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Reactions of solvated electrons with imidazolium cations in ionic liquids

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Abstract

We examined formation of solvated electrons in several ionic liquids composed of ammonium, pyrrolidinium and piperidinium cations by observing absorption spectra in the visible and near-infrared regions using pulse radiolysis. We also examined reactions of the solvated electrons with imidazolium cations in the ionic liquids. The reaction rate constants were an order of magnitude faster than the diffusion limited rate calculated from the viscosity. The electrons before full solvation (dry electrons) reacted efficiently with the imidazolium cations. These observations suggest that the electrons in the ionic liquids can move easily before solvation. The scavenging of the dry electron by the imidazolium cation was also examined using C2-alkylated-imidazolium cations. It is found that the alkylation of imidazolium suppresses the reactivity with the dry electron.

Keyword: Pulse radiolysis; Solvated electron; Dry electron; Alkylation

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1. Introduction

Room-temperature ionic liquids are salts with melting points near or below ambient temperature. They have very unique properties, such as negligible vapor pressure, excellent solvation ability and high thermal stability (Welton, 1999; Wasserscheid and Welton, 2003; Rogers and Seddon, 2003; Ranke et al., 2007). One important application of ionic liquids is as a medium for the processing of spent nuclear fuel (Allen et al., 2002; Harmon et al., 2001; Shkrob et al., 2007). Successful use of ionic liquids in radiation environments requires an understanding of radiation chemistry of ionic liquid (Grodkowski and Neta, 2002a; Grodkowski and Neta, 2002b; Grodkowski and Neta, 2002c). Wishart and Neta have for the first time observed absorption spectrum and reaction kinetics of solvated electrons in an ionic liquid methyltributylammonium bis(trifluoromethylsulfonyl)imide (R_4N -TFSI) using pulse radiolysis (Wishart and Neta, 2003). The spectrum of solvated electron was broad and the absorption maximum was located around 1400nm. Wishart et al. have also studied the solvation dynamics around the excess electron (Wishart et al., 2005). The solvation dynamics was very slow, suggesting that, in ionic liquids, not only the solvated electrons but also the pre-solvated or dry electrons play quite important roles.

Chandrasekhar *et al.* have attempted the laser-induced formation of solvated electrons in two ionic liquids, trihexyltetradecylphosphonium-bis(trifluoromethylsulfonyl)imide and butyl-methyl-pyrrolidinium-bis(trifluoromethylsulfonyl)imide (Chandrasekhar *et al.*, 2006). However, their reported spectra and kinetics are quite different from the results by the pulse radiolysis measurements previously reported. We have recently studied solvated electron in trimethyl-propylammonium-bis(trifluoromethylsulfonyl)imide (TMPA-TFSI) produced by pulse radiolysis as well as photodetachment of iodide through charge-transfer-to-solvent (CTTS) band excitation (Kato et al., 2007). The spectra obtained from the both methods were identical and broad absorption band peaking around 1100 nm. The absorption signal decay became faster by adding electron scavengers. From these experimental findings, the observed species could be attributed to solvated electrons in the ionic liquid.

The reaction of hydrated electron with imidazolium cations were previously measured in water (Behar et al., 2001). However, information about the reaction rates of the solvated electron with imidazolium cation in ionic liquid are very limited. In the present work, we examine the reaction kinetics of solvated electron formed in ionic liquids with several imidazolium cations.

2. Experiments

Electron pulse radiolysis experiments were carried out using the 30 MeV Linac installed at SANKEN, Osaka University (Kawaguchi et al., 2003). The spectrum of solvated electrons in ionic liquids were measured by injecting an 8-ns electron pulse and monitoring the optical absorption of the solvated electrons. A pulsed 100-W xenon-arc lamp provided the probe light, and the wavelength was selected using a monochromator with appropriate cutoff filters. The probe light was detected with a reverse-biased photodiode, and the data were acquired with a digital oscilloscope.

