

Short Communication

## **Ion-molecule Interaction in Solutions of Lithium Tetrafluoroborate in Propylene Carbonate: an FTIR Vibrational Spectroscopic Study**

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FTIR (Fourier transformed infrared) spectra have been collected and analyzed for solutions of lithium tetrafluoroborate in propylene carbonate (PC). It has been shown that the carbonyl stretch, symmetric ring deformation stretch and ring deformation stretch bands for PC is very sensitive to the interaction between Li<sup>+</sup> and the solvent molecule. Their half-peak breadth increases and bands split with the addition of LiBF<sub>4</sub>, indicating that a strong interaction exists between Li<sup>+</sup> and PC molecule mainly through the oxygen group of C=O and ring position of PC.

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**Keywords:** FTIR spectroscopy; Lithium tetrafluoroborate; Propylene carbonate (PC)

### **1. INTRODUCTION**

The study of organic electrolyte solutions in lithium ion battery continues to be an active field of research [1-10]. These electrolytes are of current interest because of their potential applications in lithium ion batteries [1-2]. Electrolyte of lithium ion battery consists of lithium salt (such as LiClO<sub>4</sub>, LiPF<sub>6</sub>, LiBF<sub>4</sub> etc.), mixture of organic solvents (such as propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC) etc.) and additives. The structure and composition of electrolyte plays an important role in determining the battery performance, operating temperature range and service life [1-2]. Therefore, starting from the perspective of microscopic structural elements angle, knowledge of ion-molecule and intermolecular interactions inside electrolytes is essential for the optimal choice of

solvent and electrolyte. And it is also very important and meaningful for the research and development of lithium ion battery with high performance.

Vibrational spectroscopy has been proved to be a powerful technique for probing ion-solvent and ion-ion interactions through the changes of frequency, intensity and other band properties [8]. Such studies [3-4, 6, 11-15] could help to identify the factors that affect the general properties and the performance of the electrolyte solutions. As lithium tetrafluoroborate has a proper thermal and chemical stability, a series of investigations have been carried out to study the ion solvation and association of LiBF<sub>4</sub>-based electrolytes [16] which have a excellent low temperature performance. Xuan et al. [17] studied the ion solvation and association of lithium tetrafluoroborate in acetonitrile by vibrational spectroscopic and density functional methods. Alia and Edwards [18] studied the Raman spectra of LiBF<sub>4</sub> in acrylonitrile and found the contact ion pairs and ion dimers. However, no researchers have studied the interaction of lithium tetrafluoroborate in propylene carbonate (PC).

In this paper, In order to capture the nature of ion-molecule interactions inside electrolytes, systematic FTIR spectroscopic investigations of LiBF<sub>4</sub>/PC solutions are carried out. We selected PC (64.40 at 298.15K [19]) as the solvent because it is liquid at room temperature, a number of commercial lithium batteries have adopted the mixed organic electrolyte containing PC [20]. It is commonly used in lithium ion batteries [1-6]. In order to separate out various interactions within these solutions, a series of systems with different concentrations were systematically studied, ranging from the simple pure component to the final systems of salt/solvent solutions.

## 2. EXPERIMENTAL

Lithium tetrafluoroborate (Aladdin, purity >99.99% metal basis) was dried under vacuum for 48 h at 120°C. PC (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd, cell grade, purity >99.9%, moisture <20 ppm) were used as purchased. All solution manipulations were carried out in nitrogen filled glove box. As there is no obvious absorption bands were observed around 3500 cm<sup>-1</sup> in the IR spectra, the effect of moisture in the liquid sample on ion solvation and association can be negligible. The concentration of the solutions was expressed as amount-of-substance concentration (mol/L). Different concentrations of LiBF<sub>4</sub>/PC solutions (0.2 mol/L LiBF<sub>4</sub>/PC, 0.4 mol/L LiBF<sub>4</sub>/PC and 1.2 mol/L LiBF<sub>4</sub>/PC) were prepared to be investigated. The solution preparation process was as follows: 2 mL PC solvent was pipetted into 10 mL small bottles, according to the different concentrations of LiBF<sub>4</sub>/PC, the amount of lithium salt (LiBF<sub>4</sub>) was calculated which were 0.0375 g, 0.075 g and 0.225 g, respectively. After the preparation of LiBF<sub>4</sub>/PC solutions with different concentrations, the solutions were heated at 40 °C for 48 h in order to have a completely dissolution and interaction before measurement.

