Self-Assembled Structure in Room-Temperature Ionic Liquids

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Abstract: Self-assembled vesicles, structurally equivalent to some hydrotropes, have been obtained from a Zn^{2+}–fluorous surfactant or in the mixture of Zn^{2+}–fluorous surfactant/zwitterionic surfactant in room-temperature ionic liquids (RTILs). The existence of bilayers arranged in vesicles in RTILs would be very exciting, open several new possibilities as reaction media, and increase our understanding of the physical and chemical factors for self-assembling systems in RTILs.

Introduction

Self-assembled supramolecular nanostructures constructed from various types of amphiphiles have recently received a great deal of attention.[1] The amphiphiles studied include traditional surfactants,[2] block copolymers,[3] fullerene-modified derivatives such as water-soluble penta-substituted fullerene potassium salt,[4] and the mixture of traditional surfactants/fullerene-modified derivatives,[5] and even fully hydrophilic inorganic giant ions such as polyoxometalates.[6] Solvents for this work used include water and supercritical carbon dioxide ($scCO_2$).[7] In water, amphiphilic aggregates, whose formation is driven by mainly hydrophobic forces, have been abundantly investigated.[1] Different types of stable aggregates with controlled size distribution and well-defined shapes such as spherical, wormlike or rodlike micelles, unilamellar and multilamellar vesicles,[1,8–11] and recently disk-like micelles[12] and regular hollow icosahedra[13] in dilute salt-free cationic/anionic surfactant solutions have been observed.

Even though surfactants have been extensively used to broaden the application ranges for $scCO_2$,[7,14] scarcely any work concerning surfactant aggregates in ionic liquids has been reported despite recent primary observations.[15] In the last few years, interest in the properties of room-temperature ionic liquids (RTILs) has increased considerably. RTILs have been used as clean solutions and catalysts for green chemistry and as electrolytes for batteries, in photochemistry, and in electrosynthesis because of their novel properties such as negligible vapor pressure and the fact that volatile organic components are not created during their reactions. RTILs have also been shown to be potentially excellent lubricants by us.[16] However, little is known about surfactant aggregation behavior in RTILs.

Very recently, we reported Zn^{2+}-induced vesicle formation[17] by Zn^{2+}-ligand complexation between the anionic surfactant zinc 2,2-dihydroperfluoroctanoate [Zn(OOC-$CH_2C_6F_{13}$)$_2$] and the zwitterionic surfactant tetradecyldimethylamine oxide (C_{14}DMAO) in aqueous solutions. By simply mixing C_{14}DMAO and Zn(OOCCH$_2$C$_6$F$_{13}$)$_2$, we prepared a Lα-phase with unilamellar and multilamellar vesicles in aqueous solutions and attempted to provide a new method for preparing nanoscale semiconductor ZnS particles by means of a vesicle template.[17,18]

We have placed self-assembling systems in ionic liquids, and we report herein on the first self-assembled surfactant vesicles formed by Zn(OOCCH$_2$C$_6$F$_{13}$)$_2$ alone or by mixtures of C_{14}DMAO and Zn(OOCCH$_2$C$_6$F$_{13}$)$_2$. The two common RTILs **I** and **II** were used and these RTILs are slightly

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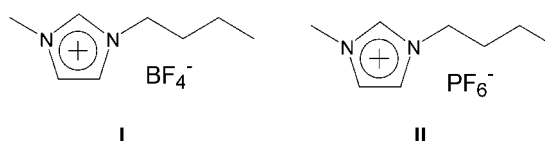
yellow and display low viscosity at room temperature. The resulting surfactant self-assemblies in the ionic liquids were characterized by negative staining transmission electron microscopy (TEM) and freeze-fracture TEM (FF-TEM) observations, small-angle X-ray scattering (SAXS), and rheological measurements. ZnS particles were obtained with the spherical and regular hexahedral structure of ZnS crystalline samples prepared by a flow of H_2S gas into vesicles in ionic liquids.

