# A New Class of Hydrophobic Ionic Liquids: Trialkyl(2-methoxyethyl)ammonium Perfluoroethyltrifluoroborate

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(Received March 1, 2004; CL-040228)

New hydrophobic ionic liquids consisting of trialkyl(2-methoxyethyl)ammonium ($[R^1R^2R^3NCH_2CH_2OCH_3]^+$, $R^1$, $R^2$, $R^3 = CH_3$ or $C_2H_5$) cation and perfluoroethyltrifluoroborate ($[C_2F_5BF_3]^-$) anion were prepared by neutralization of aq. $[R_1R_2R_3NCH_2CH_2OCH_3][OH]$ with aq. $H[C_2F_5BF_3]$. The new $[C_2F_5BF_3]^-$-based ionic liquids show much lower melting points and viscosities (58–86 cP at 25 °C), hence higher ionic conductivities, than the $[BF_4]^-$-based ones.

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The field of ionic liquids (ILs) is mainly dominated by imidazolium system, since ILs based on imidazolium have been empirically demonstrated to afford relatively low viscosities, which is a key requirement for ILs as new reaction media or electrolytes to replace conventional ones.[1] While there are a large number of imidazolium-based ILs, few ILs based on tetraalkylammonium have been reported.[2–7] Compared with the imidazolium system, tetraalkylammonium one is more electrochemically stable against oxidation and reduction, supporting it as possible safety electrolytes for 4-V class Li batteries. Tetraalkylammonium salts that are liquid at room temperature have ever been synthesized by reducing symmetry of either ammonium cation or anion in 1970s,[2,3] however, the overall size of ions involved (total C atoms $> 20$) is very large, resulting in high viscosities ($>400$ cP).[2,3b,5c] The relatively low melting and viscous ILs (50–180 cP) based on small ammonium cations (total C atoms = 5–12) have been successfully prepared by introducing fluoroanions that have relatively low symmetry and highly delocalized charge, such as bis(trifluoromethylsulfonyl)imide ($[(CF_3SO_2)_2N]^-$),[4,5a] 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide ($[(CF_3SO_2)(CF_3CO)N]^-$),[5b] and so on. Another method to prepare ammonium-based ILs with low melting points was to modify the structure of tetraalkylammonium cation slightly, i.e., replacing one alkyl group (e.g. $CH_3CH_2CH_2$–) in the four substituents of tetraalkylammonium cation with an isoelectronic ether group (e.g. $CH_3OCH_2$–).[5a,6] 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 tetraalkylammonium salts.

Recently, a new series of perfluoroalkyltrifluoroborates ($[R_FBF_3]^-$), having a lower symmetry than $[BF_4]^-$, have been reported.[8] The ILs consisting of 1-ethyl-3-methylimidazolium ($EMI^+$) and $[R_FBF_3]^-$ ($R_F = C_2F_5$, n-$C_3F_7$, and n-$C_4F_9$) have also been prepared more recently,[9] which exhibit lower melting points than [EMI][$BF_4$]. All these results stimulate us to find low melting and viscous tetraalkylammonium-based ILs by combining relatively small trialkyl(2-methoxyethyl)ammonium ($[R^1R^2R^3NCH_2CH_2OCH_3]^-$, $R^1$, $R^2$, $R^3 = CH_3$ or $C_2H_5$) with perfluoroethyltrifluoroborate ($[C_2F_5BF_3]^-$), which has a moderate size.

The new salts $[R^1R^2R^3NCH_2CH_2OCH_3][C_2F_5BF_3]$ were prepared by neutralization of aqueous solution of $[R^1R^2R^3NCH_2CH_2OCH_3][OH]$ with aqueous solution of $H[C_2F_5BF_3]$ as shown in Scheme 1. The aq. $[R^1R^2R^3NCH_2CH_2OCH_3][OH]$ were produced via anion exchange of the corresponding bromide salts, which were synthesized by reaction of trialkylamines with an equivalent of 2-bromoethyl methyl ether ($CH_3OCH_2CH_2Br$) in anhydrous acetone in an autoclave followed by recrystallization from acetone,[6] while the aq. $H[C_2F_5BF_3]$ was prepared by cation exchange of $K[C_2F_5BF_3]$.[8] For comparison, the $[BF_4]^-$-based salts were prepared similarly except for using aq. $H[BF_4]$ instead of aq. $H[C_2F_5BF_3]$.

