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Aggregation of Ions in Higher Permittivity Solvents

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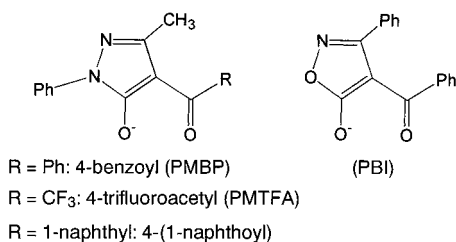
Electrolytic conductances of lithium 4-acyl-5-pyrazolonates (a kind of β -diketonates) and related salts in higher permittivity solvents, acetonitrile ($\epsilon_r = 35.95$), acetone (20.7), *N,N*-dimethylformamide (DMF) (36.71), and propylene carbonate (64.4) were measured at 25 °C. The molar conductivity–concentration ($\Lambda - c^{1/2}$) plots of lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate (LiPMBP) in acetonitrile and acetone display a minimum at 1.51×10^{-3} and 2.0×10^{-3} mol dm $^{-3}$, respectively, but not in DMF and propylene carbonate. The observed Λ values of LiPMBP in all the solvents are explained by the presence of ion pairs (LiA: A = PMBP) and higher ion aggregates, “symmetrical” triple ions ((Li $^+$) $_2$ A $^-$, Li $^+$ (A $^-$) $_2$), and quadrupoles (Li $_2$ A $_2$). The addition of small amounts of MeOH, H $_2$ O, or DMF to acetonitrile caused the c_{\min} value to be higher; with ≥ 1.0 vol % of these solvents added, the minimum disappeared completely. However, the addition of MeNO $_2$ or PhNO $_2$ caused a more distinct or deeper minimum in the $\Lambda - c^{1/2}$ curve. Upon the appearance of the minima, the effects of permittivity and viscosity of the mixed solvents were examined. The conductivity plots of the lithium salts of the 4-trifluoromethoxy derivative (LiPMTFP) and 3-phenyl-4-benzoyl-5-isoxazonolate (LiPBI) did not give minima in the solvents. The observed Λ values could not be fitted without taking into account higher ion aggregations. In DMF, LiPMTFP was much more dissociative. The association constants of the β -diketonates are discussed from the viewpoint of the electron density on the oxygen atoms. Computer calculations indicate that unilateral triple ion formation is impossible for the present system exhibited minima. The formation of bilateral triple ion species (Li $^+$) $_2$ A $^-$ and Li $^+$ (A $^-$) $_2$ (where A $^-$ = PMBP $^-$ or PBI $^-$) in acetonitrile solution was demonstrated by means of UV–visible and 7 Li NMR spectra. The formation of even 5- or 6-coordinated as well as 4-coordinated species was suggested when a large excess of *n*-Bu $_4$ NPBI was present in 0.01 mol dm $^{-3}$ LiClO $_4$ –CD $_3$ CN.

Introduction

Although the subject is still of some controversy, it is now generally accepted that alkali metal–X bonds (X = halogens, C, N, O, etc) are essentially ionic.¹ In low permittivity media ($\epsilon_r < 10$), a number of uni-univalent salts give a minimum in the conductometric curves, which has been explained by the formation of triple ions.² The formation of triple ions is based on electrostatic interaction between (spherical) ions in electric fields of low permittivity. Experimentally we have observed a linearity (slope of -1) between the triple ion formation constants and the salt concentrations at the minimum which appeared in the conductometric curves ($\Lambda - c^{1/2}$) in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), chloroform, and ethyl acetate.³ The salt concentration at the minimum varied from 1.73×10^{-4} mol dm $^{-3}$ for lithium 2,4-dinitro-1-naphtholate in THF to 2.56×10^{-2} mol dm $^{-3}$ for lithium picrate in DME. The contribution of coordination (or covalent) bonding forces as well as Coulombic forces was suspected for the aggregation of the lithium salts except for LiClO $_4$ or LiBF $_4$. For more than 15 years,⁴ we have demonstrated by means of spectroscopy, polarography, and conductometry that higher ion aggregation including triple ions may take place even in higher permittivity media ($20 < \epsilon_r < 65$) of poor solvating abilities. Salt effects on chemical equilibria in acetonitrile⁵ and kinetics in MeOH–water, acetone–water, and 1,4-dioxane–water⁶ were explained without conflicts by a

specific “chemical” interaction between the ions. The promoted formation of methoxy-substituted trityl cations from the corresponding trityl chlorides (RCI) in acetonitrile by the addition of alkali and alkaline earth metal perchlorates was confirmed by UV–visible^{7a} and 1 H NMR spectra:^{7b} $\text{RCI} + 2\text{Li}^+ \rightleftharpoons \text{R}^+ + (\text{Li}^+)_2\text{Cl}^-$; $\text{RCI} + \text{Ba}^{2+} \rightleftharpoons \text{R}^+ + \text{BaCl}^+$. A mixed-anion salt, $\text{BaCl}^+\text{ClO}_4^-$, has been isolated and characterized by IR, X-ray powder pattern, and TG-DTA.^{7c}

β -Diketones are well-known as solvent-extraction reagents. The acidities of 4-acyl-5-pyrazolones are greater than those of common β -diketones such as acetylacetone.⁸ 4-Acyl-5-pyrazolones have been utilized in extraction of alkali metal ions⁹ as well as lanthanides.¹⁰ In the present paper the conductivity of lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate (LiPMBP) and related compounds (Scheme 1) was measured in acetonitrile ($\epsilon_r = 35.95$), acetone (20.7), DMF (36.71), and propylene carbonate (64.4) at 25 ± 0.02 °C. The lithium salt of the 4-benzoyl derivative exhibited a minimum in the conductometric curves in acetonitrile and acetone, and the formation of higher ion aggregates is discussed. This is the first report that an alkali metal salt is found to give a conductometric minimum in a solvent of higher permittivity ($\epsilon_r > 10$). In benzonitrile and nitrobenzene, tributylammonium and diethylcyclohexylammonium chlorides have been observed to give a minimum in the conductometric curves.^{4d,g,h} Fuoss and Kraus² have shown

SCHEME 1: Structures of 4-Acyl-5-pyrazolonates and the 3-Phenyl-4-benzoyl-5-isoxazolonate

theoretically that triple ion formation by the electrostatic interaction becomes unstable in higher permittivity media, $\epsilon_r > 23.2$, and that a minimum in conductance due to this effect cannot appear at any concentration for $R_4N^+NO_3^-$ in dioxane–H₂O mixtures of higher permittivities. The effect on the minimum appearance of small amounts of more and less basic solvents was examined in acetonitrile. The formation of triple anions and triple cations was demonstrated by UV–visible and NMR spectroscopic techniques.

