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Journal of Fluorine Chemistry 120 (2003) 135–141

JOURNAL OF FLUORINE CHEMISTRY

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Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte

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Received 1 August 2002; received in revised form 9 September 2002; accepted 20 September 2002

Abstract

Three kinds of ionic liquids, 1-alkyl-3-methylimidazolium tetrafluoroborate ($n = 2-4$), were prepared and fundamental properties of ionic liquids and those mixed with industrially used organic solvents (PC, GBL and AN) were investigated compared to solid salts, $TEMABF_4$. It was found that degree of ionization of the ionic liquids were almost same as that of $TEMABF_4$ from the conductivity measurement in diluted system of PC. The ionic liquids and the organic solvents intermingle with each other. Some enhancement in conductivity was observed compared to $TEMABF_4$.

Keywords: Ionic liquid; 1-Alkyl-3-methylimidazolium tetrafluoroborate; Organic electrolyte

1. Introduction

Various kinds of ionic liquids have been taken as a subject for studies since a room temperature molten salt which is inert against water was reported by Wilkes and Zaworotko in 1992 [1]. Typical ionic liquids consist of organic cation with delocalized charges and organic or inorganic fluoroanions [2–10]. For example, 1-alkyl-3-methylimidazolium tetrafluorobrates is one of the most popular ionic liquids. Some of them preserve the state of liquid in wide temperature range. They are difficult to be volatile and expected to have high conductivity because they are essentially formed by ions only. These features are not seen on usual materials and receive much attention for applications [11–20].

Performances of secondary battery represented by lithium ion battery have been elevated remarkably for last decade due to earnest study on electrode materials, electrolyte and cell arrangement. Now farther improvement is required for energy storage systems of hybrid electric vehicle (HEV) and fuel cell electric vehicle (FCEV) because those devices have several drawbacks to be gotten over such as power decline at low-temperature and degradation at high temperature.

The characteristics of ionic liquids, for example, high ionic conductivity, physical stability, non-volatility, and, etc. are attracted as solutions of those problems. Several studies have been done so far and many researchers tried to apply the liquid to devices but the results pointed out high viscosity and lack of electrochemical stability [11–16].

Electrochemical double layer capacitor (EDLC) is one of the candidates for auxiliary power supply of next-generation automobile. Propylene carbonate (PC) solutions of quaternary ammonium tetrafluoroborate are often used for electrolytes of EDLC. The numerous investigations of quaternary ammonium cation structures and those solutions conclude that triethylmethylammonium tetrafluoroborates ($TEMABF_4$) and tetraethylammonium tetrafluoroborates ($TEABF_4$) are the best electrolytes at the present time [21–23]. However, these solid salts have limitations of ionic concentration and conductivity, which are caused by the solubility to solvents especially at low-temperature range.

Ionic liquids exist as liquids at room temperature and they are soluble to organic solvents. Several properties of some of 1-alkyl-3-methylimidazolium tetrafluoroborates have been described in a previous report [24]. In this work, we prepared three kinds of 1-alkyl-3-methylimidazolium tetrafluoroborates, 1-ethyl-($EMIBF_4$), 1-propyl-($MPIBF_4$) and 1-butyl-($BMIBF_4$), and investigated the physical and electrochemical properties as electrolyte.

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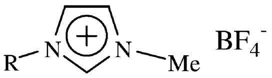
PII: S0022-1139(02)00322-6

Table 1
Physical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate



R	T_g (°C)	T_c (°C)	T_m (°C)	T_d (°C)	η (mPa s)	d (g cm^{-3})	σ (m S cm^{-1})
Ethyl	−92	−58	13	447	37	1.28	14
Propyl	−88	−38	−17	435	103	1.24	5.9
Butyl	−85	None	None	435	180	1.21	3.5

Viscosities, densities and conductivites were measured at 25 °C. T_g, glass transition temperature; T_c, crystallization point; T_m, melting point; T_d, decomposition temperature.

