1.1. Room Temperature Ionic Liquids

Room temperature ionic liquids (RTILs) are the class of salts, which are liquids at ambient temperature (20–30°C) and pressure (1 bar). They consist of bulky organic cations and anions, usually inorganic. Due to the relatively large size of their cations and the nature of the chemical substituents of the anions, the charges on the ions of these salts are usually diffuse. As a result, there is a reduction of electrostatic forces between the ionic constituents of RTILs. The steric constraint of ionic constituents and their low charge density on them make it difficult for RTILs to form a regular crystalline structure, and therefore, they are found as liquids even though at room temperature. The term ‘ionic liquid’ differs from ‘molten salt’, the latter usually represents high melting salts like NaCl with strong electrostatic interactions between cations and anions.\(^1\) The lowest melting point reported for RTILs till date is -96°C.\(^2\) These liquids have interesting physicochemical properties such as low volatility, negligible vapour pressure, non-flammability, thermal stability, broad electrochemical window and miscibility with organic compounds. Production methods of RTILs are also, in some cases, considered to be more eco-friendly when compared to the same for conventional solvents.\(^3^{18}\)

Although the first RTIL, ethylammonium nitrate, was identified in 1914\(^19\), significant attentions towards these systems were given in early 1980s when Wilkes and his coworkers\(^20,21\) developed chloroaluminate anions (AlCl\(_4^-\) or Al\(_2\)Cl\(_7^-\)) based systems. Later on, many cations such as (i) imidazolium, (ii) ammonium, (iii) phosphonium, (iv) piperdinium, (v) pyrrolidinium, (vi) morpholinium, (vii) pyridinium were used along with anions such as tetrafluoroborate (BF\(_4^-\)), hexafluorophosphate (PF\(_6^-\)), nitrate (NO\(_3^-\)) etc to develop RTILs
(Chart 1.1). In most of the cases, anion plays a vital role in determining the hydrophilic and hydrophobic characters of RTILs.\textsuperscript{12} RTILs are generally classified into three categories.

**First generation RTILs:** They are based on chloroaluminate (AlCl\textsubscript{4} or Al\textsubscript{2}Cl\textsubscript{7}) anions. They are highly hygroscopic in nature. Due to the high reactivity of these RTILs towards water, there is limitation of their applications in practical purposes.

**Second generation RTILs:** The draw backs in first generation RTILs, lead to development of “second generation RTILs”, which are mostly composed of air stable anion\textsuperscript{5}, such as BF\textsubscript{4} and PF\textsubscript{6}. However, these are highly viscous and produce detectable amount of HF acid formed by hydrolysis in the presence of trace amount of water.\textsuperscript{22}

**Third generation RTILs:** They are composed of perfluorinated anion containing RTILs such as Tf\textsubscript{2}N, fluoroalkylphosphate (FAP) and address the problem of second generation RTILs. These are mostly hydrophobic in nature and characterized with low melting points, low viscosity, and low conductivity. However, RTILs composed of these anions are more expensive and show stronger binding ability towards the Lewis acid metal ions. Due to the presence of fluorine which is toxic and harmful for human beings, disposal of these RTILs become more complicated.\textsuperscript{22-24} This problem leads to the realization of non-fluorinated
orthoborate, carborane anion containing RTILs which are low coordinating and cheaper than other RTILs.\textsuperscript{25, 26}

Recently, task specific RTILs with specific functional groups, are also developed for a particular task\textsuperscript{27-30}. For example, thiol functionalized RTILs have been used to synthesize gold nanoparticles\textsuperscript{29} and stabilize nanocrystal quantum dots\textsuperscript{30}. Recently developed amino acid based, RTILs are being extensively used for different biological applications.\textsuperscript{31, 32}

1.1.1. Properties of RTILs

RTILs have attained considerable interest from academic as well as industrial communities across the globe due to their inherent and unique properties such as negligible vapor pressure, ability to dissolve a large variety of organic and inorganic substances, high thermal and chemical stability, wide liquidous range, wide electrical conductivity, moderate to high polarity, non-flammable nature and the advantage of recyclability.\textsuperscript{3-15, 33-35} Since, these properties of RTILs are found to depend on ionic constituents, by appropriate combination and permutation of cations and anions, there is a possibility to design and develop RTILs having desired properties. Because of this they are also known as “designer solvents”\textsuperscript{3}. Molecular diagrams of some well known common imidazolium based RTILs are depicted in Chart 1.2 and physical properties of some common imidazolium based RTILs are given in Table 1.1.

