Steady-State and Time-Resolved Fluorescence Behavior of C153 and PRODAN in Room-Temperature Ionic Liquids

Rana Karmakar and Anunay Samanta*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

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Room temperature ionic liquids have emerged as nature-friendly media suitable for various applications. In this work, steady-state and time-resolved fluorescence behavior of coumarin 153 (C153) and 6-propionyl-2-dimethylaminonaphthalene (PRODAN) have been reported in two room-temperature ionic liquids based on substituted imidazolium salts. The steady-state fluorescence behavior of the two probe molecules suggests that these liquids are more polar than acetonitrile. The polarity of these media is found to be comparable to that of 2-propanol. No significant difference in the polarity of the two media could be observed although the cationic components of the two liquids contain alkyl substitutents of different chain length. Both the probe molecules display a wavelength-dependent fluorescence decay behavior. The decay profile at the red edge of the spectrum consists of an initial rise followed by a slow decay, while no rise could be observed at the blue edge of the spectrum. The solvation dynamics of the two probe molecules in the two room-temperature ionic liquids have been studied from the time-dependence of the spectral shift function constructed from the wavelength-dependent fluorescence decay profiles. The solvation of the probe molecules occurs on two different time scales with the absolute values strongly dependent on the cationic component of the ionic liquids. The average solvation time is found to be fairly long and dependent on the probe molecule used.

1. Introduction

Study of the time-dependent response of the solvent molecules to a newly created charge distribution in a dissolved solute has been an attractive topic of investigation in recent years.[1−7] From the experimental point of view, the time-dependent shift of the fluorescence spectrum of a probe molecule in polar media is quantitatively measured following excitation by an ultra-short laser pulse to obtain information on the solvation dynamics. The theoretical treatments to understanding the solvent response to the newly created charge distribution of the fluorophore immersed in a polar solvent can be broadly categorized into two approaches. The first approach, commonly referred to as "simple continuum" models, is essentially based on the initial treatments of Bakshiev[8] and Mazurenko,[9] in which the microscopic structure of the solvent is disregarded and instead, the solvent is considered as a continuous, homogeneous fluid and is characterized by bulk, frequency-dependent dielectric response function.[10−14] The continuum models predict exponential solvation kinetics with a lifetime equal to the longitudinal relaxation time, τ_L of the solvent. This bulk dielectric property is related to much slower Debye relaxation time, τ_D according to the equation $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$, where ϵ_∞ and ϵ_0 are the optical and static dielectric constants of the solvent. The second theoretical approach, initially proposed by Wolynes[15] and later developed by Rips,[16,17] and Nichols and Calef,[18] recognizes the molecular nature of the solvent. In this mean spherical approximation (MSA) model, the solvent molecules are considered as dipolar hard spheres. The dynamical MSA model predicts a more complex dynamics and a range of relaxation times between τ_L and τ_D instead of a single relaxation time τ_L predicted by the continuum theory. Some of the media in which the solvation dynamics has been extensively studied are alcohols of different polarity,[19−23] nitriles,[24] *N*-methylamides,[25] alkyl cyanides,[26] water and organized assembly in water,[1,2,27−30] inorganic molten salt at high temperature,[31−33] and ionic salt solutions.[34]

