

Laser photolysis study of anthraquinone in binary mixtures of ionic liquid [bmim][PF₆] and organic solvent

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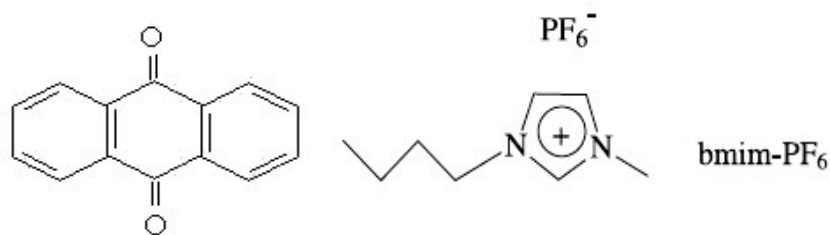
Abstract: Photochemical properties of the ionic liquid (RTIL) 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆] and its binary mixed solutions with organic solvent (DMF and MeCN) were investigated by laser photolysis at an excitation wavelength of 355 nm, using anthraquinone (AQ) as a probe molecule. It was indicated that the triplet excited state of AQ (³AQ*) can abstract hydrogen from [bmim][PF₆]. Moreover, along with the change of the ratio of RTIL and organic solvent, the reaction rate constant changes regularly. Critical points were observed at volume fraction $V_{\text{RTIL}} = 0.2$ for RTIL/MeCN and $V_{\text{RTIL}} = 0.05$ for RTIL/DMF. For both systems, before the critical point, the rate constant increases rapidly with increasing V_{RTIL} ; however, it decreases obviously with V_{RTIL} after the critical point. We conclude that the concentration dependence is dominant at lower V_{RTIL} , while the viscosity and phase transformation are dominant at higher V_{RTIL} for the effect of ionic liquid on the decay of rate constant.

Keywords: 1-butyl-3-methylimidazolium hexafluorophosphate; Laser photolysis; Anthraquinone; Rate constant

1. Introduction

Owing to their desirable properties including nonvolatility, high polarity, ease of recycling, high selectivity and chirality [1,2], room temperature ionic liquids (RTILs) are regarded as most suitable solvents for green chemistry. RTILs have been used as reaction media for a number of organic synthesis reactions, catalysis, separation processes, and polymerization [3-6]. Recently, various spectroscopic measures (NMR, IR, Raman, etc.) were utilized to characterize the properties of RTILs [7-9]. Pulse radiolysis and time-resolved fluorescence [10-16] have also been applied to study the reaction processes occurring in RTILs. These studies have provided some important information on the polarity and biphasic property of RTILs and have thrown light on the dynamics of ionic diffusion and internal motion of the dissolved solutes. As a prototype of RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆] has been used as medium in which some representative photochemical reactions have been previously studied in comparison with volatile organic compounds (VOC) [17]. It was found that molecular diffusion of solute was significantly retarded and lifetime of transient species was longer in the neat [bmim][PF₆]. Since RTILs have high viscosity and large-size organic cations, reaction kinetics in them is expected to be quite different from that in conventional aqueous or organic solutions.

In this work we have carried out kinetic studies by laser photolysis in binary mixtures of [bmim][PF₆] with N,N-dimethylformamide and acetonitrile, using anthraquinone (AQ) as the probe molecule. Our results revealed that [bmim][PF₆] itself participates in the reaction with triplet excited state of AQ (³AQ*) and the reaction kinetics is partly affected by the viscosity of [bmim][PF₆]. Along with the increasing of V_{RTIL} in the mixed solution, the decay rate constant increases at lower V_{RTIL} firstly, but then decreases at higher V_{RTIL} . One critical point is observed in both RTIL/DMF and RTIL/MeCN solutions.



Scheme 1. Chemical structures of anthraquinone (AQ) and [bmim][PF₆]

2. Experimental section

2.1. Materials

All reagents were purchased from Sigma and were of the commercially available highest purity. Anthraquinone, DMF and MeCN were all of spectral grade and used as received. The ionic liquid [bmim][PF₆] was specially treated prior to use. The [bmim][PF₆] salt was treated with activated charcoal for at least 48 h and filtered a couple of times by passing through a celite column. Then the liquid was transferred into a clean and dry reagent bottle and kept in vacuum for 12 h at 60–65 °C to

remove any volatile organic impurities and moisture. The water content in the purified ionic liquid was less than 100 ppm. The purified ionic liquid was stored in an airproof desiccator.

