Synthesis and Properties of Seven Ionic Liquids Containing 1-Methyl-3-octylimidazolium or 1-Butyl-4-methylpyridinium Cations

Nicolas Papaiconomou,[†,‡] Neal Yakelis,[§] Justin Salminen,[†,||] Robert Bergman,[‡,§] and John M. Prausnitz*[,†,‡]

Department of Chemical Engineering, 201 Gilman Hall, University of California, Berkeley, California 94720-1462, Department of Chemistry, Room 419 Latimer Hall, University of California, Berkeley, California 94720-1460, Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, and Environmental Energy Technology Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720

Syntheses are reported for ionic liquids containing 1-methyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations and trifluoromethyl sulfonate, dicyanamide, bis(trifluoromethylsulfonyl)imide, or nonafluorobutyl sulfonate anions. Densities, melting points, glass-transition temperatures, solubilities in water, and polarities have been measured. Ionic liquids containing pyridinium cations exhibit higher melting points, lower solubility in water, and higher polarity than those containing imidazolium cations.

Introduction

Room-temperature ionic liquids (RTILs) provide a new class of solvents where molecules are composed of ions. At normal temperatures, ionic liquids have essentially zero vapor pressure and are thermally stable over a wide range of temperature. Therefore, they are considered as environmentally friendly alternatives to classical organic solvents.

RTILs are also tunable solvents as some of their properties (e.g. melting points, immiscibility in other solvents, or polarity) can be changed by modifying the structure of the ionic liquid's cation or anion.

During the past decade, numerous publications have discussed properties and applications of RTILs.[1,2] Ionic liquids can serve as solvents in organic chemistry,[3−5] in electrochemistry,[6,7] as catalysts[8−12] or as extracting agents for organic or ionic solutes.[13−17] Four ionic liquids synthesized here contain pyridinium cations. These ionic liquids are used as catalysts or solvents in organic chemistry.[3,9]

For extraction of heavy-metal ions from an aqueous phase, ionic liquids need to meet specific criteria: low water solubility, low viscosity, and high affinity for the ion to be extracted. Because these properties pertain to only a limited number of known ionic liquids, it is desirable to synthesize promising new ionic liquids and to measure their physicochemical properties.

To enhance fundamental understanding concerning ionic liquids potentially suitable for extraction of heavy-metal ions, this work reports the synthesis of seven ionic liquids and some of their physicochemical properties. Three of the seven ionic liquids studied here have also been synthesized previously: 1-methyl-3-octylimidazolium trifluoromethyl sulfonate,[18] 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide,[15,19−21] and 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide.[22]

Synthesis of Ionic Liquids

We have synthesized seven ionic liquids containing 1-methyl-3-octylimidazolium $[OMIM]^+$ or 1-butyl-4-methylpyridinium $[MBPYR]^+$ cations. Figure 1 shows their structures. The $[OMIM]^+$ cation was chosen because ionic liquids containing this cation exhibit low melting points.[18−24]

The hydrophobicity of an ionic liquid increases with the length of the alkyl chain on the imidazolium ring, as shown elsewhere.[24,25] Regrettably, this increase tends to raise viscosity.[25]

Four anions were studied: trifluoromethyl sulfonate (TfO), nonafluorobutyl sulfonate (NfO), bis(trifluoromethylsulfonyl)imide (Tf_2N), and dicyanamide ($N(CN)_2$). TfO and NfO anions were chosen because they are fluorinated anions with high hydrophobicity. Several authors[16,25−27] have reported first that ionic liquids containing 1-methyl-3-butylimidazolium cation and NfO anion, such as $[BMIM]^+[NfO]^-$, are immiscible with water and, second, that ionic liquids containing TfO anions are miscible with water but less viscous than ionic liquids containing NfO anions.

