

# Modifying Properties of Aqueous Cetyltrimethylammonium Bromide with External Additives: Ionic Liquid 1-Hexyl-3-methylimidazolium Bromide versus Cosurfactant *n*-Hexyltrimethylammonium Bromide

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Understanding the effect of external additives on the properties of aqueous surfactant solutions is of utmost importance due to widespread applications of surfactant-based systems. Role of ionic liquids (ILs) in this regard may turn out to be crucial as these substances are known to possess unusual properties. To unambiguously understand and establish the role of ILs in modifying properties of aqueous surfactant systems, changes in the physicochemical properties of aqueous cetyltrimethylammonium bromide (CTAB) upon addition of an IL 1-hexyl-3-methylimidazolium bromide ([hmim][Br]) are compared with those when a cosurfactant *n*-hexyltrimethylammonium bromide (HeTAB) is added to aqueous CTAB. Important physicochemical properties, such as critical micelle concentration (cmc), aggregation number ( $N_{\text{agg}}$ ), solution conductance and microfluidity, and average aggregate size and polydispersity, are observed to change as either [hmim][Br] or HeTAB is added to aqueous CTAB; the experimental outcomes clearly imply the changes in most of the physicochemical properties to be significantly more dramatic in case of IL [hmim][Br] addition. The fact that, between the two, only IL [hmim][Br] may show cosolvent-type behavior at high concentrations is evoked to explain the differences in the behavior of the two additives. It is demonstrated that both [hmim][Br] and HeTAB show electrolytic as well as cosurfactant-type behavior within aqueous CTAB when present at low concentrations, with the changes in physicochemical properties being very similar. At high concentrations, although HeTAB still acts as a cosurfactant forming mixed micelles with CTAB, IL [hmim][Br] behaves partly as a cosolvent toward altering the physicochemical properties of aqueous CTAB. The unique role of IL in changing properties of aqueous surfactant systems is demonstrated.

## Introduction

Aqueous surfactant solutions have immense importance due to their unparalleled application potential.<sup>1</sup> This is amply manifested by the extensive research efforts invested by many research groups in both academia and industry toward understanding aqueous surfactant-based systems.<sup>2</sup> Within this context, assessment and subsequent modification of the properties of an aqueous surfactant system acquire utmost importance. At ambient conditions, physicochemical properties of an aqueous surfactant solution depend, among others, on the identity of the surfactant.<sup>1</sup> Subsequently, if the conditions remain the same, the aqueous solution of a surfactant at a given concentration possess more-or-less fixed physicochemical properties that are difficult to modulate. Other than changing temperature and pressure, the usual way to modify the physicochemical properties of a given aqueous surfactant solution is to use external additives, such as cosolvents, cosurfactants, electrolytes, polar organics, nonpolar organics, etc.<sup>1,2</sup> Because of their unusual and interesting properties ionic liquids (ILs)<sup>3</sup> as additives in modifying properties of aqueous surfactant systems, they may turn out to be of immense importance.<sup>4–7</sup> In our recent investigations we have demonstrated the uniqueness of ILs in altering the key physicochemical properties of aqueous surfactant systems composed of nonionic,<sup>5</sup> anionic,<sup>6</sup> and zwitterionic<sup>7</sup> surfactants. Most importantly, we have noted the dissimilarities in the nature of an IL to that of a salt or a cosolvent or a cosurfactant in

altering the properties of an aqueous surfactant solution. The effectiveness and uniqueness of ILs in this respect were found to be unparalleled.

Subtle, albeit distinct, differences between the chemical structure of the IL and a common salt or a cosolvent or a cosurfactant are obviously of importance in our aforementioned investigations.<sup>4–7</sup> For example, the cation (i.e., 1-butyl-3-methylimidazolium) and the anion ( $\text{PF}_6^-$  or  $\text{BF}_4^-$ ) of the IL in these investigations are different from the usual cations and anions of common salts generally used to alter properties of aqueous surfactant systems. Although the changes due to the addition of an IL as electrolyte (i.e., at low concentrations) are observed to be more pronounced as compared to those due to the addition of common salts, the similarities in changes are obvious. The changes in the physicochemical properties due to the addition of high concentration of ILs in these investigations are compared with the changes due to the addition of molecular cosolvents. Obviously, the molecular cosolvents are considerably different from ILs. The ionic nature inherent to the ILs results in highly unusual behavior of these neoteric substances as cosolvents in modifying properties of aqueous surfactant systems. Further, as far as cosurfactant-type behavior of ILs in these investigations is concerned, only the butyl functionality of the IL cation may induce any such behavior to some extent.

IL appended with longer alkyl chains may be effectively utilized to investigate cosurfactant-type behavior, if any, of these substances. The outcomes can be conveniently compared with those from the addition of a traditional cosurfactant containing an alkyl chain of the same length. This, in our opinion, will

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clearly differentiate the role of IL from that of a cosurfactant in modifying properties of aqueous surfactant solution; affording the uniqueness or anomaly associated with ILs, if any, in the process. Toward this end, we present a comparative study of changes in physicochemical properties of aqueous solution of a common cationic surfactant cetyltrimethylammonium bromide (CTAB) upon addition of an IL 1-hexyl-3-methylimidazolium bromide [hmim][Br] to that of a cosurfactant *n*-hexyltrimethylammonium bromide (HeTAB). It is noteworthy that although the surfactant, the IL, and the cosurfactant all bear the same anion, the longest alkyl chain on the IL cation is identical to that on the cosurfactant cation. It is also important to mention that although [hmim][Br] is an IL by definition (normal melting point =  $-52\text{ }^{\circ}\text{C}$ ),<sup>8a</sup> the same is not true for HeTAB (normal melting point =  $182\text{--}184\text{ }^{\circ}\text{C}$ ).<sup>8b</sup>

## Experimental Section

**Materials.** CTAB and HeTAB of highest purity were purchased from Spectrochem Ltd. and Alfa Aesar, respectively, and were used as received. IL [hmim][Br] (Merck, highest purity, water content <10 ppm) was stored under argon atmosphere and was used as received. Doubly distilled deionized water was obtained from a Millipore, Milli-Q Academic water purification system having  $\geq 18\text{ M}\Omega\cdot\text{cm}$  resistivity. The following materials were used as received: pyrene 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  $\pm 0.1\text{ mg}$ . Stock solutions of the fluorescence probes were prepared in ethanol and stored in precleaned amber glass vials at  $\sim 4\text{ }^{\circ}\text{C}$ . CTAB and CPC solutions were freshly prepared in doubly distilled deionized water. Aqueous CTAB 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 CTAB of desirable concentration was added to achieve required final probe concentration. A precalculated amount of [hmim][Br] or HeTAB was directly added to the aqueous CTAB solution.

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 measurements were done at a scattering angle of  $90^{\circ}$  and a temperature of  $25\text{ }^{\circ}\text{C}$ , which was controlled by means of a thermostat. Fluorescence spectra were acquired on model FL 3–11, Fluorolog-3 modular spectrofluorometer purchased from Horiba-Jobin Yvon, Inc. The spectrofluorometer contains single Czerny–Turner grating excitation and emission monochromators as wavelength selection devices, 450 W Xe-arc lamp as the excitation source, and PMT as the detector. All data were acquired using  $1\text{ cm}^2$  path length quartz cuvettes. Spectral response from appropriate blanks was subtracted before data analysis. All measurements were taken in triplicate and averaged. Conductivity measurements were carried out on a CM-183  $\mu\text{p}$ -based EC-TDS analyzer with ATC probe and conductivity cell (CC-03B) purchased from Elico Ltd., India.

