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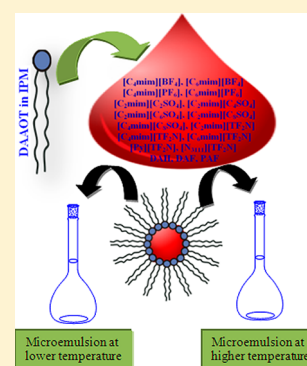
A Step toward the Development of High-Temperature Stable Ionic Liquid-in-Oil Microemulsions Containing Double-Chain Anionic Surface Active Ionic Liquid

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S Supporting Information

ABSTRACT: Owing to their fascinating properties and wide range of potential applications, interest in nonaqueous microemulsions has escalated in the past decade. In the recent past, nonaqueous microemulsions containing ionic liquids (ILs) have been utilized in performing chemical reactions, preparation of nanomaterials, synthesis of nanostructured polymers, and drug delivery systems. The most promising fact about IL-in-oil microemulsions is their high thermal stability compared to that of aqueous microemulsions. Recently, surfactant-like properties of surface active ionic liquids (SAILs) have been used for preparation of microemulsions with high-temperature stability and temperature insensitivity. However, previously described methods present a limited possibility of developing IL-in-oil microemulsions with a wide range of thermal stability. With our previous work, we introduced a novel method of creating a huge number of IL-in-oil microemulsions (Rao, V. G.; Ghosh, S.; Ghatak, C.; Mandal, S.; Brahmachari, U.; Sarkar, N. *J. Phys. Chem. B* **2012**, *116*, 2850–2855), composed of a SAIL as a surfactant, room-temperature ionic liquids as a polar phase, and benzene as a nonpolar phase. The use of benzene as a nonpolar solvent limits the application of the microemulsions to temperatures below 353 K. To overcome this limitation, we have synthesized *N,N*-dimethylethanolammonium 1,4-bis(2-ethylhexyl) sulfosuccinate (DAAOT), which was used as a surfactant. DAAOT in combination with isopropyl myristate (IPM, as an oil phase) and ILs (as a polar phase) produces a huge number of high-temperature stable IL-in-oil microemulsions. By far, this is the first report of a huge number of high-temperature stable IL-in-oil microemulsions. In particular, we demonstrate the wide range of thermal stability of $[C_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions by performing a phase behavior study, dynamic light scattering measurements, and ^1H NMR measurements and by using coumarin-480 (C-480) as a fluorescent probe molecule.



1. INTRODUCTION

Microemulsions are thermodynamically stable, isotropic, transparent mixtures of three components: a polar solvent, a nonpolar solvent (two immiscible liquids), and an amphiphilic component (usually surfactants and cosurfactants). The microheterogeneous environments present in microemulsions hold enormous promise for applications in different fields owing to the nonstandard environments they present. Often these systems exhibit chemistry entirely different than that observed in homogeneous liquid solutions.^{1,2} Owing to the capability of solubilizing polar as well as nonpolar substances, microemulsions are now being extensively used as micro-reactors for various applications.^{3,4} They have been used (i) to control the size and shape of various inorganic nanostructures synthesized in the core of the microemulsions,⁵ (ii) for the synthesis of organic nanoparticles,⁶ (iii) in purification and extraction of biomolecules,⁷ and (iv) in drug delivery systems.^{8,9}

In this work, we investigated high-temperature stable microemulsions because of the potential applications of these systems in a wide range of fields. Conventionally, micro-

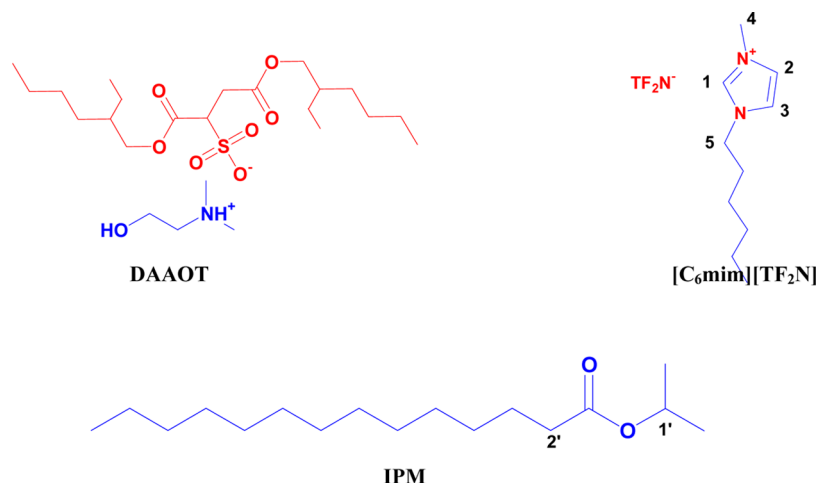
emulsions were formulated using water as the polar core, and these systems have been extensively studied in the past.^{10–17}

Most studies focused on microemulsions employ water as the polar component in combination with the standard anionic surfactant NaAOT^{10–17} (sodium 1,4-bis(2-ethylhexyl) sulfosuccinate). In this article, we used NaAOT for sodium 1,4-bis(2-ethylhexyl) sulfosuccinate and AOT[–] for 1,4-bis(2-ethylhexyl) sulfosuccinate anion. Unfortunately, these water-based microemulsions have limited thermal stability. Reports on nonaqueous microemulsions have appeared in the literature.^{18–22} Chemical reactions that require a water-free environment,¹⁸ such as the Diels–Alder reaction, esterification, and polymerization,²² can be successfully carried out in nonaqueous microemulsions. Along with the wide variety of conventional polar organic solvents¹⁹ (e.g., ethylene glycol, formamide, glycerol, etc.) that can be used to replace water as

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Scheme 1. Chemical Structure and Atom Numbering of DAAOT, $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$, and IPM

the polar core of nonaqueous microemulsions, ionic liquids are also a viable possibility.

