Conductivity Behavior of Ionomers and Ionic Liquids in Non-Aqueous Solutions

By

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ABSTRACT OF THESIS

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The conductivity behavior of ionomers and ionic liquids in non-aqueous solvents was studied. Ionic liquids (BMIM-PF₆ and EMIM-TF) were dissolved in polar (DMF) and non-polar (THF) solvents and solution conductivity was measured. When dissolved in a polar solvent, ionic groups in ionic liquids stayed as electrolytes, which resulted in the high conductivity of the solution in DMF. The conductivity measurement was also carried out on the systems of polymers (SPS-Na ionomer, PS, and PMMA) and an ionic liquid (BMIM-PF₆) dissolved in DMF and THF, respectively. Regardless of the types of polymers, all the solutions in DMF showed the same conductivity, which was identical to that of the pure ionic liquid in DMF. However, when the solvent was switched to THF, the conductivity of the solution containing both ionic liquid and ionomer was negligible compared to the other solutions. This change in conductivity was due to the aggregation between ionomer and ionic liquid in a non-polar solvent (THF). In order to further investigate the effect of the solvent polarity on the solution conductivity with both ionic liquid and ionomer, ionomer was dissolved in a series of DMF/THF solvent mixtures and the ionic liquid was added. At the same concentration of the ionic liquid, the solution conductivity increased with increasing the content of DMF. This phenomenon suggests that the ionic groups tend to dissociate in the high-polarity solvent and associate in the low-polarity solvent.

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1. Introduction

1.1 Research Motivations

Ionic liquids are the liquid electrolytes composed entirely of ions. Different from normal molten salts which are generally considered as the materials with high melting point, ionic liquids have a low melting temperature below 100°C and exist in the liquid state at room temperature [1-4]. In addition to low melting temperature, they have unique properties, such as high thermal stability, low vapor pressure, and high ion conductivity [5-6]. Because of these characteristics, ionic liquids have been considered for applications in the fields of energy generators, electrochemistry and batteries in recent years. Research has been reported on their applications in the lithium-ion battery due to the high ion conductivity and high thermal stability. Ionic liquids are also used as the electrochemical solvents for the electrodeposition of metal and semiconductor [7-10].

Ionomers are the polymers containing both neutral units and ionic groups. The content of ionic groups is up to 15 mol%. These ionic groups are randomly distributed along the backbone chains, which change the properties of ionomers in a dramatic way [11-15]. Compared to neutral polymers, modulus and viscosity are increased by several orders of magnitude. The glass transition temperature of ionomers is also significantly higher than neutral polymers. These phenomena are observed due to the presence of reversible ionic crosslinks (aggregates) in the structures of ionomers [16].

Previous research done by our group indicates that these ionic groups behave differently when they are dissolved in the solvent with different polarities by viscosity and light scattering measurements. In a high-polarity solvent, ionic groups dissociate in the solution showing polyelectrolyte behavior. In a low-polarity solvent, ionic groups tend to associate in the solution and form aggregates [11,17]. One of the goals of this study is to extend the previous work that is to investigate the effect of the solvent polarity on the ionic group's behaviors of ionomer by conductivity measurement.

While the properties of ionic liquids and ionomers have been studied separately in the literature [11,13-19], no work has been reported on the system in which both ionic liquids and ionomers are present. In order to study the interactions between ionomers and ionic liquids, the conductivity behavior of both ionomers and ionic liquids was investigated in the solvent with various polarities in this work. Considering the growing attention and wide application of these materials, it is worthwhile to study such a topic.

1.2 Electrical Conductivity Measurement

Electrical conductivity measurement has been used to determine the properties of ionic liquids mainly in aqueous solvents [19-22]. In addition, previous research has reported that the conductivity of pure ionic liquids has been measured [23]. Due to the high accuracy and precision of conductivity measurement, it can also examine solution behaviors of ionomers in a solution.

A conductivity meter, composed of an instrument and an enclosed conductivity cell, is a major tool used in electrical conductivity measurement. Several necessary term definitions are listed as follows. First, conductivity is the ability of a solution to conduct electric current. On the contrary, the definition of resistivity is the property that a material is able to oppose the flow of electric current. The resistance (ohms) of a solution is defined through Ohm's law:

R=V/I

where V represents voltage (volts) and I is current (amperes). Conductance G is defined as:

$$\mathbf{G}=1/\mathbf{R}\left(\mathbf{S}\right)$$

In addition, the observed specific conductivity κ is defined as:

$$\kappa = G \bullet K (S/cm)$$

where K is cell constant in units of cm⁻¹. Cell constant is a parameter of conductivity cell:

$$K = d/a$$

where a is the effective area of the electrodes (cm²), and d is the distance between the electrodes (cm). For solutions of low conductivity, the conductivity cell with cell constant lower than one is used for measurement, which is 0.1 cm⁻¹ or 0.01 cm⁻¹. Due to the low conductivity of the solutions, the electrodes should be placed closer or the area should be made larger so that the conductance would be raised up and it would be easier for the meter to obtain the accurate results. Similarly, the cell with the higher cell constant, such as 10 cm⁻¹, is used for solutions with high conductivity. The cell constant of the YSI 3403 conductivity cell used in this work is 1.0 cm⁻¹.

