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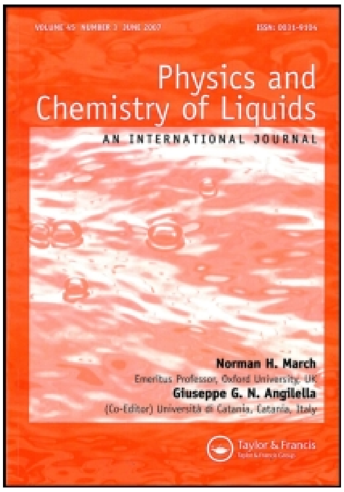

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A Vibrational Spectroscopic Study of Ion Solvation in Lithium Perchlorate/Propylene Carbonate Electrolyte

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A VIBRATIONAL SPECTROSCOPIC STUDY OF ION SOLVATION IN LITHIUM PERCHLORATE/PROPYLENE CARBONATE ELECTROLYTE

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The infrared (IR) and Raman spectra of propylene carbonate (PC) containing various concentrations of $LiClO_4$ have been measured and analyzed. The difference in spectra of PC with and without $LiClO_4$ was attributed to the interaction of the PC molecules and lithium ions. This interaction occurs mainly on the carbonyl oxygen atom of the PC molecule. The ring deformation, symmetric ring deformation, carbonyl stretching and stretching of ring oxygens for PC are sensitive to this interaction. The solvation number of Li^+ is also calculated. On the other hand, the structure of the ClO_4^- is also affected by PC molecule, forming the solvent separated ion pairs.

Keywords: Infrared and Raman spectroscopy; Ion solvation; Lithium perchlorate; Propylene carbonate

1. INTRODUCTION

Lithium batteries are often considered the future leaders in the battery industry, mainly because of their high energy and low environmental impact. As an important part of the battery, the quality of electrolytes determines the performance, operating temperature range and shelf-life. In the widely produced commercial lithium batteries, liquid

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*Corresponding author. e-mail: jwang@mail.henannu.edu.cn electrolytes are the most used. They are those containing a lithium salt dissolved in nonaqueous aprotic solvents such as propylene carbonate (PC), ethylene carbonate (EC), 1,2-dimethoxyethane (DME) or its mixtures. These liquid electrolytes must be stable, high conductivity, low viscosity and perfect cycle efficiency [1–3]. Numerous studies on the thermodynamic or electrochemical properties have been carried out to find the optimized composition of electrolyte medium [4–6]. Such studies are usually focused on the dilutions, much less is known in the high concentrations. Because the operation of electrochemical devices may cause the electrolyte to locally reach higher concentration than the normal one due to the degradation of solvent [7], the studies in highly concentrated solutions are very important. On the other hand, since a battery is an interactive system, many of the problems encountered in lithium batteries concerning the solution phase actually involve interactions between the components of the electrolyte solutions. The features of these interactions determine the performance of liquid electrolytes.

Since the spectroscopic investigation provides an insight into the interactions of ion–ion and ion–solvent at molecular level through frequencies, intensities and other band properties, it can help us to identify the factors affecting the general properties and the performance of the electrolyte. A number of reports have demonstrated the utility of spectroscopy as a powerful tool for understanding the ion–solvent interactions in electrolytic systems [8, 9].

PC is a common solvent, alone or in combination with EC, either in polymer or liquid electrolyte for lithium battery in view of its high dielectric constant (64.92 at 25°C), wide liquid range (mp −49.2°C; bp 241.7°C) and good solubilizing power for lithium salts [10]. Yeager *et al.* [11] have studied the IR spectra of $LiClO_4$/PC in nitromethane. They observed splittings of some bands of PC in the presence of Li^+. In the investigation of IR and Raman spectra, Battisti *et al.* [12] also found the evidence of strong Li^+–PC interaction, and identified the free ion, solvent-separated ion pairs and contact ion pairs from the curve fitting within the perchlorate band at $933\,cm^{-1}$. In order to understand further the nature of the interaction between lithium salt and PC, the IR and Raman spectra of $LiClO_4$/PC were studied from dilution to high concentrations and some new information is reported in the present work.

