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Solvation Dynamics of Coumarin-153 in a Room-Temperature Ionic Liquid

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Room-temperature ionic liquids are rapidly emerging as a new class of medium that is ideally suited for carrying out chemical reactions and various other applications. In this paper, steady-state and time-resolved fluorescence behavior of coumarin-153 (C153) have been reported in a room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate or [BMIM][BF$_4$]. The polarity of the solvent, as estimated from the fluorescence maximum of C153, is found to be 48.9 on the $E_T(30)$ polarity scale. The fluorescence decay behavior of C153 in [BMIM][BF$_4$] is found to be dependent on the monitoring wavelength. Although the time dependence of fluorescence in the blue region of the spectrum is represented by a multicomponent decay, that in the red region of the spectrum consists of clear growth followed by decay. The time-dependent evolution of the fluorescence spectrum of C153, constructed from the decay profiles at several wavelengths, indicates biphasic solvation dynamics similar to that observed in the case of the molten salts. In the present case, the solvation dynamics consists of two components with relaxation times of 278 ps and 3.98 ns, suggesting an average solvation time of 2.13 ns. The biphasic solvation dynamics in the room-temperature ionic liquid is proposed to be the result of a relatively fast initial response of the anion and a slow collective diffusion of the cations and the anions.

1. Introduction

In recent years, a significant effort has been directed toward finding replacements for the conventional solvents used to carry out chemical reactions because of the fact that conventional solvents, which are used in large quantities, are volatile liquids and hence are difficult to contain. The quest for “green chemistry” has led to the realization of the importance of solvent-free synthesis and the use of water, supercritical carbon dioxide, or ionic liquids as the reaction media.[1−4]

Molten organic salts have long been considered as likely solvent systems for various purposes.[5−7] Tetraalkylammonium and tetraalkylphosphonium salts not only possess relatively low melting points (between 50 and 250 °C) compared to those of the inorganic salts, which melt above 500 °C, but also have the ability to dissolve a wide variety of organic compounds. However, instability in acids and thermal decomposition of these molten salts are two of the most serious drawbacks that have restricted their usage. Room-temperature ionic liquids, on the other hand, are also organic salts that in their pure states are liquids at ambient temperature. The most commonly used salts are those with *N*-alkylpyridinium and *N*,*N′*-dialkylimidazolium cations. Some of the properties that make these ionic liquids environmentally benign solvents for carrying out chemical reactions are low vapor pressure, wide liquidus, thermal stability, high ionic conductivity, etc. However, sensitivity to moisture, high reactivity, thermal stability, and immiscibility with other solvents restricted the use of this class of compounds as solvents until very recently. The research employing ionic liquids as reaction media has received a boost since articles were published in 1992 on air- and water-stable ionic liquids based on the

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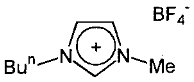
1-ethyl-3-methylimidazolium cation.[8] Several papers and some excellent review articles have appeared since then describing the physiochemical properties and applications (synthetic and electrochemical) of the room-temperature ionic liquids.[1,9−22]

The use of room-temperature ionic liquids is still rather limited in view of the fact that many of their physical properties are unknown. Hydrogen bonding interactions involving the C2 hydrogen and the anions in imidazolium salts have been well-documented.[23] A wide variety of chemical reactions such as Friedel− Crafts reactions, Diels−Alder reactions, hydrogenation, and polymerization have, however, been performed.[1,9] Also investigated rather extensively is transition-metal catalysis.[10] An EPR study in ionic liquids involving the nitroxy radicals has been reported.[17] Photophysical studies in these media are relatively few. UV−vis absorption and luminescence studies involving betaine dye, nile red, and various other fluorescent probe molecules such as pyrene and pyrene carboxaldehyde have been carried out to measure the polarity of these ionic liquids.[14,22] A recent study on four imidazolium and pyridinium ionic liquids suggests that these liquids are more polar than acetonitrile but less polar than methanol.[12] Gordon and co-workers have substantiated these results in a recent paper.[21] In addition, they have found that the polarity of an ionic liquid is largely determined by the cationic part of the solvent.