The observed molar conductivities were analyzed by a previously described method,^{3,4} outlined as follows. The formation constants of ion pairs ($M^+ + X^- \rightleftharpoons M^+X^-$, $K_1/\text{mol}^{-1} \text{ dm}^3$), triple ions ($2M^+ + X^- \rightleftharpoons (M^+)_2X^-$, $K_2/\text{mol}^{-2} \text{ dm}^6$; $M^+ + 2X^- \rightleftharpoons M^+(X^-)_2$, $K_3/\text{mol}^{-2} \text{ dm}^6$), and quadrupoles ($2MX \rightleftharpoons M_2X_2$, $K_4/\text{mol}^{-1} \text{ dm}^3$) 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 $K_2 = K_3$.

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

The equilibrium concentrations of the ion pairs, triple ions, and quadrupoles 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 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. The activity coefficients of the ions were evaluated by the Debye–Hückel equation with $a = 4 \text{ \AA}$; those of the ion pairs and the quadrupoles were taken to be unity.^{4e,f}

Experimental Section

Electrical conductances were measured at $25 \pm 0.02^\circ\text{C}$ using a Hewlett-Packard LCR meter (Model 4263A) and a conductivity cell with a cell constant of 0.4980. A Hewlett-Packard Precision LCR meter (Model HP4284A) was used for the measurement of the permittivity of mixed solvents in a liquid test fixture, Model HP 16452A. The viscosities and densities of the solutions were measured with Sibata viscosimeters (Ubbelohde type) and Vidrex pycnometers (Ostwald type, ca. 1 or 2 cm³). UV–visible spectra were measured using a Hitachi double-beam spectrophotometer (Model U-2000) and a 0.1 cm quartz cuvette at room temperature. ¹H and ⁷Li NMR measurements were carried out with a JEOL FT-NMR spectrometer Model JNM-LA400 in 5 mm sample tubes at room temperature. Acetonitrile-*d*₃ from Aldrich (99.6 atom % D) was used as solvent for the NMR measurements. The chemical shift of ⁷Li was referred to 4.0 mol dm⁻³ LiClO₄ in H₂O (90% D₂O).¹¹

The lithium and tetrabutylammonium salts of PMBP were prepared from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HP-

MBP)⁸ in methanol and equivalent amounts of LiOH and *n*-Bu₄-NOH; the lithium salt was recrystallized from acetone. LiPMBP and *n*-Bu₄NPMBP were dried in vacuo at 200 and 60 $^\circ\text{C}$, respectively. Elemental analysis of LiPMBP: Found: C, 71.36; H, 4.71; N, 9.69%. Calcd for C₁₇H₁₃N₂O₂Li: C, 71.83; H, 4.61; N, 9.86%. *n*-Bu₄NPMBP: Found: C, 75.71; H, 9.48; N, 7.99%. Calcd for C₃₃H₄₉O₂N₃: C, 76.25; H, 9.50; N, 8.09%. A hemihydrated LiPMBP was suggested by the elemental analysis of the lithium compound when dried at $\leq 150^\circ\text{C}$. Other salts were prepared in a similar way. Lithium 4-benzoyl-3-phenyl-5-isoxazolonate (LiPBI), prepared from HPBI,¹⁰ was dried at 150 $^\circ\text{C}$ and not at 200 $^\circ\text{C}$. Purification of the solvents was performed as described previously.⁴

Results and Discussion

Conductivities in Various Solvents. The physical properties and the constants of the solvents utilized in the present work are listed in Table 1. Figure 1 shows the conductometric curve of lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate (LiPMBP) in acetonitrile. A minimum was observed at $c = 1.51 \times 10^{-3} \text{ mol dm}^{-3}$. The observed Λ values were fitted by the ion pair formation constant ($K_1 = 3.48 \times 10^6$), the “symmetrical” triple ions (overall formation constant, $K_2 = K_3 = 1.55 \times 10^{10}$), and the quadrupole formation constant (the dimerization of ion pairs; $K_4 = 130$) within -1.47 to $+0.58\%$ relative error for a concentration range of $(0.40\text{--}3.0) \times 10^{-3} \text{ mol dm}^{-3}$. The Λ_T/Λ_0 value was assumed to be 0.693^{3,4,14} where Λ_0 and Λ_T are the limiting molar conductivities of the simple ion salt and the triple ion “salt” respectively. The equilibrium concentrations of the simple ions ($[Li^+, A^-]$), the ion pairs ($[LiA]$), the triple ions ($[Li_2A^+, LiA_2^-]$), and the quadrupoles ($[Li_2A_2]$) were calculated to be 1.80×10^{-5} , 1.05×10^{-3} , 8.39×10^{-5} , and $1.42 \times 10^{-4} \text{ mol dm}^{-3}$, respectively, at a concentration of the dissolved salt of $1.6 \times 10^{-3} \text{ mol dm}^{-3}$. The ion pair species amounted to 66% of the total salt concentration at this concentration. The ratios (e.g., $[X]/c_s$) of the equilibrium concentrations of the ion pairs and the single ions decreased with increasing salt concentration, whereas those of triple ions and quadrupoles increased. From the viewpoint of electrostatic interaction, one may wonder why ions associate so readily in such a high permittivity medium ($\epsilon_r = \text{ca. } 36$). We suggest that coordination forces as well as Coulombic attraction can operate between Li⁺ and the anion. The presence of Li⁺(A⁻)₂-type species is well-known.¹⁵ The formation of (Li⁺)₂A⁻-type species may seem to be destabilized due to a “possible” electrostatic repulsion. However, the presence of dilithium complexes of β -diketonates (e.g., $[Li_2(\text{acac})]^+$) in acetonitrile has been reported.¹⁶ The complexing ability of Li⁺ is discussed in the final section.

