

Vesicle Formation and Stability in Aqueous Mixtures of the Hydrolyzed Copolymer of Styrene–Maleic Anhydride and Conventional Single-Tailed Cationic Surfactants

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Vesicle formation in aqueous mixtures of the hydrolyzed copolymer of styrene–maleic anhydride (HSMA) and a series of single-tailed cationic surfactants ($C_nH_{2n+1}N(C_mH_{2m+1})_3Br$, $n = 8, 10, 12, 16$, $m = 1, 2, 3, 4$) was studied by fluorescence measurement, ζ potential measurement, and transmission electron microscopy. The driving forces of vesicle formation in this kind of system are attributed to the combination of electrostatic attraction and the hydrophobic interaction. Variation of the surfactant structure had a great influence on vesicle formation. A model for the conformation of the molecular packing in the vesicle membrane was suggested on the basis of XRD measurement and Chem3D simulation. Moreover, these vesicles showed superstability to aging time, to NaBr, and to ethanol.

Introduction

In the past few decades, vesicles have attracted much interest due to their great significance in both theoretics and applications.^{1,2} Much research has been done on exploiting new kinds of vesicle-forming systems and investigating the vesicle properties such as stability to environmental factors. Usually, vesicles formed through sonication or other mechanical disruption of the bilayer phase easily change back to flat bilayer structures or precipitate in aqueous dispersion,^{3,4} which greatly hampered the potential application of the vesicles. One approach to stabilize the vesicle structure is polymerization of the molecules before^{5,6} or after^{7–10} their orientation in model membranes, which can limit the kinetic process of reversion. Unsaturated surfactants have been specifically synthesized for this type of polymerization, and considerable progress has been made in this field.^{11,12} More recently, vesicles formed by another kind of polymer, block copolymers, have also drawn much attention.^{13–15} Another strategy is exploiting

spontaneously formed vesicle systems in which vesicles exhibit great stability to environments such as aging time, salt, and organic solvent.^{16–19} For example, in some catanionic surfactant systems, vesicles formed spontaneously can keep their stability over periods of years.^{16,17} Therefore, it is reasonable to develop a vesicle-forming system which combines the advantages of the approaches mentioned above to improve vesicle stability. In our previous work,²⁰ vesicles spontaneously formed in mixtures of a series of cationic surfactants and partially hydrolyzed polyacrylamide showed great stability, even better than the stability of the polymerized vesicles upon ethanol addition, indicating the great significance of mixtures of a polyelectrolyte and oppositely charged surfactants as a kind of vesicle-forming system.

In fact, mixtures of a polyelectrolyte and oppositely charged surfactants have received much attention from both fundamental and industrial aspects including food processing, pharmaceutical formulations, personal care products, and paints.²¹ Most of the work is concentrated on the interaction between the two components.^{22–25} The amount of research on microstructure formation and transformation in these systems is still smaller.^{26–28}

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The structure of a polyelectrolyte–surfactant complex was often regarded as micelle-like, and the “necklace” model²⁹ was proposed and widely accepted. However, there are still other kinds of microstructures³⁰ such as vesicular structures formed in the polyelectrolyte–surfactant system. Considering the similarity between vesicles formed in a mixture of a polyelectrolyte with an oppositely charged surfactant and those formed in a mixed cationic and anionic surfactant system which exhibited more advantages such as easy preparation and adjustment, some efforts were made to investigate this new kind of vesicle-forming system. In 1996, tissue-like multivesicular superstructures were found upon heating of the insoluble complex of didodecyltrimethylammonium bromide and poly(acrylic acid) in water,³¹ showing the feasibility of vesicle formation in a mixed system of an ionic surfactant and oppositely charged polyelectrolytes. However, in this system the function of polymer to vesicle formation is unclear, since the cationic surfactant itself has the capability to form vesicles. In 1997,³⁰ vesicles were found in the mixed system of polymer JR400 and its oppositely charged surfactant SDS. In this system, vesicle formation should be due to polyelectrolyte–surfactant complex formation. In 1998, Kabanov et al.³² prepared vesicles by simply mixing block copolymers containing ionic and nonionic water-soluble segments with oppositely charged single-tailed surfactants. A model for the complex structure^{32,33} was also provided. In recent years, more reports^{34–36} have revealed that vesicles can spontaneously form in polyelectrolyte–surfactant systems. The increasing but still fewer reports revealed that the system of a polyelectrolyte and an oppositely charged surfactant had already become a new kind of vesicle-forming candidate system. Unfortunately, so far the mechanism of vesicle formation in this kind of mixed system is still unclear due to the complexity of the polymer structure, which makes it difficult to clarify the relationship among the interaction of the components, the microstructure, and the properties of the aggregate. Further investigation should be made to find the final resolution.

