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Modification of photophysics of 3-hydroxyflavone in aqueous solutions of imidazolium-based room temperature ionic liquids: A comparison between micelle-forming and non micelle-forming ionic liquids

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In the present article, we have investigated the photophysical behavior of 3-hydroxyflavone (3HF), an excited state intramolecular proton transfer (ESIPT) probe, in aqueous
10 solutions of two imidazolium-based room temperature ionic liquids (RTILs), one micelle-forming and the other non micelle-forming, exploiting steady state and time resolved fluorometric techniques. The study unveils that the ESIPT process of 3HF is modified substantially in the micelle-
15 forming RTIL as compared to that in the other RTIL. The critical micellar concentration (CMC) of the micelle-forming RTIL has been determined from both steady state and time resolved data. The study suggests that 3HF resides within the micellar phase and experiences significantly less polar
20 environment in its vicinity than in the non micelle-forming ionic liquid. A comparative study with the probe in the micelle-forming ionic liquid and a conventional anionic surfactant of a similar hydrophobic chain length reveals that 3HF experiences appreciably less polar environment in the
25 RTIL micelle as compared to the conventional anionic micelle.

Introduction

The search for "green chemistry" has led to the realization of the significance of solvent free synthesis and thus, in recent past,
30 room-temperature ionic liquids (RTILs) have received extensive attention as novel media for chemical synthesis,[1] homogeneous catalysis,[2] electrochemistry[3] and separation techniques.[4] RTILs serve well as replacement of conventional solvents due to their negligible vapor pressure, wide electrochemical windows,
35 thermal stability, high ionic conductivity and a wide span of liquefying temperature (~ 96–300°C).[5–8] High reactivity and immiscibility with other solvents, however, restrict their uses to some extent.[5,7] For the last two decades, research employing the ionic liquids as reaction media has been gradually enhancing and
40 a large number of articles have already come out describing their physicochemical properties and applications.[5,7,9-11] A wide variety of chemical reactions including Friedel–Crafts reaction, Diels–Alder reaction, hydrogenation, and polymerization have been performed in RTILs.[5,12] Photophysical behavior of dyes like nile
45 red, pyrene, pyrene carboxaldehyde have been monitored to access the polarity of RTILs.[9,13-15] RTILs consisting of

imidazolium-based cation are currently the focus of extensive investigation. Recent studies on some imidazolium and pyridinium ionic liquids suggest that these ionic liquids are more
50 polar than acetonitrile but less polar than methanol.[15,16] It is also reported that the polarity of an ionic liquid is largely determined by the cationic part of it.[16] Since ionic liquids are sufficiently polar, it is interesting to study the photophysical behavior of dipolar fluorophores in these media. Recently, we have
55 investigated the photophysics of an intramolecular charge transfer (ICT) probe, namely, 3-acetyl-4-oxo-6,7-dihydro-12H indolo-[2,3-a] quinolizine, in imidazolium-based room temperature ionic liquids.[17] Ionic liquids containing long alkyl chain generally exhibit surface active properties and are known as surface active
60 ionic liquids (SAILs).[18] SAILs have achieved significant importance in the field of biochemistry because of their ability to form various self-assembled nanostructures.[19] Investigations on SAILs reveal that the surface activity of the long-chain imidazolium RTILs are superior to conventional ionic surfactants
65 with similar hydrocarbon chain length in aqueous as well as non-aqueous media.[20] Miskolczy et al. have shown that 1-butyl-3-methylimidazolium octyl sulfate ([BMIM][C_8SO_4]) forms micelle in aqueous solution with a critical micelle concentration (CMC) of 31 mM.[21] Studies on neat [BMIM][C_8SO_4] suggest that strong
70 hydrogen bonding between the ion pair leads to a fluid structure of this RTIL.[22] Tuning the hydrophobicity of the RTILs, one can modify the major characteristics such as the CMC, aggregation number, and micropolarity of the micelles dispersed in aqueous medium. Thus, the micelle-forming RTILs have developed a
75 special position in the arena of RTILs.

