Micelle-to-Vesicle Transition Induced by Organic Additives in Catanionic Surfactant Systems

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Abstract: A micelle-to-vesicle transition (MVT) induced by the addition of a series of apolar hydrocarbons (n-butylnzenzene, n-hexane, n-octane, and n-dodecane) to the catanionic surfactant system n-dodecyltriethylammonium bromide/sodium n-dodecylsulfonate (DTEAB/SDS) has been investigated for the first time by means of rheology and turbidity measurements, dynamic light scattering (DLS), and transmission electron microscopy (TEM). Interestingly, a MVT can take place within certain micellar regions, which are dependent on the structure and chain length of the hydrocarbon. However, these hydrocarbons are unable to induce a MVT in another catanionic surfactant system, namely, n-dodecyl-triethylammonium bromide/sodium n-dodecylsulfonate (DTEAB/SDSO3), in which the molecular interactions are weaker than in the DTEAB/SDS system. On the other hand, polar additives, such as n-octanol and n-octylamine, exhibit much higher efficiency and activity in inducing MVT than hydrocarbons in both DETAB/SDS and DTEAB/SDSO3. Moreover, DLS, TEM, and time-resolved fluorescence quenching (TRFQ) results demonstrate that the ratio of vesicles to micelles in the system can be actively controlled by addition of polar additives. Possible mechanisms for the above phenomena are presented, and the potential application of controllable micelle/vesicle systems in the synthesis of tailored bimodal mesoporous materials is discussed.

Keywords: micelles · surfactants · vesicles

Introduction

Aqueous mixtures of anionic and cationic surfactants (referred to as catanionic surfactants) exhibit interesting phase behavior and properties, which mainly arise from the electrostatic interactions between the oppositely charged head groups. By adjusting the composition, these interactions can be tuned to produce various microstructures with characteristic geometries ranging from spherical to cylindrical to planar, which have been studied experimentally and theoretically[1] for their potential applications in many fields.

The nature of the transition between micelle and vesicle is of great importance in a number of practical applications[2] and of fundamental interest as well.[3] For catanionic surfactant systems, much attention has focused on the influence of the micelle-to-vesicle transition (MVT) or the vesicle-to-micelle transition (VMT) of changes in surfactant composition,[1a–c] temperature variation,[4] and salt addition.[5] However, in contrast to the many studies on organized transitions induced by the solubilization of organic additives in single-surfactant systems, little work[6] has been done on the influence of organic additives in catanionic surfactant systems, since organic additives, especially apolar hydrocarbons, are usually thought to have less effect in tailoring organized assemblies of catanionic surfactant systems due to the strong electrostatic attraction in this kind of systems.

Recently, we found[8] that the addition of some short-chain alcohols, such as 2-propanol, to some catanionic surfactant systems with precipitation not only influenced the phase behavior, but also transformed the precipitate into vesicles, which indicates that suitable additives may also play an important role in the transformation of organized assemblies in catanionic surfactant systems, in which strong electrostatic interactions exist. We have now systemically studied the effects of a series of hydrocarbons (n-butylnzenzene, n-hexane, n-octane, and n-dodecane) and polar organic additives, such as n-octanol and n-octylamine, on the tran-
sition from micelle to vesicle in the catanionic surfactant systems n-dodecyltriethylammonium bromide/sodium n-dodecylsulfate (DTEAB/SDS) and n-dodecyltriethylammonium bromide/sodium n-dodecylsulfonate (DTEAB/SDSO₃).

For the first time, it was found that apolar hydrocarbons can induce a MVT in the DTEAB/SDS system within certain ranges of surfactant composition, while they are unable to induce a MVT in the DTEAB/SDSO₃ system. Moreover, the polar organic additives are much more efficient in inducing a MVT than the hydrocarbons in both systems and can actively adjust the ratio of vesicles to micelles. Possible mechanisms for the above transitions are presented, based on the theory of the aggregate packing parameter, and the different effects of the additives on a MVT are explained. Furthermore, potential application of controllable micelle/vesicle systems in the synthesis of tailored bimodal mesoporous materials is discussed.

