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Radiation-induced intermediates in irradiated glassy ionic liquids at low temperature

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HIGHLIGHTS

- An EPR signal of trapped electron was detected in several ionic liquids at 77 K.
- Absorption band in the visible range was attributed to a "hole" species.
- Aromatic scavengers react with "hole" species in ionic liquids at low temperature.

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ABSTRACT

The primary radiation-induced processes in irradiated low-temperature pyrrolidinium- and piperidinium-type ionic liquids were investigated by EPR and optical absorption spectroscopy. A narrow singlet signal in the EPR spectra of irradiated ionic liquids was attributed to the physically stabilized electron. Broad absorption band in visible region was ascribed to "hole" species. Aromatic scavengers react with "hole" species in glassy irradiated ionic liquids at 77 K.

1. Introduction

Ionic liquids (ILs) are perspective media for various fields including nuclear waste processing and electrochemical applications. The investigation of trapping and transport of excess electrons generated by light or ionizing radiation in ILs is important for better understanding of the structure, dynamics and electronic properties of these unusual media and, in particular, of their radiation chemistry and photochemistry.

Extensive experimental (Wishart and Neta, 2003; Asano et al., 2008; Wishart et al., 2005, 2012; Chandrasekhar et al., 2006; Takahashi et al., 2009, 2008; Kondoh et al., 2009; Shkrob et al., 2011a,b; Molins i Domenech et al., 2012, 2015; Musat et al., 2014, 2015) and theoretical (Shkrob and Wishart, 2009; Wang et al., 2009, 2010; Liu et al., 2013; Margulis et al., 2011; Xu et al., 2013; Xu and Margulis, 2015) studies on radiation- and light-induced intermediates in ILs were performed during past two decades. Pulse radiolysis of ILs results in appearance of two short-lived absorptions in near IR and visible regions (Molins i Domenech et al., 2015). Transient absorption in the IR region reveals a blue shift of the maximum in picosecond timescale and has a lifetime of hundreds nanoseconds (Wishart and Neta, 2003; Molins i Domenech et al., 2015). This absorption is quenched by various electron scavengers (Wishart and Neta, 2003; Asano et al., 2008; Molins i Domenech et al., 2012) and is attributed to solvated electron. However, it is still unclear, whether solvated or dry electron reacts with scavengers.

In some ionic liquids absorption band in visible region is also present (Molins i Domenech et al., 2015). Transient absorption in the visible region was ascribed to either electrons or holes (Wishart and Neta, 2003; Xu et al., 2013). Shkrob and Wishart (2009) assumed that this absorption could belong to dimeric radical cation in imidazolium-type ILs, however, it is not a case for ammonium-type ILs (Margulis et al., 2011).

On the basis of MD simulation, Wang et al. (2009, 2010) suggested that excess electron delocalizes on π-orbital of cation in

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imidazolium type of ILs. Recent calculations (Margulis et al., 2011) predict that the electron may be delocalized either on anion or on cation depending on HOMO and LUMO both the cation and the anion.

Previously we have presented the first EPR evidence of physically trapped electron in a pyrrolidinium-type ionic liquid at low temperature (Saenko et al., 2013). Here we report the results of the study on paramagnetic intermediates produced by irradiation in piperidinium and pyrrolidinium types of ionic liquids at low temperature.

2. Material and methods

N-metyl-*N*-butylpyrrolidinium *bis*(trifluoromethanesulfonyl) imide ($P_{14}NTf_2$), *N*-metyl-*N*-propylpyrrolidinium *bis*(trifluoromethanesulfonyl) imide ($P_{13}NTf_2$) and *N*-metyl-*N*-propylpiperidinium *bis*(trifluoromethanesulfonyl) imide ($PP_{13}NTf_2$) (Kanto Chemical Co., Inc) were used without additional purification. N_2O, SF_6, naphthalene and anthracene were used as scavengers. ILs were placed into SK-4B glass tubes (optically transparent at $\lambda > 370$ nm), which gave no background EPR signal after irradiation. The samples were degassed at the temperature of 363 K and irradiated with X-rays ($E_{eff} = 20$ keV) at 77 K. Total absorbed dose was in the range of 2–9 kGy. EPR spectra were measured at 77 K using an X-band (9.2–9.6 GHz) spectrometer with a 100 kHz high-frequency modulation manufactured by SPIN (St. Petersburg, Russia). Optical absorption spectra were measured at 77 K using spectrophotometer Perkin Elmer UV/Vis Spectrometer Lambda 9 (wavelength range 190–900 nm) equipped with optical quartz Dewar flask with special sample holder. A high pressure arc mercury lamp (250 W) with a series of filters was used for photobleaching experiments.

3. Results and discussion

EPR spectra of the irradiated samples of $P_{14}NTf_2$, $P_{13}NTf_2$ and $PP_{13}NTf_2$ reveal superposition of a broad multiplet signal and a narrow singlet signal ($\Delta B \approx 0.5$ mT) (Fig. 1).

The narrow singlet signal shows a strong saturation upon increasing the microwave power level and becomes almost invisible at the value of 0.5 mW. Such a saturation behavior is a typical characteristic of the signals of trapped electrons in low-temperature organic glasses. Increasing the irradiation time leads to decreasing of relative intensity of the singlet signal in the EPR spectra. This effect known as “dose saturation” is also a typical feature for stabilized electrons in molecular glasses. The intensity of the singlet signal gradually decreases at 77 K during several hours.