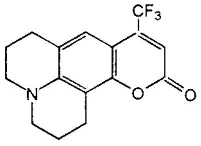
Because the ionic liquids are sufficiently polar, it is of interest to study the time-dependent fluorescence behavior of a dipolar solute in these media. The time-resolved fluorescence behavior of a dipolar solute is known to provide useful information on how the solvent molecules reorganize after an instantaneous separation of charge in the fluorophore upon absorption of photons. The study of the dynamics of solvation is an active area of interest from a theoretical as well as from an experimental point of view.[24−34] Solvation dynamics has been studied in a wide variety of polar solvents employing fluorescent probe molecules in which the charge separation reaction is much faster than the motions of the solvents. Water and alcohols are the most commonly used media for this purpose. Recently, solvation dynamics in organized assemblies has become an attractive topic for investigation.[34] Chapman and Maroncelli studied the solvation dynamics of a large number of probes in solutions containing electrolytes.[35] Huppert and co-workers have studied solvation dynamics in molten tetraalkylammonium salts a few degrees above their melting points.[36−39] Despite the limited stability of these salts above their melting points (typically 100−170 °C), they succeeded in obtaining useful information on the dynamics of the solvation process by the ionic species. The solvation dynamics in the molten salts has been found to be biphasic with separate contributions from the cations and anions. Interestingly, the relaxation times obtained from the time-resolved decay behavior of C153 in these molten salts are rather long. Although these organic salts melt at much lower temperatures than do the inorganic salts, the room-temperature ionic liquids based on *N*,*N'*-dialkylimidazolium salts possess melting points as low as −96 °C.[1] Moreover, these salts are far more air and water stable than are the tetraalkylammonium salts. In this paper, we report the picosecond time-resolved fluorescence behavior of C153 in one of the new generations of room-temperature ionic liquids.

In this study, 1-butyl-3-methylimidazolium tetrafluoroborate salt ([BMIM][BF$_4$], Chart 1) has been chosen as the medium for the study of solvation dynamics because the tetrafluoroborate salts are reported to be air and water stable.[8,20] The melting point of the tetrafluoroborate salt is lower than that of its chloride or hexafluorophosphate analogues. Moreover, even though the tetrafluoroborate salts have a greater miscibility with water, they are less hygroscopic than the halides. C153 (Chart 1) has been chosen as the probe molecule for the study of the solvation dynamics in [BMIM][BF$_4$] for several reasons: first, this system has a rigid structure; second, the charge separation following electronic excitation of C153 is known to be instantaneous; third, C153 displays a significant shift of its emission maximum as a function of the solvent polarity; and finally, the fluorescence behavior of C153, in particular, the solvation dynamics, has been extensively investigated in several other media including ionic solutions.[35,36,40−45]

CHART 1



[BMIM][BF$_4$]



C153

The relaxation time of the solvent around the photoexcited probe molecule has been estimated using the correlation function, *C*(*t*), defined by Bagchi et al.[46] as

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

where $\bar{\nu}(\infty)$, $\bar{\nu}(0)$, and $\bar{\nu}(t)$ are the peak frequencies at times ∞, 0, and *t*, respectively.

2. Experimental Section

2.1. Materials. Laser-grade C153, obtained from Eastman Kodak, was used without any further purification. The best available grade of NaBF$_4$ and 1-methylimidazole, required for the synthesis of the room-temperature ionic liquid [BMIM][BF$_4$], were procured from Lancaster, and 1-chlorobutane (HPLC grade) was obtained from Aldrich.

The 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.[20] [BMIM]Cl was first prepared from 1-methylimidazole and 1-chlorobutane in an N$_2$ atmosphere and purified according to the literature procedure.[47]

To an aqueous solution of [BMIM]Cl (18.14 g, 0.104 mol), cold NaBF$_4$ (11.42 g, 0.104 mol) was slowly added (a minimum volume of water was used to prepare the solution in each case). The reaction mixture was stirred for approximately 2 h at room temperature. The tetrafluoroborate salt was preferentially extracted by dichloromethane from the aqueous phase. The organic layer was then dried over anhydrous MgSO$_4$, filtered, and finally dried for more than 10 h under high vacuum at 70−80 °C. The purity of the salt including the water content was checked by IR and NMR.

