Solvation dynamics in room temperature ionic liquids: Dynamic Stokes shift studies of fluorescence of dipolar molecules

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Room temperature ionic liquids (RTILs) have attracted tremendous interest in recent years as promising media, which could be an alternative to the environment-polluting, volatile common organic solvents. In this article, we focus on the studies of dynamic Stokes shift of the fluorescence spectra of dipolar solutes in RTILs. These studies throw light on the nature of solvation dynamics in media that are conceptually quite different from the conventional solvents. A brief introduction to the RTILs and results of some relevant spectroscopic studies have been provided prior to the presentation of the results of dynamic Stokes shift studies. The experimental results on solvation dynamics have been discussed along with theoretical simulation studies. The current understanding of the solvation process in these media, which includes the various timescales and the mechanism of solvation dynamics, is presented to highlight the need and scope for further studies in this area.

Keywords: Dynamic Stokes shift, electron donor–acceptor molecules, fluorescence, room temperature ionic liquids, solvation dynamics.

A significant effort in recent years has been directed towards finding suitable replacement for conventional solvents, which are volatile chemicals used in large quantities and difficult to contain. The growing concern for increasing air and water pollution by these chemicals has led to the realization of the importance of solvent-free synthesis[1], use of water[2], supercritical carbon dioxide[3] and room temperature ionic liquids (RTILs)[4–11] as alternative reaction media and has given birth to 'green chemistry' as a new vibrant area of chemistry[12].

The last few years have witnessed a phenomenal growth in research involving the RTILs, primarily because of the potential of these substances as green alternative to conventional solvents[4–11]. RTILs are organic salts composed entirely of ions and unlike the common inorganic salts, which melt at higher temperatures, these are liquids at ambient condition. For example, when Na^+ in NaCl, which melts at 803°C, is replaced by a bulky organic cation, say, 1-butyl-3-methylimidazolium cation, $[bmim]^+$, the melting point of the resulting compound, [bmim]Cl, is lowered to 65°C. Further, when Cl^- is changed by a larger anion, $[BF_4]^-$, the melting point is further decreased to –81°C, thus making it an RTIL[13]. Hence, using appropriate combinations of the constituting ions, it is possible to obtain salts that are liquid at room temperature. The low melting point of these salts can be attributed to their being composed of sterically mismatched ions with low charge density, leading to hindered ion packing. Since the properties of RTILs can be tuned by appropriate combination of cations and anions, these are termed as 'designer's solvent'[4].

Some of the properties that make RTILs attractive as environmentally benign media for various applications are negligible vapour pressure, high thermal stability, high conductivity, low moisture sensitivity, wide liquid range, non-flammable and nontoxic nature, ability to dissolve both hydrophilic and hydrophobic solutes and recyclability[4–12]. Several organic reactions take place quite well in RTILs. Increasing usage of RTILs as media of organic synthesis[5–7], liquid–liquid extraction[14], electrochemical studies[15], biocatalysis[16], mass spectrometry[17], solar cells[18], synthesis of nanoparticles[19], gas sensors[20], and other applications are clearly evident from the literature. Task-specific or functionalized RTILs, wherein a functional group is incorporated in the cation or anion to achieve a particular task, are increasingly becoming popular[21]. Ionic liquid comprising magnetic anion such as $FeCl_4^-$ has also been developed recently[22].

The most widely used RTILs are the asymmetric derivatives of N,N′-dialkylimidazolium salt. The structures of some common RTILs that are based on substituted imidazolium cation are shown in Chart 1 and some of their properties are given in Table 1. The synthesis of these ionic liquids is fairly straightforward[5]. Usually, a halide salt of the imidazolium cation is first prepared by treatment of appropriate imidazole derivative with an alkyl halide. Subsequently, the halide anion is exchanged by the required anion. Purification of RTILs meant for spectroscopic studies requires special care. Usually, repeated washing with suitable solvents followed by passage through a column charged with activated charcoal and alumina gives satisfactory results.

