

Unique role of hydrophilic ionic liquid in modifying properties of aqueous Triton X-100

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Modification of important physicochemical properties of aqueous surfactant solutions can be achieved by addition of environmentally benign room temperature ionic liquids (ILs). While low aqueous solubility of “hydrophobic” ILs limits the amount of IL that may be added to achieve desired changes in the physicochemical properties, hydrophilic ILs do not have such restrictions associated to them. Alterations in the key physicochemical properties of aqueous solutions of a common nonionic surfactant Triton X-100 (TX100) on addition of up to 30 wt % hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) are reported. The presence of micellar aggregates in as high as 30 wt % [bmim][BF₄]-added aqueous TX100 solutions is established by dynamic light scattering and fluorescence probe behavior. Increasing the concentration of [bmim][BF₄] results in decrease in average micellar size and aggregation number and increase in critical micelle concentration, indicating an overall unfavorable aggregation process. Increase in the dipolarity and the microfluidity of the probe cybotactic region within the palisade layer of the micellar phase upon [bmim][BF₄] addition implies increased water penetration and the possibility of TX100-[bmim][BF₄] interactions. While the changes in some of the physicochemical properties indicate the role of [bmim][BF₄] to be similar to a cosurfactant, the IL acts like a cosolvent as far as changes in other properties are concerned. Effectiveness of IL [bmim][BF₄] in modifying physicochemical properties of aqueous TX100 is demonstrated. © 2007 American Institute of Physics. [DOI: 10.1063/1.2785178]

I. INTRODUCTION

Unusual properties of room temperature ionic liquids (ILs) are receiving increased attention from both academic and industrial research communities.¹ Almost every named chemical reaction has been reported in ILs.² Routine and often novel analytical applications of ILs are being reported, evidenced by the rapid growth in the number of publications involving ILs.³ Combined with the fact that ILs are composed entirely of cations and anions but still exist in the liquid state at ambient conditions, the recent investigations on ILs are partly also due to their *potential* environmentally benign nature. Most ILs have almost negligible vapor pressure and can be recycled easily. As a consequence, it is logical to employ these ILs in concert with other environmentally friendly systems such as supercritical fluids,⁴ aqueous⁵ and polymer⁶ solutions, surfactant-based systems,⁷ etc.

Surfactant solutions comprising of normal or reverse micelles are used as media for a variety of chemical analysis and synthesis.⁸ Normal micelles that form within aqueous surfactant solutions above a surfactant concentration (or a concentration range), usually called critical micelle concentration (cmc), are a topic of major interest due to their unusual physicochemical properties as a result of surfactant aggregation.⁸ Aqueous surfactant solutions have enjoyed more attention from the research community partly due to

the environmentally friendly nature inherent to the aqueous-based systems. Aqueous micellar systems have immense technological applications such as flow field regulators, solubilizing and emulsifying agents, membrane mimetic media, and nanoreactors for enzymatic reactions, to name just a few.⁸ At ambient conditions, properties of an aqueous surfactant solution depends, among others, on the identity of the surfactant. As a result, if conditions remain the same, aqueous solutions of a surfactant at a given concentration have more or less fixed physicochemical properties that are difficult to modulate, the usual way to alter/modify the physicochemical properties of a given aqueous surfactant solution is to use external means, such as changes in temperature/pressure and/or addition of a variety of modifiers (e.g., cosolvents, cosurfactants, electrolytes, polar organics, nonpolar organics, etc.).^{8,9} Addition of a judiciously selected environmentally benign substance to modify the desired physicochemical properties of a surfactant solution is both convenient and preferable. Due to their unusual and interesting properties, the role of ILs in this context may turn out to be crucial.

Efforts have been invested by many research groups including our own to study surfactant behavior and the possibility of surfactant self-assembly within ILs.⁷ However, the formation of micelles with altered and desired physicochemical properties within aqueous IL solutions is exciting, useful, and economically convenient. To this end, our recent attempts to modify the properties of aqueous Triton X-100 (TX100, a nonionic surfactant) by adding 2.1 wt % of a com-

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mon and popular IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), resulted in no change in cmc and aggregation number (N_{agg}), representing unchanged overall micellar structure.¹⁰ The limited aqueous solubility of “hydrophobic” [bmim][PF₆] [~2.1 wt % (Ref. 11)] severely restricts the amount of [bmim][PF₆] that may be added to induce changes in the physicochemical properties of aqueous surfactant solutions. Hydrophilic ILs, on the other hand, do not have such aqueous solubility limitations. Consequently, hydrophilic ILs can be used in appreciable amounts such that desired modifications in key physicochemical properties of aqueous surfactant systems may be achieved. Favorable modifications/alterations of the physicochemical properties of aqueous surfactant solutions upon IL addition will expand the overall capabilities and applications of aqueous surfactant systems; utilization potential of ILs will increase as well. The role of IL in property modulation for such purposes will also be established. As an effort toward this, we present the changes in the properties of aqueous TX100 (a common non-ionic surfactant) in the presence of varying concentration of a hydrophilic IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]). IL [bmim][BF₄] is completely miscible in water at ambient conditions,¹ and as a result, we are able to investigate the properties of aqueous TX100 with as high as 30 wt % added [bmim][BF₄].

II. EXPERIMENTAL

A. Materials

TX100 [polyoxyethylene(10)octylphenyl ether, scintillation grade] was obtained from SISCO Research Laboratories and was used as received. IL [bmim][BF₄] (Merck, ultrapure, halide content <10 ppm, water content <10 ppm) was also used as received. Doubly distilled de-ionized water was obtained from a Millipore, Milli-Q Academic water purification system having ≥ 18 M Ω cm resistivity. The following materials were used as received: pyrene and pyrene-1-carboxaldehyde from Sigma-Aldrich, cetylpyridinium chloride (CPC) from Acros Organics, and 1,3-bis(1-pyrenyl)propane and rhodamine 6G from Molecular Probes. Ethanol (99.9%) was obtained from sd fine-chem. Ltd.