2. EXPERIMENTAL

Lithium perchlorate (Beijing Baili Co., A.R.) was recrystallized in acetonitrile, then dried under vacuum for 36 hours at 170°C. Propylene carbonate (Luoyang Chemical Factory, A.R.) was stored over 4A molecular sieves for at least 48 hours, then distilled twice under reduced pressure. The water content, determined by Karl–Fischer method, was less than 60 ppm. All solutions were prepared by weight and concentrations are expressed as molalities (mol kg^{-1} solvent). Every precaution was taken to minimize the contamination by water.

Infrared spectra were recorded on a Bio-Rad FTS-40 FTIR spectrometer (USA) in the absorbance mode from 400 to 4000 cm^{-1}. The samples were mounted between KBr windows as liquid films. Raman spectra were taken using a Jobin-Yvon U1000 Raman spectrometer (France) equipped with a RCA31034 photomultiplier tube. The excitation line of the Ar^+ laser used is at 488 nm and the laser power on the liquid samples sealed in high quality cuvettes is 100 mW. The resolution of both infrared and Raman spectra is 2 cm^{-1}. All the measurements were made at room temperature (ca. 25°C).

3. RESULTS AND DISCUSSION

Battisti *et al.* [12] and Janz *et al.* [13] have studied the IR and Raman spectra of PC in liquid state. Assignment for most of the bands was given. Wilshurst [14] and Chabanel *et al.* [15] have measured the vibrational spectra of $LiClO_4$ and given assignments for the bands observed. In the present paper, the assignments of the bands are based on these reports. In addition, because PC is a poor anion solvator, the changes of PC spectra are considered to be the result of interaction between Li^+ and the PC molecule, the effect of ClO_4^- has been neglected [11].

When $LiClO_4$ was added, it can be seen that some bands of PC showed obvious changes in position and shape. Our analyses for changes of the bands at 1394, 1184, and 1355 cm^{-1} agree well with Yeager and co-workers [11]. We are most interested here in the carbonyl stretching (IR at 1794 cm^{-1} and Raman at 1781 cm^{-1}), the symmetric ring deformation (both IR and Raman at 712 cm^{-1}) and ring deformation (IR at 777 cm^{-1}) for PC molecule. Changes of the band of ring oxygens from 1000 to 1300 cm^{-1} also provide some useful information.

3.1. Solvation of the Lithium Ion

The solvation of lithium ion through the carbonyl oxygen atom has been reported by two groups of researches [11, 12] in $LiClO_4$/PC electrolyte. The only difference in the reported results is as follows. Yeager *et al.* [11] reported that the carbonyl stretching band at 1798 cm^{-1} exhibited a shoulder at lower frequency, whereas Battisti *et al.* [12] only observed that the width of this band became broader and no band splitting was reported in both Raman and IR spectra. In order to clarify this point, a particular attention has been paid to this band which is located at 1794 cm^{-1} in our experiment. The IR results are shown in Figure 1. It can been seen that the effect of $LiClO_4$ on PC is not obvious in the dilution solutions. However, when the $LiClO_4$ concentration reaches 1.00 mol kg^{-1}, a new band appears and its intensity increases with increasing molality of $LiClO_4$. Finally, a new band at 1774 cm^{-1} overlaps the original. The lower frequency component results from the Li^+–carbonyl interaction since its intensity showed concentration dependence. When our spectroscopic data were expressed by absorbance instead of transmittance, the result is the same as that reported by Battisti *et al.* [12]. Therefore, it seems that the difference in experimental phenomenon reported in the literature comes from the different expression of experimental data. Because the carbonyl stretching in IR is very strong and its band expressed by transmittance is very broad, it is more sensitive to express the results in absorbance for investigation of the interaction between Li^+ and PC. The carbonyl stretching vibration band in Raman is located at 1781 cm^{-1}. As shown in Figure 2, its bandwidth increases with increasing $LiClO_4$ content, but no band splitting is observed. Both the infrared and Raman spectra changes indicate that oxygen of $C{=}O$ is a solvation atom as we expected.

