

STRUCTURE OF MATTER
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FTIR Spectroscopic Study of Li⁺ Solvation in the Solutions of LiBF₄ in Propylene Carbonate, Dimethyl Sulfoxide, and Their Mixtures¹

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Abstract—Ionic solvation in solutions of lithium tetrafluoroborate (LiBF₄) in propylene carbonate (PC) + dimethyl sulfoxide (DMSO) mixtures has been studied using Fourier transformed infrared (FTIR) spectroscopy. Dimerization of DMSO molecules in the solutions was taken into account. The obtained results are discussed with respect to the electrolyte concentration and properties of the cations of the electrolyte. Band changes due to solvation interaction were detected in the region of the C=O stretching vibrations and ring deformation for PC, and the S=O stretching vibrations and C–S–C skeleton stretching modes for DMSO, indicating that there is a strong interaction between lithium cations and solvent molecules. In addition, Li⁺ was preferentially solvated by DMSO in these binary solvents as a result of the large difference in their donor number (DN) values. The structures of PC, DMSO, Li⁺-PC, Li⁺-DMSO, and Li⁺-PC+DMSO were given.

Keywords: ionic solvation, IR spectroscopy, lithium tetrafluoroborate, propylene carbonate, dimethyl sulfoxide, donor numbers

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1. INTRODUCTION

Lithium ion batteries (LIBs) have been widely used in portable electronic devices such as cellular phones, camcorders and laptop computers, due to some of their advantages, including high energy density, better safety features and more excellent cyclability [1–4]. In a typical LIB system, the most popular electrolytes include a lithium salt such as LiPF₆, LiBF₄, etc., and a mixture of organic solvents, including ethylene carbonate (EC) or propylene carbonate (PC). The properties of the electrolyte, such as conductivity, electrochemical window, cycling stability, play an important role in determining the electrochemical performance of the battery. Information about ion solvation and association is of great importance because they strongly affect the conductivity of an electrolyte.

Vibrational spectroscopy has been extensively used to study the structures and dynamics of electrolyte solutions [5–16], and it is proved to be a powerful technique for describing ion-molecule and intermolecular interactions. The fact that this method may distinguish groups of the same type in different environments, which allows one to use it to assess phenomena taking place in solutions where different types

of association are present together with unassociated species. For instance, this method is very effective in studying the ionic solvation. Such studies [17–26] could help to identify the action mechanism of lithium salt and solvent inside electrolyte and confirm the factors that affect the general properties and performance of the electrolyte solutions. Some studies have been reported on solvation of ions in organic solvents, either unitary [5] or binary [6–9] systems. Xuan studied the ion solvation and association of LiBF₄ in acetonitrile [10] and LiClO₄ in acetone [11] via vibrational spectroscopy and density functional theory methods. Alia and Edwards [12] studied the Raman spectra of LiBF₄ in acrylonitrile and found the contact ion pairs and ion dimers. Qiao et al. studied the ion solvation and ion association of LiBF₄ in *N,N*-dimethylcarbamoyl chloride-based [13] and 4-(methoxymethyl)ethylene carbonate-based [14–16] solvents by FT-Raman spectroscopic and density functional theory studies.

However, there have been no researchers studied the LiBF₄/PC+DMSO binary electrolyte solutions till now. Compared with LiPF₆, lithium tetrafluoroborate (LiBF₄) as a salt for the electrolyte [27–29] has many advantages including better thermal stability, less moisture sensitivity and a much lower charge-transfer resistance at low temperature [30]. PC (64.40

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at 298.15 K) [31] is liquid at room temperature and commonly used in lithium ion batteries. Dimethyl sulfoxide (DMSO) is a highly polar versatile solvent, which displays high salt solubility to produce well-conducting solutions with a wide electrochemical window. Therefore, the study of $\text{LiBF}_4/\text{PC}+\text{DMSO}$ electrolyte system attracts our attention. It is very interesting, worthy and meaningful for the development of electrolyte with better low temperature performance for lithium ion batteries.

Based on the above knowledge, LiBF_4 , PC, and DMSO were selected as the lithium salt and solvents in this work. In order to describe the ion-molecule and molecule-molecule interactions inside $\text{LiBF}_4/\text{PC}+\text{DMSO}$ binary solutions, a systematic FTIR spectroscopic investigations of PC+DMSO, LiBF_4/PC , $\text{LiBF}_4/\text{DMSO}$, and $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions with different concentrations are carried out. The interactions between lithium cations and the solvent molecules were analyzed, and the preferential solvation in binary solutions was evaluated. The possible ion-molecule interaction structures are given.

