

Investigation of Fundamental Transport Properties and Thermodynamics in Diglyme–Salt Solutions

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Received: January 6, 2006; In Final Form: August 25, 2006

Ionic mobility, the thermodynamics of ionic association, and the structure of associated species are studied in solutions of diglyme containing either lithium triflate or tetrabutylammonium triflate. Infrared spectroscopic, PFG NMR, thermodynamic, and crystallographic data suggest that the solute species existing in diglyme–lithium triflate are “free” ions, contact ion pairs, and dimers. Equilibrium constants, ΔS° , ΔH° , and ΔG° are calculated for processes occurring between these species. In particular, the equilibrium constant, corrected for nonideality using a modified Debye–Hückel expression, is calculated for the dissociation of contact ion pairs into “free” cations and anions. A second equilibrium constant for the formation of dimers from contact ion pairs is also calculated; these constants do not significantly vary with salt concentration up to about 1.3×10^{-3} mol cm⁻³. The measured temperature dependence of equilibrium constants was used to calculate ΔH° and ΔS° for the two processes. The value of $\Delta S^\circ = -102$ J mol⁻¹ K⁻¹ for the dissociation of contact ion pairs shows that the large entropy decrease due to cation solvation outweighs the entropy increase due to dissociation of a contact ion pair. Ionic mobilities are calculated in lithium triflate–diglyme solutions using conductivity data in conjunction with information about the nature and concentrations of solute species obtained from IR spectroscopy. Mobilities in tetrabutylammonium triflate–diglyme solutions are calculated directly from conductivity data. It was concluded that the concentration dependence of the molar conductivity is due in large part to the variation of the ion mobilities with concentration.

1. Introduction

Ion transport in liquid electrolytes has been studied for over a century. The principle goals of these studies have been experimental determination of the mobilities of the solute species and understanding of the dependence of these mobilities on concentration and on temperature. In most systems, the solute species and their concentrations are not known so that mobilities cannot be calculated. For this reason, ion transport is often studied using molar conductivity data. Molar conductivity is defined as the conductivity divided by the total salt concentration, and it is related to the mobility of the ions. Kohlrausch showed that the molar conductivity decreases linearly with the square root of the salt concentration over a substantial concentration range for 1:1 salts (both ions have a monovalent charge) in water.¹ However, this relationship occurs only in solvents with high dielectric constants. In solvents of low dielectric constant, the molar conductivity initially decreases with increasing salt concentration, reaches a minimum, increases to a maximum, and then decreases.^{2–5} There is currently no theoretical framework that explains the qualitative differences in the concentration dependence of molar conductivity observed between solvents of low and high dielectric constant.

The Debye–Hückel–Onsager theory describes ion transport for dilute, aqueous solutions of 1:1 salts, but it becomes less accurate as the dielectric constant of the solvent decreases.¹ Fuoss describes the qualitative behavior of ion transport in low dielectric constant media using the concept of charged aggregates,⁶ but it is often difficult to determine whether changes in speciation (relative amounts of “free” ions and associated species), ionic mobility, or both are responsible for the concentration dependence of ion transport. There is currently no theory that adequately describes ion transport over a wide concentration range for salts in solvents with low dielectric constants. The dependence of conductivity on salt concentration has important technological implications in the area of lithium rechargeable batteries. Electrolytes of commercialized lithium ion batteries utilize a mixture of low dielectric constant, aprotic liquids containing dissolved lithium salts. The electrolytes of prototype lithium polymer batteries often consist of an aprotic polymer, e.g., poly(ethylene oxide), complexed with a lithium salt. Alternative polymer battery systems utilize an inert polymer swollen with an aprotic, low dielectric constant liquid in which the salt is dissolved. All of these electrolytes are low dielectric constant materials and exhibit the molar conductivity behavior described in the preceding paragraph, i.e., a molar conductivity minimum followed by a molar conductivity maximum with increasing salt concentration.

This work focuses on solutions based on a solvent with a low dielectric constant: 2-methoxyethyl ether, known as di-

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glyme ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$). The salt primarily used in this study is lithium trifluoromethanesulfonate (LiCF_3SO_3), where trifluoromethanesulfonate is abbreviated as triflate (Tf). Diglyme—LiTf was chosen because the frequencies and intensities of several triflate anion vibrational modes are sensitive to ion—ion interactions; therefore, IR spectroscopy can be used to determine which species are present in the system and estimate their concentration from a curve-fitting procedure. Using this spectroscopic data in conjunction with experimentally measured conductivities allows mobilities to be calculated for this system. The behavior of the molar conductivity as a function of salt concentration in the dilute range is usually explained in terms of the formation and dissociation of associated solute species.^{6,7} However, it will be shown for the systems studied here that mobilities rather than speciation play the primary role in this behavior.

Ionic and host solvent diffusion coefficients (D) were determined from NMR pulsed field gradient (pfg) self-diffusion measurements. The resulting D -values represent an average over all mobile species, charged and neutral, and also may include the effects of rapid exchange between the various ions, pairs, and clusters. The time scale of the D measurement is several milliseconds, many orders of magnitude longer than the time scale of the vibrational spectroscopic probe used to determine the identity of the solute species. By using both analytical tools (IR and pfg NMR) on the same system and recognizing the very different time scales involved, it is hoped that a consistent description of ionic association and mobility will be achieved.

The thermodynamics of the ionic association/dissociation processes that lead to equilibria between the different species is also studied. Equilibrium constants for these processes can be calculated from the concentrations of triflate-containing species that are estimated using IR spectroscopy. The nonideal behavior of the charged species is estimated using a modified Debye—Huckel relationship. Temperature-dependent equilibrium constants are used to calculate ΔG° , ΔH° , and ΔS° for the association/dissociation processes.

2. Experimental Section

2.1. Chemicals. Diglyme (Aldrich, 99% pure) was used as received. Lithium triflate (Aldrich, 99.995%) was dried by heating at 120 °C under vacuum for 24 h. Tetrabutylammonium triflate (TbaTf) (Aldrich, 99%) was dried by heating to 100 °C for 24 h. Fumed silica (unmodified) with a surface area of 380 $\text{m}^2 \text{g}^{-1}$ was bought from Aldrich and heated at 500 °C for 24 h. All chemicals were stored and all samples were prepared in a glovebox (<1 ppm H_2O) under a nitrogen atmosphere.

2.2. Sample Preparation. **2.2.1. NMR and Conductivity Samples.** Diglyme—LiTf liquid solutions were made at room temperature by dissolving LiTf into diglyme at the appropriate O:Li ratio (molar ratio of ether oxygen atoms to lithium ions) and stirring for 24 h. Diglyme—TbaTf liquid solutions were made at room temperature by dissolving TbaTf into diglyme at the appropriate concentration and stirring for 24 h.

2.2.2. IR Samples. IR samples are made by first making the liquid electrolyte solution at a particular salt concentration as described above, but then converting this liquid into a gel by the addition of fumed silica. Fumed silica was added until its composition was 7.1 wt %. The weight percent silica was calculated to include the weight of diglyme and silica, but not salt. This mixture was stirred until the gel became homogeneous (approximately 10 min). More sample can be placed between the optical windows when it is in the form of a gel instead of a liquid. Having more sample in the cell produced a greater

intensity, which helped in the curve-fitting analysis of the more dilute samples (40:1–100:1). It is important to note that the addition of fumed silica to the solutions does not affect the cation—anion interactions of the dissolved salt to any extent measurable by vibrational spectroscopy.⁸

2.3. Instrumentation and Experimental Techniques. **2.3.1. IR.** Room-temperature IR spectra were recorded on a Bruker IFS66V FTIR spectrometer under vacuum, while a dry air purge was used at elevated temperatures. Zinc selenide windows were used in the transmission cells. The spectral resolution was 1 cm^{-1} , and each spectrum resulted from 64 scans. Curve fitting was performed with commercial software (*Galactic Grams*, v. 5.2), using a mixed Gaussian—Lorentzian function and a linear baseline. For a given salt concentration, only one batch of LiTf—diglyme—fumed silica sample was made. Nine separate portions of this batch were each analyzed with IR, resulting in 9 spectra. Each spectrum was curve-fit using the *Galactic Grams* software. This software estimated the area under the three bands (752, 757, 761 cm^{-1}) associated with the $\delta_s(\text{CF}_3)$ mode of the triflate ion. The fraction of “free” ion was taken to be the area of the 752 cm^{-1} band divided by the sum of the areas for all three bands. The areas of the 757 and 761 cm^{-1} bands were similarly used to find the fraction of ion pairs and dimers, respectively. However, it should be noted that, since a single dimer contains two different triflate ions that are each in the same environment, the actual area due to dimer would be half the area of the 761 cm^{-1} band. The concentration of each species is obtained by multiplying the fraction of that species by the total salt concentration. For a given salt concentration, curve-fitting each of the 9 spectra resulted in a fraction for each species. The average of these 9 runs was calculated for each species, and their values are reported in the paper.

