Conductivity, Viscosity, and Dissolution Enthalpy of LiNTF$_2$ in Ionic Liquid BMINTF$_2$

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The ionic conductivity, relative viscosity, and solution enthalpy of LiNTF$_2$ and NaNTF$_2$ solutions in ionic liquid BMINTF$_2$ have been measured. We observed that the conductivity decreased and the viscosity increased when the Li$^+$ and Na$^+$ salts were dissolved in BMINTF$_2$. We also observed that the dissolution is an exothermic process with a solution enthalpy of approximately -18.07 ± 4.61 kJ/mol. The experimental results indicate that the Li$^+$ ion may associate with multiple NTF$_2^-$ anions in the BMINTF$_2$ solution to form a solvated complex.

Introduction

Room-temperature ionic liquids (ILs) have recently become the focus of a growing interest due to their remarkable properties such as negligible vapor pressures, low melting points, non-flammability, being good solvents to many organic and inorganic chemicals, and high ionic conductivity.[1] These properties make ILs candidates for numerous applications including the electrolytes of electrochemical processes and in rechargeable Li/Li-ion batteries.[2−20]

There is no doubt that the Li/Li-ion batteries have many advantages, such as very high energy density or capacity, low self-discharge rate, and high voltage. The major drawback of Li/Li-ion batteries is their safety concern due to the use of Li metal and organic solvents (such as propylene carbonate and dimethoxyethane) in the electrolyte solution. While the current and future market of Li/Li-ion batteries is still burgeoning, there is an urgent need for innovative systems that reduce the risk of using these batteries and reduce the cost of several mandatory built-in safety devices, such as a shut-down circuit and a vent.

A few problems exist with these electrolyte systems. First, most of the safety problems of Li/Li-ion batteries are related to the use of organic solvents in electrolyte solutions. Organic solvents are volatile and flammable. An accident due to a Li/Li-ion battery starts from the heat generated from a short-circuit or an overcharge and is followed by several possible scenarios. If a short-circuit or overcharge makes a spark, the organic solvents (flammable liquids) can ignite. If it causes the temperature inside the battery to rise rapidly, the battery may explode because of the high vapor pressure. When the temperature increases slowly to a high value, the battery can melt, and the liquid inside can leak out. Second, Li/Li-ion batteries need oxygen-free and moisture-free electrolyte solutions. The removal of water, other protic impurities, and dissolved oxygen from the organic solvents is costly. In fact, it is the purification processes of manufacturing that contaminate the electrolyte with fine metal particles (usually, tiny pieces of lithium metal).[21] This contamination raises the risk of an internal short circuit between the anode and cathode. Third, these electrolyte solutions cannot work at very low temperatures. Most electrolyte solutions freeze at approximately −40 °C. To maintain optimal performance,

Li-ion batteries are usually used between −20 and 60 °C, and this restricts their applications.[7]

Owing to the negligible volatility and nonflammability of ILs, the inherent long life and safety features are significant advantages when ILs are used as electrolytes in these batteries. IL electrolytes also enable the use of pure Li metal electrodes for batteries, with higher energy density than Li−C materials or alloy anodes.[4,12,22] In addition, ILs prevent the dendrite formation problem of Li metal electrodes so that they can prolong the life circles of a rechargeable Li/Li-ion battery.[23,24]

A few publications reported the use of Li$^+$ salts in ILs as electrolytes.[2−20] Typical electrolytes are LiN(CF$_3$SO$_2$)$_2$ (also called LiNTF$_2$) or LiN(C$_2$F$_5$SO$_2$)$_2$. Typical ILs are imidazolium ILs with a bis(trifluormethylsulfonyl)imide (NTF$_2^-$) anion. The performance of the electrolytes and the batteries has been examined. The Li$^+$ salt−IL systems keep the advantages of negligible volatility, nonflammability, and a broad applicable temperature range. However, the conductivity of IL solutions reduced when Li$^+$ salts were dissolved in the ILs, which has been explained by the increase in viscosity.[7] On the contrary, the ionic conductivities of traditional electrolyte solutions increase with an increasing electrolyte concentration. Precisely how the dissolved Li$^+$ salts affect the viscosity of the ILs and the conductivity at a molecular level is currently unknown. The solution properties and solvation mechanisms of Li$^+$ ion in the IL solutions are not currently available.

