

Influence of Hydrocarbon Surfactant on the Aggregation Behavior of Silicone Surfactant: Observation of Intermediate Structures in the Vesicle–Micelle Transition

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Intermediate structures of the aggregates in the aqueous solution of an ABA-type silicone surfactant and in the process of an SDS-induced vesicle–micelle transition are reported. In single ABA silicone surfactant aqueous solutions, large multilamellar vesicles (MLV), small single lamellar vesicles (SLV), threadlike micelles (TLM), and spheroidal micelles were observed. Interestingly, a large amount of TLMs were found entrapped into the large MLVs, but not in SLVs. Disintegration of the small vesicles inside the MLVs indicates that the entrapped TLM are from the disintegrated membrane of the entrapped small vesicles. Addition of SDS induced a transition from vesicles or threadlike micelles to spheroidal micelles. The intermediate structures, such as the appearance of small holes in the vesicle membrane, the budding of threadlike micelles from the membrane fracture, and the clusters of spheroidal micelles, were observed with increase of the SDS concentration. The electrical conductivity measurements indicated that complex micelles of SDS and silicone surfactant were formed in the solution due to the interaction between the SDS and PEO part of the silicone surfactant.

Introduction

Silicone or siloxane surfactants consist of oxylated dimethylsilicone hydrophobe coupled to one or more polar groups. They are extensively used in industry, such as in textile manufacture,¹ in cosmetics formulations,² in polyurethane foam manufacture,³ and as paint additives.⁴ Most commonly used silicone surfactants are medium weight copolymers with rake (or comb)-type or ABA-type structures. They are surface active in both aqueous and nonaqueous media.^{5,6} It is believed that the flexibility and low cohesive energy of the dimethylsilicone chain are responsible for the unusual properties of silicone surfactants.⁷

A large amount of silicone surfactant–water binary phase diagrams have been established during the past decades, and different liquid crystal structures have been found.^{8,9} Kuniada et al. have reported, in a series of concentrated solutions of silicone surfactants that contain ethyleneoxide (EO) groups, the types of liquid crystals or self-organized structures are highly dependent on the total surfactant concentration and the ratio of EO and dimethylsilicone.¹⁰ In dilute aqueous solutions, silicone surfactants can also form globular and wormlike micelles and vesicles.⁹ Although no definite relationships between the molecular structure and aggregate's morphology have been found, it is believed that the flexible dimethylsilicone chain will fold over in the aggregates. Gradzielskie and H. Hoffmann et al. concluded from the SANS results of the micellar radii that the silicone chain must be coiled in the aggregates.¹¹ Schmaucks et al. presented evidence that the silicone hydrophobe is highly flexible.¹² Hill et al. also found that the bilayer thickness of vesicles formed by comb-type silicone surfactant is significantly smaller than the extended molecular length.¹³

Although a few studies of the aggregation of silicone surfactants in aqueous solutions have been carried out, many questions

still remain. For example, sometimes they are inevitably involved in combination with hydrocarbon surfactants, but the mixtures of silicone surfactants and hydrocarbon surfactants have received little attention. Bailey et al. claimed generally synergistic behavior for a wide range of combinations of silicone surfactants with hydrocarbon surfactants.¹⁴ Hill reported mixed cmc results and detergency measurements for several silicone surfactants with anionic, cationic, and nonionic hydrocarbon surfactants.¹⁴ The behavior of the mixtures varied from strongly synergistic to antagonistic depending on the ionic character of the hydrocarbon surfactant. Ohno et al. found that a silicone surfactant strongly lowered the surface tension of sodium dodecyl sulfate solutions but had little effect on the cmc.¹⁶ Up to date, the aggregation behaviors of these mixed systems are essentially unknown. This paper will report some results from the mixed system of an ABA-type nonionic polymeric silicone surfactant IM-22 and sodium dodecyl sulfate (SDS). First, globular and threadlike micelles and vesicles were found coexisting in the single IM-22 aqueous solution, while both the threadlike micelles and the vesicles were destroyed by the addition of SDS; after the formation of a large amount of droplike structures, extensively spheroidal micelles dominated the final aggregates. The intermediate structures between vesicles and micelles were observed. The threadlike micelles were found to grow up from the edge of the intermediate membrane structure.

Experimental Section

Chemicals. The silicone surfactant IM-22 was a gift from Wacker Co. and was used without further purification. The IM-22 is a triblock ABA-type silicone surfactant with A representing poly(ethylene oxide) (EO)₁₅ and B representing [SiO(CH₃)₂]₁₅. Sodium dodecyl sulfate (SDS) and Triton X-100 were supplied by Fluka. Sodium chloride is of analytical grade, and water was doubly distilled.