A Beer’s plot was constructed for the diglyme—LiTf—fumed silica IR data to verify that the absorbance is directly proportional to the concentration. The sum of the areas for the three peaks (752, 757, 761 cm^{-1}) was divided by the area of the CH_2 stretching peak of diglyme (2900 cm^{-1}), and this quantity was then plotted against the total LiTf salt concentration. The resulting graph is linear with $R^2 = 0.986$. Since Beer’s law is obeyed, it is feasible to extract quantitative information from the IR data.

2.3.2. Densities. Densities were measured with an 11.5 mL volume pycnometer (aluminum alloy) obtained from Fisher.

2.3.3. Conductivity. Conductivity of the liquid electrolyte solutions was determined with an Accumet Basic AB30 conductivity meter. The cell constant (1.10 cm^{-1}) was found by measuring the resistance of an aqueous solution of 0.01 M KCl and relating this value to the commonly accepted value (accepted molar conductivity of 0.01 M KCl = $1.41 \times 10^{-2} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$). The conductivity of each sample was determined by dividing the cell constant by the measured resistance. Each measurement was repeated twice. The average of the two numbers was the value reported in the paper.

2.3.4. NMR. For NMR measurements, the sealed solution vessels were placed in a drybox ($\text{H}_2\text{O} \leq 1 \text{ ppm}$) and packed into 5-mm-o.d. and 20-mm-length glass NMR tubes sealed with plastic covers and Parafilm. NMR measurements were obtained with a Chemagnetics CMX-300 spectrometer. The corresponding Larmor frequencies of ^1H , ^{19}F , and ^7Li in this field are 301.0, 283.2, and 116.9 MHz, respectively. The pfg diffusion measurements were carried out with a 5-mm double-resonance Nalorac Z-Spec gradient probe with two observation/excitation coils. A Hahn spin—echo pulse sequence ($90^\circ < \tau < 180^\circ$) was used to measure diffusion. For a diffusing system in the presence of a

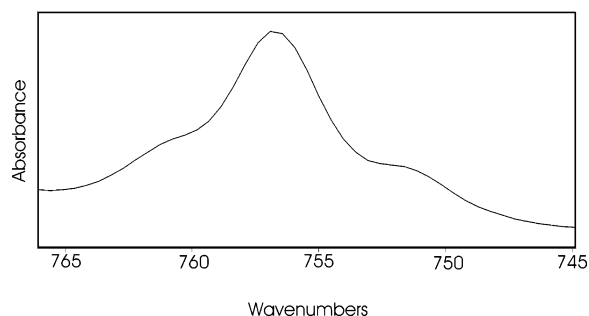


Figure 1. IR spectrum of the $\delta_s(\text{CF}_3)$ mode in diglyme–LiTf 20:1– SiO_2 7.1 wt %.

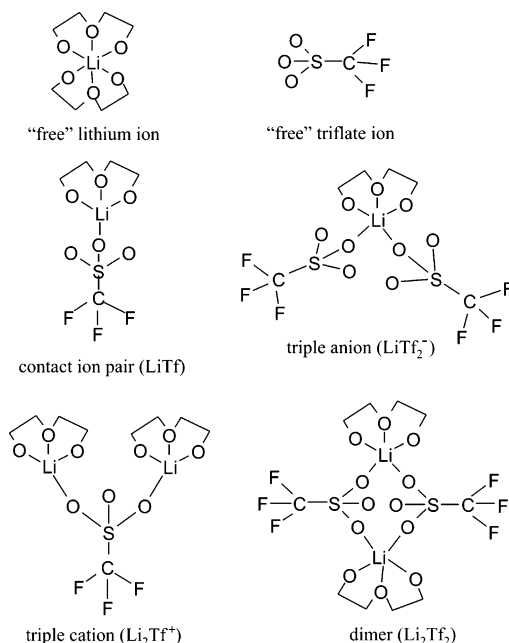


Figure 2. “Free” lithium and triflate ion, contact ion pair, triple anion, dimer, and triple cation. Li, O, S, C, and F represent lithium, oxygen, sulfur, carbon, and fluorine, respectively. The three oxygen atoms bridged by solid lines indicate the three ether oxygen atoms of a diglyme molecule.

magnetic field, the application of two square-shaped magnetic gradients, on either side of the 180° pulse, of magnitude g and duration δ results in attenuation of the echo amplitude A . This attenuation may be represented by $A(g) = \exp[-\gamma^2 g^2 D \delta^2 (\Delta - (\delta/3))]$, where γ , δ , D , and Δ represent the nuclei's gyromagnetic constant, gradient pulse width, self-diffusion coefficient, and spacing between gradient pulses, respectively. Applied gradient strengths ranged from 0.2 to 1.2 T/m, and Δ ranged from 2 to 3 and 6 to 10 ms. The resulting echo profile vs gradient strengths is fitted to the above equation and D is extracted. Uncertainties in self-diffusion coefficients are ~ 3 –5%.⁹

3. Results and Discussion

3.1. Triflate Ion Species. Figure 1 shows three bands present in the IR spectral region of the triflate ion CF_3 symmetric deformation mode, $\delta_s(\text{CF}_3)$, for a sample of diglyme–LiTf 20:1– SiO_2 7.1 wt %. The 752 cm^{-1} band is assigned to a “free” triflate ion,^{10–12} the 757 cm^{-1} band is assigned to either a contact ion pair or a triple anion, and the 761 cm^{-1} band is assigned to either a dimer or triple cation. These band assignments and their corresponding species are described in Figure 2 and the following discussion.

Figure 2 schematically represents a “free” triflate ion, “free” lithium ion, contact ion pair, triple anion, dimer, and triple

cation. Although a “free” triflate ion is not directly coordinated to a lithium ion, it is stabilized in solution by one or more lithium ions that interact with it electrostatically. A “free” lithium ion is not directly coordinated to an anion, but it is solvated by the oxygen atoms of diglyme. The 757 cm^{-1} band is attributed to either a contact ion pair (LiTf) or a triple anion (LiTf_2^-); these two species are spectroscopically indistinguishable from each other. In both species, a single oxygen atom from a triflate ion is coordinated to a lithium ion (Figure 2). Ab initio calculations have shown that, when the oxygen atoms of triflate become coordinated, there is a redistribution of charge in the anion, which alters the force constants of the bonds.¹³ As additional oxygen atoms of triflate are coordinated by cations, the $\delta_s(\text{CF}_3)$ mode shifts to higher frequencies. The 761 cm^{-1} band in the IR spectrum of diglyme–LiTf is attributed to either a dimer (Li_2Tf_2) or a triple cation (Li_2Tf^+), because these two species are also spectroscopically indistinguishable. In both cases, two different oxygen atoms on a triflate anion are each coordinated to a lithium ion (Figure 2).

