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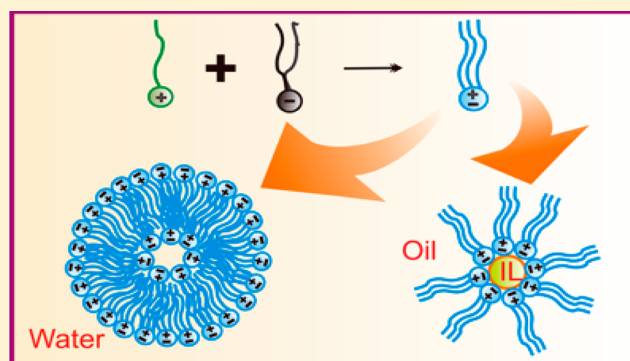
Unique Characteristics of Ionic Liquids Comprised of Long-Chain Cations and Anions: A New Physical Insight

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S Supporting Information

ABSTRACT: We have designed a unique class of surface active ionic liquids (SAILs) and utilized them to prepare IL-in-oil microemulsions as well as large unilamellar vesicles (LUVs). The IL-in-oil microemulsions were characterized by a phase behavior study, regular swelling behavior, and also by spectral shift of coumarin-480 probe molecules. The LUVs were characterized by dynamic light scattering and transmission electron microscope measurements. Our work opens up the possibility of creating a huge number of IL-in-oil microemulsions as well as LUVs simply by replacing the cation of NaAOT with a long chain cation.



1. INTRODUCTION

Room temperature ionic liquids (RTILs) have attracted much attention as a class of solvents because of their special physical and chemical properties (such as nonflammability, low volatility, and high thermal stability) and a wide range of potential applications in chemical synthesis, industrial processing, and energy storage.¹ Their unique properties and the rising necessity of sustainable, “green” chemistry have also led to an unparalleled increase in interest in such salts. RTILs are organic salts composed entirely of ions, and unlike the common organic salts, which melt at high temperatures, these salts melt at considerable low temperature, primarily due to the presence of sterically mismatched ions.^{2–4} The most popular cationic components of the RTILs are substituted imidazolium ions, while $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, and $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ are most frequently used as anionic components. Because the properties of RTILs are very much dependent on their constituent ions, it is possible to obtain a RTIL of a desired property by tuning the cationic and anionic constituents; such liquids are called “designer solvents”.^{5,6}

Microemulsions are spatially ordered and thermodynamically stable macromolecular assembly formed by two or more immiscible liquids, which are stabilized by surfactants. These microheterogeneous systems can solubilize both polar and nonpolar substances and have been applied to many fields: for chemical reaction, nanomaterial synthesis, and several organic transformations.^{7–13} The idea behind microemulsion is simple and straightforward; long-chain amphiphilic molecules (whose one end is polar and other end is nonpolar), generally called the surfactant molecules, are dissolved in a nonpolar solvent within a certain concentration range. The polar end of the amphiphilic surfactant tries to shade them from the unfavorable nonpolar

solvent interaction. As a result, they can form an aggregated structure where all the polar ends directed toward the core of the aggregates. In the last few decades a lot of studies have been performed to reveal the structure as well as the biological importance of the confined water in the pool of microemulsion. Nowadays, room-temperature ionic liquids (RTILs) are also being used as a polar solvent because they constitute “green” substituents to classic (volatile) organic solvents. The structure of microemulsions is a field of current interest. To study ionic liquid microemulsions, it is necessary to investigate the structure of the microemulsion. In particular, the research into IL-containing nonaqueous microemulsions was motivated by the fact that, in spite of the useful properties of ILs, poor solubility of nonpolar solutes in neat ILs was a major hindrance in the path of their potential applications. This can be overcome using the hydrocarbon domains provided by IL-in-oil microemulsions.^{14,15} The thermal stability of such a system over aqueous microemulsions is another important factor.¹⁶ Gao et al.¹⁷ first reported the formation of IL-in-oil microemulsions in $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{cyclohexane}$ system. The size and shape of these microemulsions were verified from SANS studies by Eastoe et al.,¹⁸ where regular swelling behavior with the addition of the IL was also observed, implying that the volume of dispersed nanodomains was proportional to the amount of IL added. Following this, several other reports on similar types of systems are available in the literature.^{19–24} From these it is evident that cyclohexane and benzene are commonly used nonpolar solvents. But the problems associated