Experimental Methods. 8% IM-22 water solutions were prepared by weighing a certain amount of IM-22 into a 100

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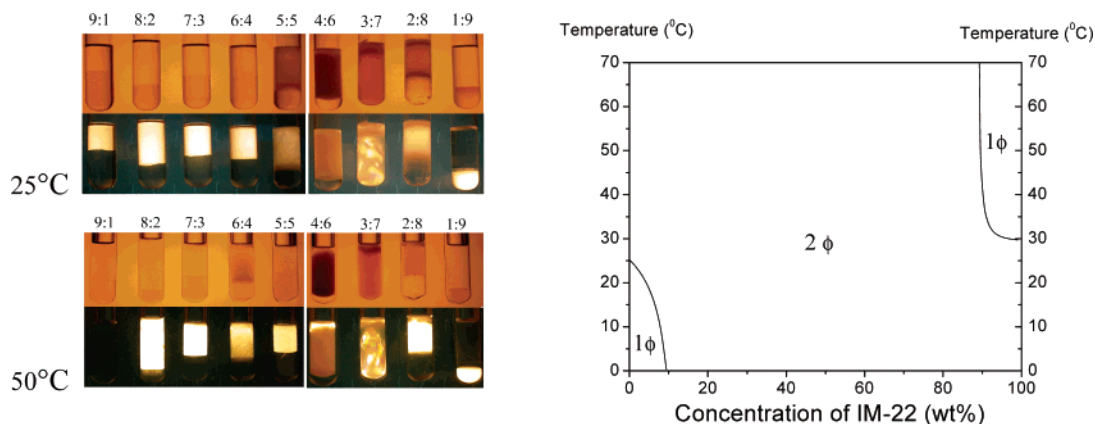


Figure 1. Left, photos for the IM-22/water system at 25 °C (upper left) and 50 °C (lower left), respectively. The numbers on the figure are the weight ratio of IM-22 to water, that is, corresponding to 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, and 10% IM-22 aqueous systems. The figure on the right is the brief phase diagram of the IM-22/water binary system.

mL glass, and water was added to the required gram. The mixture was homogenized by vortex mixing and was allowed to equilibrate for 24 h at room temperature. 1% IM-22 stock sample was obtained by dilution of the 8% solution. The 50 mM SDS stock solution was prepared by dissolving 0.72 g of solid SDS into 50 mL of water. For the 1% IM-22/SDS mixed solutions, a 1% IM-22/20 mM SDS mixed system was prepared first, and then diluted with 1% IM-22 stock solution to obtain a series of SDS in 1% IM-22 mixtures. Similarly, for the 4 mM SDS/IM-22 series solutions, the 8% IM-22/4 mM SDS stock solution was diluted with 4 mM SDS.

For cryo-transmission electron microscopy (cryo-TEM), a small drop of sample was placed on a 400 mesh copper grid, and a thin film was produced by blotting off the redundant liquid with filter paper. This thin film was then quickly dipped into liquid ethane, which was cooled by liquid nitrogen. Observation of the cryo-sample was carried out at -183 °C.

Surface tension was measured on a Lauda TE1C instrument at 25 °C with ring method. Turbidity measurement was done on a Shimadzu 250 UV spectrometer with 1 cm quartz cell in a 25 °C thermostat. Absorbance was recorded at 633 nm, at which both the polymer and the surfactant have no absorption. The conductivity measurements were performed on a microprocessor conductivity meter LF 2500 CON of WTW (Germany).

Results and Discussion

Properties of the IM-22 Single System. At room temperature, the aqueous solutions of IM-22 lower than 9% are all bluish homogeneous systems. At higher concentration, phase separation occurs. In most of the systems, bright birefringence was observed in the upper phase, which indicates the orientation of self-assemblies. Exceptions were found for the 30% and 10% systems, because the lower phase of the former system was colorful between two polarizers and the latter gave birefringence at the lower phase. At temperature higher than 30 °C, the 90% systems became homogeneous and the birefringence phenomenon disappeared. The left part of Figure 1 shows the photos of different systems at 25 and 50 °C, respectively, and the right shows the brief phase diagram. Obviously, the one-phase region can be found only in the lower left and upper right corners of the phase diagram. The phase behavior of the IM-22/water system is quite complete and will not be discussed in this paper. The following studies will focus on the homogeneous dilute IM-22 solutions.

