

FEATURE ARTICLE

Dynamic Stokes Shift and Excitation Wavelength Dependent Fluorescence of Dipolar Molecules in Room Temperature Ionic Liquids

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Room temperature ionic liquids (RTILs) are viscous media consisting entirely of ions. Because of the complex nature of various interactions in these media, the solvent properties of the RTILs are very little understood. Since the fluorescence response of molecules comprising conjugated electron donor and acceptor groups, referred to as dipolar molecules, is one of the most frequently exploited sources of information on complex media, whose properties are largely unknown, it is possible to obtain insight into the structure and dynamics of the RTILs by studying the fluorescence behavior of dipolar solutes in these complex media. The most commonly exploited utility of a fluorescent dipolar system is in the estimation of the polarity of the media from its steady state fluorescence response. While several dipolar systems do provide estimates of the polarity of various RTILs, there can be circumstances when the steady state emission frequency of a dipolar system may not truly reflect the equilibrium solvation energy and, hence, the polarity of the medium. The fluorescence response of a dipolar system can be dependent on the excitation wavelength, an observation not commonly encountered in conventional solvents of similar polarities. On the other hand, the time-resolved fluorescence behavior of a dipolar solute in polar medium is one of the primary sources of information on the time-scale of reorganization of the solvent molecules around the photoexcited species. As the RTILs are sufficiently polar media, the time-dependent fluorescence data of the dipolar systems provide insight into the dynamics and mechanism of solvation in these media, which differ considerably from the conventional solvents. These aspects have been discussed taking into consideration the inherent absorption and fluorescence behavior of the imidazolium ionic liquids.

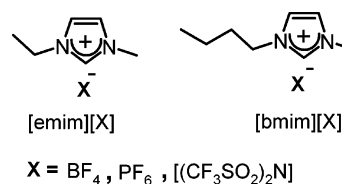
I. Introduction

Considerable effort in recent years has been directed toward finding environmentally friendly replacements for conventional solvents, which are volatile organic compounds used in large quantities and 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 room-temperature ionic liquids (RTILs) as alternative reaction media.

The RTILs, which are currently the focus of worldwide attention, are novel salts consisting entirely of ions.^{1–7} However, unlike the ionic solids, these are viscous liquids at ambient conditions. The most commonly used RTILs are the ones based on nonsymmetrically substituted *N,N'*-dialkylimidazolium cations and noncoordinating bulky inorganic anions. 1-Butyl-3-methylimidazolium ion, [bmim]⁺ and 1-ethyl-3-methylimidazolium ion, [emim]⁺ are the most common cationic components and PF₆[−], BF₄[−], and [(CF₃SO₂)₂N][−] ions are the anionic counterparts (Chart 1).

The low melting point of these salts is the consequence of weak electrostatic attraction between the ionic partners and poor packing of the crystal, arising from the bulkiness, nonsymmetry, and delocalized charge of the constituent ions. Apart from

CHART 1. Chemical Formulas and Commonly Used Abbreviations for Some Very Common Imidazolium Ionic Liquids



possessing essential solvent properties, such as wide liquid range, thermal stability, ability to dissolve a variety of organic and inorganic substances, and miscibility with other liquids, the fact that these liquids do not evaporate, do not burn, and can be recycled makes them quite appealing as environmentally friendly solvents for various fundamental studies and applications. Perhaps this explains why the utility of these substances as environmentally benign substitutes for the conventional solvents in chemical syntheses, separation processes, electrochemical studies, and several other applications has been explored within a short span of time. Since RTILs with desired properties can simply be designed by picking the right combination of the cationic and anionic constituents, these liquids are called “designer solvents”. A number of review articles dealing

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Anunay Samanta received his Ph.D. degree in 1987 from Indian Association for the Cultivation of Science (Jadavpur University) with Prof. Mihir Chowdhury. He held a postdoctoral appointment at the Radiation Laboratory, University of Notre Dame for a couple of years before joining the Chemistry faculty at University of Hyderabad in 1990, where he is a Professor since 2001. Samanta is an elected Fellow of the Indian Academy of Sciences. His primary research interests include photophysics of electron donor–acceptor molecules and design and development of fluorescence signaling systems for various guests. For the past few years he has been actively involved in studying the photophysics of molecules in room-temperature ionic liquids to obtain an understanding of these complex media.

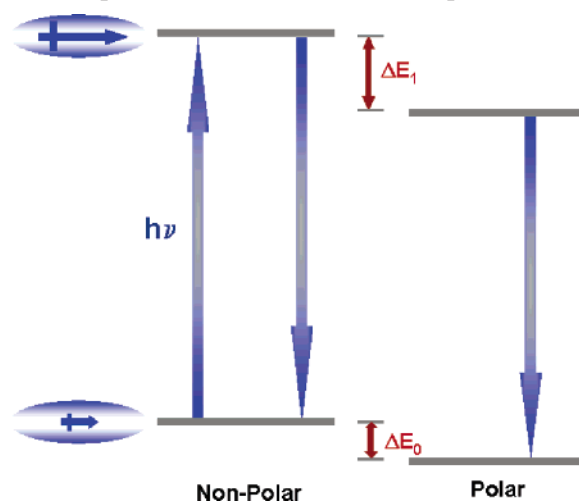
with various different aspects of the RTILs are already available.^{1–5}

This article focuses on the fluorescence response of dipolar systems in RTILs with a view to obtaining an understanding of some of the solvent properties of the RTILs at the microscopic level. Some specific questions for which we seek answers from these studies are the following: How suitable are these media for photophysical studies on dissolved solutes? How polar are these media? Are these media really homogeneous at the microscopic level? What is the mechanism and time scale of solvation in RTILs? How important are the electrostatic and specific interactions such as hydrogen bonding interaction in these media?

The fluorescence properties of dipolar molecules are remarkably sensitive to the polarity of the surrounding environment due to the intramolecular charge-transfer nature of the emitting state of these systems.⁸ As the excited state of a dipolar molecule is more polar than the ground state, the excited state is stabilized to a greater extent compared to the ground state in a polar medium, leading to a Stokes shift of the emission maximum (Scheme 1). Since the magnitude of the Stokes shift or the wavelength/energy corresponding to the fluorescence maximum of a dipolar molecule in a given solvent is a measure of the various interactions (dipolar, hydrogen bonding, electrostatic, etc.) between the two, the dipolar molecules serve as polarity probes for the study of complex systems.⁹

Since the utility of a medium for photophysical studies depends on how transparent the medium is in the optical (UV–visible) region, knowledge of the optical properties of the RTILs is desirable prior to undertaking studies involving the solute molecules. Therefore, the electronic absorption and fluorescence properties of the imidazolium ionic liquids, which have been elucidated only very recently,^{10–12} are discussed first. In this context, non-negligible absorption in the UV–visible region and an unusual fluorescence behavior of the imidazolium ionic liquids, which are commonly regarded as optically transparent substances, have been

SCHEME 1. Energy Level Diagram of a Dipolar Molecule in Nonpolar and Polar Media Illustrating the Solvent Stabilization of the Ground and Excited States and Consequent Shift of the Emission Frequencies



highlighted.^{10–12} The unusual fluorescence behavior of these liquids is shown to be the consequence of the presence of various energetically different associated forms of the ionic constituents of the RTILs.

While a majority of the dipolar systems exhibit conventional fluorescence behavior, allowing quantification of the polarity of the RTILs,^{13,14} some of the systems exhibit fairly strong excitation wavelength-dependent fluorescence spectra in these media.¹⁵ The existence of a distribution of ground-state molecules differing in their interaction energies with the RTILs and slow rates of the excited-state relaxation processes, viz. solvation and energy transfer, are shown to be responsible for the uncommon fluorescence behavior of some systems.

The remaining part of the article focuses on the time-resolved fluorescence studies of the dipolar solutes that are aimed at determining the time scale of solvation processes in RTILs. Dynamic Stokes shift of the fluorescence spectra of the dipolar solutes in the picosecond and nanosecond time scale is a common feature in RTILs. The experimental results, which suggest that solvation is a slow process in RTILs, have been discussed along with the theoretical simulation studies with a view to obtaining an understanding of the mechanism of solvation process in these media.

