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Dynamics of Solvation of the Fluorescent State of Some Electron Donor−Acceptor Molecules in Room Temperature Ionic Liquids, [BMIM][$(CF_3SO_2)_2N$] and [EMIM][$(CF_3SO_2)_2N$]

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Room temperature ionic liquids, particularly those based on the imidazolium salts, have emerged in recent years as highly promising “green” media suitable for carrying out various reactions. In this paper, picosecond time-resolved fluorescence decay behavior of three electron donor−acceptor (EDA) molecules, coumarin-153 (C153), 6-propionyl-2-dimethylaminonaphthalene (PRODAN), and 4-aminophthalimide (AP), in two room temperature ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM][$(CF_3SO_2)_2N$]) and 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide ([BMIM][$(CF_3SO_2)_2N$]), has been reported. The steady-state fluorescence behavior of the EDA molecules suggests that the polarity of the two ionic liquids in the $E_T(30)$ scale is around 47.6 for [EMIM][$(CF_3SO_2)_2N$] and 47.1 for [BMIM][$(CF_3SO_2)_2N$]. The fluorescence decay behavior of the systems in these media has been found to be dependent on the monitoring wavelength, suggesting solvent-induced relaxation of the fluorescent state of the systems in the picosecond time domain. Time-resolved fluorescence spectra of the systems, constructed from the wavelength-dependent decay profiles, show a Stokes shift of the fluorescence maxima with time. The time dependence of the spectral shift of the systems has been quantitatively analyzed to obtain information on the solvation dynamics in these media. The solvation dynamics has been found to be biphasic consisting of a short (∼0.2 ns) and a long component (∼1.0−1.2 ns). The short component has been assigned to the diffusional motion of the anion, while the long component is attributed to the collective motion of the anion and the cation. The average solvation time in the present ionic liquids is found to be faster than that in $[BF_4]^-$-based ionic liquids.

1. Introduction

The quest for green chemistry has led to the realization of the importance of solvent-free synthesis and recognition of water or supercritical carbon dioxide as the reaction media.[1−19] The efforts in this direction have also led to the identification of a number of organic salts, based mainly on the substituted imidazolium and pyridinium cations, that are liquid at ambient temperature.[20−28] These salts, which are commonly termed as room temperature ionic liquids (RTILs), are attractive alternatives to the conventional solvents that are volatile and often hazardous chemicals used in large quantities for carrying out various reactions. The properties that make these RTILs as environmentally benign media for various applications are low vapor pressure, wide liquid range, thermal stability, and the ability to dissolve a variety of substances. The most promising RTILs based on unsymmetrical imidazolium ions are moderate to highly viscous liquids at ambient temperature. The viscosity and melting point of these salts are strongly influenced by the length of the alkyl chain attached to the imidazolium ring and also by the anionic counterpart. These RTILs are conveniently synthesized by treating 1-alkylimidazole with alkyl halides of different chain length. The hydrophilicity or lipophilicity of these salts can be tuned by replacement of the anionic component by subsequent simple metathesis reaction. Though several other methods are available for improving the yield of the reactions, preparation of the RTILs in optically transparent form, particularly in the ultraviolet range, can sometimes be time consuming and laborious. A number of review articles have appeared recently where the details concerning the method of preparation and purification, properties, and utilities of the RTILs have been described.[1−4]

We have recently started exploring the suitability of various RTILs as the media for various photophysical investigations. To begin with we studied the steady state and time-resolved fluorescence behavior of some electron donor−acceptor (EDA) molecules in RTILs involving two imidazolium salts containing tetrafluoroborate (BF_4^-) as the anionic component.[29,30] These studies revealed a wavelength-dependent fluorescence decay kinetics for the probe molecules. The time-dependent changes in the fluorescence spectra of the systems were shown to be the result of solvent-induced relaxation of the fluorescent state of the molecules. A biphasic dynamics was observed in both media with an average relaxation time of around 1800 ps in [BMIM][BF_4] and 550 ps in [EMIM][BF_4]. The slow relaxation of the fluorescent state was primarily attributed to slow diffusion