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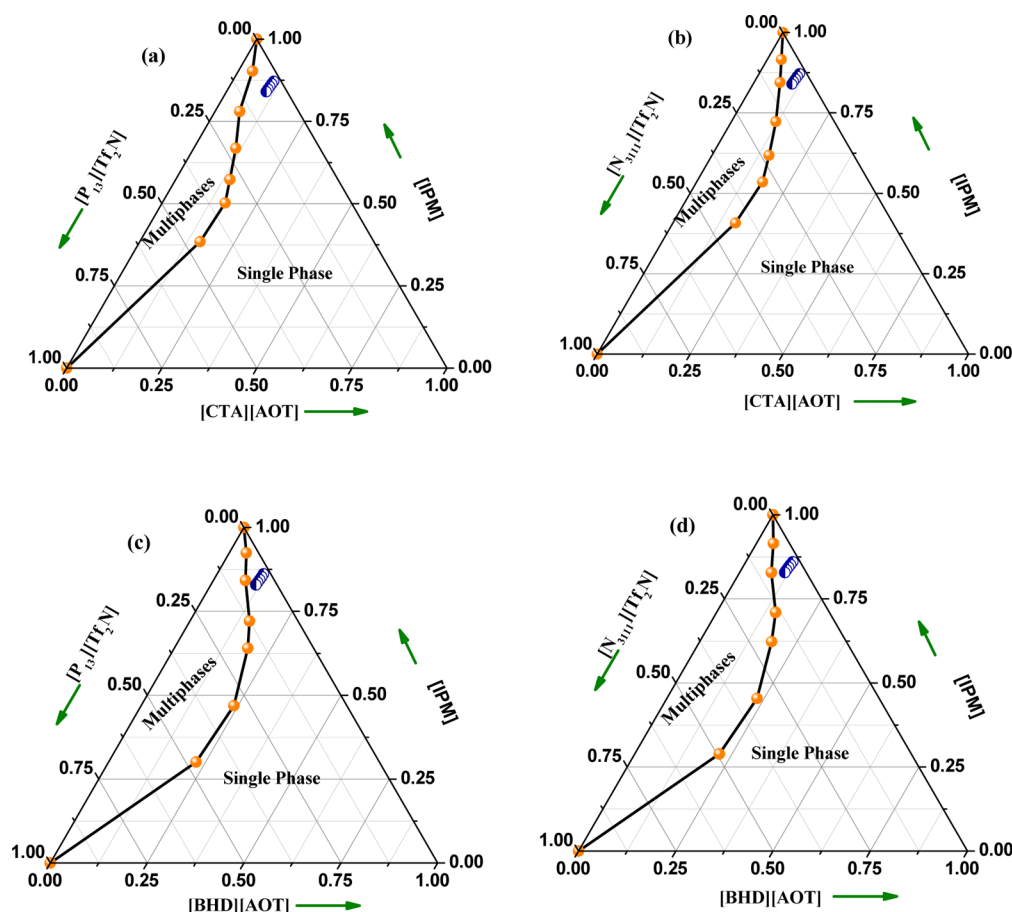


Figure 1. Phase diagram of (a) $[P_{13}][Tf_2N]/[CTA][AOT]/[IPM]$, (b) $[N_{3111}][Tf_2N]/[CTA][AOT]/[IPM]$, (c) $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$, and (d) $[N_{3111}][Tf_2N]/[BHD][AOT]/[IPM]$ ternary systems at 298 K.

with these solvents lie in the fact that they are not environment friendly and, due to their low boiling point microemulsions, are not stable at higher temperature (340–350 K). Recently, attempts have been made to construct microemulsions comprising the pharmaceutically acceptable components Tween-80/butyl lactate/isopropyl myristate (IPM)/water.^{25–28} In the present scheme of work, we used IPM instead of cyclohexane or benzene, as a nonpolar solvent due to its biocompatibility along with higher boiling point.

It is known that the mixtures of surfactants can exhibit considerable synergistic advantages in their properties as well as applications.²⁹ Sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT, AOT) or Docusate sodium is the most commonly used surfactant for reverse micelles preparation.³⁰ It is proposed that, due to the existence of favorable molecular interactions between the inorganic cations of AOT (Na^+ , NH_4^+ , Ca^{2+} , etc.) and water molecules, the formation of water-in-oil microemulsions is possible, and consequently, IL-in-oil microemulsion formation is not possible due to the absence of such favorable interactions. With these ideas, in our previous work, we have synthesized surface active ionic liquid (SAIL), $[C_4mim][AOT]$ by an anion exchange reaction between NaAOT and 1-butyl-3-methylimidazolium bromide ($[C_4mim][Br]$) and we showed that a huge number of IL-in-oil microemulsions can be prepared just by replacing the inorganic cation, Na^+ of NaAOT, by any organic cation and using different ionic liquids as the polar core.³¹ Similar type of synthesis is also reported by Brown et al., where they prepared