## Results

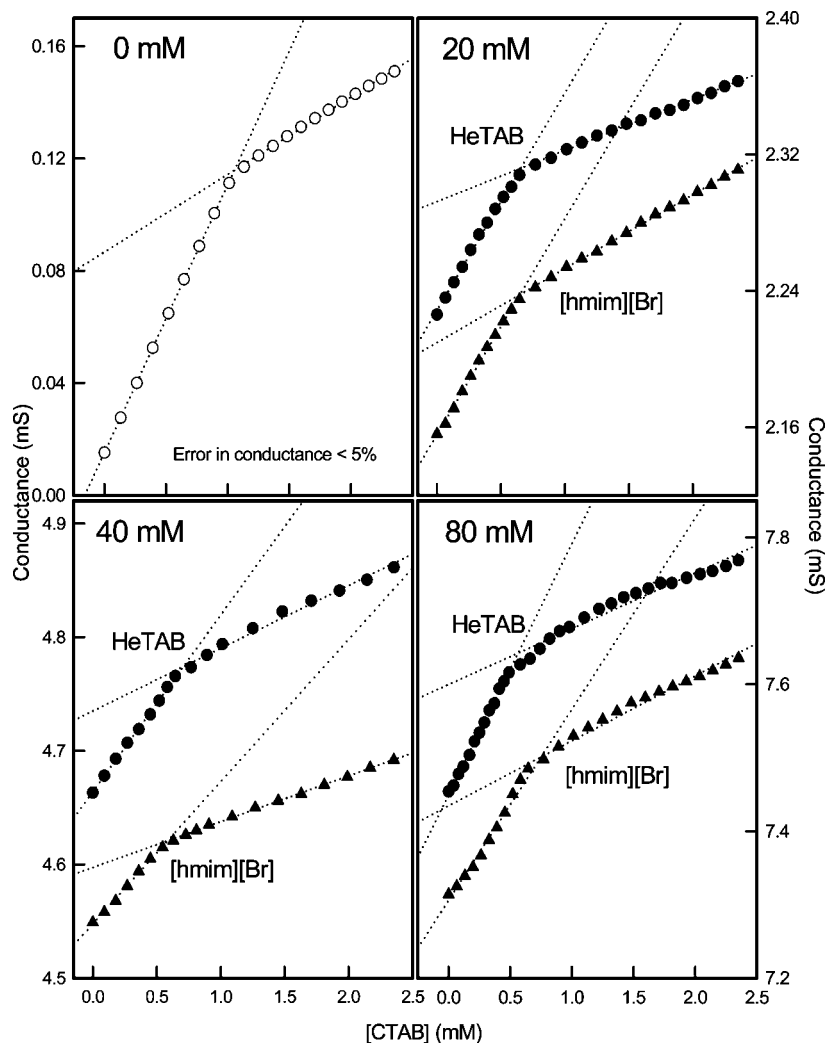
**Conductance Measurement at Low Additive Concentrations.** Conductance measurements are both easy and convenient for determining the critical micelle concentration (cmc) of aqueous solutions of ionic surfactants.<sup>1</sup> We have measured conductance as a function of [CTAB] in the presence of 0, 20,

40, and 80 mM [hmim][Br] and HeTAB, respectively, at ambient conditions (Figure 1). On the basis of the Onsager theory of electrolyte conductivity,<sup>1b</sup> one expects two linear regimes for conductance in the pre- and postmicellar regions of an aqueous ionic surfactant solution where, understandably, the slope becomes smaller once the micelles are formed. These two linear regimes are clearly evident in our data (the dotted lines in Figure 1 are the results of linear regression analysis). The cmc obtained as the *x*-intersection are reported in Table 1. A careful examination of the conductance data reveals two interesting features. First, for identical molar concentrations, the conductance of HeTAB-added aqueous CTAB is observed to be always higher than that of [hmim][Br]-added aqueous CTAB, implying the limiting molar conductivity ( $\nu_+$ ) of  $\text{HeTA}^+$  is significantly higher than that of  $\text{hmim}^+$  at ambient conditions. Second and more importantly, increasing the concentration of HeTAB or [hmim][Br] results in decreased cmc; the decrease appear to be only slightly more for [hmim][Br] addition. It is important to note that the cmc of aqueous CTAB obtained from our conductance measurement is in good agreement with that reported in literature.<sup>1c</sup> It may be inferred from the data that at low concentrations the two additives, [hmim][Br] and HeTAB, behave similarly as far as changing the cmc of the solution is concerned. It is noteworthy that at higher concentrations of these additives the conductance measurements become unreliable, rendering it impossible to extract any meaningful conclusion.

**Fluorescence Probe Behavior.** Fluorescence probes are routinely used to obtain various micellar parameters, such as cmc, aggregation number ( $N_{\text{agg}}$ ), microfluidity, and others.<sup>1,9</sup> The location of a fluorescence probe in 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.).<sup>1,9</sup>

### Critical Micelle Concentration from Pyrene Fluorescence.

We have used pyrene as the fluorescence probe to obtain the cmc of the aqueous CTAB in the presence of each of the additives, respectively. The pyrene solvent polarity scale is defined by the  $I_{\text{I}}/I_{\text{III}}$  emission intensity ratio, where  $I_{\text{I}}$  corresponds to the  $S_1(\nu = 0) \rightarrow S_0(\nu = 0)$  transition, and  $I_{\text{III}}$  denotes the intensity of the  $S_1(\nu = 0) \rightarrow S_0(\nu = 1)$  transition in pyrene. The  $I_{\text{I}}/I_{\text{III}}$  increases with increasing solvent dipolarity and is a function of solvent dielectric ( $\epsilon$ ) and refractive index ( $n$ ) via the dielectric cross term  $[f(\epsilon, n^2)]$ .<sup>10</sup> Figure 2 presents pyrene  $I_{\text{I}}/I_{\text{III}}$  versus  $\log[\text{CTAB}]$  in the presence of HeTAB and [hmim][Br], respectively. The curves represent the fit to a simplistic sigmoidal expression. A fairly drastic change in  $I_{\text{I}}/I_{\text{III}}$  implies the onset of micelle formation and hence the cmc. This is the result of “hydrophobic” pyrene being incorporated into the micellar pseudophase upon formation of micelles. On the basis of earlier reported ambiguity,<sup>11</sup> we have found empirically that by normalizing the total sigmoidal response in  $I_{\text{I}}/I_{\text{III}}$  to 1.00, the cmc can be reasonably estimated as the concentration at which the amplitude has decayed to 0.01.<sup>1f</sup> The recovered cmc of aqueous CTAB in the presence of different concentrations of HeTAB and [hmim][Br], respectively, are reported in Table 1. The cmc obtained from pyrene fluorescence in the absence and presence of up to 80 mM HeTAB and [hmim][Br], respectively, are in excellent agreement with those obtained from conductance measurements, implying a similar decrease in cmc irrespective of whether HeTAB or [hmim][Br] is added to aqueous CTAB (vide supra). Interestingly, further increasing the concentration of either of the two additives up to 1290 mM results in increase in the cmc of the solution. Most



**Figure 1.** Conductance of aqueous CTAB in the absence (○) and presence of different concentrations of HeTAB (●) and [hmim][Br] (▲), respectively, at ambient conditions. Dotted lines represent the results of linear regression analysis in pre- and postmicellar regimes in each case.

