Infrared (Attenuated Total Reflection) Study of Lithium Salts Dissolved in Non-Aqueous Aprotic Solvents

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Abstract: The role of the solvent becomes critically important during ion transport when the electrolyte solute and solvent compete for coordination. Improved ionic conductivity requires ionic dissociation. The 'hip-hop' transition of the cations requires that ion pairs split and become solvated with solvent molecules during dissolution. To achieve these hopping transitions, lithium salts are the best choice. We have investigated the vibrational spectra of lithium nitrate and lithium triflate in two different non-aqueous organic solvents, namely THF and DMSO, through ATR-FTIR spectroscopy in order to investigate ion-solvent and ion-ion interactions, to learn more about solvents' lower and higher frequency vibrations, and factors affecting the identifiable characteristics, functioning, and interaction of ionic compounds with solvents.

Keywords: FTIR; Lithium Nitrate; Lithium Triflate; THF; DMSO; Solute-Solvent Interaction

1. Introduction

The most important part of a battery is the electrolyte medium, through which the ions' transition occurs. Since solute electrolyte solute and solvent compete for coordination during ion transport, the role of the solvent becomes crucially significant. Ionic dissociation is required for improved ionic conductivity, and obviously the free energy of dissolution should be negative for the process to occur. Ion pairs must dissociate and get solvated with solvent molecules during dissolution in order to provide the 'hip-hop' transition of the cations. Lithium salts are the ideal option to achieve these hopping transitions.

Among various lithium salts, lithium nitrate ($LiNO_3$) is the most researched co-salt and additive for lithium-sulfur (Li-S) batteries for preventing the redox reactions of soluble lithium polysulfide which manifests as an improvement in the battery's coulombic efficiency and cycling stability as well as a decrease in the self-discharge rate.[1] Due to its ability to stabilize the lithium anode by forming a solid electrolyte interaction, its low degree of dissociation in aprotic solvents, and its catalytic effect against oxygen transformation response in rechargeable lithium oxide batteries, it has recently been proposed as a promising salt for lithium oxide batteries.[2]

Lithium triflate (LiTF, $LiCF_3SO_3$) is another fascinating lithium salt. If polymer hosts are used for batteries, it is worth mentioning that it reduces crystallinity and increases chemical and thermal stability.[3]

The electrolyte in which the ions are carried is the most crucial component. Transportation of ions is applicable to all kinds of electrolytes, whether it is liquid, gel, or solid polymer electrolytes. Ion transition in electrolytes depends on the heteroatom present in solvent, specifically how it coordinates with the salt. Owing to the application of organic solvents in lithium-based batteries with high energy densities, in recent years, the structure of the lithium salt solution in organic solvents has attracted a lot of interest.[4]

Dimethylsulfoxide (DMSO) is one of the dialkylsulfoxides that has found being used in this field. DMSO has its capacity to form inter-molecular self-associative formations in liquid or in solution. It should be emphasised that the self-association of DMSO molecules is caused by both intermolecular hydrogen bonds of the type SO-HC as well as dipole-dipole interactions between SO groups. Spectroscopic findings show a variety of fairly stable structural aggregates exist, notably cyclic dimers, open chains, dimers, and polymers.[5,6] It must be emphasised that in addition to Li+ cation solvation, there may be an anion-molecular interaction comprising the CH_3 groups of DMSO.[7]