Another interesting trend concerns the stretching mode of ring oxygens. Figure 3 illustrates the region including the O—C—O skeletal stretching IR band at 1184 cm^{-1} [13]. With increase of $LiClO_4$

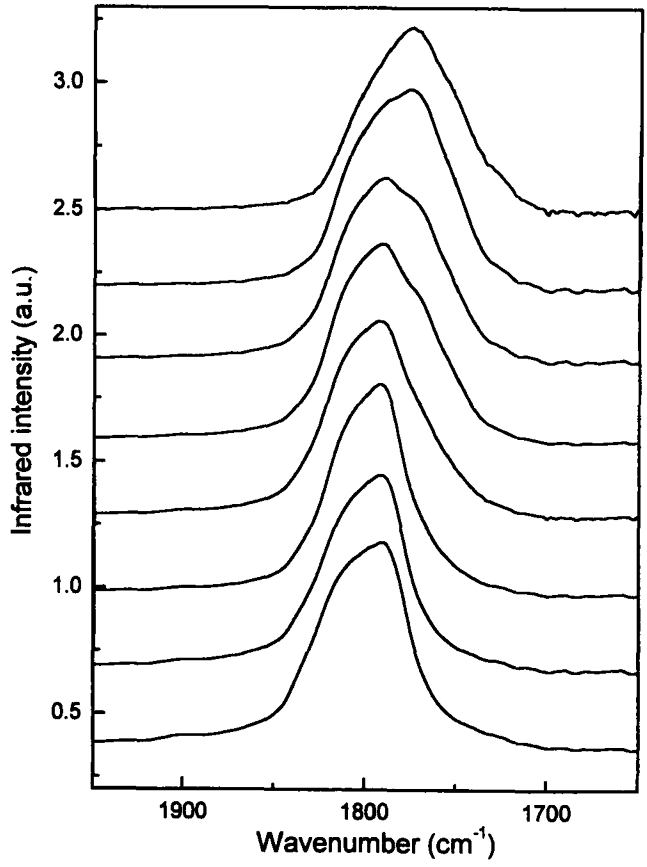

FIGURE 1 The IR spectra of carbonyl stretch for PC in solutions containing different molalities of $LiClO_4$. a: 0; b: 0.10; c: 0.50; d: 1.00; e: 1.49; f: 1.99; g: 2.98; h: 4.98 mol kg^{-1} (from bottom to top).

content, a new band appears at 1205 cm^{-1} and overlaps the original one (1184 cm^{-1}). But no concentration dependence for the band shift is observed. This is different from Yeager's result [11]. Besides this band, marked change occurs in this region. In our opinion, the Li^+–PC interaction and the perturbation of the ClO_4^- could cause such changes because the vibrational mode of free ClO_4^- is located at 1100 cm^{-1} [14]. In order to exclude the effect of ClO_4^-, we studied the IR spectra of LiBr/PC solutions. It is found that the intensity of the band at 1064 cm^{-1}, which is attributed to the ring oxygen stretching [13],

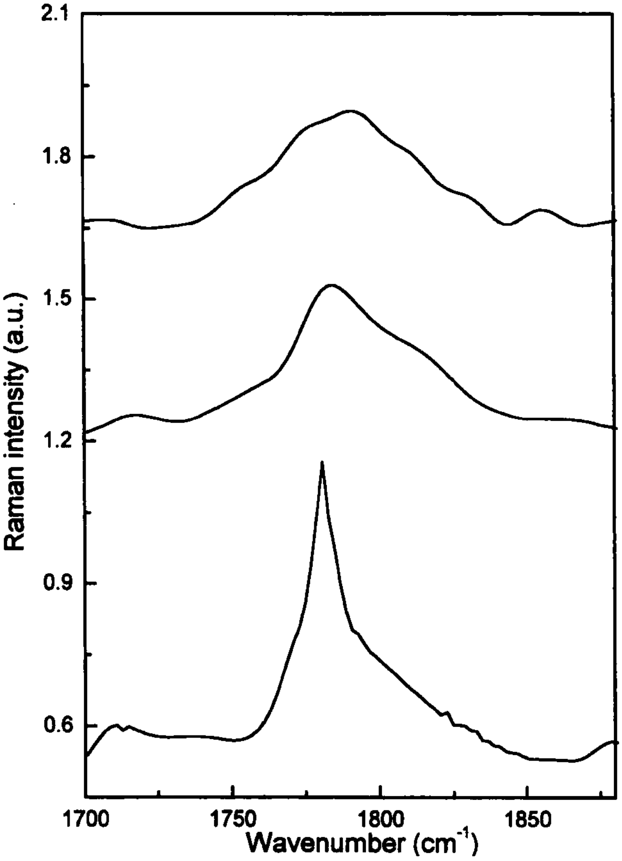

FIGURE 2 The Raman spectra of carbonyl stretch for PC in solutions containing different molalities of $LiClO_4$. a: 0; b: 1.00; c: 2.98 mol kg^{-1} (from bottom to top).

increases with the increasing Li^+ concentration. The Raman changes have also been observed in this region. All these band changes could indicate an interaction between the lithium ion and two oxygens of PC ring. The changes for the other bands in this region are very complicated, no further analysis is attempted.

