# Photoinduced Electron Transfer in an Imidazolium Ionic Liquid and in Its Binary Mixtures with Water, Methanol, and 2-Propanol: Appearance of Marcus-Type of Inversion

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S Supporting Information

ABSTRACT: The photoinduced electron transfer (PET) reaction has been investigated in a room temperature imidazolium ionic liquid (RTIL), 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO$_4$]) and also in [Emim][EtSO$_4$]—co-solvents mixtures from *N,N*-dimethyl aniline (DMA) to different Coumarin dyes using steady state and time-resolved fluorescence quenching measurements. We have used water and methanol and 2-propanol as the co-solvents of RTILs for the PET study. On going from neat ionic liquid to the RTIL—co-solvents mixtures the electron transfer rate has been largely enhanced. In neat RTIL as well as in [Emim][EtSO$_4$]—co-solvents mixtures, a Marcus type of inversion in the PET rate have been observed.
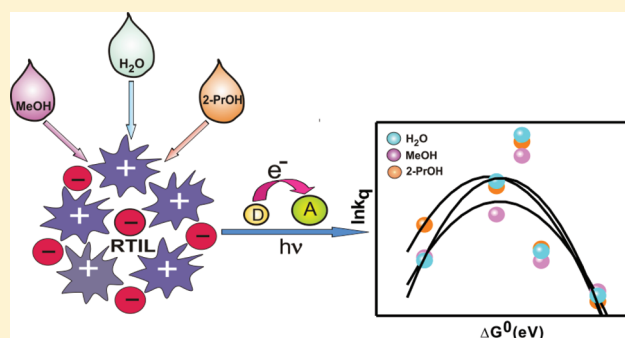
1. INTRODUCTION

Room temperature ionic liquids (RTILs) have attracted a rapidly increasing interest in recent years as the physical and chemical properties of ionic liquids can be fine-tuned through the selection of their cation and anion moieties; therefore, RTILs are also called as "designer solvents". RTILs are composed solely of ions, a bulky organic cation and non coordinating anions. RTILs became an alternative to various toxic and hazardous solvents in analytical chemistry to overcome the mentioned difficulties and are considered environmentally benign solvent media as a result of their potential low toxicity, negligible vapor pressure, high thermal stability, low flammability, and capability of dissolving a wide range of organic and inorganic compounds.[1] Ionic liquids have wide applications such as in organic synthesis and also various physical, photophysical and ultrafast spectroscopic studies were carried out in these RTILs.[2−6] RTILs are polar liquids, the polarity of neat RTIL is close to that of short chain alcohols.[2] In particular, the addition of cosolvents like water, methanol, etc. can strongly affect the physical and chemical properties of ionic liquids such as viscosity, electrical conductivity, and reactivity as well as solvation and solubility properties.[5] Previous results from our group have shown that addition of small amounts of co-solvents to ionic liquids lowers the viscosity of ionic liquids drastically.[5a−e] The lowering effect in viscosity of ionic liquids can be greatly enhanced by selecting a polar solvent. Some recent publications have demonstrated that the commonly used ionic liquids are reasonably polar solvents, having polarity greater than those of solvents like acetone, dimethyl sulfoxide, dichloromethane, etc. but less than those of water and short chain alcohols.[7a] The polarity values of the pure liquids confirm to the values reported in

the literature.[7b−d] There are several publications devoted to experimental and theoretical thermodynamic studies on pure ILs and their mixtures with water and common organic solvents most of them concerning imidazolium-based ILs.[7e−g] Properties of binary liquid mixtures have been extensively studied to understand the nature and extent of various intermolecular interactions existing between different species present in the mixtures. In binary mixtures, preferential solvation is a very common phenomenon, which leads to many interesting consequences. Of particular interest are the effects of water and numerous studies on ionic liquid/water systems have been made.[8a−c] Compared with the intensive investigations on the ionic liquid/water mixtures, there have been a few reports on solvation behavior of ionic liquid in nonaqueous molecular liquids.[8d−f] The study of time dependent solvation in neat RTILs by using dipolar solutes have been a subject of recent interest due to several unique feature of these green solvents.[2−6] These studies showed that nature of solvation dynamics in RTILs are very complex and the presence of structural heterogeneity in neat RTILs affect rates of several dynamical processes.[4d] There are some reports in the literature on the time dependent solvation in an RTILs—cosolvents mixture.[5a−d] The interaction between water and cations and anions of RTILs was investigated.[9] These studies showed that water form strong hydrogen bond with the anion of RTILs and cation also strong interaction with the water molecules.[9b,d] The interaction between RTILs with other solvents such as methanol, propanol, etc. are also studied.[9e−h] In this

paper we would like to investigate how the dynamics of photo-induced electron transfer is affected in this type of RTILs—cosolvents mixtures.

Photoinduced electron transfer (PET) from donor to acceptor as one of the most fundamental and important processes occurring in chemistry and biology.[10] The conventional ET theory is originally proposed by Marcus[10c] and thereafter further modifications on quantum-mechanical aspects have been incorporated into this. The simplified form of the rate constant of ET is given by

$$k_{ET} = \nu \exp\left[\frac{-(\Delta G^{\circ} + \lambda)^2}{4\lambda k_B T}\right] \qquad (1)$$