All Tf_2N-based ionic liquids studied previously[16,25−27] are immiscible with water. Moreover, they exhibit lower viscosities than water-immiscible ionic liquids containing PF_6^- anions or BF_4^- anions and long alkyl chains, such as $[OMIM]^+[BF_4]^-$.[28] Ionic liquids with PF_6^- may not be useful for extraction of ions from water because PF_6^- slowly reacts with water.[29]

Previous work reports that ionic liquids containing dicyanamide anion have low viscosity.[30] However, they are water soluble.

As discussed below, a two-step metathesis procedure was used to synthesize seven new ionic liquids.

***$[OMIM]^+[Tf_2N]^-$*.** In a flask containing 150 mL of acetonitrile, 6.27 g (26.7 mmol) of $[OMIM]^+[Cl]^-$ was mixed with 9.02 g (28.3 mmol, 6 % excess) of potassium bis(trifluoromethylsulfonyl)imide, used as received from Wako Chemicals (98 % purity).

After being stirred for 4 h, the solution was filtered to remove precipitated KCl. The solvent was then removed by rotary evaporation. Traces of the remaining acetonitrile were removed by placing the yellow-white product under high vacuum for 30 min. The product was washed with methylene chloride and set in a freezer for 4 h at −18 °C. The solution was filtered to remove the remaining precipitated potassium Tf_2N. Methylene

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* Corresponding author. E-mail: prausnit@cchem.berkeley.edu.
[†] Department of Chemical Engineering.
[‡] Chemical Sciences Division.
[§] Department of Chemistry.
[||] Environmental Energy Technology Division.

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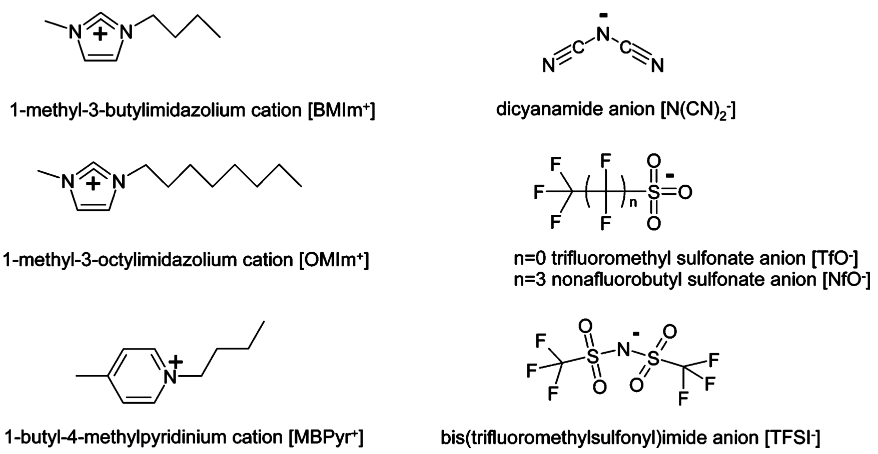

Figure 1. Structures of the cations and anions used in this work.

chloride was removed by rotary evaporation, and the product was set under high vacuum for 30 min. The resulting ionic solid was colorless. The mass of $[OMIM]^+[Tf_2N]^-$ was 10.75 g, giving a yield of 87 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.157 (1H, s, N−CH−N), 7.330 (1H, s, N−CH), 7.266 (1H, s, CH−N), 4.173−4.136 (2H, t, CH2), 3.971−3.954 (3H, d, CH_3), 1.836 (2H, s, CH_2), 1.281−1.218 (10H, m, C_5H_{10}), 0.856−0.822 (3H, t, CH_3). Anal. Calcd: C, 35.33; H, 5.58; N, 8.83. Found: C, 35.28; H, 5.08; N, 8.98.