II. Optical Properties of the RTILs

Absorption. The very fact that the spectral and temporal behavior of several systems has been studied in imidazolium ionic liquids may give an impression that these are transparent liquids in the UV–visible region.^{16,17} Interestingly, even though a large number of systems, most of which absorb above 300 nm and are strongly fluorescent, have been studied in various RTILs, a focused study on the optical properties of these liquids lacked for quite some time. Most of the remarks relating to the optical transparencies have been made during the course of study of some other properties of the imidazolium ionic liquids. These studies have indicated that these liquids are transparent in the most part of the UV region (above 240 or 300 nm) and completely transparent in the visible region.¹⁷ Even though repeated purification of an imidazolium ionic liquid, [bmim][PF₆], results in a decrease of the absorption in the 250–300 nm region, some absorption in this region remained that could not be removed by purification.¹⁸ It was left unclear whether the

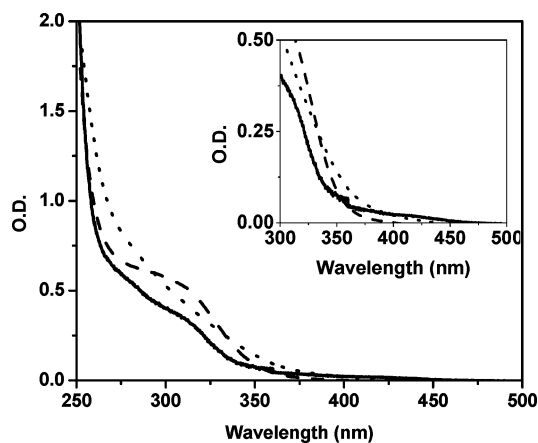


Figure 1. Absorption spectra of neat RTILs as obtained using a 1 cm path length cuvette: [emim][BF₄] (—), [bmim][BF₄] (---), [bmim][PF₆] (····). The inset shows the tail of the absorption more clearly. Adapted from Figure 1 of ref 11.

residual absorption in the 250–300 nm region was due to an impurity, which could not be completely removed from the RTIL.

We have recently studied very carefully the absorption and fluorescence behavior of a number of common imidazolium ionic liquids by adopting a strategy that is different from the one of comparing the absorption spectra of repeatedly purified samples of RTILs.^{10,11} To determine whether the residual absorption in the UV–vis region of the imidazolium ionic liquids is due to impurity or not, we have examined the absorption characteristics of the constituent imidazolium cation. This was accomplished by carrying out control experiments involving generation of the 1-methylimidazolium cation from pure 1-methylimidazole (by protonation), followed by investigation of the absorption characteristics in the region of interest.^{10,11} Since these control experiments revealed that the imidazolium cations absorb at 300 nm and above, it was evident that it would be impossible to obtain imidazolium ionic liquids with no absorption at this wavelength. The observation also indicated that the weak absorption at 300 nm and at longer wavelength had nothing to do with the impurity in the RTILs, but was clearly due to the imidazolium salts.^{10,11} The absorption characteristics of three most commonly used imidazolium ionic liquids in their neat form, as measured using a 1 cm path length cuvette, are shown in Figure 1. The figure suggests that the absorption characteristics of the common imidazolium ionic liquids such as [bmim][BF₄], [emim][BF₄], and [bmim][PF₆] are indeed very similar. [bmim]Cl, which is a solid at room temperature, also displays a similar absorption behavior in solution. While the molar extinction coefficients of the absorption at 300 nm are very low, they contribute to an absorbance of ~0.5 (neat RTIL, 1 cm cuvette) at this wavelength, implying that ~70% of the incident light is absorbed by the RTILs. At 350 nm, the absorbance due to the RTILs is around 0.07–0.15. An important feature of the absorption spectra of the RTILs is the unusually long tail that extends even beyond 400 nm. The origin of the tail portion of the absorption and its importance are evident from the later part of the discussion.

Fluorescence. We found that rigorously purified samples of the imidazolium ionic liquids are weakly fluorescent.^{10,11} A typical emission behavior of an RTIL is illustrated in Figure 2. The general emission characteristics of other imidazolium ionic liquids are quite similar. All of them exhibit a two-component emission. For short excitation wavelengths, an emission band around 340–360 nm is observed. However, when excited at

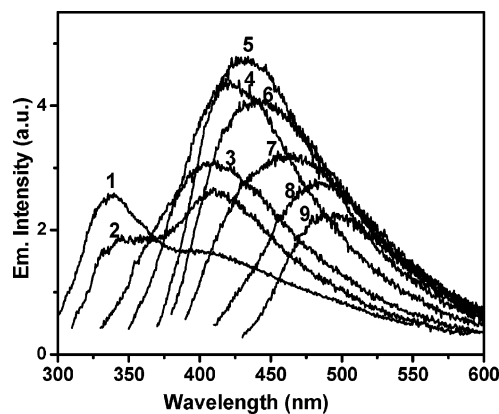


Figure 2. Excitation wavelength-dependent fluorescence spectra of neat [bmim][PF₆]. λ_{exc} values are 280 (1), 300 (2), 320 (3), 340 (4), 360 (5), 370 (6), 380 (7), 400 (8), and 420 (9) nm. Adapted from Figure 3 of ref 10.

higher wavelengths corresponding to the tail portion of the absorption, a second emission band, which appeared as a shoulder for short excitation wavelengths, becomes prominent. However, the most interesting feature of the emission is the shift of the emission maximum toward longer wavelength on increase of the excitation wavelength. No limiting value of the emission peak position is observed, and the shift, whose magnitude is quite large, is observable as long as one can record a noise-free emission spectrum. An additional point to note is that the fluorescence can be observed even when the excitation wavelength is greater than 400 nm, where the absorption due to the RTILs is insignificant.

Quantification of the fluorescence efficiency of the imidazolium ionic liquids is difficult in view of the excitation wavelength dependence of the two-component emission and its shifting nature. For neat [bmim][PF₆], the estimated value of the fluorescence quantum yield ($\lambda_{\text{exc}} = 360$ nm) is around 5×10^{-3} . Study of the fluorescence decay behavior of the RTILs by exciting the samples at different wavelengths and monitoring the decay profiles at various wavelengths reveals that the variation of the decay parameters is minimal and no definite trend of variation of the lifetime with wavelength could be observed. The lifetime components for the different ionic liquids are quite similar. The major component (~90%) of the decay consists of a lifetime that varies between 470 and 590 ps. Two other minor components with lifetime of 2.4–2.9 ns (~7%) and 8.5–9.5 ns (~3%) are also observed.

Origin of the Absorption Tail and Shifting Fluorescence. The control experiments described earlier not only confirmed that the imidazolium ion is fluorescent but also suggested that the short wavelength emission is due to the monomeric form of the imidazolium ion and the long component is due to its various associated forms.^{10,11} However, the excitation wavelength-dependent dramatic shift of the fluorescence peak of the long wavelength band, which appears to be inconsistent with Kasha's rule¹⁹ of excitation wavelength independence of the emission spectrum, is quite puzzling. Even though the nature of the shift may appear somewhat similar to that expected of a Raman band, the broad nature of the emission and the mismatch between the shift of the emission maximum and that of the excitation wavelength rules out this possibility. We figured out that this emission is observed when the excitation is made at the tail of the absorption band. We found reasons to believe that the long tail of the absorption spectra of the imidazolium ionic liquid is due to various energetically different associated species involving both the imidazolium cation and the constituting anion.^{10,11}

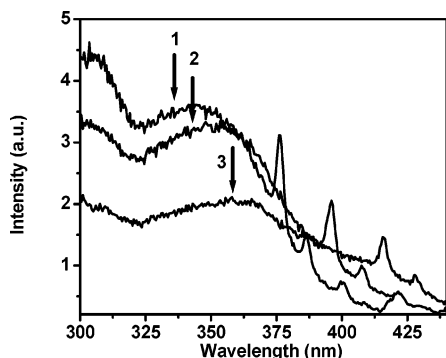


Figure 3. Fluorescence excitation spectra of [bmim][PF₆] in acetonitrile. Monitoring wavelengths are 425 nm (1), 450 nm (2), and 475 nm (3). The sharp peaks are Raman lines. Adapted from Figure 5 of ref 10.

