Electrochimica Acta 175 (2015) 254–260

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

New family of highly conductive and low viscous ionic liquids with asymmetric 2,2,2-trifluoromethylsulfonyl-N-cyanoamide anion☆

Alexander S. Shaplov[a,*], Elena I. Lozinskaya[a], Petr S. Vlasov[b], Sofia M. Morozova[a], Dmitrii Y. Antonov[a], Pierre-Henri Aubert[c], Michel Armand[d,e], Yakov S. Vygodskii[a]

[a] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, GSP-1, 119991 Moscow, Russia
[b] Department of Macromolecular Chemistry, Saint Petersburg State University, Universitetsky pr. 26, Saint Petersburg 198504, Russia
[c] Laboratoire de Physico-chimie des Polymères et des Interfaces (LPPI), Universite' de Cergy-Pontoise, 5 mail Gay-Lussac, 95031 Cergy-Pontoise Cedex, France
[d] Laboratoire de Réactivité et Chimie des Solides (LRCS), University de Picardie Jules Verne, UMR 6007CNRS, 33 rue de Saint-Leu, Amiens 80039, France
[e] CIC Energigune, C/Albert Einstein, 48 01510 Miñano, Alava, Spain

ARTICLE INFO

Article history:
Received 26 November 2014
Received in revised form 27 February 2015
Accepted 27 February 2015
Available online 28 February 2015

Keywords:
Ionic liquids
Low viscosity
Ionic conductivity
TFSAM
Asymmetric anion

ABSTRACT

The synthetic pathway for the preparation of potassium salt with novel asymmetric 2,2,2-trifluoromethylsulfonyl-N-cyanoamide (TFSAM, CF_3SO_2-N-CN) anion in high yield and purity is reported. New family of ionic liquids, based on "classical" 1-methyl-3-alkylimidazolium, N-methyl-N-propylpyrrolidinium, quaternary ammonium or phosphonium non-cyclic cations with TFSAM as counter-anion, were synthesized and their physical properties were studied. All salts were found to be low melting compounds, most being liquid at r.t., with low (for ionic liquids) viscosities and high ionic conductivities at 25 °C (for example, $\eta = 23$ cP and $\sigma = 1.1 \times 10^{-2}$ S/cm for 1-ethyl-3-methylimidazolium 2,2,2-trifluoromethylsulfonyl-N-cyanoamide). The electrochemical stability of TFSAM ILs was found to be in the range of 4.1–4.6 V.

1. Introduction

Ionic Liquids (ILs) have attracted much attention as novel reaction medium for various chemical processes [1,3–8] as well as electrolytes in different applications [9–14]. Since ILs offer great ability in the designing of cationic and anionic structures and their combinations, one can in principle manipulate their properties as desired. However, until the 90 s the field of ionic solvents was dominated only by a small number of research groups as the set of known salts with melting points below 100 °C was mostly limited to halide ILs or their mixtures with metal halides [1,2,6]. The attempts to introduce new anions, such as tetraalkylborates [15], were not very successful as demanded complicated lab-made starting materials rather than purchased ones. The real explosion of interest in ILs occurred since the discovery of tetrafluoroborate, and hexafluorophosphate anions forming air and moisture stable, easy to handle salts [16,17]. Next revolutionary step was the introduction of highly delocalized bis(trifluoromethylsulfonyl) imide ($(CF_3SO_2)_2N$, TFSI), trifluoromethane- (CF_3SO_3, TfO) and nonafluorobutanesulfonate ($C_4F_9SO_3$) anions by Grätzel and Armand [18]. This allowed for the preparation of rather fluid liquids with as low viscosity as 34 cP (25 °C) for 1-methyl-3-ethylimidazolium TFSI salt. Moreover, the outstanding electrochemical stability of the TFSI ILs was discovered as well [10–12,19]. Following, a breakthrough came as MacFarlane and Forsyth et al. in 2002 [20,21] reported that dicyanamide ($(CN)_2N$, DCA) anion forms room temperature ILs with asymmetric and cyclic aliphatic quaternary ammoniums. The lowest viscosity of DCA based salts compared to other ILs provided a new generation of reaction medium that was easier to handle in a variety of standard experimental procedures. Two years after a very similar tetracyanoborate ($(CN)_4B$, TCB) anion was patented for ILs by Merck KGaA [22]. In spite of low viscosity and high ionic conductivities (up to 10^{-2} S/cm at 25 °C), the further utilization of DCA and TCB based ILs as electrolytes was limited by their insufficient electrochemical stability [10]. In parallel the works of Matsumoto et al. [23,24] reported synthesis of new ILs with asymmetric 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide (CF_3SO_2-N-$COCF_3$, TSAC) anion. TSAC based salts showed extremely low melting points and low viscosities, however, with conductivities nearly similar to TFSI ILs, but lower than DCA based electrolytes.