Results

Microstructures of the DTEAB/SDS system: The microstructures of the DTEAB/SDS system at a fixed total surfactant concentration \( C_{\text{total}} \) of 10 mmol were determined from the results (not shown) of turbidity measurements, dynamic light scattering (DLS), and transmission electron microscopy (TEM). A partial phase diagram for the variation of \( X_{\text{DTEAB}} \) (\( X_{\text{DTEAB}} = C_{\text{DTEAB}}/C_{\text{total}} \)) is shown in Figure 1. The vertical axis is the corresponding turbidity at 500 nm of each investigated sample. In Figure 1, transitions from micelle to vesicle and finally to precipitate can be observed as \( X_{\text{DTEAB}} \) approaches 0.5, which can be understood as the result of the neutralization of oppositely charged head groups. The micellar regions are at the two edges of the diagram with \( X_{\text{DTEAB}} \) ranges from 0 to 0.33 and from 0.85 to 1. The solubilization behaviors of various organic additives were studied in these regions.

MVT induced by addition of n-butylbenzene: The micellar DTEAB/SDS system with \( C_{\text{total}} = 10 \) mmol and \( X_{\text{DTEAB}} = 0.25 \) was selected for our study. Before addition of n-butylbenzene, the sample showed obvious non-Newtonian behavior in the steady-state rheological curve (Figure 2a): shear thickening at lower shear rates and shear-thinning at higher shear rates. This behavior is a typical property of rodlike micelles in dilute solutions and has been well investigated in other work.\(^9\) On addition of n-butylbenzene to the mixed system, the non-Newtonian behavior becomes progressively weaker, and this suggests that the shape of aggregates becomes more symmetrical. In addition, a notable increase in absorbance at 500 nm on the addition of n-butylbenzene

![Figure 1](image1.png)

**Figure 1.** Partial phase diagram of DTEAB/SDS with \( C_{\text{total}} = 10 \) mmol and varying \( X_{\text{DTEAB}} \). \( A_{500} \) is the turbidity at 500 nm of each investigated sample. M = micelle, V = vesicle, P = precipitate.

![Figure 2](image2.png)

**Figure 2.** a) Steady-state rheological curves and b) variation of absorbance at 500 nm (the solid line is a guide to the eye) for the system DTEAB/SDS \( (C_{\text{total}} = 10 \) mmol, \( X_{\text{DTEAB}} = 0.25 \) with addition of n-butylbenzene.
Figure 2b) indicates that larger aggregates are formed in the system.

The microstructural transformation induced by addition of \( n \)-butylbenzene to the system was also investigated by DLS and TEM. Before addition of \( n \)-butylbenzene, the plot of the apparent hydrodynamic radius distribution \( f(R_{h,app}) \) calculated by the CONTIN method (see Experimental Section), has a single peak with an average apparent hydrodynamics radius \( \langle R_{h,app} \rangle \) of 8 nm (Figure 3a), which reflects a typical equivalent size of rodlike surfactant micelles. When 1.5 mmol of \( n \)-butylbenzene is introduced, the peak in the DLS plot shifts to the right, \( \langle R_{h,app} \rangle \) increases from 8 to 83 nm (Figure 3a), and corresponding spherical vesicles with a diameter of 100–200 nm are observed by TEM (Figure 3b). In this case, the solution becomes a Newtonian fluid (Figure 2a) and the apparent viscosity \( \eta_{app} \) of the solution is 0.93 mPas at 25°C (Figure 2a), which is quite close to the viscosity of water (0.89 mPas). The above results suggest that spherical vesicles probably become the dominant aggregates when 1.5 mmol of \( n \)-butylbenzene is added. Thus, MVT by solubilization of \( n \)-butylbenzene is confirmed.

Investigation of other micellar DTEAB/SDS systems with \( C_{total} = 10 \) mmol showed MVT by solubilization of \( n \)-butylbenzene can take place within certain surfactant compositions in Figure 1, that is, from \( X_{DTEAB} = 0.25 \) to 0.33 and from \( X_{DTEAB} = 0.86 \) to 0.96. Hereafter, such regions are referred as the \( R_{eff} \) (effective MVT regions) of the additive.