Figure 2 shows the cryo-TEM results of 1% IM-22 in water. In addition to large MLVs (multilamellar vesicles) and small SLVs (single lamellar vesicles), we also see TLMs (threadlike micelles) and even spheroidal micelles (Figure 2a,b). Surpris-

ingly, a large amount of the TLMs are found trapped in vesicles (white arrows in Figure 2b). After being slightly shaken by hand several times, the MLVs tend to transform into SLVs, but the TLMs and spheroidal micelles still exist (Figure 2c). That is to say, unlike MLVs, the TLMs can hardly be affected by shear. It can also be seen from Figure 2d the disintegration of membrane, from which threadlike micelles are budding. This is probably the reason why there are so many threadlike micelles entrapped into the large vesicles; it could be a result of the disintegration of the smaller vesicles inside. Likewise, we can conclude that the threadlike micelles outside vesicles also come from the vesicle membrane. Therefore, both the disintegrating membrane and the entrapping of a large amount of threadlike micelles in the large vesicles are the intermediate structures in the process of vesicle to micelle transition in the aqueous solution of silicone surfactant IM-22. In fact, people have observed the coexistence of MLV, SLV, TLM, and spheroidal micelles in some comblike silicone surfactants.¹⁷ The multikinds of aggregates coexisting in silicone surfactant's aqueous solution is probably caused by the polydispersed impurities in these industrial surfactants due to the polydispersity and hydrolysis nature of these polymers. The wall thickness of the IM-22 vesicles is about 5 nm, and the radii of the wormlike and spheroidal micelles are also about 5 nm, in agreement with the previous conclusion that the silicone block folds over (coiled) in aggregates.^{11–13} Moreover, the surface of the vesicles is not smooth, which is probably due to the flexible nature of the hydrophobic silicone skeleton.

Effect of SDS on the Aggregation Behavior of IM-22.

Silicone surfactants are both hydrophobic and oelophobic, which can be seen from their surface activities both in aqueous and in nonaqueous media.^{5,6} Research has found that the ionic or fluoronic surfactant will interact with the hydrophilic part of the silicone surfactant.¹⁶ However, few reports on the influence of hydrocarbon surfactant on the aggregation behavior of silicone surfactants have been addressed.¹⁸ Z. Lin et al. reported that the addition of SDS into the cationic silicone surfactant $(\text{Me}_3\text{SiO})_2\text{Si}(\text{Me})-(\text{CH}_2)^+_3\text{NMe}_2-(\text{CH}_2)_2\text{OHCl}^-$ micelle system led to the formation of vesicles.¹⁸ Excess addition of SDS to these vesicular solutions results in the formation of a cubic liquid crystal phase. Obviously, the molecular structure of IM-22 is totally different from that of the surfactant in Z. Lin's experiments. Therefore, we would like to probe the aggregation behavior of the IM-22/SDS mixed systems.

As illustrated in previous text, the 1% IM-22 solution is homogeneously bluish. However, with addition of SDS, the tur-

