Local Structure of Li⁺ in Concentrated LiPF₆-Dimethyl Carbonate Solutions

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Abstract

Neutron diffraction measurements have been carried out at 25 °C for 9.6 mol% ⁶LiPF₆-deuterated dimethyl carbonate (DMC-*d*₆) solutions in which the isotopic ratio of ⁶Li/⁷Li was changed. Local structure of Li⁺ in the solution was derived from the least squares fitting analysis of observed difference function, $\Delta_{\text{Li}}(Q)$. It was revealed that Li⁺ is surrounded by ca. 3 DMC molecules and ca. 1 PF₆⁻ with intermolecular distances of $r(\text{Li}^+\cdots\text{O}(\text{DMC})) = 2.08 \pm 0.02 \text{ \AA}$ and $r(\text{Li}^+\cdots\text{F}(\text{PF}_6^-)) = 2.03 \pm 0.06 \text{ \AA}$, respectively. Raman experimental study and DFT calculations agree well with neutron structure analysis.

1. Introduction

In recent years, the solvation structure of Li⁺ in non-aqueous solutions attracts much attention in relation with electrolytes used for lithium ion secondary batteries. Especially, formation of the contact ion pair and aggregation of ions in highly concentrated non-aqueous solutions receives considerable attraction in close connection with fast-charging and high-voltage advanced batteries [1]. Combination of LiPF₆ and carbonate solvents has mostly been employed as electrolyte solutions because of high solubility of Li salt and good electrical conductivity [2]. Mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) is often employed as a solvent in practical use to keep a wider liquid range of electrolyte solution and favorable transport property of Li⁺. In order to obtain deeper insights for the transport mechanism of Li⁺ in non-aqueous electrolyte solutions, it is necessary to determine the local structure around Li⁺. According to IR and Raman spectroscopic

studies on LiAsF₆-DMC solutions, the conformational equilibrium of DMC molecule (“cis-cis” and “cis-trans”) is modified by solvating Li⁺ [3]. The ratio of these conformers in dilute LiBF₄-DMC solution has been estimated to “cis-cis”/“cis-trans” $\approx$ 2/1 from a molecular dynamics (MD) simulation study [4]. More recent MD studies have revealed that the number of DMC molecules in the first solvation shell of Li⁺ is 2.7 [5] and 2.3 [6] in 9.1 and 7 mol% LiPF₆ solutions in DMC, respectively. The number of PF₆⁻ in the first solvation shell of Li⁺ in these solutions is estimated to be 1.7 [5] and 2.1 [6], respectively, which implies Li⁺···PF₆⁻ contact ion pairs are commonly produced. The solvation number of Li⁺ in 1.5 M LiPF₆ solution in EC + DMC mixed solvent was obtained to be 3.9 from recent Raman spectroscopic study [7], suggesting tetrahedral coordination of Li⁺ in the carbonate solution. On the other hand, much larger number of DMC molecules (8.19) associated with Li⁺ in 1.0 M LiPF₆ solution in DMC was reported from ¹⁷O NMR chemical shift of carbonyl oxygen atom within DMC molecule [8]. In order to determine the solvation number of Li⁺ in the solution, neutron diffraction with ⁶Li/⁷Li isotopic substitution method is one of the most effective experimental techniques to obtain direct information on the solvation structure of Li⁺. The ⁶Li/⁷Li isotopic substitution method was first applied for investigation of the hydration shell of Li⁺ in aqueous solutions [9-13]. This method was then adopted for non-aqueous systems. Environmental structure around Li⁺ in highly concentrated methanolic LiBr and LiI solutions has been reported [14]. Solvation structure of LiBr in concentrated acetone solution has been revealed that the first solvation shell of Li⁺ involves, on the average, ca. three carbonyl oxygen atoms of acetone molecules and ca. one Br⁻ with interatomic distances of $r_{\text{LiO}} = 2.24 \pm 0.02$ Å and $r_{\text{LiBr}} = 2.86 \pm 0.02$ Å, respectively [15]. More recently, the ⁶Li/⁷Li substitution method has been applied to investigate solvation structure of Li⁺ in concentrated propylene carbonate (PC) solution [16]. The first solvation shell of Li⁺ in the 10 mol% LiPF₆ – PC solution involves 4.5 ± 0.1 carbonyl oxygen atoms of PC molecules with interatomic distance of $r_{\text{LiO}} = 2.04 \pm 0.01$ Å. It has been found that no PF₆⁻ is involved in the first solvation shell of Li⁺ [16]. A special attention is now emerged to the solvation structure of Li⁺ in the linear carbonate such as dimethyl carbonate, since an addition of DMC to the PC solution makes more favorable physical properties (lower melting point, lower viscosity, etc.) of the electrolyte solution. However, structural properties concerning the local structure of Li⁺ in the linear carbonate solvent has not yet been obtained experimentally.