**Melting points:** The melting point is a fundamental physical property of compounds. For RTILs, melting point is especially significant because RTILs have a wide liquidus range determined by their low melting points as well as high decomposition points. Moreover, solubility of RTILs in water or organic solvents are also strongly correlated with their melting points. Melting happens when the molecules or ions fall out of their crystal structures, and become disordered liquid. Melting point values of most of RTILs are uncertain as they can undergo supercooling.\textsuperscript{12} Phase transfer temperature on RTILs depends on whether the RTIL
is heated or cooled. As the properties of the RTILs depend on the structure, attempts have been made to correlate the melting point of the RTILs to the nature of their cation or anion.\textsuperscript{36} ILs with symmetric cation exhibits the highest melting point; the melting point appear to fall gradually with increasing alkyl chain length. The melting point of RTILs generally decreases with increasing anionic radius of RTILs.\textsuperscript{38}

\[
\text{Chart 1.2. Molecular diagrams and abbreviation of some common imidazolium-based RTILs.}
\]

**Thermal phase behavior:** Thermal decomposition ($T_d$) is strongly dependent on the structures of RTILs. Unlike organic solvents, many kinds of RTILs can be kept in the liquid state above 400 °C (with $T_d$ ranging from 600 to 700 K).\textsuperscript{12} Generally, the imidazolium cations tend to be thermally more stable than the tetra-alkyl ammonium cations. High thermal stability is provided by certain kinds of anions such as $[(\text{CF}_3\text{SO}_2)_2\text{N}]^{-}$, $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^{-}$. The relative anion stabilities follows the order $\text{PF}_6^->[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^->[(\text{CF}_3\text{SO}_2)_2\text{N}]^->\text{CF}_3\text{SO}_3^->\text{BF}_4^->\text{Me}[(\text{CF}_3\text{SO}_2)_3\text{C}]^->\Gamma, \text{Br}^-, \text{Cl}^-$\textsuperscript{34}

**Glass transition temperature:** The glass transition temperature ($T_g$) is an indication of the cohesive energy within the salt, which generally decreases due to repulsive Pauli forces from the overlap of closed electron shells and increases through the attractive Coulomb and van der Waals interactions.\textsuperscript{39} Hence, $T_g$ can be decreased by minimizing the cohesive energy within the salt, which is usually achievable through modification of the cationic or anionic components of the RTILs. It has been found that with decreasing cation size and increasing
asymmetry of the cation leads to lower value of $T_g$ through the reduction of packing and cohesive energy of the RTILs.\textsuperscript{40}

**Thermal stability and volatility**: Generally RTILs are thermally stable up to 250°C. Beyond this limit (250°C), it is found that, some of the RTILs are decompose. The decomposition temperature decreases as the hydrophilicity of the anion increases. However, cations have no significant contribution in this regard. The thermal stability of the RTILs comprising different anions decreases in the order $\text{PF}_6^->[(\text{C}_2\text{F}_5\text{SO}_2)\text{2N}]^-> \Gamma^-, \text{Br}^-, \text{Cl}^-$.\textsuperscript{34}

**Table 1.1.** Physical properties of some common imidazolium RTILs

<table>
<thead>
<tr>
<th>RTILs</th>
<th>$T_{mp}$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$\rho$ (g/CC)</th>
<th>$\eta$ (cP)</th>
<th>$\sigma$ (ms/cm)</th>
<th>$E_T(30)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIMCl</td>
<td>86\textsuperscript{a}</td>
<td>-</td>
<td>solid</td>
<td>solid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>65\textsuperscript{a}</td>
<td>-</td>
<td>solid</td>
<td>solid</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EMIMTf$_2$N</td>
<td>-3\textsuperscript{b}</td>
<td>-</td>
<td>1.52\textsuperscript{b}</td>
<td>34\textsuperscript{b}</td>
<td>8.8\textsuperscript{b}</td>
<td>47.7\textsuperscript{c}</td>
</tr>
<tr>
<td>BMIMTf$_2$N</td>
<td>-4\textsuperscript{b}</td>
<td>&gt;400\textsuperscript{d}</td>
<td>1.43\textsuperscript{e}</td>
<td>52\textsuperscript{e}</td>
<td>3.9\textsuperscript{e}</td>
<td>47.2\textsuperscript{c}</td>
</tr>
<tr>
<td>EMIMPF$_6$</td>
<td>60\textsuperscript{f}</td>
<td>-</td>
<td>solid</td>
<td>solid</td>
<td>5.2\textsuperscript{g}</td>
<td>solid</td>
</tr>
<tr>
<td>BMIMPF$_6$</td>
<td>-61\textsuperscript{h}</td>
<td>-</td>
<td>1.37\textsuperscript{i}</td>
<td>371\textsuperscript{i}</td>
<td>1.5\textsuperscript{j}</td>
<td>52.3\textsuperscript{k}</td>
</tr>
<tr>
<td>BMIMBF$_4$</td>
<td>-81\textsuperscript{h}</td>
<td>435\textsuperscript{d}</td>
<td>1.2\textsuperscript{l}</td>
<td>154\textsuperscript{l}</td>
<td>3.5\textsuperscript{d}</td>
<td>48.9\textsuperscript{l}</td>
</tr>
</tbody>
</table>

$T_{mp}$: melting point, $T_d$: decomposition temperature, $\eta$: viscosity, $\rho$: density, $\sigma$: specific conductivity, $E_T(30)$: microscopic solvent polarity parameter.

