

## Fluorescence Studies in a Pyrrolidinium Ionic Liquid: Polarity of the Medium and Solvation Dynamics

Prasun K. Mandal and Anunay Samanta\*

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

Received: April 9, 2005; In Final Form: June 6, 2005

While the imidazolium ionic liquids have been studied for some time, little is known about the pyrrolidinium ionic liquids. In this work, steady-state and picosecond time-resolved fluorescence behavior of three electron donor–acceptor molecules, coumarin-153 (C153), 4-aminophthalimide (AP), and 6-propionyl-2-dimethylaminonaphthalene (PRODAN), has been studied in a pyrrolidinium ionic liquid, *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, abbreviated here as [bm<sup>+</sup>py][Tf<sub>2</sub>N<sup>-</sup>]. The steady-state fluorescence data of the systems suggest that the microenvironment around these probe molecules, which is measured in terms of the solvent polarity parameter,  $E_T(30)$ , is similar to that in 1-decanol and that the polarity of this ionic liquid is comparable to that of the imidazolium ionic liquids. All three systems exhibit wavelength-dependent fluorescence decay behavior, and the time-resolved fluorescence spectra show a progressive shift of the fluorescence maximum toward the longer wavelength with time. This behavior is attributed to solvent-mediated relaxation of the fluorescent state of these systems. The dynamics of solvation, which is studied from the time-dependent shift of the fluorescence spectra, suggests that ~45% of the relaxation is too rapid to be measured in the present setup having a time resolution of 25 ps. The remaining observable components of the dynamics consist of a short component of 115–440 ps (with smaller amplitude) and a long component of 610–1395 ps (with higher amplitude). The average solvation time is consistent with the viscosity of this ionic liquid. The dynamics of solvation is dependent on the probe molecule, and nearly 2-fold variation of the solvation time depending on the probe molecule could be observed. No correlation of the solvation time with the probe molecule could, however, be observed.

### 1. Introduction

Room-temperature ionic liquids (RTILs), especially those based on substituted imidazolium cations, are currently the focus of extensive investigation primarily because they hold promise as nature-friendly media and could be a possible alternative to the volatile organic chemicals that are used as solvents.<sup>1,2</sup> These RTILs are organic salts and are moderately to highly viscous liquids at ambient conditions. The most attractive property of the RTILs from the point of view of environmentally benign nature is their negligible vapor pressure. Wide liquidus, thermal stability, high ionic conductivity, miscibility with other solvents, and recyclable nature are some other properties that make these liquids suitable as solvents for various applications. These ionic liquids are often termed as designer solvents since an appropriate combination of the cationic and anionic constituents may provide an RTIL with desired properties. Several recent studies involving the imidazolium ionic liquids have been directed toward the characterization of their various properties. The increasing usage of these ionic liquids as media for organic synthesis,<sup>2</sup> liquid–liquid extraction,<sup>3</sup> electrochemical studies,<sup>4</sup> mass spectrometry,<sup>5</sup> solar cells,<sup>6</sup> synthesis of nanoparticles,<sup>7</sup> gas sensor,<sup>8</sup> and other applications is clearly evident from the literature.

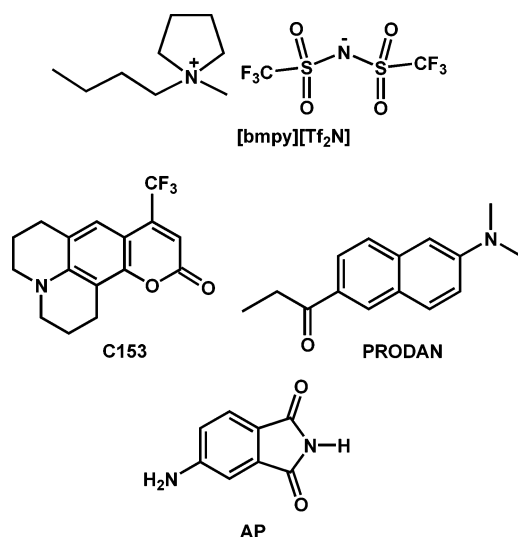
Several photophysical and spectroscopic studies have been carried out in ionic liquids during the past few years,<sup>9–20</sup> and several of them are aimed at quantifying the polarity of the various ionic liquids from the absorption and fluorescence

spectral data of the dissolved solutes.<sup>9</sup> Very recently, we have explored the absorption and fluorescence properties of the imidazolium ionic liquids and have demonstrated an excitation wavelength-dependent fluorescence behavior.<sup>11</sup> The excitation wavelength-dependent shift of the fluorescence maximum of the dipolar molecules dissolved in ionic liquids has also been observed.<sup>12</sup>

