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Publication Date

2005-09-29

Peer reviewed

Properties of some ionic liquids based on 1-methyl-3-octylimidazolium and 4-methyl-N-butylpyridinium cations

(Preliminary report, Sept. 28, 2005)

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Abstract

Syntheses are reported for ionic liquids containing 1-methyl-3octylimidazolium and 4-methyl-N-butylpyridinium cations, and trifluoromethansulfonate, dicyanamide, bis(trifluoromethylsulfonyl)imide, and nonafluorobutanesulfonate anions. Densities, melting points and glass transition points, solubility in water as well as polarities have been measured. Ionic liquids based on pyridinium cations exhibit higher melting points, lower solubility in water, and higher polarity than those based on imidazolium cations.

Introduction

Room-Temperature Ionic Liquids (RTIL) provide a new class of solvents where all molecules are ions. Because at normal temperatures, they have zero vapor pressure and because they are thermally stable over a wide range of temperature, ionic liquids are “green” solvents, i.e., environmentally safe alternatives to classical organic solvents.

RTILs are also called “tunable” solvents. Some of their properties, e.g. melting points, immiscibility in other solvents, or polarity can be controlled by modifying the nature 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].

For extraction of heavy-metal ions from an aqueous phase, ionic liquids need to meet specific criteria: water immiscibility, 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 physico-chemical properties.

To enhance fundamental understanding concerning ionic liquids potentially suitable for extraction of heavy-metal ions, this work reports the synthesis of eight ionic liquids and some of their physico-chemical properties.

Three of the eight ionic liquids studied here have also been synthesized elsewhere: 1-methyl-3octylimidazolium trifluoromethansulfonate [18], 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [15, 19-21] and 4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)imide [22, 23].

Synthesis of ionic liquids

We have synthesized eight ionic liquids based on 1-methyl-3-octylimidazolium [$OMIm^+$] or 4-methyl-N-butylpyridinium [$MBPyr^+$] cations. Figure 1 shows their structures.

The [$OMIm^+$] cation was chosen because ionic liquids based on this cation exhibit low melting points [18-24].

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

Four anions were studied: triflate, nonaflate, bis(trifluoromethylsulfonyl)imide (TFSI) and dicyanamide. Triflate and nonaflate anions were chosen because they are fluorinated anions with high hydrophobicity. Several authors (16, 25-27) have reported first, that ionic liquids based on 1-butyl-3-methylimidazolium cation and nonaflate anion, such as [$BMIm^+$] [NfO^-] are immiscible with water; and second, that ionic liquids based on triflate anions are miscible with water, but less viscous than ionic liquids containing the nonaflate anion.

All TFSI-based ionic liquids studied previously [16, 25-27] are immiscible with water. Moreover, they exhibit lower viscosities than those of well-known water-immiscible ionic liquids containing PF_6^- or BF_4^- anions [30]. Ionic liquids with PF_6^- may not be useful for extraction of ions from water because PF_6^- slowly reacts with water [28].

Previous work [26] reports that ionic liquids containing the dicyanamide anion have low viscosity [29]. However, they are water soluble.

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

OMIm-NfO

2.33 grams (10.1 mmol) of [$OMIm^+$] [Cl^-], used as received from Solvent Innovation (98% purity) and 4.27 grams (12.6 mmol, 25% excess) of potassium nonaflate, used as received from Sigma (98% purity), were mixed in a flask containing 250 mL acetonitrile. After stirring for 4 hours, the solution was filtered to remove precipitated KCl. The solvent was then removed by rotary evaporation. Traces of remaining acetonitrile were removed by placing the viscous, light-orange product under high vacuum for 30 minutes. The product was washed with methylene chloride and set in a freezer for 4 hours at -18°C. The solution was filtered to remove the remaining precipitated potassium nonaflate. Methylene chloride was removed by rotary evaporation and the product set under high vacuum for 30 minutes. The resulting ionic solid had a light-orange color. The weight of [$OMIm^+$][NfO^-] was 4.56 grams (9.3 mmol), giving a yield of 91%.

OMIm-TFSI

The above procedure was also used for [$OMIm^+$][$TFSI^-$]. In a flask containing 250mL acetonitrile, 6.27grams (26.7 mmol) of [$OMIm^+$][Cl^-] was mixed with 9.02 grams (28.3 mmol, 6% excess) of potassium bis(trifluoromethylsulfonil)imide, used as received from Wako chemicals (98% purity). After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, 10.75 grams of [$OMIm^+$][$TFSI^-$] were obtained as a light-yellow liquid. The yield was 87%.

