

Positron annihilation in the near surface of room temperature ionic liquids

T Hirade^{1,3}, B E O'Rourke² and Y Kobayashi²

¹Nuclear Science and Engineering Center, Japan Atomic Energy Agency,
Tokai, 319-1195 Japan

²National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki
305-8568, Japan

³Graduate School of Science and Engineering, Ibaraki University, 2-1-1, Bunkyo,
Mito, Ibaraki 310-8512 Japan

E-mail: t.hirade@kurenai.waseda.jp

Abstract. Positronium (Ps; a bound state of an electron and a positron) formation in insulating materials is explained by the spur reaction model. According to the model, electron and/or positron mobility affects the yield of Ps formation. A vertical slow positron beam was used to investigate the surface of a room temperature ionic liquid, N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TPMA-TFSI). Measurement of positron lifetimes indicated a higher Ps formation probability in near surface of TPMA-TFSI than in the bulk. This result suggests that the electron (and positron) mobility in the near surface may be larger than that in the bulk. Moreover, the longest annihilation lifetime of triplet Ps (ortho-Ps) in the near surface was found to be shorter than that measured in the bulk liquid. Ortho-Ps lifetimes in liquids are well correlated with the surface tension with a shorter lifetime corresponding to higher surface tension. The higher Ps formation yield and the shorter ortho-Ps annihilation lifetime were probably caused by the layered structure in near surface of TPMA-TFSI. A vertical slow positron beam is a strong tool to investigate the surface of room temperature ionic liquids.

1. Introduction

The structure of the liquid surface had been believed to be simple for a long time. However surface layering was observed by X-ray measurement for liquid metals [1]. Moreover, surface layering was also observed in molecular liquids [2]. It is very interesting to study liquid surface structure. However, the vapour pressure of molecular liquids makes studies in vacuum by many experimental methods difficult. Room temperature ionic liquids (IL's) have negligible vapor pressure and hence many experimental methods can be applied.

Slow positron beams can be applied to investigate the near surface structure. Previously, the surface of an IL was investigated using a horizontal ion beam [3]. However, it is more practical to use a vertical beam to study the stable horizontal surface of liquids. Recently a vertical slow positron beamline was developed at AIST in Tsukuba, Japan [4]. Therefore we decided to study the surface of IL's by using the AIST slow positron beam which can perform positron annihilation lifetime spectroscopy measurements. In particular the intensity and lifetime of the longest lifetime component



from the annihilation of the triplet state of positronium (Ps, a bond state of an electron and a positron) are useful to understand the surface structure of IL's.

Ps formation in insulating materials, such as liquids or solids, is well explained by the spur reaction model [5]. According to the spur reaction model, a positron can form Ps with one of the excess electrons at the terminal spur, i.e. the end part of the positron track. Ps formation time is about 1ps, because the Ps precursor is free or quasi-free electrons and positrons. Hence, Ps formation is usually difficult after localization or solvation of electrons and positrons. Therefore, the electron and positron properties in the material, such as diffusion length or mobility, affect the Ps formation intensity, i.e. the yield of Ps formation.

Measurement of the Ps formation intensity is a strong tool to investigate the electron mobility especially in very small volumes. Carbon disulphide, CS₂, is an electron scavenger. However, it was previously found that further addition of CS₂ caused enhancement of the Ps formation intensity at higher concentration of CS₂ [6]. A possible explanation for this strange phenomenon was the higher electron (and positron) mobility in CS₂ clusters, even though a small electron mobility was reported by radiation chemists. After the report of the high Ps formation intensity in CS₂ as mentioned above, the electron mobility was carefully re-measured, and the high electron mobility was successfully observed [7].

Ps has a negative work function in many materials so that Ps is energetically more stable in vacuum than in the material. Therefore, if there is a vacant space or pore in the material, Ps prefers to be inside the vacant space. The triplet Ps (ortho-Ps) has the longest annihilation lifetime in a positron annihilation lifetime spectrum. In the case of liquids, Ps creates a sub-nano meter bubble by itself and localizes in it. This bubble is called a Ps bubble. The size of the Ps bubble is controlled by the balance between the zero point energy of Ps and the surface energy of the bubble. A beautiful relation between the surface tension and ortho-Ps annihilation rate (the reciprocal lifetime) in many liquids could be seen [8]. Osada et al. reported that surface tensions of TMPA-TFSI and PP13-TFSI were about 35mN/m and 34 mN/m at 30°C [9]. The o-Ps annihilation rates for TMPA-TFSI and PP13-TFSI at 30°C were 0.27 ns⁻¹ and 0.29 ns⁻¹ [10]. The values for TMPA-TFSI and PP13-TFSI are out of the correlation between ortho-Ps annihilation rates and surface tensions for many other liquids. In the case of IL's, there must be a local structure at small scales. The ortho-Ps annihilation rate tells us about the surface energy in microscopic region, i.e. at the nanometer scale, especially for IL's. Recently, GHz oscillation of Ps bubble in IL's were reported [11]. The measurements of Ps bubble oscillation must be a strong tool to investigate the viscoelasticity of IL's. The surface tension estimated by ortho-Ps annihilation lifetime must be also a strong tool to investigate the nano structure of IL's. Here, depth profiling of Ps formation intensity and ortho-Ps lifetime was used to investigate the surface structure.

