

New Approach for Determining the Degree of Dissociation of a Salt by Measurements of Dynamic Properties of Lithium Ion Electrolytes

Hiroshi Kataoka and Yuria Saito*

National Institute of Advanced Industrial Science and Technology 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577 Japan

Received: March 13, 2002; In Final Form: September 16, 2002

A new derivation idea for the dissociation degree of the salt of an electrolyte solution using the observed diffusion coefficient and ionic mobility was proposed. The dynamic values could be measured for individual species by the pulsed gradient spin-echo NMR technique. The observed diffusion coefficient is contributed from the dissociated ion and the associated ion pair. The observed mobility, on the other hand, reflects the migration behavior of only the ion. Combining these values, we independently derived the dissociation degree of the salt. This model was applied to the actual lithium electrolyte solution samples of Li-TFSI in EC/DEC (2/3, 1 M) dispersed with 10–15 wt % of PVDF–HFP. The estimated value of the dissociation degree of the salt was 0.75–0.90 using the observed mobility by NMR. When we applied the electrical conductivity for this estimation, the dissociation degree was in the range of 0.55 to 0.70. The difference in the absolute values between two estimations is due to the difference in the absolute values of the observed mobility attributed to the different measurement techniques of the dynamic value.

Introduction

Ionic conduction mechanisms of electrolyte materials from liquid to solid have been studied for academic interest and, furthermore, the efficient development of applicable materials for batteries and sensors. Ionic conductivity is essentially dominated by the interactions between the carriers, which are generally originated from dissociation of the salt, and the local environment such as the solvent species and matrix. Therefore, the investigation of the conduction mechanism could be interpreted as the quantitative elucidation of the interactive effects on the dynamic behavior of the carrier ions.

Ionic conduction properties are generally observed using electrochemical techniques. Although the measurements of impedance and current/potential response are conventional methods, they provide comprehensive information of all the charged species in the sample. To evaluate the migration feature of the individual species to realize the essence which dominates the conduction mechanism, we have proposed a spectroscopic approach of pulsed-gradient spin-echo NMR (PGSE–NMR).^{1–4} Diffusion coefficients of the cation and anion species of lithium electrolytes could be measured independently using the probed nuclei of ⁷Li and ¹⁹F, respectively.

We have found that the observed dynamic values such as diffusion coefficient and ionic mobility are associated with the static feature of the dissociation condition of the salt through the theoretical investigation.⁵ It is generally accepted that the dissociation degree of the salt of the conventional electrolyte is not unity and depends on the salt concentration, dielectric constant, and viscosity of the material. As a result, the diffusion coefficient of each species is, due to the spectroscopic detection of the probed nuclei, contributed from both the dissociated ion and the associated ion pair represented as

$$D_{\text{obs(Li)}}^{\text{pgse-nmr}} = xD_{\text{cation}} + (1-x)D_{\text{pair}}$$

$$D_{\text{obs(F)}}^{\text{pgse-nmr}} = xD_{\text{anion}} + (1-x)D_{\text{pair}} \quad (1)$$

where D_{cation} , D_{anion} , or D_{pair} is the inherent diffusion value of the cation, anion, or ion pair, respectively, and x is the dissociation degree of the salt. The superscript represents the method from which the observable originates. It is generally impossible to distinguish D_{ion} and D_{pair} through the measurement due to the fast exchange between the ion and ion pair in the equilibrium state.

To extract the net dynamic value of the charged species that actually contribute to the charge transfer at the operation of electrochemical device, we have applied a constant electric field (E) on the PGSE–NMR.^{5,6} Only the charged species respond to the electric field drifting with a velocity (ν), which is proportional to the mobility (μ) and E . The observed echo intensity of NMR on this situation could be represented in the short pulse approximation, $\delta \ll \Delta$ as^{5,7,8}

$$M_{\nu} = M_0 \cos(q\nu_{\text{obs}}\Delta) \exp(-q^2 D_{\text{obs}}\Delta)$$

$$q = 2\gamma\delta g\pi^{-1} \quad (2)$$

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

$$\nu_{\text{obs}} = x\nu_{\text{ion}} \quad (3)$$

where D_{obs} is the observed diffusion coefficient contributed from the ion and ion pair, ν_{obs} is the drift velocity of the ion estimated from the echo intensity, D_{ion} or ν_{ion} is the inherent diffusion coefficient or drift velocity of the ion and γ , g , δ , and Δ represent the gyromagnetic ratio, strength, and width of the applied gradient pulse and interval between the two gradient pulses, respectively. We can derive ν_{obs} using the ratio of the observed echo intensities with and without the electric field as