It is assumed here that the 761 cm^{-1} band observed in the diglyme–LiTf solutions is due to dimers and not triple cations, consistent with the coordination found in the (diglyme)LiTf crystal.¹⁴ A comparative spectroscopic study of diglyme–LiTf solutions and the crystal showed local structures (associated species and diglyme conformations) in solution that correspond to those in the crystal. The crystal structure of (diglyme)LiTf is composed of discrete Li_2Tf_2 dimers. In these dimers, each lithium ion coordinates the three ether oxygen atoms of diglyme¹⁴ and two triflate oxygen atoms, one from each of two triflate ions, as illustrated in Figure 2.

At this point, it is necessary to make a further assumption in order to proceed with the analysis. It is postulated that the band at 757 cm^{-1} is due to contact ion pairs and not triple anions. Support for this assignment comes from the crystal structure of 1,1,4,7,10,10-hexamethyltriethylenetetramine complexed with lithium triflate.¹⁵ A single-crystal X-ray diffraction study shows that each lithium ion is coordinated to one oxygen atom of a triflate ion (and four nitrogen atoms of the hexamethyltriethylenetetramine compound). In other words, lithium ions and triflate ions exist only as LiTf contact ion pairs in the crystal. In the LiTf–hexamethyltriethylenetetramine crystal, there is a strong band at 757 cm^{-1} in the IR, which is consistent with our assignment of contact ion pairs in LiTf–diglyme. Furthermore, spectroscopists from other groups who are working on similar systems have attributed the 757 cm^{-1} band to ion pairs.¹¹ Ab initio calculations are also consistent with this assignment.¹³

To the extent that these two assumptions hold, the species that exist in diglyme–LiTf solution are “free” lithium ions, “free” triflate ions, contact ion pairs, and dimers. Since contact ion pairs and dimers are uncharged, the concentration of “free” lithium ions is equal to the concentration of “free” triflate ions because of mass–charge balance.

3.2. Diffusion Coefficients of Li, F, and H. Figure 3 shows diffusion coefficients for lithium, fluorine (triflate), and hydrogen (diglyme) in diglyme–LiTf as a function of salt concentration, obtained by pfg NMR measurements of ^7Li , ^{19}F , and ^1H . The diffusion coefficients for lithium and fluorine have comparable values (within 20% of each other) at every salt concentration. The mobility of triflate is identical to the mobility of lithium in both contact ion pairs and dimers (see Figure 2). Since the combined fraction of contact ion pair and dimer is approximately 80% or greater (see Table 1) at every salt concentration, the diffusion coefficients for lithium and triflate, which are averaged over all species in the system, should have

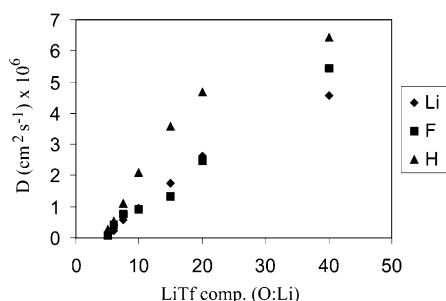
TABLE 1: Concentrations of “Free” Ion, Contact Ion Pair, and Dimer along with Conductivities, Molar Conductivities, and Mobilities of the Diglyme–LiTf Solutions as a Function of Total Salt Concentration

solution comp. (O:Li)	total salt concn (mol cm ⁻³)	concn of “free” Tf ions (mol cm ⁻³)	concn of contact ion pairs (mol cm ⁻³)	concn of dimers (mol cm ⁻³)	σ (S cm ⁻¹)	Λ (S cm ² mol ⁻¹)	$\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}$ (cm ² V ⁻¹ s ⁻¹)
5:1	3.30×10^{-3}	2.44×10^{-4}	1.10×10^{-3}	9.78×10^{-4}	1.00×10^{-3}	0.303	4.25×10^{-5}
6:1	2.85×10^{-3}	2.93×10^{-4}	1.24×10^{-3}	6.55×10^{-4}	1.70×10^{-3}	0.596	6.02×10^{-5}
7.5:1	2.38×10^{-3}	3.21×10^{-4}	1.15×10^{-3}	4.53×10^{-4}	2.59×10^{-3}	1.09	8.37×10^{-5}
10:1	1.86×10^{-3}	2.94×10^{-4}	9.95×10^{-4}	2.85×10^{-4}	3.50×10^{-3}	1.88	1.23×10^{-4}
15:1	1.29×10^{-3}	2.50×10^{-4}	7.78×10^{-4}	1.30×10^{-4}	3.60×10^{-3}	2.79	1.49×10^{-4}
20:1	9.90×10^{-4}	2.05×10^{-4}	6.24×10^{-4}	8.02×10^{-5}	3.20×10^{-3}	3.23	1.62×10^{-4}
40:1	5.10×10^{-4}	7.70×10^{-5}	3.75×10^{-4}	2.91×10^{-5}	1.70×10^{-3}	3.33	2.29×10^{-4}
70:1	2.95×10^{-4}	4.81×10^{-5}	2.25×10^{-4}	1.09×10^{-5}	8.29×10^{-4}	2.81	1.79×10^{-4}
100:1	2.10×10^{-4}	3.49×10^{-5}	1.65×10^{-4}	5.25×10^{-6}	5.10×10^{-4}	2.43	1.52×10^{-4}
150:1	1.39×10^{-4}				2.70×10^{-4}	1.94	
250:1	8.40×10^{-5}				1.30×10^{-4}	1.55	
500:1	4.17×10^{-5}				5.09×10^{-5}	1.22	
1000:1	2.11×10^{-5}				2.40×10^{-5}	1.14	
2000:1	1.09×10^{-5}				1.39×10^{-5}	1.28	
4000:1	5.43×10^{-6}				7.38×10^{-6}	1.36	
8000:1	2.72×10^{-6}				5.17×10^{-6}	1.90	

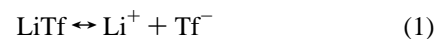
numerical values similar to each other. If the triple anionic species [LiTf₂⁻] is present to any significant extent, its concentration must be necessarily charge-balanced by either “free” Li⁺ or [Li₂Tf⁺]. In either case, the presence of at least two distinctly different LiTf-containing species would be expected to lead to differences in the Li and Tf diffusion coefficients. The behavior seen in Figure 3 provides experimental evidence for the existence of the postulated species, particularly the similarity between the lithium and fluorine diffusion coefficients. Furthermore, Figure 3 shows that the diffusion coefficient for hydrogen approaches the diffusion coefficients of lithium and fluorine as the salt concentration increases. This result may be interpreted as due to a greater fraction of diglyme molecules participating in solvation at higher solute concentrations.

Pulsed field gradient NMR has also been used to measure diffusion coefficients in other electrolyte systems such as LiCF₃SO₃ in poly(ethylene oxide),^{16,17} LiCF₃SO₃ in methyl-terminated oligo(ethylene glycol)-containing plasticizers,¹⁸ LiBF₄ in gel electrolytes,^{19,20} and Li(N(CF₃SO₂)₂) in both gel electrolytes and organic liquids.^{21,22} It is particularly useful to compare the data in Figure 3 to that obtained by Ward, who measured lithium and fluorine diffusion coefficients for LiTf–tetraglyme.^{23,24} Similarly to Figure 3, Ward observed numerical values for the lithium and triflate diffusion coefficients that were very near each other, attributing this behavior to correlated motion of the solute species in the form of neutral pairs and clusters.

It should be mentioned that the diffusion coefficient data in Figure 3 are only for the concentrated regime, and therefore, the diffusion coefficient data cannot be used to determine what aggregated species exist in the more dilute regimes.

