Low-Viscous, Low-Melting, Hydrophobic Ionic Liquids: 1-Alkyl-3-methylimidazolium Trifluoromethyltrifluoroborate

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New hydrophobic ionic liquids, 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl) trifluoromethyltrifluoroborate ($[CF_3BF_3]^-$), have been synthesized by a metathesis reaction between 1-alkyl-3-methylimidazolium halide and $K[CF_3BF_3]$. All these new ionic liquids exhibit low viscosities (26–77 cP at 25 °C) and low melting points, resulting in high conductivities correspondingly.

Ionic liquids (ILs) are being widely investigated as new reaction media and catalysts in organic synthesis and biosynthesis reactions, and as electrolytes for various electrochemical devices because of their superior properties over conventional solvents and electrolytes, such as nonflammability, nonvolatility, high thermal stability, and so on.[1] In spite of all the aforementioned advantages, ILs still have many barriers to overcome before they can be widely used in industry to replace the conventional organic solvents or electrolytes. One of the severe barriers associated with the application of ILs is the inherently high viscosity of ILs compared with conventional organic solvents. The high viscosity not only makes handling (dissolution, decantation, filtration, etc.) difficult but also leads to the reduction of the reaction rate.[2] Therefore, a great deal of effort has been made to find low viscous ILs, and a few low-viscous ILs (<30 cP at 25 °C) have been obtained by combining 1-ethyl-3-methylimidazolium (EMI^+) with some special anions, such as fluorohydrogenate ($[F(HF)_{2.3}]^-$),[3] dicyanamide ($[N(CN)_2]^-$),[4] tricyanomethanide ($[C(CN)_3]^-$),[5] bis(trifluoromethylsulfonyl)imide ($[(CF_3SO_2)_2N]^-$),[6] 2, 2, 2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide ($[(CF_3SO_2)(CF_3CO)N]^-$),[7] and so on. In this work, we report a series of low-viscous, low-melting ILs based on 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl) and trifluoromethyltrifluoroborate ($[CF_3BF_3]^-$),[8] which has a lower symmetry than tetrafluoroborate ($[BF_4]^-$).

The new salts in Table 1 were synthesized by a metathesis reaction between the purified 1-alkyl-3-methylimidazolium chloride or iodide and a little excess of $K[CF_3BF_3]$ prepared as described in a recent literature.[8b] In a typical reaction, to a stirred solution of [EMI]Cl (4.40 g, 30 mmol) in water (15 mL) was added $K[CF_3BF_3]$ (5.45 g, 31 mmol) at room temperature. The mixture was stirred for an additional 30 min. The bottom layer was separated, and washed with water twice (2 × 5 mL). The liquid obtained was dried at 70 °C and 0.02 Torr for 24 h to afford 6.32 g of $EMI[CF_3BF_3]$ (yield 85%) as a colorless liquid (water content 48 ppm).

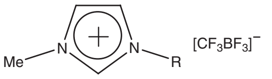
The five new $[CF_3BF_3]^-$-based salts prepared were characterized by ^1H and ^{19}F NMR, and elemental analysis.[9] The characterization data are in accordance with the expected structures and compositions. Moreover, all these ILs are immiscible with water to some extent, facilitating purification by simply washing with water to remove water-soluble impurities. More importantly, F^- (HF) content (determined by ion chromatography) in the resulting ILs is lower than 5 ppm, reflecting that $[CF_3BF_3]^-$ is stable against hydrolysis during the preparation processes probably owing to its hydrophobicity.

The physicochemical properties of the newly prepared salts are presented in Table 2. Of particular interest is the melting point (T_m), viscosity (η), and specific conductivity (κ) of these ILs. The melting points of the $[CF_3BF_3]^-$-based salts are lower than those of the $[BF_4]^-$-based ones with the same cation,[10] especially in the case of the cation with a relatively high symmetry, e.g. $MMI[CF_3BF_3]$ melting at 15 °C, which is much lower than $MMI[BF_4]$ (T_m 103 °C).[10] This result suggests that the melting points of ILs might be lowered by reduction of the fluoroanion symmetry. However, no clear relationship between the structures of these salts and their melting points is observed. The thermal stability of the salts was determined by TGA. The $[CF_3BF_3]^-$-based salts were stable up to about 200 °C, showing lower thermal stability than $EMI[BF_4]$,[11] but stable enough to be used as solvents for organic reactions or as electrolytes for electrochemical devices.