IR spectra were collected on a Thermo-Nicolet Nexus FTIR spectrometer (USA) equipped with a KBr crystal in the absorbance mode range from 400 to 4000 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. Specific test process was as follows: a moderate amount of liquid sample was sucked up using capillary and dropped in the center position of 25×4 mm KBr window. Another piece of KBr window was used to

cover the former one, and then rotating to form a liquid film. The two piece of KBr windows should be fixed before test. All the measurements were made at room temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characteristic peak assignments for PC

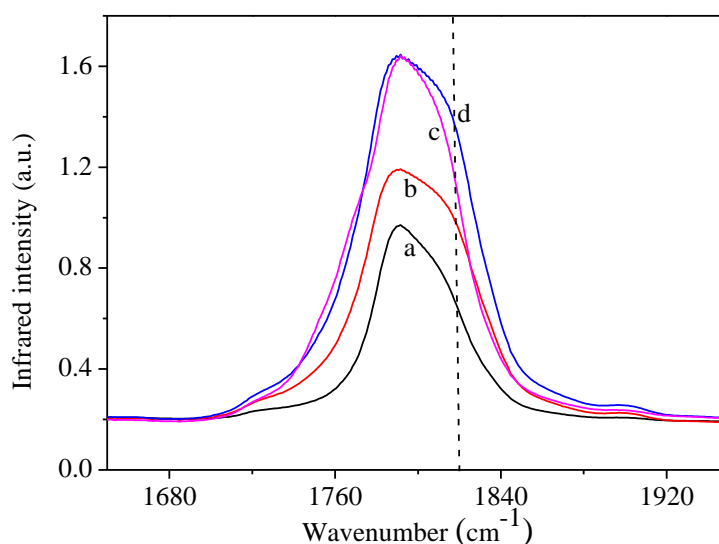
Battisti et al. [4] studied the Raman and infrared spectroscopy of PC doped with various concentrations of lithium perchlorate ( $\text{LiClO}_4$ ) and Janz et al. [21] investigated the Raman spectrum of PC. Both of them deeply researched the structure and vibrational spectra of PC, and most of the vibrational assignments have been made. In addition, Xuan [22] studied the Raman and IR vibrational spectra of  $\text{LiBF}_4/\gamma\text{-BL}$  and gave their assignments for the bands observed, the  $\nu_1$  ( $\text{BF}_4^-$ ) of  $\text{LiBF}_4$  is about  $765\text{ cm}^{-1}$ . What's more, the most significant IR characteristic peak assignments of PC were given in Table 1.

**Table 1.** Characteristic peak assignments for PC

	C=O		C-O-C		Ring	
Propylene carbonate (PC)	$1791.45\text{ cm}^{-1}$	$1794\text{ cm}^{-1}$ [3,4,8,10]	$1181.97\text{ cm}^{-1}$ as.	$1181.97\text{ cm}^{-1}$ as.	$712\text{ cm}^{-1}$ sy. $776\text{ cm}^{-1}$ def.	$711\text{-}712\text{ cm}^{-1}$ sy.[3,4,8,10] $776\text{-}777\text{ cm}^{-1}$ def.[3,4,8,10]

Note: as., asymmetric stretch; sy., symmetric stretch; def., deformation.

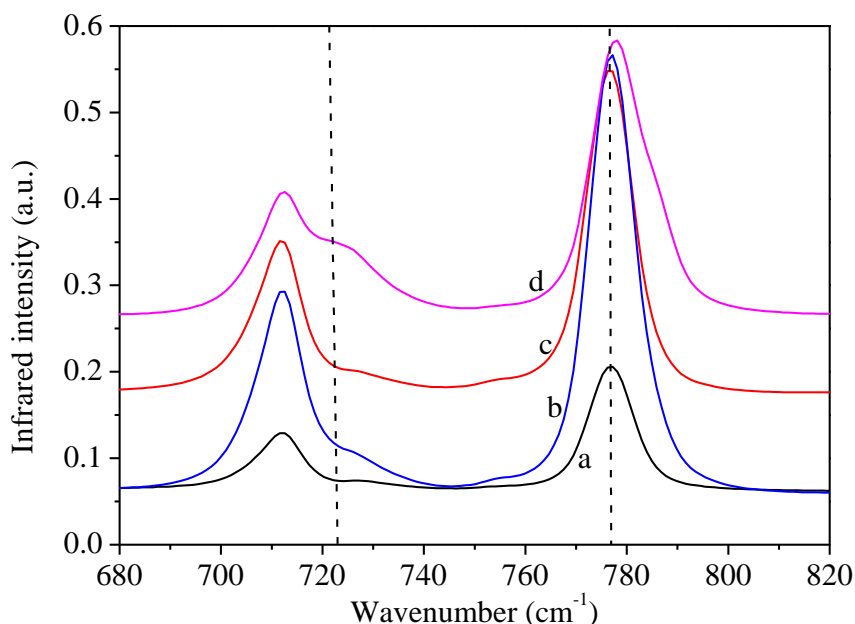
#### 3.2 Ion-molecule interactions in $\text{LiBF}_4/\text{PC}$ solutions



**Figure 1.** The IR spectra of C=O stretch for PC in solutions with different  $\text{LiBF}_4$  concentrations. a, pure PC; b, 0.2 mol/L  $\text{LiBF}_4/\text{PC}$ ; c, 0.4 mol/L  $\text{LiBF}_4/\text{PC}$ ; d, 1.2 mol/L  $\text{LiBF}_4/\text{PC}$ .