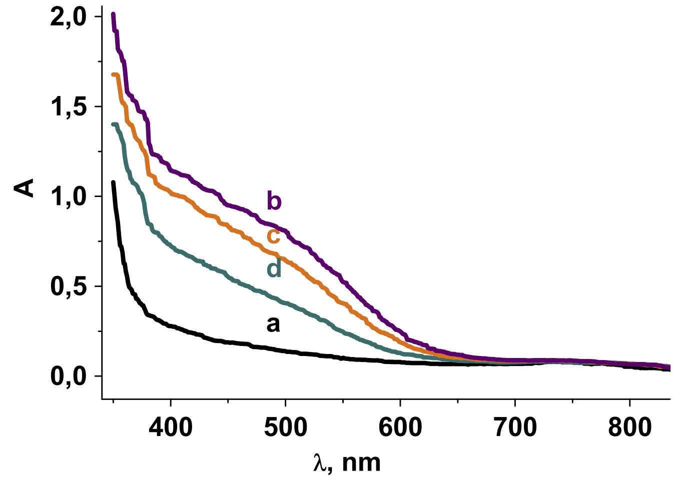

Fig. 2. Optical absorption spectra of $P_{13}NTf_2$ at 77 K: (a) initial; (b) after irradiation with X-rays for 5 min; (c) after photolysis with $\lambda > 700$ nm for 10 min; (d) after photolysis with $\lambda > 700$ nm for 40 min.

The optical spectra of irradiated ILs reveal an absorption band in the visible region with $\lambda > 500$ nm (Fig. 2).

Photolysis of $P_{13}NTf_2$ with the light at $\lambda > 700$ nm during 10 min results in decay of the narrow singlet signal in the EPR spectrum (Fig. 3). At the same time, intensity ratio of the components in the EPR spectrum is changing slightly and the absorption in the visible region gradually decreases (Fig. 2). Subsequent photolysis at $\lambda > 700$ nm during 30 min results in decay of singlet signal in the EPR spectrum and further decrease in the intensity of the absorption band.

Difference EPR spectrum (Fig. 4) shows that the bleached species are characterized by a narrow singlet signal and a broad poorly resolved multiplet. Similar singlet signal was obtained for $PP_{13}NTf_2$ and previously for $P_{14}NTf_2$ (Saenko et al., 2013). Taking into account our findings on the saturation behavior of the narrow singlet signal, “dose saturation” and decay of the singlet signal at 77 K it is quite logical to attribute the singlet signal to a physically trapped (or solvated) electron.

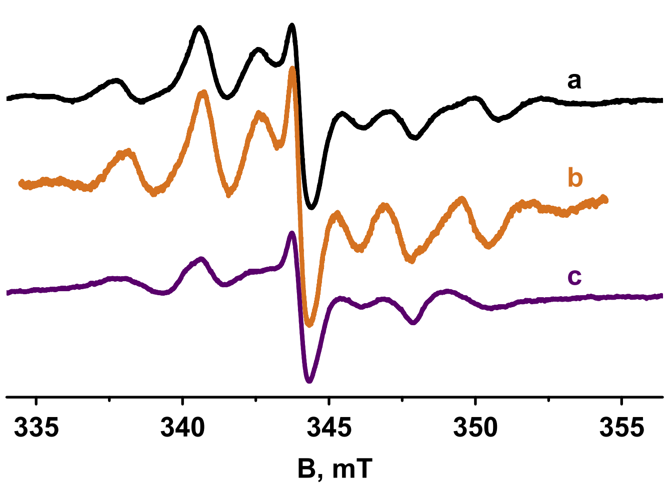

Fig. 1. EPR spectra of ionic liquids irradiated with X-rays at 77 K: (a) $P_{13}NTf_2$; (b) $P_{14}NTf_2$; (c) $PP_{13}NTf_2$. Microwave power level was 0.005 mW.

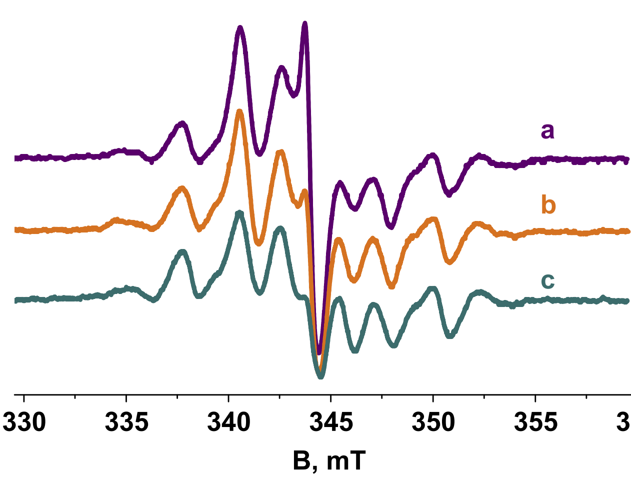

Fig. 3. EPR spectra of $P_{13}NTf_2$ at 77 K: (a) after irradiation with X-rays for 5 min; (b) after photolysis with $\lambda > 700$ nm for 10 min; (c) after photolysis with $\lambda > 700$ nm for 40 min. Microwave power level was 0.005 mW.