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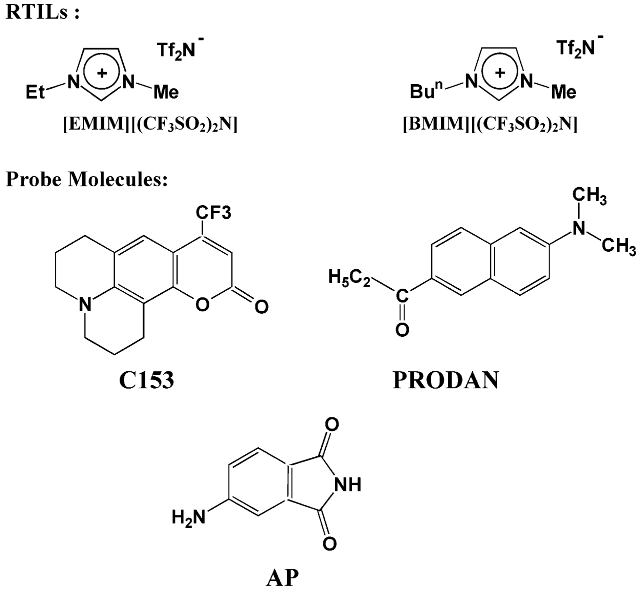
CHART 1



of the constituent ions in these viscous media. The relaxation dynamics is expected to be much faster in less viscous RTILs. That this is indeed the case is corroborated by the present study in which the solvation dynamics is investigated in two comparatively less viscous media, [EMIM][$(CF_3SO_2)_2N$] and [BMIM]-[$(CF_3SO_2)_2N$] (Chart 1). Relatively low viscosity of the [$(CF_3SO_2)_2N$]$^-$-based ionic liquids of the imidazolium salts compared to others is attributed to the weak hydrogen bonding ability of this anion.[24] Additional advantages with these salts that we have found are that they can be prepared relatively easily in greater yield and in optically pure form. High thermal stability of these salts allows removal of trace amounts of water from the liquids at elevated temperatures. Moreover, we found that it is easy to remove the parent halide, whose presence greatly increases the viscosity of the medium, by simply washing these hydrophobic ionic liquids with water.

The solvent relaxation dynamics around the photoexcited molecules has been studied employing coumarin 153 (C153), 6-propionyl-2-dimethylaminonaphthalene (PRODAN), and 4-aminophthalimide (AP) as fluorescence probes. The photophysics of these molecules are well understood.[27,31−56] Moreover, these systems have been previously employed in studies of solvation dynamics in various media.[57−71] The rationale behind using a number of probes for the study of solvation dynamics is to examine whether the solvation time is dependent on the nature of the probe molecule.

2. Experimental Section

2.1. Materials. AP was obtained from TCI and recrystallized twice from ethanol in the presence of activated charcoal. The purity of the yellow crystalline samples was confirmed by TLC with 50% ethyl acetate:hexane mixture as an eluant. C153 (laser grade) from Eastman Kodak and PRODAN from Molecular Probes were used as obtained.

1-Methylimidazole (99%) required for the synthesis of the RTILs was procured from Lancaster and distilled over KOH under vacuum. 1-Chlorobutane (HPLC grade) and 1,1,1-trichloroethane (99%) were obtained from Aldrich. Bromoethane (extra pure) was purchased from locally available grade. Both 1-chlorobutane and bromoethane were distilled fresh from P_2O_5 prior to their use. Bis(trifluoromethanesulfonyl)imide lithium salt (puriss) was obtained from Fluka and used without any purification.

2.2. Synthesis. The desired butyl salt was prepared from its chloro analogue, [BMIM][Cl], whereas the ethyl salt was prepared from the corresponding bromide salt, [EMIM][Br], by treating these salts with bis(trifluoromethanesulfonyl)imide lithium salt in water at 70 °C, according to the procedure suggested by Bonhôte et al.[24] The halide salts used for the reaction were prepared by conventional methods[24,72] and were washed several times with hot ethyl acetate until the washing was free from unreacted 1-methylimidazole. This was ensured by the absence of a strong absorption peak at around 275 nm in the UV-absorption spectrum in the ethyl acetate washing. The halides were then recrystallized from an ethyl acetate: acetonitrile mixture before proceeding to the next reaction step.

The desired products were dissolved in dichloromethane (DCM) and washed with double-distilled water until they were found free from the halide impurity (ensured by the absence of any precipitation with $AgNO_3$). To obtain the spectroscopic purity both ionic liquids were further treated with activated charcoal for at least 48 h and finally filtered twice by passing through a silica gel column. The liquids were kept under vacuum (10^{-2}−10^{-3} mbar) for 7−10 h at 50−60°C (to remove trace quantities of organic solvent or water) prior to sample preparation. The purity of the final liquid salts was assessed by IR, UV and NMR measurements.

2.3. Sample Preparation. A 2.5 mL sample of the ionic liquid was used to prepare the solution in a quartz cuvette. The cuvette was sealed with a septum and Parafilm after flushing dry nitrogen gas to prevent moisture contamination. The sample-containing cuvettes were kept sealed for a minimum of 24 h with occasional shaking (to overcome the slow solubility of the probes in ionic liquids) before any experiment was started.

