

Concentration-Dependent Dual Behavior of Hydrophilic Ionic Liquid in Changing Properties of Aqueous Sodium Dodecyl Sulfate

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Modifying physicochemical properties of aqueous surfactant solutions in favorable fashion by addition of environmentally benign room-temperature ionic liquids (ILs) has enormous future potential. Due to its unusual properties, an IL may demonstrate a unique role in altering the properties of aqueous surfactant solutions. Changes in the properties of aqueous sodium dodecyl sulfate (SDS), an anionic surfactant, upon addition of a common and popular “hydrophilic” ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] are presented. Addition of low concentrations of [bmim][BF₄] (i.e., ≤ 2 wt %) to aqueous SDS results in a decrease in critical micelle concentration (cmc) as well as an increase in aggregation number (N_{agg}) and average micellar size. An increase in dipolarity and a decrease in microfluidity of the micellar phase is reported by solvatochromic fluorescence probes pyrene and 1,3-bis-(1-pyrenyl)propane as up to 2 wt % [bmim][BF₄] is added to aqueous SDS. The IL is observed to behave similarly to common electrolytes in the concentration range $0 < [\text{bmim}][\text{BF}_4] \leq 2$ wt %. A further increase in [bmim][BF₄] concentration to 30 wt % results in an increase in cmc which is accompanied by a decrease in N_{agg} and average micellar size. Change in the microfluidity of the micellar phase is observed to become insignificant in this concentration range. Evidence of the presence of micellar aggregates at such high concentration of [bmim][BF₄] is furnished by dynamic light scattering. The role of an IL in altering the properties of aqueous SDS in the range $2 \text{ wt } \% < [\text{bmim}][\text{BF}_4] \leq 30 \text{ wt } \%$ is similar to those of polar cosolvents. The concentration-dependent dual role of the IL [bmim][BF₄] in altering physicochemical properties of aqueous SDS is demonstrated.

Introduction

Surfactant solutions comprised of normal or reverse micelles are used as media for a variety of chemical analyses and syntheses.¹ Aqueous surfactant solutions have enjoyed more attention from the research community due to their environmentally friendly nature. 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.¹ Such micellar systems have immense technological applications such as solubilizing and emulsifying agents, flow field regulators, membrane mimetic media, nanoreactors for enzymatic reactions, to name just a few.¹ At ambient conditions, properties of an aqueous surfactant solution depend on the identity of the surfactant along with its concentration in the solution. The physicochemical properties of a given aqueous surfactant solution can be modified by external means, such as changes in temperature/pressure and/or addition of different modifiers (e.g., cosolvents, cosurfactants, electrolytes, polar organics, nonpolar organics, etc.).^{1,2}

Room-temperature ionic liquids (ILs) are receiving increased attention from both academic and industrial research communities due to their unusual properties.³ Almost every named chemical reaction has been reported in ILs.⁴ Routine and often novel analytical applications of ILs are being reported, evidenced by the rapid growth in the number of publications involving ILs.⁵ 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,⁶ aqueous⁷ and polymer⁸ solutions, surfactant-based systems,⁹ and so forth.

Efforts have been invested by many research groups including our own to study surfactant behavior and the possibility of surfactant self-assembly within ILs.⁹ However, the idea of formation of micelles with desirably modified physicochemical properties within aqueous IL solutions is exciting, useful, and economically convenient. Recently, we have investigated the properties of aqueous Triton X-100 (TX100, a nonionic surfactant) in the presence of as much as 2.1 wt % of a common and popular “hydrophobic” IL 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆].¹⁰ We were surprised to learn that while [bmim][PF₆] appeared to interact with micellar TX100 preferably via hydrogen-bonding and dipole-induced dipole interactions by partitioning into the micellar phase, no significant change in cmc or aggregation number (N_{agg}) was a representation of unchanged overall micellar structure. We believe the nonionic nature of the surfactant to be the reason for these outcomes. Further, limited aqueous solubility of “hydrophobic” [bmim][PF₆] (~ 2.1 wt %)¹¹ severely restricted the amount of [bmim][PF₆] that may be added to induce changes in the physicochemical properties of aqueous surfactant solutions. “Hydrophilic” ILs do not have such aqueous solubility limitations. Consequently, “hydrophilic” ILs can be used in appreciable amounts

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such that desired modifications in key physicochemical properties of aqueous surfactant systems may be achieved. Favorably modified physicochemical properties of aqueous surfactant solutions in the presence of an IL will expand the overall capabilities and applications of aqueous surfactant systems; utilization potential of ILs will increase as well. The role of an IL in property modulation for such purposes will also be established. In this manuscript, we present the changes in the properties of aqueous sodium dodecyl sulfate (SDS, an anionic surfactant) in the presence of "hydrophilic" IL 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄]. IL [bmim][BF₄] is completely miscible with water at ambient conditions,³ and thus the properties of aqueous SDS could be investigated in the presence of much higher concentrations of [bmim][BF₄].