$$R^1R^2R^3N \xrightarrow{CH_3OCH_2CH_2Br} [R^1R^2R^3NCH_2CH_2OCH_3]Br$$

$$\xrightarrow{\text{anion exchange}} \text{aq. } [R^1R^2R^3NCH_2CH_2OCH_3][OH]$$

$$\xrightarrow{\text{aq. } H[C_2F_5BF_3]} [R^1R^2R^3NCH_2CH_2OCH_3][C_2F_5BF_3]$$

| $R^1$ | $R^2$ | $R^3$ | Notation for Cation |
|---|---|---|---|
| $CH_3$ | $CH_3$ | $CH_3$ | $N_{111.1O2}$ |
| $CH_3$ | $CH_3$ | $C_2H_5$ | $N_{112.1O2}$ |
| $CH_3$ | $C_2H_5$ | $C_2H_5$ | $N_{122.1O2}$ |
| $C_2H_5$ | $C_2H_5$ | $C_2H_5$ | $N_{222.1O2}$ |

**Scheme 1.**

All the salts prepared were characterized by $^1H$ and $^{19}F$ NMR, and elemental analyses. The characterization data are consistent with the expected compositions and structures.[10] The new $[C_2F_5BF_3]^-$-based salts are immiscible with water to some extent, and the water content in the salts was lower than 40 ppm after drying at 60 °C and 0.02 Torr for 12 h probably due to their hydrophobicity, whereas the $[BF_4]^-$-based ones are miscible with water, and still contained a relatively high amount of water (ca. 600 ppm) after rigorously drying at 80 °C and 0.02 Torr for 48 h.

The physicochemical properties of the salts prepared are summarized in Table 1. Except the salt $N_{122.1O2}[C_2F_5BF_3]$ that was not crystallized under the measurement conditions, the others (quenched to $-150$ °C) showed their melting on heating in DSC while some of the salts also showed a glass transition ($T_g$) at a very low temperature. The melting points of all the $[C_2F_5BF_3]^-$-based salts are obviously lower than those of the $[BF_4]^-$-based ones with the same cation, e.g. with the same cation $N_{1O2.112}$, but changing the anion from $[BF_4]^-$ to $[C_2F_5BF_3]^-$, results in a change of the melting point from 4 to $-33$ °C. These results strongly indicate that the melting points of the salts could be lowered significantly by reducing the symmetry of fluoroan-

**Table 1.** Synthesis yields and physicochemical properties of ionic liquid salts

| Salts | Yield / % | $T_g$[a] / °C | $T_m$[b] / °C | $T_d$[c] / °C | $d$[d] / gcm$^{-3}$ | $V_m$[e] / cm$^3$ mol$^{-1}$ | $\eta$[f] / cP | $\kappa$[g] / mScm$^{-1}$ | $\Lambda$[h] / Scm$^2$mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $N_{111.1O2}$ [$C_2F_5BF_3$] | 86 | none | 30 | 326 | solid | solid | solid | solid | solid |
| $N_{112.1O2}$ [$C_2F_5BF_3$] | 88 | −117 | −33 | 307 | 1.34 | 238.1 | 58 | 3.83 | 0.911 |
| $N_{122.1O2}$ [$C_2F_5BF_3$] | 87 | −113 | nd[i] | 322 | 1.32 | 252.3 | 68 | 3.14 | 0.792 |
| $N_{222.1O2}$ [$C_2F_5BF_3$] | 90 | −98 | 3 | 345 | 1.29 | 269.1 | 86 | 2.36 | 0.635 |
| $N_{111.1O2}$ [$BF_4$][j] | 89 | none | 54 (64) | 376 | solid | solid | solid | solid | solid |
| $N_{112.1O2}$ [$BF_4$][j] | 90 | −97 | 4 (13) | 377 | 1.21 | 181.0 | 335 (335) | 1.70 (1.70) | 0.308 |
| $N_{122.1O2}$ [$BF_4$] | 90 | −95 | 8 | 372 | 1.20 | 194.2 | 426 | 1.27 | 0.245 |
| $N_{222.1O2}$ [$BF_4$] | 92 | none | 56 | 372 | solid | solid | solid | solid | solid |

[a]Glass transition temperature determined by DSC on heating; [b]Melting point determined by DSC on heating; [c]Decomposition temperature determined by TGA; [d]Density measured by weighting 1.0 mL of ionic liquid at 25 °C; [e]Molar volume at 25 °C; [f]Viscosity measured at 25 °C. [g]Specific conductivity at 25 °C; [h]Molar conductivity ($\Lambda = \kappa V_m$) at 25 °C. [i]Not detected; [j]Data in parenthesis from Ref. 6.

