Alternative Route to Metal Halide Free Ionic Liquids

Koichiro Takao[#] and Yasuhisa Ikeda*
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550

(Received March 13, 2008; CL-080281; E-mail: yikeda@nr.titech.ac.jp)

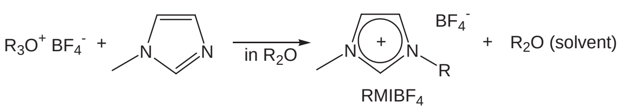
An alternative synthetic route to metal halide free ionic liquids using trialkyloxonium salt is proposed. Utility of this synthetic route has been demonstrated by preparing 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid through the reaction between 1-methylimidazole and triethyloxonium tetrafluoroborate in anhydrous ether.

Ionic liquids (ILs) consist of only ionic species, and have unique properties; low melting point, non-volatility, non-flammability, high conductivity, wide electrochemical potential window, and so on. Because of these properties, ILs have been noted as attractive media in various fields, e.g., organic syntheses,[1–5] electrochemical devices,[6] and nuclear engineering.[7,8]

The remarkable properties of ILs are nonvolatility and low melting point, which are noticeable as green solvents. However, these properties make a purification of ILs quite difficult, i.e., distillation and recrystallization of ILs are impractical usually. Actually, the physical properties of ILs having same name are different in each literature.[9,10] Such differences should arise from variety and amount of impurities in ILs. The most popular impurity in ILs is a metal halide, which contaminates ILs in the anion metathesis. It is also reported that such an impurity inhibits organic reactions in ILs, e.g. oxidation of alcohols using Ru catalyst[11] and lipase-catalyzed acylations.[12,13] From these viewpoints, innovation of synthetic and/or purification methods for ILs is required. This is necessary for its global standardization.[14]

Previously, trialkyloxonium salts ($Et_3O^+BF_4^-$ and $Me_3O^+BF_4^-$) were reported as strong alkylation agents to nucleophiles.[15–17] By-products in the alkylation using $R_3O^+BF_4^-$ will be only dialkyl ether (R_2O) and BF_4^-. The former can be removed easily by evaporation under reduced pressure, and the latter is one of the anionic components of the ILs. Therefore, it can be expected that the alkylation of a tertiary amine and the introduction of a desired anion take place simultaneously by using the trialkyloxonium salts. In addition, most of ILs are immiscible with R_2O. Therefore, use of R_2O as the solvent simplifies the reaction system, and facilitates the separation of the resulting IL from the reaction mixutre. Here, we propose a clean and simple synthetic route of ILs using the trialkyloxonium salts as shown in Scheme 1. In this study, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$), which is one of the most popular ILs, was selected as an example to demonstrate the utility of this synthetic route.

The triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) was prepared by the method described elsewhere.[15] The resulting $Et_3O^+BF_4^-$ (ca. 21 g) was suspended in anhydrous Et_2O (40 mL) under dry argon atmosphere. The freshly distilled 1-methylimidazole (MIm, 9.3 g) was added dropwise into this suspension with vigorous stirring. After stirring the mixture for 2 h on the ice bath, the lower layer of $EMIBF_4$ was separated and washed by anhydrous Et_2O (2 × 50 mL). Volatiles in the product were evaporated for 2 h at 70 °C, and then for 6 h at 110 °C. Crude $EMIBF_4$ was obtained (22 g, 95% yield). This product was dissolved in water, followed by mixing with activated charcoal. After stirring this mixture at room temperature overnight, the activated charcoal was filtered off. Then, volatiles in the filtrate were removed by evaporation at 110 °C under reduced pressure. The residual colorless liquid was recovered as a purified $EMIBF_4$.[18]



Scheme 1.

