

# Physical and electrochemical properties of 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium ionic liquids

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## Abstract

Various ionic liquids (ILs) were prepared via metathesis reaction from two kinds of 1-(2-hydroxyethyl)-3-methyl imidazolium ([HEMIm]<sup>+</sup>) and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium ([HEMMor]<sup>+</sup>) cations and three kinds of tetrafluoroborate ([BF<sub>4</sub>]<sup>-</sup>), bis(trifluoromethanesulfonyl)imide ([TFSI]<sup>-</sup>) and hexafluorophosphate ([PF<sub>6</sub>]<sup>-</sup>) anions. All the [HEMIm]<sup>+</sup> derivatives were in a liquid state at room temperature. In particular, [HEMIm][BF<sub>4</sub>] and [HEMIm][TFSI] showed no possible melting point from -150 °C to 200 °C by DSC analysis, and their high thermal stability until 380–400 °C was verified by TGA analysis. Also, their stable electrochemical property (electrochemical window of more than 6.0 V) and high ionic conductivity (0.002–0.004 S cm<sup>-1</sup>) further confirm that the suggested ILs are potential electrolytes for use in electrochemical devices. Simultaneously, the [HEMMor]<sup>+</sup> derivatives have practical value in electrolyte applications because of their easy synthesis procedures, cheap morpholinium cation sources and possibilities of high Li<sup>+</sup> mobility by oxygen group in the morpholinium cation. However, [HEMMor]<sup>+</sup> derivatives showing high viscosity usually had lower ionic conductivities than [HEMIm]<sup>+</sup> derivatives.

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**Keywords:** Ionic liquid; Imidazolium cation; Morpholinium cation; Electrochemical window; Ionic conductivity

## 1. Introduction

Ionic liquids (ILs) have been an area of interest both in clean industrial processes, such as liquid media for chemical reaction and extraction [1,2], and in electrochemical applications, such as an electrolyte for solar cell, fuel cell and lithium battery systems. Recently, various kinds of ILs have been studied mainly to promote the performance of secondary battery systems owing to their favorable characteristics, such as non-volatility, non-flammability, high ionic conductivity and wide electrochemical stability.

ILs consist of large, organic cations, such as quaternary ammonium cations [3], heterocyclic aromatic compounds [4], pyrrolidinium cations [5], with a variety of anions. The overall properties of ILs were dominated by cationic species including an alkyl chain or various functional groups and anionic species. Usually, in ILs, the anion controls their water miscibility or ionic mobility, and the cation has an impact on their hydrophobicity, viscosity, density or melting point according to the physical nature or volume size of the cation and anion species [6]. However, this trend is not exactly consistent with all species of ILs and can be altered by a change of physical state caused by supplying the thermal energy into the ILs or a different interaction between cation and anion [7].

The imidazolium family, which is extensively used for applications of electrochemical fields among vari-

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ous ILs, has been widely developed ever since 1-ethyl-3-methylimidazolium chloroaluminate was discovered by Wilkes and Zaworotko [8], indicating a wide liquid range, large electrochemical window of more than 3 V and high ionic conductivity ( $\sim 8 \times 10^{-3} \text{ S cm}^{-1}$ ) at room temperature. However, the ILs based on imidazolium cation have been reported to have the problem of chemical and electrochemical instability caused by a possible reaction with C(2) carbon. To solve this problem, 1-alkyl-2-alkyl-3-alkyl imidazolium system has been synthesized, but this system leads to a low ionic conductivity.

Recently, our laboratory has researched, for the first time, the new ILs based on *N*-alkyl-*N*-alkyl morpholinium cations [9], many of which have the merits of the easy procedure in their synthesis and purification, the low cost of the morpholinium cation source and the possibility of high  $\text{Li}^+$  mobility by oxygen group in morpholinium cation. This work helps to reveal that the *N*-butyl-*N*-methyl morpholinium bis(trifluoromethanesulfonyl)imide and *N*-ethyl-*N*-methyl morpholinium bis(trifluoromethanesulfonyl)imide possess the thermal solid–solid phase transition and useful electrochemical properties [9]. However, although these ILs based on morpholinium cation have the particular characteristics for battery system application, in order to be applied in the widespread electrochemical fields, more improvement on these ILs is required because of their solid states and low ionic conductivities due to melting points higher than room temperature.

In this work, we prepared six kinds of 3-methylimidazolium and *N*-methyl-morpholinium cations, including 2-hydroxyethyl group ( $[\text{HEMIm}]^+$  and  $[\text{HEMMor}]^+$ ) with tetrafluoroborate ( $[\text{BF}_4]^-$ ), hexafluorophosphate ( $[\text{PF}_6]^-$ ) and bis(trifluoromethanesulfonyl)imide ( $[\text{TFSI}]^-$ ) anions. While the ILs based on  $[\text{HEMIm}]^+$  have been investigated for use as an alternative recyclable and benign reaction media for chemical reactions [10], the ILs based on  $[\text{HEMMor}]^+$  may be the first trial in synthesis. Also, to our knowledge, this study will be first report for electrolyte application of the ILs based on  $[\text{HEMIm}]^+$  and  $[\text{HEMMor}]^+$ . To purify the anion impurities, the improved filtration method using existing celite was introduced when the prepared ILs are insoluble with dichloromethane solvent. Finally, the basic electrochemical and physical properties on the prepared ILs are reported together with their influences according to the change of various anions, and simultaneously, we present the possibilities for application of electrolytes through comparing these ILs with 1-3-alkyl imidazolium and *N*-*N*-alkyl morpholinium cation salts.