In the present paper, we describe the results of neutron diffraction experiments on concentrated 9.6 mol% LiPF₆ solutions in DMC. Detailed structural properties of the first solvation shell of Li⁺ was derived from the least squares fitting analysis of observed difference function obtained from the difference between scattering cross sections for the solutions with different ⁶Li/⁷Li compositions. DMC solvation number around the Li⁺ in LiClO₄ –DMC solution was also evaluated by Raman spectra to ensure neutron structure analysis. Subsequently, DFT calculations were performed to yield further insight into the Li⁺ solvation by DMC.

2. Materials and methods

2.1. Materials

^6Li -enriched $^6\text{Li}_2\text{CO}_3$ (95.6% ^6Li , Tomiyama Chemical Co. Ltd.) and natural $^{\text{nat}}\text{Li}_2\text{CO}_3$ (92.5% ^7Li , natural abundance) were respectively converted to $^6\text{LiCl}$ and $^{\text{nat}}\text{LiCl}$ by reacting with HCl in the aqueous solution. The product solution was dried under vacuum to obtain anhydrous $^*\text{LiCl}$ ($^*\text{Li}$: ^6Li , $^{\text{nat}}\text{Li}$). Enriched $^*\text{LiCl}$ was reacted with AgPF_6 in acetonitrile solution. After filtering precipitated AgCl , the filtrate was evaporated to dryness under reduced pressure to obtain anhydrous $^*\text{LiPF}_6$.

Required amounts of enriched $^*\text{LiPF}_6$ was dissolved into fully deuterated dimethyl carbonate ($\text{DMC-}d_6$, 99% D, CIL Inc.) to prepare 9.6 mol% $^*\text{LiPF}_6$ solutions in $\text{DMC-}d_6$. Density of sample was measured by a vibration tube densimeter (Kyoto Electronic, DA-310) at 25°C. Sample solutions were sealed into cylindrical fused quartz cell with inner diameter of 12 mm and 1.0 mm in wall thickness. The sample parameters are listed in Table 1.

2.2. Neutron diffraction measurements

Neutron diffraction measurements were carried out at 25 °C using the ISSP diffractometer 4G (GPTAS) installed at the JRR-3M research reactor operated at 20 MW in the Japan Atomic Energy Agency (JAEA), Tokai, Japan. The incident neutron wavelength $\lambda = 1.281(3)$ Å, was determined by Bragg reflections from KCl powder. Beam collimations were 40'-80'-80' going from the reactor to the detector. The aperture of the collimated beam was 20 mm in width and 40 mm in height. Scattered neutrons were collected over the angular range of $3.0 \leq 2\theta \leq 118.0^\circ$, corresponding to $0.26 \leq Q \leq 8.41$ Å $^{-1}$ ($Q = 4\pi\sin\theta/\lambda$). Angular step intervals were chosen to be $\Delta 2\theta = 0.5^\circ$ in the range of $3.0 \leq 2\theta \leq 40.0^\circ$ and $\Delta 2\theta = 1.0^\circ$ in the range of $41.0 \leq 2\theta \leq 118.0^\circ$, respectively. The preset times were 220 s and 140 s for $^6\text{LiPF}_6$ and $^{\text{nat}}\text{LiPF}_6$ solutions, respectively. Scattering measurements were carried out for the vanadium rod (10 mm in diameter), empty cell, and instrumental background.

