Physico-chemical properties of hydrophobic ionic liquids containing 1-octylpyridinium, 1-octyl-2-methylpyridinium or 1-octyl-4-methylpyridinium cations

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Abstract

This paper reports synthesis of some ionic liquids based on cations 1-octylpyridinium, 1-octyl-2-methylpyridinium or 1-octyl-4-methylpyridinium and anions dicyanamide \([\text{N(CN)}_2^-]\), bis(trifluoromethylsulfonyl)imide \([\text{Tf}_2\text{N}]^-\), bis(pentafluoroethylsulfonyl)imide \([\text{BETI}]^-\), trifluoromethyl sulfonate \([\text{TfO}]^-\), nonafluorobutyl sulfonate \([\text{NfO}]^-\), tetrafluoroborate \([\text{BF}_4^-]\), trifluorophenylborate \([\text{BF}_3\text{Ph}]^-\) or hexafluoroarsenate \([\text{AsF}_6^-]\). Melting points, decomposition temperatures, densities, mutual solubilities with water, and viscosities have been measured. Unlike similar ionic liquids containing imidazolium cations, pyridinium ionic liquids studied here are nearly immiscible in water. Viscosities are similar and water content is slightly lower than those for ionic liquids containing imidazolium cations.

Introduction:

Ionic liquids are room-temperature molten salts with melting points near ambient temperatures. During the past decade, ionic liquids have become a popular research topic in chemistry. Many studies have reported applications in organic chemistry\(^{1-5}\), electrochemistry\(^{6,7}\), catalysis\(^{8-11}\), and extraction\(^{12-16}\).

Ionic liquids are tunable because there are many combinations of cations and anions with distinct physico-chemical properties. To date, only a few ionic liquids, mostly those based on ammonium and imidazolium cations, have been investigated\(^{1-26}\). Recently, other types of ionic liquids, containing pyridinium cations were studied and used\(^{27,28}\). However, the physico-chemical properties of ionic liquids containing pyridinium cations are yet to be fully investigated. To increase our knowledge and
understanding of ionic liquids, and to extend the database, we report here synthesis and selected properties of some ionic liquids that contain pyridinium cations.

For metal-ion extraction ionic liquids need to be immiscible in water, with a low or moderate viscosity. Several authors report possible application of ionic liquids to metal-ion extraction.\textsuperscript{12-16} However, ionic liquids previously studied were based on imidazolium cations. Solubilities of imidazolium ionic liquids in water are too high for industrial extraction processes.\textsuperscript{13,14,23} We need hydrophobic ionic liquids, that is, cations and anions with increased hydrophobicity.

Here, we report synthesis and some physico-chemical properties of hydrophobic ionic liquids based on octylpyridinium cations. Three different cations were used: 1-octylpyridinium, 1-octyl-2-methylpyridinium and 1-octyl-4-methylpyridinium cations, toward obtaining insight into the influence of the symmetry and the nature of the cation on the properties of ionic liquids. Various anions were used: tetrafluoroborate [BF\textsubscript{4}]\textsuperscript{-}, hexafluoroarsenate [AsF\textsubscript{6}]\textsuperscript{-}, trifluoromethyl sulfonate [TfO]\textsuperscript{-}, nonafluorobutyl sulfonate [NfO]\textsuperscript{-}, dicyanamide [N(CN)\textsubscript{2}]\textsuperscript{-}, bis(trifluoromethylsulfonyl)imide [Tf\textsubscript{2}N]\textsuperscript{-}, bis(pentafluoroethylsulfonyl)imide [BETI]\textsuperscript{-}, trifluorophenylborate [BF\textsubscript{3}Ph]\textsuperscript{-} and tetraphenylborate [BPh\textsubscript{4}]\textsuperscript{-}.

Tetrafluoroborate, bis(trifluoromethylsulfonyl)imide and nonafluorobutyl sulfonate anions are useful because they are known to be hydrophobic anions.\textsuperscript{17,19,24}

To elucidate the influence of the cation on the properties of ionic liquids, trifluoromethyl sulfonate and dicyanamide anions were used with octylpyridinium cation; their properties are compared with those of 1-methyl-3-octylimidazolium trifluoromethyl sulfonate and 1-methyl-3-octylimidazolium dicyanamide, previously reported.\textsuperscript{29} Dicyanamide anions are known to yield low-viscosity ionic liquids.\textsuperscript{30}
Trifluorophenylborate and tetraphenylborate anions were used to investigate the substitution of phenyl and fluoride on a borate anion and their influence on the properties of ionic liquids containing borate anions.

Experimental:

Synthesis

1-octyl-3-methylpyridinium tetrafluoroborate was used as received from Solvent Innovation. All other ionic liquids were obtained by a two step synthesis. First, 1-octylpyridinium bromide [OPYR][Br], 1-octyl-2-methylpyridinium bromide [2MOPYR][Br], and 1-octyl-4-methylpyridinium bromide [4MOPYR][Br] were synthesized by reacting bromo-octane with pyridine, 2-methylpyridine and 4-methylpyridine, respectively, in acetonitrile at 70 °C. All syntheses were done under nitrogen atmosphere. Then, a metathesis procedure was carried out to substitute selected other anions for bromide anions.

The purity of ionic liquids synthesized was checked with NMR and elemental analysis. Except for [OPYR][Br], [2MOPYR][Br] and [4MOPYR][Br], absence of halide impurities was checked with silver nitrate: 100 mg of each ionic liquid was mixed with 1 mL of dichloromethane and 1 mL of an aqueous solution of silver nitrate. If a white-yellow precipitate (corresponding to the formation of AgBr) appeared, ionic liquids were washed with water or extracted with dichloromethane; the silver nitrate test was then repeated until no AgBr precipitate was observed.
Under nitrogen atmosphere, 25 g (150 \cdot 10^{-3} \text{ mol}) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 7.91 g (100.0 \cdot 10^{-3} \text{ mol}) of pyridine, used as received from Sigma (99.9 % purity), and 50 mL acetonitrile. After cooling to room temperature, the solvent was removed by rotary evaporation and the light yellow solid product was washed with ethyl acetate (3 \times 100 \text{ mL}) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h. 20.6 g (75.7 \cdot 10^{-3} \text{ mol}) of 1-octylpyridinium bromide, [OPYR]^+\text{[Br]}^-, was obtained as a white solid (yield: 76 %).

$^1H$ NMR (400 MHz, CDCl$_3$): \(\delta\) 9.460-9.447 (2H, d, CH$_\text{pyr-o}$), 8.513-8.475 (H, t, CH$_\text{pyr-p}$), 8.132-8.097 (2H, t, CH$_\text{pyr-m}$), 5.039-5.002 (2H, t, N-CH$_2$), 2.055-2.019 (2H, m, CH$_2$), 1.338-1.228 (10H, m,C$_5$H$_{10}$), 0.870-0.837 (3H, t, oct-CH$_3$).

[4MOPYR]^+\text{[Br]}^-

Under nitrogen atmosphere, 14.43 g (74.7 \cdot 10^{-3} \text{ mol}) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 5.0 g (53.1 \cdot 10^{-3} \text{ mol}) of 4-methylpyridine, used as received from Sigma (98 % purity), and 25 mL acetonitrile. After cooling to room temperature, the solvent was removed by rotary evaporation and the light yellow solid product was washed with ethyl acetate (3 \times 100 \text{ mL}) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h. 14.77 g (51.8 \cdot 10^{-3} \text{ mol}) of 1-octyl-4-methylpyridinium bromide, [4MOPYR]^+\text{[Br]}^-, was obtained as a white solid (yield: 96 %).