$[OMIM]^+[TfO]^-$. 5.91 g (25.2 mmol) of $[OMIM]^+[Cl]^-$ was mixed in 150 mL of acetonitrile with 6.22 g (30.24 mmol) of potassium trifluoromethyl sulfonate, used as received from Sigma (98 % purity). After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 6.86 g (20.0 mmol) of $[OMIM]^+[TfO]^-$ was obtained as a yellow liquid. The yield was 79 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.157 (1H, s, N−CH−N), 7.330 (1H, s, N−CH), 7.266 (1H, s, CH−N), 4.173−4.136 (2H, t, CH2), 3.971−3.954 (3H, d, CH_3), 1.836 (2H, s, CH_2), 1.281−1.218 (10H, m, C_5H_{10}), 0.856−0.822 (3H, t, CH_3). ^{19}F NMR (300 MHz, $CDCl_3$, δ): −77.86 (3F, s, CF_3). Anal. Calcd: C, 45.30; H, 6.70; N, 8.10. Found: C, 44.80; H, 6.72; N, 8.12.

$[OMIM]^+[NfO]^-$. 2.33 g (10.1 mmol) of $[OMIm^+]$ $[Cl^-]$, used as received from Solvent Innovation (98 % purity), and 4.27 g (12.6 mmol, 25 % excess) of potassium nonafluorobutyl sulfonate, used as received from Sigma (98 % purity), were mixed in a flask containing 150 mL of acetonitrile. After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 4.56 g of $[OMIM]^+[NfO]^-$ was obtained as a light-orange liquid. The yield was 91 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.157 (1H, s, N−CH−N), 7.330 (1H, s, N−CH), 7.266 (1H, s, CH−N), 4.173−4.136 (2H, t, CH2), 3.971−3.954 (3H, d, CH_3), 1.836 (2H, s, CH_2), 1.281−1.218 (10H, m, C_5H_{10}), 0.856−0.822 (3H, t, CH_3). Anal. Calcd: C, 38.87; H, 4.70; N, 5.66. Found: C, 38.66; H, 4.84; N, 5.64.

$[OMIM]^+[N(CN)_2]^-$. 10.55 g (45.7 mmol) of $[OMIM]^+[Cl]^-$ was mixed in 150 mL of acetonitrile with 4.99 g (56.0 mmol, 23 % excess) of sodium dicyanamide, used as received from Sigma (98 % purity). After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 9.82 g (37.5 mmol) of $[OMIM]^+[N(CN)_2]^-$ was obtained as a pale yellow liquid. The yield was 82 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.123 (1H, s, N−CH−N), 7.404−7.401 (1H, d, N−CH), 7.353−7.344 (1H, t, CH−N), 4.201−4.164 (2H, t, CH2), 3.989 (3H, s, CH_3), 1.883−1.847 (2H, t, CH_2), 1.300−1.216 (10H, m, C_5H_{10}), 0.840−0.806 (3H, t, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 136.51, 123.95, 122.50, 120.04, 50.53, 36.75, 31.76, 30.22, 29.09, 28.98, 26.34, 22.69, 14.19. Anal. Calcd: C, 64.33; H, 8.81; N, 26.80. Found: C, 61.108; H, 8.48; N, 25.50.

$[MBPYR]^+[Tf_2N]^-$. 4.36 g (18.9 mmol) of 1-butyl-4-methylpyridinium bromide, used as received from Solvent Innovation (98 % purity), was mixed with 7.56 g (24.0 mmol, 25 % excess) of potassium Tf_2N in a flask containing 150 mL of acetonitrile. After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 7.53 g (17.5 mmol) of $[MBPYR]^+[Tf_2N]^-$ was obtained as a light-yellow liquid. The yield was 93 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.299−9.283 (2H, d, pyr-CH_m), 7.844−7.829 (2H, d, pyr-CH_o), 4.933−4.896 (2H, t, CH_2), 2.647 (3H, s, CH3), 2.012−1.936 (2H, m, CH2), 1.434−1.340 (2H, m, CH_2), 0.956−0.919 (3H, t, CH_3). Anal. Calcd: C, 33.46; H, 3.70; N, 6.50. Found: C, 33.13; H, 3.53; N, 6.46.