MVT induced by addition of alkanes: When \( n \)-octane (\( C_8 \)) is gradually added to the micellar DTEAB/SDS system with \( C_{total} = 10 \) mmol and \( X_{DTEAB} = 0.25 \), the solution remains transparent and homogeneous until small droplets of oil appear that suggest the saturation limit of \( n \)-octane solubilization. Combined with the results of rheology measurements (not shown), it can be concluded that the rodlike micelles are transformed into spherical swollen micelles by solubilization of \( C_8 \), like similar reports for other surfactant systems.\(^{[10]}\) However, the situation is different for the DTEAB/SDS micellar system with \( C_{total} = 10 \) mmol and \( X_{DTEAB} = 0.33 \). A sharp increase in absorbance is observed as \( C_8 \) is added to the solution (Figure 4a). The DLS results also show that \( \langle R_{h,app} \rangle \) increases remarkably from 25 to 95 nm on addition of 2 mmol of \( C_8 \) (Figure 4b). Correspondingly, spherical vesicles with a diameter of 100–250 nm are observed by TEM (Figure 5). These results demonstrate that MVT takes place on addition of \( C_8 \) to the system. Further investigations revealed that the \( R_{eff} \) of \( C_8 \) is from \( X_{DTEAB} = 0.29 \) to 0.33 and \( X_{DTEAB} = 0.86 \) to 0.90, which is narrower than that of \( n \)-butylbenzene.

\( n \)-Hexane (\( C_6 \)) and \( n \)-dodecane (\( C_{12} \)) were also investigated. Both can induce MVT within certain ranges of surfactant composition. The \( R_{eff} \) values of the alkanes are listed in Table 1. The \( R_{eff} \) decreases with increasing hydrocarbon chain length.

Occurrence of a MVT and adjustment of the ratio of vesicles to micelles by addition of polar organic additives: Besides apolar hydrocarbons, the effects of two kinds of polar organic additives, namely, \( n \)-octanol and \( n \)-octylamine, on a MVT were also studied in the DTEAB/SDS system. A MVT by addition of \( n \)-octanol (\( C_{12} \)) can take place over the entire micellar region of Figure 1; this suggests that \( C_{12} \) is much more efficient in inducing a MVT than the above hydrocarbons. The ratio of vesicles to micelles can be conveniently controlled by addition of a small amount of \( C_{12} \).

As mentioned above, the solution of DTEAB/SDS with \( C_{total} = 10 \) mmol and \( X_{DTEAB} = 0.25 \) is composed of rodlike micelles with an average \( R_{h,app} \) of 8 nm by DLS (Figure 6a). After addition of 0.50 mmol of \( C_{12} \)OH, two distinct peaks can be clearly observed in the plot of \( f(R_{h,app}) \) versus \( R_{h,app} \) (Figure 6b), which correspond to fast and the slow diffusion modes, respectively. The fast mode has a \( \langle R_{h,app} \rangle \) of 5 nm, which is close to that of the original rodlike micelles, and it is reasonable to attribute this mode to diffusion of the micelles. The slow mode has an \( \langle R_{h,app} \rangle \) of 220 nm. Correspond-
ingly, a few spherical vesicles with a diameter of 200–500 nm were observed by TEM (Figure 7a). Therefore, it can be de-
duced that the slow mode reflects the formation of vesicles in the solution. Therefore, the two peaks are designated as the “micelle peak” and the “vesicle peak” respectively. Further addition of C₈OH causes the micelle peak to shrink while the vesicle peak grows gradually (Figure 6c and d). Moreover, the contribution of the vesicle peak to the total scattering intensity of the sample \( I_v \%), which is calculated from the weight of the vesicle peak area in the plot of \( f(R_{h,app}) \) versus \( R_{h,app} \), also increases on addition of C₈OH (Figure 8a). These results indicate growing vesicle population and increasing ratio of vesicles to micelles. This tendency is further confirmed by TEM (Figure 7b and c). The variations of \( \langle R_{h,app} \rangle \) for micelle and vesicle peaks as a function of C₈OH concentration are shown in Figure 5b. For the vesicles, \( \langle R_{h,app} \rangle \) gradually decreases with increasing C₈OH concentration. When the amount of C₈OH reaches 1.5 mmol, the micelle peak almost disappears in the DLS plot (Figure 6e), and the vesicle peak has \( \langle R_{h,app} \rangle \) of 79 nm. In this case, the rodlike micelles in the system are probably completely transformed into spherical vesicles.

