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Hydroxyl-containing ionic liquids as heat-transfer agents

Vladimir G. Krasovskiy,*[a] Elena A. Chernikova,[a] Lev M. Glukhov,[a] Elena A. Redina,[a] Gennady I. Kapustin,[a] Anatoliy A. Koroteev[b] and Leonid M. Kustov[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 137 2935; e-mail: miyusha@mail.ru*
[b] *Moscow Aviation Institute, 125993 Moscow, Russian Federation*

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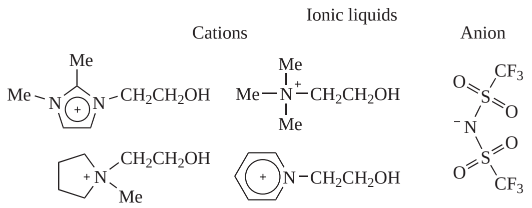
Bis(trifluoromethylsulfonyl)imide ionic liquids containing hydroxyl groups in the cation structure were synthesized. Their thermal stabilities were estimated, melting points, viscosities, and volatilities *in vacuo* were determined. The possibility of using the synthesized ionic liquids as heat-transfer agents in high vacuum is shown.



Ionic liquids (ILs) are extensively used in various fields of science and technology. The latest achievements are related to their application both as lubricants in various apparatus (for example, in combustion engines)[1–4] and as heat-transfer agents for heat management.[5–7] ILs with long alkyl chains in both cations and anions are used as lubricants. Bis(trifluoromethylsulfonyl)imide ILs mixed with various nano-objects with high thermal conductivity coefficients (graphite nanotubes, metal particles, *etc*.) are supposed to be employed as heat-transfer fluids. Hydroxyl-containing ILs are applied as solvents in organic chemistry and electrochemistry, as catalysts and substrates for catalytic reactions, for absorption and separation of gases, as reducing agents and stabilizers in the preparation of metal nanoparticles.[8] In recent years, the possibility of using ILs as heat-transfer agents for heat uptake in high vacuum have been reported[9–11] in so far as the specific nature of ILs provides a set of unique properties, *viz*. high thermal stability, low viscosity and very low volatility among all known liquids.[12–14] In our opinion, the presence of polar groups capable of intermolecular interactions should additionally reduce the volatility of the liquid *in vacuo*. This article is devoted to the synthesis of ILs containing hydroxyl groups in the cation and to the investigation of both their properties and potential for their use as heat-transfer fluids under high vacuum conditions.

ILs **1**, **2** and **4** (Figure 1) were synthesized in two stages *via* quaternization of 1,2-dimethylimidazole, *N*-methylpyrrolidine,

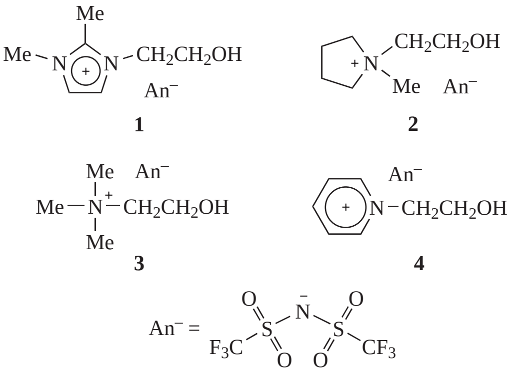


Figure 1 Hydroxyl-containing ionic liquids.

and pyridine with 2-chloroethanol, followed by the replacement of chloride anion with bis(trifluoromethylsulfonyl)imide anion (Scheme 1).[†] Choline bis(trifluoromethylsulfonyl)imide was prepared from choline chloride. The anion was chosen because it provides low viscosity and high thermal stability of the resulting ILs.[8,15]

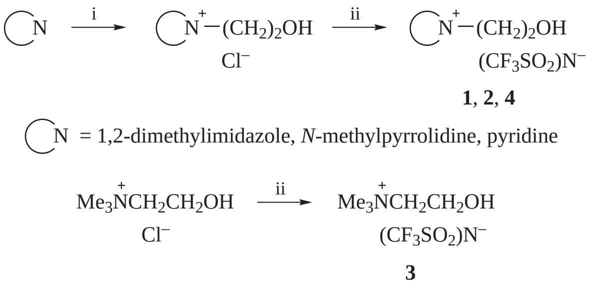
Three of the four synthesized ILs (**1**, **2** and **4**) are liquid at room temperature, and salt **3** is a solid crystalline substance.