**TABLE 1: Critical Micelle Concentration (cmc) of Aqueous CTAB in the Presence of Different Concentrations of HeTAB and [hmim][Br], Respectively, at Ambient Conditions**

concentration of additive in mM	cmc (mM) from conductance		cmc (mM) from pyrene fluorescence	
	HeTAB-added	[hmim][Br]-added	HeTAB-added	[hmim][Br]-added
0	1.10 ± 0.20	1.10 ± 0.20	1.1 ± 0.2	1.1 ± 0.2
20	0.78 ± 0.20	0.74 ± 0.20	0.8 ± 0.2	0.75 ± 0.2
40	0.65 ± 0.10	0.63 ± 0.10	0.65 ± 0.2	0.65 ± 0.2
80	0.60 ± 0.10	0.58 ± 0.10	0.6 ± 0.2	0.6 ± 0.2
410	<sup>a</sup>	<sup>a</sup>	1.5 ± 0.5	6.5 ± 2.0
840	<sup>a</sup>	<sup>a</sup>	8.0 ± 2.0	50 ± 10
1290	<sup>a</sup>	<sup>a</sup>	23 ± 7	130 ± 15

<sup>a</sup> At these high concentrations of the additives, conductance measurements fail to determine the cmc.

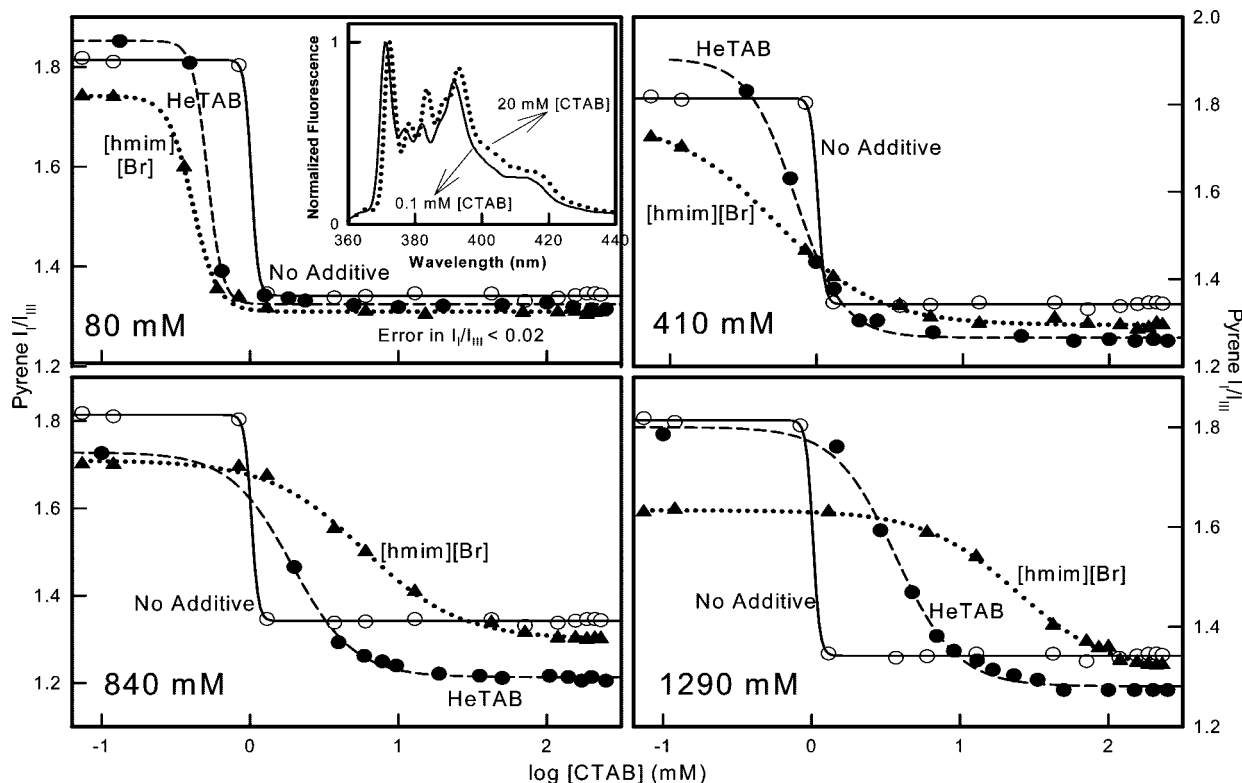
importantly, the increase in cmc is significantly more for IL [hmim][Br] addition as compared to HeTAB addition (in the presence of 1290 mM of the additive, the cmc with [hmim][Br] is observed to be more than five-times that with HeTAB). The different role of IL [hmim][Br] versus that of cosurfactant HeTAB in changing the cmc of the aqueous surfactant solution is clearly demonstrated.

**Aggregation Number from Fluorescence Quenching Method.** The aggregation number ( $N_{\text{agg}}$ ) of aqueous CTAB in the presence of HeTAB and [hmim][Br], respectively, is obtained

from fluorescence quenching of pyrene by cetylpyridinium chloride (CPC) according to the following equation:<sup>12d,13</sup>

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

where  $I_0$  and  $I_Q$  are the fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively.  $Q_{\text{micelle}}$  (i.e.,  $[\text{CPC}]_{\text{micelle}}$ ,  $[\text{micelle}]$ , and  $[\text{CTAB}]$  are the concentrations of quencher CPC within the micellar phase, micelles, and CTAB surfactant, respectively. Plots of  $\ln(I_0/I_Q)$  versus  $[\text{CPC}]_{\text{micelle}}$  for pyrene quenching by CPC within 150 mM aqueous CTAB in the presence of HeTAB and [hmim][Br], respectively, are presented in Figure 3, which suggest good linear behavior ( $0.9914 \leq r^2 \leq 0.9993$ ). It is clear that the slope decreases significantly with increasing concentration of either of the two additives. Interestingly, the decrease in slope is significantly more for [hmim][Br] addition as compared to HeTAB addition. The  $N_{\text{agg}}$  is calculated from eq 1 using the cmc obtained earlier and reported in Table 2. Our aqueous CTAB  $N_{\text{agg}}$  is in good agreement with that reported in the literature.<sup>14</sup> It is noteworthy that  $N_{\text{agg}}$  decreases on increasing the concentrations of [hmim]-



**Figure 2.** Pyrene (1  $\mu\text{M}$ )  $I_{\text{I}}/I_{\text{III}}$  versus  $\log[\text{CTAB}]$  in the absence (O) and presence of different concentrations of HeTAB (●) and [hmim][Br] (▲), respectively, at ambient conditions ( $\lambda_{\text{ex}} = 337$  nm and slit widths = 2 and 1 nm). The curves (—, ---, ···) represent fit to a simple sigmoidal expression. The inset shows pyrene emission spectra within premicellar (0.1 mM) and postmicellar (20 mM) aqueous CTAB.

[Br] and HeTAB, respectively. More importantly, however, the decrease is observed to be significantly more dramatic for [hmim][Br] addition than for HeTAB addition. Our  $N_{\text{agg}}$  results re-emphasize the difference in the behavior of HeTAB versus [hmim][Br] in modifying physicochemical properties of aqueous CTAB; IL shows a significantly more dramatic effect.