Results and Discussion

Vesicles determined by TEM and SAXS: In comparison with the considerable number of investigations of self-assembled structures of amphiphilic compounds in aqueous solutions, only a few reports of nanostructures for surfactants in ionic liquids have appeared.[15] Such nanostructures are in thermodynamic equilibrium (the samples do not change their appearance with time for more than four weeks). It is hoped that studies of such self-assembled surfactant nanospheres will increase our understanding of the physical and chemical factors that determine the self-assembly of surfactants in ionic liquids and open new ways for exploiting the wider applications of ionic liquids, particularly in chemical processes where hazardous solvents are replaced by green solvents.

$Zn(OOCCH_2C_6F_{13})_2$ has a high surface activity but is almost insoluble in water even above 70°C. However, $Zn(OOCCH_2C_6F_{13})_2$ can easily be dissolved in RTILs by heating the sample to 70–75°C under agitation. The slightly yellow and mildly viscous RTILs become transparent puce-colored viscoelastic solutions. Equilibration at 25°C for four months showed no visible change of the solutions (Figure 1a). We were surprised by the transparent puce-color of
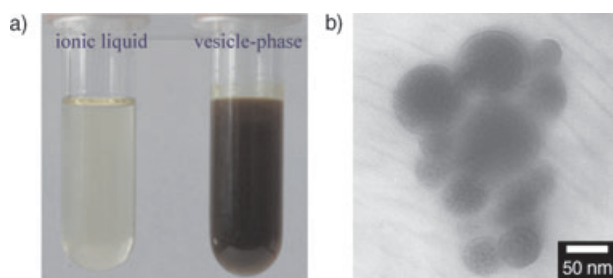
$Zn(OOCCH_2C_6F_{13})_2$ in ionic liquids to try to establish the nature of the impurity of $Zn(OOCCH_2C_6F_{13})_2$. $Zn(OOCCH_2C_6F_{13})_2$ is sparingly soluble in water or chloroform but is much more soluble in acetone and ethanol. In the latter two solvents, we observed transparent, colorless, low viscous solutions, suggesting that the purity of the sample of $Zn(OOCCH_2C_6F_{13})_2$ was very high ($>99\%$), which thus suggested that the origin of the color was not associated with an impurity. The phenomenon of colored solutions from fluorous ionic liquids functioning as surfactants in conventional room-temperature ionic liquids was also observed by Davis and co-workers.[19] In accord with their findings, we thus considered that the presence of the Zn^{2+}–fluorous surfactant in the conventional IL phase is responsible for the observed puce color, but the basis of the origin of the color is unclear. Investigations to address this issue and other facets of the chemistry of fluorous surfactants in ionic liquids, such as the phase behavior, are in progress in our laboratory, and will be reported in due course.

Preliminary measurements showed that $Zn(OOCCH_2C_6F_{13})_2$ reduces the surface tension (γ) in a manner analogous to aqueous surfactant solutions. The decrease in γ and color change might indicate that $Zn(OOCCH_2C_6F_{13})_2$ molecules can adsorb at the surface of ionic liquids and that the ionic liquid forms solvatophobic interactions with the hydrocarbon or fluorocarbon portion of $Zn(OOCCH_2C_6F_{13})_2$. Well-defined self-assembled surfactant bilayer vesicles in the ionic liquids were identified by negative-staining TEM. As shown in Figure 1b, the well-defined bilayer vesicles are clearly visible and the diameters of the nanospheres range from about 30 to more than 90 nm.

To investigate vesicle formation for the same system in water,[17] we prepared the sample by mixing $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ with a $\chi_{C_6F_{13}CH_2COO^-} = 0.18$ in **II**. The same transparent deep puce color and viscoelastic solutions were also obtained, which indicates that the mixed solutions of $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ in ionic liquids display the same self-assembled aggregation behavior as $Zn(OOCCH_2C_6F_{13})_2$ in ionic liquids. The sample was examined by negative-staining TEM and FF-TEM (Figure 2). Nanospheres similar to those in Figure 1b were observed with diameters of about 20 to 150 nm, and multilamellar
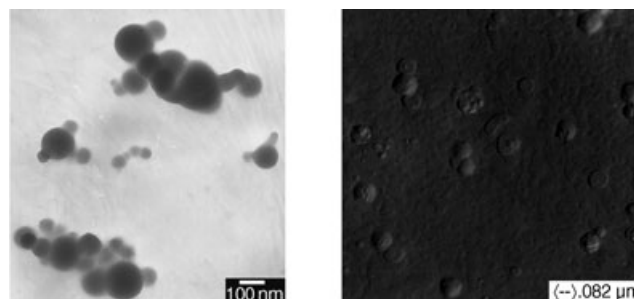

