Ionic Association of Some Lithium Salts in 1,2-Dimethoxyethane. A Raman Spectroscopic and Conductivity Study

Prakash K. Muhuri, Bijan Das, and Dilip K. Hazra*

Department of Chemistry, North Bengal University, Darjeeling 734 430, India

Received: November 8, 1996; In Final Form: February 8, 1997[⊗]

Precise measurements on electrical conductances as well as laser Raman spectra in the wavenumber range 3500−100 cm^{-1} of five lithium salts in 1,2-dimethoxyethane (DME) have been reported. The conductance data are interpreted by the Fuoss−Kraus theory, yielding values for the ion-pair and triple-ion formation constants. The Raman spectra suggest the presence of "spectroscopically free" ClO_4^-, BF_4^-, and AsF_6^-, ions in solutions, whereas there is no such evidence for either the Cl^- or Br^- ion, thus substantiating the very high ion-pair formation constants for LiCl and LiBr as obtained from conductance measurements. The observed processes have been interpreted by an Eigen multistep mechanism. Changes in the Raman bands at ca. 867, 1147, 1452, and 2805 cm^{-1} suggest that the solvation of Li^+ ion in DME occurs through the ethereal oxygen atom of the solvent molecule.

Introduction

Lithium has been considered for many years as an anode material for nonaqueous batteries.[1] In such systems, the choice of electrolyte solution and optimization of its salt concentration are two important factors. An electrolyte possessing high specific conductivity and hence with minimal ion−ion interaction is required to maintain the cell at low internal resistance. Knowledge of the state of association of the electrolytes and their interaction with the solvent molecules is essential for the optimal choice of solvent and electrolyte. To this end, a classical method such as electrical conductance has been used to study the status of association of the electrolytes. Such studies are complemented with structural studies of the metal ion solvates using Raman spectroscopy. Hopefully, this would give a molecular rationale for the choice of a given electrolyte in battery construction.

Recently, we have initiated a program[2−6] to study Li^+ ion solvation in different nonaqueous solvents from conductometric, viscometric, and laser Raman spectroscopic measurements. The study has now been extended to 1,2-dimethoxyethane (DME), a solvent particularly relevant for battery construction using lithium electrodes. This is due to its proven stability when in contact with lithium.[1,7] Here, we have investigated the solution behavior of five electrolytes, LiCl, and LiBr, LiClO$_4$, LiBF$_4$, and LiAsF$_6$, in DME using laser Raman spectroscopic and conductometric techniques in an effort to provide a picture of the effect of the anion on the process of ion complexation in this medium.

Experimental Section

1,2-Dimethoxyethane (Fluka, purum) was shaken well with FeSO$_4$ (AR, BDH) for 1−2 h, decanted, and distilled. The distillate was refluxed for 12 h and redistilled over metallic sodium,[8] and the middle fraction was collected. The purity of the solvent as checked by gas chromatography was found to be greater than 99.8%. The boiling point (357.5 K) and density (0.8613 g cm^{-3}) at 298.15 K also compared fairly well with the literature values:[9] 358.15 K and 0.8612 g cm^{-3}, respectively.

The salts were of Fluka purum or puriss grade. Lithium chloride, lithium bromide, lithium tetrafluoroborate, and lithium hexafluoroarsenate were dried under vacuum at high temperatures for 48 h and were used without further purification. Lithium perchloarte was recrystallized three times from conductivity water and then dried under vacuum for several days. To avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell (cell constant 0.13 cm^{-1}) with an accuracy of 0.01%. The cell was calibrated by the method of Lind and co-workers.[10] Measurements were made in an oil bath maintained at 298.15 ± 0.005 K, as described earlier.[11] Several independent solutions were prepared, and conductance measurements were performed with each of these to ensure the reproducibility of the results. Corrections were made for the specific conductance of the solvent.

Laser Raman spectroscopic measurements were made with a DILOR Z24 spectrometer using 4880 Å excitation. The spectral slit width was kept at 4 cm^{-1}. The laser power used was 300 mW. The spectra were recorded by the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. All spectra were scanned at least twice to ensure repeatability.

