

2016

Spectroscopic Measurements of Ionic Association in Common Lithium Salts and Carbonate Electrolytes

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Recommended Citation

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SPECTROSCOPIC MEASUREMENTS OF IONIC ASSOCIATION IN COMMON LITHIUM
SALTS AND CARBONATE ELECTROLYTES

BY

NAVID CHAPMAN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIRMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

IN

CHEMISTRY

UNIVERSITY OF RHODE ISLAND

2016

MASTER OF SCIENCE IN CHEMISTRY THESIS
OF
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2016

Abstract

FTIR and NMR spectroscopy were used to investigate the structure and composition of lithium ion solvation spheres of single salt electrolyte solutions composed of common lithium salts (LiTFSI, LiPF₆, LiBF₄, and LiClO₄) dissolved in aprotic polar linear and cyclic carbonate solvents (propylene carbonate (PC), dimethyl carbonate (DMC)). The coordination of the carbonyl oxygen of the solvents to the lithium ion is observed by FTIR spectroscopy. Determination of relative percent coordination of PC and DMC was used to calculate solvent coordination numbers in a range from 2 to 7. Solvent coordination was also monitored with ¹³C NMR spectroscopy and agreement was found when comparing the two spectroscopic methods. Solvent coordination is dependent upon the magnitude of salt dissociation. LiTFSI, LiPF₆, and LiClO₄ dissociated to approximately the same degree, while LiBF₄ had significantly less dissociation. Dissociation trends between salts were approximate under all solvent systems. The primary solvation sphere was determined to form contact ion pairs at low solvent to salt ratios (up to 4:1) and solvent separated ion pairs in dilute solutions up to (30:1). In dilute solutions, PC had preference over DMC for preferential solvation as expected by the magnitude of relative permittivity. This investigation was conducted in order to develop a fundamental understanding about the solution structure and aid as a tool for the ionic association evaluation of commonly used LIB electrolytes.

ACKNOWLEDGMENTS

I would like to express my gratitude to Professor Brett L. Lucht for advising me throughout my graduate school career. I am grateful to have Professor Lucht as well as Professor Bill Euler, Professor, Sze Yang, Professor David Heskett, and Professor Arijit Bose to have taken the time out of their busy schedules to review my thesis. I am indebted to all the brilliant minds of the Lucht lab for providing constructive feedback and helping maintain our instrumentation. This work is an extension of the work by Dr. Daniel Seo and I appreciate his years of research that made this study possible. A very special thanks for Dr. Taeho Yoon and Dr. Cao Nguyen for their invaluable input. Thank you to Partha Datta, Oleg Kazakov, and Craig Hessler for sitting in on a mock-review committee for my defense preparation. I would like to also acknowledge the University of Rhode Island Chemistry department for providing the resources required for this work and providing me with a Teaching Assistantship every semester that funded my education. This material is based upon work supported by the U.S. Department of Energy Office of Basic Energy Sciences EPSCoR Implementation award (DE-SC0007074).

Finally, my deepest and most sincere appreciation goes to my exceptionally clever, beautiful, and caring wife Ming for believing in me throughout my graduate school career.

PREFACE

This thesis is written in manuscript format and is prepared for submission to the Journal of Physical Chemistry C with authors Navid Chapman, Taeho Yoon, Cao Cuong Nguyen, and Brett L. Lucht.

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MANUSCRIPT – I

Prepared for submission to Journal of Physical Chemistry C

**Spectroscopic Measurements of Ionic Association in Common Lithium Salts
and Carbonate Electrolytes**

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CHAPTER 1

INTRODUCTION

Lithium Ion Batteries (LIBs) are of high interest in energy research due to the increased global need for energy storage sources for portable devices¹⁻⁴. There is a lack of understanding about ion solvate structures of electrolytes. Further investigation is important because ion-solvent structure, salt concentration, and temperature, to a lesser extent, directly dictate the physical properties of electrolytes and the performance in electrochemical systems⁵. These fundamental physicochemical properties affect many aspects of performance such as voltage-current curves, electrochemical stability window, working temperature range, hydrolytic stability, and ionic conductivity, which is the overall result of effects from solvent migration and solvation structure^{1,3,4,6-12}. Determining the solvation structure, and in turn preferential binding of one solvent over another, is also of interest because it dictates which solvent molecules would be preferentially reduced on the anode surface as an interfacial film dubbed the solid electrolyte interface (SEI). Understanding how co-solvents interact with lithium salts will allow for custom engineered electrochemical systems with optimal ionic mobility and SEI resistance¹³.