An ionic liquid (IL) can be defined as a material composed entirely of ions (i.e., cations and anions). Unlike simple inorganic salts like sodium chloride (NaCl), ILs are organic salts having low melting points (by convention below 100 °C) because of the presence of sterically mismatched ions^{23–25} that prevent crystal formation. Their unique properties and the growing necessity of sustainable, “green” chemistry have led to an incredible increase in interest in such salts. Room-temperature ionic liquids (RTILs) are an interesting class of tunable, designer solvents with essentially zero volatility. Therefore, we can say that ILs are a most deserving candidate for the formulation of high-temperature stable microemulsions. The IL-based microemulsions are studied by many groups.^{26–34} In the first report on the formation of IL-in-oil microemulsions, Gao et al.²⁶ developed $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{cyclohexane}$ microemulsions and characterized them by phase behavior, conductivity measurement, dynamic light scattering (DLS) measurement, freeze-fracturing electron microscopy, and UV–vis techniques. Eastoe et al.²⁷ further investigated the size and shape of the same microemulsions by small-angle neutron scattering (SANS) measurements. They noticed regular swelling behavior of microemulsions with the addition of the IL, which suggests that the volume of dispersed nanodomains is proportional to the amount of IL added.²⁷ Gao et al.³⁴ investigated the effect of temperature on the microstructure of the two IL-in-oil microemulsions $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{oil}$ (cyclohexane and toluene). In contrast to aqueous microemulsions, these systems exhibited high temperature independence. This difference in behavior was rationalized by considering the underlying stabilizing interactions that enable the formation of both types of microemulsions.³⁴

While the microemulsions mentioned above involve ILs as one of the components, they are not stable at high temperatures because they contain nonionic surfactants. The effect of temperature on microemulsions with nonionic surfactants is very pronounced. Such microemulsions are not favorable for formulating systems that are stable over a wide temperature range.³⁵ Therefore, for the formulation of high-temperature stable microemulsions, we have to look for charged surfactants. IL-based microemulsions with charged surfactants are rather scarce.^{30,35–42} Falcone et al. used cationic surfactant benzyl-*n*-hexadecyldimethylammonium chloride

(BHDC) for the formulation of $[\text{C}_4\text{mim}][\text{BF}_4]/\text{BHDC}/\text{benzene}$ and $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]/\text{BHDC}/\text{benzene}$ microemulsions and compared their behavior with $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{benzene}$ and $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]/\text{TX-100}/\text{benzene}$ microemulsions.³⁰ They compared the behavior of $[\text{C}_4\text{mim}][\text{BF}_4]$ in $[\text{C}_4\text{mim}][\text{BF}_4]/\text{BHDC}/\text{benzene}$ and $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{benzene}$ microemulsions³⁶ using a multinuclear NMR study and concluded that the structure and behavior of entrapped ILs in the microemulsions depend strongly on the surfactants used.^{30,36} We studied the solvation dynamics of coumarin dyes in $[\text{C}_4\text{mim}][\text{BF}_4]/\text{BHDC}/\text{benzene}$ ³⁷ and $[\text{Py}][\text{TF}_2\text{N}]/\text{BHDC}/\text{benzene}$ microemulsions.³⁸

ILs bearing long alkyl chains with an amphiphilic character are named surface active ionic liquids (SAILs). Recently, SAILs were employed as surfactants for the formulation of different organized assemblies.^{35,39,40,43–45} SAILs possess combined properties of ILs and surfactants.^{43–45} After observing surfactant-like behavior of SAIL 1-hexadecyl-3-methylimidazolium chloride ($[\text{C}_{16}\text{mim}][\text{Cl}]$) in EAN, Zech et al. characterized microemulsions RTIL ($[\text{C}_4\text{mim}][\text{BF}_4]$ and EAN)/ $[\text{C}_{16}\text{mim}][\text{Cl}]/\text{dodecane}$ using conductivity, DLS, and small-angle X-ray scattering (SAXS) measurements.³⁹ They concluded that for preparation of microemulsions with high-temperature stability and temperature insensitivity it is better to use ionic surfactants in combination with ILs.³⁵ Zech et al. further explored thermal stability of EAN/ $[\text{C}_{16}\text{mim}][\text{Cl}]/\text{dodecane}$ microemulsions at ambient pressure, which exhibited stability over the temperature range 303–423 K.^{35,40} We can say that SAILs are good candidates for the formulation of high-temperature microemulsions.

