

Time-resolved studies of photoinduced processes in room temperature ionic liquids

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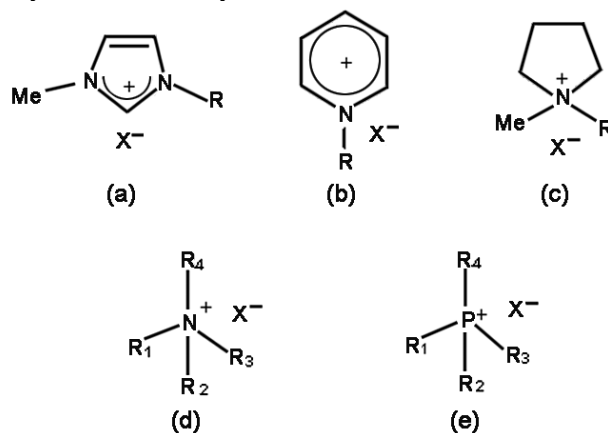
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This review summarizes the photophysical studies carried out in room temperature ionic liquids with explicit focus on those involving time-resolved measurements. Different types of photoinduced processes studied in ionic liquids are discussed with a view to understand the influence of ionic liquids in guiding the course of individual photo-reaction/process and to elucidate the difference between ionic liquids and conventional molecular solvents in this regard. Before entering into a general discussion of photoinduced processes, a short introductory note on ionic liquids and their important solvent properties are delineated. Various photoprocesses like photoinduced electron transfer, solvation and rotational dynamics, photoisomerization, excited state energy transfer, proton transfer and other reactions are discussed at length. The review concludes with an assessment of the future scope and further studies on this subject.

Keywords: Ionic liquids, Photophysical studies, Time-resolved studies, Photoprocesses, Photoisomerisation, Solvation dynamics, Rotational dynamics, Electron transfer, Proton transfer, Energy transfer

The quest for green chemistry has led to realization of the importance of alternatives to the volatile organic compounds (VOCs), one of which is ionic liquids. Ionic liquids have been invoked as environmentally benign solvents due to a number of suitable properties, but mainly because of their negligible vapor pressure, which prevents air and water pollution through emission of VOCs. Ionic liquids are simply low melting organic salts, composed entirely of ions (i.e., cation and anion). In the academic literature, the term 'ionic liquid' usually refers to liquids composed entirely of ions that are fluid at around or below 100 °C. However, room temperature ionic liquids (abbr. as ILs) are the class of ionic liquids which are free-flowing liquids at ambient temperatures (ca. 20-30 °C) and pressure (1 bar), usually having melting point near 0 °C or less. Though the history of the first ionic liquid dates back to World War I, the modern chemistry of ILs is not even two decades old.¹ With the introduction of air and water stable 1,3-dialkylimidazolium salts based on BF_4^- , PF_6^- , CF_3CO_2^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, etc., the research in ionic liquids as alternative media has received a boost. Subsequently, ILs based on different cationic moieties like (a) imidazolium, (b) pyridinium, (c) pyrrolidinium, (d) ammonium, (e) phosphonium, etc., (Scheme 1) with a large variety of anions have been reported. Since these basic cationic moieties can

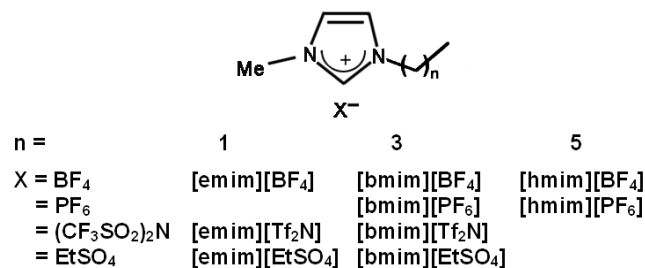
be functionalized in numerous ways and anions can be introduced through metathetic exchange, a large number of ILs can be synthesized with the desired physical and chemical properties. Most common ILs are based on unsymmetrically substituted imidazolium cations and BF_4^- , PF_6^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (commonly known as Tf_2N^-) anions (Scheme 2), though the use of alkylsulfate and dicyanamide anions is also well-known.



$\text{X} = \text{BF}_4^-, \text{PF}_6^-, \text{EtSO}_4^-, (\text{CF}_3\text{SO}_2)_2\text{N}^-$; R = alkyl group

Basic structure of some ionic liquids based on different cationic moieties. It is to be noted that with different combinations of cationic and anionic moieties as well as by varying the alkyl chain lengths, a vast number of ionic liquids can be realized, and, indeed, have been synthesized.

Scheme 1



Structures and abbreviations of some common imidazolium ionic liquids

Scheme 2

ILs possess a number of suitable solvent properties, which include wide liquidus, appreciable thermal stability, ability to dissolve a wide range of organic and inorganic substances. These properties coupled with the fact that they almost do not evaporate, make them a very popular alternative solvent system for organic and inorganic synthesis,^{2,3} catalysis^{1,4} and electrochemical⁵ and separation processes.⁶ In recent times, ILs have emerged as a versatile media with potential applicability ranging from fabrication of nanomaterials^{7,8} to development of lunar telescope.⁹ In this context we would like to note that a number of excellent review articles are already available in the literature which focus mainly on properties and various utilities of ILs.^{1-5,10,11} Because functionalization of the ILs by covalently tethering a functional group to the cation or anion (or both) imparts a particular capability to the ionic liquids, currently there is considerable interest in designing and development of various types of functionalized ionic liquids, categorized as “task-specific” ionic liquids (TSILs).¹² These TSILs serve specific purposes such as in catalysis, organic synthesis, separation of specific materials, as well as for construction of nanostructured materials and ion conductive materials, etc.¹²

The utility of the ILs as novel media for various photophysical and photochemical studies has also been explored in recent years, though such studies are still rather limited. The focus of the present article is to obtain an insight into ILs as media for studying various photophysical processes with special emphasis on those based on time-resolved measurements using small molecules. Our primary objective in this context is to understand the mechanistic details of the photoinduced processes studied in ILs, such as, to what extent these phenomena differ from those in conventional solvents

and what is the specific role of the ILs, if any, in such differential characteristics of the aforementioned photoprocesses. However, before entering into the detailed discussion on the various photophysical studies carried out in ILs, we would like to take a look at the current understanding of the physicochemical properties of ILs that can possibly be important in governing the thermodynamics and kinetic course of the photoinduced processes. In other words, we would like to begin with bare details of some crucial solvent properties of these media which ensures the scope of ILs as media for photophysical studies and then we go on to discuss these studies in detail.

