Spontaneous Vesicle Formation in Aqueous Mixtures of Cationic Surfactants and Partially Hydrolyzed Polyacrylamide

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Spontaneous vesicle formation was observed in aqueous mixtures of partially hydrolyzed polyacrylamide and single-tailed cationic surfactants. The influences of pH, addition of long-chain alcohols, variation of hydrocarbon chain length, and head group size of the cationic surfactants were investigated systematically. It was found that 30–50% hydrolyzed degree of polyacrylamide and cationic surfactants with 10 or 12 methylene groups are suitable for vesicle formation in the mixed aqueous systems at pH 9.2. Addition of long-chain alcohols was found to be helpful for vesicle formation in some cases. The vesicle stability was also investigated at various temperatures and amounts of ethanol addition. © 2001 Academic Press

Key Words: vesicle formation; polymer–surfactant interaction; organized assembly.

1. INTRODUCTION

As precursors of vesicle formation, mixed cationic–anionic surfactants have attracted more and more attention (1–3) for their great significance in both theoretics and applications. However, the research on vesicular structure formed from ionic surfactants and oppositely charged polymers is scarce (4), although some multilayer structures were observed in the 2:1 mixed system of polyvinyl sulfate and cetyltrimethylammonium bromide by Harada and Nozaleora (5). In fact, the interactions of surfactants and polymers, including neutral polymers and polyelectrolytes, have been studied extensively, but most of the reports focused on the effect of polymers on the assemblies of surfactant, such as vesicles (6) and micelles (7). Studies on the interactions between ionic surfactants and oppositely charged polyelectrolytes (8–9) were often hampered by the formation of precipitates (10–13). In 1996, Everaars *et al.* (14) showed that tissue-like multivesicular superstructures were found upon heating of the insoluble complex of didodecyldimethylammonium and polyacrylic acid in water, showing the feasibility of vesicle formation in the mixed system of ionic surfactants and oppositely charged polyelectrolytes. However, in this system the function of polymers in vesicle formation is unclear, because the cationic surfactant itself has the capability for vesicle formation. Recently, Kabanov *et al.* (15) observed vesicle formation

from complexes of cationic surfactants and block copolymers of poly(ethylene oxide) and poly(sodium methacrylate), containing ionic and nonionic water-soluble segments.

In this work, the systems of a simple polymer (partially hydrolyzed polyacrylamide) mixed with single-tailed cationic surfactants were investigated. Various cationic surfactants with different hydrophobic chain lengths and hydrophilic head groups were used in this work. However, each of them alone cannot form vesicles in an aqueous system. It was shown in this work that vesicles spontaneously formed in the mixed aqueous systems of ionic surfactant and oppositely charged polymer. Vesicles can form and show good stability in this kind of system in a broad range of pH, temperature, and other physical–chemical conditions. The simplicity of preparation, the easy availability of the raw materials, and the great stability of vesicles make these systems promising in addressing various theoretical and practical problems.

2. EXPERIMENTAL

2.1. Materials

Polyacrylamide (PAM), A.R. grade (MW = 3,000,000), was a product of Shanghai Chemical Co. Partially hydrolyzed polyacrylamide (HPAM) was prepared by boiling a mixed solution of NaOH and 1 wt% PAM solution. The hydrolysis degree of HPAM, α, was calculated from

$$\alpha = W_{\text{NaOH}} \cdot M_{\text{CH}_2\text{CHCONH}_2} / W_{\text{PAM}} \cdot M_{\text{NaOH}},$$

where W_{NaOH} and W_{PAM} are the weights of NaOH and PAM, respectively, and M_{NaOH} and $M_{\text{CH}_2\text{CHCONH}_2}$ are the molecular weight of NaOH and group weight of [$\text{CH}_2\text{CHCONH}_2$], respectively. Alkyltrimethylammonium bromide (C_mNMBr $m =$ 8, 10, 12), dodecyltriethylammonium bromide (C_{12}NEBr), and alkylpyridinium bromide (C_nPyBr $n =$ 10, 12, 14) were synthesized from *n*-alkyl bromide and trimethylamine, triethylamine, or pyridine in this lab. The crude products were recrystallized five times from the mixed solvents ethanol–acetone or ether–acetone. The purities of all the surfactants were examined by surface tension measurement using the drop volume method (16), and no surface tension minimum was found in their surface

tension curves ($\gamma - \log C$). Deionized water was treated with KMnO$_4$ and distilled before use. Other reagents were A.R.-grade products of Beijing Chemical Co.