In the present study, we have investigated the photophysical behavior of a naturally occurring bioactive plant flavonoid, 3-hydroxyflavone (3HF), in aqueous solutions of RTILs. 3HF exhibits strong antioxidant activity in membrane environment,
80 suggesting that it has the potential to act as a therapeutic agent.[23] It is also one of the best-known prototype molecules undergoing excited state intramolecular proton transfer (ESIPT) and thereby exhibiting dual fluorescence.[24-27] ESIPT process of 3HF is sensitive to the solvent polarity and proticity. Apart from the
85 conventional solvents,[28-31] ESIPT of 3HF has been extensively investigated in different biomimicking microheterogeneous environments like micelles, model membranes, DNA *etc*.[32-34] However, it is important to know how the photophysics of this

ESIPT probe is modified in aqueous RTIL environments. With this objective, we have monitored the intramolecular proton transfer process of 3HF in aqueous solutions of two different RTILs namely, 1-butyl-3-methylimidazolium tetrafluoro borate ([BMIM][BF$_4$]) and 1-butyl-3-methylimidazolium octyl sulfate ([BMIM][C$_8$SO$_4$]), both having the same imidazolium cationic part. However, the latter is capable of forming micelle in aqueous solution while the former not. The structures of both the forms of 3HF that exist during the ESIPT process and the RTILs are shown in Scheme 1. Through steady state and time resolved fluorescence techniques we have shown that the photophysical behavior of 3HF is significantly modified in the aqueous solutions of the two ionic liquids (ILs). Micelle-forming one has more pronounced effect on the ESIPT process of 3HF than its counterpart. We have determined the CMC of [BMIM][C$_8$SO$_4$] that agrees well with the literature value. Further, the photophysical behavior of the probe in the aqueous solution of micelle-forming RTIL, *i.e.*, [BMIM][C$_8$SO$_4$] has been compared with a conventional micelle, *viz.*, sodium octyl sulfate (S$_8$S), having equivalent surfactant chain length.
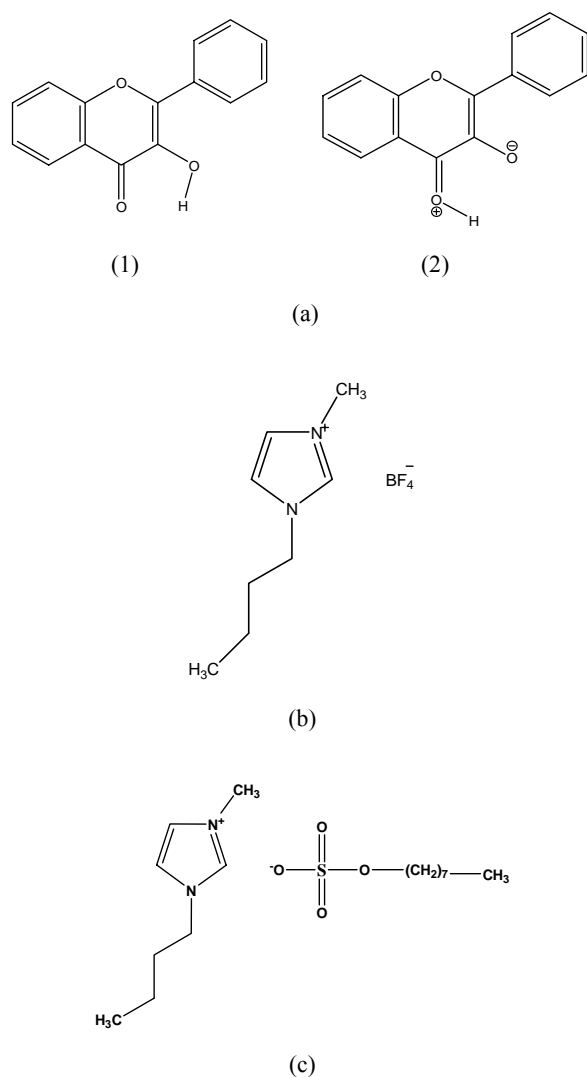
Scheme 1. Structures of (a) 3HF (normal (1) and tautomer (2) form), (b) [BMIM][BF$_4$] and (c) [BMIM][C$_8$SO$_4$].

Experimental

Materials

3HF was purchased from Fluka (USA) and used without further purification. Carbazole was procured from Aldrich (USA) and was purified by repeated crystallization from 75% alcohol. [BMIM][BF$_4$] and [BMIM][C$_8$SO$_4$] were obtained from Sigma-Aldrich (USA) and purified according to the literature procedure.[21] Sodium octyl sulfate (S$_8$S) was procured from Fluka (USA) and used as obtained. AR grade potassium iodide (KI) and potassium nitrate (KNO$_3$) were obtained from (Merck, India) and used as received. Spectroscopic grade 1,4-dioxane (Spectrochem, India) and ethanol (Merck, India) were used as received. Deionised water from a Milli-Q water purification system (Millipore) was used throughout the experiment. The concentration of 3HF was kept at ca. 20 µM throughout the study.

Methods

Shimadzu UV-2450 absorption spectrophotometer (Shimadzu Corporation, Kyoto, Japan) was used for the steady state absorption studies. Steady state fluorescence measurements were carried out in a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. All the measurements were carried out at room temperature (298 K). Freshly prepared solutions were used for the spectroscopic measurements.

