Low-melting, Low-viscous, Hydrophobic Ionic Liquids: *N*-Alkyl(alkyl ether)-*N*-methylpyrrolidinium Perfluoroethyltrifluoroborate

Zhi-Bin Zhou, Hajime Matsumoto,* and Kuniaki Tatsumi

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology,
1-8-31 Midorigaoka Ikeda, Osaka 563-8577

(Received September 10, 2004; CL-041067)

A series of new hydrophobic ionic liquids comprising *N*-alkyl (alkyl ether)-*N*-methylpyrrolidinium and perfluoroethyltrifluoroborate were prepared and characterized. The new $[C_2F_5BF_3]^-$-based salts show lower melting points than the corresponding $[BF_4]^-$-based ones. Of these new salts, five are liquids at room temperature and show very low viscosities (37–71 cP at 25 °C), high ionic conductivities (3.0–6.8 $mScm^{-1}$) and wide electrochemical windows.

Ionic liquids (ILs) are being extensively investigated as new reaction media in chemistry and as electrolytes in electrochemistry because of their desirable properties including nonvolatility, nonflammability, and high thermal stability.[1] Of the various ILs reported, the ILs based on saturated quaternary ammonium (QA) have attracted increasing attention in recent years.[1b,2-4] One of the reasons for this growing interest is that the QA salts with electrochemically stable anions, such as $[(CF_3SO_2)_2N]^-$ ($TFSI^-$), have much larger electrochemical windows than the more popular 1,3-dialkylimidazolium ones,[2–4] which may allow them as possible safety electrolytes for high-energy storage devices, such as Li batteries.[5]

Currently, the synthesis and application of chemically and electrochemically stable QA-based ILs are almost devoted to the anion $TFSI^-$, because this fluoroanion combines low symmetry, good flexibility and weakly coordinating nature, all of which are beneficial to lowering the melting point and viscosity of the ILs.[2,4,5] With the rapidly expanding applications of QA-based ILs in various fields, new robust anions that can form low-melting and/or low-viscous ILs with QA cations are certainly needed.

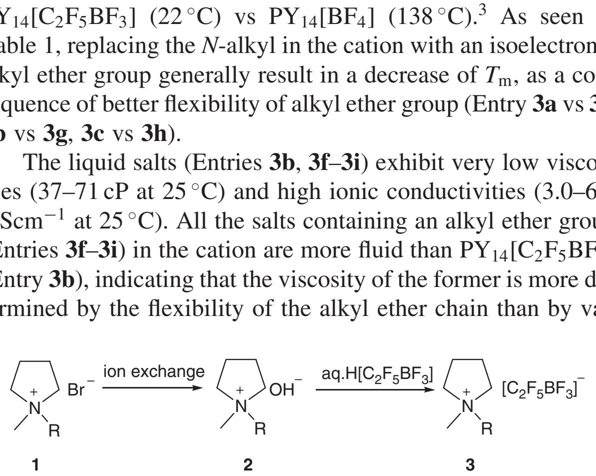
Most recently, a new class of chemically and electrochemically stable fluoroanions, namely perfluoroalkyltrifluoroborate ($[R_FBF_3]^-$, $R_F = n\text{-}C_mF_{2m+1}$, $m = 1$–4), have been successfully introduced into the ILs field.[7] Compared with the representative anion $[BF_4]^-$, $[R_FBF_3]^-$ have the obvious advantages of (1) better charge distribution and lower symmetry, thus their ILs generally exhibit very low melting points and viscosities; and (2) much better stability toward hydrolysis because of their hydrophobicity.[6] Moreover, among the series of $[R_FBF_3]^-$, perfluoroethyltrifluoroborate ($[C_2F_5BF_3]^-$) has a medium size and usually form the most fluid ILs with good thermal stability.[6d] Of the QA cations, *N*-alkyl-*N*-methylpyrrolidiniums have been demonstrated to produce low-viscous ILs due to the quasi-flat shape of pyrrolidinium core.[2b] Additionally, having an alkyl ether group in the QA cation also tends to lower the melting point and viscosity of the ILs.[4a,6c] On the base of above known knowledge, we therefore try to prepare new low-melting and/or low-viscous QA-based ILs by combining asymmetric *N*-alkyl (alkyl ether)-*N*-methylpyrrolidinium with $[C_2F_5BF_3]^-$.

