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Physical and electrochemical properties of room-temperature dicyanamide ionic liquids based on quaternary phosphonium cations

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ABSTRACT

The physicochemical and electrochemical properties of room temperature ionic liquids based on quaternary phosphonium cations together with a dicyanamide anion are presented in this report. The most dicyanamide-based phosphonium ionic liquids prepared were hydrophilic, except ionic liquids containing a long alkyl chain in the phosohonium cation. It was found that asymmetric phosphonium cations gave low-melting salts in combination with a dicyanamide anion. The dicyanamide-based phosphonium ionic liquids exhibited relatively low viscosities and high conductivities when compared to those of the corresponding ammonium ionic liquids. Particularly, the ionic liquids containing a methoxy group in the phosphonium cations indicated very low viscosities. Comparatively good electrochemical stability of the dicyanamide-based phosphonium ionic liquids was confirmed by voltammetric measurements. The thermogravimetric analysis suggested that the dicyanamide-based phosphonium ionic liquids showed higher thermal stability than those of the corresponding ammonium ionic liquids, indicating an improving effect of the phosphonium cations on the thermal stability.

1. Introduction

Room temperature ionic liquids (RTILs) have been developed for a wide variety of electrochemical applications due to their unique physicochemical properties such as favorable solubility of organic and inorganic compounds, relatively high ionic conductivity, very low volatility, high thermal stability, low flammability, *etc.* [1,2]. Another remarkable advantage of RTILs is a designability of cations and anions. Particularly, the selection of anions offers a significant change in the physicochemical properties of RTILs. Although many anions are employed for RTILs, interests in RTILs based on a dicyanamide (DCA) anion ($N(CN)_2{}^-$) have been increasing for their unique physicochemical properties. In the pioneering study published by MacFarlane et al., it is suggested that the DCA anion gives hydrophilic and low-viscous RTILs in combination with imidazolium, quaternary ammonium and pyrrolidinium cations [3,4]. Yoshida et al. have physicochemically characterized a variety of DCA-based RTILs consisted of imidazolium and the related cations [5,6]. The very low-viscous RTILs based on the DCA anion and trialkylsulfonium cations have also been reported by Wasserscheid and coworkers [7].

One of the most promising electrochemical applications of DCA-based RTILs is thought to be electrolytic media for dye-sensitized solar cells [8,9]. However, it is also known that thermal stability of the DCA-based RTILs tends to be low [10,11], so that this feature may restrict the application to dye-sensitized solar cells. On the other hand, RTILs based on quaternary phosphonium cations have been receiving a great deal of attention as potential substitutes of the corresponding ammonium counterparts due to the fact that phosphonium RTILs offer chemical and thermal stabilities as practical advantages [12,13]. We have found that bis(trifluoromethylsulfonyl)amide (TFSA) anion based phosphonium RTILs derived from triethylphosphine (TEP) and tributylphosphine (TBP) significantly exhibited relatively high thermal stability when compared to that of the corresponding ammonium RTILs [14,15]. Therefore, the thermal property of DCA-based RTILs containing the quaternary phosphonium cations is of particular interest from the viewpoint of improvement of the thermal stability. However, to the best of our knowledge, DCA-based phosphonium RTILs have been rarely investigated except trihexyl(tetradecyl)phosphonium dicyanamide [12].

Here we report the physicochemical and thermal characterizations of RTILs based on quaternary phosphonium cations in combination with the DCA anion. As shown in Fig. 1, the cations investigated are derived from TEP and TBP. This paper describes the improving effect of the phosphonium cations in the DCA-based

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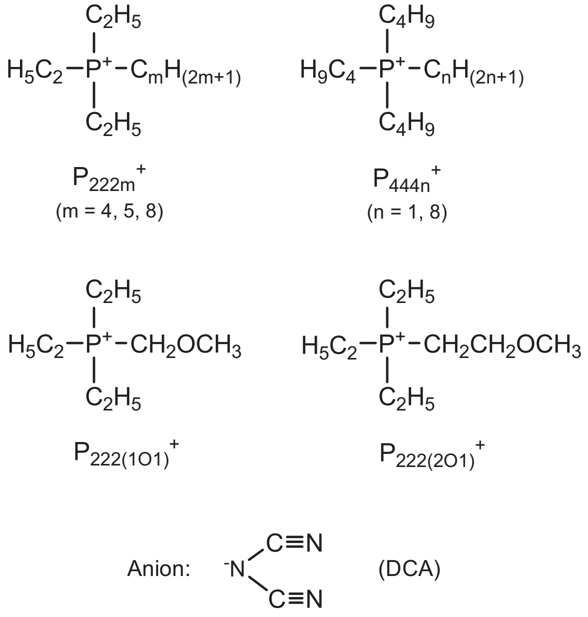

Fig. 1. Schematic illustration of DCA-based phosphonium RTILs investigated in this work.