Binary mixtures of cyclic and linear carbonates were first implemented by Tarascon and Guyomard in order to balance the cyclic carbonates that possessed high permittivity, but high viscosity with linear carbonates that possessed low

viscosity, yet low permittivity¹⁴. Binary and ternary solvent mixtures are presently commonplace in electrolyte solutions, yet there is a lack of research in understanding the cooperative effects of these mixtures in relation to single solvent systems. Previous understandings suggest that solvent relative permittivity dictates solvation ability. Using LiPF_6 as a salt, Seo et al. previously examined cation-solvent coordination via FTIR and NMR spectroscopy⁹. This study expands on Seo's work by examining solvation and ion pairing with several different salts. Spectroscopic instrumentation like FTIR, Raman, NMR can be used to indirectly observe solvent coordination by detecting changes in the local electronic environment that surrounds the solvation interactions of electrolyte components. Coordination of the solvent with the cation and the coordination of the solvent with the anion both allow for quantitative analysis of the magnitude of solvent coordination.

In this research, FTIR and NMR spectroscopy were used to investigate the molecular cation solvent interactions resulting from lithium salts dissolved in carbonate solvents. Four intermediately associated lithium salts (LiTFSI , LiPF_6 , LiBF_4 , LiClO_4) and two similar, but different types of commonly used carbonate solvents (Propylene carbonate (PC) and dimethyl carbonate (DMC)) were selected for this study¹⁵. The results suggest that the relative permittivity of the solvent is not as important in dictating the primary solvation sphere, that additional solvation effects along with salt dissociation play more significant roles than previously thought, and that solvation structure is a complicated system composed of many factors and cannot be easily defined.

EXPERIMENTAL SECTION

PC was used as-received (MP Biomedicals). DMC was used as-received (Sigma-Aldrich, anhydrous). LiTFSI, LiPF₆, LiBF₄, and LiClO₄ were also used as-received (Sigma-Aldrich). The four lithium salts (LiTFSI, LiPF₆, LiBF₄, LiClO₄) were chosen because they meet the minimal requirements for a lithium salt for usage in lithium ion batteries. These requirements are the ability to dissolve and dissociate in non-aqueous polar aprotic electrolyte solvents, have high ionic mobility, be non-reactive with electrolyte solvents, and relative stability against thermally induced reactions^{3,16,17}. These four salts possess a balance of these requirements and dissociate relatively intermediately in relation to the full scale of lithium salts^{5,18}. The solvent-to-salt ratios (30:1 to 4:1) have been selected to incorporate a full range of salt concentrations with the conventional concentration of ~1M in the middle³. Solutions were prepared in an airfree environment and analyzed shortly after creation at room temperature to minimize contamination of moisture, which is known to react with the dissociated anions and catalyze parasitic degradation reactions, and thermal effects which can occur at high and low temperatures^{3,19}. Constant temperature was maintained because temperature has a small effect on ionic association, but at the same time, minimal in comparison with the effects of salt concentration^{5,20}. These two solvents related in many properties such as both being aprotic polar solvents liquid at room temperature, low toxicity, and large lithium ion solubility, chemical and electrical stability, but they are also contrasting in a few properties; the

magnitude of ϵ is ~ 8 times higher for PC than it is for DMC, thus a large preferential solvation might be expected for PC.

Samples were prepared in an inert atmosphere (N_2) glovebox (<1 ppm of H_2O) by adding the appropriate amount of each solvent to the salts in the vials and stirring until homogeneous solutions were obtained.

Fourier transform infrared (FTIR) measurements were conducted on a Bruker FT-IR Tensor 27 spectrometer fitted with a PIKE MIRacle germanium-crystal ATR accessory. The spectra were acquired in the attenuated total reflection (ATR) mode with 4 cm^{-1} resolution with 128 total scans. All FTIR spectra were processed by OPUS software and deconvoluted with the combination of Gaussian and Lorentzian fitting function by SigmaPlot 11 software. To ensure confidence in the deconvolution, constraints of a consistent Gaussian to Lorentzian ratio was maintained on all curves in a single spectrum as well as maintaining the same full width half maximum ratio peak ratio for each functional group. The resulting peak areas were found by integrating the proposed line-fits with Mathematica 10 software.

^{13}C NMR analyses were conducted on a Bruker Avance III 300 MHz NMR Spectrometer. Deuterated DMSO was sealed in a capillary tube and placed in an NMR tube with the solution samples. All NMR spectra were referenced to d_6 -DMSO.

