Ionic Liquid Induced Transition from Wormlike to Rod or Spherical Micelles in Mixed Nonionic Surfactant Systems

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The structural changes of wormlike micelles composed of Tween 80 and Brij 30 in the presence of a common ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) were studied. Upon addition of $bmimBF_4$, the viscosities of the wormlike micelle systems decrease, or in other words, more Brij 30 is needed to attain a similar viscosity value. The changes of the storage/loss modulus and the relaxation time also show that the viscoelastic properties of the wormlike micelles decrease with increasing $bmimBF_4$ concentration. We believe that these results are attributed to a wormlike-rod/spherical micellar transition in the wormlike micelle solution, which is further confirmed by freeze-fracture transmission electron microscopy (FF-TEM) images. Additionally, the location of $bmimBF_4$ in mixed micelles was also studied to explain the structure transition in the above systems.

Introduction

Wormlike micelles have received considerable attention from theoreticians and experimentalists during the past few decades. In the late 1980s and early 1990s, an extensive study on the dynamics and rheological behavior of wormlike micelles began in long-chain ionic surfactant systems in the presence of salt.[1–4] Then, it has been found that viscoelastic wormlike micellar solutions can also be obtained by adding lipophilic surfactants such as polyoxyethylene alkyl ethers or long-chain monoglyceride.[5,6] Aramaki et al.[7] have investigated the viscoelastic properties of wormlike micelles in Tween 80 aqueous solution with trioxyethylene alkyl ether (C_mEO_3, $m = 12$, 14, and 16). We also found that wormlike micelles were formed in Tween 80 + Brij 30 ($C_{12}EO_4$) + H_2O systems.

Now many researchers have focused on the additive-induced structure changes of wormlike micelles. It is believed that knowledge of the structure and dynamics of wormlike micelles is vital for the optimization of its application. Among them, salt-induced structure changes of wormlike micelles in ionic surfactant solutions are most extensively studied.[8–12] For example, Li et al.[13] have studied the aggregation behavior of mixtures of cetyltrimethylammonium bromide (CTAB) and sodium 4-[(*E*)-phenyldiazenyl] benzoate (AZONa). With increasing the AZONa concentration, a gradual change from spherical micelles to vesicles via wormlike micellar phases was observed. In addition to the organic or inorganic salts, hydrocarbons, alcohols, and some polymers have also been shown to affect the structure of wormlike micelles to a great extent.[14–17] Although the majority of research is carried out in ionic surfactant solutions, nonionic surfactant systems are receiving much attention these days because growing environmental awareness has stimulated the search for nontoxic and biodegradable surfactants such as polyoxythylene sorbitan fatty acid esters (Tweens) and sucrose ester, and moreover, nonionic surfactant aggregations can also undergo structure transition under certain conditions.[18] Recently, Rodriguez-Abreu et al.[19] have reported the addition of small amounts of lipophilic cosurfactant to sucrose hexadecanoate induces micellar growth and leads to the formation of wormlike micelles. Linear alkyl chain oils that tend to solubilize in the micellar core have a disrupting effect on the viscoelastic properties of the wormlike micelles.

In this paper, we report the ionic liquid-induced structure transition of nonionic wormlike micelles composed of Tween 80 and Brij 30. On the one hand, room temperature ionic liquids (a kind of salt showing the liquid state) are receiving increased attention these days, and most of the investigations are driven by the possibility of their potential environmentally benign nature. So, it is logical to employ ionic liquids in concert with other environmentally friendly systems such as surfactant-based systems. Recently, modulating properties of dilute micellar solutions by adding ionic liquids have been studied extensively.[20–22] We believe utilization of ionic liquids to effectively alter or modify properties of wormlike micellar solution is still an appealing concept from both environmental and application points of view, which is still unexplored. On the other hand, there is little research about salt-induced structure changes in nonionic surfactant systems, because of the absence of electrostatic repulsion between surfactant headgroups. Here, we find the wormlike micelles composed of Tween 80 and Bij 30 are highly responsive to a popular hydrophilic ionic liquid $bmimBF_4$. Addition of $bmimBF_4$ induces a transition from wormlike to rod or spherical micelles. Rheology and freeze-fracture images provide enough information on the micellar structure changes.

Materials and Methods

Materials. Polyoxyethylene sorbitan monooleate (Tween 80, 97 %, Sigma), Brij 30 (> 99 %, Sigma), $bmimBF_4$ (water mass fraction < 10^{-5}, Shanghai Chengjie Chemical Co.), and pyrene (> 99.0 %, Aldrich) were all used as received. Water was deionized and distilled twice.

Methods. Samples with different concentrations of Tween 80 and Brij 30 were prepared in test tubes with caps, mixed on

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10.1021/je100209x

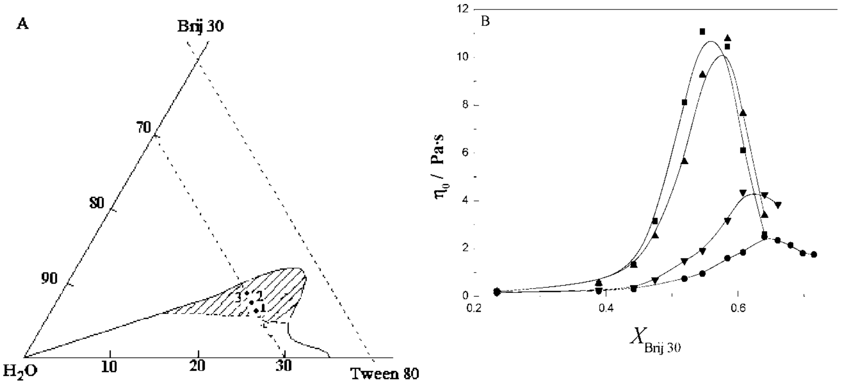


Figure 1. (A) Partial phase diagram for Tween 80 + Brij 30 + H_2O systems. (B) Variation of zero-shear viscosity (η_0) as a function of X_{Brij30} in 0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems in the absence and presence of $\mathrm{bmimBF_4}$ ($\mathrm{bmimBF_4}$/mol·L^{-1}: ■, 0; ▲, 0.03; ▼, 0.18; ●, 0.28).

a mixer for several minutes, and then controlled at (25 ± 0.1) °C for phase equilibrium.