In this paper, the enthalpy of solution, viscosity, and conductivity of Li$^+$ salt solutions in the IL 1-butyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide (BMINTF$_2$) have been systematically investigated. It was found that the conductivity of the solutions decreased proportionally with the increase of Li$^+$ salt concentration, while the viscosity increased. The dissolution of LiNTF$_2$ in BMINTF$_2$ is an exothermic process, indicating a strong interaction between the Li$^+$ cation and the NTF$_2^-$ anion. To the authors' best knowledge, this is the first report of the solution enthalpy of Li$^+$ salts in ILs.

Experimental Section

Chemicals. The IL BMINTF$_2$ (>97% pure) was purchased from EMD Chemicals Inc. LiNTF$_2$ (>99% pure) and HNTF$_2$ (>95% pure) were purchased from Fluka and were used as received. BMINTF$_2$ and LiNTF$_2$ were dried in a vacuum oven overnight at 60 °C prior to use. All other chemicals were purchased from Sigma-Aldrich and used as received. NaNTF$_2$

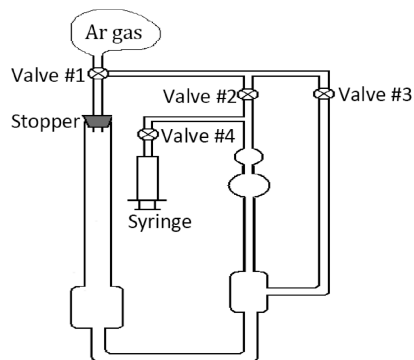* Corresponding author. Phone: 856-256-5409. Fax: 856-256-4478. E-mail: yu@rowan.edu.

Figure 1. Viscosity measurements with an Ubbelohde viscometer under an Ar atmosphere.

Figure 2. Schematic view of the "coffee-cup" calorimeter.

Figure 3. Conductivity of BMINTF$_2$ solutions as a function of H$_2$O concentration.

was prepared by neutralizing the HNTF$_2$ (an acid) with NaOH in a water solution. A 0.1 M HNTF$_2$ solution was titrated with 0.1 M NaOH. The end point was monitored by the phenolphthalein indicator. NaNTF$_2$ was recrystallized from the water solution and dried in a vacuum oven at 60 °C overnight.

Ionic Conductivity. The conductivity of pure ILs and IL solutions was measured by an AC Mode Traceable conductivity meter at a constant frequency of 3 kHz with a pair of parallel Pt plate electrodes. The cell constant is designed to be 1. ILs and IL solutions were prepared in air and treated in a vacuum oven at 60 °C overnight and then transferred into a test tube prior to the measurement.

Viscosity. The viscosities of ILs and IL solutions were measured with an Ubbelohde three-tubing viscometer. The viscometer is set in a water bath whose temperature can be precisely controlled with 0.1 °C fluctuation. Most ILs and IL solutions were prepared in air and treated in a vacuum oven at 60 °C overnight prior to the measurement. HNTF$_2$ is volatile and moisture sensitive; therefore, its solutions were prepared in a glovebox under an Ar atmosphere. The HNTF$_2$ solutions were transferred into a home-designed Ubbelohde viscometer in the glovebox and sealed under an Ar atmosphere. Then, the viscometer was moved out of the glovebox and the viscosity was measured in a water bath. The home-designed viscometer is shown in Figure 1. Valve #1 is a three-way valve, while valves #2, #3, and #4 are all two-way valves. Before loading into a glovebox, the Ar balloon is emptied and the rubber stopper is removed from the viscometer. All the valves are closed. In the glovebox, an HNTF$_2$ solution is transferred into the viscometer and the balloon is partially filled with Ar gas. The balloon is kept loose, and the Ar stored in the balloon maintained a constant pressure of the atmosphere (close to 1 atm) during the measurement. The rubber stopper is reattached to the viscometer, and the three-way valve #1 is switched on before the entire viscometer is transferred out of the glovebox. At this point, the two-way valves #2 and #3 are switched off while switching on the two-way valve #4. Then, a syringe is used to aspirate the solution to receiver bulbs. At this point, valve #4 is switched off and valves #2 and #3 are switched on to start the viscosity measurement.