Experimental

Materials. High-purity SDS 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 stored in dry conditions under argon and was also used as received. Doubly distilled deionized 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 from Molecular Probes. Ethanol (99.9%) was obtained from sd fine-chem. Ltd.

Methods. Required amounts of materials were weighed using a Mettler-Toledo AB104-S balance with a precision of ± 0.1 mg. Stock solutions of fluorescence probes were prepared in ethanol and stored in pre-cleaned amber glass vials at ~ 4 °C. SDS and CPC solutions were freshly prepared in doubly distilled deionized water. Aqueous SDS solutions of the probes were prepared taking appropriate aliquots of the probes from the stock and evaporating ethanol using a gentle stream of high-purity nitrogen gas. Aqueous SDS of desirable concentration was added to achieve the required final probe concentration. A precalculated amount of [bmim][BF₄] was added directly to the aqueous SDS 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 a model FL 3-11, Fluorolog-3 modular spectrofluorometer with single Czerny-Turner grating excitation and emission monochromators having a 450 W Xe arc lamp as the excitation source and 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. All data analysis was performed using Microsoft Excel and/or SigmaPlot 8.0 softwares.

Results

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, microfluidity, among others.^{1,12} The location of a fluorescence probe in a 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.).^{1,12} Depending on their molecular structure, fluorescence probes can locate themselves differentially in a micellar solution.^{1,12,13} Two fluorescence probes, pyrene and pyrene-1-carboxaldehyde, are utilized to obtain information on the cmc and dipolarity of aqueous SDS solutions in the presence of varying amounts of [bmim][BF₄].

Pyrene Fluorescence within [bmim][BF₄]-Added Aqueous SDS. Pyrene (Py) is one of the most popular fluorescence probes used 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, ca. 373 nm) and III (ca. 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 a change in the dipolarity of the cybotactic region of this probe; a more polar microenvironment results in a higher I_I/I_{III} and vice versa.¹⁴ Fluorescence spectra of pyrene were collected from solutions of varying [SDS] in the presence of different concentrations of [bmim][BF₄]. The variation in I_I/I_{III} versus $\log[\text{SDS}]$ for 0, 2, 10, 20, and 30 wt % added [bmim][BF₄] is shown in Figure 1. The onset of micelle formation *even* in the presence of 30 wt % added [bmim][BF₄] is 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. On the basis of 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 are reported in Table 1. It is interesting to note that addition of up to 2 wt % [bmim][BF₄] to aqueous SDS results in a significant decrease in cmc, while cmc increases dramatically on further increasing [bmim][BF₄] to 30 wt %. Most importantly, micelle formation within aqueous SDS in the presence of as high as 30 wt % [bmim][BF₄] is suggested and is confirmed by the DLS results (vide infra).

Information regarding pyrene cybotactic region dipolarity well-below and well-above cmc within [bmim][BF₄]-added aqueous SDS is obtained from Py I_I/I_{III} (Figure 2). Due to the preferential partitioning of nonpolar pyrene into micellar phase, as expected, I_I/I_{III} are observed to be significantly lower in the post-cmc region as compared to those in the pre-cmc region. Further, in the absence of micelles, statistically insignificant changes in I_I/I_{III} are observed up to 10 wt % [bmim][BF₄] followed by a slight increase in I_I/I_{III} on further addition of the IL. This slight increase could be attributed to the increased dipolarity of the solution due to the presence of dissociated [bmim][BF₄]. More interestingly, I_I/I_{III} increases dramatically upon [bmim][BF₄] addition to micellar solutions of SDS ($\Delta I_I/I_{III} \sim 0.32$ above cmc versus $\Delta I_I/I_{III} \sim 0.13$ below cmc upon 30 wt % [bmim][BF₄] addition), suggesting a more dipolar pyrene cybotactic region within the micellar phase. Since it is well-established that on average pyrene locates itself in the palisade layer,¹⁷ it is inferred that [bmim][BF₄] may be preferentially partitioning into the micellar pseudophase due to which the dipolarity of the pyrene cybotactic region is considerably increased. The observation strongly suggests the presence of interaction(s) between [bmim][BF₄] and SDS micelles.