Room-temperature ionic liquids have emerged as a new kind of media alternative to the conventionally used organic solvents, which are generally volatile, flammable, and hazardous chemicals.[35−49] Even though ionic liquids such as $[EtNH_3][NO_3]$, which has a melting point of 12° C, have been known since 1914,[36] it is only very recently that the usefulness of these systems as a new kind of media for synthetic, electrochemical, and catalytic applications is being explored.[35−52] Some of the properties that make the room-temperature ionic liquids attractive media for various applications are the wide liquid range, nonvolatility (negligible vapor pressure), nonflammable nature, less reactivity, and the ability to dissolve a large variety of organic and inorganic substances including even the polymer materials in high concentration. Many of these properties have made the room-temperature ionic liquids a nature-friendly "Green Solvent".[35,53−55] The room-temperature ionic liquids that are currently the focus of extensive investigation are generally a substituted imidazolium or a pyridinium salt. Even though the solvent properties of different halogenoaluminate(III) ionic liquids were explored as early as in 1986,[56] very little is known about the various properties of the contemporary ionic liquids despite their extensive usage in synthetic applications. Studies on the viscosity and density of the ionic liquids by Seddon and his group suggest that these are moderate to highly viscous liquids (depending on the length of the alkyl chain attached to the imidazolium moiety) at room temperature.[57] Very few photophysical studies have been carried out so far in these media. A few UV−vis absorption and fluorescence studies have been carried out with a view to measuring the polarity of these media. These studies suggest that imidazolium and pyridinium ionic liquids are sufficiently polar media. Gordon and co-

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* Corresponding author. E-mail: assc@uohyd.ernet.in.

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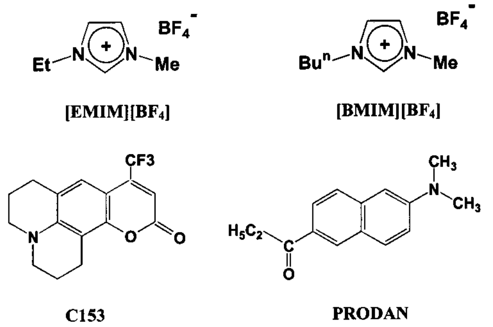
CHART 1



workers have shown recently that the polarity of an ionic liquid is largely determined by the cationic component of the solvent.[48]

In an earlier paper, we reported the solvation dynamics in a room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4]. Using C153 as the probe molecule, we observed a biphasic solvation dynamics with an average solvation time of 2.13 ns. To obtain a better understanding of the dynamics in these media it is necessary to systematically vary the constituting ions of the ionic liquids and also to examine the dynamical behavior with more than one probe molecule. This paper presents the results of a study dealing with these aspects.

In addition to [BMIM][BF_4], we have chosen 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4] (Chart 1) as the second medium for the study of solvation dynamics because of the air and water stability of these two solvents and the ease of their preparation.[58] While the constituting anionic component is identical in the two liquids, the latter possesses an imidazolium cation with a relatively shorter alkyl chain and is miscible in all proportion with water even at low temperature. The miscibility of [BMIM][BF_4] is comparatively low with ice-cold water. Even though the tetrafluoroborate ionic liquids are relatively more hygroscopic than those containing $[PF_6]^-$ or $[Tf_2N]^-$ anion,[41,59] all of them are far more stable, low-melting, less moisture sensitive, and less corrosive than the conventional halogenoaluminate ionic liquids. Moreover, the present systems, which possess a fluorinated anion, are less viscous than those containing chloride ions. This is due to the fact that the viscosity of the room-temperature ionic liquids is largely controlled by the strength of the hydrogen bonding interaction between the C2-hydrogen of the imidazolium ring and the halogen atoms in the corresponding anion.[41]

We have chosen coumarin 153 (C153) and PRODAN as the probe molecules to estimate the time-dependent Stokes shift of the emission spectrum and to determine the solvation dynamics. C153 has been extensively used as a probe for the study of the solvation dynamics in a variety of media[60,61] in view of the fact that the intramolecular charge transfer fluorescence band of C153 is highly sensitive to the polarity of the medium and also, due to the fact that the $S_0 \leftrightarrow S_1$ transition of C153 is uncomplicated by other nearby transition or interfering reactions. A recent time-resolved dielectric loss measurement indicated that the change in the dipole moment of the molecule on electronic excitation lies between 4.9 and 5.4 D.[62] PRODAN is also extensively used as a probe molecule to measure the microscopic polarity of various chemical and biological media. That the position of the fluorescence maximum of PRODAN is extremely sensitive to the polarity of the medium is evident from the fact that the molecule shows a red shift of ~130 nm when the medium is changed from cyclohexane to water.[63] Though the hypersensitivity of the fluorescence maximum of PRODAN was thought to be due to the twisted intramolecular charge transfer (TICT) nature of the emitting state, a recent study suggests that the change in the dipole moment on excitation of the systems is rather low (around 4.4−5.0 D) and the molecule emits from a locally excited state. Hydrogen bonding interaction seems to play a major role in dictating the location of the fluorescence state in alcoholic or aqueous media.[64]