In our earlier articles,^{46–48} we designed for the first time a new strategy for creating a huge number of IL-in-oil microemulsions using a SAIL as the anionic surfactant. We showed that by replacing the inorganic cation Na^+ of NaAOT with an organic cation and using different ionic liquids as polar cores, we can formulate a huge number of microemulsions.⁴⁶ In our earlier articles,^{46–48} for the formulation of microemulsions we have used a SAIL ($[\text{C}_4\text{mim}][\text{AOT}]$) as a surfactant, RTILs as a polar phase, and benzene as a nonpolar phase. Use of benzene as a nonpolar solvent cannot serve our purpose of creating high-temperature stable microemulsions, so we replaced benzene with isopropyl myristate (IPM), a biologically accepted oil phase with high boiling point (~440 K). We have synthesized *N,N*-dimethylethanolammonium 1,4-bis(2-ethyl-

hexyl) sulfosuccinate (DAAOT) and investigated the microemulsions' formation. In summary, for the first time, we have shown the possibility of creating a huge number of high-temperature stable IL-in-oil microemulsions by proper selection of the components involved in the microemulsions.

2. EXPERIMENTAL METHODS

2.1. Materials and Instrumentation. Coumarin-480 (C-480) (laser grade, Exciton) and IPM (SRL) were used as received. For the synthesis of DAAOT, we used DAF (*N,N*-dimethylethanolanmonium formate) and NaAOT. DAF was obtained from Bioniqs (>99% purity) and used as received. NaAOT (Sigma-Aldrich) was dried in vacuum for 30 h before use. The RTIL, $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$, was obtained from Merck (high-purity grade) and used as received. Doubly distilled deionized water (Milli-Q water) was used for the synthesis of DAAOT. The structures of DAAOT, IPM, and $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ are shown in Scheme 1.

For measurement of size and size distribution of aggregates in microemulsions, DLS measurements were performed with a Malvern Nano ZS instrument employing a 4 mW He–Ne laser ($\lambda = 632.8$ nm). During the process of data collection, scattering photons were collected at a scattering angle of 173° (to avoid effects of high-concentration measurements). The scattering intensity data were processed using instrumental software to obtain the hydrodynamic diameter (d_h) and size distribution of each sample. The instrument measures fluctuation in scattering intensity and uses this to calculate the size of particles within the sample. The d_h values of microemulsions were estimated from the intensity autocorrelation function of time-dependent fluctuation in intensity. The d_h is defined as

$$d_h = \frac{k_B T}{3\pi\eta D} \quad (1)$$

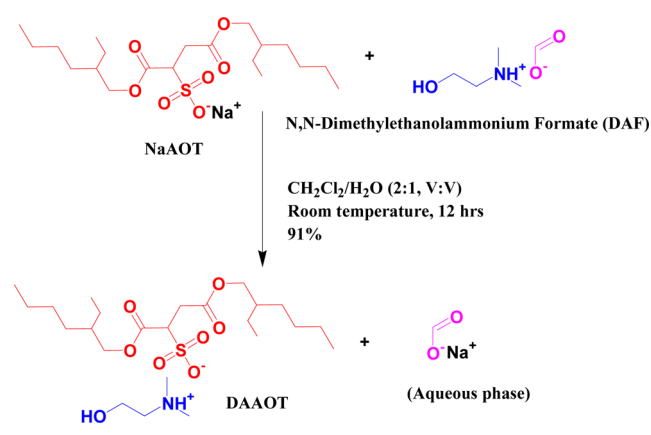
where k_B is the Boltzmann constant, η the viscosity of the solvent (in this case, viscosity of IPM) at absolute temperature T (Table S1 of Supporting Information), and D the translational diffusion coefficient. In the process of size measurement, we used the refractive index of the solvent (for IPM, 1.436).

For viscosity measurements, we used a Brookfield DV-II+ Pro viscometer. The temperature was maintained by circulating water through the cell holder using a JEIO TECH Thermostat (RW-0525GS).

The NMR measurements were carried out with a Bruker 200 and 400 MHz NMR spectrometer using C_6D_6 (Aldrich, 99.6 atom % D) as the chemical shift reference for mode locking. ^1H NMR measurements of neat ionic liquid and neat IPM were performed using D_2O as external chemical shift reference. To remove any perturbation to the studied system arising from the presence of D_2O , D_2O was packed in a capillary and then added to the NMR tube.

2.2. Synthesis of DAAOT. DAAOT was prepared by an anion exchange reaction (Scheme 2) similar to those reported in the literature.^{46,49} Equimolar (0.05 M) amounts of NaAOT salt and DAF were dissolved in a mixture of methylene chloride and water (2:1 v:v). The resulting solution was stirred for 12 h at room temperature. After the reaction was completed, the methylene chloride bottom layer was washed several times with water. The product was obtained from the lower organic layer and dried by solvent removal using a rotavapor. A high-vacuum