2.2. Methods

Vesicles were prepared by mixing the cationic surfactant and HPAM solution at room temperature (~25°C). No rigorous mechanical agitation was applied. The molar ratio of the mixture is defined as [surfactant] : [carboxylate group]. The morphology of organized assemblies was studied by electron microscopy (EM, JEM-100CXII). The freeze–fracture and negative staining (with uranyl acetate ethanol solution) techniques were used for EM sample preparation. The phase transition temperature of organized assembly in mixed systems was determined by a differential scanning calorimeter (Dupont 1090), at a heating rate of 2°C/min. The pH values were kept at 6–7 (deionized water) or 9.2 (buffered by Na$_2$B$_4$O$_7$ · 10H$_2$O, ~0.01 mol dm^{-3}) or 13 (adjusted by NaOH) in various systems.

3. RESULTS AND DISCUSSION

3.1. Vesicle Formation in C$_{12}$NMBr–HPAM Systems

At room temperature (~25°C), the aqueous system of C$_{12}$NMBr–30% hydrolyzed polyacrylamide mixture was investigated. The solubility of the mixture in water varied with the molar ratio of the surfactant–polymer mixture. Better solubility was observed when the molar ratio ([surfactant] : [carboxylate group]) was far from 5 : 5. In the mixed aqueous systems with C (the total molar concentration of surfactant and carboxylate group of HPAM) greater than 1.1×10^{-2} mol dm^{-3}, precipitation occurred at 8 : 2 to 4 : 6. However, at $C = 8.5 \times 10^{-3}$ mol dm^{-3}, the dispersions were opalescent from 9 : 1 to 4 : 6 and transparent at mixture ratios of 10 : 1, 3 : 7, 2 : 8, and
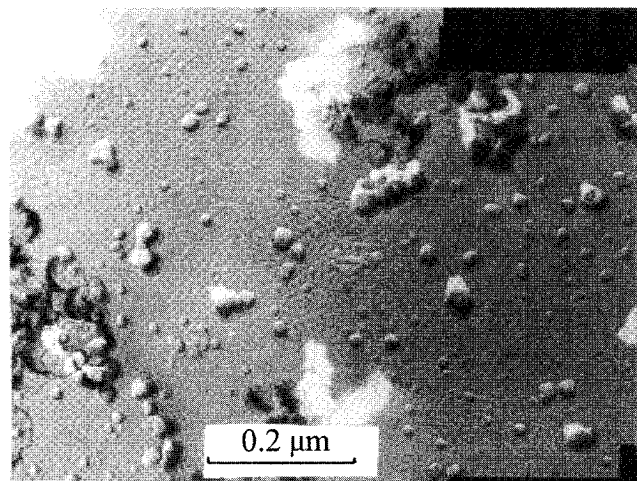

FIG. 1. Electron microscopic image for a 9 : 1 C$_{12}$NMBr–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system, observed by freeze–fracture technique.
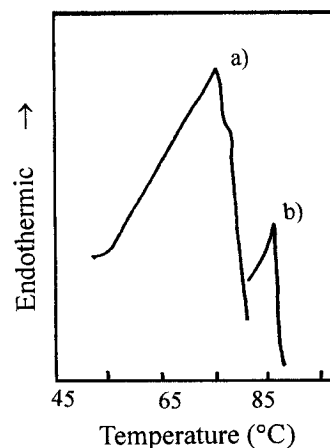

FIG. 2. DSC curves for a C$_{12}$NMBr–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system, (a) 9 : 1, (b) 4.5 : 5.5.

