

Relationship between Triple Ion Formation Constants and the Salt Concentration of the Minimum in the Conductometric Curves in Low-Permittivity Solvents

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Conductivities of a number of uni-univalent salts, including tetrabutylammonium and lithium nitrophenolates, were measured at 25.0 °C in low-permittivity solvents such as tetrahydrofuran (THF, $\epsilon_r = 7.58$), 1,2-dimethoxyethane (DME, 7.2), chloroform (4.8), and ethyl acetate (6.0). Minima in the conductometric curves ($\Lambda - C^{1/2}$) were observed for concentrations which were dependent upon both the salt and the solvent, $C_{\min} = 1.73 \times 10^{-4} \text{ mol dm}^{-3}$ for 2,4-(NO₂)₂C₁₀H₅OLi (lithium 2,4-dinitro-1-naphtholate) in THF and $2.56 \times 10^{-2} \text{ mol dm}^{-3}$ for LiPic (lithium picrate) in DME. The observed molar conductivities including C_{\min} could be completely explained by the formation of ion pairs ($M^+ + X^- \rightleftharpoons MX$, K_1), “symmetrical” triple ions ($2M^+ + X^- \rightleftharpoons M_2X^+$, K_2 ; $M^+ + 2X^- \rightleftharpoons MX_2^-$, K_3 ; $K_2 = K_3$), and (in some cases) additional formation of quadrupoles ($2MX \rightleftharpoons M_2X_2$, K_{41}). A linear relationship (the slope of -1) between the triple ion formation constants ($\log(K_2/K_1)$) and the salt concentrations at the minimum ($\log C_{\min}$) was given for all the salts in the various solvents, except for some systems in which a distinct formation of quadrupole takes place, e.g., LiNO₃ in DME ($K_1 = 3.16 \times 10^{10}$, $K_2 = 4.5 \times 10^{13}$, and $K_{41} = 35$). The formation of triple ions might be attributed to the ion sizes in solutions in which Coulombic interactions were the only main forces between ions ($R_4N^+ \cdots X^-$). However, coordination (or covalent) bonding forces as well as Coulombic forces had to be considered for the lithium salts except for LiClO₄ and LiBF₄. Gutmann’s donor and acceptor numbers of solvents (and not the permittivity) accounted for the larger difference of C_{\min} of lithium salts in THF and DME. In mixed solvents of THF and 2-ethyl-1-hexanol ($\epsilon_r = 7.58$), the C_{\min} values of LiNO₃ and 2,4-(NO₂)₂C₁₀H₅OLi increased with increasing contents of the hexanol, whereas the C_{\min} values of LiClO₄ and Bu₄NX ($X^- = \text{NO}_3^-$, 2,4-(NO₂)₂C₁₀H₅O⁻, and ClO₄⁻) remained constant for 0–30 vol % hexanol added to THF. The positive shifts in C_{\min} were explained quantitatively by the decrease in triple ion formation constants and/or by an increase in the quadrupole formation constants.

Introduction

In media of low permittivity, salts are generally so associated that the states of the ionic species in solutions are most difficult to elucidated. A number of conductometric¹ and related studies of electrolytes in nonaqueous solvents have been done, by the use of this type of electrolyte in high-energy batteries² and for further understanding of organic reaction mechanism.³

As early as 1933, Fuoss and Kraus⁴ proposed the concept of “symmetrical” triple ions, based on the electrostatic interaction between (spherical) ions in low-permittivity media. The minima observed in conductometric curves ($\Lambda - C^{1/2}$) in low-permittivity solvents ($\epsilon_r < 10$) were interpreted by the formation of this kind of species.⁵ However, some investigators have explained the appearance of conductometric minima in other ways.⁶ The controversy has not yet been settled, although conductometric theories for higher ionic fields have been sophisticatedly developed.⁷ In 1975, Fuoss⁸ improved the Fuoss–Hsia equation and related theories⁷ and noted that “it may not be applied to data for solvents of dielectric constants lower than about 10, even if the salt concentration (max) is less than $2 \times 10^{-4} \text{ mol dm}^{-3}$, because interionic Coulomb forces become strong enough to produce overlap of three or more cospheres”. Petrucci and Eyring⁹ proposed a theory based upon multibody interactions and activity coefficients of ion pairs less than unity.

In a number of studies, we have been able to explain the conductivity data of many univalent salts in solvents of higher permittivity ($20 < \epsilon_r < 65$) of poor solvation ability in terms

of the ion pairs (MX), triple ions (M_2X^+ , MX_2^-), and quadrupoles (M_2X_2).¹⁰ The role of solvation upon triple ion formation has been shown by conductivity studies in mixed solvents of isopermittivity.¹¹ Our analytical method^{10,11} is based on a rather primitive conductometric theory, Onsager’s limiting law for correcting the effects of ionic atmosphere due to the rather low concentrations of ionic species in the protophobic aprotic solvents. We would like to stress that the M_2X^+ type of species seem to exist in poorly solvating media¹² through hydrogen bonding and coordination (or covalent) bonding forces, instead of “possible” Coulombic repulsion. Recently, Barthel et al.¹³ critically commented on the M_2X^+ species.

In the present study the conductivity of uni-univalent salts was examined in low-permittivity solvents with a variety of solvation abilities, tetrahydrofuran (THF, $\epsilon_r = 7.58$,¹⁴ Gutmann’s DN = 20.0 and AN = 8.0¹⁵), 1,2-dimethoxyethane (DME, $\epsilon_r = 7.2$, DN = 23.9, and AN = 10.2), chloroform ($\epsilon_r = 4.8$ at 20 °C, DN = ~ 0 , and AN = 23.1), and ethyl acetate ($\epsilon_r = 6.0$, DN = 17.1, and AN = 9.3). Dichloromethane (CH₂Cl₂, $\epsilon_r = 8.93$) and 1,2-dichloroethane ($\epsilon_r = 10.4$) were also briefly used. The effects of solvation abilities in isopermittivity media were examined in mixed solvents between THF and 2-ethyl-1-hexanol ($\epsilon_r = 7.58$ ¹⁶). The molar conductivities were analyzed by our previously discussed method.^{10,11} The formation constants of the ion pair ($M^+ + X^- \rightleftharpoons M^+X^-$, K_1), triple ions ($2M^+ + X^- \rightleftharpoons (M^+)_2X^+$, K_2 ; $M^+ + 2X^- \rightleftharpoons M^+(X^-)_2$, K_3), and the quadrupoles ($2MX \rightleftharpoons M_2X_2$, K_{41}) were considered. The equilibrium concentration of X^- ($[X] = [M]$) at a given salt concentration (C_s) can be found by solving a fourth-order equation when $K_2 = K_3$.

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$$2K_4K_1^2[X]^4 + 3K_2[X]^3 + K_1[X]^2 + [X] - C_s = 0 \quad (1)$$

The equilibrium concentrations of the ion pair, triple ions, and the quadrupole are $[MX] = K_1[X]^2$, $[M_2X] = K_2[X]^3 = [MX_2] = K_3[X]^3$, and $[M_2X_2] = K_4K_1^2[X]^4$, respectively. The whole molar conductivity ($\Lambda/\text{S cm}^2 \text{ mol}^{-1}$) is expressed by

$$\Lambda = \Lambda_0'[X]/C_s + \Lambda_T'[MX_2]/C_s \quad (2)$$

where Λ_0' and Λ_T' are the limiting conductivity of simple ions ($[M^+, X^-]$) and of triple ions ($[M_2X^+, MX_2^-]$) when corrected by Onsager's limiting law. Activity coefficients of the ions were estimated by the Debye-Hückel equation with $a = 4 \text{ \AA}$, and those of uncharged species were taken to be unity. The Λ_0 values of the salts in the low permittivity media were evaluated from the data in acetonitrile¹⁰ by means of Walden's rule. The Λ_T/Λ_0 value was taken as 0.693. The formation of other species (such as $M_3X_2^+$, $M_2X_3^-$, and M_3X_3) was not considered.