2. Results and discussion

2.1. Synthesis of ionic liquids

Generally, 1-alkyl-3-methylimidazolium tetrafluoroborates are synthesized by ion-exchange reaction of 1-alkyl-3-methylimidazolium halide and tetrafluoroborate of metals such as silver, sodium and potassium. Here, 1-alkyl-3-methylimidazolium halides are prepared by the reaction of 1-methylimidazole and alkyl halide. However, preparation of high-purity ionic liquid is difficult because AgX (X = Cl, Br, I), which is by-product, is soluble to ionic liquids. Moreover, use of Ag salts takes much cost. Another way to synthesize them is the reaction of fluoroboric acid directly with 1-alkyl-3-methylimidazolium halide. This reaction also forms by-product HX instead of AgX but gaseous by-products is removed easily from ionic liquids and high-purity ionic liquids are synthesized with high yield. This reaction reduces the cost because fluoroboric acid is cheaper than tetrafluoroborate salts. The latter reaction was taken in order to synthesize 1-alkyl-3-methylimidazolium tetrafluoroborate to be examined in this report.

2.2. Properties of ionic liquids

Physical properties obtained in the present study (glass transition point, crystallization point, melting point, decomposition point, viscosity and conductivity) are summarized in Table 1. DSC curves of the ionic liquids are shown in Fig. 1. Samples are cooled down to −150 °C with liquid nitrogen and successively heated at the rate of 5 °C min^{-1}. The curve of $EMIBF_4$ shows glass transition, crystallization and melting. There is a small endothermic peak at −18 °C on the curve of $EMIBF_4$, which was observed repeatedly for the other samples of $EMIBF_4$. The question of whether this endothermic peak is ascribed to essential characteristics of $EMIBF_4$ or the existence of contaminants needs further research. A higher glass transition point is observed as the cation has a longer alkyl side chain. $EMIBF_4$ and $MPIBF_4$ have crystallization and melting points. The former has a lower crystallization point and higher melting point than the latter. $BMIBF_4$ does not exhibit crystallization. This might be explained by the difficulties of BMI cations and BF_4 anions to crystallize due to steric problem arising from the length of alkyl chain.

Decomposition temperature was decided by thermo-gravimetrical reduction point. The decomposition of these ionic liquids occurred at almost the same temperature regardless the length of alkyl chain.

The conductivity of $EMIBF_4$ was the highest among the ionic liquids in this study. It exists as a super-cooled liquid below the melting point during this measurement. The temperature dependence of the viscosity and conductivity of the ionic liquids are shown in Figs. 2 and 3, respectively. The length of the alkyl group influences those properties. Liquids become more viscous with the elongation of alkyl chain. Entwining of the alkyl chains is considered to be one of the reasons for the increase of viscosity.

Conductivity decreased with the increase of viscosity. In the middle temperature range, the conductivity exhibits the Arrhenius-type relation, however, not at lower temperatures.

There is no relationship between potential window and the length of alkyl chain among these ionic liquids. Linear

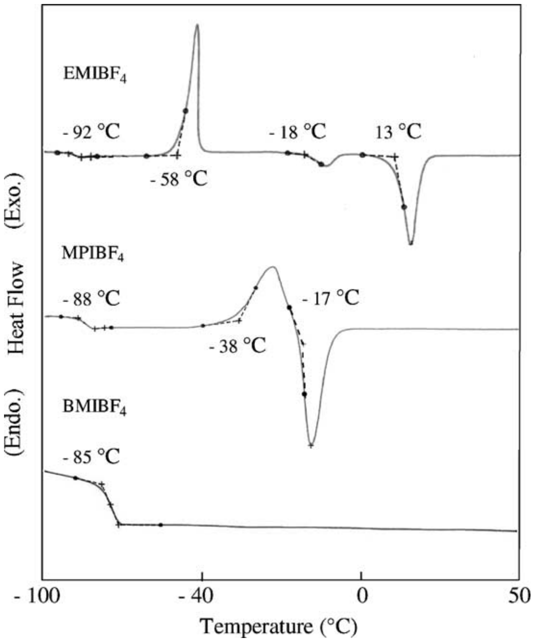


Fig. 1. DSC curves for $EMIBF_4$, $MPIBF_4$ and $BMIBF_4$.