a series of anionic surfactant ionic liquids including $[C_4mim][AOT]$ and showed that these compounds are more environmentally friendly and chemically tunable as compared to other common ILs.³² SAIL can be defined as functional ionic liquid with the combined properties of IL and surfactant; in other words, IL bearing long alkyl chains having amphiphilic character is named as SAILS.^{31,33,34} Inoue et al.³⁵ showed with evidence the existence of both lamellar (LR) and hexagonal (H1) lyotropic mesophases in mixture of the SAIL 1-dodecyl-3-methylimidazolium bromide and water over a concentration range of 10–50% (v/v), just like that for normal surfactants. After observing the surfactant-like behavior of the SAIL 1-hexadecyl-3-methylimidazolium chloride, $[C_{16}mim][Cl]$ in EAN, Zech et al. studied microemulsions of the type RTIL ($[C_4mim][BF_4]$ and EAN)/ $[C_{16}mim][Cl]$ /dodecane using conductivity, dynamic light scattering (DLS), and SAXS measurements.³⁶ The advantage associated to these ILs are they are more environmentally friendly compared to commercially other ILs.

Another interesting topic in this emerging field is to prepare large unilamellar vesicles (LUVs). Since Kaler reported the spontaneous formation of cationic and anionic (catanionic) single-tailed surfactant vesicles in aqueous solution,³⁷ a lot of work have been focused on bilayer membranes of catanionic surfactant systems.³⁸ In general, when a cationic surfactant solution and an anionic one are simply mixed, the strong reduction in area per headgroup resulting from ion pairing induces the formation of molecular bilayers at low concen-

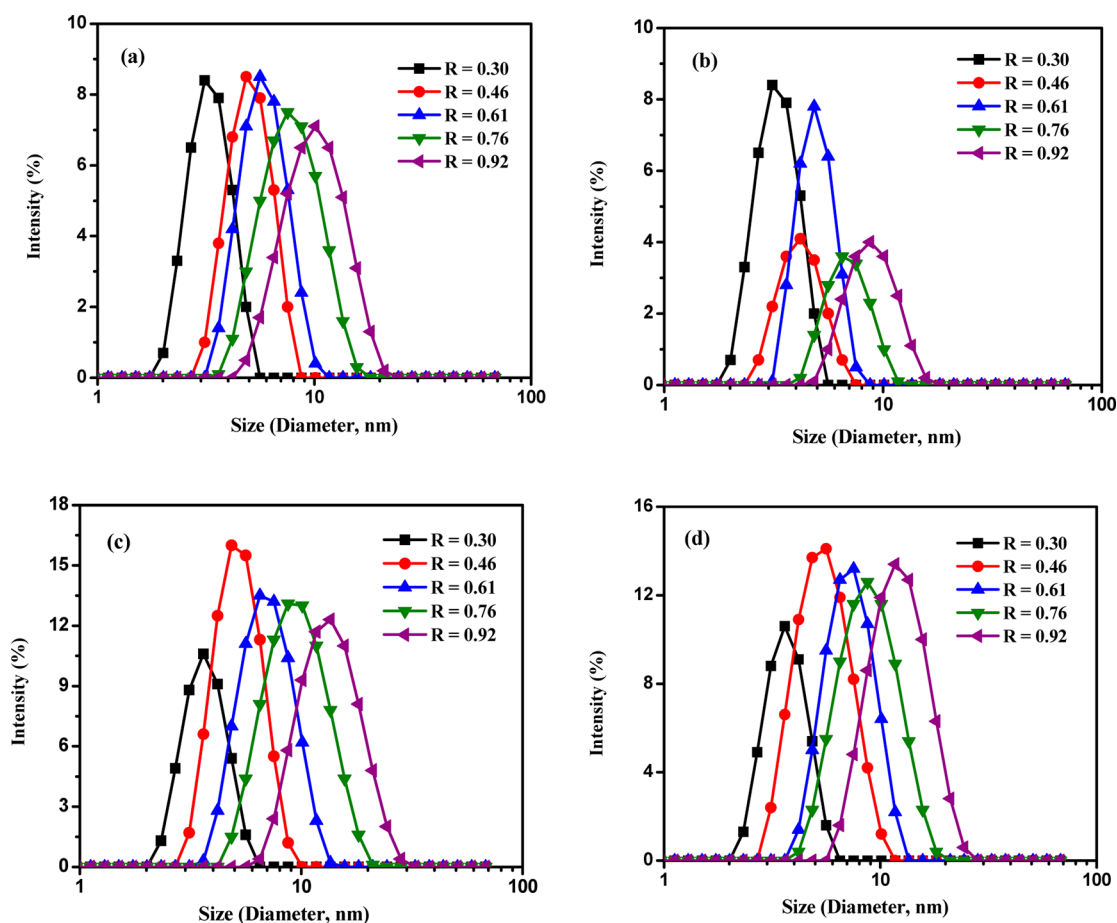


Figure 2. Size distribution of droplets (measured by dynamics light scattering study) of (a) $[P_{13}][\text{TF}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$, (b) $[\text{N}_{3111}][\text{TF}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$, (c) $[P_{13}][\text{TF}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$, (d) $[\text{N}_{3111}][\text{TF}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$ microemulsions with variation R values at 298 K.

trations. At the right mixing ratios, vesicles may be established spontaneously and are thermodynamically stable species.^{37–43} However, the formation of salt-free vesicles is still a challenging task.