In the present work, vesicle formation in mixtures of a simple polyelectrolyte, hydrolyzed styrene–maleic anhydride copolymer (HSMA), and conventional cationic surfactants was investigated. Considering the small hydrophobic part of HSMA, the interaction between HSMA and the cationic surfactant was mainly the contribution of electrostatic attraction.³⁷ Moreover, the small molecular weight ($M_n = 1600$) of SMA we selected also greatly reduces the complexity of the polymer structure. The effects of the environmental factors such as aging time, NaBr, and ethanol on the vesicle stability were also studied for further understanding the vesicle properties in this series of mixed systems.

Experimental Section

Materials. Styrene–maleic anhydride copolymer (CAS 26762-29-8) was purchased from Aldrich Co. The molecular weight and polydispersity were $M_n = 1600$ and $M_w/M_n = 2.1$. The carboxyl

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content after hydrolysis in the polymer determined through potentiometric titration (Figure 1 in the Supporting Information). Quaternary ammonium bromides including *n*-dodecyltrimethylammonium bromide ($C_{12}Me_3$), *n*-dodecyltriethylammonium bromide ($C_{12}Et_3$), *n*-dodecyltripropylammonium bromide ($C_{12}Pr_3$), *n*-dodecyltributylammonium bromide ($C_{12}Bu_3$), *n*-octyltriethylammonium bromide (C_8Et_3), *n*-decyltriethylammonium bromide ($C_{10}Et_3$), *n*-cetyltriethylammonium bromide ($C_{16}Et_3$), and *n*-octyltributylammonium bromide (C_8Bu_3) were prepared by reaction of the corresponding alkyl bromide and trialkylamine. Sodium *n*-dodecylbenzenesulfonate (SDBS) was purchased from Acros Organics Co. Sodium *n*-dodecanesulfonate (SDSO₃) was a product of AR grade of Beijing Chemical Co. All the surfactants were recrystallized five times from mixed solvents of ethanol–acetone or ether–acetone. The purity of the surfactant was examined, and no surface tension minimum was found in the surface tension curve. Pyrene was obtained from Sigma Co. and used as received. The water used was redistilled from potassium permanganate. Other reagents were products of AR grade of Beijing Chemical Co.

Polyelectrolyte Solution. The stock solution of HSMA was prepared by mixing the styrene–maleic anhydride copolymer powder, the required amount of sodium hydroxide, and buffer solution (0.01 M $Na_2B_4O_7 \cdot 10H_2O$, pH 9.2) to yield a 200 mM solution. The mixture was stirred and heated to 90 °C in a water bath for 2 h. The concentration c (HSMA) refers to the content of carboxyl groups. HSMA solutions of lower concentrations were obtained by diluting the stock solution with buffer solution.

Preparation of Samples. Surfactant solutions were obtained by dissolving the corresponding surfactant with buffer solution. The samples were prepared by directly mixing the HSMA solution and the cationic surfactant solution. The total concentration, c_T , is the total result containing the concentration of the carboxyl content of HSMA and the concentration of cationic surfactants. The mixed ratio of the mixture is defined as $X(\text{surfactant}) = n(\text{surfactant}) / \{n(\text{HSMA}) + n(\text{surfactant})\}$. The solutions were kept in airtight containers to equilibrate for at least 24 h at 25 °C before they were further analyzed.

Fluorescence Probe Experiment. An ethanol solution of pyrene was introduced into the mixtures of HSMA and surfactant. The final pyrene concentration was 5×10^{-7} M, and the ethanol volume was less than 1% of the total solution volume (usually the effect of ethanol at this concentration on the surfactant aggregates is insignificant^{38,39}). The fluorescence spectra of pyrene solubilized in the investigated solutions were recorded using a Hitachi F4500 spectrofluorometer in the range 350–450 nm at an excitation wavelength of 335 nm. I_1/I_3 corresponds to the ratio of the fluorescence intensities of the first ($\lambda = 374$ nm) and third ($\lambda = 384$ nm) vibronic peaks and was used to monitor the formation of hydrophobic microdomains. The critical aggregation concentration (cac) value can be taken as the concentration that corresponds to the intercept between the linear extrapolations of the rapidly varying portion of the curve and of the almost-horizontal portion at high concentration (Figure 2 in the Supporting Information).

Transmission Electron Microscopy (TEM). TEM micrographs were obtained with a JEM-100CX II transmission electron microscope (working voltage of 80–100 kV) by the negative-staining method with uranyl acetate solution (1%) as the staining agent. One drop of the solution was placed onto a carbon Formvar-coated copper grid (230 mesh). Filter paper was employed to suck away the excess liquid. Then one drop of the staining agent was placed onto the copper grid. The excess liquid was also sucked away by filter paper.