2.3. Data reduction

Observed scattering intensities from the sample solutions were corrected for instrumental background, absorption [17], and multiple scattering [18]. The observed count rate for sample solution was converted to the absolute scale by the use of corrected scattering intensities from the vanadium rod. Details of data correction and normalization procedures are given elsewhere [19, 20].

The first-order difference function [21-23], $\Delta_{\text{Li}}(Q)$, was obtained as the numerical difference in normalized scattering cross sections for sample solutions with different $^6\text{Li}/^7\text{Li}$ ratio. Difference function scaled at the stoichiometric unit, $(^*\text{LiPF}_6)_x(\text{DMC-}d_6)_{1-x}$, is expressed as the weighted sum of six partial structure factors relating Li atom.

$$\begin{aligned}\Delta_{\text{Li}}(Q) &= (d\sigma/d\Omega)(\text{for } ^6\text{Li sample}) - (d\sigma/d\Omega)(\text{for } ^{\text{nat}}\text{Li sample}) \\ &= A[a_{\text{LiO}}(Q) - 1] + B[a_{\text{LiD}}(Q) - 1] + C[a_{\text{LiC}}(Q) - 1] + D[a_{\text{LiP}}(Q) - 1] \\ &\quad + E[a_{\text{LiF}}(Q) - 1] + F[a_{\text{LiLi}}(Q) - 1],\end{aligned}\tag{1}$$

where, $A = 6x(1-x)(b_{6\text{Li}} - b_{\text{natLi}})b_{\text{O}}$, $B = 12x(1-x)(b_{6\text{Li}} - b_{\text{natLi}})b_{\text{D}}$, $C = 6x(1-x)(b_{6\text{Li}} - b_{\text{natLi}})b_{\text{C}}$, $D = 2x^2(b_{6\text{Li}} - b_{\text{natLi}})b_{\text{P}}$, $E = 12x^2(b_{6\text{Li}} - b_{\text{natLi}})b_{\text{F}}$, and $F = x^2(b_{6\text{Li}}^2 - b_{\text{natLi}}^2)$. The distribution function around the Li^+ , $G_{\text{Li}}(r)$, was obtained by the Fourier transform of observed $\Delta_{\text{Li}}(Q)$,

$$G_{\text{Li}}(r) = 1 + (A + B + C + D + E + F)^{-1} (2\pi^2 \rho r)^{-1} \int_0^{Q_{\text{max}}} Q \Delta_{\text{Li}}(Q) \sin(Qr) dQ$$

$$= [A g_{\text{LiO}}(r) + B g_{\text{LiD}}(r) + C g_{\text{LiC}}(r) + D g_{\text{LiP}}(r) + E g_{\text{LiF}}(r) + F g_{\text{LiLi}}(r)] \times (A + B + C + D + E + F)^{-1}. \quad (2)$$

The upper limit of the integral, Q_{max} , was set to be $8.41 \text{ \AA}^{-1}$.

Intermolecular parameters concerning the nearest neighbor $\text{Li}^+ \cdots \text{DMC}$ and $\text{Li}^+ \cdots \text{PF}_6^-$ interactions were determined through the least squares fitting for observed $\Delta_{\text{Li}}(Q)$, employing the model function $\Delta_{\text{Li}}^{\text{model}}(Q)$, involving both the short- and long-range contributions [24-26].

$$\Delta_{\text{Li}}^{\text{model}}(Q) = \sum 2x n_{\text{Li}\alpha} (b_{6\text{Li}} - b_{\text{natLi}}) b_{\alpha} \exp(-l_{\text{Li}\alpha}^2 Q^2 / 2) \sin(Qr_{\text{Li}\alpha}) / (Qr_{\text{Li}\alpha}) + 4\pi\rho (A + B + C + D + E + F) \exp(-l_0^2 Q^2 / 2) [Qr_0 \cos(Qr_0) - \sin(Qr_0)] Q^{-3}. \quad (3)$$