$^1H$ NMR (400 MHz, CDCl$_3$): \(\delta\) 9.328-9.311 (2H, d, CH$_\text{pyr-o}$), 7.865-7.849 (2H, d, CH$_\text{pyr-m}$), 4.897-4.860 (2H, t, N-CH$_2$), 2.632 (3H, s, CH$_3$C$_\text{pyr-p}$), 2.002-1.931 (2H, m, CH$_2$), 1.317-1.182 (10H, m,C$_5$H$_{10}$), 0.827-0.793 (3H, t, oct-CH$_3$).

[2MOPYR]^+\text{[Br]}^-
Under nitrogen atmosphere, 13.1 g (67.4·10^{-3} mol) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 4.5 g (49.1·10^{-3} mol) of 4-methylpyridine, used as received from Sigma (98 % purity), and 25 mL acetonitrile. After cooling to room temperature, the solvent was removed by rotary evaporation and the light yellow solid product was washed with ethyl acetate (3 × 100 mL) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h. 14.77 g (51.8·10^{-3} mol) of 1-octyl-2-methylpyridinium bromide, [4MOPYR]⁺[Br], was obtained as a white solid (yield: 96 %).

\(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 9.652-9.632 (H, d, CH\text{pyr-o}), 8.365-8.313 (H, t, CH\text{pyr-m}), 7.984-7.939 (H, t, CH\text{pyr-p}), 7.886-7.860 (H, d, CH\text{pyr-C}), 4.905-4.853 (2H, t, N-CH\text{2}), 2.940 (3H, s, CH\text{3-Cpyr-m}), 1.964-1.86 (2H, m, CH\text{2}), 1.448-1.227 (10H, m, C\text{5H}_{10}), 0.863-0.817 (3H, t, oct-CH\text{3}).

[OPYR]⁺[Tf\(_2\)N]

3.47 g (12.5·10^{-3} mol) of [OPYR]⁺[Br] and 4.79 g (15.0·10^{-3} mol) of bis(trifluoromethylsulfonyl)imide acid salt, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 mL water for 24 h. The resulting ionic liquid was extracted in 50 mL methylene chloride. Excess salt and HBr were removed by mixing the resulting liquid with water and methylene chloride (20 mL of methylene chloride and 3 × 20 mL of water). Methylene chloride phase was extracted each time. After removal of methylene chloride by rotary evaporation, the product was set under high vacuum for 24 h. 5.21 g (yield: 89 %) of [OPYR]⁺[Tf\(_2\)N] were obtained as a colorless liquid.

\(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 9.652-9.632 (H, d, CH\text{pyr-o}), 8.365-8.313 (H, t, CH\text{pyr-m}), 7.984-7.939 (H, t, CH\text{pyr-p}), 7.886-7.860 (H, d, CH\text{pyr-C}), 4.905-4.853 (2H, t, N-CH\text{2}), 2.940 (3H, s, CH\text{3-Cpyr-m}), 1.964-1.86 (2H, m, CH\text{2}), 1.448-1.227 (10H, m, C\text{5H}_{10}), 0.863-0.817 (3H, t, oct-CH\text{3}).

[2MOPYR]⁺[Tf\(_2\)N]
3.47 g (12.5·10^{-3} mol) of [2MOPYR][Br]⁻ and 4.79 g (15.0·10^{-3} mol) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 mL acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation, washing with methylene chloride (20 mL) and water (3 × 20 mL), the product was set under high vacuum for 24 h. 5.21 g (yield: 89 %) of [2MOPYR][Tf₂N]⁻ were obtained as a light-yellow liquid.

(Found: C, 39.62; H, 5.19; N, 5.71. Calc. for C_{16}H_{24}N_{2}O_{4}S_{2}F_{6}: C, 39.50; H, 4.97; N, 5.76).

[4MOPYR][Tf₂N]⁻

2.52 g (9.1·10^{-3} mol) of [4MOPYR][Br]⁻ and 3.48 g (10.9·10^{-3} mol) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 mL acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride (20 mL) and water (3 × 20 mL), the product was set under high vacuum for 24 h. 3.75 g (yield: 86 %) were obtained as a colourless liquid.

{^1}H NMR (400 MHz, CDCl₃): δ 8.615-8.599 (2H, d, CH₇pyr-o), 7.812-7.797 (2H, d, CH₇pyr-m), 4.502-4.464 (2H, t, N-CH₂), 2.656 (3H, s, CH₃-C₇pyr-p), 2.000-1.945 (2H, m, CH₂), 1.310-1.234 (10H, m,C₅H₁₀), 0.863-0.830 (3H, t, oct-CH₃).

(Found: C, 39.38; H, 5.11; N, 5.73. Calc. for C_{16}H_{24}N_{2}O_{4}S_{2}F_{6}: C, 39.50; H, 4.97; N, 5.76).

[4MOPYR][BF₄]⁻

2.57 g (9.0·10^{-3} mol) of [4MOPYR][Br]⁻ and 1.47 g (13.4·10^{-3} mol) of sodium tetrafluoroborate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 mL of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, the
product was set under high vacuum for 24 h. 2.34 g (yield: 92 %) were obtained as a white-yellow liquid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta \ 8.658-8.641 \ (2H, d, CH\text{pyr-o}), \ 7.794-7.778 \ (2H, d, CH\text{pyr-m}), \ 4.511-4.473 \ (2H, t, CH\text{pyr-N}), \ 2.596 \ (3H, s, CH_3\text{pyr}), \ 1.927-1.891 \ (2H, m, CH_2), \ 1.260-1.166 \ (10H, m, C_5H_{10}), \ 0.804-0.770 \ (3H, t, CH_3) \].

(Found: C, 57.25; H, 8.64; N, 4.90. Calc. for C_{14}H_{24}NBF_4: C, 57.36; H, 8.25; N, 4.78).

\[ [\text{OPYR}]^+[\text{TfO}]^- \]

3 g (11.4·10^{-3} mol) of [OPYR]^+[Br] and 2.57 g (13.7·10^{-3} mol) of potassium trifluoromethyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 mL of acetonitrile. After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, the product was set under high vacuum for 24 h. 3.90 g (yield: 86 %) were obtained as a white solid.

(Found: C, 49.83; H, 7.26; N, 3.90. Calc. for C_{14}H_{24}NO_3SF_3: C, 49.25; H, 6.50; N, 4.10).

\[ [\text{4MOPYR}]^+[\text{TfO}]^- \]

3 g (11.4·10^{-3} mol) of [4MOPYR]^+[Br] and 2.40 g (12.8·10^{-3} mol) of potassium trifluoromethyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 mL of acetonitrile. After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, 3.45 g (yield: 91 %) were obtained as a light yellow liquid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta \ 8.858-8.842 \ (2H, d, CH\text{pyr-o}), \ 7.879-7.804 \ (2H, m, CH\text{pyr-m}), \ 4.621-4.585 \ (2H, t, CH\text{pyr-N}), \ 2.624 \ (3H, s, CH_3\text{pyr}), \ 2.005-1.933 \ (2H, m, CH_2), \ 1.272-1.194 \ (10H, m, C_5H_{10}), \ 0.814-0.796 \ (3H, t, CH_3) \].