Small-Angle X-ray Diffraction (XRD). Self-supported cast films for the XRD studies were prepared by dispersing the vesicle suspensions in precleaned glass slides. Reflection XRD studies were carried out with a model XKS-2000 X-ray diffractometer (Scintaginc). The X-ray beam was generated with a Cu anode, and the wavelength

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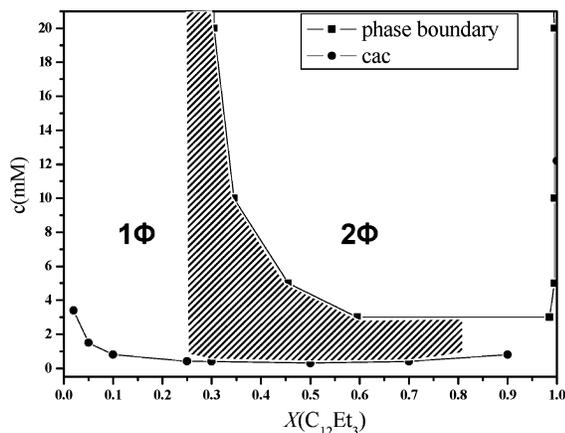


Figure 1. Partial phase diagram of aqueous mixtures of HSMA/ $C_{12}Et_3$ ($T = 25\text{ }^\circ\text{C}$, pH 9.2). Shaded area: vesicle region.

Table 1. Cac Values of Mixtures of HSMA/ $C_{12}Et_3$ at Different Mixed Ratios ($T = 25\text{ }^\circ\text{C}$, pH 9.2)

$X(C_{12}Et_3)$	cac (mM)	$X(C_{12}Et_3)$	cac (mM)
0.02	3.22	0.30	0.40
0.05	1.47	0.50	0.31
0.10	0.83	0.70	0.40
0.25	0.42	0.90	0.94

of the $K\alpha_1$ beam was 1.5406 \AA . The X-ray beam was directed toward the film edge, and the scanning was done up to a 2θ value of 10° .

ζ Potential Measurement. ζ potentials were measured using a temperature-controlled Zetasizer 2000 (Malvern Instruments Ltd.).

Results and Discussion

Vesicle Formation in Systems of HSMA Mixed with $C_{12}Et_3$

The phase behavior of the mixed system of HSMA/ $C_{12}Et_3$ ($T = 25\text{ }^\circ\text{C}$, pH 9.2) was studied and is shown in Figure 1. The mixtures showed good solubility when the total concentration was small. If the total concentration was smaller than 3 mM, the mixed solutions at any ratio were clear and homogeneous. However, a two-phase region consisting of two liquid phases appeared at the large total concentration or the rich content of $C_{12}Et_3$.

The aggregation behaviors were also investigated in this kind of mixed system. The cac values at different mixed ratios were obtained by the measurement of the I_1/I_3 of pyrene as a function of the total concentration (Figure 2 in the Supporting Information) and are listed in Table 1. The cac values plotted as a function of the mixed ratio are also shown in Figure 1. When the concentration increased over the cac, spherical vesicles with a diameter of 100–400 nm were observed by TEM (Figure 2) at mixed ratios from $X(C_{12}Et_3) = 0.25$ to $X(C_{12}Et_3) = 0.8$ (shadows in Figure 1). The size distribution investigated by dynamic light scattering showed that the average vesicle diameter is about 50–200 nm (the polydispersity index of the vesicles is 0.04) for the HSMA/ $C_{12}Et_3$ system at $c_T = 3\text{ mM}$ and $X(C_{12}Et_3) = 0.5$, which is in accordance with the TEM observation.

Vesicles in such a region were proved to be negatively charged even if $X(C_{12}Et_3)$ in the bulk solution was as high as 0.8. For example, the ζ potential values are -38.5 and -26.8 mV for the vesicles in mixed systems of $c_T = 2.5\text{ mM}$ with $X(C_{12}Et_3) = 0.6$ and $c_T = 2\text{ mM}$ with $X(C_{12}Et_3) = 0.8$, respectively. This result indicated that the component of the aggregates was usually HSMA-rich in our investigated systems no matter that of the bulk solution. This is also different from the situation for the mixture of cationic and anionic surfactants, in which negatively charged and positively charged vesicles usually formed in the anionic surfactant-rich region and cationic surfactant-rich region, respectively.¹⁶ These results in the HSMA/ $C_{12}Et_3$ system indicated that the polyelectrolyte may have the advantage to participate in the aggregates. Moreover, the phase diagram shown in Figure 1 revealed that the two-phase region was close to the $C_{12}Et_3$ side but not to the ratio of 1:1. As is known, the phase separation usually occurred when the aggregate was close to charge neutralization. This also inferred that HSMA is preferred to participate in the aggregate, so the charge neutralization occurred at $X(C_{12}Et_3) \gg 0.5$ in the bulk solution.