Solvent Properties of ILs

An appreciable number of studies have been directed towards the understanding of the various physicochemical properties of ILs like polarity, viscosity, conductivity, etc., as well as on various structural aspects of ILs and their structure-property relationships.¹³⁻²³ There are a couple of review articles which provide comprehensive discussion on this subject.^{10,11} Herein, we present an overview of the most important properties of ILs in order to understand their solvent effect on photoinduced processes. At the same time, a preliminary note on the current understanding of the structural arrangements in the liquid state of ILs with the emphasis on the possible local structures and heterogeneity, indicated by many recent studies, has also been made.¹¹

Polarity

Polarity is probably the most important property of a liquid used as solvent for photophysical studies. Often the microscopic polarity parameters like $E_T(30)$ or E_T^N have been considered to be more relevant for elucidating the photoinduced processes rather than bulk parameters like dielectric constant or dipole moment. The use of dipolar probes in measurement of various experimental polarity parameters of solvents is well documented in the literature. So it was not surprising that the first attempt to understand the polarity criteria of ILs was made by using one such probe.¹³ This and later similar studies, which include the estimation of $E_T(30)$ values using betaine dye,¹⁴ indicate that most ILs are more polar than acetonitrile but less polar than methanol.¹³⁻¹⁵ In fact, many such studies ascribed the polarity of ILs in the range of short-chain alcohols, *cf.* butanol or propanol. Other polarity parameters, like Kamlet-Taft parameters and multiple polarity parameters have also been

determined in ILs and these values have also assigned a moderate to high polarity to these novel media.¹⁶ Incidentally, recent measurements of the static dielectric constant (ϵ) using dielectric relaxation experiments for a few ILs by Weingartner *et al.*¹⁷ showed that most of these ILs have very low dielectric constant (in the range of 9-13) which is similar to that of pyridine ($\epsilon = 12.3$). The reason for such a large difference in the polarity estimates of the ILs is unclear at this moment. However, Weingartner suggested that the low value of ϵ is just the reflection of the low dipole density arising from the large molecular volumes of the constituent ions of ILs.¹¹

Viscosity

Viscosity of the ILs is much higher compared to conventional solvents like water or alcohols, and even the least viscous IL is as much as 30 times more viscous than water, though the Newtonian-fluid behavior is apparent. Generally, viscosity of ILs is extremely sensitive to moisture content and other impurities like chloride salts, etc. Often non-Arrhenius behavior is apparent in the temperature dependence of viscosity, especially when measured over a wide temperature range.¹⁸ Examining various anion-cation combinations, the increase in viscosity observed on changing selectively the anion or cation has been primarily attributed to an increase in the van der Waals forces.¹⁰ However, hydrogen bonding is also an important parameter and this effect is distinct in the case of alcohol-functionalized ILs, which are found to be more viscous than their alkyl counterparts.¹⁹ The symmetry of the anion also contributes as an additional parameter to viscosity.

Liquid structure and heterogeneity

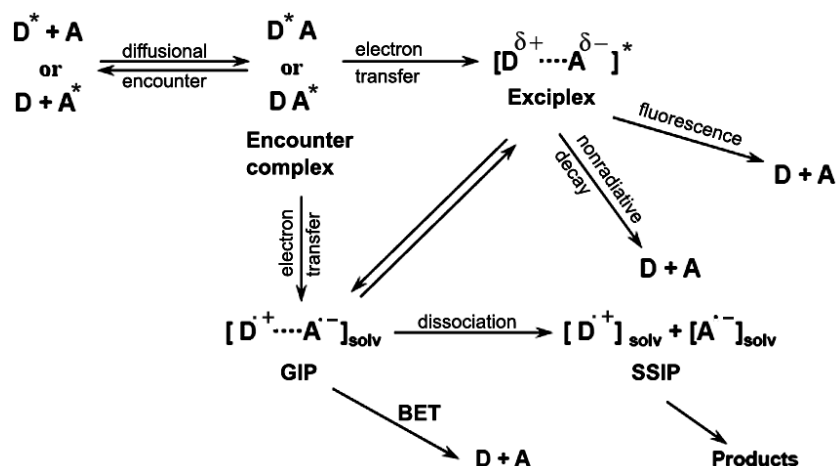
The structure of the ILs in liquid phase is considered to be more complex than that expected from extrapolation of the properties of simple inorganic salts. In the molecular level, the interaction between the ionic constituents is long range coulombic interactions, though specific interactions like hydrogen bonding and C-H $\cdots\pi$ and $\pi\cdots\pi$ type of interactions are also important.¹¹ The ionic interactions also depend on the geometry and charge distribution of the ions as well as on the relative orientation of the ions with respect to each other. Different scattering experiments indicate the possibility of the local structure originating from the broad-scale charge-ordered structures, leading to formation of different solvation shells which are more

extended as compared to that in normal solvents.^{20,21} Many simulation studies have also been performed in order to elucidate the liquid structure of ILs and different interactions and/or properties associated with it.²²⁻²⁵ Since the details of these studies are beyond the scope of this review, we would like to point out that, by and large, all these studies confirm a pronounced long-range charge order in ILs. However, there are an increasing number of studies that point to/focus on the mesoscopic level local structure of ILs. A recent X-ray scattering study on imidazolium ILs has given experimental evidence of the presence nano-structured domains in ILs, revealing the heterogeneous nature of ILs in the microscopic level.²⁶ Several molecular dynamics simulations have also suggested mesoscopic structures in even ILs with short side-chains.²² These studies have indicated the presence of polar and nonpolar domains in ILs, much similar to that in micellar media.²³ In imidazolium ILs, the liquid structure is envisaged to be composed of charge-ordered matrix formed by cationic headgroups and anions in which aggregation of the alkyl side-chains form the nonpolar domains. The implication of the heterogeneity in ILs is not well-documented, although there have been some efforts in this direction. The excitation wavelength-dependent fluorescence behavior of certain dipolar probes was predicted to be the consequence of the heterogeneous nature of ILs.²⁷ Also, a simulation study focused on this subject showed that inherent heterogeneity in ILs is primarily responsible for excitation wavelength dependence.²⁸ A recent study on microviscosity of the ILs, probed by fluorimetric measurements using a molecular rotor probe, has implied that the heterogeneous environment in microscopic level can lead to a very different experience of viscosity in microscopic level as compared to the bulk one.²⁹ Recent observation of excitation wavelength-dependent dynamics of solvation in ILs has been attributed to the dynamic heterogeneity of the media.³⁰

Photophysical Studies in Ionic Liquids

Photoinduced electron transfer

Photoinduced electron transfer (PET) reactions play an important role in numerous chemical and biological systems and have been used in a number of applications ranging from molecular photonics to solar energy conversion. In the case of PET,



GIP \equiv geminate ion-pair; SSIP \equiv solvent separated ion-pair; BET \equiv back electron transfer.