where, ν is the frequency of the motion in the reactant potential well, λ is the composite reorganization energy, given as $(\lambda_s + \lambda_i)$, λ_s being the solvent reorganization energy and λ_i being the intramolecular reorganization energy, ΔG^0 is the free energy change for the overall process and k_B is the Boltzmann constant. The most important feature of the above expression is that with increase in ΔG^0 the rate constant initially increases, reaches a maximum at $-\Delta G^0 = \lambda$ and then decreases when $-\Delta G^0 > \lambda$. The theoretical and experimental investigations have been carried out on dynamical aspect of electron transfer in different neat solvents.[11] Previously PET reactions have been well studied in homogeneous solution.[11a−g] Bagchi et al. have reported interplay between ultrafast polar solvation and vibrational dynamics in electron transfer reactions, the role of high-frequency vibrational modes and also the effects of ultrafast solvation on the rate of adiabatic outersphere electron transfer reactions.[11h,i] In organized media the local microenvironment of the reactant molecules is vastly different than that of in homogeneous media thus the dynamics and the mechanism of the reaction should also differ from homogeneous media. PET in different types of organized assembly received a considerable attention in recent studies because of its significant application in many chemical and biological processes.[12−14] PET has been reported in neat RTILs.[15a−e] The main disadvantage of using neat RTILs as a solvent media for photophysical studies is their immiscibility with solute molecules, which can be overcome by adding different cosolvents, for this the use of several binary and ternary mixtures of RTILs with cosolvents has been introduced.[15f−h] The local microenvironment surrounding the probe molecule such as viscosity, density. etc. may change due to presence of some amount of cosolvents in RTILs,[15i,j] for this reason this type system is very much interesting for photophysical studies. Margulis et al.[16a] investigated the excited state intramolecular electron transfer reaction of crystal violet lactone (CVL) in the room temperature ionic liquid (RTIL) N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide $[Pr_{31}^+][Tf_2N^-]$ using molecular dynamics simulation. Moreover, recently Lynden-Bell[16b,c] has investigated some simulation studies of model systems of two ionic liquids and compared them with acetonitrile to judge the applicability of Marcus theory in ionic liquids. The free energy and dynamics of PET reaction in a RTIL and in supercritical water and the reaction dynamics and kinetics of adiabatic electron transfer in a RTIL has been well studied by Kim et al.[16d−f] Recently, Wasielewski and co-worker has been reported the intramolecular electron transfer within a covalent, fixed-distance donor−acceptor molecule in an ionic liquid[16g] and Li et al.[16h] has reported hindered intramolecular electron transfer in a room temperature ionic liquid. We have investigated PET in a protic RTIL[15d] and observed saturation in the PET correlation curve like other homogeneous

Table 1. Absorption and Emission Maxima of the Coumarin Dyes in Neat $[Emim][EtSO_4]$ and in $[Emim][EtSO_4]-$ Co-Solvent Mixtures

system	mole fraction	$\lambda_{abs}^{max \square}$ (nm)	$\lambda_{emi}^{max \square}$ (nm)
C-153	neat RTIL	431	533
	neat RTIL+0.6 water	434	541
	neat RTIL+0.6 methanol	431	536
	neat RTIL+0.6 2-propanol	431	533
C-151	neat RTIL	387	484
	neat RTIL+0.6 water	385	488
	neat RTIL+0.6 methanol	385	485
	neat RTIL+0.6 2-propanol	387	484
C-152	neat RTIL	403	515
	neat RTIL+0.6 water	406	521
	neat RTIL+0.6 methanol	404	518
	neat RTIL+0.6 2-propanol	404	513
C-152A	neat RTIL	409	508
	neat RTIL+0.6 water	412	516
	neat RTIL+0.6 methanol	409	512
	neat RTIL+0.6 2-propanol	408	507
C-480	neat RTIL	388	465
	neat RTIL+0.6 water	392	477
	neat RTIL+0.6 methanol	387	473
	neat RTIL+0.6 2-propanol	388	469

solvents and neat solvents reported previously and also performed PET in an imidazolium ionic liquid varying excitation wavelength and observed Marcus type of inversion in the PET correlation curve.[15e] We have also performed PET in ionic liquid containing microemulsion systems[14f] and also in a ionic liquid forming micellar structure in water.[14g]

