Subscriber access provided by American Chemical Society

View the Full Text HTML

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S COMMUNICATIONS

Published on Web 05/20/2006

Coexistence of Liquid and Solid Phases of Bmim-PF$_6$ Ionic Liquid on Mica Surfaces at Room Temperature

Yaodong Liu,[†] Yi Zhang,*[,†] Guozhong Wu,*[,†] and Jun Hu[†,‡]

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China, and
Bio-X Life Science Research Center, College of Life Science and Biotechnology, Shanghai JiaoTong University,
Shanghai 200030, China

Received April 18, 2006; E-mail: wuguozhong@sinap.ac.cn; yzhang@sinap.ac.cn

Interesting phenomena occur to liquid molecules adsorbed by a solid surface.[1] Recently, it has been found that some liquids become ordered or solid-like in the layers adjacent to the surface of crystallized solid substrates and show coexistence of both liquid and solid phases.[2] In this communication, we aim to explore the unique structural patterns of a room temperature ionic liquid (IL) on a well-defined solid surface. ILs, as one of the unique types of liquids, are considered as promising alternatives to conventional organic solvents in the future for their desirable properties, such as nonvolatility, nonflammability, high thermal stability, etc.[3] ILs have many unique properties on their structural phases in bulk. Much attention has been paid to the inner bulky physical structures, including alkyl chain orientation, ionic arrangement, and interaction. Evidence,[4] including our previous work, has indicated the heterogeneous nature of pure ILs. In contrast, utilizing recoil spectroscopy,[5] neutron diffraction analysis,[6] and Raman spectroscopy,[7] several reports have revealed analogous structural patterns of 1,3-dialkylimidazolium-based ILs in both the solid and liquid phases, probably due to H-bonding and strong Coulomb forces between cations and anions. In addition, some efforts are focused on the surface[8] and interface[9] properties of ILs. It has been found that the orientation of the alkyl chains of layered ILs is normal to the solid surface, and the water contact angle of self-assembled monolayers on gold surfaces may be used as an indicator of the hydrophilicity and the hydrophobicity of ILs.[9b] Additionally, ILs have shown great promise for application, such as lubricants, that significantly improve the wear life in the microelectrical mechanical systems.[10]

We employ atomically flat mica as the substrate to adsorb a prototype ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [Bmim][PF$_6$]) and directly observe its characteristics by atomic force microscopy (AFM). The results show the coexistence of solid and liquid phases as well as the ordered phenomenon of the [Bmim][PF$_6$] on the mica surface at room temperature.

The [Bmim][PF$_6$] was prepared as described previously,[11] and its purity was confirmed by NMR spectroscopy (Supporting Information). The IL was dissolved in methanol (HPLC grade) at a concentration between 0.05 and 1.0 wt ‰. In a typical experiment, a drop of 5 μL of an IL solution was placed on a newly cleaved mica substrate (2M$_1$-muscovite, V-2 grade, Kaifeng Electrical Materials Co., Yaan, China) (1 cm × 1 cm) and dried by air flow. The microscopic morphology of the IL was investigated by tapping mode AFM (Nanoscope IIIa, Veeco /Digital Instrument) with a silicon tip (force constant of 40 N/m, MicroMasch). All images are collected at room temperature (ca. 25 °C) at a humidity of 45 ± 3%.

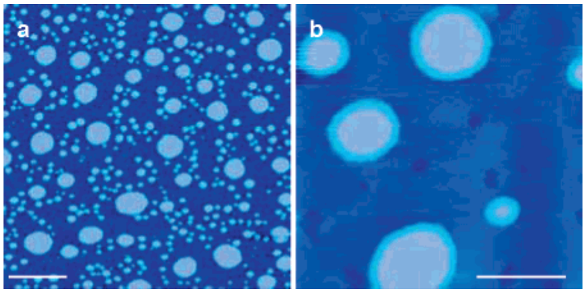

Figure 1. AFM topography images of [Bmim][PF$_6$] IL on a mica surface. (a) IL droplets with varied dimensions. (b) IL thin film under the droplets. Bars are 1 μm in (a) and 250 nm in (b).

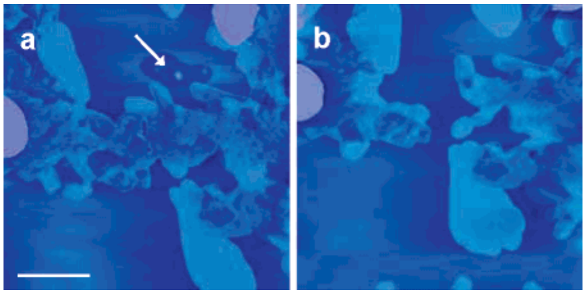

Figure 2. AFM topography images of [Bmim][PF$_6$] IL multilayers on a mica surface. The arrow in (a) indicates a hole that disappeared after a continue scanning, as shown in (b). Bar is 500 nm and applies to both (a) and (b).