The rheological measurements were performed in a rheometer Rheostess RS600 (HAAKE RheoStress) at 25 °C using a cone-plate geometry (diameter 35 mm and cone angle 1°) for highly viscous gels. Frequency sweeping measurements were performed in the linear viscoelastic regime of the samples as determined previously by dynamic strain sweeping measurements. The repeatability of this viscometer is better than 99.5 % by performing different sets of measurements of the same substances. The viscosity uncertainty was verified with water at 25 °C, finding that the deviations with the reference data are lower than 1 %. When the time scale of the reptation for an average micellar contour length (τ_{rep}) is too slow in comparison to the time scale of the scission (τ_{break}), there is a single exponential relation:

$$G(t) = G_0 \exp(-t/\tau_{\mathrm{R}}) \tag{1}$$

where G_0 is the plateau modulus, which is given by G' at high ω, and τ_{R} is the relaxation time. This kind of viscoelastic system is called Maxwell liquid,[23] described by following equations:

$$G'(\omega) = G_0 \frac{\omega^2 {\tau_{\mathrm{R}}}^2}{1 + \omega^2 {\tau_{\mathrm{R}}}^2} \tag{2}$$

$$G''(\omega) = G_0 \frac{\omega \tau_{\mathrm{R}}}{1 + \omega^2 {\tau_{\mathrm{R}}}^2} \tag{3}$$

$$|\eta^*(\omega)| = \frac{(G'^2 + G''^2)^{1/2}}{\omega} \tag{4}$$

When plotting G'' against G', there should be a semicircle called the Cole−Cole plot. It follows that:

$$(G'')^2 + \left(G' - \frac{G_0}{2}\right)^2 = \left(\frac{G_0}{2}\right)^2 \tag{5}$$

Moreover, the zero-shear viscosity (η_0) is given by the relation:

$$\tau_{\mathrm{R}} = \frac{\eta_0}{G_0} \tag{6}$$

The relaxation time τ_{R} can be estimated at $(\omega_{\mathrm{R}})^{-1}$, where ω_{R} is the frequency at which G' is equal to G''.

The freeze-fracture transmission electron microscopy (FF-TEM) investigation was carried out with a freeze-fracture apparatus (Balzers BAF 400D) on a nitrogen-cooled support and a transmission electron microscope (TEM, Tecnai 12 Philip, Holland). A small amount of sample was placed in a sample cell, which was quickly plunged into liquid nitrogen, and then the frozen sample was fractured and replicated in a freeze-fractured apparatus. Replicas were examined with a TEM. The temperature for this experiment was kept at (25 ± 0.1) °C.

Conductivity measurements were carried out on a DDS-11A digital conductometer (Xiaoshan Scientific Instrument Factory, China) at a temperature of 298 K. The respective uncertainties on the conductivity were estimated to be less than 5 %.

Steady-state fluorescence experiments were performed with a spectrofluorophotometer (RF-5301, Shimadzu Company, Kyoto, Japan) equipped with a temperature-conducted circulating water bath. Pyrene was used as the probe to determine the microenvironmental polarity of mixed micelles. The respective uncertainties on I_1/I_3 (the intensity ratio of the first peak to the third of the fluorescence spectrum of pyrene) were estimated to be less than 4 %.

^{1}H NMR experiments were carried out with a Bruker AV-600 NMR spectrometer with a ^{1}H frequency of 600.13 MHz. Sixty-four times of accumulations were acquired generally. Water was used as solvent, and D_2O (99.5 %), in which sodium 3-(trimethylsilyl)-1-propanesulfonate was added as standard substance, was used as an external standard. The respective uncertainties on ^{1}H chemical shifts of $\mathrm{bmimBF_4}$ were less than 0.3 %.

Results and Discussion

Wormlike Rod or Spherical Micelles Transition-Induced by $\mathrm{BmimBF_4}$.

Rheological Study. Steady-State Viscosity. The isotropic part of the Tween 80 + Brij 30 + H_2O systems at 25 °C in the dilute region is shown in Figure 1A. The shaded area in the phase diagram represents the viscous wormlike micelle region. Here, we will discuss the effect of $\mathrm{bmimBF_4}$ on the wormlike micellar structure. During the entire study, the mass fraction of Tween 80 + Brij 30 was fixed at 30 % in water, varying the Brij 30 concentration expressed in mole fraction of Brij 30 in total amphiphiles (X).