2.4. Instrumentation. Steady-state absorption and fluorescence spectra were recorded on a Shimadzu UV−vis−NIR spectrophotometer (UV-3101PC) and a Spex spectrofluorimeter (Fluoromax 3), respectively. Time-resolved decay measurements at various emission wavelengths were executed by using a picosecond laser-based single photon counting spectrophotometer (Model IBH 5000U). The details of this setup and the laser system are described elsewhere.[30] The instrument response time was 50 ps (fwhm). In both steady state and time-resolved experiments the excitation wavelength was maintained at 375 nm. The measured decay curves were analyzed by nonlinear least-squares iteration technique, using the measured laser profile and standard deconvolution procedure. The quality of the fit was measured by the χ^2 values and the weighted deviation obtained after fitting.

2.5. Method. The time-resolved fluorescence decay profiles were measured at 10 nm wavelength intervals across the entire emission spectrum of the probe molecule. Each decay curve was then fitted to a triexponential function with an iterative reconvolution program (IBH). This procedure increased the effective time resolution of the experiments to ~25 ps. The time-resolved emission spectra (TRES) at different times were reconstructed from the appropriately normalized intensity decay function according to the procedure described earlier.[29] The peak frequencies $\bar{\nu}(t)$ at various times were extracted by fitting each TRES to a log-normal function, known for its excellent representation of the fluorescence band shape in polar media.[57] We also estimated the peak frequencies by fitting the TRES data to various other functional forms such as Gaussian, Lorentzian, and asymmetric bi-sigmoid functions to extract the $\bar{\nu}(t)$ values. We found that though an asymmetric bi-sigmoid function gave somewhat better fit to the TRES data, the peak

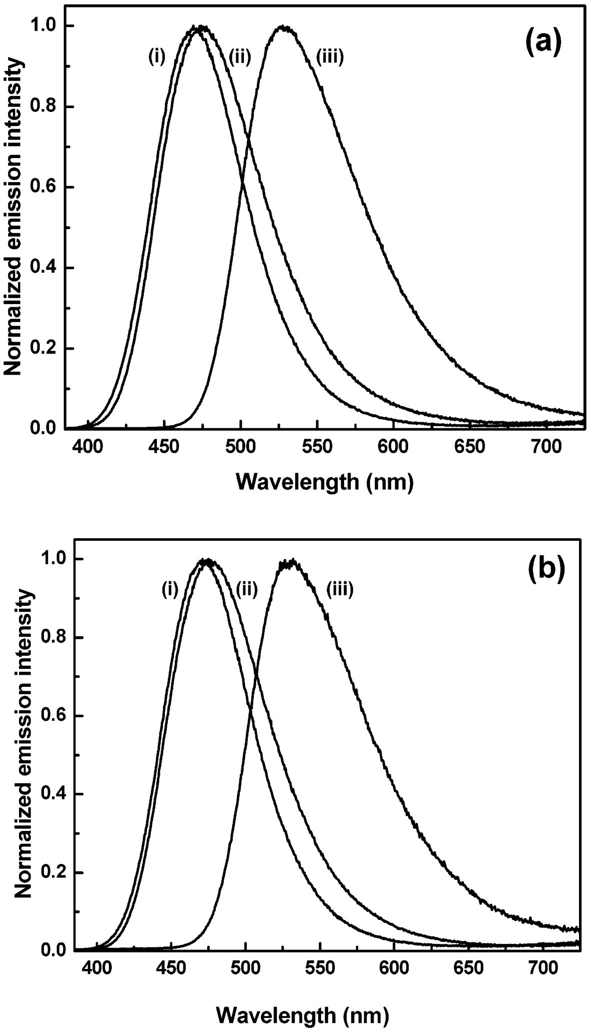


Figure 1. Steady-state fluorescence spectra of (i) PRODAN, (ii) AP, and (iii) C153 in (a) [BMIM][($CF_3SO_2)_2N$] and (b) [EMIM][($CF_3SO_2)_2N$]. The excitation wavelength was 375 nm in all cases. All spectra have been corrected for the instrumental response.

frequencies as obtained by different fitting procedures were not very different from those obtained from the log-normal fits. The normalized Stokes shift correlation function, $C(t)$,[73,74] defined as

$$C(t) = \frac{\bar{\nu}(t) - \bar{\nu}(\infty)}{\bar{\nu}(0) - \bar{\nu}(\infty)} \qquad (1)$$

where $\bar{\nu}(0)$ and $\bar{\nu}(\infty)$are the peak frequencies immediately after excitation and at infinite time after excitation (when the spectrum does not show any time-dependent Stokes shift), were evaluated. The time dependence of the correlation function in each case was fitted to a biexponential decay function, $C(t) = a_1e^{-t/\tau_1} + a_2e^{-t/\tau_2}$, where τ_1 and τ_2 are the two relaxation times having amplitudes of a_1 and a_2, respectively. Since the value of $\bar{\nu}(0)$, determined from the TRES at $t = 0$, is dependent on the finite time resolution of the instrument (~25 ps), initial response of the solvent that occurs within this very short time would not be included in our calculated $C(t)$.