1 : 9. Electron microscopic images obtained by both freeze–fracture and negative staining techniques show that in the systems ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) globular vesicles formed at molar ratios of 9 : 1 and 4.5 : 5.5 (see Fig. 1 and Table 1), providing direct evidence for vesicle formation in this kind of system. The compositions of these vesicular dispersions are just at each of the two boundaries between transparent and opalescent areas. The sizes of vesicles are ~15–30 nm as determined by the EM images obtained by the freeze–fracture technique. The differential scanning calorimeter (DSC) curves are shown in Fig. 2 and the phase transition temperatures (T_c) are listed in Table 1. It is well known that the DSC result will confirm the existence of a surfactant mesophase, and the phase transition temperature can be attributed to the "melting" of the oriented hydrocarbon chains of surfactant molecules in the mesophase. It is also well known that a vesicle is a kind of surfactant mesophase. In addition to the electron microscopic images obtained from the same systems, the DSC results further confirm vesicle formation in the mixed systems at 9 : 1 and 4.5 : 5.5.

It has been recognized that each of the components alone does not form vesicles. Vesicle formation in these mixed systems should be attributed to the interaction between the surfactants and polymers, which results in the formation of a polymer–surfactant complex. Considering the structures and sizes of

TABLE 1
Vesicle Formation in C$_{12}$NMBr and 30% Hydrolyzed Polyacrylamide Mixed Systems ($C = 8.5 \times 10^{-3}$ mol dm^{-3})

Molar ratio[a]	Solution appearance	EM observation[b]	T_c/°C
10 : 1	Transparent	−	/
9 : 1	Opalescent	+	72.0
6 : 4	Opalescent	−	/
4.5 : 5.5	Opalescent	+	84.5
3 : 7	Transparent	−	/

[a] [Surfactant] : [Carboxylate group].
[b] + Vesicle formation; − no vesicle.

FIG. 3. A scheme for the formation and structure of a surfactant–polymer complex.

FIG. 5. DSC curves for a $10:1$ mixed $C_{12}NMBr$–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system with (a) dodecanol (2.0×10^{-3} mol dm^{-3}) and (b) octanol (6.0×10^{-3} mol dm^{-3}) addition.

the surfactants and polymers, their complex can be imaged as the charged surfactant ion hanging onto the polymer backbone through electrostatic interaction between their oppositely charged hydrophilic groups. A scheme for the formation and structure of a surfactant–polymer complex is shown in Fig. 3.

It is seen from Fig. 3 that a hydrophilic area, consisting of the hydrophilic polymer, and a hydrophobic area, consisting of the hung hydrocarbon chains of surfactants, exist in the complex. Such a complex formation will have two results: (1) The solubility of the complex will be lower than that of the polymer and surfactant. The greater the degree of combination, the lower the solubility. If the amount of combination is large enough—for example, in systems of higher total concentration and in the range of molar ratio near to $5:5$—precipitation will occur. (2) The hydrocarbon tail of the surfactant will be concentrated on the polymer, which assists hydrophobic aggregation to form self-organized assemblies. The structure of the assemblies, that is, the type of self-organized assembly, will be determined by the relative size of the hydrophilic area to the hydrophobic area in the complex. That is, in aqueous systems, a hydrophilic area larger than the hydrophobic area will be beneficial to micelle formation; otherwise, the situation will be better for vesicle and bilayer structure formation. The relative size of the hydrophilic

and hydrophobic areas in the complex will be affected by many factors. Among them the hydrolysis degree of HPAM, the molar ratio of surfactant to polymer, the existence of other amphiphiles, and the pH of the aqueous system are important. The effects of these factors will be discussed as follows.