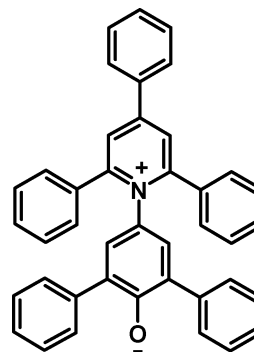
Even though the liquid state structure of the RTILs is still not fully understood, several structures with both short- and long-range spatial correlations of the cation–anion and cation–cation pairs, which we term as associated species, are indicated in a number of experimental and computer simulation studies.^{20,21} While the large anions are believed to be located mostly above and below the plane of the imidazolium ring, the existence of multiple structures, and the large region of probability of finding an anion in the vicinity of a cation and vice versa, are expected to broaden the energy states of the absorbing species and can give rise to a long tail. Recent computer simulation studies, which indicate the existence of spatially different environments in RTILs,^{22,23} suggest a further broadening of the distribution of energetically different associated species due to this heterogeneity. Since each associated species is characterized by its own absorption and fluorescence maxima, when the excitation wavelength is changed, a different species is excited and emission characteristic of that species is observed. This is evident from the gradual shift of the fluorescence excitation spectrum on changing the monitoring wavelength (Figure 3). It is important to note that mere existence of various energetically different associated species cannot ensure an excitation wavelength dependent fluorescence behavior, as is observed in the case of neat RTILs. The emission would have occurred always from the species having the most low-lying excited state had the energy transfer between the photoexcited species and the others, which are not excited and whose lowest excited-state lies below that of the photoexcited species, been efficient. Therefore, the results indicate that energy transfer from the photoexcited species to other low-lying species that are in the ground state is inefficient. Two factors can be identified for the inefficiency of the energy transfer process. First, the short fluorescence lifetime of the associated species implies that the interaction between the photoexcited species with other associated species is less probable. Second, the various associated species constitute a small fraction of the ionic liquids and, hence, the interaction between these species is expected to be minimal.

That the long-wavelength emission band indeed arises on excitation of the different associated structures, which comprise the long absorption tail of the RTILs, is also evident from the effect of dilution on the fluorescence spectra. The dilution of the RTILs with a conventional solvent leads to gradual reduction of the fluorescence intensity of the long-wavelength emission band relative to that of the short wavelength band.¹¹

III. Steady State Fluorescence of Dipolar Solutes

Conventional Behavior. One of the key parameters that characterizes how a solvent interacts with the solutes is the

CHART 2. Molecular Structure of the Betaine Dye Used in the Solvent Polarity Scales



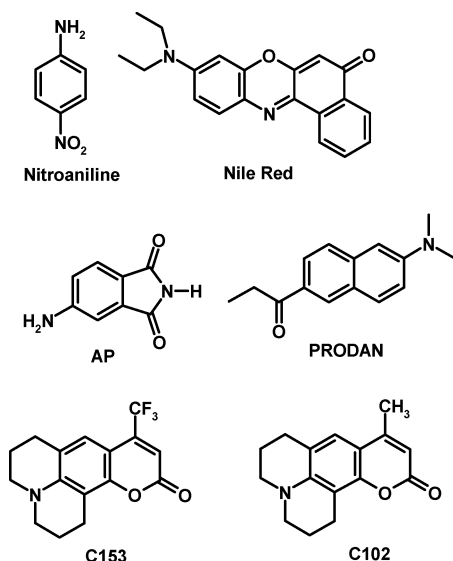
solvent polarity. For conventional solvents, quantities such as dielectric constant, refractive index, or functions involving both dielectric constant and refractive index are commonly used as macroscopic solvent polarity parameters. However, since the polarity of a solvent should reflect the multitude of its all possible interactions at the microscopic level, it is customary to express the polarity in terms of empirical parameters that take into account all possible specific and nonspecific interactions, such as electrostatic, inductive, dispersive, hydrogen bonding, etc., between the solute and the solvent.²⁴

Among the various microscopic polarity parameters, the $E_T(30)$ scale is perhaps the most common one. The $E_T(30)$ scale is based on the transition energy of a zwitterionic betaine dye (Chart 2), which exhibits exceptional negative solvatochromism (blue shift of the absorption band on increase of the polarity of the medium) as the dipole moment of the molecule in the ground state is considerably higher than that in the excited state.²⁴ The $E_T(30)$ value of a solvent is defined as the molar transition energy of this dye (in kcal/mol) at room temperature (25 °C) and normal pressure (1 bar) and is related to the wavelength corresponding to the maximum of the long wavelength absorption band of the dye as

$$E_T(30)/\text{kcal mol}^{-1} = 28591/(\lambda_{\text{max}}/\text{nm})$$

The $E_T(30)$ scale varies from 63.1 for water, the most polar solvent, to 30.7 for tetramethylsilane, the least polar solvent known. A point to note here is that even though the $E_T(30)$ scale of polarity is defined with respect to the betaine dye, the $E_T(30)$ value of a solvent is very often estimated using other substances because of convenience and sometimes because of necessity such as poor solubility of the betaine dye in the medium. Apart from the most commonly used $E_T(30)$ scale, several other polarity parameters are also used, which can be found elsewhere.²⁴

Several studies have been carried out in recent years for quantifying the polarity of the RTILs in terms of various empirical parameters using the measured frequency of the long wavelength absorption or fluorescence maximum of a number of dipolar systems. The steady state fluorescence studies of the dipolar molecules have not only revealed how polar the ionic liquids are but also have shown that photophysical behavior of the solute molecules can be studied in these media without much complication arising from the inherent absorption and fluorescence properties of the RTILs. This is because most of the dipolar molecules absorb at long wavelengths where the absorption due to the RTILs is not significant and most of the dipolar molecules are strongly fluorescent compared to the media.

CHART 3. Some of the Dipolar Molecules Used in the Measurement of the Polarity and Solvation Dynamics of the RTILs

One of the early estimations of the polarity of some imidazolium ionic liquids using dipolar probe molecules was made by Aki et al. from the fluorescence probe maxima of two aminophthalimide derivatives.¹⁴ This and several other studies in which the solvatochromic absorption or steady-state fluorescence behavior of a variety of dipolar molecules (Chart 3) has been investigated for the estimation of the solvent polarity of the RTILs suggest that most of the ionic liquids are more polar than acetonitrile but less polar than methanol.^{14,25–30} In fact, the fluorescence response of the dipolar molecules in different imidazolium or pyrrolidinium ionic liquids is found to be very similar, despite the large difference in the structures of the constituent ions. In all cases, the microenvironment experienced by these molecules is similar to that in short-chain alcohols. A very similar polarity of the different ionic liquids is perhaps a reflection of the hydrogen bonding interaction of the constituent ions of the RTILs with the probe molecules. Table 1 collects the $E_T(30)$ values of some of the RTILs estimated by us. More detailed information on the polarity of the RTILs can be found in a recent review article of Reichardt.¹⁴

Unconventional Behavior. The fact that the $E_T(30)$ values of the RTILs and short chain alcohols are very similar does not necessarily mean that the fluorescence response of a dipolar molecule would always be similar in these two types of solvents. A different fluorescence response is possible when influence from some of the solvent parameters such as viscosity, polarizability, and hydrogen bond acidity and basicity is significant.

While the fluorescence behavior of most of the dipolar molecules in ionic liquids (Figure 4) is similar to that observed in short chain alcohols, a few dipolar systems show different behavior in RTILs and short chain alcohols.¹⁵ Among the dipolar systems studied so far, two very commonly used fluorescent probe molecules, ANS and HNBD, and one not so commonly used dipolar molecule, ANF (Chart 4), exhibit an unexpected excitation wavelength-dependent fluorescence behavior in RTILs that could not be observed in short chain alcohols.¹⁵ Even though this excitation wavelength dependence is not as pronounced as that exhibited by the ionic liquids themselves, the effect cannot be ignored. The observation does not conform to the well-established Kasha's rule of photochemistry, according to which the fluorescence spectrum of a polyatomic molecule in con-

TABLE 1: Our Estimates of the Polarity of Some Commonly Used RTILs Using Various Dipolar Molecules

RTIL ^a	probe	estimated $E_T(30)$ value ^b	ref
[bmim][BF ₄]	C153	48.9	25,26
	PRODAN	47.1 (48.0)	
[emim][BF ₄]	C153	49.1	26
	PRODAN	47.5 (48.3)	
[bmim][PF ₆]	Nile Red	49.0	28
	C153	47.2	
[bmim] [(CF ₃ SO ₂) ₂ N]	PRODAN	46.0 (47.1)	27
	AP	48.2	
	C153	47.7	
	PRODAN	46.5 (47.6)	
[emim] [(CF ₃ SO ₂) ₂ N]	AP	48.5	27
	C153	47.3	
	AP	47.4 (47.7)	
	PRODAN	45.9	
[bmPy] [(CF ₃ SO ₂) ₂ N]	C153	47.3	30
	AP	47.4 (47.7)	
	PRODAN	45.9	
	betaine dye	50.1	
acetonitrile		45.6	24
methanol		55.4	24
2-propanol		48.4	24
2-butanol		47.1	24
1-decanol		47.7	24

^a The polarities of a few conventional solvents are also shown for comparison. ^b The quantities shown in parentheses are the average $E_T(30)$ values of the RTILs.

