Chinese Journal of Chemistry, **2008**, *26*, 689—692

Full Paper

Vibrational Spectroscopic Study on Ion Solvation and Ion Association of Lithium Tetrafluoroborate in 4-Ethoxymethyl-ethylene Carbonate

QIAO, Hong-Wei*,[a](乔宏伟) LUAN, He-Lin[b](栾和林) ZHOU, Zhi-Ming[a](周智明)
FANG, Xiang-Peng[c](房向鹏) YAO, Wen[b](姚文) WANG, Xin[b](汪鑫)
LI, Ji-Mei[b](李继梅)

[a] *School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China*
[b] *Beijing General Research Institute of Mining and Metallurgy, Beijing 100044, China*
[c] *Laboratory for Solid State Ionics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

Solvation and association interactions in solutions of lithium tetrafluoroborate/4-ethoxymethyl-ethylene carbonate (EEC) have been studied as a function of concentration of lithium tetrafluoroborate by infrared and Raman spectroscopy. Strong interactions between Li^+ and solvent molecules or BF_4^- anions were observed. Splitting of the ring symmetric angle deformation band, the carbonyl stretching band and the skeletal ring vibrational band suggests that the interaction between Li^+ ions and EEC molecules take place via the oxygen atom on the carbonyl group. The apparent solvation numbers of Li^+, varying from 4.32 to 1.26 with increasing the solution concentrations, were deduced. Band-fitting to the B—F stretching band of BF_4^- anion permits detailed assess of ion pairing. The spectroscopically free BF_4^- anion, contact ion pair and contact ion dimmers coexist in concentrated solutions.

Keywords vibrational spectroscopy, ion solvation and association, lithium tetrafluoroborate, solvation number

Introduction

The use of nonaqueous electrolytes in the development of lithium ion secondary batteries has been intensively investigated. In a typical lithium ion battery system, the most popular electrolytes include a lithium salt such as $LiPF_6$ and $LiBF_4$, and a mixture of alkyl carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC). Many investigations have shown that the electrolyte selection strongly affected the thermal and electrical stability of rechargeable cells.[1-3] The selection and optimization of an electrolyte for practical cells depend on a number of factors, such as low viscosity, high polarity and dielectric constant, wide electrochemical window, *etc*.

Numerous reports have demonstrated that vibrational spectroscopy is a powerful technique for probing ion-solvent and ion-ion interactions through the changes of frequency, intensity and other band properties. Such studies[4-6] could help to identify the factors that affect the general properties and the performance of the electrolyte solutions. Therefore, knowledge of ion solvation and ion association is essential for the optimal choice of solvent and electrolyte.

In our previous investigation,[7] we have reported the results of IR and Raman spectroscopic study on the ion solvation and association of lithium perchlorate in 4-methoxymethyl-ethylene carbonate (MEC), a new molecular solvent synthesized in our laboratory in order to optimize the skeletal ring structure of EC and PC. As an extension of our series of studies and in order to develop a new kind of lithium ion battery electrolyte, we designed and synthesized another molecular solvent, 4-ethoxymethyl-ethylene carbonate (EEC). In this paper, we present the results of study on ion solvation and association of $LiBF_4$/EEC electrolyte by using IR and Raman spectra, and hope it helpful for gaining further insight into the nature of solvation.

Experimental

Lithium tetrafluoroborate (Acros, purity＞98%) was twice recrystallized from acetonitrile, then dried under vacuum for 24 h at 80 ℃. EEC (purity＞99%) was synthesized by transesterification according to the reference,[8] and then refluxed with magnesium oxide and distilled three times under reduced pressure. The middle fraction was retained. As there is no obvious absorption band at about 3500 cm^{-1} in IR spectra, the influence of the moisture in air on the experimental results should be negligible. All solutions were prepared by weight, and concentrations expressed as molalities ($mol \cdot kg^{-1}$).

The IR spectra were collected on a Bruker EQUINOX 55 FT-IR spectrometer with an attenuated total

* E-mail: qiaohongwei1212@hotmail.com
Received March 14, 2007; revised January 10, 2008; accepted January 31, 2008.
Project supported by the National 973 Program (No. 2002CB211800).

