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Conductivities of 1,2-dimethoxyethane or 1,2-dimethoxyethane-related solutions of lithium salts

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Abstract

Conductometric studies of highly-concentrated solutions of lithium salts have been carried out in 1,2-dimethoxyethane (DME), a low dielectric and high DN (donor number) solvent. The formation constant of the triple ion has been determined and discussed with respect to that obtained from the measurement in a very dilute solution. Direct determination of the molar conductivity of the triple ion pair has been done and compared to conventionally assumed values. The reason for the increase in the conductivity of Li ion containing propylene carbonate (PC) solutions with the addition of DME is discussed. Preferential solvation of the Li ion by solvents with higher DN is proposed as one important factor. The solvation constants of Li ion by solvents with high DN have been determined.

Introduction

Lithium batteries have been utilized in various fields because of their high energy density at high power drains. This characteristic requires an electrolyte with high ionic conductivity. However, not only solvents with high dielectric constants (ϵ) such as propylene carbonate (PC) but also those with very low ϵ (lower than 10) such as tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and γ-butyrolactone (BL) have been used in primary and secondary Li batteries. The good conductivity of a fairly concentrated Li salt solution in a low ϵ solvent has aroused the attention of researchers. These solvents are also characterized by high donor numbers, DN ($DN > 10$), which makes it possible to dissolve large amounts of Li salts.

The existence of triple ions and dimers has been reported by many authors from conductometric studies in very dilute solutions. This aspect has been reviewed by Salomon [1]. However, very few conductometric studies have been carried out in highly-concentrated solution, perhaps because of the lack of a satisfying theory. The measurements in highly-concentrated solutions should be discussed from a practical point of view.

We have confirmed the existence of triple ions by conductometric studies from the view point of chemical equilibrium in concentrated solutions and obtained larger values for the triple ion formation constant than those obtained from a dilute solution.

In the procedure to determine the formation constant of the triple ion by the measurement in dilute solution, it is necessary to assume a relation between the molar conductivities of the ion pair and triple ion pair, Λ and Λ_T. Some investigators have used the relation $\Lambda = 3\Lambda_T$ [2–4] while others have used $\Lambda = 3/2\Lambda_T$ [5, 6].

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It seemed to us that both relations were made on an arbitrary basis without much discussion, although the values of molar conductivity of the triple ion pair could be calculated from its structure, especially ion size.

Direct determination of molar conductivity of the triple ion pair by taking into consideration that the main ionic species in a fairly-concentrated DME solution of Li ions is a triple ion, makes it possible to discuss the relation between molar conductivity of the ion pair and triple ion pair.

In a later section, the conductivity in the mixed solvent system of PC–DME is discussed. Our goal is to elucidate the reason why a mixed solvent such as PC–DME shows high conductivity even though a low dielectric solvent such as DME present. This solvent mixture is of considerable practical relevance to Li batteries.

Experimental

The purification of the solvents

1,2-dimethoxyethane was refluxed with metallic Na for 12 h, followed by the atmospheric distillation at 83 °C. PC was dehydrated with molecular sieves 4A under the pressure of 1–1.5 torr (133–200 Pa) at 65 to 70 °C. THF, dimethylsulfoxide (DMSO) and acetonitrile (ACN) were refluxed over CaH_2 and were distilled. Propionitrile (PCN) and N,N-dimethylformamide (DMF) were distilled with molecular sieve. After the distillation all the solvents were dried over molecular sieves. Physical properties of the solvents are listed in Table 1. $LiAsF_6$ (Toyama Yakuhin), $LiPF_6$ and $LiBF_4$ (Morita Kagaku) were dried at 50–80 °C at reduced pressure (0.1 torr or 13.3 Pa) for 24 h. After dissolving the Li salts, the solutions were dried again by the Li-type molecular sieves, which prevent the contamination of Na ion from molecular sieves. Lithium-type molecular sieves are prepared as follows: Na ion in molecular sieves as repeatedly replaced by Li ion in an aqueous solution of LiCl by ion exchange; then the molecular sieves were washed with water and dried; water content in the resulting electrolytic solutions were below 40 mg l^{-1}.

