

Spectroscopic Measurements of Ionic Association in Solutions of LiPF₆

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Ionic association in nonaqueous electrolytes containing LiPF₆ was investigated with infrared absorption spectroscopy. The spectral intensity of the nondegenerate ν_1 mode of the PF₆[−] anion was found to be sensitive to ion pairing. Although the ν_1 mode of an isolated PF₆[−] anion is only Raman active, coordination of Li⁺ to PF₆[−] destroys the octahedral symmetry of the anion and results in ν_1 becoming simultaneously IR and Raman active. When the dielectric constant of the solvent is increased, the IR-intensity of the ν_1 band decreases because ion pairing is not favored in high dielectric solvents. Spectroscopic studies of solutions containing LiPF₆ in diglyme show that ion pairing is also affected by specific cation–solvent interactions. The diglyme-containing solutions contain significantly fewer ion pairs than expected on the basis of the solvent's dielectric constant. It is thought that diglyme:LiPF₆ solutions consist mostly of “spectroscopically free” PF₆[−] anions because the sixfold coordination of Li⁺ by two diglyme molecules hinders Li⁺⋯PF₆[−] ion pairing.

Introduction

Lithium hexafluorophosphate dissolved in aprotic solvents has become a standard electrolyte for secondary lithium ion batteries.¹ A major focus of the research on these electrolyte systems has been devoted to optimizing the conductivity of mixed solvent solutions for practical battery applications.^{2–9} The literature covering this field of research is vast, and it is not in the interest of this communication to provide a full literature review of the subject. Ionic association in electrolytes can affect the conductivity of a solution by producing low mobility aggregates or reducing the number of charge carriers in solution through the formation of neutral ion pairs.¹⁰ Therefore, it is important to understand on a molecular level how LiPF₆ behaves in nonaqueous solvents.

Vibrational spectroscopic techniques are extremely useful for probing ionic associations in many electrolytes.^{11–18} Early work focused on solutions of LiClO₄^{12,19} or LiCF₃SO₃^{13,15} and utilized frequency shifts of nondegenerate modes in the Raman spectrum. Later work also examined frequency shifts of nondegenerate modes in the infrared spectrum.^{20,21} Several researchers have demonstrated that LiXF₆ salts (X = P, As, or Sb) form ion pairs in aprotic solvents by investigating the infrared-active modes of the XF₆[−] anion.^{22–26} Most of these studies have focused on the ν_3 (F_{1u}) and ν_4 (F_{1u}) vibrations. The symmetry labels designate the point group irreducible representations of ν_3 and ν_4 in the isolated anion. Ion–ion interactions perturb the octahedral symmetry of the XF₆[−] ion and break the 3-fold degeneracy of ν_3 and ν_4 , producing multiple bands in the spectral regions containing these vibrations.

During recent infrared transmission studies of LiPF₆-based electrolytes, bands were observed in the spectral region where the ν_1 mode is expected (approximately 740 cm^{−1}). According to theory, the ν_1 mode of isolated PF₆[−] anions is only Raman active. However, the working hypothesis of this paper is that ion–ion interactions between Li⁺ and PF₆[−] result in ν_1 being

simultaneously Raman and IR active and hence observable in an infrared transmission measurement. The modification of symmetry-based selection rules through ion–ion interactions would offer an alternative spectroscopic method for examining fundamental questions of ionic association in electrolyte solutions. It is known that ionic association decreases with increasing solution dielectric constant.^{18,27} Therefore, to test this hypothesis, infrared spectra were measured in a series of solutions whose solvents have dielectric constants that span a range of values.

Experimental Methods

Lithium hexafluorophosphate was dissolved in the following solvents (dielectric constants in parentheses): diethyl carbonate (2.8), dimethyl carbonate (3.1), ethyl acetate (6.0), 2-methoxyethyl ether [diglyme] (7.3), 2-pentanone (13.48), 2-hexanone (15.45), acetone (20.7), dimethyl sulfoxide (46.7), and propylene carbonate (64.4). All of the solvents were stored over 4 Å molecular sieves. These solvents were chosen because they do not have spectral features in the region of interest (~740 cm^{−1}) and they cover a wide range of dielectric constants. In general, solutions were prepared by dissolving the appropriate amount of LiPF₆ to make a 20:1 (solvent:LiPF₆) mole ratio solution. Some lower concentration solutions were also prepared to investigate ion–solvent interactions. All of the solutions were made under an argon atmosphere, and each sample was stirred for at least 1 h to ensure sample homogeneity.

