# In Stationary Regime, Electron Transfer Rates in RTIL Media Are Diffusion Controlled: Experimental Evidence from Pulse Radiolysis Study

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Ⓢ *Supporting Information*

ABSTRACT: We report electron transfer (ET) process from the long-lived radical anions of pyrene and benzophenone to molecular acceptors, e.g., benzophenone and fluorenone, respectively, in two RTIL media, namely, [BMIM][PF₆] and [BMIM][BF₄], as well as a few other conventional organic solvents using the nanosecond pulse radiolysis technique. Decay of the donor radical anion and concomitant formation of the acceptor radical anion ensure a bimolecular ET process. The rate constants for the bimolecular ET process in both normal organic solvents and RTILs have been found to be nearly equal to diffusion controlled rate calculated for the corresponding solvent. For long-lived anions, having lifetimes longer than a few hundred nanoseconds, quenching occurs mainly in the stationary regime. In this regime, the ET rate is fully controlled by the rate of diffusion of the reactive species in those solvents. To the best of our knowledge, this is the first experimental evidence of the diffusion controlled ET process occurring in the stationary regime in RTIL media.
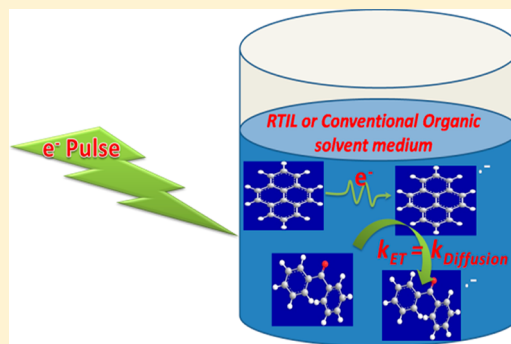
1. INTRODUCTION

Room temperature ionic liquids (RTIL) have drawn huge attention for research in recent years due to its environmental friendliness and other various potential applications.[1−10] They possess excellent properties like nonvolatility, nonflammability, recyclability, as well as good thermal and radiation stability.[3,11−14] All these properties make them good substitutes for conventional organic solvents. In addition, they can solubilize most of the inorganic and organic reagents and possess a large electrochemical window, which makes them useful for synthesis[11,13] and solar cell applications.[12,15−17] Due to their good radiation stability, they are expected to be future solvents for nuclear fuel cycle including actinide electro-refining[18] and solvent extraction.[19]

Counter ions present in RTILs generally possess low charge density, so the electrostatic interactions are not strong enough to make them solid at room temperature. Hence they appear as highly viscous solvents in ambient conditions. In spite of great research efforts in recent years, the properties of RTILs are not yet well understood. Several groups have reported the heterogeneous nature of these solvents,[1,9,10] and efforts have been made to probe the heterogeneity by studying some basic chemical processes like hydrogen atom transfer,[20] electron transfer,[21−31] solvation dynamics,[1] etc. With electron transfer (ET) being the soul of a redox process, several reports have been published on the study of ET processes in RTIL media.[21−31] Skrzypczak and Neta have reported that the ET rate in a RTIL is about an order of magnitude larger as compared to the calculated diffusion controlled rate in the same

medium.[21] To explain the reason for this difference, they predicted the existence of voids in ionic liquids and the possibility that diffusion of reacting species took place through movement of segments of ions while the viscosity was related to the movement of the whole ions. Paul and Samanta observed that the rate of photoinduced electron transfer (PET) reactions is 2−4-fold higher than the diffusion-controlled value, and they suggested that the microviscosity around the electron donor and acceptor was different from the bulk viscosity of the RTILs.[22]

Recently, Maroncelli and co-workers showed that, like in RTIL, the faster rate of an ET process could also be observed in conventional organic solvents of similar viscosity.[30] They proposed a model to explain that the following two factors were responsible for faster ET rate in highly viscous solvents. First, the quenching took place in the transient regimes due to the short-lived nature of the transients, and hence the diffusion controlled ET process was not observed. Second, the reactants possessed lower hydrodynamic radius than that of the solvent, and hence they could diffuse much more rapidly than the expected diffusion rate. Hence, they recommended that ET reaction involving long-lived transients should be an ideal probe to observe the ET process in the diffusion controlled regime.

In a recent communication, Vauthey and co-workers described the dynamics of PET reaction between N,N-

dimethylaniline and the excited state of 3-cyanoperylene in three RTILs [namely, 1-ethyl-3-methyl-imidazolium dicyanamide (BMIDCA), 1-butyl-3-methyl-imidazolium dicyanamide (EMIDCA), and 1-ethyl-3-methyl-imidazolium ethylsulfate (EMIES)] as well as in the binary mixtures of two conventional solvents (DMSO and Glycerin) of similar viscosities.[31] They concluded that, in all these cases, the diffusive motion of the reactants was very similar in RTILs and conventional solvents of comparable viscosity. They assigned the reason for the faster ET process in RTILs to the highly viscous nature of the solvents, but not related to the ionic nature of the RTILs. Faster ET rate in highly viscous solvents was explained by considering three quenching regimes, namely, *static, transient and stationary*. In the case of highly viscous solvents, transients having lifetimes of a few nanoseconds get quenched mainly in the *static and transient regime* and the average ET rate appears faster than the diffusion controlled rate.