2. Experimental

The IL sample used was N,N,N-trimethyl-N-propylammonium bis (trifluoromethanesulfonyl) imide (TMPA-TFSI) (Kanto Kagaku). The melting point of TMPA-TFSI is 19°C. TMPA-TFSI was used from a new bottle without any purification.

Positron annihilation lifetime measurements were performed using the vertical slow positron beamline installed at AIST [4]. The diameter of the positron beams was about 10mm which is small enough that almost all positrons can be injected into the IL surface. The IL was poured into a metal cup (see Figure 1(a)) which was placed in the vacuum chamber (see Figure 1(b)).

Measurements were performed at room temperature with positron energies of 1keV, 2keV and 15keV and every spectrum had 0.8-1.5 million counts. The time resolution was about 300ps (fwhm) which was enough to obtain lifetimes and intensities for the longest lifetime component from the annihilation of ortho-Ps.

3. Results and Discussion

Positron annihilation lifetime spectra obtained with positron energies of 1keV and 15keV are shown in Figure 2. We performed a free 3 component fit with the PALSfit program. [12] The results are shown in Table1. The lifetime and the intensity of the longest lifetime component for TMPA-TFSI measured

by a radioisotope based lifetime apparatus were 3.858 ns and 13.6% respectively [13]. Two interesting phenomena were found. One was the higher Ps formation probability and the other was shorter annihilation lifetimes in the near surface region.

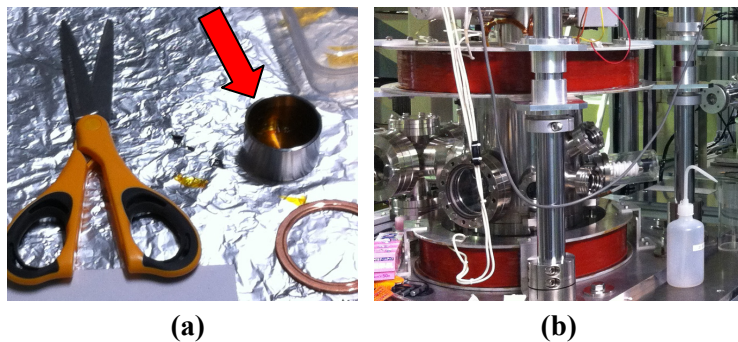


Figure 1. A metal cup indicated by an arrow in (a) was used for the sample container of IL measurements. This cup was placed in the vacuum chamber (see (b)) of the vertical slow positron beamline.

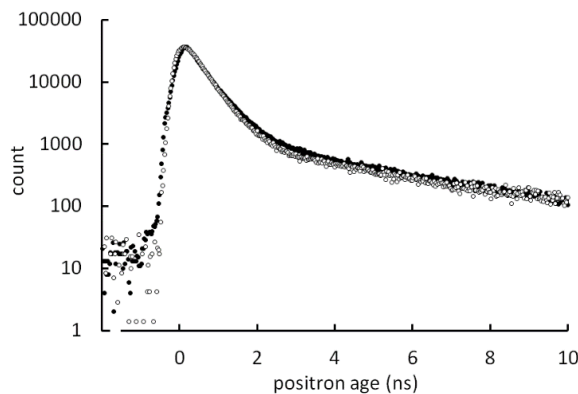


Figure 2. Positron annihilation lifetime spectra measured with positron energies of 1 keV (filled circle) and 15 keV (open circle). The 15 keV spectrum was normalized to the 1 keV spectrum for easier comparison.

Table 1. Lifetime and intensity of the longest lifetime component with free 3 component fit. Incident depth means the average depth of positron implantation at respective energies

Positron Energy (keV)	Incident Depth (nm)	τ_3 (ns)	I_3 (%)
1	25	3.75 ± 0.07	17.2 ± 0.5
2	100	3.74 ± 0.05	15.9 ± 0.1
15	3000	3.97 ± 0.12	13.7 ± 0.2

The Ps formation intensity in the near surface of several ten nm depth was higher than the value observed in bulk of TMPA-TFSI by the conventional radioisotope based lifetime apparatus. This is probably caused by the layered structure. The most top layer consists of negative anions as indicated by Nakajima et al. [3]. Neutron reflectometry measurements suggest that the inhomogeneity of the surface region extends to ~ 4 nm [14]. These things indicate that the structure in the near surface of IL's is similar to the crystalline state. Indeed, it was reported that there could be a crystalline structure on the surface of IL's even at temperature about 37°C higher than the melting point [15].

