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Impact of lithium salt addition on ionic transporting properties in a binary ionic liquid electrolyte composed of 4-(2-methoxyethyl)-4-methylmorpholinium bis(trifluoromethanesulfonyl)imide and LiTFSI

Yuan-Chung Lin[a], Chung-Wen Kuo[b], Ping-Lin Kuo[c], Lin Hao[d], Lan-Yu Tseng[e], Tzi-Yi Wu[e,*]

[a] *Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan*
[b] *Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan*
[c] *Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan*
[d] *Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan*
[e] *Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan*

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ABSTRACT

We conducted a study on the transport properties of an ionic liquid 4-(2-methoxyethyl)-4-methylmorpholin-4-ium bis(trifluoromethylsulfonyl)amide (**[MorMEOM][TFSI]**) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI)-doped **[MorMEOM][TFSI]** at various temperature and atmospheric pressure states through conductivity, viscosity, and self-diffusion coefficient characterizations. Based on the Walden rule, the α values of neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]** estimated from the slopes of Walden plots were compared to those calculated from $E_{a,\Lambda}/E_{a,\eta}$. The diffusion coefficients of ^{1}H, ^{19}F and ^{7}Li were determined using the PGSE-NMR method to carry out a study of the dynamics of the cations, anions, and ion pairs. All of the neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]** gave approximately straight lines for change in the D with $T\eta^{-1}$, demonstrating that the Stokes–Einstein equation holds for the ionic diffusivity in the ILs.

1. Introduction

For the past few years, ionic liquids (ILs) and ILs-based electrolytes have been used for a wide range of academic and industrial applications [1–9]. They are liquids at temperatures below 373.15 K and are composed entirely of ions. Their rich properties, such as nonvolatility, high electrochemical stability, and high ionic conductivity, make them attractive candidates as electrolytes in lithium ion batteries [10,11], supercapacitors [12], dye sensitized solar cells [13–17], and fuel cells [18]. In addition, ILs' properties such as transport properties or the chemical and electrochemical stability can be adjusted by changing the cyclic component or the side chain of the cation [19,20].

Development of the ionic liquids still requires relatively low cost and easy preparation. Several low cost ionic liquids have been reported, amino acid ionic liquids have attracted a great deal of attention due to their low cost, biodegradability, low viscosity, low toxicity, and potential application in large-scale energy storage [21,22]. Alkyl sulfate-based ionic liquids are prepared in large quantities from cheap alkylating agents and easily available chemicals [23,24]. Morpholinium-based ionic liquids might be applicable to electrolytes due to their low cost and good transport properties [25,26]. For example, when morpholinium-based ILs are used as the electrolytes in lithium ion batteries, the oxygen atoms in the morpholinium can dissociate the lithium salts. Moreover, the ether oxygen of Li-doped alkoxy-ILs might give rise to specific interactions with the Li^{+} cations, and result in attractive behaviors on the carrier migration mechanism. It has also been reported that the incorporation of ether groups in the alkyl side chains of the cation causes viscosity and melting point to decrease and the lithium ion transference number to increase [27]. This can be attributed to the incorporation of ether groups that increase the flexibility of ILs. Other advantages regarding the incorporation of ether groups in morpholinium salt are the suppression of self-aggregation behaviors between cations and anions [28], and the enhancement of polarity [29].

In the present study, the influence of lithium salt concentration on ion transport and dissociation in LiTFSI-doped morpholinium-based ionic liquid (**[MorMEOM][TFSI]**) electrolyte was evaluated. The relationship between the molar conductivity and the dynamic viscosity

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* Corresponding author. Tel.: +886 5 5342601x4626.
E-mail address: wuty@yuntech.edu.tw (T.-Y. Wu).

