Natural Abundance ^{17}O Nuclear Magnetic Resonance and Computational Modeling Studies of Lithium Based Liquid Electrolytes

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Abstract

Natural abundance ^{17}O NMR measurements were conducted on electrolyte solutions consisting of $\text{Li}[\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_3]$ (LiTFSI) dissolved in the solvents of ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC), and their mixtures at various concentrations. It was observed that ^{17}O chemical shifts of solvent molecules change with the concentration of LiTFSI. The chemical shift displacements of carbonyl oxygen are evidently greater than those of ethereal oxygen, strongly indicating that Li^+ ion is coordinated with carbonyl oxygen rather than ethereal oxygen. To understand the detailed molecular interaction, computational modeling of ^{17}O chemical shifts was carried out on proposed solvation structures. By comparing the predicted chemical shifts with the experimental values, it is found that a Li^+ ion is coordinated with four double bond oxygen atoms from EC, PC, EMC and TFSI anion. In the case of excessive amount of solvents of EC, PC and EMC the Li^+ coordinated solvent molecules are undergoing quick exchange with bulk solvent molecules, resulting in average ^{17}O chemical shifts. Several kinds of solvation structures are identified, where the proportion of each structure in the liquid electrolytes investigated depends on the concentration of LiTFSI.

Key words: Natural abundance ^{17}O NMR, chemical shift calculation, ethylene carbonate, propylene carbonate, ethyl methyl carbonate, and solvation structure.

1. Introduction

Electrolytes, responsible for transferring ionic components, play a critical role in energy storage systems such as rechargeable lithium ion batteries (LIBs) and redox flow batteries (RFBs), with the former based on solid-state electroactive materials while the latter on those dissolved in the electrolytes. The LIB technology has become increasingly important recently benefited from the combined high energy and high power density. Today, LIBs are widely used on cell phones, laptop computers and other portable devices, and are recently employed to revolutionize ground transportation via electric vehicles (EV) and hybrid electric vehicles (HEV).[1-3] On the other hand, RFB has enjoyed a recent renaissance fueled by the rapidly evolved global energy profile and the need for large-scale stationary energy storage devices. By providing wider electrochemically stable voltage windows, the emerging nonaqueous RFB (NRFB) has great potential to overcome the low energy density challenge present in current state-of-the-art aqueous RFB technologies.[4-7] Typically, LIBs and NRFBs share the electrolytes with similar formulations including the solvents, the charge carrier salts, the additives, and their concentrations.[8, 9] Therefore, an in-depth fundamental understanding of the electrolyte systems could shed light on both systems aiming at performance improvement.

The choice of electrolyte (i.e., solute + solvent) plays a key role in the Li^+ -based energy storage systems regardless of LIBs or NRFBs. The conductivity of the electrolytes directly influences the rating performance of the batteries, and their electrochemical stability determines the cycle life and safe operation of the batteries.[10] Alkyl carbonates were found to be the most suitable solvents for electrolytes,[11] attributed to their high electrochemical stability, a reasonable temperature range between freezing and boiling points, sufficiently low toxicity, and acceptable safety features.[12] The current model electrolyte systems prevalently use mixtures of alkyl carbonates including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl-methyl carbonate (EMC) as the solvent.[2, 3, 10, 12-14] On the other hand, among the many Li salts, lithium

bis(trifluoromethanesulfonyl)imide (LiTFSI) is one of the most attractive options because the TFSI is a large anion with delocalized charge and usually has lower binding to Li^+ thus yielding more free Li^+ cations available for charge transport (Chart 1).[15] [ENREF 12](#) Selection of the electrolyte compositions and determination of their relative ratios usually are driven by the requirements for advanced battery performance such as high conductivity, good chemical and electrochemical compatibility, low volatility of the electrolyte, etc.[2, 12, 16] The solvation phenomenon where the ions actively interact with the solvent molecules commonly exists in electrolyte systems and plays an important role in determining the properties of the electrolyte. In-depth understanding of the solvation structures of ions is critically important for designing improved electrolytes that offer optimized properties for the electrolyte and enhanced performance for batteries. Up to now, there are only a few investigations on understanding the properties of the mixed electrolytes with Li salt, where molecular dynamics (MD) simulations and diffusion measurements were employed.[15, 17-23] As this is an emerging field of research, there are indeterminate understandings reported from prior studies on the Li^+ solvation structure and the ion association in carbonate solvent.[15, 24-26] For example, in the case of EC the number of molecules bound to the Li^+ ion reported by Borodin et al. is 3.8 on average in LiTFSI/EC system,[15] while Bhatt et al. concluded that the leading component is the four-coordinated complex, $\text{Li}^+(\text{EC})_4$. For PC, on the other hand, Kameda et al. proposed a coordination number of 4.5 for LiPF₆/PC electrolyte,[24] and similar result has been calculated by Smith et al. with X-Ray absorption spectroscopy,[25] but in the study of Brooksby et al., the number of solvating PC molecules around the Li^+ ions is more consistent with 3.[26] For the mixed solvent, Vatamanu et al. obtained a total coordination number around 3.7 in the system of LiPF₆ in the mixture of EC and DMC.[22] Furthermore, little is known on the detailed changes of the solvation structures and molecular dynamics as a function of the increased solute concentration primarily due to the serious lacking of an enabling experimental investigation method.

