December, 1993] © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., **66**, 3627—3632(1993)

Study of Lithium Salts in Solvents with Low Dielectric Constant by Means of Ultrasonic Velocity and Absorption

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(Received July 8, 1993)

Ultrasonic velocity at 1.92 MHz has been measured precisely in 1,2-dimethoxyethane (DME), acetonitrile (AN), and propylene carbonate (PC) solutions of lithium tetrafluoroborate ($LiBF_4$) and in DME solution of lithium hexafluoroarsenate ($LiAsF_6$) at 25 °C. The molar relative sound velocity for the $LiBF_4$ solution has been found to show a clear inflection in the DME solution at 0.01 mol dm^{-3} and in the AN one at 0.02 mol dm^{-3} concentration though such an inflection has not been found in PC solution. The inflection for DME solution of $LiAsF_6$ is found near 0.0013 mol dm^{-3}. These sound velocity inflection points are believed to be due to formation of triple ions or dimers (quadrupoles) in solvents of low dielectric constants.

Ultrasonic absorption coefficients in DME solutions of $LiAsF_6$ and $LiBF_4$ have been measured in the frequency range from 8.5 to 220 MHz by a pulse method as a function of their concentration. A single relaxational absorption has been observed in both solutions. In DME solution of $LiBF_4$, the observed relaxational absorption mechanism has been attributed to the dimerization reaction, as reported by Maaser et al. (*J. Phys. Chem.*, **88**, 5100 (1984)). Our determination of the rate and thermodynamic constants, however, has taken into account the presence of triple ions.

The results in $LiAsF_6$ solutions are compared to those reported by Farber et al. (*J. Phys. Chem.*, **87**, 3515 (1983)) in the concentration range higher than 0.1 mol dm^{-3}. At concentrations lower than that, however, a phenomenon with a concentration dependent relaxation frequency has been found. From a consideration of various reaction models, it has been concluded that the relaxation is associated with formation of triple ions in solution. The rate and thermodynamic parameters have been determined from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength.

The solution properties of lithium salts in nonaqueous solvents have been widely investigated by various methods.[1] Ultrasonic absorption and velocity may provide useful information concerning the dynamical properties (relaxations) and the structural changes (compressibility) in such solutions. The ultrasonic methods are also used to study the solution characteristics of lithium salts in various solvents.[2] Depending upon the sizes of the anions and the characteristics of the solvents, it is believed that ion pairs, triple ions and the quadrupoles (dimers) may be formed in their solutions. Information concerning the dynamical properties of lithium salts is very important because such information may be closely related to the transport mechanisms of electrically conductive species. Farber et al.[3] reported that the ultrasonic relaxation of $LiAsF_6$ in DME is associated with the solvation process and Maaser et al.[4] showed that the relaxation of $LiBF_4$ in the same solvent is due to the dimerization process. Because of these apparent differences in the behavior of the two solutions, we wished to reexamine whether the ultrasonic relaxations observed in solutions of $LiBF_4$ and $LiAsF_6$ in the pulse frequency range reflect the processes associated with solvation or dimerization in the particular solvent. Also, we expect that the solution compressibility may be altered if higher order aggregates, such as triple ions or quadrupoles, are formed in these solutions. In the present study, the solution characteristics of some lithium salts in solvents with low dielectric constant are reconsidered by measuring the sound absorption and sound velocity.

Experimental

Chemicals: $LiBF_4$ (lithium tetrafluoroborate) and $LiAsF_6$ (lithium hexafluoroarsenate) were purchased from Morita Kagaku Co., Ltd., and were the purest grades commercially available. These salts were dried under reduced pressure at 50—80 °C. DME (1,2-dimethoxyethane), AN (acetonitrile), and PC (propylene carbonate) were purchased from Wako Pure Chemical Co., Ltd. and were dried through molecular sieves, then distilled.

Apparatus: Ultrasonic velocity measurements were carried out by a sing-around meter at 1.92 MHz. This equipment provides an accurate relative value of the sound velocity of the solvent (±5 cm s^{-1}), though the absolute value is not as well determined (±50 cm s^{-1}). Ultrasonic absorption coefficients were measured by a pulse method in the frequency range from 8.5 to 220 MHz, the details of which are described elsewhere.[5] The ultrasonic cells, which were tightly isolated from air by circulating dry N_2 gas, were immersed in a water bath maintained at a constant temperature with an accuracy better than ±0.003 °C. All measurements were carried out at 25 °C.