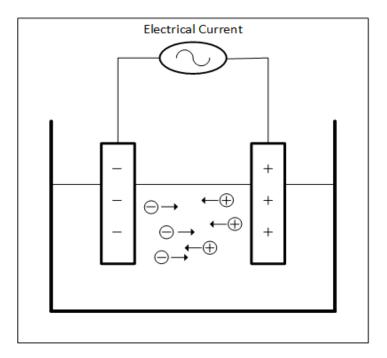


Figure 1: Conductivity measurement mechanism

When the measurement is performed, the conductivity meter actually measures the conductance G of the solution and transforms it into the observed conductivity κ as shown on the display. During the process, the cell is immersed in a solution containing electrolytes. The cations move to the negative electrode and the anions are attracted to the positive electrode. The solution conductivity is measured by determining the resistance of the solution between the two electrodes. The mechanism is shown in Figure 1.

2. Experimental Methods

2.1 Materials

Polystyrene (PS) and poly (methyl methacrylate) (PMMA), provided by Polysciences Inc., were the neutral polymers used as reference solutes in this study. In addition, a type of ionomers that is poly (styrene-co-sodium styrenesulfonate) (3.60% ion content) (SPS-Na) was prepared in this laboratory based on the sulfonation reaction method reported by Bellinger et al [24].

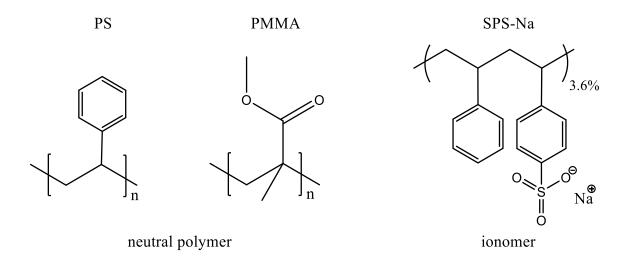


Figure 2: Chemical structures of PS,PMMA, and SPS-Na used in this study

With regard to ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) and 1-ethyl-3-methylimidazolium triflate (EMIM-TF) were obtained from Iolitech. The information and structures of both ionic liquids can be found in Table 1 and Figure 3. As shown in Figure 3, the cation of these two ionic liquids is imidazolium, which is a common cation in ionic liquids. The imidazolium ionic liquids show the properties of low vapor pressure and low glass transformation temperature [26]. The only difference between EMIM and BMIM is the side chain length, which can easily change

the properties of ionic liquids.

Table 1: A list of ionic liquids

CAS number	Abbreviation	Full Name	Formula	Molecular Weight (g/mol)	
174501-64-5	BMIM-PF ₆	1-butyl-3-methylimidaz olium hexafluorophosphate	$C_8H_{15}F_6N_2P$	284.19	
145022-44-2	EMIM-TF	1-ethyl-3-methylimidaz olium trifluoromethane sulfonate	$C_7H_{11}F_3N_2O_3S$	260.23	

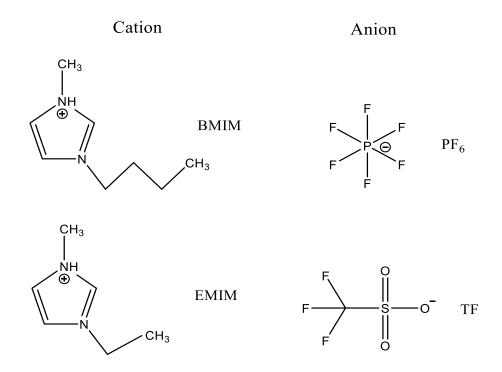


Figure 3: Chemical structures of the ionic liquids used in this study

Dimethylformamide (DMF) and tetrahydrofuran (THF) obtained from Aldrich were used in this study. DMF and THF were commonly used organic solvents with high solubility [11]. The polymers and ionic liquids described above can be easily dissolved in both solvents. Table 2 shows the dielectric constant of DMF and THF, which indicates that THF is a solvent with low polarity and DMF is a solvent with high polarity.

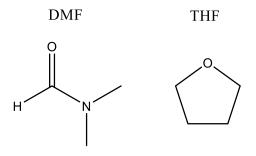


Figure 4: Chemical structures of the solvents used in this study

Table 2: A list of solvents

Solvent	Formula	Dielectric Constant (ε)
DMF	(CH ₃) ₂ NC(O)H	36.7
THF	(CH ₂) ₄ O	7.6
water	H ₂ O	80.1

2.2 Equipment

The conductivity was measured in this study at room temperature using Fisher Scientific accumet[®] model 20 pH/mV/Conductivity meter (Denver Instrument.) (Figure 6), as well as an enclosed YSI 3403 conductivity cell (Figure 5). The YSI cell has the high accuracy of $\pm 1\%$, which guarantees the accuracy of the data obtained.



