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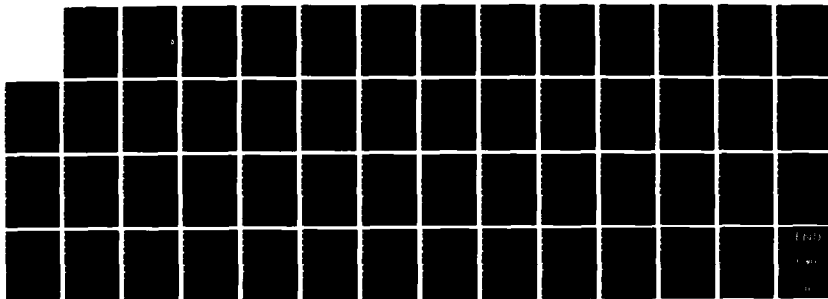
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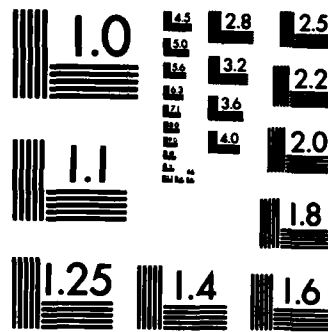
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PART A:

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Solutions of LiAsF_6 at 298.2 K were studied by audiofrequency conductance in the concentrations range 10^{-3} - 10^{-2} mol/dm³, and by radiofrequency ultrasonic absorption in the concentration range 0.05 - 0.5 mol/dm³. The solvents employed were mixtures of 4-butyrolactone with 2-methyl tetrahydrofuran varying in compositions from mole fractions $X_{\text{BL}} = 0.10$ to $X_{\text{BL}} = 0.75$. In dilute solutions the audiofrequency conductivity data yield ion association constants which appear to represent both contact and solvent-separated ion pairs for mixtures up to $X_{\text{BL}} = 0.36$. At higher LiAsF_6 concentrations and in solvent mixtures of composition $X_{\text{BL}} = 0.75$, and $X_{\text{BL}} = 0.35$, the ultrasonic spectrum shows a single relaxation process which again is attributed to the formation of both contact and solvent separated ion pairs. For $X_{\text{BL}} = 0.10$, the ultrasonic spectrum is the sum of two Debye relaxation processes identified with the equilibria $2\text{LiAsF}_6 \rightleftharpoons \text{LiAsF}_6 \cdots \text{LiAsF}_6 \rightleftharpoons (\text{LiAsF}_6)_2$.

PART B:

Electrical conductance data for LiBF_4 in 1,2-Dimethoxymethane (DMM) at 25°C reveal the electrolyte to be heavily associated to ion-pairs and triple ions. A theoretical expression for the triple ion association constant similar to the Bjerrum one for ion-pairs and to the Maaser-Bjerrum theory of dimers has been developed and applied to the present conductance data. Ultrasonic relaxation absorption data at much higher concentrations than the conductance data reveal association to dimers. This is also evident from the microwave dielectric data showing no electrolyte dielectric effect on the solvent and apparent lack of presence of dipoles. The ultrasonic data can be rationalized by a two-step dimerization mechanism.

TECHNICAL REPORT NO. 7

PART A

Molecular Dynamics and Ionic Associations of LiAsF_6
in 4-Butyrolactone Mixtures with 2-Methyl Tetrahydrofuran

Y. Harada, M. Salomon and S. Petrucci

PART B

Molecular Dynamics and Ionic Associations of LiBF_4
in 1,2-Dimethoxymethane

M. Delsignore, H. Farber and S. Petrucci

January 1, 1985 - June 30, 1985

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Polytechnic Institute of New York
Route 110
Farmingdale, NY 11735

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PART A

Molecular Dynamics and Ionic Associations of LiAsF_6 in 4-Butyrolactone Mixtures with 2-Methyl Tetrahydrofuran

Yoshifumi Harada,¹ Mark Salomon² and

Sergio Petrucci¹

Polytechnic Institute of New York

Route 110

Farmingdale, New York 11735

U. S. Army ET & DL

Power Sources Division

Ft. Monmouth, New Jersey 07703-5302

ABSTRACT

Solutions of LiAsF_6 at 298.2 K were studied by audiofrequency conductance in the concentrations range 10^{-4} - 10^{-2} mol dm⁻³, and by radiofrequency ultrasonic absorption in the concentration range 0.05 - 0.5 mol dm⁻³. The solvents employed were mixtures of 4-butyrolactone with 2-methyl tetrahydrofuran varying in compositions from mole fractions $X_{\text{BL}} = 0.10$ to $X_{\text{BL}} = 0.75$. In dilute solutions the audiofrequency conductivity data yield ion association constants which appear to represent both contact and solvent-separated ion pairs for mixtures up to $X_{\text{BL}} = 0.36$. At higher LiAsF_6 concentrations and in solvent mixtures of composition $X_{\text{BL}} = 0.75$, and $X_{\text{BL}} = 0.35$, the ultrasonic spectrum shows

¹ Polytechnic Institute of New York, Farmingdale, New York.

² U. S. Army ET & DL, Ft. Monmouth, New Jersey.

a single relaxation process which again is attributed to the formation of both contact and solvent separated ion pairs. For $X_{BL} = 0.10$, the ultrasonic spectrum is the sum of two Debye relaxation processes identified with the equilibria

$$2LiAsF_6 \rightleftharpoons LiAsF_6 \cdots LiAsF_6 \rightleftharpoons (LiAsF_6)_2.$$

Introduction

Over the past five years LiAsF_6 has emerged as the preferred electrolyte for use in rechargeable lithium batteries [1]. A major reason for this selection is that LiAsF_6 solutions generally show much higher electrolytic conductivities than corresponding solutions of other lithium salts such as LiClO_4 or LiBF_4 . In addition to a smaller tendency to form ion pairs (2-6), LiAsF_6 also has a smaller tendency to form dimers (i.e., quadrupoles) than do LiClO_4 and LiBF_4 (2,3). The use of ether based solvents is also of practical interest since lithium anodes appears to cycle well in these solvents [1]. The use of binary mixtures of an ether with a high dielectric constant solvent such as 4-butyrolactone (4-BL) and propylene carbonate (PC) has still greater practical applications since it has been shown [4,6,7 and references cited therein] that electrolytic conductances are generally greater in specific mixtures than they are in any of the pure solvents. The present study is concerned with the properties of LiAsF_6 in binary mixtures of 4-BL with 2-methyl tetrahydrofuran (2MeTHF). The systems were studied by classical audiofrequency conductance measurements at low concentrations and by more recent relaxation kinetic methods which have the advantage of being able to isolate (in the frequency spectrum) one or more multistep processes [8]. Parallel studies of LiAsF_6 in pure 2MeTHF and pure 4-BL have been reported earlier [3,5].

Experimental

Chemicals LiAsF_6 (USS Agri-Chemicals "Electrochemical Grade") was dried at 60–70°C under vacuum for 24h. 2MeTHF was distilled from benzophenone at reduced pressure (3) or was distilled from type 4A molecular sieves under an atmosphere of pure argon. 4-BL (Aldrich "Gold Label" product) was distilled from 4A and 5A molecular sieves at reduced pressure as described in [5,6]. All solvent mixtures were prepared by weight.

Solvent Properties The static dielectric constants of the solvent mixtures were measured at 25 ± 0.1 °C by the comparison method [4-6], and a precision of 0.5% or better was attained. Densities were measured at 25.0 ± 0.1 °C with a PAAR DMA 45 digital density meter. Viscosities were measured at 25.00 ± 0.02 °C with a Lauda precision viscometer with a precision of $\pm 0.1\%$. The physical properties of these solvents are given in Table 1. The data in Table 1 are fitted by least squares to the following smoothing equations

$$\epsilon(D) = 6.137 + 26.222X_{BL} + 7.6952X_{BL}^2 + 1.6939X_{BL}^3, \quad (1)$$

$$\eta(\text{cP}) = 0.4653 + 0.5691X_{BL} - 0.04594X_{BL}^2 + 0.7387X_{BL}^3, \quad (2)$$

$$d(\text{gcm}^{-3}) = 0.8475 + 0.2209X_{BL} + 0.06028X_{BL}^2 - 0.005223X_{BL}^3, \quad (3)$$

Note that the solvent compositions are mass % in Table 1, and the smoothing equations (1-3) are based upon mole fraction of 4-BL.