2. Experimental Section

2.1. Materials. Laser grade C153 from Eastman Kodak and 6-propionyl-2-dimethylaminonaphthalene (PRODAN) from Molecular Probes were used without any further purification. $NaBF_4$ (97%) and 1-methylimidazole (99%), required for the synthesis of the room-temperature ionic liquids, were procured from Lancaster and the later was distilled in vacuo before using, while 1-chlorobutane (HPLC grade), bromoethane (98%), and 1,1,1-trichloroethane (99%) were obtained from Aldrich.

2.1.1. Preparation of 1-Butyl-3-methylimidazolium Tetrafluoroborate, [BMIM][BF_4]. Air- and water-stable [BMIM][BF_4] was prepared by the metathesis of 1-butyl-3-methylimidazolium chloride [BMIM]Cl with $NaBF_4$ in water at room temperature following a standard procedure.[47] [BMIM]Cl was first prepared from 1-methylimidazole and 1-chlorobutane in N_2 atmosphere on heating at 70 °C for more than 24 h and the highly viscous oily molten salt so obtained was purified according to the literature procedure.[65]

2.1.2. Preparation of 1-Ethyl-3-methylimidazolium Tetrafluoroborate, [EMIM][BF_4]. [EMIM][BF_4] was prepared by the metathesis between 1-ethyl-3-methylimidazolium bromide, [EMIM]Br, with $NaBF_4$ in acetone at room temperature. This method is similar to the procedure adopted for the preparation of [BMIM][BF_4] by Suarez et al.[66] [EMIM]Br was synthesized by refluxing 1-methylimidazole with freshly distilled bromoethane in 1,1,1-trichloroethane at 80 °C temperature for 2 h according to the modified procedure described by Bonhote and co-workers.[41] It is to be noted that we avoided preparing [EMIM][BF_4] using conventional silver method[47] as we found that even a trace quantity of silver was enough to destroy the fluorescence probe molecules within a short time. The water content and purity of the liquid salt were checked by both IR and NMR. No precipitation of silver halide on addition of aqueous silver nitrate solution in the final tetrafluoroborate liquid salts suggests the absence of any halide impurity above the detection limit.

2.2. Instrumentation. The absorption and steady-state fluorescence spectra were recorded on Shimadzu UV−Vis−NIR spectrophotometer (UV-3101PC) and Spex spectrofluorimeter (Fluoromax 3), respectively. The time-resolved fluorescence decay profiles at various emission wavelengths were measured using a picosecond single photon counting spectrophotometer (Model IBH 5000U). In this setup, a diode-pumped Millena (5W) CW laser output (Spectra Physics) at 532 nm was used to pump a Ti-Sapphire rod in Tsunnami picosecond Mode Locked Laser system (Spectra Physics Model 4960 M3S). The frequency-doubled 375 nm output was used for excitation of the samples. The emission was detected at right angle to the excitation beam using a Hamamatsu 323P MCP photomultiplier. The instrument response time was 50 ps (fwhm).

2.3. Methods. The ionic liquids were kept in high vacuum at 70−80 °C for at least 7 h to remove any moisture present in these media. Such treated liquids were slowly allowed to cool to room temperature under vacuum prior to the sample preparation. A 2.5 mL sample of the liquid salt was used in each case to prepare the solution of the fluorescence probe at room temperature. Proper precaution was taken to avoid moisture absorption by the ionic liquid while transferring it to the quartz cuvette. The cuvettes were flushed with nitrogen prior to the transfer of the solution and were sealed by septum and Parafilm immediately after transfer to prevent moisture from contaminating the solution. The sealed solutions were found to be stable for several weeks.