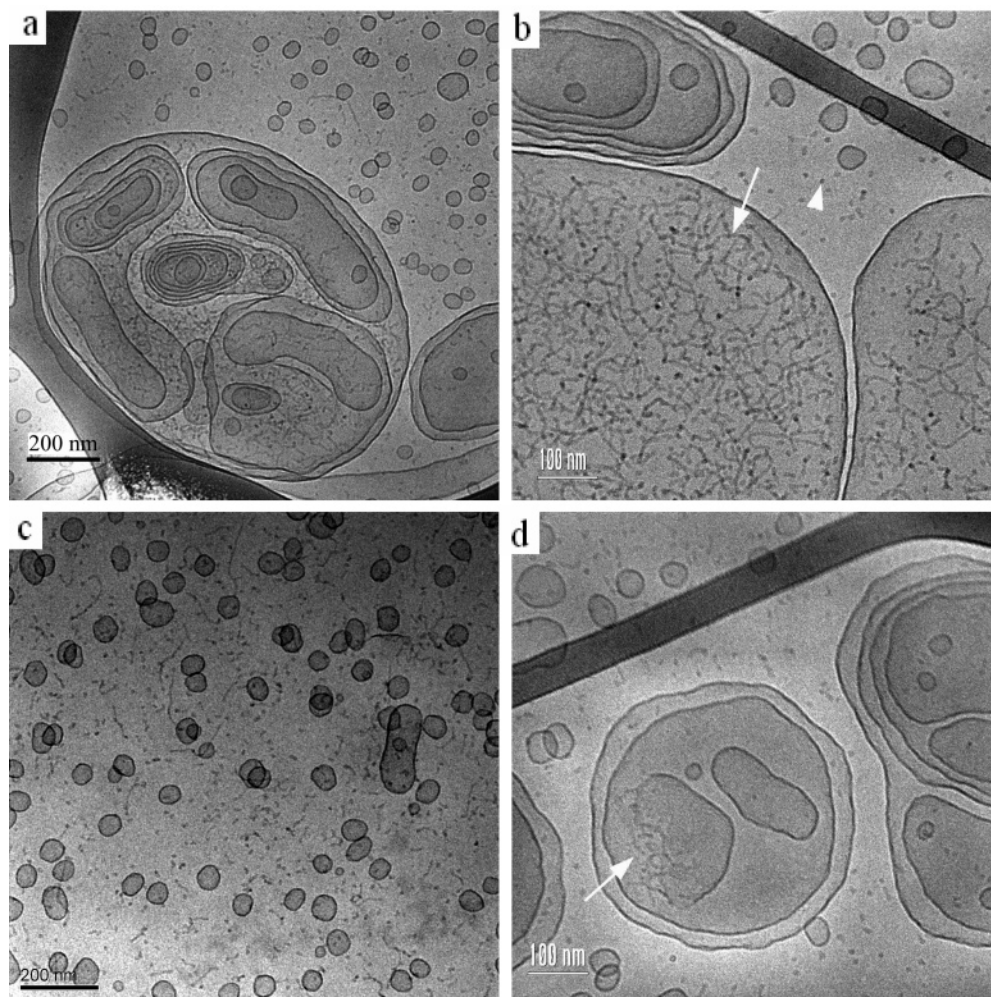


Figure 2. Cryo-TEM images of 1% IM-22 aqueous solution at room temperature. There are large multilamellar vesicles, small single lamellar vesicles, threadlike micelles, and spheroidal micelles. (a), (b), and (d) are samples without shaking, and (c) is the same sample after slightly shaking by hand several times.

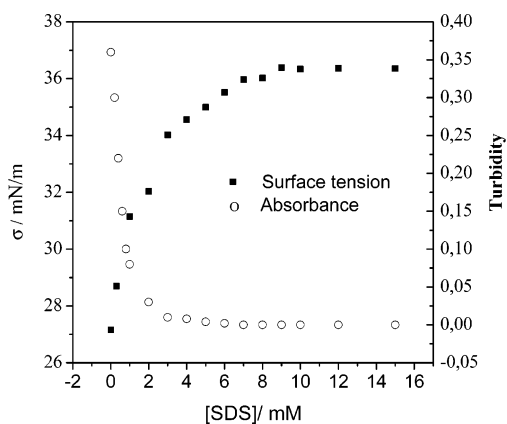


Figure 3. Surface tension and turbidity vary with SDS concentration in 1% IM-22 solution.

bidity decreases until a colorless solution is obtained at 6 mM SDS; meanwhile, the surface tension of the mixed system increases. These results are shown in Figure 3. Notice from Figure 3 that, before addition of SDS, the surface tension for 1% IM-22 is 27.15 mN/m; with the concentration of SDS increasing to 2 mM, the surface tension of the mixed system increases sharply to 32.10 mN/m; after 3 mM SDS, the increase becomes slow until the constant value of 36.04 mN/m, which is the constant surface tension of SDS at a concentration higher than the cmc (7.9 mM SDS in our experimental condition), is reached. There-

fore, the result in Figure 3 indicates that SDS molecules gradually take the place of IM-22 at the air/water interface, although IM-22 shows stronger surface activity. It also indicates that 1% IM-22 shows no apparent effect on the cmc of SDS in the bulk solution, which is similar to the results of Ohno et al.¹⁶ However, obviously some kind of interaction between IM-22 and SDS occurred in the bulk solutions because the turbidity of the mixed solutions decreases greatly with increasing SDS concentration.

The mixed systems of 1% IM-22 with different SDS concentrations were examined by cryo-TEM. It is surprising that both the vesicles and the threadlike micelles disappear after addition of the proper amount of SDS; in contrast, a large amount of droplike aggregates come into formation. Spheroidal micelles exist in all cases and finally become the dominant particles in the system. Figure 4a gives the intermediate structure in the transition from vesicles to threadlike micelles. After addition of 0.4 mM SDS into the 1% IM-22 aqueous solution, some flat membrane fractures with threadlike micelles budding from the edge are found. Figure 4b is another picture for this system, in which even the small leak in a vesicle is clearly observed (white arrow near the vesicle). Other arrows in this picture denote the flat membrane fracture, threadlike and spheroidal micelles, respectively. With increasing the concentration of SDS to 4 mM, almost all of the vesicles and threadlike micelles disappear, and some droplike particles with diameters from 20 to 50 nm are found to form. During this process, the