To boost the present knowledge and to get more information about these complicated systems, we designed this present study. Our aim in this article is to synthesize such a class of SAIL, which can form IL-in-oil microemulsion as well as salt-free LUVs. Hence, we tried to replace the inorganic cation (Na^+) of AOT by a long chain cation, and finally, we successfully synthesized $[\text{CTA}][\text{AOT}]$ and $[\text{BHD}][\text{AOT}]$ by the replacement of Na^+ . In $[\text{CTA}][\text{AOT}]$, the cation of AOT has been replaced by cetyltrimethylammonium ion, and in $[\text{BHD}][\text{AOT}]$, the same cation is replaced by benzyl-*n*-hexadecyldimethylammonium ion, yielding a waxy solid IL in the former and a comparatively low viscous IL in the latter (the scheme is shown in Supporting Information, Scheme S1). The important thing that needs to be mentioned here is that our synthesized IL, $[\text{BHD}][\text{AOT}]$, is liquid at room temperature and $[\text{CTA}][\text{AOT}]$ is a waxy solid with melting point $80 (\pm 3)^\circ\text{C}$, that is, they fulfill the basic criterion to be called them IL (organic salts with melting point less than 100°C are ILs). Brown et al.⁶ also prepared catanionic surfactants by substitution of Na^+ of NaAOT with long-chain alkylammonium ion. Where they varied the alkyl chain from C4 to C10, however, in our system, we used C16 alkylammonium ion to prepare $[\text{CTA}][\text{AOT}]$. These systems show very different

properties from the original surfactants and studies on the properties of the self-assembled aggregates in aqueous as well as nonaqueous solutions formed with this kind of SAILs are scarce. This opens the door for further and deeper investigations on these interesting supramolecular self-assemblies. We hope this work will lead to a deeper understanding on microemulsion as well as LUVs and can extend the possibility of their practical applications in biological tests.

2. MATERIALS AND INSTRUMENTATION

Coumarin 480 (C-480; laser grade, Exciton), CTAB, and BHDC were purchased from Sigma-Aldrich. NaAOT (sodium 1,4-bis(2-ethylhexyl) sulfosuccinate, Sigma-Aldrich) was dried in vacuum for 30 h before use. Isopropyl myristate (IPM; SRL, India) was used as received. The ILs *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($[P_{13}][\text{TF}_2\text{N}]$) and *N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide ($[N_{3111}][\text{TF}_2\text{N}]$) were procured from Kanto Chemicals (purity > 98%), also used as received. All the structures are shown in Supporting Information (Scheme S2). The absorption and fluorescence spectra were collected using a Shimadzu (model no. UV-2450) spectrophotometer and a Hitachi (model no. F-7000) spectrofluorimeter, respectively, and the samples were excited at 375 nm for coumarin-480 probe molecules. For DLS measurements, we used a Malvern Nano ZS instrument employing a 4 mW He–Ne laser operating at a wavelength