The time-resolved fluorescence was measured by TCSPC technique monitored at 16−20 different wavelengths across the entire emission spectrum. The detailed procedure was described elsewhere.[67] Briefly, each decay curve was fit to a sum-of-exponentials function using an iterative reconvolution program (IBH). This procedure increased the effective time-resolution of the experiments to ~25 ps. The quality of the fit was assessed by the χ^2 values and the residuals. The impulse response functions at different wavelengths were calculated from those best-fitted curves. The time-resolved emission spectra at various times were calculated from the appropriately normalized intensity decay function from steady-state intensity for different wavelengths at different times. As it is quite difficult to determine the peak frequency from the emission spectra, the time-resolved spectra were first fit to a log−normal line shape function, known for its excellent representation of the fluorescence band shape[68] and at each time the peak frequency $\bar{\nu}(t)$ was calculated. The solvation dynamics described by the normalized Stokes shift correlation function, $C(t)$, which is defined as,[10,13]

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

was calculated using the peak frequency of the time-resolved emission spectra. The quantities, $\bar{\nu}(0)$, $\bar{\nu}(t)$, and $\bar{\nu}(\infty)$ are the peak frequencies immediately after excitation, at an intermediate time and at infinite time after excitation. The correlation function in each case was found to be biexponential in nature. The decay was fit 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. The method of determination of $\bar{\nu}(0)$ from the time-resolved data is dependent on the finite time-resolution of the instrumental response. Hence, the initial response of the solvent that occurs within the first ~25 ps (time-resolution of the present setup) would not be included in the so obtained $C(t)$ function.

3. Results and Discussion

The fluorescence spectra of the two probe molecules in [EMIM][BF$_4$] are shown in Figure 1. The wavenumbers corresponding to the steady-state fluorescence maximum ($\bar{\nu}_{\mathrm{flu}}^{\mathrm{max}}$) of C153 and PRODAN in the room-temperature ionic liquids are shown in Table 1. The polarity of the two media (in terms of Reichardt's solvent polarity parameter, $E_T(30)$[69] is estimated from the linear relationship between $\bar{\nu}_{\mathrm{flu}}^{\mathrm{max}}$ and $E_T(30)$ in several conventional solvents and the measured $\bar{\nu}_{\mathrm{flu}}^{\mathrm{max}}$ values in the two ionic liquids. The estimated polarity values of the two media are shown in Table 1. Even though C153 gives a relatively higher estimate of the polarity of the media compared to that obtained with PRODAN, the data suggest that both [EMIM][BF$_4$] and [BMIM][BF$_4$] are more polar than acetonitrile ($E_T(30)$ of 45.6), but much less polar than methanol ($E_T(30)$ of 55.4). The polarity of the two media resembles more that of 2-propanol ($E_T(30)$ of 48.4). Both the probe molecules indicate that [BMIM][BF$_4$] is marginally less polar than [EMIM][BF$_4$]. This is in agreement with the presence of a relatively longer alkyl chain of the imidazolium cation in [BMIM][BF$_4$]. It is to be noted here that these estimates of the polarity of those two ionic liquids are in fairly good agreement with those obtained by Muldoon et al. from the absorption maximum of the betaine dye.[48]

