Pulse radiolysis studies of functionally substituted imidazolium-based ionic liquids

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The reactions of imidazolium-based ionic liquids having different substituent groups on the ring with hydrated electrons (e_{aq}^-), hydroxyl radicals ($^\bullet OH$), and sulfate anion radicals ($SO_4^{\bullet -}$) were investigated using nanosecond pulse radiolysis techniques. The spectra of these ionic liquids on reaction with e_{aq}^- all exhibited a similar peak at about 320 nm, and a typical peak for e_{aq}^- in aqueous ionic liquid solutions. The reaction rate constants for 1,3-disubstituted imidazolium-based ionic liquid hexafluorophosphates (BMIPF$_6$) with e_{aq}^- were deduced to be 10^{10} L mol^{-1} s^{-1}, however the values were lower for trisubstituted ionic liquids. For example, the rate constant for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (BMMIBF$_4$) was 5.5×10^9 L mol^{-1} s^{-1}. Imidazolium-based ionic liquids reacted with hydroxyl radicals via adducts to produce a mixture of isomeric OH adducts, and the pk_a value of the OH adducts was deduced to be 8.4 ± 0.4 for 1-butyl-3-methylimdazolium tetrafluoroborate (BMIBF$_4$). Moreover, imidazolium cations were also oxidized by $SO_4^{\bullet -}$ to produce bivalent cation radicals, which exhibit a peak at 320 nm, and these rate constants are of the same order of magnitude, i.e., 10^9 L mol^{-1} s^{-1}, except that for 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate with $SO_4^{\bullet -}$ ($k = 2.8 \times 10^8$ L mol^{-1} s^{-1}). Theoretical calculations were carried out to estimate the structures of the products of reduction by e_{aq}^- and the results were related to the experimental data.

pulse radiolysis, imidazolium-based ionic liquids, kinetics, rate constants

Room-temperature ionic liquids (RTILs), which have low melting points (T_m typically<100°C), are usually liquids composed of bulky organic cations and smaller inorganic anions. RTILs have been receiving increasing attention in recent years because of their low volatility, high polarity, ease of recycling, and high thermal stability compared to those of common solvents [1–3]. They have therefore been proposed as "green solvents" for chemical reactions and separation processes [4–6]. One important application of RTILs is as media for the processing of spent nuclear fuels [6,7]. It is therefore necessary to observe the characteristics of radiation chemistry in ionic liquids to understand the factors that control their stability under ionizing radiation, and to study the kinetics using pulse radiolysis methods

[8–11]. The direct observation of solvated electrons in an ionic liquid was first reported for methyltributylammonium bis(trifluoromethylsulfonyl)imide; e_{solv}^- has a lifetime of ~300 ns and a broad absorption spectrum that peaks at 1400 nm [12]. To compare the rate constants in ionic liquids with those in other solvents, Neta and co-workers [9,10,13] investigated the reactions of $CCl_3O_2^\bullet$ radicals with Trolox and chlorpromazine, which have been studied in a wide variety of solvents. However, there have been few reported radiolysis studies of functionalized ionic liquids, although many "task-specific" liquids have been designed to control solubility or to provide a specific prosthetic group such as a reagent or catalyst. Wishart et al. [14] studied the effects of functional group substitution on the spectra of solvated electrons in different types of quaternary ammonium ionic liquids. The energetics and mobilities of intermediate electron solva-

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tion states were observed for several hundred nanoseconds, and the blue shift took place in a very short time (25–40 ns).

The structures of the cations and anions are shown in Scheme 1. In the present study, the transient processes of imidazolium-based ionic liquids with various substituent groups on the imidazole ring with radicals such as $^\bullet OH$, e_{aq}^-, and $SO_4^{\bullet-}$ were observed using nanosecond pulse radiolysis techniques. The kinetics were determined, and the influences of various functional groups on the imidazolium ring and different anions on the kinetics are also discussed.