B. Methods

Required amounts of materials were weighed using Mettler Toledo AB104-S balance with a precision of ± 0.1 mg. Stock solutions of the fluorescence probes were prepared in ethanol and stored in precleaned amber glass vials at ~ 4 °C. TX100 and CPC solutions were freshly prepared in doubly distilled de-ionized water. Aqueous TX100 solutions of the probes were prepared by taking appropriate aliquots of the probes from the stock and evaporating ethanol using a gentle stream of high purity nitrogen gas. Aqueous TX100 of desirable concentration was added to achieve the required final probe concentration. Precalculated amount of [bmim][BF₄] was directly added to the aqueous TX100 solutions. Complete solubilization of each probe was confirmed via uv-vis molecular absorbance and/or fluorescence intensity measurements.

The dynamic light scattering experiments were performed on a particle size analyzer, model nano ZS90 (Malvern Instruments, UK). A He-Ne laser with a power of 4 mW was used as a light source. All the measurements were done at a scattering angle of 90° and a temperature of 25 °C, which was controlled by means of a thermostat. Fluorescence spectra were acquired on model FL 3-11, Fluorolog-3 modular spectrofluorometer with single Czerny-Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and photomultiplier tube (PMT) as the detector purchased from Horiba-Jobin Yvon, Inc. A Perkin-Elmer Lambda Bio 20 double beam spectrophotometer with variable bandwidth was used for acquisition of the uv-vis molecular absorbance. All the data were acquired using 1 cm² path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis. All the measurements were taken in triplicate and averaged. Conductivity measurements were carried out on a CM-183 μ p-based electrolyte conductivity and total dissolved solids analyzer with automatic temperature compensation probe and conductivity cell (CC-03B) purchased from Elico Ltd., India. All data analysis was performed using Microsoft Excel and/or SIGMAPLOT 8.0 softwares.

The fluorescence anisotropy (r) is given by¹²

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}, \quad (1)$$

where I_{\parallel} and I_{\perp} are the parallel and perpendicularly polarized components of the emitted radiation when the fluorophore is excited with vertically polarized light. We have used the L-format method to measure r , which is expressed as¹²

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}, \quad (2)$$

where

$$G = \frac{I_{HV}}{I_{HH}}, \quad (3)$$

where I_{VV} and I_{VH} are the vertically and horizontally polarized emissions resulting from vertically polarized excitation, respectively. In the expression for the G factor, I_{HV} and I_{HH} are similarly the vertically and horizontally polarized emissions resulting from horizontally polarized excitation, respectively.

III. RESULTS

A. Dynamic light scattering and size of micellar aggregates

Dynamic light scattering (DLS) is utilized in our case to obtain evidence of aggregate formation within aqueous TX100 in the presence of up to 30 wt % [bmim][BF₄] at ambient conditions. The size and distribution of the TX100 micellar aggregates in the presence of varying amount of [bmim][BF₄] are examined by DLS data as well. Figure 1 shows the scattering intensity for the given diameter (D) measured at room temperature of aqueous 200 mM TX100 in the absence and presence of 2, 5, 10, 20, and 30 wt %

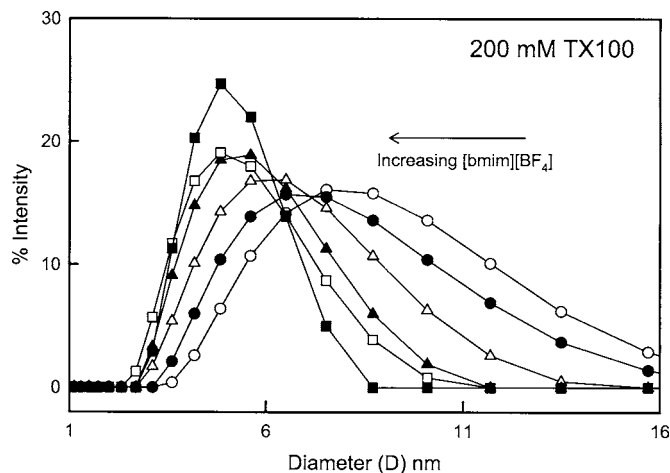


FIG. 1. Dynamic light scattering (DLS) results of 200 mM aqueous TX100 in the presence of increasing concentration of [bmim][BF₄] at ambient conditions: 0 wt % (○), 2 wt % (●), 5 wt % (△), 10 wt % (▲), 20 wt % (□), and 30 wt % (■).

[bmim][BF₄]. Monomodal distributions are observed at all added [bmim][BF₄]. The most noteworthy outcome of our DLS data is the evidence of the presence of micellelike aggregates when 30 wt % [bmim][BF₄] is added to 200 mM aqueous TX100 solution. The hydrodynamic Z-average diameters (Z_{av}) as well as the peak diameters for [bmim][BF₄]-added aqueous TX100 solutions obtained from DLS measurements for 50 and 200 mM TX100 are listed in Table I. It is clear from the DLS results that, in general, average micellar (or aggregate) size decreases as more and more [bmim][BF₄] is added to the aqueous solution of TX100. It is important to mention that our average diameter of aqueous TX100 micelles is similar to that reported in literature.¹³ Another interesting outcome is the reduction in the full width at half height of the DLS-determined size profiles as more and more [bmim][BF₄] is added. The micellar size distribution narrows considerably upon addition of [bmim][BF₄] demonstrating that the micellar assemblies are more monodisperse in the presence of IL.

B. Fluorescence probe behavior and critical micelle concentration

Fluorescence probes are routinely used to obtain various micellar parameters of interest, such as cmc, N_{agg} , dipolarity,

and microfluidity, among others.^{8,12} The location of a fluorescence probe in the micellar medium depends on the molecular structure of the fluorophore as well as on the properties of the micellar solution (e.g., type and nature of surfactant, properties of the micelles, nature of the bulk solvent, etc.).^{8,12} We have utilized two fluorescence probes, pyrene and pyrene-1-carboxaldehyde, to obtain information on cmc and dipolarity of [bmim][BF₄]-added aqueous TX100 solutions.