The adjustment of the ratio of vesicles to micelles on C₈OH addition was also characterized by time-resolved fluorescence quenching (TRFQ) experiments. The time-dependent fluorescence intensity of a probe in the micelle in the presence of a quencher is thought to obey the Infelta–Tachiya equation [Eq. (1)],[11]

\[
I(t) = I(0)\exp\left\{ -A_1t - A_2[1-\exp(-A_3t)] \right\}
\]

where \( A_1 \) and \( A_2 \) are independent of quencher concentration and \( A_3 \) is defined as Equation (2),

\[
A_3 = N[Q]/C_m
\]

where \( C_m \) is the concentration of surfactant in micellar form, \([Q]\) the concentration of quencher, and \( N \) the average aggregation number of the micelles. In vesicles and other large aggregates, the time-dependent fluorescence intensity of a probe in the presence of a quencher is thought to obey the modified Stern–Volmer equation [Eq. (3)],[12]

\[
I(t) = I(0)\exp\left\{ -A_4t - A_5t^{1/2} \right\}
\]

where \( A_4 \) and \( A_5 \) both depend on quencher concentration. When micelles and vesicles coexist in one system, the quenching kinetics will be governed by a linear combination of Equations (1) and (3). Unfortunately, the large number of parameters involved in such a combination makes quantitative analysis intractable. However, if the decay curves are
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Figure 6. Distribution of apparent hydrodynamic radii $f(R_{\text{app}})$ of the system DTEAB/SDS ($C_{\text{total}} = 10$ mmol, $X_{\text{DTEAB}} = 0.25$) with different concentrations of $C_8\text{OH}$. a) 0, b) 0.50, c) 0.70, d) 1.0, and e) 1.5 mmol.

forced to fit the form of Equation (1), $A_4$ shows dependence on quencher concentration and the ratio of vesicles to micelles. By this method, TRFQ can be used to track the transition between micelles and vesicles. The TRFQ data for DTEAB/SDS mixtures with $C_{\text{total}} = 10$ mmol, $X_{\text{DTEAB}} = 0.25$, and different concentrations of $C_8\text{OH}$ were measured. The variation of $A_4$ (obtained by fitting the data to [Eq. (1)]) as a function of $\eta$ ($\eta = [Q]/C_{\text{total}}$) for these solutions is shown in...
Before C₈OH addition, \( A₄ \) is independent of \( \eta \), that is, the solution is a pure micellar phase. The average aggregation number calculated from Equation (2) is \( 274 \pm 15 \), which is also a typical value for rodlike micelles. On addition of 0.50 mmol of \( \eta \)-octanol, the slope of \( A₄ \) versus \( \eta \) begins to deviate from zero, and this suggests the formation of vesicles. Nevertheless, the dependence of \( A₄ \) on \( \eta \) is indistinguishable, that is, the micelles are still the major component in the solution. With further addition of C₈OH, the slope of \( A₄/A₄₁ \) (\( A₄₁ \) is the value of \( A₄ \) when \( \eta = 0.002 \)) versus \( \eta \) becomes increasingly positive (Figure 9), that is, the ratio of vesicles to micelles increases, as was proved by other studies.⁷,¹³ Although the exact ratio of vesicles to micelles is difficult to obtain from the above measurements, it is confirmed that addition of C₈OH is an effective way of adjusting the ratio of vesicles to micelles in the DTEAB/SDS system.