The dielectric constant of pure solvent ($\epsilon = 7.075$ at 298.15 K) was taken from the literature.[9]

Results and Discussion

Raman Spectra. The Raman spectra of pure 1,2-dimethoxyethane and of the solutions of LiCl, LiBr, LiClO$_4$, LiBF$_4$, and LiAsF$_6$ in 1,2-dimethoxyethane in the range 3500−100 cm^{-1} have been presented in Figures 1 and 2. The principal bands observed have been listed in Table 1. Partial band assignments for the pure solvent as well as of the solutions have also been made and discussed accordingly. From Figure 1 we see that 1,2-dimethoxyethane (DME) shows $\nu_s(C-O)$ and $\nu_{as}(C-O)$ in the range 1100−1150 cm^{-1} and 800−950 cm^{-1}, respectively. The $\nu_{as}(C-H)$ stretching mode of the solvent appears in the range 1400−1500 cm^{-1} and the $\nu_s(C-H)$ mode in the range of 2700−3000 cm^{-1}. It has been observed that the spectra of the salt solutions show several remarkable changes from that of pure solvent.

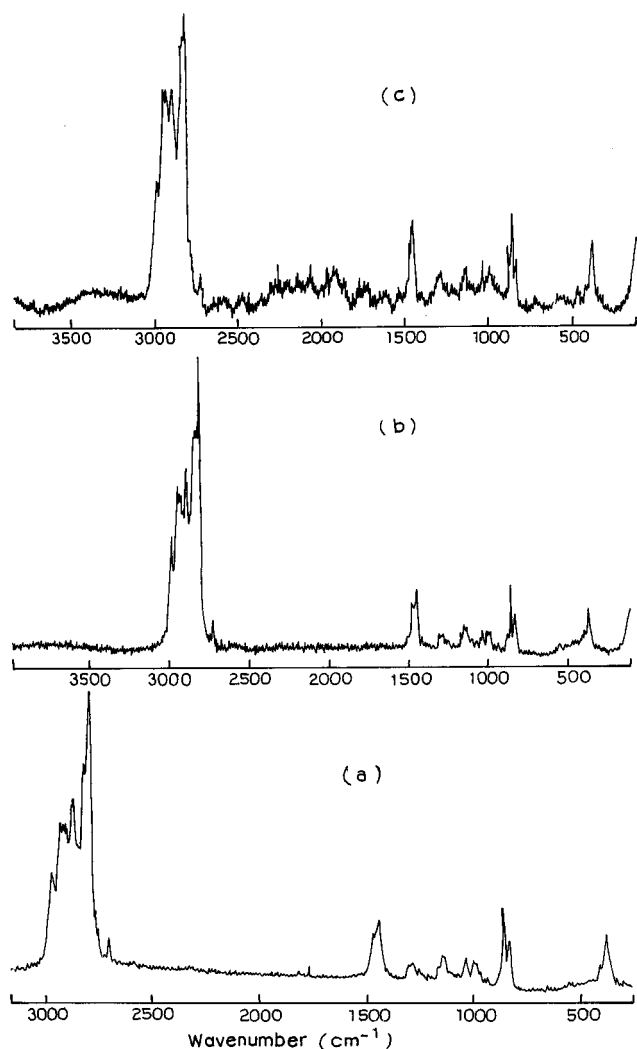For the salts a broad band near 400 cm^{-1} is obtained, and this has been assigned to the vibration primarily involving the

Figure 1. Raman spectra of (a) pure 1,2-dimethoxyethane, (b) LiCl in 1,2-dimethoxyethane, and (c) LiBr in 1,2-demethoxyethane.