In this study the PET reaction has been carried out in a room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium ethyl sulfate ($[Emim][EtSO_4]$) and also with addition different mole fraction of the cosolvents in this ionic liquid from N,N-dimethyl aniline (DMA) to different Coumarin dyes using steady-state and time-resolved fluorescence quenching measurements. Water, methanol, and 2-propanol have been used here as the cosolvents of the ionic liquid. We have already performed solvation dynamics study in this system and observed faster solvation rate in the RTIL−co-solvents mixtures than that of neat ionic liquid media due to decrease in the viscosity of the medium.[5a] In this PET study, we kept the mole fraction of the cosolvents similar to that used in our previous solvation dynamics study in the same systems to make a generalized conclusion of the ionic liquid−co-solvent mixtures from both the solvation dynamics and PET studies. The geometry optimization of $[Emim][EtSO_4]$ and $[Emim][EtSO_4]-$ co-solvent mixtures were performed by DFT calculation which confirmed the hydrogen-bonded complex formation in neat RTIL as well as in RTIL−co-solvents mixtures.[5a] For this reason we are very much interested to observe nature of the PET dynamics in this RTIL and RTIL−co-solvents mixtures systems and also we want to compare the rate of ET in neat ionic liquid media with that of ET rate in RTIL−co-solvents mixtures. Although solvation dynamics have already been reported in RTIL−co-solvents mixtures but until now there is no report available on PET study in this type of systems. Because of this reason, we have chosen this system for electron transfer study.
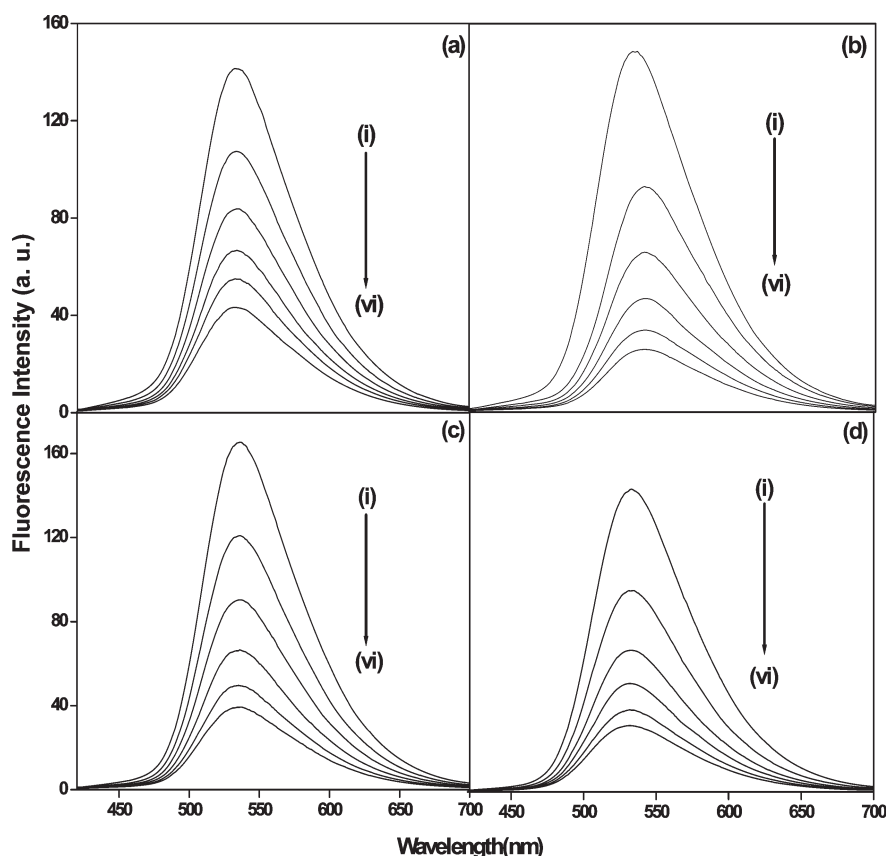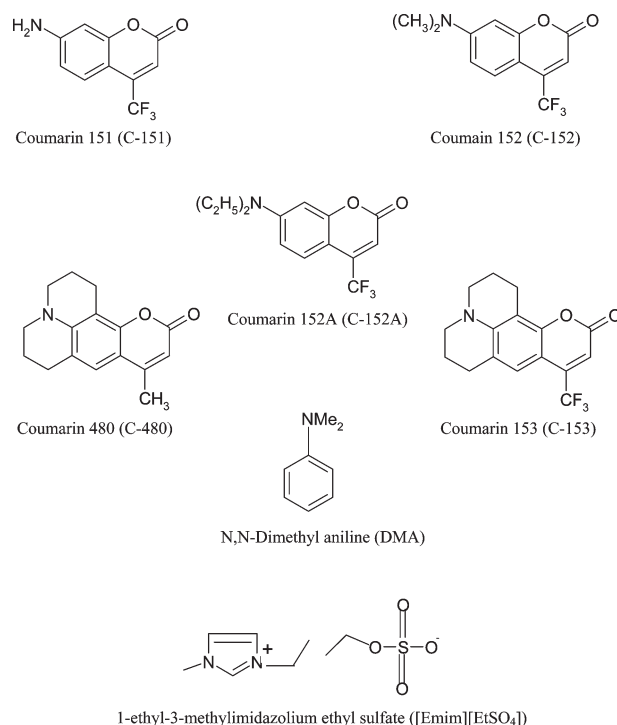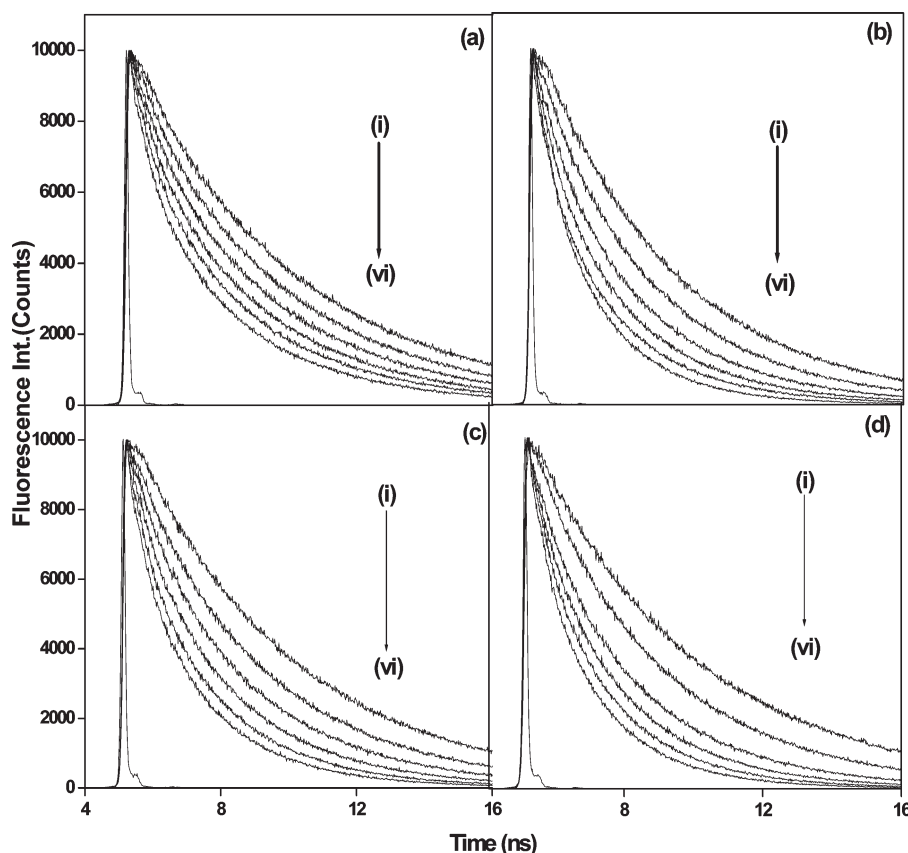
Figure 1. Steady state fluorescence quenching of C-153 with the gradual addition of 0 mM to 330 mM DMA in (a) neat $[Emim][EtSO_4]$ and with the addition of (b) 0.6 water, (c) 0.4 methanol, and (d) 0.6 2-propanol.