RESULTS AND DISCUSSION

FTIR Spectroscopy investigations on coordination. In order to develop a fundamental understanding about the solution structure and ionic association of commonly used LIB electrolytes, FTIR spectra were acquired for solutions of aprotic polar cyclic and linear carbonate solvents (PC and DMC respectively) with common lithium salts (LiTFSI, LiPF₆, LiBF₄, and LiClO₄) dissolved in them at varied solvent-to-salt ratios (30:1, 25:1, 20:1, 15:1, 10:1, 8:1, 7:1, 6:1, 5:1, and 4:1) to probe the cation inner solvation structure at different electrolyte compositions and proportions.

As seen in figure 1, Carbonate solvents possess a strong distinctive IR absorption at approximately 1700-1850 cm⁻¹ due a carbonyl band, C=O, stretching vibration. Figure 1 shows the change in the IR spectra of PC with various concentrations of dissolved salts. Upon introduction of a lithium salt to the solvent solution, a second absorption appears in this region. The second absorption results from coordination of the solvent molecule to the primary solvation sphere of the lithium cation. Coordination of the carbonyl oxygen with the lithium cation affects the local electronic environment which is manifested in an observable change in the stretching frequency of the carbon-oxygen double bond and can be observed as a shift of the absorption to lower wavelength. Coordination of the lithium cation with the electronegative carbonyl oxygen results in a decrease in the electron density of the carbonyl group, thus also a decrease in the force constant of the C=O stretch, which is observed here as a decrease of the carbonyl band absorption wavelength.^{8,9,12,21} The FT-IR spectrum

of pure PC solvent has an absorption from the carbonyl band 1805 cm^{-1} and a fermi resonance at 1790 cm^{-1} . This coordination to the lithium cation results in a shift of the carbonyl stretching band and the corresponding fermi resonance to a lower wavelength, corresponding to a higher stretching frequency, which can be observed at 1772 cm^{-1} and 1752 cm^{-1} respectively.⁹ The ratio of uncoordinated to coordinated peak intensity is directly correlated to the ratio of solvent-to-salt molecules. As the quantity of salt in solution is increased, a decrease in the peaks at 1805 cm^{-1} and 1790 cm^{-1} is observed and accompanied by the appearance of peaks at 1772 cm^{-1} and 1752 cm^{-1} . Likewise, the same effects are observed when salts are added to DMC, as seen in figure 2, where the absorption of the uncoordinated C=O stretch located at 1755 cm^{-1} decreases with increasing salt concentration and a coordinated absorption peak appears at 1724 cm^{-1} . The resolution between the uncoordinated and coordinated absorptions of both solvents is sufficient to provide meaningful deconvolution for quantitative species population analysis. The total integrated peak area of the coordinated and uncoordinated absorptions remain the same regardless of the quantity of salt added and thus, each band has equivalent IR sensitivity, thus the ratio of the area of the coordinated and uncoordinated peaks is directly proportional the population of coordinated and uncoordinated solvent. In the case of both solvents in figure 1 for PC and figure 2 for DMC, there is an isosbestic point between the two relative maxima, which provides evidence that there is an equilibrium between two species, the coordinated (in the solvation shell) and uncoordinated (bulk) solvent¹².

As shown in *equation 1*,^{5,8,9} comparing the ratio of the area of coordinated solvent, A_{CO} , to the total area, which is comprised of the uncoordinated area, A_{UC} , and A_{CO} will provide for the percentage of solvent coordination to the lithium cation. Multiplying this value by the number of solvent moles, n_{sol} , provides for the determination of the number of coordinated solvent molecules, n_{CO} . Further information in relation to the number of solvent molecules coordinated to a single lithium cation be found in equation 2 where n_{salt} is the moles of salt and N is the solvation number^{5,8,9}.

$$\text{Equation 1} \quad n_{CO} = \frac{A_{CO}}{A_{CO}+A_{UC}} \times n_{sol}$$

$$\text{Equation 2} \quad N = \frac{A_{CO}}{A_{CO}+A_{UC}} \times \frac{n_{sol}}{n_{salt}} = \frac{n_{CO}}{n_{salt}}$$

	Molar Mass (g/mol)	Density (25°C)	ϵ_r	μ (D)	η /(mPas)	$t_{mp}/^\circ\text{C}$	$t_{bp}/^\circ\text{C}$
PC	102.09	1.2 g/cm ³	64.92	16.5	2.53 (25°C)	-54.5	241.7
DMC	90.08	1.07 g/cm ³	8.93	0.91	0.59 (20°C)	4.6	90.3