© 2008 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

reflection (ATR) attachment (spectrum tech) equipped with a ZnSe crystal in the range of 4000—580 cm^{-1}. The Raman spectra were excited at 1064 nm using a Nd:YAG laser and collected on a Bruker Raman spectrometer in the range of 3500—50 cm^{-1}. The laser power was set to 300 mW. The liquid samples were sealed in transparent glass tubes and measured at room temperature (25 ℃). Both IR and Raman spectra were obtained with a resolution of 2 cm^{-1}. Each IR or Raman spectrum was the accumulation of 800 scans and collected with OPUS 6.0 software. This software package was also used to fit the Raman bands as Lorentzian functions. Relevant spectral data of EEC are as follows: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.20 (t, J=7.2 Hz, 3H), 3.54—3.62 (m, 2H), 3.68 (d, J=6.8 Hz, 2H), 4.37—4.41 (m, 1H), 4.50 (t, J=8.4 Hz, 1H), 4.79—4.83 (m, 1H); IR (KBr) ν: 2980, 2932, 2873, 2811, 1784, 1396, 1167, 1125, 1044, 848, 773, 713 cm^{-1}; MS (70 eV) *m/z* (%): 146 (M^+, 0.12), 87 (1.16), 59 (100), 57 (10.32), 44 (22.44), 31 (44.74).

Results and discussion

Ion solvation in $LiBF_4$/EEC electrolyte

The IR and Raman spectra of $LiBF_4$/EEC were recorded from 0 to 2.7 mol•kg^{-1}. Most of the bands in 580—4000 cm^{-1} show little changes in frequency and shape on addition of $LiBF_4$ except for those bands of ring symmetric angle deformation of O—C—O, ring deformation, carbonyl stretching of C=O and the skeletal ring vibration of C—O—C. In addition, because cyclic carbonates are a poor anion solvator, changes of the solvent spectra were considered to be the result of interaction between Li^+ and solvent molecules.

Figure 1 shows the IR spectra of EEC in solutions with different molalities of $LiBF_4$ in the region from 690 to 810 cm^{-1}. The ring symmetric angle deformation band is located at 713 cm^{-1}, and with the addition of $LiBF_4$, a shoulder band gradually appeared at 724 cm^{-1} and increases in intensity at the expense of the original band. The band at 773 cm^{-1} for pure EEC was attributed to the ring deformation, which gradually moved to higher wavenumbers with increasing the molality of lithium salt. Largely due to the overlap of ring deformation band with BF_4^- ν_1 modes, such as those of spectroscopically free anion (764 cm^{-1}), contact ion pairs (771 cm^{-1}), and contact ion dimers (780 cm^{-1}), it is difficult to recognize which factor resulted in the change of the 773 cm^{-1} band.

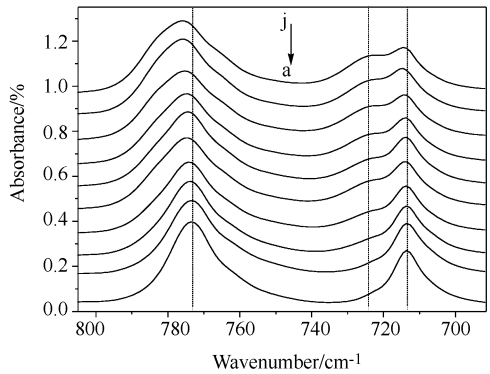

Figure 1 IR spectra of EEC in solutions with different molalities of $LiBF_4$ in the ring deformation and ring symmetric angle deformation regions. (a) 0, (b) 0.2, (c) 0.5, (d) 0.8, (e) 1.1, (f) 1.4, (g) 1.7, (h) 2.0, (i) 2.3 and (j) 2.7 mol•kg^{-1}.

Figure 2 clearly demonstrates the spectral evolution of the IR bands between 1150 and 1850 cm^{-1}. The C=O stretching of pure EEC locates at 1784 cm^{-1}. With increasing the salt content, a shoulder gradually appeared at 1761 cm^{-1} and increased in intensity, and this change procedure was especially obvious after the electrolyte concentration reached 1.1 mol•kg^{-1}.

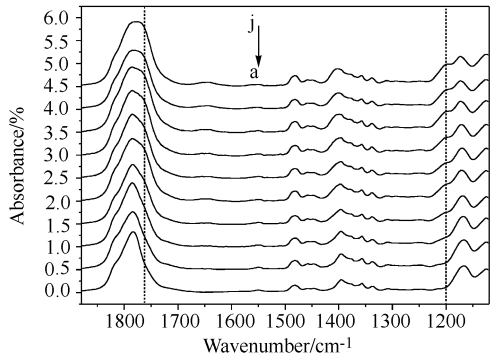

Figure 2 IR spectra of EEC in solutions containing different molalities of $LiBF_4$ in 1150—1850 cm^{-1} region. (a) 0, (b) 0.2, (c) 0.5, (d) 0.8, (e) 1.1, (f) 1.4, (g) 1.7, (h) 2.0, (i) 2.3, (j) 2.7 mol•kg^{-1}.