☆ Paper presented at the ISPE-14 Conference, Geelong, 24–29th August 2014.

* Corresponding author. Tel.: +7 499 1359244; fax: +7 499 1355085.
E-mail address: shaplov@ineos.ac.ru (A.S. Shaplov).

http://dx.doi.org/10.1016/j.electacta.2015.02.228
0013-4686/

Later on the instability of PF_6 salts towards hydrolysis [25,26] was overcome by the development of ILs with tris(perfluoroalkyl) trifluorophosphate (FAP) anions [27]. However, the conductivity of FAP ILs did not exceed 10^{-3} S/cm at 25 °C. Other attempts to improve the properties of PF_6 ILs were recently performed by Ignat'iev et al. [28] and Creager et al. [29] via synthesis of two new families of ILs with bis[bis(pentafluoroethyl) phosphinyl]imide ($[(C_2F_5)_2P(O)]_2N$) and bis(trifluoromethyl) phosphinate ($((CF_3)_2PO_2)$) anions, respectively. The reported thermal and electrochemical stabilities were raised to the level of TFSI ILs, but the viscosities of salts even when mentioned anions were coupled with imidazolium cations were as high as 100–110 cP (25 °C). To decrease melting points and the viscosity of BF_4 salts several attempts were performed resulting in the preparation of a family of ILs with weakly coordinating $B[OCH(CF_3)_2]_4$ anions [30]. Although the viscosities and conductivities of $B[OCH(CF_3)_2]_4$ – ILs were similar to TFSI and even to some of the DCA based solvents, the electrochemical stability was not high enough. Finally, the bis (fluorosulfonyl) imide ($(FSO_2)_2N$, FSI) anion was introduced in 2008 [31–34]. Its distinguishing features result from its smaller size in comparison with TFSI "brother" along with the preservation of high charge delocalization. As it was demonstrated [31], FSI ILs similarly to DCA ones possess outstanding ionic conductivity (up to 10^{-2} S/cm at 25 °C) and rather low viscosities.

Despite all the achievements the further investigation of ILs for utilization both as solvents and electrolytes in electrochemical devices turns to be impossible without the development of novel anions and cations which might particularly offer low viscosity, low melting points and high ionic conductivity.

Here we present a straightforward simple synthesis of the new $K^+[CF_3SO_2\text{-}N\text{-}CN]^-$ salt and the metathesis reactions leading to a series of 2,2,2-trifluoromethylsulfonyl-N-cyanoamide (TFSAM)-bearing ILs (Scheme 1). The newly introduced asymmetric TFSAM anion has an excellent ability to decrease melting point and viscosity of its salts containing even a small cation such as propyltrimethyl ammonium one. Simultaneously it imparts to ILs ionic conductivity higher than that of TFSI and TSAC based electrolytes and electrochemical stability exceeding the EW of salts with FSI and DCA anions.