1. Behavior of pyrene

Pyrene (Py) is one of the most popular fluorescence probes to study dipolarity within organized media.¹⁴ The pyrene polarity scale, defined by the ratio I_I/I_{III} of the monomer fluorescence intensities at bands I (0-0 band, ~373 nm) and III (~384 nm), is a function of solvent dielectric (ϵ) and refractive index (n) via the dielectric cross term [$f(\epsilon, n^2)$]. Pyrene I_I/I_{III} changes dramatically with change in the dipolarity of the cybotactic region of this probe—more polar microenvironment results in a higher I_I/I_{III} and vice versa.¹⁴ Pyrene fluorescence spectra were collected from solutions of varying [TX100] in the presence of different concentrations of [bmim][BF₄]. Figure 2 shows the variation in I_I/I_{III} versus $\log[\text{TX100}]$ for 0, 2, 10, 20, and 30 wt % added [bmim][BF₄]. The curves are the fit of the data to a simplistic sigmoidal equation. The pyrene fluorescence provides interesting and useful information on [bmim][BF₄]-added aqueous TX100 solutions. The onset of micelle formation *even* in the presence of 30 wt % added [bmim][BF₄] is clearly apparent as nonpolar pyrene partitions into the hydrophobic micellar phase upon its formation, resulting in an abrupt decrease in I_I/I_{III} . This abrupt decrease in I_I/I_{III} forms the basis of cmc determination for micelle-forming surfactant solutions. Based on earlier reported ambiguity,¹⁵ we have found empirically that by normalizing the total sigmoidal response in I_I/I_{III} to 1.00, the cmc can be reasonably estimated as the concentration at which the amplitude has decayed to 0.01.¹⁶ The recovered cmc's are reported in Table II. It is noteworthy that cmc increases with increasing concentration of [bmim][BF₄] in TX100 solutions. As a matter of fact, ~400 times increase in cmc is observed when 30 wt % [bmim][BF₄] is added to aqueous TX100. Our TX100 cmc is in good agreement with that reported in literature.^{8(h)} Most importantly, as suggested by the DLS re-

TABLE I. Effect of the addition of IL [bmim][BF₄] on the diameter of micellar aggregates within aqueous TX100 at ambient conditions obtained from DLS measurements.

Concentration of [bmim][BF ₄]		50 mM TX100		200 mM TX100	
wt %	mM	Z_{av} (nm)	Peak diameter (nm)	Z_{av} (nm)	Peak diameter (nm)
0	0	8.1±0.2	8.3±0.1	8.4±0.2	8.6±0.1
2	89	8.9±0.4	7.4±0.1	6.9±0.3	7.6±0.1
5	223	7.8±0.2	6.7±0.1	5.8±0.2	6.5±0.2
10	450	6.7±0.2	6.5±0.2	5.2±0.3	5.6±0.2
20	915	6.4±0.3	6.6±0.2	5.0±0.3	5.3±0.2
30	1397	4.9±0.2	5.1±0.1

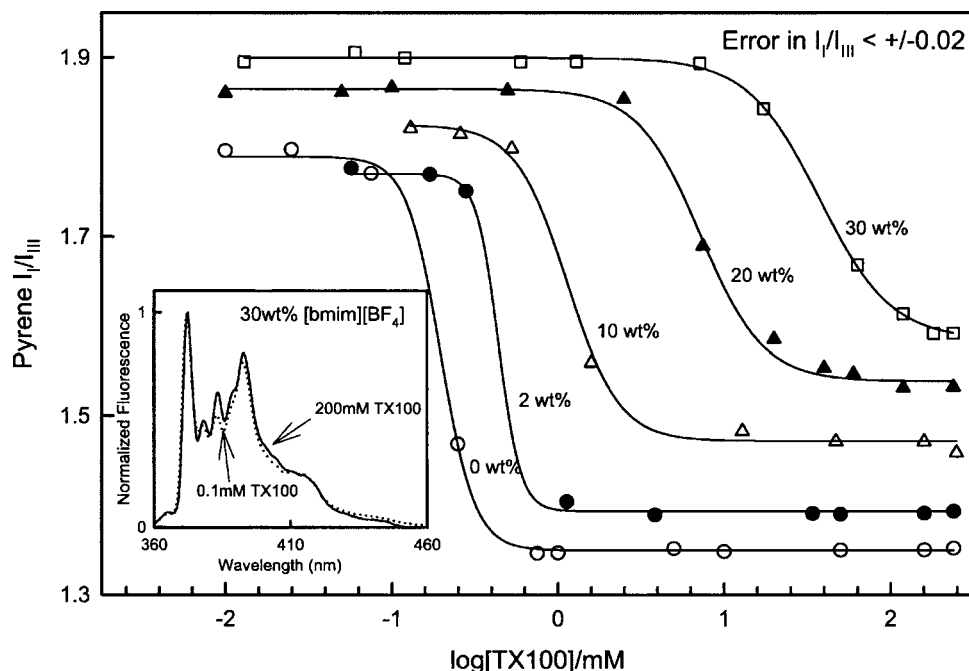


FIG. 2. Pyrene (1 μM) I_1/I_{III} vs $\log[\text{TX100}]$ in the presence of different wt % of $[\text{bmim}][\text{BF}_4]$ at ambient conditions. Inset shows pyrene emission spectra in the presence of 30 wt % $[\text{bmim}][\text{BF}_4]$ in pre-micellar (0.1 mM TX100, dotted) and post-micellar (200 mM TX100, solid) aqueous solutions ($\lambda_{\text{ex}}=337$ nm and slit widths=2 and 1 nm).

results earlier, micelle formation within aqueous TX100 in the presence of as high as 30 wt % $[\text{bmim}][\text{BF}_4]$ is clearly evident.

Information regarding the changes in the dipolarity of pyrene solubilization within TX100 upon $[\text{bmim}][\text{BF}_4]$ addition is obtained from I_1/I_{III} plateau values at $[\text{TX100}]$ well below and well above cmc [Fig. 3 panel (A)]. These results reveal several interesting outcomes. As expected based on preferential partitioning of pyrene into the micellar phase, I_1/I_{III} are much lower above cmc as compared to those below cmc irrespective of $[\text{bmim}][\text{BF}_4]$ concentration in the solution. Effect of $[\text{bmim}][\text{BF}_4]$ addition on I_1/I_{III} shows similar trends in both pre- and postmicellar regions; I_1/I_{III} increases with increase in $[\text{bmim}][\text{BF}_4]$ concentration. It is interesting to note that the increase in dipolarity is more dramatic when micelles are present ($\Delta I_1/I_{III} \sim 0.13$ below cmc versus ~ 0.24 above cmc upon 30 wt % $[\text{bmim}][\text{BF}_4]$ addition). It is important to mention that in the presence of similar $[\text{bmim}][\text{BF}_4]$ amount in *neat* water, the increase in I_1/I_{III} is

statistically insignificant (increase of only ~ 0.01 in I_1/I_{III} is observed). Based on these observations, the presence of interaction(s) between $[\text{bmim}][\text{BF}_4]$ and TX100 may be suggested. Since it is well established that on the average pyrene locates itself in the palisade layer,¹⁷ it is inferred that $[\text{bmim}][\text{BF}_4]$ may be preferentially partitioning into the micellar pseudophase due to which the dipolarity of pyrene cybotactic region is considerably increased.