(Found: C, 47.78; H, 6.89; N, 4.24. Calc. for C_{15}H_{24}NO_3SF_3: C, 50.69; H, 6.81; N, 3.94).

\[ [\text{2MOPYR}]^+[\text{TfO}]^- \]
3.3 g (12.5·10−3 mol) of [2MOPYR]+[Br]− and 2.80 g (14.9·10−3 mol) of potassium trifluoromethyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 mL of acetonitrile. After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, 3.66 g (yield: 88 %) were obtained as a light yellow liquid.

1H NMR (400 MHz, CDCl3): δ 8.842-8.826 (H, d, CHpym-o), 8.315-8.279 (H, t, CHpym-p), 7.879-7.804 (2H, m, CHpym-m), 4.591-4.552 (2H, t, N-CH2), 2.863 (3H, s, CH3-Cpym-o), 1.917-1.840 (2H, m, CH2), 1.426-1.240 (10H, m, C5H10), 0.869-0.834 (3H, t, oct-CH3).

(Found: C, 50.49; H, 6.97; N, 3.83. Calc. for C15H24N8O3S2F3: C, 50.69; H, 6.81; N, 3.94).

[OPYR]+[NfO]−

2.10 g (7.7·10−3 mol) of [OPYR]+[Br]− and 3.01 g (8.9·10−3 mol) of potassium nonafluorobutyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 mL of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3 × 25 mL). After 24 h under high vacuum, 3.44 g (yield: 91 %) were obtained as a white solid.

1H NMR (400 MHz, CDCl3): δ 8.976-8.962 (2H, d, CHpym-o), 8.466-8.427 (H, t, CHpym-p), 8.057-8.022 (2H, t, CHpym-m), 4.740-4.703 (2H, t, N-CH2), 1.991-1.980 (2H, t, CH2), 1.302-1.216 (10H, m, C5H10), 0.858-0.824 (3H, t, CH3).

(Found: C, 34.52; H, 3.75; N, 2.37. Calc. for C18H24N8O3S2F9: C, 34.61; H, 3.92; N, 2.45).

[4MOPYR]+[NfO]−

1.97 g (6.0·10−3 mol) of [4MOPYR]+[Br]− and 3.24 g (9.6·10−3 mol) of potassium nonafluorobutyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 mL of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3 × 25 mL). After 24 h under high vacuum, 2.94 g (yield: 86 %) were obtained as a white solid.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.858-8.842 (2H, d, CH$_{\text{pyr-o}}$), 7.795-7.774 (2H, m, CH$_{\text{pyr-m}}$), 4.591-4.540 (2H, t, N-CH$_2$), 2.623 (3H, s, CH$_3$-C$_{\text{pyr-o}}$), 1.949-1.925 (2H, m, CH$_2$), 1.276-1.203 (10H, m, C$_5$H$_{10}$), 0.845-0.801 (3H, t, oct-CH$_3$).

(Found: C, 43.18; H, 4.96; N, 2.69. Calc. for C$_{18}$H$_{24}$N$_3$O$_3$S$_9$: C, 42.78; H, 4.79; N, 2.77).

[2MOPYR]$^+$[NfO]$^-$

2.99 g (9.0·$10^{-3}$ mol) of [2MOPYR]$^+$[Br]$^-$ and 3.65 g (10.8·$10^{-3}$ mol) of potassium nonafluorobutyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 mL of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3 × 25 mL). After 24 h under vacuum, 4.05 g (yield: 89 %) were obtained as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.862-7.822 (H, d, CH$_{\text{pyr-o}}$), 8.315-8.279 (H, t, CH$_{\text{pyr-p}}$), 7.862-7.822 (2H, m, CH$_{\text{pyr-m}}$), 4.590-4.537 (2H, t, N-CH$_2$), 2.853 (3H, s, CH$_3$-C$_{\text{pyr-o}}$), 1.911-1.808 (2H, m, CH$_2$), 1.389-1.223 (10H, m, C$_5$H$_{10}$), 0.857-0.812 (3H, t, oct-CH$_3$).

(Found: C, 42.81; H, 4.87; N, 2.70. Calc. for C$_{18}$H$_{24}$N$_3$O$_3$S$_9$: C, 42.78; H, 4.79; N, 2.77).

[4MOPYR]$^+$[N(CN)$_2$]$^-$

2.10 g (7.3 ·$10^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 1.90 g (10.9 ·$10^{-3}$ mol) of silver dicyanamide, synthesized from silver nitrate and sodium dicyanamide, were mixed for 24 h in a flask containing 75 mL of water. After filtering and removal of the solvent by rotary evaporation, the resulting colorless liquid was washed with methylene chloride (3 × 25 mL). After 24 h under vacuum, 1.49 g (75 %) of [4MOPYR]$^+$[N(CN)$_2$]$^-$ were obtained as a colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.733-8.712 (2H, d, CH$_{\text{pyr-o}}$), 7.830-7.810 (2H, d, CH$_{\text{pyr-m}}$), 4.560-4.510 (2H, t, N-CH$_2$), 2.643 (3H, s, CH$_3$-C$_{\text{pyr-p}}$), 1.960-1.915 (2H, m, CH$_2$), 1.274-1.171 (10H, m, C$_5$H$_{10}$), 0.797-0.757 (3H, t, oct-CH$_3$).
$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 159.99, 143.70, 129.39, 120.16, 61.89, 31.84, 31.77, 29.17, 29.11, 26.30, 22.78, 22.56, 14.30.

(Found: C, 68.63; H, 9.08; N, 19.23. Calc. for C$_{16}$H$_{24}$N$_4$: C, 70.55; H, 8.89; N, 19.37).

[4MOPYR]$^+$[BF$_3$Ph]$^-$

2.02 g of [4MOPYR]$^+$[Br$^-$] (7.3 $\cdot$ 10$^{-3}$ mol) were mixed for 10 h with 2.0 g of potassium trifluorophenylborate (10.9 $\cdot$ 10$^{-3}$ mol) in 100 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was set under vacuum for 24 h. 2.14 g of [4MOPYR]$^+$[BF$_3$Ph]$^-$ (6.1 $\cdot$ 10$^{-3}$ mol) was recovered as a white-yellowish solid (yield: 84%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.262, 8.246 (2H, d, N-CH$_2$), 7.507, 7.491 (2H, d, CH-N-CH$_{pyr}$), 7.414-7.399 (2H, d, Ph-H$_m$), 7.141-7.054 (3H, m, Ph-H), 4.154-4.117 (2H, t, CH-B-CH), 2.415 (3H, s,CH$_3$-C$_{pyr}$), 1.698-1.623 (2H, m, CH$_2$), 1.240-1.105 (10H, m, C$_5$H$_{10}$), 0.849-0.815 (3H, t, oct-CH$_3$).

(Found: C, 68.07; H, 8.49; N, 3.93. Calc. for C$_{20}$H$_{29}$N$_3$F$_3$B: C, 68.38; H, 8.32; N, 3.99).