Ever since we initiated the studies on solvation dynamics in imidazolium ionic liquids,<sup>13</sup> a few groups have examined the dynamics of solvation in various ionic liquids using different probe molecules.<sup>14–20</sup> These studies have revealed that the dynamics of solvation in these media is much slower than in common organic solvents such as acetonitrile or alcohols and is nonexponential in nature. Almost 50% of the total solvation in imidazolium ionic liquids is ultrafast and could not be resolved in most of the studies. There is some disagreement among different groups on how fast this ultrafast component is.<sup>18,20</sup> There are also different opinions on the physical origin of the various components of the solvation dynamics. Many theoretical, mostly computer simulation, studies have been carried out with a view of understanding the structure of the ionic liquids and the dynamics of solvent fluctuations in these media.<sup>21–23</sup> Shim et al. has assigned the fast component of the dynamics to the translation of the anion and the slow component to the collective motion of the anion and cation.<sup>21</sup> However, according to Kobrak and Znamenskiy, the fast component arises from the collective cation–anion motion.<sup>22</sup> The probe dependence of the solvation dynamics has also been examined recently.<sup>18</sup> Solvation dynamics in mixed solvents comprising

\* Author to whom correspondence should be addressed. Fax: (+91) 40-23012460; e-mail: assc@uohyd.ernet.in.

CHART 1



ionic liquid and one conventional polar solvent as the components has also become a topic of recent interest.<sup>19</sup>

Several workers,<sup>24–29</sup> in particular, Forsyth, MacFarlane, and co-workers,<sup>24–27</sup> have recently developed some new ionic liquids that are based on pyrrolidinium ions (instead of the popular imidazolium ions). Although most of these pyrrolidinium salts are solid at room temperature, the ones comprising bis-(trifluoromethanesulfonyl)imide and dicyanamide are liquid at room temperature. For example, [bmpy][Tf<sub>2</sub>N] (Chart 1) has a melting point of  $-18\text{ }^{\circ}\text{C}$  and a viscosity of 85 cP at  $25\text{ }^{\circ}\text{C}$ .<sup>26</sup> Since little is known about this class of room-temperature ionic liquids, we examine in this manuscript the steady-state and time-resolved fluorescence behavior of three well-known probe molecules, coumarin-153 (C153), 4-aminophthalimide (AP), and 6-propionyl-2-dimethylaminonaphthalene (PRODAN) in [bmpy][Tf<sub>2</sub>N]. While the steady-state measurements allow us to determine the polarity experienced by these electron donor–acceptor (EDA) molecules, the time-resolved studies provide information on the dynamics of the diffusional motion of the constituting ions in this medium. The rationale behind using several different probe molecules instead of just one is to examine whether the solvation dynamics is dependent on the nature of the probe molecules, as has been indicated recently in an imidazolium ionic liquid.<sup>18</sup> We also give particular attention to determining whether there is any ultrafast ( $<5\text{ ps}$ ) component of the dynamics, which constitutes almost half of the solvation response in imidazolium ionic liquids but is not present in ammonium and phosphonium ionic liquids.<sup>17</sup>

## 2. Experimental Section

**2.1. Materials.** AP was obtained from TCI and was recrystallized twice from ethanol in the presence of active charcoal. The purity of the crystalline sample was verified by the single spot in the TLC plate. C153 (laser grade) and PRODAN were procured from Eastman Kodak and Molecular probes, respectively, and were used as obtained. 1-Methylpyrrolidine and lithium bis(trifluoromethanesulfonyl)imide were procured from Acros and Aldrich, respectively, and were used as received. The solvents used in this study were purified according to the literature procedure.<sup>30</sup>

**2.2.1. Preparation of [bmpy][Tf<sub>2</sub>N].** This RTIL was prepared following a standard procedure that involved two steps.<sup>29</sup> The first step consisted of the preparation of the iodide salt and the second step involved the replacement of the anion.

**Step 1.** 1-Methylpyrrolidine was added to ethyl acetate taken in a round-bottomed flask and was cooled with ice. To this ice-cooled solution was added 1-iodobutane dropwise for an hour. On completion of the addition, ice was removed and the solution was allowed to come to room temperature and then was refluxed for 36 h. The solution was cooled to room temperature and the liquid portion was decanted. The colorless powder was recrystallized from acetone/ethyl acetate mixture and was washed with ethyl acetate and then was dried over vacuum.

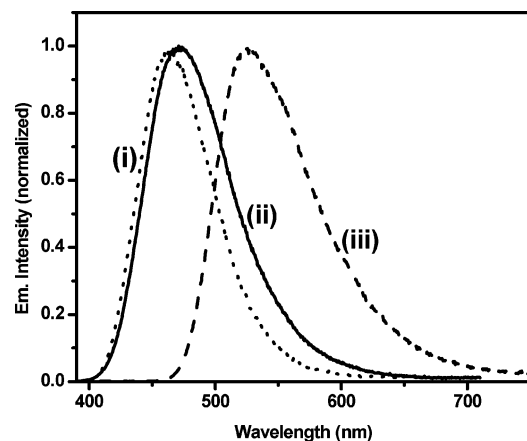
**Step 2.** The iodide salt prepared in the first step was added to triply distilled water taken in a round-bottomed flask. To this solution was added an aqueous solution of lithium bis-(trifluoromethanesulfonyl)imide with constant stirring. The resulting solution was allowed to stir for 72 h and then was filtered.