Experimental Section

Commercially obtained tetrahydrofuran (THF, Wako Pure Chemical GR grade, nonstabilizer 99.5+%), 1,2-dimethoxyethane (DME, Wako GR grade), and ethyl acetate (Wako GR grade) were distilled from freshly activated 3A molecular sieves (Wako) added to the supernatant after drying with molecular sieves for several days. The specific conductance of purified THF, DME, and ethyl acetate were $\sim 5 \times 10^{-9} \text{ S cm}^{-1}$. Chloroform (Wako GR grade), dichloromethane (Wako ∞ Pure grade), and 1,2-dichloroethane (DCE, Wako GR grade) were used as received. 2-Ethyl-1-hexanol (Wako GR grade) was used without further purification. The purification method of acetonitrile was mentioned previously.¹⁰ Lithium 2,4-dinitrophenolate (2,4-(NO₂)₂C₆H₃OLi), 2,5-dinitrophenolate (2,5-(NO₂)₂C₆H₃OLi), picrate (LiPic), 2,4-dinitro-1-naphtholate (2,4-(NO₂)₂-C₁₀H₅OLi), and the corresponding tetrabutylammonium salts were prepared as described previously.¹⁰ The lithium and tetrabutylammonium salts were dried in vacuo over P₂O₅ at 160 and 80 °C, respectively. The preparation of tetrabutylammonium *p*-toluenesulfonate (Bu₄NCH₃C₆H₃SO₃), methanesulfonate (Bu₄NCH₃SO₃), bromide, and perchlorate has also been described.¹⁰ Lithium tetrafluoroborate (LiBF₄, Aldrich 99.999%), LiClO₄ (Wako GR grade), and LiNO₃ (Wako 99.9%) were dried in vacuo over P₂O₅ at 100, 60, and 200 °C, respectively. Tetrabutylammonium chloride (TCI GR grade), iodide (Wako GR grade), thiocyanate (Fluka >99%), nitrate (Fluka >98%), and tetrahexylammonium perchlorate (Hex₄NClO₄, Fluka) were used as received or after drying at 60 °C. Sodium perchlorate (monohydrate, Wako GR grade) and LiBr (monohydrate, Wako GR 99.5%) were dried in vacuo over P₂O₅ at 200 and 180 °C, respectively. Lithium chloride (anhydrous, Wako 99.9%) was dried at 100 °C in a similar way.

Electrical conductances were measured at $25 \pm 0.02 \text{ }^\circ\text{C}$ with a Hewlett Packard LCR meter (Model 4263A) in a Yanagimoto conductivity cell with a cell constant of 0.2902. Concentrated solutions (e.g., 0.3 mol dm^{-3}) were added with a Hamilton gastight syringe to the cell containing a 14.0 mL solvent; however, the dilution method was employed when the solubility of salts was not high enough. Viscosities of the mixtures between THF and 2-ethyl-1-hexanol were measured using Sibata viscosimeters (Ubbelohde type) and Vidrex pycnometers (Ostwald type) at $25 \pm 0.02 \text{ }^\circ\text{C}$. The viscosities of 0, 2.0, 5.0, 10, 20, 30, and 50 vol % hexanol to THF were 0.46, 0.474, 0.494, 0.528, 0.605, 0.743, and 1.048 cP (1 P = 0.1 Pa s) respectively. The permittivity of the mixtures was assumed to be constant ($\epsilon_r = 7.58$). The specific conductances of mixed solvents (≤ 30

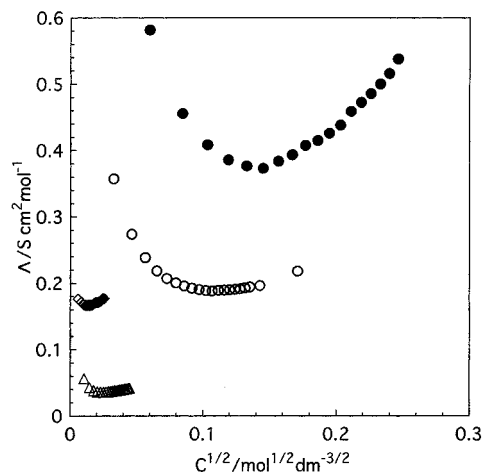


Figure 1. Observed molar conductivities (Λ) in THF at 25 °C: (●) LiClO₄; (○) LiPic; (◇) 2,4-(NO₂)₂C₁₀H₅OLi; (△) LiNO₃.

vol %) were sufficiently small ($< 6 \times 10^{-9} \text{ S cm}^{-1}$). The calculations were based upon the assumption that ϵ_r was constant and independent of the concentration of the electrolytes. Possible alteration of these results might be feasible if the changes in the permittivity of the solution with concentration (up to $\sim 0.05 \text{ mol dm}^{-3}$) were to be available and retained in the calculations.

Results and Discussion

In THF, DME, Chloroform, and Ethyl Acetate. Figure 1 shows the observed molar conductivity ($\Lambda/\text{S cm}^2 \text{ mol}^{-1}$) of the lithium salts in THF at 25 °C. The salt concentrations of minima (C_{\min}) of LiClO₄, LiPic (picrate), 2,4-(NO₂)₂C₁₀H₅OLi (2,4-dinitro-1-naphtholate), and LiNO₃ were 2.11×10^{-2} , 1.14×10^{-2} , 1.73×10^{-4} , and $6.30 \times 10^{-4} \text{ mol dm}^{-3}$, respectively (cf. Table 6). Jagodzinski and Petrucci¹⁷ have reported a minimum for LiClO₄ in THF at a similar concentration. In the same solvent, tetrabutylammonium perchlorate, picrate, 2,4-dinitro-1-naphtholate, and nitrate gave more broad minima at rather similar concentrations, i.e., 1.11×10^{-2} , 1.22×10^{-2} , 1.23×10^{-2} , and $1.13 \times 10^{-2} \text{ mol dm}^{-3}$. The C_{\min} values of 2,4-(NO₂)₂C₁₀H₅Bu₄N and Bu₄NO₃ were much higher than observed for the lithium salts; the C_{\min} values of Bu₄NClO₄ and Bu₄NPic, however, were similar to those of their lithium salts.

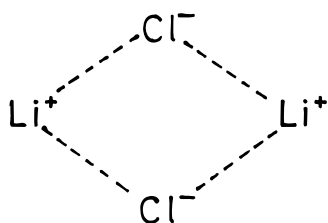
The observed molar conductivities of LiPic (cf. Table 7) were analyzed by our method.^{10,11} The Λ values at lower salt concentrations could be fitted by only considering the ion pair formation constant ($K_1 = 1.02 \times 10^8$): -0.02% and -6.6% relative error of the calculated Λ to the observed Λ value at 1.1×10^{-3} and $2.1 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. However, the calculated Λ deviated negatively as the salt concentration increased, e.g., -66.3% relative error at $C = 2.9 \times 10^{-2} \text{ mol dm}^{-3}$. The cause of the large negative error was attributed to the neglect of higher aggregates. The calculations including ion pairs ($K_1 = 1.18 \times 10^8$) and triple ions ($K_2 = K_3 = 1.08 \times 10^{10}$, $K_2/K_1 = 91.8$) accounted for the experimental Λ value in the whole concentration range. The relative error was less than $\pm 1.1\%$ for each experimental point in $\Delta C = (0.11-2.9) \times 10^{-2} \text{ mol dm}^{-3}$, cf. Table 1. The Shedlovsky analysis¹⁸ of the conductivities of LiPic in THF was not successful: the limiting molar conductivity (Λ_0) and an association constant (K_a) could not be obtained. Therefore, by employing the Walden rule using a Λ_0 value of (151.9)¹⁰ in MeCN ($\eta = 0.3409 \text{ cP}$) at 25 °C, the Λ_0 value of LiPic in THF (viscosity, $\eta = 0.460 \text{ cP}$) was evaluated to be 112.57 at 25 °C.