**Figure 3.** Diffusion coefficients for Li, F, and H in diglyme–LiTf as a function of salt concentration.

3.3. Thermodynamics of Ionic Association in Diglyme–LiTf. It is assumed the four species present in the system are involved in the following processes:



The thermodynamic equilibrium constant, K_1 , for dissociation of a contact ion pair into “free” ions (eq 1) is

$$K_1 = \frac{(\gamma_{\text{Li}^+})(c_{\text{Li}^+})(\gamma_{\text{Tf}^-})(c_{\text{Tf}^-})}{(\gamma_{\text{LiTf}})(c_{\text{LiTf}})} = \frac{(\gamma_{\pm})^2(c_{\text{free}})^2}{c_{\text{LiTf}}} \quad (3)$$

where γ_i is the activity coefficient and c_i is the molar concentration for species i ($i = \text{Li}^+, \text{Tf}^-, \text{LiTf}$). The mean ionic activity coefficient γ_{\pm} is defined by $(\gamma_{\pm})^2 = \gamma_{\text{Li}^+}\gamma_{\text{Tf}^-}$ and γ_{LiTf} is approximated as 1 since LiTf is uncharged. The concentrations of lithium and triflate ion are equal and will be written as $c_{\text{Li}^+} = c_{\text{Tf}^-} = c_{\text{free}}$.

To calculate the equilibrium constant for dissociation of a contact ion pair into “free” ions, the mean ionic activity coefficient must be determined along with the concentration of “free” ions and contact ion pairs. It was stated earlier that triflate ion bands in the $\delta_s(\text{CF}_3)$ region of diglyme–LiTf can be assigned to the solute species present in the solution. For each species, the relative integrated band intensity is proportional to the concentration of the species; therefore, a curve-fitting analysis of the $\delta_s(\text{CF}_3)$ region combined with the value of the total salt concentration provides the concentration of each species, as summarized in Table 1. All curve-fitting measurements were repeated nine times, and mean values are listed in the tables. Janz and Muller performed a similar curve-fitting procedure on Raman spectra of solutions of silver nitrate in acetonitrile.²⁵

Figure 4 shows the concentration of “free” ion, contact ion pair, and dimer versus total salt concentration. The concentration of “free” ion increases with increasing total salt concentration in the dilute region, reaches a maximum at total salt concentration of 2.38×10^{-3} mol cm⁻³ (7.5:1), and then decreases. It should be mentioned that the fraction of “free” ion generally decreases with increasing salt concentration over the entire concentration range, but the concentration of “free” ion increases until 7.5:1 because a substantial increase in total salt concentration produces only a minor reduction in the fraction of “free”

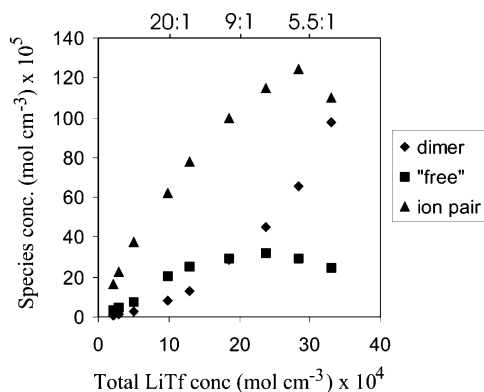


Figure 4. Concentrations of “free” triflate ions, contact ion pairs, and dimers as a function of total LiTf concentration.

ions. The concentration of contact ion pairs increases with increasing total salt concentration, reaches a maximum at a total salt concentration of $2.85 \times 10^{-3} \text{ mol cm}^{-3}$ (6:1), and then decreases. The concentration of dimer continually increases with total salt concentration.

The mean ionic activity coefficient must also be determined to calculate the equilibrium constant for dissociation of a contact ion pair into “free” ions. This can be accomplished using the Debye–Hückel ionic cloud theory, which yields the well-known expression for the mean ionic activity coefficient for dilute electrolyte solutions²⁶

$$\ln \gamma_{\pm} = \frac{-z_+|z_-|C\sqrt{I_M}}{1 + Ba\sqrt{I_M}} \quad (4)$$

where z_+ and z_- are the charges on the cation and anion, respectively, and I_M is the ionic strength. For diglyme–LiTf solutions under the previously stated assumptions, the ionic strength is

$$I_M = \frac{1}{2}(z_{\text{Li}^+}^2 c_{\text{Li}^+} + z_{\text{Tf}^-}^2 c_{\text{Tf}^-}) = \frac{c_{\text{Li}^+} + c_{\text{Tf}^-}}{2} = c_{\text{free}} \quad \text{since } c_{\text{Li}^+} = c_{\text{Tf}^-} \quad (5)$$

C and B are defined by²⁶

$$C = (2\pi N_A)^{1/2} \left[\frac{e^2}{4\pi\epsilon_0\epsilon kT} \right]^{3/2} \quad (6)$$

$$B = e \left[\frac{2N_A}{\epsilon_0\epsilon kT} \right]^{1/2} \quad (7)$$

where N_A is Avogadro’s constant, e is the proton charge, ϵ_0 is the permittivity of vacuum, ϵ is the solvent dielectric constant, k is Boltzmann’s constant, and T is the absolute temperature. For diglyme, $\epsilon = 7.3$. Substituting these values into the expressions for C and B yields

$$C = 1.31 \text{ m}^{3/2} \text{ mol}^{-1/2} \text{ and } B = 3.41 \times 10^8 \text{ m}^{1/2} \text{ mol}^{-1/2}$$

Finally, a in eq 4 is the distance from the center of an ion to the point where its ionic atmosphere begins, and it is often approximated by the sum of the cation and anion radii.²⁷ It is reasonable to assume that, in a LiTf–diglyme solution, the “free” lithium ions are sixfold coordinated by the oxygen atoms from two diglyme molecules that essentially “wrap” the lithium ion (Figure 2); the triflate ion is adjacent as a solvent-separated ion pair. This assumption is based on three published diglyme–

TABLE 2: Values of the Square of the Mean Ionic Activity Coefficient and Equilibrium Constants K_1 and K_2 at Various Salt Concentrations

solution composition (O:Li)	total salt concentration (mol cm ⁻³)	$(\gamma_{\pm})^2$	K_1 (mol m ⁻³)	K_2 (m ³ mol ⁻¹)
100:1	2.10×10^{-4}	1.09×10^{-3}	8.1×10^{-3}	1.9×10^{-4}
70:1	2.95×10^{-4}	6.81×10^{-4}	7.0×10^{-3}	2.1×10^{-4}
40:1	5.10×10^{-4}	3.46×10^{-4}	5.5×10^{-3}	2.1×10^{-4}
20:1	9.90×10^{-4}	1.00×10^{-4}	6.7×10^{-3}	2.1×10^{-4}
15:1	1.29×10^{-3}	8.14×10^{-5}	6.5×10^{-3}	2.1×10^{-4}
10:1	1.86×10^{-3}	6.87×10^{-5}	6.0×10^{-3}	2.9×10^{-4}
7.5:1	2.38×10^{-3}	6.29×10^{-5}	5.6×10^{-3}	3.4×10^{-4}
6:1	2.85×10^{-3}	6.89×10^{-5}	4.8×10^{-3}	4.2×10^{-4}
5:1	3.30×10^{-3}	8.35×10^{-5}	4.5×10^{-3}	8.1×10^{-4}

salt crystal structures consisting of solvent-separated ion pairs in which the lithium ion is present only as a “wrapped” species: the 1:1 compounds of diglyme–LiBF₄, diglyme–LiSbF₆, and diglyme–LiTFSI.²⁸ Unfortunately, the crystal structure data of the 1:1 diglyme–LiTf compound provides no insight because the crystal consists of Li₂Tf₂ dimers wherein each lithium ion is coordinated to three ether oxygen atoms of a diglyme molecule and two oxygen atoms, one from each of two triflate ions (Figure 2). Therefore, a working estimate of the parameter a is taken as the closest cation–anion distance in crystalline diglyme–LiSbF₆, which is $6.31 \times 10^{-10} \text{ m}$.