* Corresponding author: Tel. +81-727-51-9618. Fax +81-727-51-9714. E-mail yuria-saitou@aist.go.jp.

$$M_v/M = \cos(qv_{\text{obs}}\Delta) \quad (4)$$

The ionic mobility can be represented as

$$\mu_{\text{obs}}^{\text{e-nmr}} = v_{\text{obs}}/E = xv_{\text{ion}}/E = x\mu_{\text{ion}} \quad (5)$$

Equation 5 means that the observed mobility by the electric field applying PGSE–NMR (E–NMR) still includes the component of the dissociation degree of the salt similar to the form of the diffusion coefficient in eq 3. That is, the observed dynamic values are always the combination of the inherent dynamic value and the static nature, the dissociation degree of the salt of the electrolyte.

It is usual to compare the conductivities estimated from NMR diffusion and impedance measurements for the evaluation of the dissociation degree of the salt, x .^{9–11} However, in practice, this approach is not appropriate for estimation of the value unless $x = 1$ or $D_{\text{cation}} + D_{\text{anion}} \sim 2D_{\text{pair}}$ due to the component of D_{pair} in D_{obs} in eq 1.

We recognize that the D_{obs} contains contributions from the ion and ion pair although the μ_{obs} reflects only the ionic motion. This suggests that it is possible to estimate the degree of dissociation of the salt, x , and inherent dynamic values, D_{cation} , D_{anion} , D_{pair} , μ_{cation} , μ_{anion} , individually by choosing two samples of the same salt and different dissociation conditions. We are convinced that the real aspect of the electrolyte appears through the investigation of the inherent dynamic and static values independently.

In this research, we propose a new approach to estimating the dissociation degree of the salt through the theoretical derivation. We then applied the model to the real electrolyte materials of lithium for the estimation of the dissociation degree of the salt. This result provides essential information of the fundamental carrier conduction mechanism, which would be the basis for designing new ionic materials.

Theoretical Derivation of the Dissociation Degree of the Salt. Haven Ratio – Comparison of Impedance Conductivity and NMR Conductivity. Comparison of the conductivities, which are estimated from diffusion coefficient using the Nernst–Einstein equation and the experimental values measured by a.c. impedance method, has been conventionally used to roughly evaluate the dissociation condition of the salt.^{9,10} Molar conductivity can be expressed explicitly using Einstein's relation¹² as

$$\Lambda_{\text{imp}} = xF(\mu_{\text{cation}} + \mu_{\text{anion}}) = \frac{F^2x}{RT}(D_{\text{cation}} + D_{\text{anion}}) \quad (6)$$

in which $z_+ = z_- = 1$ is assumed. The molar conductivity from NMR result is conventionally defined as

$$\Lambda_{\text{NMR}} = \frac{F^2}{RT}(D_{\text{obs(Li)}}^{\text{pgse-nmr}} + D_{\text{obs(F)}}^{\text{pgse-nmr}}) \quad (7)$$

Using the relation of eq 1, Λ_{NMR} can be represented explicitly as

$$\Lambda_{\text{NMR}} = \frac{F^2}{RT}[x(D_{\text{cation}} + D_{\text{anion}}) + 2(1-x)D_{\text{pair}}] \quad (8)$$

In the case of $D_{\text{cation}} + D_{\text{anion}} \sim 2D_{\text{pair}}$ or $x \sim 1$,

$$\begin{aligned} D_{\text{obs(Li)}}^{\text{pgse-nmr}} + D_{\text{obs(F)}}^{\text{pgse-nmr}} &= D_{\text{cation}} + D_{\text{anion}} \\ \mu_{\text{obs(Li)}}^{\text{e-nmr}} + \mu_{\text{obs(F)}}^{\text{e-nmr}} &= x(\mu_{\text{cation}} + \mu_{\text{anion}}) \end{aligned} \quad (9)$$

