Mass and charge transport in 1-alkyl-3-methylimidazolium triflate ionic liquids

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Temperature-dependent transport properties in ionic liquids, such as the ionic conductivity and fluidity, are often characterized empirically through equations that require multiple adjustable fitting parameters in order to adequately describe the data. These fitting parameters offer no insight into the molecular-level mechanism of transport. Here the temperature dependence of these transport properties in 1-alkyl-3-methylimidazolium triflate ionic liquids is explained using the compensated Arrhenius formalism (CAF), where the conductivity or fluidity assumes an Arrhenius-like form that also contains a dipole density dependence in the exponential prefactor. The resulting CAF activation energies for conductivity and fluidity are much higher than those obtained from polar organic liquids and electrolytes. The CAF very accurately describes the temperature dependence of both conductivity and fluidity using only system properties (i.e., density and activation energy). These results imply that the transport mechanism in molten salts is very similar to that in polar organic liquids and electrolytes. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4832037>]

I. INTRODUCTION

Ionic liquids are a class of ionic compounds that possess sufficiently low lattice energies to exist in a molten state near room temperature ($T < 100^\circ\text{C}$). The almost exponential growth in basic and applied research in this field is driven by the extraordinary properties these materials offer in comparison with traditional solvent systems. Indeed, ionic liquids are rapidly becoming a distinct class of solvents in their own right. The synthetic versatility available in designing constituent ions of an ionic liquid allows researchers to tailor properties towards specific applications, prompting aggressive initiatives to develop ionic liquid solvents for a wide array of functions. Some potential uses for ionic liquids include electrolytes for energy storage and conversion devices; solvent systems for the extraction of natural products, chemical separations, and chemical synthesis; and the development of ionic liquids with pharmaceutical properties.

Ionic liquids exhibit a tremendous degree of variation with regard to their transport properties, and understanding the factors leading to these differences constitutes a major area of active research. The conductivity and viscosity are both fundamentally linked to the strong cohesive forces that necessarily exist between the ions. These ion-ion interactions lead to long-range, correlated motions of the ions that ultimately define the properties of the fluid as well as the overall liquid-phase structure. Therefore, it is imperative to have an adequate understanding of the molecular-level interactions in order to optimize the transport properties in these materials.

We have recently shown that mass and charge transport in polar liquids and their electrolytes can be described

very accurately using the compensated Arrhenius formalism (CAF). The CAF represents the transport coefficients for ionic conductivity,^{1–5} self-diffusion coefficient,^{4–7} dielectric relaxation rate constant,⁸ and fluidity⁹ with the same mathematical form. In each case the transport coefficient assumes an Arrhenius-like expression that also includes a static dielectric constant dependence in the exponential prefactor. All of the temperature dependence in the prefactor is due to the inherent temperature dependence of the dielectric constant. A scaling procedure can be performed that accounts for the dielectric constant dependence and allows calculation of the activation energy for transport.^{1,6,8,9}

Here, the CAF is applied to mass and charge transport phenomena in 1-alkyl-3-methylimidazolium triflate ionic liquids, where the alkyl group is either butyl, hexyl, octyl, or decyl. These four ionic liquids are abbreviated here as bmimTf, hmimTf, omimTf, and dmimTf, respectively. Application of the CAF involves measurement of both the transport coefficient of interest and the static dielectric constant of the system. However, measurement of the dielectric constant in ionic liquids is more complicated than that for polar organic liquids and electrolytes. It has been well documented that high frequency dielectric relaxation spectroscopy is required to measure the static dielectric constant of ionic liquids and that standard capacitance and voltammetric techniques produce artificially high values for the dielectric constant.¹⁰ But even dielectric relaxation spectroscopy can be problematic due in large part to the choice of fitting procedure and extrapolation of the data. The static dielectric constant is determined by fitting the dispersion portion of the frequency-dependent real part of the dielectric constant with an empirical function and then extrapolating to zero frequency. Static dielectric constants measured in this way are much less accurate than those determined from

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conventional methods.^{10,11} Furthermore, the empirical function chosen to fit the dispersion curve can greatly influence the temperature-dependent behavior of the resulting static dielectric constant. For example, it has been shown that fitting the data to one functional form leads to dielectric constants that increase with temperature, while choosing a different function results in dielectric constants that decrease with temperature.¹⁰

