

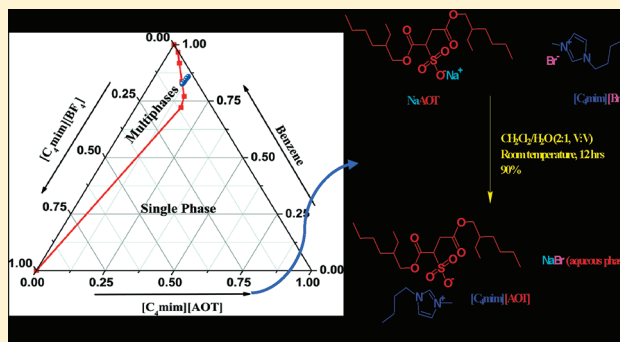
Designing a New Strategy for the Formation of IL-in-Oil Microemulsions

Vishal Govind Rao, Surajit Ghosh, Chiranjib Ghatak, Sarthak Mandal, Udit Brahmachari, and Nilmoni Sarkar*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, WB, India

S Supporting Information

ABSTRACT: Due to the increasing applicability of ionic liquids (ILs) as different components of microemulsions (as the polar liquid, the oil phase, and the surfactant), it would be advantageous to devise a strategy by which we can formulate a microemulsion of our own interest. In this paper, we have shown how we can replace water from water-in-oil microemulsions by ILs to produce IL-in-oil microemulsions. We have synthesized AOT-derived surface-active ionic liquids (SAILs) which can be used to produce a large number of IL-in-oil microemulsions. In particular, we have characterized the phase diagram of the $[\text{C}_4\text{mim}][\text{BF}_4]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ ternary system at 298 K. We have shown the formation of IL-in-oil microemulsions using the dynamic light scattering (DLS) technique and using methyl orange (MO), betaine 30, and coumarin-480 (C-480) as probe molecules.



1. INTRODUCTION

Unlike simple inorganic salts like sodium chloride (NaCl), ionic liquids (ILs) are organic salts having low melting points (by convention below 100 °C) due to the presence of sterically mismatched ions^{1–7} that hinder crystal formation. Their unique properties and the rising necessity of sustainable, “green” chemistry have led to an amazing increase in interest in such salts. Room temperature ionic liquids (RTILs) are an interesting class of tunable, designer solvents with essentially zero volatility. Because the properties of the RTILs are very much dependent on the constituent ions, various RTILs can be designed using appropriate combination of the cationic and anionic constituents to obtain some desired properties and applications. The imidazolium salts have dominated IL research ever since Wilkes et al.⁸ observed that 1,3-dialkylimidazolium electrolytes have lower melting points than their 1-alkylpyridinium cation containing counterparts. The properties of the imidazolium salts can be altered easily by varying the alkyl chain length and symmetry of the cation (leading to lowering of melting point), and by changing the anion hydrophobicity. In addition to this, 1-alkyl-3-methylimidazolium salts were used in the first-studied surface active ionic liquids (SAILs), which showed aggregation in aqueous solution.^{9,10} SAILs can be defined as functional ionic liquids with the combined properties of ILs and surfactants; in other words, ILs bearing long alkyl chains having amphiphilic character are named as surface-active ionic liquids SAILs.^{11,12} Inoue et al.¹³ 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. The imidazolium cations, as components of ILs and SAILs, are of additional interest due to their unique properties like (i) high stability due to delocalization of the positive charge over the heterocyclic moiety, (ii) presence of a proton substituent at the C-2 position which enables the imidazolium moiety to act as a catalyst by ligating to metals (the planar geometry may also be an important factor for future catalyst design), and (iii) its ability to provide an acidic medium appropriate for other types of reactions (for example, Diels–Alder or Friedel–Crafts).^{14–16}

Reverse IL-in-oil microemulsions may find various applications owing to the unique features of ILs and microemulsions: they offer a wide choice of structures (e.g., cation/anion), such as chiral structures, and allow the use of a smaller quantity of ionic liquid compared to that required for bulk-phase IL reactions. Recently, several groups have prepared and characterized RTIL containing micelles and microemulsions.^{17–26} There are many reports on microemulsions with IL as one of the components.^{27–30} Anderson et al.²⁸ have reported the formation of dry micelle of several traditional surfactants in 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}][\text{Cl}]$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$). Binks et al.³¹ have successfully prepared some novel emulsions of ILs stabilized solely by silica nanoparticles. Gao et al. have reported that under suitable condition $[\text{C}_4\text{mim}][\text{PF}_6]/\text{TX-100}/\text{water}$ system could form microemulsions.¹⁹ Han et al.