Figure 7. Micrographs of vesicles (negative-staining technique) for the system DTEAB/SDS (\( C_{\text{total}} = 10 \text{ mmol}, X_{\text{DTEAB}} = 0.25 \)) on addition of a) 0.50, b) 1.0, and c) 1.5 mmol of C₈OH.

Figure 8. a) Variation of the contribution of the vesicle peak to the total scattering intensity of the solution \( I_v \% \) as a function of the concentration of added C₈OH and b) \( < R_{\text{app}} > \) for the micelle and vesicle peaks as a function of \( C(C₈OH) \) for the system DTEAB/SDS (\( C_{\text{total}} = 10 \text{ mmol}, X_{\text{DTEAB}} = 0.25 \)). The solid lines are visual aids.

Figure 9. Normalized value of the parameter \( A₄ \) as a function of \( \eta \) (\( \eta = [Q]/C_{\text{total}} \)) with various concentrations of added C₈OH (\( A₄₁ \) is the value of \( A₄ \) when \( \eta = 0.002 \)) for the system DTEAB/SDS (\( C_{\text{total}} = 10 \text{ mmol}, X_{\text{DTEAB}} = 0.25 \)). The solid lines are visual aids.
system, and thus vesicle/micelle solutions with variable ratio of vesicles to micelles can be easily obtained.

\( n \)-Octylamine (C\(_8\)NH\(_2\)) has the same hydrocarbon chain length as C\(_8\)OH but a different polar head group. Its \( R_{\text{eff}} \) also covers the entire micellar region of the DTEAB/SDS system with \( C_{\text{total}} = 10 \) mmol. For the DTEAB/SDS system \( (C_{\text{total}} = 10 \) mmol, \( X_{\text{DTEAB}} = 0.25 \) ), only 1.0 mmol of C\(_8\)NH\(_2\) is required for complete MVT. In addition, similar to C\(_8\)OH, micelle/vesicle solutions can also be easily realized and actively controlled by addition of C\(_8\)NH\(_2\).

**MVT induced by organic additives in the DTEAB/SDSO\(_3\) system:** The solubilization behavior of the above organic additives was also studied in the \( n \)-dodecyltriethylammonium bromide/sodium \( n \)-dodecylsulfonate (DTEAB/SDSO\(_3\)) catanionic surfactant system with \( C_{\text{total}} = 10 \) mmol. None of the apolar hydrocarbons can induce a MVT in this system. However, the addition of C\(_8\)OH or C\(_8\)NH\(_2\) can still efficiently cause a MVT in the entire micellar region. Moreover, the ratio of vesicles to micelles can also be adjusted by addition of the polar additives. The solution of DTEAB/SDSO\(_3\) with \( C_{\text{total}} = 10 \) mmol and \( X_{\text{DTEAB}} = 0.25 \) is selected as an instance. The micelles in this system have \( (R_{\text{h,app}}) = 2 \) nm by DLS and an average aggregation number of 164 ± 10 by TRFQ. According to the DLS results (Figure 10) and TEM (Figure 11), the ratio of vesicles to micelles gradually increases on addition of C\(_8\)OH, and 2.5 mmol C\(_8\)OH is required for the complete MVT.

**Discussion**

Mechanism of hydrocarbon-induced MVT: As far as we know, this study is the first report that solubilization of a hydrocarbon (alkylbenzene or alkane) can induce a MVT in a surfactant system. It is known that the location, distribution,
and orientation of the solubilized molecules can significantly influence the morphology of the aggregate. Possible mechanisms for these phenomena are discussed below.

