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Short communication

Physical and electrochemical properties of phosphonium ionic liquids derived from trimethylphosphine

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ABSTRACT

Room-temperature ionic liquids based on phosphonium cations derived from trimethylphosphine are presented. The bis(fluorosulfonyl)amide-based ionic liquids showed relatively low melting point, low viscosity and high conductivity when compared to those of the corresponding bis(trifluoromethylsulfonyl)amide-based ionic liquids. The bis(trifluoromethylsulfonyl)amide-based ionic liquids were thermally stable up to at least 380 °C. The voltammetric analysis suggested that the ionic liquids exhibited high electrochemical stability. The bis(fluorosulfonyl)amide-based ionic liquids showed larger redox response of lithium than the bis(trifluoromethylsulfonyl)amide-based ionic liquids.

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1. Introduction

Room-temperature ionic liquids (RTILs) are low-melting organic compounds that are composed entirely of ions. RTILs have numbers of unique physicochemical properties, so that they have been studied for electrolytic media in various electrochemical systems [1]. The common RTILs are often based on nitrogen-based cations; however, phosphonium cation based RTILs have been recently receiving a great deal of attention as potential substitutes for ammonium counterparts [2,3]. The pioneering report by Bradaric et al. describes the preparation and properties of RTILs based on trihexyl(tetradecyl)phosphonium cation ($P_{666(14)}^{+}$) [2]. Compton and coworkers have published the electrochemical studies on redox behaviors of oxygen and hydrogen using the $P_{666(14)}$-based RTILs [4–6].

In general, lowering viscosity of RTILs is a major requirement for electrochemical applications because viscosity influences mass transport processes. The traditional phosphonium RTILs tend to have high viscosity due to their large cation sizes, so that efforts to obtain low viscosity phosphonium RTILs have been continued. For example, we have designed phosphonium RTILs derived from triethylphosphine [7]. Armel et al. have reported a low viscosity RTIL based on an asymmetric diethylmethyl(isobutyl)phosphonium cation as a dye-sensitized solar cell electrolyte [8]. Shirota et al. have designed a phosphonium cation containing a (2-ethoxyethoxy)ethyl group [9]. On the other hand, phosphonium cations derived from trimethylphosphine (TMP) have been rarely examined, despite that TMP should give the smallest phosphonium cations to form considerably low viscosity RTILs. However, to our knowledge, only trimethylhexylphosphonium cation has been reported by Matsumoto et al. [10]. In this communication, we propose a new class of low viscosity RTILs containing TMP-based phosphonium cations (P_{111x}^{+}) in combination with bis(fluorosulfonyl)amide (FSA^{-}) and bis(trifluoromethylsulfonyl)amide ($TFSA^{-}$) anions. We demonstrate here the following cation components: trimethylpropylphosphonium (P_{1113}^{+}), trimethyl(methoxymethyl)phosphonium ($P_{111(1O1)}^{+}$) and allyltrimethylphosphonium ($P_{111(Al)}^{+}$) cations.

2. Experimental

The phosphonium RTILs were prepared according to previously published papers [7]. The synthesis of precursor halides was performed by nucleophilic additions of TMP (Aldrich, 1.0 mol dm^{-3} toluene solution) to bromoalkanes (Tokyo Chemical Industry Co., Ltd.) in toluene at room temperature under nitrogen atmosphere. Despite the fact that TMP is significantly pyrophoric, the nucleophilic additions were controlled safely in diluted conditions. The aqueous ion exchange reaction of the halides with potassium FSA (Mitsubishi Materials Electronic Chemicals Co., Ltd.) or lithium TFSA (Kanto Chemical Co., Inc.) was carried out to give phosphonium FSA or TFSA salts. The resulting crude salts were extracted by dichloromethane, and then purified by washing with pure water until no residual bromide anion was detected with the use of $AgNO_3$. The products obtained were confirmed by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMRs. All RTILs were dried under high vacuum for at least 12 h at 80 °C before use. The water contents, which were measured by using a Karl Fischer moisture titrator (Mitsubishi Chemical Analytech Co., Ltd., CA-200), were less than 50 ppm.

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The melting points were estimated by a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a cooling and heating rate of 1 °C min^{-1}. The measurement of densities was carried out using a density/specific gravity meter (Kyoto Electronics Manufacturing Co., Ltd., DA-130N). The viscosities and conductivities were measured by a cone-plate type viscometer (Brookfield LVDV-II+ Pro) and an *ac* impedance analyzer (Ando Electric Co., Ltd., AG-4311 LCR Meter), respectively. The thermal decomposition temperatures were recorded by a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA6300) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

The voltammetric measurements were carried out by an automatic polarization system (Hokuto Denko Co., Ltd., HZ-5000) using a three-electrode cell in an argon-filled grove box at room temperature. A glassy carbon disk electrode (BAS Inc., surface area: 0.008 cm^2) and a Ni disk electrode (BAS Inc., surface area: 0.018 cm^2) were used as working electrodes. These surfaces were polished with diamond (d = 1 μm) and alumina paste (d = 0.05 μm), respectively. A Pt wire was mounted as an auxiliary electrode. A Ag wire immersed in 0.1 mol dm^{-3} $AgSO_3CF_3$/EMI-TFSA solution (EMI: 1-ethyl-3-methylimidazolium) with a Vycor® glass separator was employed as a Ag/Ag^+ reference electrode. The potential was calibrated using a ferrocene (Fc)/ferrocenium (Fc^+) redox couple. The electrolytes for the lithium deposition/dissolution were prepared by adding Li-TFSA (Kishida Chemical Co., Ltd.) into each IL to make the Li content a 0.5 mol kg^{-1}. A Li metal was used as a Li/Li^+ reference electrode for the voltammetric measurement.

