Phase Behavior, Rheological Property, and Transmutation of Vesicles in Fluorocarbon and Hydrocarbon Surfactant Mixtures

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ABSTRACT: We present a detailed study of a salt-free cationic/anionic (catanionic) surfactant system where a strongly alkaline cationic surfactant (tetradecyltrimethylammonium hydroxide, TTAOH) was mixed with a single-chain fluorocarbon acid (nonadecafluorodecanoic acid, NFDA) and a hyperbranched hydrocarbon acid [di-(2-ethylhexyl)phosphoric acid, DEHPA] in water. Typically the concentration of TTAOH is fixed while the total concentration and mixing molar ratio of NFDA and DEHPA is varied. In the absence of DEHPA and at a TTAOH concentration of 80 mmol L⁻¹, an isotropic L₁ phase, an L₁/L₆ two-phase region, and a single L₆ phase were observed successively with increasing mixing molar ratio of NFDA to TTAOH (n_{NFDA}/n_{TTAOH}). In the NFDA-rich region (n_{NFDA}/n_{TTAOH} > 1), a small amount of excess NFDA can be solubilized into the L₆ phase while a large excess of NFDA eventually leads to phase separation. When NFDA is replaced gradually by DEHPA, the mixed system of TTAOH/NFDA/DEHPA/H₂O follows the same phase sequence as that of the TTAOH/NFDA/H₂O system and the phase boundaries remain almost unchanged. However, the viscoelasticity of the samples in the single L₆ phase region becomes higher at the same total surfactant concentration as characterized by rheological measurements. Cryo-transmission electron microscopic (cryo-TEM) observations revealed a microstructural evolution from unilamellar vesicles to multimellar ones and finally to gaint onions. The size of the vesicle and number of lamella can be controlled by adjusting the molar ratio of NFDA to DEHPA. The dynamic properties of the vesicular solutions have also been investigated. It is found that the yield stress and the storage modulus are time-dependent after a static mixing process between the two different types of vesicle solutions, indicating the occurrence of a dynamic fusion between the two types of vesicles. The microenvironmental changes induced by aggregate transitions were probed by ¹⁹F NMR as well as ³¹P NMR measurements. Upon replacement of NFDA by DEHPA, the signal from the ¹⁹F atoms adjacent to the hydrophilic headgroup disappears and that from the ¹⁹F atoms on the main chain becomes sharper. This could be interpreted as an increase of microfluidity in the mixed vesicle bilayers at higher content of DEHPA, whose alkyl chains are expected to have a lower chain melting point. Our results provide basic knowledge on vesicle formation and their structural evolution in salt-free catanionic surfactant systems containing mixed ion pairs, which may contribute to a deeper understanding of the rules governing the formation and properties of surfactant self-assembly.

INTRODUCTION

Surfactants, which possess both hydrophobic and hydrophilic parts, have diverse applications in industries and daily life. They can adsorb onto air/water or oil/water interfaces and significantly reduce surface or interface tension. In practical applications, mixed surfactant systems are usually selected because they normally have more advantageous functions compared to systems formed by a single surfactant due to synergistic effects between different components. A typical mixed surfactant system with strong synergistic effects is a cationic/anionic (catanionic) surfactant mixture as pioneered by Kaler et al. Upon mixing, a catanionic ion pair is formed, which leads to a strong reduction of the effective area of the hydrophilic headgroup. With the variation of mixing molar ratio, diverse microstructural evolution can be induced. Of special interest is the formation of vesicles, which is a pronounced feature of catanionic surfactant systems. Due to their unique properties, vesicles have practical applications for drug and gene delivery. The hydrophobic membrane (called the vesicle wall) can be used to encapsulate oil-soluble organic compounds, while the water pool enclosed by the vesicle walls can be used to encapsulate water-soluble compounds. In addition, vesicles are able to serve as mimics of biological membranes or as micro/nanotemplates for material synthesis. However, an obstacle for further investigation and practical application of catanionic surfactant mixtures is precipitate formation, which is more pronounced at high total surfactant concentration and around equimolar.
Scheme 2. Illustration of Formation of Catanionic Ion Pairs\(^{44}\)

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\begin{align*}
\text{N(CH}_3\text{)}_2\text{OH}^- + \text{COO}^-\text{H}^+ & \rightarrow + + + \text{H}_2\text{O} \\
\text{TTAOH} & \text{NFDA} \text{TFA}^-\text{FD}^- \\
\text{N(CH}_3\text{)}_2\text{OH}^- + \text{PO}_4\text{H}^+ & \rightarrow + + + \text{H}_2\text{O} \\
\text{TTAOH} & \text{DEHPA} \text{TFA}^-\text{DEHP}^- \\
\end{align*}
\]

"The acid–base reactions between TTAOH and NFDA or DEHPA produced two different types of catanionic ion pairs bearing double and triple chains, respectively. The hydrophilic parts of NFDA and DEHPA were drawn in dissociated form to facilitate the acid–base reaction. The hydrocarbon chains are presented as flexible lines while the fluorocarbon chains are illustrated as rigid rods. For better clarity, the side chains on the hydrocarbon tails of DEHPA have been omitted.

Besides the explanation by curvature energy change in this process, many other factors, especially the interaction between the hydrophobic chains, should be considered in the current surfactant system. We also expect that the mutual phobic nature between hydrocarbons and fluorocarbons would be more crucial in explaining this transition from unilamellar vesicles to multilamellar ones if fluorocarbons are replaced with hydrocarbons. Where fluorocarbon is involved, not only can the packing parameter be cited but also the interaction between hydrocarbons and fluorocarbons should be considered.

**CONCLUSION**

We have investigated the phase behavior and microstructural evolution in a salt-free catanionic surfactant system containing one strongly alkaline cationic surfactant and two weakly acidic anionic surfactants with distinct molecular morphologies and properties. It is found that the morphologies of vesicles formed in this system can be controlled by adjusting the mixing molar ratio of the anionic surfactants. At the fluorocarbon acid NFDA-rich side, polydispersed unilamellar vesicles are dominant. Upon replacement of NFDA with the fluorocarbon acid DEHPA, aggregate transition from unilamellar vesicles to multilamellar ones and then to giant onions with deformed shapes has been detected by cryo-TEM observations. This microstructural evolution has resulted in a drastic change in the rheological properties of the system and can be also probed by $^{19}F$ and $^{31}P$ NMR measurements. The control mechanism is based on regulation of the spontaneous curvature radius, the curvature elasticity of vesicles, and even the interaction between hydrocarbons and fluorocarbons of surfactant mixtures. Our results can primarily provide a deeper understanding of the transition between bilayer structures in aqueous solutions governed by surfactant molecular structures and secondarily contribute to the realization of practical applications of salt-free catanionic surfactant mixtures, which have attracted increasing interest in recent years.

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**Notes**

The authors declare no competing financial interest.

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