The solvated electrons were also produced by an electron photodetachment from iodine by a KrF excimer laser (Lambda Physik, Lextra 100, 248 nm). For the measurements of the transient absorption signal, a 300 W xenon arc lamp (Ushio, UXL-300D) was used as a probing light source. The excitation pulse irradiated the sample in the cuvette through a 10 × 6 mm rectangular mask, while the analyzing light passed through 2-mm pinholes. A wide band-pass filter (FWHM = 40 nm, Opto-line) was used to select the analyzing wavelength. Transient signals were detected with a fast silicon photodiode (3ns rise time, NewFocus, 1801) with a 500MHz oscilloscope (Tektronix, DPO 7054). Absorption spectra of solutions were measured with an absorption spectrophotometer (Shimadzu, UV-3101PC).

Figure 1 shows the structures of ionic liquid cations used in this study as solvents and solutes. In Table 1 full and abbreviated names of the ionic liquids used are listed. All of the ionic liquids are purchased from Kanto Chemical Co., Inc (Tokyo, Japan). For the ionic liquid used as solvents, no strong absorption above 210 nm was observed, suggesting that purity of the liquids is enough both for kinetic measurements and the optical measurements in an UV wavelength range. The ionic liquid solutions were prepared in a bottle and dried under

vacuum at 60 °C for 3 hr. In both the pulse radiolysis and the photodetachment experiments, a 1 cm cuvette was used. The samples filled in the cuvettes were dried again under vacuum at 60 °C before use. As a solute molecule for the reaction with solvated electron, imidazolium based ionic liquids were used. The concentrations of KI were adjusted around 0.4 to 0.8 mM for the photodetachment experiments.

3. Results and Discussion

Figure 2 shows absorption spectra of solvated electron in the ionic liquids measured by the pulse radiolysis technique. The spectra were recorded at 10 ns after the pulse irradiation. No significant spectral shift was observed within a measured time window (10 to 1000 ns). The absorption maxima are located at 1100 nm in all ionic liquids studied, which are similar to that observed in TPA-TFSI as previously reported (Kato et al., 2007). The similarity of the peak position implies that electrons in these ionic liquids are located in sites having similar chemical environments. Probably, the electrons are localized near nitrogen atoms in the free space surrounded by ammonium cations. The peak position is located at significantly longer wavelength than those of electrons in polar solvents, such as methanol (633 nm) and 2-propanol (820 nm). Therefore, the electrons in the ionic liquid examined may be weakly solvated in the ionic liquids.

Wishart and Neta reported the absorption spectrum of solvated electrons in a similar ionic liquid (R_4N -TFSI) (Wishart and Neta, 2003). They observed the electron peak at 1400 nm, which is a longer wavelength than that obtained in the present study. This difference may be due to the increasing size of the free space for the solvated electrons because of the bulky butyl groups in R_4N -TFSI. Wishart also studied the effect of functional group substitution on the spectra of solvated electrons in ionic liquids containing ether-, alcohol-, and alkyl-functionalized ammonium dications (Wishart et al., 2005). For the alcohol-functionalized ionic liquid, the spectrum observed at 2 ns has a peak at 800 nm with a shoulder around 1200 nm. At successive time intervals the shoulder disappears and the peak shifts to 650 nm, which is typical peak position of the solvated electron in alcohols. They speculated that excess electrons are localized near the hydroxylic group of the alcohol-functionalized cation. On the contrary, for ether- and alkyl-functionalized ionic

liquids, the peak positions of absorption spectra due to electron were similar to those of the present study. This suggests that the electrons are localized near the nitrogen atoms in the free space formed by the cations.