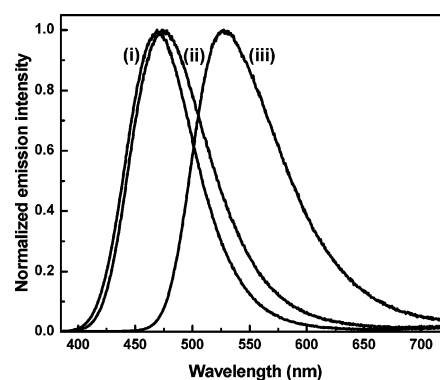
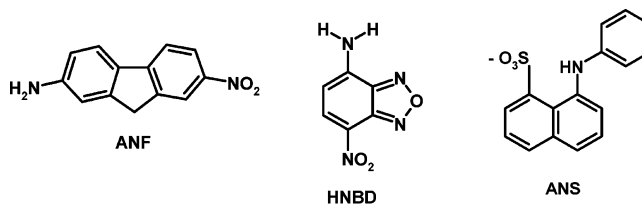


Figure 4. Steady-state fluorescence spectra of (i) PRODAN, (ii) AP, and (iii) C153 in [bmim][(CF₃SO₂)₂N]. The excitation wavelength was 375 nm in all cases. All spectra have been corrected for the instrumental response. Adapted from Figure 1(a) of ref 27.

CHART 4. Dipolar Molecules that Exhibit Red-Edge Effect in Ionic Liquids

densed media should originate from the lowest vibrational level of the first excited singlet state irrespective of the excitation.¹⁹ A typical excitation wavelength-dependent fluorescence behavior is highlighted in Figure 5. A plot of the emission peak wavelength versus the excitation wavelength is illustrated in Figure 6. In this context it should be noted that the shift of the fluorescence maximum of a dipolar solute has nothing to do with that of the RTILs, as the experimental conditions are such that weak fluorescence due to the RTILs does not interfere with relatively stronger fluorescence of the dipolar molecule. The fact that the fluorescence behavior of a dipolar system in RTILs can be different from that in short chain alcohols implies that

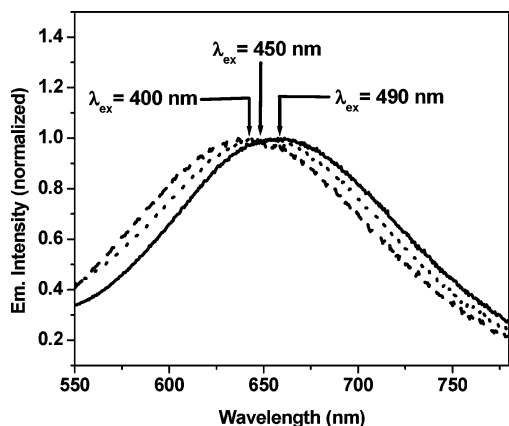


Figure 5. Normalized fluorescence spectra of ANF in [bmim][BF₄] at room temperature as a function of excitation wavelength, λ_{ex} : 400 nm (dash), λ_{ex} : 450 nm (dot), and λ_{ex} : 490 nm (solid). The fluorescence spectra have been corrected for the instrumental response. Adapted from Figure 1(b) of ref 15.

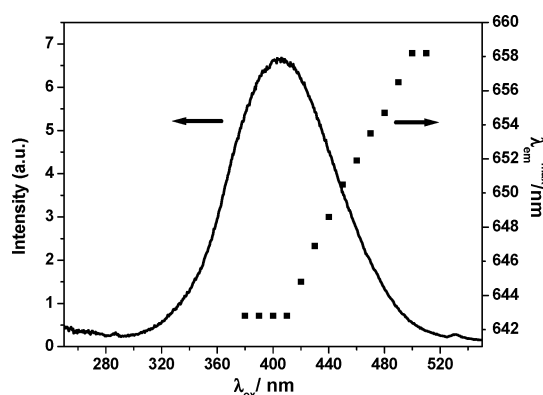


Figure 6. Wavelength corresponding to the fluorescence maximum ($\lambda_{\text{em}}^{\text{max}}$) vs excitation wavelength (λ_{ex}) plot of ANF in [bmim][BF₄] (●) superimposed on the absorption spectrum. Adapted from Figure 1(a) of ref 15.

TABLE 2: Observed Shift of the Fluorescence Maximum for Different Dipolar Molecules in RTILs and Glycerol (data from ref 15)

probe	Shift values (in nm) in			
	[emim][BF ₄]	[bmim][BF ₄]	[bmim][PF ₆]	glycerol
ANF	10	14	16	30
ANS	30	35	28	2
HNBD	14	16	13	3

solvent properties other than the polarity parameter, $E_T(30)$ value, can play important roles in determining the fluorescence behavior of the systems. To examine whether specific interactions between the solute and the solvent give rise to this kind of effect, the excitation wavelength dependence has also been investigated in a highly viscous conventional solvent, glycerol. It is found that ANF exhibits more pronounced excitation wavelength dependence in glycerol, while ANS and HNBD do not show any significant excitation wavelength dependent shift of the fluorescence maximum in this medium. This observation suggests that while the high viscosity of the RTILs is responsible for the excitation wavelength dependent fluorescence behavior of ANF, specific interactions with the solvent contribute to a similar behavior for HNBD and ANS. Table 2 collects the extent of spectral shift observed for the different systems in RTILs and glycerol.

Factors Contributing to Excitation Wavelength Dependence. Even though the excitation wavelength-dependent fluo-

rescence behavior is inconsistent with Kasha's rule, it is known for some time that the fluorescence of some systems shifts toward longer wavelength on increasing the excitation wavelength.^{31–37} Studies in different media involving a variety of fluorophores have revealed that this phenomenon can often be observed in highly viscous or frozen media such as low-temperature glasses, or in polymer matrices and organized assemblies such as membranes, proteins, etc.³¹ This phenomenon is commonly known as “red-edge effect” (REE),^{34,35} although terminologies such as edge excitation shift (EES),³³ edge excitation red shift (EERS),³⁶ and red edge excitation shift (REES)^{9,37} are also used. The phenomenon has been exploited quite extensively for studies in biological systems, and an excellent recent review on this topic is available.³¹

To observe REE, two conditions need to be satisfied. First, there must be a distribution of solute–solvent interaction energy leading to inhomogeneous broadening of the absorption spectrum. Since each molecule in a condensed medium does not necessarily experience an identical environment and since a large number of different environments are indeed possible, one can expect a variation of interaction energies between the solute and the solvent leading to a broadening of the absorption and emission spectra. This type of inhomogeneous broadening is shown to be particularly significant for a dipolar molecule in polar media, as it can be described by a simple expression according to Onsager sphere approximation:³¹

$$\Delta\nu = A \Delta\mu a^{-3/2} (kT)^{1/2}$$

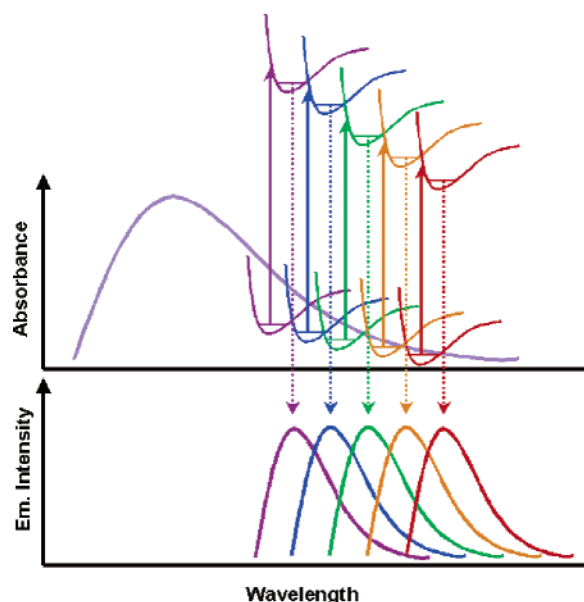
where, A is a constant dependent on the dielectric constant of the solvent, $\Delta\mu$ is the change in the dipole moment of the system on electronic excitation, and a is the Onsager cavity radius.

Additional broadening, which can be much larger compared to the one stated above, can result from specific interactions such as hydrogen bonding and electrostatic interactions. In organized assemblies, where REE is most common, the inhomogeneity also arises due to the hydrophobic and hydrophilic pockets that allow multiple solvation sites and contribute to significant additional broadening of the absorption spectra. The broadening essentially allows selective excitation of a small population of the solute molecules, whose transition energy matches with the excitation energy. However, the presence of an ensemble of energetically different molecules in the ground state, which allows photoselection of energetically different species, *alone* cannot ensure excitation wavelength dependent fluorescence behavior of a system, as rapid relaxation of the excited state most often leads to emission from the lowest excited state, irrespective of the excitation wavelength.