## 2. Materials

The list of chemicals (source, grade and purification) used in the synthesis of ionic liquids is as follows: 1-methyl-imidazole (Aldrich, 99%, used without purification), 4-methyl-morpholine (Aldrich, 99%, used with-

out purification), 2-chloroethanol (Aldrich, 99.5%, used without purification), 2-bromoethanol (Aldrich, 95%, used without purification), sodium tetrafluoroborate (Aldrich, 98%, used without purification), potassium hexafluorophosphate (Aldrich, 98%, used without purification) and bis(trifluoromethanesulfonyl)imide lithium salt (Fluka, 99%, used without purification). Solvents used include deionized water from a Millipore purification unit, dichloromethane (Merk, 99.9%), acetone (Merk, 99.9%) and acetonitrile (Merk, 99.9%).

## 3. Experimental

### 3.1. Preparation of ionic liquids

Six ionic liquids used in this study were synthesized along with the corresponding chloride or bromide precursors.

#### 3.1.1. 1-(2-Hydroxyethyl)-3-methyl imidazolium chloride $[\text{HEMIm}][\text{Cl}]$

1-Methyl-imidazole (0.14 mol) was reacted with an excess of hydroxy-ethyl chloride (2-chloroethanol, 0.2 mol) in a round-bottom flask in a nitrogen atmosphere ( $70^\circ\text{C}$ , 48 h), using 200 mL of acetonitrile as solvent, to produce the 1-(2-hydroxyethyl)-3-methyl imidazolium halide ( $[\text{HEMIm}][\text{Cl}]$ ). This molten salt of white crystalline solids was obtained by recrystallization under acetonitrile solvent in a freezer at  $-40^\circ\text{C}$  (yield 89%).

#### 3.1.2. 1-(2-Hydroxyethyl)-3-methyl imidazolium tetrafluoroborate $[\text{HEMIm}][\text{BF}_4]$

The 1-(2-hydroxyethyl)-3-methyl imidazolium chloride was reacted with an equimolar amount of sodium tetrafluoroborate in acetone ( $25^\circ\text{C}$ , 24 h), and the ionic liquid  $[\text{HEMIm}][\text{BF}_4]$  was formed. The sodium chloride was removed by filter paper and any residual sodium chloride in this ionic liquid was removed by low temperature filtration using celite. The organic liquid phase obtained from the filtration method was tested for the residual chloride salt through the concentrated  $\text{AgNO}_3$  solution, and little precipitation of  $\text{AgCl}$  was confirmed with the naked eye.

#### 3.1.3. 1-(2-Hydroxyethyl)-3-methyl imidazolium hexafluorophosphate $[\text{HEMIm}][\text{PF}_6]$

This ionic liquid was synthesized in the same manner as  $[\text{HEMIm}][\text{BF}_4]$  using  $[\text{HEMIm}][\text{Cl}]$  and potassium hexafluorophosphate to form 1-(2-hydroxyethyl)-3-methyl imidazolium hexafluorophosphate in which acetone was used as solvent. The potassium chloride was removed by filter paper, and any residual potassium chloride was cleaned in an aqueous/dichloromethane biphasic solution under an ice bath for 24 h. A concentrated  $\text{AgNO}_3$  solution test was conducted, and little precipitation of  $\text{AgCl}$  was confirmed with the naked eye.

### 3.1.4. 1-(2-Hydroxyethyl)-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide [HEMIm][TFSI]

This ionic liquid was synthesized in the same manner as [HEMIm][BF<sub>4</sub>] using [HEMIm][Cl] and bis(trifluoromethanesulfonyl)imide lithium salt to form 1-(2-hydroxyethyl)-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide in which acetonitrile was used as solvent. The lithium chloride was removed by filter paper, and any residual lithium chloride was cleaned in an aqueous/dichloromethane biphasic solution under an ice bath for 24 h. A concentrated AgNO<sub>3</sub> solution test was conducted and little precipitation of AgCl was confirmed with the naked eye.

### 3.1.5. N-(2-Hydroxyethyl)-N-methyl-morpholinium bromide [HEMMor][Br]

1-Methyl-morpholine (0.3 mol) was reacted with an excess of hydroxyethyl bromide (2-bromoethanol, 0.35 mol) in a round-bottom flask in a nitrogen atmosphere (80–90 °C, 48 h), using 200 mL of acetonitrile as solvent, to produce the N-(2-hydroxyethyl)-N-methyl morpholinium halide ([HEMMor][Br]). This molten salt of white crystalline solids was obtained by recrystallization at a room temperature (52 g, yield 77%) with acetone.

### 3.1.6. N-(2-Hydroxyethyl)-N-methyl-morpholinium tetrafluoroborate [HEMMor][BF<sub>4</sub>]

This ionic liquid was synthesized in the same manner as [HEMIm][BF<sub>4</sub>]. The residual of sodium bromide in this ionic liquid was removed by low temperature filtration using celite. The filtered organic liquid phase was tested for the residual bromide salt through the concentrated AgNO<sub>3</sub> solution.

### 3.1.7. N-(2-Hydroxyethyl)-N-methyl-morpholinium hexafluorophosphate [HEMMor][PF<sub>6</sub>]

This ionic liquid was synthesized in the same manner as [HEMMor][PF<sub>6</sub>]. The residual of sodium bromide in this ionic liquid was removed by low temperature filtration using celite. The AgNO<sub>3</sub> test was conducted as the same manner with [HEMMor][BF<sub>4</sub>].

