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Journal of Fluorine Chemistry 126 (2005) 1150–1159

JOURNAL OF FLUORINE CHEMISTRY

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New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions

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Received 10 February 2005; received in revised form 25 April 2005; accepted 30 April 2005
Available online 18 July 2005

Abstract

The synthesis of new ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions is described. The physico-chemical properties (conductivity, viscosity, electrochemical and thermal stability) of this new generation of ionic liquids (molten salts) are discussed. FAP-ionic liquids show an excellent hydrolytic stability, low viscosity and high electrochemical and thermal stability that makes them attractive for use in electrochemical devices and as a new media for application in modern technologies and chemical synthesis.

Keywords: Ionic liquids; Tris(perfluoroalkyl)trifluorophosphate; Viscosity; Conductivity; Electrochemical stability

1. Introduction

Commonly used ionic liquids with hexafluorophosphate, $[PF_6]^-$ (hydrophobic), are hydrolytically unstable, especially at elevated temperature [1]. The instability of the hexafluorophosphate anion is due to the facial protonation of the fluorine atom, followed by HF elimination and reaction with water. This mechanism of the hydrolysis of $[PF_6]^-$ salts, for example, $LiPF_6$, has been discussed in the literature [2,3]. To address this disadvantage of the hexafluorophosphate anion, the replacement of some fluorine atoms by hydrophobic perfluoroalkyl-groups looks promising as a way to increase the hydrolytic stability of fluorophosphates (see Scheme 1).

Salts with perfluoroalkylfluorophosphate anions are known for more than 40 years [4–6]. The common method of their synthesis is based on the addition of alkali metal fluorides to perfluoroalkylfluorophosphoranes [7]. Trifluoromethyl phosphoranes can be prepared by chlorination/fluorination of trifluoromethylphosphines, synthesized first by Bannett et al. [8]. These compounds were obtained by difficult, time consuming procedures, which requires high pressure (autoclave) and results in a complex mixture of trifluoromethyl containing phosphines (Scheme 2).

Later, Burg et al. have modified this procedure by generation of CF_3I in situ from silver trifluoroacetate and iodine [9] but still the isolation of individual compounds remains a difficult task. Görg et al. have recently developed an alternative method [10] (Scheme 3).

Trifluoromethyl-fluorophosphoranes undergo slow decomposition even at room temperature, releasing difluorocarbene [11]. In contrast, perfluoroalkylfluorophosphoranes with longer carbon chain are more stable [12]. Synthesis of these compounds can be carried out to the method of Emeleus [13], followed by chlorination [13] and fluorination with SbF_3 [14] (Scheme 4).

However, this method is not suitable for the preparation of tris(perfluoroalkyl)difluoro-phosphoranes [13].

In 1995, Kampa et al. [15] reported the direct fluorination of trialkylphosphines with F_2 yielding the corresponding tris(perfluoroalkyl)difluorophosphoranes. The reaction was carried out with diluted F_2 (by helium) in a mixture of CFC-11 and CFC-113 as solvent, at low temperature, with

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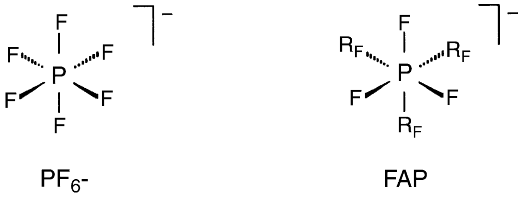
doi:10.1016/j.jfluchem.2005.04.017



Scheme 1.

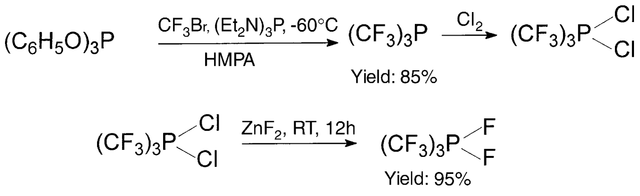
$$CF_3I + P_4 \xrightarrow[\text{Autoclave}]{\text{220-220°C, 48 h}} (CF_3)_3P + (CF_3)_2PI + (CF_3)PI_2$$

Scheme 2.

subsequent slow increase in the temperature up to RT. This difficult technique allows small quantities of tris(perfluoroalkyl)difluorophosphoranes (yield is not given) to be obtained and requires the use of expensive materials. Another synthesis of tris(perfluoroalkyl)difluorophosphoranes, developed by Semenii et al., is based on the electrochemical fluorination (Simons process) of trialkylphosphine oxides [16] (Scheme 5).

Disadvantages of this method are moderate yields of the desired perfluorinated products and formation of an equimolar quantity of toxic OF_2, which can cause a severe explosion in the mixture with hydrogen released in the electrochemical fluorination process.

Recently, we have improved this procedure by use of trialkylphosphines as starting material in an electrochemical fluorination process [17,18]. This allowed an increase in the yield of tris(perfluoroalkyl)difluorophosphoranes and avoided the formation of the dangerous side product, OF_2 (Scheme 6).



Scheme 3.

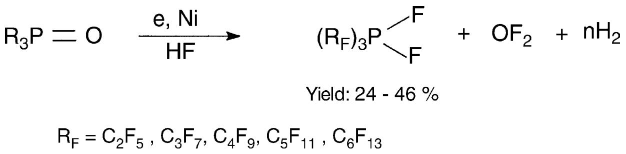
$$C_3F_7I + P_4 \xrightarrow[\text{Autoclave}]{\text{220-230°C, 8 h}} (C_3F_7)_2PI + (C_3F_7)PI_2$$

$$(C_3F_7)_2PI + AgCl \xrightarrow{\text{11 days}} (C_3F_7)_2PCl$$

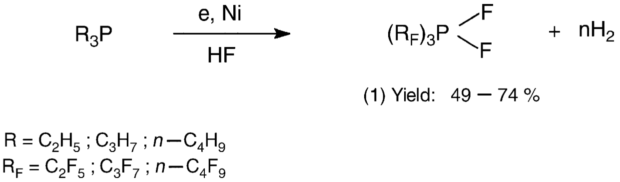
$$(C_3F_7)_2PCl + Cl_2 \xrightarrow{\text{-78°C to R.T.}} (C_3F_7)_2PCl_3$$

$$(C_3F_7)_2PCl_3 + SbF_3 \xrightarrow{\text{R.T.}} (C_3F_7)_2PF_3$$

Scheme 4.



