

Synthesis and Ionic Conductivities of Lithium-Doped Morpholinium Salts

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Abstract—A series of a new type of ionic liquids was prepared. The synthesis and purification procedure of N-alkyl-N-methylmorpholinium bromide, N-alkyl-N-methylmorpholinium tetrafluoroborate, N-alkyl-N-methylmorpholinium hexafluorophosphate, and N-alkyl-N-methylmorpholinium bis(trifluoromethanesulfonyl)imide were presented. Thermal properties of morpholinium salts and ionic conductivities of lithium-doped ionic liquids were measured in the temperature range of 303.15 to 323.15 K. In the case of the pure ionic liquids, the ionic conductivities were $10^{-4} \text{ S} \cdot \text{cm}^{-1}$.

Key words: Ionic Liquid, Electrochemical Property, N-alkyl-N-methylmorpholinium Bromide ([Mor][Br]), N-alkyl-N-methylmorpholinium Tetrafluoroborate ([Mor][BF₄]), N-alkyl-N-methylmorpholinium Hexafluorophosphate ([Mor][PF₆]), N-alkyl-N-methylmorpholinium Bis(trifluoromethanesulfonyl)imide ([Mor][TFSI]), Lithium Doped Electrolyte

INTRODUCTION

Ionic liquids (ILs) have received growing attention in both academic and industrial circles. Intrinsically, they have numerous useful characteristics such as non-volatility, high ionic conductivity, wide electrochemical window, negligible-flammability, and high thermal stability [Ngo et al., 2000; Welton, 1999; Marsh et al., 2002; Kim et al., 2004a]. Normally as conventional electrolytes in a lithium ion battery system, organic carbonates and cyclic and non-cyclic groups have been used in the form of binary solvents in order to induce high ionic conductivity [Ding et al., 2001]. However, in the case of organic solvents, relatively high vapor pressure and narrow potential window tend to cause low performance and lack of safety. Therefore the applications of ILs to electrolytes have newly been suggested for their adaptable properties in battery systems [Yoshizawa et al., 2002].

In the synthesis of ILs, innumerable combinations of organic cations, inorganic anions and alkyl chains are available, and it is possible to change the properties of ILs by the variation of the ion species [Forsyth et al., 2000; Marsh et al., 2002]. Impurities contained in ILs also affect overall properties of ILs, so the purification step is important in the synthesis process.

Until now, most of the reports concerned with the ILs have focused on 1,3-dialkylimidazolium salts, although an enormous number of ILs have been newly synthesized. The imidazolium cation based ILs have overall favorable properties compared to others, and also their physical and electrochemical information is easily accessible. However, most cation sources of ILs are expensive for various industrial applications. The investigation of novel ILs and their properties is still challenging in order to lower the cost and enhance the properties of ILs.

In this context, we suggest new ILs based on morpholinium cation.

Morpholinium ILs favorable properties are as follows. (1) Synthetic mechanism is simple and overall reaction time is short. (2) The cheaper costs of 4-methylmorpholine compared to those of imidazole could lead to low product costs. (3) The oxygen group in the morpholinium cation is expected to effectively dissociate Li salts, thereby improving ionic conductivity [Kim et al., 2004b]. In this study, we synthesized a new series of morpholinium based ILs such as N-alkyl-N-methylmorpholinium bromide ([Mor][Br]), N-alkyl-N-methylmorpholinium tetrafluoroborate ([Mor][BF₄]), N-alkyl-N-methylmorpholinium hexafluorophosphate ([Mor][PF₆]), and N-alkyl-N-methylmorpholinium bis(trifluoromethanesulfonyl)imide ([Mor][TFSI]). Thermal properties and ionic conductivities were measured in the temperature range of 303.15 to 323.15 K in the LiTFSI-doped [Mor][TFSI] systems.

