

Notes

The Structural Transition of Catanionic Vesicles Induced by Toluene

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Introduction

Vesicles are widely used as model cell membranes, drug delivery systems, and microreactors.¹ In contrast to metastable phospholipid vesicles, catanionic vesicles (formed from mixtures of cationic and anionic surfactants) are usually thought to form spontaneously and thus have many advantages over those prepared by mechanical treatment.² To facilitate the practical implementation of this kind of spontaneously forming vesicles as the microreactors and templates,³ it is desirable to know how the penetration of hydrophobic molecules into the vesicle bilayer affects the vesicle stability and its morphology. Moreover, the study on the structure transition of catanionic vesicles upon the solubilization of hydrocarbons can help to understand this vesiculation process. In this report, toluene was introduced into the catanionic vesicle bilayer, and the drastic enlargement of vesicles and the formation of lamellar structure were observed. A similar phenomenon, unilamellar DPPC vesicles transforming into multilamellar vesicles upon the solubilization of toluene, was also observed by Rehage et al.^{4,5} According to this result, a new effective way was provided to adjust the structure of catanionic surfactant aggregates.

Materials and Methods

Sodium laurate (SL) was prepared by neutralizing lauric acid (recrystallized five times from 95% ethanol) with NaOH in ethanol, then the solvent was removed and sodium laurate was vacuum-dried. Sodium dodecylbenzenesulfonate (SDBS) was used as received from Acros. Dodecyltrimethylammonium bromide (DTAB) was synthesized from *n*-alkyl bromide and trimethylamine. The crude product was recrystallized five times from the mixed solvents of ethanol–acetone or ether–acetone. The other reagents were products of Beijing Chemical Co., A.R. Grade.

The catanionic vesicles were prepared by weighing cationic surfactant and water first into the sample vial (allowing the cationic surfactant to dissolve), and then adding anionic sur-

factant stock solution of desired concentration. Samples were vortex mixed and then equilibrated in a thermostated bath controlled to 30 °C. The desired amount of toluene was added to the samples using a syringe. After the addition of toluene, the solutions were sealed, aged in airtight cuvettes, and equilibrated in a thermostatic bath controlled to 30 °C for over 3 months before investigation.

The freeze-fracture and negative-staining (with uranyl acetate ethanol solution) techniques were used for EM sample preparation. Fracturing and replication were carried out in a high-vacuum freeze-etching system (Balzers BAF-400D). A JEM-100CX electron microscope was employed in the microscopic observation. The measurement of the turbidity was performed at a Shimadzu UV-250 spectrophotometer (quartz cell path length 1 cm).

Results and Discussion

At room temperature, transmission electron microscopy (TEM) analysis of mixed sodium dodecylbenzenesulfonate (SDBS) and dodecyltrimethylammonium (DTAB) solution ($C_{\text{total}} = 0.028$ mol/L, molar ratio 1:2.5) reveals the presence of dispersed unilamellar vesicles (Figure 1a). After the addition of a small amount of toluene (0.01 mol/L), the vesicles still remain in a unilamellar structure (Figure 1b), only with the size increased. With the concentration of toluene going up to 0.04 mol/L, the size of the unilamellar vesicles further increases (Figure 1c) and the deformation of vesicles can be observed. Further increase of toluene concentration leads to the formation of large nonspherical vesicles. The striking undulations of bilayer membrane indicate a low surface tension and bending elasticity of the fluidlike membrane, which was also observed by Rehage et al. in DPPC vesicle solution upon the solubilization of toluene.^{4,5} Finally the lamellar structure is clearly revealed when the concentration of toluene increases to 0.1 mol/L (Figure 1d).

Turbidity of surfactant solutions as a function of toluene concentration was measured at 400 nm (Figure 2). The turbidity is considered as a measure of the surfactant aggregate size.⁶ The increase of turbidity indicates the size increase of surfactant aggregates upon the addition of toluene. This is in concordance with the results of TEM analysis shown above.

