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SOLUTION PROPERTIES OF IONOMERS IN LOW-POLARITY SOLVENTS  
CONTAINING IONIC LIQUIDS

By

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Masanori Hara

And approved by

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## ABSTRACT OF THESIS

### Solution Properties of Ionomers in Low-Polarity Solvents Containing Ionic Liquids

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The effect of low-polarity solvents on the properties of sulfonated polystyrene sodium salt ionomer (SPS-Na), sulfonated polystyrene calcium salt ionomer (SPS-Ca), and poly(methyl methacrylate)(PMMA-Na) ionomers were studied through viscosity experiments. Ionomers were dissolved in different low polarity solvents and viscosity measurements conducted at dilute concentrations. Intramolecular bonds between ionomer chains dominate at dilute concentrations and resulted in a decrease in solution viscosity. The relative change in viscosity was determined by the strength of the ionomer counterions as well as solvent polarity. All three ionomers were first dissolved in a mixture of benzene and methanol with the concentration of methanol in the solvent varied between 1-10% to study the change in viscosity as a function of solvent polarity. Solution viscosity increased with increasing methanol content, with a more noticeable effect occurring in PMMA-Na and SPS-Na. In addition, the solubility of the ionomers were tested in solvent mixtures of tetrahydrofuran (THF) and eight different ionic liquids in the imidazolium family. Similar viscosity behavior was observed for some of the solvent mixtures containing ionic liquids, and in some cases the ionic liquid was observed to be more effective than benzene and methanol. Finally, it was observed that the chemical structure of the ionic liquids played a part in the viscosity behavior for ionomers.

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## **1. Introduction**

### *1.1 Research Motivations*

Ionomers are types of polymer that contain ions at low concentration, typically between 5-15%, that are distributed randomly through the polymer chains and significantly enhance the material properties through the formation of ionic bonds [1-8]. Due to the presence of ionic aggregates that form, ionomers can have significantly higher impact strength, stiffness, and resistance to abrasion when compared to non-ionic polymers. In addition, the ionic crosslinks have a significant effect on the glass transition temperature, viscosity, and modulus of the polymer. This is due to the ionic bonds, as primary bonds, which are several orders of magnitudes stronger than the secondary bonds normally found between chains in non-ionic polymers [1,2].

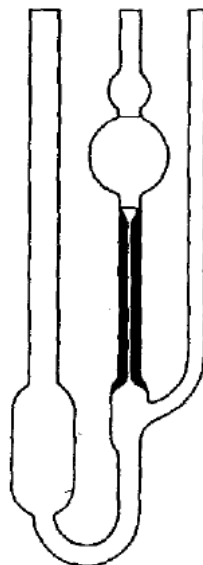
Ionomers are used in a variety of different applications, which is why it is important to study the properties. Understanding the solution properties of ionomers and the effects of different solvents is key to developing efficient processing, so the focus of this study was studying the solution properties of three different ionomers. The viscosity of poly(methyl methacrylate)(PMMA) ionomer, sulfonated polystyrene (PS) ionomer sodium salt, and sulfonated PS ionomer calcium salt were measured in different low-polarity solvents to study the ionic aggregation behavior. In addition to the viscosity, the effect of different solvents on the solution properties of the specific ionomers were examined and the viability of ionic liquids as solvents for ionomers was tested.

Ionic liquids are salts with unusually low melting points due to weakly associated cations and anions [9-13]. The unique characteristics of ionic liquids, such as extremely low vapor

pressure or high thermal and chemical stability, make them attractive for a large number of applications, including polymer science [10-13]. Recent studies have shown that ionic liquids can be incorporated into polymers as composites, be used for polymerization, and for solubilization of polymers [10-13]. However, limited work has been done on the solubilization of polymers in ionic liquids, and to our knowledge there is not yet any work documenting the effect of ionic liquids on the solubilization of ionomers. Due to the widespread use of ionomers in industry, and the growing attention on applications for ionic liquids, the interactions between ionomer and ionic liquid is an area that is valuable to investigate. Thus, in this study the solubility and viscosity of three ionomers were tested in various low-polarity solvents including eight different ionic liquids.

## *1.2 Viscosity Measurements*

Measurement of the solution viscosity is widely recognized as an effective method for studying the properties of polymers [5,14,15]. Solution viscosity is measured by comparing the efflux time of a polymer solution with a specific volume to the efflux time of the pure solvent through a capillary of a specific size [14]. Measurements of viscosity are usually performed in capillary viscometers of the Ubbelohde type, as seen in Figure 1.1, because they are independent of the amount of solution as this allows for performing measurements at a series of concentrations as opposed to a single concentration [14,16].



**Figure 1.1:** Ubbelohde Viscometer<sup>[14]</sup>

From the efflux time of the polymer solution  $t$ , the efflux time of the solvent  $t_0$ , and the solution concentration, the viscosity can be calculated from the equations listed below.

**Table 1.1:** Solution viscosity nomenclature<sup>[14]</sup>

Name	Equation
Relative Viscosity	$\eta_r = \eta/\eta_0 \cong t/t_0$
Specific Viscosity	$\eta_{sp} = \eta_r - 1 = (t - t_0)/t_0$
Reduced Viscosity	$\eta_{red} = \eta_{sp}/c$
Intrinsic Viscosity	$[\eta] = (\eta_{sp}/c)_{c=0} = [(\ln \eta_r)/c]_{c=0}$

In particular, the reduced viscosity, or the ratio of specific viscosity to the concentration, is how results are typically reported for polymer measurements because it normalizes the viscosity with respect to polymer concentration. It is known that increasing the concentration of polymer in the sample will increase the viscosity, but this is not an important or interesting observation. Thus, the viscosity is normalized with respect to

concentration in order to observe the effects of other factors, such as the presence of ionic aggregates or the type of solvent used to break the ionic aggregates.

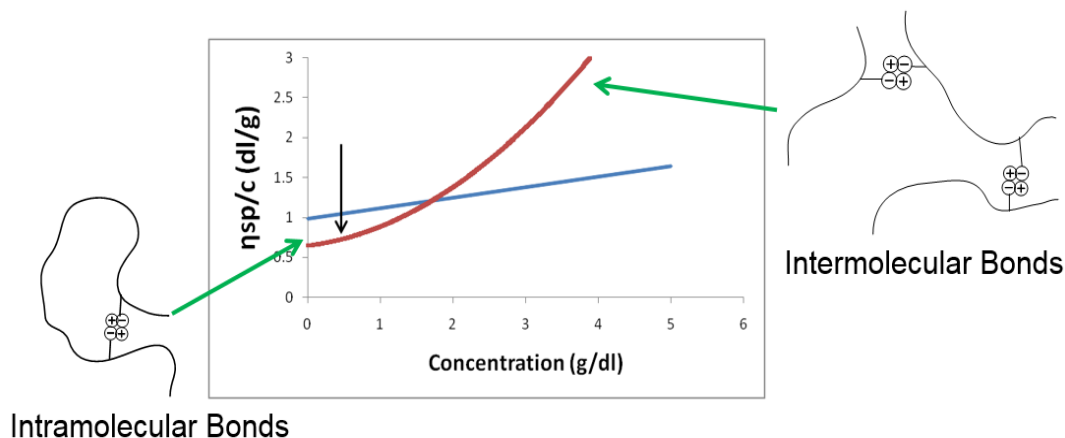
The other important value from Table 1.1 is the intrinsic viscosity which is found by extrapolating the reduced viscosity to zero concentration. The intrinsic viscosity can be used with the Mark-Houwink-Sakurada relations to estimate the molecular weight using empirical data for different polymer-solvent combinations. The Mark-Houwink-Sakurada relation will be discussed further as a method of estimating polymer molecular weights in section 2.1.

### *1.3 Aggregation Behavior of Ionomers*

In low-polarity or nonpolar solvents ionomers display aggregation behavior where counterions associate to form ionic dipoles [1-8, 17-21]. In nonpolar solvents, the electrical environment of the ionomers is similar to the solid state and is widely used to study the nature of aggregation of polymers in the solid state [17]. In polar organic solvent systems, such as DMF, ionomers display polyelectrolyte behavior which is markedly different from the aggregation behavior in low-polarity solvents [17, 23-24]. However, polar systems are outside of the scope of this work, which was instead focused on aggregation behavior and solvents with low polarity.

Viscosity measurements are a common experimental method for studying the aggregation behavior of ionomers in nonpolar or low-polarity solvents [5,14,15]. The aggregates that form in ionomer solutions have a noticeable effect on the solution viscosity, but the type of effect is very different depending on the concentration of the ionomer in the solution. If

the solution is concentrated, the aggregates cause a sharp increase in reduced viscosity, whereas if the ionomer solution is dilute, a decrease in reduced viscosity of the solution is actually observed [5, 7-8, 17]. The reason for this behavior is the type of molecular interactions that dominate at specific concentrations. Figure 1.2 shows a schematic of reduced viscosity vs. concentration and illustrates the typical viscosity behavior of ionomers and its dependence on concentration.



**Figure 1.2:** Effect of ionic aggregation of solution viscosity

At low concentrations the reduced viscosity of the ionomer is lower than the viscosity of the neutral polymer. This is attributed to the dominant presence of intramolecular ionic aggregation, which occurs between different monomers of the same polymer chain. These intramolecular bonds cause the ionomer chains to contract on itself and shrink in size [5,17]. The viscosity of the ionomer solution is determined by the strength of the ionic dipoles formed and the polarity of the solvent used. As the polarity of the solvent increases there are fewer ionic bonds able to form and less ionomers chains contract due to the ionic aggregation. This will result in the viscosity being closer to that of the neutral polymer which has no ionic aggregates. Also, the change in the viscosity as the polarity of the

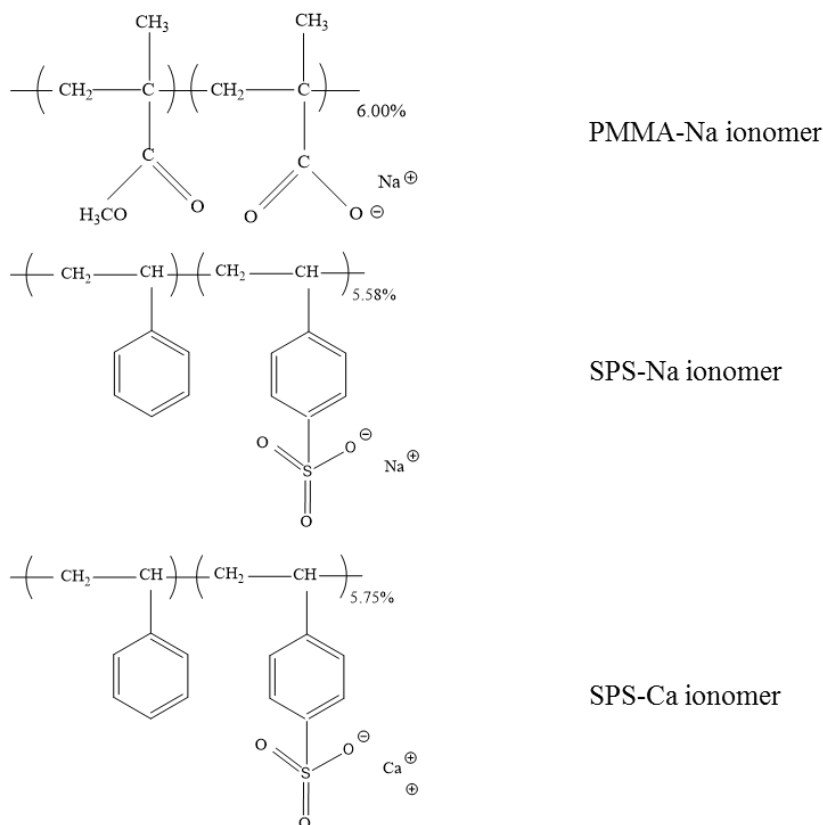
solvent changes is determined by the strength of the ionic aggregation as stronger ionic bonds will require a more polar solvent to break the bonds [17].

