SYNOPSIS

Room temperature ionic liquids (RTILs) have come up as a class of novel compounds primarily because of their interesting physicochemical properties like very low vapour pressure, wide liquid range, moderate to high viscosity, high ionic conductivity etc.\textsuperscript{1-3} It has been observed that intermolecular interactions have profound influence on many physicochemical properties of liquids and solutions.\textsuperscript{4} It is, therefore, important to have in-depth understanding of the various interactions that exist between the constituents of the RTILs and also their interaction with the added solutes so that they can be used to their full potential. In this context, studies on dynamics of solvation\textsuperscript{5-13} and rotational relaxation of solutes\textsuperscript{14, 15} have found to be quite useful in providing such information about medium. The main objective of the present thesis work is to explore solvation dynamics and rotational relaxation studies in a systematic manner 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.

Organization of thesis

The results obtained from different studies during current research investigations have been presented and discussed in this thesis, to be submitted to the Homi Bhabha National Institute for Ph.D. degree. For convenience of presentation, different aspects of the present thesis work have been discussed in a systematic manner in six different chapters. The contents of the different chapters of the present thesis are briefly described below.

Chapter 1: Introduction

This chapter starts with a brief description of RTILs and their different physicochemical properties. Applications of RTILs in chemical and biological sciences are also presented. A detailed discussion on different photophysical studies such as solvation dynamics, rotational relaxation dynamics and photoinduced electron transfer reactions in RTILs have been
described. The objective of the present work has also been discussed at the end of this chapter.

Chapter 2: Instrumentations and Methods

Brief descriptions of different instrumental techniques which have been used during the present investigation have been provided in this chapter. Working principle of the time-correlated single photon counting (TCSPC) technique has been demonstrated in details. Basic principles of the other instrumental techniques used in the present studies, such as absorption spectrophotometry, steady state spectrofluorimetry, have also been described briefly in this chapter. Various methodologies employed in the present study, such as data analysis procedure for construction of the time-resolved emission spectra from the decay curves, estimation of the solvation times and position of the time zero spectrum have also been discussed. Solvent purification techniques and experimental error limit are also provided in this chapter.

Chapter 3: Fluorescence Response of Coumarin 153 and 4-Aminophthalimide in Room Temperature Ionic Liquids: A Probe and Alkyl Chain Length Dependence Study

This chapter begins by discussing the effect of probe molecules on solvation dynamics. Solvation dynamics being a solvent property is expected to be independent of the probe molecules used. However, there are significant variations of the solvation time depending on the probe. One of the possible reasons for the probe dependent solvation dynamics may be specific solute-solvent interaction which affects the solvent reorganization time around the photoexcited probe. To understand the effect of solute-solvent interaction on solvation dynamics, we have carried out temperature dependent fluorescence response of Coumarin153 and 4-aminophthalimide in MOEMPLFAP (Chart 1).

Average solvation times for AP have been found to be six times higher than that of C153 (Figure1). Rotational coupling constants obtained from the rotational relaxation times also show a higher value for AP as compared to the same for C153. Theoretical investigation
reveals that N-H...F interaction between AP and anionic moiety of RTIL is primarily responsible for the slow solvation dynamics for AP.\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chart1.png}
\caption{Molecular diagrams of (a) Coumarin153, (b) 4-aminophthalimide and (c) MOEMPLFAP.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Decay of the spectral shift correlation function, $C(t)$, of C153 and AP in MOEMPLFAP RTIL at 298 K at $\lambda_{exc}=375$ nm. In both cases, symbols denote the experimental data points and solid lines represent the bi-exponential fit to the data points.}
\end{figure}

Although a large number of reports are available on solvation dynamics\textsuperscript{5-13}, limited number of studies on these aspects have been performed where systematic variations of the ionic constituents are made. To understand the effect of anionic alkyl chain length on the dynamics of solvation in RTILs, we have carried out studies on solvation dynamics in a series of 1-ethyl-3-methylimidazolium alkylsulfates (Chart 2) where chain length in the anion varied from butyl to octyl.
From the steady state behaviour, it has been found that C153 experiences more nonpolar character with increasing anionic alkyl chain length. A steady blue shift of the time-zero maximum of the time-resolved emission spectrum has also been found with increasing alkyl chain length which indicates that the probe molecule experiences a less polar microenvironment in the early part of the dynamics on going from butyl to octyl analogue. The average solvation time increases with increasing length of the alkyl side chain, and this is attributed to the increase in bulk viscosity of the RTILs with increasing alkyl chain length (Table 1).\textsuperscript{17}