Dissolution Enthalpy. The enthalpy of dissolution was measured with a "coffee-cup" calorimeter, as shown in Figure 2. The solute was dissolved in the solvent in a styrofoam container with a volume capacity of about 10 mL with magnetic stirring. The system was isolated with a rubber stopper. The temperature was monitored by a thermal couple connected to a computer. A temperature–time curve was recorded.
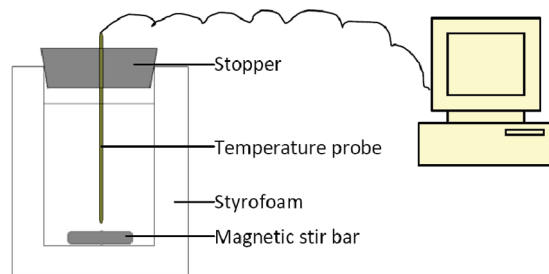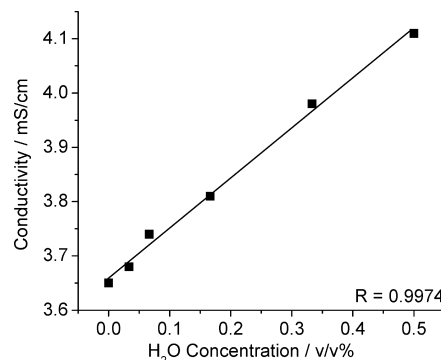
Results and Discussion

BMINTF$_2$ is a hydrophobic IL. It adsorbed a small amount of H$_2$O from the air. The effect of the adsorption of water on the IL conductivity is investigated by adding small values of deionized water into the BMINTF$_2$. Before the measurement, the IL was treated in a vacuum oven at 60 °C overnight. The concentration of water is assumed to be negligible after the treatment. As indicated by Figure 3, the conductivity of the BMINTF$_2$ solution increased from 3.65 mS/cm (pure IL) to 4.11 mS/cm (0.5 v/v% water) when water was dissolved in the BMINTF$_2$. The conductivity appears to be directly proportional to the volume percentage of water over the range 0–0.5 v/v%. While the reason that dissolving of water increased the conductivity of BMINTF$_2$ is not clear, the conductivity of BMINTF$_2$ returned to 3.66 mS/cm after the solution was retreated in a vacuum to remove all the dissolved water. This measurement indicated that vacuum treatment can effectively remove the trace amount of water adsorbed in BMINTF$_2$ and yield reproducible values of conductivity. In the later measurements, LiNTF$_2$, NaNTF$_2$, LiCl, and BMICl solutions in BMINTF$_2$ were all treated in a vacuum before the conductivity measurement.

The conductivity of LiNTF$_2$ and NaNTF$_2$ solutions in BMINTF$_2$ is shown in Figure 4. It has been reported that the conductivity values of LiNTF$_2$ solutions in the ILs 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (DMPINTF$_2$) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMINTF$_2$) decreased with the increase of LiNTF$_2$ concentration at various temperatures from 233 to 353 K.[7,10] In our measurements, the conductivity of the BMINTF$_2$ solutions decreased when the LiNTF$_2$ or NaNTF$_2$ concentration increased. The conductivity values of our measurement are at the same order of magnitude as reported results. For example, it was reported that 0.32 and 0.64 mol/kg LiNTF$_2$ solutions in DMPINTF$_2$ have conductivities of 2.3 and 1.3 mS/cm, respectively, at 30 °C.[7] At the same temperature, the pure ILs
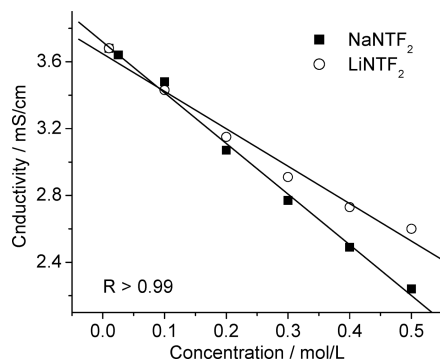
Figure 4. Conductivity of BMINTF$_2$ solutions vs LiNTF$_2$ and NaNTF$_2$ concentrations.

EMINTF$_2$ and DMPINTF$_2$ have conductivities of 10.6 and 3.41 mS/cm, respectively.[10] The exact conductivity of the ILs and IL solutions are also affected by temperature and some trace amount of contamination. DMPINTF$_2$ has a very close structure and formula mass to the IL used in this paper (BMINTF$_2$). Their conductivities measured by our group (this paper) and others (ref 10) are very close. It was noticed that the conductivity of Na$^+$ salt solutions is lower than the conductivity of Li$^+$ salt solutions when the concentration is relatively higher.

