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Dicationic disiloxane ionic liquids

Vladimir G. Krasovskiy,*[a] Gennady I. Kapustin,[a] Lev M. Glukhov,[a] Olga B. Gorbatsevich,[b] Elena A. Chernikova,[a] Anatoly A. Koroteev[c] and Leonid M. Kustov[a,d]

[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] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation*

[c] *Moscow Aviation Institute, 125993 Moscow, Russian Federation*

[d] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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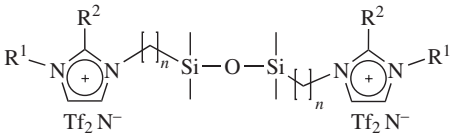
Bis(trifluoromethylsulfonyl)imide ionic liquids containing disiloxane linkers between imidazole cations were synthesized. Their hydrolytic and thermal stabilities were explored, and melting points, viscosities, and volatilities *in vacuo* were measured. The effect of nature of the substituents at imidazole cations on the set of properties of the synthesized ionic liquids was revealed.



Ionic liquids

R^1 = Me, CH_2CH_2OH, CH_2CH_2OMe, R^2 = H, Me, n = 1,3

Keywords: dicationic liquids, disiloxane linker, hydrolytic and thermal stability, viscosity, volatility.

High polarity and low volatility are the most important specific properties of ionic liquids (ILs), which make ILs useful in various fields of science and industry, in particular organic synthesis,[1,2] preparation of nanoparticles,[3,4] catalysis,[5,6] and electrochemistry.[7,8] Ionic liquids are successfully applied as extractants of various types of chemicals,[9,10] lubricants,[11,12] antistatics,[13] and heat-transfer agents.[14–16] In addition, ILs are widely used in green chemistry.[17–19]

The properties required for a practical application of ILs usually include low volatility and viscosity, as well as hydrolytic and thermal stability. The IL properties are significantly determined by the intermolecular interaction, whose strengthening leads to a decrease in volatility and an increase in viscosity of ILs. The decreased volatility is achieved *via* introducing polar groups into their structure, providing an additional interaction between the molecules due to the formation of hydrogen bonds. This usually causes a decrease in the thermal stability of ILs. An introduction of the second ion pair into the IL structure provides a decreased volatility resulting from increased Coulomb interactions, but at the same time, may lead to an increase in the IL melting point even above room temperature. Thus, a design of the IL possessing a specific set of properties is a kind of the optimization problem.

ILs containing bis(trifluoromethylsulfonyl)imide anion (Tf_2N^-) and imidazole cation without polar substituents are characterized by volatility of ~20–30 mg h^{-1} cm^{-2} at 0.013 Pa and 220 °C.[15] The presence in their cation structure of hydroxy groups capable of participating in intermolecular interactions diminishes the volatility of ILs to 10 mg h^{-1} cm^{-2}, but significantly increases their viscosity.[15,16] Introduction of a second ion pair into an IL structure reduces its volatility to values < 1 mg h^{-1} cm^{-2}, but increases the melting point up to ~60 °C or viscosity to 400–600 cSt.[19,20] To reduce the probability of crystallization of dicationic ionic liquids at room temperature, a siloxane moiety rather than methylene groups was used as a linker between cations.[20,21] The rotational energy barriers of Si–O and C–C bonds are 0.8 and 11.3 kJ mol^{-1}, and those for Si–Me and C–Me bonds are 6.7 and 15.1 kJ mol^{-1}, respectively.[22,23] The dissociation energy of the Si–O bond in hexamethyldisiloxane is 549 kJ mol^{-1}, and that of the C–C bond in ethane is 334 kJ mol^{-1}.[24]

The high bond energy and mobility of Si–O bonds are the reasons for high temperature resistance and low viscosity of siloxane compounds even at low temperatures. The operating temperature range of polydimethylsiloxane liquids is wider than 500 °C: from glass transition temperature (T_g = –70 °C) to decomposition temperatures (up to T_d = 450 °C). Introduction of polydimethylsiloxane linker allows one to obtain low-volatile *in vacuo* but rather viscous (500–1000 cSt at 30 °C) ILs even with the Tf_2N^- anion.[20] A decrease in the molecular mass of linker leads to a partial crystallization of the resulting ionic liquid. A content of the crystalline phase increases with decreasing molecular mass of the linker. The previously obtained dicationic ILs with a disiloxane linker were either solids (Mp = 50–70 °C) or very viscous liquids at room temperature (> 1300 cSt).[21,25,26] The purpose of this work was to synthesize dicationic imidazolium ILs containing the tetramethyldisiloxane linker characterized by low viscosity and volatility, high hydrolytic and thermal stability, and melting points below room temperature.