Alcohol addition. Addition of long-chain alcohols is helpful to vesicle formation in this system. No vesicle has been found in the $10:1$ $C_{12}NMBr$–30% hydrolyzed polyacrylamide system ($C = 1.0 \times 10^{-3}$ mol dm^{-3}). However, after addition of octanol (6×10^{-3} mol dm^{-3}) or dodecanol (2×10^{-3} mol dm^{-3}) to the same system, vesicles appeared. The EM and DSC results for the systems containing alcohols are shown in Figs. 4 and 5. The T_c values are 57.0 and 64.5°C for the systems containing octanol and dodecanol, respectively. As discussed in the previous section, such a DSC result supports the formation of vesicles in systems containing alcohol. This phenomenon can be explained as follows. Hydrophobic groups can participate into the complex by the electrostatic attraction between the oppositely charged groups of surfactant and polymer, as well as by the solubilization of amphiphiles into the hydrophobic area of the complex, based on the hydrophobic effect. In the $10:1$ mixed system, the amount of cationic surfactant is much more than that of carboxylic groups in HPAM. The excess of surfactants may incorporate into the hydrophobic domain through the hydrophobic effect, which makes the complex positively charged. Electrostatic repulsion between the surfactant positive charges causes

FIG. 4. Electron microscopic image for a $10:1$ mixed $C_{12}NMBr$–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system with octanol addition (6.0×10^{-3} mol dm^{-3}), observed by freeze–fracture technique.

TABLE 2
Vesicle Formation in $C_{12}NMBr$ and HPAM Systems with Different α (pH 9.2, $C = 9.1 \times 10^{-3}$ mol dm^{-3})

α	Molar ratio							
	$9:1$	$8:2$	$7:3$	$6:4$	$5:5$	$4:6$	$3:7$	$2:8$
50%	−	−	−	+	+	+	−	−
30%	+	+	+	+	+	−	−	−
15%	−	−	−	−	−	−	−	−

TABLE 3

Effect of CH Chain Variation on Vesicle Formation in HPAM and Cationic Surfactants Mixed Systems (pH 9.2)

Mixed system	C (mol dm^{-3})	Molar ratio		
		7:3	6:4	5:5
C_{10}NMBr–30% HPAM	8.5×10^{-3}	+	+	+
C_{10}NMBr–50% HPAM	9.1×10^{-3}	+	+	+
C_{10}PyBr–30% HPAM	1.0×10^{-2}		+	+
C_8NMBr–30% HPAM	1.2×10^{-2}	−	−	−
C_{14}PyBr–30% HPAM[a]	4.0×10^{-3}	/	/	/
C_{14}PyBr–50% HPAM[a]	1.3×10^{-3}	/	/	/

[a] Precipitation occurs in the mixed systems.

polymer chain extension and probably limits the relative size of the hydrophilic area to the hydrophobic area in the complex and destabilizes vesicles. On the other hand, when long-chain alcohols are added, the hydrophobic domains of the complex

TABLE 4

Effect of Head Group Variation on Vesicle Formation in HPAM and Cationic Surfactants Mixed Systems (pH 9.2, $C = 8.5 \times 10^{-3}$ mol dm^{-3})

Mixed system	Molar ratio				
	9:1	8:2	7:3	5:5	4:6
C_{12}PyBr–30% HPAM	+	+	+	+	+
C_{12}NEBr–30% HPAM			+	+	
C_{12}NEBr–50% HPAM			+	+	

prefer solubilizing the alcohol molecules to the cationic surfactants, since there is no additional electrostatic repulsion in the complex when alcohol solubilized in. Thus a larger hydrophobic area of the complex results, which is beneficial to vesicle formation.

pH effect. EM observation with the freeze–fracture and negative staining techniques showed that in C_{12}NMBr and 30% hydrolyzed polyacrylamide systems the vesicle-forming range was significantly extended as the pH changed from 6–7 (pH value of deionized water) to 9.2 (see Table 2), due to the increase of negatively charged carboxylic groups as pH rises. Thus a greater amount of cationic surfactant could be combined with the polymer, resulting in a relatively larger hydrophobic area in the complex.