At high ionomer concentration the opposite behavior is observed of the solution viscosity. The reduced viscosity increases significantly at high concentrations due to the dominant presence of intermolecular aggregation. The number of ionomer chains is much higher so ionic bonds predominately form between different chains. Instead of causing the chain to contract and reduce in size, the different polymer chains become connected and form large aggregates which cause a large increase in viscosity. At high concentration increasing the polarity of the solvent will cause the viscosity to decrease towards the viscosity of the neutral polymer because it will break the ionic aggregates holding the different chains together [5, 7-8, 17].

## 2. Experimental Methods

### 2.1 Materials

Poly(methyl methacrylate-co-sodium methacrylate)(6.00% ion content) (PMMA-Na) poly(styrene-co-sodium styrenesulfonate)(5.58% ion content) (SPS-Na), and poly(styrene-co-calcium styrenesulfonate)(5.75% ion content) (SPS-Ca) were the ionomers used in this study. SPS acid copolymer was obtained by sulfonation reaction of polystyrene in this laboratory through the preparation method described by Bellinger *et al* [25]. PMMA acid copolymer samples were obtained from Polysciences Inc, neutralized in the laboratory using sodium hydroxide (NaOH) and pure ionomer samples recovered through freeze-drying. The ionomer chemical structures are shown below in Figure 2.1.



**Figure 2.1:** Chemical structures of ionomers used in study

Molecular weights of the polymers were estimated using the relation between intrinsic viscosity and molecular weight from Mark-Houwink-Sakurada [14, 26-27]. The equation that describes this relation is the following:

$$[\eta] = K'M^a \quad (1)$$

In this equation  $[\eta]$  is the intrinsic viscosity in units of mL/g,  $K'$  and  $a$  are empirical constants found for individual polymers in different solvents, and  $M$  is the molecular weight [14, 26-27]. Using the constants from Benoit *et al.* for polystyrene in tetrahydrofuran, the molecular weight of polystyrene used was determined to be approximately 270 000 [26,28]. Both the sodium salt and the calcium salt were made from the same base polystyrene sample, so they have the same molecular weight.

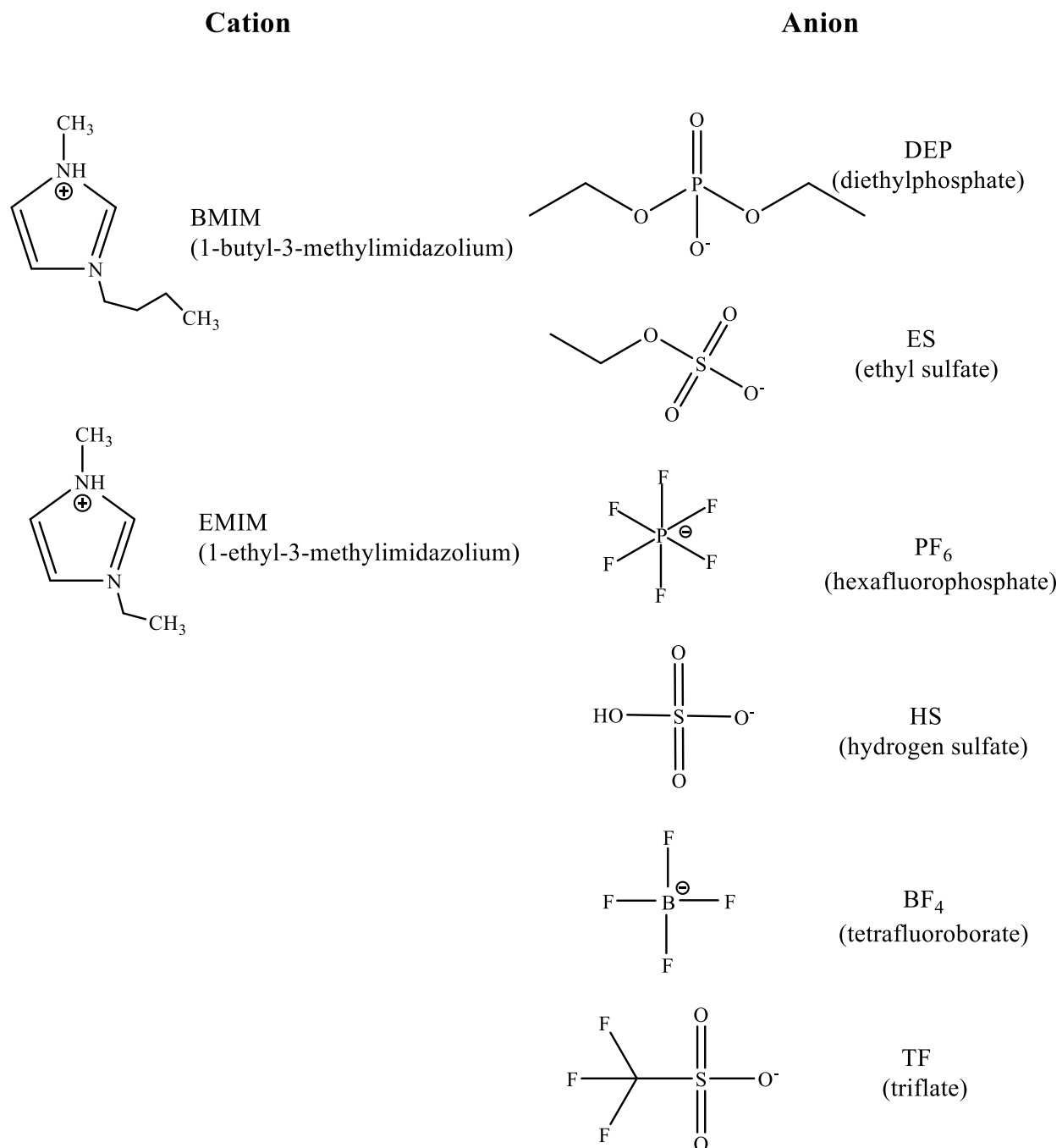
The molecular weight for the neutral PMMA sample used was calculated to be 104 000 using the empirical constants from Moore and Fort for PMMA in benzene [27,29]. The PMMA ionomer, however, was not prepared from this neutral polymer and was instead made from an acid copolymer purchased separately. Using the Mark-Houwink constants, the molecular weight of the acid sample was estimated to be around 360 000. It is assumed that there isn't a significant difference for the PMMA acid, so though there aren't Mark-Houwink constants specific for the copolymer, the value calculated is a reasonable estimate.



Solvents benzene, methanol, tetrahydrofuran (THF) and ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF<sub>6</sub>), 1-butyl-3-methylimidazolium trifluoromethane sulfonate (BMIM-TF), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF<sub>4</sub>), 1-ethyl-3-methylimidazolium diethylphosphate (EMIM-DEP), 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM-ES), 1-ethyl-3-methylimidazolium hydrogen sulfate (EMIM-HS), 1-ethyl-3-methylimidazolium trifluoromethane sulfonate (EMIM-TF), and 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIM-PF<sub>6</sub>), were obtained from Aldrich and Iolitec.

**Table 2.1:** List of ionic liquids

CAS #	Abbreviation	Full Name	Formula	Molecular Weight (g/mol)
174501-64-5	BMIM-PF <sub>6</sub>	1-butyl-3-methylimidazolium hexafluorophosphate	C <sub>8</sub> H <sub>15</sub> F <sub>6</sub> N <sub>2</sub> P	284.19
174899-66-2	BMIM-TF	1-butyl-3-methylimidazolium trifluoromethane sulfonate	C <sub>9</sub> H <sub>15</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S	288.29
143314-16-3	EMIM-BF <sub>4</sub>	1-ethyl-3-methylimidazolium tetrafluoroborate	C <sub>6</sub> H <sub>11</sub> BF <sub>4</sub> N <sub>2</sub>	197.97
848641-69-0	EMIM-DEP	1-ethyl-3-methylimidazolium diethylphosphate	C <sub>10</sub> H <sub>21</sub> N <sub>2</sub> O <sub>4</sub> P	264.26
342573-75-5	EMIM-ES	1-ethyl-3-methylimidazolium ethyl sulfate	C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S	236.29
412009-61-1	EMIM-HS	1-ethyl-3-methylimidazolium hydrogen sulfate	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S	208.24
155371-19-0	EMIM-PF <sub>6</sub>	1-ethyl-3-methylimidazolium hexafluorophosphate	C <sub>6</sub> H <sub>11</sub> F <sub>6</sub> N <sub>2</sub> P	256.13
145022-44-2	EMIM-TF	1-ethyl-3-methylimidazolium trifluoromethane sulfonate	C <sub>7</sub> H <sub>11</sub> F <sub>3</sub> N <sub>2</sub> O <sub>3</sub> S	260.23



**Figure 2.2:** Chemical structures of ionic liquid cations and anions used in study

## 2.2 *Equipment*

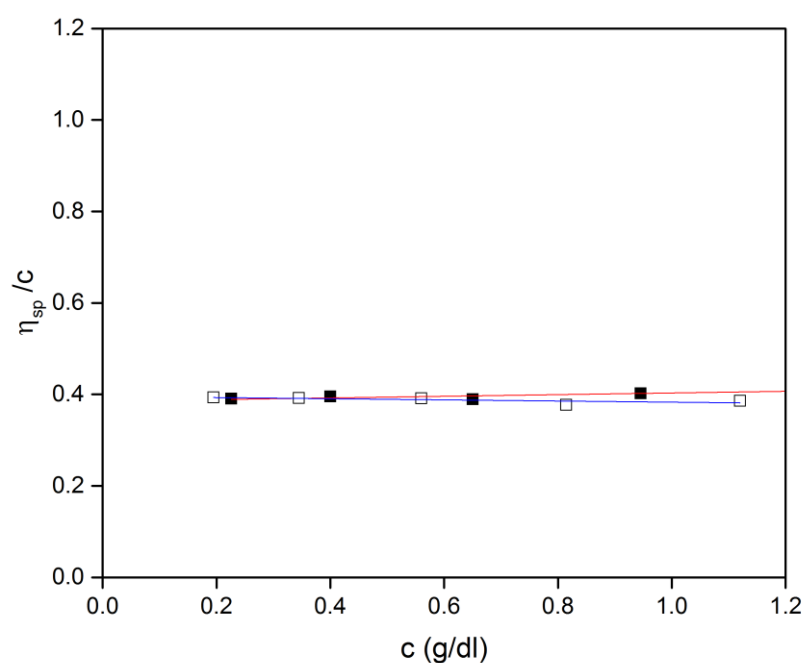
The reduced viscosity of the ionomer solutions were measured using a modified capillary viscometer of the Ubbelohde type. This type of viscometer was used so that the solution could be diluted successively allowing for a series of measurements at different concentrations [14-16]. To obtain the highest precision, viscosity measurements were performed at  $25 \pm 0.05$  °C in a thermostated bath, and caps were used to prevent exposure of the sample to air and moisture as well as evaporation of the solvent.

