ABSTRACT

SEO, DANIEL MIN. Linking Molecular-level Interactions to Lithium Battery Electrolyte Properties. (Under the direction of Dr. Wesley A. Henderson).

The molecular-level interactions within lithium battery electrolytes are the key determinant for electrolyte properties, but little is known about them at present. To better understand electrolyte interactions and how these are related to the measured bulk properties, a combination of methods has been employed in the present study: preparation of phase diagrams, X-ray single crystal determination of solvate structures, spectroscopic vibrational analysis of solvent/anion coordination and the rigorous evaluation of electrolyte properties (density, viscosity and ionic conductivity) for numerous solvent-lithium salt mixtures.

A detailed exploration of electrolyte solution structure was begun utilizing acetonitrile due to the simplicity of this solvent's interactions with Li$^+$ cations. This evaluation was then extended to other nitrile solvents (propionitrile and butyronitrile), cyclic carbonates (ethylene carbonate and propylene carbonate) and cyclic esters ($\gamma$-butyrolactone and $\gamma$-valerolactone) with various lithium salts (LiPF$_6$, LiTFSI, LiClO$_4$, LiBF$_4$, LiCF$_3$CO$_2$). Phase diagrams were prepared for the mixtures from extensive DSC measurements. The solvate species present in the solid and liquid phases were analyzed utilizing both crystal structures and Raman spectroscopy to determine how the solvent/anion structure influences the Li$^+$ cation solvation and solvate species equilibrium (i.e., ionic association). To aid in this, utilizing the crystal solvate structures obtained with the LiBF$_4$ and LiTFSI salts, detailed studies were conducted in which Raman spectra were collected to unambiguously assign the anion Raman band positions to specific forms of BF$_4^-$... and TFSI...Li$^+$ cation coordination. This is a crucial need as a large portion of the published work using spectroscopy to understand ionic
association is either incorrect or an oversimplification of the actual complex equilibrium of the solvate species present in electrolytes.

The combination of these methods provides a valuable set of tools for examining the molecular-level interactions in electrolyte solutions. Based upon the solution structure information obtained, the variations in electrolyte transport properties (viscosity, conductivity) were found to be readily explainable. This work fills a considerable gap for the study of electrolytes as no current theories aptly predict the properties of concentrated electrolytes. The methods and data obtained regarding bulk electrolyte interactions can readily be extended to the study of new solvents/salts, multi-solvent electrolytes and electrode-electrolyte interfaces—thus facilitating the transition from an entirely empirical approach to electrolyte development to tailored electrolyte formulations for specific applications (i.e., electrolytes-on-demand).
Linking Molecular-level Interactions to Lithium Battery Electrolyte Properties

by

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A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Chemical Engineering

Raleigh, North Carolina

2012

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BIOGRAPHY

Daniel Seo was born in Chicago, IL in 1981. He moved to South Korea when he was five years old and grew up in South Korea most of his life. In 2000, he started to attend Yonsei University with Chemistry major and transferred the major from Chemistry to Chemical Engineering in 2002. In 2003, he started to have military service in South Korea and it completed in 2005. He came back to college and earned B.S. degree of chemical engineering in 2007. After the graduation, he spent one year at Emmaus Bible College in Iowa for a year and headed to Raleigh to join Ph.D. program in NCSU in 2008. Since I joined to the ILEET group under the guidance of Dr. Wesley Henderson, he has been working with working on electrolyte system for Li-ion battery to understand the molecular interaction of electrolyte mixtures.
ACKNOWLEDGMENTS

First, thank God who prepare all of life and lead me in His way.

I would like to thank Dr. Henderson, who taught me, encouraged me and showed me how to deal with research problem during my Ph.D. program. Also I would like to acknowledge all members of ILEET group It is thankful for the discussion, advise and hard work. I thank to Korean colleague in NCSU whom I had great time and got lots of encourage. Finally I give thanks to my family who support me and pray for me.
# TABLE OF CONTENTS

**LIST OF TABLES** ........................................................................................................................................ vii

**LIST OF FIGURES** ........................................................................................................................................ viii

**CHAPTER 1 Introduction** ........................................................................................................................... 1

1.1 Electrical Energy Storage ......................................................................................................................... 1

1.1.1 Plug-In Hybrid Electric Vehicle ........................................................................................................... 3

1.1.2 Lithium Ion Batteries ......................................................................................................................... 5

1.2 Electrolyte of Lithium Ion Battery .......................................................................................................... 6

1.2.1 Lithium Salts ....................................................................................................................................... 7

1.2.2 Solvents ............................................................................................................................................. 9

1.3 Ionic Association and Ion Solvation ........................................................................................................ 10

1.3.1 Solvent Polarity Parameter ............................................................................................................... 10

1.3.2 Solvate Species in Mixture .............................................................................................................. 13

1.3.3 Degree of Ionic Association ........................................................................................................... 16

1.4 Motivation for the Present Study ........................................................................................................... 19

1.5 References ........................................................................................................................................... 20

**CHAPTER 2 Experimental Procedures** .................................................................................................... 25

2.1 Materials ............................................................................................................................................. 25

2.1.1 Lithium Salts .................................................................................................................................... 25

2.1.2 Solvents .......................................................................................................................................... 25

2.2 Sample Preparation ............................................................................................................................... 27

2.3 Instruments and Techniques .................................................................................................................. 28

2.3.1 Differential Scanning Calorimetry (DSC) ....................................................................................... 28

2.3.2 Raman Spectroscopy .................................................................................................................... 28

2.3.3 Solvate Crystal Structure Determination ....................................................................................... 29

2.3.4 Density/Viscosity Measurements .................................................................................................. 29

2.3.5 Conductivity Measurements .......................................................................................................... 30

2.4 References ........................................................................................................................................... 30
CHAPTER 3 Crystalline Solvates Structures and Ionic Association Interactions

3.1 Introductions

3.2 BF$_4^-$ Anion Raman Band Characterization

3.2.1 Solvate Structures and Li$^+$ Cation Coordination

3.2.2 Raman Spectroscopic Analysis of LiBF$_4$ Crystalline Solvates

3.3 TFSI$^-$ Anion Raman Band Characterization

3.3.1 Solvate Structures and Li$^+$ Cation Coordination

3.3.2 Raman Spectroscopic Analysis of LiTFSI Crystalline Solvates

3.4 Conclusions

3.5 References

CHAPTER 4 Electrolyte Solvation and Association (I): Acetonitrile (AN)-Lithium Salt Mixtures

4.1 Introduction

4.2 Thermal Phase Behavior and Solvate Crystal Structures

4.3 Ion Solvation

4.4 Ionic Association

4.5 Transport Properties

4.6 Conclusions

4.7 References

CHAPTER 5 Electrolyte Solvation and Association (II): Propionitrile (PN) and Butyronitrile (BN)-Lithium Salt Mixtures

5.1 Introduction

5.2 Thermal Phase Behavior

5.3 Ion Solvation

5.4 Ionic Association

5.5 Transport Properties

5.6 Conclusions

5.6 References
CHAPTER 6 Electrolyte Solvation and Association (III): Cyclic Carbonate and Ester-Lithium Salts Mixtures

6.1 Introduction

6.2 Thermal Phase Behavior and Solvate Crystal Structures

6.3 Ion Solvation

6.4 Ionic Association

6.5 Transport Properties

6.6 Conclusions

6.7 References

CHAPTER 7 Conclusions
LIST OF TABLES

CHAPTER 1

Table 1-1. Function and material of each component in Li-ion batteries………………..5

Table 1-2. DN, AN and permittivity of solvents……………………………………………..11

Table 1-3. Ion pair association constant of mixtures of solvent and salt…………………..11

CHAPTER 5

Table 5-1. The properties of mononitrile solvents studied.......................................115

CHAPTER 6

Table 6-1. The properties of cyclic carbonate and ester solvents studied (viscosity and density values are for 60°C…………………………………………………………………………………………141

Table 6-2. Raman vibration band positions for uncoordinated and coordinated (to a Li⁺ cation) solvents.................................................................153
LIST OF FIGURES

CHAPTER 1

Figure 1-1. Primary energy consumption by source and sector in 2010 (Quadrillion Btu)..........................................................................................................................1

Figure 1-2. Gasoline price history in dollar.................................................................2

Figure 1-3. Schematic diagram of a Li-ion battery.......................................................4

Figure 1-4. Fractions of (THF)$_n$-LiCF$_3$SO$_3$ and (glyme)$_n$-LiCF$_3$SO$_3$ solvate species determined from vibrational spectroscopic studies of ionic association at variable temperatures with a fixed concentration of EO/Li = 20..........................................................12

Figure 1-5. Types of crystalline lithium salt solvates in THF solvents......................13

Figure 1-6. DSC data and phase diagram of (G1)$_n$-LiClO$_4$ with various concentration.....16

Figure 1-7. Raman spectrum analysis of solvate structure in (G4)$_n$-LiClO$_4$ (n = 0.5)........18

CHAPTER 2

Figure 2-1. Structures and acronyms of the lithium salts used..................................25

Figure 2-2. Structures and acronyms of the solvents used..........................................26

CHAPTER 3

Figure 3-1. Examples of BF$_4$-...Li$^+$ cation coordination: (a) SSIP, (b) CIP-I, (c) CIP-II, (d) AGG-I, (e) AGG-II and (f) AGG-III............................................................32

Figure 3-2. Examples of TFSI-...Li$^+$ cation coordination: (a) SSIP-C$_1$, (b) SSIP-C$_2$, (c) CIP-I-C$_2$, (d) CIP-II-C$_1$, (e) AGG-Ia-C$_2$, (f) AGG-Ib-C$_2$, (g) AGG-IIb-C$_1$, (h) AGG-IIb-C$_2$ and (i) AGG-III-C$_2$............................................................32

Figure 3-3. BF$_4$-...Li$^+$ cation coordination in crystalline solvates and the pure LiBF$_4$ salt: (a) SSIP (G2)$_2$:LiBF$_4$, (b) CIP-I (G1)$_2$:LiBF$_4$, (c) CIP-I (G3)$_1$:LiBF$_4$, (d) AGG-I (G2)$_1$:LiBF$_4$, (e) AGG-I (EC)$_1$:LiBF$_4$, (f) AGG-II (GBL)$_1$:LiBF$_4$, (g) AGG-II (MA)$_1$:LiBF$_4$, (h) AGG-II (EA)$_1$:LiBF$_4$, (i) AGG-II (AN)$_1$:LiBF$_4$ and (j) AGG-III pure LiBF$_4$.................................35

Figure 3-4. BF$_4$-...Li$^+$ cation coordination in crystalline solvates: (a) AGG-I (AN)$_2$:LiBF$_4$, (b) AGG-I (Et-G1)$_1$:LiBF$_4$, (c) AGG-I (Et-G2)$_1$:LiBF$_4$, (d) AGG-II (THF)$_1$:LiBF$_4$, (e) AGG-II (MMA)$_1$:LiBF$_4$ and (f) AGG-II (SN)$_1$:LiBF$_4$........................................................................36
Figure 3-5. BF\(_4^-\) anion coordination in crystalline HBF\(_4\) solvates: (a) SSIP (PMDETA)$_2$:HBF\(_4\), (b) SSIP (TMEDA)$_3$:HBF\(_4\) and (c) SSIP (PHEN)$_2$:HBF\(_4\).............37

Figure 3-6. Raman spectrum of LiBF\(_4\) at 20°C........................................40

Figure 3-7. Raman spectra of the BF\(_4^-\) anion \(v_1\) vibrational band for the SSIP crystalline solvates: (a) (G2)$_2$:LiBF\(_4\), (b) (AN)$_4$:LiBF\(_4\), (c) (12C4)$_2$:LiBF\(_4\), (d) (PMDETA)$_2$:HBF\(_4\), (e) (TMEDA)$_3$:HBF\(_4\) and (f) (PHEN)$_2$:HBF (the bold curves indicate that the solvate melted)..................................................41

Figure 3-8. Raman spectra of the BF\(_4^-\) anion \(v_1\) vibrational band for the CIP crystalline solvates: (a) (G1)$_2$:LiBF\(_4\), (b) (G3)$_1$:LiBF\(_4\) and (c) (DMP)$_2$:LiBF\(_4\)..............................42

Figure 3-9. Raman spectra of the BF\(_4^-\) anion \(v_1\) vibrational band for the AGG-I crystalline solvates: (a) (G2)$_2$:LiBF\(_4\), (b) (EC)$_2$:LiBF\(_4\), (c) (AN)$_2$:LiBF\(_4\), (d) (Et-G1)$_1$:LiBF\(_4\) and (e) (Et-G2)$_1$:LiBF\(_4\)...............................................................43

Figure 3-10. Raman spectra of the BF\(_4^-\) anion \(v_1\) vibrational band for the AGG-II crystalline solvates and AGG-III LiBF\(_4\): (a) (SN)$_1$:LiBF\(_4\), (b) (AN)$_1$:LiBF\(_4\), (c) (MA)$_1$:LiBF\(_4\), (d) (GBL)$_1$:LiBF\(_4\), (e) (MMA)$_1$:LiBF\(_4\), (f) (THF)$_1$:LiBF\(_4\), (g) (EA)$_1$:LiBF\(_4\) and (h) pure LiBF\(_4\)................................................................................45

Figure 3-11. Summary of the Raman band peak position for the BF\(_4^-\) anion \(v_1\) vibrational band for the different crystalline solvates.................................................................46

Figure 3-12. Differences in the BF\(_4^-\)...Li\(^+\) cation coordination in the SSIP and CIP-I crystalline solvates: (a) SSIP (G2)$_2$:LiBF\(_4\), (b) SSIP (PMDETA)$_2$:HBF\(_4\), (c) SSIP (TMEDA)$_3$:HBF\(_4\), (d) SSIP (PHEN)$_2$:HBF\(_4\), (e) CIP-I (G1)$_2$:LiBF\(_4\) and (f) CIP-I (G3)$_1$:LiBF\(_4\) (Li\(^+\) cation is colored black)..........................................................47

Figure 3-13. Differences in the BF\(_4^-\)...Li\(^+\) cation coordination in the AGG-I crystalline solvates and AGG-III pure salt: (a) AGG-I (EC)$_2$:LiBF\(_4\), (b) AGG-I (AN)$_2$:LiBF\(_4\), (c) AGG-I (G2)$_2$:LiBF\(_4\), (d) AGG-I (Et-G1)$_1$:LiBF\(_4\), (e) AGG-I (Et-G2)$_1$:LiBF\(_4\) and (f) AGG-III pure LiBF\(_4\). (*all of the solvate structures were determined at -163°C, except for the structure for the (AN)$_2$:LiBF\(_4\) solvate which was determined at -5°C because of this solvate's solid-solid phase transition)\(^7\) (Li\(^+\) cations are colored black)..........................................................47

Figure 3-14. Differences in the BF\(_4^-\)...Li\(^+\) cation coordination in the AGG-II crystalline solvates: (a) (EA)$_1$:LiBF\(_4\), (b) (THF)$_1$:LiBF\(_4\), (c) (MMA)$_1$:LiBF\(_4\), (d) (GBL)$_1$:LiBF\(_4\), (e) (MA)$_1$:LiBF\(_4\), (f) (AN)$_1$:LiBF\(_4\)\(^{38}\) and (g) (SN)$_1$:LiBF\(_4\) (Li\(^+\) cations are colored black).............49
Figure 3-15. TFSI\(^{-}\)...Li\(^{+}\) cation coordination in crystalline solvates: (a) SSIP-C\(_2\) (G2):LiTFSI, (b) SSIP-C\(_2\) (PHEN):LiTFSI, (c) CIP-II-C\(_1\) (PMDETA):LiTFSI, (d) AGG-Ib-C\(_2\) (G1):LiTFSI, (e) AGG-Ia-C\(_2\) (EC):LiTFSI, (f) AGG-Ib-C\(_2\) (TMEDA):LiTFSI, (g) AGG-Iib-C\(_2\) (EC):LiTFSI, (h) AGG-Iib-C\(_1\) (DMPy):LiTFSI, (i) AGG-Iib-C\(_1\) (AN):LiTFSI and (j) AGG-III-C\(_2\) pure LiTFSI

Figure 3-16. Raman spectra of the TFSI\(^{-}\) anion vibrational band for the SSIP-C\(_2\) crystalline solvates: (a) (G2):LiTFSI, (b) (PHEN):LiTFSI, (c) (12C4):LiTFSI and (d) (G1):LiTFSI

Figure 3-17. Raman spectra of the TFSI\(^{-}\) anion vibrational band for the CIP and AGG-I crystalline solvates: (a) CIP-II-C\(_1\) (PMDETA):LiTFSI, (b) AGG-Ia-C\(_2\) (EC):LiTFSI, (c) AGG-Ib-C\(_2\) (G1):LiTFSI and (d) AGG-Ib-C\(_2\) (TMEDA):LiTFSI

Figure 3-18. Raman spectra of the TFSI\(^{-}\) anion vibrational band for the AGG-II crystalline solvates and AGG-III LiTFSI: (a) AGG-Iib-C\(_1\) (AN):LiTFSI, (b) AGG-Iib-C\(_1\) (2,6-DMPY):LiTFSI, (c) AGG-Iib-C\(_2\) (EC):LiTFSI, (d) AGG-III-C\(_2\) pure LiTFSI

Figure 3-19. Summary of the Raman band peak position for the TFSI\(^{-}\) anion vibrational band for the different crystalline solvates (the figure on the right is an expansion of a portion of the figure on the left)

CHAPTER 4

Figure 4-1. DSC heating traces (5\(^{\circ}\)C min\(^{-1}\)) and the corresponding phase diagrams of (a) (1-x) AN-(x) LiTFSI and (b) (1-x) AN-(x) LiPF\(_6\) mixtures

Figure 4-2. Li\(^{+}\) cation coordination in the (a) (AN):LiPF\(_6\), (b) (AN):LiPF\(_6\) and (c) (AN):LiTFSI solvate crystal structures (Li-purple, N-blue, P-orange, F-light green, O-red)

Figure 4-3. DSC heating traces (5\(^{\circ}\)C min\(^{-1}\)) and the corresponding phase diagrams for (a) (1-x) AN-(x) LiClO\(_4\) and (b) (1-x) AN-(x) LiBF\(_4\) mixtures

Figure 4-4. Li\(^{+}\) cation coordination in the (a) (AN):LiClO\(_4\), (b) (AN):LiBF\(_4\) and (c) (AN):LiBF\(_4\) and (d) (AN):LiCF\(_3\)SO\(_3\) solvate crystal structures (Li-purple, Cl-green, B-tan, F-light green, O-red)

Figure 4-5. DSC heating trace (5\(^{\circ}\)C min\(^{-1}\)) of the (AN):LiCF\(_3\)SO\(_3\) solvate

Figure 4-6. DSC heating traces (5\(^{\circ}\)C min\(^{-1}\)) of (1-x) AN-(x) LiCF\(_3\)CO\(_2\) mixtures
Figure 4-7. Raman spectra of the AN C–C (920 cm\(^{-1}\)) and C≡N (2250 cm\(^{-1}\)) stretching mode bands for (a) (AN)\(_n\)-LiBF\(_4\) and (b) (AN)\(_n\)-LiCF\(_3\)CO\(_2\) mixtures (AN/LiX ratio indicated) at 60°C.

Figure 4-8. Raman spectroscopic analysis of the solvent bands for uncoordinated AN and Li\(^+\) cation coordinated AN in (AN)\(_n\)-LiX mixtures with (a) LiPF\(_6\), (b) LiTFSI, (c) LiClO\(_4\), (d) LiBF\(_4\) and (e) LiCF\(_3\)CO\(_2\) at 60°C. The calculated Li\(^+\) cation average solvation number (N) is shown at the top.

Figure 4-9. PF\(_6^–\) anion band variation with concentration in (AN)\(_n\)-LiPF\(_6\) mixtures at (a) -80°C and (b) 60°C.

Figure 4-10. TFSI\(^–\) anion band variation with concentration in (AN)\(_n\)-LiTFSI mixtures at (a) -80°C and (b) 60°C. The mixtures with n = 3.0, 2.5, 2.0 and 1.55 are in the crystallinity gap and remain either fully amorphous liquids or glassy solids at -80°C.

Figure 4-11. TFSI\(^–\) anion band variation with temperature in (AN)\(_n\)-LiTFSI mixtures with (a) n = 6.0 (crystalline in the -80 to -45°C range) and (b) n = 4.0 (crystalline in the -100 to -35°C range).

Figure 4-12. Distribution of anion modes of Li\(^+\) cation coordination present in the (AN)\(_n\)-LiTFSI mixtures at 60°C.

Figure 4-13. Variable-temperature TFSI\(^–\) anion band variation with concentration in (AN)\(_n\)-LiTFSI mixtures with (a) n = 4.00, (b) n = 3.63, (c) n = 3.00, (d) n = 2.50, (e) n = 2.00, (f) n = 1.55, (g) n = 1.38 and (h) n = 1.00.

Figure 4-14. ClO\(_4^–\) anion band variation with concentration in the (AN)\(_n\)-LiClO\(_4\) mixtures at -80°C.

Figure 4-15. BF\(_4^–\) anion band variation with concentration in the (AN)\(_n\)-LiBF\(_4\) mixtures: (a) -80°C and (b) 60°C.

Figure 4-16. Distribution of anion modes of Li\(^+\) cation coordination present in the (AN)\(_n\)-LiBF\(_4\) mixtures at 60°C.

Figure 4-17. Temperature dependence of the BF\(_4^–\) anion bands in the (AN)\(_n\)-LiBF\(_4\) mixtures: (a) n = 8 and (b) n = 4.

Figure 4-18. Representative Li\(^+\) cation solvate species (i.e., coordination shells) extracted from the MD simulations for the (AN)\(_n\)-LiTFSI mixtures (n = 30, 20 and 10) at 60°C: (a) C\(_1\)-SSIP, (b) C\(_1\)-CIP-I, (c) C\(_2\)-AGG-I, (d) C\(_2\)-CIP-I, C\(_1\)-CIP-II (e) C\(_2\)-CIP-I (x2), C\(_1\)-AGG-I, (f)
Figure 4-19. Representative Li⁺ cation solvate species (i.e., coordination shells) extracted from the MD simulations for the (AN)_n-LiBF₄ mixtures (n = 30, 20 and 10) at 60°C: (a) SSIP, (b) CIP-I, CIP-II, (c) CIP-I, (d) CIP-II, (e) CIP-I, AGG-I, (f) AGG-I, (g) CIP-I, AGG-I (×3), (h) CIP-I, AGG-I (×3), AGG-III, (i) CIP-I, AGG-I (×2), (j) CIP-I (×2), AGG-I and (k) AGG-I (×3) (Li-purple, N-blue, B-tan, F-light green) .......................................................... 96

Figure 4-20. (a) Density of (AN)_n-LiX mixtures at 60°C (AN/LiX ratio noted in the plots) and (b) relationship between molarity vs. concentration for (AN)_n-LiX mixtures .......................... 98

Figure 4-21. Viscosity of (AN)_n-LiX mixtures (AN/LiX ratio noted in the plots) at 60°C. Data for concentrated mixtures with LiPF₆ and LiClO₄ was not gathered as these samples form crystalline solids at this temperature. ((b) is an expanded view for the dilute mixtures) .............................................................................................................. 99

Figure 4-22. Snapshot of MD simulations of (AN)_n-LiX mixtures (n = 20) with (a) LiPF₆ and (b) LiBF₄ (Li-purple, N-blue, P-orange, B-tan, F-light green) .............................. 100

Figure 4-23. Variable-temperature ionic conductivity of (AN)_n-LiX mixtures: (a) LiPF₆, (b) LiTFSI, (c) LiClO₄, (d) LiBF₄ and (e) LiCF₃CO₂ (AN/LiX ratio (n) noted in the plot) .............................................................................................................. 102

Figure 4-24. Variable-concentration ionic conductivity of (AN)_n-LiX mixtures at 60°C... 104

Figure 4-25. Molar conductivity of (a) (AN)_n-LiX mixtures (60°C) for varying AN/LiX (n) concentrations and (b) (AN)_n-LiX mixtures (n = 20 - filled circles are average values, individual measurements shown as small open circles and n = 4 - larger open circles) with varying temperature .............................................................................................................. 106

CHAPTER 5

Figure 5-1. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) PN-(x) LiPF₆ and (b) (1-x) PN-(x) LiTFSI mixtures .......................................................... 117

Figure 5-2. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) PN-(x) LiClO₄ and (b) (1-x) PN-(x) LiBF₄ mixtures ........................................................................... 118

Figure 5-3. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) BN-(x) LiPF₆ and (b) (1-x) BN-(x) LiTFSI mixtures ........................................................................... 121
Figure 5-4. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) BN-(x) LiClO₄ and (b) (1-x) BN-(x) LiBF₄ mixtures..........................................................122

Figure 5-5. Raman spectra of the PN C–C (837 cm⁻¹) and C≡N (2247 cm⁻¹) stretching bands for the (PN)ₙ–LiX mixtures: (a) LiClO₄ and (b) LiBF₄ at 60°C (PN/LiX ratio indicated)....124

Figure 5-6. Raman spectra of the BN C≡N (2250 cm⁻¹) stretching band for the (BN)ₙ–LiX mixtures with (a) LiPF₆ and (b) LiTFSI at 60°C (BN/LiX ratio indicated)…………..……125

Figure 5-7. The calculated Li⁺ cation average solvation number (N) in (a) (PN)ₙ–LiPF₆, (b) (PN)ₙ–LiTFSI, (c) (PN)ₙ–LiClO₄, (d) (PN)ₙ–LiBF₄, (e) (BN)ₙ–LiPF₆, (f) (BN)ₙ–LiTFSI, (g) (BN)ₙ–LiClO₄ and (h) (BN)ₙ–LiBF₄ mixtures at 60°C……………………….……………..126

Figure 5-8. The anion band variation with concentration in (a) (PN)ₙ– and (BN)ₙ–LiPF₆, (b) (PN)ₙ– and (BN)ₙ–LiTFSI, (c) (PN)ₙ– and (BN)ₙ–LiClO₄ and (d) (PN)ₙ– and (BN)ₙ–LiBF₄ at 60°C……………………………………………………………………………………128

Figure 5-9. Comparison of Raman band of the (solvent)ₙ–LiX (n = 6) mixtures: (a) LiTFSI, (b) LiClO₄ and (c) LiBF₄.................................................................129

Figure 5-10. Variable-concentration density (left) and relationship between molarity vs. solvent/LiX (n) (left) of (PN)ₙ–LiX (top) and (BN)ₙ–LiX mixtures (bottom) at 60°C.................................................................131

Figure 5-11. Variable-concentration viscosity of (a) (PN)ₙ–LiX and (b) (BN)ₙ–LiX mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.........................................................132

Figure 5-12. Variable-temperature ionic conductivity of (PN)ₙ–LiX mixtures: (a) LiPF₆, (b) LiTFSI, (c) LiClO₄ and (d) LiBF₄ (PN/LiX ratio (n) noted in plot).............133

Figure 5-13. Variable-temperature ionic conductivity of (BN)ₙ–LiX mixtures: (a) LiPF₆, (b) LiTFSI and (c) LiClO₄ and (d) LiBF₄ (BN/LiX ratio (n) noted in plot).............134

Figure 5-14. Variable-concentration ionic conductivity of (solvent)ₙ–LiX mixtures: (a) AN, (b) PN and (c) BN solvent at 60 °C.................................................................135

Figure 5-15. Molar conductivity of (a) (PN)ₙ–LiX and (b) (BN)ₙ–LiX mixtures (60 °C) for varying solvent/LiX (n) concentrations and (c) (PN)ₙ–LiX and (d) (BN)ₙ–LiX mixtures (n = 20) for varying temperature.................................................................136
CHAPTER 6

Figure 6-1. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiPF₆ and (b) (1-x) PC-(x) LiPF₆ mixtures……………………………………………………………….142

Figure 6-2. Li⁺ cation coordination in the (a) (EC)₄:LiPF₆ and (b) (GBL)₄:LiPF₆ (Li-purple, P-gold, F-light green, O-red ).………………………………………………………………………..143

Figure 6-3. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (1-x) GBL-(x) LiPF₆ mixtures. ………………………………………………………………………………..143

Figure 6-4. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiTFSI and (b) (1-x) PC-(x) LiTFSI mixtures……………………………..………….145

Figure 6-5. Li⁺ cation coordination in the (a) (EC)₃:LiTFSI and (b) (EC)₁:LiTFSI (Li-purple, N-blue, F-light green, O-red )……………………………………………………………………………..146

Figure 6-6. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) GBL-(x) LiTFSI and (b) (1-x) GVL-(x) LiTFSI mixtures………………………………………..………..147

Figure 6-7. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiClO₄ and (b) (1-x) PC-(x) LiClO₄ mixtures………………………………………………………………………………….149

Figure 6-8. Li⁺ cation coordination in the (a) (EC)₃:LiClO₄, (b) (EC)₂:LiClO₄, (c) (GBL)₁:LiClO₄ and (d) (GVL)₁:LiClO₄ solvate crystal structures (Li-purple, Cl-green, O-red)………………………………………………………………………………………………………..150

Figure 6-9. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) GBL-(x) LiClO₄ and (b) (1-x) GVL-(x) LiClO₄ mixtures………………………………………………………………………………..150

Figure 6-10. Raman spectra of the solvent (left) EC symmetric ring deformation mode (720 cm⁻¹) and (right) EC C-O stretching mode (900 cm⁻¹) in mixtures: (top) LiPF₆, (middle) LiTFSI and (bottom) LiClO₄ at 60°C…………………………………………………………………………………………………………………..152

Figure 6-11. Raman spectra of the solvent (left) PC symmetric ring deformation mode (720 cm⁻¹) and (right) GBL C-C stretching mode (675 cm⁻¹) in mixtures: (top) LiPF₆, (middle) LiTFSI and (bottom) LiClO₄ at 60°C…………………………………………………………………………………………………………………..155

Figure 6-12. Raman spectra of the solvent (left) GVL ring deformation mode (651 cm⁻¹) and (right) GVL C-CH₃ stretching mode (942 cm⁻¹) in mixtures: (top) LiTFSI and (bottom) LiClO₄ at 60°C…………………………………………………………………………………………………………………..156
Figure 6-13. The calculated Li$^+$ cation average solvation number ($N$) in (solvent)$_n$-LiX mixtures: (a) LiClO$_4$, (b) LiTFSI and (c) LiPF$_6$ at 60°C.