Scheme 5.



Scheme 6.

2. Results and discussion

2.1. Synthesis of ionic liquids with the FAP-anion

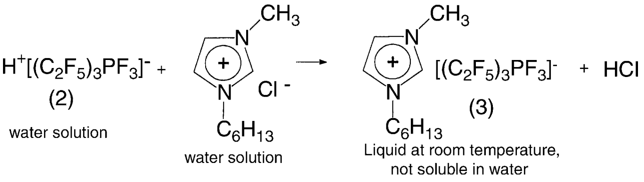
Recently Merck KGaA (Darmstadt, Germany) has developed a convenient method of the synthesis of ionic liquids with the tris(perfluoroalkyl)trifluorophosphate-anion (FAP-anion), as replacement of $[PF_6]^-$. Tris(perfluoroalkyl)difluorophosphoranes (1) [17,18] were applied as starting material for the synthesis of FAP-anions.

Tris(perfluoroalkyl)difluorophosphoranes (1) are very reactive compounds. They react readily with organic or inorganic fluorides [5–8,19–22] with formation of the corresponding salts of FAP-anions. The fluoride ion affinity of tris(perfluoroalkyl)difluorophosphoranes (1) is so high that in aqueous HF the hydrolysis of phosphoranes (1) is suppressed and the corresponding tris(perfluoroalkyl)trifluorophosphoric acid, HFAP (2) is formed in nearly quantitative yield [23,24] (Scheme 7).

HFAP is preferably formed with the meridional (unsymmetrical) structure but the subsequent formation of the facial (symmetrical) structure (up to 15 mol%) can be observed by ^{19}F NMR spectroscopy. Acid (2) is a convenient starting material for the synthesis of various salts [23,24] with ionic liquid properties (Scheme 8).

$$(C_2F_5)_3PF_2 + HF + 5H_2O \longrightarrow \underset{(2)}{[(C_2F_5)_3PF_3]^-H^+ \;.\; 5\,H_2O}$$

Scheme 7.



Scheme 8.

The imidazolium salt (3) is not soluble in water and can be separated easily from the reaction mixture as a liquid phase at the bottom of the reactor. After washing and drying, hexyl-methylimidazolium (HMIM) FAP (3) can be obtained with a very low content of chloride and residual water (10–15 ppm). HMIM FAP (3) is a hydrophobic room temperature ionic liquid, which possesses high hydrolytic stability; no detectable HF formation after 5 h in boiling water (unpublished result from the QUILL Centre, Queen's University, Belfast, UK) and a large electrochemical window (more than 5.5 V). Viscosity of HMIM FAP (3) is comparable with the viscosity of HMIM bis(trifluoromethylsulfonyl)imide.

A similar procedure was applied for the synthesis of pyridinium, pyrrolidinium, alkylammonium, alkylphosphonium, guanidinium [25], uronium [26] and thiouronium [27] salts with the FAP anion. Many of these salts are liquids at room temperature and by definition they belong to the class of room temperature ionic liquids. Alkali-metal salts with the FAP anion can be used for the synthesis of ionic liquids in the same manner as HFAP (2) [28].

2.2. Physico-chemical properties of ionic liquids with the FAP-anion

2.2.1. Water uptake by FAP-ionic liquids

The FAP-ionic liquids are hydrophobic. They are immiscible with water but miscible with polar organic solvents. The water uptake (saturation with water) for these ionic liquids is much less then for the popular ionic liquids with the bis(trifluoromethylsulfonyl)imide-anion and more than 10 times less in comparison with the commonly used ionic liquids with the $[PF_6]^-$ anion (see Table 1). This allows access to FAP-ionic liquids with a very low content of residual water, 10–15 ppm, or even less.

Table 1
Water uptake by ionic liquids containing the $[(C_2F_5)_3PF_3]^-$ (FAP) anion

Ionic liquid	Maximium water uptake (ppm)
1-Hexyl-3-methylimidazolium FAP	2030
1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	10670
1-Butyl-1-methylpyrrolidinium FAP	3500
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	14800
1-Butyl-3-methylimidazolium PF_6^-	22600

2.2.2. Thermal stability

Ionic liquids listed in Table 2 show a low melting point (glass transition point), typically below −50 °C. Ionic liquids with the FAP anion also possess high thermal stability (Table 2), for example, imidazolium based ionic liquids with the FAP-anion start to decompose at temperatures above 280 °C.

Uronium [26] and thiouronium [27] salts with FAP anion are less stable, but still show sufficient thermal stability (more than 220 °C) for practical application as ionic liquids (see Table 2 and Fig. 1.)

Table 2
Thermal stability of the ionic liquids containing the $[(C_2F_5)_3PF_3]^-$ (FAP) anion

Ionic liquid	mp (°C)	Decomposition (°C)
1-Ethyl-3-methylimidazolium FAP	−37	300
1-Pentyl-3-methylimidazolium FAP	<−50	300
1-Hexyl-3-methylimidazolium FAP	−50	290
1-Butyl-1-methylpyrrolidinium FAP	<−50	250
N,*N*,*N*′,*N*′,*N*″-Pentamethyl-*N*″-*i*-propylguanidinium FAP [25]	68–69	240
O-Ethyl-tetramethyluronium FAP [26]	32–34	220
S-Ethyl-tetramethylthiouronium FAP [27]	0–2	250

2.2.3. Electrochemical stability

Electrochemical stability is commonly determined by cyclic voltammetry. In the case of ionic liquids, small additional peaks in the cathodic and/or anodic part of cyclic voltammogram can be related to impurities (usually Cl^-, Br^-). For this reason Merck KGaA has developed and applied halogen free (Cl^-, Br^--free) technology for the preparation of some ionic liquids (for example, triflates [25–27,29–30]).

FAP-ionic liquids possess a very broad electrochemical window (Table 3). The electrochemical stability of ionic liquids with the FAP-anion is comparable with that of bis(trifluoromethylsulfonyl)imide-based ionic liquids, and much better than for tetrafluoroborates.

Tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate (mp 62 °C) shows an extremely broad electrochemical window, close to 7 V (Table 3 and Fig. 2).

This is a new non-hygroscopic conducting salt for non-aqueous supporting electrolytes in electrochemical cells.