where, $n_{\text{Li}\alpha}$ denotes the coordination number of α atom around Li^+ . Parameters, $l_{\text{Li}\alpha}$ and $r_{\text{Li}\alpha}$, are the root-mean-square displacement and internuclear distance for $\text{Li}^+ \cdots \alpha$ pair, respectively. The long-range parameter, r_0 , corresponds the distance beyond which a continuous distribution of atoms around Li^+ can be assumed. The parameter, l_0 , describes the sharpness of the boundary at r_0 . Structural parameters, $n_{\text{Li}\alpha}$, $l_{\text{Li}\alpha}$, $r_{\text{Li}\alpha}$, l_0 and r_0 are respectively determined from the least squares fit to the observed $\Delta_{\text{Li}}(Q)$. The fitting procedure was performed in the range of $0.26 \leq Q \leq 8.41 \text{ \AA}^{-1}$ with the SALS program [27], assuming that the statistical uncertainties distribute uniformly. In the present analysis, interatomic distances within DMC molecule was fixed to those reported from gas phase electron diffraction study [28]. The geometry of PF_6^- was assumed to be octahedral, with the average P-F distance of $1.597 \text{ \AA}$ [29].

2.4. Raman sample preparation and measurement.

For Raman spectra measurements, LiClO_4 salt was prepared by treating Li_2CO_3 with HClO_4 in an aqueous solution, followed by repeated evaporation to remove HClO_4 and solvent H_2O . Residual HClO_4 was checked to be negligible by a pH measurement. Thus obtained LiCO_4 salt was dried at $200 \text{ }^\circ\text{C}$ in a glass tube vacuum oven during a few days. DMC was stored with a molecular sieve 3A during several weeks to reduce water content. Samples solutions were prepared in the glove box of an Ar gas atmosphere with a water content kept less than 1 ppm. Finally, water content of thus prepared sample solutions were checked by the Karl Fischer titration. Raman spectra were measured by using a JASCO NR-1100 Raman spectrometer with the optical resolution of 2.5 cm^{-1} .

3. Results and discussion

Observed scattering cross sections for $(^6\text{LiPF}_6)_{0.096}(\text{DMC-}d_6)_{0.904}$ and $(^{\text{nat}}\text{LiPF}_6)_{0.096}(\text{DMC-}d_6)_{0.904}$ are shown in Fig. 1. Although the overall feature of observed scattering cross section for each solution looks very similar, however, the difference in the scattering intensity in the range of $1 \leq Q \leq 2 \text{ \AA}^{-1}$ can be identified. The difference function $\Delta_{\text{Li}}(Q)$ was successfully obtained by taking numerical difference between those scattering cross sections as indicated in Fig. 1. The difference function, $\Delta_{\text{Li}}(Q)$, observed for 9.6 mol% $\text{LiPF}_6 - \text{DMC}$ solution is shown in Fig. 2. Diffraction peak located at $Q \approx 1.8 \text{ \AA}^{-1}$ is obviously identified. The oscillational feature of $\Delta_{\text{Li}}(Q)$ extends to the higher- Q region. The observed distribution function around Li^+ , $G_{\text{Li}}(r)$, is represented in Fig. 3. Although resolution in r -space is not so high due to relatively small value of Q_{max} employed in the Fourier transform, a dominant first peak at $r \approx 2 \text{ \AA}$ and the second peak appearing at $r \approx 4 \text{ \AA}$ in the present $G_{\text{Li}}(r)$, clearly indicate the existence of well-defined solvation shell around the Li^+ . The first peak is attributable to the nearest neighbor $\text{Li}^+ \cdots \text{O}(\text{DMC})$ and/or $\text{Li}^+ \cdots \text{F}(\text{PF}_6^-)$ interactions from the electrostatic point of view. Since coherent neutron scattering lengths of oxygen ($b_{\text{O}} = 0.5803 \times 10^{-12} \text{ cm}$ [30]) and that of fluorine ($b_{\text{F}} = 0.5654 \times 10^{-12} \text{ cm}$ [30]) atoms are very close, the average coordination number of Li^+ was estimated to be ca. 4 from integration of the first peak of the observed $G_{\text{Li}}(r)$, indicating that Li^+ takes four fold coordination. The second peak appearing at $r \approx 4 \text{ \AA}$ is considered to involve contributions from C, D, (and O) atoms of DMC molecule and F and P atoms of PF_6^- .