Table 1: Properties of Solvents^{16,22,23}

The percentage of A_{CO} , to the total area ($A_{CO} + A_{UC}$), and the correlating solvation number (N) are presented in figure 3, for PC, and 4, for DMC, in solutions of various salt concentrations. As seen in figure 3, at a solvent to salt ratio of 4:1 with LiTFSI in PC (2.93 M), the solvation number, N , is ~ 3 and approximately 3 PC molecules are coordinated to the Li^+ cation. As the solvent to salt ratio increases and the solution becomes more dilute, more PC molecules coordinate to the Li^+ cation, which is evidenced from $N \sim 4$ at 8:1 ratio (1.47 M). Further dilution, 30:1 ratio (0.40 M) results in $N=7$, which is greater than the

typically expected coordination number between four and six.^{8,16,24,25} The large N value obtained can be attributed to either the primary solvation sphere of the lithium cation being larger than previously determined or instrumental measurement error.

Comparison of the solvation ability in relation to the salts provides information for the degree of ion dissociation of the anion. As found in lithium salt aprotic polar solvent solutions, incomplete dissociation is common for the salts with a remaining population of neutral ion clusters.²⁵ Salts with higher populations of these uncharged ion pairs will have lower quantities of dissociated ions, require fewer solvent molecules to stabilize the ions in solution and thus the lower the solvation number, the less the salt dissociated.^{3,25} According to the relative solvation numbers (figures 3 and 4) found in the varying salt concentrations and solvents; LiTFSI, LiPF₆, and LiClO₄ all consistently dissociate approximately the same intermediate degree while LiBF₄ dissociates less.^{5,16,26-28} In particular, LiBF₄ dissolved in DMC (figure 4) behaves quite differently. Even at the most dilute concentration (0.40M) with a solvent salt ratio of 30:1, $N \sim 3$ and $N \geq 4$ is never observed. As the salt concentration increases, the solvation number decreases to $N \sim 2$. This decrease in solvation number in this single solvent system is attributed to both the solvation ability of the solvent and the ionic association strength of the salt²⁹. LiBF₄, being the least disassociated salt, was expected to have a lower solvation number, as it would be stabilized with fewer solvent molecules³. The quantity of lithium available for solvent coordination is directly related to the magnitude of salt dissociation. At a solvent to salt ratio of 30:1, the

solvation number of LiBF_4 is twice as large in PC (figure 3) as the solvation number in DMC (figure 4). Since LiBF_4 dissociates less than the other three salts, it is expected that there will be more dissociated lithium available for coordination at all ratios for LiTFSI , LiPF_6 , and LiClO_4 than there was with LiBF_4 . This was found to be true as evidenced by the relatively smaller differences in solvation number with the less associated salts than found with LiBF_4 . Therefore, the significance of solvent relative permittivity in relation to solvation ability is inversely related to the quantity of dissociated ions in solution. However, this difference in solvation number between the two solvents decreases with decreasing solvent to salt ratio, which implies less influence of the solvent permittivity in concentrated electrolyte. Thus in agreement with Seo et al, relative permittivity isn't as important and solvent systems are more complicated than typically thought, especially in concentrated system.⁹

NMR Spectroscopy investigations on coordination. This change in the electronic environment of solvent's carbonyl carbon due to lithium cation coordination may also be detected via the use of ^{13}C -NMR spectroscopy as these solvents possess characteristic carbonyl resonances in ^{13}C -NMR 154.5ppm and 155.6ppm for PC and DMC respectively. Upon addition of the lithium salt to the pure solvent solution, ion-dipole coordination of the dissociated lithium cation effectively casts a deshielding effect and the carbonyl carbon experiences a downfield displacement²¹. By measuring the degree of the experienced chemical shift, it is possible to determine the degree of coordination of the solvent to cation as seen in figure 5 for LiTFSI dissolved in PC. FTIR spectroscopy measures the

relatively slow stretch of the carbonyl group, while the NMR measures the relatively rapid change in spin states, for this reason, it is possible to observe two distinct absorption via FTIR, while only one signal appears on the NMR spectrum. All chemical shift locations of single salt solutions have been plotted in figure 6a (for PC) and figure 6b (for DMC). Spectroscopic data from the NMR is useful for confirming FTIR peak area deconvolutions as linear relationships (figure 7) between the NMR weighted average shift directly correlates with the IR determined coordinated solvent percentage. Cross-method analysis and equation 2 allows for solubility comparison of the four different salts at various solvent-to-salt ratios dissolved in both linear and cyclic carbonate solvents.