Effect of hydrolysis degree. Table 2 shows the conditions of vesicle formation in the mixed cationic surfactant and HPAM with various hydrolysis degree systems. Unlike the C_{12}NMBr–30% hydrolyzed polyacrylamide system, no vesicles were found in the mixed systems of C_{12}NMBr and 15% hydrolyzed polyacrylamide at the molar ratios of [surfactant] : [carboxylate group] from 9 : 1 to 2 : 8. This may be attributed to the reduction of charged units in the polymer with the decrease of hydrolysis
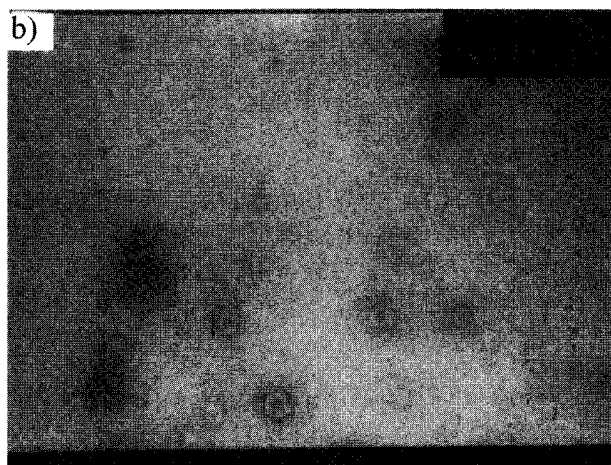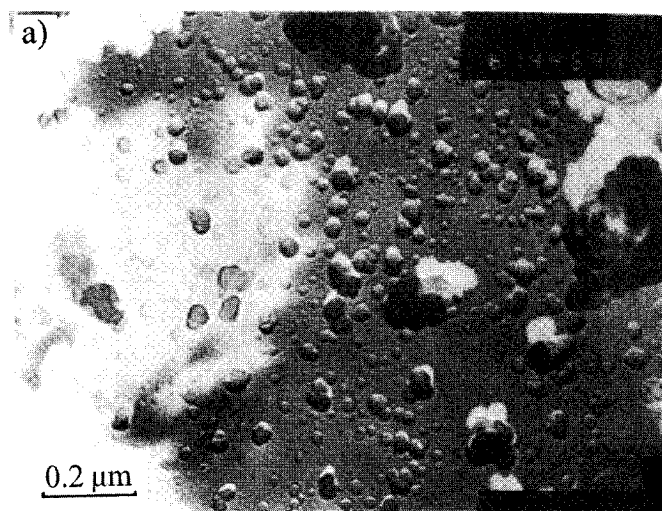
FIG. 6. Electron microscopic image for a 5 : 5 mixed C_{12}NMBr–50% hydrolyzed polyacrylamide ($C = 9.1 \times 10^{-3}$ mol dm^{-3}) system observed by (a) freeze–fracture technique and (b) negative staining technique.
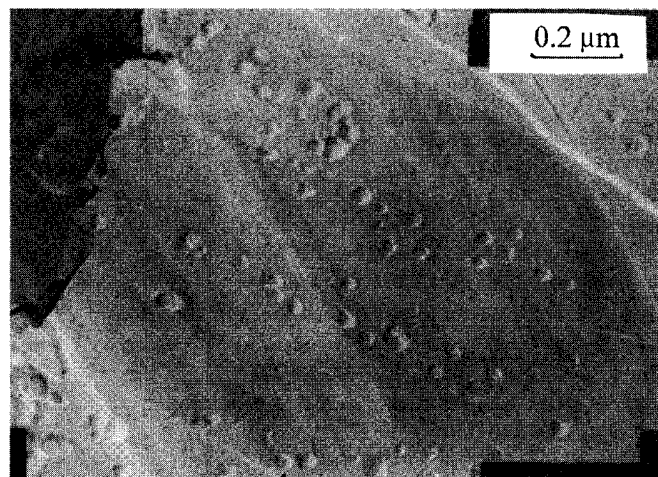