Results and Discussion

The sound velocity, v, in DME solutions of $LiBF_4$ and $LiAsF_6$ appears to increase gradually with increasing salt concentration. The difference of the sound velocity from that of solvent, v_0, divided by the analytical concentration, C_0, $V_d=(v-v_0)/C_0$, may indicate the presence of structural changes in solution.[6] The plots of V_d vs. the concentration are shown for $LiBF_4$ solutions in three solvents in Fig. 1. In DME (dielectric constant=5.5) an inflection is found at 0.01 $mol\,dm^{-3}$ and in AN (DK=36) it is observed at 0.02 $mol\,dm^{-3}$. However, in PC (DK=65) solution, the inflection could hardly be observed. These results indicate that the position of the inflection concentration increases with the solvent dielectric constant.

Barthel et al.[7] have reported that the concentration dependence of the molar conductivity for DME solution of $LiBF_4$ indicates a minimum at around 0.015 $mol\,dm^{-3}$ (0.018 mol kg^{-1}), at a concentration that is slightly higher than the inflection concentration observed by sound velocity. The dependence of the molar conductivity in DME on $LiAsF_6$ concentration was reported by Maaser et al.[4] at concentration lower than 0.09 $mol\,dm^{-3}$. We have measured it to a concentration of 0.21 $mol\,dm^{-3}$ and the results are very similar to those reported in ref. 4 in the lower concentration range.[8] The sound velocity was also measured in DME solution of $LiAsF_6$. For sake of comparison, the difference of the molar sound velocity is shown in Fig. 2 along with that of $LiBF_4$. The inflection concentration is found at 0.0013 $mol\,dm^{-3}$ for the $LiAsF_6$ solution. It is likely that the characteristic properties of the DME solutions may change at the concentrations where the difference of the molar sound velocity shows the inflection. One possible explanation for these observations is that the nature of the chemical species has changed from single ions and their pairs to triple ions, dimers or higher aggregates in these solutions.

From the results of sound velocity measurements, it may be concluded that it is difficult for lithium salts to form higher aggregates with increasing solvent dielectric constant. Also, depending upon the size of the anion, the inflection concentration may be altered. That is, the formation of the aggregate is also controlled by the structure of the counter ion. However, it is certain that these sound velocity inflection phenomena reflect a change in the adiabatic compressibility of the solution, κ_s, according to the well known Laplace equation, $\kappa_s = 1/(\rho v^2)$, where ρ is the solution density. The solution density changes gradually with solute concentration.[7]

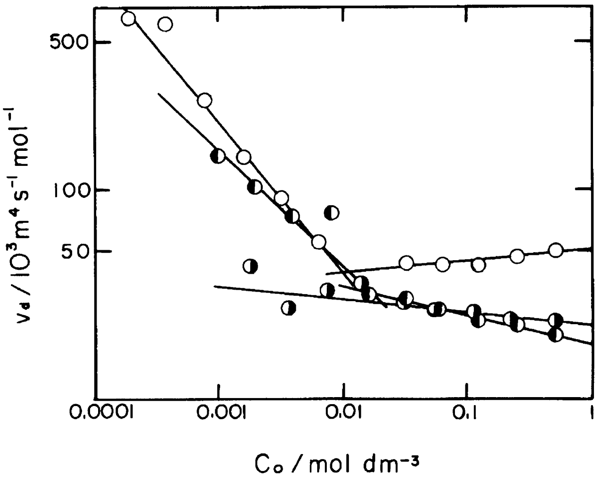

Fig. 1. Concentration dependence of the relative sound velocity per mole for $LiBF_4$ in solvents with different dielectric constant at 25 °C. ○: in DME; ◐: in AN; ◑: in PC.