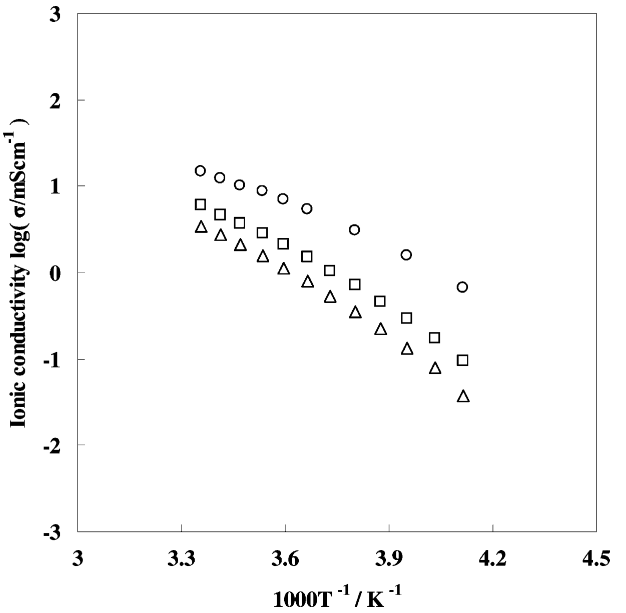


Fig. 2. Temperature dependences of the conductivity of ionic liquids. (○) $EMIBF_4$, (□) $MPIBF_4$, (△) $BMIBF_4$.

sweep voltammograms on glassy carbon electrode are shown in Fig. 4. Difference of the cations does not effect on both the oxidation and reduction potentials. The potential windows were approximately 4 V as for all these ionic liquids.

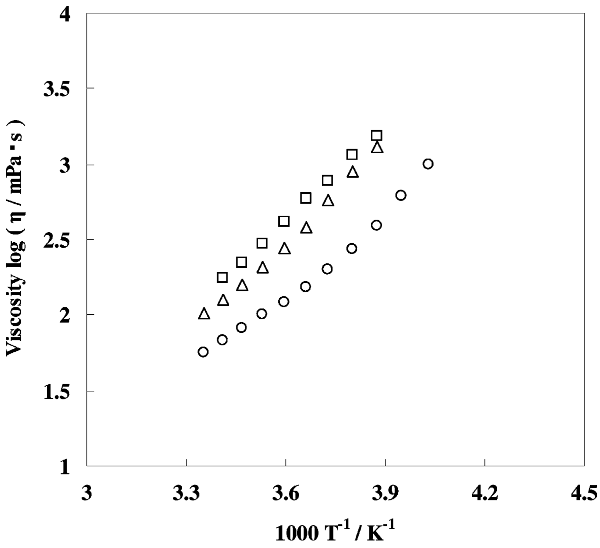


Fig. 3. Arrhenius plots for viscosity of ionic liquids. (○) $EMIBF_4$, (△) $MPIBF_4$, (□) $BMIBF_4$.

Table 2
Physical properties of selected solvents at 25 °C

Solvent	Viscosity (mPa s)	Dielectric (ε)	Liquid range (°C)
PC	2.5	65	−49 to 242
GBL	1.7	42	−44 to 204
AN	0.3	36	−49 to 82

2.3. Properties of ionic liquid mixed with solvents

As to the neat ionic liquids, the viscosity increases and the conductivity decreases with the increase of the length of alkyl chain, especially at lower temperature as explained in the previous section. We examined the properties of the mixed system of ionic liquid and organic solution to decrease the viscosity. Three kinds of solvents, propylene carbonate (PC), γ-butyrolactone (GBL) and acetonitorile (AN) were chosen in this work from the industrial point of view. Their physical properties were listed in Table 2. Propylene carbonate (PC) is often used to EDLC's electrolyte for its high dielectric, wide liquid range and electrochemical stability. It was chosen as a main solvent for this examination.