Figure 4 shows the change procedure of the IR bands at 712 (symmetric ring deformation) and 777 (ring deformation) cm^{-1} with increasing concentration of $LiClO_4$. When the molality of $LiClO_4$ is below 0.50, the spectra do not show any obvious changes from that of pure PC. At the concentration of 1.00 mol kg^{-1}, a shoulder at

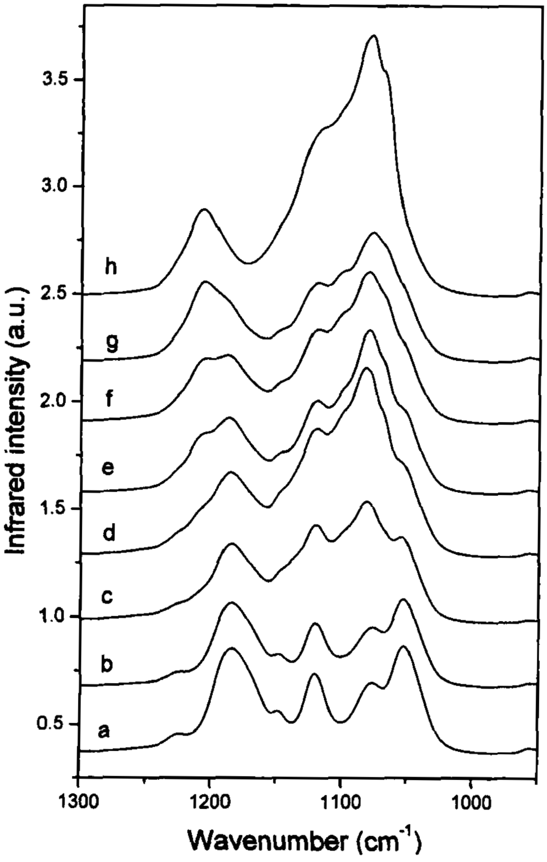

FIGURE 3 The IR spectra of ring oxygen region for PC in solutions containing different molalities of $LiClO_4$. a: 0; b: 0.10; c: 0.50; d: 1.00; e: 1.49; f: 1.99; g: 2.98; h: 4.98 mol kg^{-1}.

722 cm^{-1} appears on the high frequency side of 712 cm^{-1} and its intensity increases with the content of $LiClO_4$. At the highest concentration of 4.98 mol kg^{-1}, the band at 712 cm^{-1} becomes very weak and is overlapped by the new one at 722 cm^{-1}. Although the Raman changes of the band at 712 cm^{-1} is not as strong as the IR band, we also found the presence of new band at 722 cm^{-1} as shown in Figure 5. Splitting of the ring deformation mode has also been reported for the $LiClO_4$/EC electrolyte [16, 17]. The IR band at 777 cm^{-1} shows a maximum wavenumber shift (8 cm^{-1}) at the highest