Figure 6-14. Raman spectra of the anion P-F stretching mode (740 cm$^{-1}$) for (solvent)$_n$-LiPF$_6$ mixtures: (a) EC, (b) PC and (c) GBL at 60°C.

Figure 6-15. Raman spectra of the anion TFSI$^-$ expansion/contraction mode (740 cm$^{-1}$) for (solvent)$_n$-LiTFSI mixtures: (a) EC, (b) PC, (c) GBL and (d) GVL at 60°C.

Figure 6-16. Raman spectra of the anion Cl-O stretching mode (930 cm$^{-1}$) for (solvent)$_n$-LiClO$_4$ mixtures: (a) EC, (b) PC, (c) GBL and (d) GVL at 60°C.

Figure 6-17. Comparison of the Raman anion band for (solvent)$_n$-LiX mixtures with (a) LiTFSI ($n = 5$) and (c) LiClO$_4$ ($n = 6$) at 60°C.

Figure 6-18. Variable-concentration density and relationship between molarity vs. solvent/LiX ($n$) for (solvent)$_n$-LiPF$_6$ (top) and (solvent)$_n$-LiTFSI mixtures (bottom) at 60°C (solvent/LiX ratio noted in plots).

Figure 6-19. Variable-concentration density and relationship between molarity vs. solvent/LiX ($n$) for (solvent)$_n$-LiClO$_4$ at 60°C (solvent/LiX ratio noted in plots).

Figure 6-20. Variable-concentration viscosity of (solvent)$_n$-LiPF$_6$ and -LiTFSI mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.

Figure 6-21. Variable-concentration viscosity of (solvent)$_n$-LiClO$_4$ mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.

Figure 6-22. Variable-temperature ionic conductivity of (a) (EC)$_n$-LiPF$_6$ (b) (PC)$_n$-LiPF$_6$, (C) (EC)$_n$-LiTFSI, (d) (PC)$_n$-LiTFSI, (e) (GBL)$_n$-LiTFSI and (f) (GVL)$_n$-LiTFSI (solvent/LiX ratio ($n$) noted in plot).

Figure 6-23. Variable-temperature ionic conductivity of (solvent)$_n$-LiClO$_4$ mixtures: (a) EC, (b) PC, (c) GBL and (d) GVL (solvent/LiClO$_4$ ratio ($n$) noted in plot).

Figure 6-24. Variable-concentration ionic conductivity of (solvent)$_n$-LiX mixtures: (a) LiPF$_6$, (b) LiTFSI and (c) LiClO$_4$ at 60 °C.

Figure 6-25. Molar conductivity of (solvent)$_n$-LiX mixtures (60 °C): (a) LiPF$_6$ and (b) LiTFSI for varying solvent/LiX ($n$) concentrations and (solvent)$_n$-LiX mixtures ($n = 20$): (c) LiPF$_6$ and (d) LiTFSI for varying temperature.
Figure 6-26. Molar conductivity of (a) (solvent)$_n$-LiClO$_4$ mixtures (60 °C) for varying solvent/LiX (n) concentrations and (b) (solvent)$_n$-LiClO$_4$ mixtures (n = 20) with varying temperature.
CHAPTER 1 Introduction

1.1 Electrical Energy Storage

Energy storage technologies are one of the crucial issues in the 21st Century. Since the Industrial Revolution, the main energy source has been fossil fuels, such as coal, gas and petroleum. 83% of the total energy used in the U.S. was generated from these fuels in 2010 (Fig. 1-1). But the demand for energy parallels the rapid increase in both global population and industrial development. Furthermore, the availability of fossil fuels is limited. Recent advances in hydraulic fracturing (i.e., ‘fracking’) have greatly improved oil production in the U.S., but this simply defers the inevitable point of ‘Peak Oil’ production. The need for alternative energy sources is therefore unavoidable. A great deal of research has focused on

Figure 1-1. Primary energy consumption by source and sector in 2010 (Quadrillion Btu).
the development of alternatives for electricity production, including renewable energy sources such as solar, wind, hydropower, geothermal and biomass (i.e., torrefied wood to replace coal). Most of these energy sources are limited, however, by their location and electrical production time/rates. Therefore, the development of large-scale electrical energy storage technologies is required to greatly facilitate the storage and transportation of energy generated by renewable energy sources.

The availability of fossil fuels primarily manifests itself in what can be broadly defined as energy security. The U.S. has been a net importer of petroleum for several decades and currently imports 55% of the petroleum used. One of the main contributors to fossil fuel consumption is transportation. 36% of the total energy used in the U.S. in 2010 was generated from petroleum and 94% of this was consumed by transportation (Fig. 1-1). As petroleum supply limitations (from both limited production and increasing worldwide

![Regular Gasoline Price in Today's Dollars (9/3/2012)](image)

**Figure 1-2.** Gasoline price history in dollar.
demand) have become more restrictive, the price of gasoline has increased sharply. Fig. 1-2 shows the sharp upturn in gasoline prices just before the economic recession that occurred in 2008. The dramatic drop in the demand for fuel due to the recession led to a corresponding drop in gasoline prices, but the slow recovery of the World economy has rapidly pushed prices back to a near all-time high, despite the recent increased domestic production of petroleum due to hydraulic fracturing. Further increases, perhaps significant, in gasoline prices can therefore be expected in the future.

Finally, the combustion of petroleum is a significant contributor to CO₂ emissions. Climate Change concerns are not currently a major driving force for change in transportation, but future regulations, as well as government efforts to initiate change, could potentially drastically influence fuel usage. These issues have led to the greatly increased electrification of transportation. Electric and plug-in hybrid electric vehicles (EVs and PHEVs) have been introduced in recent years and are in the early stages of full-scale commercialization, whereas hybrid electric vehicles (HEVs) are now well accepted. One of the key factors for the success of EVs and PHEVs, however, is further advances in electric energy storage.

1.1.1 Plug-in Hybrid Electric Vehicles and Batteries

HEVs, which combine conventional combustion and an electric drive system with an external electric energy source, were introduced first by Ferdinand Porsche and in 1899. These hybrid electric vehicles were not able to be commercialized, however, because of the lack of a suitable energy storage technology. Advances in batteries in recent decades, however, have enabled the electrification of vehicles. In 1997, Toyota introduced the first commercialized HEV, the Prius. Further advances in battery technology have resulted in the
commercialization of PHEVs and a limited number of EVs. PHEVs are dual-fuel vehicles which combine a gasoline tank with the storage of electrical energy in batteries. If the electricity is supplied by a Smart Grid, the efficiency of consumption of the energy can be optimized and the usage of the electricity controlled. The widespread adoption of PHEVs with the energy storage equivalent of a driving range of 20 miles solely with electricity (PHEV20) has been projected to potentially reduce current petroleum usage by 45%. Using PHEVs as an alternative to conventional vehicles can therefore help to address all of the issues noted for above—i.e., limited petroleum supply, energy security and CO₂ production.

There are still some barriers to the widespread use of PHEVs. The most crucial barrier is electrical energy storage (i.e., batteries). To operate a PHEV, a large amount of energy capacity and power are required from a traction battery. Additional considerations for the battery include the durability (calendar life and charging/discharging lifetime), safety, volume/mass and cost. Several types of batteries have been used in PHEVs, but Li-ion

![Figure 1-3. Schematic diagram of a Li-ion battery.](image-url)
batteries are the principal focus for most commercial vehicles due to their high energy capacity. Li-ion battery technology, however, needs to be greatly improved for this application, especially with regard to safety and cost.

1.1.2 Lithium Ion Batteries

Li-ion batteries consist of two electrodes, a separator and an electrolyte (Fig. 1-3). Table 1-1 and Equation (1) below show the principle components and reactions for a Li-ion battery. When energy is applied (during charging), the cathode material is oxidized (electrons are removed and transferred to the anode active material) resulting in the deintercalation of Li$^+$ cations from the cathode and intercalation of Li$^+$ cation into the anode:

$$\text{LiMO}_x \leftrightarrow \text{Li}_{1-n}\text{MO}_x + n\text{Li}^+ + n\text{e}^-$$

$$n\text{Li}^+ + n\text{e}^- + C \leftrightarrow \text{Li}_n\text{C}$$

$$\text{C} + \text{LiMO}_x \leftrightarrow \text{Li}_{1-n}\text{MO}_x + \text{Li}_n\text{C}$$

Thus, Li$^+$ cations must be transferred from the cathode through the electrolyte to the anode.

During the discharge process, the reverse reactions occur and a current is generated through the external circuit from which useful work may be done. The cathode material typically consists of a transition metal oxide (i.e., LiCoO$_2$, LiFePO$_4$, etc.), which can be

<table>
<thead>
<tr>
<th>Component</th>
<th>Functions</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>• Emit lithium-ion to anode during charging • Receive lithium-ion during discharging</td>
<td>Lithium metal oxide powder</td>
</tr>
<tr>
<td>Anode</td>
<td>• Receive lithium-ion from anode during charging • Emit lithium-ion during discharging</td>
<td>Graphite powder</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>• Pass lithium-ions between cathode and anode</td>
<td>Lithium salts and organic solvents</td>
</tr>
<tr>
<td>Separator</td>
<td>• Prevent short circuit between cathode and anode • Pass lithium ions through pores in separator</td>
<td>Micro-porous membranes</td>
</tr>
</tbody>
</table>
oxidized/reduced and retains a structure which permits the deintercalation/intercalation of the 
Li\(^+\) cations. There is a strong demand to transition to new cathode active materials which 
have a significantly higher specific energy,\textsuperscript{13,14} as this may reduce the number of batteries 
needed for a vehicle’s battery pack and thus the total cost. One of the key challenges for 
higher capacity cathode materials is the need to charge them to a much higher voltage (i.e., > 
4.3 V instead of the 3.6 V for current Li-ion cells). New electrolyte formulations are 
necessary to enable stable battery cycling at such high voltages.

Most commercial Li-ion batteries contain graphite as the anode active material. It is 
difficult to replace graphite because of its low cost, high availability and the possibility of 
ready modifications.\textsuperscript{15} There are, however, alternative anode materials—such as Si, Sb or Li 
metal alloys—under development due to their much high capacity (relative to graphite).\textsuperscript{15–17} 
Current electrolyte formulations have been optimized for use with graphite. New 
compositions may be necessary for these alternative anode materials.

1.2 Electrolyte of Lithium Ion Battery

Li-ion battery electrolytes are a sparsely studied topic relative to the research devoted to 
battery electrodes. This is due to the fact that it is the electrodes (composition and amount) 
which determine the energy (capacity) of the battery. Frequently, however, the electrolyte is 
the bottleneck in achieving critical device performance criteria such as device power, 
low/high temperature performance, lifetime, safety, cost, etc.

The current state-of-art electrolyte consists of LiPF\(_6\) with a mixture of carbonate organic 
solvents. This electrolyte formulation has been widely utilized in commercial Li-ion batteries
for more than 25 years, but there are limitations which hinder its use at both high temperature (i.e., 60°C) due to salt degradation and low temperature (i.e., -20°C) due to increased electrolyte viscosity and solvate crystallization. This electrolyte also does not appear to be stable when used with the developmental high-voltage cathode materials and new anodes. Therefore, new electrolytes materials (i.e., salts, solvents and/or additives) are required for advanced Li-ion batteries (and Li-metal batteries) with better performance at a lower cost. To optimize the selection of electrolyte materials, however, a greatly improved understanding of the molecular-level interactions within the electrolytes is needed.

1.2.1 Lithium Salts

The typical electrolyte requirements for a lithium salt include a high thermal stability, high oxidation stability limit, low reduction stability limit, good solubility in appropriate solvents, chemical stability with the solvents, low cost and low molecular weight. Varying the anion structure strongly influences the properties of the electrolyte—such as conductivity, viscosity, the formation of solid-electrolyte interphases (SEI) on the electrodes and the passivation of the Al current collector.\textsuperscript{18} Unfortunately, no single lithium salt satisfies all of these requirements. Therefore, new materials are required or an additive can be used to compensate for deficiencies for a given lithium salt. Typical lithium salts for used for Li-ion batteries (or research) include:\textsuperscript{19}

*LiPF\textsubscript{6}:* This is the dominant salt for current commercial Li-ion battery electrolytes. Electrolytes with LiPF\textsubscript{6} generally have a very high ionic conductivity. The salt, however, is not overly thermally stable at elevated temperatures and easily crystallizes (to form solvates) at low temperature. In addition, the salt is readily hydrolyzed to form HF.
**LiTFSI:** This salt (i.e., lithium bis(trifluoromethanesulfonyl)imide or LiN(SO$_2$CF$_3$)$_2$) has extensive charge delocalization on the TFSI$^-$ anion due to the resonance. Further, the anion is quite flexible. Electrolytes with LiTFSI tend to have a high conductivity, although lower than comparable mixtures with LiPF$_6$. The salt has a much improved thermal stability relative to LiPF$_6$. Unfortunately, electrolytes with LiTFSI tend to not form a passivation layer on the Al current collector used for the composite cathode (with the metal oxide active material, conductive carbon additive and binder). Thus, extensive corrosion of the current collector occurs during battery cycling which prevents the use of this salt in commercial cells.

**LiClO$_4$:** This salt has been used for primary Li-batteries. The salt is thermally unstable and explosive, when mixed with solvents under certain circumstances. Thus, the salt is not widely used for commercial applications.

**LiBF$_4$:** This salt has an improved thermal stability (relative to LiPF$_6$), so that electrolytes with LiBF$_4$ can be used at elevated temperature (≥ 55°C). Further, the conductivity of electrolytes with LiBF$_4$ is generally higher than for those with LiPF$_6$ at low temperature. But the conductivity at ambient temperature is lower than that of comparable electrolytes with LiPF$_6$, which has limited the use of LiBF$_4$ in commercial batteries.

**LiCF$_3$SO$_3$:** This salt has been widely used for polymer electrolytes. The salt has an excellent thermal stability, but also tends to corrode Al current collectors (as for LiTFSI) when used in electrolytes with aprotic solvents. Further, the conductivity of liquid electrolytes with LiCF$_3$SO$_3$ is much lower than for comparable electrolytes with LiPF$_6$. 
1.2.2 Solvents

Solvents can be broadly categorized as protic, dipolar aprotic and low polarity/inert.\textsuperscript{20} Significant anion coordination/solvation is expected in protic solvents (i.e., H\textsubscript{2}O, MeOH, NH\textsubscript{3}, NMF, etc.) due to hydrogen bonding (in addition to cation coordination), but such solvents are poorly suited for lithium battery electrolytes due to their limited electrochemical stability. In contrast, negligible coordination of both cations and anions occurs in low polarity/inert solvents (i.e., \textit{n}-hexane, cyclohexane, etc.) resulting in negligible solubility for lithium salts. Aprotic solvents, however, are useful for electrolyte applications. Ideal aprotic solvents should have a high boiling and flash point for safety, high permittivity and low viscosity to improve the ion transport properties. However, solvents with a high permittivity have strong interactions with each other (i.e., dipole interactions, van der Waals forces, etc.) resulting in a higher viscosity. To obtain both a high permittivity and low viscosity, binary solvent mixtures are used with a high permittivity solvent (i.e., ethylene carbonate (EC)) and another a low viscosity solvent (i.e., diethyl carbonate (DEC)).\textsuperscript{18} In addition, the solvent should react with the graphite electrode to form a solid-electrolyte interface (SEI). Even though EC has a high viscosity and high melting point ($T_m$), it is widely used for electrolyte mixtures because of its high permittivity and the formation of a favorable SEI on the graphite anode. Electrochemical and thermal stability is another important factor for solvent selection. Other solvents (besides EC) for high-voltage electrolytes, such as dinitriles or sulfones, have been considered in recent years.\textsuperscript{21–28} At present, it remains unknown what combination of solvent(s) and salt(s) will provide optimal performance for the new electrode chemistries
under development. Insight into how the solvent and ion structure dictate electrolyte properties is necessary to make significant advances in electrolyte formulations.

1.3 Ionic Association and Ion Solvation

In aprotic solvent-based electrolytes, there are two competing interactions: the interaction between the Li\(^+\) cations and solvent molecules (ion solvation) and the interaction between the Li\(^+\) cations and anions (ionic association). These interactions govern the properties of electrolyte.\(^{19,29–32}\) However, very little information regarding the interactions between the Li\(^+\) cation, anion and solvent molecules is available and the solution structure of electrolytes therefore remains poorly understood.

1.3.1 Solvent Polarity Parameters

Solvent polarity is defined as the summation of all of a solvent’s intermolecular interactions.\(^ {33}\) One widely used parameter for polarity, the donor number (DN), is a qualitative measure of Lewis basicity.\(^ {34,35}\) Thus, the DN indicates the strength of the solvent’s interactions with cations. The acceptor number (AN), in contrast, is a measure of Lewis acidity and thus the solvent’s interactions with anions (typically by hydrogen bonding).

Permittivity (or dielectric constant, \(\varepsilon\)), another widely used parameter for polarity, indicates how a solvent is influenced by an electric field.

These parameters are widely utilized as indicators of the solvent’s role in influencing the ionic association present in an electrolyte. For example, several studies have indicated ionic association differences for solutions with different solvents from measured ionic association constants.\(^ {19,36}\) The association constant, \(K_A\) (ion pair constant), is obtained from a correlation
Table 1-2. *DN, AN* and permittivity of solvents.\textsuperscript{35}

<table>
<thead>
<tr>
<th>solvent</th>
<th><em>DN</em></th>
<th><em>AN</em></th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylformamide (DMF)</td>
<td>27</td>
<td>16</td>
<td>36</td>
</tr>
<tr>
<td>acetonitrile (AN)</td>
<td>14</td>
<td>19</td>
<td>38</td>
</tr>
<tr>
<td>acetone (Me2CO)</td>
<td>17</td>
<td>13</td>
<td>21</td>
</tr>
<tr>
<td>diethyl ether (Et2O)</td>
<td>19</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>tetrahydrofuran (THF)</td>
<td>20</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2-methyl-THF (2-MeTHF)</td>
<td>18</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>monoglyme (1,2-DME or G1)</td>
<td>20</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>diglyme (G2)</td>
<td>24</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>diethylamine (Et2NH)</td>
<td>&gt;50</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>ammonia (NH3)</td>
<td>50</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>ethanol (EtOH)</td>
<td>20</td>
<td>38</td>
<td>24</td>
</tr>
<tr>
<td>water (H2O)</td>
<td>18-33</td>
<td>55</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 1-3. Ion pair association constant of mixtures of solvent and salt.\textsuperscript{33,36}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Salt</th>
<th><em>K_A</em> (L·mol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-MeTHF</td>
<td>LiClO\textsubscript{4}</td>
<td>1.8×10\textsuperscript{8}</td>
</tr>
<tr>
<td>THF</td>
<td>LiClO\textsubscript{4}</td>
<td>4.8×10\textsuperscript{7}</td>
</tr>
<tr>
<td>G1</td>
<td>LiClO\textsubscript{4}</td>
<td>3.6×10\textsuperscript{6}</td>
</tr>
<tr>
<td>2-MeTHF</td>
<td>LiAsF\textsubscript{6}</td>
<td>3.3×10\textsuperscript{7}</td>
</tr>
<tr>
<td>THF</td>
<td>LiAsF\textsubscript{6}</td>
<td>2.8×10\textsuperscript{5}</td>
</tr>
<tr>
<td>G1</td>
<td>LiAsF\textsubscript{6}</td>
<td>1.3×10\textsuperscript{5}</td>
</tr>
<tr>
<td>THF</td>
<td>LiSbF\textsubscript{6}</td>
<td>2.7×10\textsuperscript{5}</td>
</tr>
<tr>
<td>G1</td>
<td>LiSbF\textsubscript{6}</td>
<td>1.1×10\textsuperscript{5}</td>
</tr>
<tr>
<td>THF</td>
<td>LiBPh\textsubscript{4}</td>
<td>2.2×10\textsuperscript{4}</td>
</tr>
<tr>
<td>2-MeTHF</td>
<td>LiBPh\textsubscript{4}</td>
<td>8.3×10\textsuperscript{4}</td>
</tr>
<tr>
<td>G1</td>
<td>LiBPh\textsubscript{4}</td>
<td>2.6×10\textsuperscript{4}</td>
</tr>
</tbody>
</table>
between the limiting molar conductivity and salt concentration. Although THF, 2-MeTHF and G1 have similar $DN$, $AN$ and permittivity values (Table 1-2), the solvents have a widely varying degree of ionic association with different lithium salts (Table 1-4). Similarly, a comparison of the ionic association of LiCF$_3$SO$_3$ in THF, G1 or G2 with the fraction of different solvate species in solution (from spectroscopic measurements) again indicates a different degree of ionic association (Fig. 1-4),$^{37}$ despite the similarity in the solvent properties (Table 1-2). These polarity parameters, therefore, do not account for all of the factors which are crucial for determining ionic association interactions and the corresponding solution structure. The degree of ionic association (solvate species present) can instead be experimentally determined directly rather than relying on such polarity parameters.

![Figure 1-4. Fractions of (THF)$_n$-LiCF$_3$SO$_3$ and (glyme)$_n$-LiCF$_3$SO$_3$ solvate species determined from vibrational spectroscopic studies of ionic association at variable temperatures with a fixed concentration of EO/Li = 20.$^{37}$](image)

$^{37}$
1.3.2 Solvate Species in Solution

When a lithium salt is dissolved in a given solvent, the Li$^+$ cations are coordinated by solvent molecules resulting in the dissolution of the salt and creation of various solvate structures. These solvates may be classified as either solvent-separated ion pair (SSIP), contact ion pair (CIP) or aggregate (AGG) solvates depending upon whether the anions are coordinated by zero, one, or more than one Li$^+$ cation, respectively (Fig. 1-5). The solvate structures present in solvent-salt mixtures are dependent upon several factors such as the type of solvent donor atoms, solvent capability of coordination as a multidentate ligands, solvent steric effects, salt concentration, etc.

The type of donor atom influences the strength of the coordinated bond formed between

\[
\text{Figure 1-5. Types of crystalline lithium salt solvates in THF solvents.}^{31}
\]
the Li\(^+\) cations and solvent molecules. This is reflected by the magnitude of the solvent donor number (\(DN\)). Li\(^+\) cations are generally coordinated by 3-8 donor atoms, with 4-6 donor atoms being typical, via the electron lone-pairs of the donor atoms.\(^{38}\) For many solvents, the donor atom is either oxygen which has two lone-pairs or nitrogen which has one. When a salt dissolves in a solvent with a high \(DN\) and a low \(AN\), the cations of the salt become coordinated by solvent molecules, as there are only weak anion-solvent interactions, with a competition existing between the solvent molecules and anions for coordination to the cations. If the strength of the solvent donor atom coordination to the Li\(^+\) cation is much stronger than that of the anions, then the cations tend to be surrounded by solvent molecules and SSIP solvates are formed (Fig. 1-5). The anions thus remain uncoordinated. Otherwise, the solvates formed are CIPs or AGGs as stronger cation-anion interactions lead to ionic association forming solvate structures in which one or more cations are coordinated to a given anion (Fig. 1-5).\(^{29,30}\)

Some solvents are able to coordinate a given cation with more than one donor atom. Such multidentate solvents (e.g., G1, G2, etc.) have a significant influence on the solvate structures formed and degree of ionic association.\(^{37,39-42}\) The strength of a specific coordination bond varies with thermal fluctuations and steric interactions with neighboring atoms in the liquid state. The solvent exchange rate indicates how frequently a solvent molecule in a solvate is replaced with a new solvent molecule (or anion) thus influencing the stability of solvates. Multidentate solvents tend to have much lower exchange rates than monodentate solvents. Although one coordination bond may be broken, the remaining coordination bond(s) to the Li\(^+\) cation keep the solvent molecule located near the cation. Thus, there is high probability
of the Li\(^+\) cation reforming the original coordination bond rather than forming a new bond with a donor atom of a different neighboring solvent molecule. G2, therefore, tends to stick to Li\(^+\) cations much better than THF thus helping to exclude anion coordination.