2. Behavior of pyrene-1-carboxaldehyde

Another fluorescence probe with distinct structural differences that has found utility in studies of solution and interfacial polarity is pyrene-1-carboxaldehyde (PyCHO).¹⁸ PyCHO has two types of closely lying excited singlet states ($n-\pi^*$ and $\pi-\pi^*$), both of which show emission in fluid solution. In a nonpolar solvent, the emission from PyCHO is highly structured and weak ($\phi_F < 0.001$) arising from the $n-\pi^*$ state. On increasing the polarity of the medium, however, the $\pi-\pi^*$ state is brought below the $n-\pi^*$ state via solvent relaxation to become the emitting state. This is manifested by a broad, reasonably intense emission (e.g., $\phi_F \approx 0.15$ in MeOH) that redshifts with increasing solvent dielectric. Change in fluorescence quantum yield (or under suitable assumptions, fluorescence intensity) and shift in fluorescence wavelength maxima can both be utilized effectively to probe a micellar system. Figure 4 presents PyCHO fluorescence intensity as a function of $\log[\text{TX100}]$ in the presence of different amounts of $[\text{bmim}][\text{BF}_4]$. As expected, fluorescence intensity decreases significantly upon micelle formation as the probe molecules are partitioned into the micellar phase where they encounter more hydrophobic microenvironment. As described earlier for pyrene, cmc's are evaluated from the sigmoidal nature of the changes (Table II)

TABLE II. Critical micelle concentration (cmc) and aggregation number (N_{agg}) of aqueous TX100 in the presence of $[\text{bmim}][\text{BF}_4]$ at ambient conditions.

$[\text{bmim}][\text{BF}_4]$ (wt %)	cmc (mM)		N_{agg}
	From pyrene I_1/I_{III}	From PyCHO fluorescence intensity	
0	0.25–0.50	0.25–0.50	94 \pm 5
2	0.5–1.0	0.5–1.0	86 \pm 6
5	1.5–2.5	1.5–2.5	72 \pm 7
10	3.0–4.5	4.0–6.0	56 \pm 8
20	20–30	25–35	45 \pm 8
30	90–110	90–110	16 \pm 9

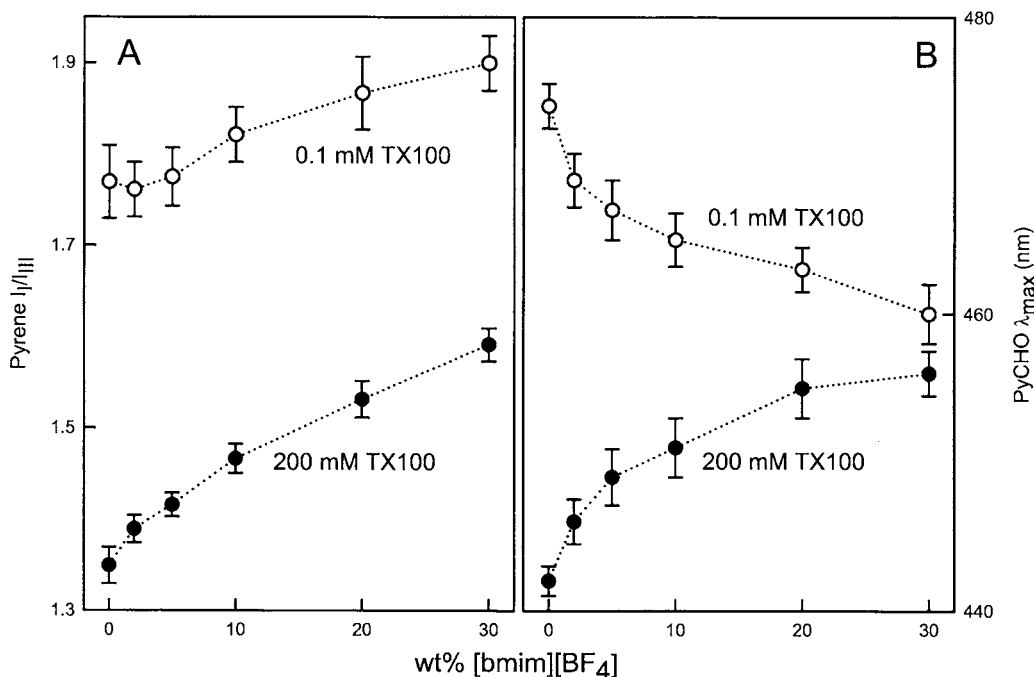


FIG. 3. Pyrene ($1 \mu\text{M}$) I_1/I_{III} [panel (A)] and PyCHO ($1 \mu\text{M}$) fluorescence maxima λ_{max} [panel (B)] vs wt % of [bmim][BF₄] in pre-micellar (0.1 mM TX100, ○) and post-micellar (200 mM TX100, ●) aqueous solutions at ambient conditions.

and are found to be statistically similar to those obtained from pyrene I_1/I_{III} .

