Development of low viscous ionic liquids: the dependence of the viscosity on the mass of the ions

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Abstract Straightforward syntheses of selected non-deuterated, partially deuterated, and fully deuterated room temperature ionic liquids (ILs) with the anions tris(pentafluoroethyl)trifluorophosphate, tetracyanoborate, and methyl sulfate were developed. The viscosity and the density of these ionic liquids were measured at various temperatures. The dissociation rate of the ionic liquid, the sizes of the cation and the anion, and the nature of the inter-ionic interaction are not influenced by deuteration, but viscosity is. All deuterated ionic liquids possess a higher viscosity and density in comparison to non-deuterated ones. The explanation of this phenomenon is given and discussed based on the modified Stokes-Einstein equation with a parameter which reflects the mass of the diffused particles. This new knowledge supports the recent development of novel low viscous inert ionic liquids which are of particular interest for the application in energy conversion devices. Deuterated ionic liquids are valuable media for the investigation of chemical reactions, natural products, and bio-materials by means of the NMR spectroscopy.

Keywords Ionic liquids · Viscosity · Density · Deuterated ionic liquids · Diffusion

Introduction

Ionic liquids are new promising materials for various applications [1–4]. The viscosity of ionic liquids (ILs) is a crucial

parameter for their practical use as reaction media and as components of electrolytes in electrochemical devices such as batteries, dye-sensitized solar cells, or super-capacitors. In particular, for electrochemical applications, low viscous ionic liquids are requested to provide optimal conditions for the diffusion of electrochemically active species. Watanabe et al. [5] have recently reported that the viscosity (particularly the self-diffusion coefficients of the ions) of ionic liquids is governed by at least three main factors: (i) size, (ii) shape, and (iii) interaction between the anion and the cation. The anion-cation interaction is developed mainly through Coulomb (electrostatic) forces, van der Waals forces, and hydrogen-bonding. Due to the ionic structure of ionic liquids, the electrostatic contribution is larger than the contribution of the van der Waals forces. Coulomb force between two charged units depends on the charges q and q' and the distance r (Eq. 1).

$$F = \frac{q \cdot q'}{r^2} \quad (1)$$

Coulomb's law is valid for two point-shaped charges separated by the distance r in vacuum. However, in reality, the cation and the anion have definite volumes and radii. In the case of ionic liquids, this means: The Coulomb interaction between a cation and an anion in ion-pairs depends on the surface charge density and the cation-anion distance. The *N,N*-dialkyl-imidazolium cation provides a very good delocalization of the positive charge. For this reason, imidazolium ionic liquids with large weakly coordinating anions like the tris(pentafluoroethyl)trifluorophosphate ion (FAP-anion) [6, 7] or the tetrakis(perfluoroalkoxy)-aluminate ions [8] have low viscosities in comparison to ionic liquids with $[PF_6]^-$ or $[BF_4]^-$ ions. By dissociation of ion-pairs, the distance between the anion and the cation increases. This reduces dramatically (in inverse ratio to r^2) the Coulomb (electrostatic) interactions

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between the ions (Eq. 1). In the case of complete dissociation (ionization) of the ion-pairs, the ions, in particular weakly coordinating cations and anions, can diffuse practically independently. This means that the ionization rate or the self-dissociativity (ionicity [9]) determines the diffusivity of the particles in ionic liquids. Viscosity and diffusivity of molecular liquids are correlated by the Stokes-Einstein equation (Eq. 2).

$$\eta = kT/C\pi D r_s \quad (2)$$

where:

k is the Stefan-Boltzmann constant,

T is the temperature, Kelvin

C is a coefficient (in the range 4–6; typically 6 for molecular liquids),

D is the translational diffusion coefficient,

r_s is the effective hydrodynamic radius (Stokes radius).

The main problem for the application of Eq. (2) to ionic liquids arises from the value of **r_s**. Ludwig et al. showed that **r_s** values are temperature dependent and thus the Stokes-Einstein equation is not valid for neat ionic liquids [10]. It seems that **r_s** values do not directly reflect the size of the ions which are involved in the mass transport in ionic liquids. It was shown that the fluidity of ionic liquids is facilitated by motion of free ions, ion-pairs, and clusters [7]. The ratio between these three types of particles in ionic liquids depends on the “ionicity” of ionic liquids [9] which is determined by the nature of the cation and the anion participating in the ion-pairing and by the temperature. In the case of ionic liquids with weakly coordinating anions and cations (“good” ILs [9]), for example for *N*-butyl-*N*-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide [BMPL] [(CF₃SO₂)₂N], the “ionicity” rate is 0.7 at RT. This means, that the mass transport in this ionic liquids is mainly facilitated by the diffusion of free anions and cations. However, the mass transport by the motion of ion-pairs or clusters still should be taken into account.

By diffusion in molecular liquids, the solute involves part of the solvent into the motion and forms a sphere with a certain hydrodynamic (Stokes) radius (**r_s**). Typically, for common solvents, **r_s** is > **r** (**r**=particle radius). However, ionic liquids consist of anionic and cationic species, which do not have a solvation shell. From this point of view, it is not obvious which radius (**r**) should be considered to calculate the diffusion coefficient (**D**) of ions in ionic liquids. For these reasons, the unification of **r_s** for all kinds of particles which move in ionic liquids is not possible and the application of the Stokes-Einstein equation in its classical form is inappropriate.

The nature of the coefficient **C** in Eq. (2) is not clear as well. In the case of ionic liquids, it is definitely not equal to 6 like for molecular solvents. Watanabe et al. have calculated

the coefficient **C** to be in the range 2.9–3.6 for *N,N*-dialkyl-imidazolium cations and 4.1–4.4 for the anion [(CF₃SO₂)₂N] depending on the counter cation [11]. This means that the coefficient **C** depends on the nature of the particles which move in the ionic liquid, and it is different for cations, anions, and ion-pairs. For these reasons, we have modified the classical Stokes-Einstein equation by separating the motions of cations, anions, and ion-pairs in ionic liquids [7].

$$\eta^{\text{IL}} = \frac{k \cdot T}{b_A \cdot D_A \cdot r_A + b_C \cdot D_C \cdot r_C + b_{A,C} \cdot D_{A,C} \cdot r_{A,C}} \quad (3)$$

where:

k is the Stefan-Boltzmann constant; **T** is the absolute temperature

η is the dynamic viscosity; **r** is the radius of the anion, cation or ion-pair (cation+anion)

D_A is the self-diffusion coefficient of the anion; **D_C** is the self-diffusion coefficient of the cation

D_{A,C} is the self-diffusion coefficient of the ion-pair

b_A=**n_A**·**m_A**·**π**; **b_C**=**n_C**·**m_C**·**π**; **b_{A,C}**=**n_{A,C}**·**m_{A,C}**·**π**

n is the transference number, **m** is the coefficient which depends on the mass, the size, and the shape of the cation, anion, or ion-pair.

Of course, cations and anions do not move completely independently. According to the Debye-Hückel theory, they are interacting with each other by their electric fields. Due to this interaction, the diffusion of the ions in ionic liquids is not a uniform motion. The movement of an ion is accelerated by approaching an ion of opposite charge (counterion). On the other hand, an ion will be decelerated upon approaching an ion of the same charge or moving away from an ion with the opposite charge. The acceleration or deceleration is modulated by the mass of the ion according to the second Newton law [12]:

$$F = m \cdot a$$

where:

F is the vector sum of the applied forces

m is the mass

a is the vector of acceleration.

