Solvation and Ion Association Studies of LiBF₄−Propylenecarbonate and LiBF₄−Propylenecarbonate−Trimethyl Phosphate Solutions

Hajime Tsunekawa,[†] **Akiko Narumi,**[†] **Mitsuru Sano,**[*,†] **Akio Hiwara,**[‡] **Miho Fujita,**[§] **and Haruhiko Yokoyama**[⊥]

Graduate School of Human Informatics, Nagoya University, Nagoya 464-8601, Japan, Electronics & Information Materials Laboratory, Mitsui Chemical, Sodegaura 299-0265, Japan, Graduate School of Natural Sciences, Nagoya City University, Nagoya 467-8501, Japan, and Department of Chemistry, Yokohama City University, Yokohama 236-0027, Japan

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Concentrated LiBF₄ solutions in propylenecarbonate (PC) or PC−trimethyl phosphate (TMP) were studied regarding the ion-association and solvation of Li⁺ ions in each solution from the measurements of conductivities, viscosities, Raman spectra, and diffusion coefficients by field gradient NMR spectroscopies. From the Walden product evaluated, the dissociation degree of LiBF₄ in the LiBF₄−PC solution was roughly deduced to be about 30% in concentrations over 1 mol dm⁻³. About 1.8 PC molecules were found bound strongly to a Li⁺ ion in the LiBF₄−PC solution, and this number was smaller than 3 for LiPF₆ in PC solutions. The small solvation number could be evidence of the formation of contact ion-pairs of Li⁺−BF₄⁻. The diffusion coefficients of BF₄⁻ came closer to those of Li⁺ ions as concentrations increased, and this is also in accordance with the assumption that the contact ion-pairs are formed. In LiBF₄−PC−TMP solutions, about 50% of LiBF₄ dissociates at 1 mol dm⁻³. TMP as a Lewis base is expected to suppress the contact ion-pairs of Li⁺−BF₄⁻ and to improve the conductivity.

Introduction

Li-ion batteries have been widely used in portable electronic devices such as cellular phones, camcorders, and laptop computers because of their relatively high specific energy density and power density. Most manufacturers use LiPF₆ as an electrolyte in Li-ion batteries. However, the obvious drawbacks of LiPF₆ are its thermal instability and moisture sensitivity. It is necessary to replace LiPF₆ with more stable lithium salts as electrolytes in Li-ion batteries. Among lithium salts commercially available, LiBF₄ is known as a qualified salt to provide a comparable and proper electrolyte solution in terms of its chemical and thermal stability.[1] However, LiBF₄ has not been used practically for Li-ion batteries because its electrolyte solution has a low ionic conductivity.[2]

As early as the mid-1980s, Matsuda et al. have studied conductivities of LiBF₄ in ether solutions for secondary lithium batteries.[3] Ue has also studied conductivities of a couple of salt solutions, and estimated the limiting molar conductivity and the ion-association constant for each salt.[4] However, no studies through such molecular-based approaches as Raman and NMR spectroscopic methods have been published on the solvation and ion-association of LiBF₄ in nonaqueous solutions. Molecular information about ion-solvations and ion-associations will be useful for understanding solvations of the ions and improving ionic conductivities from molecularscopic viewpoints. If ionic conductivities are improved by the control of ion-associations, it would surely be good progress toward electrolyte solutions for Li-ion batteries.

In the present work, we studied the solvation and ion-association in rather concentrated LiBF₄−propylenecarbonate (PC) solutions mainly using Raman and NMR spectroscopies and also report an improvement of ion conductivity in solution by the addition of trimethyl phosphate as a Lewis base.

Experimental Section

Materials. Commercially available propylenecarbonate (PC) and trimethyl phosphate (TMP) were refined by fine distillation before use. Lithium tetrafluoroborate used as an electrolyte salt was obtained from Tomiyama Chemical Co.: special grade for electrochemical use, certified to contain more than 99.9% LiBF₄, less than 10 ppm of water, and less than 50 ppm of HF as impurity. All the electrolyte solutions were prepared in a glovebox in an atmosphere of dry nitrogen gas (with a dry point below −50 °C).