Figure 3 shows the absorption spectra of KI in the ionic liquid studied here. These peaks can be assigned to the CTTS absorption band of iodide. The peak positions shift to longer wavelength with the increasing size of the cation. The following correlation between the peak position of the CTTS absorption of iodide (E_{CTTS}) and that of the solvated electron ($E_{electron}$) has been proposed previously (Fox and Hayon, 1974),

$$E_{electron} = A \times E_{CTTS}^{1.65} \quad (1)$$

where A is a proportional constant. As we reported previously, the CTTS absorption band of TMPA-TFSI appears at 225 nm, which is similar to the positions in water (228 nm) and in methanol (220 nm), but the peak is blue shifted compared to the peaks in ammonia (260 nm) (Fox and Hayon, 1974). If the above correlation is fulfilled, the peak position due to solvated electron in the ionic liquids must shift to longer wavelength with the increasing size of molecule, whereas no peak difference can be seen (Fig. 2).

Peak position of the solvated electron can be predicted from the CTTS absorption maxima. From the observed CTTS absorption maxima in TMPA-TFSI (225 nm) and in P14-TFSI (230 nm), the absorption maximum of solvated electrons can be expected to be at about 730 nm and at 830 nm, respectively. However, the predicted absorption peak is much shorter than the one we observed: 1100 nm for both liquids. This discrepancy shows that the solvation process of iodide in ionic liquid differs from that of the electrons. The peak position of the CTTS absorption band demonstrates that the solvation of iodide is relatively strong, whereas weak solvation can be seen for the electrons. This implies that the strong solvation is due to the specific interaction between iodide and ammonium cation, for example, ion-pair formation.

As shown in Fig. 3, the CTTS excitation of iodide can be made by 248-nm laser pulse and thus the solvated electrons can be produced through photodetachment reaction of iodide.

Figure 4 shows typical transient absorption signals of solvated electron excited by 248-nm laser pulse monitored at 700nm with several different concentrations of Bmim-TFSI in P14-TFSI. As clearly shown in the Figure, the decay rates became faster by adding Bmim-TFSI, indicating that an electron scavenging reaction by Bmim occurs. By fitting the decay curves with a single exponential function, pseudo-first-order reaction rate constants could be obtained. The second-order reaction rates were extracted from the pseudo-first-order reaction rates and the concentrations of Bmim. Similar measurements were performed in the ionic liquids of P13-TFSI and TMPA-TFSI. The second-order reaction rates obtained are summarized in Table 2. In the table the viscosities and the calculated diffusion limited rate constants k_{diff} based on Eq.(2) were also included.

$$k_{\text{diff}} = 8000RT/3\eta \quad (2)$$

Where η is viscosity (in Pa s), R is the gas constant ($8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature. The rate constants obtained from experiments were significantly faster than that of the calculated ones. It has been previously pointed out that the bulk viscosity of ionic liquid is not a direct determinant of the diffusion limited rate constant (Wishart and Neta, 2003; Grodkowski et al., 2003). It was suggested that the difference in the rate between the calculation and measurement was due to the voids that exist in ionic liquids and the possibility that reacting species diffuse through movement of small groups of ions, whereas viscosity is related to simultaneous movement of all ions. In the previous pulse radiolysis experiments on the reaction of solvated electron with aromatic solutes, the experimental rates were almost an order of magnitude higher than the values estimated from the viscosities of the ionic liquids (Wishart and Neta, 2003). On the other hand, the reaction rates of hydrogen atom with the aromatic molecules are two orders of magnitude higher than the calculated rate based on the viscosities in the same ionic liquid (Grodkowski et al., 2003). They speculated that a small neutral species such as hydrogen atom can move easily between voids within the ionic liquids, whereas the solvated electron, being a charged species, must interact with the ionic charges of the medium to diffuse. As a consequence, we think that the diffusion of solvated electrons is evidently hard to calculate from the bulk viscosities of ionic liquids.