Recent reports have shown that RTILs have non-negligible vapor pressure and thus, they can be distilled under reduced pressure without any thermal decomposition. In this regard, report by Earle and coworkers is noteworthy.\textsuperscript{50} They found that by vacuum distillation of RTILs, most of the commonly used aprotic RTILs can be distilled at 200-300°C and low pressure. Later, attempts have been made to separate the mixture of RTILs in pure form, which is also found to be useful for the recyclability of spent RTILs.\textsuperscript{51} Though, Earle and coworkers could not provide direct proof of ions in the gas phase of their distillation process, recently Leone et al. by tunable vacuum ultraviolet photoionization time-of-flight
mass spectrometry (PI-TOFMS) identified intact ion pair of 1-butyl-3-methylimidazolium tricyanomethanide.\textsuperscript{52}

**Density:** The density of a material depends on how closely the ions can pack together and, hence, on the size and shape of the ions and ion-ion interactions. So, the density of RTILs depends on the ionic constituents of RTILs. It is observed that the density decreases slowly as the alkyl chain length increases for alkylammonium and alkylimidazolium cations. Tributylammonium nitrate is known to have lowest density because of its bulkier cation.\textsuperscript{53, 54} It is expected that primary amines are likely to have higher densities than secondary or tertiary amines. The densities of heterocyclic amine cations are generally higher than those of the alkylammonium cations. For lactum based RTILs with fluorinated anions, it has been seen that with increasing the ring carbon number of the cation, density is decreased. This has been attributed to the modification of the cation-anion interaction due to the increase in the cation size.\textsuperscript{55}

**Viscosity:** The viscosity of RTILs is generally dependent on the cumbolic i.e. ion-ion interactions, van der Waals interaction and hydrogen bonding interactions within the ionic species. Interactions between ionic constituents lead to higher viscosities. It has been revealed that with the increase of the length of alkyl chains of the cationic moiety viscosity increases and this is due to stronger van der Waals interactions.\textsuperscript{41} Similar change in anionic constituents influence viscosity greater than the cationic constituents. Delocalization of the charge on the anion decreases the viscosity by weakening hydrogen bonds.\textsuperscript{56} Impurities like halide and water affect the RTILs viscosity considerably.\textsuperscript{2, 57} The viscosities of RTILs generally decreases with increasing temperature and it does not follow the Arrhenius behavior but it obeys Vogel-Tammann-Fulcher (VFT) equation which is given below\textsuperscript{58}

\[
\ln(\eta) = \ln(\eta_0) + \frac{DT_c}{T-T_c}
\]

(1.1)
where, $\eta_0$ is the viscosity at infinite temperature, $D$ is the fragility parameter and $T_C$ is the characteristic temperature at which viscosity diverges.

**Surface tension:** Modifications in either the cation or anion structures have a similar effect on surface tension, indicating that both ions are present at the surface of the medium.\(^{59}\) In general it is observed that surface tension is decreased when the ions have a higher packing efficiency and it is increased when the cohesiveness of the IL increases through ionic interaction or through an increase in the amount of hydrogen bonding interaction.

**Refractive index:** The refractive index, $n_D$, of a material can give the idea about its polarity. The $n_D$ values indicate that RTILs can be considered to be moderately polar media like acetonitrile but less polar than short chain alcohol. It has been shown that $n_D$ decreases slowly with increasing alkyl length, while the substitution of a hydroxyl group causes a more significant increase.\(^{59}\)

**Ionic conductivity:** The ionic conductivity (specific conductivity) of a medium is generally governed by the ionic mobility of the ions. Ionic mobility depends on the viscosity of the medium and number of charge carriers, which in turn depend on the molecular weight, density, and ion sizes.\(^{41, 54, 56, 60}\) Any association that may arise due to ion-ion interactions or hydrogen bonding interaction can reduce the ionic conductivity of the medium.\(^{61}\) The ionic conductivity of RTILs containing alkylammonium and alkylimidazolium cations decreases as the alkyl chain length increases. Larger change in conductivity is observed for short chains (C1-C4) and little change for longer chains (C4-C12).