In the same reference,[7] the decrease of the ionic conductivity has been attributed to the increase of the IL viscosity after the Li$^+$ salt is dissolved. This phenomenon of ILs has been related empirically by Walden's rule: $k\eta$ = constant, where k is the conductivity of an IL and η is its absolute viscosity.[25] We measured the relative viscosities of LiNTF$_2$ and NaNTF$_2$ solutions in BMINTF$_2$. The results are shown in Figure 5. The relative viscosity of Li$^+$ salt solutions and Na$^+$ salt solutions increased with the increase of either LiNTF$_2$ or NaNTF$_2$ concentration at 25, 30, and 35 °C. It is also noticed that, when the Li$^+$ salt and the Na$^+$ salt solutions have the same concentration, the Na$^+$ salt solution has a higher relative viscosity than the Li$^+$ salt solution at the same temperature (data not shown). The time of the LiNTF$_2$ and NaNTF$_2$ solutions flow through the capillary of the Ubbelohde viscometer was measured at different temperatures. At the same concentration, both the viscosities of LiNTF$_2$ solution and NaNTF$_2$ solution decreased with increasing temperature from 20 to 35 °C. It took a shorter time for the solutions to flow through the capillary at higher temperatures than lower temperatures.

Conductivity measures the steady-state drift velocity (ν_d in m/s) or the mobility (μ in m^2/V·s) of ions to an applied electric field across the IL solution. These two parameters are related by $\nu_d = \mu E$, where E is the applied electric field in V/m. k of an ion is proportional to μ. The ν_d value of an ion is the average velocity the ion gained with the acceleration of the electric field, the drag force from the other particles in the solution, and the collision with the other particles.[26,27] The overall conductivity of an electrolyte solution is the sum of all current carry ions: κ = $\Sigma F(Z_i)(C_i)(b_i)$, where F is Faraday's constant, Z_i is the charge of one particle, C_i is the concentration of the particle, and b_i is the internal mobility of the particle. Viscosity is a measure of the rate of transfer of momentum from the faster stream to the slower stream by the collision of faster and slower particles.[27] In a laminar flow of fluid between two plates, which may be a simplified model of the flow in a capillary viscometer, friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is described by the equation: friction (shear stress) = $\eta(\partial u/\partial y)$, where u is the

velocity of flow in the flow direction and the *y* dimension is perpendicular to the flow direction. ($\partial u/\partial y$) is the velocity gradient along the *y*-axis. In a laminar flow, momentum is transferred along the *y* dimension from higher velocity layers to lower velocity layers by the collision of particles between layers.

Since LiNTF$_2$ and NaNTF$_2$ have the same anion to the solvent BMINTF$_2$, the depression of the solution conductivity and the increase of the solution viscosity should be attributed to the addition of Li$^+$ ion or Na$^+$ ion. This hypothesis is also supported by the results when other ionic compounds are added. Addition of BMICl increased the conductivity of BMINTF$_2$ gradually from 3.65 to 3.95 mS/cm and then leveled off when the concentration was higher than 0.1 M (data not shown). This may indicate that the introduction of Cl$^-$ ion into the system increased the overall conductivity. The conductivity increased slightly (3.69 mS/cm) when the added LiCl concentration was 0.025 M and did not change significantly when more LiCl was added up to a concentration of 0.5 M. Li$^+$, Na$^+$, and BMI$^+$ ions all carry the same charge. However, Li$^+$ and Na$^+$ are much smaller ions than BMI$^+$. Therefore, addition of smaller ions such as Li$^+$ or Na$^+$ will increase the overall current carrier concentration, number of ions in a unit volume. In addition, the electrical mobility of a spherical "free ion" (not chemically bonded with other particles) in a parallel electric field is inversely proportional to the square root of the size (mass) of the ion.[28] Therefore, if the Li$^+$ or Na$^+$ ion is fully mobile in the solution, the addition of these ions will increase the overall conductivity of the IL solutions. However, this is contrary to our measured conductivity results. This may indicate that the dissolved Li$^+$ or Na$^+$ ion is solvated with the anion of IL, NTF$_2^-$, to form ion pairs or clusters, so that the Li$^+$ and Na$^+$ ions have very low activity in their solutions.