Figure 5: YSI 3403 conductivity cell



Figure 6: Fisher Scientific accumet® model 20 pH/mV/conductivity meter

2.3 Experimental Procedure

Conductivity measurement required preparations one day before the experiment day. The 25 mL of polymer solution samples was prepared in a 50 or 100 mL flask with a stirring bar and was placed on a magnetic stirrer to stir overnight. The speed of magnetic stirrer should be kept in a low range since the ionomer may aggregate in solution when stirred at high speed.

On the day of the measurement, the standardization of the conductivity meter was performed using the standard solution with the conductivity of 1409 μ s/cm before the actual measurement. The standard solution, which contains 0.07% potassium chloride and 99.3% water, was obtained from LabChem. The conductivity cell was taken out of the test tube containing distilled water and rinsed with fresh distilled water. Then the cell was dipped into the cylinder with 25 mL standard solution. The standardization procedure was

performed by setting the reading of the meter at 1409 μ s/cm. In the case that the reading was not stable, this process should be repeated until the reading on the display became stable at 1409 μ s/cm.

After standardization, the conductivity measurement of the prepared sample was carried out. The 25 mL sample solution was transferred into the cylinder using a 10 mL pipet. The cylinder was placed on a magnetic stirrer in order to get a homogeneous mixture, which was critical to the accuracy and reliability of measurement results. After taken out of the standard solution, the conductivity cell was rinsed with distilled water and the solvent (same as the solvent in the sample solution). When being dipped into the sample solution, the cell was placed in the cylinder properly without producing bubbles in the cell chamber or touching the stirring bar in order to obtain reliable data.

When stable, the reading on the display was recorded each time after the ionic liquid was added using a disposable pipet. This procedure was repeated during the whole measuring process. The total weight of the solution and cylinder was measured by the electronic balance at the beginning and at the end of the whole process.

After all the conductivity measurements were finished, the cell needed to be cleaned thoroughly. At first, it was rinsed with the organic solvent (same solvent as used for measured sample), acetone, and distilled water in order. Afterward, the cell was dipped into the cleaning solution and agitated for approximately three minutes. In the next step, the cell was kept in the test tube filled with distilled water. If the cell has been cleaned thoroughly, the conductivity value displayed on the meter should be very small because the conductivity of distilled water is relatively low. If not, the cleaning procedure should be repeated. Finally, all the pipettes, cylinders, and other glassware were cleaned.

Since most of the measurements in this work used the weight concentration of ionic liquids as the x-axis, it was important to reduce the error to a minimum when measuring the amount of ionic liquid used each time. Since BMIM-PF₆ and EMIM-TF were viscous and the amount of the ionic liquids used each time was very small, it was not practical to weigh a certain amount of ionic liquid on the electronic balance and then transfer it into the solution. Therefore, other two methods were tested and compared.

The first method was to take the cell out of the cylinder every time after adding ionic liquid into the sample solution and then measure the weight of the cylinder which contains the solution. The difference between two adjacent weights was the amount of the ionic liquid added each time. The second method was to measure the amount by only weighing the cylinder with the solution at the beginning and the end of the whole process. The weight of the ionic liquid used in every measurement was an average, which could be calculated by dividing the difference between two values of the total weights by the times of measurements.

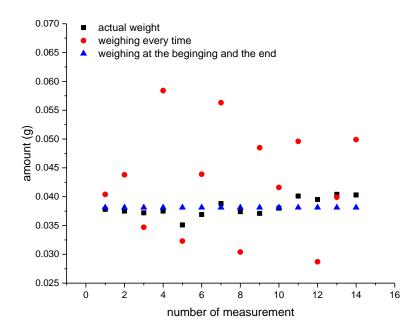


Figure 7: Amount of ionic liquid vs. number of measurement for the two methods and the actual weight

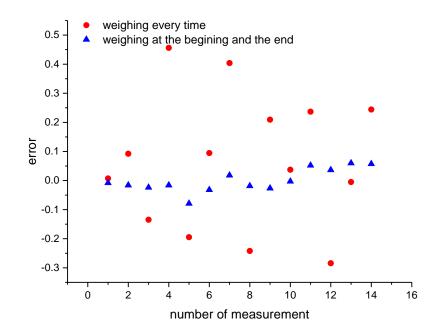


Figure 8: Weighing error vs. number of measurement of the two methods

To assess the accuracy of these two methods, we simulated the actual measuring process

by weighing the ionic liquid used each time by adding it through a disposable pipet directly into a beaker on the electronic balance. It was regarded as the actual amount of ionic liquid, which was used as the reference values. As shown in Figure 7, the weight of the ionic liquid measured by the first method is more dispersed than the second one in reference to the actual amount. In addition, the error of two methods was calculated. Figure 8 indicates that the error of the second method is smaller than the first one.