Similar microstructural transition was also observed in mixed sodium laurate (SL) and DTAB solution ($C_{\text{total}} = 0.0075$ mol/L, molar ratio 1:2) by using TEM. After the addition of toluene (0.03 mol/L), the unilamellar vesicles (Figure 3a) transform into multilamellar vesicles and lamellar structure (Figure 3b).

However, the solubilization of octane into catanionic vesicles does not lead to the same structure transition as shown above. After addition of 0.053 mol/L octane into the mixed SDBS/DTAB solution, the vesicles still remain in a unilamellar structure and their size does not show obvious change (Figure 4).

The different effects of toluene and octane on catanionic vesicles can be accredited to their different solubilization positions in the bilayer. It has been shown previously that

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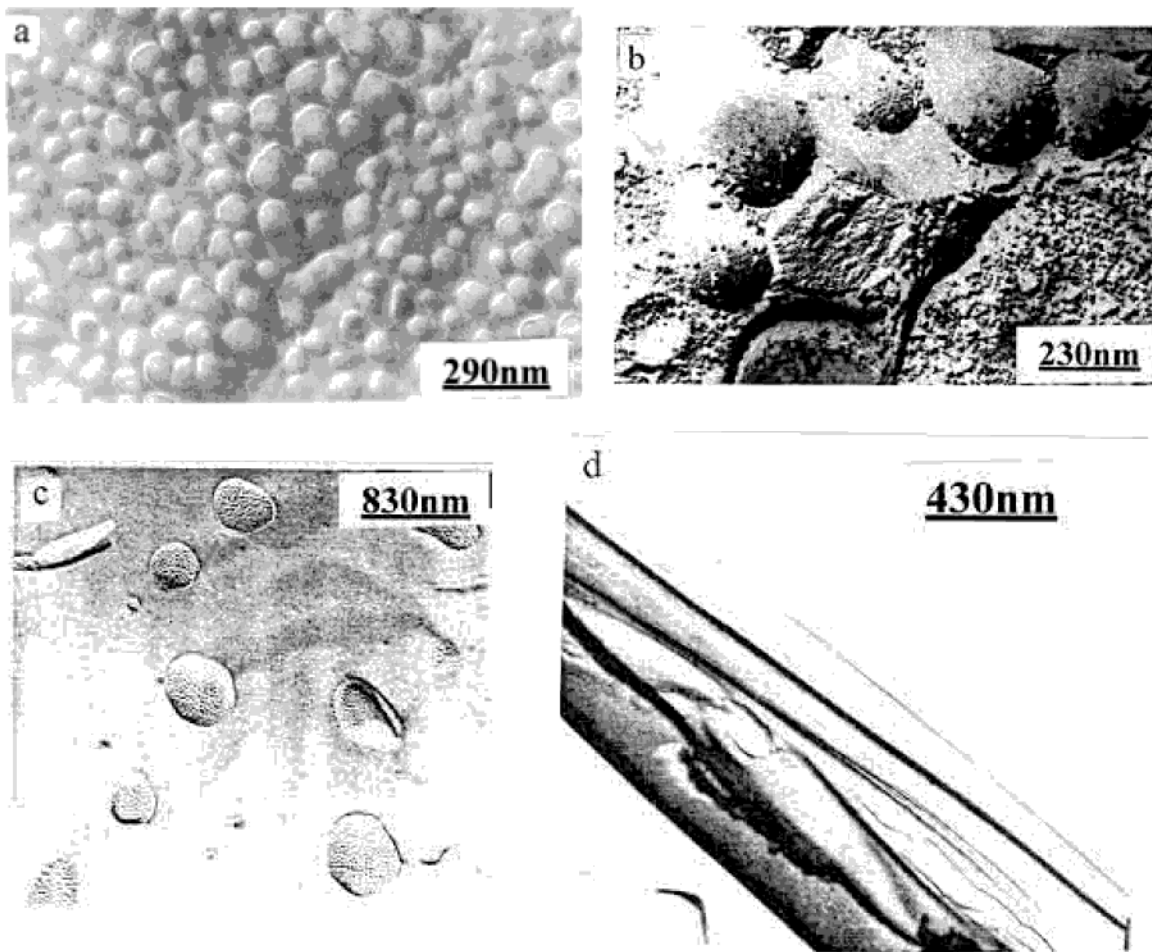