FIG. 7. Electron microscopic image for a 6 : 4 mixed C_{10}NMBr–50% hydrolyzed polyacrylamide ($C = 9.1 \times 10^{-3}$ mol dm^{-3}) system, observed by freeze–fracture technique.
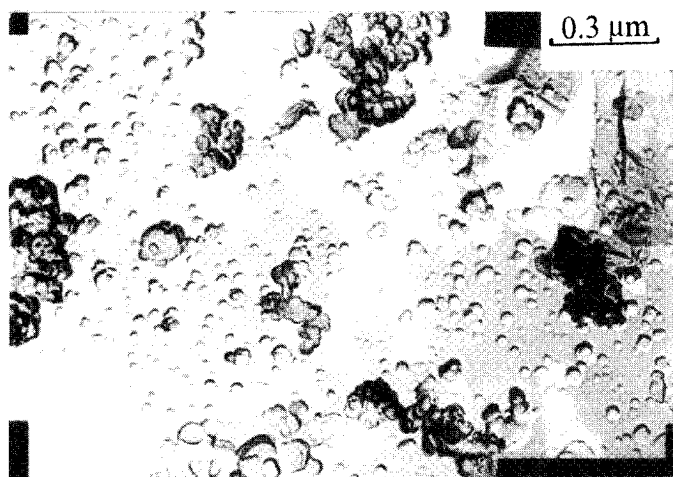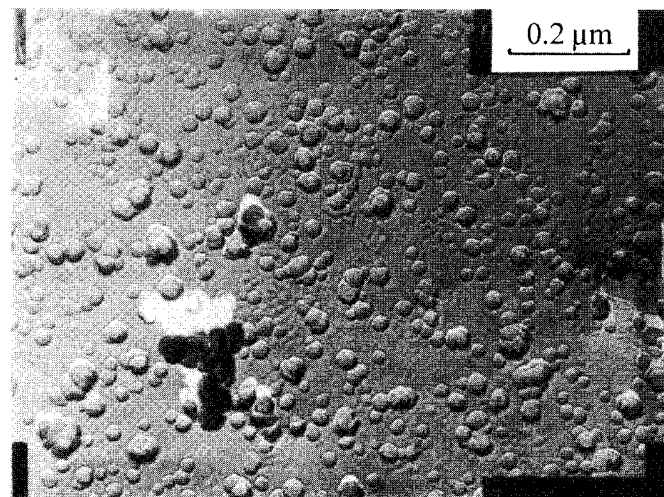
FIG. 8. Electron microscopic image for a 5:5 mixed C_{10}PyBr–50% hydrolyzed polyacrylamide ($C = 1.0 \times 10^{-2}$ mol dm^{-3}) system, observed by freeze–fracture technique.

degree. Thus the size of the hydrophobic area relative to hydrophilic area in the complex will be also reduced, greatly decreasing the vesicle forming ability in these systems. Spontaneous vesicle formation also occurred in the C_{12}NMBr–50% hydrolyzed polyacrylamide systems (see Fig. 6 and Table 2), albeit the range of molar ratio for vesicle formation in this mixed systems was smaller than that in the C_{12}NMBr and 30% hydrolyzed polyacrylamide mixed systems.

3.2. Vesicle Formation in HPAM and Different Cationic Surfactant Systems

At room temperature (~25°C), the organized assemblies in the aqueous systems of different cationic surfactants with 30

FIG. 9. Electron microscopic image for a 4:6 mixed C_{12}PyBr–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system, observed by freeze–fracture technique.

TABLE 5

Vesicle Formation in 30% Hydrolyzed Polyacrylamide and C_{12}NMBr Mixed Systems (pH 13, $C = 8.5 \times 10^{-3}$ mol dm^{-3})

Molar ratio	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8
Vesicle formation	+	+	+	+	+	+	−	−