Substituting the values for a , B , and C into the expression for the mean ionic activity coefficient yields the expression

$$(\gamma_{\pm})^2 = \exp\left(\frac{-2z_+|z_-|C\sqrt{I_M}}{1 + Ba\sqrt{I_M}}\right) = \exp\left(\frac{-2.62\sqrt{c_{\text{free}}}}{1 + 0.215\sqrt{c_{\text{free}}}}\right) \quad (8)$$

The final expression for K_1 becomes

$$K_1 = \frac{c_{\text{free}}^2}{c_{\text{LiTf}}} (\gamma_{\pm})^2 = \frac{c_{\text{free}}^2}{c_{\text{LiTf}}} \exp\left(\frac{-2.62\sqrt{c_{\text{free}}}}{1 + 0.215\sqrt{c_{\text{free}}}}\right) \quad (9)$$

Values for $(\gamma_{\pm})^2$ as a function of total salt concentration are listed in Table 2 and are obtained from the concentration of “free” ion given in Table 1 (converted to mol m⁻³). The quantity γ_{\pm} is dimensionless, but K_1 has units as can be seen from eqs 8 and 9. In the calculations using eqs 8 and 9, the concentration of free ions is expressed in units of moles per cubic meter. The mean ionic activity coefficient is much smaller in diglyme–LiTf than in aqueous electrolytes, due to the much smaller dielectric constant of diglyme. For example, with $c_{\text{free}} = 77 \text{ mol m}^{-3}$ (diglyme–LiTf 40:1) and $\epsilon = 78$, $(\gamma_{\pm})^2 = 0.66$.

Substituting the concentrations of “free” ion and contact ion pair from Table 1 (converted to mol m⁻³) and the square of the mean ionic activity coefficient from Table 2 into eq 9 gives numerical values for K_1 , which are given in Table 2. The calculated equilibrium constant has a fairly constant value over a salt concentration range of 100:1 to 15:1. For solutions more concentrated than 15:1, K_1 decreases with increasing salt concentration.

It is surprising that the calculated mean ionic activity coefficient appears to be valid at total salt concentrations as high as 1.29 mol L^{-1} (15:1). For aqueous solutions of 1:1 electrolytes, it is usually stated that the use of Debye–Hückel theory to calculate mean ionic activity coefficients is only valid up to 0.1 mol L^{-1} , assuming reasonable a values.²⁷ However, in dilute aqueous solutions of 1:1 electrolytes, there is negligible ion pairing, and therefore, the total salt concentration is equal

TABLE 3: Temperature-Dependent Values for B , C , ϵ , γ_{\pm}^2 and K_1 for Diglyme–LiTf 40:1^a

temperature (°C)	B ($\text{m}^{1/2} \text{mol}^{-1/2}$)	C ($\text{m}^{3/2} \text{mol}^{-1/2}$)	ϵ	$(\gamma_{\pm})^2$	K_1 (mol m^{-3})	K_2 ($\text{m}^3 \text{mol}^{-1}$)
27	3.43×10^8	1.33	7.17	3.51×10^{-4}	4.5×10^{-3}	2.2×10^{-4}
37	3.44×10^8	1.34	6.91	4.55×10^{-4}	3.8×10^{-3}	2.2×10^{-4}
47	3.44×10^8	1.35	6.66	6.88×10^{-4}	3.0×10^{-3}	2.4×10^{-4}
60	3.46×10^8	1.37	6.33	9.23×10^{-4}	2.4×10^{-3}	2.5×10^{-4}
70	3.48×10^8	1.40	6.07	1.22×10^{-3}	1.9×10^{-3}	2.7×10^{-4}
80						2.8×10^{-4}

^a Also included are values of K_2 for diglyme–LiTf 20:1, described later in the text.

to the concentration of “free” ion. In diglyme–LiTf, the vast majority of salt exists as uncharged ion pairs and dimers, and as seen from Table 1, the concentration of “free” ion does not exceed 0.1 mol L^{-1} until the total salt concentration is higher than 0.51 mol L^{-1} (40:1). However, the concentration of “free” ion is 0.25 mol L^{-1} at a total salt concentration of 1.29 mol L^{-1} (15:1), which is $2^{1/2}$ times greater than the commonly observed upper limit of 0.1 mol L^{-1} .

The concentrations of “free” ions, contact ion pairs, and dimers were obtained for diglyme–LiTf 20:1 and 40:1 solutions from 27 to 80°C following the curve-fitting procedures used to obtain the analogous room temperature data in Table 1. The temperature-dependent data are summarized in Supporting Information, Table S1. Figure 5 shows how the concentrations of “free” ions, contact ion pairs, and dimers vary with temperature. As the temperature increases, the concentration of “free” ion decreases while that of the dimer increases. The concentration of the contact ion pair initially increases with temperature and then levels off.

Temperature-dependent values for B (from eq 7), C (from eq 6), and ϵ were substituted into eq 8 to calculate values of γ_{\pm}^2 for a 40:1 diglyme–LiTf solution composition. These data are listed in Table 3 at various temperatures. The concentrations of “free” ions and contact ion pairs from Table S1 (converted to mol m^{-3}), along with temperature-dependent values of γ_{\pm}^2 from Table 3, were used in eq 9 to calculate values for K_1 as a function of temperature (summarized in Table 3). The equilibrium constant decreases with increasing temperature. It should be noted that the temperature dependence of B and C in Table 3 neglects the temperature dependence of a , although the change in this variable is expected to be small over the temperature range used. The temperature-dependent dielectric constants of diglyme given in Table 3 were reported in a previous study.²⁹

The van’t Hoff equation, $d(\ln K_1)/d(1/T) = -\Delta H_1^\circ/R$, is used to find the change in enthalpy ΔH_1° for the dissociation of a contact ion pair into “free” ions (eq 1) by plotting the natural logarithm of the equilibrium constant versus reciprocal temperature (Figure 6). The value of ΔH_1° is $-1.70 \times 10^4 \text{ J mol}^{-1}$ over the temperature range of Table 3 and Figure 6. This value is negative, which agrees with Le Chatelier’s principle since

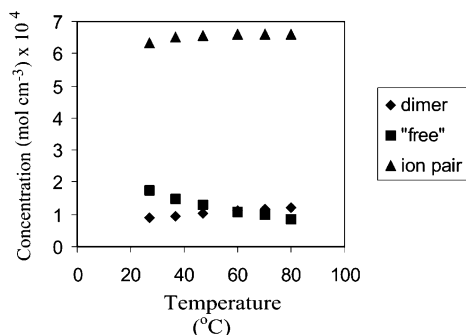


Figure 5. Concentration of “free” triflate ion, contact ion pair, and dimer as a function of temperature for diglyme–LiTf 20:1.

an increase in temperature shifts equilibrium toward the endothermic direction, decreasing the concentration of “free” ion and increasing the concentration of contact ion pair. When a contact ion pair dissociates into “free” ions, the decrease in enthalpy from cation coordination to an additional diglyme molecule is greater than the increase in enthalpy needed to break the lithium–oxygen coordinative bond. Therefore, the overall enthalpy change is negative.

The change in the Gibbs free energy for the dissociation process is easily calculated from the value of the equilibrium constant at 27°C ($K_1 = 4.5 \times 10^{-3}$) and the familiar expression $\Delta G_1^\circ = -RT \ln K_1$. The positive value of ΔG° ($1.35 \times 10^4 \text{ J mol}^{-1}$) means that equilibrium favors contact ion pairs as opposed to “free” ions. This result could have been qualitatively predicted from examination of the IR spectra in the $\delta_s(\text{CF}_3)$ region, which shows that the relative intensity of the ion pair band (757 cm^{-1}) is much larger than that of the “free” ion band (752 cm^{-1}) (see Figure 1).