CONCLUSION

Two spectroscopic methods were utilized in an investigation to probe the solvation sphere of a lithium cation. The study was conducted with four lithium salts (LiTFSI, LiPF₆, LiBF₄, and LiClO₄) and two common cyclic and linear carbonate solvents (PC and DMC) that used in lithium-ion battery systems. - Solutions were created in specific solvent-to-salt mole ratios and the quantities of coordinated and uncoordinated solvent were calculated based upon the relative areas of carbonyl IR stretching absorptions. For all systems, (LiTFSI, LiPF₆, and LiClO₄) were found to dissociate intermediately, while LiBF₄ dissociated less. At low ratios of salt to solvent, the solvation numbers were at their highest, up to ~7 in the most dissociative salts in PC (LiTFSI, LiPF₆, and LiClO₄) and up to ~3.5 with the less dissociative LiBF₄ in DMC. As the amount of solvent per salt decreased, the solvation numbers steadily decreased to ~3 in the most dissociative salts in PC and to ~2 for LiBF₄ in DMC. The solvation number was found to be dependent upon the degree of salt dissociation.

The results from IR were confirmed by comparison to the ¹³C NMR resonance spectra of the same solutions. Upon Li⁺ coordination, the ¹³C resonance of the solvent's carbonyl carbon shifts in proportion to the quantity of salt in solution, and thus is an indicator of the degree of solvent coordination. Shifts in NMR form a linear relationship when plotted with the coordinated absorption relative peak area determined from the IR deconvolution.

At high concentrations, additional solvation effects may dominate and minimal preferential solvation may exist. Prediction of ion solvent preference with the dielectric constant appears to only be valid in dilute solutions.

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	Molar Mass (g/mol)	Density (25°C)	ϵ_r	μ (D)	DN	η /(mPas)	$t_{mp}/^\circ\text{C}$	$T_{bp}/^\circ\text{C}$
PC	102.09	1.2 g/cm ³	64.92	16.5	15.1	2.53 (25°C)	-54.5	241.7
DMC	90.08	1.07 g/cm ³	8.93	0.91	15.1	0.59 (20°C)	4.6	90.3

Table 1: Properties of Solvents^{15,18,24,25}

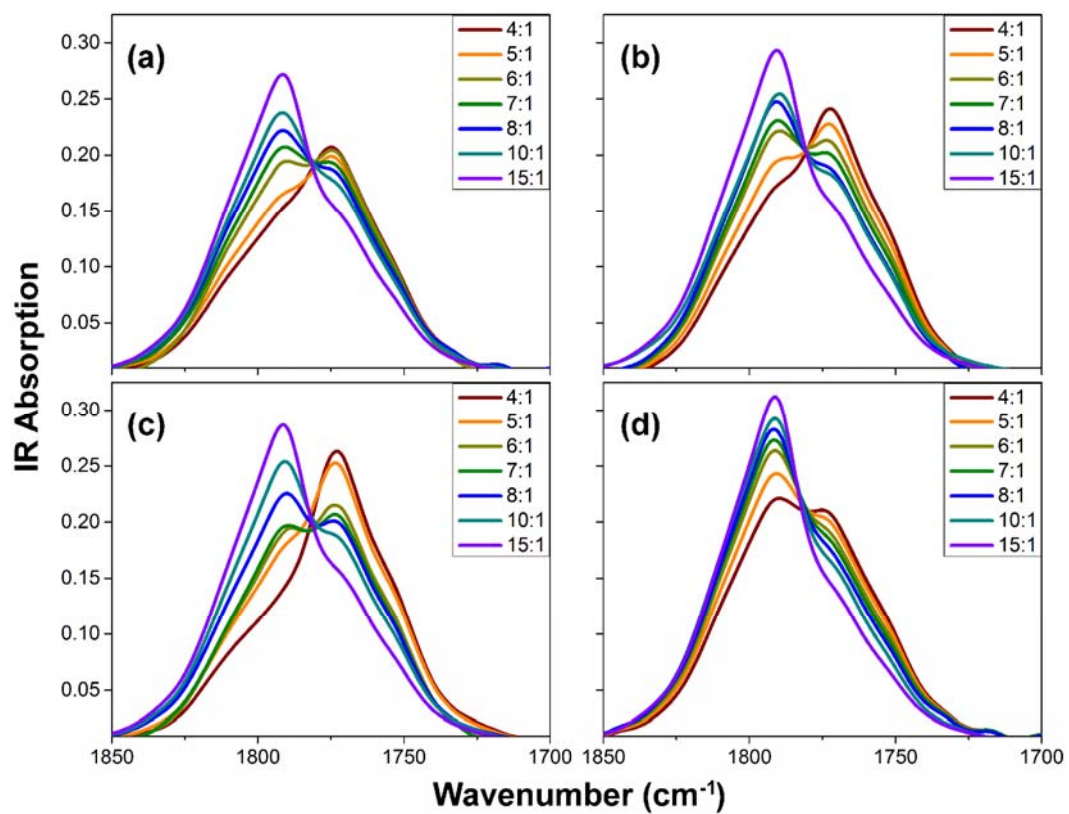


Figure 1 FTIR Propylene Carbonate (PC) carbonyl peak shifts relative to solvent:salt ratios with (a) LiTFSI (b) LiClO₄ (c) LiPF₆ (d) LiBF₄. The isosbestic point at 1781cm⁻¹ provides evidence for equilibrium between the coordinated and uncoordinated species.