TABLE 1: Formation Constants K_1 , $K_2 = K_3$, and K_{41} in THF at 25.0 °C

	K_1	K_2	K_{41}	(K_2/K_1)	$10^3 \times \Delta C^a$	rel. error ^b /%	Λ_0^c
LiNO ₃	7.5×10^{10}	1.48×10^{14}		1973.3	0.21–1.81	–2.48–+2.24	130.69
LiBr	3.36×10^{10}	2.15×10^{13}	50	639.9	0.4–5.0	–1.00–+1.10	126.73
2,4-(NO ₂) ₂ C ₆ H ₃ OLi	1.17×10^{10}	1.0×10^{14}		8547	0.07–0.34	–2.92–+2.97	112.2
LiBF ₄	2.0×10^8	1.27×10^{10}		63.5	3.7–63.0	–2.96–+2.93	130.36
LiPic	1.18×10^8	1.08×10^{10}		91.8	1.1–29.0	–1.13–+1.10	112.57
LiClO ₄	2.2×10^7	9.8×10^8		44.5	3.6–41.0	–3.66–+3.79	128.5
Bu ₄ NCl	2.96×10^7	1.0×10^{10}	11	337.8	2.2–10.0	–2.02–+1.88	120.72
Bu ₄ NCH ₃ SO ₃	2.32×10^7	5.55×10^9		239.2	1.1–15.0	–1.19–+1.39	112.72
Bu ₄ NBr	1.8×10^7	6.0×10^9	18	333.3	1.4–20.0	–1.80–+1.90	121.98
Bu ₄ NNO ₃	4.8×10^6	6.0×10^8	4.5	125	2.1–20.0	–2.58–+2.47	125.95
Bu ₄ NClO ₄	1.42×10^6	1.50×10^8	7.3	105.6	1.4–27.0	–0.84–+1.11	123.76
Hex ₄ NClO ₄	1.42×10^6	1.2×10^8		84.5	1.4–19.0	–1.22–+1.28	116.42
2,5-(NO ₂) ₂ C ₆ H ₃ OBu ₄ N	9.82×10^5	1.0×10^8	5	101.8	2.1–20.0	–1.23–+1.27	106.49
2,4-(NO ₂) ₂ C ₆ H ₃ OBu ₄ N	3.05×10^5	2.13×10^7		69.8	2.1–15.0	–0.82–+0.61	103.6
Bu ₄ NPic	2.8×10^5	1.63×10^7		58.2	1.8–16.0	–1.05–+1.13	103.38

^a The concentration range (mol dm^{–3}) examined. ^b The relative error in the calculated Λ value to the observed Λ value over the concentration range examined. ^c The limiting molar conductivity (S cm² mol^{–1}) calculated by the Walden rule with the Λ_0 in MeCN.

SCHEME 1: Quadrupole from LiCl in THF



The formation constants for other salts in THF are also listed in Table 1. The conductivity of many salts could be explained by formation of the ion pair and triple ion; in some cases, also by the additional quadrupole formation. The tendency of triple ion formation can be judged from the K_2/K_1 ratios ($MX + M^+ \rightleftharpoons M_2X^+$, K_2/K_1). This ratio was about 100 or slightly less than that for the tetrabutylammonium salts, except for the chloride, the bromide, and the methanesulfonate being from 240 to 340. The K_2/K_1 ratios of LiBF₄, LiPic, and LiClO₄ were also less than 100, although the calculated ion pair formation constants (K_1) were larger than those of the Bu₄N⁺ salts. However, K_1 and the K_2/K_1 ratios of LiNO₃ ($K_1 = 7.5 \times 10^{10}$ and $K_2/K_1 = \text{ca. } 2 \times 10^3$) and 2,4-(NO₂)₂C₆H₃OLi ($K_1 = 1.17 \times 10^7$ and $K_2/K_1 = \text{ca. } 8.5 \times 10^3$) were much larger than for the other salts. The large association between Li⁺ and the oxygen atom in the naphtholate or NO₃[–] cannot be explained by the Coulombic interaction alone, but by additional interactions, such as the coordination (or covalent) bonding forces, considering ionic sizes of the species in the solution. We have noticed that the salts with large K_2/K_1 ratios have also the lower C_{\min} values (vide infra). By the way, the minimum of LiCl in THF was not observed for $\Delta C = (0.4\text{--}18) \times 10^{-3}$ mol dm^{–3}. The formation constants for LiCl were evaluated from the experimental conductivities at lower concentrations ($\Delta C = (0.4\text{--}4.0) \times 10^{-3}$ mol dm^{–3}), leading to $K_1 = 2.8 \times 10^{10}$, $K_2 = K_3 = 1.2 \times 10^{13}$, and $K_{41} = 7 \times 10^3$. The equilibrium concentrations of simple ions ($[Li^+] = [Cl^-]$), the ion pairs ($[LiCl]$), the triple ions ($[(Li^+)_2Cl^-] = [Li^+(Cl^-)_2]$), and the quadrupoles ($[Li_2Cl_2]$) were estimated to be 9.28×10^{-8} , 2.3×10^{-4} , 0.92×10^{-8} , and 3.8×10^{-4} mol dm^{–3}, respectively, at $C_s = 1.0 \times 10^{-3}$ mol dm^{–3}. The large quadrupole formation (cf. Scheme 1) depressed definitely the formation of triple ions, compared with simple ions. Vapor-phase osmometric¹⁹ and NMR²⁰ studies have shown that LiCl is aggregated in THF. Stronger quadrupole formation with lower temperature has been reported for sodium diphenyl phosphate ($Na^+(PhO)_2PO_2^-$) in acetone.²¹

Figure 2 shows the equilibrium concentrations of the various species related to the salt concentrations (C_s) of LiPic in THF

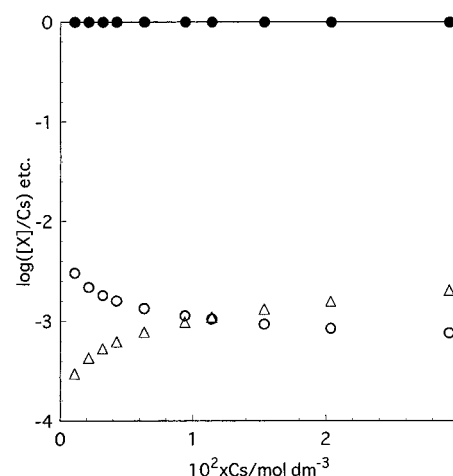


Figure 2. Changes of the ratio of each species with the LiPic concentration in THF: (○) simple ions; (●) the ion pair; (Δ) triple ions.

at 25°C. With increasing salt concentration, the equilibrium concentration of simple ions decreases, while the concentration of the triple ions increases, the concentration of the ion pair being the predominant species over the whole C_s range. At the conductance minimum ($C_{\min} = 1.144 \times 10^{-2}$ mol dm^{–3}), the equilibrium concentrations of simple ions ($[M^+] = [X^-]$), the ion pair ($[MX]$), and triple ions ($[M_2X^+] = [MX_2^-]$) were calculated to be 1.19×10^{-5} (0.10%), 1.139×10^{-2} (99.6%), and 1.24×10^{-5} mol dm^{–3} (0.11% or 0.3% as MX), respectively.