### 3.1.8. N-(2-Hydroxyethyl)-N-methyl-morpholinium bis(trifluoromethanesulfonyl)imide [HEMMor][TFSI]

This ionic liquid was synthesized in the same manner as [HEMMor][BF<sub>4</sub>] using [HEMMor][Br] and bis(trifluoromethanesulfonyl)imide lithium salt to form N-(2-hydroxyethyl)-N-methyl-morpholinium bis(trifluoromethanesulfonyl)imide in which acetonitrile was used as solvent. The lithium bromide was removed by filter paper, and any residual lithium bromide was cleaned in water for 24 h. A concentrated AgNO<sub>3</sub> solution test was conducted.

The evaluation of the purity of the prepared ILs was conducted by <sup>1</sup>H NMR, FAB mass, ionic chromatography and measurement of water contents. The <sup>1</sup>H NMR and FAB mass spectra were recorded on a Bruker DMX 300 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively. The possible presence of residual Br<sup>-</sup> or Cl<sup>-</sup> was examined by a

precipitation test of AgNO<sub>3</sub> and ionic chromatography (Bio-LC DX-300 (Dionex, Sunnyvale, CA, USA), detector: suppressed conductivity (PED2), column: ICsep AN 300 with ICsep ANSC guard). All of the ionic liquids were rigorously dried at 50 °C under 0.03 Torr for 5 days. The water contents of all prepared ILs were measured by a Karl–Fischer titration (756 KF Coulometer, Metrohm, Switzerland) in a dry atmosphere.

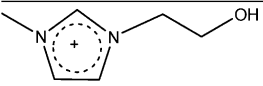
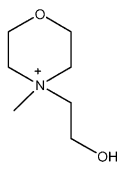
### 3.2. Low temperature filtration method using celite

In this work, a low temperature filtration method using celite was conducted. In order to investigate the removal effect of halide ions, a filtration test using celite of [HEMIm][BF<sub>4</sub>], which is not soluble in dichloromethane and soluble in water, was conducted at room temperature and a low temperature of –20 °C. The original weights of two [HEMIm][BF<sub>4</sub>] were 8.1 g, respectively. Both ILs were well mixed with 100 mL of acetone. One of the two solutions was left at room temperature and the other was kept at –20 °C in a refrigerator for 5 h. Thereafter, the two solutions were filtered through celite of 30 g. The chloride ion contents of these two ILs were analyzed by ionic chromatography after the acetone was evaporated by a rotary evaporator. The chloride ion contents of the two ILs before filtration were both 562 ppm. In the case of the ionic liquid kept and filtered at room temperature, the content of chloride ions was 540 ppm and a relatively small amount of chloride ions was removed in comparison with the initial chloride content. However, the chloride ion content of the IL maintained and filtered at –20 °C was 161 ppm. Thus, the low temperature filtration method using celite appears to be very effective in removing residual chloride ion in the case of ILs that are soluble in water and simultaneously insoluble in dichloromethane. However, when celite is used for purification, some loss of product will occur.

### 3.3. Electrochemical measurements

For evaluating the electrochemical properties of the prepared ILs, the cyclic voltammetry and the specific ionic conductivity were measured. The cyclic voltammetric measurement of 0.05 M of ionic liquid solution in acetonitrile at room temperature was performed by a Solartron 1260 A potentiostat/galvanostat in which a glassy carbon working electrode 3 mm in diameter was used with a platinum wire (Aldrich, 0.5 mm diameter, 99.99%) as a counter electrode and a silver wire (Aldrich, 1.5 mm diameter, 99.99%) as a reference electrode. The scan rate and temperature are 10 mV s<sup>-1</sup> and 25 °C, respectively. Also, the specific ionic conductivity of ionic liquids was measured by Solartron 1260 A frequency response analyzer (FRA). This apparatus was connected with a sealed cell containing a pair of SUS plate electrodes 9 mm apart and measured by our laboratory. The cell constant is 1.29 cm<sup>-1</sup>.

Table 1  
Ionic liquid cations and anions used in this study

Cations	Anions	
 [HEMIm] <sup>+</sup>	Hexafluorophosphate	[PF <sub>6</sub> ] <sup>-</sup>
	Tetrafluoroborate	[BF <sub>4</sub> ] <sup>-</sup>
 [HEMMor] <sup>+</sup>	Bis(trifluoromethanesulfonyl) imide	[(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup> or [TFSI] <sup>-</sup>
	Halides	[Cl] <sup>-</sup> , [Br] <sup>-</sup>

### 3.4. Thermal measurements

For investigating the thermal property of the prepared ILs, the differential scanning (DSC Q1000 V7.0 Build 244) data were obtained in a sealed aluminum pan with a cooling and heating rate of 10 °C min<sup>-1</sup> under the condition of He purge, 50 cm<sup>3</sup> min<sup>-1</sup>. The thermogravimetric analysis (TGA Q500 V5.0 Build 164) data were taken in air and at a heating rate of 10 °C min<sup>-1</sup> under the condition of N<sub>2</sub> purge, 100 cm<sup>3</sup> min<sup>-1</sup>.

## 4. Results and discussion

1-(2-Hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts, including anions of [Cl]<sup>-</sup>, [Br]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [PF<sub>6</sub>]<sup>-</sup> and [TFSI]<sup>-</sup>, were prepared. Table 1 shows the cations and anions of the ILs used in this study. To evaluate the basic characteristics for the application of electrolytes, their physical and electrochemical properties were determined.