1   Experimental

1.1   Materials

All ionic liquids were provided by the Chengjie Chemical Company (Shanghai, China), and were of the highest purity available commercially. Prior to use, the ionic liquids were treated with activated charcoal for at least 48 h and filtered twice by passing through a Celite column. The liquids were then transferred to a clean dry reagent bottle and kept under vacuum for 12 h at 65°C to remove any volatile organic
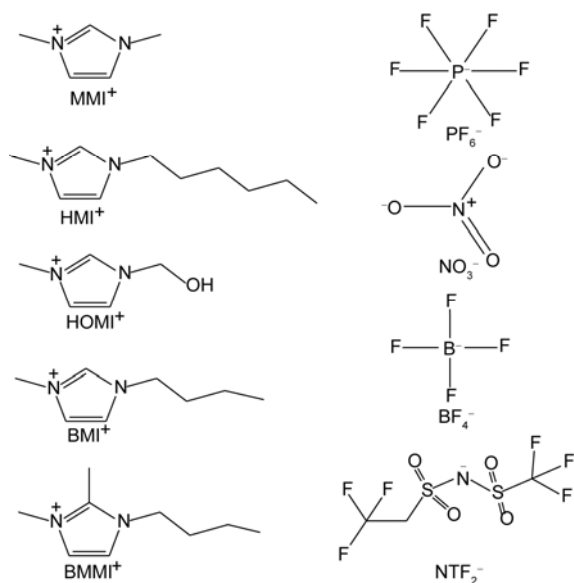
Scheme 1   Structures of imidazolium-based ionic liquids.

impurities and moisture. The purified ionic liquids were stored in an airproof desiccator. Tert-butyl alcohols and $K_2S_2O_8$ were purchased from Sigma Company (Shanghai, China).

All sample solutions were freshly prepared in triply distilled water and deaerated with high purity N_2 (99.99%) or N_2O, for different purposes, by bubbling for at least 20 min immediately before the experiments. All experiments were carried out at room temperature.

The ionic liquids used and their abbreviations are listed in Table 1. The imidazolium-based ionic liquids containing the anions BF_4^- or NO_3^- are soluble in water, whereas those with NTF_2^- and PF_6^- are less soluble. At 20°C, the solubility of $BMINTF_2$ in water is about 1.4% and that of $BMIPF_6$ is 2% [15].
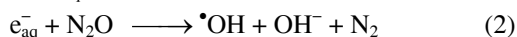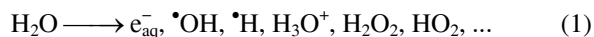
1.2   Pulse radiolysis

Pulse radiolysis experiments were performed using a 10 meV linear accelerator delivering an electron pulse with a duration of 20 ns, at the Shanghai Institute of Applied Physics. The electron pulse dosimetry was determined using a thiocyanate dosimeter with $G[(CNS)_2^{\bullet-}]=6.0$ in a 100 mmol L^{-1} KSCN solution saturated with N_2O by taking $\varepsilon_{480\,nm} = 7600$ L mol^{-1} cm^{-1} for $(CNS)_2^{\bullet-}$. G value is known as radiation chemical yield, which means the number of molecules produced or destroyed for each 100 electronvolts absorbed by a substance from ionizing radiation. The details of the setup and operating conditions have been described elsewhere [16]. The dose was about 18 Gy per pulse. The uncertainties in the measurements of wavelength, transient absorption, and least-squares fitting in obtaining the rate constants were ~1 nm, <1, and <5%, respectively.
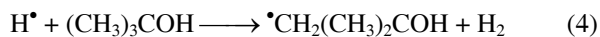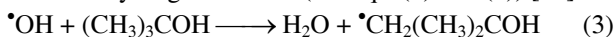
1.3   Reactions with radicals

Free radicals were generated using standard methods for converting the primary species of the radiolysis of water, such as e_{aq}^-, $^\bullet OH$, and $^\bullet H$ (eq. (1)). To study only the reactions of hydroxyl radicals, solutions were pre-saturated with N_2O, which quantitatively converts hydrated electrons to hydroxyl radicals via eq. (2) [17].

Table 1   Full and abbreviated names of ionic liquids used in the experiments

Abbreviated names	Full names
$MMIBF_4$	1,3-Dimethylimdazolium tetrafluoroborate
$BMIBF_4$	1-Butyl-3-methylimdazolium tetrafluoroborate
$HMIBF_4$	1-Hexyl-3-methylimdazolium tetrafluoroborate
$BMMIBF_4$	1-Butyl-2,3-dimethylimdazolium tetrafluoroborate
$HOMIBF_4$	1-(2'-Hydroxylethyl)-3-methylimdazolium tetrafluoroborate
$BMIPF_6$	1-Butyl-3-methylimdazolium hexafluorophosphate
$BMINTF_2$	1-Butyl-3-methylimdazolium bis(trifluoromethylsulfonyl)imide
$BMINO_3$	1-Butyl-3-methylimdazolium nitrate