Figure 2. Raman spectra of (a) LiClO$_4$, (b) LiBF$_4$, and (c) LiAsF$_6$ in 1,2-dimethoxyethane.

lithium ion. This band frequency is found to be anion dependent. The observation is similar to those found in other weakly solvating nonpolar solvents such as tetrahydrofuran[12,13] and pyridine.[14] The variation of the 400 cm^{-1} band of Li$^+$ ion with different anions indicates that the cation is associated with the anion in an intimate way in DME solutions, and this association may be primarily in the form of contact ion pairs. However, one can also expect that the cation might have some solvent molecules in its near-neighbor environment on geometrical grounds. A comparison of cation frequency in DME with that in some other solvents, 2-methoxyethanol,[6] acetone,[15] methyl acetate, and methyl formate,[16] etc., shows that the frequency of the cation vibration also varies with the solvent. This implies that the solvent affects the vibration of Li$^+$ ion in DME solution. Thus one is led to the view that the cation vibrates in a cage composed of anion and solvent molecules in DME solution and that all elements in this cage contribute (although not necessarily equally) to the factors that determine this band frequency.

For LiClO$_4$, a new nondegenerate band appearing at 942 cm^{-1} is attributed to the infrared forbidden totally symmetric stretching vibration of the perchlorate ion.[15,17] LiAsF$_6$ solution exhibits a very strong band centered at $\sim$681 cm^{-1} due to the symmetrical stretching mode of AsF$_6^-$ ion.[18,19] Raman spectrum of LiBF$_4$ solution shows two new bands peaking around 476 and 2335 cm^{-1} due to an internal vibration of the anion,[13] the latter of which being the overtone of the former. The ap-
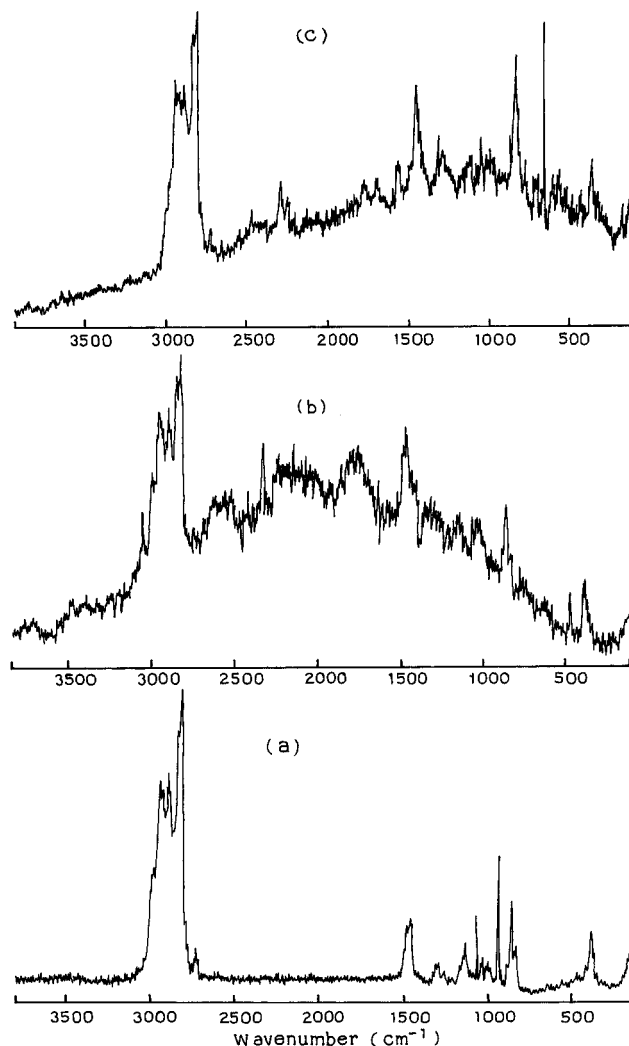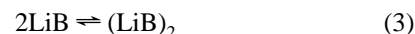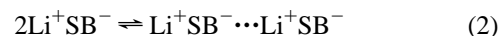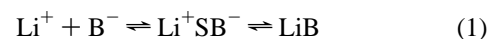
pearence of these new bands for these salts can be assigned to the "spectroscopically free" anion B$^-$ (B = ClO$_4$, AsF$_6$, and BF$_4$) in DME, that is, to the solvent-separated ion pair Li$^+$SB$^-$ (S is solvent molecule) and/or to the solvent-separated dimer, Li$^+$SB$^-$···Li$^+$SB$^-$, spectroscopically indistinguishable from each other.