3. Results and discussion

Table 1 summarizes the physicochemical properties of P_{111x}-based RTILs. All FSA-based phosphonium compounds were liquids at room temperature. On the other hand, only $P_{111(1O1)}$-TFSA was a liquid, and the other two TFSA-based compounds were crystalline solids at room temperature, which suggests that the combination of P_{111x}-based cations and the FSA anion tend to form lower melting salts.

Table 1 contains the values of density and molar volume of the RTILs. The molar volume was calculated according to the following equation:

$$V_m = M/(Nd) \tag{1}$$

where M is the molar mass, d is the density, and N is the Avogadro's constant. It was found that the densities of FSA-based RTILs were relatively low when compared to that of $P_{111(1O1)}$-TFSA. The molar volumes of FSA-based RTILs exhibited approximately similar values. In addition, these molar volumes were relatively low when compared to those of triethylphosphine-based RTILs such as triethylbutylphosphonium and triethyl(methoxymethyl)phosphonium FSA (0.469 and 0.432 nm^3, respectively) [11]. This result indicates that the sizes of P_{111x}-based cations are smaller than those of triethylphosphine-based cations.

Table 1
Physicochemical properties of various P_{111x}-based compounds.

Compound	FW[a]	T_m[b] /°C	d[c] /g cm^{-3}	V_m[d] /nm^3	η[e] /mPa s	σ[f] /mS cm^{-1}	T_{dec}[g] /°C
P_{1113}-FSA	299.30	0	1.33	0.37	31	7.1	298
P_{1113}-TFSA	399.31	40	–	–	–	–	414
$P_{111(1O1)}$-FSA	301.27	−6	1.39	0.36	21	8.9	262
$P_{111(1O1)}$-TFSA	401.28	13	1.45	0.46	43	4.1	379
$P_{111(Al)}$-FSA	297.28	−5	1.36	0.36	28	7.8	259
$P_{111(Al)}$-TFSA	397.30	–[h]	–	–	–	–	422

[a] Formula weight.
[b] Melting point as the peak temperature calculated from the DSC thermogram.
[c] Density at 25 °C.
[d] Molecular volume at 25 °C.
[e] Viscosity at 25 °C.
[f] Conductivity at 25 °C.
[g] Thermal decomposition temperature (10% weight loss).
[h] Not measured (solid at 25 °C).

Fig. 1 represents the Arrhenius plots for the transport property of the RTILs at various temperatures, and the data at 25 °C are listed in Table 1. Each plot showed a Vogel–Tammann–Fulcher (VTF)-type ionic conduction behavior. The plots for viscosity and conductivity can be fitted in the VTF equations as expressed below [12]:

$$\ln\eta = \frac{k_\eta}{T-T_0} + \frac{1}{2}\ln T - \ln A_\eta \tag{2}$$

$$\ln\sigma = -\frac{k_\sigma}{T-T_0} - \frac{1}{2}\ln T + \ln A_\sigma \tag{3}$$

where k_η and k_σ are the constants related to Arrhenius activation energy for viscosity and conductivity, respectively, A_η and A_σ are the scaling factors for viscosity and conductivity, respectively, and T_0 is an ideal glass transition temperature. The fitted parameters and the correlation coefficients (|R|) are summarized in Table 2. It was obvious that the FSA-based RTILs were less viscous than the corresponding TFSA-based RTILs at various temperatures. It is worthwhile to note that $P_{111(1O1)}$-FSA exhibited the lowest viscosity (21 mPa s at 25 °C) in the P_{111x}-based RTILs not only because of the combination with FSA anion but also because introduction of a methoxy group into the phosphonium cation might lead to a decrease in the positive charge, thereby drastically reducing the viscosity. In the case of $P_{111(Al)}$-FSA, similar reducing effect of the viscosity by an allyl group was observed, which resembles our published results demonstrating

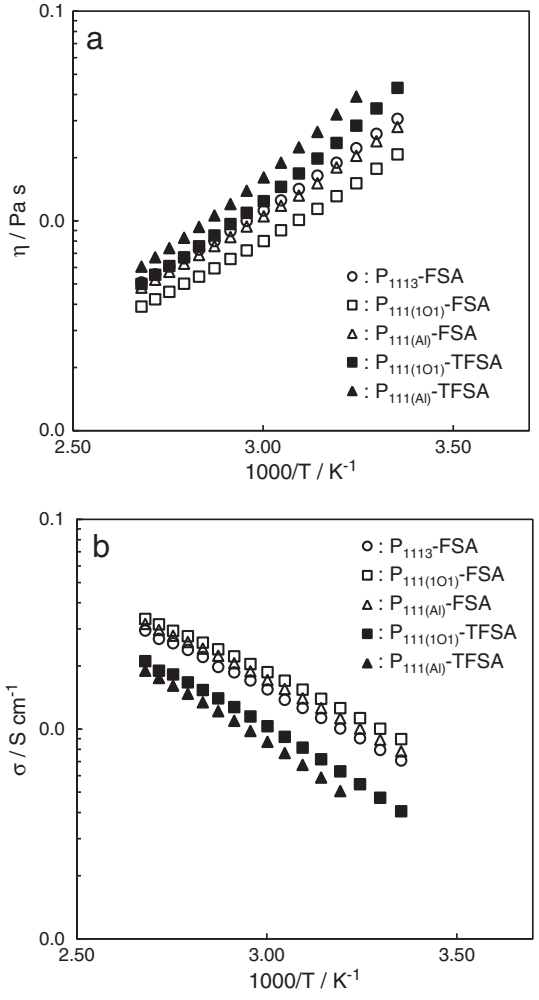

Fig. 1. Arrhenius plots of (a) viscosity and (b) conductivity for various P_{111x}-based RTILs.

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