**Synopsis**

Solute-solvent interactions play an important role in chemical reactions and also on the physicochemical properties of liquids and solutions.\(^1\) Therefore, it is important to comprehend these interactions at the microscopic level. To achieve this objective, numerous photophysical processes have been examined to a large extent in neat liquids with the aid of theoretical and experimental techniques and the outcome of these results have been well-documented in the literature.\(^2\textendash}^6\) However, understanding these interactions in binary and complex fluids such as ionic liquids and reverse micelles is not trivial compared to neat liquids. These fluids have emerged as alternative reaction media not only in various chemical processes but also in numerous industrial applications.\(^7\textendash}^{12}\) Thus, to get a better appreciation of these interactions and obtain a broad-based understanding of chemical reactivity, various photophysical processes need to be investigated in complex fluids.

Rotational diffusion provides a valuable information about the solute-solvent interactions, while studies involving photoisomerization dynamics of olefins and polyenes enables us to understand role of solute-solvent frictional coupling on unimolecular chemical reactions. Both these processes have been thoroughly investigated in conventional solvents and the ensuing findings shed light on the role of specific interactions, viscous and dielectric frictions on solute rotation and photoisomerization.\(^1,13,14\) However, understanding of these phenomena in complex fluids especially, ionic liquids and reverse micelles, is at its infancy. Thus, this thesis is an
endeavor to comprehend the complex and diverse environments of ionic liquids and reverse micelles. This task has been accomplished with the aid of steady-state and time-

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\begin{align*}
&\text{9-phenylanthracene} \\
&\text{Rhodamine 110} \\
&\text{3,3'-diethyloxadicarbocyanine iodide (DODCI)} \\
&\text{Merocyanine 540 (MC 540)}
\end{align*}
\]

**Figure 1** Molecular structures of the solutes.
resolved fluorescence spectroscopic techniques. Fluorescence parameters such as quantum yields, lifetimes and reorientation times of suitable fluorescent probes dissolved in select complex fluids have been measured. Figure 1 gives the molecular structures of the fluorescent probes used in this thesis.

1-Alkyl-3-methylimidazolium-based ionic liquids [Rmim+] with strongly associating anions such as tetrafluoroborates ([BF₄⁻]) and hexafluorophosphates ([PF₆⁻]) as well as weakly associating anions bis(trifluoromethylsulfonyl)imides ([Tf₂N⁻]) and tris(pentafluoroethyl)trifluorophosphate ([FAP⁻]) have been chosen to investigate the solute rotation. For the purpose of photoisomerization studies, 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides have been employed. These imidazolium-based ionic liquids are selected because their physicochemical properties have been well-documented in literature.⁷,⁸,¹⁵-¹⁷ It has been established that the presence of nonpolar alkyl chains on the imidazolium cation induces van der Waals interactions in addition to Coulombic and hydrogen bonding interactions between the cation and anion leading to the formation of organized structure.¹⁸-²⁰ Thus, one of the main objectives of this thesis is to understand the influence of the organized structure of ionic liquids on the dynamical processes. Apart from ionic liquids, photoisomerization studies have been performed in reverse micelles formed with the anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT). The structural parameters of AOT reverse micelles have been well-characterized.²¹ Photoisomerization studies have been carried out in this system to identify a parameter that characterizes interfacial friction in reverse micelles.
The results obtained from the investigation of solute rotation and photoisomerization in complex fluids have been presented, analyzed and discussed extensively in this thesis. Based on the theme of the work, the thesis has been divided into six different chapters. A concise account of each chapter is given below.

**Chapter 1**

Chapter 1 deals with general introduction to photo-induced fundamental processes and the motivation for investigating them in complex fluids. After presenting a detailed description of the dynamical processes that have been undertaken in the present study, this chapter describes complex fluids and how they are different from molecular solvents. An elaborate account is given on the physicochemical and structural properties of ionic liquids, in particular, how the constituent ions and substituents present on either of the ions influence the formation of organized structure. A brief portrayal of microheterogeneous systems has also been presented in this chapter. Towards the end of the chapter, significance of the work presented in this thesis has been depicted.

**Chapter 2**

Chapter 2 gives an overview of how recent advances in laser Spectroscopy have enabled researchers to investigate photo-induced processes in condensed phase. This chapter essentially deals with steady-state and time-resolved fluorescence spectroscopic techniques that have extensively been employed to carry out the work presented in this thesis. A detailed description of various experimental techniques such as absorption
spectrophotometer, steady-state spectrofluorometer and time-resolved fluorescence spectrometer, which works on the principle of time-correlated single-photon counting (TCSPC),\textsuperscript{22} has been presented. The principle involved in TCSPC and the experimental set up have been discussed. Apart from these techniques, a brief account of rheometer and refractometer that have been used to measure auxiliary parameters such as viscosities and refractive indices, respectively, of various ionic liquids is also given.