Infrared absorption spectra of the solutions were recorded on a Bruker IFS 66v spectrometer equipped with a KBr beam splitter and a DTGS detector. The solutions were sandwiched between two KBr windows (25 mm in diameter) and were measured under a dry air purge. The resolution of the spectrometer was set to 1 cm^{−1}, and each spectrum consisted of 64 scans averaged together. Raman spectra were measured with an ISA Jobin Yvon T64000 spectrometer in the triple subtractive mode. Spectra were collected in a 90° scattering geometry using a Spectra Physics Millennium Vs laser set at 80 mW and a CCD detector. The excitation wavelength was 532 nm. The samples

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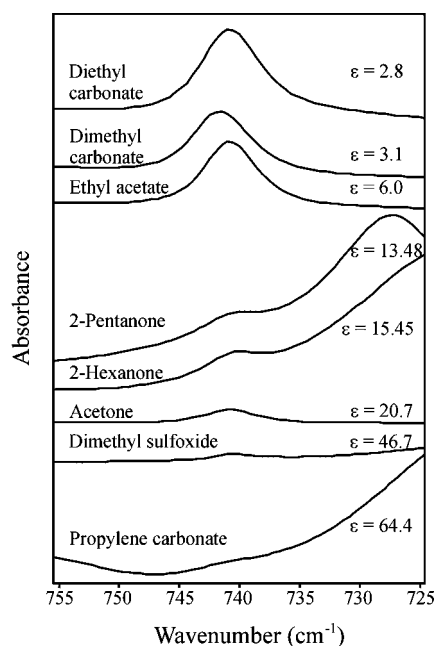


Figure 1. Infrared absorption spectra of LiPF_6 dissolved in a series of aprotic solvents (20:1 composition).

were contained in glass vials, and each spectrum consisted of 10 accumulations (2 minutes each) averaged together.

Results and Discussion

Ion–Ion Interactions. Isolated PF_6^- anions have three Raman active modes ($A_{1g} + E_g + F_{2g}$), two IR-active modes ($2F_{1u}$), and one mode that is neither IR nor Raman active (F_{2u}). The coordination of Li^+ cations to the PF_6^- anions reduces the symmetry of the PF_6^- molecule from O_h to C_{nv} ($n = 2-4$). The exact symmetry of the ion pair will depend on the coordination geometry. For example, in a bidentate configuration, the Li^+ ion interacts with two adjacent fluorine atoms of the PF_6^- molecule and the symmetry of the $\text{Li}^+\cdots\text{PF}_6^-$ species would be C_{2v} . The three possible coordination geometries of the $\text{Li}^+\cdots\text{PF}_6^-$ ion pair all destroy the center of symmetry of the PF_6^- anion and change the symmetry of the ν_1 mode from A_{1g} to A_1 . Consequently, $\nu_1(A_1)$ for ion-paired PF_6^- anions will be simultaneously Raman and IR active. Throughout the remainder of this paper, $\nu_1(A_1)$ will refer to the ν_1 mode of ion-paired PF_6^- anions while $\nu_1(A_{1g})$ denotes the ν_1 vibration of “spectroscopically free” PF_6^- anions.

Figure 1 contains infrared spectra of LiPF_6 dissolved in a series of solvents (20:1 mole ratio). As pointed out by Pereygin et al., the ν_4 band at 558 cm^{-1} is only marginally affected by salt concentration and solvent type;²² therefore, all of the spectra are scaled with respect to this band. In Figure 1, the band centered at 741 cm^{-1} gradually decreases in intensity as the dielectric constant of the solvent increases. The frequency of this band is nearly identical to the $\nu_1(A_{1g})$ mode in Raman spectra of solid KPF_6 (751 cm^{-1})²⁸ and aqueous solutions of NH_4PF_6 (741 cm^{-1}).²⁹ Accordingly, the observation of this band in the infrared spectra of LiPF_6 solutions is attributed to ν_1 and is postulated to result from a breakdown in selection rules for PF_6^- anions that participate in $\text{Li}^+\cdots\text{PF}_6^-$ ion pairs.

In high dielectric solvents such as dimethyl sulfoxide and propylene carbonate, the ν_1 band essentially vanishes. It is useful to think of solvent–cation interactions in terms of the polarizability of the solvent molecules rather than the macroscopic dielectric constant of the solvent because the number of ion

pairs in solution depends on the polarizability of the solvent molecules. Highly polarizable molecules can solvate the Li^+ ions and hinder $\text{Li}^+\cdots\text{PF}_6^-$ ion pair formation more effectively than molecules that are not very polarizable. The dielectric constant of a solvent is related to the molecular polarizability through the Clausius–Mossotti relationship.³⁰ Therefore, more ion pairs are able to form in low dielectric solvents than in high dielectric solvents, and the intensity of the $\nu_1(A_1)$ band in the infrared spectrum increases. In high dielectric solutions, it is more likely that a Li^+ ion is surrounded by a cloud of solvent molecules and counterions rather than forming a contact ion pair.