Steric effects also influence solvate structure formation. The structure of a solvent molecule coordinated to a cation may interfere with the coordination of neighboring solvent molecules to the same cation. For example, THF and Et\(_2\)O have similar structures and the same oxygen donor atom, but Et\(_2\)O solutions with lithium salt are more aggregated than those with THF. THF has a cyclic ring in which the ethyl groups are bound together, while Et\(_2\)O has two unbound ethyl groups which are free to adopt several conformations. Thus, thermal energy may cause these ethyl groups to sterically interfere with neighboring ethyl groups. Both THF and Et\(_2\)O are known to form SSIP crystalline solvates in which Li\(^+\) cations are coordinated by four solvent molecules, but THF solvates are more commonly observed due to their much higher thermal stability.\(^{43-45}\) Further, lithium salts in solutions with 2,5-dimethylTHF are more associated than those with 1,3-dioxolane and THF because of steric effects.\(^{46}\) At lower temperature, however, the steric effects are less significant due to decreased thermal motion. Thus, solutions tend to become more aggregated with increasing temperature.

The solvent to solute ratio (concentration) also affects the degree of ionic association. In dilute solutions, many solvent molecules are available for cation coordination. The actual association present in dilute solution, however, is determined by the factors just discussed. But with increasing concentration of salt, less solvent molecules are available for Li\(^+\) cation
coordination. Thus, with increasing solute concentration, ionic association also tends to increase.

1.3.3 Degree of Ionic Association

Generally, in solution, there is a dynamic equilibrium between the formations of the solvates. Through a combination of thermal, spectroscopic and x-ray structural analysis, the structures of solvates in solution and thus the degree of ionic association can be measured.

Thermal characterization of solvent-LiX salt solutions may be used to generate phase diagrams (Fig. 1-6). Phase diagrams indicate the crystalline phases present at a specific temperature and concentration. Unlike solvates in solution, crystalline solvates have a specific solvate structure determined by the solvent and ion packing constraints and the competition between the solvent and anion for Li\(^+\) cation coordination. The crystalline phases are determined by the type of solvent, the concentration of the solvent, the temperature, and

![Figure 1-6. DSC data and phase diagram of (G1)\(_n\) LiClO\(_4\) with various concentration.\(^{37}\)](image-url)
anion structures.\textsuperscript{37} Once the specific solvate compositions and thermal stability of the phases have been determined from the phase diagrams, the structure of the specified solvate crystalline phases may be obtained using X-ray structural analysis. A knowledge of the solvate structures provides a key tool for examining how the ions and solvent molecules interact with each other in a crystalline phase. Further, this information is extremely valuable when combined with vibrational analysis to determine the degree of ionic association present in electrolytes.

Raman spectroscopy is an excellent probe for identifying solvate structures, i.e., SSIPs, CIPs and AGGs, as the solvent and anion vibrational bands may be used to identify the fraction of the solvent which coordinates Li\textsuperscript{+} cations and the specific forms of anion...Li\textsuperscript{+} cation coordination and their distribution.\textsuperscript{31,40,41,47–52} As coordination bonds form between the anions and Li\textsuperscript{+} cations, the anion band positions shift. To clearly identify the ion coordination (and thus type of solvates) in the liquid (solution) phase of the solvent-lithium salt mixtures, however, it is helpful to have models of the anion spectra for specific forms of anion...Li\textsuperscript{+} cation coordination. By examining the Raman spectra of known crystalline solvate phases (from the phase diagram and crystal structures), however, it is possible to unequivocally identify the spectral fingerprint for the various forms of coordination which exist in the liquid phase and thus determine, with some accuracy, the extent of ionic association and solvation present (i.e., solution structure).

For example, a Raman spectroscopic analysis of liquid phase solvates was previously conducted after examining known (glyme)\textsubscript{n}:LiClO\textsubscript{4} crystalline solvates.\textsuperscript{41} Fig. 1-7 shows a complex, asymmetric peak in the region of the anion \(v_1\) (Cl-O stretch) vibration for a liquid
solution of \((\text{tetraglyme(G4)})_n\)-\(\text{LiClO}_4\) \((n = 0.5)\) at 70°C. This peak can be separated into three symmetric peaks, which represent different types of anion coordination. Using information obtained from known crystalline solvate structures, the Raman spectral peaks for the different forms of anion coordination may be distinguished. The peak for the uncoordinated \(\text{ClO}_4^-\) anion (SSIP) is at 933 cm\(^{-1}\). When the anion is coordinated by a single \(\text{Li}^+\) cation (CIP), the peak shifts to 939 cm\(^{-1}\), and the peak at 946 cm\(^{-1}\) originates from an anion coordinated by two \(\text{Li}^+\) cations (AGG). The area of each peak can be calculated by integration enabling the relative amount of each type of solvate to be determined. In this case, the bands provide a population of the SSIP, CIP and AGG solvates of 23, 44, and 33%, respectively. Thus, using this method, the types of solvate in solution can be determined, as well as their distribution, allowing for the determination of the degree of ionic association in the solution with varying solvents, concentrations and temperature.

![Raman spectrum analysis of solvate structure in (G4)_n-LiClO_4 (n = 0.5).](image)

**Figure 1-7.** Raman spectrum analysis of solvate structure in \((\text{G4})_n\)-\(\text{LiClO}_4\) \((n = 0.5)\).
1.4 Motivation for the Present Study

To identify promising electrolytes, many compositions (with new anions and/or solvents) have been introduced, tested and optimized by a trial-and-error method by numerous researchers. This Edisonian approach to electrolyte development is quite restrictive, however, for the rapid evolution of new battery chemistries. In aprotic solvent-based electrolytes, the competition between the solvent (solvation) and anion (ionic association) for Li\(^+\) cation coordination is crucial for dictating electrolyte properties, but little is known about this at present due to strong limitations for characterizing solution structure. Many of the widely used tools for understanding electrolyte interactions (i.e., polarity parameters, vibrational spectroscopic characterization, etc.) are misunderstood and/or misused. Thus, much of the information available about electrolyte interactions in the scientific literature is inaccurate and perhaps misleading. To address these concerns, the present study has focused on combining new tools which are not widely utilized (i.e., phase diagrams and solvate crystal structures) with greatly improved characterization methods (i.e., a rigorous evaluation of Raman anion band correlation with specific forms of anion...Li\(^+\) cation coordination). These tools have been applied to the study of the interactions within a range of electrolyte mixtures composed of solvents with varying structure (i.e., nitriles, cyclic carbonates and cyclic esters) and selecting lithium salts (chosen to have anions with varying ionic association strength). This study clearly permits the dissection of the relevant features of the solvents and anions which result in widely varying solvate formation in solution. This information (i.e., solution structure) has then been directly correlated with variations in electrolyte transport properties (i.e., viscosity, conductivity), thereby enabling a mechanistic explanation for the differences
noted in the electrolyte properties. Given that no comprehensive theory exists for predicting
the properties of concentrated (weak) electrolytes,\textsuperscript{20} this represents a tremendous advance for
the development of a "looking glass" into the molecular-level interactions in bulk
electrolytes, thereby enabling the rational design of electrolytes for a wide variety of battery
chemistries and applications (low/high temperature, high power, etc.)—electrolytes-on-
demand.

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CHAPTER 2 Experimental Procedures

2.1 Materials

2.1.1 Lithium Salts

Fig. 2-1 shows the molecular structure of the lithium salts used for this study. LiBF$_4$ (anhydrous, 99.99%), LiClO$_4$ (battery-grade, 99.998%), LiCF$_3$SO$_3$ (99.995%) and LiNO$_3$ (99.99%) were purchased from Sigma-Aldrich and used as-received. LiBF$_4$ and LiClO$_4$ (electrolyte-grade) were also purchased from Novolyte and used as-received. LiCF$_3$CO$_2$ (95%) was purchased from Sigma-Aldrich and dried at 120°C for 24 h. LiTFSI and LiPF$_6$ (battery-grade) were purchased from 3M Company and Novolyte, respectively. LiTFSI was dried at 120°C for 24 h.

![Structures and acronyms of the lithium salts used.](image)

2.1.2 Solvents

Fig. 2-2 shows a list of the solvents used and their acronyms. Acetonitrile (AN, anhydrous, 99.9%), propionitrile (PN, 99%), butyronitrile (BN, > 99%), succinonitrile (SN, > 99%), ethylene carbonate (EC, 99%, < 0.005% H$_2$O), propylene carbonate (PC, > 99.0%, < 0.01% H$_2$O), γ-butyrolactone (GBL, > 99%), γ-valerolactone (GVL, 99%), tetrahydrofuran
(THF, anhydrous, ≥ 99.9%), ethylene glycol dimethyl ether or 1,2-dimethoxyethane (monoglyme or G1, anhydrous, 99.5%), diethylene glycol dimethyl ether or 2-methoxyethyl ether (diglyme or G2, anhydrous, 99.5%), triethylene glycol dimethyl ether (triglyme or G3, 99%), 1,2-dimethoxypropane (DMP, ≥ 99%), ethylene glycol diethyl ether or 1,2-diethoxyethane (Et-G1, 98%), diethylene glycol diethyl ether (Et-G2, reagent grade, ≥ 98%), methyl acetate (MA, ≥ 98%), ethyl acetate (EA, anhydrous, 99.8%), methyl methoxyacetate

Figure 2-2. Structures and acronyms of the solvents used.
(MMA, 99%), methanol (Me-OH, anhydrous, 99.8%), 1,4,7,10-tetraoxacyclododecane or 12-crown-4 (12C4, 98%), \(\text{N},\text{N},\text{N}',\text{N}''\)-pentamethyldiethylenetriamine (PMDETA, 99%), \(\text{N},\text{N},\text{N}',\text{N}''\)-tetramethylethylenediamine (TMEDA, purified by redistillation, \(\geq 99.5\)%), phenanthroline (PHEN, \(\geq 99\)%), 2,6-lutidine or 2,6-dimethylpyridine (DMPy, \(\geq 99.0\)%)

were purchased from either Sigma-Aldrich, Novolyte and/or Fisher Scientific. These solvents were dried over 3 Å molecular sieves and the water content of the solvents was verified to be negligible (<30 ppm) using a Mettler Toledo DL39 Karl Fischer coulometer.

2.2 Sample Preparation

Samples were prepared in a Vacuum Atmospheres inert atmosphere (N\(_2\)) glovebox (<5 ppm H\(_2\)O) by combining the appropriate amounts of salt and solvent in hermetically sealed vials and heating/stirring on a hot plate to form homogeneous solutions. The compositions are generally described using three notations: \((1-x)\) solvent-(\(x\)) LiX, \((\text{solvent})_n\)-LiX and \((\text{solvent})_n\):LiX, respectively, for discussions focusing on mole fraction, ratio of solvent/Li and specific crystalline solvates.

To obtain single crystals, mixtures more dilute than the desired solvate stoichiometry were typically prepared. Single crystals grew from the mixtures upon standing either at room temperature, at 4°C (in a refrigerator) or at -23°C (in a freezer). In some case, inert solvents, such as methanol, toluene or hexane were also added. The obtained single crystals were used both for the determination of the solvate structures via single-crystal x-ray diffraction and for Raman analysis. For the latter, the crystals were ground in the glovebox into a fine powder using a mortar and pestle (if the melting point \(T_m\) of the solvate is greater than room temperature). If the solvates melt at or below room temperature, then liquid samples of the
appropriate composition were instead prepared in the glovebox and the samples were crystallized directly in the Linkam heating/cooling stage during the Raman measurements (note that this sometimes produced large crystals for which orientational effects impact the Raman peak intensities).

2.3 Instruments and Techniques

2.3.1 Differential Scanning Calorimetry (DSC)

DSC measurements were performed with a TA Instruments Q2000 DSC with liquid N\textsubscript{2} cooling. The instrument was calibrated with cyclohexane (solid-solid phase transition at -87.06°C, \(T_m\) at 6.54°C) and indium (\(T_m\) at 156.60°C). Hermetically-sealed Al sample pans were prepared in the glovebox. The sample pans were cycled (5°C min\(^{-1}\)) and annealed repeatedly at subambient temperature to fully crystallize the samples when possible. Once the samples were crystallized, the pans were cooled to -150°C and then heated (5°C min\(^{-1}\)) to fully melt the samples. The final heating traces are generally reported. Peak temperatures from these data were then used to construct the phase diagrams.

2.3.2 Raman Spectroscopy

Raman vibrational spectra were collected with a Horiba-Jobin Yvon LabRAM HR VIS high resolution confocal Raman microscope, using a 632 nm\(^{-1}\) He-Ne laser as the exciting source and a Linkam heating/cooling stage for temperature control with a long distance 50X objective. The instrument was calibrated with a monocrystalline Si wafer at 520.7 cm\(^{-1}\). The samples were contained in a stainless steel well which was hermetically sealed in the Linkam stage in the glovebox before transferring the stage to the spectrometer. Spectra were typically collected using a 10-30 s exposure time with ten accumulations to ensure that high resolution
spectra were obtained. The samples were cooled/heated at a 20°C min\(^{-1}\) rate and the spectra were collected from -100°C to 60°C at intervals of 20°C. Raman spectra were processed using LabSpec software.

### 2.3.3 Solvate Crystal Structure Determination

X-ray structural determination was conducted by Dr. P. D. Boyle in the Department of Chemistry at North Carolina State University. Crystals were typically mounted on nylon loops with a small amount of Paratone N oil. X-ray measurements were made on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer. The unit cell dimensions were determined from symmetry constrained fits of the reflections. The frame integrations were performed using SAINT.\(^1\) The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.\(^2\) The structures were solved by direct methods using either SIR92 or XS.\(^2\) All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural models were fit to the data using full matrix least-squares based on \(F^2\). The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structures were refined using the XL program from SHELXTL.\(^3\)

### 2.3.4 Density/Viscosity Measurements

Viscosity and density measurements were conducted using a Anton Paar SVM 3000 Stabinger viscometer. The instrument was calibrated using Cannon viscosity (density) standard fluids as follows: 3.689 mPa s\(^{-1}\) (0.8150 g cm\(^{-3}\)), 50.02 mPa s\(^{-1}\) (0.8209 g cm\(^{-3}\)) and 1105 mPa s\(^{-1}\) (0.8456 g cm\(^{-3}\)) at 20°C. The tests were performed from 0°C to either 60°C or
100°C (depending the boiling point \(T_b\) of solvents). Measurements were taken in 10 °C steps. Sample sizes of at least 2.6 ml were needed for the measurements and great care was taken to not expose the samples to air (and thus water) prior to and during the measurements. EA and N\(_2\) gas (> 99.99%, water concentration 2-5 ppm) were used to clean the instrument before and after the measurements. The water concentration of the samples was determined before and after the measurements to verify that no contamination occurred.

### 2.3.5 Conductivity Measurements

The ionic conductivity (\(\kappa\) or \(\sigma\)) was determined through impedance spectroscopy, using an AMEL Instruments two electrode cell with Pt electrodes. Experiments were performed from 1 MHz to 20 Hz with a 10 mV AC perturbation and no DC bias. Cell constants were determined for each conductivity cell using aqueous KCl standard solutions at 25°C. Conductivity values were measured typically while cooling from 100 °C to -40°C with the samples equilibrated at each temperature for approximately 45 min. The salt molar concentration \(C\) (mol-salt dm\(^{-3}\)) values were calculated from the concentration \(m\) (mol-salt kg\(^{-1}\)-solution) and density \(\rho\) (g-solution cm\(^{-3}\)) of each solution. Molar conductivity values were obtained from the conductivity and density data.

### 2.4 References


CHAPTER 3
Crystalline Solvates Structures and Ionic Association Interactions

3.1 Introduction

Understanding the structure of liquid electrolytes remains a key challenge for linking the solution structure with electrolyte properties. Vibrational spectroscopic analyses of electrolyte mixtures provide crucial insight regarding the molecular-level interactions between the anions and cations (i.e., ionic association), but the interpretation of the results is often challenging. In solution, solvates form which may be classified as having either solvent-separated ion pair (SSIP), contact ion pair (CIP) or aggregate (AGG) coordination depending upon whether the anions are coordinated with zero, one, or more than one Li$^+$ cations, respectively (Figs. 3-1 and 3-2). Which solvates form and their distribution directly impacts electrolyte properties. Knowledge of solvate formation in solution is therefore necessary to fully understand the origin of the properties of electrolytes—a key challenge for many electrochemical applications.

When an anion coordinates one or more Li$^+$ cations, the anion bond lengths/angles change as a result of variations in the electron density distribution. This results in the shifting of the vibrational bands for the anion. These shifts can be correlated with specific forms of anion...Li$^+$ cation coordination. Information regarding the correct assignment of the anion bands to these specific forms of coordination, however, is generally unavailable. Assignments are often made based upon computational analyses (DFT calculations), but such calculations rarely directly match experimental results and there is limited information
**Figure 3-1.** Examples of BF$_4^-$...Li$^+$ cation coordination: (a) SSIP, (b) CIP-I, (c) CIP-II, (d) AGG-I, (e) AGG-II and (f) AGG-III.

**Figure 3-2.** Examples of TFSI...Li$^+$ cation coordination: (a) SSIP-C$_1$, (b) SSIP-C$_2$, (c) CIP-I-C$_2$, (d) CIP-II-C$_1$, (e) AGG-Ia-C$_2$, (f) AGG-Ib-C$_2$, (g) AGG-IIb-C$_1$, (h) AGG-IIb-C$_2$ and (i) AGG-III-C$_2$. 
available to validate such calculations. Thus, significant guesswork remains for the Raman band assignments to determine the ionic association interactions in solvent-lithium salt mixtures. If the band assignments are misconstrued, then highly misleading conclusions can result from the analysis of electrolyte mixtures.

Although LiPF$_6$ remains the dominant salt for current state-of-the-art lithium battery electrolyte mixtures, this salt has limitations which hinder its use in electrolytes at both high temperature (i.e., 60°C) due to thermal degradation and low temperature (i.e., -20°C) due to increased electrolyte viscosity and solvate crystallization. Under similar extreme conditions, LiBF$_4$- and LiTFSI-based electrolytes have improved performance at both high and low temperature relative to those with LiPF$_6$. Further, both are highly useful salts for probing electrolyte interactions as the anions can be classified as dissociated and intermediate salt, respectively, in its association tendency with Li$^+$ cations when the salt is dissolved in aprotic solvents. To fully utilize these salts and understand their molecular-level interactions, however, it must be possible to deconvolute the complex Raman spectra obtained for liquid electrolyte mixtures which consist of overlapping Raman bands due to a wide distribution of solvate species present in solution. In the present study, therefore, the Raman band positions for various forms of BF$_4$... and TFSI…Li$^+$ cation coordination have been unambiguously assigned by correlating the Raman bands with solvate crystal structures. These solvates structures, in and of themselves, provide detailed insight into the solvation and ionic association interactions which govern solvate formation. The results suggest that the conclusions drawn about anion interactions from previously reported electrolyte studies
may be either incorrect or oversimplifications of the actual complex equilibrium of the solvate species present and thus may require reevaluation.\textsuperscript{1,18–28}

### 3.2 BF\textsubscript{4}\textsuperscript{-} Anion Raman Band Characterization

#### 3.2.1 Solvate Structures and Li\textsuperscript{+} Cation Coordination

The manner in which Li\textsuperscript{+} cations are solvated is of significant interest for understanding electrolyte interactions. Solvate crystal structures provide direct information about the coordination of the anions and solvent to the Li\textsuperscript{+} cations which is unobtainable through other means. Very limited information about solvate structures has been available, however, until quite recently. LiBF\textsubscript{4} solvate structures include (Figs. 3-3 and 3-4)—SSIP: (G2)\textsubscript{2}:LiBF\textsubscript{4},\textsuperscript{29} CIP-I: (G1)\textsubscript{2}:LiBF\textsubscript{4}\textsuperscript{30} and (G3)\textsubscript{1}:LiBF\textsubscript{4},\textsuperscript{31} AGG-I: (G2)\textsubscript{1}:LiBF\textsubscript{4}\textsuperscript{29}, (EC)\textsubscript{1}:LiBF\textsubscript{4}, (AN)\textsubscript{2}:LiBF\textsubscript{4}, (Et-G1)\textsubscript{1}:LiBF\textsubscript{4} and (Et-G2)\textsubscript{1}:LiBF\textsubscript{4}; AGG-II: (GBL)\textsubscript{1}:LiBF\textsubscript{4}, (AN)\textsubscript{1}:LiBF\textsubscript{4},\textsuperscript{32} (MA)\textsubscript{1}:LiBF\textsubscript{4}, (EA)\textsubscript{1}:LiBF\textsubscript{4}, (THF)\textsubscript{1}:LiBF\textsubscript{4}, (MMA)\textsubscript{1}:LiBF\textsubscript{4} and (SN)\textsubscript{1}:LiBF\textsubscript{4}. The crystal structure of the pure LiBF\textsubscript{4} salt (Fig. 3-3) is also known.\textsuperscript{33}

Surprising results were obtained when the synthesis of LiBF\textsubscript{4} solvates with amine solvents—PMDETA, TMEDA and PHEN (Fig. 2-2)—was attempted. To increase the solubility and make liquid-based mixtures, anhydrous methanol was added to the mixtures of LiBF\textsubscript{4} and the amine solvents. The mixtures were then heated in hermetically sealed vials in the glove box to make homogenous solutions. Upon storage at room temperature, single crystals grew from the solutions, but X-ray diffractional analysis to determine the structures produced solvates with HBF\textsubscript{4} rather than LiBF\textsubscript{4}: (PMDETA)\textsubscript{1}:HBF\textsubscript{4}, (TMEDA)\textsubscript{3/2}:HBF\textsubscript{4} and (PHEN)\textsubscript{2}:HBF\textsubscript{4} (Fig. 3-5). This indicated that a methanol deprotonated reaction occurred. To verify the reproducibility of the reaction and that it was not due to impurities, the pH of the
methanol was checked to confirm that it was not acidic. In addition, two different source of LiBF$_4$ (Sigma-Aldrich and Novolyte) were used and the same preparation procedure was repeated. The same solvates were produced in both cases.

Li$^+$ cations can have coordination numbers which vary from three to eight in crystalline solvates, but three-fold coordination is extremely rare. It is energetically favorable to

**Figure 3-3.** BF$_4^-$...Li$^+$ cation coordination in crystalline solvates and the pure LiBF$_4$ salt: (a) SSIP (G2)$_2$:LiBF$_4$, (b) CIP-I (G1)$_2$:LiBF$_4$, (c) CIP-I (G3)$_1$:LiBF$_4$, (d) AGG-I (G2)$_1$:LiBF$_4$, (e) AGG-I (EC)$_1$:LiBF$_4$, (f) AGG-II (GBL)$_1$:LiBF$_4$, (g) AGG-II (MA)$_1$:LiBF$_4$, (h) AGG-II (EA)$_1$:LiBF$_4$, (i) AGG-II (AN)$_1$:LiBF$_4$, and (j) AGG-III pure LiBF$_4$.33
Figure 3-4. BF$_4^-$...Li$^+$ cation coordination in crystalline solvates: (a) AGG-I (AN)$_2$:LiBF$_4$, (b) AGG-I (Et-G1)$_1$:LiBF$_4$, (c) AGG-I (Et-G2)$_1$:LiBF$_4$, (d) AGG-II (THF)$_1$:LiBF$_4$, (e) AGG-II (MMA)$_1$:LiBF$_4$ and (f) AGG-II (SN)$_1$:LiBF$_4$. 
generally have four-fold coordination because of steric factors between the coordinating solvent molecules and anions.\textsuperscript{35} For solvents which are flexible and have multiple donor atoms (such as glymes), however, solvates are frequently found to have higher than four-fold coordination to the Li\textsuperscript{+} cations. Examples include (G1)\textsubscript{2}:LiBF\textsubscript{4}, (G2)\textsubscript{2}:LiBF\textsubscript{4}, (Et-G2)\textsubscript{1}:LiBF\textsubscript{4}, (MMA)\textsubscript{1}:LiBF\textsubscript{4} and (G3)\textsubscript{1}:LiBF\textsubscript{4} (Figs. 3-3 and 3-4) which have five- or six-fold coordination. When greater than four-fold coordination does occur, the crowding of the

**Figure 3-5.** BF\textsubscript{4}\textsuperscript{−} anion coordination in crystalline HBF\textsubscript{4} solvates: (a) SSIP (PMDETA)\textsubscript{1}:HBF\textsubscript{4}, (b) SSIP (TMEDA)\textsubscript{3/2}:HBF\textsubscript{4} and (c) SSIP (PHEN)\textsubscript{2}:HBF\textsubscript{4}.  


donor atoms about the Li$^+$ cations results in increased coordination bond lengths (weaker bonds) due to steric factors. The (SN)$_1$:LiBF$_4$ solvate (Fig. 3-4), however, also has five-fold coordination of the solvent molecules and anions to the Li$^+$ cations. Although the SN molecules do have two donor atoms, the molecules are unable to adopt a conformation which enables the coordination of both to the same Li$^+$ cation. Thus, the SN molecules are instead coordinated to two Li$^+$ cations, in contrast to the glyme and MMA solvents. This demonstrates that five-fold coordination is found, although it is uncommon, even without solvent molecules that can form multidentate coordination bonds to the Li$^+$ cations. One of the BF$_4^-$...Li$^+$ cation bonds, however, in the (SN)$_1$:LiBF$_4$ solvate is quite long (see below) indicating a weak coordination bond. No examples of BF$_4^-$ anions with bidentate coordination to the Li$^+$ cations were identified in the present study (Figs. 3-3, 3-4 and 3-5) despite the fact that gas-phase DFT calculations of BF$_4^-$...Li$^+$ cation coordination indicate that bidentate and tridentate coordination are more favorable than monodentate coordination. Such calculations, however, neglect the interactions of the coordinated solvent (or additional anions) in the solvates present in liquid electrolytes and crystalline solvates.