A common PET reaction course

Scheme 3

the transfer of an electron occurs between the photoexcited state (singlet or triplet) and ground state molecule to generate a charge transfer species, which may either be an excited state charge transfer complex or a charge separated radical ion pair.³¹ The initial species may then undergo a variety of secondary processes like back electron transfer leading to the ground state of the molecule, ionic dissociation to free, solvent-separated ions, triplet recombination reaction, etc. In a simplified model, considering only PET involving singlet excited species where the electron transfer leads to quenching of fluorescence, there are two general possibilities: (1) formation of an exciplex which is often fluorescent, or, (2) formation of a charge separated ion pair, called geminate or contact ion pair (Scheme 3). The former is generally favored in nonpolar solvents, whereas the latter is normally realized in polar solvents. These species then undergo a number of secondary reactions and one of the most common routes is shown in Scheme 3. The thermodynamic driving force, ΔG_{ET} of the overall PET process, i.e., formation of the solvent separated species from the photoexcited species (see Scheme 3), is given by Eq. (1),³²

$$\Delta G_{ET} = E_D^{ox} - E_A^{red} - E_{0,0} - e^2/\epsilon r_q \quad \dots (1)$$

where E_D^{ox} and E_A^{red} are the oxidation and reduction potentials of the donor and the acceptor, respectively,

$E_{0,0}$ is the energy corresponding to the 0-0 transition of the photoexcited molecule (donor or acceptor) and $e^2/\epsilon r_q$ is the coulombic energy of interaction of the ion pair at the effective encounter distance of the donor and acceptor ($r_q = r_d + r_a$). The coulombic energy term depends on solvent polarity and becomes negligible when the solvent is highly polar, *cf.* acetonitrile. Rehm and Weller³² have shown that the rate of PET process (determined by fluorescence quenching constant, k_q) increases sharply with decrease of ΔG_{ET} until it reaches the diffusion controlled limit, k_d , where k_d is given by well-known Smoluchowski equation (Eq. 2),

$$k_d = \frac{8RT}{3\eta} \quad \dots (2)$$

where η is the viscosity (in cP) of media at temperature T (in K).

Given the significant role of solvents on the reaction course of a PET process and the fate of its products, it is not surprising that significant efforts have been directed to study different kinds of PET processes in ILs. One of the early examples of PET in ionic liquids is the study of electron transfer between the well-documented pair, ruthenium(II) tris(bipyridyl) (donor) and methyl viologen (acceptor), i.e., $[\text{Ru}(\text{bpy})_3]^{2+}/\text{MV}^{2+}$, in $[\text{bmim}][\text{PF}_6]$.³³ It has been found that the rate of electron transfer is within the diffusion-controlled limit and the activation energy of the process, as determined from a temperature-dependent study, is close to the activation

energy of mobility (inverse viscosity) of the given IL. However, contrary to the normal expectation, the yield of the photoproducts (the solvent-separated ions) was found to be quite high, even higher than that in acetonitrile, despite the much higher viscosity of the given IL (~1000 fold) than acetonitrile. This situation is particularly interesting because the yield of the photoproducts is directly related to the cage escape efficiency of the geminate ion pair, and, in a highly viscous solvent significantly lower escape efficiency is expected (vide Scheme 3). To address this anomaly, it has been hypothesized that the rate-determining step here is the molecular reorientation prior to back electron transfer (BET) in the geminate ion pair, which makes BET too slow to compete with the diffusional separation process (see Scheme 3).³³

Most of the studies related to intermolecular PET processes have emphasized the fact that the rate of such processes in ILs is slower than that in normal solvents. Also, higher the viscosity of the IL, slower is the rate of PET process. Considering the fact that most of the PET reaction rate constants are in the range of diffusion-controlled limit (i.e., $k_{ET} \geq k_d$), these observations were not surprising. However, some authors have preferably described the slow electron or energy transfer processes as due to the "screening effect of ionic liquids".³⁴ An interesting fact in this regard is that often the rate of electron transfer, measured in terms of fluorescence quenching rate constant (k_q), is found to be much higher (sometimes even 1-2 order higher in magnitude) than the diffusion-controlled rate constant (k_d).^{33,34,35} Although the reason behind such unusually high k_q values is not clear, it has been predicted that this observation may be a reflection of different microviscosity as compared to the bulk viscosity of these liquids.³⁵ The Rehm-Weller relationship³² between k_q and ΔG_{ET} has also been verified in ILs by using a single acceptor and a series of donors of different E_D^{ox} values.³⁶ The modest value of reorganization energy obtained from the Rehm-Weller type curve indicates a moderate interaction between the constituents of the IL and the radical ion pairs.