In our previous paper, it was found that, in the ionic liquid TMPA-TFSI, the

pre-solvated electron (or dry electron) reacts with Bmim very efficiently (Katoh et al., 2007). Similar behavior has been already observed for the reaction of electrons with some aromatic molecules in ionic liquid (R_4NNTf_2) (Wishart and Neta, 2003). As described previously, the fractional yield of the solvated electron after the fast reaction of the dry electrons can be evaluated by using the following relation,

$$G/G_0 = \exp(-C/C_{37}) \quad (3).$$

Where G_0 is the yield of solvated electron without scavengers, G is the yield of solvated electron at a given solute concentration C , and C_{37} is the concentration where only 37% ($=1/e$) of the electrons survive to be solvated. The C_{37} values for Bmim cation in the ionic liquids P13, P14, and TPA are listed in Table 2. It has been reported that the C_{37} values for various aromatic molecules in R_4NNTf_2 , for examples, 0.062 mol/L for benzophenone, 0.063 mol/L for pyrene, and 0.084 mol/L for phenanthrene. The C_{37} values for Bmim cation are about 0.05 in the ionic liquids P13, P14, and TPA, hence, it can be said that Bmim cation reacts more efficiently with the dry electron than the aromatic molecules. Because there is no significant difference in the C_{37} between P13, P14 and TPA, the reaction environment where the dry electron migrates could be almost the same for the ionic liquids P13, P14 and TPA. These results are very important in terms of the radiation damage of ionic liquids based on the imidazolium cations. Since the concentration of Bmim in a normal ionic liquid, for example Bmim-TFSI, is about 3 to 5 M, there is no chance that the dry electrons could survive to form the solvated electron in the Bmim ionic liquids. Thus, in the Bmim ionic liquid, a main reducing species is not the solvated electron but imidazolyl radical, however the dry electron can still play a very important role.

It is reported that C2-alkylation of imidazolium cation is extremely effective to extend the electrochemical redox window of the imidazolium based ionic liquid (Hayashi et al., 2005). We examined the reaction of the solvated electron with three alkylated-imidazolium cations, 1-ethyl-2,3-dimethylimidazolium (EDmim), 1-butyl-2,3-dimethylimidazolium (BDmim) and 1-hexyl-2,3-dimethylimidazolium (HDmim). TPA-TFSI was used as the solvent. The measured reaction rates for the alkylated-imidazolium cations were found to be very close each other and are 3.8×10^8 , $3.0 \times$

10^8 and 3.0×10^8 respectively. These rates are not significantly different from the reaction rate of the non-alkylated-imidazolium Bmim presented in Table 2. Hence the effect of the alkylation of imidazolium on the reaction of the solvated electron is small. On the contrary, we found that the C_{37} for these alkylated-imidazolium cations are different from that of Bmim. Fig. 5 shows a correlation between the normalized initial concentration of solvated electron G/G_0 and the concentration of alkylated-imidazolium in TMPA-TFSI. The C_{37} for EDmim, BDmim and HDmim are 0.081, 0.13, 0.12 mol/L, respectively. These values are higher than that for Bmim, indicating that it requires a higher concentration of the alkylated imidazolium cation to capture the dry electron. Since the reaction rates of the solvated electron with Bmim and the alkylated-imidazolium are quite close each other, it is concluded that the reactivity of the solvated electron and the dry electron is quite different in the ionic liquids, and the alkylation of imidazolium cation reduces the reactivity of the dry electron with the cation.

4. Conclusion

We studied the solvation properties of iodide and electrons in ionic liquids composed of ammonium, pyrrolidinium and piperidinium cations. We found that the interaction between the cation and iodide was relatively strong, whereas electrons were weakly solvated in the ionic liquids examined.

We observed electron photodetachment from iodide to the ionic liquid. The rate constants of the reaction of the solvated electrons with Bmim-TFSI were determined in the ionic liquids of P13, P14 and TMPA-TFSI. It is found that the rate constants are about 5 to $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and these rates are an order of magnitude faster than the calculated rates from the viscosities of ionic liquids. The reaction of electrons before full solvation (or dry electrons) with Bmim cation was efficient, which suggests that the electrons in P13, P14 and TMPA-TFSI are highly mobile before complete solvation. It is found that the alkylation of the imidazolium reduces the reactivity with the dry electron.