Instrumentation. The pulse gradient NMR measurements were made with a JEOL α-400 NMR spectrometer. The spectrometer was equipped with an apparatus producing a field gradient in the range 0.6−1.0 T m⁻¹. The gradient strength was calibrated and cross-checked by using the self-diffusion coefficient of 2.23×10^{-9} m² s⁻¹ known for H₂O at 25 °C.[5] The simple spin−echo pulse sequence was applied to the diffusion measurements, and the free diffusion echo signal attenuation, E, was related to experimental parameters by the following equation:[6]

$$\ln(E) = \ln(S/S_{g=0}) = -\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)$$

where S, δ, g, Δ, and γ are the spin−echo signal intensity, the duration of the field gradient with magnitude, the magnitude of the field gradient, the interval between the two gradient pulses, and the gyromagnetic ratio, respectively. The temperature
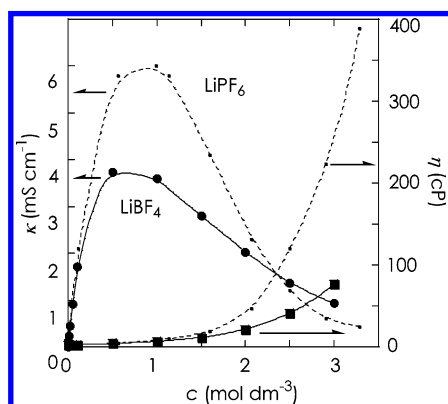

[†] Nagoya University.
[‡] Mitsui Chemical.
[§] Nagoya City University.
[⊥] Yokohama City University.

TABLE 1: Conductivities, Viscosities, and Other Parameters of LiBF$_4$−PC at 25 °C

LiBF$_4$ concn (c)/ mol dm^{-3} (PC/Li$^+$ molar ratio)	conductivity (κ)/mS cm^{-1}	molar conductivity (Λ)/S cm^2 mol^{-1}	viscosity (η)/cP^a	Walden product ($\Lambda\eta$)/ S cm^2 mol^{-1} cP	diffusion coeff (D)/10^{-10} m^2 s^{-1}		
					^{7}Li	^{19}F	^{1}H of PC
0.0		(27.3)	2.45	(66.9)			5.2
0.0001	0.0027	27	2.44	65.9			
0.001	0.0266	26.6	2.42	64.4			5.0
0.01 (1174)	0.236	23.6	2.49	58.8			5.0
0.1 (118)	1.72	17.2	2.75	47.3	2.2	4.2	4.7
0.5 (23.0)	3.74	7.48	4.05	30.3	1.2	3.1	2.2
1.0 (11.2)	3.59	3.59	6.57	23.6	.85	1.2	1.7
1.5 (7.38)	2.80	1.87	11.5	21.5	0.49	0.54	1.1
2.0 (5.40)	2.03	0.37	21.5	21.8	0.35	0.27	0.80
2.5 (4.18)	1.37	0.16	41.3	22.6	0.14	0.15	0.62
3.0 (3.39)	0.93	0.31	76.8	23.8	0.13	0.10	0.57

^{a} 1 cP = 1 mPa.

Figure 1. Conductivity (κ) and viscosity (η) of PC solutions as a function of salt concentration.

was controlled at 25.0 ± 0.5 °C with a JEOL GVT2 temperature-control unit. The accuracy of the diffusion coefficients measured is estimated at better than ±5%. Wilmad Roto Tite Valve NMR tubes were used for all the measurements.

