

Novel Hydrophobic Ionic Liquids Based on Quaternary Ammonium and Perfluoroalkyltrifluoroborate

Zhi-Bin Zhou, Hajime Matsumoto, and Kuniaki Tatsumi

Research Institute for Ubiquitous Energy Devices, AIST,
1-8-31 Midorigaoka Ikeda, Osaka 563-8577, Japan

While there are a large number of imidazolium-based ILs, few ILs based on quaternary ammonium have been reported. Compared with the imidazolium system, quaternary ammonium one is more electrochemically stable against oxidation and reduction, supporting it as possible safety electrolytes for high-energy storage devices, such as Li batteries and double-layer capacitors. Low-melting, low-viscous quaternary ammonium salts have been prepared by introducing fluoroanions that have relatively low symmetry and highly delocalized charge, such as bis(trifluoromethylsulfonyl)imide $[(CF_3SO_2)_2N]^-$,^[1] 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide $[(CF_3SO_2)(CF_3CO)N]^-$,^[2] and so on. Another method to prepare low-melting ammonium salts was to modify the structure of quaternary ammonium cation slightly, i.e., replacing one alkyl group in the four substituents of ammonium cation with a more flexible alkyl ether group.^[3] All these work suggest that both the cations and the fluoroanions, especially low symmetry ones, play an important role in determining the melting points and viscosities of quaternary ammonium salts.

Recently a new class of weakly coordinating fluoroanions, namely perfluoroalkyltrifluoroborates $[(R_F)BF_3]^-$, have been successfully synthesized via various convenient methods,^[4] whose chemistry and application in electrochemistry are currently of interest because of their good chemical and electrochemical stability. More recently, a few ILs based on the $[(R_F)BF_3]^-$ have also been reported.^[5-7] As part of our interest to find low-melting, low-viscous ILs, we herein systematically report the synthesis and characterization of a series of hydrophobic ILs based on relatively small quaternary ammonium cation $[(R^1R^2R^3R^4)N]^+$, wherein $R^1, R^2, R^3 = CH_3$ or C_2H_5 , $R^4 = CH_3(CH_2)_3, CH_3OCH_2CH_2$ and perfluoroalkyltrifluoroborate anion $[(R_F)BF_3]^-$, wherein $R_F = CF_3, C_2F_5, n-C_3F_7, n-C_4F_9$. Their electrochemical properties including ionic conductivity and electrochemical stability were also investigated.

The new salts $[(R^1R^2R^3R^4)N][R_FBF_3]$ were prepared by neutralization of aqueous solution of $[(R^1R^2R^3R^4)N][OH]$ with aqueous solution of $H[R_FBF_3]$. For comparison, the $[BF_4]^-$ -based salts were prepared similarly except for using aq. $H[BF_4]$ instead of aq. $H[R_FBF_3]$. All the salts prepared are characterized by NMR ($^1H, ^{19}F$, and ^{11}B), IR, and elemental analysis. The characterization data agree with the expected compositions and structures. The new $[(R_F)BF_3]^-$ -based salts are immiscible with water, and the water content in the resulting salts was less than 40 ppm after vacuum drying.

The physicochemical properties of these new salts were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis, density, dynamic viscosity, ionic conductivity. The key features of these new salts are their low melting points (-27 – 97 °C) or extremely low glass transition without melting. The

observed melting points of all the $[(R_F)BF_3]^-$ -based salts are generally lower than those of the $[BF_4]^-$ -based ones with the same cation, indicating that the melting points of the salts could be lowered by reducing symmetry of the fluoroanions; in our case, by replacing one fluorine atom in the $[BF_4]^-$ with R_F group. Most of these new salts are liquid at room temperature and exhibit a lower viscosity (57–210 cP at 25 °C) than the $[BF_4]^-$ -based ones with the same cation. The $[(R_F)BF_3]^-$ -based salts that are liquid at 25 °C also exhibit higher ionic conductivities than the corresponding $[BF_4]^-$ -based ones as shown in Figure 1. In addition, these new ammonium salts have a wider electrochemical window than those of the corresponding imidazolium ones.

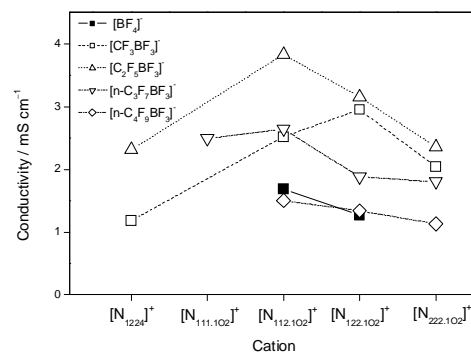


Figure 1. Specific conductivity of various ionic liquids; Notation for cation: the subscript denotes the number of carbons in each of the four substituents and an “O” denotes the oxygen atom in the substituent

This work is supported by R&D project for Li batteries by METI and NEDO.

References

1. J. Sun, M. Forsyth, and D. R. MacFarlane, *J. Phys. Chem. B* **1998**, 102, 8858.
2. H. Matsumoto, H. Kageyama, and Y. Miyazaki, *Chem. Commun.* **2002**, 1726.
3. W. Xu, E. I. Cooper, and C. A. Angell, *J. Phys. Chem. B* **2003**, 107, 6170.
4. Z. B. Zhou, M. Takeda, M. Ue, *J. Fluorine Chem.* **2003**, 123, 127.
5. Z. B. Zhou, M. Takeda, M. Ue, *J. Fluorine Chem.* **2004**, 125, 471.
6. Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, 680.
7. Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004** (in press).