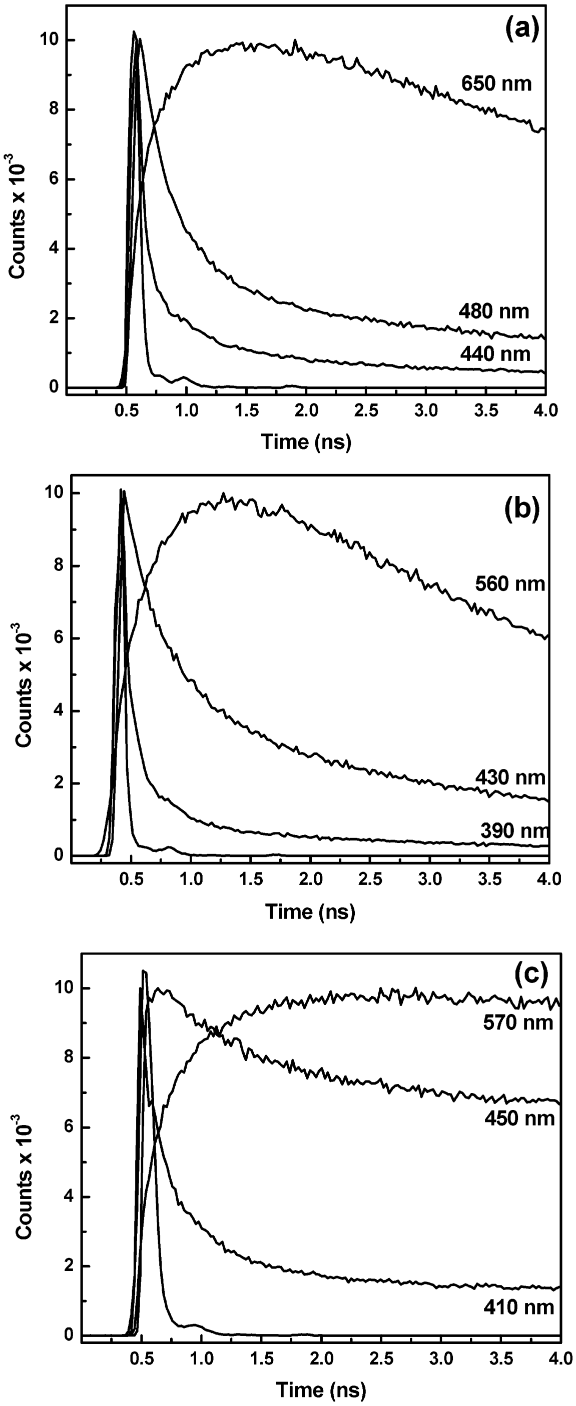


Figure 2. Wavelength dependence of the fluorescence decay profiles in [BMIM][($CF_3SO_2)_2N$]: (a) C153, (b) PRODAN, and (c) AP. The monitoring wavelengths are indicated in the figure. The excitation profiles are also shown.

TABLE 1: Steady State Fluorescence Data for the Probe Molecules and the Estimated Polarity of the Ionic Liquids in the E_T(30) Scale

probe molecule	[BMIM][($CF_3SO_2)_2N$]		[EMIM][($CF_3SO_2)_2N$]	
	$\bar{\nu}_{max}^{flu}/cm^{-1}$	est. E_T(30)	$\bar{\nu}_{max}^{flu}/cm^{-1}$	est. E_T(30)
C153	18975	47.2	18868	47.7
PRODAN	21295	46.0	21193	46.5
AP	21042	48.2	20990	48.5

The polarity of the RTILs has been described in terms of the microscopic solvent polarity parameter, E_T(30).[75] The E_T(30) value of a solvent is defined as follows: $E_T(30)$ (kcal/mol) = $28591/\lambda_{max}$, where λ_{max} is the wavelength (in nm) corresponding to the maximum of the longest absorption band of the betaine dye.[75] We have measured $\bar{\nu}_{max}^{flu}$ (wavenumber corresponding to the fluorescence maximum) values of each probe molecule in various conventional solvents and plotted these values against known E_T(30) values of the solvent to obtain the linear