It should be noted that vesicles do not form in each of the components alone and vesicle formation in the mixed system should be the result of the electrostatic interaction between the oppositely charged polyelectrolyte and surfactant. In other words, it can be regarded that the hydrophobic part was introduced to the polymer chain through electrostatic interaction.

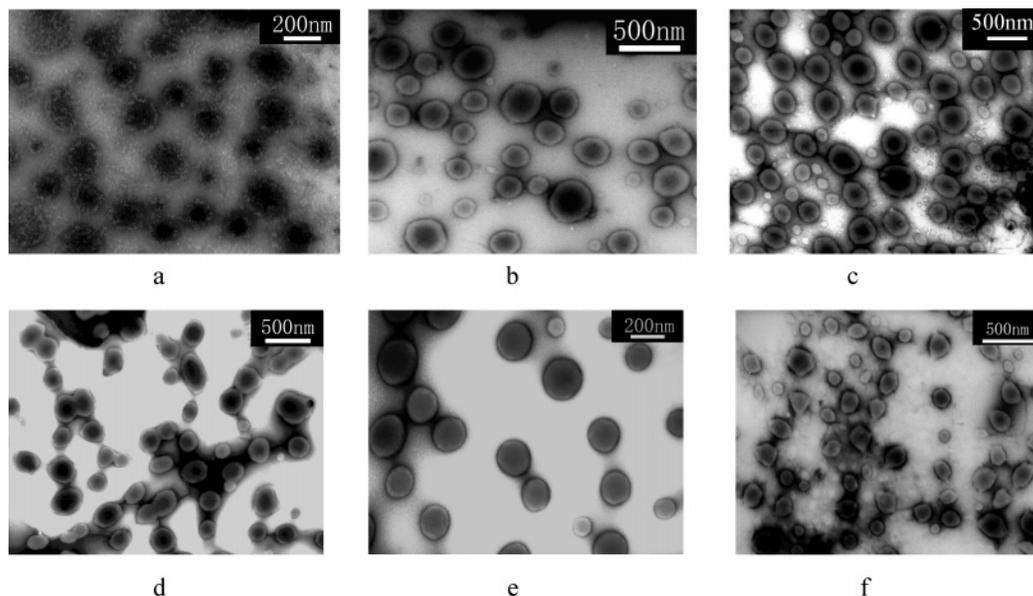
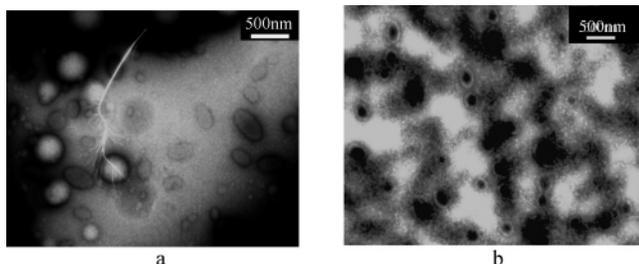


Figure 2. TEM images of vesicles formed in mixed systems of HSMA/ $C_{12}Et_3$ ($T = 25\text{ }^\circ\text{C}$, pH 9.2): (a) $c_T = 10\text{ mM}$, $X(C_{12}Et_3) = 0.25$; (b) $c_T = 3\text{ mM}$, $X(C_{12}Et_3) = 0.3$; (c) $c_T = 5\text{ mM}$, $X(C_{12}Et_3) = 0.4$; (d) $c_T = 3\text{ mM}$, $X(C_{12}Et_3) = 0.5$; (e) $c_T = 2.5\text{ mM}$, $X(C_{12}Et_3) = 0.6$; (f) $c_T = 2\text{ mM}$, $X(C_{12}Et_3) = 0.8$.

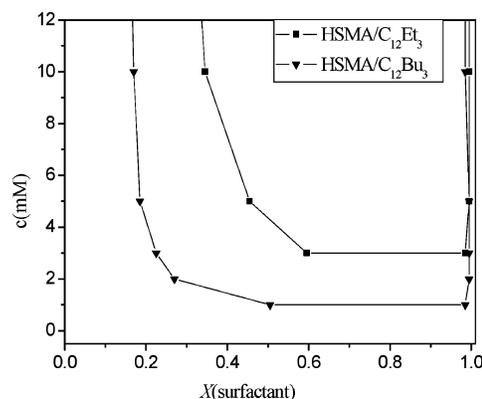
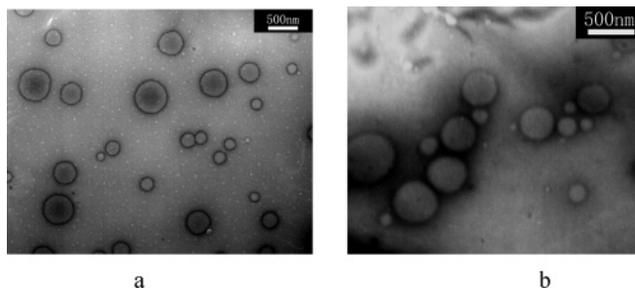
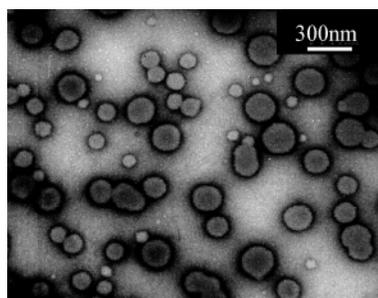
Table 2. Cac Values of Systems of HSMA Mixed with Alkyltriethylammonium Bromide ($T = 25\text{ }^{\circ}\text{C}$, pH 9.2)

