

Effect of Alkyl Chain Length in Anions on the Physicochemical Properties of Cellulose-Dissolving Protic Ionic Liquids

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A protic ionic liquid (PIL) composed of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and acetic acid can dissolve cellulose under mild conditions and catalyse its transesterification. To investigate the relationship between physicochemical properties and chemical structures, PILs composed of DBU and carboxylic acids with varying alkyl chain lengths were prepared as cellulose-dissolving solvents. The thermal behaviours of the PILs were analysed by thermogravimetry and differential scanning calorimetry, and their viscosities, ionic conductivities, and cellulose-dissolution abilities were determined. The effect of the alkyl chain length in the carboxylate ion on the physicochemical properties of the PILs was investigated. With increasing chain length, the thermal stability and ionic conductivity increased, whereas the melting point (T_m), glass-transition temperature (T_g), cellulose solubility, and viscosity decreased. The cellulose solubility increased as the difference between the pK_a values of the DBU and carboxylic acid (ΔpK_a) increased. In addition, the cellulose solubility increased with the increasing density of the PIL. It was revealed that PILs with a high ΔpK_a value and a carboxylate ion with a short alkyl chain are suitable for cellulose dissolution.

Manuscript received: 16 April 2018.

Manuscript accepted: 6 July 2018.

Published online: 20 August 2018.

Introduction

In recent years, ionic liquids (ILs) have attracted a great deal of attention across many research fields.^[1] Defined as organic salts that melt below 100°C, ILs exhibit unique properties, including non-volatility, non-flammability, high ionic conductivity, and high cellulose solubility. Protic ionic liquids (PILs), synthesised by a simple proton transfer reaction from an acid to a base, can be inexpensively obtained in high yield. In general, bulky bases and strong acids are used for the synthesis of PILs.^[2–4] The neutralisation reactions are reversible, and therefore, not only ions but also acids and bases are present in the PILs. PIL formation is best achieved when the difference between the pK_a values of the acid and base (ΔpK_a) is large. Angell and co-workers found that PILs with large ΔpK_a values (>10) showed behaviours similar to those of aprotic ILs (AILs).^[5]

PILs can be distilled when their ΔpK_a value is low (<10). By Le Chatelier's principle, the equilibrium is shifted to the reverse reaction under vacuum, and therefore, the boiling points of the PILs become lower than the decomposition temperature.^[6] According to this phenomenon, King et al. reported the PIL 1,1,3,3-tetramethylguanidinium propionate ([TMGH][OPr]) as a 'reusable cellulose solvent' via a distillation process.^[7]

Recently, we reported that PILs composed of amidines and carboxylic acids could be used as cellulose solvents and low-cost catalysts for the direct transesterification reaction of cellulose.^[8] It has already been shown that combinations of

1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and organic acids dissolve a range of synthetic and biological polymers, but no mention of distillation of the solvents has been made.^[9] We succeeded in reusing the PILs, not only as cellulose solvents but also as cellulose transesterification catalysts, after their recovery by distillation. PILs composed of DBU and carboxylic acids were suitable for cellulose transesterification.^[8] There are few reports on the physicochemical properties of amidinium carboxylates. For example, Miran et al. found that the properties of 1,8-diazabicyclo[5.4.0]-undec-7-enium ([DBUH]⁺)-based PILs, such as thermal stability and ionicity, were controlled by the differences in the pK_a values between the bases and acids (ΔpK_a) due to the generation of N–H hydrogen bonds during cation formation.^[10] In addition, Parviainen et al. found that several PILs composed of amidines and carboxylic acids, such as 1,5-diazabicyclo[4.3.0]non-5-enium propionate ([DBNH][OPr]), were good cellulose solvents because of their cellulose dissolution ability and low viscosity. Furthermore, [DBNH][OPr] was distillable and recyclable, and thus, was regarded as a 'green solvent' for cellulose.^[11] Considering PILs for cellulose transesterification, an investigation of their physicochemical properties is of paramount importance.

The physicochemical properties (thermal behaviour, viscosity, and ionic conductivity) and cellulose dissolution abilities of [DBUH]⁺-based PILs with various carboxylate ions are investigated in this study. The effect of the alkyl chain length in the carboxylate ion on cellulose solubility is discussed.

