Journal of Molecular Liquids 246 (2017) 236–243

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Physicochemical properties of phenyltrifluoroborate-based room temperature ionic liquids

Kazuki Iwasaki [a], Kazuki Yoshii [a], Tetsuya Tsuda [a,*], Susumu Kuwabata [a,b,**]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
[b] Department of Energy and Environment, Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:
Received 17 August 2017
Received in revised form 15 September 2017
Accepted 17 September 2017
Available online 20 September 2017

Keywords:
Room temperature ionic liquid
Phenyltrifluoroborate
Fluoroanion
Aromatic structure
Physicochemical properties

ABSTRACT

Novel room temperature ionic liquids (RTILs) were synthesized using phenyltrifluoroborate ($[PhBF_3]^-$), which is the simplest aryltrifluoroborate structure. The $[PhBF_3]^-$-based RTILs showed desirable transport properties, i.e., viscosity and ionic conductivity, and the anion has a rigid and bulky aromatic ring. The properties of 1-butyl-3-methylimidazolium phenyltrifluoroborate ($[C_4mim][PhBF_3]$) are comparable to those of 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$). The molecular volume of the RTILs, which was estimated using the appropriate quantum chemical calculations, highly correlated with the transport properties. The cation volume is an important factor that can control the physicochemical properties in this RTIL system. In addition, the basic skeleton structure of the cation determined the electrochemical window.

1. Introduction

Room temperature ionic liquids (RTILs), liquid salts that contain only a cation and an anion at room temperature, are a subset of molten salts that possess unique features, such as negligible vapor pressures, incombustibility, wide electrochemical windows (EWs), and relatively high ionic conductivities [1,2]. The features of RTILs, except for the handling temperatures, are very similar to those of molten salts, which are very useful anhydrous solvents for high-temperature electrochemical technologies, including the Hall-Héroult process and molten carbonate fuel cell systems. These appealing features are why many different applications have been proposed for RTILs, e.g., next generation energy devices [3–8], recyclable and nonvolatile organic synthesis processes [9,10], high-performance lubricants [11,12], and functional liquid materials for vacuum technologies [13–17]. The number of fundamental science articles related to RTILs has increased in recent years because scientists can readily design and synthesize the ionic species in RTILs but not in conventional solvents. In the past several decades, numerous cations and anions have been used to prepare various functional RTILs. The basic skeletons for typical cations include imidazolium, pyridinium, pyrrolidinium, piperidinium, quaternary ammonium, sulfonium, and phosphonium. Their common side chains include straight alkyl, aminoalkyl, hydroxyalkyl, alkoxyalkyl, and other groups, and $AlCl_4^-$, BF_4^-, PF_6^-, $CF_3SO_3^-$, $N(SO_2CF_3)_2^-$, $N(CN)_2^-$, and $(FH)_nF^-$ ($1 \le n \le 3$) have been widely used as the anion component [18,19]. The physicochemical properties of RTILs strongly depend on the cation and anion species combination [20–26]. For example, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ($[C_4mpyr][N(SO_2CF_3)_2]$) has a viscosity of 76 mPa·s, but when the cation component is changed to 1-ethyl-3-methylimidazolium ($[C_2mim]^+$), the viscosity significantly decreases to 35 mPa·s [27,28]. Changing the anion component also results in changes in the properties of the RTIL. Unfortunately, the design and synthesis of novel anion species is difficult compared to that of the cations that have been synthesized using a simple nucleophilic substitution reaction [29] because the anion synthetic process is not well-established and laborious.

Very recently, we successfully synthesized nearly 40 types of aryltrifluoroborate anions ($[ArBF_3]^-$) and reported the unique physicochemical properties of alkali metal salts with $[ArBF_3]^-$ [30]. Potassium and cesium salts with $[ArBF_3]^-$ can be easily prepared on a large scale using commercially available reagents [31]. $[ArBF_3]^-$ is an analog of tetrafluoroborate ($[BF_4]^-$), which is a typical RTIL anion first reported by Wilkes and Zaworotko [32], and in $[ArBF_3]^-$, one fluorine in $[BF_4]^-$ is replaced with a designable aromatic ring. Because of the ring, organic salts with $[ArBF_3]^-$ are likely to have favorable physicochemical properties because of the decreased interionic interaction energy between the anions and cations due to the lower surface charge density on the anions as a result of adding an electron-withdrawing phenyl group [27,33–