FT-Raman spectra were recorded on a Perkin-Elmer 2000R spectrometer equipped with a quartz beam splitter and an InGaAs detector. A 1064-nm line of a Spectron Laser System SL300 Nd:YAG laser was used as the exciting source with an output power of about 200 mW at a sample position and scattered light was collected in a 180° configuration. All spectra were accumulated for 60 scans at a 4-cm^{-1} resolution with samples kept in NMR tubes with outside diameters of 5 mm. Conductivity measurements were carried out at 25.0 ± 0.1 °C with a Toa Denpa Industries CM-40S conductivity meter at 3000 Hz. Viscosity measurements were done with a Tokyo Instrument VISCONIC-ELD viscosity meter at 25.0 ± 0.1 °C.

Molecular Orbital Calculation. The Gaussian 98 Program of the Gaussian Co. with B3LYP and 6-31G* as basis sets was used for the calculations of geometry optimizations for BF$_4$$^-$ and PF$_6$$^-$.

Results and Discussion

Conductivities (κ), viscosity coefficients (η), self-diffusion coefficients (D), and Raman spectra were measured for propylenecarbonate solutions of LiBF$_4$. Table 1 lists the values of κ, η, and D obtained as a function of the concentrations of LiBF$_4$ at 25 °C; the molar ratio of PC/Li$^+$, molar conductivity (Λ), and Walden product ($\Lambda\eta$) are also shown.

Conductivity and Salt Dissociation. Figure 1 shows the conductivities (κ) and viscosities (η) measured for LiBF$_4$ solutions against concentrations (c), and plots for those of LiPF$_6$ solutions are also included in the same graph.[7] The maximum

ionic conductivity (κ_{max}) is estimated as 3.9 mS cm^{-1} at 0.64 M (M = mol dm^{-3}) LiBF$_4$, which is much smaller than the value of 6.1 mS cm^{-1} for LiPF$_6$. Now we will discuss this smaller conductivity for LiBF$_4$ and dissociation degrees, α, of the salt in concentrated solutions. The molar conductivity, Λ, of a 1:1 electrolyte completely dissociating in a dilute solution is expressed as follows:

$$\Lambda = \Lambda^\infty - Sc^{1/2} + Ec\log(c) - J_1c + J_2c^{3/2} \quad (1)$$

where Λ^∞ and c are the limiting molar conductivity and the concentration of salt, respectively. Other parameters are as conventionally defined.[8] Among them, S, E, J_1, and J_2 depend on temperature, dielectric constant, viscosity, and Λ^∞. In addition, J_1 and J_2 also depend on the closest distance between ions. As we have no theoretically defined expessions of Λ in concentrated electrolyte solutions, a practical one for such solutions can be expressed by adding a higher order term, $O(c^2)$, to eq 1, as follows:

$$\Lambda = \Lambda^\infty - Sc^{1/2} + Ec\log(c) - J_1c + J_2c^{3/2} + O(c^2) \quad (2)$$

$$= \Lambda^\infty Q(c) \quad (3)$$

where

$$O(c^2) = O_1c^2 + O_2c^3 + O_3c^4 + \ldots$$

$$Q(c) = 1 - \{Sc^{1/2} - Ec\log(c) + J_1c - J_2c^{3/2} - O(c^2)\}/\Lambda^\infty$$

When viscosities of the solutions vary to a large extent with electrolyte concentrations, eq 3 is further modified with an additional term of the ratio of solvent to solution viscosities (η_0/η), as follows:

$$\Lambda = (\eta_0/\eta)\Lambda^\infty Q(c) \quad (4)$$

$$\Lambda\eta = \Lambda^\infty \eta_0 Q(c) \quad (5)$$

The value of $Q(c)$ is 1.0 at infinite dilution, and it decreases with increasing concentrations due to ionic interactions. When ion-pairs form, eq 5 is deformed as follows:

$$\Lambda\eta = \alpha\eta_0\Lambda^\infty Q(\alpha c) \quad (6)$$

where α is the dissociation degree of the salt in solution. Equation 6 suggests that Λ is dependent mainly on both α and η. In LiPF$_6$−PC solutions, α is almost 1.0, as shown in our previous paper.[7] As the viscosities are roughly the same for
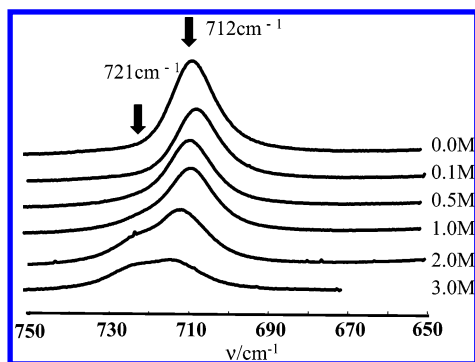
Figure 2. Raman spectra of LiBF$_4$−PC as a function of salt concentration.

both LiBF$_4$ and LiPF$_6$ solutions in concentrations less than 1.0 M, the smaller Λ of LiBF$_4$ would be attributable to a smaller α. The α values in LiBF$_4$ solutions can be estimated on the basis of eq 6 and $\eta_0 = 2.45$ cP, $\Lambda^\infty = 27.3$ S cm^2 mol^{-1}, and $Q(\alpha c) = 1.0$; the values of α are 0.70, 0.56, 0.36, and 0.28 in 0.01, 0.1, 0.5, and 1.0 M concentrations, respectively. In the previous study, $Q(\alpha c)$ was evaluated to be 0.8 at infinite dilution for LiPF$_6$ in PC solutions.[7] From the results, more than 70% of the ions turn out to be ion-pairs in concentrations over 1.0 M, and this results in lowering the conductivity in the solution.

According to the previous paper,[7] the concentration c_{max} at the maximum conductivity κ_{max} is expressed in the following equation when the salt is completely dissociated:

$$1 - Cc_{max}^2 = 0 \qquad (?)$$

where C is a parameter in the expanded Jones−Dole equation to express the viscosity in the solution.[9] The value of c_{max} is deduced to be 1.16 M by using C $= 0.86$ M^{-2}, but it is not coincident with the maximum position $c_{max} = 0.64$ M in Figure 1. Therefore, the maximum conductivity in this solution would be dependent on both the viscosity and salt-dissociation of the solution.

Raman Spectra and Solvation Numbers in Concentrated Solutions. Figure 2 shows Raman spectra of solutions of LiBF$_4$ higher than 1.0 M in the range from 650 to 750 cm^{-1}. These Raman spectra change their shapes and intensities, as LiBF$_4$ concentrations vary, as seen in Figure 2. A signal at 712 cm^{-1} is assigned to one of the ring-deformation bands of free PC molecules in solvent itself or in solutions, and its intensity decreases with an increase of LiBF$_4$ concentration, while on the contrary a signal intensity around 721 cm^{-1} increases. The arising new band centered at 721 cm^{-1} is certainly assigned to that of the ring deformation of PC molecules bound electrostatically to a Li$^+$ ion. These assignments also seem in accordance with those in Battisti et al. [10]

To estimate the ratio of free PC molecules to bound PC ones, the Raman band was taken apart into two components of 712- and 721-cm^{-1} bands by a deconvolution technique, and then their intensities of separated signals (denoted by I_{712} and I_{721}) were normalized compared with the band at 848 cm^{-1} attributable to the vibration of a methyl group of PC molecules and negligibly dependent on the salt concentration. The normalized values of I_{712} and I_{721}, and their sum of $I_{712} + I_{721}$, are summarized in Table 2. The values of I_{712} from free PC molecules decrease with increasing LiBF$_4$ concentrations, while those of I_{721}, due to the bound PC molecules, increase with the concentrations. The sum of I_{712} and I_{721} remains nearly constant over the whole range of concentration change.
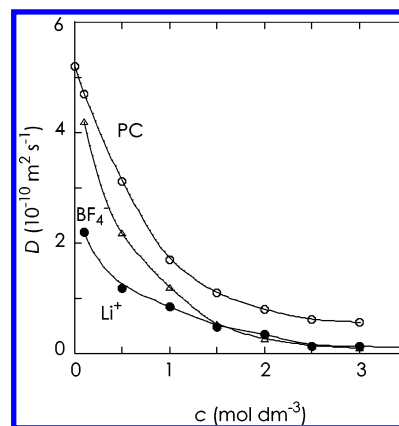

Figure 3. Diffusion coefficients (D) of ^{7}Li, ^{19}F, and ^{1}H of LiBF$_4$−PC as a function of salt concentration.