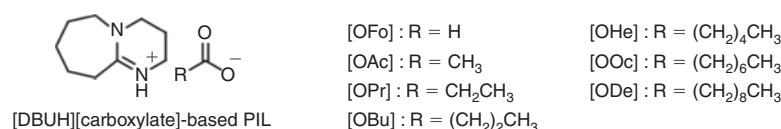


Fig. 1. Chemical structures of the PILs in this study.

Table 1. ΔpK_a , thermal properties, water solubility, and cellulose solubility of PILs

PIL	ΔpK_a ^A	pK_a of carboxylic acid	T_m ^B [°C]	T_g ^C [°C]	$T_{d-5\%}$ ^D [°C]	Water solubility	Cellulose solubility ^E [wt-%]
[DBUH][Ofo]	9.51	3.77	89	—	159	soluble	— ^F
[DBUH][OAc]	8.52	4.76	51	−43	124	soluble	28
[DBUH][OPr]	8.41	4.87	34	−45	149	soluble	27
[DBUH][OBu]	8.46	4.82	—	−54	151	partially soluble	27
[DBUH][OHe]	8.47	4.81	—	−64	161	partially soluble	24
[DBUH][OOc]	8.39	4.89	—	−68	163	insoluble	3
[DBUH][ODE]	6.88	6.40	—	−62	165	insoluble	1

^A $\Delta pK_a = (pK_a \text{ of DBUH}^+) - (pK_a \text{ of carboxylic acid})$.

^BMelting temperature (determined by first heating in DSC measurements).

^CGlass-transition temperature (determined by second heating in DSC measurements).

^D5% weight loss temperature.

^E100°C, 24 h, Ar atmosphere.

^FNo data.

Results and Discussion

Thermal Properties of PILs

The chemical structures of the PILs synthesised in this study are shown in Fig. 1. [DBUH][Ofo], [DBUH][OAc], and [DBUH][OPr] were obtained as white solids at room temperature. In contrast, the remaining PILs were transparent colourless liquids at room temperature. The DSC curves are shown in Fig. S1 (Supplementary Material). [DBUH][Ofo] exhibits the highest melting temperature (T_m) value at 89°C among the seven PILs in this study. In the case of [DBUH][Ofo], the endothermic T_m peak is observed in both the first and second heating scans, suggesting that the PIL has high crystallinity. In the cases of [DBUH][OAc] and [DBUH][OPr], the endothermic peaks corresponding to T_m are observed in the first heating scan only. [DBUH][OAc] and [DBUH][OPr] exhibit glass-transition (T_g) values of −43 and −45°C, respectively, in the second heating scan, and maintain a liquid state at room temperature. Their supercooled states are stable at room temperature. In the cases of [DBUH][OBu], [DBUH][OHe], [DBUH][OOc], and [DBUH][ODE], T_g signals are observed in both the first and second heating scans. The T_g values of the PILs decrease with increasing alkyl chain length in the carboxylate ion.

To evaluate the thermal stability of the PILs, the $T_{d-5\%}$ values, corresponding to 5 % weight loss, were measured using thermogravimetric analysis (TGA). The TGA curves are shown in Fig. S2 (Supplementary Material). The $T_{d-5\%}$ values are between 120 and 170°C for all the PILs used herein (see Table 1), and are lower than those of aprotic ionic liquids (AILs) with carboxylate ions. For example, the thermal decomposition temperatures (T_d) of 1-ethyl-3-methylimidazolium acetate ([C₂mim][OAc]) and 1-butyl-3-methylimidazolium acetate ([C₄mim][OAc]) are 221 and 216°C, respectively.^[12] Angell and co-workers reported that the boiling points of PILs increased to over 300°C when their ΔpK_a values were above 10. This was attributed to the formation of strong ionic bonds after proton transfer from the Brønsted acid to the Brønsted base.^[5] In

addition, Miran et al. found that PILs whose ΔpK_a values exceeded 15 were superior in terms of thermal stability. For the case in which the ΔpK_a value was above 20, the T_d exceeded 450°C under an N₂ atmosphere.^[10] Table 1 summarises the ΔpK_a values for this study, which were determined via the following equation: $\Delta pK_a = pK_a \text{ of DBUH}^+ (13.28) - pK_a \text{ of carboxylic acid}$ ^[13–15] (see Table 1). Since the ΔpK_a values of the PILs synthesised in this study are between 6.88 and 9.51, it is likely that proton transfer (neutralisation) insufficiently occurs during the synthesis of PILs. Lower ΔpK_a values (<10) are responsible for lower thermal stability.