For usage in lithium-oxygen (Li-O_2) batteries, Dimethylsulfoxide (DMSO)-based electrolytes are desirable due to their stable charge-discharge behaviour. The structure of the electrolyte is considered to have an impact on side products in Li-O_2 cells if the source of side products during discharge is primarily due to the dissociation of electrolytes.[8]
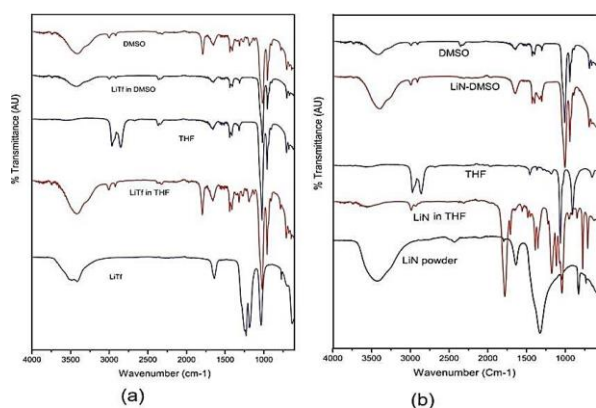
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Fig. 1. FT-IR spectra of (a) Lithium Triflate, DMSO,THF and Lithium triflate solution in DMSO and THF, (b) Lithium Nitrate, DMSO,THF and Lithium nitrate solution in DMSO and THF.
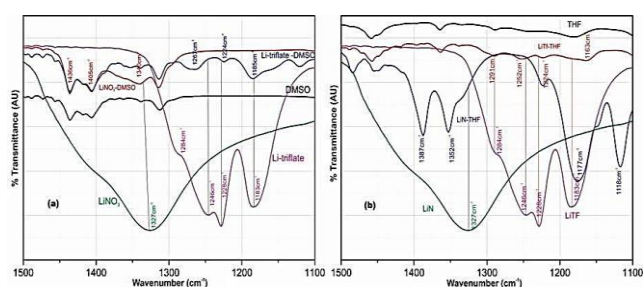

Fig. 2. Enlarge (range 1500 cm^{-1} to 1100 cm^{-1}) view of FT-IR spectra of (a) Lithium Triflate, Lithium nitrate, DMSO, Lithium triflate and Lithium nitrate solution in DMSO, (b) Lithium Triflate, Lithium nitrate, THF, Lithium triflate and Lithium nitrate solution in THF.

Tetrahydrofuran (THF) is colourless heterocyclic, water soluble with low viscosity organic liquid. Being polar with a long liquid range, it serves as a multifunctional solvent for various applications, such as in polymer science, as a solvent in several pharmaceuticals, in various synthetic processes, in organometallics, as a constituent of the mobile phases for reversed-phase liquid chromatography and for dissolution of several ionic species. Additionally, THF's extreme purity and high volatility make it easier to remove and recover solvents without leaving any traces in the target result.[9,10]

In order to investigate ion-solvent and ion-ion interactions, vibrational spectroscopy has been proven to be a useful technique for analysing alterations in frequency, intensity, and band characteristics.[11]

Vibrational analysis gives a direct mode of understanding more about solvents' lower and higher frequency vibrations. Through these analyses, it may be possible to identify the factors affecting the recognisable characteristics, functioning and interaction of ionic compounds with solvents.[12-16]

We have explored the vibrational spectra of lithium nitrate and lithium triflate in two different non-aqueous organic solvents, namely THF and DMSO, to achieve the aforementioned goal through ATR- FTIR spectroscopy.

2. Experimental Section

Lithium triflate (LiCF$_3$SO$_3$) (Mol. wt. 156.01 g/mol) and Lithium Nitrate (LiNO$_3$) (Mol. wt. 68.946 g/mol) was purchased from Sigma-

Aldrich. Prior to the preparation of polymer solution, salts were dried at 100°C for 2 h in order to remove the trace amounts of moisture in the material. Solvents namely, dimethyl sulfoxide (DMSO) and Tetrahydrofuran (THF) AR grade were purchased from SD fine Chem Ltd (India). 1 gm salt was dissolved in 5ml solvent on magnetic stirrer for 6 hours. A drop of solution was used for FT IR studies. Infrared spectroscopic measurements were carried out on a Bruker Alfa (Germany) ATR -IR spectro- photometer in the range 4000 cm^{-1} – 600 cm^{-1} at room temperature. All the spectra were recorded at a resolution 4 cm^{-1} and with an accumulation of 8-32 scans.

3. Results and Discussions

The infrared spectra of salts, solvents and salt with solvents are shown in Fig. 1. The main peaks and their assignments are given in table-1. To explain the interaction of solvents with salts, we enlarged the FT-IR spectra in the range 1500 cm^{-1} to 1100 cm^{-1} is shown in Fig. 2.