**Polarity:** Polarity of the medium is generally expressed by static dielectric constant ($\varepsilon$) of the medium. Dielectric constants of some RTILs are found to vary in a narrow range 9-13 (25°C). These data indicate that RTILs are less polar than acetonitrile ($\varepsilon=35.9$ at 25°C)\(^{62}\) and similar to pyridine ($\varepsilon=12.3$ at 25°C)\(^{63, 64}\). However, these bulk polarity values fail to explain many of the experimental observation in RTILs.\(^{65}\) Hence, microscopic polarity parameters
such as $E_T(30)$ and $E_T^N$ values which can be obtained from the micropolarity reporter probe such as betaine dye, would be the more appropriate than the dielectric constant ($\varepsilon$).$^{48, 49, 66, 67}$ These $E_T(30)$ values are defined as the molar transition energies of standard pyridinium-N-phenoxide betaine dye measured in solvents of different polarity at room temperature and normal pressure. The $E_T(30)$ values for imidazolium cation containing RTILs are generally in the range of 48-52 kcal mol$^{-1}$. With the increase in chain length of the alkyl group attached to the imidazolium cation, the polarity is found to decrease. This is also true for other cation containing RTILs as well. From the outcome of the different studies on RTILs, it is found that polarity (i.e. $E_T(30)$) of almost all RTILs is more than that of acetonitrile but less than methanol. In fact, the polarity of most of the RTILs are observed to be very similar to that of the short chain alcohols.$^{48}$

1.1.2. Structural Informations and Heterogeneity of RTILs

Structural information i.e. the organization of the chemical entities in the RTILs is extremely important since it affects the chemical reaction, solubility of different polar and nonpolar solute etc. Many experimental and theoretical investigations are carried out to understand the structural organization in solid and liquids state of RTILs. Structure of some RTILs which are solid at room temperature were determined by X-ray diffraction methods.$^{68}$ These study show that the solid consists of an extended network of cations and anions connected together by hydrogen bonding network among them. The hydrogen bond formation may be either through the aromatic hydrogen of the imidazolium ring or through the hydrogen atoms of the methyl or methylene groups, directly attached to the ring with each cation surrounded by at least three anions and each anion surrounded by at least three cations. Although the number of anions that surround the cation (and vice-versa) can change depending upon the anion size and the imidazolium alkyl substituent, the hydrogen bonding network of ions is a common feature of imidazolium crystals.$^{69}$ On a later stage, from the
neutron diffraction analysis, it was found that dialkylimidazolium cation containing RTILs have a close relationship between solid and liquidus nature, emphasizing once again the importance of hydrogen bonding interaction between ionic constituents of RTILs. The existence of hydrogen-bonded clusters both in the solid and liquid phases are also confirmed by IR and Raman spectroscopy, NMR, and mass spectrometry.

Quite interestingly, many investigations have revealed that the neat ionic liquids are also heterogeneous in nature. The multiscale coarse grained structure simulation by Wang and Voth and atomistic simulations by Lopes and Padua indicate towards a nanostructural organization in these media. Recently, optical heterodyne-detected Raman induced Kerr effect (OHD-RIKES) studies provide further indication towards heterogeneous nature of RTILs. Samanta and coworkers have also proved microheterogeneous nature of ionic liquids by exploiting excitation wavelength dependence fluorescence behaviour of several probes in RTILs. Later, Hu and Margulis through molecular dynamics (MD) simulation studies have demonstrated that the red edge excitation wavelength dependent fluorescence behavior of molecules arises from probes trapped in quasi-static solvent cages that relax in time scale longer than the fluorescence lifetime of the probes. Very recently, Maroncelli and Bhattacharyya independently have studied the excitation wavelength dependent solvation dynamics in neat ionic liquid and ionic liquid microemulsion using time-resolved emission spectroscopy. From the outcome of these investigations, it is revealed that RTILs are heterogeneous in nature and different polar and nonpolar domain formation among ionic constituents are responsible for this behavior. However, the issue of heterogeneity of ILs is not yet fully resolved. More and more theoretical and experimental investigations are further necessary to understand this phenomenon.
1.1.3. Applications of RTILs

RTILs have a number of qualities which make them unique and interesting solvents in contrast to the conventional volatile organic solvents in chemical reactions and catalysis.\textsuperscript{83-86} RTILs are of interest as stationary phases in gas-liquid chromatography or as mobile phases in liquid chromatography.\textsuperscript{87} A series of RTILs can be tried as ionic matrices for use with matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). Potential application have been found for the use RTILs with proteins, such as dissolving hydrophobic ligands to incorporate them it to crystal, improved solubility, monodispersity, as a precipitating agent and as an additive also.\textsuperscript{88} A number of RTILs have been found which can act as biocatalysts.\textsuperscript{89} RTILs are potentially very useful as ionic-conducting agents in electrochemical systems and as proton conducting agent in polymer membrane fuel cells (PEMFCs). Because of high proton conductivity, low reactivity, and wide electrochemical window provided by the ILs, these system serve as excellent electrolyte in electrochemical applications such as in lithium ion batteries, double-layer capacitors, fuel cells, and actuators.\textsuperscript{90-92} The biphasic acid scavenging utilizing ionic liquids (BASIL) method has been widely used in industrial applications for example, alkoxyphenylphosphines based raw materials for the production of photoinitiators to cure coatings and printing inks by exposure to UV light have been synthesized by this method.\textsuperscript{3, 85}