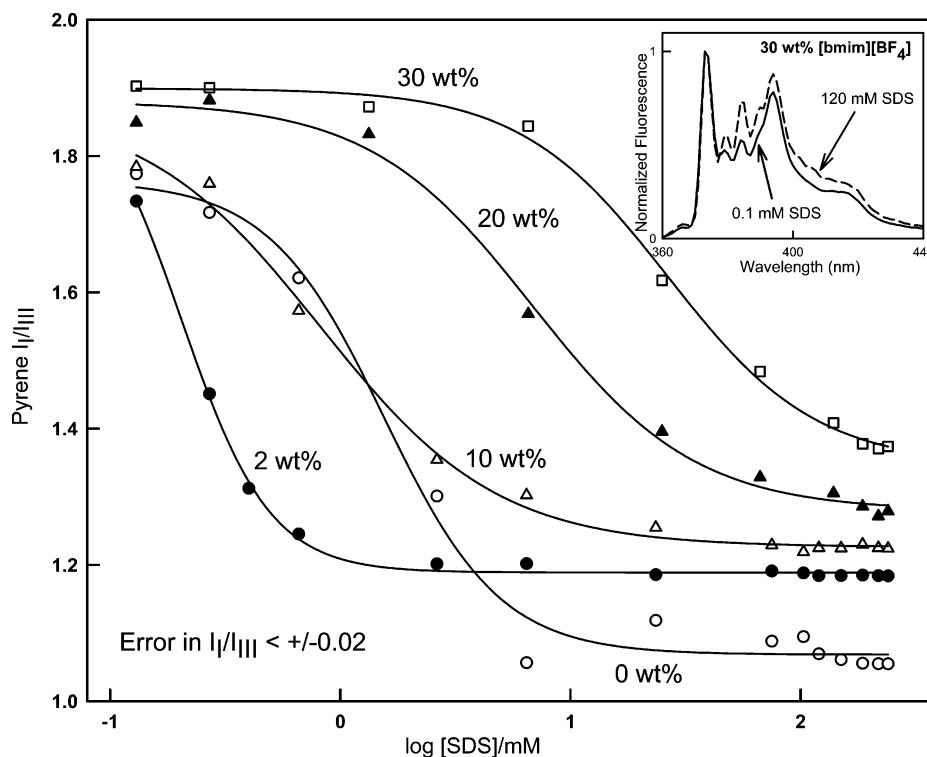


Figure 1. Pyrene (1 μM) I_I/I_{III} vs $\log[\text{SDS}]$ in the presence of different wt % $[\text{bmim}][\text{BF}_4]$ at ambient conditions (\circ : 0 wt %, \bullet : 2 wt %, \triangle : 10 wt %, \blacktriangle : 20 wt %, and \square : 30 wt %). Inset shows normalized pyrene fluorescence spectra in 0.1 mM (—) and 120 mM (---) aqueous SDS in the presence of 30 wt % $[\text{bmim}][\text{BF}_4]$ ($\lambda_{\text{ex}} = 337$ nm and slit widths = 2 and 1 nm).

TABLE 1: Effect of $[\text{bmim}][\text{BF}_4]$ Addition on Critical Micelle Concentration (cmc), Aggregation Number, and Average Size of Aqueous SDS at Ambient Conditions

concentration of $[\text{bmim}][\text{BF}_4]$		cmc (mM)			
wt %	mM	from PyCHO fluorescence intensity	from pyrene I_I/I_{III}	aggregation number (N_{agg})	peak diameter (D in nm)
0	0	7.0 ± 0.5	6.5 ± 0.5	104 ± 4	1.9 ± 0.2
0.5	22	1.5 ± 0.5	1.5 ± 0.5	111 ± 4	2.9 ± 0.3
2	88	1.0 ± 0.5	1.0 ± 0.5	126 ± 4	10.3 ± 0.4
10	442	8.5 ± 1.0	8.0 ± 1.0	96 ± 7	9.1 ± 0.3
20	885	50 ± 5	50 ± 5	38 ± 7	5.7 ± 0.3
30	1327	110 ± 10	105 ± 10	7 ± 2	4.5 ± 0.2

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).^{18,19} PyCHO has two types of close-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 red-shifts with increasing solvent dielectric.

A change in fluorescence quantum yield (or under suitable assumptions, fluorescence intensity) and shift in fluorescence wavelength maxima can both be utilized effectively to probe the micellar system. Figure 3 presents PyCHO fluorescence intensity as a function of $\log[\text{SDS}]$ 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 partition into the micellar phase where they encounter a more “hydrophobic” microenvironment. As described earlier for pyrene, cmc are evaluated from the sigmoidal nature of the

changes (Table 1), and they are found to be statistically similar to those obtained from pyrene I_I/I_{III} .

Aggregation Number Determination by Fluorescence Quenching Method. The aggregation number (N_{agg}) of SDS micelles in the presence of $[\text{bmim}][\text{BF}_4]$ was obtained by fluorescence quenching of pyrene by a cosurfactant cetylpyridinium chloride (CPC) according to the following equation:^{20d,21}

$$\ln\left(\frac{I_0}{I_Q}\right) = \frac{Q_{\text{micelle}}}{[\text{micelle}]} = \frac{[\text{CPC}]_{\text{micelle}}}{[\text{micelle}]_{\text{SDS}}} = [\text{CPC}]_{\text{micelle}} \left[\frac{N_{\text{agg}}}{[\text{SDS}] - \text{cmc}_{\text{SDS}}} \right] \quad (1)$$

where I_0 and I_Q are the fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively. Q_{micelle} (or $[\text{CPC}]_{\text{micelle}}$), $[\text{micelle}]_{\text{SDS}}$, and $[\text{SDS}]$ are the concentrations of quencher CPC within the micellar phase, SDS micelles, and SDS surfactant, respectively. Plots of $\ln(I_0/I_Q)$ versus $[\text{CPC}]_{\text{micelle}}$ for pyrene quenching by CPC within $[\text{bmim}][\text{BF}_4]$ -added 120 mM aqueous SDS presented in Figure 4 suggest good linear behavior ($0.9983 \leq r^2 \leq 0.9998$) at each addition of $[\text{bmim}][\text{BF}_4]$ in the interval 0–30 wt %. More importantly, upon