One of the major consequences of PET reaction is the formation of exciplex, mostly recognized in nonpolar solvents. In ILs, however, exciplex has not been observed even when typical exciplex-forming pair, such as pyrene-N,N'-dimethylaniline (Py-DMA) were employed.³⁵ This PET study involving Py-DMA system was carried out in a series of ILs of varying viscosity, but the exciplex emission was neither

observed in steady-state nor in time-resolved fluorescence studies. This observation has been explained in the light of high polarity of ILs, as indicated by $E_T(30)$ values of ILs and other microscopic polarity parameters, which collectively suggest that ILs are at least as polar as acetonitrile, if not more. However, ambiguity appears when one considers ILs with moderate values of static dielectric constant¹⁷ ($\epsilon = 8-11$), and on the basis of which traces of exciplex would have been expected. The fact that microscopic polarity parameters predominates in this case indicates a difference in the macroscopic and microscopic domains of ILs.³⁵ However, the effect of low dielectric constant and high viscosity of the ILs was observed in the low yield of the radical ions in the case of the aforementioned system. It was shown that the escape efficiency of the geminate ion pair to form solvent-separated ions is drastically low in highly viscous ILs such as [bmim][PF₆], which is the primary reason for nonappearance of characteristic absorptions of radical ions in laser flash photolysis study (see Scheme 3).³⁵ However, for less viscous ILs like [bmim][Tf₂N], this transient absorption due to radical ions was recorded, though the yield was very low compared to that in normal solvents. At the same time, the lifetime of the free, solvent separated radical ions was found to be quite long, indicating greater stability offered by these viscous media. Similarly, in a PET study between 2,4,6-triphenylthiapyrylium, TPTP⁺ (acceptor) and dicyclopentadiene, DCP (donor) in an IL, it was found that the transient radicals are quite long-lived, which again indicates enhanced stabilizing power of ILs for these intermediate species.³⁷ This enhanced stability of the intermediate species can be attributed to the efficient solvation by the ionic constituents of ILs and slow diffusion in these media.

While the nonspecific solvent effect of ILs over various stages of the PET reactions have been demonstrated in many of these studies, there is one evidence of direct solvent-mediated electron transfer reaction.³⁸ When pyrrolidinium ionic liquid was employed as solvent for PET reaction, it was found that the yield of PET products (i.e. radical ions) is greatly enhanced for certain systems, e.g., when duroquinone (DQ) was used as acceptor. However, in other imidazolium-based ILs, the corresponding yield of PET products was found to be significantly lower. This result was ascribed to high reduction potential of the pyrrolidinium cation, which presumably permits a secondary channel of electron migration

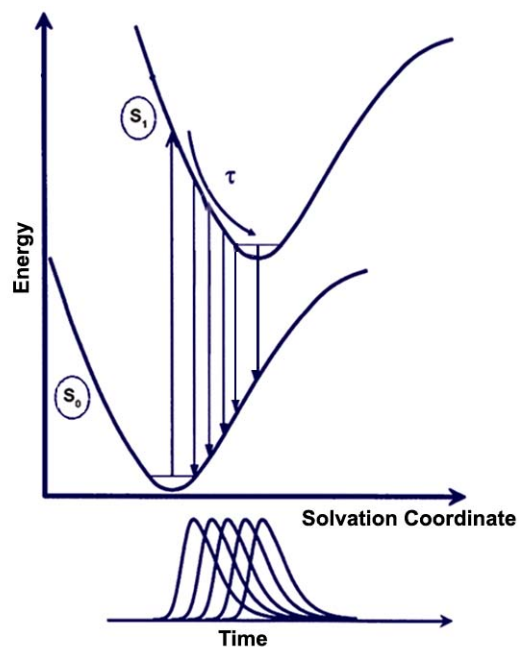
through reduction of one or more solvent cation.³⁸ However, the exact nature and the efficiency of the secondary pathway of the solvent-mediated PET process are still not clear. Apart from these intermolecular PET processes, intramolecular PET reaction within a fixed-distance donor-acceptor molecule, namely, 4-(N-pyrrolidino)naphthalene-1,8-imide-pyromellitimide, 5ANI-PI, have been studied in a low viscosity IL, [emim][Tf₂N].³⁹ It was demonstrated that both the charge separation (forward PET) and charge recombination (i.e. back electron transfer) processes occur very fast and almost at the same rate. Moreover, the rate constant values for these processes were shown to be similar to those in normal solvents of similar dielectric constant, specifically pyridine, but less than in a high dielectric solvent like acetonitrile. These findings were attributed to the significant effect of solvent polarity in terms of dielectric constant whereas viscosity seems to be innocuous in the entire reaction process.³⁹ On the other hand, when the temperature variation of both separation and recombination reaction was taken into account, the effect of viscosity was apparent in the kinetics of charge recombination reaction. Forward reaction rate was insensitive to temperature variation, but the recombination rate was found to be significantly affected by temperature. The large change in viscosity of IL in the given temperature range and the its impact on the structural reorientation required for the charge recombination process in given molecule appears to be the reason for this.³⁹

Solvation dynamics

Solvation dynamics may be described as the process of stabilization of the photoexcited state of a dipolar probe due to reorganization of solvent molecules surrounding it. Initial photoexcitation leads to an enhancement of charge transfer character (i.e. dipole moment) of the dipolar probe, thereby disrupting the equilibrium solvation structure surrounding the probe in its ground state. As a result, the solvent molecules try to reorient themselves around the newly created dipole to attain a further equilibrium and the time required in this process is known as relaxation time of the solvent, or simply solvation time. This solvation process leads to a large Stokes shift in the steady-state emission spectrum of the dipolar probe, especially in polar solvents. This solvation process is very fast in conventional molecular solvents having solvation time mostly in

