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> SHORT COMMUNICATIONS

Synthesis and Properties of Hydroxyl-Containing Ionic Liquids

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Abstract—Hydroxyl-containing ionic liquids were synthesized by quaternization of 1,2-dimethyl-1*H*-imidazole, *N*-methylpyrrolidine, and pyridine with 2-chloroethanol or 6-chlorohexan-1-ol, followed by exchange of chloride ion for bis(trifluoromethanesulfonyl)azanide, and their properties were studied.

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Ionic liquids (ILs) are organic quaternary salts melting in the range from room temperature to 100°C [1, 2]. Specific properties of ionic liquids, such as high polarity, low saturated vapor pressure, high thermal stability, and low viscosity, have determined their wide application as polar media in organic synthesis [3, 4], catalysis [5, 6], and electrochemistry [7–9]. The use of ILs in various chemical processes conforms to the main "green chemistry" principles. Herein we describe the synthesis of ionic liquids whose volatility was reduced by an order of magnitude via introduction of polar groups capable of being involved in additional intermolecular interactions.

The simplest and most convenient method for the preparation of ionic liquids is based on alkylation of nitrogen-containing compounds with alkyl halides. Quaternization of 1,2-dimethyl-1*H*-imidazole, *N*-methylpyrrolidine and pyridine with 2-chloroethanol and 6-chlorohexan-1-ol afforded the corresponding chlorides. Regardless of the side chain length, the products were solids under normal conditions. In order to obtain ILs 1–4, the chloride ion was replaced by bulky bis-(trifluoromethanesulfonyl)azanide ion. The latter was selected due to its high thermal stability and the ability to ensure low viscosity.

The thermal stability of ILs **1–4** was studied by thermogravimetric analysis. Thermal decomposition of quaternary ammonium salts with liberation of tertiary amines follows two paths, retro-Menshutkin reaction and Hofmann elimination [10]. Thermal decomposition of imidazolium cations and other cyclic ammonium ions is also accompanied by liberation of amine



via cleavage of the aromatic ring by the anion [11, 12]. The presence of a hydroxy group usually reduces thermal stability. However, all ILs **1–4** were stable up to 390–400°C (Table 1); i.e., their thermal stability was similar to the thermal stability of analogous ILs containing no hydroxy group [11, 13]. This may be rationalized by reduced reactivity of OH groups in thermal decomposition processes due to their interactions with polar fragments of ionic liquids, cations and anions. The decomposition temperature of pyrrolidine-based IL (3) almost did not differ from those of ILs 1, 2, and 4 based on imidazole and pyridine (Table 1), though cations derived from aromatic compounds are known to be more stable [10, 14].

The decomposition point determines the upper limit of the working temperature range of a ionic liquid, while the lower limit is determined by its crystallization temperature. The data on the aggregate state of ionic liquids at temperatures below ambient were obtained by differential scanning calorimetry (DSC, Table 1). For ILs **1**, **2**, and **4** with aromatic cations we succeeded in measuring experimentally only glasstransition temperature (ca. -70° C). The state of IL **3** with an aliphatic cation was characterized by two melting peaks at -21 and 14° C. This ionic liquid is likely to form a mesophase in addition to the crystalline phase [15].

The kinematic viscosity of ILs 1–4 was measured with an Ostwald viscometer (Table 1). All ILs had a viscosity lower than 200 cSt at 30°C, and the viscosity increased in the series 4 < 3 < 1 for ILs with the same hydroxyl-containing substituent in the cation. Change of the length of the side chain in imidazole derivatives from n = 2 (1) to n = 6 (2) increases the viscosity almost 2.5 times. This is difficult to rationalize taking into account only increase of the molecular weight of IL due to elongation of the substituent. Presumably, the presence of a 6-hydroxyhexyl substituent in the cation favors stronger intermolecular inter-

Table 1. Properties of hydroxyl-containing ionic liquids

Ionic liquid	t _{glass,} ℃	t _{decomp} , °C	Viscosity at 30°C, cSt	Volatility (220°C), ^a mg cm ⁻² h $^{-1}$	Density at 25°C, g/mL
1	-68	431	84.5	8.01	1.542
2	-63	401	186.4	1.07	1.416
3	14 ^b	402	52.1	2.93	1.520
4	-71	387	51.0	4.20	1.592

^a In a vacuum (~0.013 Pa).

^b Melting point for the highest temperature peak.

action of the OH group with charged structural fragments of the IL due to conformational factors, which leads to increased viscosity. The temperature dependences of the viscosities of hydroxyl-containing ILs, as well as of other ionic liquids, are well described by the Vogel–Tamman–Fulcher equation [16] for melts.

The volatility of ILs 1–4 was evaluated using a McBain quartz spring balance [17]. The vapor pressure increases in the series Pyr (3) < Py (4) < Im (1) for ILs with a 2-hydroxyethyl group in the cation and is determined by ion pair interactions. The volatilities of imidazolium derivatives 1 and 2 differ by a factor of 8, which may be due not only to increase of the molecular weight but also enhanced intermolecular interactions facilitated by increased length of the substituent. The volatility of ILs containing a hydroxy group in the cation is lower by more than an order of magnitude than that of analogous ionic liquids having no hydroxy group (30–50 mg cm⁻² h) [18].