The purity of the obtained $EMIBF_4$ was confirmed using ^1H and ^{19}F NMR spectroscopy (JEOL JNM-LA300WB, ^1H: 300.4 MHz, ^{19}F: 282.7 MHz, A neat sample with a sealed capillary tube filled by C_6D_6) and an anion chromatography (DIONEX ICS-1500). Figure 1 shows the resulting ^1H NMR spectra of the product. The ^1H NMR signals of 1-ethyl-3-methylimidazolium cation (EMI^+) are observed at 1.22 (t, 3H, N^1–CH_2CH_3), 3.69 (s, 3H, N^3–CH_3), 4.00 (quartet, 2H, N^1–CH_2CH_3), 7.26 and 7.33 (t, 2 × 1H, 4, 5-H), and 8.39 ppm (s, 1H, 2-H). In Figure 1, other small signals were detected at 3.78, 7.04, 7.09, and 8.08 ppm with a peak area ratio of 3:1:1:1. These signals arise from an impurity in the obtained $EMIBF_4$, and the peak area ratio among them corresponds to that in MIm. In addition, from the aqueous solution of the crude $EMIBF_4$, crystals of $BF_3·MIm$, which was identified by means of single-crystal X-ray analysis (see Supporting Infomation),[22]

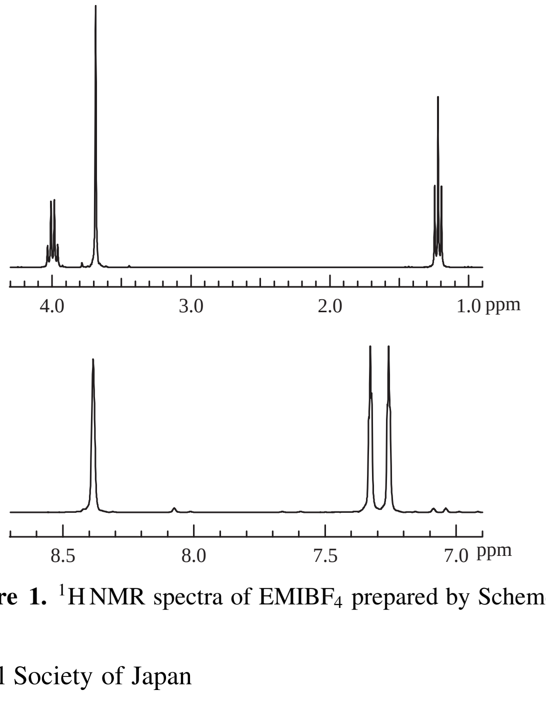


Figure 1. ^1H NMR spectra of $EMIBF_4$ prepared by Scheme 1.

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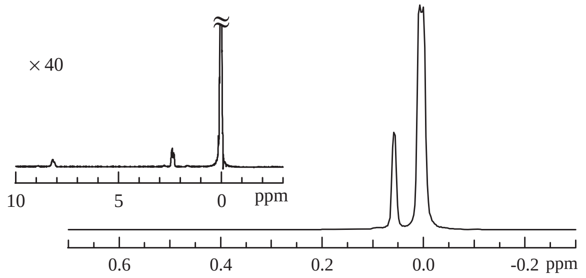

Figure 2. ^{19}F NMR spectra of EMIBF$_4$ prepared by Scheme 1. Inset shows the spectrum with the magnified longitudinal axis (×40) in the range from −4 to 10 ppm vs. $^{11}BF_4^-$.

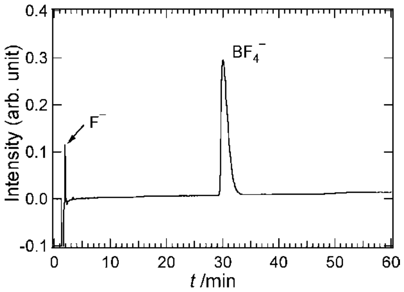

Figure 3. Anion chromatogram for EMIBF$_4$ diluted by ultrapure water. Eluent: 2.7 mM Na_2CO_3 + 0.3 mM $NaHCO_3$ aq.

deposited. This impurity is the product between MIm and the residual BF_3 in the preparation of $Et_3O^+BF_4^-$. From the peak area ratio in Figure 1, the purity of EMI$^+$ in the obtained EMIBF$_4$ was evaluated as 99 mol %.