Recently the positronium lifetime measurements were performed in several ionic liquids to investigate the mobility of the dry electrons in ionic liquids through positronium formation (Hirade, 2007). The lifetime of the positronium was anomalously long. This results suggests that the mobility of the dry electron is very fast and the positronium was formed

even at the later positron age, because if the electrons are once localized somewhere, their mobility becomes much slower and hence the positronium cannot be formed anymore. We believe that the ionic liquids are very interesting reaction medium for examining the reaction mechanisms of dry electrons.

Acknowledgments

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Table 1. Ionic Liquids Used in the Experiments and Their Full and Abbreviated Names

used as solvent

1	TMPA-TFSI	<i>N,N,N</i> -trimethyl- <i>N</i> -propylammonium bis(trifluoromethylsulfonyl)imide
2	P13-TFSI	<i>N</i> -methyl- <i>N</i> -propylpyrrolidinium bis(trifluoromethylsulfonyl)imide
3	P14-TFSI	<i>N</i> -butyl- <i>N</i> -methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
4	PP13-TFSI	<i>N</i> -methyl- <i>N</i> -propylpiperidinium bis(trifluoromethylsulfonyl)imide

used as solute

5	Bmim-TFSI	<i>N</i> -butyl- <i>N</i> -methylimidazolium bis(trifluoromethylsulfonyl)imide
6	EDmim- TFSI	<i>N</i> -Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
	BDmim- TFSI	<i>N</i> -Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
	HDmim- TFSI	<i>N</i> -Hexyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide

Table 2. The reaction rates of solvated electron with Bmim in ionic liquids.

	η^a	k^b	k_{diff}^c	C_{37}^d
P13-TFSI	55	$(7.5 \pm 1.1) \times 10^8$	1.2×10^8	0.057
P14-TFSI	69	$(6.8 \pm 0.9) \times 10^8$	9.6×10^7	0.055
TMPA-TFSI	69	$(5.3 \pm 0.8) \times 10^8$	9.6×10^7	0.057

^aViscosity, in mPa s. ^bExperimental rate constant, in $\text{M}^{-1} \text{s}^{-1}$. ^cCalculated diffusion-limited rate constant by Eq.(2), in $\text{M}^{-1} \text{s}^{-1}$. ^d C_{37} defined by Eq.(3), in M.

Figure Captions

Fig. 1. Structures of ionic liquid cations examined.

Fig. 2. Absorption spectra of solvated electron in several ionic liquids.

Fig. 3. Absorption spectra of iodide in several ionic liquids.

Fig. 4. Kinetics of the reaction of electron with Bmim in P14-TFSI observed at 700 nm after 248-nm excitation.

Fig. 5. Correlation between the normalized initial absorbance and concentration of C2-alkylated imidazolium in TMPA-TFSI.