Application of the CAF to ionic liquids using dielectric constant data obtained from dielectric spectroscopic measurements will undoubtedly lead to significant uncertainty in CAF activation energies and prefactors due to the complications described above. However, dielectric constant measurements can be avoided in the CAF procedure because Onsager developed a model that relates the static dielectric constant of an aprotic polar organic liquid to molecular and system properties.¹² The temperature dependence of the dielectric constant in this model is adequately described by the quantity N/T , where N is the liquid dipole density and T is the temperature. The dipole density is determined by dividing the liquid density by its molecular weight. We have shown that the CAF can be performed by scaling out the N/T dependence instead of the dielectric constant dependence.⁵ The calculation of N/T for ionic liquids is much more accurate than measuring the dielectric constant since it only requires measurement of the temperature-dependent density.

It has been questioned whether Onsager's equation for the dielectric constant is applicable in ionic liquids since the strong Coulombic interactions in these substances might produce charge-ordered structures that differ drastically from the structure of typical polar molecular liquids.^{13–15} However, Hunger *et al.* have demonstrated that an Onsager-type equation adequately characterizes the temperature dependence of the static dielectric constant for a variety of ionic liquids.¹⁰ Additionally, it is well-known that Onsager's equation is only applicable to aprotic liquids¹⁶ and controversy exists about whether the imidazolium cation undergoes hydrogen bonding interactions.^{17–19} The IR spectra of the alkyl-methylimidazolium triflate ionic liquids show no indication of hydrogen bonding interactions (data not shown), and consequently we assume here that Onsager's equation is a reasonable starting point for understanding the temperature dependence of transport properties in these systems. Kobrak and Li have raised concerns about the use of dielectric continuum theory in the calculation of the polarization energy, although they note that the theory gives reasonable predictions in some contexts.¹⁵ However, here we are only concerned with those variables in the Onsager's equation that control the temperature dependence.

Temperature-dependent viscosities and ionic conductivities of ionic liquids are commonly described using empirical equations that utilize multiple adjustable fitting parameters to adequately characterize these data.^{20–23} However, these fitting parameters reveal no insight into which molecular-level variables influence transport phenomena. Here we use the CAF to demonstrate that the temperature dependence of mass and charge transport in molten salts can be very accurately described using only system properties instead of empirical equations.

II. EXPERIMENTAL METHODS

The ionic liquids were obtained from Iolitec and heated under vacuum at 55 °C for three days before being transferred to a glovebox (≤ 1 ppm H_2O) under a nitrogen atmosphere. IR spectra showed no trace of water in these samples.

The conductance was measured using a HP 4192A impedance analyzer that swept a frequency range from 1 kHz to 13 MHz. The sample holder was an Agilent 16452A liquid test fixture. The conductivity, σ , is calculated from the measured conductance, G , through the equation $\sigma = LGA^{-1}$, where L is the electrode gap and A is the electrode area. A Huber Ministat 125 bath was used to regulate the temperature from 5–85 °C, in increments of 10 °C for the conductivity measurements. The density of the ionic liquids was measured over the temperature range 5 to 85 °C using an Anton Paar DMA 4500M density meter. The viscosity was measured with a Cambridge VISCOLab 4000. For viscosity measurements, the temperature was regulated over the range 25–85 °C, in increments of 10 °C, using a Huber Ministat 240 bath. Conductivity, density, and viscosity measurements were all performed in a glovebox to prevent water contamination. Subambient conductivity and density data (5 and 15 °C) could only be obtained for omimTf due to its lower melting point.