[4MOPYR]$^+$[BPh$_4$]$^-$

1.78 g of [4MOPYR]$^+$[Br$^-$] (6.2 $\cdot$ 10$^{-3}$ mol) were mixed for 10 h with 3.28 g of sodium tetraphenylborate (9.6 $\cdot$ 10$^{-3}$ mol) in 50 mL of acetonitrile. After filtering and removal of the acetonitrile by rotary evaporation, the resulting white powder was washed with methylene chloride and put in a freezer for 24 h. After filtering, methylene chloride was removed by rotary evaporation and the product was washed with water. After removal of water by rotary-evaporation, the product was set under vacuum for 24 h. 3.11 g of [4MOPYR]$^+$[BPh$_4$]$^-$ (5.9 $\cdot$ 10$^{-3}$ mol) was recovered as a white-yellowish solid (yield: 89%).
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.487 (8H, s, Ph-H$_o$), 6.927-6.878 (8H, t, Ph-H$_m$), 6.745-6.698 (4H, t, Ph-H$_p$), 6.282, 6.261 (2H, d, CH-N-CH$_2$pyr), 5.721, 5.700 (2H, d, 2CH$_2$pyr), 2.963-2.912 (2H, t, N-CH$_2$), 2.144 (3H, s, CH$_3$), 1.310-1.051 (10H, m, C$_5$H$_{10}$), 0.961-0.848 (5H, m, CH$_2$-CH$_3$).

(Found: C, 87.04; H, 8.68; N, 2.73. Calc. for C$_{38}$H$_{44}$N$_2$: C, 86.84; H, 8.44; N, 2.66).

[4MOPYR]$^+$[AsF$_6$]$	ext{-}$

1.80 g (6.2·10$^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 1.72 g (8.8·10$^{-3}$ mol) of lithium hexafluoroarsenate, were mixed in a flask containing 75 mL of water for 24 h. The product was then extracted by adding 50 mL of dichloromethane to the solution. After evaporation of the solvent by rotary evaporation, the resulting viscous liquid was washed with water (3 × 25 mL). After 24 h under vacuum, 2.29 g (yield: 93 %) of [4MOPYR]$^+$[AsF$_6$]$^-$ was obtained as a light-yellow viscous liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.486-8.469 (2H, d, CH$_{pyr-o}$), 7.776-7.760 (2H, d, CH$_{pyr-m}$), 4.470-4.432 (2H, t, N-CH$_2$), 2.626 (3H, s, CH$_3$-C$_{pyr-p}$), 1.943-1.907 (2H, m, CH$_2$), 1.288-1.209 (10H, m, C$_5$H$_{10}$), 0.841-0.807 (3H, t, oct-CH$_3$).

(Found: C, 42.56; H, 6.20; N, 3.39. Calc. for C$_{14}$H$_{24}$N$_2$F$_6$As: C, 42.54; H, 6.13; N, 3.54).

[4MOPYR]$^+$[BETI]$^-$

1.65 g (5.8·10$^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 2.47 g (6.4·10$^{-3}$ mol) of lithium BETI, were mixed in a flask containing 50 mL of water for 24 h. The product was then extracted by adding 50 mL of dichloromethane to the solution. Dichloromethane phase was collected and solvent was removed by rotary evaporation. The resulting viscous liquid was then washed with water (3 × 25 mL). After 24 h under vacuum, 3.01 g (yield: 86 %) of [4MOPYR]$^+$[BETI]$^-$ was obtained as a light-yellow viscous liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.594-8.578 (2H, d, CH$_{pyr-o}$), 7.778-7.762 (2H, d, CH$_{pyr-m}$), 4.461-4.423 (2H, t, N-CH$_2$), 2.620 (3H, s, CH$_3$-C$_{pyr-p}$), 1.920-1.899 (2H, m, CH$_2$), 1.278-1.200 (10H, m, C$_5$H$_{10}$), 0.835-0.800 (3H, t, oct-CH$_3$).
(Found: C, 36.94; H, 4.16; N, 4.89. Calc. for \( \text{C}_{18}\text{H}_{24}\text{N}_{2}\text{O}_{4}\text{S}_{2}\text{F}_{10} \): C, 36.87; H, 4.13; N, 4.78).

**Densities**

Densities were measured with a 1 mL volumetric flask in air at 25 °C and a relative humidity of 48 %. Results are precise ± 0.01 g.cm\(^{-3}\).

**Viscosities**

Viscosities of selected ionic liquids were measured using ARES Rheometric Scientific apparatus. Figure 2 shows temperature dependence of viscosities for some selected octylpyridinium ionic liquids. The samples were dried and stored in a helium gloved box prior the measurements. The measurements were carried out under dry nitrogen. Before each measurement, sample was left at least 30 minutes inside the rheometer at temperature and under nitrogen flow. Our procedure was tested with 1-octyl-3-methylpyridinium tetrafluoroborate, used as received from Solvent Innovation. Our measurements agreed within 1 % with reference data reported elsewhere.\(^{31}\)

**Melting points, glass-transition and decomposition temperatures**

Melting points and glass-transition temperatures were measured by differential scanning calorimetry (Perkin Elmer DSC 7). Ionic liquids were dried in a drying pistol at 1 mbar and 60 °C or in an antechamber for at least 48 hours in the presence of P\(_2\)O\(_5\). The ionic liquids were stored and sampled in a dry-helium glove box prior to DSC measurements. The DSC was under a dry-nitrogen hood with continuous flushing. The samples were cooled with liquid nitrogen to -120 °C and kept at this temperature for 30 min, heated well above the melting point and cooled again. The scanning rate was 10
Melting-point and glass-transition temperatures were taken from the second heating curve. Ten of the fifteen ionic liquids synthesized here are liquid at room temperature. The precision of the measurement is $\pm 1 \, ^\circ C$.

Thermo-gravimetric analysis (TGA) provides information concerning thermal stability. Perkin Elmer TGA 7 was used. The dried ionic-liquid samples were stored and sampled in a dry-helium glove box. The TGA sample holder was under dry-nitrogen flow. Similar size samples, approximately 8 mg, were studied at the same heating rate, $10 \, ^\circ C / \text{min}$. The precision of these temperatures is $\pm 5 \, ^\circ C$.

**Solubility in water:**

Solubilities of ionic liquids in water were obtained by recording the UV spectra (Beckman DU640) of an aqueous phase in equilibrium with the ionic liquid. Intensities of the absorption of ionic liquids containing $[\text{OPYR}]^+$ or $[\text{4MOPYR}]^+$ cations were recorded at 254 nm; this wavelength corresponds to the wavelength of maximum absorption for $[\text{4MOPYR}]^+$ and $[\text{OPYR}]^+$. For ionic liquids containing $[\text{2MOPYR}]^+$ cations, the intensity of absorption was recorded at 265 nm, corresponding to the wavelength of maximum absorption of 1-octyl-2-methylpyridinium cations.

Dilute aqueous solutions containing a known amount of ionic liquid, between (0.001 and 0.02) % were used for calibration. An aqueous solution saturated with ionic liquid was prepared and diluted by a factor of 100. Table 1 shows the solubilities of ionic liquids in water. The mass-fraction solubilities have a precision of $\pm 5 \%$.

**Water content of ionic liquids**
The water content of an ionic liquid was measured by Karl-Fischer method using a Metler-Toledo coulometer. Water contents were measured in two different conditions.