Three other weaker bands—at 995 cm^{-1} for LiClO$_4$, at 513 cm^{-1} for LiBF$_4$, and at 705 cm^{-1} for LIAsF$_6$—are presumed to be due to contact ion pairs, the anions having lower symmetries, based on the collateral evidence in 1,2-dimethoxyethane[19] and 2-methyltetrahydrofuran.[17] The relative intensity continues to decrease in the order LiClO$_4$ > LiBF$_4$ > LiAsF$_6$, suggesting that the proportion of the contact species decrease in the same order.

All these above observations may be interpreted in terms of the following eigen multistep mechanism:

$$\text{Li}^+ + \text{B}^- \rightleftharpoons \text{Li}^+\text{SB}^- \rightleftharpoons \text{LiB} \qquad (1)$$

$$2\text{Li}^+\text{SB}^- \rightleftharpoons \text{Li}^+\text{SB}^-\cdots\text{Li}^+\text{SB}^- \qquad (2)$$

$$2\text{LiB} \rightleftharpoons (\text{LiB})_2 \qquad (3)$$

For LiAsF$_6$, one would therefore expect only the presence of an equilibrium between the solvent-separated and contact ion pairs represented by eq 1 that is strongly shifted toward the left. The equilibrium represented by eq 2 to form the solvent-

TABLE 1: Raman Frequencies in cm^{-1} [a]

DME	LiCl	LiBr	LiClO$_4$	LiBF$_4$	LiAsF$_6$
385.4(s)	374.3(s)	377.8(s)	379.8(s)	386.5(s)	369.6(s)
				476.0(s)	
					681.2(vs)
838.7(s)	831.8(s)	831.3(m)			845.2(s)
867.2(s)	858.7(s)	857.0(vs)	860.0(s)	864.0(m)	865.3(m)
		878.8(m)			885.5(m)
			942.3(vs)		
994.8(m)	1001.5(m)	987.7(m)	995.3(m)		1003.1(m)
1034.5(m)	1036.7(m)	1031.2(m)	1034.5(m)	1039.2(m)	1025.6(m)
					1060.5(s)
1146.7(m)	1144.4(m)	1138.2(m)	1140.3(w)	1142.7(m)	1122.0(w)
		1163.9(w)	1165.8(w)	1180.5(w)	
				1289.9(m)	1294.2(m)
1452.5(s)	1463.1(s)	1456.9(s)	1461.7(m)	1463.6(w)	1447.4(w)
				2245.1(m)	1575.0(m)
				2334.7(s)	
2706.5(w)	2727.9(w)	2720.2(w)	2726.0(w)	2722.7(w)	2723.0(m)
2805.5(vs)	2825.2(vs)	2819.2(s)	2820.0(s)	2834.2(s)	2823.5(s)
2827.5(w)	2841.8(w)	2835.0(m)	2841.6(w)	2856.1(w)	2848.1(w)
2878.1(m)	2899.7(m)	2890.5(m)	2892.5(m)	2905.8(m)	2889.1(m)
					2897.2(m)
2937.5(w)	2949.4(w)	2943.4(w)	2945.5(w)	2957.1(m)	2952.6(w)
2979.2(m)	2988.7(m)	2985.5(w)	2980.7(vw)	2999.3(w)	2983.4(vw)

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

TABLE 2: Equivalent Conductances (S cm^2 mol^{-1}) and Corresponding Molarities (mol dm^{-3}) of the Lithium Salts in 1,2-Dimethoxyethane at 298.15 K