To depress halide impurities in the resultant ILs, the new pyrrolidinium perfluoroethyltrifluoroborate salts (**3**) were prepared by neutralization of aqueous solution of pyrrolidinium hydroxide (**2**) with aqueous solution of $H[C_2F_5BF_3]$ (Scheme 1), followed by an evaporation. The pyrrolidinium hydroxide (**2**) solution was prepared by passing the corresponding bromide salts (**1**) through a column filled with basic anion-exchange resin (Mitsubishi Chem., ion exchange capacity >2.0 mequiv./mL), while the aq. $H[C_2F_5BF_3]$ was prepared by cation exchange of $K[C_2F_5BF_3]$, as described in the literature.[7] The bromide salts (**1**) were synthesized by quaternizing *N*-methylpyrrolidine with equimolar *n*-alkyl (alkyl ether) bromide in acetone at room temperature and purified by recrystallization.[2b] Since the salts (**3**) are immiscible with water, the water content in the liquid salts was <50 ppm after vacuum drying at 100 °C.

The structures and compositions of these new salts were confirmed by NMR (^1H, ^{19}F, and ^{11}B), FAB-MS, and elemental analysis.[8] The thermal properties of these salts were examined by DSC on heating (heating rate: 10 °C min^{-1}) and TGA (heating rate: 10 °C min^{-1}). The data for the physicochemical properties of these salts are summarized in Table 1.

The melting points (T_m's) of these new salts are lower than 65 °C (Table 1). Of these nine salts, five (Entries **3b**, **3f**–**3i**) are liquids at room temperature. As expected, for a given cation, the T_m's of the salts with lower symmetry $[C_2F_5BF_3]^-$ are all significantly lower than those with higher symmetry $[BF_4]^-$, e.g. $PY_{14}[C_2F_5BF_3]$ (22 °C) vs $PY_{14}[BF_4]$ (138 °C).[3] As seen in Table 1, replacing the *N*-alkyl in the cation with an isoelectronic alkyl ether group generally result in a decrease of T_m, as a consequence of better flexibility of alkyl ether group (Entry **3a** vs **3f**, **3b** vs **3g**, **3c** vs **3h**).

The liquid salts (Entries **3b**, **3f**–**3i**) exhibit very low viscosities (37–71 cP at 25 °C) and high ionic conductivities (3.0–6.8 $mScm^{-1}$ at 25 °C). All the salts containing an alkyl ether group (Entries **3f**–**3i**) in the cation are more fluid than $PY_{14}[C_2F_5BF_3]$ (Entry **3b**), indicating that the viscosity of the former is more determined by the flexibility of the alkyl ether chain than by van



R	Cation	R	Cation
$n\text{-}C_3H_7$	PY_{13}	CH_3OCH_2	$PY_{1.1O1}$
$n\text{-}C_4H_9$	PY_{14}	$CH_3O(CH_2)_2$	$PY_{1.1O2}$
$n\text{-}C_5H_{11}$	PY_{15}	$C_2H_5O(CH_2)_2$	$PY_{1.2O2}$
$n\text{-}C_6H_{13}$	PY_{16}	$CH_3O(CH_2)_2O(CH_2)_2$	$PY_{1.1O2O2}$
$n\text{-}C_7H_{15}$	PY_{17}		

Scheme 1.

Table 1. Synthesis yields and physicochemical properties of ionic liquids (water content: <50 ppm)

