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New Ionic Liquids with Alkoxymethyl Hydrophobic Groups

by J. Pernak*, A. Olszówka and R. Olszewski

Poznań University of Technology, pl. Skłodowskiej-Curie 2, 60-965 Poznań, Poland

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Air and water stable new ionic liquids with alkoxymethyl hydrophobic substituents and alkyl group on C(2) in imidazolium cation have been prepared and characterized. 14 tetrafluoroborate salts and 8 hexafluorophosphate salts are liquids at r.t. The properties of obtained salts are reported. The variation of substituents on the imidazolium cation have led to useful trends in the melting point and density and have a significant influence on the thermal stability.

Key words: new ionic liquids, imidazolium tetrafluoroborates, imidazolium hexafluorophosphates

Room temperature ionic liquids (RTILs), a class of neoteric solvent, have attracted growing interest in the past few years. RTILs comprise an organic cation and weakly coordinating anion and are liquid under ambient conditions having several very interesting properties. They can solvate a wide range of organic and inorganic materials, they are highly polar and non-explosive, thermally robust, are non-volatile and have a wide liquid range. Some of them are immiscible with water and a wide range of organic solvents and are recyclable. Ionic liquids have been proposed as green solvents on laboratory and industrial scales [1] and are promising substitutes for volatile organic solvents. Several authors have reviewed the field of RTILs [2–15]. RTILs come in two main categories, namely simple salts (made of a single cation and anion) and binary ionic liquids (salt where an equilibrium is involved). By modification of the cation and anion their properties can be adapted in many ways. The change of anion dramatically affects the chemical behavior and stability of the ionic liquid; the change of cation has a profound effect on the physical properties such as melting point, viscosity and density. A binary ionic liquid system contains several different ionic species and their melting point and Lewis acidity depend upon the mole fractions of the aluminium(III) chloride or copper(I) chloride and pyridinium or imidazolium (mainly consisting of 1,3-dialkylimidazolium cation) chloride present. Chloroaluminate ionic liquids are excellent catalysts and solvents in many processes but decompose in the presence of water.

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* Corresponding author: e-mail: Juliusz.Pernak@put.poznan.pl

Numerous air and moisture-stable RTILs (simple salts) are known, in which 1-alkylpyridinium or 1,3-dialkylimidazolium cation with various anions [*e.g.* BF_4^-, PF_6^-, $N(CF_3SO_2)_2^-$, SbF_6^-, AsF_6^-, CF_3COO^-, $CF_3SO_3^-$, NO_3^-] are typically used. Also polyammonium phosphate creates a new category of ionic liquid [16].

1-Alkyl-3-methylimidazolium hexafluorophosphates are water immiscible and tetrafluoroborate are water miscible, depending on the alkyl chain length. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate are miscible with water at 25°C, where the alkyl chain length is less than 6 carbon atoms, but at or above 6 atoms, they form a separate phase when mixed with water. These media have been applied in non-catalytic and catalytic reactions as "neutral" solvents. Volatile products can be separated from the reaction mixture by distillation, as the RTIL has effectively no vapor pressure and therefore cannot be lost. There also exists the possibility of extraction with super-critical solvents or less polar organic solvents like aliphatic or aromatic hydrocarbons and diethyl ether. Recovered ionic liquid was recycled many times without any noticeable decrease in yield or regioselectivity. The development of RTILs especially in the last two years has opened numerous avenues in the areas of reaction chemistry.

Additionally, a number of applications have been demonstrated, including their use in liquid-liquid extraction processes [17–19], electrochemical technologies [20,21], in gas chromatography as a stationary phase [22], a novel versatile lubricant [23] and as a media for radiolytic generation [24]. One of the most exciting recent developments is the use of enzymes in RTILs [13–15,25].

Ionic liquids are derived from imidazolium cation mainly containing two alkyl chain lengths in N(1) and N(3) positions. Reduction of the cation symmetry is a method of lowering the melting point of the salt. In literature imidazolium salts have been described with another substituent such as fluorocarbon tails [26] and with one alkyl substituent [27] or with heteroatoms in the alkyl group [18,28].