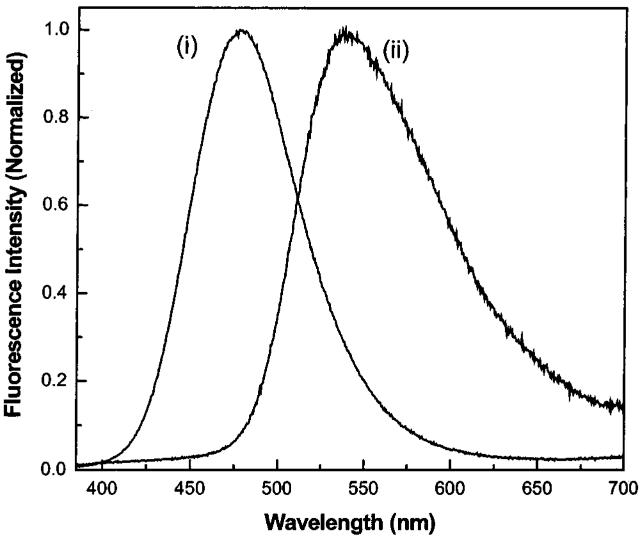


Figure 1. Normalized steady-state fluorescence spectra of PRODAN (i) and C153 (ii) in [EMIM][BF$_4$] at 25 °C; $\lambda_{\mathrm{exc}} = 375$ nm. The fluorescence spectra have been corrected for the instrumental response.

TABLE 1: Steady-State Fluorescence[a] Data of C153 and PRODAN and the Estimated Polarity Values of the Two Room-Temperature Ionic Liquids in the $E_T(30)$ Scale

	$\bar{\nu}_{\mathrm{flu}}^{\mathrm{max}}$		$E_T(30)$ value of the medium as estimated from the $\bar{\nu}_{\mathrm{flu}}^{\mathrm{max}}$ of	
medium	C153	PRODAN	C153	PRODAN
[EMIM][BF$_4$]	18587	20964	49.1	47.5
[BMIM][BF$_4$]	18622[b]	21053	48.9[b]	47.1

[a] Excitation wavelength was 375 nm. [b] From ref 67.

The time-resolved decay profiles of the probe molecules are found to be dependent on the monitoring wavelengths. When monitored at longer wavelength (toward the red edge of the fluorescence spectrum) the decay profile consisted of an initial rise followed by a slow decay. However, the rise component could not be observed when the fluorescence is monitored at the shorter wavelength region. This wavelength-dependent decay behavior of the two fluorescence probes is the signature of solvation dynamics that is occurring on the time scale comparable to that used in the measurement. Figure 2 illustrates the wavelength-dependent decay behavior of the two molecules in [EMIM][BF$_4$]. The quality of the fit to the decay profiles has been shown in Figure 3.

The time-dependent fluorescence spectra of the molecules, constructed from the decay profiles by following the procedure stated in Section 2.3, are shown in Figure 4 as dotted lines. The values of the correlation function, $C(t)$ at various times were estimated from the time-resolved emission spectra using eq 1. The time-dependence of $C(t)$ is shown in Figure 5 along with the best fit to the data. Research groups of Barbara[22] and Huppert[31−33,70] have used a stretched factor β in order to improve their biexponential fitting parameters.However, in our case, we did not find any significant improvement to the quality of the fit by varying the β value from 0.4 to 0.9. The relaxation times obtained on fitting the data are given in Table 2. The salient features of the solvation dynamics can be summarized as follows.

