ION TRANSPORT IN IONIC-LIQUID/POLYMER GEL ELECTROLYTES

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ABSTRACT

Pulsed-field-gradient spin-echo NMR has been used to determine the diffusion coefficients of the cation and anion species in 1,2-Dimethy-3-n-butyl imidazolium bis(triflyl)imide (DMBI+ N(SC>3CF3)2') ionic liquids and poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gels. The transference number of the ionic liquid and the polymer gel has been calculated. The conductivities of both the ionic liquid and polymer gel have been measured as a function of temperature and the activation energies calculated.

INTRODUCTION

Recently there has been increased interest in ionic liquids due to two innovations. First, several air stable molten salts have been developed. These molten salts use air stable anions to replace the moisture sensitive chloroaluminate anions. Several examples are: PF6-, SBF6-, BF4-, CF3SO3-, and N(CF3SO3)2- (1-6). Second, Fuller and Carlin have demonstrated that stable solid gel electrolytes and membranes can be formed by the addition of a polymer, poly-vinylidene-difluoro hexfluorophosphate (PVdF-HFP), to imidazolium based ionic liquids (7-10). These solid gel electrolytes have the potential to provide the structural and stability advantages of a polymer with the ionic conductivity approaching that of the pure molten salt. The properties of these novel electrolyte gels are strongly dependent on the type of ionic liquid, the amount of polymer, and the preparation method used.

In the present work we are investigating the effect of ionic liquid and polymer content on the transport properties of ions in the ionic liquid gels. We have employed conductivity measurements to provide information on the overall transport of charge in the gels, and we have used Pulsed-Gradient Spin-Echo NMR (PGSE) to investigate the movement of cations and anions separately (11-13).

Pulsed-Gradient Spin-Echo (PGSE) NMR is a method for determination of self-diffusion coefficients in solutions (14). The PGSE experiment utilizes a spin-echo experiment coupled with two gradient pulses. The gradient pulses create a linear gradient magnetic field that varies the precessions of the nuclei in the field. Random processes, such as diffusion, cause an attenuation of the spin-echo amplitude due to incomplete refocusing. The relationship between the spin-echo amplitude (A), the gradient pulse strength (g) and the self-diffusion coefficient (D) is given by (15),

\[ A = A_0 e^{-Dg^2} \]
\[ \ln(A_1) = -\gamma^2 g^2 \delta^2 D(\Delta - \delta/3) + \ln(A_0) \]  

where \( \gamma \) is the gyromagnetic ratio, \( \delta \) is the gradient pulse duration, and \( \Delta \) is the time interval between the two gradient pulses. The PGSE experiment involves the collection of spin-echo amplitudes as the gradient pulse strengths are varied. The value of \( D \) can be determined from the slope of a plot of \( \ln(A_1) \) versus \(-\gamma^2 g^2 \delta^2(\Delta - \delta/3)\).

**EXPERIMENTAL**

**Materials**

Preparation of the initial salt: DMBIC1. The preparation of 1,2-dimethyl-4-n-butyll-imidazolium chloride (DMBIC1) involved the reaction of 1,2-dimethyl-imidazole (Aldrich, 98%) and 1-chlorobutane (Aldrich, 99%) in a 1:1.15 molar ratio. The 1,2-dimethyl-imidazole (m.p. 38 °C) was vacuum distilled at approximately 10⁻³ Torr at 135 °C. All subsequent reactions were loaded in a dry box (O₂ and H₂O less than 1 ppm). The 1,2-dimethyl imidazole was melted at 50 °C in a dry box. The starting amount of 1,2-dimethylimidazole, 500 g, and a 15% excess of the corresponding 1-butylpropane were placed, along with 50 mL of acetonitrile, in a thick-walled, single neck, 2 liter round bottom flask. The round bottom flask was then removed from the dry box and fitted with a reflux condenser. The solution was degassed several times with dry nitrogen, gradually heated to 60 °C, and allowed to react for 2 days under nitrogen pressure. After this 2-day reaction period, the temperature was increased to 85 °C and the reaction refluxed for an additional 5 days. Cooling the solution produced a white precipitate and a very faint, yellow supernatant. 300 mL of ethyl acetate was added to the round bottom flask to precipitate all of the DMBIC1. The material was filtered and washed with five 100 mL washings of ethyl acetate in order to remove all of the unreacted 1,2-dimethyl imidazole. The solid material was dissolved in a minimum amount of hot acetonitrile and quickly crashed out of solution by the addition of a large excess of ethyl acetate. The final product was a white crystalline material. Finally, the DMBIC1 was heated to 100 °C under an active vacuum (10⁻³ Torr) for 2 days to remove the volatile contaminants with a final total yield of approximately 80%.