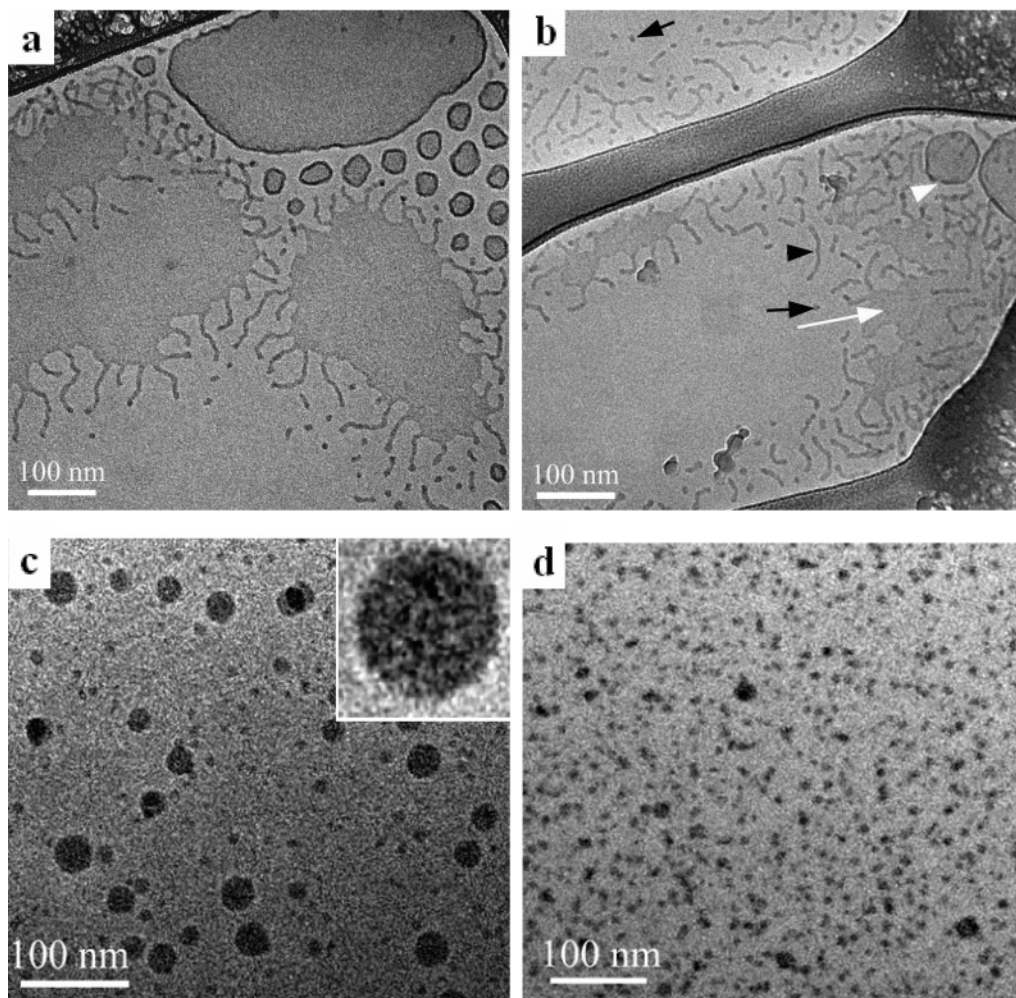


Figure 4. Cryo-TEM of (a,b) 0.4 mM, (c) 4 mM, and (d) 10 mM SDS/1%IM-22 mixed systems. The inset in (c) is the 10 times enlarged image of a droplike particle from (c). It is clear that the interior of the droplike particle is full of small particles.

small spheroidal micelles seem not to be influenced. Yet it is probably not the fact because what we see from the cryo-TEM is the morphological structures other than a detailed molecular arrangement. However, both the surface and the interior of these droplike particles are rather rough. It seems that the drops are clusters of a loosely connected large amount of small spheroidal micelles (Figure 4c, the 10 times enlarged inset). With a continuous increase of the SDS concentration to 10 mM, at which the solution is totally colorless, most of those bigger droplike particles with diameters around 20–50 nm disappear, and small micelles around 5 nm in diameter become the crowded population in the mixed system (Figure 4d).