### 4.1. Physical properties

Table 2 shows the miscibility between the prepared ILs and water along with their appearance at room temperature. All prepared ILs, except [HEMIm][TFSI], were miscible with water at room temperature. Generally, it is reported that the

Table 2  
Miscibility with H<sub>2</sub>O and water contents of prepared ILs

Ionic liquid	Miscibility with H <sub>2</sub> O	Appearance
[HEMIm][Cl]	Miscible	White solid
[HEMIm][BF <sub>4</sub> ]	Miscible	Clear colorless liquid
[HEMIm][PF <sub>6</sub> ]	Miscible	Clear colorless liquid
[HEMIm][TFSI]	Immiscible	Clear colorless liquid
[HEMMor][Br]	Miscible	White solid
[HEMMor][BF <sub>4</sub> ]	Miscible	Yellow viscous liquid
[HEMMor][PF <sub>6</sub> ]	Miscible	White solid
[HEMMor][TFSI]	Miscible	Yellow viscous liquid

anion component of ILs, and the chain length of cation influence the water miscibility; in the case of 1-3-alkyl imidazolium salts, the hydrophobicity is increased from [Cl]<sup>-</sup>, [Br]<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> to [TFSI]<sup>-</sup>, and the increase of alkyl chain length decreases the hydrophilicity of the ILs [6,13]. However, it is apparent that the miscibility with water of the imidazolium and morpholinium salts, including hydroxyethyl group, is not greatly influenced by the identity of anion.

The solid–liquid phase transition and thermal stability of the ILs prepared in this work have been examined by DSC and TGA, respectively, and the results (melting point, glass transition temperature and decomposition point) are summarized in Table 3. In our analysis, the melting points were obtained in only ILs including [PF<sub>6</sub>]<sup>-</sup> anion, and the precursor salts exhibited melting points within the range of -150 °C to 150 °C. The DSC traces (exothermic up) of 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-3-methyl morpholinium salts are shown in Figs. 1 and 2, respectively.

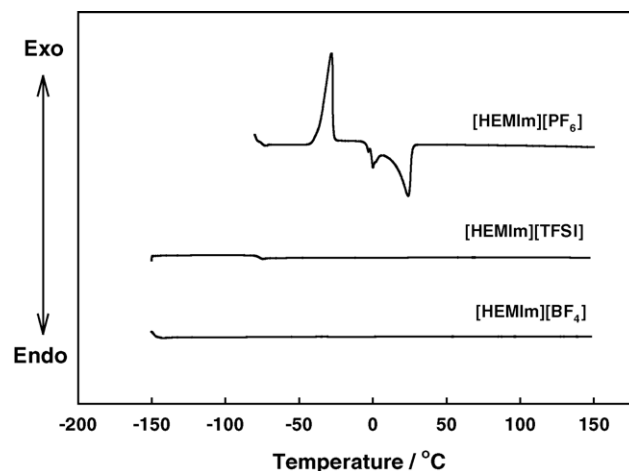


Fig. 1. Differential scanning calorimeter thermograms [HEMIm][PF<sub>6</sub>], [HEMIm][TFSI] and [HEMIm][BF<sub>4</sub>] on warming at 10 °C min<sup>-1</sup> after quenching from the liquid state (all data: second run state).

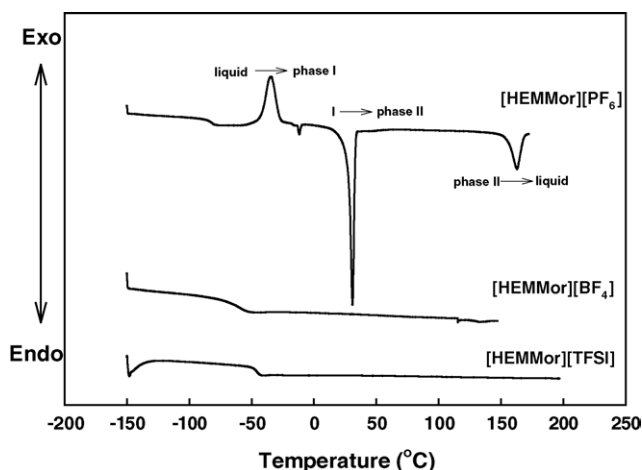


Fig. 2. Differential scanning calorimeter thermograms [HEMMor][PF<sub>6</sub>], [HEMMor][TFSI] and [HEMMor][BF<sub>4</sub>] on warming at 10 °C min<sup>-1</sup> after quenching from the liquid state (all data: second run state).

The respective samples except [HEMIm][PF<sub>6</sub>] were cooled down to about -150 °C in liquid nitrogen and successively heated up to about 200 °C at a rate of 10 °C min<sup>-1</sup>. All of the data were obtained at second heating run state. In the case of [HEMIm][PF<sub>6</sub>], the thermal analysis trace from -80 °C to 150 °C shows one possible crystalline phase transition of around -28 °C and the melting point at 23 °C. Also, the glass transition temperature does not occur at those temperatures. A small peak corresponding to the melting point was observed at 2.67 °C and has to be investigated further to determine the existence of contamination or essential thermal behavior of [HEMIm][PF<sub>6</sub>]. Unlike [HEMIm][PF<sub>6</sub>], [HEMIm][BF<sub>4</sub>] and [HEMIm][TFSI] exhibit that there are no other phase transitions or melting events in the range of -150 °C to 200 °C, indicating a glass transition temperature of -73 °C for [HEMIm][BF<sub>4</sub>] and -76.5 °C for [HEMIm][TFSI].