Fig. 2 shows the relationship between the $T_{d-5\%}$ values and the carbon number in the carboxylate ion. The boiling points of various carboxylic acids are included for comparison. Except for [DBUH][Ofo], the $T_{d-5\%}$ values increase with increasing carbon number in the carboxylate ion up to 6, and then reach a plateau. This trend differs from the boiling points (T_b) of the carboxylic acids, which increase monotonously as the carbon number increases. The $T_{d-5\%}$ values for [DBUH][OBu], [DBUH][OHe], [DBUH][OOc], and [DBUH][ODE] are lower than the T_b values of the corresponding carboxylic acids. Carboxylic acids form dimers through hydrogen bonds between the two carboxy groups. Therefore, the T_b values of carboxylic acids are higher than would be predicted from their molecular weights. In the case of PILs, proton transfer occurs between DBU and the carboxylic acid, and thus, the carboxylic acids cannot form dimers in the PILs. On the other hand, the ΔpK_a value of [DBUH][Ofo] is 9.51, which is the highest in this study. Because of its large ΔpK_a value, the high thermal stability of [DBUH][Ofo] is similar to those of AILs.

Cellulose Solubility of PILs

Cellulose solubility tests were performed at 100°C for 24 h under Ar atmosphere, and the results are summarised in Table 1. [DBUH][OAc] dissolves 28 wt-% cellulose at 100°C. The value is similar to those of AILs with acetate anions.^[16,17] The

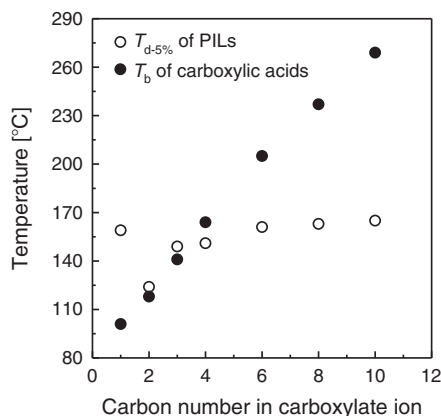


Fig. 2. Effect of carbon number in the carboxylate ion on $T_{d-5\%}$ values of the PILs and the T_b of the carboxylic acids.

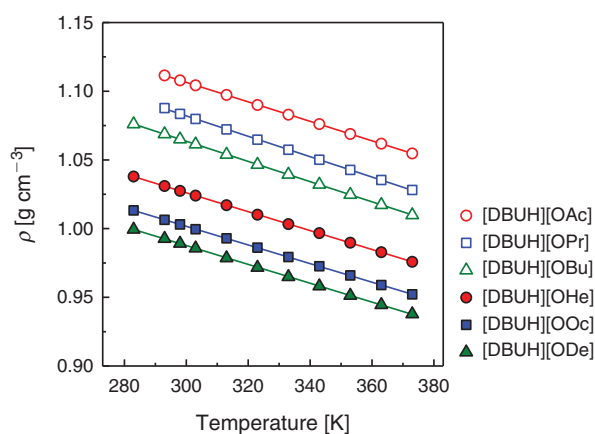


Fig. 3. Plots of density as a function of temperature for the PILs.

cellulose solubility increases with the increase in the ΔpK_a values of the PILs. However, several PILs exhibit disparate cellulose solubilities, despite very similar ΔpK_a values. [DBUH][OOc] ($\Delta pK_a = 8.39$) dissolves 3 wt-% cellulose, in contrast to the 27 wt-% cellulose that dissolves in [DBUH][OPr] ($\Delta pK_a = 8.41$). In addition, 24 wt-% cellulose dissolves in [DBUH][OHe] ($\Delta pK_a = 8.47$), whereas [DBUH][OBu] ($\Delta pK_a = 8.46$) dissolves 27 wt-% cellulose. These differences may be attributed to the alkyl chain of the carboxylate ion, according to the report by Kuzmina et al.^[18] The carboxylate ions are thought to disrupt the hydrogen bond network of the hydroxy groups in cellulose, therefore enabling the dissolution of cellulose in carboxylate-based ILs. The longer, hydrophobic alkyl chains would prevent interactions between carboxylate ions and hydroxy groups, thus decreasing cellulose solubility with increasing alkyl chain length in the carboxylate ion. The water miscibility of PILs with longer alkyl chains is low (see Table 1). This tendency is consistent with the solubility of cellulose. Although it is known that the β value of Kamlet–Taft parameters is closely related to the solubility of cellulose in ILs, we cannot determine the β value of Kamlet–Taft parameters for PILs because Reichardt’s dye becomes colourless by the protonation. Abe et al. reported that density is also an important parameter to consider for developing cellulose-dissolving ILs.^[19] An increase in the alkyl chain length in the carboxylate ion results in lower cellulose solubility owing to the decrease in density. Thus, we should consider not only the ΔpK_a value but