Therefore, both comparison results, the numerical values of the weights and the errors, show that the second method is more accurate than the first one. One of the reasons is that when the weight of ionic liquid was measured each time, there was some residue of the solution attached to the cell. Thus, the weights were not accurate. Taking account of the relatively small value of the weight of the ionic liquid used each time, the effect of the residue on the accuracy was great. As a result, we decided to use the second method, which was to weigh the total amount of cylinder and the solution at the beginning and at the end of the whole process. The amount of ionic liquid was obtained by calculating the average value.

3. Results and Discussion

3.1 Conductometric Titration

Conductometric titration is a kind of titration where the conductivity of a solution is measured when the titrant is gradually added to the solution. It is an accurate method to provide the accurate results in many cases [25]. During the titration, some of the ions in the solution are neutralized by the titrant which leads to the changes of conductivity. The endpoint could be determined graphically in the figure of the solution conductivity vs. the volume of titrant used. In this work, water based and organic solvent based titrations were performed.

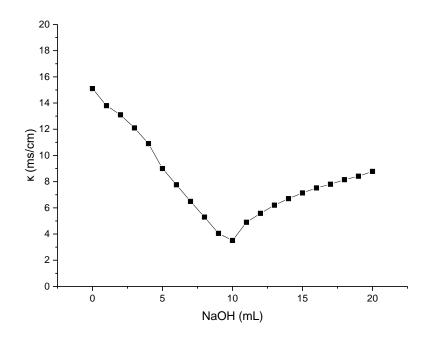


Figure 9: Conductivity vs. volume of NaOH for water-based titration

Figure 9 illustrates the conductivity curve in water based titration. At first, the conductivity decreases until it reaches the endpoint of conductivity. After that, it begins to increase with the addition of NaOH. This curve indicates that the H^+ ions of the HCl

solution, which initially existed in the solution, were gradually neutralized by the OH⁻ ions of the titrant up to the endpoint. Meanwhile, due to the neutralization reaction in the system, H_2O molecules are formed. They had no contributions to the solution conductivity. Hence, the conductivity keeps decreasing until the endpoint. When all the H^+ ions are neutralized, the conductivity reaches the endpoint where the solution conductivity is the lowest. After that point, it begins to go up because all the H^+ ions have been consumed and NaOH can produce Na⁺ and OH⁻ ions whose concentrations are increased as well.

Water based conductometric titration was also used to ensure the accuracy and reliability of the measuring system used in this work. As shown in Figure 9, the volume of NaOH solution consumed is equivalent to the initial volume of HCl solution at the endpoint under the precondition that the concentrations of NaOH and HCl solutions used were set to be equal. It proves that the system is reliable. Moreover, the conductivity curve of methanol based titration (see Figure 10) also shows the similar trend.

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Table 3: A	TISE OF	CONCINC		OI IOUS	III water

Ion	Conductivity Λ (cm ² S/mol)
H^{+}	349.82
OH-	198.0
Na ⁺	50.1
Cl ⁻	76.4

In addition, Figure 9 is not bilaterally symmetrical. Compared to the initial part of the curve before the endpoint, which decreases sharply, the rising trend of the solution

conductivity after the endpoint is relatively flat. The reason is that the OH^- ions replace the H^+ ions in the solution after endpoint. The OH^- ions has lower conductivity than H^+ ions in water. (shown in Table 3).

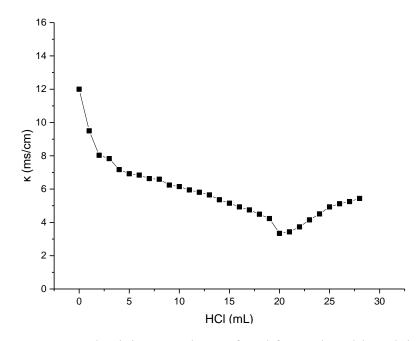


Figure 10: Conductivity vs. volume of HCl for methanol-based titration

When the water based and organic solvent based titration are compared, the trends of the solution conductivity are similar. However, the numerical changes in conductivity are different, which can be attributed to the fact that the ions have different conductivity depending on the type of solvents.

3.2 Ion Content Determination of Ionomers

Conductometric titration can be used to determine the ion content of randomly sulfonated polystyrene (SPS) ionomer because the ionic groups interact with the ions of titrant while the neutral units of the ionomer do not. The procedures were similar to methanol based titration, except the normality of titrant and the weight of ionomer used was known in advance. When the ion content determination was carried out, the SPS ionomer was dissolved in DMF and titrated by methanolic NaOH. During the process, the following reaction occurred in the system, which was similar to the neutralization reaction in the water based titration.