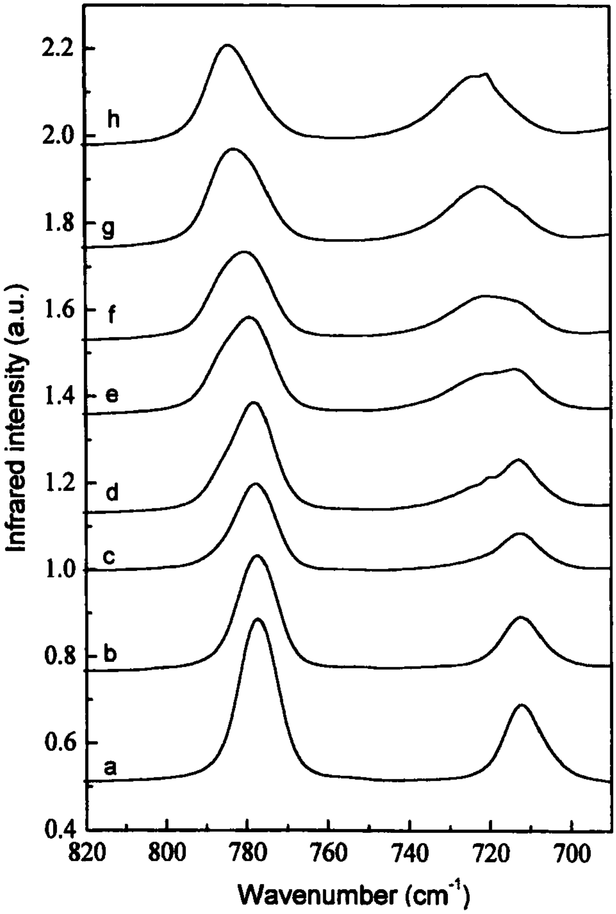

FIGURE 4 The IR spectra of symmetric ring deformation (712 cm^{-1}) and ring deformation (777 cm^{-1}) for PC in solutions containing different molalities of $LiClO_4$. a: 0; b: 0.10; c: 0.50; d: 1.00; e: 1.49; f: 1.99; g: 2.98; h: 4.98 mol kg^{-1}.

molality of $LiClO_4$ investigated. This is another evidence of interaction between Li^+ and PC.

All the spectroscopic changes observed allow us to investigate the way of the interaction between the Li^+ and PC molecule. Although PC molecule has a large dipole moment, dielectric studies have suggested little if any intermolecular association [18, 19]. So, the change of band is not the result of dissociation of the associated PC molecules at presence of $LiClO_4$. A reasonable interpretation is that

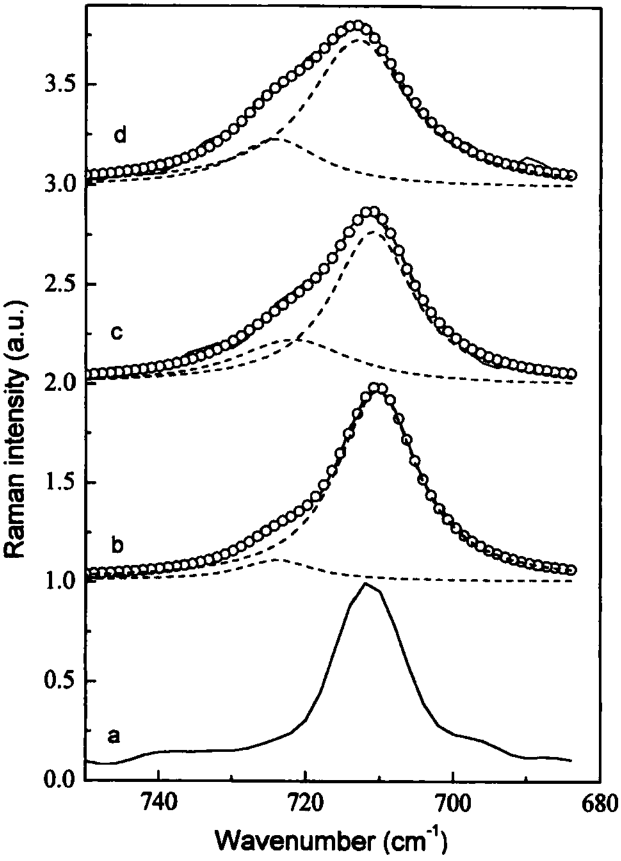

FIGURE 5 The Raman spectra of symmetric ring deformation (712 cm^{-1}) for PC in solutions containing different molalities of $LiClO_4$. a: 0; b: 1.00; c: 1.99; d: 2.98 mol kg^{-1}. (legend: solid line, experimental points; circle points, fitting profile; dashed line, fitting peak).