Under this condition, the Haven ratio, $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$, can be expressed as

$$\begin{aligned} \frac{\Lambda_{\text{imp}}}{\Lambda_{\text{NMR}}} &= \frac{x F(\mu_{\text{cation}} + \mu_{\text{anion}})}{\frac{F^2}{RT}(D_{\text{obs(Li)}}^{\text{pgse-nmr}} + D_{\text{obs(F)}}^{\text{pgse-nmr}})} = \\ &= \frac{RT(\mu_{\text{obs(Li)}}^{\text{e-nmr}} + \mu_{\text{obs(F)}}^{\text{e-nmr}})}{F(D_{\text{obs(Li)}}^{\text{pgse-nmr}} + D_{\text{obs(F)}}^{\text{pgse-nmr}})} \\ &= \frac{\frac{F^2x}{RT}(D_{\text{cation}} + D_{\text{anion}})}{\frac{F^2}{RT}(D_{\text{cation}} + D_{\text{anion}})} = x \end{aligned} \quad (10)$$

In a particular case of the condition $D_{\text{cation}} + D_{\text{anion}} \sim 2D_{\text{pair}}$, we could evaluate the dissociation degree of the salt from the Haven ratio of electrical conductivity and NMR conductivity.

Combination of Two Dynamic Values, Diffusion Coefficient and Mobility. The dynamic values obtained by the PGSE–NMR measurements with and without the electric field can be summarized as follows:

$$\begin{aligned} D_{\text{obs(Li,F)}}^{\text{pgse-nmr}} &= xD_{\text{(cation,anion)}} + (1-x)D_{\text{pair}} \\ D_{\text{obs(H)}}^{\text{pgse-nmr}} &= D_{\text{solvent}} \\ v_{\text{obs(Li,F)}}^{\text{e-nmr}} &= xv_{\text{(cation,anion)}} \Leftrightarrow \mu_{\text{obs(Li,F)}}^{\text{e-nmr}} = x\mu_{\text{(cation,anion)}} \end{aligned} \quad (11)$$

The representation with the subscript obs(Li,F) and obs(H) is the observed dynamic values using the probed species of ⁷Li or ¹⁹F and ¹H, respectively. The subscripts (cation, anion), pair, ion pair, and solvent, respectively.

The inherent diffusion coefficient of each species satisfies Einstein's relation under the ideal condition in which the species follows the Brownian motion at the equilibrium state and is expressed by

$$D_{\text{(cation,anion)}} = \mu_{\text{(cation,anion)}} \frac{RT}{F} \quad (12)$$

where $D_{\text{(cation,anion)}}$ or $\mu_{\text{(cation,anion)}}$ is a function of the viscosity and temperature, and here $z = 1$ is assumed.¹³ The viscosity is caused by the mixing of the species of different velocities and the interaction among the species. In the practical electrolyte solution, the viscosity depends on the kind of solvent, the dissolved salt, and its concentration.

We assume two electrolyte solution samples (1 and 2) of different dissociation degree of the salt dissolving the same lithium salt. They are prepared, for example, by changing the salt concentration. The inherent diffusion coefficient or mobility of each species in the solutions is inversely proportional to the viscosity according to the Stokes–Einstein relation.¹³ The observed diffusion coefficient of the solvent species probed by ¹H would represent the diffusive feature of the inherent species because the solvent species is neutral independent of the dissociating condition of the salt. We then express the relationship of the diffusion values between the two samples as

$$\alpha D_{\text{solvent}}^1 = D_{\text{solvent}}^2 \quad (13)$$

where α reflects the viscosity ratio, η_1/η_2 , of the two solutions on the assumption that the Stokes' radius is the same between them. The other inherent dynamic values also follow this relation

assuming the Stokes–Einstein equation, represented as

$$\begin{aligned}\alpha D_{(\text{cation},\text{anion})}^1 &= D_{(\text{cation},\text{anion})}^2 \\ \alpha D_{\text{pair}}^1 &= D_{\text{pair}}^2 \\ \alpha \mu_{(\text{cation},\text{anion})}^1 &= \mu_{(\text{cation},\text{anion})}^2\end{aligned}\quad (14)$$

