

## Excess Electrons in Irradiated Glassy Ionic Liquids

Lomonosov Moscow State University

Elizaveta V. Saenko\*, Ekaterina S. Shiryaeva

Kanazawa University

Kenji Takahashi

Lomonosov Moscow State University

Vladimir I. Feldman

### 1 Introduction

The investigation of trapping and transport of excess electrons generated by light or ionizing radiation in ionic liquids (IL) 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. The fate of excess electrons in ILs was extensively studied by pulse radiolysis and flash photolysis using optical absorption spectroscopy<sup>1-5</sup>); however, it is still under discussion. Meanwhile, early EPR studies on the irradiated glassy ILs at low temperatures did not provide an unequivocal sign of the electron trapping in this media<sup>6-9</sup>). Recently we presented first EPR evidence of physically trapped electron in a pyrrolidinium-type ionic liquid at low temperature<sup>10</sup>). Here we report a study on stabilization of excess electrons in a number of ionic liquids of different composition irradiated at low temperature.

### 2 Experimental

N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl) imide ( $P_{14}^+NTf_2^-$ ), N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide ( $P_{13}^+NTf_2^-$ ) and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl) imide ( $PP_{13}^+NTf_2^-$ ) (Kanto Chemical Co., Inc) were used without additional purification.

ILs were placed into SK-4B glass ampoules (optically transparent at  $\lambda > 370$  nm), which gave no background EPR signal after irradiation. Then the samples were degassed at the temperature of 363 K and irradiated with X-rays (maximum energy 33 keV) at 77 K. EPR spectra were measured at 77 K using an X-band (9.4 GHz) spectrometer with 100 kHz high-frequency modulation manufactured by SPIN (St. Petersburg, Russia).

Optical absorption spectra were measured using a Perkin Elmer UV/VIS Spectrometer Lambda 9 (wavelength range of 190 nm–900 nm) equipped with a Dewar vacuum flask made of optical quartz.

A high pressure arc mercury lamp (250 W) equipped 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 ( $\Delta B \sim 0.5$  mT) (Fig. 1).

Excess Electrons in Irradiated Glassy Ionic Liquids  
Elizaveta V. Saenko\* Ekaterina S. Shiryaeva (*Lomonosov Moscow State University*), Kenji TAKAHASHI (*Kanazawa University*), Vladimir I. Feldman (*Lomonosov Moscow State University*),

Department of Chemistry, Lomonosov Moscow State University, 1 Leninskie gory Moscow 119991 Russia  
TEL: +7-926-394-5430, E-mail: saenko@rad.chem.msu.ru

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<sup>11</sup>. 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 organic glasses. The intensity of the singlet signal gradually decreases at 77 K during several hours.

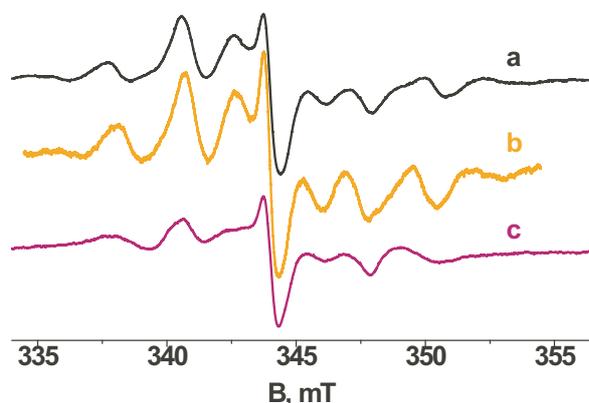


Figure 1. EPR spectra of ionic liquids irradiated with X-rays at 77 K: a)  $P_{13}^+NTf_2^-$ ; b)  $P_{14}^+NTf_2^-$ ; c)  $PP_{13}^+NTf_2^-$ . Microwave power level was 0.005 mW.