Previous studies have shown that the alkyl chain of alkylbenzene tends to dissolve in the palisade of the surfactant micelle with the benzene group located near the water/hydrocarbon interface and this increases the volume of the surfactant hydrocarbon tail. The well-known theory of the packing parameter of the packing parameter $p$, proposed by Israelachvili et al., has been widely and successfully used to explain the transformations of organized assemblies in dilute surfactant solutions: $0 \leq p \leq 1/3$ for spherical micelles, $1/3 \leq p \leq 1/2$ for cylindrical micelles, and $1/2 \leq p \leq 1$ for bilayer structures ($p$ is defined as $\nu/a_l$, where $\nu$ is the surfactant tail volume, $a_l$ is the tail length, and $a_0$ is the equilibrium area per molecule at the aggregate surface). It is conceivable that, on solubilization of alkane benzene in the DTEAB/SDS system, the variation of $a_0$ and $l_0$ will be insignificant. Therefore an increase in the aggregate parameter $p$ can be expected, and formation of larger aggregates with lower curvature is more favored. In fact, spherical micelles were found to undergo transformation to rodlike micelles in some ionic surfactant systems as the surfactant composition in the catanionic surfactant system. In particular, alkanes were usually considered to be solubilized in the micellar core of surfactant micelles and induce formation of swollen spherical micelles. However, induction of a MVT by alkyl benzene in the DTEAB/SDS system cannot be satisfactorily explained if alkane molecules are merely solubilized in the micellar core. It was proposed that alkane molecules that have shorter hydrocarbon chains than the surfactant are not restricted to the interior of the micelle and can partially penetrate into the palisade layer of the micelle, which also promote an increase in the effective hydrocarbon tail volume $\nu$ in the hydrophobic region. Hence, the solubilization of alkane, similar to the effect of $n$-alkylbenzene, may increase the packing parameter, and the MVT may then take place within certain ranges of surfactant composition in the catanionic surfactant system. In addition, the $R_{\text{eff}}$ of the alkane is generally narrower than that of $n$-butylbenzene, probably because of the alkane mole-
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High efficiency and activity of polar organic additives in inducing a MVT and adjusting the ratio of vesicles to micelles:

The $R_{eq}$ of both $C_{6}OH$ and $C_{6}NH_{2}$ are much broader than those of the hydrocarbons in the DTEAB/SDS system ($C_{total}=10 \text{ mmol}$), and the polar additives can induce a MVT even in the DTEAB/SDS system ($C_{total}=10 \text{ mmol}$), whereas the hydrocarbons fail to do so under the same conditions, which demonstrates the superiority of polar organic additives over hydrocarbons in inducing MVTs. Polar organic additives, such as $C_{6}OH$, can preferentially penetrate into the palisade of surfactant micelles with their polar head group (OH group of $C_{6}OH$) towards the surface and thus act as a kind of co-surfactant with a rather small head group. Besides the contribution of the hydrocarbon chain to increasing effective hydrocarbon tail volume $v$, the effect of the head group should also be considered. Previous work showed that solubilization of certain alcohols in lipid solution can significantly reduce the bending energy of the lipid multilayers and make the membranes more flexible.

Therefore, it is reasonable to think that the presence of the polar head group of the polar additive probably significantly alters the interactions between surfactant head groups in catanionic surfactant systems and favors the formation of vesicles. Thus, the polar additives would have much higher efficiency and activity in inducing a MVT than the apolar hydrocarbons. It is also noteworthy that for the DEAB/SDS system ($C_{total}=10 \text{ mmol}$), a lower concentration of $C_{6}NH_{2}$ (1.0 mmol) is required for a complete MVT compared with that of $C_{6}OH$ (1.5 mmol). This difference may come from the partial protonation of $C_{6}NH_{2}$ to $C_{6}NH_{3}^{+}$ in water, which can neutralize the excess negative charges in the aggregate and make an extra contribution to the increase in the packing parameter than the neutral $C_{6}OH$ molecule. Hence $C_{6}NH_{2}$ will exhibit greater efficiency in inducing a MVT in micellar phases that are rich in anionic surfactant.