**2.2.2. Purification of [bmpy][Tf<sub>2</sub>N].** The RTIL thus prepared was washed several times with triply distilled water until the washing was free from any halide (confirmed by the silver nitrate test). The resulting solution was dissolved in acetone and was treated with activated charcoal for 48 h and then was filtered with a pad of acidic alumina. The resulting colorless liquid was then kept in a dry reagent bottle and dried under vacuum (pressure of  $10^{-2}$ – $10^{-3}$  mbar) for 18 h at  $60$ – $65\text{ }^{\circ}\text{C}$  for the removal of any organic impurity or water. The purified ionic liquids were characterized by NMR spectroscopy (compared with the literature data)<sup>26,28</sup> and was stored in a desiccator under dry nitrogen wrapped by aluminum foil.

**2.3. Sample Preparation.** A 2.5 mL of the ionic liquid was taken in a quartz cuvette and a very small amount of the probe molecule was added into it. The cuvette was then sealed with a septum and Parafilm. Dry nitrogen gas was then purged for 30 minutes. The purging of the gas not only helped removal of dissolved oxygen in ionic liquid but also helped the dissolution of the solute. Finally, the cuvettes were sealed again to avoid oxygen/moisture contamination and were kept in a dry bottle and were wrapped with aluminum. The absorption of the prepared solution was checked and in all the cases it was ensured that the absorbance did not exceed 0.3 at 375 nm.

**2.4. Instrumentation.** The NMR spectrum of the ionic liquid was measured using a Bruker AV 400 MHz NMR spectrometer. Steady-state absorption and fluorescence spectra were recorded on a Shimadzu UV–Vis–NIR spectrophotometer (UV-3101 PC) and a Spex Spectrofluorometer (FluoroLog-3), respectively. Time-resolved decay measurements at various wavelengths were executed using a picosecond laser-based single-photon-counting spectrophotometer (Model IBH 5000U). The details of the instrumental setup and the laser system are described elsewhere.<sup>13,14</sup> The instrument response time was 50 ps (fwhm). Both the steady-state and time-resolved experiments were carried out by keeping the excitation wavelength at 375 nm for all the probes. The measured decay curves were analyzed by a nonlinear least-squares iteration technique using the measured laser profile following a standard deconvolution procedure. The quality of the fit was measured by the  $\chi^2$  values and the weighted deviation was obtained after fitting.

**2.5. Method.** The time-resolved emission decay profiles were measured at 10/20 nm interval across the entire range of the steady-state emission spectra. Each decay curve was then fitted to a triexponential decay function with an iterative reconvolution program (IBH). This procedure improved the effective time resolution of the experiments to  $\sim 25\text{ ps}$ . The time-resolved emission spectra (TRES) at different times were constructed according to the procedure described earlier.<sup>13,14</sup> The peak emission frequencies  $\bar{\nu}_{\text{max}}^{\text{flu}}$  ( $\text{cm}^{-1}$ ) at various times were



**Figure 1.** Steady-state fluorescence spectra of (i) PRODAN, (ii) AP, and (iii) C153 in [bmpp][CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N]. The excitation wavelength was 375 nm in all cases. All spectra have been corrected for the instrumental response.

**TABLE 1: Wavenumbers Corresponding the Fluorescence Maxima of the Systems in [bmpp][Tf<sub>2</sub>N] and the Estimated  $E_T(30)$  Values of the Medium**

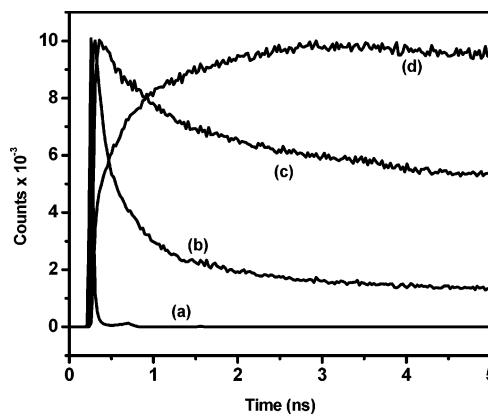
probe	$\bar{\nu}_f$ (cm <sup>-1</sup> )	$E_T(30)$ value of the medium as indicated by the $\bar{\nu}_f$ value
C153	19 010	47.3
AP	21 185	47.4
PRODAN	21 505	45.9
betaine dye		50.1 <sup>a</sup>

<sup>a</sup> This value is directly measured from the longest wavelength absorption maximum of the betaine dye in the ionic liquid.