OMIm-$N(CN)_2$

10.55 grams (45.7 mmol) of [$OMIm^+$][Cl^-] was mixed in 250mL acetonitrile with 4.99 grams (56.0 mmol, 23 % excess) of sodium dicyanamide, used as received from Sigma (98% purity). After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, 9.82 grams (37.5 mmol) of $[OMIM]^+[N(CN)_2]^-$ were obtained as a pale yellow liquid. The yield was 82%.

OMIm-TfO

5.91 grams (25.2 mmol) of [$OMIm^+$][Cl^-] was mixed in 250mL acetonitrile with 5.01 grams (56.1 mmol) of sodium dycianamide, used as received from Sigma (98% purity). After filtering, removal of acetonitrile by rotary evaporation and washing with methylene chloride, 6.86 grams (20.0 mmol) of [$OMIm^+$][TfO^-] were obtained as a yellow liquid. The yield was 79%.

MBPyr-TFSI

4.36 grams (18.9 mmol) of 4-methyl-N-butylpyridinium bromide, used as received from Solvent Innovation (98% purity), was mixed with 7.56 grams (24.0 mmol, 25% excess) of potassium TFSI in a flask containing 250mL acetonitrile. After filtering, removing acetonitrile by rotary evaporation and washing with methylene chloride, 7.53 grams (17.5 mmol) of [$MBPyr^+$][$TFSI^-$] were obtained as a light-yellow liquid. The yield was 93%.

MBPyr-NfO

5.16 grams (22.5 mmol) of 4-methyl-N-pyridinium bromide, from Solvent Innovation and recrystallized, was mixed with 10.0 grams (30.0 mmol, 33% excess) of potassium nonaflate in a flask containing 250mL acetonitrile. After filtering, removing acetonitrile by rotary evaporation and washing with methylene chloride, 9.02 grams (20 mmol) of [$MBPyr^+$][NfO^-] were obtained as a light-yellow liquid. The yield was 90%.

MBPyr-TfO

2.34 grams (10.0 mmol) of 4-methyl-N-pyridinium bromide, from Solvent Innovation and recrystallized, was mixed with 2.30 grams (12.2 mmol, 20% excess) of potassium triflate in a flask containing 100mL acetonitrile. After filtering, removing acetonitrile by rotary evaporation and washing with methylene chloride, 2.70 grams (8.9 mmol) of [$MBPyr^+$][TfO^-] were obtained as a light-yellow liquid. This ionic liquid was further purified by mixing 100mg of silver triflate with [$MBPyr^+$][TfO^-] in 15mL of methylene chloride. After filtering, removing the methylene chloride, a white-yellow solid was obtained. The yield was 89%.

MBPyr-$N(CN)_2$

12.69 grams (55.0 mmol) of 4-methyl-N-pyridinium bromide, from Solvent Innovation and recrystallized, was mixed with 6.0 grams (67.0 mmol, 22% excess) of sodium dicyanamide in a flask containing 250mL acetonitrile. After filtering, removing acetonitrile by rotary evaporation and washing with methylene chloride, the product was recrystallized twice with acetonitrile and ethyl acetate. 5.5 grams (26.0 mmol) of [$MBPyr^+$][TfO^-] were obtained as a light-yellow solid. The yield was 93%.

Physico-chemical properties

Melting and glass-transition temperatures:

Table 1 shows melting points measured by differential scanning calorimetry (DSC). Five of the eight ionic liquids synthesized here are liquid at room temperature. Ionic liquids were dried in a drying pistol and stored in a glove box prior to DSC measurements.

Ionic liquids containing nonaflate have melting points above 25°C. In air, $[OMIm^+][NfO^-]$ is metastable at room temperature because it is hygroscopic. $[OMIm^+][TFSI^-]$ exhibits no melting points. Instead, very low glass-transition temperatures are observed, e.g. -86°C.

For the same anion, melting points for ionic liquids based on $[OMIm^+]$ cations [24] are lower than those for ionic liquids based on 1-methyl-3-butylimidazolium ($[BMIM^+]$) cations. This observation is in accord with literature reports for ionic liquids based on tetrafluoroborate anions [**8**].

When the $[BMIm^+]$ cation is substituted with a $[MBPyr^+]$ cation, ionic liquids exhibit higher melting points. $[BMIm^+][TFSI^-]$, for example, shows only a glass-transition at -86°C (as compared to -81°C obtained by Crosthwaite et al. [22]) whereas $[MBPyr^+][TFSI^-]$ shows a melting point at 14°C. Surprisingly, no melting point has been observed 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:

Thermo-gravimetric analysis (TGA) provides information concerning thermal stability. All ionic liquids discussed here are thermally stable to 200°C. For most of our dried ionic liquids, the TGA curve exhibits some minor weight loss (~1%) below 200°C, indicating the presence of volatile impurities.