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have reported many ionic liquid microemulsions containing carbon dioxide.^{32,33} In our recent work, we demonstrated that the RTIL *N,N,N*-trimethyl-*N*-propylammonium bis-(trifluoromethanesulfonyl)imide ($[N_{3111}][TF_2N]$) can replace polar water and form nonaqueous microemulsions in cyclohexane with the aid of nonionic surfactant Triton X-100.²¹ Cheng et al.¹⁸ have shown formation of IL-in-IL microemulsions consisting of a hydrophobic IL, $[C_4mim][PF_6]$, a hydrophilic IL, propylammonium formate (PAF), and a surfactant sodium 1,4-bis(2-ethylhexyl) sulfosuccinate (AOT). The IL-in-oil microemulsion comprising 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) and cyclohexane, stabilized by the nonionic surfactant Triton X-100, has been studied by many other groups.^{20,34–36} It showed regular swelling behavior common to many droplet microemulsions, like AOT-stabilized w/o systems.³⁷

To the best of our knowledge, there have not been any reports of IL-in-oil (oil: benzene, cyclohexane, *n*-heptane, etc.) microemulsions using AOT or AOT-derived surfactants, while water-in-oil reverse micelle and microemulsions using AOT or AOT derived surfactants are well documented in the literature.^{38,39} So, in this paper, we have attempted to replace water by ILs to produce IL-in-oil microemulsions using AOT-derived surfactants.

2. MATERIALS AND INSTRUMENTATION

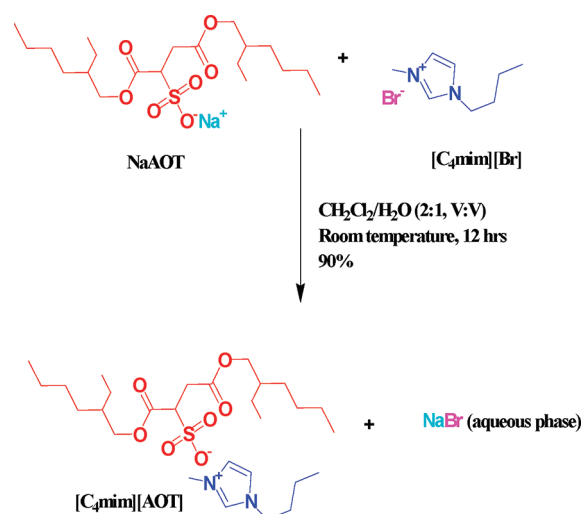
Coumarin 480 (C-480) (laser grade, Exciton), 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (betaine 30, Sigma-Aldrich), and methyl orange (MO, Merck) were used as received. NaAOT (sodium 1,4-bis(2-ethylhexyl) sulfosuccinate, Sigma-Aldrich) was dried in vacuum for 30 h before use. Benzene (Spectrochem, HPLC grade) was used as received. The absorption and fluorescence spectra were collected using a Shimadzu (model no. UV-2450) spectrophotometer and a Hitachi (model no. F-7000) spectrofluorimeter, respectively. For dynamic light scattering (DLS) measurements, we used a Malvern Nano ZS instrument employing a 4 mW He–Ne laser operating at a wavelength 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).

3. RESULTS AND DISCUSSION

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. In the case of ILs, IL-in-oil microemulsion formation is not possible due to the absence of favorable interactions of ILs with the cations of AOT (Na^+ , NH_4^+ , Ca^{2+} , etc.). This line of reasoning is supported by the fact that simple inorganic salts are not soluble in ILs.⁴⁰ It appears logical to assume, at least in theory, that replacement of the inorganic cations of AOT (Na^+ , NH_4^+ , Ca^{2+} , etc.) by organic cations could lead to the formation of IL-in-oil microemulsions.