In 1,2-dimethoxyethane (DME), lithium 2,4- and 2,5-dinitrophenolates gave minima at low salt concentrations, 3.49×10^{-3} and 6.27×10^{-3} mol dm^{–3}, respectively. In THF the C_{\min} values were too low to be observed. The formation constants of 2,4-(NO₂)₂C₆H₃OLi in DME were evaluated to be 2.65×10^9 , $K_2 = 3.75 \times 10^{12}$ ($K_2/K_1 = 1.4 \times 10^3$), and $K_{41} = 70$; those of 2,5-(NO₂)₂C₆H₃OLi were 1.43×10^9 , $K_2 = 4.0 \times 10^{11}$ ($K_2/K_1 = 2.8 \times 10^2$), and $K_{41} = 4$ (cf. Table 2). The difference in C_{\min} values and the formation constants of 2,4- and 2,5-derivatives in DME may be caused by the degree of delocalization of the negative charge in the anions.

The C_{\min} value of 2,4-(NO₂)₂C₆H₃OLi of 1.73×10^{-4} mol dm^{–3} ($K_2/K_1 = 8.5 \times 10^3$) in THF (vide supra) was observed at much larger concentration than in DME, 7.20×10^{-3} mol dm^{–3} ($K_2/K_1 = 2.6 \times 10^2$) in DME; the difference in C_{\min} of LiPic in the two solvents was less significant (cf. Table 6). Another example of the large change in C_{\min} from THF to DME was LiNO₃: from 6.30×10^{-4} mol dm^{–3} to 2.42×10^{-3} mol

TABLE 2: Formation Constants K_1 , $K_2 = K_3$, and K_{41} in DME at 25.0 °C

	K_1	K_2	K_{41}	(K_2/K_1)	$10^3 \times \Delta C^a$	rel. error ^b /%	Λ_0^c
LiNO ₃	3.16×10^{10}	4.5×10^{13}	35	1424.1	0.5–6.0	–2.19–+2.39	132.13
2,4-(NO ₂) ₂ C ₆ H ₃ OLi	2.65×10^9	3.75×10^{12}	70	1415.1	0.5–6.0	–1.87–+1.16	113.96
2,5-(NO ₂) ₂ C ₆ H ₃ OLi	1.43×10^9	4.0×10^{11}	4	279.7	1.4–13.0	–1.89–+1.40	116.73
2,4-(NO ₂) ₂ C ₁₀ H ₅ OLi	9.26×10^8	2.43×10^{11}	5	262.4	1.4–12.1	–1.12–+1.05	113.43
LiPic	6.01×10^7	2.23×10^9		37.1	2.1–38.0	–0.06–+0.29	113.81
Bu ₄ NCH ₃ SO ₃	1.11×10^7	2.4×10^9	5.7	216.2	1.4–13.0	–0.88–+0.84	113.96
LiClO ₄	2.87×10^6	9.15×10^7		31.9	3.6–34.0	–0.47–+0.37	129.92
Bu ₄ NNO ₃	2.82×10^6	3.2×10^8	7	113.5	2.1–20.0	–2.26–+2.50	127.33
2,5-(NO ₂) ₂ C ₆ H ₃ OBu ₄ N	1.38×10^6	1.3×10^8	3	94.2	3.0–28.0	–1.87–+2.52	107.66
Hex ₄ NClO ₄	1.05×10^6	1.0×10^8	3.6	95.2	1.4–19.0	–0.73–+1.21	117.7
Bu ₄ NClO ₄	9.8×10^5	1.1×10^8	12	112.2	1.4–19.0	–0.86–+0.62	125.12
Bu ₄ NPic	2.6×10^5	1.58×10^7		60.8	1.1–13.0	–1.11–+1.0	104.52

^a The concentration range (mol dm^{–3}) examined. ^b The relative error in the calculated Λ value to the observed Λ value over the concentration range examined. ^c The limiting molar conductivity (S cm² mol^{–1}) calculated by the Walden rule with the Λ_0 in MeCN.

TABLE 3: Formation Constants K_1 , $K_2 = K_3$, and K_{41} in Chloroform at 25.0 °C

	K_1	K_2	K_{41}	(K_2/K_1)	$10^3 \times \Delta C^a$	rel. error ^b /%	Λ_0^c
Bu ₄ NCH ₃ PhSO ₃	4.07×10^8	1.64×10^{11}		403	0.72–6.8	–0.73–+0.62	88.07
Bu ₄ NCH ₃ SO ₃	2.62×10^8	5.45×10^{10}		208	0.71–6.6	–0.84–+0.72	96.79
Bu ₄ NNO ₃	2.173×10^8	1.013×10^{11}	3	466	0.36–3.4	–0.99–+0.96	108.15
Bu ₄ NClO ₄	2.09×10^8	1.27×10^{11}	3	608	0.71–6.0	–0.75–+0.45	106.27
Bu ₄ NCSN	1.928×10^8	7.85×10^{10}		407	0.72–6.7	–0.51–+0.51	113.92
Bu ₄ NBr	1.75×10^8	5.57×10^{10}		318	0.72–6.7	–0.43–+0.61	104.75
Hex ₄ NClO ₄	1.74×10^8	1.05×10^{11}		603	0.35–3.3	–0.69–+0.79	99.97
Bu ₄ NCI	1.615×10^8	3.85×10^{10}		238	0.71–6.6	–0.45–+0.20	103.66
Bu ₄ NI	1.36×10^8	5.15×10^{10}		379	0.6–6.0	–0.83–+0.77	104.43
Bu ₄ NPic	2.54×10^7	4.92×10^9		194	0.72–6.7	–0.15–+0.07	88.77

^a The concentration range (mol dm^{–3}) examined. ^b The relative error in the calculated Λ value to the observed Λ value over the concentration range examined. ^c The limiting molar conductivity (S cm² mol^{–1}) calculated by the Walden rule with the Λ_0 in MeCN.

TABLE 4: Formation Constants K_1 and $K_2 = K_3$ in Ethyl Acetate at 25.0 °C

	K_1	K_2	(K_2/K_1)	$10^3 \times \Delta C^a$	rel. error ^b /%	Λ_0^c
LiPic	2.14×10^9	5.6×10^{11}	261.7	2.1–13.0	–0.91–+0.71	121.56
NaClO ₄	9.75×10^8	7.3×10^{10}	74.9	2.9–25.0	–1.22–+1.09	143.24
NaPic	8.45×10^8	1.0×10^{11}	118.3	1.4–13.0	–0.86–+0.71	125.32
LiClO ₄	7.85×10^8	5.98×10^{10}	76.2	3.6–24.0	–1.40–+1.45	138.76

^a The concentration range (mol dm^{–3}) examined. ^b The relative error in the calculated Λ value to the observed Λ value over the concentration range examined. ^c The limiting molar conductivity (S cm² mol^{–1}) calculated by the Walden rule with the Λ_0 in MeCN.

dm^{–3}. At the same time, the K_2/K_1 ratio decreased from ca. 2.0×10^3 to 1.4×10^3 . The large positive shifts in C_{\min} and the decrease in K_2/K_1 ratios from THF to DME cannot be explained by Coulombic interactions between ions since larger Coulombic interactions in DME ($\epsilon_r = 7.2$) are expected than THF ($\epsilon_r = 7.58$). In the case of the tetrabutylammonium salts (Bu₄NX), the formation constants in DME were similar to those in THF, presumably due to the Coulombic interactions between Bu₄N⁺ and X[–].

