

A Raman spectroscopic study of organic electrolyte solutions based on binary solvent systems of ethylene carbonate with low viscosity solvents which dissolve different lithium salts

Masayuki Morita,* Yoshiko Asai, Nobuko Yoshimoto and Masashi Ishikawa

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755-8611, Japan. E-mail: morita@po.cc.yamaguchi-u.ac.jp

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The ionic structure of organic electrolyte solutions has been investigated, by means of Raman spectroscopy for mixed aprotic solvents that dissolve lithium salts. The solutions consisted of binary solvent systems of a high permittivity solvent (ethylene carbonate, EC) mixed with low viscosity alkyl carbonates (dimethyl carbonate, DMC, and diethyl carbonate, DEC) or a linear alkyl ether (1,2-dimethoxyethane, DME) and of LiCF_3SO_3 , LiPF_6 and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ as the solute. The Raman shifts based on the solvents varied with the sort of dissolved lithium salts and their concentration. The ion solvation was estimated from the side-bands of the Raman scattering for the C—O stretch of single bonds of the carbonate groups and for the symmetric ring deformation of EC. The number of EC molecules interacting with the lithium cation (Li^+) was higher than that of DMC in a mixed EC + DMC (50 : 50 by volume) system. The apparent solvation number of Li^+ in 1.5 mol dm⁻³ LiCF_3SO_3 solution was about 2.8 in EC + DMC, whereas that in 1.5 M LiPF_6 solution was about 3.9. Specific solvation of Li^+ was distinguished in EC + DME (50 : 50), where DME predominantly coordinates to Li^+ . However, it was also confirmed that EC, which has a lower donicity, interacts with Li^+ even in the EC + DME system. That is, the solvation number of EC in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DME})$ remained *ca.* 1.0 even in high salt concentrations.

Introduction

Electrolyte solutions that consist of mixed alkyl carbonates which dissolve lithium salts are of special importance in the practical application to rechargeable lithium (ion) battery systems. The combination of the solvent and lithium salt often determines the battery performance.^{1,2} Thus, many research groups have been interested in the effects of the organic electrolyte solutions on battery performance.^{3,4} We believe that detailed information about the ionic structure and properties of the electrolytes would enable one to design advanced battery systems with higher performances. To date, however, little has been understood about how the electrolyte composition can lead to better performances of the positive and negative electrodes in the battery system.

There have been many publications on the theoretical and experimental work of organic electrolyte solutions for battery use. Among them, spectroscopic investigations provide important information on the structure of the electrolyte system, especially on the ion–ion and ion–solvent interactions in aprotic media.^{5–16} Vibrational spectroscopy has also been adopted to discuss the ionic structure and transport properties of organic polymers doped with alkali metal salts.¹⁷ Yeager and co-workers⁶ first reported the ionic solvation of the lithium cation (Li^+) in propylene carbonate (PC) using infrared (IR) and proton magnetic resonance (PMR) techniques. Janz *et al.*⁷ investigated Raman spectra of PC solutions that dissolve lithium perchlorate (LiClO_4/PC), and assigned each frequency to the vibrational mode of PC. Hyodo and Okabayashi^{12,13} analyzed, by Raman spectroscopy, the electrolyte system of ethylene carbonate (EC) that dissolves LiClO_4 , and reported quantitative results on the Li^+ solva-

tion in this system. Spectroscopic data in mixed solvent systems have also been published by some research groups.^{8,11,13} Recently, Aroca and co-workers¹⁶ reported Raman spectra that could be used to consistently interpret the conductance behaviour of LiClO_4 solutions with EC-based mixed solvents. However, the effects of both the solvent mixing and the sort of counter-anion on the ionic structure are still unclear.

In the present work we have examined binary solvent systems based on EC which is currently used in practical lithium ion batteries.^{3,4} The effects of solvent mixing on the conductance behaviour have so far been observed for carbonate-based solutions that dissolve lithium salts.^{8,16,18–21} We have adopted laser Raman spectroscopy to analyze ion–ion and ion–solvent interactions in practical electrolyte systems that contain different lithium salts. The effects of mixed low viscosity solvents (LVS) and counter-anions on the Li^+ solvation are discussed quantitatively.