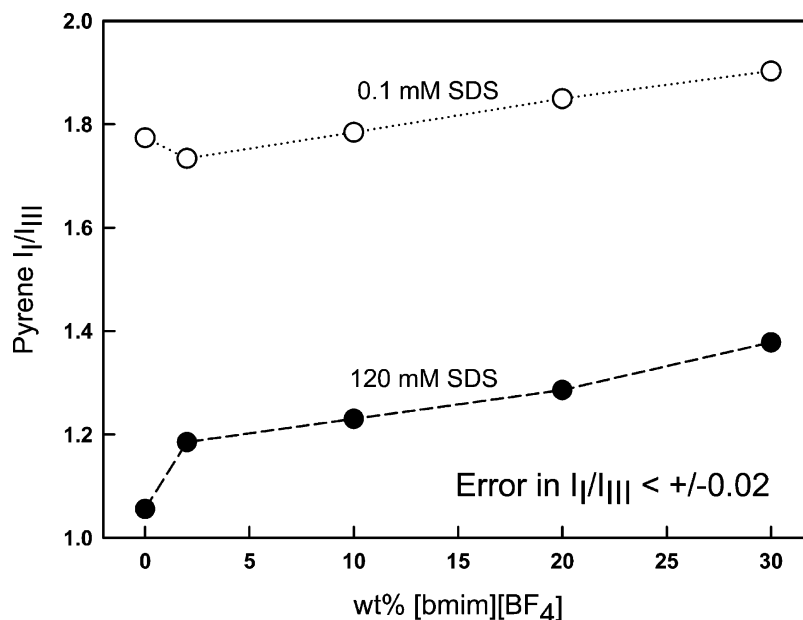


Figure 2. Pyrene I_I/I_{III} versus wt % [bmim][BF₄] within 0.1 mM (○) and 120 mM (●) aqueous SDS at ambient conditions.

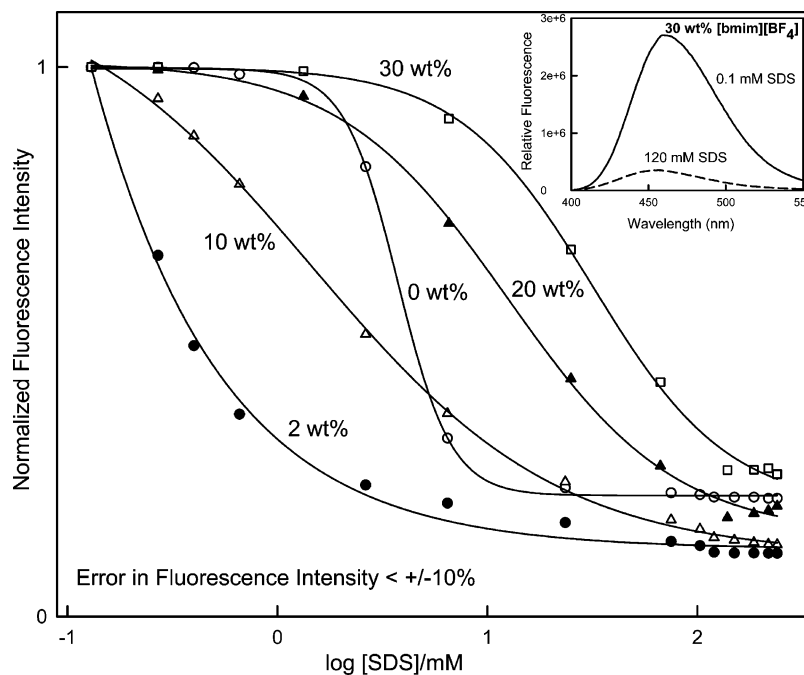


Figure 3. PyCHO (1 μ M) normalized fluorescence intensity versus $\log[\text{SDS}]$ in the presence of different wt % [bmim][BF₄] at ambient conditions (○: 0 wt %, ●: 2 wt %, △: 10 wt %, ▲: 20 wt %, and □: 30 wt %). Inset shows fluorescence emission spectra of PyCHO in the presence of 30 wt % [bmim][BF₄] within 0.1 mM (—) and 120 mM (---) aqueous SDS (λ_{ex} = 365 nm and slit widths = 2 and 2 nm).

addition of up to 2 wt % [bmim][BF₄], the slope increases; however, on further increasing the concentration of [bmim][BF₄] to 30 wt %, a drastic decrease in the slope results. N_{agg} is calculated from the slope using the cmc obtained earlier and reported in Table 1. The aggregation number increases on addition of up to 2 wt % [bmim][BF₄], and then it decreases drastically as the amount of [bmim][BF₄] is increased to 30 wt % in aqueous SDS solution.