Figure 3 [panel (B)] presents changes in lowest energy fluorescence maxima (λ_{max}) of PyCHO upon [bmim][BF₄] addition to aqueous TX100 before (0.1 mM TX100) and after (200 mM TX100) micellar formation. A hypsochromic shift in λ_{max} upon [bmim][BF₄] addition prior to cmc is easily conceivable in the light of earlier reports (PyCHO λ_{max} in

water and [bmim][PF₆] are 475 ± 2 and 428 ± 2 nm, respectively).^{5(a)} Similar decrease in λ_{max} is also observed when [bmim][BF₄] is added to neat water.¹⁹ A surprising trend in PyCHO λ_{max} is observed in the postmicellar region; the λ_{max} increases from 442 ± 2 nm in the absence of [bmim][BF₄] to 456 ± 2 nm in the presence of 30 wt % [bmim][BF₄]. Presumably, these differences reflect changes

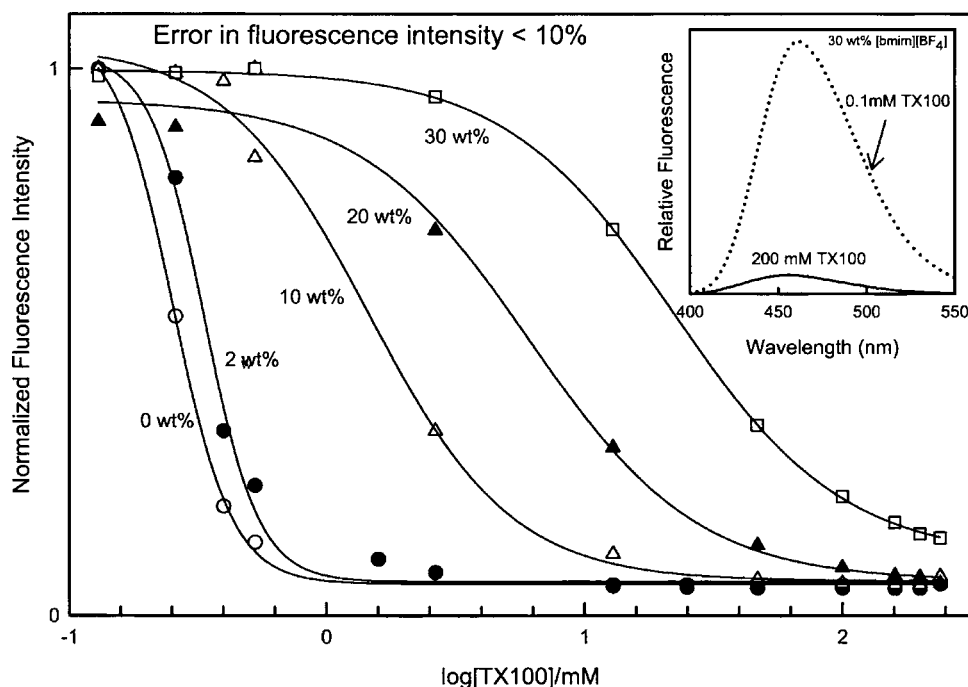


FIG. 4. PyCHO ($1 \mu\text{M}$) fluorescence intensity vs $\log[\text{TX100}]$ in the presence of different wt % of [bmim][BF₄] at ambient conditions. Inset shows PyCHO emission spectra in the presence of 30 wt % [bmim][BF₄] in pre-micellar (0.1 mM TX100, dotted) and post-micellar (200 mM TX100, solid) aqueous solutions ($\lambda_{ex}=365$ nm and slit widths=2 and 2 nm).

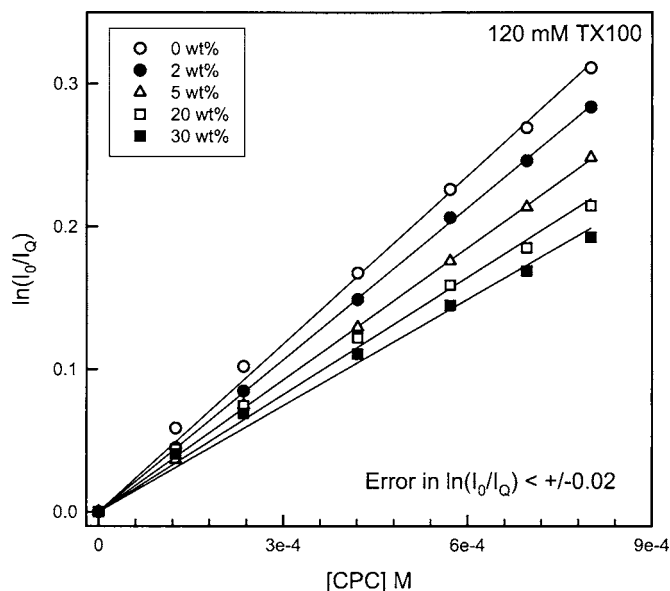


FIG. 5. Pyrene ($1 \mu\text{M}$) fluorescence quenching by CPC in 120 mM aqueous TX100 in the presence of different wt % of $[\text{bmim}][\text{BF}_4]$ at ambient conditions. Solid lines represent the results of the linear regression analysis.

in the locus of solubilization in the micellar pseudophase, the water and/or $\text{bmim}^+/\text{BF}_4^-$ accessibility, and the packing parameter.⁸ It is important to mention that the suggested increase in PyCHO cybotactic region dipolarity in the presence of $[\text{bmim}][\text{BF}_4]$ within the micellar solution is in agreement with that reported by pyrene earlier.

C. Fluorescence quenching and aggregation number

The aggregation number of TX100 micelles in the presence of $[\text{bmim}][\text{BF}_4]$ was obtained by fluorescence quenching of pyrene by cosurfactant CPC according to the following equation:^{20(d),21}

$$\begin{aligned} \ln\left(\frac{I_0}{I_Q}\right) &= \frac{Q_{\text{micelle}}}{[\text{micelle}]} \\ &= \frac{[\text{CPC}]_{\text{micelle}}}{[\text{micelle}]_{\text{TX100}}} \\ &= [\text{CPC}]_{\text{micelle}} \left(\frac{N_{\text{agg}}}{[\text{TX100}] - \text{cmc}_{\text{TX100}}} \right), \end{aligned} \quad (4)$$

where I_0 and I_Q are the fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively. Q_{micelle} (or $[\text{CPC}]_{\text{micelle}}$), $[\text{micelle}]_{\text{TX100}}$, and $[\text{TX100}]$ are the concentrations of quencher CPC within the micellar phase, TX100 micelles, and TX100 surfactant, respectively. Plots of $\ln(I_0/I_Q)$ vs $[\text{CPC}]_{\text{micelle}}$ for pyrene quenching by CPC within $[\text{bmim}][\text{BF}_4]$ -added 120 mM aqueous TX100 presented in Fig. 5 suggest good linear behavior ($0.9950 \leq r^2 \leq 0.9998$) at each addition of $[\text{bmim}][\text{BF}_4]$ in the interval of 0–30 wt %. More importantly, the recovered slope decreases significantly with increasing concentration of $[\text{bmim}][\text{BF}_4]$. From Eq. (4), N_{agg} is calculated using the cmc obtained earlier and reported in Table II. Decrease in slope in concert with increase in cmc upon $[\text{bmim}][\text{BF}_4]$ addition to aqueous TX100 results in a significant decrease in N_{agg} from 94 ± 5 in