The observation of intermediate structures such as open vesicles and pieces of lamellae was reported by Z. Lin et al. in the process of vesicle-to-micelle transition.¹⁷ They claimed that when the vesicle-to-micelle transition takes place, the vesicle first opens and then breaks into fragments of lamellae, which finally transform into either spheroidal or wormlike micelles. A. Walter et al. also observed similar intermediate structures in the vesicle–micelle transition¹⁹ of the cholate–phosphatidylcholine system. Obviously, the addition of SDS to the IM-22 aqueous solutions also leads to a vesicle-to-micelle transition, which is totally different from the role SDS plays in the $(\text{Me}_3\text{-SiO})_2\text{Si}(\text{Me})-(\text{CH}_2)_3\text{NMe}_2-(\text{CH}_2)_2\text{OHCl}^-$ micelle system.¹⁸ Revealed from the cryo-TEM results, a large amount of droplike particles with a diameter of 20–50 nm form during the disintegration of vesicles and threadlike micelles in the IM-22/SDS aqueous solution. The structure of these droplike particles

cannot be simply described with any available model of molecular self-assemblies. Although the rough surface of the particles perhaps could be explained by the highly flexible dimethylsilicone block, it is still difficult to explain why the interior is full of so many smaller micelles. To further probe the properties of this unusual phenomenon, we designed the following conductivity experiments.

Electrical Conductivity Results. Electrical conductivity experiments were done both at fixed SDS concentration while varying the concentration of IM-22 and at fixed IM-22 while changing the SDS concentration. The results are shown in Figure 5a and b.

At a fixed SDS concentration of 4 mM, which is a value lower than its cmc (7.9 mM in our experiment), the electrical conductivity was found to decrease with enhancement of IM-22 concentration, indicating a portion of the SDS molecules have been involved in the aggregates of IM-22. It is also noticeable that conductivity decreases linearly with IM-22 concentration in the range of 0–0.8% IM-22, which is probably an indication that the amount of SDS involved in the IM-22 aggregates is proportional to the concentration of IM-22 in this regime. However, the conductivity becomes constant in the IM-22 concentration range of 0.8–5%, an indication that the IM-22 aggregates have been saturated with SDS so that the increase of IM-22 concentration cannot bring a corresponding increase of SDS in the aggregates. As determined from Figure 5a, the electrical conductivity in the 4 mM SDS/1% IM-22 mixed system is 0.42 mS/cm, while that for the single 4 mM SDS

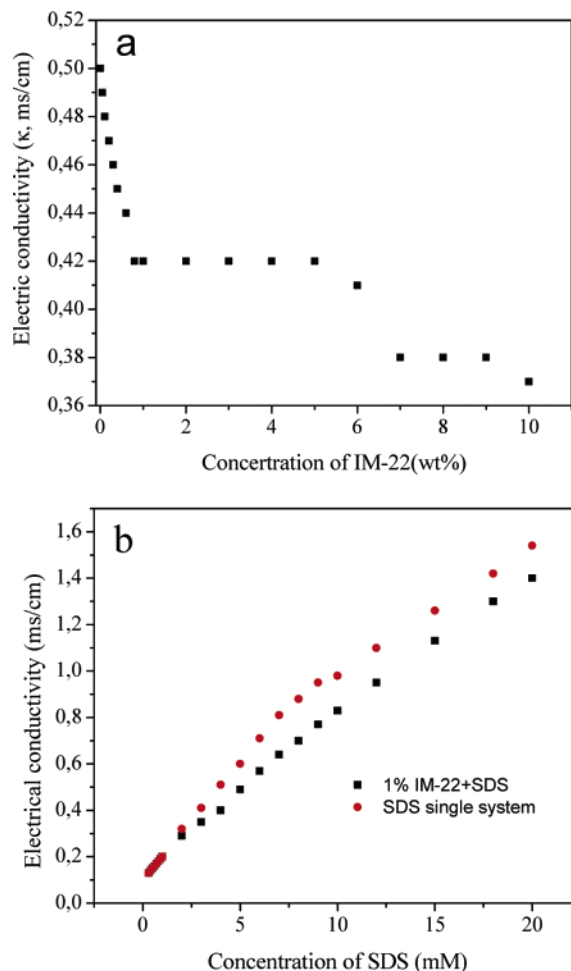


Figure 5. Electrical conductivity in the IM-22/SDS mixed systems (22 °C): (a) at a fixed SDS concentration of 4 mM, while varying the content of IM-22; (b) at a fixed IM-22 concentration of 1%, while varying the content of SDS.

solution is about 0.51 mS/cm. This suggests that approximately 20% SDS are entrapped into the spherical aggregates.

Similarly, at fixed IM-22, the conductivity also shows an interesting phenomenon with increasing SDS concentration. It is clear from Figure 5b that an obvious break at 7.9 mM SDS shows up in the conductivity curve of single SDS solution, which is a sign of SDS micelles forming at that concentration. However, in the existence of 1% IM-22, the break is almost undetectable, suggesting no sudden formation of a large amount of SDS micelles in the mixed solution. At SDS lower than 1 mM, the conductivity of the mixed system is almost the same as that of SDS single system. At greater than 2 mM SDS, the conductivities of the mixed system become lower. The decrease of conductivity at 4 mM SDS is about 22%, which agrees well with the result from the fixed SDS system (Figure 5a). It is noticeable that up to 90 mM SDS (not shown in the figure), the conductivity for the mixed system is still lower than that of the single SDS system, suggesting the amount of SDS entrapped in the IM-22 aggregates cannot be neglected.

