Physicochemical Properties of Hydrophobic Ionic Liquids Containing 1-Octylpyridinium, 1-Octyl-2-methylpyridinium, or 1-Octyl-4-methylpyridinium Cations

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This paper reports the synthesis of some ionic liquids containing cations 1-octylpyridinium $[OPYR]^+$, 1-octyl-2-methylpyridinium $[2MOPYR]^+$, or 1-octyl-4-methylpyridinium $[4MOPYR]^+$ and anions dicyanamide $[N(CN)_2]^-$, bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$, bis(pentafluoroethylsulfonyl)imide $[BETI]^-$, trifluoromethyl sulfonate $[TfO]^-$, nonafluorobutyl sulfonate $[NfO]^-$, tetrafluoroborate $[BF_4]^-$, trifluorophenylborate $[BF_3Ph]^-$, tetraphenylborate $[BPh_4]^-$, or hexafluoroarsenate $[AsF_6]^-$. 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 with water. Viscosities are similar, and water contents are slightly lower than those for ionic liquids containing imidazolium cations.

Introduction

Ionic liquids (ILs) are room temperature molten salts with melting points near ambient temperatures. During the past decade, ILs have become a popular research topic in chemistry. Many studies have reported applications, for example in organic chemistry,[1−5] electrochemistry,[6,7] catalysis,[8−11] and extraction.[12−16]

ILs are tunable because there are many combinations of cations and anions with distinct physicochemical properties. To date, only a few ILs, mostly those based on ammonium and imidazolium cations, have been investigated.[1−26] Recently, other types of ILs, containing pyridinium cations were studied.[27−29] However, the physicochemical properties of ILs containing pyridinium cations are yet to be fully investigated. To increase our understanding of ILs and to extend the database, we report here synthesis and selected properties of some ILs that contain pyridinium cations.

For metal-ion extraction from wastewaters, ILs need to be immiscible with water. Also such liquids need low or moderate viscosity. Several authors report possible application of ILs to metal-ion extraction.[12−16] However, ILs previously studied were primarily based on imidazolium cations. Solubilities of imidazolium ILs in water are too high for industrial extraction processes.[14,16,23] The solubility of an IL in water depends on the length of the alkyl chain and on the anion. Recently, we have shown that ILs containing pyridinium cations exhibit lower solubilities in water than those of imidazolium homologues.

Here, we report the synthesis and some physicochemical properties of hydrophobic ILs based on octylpyridinium cations. Three different cations were used (1-octylpyridinium $[OPYR]^+$, 1-octyl-2-methylpyridinium $[2MOPYR]^+$, and 1-octyl-4-methylpyridinium $[4MOPYR]^+$) to obtain insight into the influence of the symmetry and the nature of the cation. Several anions were used: tetrafluoroborate $[BF_4]^-$, hexafluoroarsenate $[AsF_6]^-$, trifluoromethyl sulfonate $[TfO]^-$, nonafluorobutyl sulfonate $[NfO]^-$, dicyanamide $[N(CN)_2]^-$, bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$, bis(pentafluoroethylsulfonyl)imide $[BETI]^-$, trifluorophenylborate $[BF_3Ph]^-$, and tetraphenylborate $[BPh_4]^-$ (see Figure 1 for the structures). Tetrafluoroborate, bis(trifluoromethylsulfonyl)imide, and nonafluorobutyl sulfonate anions are useful because they are known to be hydrophobic.[17,19,24] Figure 1 shows the structures of cations and anions studied in this work.

To elucidate the influence of the cation on the properties of ILs, trifluoromethyl sulfonate and dicyanamide anions were used with octylpyridinium cations; their properties are compared with those of 1-methyl-3-octylimidazolium trifluoromethyl sulfonate and 1-methyl-3-octylimidazolium dicyanamide, previously reported.[29] ILs containing dicyanamide anions exhibit low viscosities.[30] Trifluorophenylborate and tetraphenylborate anions were used to investigate the substitution of phenyl and fluoride on a borate anion and to establish their influence on the properties of ILs containing borate anions.

Experimental Section

Synthesis. 1-Octyl-3-methylpyridinium tetrafluoroborate was used as received from Solvent Innovation. All other ILs 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 bromooctane 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 ILs synthesized was checked with NMR and elemental analysis. Except for $[OPYR]^+[Br]^-$, $[2MOPYR]^+[Br]^-$, and $[4MOPYR]^+[Br]^-$, the absence of halide impurities was checked with silver nitrate: 100 mg of each IL was mixed with

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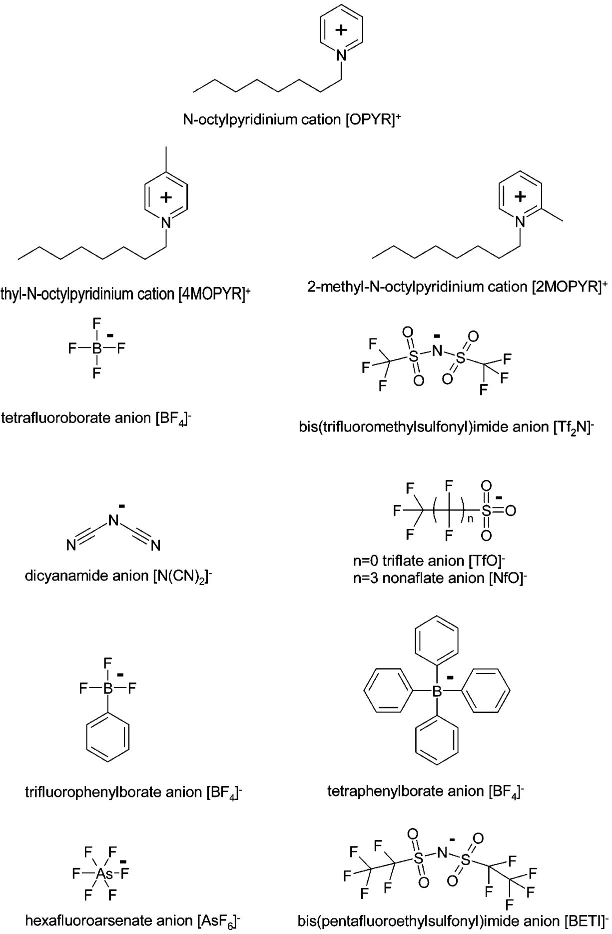

Figure 1. Structures of cations and anions used in this work.