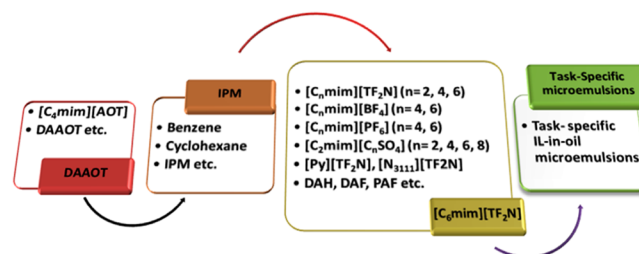
Scheme 2. Synthesis of DAAOT by Anion Exchange Reaction



pump was used for 50 h to remove any remaining traces of water, and the synthesis afforded 91% yield of DAAOT. The obtained DAAOT was characterized by ^1H , ^{13}C , and distortionless enhancement by polarization transfer (DEPT) NMR measurements and by the use of elemental microanalysis (C, H, N analyzer). All NMR measurements were carried out using C_6D_6 as the chemical shift reference for mode locking. The ^1H , ^{13}C , and DEPT NMR spectra are given in the Supporting Information (Figure S1 and Table S2). The obtained DAAOT is liquid at room temperature, whereas NaAOT is solid at room temperature. This difference in physical property can be explained by considering the decrease in crystal packing efficiency with the replacement of a small sodium cation by a large *N,N*-dimethylethanolanmonium cation. This observation is in agreement with that of Larsen and co-workers who investigated the factors that affect the melting point of imidazolium ILs.⁵⁰ The solubility of DAAOT in water at room temperature is also less than that of NaAOT, which indicates poor hydrogen-bonding interactions between the constituents of the SAIL and water. This is once again supported by the work of Coutinho et al.⁵¹ in which they showed that the solubility of ILs in water is highly dependent on the constituents of the ILs.

Following the synthesis, the solubility of DAAOT was checked in various organic solvents. DAAOT was found to be soluble in IPM. Interestingly, like $[\text{C}_4\text{mim}][\text{AOT}]$,⁴⁶ DAAOT also forms a huge number of IL-in-oil microemulsions composed of the SAIL DAAOT (as a surfactant), RTILs (as a polar phase), and IPM (as a nonpolar phase). The RTILs tested for the microemulsion formations are listed in Scheme 3. From the series of ILs which form microemulsions (Scheme 3), we have chosen $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ to further characterize the

Scheme 3. Development of a Strategy Involving Different Steps To Create Task-Specific IL-in-Oil Microemulsions



microemulsion. We have chosen TF_2N^- -containing ionic liquids because they are stable toward hydrolysis⁵² and are good absorbers of carbon dioxide (CO_2).⁵³ In addition to this, many groups are involved in the investigation of their physicochemical properties.⁵⁴

2.3. Preparation of Ionic Liquid-in-Oil Microemulsions. The phase diagram of the ternary system $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ at 298 K was constructed in the following manner: (i) the different stock solutions of DAAOT (0.05, 0.10, 0.15, 0.2, 0.25 M, etc.) in IPM were prepared. (ii) IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ was added to each solution up to the point of phase separation (based on visually observing the transition from transparent solution to turbid solution and further confirmed by UV–vis spectrophotometry). (iii) Finally, the weight fractions of all the components (DAAOT, IPM, and $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$) were calculated and plotted.

3. RESULTS AND DISCUSSION

3.1. Phase Behavior Study. The spontaneously fluctuating interface makes microemulsions dynamic systems with continuously changing microstructures. In IL-in-oil microemulsions, IL droplets are dispersed in the continuous oil phase. For characterization of the dynamic IL–oil interface, we constructed the partial phase diagram of the ternary system $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ at 298 K (see section 2.3). The partial phase diagram clearly shows a continuous stable single-phase microemulsion region over $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ or benzene content range of 0–100 wt % (Figure 1). On the basis

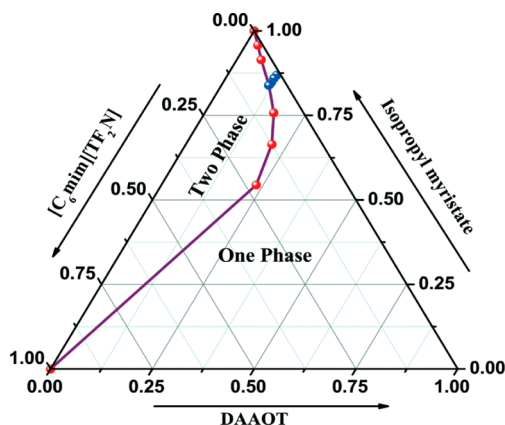


Figure 1. Phase diagram of the $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ ternary systems at 298 K. (Blue points indicate different R values selected for the system.)

of the phase diagram, a series of samples was chosen where we can have the possibility of only IL-in-oil microemulsions (blue points). Reverse IL-in-oil microemulsions were further characterized by their various applications based on the unique features of ILs and microemulsions. Ionic liquid present in IL-in-oil microemulsions can offer a wide variety of structures (e.g., cation/anion), such as chiral structures, and allows the use of a smaller quantity of ionic liquid compared to that required for bulk-phase IL reactions.

3.2. Size of the Aggregates in Microemulsions: DLS Measurements. From the phase behavior study, formation of microemulsions of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ ternary systems was verified. Additionally, we used DLS measurements to assess whether the ILs are encapsulated by the surfactant molecules to create microemulsion media.^{37,55} For all the

measurements, we used 0.2 M DAAOT in IPM solution (the exact compositions of the investigated microemulsions are given in Table S3 of the Supporting Information). Encapsulation of the IL to form IL-in-oil microemulsions is confirmed by the regular increase in the size of the droplets with the R value up to a specific level (where R is the molar ratio of RTILs to DAAOT).^{30,34,37,55,56} This regular swelling behavior is common to many well-established AOT-stabilized water-in-oil microemulsions and is consistent with the volume of dispersed nanodomains being directly proportional to the amount of added IL. The regular increase in size of the droplets (linearly with increasing R values) clearly indicates that the IL microemulsion media consist of discrete spherical and non-interacting droplets of ILs stabilized by the surfactant.³⁰ Deviation from linearity may be observed for several reasons, droplet–droplet interaction and shape of the microemulsions being the most relevant.³⁰