#### Microfluidity from 1,3-bis-(1-Pyrenyl)propane Fluorescence.

A change in the fluidity of the immediate microenvironment around a probe is effectively manifested through 1,3-bis-(1-pyrenyl)propane (BPP) steady-state emission spectra.<sup>9,10,15</sup> 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 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 within 150 mM aqueous CTAB in the presence of HeTAB and [hmim][Br], respectively, are presented in Figure 4 (insets). Due to its hydrophobic nature, BPP partitions into the micelles reporting on the microfluidity of the micellar pseudophase in the process.<sup>15</sup> BPP intramolecular excimer-to-monomer emission intensity ratio,  $I_{\text{E}}/I_{\text{M}}$ , as the function of additive concentration are plotted in Figure 4. A careful examination of Figure 4 clearly reveals the BPP cybotactic region to be significantly more fluidic in the presence of IL [hmim][Br] as compared to that in the presence of cosurfactant HeTAB. Different behavior of [hmim][Br] to that of HeTAB toward changing microfluidity of aqueous CTAB is clearly manifested; the role of IL is found to be more dramatic.

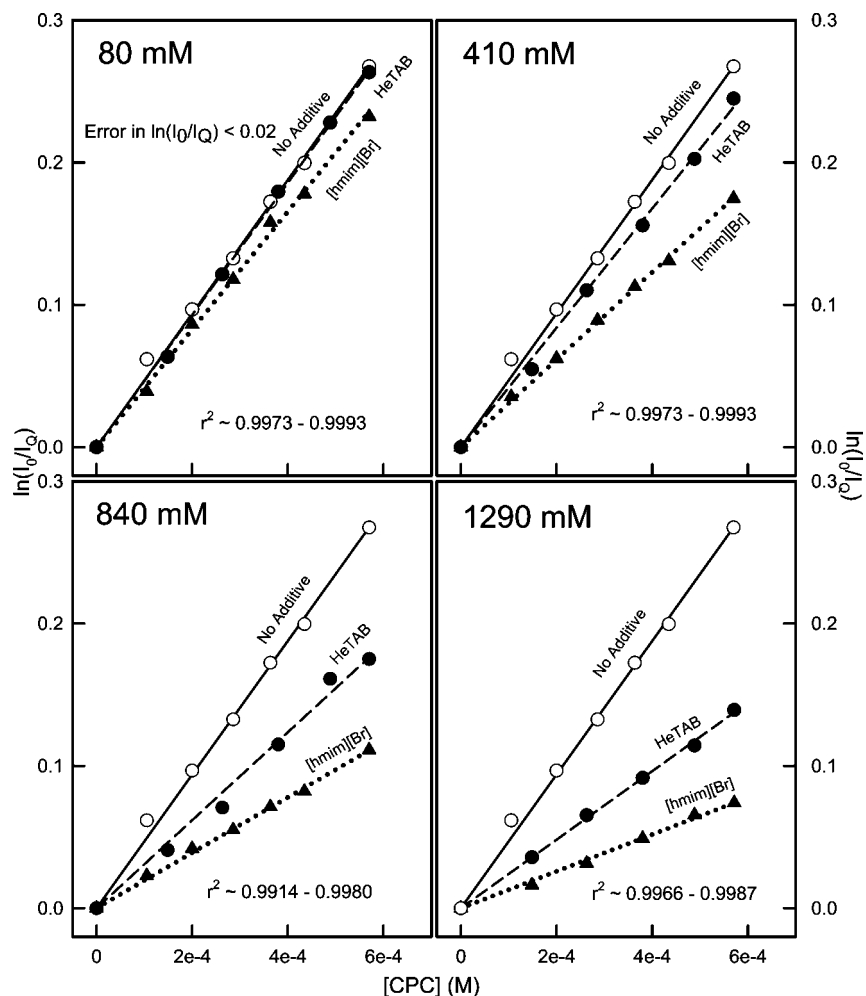
#### Dynamic Light Scattering for Average Aggregate Size.

Dynamic light scattering (DLS) is used to obtain the average size of the aggregates within aqueous CTAB in the presence of HeTAB and [hmim][Br]. Figure 5 shows the scattering intensity for the given diameter ( $D$ ) measured at ambient conditions of 150 mM aqueous CTAB upon addition of each of the two additives, respectively. Monomodal distribution is observed at each concentration of the additives. It is clear from the DLS data that although the average aggregate size appears to increase appreciably upon addition of either [hmim][Br] or HeTAB, the effect of the two on changing the average size and on the distribution of the aggregates is not the same. Drastic difference in the polydispersity is visible only for the maximum added concentration of the additives (i.e., for 1290 mM). The recovered peak diameters of the aqueous CTAB solutions in the presence of [hmim][Br] and HeTAB, respectively, are tabulated in Table 2. The increase in the average size of aggregates is found to be slightly less when [hmim][Br] is added compared to that when HeTAB is added. More importantly, although aggregates are more polydisperse in the presence of either of the additives, at 1290 mM the polydispersity in the presence of [hmim][Br] is considerably more than that in the presence of HeTAB.

#### Discussion

Our results clearly indicate the different roles and capabilities of IL [hmim][Br] versus cosurfactant HeTAB in modulating important physicochemical properties of aqueous CTAB. Specifically, when added at high concentrations (i.e., > 80 mM), IL [hmim][Br] as additive shows more dramatic increase in cmc and microfluidity and a decrease in  $N_{\text{agg}}$  as compared to when cosurfactant HeTAB is used as additive. Increase in the average aggregate size was not that different for the two additives; however, the polydispersity of the aggregates was found to be



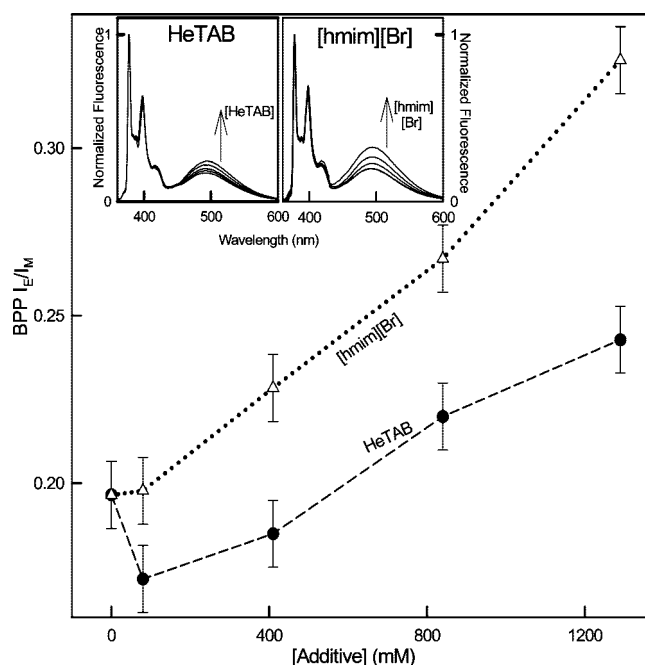


**Figure 3.** Pyrene ( $1 \mu\text{M}$ ) fluorescence quenching by CPC within  $150 \text{ mM}$  aqueous CTAB in the absence ( $\circ$ ) and presence of different concentrations of HeTAB ( $\bullet$ ) and  $[\text{hmim}][\text{Br}]$  ( $\blacktriangle$ ), respectively, at ambient conditions. The lines (—, ---, ...) represent the results of the linear regression analysis.