The ratio of vesicles to micelles can be adjusted by addition of relatively small amounts of polar organic compounds in both catanionic surfactant systems, and this may have potential applications in templated synthesis of materials. Recently, the synthesis of bimodal mesoporous materials has attracted special interest for their higher activities and better control of selectivity over monomodal porous materials. Bimodal mesoporous materials with a well-defined pore size distribution on two different scales can be easily synthesized in one step by a dual-templating method in which two different kinds of organized supramolecular assemblies simultaneously coexist in one phase (e.g., vesicle/micelle system) and separately control the bimodal pores. Although mixed vesicular/micellar phases exist in many catanionic surfactant systems and are quite promising for use as dual templates, the region of coexisting vesicle/micelle phases in the phase diagram is usually narrow. Therefore, it is difficult to actively control the ratio of vesicles to micelles by varying the surfactant ratio in catanionic surfactant systems, and so far few attempts have been made to synthesize controlled bimodal mesoporous materials with this kind of dual templates. Our work may provide a novel and universal method to realize such goal. Micelle/vesicle solutions of catanionic surfactant systems generated by addition of polar additives could act as templates for synthesis of bimodal porous materials in which the two pore size distributions are separately controlled by the micelles and vesicles. Moreover, a series of dual-template systems with different ratios of vesicle to micelle can be easily obtained by gradual addition of polar additives, and thus the connection between the dual-template solutions and the structures, as well as the properties of synthesized materials, can also be systemically investigated, which may help to understand the complex template mechanism and find suitable templates.
for other organized assemblies. Further study is ongoing in our laboratory.

**Conclusion**

It can be concluded that the induction of MVT in catanionic surfactant systems by addition of organic additives is closely related to the structure and polarity of the additive, the surfactant composition, and the interactions between the surfactant molecules. Addition of a nonpolar hydrocarbon with a certain chain length, such as n-butylbenzene or n-octane, can induce MVT at proper surfactant compositions in a catanionic surfactant system with relatively strong intermolecular interactions and high micelle aggregation number. Polar additives, such as n-octanol, are much more efficient in inducing MVT even in the system with weaker intermolecular interactions. Moreover, solubilization of the polar additive provides a series of two-template systems with variable ratios of vesicles to micelles for the synthesis of controlled bimodal mesoporous materials. This work may advance further understanding of the controlled transformation of organized assemblies in surfactant solutions and promote its applications in other fields.

**Experimental Section**

**Materials**: n-Dodecyltrimethylammonium bromide (DTEAB) was prepared by reaction of 1-bromododecane and triethylamine and was recrystallized five times from ethanol/acetone. The purity of the surfactant was examined, and no minimum was found in the surface tension curve. It was kept low (1678 DI10 mN/m) to prevent excimer formation. The amount of ethanol in the surfactant solution was controlled to less than 1 vol%. All of the solutions were degassed by nitrogen for 15 min before the measurement to eliminate the influence of oxygen. Pyrene fluorescence decay curves were monitored by an Edinburgh FLS920 time-resolved fluorescence spectrophotometer (excitation at 337 nm and emission at 385 nm). The fluorescence decay of pyrene was fitted by using modified time-resolved fluorescence quenching (TRFQ) [28] to prevent excimer formation. The amount of pyrene in ethanol and C12PyCl in water were added to the surfactant solution directly, and then the solution was stirred vigorously for 48 h. The concentration of pyrene was kept low (1 × 10−6 M) to prevent excimer formation. The amount of ethanol in the surfactant solution was controlled to less than 1 vol%. All of the solutions were degassed by nitrogen for 15 min before the measurement to eliminate the influence of oxygen. Pyrene fluorescence decay curves were monitored by an Edinburgh FLS920 time-resolved fluorescence spectrophotometer (excitation at 337 nm and emission at 385 nm). The fluorescence decay of pyrene was fitted by using modified DECAN 1.0 software from the Key Laboratory of Photochemistry, CAS.

**Absorbance measurements**: Absorbance measurements were carried out with a Varian Cary 1E spectrophotometer at 500 nm.

**Transmission electron microscopy (TEM)**: Samples for TEM were prepared by negative-staining technique with aqueous uranyl acetate solution. A JEM-100CX electron microscope was employed.

**Rheology measurements**: The rheological properties of samples were measured with a ThermoHaake RS300 rheometer. A double-gap cylindrical sensor system was used with an outside gap of 0.30 mm and an inside gap of 0.25 mm.

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