TABLE 2: Raman Data in LiBF$_4$−PC at 25 °C

LiBF$_4$ concn (c)/ mol dm^{-3}	Li$^+$:PC molar ratio	normalized Raman amplitude			no. of PC molecules bound to Li$^+$ ions
		I_{712}	I_{721}	$I_{712} + I_{721}$	
0		0.63	0.0	0.63	
1.0	1:11.2	0.56	0.07 ± 0.02	0.63	1.2 ± 0.2
1.5	1:7.38	0.49	0.12	0.61	1.5
2.0	1:5.40	0.43	0.16	0.59	1.5
2.5	1:4.18	0.38	0.22	0.60	1.5
3.0	1:3.39	0.32	0.27	0.59	1.6

We can estimate the number of PC molecules (N_s) strongly bound to a Li$^+$ ion from the results of Raman spectral measurements and analyses. The number (N_s) can be deduced from the following equation:

$$M_s = (I_{721}/(I_{712} + I_{721}))c_{pc}$$

$$N_s = M_s/C_s$$

where c_{pc} and c_s are the concentrations of PC and LiBF$_4$, respectively, and M_s is the concentration of PC molecules strongly bound to Li$^+$ ions. The results are given in Table 2. The number of PC molecules strongly bound to Li$^+$ ions is about 1.5 in each concentration and this is in sharp contrast with the number between 2.5 and 3 for LiPF$_6$−PC solutions similarly estimated from Raman spectra.[7] This difference would be due to the extent of ion-association between LiBF$_4$ and LiPF$_6$ in PC, respectively. PC molecules around a Li$^+$ ion will be pushed out of the solvation sphere by the close contact between Li$^+$ and BF$_4^-$. Therefore, the solvation number of Li$^+$ in LiBF$_4$ solutions is made smaller than that in LiPF$_6$ solutions. This is evidence of the contact ion-pair formation in LiBF$_4$ solutions. Though the PC solvation number of Li$^+$ is expected to be 4, the actual solvation number in LiPF$_6$ solutions is estimated to be as small as between 2.5 and 3.0 from the Raman intensity. This might be because the bands at 721 cm^{-1} reflect only the Raman vibration of PC molecules tightly binding to Li$^+$ ions.

Diffusion Coefficients of Li$^+$, BF$_4^-$, and PC. As mobilities of Li$^+$ and BF$_4^-$ ions and PC molecules give a significant effect to properties of electrolyte solutions, information about them is important and useful. To investigate mobilities of Li$^+$ and BF$_4^-$ and PC in solutions, their diffusion coefficients were measured with an NMR method by monitoring Li, F, and H signals, respectively. The results are summarized and drawn in Table 1 and Figure 3. In the 0.1 M solution, the diffusion coefficient of Li$^+$, 2.2 × 10^{-10} m^2 s^{-1}, is about half of that of BF$_4^-$, 4.2 × 10^{-10} m^2 s^{-1}, which is close to that of PC molecules. Diffusion coefficients of F$^-$ ions get closer to those

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TABLE 3: Conductivities, Viscosities, and Other Parameters of LiBF₄−PC−TMP at 25 °C