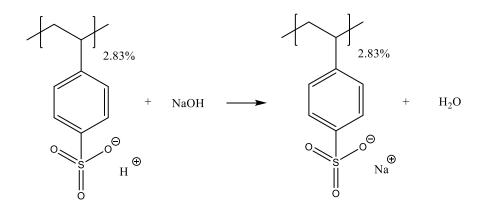


Figure 11 shows the curve of conductivity during the process of ion content determination. In general, conductivity increases with increasing volume of NaOH. However, the trend increases more after the endpoint. The volume of methanolic NaOH at the endpoint is used to calculate the ion content as follows:

Where P is the weight of the polymer in grams and x is the ion content in fraction. For example, if x equals to 0.01, then ion content is 1 mol%. N represents the normality of NaOH solution in the units of mol/liter. V is the volume of NaOH solution (liters) corresponding to the endpoint. Another equation that can be reduced from the equation above:

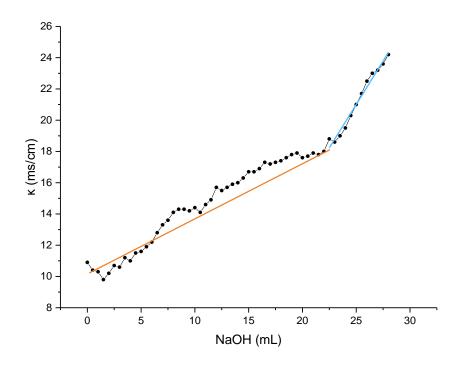


Figure 11: Conductivity vs. volume of NaOH for ion content determination

By using the volume of NaOH at the endpoint, the ion content calculated through this method is 2.861%. Comparing to the 2.83% ion content tested previously, the error was 1.1%. Thus, it also proves that using conductometric titration to determine the ion content of SPS ionomer is a reliable method.

3.3 Conductivity of Ionic Liquids in Organic Solvents

Conductivity was measured when BMIM-PF₆ was gradually added into DMF, THF, and the solvent mixtures, respectively. Figure 12 shows the conductivity of BMIM-PF₆ in the solvent mixtures of DMF and THF with several DMF content ranging from 0% to 100%. The conductivity of all the solutions increases proportionally when the BMIM-PF₆ weight concentration increases. In addition, the solutions show higher conductivity values with higher content of DMF when they are compared at the same $BMIM-PF_6$ weight concentration. It indicates that the ionic groups dissociate in the solvent with high polarity and associate in the solvent with low polarity.

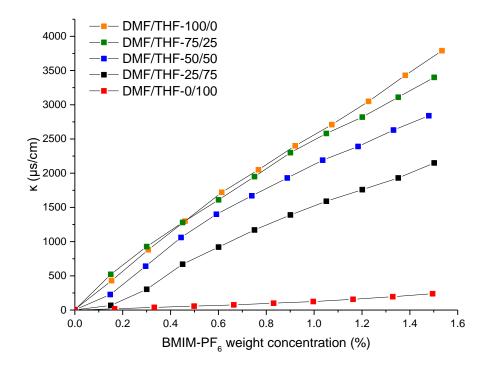


Figure 12: Conductivity vs. BMIM-PF₆ weight concentration for pure BMIM-PF₆ in solvent mixtures of THF and DMF

Particularly, the phenomenon that conductivity is larger in the solution with a higher content of DMF is most obvious under the extreme conditions, which are in pure DMF and in pure THF. When BMIM-PF₆ is dissolved in DMF, the solution conductivity is the highest among all the solutions, while the conductivity curve of THF solution is the lowest (close to the x-axis).

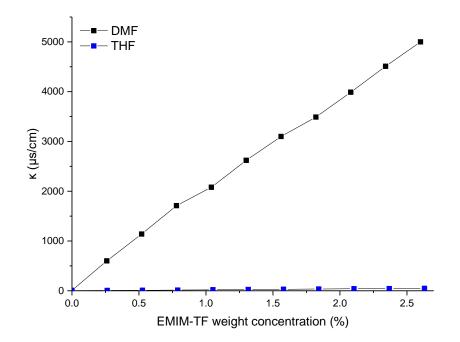


Figure 13: Conductivity vs. EMIM-TF weight concentration for EMIM-TF in DMF and THF

Conductivity measurement was also carried out on the system that EMIM-TF dissolved in pure THF and DMF. Similar to the results of BMIM-PF₆, the solution conductivity of EMIM-TF is much higher when it is dissolved in DMF than in THF as seen in Figure 13. In addition, the conductivity values of EMIM-TF are lower than that of BMIM-PF₆ in the same. The reason is that although the cation of BMIM-PF₆ and EMIM-TF is the same, the side chain length of these ionic liquids is different. As a result, their abilities to conduct electric current in the solution are not the same.