2.2. Instrumentation. A diode-pumped Millena (5W) CW laser (Spectra Physics) at 532 nm was used to pump the Ti−sapphire rod of the Tsunnami picosecond mode locked laser system (Spectra Physics model 4960 M3S). The pulse repetition rate was 82 MHz, and the fwhm was less than 2 ps. The frequency-doubled 375-nm output was used to excite the sample. The instrument response time was 50 ps. The fluorescence decays were measured by a single photon counting spectrometer (model IBH 5000U) and subsequently analyzed using the IBH data analysis software. The absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV−vis−NIR spectrophotometer (UV-3101PC) and a Spex spectrofluorimeter (Fluoromax 3), respectively.

2.3. Methods. Two milliliters of the liquid salt was used in each case to prepare the solution of the fluorescence probe at room temperature. After preparing the sample solution, the quartz cuvette was immediately sealed to avoid any moisture absorption. The sealed solution was found to be stable for weeks.

The time-resolved emission spectra were constructed from the measured fluorescence decay profiles collected at various wavelengths across the entire emission spectrum.[24] To deconvolute the instrumental response, each decay curve was fitted using a multiexponential decay function to obtain a χ^2 value between 1 and 1.2, and the impulse response function $I(\lambda, t)$ was calculated from those best-fit curve. To make the time-integrated intensity at each wavelength equal to the steady-state intensity at that wavelength, a set of $H(\lambda)$ values was calculated using

$$H(\lambda) = \frac{I_{ss}(\lambda)}{\sum_i \alpha_i(\lambda)\tau_i(\lambda)}$$

where $I_{ss}(\lambda)$ is the steady-state intensity, $\alpha_i(\lambda)$ is the preexponential coefficient, and $\tau_i(\lambda)$ is the decay time at that wavelength with $\sum\alpha_i(\lambda) = 1$. The time-resolved emission spectra at different times were calculated from the appropriately normalized intensity decay function $I'(\lambda, t)$ for different wavelengths and at different times where $I'(\lambda, t) = H(\lambda) \times I(\lambda, t)$. The emission maximum at each time $\bar{\nu}(t)$ was obtained by fitting the spectrum to a log-normal line-shape function.[48] The solvation dynamics described by the normalized Stokes shift correlation function $C(t)$ defined as[46,49]

$$C(t) = \frac{[\bar{\nu}(t) - \bar{\nu}(\infty)]}{[\bar{\nu}(0) - \bar{\nu}(\infty)]}$$

was calculated using the peak frequencies of the time-resolved emission spectra where $\bar{\nu}(\infty)$, $\bar{\nu}(0)$, and $\bar{\nu}(t)$ are the peak frequencies at times ∞, 0, and t, respectively.

3. Results

C153 is known to exhibit an intramolecular charge-transfer (ICT) fluorescence band whose location is sensitive to the polarity of the medium. With an increase in the polarity of the medium, the emission maximum of C153 shifts toward longer wavelengths. A recent time-resolved dielectric loss measurement indicated that the change in the dipole moment of the molecule on electronic excitation is between 4.9 and 5.4 D.[43] The sensitivity of the ICT emission maximum of C153 to the polarity of the medium allows one to estimate the polarity around the fluorophore from the position of the emission maximum. In [BMIM][BF$_4$], the emission maximum could be observed at ~537 nm (Figure 1), which corresponds to a polarity of 48.9 on the $E_T(30)$ scale[50] on the basis of the solvatochromic fluorescence data of C153 in homogeneous media[51] and a linear relationship between the wavenumber of the fluorescence maximum and the polarity parameter, $E_T(30)$. The measured $E_T(30)$ value suggests that [BMIM][BF$_4$] is more polar than acetonitrile (45.6) but less polar than methanol (55.4). We note that this estimate of the polarity of [BMIM][BF$_4$] is in fairly good agreement with that obtained by Muldoon et al. from the absorption maximum of the betaine dye.[21]