**Chapter 3**

Chapter 3 deals with studies involving the rotational diffusion of a nonpolar solute 9-phenylanthracene (9-PA) and a cationic solute rhodamine 110 (R110) in 1-alkyl-3-methylimidazolium (alkyl = ethyl, butyl, hexyl and octyl) tetrafluoroborates and hexafluorophosphates. The objective of this work is to understand the influence of organized structure of these ionic liquids on solute rotation. For this purpose, reorientation times ($\tau_r$) of 9-PA and R110 have been measured in [Rmim$^+$][BF$_4^-$] and [Rmim$^+$][PF$_6^-$] as a function of viscosity ($\eta$) by varying the temperature ($T$) as well as length of the alkyl chain on the imidazolium cation. The observed results have been analyzed with the aid of Stokes-Einstein-Debye (SED) hydrodynamic theory.\textsuperscript{23,24} It has been observed that for a given $\eta/T$, rotation of 9-PA becomes significantly faster with an increase in the length of the alkyl chain from ethyl to octyl on the imidazolium cation, whereas in case of R110, faster rotation of the solute has been observed at higher values of $\eta/T$. In other words, two slopes have been obtained in $\tau_r$ versus $\eta/T$ plots of R110 corresponding to lower and higher values of $\eta/T$. Despite displaying distinct trends,
rotational diffusion of both 9-PA and R110 in [Rmim\(^+\)][BF\(_4^-\)] and [Rmim\(^+\)][PF\(_6^-\)] deviates significantly from the predictions of SED theory. Even the quasihydrodynamic theories of Gierer-Wirtz (GW) and Dote-Kivelson-Schwartz (DKS), which take into consideration parameters such as solvent size and free volume, fail to explain the observed results. These trends, however, could be rationalized by taking into consideration the organized structure of the ionic liquids. The nonpolar solute 9-PA senses viscosity that is lower than the bulk viscosity due to the presence of organized domains whose size increases upon increasing in the length of the alkyl chain on the imidazolium cation and thus leading to the faster rotation of the solute. In contrast, at higher values of \( \eta/T \), diminishing hydrogen bonding interactions between the cationic solute R110 and the anions, which transpire as a consequence of the organized structure of the ionic liquids, appears to be responsible for the observed behavior.

Chapter 4

This chapter deals with the rotational diffusion of 9-PA and R110 in 1-alkyl-3-methylimidazolium-based ionic liquids (alkyl = methyl to octadecyl) with a weakly associating anion bis(trifluoromethylsulfonyl)imide ([Tf\(_2\)N\(^-\)]). From the results portrayed in the previous chapter it is evident that the presence of strongly associating anions such as [BF\(_4^-\)] and [PF\(_6^-\)] induces the formation of organized structure in ionic liquids even when length of the alkyl chain on the imidazolium cation is short and such an organized structure affects solutes rotation. Thus, the work presented in this chapter is essentially undertaken to find out the role of weakly associating anion and long alkyl chains on
solute rotation as the formation of organized structure governed by these two properties of the ionic liquids.\textsuperscript{25,26} To this effect, reorientation times of 9-PA and R110 have been measured as a function of viscosity by varying the temperature in each member of the solvent series. The observed results have been analyzed using SED hydrodynamic theory, \( \tau_r = A(\eta/T)^n \), where \( A \) is the ratio of the hydrodynamic volume of the solute to the Boltzmann constant and \( n = 1 \) as predicted by the SED theory. It has been observed that, for both the solutes, \( A \) and \( n \) decrease with an increase in the length of the alkyl chain from methyl to octadecyl on the imidazolium cation, especially from the octyl derivative onward indicating the failure of the SED theory. It may be noted that in case of imidazolium-based ionic liquids with weakly associating anions, organized structure forms only in the presence of the longer alkyl chains on the imidazolium cation. The nonpolar solute, 9-PA, resides in the nonpolar regions of the organized structure, whereas the cationic solute R110 is probably located at the interface between the nonpolar domain and ionic region. An increase in the length of the alkyl chain on the imidazolium cation leads to the formation of larger organized structure, which results in the faster rotation of the solutes at a given \( \eta/T \). In essence, an increase in the length of the alkyl chain on the imidazolium cation facilitates rotation of nonpolar as well as charged solutes despite being located in different regions of the organized structure.