Figure 1. a) RTIL **I** (left sample, slightly yellow) and $Zn(OOCCH_2C_6F_{13})_2$ in **I** (right sample, transparent deep puce color); b) a typical negative-staining TEM image of the self-assembled surfactant bilayer vesicles of $Zn(OOCCH_2C_6F_{13})_2$ in **I**, phosphotungstic acid was used as the negatively charged dye.

the solutions. Initially, we speculated that the color was attributed to an impurity of the $Zn(OOCCH_2C_6F_{13})_2$. Thus, we did some experiments and characterization such as elemental analysis, solubility measurements in different solvents, and the determination of the phase behavior of

Figure 2. Negative-staining (left) and freeze-fracture (right) TEM images of self-assembled surfactant nanospheres of $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ in **II**. Phosphotungstic acid was used as the negative charged dye.

vesicles were visible in the FF-TEM image. Clusters of nanospheres could also be seen in the negative-staining TEM image.

Small-angle X-ray scattering (SAXS) profiles of $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ and $Zn(OOCCH_2C_6F_{13})_2$ in ionic liquids (Figure 3) also clearly demonstrate the forma-
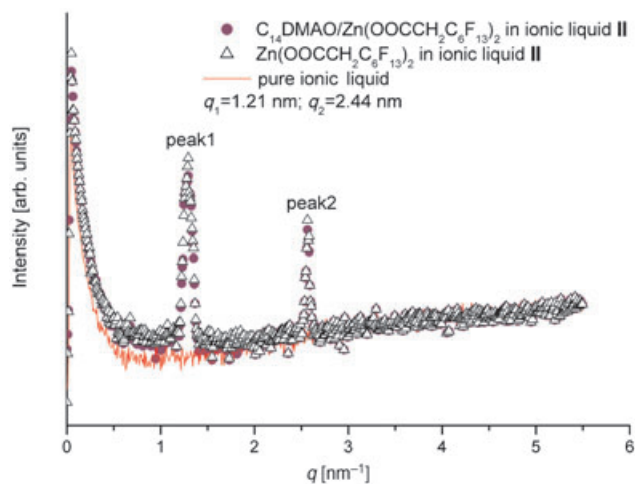

Figure 3. Small-angle X-ray scattering curves of the $C_{14}DMAO$ (100 mM)/$Zn(OOCCH_2C_6F_{13})_2$ (11 mM) mixture and $Zn(OOCCH_2C_6F_{13})_2$ (11 mM) alone in ionic liquid **II**. The scattering peaks for both systems can be indexed as a bilayer lamellar structure, but no scattering peaks for the ionic liquids were observed.

tion of lamellar aggregate structures. Both the systems have the same scattering curves with two scattering peaks at $q = 1.21$ and 2.44 nm^{-1}, which correspond to the 001 and 002 planes of a layered structure. A d spacing distance ($2\pi/q_{max}$) of 5.19 nm was obtained. The calculated length of the two surfactant molecules is about 2.70 nm,[20] indicating the d spacing of 5.19 nm includes a polar layer containing ionic liquid. Such a bilayer structure has been commonly observed in mixtures of polyelectrolyte/surfactant complexes[21] and cationic/anionic surfactant systems;[1,8] however, hardly any observations have been reported about such a bilayer structure for surfactant mixtures in ionic liquids.[15]