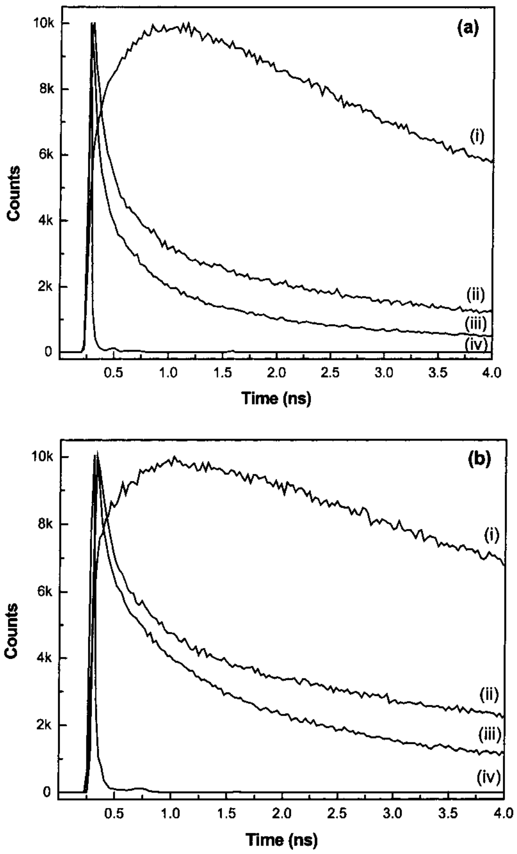


Figure 2. Time-resolved fluorescence behavior of PRODAN (a) and C153 (b) in [EMIM][BF$_4$]. The monitoring wavelengths are (i) 560, (ii) 430, and (iii) 390 nm in (a) and (i) 650, (ii) 500, and (iii) 450 nm in (b). $\lambda_{exc} = 375$ nm. The excitation lamp profile is shown in (iv) in both cases.

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

medium	viscosity[b]/ cP	probe	relaxation time/ps τ_1	relaxation time/ps τ_2	amplitude a_1	amplitude a_2	$<\tau>$[c]/ ps
[EMIM][BF$_4$]	66.5	C153	125	1290	0.73	0.27	440
		PRODAN	175	2130	0.74	0.26	680
[BMIM][BF$_4$]	154.0	C153[d]	278	3980	0.50	0.50	2130
		PRODAN	280	3330	0.62	0.38	1440

[a] At 20 °C. [b] From ref 57. [c] Average relaxation time $<\tau>$ is defined as, $<\tau> = a_1\tau_1 + a_2\tau_2$, where ($a_1 + a_2 = 1$). [d] From ref 67.

The solvation dynamics in both cases is found to be clearly biphasic consisting of a relatively fast component with a τ value of 125−175 ps in the case of [EMIM][BF$_4$] and 278−280 ps in the case of [BMIM][BF$_4$]. The long component, on the other hand, has a τ value of 1.3−2.1 ns in the case of [EMIM][BF$_4$] and 3.3−4.0 ns in the case of [BMIM][BF$_4$]. The average solvation time is calculated to be 440−680 ps in [EMIM][BF$_4$] and 1.4−2.1 ns in [BMIM][BF$_4$]. The solvation dynamics is found to be dependent on the probe molecule employed in the study. In the case of [EMIM][BF$_4$], an average solvation time of 440 ps is obtained using C153, while the relaxation time is found to be 680 ps with PRODAN. Similarly, in the case of [BMIM][BF$_4$], $\langle\tau\rangle$ value varied between 1.4 and 2.1 ns depending on the probe molecule employed.

Essentially, the main features of the solvation dynamics in the room-temperature ionic liquids, such as the biphasic nature and the probe dependence of the dynamics, are similar to what was observed in the case of the molten salts by Huppert and co-workers.[31−33] Hence, we attempt to interpret the present results in terms of the model suggested by Huppert et al. rather than using the continuum models or the MSA model, which are applicable to dynamics in molecular solvents. According to Huppert and co-workers, the biphasic nature of the dynamics is due to the difference in the transport properties of the cations and the anions, which differ in their sizes. If Huppert's model is followed, then the short-component of the dynamics has to be assigned to the motion of the smaller species, i.e., the anions, while the long-component is due to the motion of the relatively larger species, the cations. As the ionic solvation involves a cooperative movement of the ions, the absolute values of the two components, as pointed out by Huppert et al., are dependent on the size of the larger species, the cation. This is why the τ values obtained for the short and the long components in the two liquids are different. However, if the slow component were exclusively due to the cations, as proposed by Huppert, then one would have expected a smaller amplitude of this component with an increase in the size of the cations. The present results (vide Table 2) show exactly opposite behavior. Interestingly, even though Huppert also observed a similar behavior, no explanation was offered to account for the change of the amplitude of the two components. The amplitude of the two components can only be accounted for if it is assumed that the fast component is solely due to the initial response of the smaller species, i.e., the anion, while the long component arises due to

