STUDIES OF CATION TRANSPORT IN MOLTEN SALTS AND MOLTEN SALT-POLYMER GELS BY PULSED-FIELD-GRADIENT SPIN-ECHO NMR

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ABSTRACT

Pulsed-field-gradient spin-echo NMR has been used to determine the diffusion coefficients of the cation species in a series of chloroaluminate room-temperature molten salts as well as that of 1,2-dimethy-3-propyl imidazolium tetrafluoroborate (DMPI:BF₄) and a molten salt polymer gel. Based on the diffusion coefficients the activation energy for diffusion of the melt cation has been calculated. In addition the hydrodynamic radius of the melt cation has been determined using the Stokes-Einstein relation.

INTRODUCTION

Ambient-temperature chloroaluminate ionic liquids are an important class of non-aqueous solvents; they have been used for a wide variety of chemical and electrochemical studies (1-4). In addition, they show promise as electroplating baths for industrial aluminum electroplating as well as electrolytes in high energy density batteries (5-7). In addition, recently there has been increased interest in molten salts due to two innovations. First, several air stable molten salts have been developed (8-13). These
molten salts use air stable anions to replace the moisture sensitive chloroaluminate anions. Several examples are: PF$_6^-$, SBF$_6^-$, BF$_4^-$, CF$_3$SO$_3^-$, and N(CF$_3$SO$_3$)$_3^-$ (8-13). Second, various molten salts have been combined with polymers to form polymer-molten salt composites (14).

Studies of the transport properties of the ambient-temperature molten salt, 1-ethyl-3-methylimidazolium chloride:aluminum chloride (EMIC:A1Cl$_3$), found that the internal transport number of the cation, EMI$^+$, was 1.00 over a wide range of melt compositions (15). This indicates that the cation predominates charge transport in these molten salts. Efforts to measure the diffusion coefficient of the EMI$^+$ cation in these melts have met with limited success. Carlin and Osteryoung used microelectrode techniques to obtain a value of $D = 1.0 \times 10^{-7}$ cm$^2$/s in an $N = 0.44$ melt (16). Unfortunately, due to the limitations of the technique, this value is at best a crude estimate of the true diffusion coefficient.

Pulsed-Field-Gradient Spin-Echo (PGFSE) NMR is a method for determination of self-diffusion coefficients in solutions (17). The PGFSE 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 refocussing. The relationship between the spin-echo amplitude ($A$), the gradient pulse strength ($g$) and the self-diffusion coefficient ($D$) is given by (18),

$$\ln(A_1) = -\gamma^2 g^2 s^2 D(\Delta - \delta/3) + \ln(A_0)$$  \[1\]

where $\gamma$ is the gyromagnetic ratio, $\delta$ is the gradient pulse duration, and $\Delta$ is the time interval between the two gradient pulses. The PGFSE 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 $-\gamma^2 g^2 s^2(\Delta - \delta/3)$ (Figure 1).

In this manuscript we have employed PGFSE NMR to investigate the cation self-diffusion coefficients in room-temperature molten salts and gels prepared from those salts. Furthermore we have studied the affects of melt composition, counter ion, and temperature on cation self-diffusion rates.

EXPERIMENTAL

Materials

The preparation of 1-ethyl-3-methylimidazolium chloride (EMIC) was performed as previously described (5,19). Aluminum Chloride (Fluka, Puriss.>99%) was distilled in a sealed high-pressure glass tube. Chloroaluminate melts were prepared by mixing appropriate amounts of EMIC with AlCl$_3$ in a nitrogen filled Vacuum Atmospheres
drybox (O_2 and H_2O < 1 ppm). The preparation of 1,2-dimethyl-3-n-propylimidazolium chloride (DMPICl), the tetrafluoroborate salt of DMPI, and the molten salt polymer composite gels were performed as described (20).

NMR Experiments

Liquid molten salt samples where placed into 5 mm NMR tubes in a drybox and then flame sealed. Gel samples were cut into elongated strips and placed into 5 mm NMR tubes. Gel sample geometry increases the difficulty of obtaining quality spectra. In future work, it would be beneficial to prepare the gels in the NMR tubes. The NMR spectrometer used during this work was a Bruker Avance DRX-500 (500 MHz). The spectrometer was equipped with a Bruker Accustar II gradient amplifier and a Nalorac Z-Spec 5 mm indirect detection probe. The applied gradient field was varied from 5 to 50 gauss/cm in 15 increments. The longitudinal encode-decode diffusion pulse sequence was used (21). In this pulse sequence the echo decays according to T_1 rather than T_2 which is observed in the original pulse sequence. In the measurements described here we used a 90° pulse with a pulse width of 6 msec and a 5 msec gradient. The time delay used to allow for diffusion was varied between 10 and 30 msec depending upon the sample (viscous samples and gels 30 msec). Eight acquisition where accumulated at each gradient field with a 15 second relaxation between acquisitions. Sample temperature was varied from 298 to 313 K in 5 K increments. Any of the ^1H resonances on the EMI^+ could be used to determine the diffusion coefficient. We verified that the resonances on the EMI^+ were consistent. The diffusion coefficients were calculated based upon the 3-methyl resonance because this resonance provided the optimum signal to noise (singlet resonance from 3 ^1H).