$$H_2O \longrightarrow e_{aq}^-, \ ^\bullet OH, \ ^\bullet H, \ H_3O^+, \ H_2O_2, \ HO_2, ... \quad (1)$$

$$e_{aq}^- + N_2O \longrightarrow \ ^\bullet OH + OH^- + N_2 \quad (2)$$

To achieve reactions of hydrated electrons, the solutions were pre-saturated with N_2 in the presence of 1.0 mol L^{-1} *tert*-butyl alcohol (*t*-BuOH), which can be converted into the relatively inert *t*-BuOH radicals by scavenging hydroxyl radicals and hydrogen radicals (see eqs. (3) and (4)) [17].

$$^\bullet OH + (CH_3)_3COH \longrightarrow H_2O + \ ^\bullet CH_2(CH_3)_2COH \quad (3)$$

$$H^\bullet + (CH_3)_3COH \longrightarrow \ ^\bullet CH_2(CH_3)_2COH + H_2 \quad (4)$$

In the system, $^\bullet H$ and e_{aq}^- react with $S_2O_8^{2-}$ to produce $SO_4^{\bullet-}$ (eqs. (5) and (6)).

$$e_{aq}^- + S_2O_8^{2-} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (5)$$

$$^\bullet H + S_2O_8^{2-} \longrightarrow SO_4^{\bullet-} + HSO_4^- \quad (6)$$
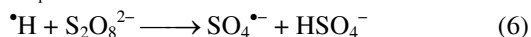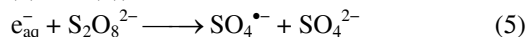
2   Results and discussion

2.1   Reactions with hydrated electrons

The transient absorption spectrum was obtained under pulse radiolysis for an aqueous solution containing $BMIBF_4$ (0.1 mmol L^{-1}) and *t*-BuOH (1.0 mol L^{-1}), deoxygenated with N_2 (Figure 1). A strong absorption spectrum appears over a broad region from 470 to 740 nm in a very short lifetime. This absorption spectrum had a maximum absorption at around 700 nm and was assigned to that of hydrated electrons, by comparison with previous studies [17]. As shown in Figure 1 and insert (a), after the decay of a hydrated electron, a new transient species with a characteristic absorption band at around 320 nm was observed; this was attributed to addition of an electron to give the neutral $BMI^\bullet$ radical.

$$e_{aq}^- + BMI^+ \longrightarrow BMI^\bullet \quad (7)$$

It is known that e_{aq}^- does not react with Cl^-, and it can be assumed that e_{aq}^- does not react with PF_6^-, BF_4^-, or other anions. The rate of e_{aq}^- decay was unchanged in other ionic liquids. The rate constants were obtained by varying the $BMIBF_4$ concentration (Figure 1, inset (b)). The values of the rate constants for e_{aq}^- with imidazolium ionic liquids are summarized in Table 2. The values were consistent with the results obtained using 1-methylimdazolium ions [18] and 1-butyl-3-methylimidazolium chloride [13].