Two Kraus-type conductivity cells (cell constant = 0.1 and 0.9 S cm^{-1}) were filled in a dry box and then thermostatted at 25 ± 0.01 °C. Cell constant was calibrated with 0.0100 M aqueous KCl solutions. The conductivity was measured at 1 kHz with Yanagimoto conductivity meter MY-8. Preparations of the electrolyte solutions and the conductivity measurements were carried out in an argon gas filled drybox. Before the measurement, we confirmed the conductivity data of $LiAsF_6$ in DME by Faber

TABLE 1

Physical properties of solvents at 25 °C

Solvent	Viscosity (cP), 25 °C	Dielectric constant, 25 °C	Donor number (DN)
Propylene carbonate (PC)	2.53	67.0	15.1
Acetonitrile (ACN)	0.341	36.0	14.1
Propionitrile (PCN)	0.389	27.2	16.1
1,2-Dimethoxyethane (DME)	0.455	7.20	20.0
Tetrahydrofran (THF)	0.460	7.39	20.0
N,N-Dimethylformamide (DMF)	0.796	36.7	26.6
Dimethylsulfoxide (DMSO)	1.99	46.5	29.8

et al. [5]. Our results, in the same concentration range as theirs, are closely similar to their published data.

Theory, results and discussion

Conductometric studies of fairly-concentrated DME solutions of lithium

According to Fuoss and Kraus [2], the procedure for the determination of the formation constant of a triple ion is as follows:

$$M^+ + L^- = ML \qquad (K_A) \tag{1}$$

$$ML + L^- = LML^- \qquad (K_{T1}) \tag{2}$$

$$ML + M^+ = MLM^+ \qquad (K_{T2}) \tag{3}$$

where K_{ij} on the right hand side of the equations are the equilibrium constants for each step. We neglect the activity coefficient for simplicity. Based on the assumption that $K_{T1} = K_{T2} = K_T$ and that $1 \gg \alpha + 3\alpha_R$, one gets the next relations:

$$K_A = (1-\alpha)/(\alpha^2 C_{ML}) \tag{4}$$

$$K_T = \alpha_T/[\alpha C_{ML}(1-\alpha-3\alpha_T)] \tag{5}$$

$$= \alpha_T/(\alpha C_{ML}) \tag{6}$$

where α and α_T are the degree of dissociated single and triple ions, respectively. The molar conductivity, Λ, is expressed using the molar conductivity of the ion pair, Λ^0, and triple ion pair, $\Lambda_T{}^0$, at infinite dilution as follows:

$$\Lambda = \alpha\Lambda^0 + \alpha_T\Lambda_T{}^0 \tag{7}$$

From eqns. (4) to (7), one gets the next relation:

$$\Lambda(C_{ML})^{1/2} = K_T{}^{-1/2}\Lambda^0 + K_T\Lambda_T{}^0 C_{ML} K_A{}^{-1/2} \tag{8}$$

The plot of $\Lambda(C_{ML})^{1/2}$ versus C_{ML} then gives the equilibrium and conductivity parameters. However, it gives us only the products of the parameters, $K_T{}^{-1/2}\Lambda_T{}^0$ and $K_T\Lambda_T{}^0K_A{}^{-1/2}$. The K_T and $\Lambda_T{}^0$ values are not separately obtained. The relationship, $\Lambda_T{}^0 = \Lambda^0/3$, is often assumed to need the K_T value [2]. This would arise from the consideration that the size of triple ion would be three times that of the single ion according to Stoke's law. Later, the assumption, $\Lambda_T{}^0 = 2/3\Lambda^0$, has been used without reasonable explanation [6].

The conductivity measurement should be done in a very dilute solution using the above procedure [2], because the assumption, $1-\alpha-3\alpha_T = 1$, should be maintained.

We noticed an abnormal relation of concentration dependence of the conductivity especially in the high concentrated region. One of authors (M.Y.) has discussed the conductivities in THF solutions of highly-concentrated aluminum compounds [7, 8]. Reger *et al.* [9] have studied the mechanism of high conductivity of aluminum bromide in toluene and concluded that the dissolution of triple ion from highly aggregates.

Figure 1 shows the relation between specific conductivity and the concentration of the total Li concentration in DME. The logarithmic plot shows that its slope is 0.6 at low concentration and 1.3 in a concentrated range. This shows that the solution state of the ionic species is completely different depending on the Li concentration.