RESULTS AND DISCUSSION

Self-diffusion coefficients of the EMI^+ cation for EMIC:AICl_3 melts were measured as a function of basic melt composition and temperature. Figure 2 shows the variation in diffusion coefficient with composition (displayed as the ratio of moles AICl_3 to moles EMIC) for a series basic EMIC:AICl_3 melts. These data correlate strongly with corresponding changes in melt viscosity. As expected, the diffusion coefficient increases as the temperature is increased.

Plots of the natural log of the cation self diffusion coefficients versus inverse absolute temperature were made for each melt sample. An example of one of these Arrhenius plots is shown in Figure 3. The slope from the least squares fit of these data for each plot times R (gas constant 8.314 J K^{-1} mol^{-1}) gave the activation energy (E_a) for diffusion for each melt composition. Figure 4 depicts the activation energies for self diffusion of the EMI^+ cation in a series of EMIC:AICl_3 melts. The E_a for diffusion of the EMI^+ cation gradually increases from 21 to 64 kJ/mol for melt ratios of 1:1 to 0.45:1
respectively. This increase in activation energy with increasing melt basicity may be the result of increasing hydrogen bonding between chloride ions and EMI⁺.

The hydrodynamic radius of the EMI⁺ cation can also be calculated from the diffusion data. The Stokes-Einstein relation is:

\[ D = \frac{kT}{6\pi\eta a} \]  

Where \( f = 6\pi\eta a \), \( k \) is the Boltzmann constant, \( T \) is temperature in Kelvin, \( \eta \) is the solution viscosity, and \( a \) is the hydrodynamic radius of the ion. Using the viscosity data of Wilkes et al. (22) and our cation self diffusion data, we were able to estimate the hydrodynamic radius of the EMI⁺ in the EMIAICI₃. These data for various basic melt compositions and temperatures are shown in Figure 5. Although the data in Figure 5 show unrealistically low values for the hydrodynamic radius (nominally 0.75 Å versus expected values of >2.5 Å) the data do seem to indicate that the hydrodynamic radius does not appear to change significantly as a function of either melt composition or temperature.

We conducted some initial measurements of the self-diffusion coefficients of the EMI⁺ cation in a poly-vinylidene-difluorohexfluorophosphate (PVDF):EMIBF₄ gel. These data are summarized in Table I. For comparison diffusion coefficients for the cations in pure melts are given. As the data in Table I indicate, the self diffusion coefficients for the cation in the molten salt gels are 5 to 10 times smaller than for the cation in the corresponding pure melt. This observation is consistent with the observed 5 to 10 fold decrease in ionic conductivity going from a pure melt to a molten salt gel (20).

Table I. Cation Diffusion Coefficients for Melts and PVDF gels

| Melt              | Temperature | Diffusion Coefficient         |
|-------------------|-------------|-------------------------------|
| EMI:AlCl₃ Melt    | 313 K       | 2.75 X 10⁻⁷ cm²/sec           |
| DMP1:BF₄ Melt     | 313 K       | 9.94 X 10⁻⁷ cm²/sec           |
| 4:1 EMIC:BF₄ PVDF Gel | 313 K | 1.67 X 10⁻⁷ cm²/sec           |
| 3:1 EMIC:BF₄ PVDF Gel | 313 K | 4.0 X 10⁻⁷ cm²/sec           |

CONCLUSIONS

Diffusion coefficients for the cation of several room-temperature molten salts have been measured. These results are in reasonable agreement with both the previous electrochemical data as well as viscosity measurements. Activation energies for the self diffusion of the melt cation show significant dependance on melt composition and are indicative of structure formation as melt basicity increases. Initial studies with molten salt polymer gels indicates a significant decrease in cation self diffusion in the gels when compared with the pure melts.
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Figure 1. Plot of \( \ln(A_1) \) versus \( -\gamma^2 g^2 (\Delta - \delta/3) \). Melt Ratio 0.69:1.0  
\( N = 0.45 \)  
Temp = 298 K  
\( D = (1.48 \pm 0.03) \times 10^{-6} \)  
\( R^2 = 0.995 \)

Figure 2. Plot of the Diffusion Coefficients of the EMI\(^+\) cation in a series of melts vs. the basic melt ratio (moles AlCl\(_3\)/moles EMIC) for the temperatures 298, 303, 308, and 313 K.
Figure 3. Arrhenius Plot of the Natural Log of the Diffusion Coefficient vs. the inverse of the temperature. Melt Ratio 0.69:1.0 \( N = 0.45 \). \( E_a = 13.3 \text{ kJ/mol} \) as determined from the slope of the least-squares fit of the data.

Figure 4. Activation energies \( (E_a) \) for diffusion of the EMI\(^+\) cation in a series of EMIC:AlCl\(_3\) melts. Melt Ratio = (moles AlCl\(_3\)/moles EMIC)

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Figure 5. Plot of hydrodynamic radius of the EMF$^+$ cation (Å) vs. the melt mole ratio for the temperatures 298, 303, 308 and 313 K. Melt Ratio = (moles AlCl$_3$/moles EMIC)