2.2.4. Viscosity

Ionic liquids appear to be more viscous then conventional organic solvents. Table 4 presents data, which demonstrate the dramatic influence of the nature of the anion on the viscosity of ionic liquids. For example, replacement of three fluorine atoms in the $[PF_6]^-$ anion by pentafluoroethyl-groups decreases drastically the viscosity of imidazolium ionic liquids (Table 4). Replacement of chloride anion in trihexyl(tetradecy)phosphonium chloride with tris(pentafluoroethyl)trifluorophosphate anion reduced the viscosity

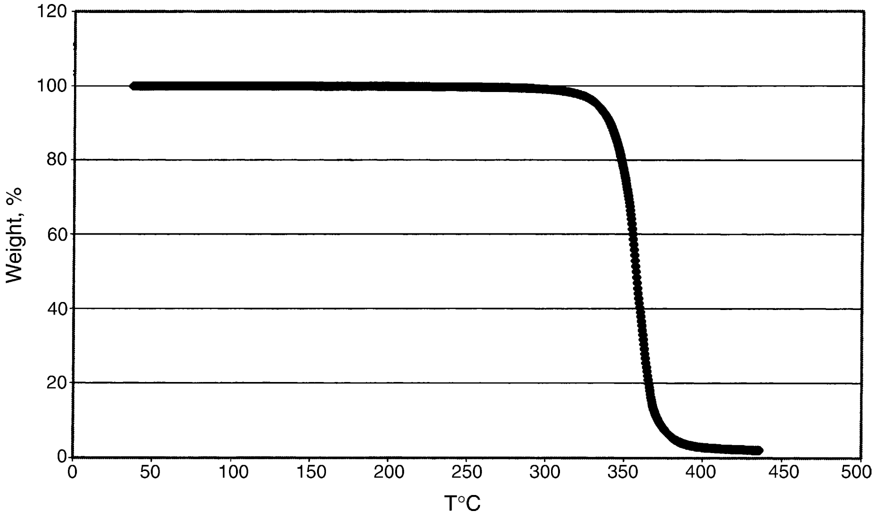


Fig. 1. TGA of *S*-ethyl-tetramethylthiouronium tris(pentafluoroethyl)trifluorophosphate (FAP).

Table 3
Redox stability of the ionic liquids containing the $[(C_2F_5)_3PF_3]^-$ (FAP) anion in comparison to the ionic liquids with bis(trifluoromethylsulfonyl)imide-anion

Ionic liquid	$E_{(ox)}$ (V) vs. ferrocene	$E_{(red)}$ (V) vs. ferrocene	Window (V)
Tetrabutylammonium FAP	3.7	−3.3	7.0
Trihexyl(tetradecyl)phosphonium FAP	3.3	−3.0	6.3
Trihexyl(tetradecyl)phosphonium Bis(trifluoromethylsulfonyl)imide	3.1	−3.4	6.5
1-Butyl-1-methylpyrrolidinium FAP	3.7	−2.9	6.6
1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide	3.5	−3.3	6.8
1-Pentyl-3-methylimidazolium FAP	3.9	−2.6	6.5
1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	3.7	−2.6	6.3
1-Ethyl-3-methylimidazolium BF_4^-	2.6	−2.6	5.2

from 2757 to 393 $mm^2 s^{-1}$ (at 20 °C), in spite of increasing the molecular weight.

Ionic liquids with long-chain perfluoroalkyl-groups in the FAP anion have a higher viscosity. For instance, 1-pentyl-3-methylimidazolium tris(nonafluorobuty)trifluorophosphate has a of viscosity 594 $mm^2 s^{-1}$, which is much higher then the viscosity of 1-hexyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophosphate and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (Table 4).

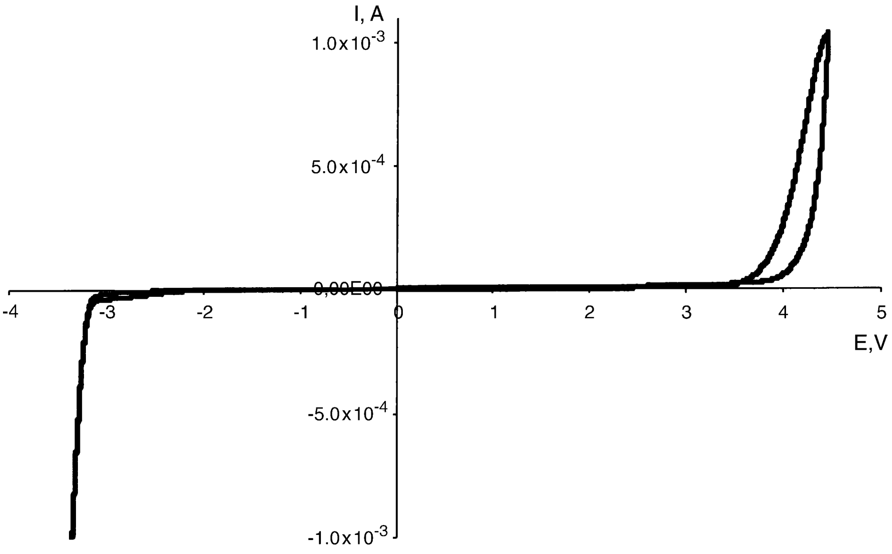


Fig. 2. CVA of tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate.

Table 4
Kinematic viscosity and density of the 1-alkyl-3-methylimidazolium ionic liquids containing different anions

Ionic liquid	Viscosity (20 °C) ($mm^2 s^{-1}$)	Density (20 °C) ($g cm^{-3}$)
1-Hexyl-3-methylimidazolium chloride	7453	1.050
1-Hexyl-3-methylimidazolium $[PF_6]^-$	548	1.297
1-Pentyl-3-methylimidazolium $[(C_4F_9)3PF_3]^-$	594	1.693
1-Hexyl-3-methylimidazolium $[(C_3F_7)3PF3]^-$	227	1.620
1-Hexyl-3-methylimidazolium $[(C_2F5)3PF_3]^-$	74	1.560
1-Hexyl-3-methylimidazolium $[(CF_3SO_2)_2N]^-$	44	1.377
1-Hexyl-3-methylimidazolium $[BF_4]^-$	195	1.150

2.2.5. Conductivity

The conductivity of a pure ionic liquid should depend on the mobility of the ions, which is greatly influenced by the viscosity, ion size and the ion association. The data of Table 5 show that the conductivity of the ionic liquids with FAP-anions decrease with increasing size of cations. Probably, this can be also correlated with the viscosity of ionic liquids, which is increasing for more bulky cations.

