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Synthesis and spectroscopic properties of symmetrical ionic liquids based on (−)-menthol

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ABSTRACT

Several symmetrical imidazolium salts were obtained from the natural chiral pool of (1*R*,2*S*,5*R*)-(−)-menthol. First 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride, which is a prototype for ionic liquids, was prepared with the use of two different methods. Furthermore, metathesis of this symmetrical imidazolium chloride with various salts was carried out. The ion exchange reaction goes smoothly, with the satisfactory yield of 97.5 to 99.5%. Obtained 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts are stable in the air, in contact with water and in commonly used organic solvents. Moreover they are non-volatile and non-flammable. Discussed symmetrical salts belong to chiral ionic liquids (CILs) where the chirality resided in the cation and is associated with the presence of optically active (1*R*,2*S*,5*R*)-(−)-menthol.
The diastereotopic protons in the ^{1}H NMR were thoroughly described. Moreover, the ^{1}H NMR and ^{13}C NMR spectra indicated notable differences in the chemical shifts depending on the anion used. Comparing the differences between values of the chemical shifts, the anions were ordered according to their increasing shielding capacities. The changing of the electron density surrounding the imidazolium ring was discussed.

1. Introduction

Ionic liquids (ILs) attract much scientific interest due to their properties and the possibility of obtaining products for distinct purposes [1–4]. Therefore during the last decade a large number of publication appearance both in the field of synthesis [5,6] and physicochemical properties [7,8], and in areas of their potential applications [9–11]. It should be highlighted that one of their major features is the 'designable' structure which can be achieved by selecting appropriate ions to obtain specific utility for various applications (e.g. in separation technology [12,13], biomass treatment [14], energy storage [15], lubrication [16,17], electrochemistry [18], catalysis [19,20], and medical chemistry [21,22]). The enormous combinations of different cations and anions for designing ionic liquids have also impact on their tunable physicochemical properties (e.g. thermal stability, density, viscosity, conductivity, polarity, solubility, hydrogen bond ability).

The asymmetry/symmetry of the cation plays an important role in changing the physicochemical properties of ionic liquids [23]. The symmetry in ILs is generally considered to the multiplicities of the cation (mainly dicationic and tricationic ILs) or to the presence of two (sometimes more) identical chains in the cation. The advantages of using those salts seem to be justified mainly due to their higher thermal stability in comparison with their asymmetric counterparts [24,25]. Moreover, other major benefits of testing them is higher flexibility in the manipulation of their physicochemical properties [26–29].

Previously, we described and tested ionic liquids based on (1*R*,2*S*,5*R*)-(−)-menthol having asymmetrical structure [30–33]. The presence of optical active monocyclic alcohol in the cationic part classified these compounds to the group of chiral ionic liquids (CILs). The promising properties have already been shown, inter alia: in organic catalysis [34], in stabilization and activation of laccase [35] and as antielectrostatic materials [30,32,33]. Moreover, the microbiological activity of some CILs with discussed terpene alcohol was definitely more pronounced than that of commercially available pattern [36]. On the other hand, the methods of synthesis of symmetrical imidazolium chloride based on (1*R*,2*S*,5*R*)-(−)-menthol have been also presented by our group [37]. In this study the synthesis, physicochemical and spectroscopic properties of new symmetrical ionic liquids based on (1*R*,2*S*,5*R*)-(−)-menthol are reported. It seems to be extremely interesting to continue the research on the issue regarding CILs with natural occurring substance: monocyclic terpene alcohol, mainly due to the possible selection of the best of them for various applications. Moreover, the impact of symmetry/asymmetry on physicochemical properties and potential use for distinct purposes is also taken into account. Furthermore, the selected anions for preparing symmetrical ionic liquids presented herein [bis(pentafluoroethylsulfonyl)imide, 1,1,2,2-tetrafluoroethanesulfonate, perfluorobutanesulfonate, dicyanamide and thiocyanate] have been nowadays often investigated mainly due to their very promising potential applications e.g. in catalysis [38], in

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extraction [39–41], in dissolution of carbohydrates [42], in electrochemistry [43,44] and in processing of cellulose [45]. Surprisingly, they have also appeared to effective stored product insect antifeedants [46].

2. Experimental

2.1. Materials

The chemicals which have been used in the synthesis of the symmetrical chiral ionic liquids were of analytical grade. They were purchased from different companies. (1*R*,2*S*,5*R*)-(−)-Menthol (≥99%), paraformaldehyde (power, 95%), imidazole (≥99%), triethylamine (anhydrous, ≥99%), hydrochloric acid (35–38%), sulfuric acid (≥96%), sodium dicyanamide (96%), potassium thiocyanate (≥99%) were purchased from Sigma-Aldrich. Lithium bis(pentafluoroethylsulfonyl)imide (99%), potassium perfluorobutanesulfonate (>98%) and potassium 1,1,2,2-tetrafluoroethanesulfonate (98%) were provided by Iolitec.

For NMR analysis, deuterated chloroform ($CDCl_3$), deuterated dimethyl sulfoxide [$(CD_3)_2SO$], deuterated acetone (CD_3COCD_3) and deuterated water (D_2O), purchased from Merck, were used. For all measurements the concentration of the tested symmetrical imidazolium salts in the deuterated solvent was constant with a value of 20 mg (±0.0001 g) in 0.60 cm^3 (±0.01 cm^3) of each solvent.

All solvents used in synthesis and purification of chiral ionic liquids were purchased from the commercial suppliers: Sigma-Aldrich and Fluka and were dried before their use. All reagents were dried and purified before the use by usual procedures, reactions were performed under anhydrous conditions and all substrates were freshly distilled before using.

2.2. Instrumentation

Melting points were determined by using an electrothermal digital-melting-point apparatus model JA 9100 (temperature resolution ±0.1 °C; accuracy ±1%; choice of ramp rate of 1.0 °C/min). The type and the shape of the crystals were analysed via optical microscope Axiolmager M1m (Zeiss) in reflection mode. Specific rotations at 578 nm were measured using an Optical Activity Ltd. Model AA-5 automatic polarimeter (resolution ±0.01°, reproducibility ±0.01°, accuracy ±0.01°, temperature probe measurement accuracy ±0.1 °C, the equipment provide four results for each measurement). The structure and purity of all of the synthesized salts were confirmed by spectral analysis. Elemental analyses were carried out for all of the synthesized substances using VARIO EL-III. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX with tetramethylsilane as the standard (at 600 and 75 MHz, respectively). Total concentration of the metal in each sample was measured in resulting solutions by high-resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS) with a contrAA 700 instrument (Analytik Jena AG).

2.3. Synthesis of symmetrical chiral ionic liquids

2.3.1. Synthesis of substrates

Chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether was obtained by passing HCl through a mixture of paraformaldehyde and (1*R*,2*S*,5*R*)-(−)-menthol, following the published method [30]. 1-(1*R*,2*S*,5*R*)-(−)-Menthoxymethylimidazole was prepared in a two-step reaction, using: trimethylamine, chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether and imidazole, following the published method [37]. 1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride (**1**) was obtained by two different methods and the details were described in our previous publication [37].