When the samples were coated with IL solution of >0.5 wt ‰, micron-sized droplets were observed on the mica surface by an optical microscope (Supporting Information), showing the typical liquid characteristics of the IL at room temperature. However, this ionic liquid presented a drop-on-the-layer structure in the nanometer scale, as revealed by AFM (Figure 1). The droplet dimension was between 10−50 nm in height and 50−300 nm in diameter. In a small-scale scanning, layered IL films under the droplets are clearly seen. This drop-on-the-layer phenomenon is believed to be a special microscopic property of liquids when in contact with a solid surface, as predicted by de Gennes' theory.[12] When the samples were well coated with IL solution at 0.1 wt ‰, the number of the droplets decreased, while the layer underneath became clearer and showed multilayer structures in the AFM images. The IL layers are fluid, and their shapes are transformed during scanning. As shown in a continuous imaging (Figure 2a,b), the hole indicated by the arrow in Figure 2a disappeared and the upper layers underwent a large morphology change. The thickness of each layer was in different multiples of 0.7−0.8 nm, which is comparable to the length of an imidazolium cation. The multilayer stack of ILs on the surface of Si(111) wafers has also been observed by Hardacre et al. by using X-ray diffraction.[13] The ILs which they studied have much longer alkyl chains (12-C, 18-C) with properties of liquid crystal;[14] their layering structure is therefore understandable. In our case, [Bmim]-

---

[†] Chinese Academy of Sciences.
[‡] Shanghai JiaoTong University.

10.1021/ja062685u CCC: $33.50 © 2006 American Chemical Society

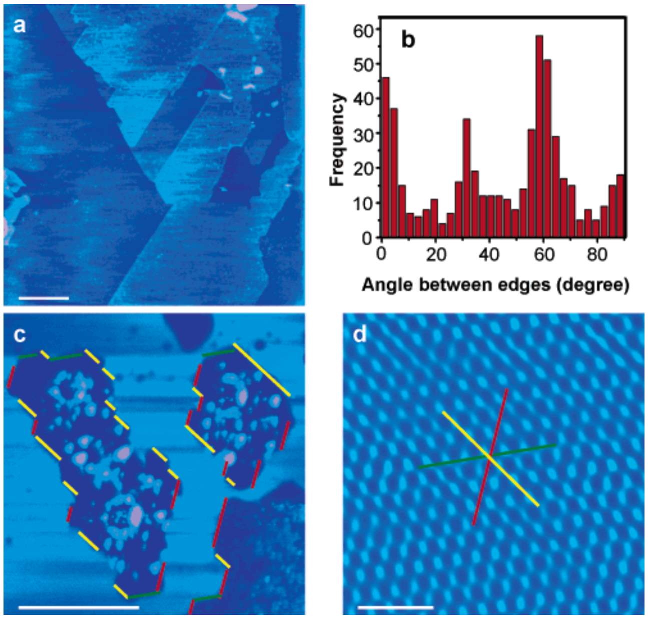

Figure 3. Solid-like structures of [Bmim][PF_6] on a mica surface. (a) AFM images of IL multilayer showing zigzag edges. (b) Statistics of the angles between zigzag edges and a randomly selected edge in AFM images. (c, d) the edges of solid-like IL structures matching well with the mica lattice. The lattice resolved image (d) was obtained by contact mode AFM after a typical investigation of a multilayer structure (c) and after recleaving the substrate. The same color (green, blue, or red) of the solid lines in (c) and (d) indicates the same direction. The bars are 500 nm in (a, c) and 2 nm in (d).

[PF_6] has a short alkyl chain (4-C), and its melting point is 6.6 °C (Supporting Information).

When the sample concentration was reduced, the layer underneath became ordered in some areas showing solid-like features that were different from the liquid-like behavior revealed earlier, indicating the coexistence of liquid and solid phases. The ordered layers could be more frequently observed when the sample concentration was <0.1 wt ‰. As shown in Figure 3a, the multilayer structure had zigzag edges with sharp angles. A statistic analysis showed that the edges presented either parallel or at specific angles, that is, multiples of 30° to each other (Figure 3b). The ordered arrangement of edges indicates a strong interaction between the mica and the IL layers. Our study further showed that the edges of the layered structures are affected by the underlying mica lattices (Figure 3c,d). In a control experiment, we did not observe the ordered layers on a chemically modified mica surface (Supporting Information). Unlike those liquid-like layers in Figure 2, the layers in Figure 3 were quite stable and their topographies remained unchanged even after they were repeatedly scanned by the AFM tip. The ordered IL structure can be attributed to the electrostatic interactions between the IL cations and the ordered anionic silicate layer on the mica surface.