Nuclear magnetic resonance (NMR) spectroscopy, a non-destructive and atomic specific tool, is ideal for such an investigation because it can offer a molecular view of the chemical sites of ions in the solvation structure. ^{13}C and ^{17}O NMR have been attempted to investigate the Li^+ solvation structures in electrolytes related to Li-ion batteries.[27-29] ^{17}O NMR is more attractive due to the large chemical shift range, i.e., a couple of thousands ppm that is a potentially very sensitive probe for investigating the subtle changes of the interaction between an O atom and a Li^+ . However, ^{17}O NMR investigations are challenging because of the extremely low natural abundance (0.037%) of the NMR-active ^{17}O , making it one of the most difficult nuclei to observe by NMR spectroscopy.[30, 31] Most of the ^{17}O NMR in the literatures used isotopic enrichment for enhanced signal to noise ratio (SNR), or took a very long time for signal averaging.[32] But isotope enrichment is often prohibitively expensive, and long-time data acquisition is too time-consuming and is unable to capture the transient changes in the structures, both making the ^{17}O NMR insufficiently practical for most research and limiting its broad application. Bogle et al. employed ^{17}O NMR for the first time as a molecular probe to understand how Li^+ from LiPF_6 interacts with EC and DMC [27], where the resonances corresponding to EC and DMC, each contributing only two well resolved peaks, were well separated from each other over the LiPF_6 concentration studied (a favorable case for NMR study).[27] A solvation structure of Li^+ with the first solvation sheath containing four EC and the 2nd solvation sheath containing six EC molecules in the mixture of EC was proposed based on results obtained by varying the ratio of EC to DMC while keeping the concentration of LiPF_6 constant, i.e., at 1.0 M. Key conclusions from these authors included that a maximum number of six EC molecules can be associated with one Li^+ and there exists fast exchange of EC molecules in the 2nd solvation sheath with bulk EC molecules under the condition of excessive EC molecules; and EC preferentially bonds with Li^+ than DMC

In this work, a highly sensitive ^{17}O NMR technique using a combination of a large-sample-volume (LSV) NMR probe and an ultrahigh magnetic field of 21.1 T was employed to study the solvation structures of LiTFSI in pure and mixed solvents of EC, PC and EMC based on changes in chemical shift

and linewidth. A total of eight resonant ^{17}O NMR peaks were observed on a mixture containing EC, PC and EMC, a case that was much more challenging than previous investigation. To obtain a detailed physical picture on how a Li^+ interacts with EC, PC and EMC, computational modeling of the ^{17}O NMR chemical shifts were used to accurately interpret the experimental results and related the experimental observations to the detailed molecular interaction associated with Li^+ solvation structures.

2. Experimental

2.1. Materials and Sample Preparations

LiTFSI, EC, PC and EMC were purchased from BASF (Florham Park, NJ) and were used as received. All the sample preparations were performed in a MBraun Labmaster Ar-filled glove box (Stratham, NH) with water and O_2 contents less than 1 ppm. A variety of samples were prepared by dissolving LiTFSI in the specified solvents, whose concentrations and compositions are summarized in Table 1.

2.2. NMR Measurements

Since EC is a solid at room temperature, EC was dissolved in dichloromethane- d_2 (CD_2Cl_2) at saturated concentration to obtain the ^{17}O NMR for neat EC. The effect of CD_2Cl_2 will be discussed in the section of computation. All the ^{17}O NMR experiments were performed on a Varian-Agilent 900MHz NMR spectrometer equipped with a homemade 15 mm outer diameter large-sample-volume probe. The details of the probe will be published in a separate paper. The corresponding Larmor frequency is 122.041 MHz. A 25 μs long hard pulse was used. The spectra were collected in 1000 - 30000 scans depending on the linewidth of the peaks, with an acquisition time of 25 ms and a recycle delay time of 0.5s. Peak positions in the ^{17}O NMR spectra were referred to the deuterium oxide (D_2O , 0 ppm) placed externally in the NMR spectrometer. Chemical shifts and linewidth of NMR signals were obtained by fitting lorentzian functions to the experimental spectra using the NUTs program (v.2012, Acorn NMR

Inc., Las Positas, CA, USA). All the NMR measurements were carried out at room temperature, i.e., 20°C.

2.3. Quantum Chemistry Calculations

Computational modeling was carried out using the *Amsterdam Density Functional* (ADF-2013) package.[33] The generalized gradient approximation (GGA) based Becke-Lee-Yang-Parr function[34, 35] with dispersion correction (BLYP-D)[36] was employed for geometry optimization. All the calculations were carried out by using the QZ4P basis set (quad Z, 4 polarization function, all-electron) with the Slater type functional[37] implemented in the ADF program. NMR calculation was performed based on the geometry optimized structures at the same level of the theory and with the same basis set to evaluate the chemical shielding for each atom.