All of the synthesized precursors of chiral ionic liquids [chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether, 1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazole and 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride (**1**)] were characterized by ^{1}H NMR and ^{13}C NMR and the results were fully comparable with those presented earlier [37].

2.3.2. Synthesis of symmetrical chiral ionic liquids (**2**–**6**)

The solid salts (0.031 mol): potassium thiocyanate, lithium bis(pentafluoroethylsulfonyl)imide, and potassium 1,1,2,2-tetrafluoroethanesulfonate were dissolved in methanol at room temperature. The potassium perfluorobutanesulfonate was also dissolved in methanol but at the elevated temperature (around 40 °C), due to its limited solubility at room temperature. In case of sodium dicyanamide the distilled water was used as a solvent (because of very low solubility of sodium dicyanamide in methanol). Then, the prepared solution was added to saturated methanol containing 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride (0.03 mol). The reaction was stirred at room temperature for 1 day. Upon evaporation of the solvents, the product was dissolved in acetone and stirred for 30 min to precipitate the halide salt (NaCl, KCl or LiCl), which was filtrated off (0.2 μm filter). The filtrate was placed in the fridge (approx. −5 °C) for one night in order to complete precipitation of the halide salt. In the case of precipitation of inorganic salt, another filtration was carried out and the resulting filtrate was evaporated. Finally, the crude product was washed with distilled water until chloride ions were no longer detected using $AgNO_3$. Obtained salts were further dried in vacuum (0.3 mm Hg) to achieve analytically pure products. Prior to any measurements 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts (**2**–**6**) samples were dried for 48 h under vacuum.

*2.3.2.1. 1,3-Bis[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium bis(pentafluoroethylsulfonyl)imide (**2**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.53 (d, J = 7.2 Hz, 6H, H9 or H10 and H9′ or H10′), 0.82–0.94 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.25–1.29 (m, 2H, H2 and H2′), 1.38–1.40 (m, 2H, H5 and H5′), 1.61–1.67 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 1.95–2.01 (m, 4H, H8, H8′Hb-6 and Hb-6′), 3.31 (td, J = 10.2 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.56 and 5.68 (d, J = 10.2 Hz, 4H, AB system, H11 and H11′), 7.475 (s, 1H, H12 or H13), 7.48 (s, 1H, H12 or H13), 9.28 (s, 1H, H14).

^{13}C NMR (300 MHz, $CDCl_3$): δ 15.4 (C9 or C10 and C9′ or C10′), 20.8 (C7 and C7′), 21.9 (C9 or C10 and C9′ or C10′), 22.8 (C3 and C3′), 25.4 (C8 and C8′), 31.1 (C5 and C5′), 34.0 (C4 and *C*4′), 40.1 (C6 and C6′), 47.7 (C2 and C2′), 77.1 (C1 and C1′), 80.3 (C11 and C11′), 113.7, 111.7, 109.75 (qxq, J^1_{CF} = 294 Hz, J^2_{CF} = 39 Hz, CF_2, anion), 120.6, 118.9, 117.0, 115.1 (txt, J^1_{CF} = 288 Hz, J^2_{CF} = 33 Hz, CF_3, anion), 122.1 (C13 and C12), 135.0 (C14).

Elemental analysis calc. (%) for $C_{29}H_{45}F_{10}N_3O_6S_2$ (785.97): C 44.31, H 5.78, N 5.35, S 8.17. Found: C 44.42, H 5.90, N 5.30, S 8.09.

*2.3.2.2. 1,3-Bis[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium 1,1,2,2-tetrafluoroethanesulfonate (**3**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.56 (d, J = 6.6 Hz, 6H, H9 or H10 and H9′ or H10′), 0.84–0.98 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.26–1.30 (m, 2H, H2 and H2′), 1.45–1.46 (m, 2H, H5 and H5′), 1.63–1.69 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 2.02 (sept d, J = 5.4 Hz, J = 2.4 Hz, 2H, H8 and H8′), 2.07–2.08 (m, 2H, Hb-6 and Hb-6′), 3.37 (td, J = 10.8 Hz, J = 4.8 Hz, 2H, H1 and H1′), 5.62 and 5.76 (d, J = 10.8 Hz, 4H, AB system, H11 and H11′), 6.31, 6.22, 6.13 (txt, J = 53.0 Hz, J = 6.0 Hz, 1H, anion), 7.49 (s, 1H, H12 or H13), 7.495 (s, 1H, H12 or H13),9.77 (s, 1H, H14). ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.6 (C9 or C10 and C9′ or C10′), 20.9 (C7 and C7′), 22.0 (C9 or C10 and C9′ or C10′), 22.8 (C3 and C3′), 25.4 (C8 and C8′), 31.1 (C5 and C5′), 34.0 (C4 and C4′), 40.2 (C6 and C6′), 47.8 (C2 and C2′), 77.3 (C1 and C1′), 80.1 (C11 and C11′), 111.70, 109.1, 107.4 (txt, J^1_{CF} = 253 Hz, J^2_{CF} = 29 Hz, anion CHF_2), 115.65, 113.8, 111.9 (txt, J^1_{CF} = 284 Hz, J^2_{CF} = 24 Hz, anion CF_2), 121.7 (C13 and C12), 136.4 (C14).

Elemental analysis calc. (%) for $C_{27}H_{46}F_4N_2O_5S$ (586.85): C 55.26, H 7.92, N 4.77, S 5.47. Found: C 55.35, H 7.87, N 4.81, S 5.38.

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*2.3.2.3. 1,3-Bis[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium perfluorobutanesulfonate (**4**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.56 (d, J = 7.2 Hz, 6H, H9 or H10 and H9′ or H10′), 0.83–0.97 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.25–1.28 (m, 2H, H2 and H2′), 1.43–1.44 (m, 2H, H5 and H5′), 1.63–1.66 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 2.00 (sept d, J = 7.2 Hz, J = 2.4 Hz, 2H, H8 and H8′), 2.06–2.07 (m, 2H, Hb-6 and Hb-6′), 3.37 (td, J = 10.2 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.61 and 5.75 (d, J = 10.8 Hz, J = 10.2 Hz, 4H, AB system, H11 and H11′), 7.49 (s, 1H, H12 or H13), 7.495 (s, 1H, H12 or H13), 9.74 (s, 1H, H14). ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.5 (C9 or C10 and C9′ or C10′), 20.8 (C7 and C7′), 21.9 (C9 or C10 and C9′ or C10′), 22.75 (C3 and C3′), 25.3 (C8 and C8′), 31.0 (C5 and C5′), 34.0 (C4 and C4′), 40.1 (C6 and C6′), 47.7 (C2 and C2′), 77.3 (C1 and C1′), 80.1 (C11 and C11′), 122.0 (C13 and C12), 136.0 (C14), 107.0–107.4, 108.3–109.5, 110.3–111.2, 111.7–112.9, 113.6–114.8, 115.6–116.7, 118.2–118.6, 120.1–120.6 (anion), 122.0 (C13 and C12), 136.0 (C14).