LiCl		LiBr		LiClO$_4$		LiBF$_4$	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
90.29	0.097	514.74	0.361	902.34	2.802	1000.81	0.952
80.15	0.100	434.96	0.367	800.46	2.659	898.32	0.900
70.00	0.104	360.32	0.378	703.44	2.465	795.82	0.828
60.36	0.108	301.13	0.392	601.56	2.299	699.36	0.782
50.22	0.115	252.22	0.408	494.83	2.126	602.90	0.735
40.07	0.124	200.75	0.434	397.80	2.004	500.40	0.688
29.93	0.138	151.85	0.474	300.74	1.882	397.91	0.639
20.29	0.162	96.51	0.557	198.90	1.836	301.45	0.622
10.14	0.220	51.47	0.716	97.03	2.063	198.96	0.633

separated dimer may also exist since Li$^+$SB$^-$ and Li$^+$SB$^-$···Li$^+$SB$^-$ are indistinguishable by Raman spectra. However, no contact quadrupole is expected to form through eq 3 for LiAsF$_6$. For both LiBF$_4$ and LiClO$_4$, where contact ion pairs are present in larger amounts than in the case of LiAsF$_6$, the formation of contact quadrupoles or dimers via eq 3 is possible. The relative amount of contact quadrupoles will be greater in LiClO$_4$ than in LiBF$_4$ for reasons described earlier.

The salts LiCl and LiBr remain essentially in the form of contact ion pairs, no solvent-separated ion pairs being detectable, since there is no evidence for the "spectroscopically free" Cl$^-$ or Br$^-$ ions in the salt solutions. A significant amount of the quadrupoles of the inner sphere type (contact quadrupole) will also be present in LiCl and LiBr solutions.

The molecular reasons for the above may be explained as follows: The donor ability of the ligands decreases in the order Cl$^-$ > Br$^-$ > ClO$_4^-$ > BF$_4^-$ > AsF$_6^-$, and the steric hindrance in the order AsF$_6^-$ > Br$^-$ > ClO$_4^-$ > Br$^-$ > Cl$^-$. Now, the ligands will compete with the solvent molecules for the first coordination positions around Li$^+$ ion, and in view of the above the probability of entering into the first solvation shell will decrease in the order Cl$^-$ > Br$^-$ > ClO$_4^-$ > BF$_4^-$ > AsF$_6^-$. This can also be seen from the Raman spectral shift of the strong symmetrical C–O–C stretching mode of DME. In pure solvent, this mode[20] appears at 867 cm^{-1}. Chelation of DME with the lithium ion has been shown to shift the frequency to a lower value. The shifting depends on the nature of the anion and decreases in the order LiCl > LiBr > LiClO$_4$ > LiBF$_4$ >

LiAsF$_6$. This is quite expected because the anion will obviously interfere with the chelation, and this interference is maximum in the case of salts remaining as contact ion pairs. This effect decreases with the gradual increase of solvent-separated ion pairs in the salt solutions. This complexation of 1,2-dimethoxyethane with the lithium ion has also been manifested by the shifts of the Raman frequencies of (i) the asymmetric C–O–C stretching mode and (ii) the CH$_3$ mode of the pure solvent. The asymmetric C–O–C stretching mode of 1,2-dimethoxyethane appears[20] at 1147 cm^{-1}, and the CH$_3$ asymmetric bending and CH$_3$ symmetric stretching modes appear respectively at 1452.5 and 2805.5 cm^{-1}. As a result of complexation through the oxygen lone pair with the Li$^+$ ion, the asymmetric C–O–C mode shifts to lower values, whereas both the bands due to the CH$_3$ mode shift to longer wavenumbers. All these salts of lithium show almost similar changes at the OCH$_3$ bending at 1452.5 cm^{-1} and at the methoxy stretching frequency at 2805.5 and above. Presumably, this may be due to strong interaction of the cation with the oxygen atom of the solvent molecule.

Electrical Conductance. The equivalent conductance (Λ) vs the concentration (c) data of LiCl, LiBr, LiClO$_4$, and LiBF$_4$ in 1,2-dimethoxyethane (LiAsF$_6$ was omitted due to its low solubility) are recorded in Table 2. When log Λ is plotted as a function of log c for these electrolytes, a minimum was observed in each case.