According to Gutmann's donor and acceptor numbers,¹⁵ Li⁺ and the active site (O[–]) of anions (the phenolates, naphtholate, or NO₃[–]) would be solvated more in DME (DN = 23.9 and AN = 10.2) than in THF (DN = 20 and AN = 8.0). Apparently, the coordination (or covalent) bonding forces between Li⁺ and the anions would be much weakened in DME. The effects of solvation in isopermittivity media (mixed solvents of THF and 2-ethyl-1-hexanol) are considered in the next section.

Table 3 shows the calculated association constants of the tetraalkylammonium salts and Hex₄NClO₄ in chloroform ($\epsilon_r = 4.8$ at 20 °C) at 25 °C. No quadrupole formation was observed except for tetrabutylammonium perchlorate and nitrate. The fit between calculated and observed Λ values was excellent ($< \pm 1.0\%$) for $\Delta C = (0.7–7) \times 10^{-3}$ mol dm^{–3}. Distinct minima on $\Lambda-C^{1/2}$ curves appeared in a narrow concentration range from 1.75×10^{-3} mol dm^{–3} for Bu₄NClO₄ to 4.74×10^{-3} mol dm^{–3} for Bu₄NCH₃SO₃. The linearity between log-

(K_2/K_1) and log C_{\min} in chloroform is presented in Figure 3. The ion pair formation constants of Bu₄NX were found to increase as Cl[–] < Br[–] < ClO₄[–], indicating that the ionic size of the anions in solution is decreasing as Cl[–] > Br[–] > ClO₄[–]. In chloroform small anions (small crystal radii) are more strongly solvated as in protic solvents (such as ethanol or hexanol). Gutmann's acceptor number of chloroform is large enough (AN = 23.1) to solvate anions, while the donor number must be too small (DN = ~0) to solvate cations. The tendency of ion pair (K_1) and triple ion formation (K_2/K_1) of Bu₄NX seems to depend on the size of anion (X[–]) and on the distribution of the negative charge in the anion.

In ethyl acetate ($\epsilon_r = 6.0$, DN = 17.1, and AN = 9.3), the higher solubility of lithium and the sodium salts of ClO₄[–] or Pic[–] (> 0.3 mol dm^{–3}) made it possible to examine the conductivities precisely. The C_{\min} values of LiClO₄ and NaClO₄ were both ca. 1.5×10^{-2} mol dm^{–3}, while those of LiPic and NaPic were 6.2×10^{-3} and 9.8×10^{-3} mol dm^{–3}, respectively. The observed conductivities were completely explained by ion pair and triple ion formation, as shown in Table 4. The linearity between log(K_2/K_1) and log C_{\min} was also observed in ethyl acetate. The lower C_{\min} (or larger K_2/K_1) value of LiPic, compared with that of LiClO₄, may suggest additional "coordination" forces between Li⁺ and Pic[–]. The C_{\min} values of LiClO₄ decreased as permittivity decreases, THF > DME > ethyl acetate; the order is quite reasonable from the electrostatic point of view. The interaction between Li⁺ and ClO₄[–] can be

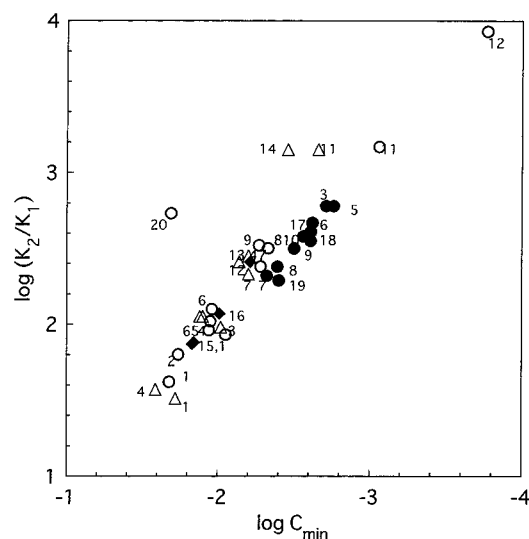


Figure 3. $\log(K_2/K_1)$ vs $\log C_{\min}$ (the salt concentration of the minimum conductivity) in THF (○), DME (△), ethyl acetate (◆), and chloroform (●) at 25.0 °C: (1) LiClO_4 ; (2) LiBF_4 ; (3) $\text{Hex}_4\text{NClO}_4$; (4) LiPic ; (5) Bu_4NClO_4 ; (6) Bu_4NNO_3 ; (7) $\text{Bu}_4\text{NCH}_3\text{SO}_3$; (8) Bu_4NCl ; (9) Bu_4NBr ; (10) Bu_4NI ; (11) LiNO_3 ; (12) $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$; (13) $2,5\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$; (14) $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$; (15) NaClO_4 ; (16) NaPic ; (17) Bu_4NSCN ; (18) $\text{Bu}_4\text{NCH}_3\text{C}_6\text{H}_4\text{SO}_3$; (19) Bu_4NPic ; (20) LiBr .

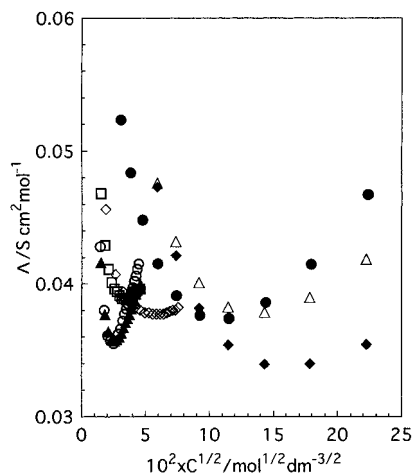


Figure 4. Molar conductivities (Λ) of LiNO_3 in THF and 2-ethyl-1-hexanol mixtures at 25.0 °C: (○) 0; (▲) 2.0; (□) 5.0; (◇) 10.0; (●) 20.0; (△) 30.0; (◆) 50.0 vol % of 2-ethyl-1-hexanol to THF.

considered to be completely electrostatic. Tetrabutylammonium picrate represents another typical example for which the C_{\min} values decrease as the permittivity decreases, $\text{THF} > \text{DME} > \text{chloroform}$. The additional quadrupole formation of Bu_4NClO_4 in THF and DME (cf. Tables 1 and 2) introduces some disorder in the C_{\min} values.

Figure 3 shows the relationship between $\log(K_2/K_1)$ and $\log C_{\min}$ of the salts in THF, DME, ethyl acetate, and chloroform. The salts examined show an almost linear relationship (with the slope of -1), the only exceptions being LiBr in THF entry 20 and LiNO_3 and $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$ in DME entries 11 and 14. The large positive deviation for these three salts can be attributed to the large quadrupole formation of LiBr ($K_{41} = 50$), LiNO_3 ($K_{41} = 35$), and $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Li}$ ($K_{41} = 70$) in each solvent. Small positive deviations were observed for other salts with smaller quadrupole formation constants, e.g., Bu_4NCl and Bu_4NBr in THF or Bu_4NClO_4 in DME.