The water content of air-saturated ionic liquid was measured first. Ionic liquids were exposed one week to air. A sample of ionic liquid was taken and the water content measured at least three times. Air humidity was also recorded.

The water content of a water-saturated ionic liquid in equilibrium with liquid water was measured by mixing water and ionic liquids for 24 hours. After that, the two-phase system was centrifuged and left in contact for another 24 h to reach equilibrium. Then, samples of the ionic liquid were taken and its water content was measured.

All measurements were repeated at least three times. The water contents of ionic liquids are reported in weight percent and are precise to ± 7 %.

**Results**

**Densities**

Table 1 shows densities for selected ionic liquids containing [4MOPYR]⁺ cations. The samples were air saturated at relative humidity 48-49 % at 25°C. The corresponding water contents for each ionic liquid are shown in table 3. For the same cation, ionic liquids containing dicyanamide anion exhibit the lowest density while [4MOPYR]⁺[BETI]⁻ exhibits the highest density (1.39 g·mL⁻¹), followed by [4MOPYR]⁺[AsF₆⁻] (1.33 g·mL⁻¹) and [4MOPYR]⁺[Te₂N⁻] (1.29 g·mL⁻¹).

The density of [4MOPYR]⁺[AsF₆⁻] appears to be higher than that of [4MOPYR]⁺[BF₄⁻]. This is in agreement with the fact that densities for perfluoroarsenate compounds are higher than those for perfluorophosphates or perfluoroborate compounds.
For the same anion, ionic liquids containing \([4\text{MOPYR}]^+\) cation exhibit densities lower than or similar to those of their 1-butyl-4-methylpyridinium homologues.\(^{29}\) As expected, density decreases with the length of alkyl chain length.

For \([\text{Tf}_2\text{N}]^-\) and \([\text{N(CN)}_2]^-\) anions, ionic liquids containing \([\text{OMIM}]^+\) cation appear to be more dense than their \([4\text{MOPYR}]^+\) homologues, in agreement with our previous report showing that ionic liquids containing 1-methyl-3-butylimidazolium cations are more dense than those containing 1-butyl-4-methylpyridinium cations.\(^{29}\)

**Melting points and glass-transition temperatures:**

Table 2 shows melting points \(t_m\) and glass-transition temperatures \(t_g\) from differential-scanning calorimetry. Most ionic liquids reported here are liquid at room temperature.

Due to the size and symmetry of the \(\text{BPh}_4\) anion, \([4\text{MOPYR}][\text{BPh}_4]\) has the highest melting point measured here, 130 °C. When phenyls are substituted with fluorides, as in the trifluorophenylborate anion, the resulting ionic liquid, \([4\text{MOPYR}][\text{BF}_3\text{Ph}]\), exhibits no melting point, and a \(t_g\) at -76 °C.

In agreement with results obtained for ionic liquids containing 1-octyl-3-methylpyridinium cations\(^{27}\), ionic liquids containing \([\text{BF}_4^-]\) or \([\text{Tf}_2\text{N}^-]\) anions exhibit no melting points. \([\text{OPYR}]^+\)[\text{Tf}_2\text{N}^-] exhibits a melting point at -8 °C, and a glass-transition temperature above -80 °C. All ionic liquids containing \(\text{NfO}^-\) anions exhibit high melting points from 68 to 78 °C and no glass-transition point. As for ionic liquids containing \(\text{BF}_4^-\) or \(\text{Tf}_2\text{N}^-\) anions, the presence of a methyl group on the octylpyridinium cation has no effect on melting points.

For ionic liquids containing \(\text{TfO}^-\) anions, on the other hand, melting points are influenced by the presence of a methyl group on the cation. For \([4\text{MOPyr}^+][\text{TfO}^-]\), for example, no melting point is observed, whereas \([\text{OPyr}^+][\text{TfO}^-]\) and \([2\text{MOPyr}^+][\text{TfO}^-]\) have melting points at 49 °C and 40 °C, respectively.
For ionic liquids containing 1-methyl-3-alkylimidazolium, previous reports showed that an increase in alkyl-chain length leads to a decrease in the melting point.\textsuperscript{18,19} This observation holds for ionic liquids containing pyridinium cations. With the same anion, table 2 shows that ionic liquids containing octylpyridinium ([OPYR\textsuperscript{+}] or [4MOPYR\textsuperscript{+}]) cations exhibit lower melting points than those for ionic liquids containing 1-butyl-4-methylpyridinium cations.\textsuperscript{29}

All ionic liquids containing 1-methyl-3-octylimidazolium cations and [Tf\textsubscript{2}N\textsuperscript{-}], [N(CN)\textsubscript{2}\textsuperscript{-}], [TFO\textsuperscript{-}] or [NfO\textsuperscript{-}] anions are liquid at room temperature.\textsuperscript{22,24,25,29} The results obtained here for ionic liquids containing octylpyridinium cations are different. Unlike [OMIM\textsuperscript{+}][NfO\textsuperscript{-}] or [OMIM\textsuperscript{+}][TfO\textsuperscript{-}], [4MOPYR\textsuperscript{+}][NfO\textsuperscript{-}] and [OPYR\textsuperscript{+}][TfO\textsuperscript{-}] are solid at room temperature.

All ionic liquids containing 1-methyl-3-octylimidazolium cations and Tf\textsubscript{2}N\textsuperscript{-}, N(CN)\textsubscript{2}\textsuperscript{-}, TFO\textsuperscript{-} or NfO\textsuperscript{-} anions are likely to be liquid at room temperature, regardless of the nature of the anion.\textsuperscript{29} Results for ionic liquids containing octylpyridinium cations are different. Here, the anion has an influence on the melting point. For ionic liquids containing [4MOPYR\textsuperscript{+}] cations, all ionic liquids studied here are liquid at room temperature, except for [4MOPYR\textsuperscript{+}][NfO\textsuperscript{-}] that melts at 68 °C. For ionic liquids containing [OPYR\textsuperscript{+}] cations, [OPYR\textsuperscript{+}][TfO\textsuperscript{-}] and [OPYR\textsuperscript{+}][NfO\textsuperscript{-}] are solid at room temperature, with melting points 49 and 73 °C, respectively.

Glass-transition temperatures for all ionic liquids reported here are higher than those for ionic liquids containing 1-methyl-3-octylimidazolium cations. For all ionic liquids containing [4MOPYR\textsuperscript{+}], glass-transition temperatures are -65 °C for [4MOPYR\textsuperscript{+}][TfO\textsuperscript{-}] and -64 °C for [4MOPYR\textsuperscript{+}][AsF\textsubscript{6}\textsuperscript{-}] and -77 °C for [4MOPYR\textsuperscript{+}][Tf\textsubscript{2}N\textsuperscript{-}]. For ionic liquids containing [OMIM\textsuperscript{+}] cations, glass-transition temperatures are between -80 °C for [OMIM\textsuperscript{+}][TfO\textsuperscript{-}]\textsuperscript{28} and -89 °C for [OMIM\textsuperscript{+}][N(CN)\textsubscript{2}\textsuperscript{-}].\textsuperscript{29}

\textit{Thermal Stability:}
Table 2 shows onset decomposition temperatures for all ionic liquids studied here. Ionic liquids containing phenylborate anions exhibit the lowest thermal stability. Our previous work has shown that the thermal stabilities of ionic liquids containing borate anions increase with the number of fluorides, and decrease with the number of phenyls appended to boron.