2. EXPERIMENTAL SECTION

The Coumarin dyes were obtained from Exciton (laser grade), used as received. N,N-Dimethyl aniline (DMA) was obtained from Aldrich chemical and distilled under reduced pressure before use. 1-Ethyl-3-methylimidazolium ethylsulfate ($[Emim][EtSO_4]$) was obtained from Solvent Innovation (>99% purity) and used as received. Methanol and 2-propanol (UV spectroscopic grade) were purchased from Spectrochem, India. The final concentration of all acceptor Coumarin molecules in the experiment was kept $\sim5 \times 10^{-6}$ M. The probe molecules were initially dissolved in methanol and transfer to a vial. The RTIL was added to the vial under nitrogen atmosphere in a glovebox and stirred for 10−20 min after removing the methanol under vacuum for several hours. Then the solution was transferred to a quartz cuvette in a glovebox and sealed with septum and parafilm. Since RTIL absorbs moisture from air so we kept the sample in a vacuum desiccators overnight between spectroscopic studies to avoid moisture absorption. During addition of DMA, each and every time the solution was allowed to mix thoroughly so that the quencher molecules adequately mixed in the solution. The absorption and fluorescence spectra were measured using a Shimadzu (model no: UV-1601) spectrophotometer and a Jobin Yvon Fluorolog-3 spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the instrument. For steady-state experiments, all samples were excited at 410 nm. The time-resolved fluorescence setup is described in detail in our earlier publication.[14] Briefly, the samples were excited at 408 nm using a picosecond laser diode (IBH, Nanoled), and the signals were collected at

Scheme 1. Structure of the Coumarin Dyes, Dimethyl Aniline, and the RTIL 1-Ethyl-3-Methylimidazolium Ethyl Sulfate ($[Emim][EtSO_4]$)

Coumarin 151 (C-151)

Coumain 152 (C-152)

Coumarin 152A (C-152A)

Coumarin 480 (C-480)

N,N-Dimethyl aniline (DMA)

Coumarin 153 (C-153)

1-ethyl-3-methylimidazolium ethyl sulfate ([Emim][EtSO₄])

Figure 2. Time-resolved fluorescence spectra of C153 with the gradual addition of 0 mM to 330 mM DMA in (a) neat $[Emim][EtSO_4]$ and with the addition of (b) 0.6 water, (c) 0.4 methanol, and (d) 0.6 2-propanol.

magic angle (54.7°) polarization using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is ∼90 ps. The same setup was used for anisotropy measurements. For the anisotropy decays, we used a motorized polarizer in the emission side. The emission intensities at parallel $(I_∥)$ and perpendicular $(I_⊥)$ polarizations were collected alternatively until a certain peak difference between parallel $(I_∥)$ and perpendicular $(I_⊥)$ decay was reached. The analysis of the data was done using IBH DAS, version 6, and decay analysis software. The same software was also used to analyze the anisotropy data. All experiments were carried out at 298 K. The chemical structure of the Coumarin dyes, DMA and the ionic liquid are shown in Scheme 1.

3. RESULTS

3.1. Steady State Absorption and Emission Measurements. With gradual addition of water in $[Emim][EtSO_4]$ the absorption peak and the emission peak of the Coumarin dyes gradually red-shifted whereas with addition of 2-propanol in $[Emim][EtSO_4]$ the absorption peak and the emission peak of the Coumarin dyes either blue-shifted or remain constant. Coumarin-153 (C-153) in neat $[Emim][EtSO_4]$ shows an emission peak at 533 nm which is close to the emission maximum of C-153 in pure methanol (∼532 nm) concludes that the polarity of $[Emim][EtSO_4]$ is close to methanol. With gradual addition of water in $[Emim][EtSO_4]$ the emission peak of C-153 gradually red-shifted, i.e., with addition of water polarity of the mixture gradually increases. Whereas with gradual addition of methanol

and 2-propanol the emission peak of C-153 remain unchanged, i.e., with addition of methanol and 2-propanol polarity of the medium remains almost same. We have tabulated the absorption and emission maxima of all the probe molecules in neat RTIL as well as in RTIL—co-solvents mixtures in Table 1.
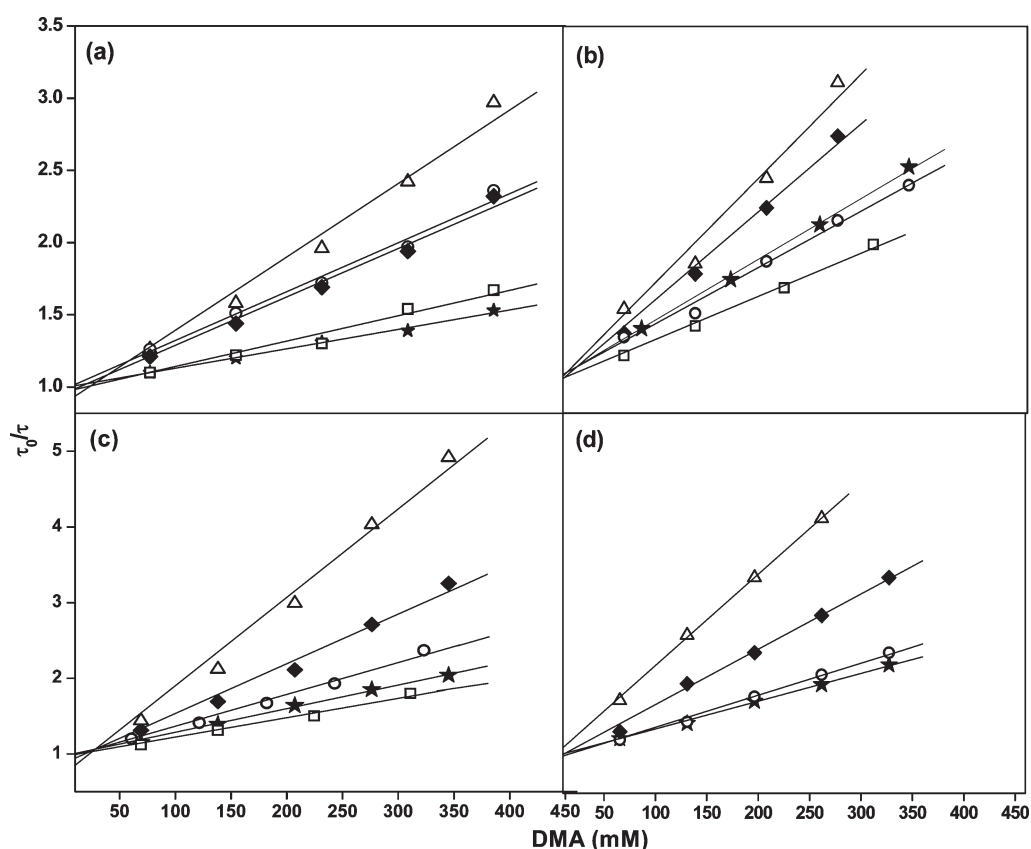
3.2. Quenching Study Using Steady State and Time-Resolved Fluorescence Measurements. We have investigated the fluorescence quenching experiments by gradual increase of the DMA concentration in the solution of Coumarin dyes in neat RTIL as well as in RTIL—co-solvents mixtures. With addition of DMA the fluorescence intensity of Coumarin dyes is continuously quenched both in case of steady state as well as time-resolved measurements (Figure 1 and Figure 2). The fluorescence-quenching constant is determined by well-known Stern—Volmer equation as