When the 2-position of the imidazole ring was alkylated, the rate constant was smaller than that for an imidazole with no alkyl group at position 2. The reaction constants of three C2-alkyl imidazolium cations [1-ethyl-2,3-dimethylimdazolium, 1-butyl-2,3-dimethylimdazolium ($BMMI^+$), 1-hexyl-2,3-dimethylimdazolium] with hydrated electrons were examined, and were found to be very close each other, 5.9×10^9, 5.5×10^9, and 5.1×10^9 L mol^{-1} s^{-1}, respectively, whereas that of the BMI^+ cation was 1.8×10^{10} L mol^{-1} s^{-1}. These findings are quite similar to those of Takahashi et al. [19]. They found that alkylation of the imidazolium suppresses reactivity with dry electrons. The influence may be less in aqueous solutions than in neat ionic liquids as a
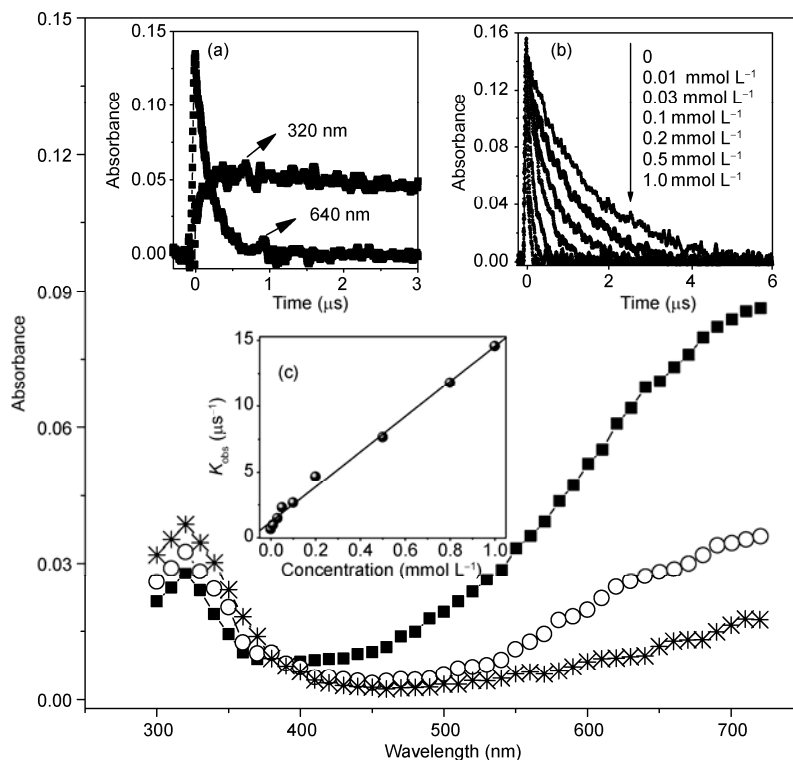

Figure 1   Transient absorption spectra of the radicals produced by radiolysis of 0.1 mmol L^{-1} BMIBF4 in N_2-saturated aqueous solutions at pH 7.1, buffered with 2 mmol L^{-1} phosphate, recorded at (■) 0.1, (○) 0.3, and (∗) 0.5 μs after the electron pulse. Insets: (a) Growth at 320 nm and decay at 640 nm; (b) time profiles observed at 640 nm for e_{aq}^-; and (c) decay rate of e_{aq}^- at 640 nm plotted as a function of $BMINTF_2$ concentration.

Table 2   Rate constants for the reactions of ionic liquids with radicals

RTILs	k (L mol^{-1} s^{-1})		
	e_{aq}^-	$^{\bullet}$OH	$SO_4^{\bullet -}$
MMIBF$_4$	2.5×10^{10}	4.2×10^9	1.0×10^9
BMIBF$_4$	1.8×10^{10}	3.3×10^9	1.2×10^9
HMIBF$_4$	1.3×10^{10}	3.1×10^9	2.5×10^9
BMMIBF$_4$	5.5×10^9	1.2×10^9	2.1×10^9
HOMIBF$_4$	1.7×10^{10}	2.6×10^9	2.8×10^8
BMINO$_3$	1.8×10^{10}	2.9×10^9	1.1×10^9
BMINTF$_2$	1.7×10^{10}	2.8×10^9	1.3×10^9
BMIPF$_6$	2.1×10^{10}	3.1×10^9	1.4×10^9

result of the high viscosities of ionic liquids. In addition Hayashi et al. [20] reported that C2-alkylation of imidazo- lium cations is extremely effective in extending the electro- chemical redox window of imidazolium-based ionic liquids.

To determine why C2-alkylation of imidazolium cations suppresses reactivity with radicals, we carried out *ab initio* molecular orbital calculations on imidazolium-based cations and neutral radicals, namely 1,3-dimethylimdazolium,1- butyl-2,3-dimethylimdazolium, 1-hexyl-3-methylimdazolium, 1-butyl-3-methylimdazolium, and 1-(2-hydroxyethyl)-3-methy- limdazolium radicals, using the Gaussian 03 suite of pro- grams [21]. All geometry optimizations were at the level of Becke's three-parameter hybrid exchange functional, and the density functional theory gradient-corrected correlation functional developed by Lee, Yang, and Parr (B3LYP) [22], and the 6-31G+(d,p) basis set were used. It was found that all spin densities lie mainly at C2 of the imidazole ring for both cations and radicals (Tables 3 and 4). The results agree with those in the corresponding report by Behar et al. [13]. The structure of the electron adducts (BMI$^{\bullet}$) is more closely represented by an allylic structure formed by the two nitro- gens and C2, and which is not conjugated with the C4=C5

double bond, rather than by a fully conjugated structure. When there is C2-alkylation of the imidazolium cations, the BMMI$^+$ structures, which are more sterically hindered than those of BMI$^+$, make it more difficult for e_{aq}^- to attack posi- tion 2 of the imidazole ring. Furthermore, CH$_3^-$, as an elec- tron-donating group, can increase the electron cloud at C2, which may be worse for the reaction of e_{aq}^- with BMMI$^+$ than for that with BMI$^+$.