The changes of the zero-shear viscosity (η_0) as a function of X_{Brij30} in the absence or presence of $\mathrm{bmimBF_4}$ are shown in Figure 1B. In the absence of $\mathrm{bmimBF_4}$, after a certain concentration, further addition of Brij 30 increases η_0 sharply until a maximum is reached, implying the formation of wormlike micelles. The micellar growth can be simply explained by the decrease of the effective cross-sectional area per amphiphile upon addition of Brij 30.[24] Thereafter, the micelles tend to form branches, and the viscosity decreases since the branch points are not fixed but are free to slide along the micelle providing an additional mode of stress relaxation.[25] In the presence of $\mathrm{bmimBF_4}$, the general shape of the plot is similar to that without

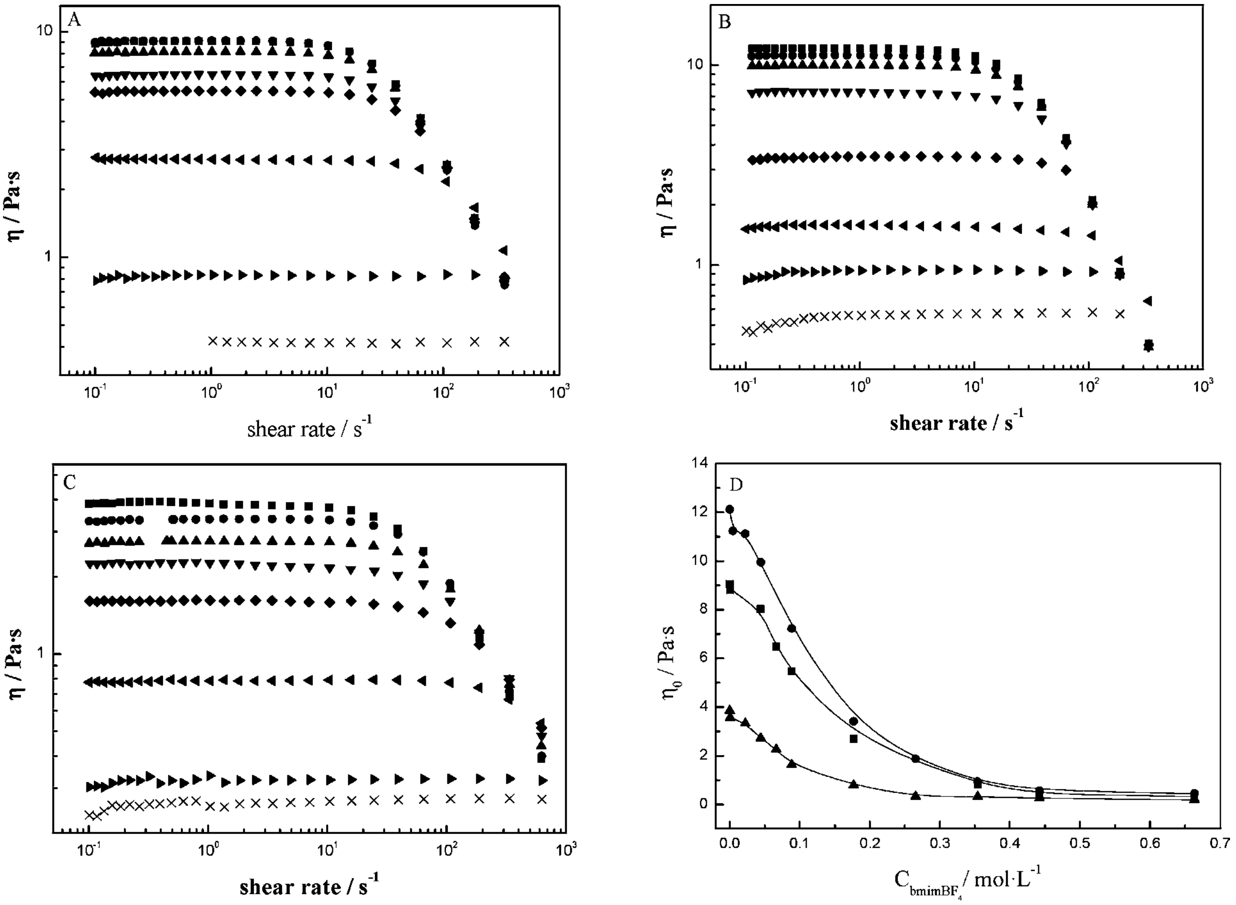


Figure 2. Steady-shear rate viscosity curves at different bmimBF$_4$ concentrations (bmimBF$_4$/mol·L^{-1}: ■, 0; ●, 0.02; ▲, 0.04; ▼, 0.07; ♦, 0.09; left-pointing triangle, 0.18; right-pointing triangle, 0.35; ×, 0.44) in 30 % (mass fraction) Tween 80 + Brij 30 surfactant systems with X_{Brij30} = (A) 0.56; (B) 0.54; (C) 0.47; and the corresponding zero-shear viscosity as a function of bmimBF$_4$ concentration (D) with X_{Brij30} = ■, 0.56; ●, 0.54; ▲, 0.47.

bmimBF$_4$, but the magnitude of η_0 becomes smaller at a similar mixing fraction of the amphiphiles, and more Brij 30 is required to attain the viscosity maximum. When bmimBF$_4$ concentration increases to 0.28 mol·L^{-1}, the system's viscosity increases to some extent with Brij 30 concentration, but it could not form viscoelastic wormlike micelles. It seems that small aggregates are favored in the presence of bmimBF$_4$, or in other words more Brij 30 is needed to induce unidimensional micellar growth. To investigate the structure changes more clearly, we studied the influence of bmimBF$_4$ on the rheological properties of the samples at $X_{\mathrm{Brij30}} = 0.47$, 0.54, and 0.56, respectively, which corresponded to the points before, at, and after the maximum viscosity (points 1, 2, and 3 shown in Figure 1A).