RTILs on the physicochemical and thermal properties of the phosphonium RTILs.

2. Experimental

2.1. Preparation

The preparation of DCA-based phosphonium RTILs was performed according to the procedure described in the literature [9]. The precursor phosphonium halides were synthesized by the nucleophilic addition of TEP (Nippon Chemical Industrial Co., Ltd., 20% toluene solution, trade name Hishicolin P-2) or TBP (Nippon Chemical Industrial Co., Ltd., trade name Hishicolin P-4) to the corresponding bromoalkanes (Tokyo Chemical Industry Co., Ltd.) at 80 °C under nitrogen atmosphere. The phosphonium halides obtained were white crystalline solids. The aqueous ion exchange reaction of the phosphonium bromides with Na-DCA (Aldrich) was carried out at ambient temperature to give quaternary phosphonium DCA salts. The resulting crude RTILs were extracted by dichloromethane and the dichloromethane solutions containing the RTILs were passed through a silica gel column using dichloromethane as an eluent to remove the ionic impurities. After evaporation of the solvent, all the RTILs were dried under high vacuum for at least 8 h at 100 °C and were stored in an argon atmosphere glove box. The isolated yields based on the precursor halides were in the range between 40 and 60%. The RTILs obtained were pale yellow transparent liquids. The water content in the RTILs thus prepared was less than 100 ppm. The products obtained were confirmed by ^{1}H, ^{13}C and ^{31}P NMRs. The residual contents of sodium cation (<10 ppm) were checked by an inductively coupled plasma spectrometer (Varian, ICP-AES Liberty LR Sequential). The corresponding ammonium RTILs were prepared by the same procedure as the phosphonium RTILs.

2.2. Measurements of physicochemical properties

The melting point of each RTIL was analyzed by using a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a cooling and heating rate of 1 °C min^{-1}. The density of each RTIL was determined by gravimetric analysis using a calibrated pipette at 25 °C. The measurements of viscosity (CBC Materials Co. Ltd., VM-10A Laboratory Viscometer calibrated with the Brookfield Viscosity Standard) and conductivity (Ivumu Technologies, CompactStat, ac impedance mode) were carried out under argon atmosphere at 25 °C. The thermogravimetric trace of each RTIL was recorded by using a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA6300) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

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 Pt disk electrode (BAS Inc., surface area: 0.020 cm^2) was used as a working electrode. The Pt electrode was polished with alumina paste (d = 0.05 μm), 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.

3. Results and discussion

3.1. Physicochemical properties

All of the DCA-based phosphonium RTILs shown in Fig. 1 were successfully prepared by the synthetic method in this work. The miscibility of the phosphonium RTILs was similar to those of the typical hydrophilic RTILs; most of the phosphonium RTILs were miscible in water, methanol, acetone, acetonitrile and dichloromethane, and were immiscible in toluene and *n*-hexane. Exceptionally, P_{4448}-DCA was miscible in toluene, which means that the hydrophobicity is increased due to its relatively long alkyl chains.

The physicochemical properties of DCA-based phosphonium and the corresponding ammonium RTILs are summarized in Table 1. The phosphonium RTILs tended to be relatively low-melting when compared to the corresponding TFSA-based RTILs. For example, the melting points (T_m) of P_{2225}-DCA and P_{4441}-DCA (−12 and 6 °C, respectively) were lower than those of P_{2225}-TFSA and P_{4441}-TFSA (17 and 16 °C, respectively) [14,15]. Even T_m of P_{2224}-DCA was 5 °C, despite the fact that the corresponding TFSA-based RTIL (P_{2224}-TFSA) is a solid at room temperature (T_m: 55 °C) [14].