Out of these, RTILs have been recognized for different application such as propellants, lubricants.\textsuperscript{93} In the last decades, various types of functionalized RTILs specifically categorized as being “task-specific” ionic liquids (TSILs) have been designed and synthesized for specific purposes such as catalysis\textsuperscript{94}, organic synthesis\textsuperscript{4}, and separation of specific materials\textsuperscript{4} as well as for the construction of nanostructure materials\textsuperscript{29} and ion conductive materials etc.
1.1.4. **Photophysical Studies in RTILs**

Utilization of new molecular solvent in practical applications requires not only the knowledge of bulk properties but also a molecular level understanding of the intermolecular interaction, structure, and dynamics of these substances. Scientific communities have immense interest to understand their structure-property relationship\textsuperscript{76-82}, molecular level picture through both simulation\textsuperscript{76, 77, 95-100} and experimental studies\textsuperscript{42, 79, 81, 82, 101-163}. Studies have also been carried out to control the photophysical\textsuperscript{164-178} and photochemical\textsuperscript{179} processes of various systems in RTILs. Many of these studies revealed that RTILs are not homogeneous like common conventional solvents.\textsuperscript{76, 77, 79, 81, 82, 101-108, 146-148} Some of the important photophysical studies in RTILs relevant to the present thesis work are discussed in the following sections.

**Solvation dynamics:** Dynamics of many chemical reactions in solution are strongly influenced by the dynamical behavior of the solvent molecules surrounding reacting species. Studies of solvent relaxation processes are thus fundamentally important to get a proper understanding on the reaction dynamics in solution, especially the processes like electron transfer, charge transfer, proton transfer, conformational relaxation, etc.\textsuperscript{180} Besides other methods, the time-dependent fluorescence Stokes shift (TDFSS) measurements have been used extensively to understand solvent relaxation dynamics in large number of systems in last few decades.\textsuperscript{109-149,181-186} In this study, the time dependent response of a polar solvent to a changing charge distribution of polar solute is investigated.\textsuperscript{180} Chemical reactions usually involve charge transfer, redistribution of electron density, stabilizations of various intermediates and products, which are formed during chemical reaction, are intimately connected to the time scale at which the surrounding solvent molecules reorganize. Understanding the time scale of solvent reorganization in RTILs may therefore be important.
Outcome of these studies are expected to be helpful in designing a solvent for carrying out a specific reaction for a desired product.

The probes for studying TDFSS should possess some special characteristics. Firstly, they should undergo large change in the dipole moment upon optical excitation. Secondly, these molecules should exhibit fluorescence with a long lifetime. Thirdly, any excited state phenomena other than solvation process should be avoided for the study of solvation dynamics. Molecular diagrams of some well know dipolar probes are shown in Chart 1.3. Molecular diagrams of some well know dipolar probes are shown in Chart 1.3.

![Molecular diagrams of some well know dipolar probes](image)

**Chart 1.3.** Some of the dipolar molecules used in the measurement solvation dynamics of the RTILs

The process of solvation can be described as follows. Let us consider that a solute molecule in its ground state is in equilibrium with the surrounding solvent molecules. Then, the equilibrium charge distribution of the solute is immediately altered through the optical excitation. This represents a non-equilibrium situation. Subsequent to the optical excitation, the surrounding solvent molecules start to reorient and rearrange themselves to stabilize the newly created charge distribution of the excited state of the probe. The time dependent
response of the solvent environment is manifested through the continuous red shift of the emission spectra of the probe with time.\textsuperscript{180} The process of solvation is schematically illustrated in Scheme 1.1 for RTILs.