Using the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, the change in entropy at 27°C is $\Delta S_1^\circ = -102 \text{ J mol}^{-1} \text{ K}^{-1}$. The change in entropy results from several contributions implied in eq 1. If one focuses on just the species described in eq 1, the dissociation of the contact ion pair into two “free” ions is accompanied by the gain of three “hindered translational” degrees of freedom at the expense of losing one Li–Tf intermolecular vibrational degree of freedom and two “hindered rotational” degrees of freedom. A “hindered translational” degree of freedom may be considered as a mixture of vibrational character and translational character resulting from an ion’s translatory motion confined to a transient cage of solvent molecules complexing the ion. In the same manner, a “hindered rotational” degree of freedom is a mixture of a large-amplitude librational motion and a partial rotational motion confined to the transient cage. If these motions occurred in the gas phase and were pure rather than hindered, one would write $\Delta S_{\text{trans}} > \Delta S_{\text{rot}} \geq \Delta S_{\text{vib}}$. It is very difficult to calculate values of the three contributions for “hindered” motion in a solution. Therefore, if the role of the solvent is neglected, the dissociation of a contact ion pair into “free” ions is expected to occur with a positive entropy change. However, there is a negative contribution to the entropy change originating in the interaction of the cation with the diglyme molecule(s). As noted

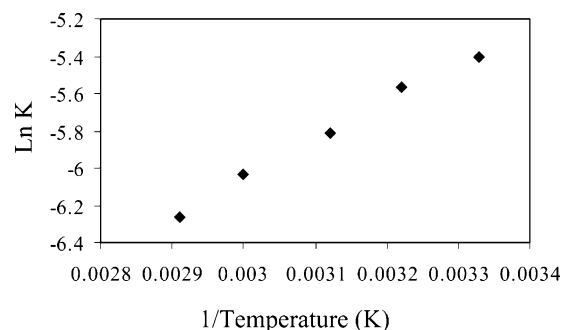


Figure 6. Van’t Hoff plot for the 40:1 diglyme–LiTf solution.

earlier, a “free” lithium ion is probably coordinated by two diglyme molecules, whereas the cation in a contact ion pair can be coordinated by at most one diglyme molecule (Figure 2). A lithium-coordinated diglyme molecule is restricted to a small number of its possible conformations; hence, its entropy is smaller than an uncoordinated diglyme molecule in solution. The number of lithium-coordinated diglyme molecules increases by 1 in the dissociation process, resulting in a negative contribution to the entropy change. The calculated value of ΔS_1° is $-102 \text{ J mol}^{-1} \text{ K}^{-1}$; therefore, the negative entropy change from the cation–diglyme interaction outweighs the small positive contribution from the change in the nature of the ionic motion as described above.

Now, consider the equilibrium described by eq 2, in which two contact ion pairs combine to form a dimer ($2\text{LiTf} \leftrightarrow \text{Li}_2\text{Tf}_2$). The equilibrium constant for this process is

$$K_2 = \frac{\gamma_{\text{Li}_2\text{Tf}_2} c_{\text{Li}_2\text{Tf}_2}}{(\gamma_{\text{LiTf}} c_{\text{LiTf}})^2} = \frac{c_{\text{Li}_2\text{Tf}_2}}{(c_{\text{LiTf}})^2} \quad (10)$$

where $\gamma_{\text{Li}_2\text{Tf}_2}$ and γ_{LiTf} are the activity coefficients of Li_2Tf_2 and LiTf , respectively, and $c_{\text{Li}_2\text{Tf}_2}$ and c_{LiTf} are the concentrations of Li_2Tf_2 and LiTf , respectively. The activity coefficients are approximated as 1, because these are electrically neutral species.

Converting the concentration of dimer and contact ion pair in Table 1 into moles per cubic meter and then substituting those concentrations into eq 10 yields numerical values for the equilibrium constant for conversion of contact ion pairs into dimer. Table 2 lists the value of K_2 for each total salt concentration. The value of the equilibrium constant is reasonably constant through a total salt concentration of $1.29 \times 10^{-3} \text{ mol cm}^{-3}$ (15:1). For concentrations higher than this, it is no longer valid to neglect activity coefficients, and the equilibrium constant changes with total salt concentration.

The temperature dependence of the equilibrium constant for dimer formation is found by substituting temperature-dependent concentrations of dimer and contact ion pair from Table S1 (converted to mol m^{-3}) for the 20:1 diglyme–LiTf composition into eq 10. Table 3 gives values for this constant for diglyme–LiTf 20:1 over a temperature range from 27 °C to 80 °C. There is a slight increase in the equilibrium constant with increasing temperature over this temperature range.

The change in enthalpy for the conversion of two contact ion pairs into a dimer is found by again using the van’t Hoff equation, yielding the value $\Delta H_2^\circ = 4.0 \times 10^3 \text{ J mol}^{-1}$. A positive value for the enthalpy change is in accordance with Le Chatelier’s principle, since shifting the equilibrium toward the endothermic direction increases the concentration of dimer. The change in Gibbs free energy is calculated as before, giving the value $\Delta G_2^\circ = 2.1 \times 10^4 \text{ J mol}^{-1}$ at 27 °C. The change in Gibbs free energy is positive, which means that equilibrium favors contact ion pairs rather than dimers. This is also seen in the $\delta_s(\text{CF}_3)$ region of an IR spectrum of diglyme–LiTf (Figure 1), which shows that the relative intensity of the contact ion pair band (757 cm^{-1}) is much larger than that of the dimer band (761 cm^{-1}). The change in entropy is $\Delta S_2^\circ = -56.7 \text{ J mol}^{-1} \text{ K}^{-1}$ at 27 °C. The formation of a dimer from two contact ion pairs would also be expected to occur with a small, negative change in entropy accompanying the net loss of “hindered translational” motion. The lithium ion of each of the two contact ion pairs undergoing association will coordinate one diglyme molecule; the two lithium ions of the resulting dimer are also each coordinated to one diglyme molecule (Figure 2). Hence, in contrast to the process described in eq 1, there is no significant

entropy contribution from any change in the number of coordinated diglyme molecules.

3.4. Ion Transport in Diglyme–LiTf. The fundamental expression for the conductivity of a system is

$$\sigma = \sum_j q_j c_j \mu_j \quad (11)$$

where σ is the conductivity, q_j , c_j , and μ_j are the absolute values of the charge, the concentration, and the mobility of species j , respectively, and the sum is over all charged species in the system. For diglyme–LiTf, subject to the assumption that “free” triflate and “free” lithium ions are the only charge-carrying species, this expression becomes

$$\sigma = q_{\text{Li}^+} c_{\text{Li}^+} \mu_{\text{Li}^+} + q_{\text{Tf}^-} c_{\text{Tf}^-} \mu_{\text{Tf}^-} = q_{\text{free}} c_{\text{free}} (\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}) \quad (12)$$

using the relations $q_{\text{Li}^+} = q_{\text{Tf}^-} = q_{\text{free}}$ and $c_{\text{Li}^+} = c_{\text{Tf}^-} = c_{\text{free}}$. The expression $(\mu_{\text{Li}^+} + \mu_{\text{Tf}^-})$ is the sum of the cation and anion mobilities, which are inherently coupled, assuming an ion cloud model of ion transport.^{1,27} Therefore, it may be more accurate to view $(\mu_{\text{Li}^+} + \mu_{\text{Tf}^-})$ as an average mobility of the system.

Table 1 gives values of the conductivity (σ), molar conductivity (Λ), and sum of the mobilities $(\mu_{\text{Li}^+} + \mu_{\text{Tf}^-})$ for the “free” lithium and “free” triflate ions as a function of total salt concentration.

The molar conductivity in diglyme–LiTf solutions is

$$\Lambda = \frac{\sigma}{c_{\text{total}}} = \frac{q_{\text{free}} c_{\text{free}} (\mu_{\text{Li}^+} + \mu_{\text{Tf}^-})}{c_{\text{total}}} \quad (13)$$

From eq 12, the sum of the mobilities can be written

$$\mu_{\text{Li}^+} + \mu_{\text{Tf}^-} = \frac{\sigma}{q_{\text{free}} c_{\text{free}}} \quad (14)$$

where the quantities on the right-hand side of eq 14 are either experimentally determined (σ , c_{free}) or known directly (q_{free}). Equation 14 is a standard equation found in many physical chemistry textbooks, and it is often used to calculate mobilities where the concentration of “free” ion is equal to the total salt concentration (i.e., 1:1 salts in water). However, when the fraction of “free” ion is less than 1 and the salt is spectroscopically sensitive to ion–ion interactions (salts containing triflate, perchlorate, or nitrate are examples), IR spectroscopic data about the solute species present and their concentrations allow mobilities to be calculated in these systems. Such is the case here.