Audiofrequency Measurements Electrolyte solutions were prepared by weight in a dry box and conversions to volume concentration units were calculated from measured densities. Aliquots of a given stock solution were placed in three 10 ml flasks which were then used for the conductivity runs using successive weight dilutions. Three Jones type conductivity cells were used in combination with an Altex RC-18 conductivity bridge. Electrolytic conductance were measured at 25.00°C (accuracy $\pm 0.02\text{K}$) is described in [4-6].

Ultrasonic Relaxation The equipment and procedures have been described elsewhere [3]. A new resonator ultrasonic cell with 1 inch diameter quartz crystals was used as it allowed measurements over a broader frequency range (0.5-16 MHz), and a better signal to noise ratio than the cell used previously [3]. After thermostating it at 25.00 °C (precision $\pm 0.01\text{K}$), for 2 hours, frequency drifts in the resonating frequencies stopped. Solutions were kept in

desiccators, used within 24 hours of preparation, and were exposed to the atmosphere during filling the resonator cell for 20-30 seconds at most.

Results and Discussion

The molar conductivities, Λ ($\text{Scm}^2\text{mol}^{-1}$), were calculated from the experimental electrolytic conductances after correcting for the solvent conductance, and the data are given in Table 2. The data in Table 2 were analyzed by means of the Fuoss-Hsia equation (9) using the method proposed by Justice [10] and the constants derived by Fernandez-Prini [11],

$$\Lambda = \Lambda^\infty - S(\alpha c)^{1/2} + E\alpha c \ln \alpha c + J_1(R_1)\alpha c - J_2(R_2)(\alpha c)^{3/2} - \Lambda \alpha c y_\pm^2 K_a^\infty \quad (4)$$

where all terms have their usual significance. The thermodynamic ion association constant and mean molar activity coefficient are defined in the usual manner:

$$K_a^\infty = (1 - \alpha) / \alpha^2 c y_\pm^2 \quad , \quad (5)$$

and

$$\ln y_\pm = -A(\alpha c)^{1/2} / [1 + B R_y (\alpha c)^{1/2}] \quad (6)$$

The distance parameters R_1 and R_y in Eqs. (4) and (6) were set equal to the Bjerrum distance q as suggested by Justice [10], and Eqs. (4-6) solved by a least squares method similar to that described by Kay [12]. Values of q (expressed in $\text{\AA}$) are given in Table 3. Table 3 also gives the results of fitting the parameters Λ^∞ , K_a^∞ , and R_2 to Eqs. (4-6). σ_Λ in this table is the standard error of estimate for the molar conductivities. Based on the σ_Λ values, the uncertainties in Λ are around 0.2% (95% level of confidence).

For electrostatic interactions, K_a^∞ can be calculated from the Bjerrum equation

$$K_a^\infty = \frac{4\pi N_A}{1000} \int_a^q R^2 \exp[z^2 e^2 / \epsilon k T R] dR \quad (7)$$

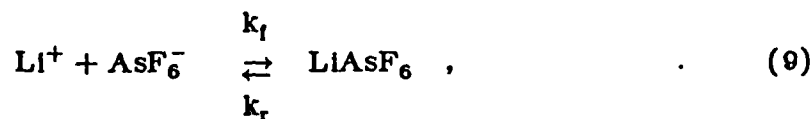
where the integration is carried out from the distance of closest approach, a , to the Bjerrum distance, q . For a contact ion pair, the distance of closest approach can be simply set equal to the sum of the ionic radii. For LiAsF_6 $a = r_+ + r_- = 4.44 \text{ \AA}$, and in which case the calculated K_a^∞ values for the mixed solvents are all much larger than the experimental K_a^∞ values given in Table 3. Calculated K_a^∞ values can be reduced by considering solvent-separated ion pairs, and in which case $a = r_+ + r_- + d$ where d is the diameter of the solvent molecule (4-7). However, taking $d \approx 3.7 \text{ \AA}$ (the approximate solvent diameter of 2MeTHF) results in calculated K_a^∞ much smaller than the experimental values. The experimental K_a^∞ values in the mixed solvents can be reproduced from Eq. (7) by taking $d \approx 1.6 \text{ \AA}$. In fact, K_a^∞ values for LiAsF_6 in dimethoxyethane mixtures with PC or 4-BL can also be reproduced within experimental error by taking $d \approx 1.6 \text{ \AA}$ (8). This low value of $1.6 \text{ \AA}$ suggests that both contact and solvent-separated ion pairs exist in these mixed solvents as proposed earlier [6]. Additional evidence for the simultaneous existence of both types of ion pairs comes from our relaxation studies discussed below.

Turning to the relaxation studies, Fig. 1 shows a representative plot of α/f^2 as a function of frequency f for LiAsF_6 in a $X_{\text{BL}} = 0.75$ mixture at 25°C . The solid line is the calculated Debye functions for a single relaxation process:

$$\alpha/f^2 = \frac{A}{1+(f/f_r)^2} + B \quad (8)$$

where α is the absorption coefficient of sound in Npcm^{-1} , f_r the relaxation frequency, and A and B are fitting parameters (8,13). The data and parameters for LiAsF_6 in the $X_{\text{BL}} = 0.75$ mixture are given in Table 4. The relaxation

parameter A in Table 4 is quite small and for $0.1 \text{ mol dm}^{-3} \text{ LiAsF}_6$ in pure 4-BL the relaxation effect is not detectable. This is consistent with the conductivity results (5) which show that LiAsF_6 is completely ionized in 4-BL at 25°C . The observed single relaxation process is interpreted in terms of ion association



for which one can write the rate expression (8)

$$\tau^{-1} = k_f \theta + k_r \quad (10)$$

In Eq. (10) τ^{-1} is the inverse of the relaxation time ($\tau^{-1} = 2\pi f_r$), and θ is a function defined by

$$\theta = 2\gamma c y_{\pm}^2 \quad (11)$$

Values of θ were estimated from Eqs. (11) and (12) taking $K_a^\infty = 39.8 \text{ mol}^{-1} \text{ dm}^3$ (obtained by interpolations from the conductivity data, Table 3). In the Davies equation (14) R_y was again set equal to the Bjerrum distance q (for X_{BL} at 25°C , $q = 9.08 \text{ \AA}$).

$$\ln y_{\pm} = \frac{-A I^{1/2}}{1 + R_y I^{1/2}} + C I \quad (12)$$

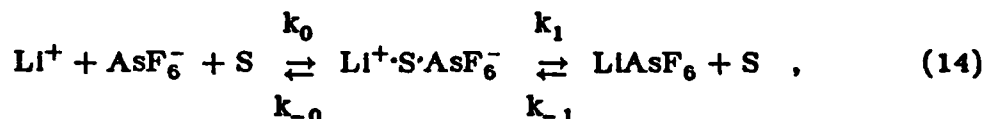
Fitting τ^{-1} and θ to Eq. (10) by the method of least squares gives $k_f = (1.79 \pm 0.49) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $k_r = (2.85 \pm 0.26) \times 10^8 \text{ s}^{-1}$ with a correlation coefficient $r^2 = 0.87$. These rate constants give an ion association constant of $K_a^\infty = k_f/k_r = 6.3 \pm 2.3 \text{ mol}^{-1} \text{ dm}^3$ which differs from that of $39.8 \text{ mol}^{-1} \text{ dm}^3$ obtained from the conductivity data. Differences of this magnitude are typical when comparing K_a^∞ values from conductivity data and rate

data, and are probably due in part to the larger experimental errors in the rate data and the use of Eq. (12) for calculating activity coefficients in highly concentrated solutions.