EXPERIMENTAL SECTION

1. Materials

4-methylmorpholine (Aldrich, 99%), bromoethane (Aldrich, 99%), 1-bromobutane (Aldrich, 99%), 1-bromooctane (Aldrich, 99%), ammonium fluoroborate (Aldrich, 99%), potassium hexafluorophosphate (Aldrich, 98%), and bis(trifluoromethanesulfonyl)imide lithium salt (Fluka, 99%) were used without other treatment. Acetonitrile (99.9%) and dichloromethane (99.9%) were obtained from Merk and used as received.

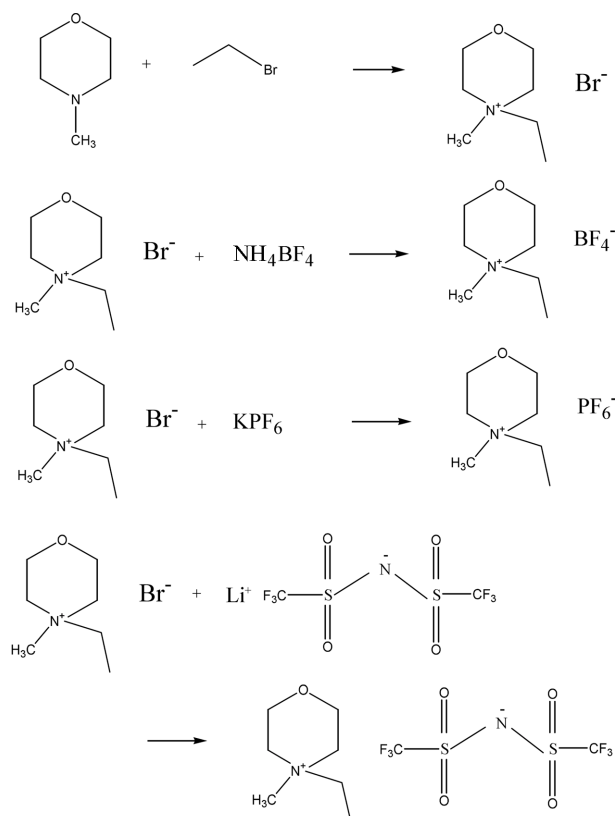
After the synthesis was finished, final products were checked by ¹H NMR spectra from a Bruker AMX FT 500 MHz NMR spectrometer and Fab Mass spectra from High Resolution Tandem Mass Spectrometer.

2. Synthesis of Ionic Liquids

We prepared [Mor][BF₄], [Mor][PF₆], and [Mor][TFSI] using the synthetic process illustrated in Scheme 1. A series of morpholinium bromides was synthesized and recrystallized. After ion exchanging, they were purified by following methods. After filtering by the filter paper, they were repeatedly washed with mixture of

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Scheme 1. Synthetic process of morpholinium cation based ILs.

water and dichloromethane for removing the by-product. The synthetic procedure of $[\text{Mor}_{1,2}][\text{BF}_4]$ was adopted in the synthesis of all ILs suggested in this study. Yield and anion contents of the product are described in Table 1.

$[\text{Mor}_{1,2}][\text{BF}_4]$ For the $[\text{Mor}_{1,2}][\text{BF}_4]$, 32.69 g (0.30 mol) of bromoethane was added dropwise over 1 h to a solution of 30.35 g (0.30 mol) of 4-methylmorpholine in 200 mL of acetonitrile while stirring vigorously, and N_2 bubbling was used. The mixture was refluxed for 5 h at 343.15 K. The molten salt was decanted, washed three times with 100 mL of dichloroethane, and dried on a rotavapor for 1 h at 343.15 K under low pressure. The solid product ($[\text{Mor}_{1,2}][\text{Br}]$) was dried under vacuum at 313.15 K for more than 48 h, and 56.67 g of the product was obtained (yield 90.00%).