Structural parameters concerning the first solvation shell of Li^+ were determined through the least-squares fitting procedure for the observed $\Delta_{\text{Li}}(Q)$, employing the model function which is described in Eq. (3). The fitting was performed in the range of $0.24 \leq Q \leq 8.41 \text{ \AA}^{-1}$ with the SALS program [27]. In the least squares fitting calculation, the Marquardt method was employed. The dynamical bi-weight method was used for weight adjustment of the observed data [27]. Prior to the fitting analysis, correction of the low-frequency systematic errors involved in the $\Delta_{\text{Li}}(Q)$ was adopted [31].

The model function, $\Delta_{\text{Li}}^{\text{model}}(Q)$, in Eq. (3), was evaluated on the basis of the following assumptions. (a) For the nearest neighbor $\text{Li}^+ \cdots \text{DMC}$ interaction, structural parameters, r_{LiO} , l_{LiO} , n_{LiO} , the bond angle α ($\angle \text{Li}^+ \cdots \text{O}=\text{C}$), and the dihedral angle β between the plane involving atoms, $\text{Li}^+ \cdots \text{O}=\text{C}$ and the plane involving $\text{O}=\text{CO}_2$ atoms within the DMC molecule were treated as independent parameters. The internuclear distances and bond angles in the DMC molecule were fixed to those determined from gas phase electron diffraction study [28]. In the preliminary analysis, it was found that the observed difference function can well be reproduced by assuming two different molecular conformations (cis-cis and cis-trans) of the DMC molecules in the first coordination shell of Li^+ , which has been predicted by the previous molecular dynamics (MD) simulation study [4]. Raman and IR studies by Doucey et al. have indicated that DMC molecules in the first solvation shell take both “cis-cis” and “cis-trans” conformers [3]. Then, molecular conformation of the DMC

molecules in the first solvation shell of Li^+ was assumed to take both “cis-cis” and “cis-trans” forms in the present analysis. The $\text{Li}^+\cdots\text{O}(\text{DMC}_{\text{cis-cis}})$ and $\text{Li}^+\cdots\text{O}(\text{DMC}_{\text{cis-trans}})$ coordination numbers were allowed to vary independently. (b) Structural parameters for the nearest neighbor $\text{Li}^+\cdots\text{PF}_6^-$ interaction, r_{LiF} , l_{LiF} , n_{LiF} , the bond angle γ ($\text{Li}^+\cdots\text{F-P}$), and the dihedral angle ϕ between plane involving $\text{Li}^+\cdots\text{F-P}$ atoms and the plane involving F-PF_3 atoms within the PF_6^- were refined independently. The molecular geometry of PF_6^- was fixed to those determined from single crystal X-ray diffraction study [29]. The first peak observed in the present $G_{\text{Li}}(r)$ function may involve both the nearest neighbor $\text{Li}^+\cdots\text{O}(\text{DMC})$ and $\text{Li}^+\cdots\text{F}(\text{PF}_6^-)$ interactions, initial value of r_{LiF} in the present analysis was set to be 2.0 Å. Values of r_{LiO} and r_{LiF} might be very close, however, the non-bonded interatomic interactions between Li^+ and P and F atoms within the PF_6^- , which is calculated from the values r_{LiF} , γ and ϕ certainly contribute to the model function in longer- r region used in the fitting procedure. (c) The second and the third solvation shell of Li^+ were also taken into account in order to improve the fit of the model function in the low- Q region. Each interaction was treated as a single interaction with the coherent scattering length b_a in Eq. (3) being the sum of scattering lengths of atoms involved in a DMC molecule ($= 3b_{\text{C}}+3b_{\text{O}}+6b_{\text{D}}$). A satisfactory agreement was obtained between observed and calculated $\Delta_{\text{Li}}(Q)$ in the whole Q -range as shown in Fig. 2. The Fourier transform of the calculated $\Delta_{\text{Li}}(Q)$ was also in good agreement with observed $G_{\text{Li}}(r)$ as depicted in Fig. 3. Final values of all independent parameters are summarized in Table 2. A possible average local structure around Li^+ adopting the determined structural parameters is depicted in Fig. 4 in the space filling model employing the van der Waals atomic radii for O, C, H, F, and P atoms and the ionic radius for Li^+ . A tetrahedral coordination around Li^+ is assumed.