3. Results and Discussions

3.1. ^{17}O NMR Experimental Results

3.1.1. ^{17}O NMR for Solvents

Figure 1a shows the ^{17}O NMR spectra of EC, PC, EMC, and the mixture of EC/PC/EMC (4:1:5 by weight). Excellent signal to noise ratio is obtained, and the peaks of each oxygen atom are clearly observed. There are three oxygen atoms in all these solvent molecules, but only two peaks are observed in the spectrum of EC (Figure 1-a1). The peak at 220.8 ppm can be assigned to carbonyl oxygen atom (Oc) of EC while the 111.9 ppm peak can be assigned to the two ethereal oxygen atoms (Oe) based on the integrated peak intensities, because the two Oe atoms are chemically equivalent in EC and thus have the same chemical shift. In addition, the spectra of PC and EMC both have three peaks for each oxygen atoms (Figure 1-a2,3). The peaks of Oc sit between 210 - 240 ppm and those of Oe are between 90 - 140 ppm (Table 2), and the linewidth range from about 114 to 370 Hz (Table S1). Figure 1-a4 shows the spectrum of mixed solvent composed of EC, PC and EMC, where we can easily distinguish the peaks of each composition. The chemical shifts have only minor changes when they are mixed. The minor changes of

chemical shifts are due to the differences between the pure electrolytes and the mixed electrolytes. In pure electrolyte of PC, or EMC, the intermolecular interaction is between the same types of molecules. While in the mixture of EC, PC and EMC, the intermolecular interaction involves a combination of different molecules.

3.1.2. LiTFSI dissolved in solvents

The spectra of LiTFSI dissolved in PC, EMC and a mixture of them (PC+EMC with 1:5 by weight) at different concentrations are shown in Figure 1b-d. Based on the spectra of PC and EMC in Figure 1a, it can be observed that with the increasing concentration of LiTFSI, the chemical shifts of the Oc in both PC and EMC experience an upfield (with decreasing ppm) displacement gradually, and the line-widths of all peaks increase significantly. The displacements of Oc of PC and EMC are up to about 30 ppm as shown in Figure 2 (expressed as positive displacements), and the line-widths of all peaks grow more than 10 times at the highest concentration (Table S1). These results are strong evidence that LiTFSI molecules interact with the solvent molecules, especially at the site of Oc. We note that the chemical shifts of Oe have downfield displacements (with increased ppm), expressed as negative displacements in Figure 2, but these changes are much less than those of Oc that are upfield shifted significantly. Whether PC or EC, the shifts of Oc (~25-30 ppm) are greater than those of Oe (~5-10 ppm), strongly indicating the direct interaction between Li^+ and Oc rather than Oe. Those upfield displacements are due to the shielding effect of Li^+ on the lone pair electron density, while the downfield displacements are attributable to an increased deshielding effect.[27] Comparing PC and EMC, the displacements of them are about the same when they are separately, but in the system of LiTFSI dissolved in the mixture of PC and EMC, shifts of Oc in PC slightly increase at the concentration of 0.25 M and 0.85 M, while shifts of Oc in EMC are less at the same concentrations. This result suggests that Li^+ ion preferably interact with PC.

Figure 1e shows the spectra acquired on LiTFSI in solvents composed of EC, PC and EMC (4:1:5 by weight). And the fitting examples of these spectral series are shown in Figure S1. The trends of chemical

shifts and linewidth are similar to those of Figure 1b-d. With the increase of LiTFSI concentration, the Oc of all three solvent molecules shifts to upfield while the Oe shifts to downfield, and line-widths of all peaks have significant increase and the results are summarized in Table 2 and Figure 3a. The results are similar to those found in the case of LiTFSI/(PC+EMC) (see above discussion). It is found that the displacements of EC and PC are similar and somewhat greater than those of EMC (See Table S2). Compared with the system of LiTFSI/(PC+EMC), the Oc of PC and EMC have smaller displacements than those at 0.25 M and 0.85 M (Figure 3a and Figure 2). Further, although the weight ratio of PC/(EC+EMC) (1:9) in this solvent mixture is smaller than that in the mixture of PC and EMC (PC/EMC=1:5), the Oc of PC in Figure 3a (Table S2) has slightly smaller displacements than those in the system of LiTFSI/(PC+EMC). It means that with the addition of EC, PC no longer dominates the primary solvation shell of Li^+ ion. In contrast, EC seems to be more preferable for the interaction with Li^+ ion than PC.