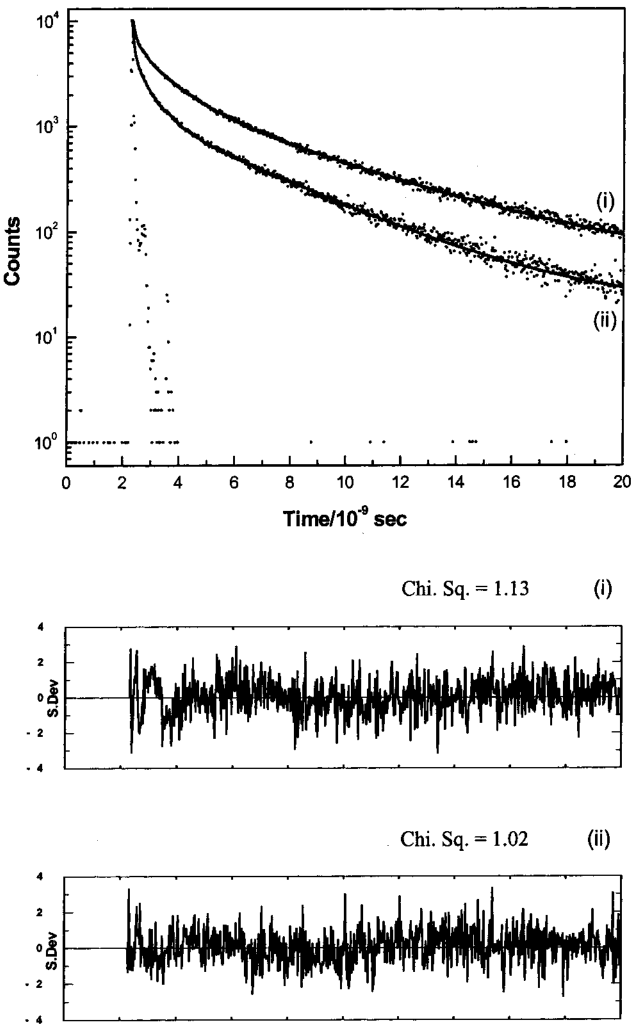


Figure 3. Fluorescence decay profile of C153 in [EMIM][BF$_4$] at 450 nm (i) and PRODAN in [EMIM][BF$_4$] at 390 nm (ii) along with the best fit (solid line). The data have been fitted to a triexponential function.