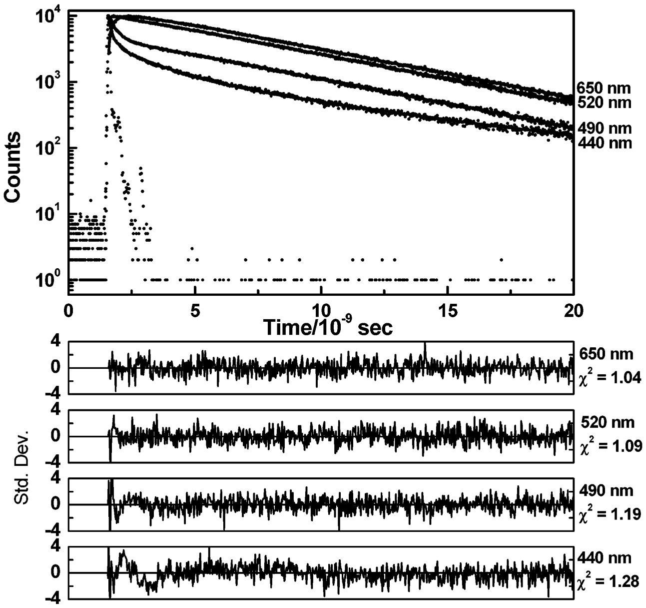


Figure 3. Fluorescence decay profiles of C153 in [EMIM][($CF_3SO_2)_2$N] at various wavelengths along with the best fits. The excitation wavelength was 375 nm.

relationship between the two quantities. By using this relationship and the measured $\bar{\nu}_{\max}^{\text{flu}}$ value of the probe in RTIL, the $E_T(30)$ value of the solvent was estimated.

3. Results and Discussion

The steady-state fluorescence spectra of the systems in [EMIM][($CF_3SO_2)_2$N] and [BMIM][($CF_3SO_2)_2$N] are depicted in Figure 1. The wavenumbers ($\bar{\nu}_{\max}^{\text{flu}}$) corresponding to the maximum fluorescence intensity of the systems are listed in Table 1. Since the $\bar{\nu}_{\max}^{\text{flu}}$ values of the chosen probe molecules are sensitive to the polarity of the media, we have estimated the polarity of the two RTILs from these values. By using the steady-state fluorescence data of the systems in conventional solvents and the measured $\bar{\nu}_{\max}^{\text{flu}}$ values in the RTILs, the $E_T(30)$[75] value of [EMIM][($CF_3SO_2)_2$N] is estimated to be between 46.5 and 48.5 (with an average value of 47.6) and the corresponding value for [BMIM][($CF_3SO_2)_2$N] lies between 46.0 and 48.2 (average of 47.1). Comparing these values with the literature $E_T(30)$ value of the conventional solvents, we find that the present RTILs are more polar than acetonitrile ($E_T(30) = 45.6$) but less polar than methanol ($E_T(30) = 55.4$). The conventional solvent, whose $E_T(30)$ value is found closest to the values estimated for the two RTILs, is 2-butanol ($E_T(30) = 47.1$). Even though [EMIM][($CF_3SO_2)_2$N] and [BMIM][($CF_3SO_2)_2$N] contain an ethyl and a butyl group respectively at the 1 position of the imidazolium ring, the polarity of the two liquids, as indicated by the average $E_T(30)$ values, is very similar. This observation is consistent with the literature report that the polarity of [EMIM][BF_4] and [BMIM][BF_4] is very similar.[30,76,77] A comparison of the $E_T(30)$ values of the tetrafluoroborate salts and the present salts reveals that the latter are slightly less polar than the tetrafluoroborate salts.

Typical wavelength dependence of the fluorescence decay profiles of the systems is illustrated in Figure 2. As can be seen, when the fluorescence is monitored in the blue edge of the spectrum, the time profile suggests a monotonic decay of the fluorescence intensity with time. On the other hand, as the monitoring wavelength approaches the red region of the