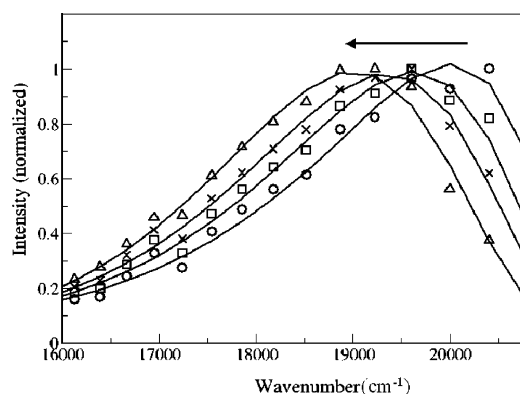
obtained by fitting each TRES to an appropriate log-normal function.<sup>31</sup> The steady-state and time-resolved measurements were carried out at 25 °C.

### 3. Results and Discussion

The steady-state emission spectra of the systems in [bmpp][Tf<sub>2</sub>N] are depicted in Figure 1, and the wavenumbers corresponding to the emission maxima are listed in Table 1. Because the emission spectra of the chosen systems are sensitive to the polarity of the surrounding medium and because the polarity of this ionic liquid is not yet known, we attempt to estimate the polarity of [bmpp][Tf<sub>2</sub>N] in terms of the microscopic solvent polarity parameter,  $E_T(30)$ <sup>32</sup> from the fluorescence spectral data of the systems. An independent and more direct estimation of the polarity of this ionic liquid is also made from the absorption spectral data of the betaine dye.<sup>32</sup> While estimating the polarity of the medium from the fluorescence measurements, we first measured the  $\bar{\nu}_f$  values of the systems in several conventional solvents (such as cyclohexane, benzene, chloroform, 1,4-dioxane, tetrahydrofuran, acetonitrile, and *N,N*-dimethylformamide) of known  $E_T(30)$  values. The linear correlation of  $\bar{\nu}_f$  and  $E_T(30)$  and the measured  $\bar{\nu}_f$  value of the probe molecule in [bmpp][Tf<sub>2</sub>N] allowed evaluation of the microscopic solvent polarity parameter,  $E_T(30)$ , of this ionic liquid. The different  $E_T(30)$  values obtained by this procedure using three probe molecules and the one directly obtained from the longest wavelength absorption maximum of the betaine dye are collected in Table 1. It can be seen that the measured  $E_T(30)$  values vary between 45.9 (obtained with PRODAN) and 50.1 (obtained by direct measurement with the betaine dye). On the basis of these measurements, an average  $E_T(30)$  value of 47.7 can be considered as an indicator of the polarity of this ionic liquid.



**Figure 2.** Wavelength dependence of the fluorescence decay profiles of AP in [bmpp][CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N]: (a) the lamp profile, (b) 410 nm, (c) 440 nm, and (d) 600 nm.  $\lambda_{exc} = 375$  nm.



**Figure 3.** Time-resolved emission spectra (normalized at the peak) of C153 in [bmpp][CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N at 0 (O), 200 (□), 500 (×), and 3000 ps (Δ), respectively.  $\lambda_{exc} = 375$  nm.

An inspection of the  $E_T(30)$  values of the conventional solvents reveals that the present ionic liquid is as polar as 1-decanol, which also has an  $E_T(30)$  value of 47.7.<sup>32</sup> It is also evident that the polarity of this pyrrolidinium ionic liquid is comparable to that of the other imidazolium ionic liquids. In fact, the  $E_T(30)$  value of [bmpp][Tf<sub>2</sub>N] is found identical to that of [emim][Tf<sub>2</sub>N].<sup>14</sup>

The fluorescence decay profiles of the probes, which are measured at several wavelengths (10–20 nm interval) across the fluorescence spectra, are strongly dependent on the monitoring wavelength. This behavior is similar to what we observed in imidazolium ionic liquids.<sup>13,14</sup> A typical behavior of this type is illustrated Figure 2. For all the systems, the decay profile consisted of a monotonic decrease of the fluorescence intensity with time when monitored at a short wavelength region of the fluorescence spectrum. On the other hand, for long monitoring wavelength, the profile comprised an initial rise followed by decay of the fluorescence intensity. This type of time- and wavelength-dependent fluorescence decay behavior of the systems, whose fluorescence properties are well-known, suggests that solvation of the photogenerated excited states is a slow process in [bmpp][Tf<sub>2</sub>N].