The steady-shear viscosity as a function of shear rate at different X_{Brij30} in the absence and presence of bmimBF$_4$ is shown in Figure 2A−C. In the absence of bmimBF$_4$, the viscosity curves are characterized at lower shear rates by a Newtonian plateau and followed by a shear-thinning region at higher shear rates, which is the typical behavior of wormlike micelles.[26] However, as the concentration of bmimBF$_4$ increases, η decreases, and the critical shear rate (shear rate at which shear thinning occurs) shifts gradually to a higher value and disappears finally. The critical shear rate is inversely proportional to the longest structural relaxation time, and a higher value of relaxation time indicates a shorter breaking time or corresponds to a smaller size of the micelles. So, this result suggests that the micellar lengths of all samples decrease, that is, the wormlike micelles are transformed into rod or spherical micelles gradually by increasing bmimBF$_4$ concentration.

The effect of bmimBF$_4$ on the viscosity of the mixed wormlike micelles is more clearly seen in Figure 2D, where zero shear viscosity, η_0, is plotted as a function of bmimBF$_4$ concentration. As can be seen from Figure 2D, η_0 at first decreases sharply with increasing bmimBF$_4$ concentration, but attains a plateau value after a certain concentration. The decrease in viscosity indicates that the network structure of wormlike micelles is destroyed after the addition of bmimBF$_4$, and the trend of the plot also suggests that the influence of bmimBF$_4$ is more profound on the structure of wormlike micelles than on that of small aggregates. At first, wormlike micelles are broken with increasing bmimBF$_4$ concentration, and η_0 decreases quickly. But, when the concentration of bmimBF$_4$ increases to 0.27 mol·L^{-1}, η_0 decreases below 2.0 Pa·s, implying that the wormlike micelles are transformed into rod or spherical micelles completely. So, η_0 scarcely decreases with further addition of bmimBF$_4$.

Temperature is another important parameter that affects the structure of wormlike micelles. Usually, there is a pronounced temperature effect in aqueous systems of nonionic surfactants, especially for poly(oxyethylene)-type surfactants (such as Tween 80 and Brij 30), because the hydration of the oxyethylene unit is sensitive to the temperature. So, the experiments carried out in (15 to 25) °C can reflect the influence of temperature on the micellar structure. Figure 3 shows a plot of η_0 as a function of X_{Brij30} in the absence or presence of bmimBF$_4$ at different temperatures. In the absence of bmimBF$_4$, when the temperature is decreased, the trend of the curve remains essentially the same, but the curve shifts to the right in the plot, or in other words,

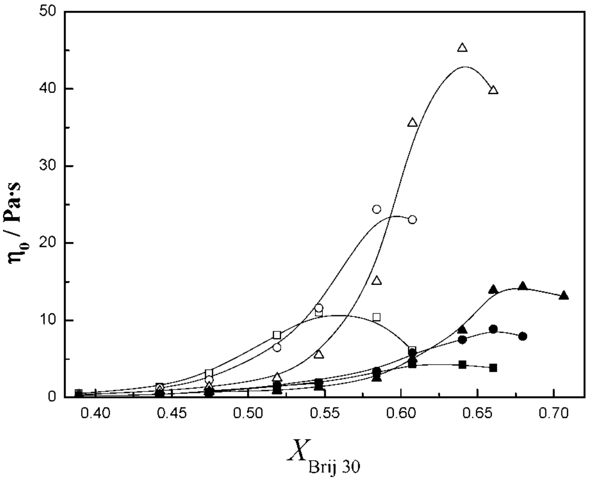


Figure 3. Variation of zero-shear viscosity with X_{Brij30} at ▲, △, 15 °C; ●, ○, 20 °C; and ■, □, 25 °C in the absence (open symbols) and presence (filled symbols) of $\mathrm{bmimBF_4}$.

more Brij 30 is required to attain a similar viscosity value. This trend is consistent with the behavior of mixed nonionic surfactant systems.[27] As the temperature decreases, the extent of hydration of the EO groups of surfactant molecules increases. Hence the extent of one-dimensional micellar growth decreases, and more Brij 30 is needed to induce a similar extent of micellar growth. However, at compositions around the viscosity maximum, the effect of temperature on the micellar growth appears to be opposite to the above conclusion. With decreasing temperature the maximum viscosity increases, which may be taken as an indication of enhanced micellar growth with decreasing temperature. Here, another factor should be considered. When the spontaneous curvature of the interface becomes more positive (at lower temperature), the end-caps are stabilized, and the energy cost associated with the formation of the interface with negative curvature becomes higher. As a result, the formation of the junction becomes less favorable, and rapid micellar branching is triggered at higher concentrations of Brij 30, which results in a larger increase in viscosity.

After the addition of $\mathrm{bmimBF_4}$ (0.18 $\mathrm{mol \cdot L^{-1}}$), the trend of plot is similar to that without $\mathrm{bmimBF_4}$. However, the viscosity decreases sharply at a same temperature, and more Brij 30 is required to attain a maximum viscosity compared with the pure surfactant systems. This rheological behavior is consistent with the above results shown in Figure 1B. Additionally, we also find that the viscosities around the maximum point are less responsive to temperature in the presence of $\mathrm{bmimBF_4}$, which may be also attributed to the structure changes of wormlike micelles induced by $\mathrm{bmimBF_4}$. It is well-known that compared with spherical or rod micelles, the structure and rheology of wormlike micelles are extremely sensitive to external factors such as temperature. But, in the presence of $\mathrm{bmimBF_4}$, the long wormlike micelles are broken into short rod micelles. So, the viscosities around the maximum point become less responsive to temperature.