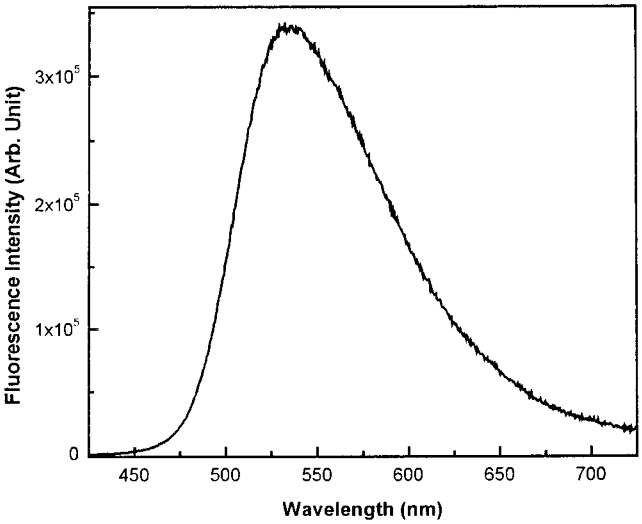


Figure 1. Steady-state fluorescence spectrum of C153 in [BMIM][BF$_4$] at 25 °C; λ_{exc} = 375 nm. The fluorescence spectrum has been corrected for the instrumental response.

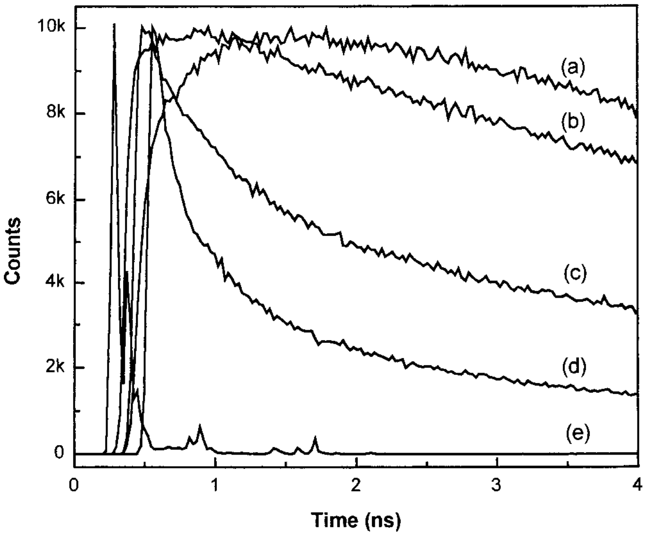


Figure 2. Time-resolved fluorescence behavior of C153 in [BMIM]-[BF$_4$] at (a) 580, (b) 530, (c) 500, and (d) 480 nm; λ_{exc} = 375 nm. The excitation profile is shown in (e).

Figure 2 shows the wavelength-dependent fluorescence decay behavior of C153 in [BMIM][BF$_4$]. At shorter wavelengths (toward the blue edge of the fluorescence spectrum), one could observe a resolution-limited rise time followed by a fast decay to some nonzero level that decays slowly. On the other hand, when monitored at longer wavelengths (red edge of the spectrum), the initial rise (which is clearly resolvable) is followed by a slow decay. The decay curves were fitted to a sum of exponentials using an iterative convolution algorithm. A typical fit to the decay profile along with the residuals is shown in Figure 3. The time constants so obtained from the fits change continuously as a function of the wavelength. This behavior is indicative of a continuous time-dependent shift of the spectrum rather than kinetics involving a few discrete states, and it is also a clear indication of nonspecific solvation dynamics.