Using imidazolium (1-butyl-3-methylimidazolium, $[C_4mim]^+$) moiety as the cationic component, we have synthesized $[C_4mim][AOT]$ by an anion exchange reaction⁴¹ (Scheme 1) between NaAOT and 1-butyl-3-methylimidazolium bromide ($[C_4mim][Br]$) (the synthetic procedure and characterization of $[C_4mim][AOT]$ are given in the Supporting

Scheme 1. Synthesis of $[C_4mim][AOT]$ by Anion Exchange Reaction



Information (Scheme S1, Figure S1, and Table S1)). Interestingly, this compound has validated all of our previous theoretical propositions. We have successfully formed IL-in-oil microemulsions using $[C_4mim][AOT]$ as SAIL, benzene as nonpolar component, and different ILs as the polar component. The results obtained using the different ILs are tabulated in Table 1.

Table 1. Tabulation of Results Obtained by the Addition of ILs to the $[C_4mim][AOT]$ /Benzene System

ionic liquid used	formation of microemulsion occurs (yes/no)
1-butyl-3-methylimidazolium tetrafluoroborate, $[C_4mim][BF_4]$	yes
1-hexyl-3-methylimidazolium tetrafluoroborate, $[C_6mim][BF_4]$	yes
1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim][PF_6]$	yes
1-hexyl-3-methylimidazolium hexafluorophosphate, $[C_6mim][PF_6]$	yes
1-ethyl-3-methylimidazolium ethylsulfate, $[C_2mim][C_2SO_4]$	yes
1-ethyl-3-methylimidazolium <i>n</i> -butylsulfate, $[C_2mim][C_4SO_4]$	yes
1-ethyl-3-methylimidazolium <i>n</i> -hexylsulfate $[C_2mim][C_6SO_4]$	yes
1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_2mim][TF_2N]$	yes
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_4mim][TF_2N]$	yes
1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[C_6mim][TF_2N]$	yes
<i>N</i> -methyl- <i>N</i> -propylpyrrolidinium bis(trifluoromethanesulfonyl)imide, $[Py][TF_2N]$	yes
<i>N,N,N</i> -trimethyl- <i>N</i> -propylammonium bis(trifluoromethanesulfonyl)imide, $[N_{3111}][TF_2N]$	yes
<i>N,N</i> -dimethylethanolammonium hexanoate, DAH	yes
<i>N,N</i> -dimethylethanolammonium formate, DAF	no
ethylammonium nitrate, EAN	no
propylammonium formate, PAF	no

From the series of ILs (Table 1), we have chosen $[\text{C}_4\text{mim}][\text{BF}_4]$ to further characterize the microemulsion. We have characterized the partial phase behavior of the ternary system $[\text{C}_4\text{mim}][\text{BF}_4]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ by observing the transition from clear transparent solution to turbid solution visually, i.e., through naked eye (Figure 1). It is evident from

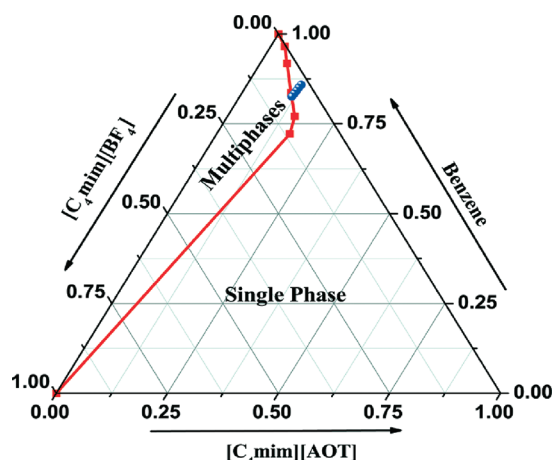


Figure 1. Phase diagram of the $[\text{C}_4\text{mim}][\text{BF}_4]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ ternary system at 298 K.