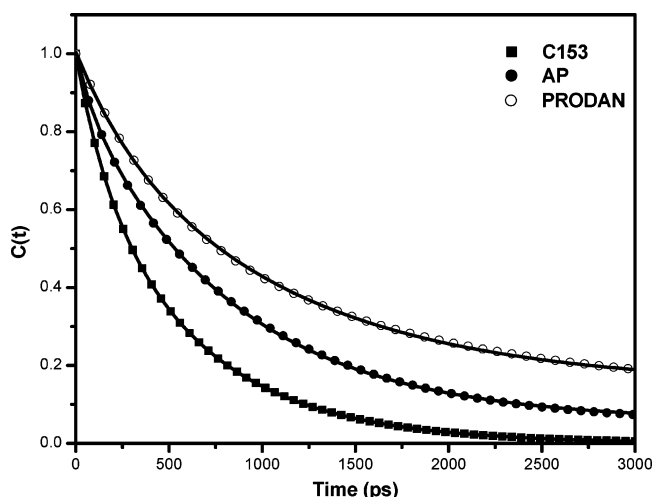
The time-resolved emission spectra (TRES) of the systems, constructed from the fitted decay profiles, show progressive red shift of the fluorescence maximum with time (Figure 3). The total Stokes shift (in cm<sup>-1</sup>) observed for the systems between  $t = 0$  and  $t = \infty$  are measured from the peak positions and are collected in Table 2.

Since the polarity of [bmpp][Tf<sub>2</sub>N] is similar to that of 1-decanol, the total spectral shift is expected to be  $\sim 1770$  cm<sup>-1</sup>

**TABLE 2: Relaxation Parameters<sup>a</sup> of the Three Probes in [bmpy][Tf<sub>2</sub>N]**

probe	$\tau_1$ (ps)	$\tau_2$ (ps)	$a_1$	$a_2$	$\langle\tau\rangle$ (ps) <sup>b,c</sup>	observed shift [ $\bar{\nu}(\infty) - \bar{\nu}(0)$ ] (cm <sup>-1</sup> )
C153	170	610	25	75	500	1000
AP	115	855	12	88	765	1050
PRODAN	440	1395	40	60	1025	1110

<sup>a</sup>  $\tau_1$  and  $\tau_2$  are the two components of the dynamics having amplitudes of  $a_1$  and  $a_2$ , respectively. <sup>b</sup> Average relaxation time defined as  $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$ , where ( $a_1 + a_2 = 1$ ). <sup>c</sup>  $\pm 5\%$ .



**Figure 4.** Time dependence of the spectral shift correlation function,  $C(t)$ , of C153, AP, and PRODAN in [bmpy][(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]. The actual points denote the calculated values of  $C(t)$  and the solid lines represent the biexponential fit to the data.

for C153 according to Maroncelli et al.<sup>31</sup> However, the observed shift for C153 between  $t(0)$  and  $t(\infty)$  is only  $\sim 1000$  cm<sup>-1</sup> (Table 2). This implies that a significant portion ( $\sim 45\%$ ) of the solvation occurs in a time scale faster than the effective time resolution (25 ps) of the present setup and is being missed here. An ultrafast component of the dynamics has been observed in imidazolium ionic liquids by several groups. While Maroncelli and co-workers<sup>18</sup> have suggested that the ultrafast component is shorter than 5 ps, the stimulated emission experiments by Petrich and co-workers,<sup>20</sup> which had subpicosecond time resolution, have indicated a time constant of 40–70 ps for this ultrafast component. There is also a difference in opinion on what contributes to this component (vide later). Interestingly, no such ultrafast component could be detected in ammonium and phosphonium ionic liquids by Maroncelli and co-workers.<sup>17</sup>

The time constant of the observable portion of solvation is obtained from the peak frequencies by constructing the spectral shift correlation function  $C(t)$ , which is defined as<sup>33</sup>

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

The time dependence of the calculated  $C(t)$  values and the fit to the biexponential function,  $C(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$ ,<sup>34</sup> are shown in Figure 4. The relaxation times obtained from the fits are collected in Table 2. The results can be summarized as follows.

The observable dynamics is biphasic in nature. The short component, which has relatively smaller amplitude, varies between 115 and 440 ps. The longer component, on the other hand, varies between 610 and 1395 ps. The average solvation

time varies between 500 and 1025 depending on the probe molecule employed.