1 cm^3 of dichloromethane and 1 cm^3 of an aqueous solution of silver nitrate. If a white-yellow precipitate (corresponding to the formation of AgBr) appeared, ILs were washed with water or extracted with dichloromethane; the silver nitrate test was then repeated until no AgBr precipitate was observed.

[OPYR]$^+$[Br]$^-$. Under nitrogen atmosphere, 25 g ($128 \cdot 10^{-3}$ mol) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 7.91 g ($100.0 \cdot 10^{-3}$ mol) of pyridine, used as received from Sigma (99.9 % purity), and 50 cm^3 of 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 cm^3) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h: 20.6 g ($76.8 \cdot 10^{-3}$ mol) of 1-octylpyridinium bromide, [OPYR]$^+$ [Br]$^-$, was obtained as a white solid (yield: 77 %).

^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.460−9.447 (2H, d, $\mathrm{CH_{pyr-o}}$), 8.513−8.475 (H, t, $\mathrm{CH_{pyr-p}}$), 8.132−8.097 (2H, t, $\mathrm{CH_{pyr-m}}$), 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]$^+$[Br]$^-$. Under nitrogen atmosphere, 14.43 g ($74.0 \cdot 10^{-3}$ mol) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 5.0 g ($53.7 \cdot 10^{-3}$ mol) of 4-methylpyridine, used as received from Sigma (98 % purity), and 25 cm^3 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 cm^3) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h; 14.77 g ($52.1 \cdot 10^{-3}$ mol) of 1-octyl-4-methylpyridinium bromide, [4MOPYR]$^+$[Br]$^-$, was obtained as a white solid (yield: 97 %).

^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.328−9.311 (2H, d, $\mathrm{CH_{pyr-o}}$), 7.865−7.849 (2H, d, $\mathrm{CH_{pyr-m}}$), 4.897−4.860 (2H, t, N-CH$_2$), 2.632 (3H, s, CH$_3$-$\mathrm{C_{pyr-p}}$), 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]$^+$[Br]$^-$. Under nitrogen atmosphere, 13.1 g ($67.2 \cdot 10^{-3}$ mol) of bromooctane, used as received from Sigma (99 % purity), was added dropwise to a solution of 4.5 g ($47.4 \cdot 10^{-3}$ mol) of 4-methylpyridine, used as received from Sigma (98 % purity), and 25 cm^3 of 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 cm^3) and filtered. Ethyl acetate was removed by rotary evaporation, and the resulting solid was set under vacuum for 12 h; 13 g ($45.9 \cdot 10^{-3}$ mol) of 1-octyl-2-methylpyridinium bromide, [4MOPYR]$^+$[Br]$^-$, was obtained as a white solid (yield: 97 %).

^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.652−9.632 (H, d, $\mathrm{CH_{pyr-o}}$), 8.365−8.313 (H, t, $\mathrm{CH_{pyr-m}}$), 7.984−7.939 (H, t, $\mathrm{CH_{pyr-p}}$), 7.886−7.860 (H, d, $\mathrm{CH_{pyr-m}}$-C), 4.905−4.853 (2H, t, N-CH$_2$), 2.940 (3H, s, CH$_3$-$\mathrm{C_{pyr-m}}$), 1.964−1.86 (2H, m, CH$_2$), 1.448−1.227 (10H, m,C$_5$H$_{10}$), 0.863−0.817 (3H, t, oct-CH$_3$).

[OPYR]$^+$[Tf$_2$N]$^-$. 3.47 g ($12.9 \cdot 10^{-3}$ mol) of [OPYR]$^+$[Br]$^-$ and 4.79 g ($16.9 \cdot 10^{-3}$ mol) of bis(trifluoromethylsulfonyl)imide acid salt, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 cm^3 of water for 24 h. The resulting IL was extracted in 50 cm^3 of methylene chloride. Excess salt and HBr were removed by mixing the resulting liquid with water and methylene chloride (20 cm^3 of methylene chloride and 3× 20 cm^3 of water). The 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: 86 %) of [OPYR]$^+$[Tf$_2$N]$^-$ was obtained as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 9.652−9.632 (H, d, $\mathrm{CH_{pyr-o}}$), 8.365−8.313 (H, t, $\mathrm{CH_{pyr-m}}$), 7.984−7.939 (H, t, $\mathrm{CH_{pyr-p}}$), 7.886−7.860 (H, d, $\mathrm{CH_{pyr-m}}$-C), 4.905−4.853 (2H, t, N-CH$_2$), 2.940 (3H, s, CH$_3$-$\mathrm{C_{pyr-m}}$), 1.964−1.86 (2H, m, CH$_2$), 1.448−1.227 (10H, m,C$_5$H$_{10}$), 0.863−0.817 (3H, t, oct-CH$_3$).

[2MOPYR]$^+$[Tf$_2$N]$^-$. 3.47 g ($12.3 \cdot 10^{-3}$ mol) of [2MOPYR]$^+$-[Br]$^-$ and 4.79 g ($14.9 \cdot 10^{-3}$ mol) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 cm^3 of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation, and washing with methylene chloride (20 cm^3) and water (3× 20 cm^3), the product was set under high vacuum for 24 h; 5.21 g (yield: 88 %) of [2MOPYR]$^+$[Tf$_2$N]$^-$ was obtained as a light-yellow liquid.

Anal. Calcd for C$_{16}$H$_{24}$N$_2$O$_4$S$_2$F$_6$: C, 39.50; H, 4.97; N, 5.76. Found C, 39.62; H, 5.19; N, 5.71.