"Room temperature ice" on the surface of mica and some salts has also been previously observed.[2b] However, the solid water layer was very fragile and could be easily disturbed by the AFM tips. Usually the average force applied on the sample in tapping mode AFM in our experiment is approximately 1 nN or 10 MPa.[15] Under this load and disturbance, the solid structures of [Bmim][PF_6] are still very stable, which may have potential applications for this IL as a new kind of lubricant.

In summary, multilayer structures, including liquid and solid phases of [Bmim][PF_6], were directly observed coexisting on mica substrates at room temperature by tapping mode AFM in air. Drop-on-the-layer structure was also revealed. The mica lattice has an effect on the orientation of solid layers. These results are helpful to advance the understanding of interfacial structures of ILs on solid surfaces, the analogous structural patterns in both of its solid and liquid phases, and its heterogeneity. The high stability of the ordered IL structures suggests that it could serve as a good model system for the study of solid−liquid interfaces.

Acknowledgment. This work was supported by the "Hundred talents" projects of the Chinese Academy of Sciences, the National Science Foundations of China (Nos. 10335070, 10404032, 20573130, and 30470441), and Shanghai Municipal Committee of Science and Technology (Nos. 0552nm033 and 04qmx1466).

Supporting Information Available: Characterization and investigation of the [Bmim][PF_6] IL. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) de Gennes, P.-G. *Rev. Mod. Phys.* **1985**, *57*, 827. (b) Alara, D. L. *Nature* **2005**, *437*, 638.
(2) (a) Oh, S. H.; Kauffmann, Y.; Scheu, C.; Kaplan, W. D.; Rühle, M. *Science* **2005**, *310*, 661. (b) Hu, J.; Xiao, X. D.; Ogletree, D. F.; Salmeron, M. *Science* **1995**, *268*, 267.
(3) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792.
(4) (a) Wong, D. S. H.; Chen, J. P.; Chang, J. M.; Chou, C. H. *Fluid Phase Equilib.* **2002**, *194*, 1089. (b) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447. (c) Wu, G. W.; Liu, Y. D.; Long, D. W. *Macromol. Rapid Commun.* **2005**, *26*, 57. (d) Paul, A.; Mandal, P. K.; Samanta, A. *Chem. Phys. Lett.* **2005**, *402*, 375.
(5) Gannon, T. J.; Law, G.; Watson, P. R.; Gamichael, A. J.; Seddon, K. R. *Langmuir* **1999**, *15*, 8429.
(6) Hardacre, C.; Holbrey, J. D.; McMath, E. J.; Bowron, D. T.; Soper, A. K. *J. Chem. Phys.* **2003**, *118*, 273.
(7) (a) Hayashi, S.; Ozawa R.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 498. (b) Ozawa, R.; Hayashi, S.; Saha, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 948.
(8) Solutskin, E.; Ocko, B. M.; Taman, L.; Kuzmenko, I.; Gog, T.; Deutsch, M. *J. Am. Chem. Soc.* **2005**, *127*, 7796.
(9) (a) Fitchett, B. D.; Conboy, J. C. *J. Phys. Chem. B* **2004**, *108*, 20255. (b) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Song, C. E.; Namgoong, S. K.; Lee, S. *J. Am. Chem. Soc.* **2004**, *126*, 480. (c) Steven, B. *J. Phys. Chem. B* **2005**, *109*, 13049.
(10) Nainaparampil, J. J.; Phillips, B. S.; Eapen, K. C.; Zabinski, J. S. *Nanotechnology* **2005**, *16*, 2474.
(11) (a) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Coummun.* **1998**, 1765. (b) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627.
(12) Brochard-Wyart, F.; di Meglio, J.-M.; Quéré, D.; de Gennes, P.-G. *Langmuir* **1991**, *7*, 335.
(13) Adrian, J. C.; Christopher, H.; John, D. H.; Mark, N.; Kenneth, R. S. *Mol. Phys.* **2001**, *99*, 795.
(14) (a) Sebastien, B.; Marie, P. V.; Anne, M. C.; Wolfgang, S.; Jurgen, P. R. *Langmuir* **1998**, *14*, 2916. (b) Xu, L.; Miquel, S. *Phys. Rev. Lett.* **2000**, *84*, 1519.
(15) Zhou, X.; Sun, J.; An, H.; Guo, Y.; Fang, H.; Su, C.; Xiao, X.; Huang, W.; Li, M.; Shen, W.; Hu, J. *Phys. Rev. E* **2005**, *71*, 062901.

JA062685U