Table 1. Some physical properties of RTILs mentioned in the text

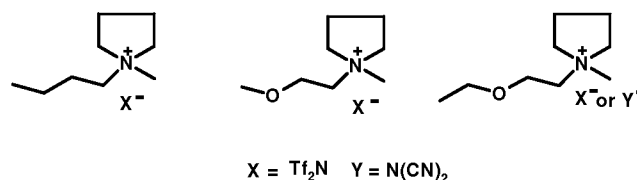| RTIL	T_{mp} (°C)	T_d (°C)	η (cP)	ρ (g/cc)	σ (ms/cm)	E_T (30)
[emim][Cl]	86[a]	–	s	s	–	–
[bmim][Cl]	65[a]	–	s	s	–	–
[emim][BF$_4$]	6[a]	447[b]	66.5[c]	1.25[c]	13[d]	49.1[e]
[prmim][BF$_4$]	–17[b]	435[b]	103[b]	1.24[b]	5.9[b]	–
[bmim][BF$_4$]	–81[f]	435[b]	154[c]	1.2[c]	3.5[b]	48.9[e]
[emim][PF$_6$]	60[g]	–	s	s	5.2[d]	s
[bmim][PF$_6$]	–61[f]	–	371[c]	1.37[c]	1.5[d]	52.3[h]
[emim][Tf$_2$N]	–3[i]	–	34[i]	1.52[i]	8.8[i]	47.7[j]
[bmim][Tf$_2$N]	–4[i]	>400[b]	52[i]	1.43[i]	3.9[i]	47.2[j]

T_{mp}, Melting point; T_d, Decomposition temperature; s, Solid; η, Viscosity; ρ, Density; σ, Specific conductivity; E_T (30), Microscopic solvent polarity parameter (see: Reichardt, C., In *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, Germany, 1988, p. 378.)
[a]Dupont *et al.*[7]; [b]Nishida, T. *et al., J. Fluorine Chem.*, 2003, **120**, 135; [c]At 20°C, Seddon *et al.*[10]; [d]At 25°C, Buzzeo *et al.*[15]; [e]Aki *et al.*[37]; [f]Watson, P. R. *et al., Langmuir*, 2001, **17**, 6138; [g]Haworth, D. *et al., Chem. Commun.*, 1994, 299; [h]Reichardt[31]; [i]At 20°C, Bonhote *et al.*[38]; [j]Karmarkar and Samanta[36].
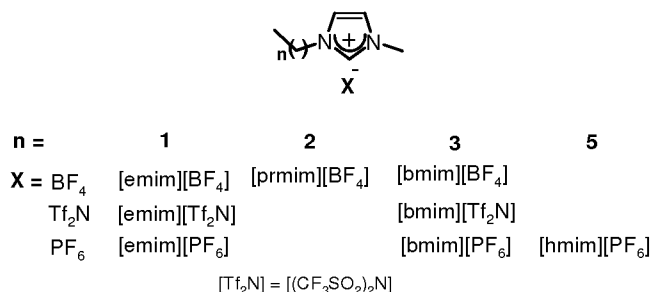
Chart 1. Structures of some imidazolium ionic liquids.

Chart 2. Structures of some pyrrolidinium ionic liquids.

Spectroscopic studies on RTILs

NMR[23–25], IR[26,27], X-ray[28–30], UV-vis absorption and fluorescence[13,31–55], and Raman[56,57] spectroscopic studies have been carried out on RTILs with a view to understanding their physical properties, nature of various interactions and structure–property relationships in solution, solid and liquid phases. These studies have provided conclusive evidence of cation–cation π-stacking interaction among the imidazolium rings, and cation–anion C–H...X and C–H...π interactions[23–25], presence of isomers of the cations[56,57] and acidity of some ionic liquids[58,59]. Multinuclear NMR studies on [emim]X (X = halide) have indicated the formation of contact ion pair even in polar solvents such as propionitrile. In dichloromethane, these salts exist in quasi-molecular states showing imidazolium stacking interactions[24]. While solvent-separated ion-pair formation has been observed in highly dilute solution of [bmim][BPh$_4$] in DMSO, the evidence of contact ion pair formation in CDCl$_3$ has been obtained by ^{1}H NOESY NMR experiments[23]. A number of pulse radiolysis studies have been carried out in RTILs by Neta and coworkers[60–62]. These include identification of the various transients produced on radiolysis of the imidazolium salts, study of reaction kinetics and investigation of the spectrum and reactivity of the solvated electrons in RTILs.

Dielectric response of some RTILs in the low frequency region (<400 cm^{-1}) has been measured by femtosecond optical heterodyne-detected Raman-induced Kerr-effect spectroscopic (OHD–RIKES) studies[63,64]. Librational ultrafast dynamics occurs within the first few picoseconds, while the subsequent slow dynamics is attributed to rotational diffusion. Quasielastic neutron scattering study on [bmim][PF$_6$] has indicated at least two different kinds of relaxation at around room temperature[65]. The ultrafast (<1 ps) component is ascribed to highly localized librational motion associated with the aromatic H-atoms, while the slower component (~10 ps) is attributed to the same relaxation related to alkyl group such as conformational transition. Recently, Shirota *et al.*[66] have also reported ultrafast molecular dynamics of several pyrrolidinium ionic liquids (Chart 2) using femtosecond optical heterodyne-detected Raman-induced Kerr effect.