Values for the sum of the mobilities for “free” lithium and triflate ion as a function of the total salt concentration are summarized in Table 1 and plotted in Figure 7. The mobilities increase with increasing concentration for low salt concentrations, reach a maximum at a total salt concentration of $5.1 \times 10^{-4} \text{ mol cm}^{-3}$ (40:1), and then decrease with increasing salt concentration. The initial increase of $\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}$ with increasing salt concentration in the dilute region is surprising, and studies are currently underway to understand this phenomenon.

Figure 8 shows the conductivity plotted against the total salt concentration for diglyme–LiTf. The conductivity increases with increasing total salt concentration until a maximum at approximately $1.53 \times 10^{-3} \text{ mol cm}^{-3}$ (12.5:1), and then decreases. The concentration of “free” ion increases with increasing salt concentration, reaches a maximum at a total salt concentration of $2.38 \times 10^{-3} \text{ mol cm}^{-3}$ (7.5:1), and then decreases (Table 1). Since the conductivity is proportional to

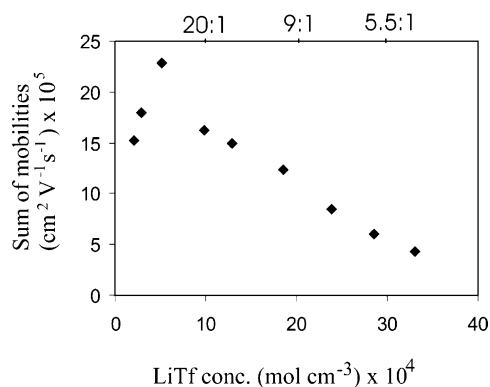


Figure 7. $\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}$ versus total salt concentration for diglyme–LiTf.

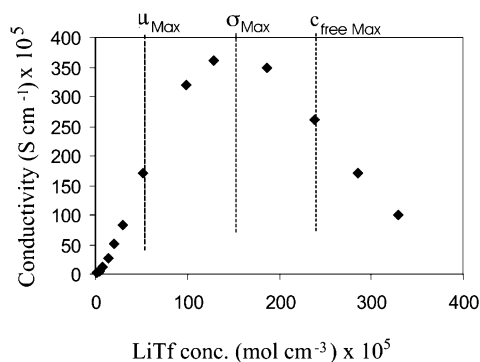


Figure 8. Conductivity versus total salt concentration for diglyme–LiTf.

the product of the concentration of “free” ion and the sum of the mobilities (eq 12), the conductivity also increases with salt concentration for low concentrations and reaches a maximum at a salt concentration that is intermediate between the salt concentration where the concentration of “free” ion and sum of mobilities reached their maxima (Figure 8). The conductivity then decreases with increasing salt concentration.

The upper half of Figure 9 shows the molar conductivity of diglyme–LiTf solutions plotted against the square root of total salt concentration (data from Table 1). Over region I, the molar conductivity is large in the very dilute region and decreases with increasing salt concentration until it reaches a minimum at a total salt concentration of approximately $2.1 \times 10^{-5} \text{ mol cm}^{-3}$ (1000:1). The molar conductivity then increases with salt concentration until a salt concentration of $5.1 \times 10^{-4} \text{ mol cm}^{-3}$ (40:1) (region II), and then decreases (region III). Similar behavior has been observed in many electrolytes based on low dielectric constant solvents; these include both low and high molecular weight polymer hosts as well as simple organic liquids and a variety of dissolved salts.^{2–5} The usual explanation for the decrease in molar conductivity in region I of Figure 9 is that, as the total salt concentration increases, $c_{\text{free}}/C_{\text{total}}$ decreases from 1 due to ion pairing.⁷ However, the lower half of Figure 9 shows that the concentration dependence of the molar conductivity for TbaTf in diglyme is qualitatively similar to that of LiTf in diglyme. The minimum in molar conductivity is also reached at approximately $2.1 \times 10^{-5} \text{ mol cm}^{-3}$; the maximum occurs at $2.7 \times 10^{-4} \text{ mol cm}^{-3}$. A TbaTf–diglyme solution has a single $\delta_s(\text{CF}_3)$ band at 752 cm^{-1} , and therefore, only “free” ions exist on the time scale of IR spectroscopy. The bulky organic groups attached to the nitrogen atom of the tetrabutylammonium cation prevent contact ion pairing or ionic aggregation in TbaTf–diglyme.^{12,13} However, dielectric relaxation data for alkylammonium salt solutions have been inter-

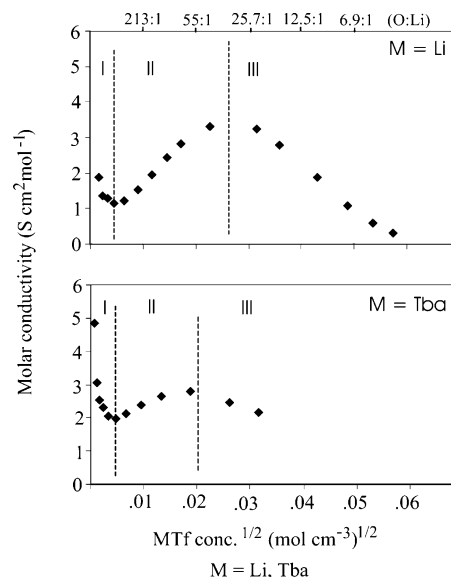


Figure 9. Molar conductivity versus the square root of the total salt concentration for diglyme–LiTf and diglyme–TbaTf.

preted in terms of the formation of ion pairs.^{1,30} There is a range of cation–anion interactions that results in what is somewhat loosely termed “ionic association”. At one extreme lies the coordinative interactions between a lithium ion and triflate oxygen atom(s), which result in long-lived, discrete solute species. The strength of these interactions leads to electronic redistribution within bonds, resulting in normal-mode frequency shifts and spectral intensity changes. By contrast, the interaction between a tetrabutylammonium cation and a triflate anion is relatively weak, because a close approach of the anion to the nitrogen atom of the cation is sterically hindered by the bulky butyl groups of the cation. Between these two extremes lie other degrees of cation–anion interaction strengths governed by Coulombic and non-Coulombic interactions between cations and anions.

The similar concentration-dependent behavior of the molar conductivity in both LiTf and TbaTf diglyme solutions argues that the decrease in molar conductivity in region I cannot be due to speciation (ionic association, e.g., ion pairing) and is more likely due to a decrease in ionic mobility. An analogous decrease in the molar conductivity at low salt concentrations has also been observed for LiTf in many other solvents (data not shown), demonstrating that the concentration-dependent behavior is not a solvent effect.