and 50% hydrolyzed polyacrylamide were investigated. The results are listed in Tables 3 and 4, and some typical electron microscopic photos are shown in Figs. 7 and 9. The solubility in mixed systems of cationic surfactants with less than 12 methylene groups and HPAM is very good. These solutions are optically transparent at any mixed ratio of surfactant and carboxylate group of HPAM, even when the total concentration is as high as 1.2×10^{-2} mol dm^{-3}. However, self-organization behavior in these mixed systems is quite different. Vesicles formed in the C_{10}NMBr–HPAM and C_{10}PyBr–HPAM systems, but no vesicles were found in the C_8NMBr–HPAM system at any composition, even if the total concentration of surfactant and the carboxylate group of HPAM was increased to 1.2×10^{-2} mol dm^{-3} (see Table 4), obviously due to the weaker hydrophobic interaction in C_8NMBr–HPAM systems. This reveals that the alkyl chain of the cationic surfactant molecule should be long enough—for example, not shorter than 10 carbon atoms—to ensure vesicle formation. However, too long a hydrocarbon chain in a cationic surfactant molecule is not good for vesicle formation in this kind of system. In fact, precipitation appeared in 30 or 50% C_{14}PyBr–HPAM (molar ratio from 7:3 to 5:5) systems in the total concentration range of 9.1×10^{-3} to 1.3×10^{-3} mol dm^{-3}.

The variation of hydrophilic head groups has no obvious effect on vesicle formation in this kind of systems. This is different from the situation of common cationic–anionic surfactant mixed systems (2). For example, when the head group changed from trimethylammonium to triethylammonium, there was no difference in vesicle formation as shown in Table 4. This may be explained by asserting that the size of the hydrophilic area per hydrophobic chain in the complex is not determined by the size of hydrophilic group of the surfactant, but by the water-soluble polymer. Thus, the increase in the head group size of cationic surfactant does not significantly influence the packing characteristics of the polymer segment and cationic surfactant.

TABLE 6

Temperature Influence[a] on Vesicle Stability in C_{12}NMBr and 30% Hydrolyzed Polyacrylamide Mixed Systems ($C = 8.5 \times 10^{-3}$ mol dm^{-3})

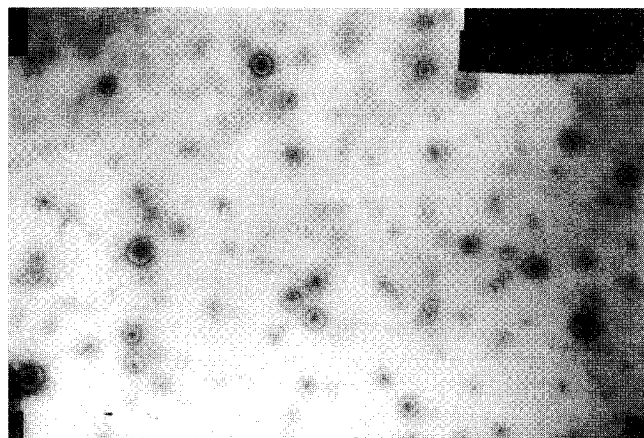| Molar ratio	50°C × 0.5 h	70°C × 0.5 h	4°C × 1 h	−17°C × 1 h
9:1	+	+	+	+
4.5:5.5	+	+	+	+

[a] EM observation after sample aging (~25°C) 4 h.

FIG. 10. Electron microscopic image for a 4.5:5.5 mixed C_{12}NMBr–30% hydrolyzed polyacrylamide ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system, after $-17°C \times 1$ h, observed by negative staining technique at room temperature.

FIG. 11. Electron microscopic image for a (a) 5:5 mixed C_{12}PyBr–30% hydrolyzed polyacrylamide and (b) 9:1 30%HPAM–C_{12}NMBr ($C = 8.5 \times 10^{-3}$ mol dm^{-3}) system, with 90% volume ethanol addition, observed by freeze–fracture technique.

3.3. Vesicle Stability

The vesicles in HPAM and cationic surfactant systems are very stable and usually can last over 10 weeks. It is worth noting that the vesicles in these systems maintain stability at very high pH, e.g., pH 13 (see Table 5), showing great vesicle stability in a strongly basic environment. Moreover, in these systems the vesicles exist over a very broad temperature range. EM observations show that either heated to 70°C (aging 0.5 h) or cooled to $-17°C$ (aging for 1 h), vesicles can be found after the samples returned to ~25°C and aged 4 h. (see Table 6 and Fig. 10). The truth might be that vesicles were destroyed at $-17°C$ (samples were frozen at that temperature) and then re-formed at 25°C. Similar results were also reported by Kaler et al. in other cationic and anionic surfactant mixed systems (17), in which the vesicles showed good stability after a freeze–thaw cycle and were called "equilibrium vesicles."