Time resolved fluorescence decay measurements were done by the time-correlated single photon counting (TCSPC) technique in Horiba–Jobin–Yvon FluoroCube fluorescence lifetime system using NanoLED (IBH, UK) as the excitation source at 370 nm and TBX photon detection module as the detector. The decays were analyzed using IBH DAS-6 decay analysis software. The lamp profile was collected by placing a scatterer (dilute micellar solution of sodium dodecyl sulfate in water) in place of the sample. Goodness of the fits was judged from the χ^2 criterion and visual inspection of the residuals of the fitted function to the data. Mean (average) fluorescence lifetimes (τ_{avg}) for triexponential iterative fittings were calculated from the decay times (τ_1, τ_2 and τ_3) and the normalized pre-exponential factors (a_1, a_2 and a_3 ; $a_1 + a_2 + a_3 = 1$) using the following relation

$$\tau_{avg} = a_1\tau_1 + a_2\tau_2 + a_3\tau_3 \qquad (1)$$

Results and discussion

Steady state absorption and emission studies

In water, 3HF shows a low energy broad absorption band with λ_{max} at ~ 345 nm with a hump at ~ 305 nm as shown in Figure 1.[34] In aqueous ionic liquid (IL) environments a decrease in the absorbance is observed without any significant shift in the peak positions. A regular modification of the absorption spectrum of 3HF with the gradual increase in the composition of the ILs in the solutions indicates that the immediate environments around the probe differ from the bulk aqueous phase. The weak band found to be developed in the longer wavelength region (λ_{max} ~ 410 nm) of the absorption spectra of 3HF in aqueous IL solutions is ascribed to the anionic form of 3HF based on the observation of the similar absorption band by Mandal and Samanta for the same probe in alcoholic solvents.[31]
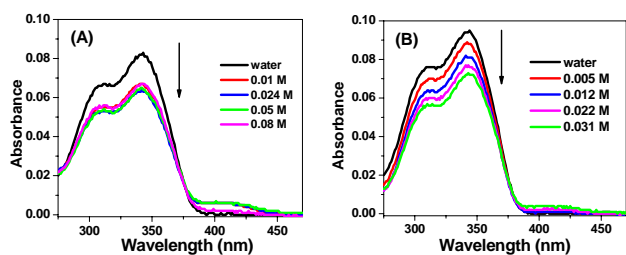
Figure 1. Absorption spectra of 3HF in water and in varying concentrations of (A) [BMIM][BF$_4$] and (B) [BMIM][C$_8$SO$_4$]. The concentrations of the ILs are provided in the legends. [3HF] = 20 μM.

In aqueous medium, photoexcitation of 3HF at 345 nm exhibits dual emission with band maxima at 410 nm and 510 nm, corresponding to the normal and the photoproduced tautomer respectively.[32,34] Figure 2 represents the variation in the emission spectra of 3HF in the presence of added ILs. Gradual addition of ILs to the aqueous solution of 3HF causes an enhancement in the emission intensity of the normal species with a concomitant decrease in the intensity of the other band corresponding to the tautomeric species; for micelle-forming IL, however, intensities of both the emission bands increase after reaching the CMC.
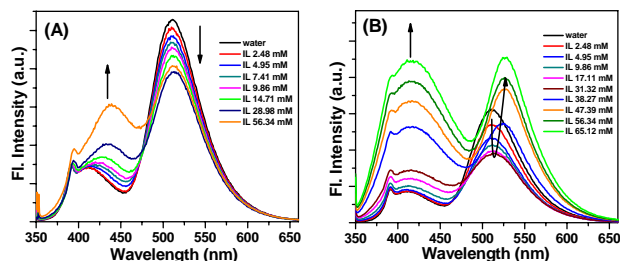
Figure 2. Variation in the emission spectra of 3HF with the addition of (A) [BMIM][BF$_4$] and (B) [BMIM][C$_8$SO$_4$]. The concentrations of the ILs are provided in the legends. The sharp peak around 392 nm arises due to the Raman scattering of the solvent medium. λ$_{exc}$ = 345 nm, [3HF] = 20 μM.