the new band at 722 cm^{-1} is attributed to the strong interaction of Li^+ with PC ring. The solvation of Li^+ through the oxygen atom of carbonyl group in PC/$LiClO_4$ solutions is unquestionable in both dilute and concentrated solutions. However, there are the other two oxygen atoms in the carbonate group of PC molecule besides the oxygen atom in the carbonyl, an interesting question is raised whether there are also interactions between these two oxygen atoms and lithium ions in the solution. If one suggests that the lithium ion interacts only with the terminus C=O oxygen atom of PC as indicated by molecular orbital approach [20], it is difficult through the induction effect of Li^+ to explain changes of the bands with respect to the oxygen atoms of PC ring such as splitting of the band at 1184 cm^{-1} and the intensity increase of the band at 1064 cm^{-1}. From the above experimental results, it seems more reasonable that the lithium ion interacts weakly with the ring oxygen atoms of the PC molecule, especially in high concentration solutions. This result is in agreement with that of NMR [17]. In fact, these two oxygen atoms have lone electron pairs and the high electron densities [11], the relatively high charge density of lithium ion and the electronegativity of oxygen atoms could easily lead to a new distinct local structure with a relatively well-defined geometry and cause significant changes of spectra.

3.2. Solvation Number of Li^+

According to the splitting of the symmetric ring deformation at 712 cm^{-1}, the interaction can be described by dividing the PC molecules into two populations: the "free" molecules and the "bound" molecules. The new band is the result of interaction between Li^+ and the PC molecule. The increase of their intensities suggests the increasing number of the bound PC molecules. So, the band at 712 cm^{-1} as an object is used to determine the solvation number of the lithium cation by PC. The band at 849 cm^{-1} in the infrared spectra was chosen as an internal standard because it remains a quasi-invariant intensity. This band serves thereafter as standard to obtain relative integrated intensities. The intensities of the bands at 712 cm^{-1} (I_f), 722 cm^{-1} (I_b) and their sum (I_t) are plotted *versus* the concentration of $LiClO_4$ in Figure 6. It can been seen that intensity of the band at 722 cm^{-1} increases at the expense of the 712 cm^{-1} with increasing concentration of $LiClO_4$. However, the total combined intensity of these bands increases to a small extent. Based on the method proposed by Irish *et al.* [21], we designate the concentration of free PC species as C_f and that of the bound species as C_b. Assuming proportionality between intensity and concentration, we can write

$$I_t = I_f + I_b = C_f J_f + C_b J_b = J_f C_t + (1 - J_f/J_b) I_b$$

where J_f and J_b are the proportional coefficients, and C_t is the total concentration of PC, which is assumed to be constant over the

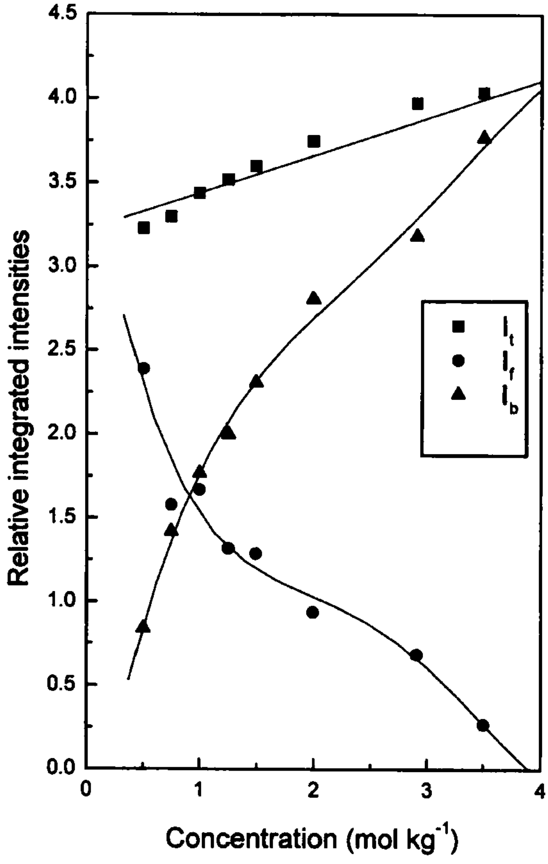

FIGURE 6 Relative integrated intensities for symmetric ring deformation of PC against the concentration of $LiClO_4$: free (I_f), bound (I_b) and their sum (I_t).