Vauthey and co-workers used the diffusional encounter theory (DET) to calculate the time-dependence of the ET rate, which decreases steadily while passing through the static and transient regimes, and the stationary value is attained only after more than a few nanoseconds even in solvents of low viscosity.[31] The most important results reported by Vauthey and co-workers revealed that while the rate of intrinsic ET reaction occurring in the static and transient regime is controlled by the free energy of reactions, solvent dynamics and concentration of the quencher and the rate of the ET reaction, as well as the onset of the stationary quenching regime, depend entirely on the viscosity of the solvent and not on its dipolar or ionic nature. Time dependence of the rate coefficients calculated using DET revealed that the stationary value, k_{diff} is attained only after a few microseconds in the case of solvents of very large viscosity (say, ~100 cP). In the *stationary regime*, quenching is possible only after substantial diffusion, and an equilibrium between the formation of the reactant pairs by diffusion and their decay upon reaction is attained giving rise to a constant reaction rate.[31]

Pulse radiolysis has been proven to be a very useful technique for studying the dynamics of ET reaction between a radical anion, which normally survives for several microseconds after its generation by an electron capture reaction, and a molecular acceptor. Therefore, this kind of ET reaction may be a useful probe for determining the rate coefficients in the *stationary quenching regime*, which is attained only after more than a microsecond following initiation of the reaction.[31]

Gordon and McLean investigated the influence of ionic liquids on the reaction rates of photoinduced electron transfer systems: the ruthenium tris-(4,4-bipyridyl)/methylviologen ($[Ru(bpy)_3]^{2+}/MV^{2+}$) or (*R^{2+}/MV^{2+}) couple.[32] The PET reaction between *R^{2+} and MV^{2+} in $[BMIM][PF_6]$ was found to occur, within experimental error, at a diffusion controlled rate. This result was the first indication of the magnitude of diffusion-controlled rate constants in such media. However, considering the fact that both reactants were ionic species, the PET reaction could be influenced by a purely ionic environment due to the charge screening effect on the formation of an encounter complex, and the rate of the back electron transfer reaction could be affected by alterations in electronic coupling between caged donor−acceptor pairs, or changes in reaction free energy and solvent reorganization energy. A combination of these effects would be expected to result in significantly different quenching rates in ionic liquids. On the other hand, Vieira and Falvey demonstrated that the rate of PET from $BP^{-\cdot}$

to MV^{2+} is an order of magnitude faster in $BuPyr-NTf_2$ than the other RTILs, namely, $BMIM-NTf_2$ and $OMIM-PF_6$, in which a solely diffusive ET pathway was observed.[25,26] This led them to suggest the solvent mediated ET pathway for $BuPyr-NTf_2$. Considering the possibilities that many factors may be operating in RTIL to affect the PET reaction, the conclusions made from only a few studies reported earlier could not be considered unanimous. Therefore, in the present work, the choice of one of the reactants in the reaction pair as a neutral molecule has eliminated the possibilities of interference of many of the factors discussed above to the ET reaction, and the rates have been determined in two RTILs and varieties of conventional solvents and compared.

We should also mention here that McLean et al. selected the exothermic triplet energy transfer from triplet benzophenone ($^3\mathbf{Bp^*}$) to naphthalene ($\mathbf{N}$) as the probe of RTIL diffusional properties using flash photolysis technique. They found that the rates of the energy transfer process observed in RTILs are up to an order of magnitude larger than the values of diffusion controlled reaction rate constants (k_{diff}) estimated theoretically (vide infra).[33]

2. EXPERIMENTAL SECTION

Purified samples of RTILs, namely, 1-butyl-3-methyl-imidazolium hexaphosphate $[BMIM][PF_6]$ (HPLC grade) and 1-butyl-3-methyl imidazolium tetraborate $[BMIM][BF_4]$ (HPLC grade), were kindly donated by Prof. A. Samanta of Hyderabad University, India, and the synthesis and purification procedures are available in refs 22 and 34. Conventional organic solvents, acetonitrile and 1-pentanol (HPLC grade) and ethylene glycol (EG) and glycerol (GL) (spectroscopic grade), were procured form Spectrochem, India. All these solvents were used as received. Fluorenone (Fl), benzophenone (BP), and pyrene (Py), procured from Sigma Aldrich, USA, were of better than 98% purity and used as received. Samples used for pulse radiolysis experiments were purged with IOLAR grade nitrogen to ensure complete removal of oxygen dissolved in pure solvents and solutions and properly sealed. Viscosities of the pure solvents as well as the solutions were measured at room temperature (298 K) using the Rheometer Model Physica MCR-101 Modular Compact adopting the coaxial cylinder mode.