2. EXPERIMENTAL

Lithium tetrafluoroborate (Aladdin, purity >99.99% on metal basis) was dried under vacuum for 48 h at 120°C PC and DMSO (Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd, cell grade, purity >99.9%, moisture <20 ppm) were used as received. Electrolyte solution preparation was carried out in a nitrogen-filled glove box (moisture <0.1 ppm, oxygen <20 ppm). As there is no obvious absorption bands around 3500 cm^{-1} in the IR spectra, the effect of moisture in the liquid sample on ion-molecule and intermolecular interactions can be negligible. The concentration of the electrolyte solutions was expressed in mol/L. Different volume ratios of $V_{\text{DMSO}}/V_{\text{PC}}$ solutions and different concentrations of LiBF_4/PC , $\text{LiBF}_4/\text{DMSO}$, and $\text{LiBF}_4/\text{PC} + \text{DMSO}$ (v/v, 1 : 1) solutions were prepared for the systematic investigations.

IR spectra were recorded on a Thermo-Nicolet Nexus FT-IR spectrometer (USA) equipped with a KBr crystal in the absorbance mode in the wavenumber range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} . All the measurements were made at room temperature.

The molecular geometries of PC, DMSO, DMSO cyclic dimers, and their solvation structures were given by Gauss View 5.0.

3. RESULTS AND DISCUSSION

3.1. Vibrational Peak Assignments and Molecular Structures for PC and DMSO

In the previous works [32–34], the FTIR spectrum of pure PC was reported. The assignments of the characteristic group peaks in this spectrum was made. The bands corresponding to C=O stretching, C–O–C stretching, symmetric ring deformation and ring deformation of PC molecule are located at 1791, 1182, 711, and 776 cm^{-1} , respectively. Forel [35] and Fawcett [36, 37] studied the structure and vibrational spectra of DMSO in detail. The DMSO molecule belongs to C_s point group, possessing only one plane of symmetry containing S and O atoms. The 24 fundamental vibrations have been discussed in detail in previous publications [35–38]. The IR spectrum of pure DMSO, showing four groups of bands is presented in Fig. 1. The bands corresponding to the skeletal C–S–C stretching vibrations of monomers and dimers of DMSO are observed between 600 and 800 cm^{-1} (Fig. 1a), and bands for the asymmetric stretching of the SO bond in monomers and dimers overlap with those for the rocking vibrations of the methyl groups in the 900–1100 cm^{-1} region (Fig. 1b). Bands corresponding to the deformational vibrations of the methyl groups are seen between 1250 and 1500 cm^{-1} (Fig. 1c), and the stretching vibrations of methyl groups are observed between 2700 and 3200 cm^{-1} (Fig. 1d). In the following discussion, analyses are based on the above peak assignments.

According to the IR spectra of pure DMSO, the self-association phenomenon of DMSO molecules is appeared. According to the literature [36], it is a fact that DMSO has a strong affinity for self-association. This type of association at high DMSO concentrations has been postulated from thermodynamic studies [39]. Such self-association could be playing a significant role in the observed change in DMSO orientation with concentration. The FTIR spectroscopic results for pure DMSO shown in Fig. 1 elucidate the nature and the quantities of DMSO self-association, and resolve existing controversies in the assignment of the bands in the DMSO vibrational spectrum. The structure of the bands due to the skeletal vibrations was found to be complex. It was shown that DMSO molecules in solutions associate in cyclic dimers. The molecular structures of PC, DMSO, and DMSO dimers are presented in Fig. 2.

3.2. Li^+ -Molecule Interactions in LiBF_4/PC and $\text{LiBF}_4/\text{DMSO}$ Solutions

As it is known, the interactions inside salt/solvent solutions include cation-solvent, anion-solvent and molecule-molecule interactions. But in the present paper, the interactions in LiBF_4/PC , $\text{LiBF}_4/\text{DMSO}$, and $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions mainly refer to the