Ion–Solvent Interactions. Lithium ion–solvent coordination is also expected to influence ionic association in these systems.¹⁸ Indeed, it has been demonstrated that Li^+ ions can interact strongly with the carbonyl groups of solvents such as dimethyl carbonate and diethyl carbonate. Aroca et al. showed that adding LiPF_6 to either diethyl carbonate or dimethyl carbonate significantly affects the carbonyl stretching frequency.²⁵ Moreover, LiAsF_6 salts strongly affect the conformational equilibrium of dimethyl carbonate.²⁴ The effect of lithium–solvent interactions on ν_1 was explored for two different solutions: LiPF_6 dissolved in ethyl acetate ($\epsilon = 6.0$) and LiPF_6 in diglyme ($\epsilon = 7.3$). The solvents were chosen because they have similar dielectric constants and are important components in practical electrolytes for lithium ion batteries.^{1,31} In addition, diglyme is a useful spectroscopic model for poly(ethylene oxide)-based polymer electrolytes.³²

Crystal structures for $\text{P(EO)}_6\text{LiXF}_6$ ^{33,34} and $(\text{diglyme})_2\text{LiXF}_6$ ^{35,36} ($X = \text{P, As, or Sb}$) have been reported in the literature. In these systems, the ether oxygen atoms of the solvent molecules fully coordinate the lithium ions, leaving “free” XF_6^- anions. For example, in the $(\text{diglyme})_2\text{LiSbF}_6$ crystals, Li^+ cations are completely wrapped by two diglyme molecules, which produces a sixfold coordination environment for the Li^+ ions. Grondin et al. used vibrational spectroscopy to identify free PF_6^- ions in $(\text{diglyme})_2\text{LiPF}_6$ crystals.³⁶ Furthermore, Seneviratne et al. demonstrated that diglyme: LiSbF_6 solutions contain mostly free SbF_6^- anions.³⁵ By way of comparison, the lithium ion coordination in diglyme: LiPF_6 solutions would be expected to be similar to the $(\text{diglyme})_2\text{LiPF}_6$ crystals and the diglyme: LiSbF_6 solutions; hence, diglyme: LiPF_6 solutions should contain predominantly free PF_6^- anions.

Figure 2 compares Raman and infrared spectra of the ethyl acetate: LiPF_6 and diglyme: LiPF_6 solutions at several different concentrations. The Raman spectra of both systems show a gradual increase in ν_1 scattering intensity (741 cm^{-1}) as the LiPF_6 concentration is increased. The relative Raman scattering intensity of the ν_1 mode in these solutions agrees with previously published results for LiPF_6 solutions at similar concentrations.²⁵ Inspection of the 741 cm^{-1} band in the infrared spectra indicates that ion pairing is much more prevalent in ethyl acetate: LiPF_6 solutions than in diglyme: LiPF_6 solutions. In fact, the diglyme: LiPF_6 solutions essentially lack any IR-activity for $\nu_1(A_1)$ over this concentration range. Figure 3 further illustrates the unique nature of the diglyme: LiPF_6 solutions. Here, an infrared spectrum of a 20:1 diglyme: LiPF_6 solution is compared to ethyl acetate: LiPF_6 and acetone: LiPF_6 solutions at the same concentration. The IR-intensity of the $\nu_1(A_1)$ band is much less in the diglyme: LiPF_6 solution than the other two solutions even though diglyme has a relatively low dielectric constant.