For pulse radiolysis study, we have used a linear electron accelerator based pulse radiolysis facility, the details of which have been described elsewhere.[35] Maximum energy of the electron beam used here was about 7 MeV. For our experiments, we have used the electron beam of 100 or 500 ns duration with the dose from a single pulse of about 15 or 35 Gy, respectively. Temporal profiles have been recorded at suitable wavelengths to determine the rate of decay or formation of the transient species. For recording the time-resolved spectra, temporal profiles were recorded at the wavelength intervals of 10 nm, and the optical densities measured at different time windows were plotted against the wavelength.

3. RESULT AND DISCUSSION

3.1. Radiolysis of Ionic Liquid and Characterization of Radical Anions.
Several studies on pulse radiolysis of ionic liquids in the nanosecond time domain,[20,27,28,36−40] as well as in the picosecond time domain,[41−44] have been published. These works indicate that, for the imidazolium ionic liquids, the

electrons produced by ionization are rapidly scavenged by the solvent molecules before they become fully solvated, while the electrons in the ammonium ionic liquids are solvated quickly to form the solvated electrons. Neta and his co-workers recorded the absorption spectra of the transient species formed upon pulse irradiation of deoxygenated liquid $[\text{BMIM}][\text{PF}_6]$.[36] The spectrum recorded at 1 μs following irradiation using electron pulses of submicrosecond duration exhibited a maximum at 325 nm and a shoulder near 370 nm. Considering the relative electron densities on the BMIM^+ (~53%) and by PF_6^- (~47%), they predicted that, in the radiolysis of this RTIL, the energy deposited in the liquid is possibly absorbed by the cation and the anion in the same ratio.[36] In both cases, the first step is ionization, forming a thermalized electron and the remaining radical.

$$\text{BMIM}^+ \rightarrow \text{BMIM}^{\cdot 2+} + e^- \tag{1}$$

$$\text{PF}_6^- \rightarrow \text{PF}_6\cdot + e^- \tag{2}$$

Geminate recombination of the primary radical species leads to formation of the excited states, and subsequently C−H and C−C bond scission reactions in the methyl and butyl groups lead to formation of H· atoms and alkyl radicals, respectively. In addition, formation of PF_5, F·, and F^- are also expected from the dissociation reaction of PF_6^- and $\text{PF}_6\cdot$ species. Thermal electrons thus produced may or may not be solvated, but these electrons and H· atoms react with BMIM^+ to form BMIM· radical (eq 3) and H· atom adduct (eq 4), respectively, and F· reacts very rapidly, possibly via addition to the ring or oxidation. These processes are complete within <10 ns and their products are observed immediately after irradiation using the electron pulse of submicrosecond duration. Therefore, those species, which have been characterized by the absorption maximum at 325 nm and a shoulder at 370 nm and is observed immediately after the electron pulse, include BMIM·, BMIM^{2+}, and three isomeric H-adducts, as well as F-adducts. Further increase of absorbance at 325 nm but decrease at the lower energy region of the spectrum occurring over next 4 μs delay time has been ascribed to the reactions of various alkyl radicals (R· as well as ·R-MIM^+) with BMIM^+. However, these radiolysis products have negligible absorption in the wavelength region of our interest (i.e., >400 nm).

$$\text{BMIM}^+ + e^- \rightarrow \text{BMIM}^\cdot \tag{3}$$

$$\text{BMIM}^\cdot + \text{H}^\cdot \rightarrow \text{H} - \text{BMIM} \tag{4}$$

The pulse radiolysis technique has been frequently used for generation, characterization, as well as study of reactions of radical anions in solutions.[20,27,28,45,46] Wishart and Neta reported that dry electron capture by aromatic solutes, such as benzophenone and pyrene, is very efficient in ionic liquids, while the reactions of the solvated electron with the same compounds are diffusion limited, and slower due to the high viscosity of the ionic liquid.[27] In this work, we have used this technique to generate and characterize the spectroscopic properties of the radical anions of pyrene, benzophenone and fluorenone in $[\text{BMIM}][\text{PF}_6]$ and $[\text{BMIM}][\text{BF}_4]$. $(3-5) \times 10^{-2}$ mol dm^{-3} of the solute dissolved in an RTIL was subjected to electron pulse irradiation and the decay kinetics of the transient species were recorded in the 400−770 nm region. The time-resolved transient spectra were constructed using these decay traces.