The sulfonyl oxygen (Os) peak of TFSI⁻ also shifts to the upfield by up to 8.5 ppm in the case of LiTFSI/PC when the concentration increases as shown in Figure 4 and Table S3. This upfield shift is suggested to be caused by ion-dipole interaction between Li^+ ion and the Os of TFSI⁻ ion.[18, 38] The results in Figure 4 indicate that the probability of interaction with Li^+ is enhanced with the increase of LiTFSI concentration. The higher ratio of LiTFSI to solvent molecules, the more probability of coordination between Li^+ and TFSI⁻. On the other hand, with the increase of carbonates, lithium ions preferentially coordinate to the Oc rather than to the Os.[39]

3.2. Computational modeling of ^{17}O NMR chemical shifts

3.2.1. Selecting ^{17}O chemical shift reference

The main goal of the computational studies of the NMR chemical shifts is to gain further insight in the structures of the solvation shell based on the NMR experimental results. Although bulk H_2O was used as the experimental reference standard, there are effects of strong hydrogen bonding among the water

molecules, which is difficult to accurately account for by the computational theory. And there are no hydrogen bonding in real LiTFSI/carbonate electrolyte systems. Therefore, in our computational study we use non-hydrogen-bonding dimethyl sulfoxide (DMSO) as the reference standard to validate our calculations. Figure S2 shows the structure of the clusters of (DMSO)_n (n=1~6, 8). The chemical shifts of ¹⁷O move to upfield when the number of molecules increases and tends to converge at -232 ppm (Table S4). It is known from literature reports that the ¹⁷O chemical shift of neat DMSO is up to ~20 ppm when referenced to H₂O.[40, 41] Therefore, the following equation is used to convert the calculated absolute shielding to the experimental chemical shift values, $\delta_{\text{obs}} = \delta_{\text{calculated}} - (-232) + 20 \text{ ppm} = \delta_{\text{calculated}} + 252 \text{ ppm}$.

3.2.2. Predicting ¹⁷O chemical shifts in neat EC, PC and EMC

¹⁷O chemical shifts associated with neat EC, PC and EMC are calculated first in gas phase, i.e., using a single molecule. Figure 5a shows the geometry optimized structures of EC, PC and EMC. The comparison of chemical shifts between the calculated and the experimental results are shown in Table S5 using DMSO as the reference by adding 252 ppm to the calculated absolute shift. It is obvious that the calculated results match the experiment results well. We note that there are still some differences between the experiments and the calculations. This may be due to intermolecular interaction in liquid phase.[42, 43] To simulate the possible intermolecular interaction, the PC and EMC are treated as dimer or trimer while one EC molecule is surrounded by one or several CD₂Cl₂ molecules as EC is a solid at room temperature and CD₂Cl₂ is, in fact, used to dissolve EC and acquire the spectrum. The calculated ¹⁷O chemical shifts are summarized in Table S6. Clearly, the differences between the calculated and the experimental values are reduced in the case of EC by using one CD₂Cl₂ interacting with the Oc of EC. However, no overall improvement is found for PC, where Oc shift is improved at the cost of two Oe oxygen positions. The ¹⁷O chemical shifts in EMC are almost independent of cluster size used.

3.2.3. Predicting ^{17}O chemical shifts in systems of Li^+ (low concentration of LiTFSI) interacting with neat PC, EC or EMC

Our experimental results have clearly shown that Li^+ ion coordinates preferentially with Oc rather than Oe. The next task is to establish the bonding direction that Li^+ is interacting with Oc. To reach this objective, chemical shift calculations are carried out using a single pair of Li^+ -PC of different initial configurations to illustrate the concept. As shown in Table S7, one Li^+ ion is placed close to each oxygen atom of a PC molecule respectively. After geometric optimization, the structures are converged at three different configurations corresponding to a global minimum (a) and local minima (b, c) in terms of bonding energy. For each complex, the chemical shift of Oc decreases (up field displacement) while those of Oe increase (down field displacement) compared with the corresponding values from isolated PC. But the displacements of the two Oe sites in (b) and (c) are quite different. Comparing with the experimental results (Table 2), only the configuration (a) is reasonable, where the Oe oxygen atoms have similar displacements of chemical shifts both experimentally and theoretically. Furthermore, the bonding energy associated with structure (a) is the lowest. The geometry optimized structure in (a) supports previous report that the Li-Oc distance in first shell is about $2\text{\AA}$ while the distance of Li-Oe is about $4\text{\AA}$ obtained using the so-called radial distribution functions (RDF) approach,[15, 21, 44, 45] but is now justified by the trend of chemical displacement observed experimentally.

Although the directions of the displacements of the calculated ^{17}O chemical shifts associated with a single pair of Li-Oc (PC) agree with experimental results, the magnitudes of displacements are much larger than the experimental observed values (comparing with Table 2). One possible reason for this discrepancy would be that one Li^+ interacts with multiple Oc rather than a single one as previously proposed.[46-49] Figure 5b-e show the structures of one Li^+ ion interacts with 1 to 4 Oc using PC as an example to illustrate the concept while the results obtained from $\text{Li}^+(\text{EC})_n$ and $\text{Li}^+(\text{EMC})_n$ are simply listed together with the case of $\text{Li}^+(\text{PC})_n$, where $n=1,2,3,4$. Table 3, Table S8 and Figure 3b summarize the calculated chemical shifts of the complexes. Comparing the results of experiment and calculation in Figure 3, it is