Combining eqs. 11, 12, 13, and 14, the dissociation degree of the salt of each solution is derived under $z = 1$ as follows:

$$\begin{aligned}x^1 &= \mu_{\text{obs}}^1 \times \frac{(\alpha \mu_{\text{obs}}^1 - \mu_{\text{obs}}^2)RT/F - (\alpha D_{\text{obs}}^1 - D_{\text{obs}}^2)}{\mu_{\text{obs}}^1 D_{\text{obs}}^2 - \mu_{\text{obs}}^2 D_{\text{obs}}^1} \\ x^2 &= \frac{\mu_{\text{obs}}^2}{\alpha} \times \frac{(\alpha \mu_{\text{obs}}^1 - \mu_{\text{obs}}^2)RT/F - (\alpha D_{\text{obs}}^1 - D_{\text{obs}}^2)}{\mu_{\text{obs}}^1 D_{\text{obs}}^2 - \mu_{\text{obs}}^2 D_{\text{obs}}^1} \\ \alpha &= D_{\text{obs(H)}}^2 / D_{\text{obs(H)}}^1\end{aligned}\quad (15)$$

The subscript obs corresponds to obs(Li) or obs(F). The superscript representing the method for observation was omitted in this equation. This result indicates that we can estimate the static values of the dissociation degree of the salt using the observed diffusion coefficients and mobilities of two samples having different dissociation condition.

In the case of $D_{(\text{cation},\text{anion})} \sim D_{\text{pair}}$, this relation can be simplified as

$$\begin{aligned}x^1 &= \frac{\mu_{\text{obs}}^1 RT}{D_{\text{obs}}^1 F} \\ x^2 &= \frac{\mu_{\text{obs}}^2 RT}{D_{\text{obs}}^2 F}\end{aligned}\quad (16)$$

This means that the dissociation degree of the salt of each sample could be estimated from its own dynamic values if $D_{(\text{cation},\text{anion})} \sim D_{\text{pair}}$ is assumed.

The ionic mobility can be obtained from the conductivity value from eqs 6 and 9 as the summation of cation and anion components:

$$\Lambda_{\text{imp}} = xF(\mu_{\text{cation}} + \mu_{\text{anion}}) = F(\mu_{\text{obs(Li)}} + \mu_{\text{obs(F)}})^{\text{imp}} \quad (17)$$

Then, x can be also estimated by applying the electrical conductivity result to eq 15 by the substitution of

$$\begin{aligned}\mu_{\text{obs}} &\Rightarrow (\mu_{\text{obs(Li)}} + \mu_{\text{obs(F)}})^{\text{imp}} = \Lambda_{\text{imp}}/F \\ D_{\text{obs}} &\Rightarrow D_{\text{obs(Li)}}^{\text{pgse-nmr}} + D_{\text{obs(F)}}^{\text{pgse-nmr}}\end{aligned}\quad (18)$$

By analogy with eq 16, the following relations could be defined when $D_{\text{cation}} + D_{\text{anion}} \sim 2D_{\text{pair}}$:

$$\begin{aligned}x_1 &= \frac{(\mu_{\text{obs(Li)}}^1 + \mu_{\text{obs(F)}}^1)RT}{(D_{\text{obs(Li)}}^1 + D_{\text{obs(F)}}^1)F} \\ x_2 &= \frac{(\mu_{\text{obs(Li)}}^2 + \mu_{\text{obs(F)}}^2)RT}{(D_{\text{obs(Li)}}^2 + D_{\text{obs(F)}}^2)F}\end{aligned}\quad (19)$$

These values correspond to eq 10. That is, the simple form of the dissociation degree is equal to the Haven ratio.