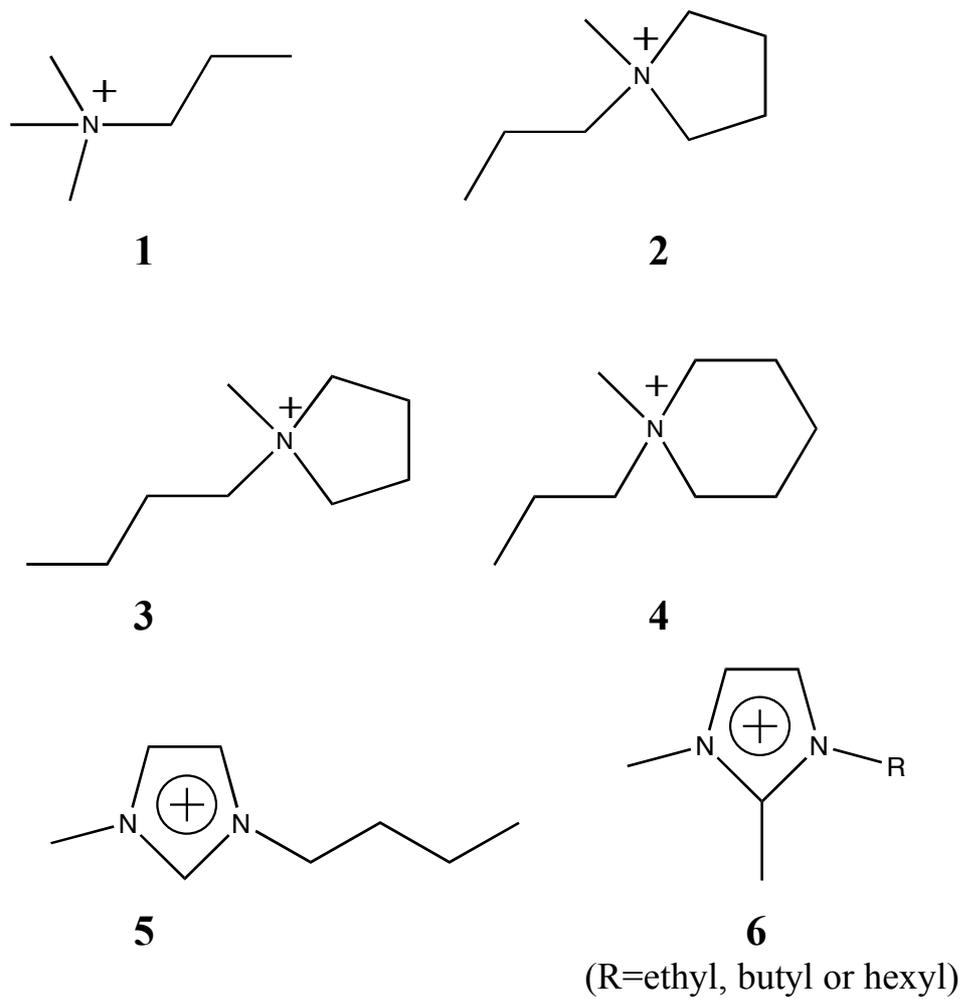


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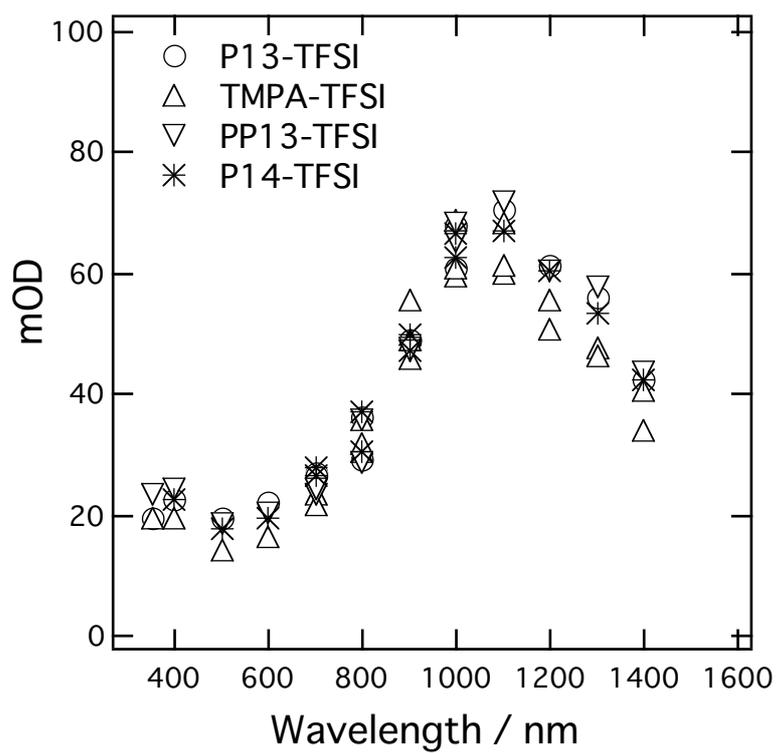


Fig. 2. Absorption spectra of solvated electron in several ionic liquids.