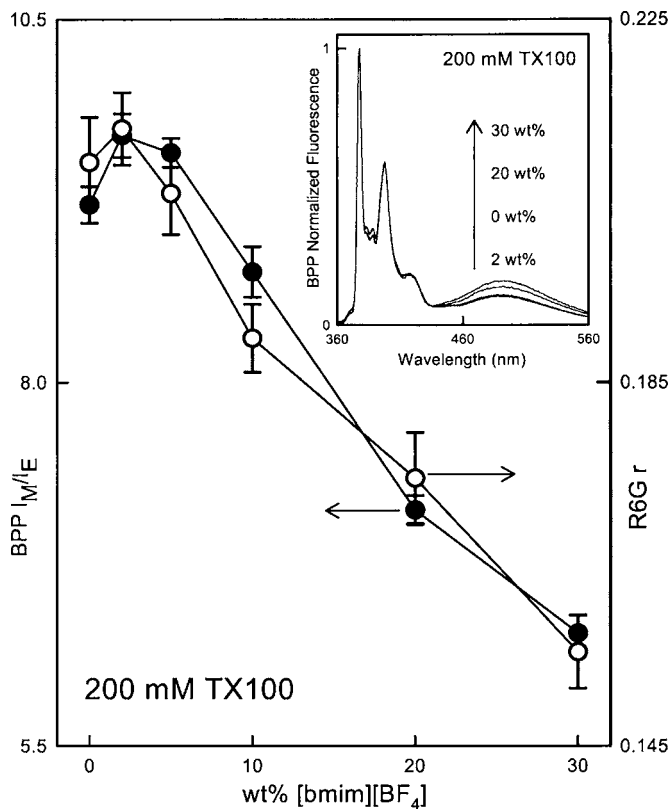


FIG. 6. BPP ($1 \mu\text{M}$) I_M/I_E (\bullet) and R6G ($1 \mu\text{M}$) r (\circ) vs wt % of $[\text{bmim}][\text{BF}_4]$ within 200 mM aqueous TX100 at ambient conditions. Inset shows BPP ($1 \mu\text{M}$) emission spectra within 200 mM aqueous TX100 in the presence of different wt % of $[\text{bmim}][\text{BF}_4]$ ($\lambda_{\text{ex}}=337 \text{ nm}$ and slit widths = 2 and 2 nm).

the absence of $[\text{bmim}][\text{BF}_4]$ to 16 ± 9 in the presence of 30 wt % $[\text{bmim}][\text{BF}_4]$. Our aqueous TX100 N_{agg} is in good agreement with that reported in the literature.²²

D. Microfluidity from 1,3-bis-(1-pyrenyl)propane and rhodamine 6G fluorescence

1. Behavior of 1,3-bis-(1-pyrenyl)propane

A change in the fluidity of the immediate microenvironment surrounding a probe is effectively manifested through 1,3-bis-(1-pyrenyl)propane (BPP) steady-state emission spectra.^{12,14,23,24} It is well established that, in addition to a usual structured monomer fluorescence band, the emission spectrum of this compound exhibits a broad and structureless band with maximum intensity in the vicinity of 450–500 nm due to the fluorescence from intramolecular excimer. In a low-viscous milieu, the two pyrenes easily fold together to form an intramolecular excimer. As the microviscosity of the cybotactic region increases, the efficiency of the excimer formation decreases and a corresponding reduction in the intensity of the excimer band is observed.

BPP emission spectra in 200 mM aqueous TX100 in the presence of 0, 2, 20, and 30 wt % $[\text{bmim}][\text{BF}_4]$ are presented in Fig. 6 (inset). Due to its hydrophobic nature, BPP preferably partitions into the micelles, thus reporting on the microfluidity of the micellar phase.²⁴ An initial slight increase in monomer to excimer emission intensity ratio (I_M/I_E , Fig. 6) on addition of 2 wt % $[\text{bmim}][\text{BF}_4]$ to aqueous TX100 is

in agreement with what was observed earlier for similar addition of hydrophobic IL [bmim][PF₆] to aqueous TX100.¹⁰ IL [bmim][BF₄] is significantly viscous,^{1(k)} and a decrease in microfluidity upon [bmim][BF₄] addition to 200 mM TX100 is easily conceivable. However, we were surprised to learn that further increase in [bmim][BF₄] concentration resulted in *decrease* in I_M/I_E (Fig. 6), manifesting an increase in microfluidity of the BPP cybotactic region upon [bmim][BF₄] addition to 200 mM TX100.

2. Behavior of rhodamine 6G

Fluorescence anisotropy, the extent of the polarization of the emitted radiation, depends on the size/shape of the rotating fluorescence probe as well as on the microfluidity of its cybotactic region.¹² In general, the higher the microfluidity of the cybotactic region, the lower the fluorescence anisotropy. As a result, fluorescence anisotropy may be used as a tool to investigate cybotactic region microfluidity in a variety of complex media, such as micelles, microemulsions, sol-gel-derived glasses, etc.⁸

Figure 6 presents rhodamine 6G steady-state fluorescence anisotropy (R6G r) within [bmim][BF₄]-added 200 mM aqueous TX100. It is convenient to note that the trend in R6G r with increasing concentration of [bmim][BF₄] is similar to that shown by BPP I_M/I_E . However, the fact that R6G r decreases with increasing wt % of [bmim][BF₄] within aqueous TX100 showing an increase in microfluidity of the R6G microenvironment remains counter-intuitive. The reason for these observations may be traced to the changes in the partitioning of these microfluidity probes and locus of solubilization within the micellar pseudophase, the water and/or $\text{bmim}^+/\text{BF}_4^-$ accessibility, and the packing parameter (*vide infra*).