The salt lithium triflouromethanesulfonate, also known as lithium triflate is having molecular formula LiCF$_3$SO$_3$. Its molecular geometry[17] with the bond angles and ionic structure of lithium triflate is represented in the Figs. 3(a) and 3(b) respectively. It is based on the conjugate bases of organic super-acids, where acid strength is enhanced due to the stabilisation of anions by the highly electron-withdrawing groups, generally per fluorinated alkyls. By integrating the inductive effect of the electron-withdrawing groups and the conjugated structures, LiTF offers the lowest conducting solution. The delocalization of the formal negative charge is actually achieved in these anions. Its low dissociation constant in low dielectric mediums and moderate ion mobility in comparison to those of other salts are thought to be the root causes of this.[18]

The absorption frequency relies on the atomic architecture, the force constant of the bonding, and the relative mass of the functional groups. It is possible to deduce from the vibrational spectrum in the triflate anion that there are 'free' ions, ion pairs, and more highly coupled ionic species.[19] The triflate anion has a tendency toward a higher frequency in the δs(CF$_3$) mode for a higher degree of connection with the cation.[20]
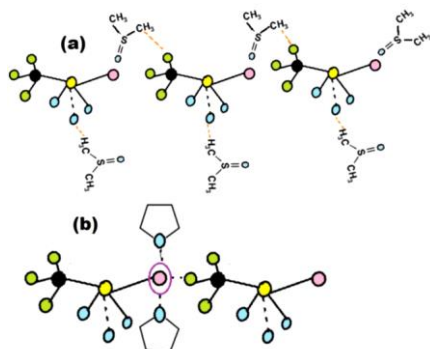
LiTF is less soluble in DMSO as compared to the LiNO$_3$. Dispersive forces are significant here because DMSO has a high degree of polarity even being an aprotic solvent (DM = 3.96D, ϵ = 46.68).

The consistent CF$_3$ symmetric deformation of the shift of the band from 772 cm^{-1} to a lower wave number is highly suggestive of the presence of ion accumulation of [Li$_2$TF]$^+$ moiety.[21] This is due to the high sensitivity of CF$_3$ stretch of LiTF towards ionic association to form ion pairs and aggregates. A peak at 1,035 cm^{-1} corresponding to the symmetric(in phase) stretching mode of SO$_3$[22] has shifted to a decreased wave number at 1,015 cm^{-1} with just a lower intensity in the presence of DMSO. The existence of monodenate ion pairs may be the cause of influencing this peak.[22,23]

The frequency peak of SO$_3$ asymmetric stretching mode is found at 1284 cm^{-1} (a small shoulder) and 1246 cm^{-1}, whereas, the frequency peak of CF$_3$ for symmetric stretching mode is found at 1,228 cm^{-1} of the triflate ion. The broad band subsequently shifts to a lower wave number at 1,224 cm^{-1} as shown in Fig. 2(a).

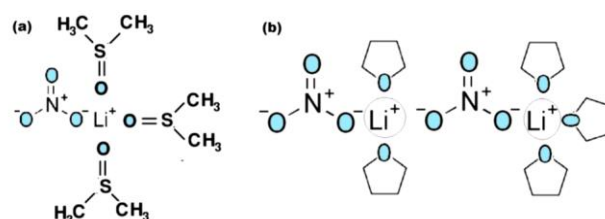**Table 1.** Peak position and their assignments of Salts -DMSO interactions