In the present system, we have assumed K_2 to be equal to K_3 ; in other words, we have used a “mean” value for the actual formation constant of the triple cation ($(Li^+)_2X^-$) and the triple anion ($Li^+(X^-)_2$) (vide infra). Our polarographic results have shown that triple anion formation is superior to triple cation formation for the interaction between Li⁺ and the benzoate ion in acetonitrile,^{4a} although the formation constants are rather similar for Li⁺–Cl⁻ in the solvent.^{4b} The formation of quadrupoles proved to be essential to account for the observed molar conductivities. In our observation,⁴ a large ion pair formation is often accompanied by rather large triple ion and quadrupole formation constants. An “apparent” limiting molar conductivity (Λ_0) of 8.65 S cm² mol⁻¹ (cf. Table 2) and an association constant (K_a) of 0 (?) were obtained by a Shedlovsky analysis¹⁷ for the lower salt concentrations of LiPMBP. The intrinsic Λ_0

TABLE 1: Physical Constants^a of the Applied Solvents at 25.0 °C

	η^b/cP	ϵ_r^c	DN ^d	AN ^d	A ^e	$10^{-8}B^e$	α^f	β^f
MeCN	0.3409	35.95	14.1	19.3	1.644	0.4857	0.7393	233.8
acetone	0.3040	20.70	17.0	12.5	3.673	0.6401	1.692	345.4
DMF	0.796	36.71	26.6	16.0	1.593	0.4807	0.7165	99.07
PC ^g	2.530	64.4	15.1	18.3	0.6858	0.3629	0.3084	23.53
H ₂ O	0.8903	78.30	(18.0)	54.8				
MeOH	0.5445	32.70	(19)	41.3				
CH ₃ NO ₂ ^h	0.627	36.67	2.7	20.5				
PhNO ₂ ^h	1.811	34.82	4.4	14.8				
PhCN ^h	1.22	25.2	11.9	15.5				

^a From ref 12, unless otherwise noted. ^b Viscosity (1 P = 0.1 Pa s). ^c Relative permittivity. ^d Gutmann's donor and acceptor numbers (ref 13). ^e Constant in the Debye-Hückel equation. ^f Constant in Onsager's equation. ^g Propylene carbonate. ^h Cf. ref 14.

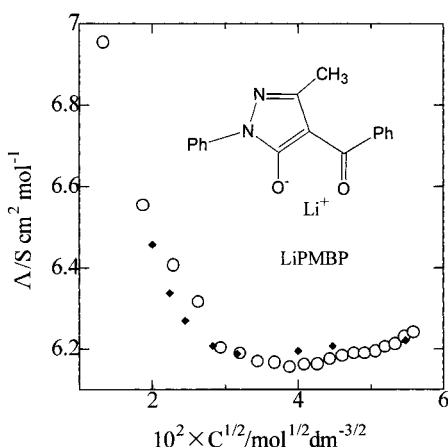


Figure 1. $\Lambda-c^{1/2}$ plots of lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate (LiPMBP) in acetonitrile at 25 °C: (○) observed; (◆) calculated with $K_1 = 3.48 \times 10^6$, $K_2 = K_3 = 1.55 \times 10^{10}$, $K_{41} = 130$, $\Lambda_0 = 134.3$, and $\Lambda_T/\Lambda_0 = 0.693$.

value of the LiPMBP was calculated to be $134.3 \text{ S cm}^2 \text{ mol}^{-1}$ in MeCN by Kohlrausch's additivity law for strong electrolytes: $\Lambda_0(\text{LiPMBP}) = \Lambda_0(\text{LiClO}_4) + \Lambda_0(n\text{-Bu}_4\text{NPMBP}) - \Lambda_0(n\text{-Bu}_4\text{NClO}_4)$. The association constants were evaluated to be $K_1 = 3.48 \times 10^6$, etc. (cf. Table 3). The difficulty in the Shedlovsky analysis has been attributed to the higher ion aggregation at the expense of ion pair formation.^{3,4,14} To avoid higher aggregation in aprotic solvents, the anion or the cation should not have specific interactions with oppositely charged ions. We have therefore made use of tetraalkylammonium (R_4N^+) and perchlorate (ClO_4^-) ions as examples of ions of nonspecific interactions.

Figure 2 shows the observed and calculated Λ values of lithium 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolonate (LiPMTFP) in acetonitrile. The observed Λ decreased monotonically with increasing salt concentration, and no minimum in the $\Lambda-c^{1/2}$ curve could be detected, even up to $c = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$. Still, the observed Λ values were never fitted by ion pair formation alone: the calculated Λ values, using $K_1 = 1.84 \times 10^5$, were always less than the observed Λ values at higher salt concentrations. The experimental Λ values in the $(0.4\text{--}3.0) \times 10^{-3} \text{ mol dm}^{-3}$ range, however, were completely explained by $K_1 = 3.0 \times 10^5$, $K_2 = K_3 = 6.0 \times 10^8$, and $K_{41} = 120$ within -0.34 to $+0.61\%$ relative error. The major difference between the 4-benzoyl and 4-trifluoroacetyl derivatives seems to be due to the K_1 and K_2/K_1 values (cf. Table 3). The large triple ion formation ($K_2/K_1 = 4.45 \times 10^3$) of LiPMBP causes a minimum in the conductivity curve to appear, but no minimum for the smaller value of $K_2/K_1 = 2.0 \times 10^3$. An increase in the quadrupole formation tends to remove the minimum even though triple ion formation is sufficient to give a minimum.^{4d}

The conductivity curves of lithium 3-phenyl-4-benzoyl-5-isoxazonolate (LiPBI) in acetonitrile gave no minimum for concentrations less than $3 \times 10^{-3} \text{ mol dm}^{-3}$. The evaluated formation constants (K_1 , $K_2 = K_3$, and K_{41}) of LiPBI are larger than expected as compared with the values for LiPMBP and LiPMTFP, based on the basicity of the β -diketonates (cf. Figure 3); the acid dissociation constants, $\text{p}K_a$ values of HPBI,¹⁰ HPMTFP, and HPMBP⁸ have been reported to be 1.23, 2.56, and 3.92, respectively. However, semiempirical calculations with AM1,¹⁸ PM3, and MNDO/H on a Cray T/94/4128 computer indicate that the electron density on the oxygen atoms of the PBI ion is larger than that of the PMTFP ion but smaller than that of the PMBP ion; the electron density on O1 and O2 is -0.432 and -0.429 for PMBP⁻, -0.396 and -0.382 for PMTFP⁻, and -0.403 and -0.419 for PBI⁻. It has been suggested that the distance between the two oxygen atoms in HPBI is too long for an intramolecular hydrogen bonding.¹⁹