III. RESULTS AND DISCUSSION

The CAF postulates that the temperature-dependent ionic conductivity $\sigma(T)$ and fluidity $F(T)$ are represented in the following form:^{1,9}

$$\sigma(T) = \sigma_o(\epsilon_s(T)) \exp(-E_a/RT), \quad (1)$$

$$F(T) = F_o(\epsilon_s(T)) \exp(-E_a/RT), \quad (2)$$

where E_a is the activation energy, ϵ_s is the static dielectric constant, $F(T)$ is the inverse of the viscosity $\eta(T)$, and $\sigma_o(\epsilon_s(T))$ and $F_o(\epsilon_s(T))$ are the exponential prefactors for conductivity and fluidity, respectively. The prefactors are written to show that their temperature dependence is due entirely to the inherent temperature dependence of the dielectric constant. Since the temperature dependence of ϵ_s is given by N/T from Onsager's work, Eqs. (1) and (2) can be rewritten in the following form:

$$\sigma(T) = \sigma_o(N(T)/T) \exp(-E_a/RT), \quad (3)$$

$$F(T) = F_o(N(T)/T) \exp(-E_a/RT). \quad (4)$$

The activation energies in Eqs. (3) and (4) are determined from a scaling procedure that cancels the prefactor.^{1,5,9} The scaling procedure can be carried out by considering the prefactor to depend on the value of ϵ_s (Eqs. (1) and (2)), or equivalently N/T (Eqs. (3) and (4)). Here we describe the scaling procedure using N/T since the CAF was applied to the ionic liquid data in this way. The scaling process is applied to a family of solvents, where a solvent family consists of members that have the same functional group but differ in alkyl chain length. For example, the members of the 1-alkyl-3-methylimidazolium triflate ionic liquid family considered in this work are bmimTf, hmimTf, omimTf, and dmimTf. Two

sets of data are required for the scaling procedure of a particular solvent family. The transport property of interest, e.g., σ , and N/T are measured isothermally for each member of the solvent family. This set of isothermal conductivities is represented as σ_r . The temperature at which these measurements are made is denoted as the reference temperature T_r . When σ_r is plotted against N/T , these isothermal data are collectively referred to as the reference curve for conductivity. Second, temperature-dependent σ measurements are collected for one particular member of the solvent family. The scaling procedure involves dividing the temperature-dependent value of σ by the reference value σ_r that corresponds to the same value of N/T . The division of σ by σ_r cancels the exponential prefactors. This procedure is repeated for each temperature in the measurement range. A more detailed description of the scaling procedure is given elsewhere.^{1,9} The final result of the scaling procedure is the compensated Arrhenius equation (CAE) for conductivity or fluidity:

$$\ln\left(\frac{\sigma(T)}{\sigma_r(T_r)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r}, \quad (5)$$

$$\ln\left(\frac{F(T)}{F_r(T_r)}\right) = -\frac{E_a}{RT} + \frac{E_a}{RT_r}. \quad (6)$$

The activation energy for conductivity or fluidity is determined from either the slope or intercept of Eq. (5) or (6), respectively.

Figure 1 shows that CAE plots from both conductivity and fluidity data are very linear. The activation energy obtained from the slope is almost identical in value to that from the intercept for all CAE plots. Changing the ionic liquid member or reference temperature has only a marginal effect on the value of the activation energy, which are trends previously observed for pure organic liquids and electrolytes.^{1,4,6} The average activation energy for conductivity in the 1-alkyl-3-methylimidazolium triflate family is 49.9 ± 0.5 kJ/mol while that for fluidity is 43.5 ± 0.7 kJ/mol. These activation energies are substantially higher than those obtained for

FIG. 1. CAE plots for (a) conductivity and (b) fluidity. Temperature-dependent data for hmimTf or omimTf are scaled to data at a reference temperature of either 35, 45, 55, or 65 °C.

FIG. 2. (a) Conductivities versus N/T for bmimTf, hmimTf, omimTf, and dmimTf over the temperature range 5–85 °C. (b) Conductivities from (a) divided by $\exp(-E_a/RT)$, where $E_a = 49.9$ kJ/mol.

typical aprotic organic liquids and electrolytes.^{1,5,9} The high E_a value for transport in molten salts is expected since ionic liquids have strong Coulombic interactions in addition to the dipole-dipole interactions that exist in a pure polar organic liquid.