The greater the distance between two ions, the lower (in quadratic relation according to the Eq. 1) are the forces between these ions. Consequently, the motion of the ions in ionic liquids is very chaotic—their velocity is being modulated by their local environment. This is probably the reason for the low correlation between viscosity and self-diffusion

coefficients found in 1-butyl-3-methyl-imidazolium (BMIM) ionic liquids with anions of different nature and mass: $[\text{PF}_6]^-$, $[\text{BF}_4]^-$, $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, $[\text{CF}_3\text{SO}_3]^-$, and $[\text{CF}_3\text{CO}_2]^-$ [13]. The high molecular mass of the heavy $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$ (M. m.=380) anion is probably the reason for the slow diffusion of this anion in comparison to the “light” imidazolium cation in *N,N*-dialkyl-imidazolium $[(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}]^-$ ionic liquids [5, 11]. Watanabe et al. noticed that the anion in ionic liquids diffuses slower than the cation even if they have the same van der Waals radii [13]. This is very probably due to the difference in the mass of heavy, fluorine-containing anions, and lighter, hydrogen-containing cations. Lengthening of the perfluoroalkyl chain in the anion structure results in an increase of the mass and consequently in the viscosity of ionic liquid in spite of the better charge delocalization in the case of highly fluorinated anions [14]. Once more, the increase of the anion’s mass determines the raise of ionic liquids’ viscosity. Similarly, for ionic liquids with the same anion, the increase of the cation mass results in a higher viscosity. For instance, the dynamic viscosity of 1-ethyl-3-methyl-imidazolium $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ at 20 °C is 34 mPa·s, but the dynamic viscosity of 1-(2’,2’,2’-trifluoroethyl)-3-methyl-imidazolium $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ is much higher: 248 mPa·s at 20 °C.

Krossing et al. have shown that the viscosity of the IL, *N*-butyl-*N*-methylnmorpholinium $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$, is higher in comparison to those of the other ionic liquids with this anion in spite of similar molecule volumes V_m [8]. The authors assume that replacement of a carbon with an oxygen atom in the cation leads to stronger contacts with the anion, which induce higher viscosity. But additionally, an increase of the cation mass upon replacement of the carbon atom by a heavier oxygen atom influences the viscosity of corresponding ionic liquids. A similar observation was made by Bonhôte et al. [14]. The authors wrote: “It was expected that replacing a butyl by a methoxyethyl substituent would decrease the viscosity by increasing the chain mobility but no such effect can be observed.” Quite opposite, the dynamic viscosity of 1-(2-methoxyethyl)-3-methyl-imidazolium $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ at 20 °C is 54 mPa·s, i.e., higher than the dynamic viscosity of 1-butyl-3-methyl-imidazolium $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ at 20 °C: 52 mPa·s [14]. All these examples demonstrate that the mass of the anion and the cation certainly influences the viscosity of ionic liquids.

In the conclusion of their article [5], Watanabe et al. state: “The relationship between the self-diffusion coefficients of the ions and the stabilization energies for the ion-pairs suggests that at least three factors (size of ions, shape of ions, and magnitude of interaction energy between anion and cation) play important roles in determining the magnitude of the self-diffusion coefficients.” We would like to insert: “... and the mass of the ions.” For this reason, we have introduced the additional coefficient *m* (reflecting the influence of the mass of the ions or ion-pair) to Eq. (3).

Experimental

For accurate measurements of the viscosity and the density, samples of high-purity ionic liquids are required. For this reason, all substances used were purified and an optimized protocol for the syntheses of high-purity deuterated and non-deuterated ionic liquids has been developed. The experimental section below describes the syntheses of high-quality deuterated ionic liquids which are of general interest for follow-up studies of these particular ILs.

Chemicals

The chemicals were purchased from reagent companies. Potassium tetracyanoborate, potassium tris(pentafluoroethyl)trifluorophosphate, 1-ethyl-3-methyl-imidazolium chloride, and triflic acid anhydride were delivered from Merck KGaA (Darmstadt). All liquid starting materials were freshly distilled under argon atmosphere. Heterocyclic nitrogen-containing bases were distilled from CaH_2 under argon atmosphere two times. All experiments were carried out under argon atmosphere. Methyl and ethyl trifluoromethanesulfonate were prepared as described before [15].

Analytical procedures

NMR spectroscopy NMR spectra were recorded in the deuterium-locked mode on a Bruker Avance III spectrometer equipped with a 9.3980 T cryomagnet. The samples were measured in 5-mm precision glass NMR tube (Wilmad 507 or 528 PPT) at 24 °C. The $^1\text{H}/^{19}\text{F}$ NMR spectra were acquired using a 5 mm combination $^1\text{H}/^{19}\text{F}$ probe head operating at 400.17 MHz (^1H) and 376.54 MHz (^{19}F). The ^{11}B (128.39 MHz), ^{13}C (100.61 MHz), and ^{31}P (161 MHz) NMR spectra were obtained using a 5-mm broad-band inverse probe head. Spectra were recorded using various memory sizes, optimal acquisition times, and relaxation delays (0.5–2 s).

The ^1H NMR chemical shifts were referenced with respect to tetramethylsilane (TMS) using the chemical shifts for the solvents CH_2Cl_2 (5.32 ppm) and CH_3CN (1.95 ppm). The ^{13}C NMR chemical shifts were referenced with respect to TMS using the chemical shifts for the solvents CH_2Cl_2 (53.5 ppm) and CH_3CN (118.7 ppm). The ^{19}F NMR spectra were referenced either with respect to CFCl_3 using the internal standards C_6F_6 (−162.9 ppm) or $\text{C}_6\text{H}_5\text{CF}_3$ (−63.9 ppm) or externally to a neat CFCl_3 reference sample at 25 °C. The ^{31}P NMR spectra were referenced externally to a H_3PO_4 (85 %) sample at 25 °C. The ^{11}B NMR spectra were referenced externally to a $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ sample at 25 °C.

Chemical shifts at lower frequency than the standard are assigned by a negative sign. The multiplicities for NMR signals were denoted as follows: s=singlet, d=doublet, t=

triplet, q=quartet, qui=quintet, sep=septet, m=multiplet; J=coupling constant.

Elemental analysis was performed by using a HEKATECH EA 3000 elemental analyzer with Callidus software.

Viscosity and density of ionic liquids were measured on Viscosimeter SVM 3000 (Anton Paar). All measurements were carried out at least two times for every batch. In most cases, two different batches of deuterated ionic liquid were prepared and measured in parallel to get a reliable data. The purity of the ionic liquids was proved by measuring of residual water (Karl-Fischer titration; 831 KF-Coulometer, Metrohm) and of chloride or bromide (ion-chromatography, Metrohm Advanced IC System; stationary phase: Metrosep A SUPP4 – 150). The content of residual water was below 180 ppm (determined after measuring of the viscosity), and the content of halides was below 20 ppm.

Syntheses

To avoid impurities of halides, we have developed the syntheses of high-purity ionic liquids with partially and fully deuterated cations by means of direct alkylation of organic bases with corresponding deuterium containing alkylating reagents.

Synthesis of trifluoromethanesulfonic acid methylester(d_3), $CF_3SO_2OCD_3$ Perdeuterated methanol (20.0 g (0.55 mol)) was slowly (3 h) added to 312.9 g (1.11 mol) trifluoromethanesulfonic acid anhydride under vigorous stirring at 0 °C. Stirring was continued for 4 h at 0 °C to complete the reaction. The product was isolated by fractionated distillation. Purification by an additional fractionated distillation gives 65.8 g (0.39 mol; yield, 71 %) perdeuterated trifluoromethanesulfonic acid methylester ($CF_3SO_2OCD_3$) (b. p. 102–104 °C) ($\rho=1.565\text{ g/cm}^3$).

Synthesis of trifluoromethanesulfonic acid ethylester(d_5), $CF_3SO_2OCD_2CD_3$ Perdeuterated ethanol (15.0 g (0.29 mol)) was diluted with 120 ml hexane. Sodium (6.61 g (0.29 mol)) was added in 20 portions under vigorous stirring at 20 °C. Stirring was continued for 4 h at 60 °C to complete the reaction, which leads to a pale yellow suspension. Trifluoromethanesulfonic acid anhydride (81.2 g (0.29 mol)) was added dropwise at 20 °C, and the color of the suspension turns into gray. The isolation of the product leads to only one main fraction with a boiling point of 68–69 °C. This main fraction was hexane with approximately 6 % (w/w) trifluoromethanesulfonic acid ethylester(d_5).

Synthesis of *N*-methylimidazole(d_3) Imidazole (99 %, Aldrich, pale yellow solid) was melted with 1 % CaH_2 and distilled fractionated at 15 hPa. The main fraction at 185–186 °C was distilled in the same manner again. Powdered

distilled imidazole (9.00 g (0.13 mol)) was suspended in 80 ml dry hexane and under vigorous stirring 22.09 g (0.13 mol) of $CF_3SO_2OCD_3$ was added dropwise during 2 h at 20 °C. After additional stirring for 1 h, two liquid phases were resulting. The upper phase was removed, and the bottom phase was washed with 50 ml hexane for two times. After the evaporation of the washed phase (31 g), a small amount of a colorless solid material precipitated. The NMR analysis of the raw product shows a 1:1:1 mixture of the desired product, protonated imidazole and two times methylated imidazole. This raw product was diluted with 20 ml of methanol and treated dropwise with a solution of 7.2 (0.13 mol) $NaOCH_3$ in 30 ml methanol at 0 °C. The solution was stirred for 2 h at 0 °C and 2 h at 20 °C. Methanol was distilled off at 20 °C. The resulting suspension was evaporated at 0.1 Pa, and residue was condensed trap to trap (160 °C; 0.1 Pa). An additional fractional distillation yields 5.9 g (0.07 mol, 52 % yield overall) of pure colorless liquid *N*-methylimidazole(d_3) at 86–87 °C (52 hPa).

Synthesis of *N*-ethylimidazole(d_5) Imidazole (99 %, Aldrich, pale yellow solid) was melted with 1 % CaH_2 and distilled fractionated at 15 mbar. The main fraction at 185–186 °C was distilled in the same manner again. The powdered distilled imidazole (10.00 g (0.15 mol)) was added in 30 portions to 483 g of the 6 % (w/w) hexane solutions of $CF_3SO_2OC_2D_5$ (29 g (0.16 mol)) within 2 h at 0 °C. Two liquid phases were resulting. The upper phase was removed, and the bottom phase was washed with 150 ml hexane for two times. After the evaporation of the washed phase (37 g), a small amount of a colorless solid material precipitated. The NMR analysis of the raw product shows a 1:1:1 mixture of the desired product, protonated imidazole and two times ethylated imidazole. The raw product was diluted with 20 ml methanol and treated dropwise with a solution of 8.0 (0.15 mol) $NaOCH_3$ in 32 ml methanol at 0 °C. The solution was stirred for 2 h at 0 °C and 2 h at 20 °C. After distilling of methanol at 20 °C, the resulting high viscous suspension was evaporated at 0.1 Pa and 9 g of a colorless liquid product can be condensed trap to trap (160 °C, 0.1 Pa). An additional fractionated distillation yields 7.3 g (0.07 mol, 49 % over all yield) of pure colorless liquid *N*-ethylimidazole(d_5) at 85–86 °C (10 hPa).

Syntheses of 1-ethyl-3-methyl-imidazolium and 1-ethylpyridinium trifluoromethanesulfonates and methyl sulfates. General protocol Non-deuterated ionic liquids with trifluoromethanesulfonate-anion were prepared according to the previously reported procedure [15]. For the syntheses of partially and fully deuterated ionic liquids, the following general procedure has been used: freshly distilled $CF_3SO_2OCD_3$ or $CF_3SO_2OC_2D_5$ (hexane solution) or $(CD_3O)_2SO_2$ or $CF_3SO_2OC_2H_5$ or $(CH_3O)_2SO_2$ (1.00–1.05 equivalent) were added dropwise to vigorously stirred 1.00

equivalent of *N*-methylimidazole(d_3) or *N*-ethylimidazole(d_5) or pyridine(d_5) at 0–20 °C. The reaction mixture was left stirring at room temperature for some hours until the reaction was completed. The product, ionic liquid, was dried in vacuum for several hours at 0.1 Pa and 25 °C. The syntheses of tetracyanoborates and tris(pentafluoroethyl)trifluorophosphates ionic liquids have been carried out by means of metathesis with potassium tris(pentafluoroethyl)trifluorophosphate, $K[(C_2F_5)_3PF_3]$, or potassium tetracyanoborate, $K[B(CN)_4]$, similar as it is described in the previously published paper [6] and in the patent application [16].

The comprehensive descriptions of the syntheses and product characterization by means of the NMR spectroscopy and elemental analysis are given below.

Synthesis of 1-ethyl-3-methyl(d_3)-imidazolium trifluoromethanesulfonate Freshly distilled $CF_3SO_2OCD_3$ (15.71 g, 94 mmol) was added dropwise into vigorously stirred *N*-ethylimidazole (8.84 g, 92 mmol) over a 5-h period at 0 °C. Magnetic stirring (800 rpm) was continued for 2 h at 0 °C and 2 h at 25 °C to complete the reaction. Finally, volatile impurities were removed from the product by evaporation during 6 h at 0.1 Pa and 25 °C. 1-Ethyl-3-methyl(d_3)-imidazolium trifluoromethanesulfonate was obtained as a pale yellow liquid in a quantitative yield (24.22 g, 92 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =1.47 (t, $^3J(H,H)$ =7.3 Hz, 3H), 4.20 (q, $^3J(H,H)$ =7.3 Hz, 2H), 7.41 (m, 1H), 7.47 (m, 1H), 8.85 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−79.3 ppm (s; CF_3S); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =15.1 (q, $^1J(C,H)$ =129 Hz; C^7), 35.7 (sep, $^1J(C,D)$ =22 Hz; C^8), 45.4 (t, $^1J(C,H)$ =144 Hz; C^6), 121.7 (q, $^1J(C,F)$ =321 Hz; CF_3), 122.6 (d, $^1J(C,H)$ =203 Hz; C^5), 124.1 (d, $^1J(C,H)$ =203 Hz; C^4), 136.6 ppm (d, $^1J(C,H)$ =220 Hz; C^2).

Synthesis of 1-ethyl(d_5)-3-methyl-imidazolium trifluoromethanesulfonate Hexane-fraction (73.3 g) with 6 % (w/w) trifluoromethanesulfonic acid ethylester(d_5) (4.4 g, 24 mmol) was added dropwise into vigorously stirred *N*-methylimidazole (1.79 g, 22 mmol) over a 5-h period at 20 °C. Magnetic stirring (800 rpm) was continued for 2 h at 25 °C to complete the reaction. Afterwards, hexane was removed at reduced pressure. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 25 °C. 1-Ethyl(d_5)-3-methyl-imidazolium trifluoromethanesulfonate was obtained as a yellow liquid in a quantitative yield (5.73 g, 22 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =3.85 (s, 3H), 7.38 (m, 1H), 7.44 (m, 1H), 8.58 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−79.3 ppm (s; CF_3S).

Synthesis of 1-ethyl(d_5)-3-methyl(d_3)-imidazolium trifluoromethanesulfonate Hexane-fraction (216.7 g) with

6 % (w/w) trifluoromethanesulfonic acid ethylester(d_5) (13.0 g, 71 mmol) was dropped into vigorously stirred *N*-methyl(d_3)imidazole (5.52 g, 65 mmol) during 9 h at 20 °C. Magnetic stirring (800 rpm) was continued for 12 h at 25 °C to complete the reaction. Afterwards, hexane was removed at reduced pressure. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 25 °C. 1-Ethyl(d_5)-3-methyl(d_3)-imidazolium trifluoromethanesulfonate was obtained as a yellow liquid in a quantitative yield (17.32 g, 65 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =7.39 (m, 1H), 7.45 (m, 1H), 8.61 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−79.3 ppm (s; CF_3S); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =13.2 (sep, $^1J(C,D)$ =19 Hz; C^7), 34.8 (sep, $^1J(C,D)$ =22 Hz; C^8), 43.8 (qui, $^1J(C,D)$ =22 Hz; C^6), 120.8 (q, $^1J(C,F)$ =321 Hz; CF_3), 121.6 (d, $^1J(C,H)$ =203 Hz; C^5), 122.5 (d, $^1J(C,H)$ =203 Hz; C^4), 135.6 ppm (d, $^1J(C,H)$ =220 Hz; C^2).

Synthesis of 1-ethyl-3-methyl-imidazolium tetracyanoborate The aqueous solutions of (12.26 g, 80 mmol) potassium tetracyanoborate and (11.67 g, 80 mmol) 1-ethyl-3-methyl-imidazolium chloride were combined and stirred at 20 °C for 1 h. The resulting emulsion was extracted with 15 ml dichloromethane for seven times. The combined dichloromethane solutions were washed with 10 ml water for three times. Then, dichloromethane was removed at reduced pressure. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. 1-Ethyl-3-methyl-imidazolium tetracyanoborate was obtained as a colorless liquid in a high yield (15.25 g, 67 mmol, 84 %). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =1.49 (t, $^3J(H,H)$ =7.3 Hz, 3H), 3.85 (s, 3H), 4.19 (q, $^3J(H,H)$ =7.3 Hz, 2H), 7.35 (m, 1H), 7.40 (m, 1H), 8.42 ppm (m, 1H); ^{11}B NMR (128.39 MHz, CD_3CN , 25 °C, Reference: $BF_3 \cdot O(C_2H_5)_2$): δ =−38.6 ppm (s; $B(CN)_4$); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =15.9 (q, $^1J(C,H)$ =129 Hz; C^7), 37.3 (q, $^1J(C,H)$ =144 Hz; C^8), 46.2 (t, $^1J(C,H)$ =144 Hz; C^6), 123.6 (q, $^1J(C,^{11}B)$ =71 Hz, sep, $^1J(C,^{10}B)$ =24 Hz; CN), 123.5 (d, $^1J(C,H)$ =203 Hz; C^5), 125.0 (d, $^1J(C,H)$ =203 Hz; C^4), 136.9 ppm (d, $^1J(C,H)$ =220 Hz; C^2).

Elemental analysis: calcd (%) for $C_{10}H_{11}N_6B$: C 53.13, H 4.90, N 37.18; found: C 53.14, H 4.64, N 37.50.

Synthesis of 1-ethyl-3-methyl(d_3)-imidazolium tetracyanoborate The aqueous solutions of (10.50 g, 68 mmol) potassium tetracyanoborate and (17.95 g, 68 mmol) 1-ethyl-3-methyl(d_3)-imidazolium trifluoromethanesulfonate were combined and stirred at 20 °C for 1 h. The resulting emulsion was extracted with 15 ml dichloromethane for seven times. The combined dichloromethane solutions were washed with 10 ml water for three times. Then, dichloromethane was removed at reduced pressure. Finally, volatile impurities were

removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. 1-Ethyl-3-methyl(d_3)-imidazolium tetracyanoborate was obtained as a pale yellow liquid in a high yield (13.59 g, 59 mmol, 87 %). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =1.49 (t, $^3J(\text{H,H})$ =7.3 Hz, 3H), 4.20 (q, $^3J(\text{H,H})$ =7.3 Hz, 2H), 7.35 (m, 1H), 7.40 (m, 1H), 8.42 ppm (m, 1H); ^{11}B NMR (128.39 MHz, CD_3CN , 25 °C, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$): δ =−38.6 (s; $\text{B}(\text{CN})_4$); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =14.1 (q, $^1J(\text{C,H})$ =129 Hz; C^7), 34.8 (sep, $^1J(\text{C,D})$ =22 Hz; C^8), 44.5 (t, $^1J(\text{C,H})$ =144 Hz; C^6), 121.6 (d, $^1J(\text{C,H})$ =203 Hz; C^5), 121.8 (q, $^1J(\text{C},^{11}\text{B})$ =71 Hz, sep $^1J(\text{C},^{10}\text{B})$ =24 Hz; CN), 123.4 (d, $^1J(\text{C,H})$ =203 Hz; C^4), 135.1 ppm (d, $^1J(\text{C,H})$ =220 Hz; C^2).

Elemental analysis: calcd (%) for $\text{C}_{10}\text{H}_8\text{D}_3\text{N}_6\text{B}$: C 52.43, H 4.84, N 36.69; found: C 52.49, H 4.56, N 37.17.

Synthesis of 1-ethyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate The aqueous solutions of (39.62 g, 82 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (21.30 g, 82 mmol) 1-ethyl-3-methyl-imidazolium triflate [12] were combined and stirred (1,000 rpm) at 20 °C for 1 h. Two colorless liquid phases were resulting. The bottom phase was separated and washed with 30 ml water for five times. Finally, the bottom phase was dried out for 8 h at 0.1 Pa and 40 °C. 1-ethyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate was obtained as a colorless liquid in a high yield (42.33 g, 76 mmol, 93 %). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =1.51 (t, $^3J(\text{H,H})$ =7.3 Hz, 3H), 3.86 (s, 3H), 4.20 (q, $^3J(\text{H,H})$ =7.3 Hz, 2H), 7.34 (m, 1H), 7.39 (m, 1H), 8.41 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−44.7 (d, $^1J(\text{F,P})$ =889 Hz, m, 1F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −68.9 (d, $^1J(\text{F,P})$ =795 Hz, m, 3F; $[(\text{C}_2\text{F}_5)_3\text{PF}_3]_{\text{f}}$), −80.9 (m, 3F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 9F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), −88.2 (d, $^1J(\text{F,P})$ =902 Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −116.2 (d, $^2J(\text{F,P})$ =83 Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −116.2 (d, $^2J(\text{F,P})$ =81 Hz, m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), −116.8 ppm (d, $^2J(\text{F,P})$ =98 Hz, m, 4F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$); Ratio of conformers $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$ (meridional): $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$ (facial)=100: 7; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): δ =−147.7 (d, $^1J(\text{F,P})$ =889 Hz, t, $^1J(\text{F,P})$ =902 Hz, t, $^2J(\text{F,P})$ =83 Hz, qui $^2J(\text{F,P})$ =98 Hz $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −147.7 ppm (q, $^1J(\text{F,P})$ =795 Hz, sep, $^2J(\text{F,P})$ =81 Hz; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =14.3 (q, $^1J(\text{C,H})$ =129 Hz; C^7), 35.7 (q, $^1J(\text{C,H})$ =144 Hz; C^8), 44.9 (t, $^1J(\text{C,H})$ =144 Hz; C^6), 122.0 (d, $^1J(\text{C,H})$ =202 Hz; C^5), 123.7 (d, $^1J(\text{C,H})$ =202 Hz; C^4), 135.5 ppm (d, $^1J(\text{C,H})$ =220 Hz; C^2).

Elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{11}\text{N}_2\text{F}_{18}\text{P}$: C 25.91, H 1.99, N 5.04; found: C 26.47, H 2.36, N 5.54.