The time-resolved transient spectra recorded following pulse radiolysis of the solutions of these solutes in $[\text{BMIM}][\text{PF}_6]$ are

presented in Figure 1. The transient absorption spectrum recorded at 0.5 μs following electron pulse radiolysis of pyrene
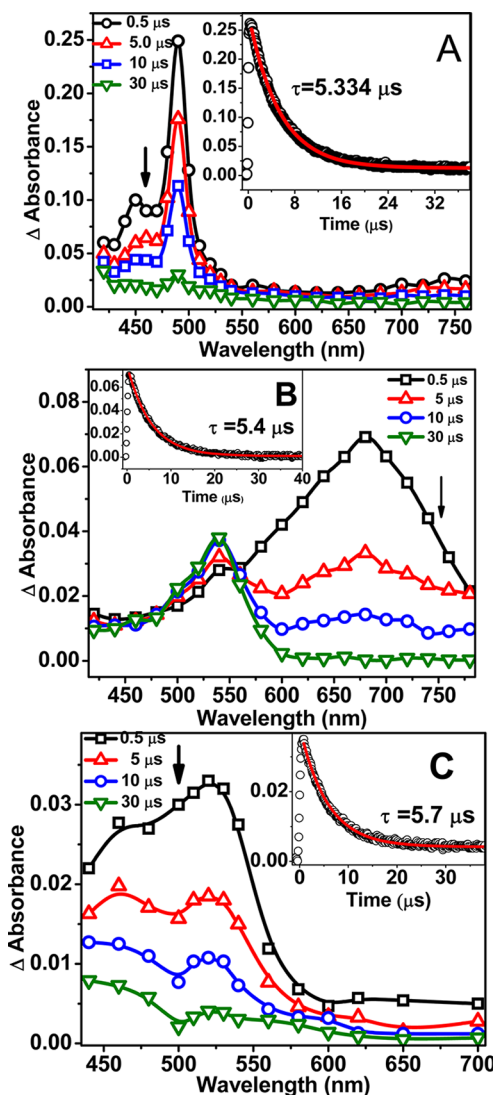

Figure 1. Time-resolved absorption spectra and decay traces at corresponding λ_{max} of the radical anions of pyrene (A), benzophenone (B), and fluorenone (C).

in this solvent has the absorption maximum at 490 nm and a shoulder at 450 nm, which can be assigned to pyrene radical anion, Py·, and radical cation, $\text{Py}^{+\cdot}$, respectively.[45] Simultaneous formation of both the pyrene radical cation and the radical anion has been observed by pulse radiolysis of pyrene in DMSO and RTIL.[20,45] We mentioned earlier that the yield of solvated electron is small in imidazolium ionic liquids because the electrons are rapidly scavenged by the solvent molecules before they become fully solvated. Therefore, in the present case, formation of these radicals can be predicted by the reactions with the dry and/or solvated electron and $\text{BMIM}^{\cdot 2+}$, respectively. Wishart and Neta reported that dry electron capture by aromatic solutes, such as benzophenone and pyrene, is very efficient in ionic liquids.[27] Therefore, formation of $\text{Py}^{+\cdot}$, and $\text{Py}^{-\cdot}$ can be predicted via reactions 5 and 6. Since the absorption coefficients of these two radicals are very similar (~2.2 × 10^4 dm^3 mol^{-1} cm^{-1}), the relative heights of the peaks

Table 1. Standard Free Energy Changes (ΔG^0) for the ET Reaction between the Anions and the Quenchers, Viscosities of the Solutions, Experimentally Determiined Rates of ET Reactions (k_{ET}), the Rates of Diffusion Controlled Reactions Calculated Using Eq 9 (k_{diff}), and the ratio between k_{ET} and k_{diff}

Pyrene−Benzophenone Pair					
solvent	ΔG^0 (eV)	viscosity (cP)	k_{ET} (dm^3.mol^{-1}s^{-1})	k_{diff}(dm^3 mol^{-1} s^{-1})	k_{ET} /k_{diff}
[BMIM][PF$_6$]	−0.26	212	$5.8 \pm 0.5 \times 10^7$	3.12×10^7	1.86
[BMIM][BF$_4$]		81.5	$14.3 \pm 1 \times 10^7$	8.10×10^7	1.77
EG + GL (0.5:0.5)		75.5	$1.3 \pm 0.2 \times 10^8$	8.80×10^7	1.48
EG + GL (0.7:0.3)		38.0	$2.3 \pm 0.2 \times 10^8$	1.74×10^8	1.32
EG		15.7	$4.7 \pm 0.1 \times 10^8$	4.21×10^8	1.12
1-decanol		12.1	$8.1 \pm 0.2 \times 10^8$	5.46×10^8	1.48
1-pentanol		3.38	$2.7 \pm 0.3 \times 10^9$	1.95×10^9	1.38
acetonitrile		0.35	$1.8 \pm 0.2 \times 10^{10}$	1.88×10^{10}	0.96
Benzophenone−Fluorenone Pair					
solvent	ΔG^0 (eV)	viscosity (cP)	k_{ET} (dm^3.mol^{-1} s^{-1})	k_{diff} (dm^3 mol^{-1} s^{-1})	k_{ET} /k_{diff}
[BMIM][PF$_6$]	−0.54	196	$4.9 \pm 0.5 \times 10^7$	3.40×10^7	1.44
[BMIM][BF$_4$]		76.5	$12.7 \pm 0.7 \times 10^7$	8.63×10^7	1.46
EG + GL (0.5:0.5)		75.7	$1.2 \pm 0.2 \times 10^8$	8.73×10^7	1.37
EG + GL (0.7:0.3)		38.1	$1.4 \pm 0.2 \times 10^8$	1.73×10^8	0.81
EG		15.8	$3.9 \pm 0.5 \times 10^8$	4.18×10^8	0.93
1-decanol		12.1	$5.7 \pm 0.2 \times 10^8$	5.50×10^8	1.04
1-pentanol		3.3	$1.5 \pm 0.2 \times 10^9$	2.0×10^9	0.75
acetonitrile		0.35	$1.4 \pm 0.1 \times 10^{10}$	1.86×10^{10}	0.75