The second condition that needs to be fulfilled for the occurrence of REE is that the excited-state relaxation of the fluorescent species, which can be solvation of the fluorescent state or energy transfer from the fluorescent state to a low lying energy state, must be slower or comparable to the fluorescence lifetime of the species. Essentially, the emission from different unrelaxed photoexcited species gives rise to the excitation wavelength dependent fluorescence, which is known as REE (Scheme 2).

With this background information, one can attempt to understand the excitation wavelength dependent fluorescence behavior of some of the dipolar molecules in RTILs. The inhomogeneous broadening of the absorption spectrum, which permits the photoselection of energetically different species, is the largest for ANF due to high $\Delta\mu$ value (25 D compared to 3–5 D for the other systems). Additional broadening due to the heterogeneity in RTILs, which has been indicated re-

SCHEME 2. Pictorial Illustration of Red-Edge Effect, which Arises from the Presence of an Ensemble of Energetically Different Molecules in the Ground State and Inefficient Relaxation in the Excited State



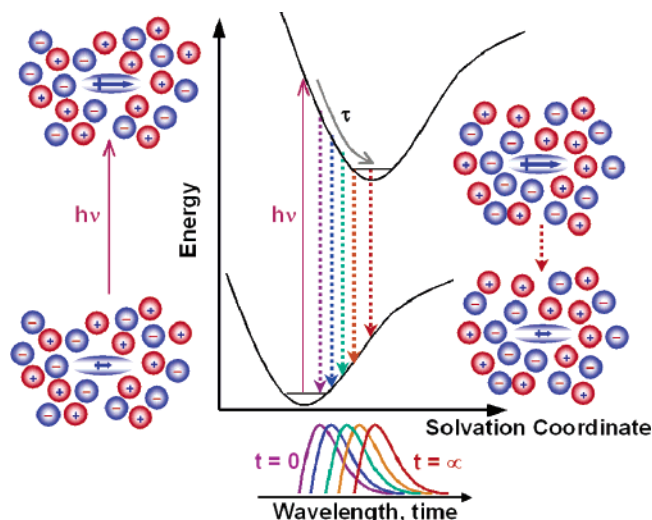
cently,^{22,23} can also be quite significant. Second, ANF has a short fluorescence lifetime in polar media ($\tau_f \approx 100$ ps in [bmim]-[BF₄]). Since the τ_f value of ANF is a much shorter than the time scale of solvation in RTILs (see later), it is possible to observe fluorescence from the unrelaxed excited state rather than from the solvent equilibrated state of this system.

However, the situation is different in the case of HNBD and ANS. Unlike ANF, these two systems do not exhibit REE in a highly viscous solvent, glycerol. Moreover, the τ_f values of ANS and HNBD are higher than the average solvation time in the RTILs. This implies that specific interaction between the solute and the solvent plays a crucial role in contributing to REE. In the case of HNBD, hydrogen-bonding interaction with the RTILs, in which the latter plays the role of H-bond acceptor, broadens the absorption spectra and facilitates the photoselection.¹⁵ In this context it is to be noted that the imidazolium ion acts as a weak hydrogen bond donor through the acidic hydrogen of the C–H moiety, which lies between two nitrogen atoms in the ring, and is capable of forming hydrogen bond with compounds having acceptor group such as the C=O functionality.¹⁴ It is also well known that the anions of the RTILs serve as hydrogen bond acceptor and can form hydrogen bonds with compounds having donor group such as the N–H functionality.¹⁴ In the case of HNBD, it is its hydrogen bonding interaction with the constituent anions that contributes to REE. For ANS, which is a charged species, electrostatic interaction with the ionic constituents of the RTILs creates a distribution of energetically different molecules in the ground state that allows their selective photoexcitation.¹⁵ Retardation of solvation due to hydrogen bonding/electrostatic interactions and/or an inefficient energy transfer between the energetically different species, perhaps contribute to the slow relaxation of the excited state.

IV. Time-resolved Fluorescence of Dipolar Molecules

General Considerations. One of the motivations behind the time-resolved fluorescence studies on dipolar solute molecules is to determine the rate at which the solvent molecules reorganize surrounding a newly created dipole following photo-

SCHEME 3. Dynamic Stokes Shift of a Dipolar Molecule in Room Temperature Ionic Liquids



induced instantaneous separation of charge. While static solvation determines the extent of stabilization of a dipolar solute in a polar medium, the dynamics of the solvation controls the rates of electron or proton transfer reaction in polar solvent.

Since solvation leads to a substantial Stokes shift of the fluorescence spectrum of a dipolar molecule, one of the most commonly exploited procedures of studying the solvation dynamics is to follow the time-dependent shift of the fluorescence spectrum of a dipolar probe molecule, termed as dynamic Stokes shift,³⁸ following its electronic excitation using a short pulse of light (Scheme 3). The experimental procedure of quantitative estimation of the solvation dynamics usually consists of the following steps. Fluorescence decay profiles are first collected at various wavelengths across the entire steady-state emission spectrum. Time-dependent emission spectra are then constructed from these decay profiles. The wavenumbers corresponding to the emission maximum at different times ($\bar{\nu}(t)$) are subsequently obtained by fitting the spectra to a line-shape function. The time constant of the solvation dynamics, described by the normalized Stokes shift correlation function, $C(t)$, is then calculated using the peak frequencies ($\bar{\nu}(t)$) of the time-resolved emission spectra

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

where, $\bar{\nu}(t)$, $\bar{\nu}(\infty)$, and $\bar{\nu}(0)$ are the peak frequencies at times t , ∞ , and 0, respectively. The time-dependence of $C(t)$ provides a quantitative measure of solvation dynamics.

Alternatively, it is possible to obtain directly the time-resolved emission spectra using devices such as a high-speed streak camera.²⁸ In this method, which is not so common, the time-resolved fluorescence spectra as well as the decay profiles at different wavelengths are conveniently extracted from a single information rich two-dimensional streak image.

In this context, one should note that solvation dynamics is an active area of interest both from theoretical and experimental point of view.³⁸ Solvation is an extremely rapid process occurring in the subpicosecond or picosecond time scale in conventional polar solvents such as acetonitrile, alcohols, and water. Study of solvation dynamics in “confined water” of various organized assemblies, which include model systems such as micelles and reverse micelles or real systems such as proteins, membranes, DNA etc., is a current topic of considerable interest.³⁹ Recent studies suggest that the solvation dynamics

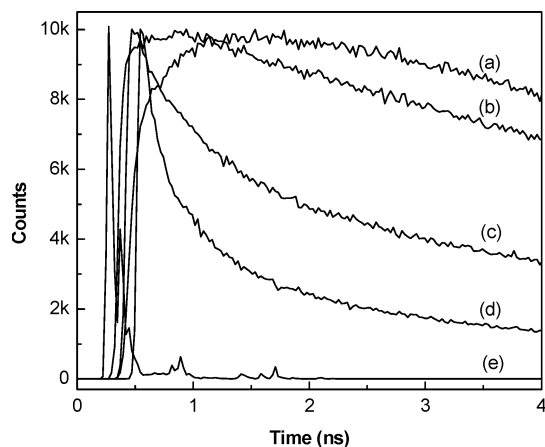


Figure 7. Time-resolved fluorescence behavior of C153 in [bmim][BF₄] at (a) 580, (b) 530, (c) 500, and (d) 480 nm; $\lambda_{\text{exc}} = 375$ nm. The excitation profile is shown in (e). Adapted from Figure 2 of ref 25.

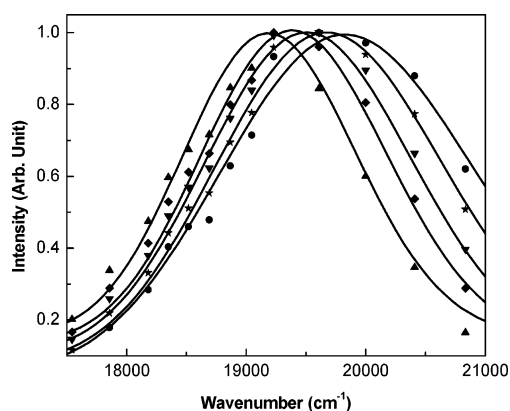


Figure 8. Time-resolved normalized emission spectra of C153 in [bmim][BF₄] at 0 (●), 100 (★), 250 ps (▼), 500 (◆), and 2000 ps (▲). Adapted from Figure 4 of ref 25.

in confined water bodies is drastically different from that in ordinary bulk water. The solvation response is biphasic in nature; a subpicosecond component and a slow component, which can be as large as hundreds to thousands of picoseconds. The slow component is assigned to dynamic exchange between the “free” and “bound” water molecules.