Microfluidity from 1,3-Bis-(1-pyrenyl)propane (BPP) Fluorescence. A change in the fluidity of the immediate microenvironment surrounding a probe is effectively manifested through BPP steady-state emission spectra.^{12–14,22} 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 the intramolecular excimer. In a low-viscous milieu, the two pyrenes easily fold together to form an intramolecular excimer. As the microfluidity of the cybotactic region decreases, the efficiency of the excimer formation decreases and a corresponding reduction in the intensity of the excimer band is observed.

BPP emission spectra in 120 mM aqueous SDS in the presence of varying amounts of [bmim][BF₄] are presented in Figure 5. Due to its “hydrophobic” nature, BPP preferably partitions into the micelles thus reporting on the microfluidity of the micellar phase.²² A significant increase in monomer-to-excimer emission intensity ratio (I_M/I_E) on addition of up to 2 wt % [bmim][BF₄] to aqueous SDS is observed. However, on further increasing the concentration of [bmim][BF₄] to 30 wt %, the increase in I_M/I_E is not as significant; the I_M/I_E appear

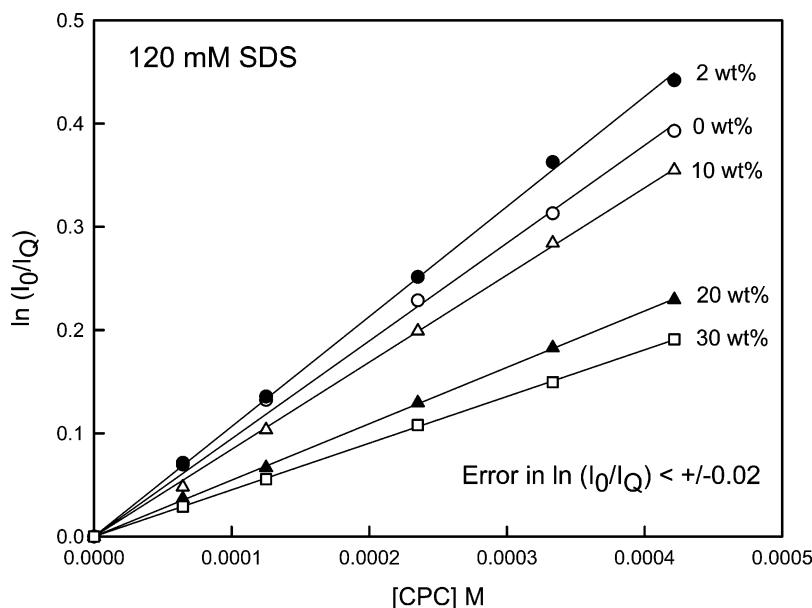


Figure 4. Pyrene ($1\ \mu\text{M}$) fluorescence quenching by CPC in 120 mM aqueous SDS in the presence of different wt % [bmim][BF₄] at ambient conditions (○: 0 wt %, ●: 2 wt %, △: 10 wt %, ▲: 20 wt %, and □: 30 wt %). Solid lines represent the results of the linear regression analysis.

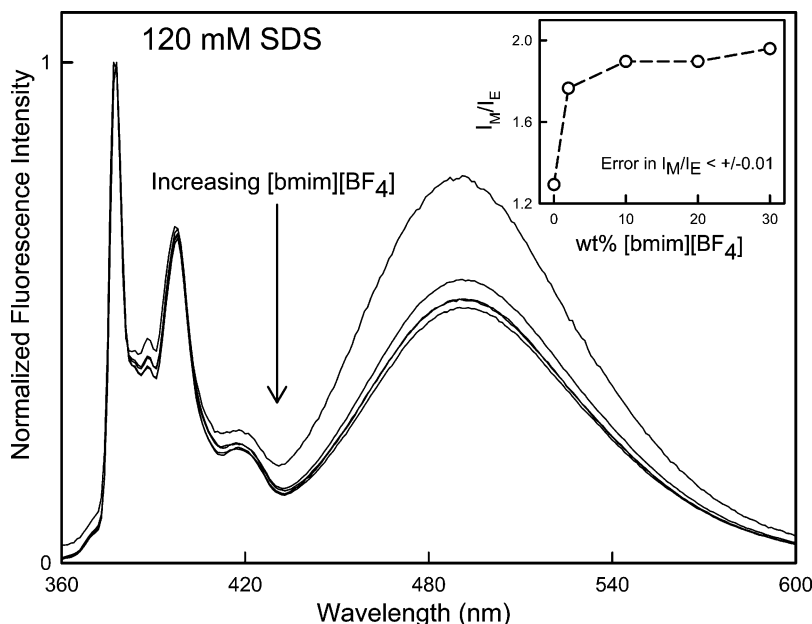


Figure 5. BPP ($1\ \mu\text{M}$) normalized fluorescence spectra within 120 mM aqueous SDS in the presence of different wt % [bmim][BF₄] at ambient conditions ($\lambda_{\text{ex}} = 337\ \text{nm}$ and slit widths = 2 and 2 nm). Inset shows the monomer-to-excimer emission intensity ratio ($I_{\text{M}}/I_{\text{E}}$) versus wt % [bmim][BF₄].

to reach a plateau value. IL [bmim][BF₄] is significantly viscous,^{3k} and a decrease in microfluidity upon [bmim][BF₄] addition to 120 mM SDS is easily conceivable. Surprisingly, the $I_{\text{M}}/I_{\text{E}}$ at higher [bmim][BF₄] concentration within SDS suggests unaltered cybotactic region microfluidity.