Several electronic absorption and fluorescence studies in RTILs have been performed with a view to estimating the polarity of these media. A number of probe molecules such as Reichardt's dye[13,31], nitroaniline[31], Nile Red[32,33], coumarin 153 (refs 34–36), 4-aminophthalimide[37], PRODAN[36] and pyrene[38] (Chart 3) have been employed for this purpose. The polarity of most imidazolium ionic liquids lies between that of acetonitrile and methanol and is comparable to the short-chain alcohols. We have recently studied the optical properties of imidazolium ionic liquids[39,40], which suggests that these liquids are not as transparent as commonly believed. Further, an excitation
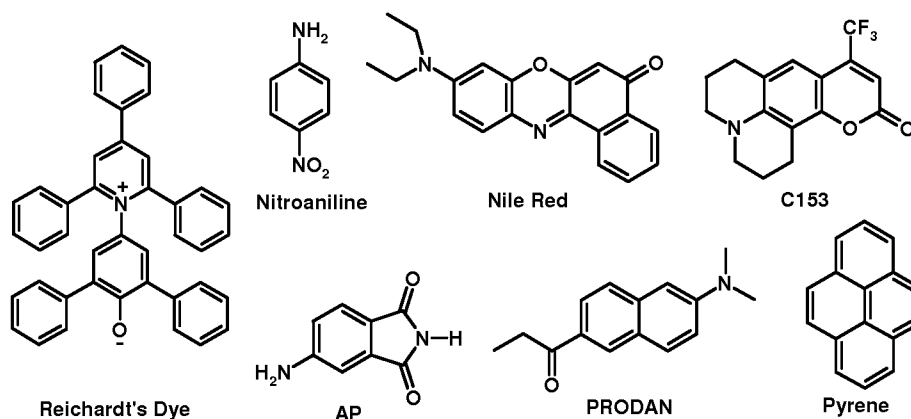
Chart 3. Structures of some probe molecules used for measurement of polarity of RTILs.

wavelength-dependent fluorescence behaviour of RTILs, which is similar to what is commonly known as 'red-edge effect', has also been observed recently[39,40]. This observation has been attributed to the presence of various energetically different associated species in RTILs. The red-edge effect of some dipolar solutes in RTILs is also reported[41]. Among the other photoprocesses studied in different RTILs, photoinduced isomerization reactions[42,43], and intramolecular excimer formation[44] are noteworthy.

Solvation dynamics

General consideration

Solvation is a fundamental process of considerable importance. It refers to stabilization of a solute by the surrounding solvent molecules and the phenomenon is most pronounced when both the solute and solvent are dipolar or charged species. Solvation dynamics represents the rate at which the solvent dipoles/charged species are rearranged surrounding a newly created dipole. The dynamics of solvation is known to dictate the reaction rates of electron or proton transfer reaction in polar solvent. Strictly speaking, solvation dynamics is an exclusive solvent property and is expected to be independent of probe molecule.

Solvation dynamics has been an active area of interest both from theoretical and experimental point of view[67–75] and has been studied in different polar solvents such as acetonitrile, alcoholic solvents and water. Solvation is an extremely rapid process in these media occurring in the subpicosecond or picosecond timescale. 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[76–82]. Recent studies suggest that solvation dynamics in confined water bodies is drastically different from that in ordinary bulk water. The solvation response is biphasic in nature; a sub-picosecond 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[76–82].

Measurement of solvent relaxation times

The commonly exploited procedure of measuring the solvation dynamics from dynamic Stokes shift of the fluorescence maximum of a dipolar probe molecule is as follows[67]. Fluorescence decay profiles at various wavelengths across the entire steady-state emission spectrum are first collected. Time-resolved emission spectra are then constructed from these measured decay profiles. The wavenumbers corresponding to the emission maximum at different times $(\bar{\nu}(t))$ are then 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 calculated using the peak frequencies of the time-resolved emission spectra

$$C(t) = [\bar{\nu}(t) - \bar{\nu}(\infty)]/[\bar{\nu}(0) - \bar{\nu}(\infty)], \qquad (1)$$

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

While the above procedure is the most common one, it is possible to obtain directly the time-resolved emission spectra using a high-speed streak camera. Time-resolved fluorescence spectra as well as decay profiles at different wavelengths are conveniently extracted from a single information-rich two-dimensional streak image. We have recently demonstrated this procedure while studying the solvation dynamics in RTIL[33].