Entry	Salts	Yield[a] / %	T_g[b] / °C	T_c[c] / °C	$T_{s\text{-}s}$[d] / °C	T_m[e] / °C	T_d[f] / °C	d[g] / g mL^{-1}	η[h] / cP	κ[i] / mScm^{-1}	Λ[j] / Scm^{2}mol^{-1}
3a	$PY_{13}[C_2F_5BF_3]$	87	—[k]	—	—	63	312	solid	solid	solid	solid
3b	$PY_{14}[C_2F_5BF_3]$	89	—	—	−93	22	311	1.30	71	3.5	0.89
3c	$PY_{15}[C_2F_5BF_3]$	93	—	—	—	36	307	solid	solid	solid	solid
3d	$PY_{16}[C_2F_5BF_3]$	93	—	—	—	58	307	solid	solid	solid	solid
3e	$PY_{17}[C_2F_5BF_3]$	95	—	—	−64, −58	52	311	solid	solid	solid	solid
3f	$PY_{1.1O1}[C_2F_5BF_3]$	70	—	—	−51, −16	26	299	1.39	37	6.8	1.55
3g	$PY_{1.1O2}[C_2F_5BF_3]$	75	—	—	−116	−3	289	1.36	52	4.5	1.10
3h	$PY_{1.2O2}[C_2F_5BF_3]$	81	−108	−53	−13	−6	290	1.33	49	3.7	0.96
3i	$PY_{1.1O2O2}[C_2F_5BF_3]$	82	−98	—	—	—	297	1.34	54	3.0	0.84

[a]Based on the amount of $H[C_2F_5BF_3]$; [b]Glass transition temperature determined by DSC; [c]Crystallization temperature determined by DSC; [d]Solid–solid transition temperature determined by DSC; [e]Melting point determined by DSC; [f]Decomposition temperature determined by TGA; [g]Density measured by weighting 1.0 mL of ionic liquid at 25 °C; [h]Viscosity measured at 25 °C. [i]Specific conductivity at 25 °C; [j]Molar conductivity ($\Lambda = \kappa M/1000\ d$, M is formula weight of the salt) at 25 °C. [k]Not detected.

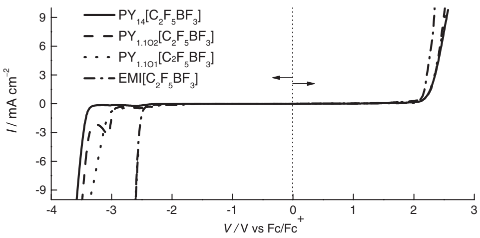


Figure 1. Linear sweep voltammogram of ionic liquids on a glassy carbon electrode (surface area: $7.85 \times 10^{-3}\ cm^{-2}$) in the first scan; scan rate: $50\ mV\ s^{-1}$; counter electrode: Pt wire; potential (V) was referred to ferrocene (Fc)/ferrocenium (Fc^+) redox couple in each salt.

der Waals interactions.

The electrochemical stability of three salts (Entries **3b**, **3f**, and **3g**) was comparatively studied with that of $EMI[C_2F_5BF_3]$[6a] (EMI^+ = 1-ethyl-3-methylimidazolium) by linear sweep voltammetry (LSV) under the same conditions. Figure 1 shows the polarization curves of these four salts, which mainly manifests the impact of the cation species on the cathodic and anodic stability. If the cathodic and anodic limits are defined as the potential at which the current density reached $1\ mA\ cm^{-2}$, the electrochemical windows for these salts show the order $[P_{14}][C_2F_5BF_3]$ (−3.41 to 2.24 V) > $[P_{1.1O1}][C_2F_5BF_3]$ (−3.03 to 2.24 V) ≈ $[P_{1.1O2}][C_2F_5BF_3]$ (−2.99 to 2.24 V) > $[EMI][C_2F_5BF_3]$ (−2.50 to 2.15 V). This result indicates that (1) these three pyrrolidinium salts show much better cathodic and anodic stability than $EMI[C_2F_5BF_3]$; and (2) having an alkyl ether group in the cation tends to reduce the cathodic stability.

In conclusion, a new series of hydrophobic ILs, *N*-alkyl (alkyl ether)-*N*-methylpyrrolidinium perfluoroethyltrifluoroborate, have been prepared and characterized. These new salts show low melting points (<65 °C). Among them, five salts are liquids at room temperature and exhibit very low viscosities, high conductivities, as well as wide electrochemical windows. All these promising properties may support them as new media for chemistry and electrochemistry.

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

References and Notes

1 a) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, **39**, 3772 (2000). b) D. MacFarlane and M. Forsyth, *Adv. Mater.*, **13**, 957 (2001). c) R. Hagiwara and Y. Ito, *J. Fluorine Chem.*, **105**, 221 (2000).