The conductivity was also examined for solutions of LiPMBP, LiPMTFP, and LiPBI in acetone, DMF, and propylene carbonate (cf. Tables 2 and 3); a minimum was observed only for LiPMBP in acetone. The evaluated association constants of LiPMBP in DMF were smaller than expected as judged by the permittivity of the solvent being close to that of acetonitrile. The molar conductivities of LiPMTFP in DMF could be explained by a weak ion-pair formation alone. In propylene carbonate (PC), large quadrupole formation constants have to be taken into account. In a previous paper,²⁰ we have obtained large quadrupole formation constants for lithium trifluoroacetate and lithium pentafluoropropionate in PC. The formation of quadrupoles of lithium salts in low permittivity media, such as THF, has been extensively investigated through spectroscopic methods by Chabanel.²¹ In THF, lithium chloride, as based on conductivity studies, has been suggested to exist mainly as ion pairs (LiCl) and as quadrupoles (Li_2Cl_2).³ Wong and Popov²² have suggested the presence of higher ionic aggregates from LiCl in THF as based upon vapor phase osmometric studies. Lithium 1-phenyl-3-methyl-4-(1-naphthoyl)-5-pyrazolonate in acetonitrile also gave a minimum at around $1.5 \times 10^{-3} \text{ mol dm}^{-3}$. However, the fitting for the observed Λ values with our model based upon higher ion aggregates was not satisfactory. The observed conductivities of LiPMBP, LiPMTFP, and LiPBI in acetonitrile at 25 °C are listed in Table IS and those of LiPMBP in acetone, DMF, and PC in Table IIS (Supporting Information).

The effect of changes in viscosity with increasing salt concentration on the minimum in the $\Lambda-c^{1/2}$ curves had to be considered. The viscosity of acetonitrile solutions of LiPMBP and LiPBI increases only slightly but linearly with the concentration of the dissolved salts: e.g., 0.3358, 0.3373, and 0.3396 cP for 1.0, 3.0, and $10 \times 10^{-3} \text{ mol dm}^{-3}$ solutions of LiPMBP in MeCN. Apparently, the minimum in the $\Lambda-c^{1/2}$ curve of LiPMBP in acetonitrile cannot be attributed to changes in the

TABLE 2: Λ_0 and Apparent K_a Values of Tetrabutylammonium and Lithium Salts in Various Solvents as Obtained by the Shedlovsky Analysis at 25.0 °C

solvent	salt	Shedlovsky analysis		
		$\Lambda_0^a/S \text{ cm}^2 \text{ mol}^{-1}$	K_a^b	$\Lambda_0(\text{calcd})^c/S \text{ cm}^2 \text{ mol}^{-1}$
MeCN	<i>n</i> -Bu ₄ NClO ₄	167.2	0	
	LiClO ₄	174.8	13.6	
	<i>n</i> -Bu ₄ NPMBP	126.7	0.6	
	<i>n</i> -Bu ₄ NPMTFP	136.6	0	
	<i>n</i> -Bu ₄ NPBI	130.0	2.9	
	LiPMBP	(8.65)	(0)	134.3
	LiPMTFP	(18.5)	(19)	144.2
	LiPBI	(14.2)	(0)	137.6
acetone	<i>n</i> -Bu ₄ NClO ₄	185.0	86.7	
	LiClO ₄	192.4	118	
	<i>n</i> -Bu ₄ NPMBP	135.8	108	
	<i>n</i> -Bu ₄ NPMTFP	146.8	64.0	
	<i>n</i> -Bu ₄ NPBI	137.9	129	
	LiPMBP ^d			143.2
	LiPMTFP	(12.2)	(0)	154.2
	LiPBI	(8.82)	(0)	145.4
DMF	<i>n</i> -Bu ₄ NClO ₄	79.0	3.2	
	LiClO ₄	78.3	1.2	
	<i>n</i> -Bu ₄ NPMBP	55.5	4.7	
	<i>n</i> -Bu ₄ NPMTFP	60.5	5.0	
	LiPMBP	(50.5)	(3.02 × 10 ³)	54.8
	LiPMTFP	57.9	66.7	59.8
propylene carbonate	<i>n</i> -Bu ₄ NClO ₄	27.87	0	
	LiClO ₄	25.98	0	
	<i>n</i> -Bu ₄ NPMBP	18.3	0	
	<i>n</i> -Bu ₄ NPMTFP	20.02	0	
	<i>n</i> -Bu ₄ NPBI	19.18	0.4	
	LiPMBP	(2.5)	(0)	16.41
	LiPMTFP	(6.1)	(651)	18.13
	LiPBI	(4.85)	(391)	17.29

^a The limiting molar conductivity. ^b Association constant: $M^+ + X^- \rightleftharpoons MX$; only the 1:1 interaction is taken into account. ^c The Λ value is calculated using Kohlrausch's additivity law for strong electrolytes. ^d The Shedlovsky analysis did not converge within 0.1% of value.