Solvation dynamics in neat RTILs

Since the ionic liquids are sufficiently polar, time-resolved fluorescence studies are expected to provide information on the reorganization of the constituent ions around the
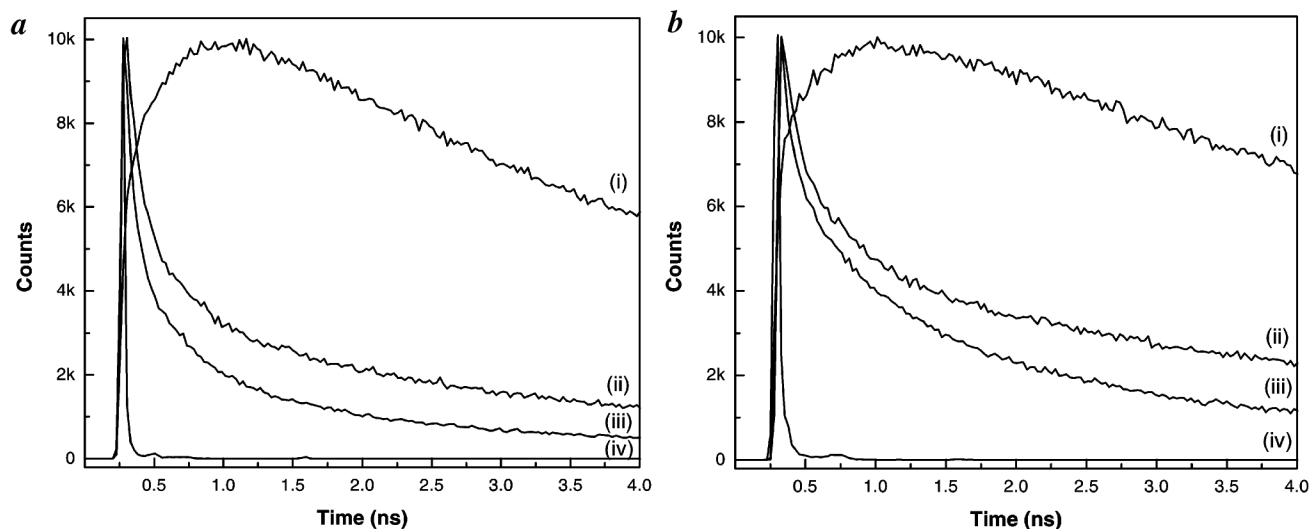
Figure 1. Time-resolved fluorescence behaviour of (*a*) PRODAN and (*b*) C153 in [emim][BF$_4$]. Monitoring wavelengths are (i) 560, (ii) 430 and (iii) 390 nm in (*a*) and (i) 650, (ii) 500 and (iii) 450 nm in (*b*). λ_{exc} = 375 nm. Excitation lamp profile is shown in (iv) in both cases. [Reprinted with permission from Karmakar and Samanta[36]; Copyright (2002) American Chemical Society].

photoexcited dipolar probe molecule. That solvation is a slow process in RTILs became evident from the wavelength dependence of the fluorescence decay profiles of some common dipolar probe molecules in these media[34-36]. In all cases, the decay profiles consisted of monotonous decrease of fluorescence intensity with time in the short-wavelength region and an initial rise followed by decay characterized the long-wavelength region (Figure 1). The RTIL in which solvation dynamics was examined for the first time from the dynamic Stokes shift of the fluorescence spectrum of dipolar molecule, C153, was [bmim][BF$_4$] (Figure 2). The dynamics was found to be biphasic in nature consisting of a fast component (~275 ps) and a slow component (3980 ps), with an average[34] solvation time (<τ>) of 2.1 ns. The biphasic nature of the dynamics in RTIL appears similar to that observed in molten ammonium salts by Huppert and coworkers[83-85]. These authors attributed the two components of the dynamics to diffusional motion of the constituting ions. The fast component was attributed to the anion, the relatively smaller species, and the slow component to the larger species, the cation. Our subsequent studies on imidazolium ionic liquids employing several probe molecules, whose photophysical properties are well known, confirm the non-exponential or biphasic nature and slowness of the solvation dynamics (Figure 3)[35,36]. The average solvation time is found to be consistent with the viscosity of RTIL. The results presented in Table 2 highlight some of the major findings. Even though some variation of solvation time with the probe molecule can be observed, no definite trend is immediately apparent from the data. It is important to note in this context that total spectral relaxation observed for C153 between zero and infinite time is substantially less than the expected value. Nearly 50% of the total spectral relaxation is missed