The interactions in LiBF<sub>4</sub>/PC solutions mainly refer to Li<sup>+</sup>-solvent interactions. Because PC is poor anion solvators, changes of solvent molecular spectra are considered to be the result of interactions between Li<sup>+</sup> and solvent molecule.

Fig. 1 shows the IR spectra of C=O stretch for PC in solutions with different LiBF<sub>4</sub> concentrations in the region of 1650-1950 cm<sup>-1</sup>. As is shown in 3.1, the band of C=O stretch of pure PC is located at 1791.45 cm<sup>-1</sup>. After the increasing addition of LiBF<sub>4</sub>, lightly shift to higher wavenumber side of the C=O stretch of PC occurs. The values of C=O stretch under different concentrations of LiBF<sub>4</sub> are 1791.45cm<sup>-1</sup> (line a), 1791.49cm<sup>-1</sup> (line b), 1791.50cm<sup>-1</sup> (line c) and 1791.67cm<sup>-1</sup> (line d), respectively. In addition, with the increasing of LiBF<sub>4</sub> concentration, it is obvious that the half-peak breadth of C=O stretch for PC increases quickly whilst a shoulder peak at 1816 cm<sup>-1</sup> is clearly visible on the higher wavenumber side, especially on the concentration of 1.2 mol/L LiBF<sub>4</sub>/PC solution (line d). Simultaneously, the intensity of the new shoulder peak gradually increases with the increasing of LiBF<sub>4</sub> concentrations. According to the above changes of C=O stretch of PC in LiBF<sub>4</sub>/PC solutions, it can be concluded that there has a strong interaction between Li<sup>+</sup> cation and PC molecules which through the oxygen atom of carbonyl group.



**Figure 2.** The IR spectra of symmetric ring deformation and ring deformation for PC in solutions with different concentrations of LiBF<sub>4</sub>. a, pure PC; b, 0.2 mol/L LiBF<sub>4</sub>/PC; c, 0.4 mol/L LiBF<sub>4</sub>/PC; d, 1.2 mol/L LiBF<sub>4</sub>/PC.

Fig. 2 illustrates another two obvious trends concern the symmetric ring deformation (711-712 cm<sup>-1</sup>) and ring deformation (776-777 cm<sup>-1</sup>) under different LiBF<sub>4</sub> concentrations in the region of 680-820 cm<sup>-1</sup>. Through the analysis of the band changes of ring deformation in this figure, obvious band shifting of ring deformation from 776 cm<sup>-1</sup> to 778 cm<sup>-1</sup> can be seen. Simultaneously, the half-peak breadth of symmetric ring deformation increases quickly whilst a shoulder peak at about 722 cm<sup>-1</sup> is clearly visible on the higher wavenumber side, especially on the concentration of 1.2 mol/L

LiBF<sub>4</sub>/PC solutions (line d). After the addition of LiBF<sub>4</sub>, the shoulder appears, even though the amount of LiBF<sub>4</sub> is not much. So, the shoulder is clearly visible when the concentration of LiBF<sub>4</sub> is 0.2 mol/L. And the intensity of the shoulder increases with the increasing of LiBF<sub>4</sub> concentrations. The intensity of the shoulder in line d (1.2 mol/L LiBF<sub>4</sub>/PC) is obviously higher than the intensity of line b (0.2 mol/L LiBF<sub>4</sub>/PC). According to the above band changes of ring deformation and symmetric ring deformation, it can be concluded that there has a strong interaction between Li<sup>+</sup> cation and PC molecules through the position of the ring in PC molecules.

According to the above FTIR vibrational spectroscopic studies of LiBF<sub>4</sub>/PC under different concentrations, it can be suggested that there is a strong interaction between Li<sup>+</sup> and PC molecules. This interaction occurs mainly on the carbonyl oxygen atom and the ring of PC molecule.

#### 4. CONCLUSIONS

The electrolyte solutions of lithium tetrafluoroborate in propylene carbonate (PC) have been investigated by FTIR spectroscopy study. Based on the above experimental and the results of salt/solvent solutions, the tentative conclusions are summarized as follows: There is a strong interaction between Li<sup>+</sup> cation and PC molecule. This interaction possibly takes place via the oxygen atom of the carbonyl group and ring position in PC, mainly through the oxygen atom of the carbonyl group.

Further experimental works and theoretical calculations are still necessary to study the structure and parameters of ion solvation and association.

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