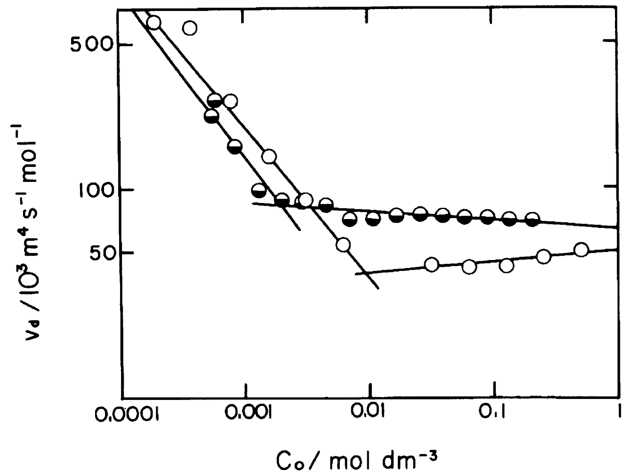

Fig. 2. Concentration dependence of the relative sound velocity per mole for DME solution of $LiAsF_6$ and $LiBF_4$ at 25 °C. ◓: $LiAsF_6$ solution; ○: $LiBF_4$ solution.

The ultrasonic absorption coefficients divided by the square of the measurement frequency, α/f^2's, were frequency independent in DME solvent per se, in DME solutions of $LiBF_4$ at concentration lower than 0.05 $mol\,dm^{-3}$, and in those of $LiBF_4$ lower than 0.005 $mol\,dm^{-3}$, while they are frequency dependent at higher than those listed concentrations. That is, the relaxational absorption was only observed in the concentration range where the higher aggregates are believed to coexist in the solutions according to conductivity and sound velocity experiments. In order to analyze the frequency dependence of the absorption coefficients, the following Debye-type single relaxational equation is applicable:

$$\alpha/f^2 = A/\{1+(f/f_r)^2\} + B, \qquad (1)$$

where A is the amplitude of the ultrasonic relaxation, f_r the relaxation frequency and B the background absorption. The three ultrasonic parameters, A, B, and f_r, were determined so as to obtain the best fit of the experimental data to Eq. 1, using a nonlinear least-mean square computer program. The ultrasonic parameters so calculated are listed along with the sound velocity data in Table 1. Figures 3 and 4 show some representative absorption spectra for DME solutions of $LiBF_4$ and $LiAsF_6$, respectively. The solid lines indicate the calculated values and it is seen that the agreement between the experimental and calculated values is excellent. These results demonstrate that a single relaxational absorption is observed in solutions of both

Table 1. Ultrasonic Parameters for DME Solutions of $LiBF_4$ and $LiAsF_6$ at 25 °C

Concn	f_r	A	B	c
	MHz	$10^{-15}\,m^{-1}\,s^2$		$m\,s^{-1}$
		$LiBF_4$		
0.000	—	—	30.8	1165.1
0.050	51±7	22±7	33.0±0.3	1168.6
0.060	22±4	34±8	35.2±0.2	1169.0
0.080	27±3	21±2	34.7±0.4	1170.0
0.090	48±3	19±1	33.3±0.2	1170.5
0.100	49±4	33±2	37.4±0.3	1171.1
0.110	38±3	25±2	35.4±0.2	1171.5
0.120	40±6	31±5	34.8±0.4	1172.0
0.150	71±8	37±2	29.0±3.0	1173.4
0.160	66±4	25±1	42.1±0.3	1173.9
0.170	87±10	35±2	38.0±2.0	1174.3
0.200	94±4	49±1	42.9±0.6	1175.8
0.300	130±18	43±2	35.0±3.0	1180.6
0.350	132±11	56±2	34.0±2.0	1183.0
0.400	126±7	38±1	49.5±1.0	1185.5
0.450	123±4	50±1	48.6±0.6	1186.9
0.470	151±13	56±2	43.0±3.0	1189.0
0.500	138±10	54±2	50.0±2.0	1190.3
		$LiAsF_6$		
0.005	56±3	13±1	29.8±0.1	1165.4
0.006	48±4	15±1	30.3±0.1	1165.5
0.007	55±8	15±2	30.2±0.3	1165.7
0.008	48±1	15±1	32.6±0.1	1165.8
0.010	58±3	19±2	32.1±0.2	1165.8
0.060	72±3	54±2	38.3±0.5	1169.6
0.070	71±2	53±1	44.3±0.4	1170.2
0.300	88±13	59±6	54.0±2.0	1184.7