system	cac (mM) at $X(\text{surfactant}) = 0.25$	cac (mM) at $X(\text{surfactant}) = 0.5$	system	cac (mM) at $X(\text{surfactant}) = 0.25$	cac (mM) at $X(\text{surfactant}) = 0.5$
HSMA/C ₈ Et ₃	9.71	6.97	HSMA/C ₁₂ Et ₃	0.42	0.31
HSMA/C ₁₀ Et ₃	1.87	1.27	HSMA/C ₁₆ Et ₃	0.11	

**Figure 3.** TEM images of HSMA/C₁₀Et₃ and HSMA/C₁₆Et₃ at $c_T = 10\text{ mM}$ and $X(\text{surfactant}) = 0.25$: (a) HSMA/C₁₀Et₃; (b) HSMA/C₁₆Et₃ ($T = 25\text{ }^{\circ}\text{C}$, pH 9.2).

Effect of Hydrophobic Interaction on Vesicle Formation in Mixed Systems of HSMA and Conventional Cationic Surfactants. Besides the electrostatic attraction, the hydrophobic effect is another important driving force for the formation of vesicles and other surfactant aggregates. To study this effect on vesicle formation, four kinds of alkyltriethylammonium bromides with different chain lengths were mixed with HSMA. The cac values of these four kinds of mixtures determined by the fluorescence probe method are listed in Table 2. As expected, the cac values decreased with an increase of the hydrocarbon chain length, demonstrating that the increase of the hydrocarbon chain length of the cationic surfactant is beneficial to form aggregates in this kind of system. TEM observation showed that vesicles only formed in the mixed systems with hydrophobic chains of the cationic surfactant bigger or equal to 10 carbon atoms (Figure 3) at a mixed ratio $X(\text{surfactant}) = 0.25$. However, no vesicle was observed in the HSMA/C₈Et₃ system even if the total concentration reached 50 mM, indicating that a large enough hydrophobic chain length of the cationic surfactant is necessary for vesicle formation in this kind of mixed system. Similar results were also observed in conventional cationic/anionic surfactant mixed systems of alkyltrimethylammonium bromide and sodium alkylcarboxylate.⁴⁰ Vesicles formed only when the total carbon atom number of the hydrocarbon chains of the two surfactants was >19 , and neither of them can be smaller than 8 carbon atoms. The study described in this paper addressed that the hydrophobic effect is an important driving force for vesicle formation in mixed systems of polyelectrolytes and cationic surfactants.

It is known that an increase of the headgroup to tributyl of the quaternary ammonium bromide cationic surfactant will enhance the aggregation ability of the surfactant as well as mixed systems containing such a surfactant.⁴¹ This is also true for mixed systems of HSMA and cationic surfactants. At a mixed ratio of $X(\text{surfactant}) = 0.5$, the cac values of the HSMA/C₁₂Me₃, HSMA/C₁₂Et₃, HSMA/C₁₂Pr₃, and HSMA/C₁₂Bu₃ systems were 0.37, 0.31, 0.33, and 0.18 mM, respectively, indicating that an increase of the headgroup to tributyl enhanced the aggregation ability of the mixed system. Moreover, compared with the system of HSMA/C₁₂Et₃, the two-phase region of HSMA/C₁₂Bu₃ moved toward a mixed ratio of 1:1 (Figure 4), indicating that the surfactant tends to participate in the aggregate more easily with an increase

**Figure 4.** Partial phase diagram of mixtures of HSMA and surfactants with various headgroups ($T = 25\text{ }^{\circ}\text{C}$, pH 9.2).**Figure 5.** Vesicles in systems of HSMA/C₁₂Bu₃: (a) $c_T = 3\text{ mM}$, $X(\text{C}_{12}\text{Bu}_3) = 0.20$; (b) $c_T = 0.25\text{ mM}$, $X(\text{C}_{12}\text{Bu}_3) = 0.5$ ($T = 25\text{ }^{\circ}\text{C}$, pH 9.2).**Figure 6.** Vesicles in the system of 10 mM HSMA/C₈Bu₃ at $X(\text{C}_8\text{-Bu}_3) = 0.25$ ($T = 25\text{ }^{\circ}\text{C}$, pH 9.2).