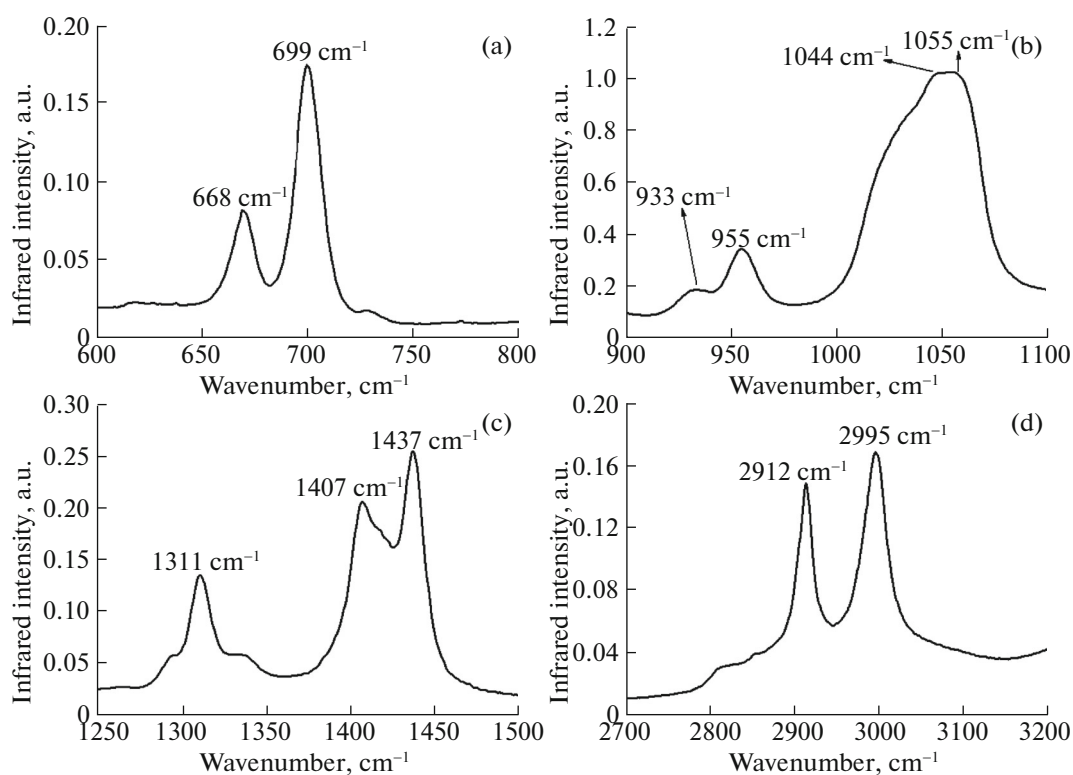


Fig. 1. IR spectra of pure DMSO. (a) 600–800 cm^{-1} region; (b) 900–1100 cm^{-1} region; (c) 1250–1500 cm^{-1} region; (d) 2700–3200 cm^{-1} region.

interactions between Li^+ cation and solvent molecules. Because both PC and DMSO are poor anion solvators, the spectra changes of solvent molecules are considered to be the result of interaction between Li^+ and solvent molecules. For LiBF_4/PC solutions, the ion-molecule interactions have been investigated in some details. According to the study of Zhang et al. [32–34], the IR spectra of pure PC and LiBF_4/PC solutions with different lithium salt concentrations have been recorded. It is shown that most of the IR bands of PC investigated present little changes of frequency and shape upon the addition of LiBF_4 , except for those at 1791, 711, and 776 cm^{-1} . With the increasing of LiBF_4 concentration, the half-peak width of C=O stretching vibrations for PC increases quickly whilst a shoulder peak at 1816 cm^{-1} is clearly visible on the higher wavenumber side. Simultaneously, the intensity of the new shoulder peak gradually increases with the LiBF_4 concentrations increase. According to the spectra of ring deformation, obvious band shifting from 776 to 778 cm^{-1} can be seen. Simultaneously, the half-peak width of symmetric ring deformation (711 cm^{-1}) also increases quickly whilst a shoulder peak at about 722 cm^{-1} is clearly visible on the higher wavenumber side. And the intensity of the new shoulder increases as the molarity of LiBF_4 increases.

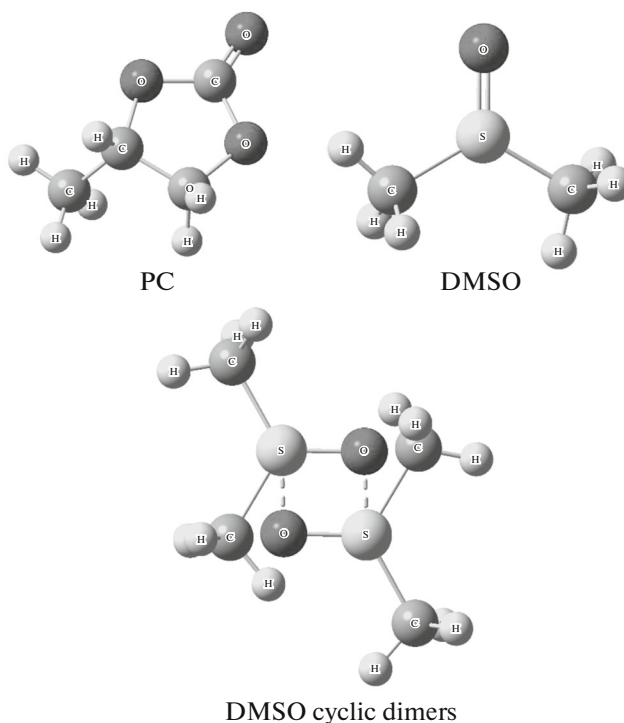


Fig. 2. The molecular structures of PC, DMSO, and DMSO cyclic dimers.