TABLE 3: Evaluated Formation Constants, K_1 , $K_2 = K_3$, and K_{41} , of the Lithium β -Diketonates in Various Solvents at 25.0 °C

solvent	salt	K_1	$K_2 = K_3$	K_{41}	K_2/K_1	$10^3 c_{\min}^a$	$10^3 \Delta c^b$	rel error ^c /%	σ error
MeCN	LiPMBP	3.48×10^6	1.55×10^{10}	130	4.45×10^3	1.51	0.40–3.0	−1.47 to +0.58	0.80
	LiPMTFP	3.0×10^5	6.0×10^8	120	2.0×10^3		0.40–3.0	−0.34 to +0.61	0.36
	LiPBI	6.80×10^5	1.5×10^9	120	2.2×10^3		0.40–3.0	−0.45 to +0.37	0.31
acetone	LiPMBP	5.11×10^7	1.5×10^{11}	115	2.9×10^3	2.00	0.40–3.0	−0.63 to +0.54	0.40
	LiPMTFP	1.05×10^6	7.2×10^8	55	6.9×10^2		0.40–3.0	−0.72 to +0.51	0.35
	LiPBI	2.96×10^6	3.0×10^9	90	1.0×10^3		0.40–3.0	−0.63 to +0.53	0.40
DMF	LiPMBP	3.63×10^3	9.0×10^5	30	2.5×10^2		0.40–3.0	−9.00 to +0.64	0.63
	LiPBI	1.0×10^2					0.40–3.0	−2.42 to +2.20	1.49
propylene carbonate	LiPMBP	3.67×10^5	2.7×10^9	250	7.4×10^3		0.40–3.0	−1.37 to +1.28	0.96
	LiPMTFP	2.15×10^4	3.6×10^7	210	1.7×10^3		0.40–3.0	−0.40 to +0.58	0.33
	LiPBI	3.80×10^4	6.0×10^7	120	1.6×10^3		0.40–3.0	−0.36 to +0.31	0.23

^a The salt concentration at which the minimum appeared. ^b The concentration range examined (mol dm^{−3}). ^c The relative error in the calculated Λ value as compared with the observed Λ value for the whole concentration range examined.

viscosity with increasing salt concentration. Changes in permittivities with increasing salt concentration²³ or changes in the activity coefficients of the ion pair²⁴ do not seem to be the cause for the appearance of the conductance minima in the present systems of low salt concentrations ($\leq 3 \times 10^{-3}$ mol dm^{−3}).

Figure 4 shows the Λ – $c^{1/2}$ curves in acetonitrile (cf. the physical constants in Table 1) which were simulated (or calculated) with variable K_3 and constant K_2 : $K_1 = 10^6$, $K_2 = 10^{10}$, $\lambda_+^\circ = \lambda_-^\circ = 67.17$, and $\lambda_{+T}^\circ = \lambda_{-T}^\circ = 46.57$, where λ° and λ^T represent the limiting (molar) single and triple ion conductivities, respectively. With $K_3 = 10^{10}$, that is, in the case of “symmetrical” triple ion formation, a minimum was observed at a low concentration, $c_{\min} = 4 \times 10^{-4}$ mol dm^{−3}. However, the c_{\min} values shifted toward larger values with decreasing K_2 values, and finally, the minimum disappeared for $K_3 \leq 10^6$. These computer calculations indicated that unilateral triple ion formation alone could not be the cause for a minimum in the

Λ – $c^{1/2}$ curve. In realistic systems, K_2 and K_3 may not attain the same value. We have explained the experimental Λ values using a “mean” value between the “real” values (K_2' and K_3') for triple ions: $K_2 = K_3 \sim \sqrt{K_2' K_3'}$.^{3,4,14,20}

Effects of Additional Solvents on the Conductivities of LiPMBP in MeCN. As described above, conductivity curves of lithium 1-phenyl-3-methyl-4-benzoyl-5-pyrazolonate (LiPMBP) displayed a minimum in acetonitrile and acetone but not in DMF and propylene carbonate. The effect of added solvents on the conductivity of LiPMBP in acetonitrile was further studied. Figure 5 shows the molar conductivity of LiPMBP in acetonitrile with increasing content of H₂O. The concentration at which the minimum appeared increased; the c_{\min} values were 1.51, 1.97, and 2.42×10^{-3} mol dm^{−3} for 0, 0.2, and 0.5 vol % H₂O. At 1.0 vol % H₂O the minimum disappeared. The effect of added MeOH on c_{\min} was similar to that of H₂O. Table 4 shows the K_1 , $K_2 = K_3$, and K_{41} values of LiPMBP in the mixed

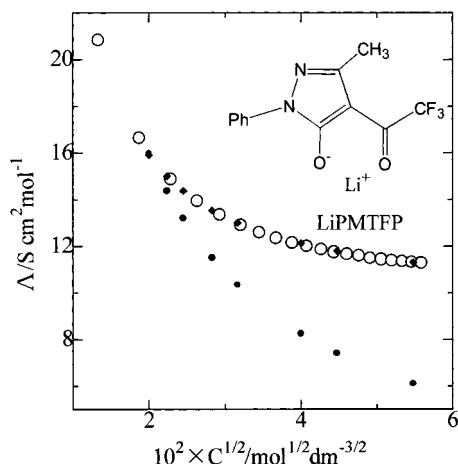


Figure 2. Observed and calculated Λ values of LiPMTFP in acetonitrile: (○) observed; (●) calculated with the only ion pair formation ($K_1 = 1.84 \times 10^5$); (◆) calculated considering the ion pair ($K_1 = 3.0 \times 10^5$), "symmetrical" triple ion ($K_2 = K_3 = 6.0 \times 10^8$), and quadrupole ($K_{41} = 120$) formation, $\Lambda_0 = 144.2$, and $\Lambda_T/\Lambda_0 = 0.693$.

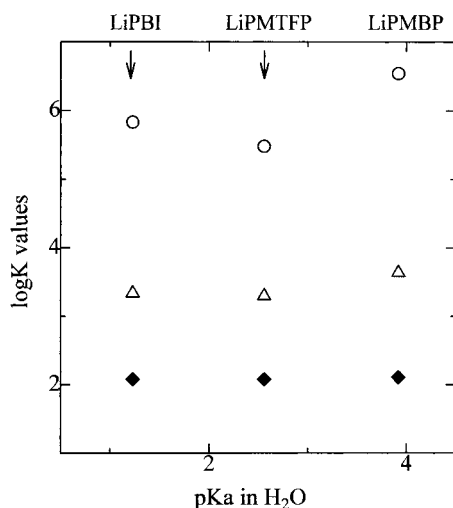


Figure 3. Relation between $\log K$ values of LiPBI, LiPMTFP, and LiPMBP in acetonitrile and Brønsted acidities (pK_a) of the β -diketones in H_2O : (○) the ion pair (K_1); (Δ) the triple ion (K_2/K_1); (◆) the quadrupole (K_{41}).