clear that the chemical shifts of Oc increase while those of Oe decrease with the ratio of Li⁺ ion to solvent molecules increasing, indicating the theoretical calculations correctly predict the trend of the experimental results. Furthermore, it is known from Table 2 and Table 3, the calculated shifts are getting closer to the experimental values with the increase of solvation number. The experimental values are basically within the range of the calculated values between ratios of Li⁺/solvent molecules of 0 (zero Li⁺) and 0.25 (Li⁺:PC=1:4). In previous report where MD simulation and DFT calculation were carried out, the fifth EC molecule has been suggested not in the first solvation shell of Li⁺ ion.[46-48] So it can be deduced that each Li⁺ ion should be coordinated with four Oc, donated by EC, PC or EMC, to form a first solvation shell. The solvent molecules in the solvation shell are undergoing fast molecular exchange with the molecules in the bulk solvent. As a result, averaged ¹⁷O chemical shifts are observed experimentally. In fact this averaged chemical shifts can be accurately predicted. In the following, we will use the system of LiTFSI/PC as an example by employing an approach similar to that used by Bogle et al..[27]

The Oc chemical shift of bulk pure PC is 220 ppm according to experiment (Table 2), and that of coordinated PC is 191.8 ppm (experimental value at saturated LiTFSI concentration in PC) or 184.8 ppm (theoretical shifts when four PC are in the first solvation sphere of each Li⁺). Under the assumption of fast molecular exchange where the exchange rate between the Li⁺ coordinated PC molecules and the PC molecules in bulk PC solvent is much fast than the difference of the peak centers in unit of Hz, i.e., $\gg (220 - 191.8) \times 122.041 = 3442$ Hz (experiments) or $\gg (220 - 184.8) \times 122.041 = 4296$ Hz (theory), a single oxygen peak for each oxygen atom in PC will be observed. The new peak center can be predicted by simply using the weighted average of the two original peaks in accordance with the following equation.

$$V_{\text{new}} = (a / (a + b)) \times V_A + (b / (a + b)) \times V_B, \quad [1]$$

where $V_A = 220$ ppm, $V_B = 191.8$ ppm (from experiment) or 184.8 ppm (from theory), “a” is the molar ratio of PC molecules that are in the bulk PC solvent while “b” is the molar ratio of PC molecules that are

in the first coordinate sphere with Li^+ . For the case of LiTFSI/PC with LiTFSI concentration of 0.25M, the molar ratio of LiTFSI/PC, or Li^+/PC , is 1/45.6 (Table 1) as determined experimentally (i.e., using the known weight of each material that was used to make the electrolyte mixture and the resulting in electrolyte volume). Thus, among each 45.6 PC molecules there are 4 PC molecules coordinated with Li^+ while there are 41.6 PC molecules are in the bulk, giving rise to $a=41.6/45.6$ and $b=4/45.6$. Based on Eq. [1], the predicted peak center under fast molecular exchange is 217.5 ppm (using experimental shifts) or 216.9 ppm (using theoretical shifts). Likewise for the case of LiTFSI/PC with LiTFSI concentration of 0.85 M, the molar ratio of LiTFSI/PC, or Li^+/PC , is 1/12.1 as determined experimentally. A 210.7 ppm (using experimental shifts) or 208.4 ppm (using theoretical shifts) are predicted. The predicted values are in excellent agreement with experimental results of 217.4 ppm for 0.25 M LiTFSI in PC and 210.5 ppm for 0.85 M LiTFSI in PC, respectively (see Table 2). These results unambiguously approve the concept that the solvent molecules in the solvation sphere of Li^+ are undergoing fast molecular exchange with the solvent molecules in the bulk solvent in the case of excessive solvent molecules. Under the excessive PC solvent, one Li^+ is solvated by four PC molecules, suggesting that the Li^+ and TFSI $^-$ are disassociated and have their respective solvation spheres. This suggestion is supported strongly by the experimental results summarized in Figure 4 and Table S3, where it is clearly shown that regardless of the solvent systems used, up to a LiTFSI concentration of about 0.85 M the changes of ^{17}O chemical shift of Os in TFSI $^-$ is small.

3.2.4. The role of TFSI

Figure 6a shows the structure of TFSI $^-$ anion. It is known from RDF studies that in electrolytes a Li^+ ion is coordinated by the Os rather than by the most electronegative nitrogen atom of the TFSI $^-$ anion,[18, 38] and the free energies of Li^+ binding to Os in TFSI $^-$ and Oc in common electrolytes are comparable in electrolyte solutions.[15] Considering the ratio of Li^+ ion to TFSI $^-$ ion of 1:1, one PC molecule may be replaced with one TFSI $^-$ ion (Figure 6b). The structures of LiTFSI(EC) $_3$ and LiTFSI(EMC) $_3$, not shown in this Figure, and their ^{17}O chemical shifts are also calculated. Besides, a model dedicated to Li^+