Experimental results by Salomon et al.²² were found to observe the linear relationship: $\log K = 1.85$ and $\log C_{\min} = -1.85$ for LiAsF_6 in methyl acetate ($\epsilon_r = 6.66$). Another example is LiAsF_6 in diethyl carbonate (DMC, $\epsilon_r = 3.1$) by

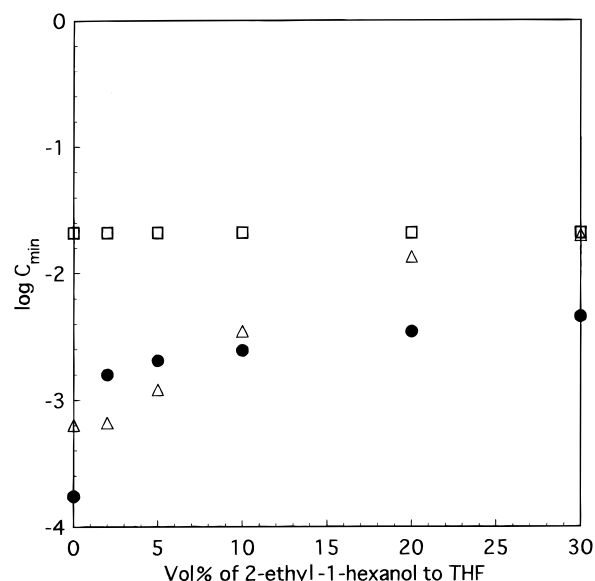


Figure 5. Variation of $\log C_{\min}$ (the salt concentration at the minimum in the conductivity plots) for (□) LiClO_4 , (△) LiNO_3 , and (●) $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Li}$ in various mixtures of 2-ethyl-1-hexanol in THF at 25.0 °C.

TABLE 5: Formation Constants K_1 , $K_2 = K_3$, and K_{41} in 2-Ethyl-1-hexanol and THF Mixtures at 25.0 °C

	K_1	K_1	K_{41}	(K_2/K_1)
Bu_4NClO_4				
0 vol % of hexanol to THF	1.42×10^6	1.50×10^8	7.3	105.6
10 vol %	1.61×10^6	1.45×10^8	6.3	90.1
20 vol %	1.82×10^6	2.2×10^8	7.5	120.9
30 vol %	1.79×10^6	2.2×10^8	7.5	122.9
Bu_4NNO_3				
0 vol % of hexanol to THF	4.8×10^6	6.0×10^8	4.5	125
2 vol %	4.52×10^6	6.15×10^8	5	136.1
5 vol %	4.6×10^6	6.3×10^8	4	136.9
10 vol %	4.4×10^6	6.05×10^8	4	137.5
20 vol %	4.04×10^6	5.64×10^8	5	139.6
30 vol %	3.469×10^6	4.8×10^8	5.5	138.4
$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$				
0 vol % of hexanol to THF	3.05×10^5	2.13×10^7		69.8
10 vol %	3.16×10^5	2.18×10^7		69
20 vol %	3.39×10^5	2.28×10^7		67.3
30 vol %	3.42×10^5	2.3×10^7		67.3
LiClO_4				
0 vol % of hexanol to THF	2.2×10^7	9.8×10^8		44.5
2 vol %	1.85×10^7	8.94×10^8		48.3
10 vol %	1.82×10^7	6.63×10^8		36.4
20 vol %	2.05×10^7	8.65×10^8		42.2
30 vol %	1.62×10^7	7.3×10^8		45.1
LiNO_3				
0 vol % of hexanol to THF	7.5×10^{10}	1.48×10^{14}		1973
2 vol %	6.74×10^{10}	1.25×10^{14}		1855
5 vol %	4.51×10^{10}	7.05×10^{13}		1563
10 vol %	2.80×10^{10}	3.49×10^{13}	35	1246
20 vol %	7.8×10^9	8.15×10^{12}	70	1045
30 vol %	3.48×10^9	3.2×10^{12}	100	919.5
$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{OLi}$				
0 vol % of hexanol to THF	1.17×10^{10}	1.0×10^{14}		8547
2 vol %	2.04×10^9	3.0×10^{12}	15	1471
5 vol %	1.54×10^9	1.8×10^{12}	16	1169
10 vol %	1.2×10^9	9.05×10^{11}	15	754.2
20 vol %	1.3×10^9	8.25×10^{11}	15	634.6
30 vol %	1.075×10^9	6.2×10^{11}	20	576.7

Delsignore et al.²³ $\log K = 2.65$ and $\log C_{\min} = -2.51$. We think that this linear relationship holds as long as the triple ion formation constants can be reasonably estimated with $\Lambda_T/\Lambda_0 = \text{ca. } 2/3$ and no or minor quadrupole formation takes place. Fuoss and Accascina²⁴ have already derived an equation, $K =$

TABLE 6: Observed C_{\min} Values of Various Salts in Various Solvents

salts	THF	DME	ethyl acetate	chloroform
LiBF ₄	1.84×10^{-2}			
LiClO ₄	2.11×10^{-2}	1.91×10^{-2}	1.45×10^{-2}	
NaClO ₄			1.47×10^{-2}	
Bu ₄ NClO ₄	1.11×10^{-2}	1.27×10^{-2}		1.75×10^{-3}
Hex ₄ NClO ₄	8.86×10^{-3}	9.57×10^{-3}		1.97×10^{-3}
LiCl				
Bu ₄ NCl	4.70×10^{-3d}			4.10×10^{-3}
LiBr	4.86×10^{-3}			
Bu ₄ NBr	5.33×10^{-3d}			3.15×10^{-3}
Bu ₄ NI				2.77×10^{-3}
Bu ₄ N SCN				2.47×10^{-3}
LiNO ₃	6.30×10^{-4}	2.42×10^{-3}		
Bu ₄ NNO ₃	1.13×10^{-2}	1.33×10^{-2}		2.41×10^{-3}
LiPic	1.14×10^{-2}	2.56×10^{-2}	6.23×10^{-3}	
NaPic			9.80×10^{-3}	
Bu ₄ NPic	1.22×10^{-2}	1.04×10^{-2}		4.00×10^{-3}
2,4-(NO ₂) ₂ C ₆ H ₃ OLi ^a		3.49×10^{-3}		
2,5-(NO ₂) ₂ C ₆ H ₃ OLi		6.27×10^{-3}		
2,5-(NO ₂) ₂ C ₆ H ₃ OBu ₄ N	1.23×10^{-2}	1.14×10^{-2d}		
2,4-(NO ₂) ₂ C ₁₀ H ₇ OLi ^b	1.73×10^{-4}	7.20×10^{-3}		
2,4-(NO ₂) ₂ C ₁₀ H ₇ OBu ₄ N	1.14×10^{-2}			
Bu ₄ NCH ₃ SO ₃	5.26×10^{-3}	6.24×10^{-3}		4.74×10^{-3}
Bu ₄ NCH ₃ PhSO ₃ ^c				2.83×10^{-3}

^a 2,4-Dinitrophenolate. ^b 2,4-Dinitro-1-naphtholate. ^c *p*-Toluenesulfonate. ^d Dilution method.