$$\frac{I_0}{I} = 1 + K_{SV}[Q] = 1 + k_q \tau_0[Q] = \frac{\tau_0}{\tau} \quad (2)$$

where, I_0 and I are the steady state fluorescence intensity and τ_0 and τ are the fluorescence lifetimes of the Coumarin dyes in absence and in presence of the quencher, K_{sv} is the Stern—Volmer constant, and $[Q]$ is the quencher concentration. The typical plot for τ_0/τ vs $[Q]$ for different Coumarin molecules with increasing concentration of DMA in neat ionic liquid as well as in RTIL—co-solvents mixtures are shown in Figure 3 and the k_q values obtained are listed in Table 2 and Table 3. The time-resolved fluorescence decays were fitted by biexponential function and the lifetime was calculated by averaging the component by using the equation

$$\langle \tau_{av} \rangle = \langle \tau \rangle = a_1\tau_1 + a_2\tau_2 \quad (3)$$

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Figure 3. Stern−Volmer plots for τ_0/τ vs [DMA] of Coumarin dyes ($\triangle$) C-151, ($\blacklozenge$) C-153, ($\bigcirc$) C-152A, ($\bigstar$) C-480, ($\square$) C-152 in (a) neat [Emim][EtSO$_4$] and with the addition of (b) 0.6 water, (c) 0.4 methanol, and (d) 0.6 2-propanol.

Table 2. Time-Resolved Quenching Constants, Ground State Redox Potentials of Donor and Acceptors, E_{00} Values, and ΔG^0 for Different Coumarin−DMA Systems Obtained in Neat [Emim][EtSO$_4$] and in [Emim][EtSO$_4$]−Alcohol Mixtures

systems	E_{00}(eV)	$E(C/C^-)$V/ (V s) SCE	$E(D/D^+)$V/ (V s) SCE	ΔG^0 (eV)	k_q^{TR} (10^9 M^{-1} S^{1-}) [Emim][EtSO$_4$] + alcohols						
					neat RTIL	0.2 MeOH	0.4 MeOH	0.6 MeOH	0.2 2-PrOH	0.4 2-PrOH	0.6 2-PrOH
C-153	2.543	−1.53	0.711	−0.392	0.745	0.967	1.447	1.662	0.987	1.312	1.698
C-151	2.846	−1.53		−0.695	0.928	1.232	1.518	1.954	1.235	1.685	2.29
C-152	2.709	−1.58		−0.508	1.204	2.373	2.607	3.562	2.404	2.981	3.724
C-152A	2.698	−1.635		−0.442	2.891	3.457	5.486	6.208	3.395	4.895	6.586
C-480	2.866	−2.00		−0.245	0.339	0.621	0.989	1.132	0.553	0.736	0.869

Table 3. Time-Resolved Quenching Constants, Ground State Redox Potentials of Donor and Acceptors, E_{00} Values, and ΔG^0 for Different Coumarin−DMA Systems Obtained in Neat [Emim][EtSO$_4$] and in [Emim][EtSO$_4$]−Water Mixtures

systems	E_{00} (eV)	$E(C/C^-)$V/(V s) SCE	$E(D/D^+)$V/(V s) SCE	ΔG^0 (eV)	k_q^{TR} (10^9 M^{-1} S^{1-}) [Emim][EtSO$_4$] + water		
					neat RTIL	0.2 water	0.4 water	0.6 water
C-153	2.543	−1.53	0.711	−0.362	0.745	1.019	1.297	1.639
C-151	2.846	−1.53		−0.665	0.928	1.207	1.334	1.457
C-152	2.709	−1.58		−0.478	1.204	2.604	3.287	3.979
C-152A	2.698	−1.635		−0.412	2.891	3.972	5.837	7.166
C-480	2.866	−2.00		−0.215	0.339	0.592	0.787	0.935

where, τ_1 and τ_2 are the two fluorescence lifetime components, and a_1 and a_2 are their relative amplitudes. The fluorescence decay parameters of the dye molecules are summarized in the Supporting Information.

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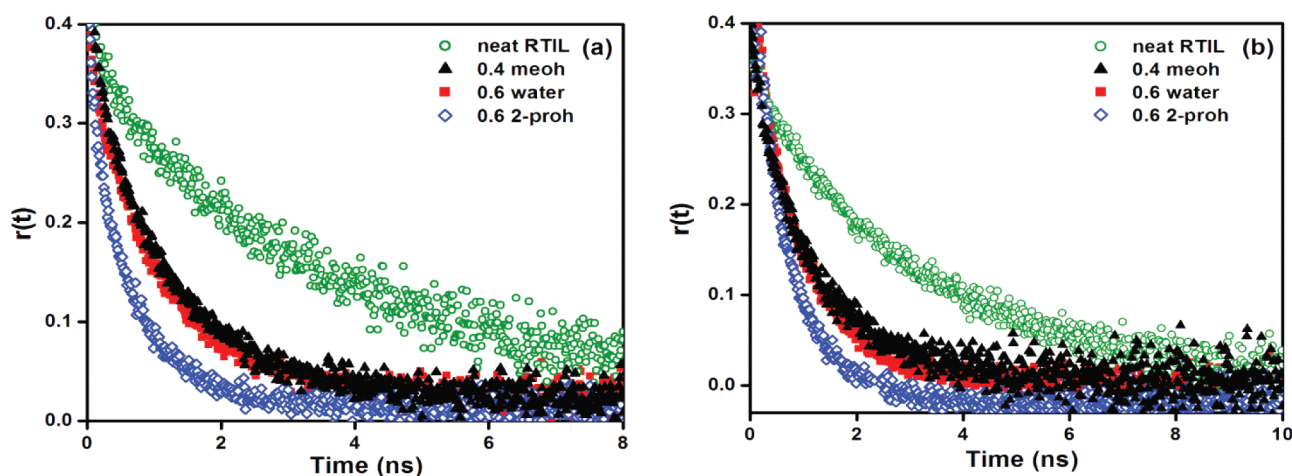
Figure 4. Decay of fluorescence anisotropy ($r(t)$) of (a) C-153 in (i) neat $[Emim][EtSO_4]$ (○) and with the addition of (ii) 0.4 MeOH (▲), (iii) 0.6 water (■), and (iv) 0.6 2-PrOH (◇) and (b) C-480 (i) neat $[Emim][EtSO_4]$ (○) and with the addition of (ii) 0.4 MeOH (▲), (iii) 0.6 water (■), and (iv) 0.6 2-PrOH (◇).