Firstly, fundamental properties of electrolyte such as the association constant and limiting molar conductivity are

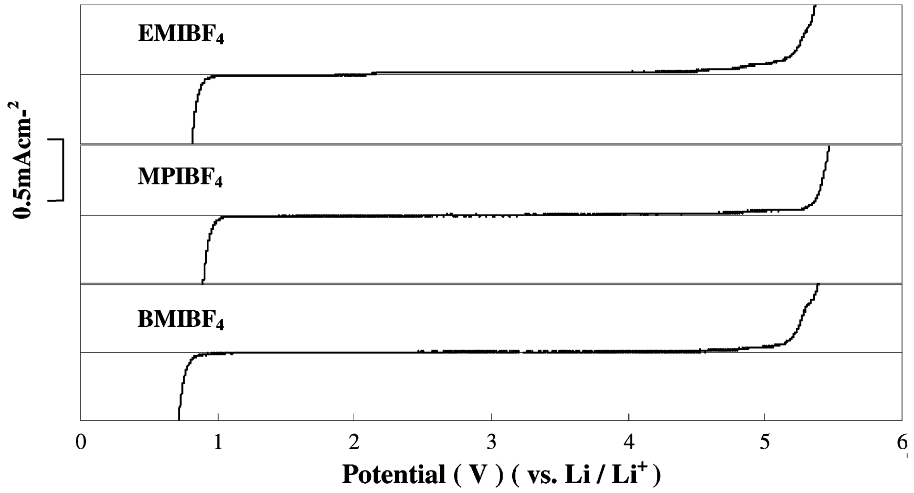


Fig. 4. Linear sweep voltammograms of $EMIBF_4$, $MPIBF_4$ and $BMIBF_4$. Scan rate was 50 mV s^{-1}.

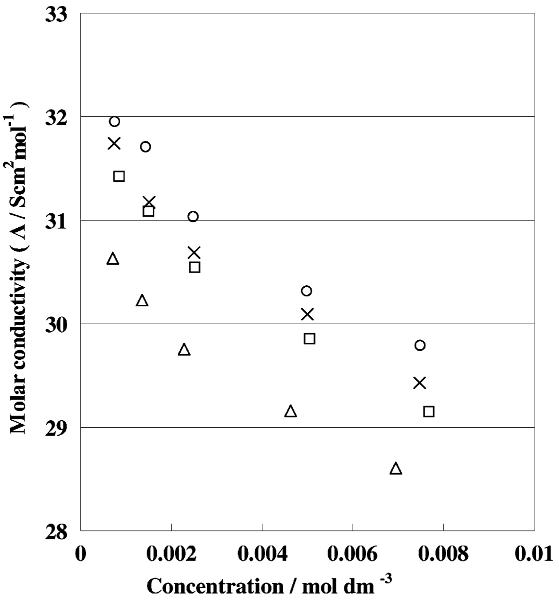


Fig. 5. Molar conductivity of ionic liquids and $TEMABF_4$ diluted with PC. (○) $EMIBF_4$, (□) $MPIBF_4$, (△) $BMIBF_4$, (×) $TEMABF_4$.

examined in diluted systems. A series of different concentrations of PC solutions of $EMIBF_4$, $MPIBF_4$, $BMIBF_4$ and $TEMABF_4$ were prepared in the range from 7.5×10^{-4} to 1.0×10^{-2} M. The relationship of the molar conductivity and concentration are shown in Fig. 5. Molar conductivities of all the samples show the same tendency. They decrease with increase of the concentration. Fuoss–Kraus Eq. (1) was used for calculations of approximate value of the limiting molar conductivities and association constants. Procedures of calculations were followed by the previous reports [25,26].

$$\frac{F_{(z)}}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_A}{\Lambda_0^2}\frac{cf^2\Lambda}{F_{(z)}} \tag{1}$$

where Λ is the molar conductivity, Λ_0, limiting molar conductivity, K_A, association constant, f, mean molar activity coefficient and $F_{(z)}$ is the Fuoss extrapolation function.

