

Vibrational Spectroscopic Study on Ion Solvation and Association of Lithium Perchlorate in 4-Methoxymethyl-ethylene Carbonate

QIAO, Hong-Wei^{*a}(乔宏伟) LUAN, He-Lin^b(栾和林)
ZHOU, Zhi-Ming^a(周智明) YAO, Wen^b(姚文)

^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

Solvation interaction and ion association in solutions of lithium perchlorate/4-methoxymethyl-ethylene carbonate (MEC) have been studied by using Infrared and Raman spectra as a function of concentration of lithium perchlorate. The splitting of ring deformation band and ring ether asymmetric stretching band, and the change of carbonyl stretching band suggest that there should be a strong interaction between Li^+ and the solvent molecules, and the site of solvation should be the oxygen atom of carbonyl group. The apparent solvation number of Li^+ was calculated by using band fitting technique. The solvation number was decreased from 3.3 to 1.1 with increasing the concentration of $\text{LiClO}_4/\text{MEC}$ solutions. On the other hand, the band fitting for the ClO_4^- band revealed the presence of contact ion pair, and free ClO_4^- anion in the concentrated solutions.

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

Introduction

Lithium ion batteries have been widely applied to portable electronic devices in the recent years due to their high energy density and low environmental impact. The composition of the non-aqueous organic electrolyte for lithium ion batteries plays an important role in determining cell performance, operating and storage temperature ranges.^{1,2} Many investigations have shown that the electrolyte selection also strongly affected the thermal and electrical stability of rechargeable cells.³⁻⁵ 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.

Ethylene carbonate (EC) and propylene carbonate (PC), which have been widely used in lithium ion batteries for many years,⁶ due to the ring structure, both have high polarity and dielectric constant, but their drawbacks are very obvious too. EC, as the boiling point is 36.4 °C, is in solid state under room temperature. While PC, due to the methyl group, can co-insert into the carbonaceous anode with Li^+ during the recharging process. In order to optimize the carbonate ring structure, we designed and synthesized 4-methoxymethyl-ethylene carbonate, hoping to develop the new kind of lithium ion battery electrolyte.

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. Such studies⁷⁻¹⁰ could help us to identify the factors that affect the general properties and the performance of the electrolyte in lithium ion batteries. In this paper, we present the result of study on ion solvation and association of $\text{LiClO}_4/\text{MEC}$ electrolyte using IR and Raman spectra, and hope it helpful for gaining further insight into the nature of solvation.

Experimental

Lithium perchlorate (Acros, purity >99.9%) was twice recrystallized in acetonitrile, then dried under vacuum for 36 h at 170 °C. MEC (purity >99%) was synthesized by transesterification according to the reference,¹¹ and then refluxed with magnesium oxide and distilled three times under reduced pressure. The middle fraction was retained. The water content, as determined by Karl-Fischer method, was less than 100 $\text{mg}\cdot\text{L}^{-1}$. All solutions were prepared by weight, and concentrations are expressed as molalities ($\text{mol}\cdot\text{kg}^{-1}$).

Infrared spectra were collected by using a Bruker FT-IR spectrometer with an attenuated total reflection (ATR) attachment (spectra tech) equipped with a ZnSe crystal in the range of 4000–580 cm^{-1} . Raman spectra were collected on a Bruker Raman spectrometer. The laser power was set to 300 mW, and 800 scans were accumulated to achieve a good signal-to-noise ratio. The liquid samples were sealed in NMR tubes and measured

* E-mail: qiaohongwei1212@hotmail.com

Received June 22, 2006; revised and accepted December 25, 2006.

Project supported by the National Basic Research 973 Program of China (No. 2002CB211800).

at room temperature (25 °C). Both IR and Raman spectra were obtained with a resolution of 2 cm⁻¹. Relevant spectral data of MEC are as follows: ¹H NMR (CDCl₃, 400 MHz) δ: 3.45 (s, 3H), 3.58 (d, *J*=10.8 Hz, 1H), 3.66 (d, *J*=11.2 Hz, 1H), 4.37–4.41 (m, 1H), 4.51 (t, *J*=8.4 Hz, 1H), 4.79–4.85 (m, 1H); IR (KBr) ν: 2993, 2933, 2895, 1782, 1399, 1168, 1042, 849, 773, 715 cm⁻¹; MS (70 eV) *m/z* (%): 132 (M⁺, 0.05), 87 (0.95), 58 (3.67), 45 (100), 29 (17.01).