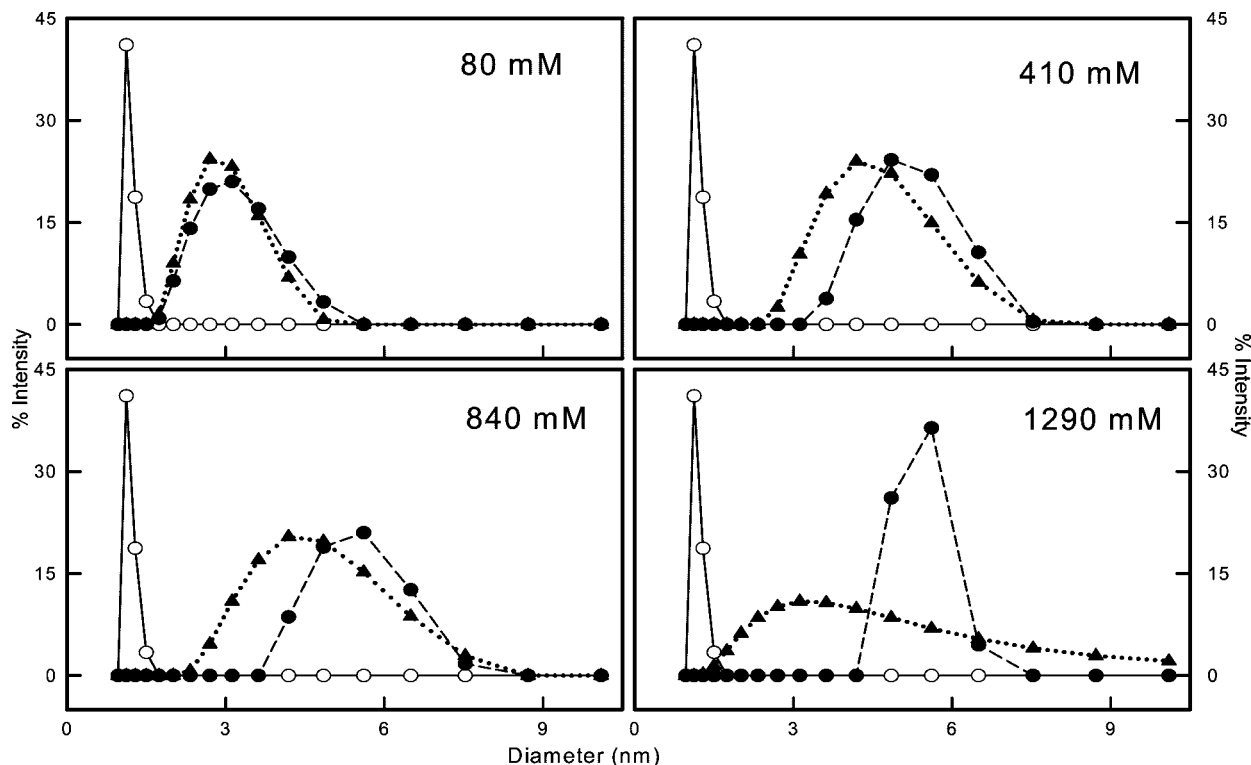
**TABLE 2: Aggregation Number ( $N_{\text{agg}}$ ) and Average Aggregate Size (Peak Diameter) of  $150 \text{ mM}$  Aqueous CTAB in the Presence of Different Concentrations of HeTAB and  $[\text{hmim}][\text{Br}]$ , Respectively, at Ambient Conditions**

concentration of additive in mM	aggregation number ( $N_{\text{agg}}$ )		peak diameter in nm (fwhm in nm)	
	HeTAB-added	$[\text{hmim}][\text{Br}]$ -added	HeTAB-added	$[\text{hmim}][\text{Br}]$ -added
0	$70 \pm 8$	$70 \pm 8$	$1.2 \pm 0.2$ ( $0.2 \pm 0.1$ )	$1.2 \pm 0.2$ ( $0.2 \pm 0.1$ )
80	$69 \pm 7$	$62 \pm 7$	$3.1 \pm 0.2$ ( $1.5 \pm 0.2$ )	$2.9 \pm 0.2$ ( $1.5 \pm 0.2$ )
410	$62 \pm 7$	$44 \pm 7$	$5.1 \pm 0.2$ ( $1.9 \pm 0.2$ )	$4.5 \pm 0.2$ ( $2.1 \pm 0.2$ )
840	$43 \pm 7$	$19 \pm 7$	$5.4 \pm 0.2$ ( $2.0 \pm 0.2$ )	$4.6 \pm 0.2$ ( $2.8 \pm 0.2$ )
1290	$30 \pm 6$	$4 \pm 2$	$5.4 \pm 0.2$ ( $1.3 \pm 0.2$ )	$5.1 \pm 0.2$ ( $3.2 \pm 0.4$ )

significantly different at very high additive concentration. Two major aspects concerning the differences between the two additives must account for these changes. First, the dissimilarities in the structure of the two cations (i.e., quaternary ammonium versus 1,3-dialkylimidazolium) must be emphasized toward any plausible explanation for the observed differences. Second, the interesting outcome from our previous studies strongly suggesting the role of IL as cosolvent at higher concentrations should also have large bearings on the outcomes, as our cosurfactant is devoid of this characteristic (maximum



**Figure 4.** BPP ( $1 \mu\text{M}$ )  $I_E/I_M$  versus  $[\text{HeTAB}]$  ( $\bullet$ ) and  $[\text{hmim}][\text{Br}]$  ( $\Delta$ ) within  $150 \text{ mM}$  aqueous CTAB. The inset shows BPP emission spectra within  $150 \text{ mM}$  aqueous CTAB in the presence of different concentrations of HeTAB and  $[\text{hmim}][\text{Br}]$ , respectively ( $\lambda_{\text{ex}} = 337 \text{ nm}$  and slit widths = 3 and 2 nm) at ambient conditions.



**Figure 5.** Dynamic light scattering results of 150 mM aqueous CTAB in the absence (○, —) and presence of different concentrations of HeTAB (●, ---) and IL [hmim][Br] (▲, ···), respectively, at ambient conditions.

IL concentration of 30 wt % in these studies are the same as those in our earlier reports).<sup>5b,6b,7a</sup>

As expected, trends in conductance of aqueous cationic CTAB in the presence of IL are similar to those observed by us earlier for aqueous anionic SDS in the presence of IL; these trends are different from those observed for aqueous nonionic triton X-100 and aqueous zwitterionic SB-12 upon addition of IL, respectively.<sup>6a,5a,7b</sup> Although the difference in the trends for triton X-100 is attributed to rather weak interactions between the surfactant and the IL, that for SB-12 is assigned to the interaction of both the cation and anion of the zwitterion headgroup of the surfactant with the anion and cation, respectively, of the IL. Specifically, H-bonding interaction between oxyethylene units of the surfactant and C2—H of bmim<sup>+</sup> cation in case of triton X-100, and electrostatic attraction between bmim<sup>+</sup> and PF<sub>6</sub><sup>-</sup>/BF<sub>4</sub><sup>-</sup> with opposite charged centers of the zwitterionic surfactant are responsible for the decrease in conductance on increasing surfactant concentration in the presence of IL, as both these surfactants have negligible contribution toward the total conductance of the solution due to their overall electrically neutral behavior. For SDS and CTAB, although the electrostatic attractive interaction takes place between the IL cation and anion with the surfactant, respectively, conductance increases on increasing surfactant concentration, as ions of both SDS and CTAB contribute significantly toward the total conductance of the solution even in the presence of IL ions.