Table 3 shows the values of limiting molar conductivities (Λ_0), association constants (K_A), and cations' single ion limiting molar conductivities (λ_{0+}) which were calculated from the anion's single ion limiting molar conductivity (20.3 m S cm^{-1}) [21]. The value of $TEMABF_4$ is slightly different from the result reported by Ue [21]. Contaminated water in the solution might cause the difference. The salts which have larger molecular weight show smaller limiting molar conductivity. The ionic liquids have almost the same association constants as $TEMABF_4$. These results suggest that the ionic liquids do not consist of only ions but some ion pairs, only dissociated ions being able to contribute to the conductance in ionic liquids.

Table 3
Calculated results of limiting molar conductivities (Λ_0), single ion molar conductivities (λ_{0+}) and association constants (K_A)

Salts	Λ_0 (S cm^2 mol^{-1})	λ_{0+} (S cm^2 mol^{-1})	K_A (dm^{-3} mol^{-1})
$EMIBF_4$	32.40	12.10	12.6
$MPIBF_4$	31.84	11.54	12.4
$BMIBF_4$	30.97	10.67	12.1
$TEMABF_4$	32.05	11.75	12.5

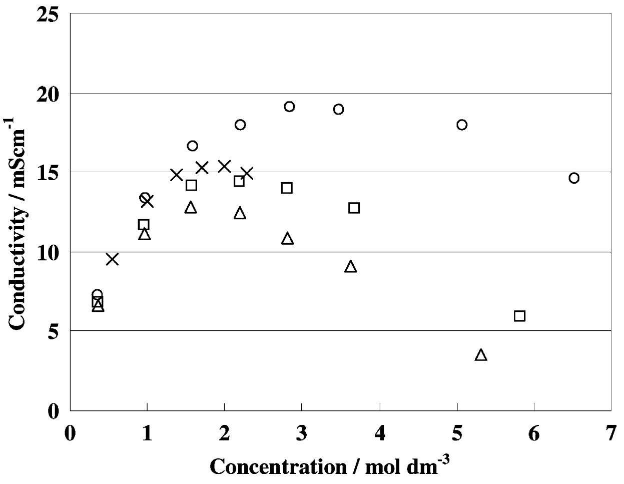


Fig. 6. Concentration dependences of conductivity of ionic liquids and $TEMABF_4$ dissolved in PC. (○) $EMIBF_4$, (□) $MPIBF_4$, (△) $BMIBF_4$, (×) $TEMABF_4$.

$TEMABF_4$/PC solution has limit concentration around 2 M though ionic liquid and PC intermingle easily with each other. The maximum solubility of $EMIBF_4$ in PC is 6.5 M. Conductivities of the mixed solutions have the maximums as shown in Fig. 6. The highest conductivity of 15 m S cm^{-1} is observed for 2 M $TEMABF_4$/PC. On the other hand, the value of $EMIBF_4$ is 19 m S cm^{-1} at 2.8 M at 25 °C, that is 40% increase in molar concentration and 25% enhancement in conductivity. The comparison among three kinds of ionic liquids/PC solutions indicates that the difference of conductivity appears over 1 M of each solution and the longer alkyl chain causes the decrease of conductivity.

The temperature dependences of conductivities of the solutions are shown in Fig. 7. Concentration of each sample

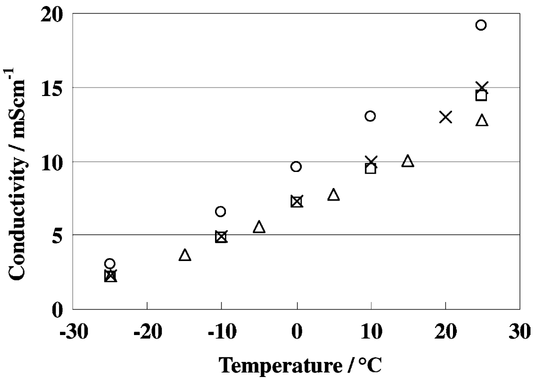


Fig. 7. Temperature dependences of conductivities of the solutions: 2.8 M $EMIBF_4$/PC (○), 2.2 M $MPIBF_4$/PC (□), 1.6 M $BMIBF_4$/PC (△) and 2.2 M $TEMABF_4$/PC (×).

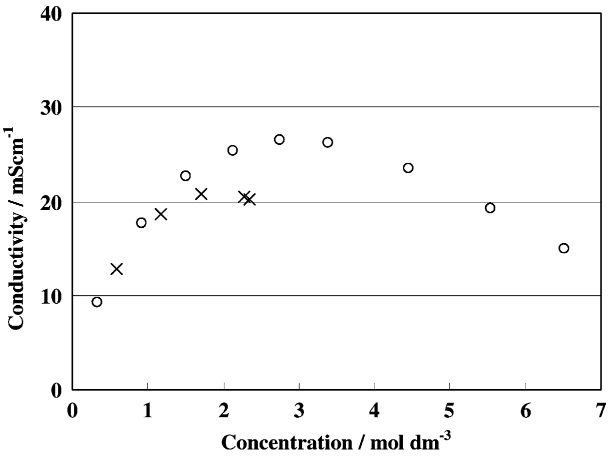


Fig. 8. Concentration dependences of conductivity of $TEMABF_4$ and $EMIBF_4$ dissolved in GBL. (○) $EMIBF_4$, (×) $TEMABF_4$.

on this figure is taken from the value which exhibits the highest conductivity of each solution in Fig. 6. Each sample of the ionic liquids shows similar dependence to that of $TEMABF_4$. The conductivities decrease as the temperature goes down. The solutions of the ionic liquids which have melting points such as $EMIBF_4$ and $MPIBF_4$ do not exhibit step-wise conductivity-drop resulting from phase separation which leads to sudden decrease in ion concentration at the lower temperatures than their melting points. DSC analysis of 2.8 M $EMIBF_4$/PC solution was carried out in order to confirm whether there was phase separation. The DSC curve did not show endothermic peak ascribed to phase separation in the temperature range of −150 to 25 °C.

Solutions of $EMIBF_4$ and $TEMABF_4$ mixed with GBL or AN exhibited higher conductivity as shown in Figs. 8 and 9. $EMIBF_4$ mingled with GBL and AN as well as PC with each other. Solubilities of $TEMABF_4$ in GBL and AN are 2.3 and 3.3 M, respectively. The maximum conductivities of $EMIBF_4$/GBL and $EMIBF_4$/AN are 26 m S cm^{-1} at 2.8 M and 68 m S cm^{-1} at 2.3 M, respectively.

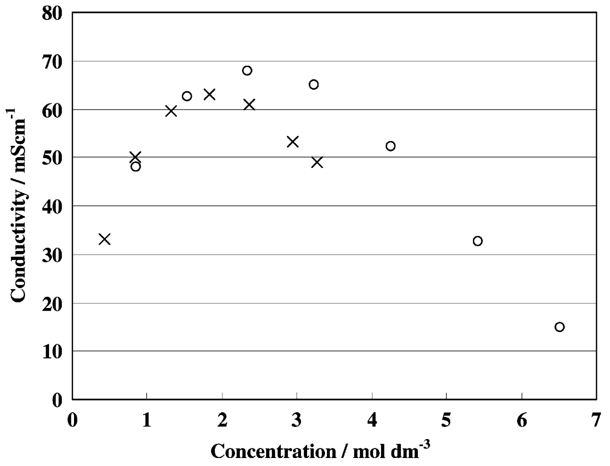


Fig. 9. Concentration dependences of conductivities of $TEMABF_4$ and $EMIBF_4$ dissolved in AN. (○) $EMIBF_4$, (×) $TEMABF_4$.

3. Experimental

3.1. General experimental procedures

Synthesis of ionic liquids is described below in detail. Thermal properties were analyzed by TG-DTA (RIGAKU, TG-8110) and DSC (RIGAKU, DSC8230B). Decomposition temperature was decided by gravimetrical reduction point of TG-DTA curve. Heating rate and terminal temperature was set at 10 °C min^{-1} and 800 °C, respectively. The glass transition point, crystallization point and melting point were decided by DSC analysis. Initial temperature was −150 °C, which is cooled with liquid nitrogen, and heated at the rate of 5 °C min^{-1}. These measurements were carried out under nitrogen atmosphere. The viscosity of solutions was measured with oscillating type viscosity meter (YAMAICHI ELECTRONICS, VM-1G). The density of solutions was measured with density meter by resonant frequency method (KYOTO ELECTRONICS, DA-130).

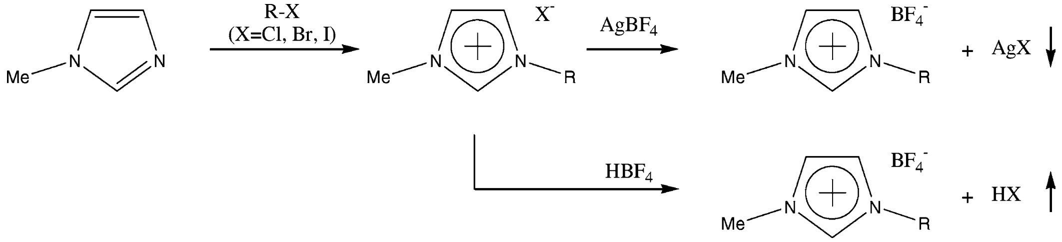
Conductivity was measured by conductivity meter (RADIOMETER ANALYTICAL, CDM210) with a glass cell with a cell constant 0.85 cm^{-1} (RADIOMETER ANALYTICAL, CDC641T). The calibration of the instrument was carried out with 0.1N KCl or 0.001N KCl solution according to conductivity range of measured sample. A glass vessel was equipped to the conductivity cell so that sample liquid is sealed up. The cell temperature was controlled to ±0.1 °C by low-temperature controlled bath into which the vessel was immersed.

Electrochemical measurement was carried out with three-electrode cell. Glassy carbon electrode (7.85×10^{-3} cm^2, BAS 11-2411) was used as working electrode. The surface of the electrode was polished before every measurement. A platinum wire was used as counter electrode. A silver wire was used as a quasi-reference electrode. Potential between a silver wire electrode and sample liquid was referred to Li^+ (0.5 M)/Li electrode in advance. For example, silver wire immersed in $EMIBF_4$ showed 3.0 V referred to lithium foil immersed in 0.5 M $LiBF_4$/$EMIBF_4$ solution separated by glass cell with a bicole glass (BAS, 11-2051). This measurement was carried out in a vacuum glove box (TAKASUGI SEISAKUSHO, G-65-MV-AV) under argon atmosphere. Electrochemical measurements were performed with an electrochemical measurement system (HOKUTO DENKO, HZ-3000).

