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Physical and electrochemical characterization of ionic liquids based on quaternary phosphonium cations containing a carbon–carbon double bond

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ABSTRACT

Physical and electrochemical characterizations of novel two ionic liquids based on quaternary phosphonium cations containing an unsaturated carbon–carbon bond (triethyl(4-pentenyl)phosphonium and allyltributylphosphonium cations) are presented in this report. It was found that both unsaturated phosphonium cations gave low-melting salts in combination with a bis(trifluoromethylsulfonyl)amide anion. The thermogravimetric analysis suggested that the unsaturated phosphonium ionic liquids showed higher thermal stability than those of the corresponding saturated phosphonium ILs. The unsaturated phosphonium ionic liquids also exhibited relatively low viscosity and high conductivities when compared to those of the corresponding saturated phosphonium ionic liquids. These results indicate an improving effect of introducing a carbon–carbon double bond into the phosphonium cations on both the thermal stability and the transport property. The voltammetric measurements suggested that the triethyl(4-pentenyl)phosphonium-based ionic liquid showed a high cathodic stability, enabling the deposition and dissolution of metallic lithium in the phosphonium ionic liquid system.

1. Introduction

Ionic liquids (ILs), i.e. organic molten salts with melting points below 100 °C, have been intensively developed for electrolytic media in various electrochemical systems due to the fact that ILs have unique physicochemical properties such as favorable solubility of organic and inorganic compounds, relatively high ionic conductivity, no measurable vapor pressure, high thermal stability, low flammability, etc. [1,2]. Another remarkable advantage of ILs is a designability of ion structures. In order to improve a particular property of ILs, the purposive design of ion structures by introducing a functional group has been attempted. For instance, introduction of unsaturated alkyl chains into the cations should give special physical and electrochemical properties arising from the unsaturated carbon–carbon bonds. From this point of view, Mizumo et al. have reported a novel class of ILs based on imidazolium cations containing an allyl group, showing an improving effect of introducing the allyl group on the transport property [3]. Grätzel et al. have applied allyl-functionalized imidazolium ILs to electrolytic media for dye-sensitized solar cells [4]. Some ILs based on an allyltrimethylammonium cation and their physicochemical properties compared with the unsubstituted ammonium ILs have also been investigated by Matsumoto et al. [5,6].

On the other hand, quaternary phosphonium based ILs have been receiving a great deal of attention as potential substitutes for the corresponding ammonium counterparts [7]. In the pioneering study by Bradaric et al., the chemical and thermal properties of the ILs based on trihexyl(tetradecyl)phosphonium cation $(C_6H_{13})_3C_{14}H_{29}P^+$ with various anions were reported from synthetic and industrial aspects [8]. Furthermore, many phosphonium ILs containing various functionalized anions have been synthesized [9–11]. We also have developed a series of ILs based on relatively small phosphonium cations derived from triethylphosphine $(C_2H_5)_3P$ and tributylphosphine $(C_4H_9)_3P$ together with a bis(trifluoromethylsulfonyl)amide (TFSA) anion in order to obtain relatively low-viscous phosphonium ILs as potential electrolytes for various electrochemical systems [12,13]. It was found that the phosphonium ILs exhibited lower viscosities, higher conductivities and thermal stabilities than those of the corresponding ammonium ILs. This characteristic feature seems to be a considerable advantage of phosphonium ILs, so that the properties of phosphonium ILs functionalized by introducing unsaturated alkyl chains are of particular interest. However, to the best of our knowledge, there has been no report on ILs containing the unsaturated phosphonium cations, except benzyl-substituted phosphonium ILs we have ever examined [14].

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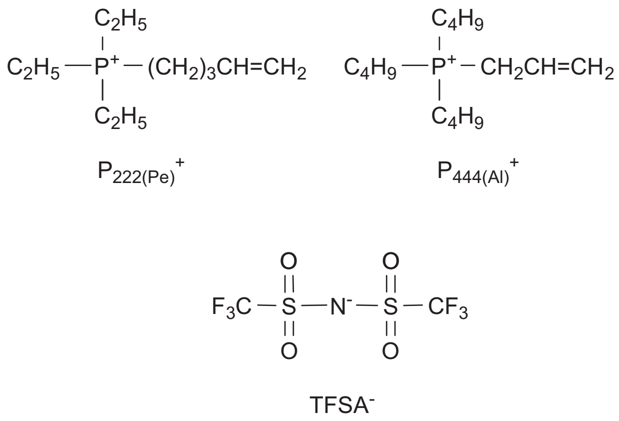

Fig. 1. Structural illustration of ionic components of ILs investigated in this work.

In this paper, we report the physicochemical characterizations of ILs based on quaternary phosphonium cations containing unsaturated alkyl chains. As shown in Fig. 1, the phosphonium cations investigated were derived from triethylphosphine and tributylphosphine: triethyl(4-pentenyl)phosphonium ($P_{222(Pe)}^{+}$) and allyltributylphosphonium ($P_{444(Al)}^{+}$) cations, respectively. The TFSA anion was employed as an anionic component since it is well known to form hydrophobic, low-melting and thermally stable salts together with various cations. This paper describes the effects of introducing unsaturated alkyl chains into the phosphonium cations on the physical, electrochemical and thermal properties of the phosphonium ILs.