The structure of the solvent is a prominent determinant for which solvate structures form. The G1, Et-G1 and DMP solvents have similar structures with two ether oxygen atoms separated by a flexible ethyl group (Fig. 2-2). From dilute mixtures, the (G1)$_2$:LiBF$_4$ solvate crystallizes as an isolated CIP-I solvate (Fig. 3-3). (Et-G1)$_n$:LiBF$_4$ mixtures, however, do not form a 2/1 crystalline phase, but instead form a 1/1 crystalline phase. Unlike the (G1)$_2$:LiBF$_4$ solvate, the (Et-G1)$_1$:LiBF$_4$ solvate is a polymeric AGG-I structure in which the Et-G1 molecules wrap around the Li$^+$ cations, while the coordinated BF$_4^-$ anions link the
solvated cations together (Fig. 3-4). A DSC characterization of a crystallized (Et-G1)\(n\)-LiBF\(_4\) (\(n = 2\)) mixture shows the melting peak of pure Et-G1 at -75°C and another melting peak above room temperature for the (Et-G1)\(_1\):LiBF\(_4\) phase indicating that a 2/1 crystalline phase does not form with this solvent, perhaps due to constraints on the Li\(^+\) cation coordination from the end ethyl groups (rather than methyl groups for G1) of the solvent molecules. A DSC characterization of a crystallized (DMP)\(n\)-LiBF\(_4\) (\(n = 2\)) mixture displayed only one sharp melting peak, which indicates the formation of a (DMP)\(_2\):LiBF\(_4\) solvate (\(T_m 3^\circ C\)). Raman data suggest that this solvate has CIP coordination (see below). Therefore, the addition of the methyl group to the ethylene portion of the G1 solvent (to form DMP) does not appear to affect the type of solvate formed. For the G2 and Et-G2 solvents, mixtures of both with LiBF\(_4\) form a 1/1 phase with AGG-I coordination. But the (G2)\(_1\):LiBF\(_4\) solvate is a dimer (Fig. 3-3),\(^{29}\) whereas the (Et-G2)\(_1\):LiBF\(_4\) solvate is instead polymeric with [BF\(_4\)^-... Li\(^+\)]\(_n\) cation chains (Fig. 3-4). Furthermore, the (Et-G2)\(n\)-LiBF\(_4\) mixtures do not form a SSIP 2/1 solvate, as occurs for (G2)\(n\)-LiBF\(_4\) mixtures (Fig 3-3).\(^{29,41}\) These comparisons demonstrate the importance of solvent structure on solvate formation.

### 3.2.2 Raman Spectroscopic Analysis of LiBF\(_4\) Crystalline Solvates

The free, tetrahedral BF\(_4^-\) anion belongs to the \(T_d\) point group with four active Raman vibrational modes—\(v_1(A_1) + v_2(E) + v_3(F_2) + v_4(F_2)\). Of the modes available, the B-F symmetric stretching mode (\(v_1\)) near 795 cm\(^{-1}\) has the strongest intensity (Fig. 3-6)\(^{22,42,43}\) and has generally been used as the probe for determining BF\(_4^-\) ionic association interactions.\(^{18-28}\) The other vibrational bands have both a low intensity and a broad shape. These bands, in contrast to the band for the \(v_1\) mode, provide inconsistent information to distinguish different
type of anion coordination. One explanation for this for some of the bands is that boron isotopes have a natural abundance of 19.9% $^{10}$B and 80.1% $^{11}$B. Two bands can thus be expected for each of the BF$_4^-$ anion vibrational modes in which the boron nucleus is displaced. In the present study, therefore, the Raman spectra of the crystalline solvates of LiBF$_4$ (and HBF$_4$) were analyzed to unambiguously assign the band positions of the $v_1$ mode for the uncoordinated BF$_4^-$ anion and the anion coordinated to one or more Li$^+$ cations.

Among the solvates analyzed, there is only one SSIP LiBF$_4$ solvate with a known structure—(G2)$_2$:LiBF$_4$ (Fig. 3-3).$^{29}$ This solvate, in which the BF$_4^-$ anions are uncoordinated to the Li$^+$ cations, has the Raman band positioned at ~764-765 cm$^{-1}$ (Fig. 3-7). (AN)$_4$:LiBF$_4$ and (12C4)$_2$:LiBF$_4$ crystalline solvate were also analyzed. From a previously reported phase diagram,$^1$ the formation of the (AN)$_4$:LiBF$_4$ solvate ($T_m$ -13°C) was confirmed and it was assumed to be a SSIP solvate, despite the lack of a known crystal structure, as for the known (AN)$_4$:LiClO$_4$ and (AN)$_4$:LiI solvate crystal structures.$^{44,45}$ The formation of a (12C4)$_2$:LiBF$_4$ solvate ($T_m$ 110°C) was confirmed with elemental analysis. This is also postulated to be a
SSIP solvate, as is found for all of the many known (12C4)$_2$:LiX solvates.\textsuperscript{46-50} The anion Raman band for both of these solvates is located in the same position as for the (G2)$_2$:LiBF$_4$ solvate (Fig. 3-7). Furthermore, the anion band for the three HF$_4$ solvates with

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-7.png}
\caption{Raman spectra of the BF$_4^-$ anion $v_1$ vibrational band for the SSIP crystalline solvates: (a) (G2)$_2$:LiBF$_4$, (b) (AN)$_4$:LiBF$_4$, (c) (12C4)$_2$:LiBF$_4$, (d) (PMDETA)$_1$:HBF$_4$, (e) (TMEDA)$_{3/2}$:LiBF$_4$ and (f) (PHEN)$_2$:HBF (the bold curves indicate that the solvate melted).}
\end{figure}
uncoordinated anions (Fig. 3-5) was also found positioned with these other SSIP solvate bands (Fig. 3-7), as expected.

Two CIP-I solvates were previously reported—(G1)₂:LiBF₄ and (G3)₁:LiBF₄ (Fig. 3-3). These CIP solvates have the Raman band positioned at ~767 cm⁻¹ (Fig. 3-8). These

![Raman spectra of the BF₄⁻ anion v₁ vibrational band for the CIP crystalline solvates: (a) (G1)₂:LiBF₄, (b) (G3)₁:LiBF₄ and (c) (DMP)₂:LiBF₄.](image)

**Figure 3-8.** Raman spectra of the BF₄⁻ anion v₁ vibrational band for the CIP crystalline solvates: (a) (G1)₂:LiBF₄, (b) (G3)₁:LiBF₄ and (c) (DMP)₂:LiBF₄.
bands are located in close proximity to the SSIP band, but they are still readily
distinguishable. DMP also formed a (DMP)$_2$:LiBF$_4$ solvate, as noted above. Because of the
similar structure with G1, the (DMP)$_2$:LiBF$_4$ solvate is expected to form a similar structure to

**Figure 3-9.** Raman spectra of the BF$_4^-$ anion $v_1$ vibrational band for the AGG-I crystalline
solvates: (a) (G2)$_2$:LiBF$_4$, (b) (EC)$_2$:LiBF$_4$, (c) (AN)$_2$:LiBF$_4$, (d) (Et-G1)$_1$:LiBF$_4$ and (e)
(Et-G2)$_1$:LiBF$_4$. 

43
the CIP-I (G1)$_2$:LiBF$_4$ solvate. The Raman band is found positioned near that for the other two CIP solvates (Fig. 3-8).

Three different types of AGG solvates—AGG-I, AGG-II and AGG-III—were also analyzed. Five AGG-I solvates are known or were determined: (G2)$_1$:LiBF$_4$, (EC)$_2$:LiBF$_4$, (AN)$_2$:LiBF$_4$, (Et-G1)$_1$:LiBF$_4$ and (Et-G2)$_1$:LiBF$_4$ (Figs. 3-3 and 3-4). All of these solvates have similar positions for the $\nu_1$ mode at ~777-779 cm$^{-1}$ (Fig. 3-9). Seven AGG-II solvates are known or were determined: (SN)$_1$:LiBF$_4$, (AN)$_1$:LiBF$_4$, (MA)$_1$:LiBF$_4$, (GBL)$_1$:LiBF$_4$, (MMA)$_1$:LiBF$_4$, (THF)$_1$:LiBF$_4$ and (EA)$_1$:LiBF$_4$ (Figs. 3-3 and 3-4). Unlike the Raman bands for the other solvates, the $\nu_1$ mode is located over a wide range of ~776-788 cm$^{-1}$ (Fig. 3-10) for the AGG-II solvates. Pure LiBF$_4$ was analyzed to characterize AGG-III coordination. The Raman band for the $\nu_1$ mode for the pure salt is positioned near ~795 cm$^{-1}$ (Fig. 3-10).

Fig. 3-11 shows a summary of the Raman band positions versus temperature for all of the solvates. This clearly indicates the assignment for each type of BF$_4^{-}$...Li$^+$ cation coordination. As such, it serves as a useful tool for understanding the ionic association behavior of liquid electrolyte mixtures containing LiBF$_4$. Notably, the SSIP, CIP-I and AGG-I anion bands are each clustered closely together, but wide variability is found for the AGG-II bands. In particular, the anion band for the AGG-II (SN)$_1$:LiBF$_4$ solvate is located at ~776 cm$^{-1}$ (Fig. 3-10), which is close to the AGG-I band position. The explanation for this variation in band position lies in the differences in the anion bond lengths and angles for the different crystalline solvates. An examination of these for the SSIP solvates reveals than none of the BF$_4^{-}$ anions have ideal tetrahedral symmetry, but the differences are minor (Fig. 3-12). This
Figure 3-10. Raman spectra of the BF$_4^-$ anion $v_1$ vibrational band for the AGG-II crystalline solvates and AGG-III LiBF$_4$: (a) (SN)$_1$:LiBF$_4$, (b) (AN)$_1$:LiBF$_4$, (c) (MA)$_1$:LiBF$_4$, (d) (GBL)$_1$:LiBF$_4$, (e) (MMA)$_1$:LiBF$_4$, (f) (THF)$_1$:LiBF$_4$, (g) (EA)$_1$:LiBF$_4$ and (h) pure LiBF$_4$.
Figure 3-11. Summary of the Raman band peak position for the BF$_4^-$ anion $v_1$ vibrational band for the different crystalline solvates.
lack of symmetry may be due to crystal lattice packing effects from the neighboring solvent molecules. For the two CIP-I solvates with the BF$_4^-$ anions coordinated to a single Li$^+$ cation, the B-F bond length for the fluorine atom coordinated to the Li$^+$ cation is notably longer than for the other three B-F bond lengths (Fig.3-12). For the AGG-I solvates with the BF$_4^-$ anions coordinated to two Li$^+$ cations, once again the B-F bonds for the fluorine atoms coordinated to the Li$^+$ cations are longer than those for the uncoordinated fluorine atoms (Fig.3-13). In addition, the F-B-F angle between the two uncoordinated fluorine atoms is greater than for the other five F-B-F angles. Finally, the explanation for the wide variability of the AGG-II anion band positions is attributed to the diversity in the manner in which three Li$^+$ cations are

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**Figure 3-12.** Differences in the BF$_4^-...$Li$^+$ cation coordination in the SSIP and CIP-I crystalline solvates: (a) SSIP (G2)$_2$:LiBF$_4$, (b) SSIP (PMDETA)$_1$:HBF$_4$, (c) SSIP (TMEDA)$_3$:HBF$_4$, (d) SSIP (PHEN)$_2$:HBF$_4$, (e) CIP-I (G1)$_2$:LiBF$_4$ and (f) CIP-I (G3)$_1$:LiBF$_4$ (Li$^+$ cation is colored black).
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Figure 3-13. Differences in the BF<sub>4</sub>...Li<sup>+</sup> cation coordination in the AGG-I crystalline solvates and AGG-III pure salt: (a) AGG-I (EC)<sub>2</sub>:LiBF<sub>4</sub>, (b) AGG-I (AN)<sub>2</sub>:LiBF<sub>4</sub>, (c) AGG-I (G2)<sub>2</sub>:LiBF<sub>4</sub>, (d) AGG-I (Et-G1)<sub>1</sub>:LiBF<sub>4</sub>, (e) AGG-I (Et-G2)<sub>1</sub>:LiBF<sub>4</sub> and (f) AGG-III pure LiBF<sub>4</sub>. (*all of the solvate structures were determined at -163°C, except for the structure for the (AN)<sub>2</sub>:LiBF<sub>4</sub> solvate which was determined at -5°C because of this solvate's solid-solid phase transition) (Li<sup>+</sup> cations are colored black).
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**Figure 3-14.** Differences in the BF$_4$...Li$^+$ cation coordination in the AGG-II crystalline solvates: (a) (EA)$_1$:LiBF$_4$, (b) (THF)$_1$:LiBF$_4$, (c) (MMA)$_1$:LiBF$_4$, (d) (GBL)$_1$:LiBF$_4$, (e) (MA)$_1$:LiBF$_4$, (f) (AN)$_1$:LiBF$_4$ and (g) (SN)$_1$:LiBF$_4$ (Li$^+$ cations are colored black).
coordinated by the BF$_4^-$ anion resulting in significant differences in the anion bond lengths and angles (Fig. 3-14). As for the other solvates, the B-F bonds for the coordinated fluorine atoms are longer than for the uncoordinated fluorine atom. Further, the F-B-F angles between the coordinated-uncoordinated fluorine atoms are greater than those between the coordinated-coordinated fluorine atoms (Fig. 3-14). Returning to the (SN)$_2$:LiBF$_4$ solvate and its deviation from the band position for the other AGG-II solvates, the F-Li$^+$ cation coordination bond lengths are longer (weaker) than for the other AGG-II solvates (Fig. 3-14) with one being particularly long. This results in two of the B-F bonds being relatively short, while two are longer. The lengths (Fig. 3-14) are comparable to those for the AGG-I solvates, thus providing the explanation for the anion band position for this particular solvate (Fig. 3-11).

No crystalline solvates with CIP-II coordination were available for spectroscopic analysis in the present study. DFT calculations, however, indicate that the BF$_4^-$ anion $v_1$ vibrational band position for such coordination may overlap with the band position for the AGG-I coordination. If this is the case, then this might make the discrimination of the CIP-II and AGG-I solvates difficult. MD simulations of (AN)$_n$:LiBF$_4$ mixtures have suggested that CIP-II coordination may be uncommon (relative to CIP-I coordination) in liquid mixtures (in contrast to results for gas phase calculations, as noted above),$^1$ but this is not yet conclusive. Thus, caution should be exercised when interpreting the results from a Raman band deconvolution of LiBF$_4$ mixtures to gauge the ionic association interactions in relevant electrolyte mixtures.
3.3 TFSI Anion Raman Band Characterizations

3.3.1 Solvate Structures and Li⁺ Cation Coordination

Some LiTFSI solvate structures have been previously reported: SSIP: (G2)_{2}:LiTFSI\(^{51}\) and (12C4)\(_2\):LiTFSI\(^{46}\); CIP-II: (PMDETA)\(_1\):LiTFSI\(^{52}\); AGG-I: (G1)\(_1\):LiTFSI\(^5\) and (TMEDA)\(_1\):LiTFSI.\(^{52}\) New crystal structures determined as part of the present study include: SSIP: (PHEN)\(_3\):LiTFSI; AGG-I: (EC)\(_3\):LiTFSI; AGG-II: (AN)\(_1\):LiTFSI,\(^{53}\) (EC)\(_1\):LiTFSI, (2,6-DMPy)\(_{1/2}\):LiTFSI. The crystal structure of the pure LiTFSI salt from powder XRD data was also previously reported,\(^{54}\) but the structure from a single crystal was determined as part of the present study (Fig. 3-15).\(^{55}\)

The TFSI⁻ anion is known to have two different conformational states: a \textit{cisoid} form (\(C_1\)) with the CF\(_3\) groups on the same side of the S-N-S plane and a \textit{transoid} form (\(C_2\)) with the CF\(_3\) groups on opposite side of the plane.\(^{5,54,56-58}\) In solution, an equilibrium exists between these conformations. However, in crystalline phases, the TFSI⁻ anion often has only one conformation, either \(C_1\) or \(C_2\). Also, the TFSI⁻ anion is able to adopt bidentate coordination easily to a single Li⁺ cation with two oxygen atoms. A more descriptive classification is necessary than for simpler anions, such as BF\(_4⁻\) and ClO\(_4⁻\);\(^2,3\) for Li⁺ cation coordination by the TFSI⁻ anion (Fig. 3-2):

<table>
<thead>
<tr>
<th>Structure</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SSIP)</td>
<td>uncoordinated anion</td>
</tr>
<tr>
<td>(CIP-I)</td>
<td>1 anion O coordinated to 1 Li⁺</td>
</tr>
<tr>
<td>(CIP-II)</td>
<td>2 anion O coordinated to 1 Li⁺</td>
</tr>
<tr>
<td>(AGG-Ia)</td>
<td>2 anion O coordinated to 2 Li⁺</td>
</tr>
<tr>
<td>(AGG-Ib)</td>
<td>3 anion O coordinated to 2 Li⁺</td>
</tr>
</tbody>
</table>
(AGG-IIa) 3 anion O coordinated to 3 Li$^+$
(AGG-IIb) 4 anion O coordinated to 3 Li$^+$
(AGG-III) 4 anion O coordinated to 4+ Li$^+$

**Figure 3-15.** TFSI...Li$^+$ cation coordination in crystalline solvates: (a) SSIP-C$_2$ (G2)$_2$:LiTFSI,$^51$ (b) SSIP-C$_2$ (PHEN)$_3$:LiTFSI, (c) CIP-II-C$_1$ (PMDETA)$_1$:LiTFSI,$^52$ (d) AGG-Ib-C$_2$ (G1)$_1$:LiTFSI,$^5$ (e) AGG-Ia-C$_2$ (EC)$_3$:LiTFSI, (f) AGG-Ib-C$_2$ (TMEDA)$_1$:LiTFSI,$^52$ (g) AGG-Iib-C$_2$ (EC)$_1$:LiTFSI, (h) AGG-Iib-C$_1$ (DMPy)$_{1/2}$:LiTFSI, (i) AGG-Iib-C$_1$ (AN)$_1$:LiTFSI$^53$ and (j) AGG-III-C$_2$ pure LiTFSI.$^{54,55}$
All of the known SSIP crystalline solvates have TFSI\(^{-}\) anions with the \(C_2\) conformation. This *transoid* anion conformation is more stable than the *cisoid* (\(C_1\)) conformation by 2.2 kJ mol\(^{-1}\) (in the gas phase), so the *transoid* conformation is likely more favorable than the *cisoid* conformation in crystalline phases in which the anion remains uncoordinated. However, for other solvates in which the anion is coordinated to Li\(^{+}\) cations, the TFSI\(^{-}\) anion instead adopts the \(C_1\) conformation (i.e., CIP-II-\(C_1\) (PMDETA)\(_2\)::LiTFSI, AGG-II-\(C_1\) (AN)\(_1\)::LiTFSI and AGG-II-\(C_1\) (DMPy)\(_{1/2}\)::LiTFSI). This conformation optimizes the coordination and packing interactions between the ions and solvent.

There are three different AGG-I solvates known: (EC)\(_3\)::LiTFSI, (G1)\(_1\)::LiTFSI and (TMEDA)\(_3\)::LiTFSI. In the (EC)\(_3\)::LiTFSI solvate, two oxygen atoms from the TFSI\(^{-}\) anion coordinate two different Li\(^{+}\) cations (i.e., AGG-Ia-\(C_2\) coordination). In the (G1)\(_1\)::LiTFSI and (TMEDA)\(_3\)::LiTFSI solvates, however, three oxygen atoms from one TFSI\(^{-}\) anion coordinate two different Li\(^{+}\) cations, including the bidentate coordination of one of the Li\(^{+}\) cations by two oxygen atoms (i.e., AGG-Ib-\(C_2\) coordination) (Fig. 3-15).

For the AGG-II solvates, there are no known examples of AGG-IIa coordination (i.e., the anion coordinated to three Li\(^{+}\) cations with three oxygen atoms). In all three AGG-II solvates studied—(AN)\(_1\)::LiTFSI, (EC)\(_1\)::LiTFSI and (2,6-DMPy)\(_{1/2}\)::LiTFSI—four oxygen atoms from one TFSI\(^{-}\) anion coordinate three different Li\(^{+}\) cations, including one with bidentate coordination (i.e., AGG-IIb coordination). However, there are differences in the conformations of the anions. The (EC)\(_1\)::LiTFSI solvate has anions with the \(C_2\) conformation, whereas the (AN)\(_1\)::LiTFSI and (2,6-DMPy)\(_{1/2}\)::LiTFSI solvates have anions with the \(C_1\) conformation (Fig. 3-2).
3.3.2 Raman Spectroscopic Analysis of LiTFSI Crystalline Solvates

The highest intensity TFSI\(^-\) anion Raman band at 740 cm\(^{-1}\) is due to the expansion and contraction of the entire anion.\(^{59–61}\) This band is the most sensitive (i.e., band positional shift) to ionic association, and many studies have examined this band.\(^{60,62–64}\) The Raman spectra of the crystalline solvates of LiTFSI were examined in the present study to unambiguously assign the band positions of the TFSI\(^-\) anion for the uncoordinated TFSI\(^-\) anion and the anion coordinated to one or more Li\(^+\) cations.

![Raman spectra of TFSI\(^-\) anion vibrational band](image)

**Figure 3-16.** Raman spectra of the TFSI\(^-\) anion vibrational band for the SSIP-C\(_2\) crystalline solvates: (a) (G2)\(_2\)::LiTFSI, (b) (PHEN)\(_3\)::LiTFSI, (c) (12C4)\(_2\)::LiTFSI and (d) (G1)\(_3\)::LiTFSI.
There are three SSIP crystalline solvates: (G2)\textsubscript{2}:LiTFSI, (12C4)\textsubscript{2}:LiTFSI and (PHEN)\textsubscript{3}:LiTFSI (Fig. 3-15). These solvates consist of uncoordinated TFSI\textsuperscript{−} anions, all of which have the \( C_2 \) anion conformation (i.e., SSIP-\( C_2 \) in Fig. 3-2). The Raman bands of these SSIP solvates are located at the same position at 741 cm\(^{-1}\), regardless of the solvent chosen for cation coordination (Fig. 3-16). A (G1)\textsubscript{3}:LiTFSI solvate is also known to form, but the structure is not yet known. It is expected to be a SSIP solvate with six-fold coordination between the \( Li^+ \) cation and six oxygen atoms from three G1 molecules, as many (G1)\textsubscript{3}:LiX crystalline solvates are known.\textsuperscript{41,51} A mixture with this composition was prepared and Raman spectra were obtained (Fig. 3-16). The TFSI\textsuperscript{−} anion Raman band in this mixture is also located at same position (741 cm\(^{-1}\) at -100°C) as for the previously studied SSIP mixtures.

(PMDETA)\textsubscript{1}:LiTFSI forms a bidentate CIP solvate (CIP-II-\( C_2 \)) in which one anion has two oxygen coordinated to one \( Li^+ \) cation (Fig. 3-15).\textsuperscript{52} A Raman band for this CIP solvate was observed at 747 cm\(^{-1}\) at -100°C (Fig. 3-17).

Six AGG solvates and the pure LiTFSI salt were also examined. AGG-Ia-\( C_2 \) coordination (i.e., (EC)\textsubscript{3}:LiTFSI) gives a Raman band at 745 cm\(^{-1}\), while AGG-Ib-\( C_2 \) coordination (i.e., (G1)\textsubscript{1}:LiTFSI and (TMEDA)\textsubscript{1}:LiTFSI) gives a Raman band at 747-748 cm\(^{-1}\) (Fig. 3-17). AGG-IIb-\( C_2 \) coordination (i.e., (EC)\textsubscript{1}:LiTFSI) gives a Raman band at 752 cm\(^{-1}\), while AGG-IIb-\( C_1 \) coordination (i.e., (AN)\textsubscript{1}:LiTFSI and (DMPy)\textsubscript{1/2}:LiTFSI) gives Raman bands at 747-750 cm\(^{-1}\) (Fig. 3-18). The pure LiTFSI salt gives a Raman band positioned near ~748 cm\(^{-1}\) (Fig. 3-18).

Fig. 3-19 shows a summary of the Raman band positions versus temperature for all of LiTFSI solvates, as well as the pure LiTFSI salt. The Raman band for the SSIP solvates,
located at 741 cm$^{-1}$, is clearly distinguishable from other solvate bands. The Raman band position for the CIP and AGG solvates, however, are closely positioned in the 747~752 cm$^{-1}$ spectral region. The Raman band position trend for the TFSI$^-$ anion differs from that found for the BF$_4^-$ and ClO$_4^-$ anions.$^{2,3}$ For the latter salts, more aggregated solvates result in Raman bands shifted to a higher wavenumber. For the LiTFSI solvates, however, increasing Li$^+$ cation coordination does not shift the band to higher wavenumber in all cases (i.e., SIP-II-$C_2$ vs. AGG-Ia-$C_2$ and AGG-III-$C_2$ vs. AGG-Ib-$C_2$ and AGG-III-$C_2$ vs. AGG-IIb-$C_1$). As

**Figure 3-17.** Raman spectra of the TFSI$^-$ anion vibrational band for the CIP and AGG-I crystalline solvates: (a) CIP-II-$C_1$ (PMDETA)$_1$:LiTFSI, (b) AGG-Ia-$C_2$ (EC)$_3$:LiTFSI, (c) AGG-Ib-$C_2$ (G1)$_1$:LiTFSI and (d) AGG-Ib-$C_2$ (TMEDA)$_1$:LiTFSI.
mentioned previously, geometry of the TFSI anion affects to Raman band position due to the different bond length and angle for each solvate. Also, there are lots of variety with flexibility to have two conformations and possibility to have bidentate coordination for TFSI-anion. While it is difficult to deconvolute the Raman spectra of solution mixture and make definite band assignment for TFSI-anion, much insight can still be gained about the ionic association of TFSI-anion in solution system.

**Figure 3-18.** Raman spectra of the TFSI anion vibrational band for the AGG-II crystalline solvates and AGG-III LiTFSI: (a) AGG-IIb-C1 (AN)1:LiTFSI, (b) AGG-IIb-C1 (2,6-DMPY)1/2:LiTFSI, (c) AGG-IIb-C2 (EC)1:LiTFSI, (d) AGG-III-C2 pure LiTFSI.
3.4 Conclusions

Many crystalline solvates structures have been introduced and determined to examine how solvent structure impacts solvate formation and to aid in determining the proper assignments for the anion vibrational modes for specific forms of BF₄⁻ and TFSI...Li⁺ cation coordination. The anion band positions have been directly correlated with the anion bond lengths and angles available from solvate crystal structures. The summary of the Raman band positions at different temperatures provides a crucial tool for aiding in the characterization of ionic association within electrolyte solutions.

3.5 References


(49) Gallucci, J. C.; Sivik, M. R.; Paquette, L. A.; Zaegel, F.; Meunier, P.; Gautheron, B. Two Derivatives of Lithium Isodicyclopentadienide: [(1,2,3,3a,7a-η)-4,5,6,7-Tetrahydro-4,7-methanoindenido](N,N,N′,N′'-tetramethylethylenediamine)lithium and Bis(1,4,7,10-tetra-oxacyclododecane)lithium(1⁺)Bis[(1,2,3,3a,7a-η)-4,5,6,7-tetrahydro-4,7-methanoindenido]lithate(1⁻). *Acta Crystallogr.* **1996**, *C52*, 1673–1679.