We now demonstrate that the temperature dependence of the conductivity and fluidity exponential prefactors is completely described by N/T . The prefactors for conductivity and fluidity are calculated from Eqs. (3) and (4), respectively, by dividing the conductivity or fluidity at each temperature by the Boltzmann factor $\exp(-E_a/RT)$, where E_a is the average activation energy obtained from the CAE plots. Figure 2(a) shows that when temperature-dependent conductivities are plotted against N/T for bmimTf, hmimTf, omimTf, and dmimTf, the data are divided into four well-separated curves with each curve giving the temperature-dependent data for a particular ionic liquid. However, Fig. 2(b) shows that all data lie on a single master curve when the exponential prefactors are plotted against N/T . The formation of a master curve supports the primary CAF postulate that all temperature dependence in the prefactor is due to N/T , and also reinforces the assumption that Onsager's model for ϵ_s can be applied to molten salts. The CAF can also be applied to the molar conductivity Λ in

FIG. 3. (a) Molar conductivities versus N/T for bmimTf, hmimTf, omimTf, and dmimTf over the temperature range 5–85 °C. (b) Molar conductivities from (a) divided by $\exp(-E_a/RT)$, where $E_a = 46.5$ kJ/mol.

FIG. 4. (a) Fluidities versus N/T for bmimTf, hmimTf, omimTf, and dmimTf over the temperature range 25–85 °C. (b) Fluidities from (a) divided by $\exp(-E_a/RT)$, where $E_a = 43.5$ kJ/mol.

order to obtain a better description of ion mobility. The molar conductivity is calculated at a given temperature by dividing the conductivity by the dipole density, and the prefactor Λ_0 results from dividing the molar conductivity by the Boltzmann factor. The average CAF activation energy for molar conductivity (46.5 ± 0.4 kJ/mol) is slightly lower than that for conductivity, but similar CAF trends are observed for Λ and Λ_0 , as shown in Fig. 3. The temperature dependence of fluidity exhibits behavior similar to that for conductivity. Figure 4(a) shows that temperature-dependent fluidity data lie on separate curves for each ionic liquid when plotted against N/T , while Fig. 4(b) shows that all data fall on the same curve when the fluidity prefactors are plotted against N/T .

IV. CONCLUSIONS

The temperature dependence of the conductivity or fluidity in the molten salts discussed here is described very well as the product of two factors: (1) an exponential prefactor whose temperature dependence is given by the temperature-dependent density of the ionic liquid using the quantity N/T , and (2) a Boltzmann factor whose temperature dependence is straightforward once the appropriate E_a value is determined from the CAF scaling procedure. Consequently, temperature-dependent mass and charge transport phenomena in ionic liquids can be characterized through the system density and activation energy instead of using empirical equations with multiple adjustable fitting parameters. The fact that the CAF describes transport in molten salts as well as in pure polar organic liquids and their electrolytes demonstrates that the transport mechanism in these systems is essentially the same except that ionic liquids have a higher energy barrier for transport compared to organic liquid systems.

Since the temperature dependence has been examined here for both conductivity and fluidity of 1-alkyl-3-methylimidazolium triflate ionic liquids, it is worthwhile to discuss the relationship between these two properties since this is commonly done in the literature for a wide range of ionic liquids. Walden's rule is often applied to ionic liquids, where the molar conductivity Λ is assumed to be directly pro-

FIG. 5. Temperature-dependent molar conductivity versus temperature-dependent fluidity for bmimTf, hmimTf, omimTf, and dmimTf. These data were measured at the same temperatures as given in Fig. 4.

portional to the fluidity.^{24–26} Figure 5 shows a Walden plot for the data studied here and demonstrates an approximate relation between molar conductivity and fluidity, with a stronger correlation in the data as the temperature decreases. It is well known that Walden's rule is at best a rough approximation in both molten salts²⁶ and organic liquid electrolytes,²⁷ although this rule is at least qualitatively valid. We have shown that the temperature dependence of both the conductivity and fluidity prefactors for the ionic liquids examined here is characterized very well by N/T . A Walden plot describes one macroscopic transport property in terms of another even though the temperature dependence of each property can be accurately described through its dependence on N/T and $\exp(-E_a/RT)$. It is likely that the approximate nature of Walden's rule, at least for these systems, is due to two factors: (1) relating the molar conductivity indirectly to N/T through the fluidity instead of treating the molar conductivity prefactor as a direct function of N/T , and (2) the difference in E_a values between fluidity and conductivity. The ionic liquid data presented here can be accessed in the supplementary material.²⁸

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