The nearest neighbor $\text{Li}^+\cdots\text{O}(\text{DMC})$ distance is determined to be 2.08 ± 0.02 Å, which is ca. 0.1 Å longer than values 1.95 ~ 1.97 Å found in various aqueous [9-13] and methanolic solutions [14] of Li-salts. The present value of r_{LiO} is very close to those observed for concentrated polyethylene oxide solutions with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (2.10 ± 0.04 Å) [32], LiClO_4 (2.07 ± 0.04 Å) [33] and LiI (2.1 Å) [34] salts in which Li^+ interacts with ether oxygen atoms of polyethylene oxide. The present $\text{Li}^+\cdots\text{O}(\text{DMC})$ distance is slightly longer than that found in 10 mol% LiPF_6 solutions in PC (2.04 ± 0.01 Å) [16] in which Li^+ interacts with carboxyl oxygen atom of PC molecule. This difference in the $\text{Li}^+\cdots\text{O}$ distance between the DMC and PC solutions may be attributable to the $\text{Li}^+\cdots\text{PF}_6^-$ contact ion pair formation occurring in the present DMC solution. On the other hand, the present $\text{Li}^+\cdots\text{O}(\text{DMC})$ distance is 0.16 Å shorter than the value, $r_{\text{LiO}} = 2.24 \pm 0.02$ Å, reported for the nearest neighbor $\text{Li}^+\cdots\text{O}(\text{acetone})$ interaction in concentrated acetone solutions [15] in which carbonyl oxygen atom of acetone molecule interacts with Li^+ . The longer value of r_{LiO} in concentrated acetone solution can be due to steric hindrance between methyl groups of acetone molecules within the first solvation shell of Li^+ , as well as the contact ion pair formation of Li^+ with bulky Br^- .

The first solvation shell of Li^+ in the present solution consists of, on the average, 2.8 DMC molecules and 1.1 PF_6^- , indicating four-fold coordination of Li^+ . In the first coordination shell of Li^+ , 1.7 of DMC molecules exist as the cis-cis conformer, while 1.1 DMC is in the cis-trans form. The

ratio of the number of DMC(cis-cis) and DMC(cis-trans) molecules in the first solvation shell of Li^+ ($= 1.7:1.1$) agrees well with the ratio 2:1 suggested from the previous MD result [4].

Recorded Raman spectra for LiClO_4 DMC solutions were shown in Fig. 5. Neat DMC has 8 Raman bands in this range; i.e., 519, 694, 800, 920 and 975 cm^{-1} for cis-cis DMC and 585, 640 and 860 cm^{-1} for cis-trans DMC, respectively. [35] By adding LiClO_4 salt, new Raman bands except those come from the ClO_4^- were observed at the higher frequency regions of Raman bands at 519, 585 and 860 cm^{-1} , which clearly indicates that newly appeared Raman bands at 525, 586 and 873 cm^{-1} can be ascribed to DMC molecules solvated to the Li^+ . As increasing the salt concentration, Raman bands that come from bulk DMC decreased in intensity, whilst those from DMC solvated to the Li^+ intensified, respectively. As aforementioned, population of the cis-trans DMC solvated to Li^+ increases relative to that in neat DMC. [3] We also observed the cis-trans isomer condensation around the Li^+ in DMC; i.e., the increase in intensity of the Raman band at 586 cm^{-1} from the cis-trans DMC was much larger than that of the Raman band at 525 cm^{-1} from cis-cis one as increasing the salt concentration. Since newly appeared Raman band at 934 cm^{-1} was seriously overlapped with the Raman band originated from ClO_4^- , we attempted to evaluate DMC solvation number to Li^+ by using a Raman band at 519 cm^{-1} . Raman band intensity from free DMC in the LiClO_4 DMC solutions I_f can be written as a function of ratio of the total DMC to the salt in solution R as

$$I_f / m = J_f(R - n) \quad (4),$$

where J_f , m and n stand for the Raman scattering coefficient of free DMC, LiClO_4 molality m and DMC solvation number to Li^+ respectively. Hence, the linear least-square slope a and intercept b yield n based on a simple relationship of $n = b/a$. As shown in Fig. 6, the plots fall on the good straight line to yield $n = 2.8$ (2). Although investigated salts are different, both DMC solvation numbers obtained in this study is similar with each other.