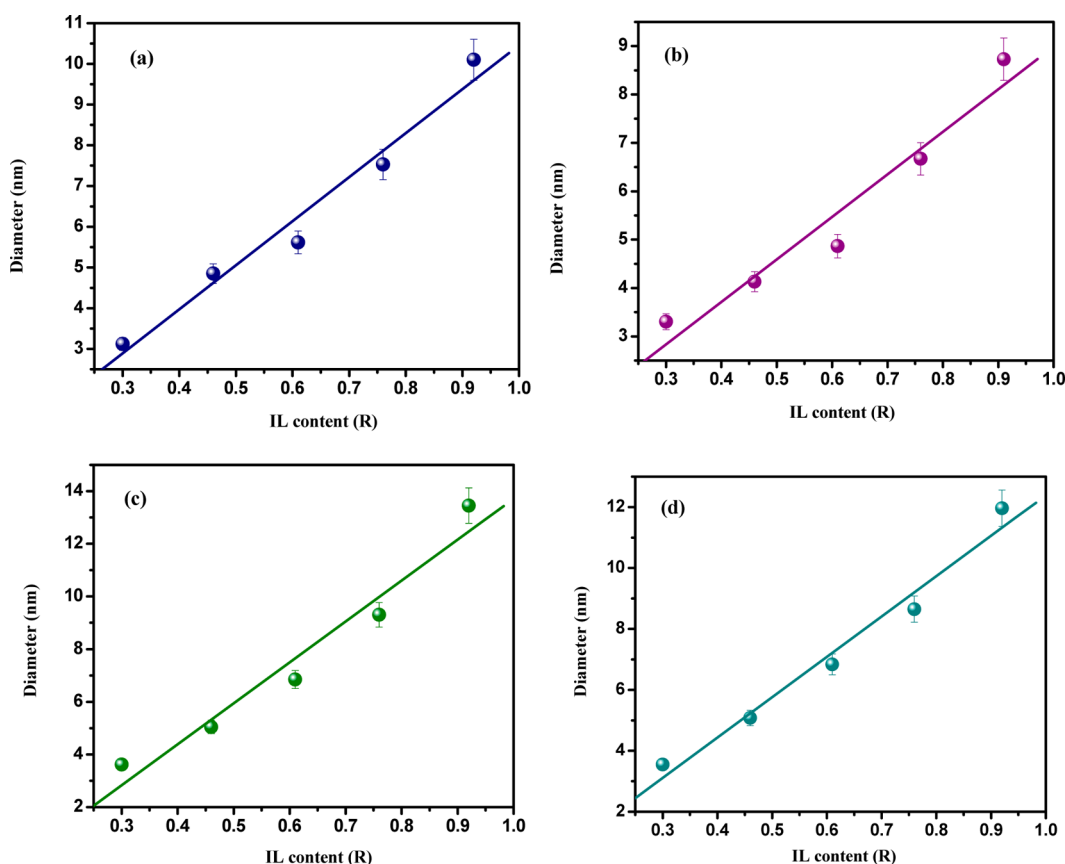


Figure 3. Diameters of droplets of (a) $[P_{13}][Tf_2N]/[CTA][AOT]/[IPM]$, (b) $[N_{3111}][Tf_2N]/[CTA][AOT]/[IPM]$, (c) $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$, and (d) $[N_{3111}][Tf_2N]/[BHD][AOT]/[IPM]$ microemulsions with different amounts of ILs at 298 K.

of 633 nm and an avalanche photodiode (APD) detector. All the experiments were performed at 298 K. The temperature was kept constant (298 K) by circulating water through the cell holder using a JEIO TECH Thermostat (RW-0525GS). TEM measurements were carried out with analytical TEM (FEI, TECNAIG220S-TWIN) instruments operating at 200 KV. Samples of TEM were prepared by blotting a carbon-coated (50 nm carbon film) Cu grid (300 mesh, Electron Microscopy Science) with a drop of vesicle solution in water and allowed to dry.

3. RESULTS AND DISCUSSION

We have characterized the partial phase behavior of the ternary systems $[P_{13}][Tf_2N]/[CTA][AOT]/[IPM]$, $[N_{3111}][Tf_2N]/[CTA][AOT]/[IPM]$, $[P_{13}][Tf_2N]/[BHD][AOT]/[IPM]$, and $[N_{3111}][Tf_2N]/[BHD][AOT]/[IPM]$, by observing the transition from clear transparent solution to turbid solution visually, that is, through the naked eye (Figure 1). In all the above-mentioned cases, $[P_{13}][Tf_2N]$ (*N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide) and $[N_{3111}][Tf_2N]$ (*N,N,N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)imide) are used as RTIL, which form the pool of the microemulsion, $[IPM]$ is used as a nonpolar solvent, and our synthesized SAILs ($[CTA][AOT]$ and $[BHD][AOT]$) are acting as a AOT-derived surfactants. It is evident from Figure 1 that a continuous stable single-phase microemulsion region can always be observed over the $[P_{13}][Tf_2N]$, $[N_{3111}][Tf_2N]$, or $[IPM]$ content range of 0–100% (wt).

The samples were also characterized by a DLS technique, a widely used and powerful technique to prove the existence of microemulsion.^{44,45} It is evident from previous studies that, if the IL is really encapsulated to form IL-in-oil microemulsions, the size of the droplets must increase regularly as the *R* value increases to a certain level.^{44–48} This regular swelling behavior is observed, which is consistent with the volume of dispersed nanodomains being directly proportional to the amount of added IL. This type of behavior is also common to many well established AOT stabilized water-in-oil systems. The regular increase in size of the droplets (linearly with increasing *R* value) clearly indicates that the IL microemulsions media consist of discrete spherical and noninteracting droplets of ILs in polar domain, which are stabilized by the surfactant within nonpolar environment.⁴⁸ Deviation from linearity could be observed due to several reasons, the most relevant ones being droplet–droplet interaction and shape of the microemulsions.⁴⁸ In our case, DLS studies revealed the formation of the IL-in-oil microemulsion in all four cases (Figure 2). In the case of $[P_{13}][Tf_2N]/[CTA][AOT]/[IPM]$ microemulsion, the droplet size (diameter) increased from 3.12 to 10.1 nm with increasing *R* values from 0.30 to 0.92 (here the *R* value implies the molar ratio of $[P_{13}][Tf_2N]$ to $[CTA][AOT]$). When we substituted the $[P_{13}][Tf_2N]$ by $[N_{3111}][Tf_2N]$, the increment in size was found to be comparatively less, with an increase from 3.30 to 8.73 nm with increment of *R* value from 0.30 to 0.92. The above two cases clearly indicate that the droplets showed regular swelling behavior with the addition of IL, $[P_{13}][Tf_2N]/[N_{3111}][Tf_2N]$ (Figure 2), suggesting the formation of IL-in-oil microemulsions. The swelling behavior is also observed in case