Unexpectedly, these new salts show very low viscosities (26–77 cP at 25 °C) (Table 2), which are obviously lower than those of the corresponding $[BF_4]^-$-based salts (37–180 cP at 25 °C),[11] although $[CF_3BF_3]^-$ has a larger size than $[BF_4]^-$. Among these new salts, $EMI[CF_3BF_3]$ shows the lowest viscosity (26 cP at 25 °C) while $MMI[CF_3BF_3]$ exhibits a bit of higher viscosity (27 cP at 25 °C). It seems that the relatively lower symmetry of $[CF_3BF_3]^-$ compared with that of $[BF_4]^-$ and the extremely low glass transition temperature (T_g) of the new salts play a crucial role in lowering the viscosities. As shown in Table 2, the viscosities of these ILs generally increase as the sizes of cations increased, indicating that a cation with a large size is unfavorable to produce low viscous ILs.

On the other hand, these new salts afford highly specific conductivities because of their low viscosities. Among them, two salts are highly conductive, 15.5 mS·cm^{-1} for MMI-

Table 1. Structure and yield of the ionic liquids prepared



Cation	R	Yield/%
MMI^+	Methyl	75
EMI^+	Ethyl	85
MPI^+	*n*-Propyl	88
BMI^+	*n*-Butyl	90
HMI^+	*n*-Hexyl	92

Table 2. Physicochemical properties of the newly prepared salts (water content in the salts is less than 50 ppm)

Salts	T_g[a]/ °C	T_m[b]/ °C	T_d[c]/ °C	η[d]/ cP	κ[e]/ $\mathrm{mS{\cdot}cm^{-1}}$
MMI[CF_3BF_3]	none	15	202	27	15.5
EMI[CF_3BF_3]	−117	−19	243	26	14.6
MPI[CF_3BF_3]	−113	−21	272	41	8.5
BMI[CF_3BF_3]	−108	nd[f]	238	49	5.9
HMI[CF_3BF_3]	−100	nd[f]	197	77	2.8

[a]Glass transition temperature determined by DSC on heating; [b]Melting point determined by DSC on heating; [c]Decomposition temperature determined by TGA; [d]Viscosity measured at 25 °C; [e]Specific conductivity at 25 °C; [f]Not detected.

[CF_3BF_3] and 14.6 $\mathrm{mS{\cdot}cm^{-1}}$ for EMI[CF_3BF_3] at 25 °C, which are a little higher than that another hydrophobic salt reported very recently, EMI[$C_2F_5BF_3$] ($\approx$12 $\mathrm{mS{\cdot}cm^{-1}}$),[12] and much higher than that EMI[$(CF_3SO_2)_2N$] (8.4 $\mathrm{mS{\cdot}cm^{-1}}$) despite of its low viscosity (28 cP at 25 °C),[6b] strongly suggesting that an anion with a medium size (e.g. $[CF_3BF_3]^-$) is favorable for improving the conductivities of ILs. Figure 1 shows the temperature dependences of the specific conductivities of the low-viscous, low-melting salt, EMI[CF_3BF_3], in comparison with EMI[BF_4]. It exhibits obviously higher conductivities than EMI[BF_4], especially in low-temperature regions, and are comparable to a conventional electrolyte for double-layer capacitors (DLCs), 1 $\mathrm{mol{\cdot}dm^{-3}}$ [Et_3MeN][BF_4] in propylene carbonate (PC).[13]

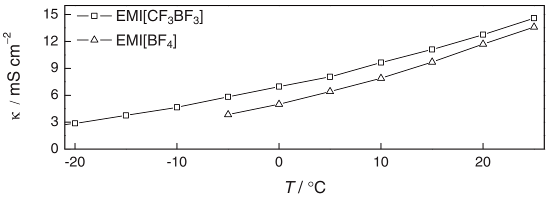


Figure 1. Temperature dependence of specific conductivities of ionic liquids (EMI[BF_4] supercooled).

The electrochemical stability of EMI[CF_3BF_3] was comparatively studied with that of EMI[BF_4] by the linear sweep voltammetry (LSV) in an argon-filled glove box (O_2 and water <5 ppm). Figure 2 shows the LSV curves of these two salts determined under the same conditions. EMI[CF_3BF_3] shows an equivalent electrochemical window to EMI[BF_4].

In conclusion, a series of new hydrophobic ionic liquids consisting of $[CF_3BF_3]^-$ anion with 1-alkyl-3-methylimidazolium (alkyl = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl) cation were synthesized and characterized. These new ILs exhibit low viscosities (high conductivities), good chemical and electrochemical stability, and might serve as new solvents for organic reactions and as potential electrolytes for electrochemical devices.