Chapter 5

Chapter 5 describes photoisomerization of a carbocyanine derivative 3,3'-diethyloxadicarbocyanine iodide (DODCI) in 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, propyl, butyl and hexyl) bis(trifluoromethylsulfonyl)imides. The present
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stigation has been undertaken to find out whether photoisomerization of DODCI in ionic liquids is any different compared to that observed in conventional solvents such as alcohols. For this purpose, nonradiative rate constants (\(k_{nr}\)) have been obtained from the measured fluorescence lifetimes and quantum yields. It may be noted that \(k_{nr}\) represents rate of photoisomerization for DODCI. The activation energy of the reaction has been calculated from the isoviscosity plots and found to be 22±3 kJ mol\(^{-1}\), which is a factor of two higher compared to that reported in alcohols (11.3 kJ mol\(^{-1}\)). The most probable reason for higher activation energy in ionic liquids compared to alcohols is due to the highly organized structure of ionic liquids,\(^{27}\) which inhibits the excited-state twisting process. To understand the reduced isomerization rate constants in terms of solvent friction, Kramers hydrodynamic theory, has been applied. However, Kramers model fails to predict the variation in the reduced isomerization rate constants with viscosity. An empirical power-law relation adequately describes the observed trends. Somewhat similar behavior that has been observed for the DODCI isomerization in alcohols in the ground and excited-states is also discussed.\(^{28,29}\) The observed deviation from Kramers hydrodynamic theory could be due to frequency-dependent frictional effect. Therefore, to improve the agreement between the experiment and theory, frequency-dependent friction of the medium needs to be considered. This aspect has been substantiated by the observed nonlinear relationship between the friction and viscosity, especially at lower viscosities.
Chapter 6

Chapter 6 presents photoisomerization of two carbocyanine derivatives, 3,3'-diethyloxadecarbocyanine iodide (DODCI) and merocyanine 540 (MC 540) in reverse micelles formed with the anionic surfactant bis(2-ethylhexyl) sodium sulfosuccinate (AOT). Essentially, this study has been performed to identify the parameter that characterizes photoisomerization process in the interfacial region of reverse micelles. For these solutes, nonradiative rate constants \( k_{nr} \) have been identified as rates of photoisomerization. Thus, nonradiative rate constants of DODCI and MC 540 have been obtained from the measured fluorescence lifetimes and quantum yields as a function of the mole ratio of water to the surfactant \( W \) in AOT/isoctane/water and AOT/cyclohexane/water reverse micellar systems. It has been established that the solutes DODCI and MC 540 are located in the interfacial region of both the reverse micellar systems at all values of \( W \) employed in this study. For DODCI and MC 540 in the two AOT reverse micellar systems, \( k_{nr} \) increases upon increasing \( W \), however, this increase is not uniform reaches saturation at higher values of \( W \). If \( k_{nr} \) values of DODCI and MC 540 were solely dependent on the water pool radius \( R_w \), they should have increased linearly with \( W \) as these two parameters \( (W \text{ and } R_w) \) have a linear dependence. However, saturation of \( k_{nr} \) has been observed at higher values of \( W \) for both the solutes in the two AOT reverse micellar systems, which is an indication that \( R_w \) is not the sole parameter that governs this process. It is a well-known fact that an increase in \( W \) not only increases \( R_w \) but also alters other structural parameters such as aggregation number \( (N_a) \) and
hydrodynamic radius \( (R_h) \) of the reverse micelles. Thus, to explain the observed results, all these structural parameters of the AOT reverse micellar systems have been considered and it may be noted that both \( N_a \) and \( R_h \) also increase with \( W \).\(^{21}\) Such an increase in \( N_a, R_w \) and \( R_h \) influences the critical packing parameter. It is defined as \( \nu/a_0 l_c \), where \( \nu, a_0 \) and \( l_c \) are respectively, volume of the hydrophobic tail, effective head group area and effective chain length of the hydrophobic tail. The critical packing parameter has been calculated with the aid of \( N_a, R_w \) and \( R_h \) using appropriate formulae.\(^{30}\) Critical packing parameter for AOT/isoctane/water and AOT/cyclohexane/water decreases upon increase in \( W \), however, this decrease is not uniform but reaches saturation at higher values of \( W \). Therefore, the steady rise and subsequent saturation observed in \( k_{nr} \) has been rationalized with the aid of critical packing parameter. An inverse correlation has been obtained between \( k_{nr} \) and \( \nu/a_0 l_c \), which indicates that the critical packing parameter can be employed to depict interfacial friction in reverse micelles.
References

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