CHAPTER 4
Electrolyte Solvation and Association (I):
Acetonitrile (AN)-Lithium Salt Mixtures

4.1 Introduction

Understanding how ion/solvent structure, temperature and salt concentration influence molecular interactions, such as ionic association and solvation, and how these, in turn, govern electrolyte physical properties and electrochemical device performance remains a critical need. Wide variability in solvates may exist in an electrolyte. Such solvated ionic species determine not only the bulk behavior (e.g., ionic conductivity, viscosity, volatility, etc.) of the mixtures, but also the interfacial interactions of the electrolyte with electrodes. Significant challenges are associated, however, with the study of structure within a liquid phase.

In a previously reported study of \((\text{glyme})_n\text{-LiX}\) mixtures, the phase behavior and crystalline solvates that formed in relatively dilute mixtures suggested the following order for increasing ionic association (ionic interactions) with varying anions\(^1\):

\[
\text{LiTFSI, LiAsF}_6 < \text{LiClO}_4, \text{LiI} < \text{LiBF}_4 < \text{LiCF}_3\text{SO}_3 < \text{LiNO}_3, \text{LiBr} < \text{LiCF}_3\text{CO}_2
\]

In the glymes, the salts were classified as follows: LiTFSI and LiAsF\(_6\) are highly dissociated; LiClO\(_4\), LiI and LiBF\(_4\) are intermediately associated; and LiCF\(_3\)SO\(_3\), LiNO\(_3\), LiBr and LiCF\(_3\)CO\(_2\) are associated or highly associated. Thus, in dilute solutions LiTFSI tends to form SSIP solvates, whereas LiCF\(_3\)CO\(_2\) tends to form AGG solvates. This previous analysis has been extended in the present study to examine the behavior of lithium salts in nitrile solvent
to determine if this classification can be broadly applied to other solvent mixtures to explain their solution behavior and properties. In aprotic solvents, the anion has only weak interactions with the solvent. Dissolution thus involves the solvation of the cations with a competition present between the solvent and anions for coordination to the Li$^+$ cations. The degree of solvation is strongly dependent upon the structure of the solvent/anions, salt concentration and temperature.

Understanding the molecular interactions in the solid phase, such as solvation and ionic association, enables a more thorough interpretation of solvate structure in the liquid phase. Molecular interactions have been studied through the combination of phase diagrams, solvate crystal structures, solvent/ionic coordination information obtained from spectroscopic characterization and molecular simulations. Also the transport properties of electrolyte have been obtained to examine how the solution structure dictates the transport properties.

AN was selected both because of its relatively straightforward solvation interactions (the solvent has only a single electron lone-pair and thus is either coordinated or uncoordinated to a single Li$^+$ cation), as well as its usefulness as a model for other nitrile or dinitrile solvents proposed as electrolyte materials such as butyronitrile, adiponitrile and glutaronitrile.$^{2-5}$ The phase behavior and solvation interactions of (AN)$_n$-LiX mixtures with LiPF$_6$, LiTFSI, LiClO$_4$, LiBF$_4$, LiCF$_3$SO$_3$, LiNO$_3$ and LiCF$_3$CO$_2$ have been examined here. This information (i.e., solution structure/molecular interactions) has then been used to explain the variations in transport properties (i.e., viscosity and ionic conductivity) noted for the different mixtures.
4.2 Thermal Phase Behavior and Solvate Crystal Structures

**Pure AN:** AN undergoes a solid-solid phase transition at $-56^\circ C$ prior to the $T_m$ at $-46^\circ C$ (Fig. 4-1). The low temperature ($\beta$ or II) and high temperature ($\alpha$ or I) phases both consist of ordered AN molecules with the phase transition consisting of a $90^\circ$ rotation of double slabs of the AN molecules packed in the crystal layers.

**AN-LiPF$_6$:** (AN)$_n$-LiPF$_6$ mixtures form both 6/1 and 5/1 AN/LiPF$_6$ crystalline solvate phases. In dilute mixture ($n \geq 10$), the 6/1 SSIP solvate crystallizes with the peak at $18^\circ C$ corresponding to the $T_m$ for this phase (Fig. 4-1). It is difficult to characterize the thermal behavior of this phase more definitively as more concentrated mixtures (i.e., $10 > n \geq 6$) form both the 6/1 and 5/1 phases. For these samples, in each case, some of the sample crystallized into the 5/1 phase upon cooling from the melt, even when a rapid cooling procedure was used. The remainder of the sample then crystallized at low temperature into the 6/1 phase resulting in the complicated thermal behavior noted (Fig. 4-1). The crystal structure of the 6/1 phase (i.e., (AN)$_6$:LiPF$_6$ solvate) has been determined as part of the present study (Fig. 4-2). This structure consists of Li$^+$ cations coordinated by four AN molecules with uncoordinated PF$_6^-$ anions and AN molecules (two per Li$^+$ cation) located between the solvated cations. The crystal structure of the 5/1 phase (i.e., (AN)$_5$:LiPF$_6$ solvate) has also been determined as part of the present study (Fig. 4-2). This resembles the 6/1 structure with Li$^+$ cations coordinated by four AN molecules, uncoordinated PF$_6^-$ anions and AN molecules (one per Li$^+$ cation) located between the solvated cations (Fig. 4-2). The same solvate structure is found for (AN)$_5$:CuPF$_6$. The 5/1 solvate with LiPF$_6$ has a $T_m$ at $67^\circ C$ with a solid-solid phase transition at $38^\circ C$. It is noteworthy that CuClO$_4$ and CuBF$_4$ form 4/1
Figure 4-1. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) AN-(x) LiTFSI and (b) (1-x) AN-(x) LiPF₆ mixtures.
phases\textsuperscript{17–21} rather than a 5/1 phase, as is also found for LiClO\textsubscript{4} and LiBF\textsubscript{4} given that the Li\textsuperscript{+} and Cu(I)\textsuperscript{+} cations are nearly identical in size.\textsuperscript{22} A eutectic point is observed for more concentrated mixtures (n < 5) between the 5/1 solvate and a more aggregated solvate (composition unknown).

\textit{AN-LiTFSI}: DSC measurements and the corresponding phase diagram for (AN)\textsubscript{n}-LiTFSI mixtures (Fig. 4-1) agree well with a previously reported partial phase diagram.\textsuperscript{23} Three

\textbf{Figure 4-2.} Li\textsuperscript{+} cation coordination in the (a) (AN)\textsubscript{6}:LiPF\textsubscript{6}, (b) (AN)\textsubscript{5}:LiPF\textsubscript{6} and (c) (AN)\textsubscript{1}:LiTFSI solvate crystal structures (Li-purple, N-blue, P-orange, F-light green, O-red).\textsuperscript{13,14,30}
different crystalline solvate phases are found, consisting of 6/1, 4/1 and 1/1 AN/LiTFSI solvates, respectively. The structures of the 6/1 and 4/1 solvates are not yet known. For the 6/1 solvate, it is possible that the Li$^+$ cations are fully solvated by six AN molecules (octahedral coordination), but several studies have suggested that it is not energetically favorable (in the gas phase) to coordinate more than four AN molecules to a Li$^+$ cation.$^{24-27}$ The spectroscopic data (see below) confirms that this is a SSIP phase with uncoordinated TFSI$^-$ anions, as expected for a solvate containing six AN molecules. The 4/1 solvate is also a SSIP phase which may have coordination similar to that found in the structures of the SSIP (AN)$_4$:LiClO$_4$.$^{28}$ and (AN)$_4$:LiI$^-$.$^{29}$ phases in which the Li$^+$ cations are fully solvated by four AN molecules (tetrahedral coordination) and the anions are uncoordinated. For compositions between the 4/1 and 1/1 phases, it was not possible to fully crystallize the samples, despite subjecting the samples to extensive heating-cooling cycles at subambient temperature. Instead, a glass transition ($T_g$) is noted (Fig. 4-1) with an amorphous glassy phase present at low temperature and a liquid phase present above the $T_g$. Thus, a crystallinity gap occurs for these compositions due to either the slow nucleation of crystalline solvates (beyond the time frame of the crystallization procedure utilized) or the inhibition of ordered crystalline solvate formation due to unfavorable packing. The crystal structure of the 1/1 phase (i.e., (AN)$_1$:LiTFSI solvate) was also determined in the present study (Fig 4-2).$^{30}$ In this phase, there are two different Li$^+$ cations. One Li$^+$ cation has six-fold coordinated by six oxygen atoms from four TFSI$^-$ anions. The second Li$^+$ cation has four-fold coordination by two oxygen atoms from two TFSI$^-$ anions and two nitrogen atoms from two AN solvent molecules. Each TFSI$^-$ anion is coordinated to three Li$^+$ cations (AGG-IIb-C$_1$ solvate).
**AN-LiClO₄:** (AN)ₙ-LiClO₄ mixtures form three phases consisting of 4/1, 2/1 and 1/1 (AN/Li) crystalline solvates, respectively (Fig. 4-3). The data agree well with and expand upon a partial phase diagram previously reported for (AN)ₙ-LiClO₄ mixtures.³¹ The structure of the SSIP 4/1 solvate (i.e., (AN)₄:LiClO₄) has been previously reported (Fig. 4-4).²⁸ The Li⁺ cations are coordinated by four AN molecules with uncoordinated ClO₄⁻ anions located between the solvated cations. This same solvate structure is found for the SSIP (AN)₄:LiI solvate.²⁹ The structure of the 2/1 crystalline solvate is not known, but may resemble the AGG (AN)₂:LiBr solvate in which each Li⁺ cation has four-fold coordination by two AN molecules and two anions.²⁹ Each Br⁻ anion is coordinated to two Li⁺ cations forming a dimer structure. The data suggests that a eutectic is present between the 4/1 and 2/1 phases and the 2/1 phase has a low energy solid-solid phase transition at approximately 30°C. The 1/1 solvate structure is also not known, but may resemble the AGG (AN)₁:LiBF₄ and (AN)₁:LiCF₃SO₃ solvates in which each Li⁺ cation is coordinated by one AN molecule and three anions.³²,³³

**AN-LiBF₄:** (AN)ₙ-LiBF₄ mixtures have similar phase behavior to those with LiClO₄ (Fig. 4-3) with the formation of 4/1, 2/1 and 1/1 crystalline solvates. The structure of the 4/1 solvate is not yet known, but likely closely resembles the same solvates with LiClO₄ and LiI. It is noteworthy that similar SSIP 4/1 solvate forms with AgClO₄, AgBF₄, CuClO₄ and CuBF₄,¹⁷,²⁰,³⁴–³⁶ as the Ag(I)⁺ and Cu(I)⁺ cations are nearly the same size as Li⁺ cations.²² The 2/1 structure, (AN)₂:LiBF₄ was determined in the present study (Fig. 4-4). In this structure, the Li⁺ cation has four-fold coordination from two anion fluorine atoms—one each from two anions—and two nitrogen atoms from two AN molecules. The 1/1 solvate structure,
Figure 4-3. DSC heating traces (5°C min$^{-1}$) and the corresponding phase diagrams for (a) (1-x) AN-(x) LiClO$_4$ and (b) (1-x) AN-(x) LiBF$_4$ mixtures.
Figure 4-4. Li⁺ cation coordination in the (a) (AN)₄:LiClO₄, (b) (AN)₂:LiBF₄, (c) (AN)₁:LiBF₄ and (d) (AN)₁:LiCF₃SO₃ solvate crystal structures (Li-purple, Cl-green, B-tan, F-light green, O-red). ²⁸, ³⁷
(AN)\(_1\):LiBF\(_4\), was also determined in the present study (Fig. 4-4).\(^{37}\) This solvate structure consists of Li\(^+\) cations coordinated by three fluorine atoms (one each from three different anions) and a single AN molecule. Each BF\(_4^-\) anion is coordinated to three Li\(^+\) cations through three anion fluorine atoms.

\textit{AN-LiCF}_3\textit{SO}_3: \textit{Although LiCF}_3\textit{SO}_3 did dissolve in AN upon heating and stirring, it was not possible to prepare a phase diagram for (AN)\(_n\)-LiCF\(_3\)SO\(_3\) mixtures. All of the samples prepared (n = 2-10) rapidly formed a high melting 1/1 crystalline phase (i.e., (AN)\(_1\):LiCF\(_3\)SO\(_3\)) on standing at room-temperature. Once this phase formed, homogeneous solutions of the samples cannot be made by heating the samples (to prepare the DSC pans for analysis) as the boiling point (\(T_b\)) of the excess AN (\(T_b\) 82°C) is much lower than the \(T_m\) for this solvate (\(T_m\) 157°C - Fig. 4-5). The AGG 1/1 solvate (Fig. 4-4) has been previously reported.\(^{33}\) The solvate structure consists of anions coordinated by the three oxygen atoms to three Li\(^+\) cations. Each Li\(^+\) cation is coordinated by three anion oxygen atoms and a single AN similar to the 1/1 phase with LiBF\(_4\). Although the anion coordination for the (AN)\(_1\):LiBF\(_4\) and (AN)\(_1\):LiCF\(_3\)SO\(_3\) solvates is similar, the ion packing in the crystal...
structures is different. The (AN)$_1$:LiBF$_4$ phase consists of planar sheets of ions, whereas the (AN)$_1$:LiCF$_3$SO$_3$ phase consists of ions arranged in a linear polymeric form of packing.

\textit{AN-LiNO$_3$}: LiNO$_3$ was essentially insoluble in AN, even in dilute mixtures. Thus, it was not possible to characterize (AN)$_n$-LiNO$_3$ solutions.

\textit{AN-LiCF$_3$CO$_2$}: LiCF$_3$CO$_2$ dissolved readily in AN forming highly concentrated solutions. No AN-LiCF$_3$CO$_2$ crystalline solvates form in the mixtures. The phase diagram for these mixtures therefore consists of the excess (uncoordinated) AN crystallizing in dilute mixtures leaving a concentrated amorphous AN-LiCF$_3$CO$_2$ phase. The DSC data (Fig. 4-6) indicate that the composition of the amorphous phase is (AN)$_n$-LiCF$_3$CO$_2$ ($n < 2$). This amorphous phase likely consists of both coordinated and uncoordinated AN molecules, the latter weakly interacting with the solvated ions and thus not crystallizing as bulk solvent.

Despite the fact that the phase diagrams for both LiPF$_6$ and LiTFSI suggests that these are highly dissociated salts (i.e., both are able to form a 6/1 phase), significant differences are also evident. In particular, LiPF$_6$ forms crystalline phases with a (relatively) high $T_m$, in

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{dsc_traces.png}
\caption{DSC heating traces (5°C min$^{-1}$) of (1-$x$) AN-($x$) LiCF$_3$CO$_2$ mixtures.}
\end{figure}
contrast with LiTFSI which forms phases which melt at low temperature. Thus, \((\text{AN})_n\)-LiTFSI mixtures remain liquid at -30°C over a large concentration range, whereas all of the \((\text{AN})_n\)-LiPF$_6$ mixtures (except for the most dilute) crystallize readily at ambient temperature. These differences are attributed to the differences in size, shape and flexibility of the anions. The PF$_6^-$ anions are essentially spherical and easily pack together symmetrically with the solvated Li$^+$ cations. At higher temperature, the uncoordinated PF$_6^-$ anions may become disordered by spinning about one axis or tumbling. The solid-solid phase transition for the 5/1 solvate is a structural change in the crystal structure which accommodates this disorder at elevated temperature. The long-range order, however, is retained. The non-spherical shape of the TFSI$^-$ anions, in contrast, likely results in a less symmetrical packing of the solvated Li$^+$ cations amongst the uncoordinated anions. Further, the anions are flexible$^{38,39}$ and may become conformationally disordered at elevated temperature thus disrupting the long-range packing of the solvate structure leading to melting instead of a disordered solid crystalline (plastic crystalline) phase.

Although LiClO$_4$ and LiBF$_4$ (i.e., salts with intermediate ionic association) form similar phases, differences do exist in the $T_m$ for these phases. In particular, it is noteworthy that the 4/1 SSIP solvate with LiClO$_4$ has a significantly higher $T_m$ than that found for LiBF$_4$ despite the fact that both anions are tetrahedral and nearly the same size (Fig. 4-3).$^{40-46}$ This is attributed to the difference in ionic association tendency between the two salts and the mechanisms for melting.$^1$ The three highly associated salts have significantly different phase behavior from LiClO$_4$ and LiBF$_4$, but also from one another. These differences, however, can be explained by the following arguments. The LiCF$_3$SO$_3$ and LiCF$_3$CO$_2$ salts both dissolve
readily, but the solvates formed, even in dilute mixtures, are likely to be primarily AGGs rather than CIPs or SSIPs. The solution AGG solvates with LiCF$_3$SO$_3$ may have ionic coordination which closely resembles that found in the (AN)$_1$:LiCF$_3$SO$_3$ crystalline phase thus facilitating the rapid nucleation and growth of this solid phase from dilute solutions (in addition to the high $T_m$ for this solvate). Similar AGG solvates may exist in the LiCF$_3$CO$_2$ solutions, but perhaps it is not possible to pack the ions into an ordered crystalline phase (due to differences in the -SO$_3$ and -CO$_2$ coordinating ends)—thus highly concentrated (AN)$_n$-LiCF$_3$CO$_2$ mixtures do not solidify. LiNO$_3$, in contrast, did not dissolve. This may be due to unfavorable AGG solvate structures with AN, perhaps due to the planar shape of the anion, which have a higher free energy relative to the crystalline LiNO$_3$ structure.$^{47}$

4.3 Ion Solvation

Uncoordinated AN has a $\nu_2$ Raman band at 2254 cm$^{-1}$ for the C≡N stretching vibration and a $\nu_4$ band at 918 cm$^{-1}$ for the C–C stretching vibration (Fig. 4-7), with the 2251 and 922 cm$^{-1}$ shoulders originating from hot bands.$^{48,49}$ When the electron lone-pair on the nitrogen is coordinated to a Li$^+$ cation, these bands shift to 2277 and 930 cm$^{-1}$, respectively (Fig. 4-7).$^{23,25,50,51}$ For the (AN)$_n$-LiClO$_4$ mixtures, only the $\nu_2$ AN band was examined because the $\nu_4$ solvent band overlaps with the Cl-O stretching vibrational mode of the ClO$_4^-$ anion.$^{52}$–$^{54}$ The fraction of solvent molecules coordinated to Li$^+$ cations (average solvation number) can be determined from the relation:

$$\frac{A_{AN-C}}{A_{AN-C} + A_{AN-UC}} = N \frac{c_{LiX}}{c_{AN}}$$  \hspace{1cm} (1)
where $A_{AN-C}$ and $A_{AN-UC}$ are the integrated area intensities of the bands for the coordinated and uncoordinated AN, respectively, $c_{LiX}$ and $c_{AN}$ are the concentrations of the salt and acetonitrile, respectively, and $N$ is the average solvate number. Therefore, from the data shown in Fig. 4-7, plots of the peak area for the coordinated and uncoordinated AN (normalized relative to the total peak area) were prepared (Fig. 4-8). This gives an indication of the fraction of solvent molecules coordinated to Li$^+$ cations. From this information, plus...
Figure 4-8. Raman spectroscopic analysis of the solvent bands for uncoordinated AN and Li$^+$ cation coordinated AN in (AN)$_n$-LiX mixtures with (a) LiPF$_6$, (b) LiTFSI, (c) LiClO$_4$, (d) LiBF$_4$ and (e) LiCF$_3$CO$_2$ at 60°C. The calculated Li$^+$ cation average solvation number ($N$) is shown at the top.
the molar ratio of AN to LiX (i.e., $c_{AN}/c_{LiX}$), the average solvation number ($N$) variation with salt concentration and different LiX salts was determined (Fig. 4-8). Errors from this analysis will be greatest for the most dilute solutions. Thus, $N$ values for data with $x < 0.10$ or thereabout are considered to be unreliable. Note that the integrated intensity $A_o$ of a band is given by:

$$A_o = KC_o$$ (2)

where $K$ is a proportionality factor which includes the Raman activity of the vibration and $C_o$ is the concentration of the species generating the band. The analysis in Fig. 4-8 is based upon the assumption that the relative activities of the bands associated with the uncoordinated and coordinated AN have equivalent Raman activity (no scaling is required) as has been suggested.$^{47,48}$ If this is not the case, the $N$ values noted in the top of Fig. 4-8 would need to be corrected appropriately. Data were collected for mixtures with LiPF$_6$, LiTFSI, LiClO$_4$, LiBF$_4$ and LiCF$_3$CO$_2$ at 60°C to ensure that the mixtures were homogeneous solutions (or melts) over a wide composition range. Selecting a particular composition for comparison, the $x = 0.20$ samples consist of mixtures with 4 AN molecules per Li$^+$ cation. At 60°C, the average solvation number is approximately 3.2 for LiPF$_6$, 2.8 for LiTFSI, 2.7 for LiClO$_4$, 2.1 for LiBF$_4$ and 1.0 for LiCF$_3$CO$_2$. A variety of solvates are actually present along with uncoordinated solvent in the liquid phase. Thus, the $N$ values do not match with the total amount of solvent present except for the most concentrated mixtures. This comparison indicates the following order for increasing Li$^+$ cation solvation (decreasing ionic association) in the liquid phase:

$$\text{LiPF}_6 > \text{LiTFSI} \geq \text{LiClO}_4 > \text{LiBF}_4 >> \text{LiCF}_3\text{CO}_2$$
in accord with the ionic association order noted previously. The more associated anions have greater coordination with the Li$^+$ cations (on average), which decreases the number of AN...Li$^+$ cation coordination bonds. Based upon the suggested order for ionic association tendency indicated previously, however, the results for LiTFSI are surprising as the TFSI$^-$ anion was proposed to be a highly dissociated anion. A comparison of the crystalline phases that form for (AN)$_n$-LiTFSI, -LiPF$_6$ and -LiClO$_4$ mixtures does indeed suggest that, in the crystalline phases, the TFSI$^-$ anions are highly dissociated (comparable to PF$_6^-$ anions). But in the liquid phase, as will be shown below, the TFSI$^-$ anions may have an ionic association tendency closer to ClO$_4^-$ than PF$_6^-$ anions. Note, however, that TFSI$^-$ also tends to form bidentate coordination to a single Li$^+$ cation to a much greater extent than anions such as PF$_6^-$, ClO$_4^-$ and BF$_4^-$. Thus, if a given TFSI$^-$ anion contributes two rather than one donor oxygens to the cation coordination, this may displace an additional AN molecule...thereby lowering the value of $N$ to some extent from what would otherwise be predicted. This could therefore be one possible explanation for the lower than expected $N$ values noted for the TFSI$^-$ anion. For (AN)$_n$-LiCF$_3$CO$_2$ mixtures, the $N$ values do not change significantly (~1) with changing salt concentration (Fig. 4-8). LiCF$_3$CO$_2$ is a highly associated lithium salt and thus tends to form AGG solvates. The data suggest that a stable amorphous 1/1 solvate is present in the (AN)$_n$-LiCF$_3$CO$_2$ mixtures and this results in an amorphous phase with some excess AN which is unable to crystallize (Fig. 4-6) due to its interactions with the solvates in solution.

4.4 Ionic Association

Fig. 4-9 shows the band variation of the PF$_6^-$ anion with varying concentration at -80°C. Based upon $O_h$ symmetry for the anion, the band assignments have been determined.\textsuperscript{30,58–62}
The most intense Raman band for the PF$_6^-$ anion is observed at 740-750 cm$^{-1}$. At -80°C, all of the samples are crystalline solids. For dilute mixtures (n ≥ 5), only a single band is evident at 744 cm$^{-1}$. This band corresponds to SSIP solvates in which the PF$_6^-$ anion is uncoordinated. There appears to be a slight shift to higher wavenumber between the 6/1 and 5/1 samples (perhaps corresponding to differences in structure (i.e., lattice packing) between the (AN)$_6$:LiPF$_6$ and (AN)$_5$:LiPF$_6$ crystalline solvates). A new band appears at 748 cm$^{-1}$ as the

![Figure 4-9. PF$_6^-$ anion band variation with concentration in (AN)$_n$:LiPF$_6$ mixtures at (a) -80°C and (b) 60°C.](image)
concentration increases \((n \leq 5)\). This band corresponds to an as yet undetermined more aggregated phase (perhaps a 1/1 phase).

For the liquid mixtures at 60°C (Fig. 4-9), the Raman band for the PF₆⁻ anion shifts to lower wavenumber and broadens. In dilute mixtures, one Raman band is observed at 741 cm⁻¹. This band corresponds to SSIP and CIP solvates. A study in progress for the PF₆⁻ Raman band assignments for crystalline LiPF₆ solvate structures (not shown) finds that the PF₆⁻ anion in SSIP and CIP solvates has a similar Raman band position, whereas the AGG-I form of coordination gives a band at 748 cm⁻¹. This indicates that it is difficult to differentiate between the SSIP and CIP forms of coordination with Raman spectroscopy. As the concentration increases (Fig. 4-9), an asymmetric shoulder at higher wavenumbers grows with increasing concentration. This is therefore attributed to one or more bands due to AGG solvates. It is clear that SSIP, and perhaps CIP, solvates dominate in the mixtures for dilute concentrations and such solvates are found even in the concentrated mixtures. This confirms that LiPF₆ is a highly dissociated salt.