solvents. K_1 and $K_2 = K_3$ values were found to decrease by addition of small amounts of the protic solvents, H_2O and MeOH. According to our measurements, the change in the relative permittivity by addition of ≤ 1.0 vol % H_2O and MeOH was very small: +1.3 and -0.8% with 1.0 vol % H_2O and MeOH, respectively. Therefore, the effect of protic solvents on the association constants of LiPMBP can hardly be attributed to a permittivity change but to an increase in the solvation ability of the mixed solvents. The disappearance of the minimum by addition of H_2O and MeOH is probably caused by the decrease in triple ion formation constants (K_2/K_1 value). Previously, we reported a similar disappearance of the minimum in the conductometric curve of diethylhexylammonium chloride ($c\text{-Hex}(\text{Et})_2\text{NH}^+\text{Cl}^-$) in benzonitrile ($\epsilon \sim 25$) by addition of EtOH, a solvent of comparable permittivity.^{4g}

The addition of more than 0.5 vol % DMF to acetonitrile caused the minimum to disappear. Due to the large donor number of DMF ($DN = 26.6$, cf. 14.1 of MeCN), this solvent strongly solvates the lithium ion in the mixed solvents while the PMBP[−] ion may not be so affected by DMF due to the small acceptor number ($AN = 16.0$, cf. 19.3 of MeCN); the

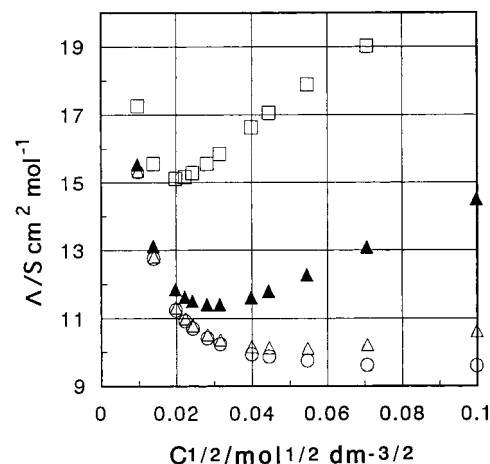


Figure 4. Computer simulation of molar conductivities (Λ) with variable K_3 at constant K_2 ($K_1 = 10^6$, $K_2 = 10^{10}$, $\lambda_+^\circ = \lambda_-^\circ = 67.17$ and $\lambda_+^T = \lambda_-^T = 46.57$ (cf. text) in acetonitrile at 25 °C: K_3 values are 10^{10} (□), 10^9 (▲), 10^8 (Δ), and 10^6 (○).

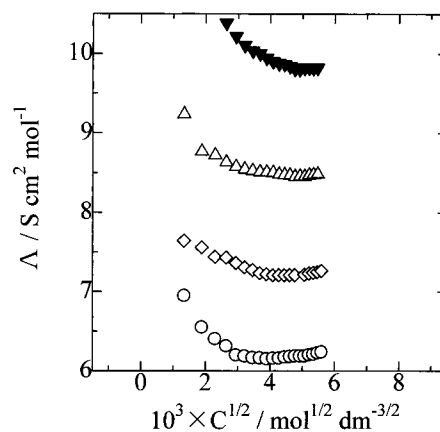


Figure 5. Observed molar conductivities (Λ) in MeCN– H_2O mixed solvents: (○) 0; (◇) 0.2 vol %; (Δ) 0.5 vol %; (▼) 1.0 vol % H_2O .

negative charge in the large PMBP[−] ion may be delocalized all over the anion. The change in ϵ_r is negligible with increasing content of DMF in MeCN. The disappearance of the minimum by the addition of DMF could not be explained by the change in the K_2/K_1 values but rather by an increase in the quadrupole formation constants (K_{41}); cf. Table 4. We have established that quadrupole formation tends to shift c_{\min} toward higher concentrations, and finally, the minimum disappears with a larger value than a critical one for K_{41} .^{4d} In 100% DMF, the association constants of LiPMBP were much smaller than in MeCN (vide supra).

Unexpectedly, the c_{\min} value was shifted toward higher concentrations by the addition of less basic solvents to acetonitrile but the minimum was more distinct (Figure 6). The addition of 1.0 vol % nitromethane caused a c_{\min} value of 2.13×10^{-3} mol dm^{-3} . The more viscous nitrobenzene showed a similar effect. The effect of 1.0 vol % benzonitrile on the minimum was ambiguous. In any case, the addition of the less basic solvents caused larger values for K_1 , $K_2 = K_3$, and K_{41} than those without the additional solvents. The physical properties of the mixed solvents (including observed viscosities) for the conductivity analyses are listed in Table IIIS (Supporting Information). The Λ_0 values of LiPMBP in the mixed solvents were evaluated by the Walden rule from the value in MeCN, $134.3 \text{ S cm}^2 \text{ mol}^{-1}$.

UV and NMR Spectra of Li^+ Complexes with the β -Diketone Ions. The complexing ability of Li^+ with the β -diketonate

TABLE 4: Formation Constants, K_1 , $K_2 = K_3$, and K_{41} , of LiPMBP in MeCN Mixed Solvents at 25.0 °C

mixed solvent	K_1	$K_2 = K_3$	K_{41}	K_2/K_1	$10^3 c_{\min}^a$	$10^3 \Delta c^b$	rel error ^c /%	σ error
MeCN ^d	3.48×10^6	1.55×10^{10}	130	4.45×10^3	1.51	0.40–3.0	–1.47 to +0.58	0.80
0.2 vol % H ₂ O	2.43×10^6	1.13×10^8	140	4.65×10^3	1.97	0.40–3.0	–0.95 to +1.38	0.75
0.5 vol % H ₂ O	1.75×10^6	8.4×10^9	130	4.8×10^3	2.42	0.40–3.0	–0.76 to +0.97	0.52
1.0 vol % H ₂ O	9.02×10^5	3.6×10^9	120	4.0×10^3		0.40–3.0	–0.27 to +0.72	0.44
0.2 vol % MeOH	3.01×10^6	1.36×10^{10}	140	4.52×10^3	2.13	0.40–3.0	–1.04 to +1.42	0.74
0.5 vol % MeOH	2.71×10^6	1.23×10^{10}	140	4.54×10^3	2.66	0.40–3.0	–1.76 to +1.72	1.12
1.0 vol % MeOH	2.15×10^6	9.0×10^9	130	4.2×10^3		0.35–3.1	–1.68 to +1.40	1.2
0.2 vol % DMF	2.45×10^6	1.1×10^{10}	165	3.65×10^3	2.41	0.40–3.0	–1.06 to +1.04	0.8
0.5 vol % DMF	1.94×10^6	9.0×10^9	170	3.7×10^3		0.40–3.0	–1.01 to +0.88	0.72
1.0 vol % DMF	1.62×10^6	7.5×10^9	175	4.6×10^3		0.40–3.0	–0.92 to +0.84	0.65
1.0 vol % MeNO ₂	3.58×10^6	1.75×10^{10}	165	4.89×10^3	2.13	0.40–3.0	–0.78 to +0.71	0.59
1.0 vol % PhNO ₂	3.66×10^6	1.76×10^{10}	160	4.76×10^3	1.82	0.40–3.0	–0.96 to +0.87	0.69
1.0 vol % PhCN	3.70×10^6	1.76×10^{10}	150	4.76×10^3	1.98	0.40–3.0	–0.69 to +0.62	0.44