2.2. Apparatus and experimental condition

Laser photolysis experiments were carried out using a Nd:YAG laser that provides 266 and 355 nm laser pulse with a duration of 5 ns and a maximum energy of 80 mJ per pulse. The probe light source was a pulsed xenon lamp. The laser and analyzing light beam passed perpendicularly through a 1 cm × 1 cm quartz cell. The transmitted light entered a monochromator equipped with a R955 photomultiplier (Hamamatsu). The signals were collected using a digital oscilloscope and then recorded by a personal computer. A detailed technical description of the equipment has been described elsewhere [18]. Prior to the irradiation, all solutions were bubbled with the appropriate gas (high-purity N₂, O₂) for at least 20 min. All experiments were carried out at room temperature.

The viscosity measurement was carried out on the Advanced Rheology Expanded System (ARES, TA instrument). Electrical conductivity of the mixtures was measured using a conductivity meter of model DDS-307 (LeiCi Co.).

3. Results and Discussion

3.1. Reactions of ³AQ* in RTIL/ MeCN solutions

In the first place we chose 355 nm laser as the irradiation light and used anthraquinone triplet excited state (³AQ*) as a probe [19, 20] to investigate its behavior in RTIL/MeCN solutions. The optical density of the neat [bmim][PF₆] at the 355 nm wavelength is about 0.13, which is similar to the report in reference 7 and there is no characteristic transient absorption upon irradiation by 355 nm laser. The transient absorption spectra were recorded for a series of RTIL/ MeCN solutions (in different ratios) containing 1 × 10⁻⁴ mol·dm⁻³ AQ solutions. In all cases, λ_{max} of ³AQ* was measured as 370 nm and remained unvaried with the addition of solvent. Fig.1 shows the representative absorption spectra recorded after 355 nm laser excitation in the mixed RTIL/MeCN solution in a volume ratio of 1/5 under N₂ and O₂ purging respectively. The decay profile of ³AQ* in the N₂ saturated solution is shown in the inset.

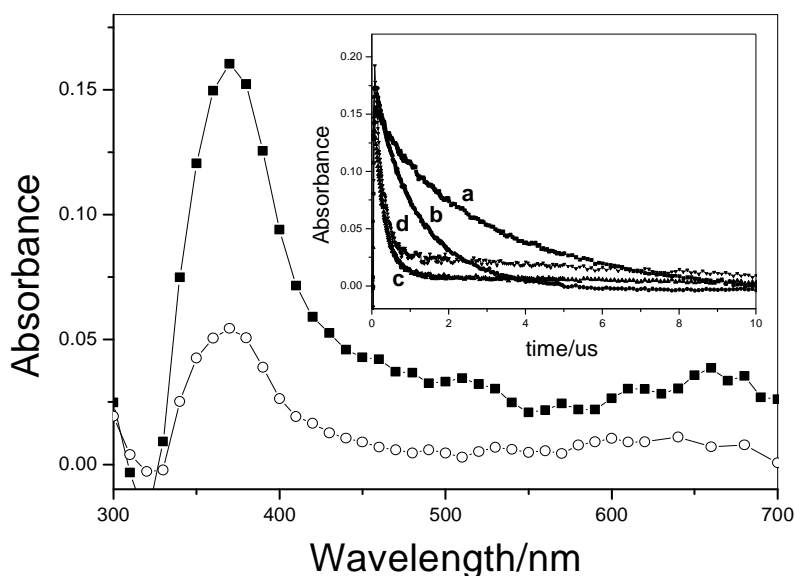


Figure 1. Transient absorption spectra of AQ recorded at 1 μ s after 355 nm laser excitation in RTIL/MeCN solution ($V_{\text{RTIL}}=0.2$, corresponding to mole fraction of 0.06) containing 1×10^{-4} mol·dm $^{-3}$ AQ under N $_2$ (■) and O $_2$ (○) purging. Inset: Decay profile monitored at 370 nm recorded in RTIL/MeCN mixed solutions in the presence of 1×10^{-4} mol·dm $^{-3}$ AQ under N $_2$ purging. Volume fraction of RTIL: (a) 0, (b) 0.01, (c) 0.2, (d) 0.5.