Experimental Section

LiN(CF₃SO₂)₂ (Li-TFSI) was dissolved into a mixed solvent composed of ethylene carbonate (EC) and diethyl carbonate

(DEC) (2:3 in volume ratio) in order to prepare a 1 M solution. To control the dissociation condition and viscosity of the solution, the polyvinylidene fluoride-type polymer (PVDF–HFP copolymer) was mixed with the solution (heated at 30 °C) to prepare a gel using acetone that eventually evaporated.¹ The polymer fraction was changed from 0 to 15 wt %. Ionic conductivity of the electrolyte solution was measured by the complex impedance technique at 25 °C in the frequency range of 1 Hz to 1 MHz. The diffusion coefficients of the ionic species were measured using the PGSE-NMR technique with the probed nuclei of ⁷Li (116.8 MHz) for the cation, ¹⁹F (282.7 MHz) for the anion, and ¹H (300.5 MHz) for the solvent species using a JNM-ECP300W wide bore spectrometer.¹ In this study, the stimulated echo sequence was used for this application. The half-sine-shaped gradient pulse was applied twice in sequence after the first and third 90° pulses to detect the attenuation of the echo intensity according to the migration property of the probed species.¹⁴ Typical values of the field gradient pulse parameters were $g = 0.17\text{--}0.62$ T/m for the pulse strength, $\delta = 0\text{--}3$ ms for the pulse width, and $\Delta = 1.5$ s for the interval between the two gradient pulses. The potential in the range of 0–10 V/cm was continuously applied from the start to the end of the spin–echo detection in order to selectively drift the ionic species. The sample cell for the NMR measurement was composed of a 10 mm diameter cylindrical glass tube having two pairs of electrodes, one pair of gold plates for the potential application placed on the top and the bottom of the tube and the other of platinum wire to detect the constant electric field at the center of the material. A direct potential was applied in a direction parallel to the static magnetic field and the gradient field. The power supply was controlled in order to keep the detected potential constant, reversing the polarity every other measurement in order to inhibit the polarization and decomposition of the electrolyte material. Temperature-controlled air was allowed to flow around the sample cell to maintain a constant temperature of 298 K \pm 0.1 K during the measurements.

Results and Discussion

To prepare the solutions of different salt dissociation degrees, we used the approach to disperse the PVDF polymer in the solution to form gels. The original idea of polymer dispersion in the solution is to inhibit thermal convection in the solution sample caused by the potential application for the mobility measurement.⁵ During the investigation of gel electrolytes, we found that the dispersed polymer for gelation affects the dissociation condition of the dissolved salt in the solution.^{1,15} Therefore, it is convenient to use gels of different gelation conditions as model samples to estimate the dissociation degree of the salt. In this study, a small amount of polymer up to 15 wt % was dispersed in the solution to form a homogeneous gel. The observed dynamic values are represented in Figure 1. With increasing the polymer fraction, the apparent viscosity increased. However, the diffusion value of the solvent species ($D_{\text{obs(H)}}$), which would reflect the microscopic viscosity, was constant in the measured region. This is apparently different from the monotonic decreasing feature with gelation in the wide range of polymer fraction in the gel.^{1,15} This suggests that the solution viscosity was not affected by the dispersed polymer network in the migration range on the order of a few μm ,¹ independent of the apparent viscosity change. This also indicates that $\alpha = 1$ in eq 13 for all the gels in this range. According to this result and eq 14, the inherent diffusion coefficient ($D_{(\text{cation},\text{anion})}$, D_{pair}) and mobility ($\mu_{(\text{cation},\text{anion})}$) of each species of the gels are still independent of the polymer content in this range.

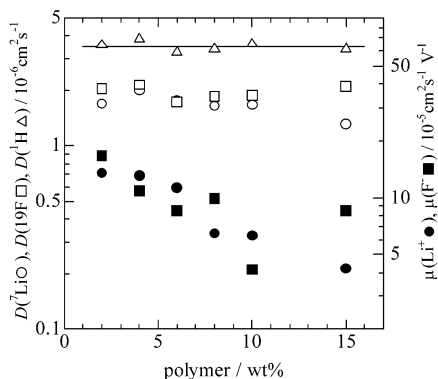


Figure 1. Observed diffusion coefficients (open marks) and mobilities (closed marks) probed by ^1H (Δ), ^7Li (\circ), and ^{19}F (\square) as a function of the dispersed polymer fraction.