This variation in the fluorometric behaviour of 3HF in aqueous IL media (in the entire range of concentrations studied for [BMIM][BF$_4$] and till the attainment of CMC in case of [BMIM][C$_8$SO$_4$]) has been ascribed to a modification of the ESIPT process, induced by the increased ionic strength of the medium with the addition of the ILs. This assignment comes from an independent experiment with the observation of a similar variation in the fluorescence spectra of the probe in aqueous solution with the gradual addition of KNO$_3$ (figure not shown). In case of the micelle-forming IL, after attainment of the CMC emission intensities of both the normal and the tautomer species increase associated with a bathochromic shift in the emission maximum of the latter. Similar bathochromic shift in the emission maximum of the tautomer of 3HF is observed in microheterogeneous environments like lipid, DNA, micelles *etc*.[32-34] A relatively lower polarity around the probe in the micellar microenvironment has been assigned responsible for this observation (see later). To obtain a clearer picture of the variation of the emission behavior of both the forms of 3HF in aqueous IL solutions, we have plotted the ratio of the emission intensities (height at the respective emission maxima) of the normal to the tautomeric species of the probe (Figure 3). Figure 3 reveals that

with increasing concentrations of ILs the ratio increases indicating that the ESIPT process of 3HF is restricted. Interestingly, for [BMIM][C$_8$SO$_4$], we observe a prominent break-point in the ratio at IL concentration 0.032 (M). This value corresponds to the CMC value of [BMIM][C$_8$SO$_4$]. The obtained value is in excellent agreement with the literature value of the CMC of [BMIM][C$_8$SO$_4$], *i.e.*, 0.031 M.[21] Once the CMC is attained the ratio becomes nearly invariant to the [BMIM][C$_8$SO$_4$] concentration. Figure 2 (B) shows that after CMC, the emission intensities of both the forms of 3HF increases appreciably. This observation can be rationalized by considering the encapsulation of the probe within the less polar region of the micelle. The substantial increment in the fluorescence intensities
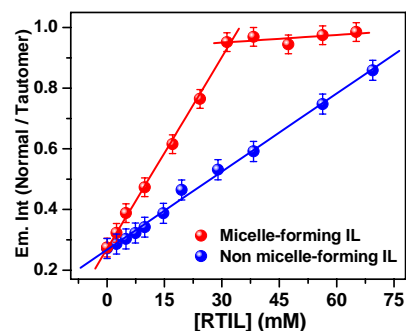
Figure 3. Variation in the ratio of emission intensities of the normal form to that of tautomeric species of 3HF in aqueous solutions of RTILs.

of both the normal and tautomer is ascribed to the decrease in non-radiative deactivation rates within the confined micellar cage. Similar enhancement in the emission intensities of both the forms of 3HF has been reported by Banerjee and Sengupta when the probe is encapsulated within the hydrophobic cavity of β-cyclodextrin (β-CD).[35] Simultaneous enhancement in emission intensities of both the normal and charge transfer bands of two twisted intramolecular charge transfer molecules, namely, dimethylamino benzonitrile and dimethylamino benzaldehyde upon encapsulation within the confined nanocavity of cyclodextrins have also been reported by Bhattacharyya *et al.* and Chattopadhyay *et al.* respectively.[36,37] We have determined the CMC of [BMIM][C$_8$SO$_4$] from the breakpoint of the plot of the emission intensity of the tautomeric species against the [BMIM][C$_8$SO$_4$] concentration (Fig S1, given in the ESI†) and the obtained value (0.030 M) is in good agreement with the literature value (0.031 M). It is pertinent to mention here that it is better to use the ratiometric plot rather than the single band based measurement for the determination of the CMC due to the fact that by adopting ratiometric method one can overcome many of the instrumental as well as experimental artefacts.[38,39] Further, we have monitored the ESIPT process of 3HF in the aqueous solution of a conventional anionic surfactant of similar hydrophobic chain length, *viz.*, sodium octyl sulfate (S$_8$S). Variation in the emission spectra of 3HF with the added surfactant is provided in the ESI† (Fig. S2). Unlike the micelle-forming IL, in case of S$_8$S a new band appears at around 460 nm (Fig. S2 in the ESI†). In tune with the work of Mandal and Samanta this band is ascribed to the anionic form of 3HF.[31] As the fluorescence band of the normal form is contaminated by this 460 nm emission band, we have not used the ratiometric plot (as