concentration range investigated ($C_t = 9.80\,\mathrm{mol\,kg^{-1}}$). A good linearity between I_t and I_b is obtained (Fig. 7) and the data give the equation:

$$I_t = 2.90 + 0.31 I_b$$

with a correlation coefficient of 0.928. Thus, $J_f = 0.30$ and $J_b = 0.43$. The solvation number 'n' of the Li^+ cation is defined as:

$$n = I_b/(C_{\mathrm{Li}} J_b)$$

where C_{Li} is the concentration of solvated Li^+ ion. Table I lists the C_{Li} and the calculated solvation number of Li^+. The solvation number of 4 is suggested for the lithium ions in the dilute $LiClO_4$/PC solutions. This is in agreement with the recent result obtained by molecular dynamic simulation [22]. Coordination numbers of 4 and

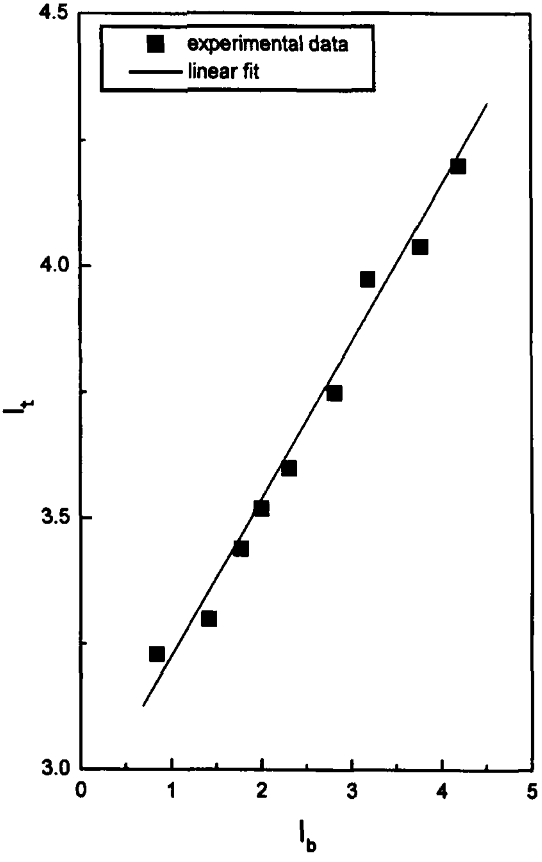

FIGURE 7 Linear plot of I_t against I_b.

TABLE I Solvation number of Li^+ deduced from the intensities of free and bound symmetric ring deformation bands for PC at different $LiClO_4$ concentrations

$C_{Li}/(mol\,kg^{-1})$	0.50	0.75	1.00	1.25	1.49	1.99	2.98	3.50	4.98
n	4.0	4.4	4.2	3.6	3.6	3.3	2.4	2.5	2.0

6 are commonly found for the lithium cation. The most favorable coordination numbers for Li^+ are expected to be 4, 5, and 6 [23, 24]. 4 has been reported for Li^+ in aqueous solutions and in some organic solutions such as EC [8], acetone [21], methyl formate or methyl acetate [25] and dimethyl carbonate [26]. However, the solvation number is much smaller than 4 in the high concentration solutions. Similar results have been reported recently by Cazzanelli and co-workers [17] for Li^+ in PC+EC mixtures. These authors suggested that a part of Li^+ ions begin to from complexes with two solvent molecules (sandwich configuration) when the molar ratio of Li^+ to (PC+EC) is above 0.2 (corresponding to about 2.0 mol kg^{-1}). It seems appropriate to state that similar configuration exists for Li^+ in PC.