The conductivity of 1-ethyl-3-methylimidazolium bis(-trifluoromethylsulfonyl)imide is slightly higher then the conductivity of 1-ethyl-3-methylimidazolium FAP, probably because the imide-anion is less bulky than the FAP-anion. The conductivity of FAP-ionic liquids is drastically increased with increasing of temperature.

Table 6 demonstrates the influence of the inter-ionic interaction in ionic liquids on the conductivity. The ionic liquids listed in Table 6 contain the same cation but different anions. We would expect an increase in the conductivity by replacement of the bulky bis(trifluoromethyl sulfonyl)imide-anion with the less bulky trifluoromethylsulfonate (triflate) anion and, in particular, with trifluoroacetate. But the differences in conductivity between these three ionic liquids are negligible. It appears, that the interaction between the weekly coordinating anions, like FAP and bis(trifluoromethylsulfonyl)imide, with the cationic part is indeed weak. The triflate anion, and especially the trifluoroacetate anion coordinate more strongly to the cation and that hinders their mobility and reduces the conductivity of ionic liquids with these anions.

Table 5
Solvent free conductivity of the ionic liquids containing the $[(C_2F_5)_3PF_3]^-$ (FAP) anion

Ionic liquid	Conductivity (20 °C) ($mS cm^{-1}$)
1-Hexyl-3-methylimidazolium FAP	1.32
1-Pentyl-3-methylimidazolium FAP	1.66
1-Ethyl-3-methylimidazolium FAP	4.40
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	7.63
1-Ethyl-3-methylimidazolium FAP (60 °C)	14.25

Table 6
Solvent free conductivity of the 1-ethyl-3-methylimidazolium ionic liquids containing different anions

Ionic liquid	Conductivity (20 °C) ($mS cm^{-1}$)
1-Ethyl-3-methylimidazolium $[(C_2F_5)3PF_3]^-$	4.40
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	7.63
1-Ethyl-3-methylimidazolium triflate	7.74
1-Ethyl-3-methylimidazolium trifluoroacetate	8.53

The electrochemical behavior of previously studied phenyl(perfluoropropyl)iodonium [31] and bis(pentafluorophenyl)iodonium salts [32] also indicates stronger interaction of the trifluoroacetate and the triflate anions with the cationic centre. The reduction potentials of these salts are more cathodic in comparison to the iodonium salts with weakly coordinated anions, like $[BF_4]^-$ and $[AsF_6]^-$.

The conductivity of ionic liquids can be increased by diluting with polar organic solvents, probably related to decreasing viscosity and separation of ion-pairs. Fig. 3 presents the conductivity of tetrabutylammonium FAP in different organic solvents. The diagram shows a typical dependence of conductivity on the concentration of conducting salt.

3. Experimental

3.1. Chemicals

Tris(perfluoroalkyl)difluorophosphoranes were synthesized via electrochemical fluorination of trialkylphosphines in anhydrous HF (Simons process) as described in [17,18]. Tris(perfluoroalkyl)trifluorophosphoric acid pentahydrate was prepared by slow addition at 0 °C of 1 mol of the corresponding tris(perfluoroalkyl)difluorophosphorane to 110.1 g of stirred aqueous HF (18.17 wt.% concentration) [23]. Imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, guanidinium, uronium and thiouronium salts with chloride, triflate and methylsulfate anions were prepared by procedures, described in the literature [25–27,33]. Tri(*n*-hexyl)tetradecylphosphonium chloride was purchased from *Cytec* company.

3.2. Analytical procedures

^1H, ^{19}F and ^{31}P NMR spectra were measured on a Brucker Avance 300 (300.13 MHz for ^1H and 282.40

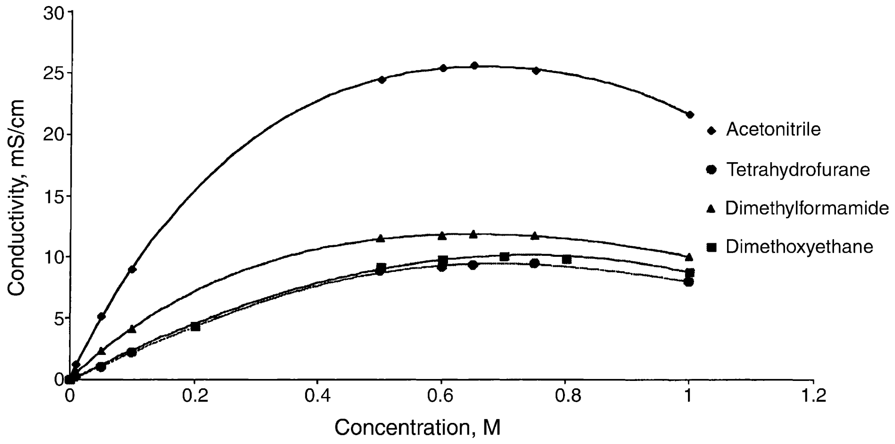


Fig. 3. Concentration dependence of tetrabutylammonium tris(pentafluoroethyl)-trifluorophosphate conductivity in different solvents at 30 °C.

for ^{19}F) and Brucker WP 80 SY spectrometers in acetonitrile-D$_3$. CCl$_3$F and TMS were used as internal references for ^{19}F NMR and the proton spectra correspondingly. The external reference for ^{31}P NMR, 85% H$_3$PO$_4$ in D$_2$O, was positioned at the frequency 230.11 Hz (measured in separate experiment in acetonitrile-D$_3$).

The purity (quality) of FAP-ionic liquids was proved by measuring of residual water (Karl-Fischer titration; 831 KF-Coulobmetr, Metrohm) and of chloride or bromide (ion-chromotography, Metrohm Advanced IC System; stationary phase: Metrosep A SUPP4–150). Contents of residual water and halides were usually below 20 ppm.

Viscosity, density and thermal stability (TGA) of ionic liquids were measured with the use of Viscosimeter SVM 3000 (Anton Paar) and TG-SDTA 851 (Mettler Toledo) correspondingly. Conductivity was measured on Conductometer 703 (Knick) and for cyclic voltammetry an Autolab PGSTAT 30 (Eco Chemie) was used. Cyclic voltammogramms were recorded for 0.5 M solutions in CH$_3$CN at glassy carbon (gc) working electrode; auxiliary electrode was Pt and Ag/AgNO$_3$ (CH$_3$CN) was used as reference electrode. The potential's values were normalized to E° of ferrocene.