Preparation of the TFSI salts. The preparation of DMBIT⁺ N(SO₂CF₃)₂⁻ was accomplished by reaction of the respective chloride salt with LiTFSI (Aldrich, 99.98%) in acetonitrile. For a typical reaction, one mole of the DMBIC1 was placed in a 1 liter reaction flask fitted with a threaded Teflon plug and dissolved in a minimum amount of acetonitrile. To this solution, an equal molar amount of the LiTFSI was added. The flask was then sealed and allowed to stir at room temperature for 7 days. After which, the flask was removed from the dry box for the last purification steps.

Upon completion of the anion exchange, the solid material (LiCl) was removed by vacuum filtration using a glass frit of medium pore size. Subsequently, all of the acetonitrile was removed by rotary evaporation, causing much of the remaining LiCl to precipitate out of solution. This impure form of the DMBITF₃S1 was then washed seven times with 200 mL of distilled water. The ionic liquid/water mixture separated into two layers. The lower water layer, which contained the remaining LiCl, was drained and
discarded. The solution was then dried for 12 hours at 85 °C under an active vacuum (10⁻³ Torr) for 1 day to remove most of the water. The solution was then diluted with 300 mL of acetonitrile, 30 g of decolorizing carbon, and 30 g of neutral alumina. The solution was allowed to stir at room temperature in a sealed reaction flask for 24 hours. After stirring, the decolorizing carbon and alumina were removed by successive filtrations. Prior to the final filtration, the solution volume was reduced by half using a rotary evaporator, and then acetone was added to restore the original volume. These ionic liquid/acetonitrile/acetone solutions were then filtered through a medium pore size glass frit, a 1 µm filter disc (Whatman, PTFE Membrane), a 0.45 µm filter disc (Whatman, PTFE Membrane), and a 0.2 µm filter disc (Whatman, PTFE Membrane). After filtration, the organic solvents were removed by rotary evaporation, and the remaining ionic liquid was washed twice with 100 mL of water to remove any remaining LiCl. For the final step in the purification process, the ionic liquids were heated to 90 °C under an active vacuum (10⁻³ Torr) for 2 days to remove the volatile components and any of the remaining water. The resulting ionic liquids were clear and colorless.

Preparation of the Polymer Gel Electrolytes. It is important to note that previous work reported for the PVdF based gels used a technique involving prolonged periods of heating and stirring (8), while several different methods have been reported for PEO gels (16). The preparation method presented here, using a sonication horn (Sonics and Materials Vibracell) resulted in much quicker preparation times, greater reproducibility and more stable composites with a significantly higher ionic liquid content. Some earlier work reported extreme difficulty in preparing gels containing more than 66% ionic liquid (8).

The polymer gels were prepared in an argon dry box (H₂O and O₂ less than 1 ppm). The PVdF-HFP (Kynar-2801-00 from Elf Atochem) was dissolved using 4-methyl-2-pentanone (98%, Aldrich) as the solvent. For each sample prepared, 0.5 g of the polymer was added to 10 mL of the solvent. The solvent/polymer mixture was sonicated for 2 minutes at high power, allowed to cool, and then resonicated for 2 additional minutes, in order to completely dissolve the polymer in the solvent. 2 grams of the ionic liquid were added, and sonication was continued, with intermittent pauses to allow for sample cooling, until there was a marked drop off in the sound of cavitation produced. The resulting ionic liquid-polymer solution was removed from the sonicator and allowed to stir at 60 °C under argon until the mixture became extremely viscous. The liquid composite material was removed from heat, poured into a 6.35 cm diameter aluminum weighing boat and cured at room temperature for 24 hours in the dry box. The aluminum boats were subsequently placed in a vacuum oven and dried an additional 24 hours under an active vacuum (approximately 10⁻³ Torr) at 75 °C. For all polymer gels prepared, the thickness of the gels was typically between 1-2 mm.