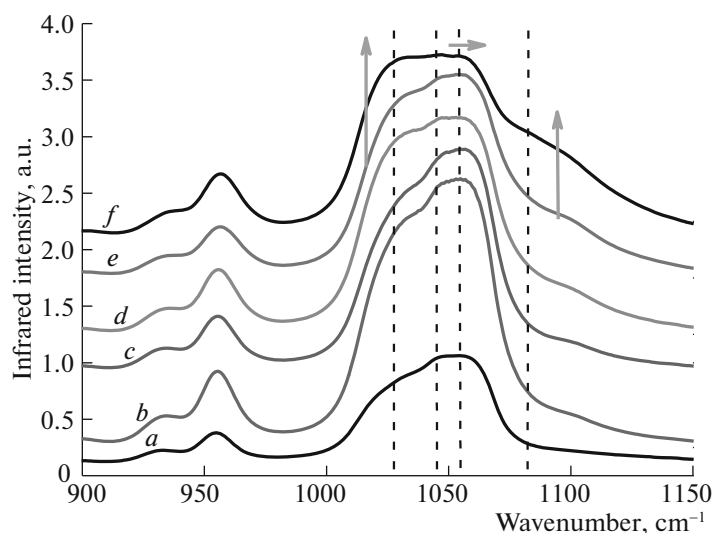


Fig. 3. The IR spectra of asymmetric stretching vibration of S=O bond and the rocking vibrations of the methyl groups in LiBF₄/DMSO solutions with different concentrations, (a) pure DMSO; (b) 0.4 mol/L LiBF₄/DMSO; (c) 0.5 mol/L LiBF₄/DMSO; (d) 0.8 mol/L LiBF₄/DMSO; (e) 1.2 mol/L LiBF₄/DMSO; (f) 1.5 mol/L LiBF₄/DMSO.

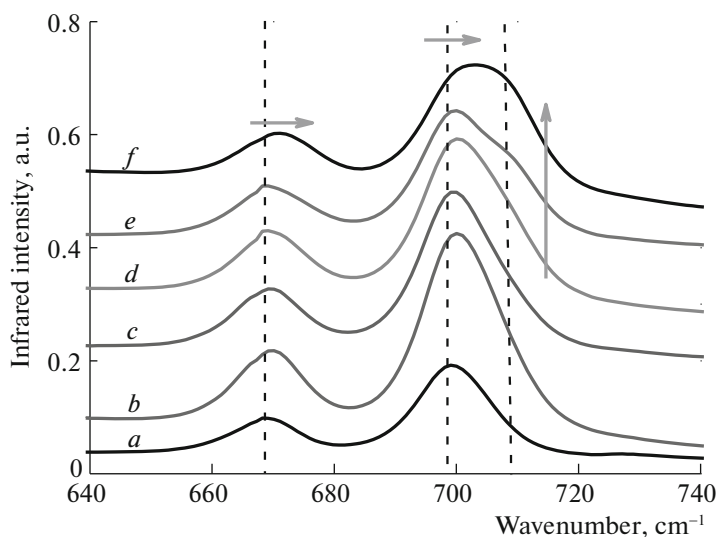


Fig. 4. The IR spectra of symmetric and asymmetric C–S–C stretching vibrations of the skeleton of DMSO monomers and dimers in LiBF₄/DMSO solutions with different concentrations, (a) pure DMSO; (b) 0.4 mol/L LiBF₄/DMSO; (c) 0.5 mol/L LiBF₄/DMSO; (d) 0.8 mol/L LiBF₄/DMSO; (e) 1.2 mol/L LiBF₄/DMSO; (f) 1.5 mol/L LiBF₄/DMSO.

The changes of all these bands mentioned above demonstrate that there is a strong interaction between Li⁺ and PC molecules. This interaction occurs mainly with the carbonyl oxygen and the ring of PC molecule. This is further verified by the observations of Battisti et al. and Janz et al. The splitting of some bands, such as PC ring deformation suggests that two kinds of PC molecules coexist in the solutions. One kind, from the bulk solvent, described as “free,” generates the 711 cm⁻¹ band. Another kind of solvent binds with

lithium cation and gives 722 cm⁻¹ band. The possible structure of the Li⁺–PC interaction in LiBF₄/PC solutions is presented in Fig. 5a.