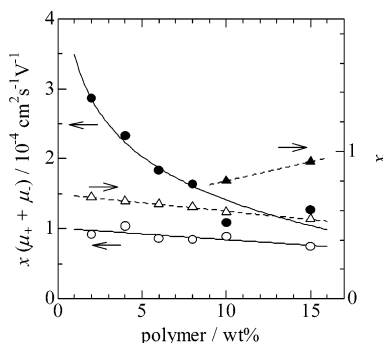


Figure 2. Observed mobility from NMR (\bullet) and the estimated mobility from impedance conductivity (\circ) and the estimated dissociation degree of the salt from NMR mobility (\blacktriangle) and impedance conductivity (\triangle).

The observed diffusion coefficients of the cation and anion species also seem to be constant with the polymer. However, this constant behavior does not mean the same diffusion tendency of the solvent species because $D_{\text{obs(Li,F)}}$ is contributed from two different species, the ion and ion pair as in eq 10, and would be expected to change with x which is affected by the polymer content. We can, rather, conclude that the independence of $D_{\text{obs(Li,F)}}$ from the polymer fraction is accidentally attributed to the relation $D_{\text{cation}} \sim D_{\text{anion}} \sim D_{\text{pair}}$. In practice, the dissociated lithium ion is solvated to be large in size comparable to that of the undissociated ion pair.³ And the dissociated anion of Li-TFSI is comparable to that of the ion pair in size. Of course, with the increase in the solution viscosity which affects the diffusivity of the species and corresponds to $\alpha \neq 1$ in eq 12, $D_{\text{obs(Li,F)}}$ decreases due to the decrease of D_{cation} , D_{anion} , and D_{pair} according to the viscosity increase. That corresponds to the diffusion results of the gel in the polymer-rich region represented in the previous results.^{1,2}

On the other hand, the observed mobility $\mu_{\text{obs(Li,F)}}$ showed a monotonous decreasing feature with the increase in the dispersed polymer content. This change proves the decrease in x of eq 5 with gelation because the inherent μ_{ion} is independent of the polymer fraction from the result of the constant $D_{\text{obs(H)}}$. The dissociation degree of the salt was affected by the dispersed polymer possibly through the interactive effect between the polymer and salt species. If we assume $D_{\text{(cation,anion)}} \sim D_{\text{pair}}$ and $\alpha = 1$, the simple form of eq 16 can be applied for the estimation of the dissociation degree of the salt.

Figure 2 represents the estimated mobility corresponding to $x(\mu_{\text{cation}} + \mu_{\text{anion}})$ from the mobilities measured by NMR and the electric conductivity from the impedance method. Except for the dispersed value due to the measurement error, both values decreased with the polymer content. The discrepancy between

the values was large for the low polymer content, but reduced at a polymer fraction over 8 wt %. The deviation in the mobility by the NMR from that of the conductivity could be explained as follows. The constant potential application by the NMR for ion drifting actually follows the a.c. method with the frequency of ~ 1 Hz by using the polarity inversion technique. On the other hand, at the conductivity measurement using the complex impedance method, the impedance value, which is estimated from the intercept of the spectra to the x -axis, was obtained at the frequency range of 1–10 Hz. Therefore, the frequency conditions for the measurement are the same between the NMR and electrochemical methods. The distinct difference between the two methods is then not attributed to the forms of d.c. and a.c. but the absolute value of the applied potential. The strength of the electric field for the NMR was about 5 V/cm, which is orderly greater than that for the impedance measurement of ~ 0.01 V/cm. We then speculate that the larger value of the mobility from the NMR compared with that estimated from the impedance in the range of small polymer fraction was caused by the instantaneous motion of the charged species which deviated from the ohmic response to the applied electric field. The interface between the solution and the polymer in the gel would motivate the migration of the solution. The electric double layer, which is prepared due to the difference in the chemical potential at the interface, induces the drift of the solution by the application of the direct potential. This motion is essentially different from the response of the charged species to the electric field (electrophoretic effect) and gives an additional drift velocity (electroosmotic effect) which appears clearly under the strong electric field.¹⁶