E. Conductance of aqueous TX100 in the presence of [bmim][BF₄]

Conductance measurements may provide information on the degree of dissociation of an electrolyte in aqueous solution.^{8,16,25} We have measured conductance as a function of [TX100] in the presence of varying amount of [bmim][BF₄] at ambient condition. Figure 7 presents conductance of aqueous TX100 in the absence (open circles) and presence (filled circles) of 20 wt % [bmim][BF₄]. The conductance of aqueous TX100 increases with increase in [TX100] in the absence of [bmim][BF₄]. This increase is attributed, in part, to the presence of increased amount of dissociated TX100. It is important to mention that conductivity is not the best of the methods to ascertain cmc of a *nonionic* surfactant.⁸ Therefore, our aim was not to determine cmc here but to obtain information on changes in the properties of aqueous TX100 solution upon [bmim][BF₄] addition. As expected, addition of 20 wt % [bmim][BF₄] increases the conductance of the solution drastically; however, the trend in conductance shown by aqueous TX100 in the presence of 20 wt % [bmim][BF₄] is unusual. Contrary to the results of aqueous TX100 with no [bmim][BF₄], conductance decreases with increase in [TX100]. It is important to mention that the trend in conductance versus [TX100] is

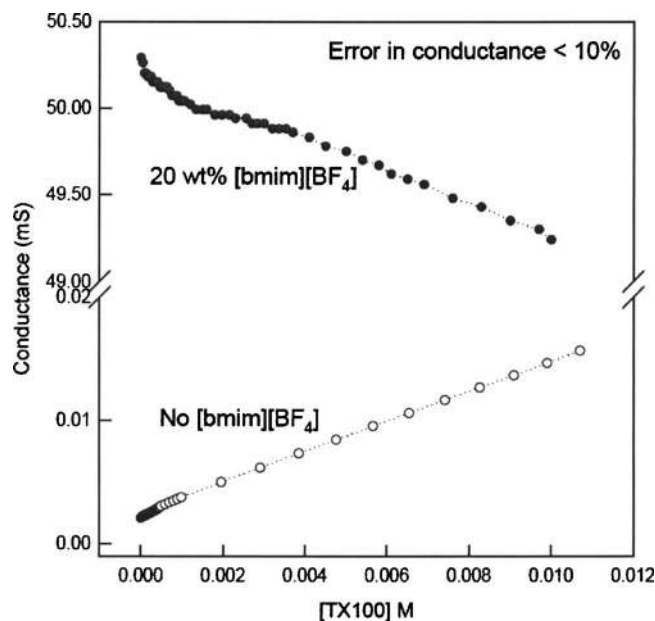


FIG. 7. Conductance of aqueous TX100 in the absence (○) and presence of 20 wt % [bmim][BF₄] (●) at ambient conditions.

similar in the presence of [bmim][BF₄] irrespective of its amount in the solution. Since the contribution of TX100 toward the total conductance of the solution in the presence of [bmim][BF₄] is rather insignificant (conductance in the microsiemen region with only TX100 in the solution, whereas it is in the millisiemen range in the presence of [bmim][BF₄]), the degree of dissociation of [bmim][BF₄] within the surfactant solution must account for the observed decrease in the conductance. It is likely that this decrease stems from the association of [bmim][BF₄] and/or $\text{bmim}^+/\text{BF}_4^-$ with surfactant monomers and/or premicellar assemblies in the solution as the [TX100] is below cmc for surfactant solution with 20 wt % [bmim][BF₄].

IV. DISCUSSION

Addition of hydrophilic IL [bmim][BF₄] results in significant changes in the properties (micellar size, cmc, N_{agg} , solute solvation environment, microfluidity, conductance, etc.) of aqueous TX100. One of the most important outcomes is the evidence of micellelike aggregation within aqueous TX100 solutions in the presence of as high as 30 wt % [bmim][BF₄]. The results presented may shed light on the role of IL [bmim][BF₄] in modifying the properties of aqueous TX100 solutions.

We have observed a decrease in average micellar size and N_{agg} along with an increase in cmc as increasing amount of [bmim][BF₄] is added to aqueous TX100 solutions. It is interesting to note that as far as micellar size is concerned, Mishael and Dubin have observed an increase in TX100 micellar diameter upon addition of up to 30 mM toluene when dissolved in 0.5M aqueous NaCl.^{13(a)} A drastic increase in Z-average diameter is also demonstrated when a cationic lipidic dendron is added to the TX100 micellar solution.^{13(b)} Surprisingly, when similar concentrations of another IL ([bmim][Br]) are added to the aqueous solutions of a block copolymer, PEO-PPO-PEO Pluronic P104, again, a dramatic

increase in the effective diameter of the micelles formed by the nonionic copolymer is observed.²⁶ Finally, addition of common alkali metal salts such as LiCl, NaCl, KCl, and CsCl to aqueous TX100 also resulted in increase in micellar size.^{22(a),27} Our results are in stark contrast with these reports. It is suggested that the role of [bmim][BF₄] in altering the properties of aqueous TX100 might be different from that of an alkali salt or a nonpolar organic cosolvent. The behavior of [bmim][BF₄], in this context, seems to be different from that of alcohols as well. The evidence originates from the fact that 0.1M methanol and ethanol do not affect TX100 cmc; however, as the alkyl chain length is increased from 1-propanol to 1-pentanol, a significant decrease in cmc results.²⁸ Considerable increase in N_{agg} is also reported when alkali metal salts are added to aqueous TX100 in amounts similar to that of [bmim][BF₄] in our studies.^{22(a),27} Finally, the microviscosity of aqueous TX100 is also shown to increase when an alkali metal salt is added to the solution.²⁹