To elucidate this behavior, the next ionization process is proposed as follows:

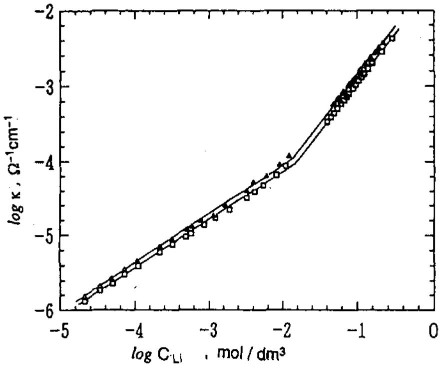


Fig. 1. log κ vs. log C_{Li} plots for (△) $LiAsF_6$ and (□) $LiPF_6$ in DME at 25.0 °C.

$$nML = M^+(ML)_{(n-1)/2} + (ML)_{(n-1)/2}L^- \tag{9}$$

The equilibrium constant is written in the concentration unit:

$$K_S = [M^+(ML)_{(n-1)/2}][(ML)_{(n-1)/2}L^-]/[ML]^n \tag{10}$$

The specific conductivity, κ, is given as follows:

$$10^3\kappa = \lambda^+[M^+(ML)_{(n-1)/2}] + \lambda^-[(ML)_{(n-1)/2}L^-] = \Lambda_M[M^+(ML)_{(n-1)/2}] \tag{11}$$

where λ^+ and λ^- are the ion molar conductivities and Λ_M is the molar conductivity. We could assume these molar and ion conductivities are essentially constant in the examined concentration range and that the concentration of ionic species would be small compared with the total concentration in the low dielectric solvent. Eqn. (11) is then rearranged into the next equation:

$$\log \kappa = 1/2\Lambda_M K + n/2 \log C_{ML} \tag{12}$$

The slope of the plots, log κ versus log C_{ML} would be 0.5 if the main ionic species is a single ion and it would be 1.5 if a triple ion.

The results obtained from Fig. 1 support that the solution state is changed at around 0.01–0.04 M and main conducting ion is a single ion in a dilute and triple ion in a concentrated solution, respectively.

The deviation of the values of slope from 0.5 would be due to the existence of small amounts of triple ions in concentrations lower than 0.01 M. The deviation from 1.5 in concentrations higher than 0.1 M can be explained by the fact that the assumption, $C_{ML} = [ML]$, may not be well satisfied in the presence of many triple ions.

Therefore, we can now determine the formation constant of the triple ions by neglecting the existence of single ions in the concentrated solution. The following equation is considered:

$$3ML = MLM^+ + LML^- \tag{13}$$

The equilibrium constant, K_S, is defined as:

$$K_S = [MLM^+]^2/[ML]^3 \tag{14}$$

$$= [MLM^+]^2/[C_{ML} - 3(MLM^+)]^3 \tag{15}$$

The specific conductivity is expressed as follows:

$$10^3\kappa = \lambda^+[\mathrm{MLM}^+] + \lambda^-[\mathrm{LML}^-] = \Lambda_T[\mathrm{MLM}^+] \qquad (16)$$

Equation (17) is derived from eqns. (15) and (16):

$$C_{ML}/10^3\kappa = 1/(K_S\Lambda_T^2)]^{1/3}(10^3\kappa)^{-1/3} + 3/\Lambda_T \qquad (17)$$

This procedure is essentially the same as the Fuoss and Kraus method. However, it is noteworthy that the concentration of the triple ions in the concentrated solution cannot be neglected. In other words, $1-\alpha-3\alpha_T$ is not 1 in the concentrated solution.

The plots of $C_{ML}/10^3\kappa$ versus $(10^3\kappa)^{-1/3}$ will then give a straight line and the values of Λ_T and K_S are calculated separately. At the same time, our assumptions would be reasonable when the linearity relation is obtained.