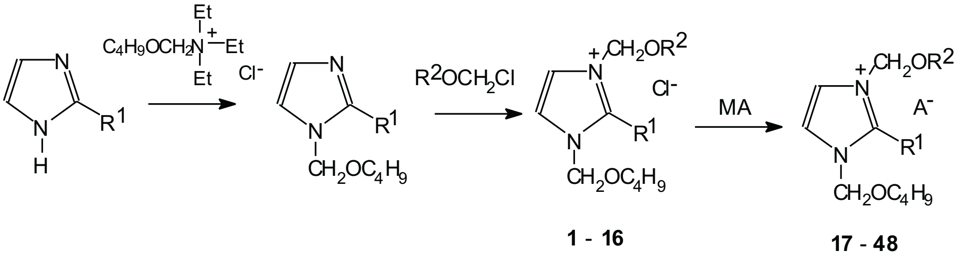
We report here on the preparation and properties of new ionic liquids with alkoxymethyl hydrophobic substituents and alkyl group on C(2) in imidazolium cation.

RESULTS AND DISCUSSION

Scheme 1 shows the strategy for synthesis of new ionic liquids with alkoxymethyl hydrophobic substituents and alkyl group on C(2) in imidazolium cation. For N-alkoxymethylation we used butoxymethyltriethylamonium chloride in toluene. This one step reaction is a new approach, which is better than the deprotonation and nucleophilic displacement [29]. We eliminated the deprotonation using solid or aqueous alkali metal hydroxides, or sodium hydride in DMF or acetonitrile.

Quaternary chlorides formed directly from 2-alkyl-1-butoxymethylimidazole were treated with an excess of alkoxymethylation agent. Chloromethyl alkyl ether is an excellent alkoxymethylation agent, but is very easily hydrolyzed. In synthesis all apparatus must be scrupulously dry and the solvent must be dried before use. Obtained imidazolium chlorides **1–16** are hygroscopic and need to be kept dry if

Scheme 1



storage is intended. They are fully soluble in water and strongly adsorb water from room air. The chemical purity of chlorides in storage in the laboratory was determined by a direct two-phase titration procedure for chlorides with alkyl long chain length (6–10 carbon atoms), presented in Table 1. They were only 90% pure, because 10% included water. Chlorides with short chain length (3–5 carbon atoms) are extremely hygroscopic and they adsorb more water than 10%. During storage they change their form from solid to liquid (water solution). The tetrafluoroborate salts **17**–**32** and hexafluorophosphate salts **33**–**48** were then readily separated from the aqueous solution in high yield and are shown in Tables 2 and 3. Anhydrous salts were obtained by heating the samples at 60°C in vacuum (10 mmHg) for 7 h. Karl-Fisher measurements show water contents of dried salts to be < 200 ppm. Also no water signals were observed in the infrared spectrum at around 3500 cm^{-1} and measurement of the ^{1}H NMR spectra anhydrous nature can be established.

Table 1. 3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium chlorides (**1**–**16**).

Chloride	R^1	R^2	M.p. (°C)	Yield (%)	Purity (%)
1	CH_3	C_3H_7	hygroscopic	94	
2	CH_3	C_4H_9	hygroscopic	94	
3	CH_3	C_5H_{11}	hygroscopic	95	
4	CH_3	C_6H_{13}	hygroscopic	94	90
5	CH_3	C_7H_{15}	hygroscopic	97	90
6	CH_3	C_8H_{17}	gel	96	91
7	CH_3	C_9H_{19}	gel	98	90
8	CH_3	$C_{10}H_{21}$	gel	98	91
9	C_2H_5	C_3H_7	131–133	88	
10	C_2H_5	C_4H_9	128–130	91	
11	C_2H_5	C_5H_{11}	hygroscopic	95	
12	C_2H_5	C_6H_{13}	hygroscopic	92	91
13	C_2H_5	C_7H_{15}	hygroscopic	92	90
14	C_2H_5	C_8H_{17}	hygroscopic	94	90
15	C_2H_5	C_9H_{19}	hygroscopic	91	90
16	C_2H_5	$C_{10}H_{21}$	hygroscopic	97	91

Table 2. 3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium tetrafluoroborate (**17**–**32**).