Measurements

Electrochemical Measurements. Temperature dependent impedance measurements were made with a Solartron Si 1260 Gain Phase Analyzer at frequencies from 100 kHz to 1 Hz, using AC amplitude of 5 mV. The sample holder was a standard t-cell composed of a polypropylene body fitted with three stainless steel swagelock fittings. Into each of the fittings was placed a stainless steel rod. All measurements were made from the initial temperature of 125 °C. The temperature intervals were approximately
10 °C. The cell was allowed to equilibrate at each temperature for approximately 1 hour before the next measurement. Sample thickness was determined by the difference between caliper measurements of the end-to-end length of the stainless steel rods with and without the polymer gel between them. The ionic conductivity was calculated from the measured resistance when the imaginary component at high frequency fell to zero.

**NMR Experiments.** Ionic liquid samples were placed into 5 mm NMR tubes. Gel samples were cut into elongated strips, coiled, and packed into 5 mm NMR tubes. Gel sample geometry increases the difficulty of obtaining quality spectra. Nonetheless, reasonable spectra were obtained of the ionic liquid in a solid polymer gel. The NMR spectrometer used during this work was a Varian INOVA (300 MHz). The spectrometer was equipped with a Varian Performa III gradient amplifier (20 amps) and a DOTY 5 mm air-cooled gradient probe. The 90° pulse width for $^1$H (299.974 MHz) was 15 μsec while the 90° pulse width for $^{19}$F (282.059 MHz) was 37 μsec. A standard refocusing gradient diffusion pulse sequence was used (15). The delay to allow for diffusion was 30 msec and the gradient pulses where applied for 1.3 msec. The applied gradient field was varied from 0 to either 200 or 375 gauss/cm in at least 30 increments. Each diffusion experiment consisted of 32 acquisitions at each gradient field with at least a 25 second relaxation between acquisitions. Sample temperature was maintained at 298 K throughout the experiments. We calculated the diffusion coefficient of the imidazolium cations from the resonances of the methyls attached to the 1 and 2 positions of the imidazolium ring because of improved signal to noise (singlet resonance from 3 $^1$H) and because movement of the butyl chain can lead to erroneously large diffusion coefficients. The diffusion coefficients for the bis(triflyl)imidide anion were determined from a single resonance that appeared in $^{19}$F spectra of both the ionic liquid and polymer gel. Surprisingly the poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer did not produce an observable $^{19}$F resonance most likely because it is in a solid state.

**RESULTS AND DISCUSSION**

The variation in conductivity with respect to temperature of the (DMBI$^+$ N(SO$_2$CF$_3$)$_2^-$) ionic liquid and a poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel have been determined (Figure 1). These data clearly show the effect of polymer content on the gel conductivity. The Arrhenius fits of the data in Figure 1 indicate activation energies for ionic conduction of 21.6 kJ/mol and 21.2 kJ/mol for the ionic liquid and polymer gel (75% ionic liquid, 25% polymer), respectively. The activation energy for conduction of both the ionic liquid and the polymer gel are essentially identical within experimental error. This result implies that the movement of the ionic liquid in the gels is not impeded by the polymer at these ionic liquid concentrations.
Figure 1. Conductivity of 1,2-Dimethy-3-n-butyl imidazolium bis(triflyl)imide (DMBI* N(SO2CF3)2) ionic liquid and 75% ionic liquid 25% poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel as a function of T^−1.

Pulsed gradient-field spin-echo (PGSE) measurements of the self-diffusion coefficients of both the cations and the anions in both the (DMBI+ N(SO2CF3)2) ionic liquid and a poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel were measured using 1H and 19F pulse field gradient NMR. In these experiments the peak integral is reduced as the gradient strength increase (Figure 2). When the natural log of the integral is plotted versus the square of the gradient pulse strength a straight line should result (Figure 3). The slope of the line is proportional to the diffusion coefficient. The quality of the least squared fit of the data is an indicator of the uncertainty of the self-diffusion coefficient and also a measure of performance of the spectrometer hardware. The self-diffusion coefficient of the cations and anions of both the (DMBI+ N(SO2CF3)2) ionic liquid and a poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel are shown in Table 1. The largest uncertainty from the least squares fit was less than 1% of the diffusion coefficient. Even so, temperature control and gradient strength uncertainties multiply the uncertainty of the self-diffusion coefficient.
Figure 2. Series of $^{19}$F Spectra of (DMBI$^+$ N(SO$_2$CF$_3$)$_2$) Ionic Liquid as the Pulsed Gradient Strength is Increased from 0 gauss/cm to 375 gauss/cm.