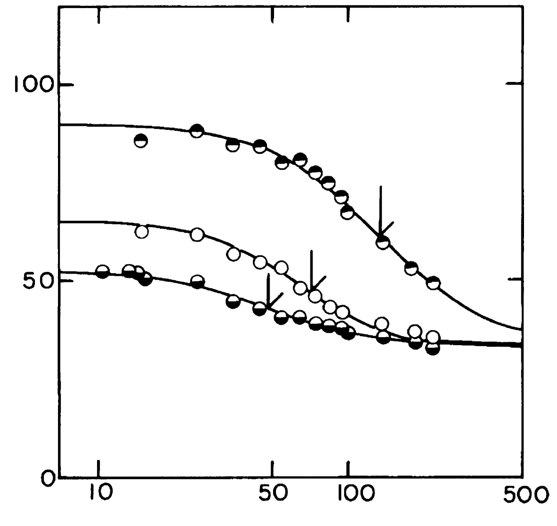

Fig. 3. Representative ultrasonic absorption spectra in DME solutions of $LiBF_4$ at 25 °C. ◒: 0.090 mol dm^{-3}; ○: 0.15 mol dm^{-3}; ◓: 0.35 mol dm^{-3}.

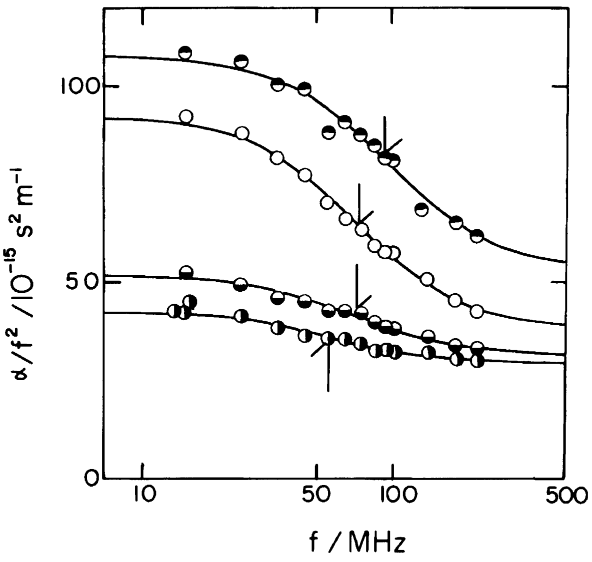

Fig. 4. Representative ultrasonic absorption spectra in DME solutions of $LiAsF_6$ at 25 °C. ◑: 0.005 mol dm^{-3}; ◒: 0.030 mol dm^{-3}; ○: 0.060 mol dm^{-3}; ◓: 0.10 mol dm^{-3}.

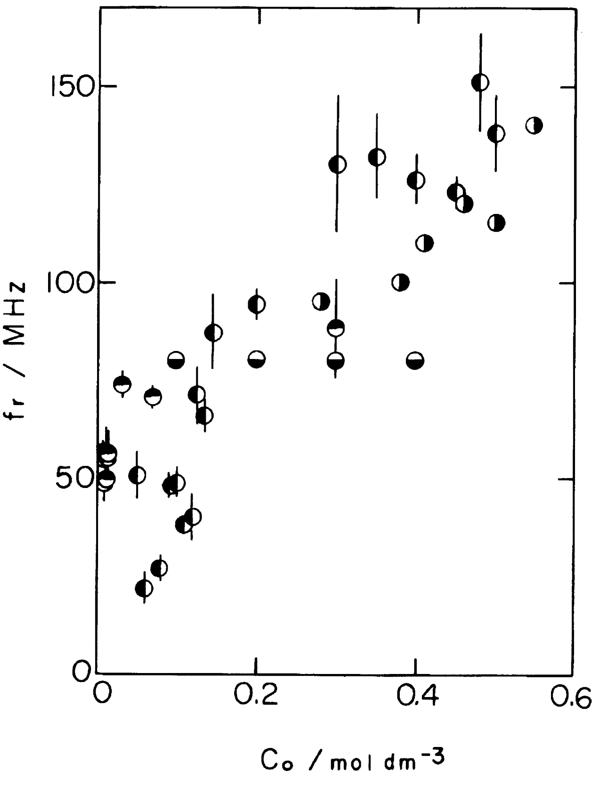

Fig. 5. Concentration dependence of the relaxation frequency. ◓: present data for $LiAsF_6$ solution; ◒: those by Farber et al. for $LiAsF_6$ solutions; ◐: present data for $LiBF_4$ solution; ◑: those by Maaser et al. for $LiBF_4$ solution.