Salt	R^1	R^2	M.p. (°C)	Yield (%)	Color
17	CH_3	C_3H_7	liquid (5–7)	90	light-yellow
18	CH_3	C_4H_9	liquid*	87	light-yellow
19	CH_3	C_5H_{11}	liquid*	88	light-yellow
20	CH_3	C_6H_{13}	liquid*	87	light-yellow
21	CH_3	C_7H_{15}	liquid*	90	light-yellow
22	CH_3	C_8H_{17}	liquid*	92	light-yellow
23	CH_3	C_9H_{19}	liquid*	92	light-yellow
24	CH_3	$C_{10}H_{21}$	liquid*	98	light-yellow
25	C_2H_5	C_3H_7	liquid*	72	colourless
26	C_2H_5	C_4H_9	35–38	85	white crystal
27	C_2H_5	C_5H_{11}	28–30	83	white, greasy
28	C_2H_5	C_6H_{13}	liquid*	81	light-yellow
29	C_2H_5	C_7H_{15}	liquid*	80	light-yellow
30	C_2H_5	C_8H_{17}	liquid*	80	light-yellow
31	C_2H_5	C_9H_{19}	liquid*	81	light-yellow
32	C_2H_5	$C_{10}H_{21}$	liquid*	80	colourless

* – after cooling form glasses

Table 3. 3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium hexafluorophosphate (**33–48**).

Salt	R^1	R^2	M.p. (°C)	Yield (%)	Color
33	CH_3	C_3H_7	38–40	88	white crystal
34	CH_3	C_4H_9	69–71	93	white crystal
35	CH_3	C_5H_{11}	34–36	87	white crystal
36	CH_3	C_6H_{13}	liquid*	88	light-yellow
37	CH_3	C_7H_{15}	liquid*	88	light-yellow
38	CH_3	C_8H_{17}	liquid*	90	light-yellow
39	CH_3	C_9H_{19}	liquid*	90	light-yellow
40	CH_3	$C_{10}H_{21}$	32–34	94	white crystal
41	C_2H_5	C_3H_7	37–39	89	white crystal
42	C_2H_5	C_4H_9	32–35	92	light-yellow crystal
43	C_2H_5	C_5H_{11}	30–33	90	light-yellow, greasy
44	C_2H_5	C_6H_{13}	liquid*	86	light-yellow
45	C_2H_5	C_7H_{15}	liquid*	85	colourless
46	C_2H_5	C_8H_{17}	liquid*	96	colourless
47	C_2H_5	C_9H_{19}	liquid*	83	light-yellow
48	C_2H_5	$C_{10}H_{21}$	32–35	96	white crystal

* – after cooling form glasses

The prepared new imidazolium salts were characterized by their ^{1}H and ^{13}C NMR spectra and microanalyses CHN. The results of elemental analysis were in agreement with the theoretical values. The purity of obtained imidazolium salts was > 99%. In the ^{1}H NMR spectra the chemical shift of the protons H(4) and H(5) is anion-dependent. For chlorides the singlet appeared at 8.13–8.05, for tetrafluoroborate salts at 7.84–7.82 and for hexafluorophosphate salts it occurred at 7.91–7.87 ppm. We also found a difference in the position of protons of the methyl group [$C(2)\text{-}CH_2CH_3$] substituted at C(2) which resonated as a singlet at 2.08 for chlorides (**1**–**8**) and at 2.71 for tetrafluoroborate and hexafluorophosphate salts (**17**–**24**, **33**–**40**). In dialkylimidazolium salts the correlation between C(2)-H and the nature of the anion exhibits that a hydrogen bond is the base of ionic liquid [28,30].