done for the ILs) for the determination of CMC of S_8S. Rather we have used only the tautomer emission to serve the purpose since this emission is far from the aforesaid band. Figure S3, in the ESI[†] depicts the variation of the tautomer emission with
5 increasing S_8S concentration. The plot shows a break at the 0.132 M S_8S concentration and this value corresponds to the CMC value of S_8S. The determined value is in agreement with the literature value of CMC of S_8S, *i.e.*, 0.136 M.[17] It is important to note that we get another break at 0.21 M S_8S concentration (Fig.
10 S3). To substantiate this observation, we have also performed an independent experiment with an excited state proton transfer probe, carbazole. At pH higher than 7, carbazole shows dual emission, one at ~ 360 nm which is due to the normal species and the other one at ~ 415 nm ascribed to the anionic form produced
15 exclusively in the photoexcited state.[40] We have recorded the emission spectra of carbazole at pH ~ 12 with increasing concentration of S_8S (Fig. S4). The variation in the ratio of emission intensities of the neutral form to that of the anionic form of carbazole in the aqueous solution of S_8S is depicted in figure
20 S5. As observed for 3HF (Fig. S3), figure S5 also shows two breaks, one at 0.139 M and the other one at 0.21 M S_8S concentration. The breakpoint around S_8S concentration 0.136 M for both 3HF and carbazole corresponds to the CMC of S_8S. The second breakpoint around 0.21 M S_8S concentration is ascribed to
25 the change in the shape of S_8S micelle. It is known that at high enough concentration, small spherical SDS micelles aggregate to yield rod-shapped units.[40] Interestingly no such literature report is available as yet on the micellar shape change at higher concentration of S_8S. The study, thus, establishes that ESIPT
30 process of 3HF can be exploited as a sensitive probe for the estimation of CMCs and the structural aspects of the micelle-forming ionic liquids as well as conventional surfactants. Comparison of the microenvironments around 3HF in both types of micelles (S_8S and $[BMIM][C_8SO_4]$) is discussed in the
35 forthcoming section.

Determination of polarity of the microenvironment

Determination of the polarity in the immediate vicinity of a probe provides an efficient way to assess the location of the probe within the microheterogeneous environment.[41] Local polarity in
40 the vicinity of a probe in a microheterogeneous environment can be estimated from a comparison of the spectral behaviour of the fluorophore in the environment with those in pure solvents or solvent mixtures of known polarities.[41,42] We have determined the micropolarity values around the vicinity of 3HF in the aqueous
45 RTIL environments and S_8S micelle in order to assess the relative values of the polarities around the probe in different environments.

For the purpose, we have used the equivalent $E_T(30)$ scale, based on the transition energy for the charge transfer absorption
50 of the betaine dye 2,6-diphenyl-4(2,4,6 triphenyl-1-pyridono)phenolate, as proposeded by Kosower and Reichardt.[43,44] We have compared the fluorescence behavior of 3HF in aqueous solutions of both the RTILs and S_8S micelle to that of a series of mixtures of dioxane and water with varying
55 composition.[45-47] The $E_T(30)$ values for different compositions of the dioxane-water mixtures are taken from the work of Kosower et al.[42] Water/dioxane mixture is chosen for this study since it covers a wider range of polarity than the commonly used

water/alcohol mixture.[42]

60 The emission maximum of 3HF tautomer shifts towards red on increasing the percentage of dioxane in the water-dioxane mixture. Representative plot monitoring the energies corresponding to the fluorescence maxima of 3HF tautomer in the water-dioxane mixtures reveals a linear correlation with $E_T(30)$
65 (Fig. 4). Interpolating the values of the energies corresponding to the 3HF tautomeric emission maxima of 3HF in aqueous solutions of 69.44 mM $[BMIM][BF_4]$, 65.12 mM $[BMIM][C_8SO_4]$ and 0.27 M S_8S on the calibration line, the micropolarity values around the probe in these media are
70 determined. The determined values are compiled in Table 1.
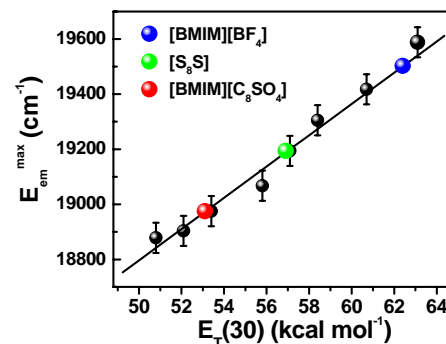
Figure 4. Variation of the energy corresponding to the maximum of 3HF tautomer emission as a function of $E_T(30)$ in water-dioxane mixtures. The interpolated values corresponds to 69.44 mM $[BMIM][BF_4]$ (blue), 0.27
75 M $[S_8S]$ (green) and 65.12 mM $[BMIM][C_8SO_4]$ (red).