Experimental

The electrolyte solutions consisted of mixed binary solvent systems that dissolve lithium salts. The high permittivity solvent, EC, was mixed with low viscosity linear alkyl carbonate, dimethyl carbonate (DMC) or diethyl carbonate (DEC), or with a linear ether, 1,2-dimethoxyethane (DME), in a volumetric ratio of 50 : 50. These solvents were used as received (Mitsubishi Chemical, Battery Grade) because of their high purity (>99.9%) and low water contents (<30 ppm). The electrolytic salts were well dehydrated LiPF_6 (Tomiyama Chemical), LiCF_3SO_3 (Central Glass) and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ (3M company), which were dissolved in the mixed solvents to make solutions with the desired salt concentration under a

dry atmosphere. The composition of the electrolyte solution is given here by the salt/solvent combination *e.g.* LiPF₆/(EC + DMC).

The ionic conductivity of the electrolytic solution was measured at 10 kHz ac using an LCR meter (AG-4311, Ando Electric) at 298 K. A Kraus-type glass cell with platinized Pt electrodes was used for the measurements. The cell constant was determined by an aqueous solution of KCl (0.1 mol dm⁻³, $\kappa = 1.286 \times 10^{-2}$ S cm⁻¹).

A laser Raman spectrometer (NR-1800, JASCO) was used to obtain spectra of the solutions. The excitation source was an argon ion laser (514.53 nm, 60 mW) and the entrance slit width was 200 μ m. A 5 mm quartz cell was used for the liquid samples. The exposure time was 10 s and the scattering spectrum was usually integrated 20 times. The wavenumber of the Raman shift was calibrated by the spectrum of an Si wafer standard. The measurements were carried out under a dry atmosphere at 298 ± 5 K. The data were collected at 0.5 cm⁻¹ steps and analyzed on a personal computer.

Results and discussion

Table 1 summarizes the molecular structure and selected properties of the solvents^{22–24} used in this work. EC has a high relative permittivity (dielectric constant; ϵ_r) and a high viscosity. The former property helps to dissociate the dissolved salt, but the latter is disadvantageous for ion transportation. The other solvents in Table 1 have lower permittivity and lower viscosity. These are the main reasons that practical batteries use mixed solvent systems based on EC with DMC or other LVSs.

Fig. 1 shows typical conductance behaviour of LiPF₆ and LiCF₃SO₃ dissolved in mixed solvent systems (50 : 50 by volume) at 298 K. The ionic conductivity has a maximum at a salt concentration in the range 0.8–1.2 mol dm⁻³ in each salt/solvent combination. Similar results for the conductance behaviour have already been reported for LiClO₄ solutions with EC-based binary solvents.¹⁶ At the same salt concentration, LiPF₆ generally has a higher ionic conductivity than LiCF₃SO₃. With respect to LVS, the conductivity increases in the order DEC < DMC < DME. These variations in the conductivity have been qualitatively explained as a result of macroscopic differences in such properties as the viscosity of the solution and the degree of ion association of the electrolytic salt.^{16,20,21} Differences in the microscopic structure of the solution can also affect the conductance behaviour. The

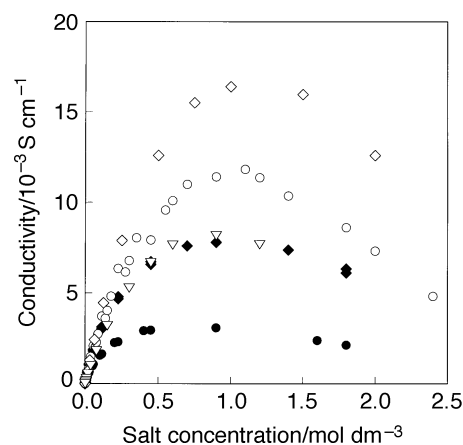


Fig. 1 Ionic conductivity of LiPF₆ (open symbols) and LiCF₃SO₃ (filled symbols) in EC-based mixed solvents. (O) LiPF₆/(EC + DMC), (◇) LiPF₆/(EC + DME), (▽) LiPF₆/(EC + DEC), (●) LiCF₃SO₃/(EC + DMC), (◆) LiCF₃SO₃/(EC + DME).

solvent–solvent and ion–solvent interactions that influence the ionic structure have widely been studied using spectroscopic techniques. We have adopted laser Raman spectroscopy to analyze the structure of the electrolytic solution based on mixed carbonate solvents.

Fig. 2 and 3 show Raman spectra for the electrolyte system LiCF₃SO₃/(EC + DMC) (50 : 50 by volume) in the 700–800 cm⁻¹ region and from 870 to 950 cm⁻¹, respectively. The Raman spectra of the solvents are generally consistent with those previously reported for PC and EC. The solvent DMC gives no Raman shift in the 700–800 cm⁻¹ region (Fig. 2). According to literature,^{7,14,25} a Raman shift at *ca.* 720 cm⁻¹ in mixed EC + DMC is assigned to symmetric ring deformation of EC, although Hyodo and Okabayashi¹² and Aroca and co-workers¹⁶ have assigned it to a C=O bending mode. The solution with a high LiCF₃SO₃ concentration shows two broad peaks in Raman scattering. The peak at *ca.* 760 cm⁻¹ is attributed to a vibration mode of SO₃⁻ combined with the CF₃ group of the CF₃SO₃⁻ anion,^{26,27} which presents some information on the ion–ion interactions (ion association), or on the formation of ion-pair and ion-aggregates,²⁶ between Li⁺ and CF₃SO₃⁻ in highly concentrated solutions. Details of the results on the ion–ion interactions in the mixed solvent systems will be discussed elsewhere. The broader peak at *ca.* 730 cm⁻¹ is based on a frequency shift of the symmetric ring deformation mode of EC (720 cm⁻¹) by the cation–solvent

Table 1 Structure and selected properties of the solvents at 298 K (unless otherwise noted)

Solvent		Molecular weight	10 ³ Density /kg m ⁻³	Relative permittivity	Viscosity /10 ⁻² P	DN ^a
EC		88.1	1.32 ^b	89.8 ^b	1.93 ^b	16.4
DMC		90.1	1.06	3.1	0.63	15.1
DEC		118.1	0.98	2.8	0.75	16.0
DME		90.1	0.87	7.3	0.46	24

^a DN: donicity. ^b At 313 K.

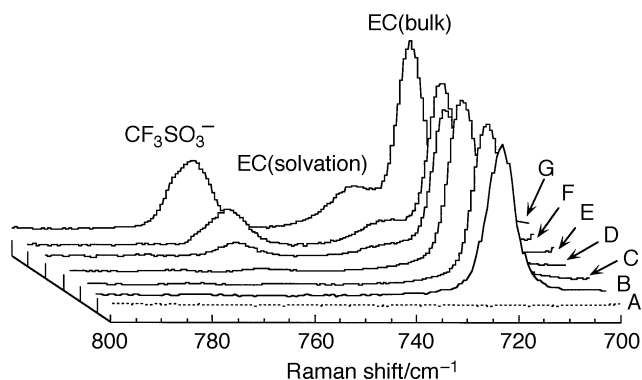


Fig. 2 Raman spectra for symmetric ring deformation of EC in the $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$ system. (A) Solvent DMC, (B) solvent EC + DMC (50 : 50 by volume), (C)–(G) EC + DMC dissolving LiCF_3SO_3 (C: 0.05, D: 0.1, E: 0.5, F: 1.0, G: 1.5 mol dm^{-3}).

interaction, or by cation solvation.^{6,12,14,16} Similar frequency shifts by cation solvation are observed for the stretching vibration band of the C—O single bond^{7,14,16} in the 870–950 cm^{-1} region (Fig. 3). The Raman shifts at about 900 and 925 cm^{-1} are, respectively, assigned to the vibration bands of EC and DMC, both of which are accompanied by satellite peaks of solvation at higher wavenumbers.

Hyodo and Okabayashi^{12,13} estimated the solvation number of Li^+ in the LiClO_4/EC system from the intensity ratio of the Raman bands. They demonstrated that the intensity ratio of “band b” (satellite band : solvated EC) to “band f” (main band : bulk EC) gives the molar ratio of the solvated EC molecule to that of bulk solvent EC, even in mixed solvent systems. In the present work, we denote the integrated scattering intensity of the band from the bulk (non-solvated) solvent as I_n and that from the solvated molecule as I_s . We need not consider any solvation for the counter-anion because the anion is too large to form complexes with these aprotic solvents.^{8,20} Spectrum deconvolution was made on the assumption that each scattering peak is expressed by a Gaussian function.¹² The intensities, I_n and I_s , were determined by integrating the area of each component peak. Here, the sensitivity of scattering may be affected by the salt concentration. Deng and Irish²⁸ employed an internal standard to determine the relative intensity of the solvent coordination of Li^+ in $\text{LiAsF}_6/\text{acetone}$ solution. They confirmed that the sum of I_n/I_0 and I_s/I_0 (I_0 : intensity of the internal standard) remained almost constant as the salt concentration varied, i.e. the sensitivity of scattering, or the scattering factor, is scarcely affected by the salt concentration. In the present case, unfortunately, we could not prove the constancy of the scattering factor over the range of salt concentration employed because

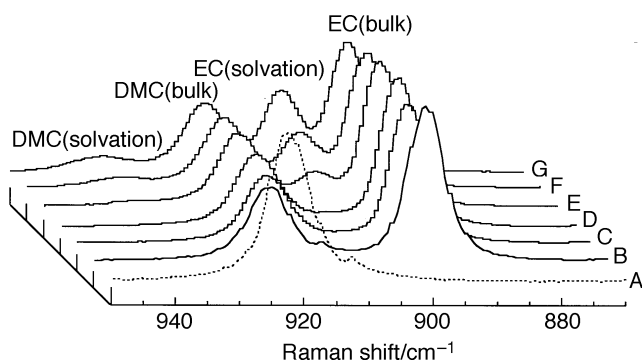


Fig. 3 Raman spectra for the symmetric stretching vibration band of C—O single bond in the $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$ system. (A) Solvent DMC, (B) solvent EC + DMC (50 : 50 by volume), (C)–(G) EC + DMC dissolving LiCF_3SO_3 (C: 0.05, D: 0.1, E: 0.5, F: 1.0, G: 1.5 mol dm^{-3}).

no scattering peak that could act as an internal standard was available in these wavenumber regions. However, the observation by Deng and Irish²⁸ in the $\text{LiAsF}_6/\text{acetone}$ system would be applicable to the present system if the discussion is limited to a comparison of the scattering intensity with respect to the same vibration mode. Consequently, we can use the intensity ratio, or relative intensity, shown in eqn. (1), instead of eqn. (2), as the measure of the Li^+ solvation.

$$I_r = I_s/(I_s + I_n) \quad (1)$$

$$I_r = (I_s/I_0)/(I_s/I_0 + I_n/I_0) \quad (2)$$

The relative intensity, I_r , is plotted as a function of the salt concentration (c_s). In Fig. 4, variations in I_r are given for the ring deformation band of EC (720 cm^{-1}) and C—O stretching bands of EC (900 cm^{-1}) and DMC (920 cm^{-1}) in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$. The relative intensity increased linearly with the salt concentration, a trend also observed in previous work.²⁸ The slope of the plot depended not only on the component solvent (EC and DMC) but also on the vibration mode (ring deformation and C—O stretching). With respect to the C—O stretching band (900–920 cm^{-1}), the relative intensity of EC showed higher slope than that of DMC. As the scattering factor is assumed to be essentially constant for the common vibration mode between EC and DMC (C—O stretching band), the higher slope of EC than DMC corresponds to a higher solvation number of EC than DMC. Selective solvation, or specific solvation, of Li^+ –EC in a mixed EC + DMC system has been suggested by Arai *et al.*, using ^{13}C NMR and MO calculations.^{29,30} On the other hand, the lower slope of the ring deformation band, compared with the C—O stretching band, of EC would reflect some differences in the influence of the solvation to the Raman shift among the vibration modes of EC.

Fig. 5 and 6 show the influences of the LVS on the variation in the relative intensity of the Li^+ –EC solvation with respect to the ring deformation band (Fig. 5) and the C—O stretching band (Fig. 6) of EC. The C—O stretching band of non-solvated DEC was, unfortunately, superimposed on the C—O stretching band of solvated EC (*ca.* 905 cm^{-1}), so that the relative intensity of the C—O stretching band of DEC could not be determined from the Raman spectra. However, almost the same result was obtained in EC + DEC as that in EC + DMC, with respect to the ring deformation band of EC (Fig. 5). On the other hand, much lower values were observed for the relative intensity of EC solvation in the EC + DME system; the relative intensity of the EC solvation in EC + DME was about 1/2 or 2/3 of that in EC + DMC, for both vibration bands (Fig. 5 and 6). This means that Li^+ preferentially forms a complex with DME molecules in mixed

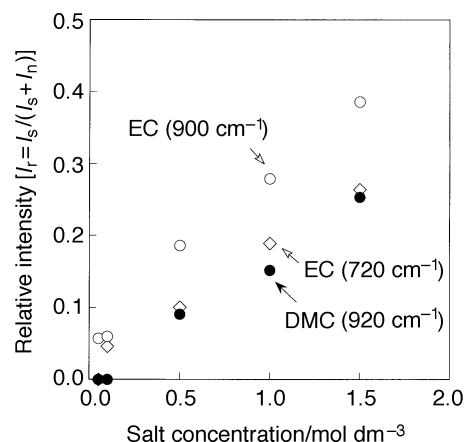


Fig. 4 Variation in the relative intensity of solvation with the salt concentration in the $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$ system. (\diamond) EC (720 cm^{-1}), (\circ) EC (900 cm^{-1}), (\bullet) DMC (920 cm^{-1}).

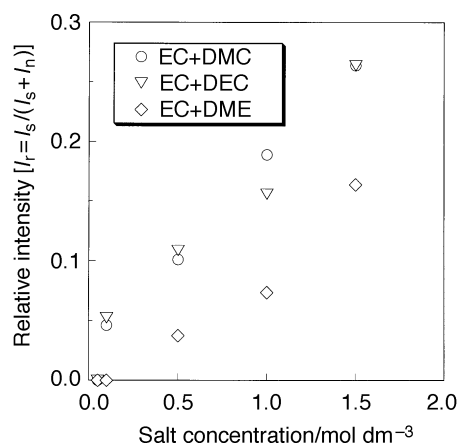


Fig. 5 Variation in the relative intensity of solvation for EC (720 cm^{-1}) in mixed EC + LVS containing LiCF_3SO_3 .

EC + DME, similar to the situation in a PC + DME system.^{8,18,20} The higher donicity (donor number: D_N) of DME would contribute to the formation of $\text{Li}^+(\text{DME})_2$ complex.⁸ It is, however, noteworthy that a part of the EC solvent still interacts with Li^+ even in the mixed EC + DME system where the donicity of one component solvent is much lower than that of the other ($D_N(\text{EC}) = 16.4$ and $D_N(\text{DME}) = 24$). Unfortunately, as DME has no active Raman scattering in these wavenumber regions, we could not obtain any direct proof that DME interacts preferentially with Li^+ in this media.

Fig. 7 shows the influence of the counter-anion on the relative intensity of the Li^+ -EC solvation in EC + DMC. The relative intensity concerning the C—O stretching band of EC was higher in solutions that dissolve LiPF_6 or $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ than in LiCF_3SO_3 solution. Similar results were obtained for the ring deformation band of EC (720 cm^{-1} region) and the C—O stretching band of DMC (920 cm^{-1} region) in the EC + DMC system. The difference in the relative intensity among the electrolytic salts is attributable to the degree of dissociation or ion-pair (ion aggregates) formation of the salt in the mixed EC + DMC system. That is, a higher degree of association or ion-pair formation of LiCF_3SO_3 ,^{21,31} which leads to lower effective concentration of the cation, would relate to a lower fraction of solvation. The relative intensity in the ring deformation band of EC in EC + DEC also gave a similar result to that in EC + DMC, with respect to the influence of the counter-anion.

Assuming that I_r is reflected by the molar ratio of the solvation to the bulk solvent, we can estimate the solvation number of Li^+ in the mixed solvent systems. The molarity of the

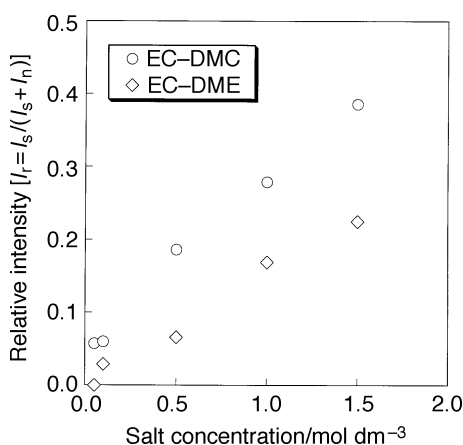


Fig. 6 Variation in the relative intensity of solvation for EC (900 cm^{-1}) in mixed EC + LVS containing LiCF_3SO_3 .

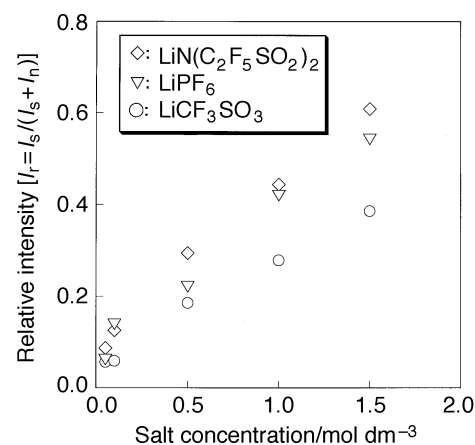


Fig. 7 Variation in the relative intensity of solvation for EC (900 cm^{-1}) in EC + DMC containing different salts.

solvent that forms Li^+ -solvation (M_s) is calculated by the following equation:

$$M_s = c_m I_r \quad (3)$$

where c_m is the total molar concentration of the solvent in the solution and I_r is the relative intensity in the spectrum of the scattering peak from the solvation, $I_s/(I_s + I_n)$. The apparent solvation number per Li^+ (N_s) is thus given by the quotient of M_s divided by the salt concentration (c_s):

$$N_s = M_s / c_s \quad (4)$$

Table 2 summarizes M_s and N_s estimated from the Raman spectra. Here the calculation was limited to systems that dissolved the salts with concentrations of 0.5 mol dm^{-3} or higher to retain reliance on the I_r value. With respect to the EC component in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$, N_s varies from 2.7 to 1.9 with the electrolyte concentration. In the same solution, the solvation number of DMC is almost constant throughout the variation in the salt concentration. Thus, the apparent total number of solvation (EC + DMC) varies from 3.7 to 2.8 in the $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$ system whose salt concentration is 0.5–1.5 mol dm^{-3} . This value is rather low compared with those reported for LiClO_4/EC ($N_s = 4.1\text{--}4.3$) by Hyodo and Okabayashi¹² and for $\text{LiAsF}_6/\text{acetone}$ ($N_s = 3.1\text{--}4.6$) by Deng and Irish.²⁸ The difference in the counter-anion would be a main cause of this disagreement. In fact, the N_s of EC in $\text{LiPF}_6/(\text{EC} + \text{DMC})$ is higher than that in the LiCF_3SO_3 solution. As the N_s of DMC remained almost constant (about 1.2) as the LiPF_6 concentration varied, the total molecular number of the solvation results in $N_s = 4.4\text{--}3.9$ for the $\text{LiPF}_6/(\text{EC} + \text{DMC})$ system. Thus, the total solvation number of Li^+ in the LiPF_6 solution shows good agreement with those obtained for LiClO_4/EC and $\text{LiAsF}_6/\text{acetone}$. The property of LiCF_3SO_3 that tends to form an ion pair or ion aggregates is probably responsible for the lower value of the apparent solvation number in EC + DMC. For example, the formation of contact-ion-pair and ion-aggregates, which is strongly suggested by the variations in the vibration band of CF_3SO_3^- ,³¹ will reduce the coordination sites of Li^+ . For both solutions that dissolve LiCF_3SO_3 and LiPF_6 , the EC molecule seems to interact more preferentially with Li^+ than does DMC. MO calculation have partly predicted this result.^{29,30}

The apparent solvation number of EC was much lower in the solutions based on mixed EC + DME where a significant donicity difference is present. We have reported the selective (specific) solvation of Li^+ -DME in $\text{LiClO}_4/(\text{PC} + \text{DME})$ under an infinite dilution condition. In the present work we also observed the preferential interaction between Li^+ and DME, as shown in lower values of EC solvation in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DME})$. However, there seems to be no

Table 2 Estimation of the apparent solvation number from Raman spectra

system	$c_s/\text{mol dm}^{-3}$	I_r	M_s^a	N_s^b
(A) EC in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$	1.5	0.39 ^c	2.8	1.9
	1.0	0.28 ^c	2.0	2.0
	0.5	0.19 ^c	1.4	2.7
(B) DMC in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DMC})$	1.5	0.25 ^d	1.4	0.9
	1.0	0.15 ^d	0.9	0.9
	0.5	0.09 ^d	0.5	1.0
(C) EC in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DME})$	1.5	0.23 ^c	1.7	1.1
	1.0	0.17 ^c	1.2	1.2
	0.5	0.07 ^c	0.5	1.0
(D) EC in $\text{LiPF}_6/(\text{EC} + \text{DMC})$	1.5	0.54 ^c	3.9	2.6
	1.0	0.42 ^c	3.0	3.0
	0.5	0.22 ^c	1.6	3.2
(E) DMC in $\text{LiPF}_6/(\text{EC} + \text{DMC})$	1.5	0.30 ^d	2.0	1.3
	1.0	0.19 ^d	1.1	1.1
	0.5	0.10 ^d	0.6	1.2

^a Molarity of the solvent forming Li^+ -solvation. ^b Apparent solvation number per Li^+ . ^c At 900 cm^{-1} . ^d At 920 cm^{-1} .

extreme selective solvation like $\text{Li}^+(\text{DME})_2$ in the system with higher salt concentrations, because the solvation number of EC remains at *ca.* 1.0 in $\text{LiCF}_3\text{SO}_3/(\text{EC} + \text{DME})$. This contrasts with the previous results reported for the mixed solvent systems with highly different donicities, $\text{EC} + \text{CH}_3\text{Cl}$ and $\text{EC} + \text{H}_2\text{O}$, the latter of which gave complete selective solvation of $\text{Li}^+-\text{H}_2\text{O}$.¹³

The estimation of the solvation number in $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ solutions gave similar results as those obtained for LiPF_6 solutions. We may conclude, therefore, that the Li^+ -solvent interaction, or the ionic atmosphere of Li^+ , in $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ solutions is generally the same as that in LiPF_6 solutions with the present mixed solvent systems. Thus, differences in the solution properties between LiPF_6 and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, if any, would come from differences in the anion itself.

Conclusions

The ionic structure of organic electrolyte solutions that consist of EC mixed with LVSS (DMC, DEC and DME) has been investigated by Raman spectroscopy. The results are summarized as follows.

- (1) The Raman shifts based on the solvents varied with both the dissolved lithium salt employed and its concentration.
- (2) The side-bands of the Raman scattering based on the C—O single bond stretch of the carbonate groups and on the symmetric ring deformation of EC enabled us to estimate the cation solvation in the mixed solvent systems.
- (3) The number of EC molecules interacting with Li^+ was higher than that of DMC in the mixed EC + DMC system.
- (4) The apparent total solvation number ($N_s(\text{EC}) + N_s(\text{DMC})$) was lower in LiCF_3SO_3 solutions than in LiPF_6 or $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ solutions.
- (5) The specific solvation of Li^+ was distinguished in the EC + DME systems (50 : 50 by volume), where DME dominantly coordinates to Li^+ .
- (6) It was also found that EC, despite having a lower donicity, still interacts with Li^+ even in the EC + DME system.

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