The degenerate ν_3 mode is also sensitive to the presence of $\text{Li}^+\cdots\text{PF}_6^-$ ion pairs in solution,^{22–25} and strong ν_3 bands appear in the infrared spectra of both systems between 800 and 900

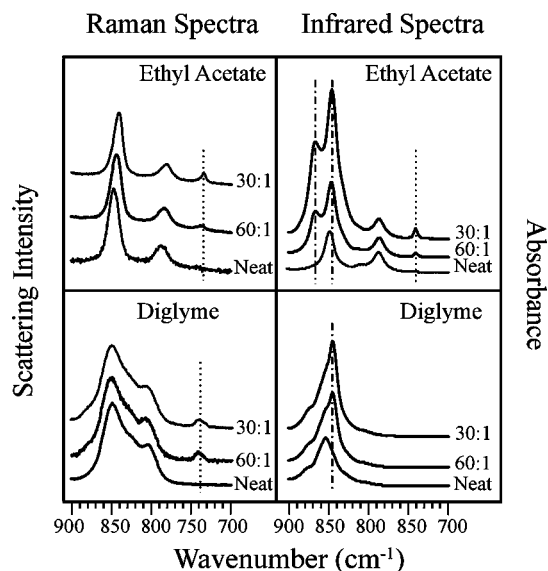


Figure 2. Raman scattering and infrared absorption spectra of diglyme:LiPF₆ and ethyl acetate:LiPF₆ solutions. The dotted lines (···) denote ν_1 vibrations and the lines with alternating dashes and dots (·-·-) mark ν_3 vibrations.

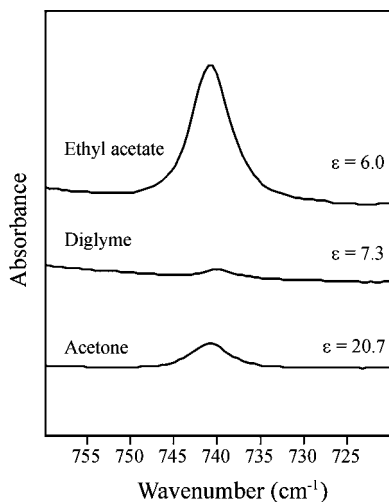


Figure 3. Infrared absorption spectra comparing diglyme:LiPF₆ solutions to ethyl acetate:LiPF₆ and acetone:LiPF₆ solutions. The composition is 20:1 for all of the electrolytes.

cm^{-1} (Figure 2). The Raman bands above 775 cm^{-1} are due to the solvent molecules. Although solvent bands overlap the PF₆[−] vibrations in the infrared spectrum, it is clear that two bands appear at 845 and 867 cm^{-1} in the ethyl acetate-based solutions, yet only one band emerges at 845 cm^{-1} in the diglyme-based solutions. Aroca et al.²⁵ and Perelygin et al.²² both assigned the 845 cm^{-1} band to free PF₆[−] anions and the 867 cm^{-1} band to Li⁺···PF₆[−] ion pairs. Therefore, the spectroscopic data suggest that the diglyme:LiPF₆ solutions contain predominantly free anions rather than Li⁺···PF₆[−] ion pairs because diglyme molecules are able to completely coordinate Li⁺ ions in a very stable configuration. This type of interaction is analogous to Li⁺ complexation by crown ethers. Molecular dynamics simulations of LiPF₆ dissolved in crown ethers show very little ionic association.³⁷ In these types of solvents, ion pairing is unfavorable even though the dielectric constant of the solvent is low enough to allow ionic association. Low dielectric, linear carbonate-based solvent molecules such as ethyl acetate are unable to solvate the Li⁺ ions as efficiently as diglyme or crown

ethers. Consequently, higher concentrations of Li⁺···PF₆[−] ion pairs may form in those solutions.

Conclusions

Cation–anion interactions (presumably ion pairs) of the PF₆[−] anion in solutions have been spectroscopically observed via an unusual mechanism involving the nondegenerate ν_1 mode. In the isolated anion, this mode can be observed only in the Raman spectrum because of the presence of a center of symmetry. In LiPF₆ solutions, the interaction of Li⁺ with PF₆[−] destroys the octahedral symmetry of the anion and results in ν_1 becoming simultaneously IR and Raman active. Ionic association in these solutions is strongly affected by the dielectric constant of the solvent. In high dielectric solvents, the solvent molecules can interact strongly with Li⁺ cations, and only a small fraction of the PF₆[−] anions can penetrate the Li⁺ solvation shell to form ion pairs. Cation–solvent interactions also influence ionic association in LiPF₆-based electrolytes. The IR-intensity of $\nu_1(\text{A}_1)$ is smaller in diglyme:LiPF₆ solutions than in ethyl acetate:LiPF₆ solutions even though the solvents have comparable dielectric constants. It is believed that two diglyme molecules wrap Li⁺ cations in a sixfold coordination environment, which severely hinders the ability of the PF₆[−] anions to coordinate with the Li⁺ cations. Although the IR-intensity of the $\nu_1(\text{A}_1)$ band is proportional to the number of Li⁺···PF₆[−] ion pairs present in solution, this avenue of quantifying the ion pairs was not pursued.

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