Fig. 4-10 shows the Raman band vibration from the expansion and contraction of the entire TFSI⁻ anion with changing concentration at -80 and 60°C. At -80°C, all of the samples are crystalline solids, except for those in the crystallinity gap which either remain liquid or are amorphous solids, depending upon the sample \(T_g\) (Fig. 4-1). Two bands are observed in the dilute mixtures \((n \geq 3.6)\) which do not vary in position with varying concentration at -80°C. Although two different crystalline solvates (6/1 and 4/1 phases) are present for this concentration range \((n \geq 4)\) (Fig. 4-1), the anion coordination to the Li⁺ cations does not change because both phases appear to consist of SSIP solvates in which the
anions are uncoordinated. As noted in Chapter 3, the TFSI anion is known to have two different low-energy conformational states: a *cisoid* form ($C_1$) with the CF$_3$ groups on the same side of the S–N–S plane and a *transoid* form ($C_2$) with the CF$_3$ groups on opposite sides of the plane. This difference in the band position was initially thought to originate from

![Figure 4-10](image)

**Figure 4-10.** TFSI$^-$ anion band variation with concentration in (AN)$_n$-LiTFSI mixtures at (a) -80°C and (b) 60°C. The mixtures with $n = 3.0$, 2.5, 2.0 and 1.55 are in the crystallinity gap and remain either fully amorphous liquids or glassy solids at -80°C.
different conformations of the anions in the solvate crystal structures. The data in Fig. 4-10 thus suggested that the 6/1 phase consists of uncoordinated TFSI\(^-\) anions with the C\(_1\) conformation, whereas the 4/1 phase consists of uncoordinated TFSI\(^-\) anions with both the C\(_1\) and C\(_2\) conformations. To confirm this, the 250-450 cm\(^{-1}\) region of the spectra from (AN)\(_n\)-LiTFSI mixtures with \(n = 6\) and 4 was examined as the anion vibrational bands in this region provide a fingerprint for the uncoordinated anion conformations (Fig. 4-11).\(^{64}\) The data, however, clearly indicate that both phases consist only of anions with the C\(_2\) conformation. Note, however, that new bands are evident at 382 cm\(^{-1}\) for the \(n = 6\) sample and 315 cm\(^{-1}\) for the \(n = 4\) samples (Fig. 4-11a) which do not correspond to the bands typically noted for either the C\(_1\) or C\(_2\) conformations, so it may be that one or more different conformations are present which would also account for the band at 741 cm\(^{-1}\). Perhaps these bands are related to a third low-energy conformation for the TFSI\(^-\) anion which has been reported,\(^{65}\) but unfortunately the Raman spectrum for this conformation is not yet known. In the crystallinity gap for more concentrated mixtures, the samples are liquid or amorphous solids at -80°C and broad bands are evident in the Raman spectra. As the concentration of LiTFSI increases, the Raman band variation indicates that the amount of SSIP solvates decreases and more aggregated solvates, i.e., CIP and AGG solvates, increase. As the composition approaches \(n = 1\), a crystalline phase is formed again (along with an amorphous phase if 1 < \(n < 1.5\)). The Raman spectra show sharper bands for the crystalline phases and broader bands for the amorphous phase. For the \(n = 1\) mixture, the entire sample is crystalline with one sharp Raman band at 751 cm\(^{-1}\), corresponding to the AGG-IIb-C\(_1\) (AN)\(_1\):LiTFSI crystalline solvate (TFSI\(^-\) anion with the C\(_1\) conformation coordinated to three Li\(^+\) cations through four oxygen atoms).
For the liquid mixtures at 60°C (Fig. 4-10), the shift of the Raman bands for the TFSI$^-$ anion varies with concentration in a similar manner to that noted for the solid phase. However, unlike the solid phase, the bands shift gradually with changing concentration. Due to the structural flexibility of the TFSI$^-$ anion, different conformations are possible and each of

![Figure 4-11. TFSI$^-$ anion band variation with temperature in (AN)$_n$-LiTFSI mixtures with (a) n = 6.0 (crystalline in the -80 to -45°C range) and (b) n = 4.0 (crystalline in the -100 to -35°C range).](image)
these may be coordinated in varying ways to one or more Li$^+$ cation(s). Therefore, numerous types of solvates are formed in the liquid mixtures with changing concentration, giving overlapping bands. This makes it challenging to deconvolute the spectra conclusively to identify specific forms of anion coordination to the Li$^+$ cations (Chapter 3). The close proximity of the bands for AGG coordination (along with other forms of AGG solvates which have not yet been characterized) suggests that it is fruitless to attempt the identification of specific forms of the AGG anion coordination in solution. Fig. 4-12 therefore notes the deconvolution of the peaks in Fig. 4-10b in terms of uncoordinated TFSI anions (SSIP at 741 cm$^{-1}$), anions coordinated to a single Li$^+$ cation (CIP at 747 cm$^{-1}$) and those coordinated to more than one Li$^+$ cation (AGG at 750 cm$^{-1}$). Such a simplified analysis suggests that dilute mixtures contain > 80% SSIP solvates, with the remainder CIP solvates. With increasing salt concentration, the fraction of both CIP and AGG solvates increases at the expense of the SSIP solvates, but the latter persist even for very concentrated mixtures.

![Graph](image)

**Figure 4-12.** Distribution of anion modes of Li$^+$ cation coordination present in the (AN)$_n$-LiTFSI mixtures at 60°C.
To examine why the crystallinity gap occurs for the (AN)$_n$-LiTFSI mixtures, variable-temperature Raman spectra have been measured for compositions within the crystallinity gap (Fig. 4-13). For the n = 4.0 mixture, the Raman bands at 741 and 743 cm$^{-1}$ (from uncoordinated TFSI$^{-}$ anions) increase as the temperature decreases, and the band at 747-749 cm$^{-1}$ (attributed to CIP and AGG-I solvates) decreases, indicating that the amount of SSIP solvates increases at lower temperature. This results in the nucleation and growth of the SSIP 4/1 crystalline phase. The n = 3.0 sample, however, did not crystallize and the Raman spectra show that even though the amount of SSIP solvates increased as the temperature decreased, there remains a sizeable amount of coordinated anions (corresponds to Raman bands at 747-752 cm$^{-1}$) thus hindering/preventing the formation of the 4/1 crystalline phase. Similarly, although the n = 2.0 sample has a dominant peak at 750 cm$^{-1}$ (corresponding to AGG-II solvate as found in the 1/1 phase), a significant fraction of the anions persist as SSIP, CIP and perhaps AGG-I solvates which hinder/prevent the nucleation and growth of the 1/1 crystalline phase. In contrast, for the n = 1.0 sample, most of the anions have AGG-II (or perhaps even higher aggregation) thus facilitating the nucleation of the 1/1 crystalline phase.

Note that in the phase diagram for the (AN)$_n$-LiTFSI mixtures in Fig. 4-1, the "×" symbols indicate the $T_g$ of the fully amorphous samples, whereas the "Δ" are the $T_g$ for the amorphous phase which remains after some portion of a sample has crystallized as the 1/1 phase. The composition of the latter amorphous phase will thus be more dilute than the composition of the sample itself. These samples have nearly the same $T_g$ value of -82°C and this value can be used to estimate the composition of the stabilized amorphous phase (i.e., $x \sim 0.25$). This value corresponds to an average of 3 AN molecules per Li$^+$ cation.
Figure 4-13. Variable-temperature TFSI anion band variation with concentration in (AN)$_n$-LiTFSI mixtures with (a) $n = 4.00$, (b) $n = 3.63$, (c) $n = 3.00$, (d) $n = 2.50$, (e) $n = 2.00$, (f) $n = 1.55$, (g) $n = 1.38$ and (h) $n = 1.00$. 
Fig. 4-14 shows the ClO$_4^-$ anion band variation with concentration for (AN)$_n$-LiClO$_4$ mixtures at -80°C. All of the samples are crystalline solids at this temperature. In this region (~930 cm$^{-1}$), Raman bands for both AN and the ClO$_4^-$ anions overlapped. For dilute samples ($n > 4$), four band are observed; uncoordinated and coordinated AN molecules at 920 and 931 cm$^{-1}$, a band at 933 cm$^{-1}$ from the anion Cl-O stretching vibrational mode and the overtone from Fermi resonance of the uncoordinated ClO$_4^-$ anion at 910 cm$^{-1}$. From a comparison with the phase diagram (Fig. 4-3), the Raman band on 933 cm$^{-1}$ corresponds to the SSIP (AN)$_4$:LiClO$_4$ solvate in which the anions are uncoordinated. A new band appears at 945 cm$^{-1}$ as the concentration is increased ($n < 4$) corresponding to the (AN)$_2$:LiClO$_4$ phase, which likely consists of AGG-I anions coordinated to two Li$^+$ cations through two oxygen atoms (similar to the (AN)$_2$:LiBF$_4$ solvate—Fig. 4-4). When the concentration of LiClO$_4$ is

![Figure 4-14. ClO$_4^-$ anion band variation with concentration in the (AN)$_n$-LiClO$_4$ mixtures at -80°C.](image-url)
increased further \((n < 2)\), another band appears at \(953 \text{ cm}^{-1}\) corresponding to the \((\text{AN})_1:\text{LiClO}_4\) phase, which likely consists of AGG-II anions coordinated to three \(\text{Li}^+\) cations through three oxygen atoms (similar to the \((\text{AN})_1:\text{LiBF}_4\) solvate—Fig. 4-4). The band at about \(938 \text{ cm}^{-1}\) appears to correspond to coordinated AN as it is found from the characterization of single crystals of the solvates that the position of the coordinated AN differs in the solid-state from that noted in solutions (Fig. 4-7), perhaps due to lattice packing effects.

Fig. 4-15a shows the anion band variation with concentration for \((\text{AN})_n-\text{LiBF}_4\) mixtures at \(-80^\circ\text{C}\). Again, all of the samples are crystalline solids at this temperature. The Raman band from the anion B-F stretching vibrational mode is observed at \(760-780 \text{ cm}^{-1}\). The study reported in Chapter 3 examined the Raman band position in this region for different forms of \(\text{BF}_4^-...\text{Li}^+\) cations coordination found in different crystalline solvates. At \(-80^\circ\text{C}\), only a single band at \(764 \text{ cm}^{-1}\) is noted for the mixtures with \(n \geq 4\) (Fig. 4-15a). A comparison of this plot with the phase diagram in Fig. 4-3, as well as the data in Chapter 3, indicates that the crystalline \((\text{AN})_4:\text{LiBF}_4\) solvate is therefore a SSIP phase in which the anions remain uncoordinated (in agreement with the same solvate for \(\text{LiClO}_4\)). A new band appears at \(778-779 \text{ cm}^{-1}\) as the concentration is increased further corresponding to an AGG-I \((\text{AN})_2:\text{LiBF}_4\) phase in which the anions are coordinated to two \(\text{Li}^+\) cations through two fluorine atoms (Chapter 3 and Fig. 4-4). For the most concentrated samples, another band appears at \(782 \text{ cm}^{-1}\) corresponding to an AGG-II \((\text{AN})_1:\text{LiBF}_4\) phase which consists of anions coordinated to three \(\text{Li}^+\) cations through three fluorine atoms (Chapter 3 and Fig. 4-4). Note that with increasing temperature, the vibrational bands shift and broaden.
For the (AN)\textsubscript{n}-LiBF\textsubscript{4} liquid mixtures at 60°C (Fig. 4-15b), bands appear at approximately 764, 767, 774-775, 783-784 and 798 cm\textsuperscript{-1} which are attributed to SSIP, CIP-I, AGG-I, AGG-II and AGG-III forms of anion coordination, respectively. The AGG-III species may be due to some large solvated aggregate ion clusters which resemble crystalline LiBF\textsubscript{4},\textsuperscript{46} as there is no evidence of solids in the most concentrated mixtures at 60°C. Interestingly, none of the crystalline phases consist of CIP solvates, but these appear to be a prominent species present.

**Figure 4-15.** BF\textsubscript{4}\textsuperscript{-} anion band variation with concentration in the (AN)\textsubscript{n}-LiBF\textsubscript{4} mixtures: (a) -80°C and (b) 60°C.
in dilute (AN)$_n$-LiBF$_4$ solutions. Thus, melting of the SSIP crystalline phase results in (or is caused by) the displacement of one (for CIP-I) or more AN molecules in the Li$^+$ cation coordination shell.

Deconvolution of the Raman bands of the BF$_4^-$ anion (Fig. 4-15b) provides an estimation of the fraction of each type of solvate present in the solutions at 60°C (Fig. 4-16). This determination assumes that the relative activities of the BF$_4^-$ bands associated with different cation coordination have equivalent Raman activity. A consideration of the information provided in Figs. 4-8 and 4-16 suggests that the solution SSIP, CIP-I, AGG-I, AGG-II and AGG-III solvates largely correspond to Li$^+$ cations coordinated by four, three, two, one and zero (or near zero) AN molecules, respectively (the AN molecules are sequentially replaced with fluorine atoms from anions).

The identity of the solvate species present in solution is also a function of temperature. Fig. 4-17 shows the BF$_4^-$ anion band variation with increasing temperature for the (AN)$_n$-

Figure 4-16. Distribution of anion modes of Li$^+$ cation coordination present in the (AN)$_n$-LiBF$_4$ mixtures at 60°C.
LiBF$_4$ (n = 8 and 4) mixtures. When these mixtures are crystalline at -80$^\circ$C, only a single band is observed corresponding to the SSIP (AN)$_4$LiBF$_4$ solvate. The Raman vibrational band of the BF$_4^-$ anion, however, shifts and splits significantly after the solid to liquid phase transition occurs. For the n = 8 mixture, bands at 764-765, 767 and 774-775 cm$^{-1}$, corresponding to SSIP, CIP-I and AGG-I solvates, respectively, are evident. Deconvolution of the Raman bands indicates that with decreasing temperature, the AGG-I solvates decrease

**Figure 4-17.** Temperature dependence of the BF$_4^-$ anion bands in the (AN)$_n$-LiBF$_4$ mixtures: (a) n = 8 and (b) n = 4.
somewhat, while the SSIP and CIP-I solvates increase. For the n = 4 mixture, the same trend is observed at a given temperature, except that the concentration of AGG-I solvates is increased at the expense of the SSIP and CIP-I solvates. The solvent competes more effectively with the anion for Li$^+$ cation coordination at lower temperature and ionic association therefore tends to increase with increasing temperature.

To further aid in understanding the in-depth solvate structures present in liquid electrolytes, molecular dynamic (MD) simulations were performed by a collaborator—Dr. Borodin at the U.S. Army Research Laboratory. Some discrepancies in the calculated average solvation number ($N$) and distribution of solvate species were identified between the simulation results and the experimental work due to the limitations for both forms of analysis. In general, however, excellent agreement was found, especially with regard to the trends in the solvation and ionic association. The simulations provide key information about plausible solvate structures in solution which is unavailable directly from the experimental techniques used.

For example, snapshot of the solvates extracted from the MD simulations show that the TFSI$^-$ anion does form solvates with bidentate coordination of the anion to the Li$^+$ cations (Fig. 4-18—d,f,g) (e.g., for the n = 10 concentration, 12% of the TFSI$^-$ anions have two oxygen atoms from the same anion bound to the same Li$^+$ cation), although this occurs to a much lesser extent than found in the AGG solvate crystal structures (Chapter 3). In contrast, the simulations indicate that bidentate coordination of an anion to a given Li$^+$ cation for semi-spherical anions such as PF$_6^-$, ClO$_4^-$ and BF$_4^-$ (Fig. 4-19—b,d) is rarely observed. This contradicts the predictions of DFT gas phase calculations for the latter anions coordination to
a single Li$^+$ cation which predict that bidentate, or even tridentate, coordination is favored. Such calculations, however, neglect the influence of neighboring solvent molecules and anions on the coordination.

Additional crucial insight was obtained from the simulations regarding the interpretation of the anion coordination information obtained from the experimental raman studies and how this correlates with the solvate species present in solution. In general, Raman data which
indicates that an anion is coordinated to a single Li$^+$ cation is understood to represent a CIP solvate (i.e., Figs. 4-18—b and 4-19—c,d), but the simulations very clearly demonstrate that this interpretation is a gross oversimplification. Many examples of AGG solvates can be identified which contain end (capping) anions which are coordinated to a single Li$^+$ cation (i.e., Figs. 4-18—d,e,f,j and 4-19—e,g,h,i,j) and thus have the same Raman spectral band as for the CIP solvates. Thus, caution should be exercised to avoid misconstruing the solution structure for a given electrolyte. A much improved picture of the solvate structures in solution emerges when both the experimental and computational results are examined in conjunction with one another, despite their discrepancies.

Figure 4-19. Representative Li$^+$ cation solvate species (i.e., coordination shells) extracted from the MD simulations for the (AN)$_n$-LiBF$_4$ mixtures ($n = 30, 20$ and $10$) at $60^\circ$C: (a) SSIP, (b) CIP-I, CIP-II, (c) CIP-I, (d) CIP-II, (e) CIP-I, AGG-I, (f) AGG-I, (g) CIP-I, AGG-I ($\times3$), (h) CIP-I, AGG-I ($\times3$), AGG-III, (i) CIP-I, AGG-I ($\times2$), (j) CIP-I ($\times2$), AGG-I and (k) AGG-I ($\times3$) (Li-purple, N-blue, B-tan, F-light green).
4.5 Transport Properties

*Concentration/density of (AN)$_n$-LiX mixtures:* The formula weights (g mol$^{-1}$) of the salts are: LiTFSI (287.09), LiPF$_6$ (151.91), LiClO$_4$ (106.39), LiBF$_4$ (93.75) and LiCF$_3$CO$_2$ (119.96). The temperature and concentration variation of the density of the (AN)$_n$-LiX mixtures was measured and the isothermal density (60°C) of the mixtures is noted in Fig. 4-20a. To discuss mechanisms for ion transport, it is helpful to relate the properties to the ratio of solvent molecules per Li$^{+}$ cation (i.e., n or AN/LiX), but most of the work reported in the scientific literature is given in terms of molarity or molality. Fig. 4-20b therefore shows the link between the concentration expressed as n vs. molarity (M or mol dm$^{-3}$). For the mixtures with n < 20, the molarity does differ notably for the different salts for a fixed n concentration. As a point of reference, a 1.0 M solution corresponds to a concentration of n ~ 15-18 (for AN solutions) (Fig. 4-20b).

**Figure 4-20.** (a) Density of (AN)$_n$-LiX mixtures at 60°C (AN/LiX ratio noted in the plots) and (b) relationship between molarity vs. concentration for (AN)$_n$-LiX mixtures.
Viscosity of (AN)$_n$-LiX mixtures: The temperature and concentration variation of the viscosity of the (AN)$_n$-LiX mixtures was obtained and the isothermal viscosity (60°C) of the mixtures is reported in Fig. 4-21. Viscosity is a measure of a fluid's resistance to deformation (internal resistance to flow) by either shear or tensile stress.Except for the most concentrated mixtures, the electrolytes studied consist of mixtures of isolated solvates and uncoordinated solvent. The identity of these solvates (SSIP, CIP and AGG) and their distribution, however, differ for the different concentrations and salts. Further, the most dissociated salts will have a greater amount of solvent coordinated to the Li$^+$ cations (and thus less uncoordinated solvent). This is evident from the MD simulations.\textsuperscript{75,76} For example, Fig. 4-22 shows the simulation results for the (AN)$_n$-LiX mixtures (n = 20) with LiPF$_6$ and LiBF$_4$. The same number of Li$^+$ cations and anions are shown for each, but only the AN solvent coordinated to Li$^+$ cations are present. Nearly all of the Li$^+$ cations have four-fold coordination to the

**Figure 4-21.** Viscosity of (AN)$_n$-LiX mixtures (AN/LiX ratio noted in the plots) at 60°C. Data for concentrated mixtures with LiPF$_6$ and LiClO$_4$ was not gathered as these samples form crystalline solids at this temperature. ((b) is an expanded view for the dilute mixtures)
solvent and anions. The LiBF$_4$ mixtures are clearly more aggregated than the LiPF$_6$ mixtures with more anions occupying the Li$^+$ cation coordination shells. The more associated mixtures will therefore have more uncoordinated solvent present. This uncoordinated solvent may, in effect, serve as a lubricant for the solvates resulting in a lower viscosity. The order of increasing ionic association in the (AN)$_n$-LiX mixtures determined previously is:

$$\text{LiPF}_6 < \text{LiTFSI} \leq \text{LiClO}_4 < \text{LiBF}_4 << \text{LiCF}_3\text{CO}_2$$

This ordering and the observed differences in viscosity for the more dilute mixtures (Fig. 4-21) agree very well. It is particularly noteworthy, however, that the viscosity data clearly contradict the conventional wisdom that less viscous solutions are more conductive. For the most concentrated mixtures (i.e., $n \leq 5$), the viscosity values for the LiTFSI and LiBF$_4$
mixtures are similar, but the viscosity of the LiCF$_3$CO$_2$ mixtures is significantly lower (Fig. 4-21). The highly concentrated mixtures begin to resemble clusters of SSIP (i.e., fully solvated Li$^+$ cations and uncoordinated anions), CIP and AGG solvates all closely packed together. There is little to no uncoordinated solvent separating the solvates. Thus, the fully or partially solvated cations are surrounded by anions (to which they are either directly coordinated or in close proximity). The reduction in the shielding and separation of the charged ions results in strong electrostatic interactions between the ions which thus begin to strongly dictate both the mobility and placement of the neighboring counter ions (i.e., influence the manner in which the ions realign relative to one another). This, in turn, greatly increases the viscosity. The explanation for the differences observed for the LiCF$_3$CO$_2$ mixtures may be attributed to the data which suggest that this salt forms AGG solvates in solution, even in very dilute mixtures, which only contain about one AN molecule per Li$^+$ cation (Fig. 4-8). Thus, even the highly concentrated mixtures with this salt still have a sizeable amount of uncoordinated solvent resulting in the much lower solution viscosity than for the other salt mixtures.

**Conductivity of (AN)$_n$-LiX mixtures:** The temperature and concentration variation of the ionic conductivity of the (AN)$_n$-LiX mixtures is given in Fig. 4-23. The data were collected after equilibrating the samples during cooling steps. The rapid drops in the conductivity are due to the crystallization of solvates in the mixtures. This was particularly problematic for the mixtures with LiPF$_6$ and LiClO$_4$, as evident from the phase diagrams (Figs. 4-1 and 4-3). It is difficult to ascribe particular meaning to the data in these figures as it is quite
Figure 4-23. Variable-temperature ionic conductivity of (AN)$_n$-LiX mixtures: (a) LiPF$_6$, (b) LiTFSI, (c) LiClO$_4$, (d) LiBF$_4$ and (e) LiCF$_3$CO$_2$ (AN/LiX ratio (n) noted in the plot).
convoluted, but some features are conspicuous. Typically, a linear relationship for conductivity data plotted on an Arrhenius plot is characterized as Arrhenius behavior:

\[ \kappa = A \exp(-E_a/RT) \quad \text{or} \quad \log(\kappa) = \log(A) - \frac{(E_a/R)(1/T)}{T} \]

with \( A \) being a fitted constant, \( R \) is the gas constant and \( E_a \) is an activation energy. If, instead, the data is curved when plotted on an Arrhenius plot, then the Vogel–Tammann–Fulcher (VTF) equation is instead applied to model the behavior:

\[ \kappa = A T^{-1/2} \exp(-B/(T - T_0)) \]

where \( A \) and \( B \) are fitted constants are generally related to the carrier number and configurational entropy, respectively, and \( T_0 \) is related to the glass transition temperature (\( T_g \)). An examination of Fig. 4-23 indicates two trends. First, the more dilute solutions have Arrhenius-like behavior, whereas the concentrated solutions have VTF-like behavior, especially at low temperature. Based upon the ionic association information previously reported (i.e., increasing association with increasing concentration), this appears to suggest that increasing ionic interactions result in a transition from Arrhenius to VTF behavior. But the second trend observable is that the most associated salts (i.e., LiBF\(_4\) and LiCF\(_3\)CO\(_2\)) have less curvature than is found for dissociated salts (i.e., LiTFSI) contradicting this interpretation. In practice, however, the VTF fitted parameters from such an analysis provide no significant insight into conductivity mechanisms.

It is more information to examine a plot of the isothermal (60°C), variable-concentration data for the conductivity (Fig. 4-24). As is widely observed for other electrolyte mixtures with aprotic solvents, the conductivity peaks near a concentration of 1 M (Figs. 4-20 and 4-
For strong (highly dissociated) electrolytes, the conductivity of an electrolyte is given by:

\[ \kappa = \Lambda n_e C \]

\[ \Lambda = \lambda_+ + \lambda_- = F(u_+ + u_-) \]

where \( n_e \) is the electrochemical valence:

\[ n_e = v_+ z_+ = |v-z| \]

of a binary salt with cationic and anionic charges \( z_+ \) and \( z_- \), stoichiometric coefficients \( v_+ \) and \( v_- \), and \( u_+ \) and \( u_- \) are the ionic mobilities of the cations and anions, respectively. When ionic association into CIP and AGG solvates occurs, however, this is complicated by the diversity of the solvates present. The conductivity is a function of the number of charge carriers (solvates) which migrate in an electric field, the charge of the charge carriers and their mobility. Thus, it is generally accepted that CIP solvates, as neutral species, do not contribute

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**Figure 4-24.** Variable-concentration ionic conductivity of (AN)_\(n\)-LiX mixtures at 60°C.
to the conductivity and AGG solvates contribute, but to a much lesser extend than fully solvate Li\(^+\) cations and uncoordinated anions due to the lower mobility of CIP and AGG solvates.

The lower conductivity values for the dilute mixtures with \(n > 20\) (Fig. 4-24) relative to more concentrated mixtures is generally attributed to the limited number of charge carriers. It is usually proposed that as the concentration becomes greater and approaches the value for the peak conductivity, the number of charge carriers increases without overly reducing the mobility of the charge carriers (solvates). But a further increase in concentration leads to the formation of CIP solvates and larger AGG species which reduces both the number of charge carriers and their mobility. A similar explanation may be used to explain the differences between the conductivity values for the different salts at a given concentration—namely, \((AN)_n\)-LiX \((n = 20)\) solutions with the most dissociated salts (i.e., LiPF\(_6\)) have the highest conductivity (Fig. 4-24) and consist principally of SSIP, and perhaps CIP, solvates (Fig. 4-22), whereas the mixtures with the more associated salts (i.e., LiBF\(_4\) or LiCF\(_3\)CO\(_2\)) have a much lower conductivity (Fig. 4-24) and contain principally CIP and AGG solvates (Fig. 4-22) which limits both the number of available charge carriers and their mobility.

When the data is replotted as molar conductivity (Fig. 4-25a), no peaks are evident. Instead relatively smooth curves are found with the most dilute mixtures having the highest molar conductivity values. If the ions were fully dissociated (i.e., strong electrolyte), then the molar conductivity would, in effect, be the conductivity normalized in terms of the available charge carriers. But since the ions are not fully dissociated, this is not the case. The same trends with regard to the conductivity and anions are found with the most associated salts.
having the lowest conductivity. For the highly concentrated mixtures (n ≤ 5), the conductivity values converge, except for the mixtures with LiCF$_3$CO$_2$. An explanation for this is similar to the one provided above for the viscosity data. The variation in properties

\[ \text{Figure 4-25. Molar conductivity of } (a) (\text{AN})_n-\text{LiX mixtures (60°C) for varying AN/LiX (n) concentrations and (b) (AN)$_n$-LiX mixtures (n = 20 - filled circles are average values, individual measurements shown as small open circles and n = 4 - larger open circles) with varying temperature.} \]
that results from different anions are exemplified in Fig. 4-25b which indicates that the molar conductivity of the dilute \((\text{AN})_n\)-LiCF\(_3\)CO\(_2\) \((n = 20)\) mixture is comparable to that for the highly concentrated \((\text{AN})_n\)-LiTFSI or -BF\(_4\) \((n = 4)\) mixtures (while the conductivity of the latter mixtures is even higher—Fig 4.24), although a different temperature dependence is found.