Elemental analysis calc. (%) for $C_{29}H_{45}F_9N_2O_5S$ (704.86): C 49.41, H 6.45, N 3.97, S 4.55. Found: C 49.56, H 6.58, N 3.92, S 4.48.

*2.3.2.4. 1,3-Bis[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium dicyanamide (**5**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.60 (d, J = 6.6 Hz, 6H, H9 or H10 and H9′ or H10′), 0.85–1.00 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.28–1.32 (m, 2H, H2 and H2′), 1.45–1.47 (m, 2H, H5 and H5′), 1.63–1.70 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 2.00–2.08 (m, 4H, H8, H8′, Hb-6 and Hb-6′), 3.38 (td, J = 10.8 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.66 and 5.75 (d, J = 10.8 Hz, J = 10.2 Hz, 4H, AB system, H11 and H11′), 7.57 (s, 1H, H12 or H13), 7.575 (s, 1H, H12 or H13), 9.62 (s, 1H, H14). ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.8 (C9 or C10 and C9′ or C10′), 20.9 (C7 and C7′), 22.1 (C9 or C10 and C9′ or C10′), 22.9 (C3 and C3′), 25.5 (C8 and C8′), 31.3 (C5 and C5′), 34.0 (C4 and C4′), 40.3 (C6 and C6′), 47.8 (C2 and C2′), 77.5 (C1 and C1′), 80.4 (C11 and C11′), 119.9 (anion), 121.9 (C13 and C12), 135.9 (C14).

Elemental analysis calc. (%) for $C_{27}H_{45}N_5O_2$ (471.74): C 67.88, H 9.51, N 5.86. Found: C 67.94, H 9.64, N 5.80.

*2.3.2.5. 1,3-Bis[(1R,2S,5R)-(−)-menthoxymethyl]imidazolium thiocyanate (**6**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.56 (d, J = 7.2 Hz, 6H, H9 or H10 and H9′ or H10′), 0.80–0.96 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.24–1.28 (m, 2H, H2 and H2′), 1.43–1.455 (m, 2H, H5 and H5′), 1.59–1.65 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 1.98 (sept d, J = 6.6 Hz, J = 2.4 Hz, 2H, H8 and H8′), 2.09–2.11 (m, 2H, Hb-6 and Hb-6′), 3.42 (td, J = 10.8 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.70 and 5.86 (d, J = 10.2 Hz, 4H, AB system, H11 and H11′), 7.50 (s, 1H, H12 or H13), 7.55 (s, 1H, H12 or H13), 9.93 (s, 1H, H14). ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.8 (C9 or C10 and C9′ or C10′), 21.0 (C7 and C7′), 22.2 (C9 or C10 and C9′ or C10′), 22.9 (C3 and C3′), 25.5 (C8 and C8′), 31.2 (C5 and C5′), 34.0 (C4 and C4′), 40.0 (C6 and C6′), 47.8 (C2 and C2′), 77.7 (C1 and C1′), 80.3 (C11 and C11′), 121.5 (C13 and C12), 132.0 (anion), 136.75 (C14).

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 0.47 (d, J = 6.6 Hz, 6H, H9 or H10 and H9′ or H10′), 0.81–0.92 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.15–1.20 (m, 2H, H2 and H2′), 1.33–1.39 (m, 2H, H5 and H5′), 1.55–1.63 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 1.94 (sept d, J = 7.2 Hz, J = 2.4 Hz, 2H, H8 and H8′), 2.04–2.505 (m, 2H, Hb-6 and Hb-6′), 3.28 (td, J = 10.8 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.64 and 5.69 (d, J = 10.8 Hz, J = 10.2 Hz, 4H, AB system, H11 and H11′), 7.99 (s, 1H, H12 or H13), 8.00 (s, 1H, H12 or H13), 9.62 (s, 1H, H14). ^{13}C NMR (300 MHz, $(CD_3)_2SO$): δ 16.05 (C9 or C10 and C9′ or C10′), 21.3 (C7 and C7′), 22.5 (C9 or C10 and C9′ or C10′), 23.0 (C3 and C3′), 25.3 (C8 and C8′), 31.25 (C5 and C5′), 34.1 (C4 and C4′), 39.6 (C6 and C6′), 47.7 (C2 and C2′), 77.6 (C1 and C1′), 78.4 (C11 and C11′), 123.2 (C13 and C12), 130.0 (anion), 137.7 (C14).

^{1}H NMR (600 MHz, CD_3COCD_3): δ 0.59 (d, J = 7.2 Hz, 6H, H9 or H10 and H9′ or H10′), 0.86–1.03 (m, 18H, Ha-4, H7, H9 or H10, Ha-6, Ha-3, Ha-4′, H7′, H9′ or H10′, Ha-6′ and Ha-3′), 1.26–1.30 (m, 2H, H2 and H2′), 1.48–1.50 (m, 2H, H5 and H5′), 1.63–1.69 (m, 4H, Hb-3, Hb-4, Hb-3′ and Hb-4′), 2.07–2.10 (m, 2H, H8 and H8′), 2.22–2.24 (m, 2H, Hb-6 and Hb-6′), 3.55 (td, J = 10.8 Hz, J = 4.2 Hz, 2H, H1 and H1′), 5.86 and 5.99 (d, J = 10.8 Hz, J = 10.2 Hz, 4H, AB system, H11 and H11′), 8.045 (s, 1H, H12 or H13), 8.05 (s, 1H, H12 or H13), 9.88 (s, 1H, H14). ^{13}C NMR (300 MHz, CD_3COCD_3): δ 15.7 (C9 or C10 and C9′ or C10′), 20.4 (C7 and C7′), 21.6 (C9 or C10 and C9′ or C10′), 22.7 (C3 and C3′), 25.52 (C8 and C8′), 31.0 (C5 and C5′), 34.0 (C4 and C4′), 40.2 (C6 and C6′), 47.9 (C2 and C2′), 77.0 (C1 and C1′), 78.9 (C11 and C11′), 122.7 (C13 and C12), 131.0 (anion), 137.2 (C14).

Elemental analysis calc. (%) for $C_{26}H_{45}N_3O_2S$ (463.84): C 67.32, H 9.80, N 9.06, S 6.92. Found: C 67.27, H 9.89, N 9.13, S 6.88.