Synthesis of 1-ethyl-3-methyl(d_3)-imidazolium tris(pentafluoroethyl)trifluorophosphate The aqueous

solutions of (10.85 g, 22 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (5.90 g, 22 mmol) 1-ethyl-3-methyl(d_3)-imidazolium trifluoromethanesulfonate were combined and stirred (1,000 rpm) at 20 °C for 1 h. The bottom phase of the resulting two colorless liquid phases was separated and washed with 20 ml water for five times. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. 1-Ethyl-3-methyl(d_3)-imidazolium tris(pentafluoroethyl)trifluorophosphate was obtained as a nearly colorless liquid in a high yield (11.78 g, 21 mmol, 94 %). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =1.53 (t, $^3J(\text{H,H})$ =7.3 Hz, 3H), 4.22 (q, $^3J(\text{H,H})$ =7.3 Hz, 2H), 7.33 (m, 1H), 7.39 (m, 1H), 8.39 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−44.7 (d, $^1J(\text{F,P})$ =889 Hz, m, 1F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −68.9 (d, $^1J(\text{F,P})$ =795 Hz, m, 3F; $[(\text{C}_2\text{F}_5)_3\text{PF}_3]_{\text{f}}$), −80.9 (m, 3F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 9F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), −88.2 (d, $^1J(\text{F,P})$ =902 Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −116.2 (d, $^2J(\text{F,P})$ =83 Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −116.2 (d, $^2J(\text{F,P})$ =81 Hz, m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), −116.8 ppm (d, $^2J(\text{F,P})$ =98 Hz, m, 4F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$); Ratio of conformers $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$ (meridional): $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$ (facial)=100: 0.5; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): δ =−147.7 ppm (d, $^1J(\text{F,P})$ =889 Hz, t, $^1J(\text{F,P})$ =902 Hz, t, $^2J(\text{F,P})$ =83 Hz, qui $^2J(\text{F,P})$ =98 Hz; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$). ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): δ =15.5 (q, $^1J(\text{C,H})$ =129 Hz; C^7), 36.4 (sep, $^1J(\text{C,D})$ =22 Hz; C^8), 46.3 (t, $^1J(\text{C,H})$ =144 Hz; C^6), 123.3 (d, $^1J(\text{C,H})$ =203 Hz; C^5), 125.0 (d, $^1J(\text{C,H})$ =203 Hz; C^4), 136.7 ppm (d, $^1J(\text{C,H})$ =220 Hz; C^2).

Elemental analysis: calcd (%) for $\text{C}_{12}\text{H}_8\text{D}_3\text{N}_2\text{F}_{18}\text{P}$: C 25.77, H 1.98, N 5.01; found: C 25.91, H 1.84, N 5.42.

Synthesis of 1-ethyl(d_5)-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate The aqueous solutions of (7.96 g, 16 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (4.36 g, 16 mmol) 1-ethyl(d_5)-3-methyl-imidazolium trifluoromethanesulfonate were combined and stirred (1,000 rpm) at 20 °C for 1 h. The bottom phase of the resulting two colorless liquid phases was separated and washed with 12 ml water for five times. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. 1-Ethyl(d_5)-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate was obtained as a nearly colorless liquid in a high yield (8.77 g, 15.6 mmol, 95 %). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): δ =3.85 (s, 3H), 7.34 (m, 1H), 7.39 (m, 1H), 8.40 ppm (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): δ =−44.7 (d, $^1J(\text{F,P})$ =889 Hz, m, 1F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −68.9 (d, $^1J(\text{F,P})$ =795 Hz, m, 3F; $[(\text{C}_2\text{F}_5)_3\text{PF}_3]_{\text{f}}$), −80.9 (m, 3F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), −82.6 (m, 9F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), −88.2 (d, $^1J(\text{F,P})$ =902 Hz, m, 2F;

$[(F_3CF_2C)_3PF_3]_m$, -116.2 (d, $^2J(F,P)=83$ Hz, m, 2F; $[(F_3CF_2C)_3PF_3]_m$, -116.2 (d, $^2J(F,P)=81$ Hz, m, 6F; $[(F_3CF_2C)_3PF_3]_f$, -116.8 ppm (d, $^2J(F,P)=98$ Hz, m, 4F; $[(F_3CF_2C)_3PF_3]_m$); Ratio of conformers $[(F_3CF_2C)_3PF_3]_m$ (meridional) : $[(F_3CF_2C)_3PF_3]_f$ (facial)=100: 0.8; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): $\delta=-147.8$ ppm (d, $^1J(F,P)=889$ Hz, t, $^1J(F,P)=902$ Hz, t, $^2J(F,P)=83$ Hz, qui, $^2J(F,P)=98$ Hz; $[(F_3CF_2C)_3PF_3]_m$); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=13.2$ (sep, $^1J(C,D)=19$ Hz; C^7), 35.6 (q, $^1J(C,H)=144$ Hz; C^8), 44.1 (qui, $^1J(C,D)=22$ Hz; C^6), 121.9 (d, $^1J(C,H)=202$ Hz; C^5), 123.6 (d, $^1J(C,H)=202$ Hz; C^4), 135.4 ppm (d, $^1J(C,H)=220$ Hz; C^2).

Elemental analysis: calcd (%) for $C_{12}H_6D_5N_2F_{18}P$: C 25.68, H 1.97, N 4.99; found: C 25.40, H 2.01, N 5.27.

Synthesis of 1-ethyl(d_5)-3-methyl(d_3)-imidazolium tris(pentafluoroethyl)trifluorophosphate The aqueous solutions of (9.96 g, 21 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (5.52 g, 21 mmol) 1-ethyl(d_5)-3-methyl(d_3)-imidazolium trifluoromethanesulfonate were combined and stirred (1,000 rpm) at 20 °C for 1 h. The bottom phase of the resulting two colorless liquid phases was separated and washed with 15 ml water for five times. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. 1-Ethyl(d_5)-3-methyl(d_3)-imidazolium tris(pentafluoroethyl)trifluorophosphate was obtained as a nearly colorless liquid in a high yield (11.14 g, 20 mmol, 96 %). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=7.34$ (m, 1H), 7.39 (m, 1H), 8.40 (m, 1H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): $\delta=-44.7$ (d, $^1J(F,P)=889$ Hz, m, 1F; $[(F_3CF_2C)_3PF_3]_m$, -68.9 (d, $^1J(F,P)=795$ Hz, m, 3F; $[(C_2F_5)_3PF_3]_f$, -80.9 (m, 3F; $[(F_3CF_2C)_3PF_3]_m$, -82.6 (m, 6F; $[(F_3CF_2C)_3PF_3]_m$, -82.6 (m, 9F; $[(F_3CF_2C)_3PF_3]_f$, -88.2 (d, $^1J(F,P)=902$ Hz, m, 2F; $[(F_3CF_2C)_3PF_3]_m$, -116.2 (d, $^2J(F,P)=83$ Hz, m, 2F; $[(F_3CF_2C)_3PF_3]_m$, -116.2 (d, $^2J(F,P)=81$ Hz, m, 6F; $[(F_3CF_2C)_3PF_3]_f$, -116.8 ppm (d, $^2J(F,P)=98$ Hz, m, 4F; $[(F_3CF_2C)_3PF_3]_m$); Ratio of conformers $[(F_3CF_2C)_3PF_3]_m$ (meridional) : $[(F_3CF_2C)_3PF_3]_f$ (facial)=100 : 0.7; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): $\delta=-147.7$ ppm (d, $^1J(F,P)=889$ Hz, t, $^1J(F,P)=902$ Hz, t, $^2J(F,P)=83$ Hz, qui, $^2J(F,P)=98$ Hz; $[(F_3CF_2C)_3PF_3]_m$); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=14.7$ (sep, $^1J(C,D)=20$ Hz; C^7), 36.5 (sep, $^1J(C,D)=22$ Hz; C^8), 45.6 (qui, $^1J(C,D)=22$ Hz; C^6), 123.4 (d, $^1J(C,H)=203$ Hz; C^5), 125.0 (d, $^1J(C,H)=203$ Hz; C^4), 136.9 ppm (d, $^1J(C,H)=220$ Hz; C^2).

Elemental analysis: calcd (%) for $C_{12}H_3D_8N_2F_{18}P$: C 25.55, H 1.96, N 4.96; found: C 25.73, H 1.97, N 5.18.