3.3. Synthesis of ionic liquids with FAP-anion

3.3.1. Tetra(n-butyl)phosphonium tris(pentafluoroethyl)trifluorophosphate, $[(C_4H_9)_4P]^+$ $[(C_2F_5)_3PF_3]^-$

A solution of tris(pentafluoroethyl)trifluorophosphoric acid, H[(C$_2$F$_5$)$_3$PF$_3$] (16.68 g, 37.4 mmol) in diethylether (14.52 g) was slowly added at room temperature to a stirred 50% solution of tetra(*n*-butyl)phosphonium chloride (10.25 g, 34.8 mmol) in toluene. The mixture was left stirring for 0.5 h and the solvent mixture was distilled off at 13.3 Pa. A white solid material (24.46 g) was obtained. The yield of tetra(*n*-butyl)phosphonium tris(pentafluoroethyl)-trifluorophosphate was quantitative. Melting point (after crystallisation from the mixture of methanol–water) was 73–74 °C.

Analyses, found: C 37.3%, H 5.1; calculated for C$_{22}$H$_{36}$F$_{18}$P$_2$ (mol. mass 704.45): C 37.5%, H 5.15%.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.7 m (CF$_3$); −81.4 m (2CF$_3$); −87.0 d, m (PF$_2$); −115.1 d, m (CF$_2$); −115.7 d, m (2CF$_2$); $^1J_{P,F}$ = 890 Hz; $^1J_{P,F}$ = 902 Hz; $^2J_{P,F}$ = 86 Hz; $^2J_{P,F}$ = 98 Hz.

^{1}H NMR spectrum, δ, ppm: 0.95 t (4CH$_3$); 1.48 m (8CH$_2$); 2.05 m (4CH$_2$); $^3J_{H,H}$ = 7.2 Hz.

^{31}P NMR, δ, ppm: 33.0 m (1P); −148.6 d, t, m (1P).

3.3.2. Tri(n-hexyl)tetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate, $[(C_6H_{13})_3(C_{14}H_{29})P]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, H[(C$_2$F$_5$)$_3$PF$_3$]·5H$_2$O (819.8 g, 1.53 mol), was added at room temperature to the stirred solution of tri(*n*-hexyl)tetradecylphosphonium chloride (793 g, 1.53 mol) in 1 l of methanol. The mixture was left stirring for 0.5 h and the solvent was distilled off on a rotary evaporator. The liquid material was washed with water until pH 6–7 and the test for chloride with silver nitrate was negative. The residue was dried at 13.3 Pa and 80 °C within 8 h. A liquid material (1395 g) was obtained. The yield of tri(*n*-hexyl)tetradecylphosphonium tris(pentafluoroethyl)-trifluorophosphate was 98.2%.

Analyses, found: C 49.2%, H 7.1%; calculated for C$_{38}$H$_{68}$F$_{18}$P$_2$ (mol. mass 928.88): C 49.1%, H 7.4%.

^{19}F NMR spectrum, δ, ppm: −43.8 d, m (PF); −79.8 m (CF$_3$); −81.4 m (2CF$_3$); −87.2 d, m (PF$_2$); −115.2 d, m (1CF$_2$); −115.7 d, m (2CF$_2$); $^1J_{P,F}$ = 890 Hz; $^1J_{P,F}$ = 902 Hz; $^2J_{P,F}$ = 87 Hz; $^2J_{P,F}$ = 97 Hz.

^{1}H NMR spectrum, δ, ppm: 0.89–0.99 m (4CH$_3$), 1.28–1.41 m (16CH$_2$), 1.42–1.62 m (8CH$_2$), 2.01–2.16 m (4CH$_2$).

^{31}P NMR, δ, ppm: 32.8 m (1P); −148.5 d, t, m (1P).

3.3.3. 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, $[C_{10}H_{19}N_2]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (2700 g, 5.04 mol) was added at room temperature to the stirred solution of 1-hexyl-3-methylimidazolium chloride (1018 g, 5.02 mol) in 1.5 l of water. The mixture was left stirring for 0.5 h. The bottom phase was separated and washed with water until pH 6–7 and the test for chloride with silver nitrate was negative. The residue was dried at 13.3 Pa and 90 °C within 22 h. A liquid material (2998 g) was obtained. The yield of 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate was 97.5%.

Analyses, found: C 31.0%, H 2.4, N 4.6; calculated for $C_{16}H_{19}F_{18}N_2P$ (mol. mass 612.29): C 31.4%, H 3.1%, N 4.7.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.7 m (CF_3); −81.4 m ($2CF_3$); −87.0 d, m (PF_2); −115.1 d, m ($1CF_2$); −115.7 d, m ($2CF_2$); $^1J_{P,F} = 891$ Hz; $^1J_{P,F} = 909$ Hz; $^2J_{P,F} = 83$ Hz; $^2J_{P,F} = 98$ Hz.

^1H NMR, δ, ppm: 0.89 m (CH_3); 1.30 m ($3CH_2$); 1.81 m (CH_2); 3.80 s (CH_3); 4.10 t (CH_2); 7.30 d, d (CH); 7.34 d, d (CH); 8.35 br.s (CH); $^3J_{H,H} = 7.2$ Hz; $^3J_{H,H} = 1.5$ Hz.

^{31}P NMR, δ, ppm: −148.0 d, t, m.

3.3.4. 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, $[C_9H_{20}N]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (214 g, 0.399 mol) was added at room temperature to the stirred solution of 1-butyl-1-methylpyrrolidinium methylsulfate (100 g, 0.395 mol) in 300 cm^3 of water. The mixture was left stirring for 10 min. The bottom phase was separated and washed with water until pH 6–7. The residue was dried at 13.3 Pa and 80 °C within 8 h. A liquid material (215.1 g) was obtained. The yield of 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate was 92.7%.

Analyses, found: C 30.6%, H 3.1%, N 2.6%; calculated for $C_{15}H_{20}F_{18}NP$ (mol. mass 587.28): C 30.7%, H 3.4%, N 2.4%.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.7 m (CF_3); −81.4 m ($2CF_3$); −87.0 d, m (PF_2); −115.0 d, m ($1CF_2$); −115.7 d, m ($2CF_2$); $^1J_{P,F} = 888$ Hz; $^1J_{P,F} = 903$ Hz; $^2J_{P,F} = 82$ Hz; $^2J_{P,F} = 98$ Hz.