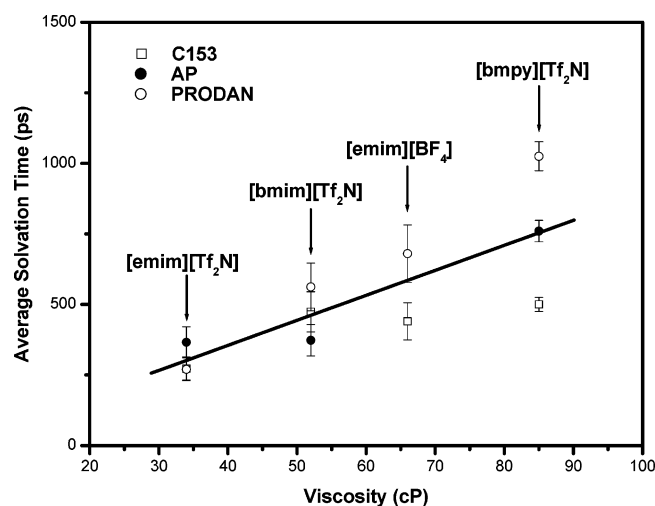
It is well-known that the solvation process in ionic liquids is fundamentally different from that in polar molecular solvents. While in the case of molecular solvents the reorientation of the solvent molecules around the photoexcited molecule is responsible for solvation, the diffusional motion of the constituent ions contributes to solvation in the case of ionic liquids. Having observed a similar biphasic solvation dynamics in imidazolium ionic liquids,<sup>13–15</sup> we attributed the fast component to the anion and the long component to the collective motion of both anion and cation after taking into consideration the literature available on the dynamics in molten salts<sup>35</sup> and the amplitude of the two components. However, according to Maroncelli and co-workers, the ultrafast component of dynamics in imidazolium ionic liquids arises because of small amplitude motions of one or more cations in close contact with the solute and is facilitated by coplanar arrangements of the solute with imidazolium nearest neighbors.<sup>18</sup> The slow component is attributed to large-scale rearrangement of the ions around the photoexcited system. Petrich and co-workers, on the other hand, speculated that the polarizability of the cation is responsible for the fast component.<sup>20</sup> The theoretical results, mostly the computer simulation studies, also present conflicting pictures. While Shim et al. have shown that the short component is due to the translational motion of the anion,<sup>21</sup> Kobrak and Znamenskiy, on the other hand, have demonstrated that collective cation–anion motion is responsible for the fast component.<sup>22</sup> It thus appears that with the present state of knowledge (both theory and experiment) no unambiguous assignment of the various components of the dynamics is possible. We therefore refrain from commenting on the individual components and instead concentrate on the general trends.

An important point that should not be neglected here is the missed ultrafast component of the dynamics. Since an ultrafast component has been observed previously in the case of imidazolium ionic liquids, but not in the case of ammonium or phosphonium ionic liquids,<sup>17</sup> the presence of this component in the present ionic liquid, where the pyrrolidinium ion is devoid of  $\pi$ -bonds and is structurally similar to the ammonium ion, is unexpected. Since some of the earlier interpretations offered for the ultrafast component involved the planarity or the polarizability of the cation,<sup>18,20</sup> a reassignment for this component seems necessary in light of the present results as the pyrrolidinium cation is nonplanar and is much less polarizable compared to the imidazolium cation.

The solvation time in viscous ionic liquid is expected to be dependent on the viscosity of the medium. Previous studies have indicated that for moderately viscous ionic liquids, the average solvation time is linearly dependent on the viscosity of the medium.<sup>17</sup> Figure 5 shows a plot of the various solvation times (as measured by us with different probe molecules) versus the viscosity of the medium for relatively less viscous ionic liquids. For ionic liquids with viscosity values higher than 100 cP (such as [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>]), as has been noted previously,<sup>17</sup> a substantial deviation from the linearity could be observed. Since the viscosity of the present ionic liquid is 85 cP,<sup>26</sup> the present data falls within the linear portion of the plot. Therefore, the measured solvation time is consistent with the viscosity of the pyrrolidinium ionic liquid.<sup>26</sup>

Another point that requires attention is the dependence of the average solvation time on the probe molecule. Maroncelli and co-workers have highlighted the probe dependence of the solvation times in one of their recent papers.<sup>18</sup> While in our previous studies we did observe some variation of solvation





**Figure 5.** Viscosity dependence of the average solvation times, as obtained using different probes, in moderately viscous ionic liquids ( $\eta < 100$  cP). A linear fit to the data points is also shown. The data points shown in the plot are taken from refs 13b, 14, and the present work.

**TABLE 3: Average Solvation Times (in ps) of Different Probes in Different RTILs**

RTIL	C153	AP	PRODAN	reference
[emim][Tf <sub>2</sub> N]	280	370	270	14
[bmim][Tf <sub>2</sub> N]	480	380	560	14
[emim][BF <sub>4</sub> ]	440		680	13b
[bmim][BF <sub>4</sub> ]	2130		1440	13b
[bmim][PF <sub>6</sub> ]	1000	1600	1800	18
[bmpy][Tf <sub>2</sub> N]	500	765	1025	this work

time with the probe molecule, the extent of variation was not so appreciable (see Table 3 or Figure 5). In the present case, the solvation times differ by a factor of  $\sim 2$ . The various solvation times measured for different ionic liquids with different probe molecules are collected in Table 3 to determine whether any particular trend is apparent from these data. It can be seen that the average solvation time in [emim][Tf<sub>2</sub>N], as measured by us, is the lowest with PRODAN and the highest with AP.<sup>14</sup> However, in [bmim][Tf<sub>2</sub>N], the trend is exactly opposite, that is, the lowest value is obtained with AP and the highest with PRODAN.<sup>14</sup> In [bmim][PF<sub>6</sub>], Maroncelli et al. found that the average solvation time is lowest for C153 and highest for PRODAN,<sup>18</sup> which is similar to the trend observed in the present case of [bmpy][Tf<sub>2</sub>N]. However, the numbers collected in Table 3 suggest that there is no definite pattern of the variation of the solvation time with the probe molecule.