Here, DLS studies revealed the formation of the IL-in-oil microemulsion (Figure 2a). Aggregate size increased from 7.9 to 91.0 nm with R values increasing from 0.10 to 0.45 (Table 1). We observed almost linear variations of size at R values lower than 0.33 (Figure 2b), and further addition of IL causes deviation from linearity that may be attributed to the increased droplet–droplet interaction at higher R values.³⁰

3.3. Influence of Temperature on the Size of the Aggregates in Microemulsions: Wide Temperature Range Stability. We investigated the effect of temperature on the size of the aggregates in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.33$ and 0.40 (Figure 3). It is evident from the DLS measurements that the size of the aggregates in microemulsions decreases with increasing temperature and increases with decreasing temperature. The observed decrease in size with increase in temperature suggests the noninteracting hard sphere nature of the aggregates in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.33$ and 0.40 and the absence of any droplet-coalescing processes.^{30,47,48,57} The decrease in size with increase in temperature corroborates our earlier reports^{37,47,48} where we showed that the size of $[\text{C}_4\text{mim}][\text{BF}_4]/\text{BHDC}/\text{benzene}$, $[\text{Py}][\text{TF}_2\text{N}]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$, and $[\text{C}_n\text{mim}][\text{TF}_2\text{N}]/[\text{C}_4\text{mim}][\text{AOT}]/\text{benzene}$ aggregates in microemulsions decreases with an increase in temperature.^{37,47,48}

Interestingly, $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.33$ are stable at temperatures as low as 278 K, whereas $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.40$ is unstable below 295 K. This difference can be accounted for by the presence of different amounts of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in the microemulsions. The size of aggregates in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.33$ increased from 24.6 to 60.2 nm when the temperature decreased from 298 to 278 K. At 298 K, aggregate sizes were 24.6 and 59.2 nm for $R = 0.33$ and 0.40, respectively (Table 2).

To confirm their high-temperature stability, we heated $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.33$ and 0.40 to ~ 423 K. Unlike microemulsions containing a nonionic surfactant, the $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions did not display phase separation, indicating high-temperature stability.

Size variation of the microemulsions with increasing temperature was measured by a Malvern Nano ZS instrument. Because of the limitation of our instrumental setup, we were unable to measure size variation above 358 K. With increasing temperature from 298 to 358 K, the size of the aggregates in

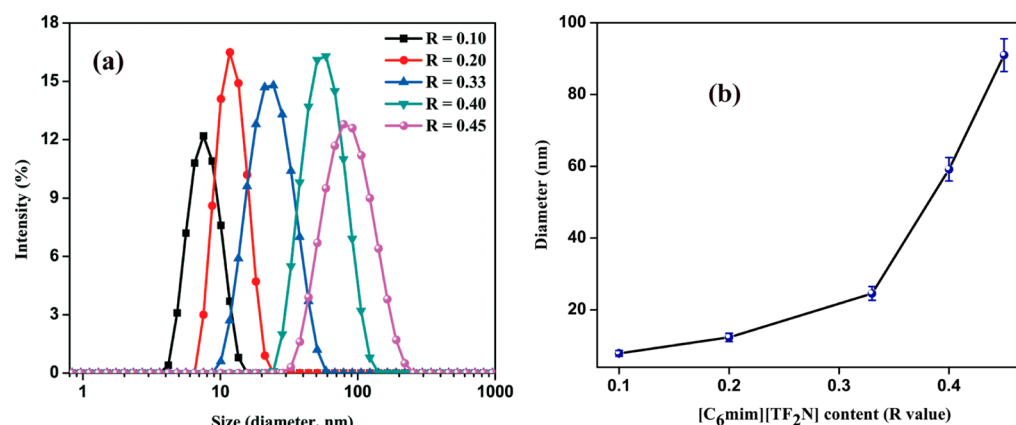


Figure 2. (a) Size distribution and (b) diameter of the droplets (measured by DLS) of [C₆mim][TF₂N]/DAAOT/IPM microemulsions at different R values.

Table 1. Size (Diameter) of the Droplets of [C₆mim][TF₂N]/DAAOT/IPM Microemulsions as a Function of Concentration of RTILs (R value) at 298 K

system	R value	size (diameter, nm) ^a
[C ₆ mim][TF ₂ N]/DAAOT/IPM	0.10	7.9 ± 0.8
	0.20	12.3 ± 1.2
	0.33	24.6 ± 1.9
	0.40	59.2 ± 3.3
	0.45	91.0 ± 4.5

^aThe uncertainties for the aggregate sizes denote the uncertainties in the peak position (maxima) of the DLS measurement.

[C₆mim][TF₂N]/DAAOT/IPM microemulsions at R = 0.33 and 0.40 decreases from 24.6 to 5.4 nm and 59.2 to 13.3 nm, respectively. This shows that the microemulsions retain their structural integrity across the temperature range used in the study.