Ionic liquids **1**–**5** (Table 1) were synthesized in three steps (Scheme 1). At the first step, 1,3-di(chloroalkyl)tetramethyldisiloxane was obtained by hydrolytic condensation of the corresponding chlorosilane. The substituted imidazole was then quaternized with di(chloroalkyl)tetramethyldisiloxane in MeCN at its boiling point, giving the dichloride salt of target cation with the disiloxane linker. Finally, the chloride anion was exchanged for the Tf_2N^- one in MeCN solution. The target product was washed with water to remove the LiCl precipitate and dried using azeotropic distillation with thoroughly dehydrated CH_2Cl_2. The structures of synthesized ILs were confirmed by IR and ^1H, ^{13}C and ^{29}Si NMR spectroscopy and elemental analysis.

Table 1 Thermophysical characteristics of dicationic disiloxane ILs.

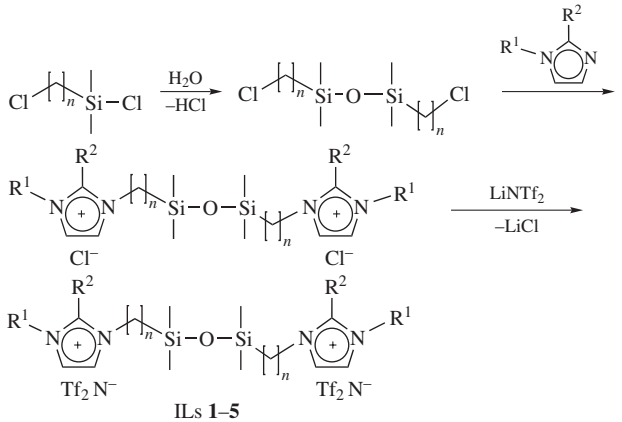
IL	Viscosity/cSt (30 °C)	Mp/°C (DSC)	T_d/°C (TGA)	Volatility/mg h^{-1} cm^{-2} at 150/190/220 °C[a]
1	–	69	437	0.00/0.03/0.04
2	–	59	419	0.01/0.02/0.17
3	602	–53[b]	391	0.02/0.12/0.35
4	555	–48[b]	416	0.02/0.22/0.94
5	344	–58[b]	402	0.03/0.33/0.95

[a] *In vacuo* (~0.013 Pa). [b] T_g.

The chloride precursors of ILs **1** and **2** obtained by quaternization of 1,2-dimethylimidazole, despite the different length of the spacer between the N and Si atoms, are crystalline solids at room temperature, while those of ILs **3**, **4** and **5** are highly viscous liquids at room temperature. All these chloride salts are soluble in water. The resulting disiloxane ionic liquids **1**–**5** are insoluble in water, even compound **3** with 2-hydroxyethyl groups.

The ionic liquids are characterized by low hydrolytic stability in the case of methylene group being a spacer between the imidazole and the silicon atom. During alkylation of 1,2-dimethylimidazole with 1,1,3,3-tetramethyl-1,3-di(chloromethyl)disiloxane, 1,2,3-trimethylimidazolium chloride is formed as a byproduct in the presence of even traces of water. The use of propylene spacer instead of methylene groups allows one to synthesize hydrolytically stable dicationic disiloxane ionic liquids due to an increase of the distance between the cations (Scheme 2).