^1H NMR, δ, ppm: 0.96 t (CH_3); 1.37 m (CH_2); 1.71 m (CH_2); 2.14 m ($2CH_2$); 2.92 s (CH_3); 3.20 m (CH_2); 3.38 m ($2CH_2$); $^3J_{H,H} = 7.4$ Hz.

^{31}P NMR, δ, ppm: −148.1 d, t, m.

3.3.5. 1-Butyl-4-methylpyridinium tris(pentafluoroethyl)trifluorophosphate, $[C_{10}H_{16}N]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (537 g, 1.002 mol) was added at room temperature to the stirred solution of 1-butyl-4-methylpyridinium chloride (185 g, 0.996 mol) in 300 cm^3 of water. The mixture was left stirring for 15 min. The bottom phase was separated and washed with water until pH 6–7 and the test for chloride with silver nitrate was negative. The residue was dried at 13.3 Pa and 100 °C within 12 h. A liquid material (581 g) was obtained. The yield of 1-butyl-4-methylpyridinium tris(pentafluoroethyl)trifluorophosphate was 98.0%.

Analyses, found: C 32.4%, H 2.2, N 2.6; calculated for $C_{16}H_{19}F_{18}N_2P$ (mol. mass 595.25): C 32.3%, H 2.7%, N 2.4.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.7 m (CF_3); −81.4 m ($2CF_3$); −87.0 d, m (PF_2); −115.0 d, m ($1CF_2$); −115.6 d, m ($2CF_2$); $^1J_{P,F} = 888$ Hz; $^1J_{P,F} = 903$ Hz; $^2J_{P,F} = 85$ Hz; $^2J_{P,F} = 98$ Hz.

^1H NMR, δ, ppm: 0.95 t (CH_3); 1.35 m (CH_2); 1.91 m (CH_2); 2.61 s (CH_3); 4.42 t (CH_2); 7.79 m (2CH); 8.46 m (2CH); $^3J_{H,H} = 7.4$ Hz; $^3J_{H,H}(A, B) = 6.6$ Hz.

^{31}P NMR, δ, ppm: −148.0 d, t, m.

3.3.6. Tetraethylammonium tris(pentafluoroethyl)trifluorophosphate, $[(C_2H_5)_4N]^+$ $[(C_2F_5)_3PF_3]^-$

A 20% aqueous solution (11.37 g, 15.44 mmol) of tetraethylammonium hydroxide was slowly, within 2 min, added to tris(pentafluoroethyl)trifluoro-phosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (8.28 g, 15.44 mmol) by stirring and cooling of the reaction mixture with ice–water bath. The reaction mixture was diluted with 100 cm^3 of water and stirred additionally 10 min at room temperature. White precipitate was filtered off and washed two times with 30 cm^3 of water. After drying on air over the night, a white solid material (8.55 g) was obtained. The yield of tetraethylammonium tris(pentafluoroethyl)trifluorophosphate was 96.3%. Melting point was 95 °C. After crystallization of this product from the mixture of methanol–water, the melting point was not changed.

Analyses, found: C 29.1%, H 3.4%, N 2.5%; calculated for $C_{14}H_{20}F_{18}NP$ (mol. mass 575.26): C 29.2%, H 3.5%, N 2.4%.

^{19}F NMR spectrum, δ, ppm: −43.5 d, m (PF); −79.6 m (CF_3); −81.3 m ($2CF_3$); −86.9 d, m (PF_2); −115.0 d, m (CF_2); −115.7 d, m (CF_2); $^1J_{P,F} = 888$ Hz; $^1J_{P,F} = 902$ Hz; $^2J_{P,F} = 86$ Hz; $^2J_{P,F} = 98$ Hz.

^1H NMR spectrum, δ, ppm: 1.39 t, m ($4CH_3$), 3.48 q ($4CH_2$); $^3J_{H,H} = 7.3$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m.

3.3.7. Tetrabutylammonium tris(pentafluoroethyl)trifluorophosphate, $[(C_4H_9)_4N]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (407.5 g, 0.76 mol) was slowly, within 1 h, added by stirring and cooling of the reaction mixture with ice–water bath to of 40% aqueous (493.2 g, 0.76 mol) solution of tetrabutylammonium hydroxide, diluted with 2 l of water. White precipitate was filtered off and washed two times with 300 cm^3 of water. After drying at 13.3 Pa and 50 °C within 8 h a solid material (504.6 g) was obtained. The yield of tetrabutylammonium tris(pentafluoroethyl)-trifluorophosphate was 96.6%. Melting point was 62 °C.

Analyses, found: C 38.3%, H 5.1%, N 1.8%; calculated for $C_{22}H_{36}F_{18}NP$ (mol. mass 687.48): C 38.4%, H 5.3%, N 2.0%.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.6 m (CF_3); −81.3 m ($2CF_3$); −87.0 d, m (PF_2); −115.0 d, m ($1CF_2$); −115.6 d, m ($2CF_2$); $^1J_{P,F} = 889$ Hz; $^1J_{P,F} = 902$ Hz; $^2J_{P,F} = 83$ Hz; $^2J_{P,F} = 97$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.00 t ($4CH_3$), 1.38 q, t ($4CH_2$); 1.63 m ($4CH_2$); 3.11 m ($4CH_2$); $^3J_{H,H} = 7.3$ Hz; $^3J_{H,H} = 7.4$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m.

3.3.8. *O-ethyl-tetramethyluronium tris(pentafluoroethyl)trifluorophosphate,* $[(CH_3)_2N]_2C(OC_2H_5)]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (36.0 g, 0.067 mol) was added at room temperature to the stirred solution of *O*-ethyl-tetramethyluronium triflate [26] (18.8 g, 0.064 mol) in 70 cm^3 of water. White precipitate was filtered off and washed four times with 30 cm^3 of water. After drying at 7.0 Pa and 60 °C within 3 h a solid material (36.7 g) was obtained. The yield of *O*-ethyl-tetramethyluronium tris(-pentafluoroethyl)trifluorophosphate was 97.3%. Melting point was 32–34 °C.