2.4. The purity of the prepared CILs – metal content in CIL

Samples (100 mg) of solid CILs were wet digested in ACS grade concentrated HNO_3 (5 ml). A digestion block DigiPrep Jr. (SCP Science) was used. The digestion was carried out at 120 °C for 2 h in semi-closed vessels. Later on, the samples' solutions were evaporated nearly to dryness and finally reconstituted in deionized water to 5.0 g. The total concentrations of the proper metal (Li in the case of [Men-Im-Men][PFSI] – **2**; K in the case of [Men-Im-Men][TFES] – **3**, [Men-Im-Men][PFBS] – **4**, [Men-Im-Men][SCN] – **6**, and Na in the case of [Men-Im-Men][DCA] – **5**) were measured in resulting solutions by high resolution continuum source flame atomic absorption spectrometry (HR-CS-FAAS). Simple standard solutions of K, Li or Na (0.05, 0.1, 0.2 and 0.5 μg/g) were used for calibration. It was found that the samples' solutions of the investigated CILs contain proper metal below its limit of quantification (LOQ) assessed for HR-CS-FAAS as 0.005 μg/g. Considering the sample masses and the final volumes of the samples' solution it corresponded to the metal content below 0.25 μg/g.

2.5. Solubility

The solubility of obtained CILs was determined according to Vogel's Textbook of Practical Organic Chemistry [47]. The investigations were carried out for the synthesized salts (**2**–**6**) at 20 °C (±0.5 °C) and at 50 °C (±0.5 °C) under ambient pressure using popular solvents. The phrase *complete solubility* describe those salts which are soluble (0.1 g ± 0.01 g of each) in 1 mL (±0.01 mL) of solvent, while the *limited solubility* specifies those CILs in which 0.1 g (±0.01 g) of each salts is soluble in 3 mL (±0.1 mL) of solvent. The expression *insoluble* was used to characterize insolubility of the compound (0.1 g ± 0.01 g of the salt in 3 mL ± 0.1 mL of solvent).

3. Results and discussion

The studied new symmetrical chiral ionic liquids based on (1*R*,2*S*,5*R*)-(−)-menthol (**2**–**6**) were synthesized as shown in Scheme 1. In the first step, chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether was obtained by chloromethylation of (1*R*,2*S*,5*R*)-(−)-menthol [30]. Then 1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazole was prepared following the published method: trimethylamine reacted with terpene ether in toluene, then imidazole was added in order to perform *N*-alkoxymethylation [37]. Previously, we described two different methods of obtaining 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride (**1**) [37]. In the first method chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether reacted with stoichiometric amount of 1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazole in hexane. In the second method the reaction between two equivalents of chloromethyl (1*R*,2*S*,5*R*)-(−)-menthyl ether and one equivalent of imidazole took place in DMF. In this study the symmetrical chloride with two monocyclic terpene moieties (**1**) has been used as a precursor of new chiral ionic liquids via metathesis reaction.

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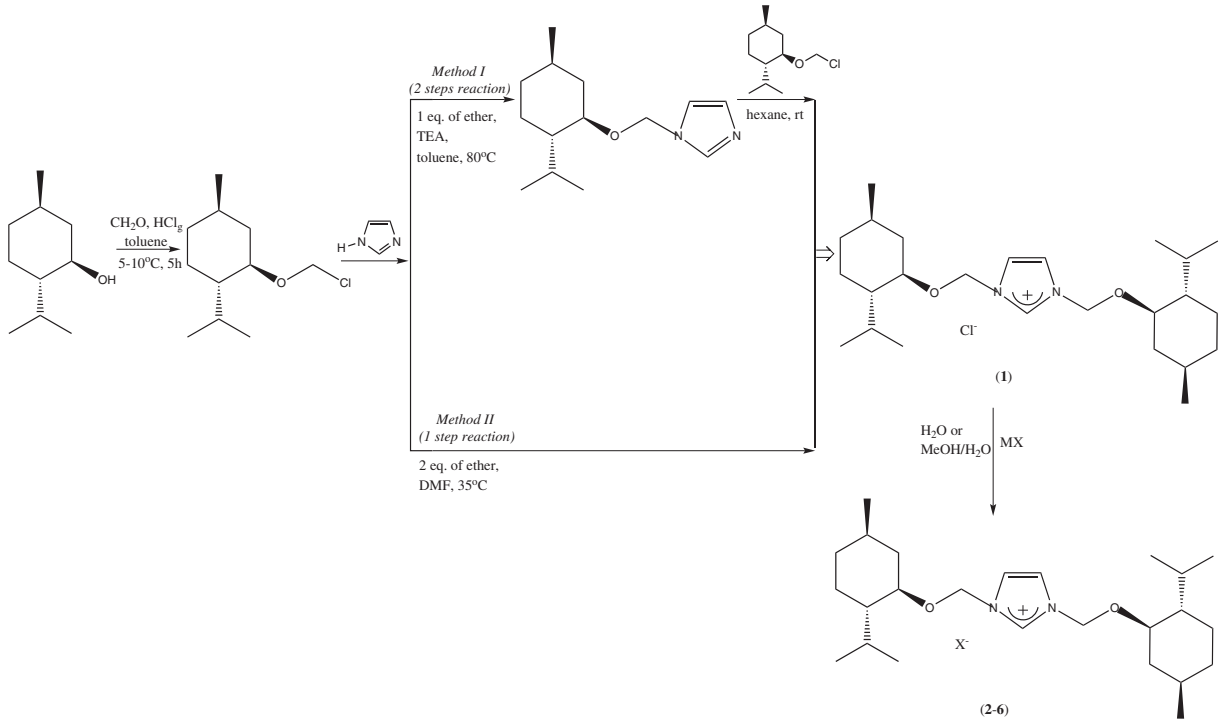

Scheme 1. Preparation of symmetrical chiral ionic liquids (**2**–**6**). MX = $(C_2F_5SO_2)_2NLi$, $C_2F_4HSO_3K$, $C_4F_9SO_3K$, $NaN(CN)_2$, KSCN.

The anion exchange processes proceeded smoothly, with the efficiency exceeding 97% in each case (Table 1). Due to very low solubility of 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium chloride in water the metathesis reaction was conducted using saturated methanol solution of salt **1**. In the case of obtaining [Men-Im-Men][PFSI], [Men-Im-Men][TFES] and [Men-Im-Men][SCN] the reaction was carried out in methanol solution at room temperature, while [Men-Im-Men][PFBS] was synthesized in the same solvent, but at elevated temperature, since potassium perfluorobutanesulfonate shows limited solubility in methanol at room temperature. The mixture of methanol/water was used for synthesis of [Men-Im-Men][DCA] due to very low solubility of sodium dicyanamide in methanol. Sodium, potassium or lithium chloride were by-products of the exchange reactions and were removed using acetone, in which those inorganic salts precipitate. The details about metathesis reaction as well as structures and abbreviations of obtained salts are presented in the Table 1.

All of the synthesized 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl] imidazolium salts (**2**–**6**) are solid. The melting point, crystallization conditions, crystal shape and specific rotation of each salt are given in Table 2. The melting points of new symmetrical imidazolium salts based on (1*R*,2*S*,5*R*)-(−)-menthol suggest that they should be considered as ionic liquids, except 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium thiocyanate (**6**) with higher melting point: 134.1–134.5 °C. The general trend which can be observed for discussed CILs is that there is a major influence of lowering the melting point with changing the type of the anion. In case of comparing chloride (**1**) with perfluorobutanesulfonate (**4**) the difference is over 70 °C: from 126 to 127.7 °C for salt **1** [37] to 51.7–52.3 °C for salt **4**. Surprisingly, the melting point of [Men-Im-Men][SCN] is higher than its precursor.

The obtaining of the crystal structure was possible to achieve for majority of discussed salts. The solids: [Men-Im-Men][PFSI] and [Men-Im-Men][PFBS] crystallize easily from mixture water/ethanol, while [Men-Im-Men][TFES] from hexane/chloroform. In the case of performing the crystal structure of [Men-Im-Men][SCN] the mixture of solvents of ethyl acetate/acetone was used. The various form of the crystals were observed: for bis(pentafluoroethylsulfonyl)imide (**2**) and thiocyanate (**6**) derivatives structure of plates were recognized, while crystals of 1,1,2,2-tetrafluoroethanesulfonate (**3**) and perfluorobutanesulfonate (**4**) compounds are in the shape of needles (Table 2). Unfortunately, repeated efforts have not succeeded in obtaining the crystal structure for [Men-Im-Men][DCA]. In spite of using different types of solvents for crystallization the salt has exhibited the tendency to oil and the crystal form hasn't been observed.

All of the synthesized 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl] imidazolium salts (**2**–**6**) are stable in air, in aqueous solutions and in commonly used organic solvents. The solubility test has been performed using popular polar and nonpolar solvents according to the method described by Vogel et al. [47]. The results are shown in Table 2. All of the obtained chlorides are soluble in various commonly used solvents, e.g.: acetone, acetonitrile, chloroform, THF, DMSO, DMF and in low molecular weight alcohols. The solubility in toluene and ethyl acetate is also excellent at room temperature in case of salts **2**–**5**. The thiocyanate derivative (**6**) might be completely soluble in toluene at elevated temperatures, while in ethyl acetate it is totally insoluble even at elevated temperatures (Table 3). All of the synthesized salts are not soluble in diethyl ether and hexane independently from the set of the measurement temperature. In case of water there is an interesting point to discuss: at room temperature majority of 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts are insoluble, only [Men-Im-Men][DCA] shows partial solubility. In 50 °C salts from **1** to **5** are completely soluble in water, except [Men-Im-Men][SCN], which is totally insoluble. Furthermore, it should be pointed that the change of the anion influence the solubility of the obtained salts in water. This pattern refers to CILs from **1** to **5**, which are soluble in water at 50 °C, while its chloride precursor is almost insoluble even at elevated temperatures.

The changes of the solubility of [Men-Im-Men][DCA] **5** were confirmed by ^1H NMR, using D_2O as a solvent. The spectra were performed for various amounts of the compound (m = 0.02 g, 0.01 g and 0.005 g; $V_{D2O} = 0.60\ cm^3$; $T = 20\ °C$) and various temperatures of the measurement (T = 20 °C, 30 °C, 40 °C, 50 °C, 60 °C). With increasing the amount of the dicyanamide salt and with increasing the temperature of the measurement the observed picks are more pronounced and more sharp (all spectra are provided in Supporting Information S22-S26).

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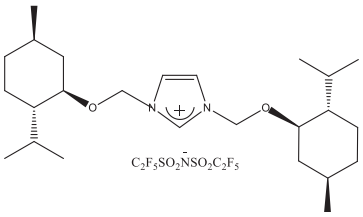
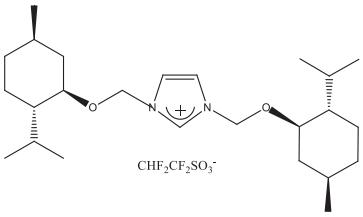
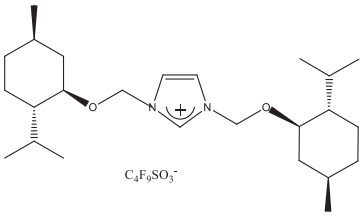
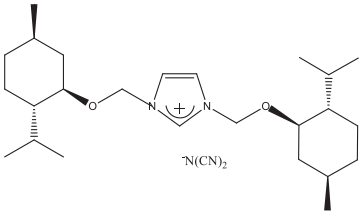
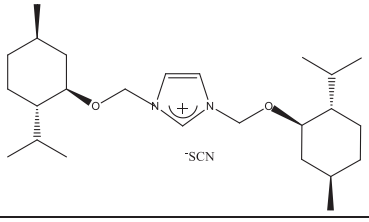
Table 1
Structure and metathesis conditions of symmetrical chiral ionic liquids (**2–6**).

Salt number	Chiral ionic liquid	Abbreviation	Structure	Conditions of metathesis	Yield[a] (%)
2	1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium bis(pentafluoroethylsulfonyl)imide	[Men-Im-Men][PFSI]		MeOH, 25 °C, 24 h	99.0
3	1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium 1,1,2,2-tetrafluoroethanesulfonate	[Men-Im-Men][TFES]		MeOH, 25 °C, 24 h	98.0
4	1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium perfluorobutanesulfonate	[Men-Im-Men][PFBS]		MeOH, 40 °C, 24 h	99.5
5	1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium dicyanamide	[Men-Im-Men][DCA]		MeOH/H_2O, 25 °C, 24 h	97.5
6	1,3-Bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium thiocyanate	[Men-Im-Men][SCN]		MeOH, 25 °C, 24 h	98.5

[a] Accuracy ±0.1%.

Synthesized new symmetrical chiral ionic liquids containing (1*R*,2*S*,5*R*)-(−)-menthol moieties were characterized by ^1H and ^{13}C NMR (for spectra see Supporting Information), and by elemental analysis.

Table 2
Properties of symmetrical chiral ionic liquids (**2–6**).

CILs	M.p.[a] (°C)	Crystallization solvents	Crystal shape	Specific rotation[b,c,d] $[\alpha]_D^{25}$
2	81.2–81.4	Water/ethanol	Irregular plates	−77.02 (*c* 1.014)
3	94.2–94.6	Hexane/chloroform	Long, regular needles	−102.90 (*c* 1.076)
4	51.7–52.3	Water/ethanol	Long, regular needles	−83.03 (*c* 1.034)
5	71.1–71.4	–	–	−112.18 (*c* 1.054)
6	134.1–134.5	Ethyl acetate/acetone	Regular, squared plates	−123.38 (*c* 1.003)

[a] Accuracy ±0.1 °C.
[b] *c* in methylene chloride.
[c] Standard uncertainty for specific rotation u is u(α) = ±0.5°.
[d] Standard uncertainty for concentration u is u(*c*) = ±0.002 g/100 mL.