If we accept the NMR mobility in the range over a 10 wt % polymer dispersion as real, the dissociation degree was estimated to be 0.75–0.90 using eq 15. When we apply the higher mobility values in the range of the lower polymer fraction for this estimation, the dissociation degree of the salt exceeds unity, which is meaningless and also proves the overestimation of the mobility. The estimated value using the observed conductivity was, slightly smaller than that from mobility, 0.55 to 0.70 for the gels over the range of polymer fraction from 2 to 15 wt %. All estimated values of the dissociation degree were plotted in Figure 2. The difference in the absolute value of x estimated from NMR and impedance results is due to the difference in the absolute values of the mobility.

A set of solutions for this evaluation can be prepared by other approaches. One candidate is a set of solutions dissolved in different solvents if it is assumed that the Stokes' radius of the probed species is the same between the solutions. Depending on the dielectric constant and viscosity of the solvent, the dissociation degree of the salt would change. It would be important to confine the dissolved salts to the same one to negate any other effects coming from the morphological difference on α except for the viscosity. The dissociation degree of molten salts (ionic liquids) also depends on their structure. If we select two samples having different dissociation degrees and the same cation or anion, it is possible to use them for the estimation of the static values using the observed diffusion coefficient and mobility.

Conclusions

We theoretically derived correlation between the static value of the dissociation degree of the salt and the dynamic values, diffusion coefficient and mobility. Based on the result, the dissociation degree of the salt was proved to be 0.75–0.90 for

the lithium electrolyte composed of 1 M Li-TFSI/EC-DEC/10–15 wt %PVDF–HFP.

References and Notes

- (1) Saito, Y.; Kataoka, H.; Capiglia, C.; Yamamoto, H. *J. Phys. Chem. B* **2000**, *104*, 2189.
- (2) Saito, Y.; Capiglia, C.; Kataoka, H.; Yamamoto, H.; Ishikawa, H.; Mustarelli, P. *Solid State Ionics* **2000**, *136–137*, 1161.
- (3) Saito, Y.; Yamamoto, H.; Kageyama, H.; Nakamura, O.; Miyoshi, T.; Matsuoka, M. *J. Mater. Sci.* **2000**, *35*, 809.
- (4) Saito, Y.; Kataoka, H.; Stephan, A. M. *Macromolecules* **2001**, *34*, 6955.
- (5) Kataoka, H.; Saito, Y.; Sakai, T.; Deki, S.; Ikeda, T. *J. Phys. Chem. B* **2001**, *105*, 2546.
- (6) Saito, Y.; Kataoka, H.; Deki, S. *J. Electrochem. Soc.* **2001**, *148*, E382.
- (7) Price, W. S.; Kuchel, P. W. *J. Magn. Reson.* **1991**, *94*, 133.
- (8) Holz, M. *Chem. Soc. Rev.* **1994**, 165.
- (9) Clericuzio, M.; Parker, W. O., Jr.; Soprani, M.; Andrei, M. *Solid State Ionics* **1995**, *82*, 179.
- (10) Hayamizu, K.; Aihara, Y.; Arata, S.; Price, W. S. *Solid State Ionics* **1998**, *107*, 1.
- (11) Kataoka, H.; Saito, Y.; Uetani, Y.; Murata, S.; Kii, K. *J. Phys. Chem. B*, submitted.
- (12) West, A. R. in *Solid State Chemistry and its Applications*; John Wiley & Sons: New York, 1985; p 453.
- (13) Atkins, P. W. In *Physical Chemistry*, sixth edition; Oxford University Press: Oxford, 1998; p 740.
- (14) Tanner, J. E. *J. Chem. Phys.* **1970**, *2*, 2523.
- (15) Saito, Y.; Capiglia, C.; Yamamoto, H.; Mustarelli, P. *J. Electrochem. Soc.* **2000**, *147*, 1645.
- (16) Mishchuk, N. A.; Barany, S.; Tarovsky, A. A.; Madai, F. *Colloids Surf.* **1998**, *140*, 43.