The optical spectra of irradiated ILs in the visible region reveal an absorption band with  $\lambda \approx 500$  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 is characterized by a narrow singlet signal. Similar results were obtained for  $P_{14}^+NTf_2^-$  and  $PP_{13}^+NTf_2^-$ . Taking into account our findings on the saturation behavior of the narrow singlet signal, “dose

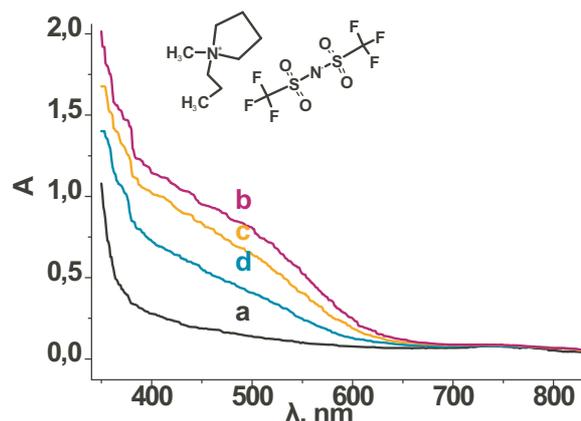


Figure 2. Optical absorption spectra of  $P_{13}^+NTf_2^-$  at 77 K: a) initial; b) after irradiation with X-rays for 5 min; c) after photolysis with  $\lambda > 700$  nm for 10 min; d) after photolysis with  $\lambda > 700$  nm for 40 min.

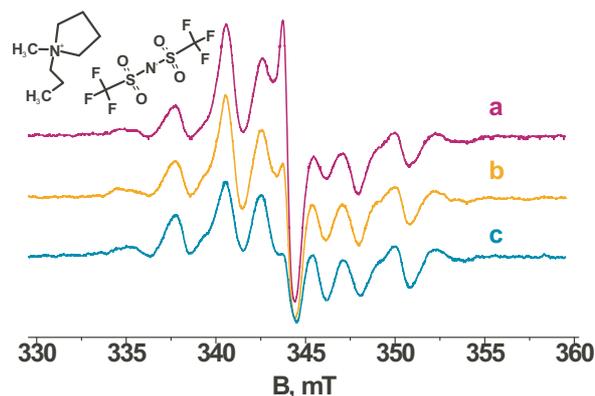


Figure 3. EPR spectra of  $P_{13}^+NTf_2^-$  at 77 K: a) after irradiation with X-rays for 5 min; b) after photolysis with  $\lambda > 700$  nm for 10 min; c) after photolysis with  $\lambda > 700$  nm for 40 min. Microwave power level was 0.005 mW.

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.

It is worth noting that solvated electrons in room temperature ionic liquids exhibit absorption bands in the near IR region (1000 nm–1400 nm)<sup>1,3–5</sup>. Taking into account this observation, the absorption band at  $\lambda_{\max} \approx 500$  nm observed in our study could be hardly attributed to a stabi-

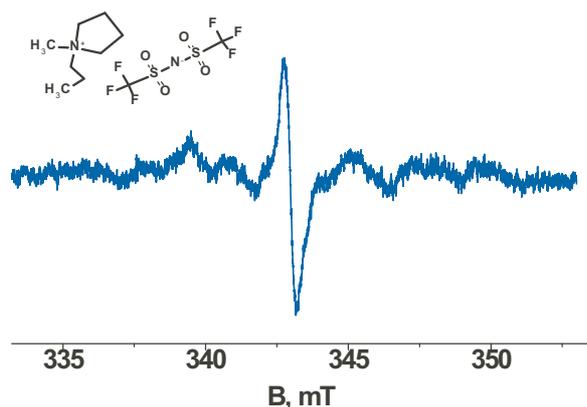


Figure 4. Difference EPR spectrum of photolyzed species.

lized electron, even assuming a reasonable blue shift of the absorption band with decreasing the temperature. Thus, the absorption band with the  $\lambda_{\max} \approx 500$  nm may be presumably attributed to a “hole” species.

A decay of singlet signal attributed to the trapped electron and decrease of the absorption band under photolysis may be explained by the recombination of trapped electron and the “hole” species. Weak lines in the difference EPR spectrum may be attributed to the “hole” species disappearing together with the trapped electron. It should be noted that it is still unclear, where the excess electron comes from - either from cation or from anion. Thus, the nature of the primary “hole” species is still under discussion. Generally, it could be a N-centered neutral radical from anion or radical dication from the cation. Meanwhile, at this stage, our EPR data do not provide definite identification because of poor intensity and broadening of the corresponding signal.