Ion pairs are neutral in charge. The formation of ion pairs reduced the concentration of current carriers. Ion clusters are larger in size and reduced the ion drift velocity and mobility. Both effects will cause a conductivity depression. The interaction between Cl$^-$ ion and BMI$^+$ ion is relatively weaker compared to the interaction between cations and anions of typical inorganic salts. In fact, BMICl is an ionic liquid itself. Therefore, the Cl$^-$ ion may have a relative larger activity compared with cations, such as Li$^+$ and Na$^+$, and, hence, may increase the conductivity. In the LiCl solution, the effects of Li$^+$ and Cl$^-$ ion on conductivity may cancel out partially. This molecular mechanism can also qualitatively explain the observed increase of viscosity. During the laminar flow, the flow layers are cylindrical in structure in a capillary tube; faster moving particles transfer momentum to the slower moving particles in an adjunct layer by collision. The ions in the faster layer bump against the adjunct ions in the slower layer as they pass. On average, the ions in the faster stream are slowed down and those in the slower stream are sped up. According to Newtonian mechanics, it will be easier to transfer momentum to a smaller particle than to a larger particle. Again, if the dissolved Li$^+$ and Na$^+$ ions have large activity, the smaller particles will decrease the solution viscosity. The measured increase of viscosity may indicate that the Li$^+$ and Na$^+$ ions either interact strongly with the NTF$_2^-$ anion or bond with the anion to form larger and heavier particles. Therefore, more kinetic energy will dissipate when transferring momentum to larger particles or by breaking the interactions between the cation and anion in the cluster. When temperature is increased, more small particles will have enough kinetic energy to escape temporarily from the ion pairs or ion clusters. Thus, the transfer of momentum will be faster, yielding a smaller viscosity. For most liquids, an increase in temperature will
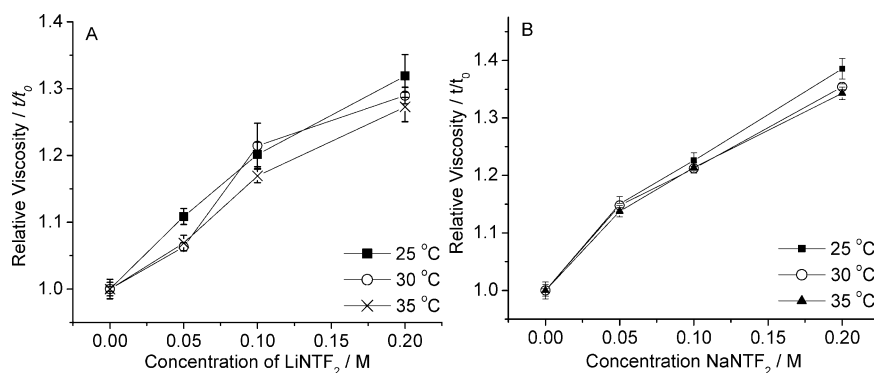
Figure 5. Relative viscosities of LiNTF$_2$ (A) and NaNTF$_2$ (B) solutions in BMINTF$_2$ at various temperatures.

TABLE 1: Measurement of the LiNTF$_2$ Dissolution Enthalpy in BMINTF$_2$

mass of LiNTF$_2$[a]	volume of BMINTF$_2$	density of BMINTF$_2$	concentration[a]	heat capacity	change of temperature	enthalpy of dissolution
ca. 0.1435 g	5 mL	1.3984 g/mL	ca. 0.1 M	0.56733 kJ/K·mol[29]	0.55 ± 0.16 °C ($n = 14$)	−18.07 ± 4.61 kJ/mol ($n = 14$)

[a] Mass and concentration may change in different trails.

decrease the viscosity, also seen in the ILs and IL solutions. When LiBF$_4$ is dissolved in EMIBF$_4$ (ethyl-methyl-imidazolium tertrafluoroborate), an increase in viscosity and a decrease in conductivity have also been observed.[8] Further measurement of the transport number of Li$^+$ ions indicates the major current carrier is EMI$^+$ in the solution. We dissolved a "molecular" compound, HNTF$_2$, in BMINTF$_2$. The reduction of the conductivity and the increase of the viscosity was insignificant (data not shown), probably because the solute did not completely dissociate in the BMINTF$_2$ solution.