Table 3
Solubility of prepared symmetrical chiral ionic liquids at 20 °C and 50 °C.

Solvent	Temperature (°C)	CILs				
		2	**3**	**4**	**5**	**6**
Water	20 °C	−	−	−	±	−
	50 °C	+	+	+	+	−
Methanol	20 °C	+	+	+	+	+
Ethanol	20 °C	+	+	+	+	+
Propanol	20 °C	+	+	+	+	+
Acetone	20 °C	+	+	+	+	+
Acetonitrile	20 °C	+	+	+	+	+
Diethyl ether	20 °C	−	−	−	−	−
Hexane	20 °C	−	−	−	−	−
	50 °C	−	−	−	−	−
Chloroform	20 °C	+	+	+	+	+
Ethyl acetate	20 °C	+	+	+	+	−
	50 °C	+	+	+	+	−
THF	20 °C	+	+	+	+	+
Toluene	20 °C	+	+	+	+	±
	50 °C	+	+	+	+	+
DMSO	20 °C	+	+	+	+	+
DMF	20 °C	+	+	+	+	+

Complete soluble: '+'. Limited solubility: '±'. Insoluble: '−'.

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3.1. Diastereotopic protons

There are two characteristic doublets observed in the ^{1}H NMR spectra around 5.60 and 5.75 ppm, depending on the anion used. These signals described CH_2 groups, which link menthol and amine derivatives, appear in the spectra in the form of two doublets as an AB spin system. This is a typical situation of diastereotopic protons presence, which are generally seen in CH_2 group of chiral molecules. The diastereotopic protons are the ones that topologically are identical, but at the same time they are non-alternate towards symmetry operations of the molecule. For the discussed protons different chemical shifts are observed, because the molecule has C1 symmetry and due to it the methylene groups are diastereotopic.

3.2. Chemical shifts

NMR spectra are usually used to assess the purity and the stability of ILs. A more thorough analysis of the chemical shifts value provides information about the acidity of the hydrogen atoms and of the electron density distribution within the cation and anion. The signal of H-2 atom in imidazolium ring (numbered as HC-14 in figure in Table 4) is registered in the lowest field, which means the lowest electron density surrounds this atom.

^{1}H and ^{13}C NMR spectra indicated notable differences in the chemical shifts depending on the anion used. The chemical shifts of the 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts, but also numbered protons and carbons, are presented in Table 4. These chemical shifts are evident for the protons and the carbons localized adjacent to the quaternary nitrogen atom. It is caused mainly by the steric effect of electron clouds and changing of the electrostatic interactions between ionic charges.

^{1}H NMR spectra of the 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl] imidazolium chloride and the additional 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts indicate different chemical shifts for the imidazolium ring protons and methylene protons adjacent to the oxygen atoms. A strong anionic effect was evident. The substitution of the Cl^- anion with $(C_2F_5SO_2)_2N^-$, $CHF_2CF_2SO_3^-$, $C_4F_9SO_3^-$, $(CN)_2N^-$ and SCN^- resulted in changes in the electron density near the quaternary nitrogen atom. The most significant chemical shifts were observed in the case of the proton in imidazolium ring, numbered HC-14, for all of the exchanged anions. A shift of 2.10 ppm between the salt [Men-Im-Men][Cl] and the [Men-Im-Men][PFSI] in the case of the HC-14 group, exemplifies the dramatic effect of the change in the electron density resulting from changing the anion. Whereas the value of the chemical shift for protons in methylene groups, numbered H_2C-11 and H_2C-11′, amounts to 0.24 ppm, also for bis(pentafluoroethylsulfonyl) imide. Surprisingly, for other protons in the imidazolium ring, numbered HC-13 and HC-12, no particular effect of the change in the electron density was observed, since the value of the chemical shifts for these protons where of a maximum of around 0.1 ppm.

The greatest effect of the chemical shifts for all the discussed protons, localized adjacent to the quaternary nitrogen atom, were observed for bis(pentafluoroethylsulfonyl)imide anion. The replacement of the chloride anion with much bigger $(C_2F_5SO_2)_2N^-$ one was associated with the chemical proton signal shifts in the direction of the higher field. Such changes of the chemical shifts indicate lower electron acceptability of positively charged nitrogen atom, resulting from improved solvation of the cation via the molecules of deuterated chloroform in the case of anions with greater steric hindrance.

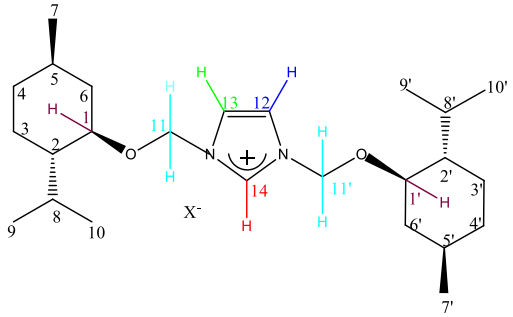
Comparing the differences between the values of the chemical shifts, the anions are ordered according to their increasing shielding capacities as follows:

$$Cl^- < SCN^- < CHF_2CF_2SO_3^- < C_4F_9SO_3^- < (CN)_2N^- < (C_2F_5SO_2)_2N^-$$

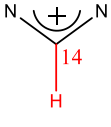
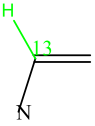
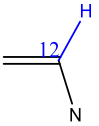
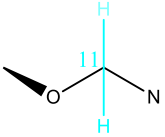
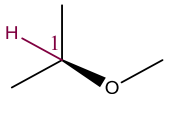
As mentioned earlier, the ^{13}C NMR spectra also indicated notable differences in the chemical shifts of the carbons, depending on the anion used. The shifts were most evident for carbon surrounded of two nitrogen atoms in the imidazolium ring (numbered HC-14) and were of the ranged of 2.7 ppm for $(C_2F_5SO_2)_2N^-$, around 2 ppm for $(CN)_2N^-$ and $C_4F_9SO_3^-$ anions, 1.3 ppm for $CHF_2CF_2SO_3^-$ and nearly 1 ppm for SCN^-. The ordering of the anions according to their increasing shielding capacities is identical as the one presented for protons.

Some examples about the chemical shifts depending on the anion used have already been shown in the literature [48–50]. In those manuscripts the differences in the chemical shifts have been noticed only in

Table 4
The chemical shifts in ^{1}H NMR.