of the surfactant headgroup to tributyl. In fact, vesicles can form at lower concentration (0.25 mM at $X(\text{C}_{12}\text{Bu}_3) = 0.5$) and smaller $X(\text{C}_{12}\text{Bu}_3)$ ($X(\text{C}_{12}\text{Bu}_3) \geq 0.15$) in the HSMA/C₁₂Bu₃ system (Figure 5) than that in the HSMA/C₁₂Et₃ system. That is to say, an increase of the number of $-\text{CH}_2-$ segments on the surfactant headgroup will increase the hydrophobic effect between the headgroups, which will also enhance the hydrophobic effect of the surfactant and promote vesicle formation.

A mixture of HSMA/C₈Bu₃ was investigated to test the effect of an increase of the hydrophobic interaction of the surfactant headgroup on vesicle formation mentioned above. As expected, vesicles were observed in the system at $c_T = 10\text{ mM}$ with $X(\text{C}_8\text{-Bu}_3) = 0.25$ (Figure 6), although there were no vesicles formed in systems of HSMA/C₈Et₃ where the tail length of the cationic surfactant is the same.

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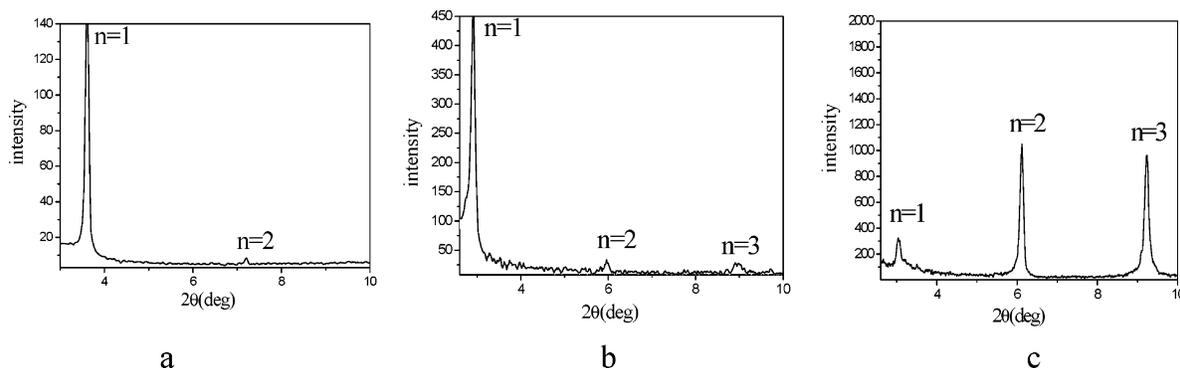
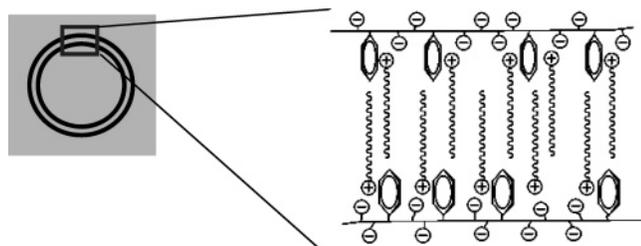


Figure 7. XRD patterns of vesicles in the following systems: (a) HSMA/C₁₂Et₃ at $c_T = 10$ mM and $X(\text{C}_{12}\text{Et}_3) = 0.30$; (b) HSMA/C₁₆Et₃ at $c_T = 10$ mM and $X(\text{C}_{16}\text{Et}_3) = 0.25$; (c) HSMA/C₁₂Bu₃ at $c_T = 10$ mM and $X(\text{C}_{12}\text{Bu}_3) = 0.15$.

Scheme 1. Illustration of the Molecular Arrangement in Vesicle Membranes



Molecular Packing in the Vesicle Membrane. Combined with the above results, vesicles formed easily in the systems of HSMA mixed with conventional surfactants, which is the result of the strong electrostatic interaction and the hydrophobic interaction. Considering the structure of the surfactants and polyelectrolyte, their complex can be imagined as the charged surfactant ion hanging onto the polymer backbone through electrostatic interaction between their oppositely charged hydrophilic groups. The hydrocarbon tails of the surfactants associated together through the hydrophobic effect, constituting the hydrophobic layer. Hence, it is understandable that the cationic surfactant should have a large enough hydrophobic chain length to form the hydrophobic part of the vesicle. Moreover, benzene rings hung on the polymer main chain will fix the surfactant headgroup near the benzene ring through cation- π interaction.^{42,43}