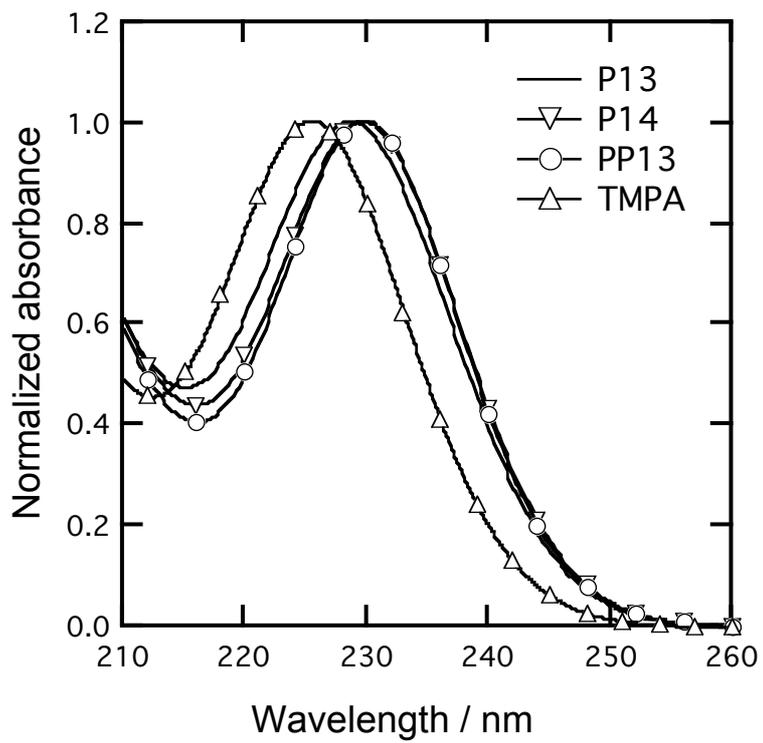


Fig. 3. Absorption spectra of iodide in several ionic liquids.