To obtain further insight into Li^+ solvation, DFT calculations performed at the B3LYP/6-311+(d,p) level of theory for the stepwise solvation of H_2O , PC, cis-cis DMC and cis-trans DMC in a gas phase as shown in Fig. 7. For $n = 1$, the order of stability in Gibbs free energy was $\text{PC} > \text{cis-trans DMC} > \text{cis-cis DMC} > \text{H}_2\text{O}$, which suggests that steric repulsion among the solvated molecules is rejected the essential reason why the cis-trans DMC condensation in the first Li^+ solvation shell. As increasing n , ΔG monotonically decreased (became more negative) up to $n = 3$ for all of solvents examined here. In the case of H_2O and PC, ΔG increased toward larger n via a minim at $n = 4$. On the other hand, ΔG for $n = 3$ and 4 are similar for both cis-cis and cis-trans DMC. Please note that from $n = 3$ to 4 ΔG for cis-cis DMC becomes positive, whilst that for cis-trans DMC varied more negative. It implied that steric repulsion might be significant when 4 cis-cis DMC molecules solvates to Li^+ . Preference of cis-trans DMC to cis-cis one at the neighboring Li (the difference between $\Delta G(\text{cis-trans DMC})$ and $\Delta G(\text{cis-cis DMC})$) became larger as the increase of n , suggesting

that the charge–dipole interaction contributes to the cis-trans preference due to the larger dipole moment for cis-trans DMC than that for the other. Estimated dipole moments are 0.04 and 3.80 D for cis-cis and cis-trans DMC, respectively, based on the ESP charge derived from the DFT calculations. Therefore, it is deduced that the cis-trans conformer condensation in the first Li^+ solvation shell observed in neutron and Raman experiments could be ascribed to the larger charge–dipole interaction between Li^+ and cis-trans DMC.

4. Conclusion

Neutron diffraction measurements were carried out on isotopically substituted 9.6 mol% $^*\text{LiPF}_6\text{-DMC-}d_6$ solutions. Observed first-order difference function $\Delta_{\text{Li}}(Q)$ was analyzed in term of short range local structure of Li^+ by the use of least squares fitting procedures. The first solvation shell of Li^+ consists of 2.8 DMC molecules and 1.1 PF_6^- with interatomic distances of 2.08 ± 0.02 and 2.03 ± 0.06 Å, respectively, indicating that tetrahedral coordination of Li^+ and $\text{Li}^+\cdots\text{PF}_6^-$ contact ion pairs are extensively formed in the present solution. DMC molecules in the first solvation shell of Li^+ take both “cis-cis” and “cis-trans” conformations. DMC solvation number to Li^+ evaluated by Raman spectroscopy agrees well with neutron structure analysis. Existence of cis-trans DMC in the first Li^+ solvation shell was observed by both neutron and Raman experiments. On the basis of DFT calculations, it is deduced that larger charge–dipole interaction mainly contributes to the stability of cis-trans isomer at the closest neighbor of Li^+ .

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Figure Captions

Fig. 1 Scattering cross section, $(d\sigma/d\Omega)$, observed for 9.6mol% $^6\text{LiPF}_6$ and $^{\text{nat}}\text{LiPF}_6$ solutions in DMC- d_6 . Observed first-order difference function, $\Delta_{\text{Li}}(Q)$, is shown below.

Fig. 2 (a) $\Delta_{\text{Li}}(Q)$ observed for 9.6 mol% LiPF_6 solutions in DMC- d_6 (dots), and the best-fit of the calculated $\Delta_{\text{Li}}^{\text{model}}(Q)$ (solid line). (b) Residual function (dots).

Fig. 3 Distribution function, $G_{\text{Li}}(r)$, observed for 9.6 mol% LiPF_6 solutions in DMC- d_6 (thick solid line). Fourier transform of the calculated $\Delta_{\text{Li}}^{\text{model}}(Q)$ is shown by a thin solid line. The short-range $\text{Li}^+\cdots\text{DMC}(\text{cis-cis})$ and $\text{Li}^+\cdots\text{DMC}(\text{cis-trans})$ contributions are denoted by dotted and dashed-dot lines, respectively. Contributions from $\text{Li}^+\cdots\text{PF}_6^-$, the second and third nearest neighbor $\text{Li}^+\cdots\text{DMC}$ interactions are indicated by broken lines.