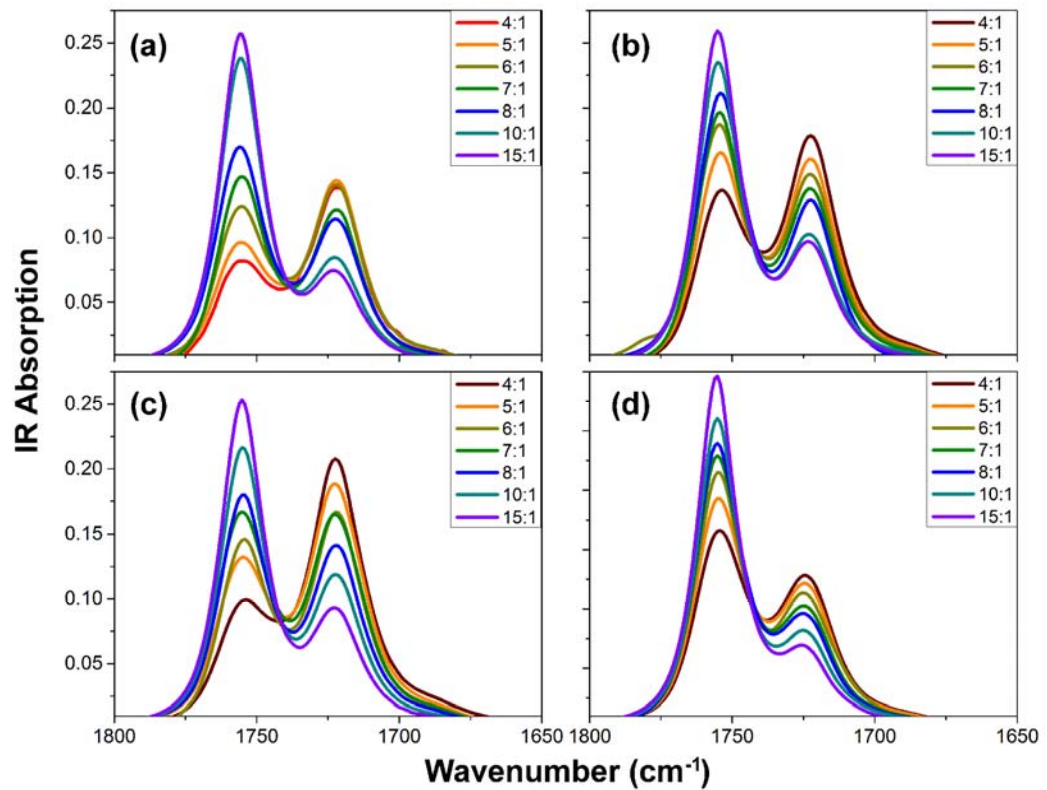


Figure 2 FTIR Dimethyl Carbonate (DMC) carbonyl peak shifts relative to solvent:salt ratios with (a) LiTFSI (b) LiClO₄ (c) LiPF₆ (d) LiBF₄. The isosbestic point at 1738 cm^{-1} provides evidence for equilibrium between the coordinated and uncoordinated species.