**Table 1.** Summary of the solvent relaxation parameters of C153 in 1-ethyl-3-methylimidazolium alkylsulfates at 298K.

<table>
<thead>
<tr>
<th>RTILs</th>
<th>Vis.(cP)\textsuperscript{a}</th>
<th>a\textsubscript{1}</th>
<th>(\tau\textsubscript{1}(ns))</th>
<th>a\textsubscript{2}</th>
<th>(\tau\textsubscript{2}(ns))</th>
<th>(\langle \tau\textsubscript{c} \rangle (ns))\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIMBSU</td>
<td>141</td>
<td>0.70</td>
<td>0.42</td>
<td>0.30</td>
<td>1.39</td>
<td>0.71</td>
</tr>
<tr>
<td>EMIMHSU</td>
<td>284</td>
<td>0.65</td>
<td>0.43</td>
<td>0.35</td>
<td>2.48</td>
<td>1.15</td>
</tr>
<tr>
<td>EMIMOSU</td>
<td>453</td>
<td>0.61</td>
<td>0.42</td>
<td>0.39</td>
<td>2.98</td>
<td>1.42</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental error 5%.

**Chapter 4. Effect of Anions and Alkyl Chain Length on the Rotational Relaxation of Coumarin153 and 4-Aminophthalimide in Room Temperature Ionic Liquids**

This chapter describes the effect of various anions on the rotational relaxation dynamics of organic solutes. Specifically, the effects of H-bond basicity and alkyl chain lengths of anions on the rotational diffusion behavior of two well known fluorescent dipolar probes, C153 and AP (Chart 2, 3), have been discussed in this chapter.

![Molecular diagrams of 1-ethyl-3-methylimidazolium alkylsulfates](image)

**Chart 2.** Molecular diagrams of 1-ethyl-3-methylimidazolium alkylsulfates.

The results obtained from the rotational diffusion measurements indicate two distinct rotational environments for these two different probes. The rotational dynamics of C153 lie between stick and slip boundary condition in the ethyl analogue and finally reaches the
subslip condition in the case of octyl substituent. The rotational dynamics of C153 becomes faster with an increase in the alkyl chain length, primarily because of the fact that larger solvent molecules offer lower friction to the rotating solute (Figure 2). We have also observed fractional viscosity dependency on the rotation of C153 in these RTILs. The observation indicates a significant diffusion–viscosity (d-\(\eta\)) decoupling during rotational relaxation of C153 in these RTILs. The decoupling is analyzed through fractional viscosity dependence of the measured rotational times \(\langle \tau_r \rangle\): \(\langle \tau_r \rangle \propto (\eta/T)^p\) (p is the exponent, and T is the temperature). The fractional viscosity dependency (p = 0.76 to 0.48) increases with increasing anionic alkyl chain length of the anions from butyl to octyl. Generally, fractional viscosity dependence arises due to diffusion-viscosity decoupling during the solute rotation in highly organized and microheterogeneous medium.\(^{18, 19}\) From d-\(\eta\) decoupling, it can be concluded that structural organization and heterogeneity increases with increase in anionic alkyl chain length in these RTILs.\(^{17, 20}\)

For AP, hydrodynamic behavior changes from superstick to stick with the increase of the alkyl chain length. Superstick behavior has been attributed to the strong solute-solvent H-bonding interaction between AP and the ionic liquid. Rotational coupling constant values have been found to decrease with increasing length of alkyl side chains. Theoretical calculation (DFT) shows that charge density of sulphate moiety decreases with increasing alkyl chain length of anion in RTILs.
The second part of this chapter discusses the role of solute-solvent H-bonding interaction during the rotational diffusion of organic solutes. To find a correlation between H-bond basicity of anions and average rotational relaxation time of solute, we have investigated rotational diffusion of AP and C153 in several RTILs (Chart 3) that differ in their H-bond basicity. Among the solutes AP is known to form H-bond with H-bond acceptors. While the reorientation times of C153 depends upon the viscosity of the ionic liquids and follows normal hydrodynamics, rotational diffusion of AP has been found to be significantly influenced by H-bond basicity of anions. AP shows superstick behavior in EMIMESU and EMIMTFA and follows stick hydrodynamics in EMIMTFB and EMIMTCB (Figure 3). The superstick behavior is attributed to the strong specific solute solvent interaction. Rotational coupling constant values for AP are found to decrease in the order TFA>ESU>TCB>TFB. The variation in the rotational coupling constants, the measure of extent of departure from the normal hydrodynamics behavior due to specific solute-solvent interaction, is explained by considering the H-bond basicity of the anionic moiety of the corresponding RTILs.
Chapter 3. Molecular diagrams of RTILs used under the present study.

Figure 3. log-log plots for \( \tau_r \) vs. \( \eta/T \) for AP in different RTILs. Computed data are with stick (—), slip (----) boundary conditions and experimentally measured data are shown by symbol.