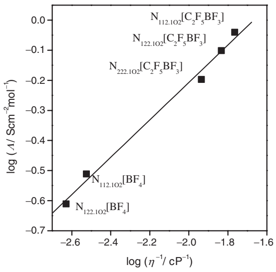

**Figure 1.** A plot of the molar conductivity ($\Lambda$) against the reciprocal of the viscosity ($\eta^{-1}$) for the salts that are liquid at room temperature.

ions, in our case, by replacing one fluorine atom of $[BF_4]^-$ with $C_2F_5$ group. The cation of the salts also show a similar effect on the melting points, e.g. keeping the anion $[BF_4]^-$ or $[C_2F_5BF_3]^-$ constant, the salts containing the less symmetrical cations, $N_{112.1O2}$ and $N_{122.1O2}$, exhibit lower melting points than those containing the more symmetrical ones, $N_{111.1O2}$ and $N_{222.1O2}$ (see Table 1). More importantly, the $[C_2F_5BF_3]^-$-based salts that are liquid at 25 °C exhibit much lower viscosities (56–86 cP at 25 °C) and higher ionic conductivities (2.3–3.8 mScm$^{-1}$ at 25 °C) than the $[BF_4]^-$-based ones (330–430 cP and 1.2–1.7 mScm$^{-1}$ at 25 °C), although the size of $[C_2F_5BF_3]^-$ is much larger than that of $[BF_4]^-$. It seems that the lower glass transition and melting points of the former salts compared with those of the later ones may contributed to their lower viscosities, resulting in higher ionic conductivities. This is further supported by a linear relationship between the molar conductivity ($\Lambda$) and the reciprocal of the viscosity ($\eta^{-1}$) of these salts as shown in Figure 1 ($r = 0.996$).

The thermal stability of these salts was determined by TGA. The $[C_2F_5BF_3]^-$-based salts were stable up to ca. 300 °C, showing a less thermal stability than the $[BF_4]^-$-based ones.

In summary, a new class of hydrophobic ionic liquids, trialkyl(2-methoxyethyl)ammonium perfluoroethyltrifluoroborate, have been prepared and characterized. Most of them exhibit low viscosities (high conductivities) and low melting points, and might be used as potential electrolytes for electrochemistry and as new solvents for organic reactions.

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

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10 Chemical shift values are reported with respect to internal TMS for $^1$H (400 MHz) and external $CCl_3F$ for $^{19}$F (376 MHz), and acetone-$d_6$ was used as solvent. $N_{1O2.111}$**[$C_2F_5BF_3$]**. $^1$H NMR: $\delta$ 3.37 (s, 3 × 3H), 3.40 (s, 3H), 3.76 (s, 2H), 3.94 (s, 2 H). Anal. Calcd. for $C_8H_{16}BF_8NO$: C, 31.5; H, 5.3; N, 4.6%. Found: C, 31.2; H, 5.2; N, 4.6%. $N_{1O2.112}$**[$C_2F_5BF_3$]**. $^1$H NMR: $\delta$ 1.45 (t, 3H, $J = 7.2$ Hz), 3.28 (s, 2 × 3H), 3.39 (s, 3H), 3.64 (q, 2H, $J = 7.2$ Hz), 3.71 (t, 2H, $J = 4.8$ Hz), 3.92 (s, 2H). Anal. Calcd. for $C_9H_{18}BF_8NO$: C, 33.9; H, 5.7; N, 4.4%. Found: C, 33.7; H, 5.6; N, 4.3%. $N_{1O2.122}$**[$C_2F_5BF_3$]**. $^1$H NMR: $\delta$ 1.41 (t, 2 × 3H, $J = 7.2$ Hz), 3.19 (s, 3H), 3.39 (s, 3H), 3.59 (q, 2 × 2H, $J = 7.2$ Hz), 3.67 (t, 2H, $J = .8$ Hz), 3.91 (s, 2H). Anal. Calcd. for $C_{10}H_{20}BF_8NO$: C, 36.1; H, 6.1; N, 4.2%. Found: C, 35.8; H, 5.9; N, 4.1%. $N_{1O2.222}$-**[$C_2F_5BF_3$]**. $^1$H NMR: $\delta$ 1.37 (t, 3 × 3H, $J = 7.2$ Hz), 3.38 (s, 3H), 3.56 (q, 3 × 2H, $J = 7.2$ Hz), 3.63 (t, 2H, $J = 4.8$ Hz), 3.87 (s, 2H). Anal. Calcd. for $C_{11}H_{22}BF_8NO$: C, 38.1; H, 6.4; N, 4.0%. Found: C, 38.1; H, 6.4; N, 4.0%. All above salts have the same anion $[CF_3CF_2BF_3]^-$, and show an equivalent chemical shift value and coupling constant in $^{19}$F NMR. $^{19}$F NMR: $\delta$ −83.0 (s, C$F_3$), −135.8 (q, C$F_2$, $^2J_{BF} = 19.4$ Hz), −153.0 (q, B$F_3$, $^1J_{BF} = 39.7$ Hz).

Published on the web (Advance View) June 21, 2004; DOI 10.1246/cl.2004.886