Figure 1 that a continuous stable single-phase microemulsion region can always be observed over the $[\text{C}_4\text{mim}][\text{BF}_4]$ or benzene content range of 0–100% (wt). Based on the phase diagram, a series of samples were chosen where we can have the possibility of IL/O microemulsions only. The samples were characterized by dynamic light scattering (DLS) technique. DLS has been widely used as a powerful technique to assess whether the ILs are encapsulated by the surfactant molecules to create microemulsion media.^{42,43} Owing to the extensive studies on characterization of microemulsion using DLS, we can say 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.^{19,35,42–44} This regular swelling behavior is consistent with the volume of dispersed nanodomains being directly proportional to the amount of added IL. This type of behavior is common to many well-established AOT stabilized w/o microemulsions. The regular increase in size of the droplets (linearly with increasing R value) clearly indicates that the IL microemulsion media consist of discrete spherical and noninteracting droplets of ILs stabilized by the surfactant.⁴⁴ Deviation from linearity could be observed due to several reasons, the most relevant ones being droplet–droplet interaction and shape of the microemulsions.⁴⁴ In our case, DLS studies revealed the formation of the IL-in-oil microemulsion (Figure 2). The sizes of the aggregates increased from 5.2 to 18.7 nm with increasing R values from 0.4 to 1.2 (here the R value is defined as the molar ratio of $[\text{C}_4\text{mim}][\text{BF}_4]$ to $[\text{C}_4\text{mim}][\text{AOT}]$). The microemulsions showed regular swelling behavior with the addition of IL, $[\text{C}_4\text{mim}][\text{BF}_4]$ (Figure 3), indicating the formation of IL-in-oil microemulsion. We have observed almost linear variations of size at R values lower than 1.0 for the addition of IL, $[\text{C}_4\text{mim}][\text{BF}_4]$. We have observed deviation from the linearity at R values higher than 1.0, which may be attributed to the increased droplet–droplet interaction at higher R value.

Methyl orange (MO) is often used as a solvatochromic probe.⁴⁵ It is sensitive to the local environment, and the UV–

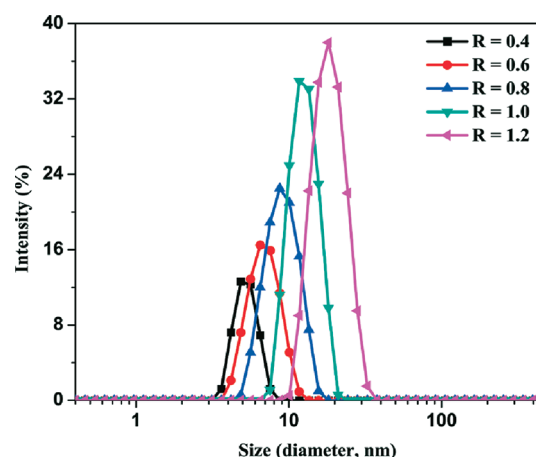


Figure 2. Size distribution of the droplets (measured by dynamic light scattering) of $[\text{C}_4\text{mim}][\text{BF}_4]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ microemulsion at different R values.

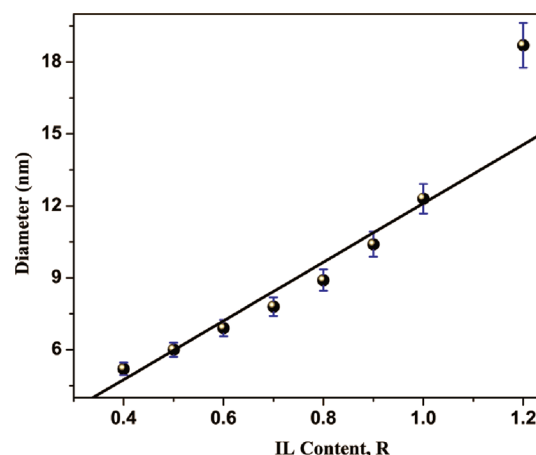


Figure 3. Diameter of the droplets of $[\text{C}_4\text{mim}][\text{BF}_4]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ microemulsion as a function of $[\text{C}_4\text{mim}][\text{BF}_4]$ concentration (R value).