The fitted decay profiles at various wavelengths were then normalized such that the time-integrated intensity is proportional

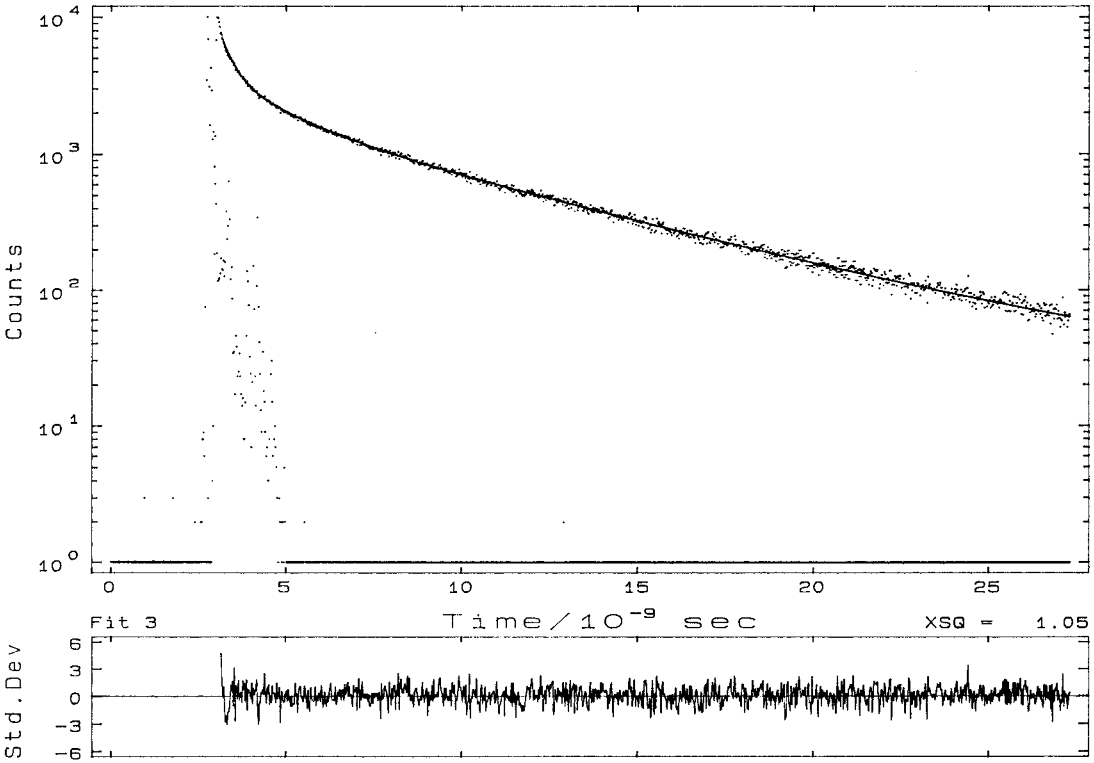


Figure 3. Fluorescence decay profile of C153 at 480 nm along with the best fit (solid line). The data have been fitted to a triexponential function using lifetimes of 350 ps, 1.64 ns, and 6.51 ns, and the corresponding amplitudes are 0.50, 0.24, and 0.26, respectively.

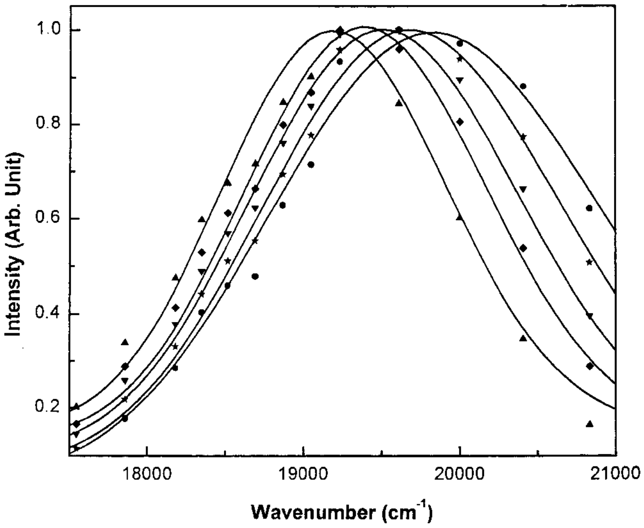


Figure 4. Time-resolved normalized emission spectra of C153 in [BMIM][BF$_4$] at 0 ps (●), 100 ps (★), 250 ps (▼), 500 ps (♦), and 2000 ps (▲).