The melting points of 3-alkoxymethyl-2-alkyl-1-butoxymethylimidazolium salts are a function of the length of the alkoxymethyl and alkyl groups. The tetrafluoroborate salts were obtained as white solids (**26**, **27**) with a low melting point or colorless (**25**, **32**) to light-yellow (**17**–**24**, **28**–**31**) liquids and the hexafluorophosphate salts as white and light-yellow solids (**33**–**35**, **40**–**43**, **48**) or colorless (**45**, **46**) and light-yellow (**36**–**39**, **44**, **47**) liquids. The asymmetry of imidazolium cation reduces the energy of the crystalline form and hence lowers the melting point that causes salt to be liquid at r.t. All prepared salts are air and water stable under ambient conditions and may be handled under normal laboratory conditions. They are soluble in DMSO, DMF, acetone, $CHCl_3$, CH_2Cl_2 and ethyl acetate. They form a separate phase when mixed with water and are completely insoluble in hexane.

The acidity of the C(2)-H in imidazolium cation is well known and they can be deprotonated to form carbenes by basic ligands of a metal compound. In most cases the imidazolium cation is an inert component of a solvent system and not directly involved in a catalytic cycle. In literature there are examples that imidazolium cation reacts with low valent metals to form carbene complexes [31–33]. Alkyl substituent at C(2) position in prepared salts delimit this possibility. In general an alkyl group in this position increases the melting point. This implies that the effect of the van der Waals interaction *via* alkyl group dominates the electrostatic interaction *via* proton on C(2).

The thermal stability of the anhydrous ionic liquids were investigated by the TGA and DTA curves over the temperature range between 20 to 450°C. The TGA curve has a sigmoidal shape and it can be split into three segments. The first one, corresponding to temperatures below *ca*. 200°C, shows a small weight (~ 1%) loss. The second segment of the plot is located between 200 and 290°C. This part of the plot attributes to the thermal decomposition of the sample. The slope of this part of the plot corresponds to 0.94 mass%/°C, indicating a single catastrophic weight loss located between 255 and 265°C. This maximum decomposition is a result of dealkoxymethylation of the imidazolium ring generating volatile compounds. The third segment of the plot located above *ca*. 290°C can be represented as a straight line parallel to the temperature axis. It indicates that the increase in temperature does not produce a further decrease in mass.

The practical thermal stability of salts obtained in contact with air is lower. We can state that both the synthesized homologous series are thermally stable and they can be safely stored and used up to *ca.* 175°C for tetrafluoroborate salts and *ca.* 160°C for hexafluorophosphate salts. The product does not change color until the above temperature is reached. The prepared new salts may be classified as "soft" thermal stable ionic liquids in comparison with 1-alkyl-3-methylimidazolium tetrafluoroborates [30]. Thus, it is expected that the thermal stability of imidazolium salts is relatively high and the choice of the anions and the kind of substituents in the imidazole ring often determines the decomposition temperature.

The densities of obtained RTILs are measured at r.t. range 1.19–1.03 g/ml. All are heavy with water. There is an interesting tendency, which is seen in Figure 1.

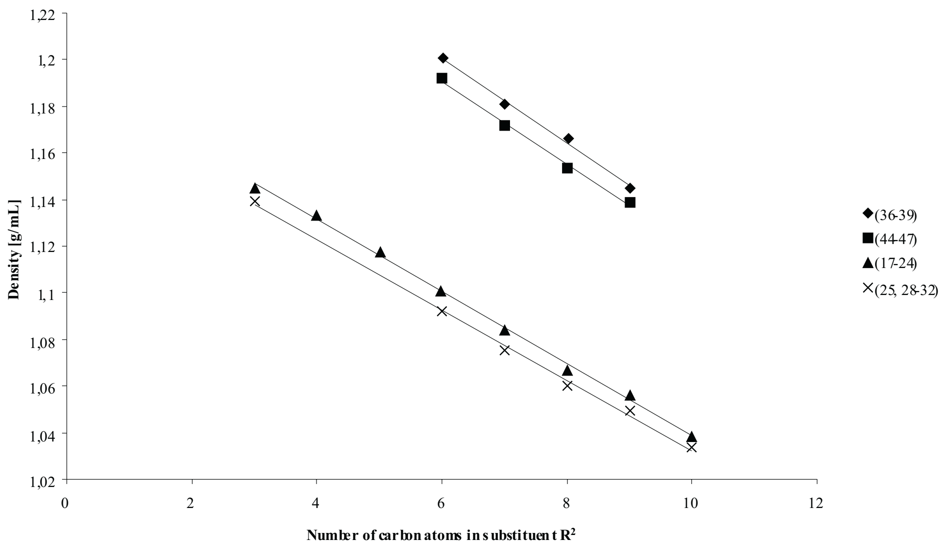


Figure 1. Density for tetrafluoroborate and hexafluorophosphate salts prepared.

Increasing molecular weight of the cation leads to a decreasing density. A linear relationship exists between the density and the number of carbon atoms in the alkoxy group according to:

for 3-alkoxymethyl-1-butoxymethyl-2-methylimidazolium tetrafluoroborates (**17**–**24**)

$$y = -0.0162\,x + 1.1934 \quad (r^2 = 0.9873)$$

for 3-alkoxymethyl-1-butoxymethyl-2-ethylimidazolium tetrafluoroborates (**25**, **28**–**32**)

$$y = -0.0149\,x + 1.1823 \quad (r^2 = 0.9965)$$

for 3-alkoxymethyl-1-butoxymethyl-2-methylimidazolium hexafluorophosphates (**36**–**39**)

$$y = -0.0217\,x + 1.33 \quad (r^2 = 0.9032)$$

for 3-alkoxymethyl-1-butoxymethyl-2-ethylimidazolium hexafluorophosphates (**44**–**47**)

$$y = -0.017\,x + 1.2922 \quad (r^2 = 0.9886)$$

where: y – density, x – the number of carbon atoms in the alkoxy group, r – the correlation coefficient. The density of hexafluorophosphates is significantly higher than the density of tetrafluoroborates.

CONCLUSIONS

We have described the preparation and properties of imidazolium tetrafluoroborate and hexafluorophosphate salts with alkoxymethyl hydrophobic groups, which are liquid at r.t. 3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium tetrafluoroborates and hexafluorophosphates were derived from chloride salts, which were prepared by alkoxymethylation of 1-alkoxymethylimidazole. Anhydrous RTILs were obtained by heating at 60°C under vacuum for 7 h. They can solvate a wide range of organic materials, are immiscible with water and hexane and they have a nonvolatile nature. All prepared salts are air and water stable under ambient conditions and may be handled under normal laboratory conditions. The variation of substituents on the imidazolium cation have led to useful trends in the melting point, and density and have a significant influence on the thermal stability. The density and asymmetry of salts can be varied by changes to the structure of cation.

EXPERIMENTAL

Melting points were determined by using an electrothermal digital-melting-point apparatus model JA 9100. NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, with TMS as standard. Elemental analyses CHN were done at the A. Mickiewicz University, Poznań. For all synthesized salts, satisfactory microanalysis was obtained C ± 0.36; H ± 0.37 and N ± 0.35. A Mettler Toledo DA 110M scale was used for the mass/density measurements (temperature = 20 ± 2°C, sample volume = 2 ml). The thermal stability of the tetrafluoroborate and hexafluorophosphate salts were investigated using thermogravimetrical analyzer TGA-50 (Shimadzu), and differential thermal analyzer DTA-50 equipped with personal computer. The samples were analyzed in alumina crucibles using α-Al_2O_3 as a reference substance. In all analysis the heating rate was 5°C/min. and the sampling frequency of 0.5 s was applied. Direct two-phase titration procedure was used for the determination of the purity of chlorides **4**–**8** and **12**–**16** [34].

Preparation of 2-alkyl-1-butoxymethylimidazole. Chloromethyl butyl ether (61.3 g, 0.5 mol) was slowly added to a stirred anhydrous solution of triethylamine (50.6 g, 0.5 mol) in toluene (500 ml) and stirred at r.t. for 15 min. 2-Alkylimidazole (0.5 mol) was then added. After 2 h the mixture was refluxed and filtered from triethylamine hydrochloride. The solvent was evaporated and the obtained oil was vacuum distilled to give 2-alkyl-1-butoxymethylimidazole with 85% yield.

1-Butoxymethyl-2-methylimidazole. ^{1}H NMR (DMSO-d_6) δ ppm: 7.15 (d, J = 1.4 Hz, 1H), 6.74 (d, J = 1.4 Hz, 1H), 5.35 (s, 2H), 3.35 (t, J = 6.3 Hz, 2H), 2.31 (s, 3H), 1.46 (t, J = 4.8 Hz, 2H), 1.41 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR (DMSO-d_6) δ ppm: 144.3, 126.0, 120.4, 74.6, 67.1, 30.9, 18.7, 13.6, 12.6.

1-Butoxymethyl-2-ethylimidazole. ^{1}H NMR (DMSO-d_6) δ ppm: 7.16 (d, J = 1.4 Hz, 1H), 6.78 (d, J = 1.4 Hz, 1H), 5.28 (s, 2H), 3.38 (t, J= 6.4 Hz, 2H), 2.71 (q, J = 7.5 Hz, 2H), 1.46 (m, 2H), 1.28 (m, 5H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR (DMSO-d_6) δ ppm: 149.2, 126.1, 120.4, 74.5, 67.2, 30.9, 19.3, 18.7, 13.4, 12.0.

Synthesis of 3-alkoxymethyl-2-alkyl-1-butoxymethylimidazolium chlorides. Chlorides **1**–**16** were prepared by dissolving 2-alkyl-1-butoxymethylimidazole in anhydrous hexane and adding an equimolar amount of the appropriate chloromethyl alkyl ether. The mixture was stirred for 1 h at r.t. The separated product was purified by extraction with hexane or crystallized from ethyl acetate. All prepared chlorides were stored over phosphorus pentoxide. Chloromethyl alkyl ether was prepared by passing HCl-gas through a mixture of formaldehyde and the appropriate alcohol.

1-Butoxymethyl-2-methyl-3-propoxymethylimidazolium chloride **1**. ^{1}H NMR (DMSO-d_6) δ ppm: 8.13 [s, H(4)H(5)], 5.78 (s, 2NCH$_2$O), 3.55 (m, 4H), 2.08 (s, 3H), 1.52 (m, 4H), 1.31 (m, 2H), 0.86 (t, J = 7.4 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 149.6, 121.6, 77.2 (NCH$_2$O), 70.5, 68.6, 30.7, 22.0, 18.5, 13.4, 10.2, 9.8.

1-Butoxymethyl-2-ethyl-3-propoxymethylimidazolium chloride **9**. ^{1}H NMR (DMSO-d_6) δ ppm: 8.11 [s, H(4)H(5)], 5.75 (s, 2NCH$_2$O), 3.54 (m, 4H), 3.25 (q, J = 7.5 Hz, 2H), 1.53 (m, 4H), 1.34 (m, 2H),), 1.26 (t, J=7.6 Hz, 3H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 149.6, 121.7, 77.1 (NCH$_2$O), 70.5, 68.6, 30.8, 22.1, 18.6, 16.7, 13.4, 12.0, 10.3.