Results and discussion

Ion solvation in LiClO₄/MEC electrolyte

The IR and Raman spectra of LiClO₄/MEC were recorded from 0 to 3 mol·kg⁻¹. Most of the bands in 580–4000 cm⁻¹ show little changes in frequency and shape on addition of LiClO₄ except for those bands of ring symmetric deformation O—C—O, ring deformation, ring ether asymmetric stretching C—O—C and carbonyl stretching C=O. In addition, because MEC is 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 change procedure of the bands in region from 690 to 810 cm⁻¹. Ring symmetric deformation O—C—O was located at 715 cm⁻¹. With the addition of lithium perchlorate, a shoulder peak appeared at 724 cm⁻¹ and increased in intensity as the molality of LiClO₄ increased. The ring deformation band was located at 773 cm⁻¹, and with increasing the molality of LiClO₄, a new band appeared at 779 cm⁻¹ and increased in intensity at the expense of the 773 cm⁻¹ band.

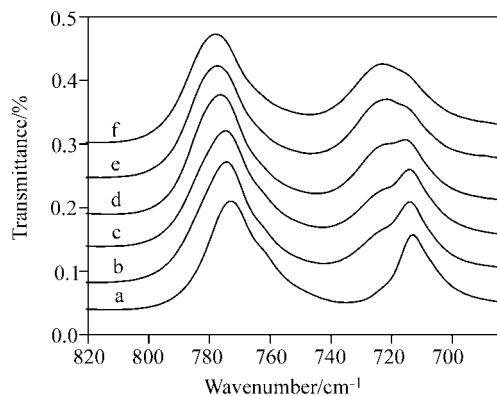


Figure 1 IR spectra of MEC in solutions with different molalities of LiClO₄ in the ring deformation and ring symmetric deformation region (a) 0, (b) 0.5, (c) 1.1, (d) 2.0, (e) 2.5, (f) 3.0 mol·kg⁻¹.

Figure 2 shows the effect of LiClO₄ concentration on the strong IR absorption at 1781 cm⁻¹, which was attributed to C=O carbonyl stretching band. With the increasing addition of LiClO₄, this band was gradually moved to the lower wave number. The maximum shift is 21 cm⁻¹ in the present study.

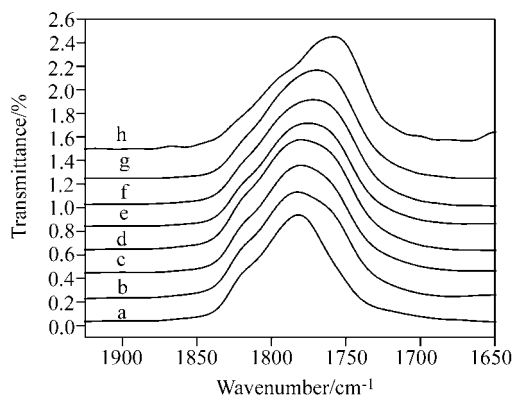


Figure 2 IR spectra of MEC in solutions containing different molalities of LiClO₄ in the carbonyl stretching regions (a) 0, (b) 0.5, (c) 0.8, (d) 1.1, (e) 1.4, (f) 1.7, (g) 2.0, (h) 2.5 mol·kg⁻¹.