The rate constant for a diffusion controlled ionic encounter can be calculated from the Debye-Smoluchowsky equation (15)

$$k_D = \frac{8RT}{3000\eta} \cdot \frac{b}{1 - e^{-b}} \quad (13)$$

where b is the Bjerrum parameter $|z_+z_-|e^2/q\epsilon kT$. For $X_{BL} = 0.75$ the quantities $\epsilon(30.85D)$ and $\eta(1.178cP)$ were obtained from Eqs. (1-2), and thus $k_D = 1.29 \times 10^{10} \text{ mol}^{-1}\text{dm}^3 \text{ s}^{-1}$ which is an order of magnitude greater than the experimental value of $1.79 \times 10^9 \text{ mol}^{-1}\text{dm}^3 \text{ s}^{-1}$ for k_f . This result leads us to conclude that for LiAsF_6 in $X_{BL}=0.75$ the association process takes place with a energy barrier larger than viscous flow. Elimination of solvent from the first coordination of the ions is the likely source of the above differences in the k_f 's. We then propose the Eigen mechanism [8] for the association process:

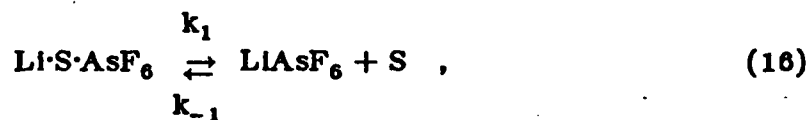


where $\text{Li}^+ \cdot \text{S} \cdot \text{AsF}_6^-$ is the solvent-separated (intermediate) ion pair.

Considering LiAsF_6 in mixtures where $X_{BL} = 0.35$, Fig. 2 shows a representative plot of the excess sound absorption per wavelength $\mu = (\alpha - Bf^2)u/f = \alpha_{exc}\lambda$ against the frequency f . Here $\lambda = u/f$ is the wavelength and B is the value of α/f^2 for $f \gg f_r$ (cf. Eq. (8)). The solid line in Fig. 2 is the Debye function for a single relaxation process

$$\mu = 2 \mu_{\max} \frac{f/f_r}{1 + (f/f_r)^2} \quad (15)$$

where $\mu_{\max} = A\omega f_r/2$. Table 5 gives $\mu_{\max}, f_r, B$, and the sound velocity u for LiAsF_6 solutions in $X_{\text{BL}} = 0.35$ mixtures at 25°C . From Table 5 it is seen that within experimental error, f_r is independent of the LiAsF_6 concentration, and that $\mu_{\max}$ is a linear function of concentration. From the conductivity data, K_a^∞ interpolated from a plot of $\log K_a^\infty$ vs. $1/\epsilon$ is $457\text{mol}^{-1}\text{dm}^3$, which means that the concentration of free ions in the solutions of composition $X_{\text{BL}} = 0.35$ is small. Under these conditions the scheme presented in (14) above probably reduces to



i.e., to a pseudo first order process, the solvent S being in large excess. For this pseudo first order process, the rate equation is therefore (8)

$$\tau^{-1} = k_1 + k_{-1} = (4.3 \pm 0.2) \times 10^8 \text{s}^{-1} \quad .$$

The value of $\mu_{\max}$ is also given by (2)

$$\mu_{\max} = \frac{\pi}{2\beta_s} \frac{(\Delta V_s)^2}{RT} \cdot \frac{K_1}{(1+K_1)^2} c \quad , \quad (17)$$

where $K_a^\infty = K_0(1+K_1) = 457\text{mol}^{-1}\text{dm}^3$ K_0 and K_1 are the equilibrium constants for the two steps given in Eq. (14) and the adiabatic compressibility $\beta_s = (d_0 u^2)^{-1} = 62.9 \times 10^{-12} \text{g}^{-1} \text{cm s}^2$. At the present time K_1 is not known and ΔV_s cannot therefore be calculated.

Considering LiAsF_6 solutions at 25°C in $X_{\text{BL}} = 0.10$, a representative plot of μ as a function of f is shown in Fig. 3. The data in this figure cannot be fitted satisfactorily in terms of a single Debye relaxation. The solid line in Fig. 3 was obtained by fitting the data to two Debye functions given by the relation

$$\mu = 2\mu_{\max,I} \frac{f/f_I}{1+(f/f_I)^2} + 2\mu_{\max,II} \frac{f/f_{II}}{1+(f/f_{II})^2} \quad (18)$$

Table 6 gives the parameters $\mu_{\max,I}$, f_I , $\mu_{\max,II}$, f_{II} , the background absorption B, and the velocity u as a function of LiAsF₆ concentration. The inset in Fig. 3 shows the tail of the α/f^2 vs. f corresponding plot, with the solid line calculated from the parameters of Table 6, indicating that the choice of B is rather unequivocal and subject to an error not larger than ± 0.5 to $\pm 1.0 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2$: i.e., the second relaxation is required to accurately describe the processes in $X_{BL} = 0.10$ solutions. From the plot of $\log K_a^\infty$ vs. $1/\epsilon$ based on the data in Table 3, for $X_{BL} = 0.10$ we find that $K_a^\infty x = 2 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ which means that ion association is virtually complete, and that no ultrasonic relaxation can arise from dissociation to free ions. Outer-sphere inner-sphere processes are first order (or pseudo first order as described above for LiAsF₆ in $X_{BL} = 0.35$ mixtures) which, for LiAsF₆ in $X_{BL} = 0.10$ mixtures, cannot explain the concentration dependencies of the relaxation frequencies f_I and f_{II} . In order to explain these concentration dependencies we propose (see also (3)) that the two Debye processes are associated with the dimerization of ion pairs to form quadrupoles according to:



where the dimerization (or quadrupole formation) constant is given by:

$$K_q = K_2(1+K_3) \quad (20)$$

In (19) we propose a solvent separated intermediate quadrupole, LiAsF₆...S...LiAsF₆, on the basis of the two observed Debye relaxations. LiAsF₆ solutions in pure 2MeTHF (3) show only a single Debye process, and

at this time we cannot determine which solvent component S represents in Eq. (19). According to the scheme in Eq. (19), one would expect the two relaxation times to be described by the relation (3)

$$\tau_{I,II}^{-1} = [S \pm (S^2 - 4P)^{1/2}] / 2 \quad (21)$$

where

$$S = \tau_I^{-1} + \tau_{II}^{-1} = 4k_2[AB] + k_{-2} + k_3 + k_{-3} \quad (22)$$

and

$$P = \tau_I^{-1} \tau_{II}^{-1} = 4k_2[AB](k_3 + k_{-3}) + k_{-2}k_{-3} \quad (23)$$

When the dimerization constant K_q is small, then the ion pair concentration $[AB]$ can be safely approximated by the stoichiometric concentration $c/\text{mol dm}^{-3}$. Linear regression of S vs. c gives a determination coefficient $r^2 = 0.985$, a slope = 1.29×10^9 , and an intercept = 8.15×10^8 . Linear regression of P vs. c gives $r^2 = 0.972$, slope = 4.88×10^{17} , and intercept = 1.19×10^{17} . Similar to the treatments for LiBF_4 in pure 2MeTHF (3), the above slopes and intercepts are used to calculate the following rate constants and equilibrium constants:

$$k_2 = 3.2 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}; \quad k_{-2} = 4.4 \times 10^8 \text{ s}^{-1}$$

$$K_2 = k_2/k_{-2} = 0.73 \text{ mol}^{-1} \text{ dm}^3$$

$$k_3 = 1.1 \times 10^8 \text{ s}^{-1}; \quad k_{-3} = 2.7 \times 10^8 \text{ s}^{-1}$$

$$K_3 = 0.41$$

$$K_q = K_2(1+K_3) = 1.0 \text{ mol}^{-1} \text{ dm}^3$$

This value of K_q in the $X_{\text{BL}} = 0.10$ mixture is consistent with the value of

$1.8 \text{ mol}^{-1} \text{ dm}^3$ for LiAsF_6 in pure 2MeTHF (3).