In diglyme–LiTf, as well as in many polymer electrolytes, the molar conductivity increases with salt concentration after its initial decrease as seen in region II of Figure 9. The usual explanation for the increase in molar conductivity in region II is that either mobile triple ions are formed or there is increased dissociation of ion pairs into “free” ions.^{6,7} Again, TbaTf cannot form contact ion pairs or aggregates. Furthermore, as seen from the data for diglyme–LiTf in Table 1, the ratio $c_{\text{free}}/C_{\text{total}}$ changes very little in the composition range from 100:1 ($c_{\text{free}}/C_{\text{total}} = 0.17$) to 40:1 ($c_{\text{free}}/C_{\text{total}} = 0.15$). However, the sum of the ionic mobilities increases with increasing salt concentration over this composition range as seen in Figure 7. It is expected that the sum of the mobilities also increases with increasing salt concentration beginning at low concentrations (i.e., compositions starting at 1000:1 for LiTf), but at the present time, this cannot be verified because of the detection limits of IR spectroscopy. Therefore, the increase in molar conductivity in region II of Figure 9 is attributed to the increase in mobility. This is clearly

TABLE 4: Comparison of Self-Diffusion Coefficients ($\text{cm}^2 \text{s}^{-1} \times 10^6$) in 20:1 Solutions of Diglyme–Li(N(CF₃SO₂)₂) and Diglyme–LiTf

	$D(\text{Li})$	$D(\text{F})$	$D(\text{H})$
this work	2.64	2.47	4.67
Hayamizu et al.	4.5	5	9.3

the case in diglyme–TbaTf and presumably true in diglyme–LiTf. The idea that the concentration dependence of molar conductivity is mobility-based has been previously postulated by the Torell group, who studied triflate salts in solid polymer electrolytes.³¹ Torell used Raman spectroscopy to examine ionic association over an extensive concentration range and reached the conclusion that speciation changes are not responsible for the concentration dependence of molar conductivity.

4. Conclusions

In solutions of diglyme–LiTf, IR spectroscopy provides information about the nature of the solute species present and their concentrations. These concentrations have been corrected for nonideality by a form of the Debye–Huckel equation and were used to calculate equilibrium constants in a series of diglyme–LiTf solutions for the dissociation of a LiTf contact ion pair into “free” ions. Equilibrium constants were also calculated for the association of two contact ion pairs into a dimer. From ΔG° and the temperature dependence of the equilibrium constants, ΔH° and ΔS° are calculated for the processes. A careful examination of the ΔS° values for the two processes underscores the important contribution of the solvation entropy to the overall entropy change.

The enthalpy change for the dissociation of a LiTf contact ion pair into “free” ions ($\Delta H_1^\circ = -1.70 \times 10^4 \text{ J mol}^{-1}$) is negative. This is expected because the energy required to break a coordinative bond between the lithium ion and the oxygen atom of a triflate anion is smaller than the energy released in the coordinative interaction of the lithium ion with an additional diglyme molecule, assuming that the “free” lithium ion is sixfold coordinated by two diglyme molecules after dissociation. The enthalpy change for the association of two LiTf contact ion pairs into a dimer is positive ($\Delta H_2^\circ = 4.0 \times 10^3 \text{ J mol}^{-1}$). Here, the major contribution is the formation of two Li–Tf coordinative interactions, since there is no significant change in the interaction of the cations with the diglyme molecules (Figure 2). The fact that ΔH_2° is positive suggests that the contact ion pair is more tightly packed than the dimer, thereby costing more energy to dissociate than is gained in the formation of two additional Li–Tf coordinative bonds in the association process. More experimental support for this claim is observed from the crystal structures of diglyme–LiTf and the 1:1 complex of 1,1,4,7,10,10-hexamethyltriethylenetetramine with LiTf. As mentioned previously, the LiTf–diglyme crystal consists of dimers, while the LiTf–hexamethyltriethylenetetramine crystal is composed of contact ion pairs. The lithium–triflate oxygen bond distance is shorter in the LiTf–hexamethyltriethylenetetramine crystal (1.902 Å)¹⁵ than in the LiTf–diglyme crystal (1.944–1.965 Å),¹⁴ consistent with a contact ion pair being more compact with stronger lithium–oxygen bonds than a dimer. It is also possible that the positive change in enthalpy for dimer formation results from solvent rearrangement.

The dependence of the molar conductivity on LiTf concentration in diglyme has a characteristic behavior observed in other electrolyte solutions with low dielectric constants. In the very dilute region, the molar conductivity sharply decreases to a minimum with increasing salt concentration (region I), then

increases to a maximum (region II) before again decreasing (region III). Ionic association has long been thought to play a significant role in the behavior in regions I and II. However, the same concentration dependence was observed in diglyme solutions containing dissolved TbaTf, where ionic association is minimized due to the steric effect of the bulky cation. This comparison suggests that, although ionic association plays an important role in controlling the ionic transport, other factors are equally significant.

Knowledge of the concentration of the “free” ion present at various solution compositions and measurement of σ allows a calculation of $\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}$ using eq 14. The decrease of $\mu_{\text{Tba}^+} + \mu_{\text{Tf}^-}$ in region I followed by the increase of both $\mu_{\text{Tba}^+} + \mu_{\text{Tf}^-}$ and $\mu_{\text{Li}^+} + \mu_{\text{Tf}^-}$ in region II suggest that the change in ionic mobilities plays an essential role in the mechanism of ionic transport in these two regions.

The values of the lithium and fluorine self-diffusion coefficients measured in this study are similar to those reported in comparable studies. Hayamizu et al. measured the proton, lithium, and fluorine self-diffusion coefficients in a series of 14 organic solvents, including diglyme, containing Li(N(CF₃SO₂)₂), all at a molar solvent/salt ratio of 20:1.²² Their diffusion coefficients were in the range of 1×10^{-6} to $1 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$. A comparison of their measured diffusion coefficients and ours is summarized in Table 4.

The values reported by Hayamizu et al. are about twice as large as those measured in this work. This difference may lie in the different anions. Charge delocalization occurs to a greater extent in the (N(CF₃SO₂)₂)[−] anion studied by Hayamizu et al. than in the triflate anion used in this work. Consequently, there are stronger cation–anion interactions in the triflate system, and these may lead to smaller diffusion coefficients because bulkier contact ion pairs and aggregates presumably have smaller mobilities than “free” ions.

Saito et al. used PFG-NMR to measure the diffusion of various species in gel electrolytes consisting of copolymers of poly(vinylidene fluoride) and hexafluoropropylene (Kynar 2751) containing ethylene carbonate and diethylene with dissolved Li(N(CF₃SO₂)₂).²¹ They found that the diffusion coefficients of the cationic and anionic species approached each other with increasing polymer fraction in the gel. The authors attributed this trend to an increase in the association of the salt as the polymer content increased. This trend is similar to the behavior shown in Figure 3 as the salt concentration increases and the degree of association increases. The diffusion coefficients reported by Saito et al. ranged from about 10^{-7} to $10^{-5} \text{ cm}^2 \text{s}^{-1}$ over a solution fraction from 40% to 80%. The diffusion coefficients in this study fell in the range from 0.08×10^{-6} to $6.4 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ over a series of compositions from O:Li = 5:1 to 40:1.

The conclusions reached in this paper result from the assumptions made about the type of species present in solution. It was presumed that dimers, contact ion pairs, and “free” ions are the existing species, and abundant experimental data supports this claim: (1) A dimeric structure is known to exist for the crystal structure of diglyme–LiTf, and it is very reasonable to assume that dimers are also present in solution. (2) Contact ion pairs are known to exist in crystal structures involving lithium triflate. (3) NMR data show that the diffusion coefficients for lithium and triflate are similar, consistent with the existence of contact ion pairs and dimers. If triple ions existed in solution, it is expected that lithium and triflate’s diffusion coefficients would be substantially different from each other. (4) The equilibrium constant for dimer formation is constant over a wide

concentration range. If triple ions existed in solution, activity coefficients would be necessary for the equilibrium constant to remain constant as a function of salt concentration. However, this is not the case. (5) Calculated values for the change in enthalpy agree with Le Chatelier's principle, and (6) triple ion formation is often invoked as a necessity for explaining the increase in molar conductivity as a function of salt concentration in region II for electrolytes with a low dielectric constant solvent. However, solutions of tetrabutylammonium triflate in low dielectric constant solvents also exhibit an increase in molar conductivity in region II. IR spectroscopy has confirmed that tetrabutylammonium triflate cannot form ion pairs or aggregates, eliminating triple ions as the cause of this behavior.

Acknowledgment. We thank the Department of Chemistry and Biochemistry, University of Oklahoma, for financial support of this project.

Supporting Information Available: Additional experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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