The ^{19}F NMR spectrum and the anion chromatogram of the obtaind EMIBF$_4$ are displayed in Figures 2 and 3, respectively. In Figure 2, two intense ^{19}F NMR signals due to BF_4^- were observed with the area ratio of 1:4, which is comparable with the ratio of natural abundances of boron isotopes (^{10}B: 19.9%, ^{11}B: 80.1%). The separation between the ^{19}F NMR signals of $^{10}BF_4^-$ and $^{11}BF_4^-$ ($\Delta\delta = 0.06$) for the isotope effect is consistent with that ($\Delta\delta = 0.050 \pm 0.002$) reported previously.[19] In the inset of Figure 2, additional ^{19}F peaks other than BF_4^- were detected at 2.4 and 8.2 ppm vs. $^{11}BF_4^-$. These signals are indicative of the presence of the impurities in the obtained EMIBF$_4$. From the peak integrals in Figure 2, the purity of BF_4^- was estimated as 99 mol %.

In the anion chromatogram (Figure 3), two peaks due to F$^-$ and BF_4^- were observed. The mole fractions of F$^-$ and BF_4^- were determined as 0.04 and 0.96, respectively. Since BF_4^- may convert to F$^-$ and $BF_3(OH)^-$ through its hydrolysis,[20] the detected F$^-$ in Figure 3 cannot be assigned to the impurity in the obtained EMIBF$_4$ or the hydrolysis product of BF_4^- during the sample preparation for the anion chromatography. Thus, the purity of the obtained EMIBF$_4$ cannot be estimated using the data in Figure 3. It is noteworthy that no other anions were detected in this chromatogram. This is the important evidence, because one of the advantages of our synthetic route is no contamination by metal halides into ILs.

The noticeable significance of the synthetic route of ILs using the trialkyloxonium salts is the simultaneous introduction of BF_4^- and alkyl group to tertiary N. In this method, any contamination of metal halides can be avoided, because the preparation of onium halide and the anion metathesis using metal salts are no longer required. Since the trialkyloxonium salts are the strong alkylation agents, high yield of ILs can be expected. The by-product of this method is only R_2O. The use of R_2O as a solvent simplifies the reaction system, and facilitates the separation of the resulting ILs. The utility of this method was successfully demonstrated by the preparation of EMIBF$_4$. Further, all chemicals used here do not have large molecular weights, and are commonly available. These are additional merits in an aspect of synthetic cost of ILs. A small amount of BF_3·MIm was detected as an impurity in the obtained EMIBF$_4$. According to Fratiello et al., BF_3 is preferentially coordinated by MIm, and forms a stable complex.[21] In our experiment, BF_3·MIm in EMIBF$_4$ was durable up to 110 °C, and seems to be stable under the presence of water, even in the aqueous solution, despite the strong Lewis acidic character of BF_3. Hence, this impurity might be inert in ILs. Further investigation for the removal of BF_3·MIm from the resulting ILs is in progress. Nowadays, several trialkyloxonium salts ($Et_3O^+BF_4^-$, $Me_3O^+BF_4^-$, $Et_3O^+PF_6^-$, and $Et_3O^+SbCl_6^-$) are commercially available. Thus, wide variety of metal halide free ILs will be covered by our synthetic route.

References and Notes

\# This author's last name has been changed from "Mizuoka." His present address is Institute of Radiochemistry, Forschungszentrum Dresden–Rossendorf (FZD), Germany. E-mail: k.takao@fzd.de.

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18 The obtained EMIBF$_4$ was neutral. This means that there were no contamination of water through the reactions and no hydrolysis of BF_4^- during the purification using the activated charcoal.

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22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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