[4MOPYR]$^+$[Tf$_2$N]$^-$. 2.52 g ($8.9 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$-[Br]$^-$ and 3.48 g ($10.8 \cdot 10^{-3}$ mol) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako Chemicals (99 % purity), were mixed in a flask containing 100 cm^3 of acetonitrile for 24 h. After filtering, removal of acetonitrile by rotary evaporation, and washing with methylene chloride (20 cm^3) and water (3× 20 cm^3), the product was set under high vacuum for 24 h; 3.75 g (yield: 87 %) was obtained as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.615−8.599 (2H, d, $\mathrm{CH_{pyr-o}}$), 7.812−7.797 (2H, d, $\mathrm{CH_{pyr-m}}$), 4.502−4.464 (2H, t, N-CH$_2$), 2.656 (3H, s, CH$_3$-$\mathrm{C_{pyr-p}}$), 2.000−1.945 (2H, m, CH$_2$), 1.310−1.234 (10H, m, C$_5$H$_{10}$), 0.863−0.830 (3H, t, oct-CH$_3$).

Anal. Calcd for $C_{16}H_{24}N_2O_4S_2F_6$: C, 39.50; H, 4.97; N, 5.76. Found: C, 39.38; H, 5.11; N, 5.73.

[4MOPYR]$^+$[BF$_4$]$^-$. 2.57 g ($9.1 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 1.47 g ($13.1 \cdot 10^{-3}$ mol) of sodium tetrafluoroborate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 cm^3 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: 89 %) was obtained as a white-yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.658−8.641 (2H, d, CH_{pyr-o}), 7.794−7.778 (2H, d, CH_{pyr-m}), 4.511−4.473 (2H, t, N-CH_2), 2.596 (3H, s, CH_3-C_{pyr-p}), 1.927−1.891 (2H, m, CH_2), 1.260−1.166 (10H, m,C_5H_{10}), 0.804−0.770 (3H, t, oct-CH_3).

Anal. Calcd for $C_{14}H_{24}NBF_4$: C, 57.36; H, 8.25; N, 4.78. Found: C, 57.25; H, 8.64; N, 4.90.

[OPYR]$^+$[TfO]$^-$. 3 g ($11.2 \cdot 10^{-3}$ mol) of [OPYR]$^+$[Br]$^-$ and 2.57 g ($13.4 \cdot 10^{-3}$ mol) of potassium trifluoromethane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 cm^3 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; 3.7 g (yield: 98 %) was obtained as a white solid.

Anal. Calcd for $C_{14}H_{24}NO_3SF_3$: C, 49.25; H, 6.50; N, 4.10. Found: C, 49.83; H, 7.26; N, 3.90.

[4MOPYR]$^+$[TfO]$^-$. 3 g ($10.6 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 2.40 g ($12.5 \cdot 10^{-3}$ mol) of potassium trifluoromethane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 cm^3 of acetonitrile. After filtering, removal of acetonitrile by rotary evaporation, and washing with methylene chloride, 3.45 g (yield: 92 %) was obtained as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.858−8.842 (2H, d, CH_{pyr-o}), 7.879−7.804 (2H, m, CH_{pyr-m}), 4.621−4.585 (2H, t, N-CH_2), 2.624 (3H, s, CH_3-C_{pyr-o}), 2.005−1.933 (2H, m, CH_2), 1.272−1.194 (10H, m, C_5H_{10}), 0.814−0.796 (3H, t, oct-CH_3).

Anal. Calcd for $C_{15}H_{24}NO_3SF_3$: C, 50.69; H, 6.81; N, 3.94. Found: C, 47.78; H, 6.89; N, 4.24.

[2MOPYR]$^+$[TfO]$^-$. 3.3 g ($11.7 \cdot 10^{-3}$ mol) of [2MOPYR]$^+$[Br]$^-$ and 2.80 g ($14.6 \cdot 10^{-3}$ mol) of potassium trifluoromethane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 100 cm^3 of acetonitrile. After filtering, removal of acetonitrile by rotary evaporation, and washing with methylene chloride, 3.66 g (yield: 89 %) was obtained as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.842−8.826 (H, d, CH_{pyr-o}), 8.315−8.279 (H, t, CH_{pyr-p}), 7.879−7.804 (2H, m, CH_{pyr-m}), 4.591−4.552 (2H, t, N-CH_2), 2.863 (3H, s, CH_3-C_{pyr-o}), 1.917−1.840 (2H, m, CH_2), 1.426−1.240 (10H, m, C_5H_{10}), 0.869−0.834 (3H, t, oct-CH_3).

Anal. Calcd for $C_{15}H_{24}NO_3S\ F_3$: C, 50.69; H, 6.81; N, 3.94. Found: C, 50.49; H, 6.97; N, 3.83.

[OPYR]$^+$[NfO]$^-$. 2.10 g ($7.8 \cdot 10^{-3}$ mol) of [OPYR]$^+$[Br]$^-$ and 3.01 g ($8.7 \cdot 10^{-3}$ mol) of potassium nonafluorobutane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 cm^3 of acetonitrile for 24 h. After filtering, acetonitrile was removed by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3× 25 cm^3). After 24 h under high vacuum, 3.44 g (yield: 91 %) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.976−8.962 (2H, d, CH_{pyr-o}), 8.466−8.427 (H, t, CH_{pyr-p}), 8.057−8.022 (2H, t, CH_{pyr-m}), 4.740−4.703 (2H, t, N-CH_2), 1.991−1.980 (2H, t, CH_2), 1.302−1.216 (10H, m, C_5H_{10}), 0.858−0.824 (3H, t, CH_3).

Anal. Calcd for $C_{18}H_{24}NO_3SF_9$: C, 34.61; H, 3.92; N, 2.45. Found: C, 34.52; H, 3.75; N, 2.37.

[4MOPYR]$^+$[NfO]$^-$. 1.97 g ($7.0 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 3.24 g ($9.4 \cdot 10^{-3}$ mol) of potassium nonafluorobutane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 cm^3 of acetonitrile for 24 h. After filtering, acetonitrile was removed by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3× 25 cm^3). After 24 h under high vacuum, 2.94 g (yield: 84 %) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.858−8.842 (2H, d, CH_{pyr-o}), 7.795−7.774 (2H, m, CH_{pyr-m}), 4.591−4.540 (2H, t, N-CH_2), 2.623 (3H, s, CH_3-C_{pyr-o}), 1.949−1.925 (2H, m, CH_2), 1.276−1.203 (10H, m, C_5H_{10}), 0.845−0.801 (3H, t, oct-CH_3).

Anal. Calcd for $C_{18}H_{24}NO_3SF_9$: C, 42.78; H, 4.79; N, 2.77. Found: C, 43.18; H, 4.96; N, 2.69.