at 495 and 450 nm clearly suggest much larger yield of the radical anion.[42]

$$Py + e^- \rightarrow Py^{\cdot-} \tag{5}$$

$$Py + BMIM^{\cdot 2+} \rightarrow Py^{\cdot+} \tag{6}$$

Formation of the radical anions of benzophenone and fluorenone is also confirmed by the absorption bands with the maxima at 680 and 530 nm (and a shoulder at 470 nm), respectively (Figure 1B and C).[27,46,47] While the time evolution of the transient spectra reveals that the radical anion of pyrene decays monotonously without formation of any other radiolysis products (insets of Figure 1A), the decay of the benzophenone radical anion band with the maximum at 680 nm leads to the concomitant rise of another band with the maximum at 540 nm. The latter can be attributed to the formation of ketyl radical of benzophenone.[48] In the case of fluorenone also, the change in the shape of the time-resolved spectra during the course of decay of the fluorenone radical anion is a clear indication of formation of ketyl radical of fluorenone, which has already been characterized by an absorption spectrum with the maxima at 350 and 500 nm.[49] Formation of ketyl radicals of benzophenone and fluorenone can be envisioned by the reaction of the anion radical with the H· atom generated by radiolytic C−H bond scission of the methyl and butyl group of [BMIM][PF$_6$] (vide supra).

For determination of the lifetimes of these radical anions, we have analyzed the decay profiles recorded at several wavelengths of the absorption spectra and found that each of them could be well-fitted using an exponential function with a single lifetime component. Only one decay trace, recorded at the wavelength of maximum absorption of each of the radical anions, is given in the insets of Figure 1 along with the best fit single exponential function and the associated lifetime. The lifetimes of the anion radicals of pyrene, benzophenone, and fluorenone in [BMIM][PF$_6$] are 5.3, 5.4, and 5.7 μs, respectively. We discussed earlier that, for investigation of the electron transfer processes occurring in the diffusion controlled

regime in viscous RTIL media, the electron donor needs to be long-lived enough to survive for several hundreds of nanoseconds. Therefore, these radical anions could be used as promising electron donors for this purpose.

Characteristics of the radical anions of these solutes have also been studied in [BMIM][BF$_4$] (see Supporting Information). Absorption spectra of the anions in this solvent have been found to be very similar to those recorded in the other RTIL. The lifetimes have been determined to be 9.9, 6.9, and 6.2 μs for the radical anions of benzophenone, fluorenone, and pyrene, respectively.

3.2. Electron Transfer Study. We have investigated the dynamics of ET from a radical anion, which is formed by capturing a thermal electron, to an acceptor molecule in the ground electronic state. We have chosen the donor−acceptor pairs of molecules on the basis of the consideration that the absorption band of the donor radical anion does not have significant overlap with that of the radical anion of the acceptor molecule so that the decay of the former and formation of the later can be monitored without any interference. Therefore, we have chosen pyrene−benzophenone and benzophenone−fluorenone pairs for our study. In these systems, concentration used for pyrene (or benzophenone) (3 or 5 × 10^{-2} mol dm^{-3}) is about ten times larger than that of the acceptor molecule, benzophenone (or fluorenone) (varying in the range (1−8) × 10^{-3} mol dm^{-3}). In this condition, the thermal electrons are preferentially captured by pyrene (or benzophenone) to form the radical anion, which transfers its extra electron to benzophenone (or fluorenone). The ΔG values[48] for these two pairs of donor radical anion and molecular acceptor systems have also been calculated using eq 7 (Table 1) and has been found to be negative, suggesting the fact that these pairs are suitable for study of ET process in RTILs.

$$\Delta G = -E_{red}(A/A^-) + E_{red}(M/M^-) \tag{7}$$

where $E_{red}(M/M^-)$ and $E_{red}(A/A^-)$ are the reduction potentials for the quencher molecule and the radical anion, respectively. In the present case, since one of the reactants undergoing ET

reaction and one of the products formed are neutral molecules, the work function term arising due to columbic interaction between the ionic species will have negligible contribution and is not considered here.