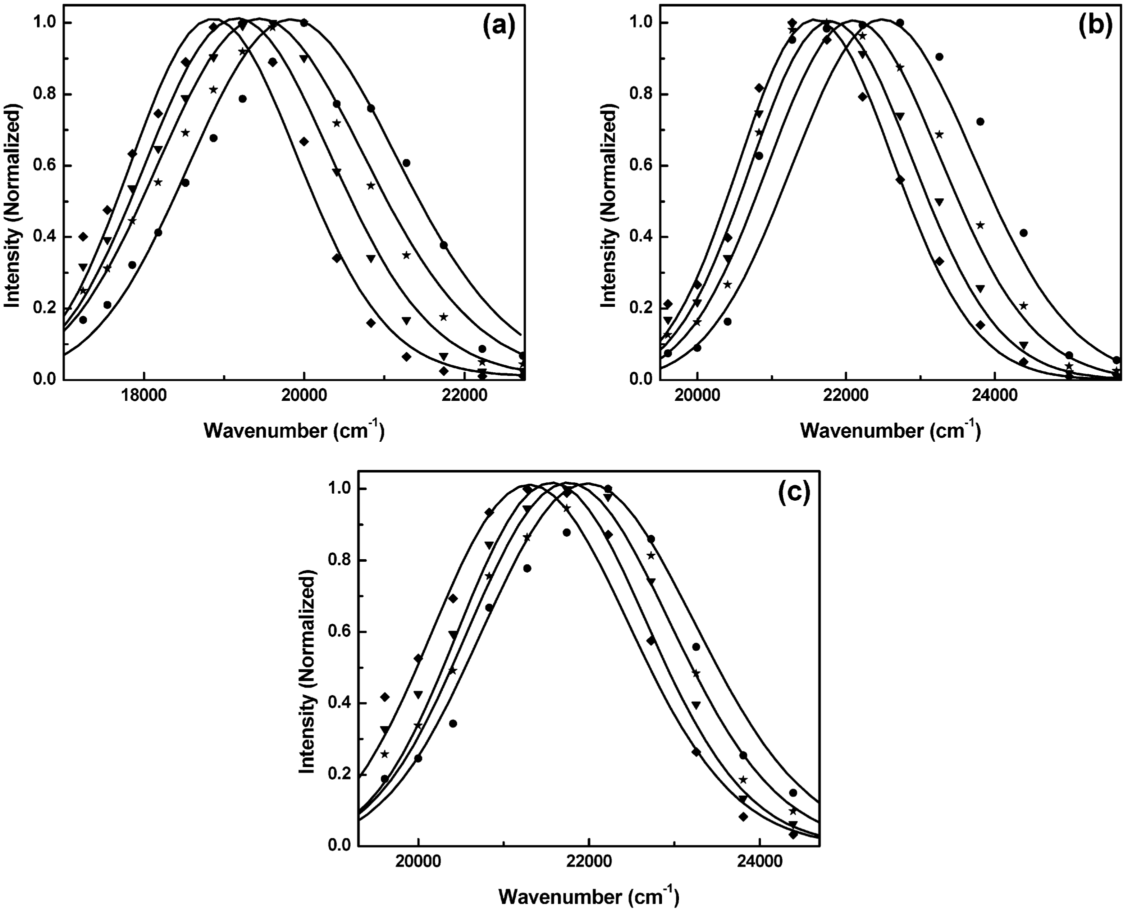


Figure 4. Time-resolved emission spectra (normalized at the peak) of (a) C153, (b) PRODAN, and (c) AP in [EMIM][($CF_3SO_2)_2$N] at 0 (●), 100 (★), 250 (▼), and 2000 ps (◆), respectively.