The onset decomposition temperatures of $[4\text{MOPYR}]^+\text{[BPh}_4^-]$ and $[4\text{MOPYR}]^+\text{[BF}_3\text{Ph}]^-$ are, respectively, 190 and 205 °C.

Previous work$^{29}$ showed that $[\text{OMIM}]^+\text{[N(CN)}_2\text{]}^-$ has a lower thermal stability than those of $[\text{OMIM}]^+\text{[TfO]}^-$, $[\text{OMIM}]^+\text{[NfO]}^-$, $[\text{OMIM}]^+\text{[BF}_4^-]$ or $[\text{OMIM}]^+\text{[Tf}_2\text{N}]^-$ anions. In agreement with our previous results, onset decomposition temperature $t_d$ for $[4\text{MOPYR}]^+\text{[N(CN)}_2\text{]}^-$ is lower (228 °C) than for $[4\text{MOPYR}]^+\text{[TfO]}^-$ (296 °C), $[4\text{MOPYR}]^+\text{[NfO]}^-$ (298 °C), $[4\text{MOPYR}]^+\text{[BF}_4^-]$ (290 °C) or $[4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-$ (315 °C).

For the same anion, the methyl group on the octylpyridinium cation has only minor influence on the thermal stability of ionic liquids. For ionic liquids containing $\text{[NfO]}^-$ anions, $t_d$ varies from 298 to 294 °C and 292 °C for $[4\text{MOPYR}]^+\text{[NfO]}^-$, $[\text{OPYR}]^+\text{[NfO]}^-$, and $[2\text{MOPYR}]^+\text{[NfO]}^-$, respectively. For ionic liquids containing $\text{[TfO]}^-$ anions, $t_d$ varies from 280 to 296 °C for $[\text{OPYR}]^+\text{[TfO]}^-$ and $[4\text{MOPYR}]^+\text{[TfO]}^-$, respectively.

The onset decomposition temperature for $[3\text{MOPYR}]^+\text{[BF}_4^-]$ measured here is 310 °C, higher than 274 °C previously reported by Crosthwaite et al.$^{27}$ With a decomposition temperature of 290 °C, $[4\text{MOPYR}]^+\text{[BF}_4^-]$ appears to have a slightly lower thermal stability than $[3\text{MOPYR}]^+\text{[BF}_4^-]$.

As expected, considering the large and symmetric shape of the anion, $[4\text{MOPYR}]^+\text{[AsF}_6^-]$ exhibits higher thermal stability, with decomposition temperature 305 °C.

Ionic liquids containing bis(perfluoroalkylsulfonyl)imide anions exhibit the highest thermal stabilities measured here: $t_d$ for $[4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-$ and $[4\text{MOPYR}]^+\text{[BETI]}^-$ are 315 and 325 °C, respectively. $[4\text{MOPYR}]^+\text{[BETI]}^-$ is more thermally stable than $[4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-$ due to the increased number of
fluorinated carbons. It shows the highest thermal stability of all ionic liquids containing [4MOPYR]+ studied here.

The thermal stabilities $t_d$ of ionic liquids containing [4MOPYR]+ cations are in the order: BETI− > Tf$_2$N− > AsF$_6$− > NfO− > TfO− ~ BF$_4$− > N(CN)$_2$− > BF$_3$Ph− > BPh$_4$−.

**Solubility in water:**

All ionic liquids studied here are nearly immiscible with water. This result is surprising, because previous studies of ionic liquids containing 1-methyl-3-octylimidazolium cations did not always yield immiscible ionic liquids$^{19,29}$. For example, [OMIM][TfO]− and [OMIM][N(CN)$_2$]− are miscible with water. Here, [4MOPYR][TfO]− and [4MOPYR][N(CN)$_2$]− are nearly immiscible with water. The solubilities in water for [4MOPYR][TfO]− and [4MOPYR][N(CN)$_2$]− are 1.59 %, and above 5 %, respectively, the highest measured in this work. The solubility in water for [4MOPYR][TfO]− is very close to that for [4MOPYR][BF$_4$]−. Considering the water miscibility of [OMIM][TfO]− as opposed to [OMIM][BF$_4$], [4MOPYR][BF$_4$]− and [4MOPYR][TfO]−, it appears that the higher solvation energy of the [TfO]− anion is compensated by the decreased solvation energy of [4MOPYR]+ cation, as compared to that of the [OMIM]+ cation.

Due to the high hydrophobicity of the tetraphenylborate anion, [4MOPYR][BPh$_4$]− has the lowest solubility in water.

Surprisingly, the solubility of [4MOPYR][BF$_4$]− in water is very close to those for [OMIM][BF$_4$]−. The solubility in water of [4MOPYR][BF$_3$Ph]− (0.49 %) is also similar to that for [OMIM][BF$_3$Ph]− (0.51 %).

The solubility in water of ionic liquids containing borate anions appears to be mainly influenced by the anion.
As expected, low solubilities in water are obtained for ionic liquids containing \([\text{Tf}_2\text{N}]^-, [\text{NfO}]^-, [\text{BETI}]^-, \text{or [AsF}_6^-\text{]}\) anions. The water solubilities are 0.013 %, 0.022 %, 0.036 %, and 0.027 % for \([4\text{MOPYR}]^+[\text{BETI}]^-, [4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-, [4\text{MOPYR}]^+[\text{NfO}]^-, \text{and [4MOPYR]}^+\text{[AsF}_6^-\text{]}, \) respectively. Due to the increased hydrophobicity of the BETI anion, \([4\text{MOPYR}]^+[\text{BETI}]^-\) is the room-temperature ionic liquid with the lowest solubility in water found in this work.

The solubilities shown here are an order of magnitude lower than those previously reported for ionic liquids based on 1-octyl-3-methylimidazolium cation.$^29$

The water solubilities obtained for \([\text{OPYR}]^+\text{[Tf}_2\text{N}]^-\) and \([\text{OPYR}]^+[\text{NfO}]^-\) are 0.035 % and 0.046 %, respectively. Ionic liquids containing \([\text{OPYR}]^+\) cations appears to be slightly more soluble in water than their \([4\text{MOPYR}]^+\) homologues.

On the other hand, ionic liquids containing \([2\text{MOPYR}]^+\) cations show higher solubilities in water than ionic liquids containing \([\text{OPYR}]^+\) or \([4\text{MOPYR}]^+\) cations. For example, 0.10 % is obtained for the solubility in water of \([2\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-\), compared to 0.035 and 0.020 % obtained for \([\text{OPYR}]^+\text{[Tf}_2\text{N}]^-\) and \([4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-\). Similarly, the solubility in water for \([2\text{MOPYR}]^+[\text{NfO}]^-\) is 0.12 % compared to 0.036 and 0.045 % for \([\text{OPYR}]^+[\text{NfO}]^-\) and \([4\text{MOPYR}]^+[\text{NfO}]^-\), respectively.

The significant influence of a minor change in structure of ionic liquid to physical properties is clearly shown.