Synthesis of 1-ethyl-3-methyl-imidazolium methylsulfate Freshly distilled $(CH_3O)_2SO_2$ (4.15 g, 33 mmol, 1 % excess) was added dropwise into vigorously stirred *N*-

ethylimidazole (3.13 g, 33 mmol) over a period of 8 h at 0 °C. Magnetic stirring (800 rpm) was continued for 12 h at 25 °C and 1 h at 50 °C to complete the reaction. Finally, volatile impurities were removed from the product by evaporation during 16 h at 0.1 Pa and 35 °C. 1-Ethyl-3-methyl-imidazolium methylsulfate was obtained as a colorless liquid in a quantitative yield (7.22 g, 33 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=1.45$ (t, $^3J(H,H)=7.3$ Hz, 3H), 3.53 (s, 3H; $[CH_3SO_4]^-$), 3.87 (s, 3H), 4.21 (q, $^3J(H,H)=7.3$ Hz, 2H), 7.48 (m, 1H), 7.55 (m, 1H), 8.96 ppm (m, 1H); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=15.8$ (q, $^1J(C,H)=129$ Hz; C^7), 36.8 (q, $^1J(C,H)=144$ Hz; C^8), 45.8 (t, $^1J(C,H)=144$ Hz; C^6), 54.4 (q, $^1J(C,H)=145$ Hz; $[CH_3SO_4]^-$), 123.1 (d, $^1J(C,H)=202$ Hz; C^5), 124.7 (d, $^1J(C,H)=202$ Hz; C^4), 137.7 ppm (d, $^1J(C,H)=221$ Hz; C^2).

Elemental analysis: calcd (%) for $C_7H_{14}N_2O_4S$: C 37.83, H 6.35, N 12.60, S 14.42; found: C 37.84, H 6.11, N 12.58, S 12.84.

Synthesis of 1-ethyl-3-methyl(d_3)-imidazolium methyl(d_3)sulfate Freshly distilled $(CD_3O)_2SO_2$ (6.50 g, 49 mmol, 1 % excess) was added dropwise into vigorously stirred *N*-ethylimidazole (4.68 g, 49 mmol) over a period of 8 h at 0 °C. Magnetic stirring (800 rpm) was continued for 12 h at 25 °C and 1 h at 50 °C to complete the reaction. Finally, volatile impurities were removed from the product by evaporation during 16 h at 0.1 Pa and 35 °C. 1-Ethyl-3-methyl(d_3)-imidazolium methyl(d_3)sulfate was obtained as a colorless liquid in a quantitative yield (11.10 g, 49 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=1.43$ (t, $^3J(H,H)=7.3$ Hz, 3H), 4.20 (q, $^3J(H,H)=7.3$ Hz, 2H), 7.52 (m, 1H), 7.59 (m, 1H), 8.99 ppm (m, 1H); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=15.7$ (q, $^1J(C,H)=129$ Hz; C^7), 36.0 (sep, $^1J(C,D)=22$ Hz; C^8), 45.6 (t, $^1J(C,H)=144$ Hz; C^6), 53.5 (sep, $^1J(C,D)=22$ Hz; $[CD_3OSO_3]^-$), 123.0 (d, $^1J(C,H)=203$ Hz; C^5), 124.6 (d, $^1J(C,H)=203$ Hz; C^4), 137.6 ppm (d, $^1J(C,H)=221$ Hz; C^2).

Elemental analysis: calcd (%) for $C_7H_8D_6N_2O_4S$: C 36.83, H 6.18, N 12.27, S 14.04; found: C 36.47, H 6.24, N 12.20, S 14.04.

Synthesis of 1-ethyl(d_5)-3-methyl(d_3)-imidazolium methyl(d_3)sulfate Freshly distilled $(CD_3O)_2SO_2$ (3.97 g, 30 mmol, 1 % excess) was added dropwise into vigorously stirred 1-ethyl(d_5)-imidazole (3.01 g, 30 mmol) over a period of 8 h at 0 °C. Magnetic stirring (800 rpm) was continued for 12 h at 25 °C and 1 h at 50 °C to complete the reaction. Finally, volatile impurities were removed from the product by evaporation during 16 h at 0.1 Pa and 35 °C. 1-Ethyl(d_5)-3-methyl(d_3)-imidazolium methyl(d_3)sulfate was obtained as a yellow liquid in a quantitative yield (6.89 g, 30 mmol). 1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=7.52$ (m, 1H), 7.59 (m, 1H), 8.99 ppm (m, 1H); ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=14.6$ (sep, $^1J(C,D)=20$ Hz; C^7),

35.9 (sep, $^1J(\text{C},\text{D})=22$ Hz; C^8), 44.8 (qui, $^1J(\text{C},\text{D})=22$ Hz; C^6), 53.5 (sep, $^1J(\text{C},\text{D})=22$ Hz; $[\text{CD}_3\text{OSO}_3]^-$), 123.0 (d, $^1J(\text{C},\text{H})=203$ Hz; C^5), 124.5 (d, $^1J(\text{C},\text{H})=203$ Hz; C^4), 137.6 ppm (d, $^1J(\text{C},\text{H})=221$ Hz; C^2).

Elemental analysis: calcd (%) for $\text{C}_7\text{H}_3\text{D}_{11}\text{N}_2\text{O}_4\text{S}$: C 36.03, H 6.04, N 12.01, S 13.74; found: C 36.17, H 6.01, N 12.51, S 13.22.

Synthesis of *N*-ethylpyridinium trifluoromethanesulfonate Freshly distilled ethyl trifluoromethanesulfonate (25.00 g (0.14 mol)) [12] was dissolved in 120 ml hexane and under vigorously stirring (10.28 g, 0.13 mol) pyridine was added dropwise over a 6-h period at 25 °C. Magnetic stirring (800 rpm) was continued for 2 h at 25 °C to complete the reaction. The bottom phase of the resulting two phases was separated and washed with 30 ml hexane for four times. Finally, volatile impurities were removed from the product by evaporation during 6 h at 0.1 Pa and 25 °C. *N*-ethylpyridinium trifluoromethanesulfonate was obtained as a colorless solid material (m. p.: 40–41 °C) in a quantitative yield (32.42 g, 0.13 mol). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=1.61$ (t, $^3J(\text{H},\text{H})=7.3$ Hz, 3H), 4.64 (q, $^3J(\text{H},\text{H})=7.3$ Hz, 2H), 8.06 (m, 2H), 8.54 (m, 1H), 8.85 ppm (m, 2H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): $\delta=-79.1$ ppm (s; CF_3S).

Synthesis of *N*-ethylpyridinium tris(pentafluoroethyl)trifluorophosphate The aqueous solutions of (18.64 g, 38 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (9.90 g, 38 mmol) *N*-ethylpyridinium trifluoromethanesulfonate were combined and stirred (1,000 rpm) at 20 °C for 1 h. The bottom phase of the resulting two colorless liquid phases was separated and washed with 25 ml of water for five times. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. *N*-ethylpyridinium tris(pentafluoroethyl)trifluorophosphate was obtained as a colorless liquid in a high yield (20.04 g, 36 mmol, 94 %).