The thermal stability of the synthesized ILs was studied by thermogravimetric analysis (TGA).[†] Thermal decomposition of

[†] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer (300.13 and 75.47 MHz). FT-IR spectra were measured on a Nicolet iS50 IR spectrometer using an attenuation total reflectance (built-in attachment, crystal-diamond, resolution 4 cm^{-1}, 32 Sc). TGA was performed on a Derivatograph-C instrument (MOM) in argon atmosphere at a heating rate of 10 K min^{-1} (sample mass was ~20 mg). The melting points and glass transition temperatures of ILs were determined *via* DSC using a DSC-822e instrument (Mettler-Toledo). Glass transition temperatures were determined in the temperature range of –100 to 100 °C at a heating rate of 10 K min^{-1} in argon atmosphere. Kinematic viscosity was measured using an Ostwald viscosimeter placed in a well-stirred thermostatic (±0.5 °C) oil bath and calibrated at 25 °C using ethylene glycol (Aldrich, 99.8%) as the reference liquid. The evaporation of ILs *in vacuo* was studied using a McBain quartz spring balance. Each sample (~0.2 g) was placed in a quartz cup attached to the movable end of the spring of the balance. The surface area of the liquid was about 1.7 cm^2. Tubes containing the samples were placed in a thermostated aluminum block. Spring elongation was determined from the change in the positions of reference marks using a KM-8 cathetometer with the accuracy of ±0.02 mm. The spring had a sensitivity of 0.3709 mm mg^{-1}. The setup was evacuated with a diffusion pump. Before measurements, the samples were dried to constant weight (for ~15 h) directly in the setup *in vacuo* (at least 10^{-4} Torr) at 100 °C.

General procedure for the synthesis of compounds **1**–**4**. The reaction of quaternization was carried out in acetonitrile (50% solution) at the solvent boiling point for 48 h. The reagents were taken in an equimolar ratio. Lithium bis(trifluoromethylsulfonyl)imide (10% excess) was added to the solution, and the reaction mixture was stirred for 30 min. After that, the solvent was evaporated *in vacuo* and the residue was washed with water to remove lithium salts. The obtained ILs were dried *in vacuo* at 100 °C for 10 h. Choline bis(trifluoromethylsulfonyl)imide was prepared from choline chloride (Sigma-Aldrich).

For more details, see Online Supplementary Materials.



Scheme 1 *Reagents and conditions*: i, $ClCH_2CH_2OH$, ii, $LiN(SO_2CF_3)_2$.

quaternary ammonium salts affords tertiary amines *via* two ways, reverse Menschutkin reaction and Hofmann elimination.[16] In the course of thermal decomposition of imidazolium and other cyclic cations, the amines are formed resulting from cleavage of the ring by an anion.[17,18] Commonly, the presence of hydroxyl groups in the structure decreases its thermal stability. Nevertheless, all the synthesized ILs show high thermal stability up to 390–400 °C (Table 1). That fact is most likely caused by a decrease in the OH group activity due to the interaction between OH groups and polar fragments of the IL, both cations and anions. The decomposition temperature of ILs **2**, **3** with aliphatic cations (Figure 2, curves *2* and *3*) is practically the same as that of imidazolium and pyridinium ILs **1**, **4** (curves *1* and *4*) in spite of the fact that the thermal stability of ILs with aromatic cations is known to be generally higher.[8,16]

1,2-Dimethyl-3-(2-hydroxyethyl)imidazolium bis(trifluoromethylsulfonyl)-imide **1**. Yield 91%. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ: 2.58 (s, 3H, MeC), 3.70 (m, 2H, CH_2O), 3.76 (s, 3H, MeN), 4.18 (m, 2H, CH_2N), 5.08 (br. s, 1H, OH), 7.60 (m, 2H). ^{13}C NMR (76.47 MHz, DMSO-d_6) δ: 9.65 (C*Me*), 34.90 (NMe), 50.71 (CH_2O), 60.04 (CH_2N), 113.53, 117.79, 122.05, 126.31 (quart., CF_3, *J* 321.55 Hz), 121.61, 122.48, 145.22 ($C_3H_2N_2$). FTIRS (ATR, ν/cm^{-1}): 3538 (OH), 3188–3094 (CH in $C_3H_2N_2$), 2962–2891 (CH in Me and CH_2), 1591 (C=C), 1346 (SO_2), 1177 (CF_3), 1132 (SO_2), 1050 (SO_2), 740 (CF_3), 568 (CF_3), 519 (CF_3). Found (%): C, 25.57; H, 3.04, F, 27.15; S, 15.05; N, 10.01. Calc. for $C_9H_{13}N_3O_5F_6S_2$ (%): C, 25.66; H, 3.11; F, 27.05; S, 15.22; N, 9.97.