We have recorded the temporal profiles for the transient species formed following radiolysis of 3×10^{-2} mol dm^{-3} of pyrene and 3×10^{-3} mol dm^{-3} of benzophenone in [BMIM][PF$_6$] in the 420−770 nm region, and the time-resolved spectra of the transient species thus constructed using these temporal profiles are shown in Figure 2. We find a rapid
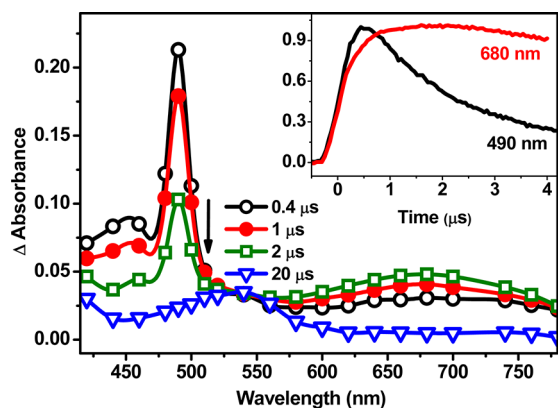
Figure 2. (a) Time-resolved transient absorption spectra recorded following pulse radiolysis of 3×10^{-2} mol dm^{-3} of pyrene and 3×10^{-3} mol dm^{-3} of benzophenone in [BMIM][PF$_6$]. (b) Decay trace of pyrene anion radical at 490 nm and formation of benzophenone radical anion at 530 nm.

decay of the transient absorption band with the maximum at 490 nm and the concomitant growth of a transient absorption band with the maximum at 680 nm. This time evolution of the transient spectra suggests the transfer of an electron from the radical anion of pyrene to benzophenone forming the benzophenone radical anion. This has been further confirmed by monitoring the decay of the pyrene radical anion at 490 nm and the growth of the benzophenone radical anion at 680 nm following pulse radiolysis of the solutions containing pyrene of fixed concentration (3×10^{-2} mol dm^{-3} of pyrene) but varying concentrations of benzophenone in the range $(1.6-6.8) \times 10^{-3}$ mol dm^{-3}. The results have been presented in Figure 3, which clearly reveals that the decay rate of pyrene radical anion increases with the increasing concentration of benzophenone in solution. This observation confirms the electron transfer interaction between the pyrene radical anion and benzophenone in its ground electronic state.

The decay traces are fitted single exponentially and the pseudo first order rate constants (the inverse of the corresponding lifetimes) for the ET reaction in the presence of different concentrations of benzophenone are determined (Table 1). The bimolecular rate constant for the ET process from pyrene radical anion to benzophenone molecule in [BMIM][PF$_6$] has been determined from the slope of the linear plot of the pseudo first order rate constants vs the concentration of benzophenone. The rate constant thus determined is 5.8×10^7 dm^3 mol^{-1} s^{-1}.

Quenching of benzophenone radical anion as the electron donor has been studied using fluorenone as the electron acceptor in [BMIM][PF$_6$]. Figure 4 presents the time-resolved spectra of the transients following pulse radiolysis of 5×10^{-2} mol dm^{-3} of benzophenone and 5×10^{-3} mol dm^{-3} of
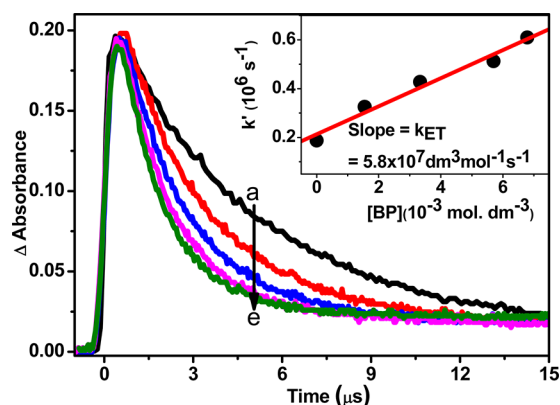

Figure 3. Decay of pyrene radical anion measured at 490 nm in absence of benzophenone (a) and in presence of 1.6 (b), 3.3 (c), 5.7 (d), and 6.8 (e) $\times 10^{-3}$ mol dm^{-3} of benzophenone in acetonitrile. Inset: Linear plot of the pseudo first order rate constants vs the concentration of benzophenone ([BP]) in [BMIM][PF$_6$].
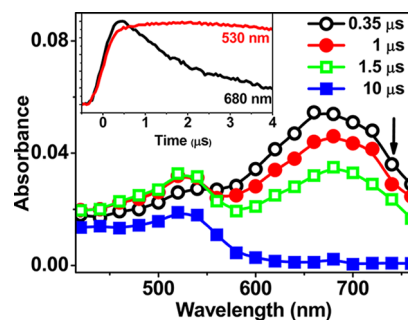