TABLE 7: Conductivities of LiClO₄, LiPic, 2,4-(NO₂)₂C₁₀H₇OLi, and LiNO₃ in THF at 25.0 °C

LiClO ₄		LiPic		2,4-(NO ₂) ₂ C ₁₀ H ₇ OLi		LiNO ₃	
10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ	10 ⁴ C	Λ
35.7189	0.5815	10.768	0.3572	0.3514	0.1761	1.0683	0.0562
71.1844	0.4557	21.4596	0.2738	0.7004	0.1715	2.1291	0.0428
106.399	0.4086	32.0756	0.2383	1.0469	0.1677	3.1824	0.038
141.366	0.3859	42.6169	0.2183	1.3909	0.1665	4.2283	0.0361
176.088	0.3767	53.0842	0.2071	1.7325	0.1664	5.2667	0.0357
210.566	0.373	63.4783	0.2004	2.0717	0.1665	6.2979	0.0355
244.805	0.3838	73.8	0.1957	2.4085	0.1666	7.3219	0.0357
278.806	0.3935	84.05	0.1925	2.7431	0.1672	8.339	0.0362
312.571	0.4076	94.2291	0.1901	3.0753	0.1687	9.3488	0.0366
346.103	0.415	104.338	0.1887	3.4052	0.1701	10.3518	0.0372
379.406	0.426	114.377	0.1882	3.7329	0.1707	11.3479	0.0377
412.479	0.4381	124.348	0.189	4.0582	0.1707	12.337	0.0381
445.328	0.4588	134.251	0.1894	4.3814	0.1709	13.3196	0.0385
477.952	0.4724	144.086	0.1899	4.7024	0.1715	14.2952	0.0389
510.356	0.4858	153.854	0.1906	5.0211	0.1723	15.2643	0.0394
542.541	0.5002	163.557	0.1914	5.3378	0.1729	16.227	0.0397
574.508	0.5159	173.194	0.1926	5.6524	0.1743	17.1831	0.0402
606.262	0.5379	182.766	0.1941	5.9648	0.176	18.133	0.0406
		203.876	0.1964	6.2751	0.1763	19.0762	0.0411
		292.819	0.2182	6.5834	0.1767	20.0134	0.0415

$(\lambda_0/\Lambda_0)C_{\min}$, where K is the dissociation constant of the triple ion (assumed to form through complete electrostatic forces) and λ_0 and Λ_0 are the limiting molar conductivity of triple ions and the single ions, respectively.

Tetrabutylammonium perchlorate gave a minimum at 2.8×10^{-2} mol dm⁻³ in dichloromethane (CH₂Cl₂, $\epsilon_r = 8.93$, $\eta = 0.393$ cP (at 30 °C)). The observed molar conductivity in a lower salt concentration range and not covering C_{\min} (1.1×10^{-3} to 1.0×10^{-2} mol dm⁻³) could be explained by our model; $K_1 = 4.45 \times 10^4$ and $K_2 = K_3 = 1.80 \times 10^6$. In 1,2-dichloroethane ($\epsilon_r = 10.4$, $\eta = 0.73$ cP (at 30 °C), DN = 0, and AN = 16.7), however, Bu₄NClO₄ did not give a minimum for $\Delta C = 3.5 \times 10^{-3}$ to 9.7×10^{-2} mol dm⁻³. Association constants, $K_1 = 8.0 \times 10^3$ and $K_2 = K_3 = 9.0 \times 10^6$, were roughly estimated by the lower molar conductivities of $\Delta C = (0.4\text{--}4.0) \times 10^{-3}$ mol dm⁻³. Inami et al.²⁵ have reported the ion pair formation constants of Bu₄NClO₄ in 1,1- and 1,2-dichloroethane to be 4.67×10^4 and 6.41×10^3 , respectively, based upon the conductivity data of an extremely low salt concentrations (ca. 1×10^{-5} to 1×10^{-4} mol dm⁻³). Higher

concentrations of ionic species from Bu₄NClO₄ in 1,2-dichloroethane, based on the small K_1 value of 8.0×10^3 (cf., $K_1 = 4.45 \times 10^4$, 1.42×10^6 and 2.09×10^8 in CH₂Cl₂, THF, and CHCl₃, respectively) should introduce higher Coulombic effects to the system.

Mixed Solvents of THF and 2-Ethyl-1-hexanol. In the previous section effects of permittivity and solvation ability of solvents were discussed. In the present section the effects of solvation abilities are independently examined in almost iso-permittive mixtures from THF ($\epsilon_r = 7.58$) and 2-ethyl-1-hexanol ($\epsilon_r = 7.58$);¹⁶ the latter solvent is expected to have larger solvation abilities, especially toward anions (AN = ~30 ?, cf. 33.5 for 2-propanol). With increasing content of the hexanol, the observed viscosities of the solvent mixtures increased distinctly while the permittivity was thought not to differ so much from 7.58.

Figure 4 shows the molar conductivities (Λ) of LiNO₃ in the various contents of 2-ethyl-1-hexanol and THF. At low salt concentrations, the Λ values increased with increasing content of the hexanol, although the viscosity increases; the phenomenon

indicates clearly that the association of LiNO_3 is decreasing by the increased solvation. C_{\min} increased with increasing content of the hexanol, $C_{\min} = 6.3 \times 10^{-4}$, 6.6×10^{-4} , 1.2×10^{-3} , 3.6×10^{-3} , 1.58×10^{-2} , and 1.99×10^{-2} mol dm^{-3} for 0, 2.0, 5.0, 10, 20, and 30 vol % of the hexanol, cf. also Figure 5. By the way, the C_{\min} values of Bu_4NClO_4 and $2,4\text{-(NO}_2)_2\text{C}_{10}\text{H}_5\text{-OBu}_4\text{N}$ remained constant, i.e., $C_{\min} = 1.11 \times 10^{-2}$ and 1.14×10^{-2} mol dm^{-3} for 0 and 30 vol % hexanol. In the case of Bu_4NNO_3 , however, the C_{\min} values were slightly decreased: $C_{\min} = 1.13 \times 10^{-2}$, 9.3×10^{-3} , and 8.3×10^{-3} mol dm^{-3} for 0, 2.0, and ≥ 5.0 vol % of hexanol, respectively. This reduction in C_{\min} of Bu_4NNO_3 with increasing content of the hexanol (by the increase of solvation ability) was not readily explained. Variation in $\log C_{\min}$ of LiClO_4 and $2,4\text{-(NO}_2)_2\text{C}_{10}\text{H}_5\text{OLi}$ with increasing content of 2-ethyl-1-hexanol in THF are also shown in Figure 5.