Size of Micellar Aggregates by Dynamic Light Scattering (DLS). Dynamic light scattering (DLS) is utilized to further substantiate the evidence of aggregate formation within aqueous SDS in the presence of up to 30 wt % [bmim][BF₄] at ambient conditions. The size and distribution of the SDS micellar aggregates in the presence of varying amounts of [bmim][BF₄] are examined by DLS data as well. Figure 6 shows the scattering intensity for the given diameter (D) measured at room temperature of aqueous 120 mM SDS in the presence of 0, 2, 10, 20, and 30 wt % [bmim][BF₄]. Monomodal distributions are

observed at all amounts of added [bmim][BF₄]. The most noteworthy outcome of our DLS data is the evidence of the presence of micelle-like aggregates in the presence of as high as 30 wt % [bmim][BF₄]. The peak diameters for [bmim][BF₄]-added aqueous SDS obtained from DLS measurements for 120 mM SDS are listed in Table 1. It is interesting to note that the average micellar (or aggregate) size increases drastically upon addition of up to 2 wt % [bmim][BF₄]. However, a subsequent gradual decrease in average micellar diameter is clearly evident on further addition of up to 30 wt % [bmim][BF₄]. It is important to mention that our average diameter of aqueous SDS micelles is similar to that reported in the literature.¹ Another interesting outcome of our DLS data is the FWHM of the distribution at each addition of [bmim][BF₄] which parallels the trend of average micellar size (inset of Figure 6). The micellar size

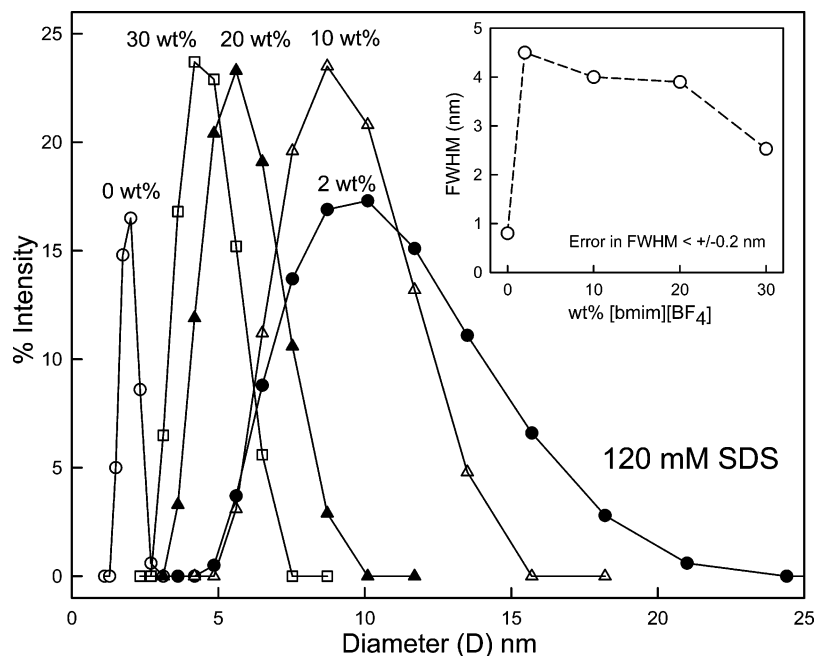


Figure 6. Dynamic light scattering (DLS) results of 120 mM aqueous SDS in the presence of increasing concentration of [bmim][BF₄] at ambient conditions (0 wt % (○), 2 wt % (●), 10 wt % (△), 20 wt % (▲), and 30 wt % (□)). Inset shows full width at half-maximum (FWHM) versus wt % [bmim][BF₄].

distribution becomes significant from no [bmim][BF₄] to 2 wt % [bmim][BF₄]; however, it narrows gradually upon further addition of up to 30 wt % [bmim][BF₄], demonstrating that the micellar assemblies are more monodisperse in the presence of high concentrations of IL as compared to 2 wt % [bmim][BF₄].