Table 1. Emission Maxima of C-480 in Different Systems

R values	system λ_{max} (emission, nm)			
	$[\text{P}_{13}][\text{Tf}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$	$[\text{N}_{3111}][\text{Tf}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$	$[\text{P}_{13}][\text{Tf}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$	$[\text{N}_{3111}][\text{Tf}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$
$R = 0$	432	432	433	433
$R = 0.30$	435	433	435	434
$R = 0.46$	437	434	436	436
$R = 0.61$	439	436	438	438
$R = 0.76$	441	437	441	440

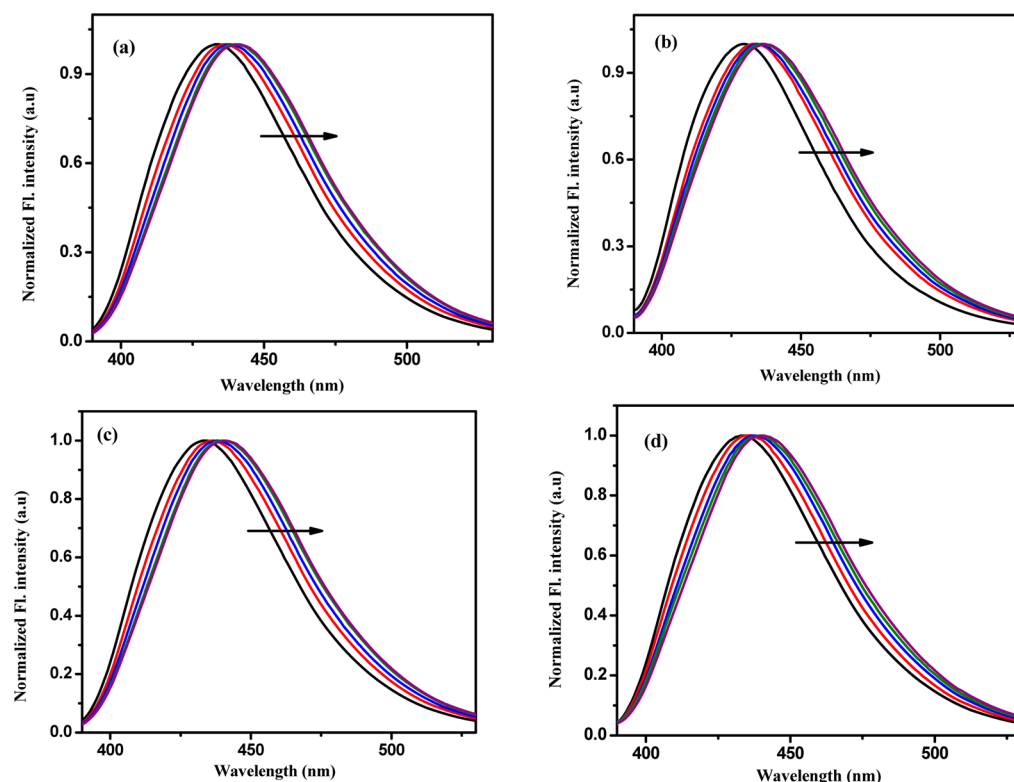


Figure 4. Normalize fluorescence spectra of C-480 in (a) $[\text{P}_{13}][\text{Tf}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$, (b) $[\text{N}_{3111}][\text{Tf}_2\text{N}]/[\text{CTA}][\text{AOT}]/[\text{IPM}]$, (c) $[\text{P}_{13}][\text{Tf}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$, and (d) $[\text{N}_{3111}][\text{Tf}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$ microemulsions with a variation of R values (0.30–0.76) at 298 K.