[2MOPYR]$^+$[NfO]$^-$. 2.99 g ($10.6 \cdot 10^{-3}$ mol) of [2MOPYR]$^+$[Br]$^-$ and 3.65 g ($10.6 \cdot 10^{-3}$ mol) of potassium nonafluorobutane sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 60 cm^3 of acetonitrile for 24 h. After filtering, acetonitrile was removed by rotary evaporation. The resulting white solid was then washed with methylene chloride and then water (3× 25 cm^3). After 24 h under vacuum, 4.05 g (yield: 76 %) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.862−7.822 (H, d, CH_{pyr-o}), 8.315−8.279 (H, t, CH_{pyr-p}), 7.862−7.822 (2H, m, CH_{pyr-m}), 4.590−4.537 (2H, t, N-CH_2), 2.853 (3H, s, CH_3-C_{pyr-o}), 1.911−1.808 (2H, m, CH_2), 1.389−1.223 (10H, m, C_5H_{10}), 0.857−0.812 (3H, t, oct-CH_3).

Anal. Calcd for $C_{18}H_{24}NO_3SF_9$: C, 42.78; H, 4.79; N, 2.77. Found: C, 42.81; H, 4.87; N, 2.70.

[4MOPYR]$^+$[N(CN)$_2$]$^-$. 2.10 g ($7.4 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$[Br]$^-$ and 1.90 g ($10.9 \cdot 10^{-3}$ mol) of silver dicyanamide, synthesized from silver nitrate and sodium dicyanamide, were mixed for 24 h in a flask containing 75 cm^3 of water. After filtering and removal of the solvent by rotary evaporation, the resulting colorless liquid was washed with methylene chloride (3× 25 cm^3). After 24 h under vacuum, 1.49 g (75 %) of [4MOPYR]$^+$[N(CN)$_2$]$^-$ was obtained as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.733−8.712 (2H, d, CH_{pyr-o}), 7.830−7.810 (2H, d, CH_{pyr-m}), 4.560−4.510 (2H, t, N-CH_2), 2.643 (3H, s, CH_3-C_{pyr-p}), 1.960−1.915 (2H, m, CH_2), 1.274−1.171 (10H, m, C_5H_{10}), 0.797−0.757 (3H, t, oct-CH_3).

^{13}C NMR (400 MHz, $CDCl_3$, δ): 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.

Anal. Calcd for $C_{16}H_{24}N_4$: C, 70.55; H, 8.89; N, 19.37. Found: C, 68.63; H, 9.08; N, 19.23.

[4MOPYR]$^+$[BF$_3$Ph]$^-$. 2.02 g of [4MOPYR]$^+$[Br]$^-$ ($7.1 \cdot 10^{-3}$ mol) was mixed for 10 h with 2.0 g of potassium phenyltrifluoroborate ($9.2 \cdot 10^{-3}$ mol) in 100 cm^3 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]$^-$ ($5.7 \cdot 10^{-3}$ mol) was recovered as a white-yellowish solid (yield: 80 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 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_5H_{10}), 0.849−0.815 (3H, t, oct-CH_3).

Anal. Calcd for $C_{20}H_{29}NF_3B$: C, 68.38; H, 8.32; N, 3.99. Found: C, 68.07; H, 8.49; N, 3.93.

[4MOPYR]$^+$[BPh$_4$]$^-$. 1.78 g of [4MOPYR]$^+$[Br]$^-$ ($6.3 \cdot 10^{-3}$ mol) was mixed for 10 h with 3.28 g of sodium tetraphenylborate ($9.5 \cdot 10^{-3}$ mol) in 50 cm^3 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$_4$]$^-$ ($6.0 \cdot 10^{-3}$ mol) was recovered as a white-yellowish solid (yield: 95 %).

^{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$_{pyr}$), 5.721, 5.700 (2H, d, 2CH$_{pyr}$), 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$_3$).

Anal. Calcd for $C_{38}H_{44}NB$: C, 86.84; H, 8.44; N, 2.66. Found: C, 87.04; H, 8.68; N, 2.73.

[4MOPYR]$^+$[AsF$_6$]$^-$. 1.80 g ($6.4 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$-[Br]$^-$ and 1.72 g ($8.8 \cdot 10^{-3}$ mol) of lithium hexafluoroarsenate were mixed in a flask containing 75 cm^3 of water for 24 h. The product was then extracted by adding 50 cm^3 of dichloromethane to the solution. After evaporation of the solvent by rotary evaporation, the resulting viscous liquid was washed with water (3× 25 cm^3). After 24 h under vacuum, 2.29 g (yield: 91 %) 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$_3$).

Anal. Calcd for $C_{14}H_{24}NF_6As$: C, 42.54; H, 6.13; N, 3.54. Found: C, 42.56; H, 6.20; N, 3.39.

[4MOPYR]$^+$[BETI]$^-$. 1.65 g ($5.8 \cdot 10^{-3}$ mol) of [4MOPYR]$^+$-[Br]$^-$ and 2.47 g ($6.4 \cdot 10^{-3}$ mol) of lithium bis(pentafluoroethylsulfonyl)imide were mixed in a flask containing 50 cm^3 of water for 24 h. The product was then extracted by adding 50 cm^3 of dichloromethane to the solution. Dichloromethane phase was collected, and the solvent was removed by rotary evaporation. The resulting viscous liquid was then washed with water (3× 25 cm^3). After 24 h under vacuum, 3.01 g (yield: 89 %) 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$_3$).

Anal. Calcd for $C_{18}H_{24}N_2O_4S_2F_{10}$: C, 36.87; H, 4.13; N, 4.78. Found: C, 36.94; H, 4.16; N, 4.89.

Densities. Densities were measured with a 1 cm^3 volumetric flask in air at 25 °C and relative humidity (RH) of 48 %. The uncertainty of the density measurement is ± 0.01 g cm^{-3}.

Melting Points, Glass Transition, and Decomposition Temperatures. Melting points and glass transition temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC 7). ILs were dried in a drying pistol at 1 mbar and 60 °C or in an antechamber for at least 48 h in the presence of P$_2$O$_5$. The ILs were stored and sampled in a dry-helium glovebox 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, kept at this temperature for 30 min, heated well above the melting point, and cooled again. The scanning rate was 10 °C/min. Melting point and glass transition temperatures were taken from the second heating curve. The uncertainty of the measurement is ± 1 °C.