As seen in Figure 2, the IR spectrum of the skeletal ring vibration C—O—C (1167 cm^{-1}) of pure EEC is also very sensitive to the variation of salt concentrations. With increasing the content of $LiBF_4$ in electrolyte solutions, this band gradually blue-shifted to higher wavenumbers, and the maximum shift in the present study was 7 cm^{-1}; whilst a new band was split at 1200 cm^{-1} and increased in intensity quickly. As there is no other band observable for the pure EEC in this region, the band splitting at 1200 cm^{-1} must result from the interaction between Li^+ and EEC molecules.

All the spectroscopic changes observed above suggested the strong interactions between Li^+ and EEC molecules. The lithium cation probably binds with the oxygen atom of carbonyl functional group of EEC. The electrons on the EEC molecules will be transferred to lithium cations after the solvation clusters are formed, and as a result, some spectral bands are moved or split gradually. The splitting of the ring symmetric angle deformation band suggests that there should be two kinds of EEC molecules coexisting in the electrolyte solutions: isolated EEC in bulk solvent and coordinated EEC with Li^+ in solvation clusters. The shoulders in all the selected spectral regions were assigned to EEC molecules located in the first solvation shell.

© 2008 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Ion association and solvation number of $LiBF_4$/EEC solutions

The free BF_4^- belongs to the T_d point group and has a tetrahedral structure with four vibrational modes,[9] ν_1 (A_1), ν_2 (E), ν_3 (F_2), and ν_4 (F_2), which are very similar to those of ClO_4^-. Papke[10] studied the IR and Raman spectra of $LiBF_4$ in solid polymer PEO and summarized the absorption positions for the four vibrational modes. The symmetric B—F stretch mode (ν_1), which is always located at around 764 cm^{-1}, can be used to study the ion association in concentrated electrolytes. Xuan *et al.*[11] reported their band-fitting results of IR and Raman bands of B—F stretch in $LiBF_4$/acetonitrile solutions, and ascribed the band at 763 cm^{-1} to spectroscopically free anions, and that at 771 cm^{-1} to contact ion pairs. Alia and Edwards[12] studied the ion association of $LiBF_4$ and $AgBF_4$ in acrylonitrile, and ascribed the band at 766 cm^{-1} to BF_4^- free anion, 773 cm^{-1} to contact ion pair, and 782 cm^{-1} to contact ion dimers.

Figure 3 illustrates the Raman spectra of EEC in solutions with $LiBF_4$ at different molalities in the 700—780 cm^{-1} region. For the isolated EEC molecule, the ring symmetric angle deformation band locates at 715 cm^{-1}. With increasing the molar content of $LiBF_4$, a shoulder split at 725 cm^{-1} and increased in intensity gradually. As seen in Figure 3, the 765 cm^{-1} band gradually became stronger with the addition of $LiBF_4$, and a weak shoulder at 770 cm^{-1} gradually appeared in the concentrated solutions.

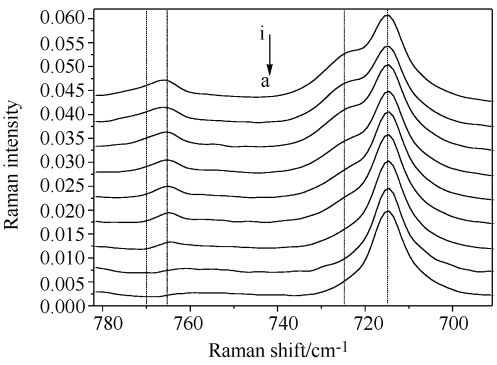

Figure 3 Raman spectra of EEC in solutions with $LiBF_4$ at different molalities in the 700—780 cm^{-1} region: (a) 0, (b) 0.2, (c) 0.5, (d) 0.8, (e) 1.4, (f) 1.7, (g) 2.0, (h) 2.3, (i) 2.7 mol•kg^{-1}.