LiBF₄ concn (c)/ mol dm^{-3}	conductivity (κ)/ mS cm^{-1}	viscosity (η)/ cP	Walden product ($\Lambda\eta$)/ S cm^2 mol^{-1} cP	diffusion coeffs (D)/10^{-10} m^2 s^{-1}			
				^{7}Li	F	^{1}H of PC	^{1}H of TMP
0	(27.3)^a	2.45	67			6.0	6.5
0.0001	0.0027	2.44	66				
	(27)		(0.99)^b				
0.001	0.0266	2.42	64				
	(26.6)		(0.96)				
0.01	0.236	2.49	59				
	(23.6)		(0.88)				
0.1	2.17	2.37	51	2.3	5.4	5.1	5.4
	(21.7)		(0.77)				
1.0	6.21	5.16	32	1.1	2.0	2.9	1.5
	(6.21)		(0.49)				

^{a} Values in parentheses are the molar conductivities in S cm^2 mol^{-1}. ^{b} Values in parentheses are the ratios of $\Lambda\eta$ to $\Lambda_0\eta_0$.
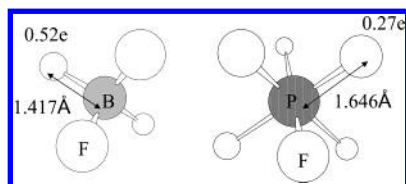
Figure 4. Result of molecular orbital calculations for BF₄⁻ and PF₆⁻.

Figure 5. Raman spectra of PC, PC−TMP, and 0.1 and 1.0 M LiBF₄− PC−TMP.

of Li⁺ with an increase in salt concentrations. In concentrations higher than 1.5 M, approximately 70% of the ions are deduced from the Walden product to form ion-pairs and the ion-association makes Li⁺ and BF₄⁻ mobilize together. This results in similar diffusion coefficients for both Li⁺ and BF₄⁻.

As shown in Figure 1, the viscosity of LiPF₆ solutions becomes sharply larger than that of LiBF₄ solutions in higher concentrations. In the previous work,[7] we discussed the remarkable increase in viscosity of the LiPF₆ solution due to some aggregation or cluster formation by bridges between Li⁺ ions with PC molecules. On the contrary, for LiBF₄ the contact ion-pair formation between Li⁺ and BF₄⁻ exists in PC solutions, suggesting that interactions between a Li⁺ ion and PC molecules are weaker than those in clusters in LiPF₆ solutions due to the electric neutralization of Li⁺ ions by the contact ion-pair formation with BF₄⁻ ions. Thus, the viscosity of the LiBF₄ solution becomes smaller than that of the LiPF₆ solution.

Estimated Charges by MO Calculations and Their Contribution to Degree of Ion-Associations. We consider the ion-association between Li⁺ and BF₄⁻ from a molecular point of view. Theoretical calculations of molecular orbitals were done for BF₄⁻ and for PF₆⁻ as well for comparison. Results are given in Figure 4. The charges on equivalent F atoms are 0.52e and 0.27e in BF₄⁻ and PF₆⁻, respectively, and the atomic distances between F and the center atoms are 1.42 and 1.65 Å in BF₄⁻ and PF₆⁻, respectively. In a BF₄⁻ ion, negative charge is higher in F atoms in a tight space, while in PF₆⁻ comparatively little negative charge spreads into the atoms in a comparatively wide space. Thus, a BF₄⁻ ion can strongly attract a positive ion like a Li⁺ ion to result in easier formation of a contact ion-pair.

Improvement of Ionic Conductivity by the Addition of Trimethyl Phosphate. Previously, the ion-association was discovered to contribute greatly to the low conductivity in the LiBF₄−PC solution. Thus, conductivity could be improved by suppression of the ion-association. One method of suppression is to make Li⁺ bind with a Lewis base, so that the tighter ion-association between Li⁺ and BF₄⁻ could be weakened. The following reaction is expected:

$$Li^+-BF_4^- + \text{Lewis base} \rightarrow Li^+-\text{Lewis base} + BF_4^-$$
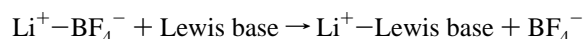
For this purpose, we focused on trimethyl phosphate (TMP) as
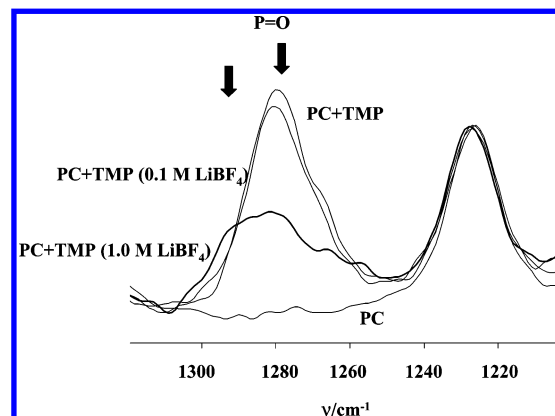
a Lewis base in the present work, and added it to 0.1 and 1 M LiBF₄−PC solutions (TMP:PC = 2:3 by weight).

Table 3 lists the values of κ, η, and D and others on the addition of TMP. The conductivities are 2.17 and 6.21 mS cm^{-1} for 0.1 and 1.0 M, respectively, and they are compared with 1.72 and 3.59 mS cm^{-1} for LiBF₄−PC solutions without TMP addition. The α values are estimated to be 0.77 and 0.49 in 0.1 and 1.0 M solutions, respectively, from the above derivation as $Q(\alpha c) = 1.0$. These values are larger than the corresponding values, 0.71 and 0.35, for the LiBF₄−PC system. Therefore, TMP as a Lewis base does bring a decrease or suppression of ion-association and thus an increase of ionic conductivity. Besides this effect, the corresponding decrease of viscosity would also contribute to an improvement of conductivity.

To obtain more information of the solvation on addition of TMP, we measured the diffusion coefficients of Li⁺, BF₄⁻, and PC by monitoring the NMR signals of ^{7}Li, F, ^{1}H of PC, and ^{1}H of TMP in the solutions. Table 3 also shows the results. The large decrease of ^{1}H TMP was observed from 6.5 down to 1.5 × 10^{-10} m^2 s^{-1} in comparison with the values of ^{1}H of PC, and this result suggests the presence of TMP molecules bound to a Li⁺ ion. Raman spectra were also measured for LiBF₄− PC−TMP solutions. On their spectra shown in Figure 5, a signal of 1280 cm^{-1} can be assigned to a P=O stretching band of free TMP and a shifting signal of 1292 cm^{-1} to that of TMP bound to Li⁺. The number of TMP molecules bound to Li⁺ ions is estimated at 2.2 and 1.5 from the intensities for 0.1 and 1.0 M solutions, respectively. The contact ion pair formation between Li⁺ and BF₄⁻ depends on the solvation of Li⁺ ions with additional TMP.

Conclusion

Ion-associations and solvations of Li^+ ions have been studied in concentrated $LiBF_4$ solutions in propylenecarbonate and also solutions containing trimethyl phosphate with measurement of conductivities, self-diffusion coefficients by field gradient NMR spectroscopy, and Raman spectra. The results obtained are summarized below:

(1) In $LiBF_4$–propylenecarbonate solutions, about 30% of $LiBF_4$ is found to dissociate in concentrations higher than 1 M, as estimated from the Walden product. The diffusion coefficients of BF_4^- ions become closer to those of Li^+ ions as the fraction of ion-pairs is increased with increasing concentration. The number of PC molecules strongly bound to a Li^+ ion is determined to be about 1.8 from the analysis of Raman spectra. This strongly suggests the presence of contact ion-pairs of Li^+–BF_4^- association in the solution.

(2) In $LiBF_4$–PC–TMP solutions, about 50% of $LiBF_4$ dissociates in the 1 M $LiBF_4$ solution. TMP as a Lewis base strongly binds to Li^+ ions and suppresses or disturbs the ion association between Li^+ and BF_4^-, and eventually improves the conductivity.

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