3.4. Emission Spectra of Coumarin-480. The phase behavior study and regular increase in size of the aggregates in [C₆mim][TF₂N]/DAAOT/IPM microemulsions with increasing R values clearly indicate penetration of [C₆mim][TF₂N] in the polar core of the microemulsions. 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 sensitive to the local environment, and the emission maximum increases

Table 2. Size (Diameter) of the Droplets of [C₆mim][TF₂N]/DAAOT/IPM Microemulsions at R = 0.33 and 0.40 as a Function of Temperature

system	temperature (K)	size (diameter, nm) ^a
[C ₆ mim][TF ₂ N]/DAAOT/IPM (R = 0.33)	278	60.2 ± 3.8
	288	30.9 ± 2.5
	298	24.6 ± 2.1
	308	21.3 ± 1.9
	318	17.9 ± 1.6
	328	13.8 ± 1.4
	338	10.4 ± 1.3
	348	7.5 ± 1.3
	358	5.4 ± 1.1
	368	3.3 ± 1.1
[C ₆ mim][TF ₂ N]/DAAOT/IPM (R = 0.40)	298	59.2 ± 3.2
	308	37.2 ± 2.2
	318	26.5 ± 1.6
	328	20.2 ± 1.4
	338	18.2 ± 1.2
	348	16.2 ± 1.1
	358	13.3 ± 1.3

^aThe uncertainties for the aggregate sizes denote the uncertainties in the peak position (maxima) of the DLS measurement.

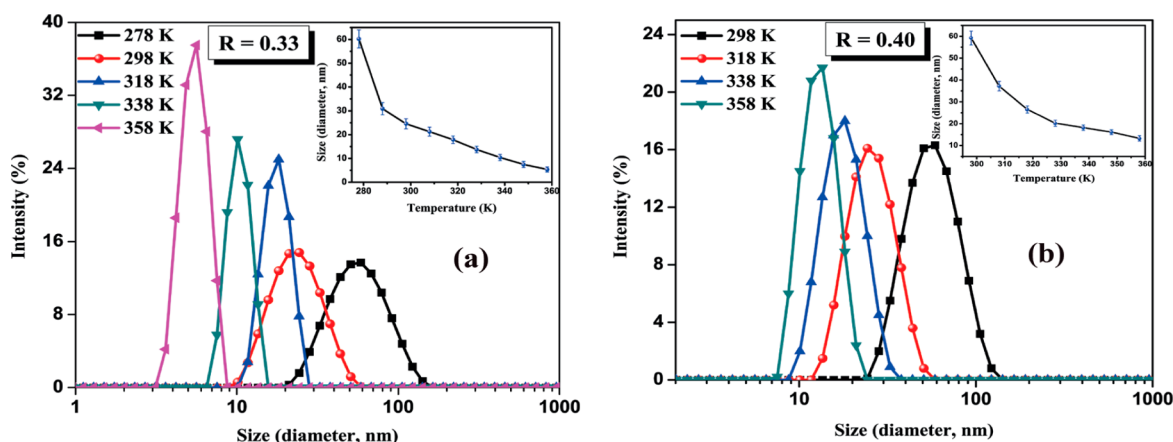


Figure 3. Size distributions of the droplets (measured by DLS) of [C₆mim][TF₂N]/DAAOT/IPM at different temperatures at (a) R = 0.33 and (b) R = 0.40.

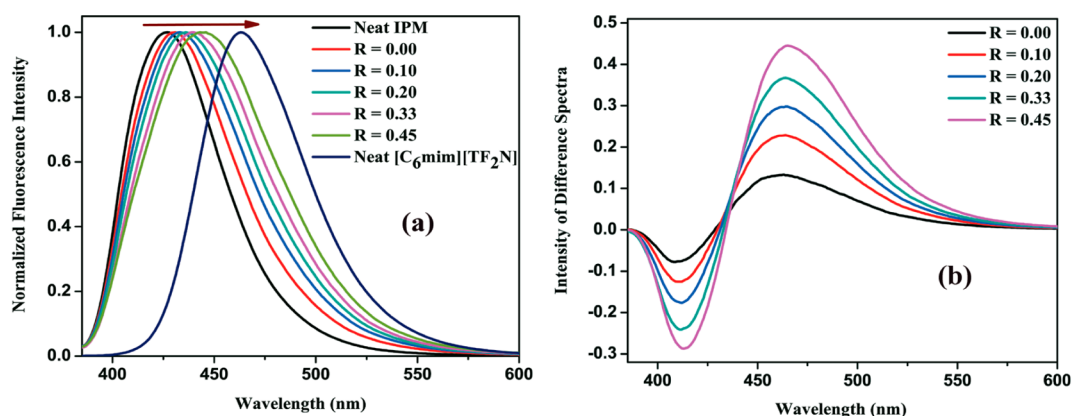


Figure 4. (a) Emission spectra of C-480 in neat IPM, [C₆mim][TF₂N]/DAAOT/IPM microemulsions at different *R* values, and in neat [C₆mim][TF₂N]. (b) Difference spectra of C-480 in [C₆mim][TF₂N]/DAAOT/IPM microemulsions at different *R* values with C-480 in IPM.