Discussion

Our results clearly demonstrate that addition of a commonly used “hydrophilic” IL [bmim][BF₄] results in significant changes in the properties (i.e., cmc, N_{agg} , micellar size, solute solvation environment, microfluidity) of aqueous SDS. Careful analyses of the results reveal an interesting outcome: IL [bmim][BF₄] shows concentration-dependent dual behavior in changing the properties of aqueous SDS. While addition of up to 2 wt % [bmim][BF₄] results in decreased cmc and increased N_{agg} and micellar size, on further addition of IL up to 30 wt %, cmc is increased and N_{agg} and micellar size decrease. Presence of micelle-like aggregates within aqueous SDS solutions in the presence of as high as 30 wt % [bmim][BF₄] is clearly evident. One may be able to assess the role of IL [bmim][BF₄] in changing the properties of aqueous SDS from these results. The only other investigation on cmc change of aqueous SDS on IL addition that we are aware of reports that while addition of 30 mM 1,3-dimethylimidazolium iodide (mmimI) and 1-butyl-3-methylimidazolium chloride (bmimCl) increases the cmc of aqueous SDS to 170 and 70 mM from 7 mM, respectively, the decrease to 2.8, 1.9, and 1.9 mM were observed when the same amount of 1-hexyl-3-methylimidazolium chloride (hmimCl), 1-methyl-3-octylimidazolium chloride (moimCl), and 1-methyl-3-octylimidazolium tetrafluoroborate (moimBF₄), respectively, were added.²³

The effect of various external additives on the properties of aqueous SDS has been investigated by many researchers.² It is reported that the cmc of SDS may not depend on the anions of the added salt, and for four different cations investigated, the cmc generally decreased in the order $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+}$.^{2a} A decrease in cmc of aqueous SDS is also observed with other electrolytes, such as sodium acetate and propionate,^{2c}

TbCl₃,^{2d} tris(hydroxymethyl)methylammonium chloride,^{2b} and so forth. Our observation of reduction in cmc of aqueous SDS in the presence of low concentration of [bmim][BF₄] is similar to the above results. The extent of cmc decrease with 2 wt % [bmim][BF₄] addition in our investigation was observed to be similar to that for Mg^{2+} , one of the most efficient cations for SDS cmc reduction.^{2a} We were surprised to learn that the presence of similar concentrations of tetraalkylammonium cations, such as $(\text{C}_3\text{H}_7)_4\text{N}^+$, $(\text{C}_2\text{H}_5)_4\text{N}^+$, and $(\text{CH}_3)_4\text{N}^+$, appear to increase the cmc.^{2k} The nature of bmim^+ –SDS interactions appears to be significantly different from tetraalkylammonium cations–SDS interactions at low cation concentrations. It is important to mention that addition of polar cosolvents, in general, increases the SDS cmc.^{2h,i} It is shown that the increase in SDS cmc is not as significant in the cases of added methanol, ethylene glycol, and glycerol^{2h} as in the cases of added acetonitrile and tetrahydrofuran.²ⁱ On the basis of our observations, it may be proposed that the role of [bmim][BF₄] in changing the cmc of aqueous SDS at higher concentrations (i.e., 2 wt % $< [\text{bmim}][\text{BF}_4] \leq 30$ wt %) is similar to that of a polar cosolvent.

The trends in cmc and N_{agg} of aqueous SDS upon [bmim][BF₄] addition complement each other nicely; N_{agg} increases upon addition of up to 2 wt % [bmim][BF₄] before decreasing dramatically as the concentration of IL is increased to 30 wt % in the solution. To our convenience, an increase in SDS N_{agg} is reported upon addition of salts such as, NaCl, NH₄Cl,^{24a} sodium acetate, propionate, butyrate,^{24b} and some “hydrophobic” salts (e.g., aniline hydrochloride, *o*-toluidine hydrochloride, and *m*-toluidine hydrochloride).^{24c} Again, at lower concentrations (i.e., ≤ 2 wt %), the role of [bmim][BF₄] in changing N_{agg} is similar to that of common electrolytes. The reason for a decrease in cmc and an increase in N_{agg} in the presence of up to 2 wt % [bmim][BF₄] is analogous to that established for common electrolytes—it is due to the electrostatic attraction between bmim^+ and the anionic head group of SDS resulting in decreased Coulombic repulsive interactions between the surfactant head groups allowing more surfactant monomers to form micelles.^{1,2}

A decrease in N_{agg} of SDS micelles is observed for additives such as propylene carbonate,^{24d} propanol and allyl alcohol,^{24e} and poly(propylene oxide)methacrylate.^{24f} The trends in N_{agg} in the presence of these cosolvents are similar to those we observe for [bmim][BF₄] at higher concentrations. Again, the role of [bmim][BF₄] as a polar cosolvent at higher concentrations (2 wt % < [bmim][BF₄] ≤ 30 wt %) is reaffirmed. While the dissociation of [bmim][BF₄] within aqueous SDS may be significant at lower IL concentrations, at higher concentrations the dissociation of [bmim][BF₄] is decreased to such an extent to force IL to show cosolvent-like behavior. The decrease in N_{agg} and increase in cmc at higher concentrations of [bmim][BF₄] result from the reduction in the “hydrophobic” effect that is usually the major contributor to micelle formation.¹¹ It is important to pinpoint that at higher concentrations of [bmim][BF₄] the molar ratio of [IL]/[SDS] is much greater than 1.