of $[\text{P}_{13}][\text{Tf}_2\text{N}]/[\text{BHD}][\text{AOT}]/[\text{IPM}]$ microemulsion, where the droplet size (diameter) increased from 3.61 to 13.45 nm with increasing R values from 0.30 to 0.92 (here the R value implies the molar ratio of $[\text{P}_{13}][\text{Tf}_2\text{N}]$ to $[\text{BHD}][\text{AOT}]$). After substitution of $[\text{P}_{13}][\text{Tf}_2\text{N}]$ by $[\text{N}_{3111}][\text{Tf}_2\text{N}]$, the increment of the droplet size is comparatively smaller, which is consistent with the previous case. The droplet size increased from 3.55 to 11.96 nm with the same increment of R values. In all the cases, we observed almost linear variations of size with variation of R values, implying the formation of spherical droplets (Figure 3). The little deviation from linearity may be attributed to the increased droplet–droplet interaction at higher R values.

To further support the concept of formation of IL pools in the IL-in-oil microemulsions, we have used coumarin-480 (C-480) as a probe molecule. It is also sensitive to the local environment and the emission maximum increases with the polarity of the environment. In recent years our group has used C-480 for the characterization of different IL-in-oil microemulsions.^{44,45} Owing to these studies, we can say that the red shift in emission maximum of C-480 with gradual addition of ILs is a clear indication of the existence of IL-in-oil

microemulsions. In neat IPM, C-480 shows emission maximum at 425 nm and with the addition of $[\text{CTA}][\text{AOT}]$ and $[\text{BHD}][\text{AOT}]$ the emission maximum gets shifted to 432 and 433 nm (Table 1). This marked red shift of emission maxima (7–8 nm) clearly indicates the transfer of the probe molecule from bulk IPM to the polar interior of the $[\text{CTA}][\text{AOT}]$ and $[\text{BHD}][\text{AOT}]$ reverse micelle. Further addition of ILs $[\text{P}_{13}][\text{Tf}_2\text{N}]$ and $[\text{N}_{3111}][\text{Tf}_2\text{N}]$ to $[\text{CTA}][\text{AOT}]/[\text{IPM}]$ reverse micelles causes red shift in the emission maxima. With an increase in ionic liquid content from $R = 0.30$ to 0.76, the emission maxima is red-shifted from 435 to 441 nm (Figure 4, Table 1) for $[\text{P}_{13}][\text{Tf}_2\text{N}]$ and the same value changed from 433 to 437 nm in the case of $[\text{N}_{3111}][\text{Tf}_2\text{N}]$. We also measured the red-shift for the other microemulsion, that is, $[\text{BHD}][\text{AOT}]/[\text{IPM}]$, and found that, with an increase in ionic liquid content from $R = 0.30$ to 0.76, the emission maxima is red-shifted from 435 to 441 nm (Figure 4, Table 1) for $[\text{P}_{13}][\text{Tf}_2\text{N}]$, while the same value changed from 434 to 440 nm in the case of $[\text{N}_{3111}][\text{Tf}_2\text{N}]$. The gradual red shift of emission maxima with the addition of $[\text{P}_{13}][\text{Tf}_2\text{N}]$ and $[\text{N}_{3111}][\text{Tf}_2\text{N}]$ clearly indicates the movement of probe

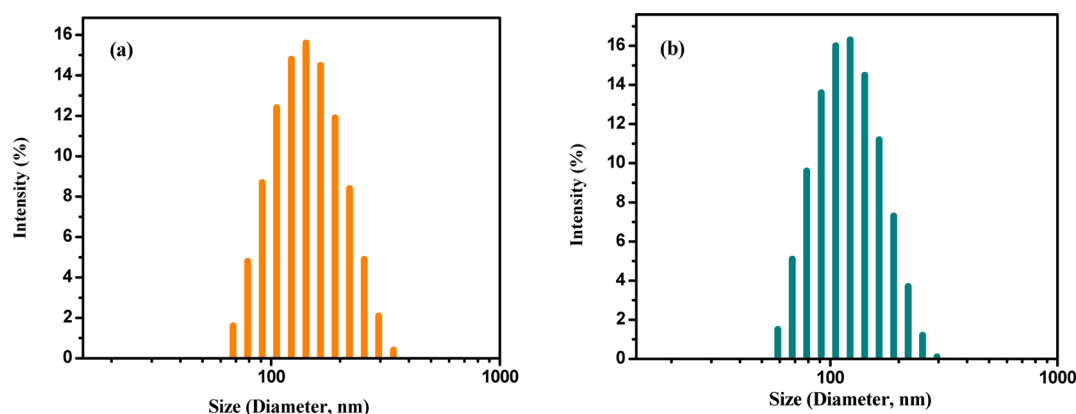


Figure 5. DLS size distribution plots of vesicles formed by (a) [CTA][AOT] and (b) [BHD][AOT] ILs in water at 298 K.

molecules toward the polar IL pool of the microemulsions. The partition of these long chain SAILs at the interface is still unknown and it required a lot of work to reveal the exact structure of these microemulsions, which is also a field of current interest.