For LiBF₄/DMSO solutions, according to the analysis of the IR spectra of pure DMSO and LiBF₄/DMSO solutions, most of the DMSO bands show little changes in frequency, intensity and shape after addition of LiBF₄, except for the 900–1150 cm⁻¹ and 640–740 cm⁻¹ region, which is attributed to S=O asymmetric stretch vibrations of DMSO monomers,

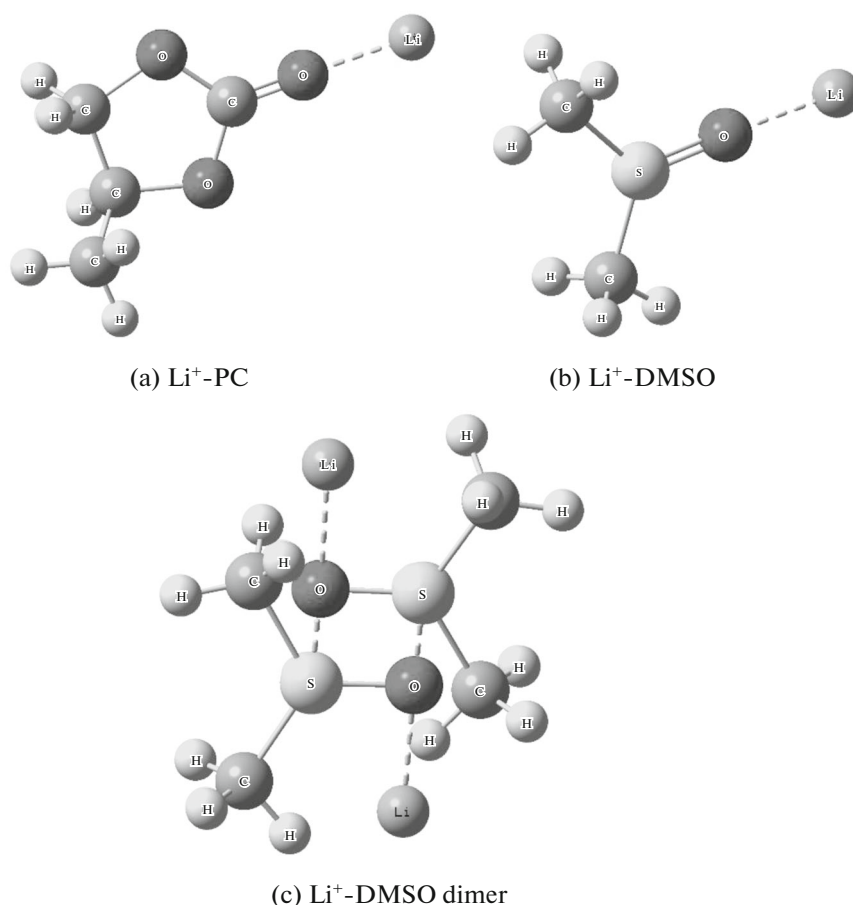


Fig. 5. The possible interaction structures of Li⁺-PC, Li⁺-DMSO, and Li⁺-DMSO dimer.

DMSO cyclic dimers, rocking vibrations of methyl groups and C–S–C skeleton stretch. IR spectra of pure DMSO and LiBF₄/DMSO with different concentrations in the frequency range 900–1150 cm⁻¹ are shown in Fig. 3. In the spectrum of pure DMSO (Fig. 3a), a very intense band is observed at 1055 cm⁻¹, which has two shoulders, a rather intense one at 1044 cm⁻¹, and another one arising from the overlapping peaks at 1027 and 1013 cm⁻¹ due to the rocking vibrations of the methyl groups. The positions of the peaks at 1055 and 1044 cm⁻¹ belong to the asymmetric stretching vibration of S=O bond in DMSO monomers and dimers.

With increasing salt concentrations, the higher frequency band (1055 cm⁻¹) increases its intensity at the expense of the 1044 cm⁻¹ component. This suggests that cation modified the dimerization equilibrium of 2DMSO ~ (DMSO)₂, and promoted the formation of monomelic DMSO molecules, which can solvate the lithium ion more effectively. Furthermore, as the concentration of LiBF₄/DMSO solution increases, the half-peak width of S=O asymmetric stretching vibrations also increases quickly whilst slightly blue-shift

appeared. With the increasing of LiBF₄ concentrations, an obvious shoulder appears at 1080 cm⁻¹, and the intensity of the new shoulder peak gradually increases. Besides the changes of S=O stretching vibrations, the half-peak width of rocking vibrations of methyl groups also increases and its intensity becomes stronger.

The IR spectra of symmetric and asymmetric stretching vibrations of the C–S–C skeleton of DMSO monomers and dimers in LiBF₄/DMSO solutions with different concentrations are shown in Fig. 4. The IR spectra changes of LiBF₄/DMSO illustrated in Fig. 4 show an obvious band shift. The two bands at 668 and 699 cm⁻¹ can be ascribed to the CS-C skeleton stretching of DMSO monomers and dimers. A considerable shift to the higher wavenumber side and a decrease in intensity for the band at 668 cm⁻¹ and a split for band at 699 cm⁻¹ were observed. A new band at higher frequency side arises from the lithium ion solvation with DMSO molecules.