Neat RTILs. Since the RTILs are sufficiently polar, we thought that it might be possible to obtain useful information on the time scale of reorganization of the constituent ions around the photoexcited dipolar molecules in these novel media from the time-resolved fluorescence behavior of the systems. With this in mind, we made the first measurement of solvation dynamics in these media using C153 as the dipolar probe molecule.²⁵ The choice of C153 as probe molecule was guided by the facts that it has a rigid structure, the photoinduced charge separation in C153 is instantaneous, it displays a significant shift of its emission maximum as a function of the solvent polarity, and it has been extensively used in studies of solvation dynamics in various media. The decay profiles of C153 in [bmim][BF₄] are found to be dependent on the monitoring wavelength. When measured in the short wavelength region of the fluorescence spectrum, the decay profile showed a monotonic decrease of the fluorescence intensity with time. However, in the long wavelength region, the profiles showed a rise time (component with a negative preexponential factor) along with the expected decay (Figure 7). The time-resolved fluorescence spectra constructed from these decay profiles show a gradual Stokes shift in the ps–ns time domain (Figure 8). The slow relaxation

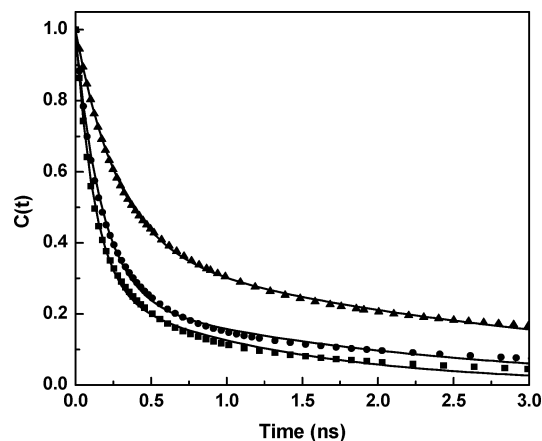


Figure 9. Decay profile of the response function, $C(t)$ of PRODAN in [emim][BF₄] (●), PRODAN in [bmim][BF₄] (▲), and C153 in [emim][BF₄] (□). The points denote the actual values of $C(t)$, while the solid line represents the biexponential fit. Adapted from Figure 5 of ref 26.

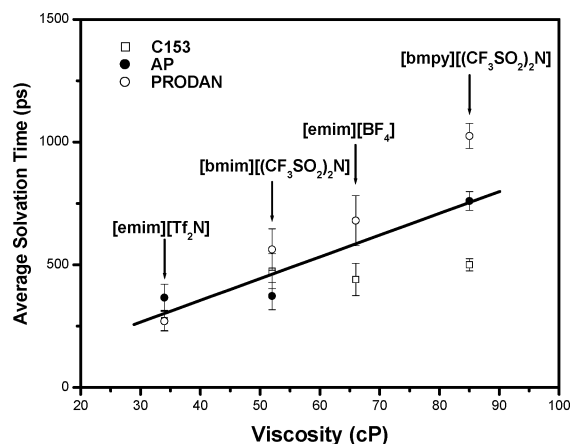


Figure 10. Viscosity dependence of the average solvation times, as obtained using different probes, in moderately viscous ionic liquids ($\eta < 100$ cP). A linear fit to the data points is also shown. Adapted from Figure 5 of ref 30.

of the fluorescence state of C153 immediately suggested that solvation is a slow process in [bmim][BF₄]. Our subsequent studies on other imidazolium ionic liquids, in which we employed a few other probe molecules with well-known photophysical properties, led us to conclude that “slow dynamics” is a common feature to all viscous RTILs.^{26–29,40} We found that the time dependence of the Stokes shift correlation function $C(t)$ in all cases could be satisfactorily fit to a biexponential function (Figure 9) yielding a component with lifetime of a few hundreds of ps and another with a few thousands of ps. The average solvation time was found to be consistent with the viscosity of the RTIL (Figure 10). The results presented in Table 3 substantiate these observations. Even though some variation of the solvation time with the probe molecules is evident, no definite trend can be deduced from the data. One important point to note here is that total spectral shift (relaxation) observed for C153 in these RTILs between zero and infinite time is found substantially ($\sim 50\%$) less than that expected from consideration of the polarity of the RTILs. The fact that almost half of the expected spectral relaxation could not be observed and hence, missed in these measurements, implies that a substantial portion of the solvation dynamics is ultrafast (< 25 ps, the instrument response time) even in these highly viscous media.

Our initial studies of solvation dynamics in RTILs were followed by works from a few other groups in neat RTILs and

TABLE 3: Results of Biexponential Fit to Our C(t) Data in RTILs Using Various Probe Molecules

RTIL	probe	τ_1^a / ns	a_1	τ_2^a / ns	a_2	$\langle\tau\rangle^b$ / ns	ref
[bmim][BF ₄] (154 cP)	C153	0.28	0.50	3.98	0.50	2.13	25,26
	PRODAN	0.28	0.62	3.33	0.38	1.44	
[emim][BF ₄] (66.5)	C153	0.13	0.73	1.29	0.27	0.44	26
	PRODAN	0.18	0.74	2.13	0.26	0.68	
[bmim][PF ₆] (207 cP)	Nile Red	0.13	0.32	1.25	0.68	1.01	28
[bmim][(CF ₃ SO ₂) ₂ N] (52 cP)	C153	0.23	0.67	0.98	0.33	0.48	27
	PRODAN	0.21	0.68	1.30	0.32	0.56	
	AP	0.15	0.63	0.76	0.37	0.38	
[emim][(CF ₃ SO ₂) ₂ N] (34 cP)	C153	0.17	0.78	0.66	0.22	0.28	27
	PRODAN	0.18	0.92	1.30	0.08	0.27	
	AP	0.24	0.90	1.50	0.10	0.37	
[bmPy][(CF ₃ SO ₂) ₂ N] (85 cP)	C153	0.17	0.25	0.61	0.75	0.50	30
	AP	0.12	0.12	0.86	0.88	0.77	
	PRODAN	0.44	0.40	1.40	0.60	1.03	

^a τ_1 and τ_2 are the two components of the dynamics having amplitudes of a_1 and a_2 respectively. ^b Average relaxation time defined as, $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$, where ($a_1 + a_2 = 1$). The viscosities of the RTILs at 25 °C are indicated in the parentheses in the first column.

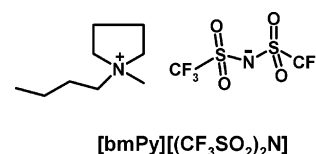
TABLE 4: Average Solvation Times (at 25 °C) in Some Neat RTILs, As Measured by Other Groups Using Different Dipolar Molecules

RTIL	probe	$\langle t \rangle$ /ns	ref
[bmim][PF ₆]	C153	1.0	44
	PRODAN	1.8	
	AP	1.6	
	C102	1.8 ^a	
[bmim][PF ₆]	C153	1.00	50
[bmim][BF ₄]	C153	0.46	50
[bmim] [(CF ₃ SO ₂) ₂ N]	C153	0.72	50
[bmim][PF ₆]	C153	3.35	45
	C152	2.76	

^a At 300 K.

in mixed solvents containing RTIL as one of the components.^{41–50} In particular, research groups of Maroncelli and Sarkar have extensively studied various different aspects of solvation dynamics. These studies have corroborated the slow, non-exponential or biphasic nature of the dynamics and the viscosity and probe dependence of the solvation times. Moreover, these studies also indicate that nearly half of the spectral relaxation is extremely rapid to be measured in an experimental setup having a time resolution of 25 ps. The measured solvation times by various groups agree reasonably well for moderately viscous RTILs (Table 4). However, the measured values differ significantly in the case of highly viscous RTILs. One of the primary factors responsible for the difference in the measured solvation times of different groups is the quality of the RTILs employed in these studies. Both the source and method of purification (if adopted at all) of the RTILs differ significantly for different groups. Since the solvation time is closely related to the viscosity of the RTILs and the latter is highly dependent on the purity of the samples, a difference of this kind is not unexpected. It is perhaps necessary to point out here that the treatment of the dynamic Stokes shift data also differed in some cases. While we fitted the $C(t)$ data to multiexponential function (a biexponential fit was found quite satisfactory in all cases) to obtain two “resolvable” relaxation times,^{25–30} Maroncelli and co-workers preferred fitting their $\bar{\nu}(t)$ data to stretched exponential representation of the following form^{41–44}