^a The salt concentration at which the minimum appeared. ^b The concentration range examined (mol dm^{–3}). ^c The relative error in the calculated Λ value as compared with the observed Λ value for the whole concentration range examined. ^d Cf. Table 3.

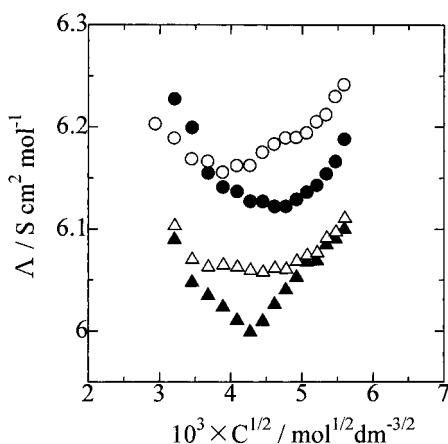


Figure 6. Observed molar conductivities (Λ) in acetonitrile and in mixed solvents: (○) MeCN; (●) 1.0 vol % MeNO₂; (Δ) 1.0 vol % PhCN, (▲) 1.0 vol % PhNO₂.

ions was examined in acetonitrile. Figure 7 shows the UV spectra of n -Bu₄N⁺PBI[–] in the presence of various concentrations of LiClO₄. Without LiClO₄ added, a 1.0×10^{-3} mol dm^{–3} solution of n -Bu₄N⁺PBI[–] in MeCN showed an absorption band at 324 nm ($\epsilon = 6.5 \times 10^3$). However, with increasing concentration of LiClO₄ up to 1 equiv, the absorption band showed a hypsochromic shift accompanied by a hyperchromic effect giving isosbestic points at 268 and 326 nm (cf. Figure 7, upper). The appearance of isosbestic points indicates an equilibrium between the free PBI[–] ion and the ion pair Li⁺PBI[–]. On the other hand, with [LiClO₄] > 1.0×10^{-3} mol dm^{–3}, the isosbestic point of 326 nm shifted to 310 nm (cf. Figure 7, lower). Upon addition of 1.0 mol dm^{-3} LiClO₄, λ_{\max} shifted to 301 nm ($\epsilon = 9.5 \times 10^3$). The further hypsochromic shift accompanied by hyperchromic effects for $>1.0 \times 10^{-3}$ mol dm^{–3} LiClO₄ could not be explained by the formation of only an ion pair Li⁺PBI[–] but is probably due to formation of “reverse” coordinated⁵ species, (Li⁺)₂PBI[–] (in other word, a triple cation). We propose that the isosbestic point observed at 310 nm indicates an equilibrium between Li⁺PBI[–] and (Li⁺)₂PBI[–] in acetonitrile. The ¹H NMR spectra of LiPBI in the presence of increasing concentration of LiClO₄ gave downfield shifts which may be consistent with the formation of (Li⁺)₂PBI[–]. Similarly, the UV spectra of n -Bu₄N⁺PMBP[–] in the presence of various concentrations of LiClO₄ also suggested the formation of both the ion pair, Li⁺PMBP[–], and the triple cation, (Li⁺)₂PMBP[–]. The triple cation formation has also been demonstrated for the 2,4-dinitrobenzoate ion in acetonitrile by UV absorption spectra with increasing concentration of LiClO₄.^{4c}

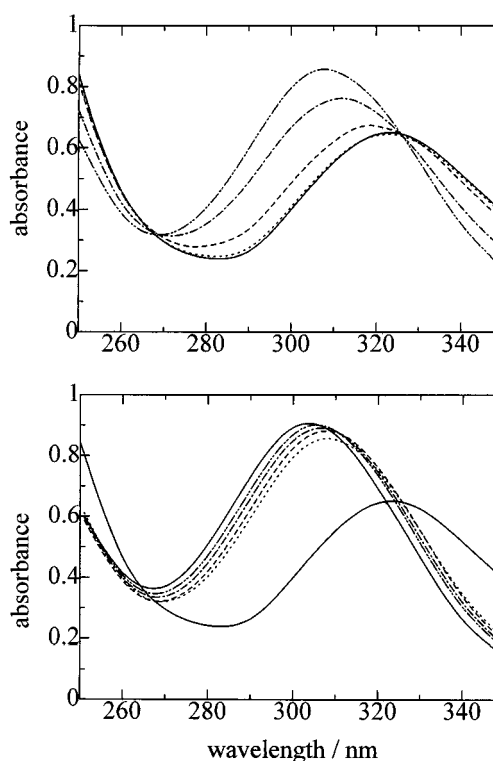


Figure 7. Effect of LiClO₄ on the absorption spectra of the PBI[–] ion ([Bu₄NPBI] = 1.0×10^{-3} mol dm^{–3}; 0.1 cm path length) in acetonitrile: (upper): (—) 0; (---) 1.0×10^{-4} ; (—) 2.0×10^{-4} ; (— · —) 5.0×10^{-4} ; (— · · —) 1.0×10^{-3} mol dm^{–3} LiClO₄; (lower): (—) 0; (---) 1.0×10^{-3} ; (—) 1.0×10^{-2} ; (— · —) 0.1; (— · · —) 0.2; (—) 0.5 mol dm^{–3} LiClO₄.