Figure 14: Ionic liquid in DMF and THF

The results of BMIM-PF₆ and EMIM-TF suggests that such conductivity phenomena are general to the ionic liquids that have similar structures to BMIM-PF₆ and EMIM-TF. Figure 14 is a schematic figure showing the dissociation and association of the ionic groups in a polar solvent and in a non-polar solvent. The dissociation of ionic groups leads to the high conductivity in solutions with high polarity, and the association results in the low conductivity in low-polarity solutions.

3.4 Conductivity of Polymers and Ionic Liquids in Organic Solvents

To study ionic aggregation between ionomers and ionic liquids, conductivity measurement was performed on the system in which both ionomer and ionic liquid are present. In addition, neutral polymers were used in order to be compared with the results on ionomer. First, PS and SPS-Na ionomer were dissolved in THF and DMF initially as sample solutions. The conductivity of pure BMIM-PF₆ solutions could be used as a reference. In these measurements, the concentrations of neutral polymers and ionomer were fixed in order to avoid the effect of solute concentration. In the measurement, BMIM-PF₆ was added to the sample solutions and conductivity was measured after each

time of BMIM-PF₆ addition.

Figure 15 shows the conductivity vs. BMIM-PF₆ weight concentration for six cases, which are conductivity values of pure BMIM-PF₆, PS, and SPS-Na in DMF, as well as these substances in THF. For solutions in THF, the conductivity of all three solutions was identical, which shows increasing trends with increasing the BMIM-PF₆ weight concentration. It indicates that adding PS or SPS-Na into the solution in DMF has no effect on the conductivity. Hence, there is no almost no interactions between ionomer (or neutral polymers) and ionic liquid when they are dissolved in the solvent with high polarity. The ionomer (or neutral polymers) has no effect on the behavior of ionic liquids.

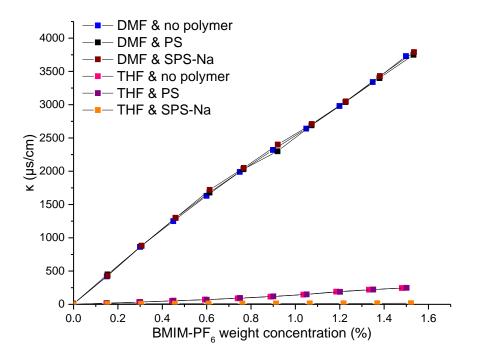
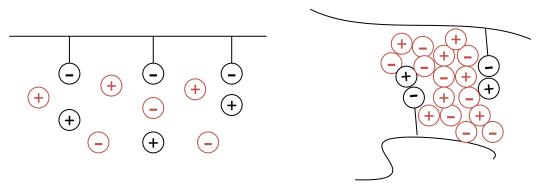


Figure 15: Conductivity vs. BMIM-PF₆ weight concentration for different solutes with BMIM-PF₆ in DMF and THF

While the solution conductivity of PS is also the same as pure BMIM-PF₆ in THF, it is smaller compared with the solution conductivity in DMF. However, the conductivity of

SPS-Na sample in THF shows a big difference from the other solutions. It is almost negligible compared with the other two samples in THF. THF was a non-polar solvent so that the ionic groups of ionomer and ionic liquid form aggregates. Since the aggregates have no contributions to the solution conductivity, the curve almost falls on the x-axis. Figure 16 is a schematic figure showing the dissociation and association of the ionic groups in ionic liquid and ionomer in a polar solvent and in a non-polar solvent. The red ions represent the ions of ionic liquids, and the black ones are ionic groups of ionomers.



polar solvent

non-polar solvent

Figure 16: Ionomers and ionic liquids in DMF and THF

In order to exclude the possibility that the extremely low conductivity of ionomer and ionic liquid in THF solvent was influenced by the high polarity of ionomer, PMMA was also used in this work. PMMA and PS are both neutral polymers while PMMA is more polar. By dissolving the same amount of PMMA in THF as a sample solution, the conductivity was measured with BMIM-PF₆ added. The results were compared with the others to determine whether there were interactions between PMMA and BMIM-PF₆.

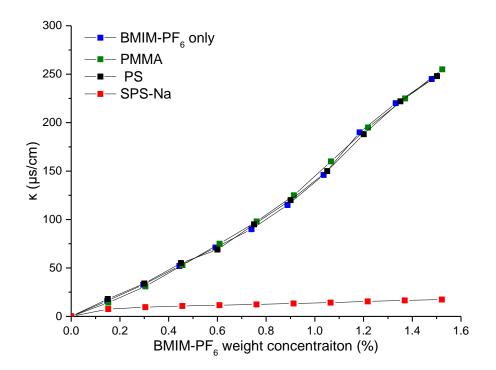


Figure 17: Conductivity vs. BMIM-PF₆ weight concentration for pure BMIM-PF₆, PMMA, and SPS-Na in THF

Figure 17 illustrates that the conductivity of PMMA solution is the same as the pure BMIM-PF₆ solution as well as the SPS-Na solution. It indicates that PMMA has no interactions with BMIM-PF₆ in THF. Since PMMA has no ionic groups, the ions of BMIM-PF₆ could not form ion pairs with it. These ions could dissociate in the solution and contribute to conductivity instead of being trapped in the ionic aggregation. Therefore, the polarity of the neutral polymers is not one of the essential factors that would influence ionic aggregation behavior in low polarity solvent. Compared with neutral polymers, only ionomers can form ion pairs with the ionic liquid and cause the extremely low solution conductivity in the non-polar solvent.