Table 1. Air-Saturated Densities ρ of Selected Ionic Liquids[a]

ionic liquid	ρ/g·cm^{-3}
[4MOPYR]$^+$[BF$_4$]$^-$	1.08
[4MOPYR]$^+$[AsF$_6$]$^-$	1.33
[4MOPYR]$^+$[Tf$_2$N]$^-$	1.29
[4MOPYR]$^+$[BETI]$^-$	1.39
[4MOPYR]$^+$[TfO]$^-$	1.17
[4MOPYR]$^+$[N(CN)$_2$]$^-$	0.98

[a] The relative humidity (RH) was 49 %.

Thermogravimetric analysis (TGA) provides information concerning thermal stability. Perkin-Elmer TGA 7 was used. The dried IL samples were stored in a dry-helium glovebox. The TGA sample holder was under dry-nitrogen flow during the sampling. Similar size samples, approximately 8 mg, were used at the same heating rate, 10 °C/min. The precision of the measurement was ± 5 °C.

Solubility in Water. Solubilities of ILs in water were obtained by recording the UV spectra (Beckman DU640) of an aqueous phase in equilibrium with the IL. Intensities of the absorption of ILs containing [OPYR]$^+$ or [4MOPYR]$^+$ cations were recorded at 254 nm; this wavelength corresponds to the wavelength of maximum absorption for [4MOPYR]$^+$ and [OPYR]$^+$. For ILs containing [2MOPYR]$^+$ cations, the intensity of absorption was recorded at 265 nm, corresponding to the wavelength of maximum absorption of [2MOPYR]$^+$ cations.

Dilute aqueous solutions containing a known amount of IL, between (0.001 and 0.02) wt %, were used for calibration. An aqueous solution saturated with IL was prepared and diluted by a factor of 100. Table 2 shows the solubilities of ILs in water. The mass fraction solubilities have a precision of ± 5 %.

Water Content of ILs. The water content of an IL was measured by the Karl Fischer method using a Metler-Toledo coulometer. Water contents were measured at two different conditions.

The water content of an air-saturated IL was measured first. The IL was exposed one week to air. Then, a sample of the IL was taken, and the water content was measured at least three times. Air humidity was also recorded.

Second, the water content of a water-saturated IL in equilibrium with liquid water was measured by mixing water and IL for 24 h. After that, the two-phase system was centrifuged and left in contact for another 24 h to reach equilibrium. Then, samples of the IL were taken, and its water content was measured. All measurements were repeated at least three times. The water contents of ILs are reported in mass fraction; they are precise to ± 7 %.

Viscosities. Viscosities of selected ILs were measured using an ARES Rheometric Scientific apparatus. Samples were dried and stored in a helium glovebox prior to measurement. Sampling and measurements were carried out under dry nitrogen. Before each measurement, the sample was left at least 30 min inside the rheometer at 100 °C under dry-nitrogen flow. The procedure was tested with 1-octyl-3-methylpyridinium tetrafluoroborate, used as received from Solvent Innovation. Our measured viscosities of [OMPYR]$^+$[BF$_4$]$^-$ at (25 and 75) °C agree within 1 % with those reported in the literature.[31]

Results

Densities. Table 1 shows densities for selected ILs containing [4MOPYR]$^+$ cations. The samples were exposed to air at RH

Table 2. Melting Points (t_m), Glass Transition Temperatures (t_g), Onset Decomposition Temperatures (t_d), and Mass-Fraction Solubilities in Water (w) for Several Ionic Liquids

ionic liquid	t_m/°C	t_g/°C	t_d/°C	100 w
$[4MOPYR]^+[BF_4]^-$	*a*	−64	290	1.68
$[3MOPYR]^+[BF_4]^-$	*a*	−70	310	1.65
$[OPYR]^+[Tf_2N]^-$	−12	−78	320	0.035
$[4MOPYR]^+[Tf_2N]^-$	7	−77	300	0.022
$[2MOPYR]^+[Tf_2N]^-$	*a*	−72	290	0.10
$[OPYR]^+[TfO]^-$	49	*b*	280	1.46
$[4MOPYR]^+[TfO]^-$	*a*	−65	296	1.59
$[2MOPYR]^+[TfO]^-$	40	*b*	275	*c*
$[OPYR]^+[NfO]^-$	73	*b*	294	0.046
$[4MOPYR]^+[NfO]^-$	68	*b*	298	0.065
$[2MOPYR]^+[NfO]^-$	78	*b*	292	0.14
$[4MOPYR]^+[N(CN)_2]^-$	*a*	−69	228	>5.0
$[4MOPYR]^+[BF_3Ph]^-$	*a*	−57	205	0.49
$[4MOPYR]^+[BPh_4]^-$	130	*b*	190	<0.0005
$[4MOPYR]^+[AsF_6]^-$	8	−64	305	0.027
$[4MOPYR]^+[BETI]^-$	2	−75	325	0.013

[a] No melting point observed. [b] No glass-transition point observed. [c] Not measured.

Table 3. Water Content in Mass-Fraction 100 w of Some Selected Air-Saturated and Water-Saturated Ionic Liquids at 25 °C

ionic liquid	RH/%	100 w(air-sat)	100 w(wat-sat)
$[4MOPYR]^+[BF_4]^-$	49	1.81	11.3
$[3MOPYR]^+[BF_4]^-$	48	1.25	13.6
$[OPYR]^+[Tf_2N]^-$	49	0.13	0.86
$[2MOPYR]^+[Tf_2N]^-$	49	0.31	0.78
$[4MOPYR]^+[Tf_2N]^-$	49	0.10	0.73
$[4MOPYR]^+[BETI]^-$	49	0.20	0.52
$[4MOPYR]^+[TfO]^-$	49	0.23	17.2
$[4MOPYR]^+[N(CN)_2]^-$	49	1.84	54.9
$[4MOPYR]^+[AsF_6]^-$	49	0.25	0.90

of (48 or 49) % at 25 °C. The corresponding water contents for each IL are shown in Table 3. For the same cation, ILs containing dicyanamide anion exhibit the lowest density (0.98 g cm^{-3}) while $[4MOPYR]^+[BETI]^-$ has the highest density (1.39 g cm^{-3}), followed by $[4MOPYR]^+[AsF_6]^-$ (1.33 g cm^{-3}) and $[4MOPYR]^+[Tf_2N]^-$ (1.29 g cm^{-3}).