The trend in the cmc of aqueous cationic CTAB as [hmim][Br] is added is the same as that observed for the cmc of aqueous anionic SDS and zwitterionic SB-12 upon addition of [bmim][BF<sub>4</sub>] (a decrease at lower [IL] is followed by an increase as the [IL] is increased).<sup>6b,7a</sup> It is noteworthy that the cmc of aqueous nonionic triton X-100 monotonically increases upon addition of IL [bmim][BF<sub>4</sub>].<sup>5b</sup> A similar decrease in cmc upon addition of either HeTAB or [hmim][Br] at low concentrations to aqueous CTAB indicates the electrolytic behavior of

the two additives to be fairly identical. An increase in the cmc at high additive concentrations, however, is more dramatic upon [hmim][Br] addition as compared to that upon HeTAB addition. Although mixed micelles are formed within the CTAB + HeTAB system, IL [hmim][Br], apart from forming mixed micelles with CTAB, may also act like a cosolvent. As mentioned earlier, two factors may contribute toward this. First, although within CTAB + HeTAB mixed micelles CTA<sup>+</sup> and HeTA<sup>+</sup> both have similar headgroups, the headgroups of CTA<sup>+</sup> and hmim<sup>+</sup> forming CTAB + [hmim][Br] mixed micelles are significantly different. The second fact concerns our previous observation of the role reversal of the IL to a cosolvent at higher concentrations.<sup>5b,6b,7a</sup> Addition of a cosolvent is known, in general, to increase the cmc of aqueous surfactant systems (vide infra). We can conclude that a more dramatic increase in cmc of aqueous CTAB upon [hmim][Br] addition is due in part to the structural dissimilarities between hmim<sup>+</sup> and CTA<sup>+</sup> and in part to the presence of [hmim][Br] as cosolvent within the aqueous surfactant system.

It is important to put our cmc results in context with those reported in the literature to draw further support to our propositions. It is reported that addition of electrolytes KBr to aqueous CTAB<sup>16a</sup> and NaBr to aqueous HeTAB,<sup>16b</sup> respectively, resulted in decreased cmc of the solution. The decrease in cmc of aqueous CTAB is also observed in the presence of long chain alcohols possessing cosurfactant-type behavior.<sup>16c</sup> Cosurfactants, such as cationic benzylhexadecyldimethylammonium chloride and nonionic Brij-58, when added at lower concentration, make the cmc of aqueous CTAB lower as well.<sup>16d</sup> Addition of ILs propyl-(2-hydroxyethyl)-dimethylammonium bromide,<sup>17a</sup> butyl-(2-hydroxyethyl)-dimethylammonium bromide,<sup>17a</sup> and didecyl-dimethylammonium nitrate,<sup>17b</sup> results in decreased cmc of aqueous CTAB. Addition of cosolvent ethylene glycol, however, results in an increase in the cmc of aqueous CTAB, DTAB, and TTAB.<sup>18a</sup> Other cosolvents such as tetrahydrofuran,<sup>18b</sup>

acetonitrile,<sup>18b</sup> and glycerol,<sup>14a</sup> also increase the cmc of aqueous CTAB upon addition. Cosurfactants such as polyoxyethylene sorbitan monolaurate,<sup>19a</sup> chlorohexidine digluconate, DTAB, and TTAB,<sup>19b</sup> form mixed micelles within aqueous CTAB and increase the cmc.

On a similar note, the extent of decrease in  $N_{agg}$  is observed to be significantly more when IL [hmim][Br] is added to aqueous CTAB as compared to when cosurfactant HeTAB is added to the same system. It is reported that increasing the mole fraction of a cosurfactant chlorohexidine digluconate (a dicationic surfactant) to the mixture containing cationic TTAB results in decreased  $N_{agg}$ .<sup>19b</sup> Cosolvents such as glycerol,<sup>14a</sup> ethylene glycol,<sup>18a</sup> and phenol<sup>20</sup> present at higher concentrations within aqueous CTAB also result in decreased  $N_{agg}$ . In line with the cosolvent nature of IL, we have earlier demonstrated that  $N_{agg}$  decreases as higher concentrations of IL [bmim][BF<sub>4</sub>] are added to aqueous nonionic triton X-100,<sup>5b</sup> anionic SDS,<sup>6b</sup> and zwitterionic SB-12.<sup>7a</sup> It is easy to conceive that the presence of a cosolvent [hmim][Br] within aqueous CTAB is able to reduce the  $N_{agg}$  to a greater extent.

A more dramatic increase in the microfluidity of aqueous micellar CTAB upon addition of IL [hmim][Br] as compared to the addition of cosurfactant HeTAB is a complex interplay of many factors. Because of the relatively high bulk viscosity of IL [hmim][Br],<sup>21</sup> one may argue that addition of this IL should result in a decrease in the microfluidity of the micellar pseudophase. However, a small  $N_{agg}$  value along with increased average size in the presence of [hmim][Br] hints at aggregates having considerable water penetration, thus demonstrating increased microfluidity; the water penetration is more apparent in the presence of [hmim][Br] than that in the presence of HeTAB as the decrease in  $N_{agg}$  is significantly more in the presence of [hmim][Br]. The difference in the partitioning of the probe BPP into the micellar pseudophase within HeTAB-versus [hmim][Br]-added aqueous CTAB may also contribute toward increased microfluidity, as the [hmim][Br]-added system may result in decreased partitioning of the probe into the micellar pseudophase. Again, the presence of IL [hmim][Br] as cosolvent appears to be responsible for a relatively more dramatic increase in the microfluidity of aqueous CTAB.

Interestingly, the average size of the aggregate appears to increase as either HeTAB or [hmim][Br] is added to aqueous CTAB; the increase is a little less for the [hmim][Br] addition, especially at higher concentrations. As far as additive-induced changes in the average micellar size is concerned, it is reported that increasing concentration of KBr results in an increase in the micellar size of aqueous CTAB and aqueous alkanediyl- $\omega$ -bis(dimethylcetyl ammonium bromide), a gemini surfactant.<sup>22</sup> Addition of *n*-butanol, *n*-pentanol, and *n*-hexanol, respectively, also result in increased average micellar hydrodynamic diameter of the same gemini surfactant. Importantly, the extent of increase is more as alkyl chain length of the alcohol is increased (i.e., increasing the cosurfactant nature of the alcohol). Although the addition of IL [bmim][Br] to an aqueous solution of block copolymer, PEO-PPO-PEO Pluronic P104, resulted in a dramatic increase in the effective diameter of the micelles formed by this nonionic copolymer,<sup>4w</sup> we reported a decrease in the average aggregate size of aqueous nonionic triton X-100<sup>5b</sup> and zwitterionic SB-12<sup>7a</sup> upon addition of IL [bmim][BF<sub>4</sub>]. However, an increase followed by a decrease in average aggregate size was noted by us when the same IL was added to aqueous anionic SDS.<sup>6b</sup> The monotonous increase in average aggregate size upon [hmim][Br] addition to aqueous CTAB is a unique feature inherent to this system. The interactions

involving IL ions and the surfactant are very different for a nonionic or a zwitterionic versus an anionic surfactant. One would expect these interactions for CTAB to be similar to those for SDS; however, one must realize that although the cation of the IL (i.e., bmim<sup>+</sup>) and -SO<sub>4</sub><sup>-</sup> of SDS are involved in electrostatic attractive interactions, in the present case the major interaction is between Br<sup>-</sup> of IL and -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> of CTAB. Further, the hexyl chain at position 1 of hmim<sup>+</sup> renders its involvement as a cosurfactant as well. ILs [bmim][BF<sub>4</sub>] and [hmim][Br] also have different properties as far as a cosolvent is concerned.