Figure 4. Time-resolved transient absorption spectra recorded following pulse radiolysis of 5×10^{-2} mol dm^{-3} of benzophenone and 5×10^{-3} mol dm^{-3} of fluorenone in [BMIM][PF$_6$], Inset: Decay trace of benzophenone radical anion at 680 nm and formation of fluorenone radical anion at 530 nm.

fluorenone in this RTIL. We determined the bimolecular rate constant for the ET reaction between benzophenone radical anion and fluorenone using different concentrations of fluorenone in the range $(2-8) \times 10^{-3}$ mol dm^{-3} as the quencher (Figure 5).
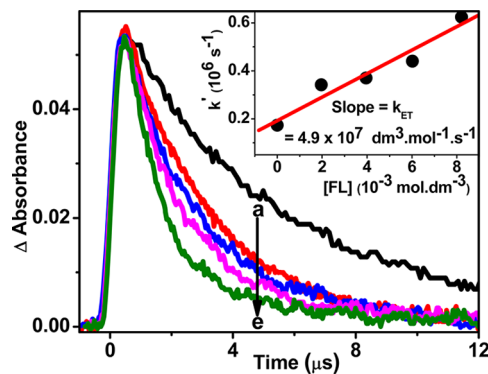

Figure 5. Decay of benzophenone radical anion measured at 680 nm in absence of fluorenone (a) and in presence of 1.9 (b), 3.8 (c), 6.0 (d), and 8.0 (e) $\times 10^{-3}$ mol dm^{-3} of fluorenone in acetonitrile. Inset: Linear plot of the pseudo first order rate constants vs the concentration of fluorenone ([FL]) in [BMIM][PF$_6$].

In the pulse radiolysis experiments with the ionic liquids in the presence of pyrene or benzophenone, thermalized electrons (either from the pulse or generated via reactions 1 and 2) are captured by the added solutes and formation of the solute anion is observed immediately after the electron pulse. In the present study, although we have not been concerned with the different reactions between the anion and other radiolysis products, the total decay rate (inverse of the lifetime given in the insets of Figure 1) includes all the processes or reactions by the anion following its formation. This decay rate also includes the effect due to formation of charged radical species, if any, due to irradiation of the solvent. Due to gradual increase in concentration of the quencher molecule (benzophenone or fluorenone), the decay rate of the anion radical increases, obeying the linear relationship between the decay rate of the anion radical and the concentration of the quencher molecule. This suggests that the rates of the reaction determined from the linear plots presented in the insets of Figures 3 and 5 represent entirely the interaction between the anion radical and the acceptor solute, but no other processes associated with the decay of the anion radicals.

Similar studies as described in the earlier sections using $[BMIM][PF_6]$ as the solvent were extended for the other RTIL, namely, $[BMIM][BF_4]$, as well as other conventional solvents, namely, acetonitrile, 1-pentanol, and 1-decanol, as well as ethylene glycol (EG) and ethylene glycol−glycerol (GL) solvent mixtures. The bimolecular rate constants for the ET reactions for the pyrene−benzophenone and benzophenone−fluorenone pairs have been estimated. Results obtained are presented in Table 1 and the decay traces and the linear plots are given in the Supporting Information.

In conventional liquids, the value of k_{diff} can be evaluated using the simple Smoluchowski prediction for the diffusion-limited rate constant (assuming the sizes of the reactants larger than the solvents),[50,51]

$$k_{diff} = \frac{8 \times 10^6 RT}{3\eta} \left(\frac{(R_D + R_A)^2}{4R_D R_A} \right) \qquad (8)$$

where R_D and R_A are the radii of the donor anion and the acceptor molecule, R is the gas constant (8.3144 J K^{-1} mol^{-1}), T is the room temperature (25 °C) and η is bulk or macroscopic viscosity of the solvent in cP unit. In a first approximation, i.e., assuming spherical reactants of identical radii, we have calculated the diffusion values of k_{diff} for all those solvents and solvent mixtures used in the present study (Table 1) using the eq 9 and the values are given in Table 1[30,31]

$$k_{diff} = \frac{8 \times 10^6}{3\eta} RT \qquad (9)$$

At 25 °C, the bulk viscosities of the pure solvents as well as the solutions in the presence of the highest concentrations of the donor and acceptor molecules have been measured and the values are given in Table 1. We find that, in the presence of the donor and acceptor molecules, the bulk viscosities of both the RTILs used here are reduced significantly, e.g., the viscosity of pure $[BMIM][PF_6]$ at 298 K is 270 cP, but the viscosity of the RTIL decreases to 212 cP in the presence of 3×10^{-2} mol dm^{-3} of pyrene and 5×10^{-3} mol dm^{-3} of benzophenone and to 196 cP in the presence of 5×10^{-2} mol dm^{-3} of benzophenone and 5×10^{-3} mol dm^{-3} of fluorenone. Here we have assumed that, due to variation of the concentration of the acceptor molecule in the range $(1.5−8) \times 10^{-3}$ mol dm^{-3}, the

viscosities of the solutions do not change significantly. Conventional solvents, e.g., acetonitrile, 1-pentanol, 1-decanol, and EG, have much lower viscosities as compared to those of RTILs, and ethylene glycol−glycerol mixtures have moderate viscosities. Viscosities of liquids may change by irradiation due to various reasons, such as polymer formation, changes of composition due to degradation of the solvent, etc. Our observation is that viscosities of the RTILs used here remain unchanged before and after irradiation in our experimental conditions.