The above manifestation of interactions in the studied solutions based on the IR spectroscopic data leads to the conclusion that there is a strong interac-

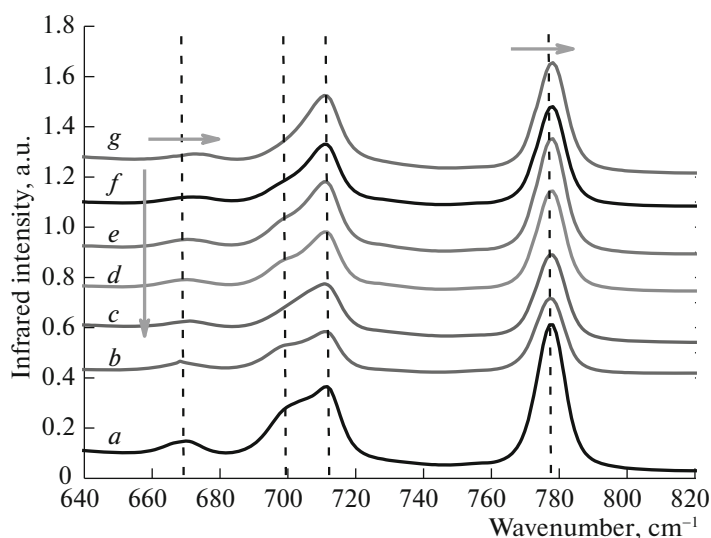


Fig. 6. IR spectra of $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions with different LiBF_4 concentrations in the region of $640\text{--}820\text{ cm}^{-1}$, (a) $\text{PC}+\text{DMSO}$ ($v/v = 1 : 1$); (b) $0.4\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$; (c) $0.5\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$; (d) $0.8\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$; (e) $1.0\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$; (f) $1.2\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$; (g) $1.5\text{ mol/L LiBF}_4/\text{PC}+\text{DMSO}$.

tion between Li^+ and DMSO molecules, and this interaction occurs mainly through the oxygen atom of S=O group. Because the coexistence of DMSO monomers and DMSO cyclic dimers inside the system, there are two kinds of Li^+ -DMSO molecule interaction structures. One is Li^+ -DMSO monomer, the other is Li^+ -DMSO dimer. The possible structures of the Li^+ -DMSO and Li^+ -DMSO dimer interactions in $\text{LiBF}_4/\text{DMSO}$ solutions are presented in Figs. 5b, 5c.

3.3. Molecule–Molecule Interaction in $\text{PC}+\text{DMSO}$ Solutions

In order to study the interaction between PC and DMSO molecules, the IR spectra of $\text{PC}+\text{DMSO}$ mixtures with different volume ratios of $V_{\text{DMSO}}/V_{\text{PC}}$ ($V_{\text{DMSO}}/V_{\text{PC}} = 0, 1, 2, 3, 5, 7, 10, 12, 15, 20$) have been investigated. According to the study of the position of C=O stretching vibrations band for PC in $\text{PC}+\text{DMSO}$ mixtures on volume ratios of $V_{\text{DMSO}}/V_{\text{PC}}$, the C=O stretching for PC did not change obviously. The minimum value is 1790.23 cm^{-1} and the maximum value is 1793.11 cm^{-1} . As the resolution of IR is 2 cm^{-1} , therefore, the values are all within the spectral analysis error. In other words, they are the same band position. This is very different from $\text{LiBF}_4/\text{PC}+\text{DEC}$ solutions [33], which show a strong interaction between solvent molecules. Simultaneously, most of the PC and DMSO bands did not show any observable changes within the experimental error, so, it can be deduced that no or very weak interactions are present between PC and DMSO molecules. This weak interaction can be explained as follows: both PC and

DMSO are aprotic solvents in which the autoprotolysis is extremely weak. Besides this, there is no association phenomenon, according to the experiment. Therefore, no obvious association between PC and DMSO would be present in the mixtures. Based on these analyses, it can be concluded that there is a very weak interaction between PC and DMSO molecules. This is in accordance with their structural characterization.

3.4. Li^+ -PC+DMSO Interactions in $\text{LiBF}_4/\text{PC}+\text{DMSO}$ Solutions

For convenient observation of the changes of the bands, we respectively enlarge the bands where changes happened in $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions. Figure 6 illustrates the IR spectra of $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions with different LiBF_4 concentrations in the region of $640\text{--}820\text{ cm}^{-1}$.

The intensity of the C-S-C skeleton stretching vibrations of DMSO in binary solutions gradually decreases with the increase in the lithium salt concentrations. Meanwhile, an obvious band shift to the higher wavenumber at 668 and 699 cm^{-1} happened, which is similar with the shift changes in $\text{LiBF}_4/\text{DMSO}$ solutions. For the symmetric ring deformation (711 cm^{-1}) and ring deformation (776 cm^{-1}) of PC, the 1816 cm^{-1} shoulder peak appeared in LiBF_4/PC solutions, which does not exist in binary solutions, and is different from LiBF_4/PC system. However, the band shift from 776 to 778 cm^{-1} can be seen in binary solutions.