20.96 g (0.20 mol) of NH_4BF_4 was added to 41.98 g (0.20 mol) of $[\text{Mor}_{1,2}][\text{Br}]$ in 150 mL of acetonitrile. The mixture was stirred for 2 days at 343.15 K, and NH_4Br was filtered by the filter paper. Then, the mixture was washed with the mixture including water and dichloromethane. After roto-evaporation of the solvent, the $[\text{Mor}_{1,2}][\text{BF}_4]$ was dried product under vacuum at 313.15 K for more than

48 h, and obtained 35.55 g of the product (yield 82.20%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.14–4.04 (m, 4H), 3.79–3.75 (q, 2H), 3.67–3.61 (m, 4H), 3.39–3.36 (s, 3H), 1.50–1.46 (t, 3H). FAB MS : $m/z=130$ $[\text{Mor}_{1,2}]^+$. Br-content : 5.60 ppm.

$[\text{Mor}_{1,4}][\text{BF}_4]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. For $[\text{Mor}_{1,4}][\text{BF}_4]$, 41.11 g (0.30 mol) of 1-bromobutane was used instead of bromoethane and got 58.52 g of $[\text{Mor}_{1,4}][\text{Br}]$ (yield 82.00%). 40.00 g of $[\text{Mor}_{1,4}][\text{BF}_4]$ was obtained from 47.58 g (0.20 mol) of $[\text{Mor}_{1,4}][\text{Br}]$ (yield 81.70%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.12–4.03 (m, 4H), 3.67–3.60 (m, 6H), 3.36 (s, 3H), 1.92–1.85 (m, 2H), 1.48–1.40 (m, 2H), 1.00–0.97 (t, 3H). FAB MS : $m/z=158$ $[\text{Mor}_{1,4}]^+$. Br-content : 145.00 ppm.

$[\text{Mor}_{1,8}][\text{BF}_4]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. For $[\text{Mor}_{1,8}][\text{BF}_4]$, 57.94 g (0.30 mol) of 1-bromooctane was used instead of bromoethane and got 81.12 g of $[\text{Mor}_{1,8}][\text{Br}]$ (yield 92.00%). 51.14 g of $[\text{Mor}_{1,8}][\text{BF}_4]$ was obtained from 58.78 g (0.20 mol) of $[\text{Mor}_{1,8}][\text{Br}]$ (yield 85.10%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.13–4.05 (m, 4H), 3.70–3.63 (m, 6H), 3.39 (s, 3H), 1.97–1.90 (m, 2H), 1.44–1.36 (m, 4H), 1.35–1.26 (m, 6H), 0.88–0.86 (t, 3H). FAB MS : $m/z=214$ $[\text{Mor}_{1,8}]^+$. Br-content : 101.10 ppm.

$[\text{Mor}_{1,2}][\text{PF}_6]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. 49.42 g of $[\text{Mor}_{1,2}][\text{PF}_6]$ was obtained from 41.98 g (0.20 mol) of $[\text{Mor}_{1,2}][\text{Br}]$ and 38.81 g (0.20 mol) of KPF_6 (yield 89.86%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.16–4.07 (m, 4H), 3.82–3.78 (q, 2H), 3.69–3.66 (m, 4H), 3.40 (s, 3H), 1.52–1.48 (t, 3H). FAB MS : $m/z=130$ $[\text{Mor}_{1,2}]^+$. Br-content : 57.4 ppm.

$[\text{Mor}_{1,4}][\text{PF}_6]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. 40.64 g of $[\text{Mor}_{1,4}][\text{PF}_6]$ was obtained from 47.58 g (0.20 mol) of $[\text{Mor}_{1,4}][\text{Br}]$ and 38.81 g (0.20 mol) of KPF_6 (yield 83.30%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.13–4.11 (m, 4H), 3.73–3.67 (m, 6H), 3.43 (s, 3H), 1.96–1.90 (m, 2H), 1.48–1.43 (m, 2H), 1.01–0.98 (t, 3H). FAB MS : $m/z=158$ $[\text{Mor}_{1,4}]^+$. Br-content : 80.10 ppm.