The density of $[4MOPYR]^+[AsF_6]^-$ appears to be higher than that of $[4MOPYR]^+[BF_4]^-$, in agreement with the observations that densities for perfluoroarsenate liquids are higher than those liquids containing perfluorophosphates or perfluoroborate.

For the same anion, densities of ILs containing $[4MOPYR]^+$ cation are lower or similar to those liquids containing 1-butyl-4-methylpyridinium homologues.[29] As expected, density decreases with the length of the alkyl chain. For $[Tf_2N]^-$ and $[N(CN)_2]^-$ anions, ILs containing $[OMIM]^+$ cation appear to be more dense than $[4MOPYR]^+$ homologues, in agreement with our previous report showing that ILs 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 ILs reported here are liquid at room temperature.

Due to the size and symmetry of the $[BPh_4]^-$ anion, $[4MOPYR]^+[BPh_4]^-$ has the highest melting point measured here, 130 °C. When phenyls are substituted with fluorides, as in the trifluorophenylborate anion, the resulting IL, $[4MOPYR]^+[BF_3Ph]^-$, shows no melting point and a t_g at −57 °C.

In agreement with results obtained for ILs containing 1-octyl-3-methylpyridinium cations,[27] ILs containing $[BF_4]^-$ or $[Tf_2N]^-$ anions show no or low melting points. $[OPYR]^+[Tf_2N]^-$ shows a melting point at −12 °C and a glass transition temperature at −78 °C. All ILs containing $[NfO]^-$ anions exhibit high melting points from (68 to 78) °C and no glass transition point. As for ILs containing $[BF_4]^-$ or $[Tf_2N]^-$ anions, a methyl group on the octylpyridinium cation has no effect on melting points.

For ILs containing $[TfO]^-$ anions, on the other hand, melting points are influenced by a methyl group on the cation. For $[4MOPYR]^+[TfO]^-$, for example, no melting point is observed, whereas $[OPYR]^+[TfO]^-$ and $[2MOPYR]^+[TfO]^-$ have melting points at (49 and 40) °C, respectively.

For ILs containing 1-methyl-3-alkylimidazolium, previous reports showed that an increase in alkyl chain length leads to a decrease in the melting point.[18,19] This observation holds for ILs containing pyridinium cations. With the same anion, Table 2 shows that ILs containing octylpyridinium ($[OPYR]^+$ or $[4MOPYR]^+$) cations show lower melting points than those for ILs containing 1-butyl-4-methylpyridinium cations.[29]

All ILs containing 1-methyl-3-octylimidazolium cations and $[Tf_2N]^-$, $[N(CN)_2]^-$, $[TfO]^-$, or $[NfO]^-$ anions are liquid at room temperature.[29] The results obtained here for ILs containing octylpyridinium cations are different. Unlike liquids containing $[OMIM]^+[NfO]^-$ or $[OMIM]^+[TfO]^-$, ILs containing $[4MOPYR]^+[NfO]^-$ and $[OPYR]^+[TfO]^-$ are solid at room temperature.

Glass transition temperatures for all ILs reported here are (10 or 15) °C higher than those for ILs containing 1-methyl-3-octylimidazolium cations. Glass transition temperatures are −64 °C for $[4MOPYR]^+[BF_4]^-$ and $[4MOPYR]^+[AsF_6]^-$, −65 °C for $[4MOPYR]^+[TfO]^-$, −69 °C for $[4MOPYR]^+[N(CN)_2]^-$, −75 °C for $[4MOPYR]^+[BETI]^-$, −57 °C for $[4MOPYR]^+[BF_3Ph]^-$, and −77 °C for $[4MOPYR]^+[Tf_2N]^-$. For ILs containing $[OMIM]^+$ cations, glass transition temperatures are between −80 °C for $[OMIM]^+[TfO]^-$ and −89 °C for $[OMIM]^+[N(CN)_2]^-$.[29]

Thermal Stability. Table 2 shows onset decomposition temperatures for all ILs studied here. ILs containing phenylborate anions exhibit the lowest thermal stability. Our previous work has shown that the thermal stabilities of ILs containing borate anions increase with the number of fluorides and decrease with the number of phenyls appended to boron. The onset decomposition temperatures of $[4MOPYR]^+[BPh_4]^-$ and $[4MOPYR]^+[BF_3Ph]^-$ are, respectively, (190 and 205) °C.

Previous work[29] showed that $[OMIM]^+[N(CN)_2]^-$ has a lower thermal stability than those of $[OMIM]^+[TfO]^-$, $[OMIM]^+[NfO]^-$, $[OMIM]^+[BF_4]^-$, or $[OMIM]^+[Tf_2N]^-$ anions. In agreement with our previous results, onset decomposition temperature (t_d) for $[4MOPYR]^+[N(CN)_2]^-$ is lower (228 °C) than those for $[4MOPYR]^+[TfO]^-$ (296 °C), $[4MOPYR]^+[NfO]^-$ (298 °C), $[4MOPYR]^+[BF_4]^-$ (290 °C), or $[4MOPYR]^+[Tf_2N]^-$ (300 °C).

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

The onset decomposition temperature for $[3MOPYR]^+[BF_4]^-$ measured here is 310 °C, higher than 274 °C previously reported by Crosthwaite et al.[27] With a decomposition temperature of 290 °C, $[4MOPYR]^+[BF_4]^-$ appears to have a slightly lower thermal stability than $[3MOPYR]^+[BF_4]^-$. As expected, considering the large symmetric shape of the anion, $[4MOPYR]^+[AsF_6]^-$ exhibits higher thermal stability with a decomposition temperature of 305 °C.