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in the neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]** was analyzed using the Walden rule. By using the PGSE-NMR method, the temperature-dependent diffusion coefficients of the **MorMEOM** cation (D_{MorMEOM^+}), TFSI anion (D_{TFSI^-}), and the lithium ion (D_{Li^+}) as a function of the lithium salt concentration were measured using ^{1}H, ^{19}F, and ^{7}Li NMR, respectively. The lithium transference number (t_{Li}) in an electrolyte formed by doping **[MorMEOM][TFSI]** with the lithium salt LiTFSI was also estimated using PGSE-NMR method.

2. Experimental

2.1. Materials and measurements

2-Chloroethyl methyl ether (98%), 4-methylmorpholine (98%), and LiTFSI (99%) were obtained from Alfa Aesar, TCI, Acros, and Aldrich and used as received. Poly(1-(benzo[d][1,3]dioxol-5-yl)-2,5-di(thiophen-2-yl)-pyrrole) (PMDOB) was prepared from previously published procedures [30]. The conductivity of the ILs was measured using a conductivity meter LF 340 and a standard conductivity cell TetraCon 325 (Wissenschaftlich-Technische Werkstätten GmbH, Germany). The cell was calibrated before each sample measurement using an aqueous 0.01M KCl solution. The density of ILs was measured with a dilatometer, which was calibrated by measuring the density of neat glycerin at 303.15, 313.15, 323.15, 333.15, 343.15, and 353.15 K. The dilatometer was placed in a thermostatic water bath (TV-4000, TAMSON), and its temperature was adjusted to within ±0.01 K. To measure density, ILs were placed into the dilatometer up to the mark, the top of the capillary tube (located on the top of the dilatometer) was sealed, and the dilatometer (with capillary tube) was placed into a temperature bath for 10 min to allow the temperature to equilibrate. The major interval between the two marks in the capillary tube was 0.01 cm^3, and the minor interval between two marks was 0.001 cm^3. From the correction coefficient of neat glycerin in capillary tube at different temperatures, the ρ of ILs by the expanded volume of liquid in the capillary tube at various temperatures can be estimated. Each sample was measured at least three times to determine an average value, and the measured values of density were ±0.0001 g/mL. The viscosity (η) of the ILs was measured using a calibrated modified Ostwald viscometer (Cannon–Fenske glass capillary viscometers, CFRU, 9721-A50) [31,32]. The viscometer was placed in a thermostatic water bath (TV-4000, TAMSON), in which the temperature was adjusted to within ±0.01 K. For each IL, the experimental viscosity was obtained by averaging three to five flow time measurements. The water content of the synthesized IL was detected using a Karl–Fischer moisture titrator (Metrohm 73KF coulometer), and the water content was less than 100 ppm.

2.2. Synthesis of 4-(2-methoxyethyl)-4-methylmorpholin-4-ium chloride [MorMEOM][Cl]

2-Chloroethyl methyl ether (89.8 g, 0.95 mol) and 4-methylmorpholine (63.7 g, 0.63 mol) were added to a reactor and stirred at 80 °C for 24 h. After the mixture was cooled, diethyl ether was added to the crude product and mixed thoroughly. The diethyl ether was decanted, and the remaining diethyl ether was removed by a rotavapor. The neat product was dried in a vacuum for 2 days. Yield: 77%. ^{1}H NMR (300 MHz, D_2O, ppm): δ 3.19 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 3.46 (t, 2H, CH_2), 3.52 (t, 2H, CH_2), 3.65 (t, 2H, CH_2), 3.85 (t, 2H, CH_2), 3.97 (m, 4H, CH_2). Elem. Anal. Calcd. for $C_8H_{18}ClNO_2$: C, 49.10%; H, 9.27%; N, 7.16%. Found: C, 49.15%; H, 9.18%; N, 7.14%.