Peak position of DMSO (cm⁻¹)	Peak position of LiTF (cm⁻¹)	Peak position of LiNO₃ (cm⁻¹)	Peak position of LiTF-DMSO (cm⁻¹)	Peak position of LiNO₃- DMSO cm⁻¹)	Assignments
3431	3409	3422	3411	3407 (red shift)	H_2O- OH stretching
2998			2998	2998	S-CH_3, out of phase stretching
2917			2919	2917	S-CH_3, in phase stretching
2358			2367		
			2334		
	1641		1655	1656	
		1639			O-NO_2 stretching
1437				1436	S-CH_3 out of phase bending
1413			1407	1405	S-CH_3 out of phase stretching
1340			1340	1340	S-CH_3 in phase stretching
		1327			out of phase stretching of NO_3
1312			1312	1311	In phase bending
	1228		1224		SO_3 out of phase stretching
	1183		1185		SO_3 out of phase stretching
1016	1035	1050	1015	1014	S=O in phase stretching
			951	951	SO_3 out of phase stretching
915					CH_3 rock
	772				CF_3sym.deform
702	701		700	702	C-S-C out of phase stretching, C-S stretching
667			669	671	C-S-C in phase stretching
	634				SO_3sym.deform.
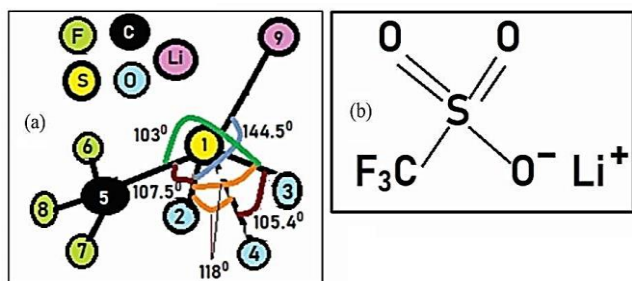
Fig. 3. Schematic representation of (a) molecular representation and (b) Ionic structure of lithium triflate.

Fig. 5. Representation of solute-solvent interaction between lithium nitrate with DMSO and THF molecules

Fig. 4. Representation of solute-solvent interaction between lithium triflate with DMSO and THF molecules.

The peak at 1183 cm⁻¹ in the spectra of pure LiTF (Fig. 2a) is attributed to the asymmetric stretching of CF_3 (Fig. 2a). Due to the formation of ion pairs and aggregates, the symmetric deformation of CF_3 is very sensitive to ionic association.[24]

In the LiTF-DMSO system, the asymmetric stretching frequency of CF_3 at 1,228 cm⁻¹ of the triflate ion is greatly reduced and shifted to 1,224 cm⁻¹, exhibiting ion pairing and ion association of the triflate ion with DMSO molecule. In the LiTF - DMSO mixture, the shoulder peak at 1,284 cm⁻¹ and 1246 cm⁻¹, which were attributed to asymmetric stretching of LiTF 's SO_3 group, merges to create a broader and less intense peak at 1267 cm⁻¹, indicating the lack of free SO_3 group availability due to engagement with the DMSO molecule in H-bonding. The oxygen end of DMSO gets oriented towards Lithium ion and its C-H group point towards F of triflate ion. Lithium ion of one molecule and F of another molecule of triflate ion orient towards each other also showing intermolecular interactions facilitating H-bonding between solute and solvent. The bond angles and bent structure (shown in Fig. 3) of LiTF supports the solute-solvent dispersive interaction and aforementioned explanation provides its strong evidence (shown in Fig. 4).

Shifting of a weak peak in LiTF-DMSO at 2919 cm⁻¹ from 2917 cm⁻¹ of DMSO indicates strengthening of S-CH_3 in phase stretch. The peak of DMSO 3431 cm⁻¹ is shifted to 3411 cm⁻¹ with increased intensity of OH stretch may be assigned to the presence of ambient moisture within the LiTF-DMSO solution. In Li-batteries, the intermediate LiO_2, is anticipated to quickly vanish prior to chemical reactivity with electrolytes, on the cathode surface and get further reduce on the surface to produce film-like depositions of Li_2O_2, so it is widely accepted that a lower donor number of solvents restrict side products on the cathode surface.

Therefore, the $LiNO_3$/DMSO (interaction with $LiNO_3$ and DMSO is shown in Fig. 5) electrolyte are preferred in Li-batteries, however, it behaves as a low donor number of solvent in LiO_2 cells despite having a high donor number of anion (NO_3)⁻ and solvent (DMSO).[25-27]

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LiNO$_3$ dissolves relatively less soluble in ethanol than it does in DMSO. Although the dielectric constant of DMSO is sufficient, the other parameters like hydrogen-bond formation and dispersion forces also influences solubility of lithium salts. The polarity of the solvent has a considerable impact on solubility. In polar DMSO solvent, lithium nitrate dissolves quite quickly.[28] At 1357 cm^{-1} a broad peak due to out-of-phase NO$_3$ nitrate stretching is observed. But when DMSO is mixed, DMSO is dominated in the mixed system. At 1437 cm^{-1} out of phase bending frequency of S-CH$_3$ and at 1311 cm^{-1} in phase bending of S are common in both DMSO and mixed coordinate system. The S=O stretching frequency at 1016 cm^{-1} of DMSO is there with a little shifting at 1014 cm^{-1} in mixed system, while S-CH$_3$ rock mode is observed at 915 cm^{-1} in both the cases.