ILs containing bis(perfluoroalkylsulfonyl)imide anions exhibit the highest thermal stabilities measured here: t_d for $[OPYR]^+$-

$[Tf_2N]^-$ and $[4MOPYR]^+[BETI]^-$ are (320 and 325) °C, respectively. $[4MOPYR]^+[BETI]^-$ is more thermally stable than $[4MOPYR]^+[Tf_2N]^-$ due to the increased number of fluorinated carbons. $[BETI]^-$ shows the highest thermal stability of all ILs containing $[4MOPYR]^+$ studied here. Thermal stabilities (t_d) of ILs containing $[4MOPYR]^+$ cations are in the order: $[BETI]^- > [AsF_6]^- > [Tf_2N]^- > [NfO]^- > [TfO]^- \sim [BF_4]^- > [N(CN)_2]^- > [BF_3Ph]^- > [BPh_4]^-$.

Solubility in Water. All ILs studied here are nearly immiscible with water. This result is surprising because previous studies of ILs containing 1-methyl-3-octylimidazolium cations did not always yield water-immiscible ILs.[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 mass fraction (w) of $[4MOPYR]^+[TfO]^-$ and $[4MOPYR]^+[N(CN)_2]^-$ in water 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 solubility 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 that for $[OMIM]^+[BF_4]^-$. The solubility in water of $[4MOPYR]^+[BF_3Ph]^-$ (0.49 %) is similar to that for $[OMIM]^+[BF_3Ph]^-$ (0.51 %). The borate anions appear to determine the solubility of ILs in water.

As expected, low solubilities in water are obtained for ILs containing $[Tf_2N]^-$, $[NfO]^-$, $[BETI]^-$, or $[AsF_6]^-$ anions. The mass fractions w of ILs in water are 0.013 %, 0.022 %, 0.065 %, and 0.027 % for $[4MOPYR]^+[BETI]^-$, $[4MOPYR]^+[Tf_2N]^-$, $[4MOPYR]^+[NfO]^-$, and $[4MOPYR]^+[AsF_6]^-$, respectively. Due to the increased hydrophobicity of the $[BETI]^-$ anion, $[4MOPYR]^+[BETI]^-$ is the room temperature IL 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 ILs containing 1-octyl-3-methylimidazolium cation.[29]

The water solubilities w obtained for $[OPYR]^+[Tf_2N]^-$ and $[OPYR]^+[NfO]^-$ are 0.035 % and 0.046 %, respectively. ILs containing $[OPYR]^+$ cations appear to have similar solubilities in water as compared to those of their $[4MOPYR]^+$ homologues.

On the other hand, ILs containing $[2MOPYR]^+$ cations show higher solubilities in water as compared to ILs containing $[OPYR]^+$ or $[4MOPYR]^+$ cations. For example, 0.10 % is obtained for the solubility in water of $[2MOPYR]^+[Tf_2N]^-$ as compared to (0.035 and 0.022) % obtained for $[OPYR]^+[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$. Similarly, the solubility in water for $[2MOPYR]^+[NfO]^-$ is 0.14 % as compared to (0.046 and 0.065) % for $[OPYR]^+[NfO]^-$ and $[4MOPYR]^+[NfO]^-$, respectively. The significant influence of a minor change in molecular structure is clearly evident.

Water Content. Table 3 gives water contents for "air-saturated" and "water-saturated" ILs for $[2MOPYR]^+[Tf_2N]^-$, $[4MOPYR]^+[Tf_2N]^-$, $[4MOPYR]^+[BETI]^-$, $[4MOPYR]^+[TfO]^-$, $[4MOPYR]^+[N(CN)_2]^-$, and $[4MOPYR]^+[AsF_6]^-$.

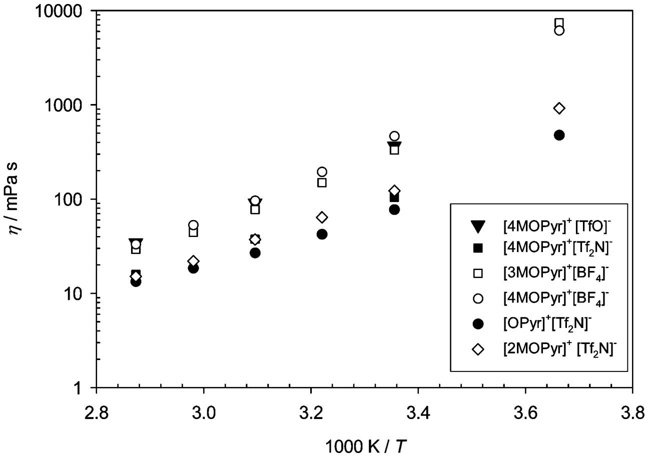

Figure 2. Viscosities η for selected ionic liquids containing 1-octylpyridinium cations.

In agreement with the high solubilities in water obtained for $[3MOPYR]^+[BF_4]^-$, $[4MOPYR]^+[BF_4]^-$, $[4MOPYR]^+[TfO]^-$, and $[4MOPYR]^+[N(CN)_2]^-$, water contents for these four ILs are the highest measured in this study. Water contents for water-saturated samples of $[3MOPYR]^+[BF_4]^-$ and $[4MOPYR]^+[BF_4]^-$ are lower than those for $[4MOPYR]^+[TfO]^-$ (17.2 %). When saturated with water, $[4MOPYR]^+[N(CN)_2]^-$ shows a water content of 54.9 %. All other ILs studied here have lower water contents (0.10, 0.20 and 0.25) % for air-saturated $[4MOPYR]^+[Tf_2N]^-$, $[4MOPYR]^+[BETI]^-$, and $[4MOPYR]^+[AsF_6]^-$, respectively.

The water content of air-saturated $[4MOPYR]^+[BETI]^-$ (0.20 %) at 25 °C and RH of 49 % is twice that for $[4MOPYR]^+[Tf_2N]^-$ (0.10 %), even though $[4MOPYR]^+[BETI]^-$ is less soluble in water than $[4MOPYR]^+[Tf_2N]^-$. These water contents w are unexpectedly high as compared to that for $[4MOPYR]^+[TfO]^-$ (0.23 %), a much less hydrophobic IL than $[4MOPYR]^+[Tf_2N]^-$ 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 $[4MOPYR]^+[Tf_2N]^-$ is 0.73 %.