**Scheme 1.1.** Pictorial illustration of dynamic Stokes shift in RTILs.

Since RTILs are sufficiently polar\textsuperscript{48, 49}, time dependent fluorescence Stokes shift measurements on dipolar solute probe molecules can give valuable information on the time scale of the reorganization of the ionic constituents of the RTILs. To get an insight into the solute-solvent and solvent-solvent interactions, first Samanta and coworkers\textsuperscript{109-117} have carried out the pioneering work on dynamics on solvation by monitoring this time-dependent fluorescence Stokes shift (TDFSS) of a dipolar solute in RTILs. Subsequently Maroncelli\textsuperscript{118-128}, Sarkar\textsuperscript{129-135}, Bhattacharyya\textsuperscript{82}, Petrich\textsuperscript{136, 137} and Biswas\textsuperscript{138-143} have also made significant contribution to this area. The main findings of these works are collected in the recent review articles.\textsuperscript{112, 113, 116} These studies have revealed that solvation dynamics in RTILs is slow compared to that of the common molecular solvents such as acetonitrile, methanol, or water. The time-resolvable component of the dynamics is bi-exponential or non-exponential in nature, with the average solvation time dependent on the viscosity of the media. Almost 50\% of the spectral relaxation dynamics is quite fast (<25 ps). Though, time scale and origin of
ultrafast component is under debate, recent studies based on femtosecond fluorescence upconversion technique show that only 10-20% of the dynamics is ultrafast and occurs within 10 ps timescale. The solvation dynamics in RTILs is found to be probe dependent. Recently, Solvation dynamics studies have also been carried out in mixtures of RTILs with conventional solvents and also in micellar solutions.

The mechanism of solvation process in RTILs is fundamentally different from that in polar conventional solvents. Dipolar solvent molecules undergo reorientation around the photoexcited species without moving from their original positions i.e. reorientation of solvent molecule is primarily responsible for the stabilization of the photoexcited probe. However, because of their ionic charge, the ionic species of the RTILs 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 significantly to solvation process in the case of RTILs. This fundamental difference of the mechanism of solvation has been illustrated in the form of an oversimplified diagram in Scheme 1.2.

**Scheme 1.2.** Oversimplified diagram illustrating the fundamental difference in the mechanism of solvation of a dipolar molecule in conventional molecular solvents and in RTILs.
Simulation studies have also been carried out to have a better understanding of solvation dynamics in RTILs on these aspects. However, different pictures have emerged while assigning fast and slow component to molecular motion. For example, Shim et al. reported that the fast component is due to the translational motion of the anions\textsuperscript{95}, whereas Kobrak and Znamenskiy considered it because of collective cation-anion motion\textsuperscript{96, 97}. Later on, Shim et al.\textsuperscript{98} attributed the ultrafast dynamics to the local density of the ions near the solvation probe molecule. When the local density is high, few ions in close proximity to the probe molecule are responsible for the ultrafast component and when the local density is low, the ions from the region further away contribute significantly to the ultrafast component.

**Excitation wavelength dependence fluorescence study:** According to Kasha’s rule, fluorescence generally originates from the lowest vibrational energy level of the lowest excited state of the same spin multiplicity. Hence, emission spectrum is expected to be independent of excitation wavelength.\textsuperscript{188} However, under certain conditions fluorescence of some organic fluorophore are observed to shifts towards longer wavelength upon increasing the excitation wavelengths particularly at the red region of the absorption spectra.\textsuperscript{189-195} This phenomenon is commonly known as “red-edge effect” (REE)\textsuperscript{192, 193}, although some other terminologies such as edge excitation shift (EES)\textsuperscript{191}, edge excitation red shift (EERS)\textsuperscript{194}, and red edge excitation shift (REES)\textsuperscript{193} are also used to describe this unusual observation. Two conditions have to be satisfied by fluorescence organic molecules for observing this unusual phenomenon.\textsuperscript{189, 190} There must be presence of ensemble of energetically different molecules in the ground state which may arise due to solute-solvent interaction energy which leads to inhomogeneous broadening of the absorption spectrum. Again, another necessary condition that needs to be fulfilled for the occurrence of REE phenomenon is that excited state relaxation of the fluorescent solute molecule must be slower or comparable to the excited state lifetime of the molecule. Since each molecule in a condensed system does not
necessarily experience an equal environment, large numbers of different environments are indeed possible and one can expect a variation of interaction energies between the solute and the solvent leading to a broadening of the absorption. If the media is heterogeneous, this will also allow different ensemble of solvation sites and contribute to significant additional broadening of the absorption spectra. REES has been observed for some organic fluorescent dipolar molecules in RTILs. Molecular basis of this phenomenon is illustrated pictorially by a schematic diagram which is shown in scheme 1.3.

**Scheme 1.3.** Pictorial illustration of red-edge effect (REE).

*Fluorescence anisotropy; rotational dynamics:* Fluorescence anisotropy is a measure of emission depolarization of a fluorescent molecule that absorbs polarized light. Rotational motion in the excited state is the common cause of emission depolarization. In a homogeneous solution, the ground-state fluorophores are all randomly oriented in the medium. When such an isotropic ensemble of chromophores is preferentially excited with a polarized light beam, an anisotropic distribution is generated in the excited state due to the selective excitation of the suitably oriented chromophoric molecules in the solution. This
preferential excitation of molecules creates anisotropy in excited electronic state. The anisotropy measurements reveal the average angular displacement of the fluorophore that occurs between the absorption and the subsequent emission of fluorophore. This angular displacement is dependent upon the rate and the extent of the rotational diffusion of the excited species during the lifetime of the excited state. Rotational diffusion of a molecule depends upon its size and shape as well as on the viscosity or the rigidity of its local microenvironment. In view of this, studies on the fluorescence anisotropy have been utilized extensively to explore the local environment of the fluorescence dyes as well as to investigate their interactions in host-guest assembly. Probing interactions of solvents with molecules through rotational dynamics study is also expected to be very useful in a sense that well-developed theoretical frameworks for the analysis of the experimental data are available in literature. Solute–solvent interactions play an important role in determining the physicochemical properties of liquids and solutions\textsuperscript{197} proper understanding of which is highly desirable.