In Fig. 2, the [HEMMor][PF<sub>6</sub>] exhibits multiple thermal transitions, possessing the richest crystalline behavior among the family of the compounds described here. In detail, we can describe that glass transition temperature was observed around -74 °C and one exothermic peak appears at around -50 °C that represents the crystallization behavior from supercooled liquid to low temperature stable solid phase (phase I). Phase I then transformed into higher temperature solid phase (phase II) at 30 °C exhibiting the final melting point of 160.4 °C. However, the appropriate researches might be needed in order to identify the small endothermic peak at -10 °C whether it represents the essential thermal quality or the existence of contaminants.

Like 1-(2-hydroxyethyl)-3-methyl imidazolium salts of Fig. 1, [HEMMor][BF<sub>4</sub>] and [HEMMor][TFSI], but not [HEMMor][PF<sub>6</sub>], exhibit no other solid phase transition or melting event from -150 °C to 200 °C, indicating the glass transition temperatures, -59 °C for [HEMMor][BF<sub>4</sub>] and -74 °C for [HEMMor][TFSI] (Fig. 2).

The thermal stabilities of the prepared ILs were determined on the thermogravimetric analysis (TGA), as

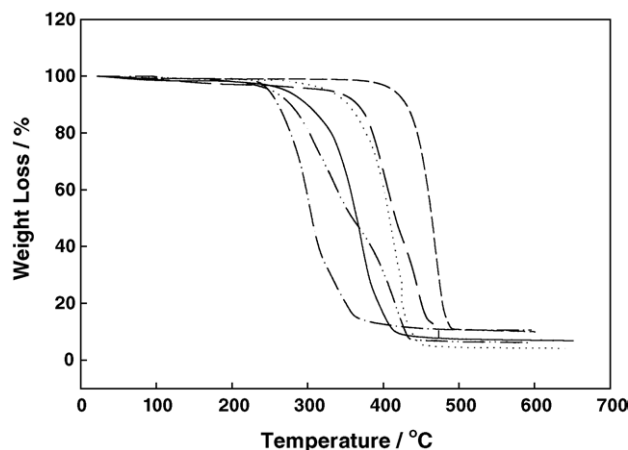


Fig. 3. Thermogravimetries of prepared ILs (dotted: [HEMIm][BF<sub>4</sub>], solid: [HEMIm][PF<sub>6</sub>], short dash: [HEMIm][TFSI], dash-dot-dot: [HEMMor][BF<sub>4</sub>], dash-dot: [HEMMor][PF<sub>6</sub>], long dash: [HEMMor][TFSI]).

shown in Fig. 3. In general, while the [HEMIm][PF<sub>6</sub>], [HEMMor][BF<sub>4</sub>] and [HEMMor][PF<sub>6</sub>] were stable around 300 °C, the [HEMIm][BF<sub>4</sub>] and [HEMMor][TFSI] were stable around 400 °C. Particularly, [HEMIm][TFSI] showed the stable thermal property until 450 °C.

#### 4.2. Electrochemical behavior

Figs. 4 and 5 show cyclic voltammograms on the prepared 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts at room temperature, respectively. A glassy carbon was used as working electrode with platinum wire as a counter electrode and silver wire as reference electrode. Fig. 4 shows that the windows of electrochemical stability between reduction and oxidation potentials were 6.4 V for the [HEMIm][BF<sub>4</sub>], 6.2 V for [HEMIm][TFSI] and 5.4 V for [HEMIm][PF<sub>6</sub>], respectively. The electrochemical stabilities of the 1-(2-hydroxyethyl)-3-methyl imidazolium salts obtained by anion exchange reaction were enhanced up to about 2.7–3.6 V as reported in the case of 1,3-alkyl imidazolium salts [11]. The oxidation of anions, which is presumed to be related to anodic reaction [15–19], starts at about 3 V ver-

Table 3  
Thermal properties of prepared ILs

Ionic liquid	$T_m$ (±2 °C)	$T_g$ (±2 °C)	$T_d$ (±2 °C)
[HEMIm][Cl]	60.8	–	–
[HEMIm][BF <sub>4</sub> ]	–	-73	380
[HEMIm][PF <sub>6</sub> ]	23	–	310
[HEMIm][TFSI]	–	-76.5	420
[HEMMor][Br]	150	–	–
[HEMMor][BF <sub>4</sub> ]	–	-59	300
[HEMMor][PF <sub>6</sub> ]	160.4	-85	280
[HEMMor][TFSI]	–	-50	370

$T_m$ : melting temperature;  $T_g$ : glass transition temperature,  $T_d$ : decomposition temperature.