3.3. Time-Resolved Anisotropy Measurements. Time resolve fluorescence anisotropy measurements have been carried out to determine of the location of the probe molecules in the RTIL—co-solvents mixtures. The expression used to calculate the fluorescence anisotropy is as follows:

$$r(t) = \frac{I_\parallel(t) - GI_\perp(t)}{I_\parallel(t) + 2GI_\perp(t)} \quad (4)$$

Here, $I_{//}(t)$ and $I_\perp(t)$ are the fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. G is the correction factor for detector sensitivity to the polarization direction of the emission. The emission intensities at parallel ($I_\parallel$) and perpendicular ($I_\perp$) polarizations were collected alternatively until a certain peak difference between parallel ($I_\parallel$) decay and perpendicular ($I_\perp$) decay was reached. The absorption and emission spectra can give a qualitative idea regarding the location of the probe molecules. This can be more accurately predicted by the time-resolved fluorescence anisotropy measurements. Our system is a binary solvent mixture system, i.e., ionic liquid—water and ionic liquid—alcohol. With addition of cosolvents in the RTIL [Emim][EtSO_4] the rotational relaxation time of the Coumarin molecules gradually decreases. The anisotropy decays were fitted to a biexponential function in all the RTIL—co-solvents mixtures. The fitted results of average rotational relaxation time for all the Coumarin dyes in neat ionic liquid and in ionic liquid—co-solvent systems are summarized in Table 4. The representative decays of time-resolved fluorescence anisotropy plots in neat ionic liquid and in RTIL—co-solvents mixtures of C-153 and C-480 molecules are given in Figure 4.

4. FREE ENERGY CHANGE

The electron transfer (ET) rate depends on the free energy change of the system. In the Marcus type of system, the ET rate initially increases with negative change in the free energy gap, reaches a maximum and then decreases with further negative change in the free-energy gap. The last region is called the Marcus inverted region. The common expression for calculating ΔG^0 is given by the famous Rehm—Weller equation[17a] and we have calculated free energy change using the following equation

$$\Delta G^\circ = E(D/D^+) - E(A/A^-) - E_{IPS} - E_{00} \quad (5)$$

where, E_{00} is the energy difference between S_0 and S_1 states, which was obtained from the intersecting point of normalized fluorescence and normalized absorption spectra. $E(D/D^+)$ and $E(A/A^-)$ denote the oxidation potential of the donor and reduction potential of the acceptor, respectively. We have used the standard values of oxidation and reduction potentials of ethanol for free energy change calculation as the emission maxima of most of the probe molecules in neat $[Emim][EtSO_4]$, $[Emim][EtSO_4]$—methanol, and $[Emim][EtSO_4]$—2-propanol are almost similar to ethanol medium.[17b] Since the position of the emission maxima depends on the polarity of the medium, and thus it can be expected the similar type of polarity of both the system. The expression for E_{IPS} is

$$E_{IPS} = \frac{e^2}{\varepsilon_0 r} \quad (6)$$

where e is the charge of the electron and ε_0 is the static dielectric constant of the medium. We have used the dielectric constant of ethanol for calculation of E_{IPS} for the same reason. But in the case of $[Emim][EtSO_4]$—water systems, the emission maxima of the Coumarin dyes largely red-shifted and becomes almost similar to that of the emission maxima in 50% ethanol.[17b] For this reason we have calculated the ΔG^0 value in $[Emim][EtSO_4]$—water systems using the dielectric constant of 50% ethanol. Here "r" is the distance between the donor and the acceptor, is assumed to be the sum of the radii of the donors and the acceptors. The radii of the donor and acceptor molecules were estimated by following Edward's volume addition method assuming the molecules to be spherical.[17c] We have calculated ΔG^0 values in all the systems for each Coumarin—amine systems, and the results thus obtained are summarized in Tables 2 and 3.

5. DISCUSSION

In this study, we have investigated the dynamics of photoinduced electron transfer process between N,N-dimethylaniline and Coumarin dyes in a room temperature ionic liquid [Emim][EtSO_4], and in $[Emim][EtSO_4]$—co-solvent mixtures. The PET reaction between Coumarin dyes and amines have been extensively studied in homogeneous acetonitrile solution.[11] In homogeneous solution, the donor and acceptor are free to move as they