2. Experimental

2.1. Praparation

The preparation of the phosphonium ILs was carried out according to the procedure described elsewhere [12,13]. Triethyl(4-pentenyl)phosphonium bromide was synthesized by the nucleophilic addition of triethylphosphine (Nippon Chemical Industrial Co., Ltd., 20% toluene solution, trade name Hishicolin® P-2) to 5-bromopentene (Tokyo Chemical Industry Co., Ltd.) at 80 °C under nitrogen atmosphere. Allyltributylphosphonium bromide was used as supplied by Nippon Chemical Industrial Co., Ltd. (trade name Hishicolin® PX-4ALB). The aqueous ion exchange reactions of these phosphonium bromides with Li–TFSA (Kanto Chemical Co., Inc.) were carried out at ambient temperature to obtain the corresponding TFSA salts. The resulting crude compounds were extracted by dichloromethane, and then purified by washing with pure water several times until no residual bromide anion was detected with the use of $AgNO_3$. All the compounds were dried under high vacuum for at least 8 h at 120 °C and were stored in an argon atmosphere glove box. The water content in each compound, which was measured by using a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing Co., Ltd., MKC-610), was less than 50 ppm. The products obtained were confirmed by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMRs. The residual contents of bromide anion (<50 ppm) and lithium cation (<5 ppm) were checked by an ion chromatography and an inductively coupled plasma spectrometer (Varian, ICP-AES Liberty LR Sequential), respectively.

2.2. Measurements of physicochemical properties

The melting point of each IL was analyzed by using a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a cooling and heating rate of 3 °C min^{-1}. The density of each IL was determined by gravimetric analysis using a calibrated pipette at 25 °C. The viscosity of each IL was measured by using a vibration type viscometer (CBC Materials Co. Ltd., VM-10A Laboratory Viscometer calibrated with the Brookfield Viscosity Standard) under argon atmosphere at 25 °C. The measurement of conductivity (Ivium Technologies, CompactStat, using an ac impedance mode) was carried out using a two Pt-electrode cell (cell constant: 1.27 cm^{-1}) under argon atmosphere at various temperatures. The thermogravimetric trace of each IL was recorded by using a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA6300) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Table 1
Thermal properties of unsaturated and the corresponding saturated phosphonium ILs.

Ionic liquid	FW[a]	T_m [b]/°C	T_{dec} [c]/°C	Ref.
$P_{2225(Pe)}$–TFSA	467.43	12	424	This work
P_{2225}–TFSA	469.44	17	380	[12]
$P_{444(Al)}$–TFSA	523.57	29	419	This work
P_{4441}–TFSA	497.50	16	379	[13]
P_{4443}–TFSA	525.55	65	–	[15]

[a] Formula weight.
[b] Melting point.
[c] Thermal decomposition temperature (10% weight loss).

2.3. Voltammetric measurement

The voltammetric measurements were carried out using a conventional three-electrode cell configuration under argon atmosphere at 25 °C. The electrode potential was controlled by an automatic polarization system (Hokuto Denko Co., Ltd., HZ-5000). 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. The glassy carbon and Ni electrodes were polished with diamond paste ($d = 1$ μm) and alumina paste ($d = 0.05$ μm), respectively, and then dried *in vacuo* before voltammetric measurements. A Pt wire was mounted in the cell as an auxiliary electrode. An 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 an Ag/Ag^{+} reference electrode. The potential was calibrated using a ferrocene (Fc)/ferrocenium (Fc^{+}) redox couple. The electrolytes used for the lithium deposition/dissolution measurements were prepared by adding Li–TFSA (Kishida Chemical Co., Ltd.) into each IL to make the Li content a 0.8 mol dm^{-3}, and then dried under high vacuum at 120 °C before use (residual water content: <50 ppm).

3. Results and discussion

3.1. Thermal property

The data of melting point (T_m) and thermal decomposition temperature (T_{dec}) of $P_{222(Pe)}$–TFSA, $P_{444(Al)}$–TFSA and the corresponding saturated phosphonium ILs were listed in Table 1. $P_{222(Pe)}$–TFSA was a liquid at room temperature (the so-called room temperature ionic liquid, RTIL), showing a T_m at 12 °C. This T_m was lower than that of the corresponding saturated phosphonium IL (P_{2225}–TFSA, T_m: 17 °C). Although the T_m of $P_{444(Al)}$–TFSA was somewhat high (29 °C), $P_{444(Al)}$–TFSA was also lower melting than the corresponding saturated phosphonium IL (P_{4443}–TFSA, T_m: 65 °C). This finding indicates that introduction of a carbon–carbon double bond into the alkyl chain of phosphonium cations gives relatively low-melting ILs, which is closely similar to the low-melting effect observed in several imidazolium IL systems reported by Mizumo et al. [3].