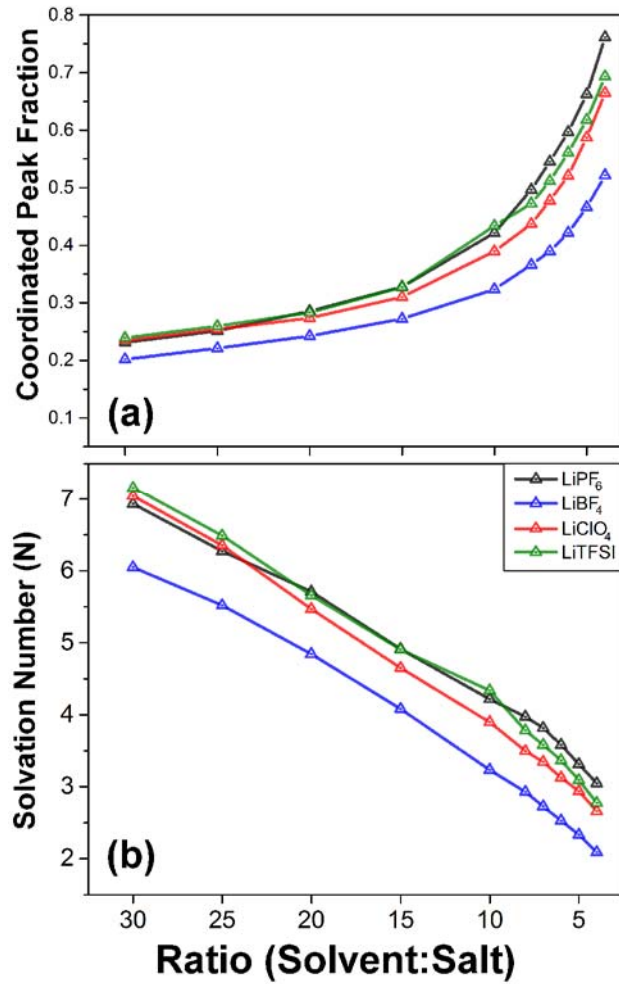


Figure 3 (a) Proportion of coordinated solvent fraction in LiPF₆, LiBF₄, LiClO₄, and LiTFSI dissolved in PC at various solvent:salt ratios. (b) Calculated solvation number for LiPF₆, LiBF₄, LiClO₄, and LiTFSI dissolved in PC at various solvent:salt ratios.

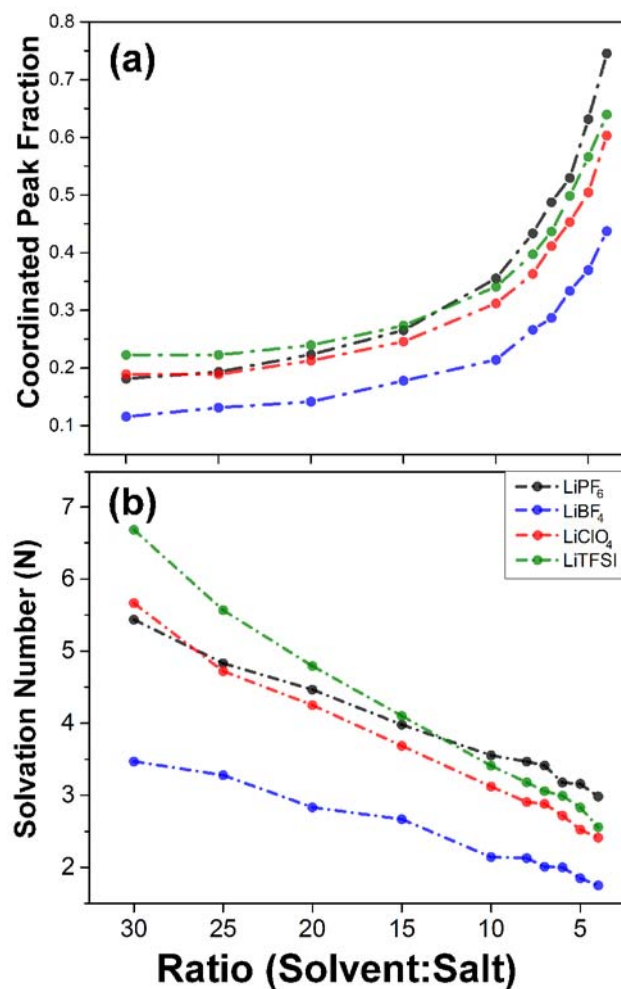


Figure 4 (a) Proportion of coordinated solvent fraction in LiPF₆, LiBF₄, LiClO₄, and LiTFSI dissolved in DMC at various solvent:salt ratios. (b) Calculated solvation number for LiPF₆, LiBF₄, LiClO₄, and LiTFSI dissolved in DMC at various solvent:salt ratios.