Conductivities of highly-concentrated solutions are tabulated in Table 2. Figure 2 shows the plots of $C_{ML}/10^3\kappa$ versus $(10^3\kappa)^{-1/3}$ and the obtained parameters using a least mean square method are listed in Table 3. According to our results, more than 15% of the molecules exist as triple ions at 0.1 M. Therefore, high conductivities of Li salts in a low dielectric and high DN solvents would be due to the existence of a high concentration of triple ions. On the contrary, the values obtained at a dilute solution shows the less amount of existence of triple ion ($K_A = 1\times10^5$, $K_T = 28$) [5] as shown in Table 3.

For $LiAsF_6$ in DME, Faber *et al.* [5] have obtained the values of $\Lambda_T{}^0 = 99.3\ \Omega^{-1}$ cm^2 mol^{-1}, assuming that $\Lambda_T{}^0 = 2/3\Lambda^0$ and that Λ^0 was estimated from the value at

TABLE 2

Specific conductivities of DME solutions of $LiAsF_6$ or $LiPF_6$ at 25.0 °C

$LiAsF_6$		$LiPF_6$	
C (M)	$\kappa\times10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$	*C* (M)	$\kappa\times10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$
0.0480	0.5716	0.0404	0.3375
0.0495	0.5962	0.0451	0.3905
0.0546	0.6709	0.0495	0.4405
0.0566	0.7047	0.0551	0.5073
0.0634	0.8082	0.0615	0.5842
0.0660	0.8534	0.0673	0.6556
0.0754	1.004	0.0727	0.7289
0.0792	1.076	0.0777	0.7946
0.0834	1.135	0.0781	0.8050
0.0880	1.219	0.0886	0.9423
0.0932	1.285	0.0958	1.031
0.0990	1.369	0.104	1.116
0.106	1.519	0.113	1.284
0.112	1.628	0.121	1.419
0.123	1.813	0.125	1.467
0.129	1.953	0.140	1.687
0.145	2.190	0.158	1.953
0.152	2.370	0.160	2.028
0.171	2.679	0.212	2.794
0.176	2.794	0.290	4.196
0.189	3.044		
0.194	3.180		
0.219	3.641		

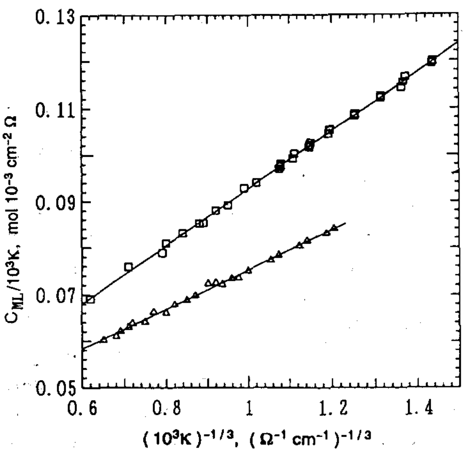


Fig. 2. $C_{ML}/(10^3\ \kappa)$ vs. $(10^3\ \kappa)^{-1/3}$ plots for (△) ML = $LiAsF_6$ and (□) $LiPF_6$ in DME at 25.0 °C.

TABLE 3

Λ_T and K_S values for DME solutions of $LiAsF_6$ or $LiPF_6$ at 25.0 °C

	$LiAsF_6$		$LiPF_6$
Λ_T (Ω^{-1} cm^2 mol^{-1})	91.3 ± 1.2	99.3[a]	97.0 ± 0.9
K_S (dm^3 mol^{-1})	1.57 ± 0.02	0.08[b]	0.448 ± 0.005

[a]Value assumed in ref. 5.
[b]Value calculated from ref. 5 by using the relation, $K_S = K_t^2/K_A$.

infinite dilution in acetonitrile (ACN). As seen in Table 3, the Λ_T value obtained in the study is very close to the assumed value by Faber. The size of the triple ion may be 1.5 times larger than that of a single ion. This means that the size of the triple ion gets smaller than that algebraically expected. Although, Hojo [10] reported by measuring a tertiary ammonium salt in a low dielectric solution that the assumption of $\Lambda_T^0 = 1/3\Lambda^0$ is reasonable. These results show that the values of Λ_T^0 can not be easily assumed, because the size of a triple ion would change depending on the structure of the ions. Much attention should be directed toward the validity of this assumption.

There are discussions to explain the abnormally high conductivities of Li salts in a highly-concentrated and a low dielectric constant solvent.