Now the most stimulating motive in this article is to examine the property of the synthesized surfactant in water. First, we studied the properties of [CTA][AOT] in water and found that, when it was dissolved in water, an opalescent solution was obtained, which was stable for more than a month. Hence, the possibility of the formation of vesicle was not ignored. Based on these observations, we followed the vesicle formation steps.^{49,50} The synthesis procedure is given in the Supporting Information. We then undertook the DLS measurement and observed that the size (diameter) of the aggregate is around 150 nm, which is nearly unchanged with the variation of concentration of [CTA][AOT]. It is a well-known characteristic of the vesicles that the size of the vesicles at low concentration of [CTA][AOT] should not change compared with the size obtained at higher concentration of [CTA][AOT]. During the size measurement experiment, another notable observation was that we obtained a very low polydispersity index (PDI) with variation of [CTA][AOT]. This is a clear manifestation of the formation of unilamellar vesicles. Following these initial observations, we carried out the TEM measurement to confirm the vesicles formation. The TEM pictures are shown in Figure 6. The TEM picture validates our approach, that is, the formation of the unilamellar vesicles occurs when [CTA][AOT] is dissolved in water. However, we obtained relatively larger vesicles (200–300 nm) compared to the size obtained from the DLS experiment (151

nm, Figure 5). This could be due to fusion of the unilamellar vesicles on the TEM grid during the drying procedure. The fusion of the vesicles is also shown in Supporting Information (Figure S3). After obtaining the unilamellar vesicles with [CTA][AOT], we repeated the same experiments with another synthesized IL, [BHD][AOT], and found similar observations with [CTA][AOT]. The size of the vesicle obtained from the DLS experiment was 120 nm (Figure 5), but after the analysis of the TEM picture, we obtained the average size of the vesicles, which was nearly 150–200 nm. This also supports the fusion mechanism we proposed in the previous case.

4. CONCLUSION

In conclusion, a new type of SAILs ([CTA][AOT]/[BHD]-[AOT]) was synthesized from three commercially available traditional surfactants, CTAB, NaAOT, and BHDC. The ILs obtained by the ion-exchange reaction not only form an IL-in-oil microemulsion, but also form a unilamellar vesicle. By using these SAILs, there are possibilities to synthesize a huge number of IL-in-oil microemulsions like our earlier study.³¹ We have characterized [P₁₃][Tf₂N]/[CTA][AOT]/[IPM], [N₃₁₁₁][Tf₂N]/[CTA][AOT]/[IPM], [P₁₃][Tf₂N]/[BHD][AOT]/[IPM], and [N₃₁₁₁][Tf₂N]/[BHD][AOT]/[IPM] microemulsions and showed that the polarity of ILs pooled inside the microemulsion is less compared with neat ILs. Our work opens up the potential of creating a huge number of IL-in-oil microemulsions simply by replacing the inorganic cation, Na⁺ of NaAOT, with any long chain cation and using different ionic liquids as the polar core. Our synthesized ILs are not only efficient to form IL-in-oil microemulsion, but they also have the ability to form LUVs spontaneously. This is a very interesting and novel finding, as these types of aggregates are well-known drug carriers, which is a field that is being currently investigated. We believe our present findings will stimulate interest because of the new exciting SAILs presented. The unique capacity of the new SAILs, [CTA][AOT] or [BHD][AOT], to form different stable organized media, depending on the surrounding solvents, microemulsion in IPM and spontaneous LUVs in water, may make a significant impact on surfactant and IL research. Also, these aggregates have the potential to serve as good biomimicry models to study various processes occurring in biological molecules embedded in biomembranes.

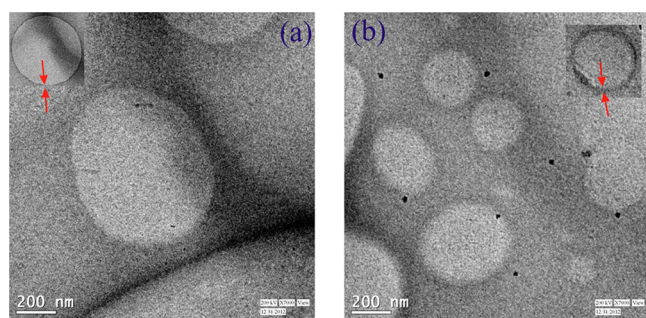


Figure 6. TEM microscopic images of vesicles formed by (a) [CTA][AOT] and (b) [BHD][AOT] ILs in water at 298 K.

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of ILs, schematic presentation, NMR characterizations, size vs R plot, and vesicles preparation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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