## Conclusions

The presence of IL [hmim][Br] or cosurfactant HeTAB results in modified physicochemical properties of aqueous CTAB; [hmim][Br] appears to be more severe in altering most of the properties investigated. We recognize the difference in the structure of the two cations (hmim<sup>+</sup> versus HeTA<sup>+</sup>) to play a role toward this, especially when these cations are acting as cosurfactants. However, the fact that IL [hmim][Br] possesses characteristics of a cosolvent and HeTAB does not, this should be the major contributor to the observation that the property changes are significantly more dramatic for IL [hmim][Br] addition as opposed to cosurfactant HeTAB addition. It can be concluded from our observations that both [hmim][Br] and HeTAB show electrolytic as well as cosurfactant behavior when present at lower concentrations. At higher concentrations, HeTAB continues to act as a cosurfactant, forming mixed micelles with CTAB; part of IL [hmim][Br] switches to the role of a cosolvent in modulating the properties of aqueous CTAB. The unique role of IL in modifying physicochemical properties of aqueous surfactant solution is thus amply established.

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## References and Notes

- (1) (a) Moroi, Y. *Micelles: Theoretical and Applied Aspects*; Springer: New York, 1992. (b) Jones, M. J.; Chapman, D. *Micelles, Monolayers, and Biomembranes*; Wiley-LISS: New York, 1995. (c) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989. (d) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; Wiley-Interscience: New York, 1973. (e) Holmberg, K.; Johnsson, B.; Kronberg, B.; Lindman, B. *Surfactants and Polymers in Aqueous Solution*, 2nd ed.; John Wiley & Sons: Chichester, 2003. (f) Baker, G. A.; Pandey, S.; Pandey, S.; Baker, S. N. *Analyst* **2004**, *129*, 890.
- (2) (a) Paul, B. C.; Islam, S. S.; Ismail, K. J. *Phys. Chem. B* **1998**, *102*, 7807. (b) Neves, A. C. S.; Valente, A. J. M.; Burrows, H. D.; Ribeiro, A. C. F.; Lobo, V. M. M. *J. Colloid Interface Sci.* **2007**, *306*, 166. (c) Bales, B. L.; Messina, L.; Vidal, A.; Peric, M.; Nascimento, O. R. *J. Phys. Chem. B* **1998**, *102*, 10347. (d) Dutkiewicz, E.; Jakubowska, A. *J. Phys. Chem. B* **1999**, *103*, 9898. (e) Srinivasan, V.; Blankschtein, D. *Langmuir* **2003**, *19*, 9946. (f) Ranganathan, R.; Peric, M.; Bales, B. L. *J. Phys. Chem. B* **1998**, *102*, 8436. (g) Wydro, P. *J. Colloid Interface Sci.* **2007**, *316*, 107. (h) Christov, N. C.; Denkov, N. D.; Kralchevsky, P. A.; Ananthapadmanabhan, K. P.; Lips, A. *Langmuir* **2004**, *20*, 565. (i) Nordstierna, L.; Furo, I.; Stilbs, P. *J. Am. Chem. Soc.* **2006**, *128*, 6704.
- (3) (a) *Ionic Liquids: Industrial Applications for Green Chemistry*; Rogers, R. D.; Seddon, K. R. Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002. (b) *Ionic Liquids III: Fundamentals, Challenges, and Opportunities*; Rogers, R. D.; Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2005. (c) Seddon, K. R. *Green Chem.* **2002**, *4*, G25–G26. (d) Crabb, C.

*Chem. Eng.* **2001**, March, 33. (e) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broken, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3, 156. (f) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003. (g) Welton, T. *Chem. Rev.* **1999**, 99, 2071. (h) Pandey, S. *Anal. Chim. Acta* **2006**, 556, 38. (i) Baker, G. A.; Baker, S. N.; Pandey, S.; Bright, F. V. *Analyst* **2005**, 130, 800. (j) Fletcher, K. A.; Pandey, S. *Appl. Spectrosc.* **2002**, 56, 266. (k) Pandey, S.; Fletcher, K. A.; Baker, S. N.; Baker, G. A. *Analyst* **2004**, 129, 569. (l) Baker, S. N.; Baker, G. A.; Bright, F. V. *Green Chem.* **2002**, 4, 165. (m) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. *J. Am. Chem. Soc.* **2002**, 124, 10276. (n) Solinas, M.; Pfaltz, A.; Cozzi, P. G.; Leitner, W. *J. Am. Chem. Soc.* **2004**, 126, 16142. (o) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, 399, 6731. (p) Malham, I. B.; Letellier, P.; Turmine, M. *J. Phys. Chem. B* **2006**, 110, 14212. (q) Triolo, A.; Russina, O.; Keiderling, U.; Kohlbrecher, J. *J. Phys. Chem. B* **2006**, 110, 1513. (r) Wang, L.; Chen, X.; Cahi, Y.; Hao, J.; Sui, Z.; Zhuang, W.; Sun, Z. *Chem. Commun.* **2004**, 24, 2840. (t) Pal, A.; Samanta, A. *J. Phys. Chem. B* **2007**, 111, 4724. (u) Singh, T.; Kumar, A. *J. Phys. Chem. B* **2007**, 111, 7843. (v) Singh, T.; Kumar, A. *J. Phys. Chem. B* **2008**, 112, 4079.

(4) (a) Fletcher, K. A.; Pandey, S. *Langmuir* **2004**, 20, 33. (b) Merrigan, T. L.; Bates, E. D.; Dorman, S. C.; Davis, Jr. J. H. *Chem. Commun.* **2000**, 2051. (c) Wang, J.; Wang, H.; Zhang, S.; Zhang, H.; Zhao, Y. *J. Phys. Chem. B* **2007**, 111, 6181. (d) Liu, J.; Cheng, S.; Zhang, J.; Feng, X.; Fu, X.; Han, B. *Angew. Chem.* **2007**, 46, 3313. (e) Li, N.; Cao, Q.; Gao, Y.; Zhang, J.; Zheng, L.; Bai, X.; Dong, B.; Li, Z.; Zhao, M.; Yu, L. *Chem. Phys. Chem.* **2007**, 8, 2211. (f) Gao, Y.; Li, N.; Zheng, L.; Bai, X.; Yu, L.; Zhao, X.; Zhang, J.; Zhao, M.; Li, Z. *J. Phys. Chem. B* **2007**, 111, 2506. (g) Dong, B.; Li, N.; Zheng, L.; Yu, L.; Inoue, T. *Langmuir* **2007**, 23, 4178. (h) He, Y.; Lodge, T. P. *J. Am. Chem. Soc.* **2006**, 128, 12666. (i) Simone, P. M.; Lodge, T. P. *Macromol. Chem. Phys.* **2007**, 208, 339. (j) He, Y.; Lodge, T. P. *Chem. Commun.* **2007**, 26, 2732. (k) Velasco, S. B.; Turmine, M.; Di Caprio, D.; Letellier, P. *Colloids Surfaces A* **2006**, 275, 50. (l) Atkin, R.; Warr, G. G. *J. Am. Chem. Soc.* **2005**, 127, 11940. (m) Araos, M. U.; Warr, G. G. *J. Phys. Chem. B* **2005**, 109, 14275. (n) Atkin, R.; Warr, G. G. *J. Phys. Chem. B* **2007**, 111, 9309. (o) Seth, D.; Chakraborty, A.; Setua, P.; Sarkar, N. *J. Phys. Chem. B* **2007**, 111, 4781. (p) Seth, D.; Chakraborty, A.; Setua, P.; Sarkar, N. *J. Chem. Phys.* **2007**, 126, 224512. (q) Yan, F.; Texter, J. *Angew. Chem.* **2007**, 46, 2440. (r) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. *Chem. Commun.* **2003**, 19, 2444. (s) Adhikari, A.; Sahu, K.; Dey, S.; Ghosh, S.; Mandal, U.; Bhattacharyya, K. *J. Phys. Chem. B* **2007**, 111, 12809. (t) Canilho, N.; Scholl, M.; Klok, H.; Mezzenga, R. *Macromolecules* **2007**, 40, 8374. (u) Sifaoui, H.; Lugowska, K.; Domanska, U.; Modaressi, A.; Rogalski, M. *J. Colloid Interface Sci.* **2007**, 314, 643. (v) Beyaz, A.; Woon, S. O.; Reddy, V. P. *Colloids Surfaces B* **2004**, 35, 119. (w) Zheng, L.; Guo, C.; Wang, J.; Liang, X.; Chen, S.; Ma, J.; Yang, B.; Jiang, Y.; Liu, H. *J. Phys. Chem. B* **2007**, 111, 1327.