## 2.3 *Solvents Used*

Reduced viscosity of the three ionomer compounds, PMMA-Na, SPS-Na, and SPS-Ca were measured at dilute concentrations. Solvents for each ionomer sample were determined experimentally in the lab and chosen out of research interest. To study the aggregation behavior of the ionomer samples, organic solvents of low-polarity were chosen as the base solvent including benzene ( $\epsilon = 2.26$ ) and THF ( $\epsilon = 7.6$ ). In addition, small amounts of polar additives were mixed with the organic solvent. Due to the presence of ionic aggregates, a polar additive is used to weaken the bonds and make the ionomer solution a homogenous mixture [5]. The effectiveness of the solvent in breaking ionic aggregates depends partially on the dielectric constant of the solvent [17].

While being highly polar and capable of breaking ionic bonds, water cannot be used as a solvent for ionomer solutions because an organic solvent is needed for the polymer backbone chains [17]. Ionomers contain ionic groups at low percentages, the highest percentage used in this study was 6.00%, thus many units of the polymer chain do not

contain ionic groups. This makes solvents of high polarity, such as water, ineffective for ionomers and will result in the formation of solid precipitate. The percentage of polar additive in the solution was varied to observe its effect on the solution viscosity of the ionomers. Mixtures of benzene and methanol were used, with the methanol content ranging from 1% to 10%, to dissolve PMMA (ionomer and acid), SPS-Na and SPS-Ca. To be sure that the changes in reduced viscosity observed were due to the presence of ionic aggregates and not the changing concentration of the solvent mixture, PMMA was tested in a mixture with methanol concentrations of 10% and 1%.



**Figure 2.3:** Reduced viscosity vs. concentration for PMMA in solvent mixture of benzene and methanol

-■- 90/10 benzene/methanol

-□- 99/1 benzene/methanol

As seen in Figure 2.3., the reduced viscosity was almost identical which means that changing the methanol concentration does not have a meaningful effect on the solution viscosity of the polymer.

Further experiments were conducted on the three ionomer systems using THF as the base organic solvent with small amounts of ionic liquid added to break the ionic aggregates. The ionic liquids were taken from the imidazolium family with different combinations of two cations and six anions. Table 2.2 summarizes the solubility of the ionomers in the ionic liquids found experimentally in the laboratory.

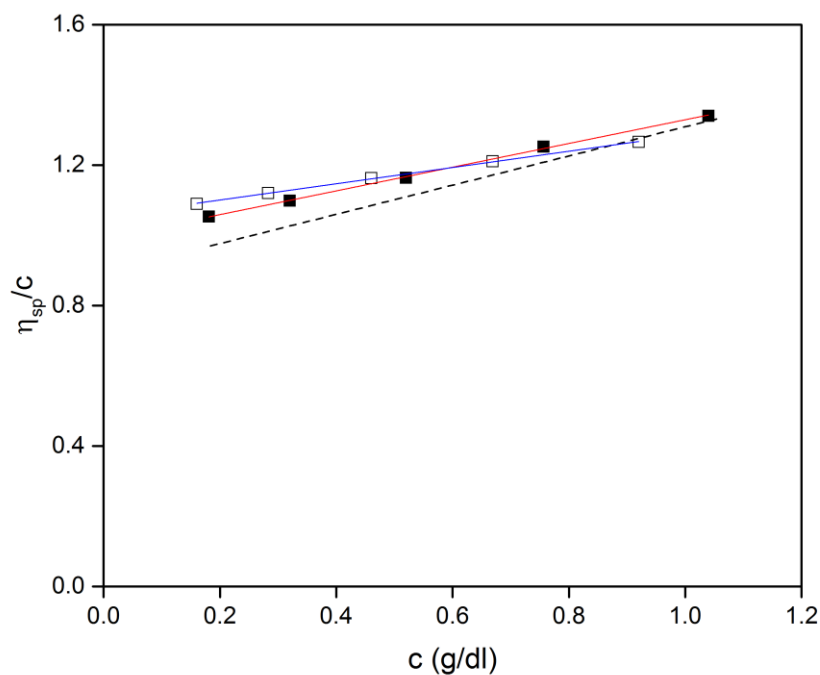
**Table 2.2:** Solubility of ionomers in ionic liquids

Ionic liquid	Dissolved PMMA-Na	Dissolved SPS-Na	Dissolved SPS-Ca
BMIM-PF <sub>6</sub>	Yes	Yes	Yes
BMIM-TF	No	No	No
EMIM-BF <sub>4</sub>	Yes	No	No
EMIM-DEP	No	Yes	Yes
EMIM-ES	No	Yes	Yes
EMIM-HS	No	No	No
EMIM-PF <sub>6</sub>	Yes	No	Yes
EMIM-TF	Yes	Yes	Yes

Of the eight ionic liquids used, two were successful in dissolving all three ionomers, BMIM-PF<sub>6</sub> and EMIM-TF, and two were unable to dissolve any of the three, BMIM-TF and EMIM-HS. The remaining four showed varying success with EMIM-BF<sub>4</sub> working only with PMMA-Na, EMIM-DEP and EMIM-ES working for the polystyrene ionomers, and EMIM-PF<sub>6</sub> working with PMMA-Na and SPS-Ca, but not SPS-Na.

The amount of ionic liquid used in preparation of samples was measured as the ratio of moles of ionic liquid over the moles of ionic groups in the ionomers. This ratio is denoted

as  $[\text{IL}]/[\text{Ion}]$  in this report, and is the number reported next to the name of the ionic liquids for discussion of the results.



**Figure 2.4:** Reduced viscosity vs. concentration for PS in solvent mixtures of THF and EMIM-TF and BMIM-PF<sub>6</sub>

-■- EMIM-TF

-□- BMIM-PF<sub>6</sub>

As done previously with benzene and methanol, the effect of ionic liquids on the solution viscosity was tested. In this case, the viscosity of polystyrene in solvent mixtures of THF/EMIM-TF and THF/BMIM-PF<sub>6</sub> were compared to the viscosity of polystyrene in pure THF. Figure 2.4 shows that there is minimal change in viscosity compared to PS in THF, so it was determined that the addition of ionic liquids does not have a significant effect on the viscosity.

## 2.4 *Experimental Procedure*

Samples for viscosity measurement were prepared at least a day in advance. This was done by placing ionomer, weighing between 80 mg and 150 mg depending on the desired concentration, in an erlenmeyer flask. Then 10 mL of the chosen solvent mixture, or pure solvent, was measured using a pipette and added to the flask. Samples made using a solvent mixture of benzene/methanol were set on a magnetic stirrer for at least a day at room temperature to ensure that the sample would dissolve into a homogenous mixture for measurements. Magnetic stirring was not used for solvent mixtures of THF and ionic liquids. In some of these samples aggregation was observed, which may have been shear-induced from the stirring. Samples that showed solid precipitation in the flask could not be used for experimentation because the particles could get stuck in the viscometer capillary and effect the measurement.

On the day of the experiment the viscometer was removed from storage in the hood and rinsed with water for at least five minutes. Acetone was used after to remove water from the viscometer before it was put into the oven for at least 10 minutes to dry. Upon removal from the oven, an aspirator was used to remove hot air from the viscometer until it reached room temperature. This was done to avoid condensation of water inside the viscometer, which would adversely affect the sample. Once the viscometer was prepared, 8 mL of the solvent used for the sample was added to the viscometer and it was placed in a thermostated bath at 25 °C. Viscosity measurements were then carried out on the solvent until the relative error of three successive measurements did not exceed 0.5% and the results did not show an increasing or decreasing trend. Values from the solvent measurement were used as calibration and in calculations of the reduced viscosity.

Following solvent measurement, the viscometer was removed from the bath and cleaned once again before measuring the ionomer solution. The viscometer was first rinsed with acetone to remove the solvent and then placed in the oven for 10 minutes until completely dry. And as done previously, hot air was removed from the viscometer using an aspirator to prevent condensation. In this way the viscometer was cleaned of any solvent so that the concentration of the ionomer sample would be preserved for measurement.

After the viscometer was cleaned, 8 mL of the ionomer sample was measured and added to the viscometer. The viscometer was then returned to the thermostated bath and measurements conducted in the same manner done for the solvent. After measurement of the ionomer solution, the sample was diluted four times in the viscometer. The amounts added for these dilutions were 3 mL, 5 mL, 10 mL, and 20 mL of solvent, with measurements conducted at each dilution.

To obtain good data, the viscometer was thoroughly cleaned after each experiment. First, the sample was emptied and the viscometer rinsed with the solvent. After the solvent, the viscometer was rinsed with acetone, and then with water using an aspirator to ensure that the water flowed through the capillary for at least five minutes. Finally, the viscometer was filled with sulfuric acid and stored in the hood overnight for the next experiment.



### 3. Results and Discussion

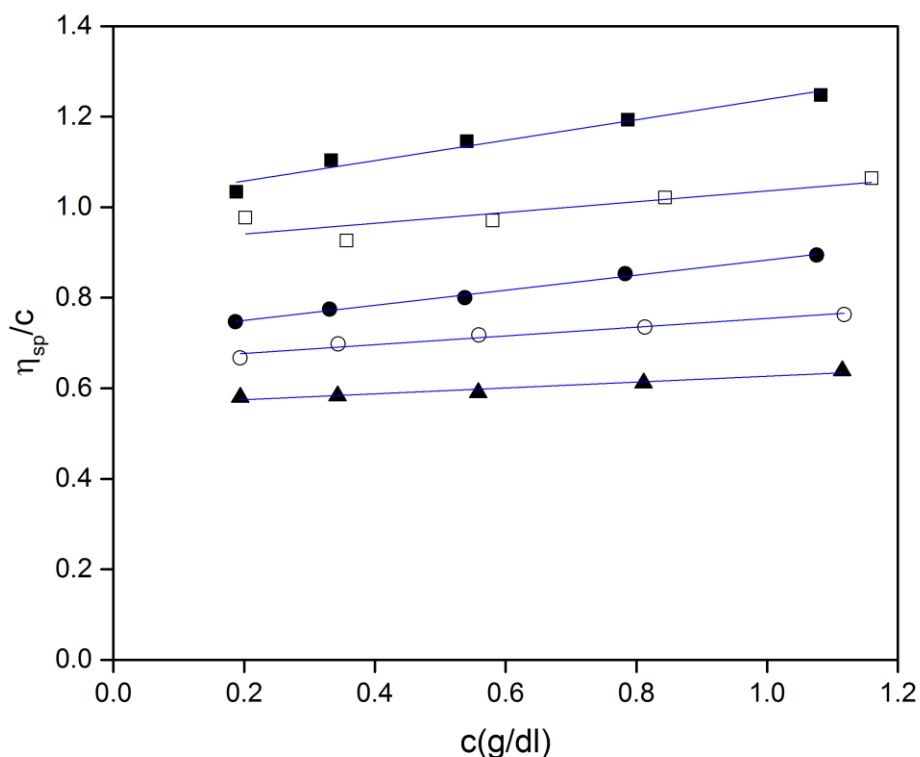
#### 3.1 Viscosity of PMMA

Viscosity experiments were performed on the PMMA acid copolymer and ionomer samples. First, they were studied at dilute concentrations in solvent mixtures of benzene and methanol.