Compound **1** is a solid with melting point of 69 °C (see Table 1). Replacement of methylene group between the Si and N atoms with propylene spacer reduces the melting point only by 10 °C (IL **2**, see Table 1). It is known that the introduction of polar groups into the cation reduces the tendency of an IL to crystallization.[15,27] IL **3** obtained from 1-(2-hydroxyethyl)imidazole remains in the liquid state at room temperature. However, the presence of a mobile proton and OH groups in the IL structure, which are involved in intermolecular interaction, leads to a high viscosity (~600 cSt at 30 °C) of this ionic liquid. Replacement of a hydroxy group with a methoxy one and the introduction of a methyl group at the second position of imidazole significantly reduces the IL viscosity (IL **4**), which is also liquid at room temperature. The lowest viscosity and melting point values were achieved for IL **5**. Ionic liquids **3**–**5** possess glass transition temperatures (T_g) from –58 to –48 °C, characteristic of siloxane compounds, due to the presence of functional groups capable of intermolecular interactions (*i.e.*, CH_2CH_2OH group) in the cation structure, or groups increasing its flexibility (like 2-methoxyethyl groups).

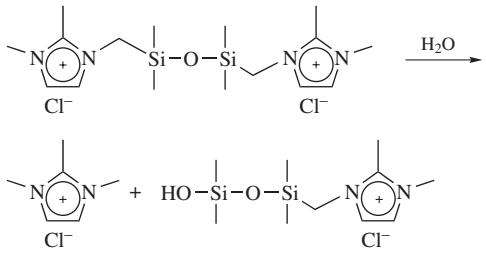


ILs **1**–**5**

Tf = CF_3SO_2

1 $R^1 = R^2 = Me$, $n = 1$
2 $R^1 = R^2 = Me$, $n = 3$
3 $R^1 = CH_2CH_2OH$, $R^2 = H$, $n = 3$
4 $R^1 = CH_2CH_2OMe$, $R^2 = Me$, $n = 3$
5 $R^1 =$ Me, $R^2 = H$, $n = 3$

Scheme 1



Scheme 2

The presence of polar groups in the IL cation affects not only their aggregate state, but also their thermal stability. If IL **1** (without polar groups in the cation) is characterized by the decomposition temperature of 437 °C (Figure 1), IL **3** bearing 2-hydroxyethyl groups shows the value of 391 °C. Replacement of the hydroxy group with a methoxy one leads to a lesser decrease in the decomposition temperature, only to 416 °C (IL **4**). The presence of mobile hydrogen atom at 2-position of imidazolium ring capable of interacting with an IL anion reduces the thermal stability of the disiloxane IL to 402 °C (IL **5**). Changing the aliphatic spacer length from C_1 to C_3 leads to a decrease in the thermal stability of IL **2** as compared to IL **1** by almost 20 °C (see Figure 1). Thus, dicationic disiloxane liquids with imidazole cations without polar groups and substituents at 2-position are the most thermally stable ones, but they are crystalline at room temperature. Either introduction of polar groups into the cation in order to reduce the IL melting point or elongation of a spacer between the N and Si atoms to increase the hydrolytic stability lead to a decrease in the thermal stability of disiloxane ILs.

The difference in the coke mass in TGA experiments for ILs **1**–**3** and **4**–**5** (see Figure 1) indicates various destruction mechanisms for ILs with different substituents in the cation.

Temperature dependences of the kinematic viscosity for ILs **3**–**5** (Figure 2), like for most other ionic liquids, are well approximated ($R^2 > 0.99$) by the Vogel–Tamman–Fulcher equation,[28] describing the temperature dependence of melt viscosity. The presence of polar groups in the cation strengthening intermolecular interactions increases the IL viscosity. The viscosities of ILs **3**–**5** are determined by the nature of the substituents at the imidazole cation and increase in the following order: H < $MeOCH_2CH_2$ < $HOCH_2CH_2$ (see Figure 2). The influence of siloxane nature of the linker in dicationic liquids is clearly seen in the temperature dependences of their viscosities. The viscosities of ILs at temperatures above 60 °C have almost the same values in spite of a significant difference at room temperature (see Figure 2).