Mechanism of the SDS-Induced Vesicle-to-Micelle Transition. How were these SDS molecules entrapped in the IM-22 aggregates? The following release of entrapped electrolyte experiment perhaps helps in explaining the mode of this “entrapment”. 10 mM NaCl was added into 1% IM-22 solution. The system was mixed adequately to make sure that the concentration of NaCl in and out of the IM-22 vesicles is in balance. The conductivity for a series of 1% IM-22/10 mM NaCl

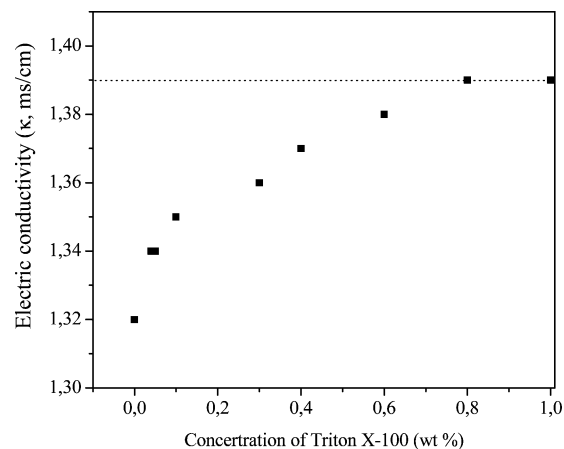


Figure 6. Change of electrical conductivity in the 1% IM-22/10 mM NaCl mixed solution with concentration of Triton X-100 (22 °C). The dotted line in the figure is the electrical conductivity of 10 mM NaCl solution, $\kappa = 1.39$ ms/cm.

solutions with different contents of Triton X-100 was then measured. It is well known that by addition of Triton X-100, vesicles in the aqueous solution of amphiphiles can be broken. Therefore, it is expected that with increasing Triton X-100, the electrical conductivity for the 1% IM-22/10 mM NaCl mixed system will be enhanced. The results are shown in Figure 6.

It is clear that the electrical conductivity monotonically increases with the content of Triton X-100. At Triton X-100 higher than 0.8%, the conductivity of the system becomes the same as that of the 10 mM NaCl solution. This result suggests that before addition of Triton X-100, some NaCl molecules have been entrapped into the interior of IM-22 vesicles, and these vesicles are destroyed by 0.8% Triton X-100. The amount of entrapped NaCl is calculated to be around 8%, which is far lower than the amount of entrapped SDS from Figure 4 (23%). This is an indication that the SDS molecules have been involved in the formation of the mixed aggregates with IM-22.

It has been reported that SDS shows a remarkable interaction with poly(ethylene oxide) (PEO) in aqueous solution by formation of micelles with a smaller aggregation number along the PEO chain.^{20–22} The calorimetric titration curves from addition of 10% SDS to 0.1% PEO gave an enthalpy as much as 6 kJ/mol.²² One of the proposed mechanisms for the formation of PEO/SDS complexes is based on the notion of the weakly electronegative nature of the PEO chain. In this picture, the surfactant’s counterion (Na^+) will coordinate with the PEO chain to form a “pseudopolycation” in which positive charges are distributed along the polymer coil.^{23–25} This charge distribution along the chain is not strong enough to produce an appreciable expansion of the coil in the absence of surfactant, but it is enough to induce polymer/surfactant interactions. At SDS below the concentration at which the surfactant begins to bind to the polymer molecules, the SDS and PEO molecules are dissolved without intermolecular interactions. As the concentration of SDS in the solution increases, the concentration of sodium cations in solution also increases and the pseudopolycation is formed. At a specific SDS concentration (the critical aggregation concentration, c_{ac} , reported to be in the range of 4.1–5.4 mM at 20 °C), surfactant aggregates are formed along the polymer chains. Once formed, the hydrophilic, negatively charged ends of the micellar aggregates associate with the positive charges along the PEO chain. In addition, there is evidence that a significant portion of the PEO chain exhibits hydrophobic interactions with the micellar aggregates, a fact indicating that part of the chain penetrates into the aggregate.^{26–28}

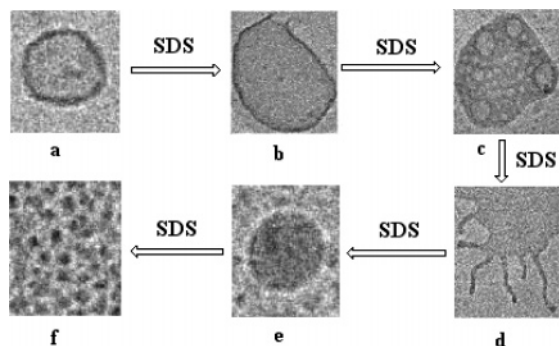


Figure 7. Influence of SDS on the vesicles of IM-22. All of the images are cut from the cryo-TEM results.