As shown in Table 1, the viscosity of the phosphonium RTILs was significantly decreased with decreasing the cation size. This seems to be attributed to decrease in the Stokes radii of the phosphonium cations. The P_{2224} cation is the smallest in phosphonium cations containing side chains without heteroatoms, so that P_{2224}-DCA shows relatively low viscosity (60 mPa s at 25 °C). Further low viscosities were observed in $P_{222(1O1)}$-DCA and $P_{222(2O1)}$-DCA (29 and 39 mPa s at 25 °C, respectively), which indicates that introducing a methoxy group into the phosphonium cations drastically reduce their viscosities. Especially, $P_{222(1O1)}$-DCA exhibited very low viscosity when compared to not only the corresponding ammonium IL having a methoxymethyl group, $N_{222(1O1)}$-DCA (42 mPa s at 25 °C), but also the corresponding TFSA-based phosphonium IL, $P_{222(1O1)}$-TFSA (35 mPa s at 25 °C [14]).

In the case of TFSA-based RTILs, it has been generally accepted that the effect is due to an electron donation from the methoxy group into the cation center to decrease the positive charge of the cation [16]. Hence, an electrostatic interaction between the cation and the anion is weakened, which results in reducing both the vis-

Table 1
Physicochemical properties of DCA-based phosphonium and the corresponding ammonium RTILs.

Ionic liquid	FW[a]	T_m[b]/°C	d[c]/g cm^{-3}	η[d]/mPas	σ[e]/mS cm^{-1}	T_{dec}[f]/°C
P_{2224}-DCA	241.31	5	1.00	60	5.7	394
P_{2225}-DCA	255.34	−12	0.99	72	4.0	393
P_{2228}-DCA	297.42	<−50	0.97	104	2.0	394
$P_{222(101)}$-DCA	229.26	−11	1.06	29	12.8	278
$P_{222(201)}$-DCA	243.29	<−50	1.05	39	8.2	244
P_{4441}-DCA	283.39	6	0.96	167	1.2	387
P_{4448}-DCA	381.58	<−50	0.95	245	0.45	389
N_{2225}-DCA	238.37	−7	0.99	121	2.8	270
N_{2228}-DCA	280.45	<−50	0.99	241	1.0	271
$N_{222(101)}$-DCA	212.29	<−50	1.05	42	8.2	154
N_{4441}-DCA	266.43	12	0.98	410	0.57	260

[a] Formula weight.
[b] Melting point.
[c] Density at 25 °C.
[d] Viscosity at 25 °C.
[e] Conductivity at 25 °C.
[f] Thermal decomposition temperature (10% weight loss).

cosity and the melting point of the RTILs. It seems reasonable to give similar explanations to the DCA-based phosphonium RTILs. Furthermore, as shown in Table 1, it is obvious that DCA-based phosphonium RTILs were less viscous and more conductive than those of the corresponding ammonium RTILs. Similar results have been reported in a previously published paper describing transport property data of TFSA-based phosphonium RTILs [14].

In order to discuss the correlation between viscosity and conductivity, the plot of the molar conductivity Λ against the inverse viscosity η^{-1} (the so-called Walden plot [17,18]) for DCA-based phosphonium and the corresponding ammonium RTILs is depicted in Fig. 2. All the points were positioned below the ideal Walden line as in the case of typical RTILs. In the case of relatively low-viscous RTILs such as $P_{222(101)}$-DCA, $P_{222(201)}$-DCA and P_{2224}-DCA, there seems to be no essential difference in the deviation of the points from the ideal Walden line. However, the points of the phosphonium RTILs having long alkyl chains (e.g., P_{2228}-DCA, P_{4441}-DCA and P_{4448}-DCA) tended to be slightly deviated from those of the corresponding ammonium RTILs. According to the general interpretation of the Walden plot, the deviation from the ideal line indicates a lack of complete ion dissociation of the salt [19,20]. Therefore, the result in Fig. 2 suggests slightly high degree of association between the phosphonium cations and the DCA anion.

One of the differences between phosphonium and the corresponding ammonium cations is a presence of empty *d*-orbitals in the phosphorus atom. It has been reported and generally accepted that quaternary phosphonium compounds are more covalent in nature than corresponding ammonium compounds due to empty *d*-orbitals in the phosphorus atom [21,22]. This allows us to infer that the empty *d*-orbitals in the phosphonium cations might more or less interact with the counteranions, leading to reduce the charges of cations and anions, in other words, to weaken the electrostatic force between cations and anions. Although the improving effect of the transport property by phosphonium cations is not sufficiently clarified at present, such an interaction seems likely to afford a decrease in the viscosity.