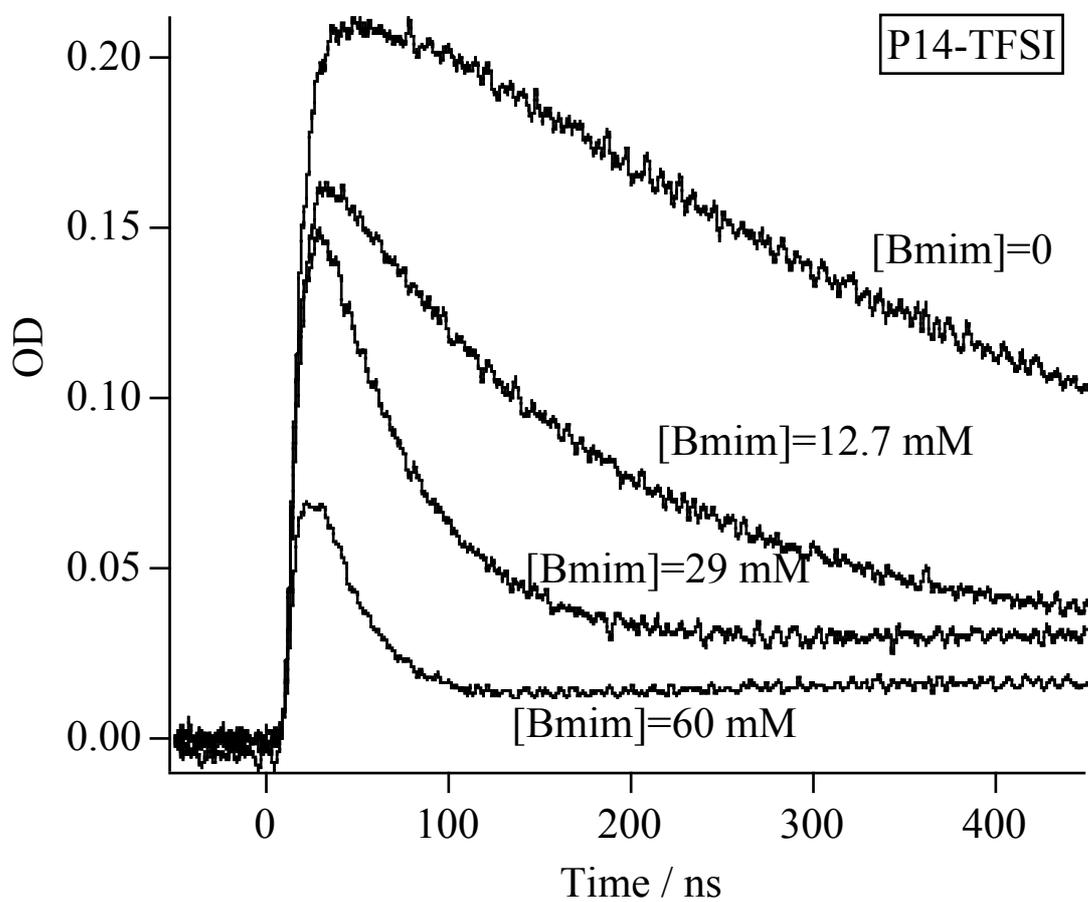


Fig. 4. Kinetics of the reaction of electron with Bmim in P14-TFSI observed at 700 nm after 248-nm excitation.

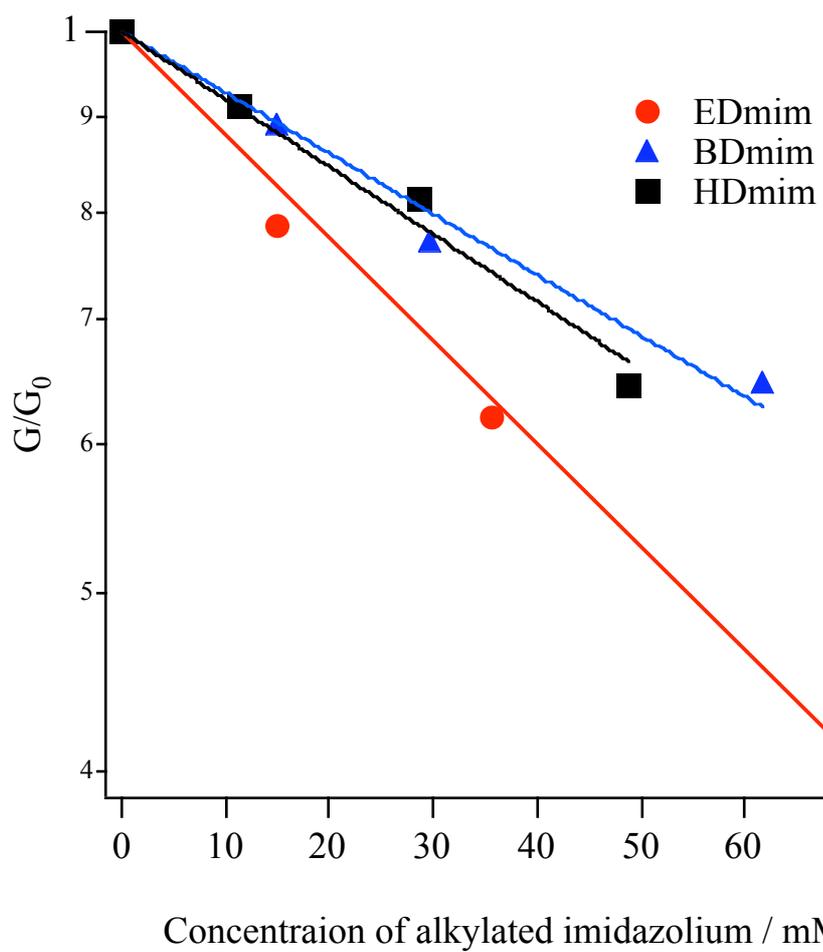


Fig. 5. Correlation between the normalized initial absorbance and concentration of C2-alkylated imidazolium in TPA-TFSI.