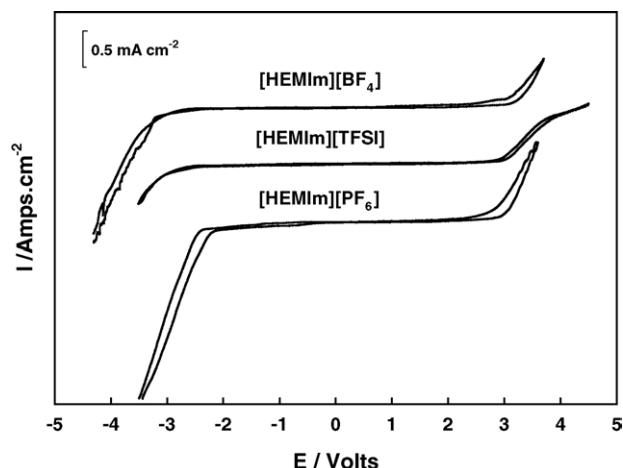


Fig. 4. Cyclic voltammograms for 0.05 M [HEMIm][BF<sub>4</sub>], 0.05 M [HEMIm][TFSI] and 0.05 M [HEMIm][PF<sub>6</sub>] solution in acetonitrile at 25 °C. Scan rate: 10 mV s<sup>-1</sup>, working electrode: glassy carbon, counter electrode: platinum, reference electrode: silver wire.

versus Ag/Ag<sup>+</sup> in all [HEMIm][BF<sub>4</sub>], [HEMIm][TFSI] and [HEMIm][PF<sub>6</sub>], in spite of the difference of anions. On the other hand, the reduction of imidazolium cations, usually considered by cathodic reaction [15–17], starts below -3.4 V, -3.2 V and -2.5 V versus Ag/Ag<sup>+</sup> for [HEMIm][BF<sub>4</sub>], [HEMIm][TFSI] and [HEMIm][PF<sub>6</sub>], respectively, although all of the related salts have the same cation. From the results of this cyclic voltammogram, it is estimated that, in the case of 1-(2-hydroxyethyl)-3-methyl imidazolium salts, the anodic and cathodic limits are not significantly influenced by the nature of cation and anion, as the cathodic limits of imidazolium salts having different anions, such as 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]) and 1-butyl-3-methyl-

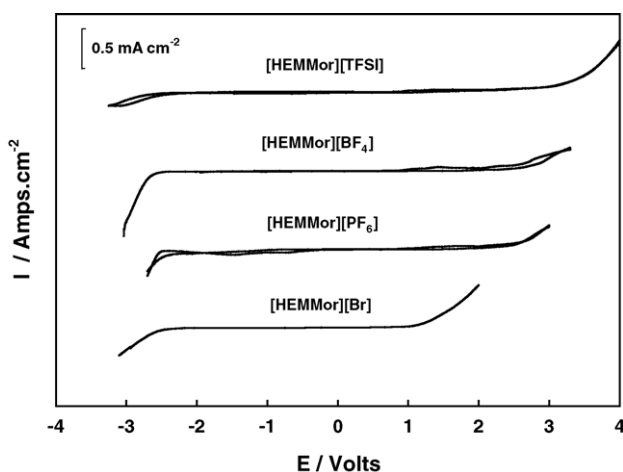


Fig. 5. Cyclic voltammograms for 0.05 M [HEMMor][PF<sub>6</sub>], 0.05 M [HEMMor][TFSI], 0.05 M [HEMMor][BF<sub>4</sub>] and 0.05 M [HEMMor][Br] solution in acetonitrile at 25 °C. Scan rate: 10 mV s<sup>-1</sup>, working electrode: glassy carbon, counter electrode: platinum, reference electrode: silver wire.

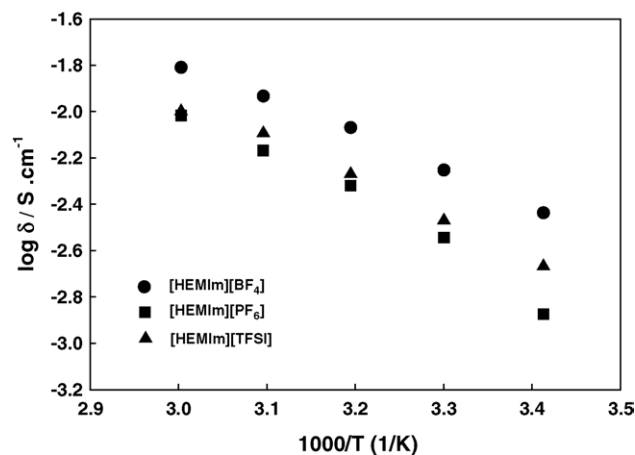


Fig. 6. Arrhenius plot of ionic conductivity ( $\delta$ ) for [HEMIm][PF<sub>6</sub>], [HEMIm][TFSI] and [HEMIm][BF<sub>4</sub>].

imidazolium hexafluorophosphate ([BMIm][PF<sub>6</sub>]), indicate different potentials of -1.8 V and -2.5 V versus Pt at the glassy carbon working electrode, respectively [11].

The electrochemical windows between the onset of oxidation and reduction of [HEMMor][TFSI], [HEMMor][BF<sub>4</sub>], [HEMMor][PF<sub>6</sub>] and [HEMMor][Br] are, respectively, 6.2 V, 5.7 V, 5.2 V and 4 V (Fig. 5). Unlike imidazolium salts including the hydroxyethyl group, the cathodic and anodic limiting potentials of *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts showed common behavior according to the different anions [12]. The cathodic limits, about -2.5 V versus Ag/Ag<sup>+</sup>, were only slightly changed by different anions; on the other hand, the anodic limits were roughly changed from 2.7 V versus Ag/Ag<sup>+</sup> for [HEMMor][PF<sub>6</sub>] to the highest value, 3.8 V versus Ag/Ag<sup>+</sup> for [HEMMor][TFSI].

In the case of 1-(2-hydroxyethyl)-3-methyl imidazolium salts, the outstanding wide electrochemical windows of more than 6.0 V and the lower limiting reduction potential of less than -3.0 V versus Ag/Ag<sup>+</sup> will strengthen their electrolyte candidacy compared to *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts. However, in the case of PF<sub>6</sub><sup>-</sup> salts, further studies are necessary to characterize oxidation reactions at anodic limits of prepared ILs, because formation of atomic fluorine and PF<sub>5</sub> has been proposed to explain the gas evolution on the anode [12,18,19].