In this way, the polymer coils act as a nucleus for micellization in the PEO/SDS mixed systems. The SDS micellar aggregates formed along the PEO chain are negatively charged; hence, they repel each other and the polymer coils expand.

Similarly, SDS will interact with the PEO part in the IM-22 molecules. With the formation of complex SDS-PEO micelles along the PEO chains, repulsion between the PEO chains of the vesicle membrane increases. Therefore, the neighboring IM-22 molecules in the vesicle membrane tend to be far away from each other, which finally causes the leak or holes in the vesicle membrane (Figure 7b). With the appearance of more and more holes in the vesicles (Figure 7c), the vesicles finally disintegrate to membrane fractures (Figure 7d). To minimize the energy introduced by the exposed polydimethylsilicone, the IM-22 molecules on the edge of the tiny membrane fractures tend to change their conformation to form threadlike micelles (Figure 7d). It should be figured out that both the vesicles with holes and the membrane fractures with threadlike micelles budding (Figure 7b-d) were observed in the 0.4 mM SDS/1% IM-22 mixed systems. The above results give two messages: (1) SDS molecules start binding to the IM-22 molecules at a very low concentration, even lower than 0.4 mM, which is far lower than the reported cac values of SDS in the existence of PEO molecules; and (2) SDS molecules are not averagely distributed in the system. However, this can be reasonable under the condition that SDS molecules bind to the PEO chains before SDS micelles start formation. Because the rate of interaction between SDS and PEO is faster than that of the diffusion of SDS in the solution, it is destined that the small amount of SDS molecules are "consumed" by the nearby PEO chains in the IM-22 vesicles. Therefore, the intermediate structures from single-hole via multiholes in vesicles to membrane fractures with threadlike micelles budding on the edge recorded the history of the interaction between SDS molecules and the IM-22 vesicles. As more and more SDS micelles bind to the PEO chains, the repulsion finally drives the threadlike micelles to disintegrate to loosely aggregated micellar clusters (Figure 7e). These micellar clusters are supposed to be linked together by the bridging of the PEO chains. Further increasing the concentration of SDS leads to a saturated binding of SDS to the PEO chains. In that case, the bridging of PEO chains will disappear and free SDS micelles will form. It is proved by the calorimetric titration experiments that at higher SDS concentration, the addition of PEO is only to dilute the SDS micelle solution.²² Therefore, we concluded that at 10 mM SDS, the small micelles observed in our experiment could contain both the free SDS micelles and the micelles of IM-22 with a silicone core and PEO corona shells (Figure 7f).

Conclusions

The intermediate structures of the different aggregates in the aqueous solution of ABA-type silicone surfactant EO₁₅-

[Si(CH₃)₂]₁₅-EO₁₅ and of the SDS-induced vesicle-micelle transition are reported in this paper. Large multilamellar vesicles, small single lamellar vesicles, threadlike micelles, and spheroidal micelles were found to coexist in the EO₁₅-[Si(CH₃)₂]₁₅-EO₁₅ aqueous solution. In addition to threadlike micelles in the bulk solution, a large amount of threadlike micelles were found to be entrapped in the large vesicles. The observation of disintegrating vesicle membrane proves that this interesting entrapment is the result of the disintegration of small vesicles inside of the large multilamellar vesicles. Addition of SDS led to the disappearance of vesicles and threadlike micelles due to increasing repulsion in the vesicle membrane or the thread body. The intermediate structures, such as single hole and multiholes, were observed in the vesicle membrane with addition of 0.4 mM SDS. With more SDS added, the vesicles were broken into membrane fractures with threadlike micelles budding from the edge. At 4 mM SDS, both the vesicles and the threadlike micelles vanished, and a large amount of spheroidal micellar clusters formed. Further increasing the SDS concentration to 10 mM, the micellar clusters collapsed and small micelles began to govern the mixed system. The formation of SDS micelles along PEO chains of the silicone surfactants and the mutual phobic nature of the hydrocarbon and dimethylsilicone oxide are considered to be responsible for the aggregate transition.

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