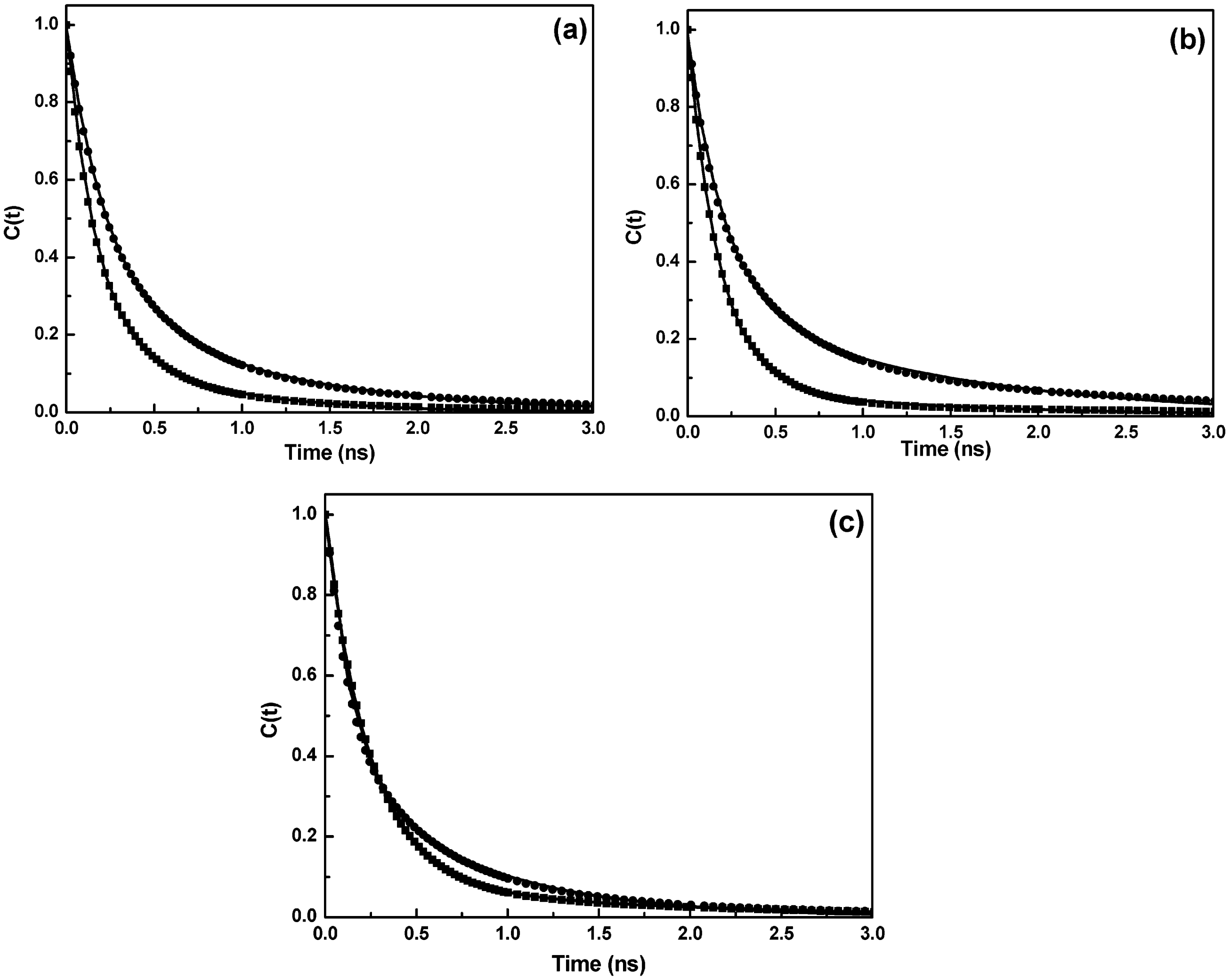


Figure 5. Time dependence of the spectral shift correlation function, $C(t)$, of (a) C153, (b) PRODAN, and (c) AP in [BMIM][$(CF_3SO_2)_2N$] (●) and [EMIM][$(CF_3SO_2)_2N$] (■), respectively. The actual points denote the estimated values of $C(t)$ and the solid lines represent the biexponential fit to the data.

spectrum, a growth of the fluorescence intensity with time is observed initially before the usual decay of the fluorescence could be observed. The time and wavelength dependence of the fluorescence intensity of the systems suggests an excited state relaxation occurring on a time scale comparable with that used in the measurements. Each decay curve was fitted to a sum of exponentials by using an iterative convolution algorithm. Figure 3 depicts typical fits to the decay profiles along with the plots of the residuals. The time constants obtained from these fits have been found to vary continuously with the monitoring wavelength.

The time-resolved emission spectra (TRES) of the systems, constructed from the fitted decay profiles and the steady-state fluorescence data, are shown in Figure 4. In all cases, a shift of the spectral maximum with time toward the red region is evident. The time-dependent spectral evolution of the systems is characteristic of solvent relaxation around the photoexcited molecules during the excited-state lifetime of the probe molecules. No significant time-dependent change in the spectral width could be observed.

The spectral shift correlation function $C(t)$, which is a measure of the solvent relaxation time, has been estimated at various times from the time-resolved spectral shift data (see Section 2.5), and its time dependence is illustrated in Figure 5 along with the best fit to the data. The relaxation times obtained from the analysis of the data are listed in Table 2. Inspection of these data reveals the following features: First, the relaxation process is characterized by a biphasic dynamics in all cases. Second, while the average relaxation time in [EMIM][$(CF_3SO_2)_2N$] varies between 0.27 and 0.37 ns (depending on the choice of the probe molecule), that in [BMIM][$(CF_3SO_2)_2N$] lies between 0.38 and 0.56 ns. Third, although the average solvation time is found to vary to some extent depending on the choice of the probe molecule, no clear trend is evident from the data.

The process of solvation of a dipolar species in RTILs is fundamentally different from that in conventional polar molecular solvents. While in the case of the latter, the solvent molecules reorient themselves after the creation of the new dipole in the photoexcited probe molecule, in the case of the former, the relaxation of the photoexcited molecule occurs due to diffusional motion of the constituent ions around it. Despite this difference in the nature of the solvation process, previous studies on molten salts,[78−80] ionic solutions,[60] and RTILs[29,30] have shown that the solvation in these media can indeed be represented by the correlation function, $C(t)$, which was originally proposed to characterize the solvation dynamics in polar molecular solvents.