* Corresponding author.
** Correspondence to: Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan.
E-mail addresses: ttsuda@chem.eng.osaka-u.ac.jp (T. Tsuda), kuwabata@chem.eng.osaka-u.ac.jp (S. Kuwabata).

https://doi.org/10.1016/j.molliq.2017.09.067
0167-7322/

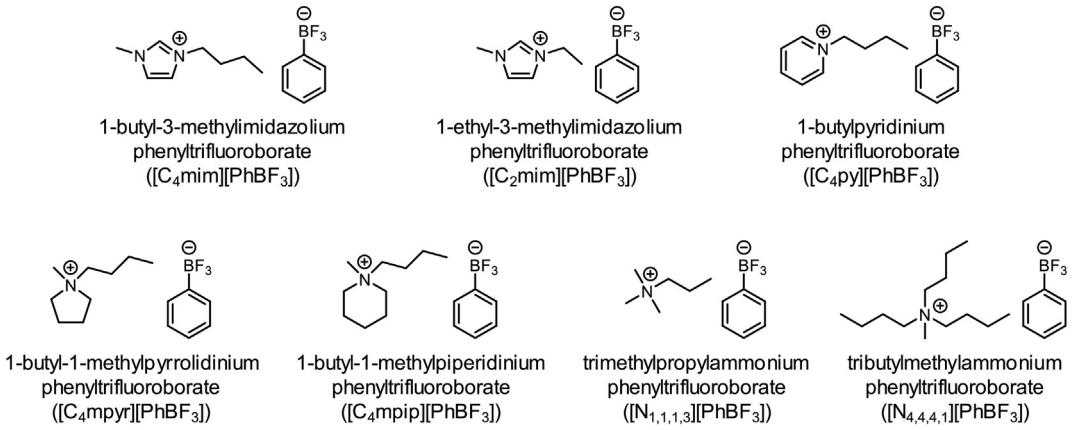

Fig. 1. Chemical structures of $[PhBF_3]^-$-based RTILs with different organic cations and their abbreviations.

40]. In this study, we attempted to produce undiscovered RTILs by combining different onium cations, e.g., imidazolium, pyridinium, pyrrolidinium, piperidinium, and quaternary ammonium, with the phenyltrifluoroborate ($[PhBF_3]^-$) anion, which has the simplest structure among the $[ArBF_3]^-$ anions. The physicochemical properties of the resulting $[PhBF_3]^-$-based salts were examined. The factors controlling their properties were explored via systematic data gathering.

2. Experimental section

Potassium phenyltrifluoroborate ($K[PhBF_3]$) was synthesized using phenylboronic acid ($PhB(OH)_2$) (Wako Pure Chemical Industries, Ltd.), potassium fluoride (KF) (Wako Pure Chemical Industries, Ltd.), and L-tartaric acid (Wako Pure Chemical Industries, Ltd.) in the following procedure [31]. An aqueous solution of KF (200 mmol, 20 mL) was added to a solution of $PhB(OH)_2$ (50 mmol) in acetonitrile (200 mL), and the mixture was stirred for 15 min at ambient temperature. L-Tartaric acid (2.05 equiv.) dissolved in tetrahydrofuran (THF) (100 mL) was slowly added to the mixture, and then, a white by-product immediately precipitated. The reaction mixture was vigorously stirred for 1 h at ambient temperature and filtered to remove the precipitate. The resultant filtrate was concentrated in vacuo, and the crude potassium salt was obtained as a solid. The crude product was purified by recrystallization to obtain pure $K[PhBF_3]$. The obtained salt was dried at 353 K under vacuum for 1 h. The final product was confirmed by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis.