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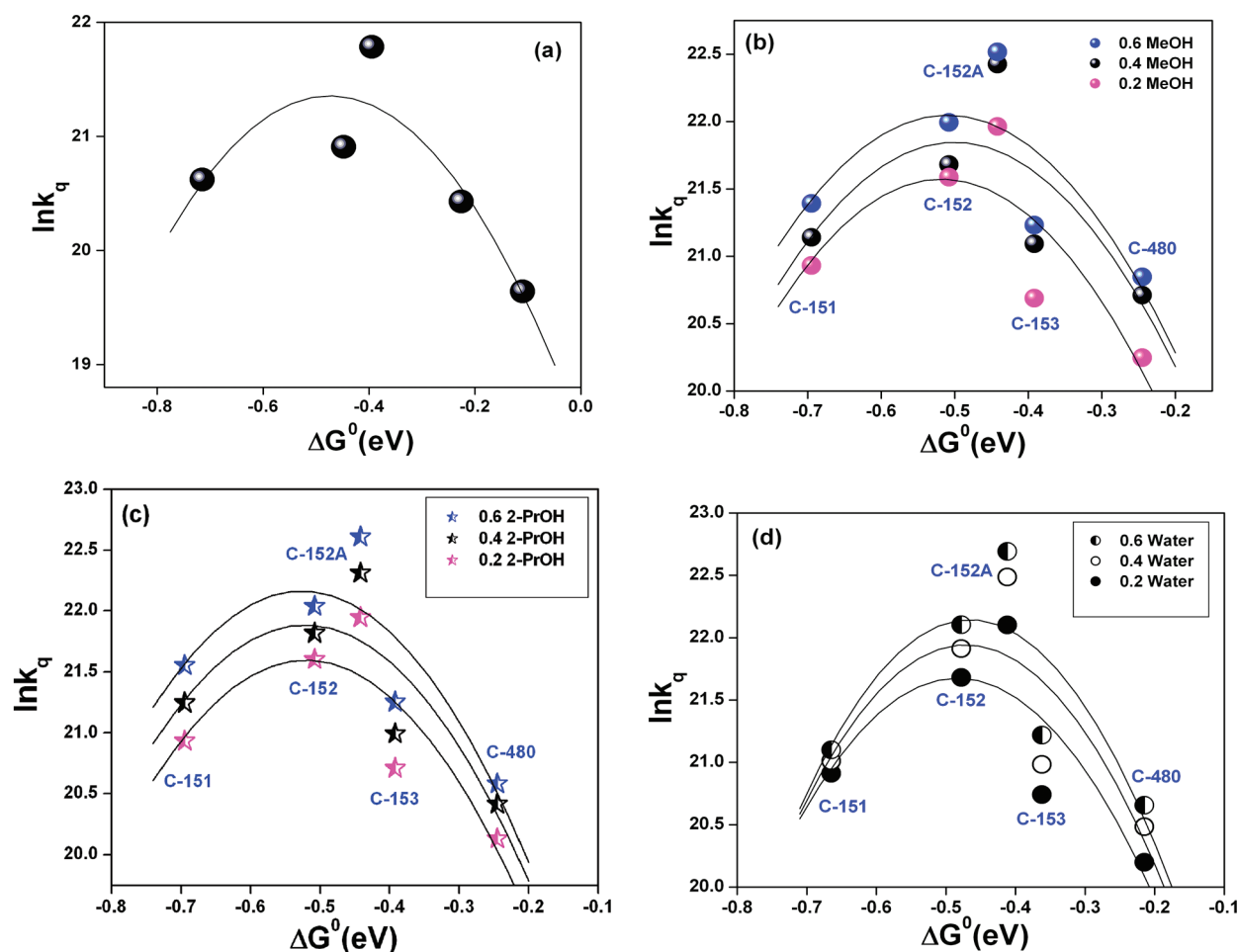
Figure 5. (a) Plot of ln k_q vs ΔG^0 for Coumarin—DMA system in (a) neat [Emim][EtSO$_4$], and 0.2, 0.4, and 0.6 mol fraction of (b) methanol, (c) 2-propanol, and (d) water.

can efficiently diffuse to a close contact to form the encounter complex but in the case of neat ionic liquid due to higher viscosity of the medium the diffusion of the reactants are restricted and as a result of that ET rate becomes slower than that of observed in the homogeneous solution. In our previous study on solvation dynamics in this ionic liquid—co-solvent system,[5a] we observed a faster solvation dynamics with addition of cosolvent because with addition of cosolvents the separation between cation and anion increases, which leads to a decrease in the electrostatic interaction between cation and anion. As a result of this, the bulk viscosity of [Emim][EtSO$_4$] gradually decreases with addition of cosolvents. For this reason, the diffusion of the donor and acceptor becomes more and more feasible which is also reflected in the present study on photoinduced electron transfer in this system. The electron transfer rate becomes 2 times faster or greater in RTIL—co-solvents mixtures rather than in neat ionic liquid.

We have plotted the Electron transfer rate constant k_q^{TR} with the free energy change (ΔG^0) for the system, in neat ionic liquid as well as in RTIL—co-solvents mixtures. In all these plots, initially PET rate increases with change in the free energy, reaches a maximum and then falls off; i.e., in the present case, we observed retardation in the electron transfer rate at higher free energy region (Figure 5) as predicted by Marcus ET theory.[10d] In our previous solvation dynamics study in this media we have observed the formation of hydrogen bonded complexes between

both the system in RTIL-water and also in RTIL-alcohols by B3LYP/6-31++G(d,p) level of optimization in the gas phase as well as by B3LYP/6-31+G(d,p) level optimization in solution phase. Recently Gopidas and co-workers showed that the Marcus inverted region could be obtained in a series of donors and acceptors when they are hydrogen bonded.[18] Thus, it can be predicted that the microenvironment of the probe molecules in RTIL—co-solvents mixtures is not at all like homogeneous solvents. The observed inversion at higher exergonicity has been attributed to the heterogeneous distribution of the probe molecules in this microenvironment. There are several reports available in the literature on PET in these type of microheterogeneous media, where Marcus type of inversion has been found due to the retardation of solvent motion and confinement of reactant molecules.[12−14] Here in both neat ionic liquid as well in all the mole fraction of RTIL—co-solvents mixtures, we observed an inversion in the ET rate at higher free energy region. The observation of Marcus inversion in the neat RTIL is particularly interesting because such inversion is rarely observed in a bulk liquid.[13e] Recently we have performed excitation wavelength dependent PET in a neat ionic liquid and observed a retardation in the PET rate at higher free energy region due to inherent heterogeneous behavior of the ionic liquid medium.[15e] The inversion appears for the C-151 probe molecule. C-151 is a hydrophilic probe so the dipole moment increases on excitation and it migrates toward the more polar region and also