Macroproperties of the vesicle-phase and preparation of ZnS precipitates by using the vesicle-phase as the reaction medium: The macroproperties of $Zn(OOCCH_2C_6F_{13})_2/C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ ionic liquid solutions were characterized by rheological measurements of the oscillatory shear. Two typical rheograms of the oscillatory shear for two samples of 100 mM $C_{14}DMAO$/11 mM $Zn(OOCCH_2C_6F_{13})_2$ ($\chi_{C_6F_{13}CH_2COO^-} = 0.18$) and 11 mM $Zn(OOCCH_2C_6F_{13})_2$ in ionic liquid **II** at $25.0 \pm 0.1\,°C$ are shown in Figure 4. The rheograms of the two samples display the typical characteristics for solutions consisting of vesicles, and phase behavior similar to that for the same surfactant composition but with charged surfactant vesicle phases in aqueous solutions.[11,17] Both moduli are nearly fre-
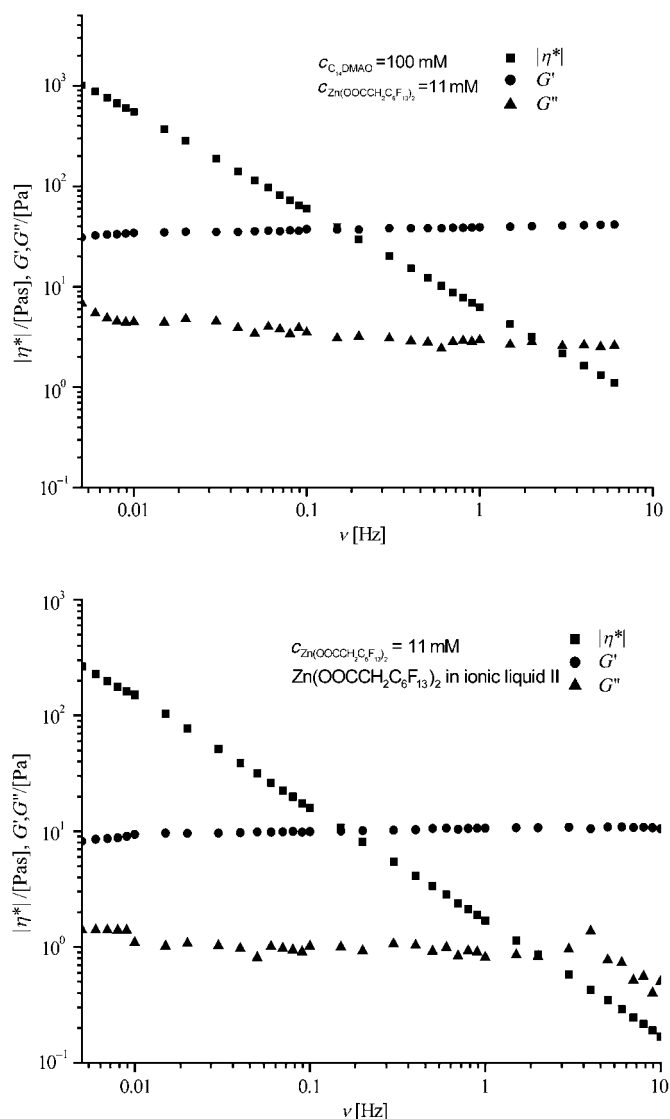

Figure 4. Rheograms for the $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ mixture (top) and $Zn(OOCCH_2C_6F_{13})_2$ alone (bottom) in ionic liquid **II**. Plots of the storage modulus G', loss modulus G'', and complex vesicosity $|\eta^*|$ as a function of the angular frequency. $T = 25.0 \pm 0.1\,°C$.

quency-independent in the $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ and $Zn(OOCCH_2C_6F_{13})_2$ systems. For the $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ system, the storage modulus with $G' \approx 40$ Pa, is about one order of magnitude higher than the loss modulus with $G'' \approx 4.0$ Pa. For the $Zn(OOCCH_2C_6F_{13})_2$ system, $G' \approx 10$ Pa and $G'' \approx 1.0$ Pa. The complex viscosity ($|\eta^*|$) values linearly decrease over the whole frequency range from 0.005 to 10 Hz; the slope is -1 for the two systems. Comparing the two rheograms, one can see that the G', G'', and $|\eta^*|$ values in the $Zn(OOCCH_2C_6F_{13})_2$ system are much lower than those in the $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ system.