Conclusions

The combination of two completely different methods of investigation, albeit in different concentration ranges, has shown a consistent description of the status of the electrolyte, as being practically all ionized (up to $c \approx 0.1 \text{ M}$) in 4-BL, and practically all associated with a small percentage of dimerization, in 2MeTHF. The addition of 4 BL to 2MeTHF causes solvation of the dimers and increases the ionization of the electrolyte. Perhaps, the potentially chelating ability of 4 BL causes preferential solvation of Li^+ , a point that would be desirable to check experimentally by tools others than the ones used in the present study.

It is clear from the above investigation, that no method has the capability of giving a complete picture of a given system. Rather, the information gathered by several parallel investigations by different technologies will give enough complementary data as to offer an adequate insight for a molecular description of the system.

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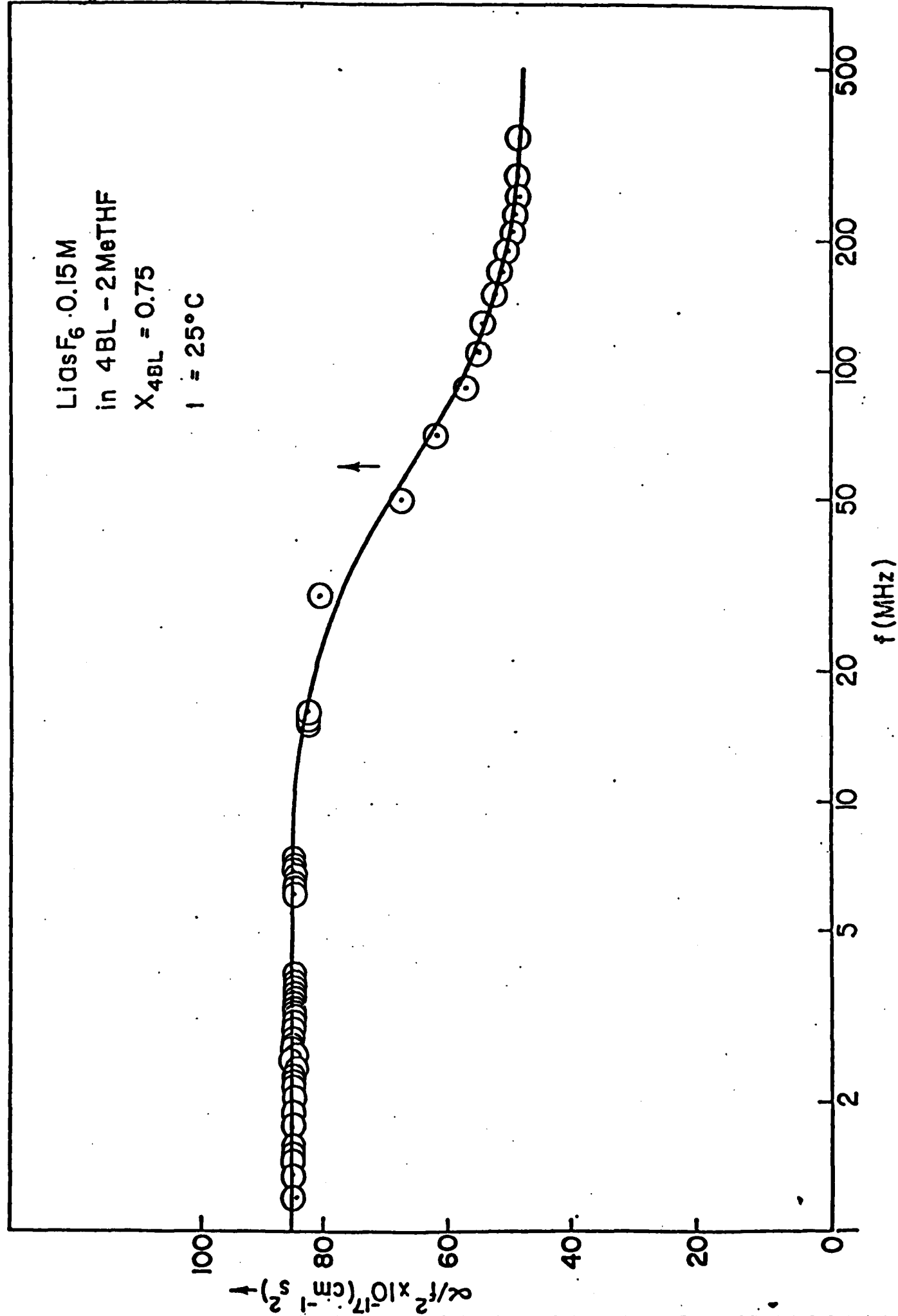
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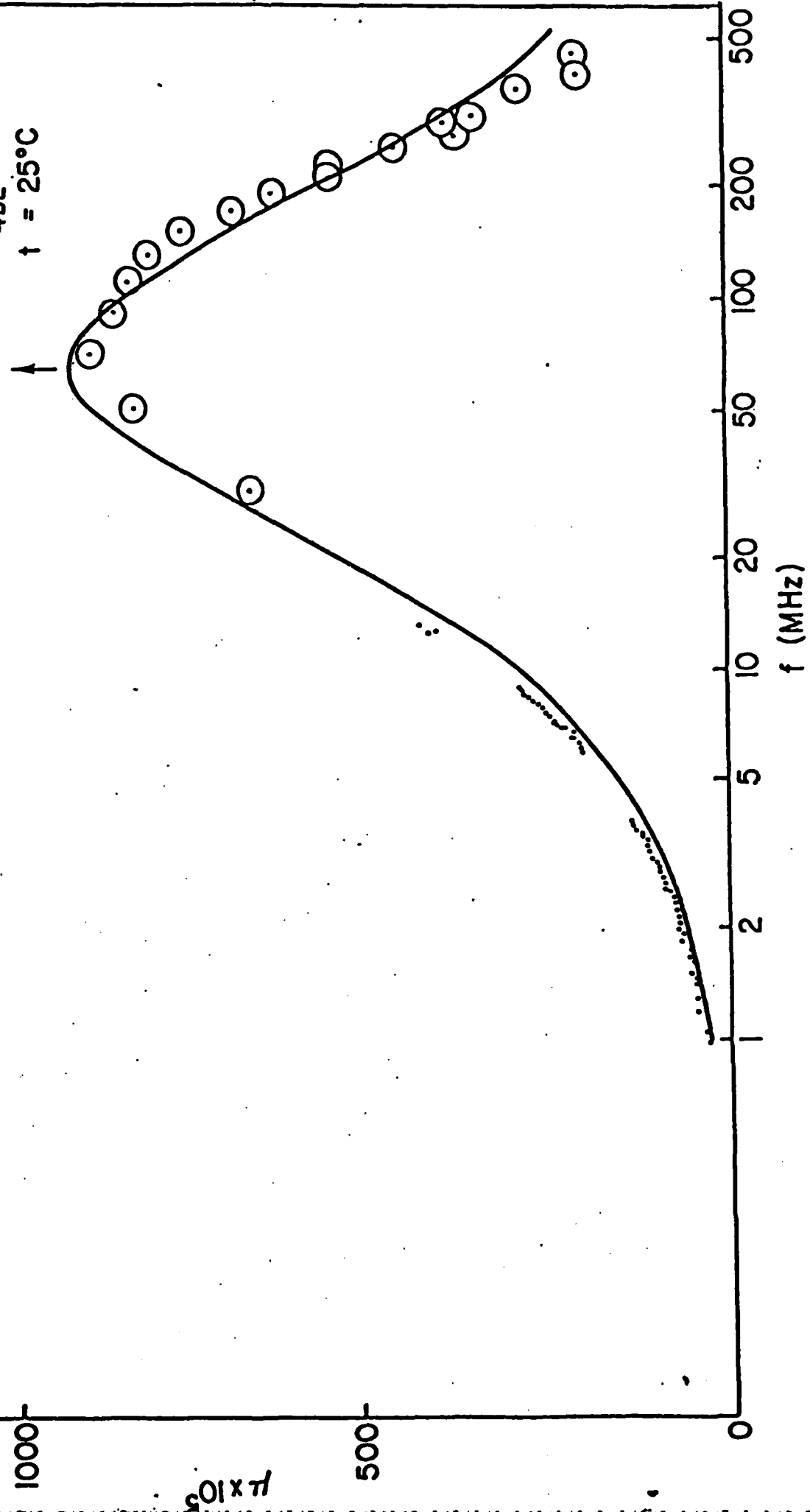
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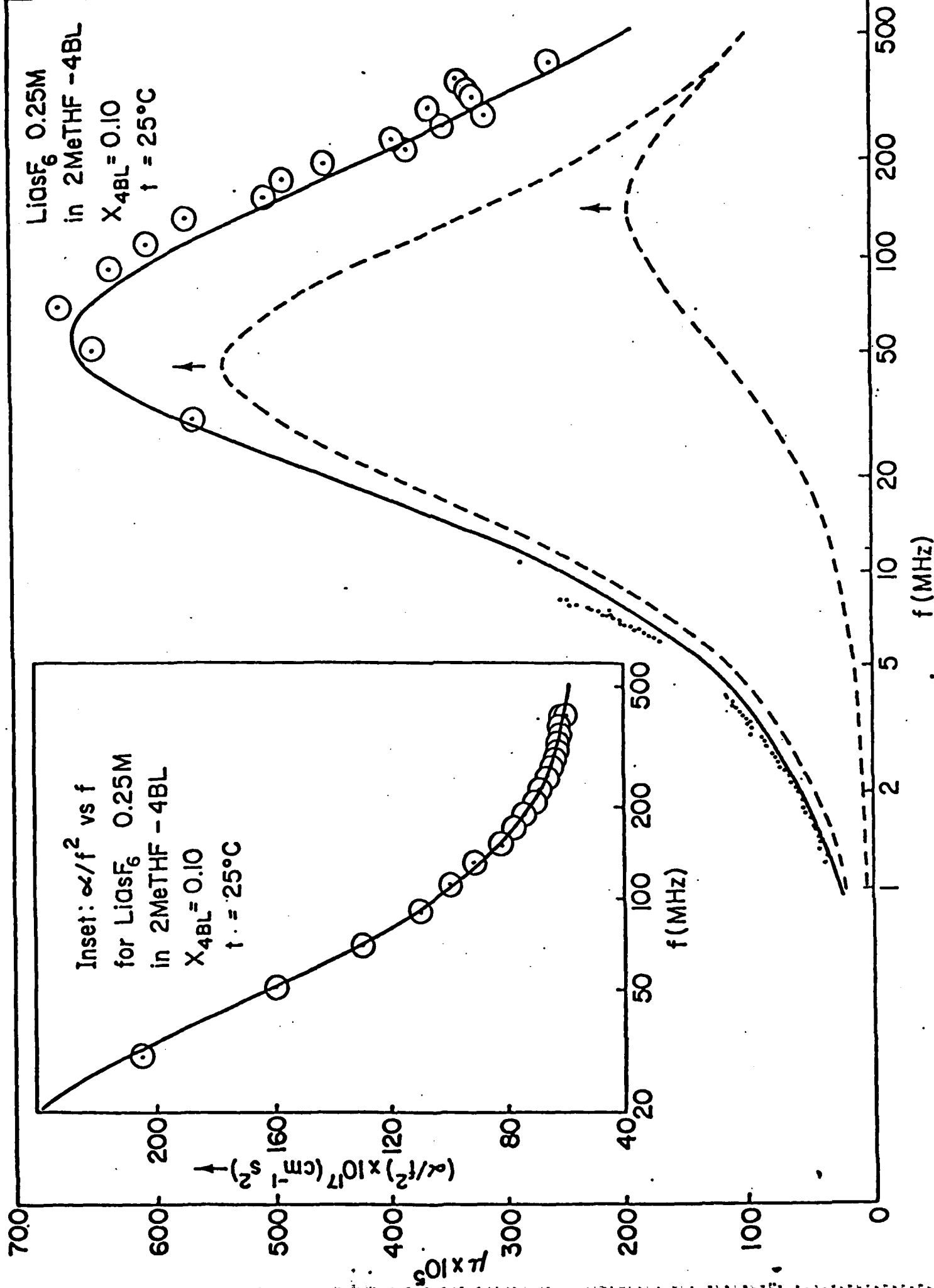
- Fig. 1 Representative plot of the quantity (α/f^2) vs. frequency f , for LiAsF_6 in the solvent mixture 2MeTHF-4-BL of composition $X_{4\text{BL}} = 0.75$ at $t = 25^\circ\text{C}$.
- Fig. 2 Representative plot of the quantity μ vs. f for LiAsF_6 in the solvent mixture 2MeTHF-4BL of composition $X_{4\text{BL}} = 0.35$ at $t = 25^\circ\text{C}$.
- Fig. 3 Representative plot of the quantity μ vs. f for LiAsF_6 in the solvent mixture 2MeTHF-4BL of composition $X_{4\text{BL}} = 0.10$ at 25°C .