Thermal stability is mostly determined by the nature of the anion. For every type of cation, the thermal stability follows the trend: $T_d(\mathrm{TFSI}) > T_d(\mathrm{NfO}) > T_d(\mathrm{TfO}) > T_d(\mathrm{N(CN)_2})$.

Density:

Densities of ionic liquids were measured gravimetrically with a 1-ml volumetric flask. Results are collected in Table 1.

All ionic liquids that are liquid at room temperature are more dense than water, due to the anions used. The density of $[MBPyr^+][TfO^-]$ has been measured before its purification with silver triflate. The density of $[OMIm^+][TFSI^-]$ has already been reported previously [15, 19]. Reported values are $1.36 g.cm^{-3}$ [15] and $1.32 g.cm^{-3}$ [19]. The latter density is in accord with our measurement, 1.31 ± 0.01 $g.cm^{-3}$.

Compared to ionic liquids based on $[BMIm^+]$, $[OMIm^+]$ cations lead to less dense ionic liquids, due to an increase in the alkyl chain length, as reported previously [12, 19 24]. Substitution of imidazolium cation with $[MBPyr^+]$ cation, on the other hand, leads to an increase in density when the imidazolium cation is $[BMIm^+]$ or $[OMIm^+]$.

Solubility:

Only ionic liquids based on nonaflate and TFSI 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 211nm; this wavelength corresponds to the wavelength of maximum absorption for the N-methylimidazole group. For an ionic liquid 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 concentration of ionic liquid (between 0.001 and 0.02 wt%) 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.

[$OMIm^+$][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.

Ionic liquids based on dicyanamide or triflate anions are soluble in water. For nonaflate or TFSI anions, ionic liquids based on [$OMIm^+$] and [$MBPyr^+$] cations are insoluble in water.

For the same cation ($TFSI^-$ or NfO^-), ionic liquids based on [$OMIm^+$] and [$MBPyr^+$] cations have lower solubilities in water than ionic liquids based on [$BMIm^+$] cation. For TFSI anions, the solubility in water decreases from 1.6 wt% [25] (or 0.8 wt% [15]) for [$BMIm^+$][$TFSI^-$] to 0.22 wt% for [$OMIm^+$][$TFSI^-$] (literature reports 0.21 wt% [15] for [$OMIm^+$][$TFSI^-$]) and to 0.48 wt% for [$MBPyr^+$][$TFSI^-$]. For nonaflate anions, the solubility in water decreases from 17.5 wt% [25] for [$BMIm^+$][NfO^-] to 0.16 wt% for [$OMIm^+$][NfO^-] and 2.29 wt% for [$MBPyr^+$][NfO^-].

In general, longer alkyl chains lead to lower solubilities in water, due to the increase in hydrophobicity of the alkyl chain. This observation is in accord with literature reports [16, 24, 25]. Pyridinium cations lead to lower solubilities as compared to imidazolium cations, perhaps due to the presence of one nitrogen in the pyridinium cation, as compared to two nitrogens in the imidazolium cation.

Solvent polarity: $E_T(30)$ 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 [30].

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 in kcal/mol units, corresponding to the energy required to go from the ground state to the excited state.

For a given solvent, the $E_T(30)$ scale is obtained from the wavelength of maximum absorption λ_{max} of Reichardt's dye dissolved in that solvent:

$$E_T(30) \text{ (in kcal/mol)} = 28591/\lambda_{max}$$

with λ_{max} in nm.

$E_T(30)$ polarities have been reported in the literature [24] for several ionic liquids based on imidazolium cations but, to our best knowledge, there are no published data for ionic liquids containing pyridinium cations. Polarities for the latter type of ionic liquid are reported here.

Table 2 gives polarity data for four ionic liquids: $[OMIm^+]$ $[TFSI^-]$, $[OMIm^+]$ $[N(CN)_2^-]$, $[OMIm^+][TfO^-]$ and $[MBPyr^+][TFSI^-]$. Table 2 shows the wavelength of maximum absorption for Reichardt's dye in these ionic liquids, along with the resulting $E_T(30)$ scales. 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, 31], the polarities of ionic liquids based on imidazolium cations mostly depend on the nature of 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; $[OMIm^+][TFSI^-]$ and $[OMIm^+]$ $[N(CN)_2^-]$ have essentially the same $E_T(30)$.

Four ionic liquids synthesized here contain pyridinium cations. These ionic liquids are used as catalysts or solvents in organic chemistry [3, 9].

Table 2 shows that pyridinium ionic liquids are more polar than those containing imidazolium cations. $[OMIm^+][TFSI^-]$ polarity is 51.5, whereas that for $[MBPyr^+]$ $[TFSI^-]$ is 58.8. This difference in polarity is consistent with the previous observation that the polarity of an ionic liquid is mainly determined by the nature of the cation.