Table 2. Density equation parameters ($\rho = aT + b$) of PILs

PILs	$a (\times 10^{-4})$ [g cm ⁻³ K ⁻¹]	b [g cm ⁻³]	R^2
[DBUH][OAc]	-7.09	1.32	1.0000
[DBUH][OPr]	-7.41	1.30	0.9999
[DBUH][OBu]	-7.34	1.28	1.0000
[DBUH][OHe]	-6.88	1.23	1.0000
[DBUH][OOc]	-6.78	1.20	1.0000
[DBUH][ODE]	-6.89	1.19	1.0000

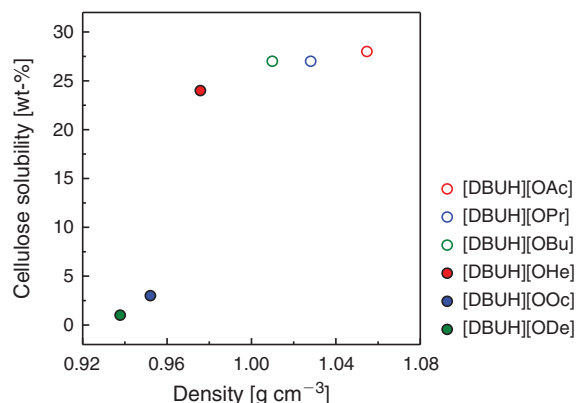


Fig. 4. Relationship between density and cellulose solubility for the PILs at 100°C.

also the density of the ILs when assessing cellulose solubility. The densities of the PILs prepared in this study are discussed in the next section. Nevertheless, PILs with a high ΔpK_a value and a short alkyl chain in the carboxylate ion are revealed as suitable for cellulose dissolution.

Density of PILs

The density of the PILs at various temperatures was investigated. Fig. 3 shows the temperature dependence of the PILs’ densities in the 10–100°C range. The density decreases linearly with increasing temperature. Table 2 summarises the best-fit parameters for the linear fits of density as a function of temperature. The best-fitted results are also depicted as the solid lines in Fig. 3. The a values of the PILs are nearly the same at about -7×10^{-4} g cm⁻³ K⁻¹. The b values range from 1.19 to 1.32 g cm⁻³, and increase with the increase in the alkyl chain length. The density values monotonously decrease with decreasing ΔpK_a values and increasing alkyl chain lengths. These trends are consistent with the cellulose solubility results.

Fig. 4 shows the density dependence of cellulose solubility in the PILs at 100°C. The cellulose solubility decreases with decreasing PIL density. This trend is consistent with the literature.^[19] The cellulose solubility of the PILs drastically decreases when the alkyl chain increases from 6 to 8, even though the difference in density is small. According to Table 1, the hydrophilicity of the PILs drastically changes at a carbon number of 8, such that the PILs become hydrophobic. As mentioned in the *Cellulose Solubility of PILs* section, cellulose solubility increases with the increasing ability of the carboxylate ion to function as a hydrogen-bond acceptor with cellulose. The hydrophilicity of the PIL is an important factor for increasing cellulose solubility.

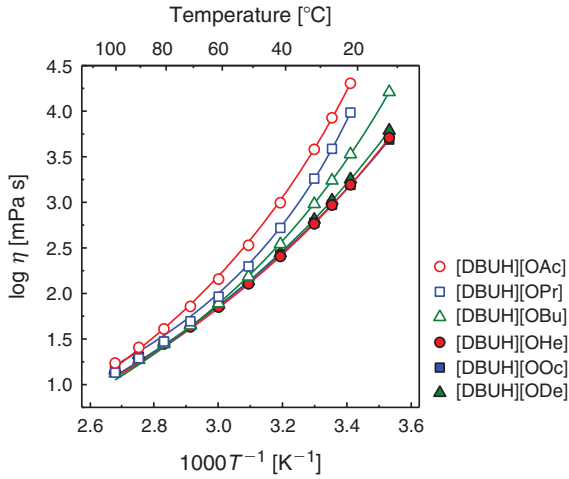


Fig. 5. Arrhenius plots of viscosity for the PILs.