Ion association constant (K_A) decreases with increase in concentration due to the change in dielectric constant and activity term of the electrolyte [11]. The value of K_A in $LiAsF_6$–DME system is decreased from 4×10^4 at in a infinite dilute solution to 1×10^4 at 0.006 M, according to the their calculations [11]. These show that dissociation of $LiAsF_6$ proceeds with increase in the concentration.

However, their theory extended from the theory established in dilute solution cannot explain the conductometric behavior of a concentrated solution. For example, incredible value of $K_A = 10^{-2000}$ at 0.1 M will be obtained according to their calculation [11]. Otherwise their calculation will lead to the conclusion that the electrolyte, LiAsF$_6$–DME, is a strong electrolyte, for example, having a $K_A = 10^2$ in a concentrated solution. Thus, their approach would not extend to the highly-concentrated solution.

There would be an another way to describe the conductometric behavior in a highly-concentrated solution. The authors have successfully applied a law of mass action under the assumptions. The linear relation between $C_{ML}/10^3$ versus $(10^3\kappa)^{-1/3}$ is obtained in a wide concentration range. This reflects that our assumptions that K_S and Λ_T could be regarded as constant as a first approximation and that a triple ion is main ionic species, would be reasonable.

Conductometric studies of propylene carbonate- or acetonitrile-based mixed solutions of lithium salts

When DME is added to a propylene carbonate (PC) solution of Li salts, a large increase in the conductivities is shown in Fig. 3. The conductivity of the Li salt in a PC–DME mixed solvent shows a maximum for an electrolyte mixture with 50–60 vol.% DME at 1 M of Li. As Matsuda *et al.* [13] have described, the main reason for the initial increase in the conductivity by the addition of DME would be the decrease in viscosity while the decrease in the conductivity at the high DME content would be explained by the decrease in the dielectric constant of the mixed solution.

However, from another point of view, it is considered that specific solvation (preferential solvation) of DME to Li ions comes out in the PC–DME system and it increases the conductivity because of its higher DN.

The effect of the addition of donor solvents (S) on the conductivity of LiBF$_4$ in a PC or an ACN solution will be discussed using the molar ratio method from the view point of specific solvation of donor solvents to Li ion.

The molar ratio method, where the specific conductivity is plotted versus the molar ratio of C_S/C_{Li} in a mixed solution of PC–S under the condition of constant Li concentration, was applied to determine the next formation constants. The relation between solvated ions can be written as follows:

$$\mathrm{Li}^+ + \mathrm{S} = \mathrm{LiS}^+ \ (K_1) \tag{18}$$

$$\mathrm{LiS}^+ + \mathrm{S} = \mathrm{LiS_2}^+ \ (K_2) \tag{19}$$

Hence, Li^+ denotes the Li ion solvated by the solvent with a DN lower than DME (in this case PC or ACN) and LiS^+ and $\mathrm{LiS_2}^+$ denote the solvated Li ion with

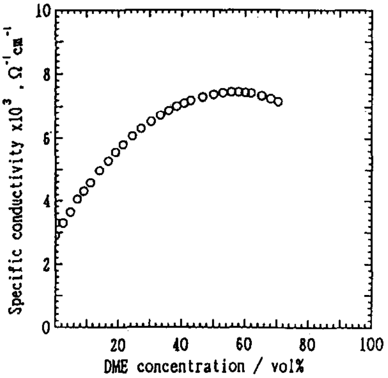


Fig. 3. Specific conductivity of LiBF$_4$ in mixed PC–DME system under the constant concentration of Li (1 M) at 25.0 °C.

the solvent, S, of higher DN (in this case DME or others). C_{Li} and C_S are written as follows:

$$C_{Li} = [Li^+] + [LiS^+] + [LiS_2^+] \tag{20}$$

$$C_S = [S] + [LiS^+] + 2[LiS_2^+] \tag{21}$$

The specific conductivity of the electrolyte is written using each concentration and molar conductivity:

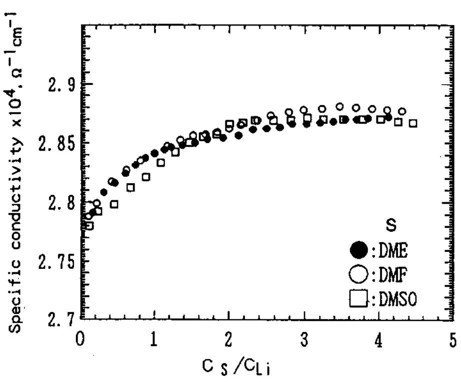
$$10^3\kappa = \lambda_{Li^+}[Li^+] + \lambda_{LiS^+}[LiS^+] + \lambda_{LiS2^+}[LiS_2^+] \tag{22}$$

At first, all the concentrations of the chemical species are calculated from eqns. (18) to (21) using the assumed values of K_1, K_2, λ_{LiS} and λ_{LiS_2}. The specific conductivities can then be calculated from eqn. (22). This procedure is repeated, using a computer, until the difference between the calculated and measured values are within the set minima.

During the experiments, the concentration of Li is maintained at 10^{-2} M in the PC–S mixed solution and 10^{-3} M in the ACN–S mixed solution. The concentration of associated species (ion pair) can be neglected under these conditions. The change in the viscosity and dielectric constant are very small during the measurements, because the amount of the second solvent (S) is less than 0.2%.

The conductometric titration of PC or ACN solutions of $LiBF_4$ with various donor solvents (S) under constant Li concentration is shown in Figs. 4 and 5. An initial increase in the conductivity in Figs. 4 and 5 is mainly due to the formation of solvated species like LiS^+.

A typical computer analysis is shown in Fig. 6. A rapid increase in the conductivities of PC solutions by the addition of DME is related to the formation of the solvated species, $Li(DME)^+$. The formation constant between Li and DME in PC solution, K_1, and ion molar conductivity, λ_{LiS}, was found to be 8.8×10^2 l mol^{-1} and 28.7 Ω^{-1} cm^{-1}, respectively. The existence of the 1:2 complex, LiS_2^+, cannot be confirmed.



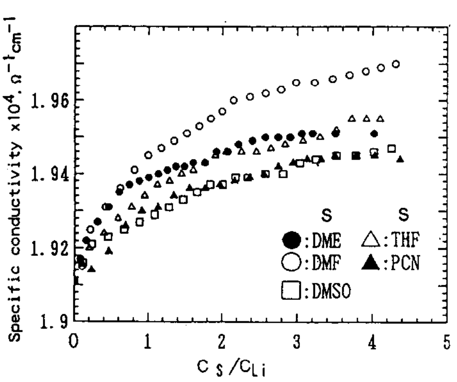
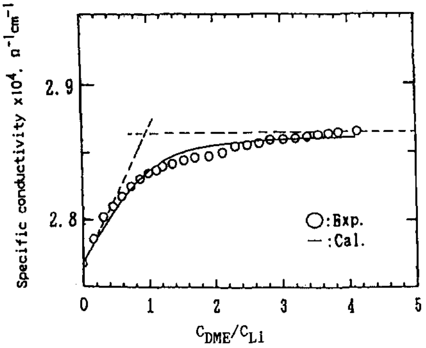


Fig. 4. Specific conductivity vs. molar ratio of C_S/C_{Li} under the constant concentration of C_{Li} = 0.01 M in PC at 25.0 °C.

Fig. 5. Specific conductivity vs. molar ratio of C_S/C_{Li} under the constant concentration of C_{Li} = 0.001 M in ACN at 25.0 °C.



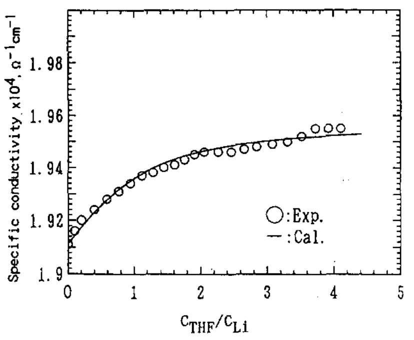


Fig. 6. Calculated and experimental curves of specific conductivity vs. molar ratio of C_{DME}/C_{Li} under the constant concentration of $C_{Li}=0.01$ M in PC at 25.0 °C, calculated using $K_1=8.8\times10^2\pm5\times10^1$ l mol^{-1} and $\Lambda_{LiS^+}=28.7\pm6$ Ω^{-1} cm^2 mol^{-1}.