2.2 Reactions with $^{\bullet}$OH

An aqueous N$_2$O-saturated solution of 0.1 mmol L^{-1} BMIBF$_4$ at pH 7.1 was pulse-irradiated. The transient spec- tra showed a strong narrow absorption band at around 320 nm, and another quite broad absorption band in the 390–460 nm range (Figure 2). These absorption bands were similar to those previously observed for OH adducts of imidazoles, as shown in eq. (8) [13,18]. The rate constant was determined for the rate of absorption buildup at 320 nm, and was found to be 3.5×10^9 L mol^{-1} s^{-1} at pH 7.1 (Figure 2, inset), only slightly lower than the value reported for the *N*- methylimidazolium cation (5×10^9 L mol^{-1} s^{-1}) [18].

$$BMI^+ + {}^{\bullet}OH \longrightarrow HO\text{-}BMI^{\bullet +} \qquad (8)$$

On varying the pH values from 5.5 to 11, the rate con- stants of BMIBF$_4$ reacting with OH radicals decreased from 3.5×10^9 to 0.9×10^9 L mol^{-1} s^{-1}. This change indicated the existence of an acid-base equilibrium. Figure 3 shows the dependence of rate constants on pH values. Sigmoidal fitting of the origin showed that the pK_a value of the OH adducts was 8.4±0.4. The OH adducts therefore possibly undergo ionization followed by rearrangement, as shown in eq. (9).

$$HO\text{–}BMI^{\bullet +} + OH^- \rightleftharpoons {}^-O\text{-}BMI + H_2O \qquad (9)$$
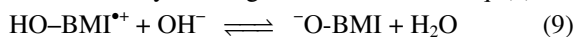
Table 3   Spin densities at the atomic centers of the imidazolium ring computed at the B3LYP/6-31+G (d,p) level of theory

Atom center	MMI$^{\bullet}$	BMI$^{\bullet}$	HMI$^{\bullet}$	BMMI$^{\bullet}$	HOMI$^{\bullet}$
N1	0.083958	0.109141	0.084024	0.021877	0.093384
C2	0.739019	0.797163	0.768075	1.078353	0.735911
N3	0.083932	0.037844	0.095249	0.115888	0.076351
C4	0.023402	−0.012617	0.060588	0.096584	0.026606
C5	0.023640	0.074464	0.051850	−0.009596	0.015200

Table 4   Spin densities at the atomic centers on the imidazolium cation computed at the B3LYP/6-31+G (d, p) level of theory[1)]

Atom center	MMI$^+$	BMI$^+$	HMI$^+$	BMMI$^+$	HOMI$^+$
N1	−0.14896	−0.151186	−0.129232	−0.1633	−0.22799
C2	0.00285	0.027827	0.046322	0.193593	−0.002439
N3	−0.148959	−0.085711	−0.074808	−0.076189	−0.133267
C4	−0.061262	−0.047189	−0.038762	−0.006593	−0.030661
C5	0.023640	0.074464	0.051850	−0.009596	0.015200
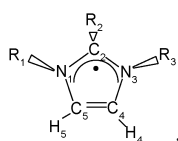
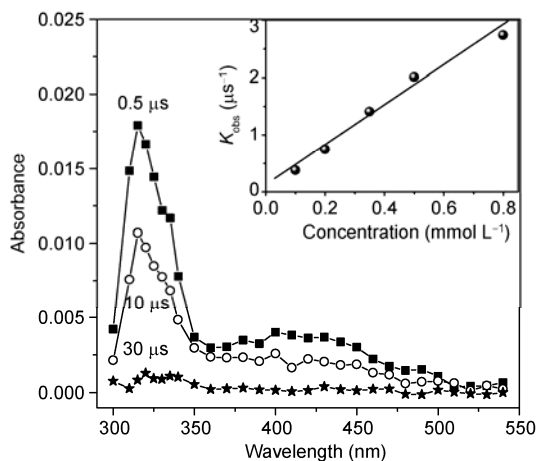1) The scheme of imidazolium radical as