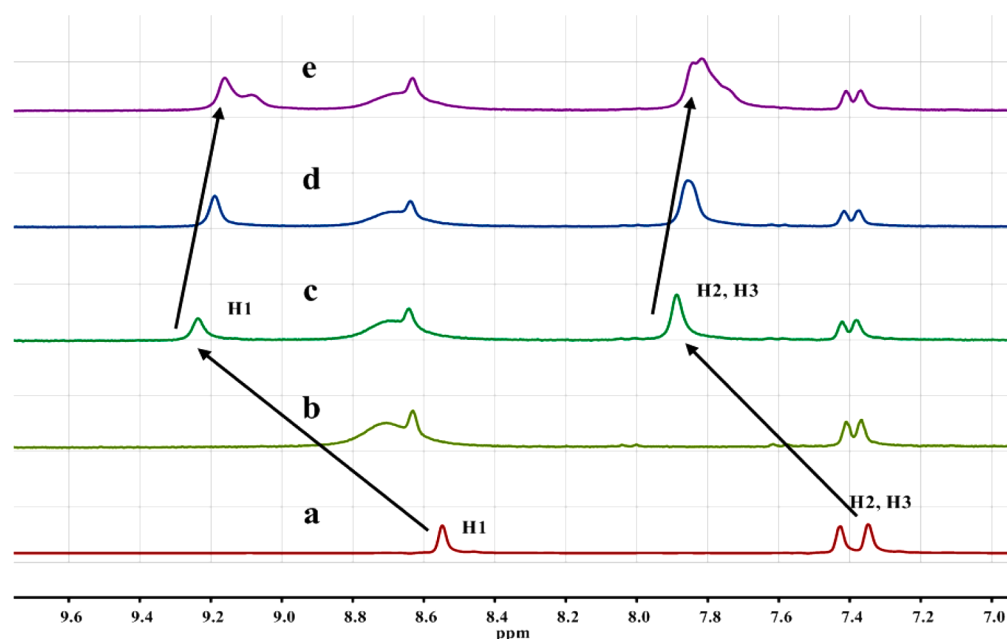


Figure 5. Partial ¹H NMR spectra of neat [C₆mim][TF₂N] (a) and [C₆mim][TF₂N]/DAAOT/IPM microemulsions at *R* = 0.00 (b), 0.20 (c), 0.33 (d), and 0.45 (e).

with the polarity of the environment. In recent years, our group has used C-480 for the characterization of different IL-in-oil microemulsions.^{37,46,55,58} Owing to these studies, we can say that the red shift in emission maximum of C-480 with the gradual addition of ILs is a clear indication of the existence of IL-in-oil microemulsions.

In neat IPM, C-480 shows an emission maximum at 427 nm, and with the addition of DAAOT, the emission maximum gets shifted to 431 nm (Figure 4a). This red shift of emission spectra indicates the partition of the probe molecule from bulk IPM to the polar interior of the DAAOT reverse micelle. Further addition of IL ([C₆mim][TF₂N]) to DAAOT/IPM reverse micelles causes the red shift in the emission maxima. With an increase in ionic liquid content from *R* = 0 to 0.45, the emission maximum is red shifted from 431 to 445 nm (Figure 4a). The gradual red shift of emission maxima with the addition of [C₆mim][TF₂N] clearly indicates the movement of probe molecules toward the polar IL pool of the microemulsion. In neat [C₆mim][TF₂N], C-480 shows emission maximum at 463 nm, indicating higher polarity of neat [C₆mim][TF₂N]

compared to that of the [C₆mim][TF₂N] pool inside the microemulsion. The higher polarity of neat ILs compared to that of the ILs present in the polar core of the microemulsions is well-supported by our earlier observation.⁴⁶

To further support the movement of C-480 toward the IL pool of the microemulsion, we have constructed the fluorescence difference spectra of C-480 in neat IPM and C-480 in [C₆mim][TF₂N]/DAAOT/IPM microemulsions at different *R* values (Figure 4b). Difference spectra of C-480 in [C₆mim][TF₂N]/DAAOT/IPM microemulsions at different *R* values with C-480 in IPM exhibit a negative fluorescence intensity around 412 nm, and there is a distinct peak around 462 nm. The peak centered on ~412 nm is the contribution from C-480 in IPM. With the addition of DAAOT and subsequently [C₆mim][TF₂N] in IPM, the intensity of the peak around 412 nm decreases and the intensity of the peak around 462 nm increases. This clearly indicates that with the addition of IL ([C₆mim][TF₂N]) in DAAOT/IPM reverse micelles, the population of the probe molecule (C-480) in IPM decreases