in our measurements having a time resolution of 25 ps. This implies that a substantial portion of the solvation dynamics is ultrafast and occurs within 25 ps, despite the high viscosity of the RTILs. In addition to the studies based on the conventional method of construction of time-resolved emission spectra, we have recently investigated solvation dynamics from the two-dimensional images captured by a fast streak camera[33]. The findings of this study are consistent with those obtained by the conventional technique.

Subsequent to our initiation of studies on solvation dynamics and demonstration that solvation is a slow process in RTILs, several other groups have studied solvation dynamics in neat RTILs[45-50]. These results corroborate slow non-exponential or biphasic nature of the dynamics, as well as the viscosity and probe dependency of the solvation times. While the measured solvation times by different groups differ significantly for highly viscous RTILs such as [bmim][PF$_6$], the values agree fairly well for moderately viscous RTILs (Table 3). A feature common to all studies is that nearly 50% of the spectral relaxation is extremely rapid to be measured even in a picosecond set-up.

Maroncelli and coworkers[46,48] have recently studied the solvation dynamics in RTILs comprising various ammonium or phosphonium ions as the cationic component. While the solvation times are consistent with the viscosity of these RTILs, the most important observation of these studies is that the ultrafast component of the solvation, which could not be time-resolved in the case of immidazolium ionic liquids, is completely absent in these cases.

Recently, we have studied the solvation dynamics in a pyrrolidinium ionic liquid, [*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, [bmpy][Tf$_2$N] using three different solvation probes[52]. The solvation

Table 2. Results of some of the early measurements of solvation dynamics

RTIL	Viscosity (cP)	Probe	τ_1 (ps)	τ_2 (ps)	a_1	a_2	$<\tau>$ (ps)	Reference
[emim][BF$_4$]	66	C153	125	1290	0.73	0.27	440	36
		PRODAN	175	2130	0.74	0.26	680	36
[bmim][BF$_4$]	154	C153	278	3980	0.5	0.5	2130	34, 36
		PRODAN	280	3330	0.62	0.38	1440	36
[emim][Tf$_2$N]		C153	165	650	0.78	0.22	280	35
	34	AP	240	1500	0.9	0.1	370	35
		PRODAN	180	1300	0.92	0.08	270	35
[bmim][Tf$_2$N]		C153	225	980	0.67	0.33	480	35
	52	AP	145	760	0.63	0.37	380	35
		PRODAN	205	1320	0.68	0.32	560	35
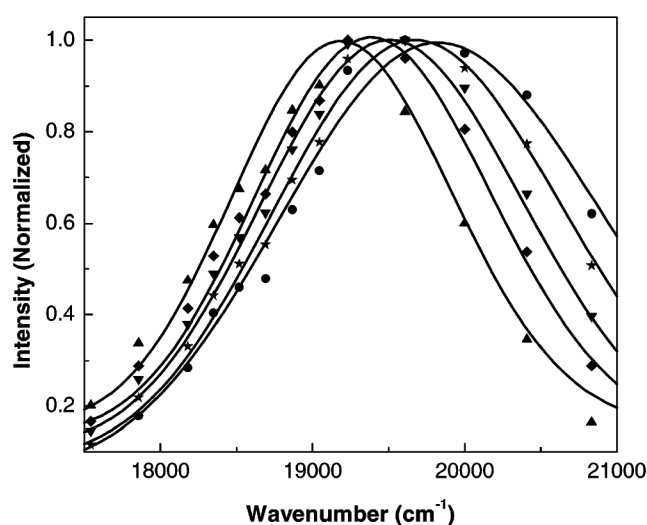
Figure 2. Time-resolved normalized emission spectra of C153 in [bmim][BF$_4$] at 0 (), 100 (✶), 250 ps (), 500 (◆) and 2000 ps (). [Reprinted with permission from the Karmakar and Samanta[34]; Copyright (2002) American Chemical Society].