Further investigation of the vesicle membrane structure is performed through the small-angle XRD method in mixtures of HSMA and cationic surfactants. The XRD patterns of cast films for dispersions of HSMA/C₁₂Et₃, HSMA/C₁₆Et₃, and HSMA/C₁₂Bu₃ are illustrated in Figure 7. A series of reflections were obtained for all the samples, which are similar to those reported in other amphiphiles' cast films.^{44,45} According to the Bragg equation, the layer spacing corresponding to the first peak at the lowest 2θ value was calculated to be 2.4, 3.0, and 2.9 nm for HSMA/C₁₂Et₃, HSMA/C₁₆Et₃, and HSMA/C₁₂Bu₃, respectively. The molecular length of C₁₂Et₃, C₁₆Et₃, and C₁₂Bu₃ was estimated to be about 1.8, 2.3, and 2.0 nm on the basis of the Chem3D simulation, respectively. It is clear that the thickness of the vesicle membranes is shorter than twice the molecular length but slightly longer than the molecular length of the corresponding cationic surfactant, indicating that the surfactant molecules probably adopt

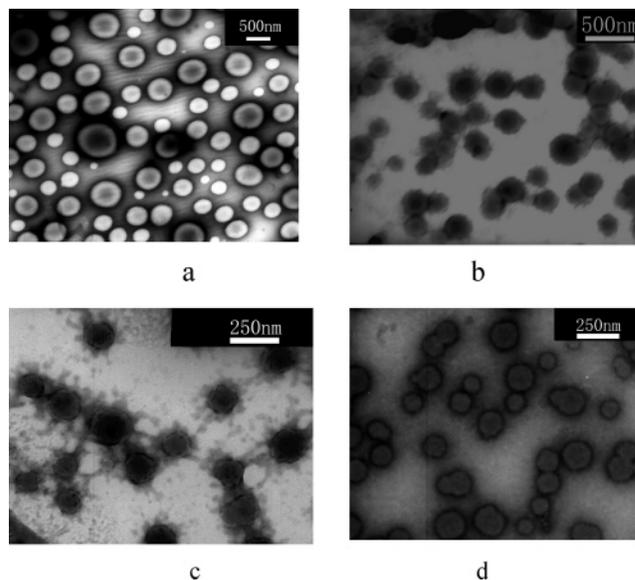


Figure 8. TEM images of vesicles in systems of HSMA/C₁₂Et₃: (a) $c_T = 3$ mM, $X(\text{C}_{12}\text{Et}_3) = 0.3$, after 9 months; (b) $c_T = 3$ mM, $X(\text{C}_{12}\text{Et}_3) = 0.5$, after 9 months; (c) $c_T = 3$ mM, $X(\text{C}_{12}\text{Et}_3) = 0.5$, cooled to -25 °C and then returned to 25 °C; (d) $c_T = 3$ mM, $X(\text{C}_{12}\text{Et}_3) = 0.5$, heated to 70 °C and then returned to 25 °C.

the interdigitated chain packing model. A scheme for the molecular arrangement in the vesicle membrane is proposed in Scheme 1.

Vesicle Stability. Vesicles formed in mixed systems of HSMA and conventional cationic surfactants showed superstability. The vesicle solutions remained clear during our investigation time. TEM results revealed that vesicles can keep their morphology for at least 9 months at room temperature (22–27 °C) (Figure 8a,b). Moreover, TEM observations show that, either heated to 70 °C (aging for 1 h) or cooled to -25 °C (aging for 1 h), vesicles can be found after the samples are returned to 25 °C and aged for 5 h (Figure 8c,d). The truth might be that the vesicles are destroyed at -25 °C (samples frozen at that temperature) or 70 °C and then re-formed at 25 °C.

Usually, addition of salt will screen the electrostatic interaction in the surfactant aggregates and among them. Due to these two effects, vesicles usually will be destroyed on adding salt. For example, vesicles changed to micelles after addition of 4 wt % NaBr to a cetyltrimethylammonium bromide (CTAB) and sodium octyl sulfate (SOS) system.¹⁸ However, it is interesting to note that vesicles in the HSMA/C₁₂Et₃ system showed great stability in the presence of NaBr, even at a NaBr concentration of 2 M (Figure 9). The vesicles are only slightly larger at 1 M NaBr than without NaBr.

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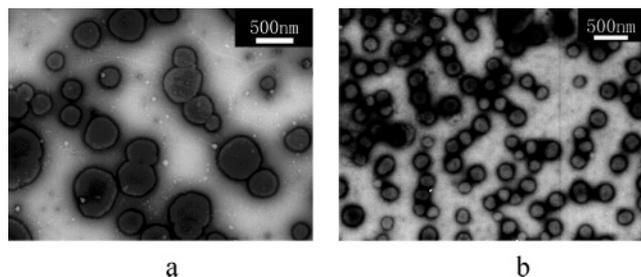


Figure 9. TEM images of vesicles in systems of HSMA/C₁₂Et₃ at $c_T = 3$ mM and $X(C_{12}Et_3) = 0.5$ with addition of NaBr: (a) 1 M; (b) 2 M.