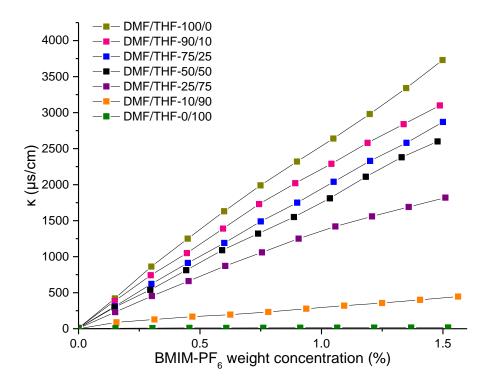


Figure 18: Conductivity vs. BMIM-PF₆ weight concentration for SPS-Na in solvent mixtures of DMF and THF

Moreover, in order to determine the effect of the polarity of solvent on ionic aggregation behavior, SPS-Na was dissolved in solvent mixtures of DMF and THF, with DMF content ranging from 0% to 100%. Figure 18 plots the conductivity vs. BMIM-PF₆ weight concentration for SPS-Na in the solvent mixtures. All curves of conductivity show the same trend: conductivity increases with increasing weight concentration of BMIM-PF₆. The solution conductivity is higher when it is measured in the solvent with higher content of DMF. As the DMF content increases, ionic groups tend to dissociate in the solution and contribute to conductivity. The lowest value of conductivity shown in Figure 18 is ionomer and ionic liquid dissolved in pure THF solvent, which almost falls on the x-axis. It suggests that the cations and anions form aggregates in the non-polar solvent. As a consequence, conductivity is significantly small since the ion pairs are electroneutral. The highest conductivity appears in the solution with the highest content of DMF, where cations and anions dissociate and move to the poles of conductivity meter more easily. Therefore, the conductivity of solutions of ionomer and ionic liquid increases when they are dissolved in the high-polarity solvents.

4. Conclusion and Future Work

The conductivity behavior of ionomers and ionic liquids in non-aqueous solvents was investigated in this study. The conductivity of two ionic liquids was measured in the organic solvents with various polarities. In addition, the solution conductivity of ionomers and neutral polymers was also measured with an ionic liquid in the solvents, and the results were compared.

BMIM-PF₆ and EMIM-TF were added gradually to the solvent mixtures of DMF and THF with the DMF content ranging from 0% to 100%. For BMIM-PF₆, the conductivity of all the solutions increased proportionally when BMIM-PF₆ weight concentration increased. The conductivity was higher in the solution with a higher content of DMF when it was compared at the same BMIM-PF₆ weight concentration. For EMIM-TF, the conductivity was measured in pure THF and DMF, respectively. Similar to the results on BMIM-PF₆, the conductivity of the solution in DMF was significantly higher than the conductivity of the solution in THF.

Moreover, the same amount of PS, PMMA, and SPS-Na were separately dissolved in DMF and THF. Conductivity measurement was carried out when BMIM-PF₆ was added to these solutions. For solutions with DMF, the conductivity values of PS, PMMA, and SPS-Na samples were all identical, which were also the same as the conductivity of the pure BMIM-PF₆ in DMF solvent. For solutions with THF, the conductivity values of PS and PMMA were the same as the pure BMIM-PF₆ in THF. The conductivity of SPS-Na in THF solvent with BMIM-PF₆ was the lowest one, which was negligible compared to the others. Finally, it is observed that the solutions with ionomer and ionic liquid showed lower conductivity in the non-polar solvent (THF) than in the high-polarity solvent

(DMF).

In order to further investigate the effect of the solvent polarity on the conductivity of the solution in which both ionomer and ionic liquid were present, SPS-Na was dissolved in a series of DMF/THF solvent mixtures with the DMF content ranging from 0% to 100%. The conductivity increased when the content of DMF increased at the same BMIM-PF₆ weight concentration. The highest and lowest conductivity appeared correspondingly in the solutions with pure DMF and THF. The conclusion can be drawn that ions of ionomer and ionic liquid tend to dissociate in the solvent with high polarity and associate in the solvent with low polarity.