$LiBF_4$ and $LiAsF_6$. The complete sets of α/f^2 values at various concentrations of salts are available on request from one of the authors (S.N.). Figures 5 and 6 show the concentration dependencies of the relaxation frequency and the amplitude of the ultrasonic relaxation, respectively. The results reported by Farber et al.[3] and Maaser et al.[4] in DME solutions of $LiAsF_6$

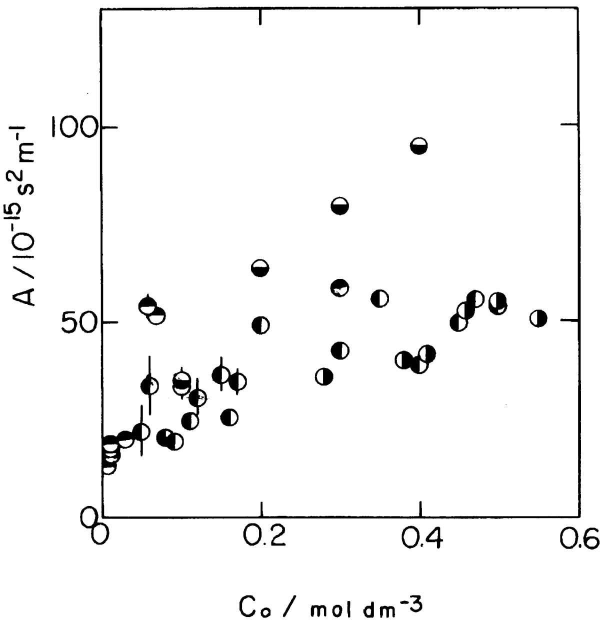

Fig. 6. Concentration dependence of the amplitude of the ultrasonic relaxation. ◓: present data for $LiAsF_6$ solution; ◒: those by Farber et al. for $LiAsF_6$. Their data at more than 0.3 mol dm^{-3} are off this scale; ◐: present data for $LiBF_4$ solution; ◑: those by Maaser et al. for $LiBF_4$.

and $LiBF_4$ are also shown in the figures for comparison. The facts that the similar ultrasonic absorption results are obtained in a similar concentration range may indicate that the salt solutions used in this study are fully applicable to the ultrasonic study. The source of the relaxation in $LiAsF_6$ solution was attributed to a unimolecular reaction associated with the solvation process, since the observed relaxation frequency was reported to be independent of the concentration.[3] However, our new finding is the result that the observed relaxation frequency does depend on the concentration at the lower $LiAsF_6$ concentrations.

In order to clarify the absorption mechanisms, it is very important to determine the nature of the chemical species present in the solutions. It may be certain that the higher aggregates exist in the lithium salt solutions of which solvents have low dielectric constant. In consistent with previous studies carried out by other investigators,[3,4] we also assume the following equilibria.

$$\begin{array}{l} M^+ + L^- \underset{k_{21}}{\overset{\overset{\text{I}}{k_{12}}}{\rightleftharpoons}} ML \underset{\substack{k_{32}\\ M^+(\text{or } L^-)}}{\overset{\overset{\text{II}}{k_{23}}}{\rightleftharpoons}} MML^+(\text{or } MLL^-), \\ 2ML \underset{k_{43}}{\overset{\overset{\text{III}}{k_{34}}}{\rightleftharpoons}} (ML)_2, \end{array} \qquad (2)$$

where M^+ and L^- are the cation and anion, ML the ion pair, MML^+ or MLL^- the triple ion and $(ML)_2$ the quadrupole (dimer). We define the ion pair formation constant, K_a, as $K_a = [ML]/[M][L]$, the triple ion formation constant, K_T, as $K_T = [MML]/[M][ML] = [MLL]/[L][ML]$ and the dimer formation constant, K_q, as $K_q = [(ML)_2]/[ML]^2$. The analytical concentration of the lithium salts is then expressed by retaining the symmetrical approximation for triple ions as

$$\begin{aligned} C_0 = {} & [ML]^{1/2} K_a^{-1/2} + [ML] \\ & + 3K_a K_T^{-1/2} [ML]^{3/2} + 2K_q [ML]^2. \end{aligned} \qquad (3)$$