The volatility of ILs **1**–**5** was measured using MacBain quartz spiral balances[19] at temperatures of 150, 190 and 220 °C and a vacuum of ~0.013 Pa. These results are summarized in Table 1. The volatility values measured experimentally serve as a total estimation of the actual congruent evaporation of the heat transfer agents and of the processes of slow thermal decomposition with the volatile products formation, when the heat transfer agent samples

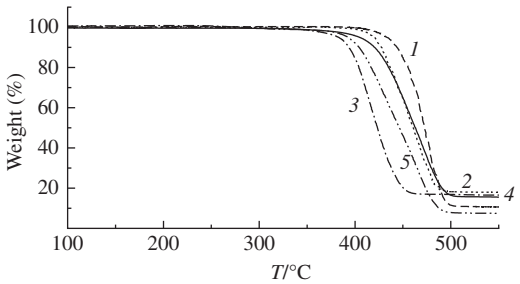


Figure 1 TGA curves of dicationic disiloxane ILs (*1*)–(*5*) **1**–**5**, respectively, under Ar atmosphere.

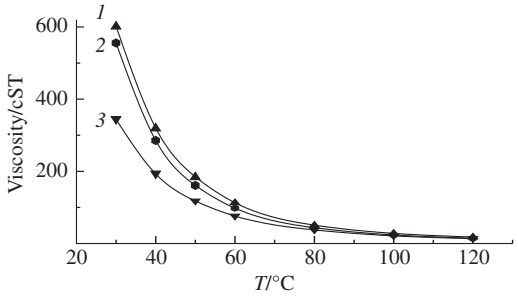


Figure 2 Temperature dependence of viscosity for ILs (*1*) **3**, (*2*) **4** and (3) **5**.

are heated *in vacuo*. All the studied dicationic ionic liquids do not practically evaporate at 150 °C. The dependence of the volatility on the IL structure begins to appear at the experiment temperatures ⩾190 °C. The decrease in the volatility of IL **2** at 190 °C compared to IL **1** is due to the higher molecular weight of IL **2**. With an increase in the evaporation temperature of IL to 220 °C, the volatility of IL **2** increases significantly, compared to IL **1**, due to a higher degree of thermal degradation of IL **2**, which has a propylene spacer in the structure.

The volatility of IL **3** is significantly higher than those of IL **1** and IL **2**, although the introduction of OH groups into the cation structure providing additional intermolecular interactions should reduce the values of this parameter.[15] However, the hydroxy groups presented in IL **3** structure cause the cleavage of hydrolytically unstable under experimental conditions Si–O–Si and Si–C bonds and formation of volatile decomposition products. The increased (as compared to IL **3**) evaporation rate *in vacuo* for IL **4** can be explained by the larger shielding of imidazole cation that leads to a weakening of the Coulomb interaction between ions, a weaker additional intermolecular interaction (energy of H-bonds in MeO groups is lower than in OH groups) and the presence, albeit to a lesser extent, of thermal destruction. The greatest volatility of IL **5** can be explained by the largest contribution of destruction processes *in vacuo* to the observed changes in the sample mass. This fact is consistent with the lowest decomposition temperature of IL **5** measured by TGA and is explained by the presence of a mobile hydrogen atom at 2-position of imidazole. This trend continues at 220 °C, although the destruction and evaporation of the IL occur more intensively. The increase in the volatility of IL **2** as compared to IL **1** at 220 °C can most likely be caused by thermal destruction processes due to the elongation of organic spacer between the imidazole and the silicon atom. Thus, the volatility of dicationic disiloxane liquids *in vacuo* at high temperatures is mainly determined by the thermal destruction processes resulted from the presence of polar groups in their structures. The introduction of polar groups in the dicationic ILs structure reduces the volatility (as it happens in monocationic ILs), but in lesser extent than increases it due to destructive processes with their participation (see Table 1).

In summary, it has been revealed that the presence of polar substituents at the imidazole cation of disiloxane dication liquids affects the whole set of IL properties. The replacement of methyl group with 2-methoxyethyl one leads to a significant decrease in the melting point, but increases the IL volatility *in vacuo*. In comparison with IL bearing a methyl group at the second position, the ionic liquids with unsubstituted 2-position of the imidazole ring exhibit lower melting points, higher volatilities *in vacuo*, and low decomposition temperatures. The presence of 2-hydroxyethyl group in the cation reduces the volatility as compared to the methyl analogue, but leads to a significant increase in the viscosity and a decrease in the decomposition temperature.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.038.

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