For spherical micelles of a given surfactant, it is observed that an increase in N_{agg} is usually accompanied by increased size of the micellar aggregates and vice versa.¹¹ Our DLS results are in agreement with this observation. An increase in SDS micellar size is observed as up to 2 wt % [bmim][BF₄] is added to the solution; further addition to 30 wt % results in decreased average micellar size. An increase in average micellar size upon addition of electrolytes is reported by other researchers as well; the electrolytes used were NaCl,^{25a,d} tetrabutylammonium bromide,^{25b} and anilinium nitrate,^{25c} among others. In the presence of cosolvents, on the other hand, the average micellar size appears to decrease.

The results of a BPP probe regarding information on microfluidity of aqueous SDS upon [bmim][BF₄] addition are very different from those obtained by the addition of a “hydrophobic” IL [bmim][PF₆] to nonionic TX100.¹⁰ While only a slight decrease in microfluidity was observed on ~2 wt % [bmim][PF₆] addition to 10 mM aqueous TX100, a similar addition of [bmim][BF₄] to 120 mM aqueous SDS results in a drastic decrease in the microfluidity of the probe cybotactic milieu. Interestingly, upon further addition of up to 30 wt % [bmim][BF₄] the decrease in microfluidity as reported by BPP becomes considerably less significant. On average, BPP is considered to be solubilized within the micellar phase in the palisade layer.²² A decrease in the microfluidity could be a manifestation of the presence of significantly viscous [bmim][BF₄]^{3k} within the micellar phase. This provides further evidence of the interactions between SDS and bmim⁺ at low IL concentrations. However, the fact that the BPP cybotactic region within the micellar phase is specific to the surfactant type and structure cannot be ignored. Specifically, BPP within TX100 micelles shows a fairly viscous microenvironment to begin with, and addition of [bmim][PF₆] may not alter it as dramatically.¹⁰ However, a BPP solvation microenvironment within SDS micelles suggests a relatively fluidic milieu, and hence, addition of [bmim][BF₄] may result in a rather dramatic decrease in microfluidity. It is important to recognize that due to a reduced micellar surface charge in the presence of up to 2 wt % [bmim][BF₄], probe BPP is solubilized within larger micelles with less water penetration that are similar more to the nonionic micelles in properties. Hence, the dramatic reduction in microfluidity could also have a contribution from the significantly altered nature of the BPP cybotactic region. Upon further addition of [bmim][BF₄], the increase in microfluidity due to a decrease in micellar size and N_{agg} is compensated by the presence of an increased amount of highly viscous [bmim][BF₄] as cosolvent. This results in a rather insignificant decrease in microfluidity.

The changes in the dipolarity reported by the solvatochromic fluorescence probe pyrene due to the presence of [bmim][BF₄] within aqueous SDS provides important information regarding the solute solvation environment. Increased dipolarity of the pyrene cybotactic milieu within the micellar solutions of SDS upon addition of [bmim][BF₄] suggests the presence of bmim⁺ and/or BF₄[−] close to the probe molecule. This is similar to what is observed for aqueous nonionic TX100 in the presence of IL [bmim][PF₆].¹⁰ Since it is well-established that pyrene is solubilized in the micellar palisade layer,¹⁷ it can be inferred that [bmim][BF₄], in part, may also be localized within the palisade layer of the micellar phase. In the presence of higher [bmim][BF₄] concentrations, a drastic reduction in N_{agg} may allow increased water penetration into the micelles which may lead to increased dipolarity as well.

Conclusions

Properties of aqueous solutions of an anionic surfactant SDS can be effectively changed by adding a “hydrophilic” IL [bmim][BF₄]. Micelles form at much lower surfactant concentrations with higher aggregation number in the presence of up to 2 wt % [bmim][BF₄]. Micelles thus formed are bigger in size with increased dipolarity and decreased microfluidity as reported by fluorescence probes. Further increase in concentration of [bmim][BF₄] to 30 wt %, however, results in increased critical micelle concentration and decreased aggregation number that is accompanied by decreased average micellar size. While the dipolarity of the probe cybotactic region continues to increase, the decrease in microfluidity becomes less significant in this IL concentration range (i.e., 2 wt % < [bmim][BF₄] ≤ 30 wt %). Concentration-dependent dual behavior of IL [bmim][BF₄] in altering important properties of aqueous SDS is clearly evident. At lower concentrations (i.e., ≤ 2 wt %) the role of an IL appears to be similar to that of common electrolytes, while its behavior is closer to those of polar cosolvents in the concentration range 2 wt % < [bmim][BF₄] ≤ 30 wt %. SDS aggregation to form micelles is clearly evident even in the presence of as high as 30 wt % [bmim][BF₄]. Key physicochemical properties of aqueous anionic surfactants may be altered favorably by adding an appropriate amount of “hydrophilic” ionic liquids.

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