3.2. Electrochemical stability

Fig. 3 illustrates the linear sweep voltammograms measured in the neat DCA-based RTILs at a Pt electrode. The shapes of the voltammograms thus observed closely resemble those of the imidazolium based DCA-ILs reported by Yoshida et al. [6]. Slight oxidation currents were observed around +1.0 V vs. Ag/Ag$^+$, which might be due to the electrochemical oxidation of trace amount of impurities. It is noted that RTILs based on methoxy-substituted phosphonium

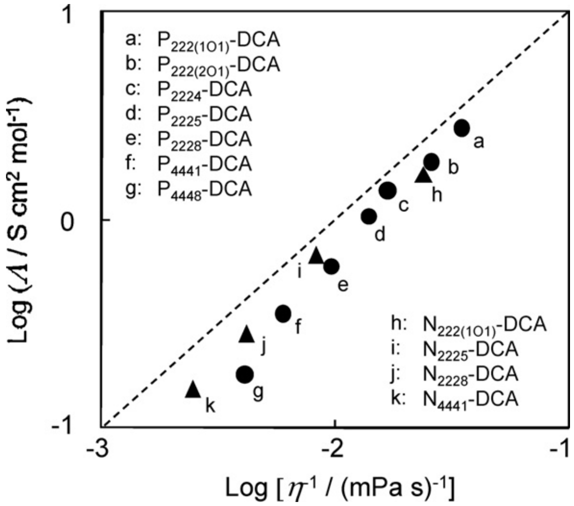

Fig. 2. Plots of the molar conductivity against the inverse viscosity for DCA-based phosphonium and the corresponding ammonium RTILs. The dotted line indicates the ideal Walden line (dilute aqueous KCl solution).

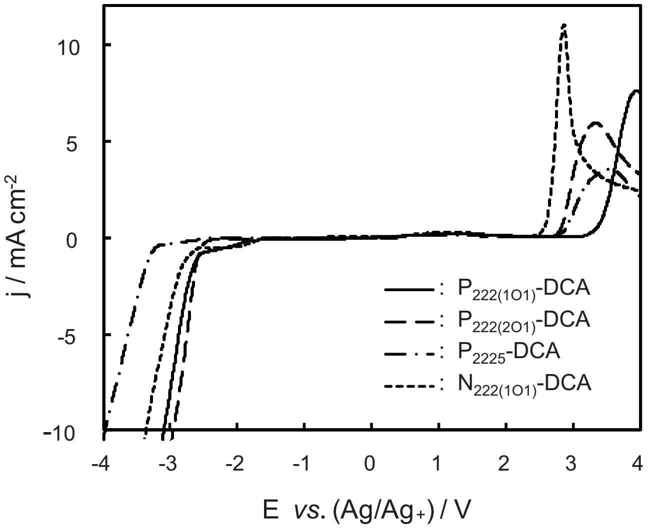

Fig. 3. Linear sweep voltammograms for neat DCA-based phosphonium and the corresponding ammonium RTILs at a Pt electrode with a 5 mV s^{-1} potential sweep rate.