^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): $\delta=1.64$ (t, $^3J(\text{H},\text{H})=7.3$ Hz, 3H), 4.61 (q, $^3J(\text{H},\text{H})=7.3$ Hz, 2H), 8.04 (m, 2H), 8.52 (m, 1H), 8.73 ppm (m, 2H); ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): $\delta=-44.7$ (d, $^1J(\text{F},\text{P})=889$ Hz, m, 1F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -68.9 (d, $^1J(\text{F},\text{P})=795$ Hz, m, 3F; $[(\text{C}_2\text{F}_5)_3\text{PF}_3]_{\text{f}}$), -80.9 (m, 3F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -82.6 (m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -82.6 (m, 9F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), -88.2 (d, $^1J(\text{F},\text{P})=902$ Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -116.2 (d, $^2J(\text{F},\text{P})=83$ Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -116.2 (d, $^2J(\text{F},\text{P})=81$ Hz, m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), -116.8 ppm (d, $^2J(\text{F},\text{P})=98$ Hz, m, 4F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$); Ratio of conformers $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$ (meridional) : $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$ (facial) = 100 : 0.8; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): $\delta=-147.7$ (d, $^1J(\text{F},\text{P})=889$ Hz, t, $^1J(\text{F},\text{P})=902$ Hz, t, $^2J(\text{F},\text{P})=83$ Hz, qui, $^2J(\text{F},\text{P})=98$ Hz; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$); ^{13}C NMR

(100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=15.4$ (q, $^1J(\text{C},\text{H})=130$ Hz; C^8), 57.3 (t, $^1J(\text{C},\text{H})=147$ Hz; C^7), 128.3 (d, $^1J(\text{C},\text{H})=202$ Hz; $\text{C}^{3,5}$), 144.0 (d, $^1J(\text{C},\text{H})=190$ Hz; $\text{C}^{2,6}$), 145.6 ppm (d, $^1J(\text{C},\text{H})=169$ Hz; C^4).

Elemental analysis: calcd (%) for $\text{C}_{13}\text{H}_{10}\text{NF}_{18}\text{P}$: C 28.23, H 1.82, N 2.53; found: C 28.29, H 2.27, N 2.83.

Synthesis of *N*-ethyl(d_5)pyridinium(d_5) trifluoromethanesulfonate Hexane-fraction (200.0 g) with 6 % (w/w) trifluoromethanesulfonic acid ethylester(d_5) (12.0 g, 65 mmol) was dropped into vigorously stirred pyridine(d_5) (5.00 g, 59 mmol) during 9 h at 20 °C. Magnetic stirring (800 rpm) was continued for 12 h at 25 °C to complete the reaction. The lower phase of the resulting two phases was isolated and washed with 15 ml hexane for four times. Finally, volatile impurities were removed from the product by evaporation during 6 h at 0.1 Pa and 25 °C. *N*-ethyl(d_5)pyridinium(d_5) trifluoromethanesulfonate was obtained as a colorless solid material (m. p.: 42–43 °C) in a quantitative yield (15.72 g, 0.59 mmol). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): no signals; ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): $\delta=-79.1$ ppm (s; CF_3S).

Synthesis of *N*-ethyl(d_5)pyridinium(d_5) tris(pentafluoroethyl)trifluorophosphate The aqueous solutions of (17.55 g, 36 mmol) potassium tris(pentafluoroethyl)trifluorophosphate and (9.69 g, 36 mmol) *N*-ethyl(d_5)pyridinium(d_5) trifluoromethanesulfonate were combined and stirred (1,000 rpm) at 20 °C for 1 h. The bottom phase of the resulting two colorless liquid phases was separated and washed with 15 ml of water for five times. Finally, volatile impurities were removed from the product by evaporation during 8 h at 0.1 Pa and 30 °C. *N*-ethyl(d_5)pyridinium(d_5) tris(pentafluoroethyl)trifluorophosphate was obtained as a colorless liquid in a high yield (19.57 g, 35 mmol, 95 %). ^1H NMR (400.17 MHz, CD_3CN , 25 °C, TMS): No signals; ^{19}F NMR (376.54 MHz, CD_3CN , 25 °C, CCl_3F): $\delta=-44.7$ (d, $^1J(\text{F},\text{P})=889$ Hz, m, 1F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -68.9 (d, $^1J(\text{F},\text{P})=795$ Hz, m, 3F; $[(\text{C}_2\text{F}_5)_3\text{PF}_3]_{\text{f}}$), -80.9 (m, 3F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -82.6 (m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -82.6 (m, 9F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), -88.2 (d, $^1J(\text{F},\text{P})=902$ Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -116.2 (d, $^2J(\text{F},\text{P})=83$ Hz, m, 2F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$), -116.2 (d, $^2J(\text{F},\text{P})=81$ Hz, m, 6F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$), -116.8 ppm (d, $^2J(\text{F},\text{P})=98$ Hz, m, 4F; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$); Ratio of conformers $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$ (meridional) : $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{f}}$ (facial) = 100 : 0.8; ^{31}P NMR (161.99 MHz, CD_3CN , 25 °C, H_3PO_4 (85 %)): $\delta=-147.6$ ppm (d, $^1J(\text{F},\text{P})=889$ Hz, t, $^1J(\text{F},\text{P})=902$ Hz, t, $^2J(\text{F},\text{P})=83$ Hz, qui $^2J(\text{F},\text{P})=98$ Hz; $[(\text{F}_3\text{CF}_2\text{C})_3\text{PF}_3]_{\text{m}}$). ^{13}C NMR (100.61 MHz, CD_3CN , 25 °C, TMS): $\delta=14.5$ (sep, $^1J(\text{C},\text{D})=20$ Hz; C^8), 56.7 (quin, $^1J(\text{C},\text{D})=22$ Hz; C^7), 128.1 (t, $^1J(\text{C},\text{D})=27$ Hz; $\text{C}^{3,5}$), 143.7 (t, $^1J(\text{C},\text{D})=29$ Hz; $\text{C}^{2,6}$), 145.3 ppm (t, $^1J(\text{C},\text{D})=26$ Hz; C^4).

Fig. 1 Linear correlation between increase in the molar mass and increase in the density of ILs

Elemental analysis: calcd (%) for $C_{13}D_{10}NF_{18}P$: C 27.72, H 1.79, N 2.49; found: C 27.78, H 1.77, N 2.55.

Results and discussion

To examine the validity of our hypothesis, we have prepared a number of ionic liquids with partially and completely deuterated cations and anions and compared their viscosity and density with that of non-deuterated ILs. By deuteration, we change neither the ionicity rate of the ionic liquid nor the cation or anion size or shape, nor the nature of the inter-ionic interaction. Only the mass of the cation or the anion is changed by the replacement of hydrogen with deuterium. This

statement is strongly supported by the linear correlation between the increase in the molar mass and the resulting increase in the density (Fig. 1). In our study, we have found that with increasing number of deuterium atoms in the cation and anion, the viscosity of ionic liquids systematically increases in some units (see Table 1). This is particularly evident at 20 °C. At higher temperature (80 °C), the gap between the viscosity of deuterated and non-deuterated ionic liquids becomes much smaller. Probably at elevated temperatures (above 80 °C) due to the high degree of ion-pairs self-dissociation, the viscosity of ionic liquids depends predominantly on the mobility (diffusivity) of the cations and anions, but not on the diffusivity of the ion-pairs [17]. In other words, at elevated temperatures the equilibrium $Ct^+A^- \rightleftharpoons Ct^+ + A^-$ is strongly shifted to the right side. This phenomenon was also found in the previously described studies with ionic liquids having the same anion but various cations [14, 17, 18] or the imidazolium cation with different alkyl chains [11].

It seems that at temperatures above 80 °C, ionic liquids reach a critical state. In this state, the physical properties of ILs (viscosity, conductivity etc.) in liquid phase depend faintly on the chemical nature of the ions and their intra-ionic interactions [19].

A reasonable correlation was observed between the increase of the molar mass of the deuterated ILs and the corresponding increase of the viscosity. The linear correlation $y = 3.1x$ (Fig. 2) indicates that percentage increase in the viscosity (y) of various ILs is approximately three times higher than the percentage increase in their molar mass (x).