IR peaks from 1300 cm^{-1} to 1450 cm^{-1} range, some unusual behaviour of said coordinated system is noticed. Even at higher notes, S-CH$_3$, out of phase stretching and S- CH$_3$, in phase stretching frequencies lie at same position in DMSO and mixed coordinated system at 2998 cm^{-1} and 2917 cm^{-1} respectively. The same IR peak positions of mixed system and of DMSO curve in this region indicates that DMSO molecules orient around the LiNO$_3$ molecule most probably in a tetrahedral fashion, as Li$^+$ ion displays a coordination number of 4- regardless of the types of anions or concentrations,[29] exhibiting proper ion – dipole interaction in the coordinated solution shown in Fig. 5.

Investigation reveals that the individual THF peak at 1064 cm^{-1} is caused by the asymmetric C-O-C out of phase stretching when combined with the symmetric stretch of SO$_3$ at 1035 cm^{-1} of the free triflate ion, upon interaction, a red shift is observed at 1014 cm^{-1} in the LiTF- THF complex, indicating the formation of a stable mixed complex, as the energy of the system is lowered. The energy of the peak indicating 5 membered ring of THF at 907 cm^{-1} is also lowered in the complex observed at 897 cm^{-1}.
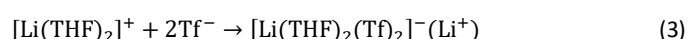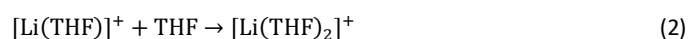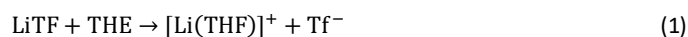
All of the peaks observed in the plain THF IR curve in the range of 1100 cm^{-1} to 1500 cm^{-1} exhibit low intensity peaks. Peak at 1461 cm^{-1} is generated by the vibration mode -CH$_2$ bend, at 1365 cm^{-1} by -CH$_2$ wagging, and at 1182 cm^{-1} by the vibrations of the C-O-C asymmetric stretching mode.

In LiTF-based electrolytes, severe ion pairing is anticipated, especially when low dielectric constant solvents like ethers are added.[18]

Spectral Bands attributed to the anti-symmetric stretching of SO$_3$ of the triflate anions are visible in the region between 1100 and 1500 cm^{-1}. These are designated for two different forms of contact ion pairs, namely, the outer sphere and inner sphere triflate anions, also known as SSIP (for Solvent Separated Ion Pair) and CIP (for Contact Ion Pair), accordingly.[30]

A broad peak cantering at 1224 cm^{-1} is most likely a mixture of two spectral components: CIP at 1210 cm^{-1}, which is associated with triflate anions' C- S vibrations combined with SO$_3$ vibrations and SSIP at 1220 cm^{-1}, which is associated with SO$_3$'s asymmetric stretching frequency.[31] SO$_3^-$M$^+$ out of phase SO$_3$ stretch vibrations are visible at the peak at 1252cm^{-1}. The peak at 1365 cm^{-1} is assigned to the CH$_2$ wagging that is also present in the plain THF curve and indicates interaction of THF with triflate ion upon access of an extra triflate anions to the inner solvation sphere of the Li$^+$ cation. A second faint peak arises at about 1350 cm^{-1}. We assign this peak to a third group