$$\bar{\nu}(t) = \bar{\nu}(\infty) + \Delta\bar{\nu} \exp\{-(t/\tau)^\beta\}$$

CHART 5. Chemical Formula of a Typical Pyrrolidinium Ionic Liquid

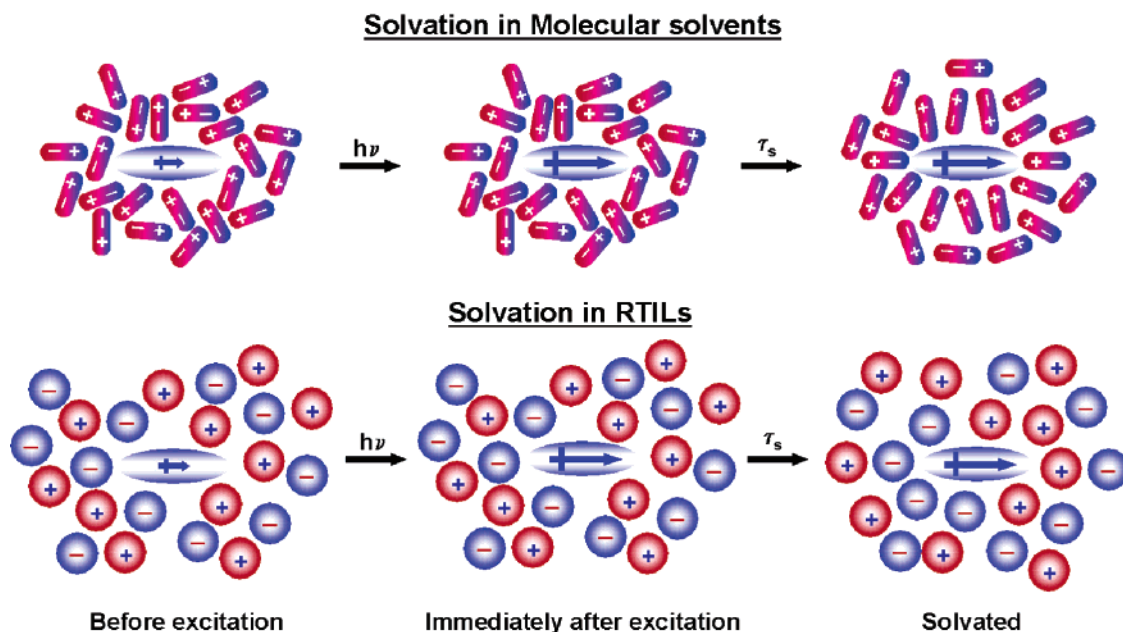
with the stretching exponent, β , having a value between 0.4 and 0.8 to obtain a single “resolvable” solvation component.

The dynamic Stokes shift studies have recently been performed on various ammonium or phosphonium ionic liquids. While most of the findings of these studies are consistent with those obtained for the imidazolium ionic liquids, it has been found that none of these liquids displays the ultrafast solvation component observable in the case of the imidazolium ionic liquids.⁴²

Absence of the ultrafast component of solvation in the case of ammonium or phosphonium ionic liquids suggested that this component would be absent in the case of pyrrolidinium ionic liquids, where the cationic component is structurally similar to the ammonium ion. However, our recent study on a pyrrolidinium ionic liquid, [bmPy][(CF₃SO₂)₂N], revealed that nearly 45% of the solvent relaxation was too rapid to be resolved using an experimental setup having a time resolution of 25 ps.³⁰ In this RTIL, the average solvation time was found to be consistent with the viscosity of the medium. We could also observe nearly 2-fold variation of the solvation time depending on the probe molecule, though no correlation of the time with the probe molecule could be established (Table 3).

Binary Solvents Containing RTILs. One of the limitations of most of the imidazolium RTILs is the limited solubility of many solutes. Since this problem can be overcome by addition of conventional solvents as co-solvent and that such addition allows modulation of some of the solvent properties of the RTILs to a great extent, study of the solvation properties in mixed solvents comprising ionic liquid as one of the constituents is also a topic of considerable interest. The effect of acetonitrile, water, ethanol, aqueous ethanol, etc. on the steady-state absorption and fluorescence properties of a number of solvatochromic dye molecules has been explored. One of the very first studies on solvation dynamics in a binary mixture containing an RTIL was made by Baker et al. in which the authors examined the effect of addition of water in [bmim][PF₆] on the dynamic Stokes shift of PRODAN.⁴⁹ Nearly 40% reduction of the solvation time was observed in the presence of water. Later, Sarkar and co-workers have studied solvation dynamics in several binary mixtures of RTILs containing water, methanol, acetonitrile etc.^{46,47} The solvation in these media also occurs in two well-separated time regimes, and a substantial portion of the solvation dynamics was found too fast to be time-resolved. The addition of the co-solvents, which leads to lowering of the viscosity of the media, results in a decrease of the solvation time. Exploiting a recent report of the formation of “water-in-oil” type microemulsion by surfactant (Triton-X-100) stabilized [bmim][BF₄] in cyclohexane,⁵¹ Sarkar and co-workers have recently studied the effect of confinement of the RTILs to nanometer-sized microemulsions on the solvation dynamics.⁴⁸ Solvation dynamics has been found to be biphasic occurring in two different time scales with the solvation time independent of the weight ratio of [bmim][BF₄] to [surfactant]. Further, the solvation dynamics in the core of the microemulsions have been found to be retarded by a factor of ~4 compared to the time constant of solvation in neat RTILs.

SCHEME 4. Oversimplified Diagram Illustrating the Fundamental Difference in the Mechanism of Solvation of a Dipolar Molecule in Conventional Molecular Solvents and in Room Temperature Ionic Liquids



Nature of Biphasic Solvation Components. The mechanism of solvation in RTILs is fundamentally different from that in polar molecular solvents. In the case of conventional molecular solvents, the net force acting on the solvent molecules due to the change in the electric field of the dipolar molecules can be taken to be zero. Consequently, the dipolar solvent molecules undergo reorientation around the photoexcited species without moving from their original positions. However, because of their charge, the ionic constituents of the ionic liquids experience a net force when the dipole moment of the solute changes on photoexcitation. As a result, the ions move from their initial position and, hence, the translational motion of the constituent ions mainly contributes to solvation in the case of RTILs. This fundamental difference of the mechanism of solvation has been illustrated in the form of an oversimplified diagram (Scheme 4). It is to be noted here that even though the ionic constituents of the RTILs have been represented by charged spheres in Schemes 3 and 4, most of them are not spherical and the charges are distributed over a certain distance among different atoms. A typical charge distribution in $[\text{emim}]^+$ and $[\text{PF}_6]^-$ is illustrated in Figure 11.

An understanding of the mechanism of the solvation process in RTILs requires a knowledge of the physical origin of the various components of the dynamics. What are the different motions that contribute to the dynamics? Our original interpretation was based on the similarity of the resolvable components of the dynamics in imidazolium ionic liquids and in molten ammonium salts, studied earlier by Huppert and co-workers.⁵² In both cases the resolvable part of the dynamics consist of two components. Huppert and co-workers attributed the fast component of the dynamics to the translational motion of the anion, the relatively smaller species and the slow component to the larger species, the cation. Taking into consideration the literature on the dynamics in molten ammonium salts and the amplitudes associated with the slow and fast components of the dynamics, we proposed a model according to which the resolvable fast component was due to the translational movement of the relatively smaller species, the anion and the longer component to the combined translational motion of cation and anion.^{25,26} However, a different speculation was made by

Maroncelli and co-workers.^{41–44} They concentrated on the ultrafast component that could not be time resolved and the integral solvation time, $\langle\tau\rangle$, which is the averaged value of the observable solvation time. The ultrafast component was attributed to the translational adjustments of the ions in close proximity with the solute and the slow component to large scale spatial rearrangement of the ions.⁴¹ Based on the absence of the ultrafast component in the case of phosphonium and ammonium liquids, it was later conjectured that the ultrafast component of the dynamics in imidazolium ionic liquids arises due to small amplitude motions of one or more cations in close contact with the solute and was facilitated by the coplanar