Figure 2 Transient absorption spectra of radicals produced by reaction of $^\bullet OH$ with 0.1 mmol L^{-1} BMIBF$_4$ in N$_2$O-saturated aqueous solutions at pH 7.1, buffered with 2 mmol L^{-1} phosphate. Inset: Decay rates of the radicals produced by reaction of $^\bullet OH$ with BMIBF$_4$ at 320 nm plotted as a function of BMIBF$_4$ concentration.
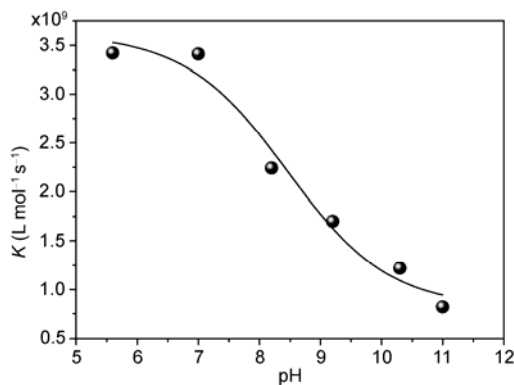

Figure 3 Growth rate constants of $^\bullet OH$ reacting with BMIBF$_4$ at 320 nm as a function of pH.

2.3 Reactions with SO$_4^{\bullet-}$

The pulse radiolysis of N$_2$-saturated aqueous solutions containing 0.5 mmol L^{-1} imidazolium-based ionic liquid, 50 mmol L^{-1} K$_2$S$_2$O$_8$, and 1.0 mol L^{-1} *t*-BuOH gave a transient optical absorption spectra, as shown in Figure 4. The absorption peak which appeared after a short time at 460 nm was attributed to SO$_4^{\bullet-}$. SO$_4^{\bullet-}$ is a strong oxidant and can completely oxidize imidazolium cations to BMI$^{\bullet 2+}$, as shown in eq. (10). However, another weaker peak appeared at around 320 nm after 2 μs. To test the attribution of the absorption band at around 320 nm, the spectrum of 50 mmol L^{-1} K$_2$S$_2$O$_8$ without imidazolium salts was determined, and there was a very weak SO$_4^{\bullet-}$ absorption at 320 nm. The absorption peak at 320 nm was therefore mainly attributed to the cation radical BMI$^{\bullet 2+}$. However, the spectra of BMI$^+$ reacting with SO$_4^{\bullet-}$ were quite different from that observed for the OH adduct BMI–OH$^{\bullet+}$. The latter showed a typical maximum absorption band at 325 nm and another-
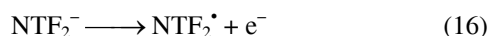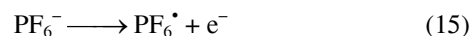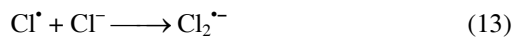
broad band at around 390–460 nm.

$$SO_4^{\bullet-} + BMI^+ \longrightarrow BMI^{\bullet 2+} + SO_4^{2-} \qquad (10)$$

Using five BMIBF$_4$ concentrations varying from 0.15 to 1.5 mmol L^{-1}, the rate constant was calculated to be 1.2×10^9 L mol^{-1} s^{-1}. Except in the case of HOMIBF$_4$, the rate constants of other tested ionic liquids with SO$_4^{2-}$ were almost the same as those in Table 2. The value for HOMIBF$_4$ was slightly lower, 2.8×10^8 L mol^{-1} s^{-1}. This may be because of the hydroxyethyl substituent, which is an electron-withdrawing group, on the imidazolium ring.