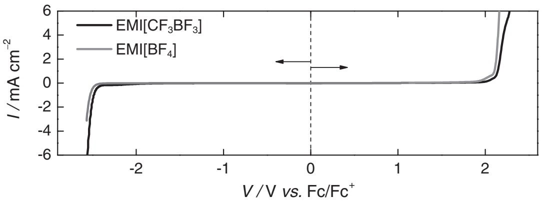


Figure 2. Linear sweep voltammogram for ionic liquids on a glassy carbon electrode ($8 \times 10^{-3}\ \mathrm{cm^{-2}}$); scan rate: 50 $\mathrm{mV\,s^{-1}}$; counter electrode: Pt wire; potential (V) was referred to ferrocene (*F*c)/ferrocenium (*F*c^+) redox couple.

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9 Chemical shift values are referenced to internal TMS for ^1H (400 MHz) and external CCl_3F for ^{19}F (376 MHz), and acetone-d_6 was used as solvent. **MMI[CF_3BF_3]**. Anal. Calcd. (Found): C, 30.8 (30.5); H, 3.9 (4.0); N, 12.0 (11.9)%. ^1H NMR: $\delta = 4.02$ (s, 2 × 3H, $\mathrm{NC}H_3$), 7.66 (m, 2H, N–CH=CH–N), 8.89 (s, 1H, N–CH–N). **EMI[CF_3BF_3]**. Anal. Calcd. (Found): C, 33.9 (33.9); H, 4.5 (4.4); N, 11.3 (11.4)%. ^1H NMR: $\delta = 1.56$ (t, $J = 7.4$ Hz, 3H, $\mathrm{CC}H_3$), 4.03 (s, 3H, N–CH_3), 4.38 (q, $J = 7.3$ Hz, 2H, $\mathrm{NC}H_2$–), 7.67 and 7.74 (s, 2H, N–CH=CH–N), 8.94 (s, 1H, N–CH–N). **MPI[CF_3BF_3]**. Anal. Calcd. (Found): C, 36.7 (36.5); H, 5.0 (5.1); N, 10.7 (10.8)%. ^1H NMR: 0.96 (t, $J = 7.2$ Hz, 3H, $\mathrm{CC}H_3$), 1.98 (m, 2H, $\mathrm{CH_3C}H_2$–), 4.06 (s, 3H, N–CH_3), 4.32 (q, $J = 7.3$ Hz, 2H, $\mathrm{NC}H_2$–), 7.71 and 7.75 (s, 2H, N–CH=CH–N), 8.99 (s, 1H, N–CH–N). **BMI[CF_3BF_3]**. Anal. Calcd. (Found): C, 39.2 (38.9); H, 5.5 (5.8); N, 10.2 (10.2)%. ^1H NMR: $\delta = 0.95$ (t, $J = 7.2$ Hz, 3H, $\mathrm{CC}H_3$), 1.40 (m, 2H, $\mathrm{CH_3C}H_2$–), 1.93 (m, 2H, $\mathrm{CH_3CC}H_2$–), 4.04 (s, $\mathrm{NC}H_3$), 4.35 (q, $J = 7.3$ Hz, 2H, $\mathrm{NC}H_2$–), 7.68 and 7.74 (s, 2H, N–CH=CH–N), 8.95 (s, 1H, N–CH–N). **HMI[CF_3BF_3]**. Anal. Calcd. (Found): C, 43.5 (43.2); H, 6.3 (6.0); N, 9.2 (9.3)%. ^1H NMR: $\delta = 0.87$ (t, $J = 7.0$ Hz, 3H, $\mathrm{CC}H_3$), 1.34 (m, 3 × 2H, $\mathrm{CH_3(C}H_2)_3$–), 1.95 (m, 2H, $\mathrm{NCH_2C}H_2$–), 4.04 (s, 3H, $\mathrm{NC}H_3$), 4.35 (t, $J = 7.2$ Hz, 2H, $\mathrm{NC}H_2$–), 7.69 and 7.75 (s, 2H, N–CH=CH–N), 8.97 (s, 1H, N–CH–N). All above salts have the same anion $[CF_3BF_3]^-$, and show an equivalent chemical shift value and coupling constant in ^{19}F NMR. ^{19}F NMR: $\delta = -74.8$ (q, $^2J_{BF} = 32.6$ Hz, 3F, $\mathrm{C}F_3$), -155.2 (q, $^1J_{BF} = 39.6$ Hz, 3F, $\mathrm{B}F_3$).

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