Seven kinds of onium salts, 1-ethyl-3-methylimidazolium chloride ($[C_2mim]Cl$) (Tokyo Chemical Industry Co., Ltd.), 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) (Kanto Chemical Co., Inc.), 1-butylpyridinium chloride ($[C_4py]Cl$) (Tokyo Chemical Industry Co., Ltd.), 1-butyl-1-methylpyrrolidinium chloride ($[C_4mpyr]Cl$) (Sigma-Aldrich, Inc.), 1-butyl-1-methylpiperidinium chloride ($[C_4mpip]Cl$) (Tokyo Chemical Industry Co., Ltd.), trimethylpropylammonium bromide ($[N_{1,1,1,3}]Br$) (Tokyo Chemical Industry Co., Ltd.), and tributylmethylammonium chloride ($[N_{4,4,4,1}]Cl$) (Sigma-Aldrich, Inc.) were used as the cationic species for the preparation of the $[PhBF_3]^-$-based organic salts. $K[PhBF_3]$ was prepared via the previously mentioned protocol and was used as the anion source. The synthesis of the $[PhBF_3]^-$-based organic salts was performed using the metathesis protocol explained below. $K[PhBF_3]$ (40 mmol) was added to a solution of an onium halide (40 mmol) in acetonitrile (60 mL), and the mixture was stirred for 1 h at ambient temperature. After the reaction, the mixture was filtered to remove the precipitated by-product, KCl or KBr, and the filtrate was condensed under vacuum. The crude product was extracted by CH_2Cl_2 and rinsed with ultrapure water several times to remove the unreacted halides and by-product. The organic layer was concentrated in vacuo. The resultant onium phenyltrifluoroborate was dried at 373 K under vacuum for 12 h. The final product was confirmed by NMR spectroscopy, mass spectrometry, and elemental analysis. 1-Butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) was purchased from Kanto Chemical Co. and used for comparison. It was thoroughly vacuum dried for 24 h before use to remove any residual water.

Thermogravimetric (TG) analyses were performed using a Bruker TG-DTA2000SA instrument. Samples were placed on an open aluminum pan and heated from room temperature to 773 K at a rate of 5 $K \cdot min^{-1}$ under flowing dry nitrogen gas. The thermal degradation temperature was determined from the 5 wt% loss point of the TG curve. Differential scanning calorimetry (DSC) was conducted using a Bruker DSC3100SA instrument. The samples were sealed in an aluminum pan with an aluminum top. The sealed pan was heated and cooled at a rate of 5 $K \cdot min^{-1}$. The glass-transition temperature and melting point were obtained from the DSC curve of the second heating process. These values were estimated using the tangential intersection method near the temperature at which a phase transformation occurred. These two instruments were controlled with a Bruker MTC1000SA workstation utilizing the Bruker WS003 software. All the specimens for these measurements were prepared in an argon gas-filled glove box (Vacuum Atmospheres Co., Omni-Lab, O_2 and $H_2O < 1$ ppm).

Density measurements were conducted using a Kyoto Electronics Manufacturing DA-640 resonant frequency oscillation density/specific gravity meter in the range of 298–353 K. The viscosity was measured

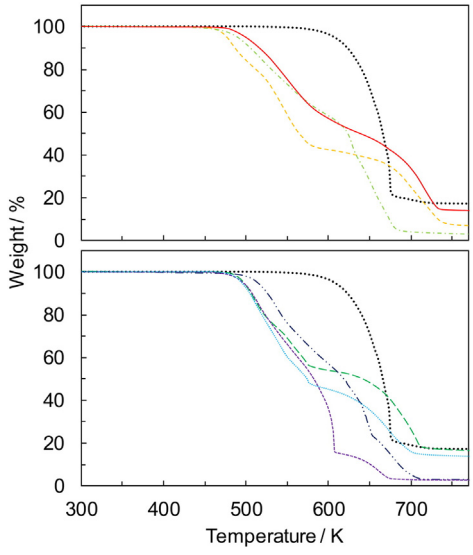

Fig. 2. Results of the TG analysis for (•••) $[C_4mim][BF_4]$, (——) $[C_4mim][PhBF_3]$, (– – –) $[C_2mim][PhBF_3]$, (—·—) $[C_4py][PhBF_3]$, (— —) $[C_4mpyr][PhBF_3]$, (—··—) $[C_4mpip][PhBF_3]$, (····) $[N_{1,1,1,3}][PhBF_3]$, and (- - -) $[N_{4,4,4,1}][PhBF_3]$. The measurements were conducted at a rate of 5 $K \cdot min^{-1}$.