2.4 Pulse radiolysis of neat ionic liquids

In general, pulse radiolysis of neat imidazolium-based ionic liquids BMI$^+$X$^-$ initially produces solvated electrons (e_{solv}^-) and other radical cations and anions such as BMI$^{\bullet 2+}$, NTF$_2^\bullet$, Br$_2^{\bullet-}$, and Cl$_2^{\bullet-}$, as shown in eqs. (11)–(16). The solvated electrons, which had typical absorptions above 1100 nm, reacted with BMI$^+$ very quickly to produce BMI$^\bullet$. The transient absorption spectra of imidazolium-based ionic liquids with different anions showed slight differences in the maximum absorption peaks. For BMIPF$_6$ and BMINTF$_2$, the peaks were very similar (Figure 5(a) and (b)), which indicated that these anions were inert. However, for BMICl and BMIBr, the absorption peaks were about 340 and 360 nm, respectively (Figure 5(c) and (d)). It is expected that similar to the case in aqueous solutions, halide atoms would be stabilized through the formation of complex radical anions (eqs. (13) and (14)). The radical anions Cl$_2^{\bullet-}$ and Br$_2^{\bullet-}$ had typical absorptions at around 340 and 360 nm, respectively [23,24]. In ionic liquids, the stabilization effect should be even stronger as a result of the smaller energy of solvation of the anions and the greater stabilization by large radical anions. Michalski et al. [25] also showed that at ambient temperature and at −196°C , the radical anion Br$_2^{\bullet-}$ was the major product upon radiolysis of neat ionic liquid BMIBr. The redox potentials of the dihalide anion radicals (Br$_2^{\bullet-}$ and Cl$_2^{\bullet-}$) in aqueous solutions were 2.09 and 1.6 V for $E^\circ(Cl_2^{\bullet-}/2Cl^-)$ and $E^\circ(Br_2^{\bullet-}/2Br^-)$, respectively [26]. It is therefore very likely that the use of ionic liquids, with different halide anions, as additives to organic solvents would result in the formation of oxidizing species analogous to those formed in non-aqueous environments.

$$BMI^+X^- \longrightarrow BMI^\bullet, BMI^{\bullet 2+}, X^\bullet, e_{solv}^- \qquad (11)$$