The conductance data have been analyzed by the Fuoss– Krauss triple-ion theory[21] in the form

$$\Lambda g(c) c^{1/2} = \frac{\Lambda_0}{K_P^{1/2}} + \Lambda_0^T \frac{K_T}{K_P^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \qquad (4)$$

$$g(c) = \frac{\exp\left[-\frac{2.303}{\Lambda_0^{1/2}} \beta'(c\Lambda^{1/2})\right]}{\left(1 - \frac{S}{\Lambda_0^{3/2}}(c\Lambda)^{1/2}\right)\left(1 - \frac{\Lambda}{\Lambda_0}\right)^{1/2}} \qquad (5)$$

where $g(c)$ is a term lumping all the interionic terms together. Here, $\beta' = 1.8247 \times 10^6/(DT)^{3/2}$ is the Debye–Huckel term of the activity coefficient, $f = \exp[(-2.303/\Lambda_0^{3/2})\beta'(c\Lambda)^{1/2}]$, and $S = [0.8204 \times 10^6/(DT)^{3/2}]\Lambda_0 + 82.501/\eta(DT)^{1/2}$ is the Onsager coefficient of the conductance equation: $\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)^{1/2}$. Also, Λ_0 is the sum of the equivalent conductances of the simple ions at infinite dilution and Λ_0^T the sum of the values for the two kinds of triple ions, LiB_2^- and Li_2B^+; K_P and K_T are the ion-pair and triple-ion formation constants, respectively. The symmetrical approximation of the two possible formation constants of triple ions equal to each other has been considered.

Neglect of Λ/Λ_0 and $(S\Lambda_0^{3/2})(c\Lambda)^{3/2}$ together with the assumption of $f_\pm = 1$ leads to $g(c) = 1$ and hence

$$\Lambda c^{1/2} = \frac{\Lambda_0}{K_P^{1/2}} + \Lambda_0^T \frac{K_T}{K_P^{1/2}} \qquad (6)$$

For the present data, it was found that eq 6 was inadequate, the data showing a downward curvature when plotted as $\Lambda c^{1/2}$ vs c. On the contrary, eq 4 gives reasonably straight lines, the curvature having almost disappeared.

To apply eq 4, it is necessary to have estimates of Λ_0 and to assume a value of Λ_0^T. Assuming $\Lambda_0^T = 2\Lambda_0/3$ and using the Walden product values $(\Lambda_0\eta)$ at 298.15 K equal to 0.675, 0.670, 0.614, and 0.564 for LiCl, LiBr, LiClO$_4$, and LiBF$_4$, respectively, and $\eta_{DME} = 0.004\,236$ P, the Λ_0 values are found to be 159.0, 158.0, 153.9, and 150.8 respectively for LiCl, LiBr, LiClO$_4$, and LiBF$_4$. Table 3 reports Λ_0, K_P, K_T, and r^2 values for the salts.

The concentrations of the ion pairs and triple ions (c_P and c_T, respectively) at the highest concentration for each electrolyte have been calculated using the following relations,

$$c_P = c(1 - \alpha - 3\alpha_T) \qquad (7)$$

$$\alpha = (K_P c)^{-1/2} \qquad (8)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \qquad (9)$$

$$c_T = (K_T/K_P^{1/2})c^{3/2} \qquad (10)$$

and are also included in Table 3. We see that the major proportion of these electrolytes exist as ion pairs with only a minor proportion as triple ions.

Electrical conductances of LiBF$_4$ and LiClO$_4$ in 1,2-dimethoxyethane have been reported earlier by Petrucci et al.[7,22] and our K_P and K_T values for these salts are found to be in good agreement with their values.

We also tried to identify triple ions and quadrupoles by analyzing the conductivity data on the basis of Newton's method, as done by Hojo et al.[23,24] However, our data did not fit well with the equation. This was also true for the conductance data of the salts in 1,2-dimethoxyethane[19] and 2-methyltetrahydrofuran[16] taken from the works of Petrucci et al.