Samples of the acid copolymer system were successfully dissolved in solvent mixtures containing methanol percentages of 10%, 5%, 2.5%, 2% and 1%. The minimum methanol content tested to dissolve the acid copolymer was 1%, but the results suggest that the polymer could still be successfully dissolved when further lowering the methanol content without the formation of a solid precipitate.

The reduced viscosity for the acid copolymer system showed an increasing trend with increasing methanol content. Despite not containing any ionic groups, the viscosity follows the behavior of dilute ionomer solutions which can be attributed to the presence of secondary hydrogen bonds that form between polymer chains [3,17,30].

The increasing viscosity with increasing concentrations of methanol in the solvent indicates that the hydrogen bonds that form are predominately intramolecular bonds. This is consistent with the behavior of ionomers in the dilute concentration, but because hydrogen bonds are several orders of magnitude weaker than ionic bonds, the effect they have on the solution viscosity is relatively small [30]. This is illustrated in Figure 3.1 which plots the reduced viscosity versus methanol content of the acid copolymer at a specific concentration.

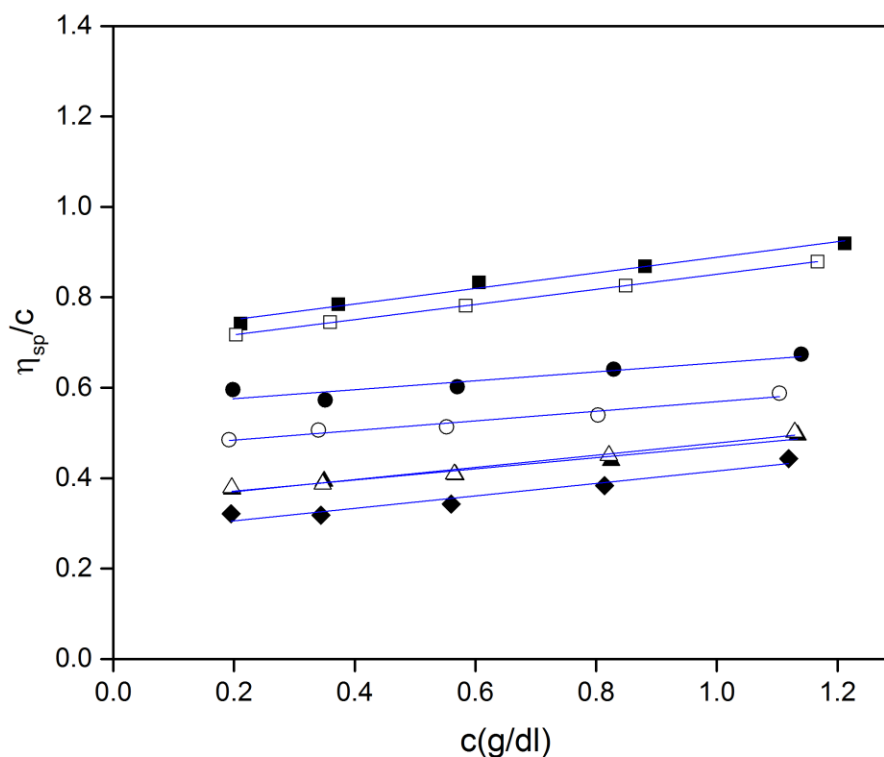


**Figure 3.1:** Reduced viscosity vs. concentration for PMMA acid copolymer in solvent mixture of benzene and methanol

- 90/10 benzene/methanol    -□- 95/5 benzene/methanol
- 97.5/2.5 benzene/methanol    -○- 98/2 benzene/methanol
- ▲- 99/1 benzene/methanol

To demonstrate the effect of ionic aggregations on the properties of ionomers, the PMMA-Na ionomer was also dissolved in solvent mixtures of benzene and methanol and compared to the results of the acid copolymer. Samples of PMMA-Na ionomer were successfully dissolved in solvent mixtures with methanol content of 10%, 5%, 4%, 3.5%, 3%, and 2%. Solid precipitation was observed in samples containing methanol content lower than 2%,

so that was determined to be the minimum methanol concentration able to dissolve the PMMA-Na ionomer.

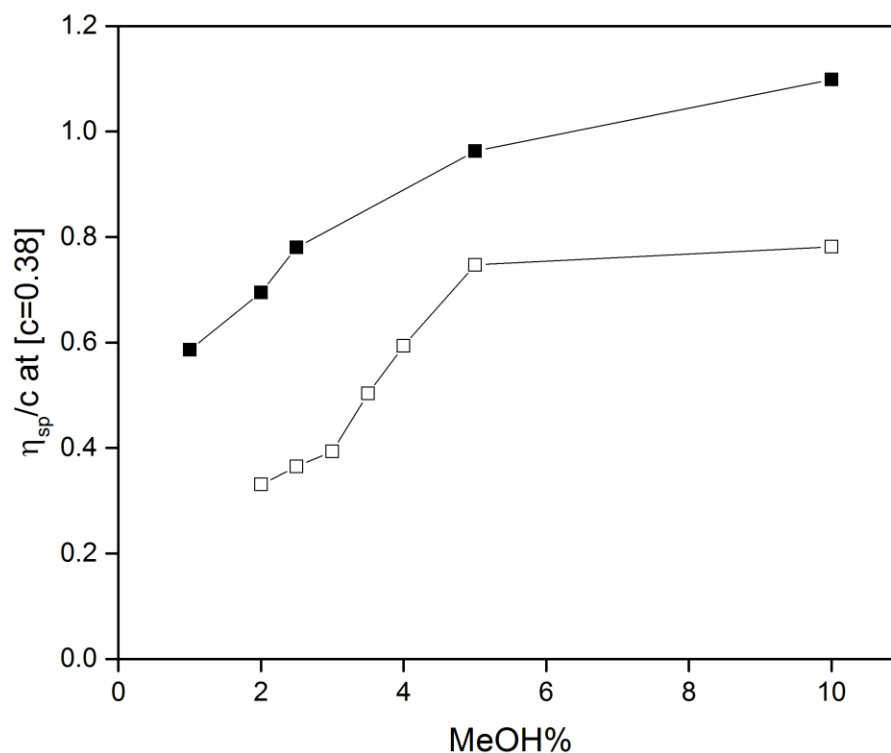


**Figure 3.2:** Reduced viscosity vs. concentration for PMMA-Na ionomer in solvent mixture of benzene and methanol

- 90/10 benzene/methanol -□- 95/5 benzene/methanol -●- 96/4 benzene/methanol
- 96.5/3.5 benzene/methanol -◆- 97/3 benzene/methanol
- ◇- 97.5/2.5 benzene/methanol -▲- 98/2 benzene/methanol

Similar to the results for the acid copolymer system, the reduced viscosity of the PMMA-Na ionomer showed an increasing trend with increasing methanol content. This trend, which is characteristic of dilute concentration ionomers, is observed in Figure 3.2 which

plots reduced viscosity vs. concentration for the PMMA-Na ionomer samples [5,17]. While both systems show the same trend, there are noticeable differences when the results between the acid copolymer and the ionomer are compared.



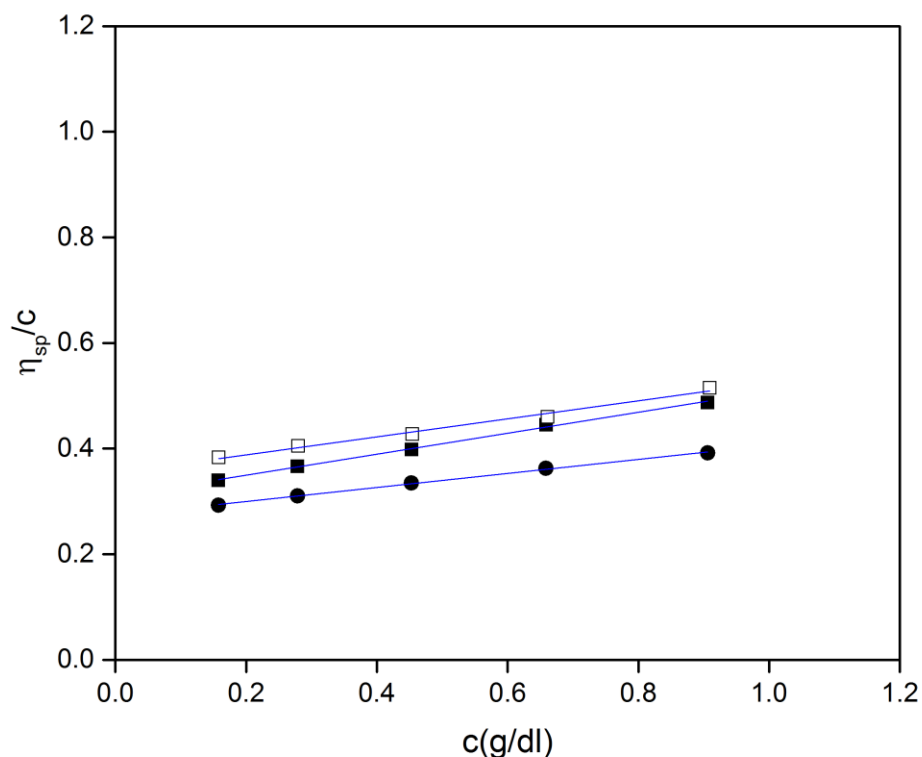
**Figure 3.3:** Reduced viscosity vs. methanol concentration for PMMA acid copolymer and ionomer in a solvent mixture of benzene and methanol at a fixed concentration

-■- Acid -□- Ionomer

First, because ionic bonds are much stronger than hydrogen bonds, the change in reduced viscosity with changing methanol content was larger for the ionomer than the acid copolymer [30]. This is illustrated in Figure 3.3 which plots reduced viscosity versus changing methanol content of the PMMA-Na ionomer at a fixed concentration.