3.2. Synthetic procedures

3.2.1. Synthesis of 1-ethyl-3-methylimidazolium bromide

The equipments are set up as follows. Reflux condenser, 300 ml dropping funnel and nitrogen gas line (20–30 ml min^{-1}) were connected to three-neck flask to keep the reactors dry. Stirring was done by magnetic stirrer. Ethylbromide (1.1 mol, TCI) was dropped into 300 ml dehydrated toluene solution of 1-methylimidazole (1 mol, TCI) for 3 h at 30 °C. After stirring for 5 h, the reaction solution was



Scheme 1. Synthetic methods of 1-alkyl-3-methylimidazolium tetrafluoroborate.

cooled to 0 °C. The precipitated crystal was filtered. Each starting material was distilled in advance under reduced pressure with molecular sieve 4A (WAKO). Filtered crystal was dissolved into 100 ml dehydrated acetonitrile and re-crystallized by addition of dehydrated ethylacetate (300 ml, TCI). Whole operations were carried out under nitrogen atmosphere.

Melting point: 74.5 °C. 1H-NMR (Me_2SO_2-d_6, σ (ppm) relative to Me_4Si): 9.27 (s, 1H), 7.83 (t, 1H), 7.74 (t, 1H) 4.20 (q, 2H), 3.85 (s, 1H), 1.40 (t, 3H).

3.2.2. *Synthesis of 1-methyl-3-propylimidazolium bromide*

Same equipments for synthesis of 1-ethyl-3-methylimidazolium bromide were applied. Reaction temperature was 70 °C. Melting point was 35.3 °C. 1H-NMR (Me_2SO_2-d_6, σ (ppm) relative to Me_4Si): 9.32 (s, 1H), 7.86 (t, 1H), 7.79 (t, 1H) 4.17 (t, 2H), 3.89 (s, 1H), 1.82 (m, 2H), 0.86 (t, 3H).

3.2.3. *Synthesis of 1-butyl-3-methylimidazolium bromide*

Same equipments for synthesis of 1-ethyl-3-methylimidazolium bromide were applied. Reaction temperature was 70 °C. Melting point was 77.6 °C. 1H-NMR (Me_2SO_2-d_6, σ (ppm) relative to Me_4Si): 9.11 (s, 1H), 7.77 (t, 1H), 7.70 (t, 1H) 4.16 (t, 2H), 3.84 (s, 3H), 1.76 (m, 2H), 1.26 (m, 2H), 0.90 (s, 3H).

3.2.4. *Synthesis of 1-alkyl-3-methylimidazolium tetrafluoroborate*

Hydrogen bromide is generated when 1-alkyl-3-methylimidazolium bromide and tetrafluoroboric acid are directly reacted as shown in Scheme 1.

1-Alkyl-3-methylimidazolium bromide was dissolved in methanol on which tetrafluoroboric acid (40%) in methanol solution was slowly added. The mixed solution was dried with a rotary pump after condensation under reduced pressure. All the operations were carried out under nitrogen atmosphere. The impurity contents of the ionic liquids are shown in Table 4.

Table 4
Impurity contents of ionic and analysis method

H_2O	Karl Fischer's method	<50 ppm
Br^-	Turbidimetry	<1 ppm
Metals (Ca, Cr, Fe, Mg, Na, Ni, Al)	ICP-AES	<1 ppm

4. Conclusions

From the conductivity measurement in diluted system, the association constants and limiting molar conductivities of 1-alkyl-3-methylimidazolium tetrafluoroborates and TEMABF_4 in PC were examined. The limiting molar conductivities of the salts became smaller as their molecular weights increased. Association constants of the ionic liquids were almost same as that of the solid solute such as TEMABF_4. This suggests that the ionic liquids do not consist of only ions but some ion pairs. The ionic liquids mingled with PC, GBL and AN with each other. These solutions showed some enhancement in conductivity compared to TEMABF_4 solutions.

Acknowledgements

We are thankful to the JSPS 155th Committee on Fluorine Chemistry for providing us such a valuable opportunity to present our activity.

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