$[\text{Mor}_{1,8}][\text{PF}_6]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. 70.36 g of $[\text{Mor}_{1,8}][\text{PF}_6]$ was obtained from 58.78 g (0.20 mol) of $[\text{Mor}_{1,8}][\text{Br}]$ and 38.81 g (0.20 mol) of KPF_6 (yield 98.00%).

$^1\text{H-NMR}$ (Acetone, δ ppm) 4.12–4.11 (m, 4H), 3.73–3.66 (m, 6H), 3.44 (s, 3H), 1.98–1.95 (m, 2H), 1.45–1.38 (m, 4H), 1.35–1.26 (m, 6H), 0.88–0.86 (t, 3H). FAB MS : $m/z=214$ $[\text{Mor}_{1,8}]^+$. Br-content : 89.30 ppm.

$[\text{Mor}_{1,2}][\text{TFSI}]$ The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. 28.00 g of $[\text{Mor}_{1,2}][\text{TFSI}]$ was obtained from 21.00 g (0.10 mol) of $[\text{Mor}_{1,2}][\text{Br}]$ and 28.71 g (0.10 mol) of LiTFSI (yield 70.00%).

$^1\text{H-NMR}$ (D_2O , δ ppm), 4.08 (m, 4H), 3.59–3.50 (m, 6H), 3.19

Table 1. Summary of ionic liquids

	Ionic liquids							
	$[\text{Mor}_{1,2}][\text{BF}_4]$	$[\text{Mor}_{1,4}][\text{BF}_4]$	$[\text{Mor}_{1,8}][\text{BF}_4]$	$[\text{Mor}_{1,2}][\text{PF}_6]$	$[\text{Mor}_{1,4}][\text{PF}_6]$	$[\text{Mor}_{1,8}][\text{PF}_6]$	$[\text{Mor}_{1,2}][\text{TFSI}]$	$[\text{Mor}_{1,4}][\text{TFSI}]$
Yield (%)	82.2	81.7	85.1	89.86	83.30	98.0	70.0	75.0
Br^- concnts. (ppm)	5.6	145	101.1	57.4	80.1	89.3	-	-

(s, 3H), 1.41 (t, 3H). FAB MS : $m/z=130.00$ $[\text{Mor}_{1,2}]^+$. Br-content: not detected by ion chromatography.

[Mor_{1,4}][TFSI] The same apparatus and similar procedure were used as for $[\text{Mor}_{1,2}][\text{BF}_4]$. 33.00 g of $[\text{Mor}_{1,4}][\text{TFSI}]$ was obtained from 24.00 g (0.10 mol) of $[\text{Mor}_{1,4}][\text{Br}]$ and 28.71 g (0.10 mol) of LiTFSI (yield 75.00%).

¹H-NMR (D_2O , δ /ppm), 4.08 (m, 4H), 3.56-3.47 (m, 6H), 3.21 (s, 3H), 1.82-1.80 (m, 2H), 1.46-1.42 (m, 2H), 1.01-0.98 (t, 3H). FAB MS : $m/z=158$ $[\text{Mor}_{1,4}]^+$. Br-content: not detected by ion chromatography.

3. Apparatus and Procedure

Ionic conductivities The ionic conductivities of the morpholinium cation based ionic liquids were measured by complex impedance analysis using a Solartron 1260A frequency response analyzer over a frequency range of 100 Hz-1 MHz. In this work, the ionic conductivity could be calculated from the bulk resistance (R_b) found in complex impedance diagram. Ionic conductivities of $[\text{Mor}_{1,2}][\text{TFSI}]$ and $[\text{Mor}_{1,4}][\text{TFSI}]$ were measured in the temperature range from 303.15 to 323.15 K. For measuring the ionic conductivity, Kynar 761 (ATOCHEM) was used to make film samples. Kynar 761 was mixed with each IL, 30 weight% Kynar and 70 weight% IL, in N,N-dimethylformamide (DMF) at room temperature for 24 h. The mixture was poured and flattened on a flat glass by doctor blade. After drying in vacuum oven for 48 h, films were obtained.