For the solution of $LiBF_4$, the equilibrium constants for the individual steps can be estimated from conductivity data.[3] They are $K_a = 1.2 \times 10^7$ mol^{-1} dm^3, $K_T = 50$ mol^{-1} dm^3, and $K_q = 2$ mol^{-1} dm^3. From these data one can calculate numerically the ion pair concentration, [ML], at each analytical salt concentration. This was performed on a computer (NEC PC-9801). Once the ion pair concentration is determined, the concentration of other chemical species can also be calculated. As the concentration of the ions in $LiBF_4$ solution is too small (less than 10^{-4} mol dm^{-3}), the ion pair formation process (process I in Eq. 2) may be ruled out as the cause of the observed relaxational absorption. If the second step (II) is associated with the observed ultrasonic relaxation, then the relationship between the relaxation frequency and the concentration, and the maximum absorption per wavelength is given by

$$2\pi f_r = k_{12}([M] + [ML]) + k_{21}, \qquad (4)$$

$$\mu_{max} = 0.5 A f_r c = \pi (\Delta V)^2 / (2\kappa_s RT) \Gamma, \qquad (5)$$

$$\Gamma = (1/[M] + 1/[ML] + 1/[MML])^{-1},$$

where ΔV is the volume change of the reaction, R the gas constant and T the absolute temperature. The plots of f_r vs. ([M]+[ML]) provide a reasonable straight line from which the rate constants of the order of 10^8 mol^{-1} dm^3 s^{-1} and 10^8 s^{-1} can be deduced. However, the calculated volume change for the reaction is 180 cm^3 mol^{-1} which is implausible even if the presence of another triple ion formation process, $L^- + ML \rightleftharpoons MLL$, is taken into account. This suggests that the second step in Eq. 2 is not the cause of the observed relaxation. Next, the intervention of a dimerization process is tested with the following:

$$2\pi f_r = 4k_{34}[ML] + k_{43}, \qquad (6)$$

$$\mu_{max} = \pi (\Delta V)^2 / (2\kappa_s RT) \Gamma, \qquad (7)$$

$$\Gamma = K_q [ML]^2 / (1 + 4K_q [ML]).$$

The calculated rate constants from the plots of f_r vs. the ion pair concentration are $k_{34} = (7.9 \pm 0.5) \times 10^8$ mol^{-1} dm^3 s^{-1} and $k_{43} = (7.5 \pm 3.1) \times 10^7$ s^{-1}. The ratio, k_{34}/k_{43}, is (10 ± 4) mol^{-1} dm^3, which can be considered similar in magnitude to the dimer formation constant, K_q, used for calculating the distribution of chemical species in Eq. 2. The above forward and reverse rate constants are slightly larger than those reported by others.[4] This might be due to their use of the approximation that the analytical concentration is similar to the ion pair concentration. Further, the volume change of the reaction was determined from plots of $\mu_{\max}$ vs. $\pi/(2\kappa_s RT)\Gamma$ using Eq. 7 as (10.8 ± 0.7) cm^3 mol^{-1}, a reasonable value.

Next, we turn to an analysis of the relaxation observed in LiAsF$_6$ solution. According to the conductivity experiments, it was concluded that formation of the dimer is rare. Therefore, we neglect the fourth term on the right hand side of Eq. 3. The ion formation constant, $K_a=1.03\times10^5$ mol^{-1} dm^3, and the triple ion formation constant, $K_T=28$ mol^{-1} dm^3 are used in this solution.[3] The ion pair concentration was calculated at each analytical concentration of salt, and the concentrations of the single and triple ions were also deduced. The ion pair formation constant is not very large, therefore the possibility of ion pair formation as the cause of the relaxation cannot be excluded. The plots of the observed relaxation frequency, f_r, vs. γ^2[M] gave the rate constants, k_{12} and k_{21}, from the slope and the intercept, respectively, assuming that the relaxation is due to ion pair formation. However, the calculated value, k_{12}, is 7×10^{10} mol^{-1} dm^3 s^{-1}, which is unreasonably large. Also, the volume change of the reaction was calculated to be 65 cm^3 mol^{-1}. These calculations indicate that the cause of the observed relaxation is unlikely to be the ion pair formation process. Farber et al.[3] reported that the observed relaxation can be attributed to the solvation and desolvation process of the ion pair, since their experimental results showed that the relaxation frequency is independent of the concentration. However, our results show that the relaxation frequency is indeed concentration dependent in the low concentration range, as seen in Table 1 and in Fig. 5. Therefore, the solvation process might be couple to the ion pair formation process. Under these conditions, step I in Eq. 2 takes on a more complex form:

$$\mathrm{M}^+ + \mathrm{L}^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{M(S)L} \underset{k'_{21}}{\overset{k'_{12}}{\rightleftharpoons}} \mathrm{ML}, \qquad (8)$$

where M(S)L is the solvent separated ion pair. If the observed relaxation is associated with coupling of the first and the second processes in Eq. 8. The expression for the relaxation frequency is given by:

$$2\pi f_r = k'_{12}2K_{12}\gamma^2[\mathrm{M}]/(1+2K_{12}\gamma^2[\mathrm{M}]) + k'_{21}, \qquad (9)$$

where K_{12} is defined as $K_{12}=k_{12}/k_{21}$ and γ the activity coefficient calculated from the Debye equation. The concentration of the ion pair, ML, is very low compared with that of the solvent separated ion pair, M(S)L. Therefore, K_{12} can be approximated to equal to the association constant, K_a. However, the plots of f_r vs. $2K_a\gamma^2[\mathrm{M}]/(1+2K_a\gamma^2[\mathrm{M}])$ provided a negative intercept and unreliable rate constants. Therefore, we have to rule out this mechanism as the cause of the relaxational absorption. The only mechanism remaining for consideration is the formation of triple ions. The concentration of ion pair, including the solvent separated ion pairs, is not very small compared to that in LiBF$_4$ solutions and the sound velocity and the conductivity data indicate the existence of triple ions. Figure 7 shows the plots of f_r vs. ([M]+[ML]) according to Eq. 4. The rate constants are $k_{23}=(8\pm1)\times10^8$ mol^{-1} dm^3 s^{-1} and $k_{32}=(3.5\pm0.2)\times10^8$ s^{-1}. The ratio of the rate constants, k_{23}/k_{32}, is about 2 mol^{-1} dm^3 with a quite significant error. Therefore, it is believed that this ratio may be close to the triple ion formation constant, K_T, used for the calculation of the concentration of various chemical species. Further, the volume change of the reaction was calculated from Eq. 5 using the same procedure as for LiBF$_4$. The plots of $\mu_{\max}$ vs. $\pi/(2\kappa_s RT)\Gamma$ are shown in Fig. 8 and the slope provided $\Delta V=53\pm5$ cm^3 dm^{-1}. The fact that the line does not pass through the origin may indicate that the observed relaxation is not only due to volume relaxation but also to thermal relaxation. That is, the volume change in Eq. 5 should be expressed precisely as $\Delta V=\Delta V_{re}-\alpha_p\Delta H/\rho C_p$, where ΔV_{re} is the real volume change of the reaction, α_p the thermal expansion coefficient, ΔH the enthalpy change and C_p the specific heat at constant pressure. Therefore, the volume change given above may be overestimated if we