Figure 1. The structure transition of SDBS–DTAB vesicles upon the addition of toluene: (a) without toluene; (b) [toluene] = 0.01 M; (c) [toluene] = 0.04 M; (d) [toluene] = 0.1 M.

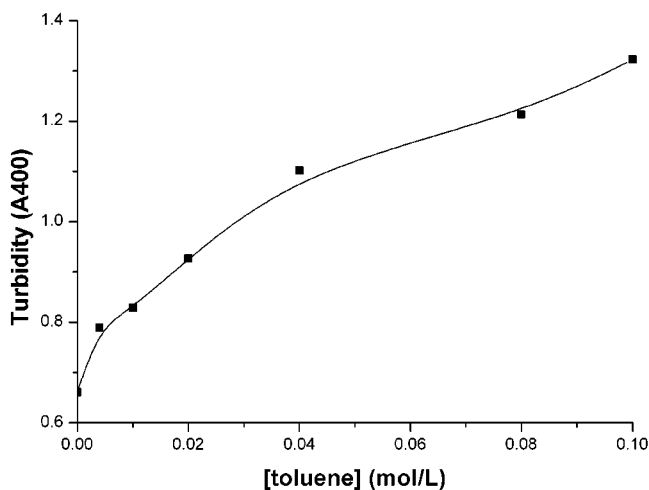


Figure 2. Turbidity for mixed SDBS–DTAB solutions as a function of toluene concentration.

toluene is mainly solubilized at the interface of the surfactant aggregates,^{7,8} at least in the initial stage of the solubilization process, while aliphatic hydrocarbons are solubilized in the hydrocarbon core part of the aggregates.⁹ Because the interfacial tension of the toluene/water

interface (35 mN/m) is lower than that of the octane/water interface (50.8 mN/m),¹⁰ toluene is surface active at the water/hydrocarbon interface and therefore solubilized in the palisade layer between the surfactant headgroups. Because the vesicles are positively charged due to the excess of cationic surfactant, solubilized toluene molecules would move the surfactant headgroups further apart and decrease the repulsion between the headgroups of the surfactants. Moreover, the delocalized π -electrons of benzene ring can interact with the cationic groups and have the charge shielding effect between the positively charged headgroups.¹¹ Such effects would decrease the surface charge density of the surfactant aggregates,¹² which has been proven to play an important role for surfactant aggregates.^{13,14} Since the decreased surface charge density favors the formation of aggregate with small curvature (large radius),¹⁴ the cationic vesicles would enlarge and transform into lamellar structure. In addition, the penetration of toluene molecules into the inner and outer interfaces of vesicle bilayer would decrease the interfacial tension of the water/hydrophobic region of vesicles, as well as the bending elastic modulus of the