(5) (a) Behera, K.; Dahiya, P.; Pandey, S. *J. Colloid Interface Sci.* **2007**, 307, 235. (b) Behera, K.; Pandey, M. D.; Porel, M.; Pandey, S. *J. Chem. Phys.* **2007**, 127, 184501.

(6) (a) Behera, K.; Pandey, S. *J. Colloid Interface Sci.* **2007**, 316, 803. (b) Behera, K.; Pandey, S. *J. Phys. Chem. B* **2007**, 111, 13307.

(7) (a) Behera, K.; Pandey, S. *Langmuir* **2008**, 24, 6462. (b) Behera, K.; Pandey, S. *J. Colloid Interface Sci.* DOI: 10.1016/j.jcis.2008.11.008.

(8) (a) Lopez-Martin, I.; Burello, E.; Davey, P. N.; Seddon, K. R.; Rothenberg, G. *ChemPhysChem* **2007**, 8, 690. (b) The melting point of

HeTAB was obtained on an electrothermal melting point apparatus obtained from M/S Toshniwal.

(9) (a) Acree Jr., W. E. Absorption and luminescence probes. In *Encyclopedia of Analytical Chemistry: Theory and Instrumentation*, Meyer, R. A. Ed.; John Wiley & Sons, Ltd.: Chichester, 2000. and references cited therein. (b) Suppan, P.; Ghoneim, N. *Solvatochromism*; Royal Society of Chemistry: Cambridge, 1997. (c) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer Publisher: New York, 2006. and references cited in each of the chapters.

(10) (a) Pandey, S.; Redden, R. A.; Fletcher, K. A.; Palmer, C. P. *Macromol. Chem. Phys.* **2003**, 204, 425. (b) Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, 99, 3951. (c) Waris, R.; Acree Jr., W. E.; Street Jr., K. W. *Analyst* **1988**, 113, 1465. (d) Fletcher, K. A.; Pandey, S. *J. Phys. Chem. B* **2003**, 107, 13532. (e) Baker, G. A.; Bright, F. V.; Pandey, S. *Chem. Educ.* **2001**, 6, 223.

(11) (a) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, 99, 2039. (b) Ananthapadmanabhan, K. P.; Goddard, E. D.; Turro, N. J.; Kuo, P. L. *Langmuir* **1985**, 1, 352.

(12) (a) Dutta, P.; Sen, S.; Mukherjee, S.; Bhattacharyya, K. *Chem. Phys. Lett.* **2002**, 359, 15. (b) Sen, S.; Sukul, D.; Dutta, P.; Bhattacharyya, K. *J. Phys. Chem. B* **2002**, 106, 3763. (c) Sarkar, N.; Bhattacharyya, K. *Chem. Phys. Lett.* **1991**, 180, 283. (d) Karukstis, K. K.; McDonough, J. R. *Langmuir* **2005**, 21, 5716.

(13) (a) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, 100, 5951. (b) Sabate, R.; Estelrich, J. *J. Phys. Chem. B* **2003**, 107, 4137. (c) Tachiya, M. *Chem. Phys. Lett.* **1975**, 33, 289. (d) Tachiya, M. *J. Chem. Phys.* **1982**, 76, 340.

(14) (a) Errico, G. D.; Ciccirelli, D.; Ortona, O. *J. Colloid Interface Sci.* **2005**, 286, 747. (b) Ferreira, T. L.; Seoud, O. A. E.; Bertotti, M. *J. Electroanal. Chem.* **2007**, 603, 275.

(15) (a) Snare, M. J.; Thistlethwaite, P. J.; Ghiggino, K. P. *J. Am. Chem. Soc.* **1983**, 105, 3328. (b) Zachariasse, K. A. *Chem. Phys. Lett.* **1978**, 57, 429.

(16) (a) Singh, H. N.; Swarup, S.; Salim, S. M. *J. Colloid Interface Sci.* **1979**, 68, 128. (b) Mosquera, V.; Rio, J. M.; Attwood, D.; Garcia, M.; Jones, M. N.; Prieto, G.; Suarez, M. J.; Sarmiento, F. *J. Colloid Interface Sci.* **1998**, 206, 66. (c) Munoz, M.; Graciani, M. D. M.; Rodriguez, A.; Moya, M. L. *Int. J. Chem. Kinet.* **2004**, 36, 634. (d) Dar, A. A.; Rather, G. M.; Das, A. R. *J. Phys. Chem. B* **2007**, 111, 3122.

(17) (a) Modaressi, A.; Sifaoui, H.; Grzesiak, B.; Solimando, R.; Domanska, U.; Rogalski, M. *Colloids Surfaces A* **2007**, 296, 104. (b) Sifaoui, H.; Lugowska, K.; Domanska, U.; Modaressi, A.; Rogalski, M. *J. Colloid Interface Sci.* **2007**, 314, 643.

(18) (a) Rodriguez, A.; Munoz, M.; Graciani, M. D. M.; Moya, M. L. *J. Colloid Interface Sci.* **2006**, 298, 942. (b) Misra, P. K.; Mishra, B. K.; Behera, G. B. *Colloids Surf.* **1991**, 57, 1.

(19) (a) Das Gupta, P. K.; Moulik, S. P. *Colloid Polym. Sci.* **1989**, 267, 246. (b) Attwood, D.; Patel, H. K. *J. Colloid Interface Sci.* **1989**, 129, 222.

(20) Mata, J. P.; Aswal, V. K.; Hassan, P. A.; Bahadur, P. *J. Colloid Interface Sci.* **2006**, 299, 910.

(21) Bulk viscosity of dried samples of the IL [hmim][Br] at ambient conditions is separately measured in our laboratory using an Automated Microviscometer (model AMVn) purchased from Anton Paar, Austria.

(22) Siddiqui, U. S.; Ghosh, G.; Din, K. *Langmuir* **2006**, 22, 9874.

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