In future studies, the interactions between ionomers and ionic liquids, as well as their effect on solution conductivity can continue to be investigated. The work would be extended to other systems of ionomers and ionic liquids with different structures. The unique aggregation behavior between ionomers and ionic liquids can be used in lots of applications, such as batteries. Because the polarity of solvent has influence on the aggregation behavior, the electrons can be either reserved or released by changing the solvent polarity. Furthermore, other factors that would affect the aggregation behaviors of ionomers and ionic liquids can be an interesting area to explore, for example, temperature and ionomer concentration.

5. References

[1] Electrochemical aspects of ionic liquids. John Wiley & Sons, 2011.

[2] Dupont J, de Souza R F, Suarez P A Z. Ionic liquid (molten salt) phase organometallic catalysis. Chemical reviews, 2002, 102(10): 3667-3692.

[3] Wasserscheid P, Keim W. Ionic liquids—new "solutions" for transition metal catalysis. Angewandte Chemie International Edition, 2000, 39(21): 3772-3789.

[4] Rogers R D, Seddon K R. Ionic liquids--solvents of the future? Science, 2003, 302(5646): 792-793.

[5] Chiappe C, Pieraccini D. Ionic liquids: solvent properties and organic reactivity. Journal of Physical Organic Chemistry, 2005, 18(4): 275-297.

[6] Marsh K N, Boxall J A, Lichtenthaler R. Room temperature ionic liquids and their mixtures—a review. Fluid Phase Equilibria, 2004, 219(1): 93-98.

[7] Earle M J, Seddon K R. Ionic liquids. Green solvents for the future. Pure and applied chemistry, 2000, 72(7): 1391-1398.

[8] Armand M, Endres F, MacFarlane D R, et al. Ionic-liquid materials for the electrochemical challenges of the future. Nature materials, 2009, 8(8): 621-629.

[9] Plylahan N, Kerner M, Lim D H, et al. Ionic liquid and hybrid ionic liquid/organic electrolytes for high temperature lithium-ion battery application. Electrochimica Acta, 2016, 216: 24-34.

[10] Abbott A P, McKenzie K J. Application of ionic liquids to the electrodeposition of metals. Physical Chemistry Chemical Physics, 2006, 8(37): 4265-4279.

[11] Hara M, Wu J, Lee A H. Effect of intra-and intermolecular interactions on solution properties of sulfonated polystyrene ionomers. Macromolecules, 1988, 21(7): 2214-2218.

[12] Ion-containing polymers: physical properties and structure. Elsevier, 2012.

[13] Hara M, Lee A H, Wu J. Solution properties of ionomers. I. Counterion effect. Journal of Polymer Science Part B: Polymer Physics, 1987, 25(7): 1407-1418.

[14] Hara M, Wu J, Lee A H. Solution properties of ionomers. 2. Simple salt effect. Macromolecules, 1989, 22(2): 754-757.

[15] Zhou Z, Peiffer D G, Chu B. Light scattering studies of block ionomer aggregation characteristics in nonpolar solvent. Macromolecules, 1994, 27(6): 1428-1433.

[16] Structure and properties of ionomers. Springer Science & Business Media, 2012.

[17] Hara M, Wu J L. Light scattering study of ionomers in solution. 2. Low-angle scattering from sulfonated polystyrene ionomers. Macromolecules, 1988, 21(2): 402-407.

[18] Vila J, Gines P, Rilo E, et al. Great increase of the electrical conductivity of ionic liquids in aqueous solutions. Fluid phase equilibria, 2006, 247(1): 32-39.

[19] Boruń A, Bald A. Ionic association and conductance of [emim][BF4] and [bmim][BF4] in 1-butanol in a wide range of temperature. The Journal of Chemical Thermodynamics, 2016, 96: 175-180.

[20] Inoue T, Ebina H, Dong B, et al. Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. Journal of colloid and interface science, 2007, 314(1): 236-241.

[21] Liu W, Zhao T, Zhang Y, et al. The physical properties of aqueous solutions of the ionic liquid [BMIM][BF4]. Journal of solution chemistry, 2006, 35(10): 1337-1346.

[22] Galiński M, Lewandowski A, Stępniak I. Ionic liquids as electrolytes. Electrochimica Acta, 2006, 51(26): 5567-5580.

[23] Widegren J A, Saurer E M, Marsh K N, et al. Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. The journal of chemical thermodynamics, 2005, 37(6): 569-575.

[24] Bellinger M A, Sauer J A, Hara M. Tensile fracture properties of rigid-rigid blends made of sulfonated polystyrene ionomer and polystyrene. Macromolecules, 1994, 27(21): 6147-6155.

[25] Grunwald E. End Point Calculation in Conductometric and Photometric Titrations. Analytical Chemistry, 1956, 28(7): 1112-1116.

[26] Ngo H L, LeCompte K, Hargens L, et al. Thermal properties of imidazolium ionic liquids. Thermochimica Acta, 2000, 357: 97-102.