All the spectroscopic changes observed above suggested that there should be a strong interaction between Li⁺ and MEC molecules. The lithium cation probably binds with the oxygen atom of carbonyl functional group of MEC. Splitting of MEC ring and symmetric ring deformations suggests that there should be two kinds of MEC molecules in the solution: free MEC in bulk solvent, and coordinated MEC with lithium cation in solvation shell. The new component at higher wavenumbers than the main band was assigned to MEC molecules located in the first solvation shell. Because the Raman intensity is linear to the concentration of the solvent,¹² intensity of the new band, resulting from the coordinated MEC, and the intensity of original band of free MEC can be used to calculate the solvation numbers by using Irish method.^{13,14}

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

$$I_t = I_b + I_f = J_b C_b + J_f C_f$$

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

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

where *I_f* and *I_b* are the intensities of the bands for free and coordinated MEC molecules, *J_f* and *J_b* are molar diffusing coefficients of the two MEC molecules, *C_t* is the molality of MEC molecule. From the Raman intensities, we can achieve the linear equation as follows: *I_t* = 0.5327*I_b* + 2.0118, and the relevant linear coefficient is 0.91. Figure 3 shows the effect of LiClO₄ concentrations on the solvation number of Li⁺. In this way, solvation numbers varying between 3.3 and 1.1 were obtained, depending on the concentration of salt. The solvation number of Li⁺ in MEC is lower than 4.¹⁵⁻¹⁷ The reason can be deduced as follows: at the high salt concentrations, Li⁺ has more chances to contact with the ClO₄⁻ anion to form ion pairs or ion aggregates, which results in a lower concentration of the solvated Li⁺ and a smaller solvation number. While in infinite diluted solutions, it can be expected that the solvation number

of Li^+ in MEC is close to 4, because ion association is negligible in this situation. Figures 4 and 5 show the changing intensity of the two symmetric ring deformation bands with increasing concentration of LiClO_4 , and curve fitting of Raman spectra for symmetric ring deformation band of MEC molecule in $1.7 \text{ mol}\cdot\text{kg}^{-1}$ $\text{LiClO}_4/\text{MEC}$ solution, respectively.

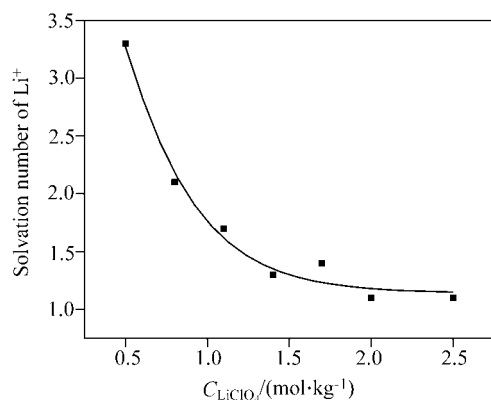


Figure 3 Effect of LiClO_4 concentrations on the solvation number of Li^+ .

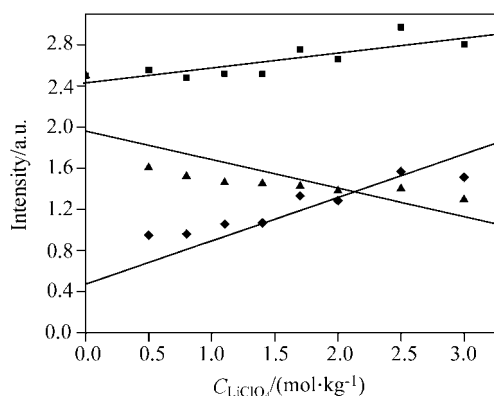


Figure 4 Effect of LiClO_4 concentrations on IR intensity of MEC symmetric ring deformation ($\blacktriangle I_f$; $\blacklozenge I_b$; $\blacksquare I_t$).

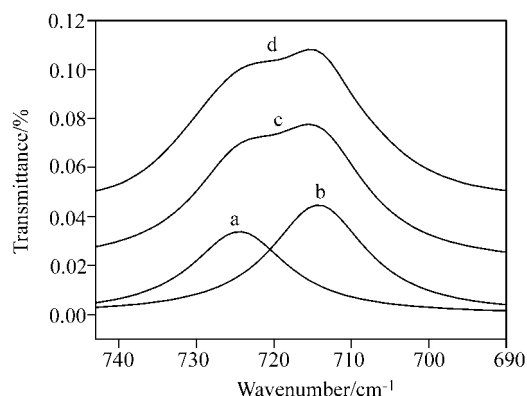


Figure 5 Curve fitting of Raman spectra for the symmetric ring deformation band (at 715 cm^{-1}) of MEC in the $1.7 \text{ mol}\cdot\text{kg}^{-1}$ $\text{LiClO}_4/\text{MEC}$ solution (a), (b) fitted components; (c) fitted spectrum; (d) raw data.