LiOsF_6 0.15M
in 4BL-2MeTHF
 $X_{4\text{BL}} = 0.75$
 $t = 25^\circ\text{C}$



LiOsF_6 0.55 M in
2MeTHF - 4BL
 $X_{4\text{BL}} = 0.35$
 $T = 25^\circ\text{C}$





PART B

**Molecular Relaxation Dynamics and Ionic Association
of LiBF_4 in 1,2-Dimethoxymethane**

by

M. Delsignore, H. Farber, S. Petrucci

Depts. of Chemistry and Electrical Engineering

Polytechnic Institute of New York

Long Island Center

Farmingdale, NY 11735

Abstract

Electrical conductance data for LiBF_4 in 1,2-Dimethoxymethane (DMM) at 25°C reveal the electrolyte to be heavily associated to ion-pairs and triple ions. A theoretical expression for the triple ion association constant similar to the Bjerrum one for ion-pairs and to the Maaser-Bjerrum theory of dimers has been developed and applied to the present conductance data. Ultrasonic relaxation absorption data at much higher concentrations than the conductance data reveal association to dimers. This is also evident from the microwave dielectric data showing no electrolyte dielectric effect on the solvent and apparent lack of presence of dipoles. The ultrasonic data can be rationalized by a two-step dimerization mechanism.

Introduction

A previous conductance study of the ionic association of LiBF_4 in 2-Methyltetrahydrofuran¹ and in 1,2-Dimethoxyethane² of respective static permittivities $\epsilon = 6.2$ and $\epsilon = 7.0$ has been reported. In the same works,^{1,2} the diffusional rotational relaxation dynamics of ion pairs was studied by dielectric relaxation. In addition, ultrasonic relaxation revealed some dimerization of the ion-pairs and a kinetic investigation of this additional process was reported.