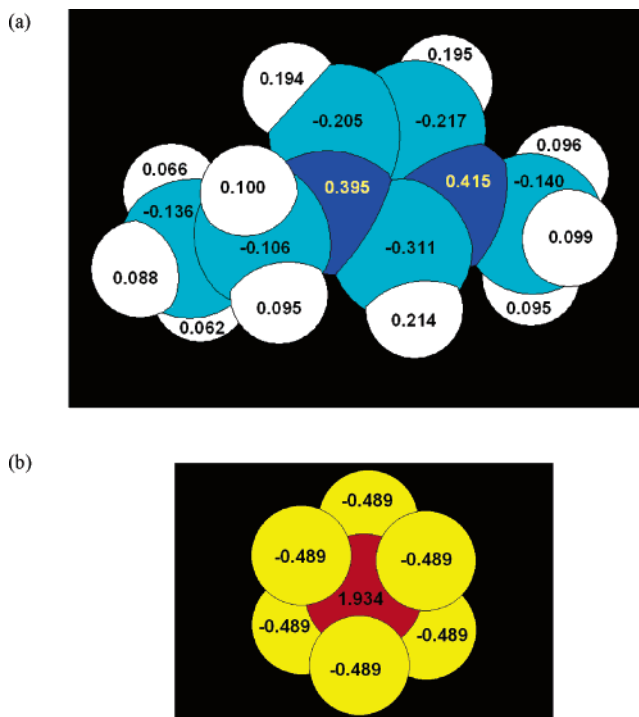


Figure 11. Charge distribution in the PM3-optimized geometries of (a) $[\text{emim}]^+$, (b) $[\text{PF}_6]^-$. The calculations have been carried out using Hyperchem program (Hypercube Inc.).

arrangement of the solute and its nearest imidazolium neighbors.⁴² Petrich and co-workers considered the polarizability of the cation responsible for the fast component.⁵⁰ However, the presence of the ultrafast component in the case of pyrrolidinium ionic liquids, where the cation is devoid of any π -bond and is structurally similar to the ammonium ion, implies that the interpretations offered for the ultrafast component involving the planarity or the polarizability of the cationic constituent may not be correct.³⁰ Clearly, there is disagreement on the origin of the various time components of solvation. There is also disagreement between different groups on how fast the ultrafast component is. While some groups have suggested the ultrafast component to be shorter than 1 ps,⁴³ the stimulated emission experiments by Petrich and co-workers, which had subpicosecond time resolution, suggest 40–70 ps as the time constant for the ultrafast component.⁵⁰

Since the thermal properties of the RTILs are strikingly similar to those of ordinary (non ionic) molecular glass-forming liquids, one may expect some similarities in the solvation dynamics in these media.⁵³ Berg and co-workers observed that the solvation in glass-forming molecular liquids occurs in two well-separated time scales, quite similar to that observed in the case of imidazolium RTILs.^{54,55} They attributed the fast component to the inertial motion and the slow component to the diffusive motion. However, latter report seems to suggest that spatial heterogeneity is responsible for the nonexponential dynamics in supercooled liquids and glasses.⁵⁶

Probe dependency of the solvation dynamics is another unresolved issue. Solvation dynamics being a solvent property is expected to be independent of the probe molecules used. However, as can be seen from the data (Tables 3 and 4), there is significant variation of the solvation time depending on the probe molecule used. It can be seen that the average solvation time for [emim][Tf₂N], as measured by us is the lowest with PRODAN and highest with AP. However, for [bmim][Tf₂N], the trend is exactly opposite. In the case of [bmim][PF₆], the estimated solvation time is the lowest with C153 and highest with PRODAN. Clearly, there is no definite pattern of the variation of the solvation times with the probe molecules. The recent study of Ito et al. on the solvation dynamics in [bmim][PF₆], wherein a large number of probe molecules have been used with a view to understanding the probe dependence of the solvation time, is inconclusive.⁴⁴

Recent femtosecond time-resolved ultrafast dynamical studies based on the Kerr effect have revealed the time scales of the different relaxation processes in imidazolium and pyrrolidinium ionic liquids.⁵⁷ However, it is difficult to comment on whether some of the motions identified in these experiments are responsible for the dynamic Stokes shift of the dipolar molecules. Several molecular dynamics simulation studies have been performed in recent years with a view to understanding the structure and dynamic properties of the RTILs.^{20–23,58–60} The molecular dynamics simulation studies of [emim]Cl and [emim][PF₆] by Shim et al. using a *diatomic* probe molecule suggested a subpicosecond component of the dynamics due to the anion translation.⁵⁸ However, Kobrak and Znamenskiy found that collective cation and anion motions are responsible for the fast component.⁵⁹ This disagreement can probably be attributed to the difference in the treatment of the probe molecules by the two groups. Shim et al. considered a diatomic molecule of 3.5 Å bond length, whereas Kobrak and Znamenskiy used a much larger and more realistic betaine dye as the probe molecule. Therefore, while the model of Shim et al. may be relevant to small molecule dynamics, the latter model is more pertinent to

studies involving large aromatic probe molecules used in solvation studies. The results of Kobrak and Znamenskiy contradict the suggestion that cation and anion motions occur on different time scales and instead, attribute the two different time scales of the solvation process to different length scales for solvation response. Shim et al. have recently examined the solvation structure and dynamics in RTILs by molecular dynamics simulations using both diatomic and benzene like probes.^{21,60} Both equilibrium and non-equilibrium solvation dynamics are characterized by a subpicosecond inertial regime and a slow diffusional regime. The solvent region contributing to the subpicosecond dynamics is found to vary significantly with inertial solvent configuration near the solute, whereas the slower component is ascribed to the ion transport. In case of high local solvent density near the probe at the moment of excitation, the subpicosecond relaxation is governed mainly by the motion of a few ions close to the probe molecule. However, for low initial density, the solvent ions, which are even farther away, contribute to the subpicosecond solvent relaxation process.

Concluding Remarks

It is shown that the fluorescence response of dipolar molecules in RTILs provides fundamental information relating to the structure and dynamics of these novel media. The complex nature of the various interactions in these media gives rise to effects that are not commonly observed in homogeneous media. These have been discussed in the context of the optical properties of the imidazolium ionic liquids.

Recent findings of non-negligible absorption in the UV and visible region due to the imidazolium ionic liquids, which suggest that these are not so optically transparent media as commonly believed, are consistent with the chemical formulas of the substances and the optical properties of the constituent ions and their various associated forms. These liquids display weak but highly interesting fluorescence covering a large part of the visible region. The unusual shift of the fluorescence maximum with the excitation wavelength can be rationalized by taking into account the presence of various energetically different associated forms of the constituent ions and the inefficiency of the energy transfer process between the photo-excited species and other species having low-lying excited states. As such, the weak absorption and fluorescence due to the imidazolium ionic liquids may not be a matter of concern while studying strongly fluorescent samples in these media. However, this can be a serious problem for weakly emitting species, and extreme care is needed while carrying out such measurements.

Care is also needed while estimating the polarity of an RTIL from the measured fluorescence maximum of the dipolar systems. Since solvation is a slow process in RTILs, only those systems having fluorescence lifetime longer than the solvation time can perhaps ensure that the frequency corresponding to the maximum represents the equilibrium solvation energy and qualify as polarity indicators.

The excitation wavelength-dependent fluorescence of some dipolar systems in these media can be a consequence of the short fluorescence lifetime of these systems compared to the solvation time. However, additional factors such as hydrogen bonding and electrostatic interactions can also contribute to this effect. Essentially, it is shown that the presence of a distribution of ground-state molecules differing in their interaction energies with the RTILs and slow excited-state relaxation processes such as solvation and/or energy transfer is responsible for this behavior.

The dynamic Stokes shift of the fluorescence spectra of dipolar molecules in the ps–ns time scale is a reflection of slow solvation in these media. Some of the salient features of the dynamics that have emerged from these studies are the following. The average solvation time is fairly long and consistent with the viscosity of the medium. A significant portion (40–50%) of the dynamics is, however, too rapid to be measured and hence, missed in most of the studies. The solvation dynamics is dependent on the probe molecule.

While these features of the dynamics are known with certainty, the mechanism of the solvation process in RTILs is far from clear. As far as the ultrafast component of the dynamics is concerned, even though it is reasonable to assume that this component is due to small amplitude motion of the solvent in the vicinity of the probe molecule, whether the motion is due to the cation or anion is a matter of debate and speculation. The nature of the physical motion contributing to this ultrafast component of the dynamics is also a matter of conjecture. It is difficult to understand why the ultrafast component, which is absent in ammonium and phosphonium ionic liquids, is present in pyrrolidinium ionic liquids. As far as the “resolvable part” of the dynamics is concerned, while the average solvation time is related to the viscosity of the medium for the moderately viscous RTILs, we are not sure whether to attach importance to the two components detected in the dynamic Stokes shift measurements. The probe dependence of the dynamics is another aspect that is least understood. It is therefore obvious that it will take quite some time before we can fully understand the mechanism of solvation dynamics in RTILs because of the complex nature of the problem and lack of convincing theoretical results. Understanding of the solvation process in binary mixtures involving an RTIL as one of the components is an even more difficult problem.

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