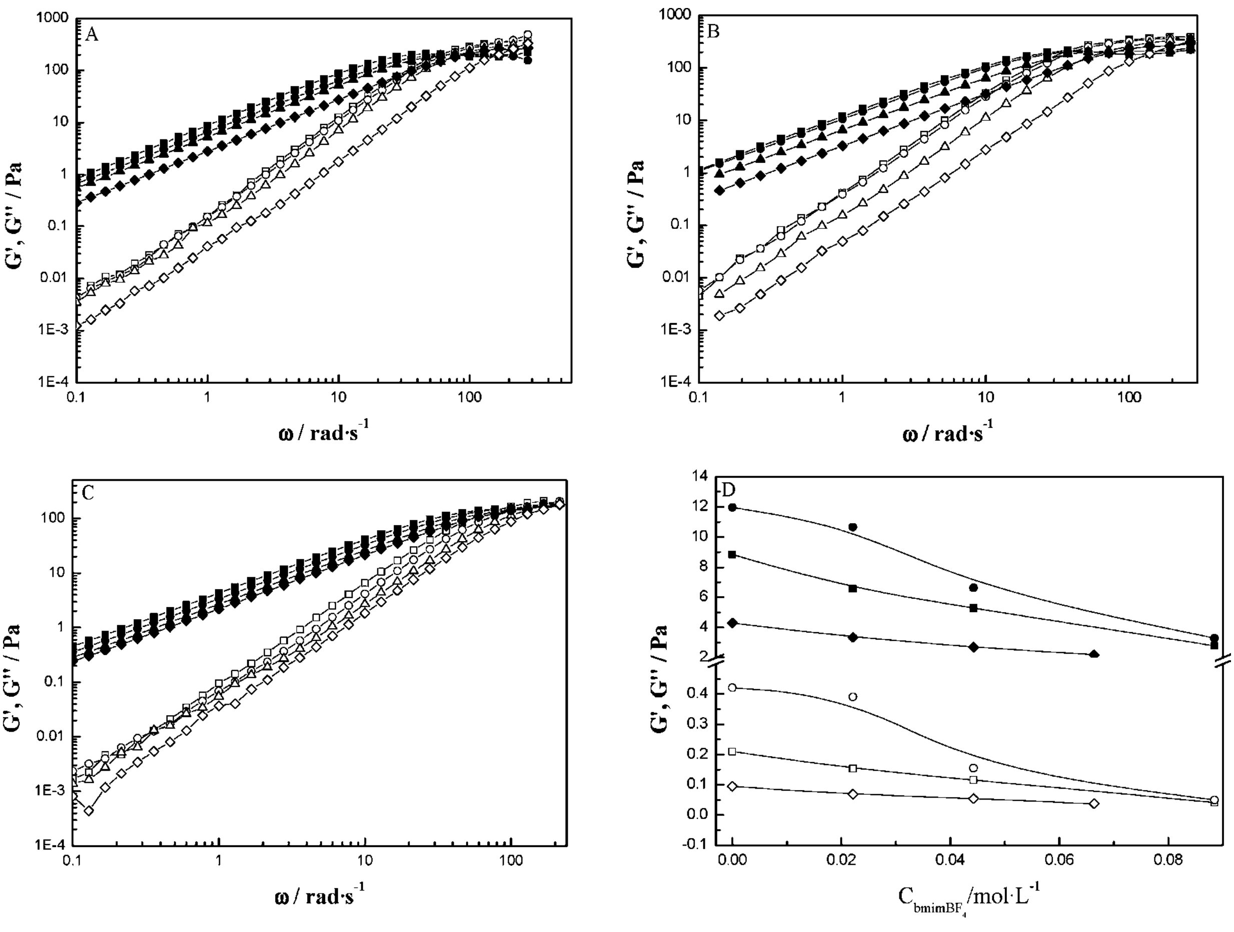


Figure 4. Variation of elastic modulus, G' (open symbols), and viscous modulus, G'' (filled symbols), as a function of oscillatory-shear frequency (ω) in 0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems with X_{Brij30} = (A) 0.56; (B) 0.54; (C) 0.47 ($\mathrm{bmimBF_4/mol \cdot L^{-1}}$: (A, B) ■, □, 0; ●, ○, 0.02; ▲, △, 0.04; ♦, ◇, 0.09; (C) ■, □, 0; ●, ○, 0.02; ▲, △, 0.04; ♦, ◇, 0.07); and the corresponding G' (open symbols) and G'' (filled symbols) as a function of $\mathrm{bmimBF_4}$ concentration at ω = 1.0 Pa (D) with X_{Brij30} = ■, □, 0.56; ●, ○, 0.54; ♦, ◇, 0.47.

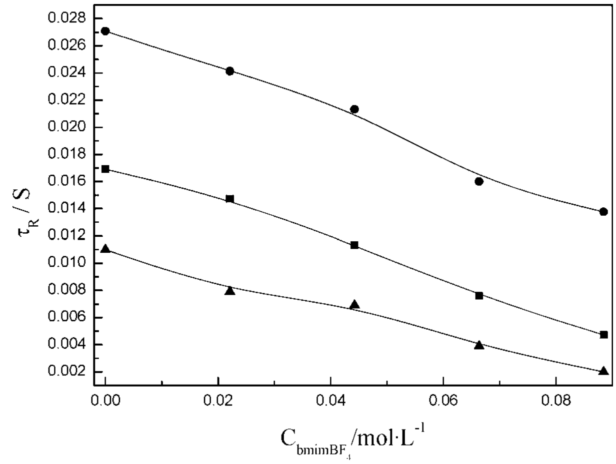


Figure 5. Variation of τ_R as a function of bmimBF$_4$ concentration in 0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems with X_{Brij30} = ■, 0.56; ●, 0.54; ▲, 0.47.