Table 2 presents the percentage's increase in the molar mass of the ionic liquid and separately of the anion and the cation. A clear tendency can be elucidated: increasing of the molar mass

Table 1 Viscosity and density of deuterated ILs (given in the order of increasing viscosity at 20 °C)

Ionic liquid (IL)	Viscosity ^a (mPa·s) temperature (°C)				Density ^b (g/cm ³) temperature (°C)			
	20	40	60	80	20	40	60	80
[EMIM][B(CN) ₄]	21.96	11.24	6.84	4.68	1.041	1.026	1.011	0.996
[EM(d ₃)IM][B(CN) ₄]	22.58	11.52	6.98	4.76	1.055	1.041	1.025	1.010
[EMIM][(C ₂ F ₅) ₃ PF ₃]	76.57	34.45	18.67	11.65	1.715	1.693	1.669	1.646
[EM(d ₃)IM][(C ₂ F ₅) ₃ PF ₃]	78.04	35.09	19.04	11.73	1.726	1.704	1.681	1.658
[E(d ₅)MIM][(C ₂ F ₅) ₃ PF ₃]	80.10	34.58	19.17	11.74	1.733	1.711	1.688	1.663
[E(d ₅)M(d ₃)IM][(C ₂ F ₅) ₃ PF ₃]	80.93	36.01	19.38	11.87	1.745	1.722	1.699	1.674
[EMIM][CH ₃ OSO ₃]	88.41	38.70	20.54	12.50	1.285	1.272	1.259	1.245
[EM(d ₃)IM][CD ₃ OSO ₃]	95.86	41.38	21.87	13.25	1.321	1.307	1.293	1.280
[E(d ₅)M(d ₃)IM][CD ₃ OSO ₃]	101.52	43.64	22.95	13.86	1.351	1.337	1.323	1.309
[EPy][(C ₂ F ₅) ₃ PF ₃]	118.04	47.87	24.35	14.34	1.733	1.710	1.688	1.665
[E(d ₅)Py(d ₅)][(C ₂ F ₅) ₃ PF ₃]	124.68	50.30	25.49	14.99	1.766	1.744	1.721	1.698

[E(d₅)M(d₃)IM] 1-ethyl-3-methyl-imidazolium-cation with perdeuterated alkyl chains, [E(d₅)Py(d₅)] perdeuterated *N*-ethylpyridinium-cation

^a Viscosity was determined correct to three decimal digits; accuracy is estimated to be with 0.01 mPa·s

^b Density was determined correct to four decimal digits; accuracy is estimated to be with 0.001 g/cm³

Fig. 2 Linear correlation between increase of the molar mass of IL and increase in the viscosity

of ionic liquids (anion+cation) by increasing the number of deuterium atoms leads to an increase in the viscosity.

This new knowledge gained in our study explicates the properties of recently developed ionic liquids of particularly low viscosity. Table 3 presents the viscosity of ionic liquids consisting of the 1-ethyl-3-methyl-imidazolium cation [EMIM] and small weakly coordinating anions of different mass. The tendency is evident: Less heavy anions secure a low viscosity of the corresponding ionic liquids. An

Table 3 Viscosity and density of 1-ethyl-3-methyl-imidazolium ([EMIM]) ionic liquids with $[B(CN)_4]^-$ (TCB), $[FB(CN)_3]^-$, $[HB(CN)_3]^-$, $[F_2B(CN)_2]^-$, and $[H_2B(CN)_2]^-$ anions

Ionic liquid	MM (g/mol) of the anion	Viscosity at 20 °C, mPa·s	Density at 20 °C, g/cm ³
[EMIM][B(CN) ₄][16]	115	22.0	1.04
[EMIM][FB(CN) ₃][20]	108	12.6	1.07
[EMIM][HB(CN) ₃][21]	90	12.2	1.01
[EMIM][F ₂ B(CN) ₂][22]	101	11.1	1.12
[EMIM][H ₂ B(CN) ₂][23]	65	10.2	0.98

MM molar mass

extraordinarily large decrease of the viscosity of ionic liquids containing borate-anions is observed by replacement of the tetracyanoborate anion, $[B(CN)_4]^-$, with other cyanoborates. Substitution of one cyano group with fluorine or hydrogen reduces the mass of the $[B(CN)_4]^-$ anion and breaks also the symmetry of the tetracyanoborate anion.

The difference in the viscosities of [EMIM][FB(CN)₃] and [EMIM][F₂B(CN)₂] is not as big as in the case of [EMIM][B(CN)₄] and [EMIM][FB(CN)₃]. The $[F_2B(CN)_2]^-$ -anion is a little bit lighter than the $[FB(CN)_3]^-$ -anion, but has a symmetrical structure and is probably more coordinative than the tricyanofluoroborate anion. The same applies to the assessment of [EMIM][HB(CN)₃] and [EMIM][H₂B(CN)₂] ILs.

Table 2 Comparison of the molar mass and the viscosity of deuterated and non-deuterated ILs

Ionic liquid (IL)	MM (g/mol) of IL (mass increase in %) ^[a]	MM (g/mol) of cation (mass increase in %) ^a	MM (g/mol) of anion (mass increase in %) ^a	Increase of viscosity at 20 °C in % ^{a, b}	Increase of density at 20 °C in % ^{a, c}
[EMIM][B(CN) ₄]	226.05	111.17	114.88		
[EM(d3)IM][B(CN) ₄]	229.06 (1.33 %)	114.18 (2.71 %)	114.88	2.82 %	1.35 %
[EMIM][(C ₂ F ₅) ₃ PF ₃]	556.18	111.17	445.01		
[EM(d3)IM][(C ₂ F ₅) ₃ PF ₃]	559.20 (0.54 %)	114.18 (2.71 %)	445.01	1.92 %	0.64 %
[E(d5)MIM][(C ₂ F ₅) ₃ PF ₃]	561.21 (0.91 %)	116.20 (4.52 %)	445.01	4.61 %	1.05 %
[E(d5)M(d3)IM][(C ₂ F ₅) ₃ PF ₃]	564.23 (1.45 %)	119.22 (7.24 %)	445.01	5.69 %	1.75 %
[EMIM][CH ₃ OSO ₃]	222.26	111.17	111.09		
[EM(d3)IM][CD ₃ OSO ₃]	228.29 (2.71 %)	114.18 (2.71 %)	114.11 (2.72 %)	8.43 %	2.80 %
[E(d5)M(d3)IM][CD ₃ OSO ₃]	233.33 (4.89 %)	119.22 (7.24 %)	114.11 (2.72 %)	14.83 %	5.14 %
[EPy][(C ₂ F ₅) ₃ PF ₃]	553.17	108.16	445.01		
[E(d5)Py(d5)][(C ₂ F ₅) ₃ PF ₃]	563.23 (1.82 %)	118.22 (9.30 %)	445.01	5.63 %	1.90 %

[E(d5)M(d3)IM] 1-ethyl-3-methyl-imidazolium-cation with perdeuterated alkyl chains, [E(d5)Py(d5)] perdeuterated *N*-ethylpyridium-cation, MM molar mass

^a In every case is related to the non-deuterated ionic liquid

^b ±0.1 %

^c ±0.2 %

In spite of a quite big difference in the molecular mass of $[\text{FB}(\text{CN})_3]$ and $[\text{HB}(\text{CN})_3]$ anions, the viscosities of $[\text{EMIM}]$ ionic liquids with these anions have a comparable value (Table 3). This means, not only reduction of the mass of the anion but also its coordination to the cation strongly influences the viscosity of the ionic liquid. Weakly coordinating anions provide an access to low-viscosity ionic liquids [7]. Fluorine is strongly participating in the delocalization of the negative charge of the $[\text{FB}(\text{CN})_3]$ -anion. This makes this anion less coordinative in comparison to the $[\text{HB}(\text{CN})_3]$ -anion. Table 3 summarizes that the mass, the shape (or symmetry), and coordination ability of the anion modulate the viscosity of ionic liquids. This makes the prognoses of the properties (i.e., viscosity) of unknown ionic liquids thorny.

Conclusions

The properties of ionic liquids (like viscosity, conductivity, etc.) are determined not only by the size of the ions, the shape of the ions, and the magnitude of the interaction's forces between anion and cation, but also by the mass of the ions which form ionic liquids. ILs which possess a low viscosity are of particular interest for application in energy conversion devices.

Deuterated ILs are valuable media to study chemical reactions, natural products, and bio-materials by means of NMR spectroscopy and other physical methods.

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