Analyses, found: C 26.5%, H 3.0%, N 4.8%; calculated for $C_{13}H_{17}F_{18}N_2OP$ (mol. mass 590.24): C 26.5%, H 2.9%, N 4.8%.

^{19}F NMR spectrum, δ, ppm: −43.5 d, m (PF); −79.5 m (CF_3); −81.2 m ($2CF_3$); −86.9 d, m (PF_2); −114.9 d, m ($1CF_2$); −115.5 d, m ($2CF_2$); $^1J_{P,F} = 889$ Hz; $^1J_{P,F} = 900$ Hz; $^2J_{P,F} = 84$ Hz; $^2J_{P,F} = 98$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.42 t (CH_3); 3.05 s ($4CH_3$), 4.37 q (CH_2); $^3J_{H,H} = 7.0$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m; $^1J_{P,F} = 888$ Hz; $^1J_{P,F} = 902$ Hz.

3.3.9. *S-ethyl-tetramethylthiouronium tris(pentafluoroethyl)trifluorophosphate,* $[(CH_3)_2N]_2C(SC_2H_5)]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (31.0 g, 0.058 mol) was added at room temperature to the stirred solution of *S*-ethyl-tetramethylthiouronium triflate [27] (17.1 g, 0.055 mol) in 70 cm^3 of water. The bottom phase was separated and washed four times with 30 cm^3 of water. After drying at 7.0 Pa and 60 °C within 3 h a liquid material (30.0 g) was obtained. The yield of *S*-ethyl-tetramethylthiouronium tris(pentafluoroethyl)trifluorophosphate was 89.8%.

Analyses, found: C 25.6%, H 2.9%, N 4.6%; calculated for $C_{13}H_{17}F_{18}N_2PS$ (mol. mass 606.30): C 25.8%, H 2.8%, N 4.6%.

^{19}F NMR spectrum, δ, ppm: −43.6 d, m (PF); −79.6 m (CF_3); −81.3 m ($2CF_3$); −86.9 d, m (PF_2); −114.9 d, m ($1CF_2$); −115.5 d, m ($2CF_2$); $^1J_{P,F} = 890$ Hz; $^1J_{P,F} = 904$ Hz; $^2J_{P,F} = 86$ Hz; $^2J_{P,F} = 97$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.34 t (CH_3); 3.03 q (CH_2); 3.25 s ($4CH_3$); $^3J_{H,H} = 7.4$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m; $^1J_{P,F} = 890$ Hz; $^1J_{P,F} = 902$ Hz.

3.3.10. *N-i-Propyl-N-pentamethylguanidinium tris(pentafluoroethyl)trifluorophosphate,* $[(CH_3)_2N]_2C[N(CH_3)(i\text{-}C_3H_7)]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (11.4 g, 0.021 mol) was added at room temperature to the stirred solution of *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-*i*-propyl-guanidinium triflate [25] (6.8 g, 0.021 mol) in 100 cm^3 of water. White precipitate was filtered off and washed three times with 30 cm^3 of water. After drying at 7.0 Pa and 60 °C within 3 h a solid material (12.3 g) was obtained. The yield of *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-*i*-propyl-guanidinium tris(pentafluoroethyl)trifluorophosphate was 94.0%. Melting point was 68–69 °C.

Analyses, found: C 29.3%, H 3.5%, N 6.8%; calculated for $C_{15}H_{22}F_{18}N_3P$ (mol. mass 617.30): C 29.2%, H 3.6%, N 6.8%.

^{19}F NMR spectrum, δ, ppm: −43.5 d, m (PF); −79.6 m (CF_3); −81.2 m ($2CF_3$); −86.8 d, m (PF_2); −114.9 d, m ($1CF_2$); −115.5 d, m ($2CF_2$); $^1J_{P,F} = 889$ Hz; $^1J_{P,F} = 901$ Hz; $^2J_{P,F} = 87$ Hz; $^2J_{P,F} = 97$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.22 br.s (CH_3); 1.33 br.s (CH_3); 2.77 s (CH_3); 2.91 s ($4CH_3$); 3.74 hep (CH); $^3J_{H,H} = 6.6$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m; $^1J_{P,F} = 890$ Hz; $^1J_{P,F} = 902$ Hz.

3.3.11. *1,3-Dimethyl-2-diethylaminoimidazolidinium tris(pentafluoroethyl)trifluorophosphate,* $[C_9H_{20}N_3]^+$ $[(C_2F_5)_3PF_3]^-$

Tris(pentafluoroethyl)trifluorophosphoric acid pentahydrate, $H[(C_2F_5)_3PF_3]\cdot 5H_2O$ (41.0 g, 0.077 mol) was added at room temperature to the stirred solution of 1,3-dimethyl-2-diethylaminoimidazolidinium chloride [25] (15.0 g, 0.073 mol) in 200 cm^3 of water. White precipitate was filtered off and washed three times with 50 cm^3 of water. After drying at 7.0 Pa and 60 °C within 3 h a solid material (43.9 g) was obtained. The yield of 1,3-dimethyl-2-diethylaminoimidazolidinium tris(pentafluoroethyl)trifluorophosphate was 97.8%. Melting point was 36–37 °C.

Analyses, found: C 29.2%, H 2.9%, N 7.0%; calculated for $C_{15}H_{20}F_{18}N_3P$ (mol. mass 615.29): C 29.3%, H 3.3%, N 6.8%.

^{19}F NMR spectrum, δ, ppm: −43.5 d, m (PF); −79.6 m (CF_3); −81.3 m ($2CF_3$); −86.9 d, m (PF_2); −114.9 d, m

(1CF$_2$); −115.5 d, m (2CF$_2$); $^1J_{P,F} = 888$ Hz; $^1J_{P,F} = 900$ Hz; $^2J_{P,F} = 85$ Hz; $^2J_{P,F} = 98$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.20 t (2CH$_3$); 2.94 s (2CH$_3$); 3.34 q (2CH$_2$); 3.68 s (2CH$_2$); $^3J_{H,H} = 7.1$ Hz.

^{31}P NMR, δ, ppm: −148.6 d, t, m; $^1J_{P,F} = 890$ Hz; $^1J_{P,F} = 902$ Hz.