Table 3. Stability of Vesicles to NaBr in Different Cationic Systems and after Addition of PEG 2000

system ^a	$c(\text{NaBr})^b$ (mM)	system ^a	$c(\text{NaBr})^b$ (M)
SDSO ₃ /C ₁₂ Et ₃	120	SDSO ₃ /C ₁₂ Et ₃ /PEG 2000	> 1.2
SDBS/C ₁₂ Et ₃	200	SDBS/C ₁₂ Et ₃ /PEG 2000	> 1.2

^a The total surfactant concentration of the mixture is 3 mM, the mixed ratio is 1:6, and the PEG 2000 content is 2.5 wt %. ^b $c(\text{NaBr})$ represents the concentration of NaBr at which the vesicles were destroyed.

The superstability of the vesicles formed in the HSMA/C₁₂Et₃ system in the presence of a high concentration of NaBr may be due to the contribution of the introduction of a macromolecule, the strong electrostatic attraction, and the cation- π interaction between the two components. By the use of TEM and dynamic light scattering, control experiments were carried out to clarify the contribution of each aspect (Figure 3 in the Supporting Information). Two systems (SDSO₃/C₁₂Et₃ and SDBS/C₁₂Et₃) with the same mixed ratio and total concentration were selected to determine the contribution of the cation- π interaction. The polymer poly(ethylene glycol) 2000 (PEG 2000) was added to the above systems to verify the effect of introducing of a macromolecule. The results are listed in Table 3.

From Table 3, it is found that vesicles in the system of SDBS/C₁₂Et₃ have better stability to NaBr than those in the system of SDSO₃/C₁₂Et₃, indicating that the cation- π interaction is helpful to vesicle stability against a salt. However, the dramatic increase of vesicle stability to NaBr after addition of PEG 2000 clearly demonstrated that the introduction of a macromolecule is the main contribution to the vesicle stability in a high concentration of NaBr.

The effect of ethanol addition to the vesicle stability was also investigated in the HSMA/C₁₂Et₃ system. TEM observation revealed that vesicles still existed in HSMA/C₁₂Et₃ in 1:1 (v/v) ethanol/water solutions (Figure 10) and the vesicle size had no

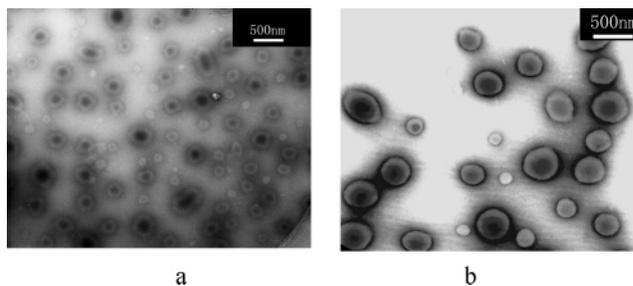


Figure 10. TEM images of vesicles in systems of HSMA/C₁₂Et₃ in ethanol/water (1:1, v/v): (a) $c_T = 3$ mM, $X(C_{12}Et_3) = 0.3$; (b) $c_T = 3$ mM, $X(C_{12}Et_3) = 0.5$.

obvious change, indicating that vesicles in these systems had good stability to ethanol which is even better than that of some polymeric vesicles. The great stability to ethanol can be attributed to the compensation of electrostatic attraction due to the effect of the medium dielectric constant we suggested in 1997.¹⁹

Conclusion

Spontaneous vesicle formation was observed in mixed systems of HSMA and various cationic surfactants. The driving forces of vesicle formation in such systems were attributed to the electrostatic interaction between the surfactant ionic headgroups and the oppositely charged units of the polymer as well as the hydrophobic effect of the surfactant tails. An increase of the hydrocarbon tail length influenced vesicle formation, and it was proved that vesicles in the systems of HSMA mixed with *n*-alkyltriethylammonium bromide only formed when the carbon number of the cationic surfactant tail was more than 10. An increase of the hydrocarbon length of the headgroup to tributyl also enhanced the vesicle formation ability. Moreover, vesicles in such systems showed superstability to aging time, ethanol, and NaBr. Our results provided a new vesicle-forming system with superstability based on the interaction of a polyelectrolyte and oppositely charged surfactants. We hope this work will advance the understanding of vesicle formation and stability and promote its applications in related fields.

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Supporting Information Available: Determination of the carboxyl content, determination of cac values of HSMA/C₁₂Et₃ systems at different mixed ratios by the fluorescence method, and control experiments of vesicle stability to NaBr. This material is available free charge via the Internet at <http://pubs.acs.org>.

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