It was of interest to extend the above studies in a medium of lower permittivity as Dimethoxymethane (DMM) of $\epsilon = 2.76$ at 25°C , where presumably, the electrolyte exists completely as ion-pairs at all finite concentrations, but where the extent of triple ion formation and quadruple formation is sizable and may become preponderant at high concentrations ($C > 0.1, 0.2\text{M}$). On the practical side, LiBF_4 dissolved in ethers is a system relevant to secondary batteries construction. It was of interest to report a quantitative study in a solvent of very low permittivity as DMM ($\epsilon = 2.76$ at 25°C) which may constitute an extreme limit for an electrolyte solution. In the process, we have derived a new Bjerrum-like expression for the association to triple ions as reported below. This expression and the corresponding one for dimer formation, already presented,² may give some theoretical guidelines to the extent of association up to the quadrupoles, but below the larger aggregates which may precede the eventual separation of the electrolyte from the liquid phase. For the sake of clarity, after the experimental part the conductance and theoretical aspects leading to the triple ion formation constant will be dealt with first, followed by the relaxation dynamics study by ultrasonic and microwave dielectric relaxation which involves itself with dimer formation.

Experimental Part

The equipment for the conductance³ and microwave dielectric relaxation⁴ has already been described. For the ultrasonic work the pulse instrumentation has been automated, in data capturing, by mounting over the dual crystals interferometric cell a Mitutoyo Series 164 digital micrometer (resolution ± 0.00005 inch) and associated interfaced digital counter and printer, giving a hardcopy of the displacements for attenuation increments (expressed in decibels) of the standard comparison signal.

For the chemicals, the solvent DMM (Aldrich) was refluxed over sodium and benzophenone until a bluish coloration indicating absence of peroxides was present. It was then distilled in the same all pyrex apparatus and used shortly afterwards. LiBF_4 (Aldrich) was dried in in vacuo at $\sim 60^\circ\text{C}$ overnight.

Results and Discussion

a) Electrical Conductance

Figure 1A reports the electrical conductance data in the form of $\log_{10}\Lambda$, vs. $\log_{10}C$ at $t=25.00^\circ\text{C}$ for LiBF_4 in DMM. Several runs with independently prepared stock solutions and solvent were used in order to insure reproducibility of the results. Figure 1B reports the same data for $C \leq 0.1\text{M}$ elaborated in accord to the Fuoss-Kraus triple ions theory.⁵

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_A}} + \frac{\Lambda_0^T K_T}{\sqrt{K_A}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) C \quad (\text{I})$$

where $g(c)$ is a term lumping together all the interionic terms, K_A and K_T are the ion-pairs and triple ions formation constants, Λ_0 and Λ_0^T the limiting conductivities of the single ions and triple ions respectively. In the above, the arbitrary condition $\Lambda_0^T = \frac{2}{3}\Lambda_0$ has been retained as done previously.^{1,2} Further, for the calculations of Λ_0 , the Walden rule has been used with the following

data from the literature:

- in THF at 25°C (viscosity $\eta=0.0046$ poise)⁶ $\lambda_{Li}^O=36.6\Omega^{-1}cm^2eq^{-1}$,⁷ hence $\lambda_{Li}^O\eta=0.168$.
- in nitrobenzene ($\eta=0.01823$ poise)⁸ $\lambda_{BF_4}^O=22.1\Omega^{-1}cm^2eq^{-1}$; ^{8a} hence $\lambda_{BF_4}^O\eta=0.403$.

It results that in DMM ($\eta=0.00315$ poise)⁹ $\lambda_{Li}^O=53.3\Omega^{-1}cm^2eq^{-1}$ and $\lambda_{BF_4}^O=127.9\Omega^{-1}cm^2eq^{-1}$, or, $\Lambda_{LiBF_4}^O=181\Omega^{-1}cm^2eq^{-1}$ and $\Lambda_O^T=\frac{2}{3}\Lambda_O=121\Omega^{-1}cm^2eq^{-1}$ in DMM at 25°C.

From Figure 1B, the solid line calculated by linear regressions gives $r^2=0.98$, Intercept= $\frac{\Lambda_O}{\sqrt{K_A}}=7.20\times 10^{-7}$ and slope= $\frac{\Lambda_O^TK_T}{\sqrt{K_A}}=3.98\times 10^{-4}$, from which $K_A=6.3\times 10^{16}M^{-1}$ and $K_T=826M^{-1}$.

By equating K_A to the Fuoss-Jagodzinski expression

$$K_{FJ} = \frac{4\pi L d^3}{3000} e^{-1/2} e^b \quad (II)$$

it results in a charge to charge separation in the pair $d = 5.1\times 10^{-8}cm$. Similarly by equating K_T to the Fuoss-Jagodzinski¹⁰ triple ion theoretical expression

$$K_T^{FJ} = \frac{\pi L a^3}{1000} e^{-3/2} e^{e^2/2\epsilon kT} \quad (III)$$

it results in ion to ion-pair separation $a=16.9\times 10^{-8}cm$, a value that seems too high to be reconciled with the triple ions model and definition envisaging the three ions at contact, whereas, the value $a\sim 1.5d=7.7\times 10^{-8}cm$ would appear to be a more reasonable parameter. Therefore, we have decided to re-examine the triple ion theory for K_T without the constriction that the complexing ion be in contact with the pair to be defined as a triple ion. We shall follow the guidelines of the Bjerrum theory for comparison and the one for the dimers (Maaser-Bjerrum theory) already presented.² In the past, dealing with the three

ion interactions Fuoss and Kraus¹¹ have indeed derived a triple ion expression based on the Bjerrum model. Their derivation lead to a integral which, to date, is difficult to solve, short of resolving to a graphical integration. We thought it worthwhile to try to arrive at a more manageable solution of the problem by a simplified derivation based on the interaction between an ion and a permanent dipole of moment μ .

b) Ion-dipole interaction

We will start by defining r_- as the distance between a given positive ion and the negative end of a dipole ion-pair. Let r be the distance between the same ion and the center of the dipole and r_+ the distance between the ion and the positive end of the dipole ion pair. θ' is the angle between r_- and the line passing through the dipole axis, and d is the separation of the two charges in the dipole. We have then (Fig. 2A) $r_- - r_+ = d \cos \theta'$, and the ion-dipole potential will be

$$\phi = \frac{e}{\epsilon} \left(\frac{1}{r_-} - \frac{1}{r_+} \right) = \frac{e}{\epsilon} \frac{r_+ - r_-}{r_+ r_-} \cong - \frac{ed \cos \theta'}{\epsilon r^2}$$

In the above, ϵ is the static permittivity of the solvent and the approximation $r_+ r_- \approx r^2$. If concomitantly one writes $\theta' \approx \theta$ where θ is the angle between r and the line passing through the dipole, one has

$$\phi \cong - \frac{\mu \cos \theta}{\epsilon r^2} \quad (\text{IV})$$

where $\mu = ed$ is the dipole moment of the dipole separated by a distance $r > d$ from the positive ion. The ion-dipole potential energy will then be

$$U = \phi e \cong - \frac{e \mu \cos \theta}{\epsilon r^2} \quad (\text{V})$$

The probability of finding an ion around a dipole taken as the reference of a coordinate system, will be a function of the concentration of the ions

$(Nc\sigma/1000)e^{-U/kT}$ surrounding the dipole;* of the volume shell element $4\pi r^2 dr$; and of the solid angle ratio $dw/4\pi$, expressing the point-to-point spatial orientational probability between the ion and the central dipole (Fig. 2B). In polar coordinates r , θ and ψ , we will have

$$\frac{dw}{4\pi} = \frac{r \sin\theta d\psi r d\theta}{4\pi r^2} = \frac{\sin\theta d\theta d\psi}{4\pi},$$

and

$$dP(r, \theta, \psi) = \left(\frac{Nc\sigma}{1000} e^{\frac{e\mu \cos\theta}{\epsilon r^2 kT}} \right) (4\pi r^2 dr) \left(\frac{\sin\theta d\theta d\psi}{4\pi} \right)$$