Table 1. $E_T(30)$ values of 3HF in aqueous and other environments

Environment	Concentration (M)	$E_T(30)$ (kcal mol^{-1})
Water	-	63.1
$[BMIM][BF_4]$	0.069	62.4
$[BMIM][C_8SO_4]$	0.065 (~ 2 times CMC)	53.1
S_8S	0.270 (~ 2 times CMC)	56.9

A close inspection of Table 1 suggests that at similar concentrations of the two RTILs studied, the micropolarity
80 around the probe in micelle-forming IL environment is substantially lower than that of the other RTIL. A similar value of micropolarity (52.8 kcal mol^{-1}) around 3HF is reported by Jana *et al.* in ctDNA environment.[34] By looking at the comparable micropolarity values of 3HF in $[BMIM][C_8SO_4]$ environment and
85 ctDNA medium, we can infer that the probe resides within the micellar units where the polarity is lower than the bulk aqueous phase whereas the polarity in the non micelle-forming IL environment is reduced marginally from that of the bulk aqueous medium. A slight lowering of polarity in the non micelle-forming
90 IL environment may be ascribed to the overall lowering of the medium polarity since ILs are known to be less polar than water. Further, a comparison of the $E_T(30)$ values of the probe in $[BMIM][C_8SO_4]$ micelle and S_8S micelle at their respective two times CMCs reveals that the polarity within the RTIL micelle is
95 appreciably less than that in the conventional micelle (S_8S) with the same hydrophobic chain length. As the chain lengths of the anionic components of both the surfactant systems are the same, the cationic counterpart is assigned to be responsible for this differential observation, consistent with the literature.[16]
100 The estimated $E_T(30)$ values of the immediate vicinity of 3HF

in the IL media suggest that the probe resides within the micellar phase in the micelle-forming IL. NMR spectral study can serve as an useful tool to monitor the inclusion of probes in microheterogeneous environments, provided the solubility of the probe in the environment is sufficiently high.[48] Unfortunately, in the present case, poor solubility of 3HF (in the range of tens of micromolar) could not provide any support to the inclusion of 3HF in the RTIL micellar environment through NMR study. However, fluorometric techniques are sensitive enough to monitor such processes and hence we have adopted them.
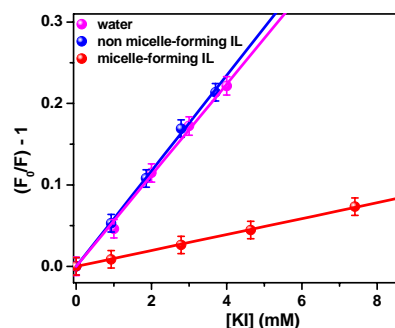
Fluorescence quenching study

Fluorescence quenching study provides information about the accessibility of the fluorophore towards the quencher and hence, it is exploited to find the location of the fluorophores in various microheterogeneous environments.[34,41,45] In the present work, quenching studies of 3HF in water and in the two RTIL media have been performed using potassium iodide as quencher to substantiate the encapsulation of 3HF within the RTIL micellar phase. The experimental data follows the Stern-Volmer equation

$$F_0/F = 1 + K_{SV} [Q] \qquad (2)$$

$$\text{or, } F_0/F - 1 = K_{SV} [Q] \qquad (3)$$

where F_0 and F are the fluorescence intensities in the absence and in the presence of the quencher, $[Q]$ is the molar concentration of the quencher (KI) and K_{SV} is the Stern-Volmer quenching constant. K_{SV} acts as an indicator to judge the exposure of the fluorophore to the quencher. Higher the value of K_{SV} higher is the degree of accessibility of the fluorophore to the quencher. Figure 5 represents the Stern-Volmer plots and depicts the relative extent of quenching of 3HF in water and the two RTIL media. The slopes of the Stern-Volmer plots (Figure 5) provide the values of K_{SV} to be 56.0 M^{-1}, 9.8 M^{-1}, and 58.6 M^{-1} for water, micelle-forming IL and non micelle-forming IL respectively. Figure 5 and the determined K_{SV} values clearly indicate that in the non micelle-forming IL medium, the accessibility of the probe to the quencher is almost the same as that in water whereas in the micelle-forming IL medium the accessibility of the probe is reduced drastically. It is known that the ionic quencher (I^-) is preferentially available in polar region, *i.e.*, in the bulk aqueous phase and the water-micelle interface but not expected to be available in the micellar phase due to the low polarity of the region. The observations of the quenching study thus, establish that 3HF resides in the less polar RTIL micellar phase where the availability of the ionic quencher is appreciably low. It is pertinent to mention here that we have used the emission intensity values of the normal form (410 nm) to construct the Stern-Volmer plots (Figure 5). However, tautomer emission (510 nm) data also produces a similar result.


Figure 5. Stern-Volmer plots for the fluorescence quenching of 3HF by I^- ion in water and two RTIL media as mentioned in the figure legends.