$[MBPYR]^+[TfO]^-$. 2.34 g (10.0 mmol) of 1-butyl-4-methylpyridinium bromide, from Solvent Innovation, washed with ethyl acetate, was mixed with 2.30 g (12.2 mmol, 20 % excess) of potassium trifluoromethyl sulfonate in a flask containing 100 mL of acetonitrile. After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 2.70 g (8.9 mmol) of $[MBPYR]^+[TfO]^-$ was obtained as a light-yellow liquid. This ionic liquid was further purified by mixing 100 mg of silver trifluoromethyl sulfonate with $[MBPYR]^+[TfO]^-$ in 15 mL of methylene chloride. After filtering and removing the methylene chloride, a white-yellow solid was obtained. The yield was 89 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.846−8.831 (2H, d, pyr-CH_m), 7.787−7.771 (2H, d, pyr-CH_o), 4.601−4.563 (2H, t, CH_2), 2.603 (3H, s, CH3), 1.939−1.883 (2H, m, CH2), 1.395−1.301 (2H, m, CH_2), 0.944−0.907 (3H, t, CH_3). ^{19}F NMR (300 MHz, $CDCl_3$, δ): −77.74 (3F, s, CF_3). Anal. Calcd: C, 43.30; H, 5.39; N, 4.68. Found: C, 41.20; H, 5.11; N, 4.95.

$[MBPYR]^+[NfO]^-$. 5.16 g (22.5 mmol) of 4-methyl-*N*-pyridinium bromide, from Solvent Innovation, washed with acetyl acetate, was mixed with 10.0 g (30.0 mmol, 33 % excess) of potassium nonafluorobutyl sulfonate in a flask containing 150 mL of acetonitrile. After filtering, removing acetonitrile by rotary evaporation, and washing with methylene chloride, 9.02 g (20 mmol) of $[MBPYR]^+[NfO]^-$ was obtained as a light-yellow liquid. The yield was 90 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.785−8.769 (2H, d, pyr-CH_m), 7.787−7.771 (2H, d, pyr-CH_o), 4.601−4.563 (2H, t, CH_2), 2.627 (3H, s, CH3), 1.959−1.883 (2H, m, CH2), 1.387−

Table 1. Densities ρ at 25 °C, Melting Points t_m, Glass-Transition Temperatures t_g, Decomposition Temperatures t_d, and Mass Fraction Solubilities w in Water at 25 °C for Several Ionic Liquids

ionic liquid	ρ/g·mL^{-1}	t_m/°C	t_g/°C	t_d/°C	100 w[b]
$[OMIM]^+[Tf_2N]^-$	1.31, 1.32[19], 1.36[15]	*a*	−86	325	0.21
$[OMIM]^+[TfO]^-$	1.12	5	−80	250	S
$[OMIM]^+[NfO]^-$	1.33	32	−86	250	0.16
$[OMIM]^+[N(CN)_2]^-$	1.00	−49	−89	150	S
$[MBPYR]^+[Br]^-$	solid	78	−38	225	S
$[MBPYR]^+[Tf_2N]^-$	1.35	10	−80, −84[15]	275	0.48
$[MBPYR]^+[TfO]^-$	1.17	38	−68	200	S
$[MBPYR]^+[NfO]^-$	solid	70	32	275	2.29
$[BMIM]^+[Tf_2N]^-$	1.43[25,34], 1.44[31]	−4, −3[25,34], −4[25], −2[31]	−91, −87[34], −86[31]	330, 330[31]	0.71, 0.80[15]
$[BMIM]^+[TfO]^-$	1.30[34,31],1.29[25]	15, 16[15], 17[34], 13[31]		340[31], 409[34]	S
$[BMIM]^+[NfO]^-$	1.47[25]	20[25]	nd	225	1.69
$[BMIM]^+[N(CN)_2]^-$	1.06[31]	−6[31]	−90[31]	240[31]	S

[a] $[OMIM]^+[Tf_2N]^-$ has no melting point. [b] S indicates an ionic liquid miscible in water. nd indicates no data available.

1.293 (2H, m, CH_2), 0.938−0.901 (3H, t, CH_3). Anal. Calcd: C, 37.43; H, 3.78; N, 3.12. Found: C, 37.47; H, 3.37; N, 3.10.