The formation of ion pairs or ion clusters will release the potential energy carried by the positively and negatively charged ions, which is converted to heat. The dissolution enthalpy of LiNTF$_2$ in BMINTF$_2$ has been measured at a constant pressure, and the results are shown in Table 1. Typically, a small quantity of BMINTF$_2$ (5 mL) and LiNTF$_2$ (ca. 0.1435 g) was used, in order to save the relatively expensive chemicals. The systematic error (loss of heat) was calibrated with the dissolution of CaCl$_2$ in H$_2$O. Comparing the measured and standard dissolution enthalpy of CaCl$_2$ in H$_2$O, we identified a 28.0 ± 2.7% ($n = 9$) heat loss when 5 mL of solvent was used, and the maximum temperature was reached within 2 min. This 28.0 ± 2.7% heat loss was compensated when the dissolution enthalpy of LiNTF$_2$ in BMINTF$_2$ was computed. We also used the same system to measure the heat capacity of BMINTF$_2$; the measured results were consistent with the reported values in the literature.[29] The change of temperature and the enthalpy of dissolution data shown in Table 1 have a relatively large percentage uncertainty, ca. 25−30%. This is because the relatively smaller enthalpy of dissolution and larger viscosity of IL systems were compared with aqueous systems. However, in all the trials (number of 14), an increase in temperature and an exothermic dissolution enthalpy were unambiguously observed. The temperature fluctuations of the background were also monitored. It is within 0.1 °C during the experimental time scale. This result may rule out the possibility that the increments of temperature were from the mechanical friction of magnetic stirring. A typical curve of temperature change vs time is shown in Figure 6. Since the styrofoam is a good heat isolation material, we can observe a quick increase in temperature when the LiNTF$_2$ is dissolving. After a maximum temperature has been reached, it decreases slowly back to the original room temperature.
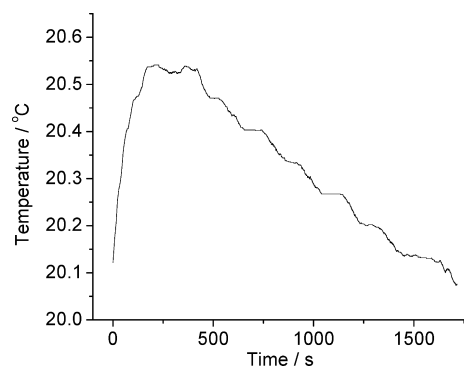

Figure 6. Temperature vs time during a typical calorimetry process of LiNTF$_2$ dissolution in BMINTF$_2$. The curve has been smoothed from the original data by adjacent averaging.
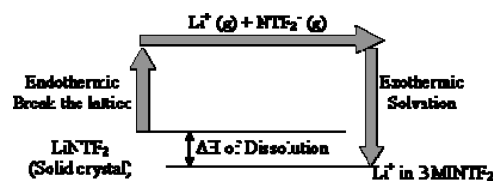

Figure 7. Schematic view of the dissolution processes.

The dissolution of a salt in a solvent includes three processes at the molecular level: an endothermic process breaking the attractions of solute ions, another endothermic process breaking the attractions of solvent ions, and an exothermic process of solvation, as shown in Figure 7. A solution of LiNTF$_2$ in BMINTF$_2$ consists merely of ions. The solute and the solvent share the same anion. We can assume the Li$^+$ ion is solvated only by the anion of NTF$_2^-$. The addition of extra NTF$_2^-$ from LiNTF$_2$ will not result in an enthalpy change of the system. The solvation of the additional NTF$_2^-$ will form new interactions between the NTF$_2^-$ and BMI$^+$ ions. Occurring simultaneously, an equivalent interaction will be broken between the BMI$^+$ and NTF$_2^-$ ions. Therefore, the solvation enthalpy should solely come from the solvation of Li$^+$ ion. The exothermic dissolution enthalpy indicates that the solvation enthalpy of Li$^+$ ion should be greater than the lattice enthalpy in absolute value. Since the anions in the Li$^+$ salt and in the IL are the same, this greater solvation enthalpy may indicate that a Li$^+$ ion in the solution is
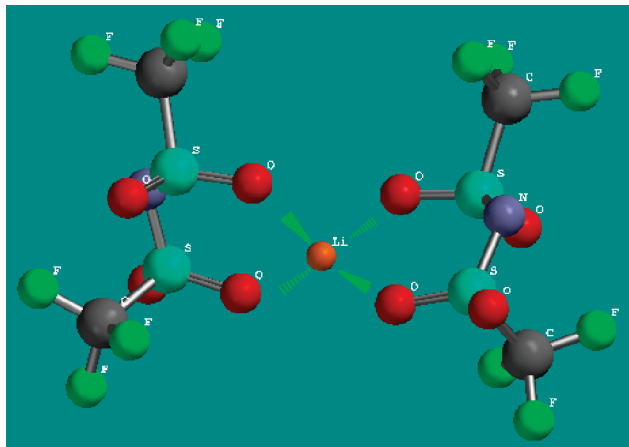
Figure 8. Structure of a Li$^+$ ion solvated with two NTF$_2^-$ ions. (The structure was obtained by Spartan 04 with the best conformation search. The wedged bonds and hashed wedged bonds between Li and O are not produced by Spartan. The authors added these bonds in order to indicate the 3-D positions of Li and O in the complex.)