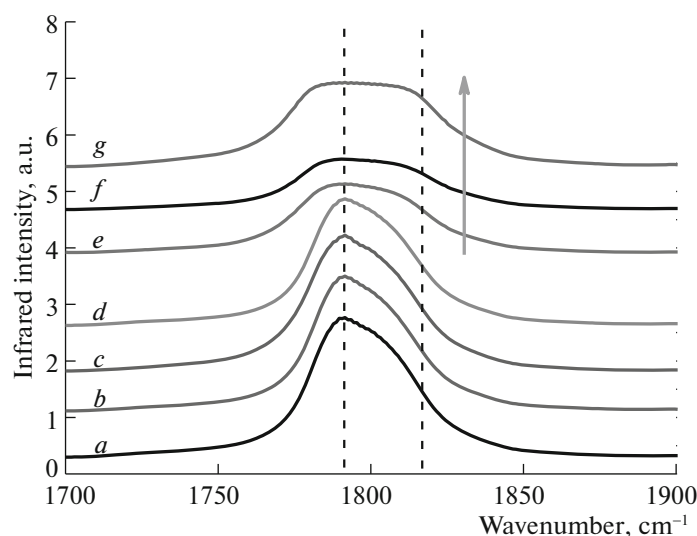


Fig. 7. The IR spectra of C=O stretch of PC in LiBF₄/PC+DMSO solutions with different concentrations, (a) PC+DMSO ($v/v = 1 : 1$); (b) 0.4 mol/L LiBF₄/PC+DMSO; (c) 0.5 mol/L LiBF₄/PC+DMSO; (d) 0.8 mol/L LiBF₄/PC+DMSO; (e) 1.0 mol/L LiBF₄/PC+DMSO; (f) 1.2 mol/L LiBF₄/PC+DMSO; (g) 1.5 mol/L LiBF₄/PC+DMSO.

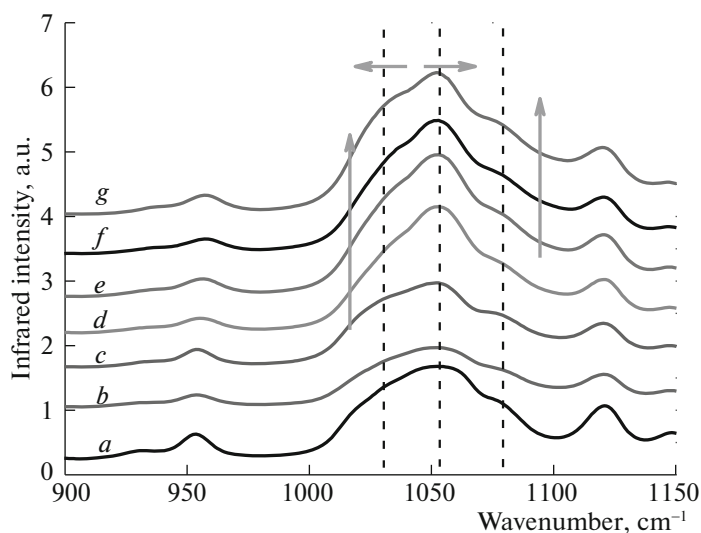


Fig. 8. The IR spectra of asymmetric stretching vibration of S=O bond and the rocking vibrations of the methyl groups in LiBF₄/PC+DMSO solutions with different concentrations, (a) PC+DMSO ($v/v = 1 : 1$); (b) 0.4 mol/L LiBF₄/PC+DMSO; (c) 0.5 mol/L LiBF₄/PC+DMSO; (d) 0.8 mol/L LiBF₄/PC+DMSO; (e) 1.0 mol/L LiBF₄/PC+DMSO; (f) 1.2 mol/L LiBF₄/PC+DMSO; (g) 1.5 mol/L LiBF₄/PC+DMSO.

Figure 7 shows the changes of IR spectra of C=O stretching vibrations of PC in LiBF₄/PC+DMSO solutions containing different LiBF₄ concentrations. The carbonyl stretching band of PC in the binary solutions without LiBF₄ is located at 1792 cm⁻¹. It is shown in Fig. 7 that the half-peak width of C=O stretching vibrations band for PC increases quickly whilst a shoulder peak at 1816 cm⁻¹ is clearly visible on the higher wavenumber side with the increasing of LiBF₄

concentration. Simultaneously, the intensity of the new shoulder peak gradually increases with the LiBF₄ concentrations increase. These illustrate the existence of Li⁺-PC interactions in LiBF₄/PC+DMSO binary solutions.