Physicochemical Properties

Melting and Glass-Transition Temperatures. Table 1 shows melting points and glass-transition temperatures 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 3 days in the presence of P_2O_5. The ionic liquids were stored and sampled in a dry-helium glovebox prior to DSC measurements. The DSC apparatus was under a dry-nitrogen hood. The samples were cooled to −120 °C and kept at this temperature for 30 min, heated well above the melting point, and cooled again. The scanning rate used was 10 °C/min. Melting points and glass-transition temperature were taken from the second heating curve. Five of the seven ionic liquids synthesized here are liquid at room temperature. Values for the temperatures are given ± 1 °C.

Ionic liquids synthesized in this work containing the NfO anion have melting points above 25 °C. $[OMIM]^+[Tf_2N]^-$ exhibits no melting points. Instead, a glass-transition temperature is observed at −86 °C.

To compare the properties of ionic liquids containing $[OMIM]^+$ and $[MBPYR]^+$ cations with those of ionic liquids containing $[BMIM]^+$ cations, Table 1 shows densities, melting points, glass-transition temperatures, and solubilities of ionic liquids containing $[BMIM]^+$ cations, as reported in the literature. We also show our melting points and glass-transition temperatures.

For all anions except NfO, melting points for ionic liquids containing $[OMIM]^+$ cations are lower than those for ionic liquids containing 1-methyl-3-butylimidazolium, $[BMIM^+]$ cations. This is in agreement with results for ionic liquids containing tetrafluoroborate anions.[28]

When the $[BMIM]^+$ cation is replaced by a $[MBPYR]^+$ cation, the latter ionic liquids exhibit higher melting points. In the case of $[BMIM]^+[Tf_2N]^-$, for example, our measurements show a glass-transition at −91 °C as compared to −81 °C obtained by Crosthwaite et al.,[22] −86 °C by Tokuda et al.,[19] and −87 °C by Bonhote et al.[25] and a melting point at −5 °C as compared to −3 °C by Tokuda et al.,[19] −4 °C by Bonhote et al.,[25] and −2 °C by Fredlake et al.[31] Our 1-butyl-4-methylpyridinium Tf_2N shows a glass-transition temperature at −80 °C and a melting point at 10 °C. No melting point was observed for 1-butyl-3-methylpyridinium Tf_2N by Crosthwaite et al.[22] For all other ionic liquids, it appears that substitution of imidazolium with pyridinium yields ionic liquids melting above room temperature.

Thermal Stability. Thermogravimetric 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 glovebox. The TGA sample holder was under dry-nitrogen flow. Similar size samples, near 12 mg, and the same heating rate, 10 °C/min, were used for all our ionic liquids. Values for the temperatures are given ± 5 °C.

For most of our dried ionic liquids, the TGA curve exhibits some minor weight loss, < 1 %, below 200 °C. Two of our samples show lower thermal stability than 200 °C; $[OMIM]^+$-$[N(CN)_2]^-$ shows an onset temperature at 150 °C and $[MBPYR]^+[N(CN)_2]^-$ at 180 °C.

Thermal stability is primarily related to the nature of the anion. For every cation studied here, the thermal stability follows the trend: $T_d(Tf_2N) > T_d(NfO) > T_d(TfO) > T_d(N(CN)_2)$.

Density. Densities of ionic liquids were measured at 20 °C gravimetrically with a 1 mL volumetric flask. Values for the densities are given ± 0.01 g·mL^{-1}. Table 1 shows the results.

All ionic liquids at room temperature are more dense than water due to the anions used. The density of $[OMIM]^+[Tf_2N]^-$ has been reported previously.[15,19] Reported values are 1.36[15] and 1.32.[19] The latter density is in accord with our measurement, (1.31 ± 0.01) g·cm^{-3}.