of contact ion pairs, or CIP,[32] which may be shown as [Li(THF)$_2$(TF)$_2$]$^-$. Due to -CF alkyl stretching, a shifting of the peak at 1163 cm^{-1} is also observed. According to the rationale given above, the solute-solvent interaction may result to a tetrahedral orientation around the lithium cation (Fig. 4(b)). There may be three ion- dipole interactions between Li$^+$ - O(of THF) and Li$^+$ - F(of another Triflate ion) and the fourth one is the polar covalent bond between S and Li of same molecule. The resulting tetrahedral geometry[29] of the complex may be understood with help of following equations:

$$\text{LiTF} + \text{THE} \rightarrow [\text{Li(THF)}]^+ + \text{Tf}^- \qquad (1)$$

$$[\text{Li(THF)}]^+ + \text{THF} \rightarrow [\text{Li(THF)}_2]^+ \qquad (2)$$

$$[\text{Li(THF)}_2]^+ + 2\text{Tf}^- \rightarrow [\text{Li(THF)}_2(\text{Tf})_2]^-(\text{Li}^+) \qquad (3)$$

Shifting of and much reduction in the intensities of characteristic peak of THF at 2971 and 2857 cm^{-1} to 2995 and 2916 cm^{-1} respectively on complexation is also supporting the coordination of THF with lithium triflate molecule.

Here also shifting of and reduction in the intensities of characteristic peak of THF at 2971 and 2857 cm^{-1} to 2985 and 2932 cm^{-1} respectively on complexation is also supporting the coordination of THF with lithium nitrate molecule. The peak at 1779 cm^{-1} in the spectra of LiNO$_3$, is actually the overtone of 1056+723 cm^{-1} of out of phase NO$_3^-$ stretching frequency. In the case of LiNO$_3$-THF system, the intensity of some peaks enhanced surprisingly indicating better solute-solvent interaction. Ring CH$_2$ bending mode vibrations appeared at 1461 cm^{-1} and a broad peak at 1450 cm^{-1} appeared. Twin peak at 1387 cm^{-1} and 1352 cm^{-1} indicates NO$_2$ in phase stretching with CH$_2$-O-CH$_2$ wagging vibrations and CH$_2$ bending vibrations. The intense peak is actually shifting of 1182 cm^{-1} of C-O-C asymmetric stretching to 1177 cm^{-1} and the aliphatic ethereal bending peak appears at 1118 cm^{-1} indicating nitrate interaction with THF. LiNO$_3$ with THF responded similar to the LiTF, but in this case, LiNO$_3$ and THF shows better SSIP and CIP solute-solvent interactions forming regular tetrahedral orientation symmetry. Here, oxygen of two THF molecules and O$^-$ of another salt molecule get oriented around Li$^+$ ion of nitrate salt tetrahedrally associated through ion-dipolar interactions. The aforesaid interaction is further supported by the C-O-C out of phase stretching peak of THF shifting from 1064 cm^{-1} to 1074 cm^{-1} and 907 cm^{-1} (of a 5 membered ring) to 917 cm^{-1} in the LiNO$_3$-THF complex. A layout of the interaction is represented in Fig. 5(b).

4. Conclusions

The interactions of LiTF and LiNO$_3$ with DMSO and THF are investigated with the assistance of the assignments for the observed IR spectra. Both the mixed coordinated system reveals intermolecular interactions that support H-bonding between the solute and solvent. The abnormal behaviour of the mixed coordinated system between 1100 cm^{-1} to 1450 cm^{-1} frequency range unfolded the specific interactions between them. The solute-solvent dispersive interaction is supported by the bond angles and bent structure of LiTF. The Li$^+$ ion exhibits a coordination number of 4

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and exhibits proper ion - dipole interaction in the coordinated solution, and the similar IR peak positions of the mixed system and the DMSO curve in particular region suggest that DMSO molecules orient around the $LiNO_3$ molecule most likely in a tetrahedral fashion resulting from the solute-solvent interaction. There could be ion-dipole interactions with THF coordination. $LiNO_3$ and THF exhibited better SSIP and CIP solute-solvent interactions for establishing regular tetrahedral orientation symmetry. The shifting of the vibrational peaks provides as much evidence for the aforementioned interaction.

Conflicts of Interest

The authors declare no conflict of interest.

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