The rheological variation from the low viscosity of the ionic liquids to the viscoelastic fluid of surfactants in ionic liquids demonstrates that the solutions are highly viscoelas-

tic, have high yield stress values, and therefore behave like Bingham fluids—typical properties of vesicle solutions.[11,17] Conductivity measurements of the aggregate solutions show that the conductivity values do not significantly change for the aggregate solutions compared with the ionic liquids (**I** and **II** have $\kappa \approx 3.8$ and $\approx 1.8 \, mS \, cm^{-1}$, respectively). Both samples of 11 mM $Zn(OOCCH_2C_6F_{13})_2$ or 100 mM $C_{14}DMAO/11$ mM $Zn(OOCCH_2C_6F_{13})_2$ in ionic liquid **I** have the same value, $\kappa \approx 3.8 \, mS \, cm^{-1}$, which demonstrates that the ionic liquid is the continuous phase and that the ionic surfactant makes no contribution to the conductivity.

The first aim of the present study was to prepare self-assembled nanostructures formed by surfactants in ionic liquids, which should open up several new possibilities as reaction media. The second aim, and why we chose $Zn(OOCCH_2C_6F_{13})_2$ as an organozinc precursor in ionic liquids, was provide a route to synthesize nanoscale semiconductor ZnS particles with an S source. ZnS particles were obtained by allowing H_2S gas to flow at room temperature into $Zn(OOCCH_2C_6F_{13})_2$ and $C_{14}DMAO$ bilayer vesicle solutions prepared in ionic liquids. In this reaction, when H_2S gas is injected into the $Zn(OOCCH_2C_6F_{13})_2$ and $C_{14}DMAO$ mixed solutions, Zn^{2+} is precipitated by H_2S to form nanoscale semiconductor ZnS particles. After H_2S gas was injected into the $Zn(OOCCH_2C_6F_{13})_2$ and $C_{14}DMAO$ bilayer vesicle solutions (24 h), stable transparent puce-colored viscoelastic solutions were obtained.

The spherical and regularly hexahedral re-united structures of crystalline ZnS are clearly visible in the TEM images of the resulting ZnS particles (Figure 5). We will not

behaves as a solvophilic group. Taken together these then would provide the driving force to form the nanostructures through weak attractive intermolecular interactions such as dipole–dipole and van der Waals forces. However, the ionic groups could also display strong electrostatic interactions between the ionic liquids and the surfactants, and the mechanism of the self-assembly of surfactant nanostructures in ionic liquids merits further discussion.[19] Thus, the formation of the mixed complex is not essential for the assembly. However, we would like to confirm that the phase behavior of $Zn(OOCCH_2C_6F_{13})_2$ alone differs from that of the mixture of $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ in ionic liquids. This should be compared with the results of $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ in water,[17] in which we did not find the self-assembled structure for $Zn(OOCCH_2C_6F_{13})_2$ alone.

Conclusion

Herein we report the self-assembly of stable surfactant nanospheres from a Zn^{2+}–fluorous surfactant, which should open unique opportunities to design nanoscale architectures in green solvents. Such nanostructures are interesting not only from the standpoint of the assembly of advanced materials and environmental concerns, but also may be useful in applications in nanoscience such as the present synthesis of semiconductor ZnS particles and in formulations for the pharmaceutical, personal care, or household products, and even ultimately as drug and gene delivery systems.

Experimental Section

Figure 5. TEM images showing the spherical and regularly hexahedral re-united ZnS masses obtained from $Zn(OOCCH_2C_6F_{13})_2$ and $C_{14}DMAO$ bilayer vesicle ionic liquid solutions on injecting H_2S. Some regularly hexahedral re-united masses were visible and marked by hexagons.

discuss controlling the size and morphology of ZnS particles by the present synthesis route, because it is clear that neither the size nor the shape of the original vesicles is preserved.