Oscillatory Measurements. The influence of bmimBF$_4$ on the viscoelastic properties of the wormlike micellar solution has been studied by oscillatory shear measurements.

Figure 4A−C gives the variation of the elastic modulus (G') and the viscous modulus (G'') with oscillation frequency (ω) at different bmimBF$_4$ concentrations. As can be seen from Figure 4A−C, at low ω, all of the samples show a viscous behavior ($G'' > G'$), whereas at high ω, the samples exhibit elastic behavior ($G' > G''$). This is the typical viscoelastic behavior of wormlike micellar solutions, which is attributed to the entanglement of the wormlike micelles. But, compared with the sample without bmimBF$_4$, the viscoelastic properties of the wormlike micelles are gradually lost with increasing bmimBF$_4$ concentration. First, G' and G'' decrease with bmimBF$_4$ concentration at lower ω (Figure 4D). Second, the shear frequencies corresponding to the G' and G'' crossover, ω_R, shift to higher values. ω_R is equivalent to the inverse of relaxation time, τ_R, which is related to the average length of the wormlike micelles. τ_R decreases with increasing bmimBF$_4$ concentration (Figure 5), indicating that the length of the wormlike micelle decreases and the transition from wormlike micelles to rod or spherical micelles occurs.

Usually, the rheological behavior at low ω (Figure 4) can be described by the Maxwell model, but at high ω, experimental data show significant deviation, which is probably caused by the Rouse model of stress relaxation. A Cole−Cole plot (plot of G'' as a function of G') can easily visualize how well the data correspond to the Maxwell model. It can be seen from Figure 6 that a large deviation from the Maxwellian behavior is observed at higher frequencies and the deviation becomes larger after the addition of bmimBF$_4$, which is also an indication of a less structured system with poor viscoelastic behavior in the presence of bmimBF$_4$.

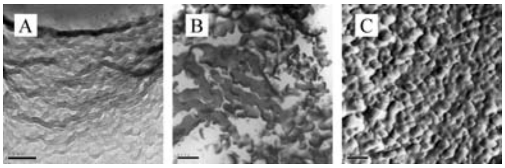


Figure 7. Freeze-fractured images of micelles (0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems with $X_{\text{Brij30}} = 0.54$) at different bmimBF$_4$ concentrations. The scale mark is 0.2 μm.

Freeze-Fractured Transmission Electron Microscopy. To confirm the structural transition of the wormlike micelles, FF-TEM measurements were carried out. We chose the sample with the maximum viscosity (corresponding to point 2 in Figure 1A) in 0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems as a typical example and studied the influence of bmimBF$_4$.

The structural transition from wormlike micelles to rod or spherical micelles induced by bmimBF$_4$ is clearly shown in Figure 7. Figure 7A shows the image of the wormlike micelles without bmimBF$_4$, from which we can see many flexible wormlike micelles entangle with each other and form network structures. Therefore, the viscosity is very high. But, when bmimBF$_4$ (0.04 mol·L^{-1}) is added to the system (Figure 7B), the micellar length decreases, and the coexistence of some spherical and rodlike particles also suggests that the wormlike structures are destroyed. Then, by further increasing the bmimBF$_4$ concentration (0.22 mol·L^{-1}), only spherical micelles can be observed (Figure 7C), corresponding to the low zero-shear viscosity. This result is consistent with that obtained from rheology data.

Mechanism of Structural Transition.

It is well-known that shapes of surfactant aggregates are determined by geometrical structures of surfactant molecules, as discussed by Israelachvili et al.[28] A simple dimensionless molecular parameter that connects the shape of the aggregates to the molecular geometrical structure is given as the surfactant packing parameter, which is defined via[29]

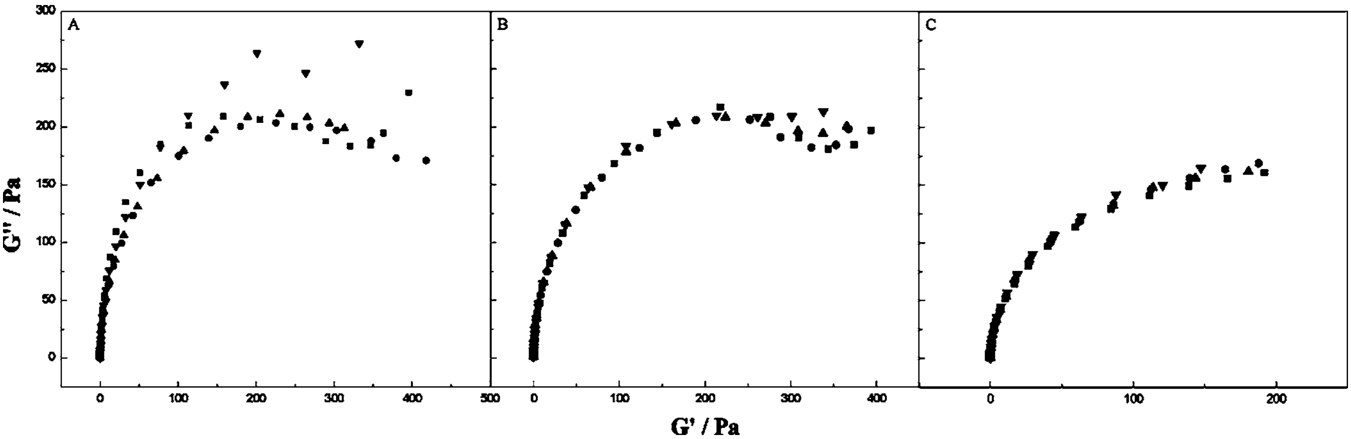


Figure 6. Cole−Cole plots of the values shown in Figure 4 in 0.30 (mass fraction) Tween 80 + Brij 30 surfactant systems with X_{Brij30} = (A) 0.56; (B) 0.54; (C) 0.47; in the absence and presence of bmimBF$_4$ (bmimBF$_4$/mol·L^{-1}: (A, B) ■, 0; ●, 0.02; ▲, 0.04; ▼, 0.09; (C) ■, 0; ●, 0.02; ▲, 0.04; ▼, 0.07).