3.3. Spectral Evidence for Ion Pairing in $LiClO_4$/PC Electrolyte

The ClO_4^- anion has a tetrahedral symmetry (T_d) and thus its nine vibrational freedom degrees are divided into four modes of vibration: $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(T_2)$, $\nu_4(T_2)$. Chabanel *et al.* [15] have performed an extensive investigation for perchlorates in different solvents and deduced average frequencies of free perchlorate anion: $\nu_1(A_1) = 931\,cm^{-1}$, $\nu_2(E) = 458\,cm^{-1}$ (Raman active), $\nu_3(T_2) = 1100\,cm^{-1}$, $\nu_4(T_2) = 624\,cm^{-1}$. Because of the perturbation of Li^+ or other species, all these four modes can split into new bands corresponding to the particular interaction. Our band fitting of Raman band at 931 cm^{-1} produces a new band at 938 cm^{-1}, which is assigned to the solvent-separated-ion pair [27], when the concentration is above 1.00 mol kg^{-1}. This result agrees well with that reported by Battisti and co-workers [12]. ν_3 band is very strong in IR and weak in Raman, we only identified the band at 1076 cm^{-1}, which is attributed to the free ClO_4^-, the other changes are obscured by the interactions between lithium ions and PC molecule. In addition, it was shown in a recent report [28] that the ν_4 and ν_2 are also sensitive to the ion association. In our experiment, the IR and Raman at 624 cm^{-1} and the Raman band at 462 cm^{-1} show changes with increasing concentration of $LiClO_4$ as partially shown in Figure 8. The Lorentzian deconvolution of 624 cm^{-1} revealed two bands centered at 624 and 634 cm^{-1},

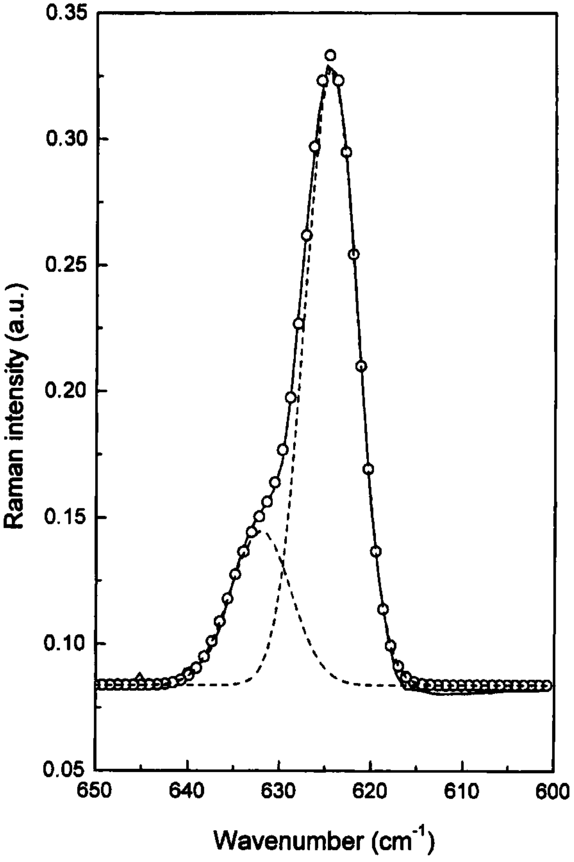

FIGURE 8 ν_4 band (Raman) of perchlorate anion in 1.00 mol kg^{-1} LiClO$_4$/PC solutions. (legend: solid line, experimental points; circle points, fitting profile; dashed line, fitting peak).

respectively. Although the latter could not be assigned definitively to one of some kinds of ion pairs, it is an indication of the changes of local structure of ClO_4^- at least.

The above Raman and IR analysis for perchlorate anion indicate that the symmetry of ClO_4^- changes with increasing LiClO$_4$ concentration. The appearance of the new band at 938 cm^{-1} could be used to probe the ion association. When the concentration is below 1.00 mol kg^{-1}, free ClO_4^- ions are predominant in solutions. However, with the increase of LiClO$_4$ content, the free Li$^+$ becomes bound with the ClO_4^- ions to form solvent separated ion pair. The formation of ion pairs can lead to increase of viscosity and decrease of ion mobility. These factors can explain well the phenomenon of decreasing conductivity of $LiClO_4$/PC electrolytes.

4. CONCLUSIONS

A comparative Raman and Infrared spectra has been made on a $LiClO_4$/PC electrolyte. The analysis for changes of PC spectra shows that the lithium ions probably interact with the three oxygen atoms of PC molecules. Some bands such as the symmetric ring deformation at $712\,cm^{-1}$ (both in IR and Raman) are very sensitive to the interaction between Li^+ and PC molecule and split into new bands when enough $LiClO_4$ is added. Solvation numbers of 4 for lithium cation in the diluted PC/$LiClO_4$ solutions and about 2 in the high concentration solutions have been inferred, and the coexistence of solvent separated ion pairs and free ClO_4^- is also proposed at higher salt concentrations.

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