interacting with TFSI-EC-PC-EMC is shown in Figure 6c. After geometric optimization, the solvent molecules in both Figure 6c and 6d seem to move close to TFSI⁻ anion that can be regarded as that Li⁺ and TFSI⁻ are sharing solvent shell as contact ion-pair. The calculated chemical shifts are summarized in Table 4, Table S8 and Table S9. We note that these values of δ_{O} are close to those of Li⁺(solvent)₄ (i.e., with Li⁺/(solvent molecules) ratio of 0.25) in Table 3, indicating that the effect of replacing one solvent molecule with one TFSI⁻ is small on the chemical shifts of δ_{O} sites of solvent EC, PC or EMC. Therefore, it is not possible to tell whether the Li⁺ and TFSI⁻ in LiTFSI is dissociated in electrolytes and form their own solvation sphere based only on the δ_{O} site chemical shift changes. In contrast to δ_{O} , the predicted ¹⁷O chemical shift of δ_{S} sites in TFSI changes significantly by 5 ppm or more if one TFSI⁻ is replaced into the Li⁺(solvent)₄ structures (Table 4, Table S9). Experimentally, we observe only small changes in ¹⁷O chemical shifts of the δ_{S} sites up to a LiTFSI concentration of about 0.85 M but significant upfield shift of the δ_{S} peak associated with TFSI⁻ are indeed observed at, or at close to saturated TFSI⁻ concentration (see Table S3). These combined experimental and theoretical results approve that under the condition of excessive electrolytes (i.e., low concentration of LiTFSI, i.e., < 0.85 M), Li⁺ and TFSI⁻ in LiTFSI are dissociated in electrolytes and form their own solvation spheres. The small upfield ¹⁷O shifts of δ_{S} at low LiTFSI concentration can be explained by a model where one solvent molecule bonded to Li⁺ is replaced by one TFSI⁻ which is under fast exchange with the solvent solvated TFSI⁻ anion, resulting in an averaged ¹⁷O chemical shifts that is shifted slightly upfield. Between the low and saturated LiTFSI concentration, the ratio of TFSI⁻ anion participating in bonding to Li⁺ increases and thus more upfield shifts are observed. The concept of exchange is supported by previous MD simulations that the residence time of δ_{S} in the Li⁺ first solvation shell is less than 1 ns.[15] Our results (both experimental and computational modeling of ¹⁷O chemical shifts combined with the concept of molecular exchange) justify previous proposal based on the results obtained from phase diagrams prepared from differential scanning calorimeter (DSC) heating curves,[50] and pulse-gradient spin-echo (PGSE) NMR,[51] that LiTFSI is one of the most highly dissociated Li salt. It can be deduced that most of LiTFSI ion-pairs are fully dissociated at low concentrations, e.g. 0.05 to 0.25 M, in our systems, and

the chemical shifts of Os should be similar to that of isolated TFSI⁻ anion. Therefore, we can re-reference the ¹⁷O chemical shift of Os of isolated TFSI⁻ anion to the experimental value of 162.1 ppm at low concentration, i.e., the 0.25 M LiTFSI/PC result from Table S3 so that the effect of Os bonded to Li⁺ can be more easily visualized theoretically. As shown in Table 4, the referenced Os chemical shifts of TFSI⁻ anion coordinated with Li⁺ ion are 156.9~158.2 ppm, which are in agreement with the experimental results.

In saturated electrolyte solutions of LiTFSI/PC, LiTFSI/EMC, and LiTFSI/(PC+EMC), the concentration of Li⁺ ion is high and the ratio of solvent molecules in the bulk solvent phase declines. From experimental section, it is known that the molar ratios are [LiTFSI]:[PC] = 1:2 in LiTFSI/PC at 3.2 M, [LiTFSI]:[EMC] = 1:1.6 in LiTFSI/EMC at 3.2 M and [LiTFSI]:[PC]:[EMC] = 1:0.3:1.5 in LiTFSI/(PC+EMC) at 3.1 M. This leads to a condition where the solvent molecules are not enough to form 4-coordination for every Li⁺ ion. In this case, a different structure, (LiTFSI)₂(PC)₄, have been previously proposed.[15] The geometry optimized structure of (LiTFSI)₂(PC)₄ is shown in Figure 6d, where each Li⁺ ion is still coordinated by 4 oxygen atoms albeit with two of which are donated by TFSI⁻ anions, i.e., each TFSI⁻ donates two Os. Thus, only two PC molecules are needed for each Li⁺ ion, which is in excellent agreement with the ratio in LiTFSI/PC at saturation of 3.2 M. The predicted ¹⁷O chemical shift of Os in (LiTFSI)₂(PC)₄ is 155.8 ppm (Table 4), in excellent agreement with the experimental value of 153.6 ppm at LiTFSI saturation of 3.2 M in PC (Table S3). This result validates the existence of (LiTFSI)₂(PC)₄ at saturation. Since no extra PC to form a bulk PC phase in the solution, the molecular motion is restricted, resulting in significantly increased ¹⁷O linewidth observed for both Oc and Os sites experimentally when the LiTFSI concentration is approaching or at saturation. Likewise, one EMC molecule may coordinated with two Li⁺ ions as shown in Figure 6e, i.e., forming the complex of (LiTFSI)₂(EMC)₃, whose theoretical molar ratio of LiTFSI to EMC is 1:1.5 that is again in excellent agreement with the experimental molar concentration ratio of LiTFSI to EMC, i.e., 1:1.6. Again, the predicted ¹⁷O chemical shift of Os, 155.8 ppm (Table 4), is in excellent agreement with experimental

value of 154.4 ppm (Table S3) at LiTFSI saturation concentration. Thus, it can be concluded that at the saturated solutions of LiTFSI/EMC, $(\text{LiTFSI})_2(\text{EMC})_3$ is the main structure.