The Stokes-Einstein-Debye (SED) theory has been found to be suitable for explaining the rotational diffusion of medium sized solute molecules when the coupling between solute and solvent is purely hydrodynamic in nature. It has been observed that the SED theory correctly predicts the linear dependence of the rotational diffusion times of solutes on the solvent viscosity. According to this theory rotational time ($\tau_r^{SED}$) of non-interacting solute in a solvent continuum of viscosity $\eta$ is given by\textsuperscript{196}

$$\tau_r^{SED} = \frac{V_h\eta}{k_BT}$$

(1.2)

where $V_h$ is the hydrodynamic volume of the solute molecule, and $V_h$ is the product of the van der Waals volume $V$ of the molecule, its shape factor $f$ and the boundary condition
parameter \( C \). \( T \) is the absolute temperature and \( k_B \) is the Boltzmann constant. The shape factor \( f \) depends on the axial ratio of the semi axes. For a spherical solute \( f \) is unity, and is greater than 1 for an asymmetric ellipsoid. When the size of the rotating solute is much bigger than the solvent molecule, the boundary condition parameter, \( C \), is unity, and is represented as the stick boundary condition. In the case of a solute of comparable size, \( C \) is less than unity and remains commonly within the range 0<\( C \)<1. SED theory is helpful for the calculation of rotational coupling constants (\( C_{\text{rot}} \)) values which measure the departure from the normal hydrodynamic behavior.

It is also observed that the experimentally measured rotational reorientation times of a number of solutes could not be well described by the SED theory. Sometime, it is found that hydrodynamic behavior of rotating solute goes beyond slip boundary. This discrepancy arises due to the fact that SED theory takes in to account only the size of the solute molecule and not that of the solvent. In this regard, quasihydrodynamic theories\(^{198, 199} \) were developed to take care of size of the solvent molecules.

An in-depth understanding of various interactions that exist between constituents of RTILs and also their interaction with added solute are important to improvise their application in new avenues. Recently, a number of studies have been carried by different groups including ourselves towards attaining this goal.\(^{150-163} \) These studies indicate that apart from viscosity, solute–solvent hydrogen bonding interaction significantly hinders solute rotation.\(^{114, 151, 152} \) It is also found that the solvent size controls the solute rotation in the absence of specific interactions.\(^{151} \) As RTILs are composed of ions, and it is obvious to expect that it will influence the rotational dynamics of either cationic and/or anionic charged probe molecules. Interestingly, most of the rotational relaxation studies reveal that the rotational times of the charged species in RTILs depend on the viscosity of the medium and
the effect of ionic constituents of the RTILs on the rotational dynamics is found to be negligible.\textsuperscript{150} However, as it is possible to design RTILs with proper choice of different ionic constituents, and tailor their physicochemical properties, it may be possible that the scenario of molecular rotation is changed with the modification of ionic constituents in RTILs.

**Photoinduced electron transfer:** Photoinduced electron transfer (PET) is the basis of the design and development of systems for solar energy conversion\textsuperscript{200, 201} and making components of electronic devices\textsuperscript{202}. Electron transfer reaction also plays important role in many applications of ionic liquids such as their use in photovoltaic cells.\textsuperscript{203} Hence, it is important to understand electron transport and transfer in ionic liquids. In particular, it is important to learn the similarities and differences in rate of electron transfer between conventional solvents and RTILs. Study of Intermolecular PET reaction between pyrene and N, N-dimethylaniline (DMA) by Paul and Samanta\textsuperscript{204} have revealed that the mechanism of electron transfer depends on the microscopic properties of the ionic liquids but not on their bulk properties. The rate constant of PET induced fluorescence quenching ($k_q$) is found to be higher than the diffusion controlled rate constant ($k_{diff}$) suggesting that the microviscosity around the donor-acceptor pair is different from the bulk viscosity of the RTILs. However, similar observation have also found by Maroncelli\textsuperscript{205} and Vauthey\textsuperscript{206} independently in conventional organic solvents having comparably high viscosities, indicating that this behavior is not unique to ionic liquids and rate of electron transfer is not faster in RTILs compared to conventional solvents.