In Table 1, we observe that the ratios of the experimentally determined values of k_{ET} for both the donor−acceptor pairs and the estimated values of k_{diff} using eq 9 (i.e., the k_{ET}/k_{diff} ratio) in the case of conventional solvents are nearly equal to unity, revealing the diffusion controlled ET rates. However, we find that the k_{ET}/k_{diff} ratios determined in RTILs are significantly larger than unity. To explain this, one should consider the fact that eqs 8 and 9 are valid for the case when the hydrodynamic radii of the reactants are much larger than that of the solvent, so that there is no slip at the surface of the diffusing particle.[52] However, the recently published work of Maroncelli and co-workers revealed that the hydrodynamic radii of the ionic solvents are much larger than those of the reactant solutes used in the present study.[30] In this case, one should use the coefficient of the viscosity term (η) (i.e., in the denominator of eq 9) smaller than 3. Therefore, in RTILs, the estimated value of k_{diff} becomes larger and hence the k_{ET}/k_{diff} becomes smaller and nearly equal to unity.

Vauthey and co-workers observed time-dependence of the rates of bimolecular quenching reactions in RTIL as well as in other viscous solvents and explained the phenomenon by predicting the existence of three distinct quenching regimes.[31] In the *static* regime, the reactant pairs are already in contact with each other, and no diffusion is necessary for the reaction to take place and the quenching rate is the intrinsic ET rate, k_0. In the next regime, namely, the *nonstationary* or *transient* regime, the reaction rate constantly decreases with time, because of the fact that, immediately after the reactions between the reactants in close contact, the hole created by the reaction in the pair distribution distance between the reactants gradually increases and the reactants needs to diffuse to react. This continues as long as an equilibrium is established between the rate at which the intrinsic reaction occurs and the rate of diffusion of the reactants to give rise to a constant reaction rate. This is called the stationary regime. The duration of the static regime depends on the intrinsic ET rate constant, k_0, whereas that of the transient regime depends on the viscosity of the solvent. Therefore, while the stationary regime may be reached after a few nanoseconds in the case of low viscosity solvents, such as acetonitrile, it may take several hundreds of nanoseconds to reach the same regime in the case of viscous solvents, like RTIL.[31] In the case of highly viscous solvents, the reaction rate (here k_{ET}), which is controlled entirely by the rates of approach of the reacting pairs through diffusion to the optimal distance to form an encounter complex (and can be represented as k_{diff}), is significantly slower than the intrinsic ET rate constant, k_0.

In the present study, because of long duration of the electron pulse (~500 ns), the static and transient quenching regime is not resolvable and hence the value of k_0 could not be determined even in the case of conventional solvents of low viscosity. But the long lifetimes of the donor radical anions allow us to monitor the quenching rates in the *stationary regime*, and the transient decay of the donor radical anions appears to

follow single exponential kinetics. This suggests that the rate of the bimolecular ET process is determined only by the diffusion rate of the reactants in all kinds of solvents. We observe that, like in conventional organic solvents, the ET process is diffusion controlled in RTILs too.

4. SUMMARY AND CONCLUSION

For the first time we have given direct evidence that, in the stationary regime, the rate of electron transfer reaction is controlled by the rate of diffusion of the reactants in highly viscous RTIL media and in conventional solvents with both high as well as very low viscosities. Electron transfer reaction between a long-lived anion radical and neutral molecule is an ideal probe for investigation of diffusion controlled reactions in highly polar and viscous media. There may be several reasons, we predict, for the reaction rates reported earlier to be much faster than the diffusion controlled rate in ionic liquids. First, the rates of the reactions determined in the pico or nanosecond time domain may also have contributions from the static and transient quenching processes.[30,31] Second, the diffusion coefficients of the reactants increase due to significant reduction of the viscosity of the solvent in the presence of high concentration of reactant solutes. Finally, much smaller sizes of the reactants as compared to that of the ionic liquid may also be a factor responsible for the much lower value of the estimated k_{diff} and hence the apparent faster rate of the reaction as compared to that of estimated k_{diff}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Time resolved anion radical spectrum and decay profile of (a) pyrene, (b) benzophenone, and (c) fluorenone anion radicals in [BMIM][BF$_4$] (Figure S1). Decay profile collected for different quencher concentration and k' vs quencher concentration plot for pyrene-benzophenone and benzophenone-fluorenone pair at different solvents are (Figures S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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