A crystalline structure in near surface of TMPA-TFSI is quite possible at room temperature (about 25°C) which is just 6°C higher than the melting temperature. In crystalline structures, light particles, such as electron, positron and Ps, are usually in a delocalized state. Therefore, the mobility of electrons (and positrons) in the near surface are probably higher than in the homogeneous structure found in the bulk liquid. This is the reason why Ps intensity is higher in the near surface.

Although a higher electron density at the surface was reported [16], the layer with higher electron density was only 2-3 nm which is much smaller than the distribution of the terminal spur of the

positron track. Therefore the higher electron density at the surface may not be the reason of the higher Ps formation intensity.

For the measurement at 2keV a time resolution of around 200ps was obtained which is sufficient to extract a GHz oscillation signal. Analysis of the 2keV spectrum found an oscillation of the annihilation rate which had a frequency of about 4.6GHz. It is known that this oscillation is caused by the oscillation of Ps bubble and the frequency corresponds to the oscillation at about 28°C according to the temperature dependence measurements performed by the conventional radioisotope based positron annihilation lifetime measurement apparatus [9]. We performed the experiments at the room temperature but did not know the precise temperature of the sample in this experiment. In the future we intend to study the temperature dependence of ortho-Ps lifetime and the oscillation of Ps bubble to understand the surface of IL's in detail.

4. Conclusion

We successfully observed the effect of the surface of TMPA-TFSI on the ortho-Ps lifetime and intensity. The lifetimes in near surface were shorter than that in bulk, indicating that the surface energy in near surface was larger, probably. The intensity of the long lifetime component was higher in near surface region. This increase was probably caused by the higher electron (and positron) mobility in crystalline like structure. Moreover, the oscillation of Ps bubble was also obtained successfully. Further investigation will be needed to understand more in detail. The vertical positron beamline installed at AIST will be a strong tool to investigate surface of IL's.

Acknowledgement

This research was partially supported by a Ministry of Education, Culture, Sports, Science and Technology Grant-in-Aid for Scientific Research (C), 23600011, 2011-2014 and 16K05026, 2016-2018.

References

- [1] Magnussen O M, Ocko B M, Regan M J, Penanen K, Pershan P S, and Deutsch M 1995 *Phys. Rev. Lett.* **74** 4444
- [2] Mo H, Evmenenko G, Kewalramani S, Kim K, Ehrich S N and Dutta P 2006 *Phys. Rev. Lett.* **96** 096107
- [3] Nakajima K, Ohno A, Suzuki M and Kimura K 2009 *Nuclear Instruments and Methods in Physics Research B* **267** 605
- [4] O'Rourke B E, Oshima N, Kinomura A and Suzuki R 2014 *Jpn. J. Appl. Phys. Conf. Proc.* **2** 011304
- [5] Mogensen O E 1974 *J. Chem. Phys.* **60** 998
- [6] Jansen, P and Mogensen, O E, 1977. *Chem. Phys.* **25** 75
- [7] Gee N and Freeman G R 1989 *J. Chem. Phys.* **90** 5399
- [8] Tao S J 1972 *J. Chem. Phys.* **56** 5499
- [9] Hirade T, "Temperature dependence of positronium bubble oscillation in room temperature ionic liquids" 17th international conference on positron annihilation, Wuhan, China 20-25 September, 2015
- [10] Osada R, Hoshino T, Okada K, Ohmasa Y and Yao M. 2009 *J. Chem. Phys.* **130** 184705
- [11] Hirade T 2014 *JJAP Conf. Proc.* **2** 011003
Hirade T 2015 *Journal of Physics: Conference Series* **618** 012004
- [12] Kirkegaard P, Olsen J V, Eldrup M and Pedersen N J 2009 PALSfit Risø-R-1652(EN)
- [13] Hirade T 2009 *Materials Science Forum* **607** 232
- [14] Bowers J and Vergara-Gutierrez M C 2004 *Langmuir* **20** 309
- [15] Jeon Y, Vaknin D, Bu W, Sung J, Ouchi Y, Sung W and Kim D 2012 *Phys. Rev. Lett.* **108** 055502
- [16] Slutskin E, Ocko B M, Tamam L, Kuzmenko I, Gog T and Deutsch M 2005 *J. Am. Chem. Soc.* **127** 7796