#### 4. Conclusion

The steady-state and time-resolved fluorescence behavior of C153, AP, and PRODAN has been studied for the first time in an ionic liquid on the basis of pyrrolidinium cation with a view to characterizing the polarity of this medium and determining the dynamics of solvation. The polarity experienced by the dipolar probe molecules in this medium is found comparable to that of 1-decanol. An ultrafast component of the dynamics, which could not be observed previously in ammonium and phosphonium ionic liquids, has been detected in this pyrrolidinium ionic liquid even though the pyrrolidinium ion resembles the ammonium ion. The observation points to the complex nature of the solvation in ionic liquids and requires a reassignment of the ultrafast component of the dynamics. The average of the time-resolved portion of the solvation time is found consistent with the viscosity of the medium. The average

solvation time is dependent on the probe molecule. However, no definite pattern of variation of the solvation time with the probe molecule could be identified.

**Acknowledgment.** This work has been supported by the Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST), Government of India, and the UPE Program of University Grants Commission (UGC). P.K.M. thanks CSIR for a Fellowship. We thank Profs. P. Natarajan, P. Ramamurthy, and Mrs. V. K. Indirapriyadarsini for their help during the collection of picosecond time-resolved fluorescence data at the National Centre for Ultrafast Processes (NCUPP), Chennai, India.

#### References and Notes

- (1) (a) Seddon, K. R. *Nature (Materials)* **2003**, 2, 363. (b) Seddon, K. R.; Stark, A.; Torres, M. J. In *Clean Solvents: Alternative Media for Chemical Reactions and Processing*; Abraham, M. A.; Moens, L., Eds.; ACS Symposium Series 819; American Chemical Society: Washington, DC, 2002. (c) *Ionic Liquids, Industrial Applications for Green Chemistry*; Rodgers, R.; Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002. (d) Brennecke, J. F.; Maginn, E. J. *AIChE J.* **2001**, 47, 2384.
- (2) (a) Welton, T. *Chem. Rev.* **1999**, 99, 2071. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, 102, 3667. (c) *Ionic Liquids in Synthesis*; Welton, T.; Wasserscheid, P., Eds.; VCH-Wiley: Weinheim, Germany, 2002. (d) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772. (e) Sheldon, R. *Chem. Commun.* **2001**, 2399.
- (3) Huddleston, J. G.; Rogers, R. D. *Chem. Commun.* **1998**, 1765.
- (4) (a) Dickinson, V. E.; Williams, M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.* **1999**, 121, 613. (b) Ding, J.; Zhou, D.; Spinks, G.; Wallace, G.; Forsyth, S.; Forsyth, M.; MacFarlane, D. *Chem. Mater.* **2003**, 15, 2392. (c) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *Chem. Phys. Chem.* **2004**, 5, 1106.
- (5) Armstrong, D. W.; Zhang, L. K.; He, L.; Gross, M. L. *Anal. Chem.* **2001**, 73, 3679.
- (6) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Gratzel, M. *J. Phys. Chem. B* **2003**, 107, 13280.
- (7) Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, 126, 3026.
- (8) Buzzeo, M. C.; Hardacre, C.; Compton, R. G. *Anal. Chem.* **2004**, 76, 4583.
- (9) (a) Aki, S. N. V. K.; Brennecke, J. F.; Samanta, A. *Chem. Commun.* **2001**, 413. (b) Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2* **2001**, 433. (c) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, 35, 1168. (d) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2003**, 5, 2790. (e) Carmichael, A. J.; Seddon, K. R. *J. Phys. Org. Chem.* **2000**, 13, 591.
- (10) (a) Karmakar, R.; Samanta, A. *Chem. Phys. Lett.* **2003**, 376, 638. (b) Yang, Y.; Kou, Y. *Chem. Commun.* **2004**, 226. (c) Katayanagi, H.; Hayashi, S.; Hamaguchi, H.; Nishikawa, K. *Chem. Phys. Lett.* **2004**, 392, 460. (d) Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dolle, A.; Carper, W. R. *J. Phys. Chem. B* **2004**, 108, 13177. (e) Behar, D.; Neta, P.; Schultheisz, C. *J. Phys. Chem. A* **2002**, 106, 3139. (f) Skrzypczak, A.; Neta, P. *J. Phys. Chem. A* **2003**, 107, 7800. (g) Grodkowski, J.; Neta, P. *J. Phys. Chem. A* **2002**, 106, 5468. (h) Chakrabarty, D.; Chakraborty, A.; Hazra, P.; Seth, D.; Sarkar, N. *Chem. Phys. Lett.* **2004**, 397, 216. (i) Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. *Inorg. Chem.* **2003**, 42, 1726. (j) Fletcher, K. A.; Baker, S. N.; Baker, G. A.; Pandey, S. *New J. Chem.* **2003**, 27, 1706. (k) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. *J. Phys. Chem. B* **2001**, 105, 9663.
- (11) (a) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, 402, 375. (b) Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, 109, 9148.
- (12) Mandal, P. K.; Sarkar, M.; Samanta, A. *J. Phys. Chem. A* **2004**, 108, 9048.
- (13) (a) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, 106, 4447. (b) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, 106, 6670.
- (14) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2003**, 107, 7340.
- (15) Saha, S.; Mandal, P. K.; Samanta, A. *Phys. Chem. Chem. Phys.* **2004**, 6, 3106.
- (16) (a) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2003**, 107, 5926. (b) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. *J. Phys. Chem. B* **2004**, 108, 5771. (c) Chakrabarty, D.; Hazra, P.; Chakraborty, A.; Seth, D.; Sarkar, N. *Chem. Phys. Lett.* **2003**, 381, 697.
- (17) Arzhantsev, S.; Ito, N.; Heitz, M.; Maroncelli, M. *Chem. Phys. Lett.* **2003**, 381, 278.