2.3. Synthesis of 4-(2-methoxyethyl)-4-methylmorpholin-4-ium bis(trifluoromethylsulfonyl)amide [MorMEOM][TFSI]

LiTFSI (100 mmol, 28.7 g), **[MorMEOM][Cl]** (100 mmol, 19.6 g), and a 100 mL of H_2O were added to a 250-mL two-necked glass reactor. The mixture was stirred at 60 °C for 3 h. After cooling, an oily crude product was formed, which was extracted with chloroform (100 mL). After extracting, an oily product was obtained by removing the solvent and the neat product was dried in a vacuum at 100 °C to remove the water. Yield: 91%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 3.26 (s, 3H, CH_3), 3.40 (s, 3H, CH_3), 3.47 (t, 2H, CH_2), 3.58 (t, 2H, CH_2), 3.69 (t, 2H, CH_2), 3.86 (t, 2H, CH_2), 4.01 (m, 4H, CH_2). ^{19}F NMR (400 MHz, DMSO-d_6): 84.0 ppm. Elem. Anal. Calcd. for $C_{10}H_{18}F_6N_2O_6S_2$: C, 27.27%; H, 4.12%; N, 6.36%. Found: C, 27.25%; H, 4.08%; N, 6.28%. The Cl^- content was confirmed using ICP-MS, and it was below 0.5% (w/w). The structure of **[MorMEOM][TFSI]** is shown in Fig. 1.

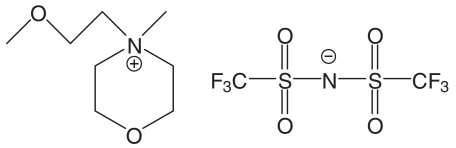

Fig. 1. Chemical structure of 4-(2-methoxyethyl)-4-methylmorpholin-4-ium bis(trifluoromethylsulfonyl)amide **[MorMEOM][TFSI]**.

2.4. Self-diffusion coefficient measurements

ILs were degassed and sealed in a cylindrical Pyrex tube under high vacuum conditions. The sealed sample tube was inserted into a 5 mm tube filled with an external lock D_2O solvent. ^{1}H, ^{19}F, and ^{7}Li NMR diffusion coefficient measurements were implemented on a Bruker Avance 400 with a 5 mm PFG probe. The signals of ^{1}H in [MorMEOM]$^+$, ^{7}Li in Li$^+$, and ^{19}F in bis(trifluoromethanesulfonyl)imide anion were used for the determination of D_{MorMEOM^+}, D_{Li^+}, and D_{TFSI^-}, respectively. The sample temperature was controlled within ±0.1 K using a temperature control meter (Bruker, Germany).

PGSE-NMR diffusion measurements were implemented using a stimulated spin-echo sequence. In the NMR experiment, the self-diffusion coefficient (D) of cations and anion can be determined from the following equation [33]:

$$\ln\left(\frac{A}{A_0}\right) = -D\gamma^2\left(\Delta - \frac{\delta}{3}\right)\delta^2 g^2 \tag{1}$$

where A and A_0 are the signal integrals in the presence and absence of the PFG, respectively, γ is the nuclear magnetogyric ratio, Δ is the interval between the two gradient pulses, δ is the width of gradient pulse, and g is the magnitude of gradient. In this work, the pulse-field-gradient interval Δ determines the diffusion time and was below 1.0 s, δ was set between 1 and 3 ms, and g was set using a suitable strength [34,35]. The experimental D_{MorMEOM^+}, D_{Li^+}, and D_{TFSI^-} values were measured five or more times at each temperature, and their errors were evaluated to be less than 3%.

3. Results and discussion

3.1. Ionic conductivity and viscosity of neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]**

The fundamental properties of neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]**, including the physicochemical quantities of density (ρ), viscosity (η), and conductivity (σ), were measured at 303.15–353.15 K. As shown in Fig. 2, a strong linear relationship of ρ *vs.* T was observed for neat **[MorMEOM][TFSI]** and LiTFSI-doped **[MorMEOM][TFSI]**. The following equation expresses this dependence:

$$\rho = a + bT \tag{2}$$

where a, b, and T are the density at 0 K (g/cm^3), the volume expansion coefficient (g/cm^3 K), and absolute temperature (K), respectively. The

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