The above expression can be integrated for $\psi=0$ to 2π obtaining the probability that the ion is contained in a solid annulus

$$\begin{aligned} dP(r, \theta) &= \left(\frac{Nc\sigma}{1000} e^{e\mu \cos\theta / \epsilon r^2 kT} \right) (4\pi r^2 dr) \left(\frac{\sin\theta d\theta}{2} \right) \\ dP(r, \theta) &= \frac{2\pi Nc\sigma}{1000} r^2 dr \left(e^{e\mu \cos\theta / \epsilon r^2 kT} \right) \sin\theta d\theta \end{aligned} \quad (VI)$$

Call $\cos\theta=y$, $dy=-\sin\theta d\theta$. Then, given

$$dP(r) = \frac{2\pi Nc\sigma}{1000} r^2 dr \int_0^\pi \left(e^{e\mu \cos\theta / \epsilon r^2 kT} \right) \sin\theta d\theta,$$

we shall have:

$$dP(r) = \frac{2\pi Nc\sigma}{1000} r^2 dr \int_{-1}^1 e^{(e\mu / \epsilon r^2 kT)y} dy.$$

The integral

$$\begin{aligned} \int_{-1}^1 e^{(\mu e / \epsilon r^2 kT)y} dy &= \frac{1}{(\mu e / \epsilon r^2 kT)} \int_{-1}^1 e^{(\mu e / \epsilon r^2 kT)y} d\left(\frac{e\mu}{\epsilon r^2 kT} y \right) \\ &= \frac{e^{\mu e / \epsilon r^2 kT} - e^{-\mu e / \epsilon r^2 kT}}{(\mu e / \epsilon r^2 kT)} = \frac{2\sinh[\mu e / \epsilon r^2 kT]}{(\mu e / \epsilon r^2 kT)}. \end{aligned}$$

Then

$$dP(r) = \frac{2\pi Nc\sigma}{1000} r^2 dr \left(\frac{e^{\mu e / \epsilon r^2 kT} - e^{-\mu e / \epsilon r^2 kT}}{(\mu e / \epsilon r^2 kT)} \right) \quad (VII)$$

In order to integrate with respect to r one has to set a finite upper limit to r .

* σ is the degree of dissociation of the electrolyte

The above function, for a given finite thickness Δr shows a minimum with r , defined by

$$\frac{\partial}{\partial r} \left(\frac{\Delta P(r)}{\Delta r} \right) = \frac{4\pi Nc\sigma}{1000} \frac{1}{\mu e/\epsilon kT} \frac{\partial}{\partial r} \left[r^4 \sinh \left(\frac{\mu e}{\epsilon r^2 kT} \right) \right] = 0$$

which, operating the derivative leads to

$$4r^3 \sinh \left(\frac{\mu e}{\epsilon r^2 kT} \right) + r^4 \left[\cosh \left(\frac{\mu e}{\epsilon r^2 kT} \right) \right] \left(-\frac{2\mu e}{\epsilon r^3 kT} \right) = 0$$

$$4r^3 \tanh \left(\frac{\mu e}{\epsilon r^2 kT} \right) - \frac{2\mu e}{\epsilon r^2 kT} r^3 = 0$$

Call $Y = (\mu e/\epsilon r^2 kT)$. Then $2 \tanh Y - Y = 0$

$$\frac{\tanh Y}{Y} = 0.5 \quad (\text{VIII})$$

which is satisfied for $Y = 1.915 \approx 2$. The probability function will have a minimum for $Y \approx 2$ which means physically that the probability will go through a minimum for a squared distance $r^2 = q^2$ that corresponds to an aligned ($\theta = 0$) ion-dipole configuration of energy equal to $2kT$ or;

$$q = \left(\frac{e\mu}{2\epsilon kT} \right)^{1/2} \quad (\text{IX})$$

For an electrolyte as LiBF_4 of $\mu = 16 \times 10^{-18} \text{esu cm}$ in the solvent 1,2-Dimethoxyethane ($\epsilon = 7.0$ at 25°C) $q = 11.5 \times 10^{-8} \text{cm}$, whereas in DMM ($\epsilon = 2.76$ at 25°C), by retaining the same μ , it results in $q = 18.4 \times 10^{-8} \text{cm}$. Following Bjerrum, we shall integrate $dP(r)$ for r between a and q - a being the minimum distance accessible to an ion to approach a dipole.

$$P(r) = \frac{4\pi Nc\sigma}{1000} \int_a^q r^2 \frac{(e^{\mu e/\epsilon r^2 kT} - e^{-\mu e/\epsilon r^2 kT})/2}{(\mu e/\epsilon r^2 kT)} dr$$

and given

$$Y = \frac{e\mu}{\epsilon r^2 kT}, \quad r = \left(\frac{\mu e}{\epsilon kT} \right)^{1/2} Y^{-1/2}, \quad dr = - \left(\frac{\mu e}{\epsilon kT} \right)^{1/2} Y^{-3/2} dY$$

$$r^2 dr = - \left(\frac{\mu e}{\epsilon kT} \right)^{3/2} Y^{-5/2} dY$$

$$\begin{array}{ll} \text{also} & \text{for } r = q \quad Y = 2, \text{ and} \\ & \text{for } r = a \quad Y = \frac{e\mu}{\epsilon a^2 kT} = b \end{array}$$

Then

$$\begin{aligned} P(Y) &= -\frac{4\pi Nc\sigma}{1000} \int_b^2 \left(\frac{\mu e}{\epsilon kT} \right)^{3/2} \frac{1}{2} Y^{-5/2} \frac{\sinh Y}{Y} dY \\ P(Y) &= \frac{2\pi Nc\sigma}{1000} \int_2^b \left(\frac{\mu e}{\epsilon kT} \right)^{3/2} \frac{\sinh Y}{Y^{7/2}} dY \end{aligned} \quad (X)$$

and by multiplying and dividing by a^3

$$P(Y) = \frac{2\pi Nc\sigma a^3}{1000} b^{3/2} \int_2^b \frac{\sinh Y}{Y^{7/2}} dY$$

The integral can be solved by expanding in series the convergent function

$$\sinh Y = Y + \frac{Y^3}{3!} + \frac{Y^5}{5!} + \dots$$

$$Q = \int_2^b \frac{\sinh Y}{Y^{7/2}} dY = \int_2^b \left(Y^{-5/2} + \frac{1}{3!} Y^{-1/2} + \frac{1}{5!} Y^{3/2} + \frac{1}{7!} Y^{7/2} \right) dY$$

$$Q = \frac{-Y^{-3/2}}{1!(3/2)} + \frac{Y^{1/2}}{3!(1/2)} + \frac{Y^{5/2}}{5!(5/2)} + \frac{Y^{9/2}}{7!(9/2)} + \dots \Big|_2^b$$

$$Q = \sum_n \frac{Y^{(n-(5/2))}}{(n-(5/2))n!} \Big|_2^b, \text{ for all odd } n's.$$

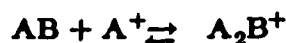
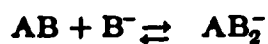
Therefore

$$P(Y) = \frac{2\pi Nc\sigma a^3}{1000} b^{3/2} Q = \frac{2\pi Nc\sigma a^3}{1000} b^{3/2} \left[\sum_{n, \text{ odd}} \frac{Y^{(n-5/2)}}{(n-5/2)n!} \right]_{Y=2}^{Y=b} \quad (XI)$$

The function Q is a converging function by increasing n . By limiting n to $n=15$ one obtains

$$\begin{aligned} Q_{n=15} &= -\frac{b^{-3/2}}{1.5} + \frac{b^{1/2}}{0.5 \times 3!} + \frac{b^{5/2}}{2.5 \times 5!} + \frac{b^{9/2}}{4.5 \times 7!} + \frac{b^7}{7 \times 9!} \\ &\quad + \frac{b^{17/2}}{8.5 \times 11!} + \frac{b^{21/2}}{10.5 \times 13!} + \frac{b^{25/2}}{12.5 \times 15!} - 0.2556 \end{aligned}$$

and we shall identify the ratio $P(Y)/c\sigma$ as the triple ion formation constant K_T , associated to either of the two processes.



taken to occur to the same extent (symmetrical approximation)

$$K_T = \frac{\sigma_T c}{(1 - \sigma - 3\sigma_T) c \sigma c} \approx \frac{\sigma_T}{c \sigma}$$

namely, a degree of triple ion formation σ_T per unit concentration of free ions.