Table 3. Measured average solvation time, $<\tau>$, in different imidazolium RTILs

RTIL	Viscosity (cP)	Probe	$<\tau>$ (ps)	Reference
[emim][BF$_4$]		C153	440	36
	66.5	PRODAN	680	36
[bmim][BF$_4$]		C153	2130	36
	154	PRODAN	1440	36
		C153	460	50
		C102	850	51
		C153	280	35
[emim][Tf$_2$N]	34	AP	370	35
		PRODAN	270	35
[bmim][Tf$_2$N]		C153	480	35
	52	AP	380	35
		PRODAN	560	35
		C153	720	50
[bmim][PF$_6$][†]		AP	1400	45
		C102	1800	45
		PRODAN	1800	49
		C153	1000	49
	207	AP	1600	49
		C153	1000	50
		C153	3350	47
		C152	2760	47
		Nile Red	1010	33
[hmim][PF$_6$]		C153	6960	47
	363	C153	6090	47

[†]Viscosity of [bmim][PF$_6$] is reported to be 260 and 371 cP in Ito et al.[49] and Chowdhury et al.[50] respectively.

dynamics is found to be biphasic in nature. Time-dependent shift of the fluorescence spectra suggests that nearly 45% of the relaxation is too rapid to be measured by the instrument having a time resolution of 25 ps. The remaining observable components of the dynamics consist of a fast component of 115–440 ps (with smaller amplitude) and a slow component of 610–1395 ps. The average solvation time is found to be consistent with the viscosity of this RTIL. Further, nearly two-fold variation of the solvation time depending on the probe molecule is observed, though no correlation of time with the probe molecule could be established.

Solvation dynamics in binary solvents containing RTILs

Since limited solubility of many solutes in neat RTILs can be overcome by addition of conventional solvents as co-solvents and that such addition allows modulation of some of the solvent properties of RTILs to a great extent, study of solvation properties in mixed solvents comprising ionic liquid as one of the constituents is also a topic of considerable interest[86]. The effect of 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 first studies on solvation dynamics in binary mixture containing RTIL was made by Baker et al.[87], in which the authors examined the effect

of addition of water in [bmim][PF$_6$] on the dynamic Stokes shift of PRODAN. Nearly 40% reduction of the solvation time was observed in the presence of water. Sarkar and coworkers[53,54] have studied solvation dynamics
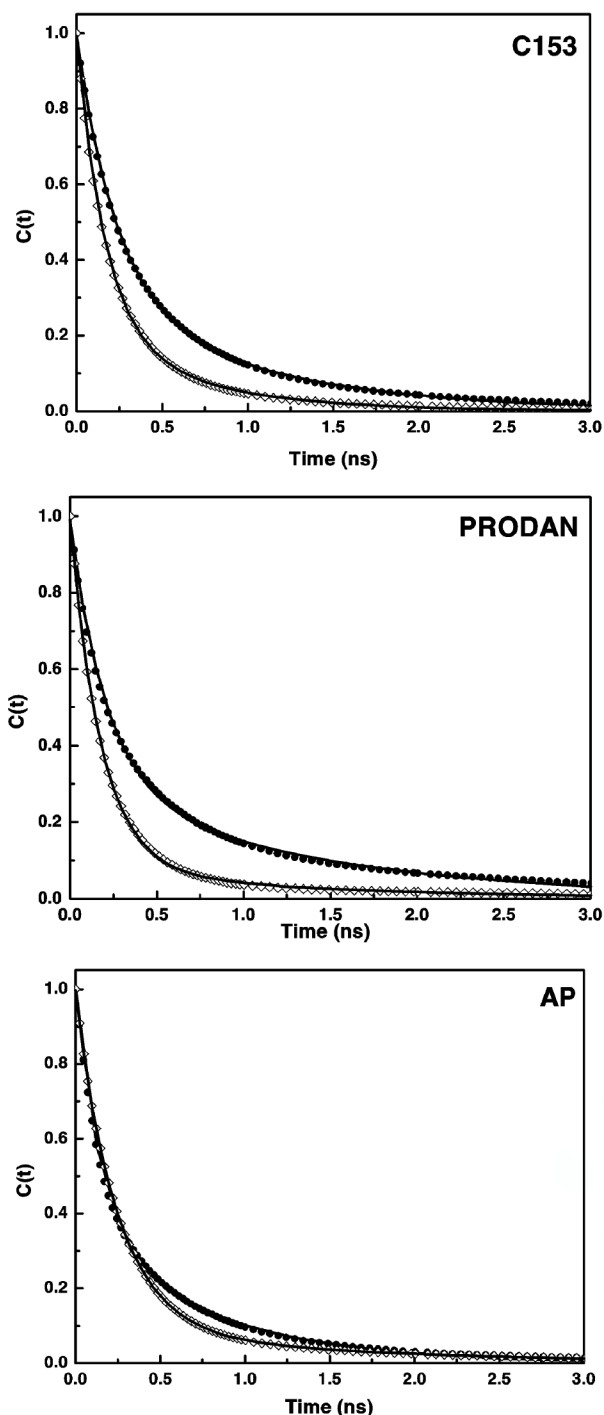

Figure 3. Time-dependence of spectral shift correlation function, $C(t)$ of different probe molecules in [bmim][Tf$_2$N] (●) and [emim][Tf$_2$N] () respectively. Points denote estimated values of $C(t)$ and solid lines represent the bi-exponential fit to the data. [Reprinted with permission from Karmakar and Samanta[35]; Copyright (2003) American Chemical Society].

in several binary mixtures of [bmim][PF$_6$] and [hmim][PF$_6$] containing water, methanol, acetonitrile, etc. In these media also, solvation occurs in two well-separated time regimes and a substantial portion of the solvation dynamics was found too fast to be time-resolved. Addition of the co-solvents, which leads to lowering of viscosity of the media, results in a decrease in solvation time. Exploiting a recent report on formation of 'water-in-oil' type microemulsion by surfactant (Triton-X-100)-stabilized [bmim][BF$_4$] in cyclohexane[88], Sarkar and coworkers[55] have recently studied the effect of confinement of the RTILs to nanometre-sized microemulsions on solvation dynamics. Solvation dynamics has been found to be biphasic occurring in two different timescales, with the solvation time independent of the weight ratio of [bmim][BF$_4$] to [surfactant]. Further, solvation dynamics in the cores of the microemulsions has been found to be retarded by a factor of ~4 compared to the time constant of solvation in neat RTILs.

Nature of biphasic solvation components

The mechanism of solvation in RTILs is fundamentally different from that in polar molecular solvents. While in the case of molecular solvents, reorientation of the solvent molecules around the photoexcited dipole is responsible for solvation, diffusional motion of the constituent ions mainly contributes to solvation in the case of RTILs. This is illustrated using an over-simplified diagram (Scheme 1).

Since the thermal properties of RTILs are strikingly similar to those of ordinary molecular glass-forming liquids, a number of similarities in their solvation dynamics are expected and this is indeed the case. While studying the solvation dynamics of glass-forming molecular liquids, Berg *et al.*[89,90] observed the dynamics in two well-separated timescales, quite similar to that observed in the case of imidazolium RTILs. The fast component was ascribed to 'phonon-induced' or 'inertial motion', whereas the slow
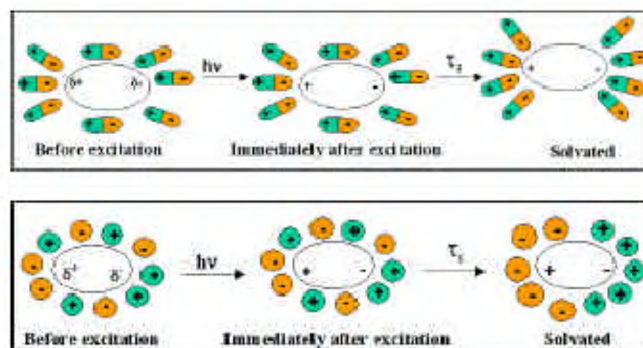
Scheme 1. Schematic representation of solvation of a dipolar solute in conventional solvents (top) and RTILs (below). In this oversimplified diagram, the shape and size of the probe/solvent molecules and constituting ions of the RTILs have not been taken into account. Also, solvation process only in the immediate neighbourhood of the probe molecule is highlighted.

component to the 'diffusive' or 'structural relaxation'. The slow solvation component is found to track solvent viscosity. Ediger *et al.*[91,92] also observed similar non-exponential dynamics in supercooled liquids and glasses. Even though there is some controversy on the homogenous versus heterogeneous origin of such non-exponential relaxation in glass-forming liquids, spatial heterogeneity is proposed to be the cause of distribution kinetics in those systems.