1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium salts with numbered atoms

Salt number	Abbreviation	Anion X^-	Characteristic protons				
							
1	[Men-Im-Men][Cl]	Cl^-	11.38	7.48		5.68 and 5.92	3.39
2	[Men-Im-Men][PFSI]	$(C_2F_5SO_2)_2N^-$	9.28	7.48	7.475	5.56 and 5.68	3.31
3	[Men-Im-Men][TFES]	$CHF_2CF_2SO_3^-$	9.77	7.495	7.49	5.62 and 5.76	3.37
4	[Men-Im-Men][PFBS]	$C_4F_9SO_3^-$	9.74	7.495	7.49	5.61 and 5.75	3.37
5	[Men-Im-Men][DCA]	$(CN)_2N^-$	9.62	7.575	7.57	5.66 and 5.75	3.38
6	[Men-Im-Men][SCN]	SCN^-	9.93	7.55	7.50	5.70 and 5.86	3.42

Spectra in $CDCl_3$; shifts in ppm.

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the ^{1}H NMR. Interestingly, in the cited reports it is emphasized that ^{13}C NMR spectra indicated no significant variation in the carbon signal shifts.

4. Conclusions

New symmetrical imidazolium ionic liquids based on (1*R*,2*S*,5*R*)-(−)-menthol were prepared successfully and with very high efficiency. All of the synthesized salts are solid, are stable in the air, in contact with water and in commonly used organic solvents. The salts **2**–**5** fall within the category of ionic liquids (i.e. m.p. <100 °C). The only exception is 1,3-bis[(1*R*,2*S*,5*R*)-(−)-menthoxymethyl]imidazolium thiocyanate (**6**) with higher melting point: 134.1–134.5 °C. Studied compounds belong to the group of chiral ionic liquids due to the presence in cationic part two molecules of natural, monocyclic terpene alcohol with three chiral centers.

In ^{1}H NMR, characteristic diastereotopic protons of the CH_2 group (AB spin system), which links menthol and amine derivatives, were observed for all the presented salts.

^{1}H and ^{13}C NMR spectra indicated notable differences in the chemical shifts depending on the anion used. The most pronounced shielding abilities were noted for the bis(pentafluoroethylsulfonyl)imide and dicyanamide salts with the value of chemical proton shifts 2.1 and 1.76 ppm respectively. On the other hand, in the ^{13}C NMR spectra the shift of 2.7 ppm was observed again for bis(pentafluoroethylsulfonyl) imide salt. The most significant chemical shifts were noted for the proton and the carbon surrounded of two nitrogen atoms in the imidazolium ring.

The selection of the anions for preparing symmetrical ionic liquids: bis(pentafluoroethylsulfonyl)imide, 1,1,2,2-tetrafluoroethanesulfonate, perfluorobutanesulfonate, dicyanamide and thiocyanate were intended, since currently these anions are strongly investigated in various applications, e.g. separation science, electrochemistry, catalysis. Further research to evaluate the potential used of the salts described herein is currently ongoing in our laboratories. We believe we will find applications for ionic liquids based on (1*R*,2*S*,5*R*)-(−)-menthol with untested earlier anions, especially since successful examples with different anions we already have.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2016.08.112.