The most noteworthy phenomenon is that the water-insoluble surfactant, $Zn(OOCCH_2C_6F_{13})_2$, is highly soluble in ionic liquids and forms self-assembled supramolecular nanostructures. A tempting explanation is to assume that the zinc moiety of $Zn(OOCCH_2C_6F_{13})_2$ or the zinc complex moiety of $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ may act as a solvophobic group, whereas the hydro- and fluorocarbon part of $Zn(OOCCH_2C_6F_{13})_2$ or $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$

Methods: The required amount of $Zn(OOCCH_2C_6F_{13})_2$ only or mixed with $C_{14}DMAO$ was added to the ionic liquid. The samples were prepared at 70 °C under stirring and then thermostated at 25 °C for equilibrium (4 months). Very stable, transparent deep puce-colored solutions were obtained.

For the negative-staining TEM images, about 4 μL of the ionic liquid solution was transferred onto a TEM grid (copper grid, 3.02 mm, 200 mesh, coated with Formvar film) and stained with 2% phosphotungstic acid. After drying the solution by using a filter paper in air, negative-staining TEM images were recorded on a CEM 902 electron microscope (Zeiss, Germany) operating at an accelerating voltage of 80 kV. For the FF-TEM images, about 4 μL of the sample solution was placed on a 0.1-mm thick copper disk and covered with a second copper disk. The copper sandwich with the sample was frozen by plunging this sandwich into
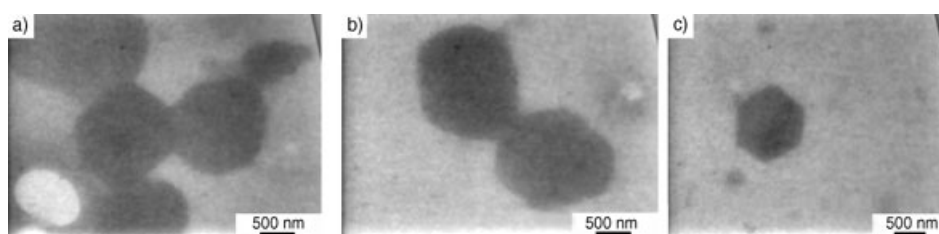
liquid propane which had been cooled with liquid nitrogen. For fracturing and replication, a freeze-fracture apparatus (Balzer BAF 400, Germany) was used at a temperature of $-140\,°C$. Pt/C was deposited at a $45°$ angle. The samples were examined with a Zeiss CEM 902.

Small-angle X-ray scattering (SAXS) measurements were carried out at room temperature on a modified Kratky compact camera. The evacuated camera was mounted on a sealed X-ray tube equipped with a copper target. The scattering intensities were measured with a linear position-sensitive, gas-filled detector (Mbraun, Germany) by monitoring the scattering curves in the q range ($q = 4\pi/\lambda \sin\theta/2$, θ is the scattering angle and λ is the wavelength of the radiation). The sample solutions were injected into a 1-mm diameter quartz capillary mounted in a steel cuvette. The data collection time for each scattering curve was about 15 h.

The rheological measurements were carried out with a Bohlin CS 10 stress-controlled rheometer using a cone plate measuring system and a double gap system. The lowest possible stress value was about 3 mPa. The viscoelastic properties of $C_{14}DMAO/Zn(OOCCH_2C_6F_{13})_2$ and $Zn(OOCCH_2C_6F_{13})_2$ alone vesicle-phase samples were determined from the oscillatory measurements from 0.001 to 10 Hz, whereby alternatively the strain amplitude or the stress amplitude were kept constant.

For the TEM images of the ZnS particles, a drop of the resulting transparent puce-colored viscoelastic solution of the ZnS particles was placed on a carbon-coated, Formvar-covered TEM grid (copper grid, 3.02 mm, 200 mesh) and subsequently the excess solution was drawn off. The grids were then examined by using a JEOL 100CX-II transmission electron microscope operating at 100 kV.

Acknowledgements

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