However, another difference that we see is that while the ionomer shows a larger change with changing methanol concentration, this effect plateaus after a certain point. From Figure 3.3 we can see that the reduced viscosity changes only slightly when the methanol concentration is doubled from 5% to 10% which indicates that the effect of increasing the polar solvent stopped having an effect on the viscosity. In addition, even at 10% methanol concentration there is still a noticeable gap between the viscosity of the ionomer and that of the acid polymer. The large gap for the ionomer indicates that not all of the ionic aggregates could be broken by the polar solvent. This comparison suggests that there is a limit to the effectiveness of methanol as a polar solvent for the PMMA-Na ionomer.

In addition to solvent mixtures of benzene and methanol, PMMA-Na ionomer was successfully dissolved in solvent mixtures of THF and different ionic liquids. Of the eight ionic liquids tested, PMMA-Na was successfully dissolved in the following four: EMIM-BF<sub>4</sub>, EMIM-TF, EMIM-PF<sub>6</sub>, and BMIM-PF<sub>6</sub>.

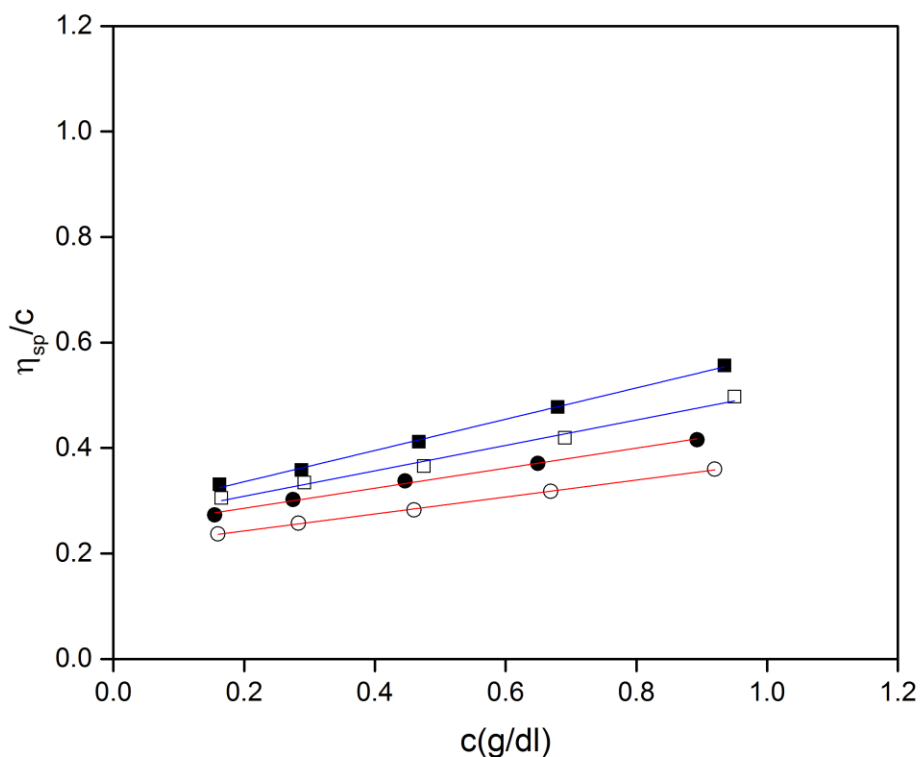


**Figure 3.4:** Reduced viscosity vs. concentration for PMMA-Na ionomer in solvent mixture of THF and EMIM-BF<sub>4</sub>

-□- EMIM-BF<sub>4</sub> 30    -■- EMIM-BF<sub>4</sub> 26    -●- EMIM-BF<sub>4</sub> 17.5

Shown in Figure 3.4 is the graph of reduced viscosity vs. concentration for samples dissolved in a solvent mixture of EMIM-BF<sub>4</sub> and THF. PMMA-Na was successfully dissolved in solvents with [IL]/[Ion] ratios of 17.5, 25, and 30. Samples attempted with a ratio lower than 17.5 were unable to fully dissolve the ionomer and solid precipitation was observed. For the three successfully samples, PMMA-Na in EMIM-BF<sub>4</sub> shows the characteristic increase in viscosity with increasing solvent polarity. It is worth noting that while EMIM-BF<sub>4</sub> was unsuccessful in dissolving the polystyrene ionomers, it performed as expected for the PMMA system.

In addition to EMIM-BF<sub>4</sub>, samples dissolved in solvent mixtures of EMIM-TF and THF also showed the characteristic viscosity behavior of ionomers in dilute concentration.



**Figure 3.5:** Reduced viscosity vs. concentration for PMMA-Na ionomer in solvent mixture of THF and EMIM-TF, EMIM-PF<sub>6</sub>, BMIM-PF<sub>6</sub>

-■- EMIM-TF 32 -□- EMIM-TF 24

-●- BMIM-PF<sub>6</sub> 22.2 -○- EMIM-PF<sub>6</sub> 16.1

Figure 3.5 shows reduced viscosity vs. concentration for samples successfully dissolved with [IL]/[Ion] ratios of 24 and 32. Samples tested with ratios lower than 20 were all unsuccessful with precipitation observed, so fewer results were obtained for PMMA-Na in EMIM-TF and THF.

For the remaining two ionic liquids, EMIM-PF<sub>6</sub> and BMIM-PF<sub>6</sub>, only a very narrow range of ratios were able to successfully dissolve the ionomer. For EMIM-PF<sub>6</sub> the successful sample was obtained with a ratio of 16. Samples with ratios much higher and lower than 16 showed solid precipitation which can likely be attributed to the fact that the polarity of the sample becoming too low or too high. It is also worth noting that of the viscosity experiments performed with PMMA ionomer and ionic liquids, EMIM-PF<sub>6</sub> had the lowest viscosity and therefore was the least effective at breaking the ionic aggregation. For BMIM-PF<sub>6</sub>, a successful sample was obtained with a ratio of 22, but like EMIM-PF<sub>6</sub>, ratios much higher or lower resulted in solid precipitation.

Compared to the polystyrene ionomers, the successful samples for the PMMA-Na ionomer with ionic liquids required higher ratios to fully dissolve into a homogenous solution. For comparison, the minimum ratio of EMIM-TF needed to dissolve SPS-NA was 2.4, but the lowest sample PMMA that was successful was ten times higher at 24. This observation may be attributable to the overall polarity of the ionomer.

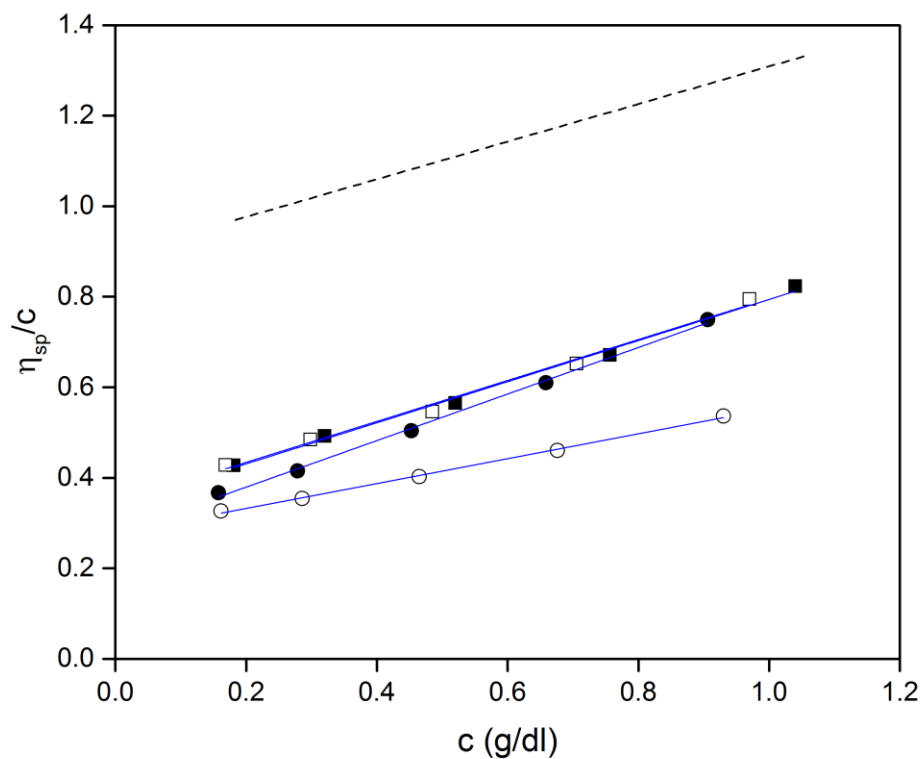


### 3.2 Viscosity of SPS-Ca

Two sets of experiments were carried out with the SPS-Ca. First, the viscosity was measured for SPS-Ca dissolved in solvent mixtures of benzene and methanol with the methanol content varying from 3 to 10%.

Samples of SPS-Ca successfully dissolved in solvent mixtures with methanol content of 10%, 5%, 4% and 3%. Decreasing the methanol content further caused the ionomer to precipitate on the bottom of the flask, so it was determined that the minimum methanol content that could successfully dissolve SPS-Ca was 3%. This is slightly higher than the 2.7% needed to dissolve SPS-Na, which perhaps can be attributed to the stronger calcium bonds.

Figure 3.6 plots the reduced viscosity vs. concentration for SPS-Ca in benzene and methanol and it can be seen that the behavior does not follow the characteristic trend for dilute ionomer solutions [5,7,17,31]. For methanol concentrations of 4%, 5%, and 10%, the viscosity is very close, with no increasing or decreasing trend. The exception is the 3% methanol sample which is notably lower than the other samples, which suggests that the ionomer was not fully dissolved at 3%. Also, the lack of a significant viscosity change in the other three samples indicates that methanol may be a poor solvent for SPS-Ca because divalent calcium ions are stronger than sodium ions. Compared to PMMA-Na which showed the increasing viscosity with increasing methanol trend, SPS-Ca showed very little change.