**Water content**

Table 3 gives water contents for “air-saturated” and “water-saturated” ionic liquids for \([2\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-\), \([4\text{MOPYR}]^+\text{[Tf}_2\text{N}]^-\), \([4\text{MOPYR}]^+[\text{BETI}]^-\), \([4\text{MOPYR}]^+\text{[TfO]}^-\), \([4\text{MOPYR}]^+[\text{N(CN)}_2]^-\) and \([4\text{MOPYR}]^+\text{[AsF}_6^-\text{]}\).

In agreement with the high solubilities in water obtained for \([3\text{MOPYR}]^+\text{[BF}_4^-\text{]}\), \([4\text{MOPYR}]^+\text{[BF}_4^-\text{]}\), \([4\text{MOPYR}]^+[\text{TfO}]^-\) and \([4\text{MOPYR}]^+[\text{N(CN)}_2]^-\), water contents for these four ionic liquids are the
highest measured in this study. Water contents for water-saturated samples of [3MOPYR][BF₄] and [4MOPYR][BF₄] are lower than those for [4MOPYR][TfO]⁻ (17.2 %). When saturated with water, [4MOPYR][N(CN)$_2$] exhibit a water content of 54.9 %.

All other ionic liquids studied here have lower water contents: 0.11, 0.20 and 0.23 % for air-saturated [4MOPYR][Tf$_2$N], [4MOPYR][BETI] and [4MOPYR][AsF$_6$], respectively.

The water content of RH 49 %, 25°C air-saturated [4MOPYR][BETI] (0.20 %) is twice that for [4MOPYR][Tf$_2$N] (0.10 %), even though [4MOPYR][BETI] is less soluble in water than [4MOPYR][Tf$_2$N].

These water contents are unexpectedly high compared to that for [4MOPYR][TfO]⁻ (0.23 %), which is a much less hydrophobic ionic liquid than [4MOPYR][Tf$_2$N]⁻ or [4MOPYR][BETI].

When air-saturated [4MOPYR][BETI] is in contact with liquid water, the water content increases to 0.52 %. Water content of water-saturated [4MOPYR][Tf$_2$N] is 0.73 %.

When the methyl group on the octylpyridinium cation changes from ortho to para position, the water content decreases for ionic liquids containing Tf$_2$N anions. For air-saturated [2MOPYR][Tf$_2$N] and [4MOPYR][Tf$_2$N], the water content decreases from 0.31 to 0.10 %, respectively. The influence of the position of the methyl group on water content of water-saturated [2MOPYR][Tf$_2$N] and [4MOPYR][Tf$_2$N] is much smaller: the water content decreases from 0.78 to 0.73 %, respectively.

The higher water content of [2MOPYR][Tf$_2$N], as compared to that for [4MOPYR][Tf$_2$N], is consistent with results obtained for the water solubilities of [2MOPYR][Tf$_2$N] and [4MOPYR][Tf$_2$N], suggesting that the interaction between water and 1-octyl-2-methylypyridinium cation is stronger than that between water and 1-octyl-4-methylpyridinium cation.
The few data available for the water content of ionic liquids containing imidazolium cations\textsuperscript{17,19} are similar to those obtained in this study. The water content of water-saturated [BMIM][Tf$_2$N] is close to that of [OPYR][Tf$_2$N], [2MOPYR][Tf$_2$N] or [4MOPYR][Tf$_2$N].

Water contents for [4MOPYR][AsF$_6$] and [3MOPYR][BF$_4$] or [4MOPYR][BF$_4$] were higher than [OPYR][Tf$_2$N], [2MOPYR][Tf$_2$N] or [4MOPYR][Tf$_2$N] ionic liquids. That is in agreement with previous measurements indicating that ionic liquids containing fluorinated spherical anions such as [PF$_6$] have water content higher than those of other ionic liquids containing [Tf$_2$N] anions.\textsuperscript{19}

Considering the similar results obtained for ionic liquids containing imidazolium or pyridinium cations, the water content of ionic liquids appears to be mostly influenced by the anion.

*Viscosity*

Viscosities for [3MOPYR][BF$_4$], [4MOPYR][BF$_4$], [4MOPYR][TfO], [OPYR][Tf$_2$N], [2MOPYR][Tf$_2$N] and [4MOPYR][Tf$_2$N] are shown in table 4. A plot of viscosities in shown in Figure 2. Viscosities measured for [OMIM][BF$_4$] are also shown in table 4.

Two groups appear in the plot. The group of ionic liquids with the lower viscosities contains, as expected, ionic liquids containing Tf$_2$N anions, [OPYr][Tf$_2$N], [2MOPyr][Tf$_2$N] and [4MOPyr][Tf$_2$N].

The lowest viscosities are measured for [OPYr][Tf$_2$N] which has a viscosity of 77.1 mPa s at 25 °C. The absence of methyl group on the pyridinium explains the lower viscosity as compared to [2MOPyr][Tf$_2$N] or [4MOPyr][Tf$_2$N]. Values for [4MOPyr][Tf$_2$N] are very close to those for [4MOPyr][Tf$_2$N] and those for [3MOPyr][Tf$_2$N] reported by Crosthwaite et al.\textsuperscript{29}

The position of the methyl group on the pyridinium cation has little influence on the viscosity of ionic liquids containing Tf$_2$N anion.
The second group of ionic liquids with higher viscosities contains [3MOPyr]⁺[TfO]⁻, [4MOPyr]⁺[BF₄]⁻ and [4MOPyr]⁺[TfO]⁻.

The difference between the viscosities for [3MOPyr]⁺[BF₄]⁻ and [4MOPyr]⁺[BF₄]⁻ are here higher than the one observed for [3MOPyr]⁺[Tf₂N]⁻ and [4MOPyr]⁺[Tf₂N]⁻. At 25 °C, for instance, viscosities for [3MOPyr]⁺[BF₄]⁻ and [4MOPyr]⁺[BF₄]⁻, respectively, are 331.7 and 464.4 mPa s. For [3MOPyr]⁺[Tf₂N]⁻ and [4MOPyr]⁺[Tf₂N]⁻ the viscosities are 112 mPa s and 104.6 mPa s.

The position of the methyl group here has an increased influence on the viscosities of ionic liquids containing BF₄ anions.

The viscosities measured here appear in general to be similar to the ones obtained for ionic liquids containing 1-octyl-3methylimidazolium cations. At 25 °C, viscosities for [OMIM]⁺[BF₄]⁻ and [3MOPYR]⁺[BF₄]⁻ are 345 and 331 mPa s, respectively.

It appears here that viscosities of ionic liquids are mainly influenced by the nature of the anions. Nevertheless, changes of cation structure such as the presence and position of a methyl group on the pyridinium cations also might have some influence on the viscosities.

**Conclusion**

Ionic liquids containing octylpyridinium-type cations have physico-chemical properties significantly different from those that contain 1-methyl-3-octylimidazolium cation. Melting points are more influenced here by the nature of the anion than those for their imidazolium homologues. Glass-transition temperatures are found to be 10 to 20 °C higher. Thermal stabilities are similar to those for ionic liquids containing [OMIM]⁺ cations. Viscosities for ionic liquids containing octylpyridinium-type cations are also very close to those containing [OMIM]⁺ cations. But most important, all ionic liquids based on octylpyridinium-type cations are nearly water-immiscible. Solubilities in water are an order of magnitude lower than those for their imidazolium homologues. Ionic liquids containing octylpyridinium
cations, therefore, may provide an alternative to ionic liquids containing imidazolium for application in extraction of heavy metal cations from wastewaters.