C-151 has a free $-NH_2$ group and it may be hydrogen bonded with ionic liquid as well as in polar RTIL—co-solvents mixtures as because C-151 most probably forms ground-state complexes and can faced a restricted environment compared to the other Coumarin molecules which lead to the decrease in the electron transfer rate at higher free energy region. In bimolecular electron transfer reaction under diffusive condition,[17] the donor and acceptor are freely diffusing to the medium and the ET does not take place at a fixed donor—acceptor separation and occurs over a wide range of distance. The diffusional motion becomes faster due to decrease in viscosity of the medium. Here the diffusion of the reactant molecules increases from neat ionic liquid to that of IL—co-solvent mixtures due to decrease in the medium viscosity. As a result the donor and acceptor are more accessible to each other for reaction leads to an increase in the PET rate in IL—co-solvent system than that of in neat ionic liquid media. Under diffusive condition, the solvent reorganization energy is a dominating factor governing the ET kinetics. In a system if the ET rate (k_q^{TR}) is either higher or comparable with the solvation rate that causes a partial contribution to solvent reorganization energy. In such case many groups have used 2D-ET model.[12,13] In this 2DET model, the reorganizations along the intramolecular modes occur much faster than the solvent modes. Thus, the reactants can reach the transition state for ET via the involvement of these intramolecular modes even when the solvent modes are frozen altogether.[12] Under this situation, the ET rates can thus become faster than the solvation rates.[12,13] In our case the solvation rate is 3—3.5 times faster than the ET rate which results in full contribution of the solvent reorganization energy toward the activation barrier for the ET reaction.[12d]

The ET rates in $[Emim][EtSO_4]$—co-solvent mixtures are lesser than the PET rate in pure acetonitrile media but higher than ET rate in neat ionic liquid or other confined micellar, reverse micellar systems. In this case the PET rate is higher than the PET rate of RTIL micelle[14f] and RTIL-containing microemulsions,[14g] SDS micelle,[12b] and CTAB and DTAB micelle[12d] and almost similar to that of the PET rate in TX-100 micelle.[12c] Because

of the heterogeneity in the system of both neat RTIL and RTIL—co-solvents mixtures, the diffusion of the different Coumarin molecules should not be the same due to the differing strength in the binding of different Coumarin molecules in that environment and we have observed that the PET rate is highly retarded for C-151.

With addition of cosolvents in the RTIL the bulk viscosity of the mixture gradually decreases leads to decrease in rotational relaxation time. We observed from Table 4 that for all the probe molecules with the addition of alcohols in neat $[Emim][EtSO_4]$ the rotational relaxation time decreases more compared to the addition of water. The reason behind the anomalous behavior of the rotational relaxation data has been already explained in our previous study on solvation dynamics in this system,[5a] which was explained on the basis of microviscosity calculation that suggested that the calculated microviscosity of C-153 molecule in water was higher than that of 2-propanol and methanol, i.e., the probe molecules was facing more restricted environment in water than alcohols. In this PET study, also, we have observed the same effect in the rotational data for all the Coumarin molecules. In case of C-151, the PET rate is retarded at higher free energy region and we can see from Table 3 that with increase in mole fraction of water there is very little change in the k_q value but in case of methanol and 2-propanol (Table 2) there was certain increase in the k_q values. From Figure 5d we can see that the location of the C-151 molecule is almost fixed in the inverted region in all the plots of different mole fraction of water due to its restricted rotational motion in $[Emim][EtSO_4]$—water system. Finally we have demonstrated that both the neat $[Emim][EtSO_4]$ as well as the $[Emim][EtSO_4]$—co-solvent mixtures are inhomogeneous in nature.

6. CONCLUSION

The photoinduced electron transfer in a room temperature ionic liquid $[Emim][EtSO_4]$ and $[Emim][EtSO_4]$—co-solvents

Table 4. Rotation Relaxation Parameters of the Coumarin Dyes on Addition of Different Co-Solvents in $[Emim][EtSO_4]$

system	mole fraction	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$\langle\tau_r\rangle$ (ns)
C-153	neat RTIL	0.40	0.20	0.181	0.80	3.49	2.83
	neat RTIL + 0.6 water	0.40	0.17	0.088	0.83	1.089	0.92
	neat RTIL + 0.6 methanol	0.34	1	0.479	-	-	0.479
	neat RTIL + 0.6 2-propanol	0.39	0.28	0.112	0.72	0.728	0.555
C-151	neat RTIL	0.35	1	4.358	-	-	4.358
	neat RTIL + 0.6 water	0.39	0.09	0.087	0.91	1.050	0.963
	neat RTIL + 0.6 methanol	0.39	0.25	0.360	0.75	0.871	0.748
	neat RTIL + 0.6 2-propanol	0.40	1	0.776	-	-	0.776
C-152	neat RTIL	0.39	0.26	0.139	0.74	3.016	2.268
	neat RTIL + 0.6 water	0.37	1	0.974	-	-	0.974
	neat RTIL + 0.6 methanol	0.35	1	0.536	-	-	0.536
	neat RTIL + 0.6 2-propanol	0.35	1	0.716	-	-	0.716
C-152A	neat RTIL	0.32	1	2.284	-	-	2.284
	neat RTIL + 0.6 water	0.34	1	1.044	-	-	1.044
	neat RTIL + 0.6 methanol	0.30	1	0.487	-	-	0.487
	neat RTIL + 0.6 2-propanol	0.38	1	0.745	-	-	0.745
C-480	neat RTIL	0.40	0.18	0.124	0.82	3.070	2.540
	neat RTIL + 0.6 water	0.40	0.18	0.325	0.82	1.003	0.881
	neat RTIL + 0.6 methanol	0.35	0.50	0.321	0.50	0.695	0.508
	neat RTIL + 0.6 2-propanol	0.36	0.27	0.261	0.73	0.839	0.683

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mixtures have been successfully investigated by steady state and time-resolved fluorescence quenching measurements. Interestingly we have observed a Marcus type of inversion in the electron transfer rates vs free energy correlation curves in both the systems in neat RTIL as well as in RTIL—co-solvents mixtures indicating the presence heterogeneity in the systems. The nanostructural organization of neat ionic liquid and their nature as microsegregated media and our previous results on the geometry optimization by DFT calculation confirms the formation of hydrogen-bonded complex between in both the system of [Emim][EtSO$_4$]—water and [Emim][EtSO$_4$]—alcohols proves the heterogeneous behavior of both the systems. The diffusion of the molecules plays a very crucial role in governing the PET kinetics. The diffusion and the PET rate in the neat RTIL are slower than that in RTIL—co-solvents mixtures due to high viscosity of neat ionic liquid.

■ ASSOCIATED CONTENT

ⓈSupporting Information. Fluorescence decay parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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