Band-fitting to the Raman spectrum of 2.7 mol•kg^{-1} $LiBF_4$/EEC solution between 760—795 cm^{-1} region gives three bands located at 765, 772, and 786 cm^{-1}, respectively (Figure 4). The band at 765 cm^{-1} should be due to the spectroscopically free anion, and that at 772 cm^{-1} could be attributed to the contact ion pairs. The mode to result in the appearance of the component band at 786 cm^{-1} is not clear, and we supposed it to be due to the contact ion dimers here. With increasing the molalities of lithium salt, the intensities of the two components at 772 and 786 cm^{-1} gradually increased, which is in accordance with the reference.[11] Comparing the bands of contacted ion pairs at 772 cm^{-1} with those reported

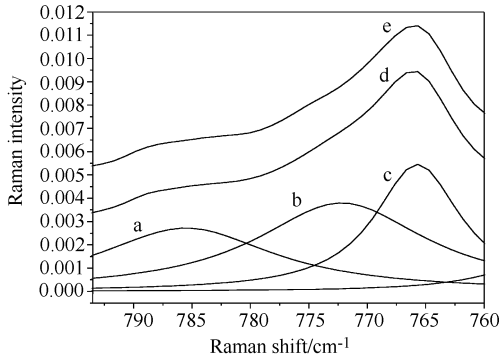

Figure 4 Band-fitting results of the Raman spectrum of the BF_4^- ν_1 mode in 2.7 mol•kg^{-1} solution. (a), (b), (c) fitted components, (d) fitted spectrum and (e) raw data.

by Xuan *et al.*, the intensities are obviously lower than those in $LiBF_4$/acetonitrile solutions. In our opinion, this is largely due to the relatively high dielectric constant of cyclic carbonate and good solubility of $LiBF_4$ in EEC solvents.

Figure 5 gives the results of band-fitting to the ring symmetric angle deformation band of an EEC molecule in 2.7 mol•kg^{-1} $LiBF_4$/EEC solution. The new band, resulting from the interaction between Li^+ and EEC molecules, is located at 725 cm^{-1}. Throughout the investigated salt contents, the Raman bands at 850 cm^{-1} show no detectable change in position and relative intensity. Therefore, the integrated intensity of this band was taken as the reference for calculating the relative intensities of other bands. Because the Raman intensity is linear to the content of specific species in the solution, intensity of the new band, resulting from the coordinated EEC, and the intensity of original band of free EEC can be used to calculate the solvation numbers by using an Irish method.[13,14] The model is based on the following equations:

$$I_f = J_f C_f,\ I_b = J_b C_b,\ C_t = C_f + C_b,\ I_t = I_b + I_f = J_b C_b + J_f C_f$$

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

$$n_s = C_b / C_{Li} = I_b / C_{Li} J_b$$

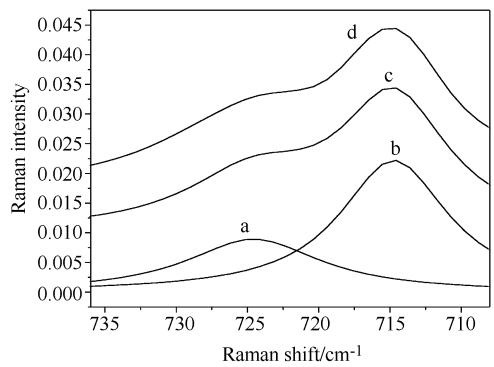

Figure 5 Band-fitting results of the Raman spectrum in the range 705—735 cm^{-1} in 2.7 mol•kg^{-1} $LiBF_4$/EEC solution. (a), (b) fitted components, (c) fitted spectrum and (d) raw data.

© 2008 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

where I_f and I_b are the intensities of the bands for free and coordinated EEC molecules, J_f and J_b are molar diffusing coefficients of the two EEC molecules, C_{Li} is the concentration of solvated lithium cations, and C_t (6.849 mol•kg^{-1}) is the total molality of free EEC molecule (C_f) and coordinated one (C_b). From the Raman intensities of the components in the ring symmetric angle deformation envelops, we can achieve the linear equation as follows: $I_t = -0.5974I_b + 1.4396$, with the linear coefficient of 0.9519. In this way, solvation numbers varying between 4.32 and 1.26 were obtained. Figure 6 shows the effect of $LiBF_4$ concentrations on the solvation numbers of Li^+. As we can see from this plot, the apparent solvation numbers decrease quickly with increasing the concentration of $LiBF_4$. The reason can be deduced as follows: in concentrated solutions, Li^+ ions have more chances to contact with the BF_4^- anions to form contact ion pairs and their dimers than in infinitely diluted solutions. With increasing salt contents, more and more EEC molecules will be pushed out of the solvation shell by the close contact between solvated Li^+ cations and BF_4^- anions. This is why a decreasing tendency of the apparent solvation number was obtained.