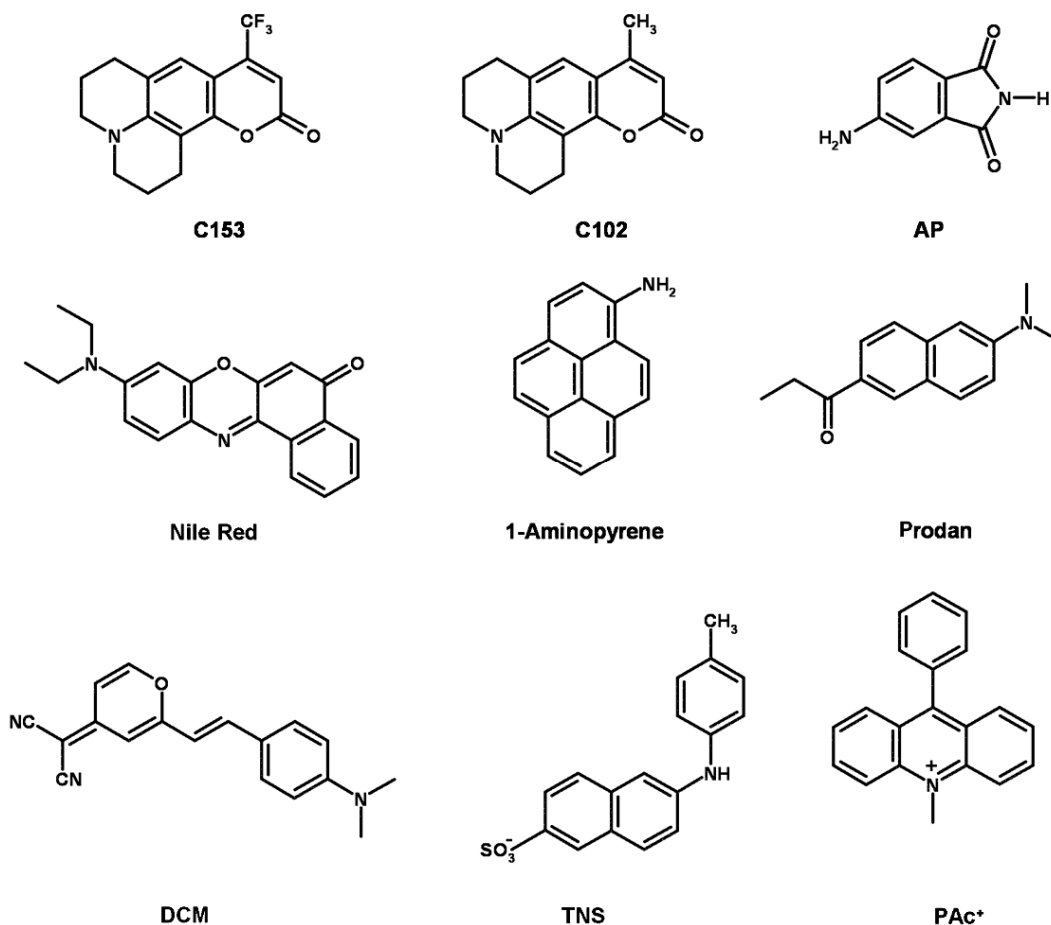
the subpicosecond range at room temperature. Since the fluorescence lifetimes of the probes are mostly in the nanosecond range, this means the excited state equilibrium through solvation is attained prior to fluorescence of the probe. However, in viscous media and organized assemblies like micelles or microemulsions or proteins, the solvation dynamics is slowed down appreciably to allow monitoring of the intermediate stages of the solvation process through time-resolved fluorescence studies in ps-ns regime.

Since solvation leads to a substantial Stokes shift of the fluorescence spectrum of a dipolar molecule, the most commonly exploited procedure for studying the solvation dynamics is to follow the time-dependent shift of the fluorescence spectrum of a dipolar probe molecule following its electronic excitation using a short pulse of light. This time-dependent shift of the emission spectra, called the dynamic Stokes shift, is the typical signature of solvation dynamics process. This is illustrated in a simplified manner in the Scheme 4. The probe molecules for solvation dynamics studies are carefully chosen dipolar molecules having intense single emission, mostly of charge-transfer type, with moderate fluorescence lifetime. Also, an ideal probe molecule for solvation dynamics study should not undergo any other secondary excited state process which may interfere



Schematic representation of the dynamic Stokes shift

Scheme 4



Scheme 5

or occur simultaneously with the dynamic solvation process. Some typical probe molecules used for solvation dynamic studies are depicted in Scheme 5. It should be noted that wavelength-dependent decay profiles are invariably observed for any given probe, which is the characteristic feature of the solvation dynamics process. One representative wavelength-dependent decay behavior is illustrated in Fig. 1. When monitored at the shorter wavelength region, only monotonous decays are observed whereas at longer wavelengths, the time profiles are characterized by a slow rise followed by the decay. In a typical measurement, the time-resolved emission decay profiles are recorded at 5/10 nm interval across the entire steady-state emission spectra of a given dipolar probe. Now, each decay curve is fitted to suitable multiexponential decay function using an iterative reconvolution program. From the fitted parameters, time-resolved emission spectra (TRES)

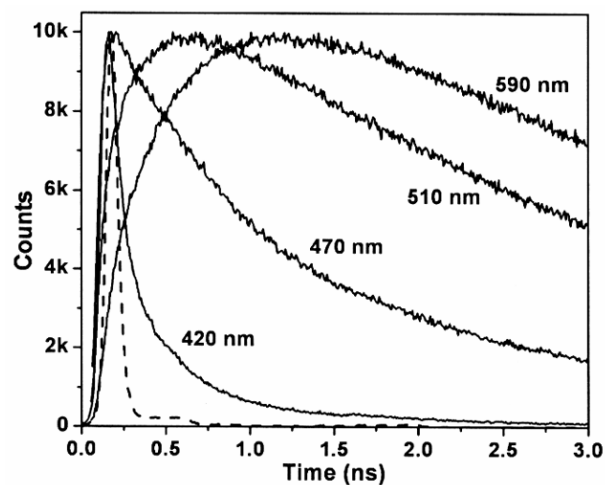


Fig. 1 — Wavelength-dependent decay profiles of prodan in [OH-emim][Tf₂N]. [The monitoring wavelengths are indicated in the respective graphs. The lamp profile in each case is shown as dotted line. OH-emim ≡ 1-hydroxyethyl-3-methylimidazolium].

are constructed using spectral reconstruction technique. The peak emission frequencies $\bar{\nu}(t)$ (in cm^{-1}) at various times are then obtained by fitting each TRES to appropriate function, usually the log-normal function of the following form (Eq. 3),

$$I = h \exp[-\ln 2 \{ \ln(1 + \alpha) / \gamma \}^2] \quad \text{for } \alpha > -1 \\ = 0 \quad \text{for } \alpha \leq -1 \quad \dots(3)$$

where $\alpha = \frac{2\gamma(\bar{\nu} - \bar{\nu}_{\text{peak}})}{\Delta}$, $\bar{\nu}_{\text{peak}}$ = wave number

corresponding to the peak, h = peak height, Δ = full width at half-maxima and γ corresponds to the asymmetry of the band shape. Optimizing these four parameters by non-linear least-squares iteration technique, the best fitted curve was obtained. When the $\bar{\nu}(t)$ values thus obtained are plotted as a function of time, the solvation time (s) is obtained from appropriate fitting to the curve.