References

[1] R.D. Rogers, K.R. Seddon, Ionic liquids - solvents of the future? Science 302 (2003) 792–793.
[2] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, 2nd edn Wiley-VCH VerlagGmbh& Co. KGaA, Weinheim, 2008.
[3] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, Chem. Rev. 99 (1999) 2071–2083.
[4] C.A. Angell, Y. Ansari, Z. Zhao, Ionic liquids: past, present and future, Faraday Discuss. 154 (2012) 9–27.
[5] J.P. Hallet, T. Welton, Room-temperature ionic liquids: solvents for synthesis and catalysis2 Chem. Rev. 111 (2011) 3508–3576.
[6] Z. Fei, T.J. Geldbach, D. Zhao, P.J. Dyson, From dysfunction to bis-function: on the design and applications of functionalised ionic liquids, Chem. Eur. J. 12 (2006) 2122–2130.
[7] M. Bendová, Z. Wagner, Thermodynamic description of liquid–liquid equilibria in systems 1-ethyl-3-methylimidazolium ethylsulfate + C7-hydrocarbons by polymer-solution models, Fluid Phase Equilib. 284 (2009) 80–85.
[8] J. Jacquemin, J. Feder-Kubis, M. Zorębski, K. Grzybowska, M. Chorążewski, S. Hensel-Bielówka, E. Zorębski, M. Paluch, M. Dzida, Structure and thermal properties of salicylate-based-protic ionic liquids as new heat storage media. COSMO-RS structure characterization and modeling of heat capacities, PCCP 16 (2014) 3549–3557.
[9] N.V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123–150.
[10] M. Smiglak, J.M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D.R. MacFarlane, R.D. Rogers, Ionic liquids for energy, materials, and medicine, Chem. Commun. 50 (2014) 9228–9250.
[11] D.D. Patel, J.M. Lee, Applications of ionic liquids, Chem. Rec. 12 (2012) 329–355.
[12] X. Han, D.W. Armstrong, Ionic liquids in separations, Acc. Chem. Res. 40 (40) (2007) 1079–1086.
[13] S. Werner, M. Haumann, P. Wasserscheid, Ionic liquids in chemical engineering, Annu. Rev. Chem. Biomol. Eng. 1 (2010) 203–230.
[14] K. Staerk, N. Taccardi, A. Bösmann, P. Wasserscheid, Oxidative depolymerization of lignin in ionic liquids, Chem. Sus. Chem. 3 (2010) 719–723.
[15] G.G. Eshetu, M. Armand, H. Ohno, B. Scrosati, S. Passerini, Ionic liquids as tailored media for the synthesis and processing of energy conversion materials, Energy Environ. Sci. 9 (2016) 49–61.
[16] R. Gusain, O.P. Khatri, Fatty acid ionic liquids as environmentally friendly lubricants for low friction and wear, RSC Adv. 6 (2016) 3462–3469.
[17] A.H. Batteza, M. Bartolomé, D. Blanco, J.L. Viesca, A. Fernández-González, R. González, Phosphonium cation-based ionic liquids as neat lubricants: physicochemical and tribological performance, Tribol. Int. 95 (2016) 118–131.
[18] P. Hapiot, C. Lagrost, Electrochemical reactivity in room-temperature ionic liquids, Chem. Rev. 108 (2008) 2238–2264.
[19] A. Wirwis, W. Gila, J. Pernak, A.M. Trzeciak, The effect of Al_2O_3 and ionic liquids in palladium catalyzed arylation of cyclohexene. Interaction of Hg(0) with immobilized palladium, J. Mol. Catal. A-Chem. 411 (2016) 188–195.
[20] V.I. Pârvulescu, C. Hardacre, Catalysis in ionic liquids, Chem. Rev. 107 (2007) 2615–2665.
[21] S.V. Malhotra, V. Kumar, A profile of the in vitro anti-tumor activity of imidazolium-based ionic liquids, Bioorg. Med. Chem. Lett. 20 (2010) 581–585.
[22] J.N. Pendleton, B.F. Gilmore, The antimicrobial potential of ionic liquids: a source of chemical diversity for infection and biofilm control, Int. J. Antimicrob. Agents 46 (2015) 131–139.
[23] J.L. Anderson, R. Ding, A. Ellern, D.W. Armstrong, Structure and properties of high stability geminal dicationic ionic liquids, J. Am. Chem. Soc. 127 (2005) 593–604.
[24] W. Zheng, A. Mohammed, L.G. Hines Jr., D. Xiao, O.J. Martinez, R.A. Bartsch, S.L. Simon, O. Russina, A. Triolo, E.L. Quitevis, Effect of cation symmetry on the morphology and physicochemical properties of imidazolium ionic liquids, J. Phys. Chem. B 115 (2011) 6572–6584.
[25] X. Han, D.W. Armstrong, Using geminal dicationic ionic liquids as solvents for high-temperature organic reactions, Org. Lett. 7 (2005) 4205–4208.
[26] S.V. Dzyuba, R.A. Bartsch, New room-temperature ionic liquids with C_2-symmetrical imidazolium cations, Chem. Commun. 1466–1467 (2001).
[27] J. Zimmermann, B. Ondruschka, A. Stark, Efficient synthesis of 1,3-dialkylimidazolium-based ionic liquids: the modified continuous Radziszewski reaction in a microreactor setup, Org. Process. Res. Dev. 14 (2010) 1102–1109.
[28] H. Xing, X. Zhao, R. Li, Q. Yang, B. Su, Z. Bao, Y. Yang, Q. Ren, Improved efficiency of ethylene/ethane separation using a symmetrical dual nitrile-functionalized ionic liquid, ACS Sustain. Chem. Eng. 11 (2013) 1357–1363.
[29] F.A. Silva, F. Siopa, B.F.H.T. Figueiredo, A.M.M. Gonçalves, J.L. Pereira, F. Gonçalves, J.A.P. Coutinho, C.A.M. Afonso, S.P.M. Ventura, Sustainable design for environment-friendly mono and dicationic cholinium-based ionic liquids, Ecotoxicol. Environ. Saf. 108 (2014) 302–310.
[30] J. Pernak, J. Feder-Kubis, Synthesis and properties of chiral ammonium-based ionic liquids, Chem. Eur. J. 11 (2005) 4441–4449.
[31] J. Pernak, J. Feder-Kubis, Chiral pyridinium-based ionic liquids containing the (1*R*,2*S*,5*R*)-(−)-menthyl group, Tetrahedron-Asymmetry 17 (2006) 1728–1737.
[32] J. Pernak, J. Feder-Kubis, A. Cieniecka-Rosłonkiewicz, C. Fischmeister, S. Griffin, R. Rogers, Synthesis and properties of chiral imidazolium ionic liquids with a (1*R*,2*S*,5*R*)-(−)-menthoxymethyl substituent, New J. Chem. 31 (2007) 879–892.
[33] J. Feder-Kubis, M. Kubicki, J. Pernak, 3-Alkoxymethyl-1-(1*R*,2*S*,5*R*)-(−)-menthoxymethylimidazolium salts-based chiral ionic liquids, Tetrahedron-Asymmetry 21 (2010) 2709–2718.
[34] X. Miao, J. Feder-Kubis, C. Fischmeister, J. Pernak, P. Dixneuf, Catalytic cycloisomerisation of 1,6-dienes in ionic liquids, Tetrahedron 64 (2008) 3687–3690.
[35] J. Feder-Kubis, J. Bryjak, Laccase activity and stability in the presence of menthol-based ionic liquids, Acta Biochim. Pol. 60 (2013) 741–745.
[36] J. Feder-Kubis, K. Tomczuk, The effect of the cationic structures of chiral ionic liquids on their antimicrobial activities, Tetrahedron 69 (2013) 4190–4198.
[37] J. Feder-Kubis, B. Szefczyk, M. Kubicki, Symmetrical imidazolium chloride based on (−)-menthol: synthesis, characterization, and theoretical model of the reaction, J. Org. Chem. 80 (2015) 237–246.
[38] A.H. Jadhav, K. Lee, S. Koo, J.G. Seo, Esterification of carboxylic acids with alkyl halides using imidazolium based dicationic ionic liquids containing bis-trifluoromethane sulfonimide anions at room temperature, RSC Adv. 5 (2015) 26197–26208.
[39] S. García, J. García, M. Larriba, J.S. Torrecilla, F. Rodríguez, Sulfonate-based ionic liquids in the liquid-liquid extraction of aromatic hydrocarbons, J. Chem. Eng. Data 56 (2011) 3188–3193.

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[40] P.F. Requejo, E. Gómez, N. Calvar, Á. Domínguez, Application of pyrrolidinium-based ionic liquid as solvent for the liquid extraction of benzene from its mixtures with aliphatic hydrocarbons, Ind. Eng. Chem. Res. 54 (2015) 1342–1349.
[41] H. Gao, S. Zeng, X. Liu, Y. Nie, X. Zhang, S. Zhang, Extractive desulfurization of fuel using *N*-butylpyridinium-based ionic liquids, RSC Adv. 5 (2015) 30234–30238.
[42] B. Kirchner, Topics in Current Chemistry, Ionic liquids. Springer-Verlag, Berlin Heidelberg, 2009 32.
[43] D.R. MacFarlane, N. Tachikawa, M. Forsyth, J.M. Pringle, P.C. Howlett, G.D. Elliott, J.H. Davis Jr., M. Watanabe, P. Simonf, C.A. Angell, Energy applications of ionic liquids, Energy Environ. Sci. 7 (2014) 232–250.
[44] S. Shen, S. Fang, L. Qu, D. Luo, L. Yang, S. Hirano, Low-viscosity ether-functionalized pyrazolium ionic liquids based on dicyanamide anions: properties and application as electrolytes for lithium metal batteries, RSC Adv. 5 (2015) 93888–93899.
[45] H. Wang, G. Gurau, R.D. Rogers, Ionic liquid processing of cellulose, Chem. Soc. Rev. 41 (2012) 1519–1537.
[46] J. Pernak, J. Nawrot, M. Kot, B. Markiewicza, M. Niemczak, Ionic liquids based stored product insect antifeedants, RSC Adv. 3 (2013) 25019–25029.
[47] A.I. Vogel, A.R. Tatchell, B.S. Furnis, A.J. Hannaford, P.W.G. Smith, Vogel's Textbook of Practical Organic Chemistry, Longman, 5th edn., 1989.
[48] S. Jankowski, NMR studies of ionic liquids, Przem. Chem. 92 (2013) 1606–1608.
[49] J. Pernak, A. Syguda, I. Mirska, A. Pernak, Choline-derivative-based ionic liquids, Chem. Eur. J. 13 (2007) 6817–6827.
[50] J. Pernak, K. Sobaszkiewicz, J. Foksowicz-Flaczyk, Ionic liquids with symmetrical dialkoxymethyl-substituted imidazolium cations, Chem. Eur. J. 10 (2004) 3479–3485.

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