When the methyl group on the octylpyridinium cation changes from the ortho to para position, the water content decreases for ILs containing $[Tf_2N]^-$ anions. For air-saturated $[2MOPYR]^+[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$, the water content decreases from (0.31 to 0.10) %. The influence of the position of the methyl group on water content of water-saturated $[2MOPYR]^+[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$ is much smaller: the water content decreases from (0.78 to 0.73) %.

The higher water content of $[2MOPYR]^+[Tf_2N]^-$, as compared to that for $[4MOPYR]^+[Tf_2N]^-$, is consistent with results obtained for the water solubilities of $[2MOPYR]^+[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$, suggesting that the interaction between water and 1-octyl-2-methylpyridinium cation is stronger than that between water and 1-octyl-4-methylpyridinium cation.

The few data available for the water contents of ILs containing imidazolium cations[17,19] are similar to those obtained in this study. The water content of water-saturated $[BMIM]^+[Tf_2N]^-$ is close to that of $[OPYR]^+[Tf_2N]^-$, $[2MOPYR]^+[Tf_2N]^-$ or $[4MOPYR]^+[Tf_2N]^-$.

Water contents for $[4MOPYR]^+[AsF_6]^-$ and $[3MOPYR]^+[BF_4]^-$ or $[4MOPYR]^+[BF_4]^-$ were higher than those for $[OPYR]^+[Tf_2N]^-$, $[2MOPYR]^+[Tf_2N]^-$, or $[4MOPYR]^+[Tf_2N]^-$ ILs, in agreement with previous measurements indicating that ILs containing fluorinated spherical anions such as $[PF_6]^-$ have water content higher than those of other ILs containing $[Tf_2N]^-$ anions.[19] Considering that results obtained for ILs containing imidazolium are similar to those for pyridinium cations, the water content of an IL appears to be mostly influenced by the anion.

Table 4. Viscosities η for Selected Ionic Liquids from (0 to 75) °C

	t/°C					
η/mPa·s	0	25	37.5	50	62.5	75
$[3MOPYR]^+[BF_4]^-$	7410	332	149	77.3	44.3	29.3
$[4MOPYR]^+[BF_4]^-$	6120	460	194	96.1	52.8	33.1
$[OPYR]^+[Tf_2N]^-$	476	77.1	42.2	26.8	18.5	13.3
$[2MOPYR]^+[Tf_2N]^-$	919	122	64.0	37.2	22.0	15.1
$[4MOPYR]^+[Tf_2N]^-$	*a*	105	*a*	37.6	*a*	15.9
$[4MOPYR]^+[TfO]^-$	*a*	365	*a*	90.8	*a*	34.3
$[OMIM]^+[BF_4]^-$	*a*	345	*a*	87.3	*a*	37.9

[a] Not measured.

Viscosity. Table 4 shows viscosities for $[3MOPYR]^+[BF_4]^-$, $[4MOPYR]^+[BF_4]^-$, $[4MOPYR]^+[TfO]^-$, $[OPYR]^+[Tf_2N]^-$, $[2MOPYR]^+[Tf_2N]^-$, and $[4MOPYR]^+[Tf_2N]^-$. A plot of viscosities is shown in Figure 2. Viscosities measured for $[OMIM]^+[BF_4]^-$ are also shown in Table 4.

Two groups appear in the plot. The first group of ILs with lower viscosities includes, as expected, ILs containing $[Tf_2N]^-$ anions: $[OPYR]^+[Tf_2N]^-$, $[2MOPYR]^+[Tf_2N]^-$, and $[4MOPYR]^+$-$[Tf_2N]^-$.

The lowest viscosities are those for $[OPYR]^+[Tf_2N]^-$, which shows a viscosity of 77.1 mPa·s at 25 °C. The absence of a methyl group on the pyridinium explains the lower viscosity as compared to those for $[2MOPHR]^+[Tf_2N]^-$ or $[4MOPYR]^+$-$[Tf_2N]^-$. Viscosities for $[4MOPYR]^+[Tf_2N]^-$ are close to those for $[3MOPYR]^+[Tf_2N]^-$ reported by Crosthwaite et al.[27]

The position of the methyl group on the pyridinium cation has little influence on the viscosity of IL containing the $[Tf_2N]^-$ anion. The second group of ILs with higher viscosities are those containing $[3MOPYR]^+[BF_4]^-$, $[4MOPYR]^+[BF_4]^-$, and $[4MOPYR]^+[TfO]^-$.

The difference between the viscosities for $[3MOPYR]^+[BF_4]^-$ and $[4MOPYR]^+[BF_4]^-$ are higher than that observed for $[3MOPYR]^+[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$. For example, at 25 °C, viscosities for $[3MOPYR]^+[BF_4]^-$ and $[4MOPYR]^+$-$[BF_4]^-$, respectively, are (332 and 460) mPa·s. For $[3MOPYR]^+$-$[Tf_2N]^-$ and $[4MOPYR]^+[Tf_2N]^-$, the viscosities are 112 mPa·s[27] and 105 mPa·s. The position of the methyl group influences the viscosities of ILs containing $[BF_4]^-$ anions.

The viscosities measured here are similar to those obtained for ILs containing 1-octyl-3-methylimidazolium cations. At 25 °C, viscosities for $[OMIM]^+[BF_4]^-$ and $[3MOPYR]^+$-$[BF_4]^-$ are (345 or 332) mPa·s, respectively. It appears that viscosities of ILs are mainly influenced by the nature of the anions. Nevertheless, cation structure such as the presence and position of a methyl group on the pyridinium cations also has some influence on viscosity.

Conclusion

ILs containing octylpyridinium-type cations have some physicochemical properties similar to and others significantly different from those that contain 1-methyl-3-octylimidazolium cation. Melting points are more influenced by the nature of the anion than those for their imidazolium homologues. Glass transition temperatures are (10 to 20) °C higher. Thermal stabilities are similar to those for ILs containing $[OMIM]^+$ cations. Viscosities for ILs containing octylpyridinium-type cations are close to those containing $[OMIM]^+$ cations. But most important, all ILs containing octylpyridinium-type cations are nearly water immiscible. Solubilities in water are an order of magnitude lower than those for their imidazolium homologues. ILs containing octylpyridinium cations, therefore, may provide an alternative to ILs containing imidazolium for application in extraction of heavy metal cations from wastewaters.

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