solvated by multiple NTF$_2^-$ anions (2−4). The reported diffusion coefficients of Li$^+$ and NTF$_2^-$ measured by pulsed gradient spin−echo NMR also suggested the formation of solvated species such as [Li(NTF$_2$)$_2$]$^-$, [Li(NTF$_2$)$_3$]$^{2-}$, or [Li(NTF$_2$)$_4$]$^{3-}$.[30,31] Thus, ion clusters are formed with a much greater size than that of NTF$_2^-$ ion. Molecular modeling results indicated that the apparent radii of solvated species are about 0.8 nm, Li(NTF$_2$)$_4$$^{3-}$, and 0.7 nm, Li(NTF$_2$)$_2$$^-$.[31] This assumption agrees with the aforementioned results of conductivity and viscosity. Considering that Li$^+$ ion has a very small ion radius, a more plausible structure is that a Li$^+$ ion is coordinated with two NTF$_2^-$ ions ([Li(NTF$_2$)$_2$]$^-$), shown in Figure 8. Since the measured conductivity, viscosity, and apparent diffusion coefficient provide some macroscopic information of the overall solution; the exact solvation structure is still unknown based on the current available data. Further measurement of the lattice enthalpy and solvation enthalpy may add additional insight to this discussion. Raman spectroscopy results also suggest that the Li$^+$ is directly solvated by the oxygen atom in the NTF$_2^-$ anions.[32,33] While Na$^+$ is a larger cation, it may solvate with more NTF$_2^-$ ions, which makes the depression of conductivity and increasing viscosity even more significant. NaNTF$_2$ dissolves in BMINTF$_2$ very slowly when a solution has a molarity of 0.1 M or above. It took about 30 min to 2 h in an ultrasound bath when grinded NaNTF$_2$ powder was dissolved into BMINTF$_2$ to make solutions of 0.1−0.4 M. At lower concentration, the dissolving processes were still slow and the changes of temperature were very small, close to the fluctuations of background temperature. Many factors may affect the dissolution rate of solid solutes in a liquid solvent. The relative larger lattice energy (yields a higher activation energy) of NaNTF$_2$ compared to that of LiNTF$_2$ may be one of the reasons to cause the slow dissolution of NaNTF$_2$.[34] The larger lattice energy can be supported by the higher melting point of NaNTF$_2$ (262−266 °C), while the melting point of LiNTF$_2$ is 234−238 °C, provided by Sigma-Aldrich Inc. Therefore, the dissolution enthalpy of NaNTF$_2$ has not been obtained by calorimetry.

Conclusions

In this paper, we measured the conductivity, viscosity, and enthalpy of the IL BMINTF$_2$ and its solutions. The conductivity

decreased and the viscosity increased when LiNTF$_2$ and NaNTF$_2$ were dissolved in the IL. The dissolution enthalpy of LiNTF$_2$ in BMINTF$_2$ has been measured. It is an exothermic process and the value of the dissolution enthalpy is −18.07 ± 4.61 kJ/mol. All of these experimental results suggest that when a Li$^+$ ion is solvated in the BMINTF$_2$, it makes ion clusters with two to four NTF$_2^-$ anions by the strong interactions of Li$^+$ ion and the O and N atoms in the anion. The conclusions would then be usable to provide better insight about the ionic liquid electrolyte in order to develop a more efficient electrolyte system, as well as a more reliable and longer-lasting battery based on ILs.

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