### Time resolved fluorescence decay measurements

Fluorescence lifetime measurement often serves as a sensitive indicator of the local environment around a fluorophore and is responsive toward excited state interactions.[42,49] In an attempt to follow a generalized picture of the effect of ILs on the ESIPT process of 3HF, we have recorded the fluorescence decays of 3HF in the presence of varying concentrations of ILs. Figures 5 and 6 represent the characteristic decay profiles of both the forms of 3HF in aqueous solutions of RTILs. We have collected the decays at higher wavelength (550 nm) than the corresponding emission maxima of the tautomer to exclude any possible contribution coming from the emission of the normal species. The deconvoluted data are compiled in Tables S1 − S4, in the ESI[†]. Although some of the reported lifetime values are quite short (within the instrument response function (IRF)), they earn reliability since deconvolution can produce reliable values below the IRF for experiments where the instrument as well as the measuring systems are stable. Moreover, the relative changes in the lifetime values with a change in the medium are meaningful under similar experimental conditions. Further, in case of excited state prototropic process like ESIPT one might expect a grow-in component with negative pre-exponential factor for the fluorescence decay of the tautomeric species produced exclusively in the photoexcited state. However, we were unable to monitor it since the rate of the ESIPT process for the studied probe (in the range of femtosecond[50]) is well below the resolution of our set-up. Figures 6 and 7 reveal that in water both the forms of 3HF show biexponential decay pattern with average fluorescence lifetime values of 0.20 ns and 0.26 ns for the normal and tautomeric species respectively. With the addition of the RTILs the fluorescence decays of both the forms of 3HF become triexponential (Figs. 6 and 7). Triexponential fluorescence decays of probes are quite common in microheterogeneous environments.[42,46,49] The multiexponential decay of a polarity-sensitive probe molecule in microheterogeneous environments like the present case is ascribed to originate from the location of the different molecules of the same probe in regions differing in polarity.[42,46,49,51-55] For our purpose, we have exploited the average (mean) fluorescence lifetime of the probe for exploring its behavior within the microheterogeneous environment, rather than emphasizing on the individual decay constants.

    Figures 6 and 7 reveal that the decays of both the forms of 3HF become slower with the addition of the RTILs. Furthermore, it is obvious from the figures that the effect of the micelle-forming IL on the fluorescence decays of both the forms of the probe is more

prominent than that of the non micelle-forming IL. With the addition of [BMIM][BF$_4$], *i.e.*, non micelle-forming IL, the average lifetime value of the normal form of 3HF increases gradually from 0.20 ns in aqueous medium and ultimately saturates at a value of 0.47 ns (Table S1). The lifetime value of the same form of the probe increases much more rapidly with the addition of [BMIM][C$_8$SO$_4$], *i.e.*, the micelle-forming IL and attain its saturation at around 1.55 ns (Table S2). Similar trend is
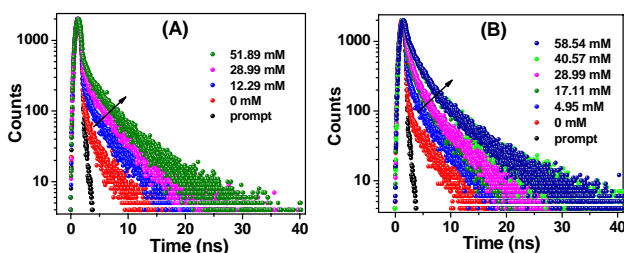

Figure 6. Decay pattern of the normal species of 3HF in (A) BMIMBF$_4$ and (B) BMIMC$_8$SO$_4$ media. The sharp black profile is the lamp profile. λ_{exc} = 370 nm, λ_{em} = 410 nm. [3HF] = 20 μM.
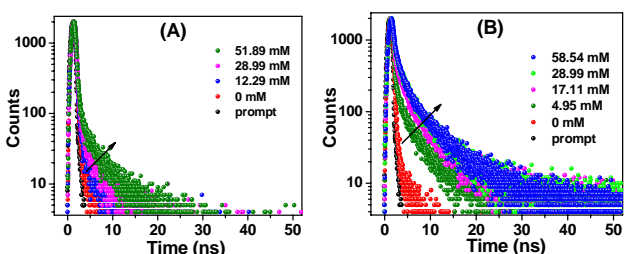
Figure 7. Decay pattern of the tautomer species of 3HF in (A) BMIMBF$_4$ and (B) BMIMC$_8$SO$_4$ media. The sharp black profile is the lamp profile. λ_{exc} = 370 nm, λ_{em} = 550 nm. [3HF] = 20 μM.

