使非水溶剂中聚集体的研究更加丰富多彩.

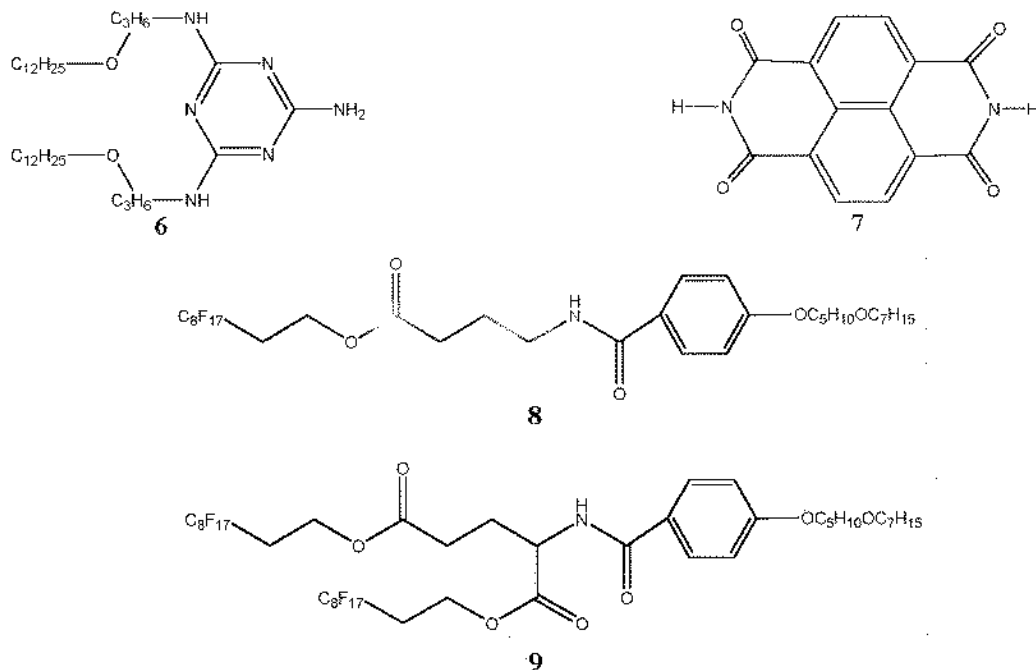
磷脂类分子可在有机溶剂中形成反胶团. Barclay 等^[38]于 1984 年报道了二棕榈酰卵磷脂等分子在水/磷脂摩尔比为 20:1 时, 可在苯、氯苯、邻二氯苯中形成反胶团, 聚集数为 80~100. 但若水/磷脂比例为 2~16 时, 有机溶剂中既有表面活性剂单体存在, 又有聚集体存在, 聚集体数目随含水量增加规则地增加.

表面活性剂分子亦可在非极性有机溶剂中形成反向的囊泡 (即亲水基团朝内、疏水部分朝外的双分子层膜). 1993 年, Kunieda 等^[39]用单羧酸蔗糖酯在癸烷/己醇/水溶剂中形成反向的囊泡. 单羧酸蔗糖酯在癸烷中不溶, 加入少量水后, 溶解生成层状液晶. 再加入己醇, 超声后层状液晶卷曲形成反向的囊泡. 此反向囊泡周围及内部都是油, 水全部存在于极性区. 这种结构有着好的时间稳定性及热稳定性.

磷脂分子 **5** (结构式见下图), 则可在 Ca^{2+} 的诱导下, 在氯仿、甲苯中形成反向的囊泡^[40].



1989 年, McIntosh 等^[41]报道了在甲酰胺、1,3-丙二醇中形成排列整齐的卵磷脂及卵磷脂/胆固醇



的多层膜结构,并用 XRD 测量了分子层的厚度。

1995 年, Kimizuka 等^[42]报道了分子 6 和分子 7 (结构式见上图)靠氢键作用,在甲基环己烷中形成的直径为 10 nm 管状结构。往溶液中加入 50% 的乙醇,出现 7 的沉淀,因为乙醇将氢键结构破坏,原本不溶于甲基环己烷的分子 7 沉淀出来。

对于有着特殊的憎水憎油性质的碳氟类表面活性剂在非水体系中的聚集性质的研究也已经出现。1989 年 Kunitake 等^[16]报导了碳类表面活性剂在非水溶剂中形成的囊泡。对于分子 8、9(结构式见上图),可在环己烷中形成宽 160 nm 的卷曲的带状物和直径为 20~100 nm 的球形囊泡。这是由碳氟链的疏溶剂效应与碳氢链的亲溶剂效应共同作用的结果。对于碳氟类表面活性剂在非水溶剂中形成的聚集体还有报道^[43-45],其聚集体形成原理普遍在于碳氟链对碳氢溶剂的疏溶剂效应。

对非水溶剂中表面活性剂聚集行为的研究是一项非常重要的工作,该领域的研究必将对膜模拟化学及合成化学、材料化学等相关领域的发展起到极大的推动作用。

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Vesicles and Other Self-organized Molecular Assemblies Formation in Nonaqueous Solvents*

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Abstract Formation of vesicles, micelles and other self-organized molecular assemblies in nonaqueous and mixed solvents was reviewed. Especially, the influences of dielectric constant variation on aggregation behavior of cationic surfactant mixtures in nonaqueous solvents were fully discussed. The situation about the formation of reverse micelles and other self-organized molecular assemblies in nonaqueous solvents was also summarized.

Keywords: Nonaqueous solvent, Vesicle, Micelle, Self-organized molecular assembly