2 a) J. Sun, M. Forsyth, and D. R. MacFarlane, *J. Phys. Chem. B*, **102**, 8858 (1998). b) D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, *J. Phys. Chem. B*, **103**, 4164 (1999). c) D. MacFarlane, J. Huang, and M. Forsyth, *Nature*, **402**, 792 (1999).

3 S. Forsyth, J. Golding, and D. R. MacFarlane, and M. Forsyth, *Electrochim. Acta*, **46**, 1753 (2001).

4 a) H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, and Y. Miyazaki, *Chem. Lett.*, **2000**, 922. b) H. Matsumoto, H. Kageyama, and Y. Miyazaki, *Chem. Lett.*, **2001**, 182.

5 a) H. Sakaebe and H. Matsumoto, *Electrochem. Commun.*, **5**, 594 (2003). b) P. C. Howlett, D. R. MacFarlane, and A. F. Hollenkamp, *Electrochem. Solid-State Lett.*, **7**, A97 (2004).

6 a) Z. B. Zhou, M. Takeda, and M. Ue, *J. Fluorine Chem.*, **125**, 471 (2004). b) Z. B. Zhou, H. Matsumoto, and K. Tatsumi, *Chem. Lett.*, **33**, 680 (2004). c) Z. B. Zhou, H. Matsumoto, and K. Tatsumi, *Chem. Lett.*, **33**, 886 (2004). d) Z. B. Zhou, H. Matsumoto, and K. Tatsumi, *Chem.—Eur. J.*, (2004), in press.

7 Z. B. Zhou, M. Takeda, and M. Ue, *J. Fluorine Chem.*, **123**, 127 (2003).

8 Selected characterization data: **3a**. Anal. Calcd. for $C_{10}H_{18}BF_8N$: C, 38.12; H, 5.76; N, 4.45%. Found: C, 37.48; H, 5.65; N, 4.41%. **3b**. Anal. Calcd. for $C_{11}H_{20}BF_8N$: C, 40.15; H, 6.13; N, 4.26%. Found: C, 39.94; H, 5.82; N, 4.20%. **3c**. Anal. Calcd. for $C_{12}H_{22}BF_8N$: C, 42.01; H, 6.46; N, 4.08%. Found: C, 41.72; H, 6.37; N, 4.14%. **3d**. Anal. Calcd. for $C_{13}H_{24}BF_8N$: C, 43.72; H, 6.77; N, 3.92%. Found: C, 43.57; H, 6.61; N, 3.86%. **3e**. Anal. Calcd. for $C_{14}H_{26}BF_8N$: C, 45.30; H, 7.06; N, 3.77%. Found: C, 45.21; H, 6.81; N, 3.72%. **3f**. Anal. Calcd. for $C_9H_{16}BF_8NO$: C, 34.10; H, 5.09%; N, 4.42. Found: C, 33.84; H, 5.11; N, 4.39%. **3g**. Anal. Calcd. for $C_{10}H_{18}BF_8NO$: C, 36.28%; H, 5.48; N, 4.23. Found: C, 36.10; H, 5.47; N, 4.24%. **3h**. Anal. Calcd. for $C_{11}H_{20}BF_8NO$: C, 38.29%; H, 5.84; N, 4.06. Found: C, 38.02; H, 5.58; N, 4.06%. **3i**. Anal. Calcd. for $C_{12}H_{22}BF_8NO_2$: C, 38.42; H, 5.91%; N, 3.73. Found: C, 38.12; H, 5.60; N, 3.66%. All above salts have the same anion $[C_2F_5BF_3]^-$ and show an equivalent chemical shift value and coupling constant in the respective ^{19}F and ^{11}B NMR. ^{19}F NMR (376 MHz/acetone-d_6, δ ppm relative to external CCl_3F): δ −83 (s, CF_3), −136 (q, CF_2, $^2J_{BF}$ = 19.6 Hz), −153 (q, BF_3, $^1J_{BF}$ = 39.9 Hz). ^{11}B NMR (128 MHz/acetone-d_6, δ ppm relative to external $BF_3 \cdot Et_2O$): 0.21 (qt, $^1J_{BF}$ = 40.9 Hz, $^2J_{BF}$ = 19.1 Hz).

Published on the web (Advance View) November 20, 2004; DOI 10.1246/cl.2004.1636