It is interesting to note that addition of common cationic surfactants, cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), and dodecyltrimethylammonium bromide (DTAB), to aqueous TX100 results in increase in the cmc of mixed micelles thus formed.^{30(a)} The trends in increase in cmc upon addition of alkyltrimethylammonium bromides are similar to what we have observed with [bmim][BF₄] addition to aqueous TX100. Importantly, the increase in cmc becomes more prominent as the alkyl chain length of the cationic cosurfactant is decreased. It is important to pinpoint that the extent of increase in cmc with [bmim][BF₄] addition is significantly more drastic than that with DTAB addition to aqueous TX100. Addition of an anionic surfactant sodium dodecylsulfate (SDS) to aqueous TX100 also results in an increase in cmc.^{30(b)} Consequently, it may not be too farfetched to infer that bmim⁺ with associated butyl chain may align itself along with the TX100 within the micelles to act similar to a cosurfactant than a cosolvent or a salt. A decrease in size and N_{agg} also suggests the same. However, one should refrain from any generalized proposition indicating the role of [bmim][BF₄] to be similar to that of a cosurfactant *alone*. As the fluorescence probes pyrene and PyCHO are preferentially solubilized close to the micellar surface in the palisade layer, the average dipolarity of the cybotactic region reported by these probes may reflect the extent of water and/or IL [bmim][BF₄] penetration into the micellar phase. The state of IL [bmim][BF₄] [e.g., degree of dissociation, interaction(s) with TX100, etc.] within the palisade layer will also have significant contribution to the probe response. With addition of DTAB, TTAB, and CTAB to aqueous TX100, the dipolarity reported by pyrene I_1/I_{III} decreases, indicating a smaller water penetration into the mixed micellar phase.^{30(a)} In contrast, our observations indicate an increase in the dipolarity of the microenvironment of pyrene and PyCHO in the postmicellar region on [bmim][BF₄] addition. As argued in the case of cationic surfactant addition to TX100, the reason for these observations may be tentatively attributed to the interaction(s) of bmim⁺ and/or BF₄⁻ with TX100 within the micellar phase in such a manner to “open up” the micelles to allow increased water penetration. However, the

presence of bmim⁺ and/or BF₄⁻ within the first few solvation shells of the probes will also result in an increase in the dipolarity of the cybotactic region (or the palisade layer).

Significant increase in cmc and decrease in N_{agg} upon [bmim][BF₄] addition imply a thermodynamically “unfavorable” micellization within aqueous TX100. These outcomes may also result from the reduction in hydrophobic effects that are responsible for micelle formation.⁸⁽ⁱ⁾ Addition of a polar cosolvent, e.g., acetonitrile, ethanol, etc., to aqueous TX100 also results in similar changes; the extent of changes is not as prominent though.⁸⁽ⁱ⁾ In this context, the role of [bmim][BF₄] as a polar cosolvent when present in higher concentrations may not be ignored. Decrease in conductance as the [TX100] is increased in the presence of [bmim][BF₄] provides additional support to this claim. This decrease in conductance is attributed to the presence of [bmim][BF₄] within TX100 micelles in the state of decreased ionic dissociation as a result of the nature of the [bmim][BF₄] solubilization site within TX100 micelles which is relatively hydrophobic/nonpolar in nature. Consequently, in this respect, the [bmim][BF₄] is more like a cosolvent. It is important to mention, however, that interaction of TX100 with bmim⁺ and/or BF₄⁻ via ion-dipole (ion of IL and dipole of TX100) and/or hydrogen bonding (hydroxyl H of TX100 and BF₄⁻ and/or hydroxyl/ethoxy oxygens of TX100 with C-2 hydrogen of bmim⁺) may decrease the overall ionic character of the solution resulting in decreased solution conductance. On the molar basis, [bmim][BF₄] is always in abundance as compared to TX100. Both of the reasons mentioned above would result in decreased overall conductance of the aqueous TX100 solution.

The most counterintuitive are the results of the microfluidity probes BPP and R6G due to significantly high viscosity associated to most ILs including [bmim][BF₄].^{1(k)} As a result, increase in microfluidity within aqueous TX100 on addition of up to 30 wt % [bmim][BF₄] is not easily conceivable. One may erroneously wish to assign the increase in microfluidity on [bmim][BF₄] addition to the decreased micellar concentration, thus decreasing equilibrium concentration of probes partitioned into the micellar phase. However, calculations suggest an increase in micelle concentration $[\text{micelles}] = ([\text{TX100}] - \text{cmc})/N_{agg}$ as the amount of [bmim][BF₄] in aqueous TX100 is increased. Therefore, the increased microfluidity of micellar TX100 on [bmim][BF₄] addition may be tentatively attributed to the increased water penetration to the micellar phase. Apparently, interaction of bmim⁺ and/or BF₄⁻ with TX100 along with the presence of [bmim][BF₄] within the micellar phase allows increased water penetration. This is further substantiated by decreased N_{agg} and micellar size and increased cmc (*vide supra*). Microfluidity probes BPP and R6G that are solubilized within a more viscous (and protected) TX100 micellar phase in the absence of [bmim][BF₄] are exposed to more water as micelles become smaller with less number of TX100 monomers to form them as a significant amount of [bmim][BF₄] is added to aqueous TX100 solutions. Another contribution to the aforementioned observation may come from the possibility that [bmim][BF₄] and/or bmim⁺/BF₄⁻ are incorporated into the micelles resulting in more loosely bound, albeit

well-defined, assemblies. Based on DLS results, assuming nearly spherical micelles, the micellar volume decreases ~ 4.8 -fold from 0 to 30 wt % [bmim][BF₄], while N_{agg} decrease ~ 5.9 -fold. This further suggests incorporation of [bmim][BF₄] and/or bmim⁺/BF₄⁻ within TX100-based micelles in the solution.

V. CONCLUSIONS

The unique role of hydrophilic IL [bmim][BF₄] in modifying the properties of aqueous TX100 is established. Surfactant aggregation is clearly evident in the presence of as high as 30 wt % [bmim][BF₄]. Addition of up to 30 wt % [bmim][BF₄] to aqueous TX100 results in decreased micellar size, increased cmc, and decreased N_{agg} , thus indicating an overall unfavorable micellization process when the IL is present. These observations strongly imply interactions between [bmim][BF₄] and TX100. This is further supported by the increased dipolarity of the probe cybotactic region within the micellar phase (i.e., the palisade layer) upon [bmim] × [BF₄] addition. Smaller micellar size with significantly lower N_{agg} due to the presence of [bmim][BF₄] within aqueous TX100 results in more water penetration into the micellar phase giving rise to increased microfluidity as reported by the fluorescence probes. Decreased ionic character of [bmim][BF₄] within micellar TX100 may be a result of interactions between bmim⁺ and/or BF₄⁻ with TX100; however, the possibility of the presence of undissociated [bmim][BF₄] within the micellar phase should also be considered. As far as changing the properties of aqueous solution of a nonionic surfactant TX100 is concerned, in some aspects, hydrophilic IL [bmim][BF₄] acts like a cosurfactant, while in others, its behavior is similar to a cosolvent.

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