Compared to ionic liquids containing $[BMIM]^+$, $[OMIM]^+$ cations lead to less dense ionic liquids due to an increase in the alkyl chain length, as reported previously.[12,19,24] Replacing the imidazolium cation with $[MBPYR]^+$, on the other hand, leads to an increase in density when the imidazolium cation is $[BMIM]^+$ or $[OMIM]^+$.

Solubility in Water. Only ionic liquids containing NfO and Tf_2N anions appear to be essentially immiscible with 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. The intensity of the absorption of ionic liquids containing $[OMIM]^+$ cations was recorded at 211 nm; this wavelength corresponds to the wavelength of maximum absorption for the 1-methylimidazole group. For ionic liquids containing $[MBPYR]^+$ cations, the intensity of absorption was recorded at 254 nm, corresponding to the wavelength of maximum absorption of 4-methylpyridine.

Dilute aqueous solutions containing a known mass fraction of ionic liquid, between (0.001 and 0.02) % were used for calibration. An aqueous solution saturated with ionic liquid was prepared and diluted 100 times. Table 1 shows the solubilities of ionic liquids in water. Values for the mass fraction solubilities are given ± 0.01 %. $[OMIM]^+[NfO]^-$ appears to be a strongly hydrophobic ionic liquid; its solubility in water is lower than that of any ionic liquid reported in the literature.

Table 2. Solvatochromic Shifts of Reichardt's Dye in Several Ionic Liquids and the Corresponding E_T^N Scale[a]

liquid	λ_{max}/nm	E_T^N
$[BMIM]^+ [PF_6]^-$	546 [24]	0.667
$[OMIM]^+ [Tf_2N]^-$	559	0.629
$[OMIM]^+[N(CN)_2]^-$	559	0.629
$[OMIM]^+[TfO]^-$	558	0.631
$[MBPYR]^+[Tf_2N]^-$	481	0.884
water[24]	453	1.000
ethanol[24]	551	0.653
DMSO[24]	634	0.443

[a] For comparison, results are also shown for three common solvents.

Ionic liquids containing dicyanamide or TfO anions are soluble in water. For NfO or Tf_2N anions, ionic liquids containing $[OMIM]^+$ and $[MBPYR]^+$ cations are essentially insoluble in water. For the same anion (Tf_2N^- or NfO^-), ionic liquids containing $[OMIM]^+$ or $[MBPYR]^+$ cations synthesized in this work have mostly mass fraction in water lower than those for ionic liquids containing the $[BMIM]^+$ cation. For Tf_2N anions, the solubility in water decreases from 0.71 % (or 0.80 %[15]) for $[BMIM]^+[Tf_2N]^-$ to 0.22 % (0.21 %[15]) for $[OMIM]^+[Tf_2N]^-$, and 0.48 % for $[MBPYR]^+[Tf_2N]^-$. For NfO anions, the solubility in water is 0.16 % for $[OMIM]^+[NfO]^-$ and 2.29 % for $[MBPYR]^+[NfO]^-$. The mass fraction of $[BMIM]^+[NfO]^-$ in water is 1.69 %, which is lower than the value of 2.29 % for $[MBPyr]^+[NfO]^-$ synthesized in this work. In general, longer alkyl chains lead to lower solubilities in water, in accord with literature.[16, 24, 25]

Solvent Polarity: E_T^N Scale with Reichardt's Dye. The polarity of a solvent provides a measure of a solvent's overall solvation capability. A common polarity scale is the $E_T(30)$ scale where 30 corresponds to the number assigned to this dye by Reichardt while studying a wide set of solvatochromic dyes.[32]

Reichardt's dye is a zwitterion exhibiting negative solvatochromic properties (i.e., the wavelength corresponding to maximum absorption shifts to lower wavelength as the polarity of the solvent increases). The solvatochromism of the dye is due to a change from the ground state to an excited state that is influenced by the polarity of its surroundings (i.e., the solvent). For Reichardt's dye, the more polar the solvent, the more stable the ground state of the dye, and the more energy is required to move to the excited state. The $E_T(30)$ scale is usually in $kcal \cdot mol^{-1}$ units, corresponding to the energy required to go from the ground state to the excited state.