2. Experimental

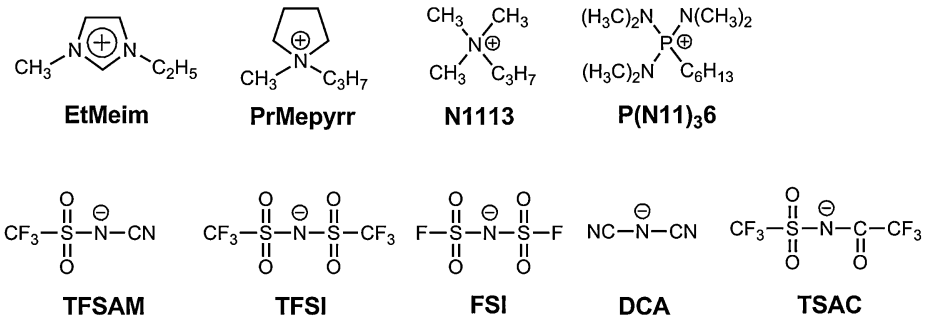
2.1. Materials

tert-Butanol (99.5%, extra pure, Acros), cyanogen bromide solution (5.0 M in acetonitrile, Aldrich), trimethylamine (33 wt.% solution in ethanol, Acros), trifluoroacetic anhydride (>99%, Aldrich) and methanol (>99.9%, Aldrich) were used without further purification. Reagent-grade dichloromethane, acetonitrile, hexane, ethyl acetate and diethyl ether were obtained from Aldrich or Merck and were dried by vacuum distillation over P_2O_5. N-methylimidazole (98%, Aldrich), N-methylpyrrolidine (98%, Acros), bromoethane (98%, Acros), 1-bromopropane (99%, Acros) and 1-bromohexane (99 + %, Aldrich) were distilled under inert atmosphere over CaH_2. Tris(dimethylamino) phosphine (97%, ABCR) was distilled under reduced pressure over CaH_2. Trifluoromethanesulfonamide (97%, ABCR) and potassium *tert*-butoxide (Acros, 98%) were sublimed in high vacuum (<1 mm Hg) at 75-80 and 200-210 °C, respectively. 1-Ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide ([EtMeim]TFSI, electrochemistry grade 99.9%, Solvionic), 1-ethyl-3-methyl imidazolium dicyanamide ([EtMeim]DCA, >98%, Iolitec), 1-ethyl-3-methyl imidazolium bis (fluorosulfonyl) imide ([EtMeim]FSI, 99.5%, Solvionic) and N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([PrMepyrr]TFSI, 99.5%, Solvionic) were additionally dried at 55 °C/1 mm Hg for 12 h with a special flask filled with P_2O_5 and introduced into the vacuum line.

2.2. Potassium 2,2,2-trifluoromethylsulfonyl-N-cyanoamide K [CF_3SO_3-N-CN](KTFSAM)

Potassium t-butoxide (29.6 g, 0.264 mol) was slowly dissolved in 300 mL of anhydrous *t*-butanol at 50 °C under inert atmosphere. The prepared solution was transferred to the funnel and added dropwise to the stirred solution of trifluoromethanesulfonamide (39.4 g, 0.264 mol) in 150 mL of *t*-butanol under inert atmosphere. Then the temperature was raised to 85 °C and the reaction was continued for 8 h. Afterwards the reaction mixture was concentrated and allowed to slowly cool down to r.t. The precipitated white crystals were collected by filtration under inert atmosphere, washed with anhydrous *t*-butanol, anhydrous diethyl ether and dried at 55 °C/1 mm Hg for 4 h. Yield: 43.5 g (88%).

Cyanogen bromide solution (23.2 mL, 0.116 mol) in acetonitrile was slowly injected at r.t. to the solution of CF_3SO_2NHK (43.4 g, 0.232 mol) in 200 mL of anhydrous acetonitrile placed under inert atmosphere in a Schlenk flask. After 15 minutes of stirring the precipitation of a white solid was observed and an exothermic reaction was occurred to 40 °C. The stirring was continued at 35 °C for 24 h. The reaction mass was filtered and the solvent was removed under reduced pressure at 55 °C. The solid residue was washed with anhydrous diethyl ether (4 × 200 mL), dried for 2 h at r.t./1 mm Hg and finally for 5 h at 85 °C/1 mm Hg. The resultant CF_3SO_2-N-CNK salt was obtained as white powder. Yield: 23.6 g (96%); mp = 132-133 °C; ^{13}C NMR (100 MHz, D_2O): 124.8-115.2 (q, $^1J_{CF}$ = 322 Hz), 116.2 (s, CN); ^{19}F NMR (376 MHz, D_2O): -78.0; IR (KBr pellet): 2221 (vs, ν_{CN}), 2202 (vs, ν_{CN}), 1346 (vs, ν_{asSO2}), 1327 (s), 1253 (vs), 1218 (vs, ν_{CF}), 1172 (m, ν_{sSO2}), 1115 (s, ν_{CF}), 837 (s), 641 (m), 601 (s), 481 (w), 454 (w).



Scheme 1. Structure of cations and anions used for the synthesis of ILs.