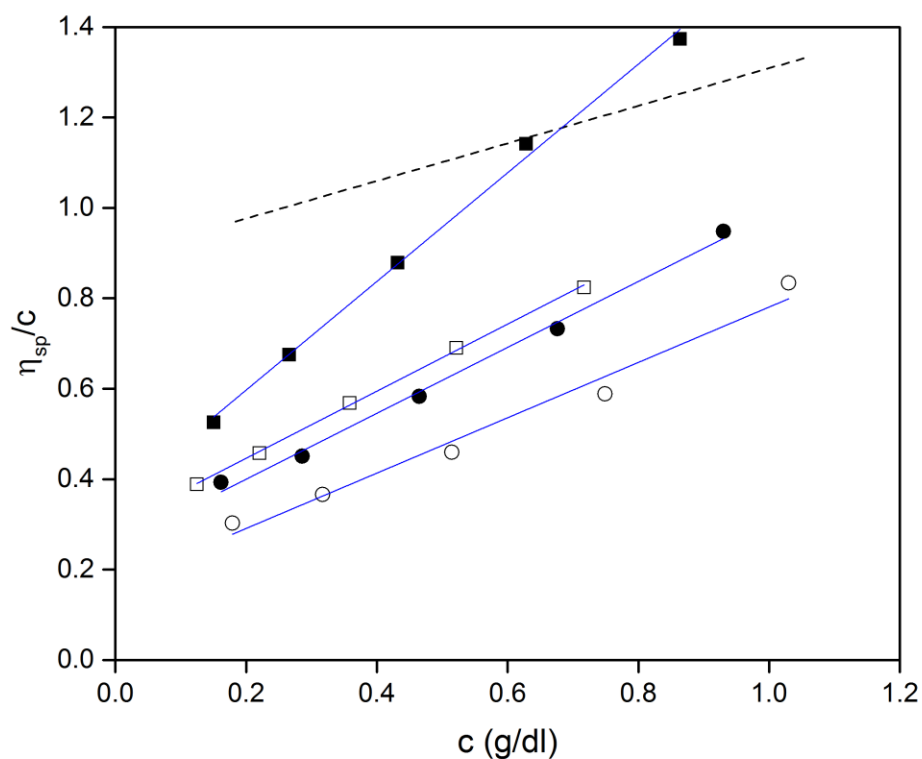


**Figure 3.6:** Reduced viscosity vs. concentration for SPS-Ca in solvent mixture of benzene and methanol

-■- 90/10 benzene/methanol -□- 95/5 benzene/methanol  
 -●- 96/4 benzene/methanol -○- 97/3 benzene/methanol

In addition to solvent mixtures of benzene and methanol, the viscosity of SPS-Ca was measured in solvent mixtures containing the ionic liquids detailed in sections 2.1 and 2.2. Of the 8 ionic liquids tested, the following successfully dissolved the ionomer: BMIM-PF<sub>6</sub>, EMIM-TF, EMIM-PF<sub>6</sub>, EMIM-ES, and EMIM-DEP.

The amount of ionic liquid was measured in a ratio of moles of ionic liquid added to the moles of sulfonate ion present in the ionomer chain. Figure 3.7 shows the viscosity measurements of SPS-Ca dissolved in a mixture of EMIM-TF and THF with [IL]/[Ion] ratios ranging from 6.08 to 33.73.



**Figure 3.7:** Reduced viscosity vs. concentration for SPS-Ca in a solvent mixture of THF and EMIM-TF

-■- EMIM-TF 33.7 -□- EMIM-TF 23.6  
 -●- EMIM-TF 14.7 -○- EMIM-TF 6

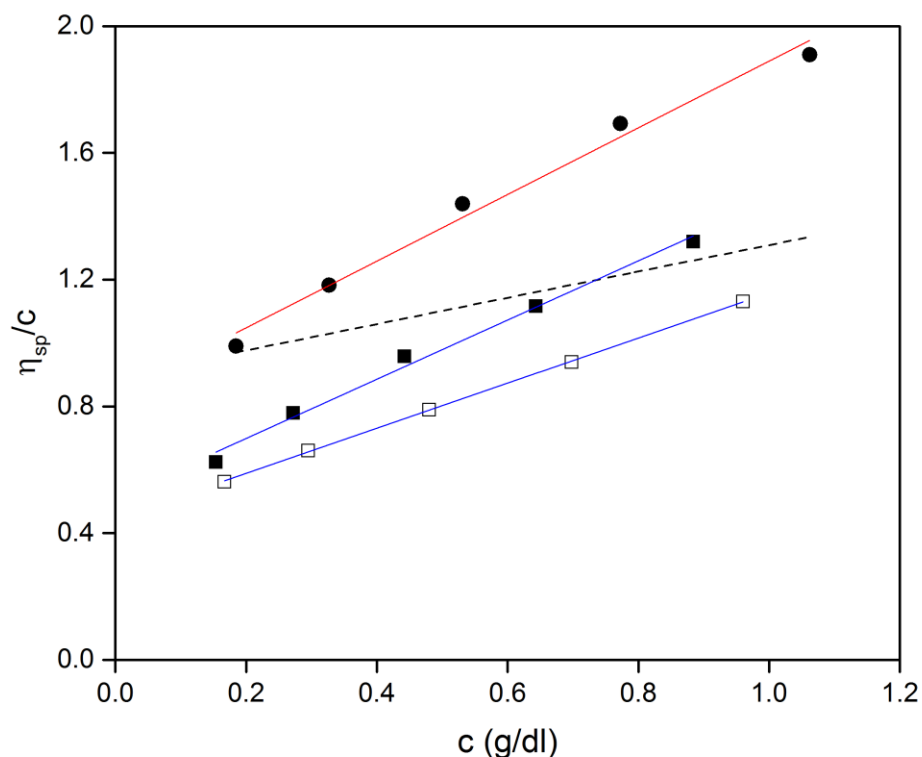
For [IL]/[Ion] ratios lower than 6.08 solid precipitation occurred, and higher than 33.73 precipitation also occurred due to saturation by the polar solvent. Unlike the results for

benzene and methanol, the reduced viscosity of samples dissolved with EMIM-TF shows an increasing trend with ionic liquid content. This behavior is consistent with ionomers in dilute concentration in low-polarity solvents, so this demonstrates the capability of ionic liquids to dissolve ionomers, and in some cases, perform better than traditional solvents.

At the highest ionic liquid content, 33.73, the viscosity results approach the viscosity of neutral polystyrene which shows that in addition to being able to dissolve the ionomer, the ionic liquid is able to break many of the bonds in the solution. It should also be noted that additional ionic liquid was not added when diluting the sample. This means that while the  $[\text{IL}]/[\text{Ion}]$  ratio is consistent, the overall concentration of ionic liquid in the solution decreases with subsequent dilutions of THF.

In addition to EMIM-TF, SPS-Ca was also successfully dissolved in ionic liquid EMIM-PF<sub>6</sub>. Similar to EMIM-TF, the results of EMIM-PF<sub>6</sub> show the increasing viscosity trend with increasing ionic liquid content, which can be seen in Figure 3.8. Samples were successfully dissolved with  $[\text{IL}]/[\text{Ion}]$  ratios of 5.3 and 15.14 and precipitation occurring in samples containing lower ratios, such as 2.6, and at higher ratios, in samples tested in the range of 20-29.

Compared to EMIM-TF, results for EMIM-PF<sub>6</sub> were successful for a smaller range. However, it also achieved similar reduced viscosity results using half the ionic liquid ratio needed for EMIM-TF (compare EMIM-TF 33 to EMIM-PF<sub>6</sub> 15). This may be due to the fact that the ionic bonds formed by EMIM-PF<sub>6</sub> are stronger than that of EMIM-TF and so less is required to break the ionomer bonds.

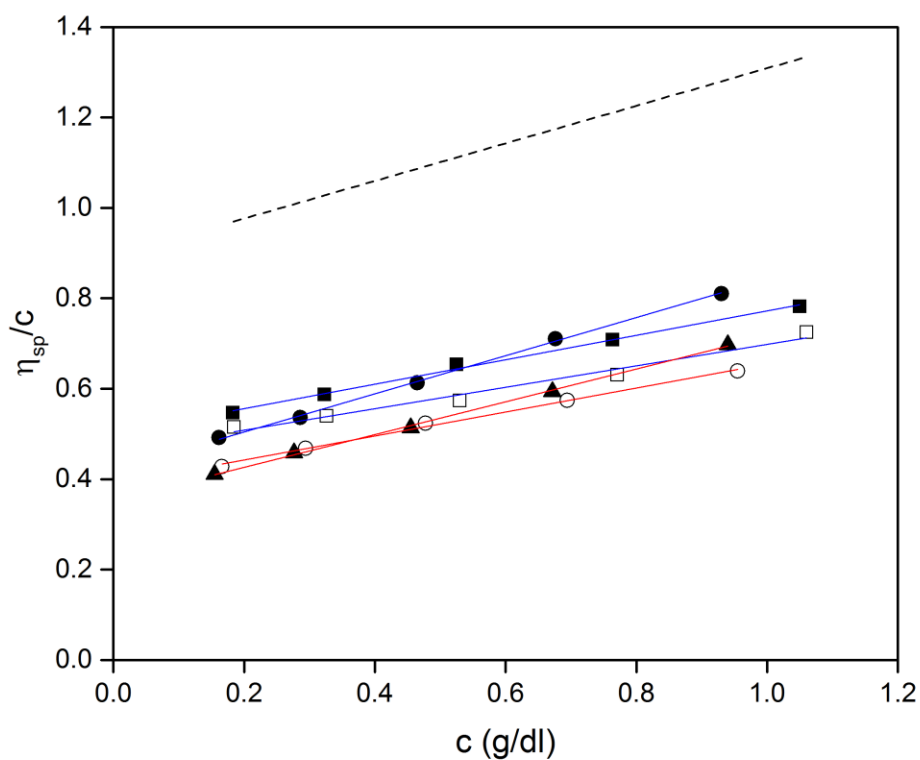


**Figure 3.8:** Reduced viscosity vs. concentration for SPS-Ca in solvent mixtures of THF and EMIM-PF<sub>6</sub> and BMIM-PF<sub>6</sub>

-■- EMIM-PF<sub>6</sub> 15.1 -□- EMIM-PF<sub>6</sub> 5.3 -●- BMIM-PF<sub>6</sub> 36.7

What can also be compared is the relative effectiveness of the ionic liquids as solvents for SPS-Ca compared to methanol. While samples dissolved in methanol showed a relatively large plateau, the ionic liquids overall performed better. EMIM-DEP and EMIM-ES compared similarly to methanol as they showed little to no change in viscosity even after the concentration was doubled. On the other hand, EMIM-TF and EMIM-PF<sub>6</sub> showed the characteristic increasing trend as well as a much larger range of viscosities. Also, at high concentrations, both EMIM-TF and EMIM-PF<sub>6</sub> approach the viscosity of pure polystyrene, which means that they were able to break many of the bonds.

However, some of the ionic liquids were not consistent with the behavior of ionomers in dilute concentrations. While able to dissolve SPS-Ca ionomer, the reduced viscosity results for EMIM-DEP and EMIM-ES showed different behavior. Compared to the increasing viscosity trend with increasing ionic liquid ratio for EMIM-TF and EMIM-PF<sub>6</sub>, both EMIM-DEP and EMIM-ES remain constant over the range of ratios tested.



**Figure 3.9:** Reduced viscosity vs. concentration for SPS-Ca in solvent mixtures of THF and EMIM-DEP and EMIM-ES

-■- EMIM-DEP 24.5 -□- EMIM-DEP 14.7 -●- EMIM-DEP 6.4  
 -○- EMIM-ES 28.9 -▲- EMIM-ES 15.5

Figure 3.9 compares the results for EMIM-DEP and EMIM-ES. EMIM-ES was tested at two ratios, 15.5 and 28.9, and despite almost doubling the  $[IL]/[Ion]$  the reduced viscosity

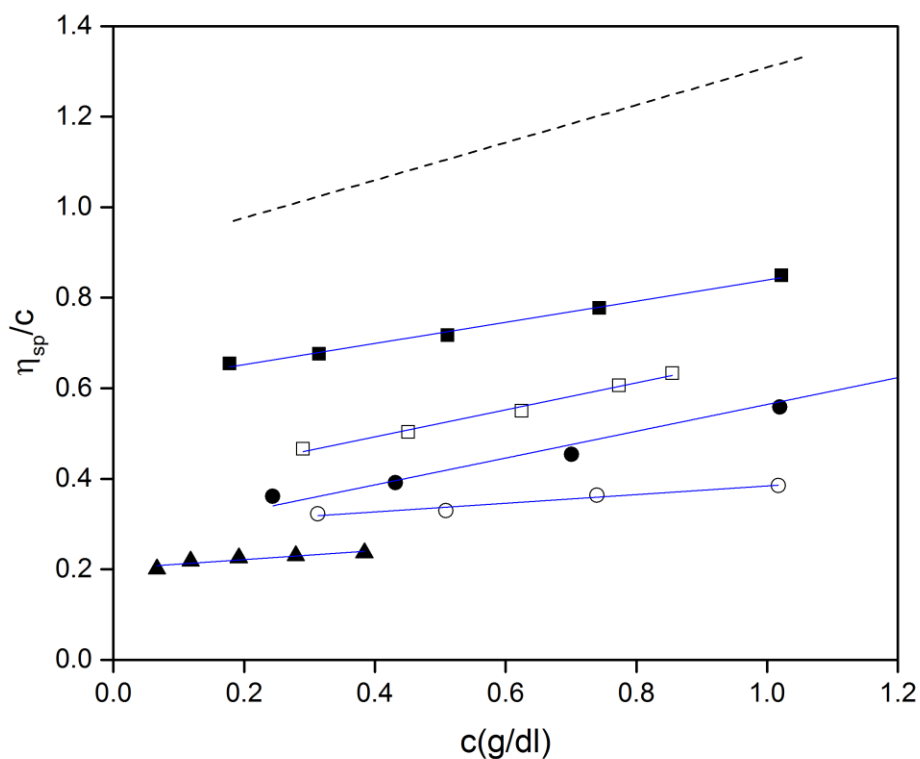
remains almost constant. Similarly, EMIM-DEP was tested at three ratios, 6.4, 14.7, and 24.5, and like EMIM-ES remained almost constant over the entire range.

The solution behavior for EMIM-ES and EMIM-DEP may be attributed to the large dipoles in the ionic liquid structure due to the non-polar ethyl branches found on the anion structures. As discussed previously, these dipoles result in visible phase separation in the solvent and the presence of THF (which is much less polar) may be preventing the ionic liquid from fully interacting with the ionomer.

### *3.3 Viscosity of SPS-Na*

SPS-Na was successfully dissolved in solvent mixtures of benzene and methanol with methanol content ranging from 1-10%. Samples were successfully dissolved in samples containing 10%, 5%, 4%, 3% and 2.7% methanol concentration. Samples precipitated at methanol concentrations of 2.5% and lower, so the minimum methanol concentration successfully able to dissolve SPS-Na was determined to be 2.7%.

Figure 3.10 plots the reduced viscosity vs. concentration for the five successful samples. It can be seen that the behavior of SPS-Na in solvent mixtures of benzene and methanol follows the characteristic trend of ionomers in dilute concentration. As the methanol concentration increases, the viscosity of the ionomer sample also increases and approaches the viscosity of polystyrene.



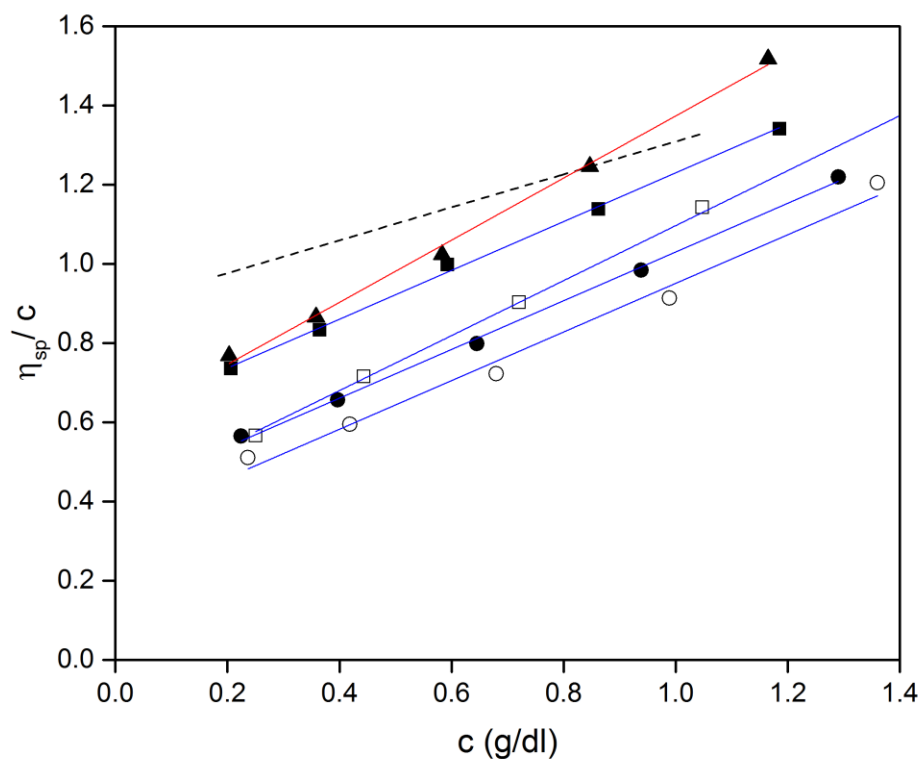
**Figure 3.10:** Reduced viscosity vs. concentration for SPS-Na in a solvent mixture of benzene and methanol

- 90/10 benzene/methanol -□- 95/5 benzene/methanol
- 96/4 benzene/methanol -○- 97/3 benzene/methanol
- ▲- 97.3/2.7 benzene/methanol

The ionomer was successfully dissolved at all concentrations except for 2.5%. At this concentration, solid precipitation was observed and viscosity measurements could not be performed. By increasing the concentration of methanol it was determined that the minimum needed to dissolve sulfonated PS was 2.7%.



As was done with the previous two ionomers, SPS-Na was dissolved in ionic liquids. Of the 8 ionic liquids tested, the following four successfully dissolved the ionomer: EMIM-TF, BMIM-PF<sub>6</sub>, EMIM-DEP, and EMIM-ES. The list is similar to SPS-Ca with the sole difference of EMIM-PF<sub>6</sub>. SPS-Na showed precipitation in all samples with ratios ranging from 5 to 24. It may be that EMIM-PF<sub>6</sub> is too polar for SPS-Na, but further investigation will be required to understand the interactions.



**Figure 3.11:** Reduced viscosity vs. concentration for SPS-Na in solvent mixtures of THF and EMIM-TF and BMIM-PF<sub>6</sub>

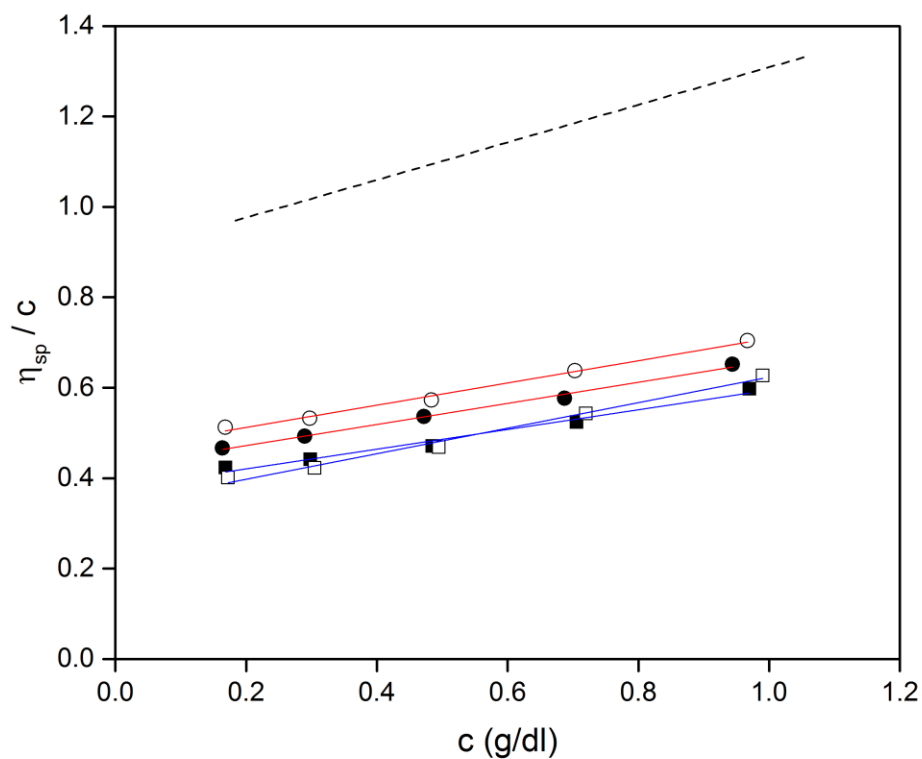
-■- EMIM-TF 26 -□- EMIM-TF 14.4 -●- EMIM-TF 7.8  
 -○- EMIM-TF 2.4 -▲- BMIM-PF<sub>6</sub> 28

With the exception of the aforementioned EMIM-PF<sub>6</sub>, the viscosity behavior of SPS-Na in the successful ionic liquid samples was similar to that found with SPS-Ca. EMIM-TF showed the characteristic trend of increasing viscosity with increasing ionic liquid content and was successful over a range of ratios from 2.4 to 26. Figure 3.11 plots the viscosity results of EMIM-TF/THF and it can be seen that at the highest tested ionic liquid ratio, the viscosity comes close to the neutral polymer line, indicating that EMIM-TF performs well as a solvent for the ionomer. It should also be noted that the lower limit of 2.41 is lower than that of SPS-Ca, which likely can be attributed to the fact that sodium bonds are weaker than calcium bonds.

For BMIM-PF<sub>6</sub> there was only one successful sample obtained with a [IL]/[Ion] ratio of 28. Samples with ratios higher precipitated due to the polarity of the solvent being too high, while lower ratios resulted in small pieces of solid undissolved in the flask. It should also be noted that the time scale for dissolving samples in BMIM-PF<sub>6</sub> were much higher than for any of the samples with the cation EMIM. A successful sample dissolved in BMIM-PF<sub>6</sub> took a week, whereas all the other samples were ready for viscosity experiments in a day at most. This large difference in time may be due to the presence of longer chains, butyl compared to ethyl, in BMIM which may interfere with dissolving the ionomer.