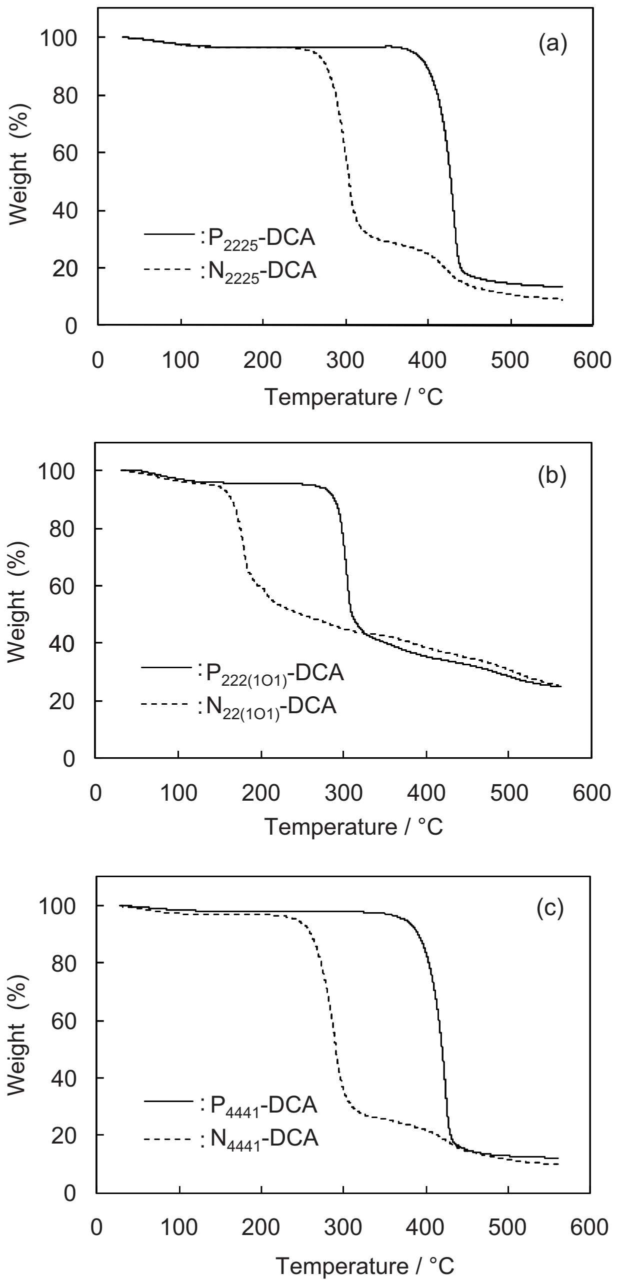

Fig. 4. Thermogravimetric traces for DCA-based phosphonium (solid line) and the corresponding ammonium (dotted line) RTILs: (a) P_{2225}-DCA and N_{2225}-DCA, (b) $P_{222(1O1)}$-DCA and $N_{222(1O1)}$-DCA, (c) P_{4441}-DCA and N_{4441}-DCA.

cations, *i.e.* $P_{222(1O1)}$-DCA and $P_{222(2O1)}$-DCA, reduced their cathodic stabilities, which is a similar tendency observed in the TFSA-based phosphonium systems [14]. On the other hand, the anodic limits of the DCA-based phosphonium RTILs were somewhat shifted to positive potentials when compared to the corresponding ammonium RTIL ($N_{222(1O1)}$-DCA), indicating the anodic stability improved by the phosphonium cation system. As a result, it was found that each DCA-based phosphonium RTIL seems to be electrochemically stable in a potential range between approximately −2.5 and +2.5 V vs. Ag/Ag^+. This fact suggests that the DCA-based phosphonium RTILs can be used as dye-sensitized solar cell electrolytes since the electrochemical windows cover the redox potentials of the iodide–triiodide mediator system employed in the electrolytic media (ca. 0.3 V vs. NHE in acetonitrile [23]).

3.3. Thermal stability

Thermal stability is of practical importance for various electrochemical applications. Fig. 4 shows the thermogravimetric traces of several DCA-based phosphonium and the corresponding ammonium RTILs. Additionally, the onset thermal decomposition temperatures (T_{dec}) at 10% weight loss are listed in Table 1. It was clearly found that the T_{dec} of the phosphonium RTILs were considerably high when compared to those of the corresponding ammonium RTILs. In each case, the drastic increase in the thermal stability was observed (ca. 120 °C). It should also be noted that the phosphonium RTILs having no methoxyalkyl group (P_{2224}-DCA, P_{2225}-DCA, P_{2228}-DCA, P_{4441}-DCA and P_{4448}-DCA) were stable up to nearly 400 °C, indicating the high thermal stability comparable with those of the TFSA-based phosphonium RTILs [14,15]. These results reveal that the phosphonium cations favorably improve the thermal stability of DCA-based RTILs. At present, the detailed thermal decomposition mechanism for the phosphonium RTILs remains unclear; however, the presence of empty *d*-orbitals might play an essential role in a significant increase in the bond strength, thereby resulting in the high thermal stability.

4. Conclusions

New DCA-based RTILs based on quaternary phosphonium cations were physically and thermally characterized. The phosphonium RTILs showed relatively low viscosities and high conductivities when compared to the corresponding ammonium RTILs. It was found that voltammetric measurements indicated the comparatively good electrochemical stability of the phosphonium RTILs. The excellent thermal stability of the phosphonium RTILs was also confirmed by the thermogravimetric analysis. These findings allow us to suggest that low-viscous and thermally stable DCA-based phosphonium RTILs can be good candidates for electrolytic media used in dye-sensitized solar cells. Further electrochemical characterization of DCA-based phosphonium RTILs will be conducted.

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