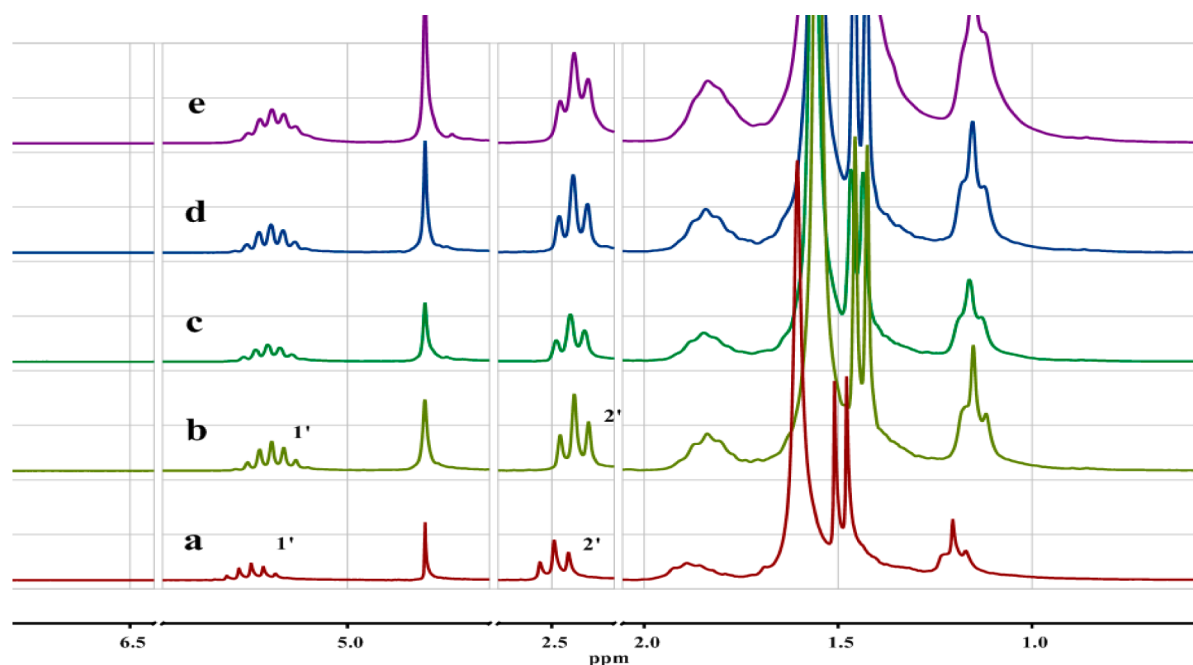


Figure 6. Partial ^1H NMR spectra showing peaks corresponding to IPM solvent in neat IPM (a) and in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at $R = 0.00$ (b), 0.20 (c), 0.33 (d), 0.45 (e).

and the population of C-480 in the IL pool of the microemulsion increases.

3.5. ^1H NMR Spectra. ^1H NMR spectra are taken to provide more detailed information about the intra- and intermolecular interactions and thus provide the microstructure characteristics of the IL-in-oil microemulsions, including the locations of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions. For all the measurements, we used 0.2 M DAAOT in IPM solution. Figure 5 shows a part of the ^1H NMR spectra of neat $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ and $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions at different R values (full NMR spectra are shown in Figure S2 of the Supporting Information). With the addition of IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in DAAOT/IPM reverse micelle, the H1 proton of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ is significantly shifted downfield compared to that of the neat $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ ($\delta = 8.548\text{ ppm}$) (Figure 5). In $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions ($R = 0.2$), the signal associated with the H1 proton of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ appears at $\delta = 9.236\text{ ppm}$, which is 0.688 ppm shifted downfield compared to that of neat $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$. This huge downfield shift is well-supported by many other studies and confirms the incorporation of IL inside the reverse micelle.^{36,59} With further addition of the IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$, that is, with increasing R values from 0.2 to 0.45 , the peak associated with the H1 proton of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ is shifted upfield from 9.236 to 9.116 ppm (Figure 5). This observation is also supported by our earlier work⁴⁸ and by the observations of Falcone et al.³⁶ and Ferreyra et al.⁵⁹ Even though the H1 proton signal of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in microemulsions shifted upfield toward the neat IL with increasing R values, it remains substantially different from that of neat $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$. This once again indicates a new environment for $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions.⁴⁸ The other two protons of the imidazolium ring (H2 and H3) also shifted to downfield positions with the addition of the IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ in DAAOT/IPM reverse micelles, but the shift is relatively small compared to that of the H1 protons. This can be accounted for

by the acidity of the H1 atom, which makes it most sensitive to its environment.^{36,57}

Furthermore, we observed the peak associated with the nonpolar solvent, IPM. A small upfield shift in all the peaks associated with IPM was observed with the addition of DAAOT. This can be accounted for by the interaction of DAAOT with IPM and subsequent formation of reverse micelles. Moreover, with the addition of IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$, the peaks associated with IPM in DAAOT/IPM reverse micelles remain unchanged. This clearly indicates that the added IL $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ gets solubilized in the polar core of the reverse micelle and does not interact with the nonpolar solvent, IPM (Figure 6).

4. CONCLUSIONS

In conclusion, we demonstrated a strategy by which we can formulate IL-in-oil microemulsions exhibiting stability over a wide range of temperatures (278 to $\geq 423\text{ K}$). We characterized $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ microemulsions and showed that the amount of IL within the core of aggregates in microemulsions can be easily manipulated to affect the size of the aggregates directly. We showed that by the use of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ as the polar component we can tune the size of the aggregates in microemulsions from 7.9 to 91.0 nm . This wide range of available nano-sized containers can serve as interesting media in which to perform different reactions. Moreover, the polarity of the $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ pool inside the microemulsion is less than that of neat $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$, which indicates a different environment of the IL.

These high-temperature stable IL-in-oil microemulsions can dissolve a wide variety of ionic liquids, making them suitable for a wide field of potential applications, such as for the synthesis of nanostructured polymers⁶⁰ and for performing chemical reactions.⁶¹

■ ASSOCIATED CONTENT

■ Supporting Information

Information regarding synthesis and characterization of DAAOT and ^1H NMR spectra of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]/\text{DAAOT}/\text{IPM}$ ternary systems. 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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