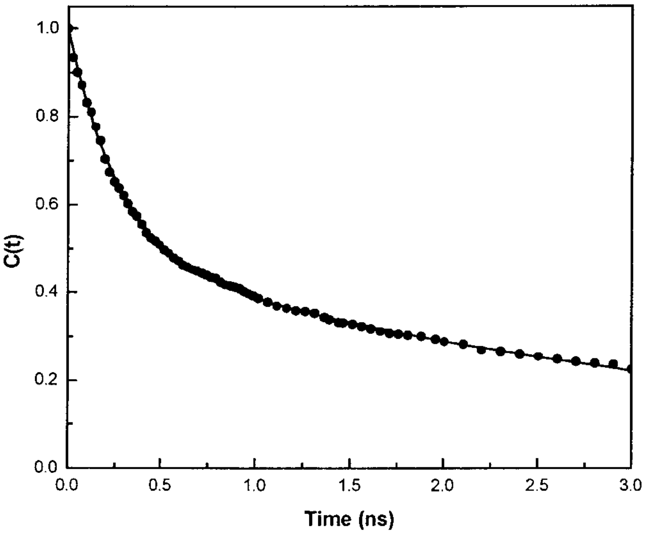


Figure 5. Decay of the response function $C(t)$ of C153 in [BMIM]-[BF$_4$]. The points denote the actual values of $C(t)$, and the solid line represents a biexponential fit.

to the intensity of the steady-state fluorescence spectrum at each wavelength. The time-dependent spectra of C153 obtained by this procedure are shown as points in Figure 4. Because it is difficult to determine the peak frequencies from these data manually, the spectral data were fitted to a log-normal line-shape function. It has been shown earlier that this procedure gives an excellent representation of the fluorescence band shape and a reliable estimate of the wavenumber corresponding to the maximum.[52] The fitted spectra are also shown in Figure 4. We note here that the time-dependent spectral shift observed for C153 in this medium is ~900 cm^{-1}. Because the present medium is as polar as 2-propanol, one should have observed, according to Maroncelli and co-workers,[53] a shift of ~1900 cm^{-1} between $t(0)$ and $t(\infty)$ The fact that we are missing nearly 1000 cm^{-1} of shift at early times (hence, the early part of the dynamics) is due to the low time resolution of the instrument. $\bar{\nu}(t)$ values obtained from the fitted spectra (Figure 4) have been used to estimate the $C(t)$ values using eq 1. The time-dependent variation of $C(t)$ is shown in Figure 5. These data could be fitted to a biexponential decay function, $C(t) = a_1e^{-t/\tau_1} + a_2e^{-t/\tau_2}$ (with $a_1 + a_2 = 1$), to obtain 278 ps and 3.98 ns as the two solvent correlation times. As the time dependence of $C(t)$ in ionic solutions or molten ionic salts usually consists of more than one component, it is customary to express the solvation time as an average.[35,36] The average relaxation time, $\langle\tau\rangle$, in the present solvent system as obtained using C153 is estimated to be 2.13 ns.

4. Discussion

An important point to note here is that solvation in ionic liquids is distinctly different from that in other polar solvents. In polar molecular solvents such as water or alcohol, the solvent molecules reorient themselves around the photoexcited molecule. On the contrary, the time-dependence of the fluorescence spectrum of the probe in ionic liquids arises mainly from the motion of the ions. In view of this situation, the solvation dynamics in a room-temperature ionic liquid is likely to be different from that in conventional molecular solvents. Even though no studies on the solvation dynamics have been undertaken thus far in any room-temperature ionic liquid such as the present one, dynamical results are available in molten salts as well as in ionic solutions.[35−39] It is therefore pertinent to compare our results with those in molten salts and ionic solutions. These studies have already shown that even though there is a fundamental difference in the nature of the solvation process in conventional polar media and in media containing ions, the solvation dynamics by the ions can indeed be represented by the function $C(t)$ that was originally proposed to characterize solvation dynamics in polar molecular solvents.