vis absorption maximum (λ_{max}) increases with the polarity of the environment. It has been widely used by many groups to characterize the formation of different microemulsions.^{19,46–50} We have also used this (MO) as a probe molecule to show the formation of IL-in-oil microemulsions. The absorption spectra of MO are shown in Figure 4, which clearly shows that the absorption maximum (λ_{max}) increases with the addition of IL, $[\text{C}_4\text{mim}][\text{BF}_4]$. On increasing the ionic liquid content from $R = 0$ to $R = 1.2$, the absorption maxima is red-shifted from 415 to 421 nm. This red shift in absorption maxima clearly indicates that with increasing R value the MO gets solubilized inside the ionic liquid pool formed in the microemulsion and the micropolarity around MO increases. One more point to be noted is that the absorption maxima of MO in neat $[\text{C}_4\text{mim}][\text{BF}_4]$ was found to be 430 nm, which clearly indicates that the polarity of the ionic liquid pool ($[\text{C}_4\text{mim}][\text{BF}_4]$ pool) inside the microemulsion is less compared to the neat IL ($[\text{C}_4\text{mim}][\text{BF}_4]$).

We have also utilized one of the most typical polarity probes, betaine 30 ($E_T(30)$ probe),^{51–53} to show the formation of IL-in-oil microemulsions. Due to its exceptionally large negative solvatochromism (a pronounced hypsochromic band shift with increasing solvent polarity), the $E_T(30)$ probe has been widely

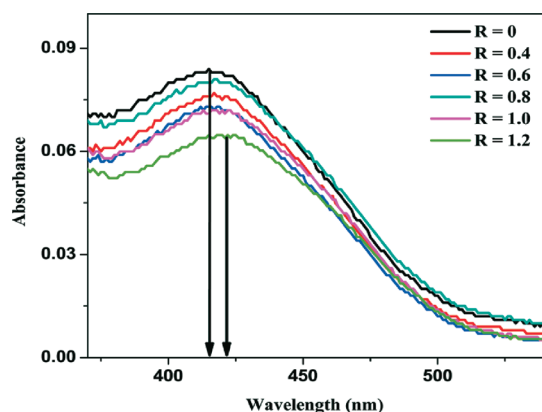


Figure 4. Absorption spectra of methyl orange (MO) in $[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ microemulsion at different R values.

used by many groups to determine the polarity of different systems.^{51–57} It has been also utilized for the characterization of different microheterogeneous media. The absorption spectra of $E_T(30)$ probe are shown in Figure 5, which clearly shows that

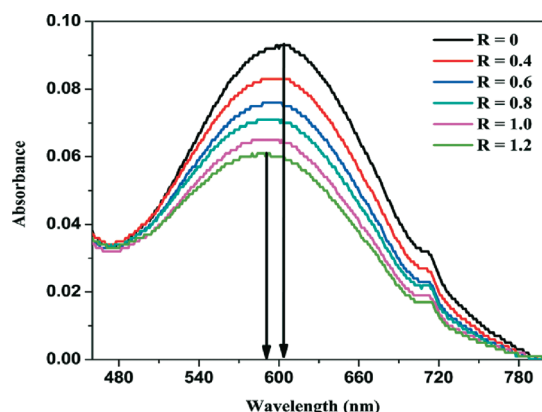


Figure 5. Absorption spectra of betaine 30 in $[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ microemulsion at different R values.

the absorption maximum (λ_{max}) decreases with the addition of IL, $[C_4mim][BF_4]$. On increasing the ionic liquid content from $R = 0$ to $R = 1.2$, the absorption maxima is blue-shifted from 603 to 590 nm. This blue shift in absorption maxima clearly indicates that with increasing R value the $E_T(30)$ probe gets solubilized inside the ionic liquid pool formed in the microemulsion and the micropolarity around $E_T(30)$ probe increases. We have also determined the $E_T(30)$ value using eq 1.⁵⁷

$$E_T(30) = h\nu_{max}N_A = \frac{28591}{\lambda_{max} \text{ (nm)}} \frac{\text{kcal}}{\text{mol}} \quad (1)$$

In this equation h , c , and N_A are Planck's constant, speed of light, and Avogadro's number, respectively. λ_{max} and ν_{max} are the wavelength (in nm) and frequency of the maximum absorption of the $E_T(30)$ probe, respectively. With increase in ionic liquid content from $R = 0$ to 1.2, the $E_T(30)$ value changes from 47.41 to 48.46 kcal mol^{−1}. This change in $E_T(30)$ value clearly indicates the with increasing R value $E_T(30)$ probe molecules experience more polar environment. The $E_T(30)$ value of neat $[C_4mim][BF_4]$ was found to be 52.56 kcal mol^{−1}, which is well in agreement with the literature value. The higher $E_T(30)$ value of neat $[C_4mim][BF_4]$ compared to that of $[C_4mim][BF_4]$

inside the microemulsion clearly indicates that the polarity of $[C_4mim][BF_4]$ pool inside the microemulsion is less compared to that in neat IL ($[C_4mim][BF_4]$).