Fig. 4 Possible local structure around Li^+ in 9.6 mol% LiPF_6 solutions in DMC- d_6 (Li: yellow, H: white, C: black, O: red, F: green, P: purple).

Fig. 5 Raman spectra for LiCO_4 DMC solutions at the frequency range .of (a) $480 - 720 \text{ cm}^{-1}$ and (b) $840 - 1000 \text{ cm}^{-1}$, respectively.

Fig. 6 I_f vs. R plots for evaluation of DMC solvation number to Li^+ .

Fig. 7 Gibbs free energy change for the stepwise solvation reaction $\text{Li}(\text{solvent})_{n-1} + \text{solvent} \rightarrow \text{Li}(\text{solvent})_n$ of H_2O , PC, cis-cis DMC and cis-trans DMC.

Table 1

Isotopic composition, average scattering length, b_{Li} , of lithium ion, total cross section, and number density of samples in the stoichiometric unit $(^*\text{LiPF}_6)_{0.096}(\text{DMC-}d_6)_{0.904}$, σ_t and ρ , respectively.

Sample	$^6\text{Li}/\%$	$^7\text{Li}/\%$	$b_{\text{Li}}/10^{-12}\text{cm}$	σ_t/barns^a	$\rho/\text{\AA}^{-3}$
$(^6\text{LiPF}_6)_{0.096}(\text{DMC-}d_6)_{0.904}$	95.6	4.4	0.182	116.866	0.007942
$(^{\text{nat}}\text{LiPF}_6)_{0.096}(\text{DMC-}d_6)_{0.904}$	7.5	92.5	-0.190	60.311	

^a For incident neutron wavelength of 1.281 Å.

Table 2

Results of the least squares fitting analysis of $\Delta_{\text{Li}}(Q)$ observed for 9.6 mol% LiPF_6 -DMC- d_6 solutions.^a

Interaction	$i \cdots j$	$r_{ij}/\text{\AA}$	$l_{ij}/\text{\AA}$	n_{ij}
$\text{Li}^+ \cdots \text{DMC}(\text{cis-cis} \ \& \ \text{cis-trans})$	$\text{Li}^+ \cdots \text{O}$	2.08(2)	0.259(6)	
$\text{Li}^+ \cdots \text{DMC}(\text{cis-cis})$	$\alpha = 153(22)^\circ$ ^b	$\beta = 14(20)^\circ$ ^c		1.7(2)
$\text{Li}^+ \cdots \text{DMC}(\text{cis-trans})$	$\alpha = 92(2)^\circ$	$\beta = 26(3)^\circ$		1.14(2)
$\text{Li}^+ \cdots \text{PF}_6^-$	$\text{Li}^+ \cdots \text{F}$	2.03(6)	0.2(1)	
	$\gamma = 164(7)^\circ$ ^d	$\phi = 61(30)^\circ$ ^e		1.07(4)
$\text{Li}^+ \cdots \text{DMC}(\text{II})$	$\text{Li}^+ \cdots \text{DMC}$	4.98(7)	0.65(3)	3.6(5)
$\text{Li}^+ \cdots \text{DMC}(\text{III})$	$\text{Li}^+ \cdots \text{DMC}$	6.92(3)	0.74(2)	7.18(8)
		$r_0/\text{\AA}$	$l_0/\text{\AA}$	
Long-range		7.58 (2)	0.38(2)	

^a Standard deviations are given in parentheses. ^b Bond angle $\angle \text{Li}^+ \cdots \text{O}=\text{C}$. ^c Dihedral angle between a plane involving atoms $\text{Li}^+ \cdots \text{O}=\text{C}$ and molecular plane of DMC molecule. ^d Bond angle $\angle \text{Li}^+ \cdots \text{F}-\text{P}$.

^e Dihedral angle between a plane involving atoms $\text{Li}^+ \cdots \text{F}-\text{P}$ and the plane formed by atoms $\text{F}-\text{PF}_3$.

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