$$e_{solv}^- + BMI^+ \longrightarrow BMI^\bullet \qquad (12)$$

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^{\bullet-} \qquad (13)$$

$$Br^\bullet + Br^- \longrightarrow Br_2^{\bullet-} \qquad (14)$$

$$PF_6^- \longrightarrow PF_6^\bullet + e^- \qquad (15)$$

$$NTF_2^- \longrightarrow NTF_2^\bullet + e^- \qquad (16)$$

3 Conclusion

The rate constants of various imidazolium-based cations
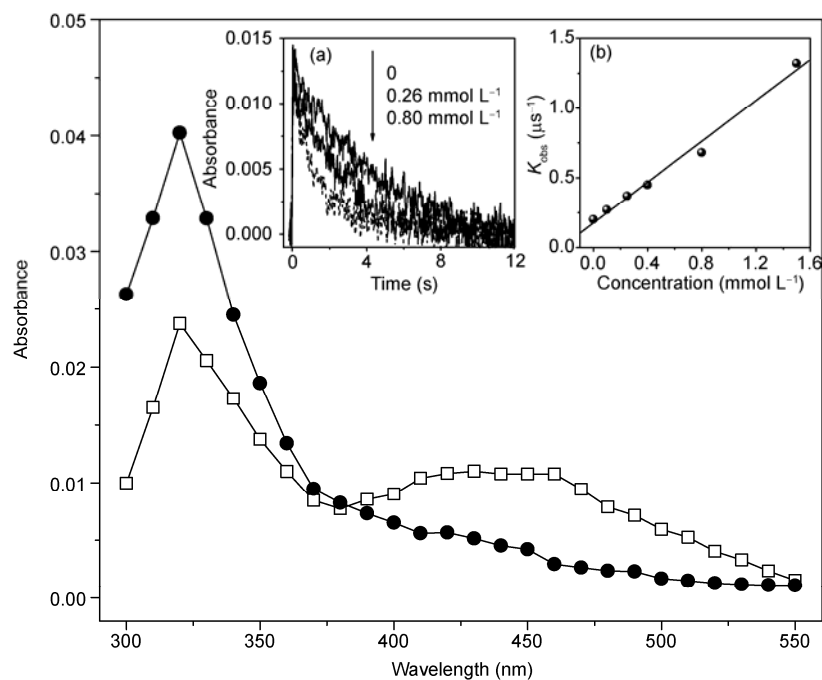
Figure 4   Transient absorption spectra of BMIBF$_4$ produced by reaction of BMI$^+$ with SO$_4^{\bullet-}$ radicals in N$_2$-saturated aqueous solutions at pH 7.1 containing 1.0 mol L^{-1} *tert*-butyl alcohols buffered with 2 mmol L^{-1} phosphate, recorded at (□) 0.2 and (●) 2 μs after the pulse. Inset: (a) Time profiles observed at 460 nm for SO$_4^{\bullet-}$ and (b) decay rate of SO$_4^{\bullet-}$ at 460 nm plotted as a function of BMIBF$_4$ concentration.
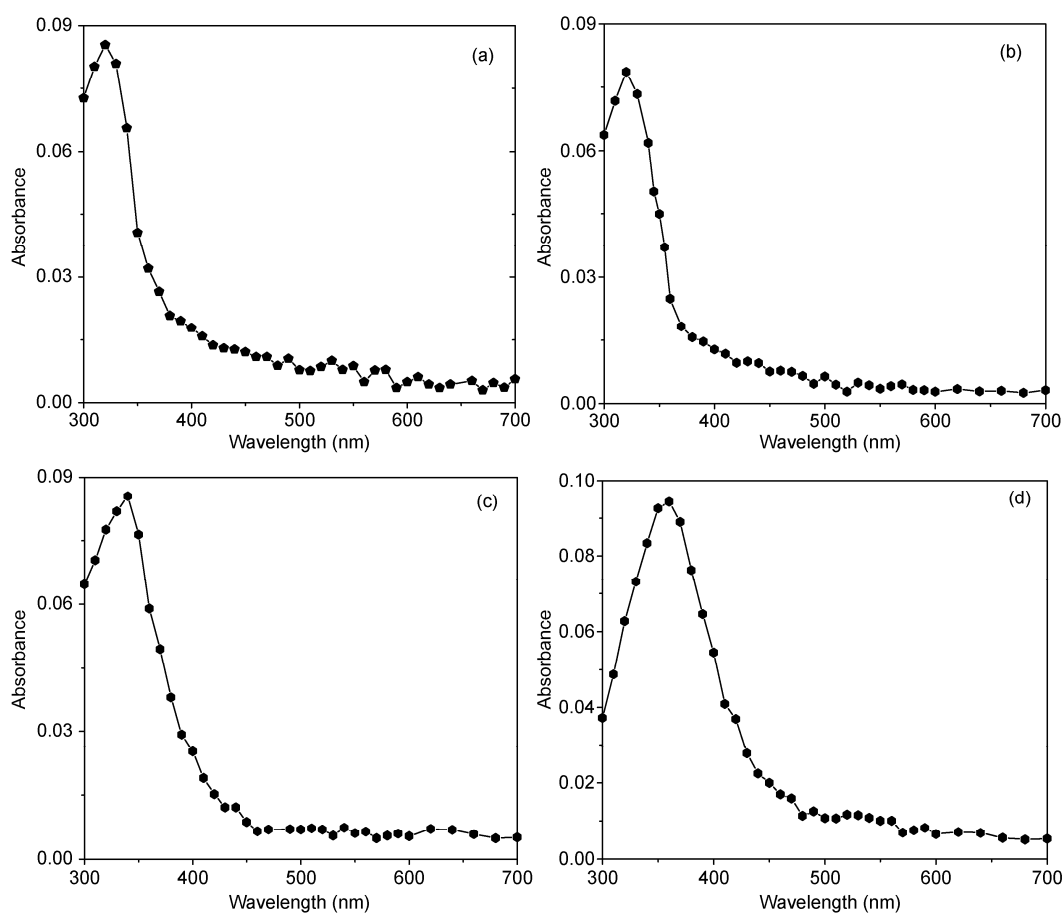

Figure 5   Transient absorption spectra measured 0.5 μs after the electron pulse radiolysis of neat ionic liquids under the same conditions: N$_2$-saturated (a) BMIPF$_6$; (b) BMINTF$_2$; (c) BMICl; and (d) BMIBr.

with hydrated electrons, hydroxyl radicals, and sulfate anion radicals were investigated using nanosecond pulse radiolysis techniques. The values were deduced to be of the order of magnitude 10^9–10^{10} L mol^{-1} s^{-1}. Under the experimental conditions, it was found that the length of the alkyl chain on the imidazole ring and the anion type had hardly any influence on the reactions with hydroxyl radicals and sulfate anion radicals. However, when the imidazolium rings were substituted at the 2-position, the rate constants with hydrated electrons were a little lower. For example, for BMMIBF$_4$ and BMIBF$_4$, the values were 5.5×10^9 and 1.8×10^{10} L mol^{-1} s^{-1}, respectively. Gaussian calculations further confirmed that the electron cloud changed with the substituent on the imidazolium ring, and this influenced the reactivities of ionic liquids with various radicals.

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