Thermal properties N-alkyl-N-methylmorpholinium salts were measured by Dupont TA 2000 differential scanning calorimetry (DSC) under nitrogen gas at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Two-step synthesis was used to prepare morpholinium salts. All final products were in solid state. Recrystallization was applicable to separate byproduct from primary product using proper solvents. ¹H NMR and Fab Mass spectra were used for structural analysis of the prepared ILs. Also, Br⁻ contents were recorded, which is important because the thermophysical properties such as melting points and viscosities might depend on the halogen anion contents. Table 1 indicates the summary of the yield and contents of anion for each IL.

Thermal data of morpholinium salts are summarized in Table 2. Except $[\text{Mor}_{1,8}][\text{PF}_6]$, the melting points of morpholinium salts are below 373.15 K. Especially, it is very noticeable that the melting points of $[\text{Mor}][\text{TFSI}]$ were recorded near room temperature. Melting temperature was illustrated by anion species sequence, $[\text{Mor}][\text{PF}_6]>[\text{Mor}][\text{BF}_4]>[\text{Mor}][\text{TFSI}]$.

Three samples, 10 mol%, 20 mol%, and 30 mol% of LiTFSI in $[\text{Mor}][\text{TFSI}]$, were used for ionic conductivity measurements. Fig. 1 and 2 illustrated ionic conductivities for pure ILs and lithium doped morpholinium based ILs at the various concentrations and temper-

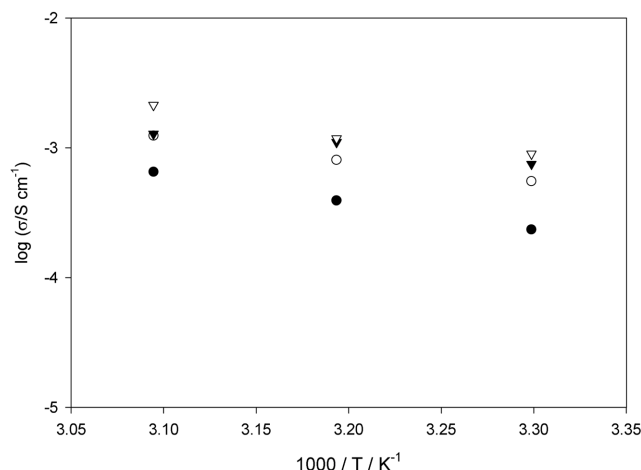


Fig. 1. Ionic conductivity of $[\text{Mor}_{1,2}][\text{TFSI}]$ (●), 10% Lithium ion doped $[\text{Mor}_{1,2}][\text{TFSI}]$ (○), 20% Lithium ion doped $[\text{Mor}_{1,2}][\text{TFSI}]$ (▼), 30% Lithium ion doped $[\text{Mor}_{1,2}][\text{TFSI}]$ (▽).

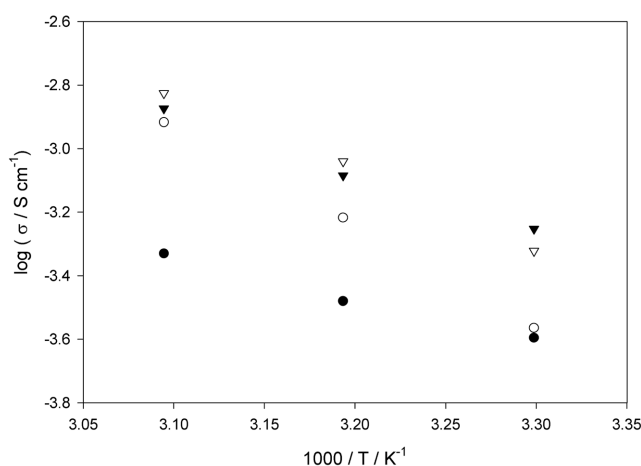


Fig. 2. Ionic conductivity of $[\text{Mor}_{1,4}][\text{TFSI}]$ (●), 10% Lithium ion doped $[\text{Mor}_{1,4}][\text{TFSI}]$ (○), 20% Lithium ion doped $[\text{Mor}_{1,4}][\text{TFSI}]$ (▼), 30% Lithium ion doped $[\text{Mor}_{1,4}][\text{TFSI}]$ (▽).