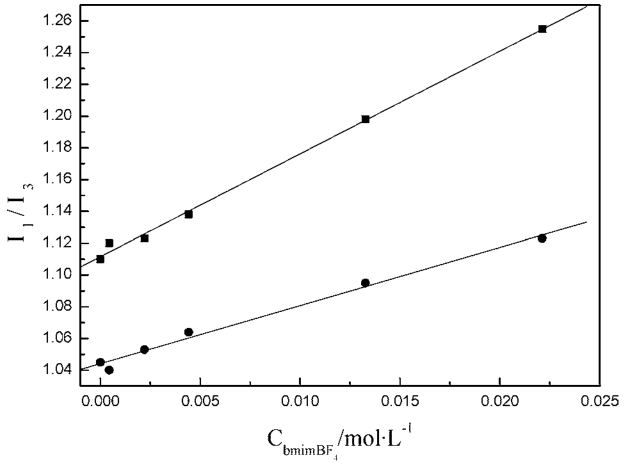


Figure 8. Plots of I_1/I_3 of pyrene against bmimBF$_4$ concentration in surfactant solutions (Tween 80/mmol·L^{-1}: ■, 0.03; ●, 0.06).

$$R_p = \frac{V_o}{A_h L_o} \qquad (7)$$

where A_h is the area at the micellar surface of surfactant headgroup(s), V_o is the volume occupied by the alkyl chain, and L_o is the length of the chain. R_p is the fundamental geometric quantity for some of the possible aggregation shapes.[30] Surfactants with smaller headgroup areas (high R_p) tend to form larger aggregates. So, we believe that the addition of bmimBF$_4$ to mixed micelles may increase A_h of surfactant molecules and decrease R_p. Consequently, the wormlike micelles are transformed into rod or spherical micelles, which results in a decrease in viscoelastic properties.

If this explanation holds true, bmimBF$_4$ should be located in the outer palisade layer of the mixed micellar phase. The results from conductivity, steady-state fluorescence probe techniques, and ^{1}H NMR confirm our hypothesis.

In the following experiments, the location of bmimBF$_4$ in the mixed micelles in dilute solution was studied, and X_{Brij30} is still fixed at 0.54. We use Tween 80 concentration instead of total surfactant concentration in following plots.

Behavior of Pyrene. Pyrene was usually used as a probe to determine the microenvironmental polarity of micelles. The steady state emission spectrum of pyrene shows five vibronic bands in (350 to 420) nm region. The intensity ratio of the first peak to the third (I_1/I_3) of the fluorescence spectrum of pyrene shows the microenvironmental polarity where the probe exists.[31]

Figure 8 presents I_1/I_3 as a function of bmimBF$_4$ concentration at a fixed concentration of surfactants. It appears that I_1/I_3 increases with bmimBF$_4$ concentration implying that the dipolarity as indicated by I_1/I_3 is significantly higher in the presence of bmimBF$_4$. Because it has been established that pyrene is solubilized in the palisade layer of the micellar moiety,[32,33] it can be inferred from I_1/I_3 and the hydrophilic property of bmimBF$_4$ that bmimBF$_4$ can partition into the mixed micellar phase and may be located on the outer side of pyrene molecules.

Conductivity. Conductivity was also used to study the interaction between the mixed micelles and the bmimBF$_4$. Figure 9 presents the conductivity of Tween 80 + Brij 30 + H$_2$O mixed systems in the absence and presence of bmimBF$_4$. It shows that the conductivity of the Tween 80 + Brij 30 + H$_2$O mixed systems increases with surfactant concentration but decreases in the presence of bmimBF$_4$. We believe that this unusual trend should be due to the interaction between bmimBF$_4$ and amphiphile molecules. Behera et al.[20] have studied changes in the properties of Triton X-100 micelles upon addition of 0.021 (mass fraction) bmimPF$_6$. They proposed that the interactions (e.g., H-bonding, dipole−induced dipole, among others) between bmimPF$_6$ and TX-100 probably decrease the overall ionic character of the solution and thus decrease the conductivity. Another appropriate reason may be that the bmimPF$_6$ solubilization site in TX-100 micelles could be relatively hydrophobic, resulting in decreased ionic dissociation of bmimPF$_6$. Contrary to bmimPF$_6$, bmimBF$_4$ is hydrophilic. Therefore, it can be speculated that the decrease in conductivity here is mainly due to the association of Tween 80 and/or Brij 30 with bmim$^+$ and/or BF$_4^-$ via ion−dipole and/or hydrogen-bonding interactions.