The slow kinetics of trapped electron decay at 77 K is in agreement with the assumption of recombination of electron with “hole” species through the tunneling mechanism<sup>12</sup>.

Regarding the detailed structure of “physically trapped” electron in ILs, we may notice that it is still not fully understood and it may be substantially different from those of electrons observed in molecular liquids and glasses, taking into account the theoretical findings on this issue<sup>13–16</sup>. It is worth noting that the signals of trapped electrons in molecular low temperature glasses usually exhibit  $g$ -values very close to that of free electron ( $g_e = 2.0023$ ) or slightly below it. Meanwhile, the  $g$ -value of the singlet signal in EPR

spectrum attributed to the trapped electron ( $g = 2.004$ )<sup>11</sup> is somewhat higher than  $g_e$ . This may be an indication of specific character of the electron wave function in the species observed in ILs.

#### 4 Conclusions

Our investigations demonstrate the EPR evidence of physically trapped electron in pyrrolidinium- and piperidinium-type glassy ionic liquids at low temperature. These species decay slowly even at 77 K and can be easily photobleached with visible and near IR light (presumably, due to recombination with “hole” species).

This work was supported by the Russian Foundation for Basic Research (project no. 14-03-31978).

#### References

- 1) J. F. Wishart, P. Neta, *J. Phys. Chem. B*, 107 (2003) 7261.
- 2) J. F. Wishart, I. Lall-Ramnarine, R. Raju, A. Scumpia, S. Bellevue, R. Ragbir, R. Engel, *Radiat. Phys. Chem.*, 72 (2005) 99.
- 3) T. Kondoh, A. Asano, J. Yang, K. Norizawa, K. Takahashi, M. Taguchi, R. Nagaishi, R. Katoh, Y. Yoshida, *Radiat. Phys. Chem.*, 78 (2009) 1157.
- 4) K. Takahashi, T. Sato, Y. Katsumura, J. Yang, T. Kondoh, Y. Yoshida, R. Katoh, *Radiat. Phys. Chem.*, 77 (2008) 1239.
- 5) J. F. Wishart, A. M. Funston, T. Szreder, A. R. Cook, M. Gohdo, *Faraday Discuss*, 154 (2012) 353.
- 6) I. A. Shkrob, T. W. Marin, S. D. Chemerisov, J. F. Wishart, *J. Phys. Chem. B*, 115 (2011) 3872.
- 7) I. A. Shkrob, T. W. Marin, S. D. Chemerisov, J. L. Hatcher, J. F. Wishart, *J. Phys. Chem. B*, 115 (2011) 3889.
- 8) I. A. Shkrob, J. F. Wishart, *J. Phys. Chem. B*, 113 (2009) 5582.
- 9) I. A. Shkrob, S. D. Chemerisov, J. F. Wishart, *J. Phys. Chem. B*, 111 (2007) 11786.
- 10) E. V. Saenko, K. Takahashi, V. I. Feldman, *J. Phys. Chem. Lett.*, 4 (2013) 2896.
- 11) J. Lin, K. Tsuji, F. Williams, *J. Am. Chem. Soc.*, 90 (1968) 2776.
- 12) R. F. Khairutdinov, K. I. Zamaraev, *Top. Curr. Chem.*, 163 (1992) 1.
- 13) C. J. Margulis, H. V. R. Annapureddy, P. M. De Bi-

- ase, D. Coker, J. Kohanoff, M. G. Del Popolo, J. Am. Chem. Soc., 133 (2011) 20186.
- 14) Z. P. Wang, L. Zhang, X. H. Chen, R. I. Cukier, Y. X. Bu, J. Phys. Chem. B, 113 (2009) 8222.
- 15) Z. P. Wang, L. Zhang, R. I. Cukier, Y. X. Bu, Phys. Chem. Chem. Phys., 12 (2010) 1854.
- 16) F. M. Domenech, B. FritzPatrick, A. T. Healy, D. A. Blank, J. Chem. Phys., 137 (2012) 034512.