The solvation dynamics of C153 in [BMIM][BF_4] is biphasic in nature; the short component of $C(t)$ is ∼278 ps (50%), and the long component is 3.98 ns (50%). Even though biphasic dynamics is in contrast to monophasic dynamics of C153 and other probes in molecular solvents, Huppert and co-workers observed similar solvation dynamics of C153 in molten tetraalkylammonium salts.[36,37] Chapman and Maroncelli, while studying the solvation dynamics of several probes in solutions containing various electrolytes, found that the ionic solvation dynamics is rather slow, taking place on a 1−10 ns time scale, and is dependent on the viscosity of the media.[35] A model based on an activated exchange between ions and solvent molecules in the first solvation shell of the probe was proposed to account for the dynamics. Although this model cannot be applied to the present medium in which no solvent molecules other than the ions are available, our results do confirm slow dynamics that is dependent on the viscosity of the media. Huppert and co-workers, on the other hand, attributed a similar observation in ionic solutions to the slow translational dynamics of the ion pairs.[54,55] In molten salts, the biphasic nature of the solvation dynamics was attributed to the difference in the transport properties of the cations and the anions. According to Huppert and co-workers, the short component arises from the motion of the anions, and the longer component arises from the cations.[36,37] This interpretation was based on the consideration of the sizes of the cations and the anions. As the ionic solvation involves a cooperative movement of the ions, the absolute values of both the short and the long components are dependent on the size of the larger species, the cation. On the basis of this model, the short component observed by us has to be attributed to the anion (which is considerably smaller than its cationic counterpart), and the long component, to the cation. We note, however, that the present values are considerably higher than those obtained by Huppert and co-workers in the molten tetraalkylammonium salts. The most important factor that perhaps contributes to the difference in the magnitude of the solvation times between our values and those obtained in the case of molten salts is the viscosity. Even though the exact viscosities of the molten tetraalkylammonium salts used by Huppert at the temperature of the measurements are not available, the values are expected to be in the range of 2−30 cP.[56] On the other hand, the viscosity of [BMIM][BF_4] is reported to be 90 cP at room temperature.[57] Assuming a similar mechanism of solvation dynamics in molten salts and in room-temperature ionic liquids, slower dynamics in the latter solvents is expected on the basis of the consideration of the viscosity values.

Another important point that deserves attention is the amplitudes of the short and the long components. If translational diffusion of the ions is the sole deciding factor of the magnitude of the solvation times, then the faster-moving smaller species, the anion, is expected to contribute more to the amplitude, which is why the smaller ions (with the same charge) contribute more to the transport of charge or conductance. However, the amplitudes of the short and long components are identical in the present case. Clearly, the short component of the dynamics does not represent the total contribution of the anions. If the slow component were solely due to the motion of the cations, then one would have expected a smaller amplitude of this component on increasing the size of the cation. However, our own results (which are currently underway) and those of Huppert and co-workers[36] indicate exactly the opposite behavior. The amplitudes of the slow and the fast components can be accounted for if it is assumed that the relatively fast component arises solely from the initial response of the anions to the newly created charge separation but the long-component arises from a collective motion involving both of the ions and its magnitude is determined largely by the significantly larger and slower moving species, the cations. In view of the close proximity of the oppositely charged ions in ionic liquid, this mechanism is more likely than the alternative mechanism in which the two components are assigned to separate contributions of the anions and the cations.

5. Conclusions

The steady-state and time-resolved fluorescence behavior of C153 have been studied for the first time in a room-temperature ionic liquid, [BMIM][BF_4]. The static fluorescence measurements indicate this solvent to be as polar as 2-propanol. This study shows that the time dependence of the spectral shift function $C(t)$ of C153 is biexponential, with a short component of 278 ps and a much longer component of 3.98 ns. The results confirm that the solvation in ionic liquids that is primarily governed by the translational motion of the ions is considerably slower than that in polar molecular liquids. An initial motion of the anions and a collective motion of the cations and the anions have been proposed to account for the biphasic solvation dynamics. Synthesis of several other room-temperature ionic liquids for the purpose of investigating the solvation dynamics of C153 and other probes is currently underway.

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