The variations in K_1 , K_2/K_1 , and K_{41} values for LiNO_3 , $2,4\text{-(NO}_2)_2\text{C}_{10}\text{H}_5\text{OLi}$, and LiClO_4 with increasing amount of 2-ethyl-1-hexanol to THF were also examined. With increasing content of hexanol, $\log K_1$ of LiNO_3 decreased linearly while $\log(K_2/K_1)$ decreased slightly; however, $\log K_{41}$ increased substantially (cf. Table 5). For $2,4\text{-(NO}_2)_2\text{C}_{10}\text{H}_5\text{OLi}$, the $\log K_1$ and $\log(K_2/K_1)$ decreased suddenly by the addition of 2.0 vol % hexanol and then decreased gradually by further addition of hexanol; the $\log K_{41}$, however, remains almost constant at 2.0% and more of hexanol. On the other hand, the $\log K_1$ and $\log(K_2/K_1)$ values of LiClO_4 , for which only Coulombic interactions occur, are almost constant. The variation in the $\log C_{\min}$ values of the lithium salts (in Figure 5) seems to be in accordance with the variation in the $\log(K_2/K_1)$ values of the salts. The addition of 2-ethyl-1-hexanol to THF definitely caused an increased solvation, judging from the decreases in K_1 and K_2/K_1 of LiNO_3 and $2,4\text{-(NO}_2)_2\text{C}_{10}\text{H}_5\text{OLi}$. The possible increase of the dipole moment of LiNO_3 by the increased solvation may also cause the large quadrupole formation in ≥ 10 vol % hexanol. Wang and Hemmes²⁶ suggested formation of a quadrupole from LiNO_3 even in THF. The effects of the increase in K_{41} value on C_{\min} at constant K_1 and K_2 values were examined by computer simulations: in a mixed solvent (10 vol % of 2-ethyl-1-hexanol to THF, $\epsilon_r = 7.58$, $\eta = 0.528$ cP at 25 °C) with $K_1 = 2.8 \times 10^9$, $K_2 = K_3 = 3.5 \times 10^{13}$, and various K_{41} values. Values of K_{41} up to 50 shifted C_{\min} to higher concentrations; the minimum disappeared at $K_{41} \geq 75$ for that system. The computer simulation indicated that the increase in K_{41} also causes an increase in C_{\min} . The increase in C_{\min} of LiNO_3 in ≥ 10 vol % hexanol may be caused by an increase in K_{41} because the decrease of the K_2/K_1 was not so significant (ca. 2.0×10^3 to 9.2×10^2 for 0–30 vol % hexanol). The positive deviation from linearity in the $\log(K_2/K_1)$ vs $\log C_{\min}$ plot of Figure 3 may also be assisted by the large quadrupole formation, e.g., $K_{41} = 35$ and 75 for LiNO_3 and $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_5\text{OLi}$, respectively, in DME. The lack of a minimum in the conductivity plot of LiCl in THF (vide supra) may also be caused by the large quadrupole formation constant.

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References and Notes

- (1) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic: New York, 1972; Vol. 1.
- (2) Salomon, M. *Pure Appl. Chem.* **1987**, 59, 1165. Salomon, M. J. *Power Sources* **1989**, 26, 9. Matsuda, Y.; Morita, M.; Yamashita, T. *J. Electrochem. Soc.* **1984**, 131, 2821. Salomon, M. J. *Solution Chem.* **1993**, 22, 715. James, S. D. *J. Chem. Eng. Data* **1978**, 23, 313.
- (3) Arnett, E. M.; Moe, K. D. *J. Am. Chem. Soc.* **1991**, 113, 7288. Krom, J. A.; Petty, J. T.; Streitwieser, A. *J. Am. Chem. Soc.* **1993**, 115, 8024. Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, 110, 3829.
- (4) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1933**, 55, 2387. Kraus, C. A. *Trans. Electrochem. Soc.* **1934**, 66, 179. Fuoss, R. M. *Chem. Rev.* **1935**, 17, 27. Kraus, C. A. *Science* **1939**, 90, 281.
- (5) Barthel, J.; Gerber, R.; Gores, H.-J. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, 88, 616. Salomon, M.; Uchiyama, M. C. *J. Solution Chem.* **1987**, 16, 21.
- (6) Grigo, M. J. *Solution Chem.* **1982**, 11, 529. Gestblom, B.; Svorstol, I.; Songstad, J. J. *Phys. Chem.* **1986**, 90, 4684.
- (7) Spiro, M. In *Physical Methods of Chemistry*, Vol. 2: *Electrochemical Methods*, 2nd ed.; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Chapter 8.
- (8) Fuoss, R. M. *J. Phys. Chem.* **1975**, 79, 525.
- (9) Petrucci, S.; Eyring, E. M. *J. Phys. Chem.* **1991**, 95, 1731.
- (10) Hojo, M.; Takiguchi, T.; Hagiwara, M.; Nagai, H.; Imai, Y. *J. Phys. Chem.* **1989**, 93, 955. Hojo, M.; Watanabe, A.; Mizobuchi, T.; Imai, Y. *J. Phys. Chem.* **1990**, 94, 6073. Hojo, M.; Miyauchi, Y.; Tanio, A.; Imai, Y. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 3847. Miyauchi, Y.; Hojo, M.; Ide, N.; Imai, Y. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 1425. Miyauchi, Y.; Hojo, M.; Moriyama, H.; Imai, Y. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 3175. Hojo, M.; Miyauchi, Y.; Ide, N.; Tanio, A.; Imai, Y. *J. Electroanal. Chem.* **1992**, 340, 197. Hojo, M.; Fujime, C.; Yoneda, H. *Chem. Lett.* **1993**, 37. Hojo, M.; Hasegawa, H.; Miyauchi, Y.; Moriyama, H.; Yoneda, H.; Arisawa, S. *Electrochim. Acta* **1994**, 39, 629. Hojo, M.; Hasegawa, H.; Morimoto, Y. *J. Phys. Chem.* **1995**, 99, 6715. Hojo, M.; Hasegawa, H.; Hiura, N. *J. Phys. Chem.* **1996**, 100, 891. M. Hojo, Hasegawa, H.; Chen, Z. *Bull. Chem. Soc. Jpn.* **1996**, 69, 2215.
- (11) Hojo, M.; Moriyama, H. *J. Solution Chem.* **1996**, 25, 681.
- (12) Hojo, M.; Imai, Y. *Bull. Chem. Soc. Jpn.* **1983**, 56, 1963. Hojo, M.; Tanio, A.; Miyauchi, Y.; Imai, Y. *Chem. Lett.* **1991**, 1827. Hojo, M.; Nagai, H.; Hagiwara, M.; Imai, Y. *Anal. Chem.* **1987**, 59, 1770. Hojo, M.; Hasegawa, H.; Yoneda, H. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1855. Hojo, M.; Hasegawa, H.; Mizobe, A.; Ohkawa, Y.; Miimi, Y. *J. Phys. Chem.* **1995**, 99, 16609. Hojo, M.; Hasegawa, H.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1996**, 69, 971.
- (13) Barthel, J.; Gores, H.-J.; Kraml, L. *J. Phys. Chem.* **1996**, 100, 3671.
- (14) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Techniques of Chemistry*, Vol. 2: *Organic Solvents*, 4th ed.; Weissberger, A., Ed.; John Wiley: New York, 1986. The permittivities and viscosities of all the solvents were cited from this reference book, unless otherwise noted.
- (15) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978; Chapter 2. The donor and acceptor numbers of all the solvents were cited from this book.
- (16) Lide, D. R. *Handbook of Organic Solvents*; CRC Press: Boca Raton, 1995; p 235.
- (17) Jagodzinski, P.; Petrucci, S. *J. Phys. Chem.* **1974**, 78, 917.
- (18) Shedlovsky, T. *J. Franklin Inst.* **1938**, 225, 739. Fuoss, R. M.; Shedlovsky, T. *J. Am. Chem. Soc.* **1949**, 71, 1496.
- (19) Wong, M. K.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1972**, 34, 3615.
- (20) Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.* **1993**, 115, 8728.
- (21) Hojo, M.; Hasegawa, H.; Morimoto, Y. *Anal. Sci.* **1996**, 12, 521.
- (22) Salomon, M.; Uchiyama, M.; Xu, M.; Petrucci, S. *J. Phys. Chem.* **1989**, 93, 4374.
- (23) Delsignore, M.; Farber, H.; Petrucci, S. *J. Phys. Chem.* **1985**, 89, 4968.
- (24) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959; p 256.
- (25) Inami, H.; Bodenseh, H. K.; Ramsey, J. B. *J. Am. Chem. Soc.* **1961**, 83, 4745.
- (26) Wang, H.; Hemmes, P. *J. Am. Chem. Soc.* **1973**, 95, 5119.