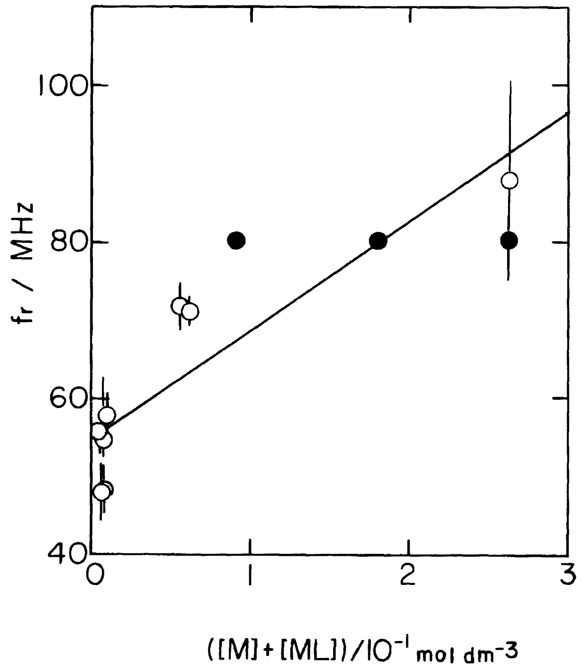

Fig. 7. Plots of the relaxation frequency vs. the concentration of single ions and ion pairs for DME solution of LiAsF$_6$ at 25 °C. ○: present data; ●: those by Farber et al.

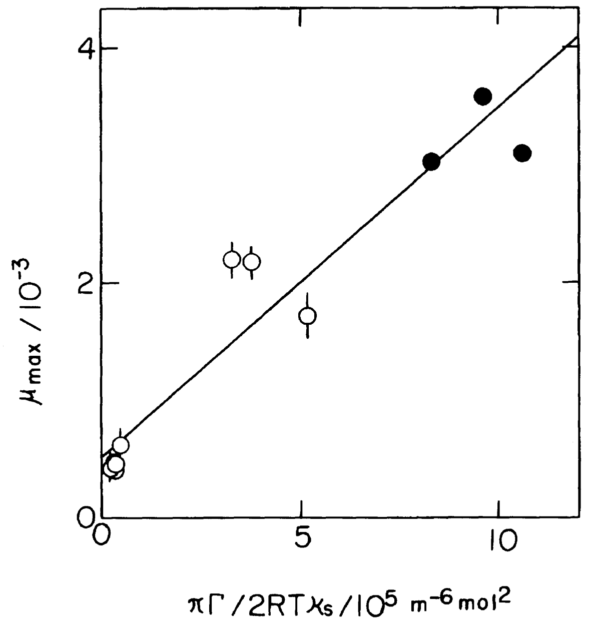

Fig. 8. Plots of the maximum absorption per wave length, $\mu_{\rm max}$ vs. $\pi/(2\kappa_s RT)\Gamma$ for DME solution of LiAsF$_6$ at 25 °C. ○: present data; ●: those by Farber et al.

take into account of the thermal relaxational term. It is not possible at this stage to analyze quantitatively how much the thermal relaxation contributes to the absorption because of lacks of other thermodynamic parameters, i.e., α_p, ΔH and C_p. There may be other two reasons for such a large volume change. One is associated with the structure of the triple ion. We have assumed that the triple ion formation processes are identical, even though there may exist two forms of triple, MML and MLL. These two processes are considered to superimpose in the same frequency range. It is impossible to differentiate between them at this stage. The second reason for the large ΔV may be that the major species among the ion pairs are those separated by a solvent molecule. This is consistent with the model proposed by Firman et al.[1)]

In summary, the observed behavior of the sound velocity reflects the change of the solution characteristics of lithium salts in low dielectric solvents. Depending upon the size of the counter anion for lithium and the dielectric constant, the concentration where the molar relative sound velocity exhibits inflection may change. Therefore, it is possible to estimate from the sound velocity measurement how the solution structure is being changed.

The ultrasonic relaxations observed in DME solutions of LiBF$_4$ and LiAsF$_6$ have been attributed to the formation of dimers and of triple ions. We speculate that these results are mainly due to the magnitudes of the ion pair formation constant, $K_{\rm a}$, the triple ion formation constant, $K_{\rm T}$, and the dimer formation constant, $K_{\rm q}$. The concentration of triple ions for LiBF$_4$ solutions (2×10^{-3}—1.3×10^{-4} mol dm^{-3}) is one order of magnitude lower than that for the LiAsF$_6$ solution at each analytical salt concentration. This is because of the large difference of their ion pair formation constants and because of the formation of the dimer of LiBF$_4$. In LiAsF$_6$ solution, the dimer is not formed and the related relaxation is not observed. Even if the rate constants for triple ion formation of LiBF$_4$ might be similar to those for formation of triple ions from LiAsF$_6$, the relaxational amplitude would be very small and the relaxation frequency would appear at frequency range lower than that used in this study.

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