#### 4.3. Ionic conductivity

Figs. 6 and 7 indicate the Arrhenius plots on the ionic conductivity at different temperatures of prepared 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts, respectively. The temperature dependence of the ionic conductivity of both salts follows the Arrhenius relation in the high temperature region. The ionic conductivities of 1-(2-hydroxyethyl)-3-methyl imidazolium salts were higher than those of *N*-

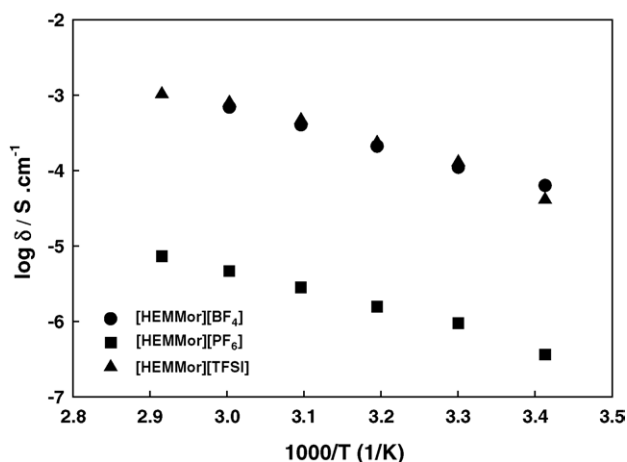


Fig. 7. Arrhenius plot of ionic conductivity ( $\delta$ ) for [HEMMor][PF<sub>6</sub>], [HEMMor][TFSI] and [HEMMor][BF<sub>4</sub>].

(2-hydroxyethyl)-*N*-methyl morpholinium salts, particularly showing the high order of  $10^{-2}$  in the vicinity of 60 °C. The low conductivities of *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts can be explained by the high viscosities of [HEMMor][X] (X = BF<sub>4</sub> and TFSI) and the solid state of [HEMMor][PF<sub>6</sub>] caused by a high melting point. Generally, the variance of anion under the conditions of the same cation is widely known to be related with an ionic conductivity. Above the melting point, it is reported that the ionic conductivity for room temperature ionic liquid is restricted by ion size [7]. From the literature, the ionic conductivities of [EMIm][X] (X = [BF<sub>4</sub>]<sup>-</sup>, [TFSI]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup>) were determined in the order of BF<sub>4</sub><sup>-</sup> (48 Å<sup>3</sup>, 13 mS cm<sup>-1</sup>) > TFSI<sup>-</sup> (143 Å<sup>3</sup>, 8.4 mS cm<sup>-1</sup>) > PF<sub>6</sub><sup>-</sup> (68 Å<sup>3</sup>, 5.2 mS cm<sup>-1</sup>) > Beti-(bis(perfluoroethylsulfonyl)imide, 189 Å<sup>3</sup>, 3.6 mS cm<sup>-1</sup>) in which, compared to the anion volume, the ionic conductivity of [EMIm][PF<sub>6</sub>] was relatively low due to its supercooled state at room temperature [7]. As shown in Fig. 6, in 1-(2-hydroxyethyl)-3-methyl imidazolium salts, the value of ionic conductivity according to the different anions agrees with the value of the ionic conductivity of [EMIm][X].

The room temperature ionic conductivities and activation energies calculated from the slope of the linear Arrhenius region around 298 K are listed in Table 4. Compared with common 1-butyl-3-methyl imidazolium salts ([BMIm][X]) [14] and *N*-butyl-*N*-methyl pyrrolidinium salts ([P<sub>N,N</sub>][X]) [5], [HEMIm][X] (X = BF<sub>4</sub>, TFSI, PF<sub>6</sub>) has similar or higher conductivities at room temperature; for example, in [BF<sub>4</sub>]<sup>-</sup> anion, the ionic conductivity of [HEMIm][BF<sub>4</sub>] (0.0046 S cm<sup>-1</sup>) is absolutely higher than that of [BMIm][BF<sub>4</sub>] (0.00173 S cm<sup>-1</sup>) or [P<sub>1,4</sub>][BF<sub>4</sub>] (solid at room temperature), and in [TFSI]<sup>-</sup> anion, the ionic conductivity of [HEMIm][TFSI] (0.0028 S cm<sup>-1</sup>) is lower than [BMIm][TFSI] (0.0039 S cm<sup>-1</sup>) but higher than [P<sub>1,4</sub>][TFSI] (0.0022 S cm<sup>-1</sup>).