Samples dissolved in EMIM-DEP and EMIM-ES followed the trend established with samples of SPS-Ca. EMIM-DEP was tested at two ratios, 14.6 and 27.6, and EMIM-ES at 16 and 27. Just like with SPS-Ca the two ionic liquids in SPS-Ca were constant even after doubling the ionic liquid ratios. This indicates that while able to dissolve the ionomer, EMIM-DEP and EMIM-ES are not good solvents. As illustrated in Figure 3.12, the reduced

viscosity obtained from samples of EMIM-DEP and EMIM-ES are low compared to the viscosity of polystyrene, so that means that many ionic aggregates remain.

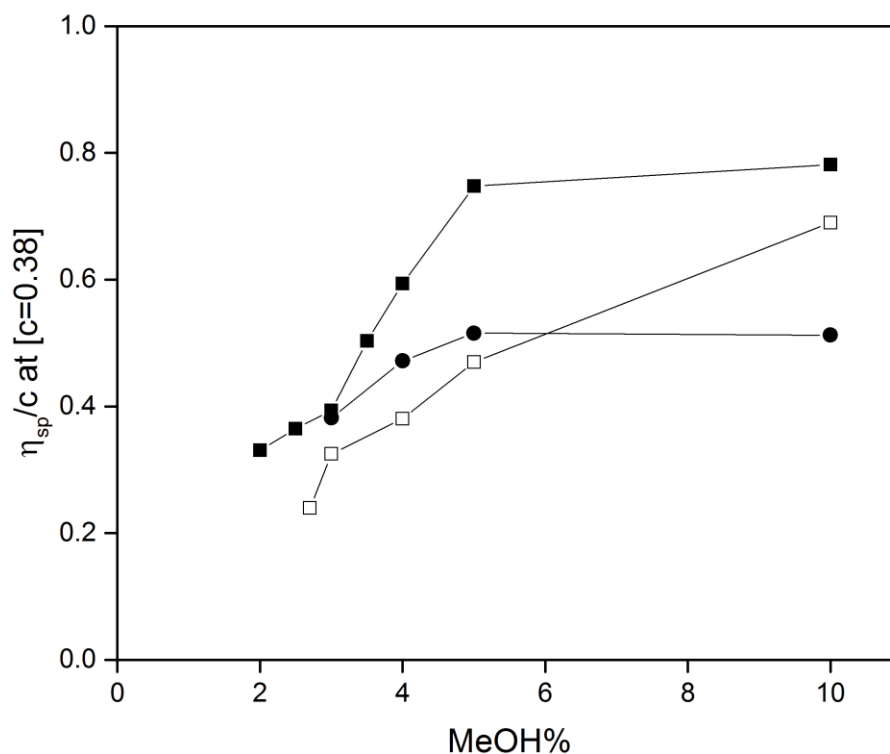


**Figure 3.12:** Reduced viscosity vs. concentration for SPS-Na in solvent mixtures of THF and EMIM-DEP and EMIM-ES

-■- EMIM-ES 27 -□- EMIM-ES 16  
 -●- EMIM-DEP 27.6 -○- EMIM-DEP 14.6

### 3.4 Results Comparison

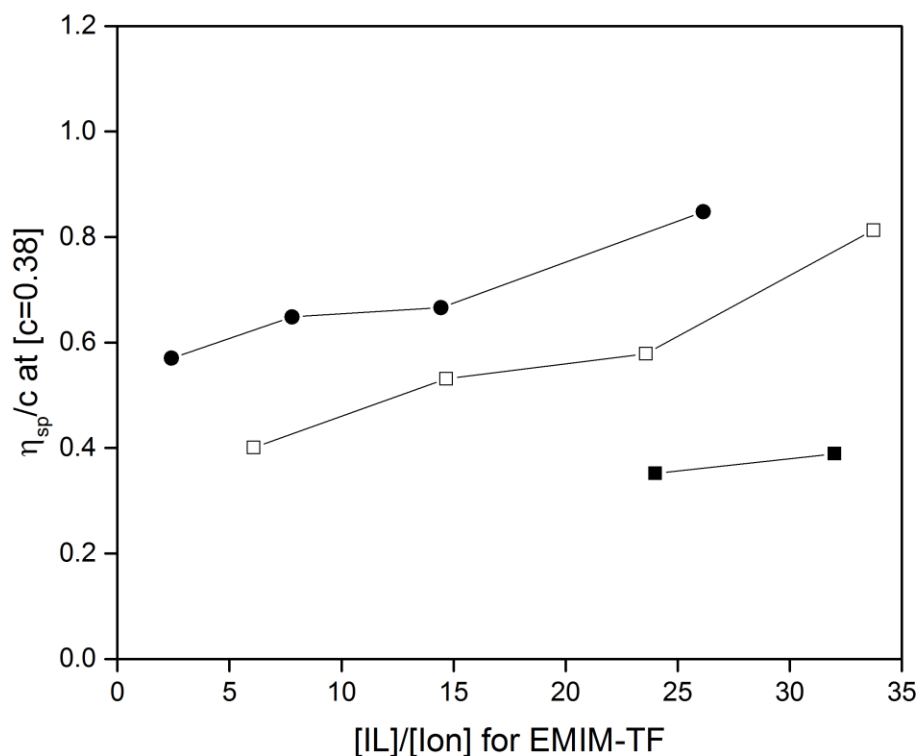
This section attempts to gain a better understanding of the effectiveness of different solvent mixtures on the individual ionomers. Figure 3.13 plots the reduced viscosity vs. methanol concentration for each of the three ionomers at a fixed concentration. As the methanol increases, and therefore the polarity of the solvent mixture increases, the expectation is that the reduced viscosity will also increase for dilute concentrations, and this is illustrated in all three ionomer systems.



**Figure 3.13:** Reduced viscosity vs. methanol concentration for PMMA-Na, SPS-Na, and SPS-Ca in a solvent mixture of benzene and methanol at a fixed concentration

-■- PMMA-Na -□- SPS-Na -●- SPS-Ca

However, as can be seen in Figure 3.13, the relative change in reduced viscosity is different for each ionomer system, which indicates that effectiveness of the solvent is very different. As mentioned previously, SPS-Ca showed little change in viscosity while changing the concentration of methanol, while PMMA-Na and SPS-Na show a greater change in viscosity. There are some similarities as well, though, as seen in how both PMMA-Na and SPS-Ca remain almost constant when the methanol concentration is increased from 5% to 10%.



**Figure 3.14:** Reduced viscosity vs.  $[IL]/[Ion]$  for PMMA-Na, SPS-Na, and SPS-Ca in a solvent mixture of THF and EMIM-TF at a fixed concentration

-■- PMMA-Na -□- SPS-Ca -●- SPS-Na

A similar comparison can also be done across ionomer systems for EMIM-TF because it is one of only two ionic liquids that worked as a solvent for all three ionomers. Figure 3.14 plots reduced viscosity at a fixed concentration for three ionomers against increasing  $[\text{IL}]/[\text{Ion}]$  ratios for EMIM-TF. The graph makes it easier to see the differences seen when EMIM-TF was used in the solvent mixture. While it did not appear to be very effective for PMMA-Na (limited range and small change in viscosity), EMIM-TF performed similarly for both SPS-Ca and SPS-Na. In addition they were also effective over a much larger range of ratios. It is also observed that while SPS-Ca showed a plateau at higher methanol concentration, the same behavior was not observed for a THF/EMIM-TF solvent mixture.

Another method of comparison that can be made between systems dissolved in ionic liquids and those in benzene and methanol is to compare molar ratios in the solvent. Just like how the  $[\text{IL}]/[\text{Ion}]$  ratio used to measure the amount of IL, the ratio of moles of methanol to moles of ions in the ionomers can be calculated at the initial sample concentration. For PMMA-Na, the methanol concentration ranged from 2% to 10% with  $[\text{MeOH}]/[\text{Ion}]$  ratios ranging from 73 to 340 respectively. SPS-Ca ranged from 3-10% methanol concentration and  $[\text{MeOH}]/[\text{Ion}]$  ratios of 150 to 466. Finally, SPS-Na, ranged from 3-10% with ratios from 144-480. Compared to the ratios for various ionic liquids, the ratio of methanol used is significantly higher. For ionic liquids the highest molar ratio used was about 33, while even the lowest for methanol was more than double that at 73 in the 2% methanol sample of PMMA-Na. Comparing the ratios needed shows that certain ionic liquids are able to achieve similar effects on viscosity to methanol while requiring a fraction of the molar ratio. In some cases, such as EMIM-DEP and EMIM-ES for the sulfonated PS ionomers,

little viscosity change was observed and methanol was shown to be more effective. But in other cases, such as EMIM-TF for SPS-Ca, the ionic liquid was more effective while the effects of methanol were small even with ratios that were over 10 times higher. Also, the lower limit for EMIM-TF with SPS-Na was 2.41 which was significantly lower than the 150 of methanol at 3% concentration. Overall, this shows that significantly smaller amounts of ionic liquid are required to achieve comparable, and in some cases better, changes in reduced viscosity of the three ionomers.

#### 4. Conclusions

The effect of different polar solvents on the intramolecular bonds in ionomer solutions were examined in this study using viscosity experiments. The reduced viscosity for three different ionomer systems were measured with variable solvents and solvent concentrations, and their results compared.

PMMA-Na, SPS-Ca, SPS-Na were dissolved in a solvent mixture of benzene and methanol with the methanol content ranging from 1 to 10%. In the solvent mixture, PMMA-Na was successfully dissolved in 2% methanol content, but showed solid precipitation at lower percentages. Viscosity increases were achieved by increasing methanol concentration to 5% with little to no change occurring when methanol concentration was increased further to 10%. The lowest methanol content necessary to dissolve SPS-Na was found to be 2.7% with solid precipitation occurring at lower concentrations. For SPS-Ca, the lower limit was determined to be 3% with minimal changes in viscosity all the way to 10% methanol.

In addition to benzene and methanol, mixtures of THF and eight different ionic liquids were tested as solvents for the three ionomers. Samples of PMMA-Na were successfully dissolved using BMIM-PF<sub>6</sub>, EMIM-BF<sub>4</sub>, EMIM-PF<sub>6</sub>, and EMIM-TF, while precipitating was observed in the other four. SPS-Ca was dissolved in BMIM-PF<sub>6</sub>, EMIM-DEP, EMIM-ES, EMIM-PF<sub>6</sub>, and EMIM-TF, and SPS-Na was dissolved in BMIM-PF<sub>6</sub>, EMIM-DEP, EMIM-ES, and EMIM-TF. In some ionic liquids, such as EMIM-DEP and EMIM-ES, little change in viscosity was observed even when increasing the concentration. In other cases, such as EMIM-PF<sub>6</sub> and EMIM-TF, the characteristic increase in viscosity with increasing polarity of the solvent for dilute ionomer solutions was observed.



In future studies, the performance of ionic liquids as solvents for ionomers and their effect on solution viscosity can continue to be explored. The goal would be to develop a relationship between the structure of ionic liquids and their effect on the solution properties of ionomers. In addition to using ionic liquids as co-solvents, the solubility of ionomers in pure ionic liquid is also an avenue that will be interesting to investigate. Just as ionic liquids have started seeing use as solvents and composite materials for polymers, the interactions with ionomers is an area in which exciting new discoveries can be made.

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