Biphasic dynamics in molten salts or in RTILs has been observed previously. Huppert et al. attributed the biphasic nature of the dynamics in molten salts to the difference in the transport properties of the constituting ions that differed in their sizes.[78−80] According to the model put forward by Huppert and co-workers, the short component of $C(t)$ of the dynamics represents the movement of the smaller species and the long component is

TABLE 2: Relaxation Parameters of the Probe Molecules in the Room Temperature Ionic Liquids[a]

			relaxation time[c]/ns		amplitude		
medium	viscosity[b]/cP	probe	τ_1	τ_2	a_1	a_2	$\langle\tau\rangle^{d,e}$/ns
[EMIM][$(CF_3SO_2)_2N$]	34	C153	0.17	0.66	0.78	0.22	0.28
		PRODAN	0.18	1.3	0.92	0.08	0.27
		AP	0.24	1.5	0.90	0.10	0.37
[BMIM][$(CF_3SO_2)_2N$]	52	C153	0.23	0.98	0.67	0.33	0.48
		PRODAN	0.21	1.3	0.68	0.32	0.56
		AP	0.15	0.76	0.63	0.37	0.38

[a] At 20 °C. [b] From ref 24. [c] Since some of the log-normal fits to the spectral data points, particularly those at early times, are not the best one can possibly obtain from a given set of data points, we also fitted some of the spectral data to Gaussian, Lorentzian, and asymmetric bi-sigmoid functions as well. The relaxation times obtained from the estimated $\bar{\nu}(t)$ values of the Gaussian/Lorentzian/asymmetric bi-sigmoid fit differ from the values shown here by 4−11%. [d] Average relaxation time $\langle\tau\rangle$ is defined as, $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2,$ where $(a_1 + a_2 = 1)$. [e] ±15%.

due to the larger species. Since ionic solvation involves cooperative motion of both the anion and the cation, the absolute values of the two components were found to be dependent on the size of the larger species. However, consideration of the amplitudes associated with the two components in our previous studies on [EMIM][BF_4] and [BMIM][BF_4] led us to conclude that while the short component of the dynamics is due to the anion, the long component arises due to the collective motion of both the anion and the cation.[29,30]

In the present case, the cationic component of the two ionic liquids is the only difference. According to Huppert's model, the short and long components observed here are to be assigned to the translational diffusion of $[(CF_3SO_2)_2N]^-$ and $[BMIM]^+$/$[EMIM]^+$ respectively as the size of the anion is significantly smaller than that of the cation.[81] However, if the long component were exclusively due to the cations, as proposed by Huppert and co-workers, one would have expected a smaller amplitude of this component where the cation is bigger. However, the data presented in Table 2 show that the amplitude of the long component in [BMIM][$(CF_3SO_2)_2N$] is higher than that in [EMIM][$(CF_3SO_2)_2N$]. Obviously, the long component arises due to some anions too. Taking into consideration the close proximity of the ions in ionic liquids we think it is more realistic to assume that the long component perhaps represent collective diffusion involving both the cations and the anions. Since our previous studies on tetrafluoroborate anion based ionic liquids have also indicated a similar picture, we think that the trend observed here and the mechanism offered are somewhat quite general for the molten salts or the room temperature ionic liquids.

A recent paper by Maroncelli and co-workers came into our attention during the revision of the manuscript wherein the authors have reported solute rotation and solvation dynamics in [BMIM][PF_6] over a certain temperature range.[82] As far as the solvation dynamics is concerned, the results reported in this paper are quite similar to those reported here and elsewhere.[29,30] The two observable time components of the dynamics are measured to be 0.26 and 2.00 ns at room temperature. In addition, these authors have shown that more than half of the dynamics, which could not be resolved, occur within 5 ps.

4. Conclusion

The fluorescence behavior of C153, PRODAN, and AP has been investigated in two room temperature ionic liquids. The steady-state fluorescence behavior of the systems suggests that the polarity of [EMIM][$(CF_3SO_2)_2N$] and [BMIM][$(CF_3SO_2)_2N$] is comparable to that of 2-butanol. It is also evident that these RTILs are slightly less polar than those based on the tetrafluoroborate anion. The solvation dynamics in the present RTILs is also found to be biphasic in nature though relatively faster compared to that in [EMIM][BF_4] and [BMIM][BF_4], because of the less viscous nature of the $[(CF_3SO_2)_2N]^-$-based ionic liquids. This study substantiates that the two components observed in the dynamics arise from the anion and collective motion of the anion and the cation. It is also evident that specific interaction of the constituting ions of the RTILs with the probe molecules does not influence the fluorescence response of the molecules to any significant extent.

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