4.6 Conclusions

Five phase diagrams of \((\text{AN})_n\)-LiX \((X = \text{PF}_6^-, \text{TFSI}^-, \text{ClO}_4^-, \text{BF}_4^- \text{and CF}_3\text{CO}_2^-)\) mixtures were determined and the phase behavior was compared/ contrasted. Widely varying phase behavior (i.e., solvate formation) was found for different anions. Solvate crystal structures were determined to add additional insight into the phase behavior. This work was complemented by a Raman spectroscopic analysis used to examine both the solvent and anion interactions with the Li\(^+\) cations. An average Li\(^+\) cation solvation number \((N)\) in solution was determined as a function of salt concentration with wide variability noted for different anions. Utilizing the information obtained from the crystal structure and the spectroscopic characterization of both the average solvation number \((N)\) and anion coordination at a given composition and temperature, it is possible to glean considerable insight into the structure of the solvates in the liquid phase. Examining electrolytes composed of varying salts with a single solvent, AN, greatly aids in understanding the significance of ionic association interactions within the liquid phase (i.e., solution structure) with regard to the origin of widely varying electrolyte properties.
4.7 References


CHAPTER 5

Electrolyte Solvation and Association (II):

Propionitrile (PN) and Butyronitrile (BN)-Lithium Salt Mixtures

5.1 Introduction

As a continuation of the work from Chapter 4, propionitrile (PN) and butyronitrile (BN), which have a longer alkyl chain than AN, were studied with various lithium salts to examine how solvent structure dictates the properties of the mixtures. These solvents have only one nitrogen donor atom, as for AN. The manner in which they coordinate Li\(^{+}\) cations is therefore similar. The properties of PN and BN are shown in Table 5-1.\(^1,2\) It is interesting to note that the two solvent polarity parameters—\(DN\) and \(\varepsilon\)—show an opposite trend relative to one another. It is therefore worthwhile to study how differences in the solvent alkyl chain length affect the molecular interactions (i.e., both ion solvation and ionic association) and how this governs the properties of the electrolyte mixtures. This study will be useful for comparison with a similar evaluation (not part of the present study) of dinitrile solvents—SN and glutaronitrile (GLN)—which are one class of alternative solvents for electrolyte with a wide temperature window of operation and high electrochemical stability.\(^3-6\) For this study, mixtures with four lithium salts were evaluated: LiPF\(_6\), LiTFSI, LiClO\(_4\) and LiBF\(_4\).

| Table 5-1. The properties of mononitrile solvents studied. (viscosity and density values are for 25\(^{\circ}\)C)\(^1,2\) |
|-----------------------------------------------|---------|---------|---------|---------|---------|---------|
| Solvent                       | \(T_m\) (\(^{\circ}\)C) | \(T_b\) (\(^{\circ}\)C) | \(DN\)   | \(\varepsilon\) | \(\eta\) (mPa s) | \(\rho\) (g cm\(^{-3}\)) |
| acetonitrile                  | -49     | 82      | 14.1    | 36       | 0.30    | 0.78     |
| propionitrile                 | -93     | 97      | 16.1    | 26       | 0.41    | 0.77     |
| butyronitrile                 | -112    | 118     | 16.6    | 21       | 0.53    | 0.79     |
5.2 Thermal Phase Behavior

*Pure Solvent:* PN undergoes a solid-solid phase transition at \(-96^\circ\text{C}\) prior to the \(T_m\) at \(-92^\circ\text{C}\) (Figs. 5-1 and 5-2), while BN has \(T_m\) at \(-108^\circ\text{C}\) (Figs. 5-3 and 5-4). Unlike AN and PN (which crystallize readily on cooling), BN is only able to crystallize after cycling/annealing the sample at low temperature. In contrast with AN and PN, BN is known to have two different conformations in the liquid phase—*anti* and *gauche* conformers. From *ab initio* calculations, it has been shown that the *gauche* conformer is more stable than the *anti* conformer. From a Raman analysis, however, BN has only the *anti* conformer in the solid (crystalline) phase.\(^7\) This is likely to be the reason why BN cannot be crystallized easily. In addition, the longer alkyl chain on BN may make the ordered packing of the solvent molecules more difficult for the formation of the crystalline phase.

The thermal phase behavior of the mixtures was examined. Figs. 5-1 and 5-2 show DSC heating trace for the varying concentrations and the corresponding phase diagram for the (PN)\(_n\)-LiX mixtures, while Figs. 5-3 and 5-4 show similar data for the (BN)\(_n\)-LiX mixtures.

*PN-LiPF\(_6\):* Similar to the (AN)\(_n\)-LiPF\(_6\) mixtures, it was difficult to crystallize the dilute samples into thermodynamically favored phases. A 4/1 PN/LiPF\(_6\) solvate (i.e., (PN)\(_4\):LiPF\(_6\)) clearly forms with two low-energy solid-solid phase transition at \(-120\) and \(-114^\circ\text{C}\) prior to \(T_m\) at 36\(^\circ\text{C}\). But more dilute mixtures also form a different (more dilute) phase, as well as the 4/1 phase. Sharp peaks are noted near \(-55^\circ\text{C}\), while broader peaks are found near \(-20^\circ\text{C}\) (Fig. 5-1). It is possible that these correspond to different phases, but another possibility is that the peaks actually correspond to a single phase (i.e., perhaps (PN)\(_6\):LiPF\(_6\)) with the \(-55^\circ\text{C}\) peak representing a solid-solid phase transition and the higher temperature peak the \(T_m\). A eutectic
**Figure 5-1.** DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) PN-(x) LiPF₆ and (b) (1-x) PN-(x) LiTFSI mixtures.
Figure 5-2. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) PN-(x) LiClO₄ and (b) (1-x) PN-(x) LiBF₄ mixtures.
forms for the concentrated compositions between the 4/1 solvate and a more aggregated (concentrated) phase (i.e., perhaps a (PN)$_1$:LiPF$_6$ solvate). Due to limitation for the salt dissolution in the highly concentrated mixtures, the composition of the aggregated solvate was not determined.

*PN-LiTFSI:* Many of the (PN)$_n$-LiTFSI mixtures (i.e., $n \leq 8$) remain completely amorphous phase (Fig. 5-1). For the most dilute samples, some of the pure PN solvent could be crystallized. These samples are semicrystalline with the solvated LiTFSI remaining in an amorphous phase (the $T_g$ is $< -150^\circ$C for these samples). The large size and flexibility of the TFSI$^-$ anion appears to readily disrupt the ordered packing of the solvated Li$^+$ cations solvates necessary for the growth of a crystalline phase. Note that this does not mean that crystalline phases cannot form in these mixtures. Rather, it indicates that crystalline solvates cannot form under the experimental cycling/annealing conditions used (not shown).

*PN-LiClO$_4$: Four crystalline solvate phases form in the (PN)$_n$-LiClO$_4$ mixtures (Fig. 5-2). 3/1 and 2/1 solvates were clearly identified with sharp peaks of $T_m$ at 11 and 17$^\circ$C, respectively. It was difficult to characterize the thermal behavior of the (PN)$_n$-LiClO$_4$ ($n > 3$) mixtures due to the formation of both the 3/1 phase and a more dilute phase of unknown composition. Two different eutectic compositions are found, with one between the 3/1 and 2/1 phases and another between the 2/1 phase and a more aggregated solvate. The $n = 1$ sample still has a melting peak for the 2/1 solvate, as well as a peak for a more aggregate solvate (unknown composition, but likely more concentrated than 1/1). Due to limitations for the salt dissolution, it was not possible to analyze more concentrated mixtures than the 1/1 mixture.
PN-LiBF₄: Three crystalline solvate phases appear to form in the (PN)ₙ-LiBF₄ mixtures consisting of 3/1, 2/1 and a more aggregated solvate (than 1/1) (Fig. 5-2). The 3/1 and 2/1 solvates have a $T_m$ at -30 and -9°C, respectively. Due to limitations for the salt dissolution, it was not possible to analyze more concentrated mixtures than the 1/1 mixture.

BN-LiPF₆: Two crystalline solvate phases form in the (BN)ₙ-LiPF₆ mixtures, with a 4/1 phase clearly identifiable (Fig 5-3). The most dilute (n ≥ 20) mixtures could not be crystallized and only a $T_g$ was noted at low temperature. The more concentrated (n < 20) mixtures, however, could be crystallized. For the (10 ≥ n > 4) samples, the DSC data shows $T_m$ peaks corresponding to both the pure BN and the 4/1 solvate. The 4/1 solvate has a $T_m$ at -14°C. For the n < 4 samples, a eutectic was found between the 4/1 phase and a more aggregated solvate (unknown composition). Due to limitations for the salt dissolution, it was not possible to analyze more concentrated mixtures than the 2.3/1 mixture.

BN-LiTFSI: No crystalline phases were found in the (BN)ₙ-LiTFSI mixtures (Fig 5-3, despite extensive cycling/annealing of the samples at low temperature. Only for the 40/1 mixture was it possible to crystallize some of the BN solvent.

BN-LiClO₄: Two crystalline phases were found in the (BN)ₙ-LiClO₄ mixtures, consisting of 5/1 (perhaps 4/1) and 2/1 solvates (Fig. 5-4). As for the (BN)ₙ-LiPF₆ mixtures, the dilute mixtures (n ≥ 10) could not be crystallized. The $T_m$ at -80°C is believed to correspond to a 5/1 solvate, but it is possible that this may instead be a 4/1 solvate (even though the samples with a n = 4 composition did not crystallize). If it is a 5/1 solvate, then this solvate may have a similar structure to the (AN)₅:LiPF₆ and (AN)₆:LiPF₆ solvates, which have a Li⁺ cation
coordinated by four AN molecules and one and two additional uncoordinated AN solvent molecules, respectively, in crystal structure.\textsuperscript{8,9} A crystallinity gap is found for samples with a composition intermediate between these two crystalline phases. The 2/1 solvate has a $T_m$ at -13°C. Samples more concentrated than the 2/1 phase could not be crystallized.

Figure 5-3. DSC heating traces (5°C min\textsuperscript{-1}) and the corresponding phase diagrams of (a) (1-x) BN-(x) LiPF\textsubscript{6} and (b) (1-x) BN-(x) LiTFSI mixtures
Figure 5-4. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-\(x\)) BN-(\(x\)) LiClO₄ and (b) (1-\(x\)) BN-(\(x\)) LiBF₄ mixtures.
**BN-LiBF₄**: Thermal phase behavior of the (BN)ₙ-LiBF₄ mixtures is similar to that of the (BN)ₙ-LiTFSI mixtures. No crystallization occurred for any of the concentrations studied (Fig. 5-4).

The thermal phase behavior can be linked with the ionic association of LiX salts in PN and BN mixtures, as has already been seen for the (AN)ₙ-LiX (Chapter 4) and (glyme)ₙ-LiX mixtures. The solvates tend to melt at lower temperature and/or the first phase to form from dilute solutions tends to be more aggregated for salts with increasing ionic association (i.e., (PN)ₙ-LiClO₄ vs. (PN)ₙ-LiBF₄). Furthermore, the differences in the solvent structure also affect the phase behavior. The Tₘ of the LiX solvates with AN are generally higher than those for the PN and BN mixtures, while the solvates with PN generally have a higher Tₘ than those for the BN mixtures. The disruption to the ordered packing caused by the rotation and/or conformational changes of the nitrile solvent molecules with longer alkyl chains due to thermal energy is the likely explanation for the reduction in the solvate Tₘ values with increasing solvent alkyl chain length.

### 5.3 Ion Solvation

Uncoordinated PN has a ν₂ Raman band at 2247 cm⁻¹ for the C≡N stretching vibration and a ν₄ Raman band at 837 cm⁻¹ for the C–C stretching vibration (Fig. 5-5). When the PN nitrogen atom is coordinated to a Li⁺ cation with its electron lone-pair, these bands shift to 2273 and 845 cm⁻¹, respectively (Fig. 5-5). BN has a ν₂ Raman band at 2250 cm⁻¹ for the C≡N stretching vibration with a shoulder at 2237 cm⁻¹ (Fig. 5-6). Unlike AN and PN, only the C≡N stretching band for BN shifts (to 2273 cm⁻¹) upon coordination of the solvent to a
Li$^+$ cation (Fig. 5-6). The PN C-C stretching band at 830 cm$^{-1}$ does not shift upon Li$^+$ cation coordination. Thus, only the $\nu_2$ Raman band was analyzed for the (BN)$_n$-LiX mixtures.

The average solvation number for the liquid mixtures (at 60°C) was calculated from the solvent Raman band(s) based upon the assumption that the uncoordinated and coordinated PN and BN bands have equivalent Raman activity, as was done for Chapter 4.$^{13,14}$ Fig. 5-7
shows the average solvation number of the \((\text{PN})_n\)-LiX and \((\text{BN})_n\)-LiX mixtures. Selecting a particular composition for comparison (as was done in Chapter 4), for the \(n = 0.20\) (AN/Li = 4/1) mixtures, the average solvation number of the PN mixtures is approximately 3.0 for LiPF\(_6\), 2.8 for LiTFSI, 2.6 for LiClO\(_4\) and 2.0 for LiBF\(_4\). The PN mixtures thus have slightly lower \(N\) values than those for the \((\text{AN})_n\)-LiX mixtures (Fig. 4.8). For the \((\text{BN})_n\)-LiX \((n = 0.20)\) mixtures, the \(N\) values are 2.7 for LiPF\(_6\), 2.4 for LiTFSI, 2.2 for LiClO\(_4\) and 1.3 for LiBF\(_4\). The BN mixtures therefore have a significantly lower degree of solvation than the PN mixtures.

\[\text{Figure 5-6. Raman spectra of the BN } \equiv \text{N} (2250 \text{ cm}^{-1}) \text{ stretching band for the } (\text{BN})_n\text{-LiX mixtures with (a) LiPF}_6 \text{ and (b) LiTFSI at 60°C (BN/LiX ratio indicated).}\]
and AN mixtures. This can be relate (perhaps) with the lower dielectric constant of the PN and BN solvents, as well as the longer alkyl chains which may hinder Li$^+$ cation coordination because of steric effects. Therefore, the degree of solvation for the solvent molecule can be ordered based upon the average solvation number ($N$) as follows:

$$AN > PN > BN$$
Moreover, this comparison shows the same trends found previously with glyme and AN for the association of different lithium salts\(^{10,13,14}\):

\[
\text{LiPF}_6 < \text{LiTFSI} \leq \text{LiClO}_4 < \text{LiBF}_4
\]

### 5.4 Ionic Association

To understand the ionic association interactions in solution, the Raman bands of the anions were examined. For the (PN)\(_n\)- and (BN)\(_n\)-LiPF\(_6\) mixtures, Fig. 5-8 shows the band variation of the PF\(_6^-\) anion. As for the (AN)\(_n\)-LiPF\(_6\) mixtures (Chapter 4), a band at 741 cm\(^{-1}\) is observed for the dilute samples, which is from the PF\(_6^-\) anion with either SSIP or CIP coordination (as noted above). As the salt concentration increases, this band shifts slightly to higher wavenumber due to the formation of AGG solvates. A comparison of the PF\(_6^-\) anion band variation in the different solvents is not particularly useful, however, because all of the spectra are essentially identical for the three sets of mixtures at a given concentration. This may be due to the fact that SSIP and CIP solvates dominate for the dilute mixtures and it is not possible to estimate the amounts of these because of the overlap of the respective PF\(_6^-\) anion bands. Thus, the distribution of the SSIP and CIP may well vary for the different solvents (as indicated by the different average solvation numbers for the different solvents). Only a few AGG solvates may form in these dilute mixtures irrespective of the nitrile solvent. In contrast, for the most concentrated samples, the solvation numbers converge (for the different solvents) and thus the distribution of the solvate species may be similar (resulting in similar anion spectra).

For the (PN)\(_n\)- and (BN)\(_n\)-LiTFSI mixtures, Fig. 5-8 shows the band variation of the TFSI\(^-\) anion. As for the (AN)\(_n\)-LiTFSI mixtures, the Raman band intensities shift smoothly as the
Figure 5-8. The anion band variation with concentration in (a) (PN)$_n^-$ and (BN)$_n^-\text{LiPF}_6$, (b) (PN)$_n^-$ and (BN)$_n^-\text{LiTFSI}$, (c) (PN)$_n^-$ and (BN)$_n^-\text{LiClO}_4$ and (d) (PN)$_n^-$ and (BN)$_n^-\text{LiBF}_4$ at 60°C.
Figure 5-9. Comparison of Raman band of the (solvent)$_n$-LiX ($n = 6$) mixtures: (a) LiTFSI, (b) LiClO$_4$ and (c) LiBF$_4$. 
concentration is increased due to the formation of CIP and AGG solvates. A comparison of the spectra for the n = 6 samples with the different solvents (Fig. 5-9a) indicates that there is a significant difference in the fraction of solvates present. The ionic association (increase in CIP coordination at the expense of SSIP coordination) therefore increases in the order:

\[ \text{AN} < \text{PN} < \text{BN} \]

This is in complete accord with the \( N \) values noted above.

For the \((\text{PN})_n\) and \((\text{BN})_n\)-LiClO\(_4\) mixtures, Fig. 5-8 shows the band variation of the ClO\(_4^−\) anion. The assignments for the ClO\(_4^−\)...Li\(^+\) cation coordination have been previously reported.\(^{15−17}\) The solvate bands (at -100°C) are positioned at: SSIP (933 cm\(^{-1}\)), CIP-I (942 cm\(^{-1}\)), AGG-I (945 cm\(^{-1}\)), AGG-II (955 cm\(^{-1}\)) and AGG-III (962 cm\(^{-1}\)) solvates.\(^{17}\) A comparison of the solvate distribution in these mixtures shows a similar trend with that found for the LiTFSI mixtures (Fig. 5-9). Note that the AN solvent bands overlap with the anion bands so data for AN is not shown.

For the \((\text{PN})_n\) and \((\text{BN})_n\)-LiBF\(_4\) mixtures, Fig. 5-8 shows the band variation of the BF\(_4^−\) anion. For the \((\text{BN})_n\)-LiBF\(_4\) mixtures, the Raman analysis for the BF\(_4^−\) anion is not possible due to the band overlap between the B-F stretching mode of the anion and the CH\(_2\) rocking mode of the solvent.\(^7\) Data for the BN mixtures is therefore not included in Fig. 5-9. A comparison between the AN and PN mixtures, however indicates that the AN mixture is less aggregated than the PN mixture (Fig. 5-9), as observed for the other salts.

### 5.5 Transport Properties

**Concentration/density:** The isothermal density (60°C) of the mixtures is reported in Fig. 5-10. The relationship between the molarity (M or mol dm\(^{-3}\)) and the ratio of solvent
molecules per Li\(^+\) cation (i.e., n or solvent/LiX) is also shown in Fig. 5-10. A 1.0 M solution corresponds to a concentration of n \sim 12-15 for the PN solutions and n \sim 9-11 for the BN solutions. From this information, the (BN)\(_n\)-LiX mixtures have the lowest density, and the
**Figure 5-11.** Variable-concentration viscosity of (a) (PN)$_n$-LiX and (b) (BN)$_n$-LiX mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.
(AN)ₙ-LiX mixtures have the highest density, in accord with the differences of the pure solvent density.

**Viscosity**: The isothermal viscosity (60°C) of the (PN)ₙ- and (BN)ₙ-LiX mixtures is reported in Fig. 5-11. The BN and AN mixtures have the highest and lowest viscosity, respectively, for a specific salt concentration. Furthermore, the same trend as found for the
(AN)$_n$-LiX mixtures was noted for the (PN)$_n$- and (BN)$_n$-LiX mixtures, with the viscosity increasing in the order:

$$\text{LiPF}_6 > \text{LiTFSI} > \text{LiClO}_4 > \text{LiBF}_4$$

Thus, higher salt dissociation (i.e., increased Li$^+$ cation solvation) results in a higher viscosity. In addition to the solvates formed and their distribution, the viscosity is largely
influenced by the amount of free (uncoordinated) solvent present, especially for dilute mixtures. The less aggregated mixtures have a lower amount of free solvent due to the increased solvation of the Li$^+$ cations.

**Conductivity:** The temperature and concentration variation of the ionic conductivity of the (PN)$_n$- and (BN)$_n$-LiX mixtures is given in Figs. 5-12 and 5-13. In these figures, the conductivity of the more dilute concentrations (with lower ion aggregation) follows Arrhenius behavior, whereas the concentrated mixtures (with higher ion aggregation) follow the VTF model. In contrast with this, however, the more aggregated mixtures (with LiBF$_4$) are more Arrhenius-like than the less aggregated mixtures (with LiTFSI). A plot of the isothermal (60°C), variable-concentration data for the conductivity is shown in Fig. 5-14.
Figure 5-15. Molar conductivity of (a) (PN)$_n$-LiX and (b) (BN)$_n$-LiX mixtures (60 °C) for varying solvent/LiX (n) concentrations and (c) (PN)$_n$-LiX and (d) (BN)$_n$-LiX mixtures (n = 20) for varying temperature.
The order of increasing conductivity for the mixtures is as follows:

$$\text{AN} > \text{PN} > \text{BN}$$

This is perhaps related to the higher viscosity of the mixtures and the increasing solvate aggregation with increasing solvent alkyl chain length. As for the (AN)$_n$-LiX mixtures, the conductivity of the (PN)$_n$- and (BN)$_n$-LiX mixtures follows the order:

$$\text{LiPF}_6 > \text{LiTFSI} > \text{LiClO}_4 > \text{LiBF}_4$$

The peak conductivity is found near 1.2-1.5 M for the (PN)$_n$-LiX mixtures and 1.1-1.3 M for the (BN)$_n$-LiX mixtures. This is dependent upon the optimization of the number of available charge carriers and their mobility. Fig. 5-15 shows the molar conductivity of the (PN)$_n$- and (BN)$_n$-LiX mixtures. The data closely resembles that found for the (AN)$_n$-LiX mixtures (Fig. 4-23) with an increase noted in the molar conductivity in the order:

$$\text{AN} > \text{PN} > \text{BN}$$

as found for the conductivity.

**5.6 Conclusions**

For comparison with the (AN)$_n$-LiX work reported in Chapter 4, (PN)$_n$- and (BN)$_n$-LiX mixtures were examined to understand how the solvent structure influences the molecular interactions and transport properties of the electrolytes. Using four different salts (LiPF$_6$, LiTFSI, LiClO$_4$ and LiBF$_4$) and two solvents (PN and BN), eight phase diagrams were obtained and compared with the (AN)$_n$-LiX mixtures to identify how the different solvents affect the thermal phase behavior. Raman spectra were obtained to examine both the ion solvation and ionic association interactions in the liquid phase. Increasing the solvent alkyl chain length tends to lower the Li$^+$ cation solvation and increase the ion association, likely
due to increased steric hindrance from the coordinating solvent molecules. The conductivity decreases and the viscosity increases with increasing solvent alkyl chain length. This is readily explained by the solution structure, noted from the variations in the phase diagrams and Raman spectroscopy, which varies significantly upon changing the solvent structure. This work is, therefore, able to show a strong correlation between the molecular interactions and the properties of the electrolyte mixtures.

5.7 References


CHAPTER 6

Electrolyte Solvation and Association (III):

Cyclic Carbonate and Ester-Lithium Salts Mixtures

6.1 Introduction

Current state-of-art electrolytes for commercial Li-ion batteries use a mixture of cyclic and acyclic carbonate solvents with LiPF$_6$. EC is the most widely used cyclic carbonate solvents, although EC has some drawbacks including a high $T_m$ (32 °C), a high viscosity and a tendency to form crystalline solvates when mixed with LiX salts. To decrease the viscosity, increase conductivity and avoid crystallization, an acyclic carbonate (i.e., dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (MEC), etc.) is typically added to EC-LiPF$_6$ mixtures. Despite its drawbacks, EC is a crucial solvent for electrolyte because it is able to strongly solvate Li$^+$ cations and it forms a passivation layer, the so-called solid-electrolyte interface (SEI), on the graphite anode used in Li-ion batteries. As demands for new advanced electrolytes have grown for new lithium battery chemistries, alternative solvents and LiX salts have once again become a focus. The present study is not aimed at developing practical electrolytes, but rather to understand how solvent and anion structure (as well as composition and temperature) influence electrolyte solution structure and properties.

This chapter focuses on the investigation of cycle carbonate (EC and PC) or ester (GBL and GVL) solvent-LiX mixtures with three lithium salts: LiClO$_4$, LiTFSI and LiPF$_6$. These four solvent have a very similar structure—differing in an extra oxygen atom and/or methyl group in/on the solvent ring (Fig. 2-2). Table 6-1 shows the properties of these solvents.
For polarity solvent parameters, $DN$ and $\varepsilon$, have different trends, as was noted for the nitrile solvents in Chapter 5. Very little information is available regarding how varying the structure of the solvent influences the molecular interaction, as well as the properties of electrolytes. Utilizing the combination of structural information (phase diagrams and solvate crystal structures) and Raman spectroscopy to examine the ion solvation and ionic association interactions, the solution structure (molecular-level interactions) of the carbonate- and ester-LiX mixtures was determined and linked with the transport properties of the electrolyte mixtures as was done in Chapters 3 and 4 for the nitrile-LiX mixtures.

6.2 Thermal Phase Behavior and Solvate Crystal Structures

**Pure Solvents:** EC has an unusually high $T_m$ of 32 °C (Table 6-1). The crystal structure of EC has been reported. Unlike EC, the solvents PC, GBL and GVL have a relatively low $T_m$ of -49, -44 and -31°C, respectively (Table 6-1).

**EC-LiPF$_6$:** Two crystalline solvates form in (EC)$_n$-LiPF$_6$ mixture (Fig. 6-1), with a 4/1 solvate clearly identified. The structure of 4/1 (i.e., (EC)$_4$:LiPF$_6$) solvate has been previously reported and is known to be SSIP solvate in which the Li$^+$ cations are fully solvated by four EC molecules and the PF$_6^-$ anions are uncoordinated (Fig. 6-2). A more aggregated solvate

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_m$ (°C)</th>
<th>$T_b$ (°C)</th>
<th>$DN$</th>
<th>$\varepsilon$</th>
<th>$\eta$ (mPa s)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene carbonate (EC)</td>
<td>32</td>
<td>248</td>
<td>16.4</td>
<td>89</td>
<td>1.44</td>
<td>1.29</td>
</tr>
<tr>
<td>propylene carbonate (PC)</td>
<td>-49</td>
<td>242</td>
<td>15.1</td>
<td>69</td>
<td>1.23</td>
<td>1.16</td>
</tr>
<tr>
<td>$\gamma$-butyrolactone (GBL)</td>
<td>-44</td>
<td>204</td>
<td>18.0</td>
<td>42</td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td>$\gamma$-valerolactone (GVL)</td>
<td>-31</td>
<td>208</td>
<td>-</td>
<td>34</td>
<td>1.10</td>
<td>1.02</td>
</tr>
</tbody>
</table>
Figure 6-1. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiPF₆ and (b) (1-x) PC-(x) LiPF₆ mixtures.
Figure 6-2. Li$^+$ cation coordination in the (a) (EC)$_4$:LiPF$_6$ and (b) (GBL)$_4$:LiPF$_6$ (Li-purple, P-gold, F-light green, O-red).