Ion association in $\text{LiClO}_4/\text{MEC}$ solutions

The free ClO_4^- anion has a tetrahedral symmetry (T_d) and thus its nine vibrational degrees of freedom are divided into four modes of vibration: ν_1 (A_1), ν_2 (E), ν_3 (F_2), and ν_4 (F_2). The F_2 modes are IR active, while others are Raman active. All the four modes are very sensitive to the interactions between ion-ion and ion-solvent, and can be used to detect the existing form of ion association and ion pairs in solutions. Chabanel *et al.*¹⁸ deduced average frequencies for the unperturbed perchlorate anion as follows: ν_1 (A_1) = 931 cm^{-1} , ν_2 (E) = 458 cm^{-1} , ν_3 (F_2) = 1100 cm^{-1} , ν_4 (F_2) = 624 cm^{-1} . Change in the shapes of the totally symmetric band ν_1 of the free ClO_4^- anion has been attributed by some authors¹⁸⁻²⁰ to ion association in the solution. James and Mayes^{19,20} have identified ion-solvent interaction in the Raman spectra of perchlorate solutions. However, because the ν_1 mode is not IR active for unperturbed ClO_4^- , no ν_1 band can be observed in the IR spectrum if the ClO_4^- is completely free. We can use Raman spectrum to study changes around the ion. Figure 6 shows the change of Raman absorption bands of free ClO_4^- anions, and multiple ion aggregates with increasing the concentration of LiClO_4 .

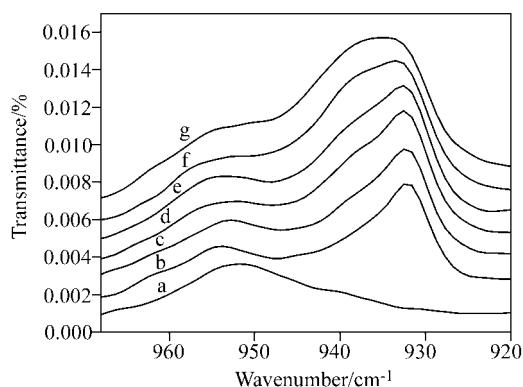


Figure 6 Raman spectra of ClO_4^- and ion aggregates with increasing molality of solutions (a) 0, (b) 1.1, (c) 1.4, (d) 1.7, (e) 2.0, (f) 2.5, (g) $3.0 \text{ mol}\cdot\text{kg}^{-1}$.

In the present investigation, as shown in Figure 6, the intensity of the band at 931 cm^{-1} , which is attributed to free ClO_4^- anions, increases with increasing LiClO_4 content. Figure 7 shows the band fitting result for the ν_4 IR band (*ca.* 624 cm^{-1}) of free ClO_4^- anion. We can see the ν_4 band splitting into two components at $1.7 \text{ mol}\cdot\text{kg}^{-1}$ $\text{LiClO}_4/\text{MEC}$ solutions and the shoulder peak locates at 634 cm^{-1} . The former should be attributed to the free ClO_4^- anion, and the latter to the contact ion pairs or ion aggregates, which is in accordance with the reference.²¹

The above phenomena indicate that the symmetry and shape of the ClO_4^- anion change with increasing the concentration of LiClO_4 . That is, part of the free Li^+ cations become bound with ClO_4^- anion to form contact ion pairs, which leads to splitting of the vibrational modes of ClO_4^- anion. Moreover, these species are lar-

ger in size and hence reduce the mobility of ions and increase the viscosity of solutions, causing decreased conductivity. That is to say, the optimal concentration should be found during the preparation of liquid electrolyte.