3.3.12. 1-Hexyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophosphate, $[C_{10}H_{19}N_2]^+$ $[(C_3F_7)_3PF_3]^-$

Tris(heptafluoropropyl)trifluorophosphoric acid pentahydrate, $H[(C_3F_7)_3PF_3]\cdot 5H_2O$ (27.0 g, 39.4 mmol) was added at room temperature to the stirred solution of 1-hexyl-3-methylimidazolium chloride (7.97 g, 39.3 mmol) in 20 cm^3 of water. The mixture was left stirring for 10 min. The bottom phase was separated and washed five times with 50 cm^3 of water until the test for chloride with silver nitrate was negative. The residue was dried at 13.3 Pa and 50 °C within 6 h. A liquid material (26.4 g) was obtained. The yield of 1-hexyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophosphate was 88.1%.

Analyses, found: C 30.2%, H 2.1%, N 4.1%; calculated for $C_{19}H_{19}F_{24}N_2P$ (mol. mass 762.31): C 29.9%, H 2.5%, N 3.7%.

^{19}F NMR spectrum, δ, ppm: −43.8 d, m (PF); −79.6 t (2CF$_3$); −80.0 t (CF$_3$); −84.7 d, m (PF$_2$); −111.8 d, m (1CF$_2$); −112.9 d, m (2CF$_2$); −122.8 m (1CF$_2$); −124.6 m (2CF$_2$); $^1J_{P,F} = 897$ Hz; $^1J_{P,F} = 930$ Hz; $^2J_{P,F} = 82$ Hz; $^2J_{P,F} = 101$ Hz; $^4J_{F,F} = 12$ Hz.

^{1}H NMR, δ, ppm: 0.88 m (CH$_3$); 1.30 m (3CH$_2$); 1.81 m (CH$_2$); 3.80 s (CH$_3$); 4.09 t (CH$_2$); 7.30 m (CH); 7.34 m (CH); 8.35 br.s (CH); $^3J_{H,H} = 7.3$ Hz.

^{31}P NMR, δ, ppm: −142.4 d, t, m.

3.3.13. 1-Pentyl-3-methylimidazolium tris(nonafluorobutyl)trifluorophosphate, $[C_9H_{17}N_2]^+$ $[(C_4F_9)_3PF_3]^-$

Tris(nonafluorobutyl)trifluorophosphoric acid pentahydrate, $H[(C_4F_9)_3PF_3]\cdot 5H_2O$ (133.2 g, 159.3 mmol) was added within 5 min at room temperature to the stirred solution of 1-pentyl-3-methylimidazolium chloride (30.0 g, 159.0 mmol) in 100 cm^3 of water. The mixture was left stirring for 10 min. The bottom phase was separated and washed 5 times with 50 cm^3 of water until the test for chloride with silver nitrate was negative. The residue was dried 13.3 Pa and 50 °C within 5 h. A liquid material (128.4) g was obtained. The yield of 1-pentyl-3-methylimidazolium tris(nonafluorobutyl)trifluoro-phosphate was 89.9%.

Analyses, found: C 28.4%, H 2.1%, N 3.7%; calculated for $C_{19}H_{19}F_{24}N_2P$ (mol. mass 898.31): C 28.1%, H 1.9%, N 3.1%.

^{19}F NMR spectrum, δ, ppm: −44.0 d, m (PF); −80.7 t, t (1CF$_3$); −80.8 t, t (2CF$_3$); −84.5 d, m (PF$_2$); −111.4 d, m (1CF$_2$); −112.5 d, m (2CF$_2$); −119.2 m (1CF$_2$); −121.2 m (2CF$_2$); −124.7 t, m (2CF$_2$); −125.2 m (CF$_2$); $^1J_{P,F} = 905$ Hz; $^1J_{P,F} = 935$ Hz; $^2J_{P,F} = 83$ Hz; $^2J_{P,F} = 97$ Hz; $^4J_{F,F} = 10$ Hz; $^5J_{F,F} = 4$ Hz.

^{1}H NMR, δ, ppm: 0.92 t (CH$_3$); 1.34 m (2CH$_2$); 1.86 t, t (CH$_2$); 3.84 s (CH$_3$); 4.13 t (CH$_2$); 7.32 d, d (CH); 7.36 d, d (CH); 8.41 br.s (CH); $^3J_{H,H} = 7.1$ Hz; $^3J_{H,H} = 7.4$ Hz; $^3J_{H,H} = 1.8$ Hz.

^{31}P NMR, δ, ppm: −141.9 d, t, m.

3.3.14. Tetraethylammonium bis(nonafluorobutyl)tetrafluorophosphate, $[(C_2H_5)_4N]^+$ $[(C_4F_9)_2PF_4]^-$

A 85.9%-ige (wt.%) aqueous bis(nonafluoro-*n*-butyl)tetrafluorophosphoric acid (3.95 g) was slowly, within 3 min, added to aqueous tetraethylammonium hydroxide (54.58 g; prepared from 4.58 g of 20%-ige aqueous $(C_2H_5)_4N^+$ ^-OH and 50 cm^3 of water), by stirring and cooling of the reaction mixture with ice–water bath. The reaction mixture was stirred additionally 10 min at room temperature. White precipitate was filtered off and washed two times with 10 cm^3 of water. After drying on air over the night, a white solid material (3.05 g) was obtained. The yield of tetraethylammonium bis(nonafluoro-*n*-butyl)tetrafluorophosphate is 72.6%. Melting point was 148–149 °C.

Analyses, found: C 38.5%, N 2.0%; calculated for $C_{22}H_{36}F_{18}NP$ (mol. mass 687.48): C 38.4%, N 2.0%.

^{19}F NMR spectrum, δ, ppm: −70.3 d, m (PF$_4$); −80.7 m (2CF$_3$); −116.0 d, m (2CF$_2$); 122.4 m (2CF$_2$); 124.4 t (2CF$_2$); $^1J_{P,F} = 931$ Hz; $^2J_{P,F} = 100$ Hz; $^4J_{F,F} = 15.3$ Hz.

^{1}H NMR spectrum, δ, ppm: 1.20 t, m (4CH$_3$), 3.15 q (4CH$_2$); $^3J_{H,H} = 7.1$ Hz.

^{31}P NMR, δ, ppm: −148.2 quin, quin; $^1J_{P,F} = 932$ Hz; $^2J_{P,F} = 100$ Hz.

Acknowledgements

Authors thank Dr. O. Korbut and Mrs. A. Amann for the measurements of physico-chemical properties of ionic liquids.

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