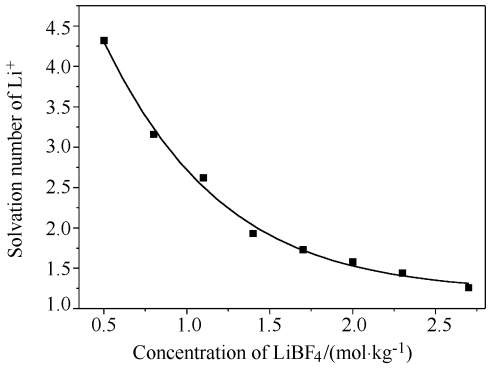

Figure 6 Effect of $LiBF_4$ concentrations on the solvation number of Li^+.

All the phenomena observed above indicate that the degree of ion association of $LiBF_4$ increases quickly with increasing the concentration of solutions, which is especially obvious in the concentrated electrolytes. As the contact ion pairs and their dimers appeared in electrolyte solutions, the number of conductive lithium cations decreased and the viscosity of the solution increased, and as a result, causing a reduced conductivity. That is to say, the optimal concentration should be found during the preparation of liquid electrolyte.

Conclusion

From the IR and Raman spectra of EEC in different concentrations of $LiBF_4$, it can be deduced that there is a strong interaction between Li^+ and EEC, and the site of solvation is supposed to be the carbonyl oxygen atom of EEC. The apparent solvation numbers of Li^+ varied from 4.32 to 1.26 with increasing the electrolyte concentration. The spectroscopically free anion, contact ion pairs and contact ion dimers could be found in the concentrated solutions. As the EEC compound is a new molecular solvent for lithium battery electrolyte, the scientific values exhibited in this paper are useful for the further electrochemical studies on the EEC-based electrolytes.

Acknowledgements

Professor Wang Zhao-xiang in Chinese Academy of Sciences, Associate Professor Xuan Xiao-peng at Henan Normal University, and Professor Zhang Shao-wen and Dr. Wu Yu-kai at Beijing Institute of Technology are sincerely appreciated for helpful suggestions.

References

1 Salomon, M. *Pure Appl. Chem.* **1998**, *70*, 1905.
2 Ogumi, Z.; Inaba, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 5211.
3 Dudley, J. T.; Wilkinson, D. P.; Thomas, G.; Levae, R.; Woo, S.; Blom, H.; Horvah, C.; Juzkow, M. W.; Denis, B.; Juric, P.; Aghakian, P.; Dahh, J. R. *J. Power Sources* **1991**, *35*, 59.
4 Klassen, B.; Aroca, R.; Nazri, M.; Nazri, G. A. *J. Phys. Chem. Sect. B* **1998**, *102*, 4795.
5 Morita, M.; Asai, Y.; Yoshimoto, N.; Ishikawa, M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3451.
6 Xuan, X. P.; Wang, J. J.; Tang, J. M.; Qu, G. R.; Lu, J. S. *Spectrochim. Acta* **2000**, *56*, 2131
7 Qiao, H. W.; Luan, H. L.; Zhou, Z. M.; Yao, W. *Chin. J. Chem.* **2007**, *25*, 461
8 Wu, M.; Wu, F.; Luan, H. L.; Chen, R. J. *Acta Chim. Sinica* **2005**, *63*, 787 (in Chinese).
9 Xuan, X. P. *Doctoral Thesis*, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, **2004** (in Chinese).
10 Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **1982**, *129*, 1434.
11 Xuan, X. P.; Zhang, H. C.; Wang, J. J.; Wang, H. Q. *J. Phys. Chem. A* **2004**, *108*, 7513.
12 Alia, J. M.; Edwards, H. G. M. *J. Solution Chem.* **2000**, *29*, 781.
13 Deng, Z.; Irish, D. E. *Can. J. Chem.* **1991**, *69*, 1766.
14 Xuan, X. P.; Wang, J. J.; Zhao, Y.; Zhuo, K. L. *Acta Chim. Sinica* **2005**, *63*, 1693 (in Chinese).

(E0703142 LU, Y. J.)

© 2008 SIOC, CAS, Shanghai, & WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim