

## Ionic Diffusion and Salt Dissociation Conditions of Lithium Liquid Crystal Electrolytes

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Salt dissociation conditions and dynamic properties of ionic species in liquid crystal electrolytes of lithium were investigated by a combination of NMR spectra and diffusion coefficient estimations using the pulsed gradient spin-echo NMR techniques. Activation energies of diffusion ( $E_a$ ) of ionic species changed with the phase transition of the electrolyte. That is,  $E_a$  of the nematic phase was lower than that of the isotropic phase. This indicates that the aligned liquid crystal molecules prepared efficient conduction pathways for migration of ionic species. The dissociation degree of the salt was lower compared with those of the conventional electrolyte solutions and polymer gel electrolytes. This is attributed to the low concentration of polar sites, which attract the dissolved salt and promote salt dissociation, on the liquid crystal molecules. Furthermore, motional restriction of the molecules due to high viscosity and molecular oriented configuration in the nematic phase caused inefficient attraction of the sites for the salt. With a decreased dissolved salt concentration of the liquid crystal electrolyte, salt dissociation proceeded, and two diffusion components attributed to the ion and ion pair were detected independently. This means that the exchange rate between the ion and the ion pair is fairly slow once the salt is dissociated in the liquid crystal electrolytes due to the low motility of the medium molecules that initiate salt dissociation.

## Introduction

The development of energy storage devices with high capacity and sufficient safety performance is an urgent and significant subject from the aspect of energy storage and environmental preservation. For this goal, it is indispensable to prepare a new type of electrolyte material having high ion diffusivity and safety, which is superior to the conventional electrolytes such as solid polymer and polymer gel electrolytes.

The fundamental concepts of electrolyte design can be categorized into two points. One is the way of securing mobile ions responsible for charge transport in the medium. The introduction of the polar groups or sites in the medium structure, which has been tried in several polymer electrolytes, is a representative approach.<sup>1,2</sup> This is based on the idea that the Coulombic effect of the polar sites on the dissolved salt could promote salt dissociation to prepare net mobile ions. Another point that has to be considered for electrolyte design is mobility enhancement of the dissociated ions. Ionic mobility is dominated by the morphology or the chemical structure of the conduction pathway and the motional activity (plasticity) of the entire medium. The latter is typically represented by the flexibility of the polymer chains of polymer electrolytes and by the disordered alignment of the medium molecules such as liquid solvents, amorphous polymers, polymer gels, and amorphous glasses. It is generally accepted that the amorphous and flexible medium structures provide a random network of ion transport pathways

in which the ion migrates with lower activation energy compared with that of the migration in ordered crystal structures. This feature of ion transport contrasts well with the electron conduction mechanism in which the ordered structure has the advantage over the disordered structure for fast electronic conduction. This would be mainly attributable to the orderly difference in size between the ion and electron. It is presumed that an ion, which is  $10^4$  times greater in size than an electron, is sensitively affected by the atomic species forming the framework structure of the medium in the course of migration. In practice, it is not easy to design the structure of conduction pathways for fast ion transport under the consideration of chemical and physical interactions between the mobile ions and the atomic species of the medium. We could find only a few successful electrolytes of inorganic crystals such as Na super-ionic conductors (NASICON) and Li super-ionic conductors (LISICON).<sup>3,4</sup>

Recently, it was reported that a crystalline polymer electrolyte based on poly(ethylene oxide) (PEO) had higher conductive pathways in a direction parallel to a crystal axis.<sup>5</sup> In addition, recent research on the ion conduction mechanism in amorphous PEO-type polymer electrolytes revealed anisotropy in lithium diffusivity after applying a stress by stretching the electrolyte membrane.<sup>6,7</sup> It was expected that the stretching operation induced partial molecular alignment in amorphous PEO to prepare effective pathways for ion transport. Furthermore, we confirmed that ion ordering was a dominant factor in the ionic mobility of dialkylimidazolium ionic liquids.<sup>8</sup> Several cations and anions in the salt are aggregated in the liquid phase forming a domain particle,  $A(\text{AX})_m^+$  or  $(\text{AX})_n\text{X}^-$ , as a unit of fluid particles responsible for charge transport. With the increased

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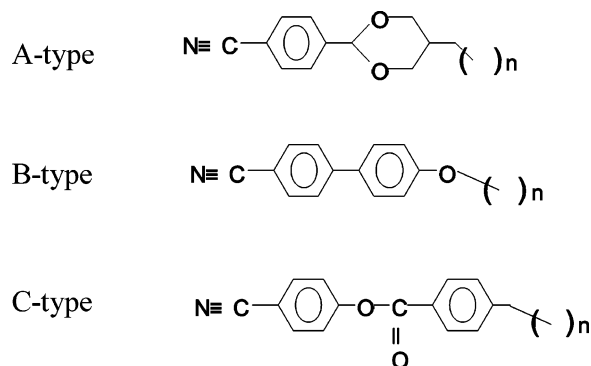
ordering of a domain particle represented by increased  $m$  and  $n$ , ionic conductivity and diffusivity are enhanced.

These results concerning the polymer electrolytes and ionic liquids suggest that molecular alignment or ordering could be a key approach for designing the medium structure for fast ion migration even in plastic or fluid materials if the aligned molecules could provide effective pathways for fast ion transport.<sup>9–11</sup> We suppose that it is a new departure to prepare the electrolytes having both plasticity and molecular orientation and investigate the ion transport mechanism in the electrolyte.

Along this consideration, we prepared lithium liquid crystal electrolytes composed of a lithium salt and liquid crystal medium in this research. Liquid crystals have phase transition points at which the molecular ordering condition changes. In the isotropic phase, the molecules with a long axis are directed randomly with each other. In the anisotropic (nematic or smectic) phase, the molecules are oriented in a direction, which is confirmed by the transmittance measurement by polarized microscope. The dissolved ions diffuse and migrate in the space of the liquid crystal medium affected by the Coulombic force of the polar sites on the molecules as well as by the physical barrier effect of the long molecules. It is expected that the ion migration in the anisotropic phase would reflect the anisotropy of the aligned molecules different from the migration in the isotropic phase of a random molecular configuration. Furthermore, the promotion of salt dissociation is a significant subject for electrolyte material preparation. The dissociation degree of the salt is dominated by the ability and efficiency of ion attraction on the polar sites of the liquid crystal molecules. We would like to investigate the effect of molecular orientation on ionic mobility, the effect of the polar sites on salt dissociation, and the consequent states of the ions and ion pairs in liquid crystal electrolytes. This research is the first clue for material development taking advantage of the aligned molecular structure of fluid materials.

## Experimental Section

In the selection of liquid crystal materials for the electrolyte medium, the abilities of salt dissolution and dissociation are the most significant factors to prepare a large number of mobile ions. We then chose the liquid crystals having effective polar sites such as  $\text{C}\equiv\text{N}$  and  $-\text{O}-$ , which attract ions and promote salt dissociation. The starting liquid crystal materials, A-I, *trans*-4-(5-propyl-1,3-dioxane-2-yl)benzonitrile; A-II, *trans*-4-(5-pentyl-1,3-dioxane-2-yl)benzonitrile; B-I, 4'-pentyloxy-biphenyl-4-carbonitrile; B-II, 4'-heptyloxy-biphenyl-4-carbonitrile; C-I, 4-cyanophenyl-4-hexylbenzoate; C-II, 4-cyanophenyl-4-heptylbenzoate, purchased from Wako Pure Chemical Industries, Ltd., were recrystallized several times by dissolving in ethanol. The chemical formula of each liquid crystal medium is represented in Figure 1. I and II of the A, B, or C types were mixed in the molar ratios of 47.5:47.5, 38:57, and 47.5:47.5 for A, B, and C, respectively, to obtain the final liquid crystal media, A, B, and C. The mixing ratios were determined to lower the phase transition temperature in each mixture after dissolving 5 mol % lithium salt. A lithium salt,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (Li-TFSI) from Kishida Chemical Co. Ltd. was dissolved in A, B, or C in Ar atmosphere at 100 °C with the concentration of 1, 3, or 5 mol % to form the liquid crystal electrolyte (LCE). The final electrolyte compounds are abbreviated as LCE-A, LCE-B, and LCE-C. The phase transition temperature and molecular ordering in the nematic phase of the liquid crystals and LCEs were confirmed by the transmittance observation of visible light using a polarized microscope.



**Figure 1.** Chemical formulas of liquid crystals: A, *trans*-4-(5-alkyl-1,3-dioxane-2-yl)benzonitrile; B, 4'-alkyloxy-biphenyl-4-carbonitrile; C, 4-cyanophenyl-4-alkylbenzoate. The values for  $n = 3$  and 5 of A,  $n = 5$  and 7 of B, and  $n = 6$  and 7 of C were mixed to prepare the electrolyte with the lower phase transition temperature.

The ionic conductivities of the electrolytes were measured by the complex impedance technique over the temperature range of 20–80 °C. The frequency was changed from 20 Hz to 1 MHz using an LCR meter (4284A, Hewlett-Packard).

To observe the conductivity along the long axis of the oriented molecules in the nematic phase, we used a home-made conductivity cell with a couple of conductive glass electrodes sandwiching a poly(phenylene sulfide) separator of 24  $\mu\text{m}$  in thickness having a hole of 6 mm in diameter in which the electrolyte sample is held. We confirmed using the polarized microscope that the liquid crystal molecules were aligned directing the long axis perpendicular to the electrode plates below the phase transition temperature. Measured conductance using the special conductivity cell were corrected in reference to the values of the isotropic condition using the conventional conductivity cell with a cell constant of  $\sim 0.1 \text{ cm}^{-1}$ .

The diffusion coefficients of the cation and anion species and liquid crystal molecule in the electrolytes were measured using the pulsed gradient spin-echo (PGSE) NMR technique with a JNM-ECP300W spectrometer (7.04 T) and wide-bore probe units best tuned to (a)  $^7\text{Li}$  (116.8 MHz) for the cation species and (b)  $^{19}\text{F}$  (282.7 MHz) and  $^1\text{H}$  (300.5 MHz) for the anion species and liquid crystal molecules, respectively.<sup>12</sup> The stimulated echo sequence was used for this measurement.<sup>13,14</sup> Two gradient pulses were applied in the sequence after the first and third  $\pi/2$  pulses with a time interval  $\Delta$ . A half-sine-shaped pulse was used for the field gradient pulse because of the advantage for matching the two pulses as compared with a square-shaped pulse.<sup>15</sup> In this PGSE-NMR experiment, the signal attenuation is described as

$$M \propto \exp[-\gamma^2 g^2 \delta^2 D(\Delta - \delta)/\pi^2] \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio of the observe nuclei,  $g$  is the strength of the field gradient pulse,  $\delta$  is the width of the field gradient pulse, and  $D$  is the diffusion coefficient. Typical values of the parameters are  $g = 5\text{--}10 \text{ T m}^{-1}$ ,  $\delta = 0\text{--}5 \text{ ms}$ , and  $\Delta = 80 \text{ ms}$ . In this static magnetic field (7.04 T), the molecules are aligned parallel to the direction of the applied field in the nematic phase region.<sup>16,17</sup> As the gradient pulses are applied in the direction parallel to the static field, observed diffusion coefficients in the nematic phase reflect the migration along the long axis of the aligned molecules. In the case of  $^7\text{Li}$ , a split peak appeared over the entire temperature range, and the split interval changed with the salt concentration. However, the signal shape of the  $^{19}\text{F}$  peak changed drastically depending on the phase condition. In the isotropic phase, a split peak,

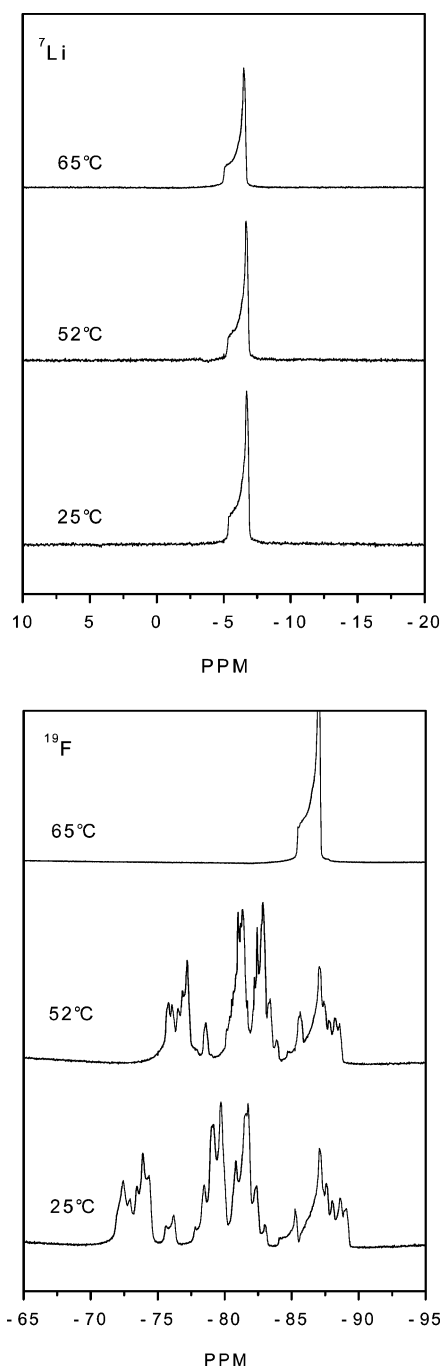
similar to the form of  $^7\text{Li}$ , was observed. In the nematic phase, several peaks in symmetry were observed. These features of peak patterns reflect the ionization state of the salt and existing state of the species in the liquid crystal molecules. For the diffusion coefficient estimation of each overlapped component that would be attributed to the different ionization state, we first separated the signal into each component analytically using the ECP analytical program from JEOL and evaluated the diffusion value from the peak intensity (area) attenuation of each separated component.

## Results and Discussion

**Confirmation of Molecular Alignment in Liquid Crystal Electrolytes.** We measured the phase transition temperature of liquid crystal electrolytes set in a home-made conductivity cell using the polarized microscope. The liquid crystal molecules were aligned below the temperatures 20–23 °C for LCE-A, 52 °C for LCE-B, and 35–40 °C for LCE-C corresponding to the phase transition points. The temperature widths at the phase transition points of LCE-A and LCE-C are due to the dissolved lithium salt which, as an impurity, contributes to reduce the orientation degree of the liquid crystal molecules and make the transition point ambiguous.

We also confirmed the molecular orientation condition in each phase under the NMR static field by the observation of  $^7\text{Li}$  and  $^{19}\text{F}$  NMR spectra. Figure 2 shows the comparison of the echo signal of LCE-B with 5 mol % Li-TFSI at several temperatures. Three spectra on each nuclear species represent the states of the isotropic liquid phase (65 °C), in the middle of the phase transition point (52 °C), and the nematic mesophase (25 °C). The shape and position of  $^7\text{Li}$  spectra were independent of the phase condition, indicating that the state of the cation species was not affected seriously by the orientation condition of the liquid crystal molecules. The asymmetrical line shape of lithium is the same as that of the polymer gel electrolyte or polymer electrolyte in which the salt is dissolved in the high-viscosity medium. We suppose that the shape reflects the inhomogeneity of the static field on the species of low motility or the existence of different states of the lithium species, i.e., the dissociated ionic species and associated molecular species in the solvent environment. However,  $^{19}\text{F}$  spectra reflected the liquid crystal phase condition. The peak number increased showing a symmetrical pattern with the progress of molecular alignment. This is attributed to the nuclear spin coupling of the fluoride nucleus.<sup>18</sup> According to the orientation of liquid crystal molecules in the nematic phase, the configuration of the large anion species would follow the ordering. As the spin–spin interaction depends on the direction of the magnetic field against the anion species orientation, several peak appearances reflect the number of orientation directions of the anion species. With increased temperature promoting the molecular disordering in the isotropic phase, the peaks converged and became singular due to the averaging of the states by motion activation. These features represent the fact that the molecular orientation of the conduction medium practically affects the existing state and/or configuration of the anion species. This apparent difference in peak pattern between the cation and anion is attributed to the fact that the anion species comprises several nuclei,  $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ , in contrast to the spherical cation composed of a single lithium nucleus.

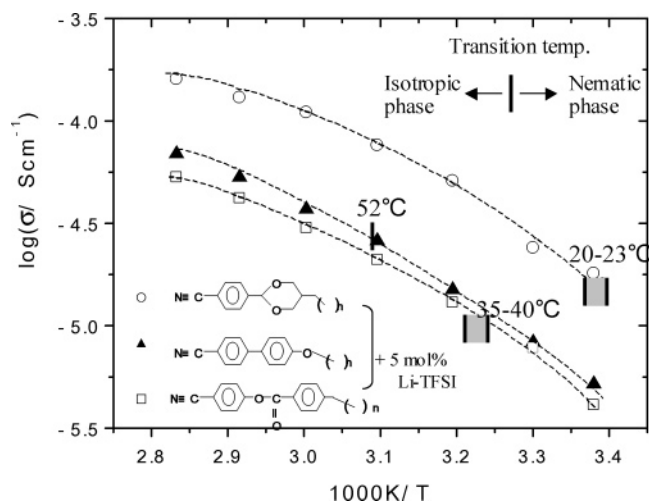
**Dynamic Features of Liquid Crystal Electrolytes.** Figure 3 shows the temperature dependence of the ionic conductivity of LCE-A, LCE-B, and LCE-C with 5 mol % lithium salt. It is characteristic that the conductivity change showed a monotonically curved feature over the observed temperature range in a



**Figure 2.**  $^7\text{Li}$  and  $^{19}\text{F}$  NMR spectra of LCE-B with 5 mol % Li-TFSI observed above and below the phase transition temperature, 52 °C.  $^{19}\text{F}$  spectra showed the symmetrical feature attributed to the anion orientation according to the alignment of liquid crystal molecules in the nematic phase.

similar manner for three samples. As we said in the Experimental Section, the liquid crystal molecules are aligned perpendicular to the electrode plates at the nematic phase. Therefore, the conductivity reflects the ion migration along the long axis of the oriented molecules below the transition temperature different from the conductivity in the disordered medium above the transition temperature. Despite the change in the molecular ordering condition at the transition point, there was no apparent change in temperature dependence of conductivity as a variation of activation energy around the temperature.

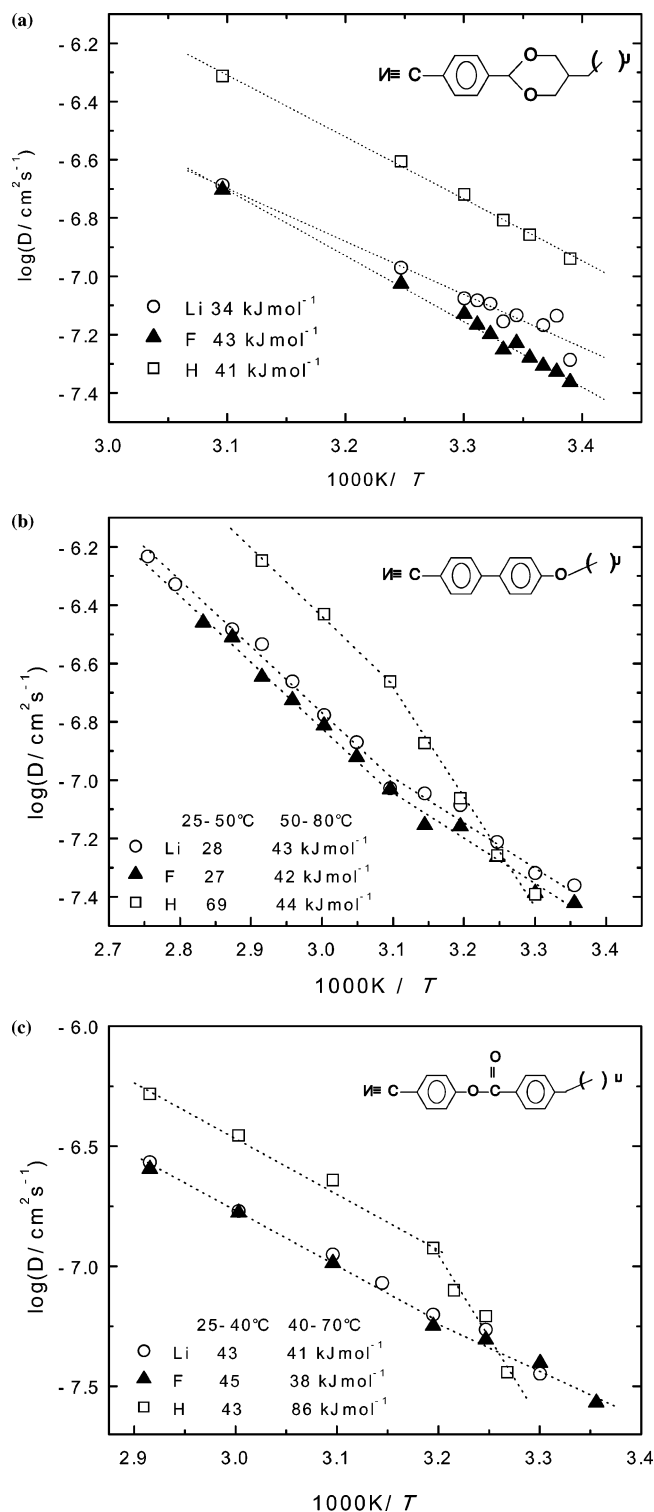
To elucidate the migration features associated with the morphological properties of the medium, we observed the diffusion behaviors of the cation and anion species individually



**Figure 3.** Temperature dependence of the ionic conductivity of LCE-A (○), LCE-B (▲), and LCE-C (□) with the lithium salt concentration of 5 mol %. Phase transition temperatures were 20–23 °C for LCE-A, 52 °C for LCE-B, and 35–40 °C for LCE-C.

using the pulsed gradient spin-echo NMR technique. The echo intensity attenuation by the application of stepwise-changed gradient pulse strengths showed a linear change in  $\log$  intensity versus  $\delta^2\Delta$ , indicating the random walk migration of the ionic species. This means that the liquid crystal molecules provide uniform conduction pathways at least along the direction of diffusion detection without any restricting barriers that disturb free migration. Then, we estimated the diffusion coefficient,  $D$ , from the echo attenuation rate.<sup>12</sup>

Figure 4 represents the temperature dependence of diffusion coefficients of the cation ( $D_{Li}$ ) and anion ( $D_F$ ) species and the liquid crystal molecule ( $D_H$ ) in LCE-A, LCE-B, and LCE-C with 5 mol % Li-TFSI. The estimated diffusion coefficients from different peaks, which were separated analytically first in case where the peaks are overlapped, in each nuclear species were almost the same within the experimental error. Therefore, it is acceptable that  $D_{Li}$  or  $D_F$  is contributed from a single species. Then, the diffusion coefficients  $D_{Li}$ ,  $D_F$ , and  $D_H$  were finally determined by averaging the estimated value from each peak. Plots of LCE-B and LCE-C showed the change in slope at the phase transition temperature, indicating the variation of the ion migration mechanism depending on the molecular orientation condition. There was no apparent change in the slope for the diffusion of LCE-A over the observed temperature range because the phase transition temperature range, 20–23 °C, was below the observed temperature region. It is characteristic that the changing tendency of the activation energy of diffusion ( $E_a$ ) across the phase transition point was reversed between the ionic species and the liquid crystal molecules. That is,  $E_a$  of the cation or anion diffusion in the nematic phase was lower than that in the isotropic phase. However,  $E_a$  of the diffusion of the liquid crystal molecules became steeper with going to the nematic phase. This difference could be attributed to a fundamental difference in the migration mechanism of the dissolved small species and large medium molecules: Ionic species, which are smaller compared with the liquid crystal molecules, migrate in the space between the molecules colliding and interacting with the medium molecules. Then the motion is random in the isotropic phase, which is fundamentally similar to the behavior of dissolved ions in conventional solvents such as propylene carbonate (PC) and diethyl carbonate (DEC). However, ionic species migration in the nematic phase is different and dominated by the molecular orientation condition of the medium molecules. The ionic species could smoothly transport in the



**Figure 4.** Temperature dependence of the diffusion coefficient of the cation (○), anion (▲), and solvent species (□) from the nuclear species of  $^7\text{Li}$ ,  $^{19}\text{F}$ , and  $^1\text{H}$ , respectively, of (a) LCE-A with 5 mol % Li-TFSI, (b) LCE-B with 5 mol % Li-TFSI, and (c) LCE-C with 5 mol % Li-TFSI. Activation energies of diffusion are incorporated in the figure.

systematic space of the oriented molecules along the aligned long axis. This may be the reason  $E_a$  of ion diffusion in the nematic phase was lower than that in the isotropic phase. Migration of the large liquid crystal molecules themselves would be fundamentally different from that of the smaller ionic species. Molecular orientation in the nematic phase would rather reduce the free space for molecular migration, resulting in the increase in  $E_a$  for diffusion.



It should be noted that the  $E_a$  change at the phase transition temperature appeared in the diffusion coefficient change and did not appear in the conductivity change. We suppose there are two possible explanations for the different features. One is attributed to the difference in the contributing species between the diffusion and the conductivity measurements. Electrical conductivity detects the motion of charged ions regardless of the amount. However, the diffusion coefficient is contributed from both the dissociated ions and the associated ion pairs as long as they coexist and contain the same probed nucleus such as  $^7\text{Li}$  or  $^{19}\text{F}$ .<sup>19</sup> Therefore, in the case of the low salt dissociation condition that is discussed later, observed diffusion coefficients mainly reflect the ion pair migration. It is expected that the neutral ion pair migration would simply depend on the morphology prescribed by molecular alignment although the charged ion migration is affected by the Coulombic effect of the polar sites on the medium molecules in addition to the physical effect of the migration pathway. As a result,  $E_a$  of the diffusion strongly reflected the molecular alignment condition depending on the phase change. Another reason for the  $E_a$  change difference between the diffusion and conductivity would be the difference in the migration distance of the species during the measurement. In the case of the diffusion coefficient measurement, probed species migrate about  $5\text{ }\mu\text{m}$  when  $D_{\text{obs}} \approx 10^{-6}\text{ cm}^2\text{ s}^{-1}$ . In the conductivity measurement for the same mobile species, the migration distance corresponds to  $0.005\text{ }\mu\text{m}$ , assuming the detected frequency of  $1\text{ kHz}$ . Micrometer distance diffusion migration is enough to reflect the morphological feature of the transport pathway for diffusion coefficient values. On the contrary, the conductivity is estimated from the vibrational motion between the sites on, at most, several molecules. Therefore, the  $E_a$  value of the conductivity could not give information about the molecular alignment condition different from the  $E_a$  value of the diffusion.

The absolute values of  $D_{\text{H}}$  were larger than those of  $D_{\text{Li}}$  and  $D_{\text{F}}$  in the isotropic phase. This is similar to the situation in conventional electrolyte solutions and polymer gel electrolytes in which the diffusion coefficient of the solvent species was larger than that of the ionic species.<sup>20,21</sup> This feature indicates that the neutral species could migrate faster than the ionic species without deceleration attributed to the Coulombic interaction. Several reports concerning the diffusivity of liquid crystals said that the doped impurity in the liquid crystal showed a larger diffusion coefficient than that of the liquid crystal molecule itself.<sup>16,22</sup> Our result of  $D_{\text{Li}}, D_{\text{F}} < D_{\text{H}}$  is opposite to the tendency of the reports. This discrepancy is due to the fact that the doped impurities in the previous research were neutral and small molecules different from the salt accompanied by dissociation to charged ions. In those cases, there was no effect of Coulombic interaction on the carrier species causing the reduction of the absolute diffusion values.

It should be noted that  $D_{\text{Li}}$  and  $D_{\text{F}}$  were almost the same over the entire temperature range in LCE-B and LCE-C. In case of LCE-A, the difference between  $D_{\text{Li}}$  and  $D_{\text{F}}$  increased with the decrease in temperature. On the basis of our previous research, the agreement in  $D_{\text{Li}}$  and  $D_{\text{F}}$  indicates that the dissociation degree of the salt is low and the probed species for the  $D_{\text{Li}}$  and  $D_{\text{F}}$  measurements are the same ion pair.<sup>12,20</sup> The difference between  $D_{\text{Li}}$  and  $D_{\text{F}}$  becomes larger over the course of salt dissociation because the size and interactive effect on the surrounding atoms of the cation and anion are essentially different.<sup>20</sup> In the dissociated condition,  $D_{\text{Li}}$  is generally smaller than  $D_{\text{F}}$  in electrolyte solutions and polymer gel electrolytes that dissolve Li-TFSI salt due to the solvation effect of several

**TABLE 1: Estimated Haven Ratio,  $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$  of Several Types of Electrolyte Materials Using Molar Conductivity and Diffusion Coefficients ( $D_{\text{Li}}$  and  $D_{\text{F}}$ ) at 25 °C**

	$\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$
Li-TFSI-PC (0.01 M)	0.9 <sup>a</sup>
Li-TFSI-PC (0.1 M)	0.5 <sup>a</sup>
Li-TFSI-PC (1.0 M)	0.3 <sup>a</sup>
LiPF <sub>6</sub> -EC/EMC-PEO (5 wt % of LiPF <sub>6</sub> -EC/EMC)	0.4 <sup>b</sup>
Li-TFSI-LCE-B (5 mol % of Li-TFSI)	0.08

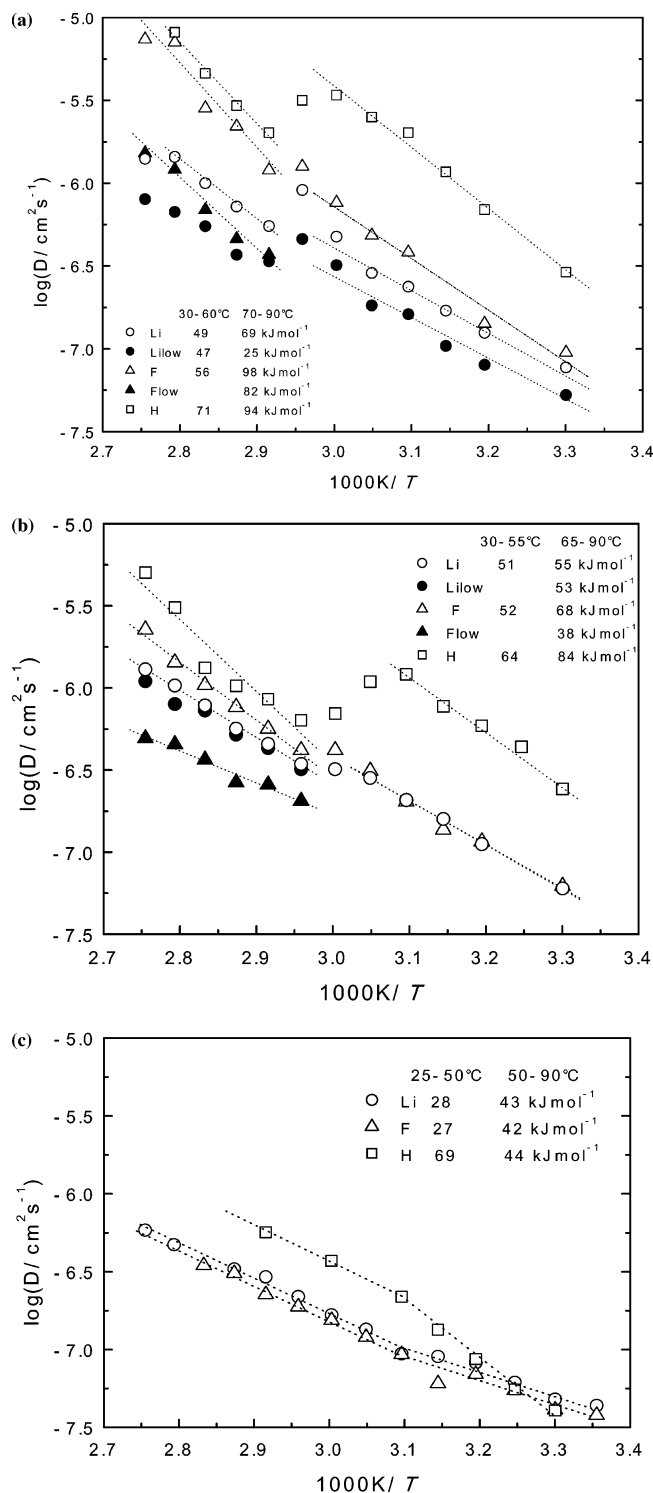
<sup>a</sup> Estimation from the observed conductivity and diffusion coefficients in ref 20. <sup>b</sup> Estimation from the observed conductivity and diffusion coefficients in ref 21.

polar solvent molecules on  $\text{Li}^+$  to form a larger hydrodynamic species than the free anion.<sup>20,23</sup> According to this consideration, it is presumed that the agreement in  $D_{\text{Li}}$  and  $D_{\text{F}}$  in LCE-B and LCE-C over the entire temperature range is ascribed to (1) the low dissociation condition of the salt in the liquid crystal molecules, and  $D_{\text{Li}}$  and  $D_{\text{F}}$  reflect diffusivity of the dominant ion pair, or (2) a coincidental result under the situation of comparable size of the cation and anion species as hydrodynamic particles after the solvation of the liquid crystal molecules. Low salt dissociation could be supported from the consideration of the  $E_a$  value difference between the diffusion coefficient and the conductivity.

#### Salt Dissociation Condition of Liquid Crystal Electrolytes.

For the evaluation of the salt dissociation condition, estimation of the Haven ratio,  $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ , is one of the convenient approaches when both the conductivity and the diffusion data are obtained. We have previously reported that the Haven ratio is approximated by the dissociation degree of the salt,  $x$  in case of  $D_{\text{cation}} + D_{\text{anion}} \approx 2D_{\text{pair}}$  or  $x \approx 1^8$  where  $D_{\text{cation}}$ ,  $D_{\text{anion}}$ , and  $D_{\text{pair}}$  represent the diffusion coefficients of the cation, anion, and ion pair, respectively. Except the condition, the ordering of the magnitudes of the Haven ratios of different samples is not necessarily consistent with the ordering of  $x$ .<sup>8</sup> After due consideration of this assumption, we compared the Haven ratios estimated from the conductivity and diffusion coefficient of several electrolyte materials in Table 1. The value decreased with the increase in salt concentration and solvent viscosity. Then, it is acceptable that the estimated Haven ratios relatively reflect the dissociation condition of the salt. In practice, the value of the liquid crystal electrolyte was significantly smaller compared with the values of other electrolytes, indicating the possibility of a lower dissociation degree of the salt. This result fundamentally agrees with the consideration in the section of dynamic features. It is supposed that the polar sites on the liquid crystal molecules are not so effective, in number and strength, to attract and dissociate the salt compared with polar solvents as the PC or the aligned ether oxygen sites on PEO-type polymer chains.

It is expected that salt dissociation is promoted by decreasing the salt concentration in liquid crystal electrolytes by analogy with the electrolyte solutions and polymer gel electrolytes.<sup>12,20</sup> To elucidate the dissociation condition of the salt in liquid crystals in detail, we next changed the salt concentration of the liquid crystal electrolytes and observed the NMR spectral changes and diffusion behaviors of each mobile species. Figure 5 shows the temperature dependence of the diffusion coefficients  $D_{\text{Li}}$ ,  $D_{\text{F}}$ , and  $D_{\text{LC}}$  of LCE-B with three different salt concentrations (5, 3, and 1 mol %). In the process of diffusion coefficient estimation, two overlapped peaks were first separated into two components. Then diffusion values were estimated from the intensity attenuation of each component. In the case where the



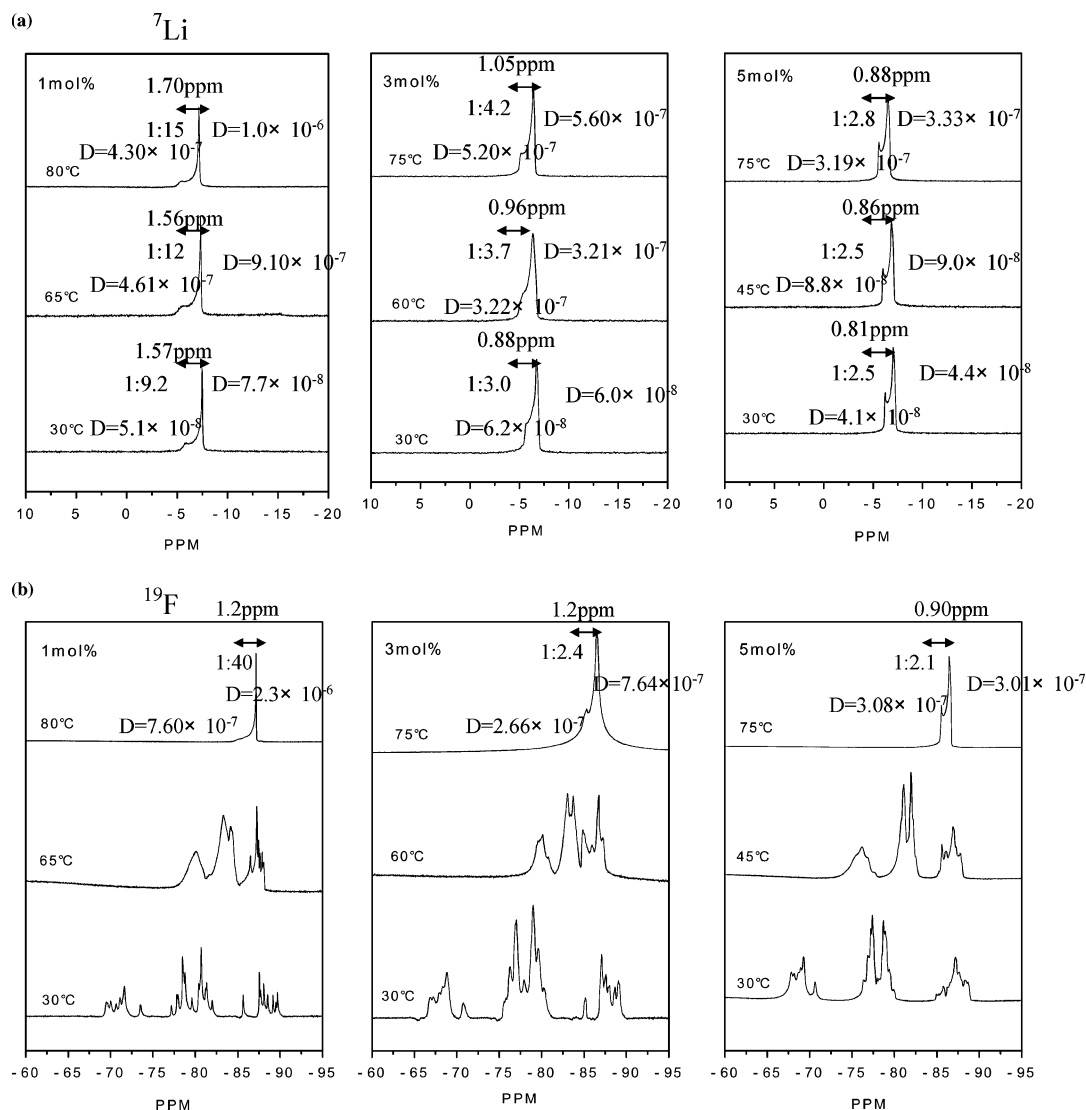
**Figure 5.** Temperature dependence of the diffusion coefficient of the cation (○,●), anion (□,▲), and solvent species (□) from the nuclear species  $^7\text{Li}$ ,  $^{19}\text{F}$ , and  $^1\text{H}$ , respectively, of (a) LCE-B with 1 mol % Li-TFSI, (b) LCE-B with 3 mol % Li-TFSI, and (c) LCE-B with 5 mol % Li-TFSI.

difference between the two values from the separated components was over the experimental error, both values were plotted in the figure. We could find several characteristic features by changing the salt concentration in the electrolytes: (1) the absolute values of the observed diffusion coefficients increased with decreased salt concentration, (2) the temperature dependence of  $D_{\text{LC}}$  of LCE-B 3 mol % and LCE-B 1 mol % showed minimum points at the phase transition temperature, (3) the

difference between  $D_{\text{Li}}$  and  $D_{\text{F}}$  enhanced especially in the isotropic phase with decreased salt concentration, (4)  $D_{\text{Li}}$  of LCE-B 1 mol %,  $D_{\text{F}}$  of LCE-B 3 mol %, and LCE-B 1 mol % showed two diffusion values (e.g.,  $D_{\text{Li}}^{\text{high}}$  and  $D_{\text{Li}}^{\text{low}}$ ) from the separated components, and (5) the  $E_a$  value of the diffusion of each species almost increased with the decreased salt concentration. These features are attributed to the changes in (a) the degree of orientation of the liquid crystal molecules, (b) the degree of the salt dissociation, and (c) the macroscopic viscosity, depending on the salt concentration. We could interpret the characteristic results denoted above based on these points as follows: (1) Increased diffusion values with the salt concentration decrease reflect the decrease in the viscosity of the medium. (2) Minimum appearance in the  $D_{\text{LC}}$  change with temperature variation represents the typical diffusivity of the liquid crystal molecules accompanied with the phase transition. Several reports of the diffusion coefficient change of the liquid crystal molecule with temperature showed abrupt discontinuity at the phase transition point.<sup>16,22,24</sup> Inversion of  $D_{\text{LC}}$  in the vicinity of the phase transition point indicates that the diffusion mechanism is fundamentally different between the two phases and the aligned condition is more appropriate for the long molecule migration. With decreased dissolved salt concentration, the degree of molecular orientation became higher, and discontinuous change appeared. This is because the dissolved salt would act as an impurity species disturbing the molecular orientation and making the transition point ambiguous. This is the reason that  $D_{\text{LC}}$  of LCE-B 5 mol % in Figure 4 showed continuous change at the phase transition point. (3) Enhanced difference between  $D_{\text{Li}}$  and  $D_{\text{F}}$  with decreasing salt concentration proves that the salt dissociation was promoted with the salt concentration decrease. This agrees with the situation of the conventional electrolyte solution and polymer gel electrolytes.<sup>12,20</sup> The larger separation between  $D_{\text{Li}}$  and  $D_{\text{F}}$  in the isotropic phase than that in the nematic phase would indicate that the random configuration of the liquid crystal molecules is more efficient for polar sites on the molecules to attack the salt and induce salt dissociation. (4) Two diffusion components in  $D_{\text{Li}}$  or  $D_{\text{F}}$  observed in LCE-B 3 mol % and LCE-B 1 mol % could be simply assumed as contributions from the ions and ion pair species. A single diffusion component of  $D_{\text{Li}}$  or  $D_{\text{F}}$  observed in LCE-B 5 mol % then reflects the migration of the ion pairs as the dominant species in the low salt dissociation condition. With the increased relative amount of the ion to the ion pair with the salt concentration decrease, two independent values were detected in  $D_{\text{Li}}$  or  $D_{\text{F}}$ . (5) Enhanced  $E_a$  with the salt concentration decrease would be due to the change in the dominant mobile species from the ion pair to the ion. In the course of the migration, ions are affected by the Coulombic interaction of the polar sites on the medium molecules. This effect would dominate the ionic mobility, leading to an  $E_a$  value larger than that of the ion pair diffusion, which is free from the Coulombic effect.

When the two diffusion components (e.g.,  $D_{\text{Li}}^{\text{high}}$  and  $D_{\text{Li}}^{\text{low}}$ ) can be assigned to the ion and the ion pair, this situation indicates that the exchange rate between the ion and the ion pair is fairly slow in the liquid crystal electrolytes, enough to be distinguished from each other. This is completely different from the coexisting states of the ion and the ion pair in conventional electrolyte solutions or polymer gel electrolytes in which they exchange with each other fast, and the observed single diffusion coefficient is the average of two contributions represented by<sup>19</sup>

$$D_{\text{obs}} = xD_{\text{ion}} + (1 - x)D_{\text{pair}} \quad (2)$$



**Figure 6.** (a)  $^7\text{Li}$  and (b)  $^{19}\text{F}$  NMR spectra of LCE-B with changing salt concentrations and observed temperature of the liquid crystal electrolytes.

where  $x$  is the existence probability of the ion and equal to the dissociation degree of the salt.<sup>19</sup>

To confirm the static features of the ion and the ion pair in detail, we compared the  $^7\text{Li}$  and  $^{19}\text{F}$  NMR spectra in different salt concentrations and observed temperatures in Figure 6. The  $^7\text{Li}$  spectra showed two peaks changing the splitting width with the parameters' change. With a decrease in the salt concentration (moving from the right side to the left side in Figure 6), (1) the splitting width broadened, and (2) the echo intensity and diffusion value from each peak became different. With an increase in the observed temperature (moving from the bottom to the top in Figure 6), the variation of splitting width and the signal intensity difference between the two peaks followed the change with the salt concentration decrease.

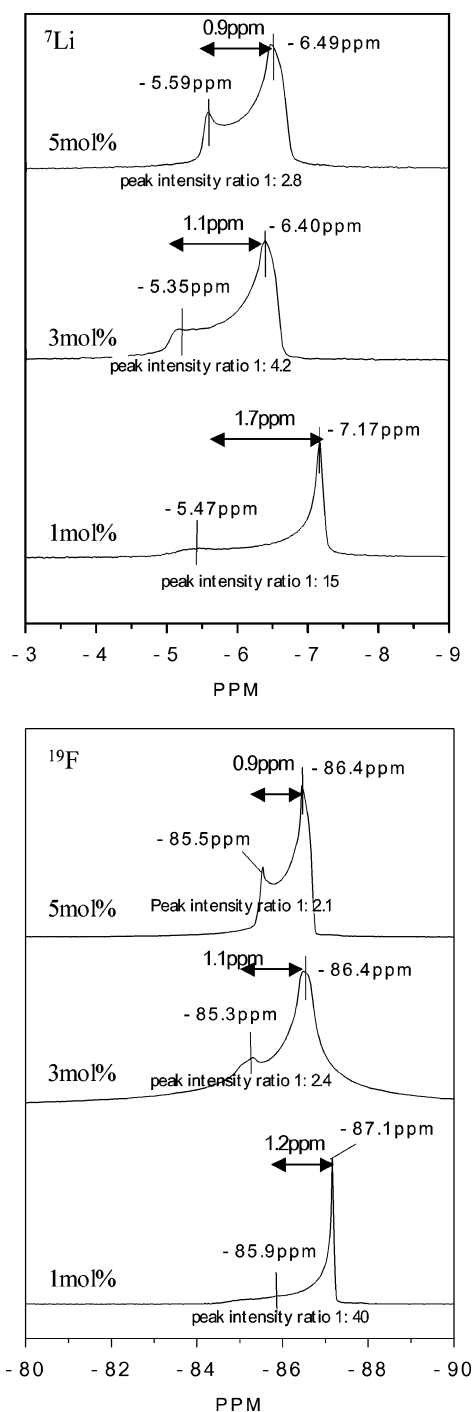
As is depicted in the diffusion coefficient features in Figure 5, the salt concentration decrease and the temperature increase lead to promoting the salt dissociation. Therefore, an increase in the interval between the two peaks with their different diffusion values represents the appearance of two independent species, the ion and the ion pair in the progress of salt dissociation.

The spectral pattern change of  $^{19}\text{F}$  above the phase transition temperature was similar to the behavior of  $^7\text{Li}$  with the salt concentration change, including the appearance of two diffusion values from the split peak. This feature supports the existing

state of the ion and the ion pair, which exchange with each other slowly, denoted by the  $^7\text{Li}$  spectral feature.

Figure 7 represents the magnified echo peaks of  $^7\text{Li}$  and  $^{19}\text{F}$  in the isotropic phase to clarify the peak shift with the changing the salt concentration. The interval between the two peaks increased with the salt concentration decrease. Furthermore, it is characteristic that the right-side peaks of  $-6.4$  ppm in  $^7\text{Li}$  and  $-86.4$  ppm in  $^{19}\text{F}$  of the 3 and 5 mol % samples significantly shifted to the right,  $-7.1$  ppm in  $^7\text{Li}$  and  $-87.1$  ppm in  $^{19}\text{F}$  in the 1 mol % sample. We suppose that the right-side peaks of the 1 mol % sample are assigned to the different species responsible for the right-side peaks of the 3 mol % and 5 mol % samples. As the estimated diffusion coefficients from the two peaks in LCE-B 5 mol % were the same within an experimental error, the two peaks with a narrow interval are attributed to the inhomogeneous contribution of the static field to the low motility species and could be assigned to the dominant ion pair species. However, the two peaks of LCE-B 1 mol % are attributed to the different species; the larger peak corresponds to the ion and the weak peak to the ion pair due to the apparent peak shift and different diffusion values estimated from each peak.

Under this assignment, higher diffusion components ( $D_{\text{Li}}^{\text{high}}$  and  $D_{\text{F}}^{\text{high}}$ ) estimated from the right-side peaks are of the ion, and lower diffusion components ( $D_{\text{Li}}^{\text{low}}$  and  $D_{\text{F}}^{\text{low}}$ ) are of the



**Figure 7.**  $^7\text{Li}$  and  $^{19}\text{F}$  NMR spectra of LCE-B for the comparison of the peak shift with changing the salt concentrations of the liquid crystal electrolytes.

ion pair in LCE-B 1 mol %. If two diffusion components ( $D^{\text{high}}$  and  $D^{\text{low}}$ ) in a signal discretely reflect the ion and the ion pair, respectively, then  $D_{\text{Li}}^{\text{low}}$  and  $D_{\text{F}}^{\text{low}}$  have to be consistent with each other because they were assigned to the same ion pair. In practice, their estimated values were different especially in the higher temperature region as shown in Figure 5. This may be due to difficulty in the explicit estimation of the diffusion value from the separation of the overlapped peaks and especially from the small peak attenuation.

It is anomalous that  $D_{\text{ion}}$  and  $D_{\text{pair}}$  were observed simultaneously from an individual peak. That is contrasted with the situation of conventional electrolyte solutions and polymer gel electrolytes in which the ion and the ion pair coexist and

exchange fast with each other. In the case, an averaged single diffusion coefficient, represented by eq 2, is observed for the cation and anion species. This fundamental difference would be attributed to the difference in the chemical effect of the medium molecules on the dissolved salt. It is expected that once the dissolved salt interacts with the polar sites on the liquid crystal molecules to be dissociated the interacting sites have to keep the ion for a certain time. This is because there is no appropriate site for ion hopping in the neighborhood such as the efficient alignment of the ether oxygen on PEO chains. Furthermore, the higher viscosity (73–140 mPa s) and the lower motility of the liquid crystals as compared with those of low molecular weight solvents reduce the exchange rate between the ion and the ion pair.

## Summary

Liquid crystal electrolytes of lithium showed the characteristic diffusivity of the ionic species reflecting the molecular orientation of the liquid crystal medium. The activation energies of diffusion of the cation and the anion species along the aligned molecules were lower than those of diffusion in randomly oriented molecules. This indicates that the oriented structure provides efficient ion transport pathways along the direction of the long axis of the oriented molecules.  $D_{\text{LC}}$  changes with temperature in the liquid crystal electrolytes with lower salt concentration showed discontinuity at the phase transition temperature. That is, in the vicinity of the phase transition temperature,  $D_{\text{LC}}$  in the nematic phase was higher than that in the isotropic phase despite the lower temperature region. We expect from these results that the molecular oriented structure of liquid crystals can be used for an electrolyte medium providing high ion mobility.

Concerning the salt dissociation ability, liquid crystal molecules were not so effective to attract and dissociate the salt compared with the polar solvents such as PC and ethylene carbonate (EC) or PEO chains having an alignment of ether oxygen on each chain. This is attributed to the fewer number of sites on a molecule. In addition, in the orientated molecular configuration of the nematic phase, motional restriction causes the inefficient attraction of the polar sites on the molecules for the salt. Therefore, it is a key point to design the liquid crystal molecules having polar sites that are effective in number and strength for the preparation of net mobile ions.

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