Figure 8 shows the IR spectra of asymmetric stretching vibration of S=O bond and the rocking vibrations of the methyl groups in LiBF₄/PC+DMSO solutions with different concentrations in the region of

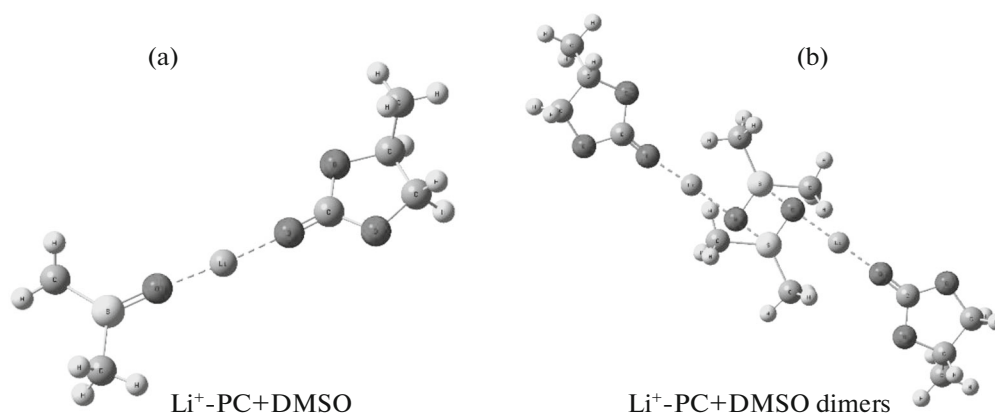


Fig. 9. The possible interaction structures of Li^+ -PC+DMSO and Li^+ -PC+DMSO dimers.

900–1150 cm^{-1} . As the concentration of $\text{LiBF}_4/\text{DMSO}$ solution increases, it is obvious that the half-peak width of S=O asymmetric stretching vibrations increases quickly. A distinctive shoulder appears at the position of 1080 cm^{-1} , and the intensity of the new shoulder peak gradually increases with the increase in the lithium salt concentrations. This is similar with the changes in $\text{LiBF}_4/\text{DMSO}$ solutions. Besides the changes of S=O stretching vibrations band, the half-peak width of rocking vibrations of methyl groups also increases and the intensity becomes stronger.

According to the above analysis, it can be concluded that there is a rather strong coexistence of Li^+ -PC and Li^+ -DMSO interactions appear in $\text{LiBF}_4/\text{PC}+\text{DMSO}$ binary solutions. This interaction affects the structure of the solvent molecules, and causes the changes in the spectra. The strong interaction occurs mainly through the oxygen atoms of C=O group of PC and the oxygen atoms of S=O group of DMSO. Given the coexistence of DMSO monomers and DMSO cyclic dimers in the system, the possible interaction structures of Li^+ -PC+DMSO and Li^+ -PC+DMSO dimers are shown in Fig. 9.

3.5. Preferential Solvation of the Solvent Molecules with Li^+

It is an interesting question, which kind of molecules (PC or DMSO) in the studied system interact preferentially with Li^+ ?

According to the IR spectra changes for the solutions based on single and binary solvents, especially considering the difference between LiBF_4/PC and $\text{LiBF}_4/\text{PC}+\text{DMSO}$ solutions, we can conclude that lithium ion is preferentially solvated by DMSO in the mixed solvents. The preferential solvation can well be explained by the donor-acceptor approach. The magnitude of the donor number (DN) of a solvent is a measure of the solvation power, and is very useful in

determining the solvent environment around cation in mixed solutions. The donor number values of the solvents investigated in the present work are 29.8 for DMSO, and 15.1 for PC, respectively, so the DN value of DMSO is considerably higher than that of PC. The Lewis basicity of DMSO is higher than that of PC on the basis of its donor number. Therefore, DMSO is a better solvent for cations, interacting rather strongly with lithium ions. Thus, the interactions between Li^+ and DMSO is stronger than that between Li^+ and PC, and lithium ion is preferentially solvated by DMSO.

CONCLUSIONS

The electrolyte solutions of lithium tetrafluoroborate (LiBF_4) in PC, DMSO, and PC+DMSO solutions have been systematically investigated by FTIR spectroscopy. The tentative conclusions can be summarized as follows:

(I) Strong Li^+ -PC and Li^+ -DMSO interactions are observed in LiBF_4/PC , $\text{LiBF}_4/\text{DMSO}$, and $\text{LiBF}_4/\text{PC}+\text{DMSO}$ electrolyte solutions. It is possible that these interactions occur mainly through the oxygen atoms of carbonyl group of PC and the oxygen atoms of S=O group of DMSO.

(II) The interaction between PC and DMSO molecules in PC+DMSO mixtures is very weak and could not be detected by IR spectroscopy.

(III) The specific solvation of Li^+ was distinguished in $\text{LiBF}_4/\text{PC}+\text{DMSO}$ binary solutions, where lithium ion was preferentially solvated by DMSO due to the large difference in DN values for PC and DMSO.

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