Figure 6-3. DSC heating traces (5°C min$^{-1}$) and the corresponding phase diagrams of (1-x) GBL-(x) LiPF$_6$ mixtures.
is also formed in the concentrated samples, but due to the limitation for the salt dissolution, the composition of this solvate is unknown. Two eutectics are found—one between the pure EC and 4/1 solvate, and another between the 4/1 solvate and the more aggregated solvate.

**PC-LiPF₆:** A 4/1 crystalline solvate forms in the (PC)ₙ-LiPF₆ mixtures, but only for mixtures close to the composition of this solvate (Fig. 6-1). The other compositions studied could not be crystallized. The structure is this solvate is not known, but it may resemble the SSIP (EC)₄:LiPF₆¹¹ and (GBL)₄:LiPF₆ solvates (Fig. 6-2).

**GBL-LiPF₆:** Four crystalline solvates appear to form in the (GBL)ₙ-LiPF₆ mixtures (Fig. 6-3), with a 5/1, 4/1, 3/1 and 2/1 composition. The structure of 4/1 solvate (i.e., (GBL)₄:LiPF₆) was determined as part of the present study. This SSIP solvate resembles the (EC)₄:LiPF₆ solvate¹¹ with Li⁺ cations coordinated by four GBL molecules and uncoordinated PF₆⁻ anions (Fig. 6-2). A eutectic is found between the pure GBL and 5/1 solvate.

**GVL-LiPF₆:** When (GVL)ₙ-LiPF₆ mixtures were prepared and heated/stirred, none of the compositions formed homogenous solutions. Instead, it appears that a degradation reaction occurred as the colorless mixtures became brown and a precipitate accumulated on the bottom of vials. Therefore, the (GVL)ₙ-LiPF₆ mixtures could not be analyzed for comparison with the other mixtures.

**EC-LiTFSI:** Two crystalline solvates form in the (EC)ₙ-LiTFSI mixtures (Fig. 6-4), with a 3/1 and 1/1 composition. The structure of both solvates (i.e., (EC)₃:LiTFSI and (EC)₁:LiTFSI) was determined as part of the present study (Fig.6-5). The (EC)₃:LiTFSI solvate consists of Li⁺ cations coordinated by five oxygen atoms (three from three EC
Figure 6-4. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiTFSI and (b) (1-x) PC-(x) LiTFSI mixtures.
molecules and two from two TFSI$^-$ anions). The TFSI$^-$ anions are coordinated to two Li$^+$ cations (i.e., AGG-Ia-C$_2$ coordination) thus forming linear polymeric aggregates. The (EC)$_1$:LiTFSI solvate consists of Li$^+$ cations coordinated by five oxygen atoms (two from two EC molecules and three from two TFSI$^-$ anions). The TFSI$^-$ anions have four-fold coordination to three Li$^+$ cation (i.e., AGG-IIb-C$_2$ coordination). A eutectic is present between the pure EC and 3/1 solvate, while a crystallinity gap is found between the 3/1 and 1/1 solvates.

**PC-, GBL-, GVL-LiTFSI:** No crystalline solvates formed in the mixtures with PC, GBL and GVL (Figs. 6-4 and 6-6). Only some of the pure solvent can be crystallized for the very dilute mixtures for (GBL)$_n$- and (GVL)$_n$-LiTFSI. The pure PC solvent could not be crystallized for the mixtures with LiTFSI even for the very dilute mixtures (n = 40 and 30). PC and GVL are both racemic with (R)-(+) and (S)-(+) molecules. The two different type of
Figure 6-6. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-\(x\)) GBL-(\(x\)) LiTFSI and (b) (1-\(x\)) GVL-(\(x\)) LiTFSI mixtures.
PC isomer may hinder the ability of the solvent to crystallize, but it was possible to crystallize some of the GVL.

**EC-LiClO₄:** Two crystalline phases form in (EC)ₙ-LiClO₄ mixtures (Fig. 6-7), with a 3/1 and 2/1 composition. The structures of both solvates (i.e., (EC)₃:LiClO₄ and (EC)₂:LiClO₄) were determined as part of the present study (Fig. 6-8). The (EC)₂:LiClO₄ solvate consists of Li⁺ cations coordinated by four oxygen atoms (three from three EC molecules and one from a ClO₄⁻ anion). The ClO₄⁻ anions are coordinated to a single Li⁺ cation (i.e., CIP-I coordination). The (EC)₃:LiClO₄ solvate consists of Li⁺ cations coordinated by four oxygen atoms (two from two EC molecules and two from two ClO₄⁻ anions). The ClO₄⁻ anions are coordinated to two Li⁺ cations (i.e., AGG-I coordination). A eutectic is present between the pure EC solvent and 3/1 solvate, and the 3/1 solvate has a solid-solid phase transition at -94°C. For mixtures more concentrated than the 2/1 composition, some of the sample crystallized as the 2/1 phase while the remainder could not be crystallized. The mixture with n = 1 remained completely amorphous.

**PC-LiClO₄:** No crystalline solvate forms in the (PC)ₙ-LiClO₄ mixtures (Fig. 6-7). Furthermore, the pure PC solvent could not be crystallized, even for the very dilute mixtures (n = 40), as for the (PC)ₙ-LiTFSI mixtures.

**GBL-LiClO₄:** Three crystalline phases form in the (GBL)ₙ-LiClO₄ mixtures (Fig. 6-9), with a 4/1, 3/1 and 1/1 composition. The 1/1 (i.e., (GBL)_1:LiClO₄) solvate structure was determined as part of the present study (Fig. 6-8). The (GBL)_1:LiClO₄ solvate consists of Li⁺ cation coordinated by four oxygen atoms (two from two GBL molecules and two from two ClO₄⁻ anions). The ClO₄⁻ anions are coordinated to two Li⁺ cations (i.e., AGG-I
Figure 6-7. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) EC-(x) LiClO₄ and (b) (1-x) PC-(x) LiClO₄ mixtures.
Interestingly, the carbonyl oxygen atoms of the GBL are coordinated to two Li$^+$ cations. Two eutectics were found—one between the pure GBL and 4/1 solvate, and another between the 4/1 and 3/1 solvates. The 3/1 solvate has a solid-solid phase transition at -92°C prior to the $T_m$ at -9°C. Between the n = 3 and 1 compositions, some exothermic peaks were noted, perhaps due to the formation of a metastable phase.

Figure 6-8. Li$^+$ cation coordination in the (a) (EC)$_3$:LiClO$_4$, (b) (EC)$_2$:LiClO$_4$, (c) (GBL)$_1$:LiClO$_4$ and (d) (GVL)$_1$:LiClO$_4$ solvate crystal structures (Li-purple, Cl-green, O-red).
**GVL-LiClO₄:** One crystalline phase forms in the (GVL)ₙ-LiClO₄ mixtures (Fig. 6-9), with a 1/1 composition. This phase forms, however, only for mixtures close to this composition. Most of the other samples could not be crystallized. The 1/1 (i.e., (GVL)₁:LiClO₄) solvate structure was determined as part of the present study (Fig. 6-8). The (GVL)₁:LiClO₄ solvate consists of Li⁺ cation coordinated by four oxygen atoms (two from two GVL molecules and two from two ClO₄⁻ anions). The ClO₄⁻ anions are coordinated to two Li⁺ cations (i.e., AGG-I coordination). This solvate is nearly isostructural with the (GBL)₁:LiClO₄ solvate (Fig. 6-8). The GVL molecules in the structure are disordered over two positions due to the inclusion of both isomers in the solvate structure. Notably, the EC mixtures do not form a 1/1 solvate. Instead this solvent forms a 2/1 solvate in which the carbonyl oxygen atoms are only coordinated to a single Li⁺ cation.

The comparison of the phase diagrams confirms the order of ionic association previously noted for the lithium salts (Chapters 4 and 5). For the (EC)ₙ-LiX electrolytes, a 4/1 SSIP crystalline solvate is able to form in the LiPF₆ mixtures. In contrast, the LiTFSI and LiClO₄ mixtures with EC do not form a 4/1 phase, but instead form a 3/1 CIP or AGG-I crystalline solvate from the dilute mixtures. For the (GBL)ₙ-LiX electrolytes, the LiPF₆ mixtures form 5/1 and 4/1 crystalline SSIP solvates, while the LiClO₄ mixtures form a 4/1 solvate, but not a 5/1 solvate. The \( T_m \) of the 4/1 solvate in the (GBL)ₙ-LiPF₆ mixture is higher than that for the same solvate in the (GBL)ₙ-LiClO₄ mixtures further supporting the previously identified correlation between the ionic association strength of an anion and the \( T_m \) of SSIP and CIP solvates.¹²
Figure 6-9. DSC heating traces (5°C min⁻¹) and the corresponding phase diagrams of (a) (1-x) GBL-(x) LiClO₄ and (b) (1-x) GVL-(x) LiClO₄ mixtures.
The addition of the methyl group to the solvent ring (i.e., PC and GVL) clearly restricts/hinders the formation of crystalline phases. This extra methyl group, as well as the presence of isomers of the solvents, may inhibit the process of packing the solvates efficiently in an ordered manner. A comparison of the phase behavior of the EC and GBL mixtures indicates that the GBL mixtures tend to have less aggregated (more highly solvated) solvates than the EC mixtures. For example, for the electrolytes with LiClO$_4$, the GBL mixtures form a 4/1 SSIP crystalline solvate, but the EC mixtures do not. Instead a 3/1 CIP crystalline solvate forms from dilute mixtures. Similarly, for the electrolytes with LiPF$_6$, the GBL mixtures form both 5/1 and 4/1 SSIP crystalline solvates, while the EC mixtures only form a 4/1 solvate. This suggests that GBL coordinates Li$^+$ cations more effectively than EC, despite the fact that GBL has a much lower permittivity than EC (Table 6-1). The GBL solvates do, however, tend to melt at a lower temperature than the EC solvates.

6.3 Ion Solvation

The Raman vibrations bands for EC, PC, GBL and GVL may be used to examine the solvation interactions with the Li$^+$ cations (Table 6-2). Raman data were

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Uncoordinated (cm$^{-1}$)</th>
<th>Coordinated (cm$^{-1}$)</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>717 795</td>
<td>728 905</td>
<td>symmetric ring deformation</td>
</tr>
<tr>
<td>PC</td>
<td>712</td>
<td>722</td>
<td>symmetric ring deformation</td>
</tr>
<tr>
<td>GBL</td>
<td>675 690</td>
<td></td>
<td>C-C stretching</td>
</tr>
<tr>
<td>GVL</td>
<td>651 942</td>
<td>660 951</td>
<td>ring deformation</td>
</tr>
</tbody>
</table>

Table 6-2. Raman vibration band positions for uncoordinated and coordinated (to a Li$^+$ cation) solvents. 

13-25
collected at 60°C for mixtures of the four solvents (EC, PC, GBL and GVL) and three salts (LiClO$_4$, LiTFSI and LiPF$_6$) (Figs. 6-10, 6-11 and 6-12). The relative area of each band was calculated and plotted in Fig. 6-13, from which the average solvation number ($N$) variation was calculated (as in Chapters 4 and 5). As before, this analysis is based upon the assumption that the Raman activities of the uncoordinated and coordinated solvent are equivalent (no scaling of the bands is required for the analysis).
From the comparison of a given salt with different solvents, the same trend of increasing solvation number is observed with solvation increasing in the order:

$$\text{GBL} \geq \text{GVL} \geq \text{EC} \geq \text{PC}$$

The differences in the solvent structure significantly influence both the ion solvation in the liquid phase, as well as the phase behavior as noted above. One structural factor is the
Figure 6-12. Raman spectra of the solvent (left) GVL ring deformation mode (651 cm\(^{-1}\)) and (right) GVL C-CH\(_3\) stretching mode (942 cm\(^{-1}\)) in mixtures: (top) LiTFSI and (bottom) LiClO\(_4\) at 60°C.\(^{24,25}\)

Figure 6-13. The calculated Li\(^+\) cation average solvation number (\(N\)) in (solvent)\(_n\)-LiX mixtures: (a) LiClO\(_4\), (b) LiTFSI and (c) LiPF\(_6\) at 60°C.
number of oxygen atoms in the solvent ring (in addition to the carbonyl oxygen which all of the solvents have). GBL and GVL both have one oxygen, whereas EC and PC both have two. Each oxygen atom has two electron lone-pairs. These lone-pairs will have repulsive interactions with the lone-pairs on neighboring solvent molecules, as well as anions, making it more difficult for multiple EC or PC solvent molecules to fully solvate a Li\(^+\) cation than for GBL and GVL. Thus, despite the fact that GBL and GVL have a lower permittivity than EC and PC, the data indicate that GBL and GVL solvate the Li\(^+\) cations to a greater extent than EC and PC. Another factor to consider is the methyl group on the solvent ring for both PC and GVL. The Raman analysis suggests that the methyl group results in a lower Li\(^+\) cation solvation number. As for the extra oxygen atom on the solvent ring, the methyl groups likely cause more repulsive interactions when the solvent molecules solvate a Li\(^+\) cation. Therefore, EC and GBL solvate the Li\(^+\) cations to a greater extent at a given concentration than PC and GVL, respectively. This analysis thus indicates the influence of solvent structure for the determination of the degree of solvation of Li\(^+\) cations in solution.

The comparison between the different salt mixtures with the same solvent shows the same trend as previously observed with the nitrile solvents (Chapters 4 and 5). The solvation numbers thus increase in the following order (Fig. 6-13):

LiPF\(_6\) > LiTFSI > LiClO\(_4\)

### 6.4 Ionic Association

As well as ion solvation, the ionic association in the mixtures was examined using the Raman spectra of the anion vibrational bands. Each anion (PF\(_6^–\), TFSI\(^–\) and ClO\(_4^–\)) has one specific Raman band as a probe for determining ionic association: \(\nu_1\) mode at 740–745 cm\(^{-1}\)
Figure 6-14. Raman spectra of the anion P-F stretching mode (740 cm⁻¹) for (solvent)ₓLiPF₆ mixtures: (a) EC, (b) PC and (c) GBL at 60°C.

Figure 6-15. Raman spectra of the anion TFSI expansion/contraction mode (740 cm⁻¹) for (solvent)ₓLiTFSI mixtures: (a) EC, (b) PC, (c) GBL and (d) GVL at 60°C.
for the PF$_6^-$ anion, expansion/contraction mode at 740-750 cm$^{-1}$ for the TFSI anion, and Cl-O stretching mode at 930-960 cm$^{-1}$ for the ClO$_4^-$ anion. These Raman spectra were collected at 60°C and the results are shown in Figs. 6-14, 6-15 and 6-16. All of the Raman spectra are shifted to higher wavenumber as the concentration of the LiX salt increases due to the formation of more aggregated solvates.

For the LiPF$_6$ mixtures, it is hard to observe a difference in the PF$_6^-$ anion band between the cyclic carbonate and ester solvent mixtures (Fig. 6-14). LiPF$_6$ is the most disassociated salt studied, so it is to be expected that the solvates in the electrolytes consist mostly of SSIP, and perhaps some CIP solvates. Furthermore, the Raman band assignments for the PF$_6^-$ anion indicate that the Raman bands for the SSIP and CIP solvates are located at essentially

![Raman spectra](image)

**Figure 6-16.** Raman spectra of the anion Cl-O stretching mode (930 cm$^{-1}$) for (solvent)$_n$-LiClO$_4$ mixtures: (a) EC, (b) PC, (c) GBL and (d) GVL at 60°C.
the same position (i.e., 741 cm$^{-1}$). So it is therefore not possible to deconvolute the Raman band to distinguish between the SSIP and CIP solvates present. Thus, no notable differences are found for the Raman band of the $v_1$ PF$_6^-$ mode with the different solvents, even though there may actually be differences in the distribution of SSIP and CIP solvates.

For the LiTFSI mixtures, a significant number of SSIP solvates may be noted (Fig. 6-15), even for highly concentrated ($n \geq 3$) mixtures. To facilitate a comparison of the differences in solvation for the different solvents, the spectra for the four mixtures with $n = 5$ are shown in Fig. 6-17. The PC mixture has the higher relative intensity for the band at 747 cm$^{-1}$, which is attributed to CIP and AGG-I solvates (Chapter 3), whereas the GBL mixture has the lowest intensity. This comparison indicates that the relative amount of SSIP solvates (i.e., decreasing anion coordination) increases in the order:

$$\text{GBL} > \text{GVL} \geq \text{EC} > \text{PC}$$

Similar results were noted from the analysis of the LiClO$_4$ mixtures (Figs. 6-16 and 6-17). This order agrees well with the ion solvation data noted above.

\[\text{Figure 6-17. Comparison of the Raman anion band for (solvent)$_n$-LiX mixtures with (a) LiTFSI (n = 5) and (c) LiClO}_4 (n = 6) at 60^\circ\text{C.}\]
6.5 Transport Properties

*Concentration/density:* The isothermal density (60°C) of the mixtures is reported in Figs. 6-18 and 6-19. The density of the mixtures is more closely related with the solvent selected.

![Graph showing density and molarity vs. solvent/LiX](image)

**Figure 6-18.** Variable-concentration density and relationship between molarity vs. solvent/LiX (n) for (solvent)$_n$-LiPF$_6$ (top) and (solvent)$_n$-LiTFSI mixtures (bottom) at 60°C (solvent/LiX ratio noted in plots).
than the identity of the lithium salts. As for the pure solvents (Table 6-1), the EC mixtures have the highest density (for a given salt), while the GVL mixtures have the lowest density. Also the relationship between the molarity and the ratio of solvent molecules per Li$^+$ cation (i.e., n or solvent/LiX) is shown in Figs. 6-18 and 6-19. For reference, a 1.0 M solution corresponds to a concentration of n ~ 9-15 for all of the mixtures with the cyclic carbonate and ester solvents.

**Viscosity**: The isothermal viscosity (60°C) of the mixtures is shown in Figs. 6-20 and 6-21. A comparison of the data indicates that, for the dilute mixtures, the pure solvent properties (Table 6-1) dominate the viscosity of mixtures with the viscosity increasing in the order:

\[
\text{EC} > \text{PC} > \text{GVL} \geq \text{GBL}
\]
Figure 6-20. Variable-concentration viscosity of (solvent)$_n$-LiPF$_6$ and -LiTFSI mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.
Figure 6-21. Variable-concentration viscosity of (solvent)$_n$-LiClO$_4$ mixtures at 60°C (solvent/LiX ratio noted in plots). The bottom figures are expanded views of the low concentrated portion of the top figures.
Figure 6-22. Variable-temperature ionic conductivity of (a) (EC)$_n$-LiPF$_6$, (b) (PC)$_n$-LiPF$_6$, (C) (EC)$_n$-LiTFSI, (d) (PC)$_n$-LiTFSI, (e) (GBL)$_n$-LiTFSI and (f) (GVL)$_n$-LiTFSI (solvent/LiX ratio (n) noted in plot).
Unlike the nitrile-LiX mixtures, only minor differences in the viscosity values are noted for the three different salts studied for the dilute mixtures. It is unknown why this relationship differs from that noted for the nitrile solvents. For the concentrated mixtures, the LiPF$_6$ mixtures have the highest viscosity, while the LiTFSI mixtures have the lowest.

**Conductivity:** The temperature and concentration variation of the ionic conductivity of the mixtures are given in Figs. 6-22 and 6-23. Over the entire concentration range, the
conductivity of these mixtures appears more VTF-like than Arrhenius, which contrast strongly with what was found for the dilute nitrile mixtures (Chapters 4 and 5).

Fig. 6-24 is a plot of the isothermal (60°C), variable-concentration data for the conductivity. It is interesting to note the relationship between the viscosity and conductivity of the mixtures. Generally more viscous electrolytes are expected to have a lower conductivity due to the lower mobility of the charge carriers. A comparison of the conductivity data, however, shows a somewhat different trend from that noted above for the viscosity data. Namely, the conductivity increases in the order:

\[ \text{GBL} > \text{EC} \geq \text{GVL} > \text{PC} \]

In contrast with the viscosity, for which a clear link is not evident, this trend matches very
well with the relative order of the molecular-level interactions (i.e., solvation number and ionic association) from the Raman analysis noted above.

Figs. 6-25 and 6-26 show the molar conductivity for the mixtures. No peaks are evident. Instead, the highest molar conductivity is found for the most dilute mixtures. As shown in the previous chapters, LiTFSI and LiClO$_4$ have a similar degree of ion association and thus the molar conductivity values of both sets of mixtures are similar, while the values for the LiPF$_6$ mixtures are higher, as expected. For the mixtures with a given salts and different solvents, the trend in the molar conductivity resembles that noted for increasing ion solvation and decreasing ionic association, namely:

$$\text{GBL} > \text{GVL} \geq \text{EC} > \text{PC}$$

This is not followed exactly, however, as in some cases the PC mixtures have a higher molar conductivity than the corresponding EC mixtures. Molecular dynamics (MD) simulation are now in progress with collaborators. These are expected to provide additional insight to aid in understanding the link between the molecular-level interactions/solution structure and the variations in the transport properties.

### 6.6 Conclusions

Mixtures with cyclic carbonate (i.e., EC, PC) or cyclic ester (i.e., GBL, GVL) solvents with three different salts (i.e., LiClO$_4$, LiTFSI and LiPF$_6$) were extensively characterized. The solvents were selected to examine how small structural differences influence the molecular-level interactions and the resulting electrolyte properties. Eleven phase diagrams and some of the relevant solvate crystal structures were obtained in this study. Raman spectra were used to determine the degree of ion solvation and ionic association in the liquid
Figure 6-25. Molar conductivity of $(\text{solvent})_n$-LiX mixtures (60 °C): (a) LiPF$_6$ and (b) LiTFSI for varying solvent/LiX ($n$) concentrations and $(\text{solvent})_n$-LiX mixtures ($n = 20$): (c) LiPF$_6$ and (d) LiTFSI for varying temperature.
Figure 6-26. Molar conductivity of (a) (solvent)$_n$-LiClO$_4$ mixtures (60 °C) for varying solvent/LiX (n) concentrations and (b) (solvent)$_n$-LiClO$_4$ mixtures (n = 20) with varying temperature.
electrolytes. From this analysis, small structural differences in the solvent (i.e., the inclusion of an extra oxygen atom or methyl group in/on the solvent ring) are found to strongly affect the molecular-level interactions. Due to this, the mixtures with GBL, which has a single ring oxygen atom and no methyl group, are much less aggregated than the mixtures with PC, which has two ring oxygen atoms and a methyl group. Variations in the transport properties (viscosity and conductivity) can be readily explained based upon the pure solvent properties and electrolyte molecular-level interactions, as was previously done for the nitrile-LiX mixtures.

6.7 References


CHAPTER 7 Conclusions

The purpose of this research was to determine the molecular-level interactions (ion solvation and ionic association) between the Li\(^+\) cations, anions and solvent molecules present in battery electrolytes to aid in explaining the wide variations found for concentrated electrolyte properties with differing solvents and/or lithium salts. Utilizing DSC, XRD and Raman spectroscopy, a set of tools was introduced to enable an understanding of the solvate structures present in electrolyte solutions. Once a detailed examination of the solution structure was completed, the information was directly correlated with electrolyte viscosity and ion conductivity data to determine how the interactions govern the transport properties of electrolytes.

To enable the spectroscopic characterization of the liquid electrolyte ionic association interactions, the anion Raman bands of crystalline solvates (with known structures) were unambiguously assigned to specific forms of anion...Li\(^+\) cation coordination. These studies, when combined with DFT calculation and MD simulation work from a collaborator, made it very evident what information can, and what cannot, be obtained about ionic association interactions in electrolyte solutions. Such information is demonstrated to be much more useful when applied systematically to electrolyte mixtures with varying solvent/anion structures and when examined in concert with information obtained from other techniques (phase diagrams, solvate crystal structures).

Acetonitrile (AN)-based mixtures with differing lithium salts were initially prepared and examined by both DSC (to prepare phase diagrams) and Raman spectroscopy. Solvate crystal structures were determined for a number of the solvate phases identified from the phase
diagrams. It became evident that the relative ionic association tendency of the lithium salt (anion) strongly influences the thermal phase behavior (i.e., formation of specific solvate phases). The average solvation number and the degree of ionic association in the liquid mixtures were determined by Raman analysis. The mixtures with more weakly associating anions have a higher solvation number and lower degree of ionic association with the order of decreasing association being:

\[
\text{LiPF}_6 > \text{LiTFSI} \geq \text{LiClO}_4 > \text{LiBF}_4 >> \text{LiCF}_3\text{CO}_2
\]

The combination of the phase behavior (phase diagrams and solvate crystal structures) and Raman analysis provides tremendous insight into the solution structure present in electrolyte liquid phases. This was complemented by the DFT calculations and MD simulations. The transport properties (viscosity, conductivity) were measured and explained using the solution structure information. As expected, mixtures with greater ionic association have a lower conductivity. In contrast, the viscosity of the more dilute mixtures is determined by both the solvate distribution and the corresponding amount of free solvent molecules present.

Following the work with AN, other nitrile (propionitrile (PN) and butyronitrile (BN)), cyclic carbonate (ethylene carbonate (EC) and propylene carbonate (PC)) and cyclic ester (\(\gamma\)-butyrolactone (GBL) and \(\gamma\)-valerolactone (GVL)) solvents were studied using a similar methodology. The AN, PN and BN studies, taken together, provide direct information about how the length of the solvent alkyl chain (solvent structure) influences the electrolyte molecular-level interactions and transport properties. As expected, a longer solvent alkyl chain is more restrictive to \(\text{Li}^+\) cation solvation with the result that the increase in the average solvation number and decrease in the ionic association follows the order:
A comparison of the results for the cyclic carbonate and ester solvents also permits an examination of the influence of solvent structure. The inclusion of an extra oxygen atom and/or methyl group in/on the solvent ring results in a decrease in the Li$^+$ cation solvation and increase in the ionic association due to increased repulsive interactions with neighboring solvent molecules and/or anions. Thus, the increase in the average solvation number and decrease in the ionic association follows the order:

$$GDL > GVL \geq EC > PC$$

This study clearly shows how the transport properties of the mixtures (i.e., nitrile, cyclic carbonate and cyclic ester solvents with varying lithium salts) are governed by the molecular-level interactions due to both solvent and anion structure, as well as concentration and temperature. From the information gathered, it was demonstrated that the solvent structure, even for relatively modest structural differences, is one of critical factors for determining the molecular interactions and resulting solution structure of an electrolyte. A strong correlation between the solvent/ion interactions and the properties of the electrolyte mixtures was found. This research, therefore, provides the tools necessary to more fully identify the molecular-level interactions in solution and thus to develop a comprehensive understanding of the link between solvent/anion structure and properties for liquid electrolytes.