N-*Methyl*-N-*(2-hydroxyethyl)pyrrolidinium bis(trifluoromethylsulfonyl)-imide* **2**. Yield 87%. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ: 2.08 (m, 4H, CH_2 pyrrolidine), 3.04 (s, 3H, Me), 3.42 (m, 2H, CH_2N), 3.51 (m, 4H, NCH_2 pyrrolidine), 3.84 (m, 2H, CH_2O), 5.27 (br. s, 1H, OH). ^{13}C NMR (76.47 MHz, DMSO-d_6) δ: 21.23 (CH_2 pyrrolidine), 48.38 (Me), 55.96 (NCH_2 pyrrolidine), 64.74 (CH_2O), 65.10 (CH_2N), 113.52, 117.79, 122.05, 126.31 (quart., CF_3, *J* 321.55 Hz). FTIRS (ATR, ν/cm^{-1}): 3537 (OH), 2979–2902 (CH in Me and CH_2), 1347 (SO_2), 1177 (CF_3), 1131 (SO_2), 1050 (SO_2), 741 (CF_3), 569 (CF_3), 509 (CF_3). Found (%): C, 26.41; H, 3.99; F, 27.71; S, 15.45; N, 6.87. Calc. for $C_9H_{16}N_2O_5F_6S_2$ (%): C, 26.34; H, 3.93; F, 27.78; S, 15.63; N, 6.83.

Trimethyl(2-hydroxyethyl)ammonium bis(trifluoromethylsulfonyl)imide **3**. Yield 81%. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ: 3.10 (m, 9H, 3Me), 3.41 (m, 2H, CH_2N), 3.84 (m, 2H, CH_2O), 5.27 (br. s, 1H, OH). ^{13}C NMR (76.47 MHz, DMSO-d_6) δ: 53.61 (t, Me, *J* 3.90 Hz), 55.59 (CH_2O), 67.51 (t, CH_2N, *J* 2.80 Hz), 113.50, 117.76, 122.02, 126.28 (quart., CF_3, *J* 321.55 Hz). FTIRS (ATR, ν/cm^{-1}): 3531 (OH), 2971–2852 (CH in Me and CH_2), 1346 (SO_2), 1177 (CF_3), 1131 (SO_2), 1050 (SO_2), 741 (CF_3), 570 (CF_3), 510 (CF_3). Found (%): C, 21.74; H, 3.71; F, 29.67; S, 16.69; N, 7.25. Calc. for $C_7H_{14}N_2O_5F_6S_2$ (%): C, 21.87; H, 3.67; F, 29.66; S, 16.97; N, 7.29.

N-*(2-Hydroxyethyl)pyridinium bis(trifluoromethylsulfonyl)imide* **4**. Yield 92%. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ: 3.38 (m, 2H, CH_2O), 4.67 (m, 2H, CH_2N), 5.26 (br. s, 1H, OH), 8.14–8.99 (m, 5H, C_5H_5N). ^{13}C NMR (76.47 MHz, DMSO-d_6) δ: 60.37 (CH_2O), 63.85 (CH_2N), 113.50, 117.75, 122.01, 126.27 (quart., CF_3, *J* 321.55 Hz), 127.94–145.73 (C_5H_5N). FTIRS (ATR, ν/cm^{-1}): 3531 (OH), 3221–3073 (CH in C_5H_5N), 2947–2891 (CH in CH_2), 1637 (C=C), 1346 (SO_2), 1175 (CF_3), 1131 (SO_2), 1050 (SO_2), 740 (CF_3), 569 (CF_3), 519 (CF_3). Found (%): C, 26.59; H, 2.44; F, 28.17; S, 15.73; N, 6.91. Calc. for $C_9H_{10}N_2O_5F_6S_2$ (%): C, 26.74; H, 2.49; F, 28.19; S, 15.86; N, 6.93.

Table 1 Thermophysical characteristics of hydroxyl-containing ionic liquids.

IL	mp / °C [a]	$T_{decomp.}$ / °C	Viscosity (30 °C) / cSt	Volatility [c] (220 °C) / mg cm^{-2} h^{-1}
1	–72 [b]	431	84.5	8.01
2	14	402	52.1	2.93
3	34	391	–	1.73
4	–71 [b]	387	51.0	4.20

[a] The value corresponding to the DSC peak with highest temperature. [b] T_g. [c] *In vacuo* (~0.013 Pa).