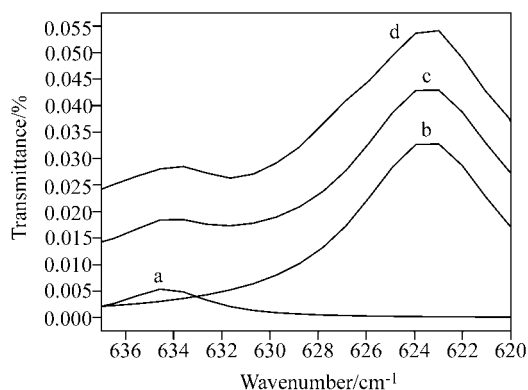


Figure 7 Curve fitting of IR spectra for the ν_4 band (at 624 cm^{-1}) of ClO_4^- anion in the $1.7 \text{ mol} \cdot \text{kg}^{-1}$ $\text{LiClO}_4/\text{MEC}$ solution (a), (b) fitted components; (c) fitted spectrum; (d) raw data.

Conclusion

From IR and Raman spectra of MEC in the presence of LiClO_4 , it can be seen that there is an interaction between Li^+ cation and MEC. The site of solvation is the oxygen atom of carbonyl group. The apparent solvation numbers of Li^+ were varied from 3.3 to 1.1 with increasing electrolyte concentration. The free ClO_4^- anion, and contact ion pairs can be detected in the concentrated solutions.

Acknowledgements

Professor Wang Zhao-Xiang in Chinese Academy of Sciences, and associate professor Xuan Xiao-Peng in Henan normal university are sincerely appreciated for helpful suggestions.

References

- 1 Barthel, J.; Gores, H. J. *Pure Appl. Chem.* **1985**, *57*, 1071.
- 2 Venkatesetty, H. V. In *Lithium Battery Technology*, Ed.: Venkatesetty, H. V., Wiley, New York, **1984**.
- 3 Salomon, M. *Pure Appl. Chem.* **1998**, *70*, 1905.
- 4 Ogumi, Z.; Inaba, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 5211.
- 5 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.
- 6 Wu, Y. P.; Dai, X. B.; Ma, J. Q.; Cheng, Y. J. *Lithium Ion Battery—Application and Practice*, Chemical Industry Press, Beijing, **2004**, Chapter 9.1 (in Chinese).
- 7 Buxton, T. L.; Caruso, J. A. *J. Phys. Chem.* **1973**, *77*, 1882.
- 8 Klassen, B.; Aroca, R.; Nazri, M.; Nazri, G. A. *J. Phys. Chem. B* **1998**, *102*, 4795.
- 9 Morita, M.; Asai, Y.; Yoshimoto, N.; Ishikawa, M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3451.
- 10 Xuan, X. P.; Wang, J. J.; Tang, J. M.; Qu, G. R.; Lu, J. S. *Spectrochim. Acta* **2000**, *56*, 2131.
- 11 Wu, M.; Wu, F.; Luan, H. L.; Chen, R. J. *Acta Chim. Sinica* **2005**, *63*, 787 (in Chinese).
- 12 Xuan, X. P.; Zhang, H. C.; Wang, J. J.; Wang, H. Q. *J. Phys. Chem. A* **2004**, *108*, 7513.
- 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).
- 15 Barthel, J.; Buchner, R.; Wismeth, E. *J. Solution Chem.* **2000**, *29*, 937.
- 16 Seo, J.; Cheong, B.; Cho, H. *Spectrochim. Acta* **2002**, *58A*, 1747.
- 17 Loring, J. S.; Fawcett, W. R. *J. Phys. Chem. A* **1999**, *103*, 3608.
- 18 Chabanel, M.; Legoff, D.; Touaj, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4199.
- 19 James, D. W.; Mayes, R. E. *Aust. J. Chem.* **1988**, *35*, 1775.
- 20 James, D. W.; Mayes, R. E. *Aust. J. Chem.* **1988**, *35*, 1785.
- 21 Salomon, M.; Xu, M.; Eyring, E.; Petrucci, S. *J. Phys. Chem.* **1994**, *98*, 8234.

(E0606222 SONG, J. P.)