## 5. Conclusions

Ionic liquids based on 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium cations with three different anions ([BF<sub>4</sub>]<sup>-</sup>, [TFSI]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup>) have been prepared, and their desirable physical and electrochemical properties for electrolyte application have been studied. An improved filtration method using existing celite was effectively applied to remove the anion impurities of the ILs insoluble with dichloromethane solvent. The ILs based on 1-(2-hydroxyethyl)-3-methyl imidazolium and *N*-(2-hydroxyethyl)-*N*-methyl morpholinium cations with anions of [BF<sub>4</sub>]<sup>-</sup> and [TFSI]<sup>-</sup> are liquid at room temperature, at which *N*-(2-hydroxyethyl)-*N*-methyl morpholinium salts are in a far more viscous liquid state than 1-(2-hydroxyethyl)-3-methyl imidazolium salts. The valuable characteristics of [HEMIm][BF<sub>4</sub>] as a strong electrolyte candidate were proven by an outstanding electrochemical window of about 6.4 V and ionic conductivity of 0.0046 S cm<sup>-1</sup>. The prepared [HEMIm][TFSI] can be considered as another candidate because of the resulting properties, such as hydrophobic nature at room temperature, liquid state in a wide temperature range (-150 °C to 200 °C), high thermal stability (400 °C of *T*<sub>d</sub>), high ionic conductivity (0.0028 S cm<sup>-1</sup>) and remarkable electrochemical stability (electrochemical window of 6.2 V). Compared with common 1-alkyl-3-alkyl imidazolium TFSI [HEMIm][TFSI] indicates the improvements, such as maintenance of liquid state in a wider temperature range than [BMIm][TFSI] (melting point of -25 °C), and more wide electrochemical window than [EMIm][TFSI] (electrochemical window of about 4 V)—although the ionic conductivity of [HEMIm][TFSI] is 0.7 times lower than [BMIm][TFSI] (0.0039 S cm<sup>-1</sup>) [2]. On the other hand, [HEMMor] salts have the advantages of an easy synthesis process and the low cost of a morpholinium cation source, although the physical and electrochemical properties are more or less inferior to [HEMIm] salts. Particularly, [HEMMor][BF<sub>4</sub>] and [HEMMor][TFSI] possess better ionic conductivities than *N*-methyl-*N*-alkyl-morpholinium salts, which are in a solid state at room temperature due to their liquid state at the wider temperature range (-150 °C to 200 °C). Also, in the case of [HEMMor][PF<sub>6</sub>], we can expect elevated performances in ionic conductivity through battery

Table 4  
Ionic conductivities  $\sigma$  (S cm<sup>-1</sup>) of the prepared ILs at 298 K and activation energies  $E_A$  (kJ mol<sup>-1</sup>) obtained from the corresponding Arrhenius plots

Ionic liquid	$\sigma$ (S cm <sup>-1</sup> )	
	25 °C	$E_A$ (kJ mol <sup>-1</sup> )
[HEMIm][BF <sub>4</sub> ]	$4.6 \times 10^{-3}$	29.48
[HEMIm][TFSI]	$2.8 \times 10^{-3}$	32.13
[HEMIm][PF <sub>6</sub> ]	$2.1 \times 10^{-3}$	39.29
[HEMMor][BF <sub>4</sub> ]	$8.7 \times 10^{-5}$	49.24
[HEMMor][TFSI]	$8.5 \times 10^{-5}$	53.54
[HEMMor][PF <sub>6</sub> ]	$6.6 \times 10^{-7}$	–

system application by exhibiting solid–solid phase transition behavior.

## 6. Purity of ionic liquids

### 6.1. [HEMIm][Cl]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.72(q, 2H), 3.88(s, 3H), 4.21(t, 2H), 5.29(t, 1H), 7.71(d, 1H), 7.75(d, 1H), 9.18(s, 1H). FAB mass showed  $m/z = 127.17$  [HEMIm] $^+$ .

### 6.2. [HEMIm][BF<sub>4</sub>]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.72(q, 2H), 3.88(s, 3H), 4.21(t, 2H), 5.29(t, 1H), 7.71(d, 1H), 7.75(d, 1H), 9.18(s, 1H). FAB mass showed  $m/z = 127.17$  [HEMIm] $^+$ . The content of chloride anion was 24 ppm. The water content was 266 ppm.

### 6.3. [HEMIm][PF<sub>6</sub>]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.72(q, 2H), 3.88(s, 3H), 4.21(t, 2H), 5.29(t, 1H), 7.71(d, 1H), 7.75(d, 1H), 9.18(s, 1H). FAB mass showed  $m/z = 127.17$  [HEMIm] $^+$ . The content of chloride anion was 48 ppm. The water content was 183 ppm.

### 6.4. [HEMIm][TFSI]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.72(q, 2H), 3.88(s, 3H), 4.21(t, 2H), 5.29(t, 1H), 7.71(d, 1H), 7.75(d, 1H), 9.18(s, 1H). FAB mass showed  $m/z = 127.17$  [HEMIm] $^+$ . The water content was 54 ppm.

### 6.5. [HEMMor][Br]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed  $m/z = 146$  [HEMMor] $^+$ .

### 6.6. [HEMMor][BF<sub>4</sub>]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed  $m/z = 146.03$  [HEMMor] $^+$ . The content of bromide anion was 130 ppm. The water content was 192.4 ppm.

### 6.7. [HEMMor][PF<sub>6</sub>]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.47(t, 2H), 3.53(t, 2H), 3.6(t, 2H), 3.89(s, 2H), 3.95(s, 4H), 5.32(t, 1H). FAB mass showed  $m/z = 146.1$  [HEMMor] $^+$ . The content of bromide anion was 158 ppm. The water content was 78 ppm.

### 6.8. [HEMMor][TFSI]

The  $^1\text{H}$  NMR (DMSO,  $\delta$  (ppm), relative to TMS) spectrum consists of the following peaks: 3.21(s, 3H), 3.42–3.48(t, 2H), 3.49–3.53(t, 2H), 3.6(t, 2H), 3.87–3.89(s, 2H), 3.92–3.56(m, 4H), 5.32(t, 1H). FAB mass showed  $m/z = 146.1$  [HEMMor] $^+$ . The content of bromide anion was 129.3 ppm. The water content was 123 ppm.

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