A previous attempt to increase the polarity of imidazolium ionic liquids has been made [27] by inserting ether, ketone or alcohol groups into the alkyl chain of the cation. For example, the polarity for $[BMIm^+][TFSI^-]$, 51.9, increases to 60.8 for 1-(2-hydroxyethyl)-3-methyl imidazolium TFSI.

Considering the high polarities of alkyl-pyridinium ionic liquids, substitution of hydroxyl groups into the alkyl chain of the pyridinium cation may lead to a new class of tunable solvents with high polarities.

Conclusion

Eight ionic liquids have been synthesized; they are based on 1-methyl-3-octylimidazolium or 4-methyl-N-butylpyridinium cations. Their densities, melting points and decomposition temperatures have been measured.

We find a general trend in the influence the alkyl-chain length and the nature of the cation on the physico-chemical properties of ionic liquids: with similar anions, ionic liquids based on 1-methyl-N-butylpyridinium cations exhibit higher melting points, higher densities but lower water solubilities than those for ionic liquids based on 1-methyl-3-butylimidazolium or 1-methyl-3-octylimidazolium cations. On the other hand, ionic liquids based on 1-methyl-3-octylimidazolium have lower melting points, lower densities and lower water solubilities than their 1-methyl-3-butylimidazolium homologues.

Polarities were measured spectroscopically using Reichardt's dye. The polarities of ionic liquids are mostly determined by the cation. Ionic liquids based on 1-methyl-3-octylimidazolium cations have polarities similar to that of ethanol. Ionic liquids based on 1-methyl-3-butylpyridinium cations have higher polarities.

Table 1- Densities, melting points (T_m), glass-transition temperatures (T_g) and decomposition temperatures (T_d) and solubilities in water for several ionic liquids. All temperatures are °C.

Ionic Liquid	Density (g/ml) at 25°C	T_m [a]	T_g	T_d	Solubility in water (wt%) at 25°C [b]
OMIM TFSI	1.31	-	-86	>300	0.21
OMIM TfO	1.12	-40	-5	>275	S
OMIM NfO	1.33	36	-86	>250	0.16
OMIM $N(CN)_2$	1.00	-49	-89	>150	S
MBPyr TFSI	1.35	14	-82	>300	0.48
MBPyr TfO	1.17	38	-68	>250	S
MBPyr NfO	solid	70	32	>250	2.29
MBPyr $N(CN)_2$	solid	51	-38	>180	S
BMIM TFSI	1.44[c]	-2[c] (-6[d])	-86[c] (-87[d])	330[c]	1.6[d] (0.8[e])
BMIM TfO	1.30[c]	13[c] (16[d])	-19[c]	230[c]	S
BMIM NfO		20[d]		>250	17.5[d]
BMIM $N(CN)_2$	1.06[c]	-6[c]	-90[c]	240[c]	S

[a] [OMIM$^+$][TFSI$^-$] has no melting point. [b] S indicates an ionic liquid soluble in water. [c]: Taken from ref. 19. [d]: Taken from ref. 25. [e]: Taken from ref. 15.

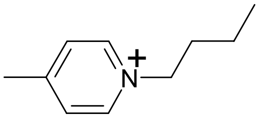
Table 2- Solvatochromic shifts of Reichardt's dye in several ionic liquids and the corresponding $E_T(30)$ polarity scales. For comparison, results are also shown for three common solvents.

Liquid	λ_{max} (nm)	$E_T(30)$ (kcal/mol)
$[BMIM]^+ [PF_6]^-$	546 ^{b}	52.4
$[OMIM]^+ [TFSI]^-$	559	51.1
$[OMIM]^+[N\text{-}(CN)2]^-$	559	51.1
$[OMIM]^+[TfO]^-$	558	51.2
$[MBPyr]^+[TFSI]^-$	485	59.0
Water ^{a}	453	63.1
Ethanol ^{a}	551	51.9
DMSO ^{a}	634	45.1

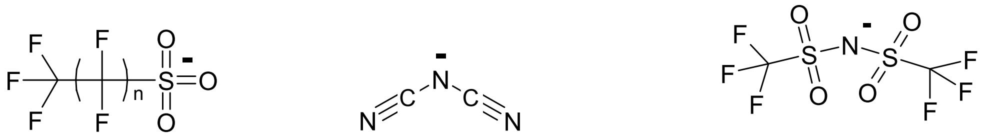
^{a} From ref. 24. ^{b} literature value: 546 nm [24].

1-Methyl-3-butylimidazolium cation [BMIm$^+$]

1-Methyl-3-octylimidazolium cation [OMIm$^+$]



4-Methyl-N-butylpyridinium cation [MBPyr$^+$]



n=0 triflate anion
n=3 nonaflate anion

dicyanamide anion

bis(trifluoromethylsulfonyl)imide anion (TFSI)

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

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