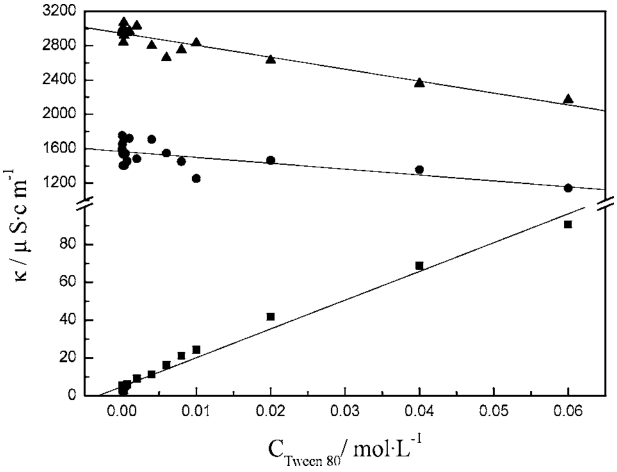
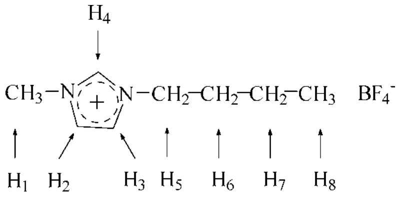


Figure 9. Conductivity of the mixed micelles in the absence and presence of bmimBF$_4$ (bmimBF$_4$/mol·L^{-1}: ■, 0; ●, 0.02; ▲, 0.04).

Scheme 1. bmimBF$_4$ Molecular Structure



^{1}H NMR. The interaction between bmimBF$_4$ and mixed micelles was further studied by ^{1}H NMR. The mixed critical micelle concentration, cmc (0.02 mmol·L^{-1}), of Tween 80 + Brij 30 with $X_{\text{Brij30}} = 0.54$ in aqueous solution was determined by steady-state fluorescence spectroscopy using pyrene as a fluorescence probe (see Figure S1 in the Supporting Information). Because the concentration of bmimBF$_4$ is low (0.004 mol·L^{-1}), its influence on the mixed cmc is negligible.

The number of H atoms in a bmimBF$_4$ molecule is shown in Scheme 1, and the ^{1}H NMR spectrum of bmimBF$_4$ is given in Figure S2 in the Supporting Information. The effect of surfactant on the ^{1}H chemical shifts of bmimBF$_4$ are shown in Table 1. As can be seen from Table 1, at lower concentrations of Tween 80 (< 0.02 mmol·L^{-1}), the chemical shifts of the protons of H1, H4, H5, H6, H7, and H8 undergo negligible downfield shifts, whereas the protons of H2 and H3 exhibit significant chemical shifts. Miki et al.[34] have found that the hydrogen atoms on the imidazolium ring are all involved in the formation of hydrogen bonds with water in the H$_2$O-rich mixture. In our system, ethoxy oxygens of Tween 80 and Brij 30 can also accept protons. So, we believe that the upfield shifts of H2 and H3 may be ascribed to their hydrogen-bonding interactions with ethoxy oxygens of Tween 80 and/or Brij 30 and the conjugated effect of ethoxy oxygens of Tween 80 and/or Brij 30 and

Table 1. Effect of Surfactant on the ^{1}H Chemical Shifts of bmimBF$_4$

	C_{Tween80}/mmol·L^{-1}				
$\Delta\delta$H	0.004	0.008	0.02	0.03	0.04
$\Delta\delta$H1	−0.001	0.002	0.242	0.242	0.241
$\Delta\delta$H2	−0.053	−0.053	0.189	0.189	0.187
$\Delta\delta$H3	−0.048	−0.048	0.194	0.194	0.193
$\Delta\delta$H4	0	0	0.242	0.243	0.241
$\Delta\delta$H5	0	0.001	0.242	0.242	0.240
$\Delta\delta$H6	0	0.002	0.242	0.242	0.241
$\Delta\delta$H7	0	0.002	0.241	0.241	0.240
$\Delta\delta$H8	−0.001	0.002	0.242	0.242	0.241

imidazolium ring may also play an important role in this process. But, H4, the most active proton on imidazolium ring, does not show significant chemical shifts. We suspect that this should be due to its strong hydrogen bonds with H_2O. So, the influence of surfactants on the chemical shift of H4 is negligible. However, when the concentration of surfactant is higher than the mixed cmc, the chemical shifts of the protons of bmim$^+$ all exhibit significant chemical shifts toward downfield. This can be explained by the variation of micropolarity of bmim$^+$ as a result of partitioning of bmimBF$_4$ into the mixed micellar phase. Then, by further addition of surfactants, no obvious variations are observed.

On the basis of the overall data, it can be inferred that bmim$^+$ can partition into the mixed micellar phase and is close to the hydrophilic moiety of Tween 80 and/or Brij 30, because of favorable interactions (ion−dipole and hydrogen-bonding interactions between bmimBF$_4$ and surfactant molecules).

Summary

Salt-induced micellar structure changes of nonionic surfactant solution are always neglected, because of the absence of complicated interactions between the counterions and the head groups. In this paper, we find that the wormlike micelles composed of Tween 80 and Brij 30 are highly responsive to bmimBF$_4$ (a kind of salt showing the liquid state). Addition of bmimBF$_4$ decreases viscoelastic properties of wormlike micelles due to a wormlike to rod or spherical micellar transition, and it is further confirmed by the freeze-fracture images. These results may be attributed to the location of bmim$^+$ in mixed micelles because the location of bmim$^+$ in the palisade layer of mixed micelles increases the area of surfactant headgroup at the micellar surface and thus induces the structure changes. We think the present study has unambiguously shown a possible route to control the microstructure of nonionic wormlike micelles.

Supporting Information Available:

Plots of I_1/I_3 of pyrene against Tween 80 concentration and ^{1}H NMR spectrum of bmimBF$_4$ are shown in Figures S1 and S2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review March 5, 2010. Accepted May 17, 2010. This research work was supported by the National Nature Science Foundation of China (No. 20633010 and 20773106).

JE100209X