Fig. 7. Calculated and experimental curves of specific conductivity vs. molar ratio of C_{THF}/C_{Li} under the constant concentration of $C_{Li}=0.001$ M in ACN at 25.0 °C, calculated using K_1, K_2, Λ_{LiS^+}, $\Lambda_{LiS_2^+}$: $K_1=2.0\times10^3\pm3\times10^2$ l mol^{-1}; $K_2=2.0\times10^2\pm3\times10^1$ l mol^{-1}; $\Lambda_{LiS^+}=196\pm30$ Ω^{-1} cm^2 mol^{-1}; $\Lambda_{LiS_2^+}=195\pm30$ Ω^{-1} cm^2 mol^{-1}.

TABLE 4

Formation constant, K_1, and molar conductivities, Λ_{LiS^+}, for LiS$^+$ complexes in PC and ACN at 25.0 °C

Solvent PC	K_1 ($C_{Li}=0.01$ M)	Λ_{LiS^+} ($C_{Li}=0.01$ M)	Λ_{LiPC^+} ($C_{Li}=0.01$ M)
DME	$8.8\times10^2\pm5\times10^1$	28.7 ± 6	27.7
DMF	$7.7\times10^2\pm9\times10^1$	28.7 ± 5	27.7
DMSO	$2.2\times10^2\pm4\times10^1$	28.8 ± 5	27.7
Solvent ACN	**K_1 ($C_{Li}=0.001$ M)**	**Λ_{LiS^+} ($C_{Li}=0.001$ M)**	**Λ_{LiACN^+} ($C_{Li}=0.001$ M)**
PCN	$1.3\times10^3\pm2\times10^2$	195 ± 30	191
THF	$2.3\times10^3\pm4\times10^2$	196 ± 30	191
DME	$5.9\times10^3\pm2\times10^2$	196 ± 30	191
DMF	$5.7\times10^3\pm3\times10^2$	197 ± 40	191
DMSO	$1.2\times10^3\pm2\times10^2$	196 ± 30	191

This shows that counter anions in a lower DN solvents can be easily replaced by solvent molecules with higher DN. So, this covalent interactions would decrease the association constant of Li salts in the lower DN solvent.

The conductometric study of LiClO$_4$ in very dilute DME solutions showed the existence Li(DME)$_2{}^+$ at infinite dilute solution as suggested by Matsuda [12]. The solution state of Li ions in a concentrated solution would be different from that in a dilute solution. However, for some cases, we got the value of K_2, which is shown in Fig. 7. THF is a monodendate ligand and DME is a bidendate ligand. So, the THF complex makes a 1:2 complex, Li(THF)$_2{}^+$, although the calculation is possible by taking into consideration only the existence of the 1:1 complex as shown in Table 4.

The DN value of the solvent is defined as the enthalpy change (kcal mol^{-1}) when $SbCl_5$ is reacted with the solvents. If we assume that the enthalpy change, when the Li ion is transferred from the lower DN solvent to the higher DN solvent, is the same as that in the case of $SbCl_5$, we can roughly calculate the formation constant in PC–S solution using the relation $\Delta G = -RT \ln K$. The formation constant in PC–DME (difference of DN = 5 is corresponding to 5 kcal mol^{-1}) would be $10^{3.7}$ under the condition of neglecting the entropy term. Formation constant obtained in our measurement are in the range of 10^3 to 10^4, while DNs are in the range of 5 to 14. This result means one of the important factors that determines the formation constant would be the DN of the solvent, nevertheless the calculated values from DN not fully coincide with the experimental values.

Conclusions

Triple ion formation constants of two Li salts in a low dielectric and high DN solvent, DME, are determined from the view point of equilibrium in a highly-concentrated solutions of by conductivity measurements. The method proposed here enables direct measurement of the molar conductivity of triple ion, while its value have been arbitrary assumed without reasonable explanation.

The reason why the conductivity of the Li salts in a high dielectric solvent such as PC is increased by the addition of low dielectric – but high DN solvent such as DME, THF, etc. – is elucidated from the view point of coordination chemistry.

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