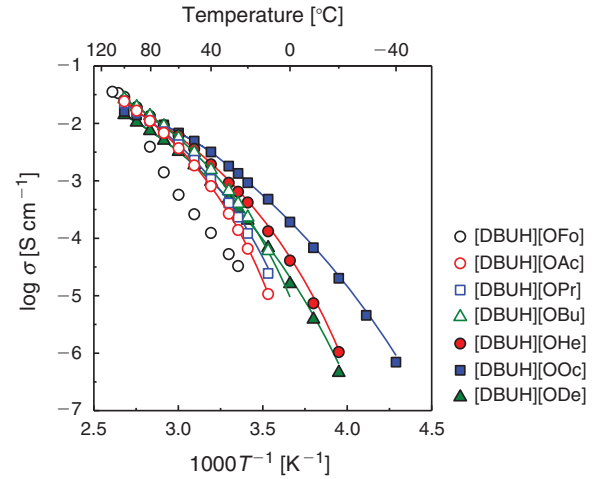


Fig. 6. Arrhenius plots of ionic conductivity for the PILs.

Table 3. VFT equation parameters of viscosity data for PILs

PIL	η_0 [mPa s]	B [K]	T_0 [K]	R^2
[DBUH][OAc]	2.33×10^{-2}	9.91×10^2	221	1.0000
[DBUH][OPr]	2.38×10^{-1}	5.63×10^2	240	0.9999
[DBUH][OBu]	2.81×10^{-2}	9.84×10^2	209	0.9999
[DBUH][OHe]	2.10×10^{-2}	1.17×10^3	189	1.0000
[DBUH][OOc]	1.62×10^{-2}	1.26×10^3	183	1.0000
[DBUH][ODE]	2.29×10^{-2}	1.14×10^3	192	1.0000

Viscosity of PILs

The viscosity (η) of the PILs was investigated by viscometry in the range of 10 to 100°C. Fig. 5 shows the temperature dependence of the viscosity for the PILs, which obeys the Vogel–Fulcher–Tamman (VFT) equation (Eqn 1):

$$\eta = \eta_0 \exp[B/(T - T_0)] \quad (1)$$

where η_0 , B , and T_0 are adjustable parameters. The best-fit parameters are summarised in Table 3 and depicted as solid lines in Fig. 5. Except for [DBUH][ODE], the viscosities of the PILs decrease with increasing alkyl chain length in the carboxylate ion. This phenomenon is consistent with the trend of T_g values determined by the DSC measurements. Decreases in the polarity, density, and molecular packing of the carboxylate ions are caused by the increases in their alkyl chain lengths.^[20] The viscosities of ILs with carboxylate ions, such as imidazolium carboxylate, ammonium carboxylate, and choline carboxylate,^[21–23] increase with the increasing bulkiness of the ion species, whether cationic or anionic. The PILs used in this study exhibit a different trend. On the other hand, the viscosity of [DBUH][ODE] is 1.79×10^3 mPa s at 20°C, which is higher than that of [DBUH][OOc]. In general, the viscosity of a molecular liquid increases because the van der Waals force is strengthened as the number of atoms in the molecules increase. Thus, the greater viscosity in the case of [DBUH][ODE] versus [DBUH][OOc] indicates the stronger van der Waals interactions.

Ionic Conductivity of PILs

Fig. 6 shows the Arrhenius plots of the ionic conductivity (σ) for the PILs in the cooling process. The plots of the temperature

Table 4. VFT equation parameters of ionic conductivity data for PILs

PIL	σ_0 [S cm⁻¹]	B [K]	T_0 [K]	R^2
[DBUH][OAc]	3.88	7.59×10^2	223	1.0000
[DBUH][OPr]	2.83	7.53×10^2	217	1.0000
[DBUH][OBu]	2.81	7.41×10^2	214	1.0000
[DBUH][OHe]	4.19	9.26×10^2	192	0.9998
[DBUH][OOc]	1.66	7.99×10^2	186	0.9997
[DBUH][ODE]	1.81	8.36×10^2	201	0.9998

dependence of the ionic conductivity appear as upper convex curves and are well fitted by the VFT equation (Eqn 2):

$$\sigma = \sigma_0 \exp[-B/(T - T_0)] \quad (2)$$

where σ_0 , B , and T_0 are adjustable parameters. The best-fit parameters are summarised in Table 4 and depicted as solid lines in Fig. 6. The ionic conductivity of [DBUH][OAc] drastically increases between 80 and 90°C, because the T_m value of [DBUH][OAc] is 89°C. The ionic conductivity in the low-temperature range increases with the increasing alkyl chain length in the carboxylate ion. Fig. 7 shows the ionic conductivity and viscosity at 25°C as a function of the carbon number in the carboxylate ion. The ionic conductivity increases as the carbon number increases to 8, whereas the viscosity decreases for the same carbon number range. The ionic species can be transported more easily due to the decrease in the viscosity.^[24] Thus, the ionic conductivity is correlated with the viscosity.