atures. The values of ionic conductivities of Li doped $[\text{Mor}][\text{TFSI}]$ systems are summarized in Table 3 and Table 4. Ionic conductivities increased with increasing the temperature and in the proportion to the mol concentration of LiTFSI. The ionic conductivities of pure $[\text{Mor}_{1,2}][\text{TFSI}]$ and $[\text{Mor}_{1,4}][\text{TFSI}]$ were $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ to $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ over the given temperature range. The ionic conductivities of lithium doped ILs are higher than those of pure ILs because the polar oxygen group in morpholinium cation might facilitate to dissociate Li salts.

It is of interest to indicate the overall comparison between mor-

Table 2. Thermal data of $[\text{Mor}][\text{BF}_4]$, $[\text{Mor}][\text{PF}_6]$, and $[\text{Mor}][\text{TFSI}]$

	Ionic liquids							
	$[\text{Mor}_{1,2}][\text{BF}_4]$	$[\text{Mor}_{1,4}][\text{BF}_4]$	$[\text{Mor}_{1,8}][\text{BF}_4]$	$[\text{Mor}_{1,2}][\text{PF}_6]$	$[\text{Mor}_{1,4}][\text{PF}_6]$	$[\text{Mor}_{1,8}][\text{PF}_6]$	$[\text{Mor}_{1,2}][\text{TFSI}]$	$[\text{Mor}_{1,4}][\text{TFSI}]$
Melting point (K)	324.19	350.77	319.61	358.75	366.68	380.06	302.35	301.85

Table 3. Ionic conductivities as a function of inverse temperature for Li doped Mor_{1,2}TFSI systems

Temperature (1000/T/K)	Ionic conductivity (log (S·cm ⁻¹)) of Mor _{1,2} TFSI			
	0% LiTFSI	10% LiTFSI	20% LiTFSI	30% LiTFSI
3.2987	-3.6289	-3.2572	-3.1250	-3.0468
3.1934	-3.4060	-3.0934	-2.9570	-2.9289
3.0945	-3.1846	-2.9067	-2.8934	-3.6711

Table 4. Ionic conductivities as a function of inverse temperature for Li doped Mor_{1,4}TFSI systems

Temperature (1000/T/K)	Ionic conductivity (log(S·cm ⁻¹)) of Mor _{1,4} TFSI			
	0% LiTFSI	10% LiTFSI	20% LiTFSI	30% LiTFSI
3.2987	-3.5951	-3.5643	-3.2525	-3.3220
3.1934	-3.4800	-3.2175	-3.0847	-3.0400
3.0945	-3.3300	-2.9169	-2.8736	-2.8259

pholinium and imidazolium salts. The reaction time of morpholinium salts is shorter than that of imidazolium salt, and the cost of 4-methylmorpholine as a cation source of morpholinium salts is cheaper than 1-methylimidazole. In both salts, synthesis and purification processes are easy and product reproducibility is good. These morpholinium salts melt above room temperature, and the overall melting points are higher than those of imidazolium salts.

CONCLUSION

A series of morpholinium cation based ILs was prepared and their thermal properties and ionic conductivities were measured. The synthetic and purification processes were also described. Relatively [Mor_{1,2}][TFSI] and [Mor_{1,4}][TFSI] have low melting point near room temperature when compared to [BF₄] and [PF₆] salts. The ionic conductivities were investigated for the lithium doped [TFSI] salts. It is believed that the [TFSI] salts effectively dissociate the lithium salts, which could lead to overall high ionic conductivities.

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