To further support the 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.^{21,42,43} Owing to these studies, we can say that the red shift in emission maximum of C-480 with gradual addition of ILs is clear indication of the existence of IL-in-oil microemulsions. In neat benzene, C-480 shows emission maximum at 430 nm and with the addition of $[C_4mim][AOT]$ the emission maximum gets shifted to 454 nm (Table 2). This marked red shift of emission

Table 2. Emission Maxima of C-480 in Different Systems

system	$\lambda_{max}(\text{emission})$ (nm)
benzene	430
$[C_4mim][AOT]/benzene$	454
$[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ ($R = 0.4$)	457
$[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ ($R = 0.6$)	458
$[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ ($R = 0.8$)	458
$[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ ($R = 1.0$)	459
$[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ ($R = 1.2$)	460
$[C_4mim][BF_4]$	463

maxima (24 nm) clearly indicates the transfer of the probe molecule from bulk benzene to the polar interior of the $[C_4mim][AOT]$ reverse micelle. Further addition of IL ($[C_4mim][BF_4]$) to $[C_4mim][AOT]/benzene$ reverse micelles causes red shift in the emission maxima. With increase in ionic liquid content from $R = 0$ to $R = 1.0$ the emission maxima is red-shifted from 454 to 459 nm (Figure 6, Table 2). The

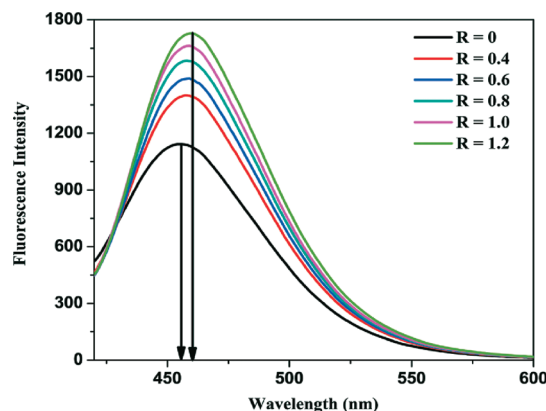


Figure 6. Fluorescence spectra of C-480 in $[C_4mim][BF_4]/[C_4mim][AOT]/benzene$ microemulsion at different R values.

gradual red shift of emission maxima with the addition of $[C_4mim][BF_4]$ clearly indicates the movement of probe molecules toward the polar IL pool of the microemulsion. In neat $[C_4mim][BF_4]$, C-480 shows emission maximum at 463 nm indicating higher polarity of neat $[C_4mim][BF_4]$ compared to that of $[C_4mim][BF_4]$ pool inside the microemulsion.

We have also performed DLS measurements for other ionic liquid microemulsions; the size variation is shown in Figure 7. Figure 7 clearly indicates the swelling behavior of IL-in-oil microemulsions with the addition of ILs. In the case of all the