3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium tetrafluoroborates (17–32). A solution of NaBF$_4$ (3.3 g, 0.03 mol) in water (20 ml) was added to a solution of 3-alkoxymethyl-2-alkyl-1-butoxymethylimidazolium chloride (0.03 mol) in water (20 ml). During the addition the product precipitates. After 24 h the water was removed, the residue was dissolved in ethyl acetate and then the organic layer was washed with water (3 × 50 ml). In water eluent chlorine ion was controlled by a water solution of AgNO$_3$. The solvent was removed to yield the tetrafluoroborate salt. The product dried in vacuum (10 mmHg, heat, 7 h).

1-Butoxymethyl-3-decyloxymethyl-2-methylimidazolium tetrafluoroborate **24**. ^{1}H NMR (DMSO-d_6) δ ppm: 7.84 [s, H(4)H(5)], 5.60 (s, 2NCH$_2$O), 3.50 (m, 4H), 2.71 (s, 3H), 1.50 (m, 4H), 1.31 (m, 16H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 146.0, 121.5, 77.3 (NCH$_2$O), 69.0, 68.7, 31.3, 30.7, 28.9, 28.6, 25.3, 22.0, 18.5, 13.8, 13.4, 9.4.

1-Butoxymethyl-3-decyloxymethyl-2-ethylimidazolium tetrafluoroborate **32**. ^{1}H NMR (DMSO-d_6) δ ppm: 7.91 [s, H(4)H(5)], 5.66 (s, 2NCH$_2$O), 3.56 (m, 4H), 3.18 (q, J = 7.5 Hz, 2H), 1.52 (m, 4H), 1.33 (m, 16H),), 1.28 (t, J =7.6 Hz, 3H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 149.8, 121.7, 77.3 (NCH$_2$O), 69.1, 68.8, 31.3, 30.8, 28.9, 28.72, 28.67, 25.4, 22.1, 18.5, 16.5, 13.8, 13.4, 11.7.

3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium hexafluorophosphates (33–48). 3-Alkoxymethyl-2-alkyl-1-butoxymethylimidazolium chloride (0.03 mol) dissolved in water (20 ml) and a solution of KPF$_6$ (5.52 g, 0.03 mol) in water (25 ml) are mixed by stirring for 2 h at r.t. After 24 h the water was removed and the precipitate was washed with water (3 x 40 ml). In eluent chlorine ion was controlled by a solution of AgNO$_3$. The obtained hexafluorophosphate without chlorine ion dried in vacuum (10 mmHg, heat, 7 h).

1-Butoxymethyl-3-decyloxymethyl-2-methylimidazolium hexafluorophosphate **40**. ^{1}H NMR (DMSO-d_6) δ ppm: 7.83 [s, H(4)H(5)], 5.60 (s, 2NCH$_2$O), 3.51 (m, 4H), 2.70 (s, 3H), 1.53 (m, 4H), 1.35 (m, 16H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 146.0, 121.5, 77.3 (NCH$_2$O), 69.1, 68.7, 31.3, 30.7, 29.0, 28.7, 25.4, 22.1, 18.6, 13.6, 13.4, 9.4.

1-Butoxymethyl-3-decyloxymethyl-2-ethylimidazolium hexafluorophosphate **48**. ^{1}H NMR (DMSO-d_6) δ ppm: 7.87 [s, H(4)H(5)], 5.62 (s, 2NCH$_2$O), 3.54 (m, 4H), 3.18 (q, J = 7.5 Hz, 2H), 1.54 (m, 4H), 1.32 (m, 16H), 1.29 (t, J =7.6 Hz, 3H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ ppm: 149.6, 121.6, 77.2 (NCH$_2$O), 69.0, 68.7, 31.3, 30.8, 29.0, 28.71, 28.66, 25.4, 22.1, 18.5, 16.5, 13.9, 13.5, 11.9.

The order number of obtained chlorides, tetrafluoroborates and hexafluorophosphates are given in Tables 1, 2 and 3. Tetrafluoroborates and hexafluorophosphates exhibited a marked tendency to supercool to form glasses.

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