Let us now attempt to determine the various motions that can contribute to the fast and slow components of solvation dynamics in RTILs. In order to account for the two observable components of the solvation dynamics in RTILs, different models have been proposed. Taking into account the literature on the dynamics in molten ammonium salts and the amplitudes associated with the slow and fast components of the dynamics[83–85], we proposed a model according to which the faster component was due to the translational movement of the relatively smaller species, the anion and the longer component arose due to the combined translational motion of cation and anion[33–36,51]. This assignment is in accordance with the molecular dynamics simulation studies by Shim and coworkers[93]. On the other hand, Maroncelli and coworkers[48] attributed the ultrafast response to the small amplitude motion of one or more cations in close contact with the solute and the slow component to large scale spatial rearrangement of the ions. Chowdhury *et al.*[50], however, considered the polarizability of the cation responsible for the fast component. Clearly, there is disagreement on the origin of the two components of solvation. There is also disagreement between different groups on how fast the ultrafast component is. According to Maroncelli and coworkers[48], the ultrafast component is shorter than 5 ps. However, the stimulated emission experiments[50] which had subpicosecond time resolution, suggest 40–70 ps as the time constant for the ultrafast component.

Theoretical studies

Several theoretical molecular dynamics simulation studies[93–99] have been made by different groups to investigate the structure and dynamic properties of the RTILs. Shim and coworkers have studied solvation using molecular dynamics simulation of [emim]Cl and [emim][PF₆] using a diatomic probe molecule. They found a sub-picosecond component of the dynamics due to anion translation[93]. Kobrak and Znamenskiy[97], on the other hand, have shown that collective cation and anion motions are responsible for the fast component. This disagreement can probably be attributed to the difference in the treatment of the probe molecules by the two groups. Shim and coworkers considered a diatomic molecule of 3.5 Å bond length, whereas Kobrak and Znamenskiy used a much larger and more realistic betaine 30 as the probe molecule. Thus, while the model of Shim and coworkers 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 timescales and instead, these attribute the two different timescales of the solvation process to different length scales for solvation response. Shim *et al.*[98,99] have recently examined the solvation structure and dynamics in RTILs by molecular dynamics simulations using both diatomic and benzene-like probes. Both equilibrium and nonequilibrium solvation dynamics are characterized by a sub-picosecond inertial regime and a slow diffusional regime. Solvent region contributing to sub-picosecond 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 sub-picosecond 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 sub-picosecond solvent relaxation process.

Probe dependency

Another point that requires attention is the probe dependency of solvation dynamics. Solvation dynamics being a solvent property, is expected to be independent of the probe molecules used. Maroncelli and coworkers[49] have highlighted the probe dependency of solvation dynamics. Our recent study on pyrrolidinium cation-based RTIL also indicates significant probe dependency[52]. The solvation times, measured using different RTILs with various probe molecules by different groups, are given in Table 4. 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. Maroncelli *et al.*[49] found that the average solvation time for [bmim][PF₆] is the lowest with C153 and highest for PRODAN, which is though similar to the trend observed in the case of [bmpy][Tf₂N]. Table 4 suggest that there is no definite pattern of variation of solvation times with the probe molecules.

Table 4. Probe dependency of average solvation times (in ps) in different RTILs

RTIL	C153	PRODAN	AP	Reference
[emim][Tf₂N]	280	270	370	35
[bmim][Tf₂N]	480	560	380	35
[emim][BF₄]	440	680	–	36
[bmim][BF₄]	2130	1440	–	34, 36
[bmim][PF₆]	1000	1800	1600	49
[bmpy][Tf₂N]	500	1025	765	52

Concluding remarks

Some of the general features that have emerged from the dynamic Stokes shift studies of fluorescence spectra of dipolar solute molecules in imidazolium ionic liquids are the following: The observable part of the dynamics is characterized by two components; one typically few hundreds of picoseconds and the other, few thousands of picoseconds. The nonexponential nature of solvation dynamics in RTILs is similar to that of glass-forming molecular liquids. The average solvation time is consistent with the viscosity of the medium. A significant portion (40–50%) of the dynamics is too rapid to be measured and hence, missed in most studies. The solvation dynamics is dependent on the probe molecule. While the salient features of the dynamical studies are known with certainty, the mechanism of solvation process in ionic liquids is far from clear. Though recent molecular dynamics simulation studies have shed light on the timescales of motions of the constituent ions in the vicinity of the probe molecule and at some distance from it, what kind of physical motion contributes to the various components of the dynamics is still a matter of debate and speculation. It is not known at present why the ultrafast component, which is absent in ammonium and phosphonium ionic liquids, is present in imidazolium and pyrrolidinium ionic liquids. The probe dependence of the dynamics is also not understood. It will certainly take some more time before we 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 containing ionic liquid as one of the components, will certainly be an even more difficult job.

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