Chapter 5. Effect of Nonpolar and Polar Cosolvents on the Solute Rotation and Solvation Dynamics in Room Temperature Ionic Liquids

This chapter attempts to demonstrate the role of various cosolvents toward solvation and rotational relaxation dynamics of C153 in RTIL. The present work is undertaken, keeping in mind the potential of mixed ionic liquid-cosolvent system in real application. To study the effect of nonpolar cosolvent, we have explored the solvation and rotational relaxation behavior of C153 in a hydrophobic IL, MOEMPLFAP and IL-toluene mixture.

Time-resolved fluorescence anisotropy measurements show that the rotational diffusion of the probe becomes faster in presence of toluene. Solvation dynamics in ionic liquid–toluene mixtures is found to be biphasic, and the average solvation time is found to decrease with the addition of nonpolar cosolvent to the ionic liquid. A significant blue shift of the
time-zero maximum of time-resolved fluorescence spectrum upon addition of toluene indicates a more nonpolar environment around C153 at the initial stage of dynamics in the mixed solvent system. A comparison of the dynamics of solvation data in ionic liquid and ionic liquid–toluene mixture suggests that toluene can effectively penetrate into the ionic liquid-rich cybotactic region of the probe. This behaviour is explained in terms of favourable hydrophobic interaction between ionic liquid and toluene.\textsuperscript{22}

Again in order to understand the effect of polar solvent on solute rotation and solvation dynamics, we have carried out the fluorescence response of C153 in 1-butyl-3-methylimidazolium trifluoroacetate (BMIMTFA) (Chart 4), and also its mixture with water, methanol. Steady state absorption and emission maxima of C153 has found to be unaffected (no blue or red shift) by the addition of these cosolvents. Solvation as well as solute rotational relaxation times is found to be faster due to the lowering viscosity of the medium only. Theoretical calculations (DFT studies) have been performed on ground state structure of neat BMIMTFA, BMIMTFA-H\textsubscript{2}O and BMIMTFA-CH\textsubscript{3}OH systems to rationalize the experimental observations.\textsuperscript{23}

![Chart 4. Molecular diagram of BMIMTFA](image)

**Chapter 6. Solute Rotation and Solvent Relaxation of Coumarin153 in Moderate and High Viscous Room Temperature Ionic Liquids: An Excitation Wavelength Dependence Study**

Some recent studies depicts that RTILs are microheterogeneous in nature\textsuperscript{5, 6, 24, 25}. Again, recent literature reports reveal that the solute rotation and solvation dynamics in deep eutectic melts are decoupled from the medium viscosity due to heterogeneity of the medium.\textsuperscript{18, 19} Thus, it is expected that this microheterogeneous behaviour of the medium may
contribute significantly towards the solvent reorganization. To investigate whether microheterogeneous nature of the media has any bearing on solvation and solute relaxation dynamics, we have carried out the temperature as well as excitation wavelength dependence solvation and rotational relaxation of C153 in a highly viscous MOEMMOFAP and moderately MOEMPLFAP (Chart 5).

![Molecular diagram of MOEMMOFAP](chart5)

**Chart 5.** Molecular diagram of MOEMMOFAP used in the present study.

The average solvation times are found to depend on the excitation wavelengths. In case of a more viscous, morpholinium cation containing ionic liquid, the solvation and rotational relaxation times are found not to be as slow as are expected from the bulk viscosity of the medium. The breakdowns of both Stokes-Einstein (SE) and Stokes-Einstein-Debye (SED) relationships have been observed. The observation indicates a significant viscosity-diffusion decoupling during solvation and rotational relaxation of C153 in highly viscous IL. The observation seems to suggest that both static and dynamic heterogeneity may play an important role for the observed viscosity-diffusion (d-η) decoupling in highly viscous ionic liquid (Figure 4).\(^{26,27}\)
In conclusion, solvation and rotational relaxation dynamics of some well known organic dipolar probes have been investigated in several RTILs. Many interesting features with regard to understanding the fundamentals of solvation and rotational dynamics have come out from the present study. (1) Specific solute-solvent interaction even though weak in nature can influence the solvation dynamics in RTILs. (2) Rotational relaxation of organic solute becomes faster with the increase of alkyl chain length in anion because larger solvent molecules offer lower friction to the rotating solute. (3) Hindered rotational motion of organic solute (capable of H-bond formation) can be correlated with the hydrogen bond basicity of anion. (4) Trace amount of cosolvents can affect the solvation and rotational relaxation dynamics in RTILs in a significant manner. (5) The highly organised and heterogeneous nature of RTILs is revealed through diffusion-viscosity decoupling (d-η).

The future prospect and challenges are outlined at the end of the thesis.

References