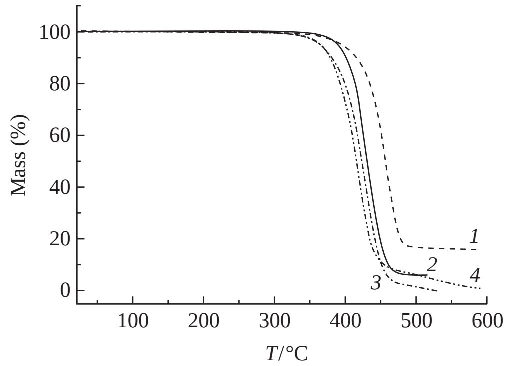


Figure 2 TGA curves (*1*)–(*4*) of ILs **1**–**4**, respectively, in argon atmosphere.

The decomposition temperature defines the upper limit of the working temperature interval of IL. The lower limit is restricted by its crystallization temperature. Data on the states of ILs below room temperature measured by differential scanning calorimetry (DSC) are given in Table 1. Under the experimental conditions, it was impossible to measure the melting temperatures of ILs **1** and **4** with heteroaromatic cations. Their glass transition temperatures (*ca.* –70 °C) were only determined. ILs **2** and **3** with aliphatic cations show more complex DSC curves with several melting peaks observed at –21 and 14 °C (**2**), −9, 1, 27 and 34 °C (**3**). For these liquids, along with the crystalline phase, the existence of the mesophase can be assumed.[18]

The viscosity measured at 30°C for all studied ILs is lower than 100 cSt and increases depending on the cation type in the order pyridinium < *N*-methylpyrrolidinium < 1,2-dimethylimidazolium (see Table 1).† The viscosity *vs*. temperature dependences for the hydroxyl-containing ILs (Figure 3), like for most other ILs, are well approximated ($R^2 > 0.99$) by the Vogel–Tammann–Fulcher equation[19] for melts.

The study of the IL volatilities (Table 1, Figure 4)† has shown that ILs containing OH groups in the cation structure possess more than an order of magnitude lower volatility as compared with similar ILs without hydroxyl groups (30–50 mg cm^{-2} h^{-1}).[20] The order of decrease in the volatility values (**1** > **4** > **2** > **3**)

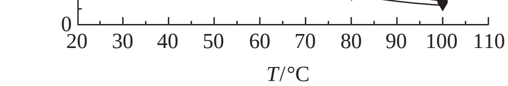


Figure 3 The temperature dependence of viscocity (*1*)–(*4*) for ILs **1**–**4**, respectively.

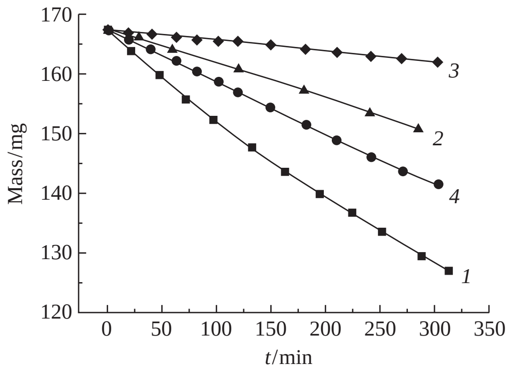


Figure 4 Normalized mass loss *vs*. time dependences (volatility) (*1*)–(*4*) for ILs **1**–**4**, respectively, *in vacuo* (~0.013 Pa) at 220 °C.

is in agreement with the values of the positive charge on the nitrogen atom in the IL cation estimated by XPS,[21–23] which increase in the same order. Probably, due to that, the interaction between structural fragments (ions and OH groups) of IL is enhanced affecting the volatility of ILs.

Thus, in this work we have shown that ILs with hydroxyl group are characterized by low viscosity, high thermal stability and by an order of magnitude lower volatility as compared with conventional (1,3-dialkylimidazolium, *N*-alkylpyridinium) ILs without hydroxyl groups. Being related with the nature of the cation, the volatility decreases by a factor of four within the following series of 2-hydroxyethyl substituted cations: 1,2-dimethylimidazolium > pyridinium > *N*-methylpyrrolidinium > trimethylammonium. The investigated hydroxyl-containing ILs possess a set of physical and chemical properties that allows one to use such ILs as heat-transfer fluids in high vacuum and even in space.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.11.022.

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