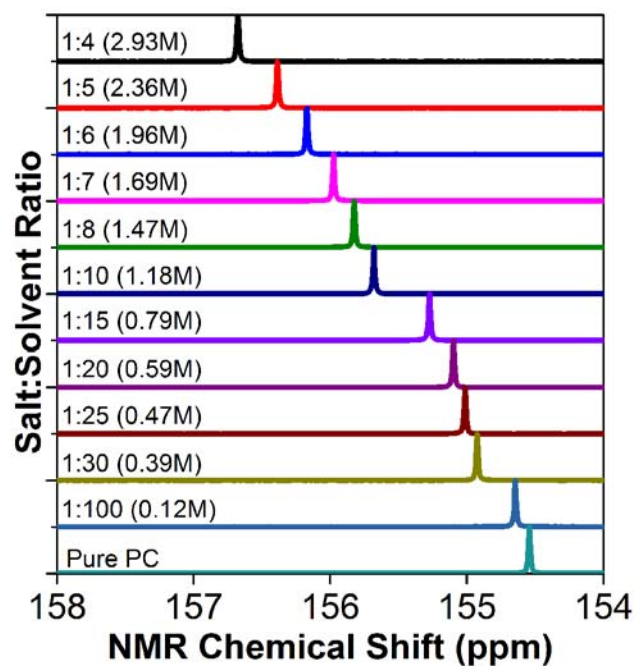


Figure 5 NMR ^{13}C spectrum of the carbonyl carbon chemical shifts of PC solvent with various amounts of LiTFSI dissolved in. Solvent coordination to the lithium cation has a deshielding effect on the carbonyl carbon.

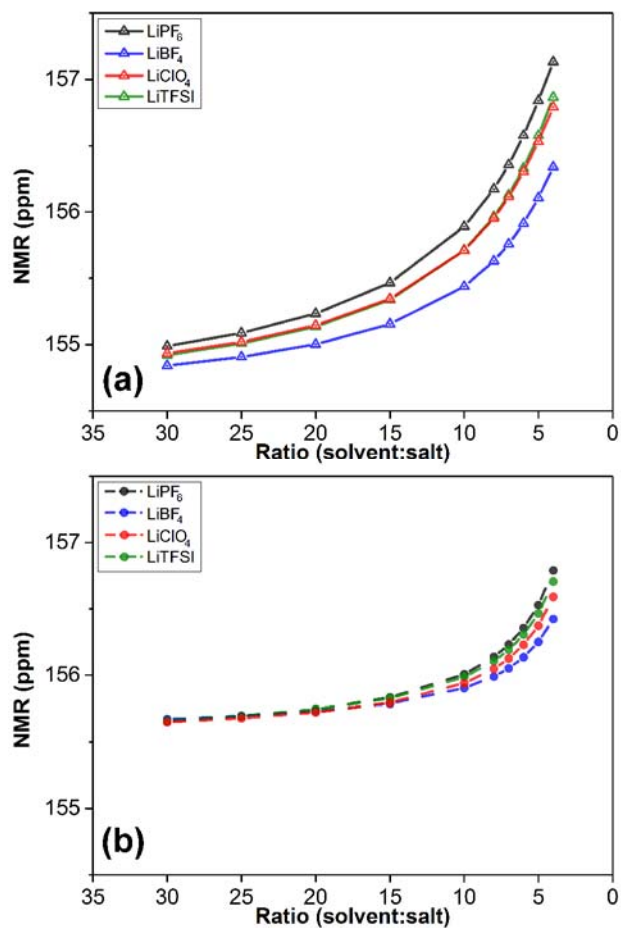


Figure 6 (a) NMR ¹³C spectrum of the carbonyl carbon chemical shifts of PC solvent with various amounts of salts; LiPF₆, LiBF₄, LiClO₄, LiTFSI dissolved in single salt solutions. (b) NMR ¹³C spectrum of the carbonyl carbon chemical shifts of DMC solvent with various amounts of salts; LiPF₆, LiBF₄, LiClO₄, LiTFSI dissolved in single salt solutions.

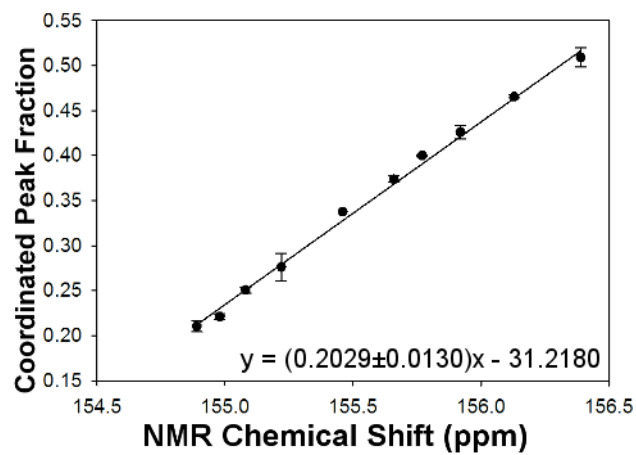


Figure 7 Plot of the FTIR solvent coordination percentage (LiBF_4 dissolved in PC) against the ^{13}C -NMR chemical shift. Agreement between the two spectroscopic methods increases confidence in the results.