4. Conclusions

In this work, natural abundance ^{17}O NMR and computational modeling of ^{17}O NMR chemical shifts were used to study the solvation mechanism of LiTFSI dissolved in solvents of EC, PC, and EMC, including mixtures of these solvents. ^{17}O NMR spectra on various systems at LiTFSI concentrations varied from zero up to saturation were acquired with high signal to noise ratio by taking advantages of ultra-high field and a large sample volume probe. The results clearly indicate that the Li^+ ion is coordinated by 4 oxygen atoms donated by solvent molecules of EC, PC, EMC and TFSI $^-$ anions to form a first solvation shell. The solvent molecules in the solvation shell quickly exchange with bulk solvent under the condition of excessive solvent molecules. The experimentally observed ^{17}O chemical shifts is a weighted average between free and solvation shell-containing solvent molecules. The observed ^{17}O chemical shifts can be quantitatively interpreted based on the principle of fast exchange and the molar ratios of Li^+ and solvent. At low LiTFSI concentrations, e.g. 0.05M and 0.25M, the Li^+ ion is dissociated with TFSI $^-$ and fully solvated by solvent, forming its own respective solvation spheres, i.e., with $\text{Li}^+(\text{PC})_4$ and $\text{Li}^+(\text{EMC})_4$ as the solvated structures in pure PC and pure EMC, respectively. At high LiTFSI concentrations, in particular at saturated concentrations, $(\text{LiTFSI})_2(\text{PC})_4$ for LiTFSI in PC, and $(\text{LiTFSI})_2(\text{EMC})_3$ for LiTFSI in EMC are the preferred structures. Because all of the solvent molecules are bonded with Li^+ cations at saturation and molecular motion is severely hindered, resulting in dramatically increased ^{17}O linewidth. For LiTFSI concentration between low and saturation, $(\text{LiTFSI})(\text{PC})_3$ for LiTFSI in PC, and $(\text{LiTFSI})(\text{EMC})_3$ for LiTFSI in EMC are the preferred structures. There are quick exchanges between free and solvation shell-containing TFSI $^-$ anions in addition to quick exchanges of free and solvation shell-containing solvent molecules, resulting in an average ^{17}O chemical shift values for the O sites. For an electrolyte system containing LiTFSI dissolved in EC, PC and EMC, the fundamentals are similar to those in a pure solvent except EC. Solvent molecules and TFSI $^-$ anion will compete for the opportunity of bonding with Li^+

cation, resulting in one Li^+ associated with the Oc and Os in the first solvation shell of a composite of EC, PC, EMC and TFSI⁻ depending on the Li^+ concentration.

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Table 1. The molar ratio of each solvent with respect to LiTFSI in corresponding electrolyte mixtures.

Systems	Concentration/M	EC ^a	PC ^a	EMC ^a
LiTFSI/PC	0.25		45.6	
	0.85		12.1	
	1.6		5.7	
	3.2		2	
LiTFSI/EMC	0.25			37.0
	0.85			10.0
	1.4			5.5
	3.2			1.6
LiTFSI/(PC+EMC)	0.25		6.5	31.7
	0.85		1.7	8.5
	1.5		0.9	4.3
	3.1		0.3	1.5
LiTFSI/(EC+PC+EMC)	0.05	103.0	22.2	109.0
	0.25	20.0	4.3	21.2
	0.85	5.5	1.2	5.8
	1.7	2.3	0.5	2.5
	2.5	1.3	0.3	1.4

^a The relative molar ratio of solvent molecules when the concentration of LiTFSI is normalized to 1 M.

Table 2. The experimentally obtained ^{17}O chemical shifts.

System/Concentration of LiTFSI(M)	EC			PC			EMC		
	O1	O2	O3	O1	O2	O3	O1	O2	O3
EC in CD_2Cl_2	220.8	111.9	111.9						
Pure PC				220.0	138.6	114.8			
Pure EMC							241.3	121.8	92.9
EC+PC+EMC ^a	218.7	110.6	110.6	219.6	138.0	114.1	239.4	122.2	93.5
LiTFSI/PC	0.25			217.4	139.2	115.4			
	0.85			210.5	141.1	117.4			
	1.6			202.3	144.9	120.1			
	3.2			191.8	147.0	126.9			
	0.25						238.5	122.2	93.3
LiTFSI/EMC	0.85						231.4	123.5	94.8
	1.4						224.1	124.6	95.9
	3.2						212.4	128.4	100.9
	0.25			216.5	139.1	115.2	238.7	122.6	93.8
LiTFSI/PC +EMC ^b	0.85			206.0	141.4	117.4	231.5	123.6	94.9
	1.5			199.3	144.1	120.5	223.3	125.4	96.9
	3.1			189.6	146.9	124.3	211.1	128.4	100.2
	0.05	218.2	110.9	219.2	138.4	114.3	239.2	122.5	93.7
LiTFSI/EC +PC+EMC ^a	0.25	215.5	111.5	216.5	139.0	114.9	237.5	122.7	94.0
	0.85	208.8	113.3	210.1	140.8	116.5	231.8	123.7	95.2
	1.7	199.2	115.4	201.3	142.8	119.3	221.0	125.4	97.6
	2.5	195.4	117.4	196.8	144.4	121.4	217.6	127.7	99.0

^a Mixed solvent is composed of EC, PC and EMC (4:1:5 by weight).^b Mixed solvent is composed of PC and EMC (1:5 by weight).