Since ILs are quite polar and viscous media, the dynamics of solvation is expected to be sufficiently slower to allow monitoring of this process by measuring the time-resolved fluorescence behavior of the systems. Ever since the early work of Karmakar and Samanta,⁴⁰⁻⁴² many researchers have studied the solvation dynamics in ILs with a view to elucidating different features of this process.⁴³ These studies have revealed that solvation dynamics is a slow process in ILs, much slower than that in conventional molecular solvents. The average solvation time in moderate to high viscosity solvents, in fact, lies in the nanosecond regime. However, in most of the dynamical studies, an appreciable portion of the dynamics, say 40-50 %, has been found to be too fast to be recorded due to limited time-resolution of most setups (typically 25 ps). The precise origin of the ultrafast component and its exact nature is one of the complex features of the dynamics and has remained a matter of considerable speculation and debate.

To describe the observable dynamics, generally, a correlation function $C(t)$ of the following form is constructed (Eq. 4),

$$C(t) = \frac{\bar{\nu}(t) - \bar{\nu}(\infty)}{\bar{\nu}(0) - \bar{\nu}(\infty)} \quad \dots (4)$$

where the peak frequencies (in cm^{-1}) of the measured spectra at any time t is $\bar{\nu}(t)$. At $t = 0$

(zero time), $\bar{\nu}(t) = \bar{\nu}(0)$ and at $t = \infty$ (infinite time), $\bar{\nu}(t) = \bar{\nu}(\infty)$. The $C(t)$ values are then plotted against time and usually fitted to a biexponential function of the following form (Eq. 5),

$$C(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \quad \dots (5)$$

where τ_1 and τ_2 are the solvent relaxation time constants. Accordingly, the dynamics has been depicted as biphasic with two components typically in the picosecond and nanosecond region.⁴⁴⁻⁴⁸ However, while this biphasic description seems to be adequate in terms of fitting, the interpretation of the two-component dynamics is not so straightforward. Since the amplitude of the individual components varies rather widely from one IL to another, irrespective of the viscosity or ionic constituents of the ILs, the assignment of these components individually to any particular interaction or motion is rather difficult. However, if the average solvation time (average solvation time $\tau_{\text{av}} = a_1\tau_1 + a_2\tau_2$, where $a_1 + a_2 = 1$) is considered instead of individual components, a rough correlation can be drawn between viscosity and the average solvation time, only if the ILs are not too viscous (<100 cP).^{44,45} Therefore, one can point out that the average solvation time is a reflection of the overall motion of cations and anions. However, no correlation can be drawn between the average solvation time and viscosity of the highly viscous ILs. Though many researchers have favored the biexponential fitting and hence the biphasic description of dynamics, others have sought for an alternative description of the observable dynamics. Notably, Maroncelli and coworkers⁴⁹⁻⁵² treated the observable dynamics as non-exponential and fitted their data to a stretched exponential equation (Eq. 6),

$$\bar{\nu}(t) = \bar{\nu}(\infty) + \Delta\bar{\nu} \exp(-(t/\tau_0)^\beta) \quad \dots (6)$$

where $0 < \beta \leq 1$

The average time of solvation is obtained by Eq. (7),

$$\langle \tau_{\text{solv}} \rangle = \frac{1}{\Delta\bar{\nu}} \int_0^\infty [\bar{\nu}(t) - \bar{\nu}(\infty)] dt = \frac{\tau_0}{\beta} \Gamma(\beta^{-1}) \quad \dots (7)$$

where Γ is the gamma function. In this case, instead of individual components, the focus is on the average solvation time assigned to the large scale diffusion of the constituent ions.⁴⁹ Recently, Maroncelli and

coworkers⁵² have also demonstrated that for a given probe (C153) in a large number of different ILs, the solvation dynamics can roughly be depicted by the following empirical relationship:

$\langle \tau_{\text{solv}} \rangle \propto \left(\frac{\eta}{T} \right) (r_{\text{cation}})^4$, where η and r_{cation} are viscosity

and cationic radius of IL, respectively. Though the physical interpretation of such relationship is not very clear, the $(r_{\text{cation}})^4$ dependence indicated a very strong influence of the cation on the observable dynamics. In this context we would like to point out that for a given set of data it can be shown that the average solvation times obtained by both methods (biphasic and nonexponential) are essentially the same.⁴⁵ Therefore, any interpretation about the physical origin of the observable dynamics in terms of average solvation time is expected to be similar for both descriptions of dynamics.

To understand the dynamic solvation behavior of ILs, one must remember that this process in ILs is fundamentally different from that in ordinary polar solvents. In molecular solvents, reorientation of the solvent dipoles around the probe molecule mainly contributes to solvation, whereas the diffusional motion of the constituent ions is expected to contribute significantly to the relaxation process in ILs. This could be the motion of the individual ions and/or the collective motion of the cation and anion. At the same time, small amplitude motions of the ions in the immediate vicinity of the probe molecule is likely to play an important role, especially in the early part of the solvation dynamics. In the case of dipolar ionic constituents, reorientation of the individual ions close to the probe molecule can also contribute to the early part of the dynamics. In the case of polarizable ionic constituents of the ILs, electron redistribution in these ions influenced by the change in the dipole moment of the photoexcited probe molecule may also contribute to the short time domain of the dynamics. Clearly, understanding the mechanism of solvation dynamics in ILs is a complex problem and at this stage it is impossible to pinpoint what are the various motions that contribute to the different components of the dynamics.

The solvation dynamics in ILs is also probe dependent.^{44,45,50} The value of average solvation time varies significantly and rather irregularly with changing probe molecule. Since it is difficult at present to interpret the different kinds of interactions present between the probe and the constituent ions

of the IL, the probe-dependent dynamics is rather hard to explain. However, sometimes strong specific interactions (*cf.* hydrogen bonding) between the particular probe and IL can change the entire scenario and impart a unique probe-dependency to the dynamical course.⁴⁵

Another distinguished feature of solvation dynamics in ILs is the ultrafast or missed dynamics which is invariably associated with the most of the dynamical studies. The actual time scale and physical origin of the ultrafast dynamics has been a matter of considerable speculation and debate. Maroncelli and his coworkers⁴⁹ suggested that the time scale of ultrafast component is <1 ps in the case of imidazolium ionic liquids and attributed it to small amplitude motion of imidazolium cations in close contact with the probe, facilitated by the coplanar arrangement of the probe and imidazolium moiety. On the other hand, Petrich and his coworkers⁵³ indicated that at least 50 % of the initial dynamics occurs with a time scale of 40-70 ps and speculated that it could be due to polarizability of the cation. The importance of role of the cation having planar and polarizable ring system was reinforced by the fact that no ultrafast component was found in alkylammonium or alkylphosphonium ionic liquids where the cationic moieties lack these criteria.⁵¹ However, in the case of pyridinium ionic liquid, which is basically the cyclic analogue of ammonium ionic liquid, almost 50 % of the dynamics was found to be ultrafast, which means that planarity and polarizability are not the sole criterion for ultrafast dynamics.⁴⁴

Complete solvation response with imidazolium ILs has also been observed by using femtosecond Kerr-gated emission (KGE) spectroscopy combined with picosecond time-correlated single photon counting as well as by employing femtosecond upconversion technique.^{54,55} While from KGE a 300-700 fs time-scale was suggested for ultrafast dynamics,⁵⁴ the upconversion procedure indicated that 10-20 % of dynamics occurs with 5 ps.⁵⁵ In the latter study, the authors have also pointed out that due to factors such as conformational changes of the fluorophore in polar and nonpolar solvents, superimposition of the internal relaxation of the probe with the early part of solvent relaxation, etc., it may not be possible to precisely determine the extent to which the dynamics is missed. Femtosecond solvation dynamics studies by Bhattacharyya and coworkers⁵⁶ have indicated that

the amount of ultrafast component may depend on excitation wavelength. Up to 40-60 % dynamics was shown to occur in the ultrafast time scale (<5 ps) when the excitation wavelength is more towards the red-edge of the absorption band.⁵⁶ Many simulation studies have been performed in order to have a better insight into the solvation dynamics in ILs and these studies have revealed many useful information on the various aspects of the dynamical process.^{24,25,57-61} Since the scope of this review is limited we are not going into the details of these studies. Kobrak and Znamenskiy⁵⁷ in a simulation study assigned the ultrafast component of the dynamics to the collective cation-anion motion. Kobrak⁵⁸ in a recent study has also suggested that almost 15 % of the total dynamics is ultrafast whereas Kim and his coworkers⁵⁹ have suggested that nearly 50 % of the dynamics may be ultrafast if solvent polarizability is incorporated into the molecular dynamics simulation. The latter group has also indicated that the local density of the ions near the probe molecule is an important factor in governing the ultrafast dynamics.⁶⁰ In our opinion, the ubiquitous presence of ultrafast component in ionic liquids of varying viscosity does suggest that the initial dynamics is less sensitive to viscosity and some local effect is therefore an important criterion. In a recent study we have shown that an enhanced hydrogen bonding interaction between probe and IL may lead to retardation of the dynamics with a substantial (~10-20 %) reduction of the ultrafast component.⁴⁵

Apart from neat ILs, the dynamical studies have also been carried out in mixtures of IL and conventional solvents and also in IL-based microheterogeneous systems.⁶¹⁻⁶⁷ It was shown that the polar solvents can affect the dynamics in ILs due to their enrichment in the cybotactic region of the probe.^{61,62} However, in a recent paper, it has been shown that even nonpolar solvents like toluene can significantly influence the dynamical course in imidazolium ILs, probably due to favorable interaction between toluene and polarizable π -cloud of imidazolium moiety.⁶³ There have also been a few studies on solvation dynamics in IL-based microheterogeneous systems such as microemulsions and micelles as well as in IL-swollen triblock copolymers.⁶⁴⁻⁶⁷ These studies have revealed many interesting aspects regarding the dynamical characteristics of ILs present in a confined

environment. For example, Sarkar and coworkers⁶⁴ have found that ultrafast dynamics is substantially retarded in an imidazolium IL-based microemulsion as compared to the bulk IL. Also, in a recent study Bhattacharyya and coworkers^{66,67} have elucidated the differential dynamical behavior for a probe situated in different locations in a large aggregate of IL and block copolymer. Together these studies definitely suggest that much can be explored in the IL-based mixed systems as media for solvation dynamics.

Rotational dynamics

Time-resolved fluorescence anisotropy, $r(t)$, is calculated using the following equation (Eq. 8),

$$r(t) = \frac{I_{\parallel}(t) - G I_{\perp}(t)}{I_{\parallel}(t) + 2G I_{\perp}(t)} \quad \dots (8)$$

where G is the correction factor for the detector sensitivity to the polarization direction of the emission and $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the fluorescence decays, polarized parallel and perpendicular to the polarization of the excitation light, respectively. In most cases, the anisotropy decay for fluorescence probes in ILs can be adequately described by single-exponential or biexponential fitting to the data, with biexponential fitting being more suitable (generally) than the single-exponential one. However, the average rotational time obtained by the biexponential fitting corroborates well with the rotational time obtained through single-exponential method.⁴⁵ It has been found that the rotational correlation time (τ_r) for any given probe is much higher in ILs than in conventional solvents, primarily due to the high viscosity of the ILs. Also, in some ILs the nonexponential behavior of the anisotropy decay is quite apparent, especially in the case of the alkylphosphonium ILs.⁵¹ Maroncelli and his coworkers^{49,51} have treated the anisotropy decay with the stretched exponential fitting describe by the following equation (Eq. 9),

$$r(t) = r_0 \exp \left[\left(- \frac{t}{\tau_r} \right)^{\beta_r} \right] \quad \dots (9)$$

where r_0 is the initial anisotropy (often with a fixed assigned value) and β_r is the stretched parameter. However, since both stretched exponential and biexponential fitting leads to similar τ_r values within

the experimental error limit, no particular emphasis can be invoked from different treatments to the anisotropy data. Also, the τ_r values do not alter much by varying the excitation wavelength and are quite insensitive to the monitoring wavelengths. The clear evidence of negligible excitation wavelength dependence of τ_r suggests the absence of heterogeneity in rotational dynamics in ILs. However, Castner *et al.*⁶⁹ have studied rotational dynamics in supercooled regime of tertaalkylammonium ILs and they have shown that the relaxation of rotational anisotropy can occur in a very long-time scale with multiexponential decay parameters. They have assigned this observation to the long-lived local structures in the environment of the probe molecule.

Apart from the general solvent effect on rotational dynamics in ILs, specific solute-solvent interactions have also been investigated.^{45,49,50,70-72} According to the stick hydrodynamic prediction, the rotational time-constant (τ_r) of a nonspherical solute of volume V , rotating along the longest axis of the ellipsoid in a medium of viscosity η at temperature T is given by Eq. 10,

$$\tau_r = C_r(Vf_{\text{stk}}\eta / k_B T) \quad \dots (10)$$

where f_{stk} is a factor accounting for the non-spherical shape of the solute, k_B is the Boltzman constant and C_r is the rotational coupling constant. The latter is a measure of the extent of departure from normal hydrodynamic behavior of a solute due to specific interactions. Maroncelli and co-workers⁴⁹ have shown that for ILs of varying viscosity, τ_r versus η/T plots are linear for a given probe and the values are well within the Stick boundary condition. As such C_r values for most probes in ILs are also in the normal range, i.e., in the range of conventional, less viscous solvents. However, in some cases, notably in the case of 4-aminophthalimide in a protic IL, the C_r value was appreciably higher, reflecting the influence of specific interaction (hydrogen bonding) between the probe and IL moieties.⁴⁵

Similar specific solute-solvent interaction and its influence on rotational dynamics in ILs have also been demonstrated in other studies.^{70,71} It has been shown that in [bmim][PF₆], certain ionic probes can behave very differently from a neutral probe of similar hydrodynamic volume due to specific hydrogen bonding and (possibly) favorable

ionic interactions.⁷¹ Significant specific solute-solvent interaction has also been depicted with 2-aminoquinoline (2-AQ) in imidazolium ILs, whence addition of a small amount of polar solvent leads to significant reduction in τ_r values, apparently due to the disruption of such interaction.⁷² In other 'nonaromatic' ILs (i.e. those devoid of polarizable π -cloud), no such abrupt effect of the polar solvents was registered which indicates the lack of aforementioned favorable association between probe and IL.

Other photophysical studies

The first report on the study of photoisomerization in ILs was the photoinduced *cis-trans* isomerization of *trans*-stilbene in a highly viscous IL.⁷³ This molecule undergoes a twisting around the double bond in the excited state leading to the formation of a different diastereoisomer than that existing in ground state. It has been found that the rate of the photoisomerization in the IL is much larger than that expected from its polarity and shear viscosity. Another study focused on a similar photoinduced twisting around the double bond of a carbocyanine dye demonstrated the viscosity-driven drastic retardation of the rate and consequent increase in activation energy of the photoisomerization process.⁷⁴ Possible effect of specific solute-solvent interaction on the photoisomerization in an IL has also been investigated.⁷⁵

The triple-triplet energy transfer between benzophenone and naphthalene has been studied using laser flash photolysis (LFP) method in the ILs of varying viscosity at different temperatures.⁷⁶ The diffusion-controlled rate equation (Eq. 2) holds good in this case and the activation energy of the given process was found to be nearly equal to the viscosity activation energy of the respective IL. Another LFP study involving benzophenone in ILs, focusing on the H-abstraction by triplet benzophenone from the ILs, revealed higher activation energy of this process in ILs as compared to that in conventional solvents.⁷⁷ This high activation energy was attributed to the strong electrostatic interactions between the ions in the ILs. Recently, fluorescence resonance energy transfer (FRET) was studied in an IL-based microemulsion by using coumarin 480 as donor and rhodamine 6G as acceptor by using femtosecond upconversion technique.⁷⁸ The time-constants of the FRET in this study ranges from subpicosecond to several nanoseconds, indicating different locations of

the donor in the microemulsion as compared to the acceptor sitting in the IL pool.

Excited state intramolecular proton transfer in a hydroxyflavone derivative has been studied in ILs by using time-resolved picosecond Streak camera.⁷⁹ The results suggested that the intramolecular proton transfer is quite slow in ILs as compared to that in conventional solvents and (somewhat surprisingly) it is strongly influenced by the ultrafast dynamics of solvation. Excited-state proton transfer (ESPT) reaction of 7-hydroxyquinoline (7-HQ) mediated by methanol molecules has been studied in a couple of ILs and the result suggested that a considerable solvent reorganization is required prior to the methanol mediated relay of proton from one part of the molecule to the other.⁸⁰ The kinetic parameters of the proton transfer process were evaluated and interpreted in terms of microheterogeneous nature of ILs and the role of microviscosity at the probe environment.

Intramolecular excimer formation between two pyrenyl moieties attached through a covalent linkage (propyl chain) has been studied in different ILs by time-resolved fluorescence measurements.⁸¹ The formation kinetics revealed that though the mechanism of excimer formation is similar to that in normal solvents, the rate of excimer formation is very slow in ILs, presumably owing to the high viscosity of ILs which hinders the excited state dimerization process.

Conclusions

In the current review, we have summarized various photoprocesses studied in ILs. Though only a limited number of studies have been carried out so far and the future scope is still wide open, these studies have indeed reflected many of the differential characteristics of ILs compared to conventional molecular solvents. While various aspects of solvent properties of ILs have been beautifully elucidated by the solvation and rotational dynamics studies, investigations on photoinduced electron transfer and other such photoprocesses have provided the opportunity to explore the horizon of ILs as media for photophysical studies. We have seen that the general as well as specific solvent effects of ILs on a given photoprocess are singularly different from conventional solvents and sometimes these may lead to an entirely different course or provide a different mechanism for the given photoprocess. However, there are various aspects of these photophysical

processes which are still not well understood. For example, the physical origin of different components of dynamic solvation process, especially those which occur in ultrafast time-scale, is not well resolved. Also, the full significance of specific solvent-solute interactions in ILs on photoinduced processes like electron transfer, proton transfer, isomerization and charge-separation processes is still not well understood. Hence, controlled experiments directed to resolve these issues are required to have a detailed understanding on this subject. At the same time, only a few types of photophysical processes have so far been attempted in ILs. To understand the full potential of ILs as a novel media for such studies, a variety of other photoinduced processes are to be probed in detail. Mixtures of ILs and conventional solvents, as well as heterogeneous media composed of IL as a key component, are emerging as potential new media for various applications. However, only a few photoinduced processes have so far been studied in these media and hence a lot more similar studies are required to comprehend the full potential of these IL-based systems.

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