Nevertheless, it is interesting to note that vesicles in these kinds of systems can maintain their stability at very large ethanol/water ratios (see Table 7 and Fig. 11), albeit the ethanol addition improves the solubility of the complex very well. The solution is optically transparent when the volume ratio of ethanol/water is higher than 0.5. The vesicle stability in these systems is similar to that of 1:1 mixed cationic and ionic surfactant systems (2, 18), and better than that of the phospholipid liposome and polymerized vesicle systems (19).

However, the vesicles will be destroyed if NaBr is added at a concentration of 0.1 mol dm^{-3}. This is similar to the stability of the usual phospholipid liposome systems (19) and worse than that of vesicles formed from cationic surfactants. In the latter situation vesicles still exist at 0.2 mol dm^{-3} NaBr in some cases (2).

4. SUMMARY

Spontaneous vesicle formation was observed in mixed systems of HPAM and various cationic surfactants. It was explained that the surfactant ionic head groups bound to the oppositely charged units of the polymer and formed a complex. The water-soluble polymer and the head groups of the surfactant formed a hydrophilic area, and the hydrophobic groups of the bound surfactant tails formed hydrophobic domains in the complex. Therefore, such a complex constitutes a special polymeric surfactant, showing the typical characteristics of a surfactant: self-organization. It was shown that (1) pH 9.2 and HPAM of 30–50% hydrolyzed degree are the better conditions for vesicle formation. (2) Addition of long-chain alcohols is helpful for vesicle formation in some cases. (3) Decreasing the hydrocarbon chain length of cationic surfactants can improve their solubility but decrease their vesicle-forming capability. The cationic surfactants with 10–12 methylene groups will be better for vesicle formation. (4) The size variation of the head group of cationic surfactants did not influence the vesicle formation significantly. All of these phenomena have been explained preliminarily by the variation of the relative sizes of the hydrophobic area and the hydrophilic area in the surfactant–polymer complex. Furthermore, the vesicles formed in this kind of systems showed

TABLE 7
Influence of Ethanol Addition on Vesicle Stability in 30% Hydrolyzed Polyacrylamide and Cationic Surfactant Mixed Systems ($C = 8.5 \times 10^{-3}$ mol dm^{-3})

Mixed system[a]	Molar ratio	$V_e/V_t = 0.3$	$V_e/V_t = 0.7$	$V_e/V_t = 0.9$
C_{12}NMBr–30% HPAM	9:1	+	+	+
C_{12}NMBr–30% HPAM	4.5:5.5	+	+	+
C_{12}PyBr–30% HPAM	5:5	+	+	+

[a] Solution is opalescent and optically transparent before and after $V_e/V_t = 0.5$. V_e/V_t is the ratio of ethanol volume and total volume.
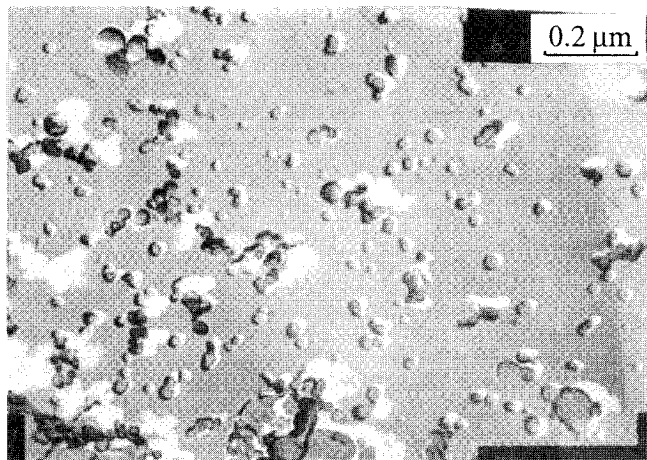
great stability to ethanol addition and the variation of pH or temperature.

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