Table 3. Predicted ^{17}O chemical shifts of $\text{Li}^+(\text{EC})_n$, $\text{Li}^+(\text{PC})_n$ and $\text{Li}^+(\text{EMC})_n$.^a

Proportion of Li ion to solvent molecule	EC			PC			EMC		
	O1	O2	O3	O1	O2	O3	O1	O2	O3
0	223	103.5	103.5	228	138.5	118.5	240.1	128.8	97.1
0.25	185.7	121.5	121.5	184.8	151.1	132.0	198.5	142	111.5
0.33	168.3	125.8	125.8	170.7	154.5	134	190.1	143.1	112.5
0.50	147.6	132.2	132.2	146.8	164.7	143.8	163.1	148.3	115.5
1.00	133.5	139.3	139.3	133.6	171.8	150.2	152.2	152.9	120.6

^a DMSO is used as the reference by adding 252 ppm to the calculated absolute shift.

Table 4. Predicted double-bond oxygen (i.e., the Oc and Os) ^{17}O chemical shifts of Li^+ -TFSI $^-$ ion-pair with different solvent bonding structures. ^a

System	EC	PC	EMC	TFSI ^b	TFSI ^c
TFSI (gas phase)				172.3	162.1
LiTFSI(EC) ₃	186.4			167.6	157.4
LiTFSI(PC) ₃		185.2		167.9	157.7
LiTFSI(EMC) ₃			200.0	167.1	156.9
LiTFSI-EC-PC-EMC	183.2	182.4	203.0	168.4	158.2
(LiTFSI) ₂ (EC) ₄	184.6			162.3	152.1
(LiTFSI) ₂ (PC) ₄		192.8		166.0	155.8
(LiTFSI) ₂ (EMC) ₃			197.5	166.0	155.8

^a DMSO is used as the reference by adding 252 ppm to the calculated absolute shift.

^b The value of TFSI is the average of the four Os.

^c Re-reference the Os chemical shift of the 0.25Mole/L LiTFSI/PC to the experimental value of 162.1 ppm by subtracting 10.2 ppm from the predicted values for all other cases in the Table.

Figure captions

Chart 1. The labeling of the oxygen sites and the formula of EC, PC, EMC and TFSI⁻

Figure 1. Natural abundance ^{17}O NMR spectra of: (a) The solvents, (a1) EC dissolved in CD_2Cl_2 , (a2) Pure PC, (a3) Pure EMC, (a4) Mixture of EC, PC and EMC (4:1:5 by weight); (b) LiTFSI in PC, (c) LiTFSI in EMC, (d) LiTFSI in mixture of PC and EMC (1:5 by weight), (e) LiTFSI in mixture of EC, PC and EMC (4:1:5 by weight). Concentration: (b1~b4) 0.25M, 0.85M, 1.6M and 3.2M (saturated); (c1~c4) 0.25M, 0.85M, 1.4M and 3.1M (saturated); (d1~d4) 0.25M, 0.85M, 1.5M and 3.2M (saturated); (e1~e5) 0.05M, 0.25M, 0.85M, 1.70M, 2.5M.

Figure 2. Displacement of ^{17}O chemical shifts. (a) LiTFSI dissolved in pure PC and pure EMC respectively; (b) LiTFSI dissolved in the mixture of PC + EMC with PC/EMC=1:5.

Figure 3. Displacements of ^{17}O chemical shifts according to (a) the experimental results obtained from LiTFSI in mixture of EC+PC+EMC with EC/PC/EMC of 4:1:5 by weight; (b) predicted (theoretical) displacements of ^{17}O chemical shifts of structures $\text{Li}(\text{Solvents})_n$ ($n=1, 2, 3, 4$).

Figure 4. Experimentally obtained ^{17}O chemical shifts of Os in pure or mixed solvents with different LiTFSI concentrations according to Table S3.

Figure 5. Geometry optimized structures. (a) EC, PC, EMC. (b-e) Li^+ ion bonded with 1~4 PC.

Figure 6. Geometry optimized structures of Li^+ solvation shell by including TFSI⁻. (a) TFSI⁻. (b) Li^+ ion bonded with TFSI⁻ ion and 3 PC. (c) Li^+ bonded with EC, PC, EMC and TFSI⁻. (d) $(\text{LiTFSI})_2(\text{PC})_4$. (e) $(\text{LiTFSI})_2(\text{EMC})_3$.

EC

PC

EMC

TFSI⁻

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6