For convenience a normalized E_T^N scale is used, where $E_T^N = 1.0$ for water ($E_T(30) = 63.1$) and $E_T^N = 0.0$ for tetramethylsilane ($E_T(30) = 30.7$). The E_T^N scale is obtained from the wavelength of maximum absorption λ_{max} of Reichardt's dye dissolved in that solvent:

$$E_T^N = \frac{(\{28591\}/\{\lambda_{max}\}) - 30.7}{32.4} \quad (1)$$

with λ_{max} in nm.

E_T^N values have been reported in the literature[24] for several ionic liquids containing imidazolium cations but, to the best of our knowledge, there are no published data for ionic liquids containing pyridinium cations and $[Tf_2N]^-$ anions. Polarities for these ionic liquids are reported here.

Table 2 gives polarity data for four new ionic liquids: $[OMIM]^+[Tf_2N]^-$, $[OMIM]^+[N(CN)_2]^-$, $[OMIM]^+[TfO]^-$, and $[MBPYR]^+[Tf_2N]^-$. Table 2 shows the wavelengths of maximum absorption for Reichardt's dye in these ionic liquids, along with the resulting E_T^N values. Because $[OMIM]^+[NfO]^-$, $[MBPYR]^+[TfO]^-$, $[MBPYR]^+[NfO]^-$ and $[MBPYR]^+[N(CN)_2]^-$ are solid at ambient temperature, their polarities were not measured.

As reported previously,[24,33] the polarities of ionic liquids containing imidazolium cations mostly depend on the cation and on the length of the cation's alkyl chain. For example, previous results show that ionic liquids containing $[BMIM]^+$ cations are more polar than those containing $[OMIM]^+$ cations, regardless of the anion. The results obtained here are consistent with these earlier observations; $[OMIM]^+[Tf_2N]^-$ and $[OMIM]^+[N(CN)_2]^-$ have essentially the same E_T^N value.

Table 2 shows that pyridinium ionic liquid $[MBPYR]^+[Tf_2N]^-$ has a higher value for the $E_T(30)$ scale than ionic liquids containing imidazolium cations studied in this work. The E_T^N value for $[OMIM]^+[Tf_2N]^-$ is 0.629, whereas that for $[MBPYR]^+[Tf_2N]^-$ is 0.884.

A previous attempt to increase the polarity of imidazolium ionic liquids has been made by inserting ether, ketone or alcohol groups into the alkyl chain of the cation.[27] The normalized polarity value for $[BMIM]^+[Tf_2N]^-$, 0.64, increases to 0.93 for 1-(2-hydroxyethyl)-3-methyl imidazolium Tf_2N.

Considering the $E_T(30)$ value obtained for $[MBPYR]^+[Tf_2N]^-$, substitution of hydroxyl groups into the alkyl chain of the pyridinium cation may lead to a new class of solvents with high polarities.

Conclusions

Seven ionic liquids have been synthesized; they contain 1-methyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations. Their densities, glass-transition temperatures, melting points, and decomposition temperatures have been measured.

We find a general trend in the influence of the alkyl chain length and the nature of the cation on the physicochemical properties of ionic liquids: with similar anions, ionic liquids containing 1-butyl-4-methylpyridinium cations exhibit higher melting points, higher densities, but lower water solubilities than those for ionic liquids containing 1-methyl-3-butylimidazolium or 1-methyl-3-octylimidazolium cations. On the other hand, ionic liquids containing 1-methyl-3-octylimidazolium have lower melting points, lower densities and lower water solubilities than those containing 1-methyl-3-butylimidazolium ions.

Polarities were measured spectroscopically using Reichardt's dye. The polarities of ionic liquids are mostly determined by their cation. Ionic liquids containing 1-methyl-3-octylimidazolium cations have polarities similar to that of ethanol. $[MBPYR]^+[Tf_2N]^-$ has higher polarity.

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