Ionic liquids 1-4 have a fairly high density (1.5– 1.6 g/mL; Table 1). The presence of a hexyl substituent in the cation of **2** is likely to be responsible for the lower density of this ionic liquid.

Thus, hydroxyl-containing ionic liquids are characterized by low viscosity, high thermal stability, and low volatility which is lower by an order of magnitude than the volatility of classical (i.e., containing no OH groups) ionic liquids.

Compounds 1-4 (general procedure). Quaternization of 1,2-dimethyl-1*H*-imidazole, 1-methylpyrrolidine, and pyridine with an equimolar amount of 2-chloroethanol or 6-chlorohexan-1-ol was carried out in acetonitrile (50% solution) under reflux for 48 h. A 50% solution of lithium bis(trifluoromethanesulfonyl)azanide (1.1 equiv) in acetonitrile was then added, and the mixture was stirred for 30 min. The solvent was distilled off under reduced pressure, and the residue was washed with water to remove lithium salts. The product was dried under reduced pressure at 100°C for 10 h.

1-(2-Hydroxyethyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)azanide (1). Yield 91%. ¹H NMR spectrum, δ, ppm: 2.58 s (3H, 2-CH₃), 3.70 m (2H, CH₂O), 3.76 s (3H, 3-CH₃), 4.18 m (2H, CH₂N), 5.08 br.s (1H, OH), 7.60 m (2H, 4-H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 9.65, 34.90, 50.71, 60.04, 113.53, 117.79, 121.61, 122.05, 122.48, 126.31. Found, %: C 25.57; H 3.04; F 27.15; N 10.01; S 15.05. C₉H₁₃F₆N₃O₅S₂. Calculated, %: C 25.66; H 3.11; F 27.05; N 9.97; S 15.22. **1-(6-Hydroxyhexyl)-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)azanide (2).** Yield 91%. ¹H NMR spectrum, δ , ppm: 1.29 m (4H, CH₂), 1.39 m (2H, CH₂), 1.70 m (2H, CH₂), 2.57 s (3H, 2-CH₃), 3.38 m (2H, CH₂O), 3.74 s (3H, 1-CH₃), 4.09 m (2H, CH₂N), 4.35 br.s (1H, OH), 7.62 m (2H, 4-H, 5-H). ¹³C NMR spectrum, δ_{C} , ppm: 9.25, 25.32, 25.81, 29.55, 32.61, 34.85, 48.00, 61.01, 113.52, 117.78, 121.13, 122.04, 122.60, 126.31, 144.49. Found, %: C 32.47; H 4.28; F 23.94; N 9.01; S 13.48. C₁₃H₂₁F₆N₃O₅S₂. Calculated, %: C 32.70; H 4.43; F 23.88; N 8.80; S 13.43.

1-(2-Hydroxyethyl)-1-methylpyrrolidinium bis-(trifluoromethanesulfonyl)azanide (3). Yield 87%. ¹H NMR spectrum, δ, ppm: 2.08 m (4H, 3-H, 4-H), 3.04 s (3H, CH₃), 3.42 m (2H, CH₂O), 3.51 m (4H, 2-H, 5-H), 3.84 m (2H, CH₂N), 5.27 br.s (1H, OH). ¹³C NMR spectrum, δ_{C} , ppm: 21.23, 48.38, 55.96, 64.74, 65.10, 113.52, 117.79, 122.05, 126.31. Found, %: C 26.41; H 3.99; F 27.71; N 6.87; S 15.45. C₉H₁₆F₆N₂O₅S₂. Calculated, %: C 26.34; H 3.93; F 27.78; N 6.83; S 15.63.

1-(2-Hydroxyethyl)pyridinium bis(trifluoromethanesulfonyl)azanide (4). Yield 92%. ¹H NMR spectrum, δ, ppm: 3.38 m (2H, CH₂O), 4.67 m (2H, CH₂N), 5.26 br.s (1H, OH); 8.14 m (2H), 8.60 m (1H), and 8.99 m (2H) (C₅H₅N). ¹³C NMR spectrum, δ_{C} , ppm: 60.37, 63.85, 113.50, 117.75, 122.01, 126.27, 127.94, 145.25, 145.73. Found, %: C 26.59; H 2.44; F 28.17; N 6.91; S 15.73. C₉H₁₀F₆N₂O₅S₂. Calculated, %: C 26.74; H 2.49; F 28.19; N 6.93; S 15.86.

The ¹H and ¹³C NMR spectra were measured on a Bruker AM-300 spectrometer from solutions in DMSO- d_6 using tetramethylsilane as internal standard. Thermogravimetric analysis was performed on a MOM Derivatograph-C (Hungary) in an argon atmosphere at a heating rate of 10 deg/min (sample weight ~20 mg). The glass transition temperatures were determined by differential scanning calorimetry with a Mettler-Toledo DSC-822e instrument (temperature range -100 to 100°C; heating rate 10 deg/min, argon atmosphere). The kinematic viscosities were measured using an Ostwald viscometer (capillary diameter 1.2 mm); the viscometer was calibrated at 25°C using ethylene glycol (Aldrich, 99.8%, water content < 0.01%) as reference. The densities were determined with a 1-mL pycnometer calibrated against distilled water. The volatilities of ILs in a vacuum were determined with a McBain quartz spring balance. Stretching of the

spring was measured with an accuracy of ± 0.02 mm using a KM-8 cathetometer.

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