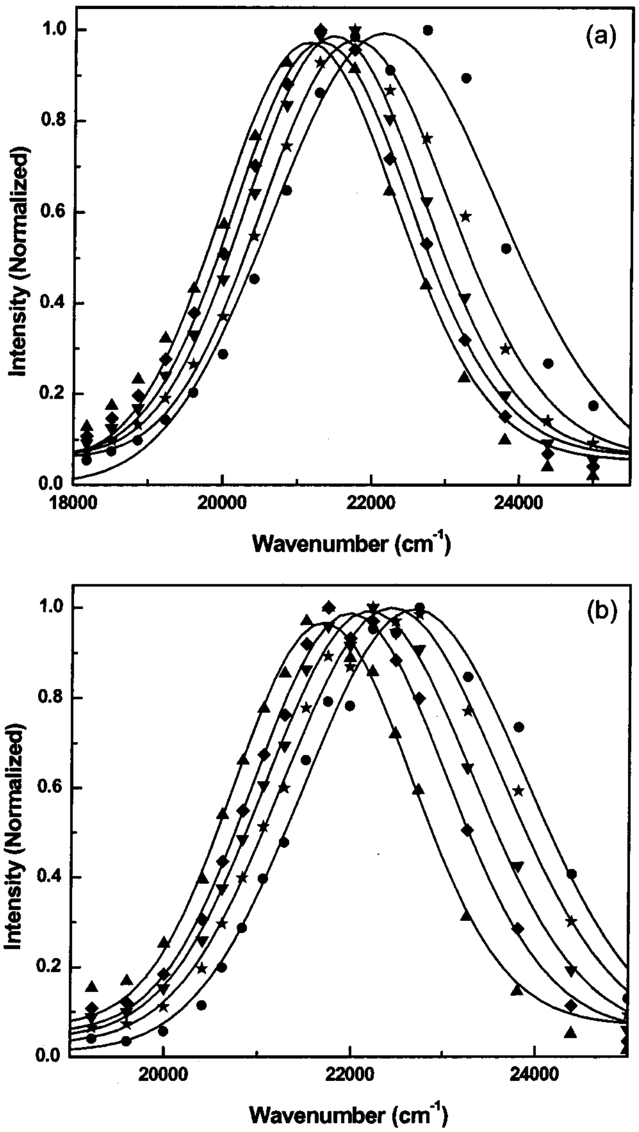


Figure 4. Time-resolved emission spectra (normalized at the peak position) of PRODAN in [EMIM][BF$_4$] (a), and [BMIM][BF$_4$] (b) at 0 (●), 100 (★), 250 (▼), 500 (◆), and 2000 ps (▲), respectively.

a collective diffusion involving both the cations and the anions. The close proximity of the ions makes this mechanism more realistic than the one involving separate contributions of the ions.

4. Conclusion

Steady-state and time-resolved fluorescence behavior of C153 and PRODAN in two different room-temperature ionic liquids, [EMIM][BF$_4$] and [BMIM][BF$_4$] have been studied. The steady-state fluorescence behavior of the two probe molecules suggests that both the ionic liquids are more polar than acetonitrile but less polar than methanol. Very little difference in the polarity of the two media could be observed even though the cationic components of the ionic liquids contain alkyl chains of different length. Both the probe molecules exhibit wavelength-dependent decay profiles and time-dependent Stokes shift of the fluorescence spectrum. The solvation dynamics of the probe molecules in these media, as characterized by the time-correlated spectral shift function, $C(t)$, are biexponential in all cases consisting of a short and a long component. The average solvation time, which is found to depend on the probe molecule used, lies in the nanosecond time scale. On the basis of the present results, the fast initial response of the biphasic dynamics is attributed to the motion of the relatively smaller species, the anions, while the slow component originates from the collective motion of the cations and the anions.

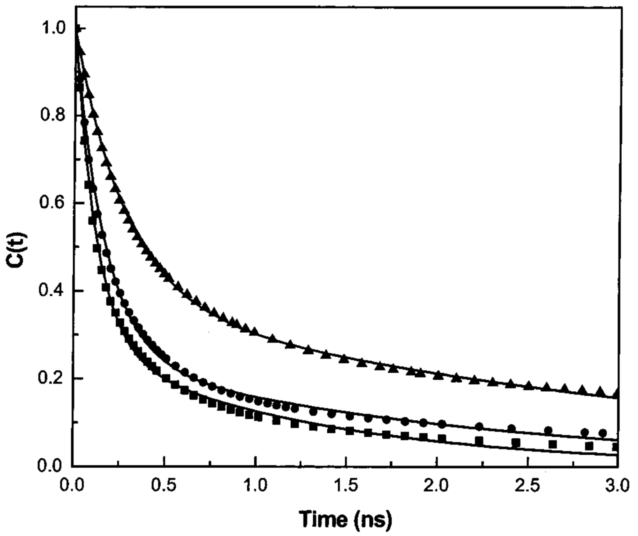


Figure 5. Decay profile of the response function, $C(t)$ of PRODAN in [EMIM][BF$_4$] (●), PRODAN in [BMIM][BF$_4$] (▲), and C153 in [EMIM][BF$_4$] (■). The points denote the actual values of $C(t)$, while the solid line represents the biexponential fit.

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