also observed for the other form of the probe, *i.e.*, the tautomeric form. For a better understanding of the relative variation of the average lifetime values of the two species of 3HF in the two RTIL media, we have plotted the average lifetimes of both the species against the IL concentrations (Fig. 8). Figure 8 depicts that the average lifetime value of both the forms of 3HF is modified drastically in the micelle-forming IL. The interesting feature of Figure 8 is that we observe definite break points in the variation patterns of both the forms of 3HF in the micelle-forming IL whereas in the non micelle-forming IL we do not get such breaks. For the micelle-forming IL, we get breakpoints at 34 mM [BMIM][C$_8$SO$_4$] monitoring both the species of 3HF. This breakpoint, as before, correspond to the CMC value of [BMIM][C$_8$SO$_4$]. The determined value is, again, in good agreement with the literature value of CMC of [BMIM][C$_8$SO$_4$], *i.e.*, 31 mM.[21] It is pertinent to mention here that the observed lifetime value of the tautomeric species of 3HF in the micelle-foming IL is comparable with the values reported by Sengupta *et al.* for the 3HF tautomer in the liposomal membrane and β-CD environment where the polarity is much less than that of the bulk aqueous milieu.[35,56] It is, therefore, reasonable to conclude that 3HF resides in a less polar region within the micellar environment formed by the micelle-forming IL. The little increase in the lifetime value of both the normal and the tautomeric forms of the probe in [BMIM][[BF$_4$] medium can be justified, as before, by considering the slight lowering of the

overall polarity in the non micelle-forming IL medium (*vide supra*). The time resolved fluorescence decay measurements, thus, corroborate the outcomes of the steady state fluorometric study.
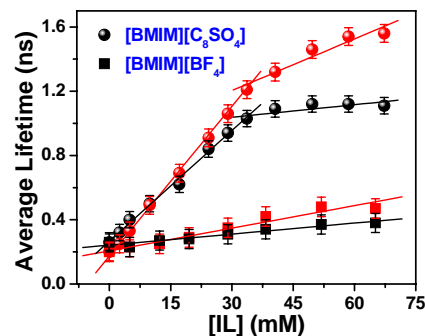
Figure 8. Variation of the relative values of average fluorescence lifetime of normal form (red) and tautomeric form (black) of 3HF as a function of the concentrations of RTILs.

Conclusion

The present work articulates the modification in the photophysical behavior of the ESIPT probe 3HF in the aqueous solutions of two imidazolium-based room temperature ionic liquids. The ESIPT process of 3HF is significantly modified in the micelle-forming ionic liquid as compared to the other one, *i.e.*, the non micelle-forming ionic liquid. Both steady state and time resolved fluorescence data are exploited to determine the critical micellar concentration (CMC) of the micelle-forming ionic liquid and the obtained value is in good agreement with the literature value. Micropolarity study suggests that the polarity around the probe is much reduced in the aqueous solution of the micelle-forming ionic liquid compared to that of the pure aqueous medium. Fluorescence quenching experiment confirms that 3HF resides within the RTIL micelle. Further, a comparative study between the micelle-forming ionic liquid and a conventional surfactant sodium octyl sulfate, both having the same hydrophobic chain length, reveals that 3HF experiences a lesser polar microenvironment in the RTIL micelle than the conventional one. The present study is expected to provide an insight into the photophysical behavior of ESIPT probes in various room temperature ionic liquids capable or incapable of forming micelles in aqueous solution.

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Notes and references

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† Electronic Supplementary Information (ESI) available: figures corresponding to the variation in the tautomer emission against the

[BMIM][C$_8$SO$_4$] concentration, emission spectra of 3HF in the S$_8$S media, plot of variation of the tautomer emission of 3HF against the S$_8$S concentration, variation in the emission intensities of the normal and the deprotonated forms of carbazole at a particular pH in the aqueous solutions of S$_8$S and tables containing time resolved fluorescence decay parameters of both the species of 3HF in the two RTIL media. See DOI: 10.1039/b000000x/

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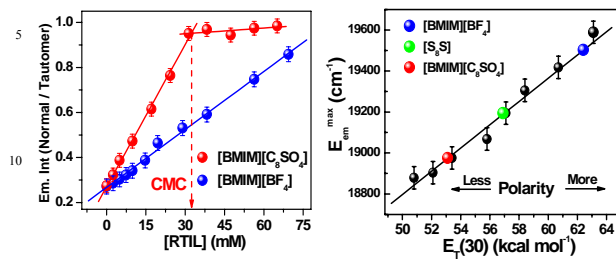
Fluorometric techniques have been exploited to study the photophysical behaviour of an excited state intramolecular proton transfer probe, 3HF, in two imidazolium-based room teperature ionic liquids, one micelle-forming and the other non micelle-forming.