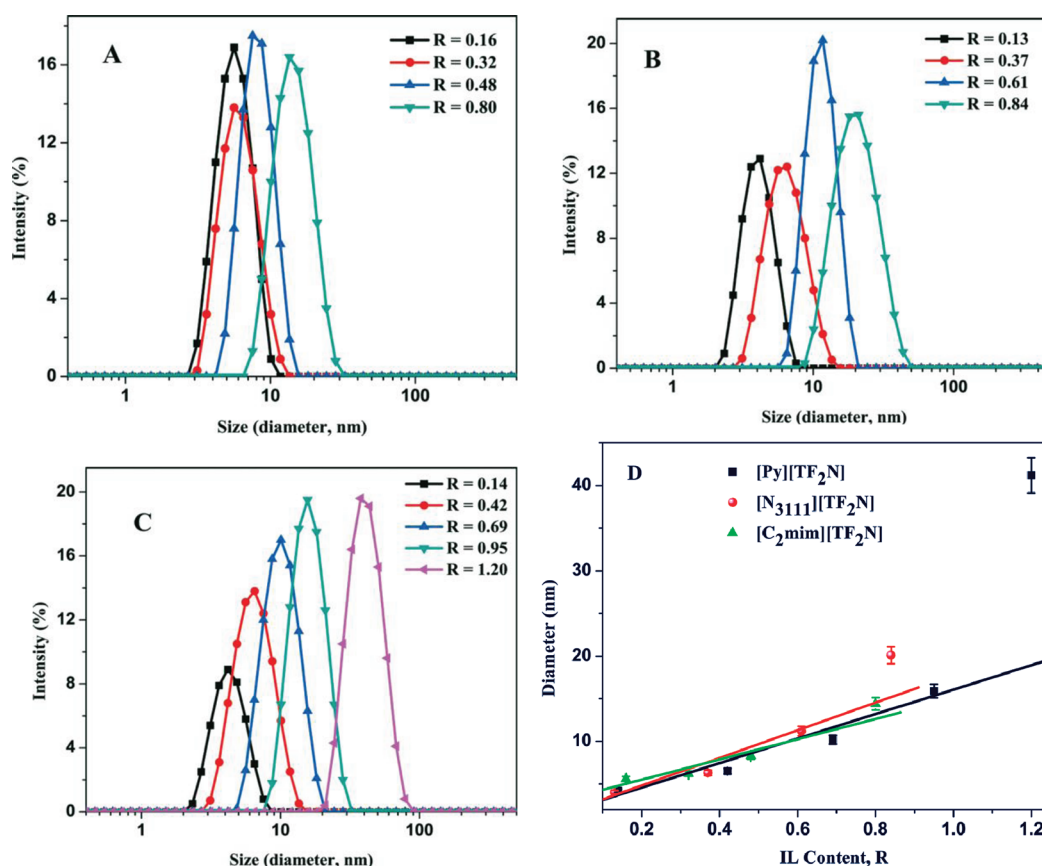


Figure 7. Size distribution of the droplets (measured by dynamic light scattering) of (A) [C₂mim][TF₂N]/[C₄mim][AOT]/benzene; (B) [N₃₁₁₁][TF₂N]/[C₄mim][AOT]/benzene; and (C) [Py][TF₂N]/[C₄mim][AOT]/benzene microemulsions at different *R* values. (D) Diameter of the droplets of IL/[C₄mim][AOT]/benzene microemulsion as a function of ILs concentration (*R* value).

ILs, we have observed linear relationship between size and *R* which continues up to a certain value of *R*. Deviation from linearity is observed at higher *R* values of ILs. We are trying to carry out further structural characterization for all the microemulsions in our lab. Also, by an analogous reaction, we have replaced the inorganic cation, Na⁺, of NaAOT by an organic cation, *N,N*-dimethylethanolammonium (DA⁺) (HOH₂CCH₂N⁺(CH₃)₂H), through anion exchange reaction. From the initial studies we have found that DAAOT also forms IL-in-oil microemulsions with many of the ILs listed in Table 1 (work related to DAAOT is not reported here). This provides additional support to our previously stated propositions.

4. CONCLUSION

In conclusion, we have shown how we can replace water from water-in-oil microemulsions by ILs to produce IL-in-oil microemulsions using AOT-derived surface active ionic liquids (SAILs). We have characterized [C₄mim][BF₄]/[C₄mim][AOT]/benzene microemulsion and showed that the polarity of [C₄mim][BF₄] pool inside the microemulsion is less compared to that of neat [C₄mim][BF₄]. Our work opens up the possibility of creating a huge number of IL-in-oil microemulsions just by replacing the inorganic cation, Na⁺ of NaAOT, by any organic cation and using different ionic liquids as the polar core. We can use task-specific organic cations to replace the Na⁺ of NaAOT to synthesize different nano materials and perform different organic reactions and biological extractions, and for many more applications.

■ ASSOCIATED CONTENT

Supporting Information

Information regarding synthesis and characterization of [C₄mim][AOT]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nilmoni@chem.iitkgp.ernet.in. Fax: 91-3222-255303.

Notes

The authors declare no competing financial interest.

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