Conclusions

We investigated the physicochemical properties of PILs composed of DBU and various carboxylic acids, which can dissolve cellulose. The thermal stability of the PILs depended on their ΔpK_a value and alkyl chain length in the carboxylate ion. The T_g and viscosity values of the PILs decreased with increasing alkyl chain length, following the same trend as cellulose solubility. These trends were closely related to the density of the PILs. [DBUH][OAc] could dissolve 28 wt-% cellulose at 100°C, which was the highest value in this study. The PILs composed of

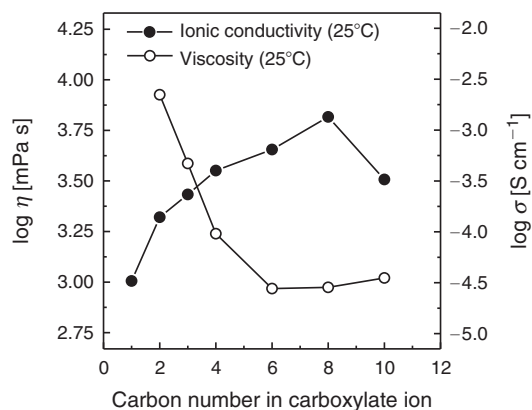


Fig. 7. Viscosity and ionic conductivity at 25°C as a function of carbon number in the carboxylate ions.

carboxylate ions with short alkyl chains were most suitable for cellulose dissolution.

Experimental

Materials

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, >98.0%), propionic acid (>98.0%), butyric acid (>98.0%), hexanoic acid (>98.0%), *n*-octanoic acid (>98.0%), and decanoic acid (>98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Formic acid (>99.0%) and acetic acid (>99.7%) were purchased from Wako Pure Chemical Industries Ltd, and used as obtained. All materials except formic acid and acetic acid were distilled under vacuum before use.

Preparation of PILs

All PILs were prepared by a simple neutralisation reaction without any solvent. The carboxylic acids were added into the amidine under Ar atmosphere in a two-necked round-bottomed flask kept in an ice bath. The mixtures were stirred at room temperature for 24 h, to afford colourless transparent liquids or white solids. The synthesised PILs are designated according to the carbon number in the carboxylate ions ([O_Fo], [OAc], [OPr], [OBu], [OHe], [OOc], and [ODE]).

Measurements

The 5% weight loss temperature ($T_{d-5\%}$) was measured by thermogravimetry (TG-DTA; TG-DTA7200, Hitachi High-Technologies). The samples were heated from room temperature to 500°C at a scan rate of 20°C min⁻¹ under a nitrogen atmosphere. The melting temperature (T_m) and glass-transition temperature (T_g) were measured by differential scanning calorimetry (DSC; DSC7020, Hitachi High-Technologies) in the temperature range of -100 to 100°C at heating and cooling rates of 10°C min⁻¹. The samples were tightly sealed in Al pans under an Ar atmosphere in a dry glove box. Density and viscosity were measured with a viscometer (SVM3000, Anton Paar) in the temperature range of 10 to 100°C.

Ionic conductivity was measured with an impedance analyser (VSP-300, BioLogic) and a thermostatic chamber (SU-262, Espec Corp.) in the temperature range of -40 to 110°C. The samples were tightly sealed in cells with two platinum electrodes under an Ar atmosphere in a glove box. After the cells were

maintained at each temperature for 20 min, the ionic conductivity was measured (frequency range: 5 Hz to 1 MHz; applied voltage: 10 mV). The cell constant was determined with 0.1 M KCl aq. at 25 and 50°C.

Supplementary Material

The results of differential scanning calorimetry and thermogravimetric analysis of protic ionic liquids used in this study are available on the Journal's website.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

This work was supported by a Sophia University Special Grant for Academic Research.

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