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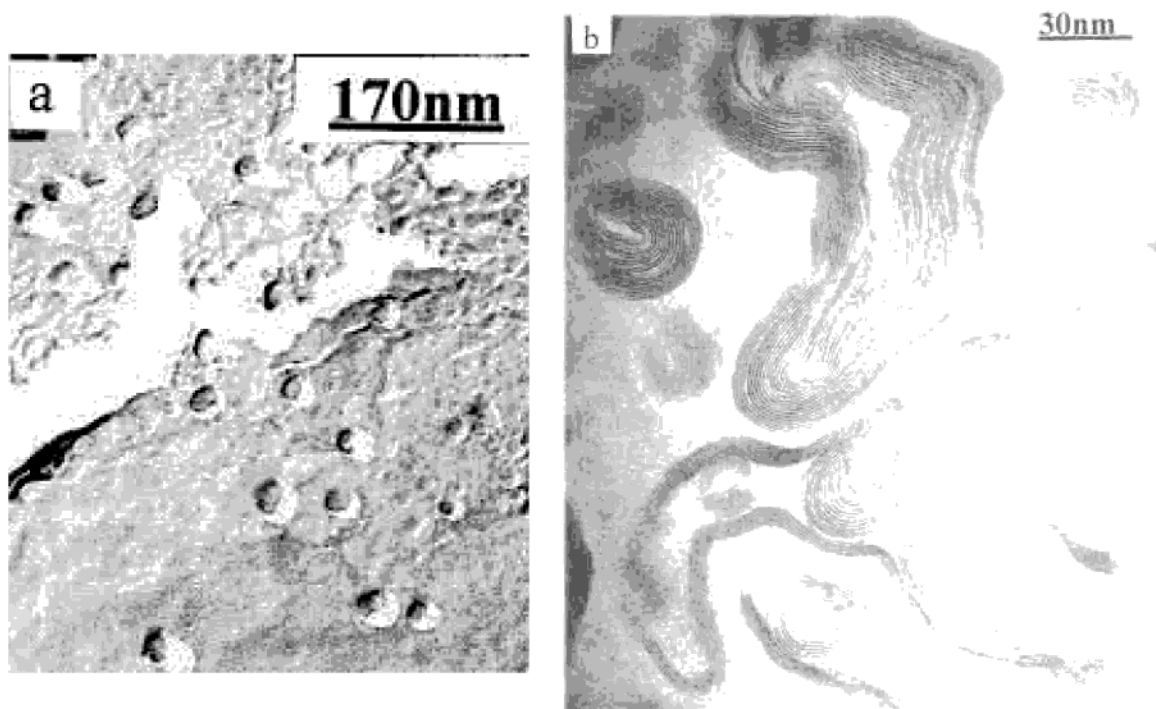


Figure 3. The structure transition of SL-DTAB vesicles upon the addition of toluene: (a) without toluene; (b) [toluene] = 0.03 M (by negative staining technique).

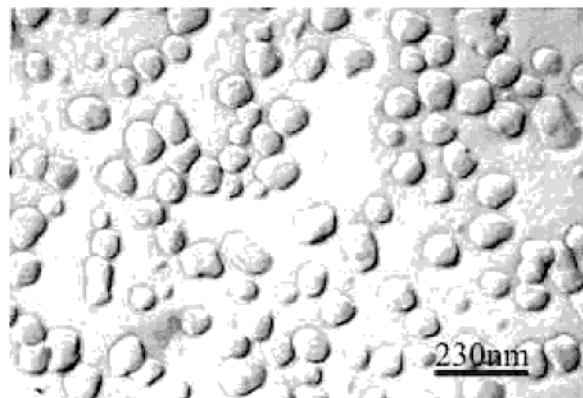


Figure 4. The structure of SDBS-DTAB vesicles upon the addition of 0.053 mol/L octane.

bilayer.⁴ This may enhance the undulation motions of bilayer and the deformations of the vesicles.^{4,5} Hence it is understandable that the unilamellar vesicles can

transform into multilamellar vesicles or lamellar structure.

Conclusion

The solubilization of toluene into the cationic vesicle bilayer of SDBS-DTAB and SL-DTAB mixed systems leads to the enlargement and deformation of vesicles and the formation of lamellar structure. However, cationic vesicles still remain in a unilamellar structure upon the solubilization of octane. The penetration of toluene into the cationic vesicle bilayer can decrease the surface charge density of the cationic vesicles, decrease the bending elastic modulus, and enhance the undulation motions of bilayer membrane. On comparison of the different results of octane or toluene addition, the various effects of solubilization of hydrocarbons on the cationic vesicles were accredited to the positions they occupy in the bilayer.

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