Figure 3. Natural Log of the Peak Integral of a Series of $^1$H Spectra of (DMBI$^+$ N(SO$_2$CF$_3$)$_2$) Ionic Liquid versus the Strength of the Gradient Pulse Squared. Pulsed Gradient Strength Increases from 0 to 200 gauss/cm.
Table 1. Diffusion Coefficients for the Cation and the Anion of Both the (DMBI⁺ N(SO₂CF₃)₂⁻) Ionic Liquid and a Poly-Vinylidene-Difluoro Hexfluorophosphate (PVdF/HFP) polymer gel (75% Ionic Liquid, 25% Polymer).

| Sample                  | \(^1\text{H}\) (cm²/sec) Cation | \(^{19}\text{F}\) (cm²/sec) Anion |
|-------------------------|---------------------------------|----------------------------------|
| DMBI bis(triflyl)imide  | \(1.83 \times 10^{-7}\)        | \(1.58 \times 10^{-7}\)        |
| 75% DMBI bis(triflyl)imide, 25% PVDF/HFP | \(1.38 \times 10^{-7}\)        | \(1.46 \times 10^{-7}\)        |

The ionic liquid cation and anion diffusion coefficients are both larger than those in the polymer gel. However, the reduction in the diffusion coefficient is within the uncertainty of these measurements. It is interesting to note that the reduction in conductance between the ionic liquid and polymer gel is similar to the reduction in the cation diffusion coefficient (Table 2). Additional measurements to be taken in the future will reduce the uncertainty so we can ascertain whether this effect is authentic.

With both the cation and anion self-diffusion coefficients determined, the transport number can be calculated (Table 2). For both the (DMBI⁺ N(SO₂CF₃)₂⁻) ionic liquid and the poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel the transport number is approximately 0.5. This is because the cation and anion are diffusing at roughly the same rate in the ionic liquid and in the polymer gel.

Table 2. Transport Number of (DMBI⁺ N(SO₂CF₃)₂⁻) Ionic Liquid and a Poly-Vinylidene-Difluoro Hexfluorophosphate (PVdF/HFP) polymer gel (75% Ionic Liquid, 25% Polymer). Reduction in Diffusion Coefficient between the Ionic Liquid and Polymer Gel Compared to the Reduction in Conductance.

| Sample                  | Transport Number | Reduction in Diffusion Coefficient | Reduction in Conductance |
|-------------------------|------------------|-----------------------------------|--------------------------|
| DMBI bis(triflyl)imide  | 0.54             | -                                 | -                        |
| 75% DMBI bis(triflyl)imide, 25% PVDF/HFP | 0.49             | 25%                               | 8%                       | 29%                      |

CONCLUSIONS

Conductance measurements for both the (DMBI⁺ N(SO₂CF₃)₂⁻) ionic liquid and a poly-vinylidene-difluoro hexfluorophosphate (PVdF/HFP) polymer gel as a function of temperature have been determined. The activation energy for conduction of both the ionic liquid and the polymer gel are essentially the same within experimental error. The
diffusion coefficients for the cation and anion of both the ionic liquid and the polymer gel have been measured as well. A slight decrease in self-diffusion coefficient is observed between the ionic liquid and the polymer gel. However, the decrease is less than the current level of experimental uncertainty. Additional measurements will be conducted to ascertain whether this effect is authentic. The transport numbers of both the ionic liquid and of the polymer gel are 0.5. We will continue this work to include: the effect of temperature on diffusion coefficients, the effect of composition of the polymer gel on both conductivity and diffusion, the effect of variation of polymer identity on both conductivity and diffusion, and the effect of inclusion of lithium cation on both conductivity and diffusion.

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