Acknowledgement

The authors are grateful to the office for Basic Sciences, US Dept. of Energy and TEKES for financial support.


Figure 1 - Structures of cations and anions used in this work.
Figure 2. Viscosities \( \eta \) for selected ionic liquids containing 1-octylpyridinium cations.

Table 1 – Densities of selected ionic liquids in g·cm\(^{-3}\). RH is 49%.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Density/g·cm(^{-3})</th>
</tr>
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<tbody>
<tr>
<td>[4MOPYR][BF(_4)]</td>
<td>1.08</td>
</tr>
<tr>
<td>[4MOPYR][AsF(_6)]</td>
<td>1.33</td>
</tr>
<tr>
<td>[4MOPYR][Tf(_2)N]</td>
<td>1.29</td>
</tr>
<tr>
<td>[4MOPYR][BETI]</td>
<td>1.39</td>
</tr>
<tr>
<td>[4MOPYR][TfO]</td>
<td>1.17</td>
</tr>
<tr>
<td>[4MOPYR][N(CN)(_2)]</td>
<td>0.98</td>
</tr>
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</table>
Table 2- Melting points ($t_m$), glass transition temperatures ($t_g$) and onset decomposition temperatures ($t_d$) and mass fraction solubilities in water ($w$) for several ionic liquids.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>$t_m/°C$</th>
<th>$t_g/°C$</th>
<th>$t_d/°C$</th>
<th>100 $w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4MOPYR][BF$_4$]</td>
<td>$^{a}$-64</td>
<td>290</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>[3MOPYR][BF$_4$]</td>
<td>$^{a}$-70</td>
<td>310</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>[OPYR][Tf$_2$N]$^-$</td>
<td>-9</td>
<td>-78</td>
<td>320</td>
<td>0.035</td>
</tr>
<tr>
<td>[4MOPYR][Tf$_2$N]$^-$</td>
<td>16</td>
<td>-77</td>
<td>300</td>
<td>0.022</td>
</tr>
<tr>
<td>[2MOPYR][Tf$_2$N]$^-$</td>
<td>12</td>
<td>-74</td>
<td>290</td>
<td>0.10</td>
</tr>
<tr>
<td>[OPYR][TfO]$^-$</td>
<td>49</td>
<td>$^{b}$280</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][TfO]$^-$</td>
<td>$^{a}$-65</td>
<td>296</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>[2MOPYR][TfO]$^-$</td>
<td>40</td>
<td>$^{b}$275</td>
<td>$^{c}$</td>
<td></td>
</tr>
<tr>
<td>[OPYR][NfO]$^-$</td>
<td>73</td>
<td>$^{b}$294</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][NfO]$^-$</td>
<td>68</td>
<td>$^{b}$298</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>[2MOPYR][NfO]$^-$</td>
<td>78</td>
<td>$^{b}$292</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][N(CN)$_2$]$^-$</td>
<td>$^{a}$-69</td>
<td>228</td>
<td>&gt;5.0</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][BF$_3$Ph]$^-$</td>
<td>$^{a}$-76</td>
<td>205</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][BPh$_4$]$^-$</td>
<td>130</td>
<td>$^{b}$190</td>
<td>&lt;0.0005</td>
<td></td>
</tr>
<tr>
<td>[4MOPYR][AsF$_6$]$^-$</td>
<td>-20</td>
<td>-64</td>
<td>305</td>
<td>0.027</td>
</tr>
<tr>
<td>[4MOPYR][BETI]$^-$</td>
<td>2</td>
<td>-75</td>
<td>325</td>
<td>0.013</td>
</tr>
</tbody>
</table>

$^{a}$: no melting point observed. $^{b}$: no glass-transition point observed. $^{c}$: not measured.

Table 3 – Water content $m$ in % of some selected air-saturated and water-saturated ionic liquids at 25 °C.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>RH/%</th>
<th>$m$(air-sat)/%</th>
<th>$m$(wat-sat)/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[4MOPYR][BF$_4$]$^-$</td>
<td>49</td>
<td>1.81</td>
<td>11.3</td>
</tr>
<tr>
<td>[3MOPYR][BF$_4$]$^-$</td>
<td>48</td>
<td>1.25</td>
<td>13.6</td>
</tr>
<tr>
<td>[OPYR][Tf$_2$N]$^-$</td>
<td>49</td>
<td>0.13</td>
<td>0.86</td>
</tr>
<tr>
<td>[2MOPYR][Tf$_2$N]$^-$</td>
<td>49</td>
<td>0.31</td>
<td>0.78</td>
</tr>
<tr>
<td>Ionic Liquid</td>
<td>0 °C</td>
<td>25 °C</td>
<td>37.5 °C</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>[4MOPYR][Tf₂N]⁻</td>
<td>49</td>
<td>0.10</td>
<td>0.73</td>
</tr>
<tr>
<td>[4MOPYR][BETI]⁻</td>
<td>49</td>
<td>0.20</td>
<td>0.52</td>
</tr>
<tr>
<td>[4MOPYR][TfO]⁻</td>
<td>49</td>
<td>0.23</td>
<td>17.2</td>
</tr>
<tr>
<td>[4MOPYR][N(CN)₂]⁻</td>
<td>49</td>
<td>1.84</td>
<td>54.9</td>
</tr>
<tr>
<td>[4MOPYR][AsF₆]⁻</td>
<td>49</td>
<td>0.25</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 4 – Viscosity $\eta$ in cP for selected ionic liquids from $t = 0$ °C to 75 °C.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>0 °C</th>
<th>25 °C</th>
<th>37.5 °C</th>
<th>50 °C</th>
<th>62.5 °C</th>
<th>75 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3MOPYR][BF₄]⁻</td>
<td>7407.7</td>
<td>331.7</td>
<td>149.0</td>
<td>77.3</td>
<td>44.3</td>
<td>29.3</td>
</tr>
<tr>
<td>[4MOPYR][BF₄]⁻</td>
<td>6124.7</td>
<td>464.4</td>
<td>194.0</td>
<td>96.1</td>
<td>52.8</td>
<td>33.1</td>
</tr>
<tr>
<td>[OPYR][Tf₂N]⁻</td>
<td>475.9</td>
<td>77.1</td>
<td>42.2</td>
<td>26.8</td>
<td>18.5</td>
<td>13.3</td>
</tr>
<tr>
<td>[2MOPYR][Tf₂N]⁻</td>
<td>918.9</td>
<td>122.3</td>
<td>64.0</td>
<td>37.2</td>
<td>22.0</td>
<td>15.1</td>
</tr>
<tr>
<td>[4MOPYR][Tf₂N]⁻</td>
<td>a</td>
<td>104.6</td>
<td>a</td>
<td>37.6</td>
<td>a</td>
<td>15.9</td>
</tr>
<tr>
<td>[4MOPYR][TfO]⁻</td>
<td>a</td>
<td>365.4</td>
<td>a</td>
<td>90.8</td>
<td>a</td>
<td>34.3</td>
</tr>
<tr>
<td>[OMIM][BF₄]⁻</td>
<td>a</td>
<td>345</td>
<td>a</td>
<td>87.3</td>
<td>a</td>
<td>37.9</td>
</tr>
</tbody>
</table>

a: not measured.