TABLE 3: Conductance Parameters in 1,2-Dimethoxyethane

electrolyte	Λ_0	K_P	K_T	r^2	$10^4 c_P$	$10^6 c_T$
LiCl	159.0	5.96×10^8	52.39	0.9994	90.20	1.84
LiBr	158.0	1.38×10^7	10.77	0.9999	513.11	33.86
LiClO$_4$	153.9	1.34×10^6	18.24	0.9890	886.93	427.10
LiBF$_4$	150.8	9.76×10^6	29.66	0.9988	990.78	300.59

From Table 3, we see that the K_P and K_T values decrease in the order LiCl > LiBr > LiBF$_4$ > LiClO$_4$, which suggests that the total amount of ion pairs decreases in the same order on going from LiCl to LiClO$_4$. From spectral data we have seen that LiCl and LiBr exist as contact ion pairs (and contact quadrupoles) with no solvent-separated species, and this view is also supported by the conductance data. In LiBF$_4$ and LiClO$_4$ solutions both contact and solvent-separated ion pairs could be present, as observed from Raman study, the relative amount of the contact species being greater in LiClO$_4$ solution. From the present conductance study it also appears that the solvent-separated ion pairs may be present in smaller amounts in LiClO$_4$ solution.

It may thus be concluded that LiCl and LiBr remain essentially in the form of contact ion pairs along with quadrupoles of inner sphere type. On the other hand, LiClO$_4$, LiBF$_4$, and LiAsF$_6$ are found to exist in DME solution as solvent-separated ion pairs and/or solvent-separated dimers, thus exhibiting a very intense peak for the "spectroscopically free" anion. Moreover, chelation of DME with lithium ion is taking place through the lone pairs of ethereal oxygen atom.

References and Notes

(1) Christie, A. M.; Vincent, C. A. *J. Phys. Chem.* **1996**, *100*, 4618.
(2) Nandi, D.; Das, S.; Hazra, D. K. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1531.
(3) Nandi, D; Hazra, D. K. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 4227.
(4) Muhuri, P. K.; Hazra, D. K. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3511.
(5) Muhuri, P. K.; Hazra, D. K. *Z. Naturforsch.* **1993**, *48a*, 523.
(6) Das, B.; Hazra, D. K. *J. Phys. Chem.* **1995**, *99*, 269.
(7) Maaser, H. E.; Delsignore, M.; Newstein, M.; Petrucci, S. *J. Phys. Chem.* **1984**, *88*, 5100.
(8) Ghosh, S. K.; Hazra, D. K.; Lahiri, S. C. *Thermochim. Acta* **1989**, *147*, 41.
(9) Renard, E.; Justice, J-C. *J. Solution Chem.* **1974**, *3*, 633.
(10) Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1557.
(11) Dasgupta, D.; Das, S.; Hazra, D. K. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1057.
(12) Edgell, W. F.; Lyford, J., IV.; Wright, R.; Risen, W., Jr.; Watts, A. *J. Am. Chem. Soc.* **1970**, *92*, 2240.
(13) Chang, S.; Severson, M. W.; Schmidt, P. P. *J. Phys. Chem.* **1985**, *89*, 2892.
(14) McKinney, W. J.; Popov, A. I. *J. Phys. Chem.* **1970**, *74*, 535.
(15) Pullin, A. D. E.; Pollock, J. M. *Trans. Faraday Soc.* **1958**, *54*, 11.
(16) Deng, Z.; Irish, D. E. *Can. J. Chem.* **1991**, *69*, 1766.
(17) Maaser, H.; Xu, M.; Hemmes, P.; Petrucci, S. *J. Phys. Chem.* **1987**, *91*, 3047.
(18) Deng, Z.; Irish, D. E. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2891.
(19) Farber, H.; Irish, D. E.; Petrucci, S. *J. Phys. Chem.* **1983**, *87*, 3515.
(20) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964.
(21) Fuoss, R. M.; Accascina, F. *Electrolytic Conductance*; Interscience: New York, 1959.
(22) Onishi, S.; Farber, H.; Petrucci, S. *J. Phys. Chem.* **1980**, *84*, 2922.
(23) Hojo, M.; Watanabe, A.; Mizobuchi, T.; Imai, Y. *J. Phys. Chem.* **1990**, *94*, 6073.
(24) Hojo, M.; Hasegawa, H.; Miyauchi, Y.; Moriyama, H.; Yoneda, H; Arisawa, S. *Electrochim. Acta* **1994**, *39*, 629.