It was found that the decay of $^3\text{AQ}^*$ under N $_2$ atmosphere follows a mono-exponential kinetics in MeCN. Under this condition, $^3\text{AQ}^*$ can be self-quenched by the ground state molecule. However, the decay profile of AQ in RTIL/MeCN is composed by a fast component and a slow component. According to the literature [21], triplet excited state of benzophenone ($^3\text{BP}^*$) can decay via the hydrogen abstraction from alkyl hydrogen atoms on the cation substituents of [bmim][PF $_6$]. It was speculated that the slow component is AQH $^\bullet$ formed via H abstraction of $^3\text{AQ}^*$ from [bmim][PF $_6$] and the fast component is the residue of $^3\text{AQ}^*$. The possible processes are suggested as follows:



Upon excitation by 355 nm laser, the ground state AQ molecule is excited to singlet excited state $^1\text{AQ}^*$, then $^3\text{AQ}^*$ is formed through inter-system crossing (ISC) (Eq.1). $^3\text{AQ}^*$ is self-quenched by the ground state molecule (Eq.2), its rate constant is reported to be 1×10^9 M $^{-1}$ ·s $^{-1}$ in acetonitrile [22]. The triplet excited state can also be quenched by the cation (abbreviated as RH $^+$) of [bmim][PF $_6$] via hydrogen transfer (Eq.3). In our case, when the concentration of [bmim][PF $_6$] is 0.96 mol·dm $^{-3}$ (corresponding to the critical points where $V_{\text{RTIL}}=0.2$, see 3.3) which is much higher than that of AQ, hence reaction 3 is dominant over reaction 2 in the RTIL/MeCN binary solutions.

3. 2. Reactions of $^3AQ^*$ in RTIL/DMF solutions

To compare the reaction of $^3AQ^*$ in solution of RTIL mixed with different organic solvent, the same investigations were also done in RTIL/DMF mixed solutions under identical conditions. Fig.2 shows the transient absorption spectra of AQ solution recorded after 355nm laser excitation in DMF solution under N_2 and O_2 purging.

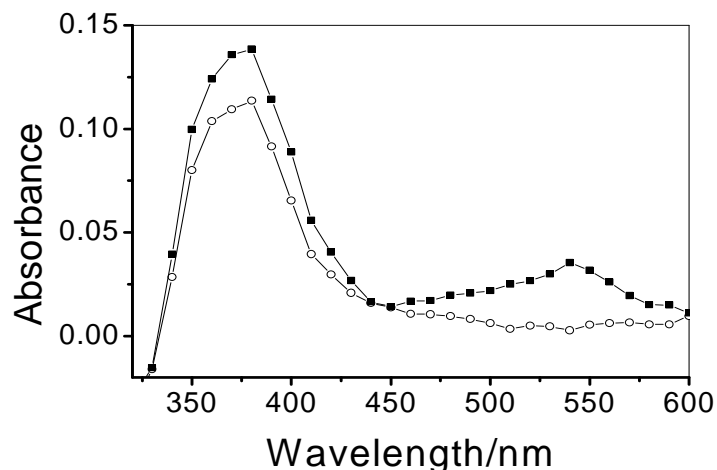
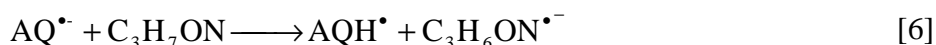
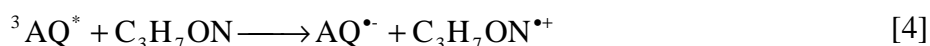


Figure 2. Transient absorption spectra of AQ recorded at $3\mu s$ after 355 nm laser excitation in DMF solution containing $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ AQ under N_2 (■) and O_2 (○) purging.

It is seen that the transient absorption spectrum in N_2 -saturated solution has two bands: one centered at 380 nm and the other at 540 nm, which may be attributed to two different components. As previously shown by Görner [22], a radical anion $AQ^{\bullet-}$ centered at 530 nm is produced via electron transfer between the $^3AQ^*$ and triethylamine (TEA). It has also been suggested by theoretical work that DMF can act as an electron donor in the process of some charge-transfer complexes [23]. Since the 540nm band disappears while the 380 nm band remains almost unchanged in shape and intensity when the solution is purged with oxygen, the 540 nm band is assigned to $AQ^{\bullet-}$ that is produced via electron transfer between the $^3AQ^*$ and DMF (Eq.4). As shown in Eq.5, another possibility is an electron transfer from AQ to $^3AQ^*$ [24]. Then AQH^{\bullet} can be formed by the protonation of $AQ^{\bullet-}$ (Eq.6). The $AQ^{\bullet-}$ can be quenched by oxygen (Eq.7). Therefore the 380 nm band, which is not disappeared under oxygen purging, cannot be entirely assigned to the $^3AQ^*$. It should contain the contribution of AQH^{\bullet} or the radical cation $AQ^{\bullet+}$.



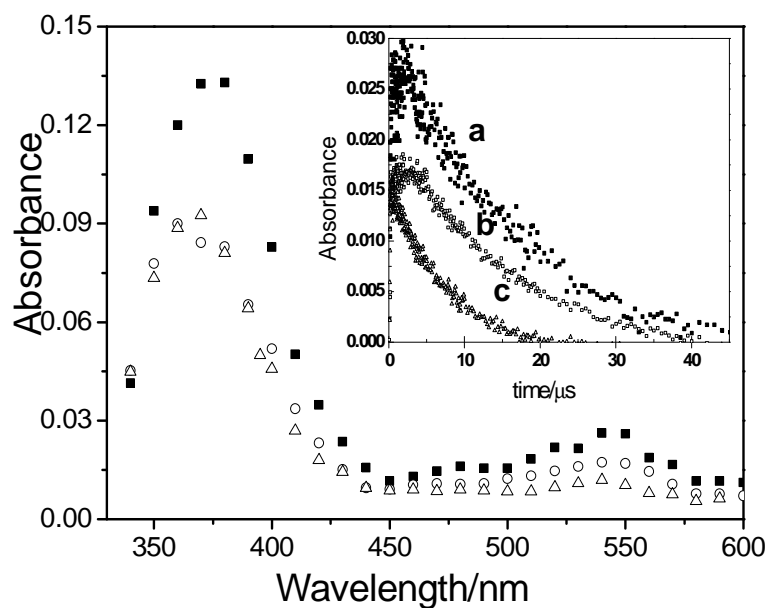


Figure 3. Transient absorption spectra of AQ recorded at 3 μ s after 355 nm laser excitation in RTIL/DMF mixed solution containing 1×10^{-4} mol·dm $^{-3}$ AQ under N $_2$ purging. Inset: Decay profile of AQ* $^-$ monitored at 540 nm. Volume fraction of RTIL: (a) 0 (■), (b) 0.01 (○), (c) 0.05 (△).

Figure 3 shows the transient absorption spectra of AQ solution recorded after 355 nm laser excitation in the mixed RTIL/DMF solutions under N $_2$ purging. The inset shows the decay profiles of AQ* $^-$ in RTIL/DMF binary solutions. It is concluded that there is a competition between the decay of 3 AQ* by hydrogen abstraction (Eq.3) and by electron transfer (Eq.4 and Eq.5), as the intensity of the 540 nm band decreases with increasing the fraction of [bmim][PF $_6$] in mixed solution.

3.3. Effect of RTIL/organic ratio on the reaction rate constant

The change in solvent property with the addition of RTIL was further examined by comparing the observed pseudo-first-order rate constants (k_{obs}) of transient species in different AQ solutions with varying the volume fraction of [bmim][PF $_6$] (V_{RTIL}). The rate constants were calculated from the decay at 370 nm for RTIL/MeCN solutions and at 540 nm for RTIL/DMF solutions. As shown in Fig.4, k_{obs} increases with V_{RTIL} and reaches a maximum but decreases with further increasing of V_{RTIL} , one critical point was observed in both the systems. In RTIL/MeCN system, the critical point is observed at volume fraction $V_{\text{RTIL}}=0.2$; and in RTIL/DMF system, the critical point is at volume fraction $V_{\text{RTIL}}=0.05$. Before the critical point, the quenching rate constant increases obviously with the increasing of V_{RTIL} ; after the critical point, however, the quenching rate constant decreases rapidly with the increasing of V_{RTIL} .

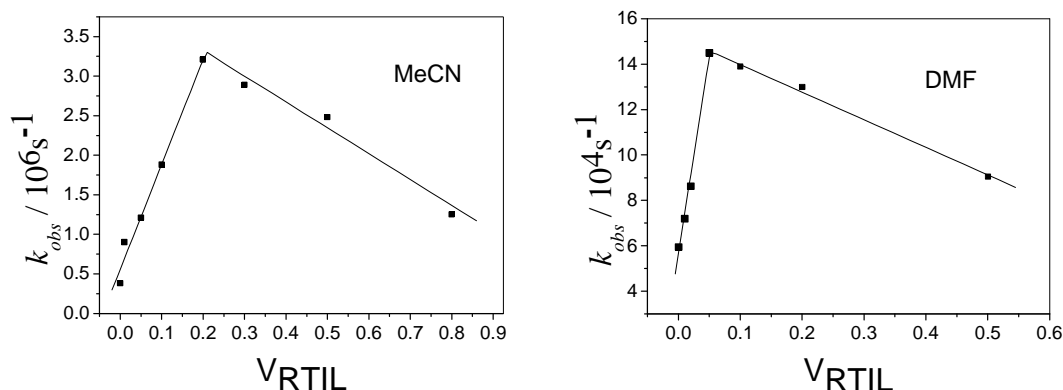


Figure 4. Dependences of ${}^3AQ^*$ (370 nm) and $AQ^{\bullet-}$ (540 nm) decay rate constants k_{obs} on volume fraction of RTIL in RTIL/MeCN and RTIL/DMF mixed solutions, respectively.

According to the theory of Dupont [25], when the concentration of imidazolium ionic liquid is substantially smaller than that of the organic solvent, solvent-separated ion pairs of ionic liquid can be formed. The increasing of k_{obs} with V_{RTIL} before the critical point can be explained by the quenching of ${}^3AQ^*$ via the hydrogen abstraction from [bmim][PF₆]. With the increase of imidazolium salt concentration, ions of [bmim][PF₆] collapse to form contact ion pairs through hydrogen bonding and a further increase of salt concentration leads to the formation of triple ions, etc. Pure imidazolium ionic liquid can be considered as hydrogen-bonded polymeric supramolecule in which some typical photochemical characters have been proved in reference [17]. Probably, phase transformation leads to the decrease of k_{obs} with further increasing of [bmim][PF₆] after the critical point.

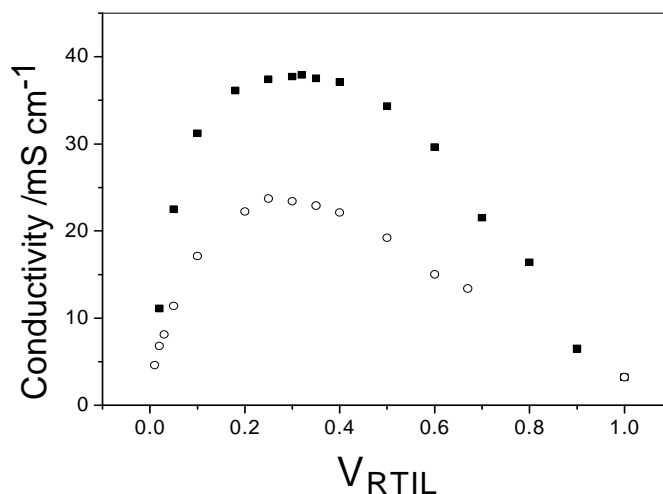


Figure 5. Electrical conductivity, σ vs. the volume fraction of [bmim][PF₆] for RTIL/MeCN (■), and RTIL/DMF (○) solutions.

Because RTIL are entirely composed of special organic cations and anions, electrical conductivity change can indicate the phase transformation of RTIL/organic mixed solutions [25, 26]. We measured the electrical conductivity of the binary mixtures to clarify whether there is phase transformation in our case. As shown in Fig.5, the maximum of conductivity for RTIL/MeCN is 37.9 mS cm⁻¹ at $V_{RTIL}=0.32$, and maximum value for RTIL/DMF is 23.7 mS cm⁻¹ at $V_{RTIL}=0.25$. The conductivity of RTIL/MeCN is

higher than that of RTIL/DMF at the same concentration of [bmim][PF₆]. These differences may be explained by the different interactions between [bmim][PF₆] with MeCN and DMF. It is considered that the change of k_{obs} may be due to many factors such as concentration change and phase transformation. As a result, the maxima of k_{obs} are different in RTIL/MeCN and RTIL/DMF binary mixtures.

3.4. Effect of viscosity on the kinetics in RTIL/DMF

Since [bmim][PF₆] is a kind of high viscosity liquid compared with organic solvent, viscosity also plays an important role in the rate constants of transient species. Before and after the critical point, two different factors dominate the quenching of ³AQ*. In the lower V_{RTIL} region, the concentration of RTIL is substantially smaller than that of the organic solvent, the effect of viscosity is unimportant, so the rate constant increases and the lifetime decreases steadily with an increasing of V_{RTIL} . In the higher V_{RTIL} region, the viscosity of the mixed solution increases with the increasing of V_{RTIL} , which partly leads to a decrease in the decay rate constant and an increase in lifetime. For a better understanding, viscosities of the mixed RTIL/organic solutions should be measured and correlated to the decay rate constant.

Fig.6 shows a plot of the viscosity of binary RTIL/DMF mixture as a function of the volume fraction of RTIL, V_{RTIL} , at a shear rate of 15.8 s⁻¹. It is clear that the viscosity decreases substantially when DMF is added to the ionic liquid [bmim][PF₆]. The viscosity of DMF is 1.30 mPa s, very close to that of water at room temperature, while the viscosity of the pure [bmim][PF₆] is about 278 mPa s, approximately 200 times higher than that of DMF.

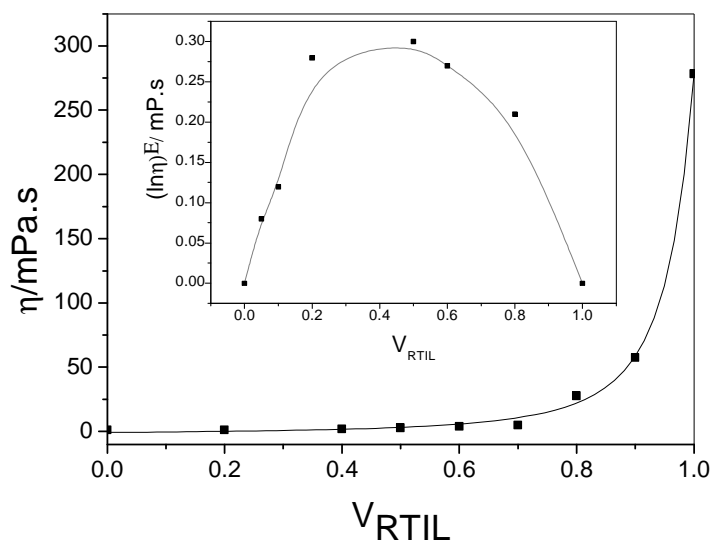


Figure 6. Viscosities of the binary mixture vs. volume fraction of RTIL in RTIL/DMF mixed solvent at 298.15 K. Insert : The excess logarithm viscosities $(\ln \eta)^E$ for mixtures of [bmim][PF₆] and DMF.

Based on the measured viscosity of the mixed solution, the diffusion controlled rate constant can be calculated by applying the Smoluchowski equation [27]

$$k_{\text{diff}} = 8000RT/3\eta$$

where R is the gas constant ($8.3144 \text{ J K}^{-1}\text{mol}^{-1}$), T the absolute temperature, and η the viscosity (in Pa s). The values of the diffusion controlled rate constant for AQ in RTIL/DMF solutions with varying V_{RTIL} are presented in table 1.

Table 1. Decay rate constants, diffusion rate constants of $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ AQ in mixed RTIL/DMF solutions

Volume fractions V_{RTIL}	$\eta(\text{mPa s})$	k_{diff} ($\text{LM}^{-1}\text{s}^{-1}$)/ 10^9	k_{obs} (s^{-1})/ 10^5
0	1.30	5.08	0.60
0.05	1.32	5.00	1.45
0.10	1.36	4.86	1.39
0.20	1.99	3.32	1.30
0.50	5.09	1.30	0.90
0.60	27.75	0.18	0.65
0.80	57.68	0.14	0.52

Because there is a competition between the decay of $^3\text{AQ}^*$ by hydrogen abstraction and by electron transfer, rate constants of the $\text{AQ}^{\bullet-}$ decay cannot be obtained in RTIL/DMF mixed solutions. However, a similar critical point is not obtained for the calculated k_{diff} values (Table 1). We conclude from the above results that phase transformation in the mixed solvent leads to the possible change from the DMF enriched phase to the RTIL enriched phase in addition to the viscosity change [5], and the effective concentration of RTIL is changed.

4. Conclusion

Laser photolysis studies were carried out in the binary mixtures of RTIL and conventional organic solvents. Our results revealed that the mixed solvents characterize some new particular properties differing from the neat RTIL and pure organic solvent. It was indicated that RTIL itself participates in the reaction, and along with the change of the ratio of RTIL and organic solvent, the reaction rate constants change regularly. At lower V_{RTIL} , the concentration factor is dominant and the rate constant increases steadily with the increasing of V_{RTIL} ; To the contrary, at higher V_{RTIL} , the viscosity and phase transformation are dominant and the rate constant decreases obviously with the increasing of V_{RTIL} . Mixed [bmim][PF₆]/organic solution may be considered as a new type of medium for investigation of photochemical reactions.

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References

1. Welton, T. Room-Temperature Ionic Liquids. Solvents for synthesis and catalysis, *Chem. Rev.* **1999**, *99*: 2071-2083.
2. Rogers, Robin D.; Seddon, Kenneth R. Ionic liquids—Solvents of the future? *Science*, **2003**, *302*: 792-793
3. Gutowski, K. E.; Broker, G. A. Controlling the aqueous miscibility of ionic liquids: Aqueous biphasic systems of water-miscible ionic liquids and Water-Structuring salts for recycle, metathesis, and separations, *J. Am. Chem. Soc.* **2003**, *125*, 6632-6633.
4. Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic liquid (molten salt) phase organometallic catalysis, *Chem. Rev.* **2002**, *102*, 3667-3692.
5. Wu, G.Z.; Liu, Y.D.; Long, D.W., Effects of ionic liquid $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}]^{(+)}$ $[\text{ZnCl}_3]^{(-)}$ on gamma-radiation polymerization of methyl methacrylate in ethanol and N,N-dimethylformamide, *Macromol. Rapid. Commun.* **2005**, *26*, 57-61.
6. Gordon, C. M.; McLean, A. J. Photoelectron transfer from excited-state ruthenium(II) tris(bipyridyl) to methylviologen in an ionic liquid, *Chem. Commun.* **2000**, 1395-1396
7. Paul, A.; Mandal, P.; Samanta, A. How transparent are the imidazolium ionic liquids? A case study with 1-methyl-3-butylimidazolium hexafluorophosphate, $[\text{bmim}][\text{PF}_6]$, *Chem. Phys. Lett.* **2005**, *402*, 375-379.
8. Talaty, E.R.; Raja, S.; Storhaug, V.J.; Dolle, A.; Carper, W.R. Raman and Infrared spectra and ab Initio calculations of C_{2-4}MIM imidazolium hexafluorophosphate ionic liquids, *J. Phys. Chem. B*, **2004**, *108*, 13177-13184.
9. Liu, Y.D.; Zhang, Y.; Wu, G.Z.; Hu, J. Coexistence of liquid and solid phases of Bmim- PF_6 ionic liquid on mica surfaces at room temperature, *J. Am. Chem. Soc.* **2006**, *128*, 7456-7457
10. Marcinek, A.; Zielonka, J.; Gebicki, J. Ionic Liquids: Novel media for characterization of radical ions, *J. Phys. Chem. A*, **2001**, *105*, 9305-9309.
11. Wishart, J.F.; Neta, P. Spectrum and reactivity of the solvated electron in the ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide, *J. Phys. Chem. B*, **2003**, *107*, 7261-7267.
12. Baker, S.N.; Baker, G.A.; Kane, M.A.; Bright, F.V. The cybotactic region surrounding fluorescent probes dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate: effects of temperature and added carbon dioxide, *J. Phys. Chem. B*, **2001**, *105*, 9663-9668.
13. Karmakar, R.; Samanta, A.R. Intramolecular excimer formation kinetics in room temperature ionic liquids, *Chem. Phys. Lett.* **2003**, *376*, 638-645.
14. Grodkowski, J.; Neta, P. Reaction kinetics in the ionic liquid methyltributylammonium bis(Trifluoromethylsulfonyl) imide. Pulse radiolysis study of CF_3 radical reactions, *J. Phys. Chem. A*, **2002**, *106*, 5468-5473
15. Karmakar, R.; Samanta, A.R. Steady-state and time-resolved fluorescence behavior of C_{153} and PRODAN in room-temperature ionic liquids, *J. Phys. Chem. A*, **2002**, *106*, 6670-6675.
16. Karmakar, R.; Samanta, A. Dynamics of solvation of the fluorescent state of some electron donor-acceptor molecules in room temperature ionic liquids, $[\text{BMIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$ and $[\text{EMIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$, *J. Phys. Chem. A*, **2003**, *107*, 7340-7346.

17. Avaro, M.; Ferrer, B.; Garcia, H.; Narayana, M. Screening of an ionic liquid as medium for photochemical reactions, *Chem. Phys. Lett.* **2002**, *362*, 435-440.
18. Zuo, Z.H.; Yao, S.D.; Luo, J. Wang, W.F.; Zhang, J.S. Lin, N.Y. Laser photolysis of cytosine, cytidine and dCMP in aqueous solution, *J. Photochem. Photobiol. B: Biol.* **1992**, *15*, 215-222.
19. Kausche, T.; Suberlich, J.; Trobitzsch, E.; Beckert, D. and Dinse, K. P. Photoreduction of 9, 10-anthraquinone by triethylamine: a Fourier-transform EPR study. *Chem. Phys.* **1996**, *208*, 375-390.
20. Carlson, S. A. and Hercules, D. M. Studies of some intermediates and products of the photoreduction of 9, 10-anthraquinone. *Photochem. Photobiol.* **1973**, *17*, 123-131.
21. Muldoon, Mark J.; McLean, Andrew J.; Charles M. Gordon and Ian R. Dunkin, Hydrogen abstraction from ionic liquids by benzophenone triplet excited states, *Chem. Commun.* **2001**, 2364-2365.
22. Görner, H. Photoreduction of 9, 10-Anthraquinone derivatives: Transient spectroscopy and effects of alcohols and amines on reactivity in solution, *Photochem. Photobiol.* **2003**, *77*, 171-179.
23. Ohtaki, H.; Niwa, Y.; Ozutsumi, K.; etc. Anomaly of the basicity of water in mixed solvents, *J. Mol. Liq.* **2006**, *129*, 49-56.
24. Görner, H. Photoprocesses of *p*-benzoquinones in aqueous solution, *J. Phys. Chem. A*, **2003**, *107*, 11587-11595.
25. Dupont, J. On the solid, liquid and solution structural organization of imidazolium ionic liquids, *J. Braz. Chem. Soc.* **2004**, *15*, 341-350.
26. Jarosik A.; Krajewski, S. R.; Lewandowski, A.; Radzimski, P., Conductivity of ionic liquids in mixtures, *J. Mol. Liq.* **2006**, *123*, 43-50.
27. Espenson, J.H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed. McGraw-Hill: New York, **1995**, 201-202.