Samanta\textsuperscript{207, 208} and Manocelli\textsuperscript{209} independently reported that intramolecular PET reactions are solvent controlled in RTILs. Recent report by Wu\textsuperscript{210} and Lee\textsuperscript{211} et al. have also shown that rate of intramolecular PET reactions in RTILs is hindered compare to conventional solvents and this is due to slow solvent relaxation of RTILs compared to common conventional solvents. These studies have also revealed that intramolecular electron
transfer reaction in RTILs should be treated using a solvent controlled electron-transfer model where solvent relaxation time has a significant role in controlling this process.

Apart from solvation dynamics and rotational diffusion studies, photophysical studies by employing fluorescence correlation spectroscopy (FCS) have also been carried out to understand structure-property relationship in RTILs and these studies have provided evidence in support of microheterogeneous nature of RTILs.\textsuperscript{103, 108}

1.2. Objective behind the thesis

The main interest is to explore solvation dynamics and rotational diffusion studies in systematic way in a variety of RTILs such that a comprehensive and quantitative understanding of the relationship among structure, intermolecular interaction and dynamics in ionic liquids is obtained.

Solvation dynamics in RTILs depends on the choice of probe molecule.\textsuperscript{128, 132,136} As solvation dynamics is a solvent property, solvent organization times is normally expected to be independent of the probe molecules used. However, it is observed that the value of average solvation time varies significantly with change in the probe molecules. To understand the probe dependency on solvation dynamics, we have investigated the fluorescence response of C153 and AP in a hydrophobic RTIL, 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluorethyl)trifluorophosphate (MOEMPLFAP)(Chart 1.4). Again, although a large number of reports are available on solvation dynamics\textsuperscript{109-149}, very limited numbers of studies on solvation dynamics have been performed with the systematic variation of the ionic constituents. Keeping this fact in mind, we have carried out studies on solvation dynamics in 1-ethyl-3-methylimidazolium alkylsulfate to understand the effect of alkyl chain length on the dynamics of solvation in RTILs. (Chapter 3)

As discussed earlier, rotational diffusion studies provide a great deal of information about the solute-solvent interaction and microenvironment of the solute in these media; study
of the rotational dynamics by doing the systematic variations in the constituents of the ILs would be helpful to understand the nature of various forces that are responsible for solute-solvent interactions, also the interactions between the constituents of the ILs and microenvironment of the added solute. In view of this, we have undertaken the dynamics of rotational diffusion of two neutral organic solutes, AP and C153 in a series of 1-ethyl-3-methylimidazolium alkyl sulfate and 1-ethyl-3-methylimidazolium cation containing ILs to understand the effect of alkyl chain lengths and H-bond basicity of anions on the rotational diffusion behavior of C153 and AP. (Chapter 4)

RTILs are not easily available like common conventional solvents and are also expensive. Hence, the scale at which the neat RTILs should be used in the practical applications has not been reached till date. One of the possible approaches to expand the uses of RTILs would be to use various molecular solvent as cosolvents with RTILs.\textsuperscript{212, 213} RTIL-cosolvent mixtures are also known to show interesting physicochemical properties. However, a deeper understanding of their physicochemical properties in terms of IL-cosolvent interactions and their response to the photoexcited probe are extremely important so that the systems can be used more efficiently. To understand the effect of nonpolar cosolvent, we have investigated the solvation and rotational relaxation behavior C153 in MOEMPLFAP and its toluene mixture. Again to understand the effect of polar cosolvents in these dynamical phenomena, the solute and solvation dynamics of C153 in 1-butyl-3-methylimidazolium trifluoroacetate (BMIMTFA) and also its mixture with water and methanol have also been carried out separately. (Chapter 5)

Since the RTILs are heterogeneous in nature, this factor may also contribute significantly towards the solvent reorganization in these media. Therefore, it is of paramount importance to study solvation dynamics in ionic liquids as a function of excitation wavelengths so that a clearer picture about the heterogeneous nature of this media comes out.
Keeping all this aspects in mind we have carried out the temperature as well as excitation wavelength dependence on solvation and rotational relaxation of C153 in 1-(2-methoxyethyl)-1-methylpyrrolidinium [MOEMPL], 1-(2-methoxyethyl)-1-methylmorpholinium [MOEMMO] cation containing RTILs with a fixed anionic moiety such as FAP. (Chapter 6)

Chart 1.4. Molecular diagrams of RTILs under the present study. EMIM, 1-ethyl-3-methylimidazolium; ESU, ethylsulfate; BSU, butylsulfate; HSU, hexylsulfate, OSU, octylsulfate; MOEMPL, 1-(2-methoxyethyl)-1-methylpyrrolidinium; MOEMMOFAP, 1-(2-methoxyethyl)-1-methylmorpholinium; FAP, tris(pentafluoroethyl)trifluorophosphate.