- (18) Ito, N.; Arzhantsev, S.; Maroncelli, M. *Chem. Phys. Lett.* **2004**, 396, 83.
- (19) (a) Baker, S. N.; Baker, G. A.; Munson, C. A.; Chen, F.; Bukowski, E. J.; Cartwright, A. N.; Bright, F. V. *Ind. Eng. Chem. Res.* **2003**, 142, 6457. (b) Chakrabarty, D.; Chakraborty, A.; Seth, D.; Hazra, P.; Sarkar, N. *Chem. Phys. Lett.* **2004**, 397, 469. (c) Chakrabarty, D.; Chakraborty, A.; Seth, D.; Sarkar, N. *J. Phys. Chem. A* **2005**, 109, 1764.
- (20) Chowdhury, P. K.; Halder, M.; Sanders, L.; Calhoun, T.; Anderson, J. L.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. B* **2004**, 108, 10245.
- (21) Shim, Y.; Duan, J. S.; Choi, M. Y.; Kim, H. J. *J. Chem. Phys.* **2003**, 119, 6411.
- (22) Kobrak, M. N.; Znamenskiy, V. *Chem. Phys. Lett.* **2004**, 395, 127.
- (23) (a) Margulis, C. J.; Stern, H. A.; Berne, B. J. *J. Phys. Chem. B* **2002**, 106, 12017. (b) Del Popolo, M. G.; Lynden-Bell, R. M.; Kohanoff, J. *J. Phys. Chem. B* **2005**, 109, 5895. (c) Lynden-Bell, R. M.; Kohanoff, J.; Del Popolo, M. G. *Faraday Discuss.* **2005**, 129, 57.
- (24) (a) Forsyth, S.; Golding, J.; MacFarlane, D. R.; Forsyth, M. *Electrochim. Acta* **2001**, 46, 1753. (b) Golding, J.; Hamid, N.; MacFarlane, D. R.; Forsyth, M.; Forsyth, C.; Collins, C.; Huang, J. *Chem. Mater.* **2001**, 13, 558.
- (25) MacFarlane, D. R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G. B. *Chem. Commun.* **2001**, 1430.
- (26) MacFarlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, 103, 4164.
- (27) (a) Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. *Chem. Mater.* **2002**, 14, 2103.
- (28) Lancaster, N. L.; Salter, P. A.; Welton, T.; Young, G. B. *J. Org. Chem.* **2002**, 67, 8855.
- (29) Henderson, W. A.; Passerini, S. *Chem. Mater.* **2004**, 16, 2881.
- (30) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.
- (31) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, 99, 17311.
- (32) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, Germany, 1988.
- (33) (a) Bagchi, B.; Oxtoby, D. W.; Flemming, G. R. *Chem. Phys.* **1984**, 86, 257. (b) van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1985**, 89, 4181.
- (34) Bart et al. (see ref 35) fitted the spectral shift correlation function  $C(t)$  a stretched exponential of the form  $C(t) = a_1 \exp(-t/\tau_1)^\beta + a_2 \exp(-t/\tau_2)^\beta$  while examining the dynamics in molten ammonium and phosphonium salts. However, our attempts to fit the present set of data yielded a  $\beta$  value of unity.
- (35) (a) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, 98, 3295. (b) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1994**, 98, 10819. (c) Bart, E.; Meltsin, A.; Huppert, D. *J. Phys. Chem.* **1995**, 99, 9253.