SCHEME 2: The (Li⁺)₂PBI[–] and Li⁺(PBI[–])₂ Complexes

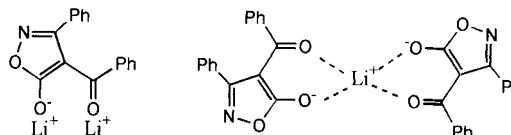


Figure 8 shows the chemical shifts of the ⁷Li signal of LiClO₄ in the presence of various concentrations of n -Bu₄N⁺X[–] (X[–] = PBI[–], PMBP[–], and PMTFP[–]). With increasing amounts of PBI[–] and PMBP[–], downfield shift of ⁷Li approached an asymptotic value after [X[–]]/[Li⁺] ≥ 2.0 suggesting the formation of a Li⁺(X[–])₂-type complex for both PBI[–] and PMBP[–] in acetonitrile. As for PMTFP[–], a 5-fold excess of the ligand to Li⁺ was needed to attain a constant δ value, probably because of the weaker interaction between Li⁺ and PMTFP[–]; cf. Table

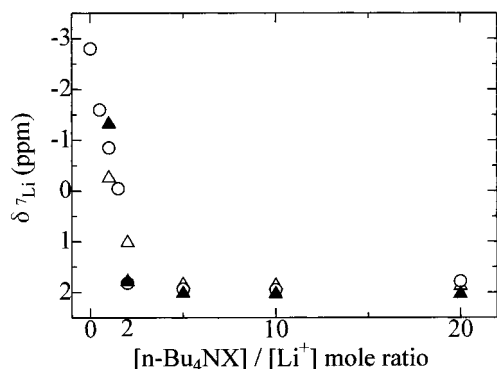


Figure 8. Chemical shift of ^7Li as a function of $[\text{n-Bu}_4\text{NX}]/[\text{LiClO}_4]$ mole ratio, 0.01 mol dm^{-3} LiClO_4 in CD_3CN : (O) X = PBI; (\blacktriangle) X = PMBP; (\triangle) X = PMTFP.

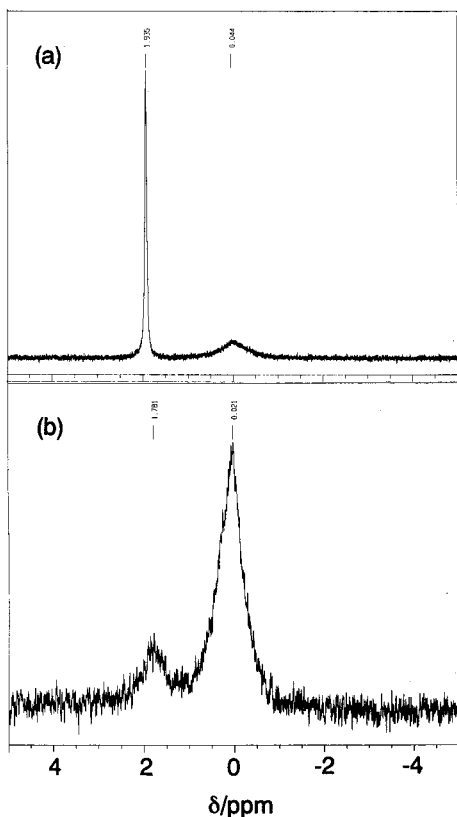


Figure 9. ^7Li NMR spectra of 0.01 mol dm^{-3} LiClO_4 in the presence of $n\text{-Bu}_4\text{NPBI}$ in CD_3CN : (a) 0.15 , (b) 0.20 mol dm^{-3} $n\text{-Bu}_4\text{NPBI}$.

3. By a similar procedure, Schmidt et al.¹¹ have demonstrated the presence of a $\text{Li}^+(\text{BP})_2$ complex (BP = 2,2'-bipyridine) in nitromethane. However, at higher concentrations of $n\text{-Bu}_4\text{N}^+\text{-PBI}^-$ as compared to $\text{Li}^+\text{ClO}_4^-$, a second peak was observed around $\delta = 0.03$; cf. Figure 9. The second peak was broadened while the first peak was sharp for $[\text{PBI}^-] \leq 0.15 \text{ mol dm}^{-3}$. Even with $[\text{PBI}^-] = 0.3 \text{ mol dm}^{-3}$, the lower field peak ($2.0 > \delta > 1.5$) was still observable. The broad second peak may be assigned to some species of higher coordination numbers ($n > 4$). Olsher et al.²⁵ have reviewed the coordination chemistry of the lithium ion and concluded that the most favorable coordination numbers of Li^+ are expected to be 4, 5, and 6. Two forms of 5-fold coordination are common, i.e., a trigonal bipyramid (TBP) and a square pyramid (SP); these configurations can be interconverted. The octahedral structure with a coordination number of 6 can be distorted to other structures. We suggest that various configurations of 5- or 6-coordinated species may

give rise to the broad ^7Li signal. An X-ray diffraction study has shown that the 6-coordinated (octahedral) $\text{Li}^+ \cdots \text{N}$ bond is longer than the 4-coordinated (tetrahedral) bond.²⁶

On the other hand, addition of $\leq 0.4 \text{ mol dm}^{-3}$ $n\text{-Bu}_4\text{N}^+\text{-PMBP}^-$ to 0.01 mol dm^{-3} LiClO_4 in CD_3CN gave almost no ^7Li second signal around $\delta = \pm 0$. The two 1-phenyl groups in the PMBP $^-$ anion may probably hinder 5- or 6-coordinated species of Li^+ . The higher coordination numbers may also be based on the long $\text{O} \cdots \text{O}$ distance of the PBI^- ion (vide supra).¹⁹ It should also be noted that the ^7Li signal of LiPMBP was shifted to lower fields without line broadening when water, 0.5, 1.0, and 2.0 vol %, was added to CD_3CN .

Supporting Information Available: Supporting Information Available: Table IS, observed molar conductivities of LiPMBP , LiPMTFP , and LiPBI in acetonitrile at 25°C ; Table II, observed molar conductivities of LiPMBP in acetone, DMF, and propylene carbonate; Table IIIS, variations in the physical properties of MeCN at 25°C by the addition of small amount of other solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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