Then:

$$K_T = \frac{2\pi N a^3}{1000} b^{3/2} Q = K_O b^{3/2} Q \quad (XII)$$

Table I reports the calculated values of K_T as a function of a for $LiBF_4$ in DME ($= 1,2$ Dimethoxyethane) of permittivity $\epsilon = 7.0$ for which $\mu = 15.8 \times 10^{-18}$ esu cm. ² It was found² that $K_t(\text{exp}) = 50 \text{ M}^{-1}$ from conductance experiments. Judging from the above figure it would result $a \approx 5.7 \times 10^{-8}$ cm, a very reasonable figure when compared with the charge separation of the dipole $d = \mu/e = (15.8 \times 10^{-18} / 4.8 \times 10^{-10}) = 3.3 \times 10^{-8}$ cm and the axion¹¹ $a_T = 1.5d = 4.9 \times 10^{-8}$ cm. The last model envisages the triple ion as composed of three identical spheres in an aligned configuration (corresponding to a minimum in the potential energy). Very reliable data for K_T as a function of the permittivity exist in the literature for the system $I-Am_4N \cdot NO_3$ in H_2O dioxane at $25^\circ C$.

Table II compares the experimental data for $\log_{10} K_T$ with the calculated $\log K_T$'s and the corresponding values of a used. The calculated K_T corresponds to the best fit by varying a . The values of $K_T(\bar{a})$ using the averaged a 's are also shown. Figure 3 reports the $\log_{10} K_T$ vs. $1/\epsilon$ for the above system. The solid lines are the calculated values of $\log_{10} K_T(9.6_4)$. The fit to the experimental data is comparable with the one obtainable with the Fuoss-Jagodzinski function K^{FJ} and the parameter $a = 10.7 \times 10^{-8}$ cm

$$K_T^{FJ} = \frac{\pi L a^3 e^{-3/2}}{1000} \exp(\beta)$$

with $\beta = e^2 / 2\epsilon akT$.

In fact, the average $|\bar{\Delta}| = \log K_T(\text{calc}) - \log K_T(\text{exp}) = 0.14$ with $a = 9.6_4 \times 10^{-8} \text{ cm}$, whereas $|\bar{\Delta}| = \log K_T^{\text{FJ}} - \log K_T(\text{exp}) = 0.15$ with $a = 10.7 \times 10^{-8} \text{ cm}$. The present approach however, does not contain constraints in defining a triple ion only when the ion is "in contact" with a dipole. Rather, it defines a triple for r varying between a and q .

We then wish to compare K_T (Eq. XII) with the experimental result for LiBF_4 in DMM at 25°C . Using the value of $\mu = 16 \times 10^{-18} \text{ esu cm}$, obtained in DME solvent by dielectric relaxation, Table I reports the values of K_T as a function of the parameter a . The fit with the experimental value $K_T = 826 \text{ M}^{-1}$ is obtained for $a = 8.0 \times 10^{-8} \text{ cm}$. This value is remarkably close to the one calculable from the axiom $a = 1.5d = 7.7 \times 10^{-8} \text{ cm}$, $d = 5.1 \times 10^{-8} \text{ cm}$ being calculable from the K_A obtained from the conductance data.

Table I

Calculated K_T for LiBF_4 in DME ($\epsilon=7.0$) and in DMM ($\epsilon=2.76$) at $T=298.2\text{K}$ as a function of the separation distance a between ions and dipoles.

Solvent: DME; $q=(\frac{e\mu}{2\epsilon kT})^{1/2}=11.47\times 10^{-8}\text{cm}$; $\mu=15.8\times 10^{-18}\text{esu cm}$

$a\times 10^8$ (cm)	b --	K_o (M^{-1})	Q --	K_T (M^{-1})	$K_T(\text{exp})$ M^{-1}
4	16.455	0.2421	398.5	6.4×10^3	50
5	10.531	0.4728	12.071	195.	
5.5	8.704	0.6293	4.115	66.5	
5.6	8.395	0.6643	3.465	56.0	
5.7	8.103	0.7005	2.955	47.7	
6	7.313	0.8170	1.463	31.7	
7	5.373	1.2974	0.828	13.4	
9	3.250	2.7574	0.3055	4.94	
11	2.176	5.0345	0.0532	0.86	

Solvent: DMM; $q=18.39\times 10^{-18}\text{cm}$; $\mu=16\times 10^{-18}\text{esu cm}$

7	13.802	1.2974	86.34	5474.	826
7.99	10.594	1.9294	12.535	834.	
8	10.567	1.9366	12.336	821.	
10	6.7630	3.7825	1.5071	100.	
12	4.6965	6.5362	0.6283	41.8	
14	3.4505	10.379	0.3469	23.1	
16	2.6418	15.493	0.1722	11.5	
18	2.0873	22.060	0.0268	1.78	

Table II

Experimental values of $\log_{10}K_T$ and calculated values of $\log_{10}K_T(a)^*$ for the system isoamylammonium nitrate in H_2O -dioxane mixtures at $25^\circ C$. The values of $\log_{10}K_T(a)$ have been approximated to $\log_{10}K_T(\exp)$ by varying a in steps of $0.1 \times 10^{-8} \text{ cm}$. The value of $\log_{10}K_T(\bar{a})$ corresponds to the calculated K_T for the averaged a for the system, $\bar{a} = 9.64 \times 10^{-8} \text{ cm}$

$\%H_2O$	ϵ	$\log_{10}K_T(\exp)$	$\log_{10}K_T(a)$	$a \times 10^8$ (cm)	$\log_{10}K_T(\bar{a})$
0.60	2.38	4.68	4.65	9.6	4.62
1.24	2.56	4.12	4.11	9.9	4.30
2.35	2.90	3.50	3.50	10.1	3.79
4.01	3.48	3.00	2.98	9.9	3.12
6.37	4.42	2.50	2.51	9.4	2.41
9.50	5.84	2.00	2.01	8.9	1.80

* The value $\mu = 29 \times 10^{-18} \text{ esu cm}$, corresponding to $d = 6.04 \times 10^{-8} \text{ cm}$ ($\mu = de$) has been used to calculate $K_T(a)$. a is the experimental value for the ion-dipole separation distance. d is the dipole charge to charge separation distance.

c) Dielectric and ultrasonic relaxation

Figure 4A reports the real part ϵ' of the complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ plotted vs. the frequency f for LiBF_4 0.35M in DMM at 25°C. The solid line is the fitted function which appears capable to interpret the available data according to a single Debye relaxation process

$$\epsilon' = (\epsilon_0 - \epsilon_\infty) \frac{1}{1+(f/f_r)^2} + \epsilon_\infty \quad (\text{XIII})$$

Figure 4B is the Cole-Cole plot of ϵ'' vs. ϵ' and the semi-circle corresponds to a single relaxation process with ϵ' given by the equation above and ϵ''

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) \frac{f/f_r}{1+(f/f_r)^2} \quad (\text{XIV})$$

with parameters $\epsilon_0 = 2.78$, $\epsilon_\infty = 2.02$ and $f_r = 60$ GHz. Notice that Saar et.al.⁹ reported for the solvent DMM $\epsilon_0 = 2.76$, $\epsilon_\infty = 2.18$ and $f_r = 75$ GHz. Hence, the presence of 0.35M is only detectable in a shift of the solvent relaxation to lower frequencies and a change of the relaxation strength $(\epsilon_0 - \epsilon_\infty)$ which is apparently due mostly to a change in ϵ_∞ . The latter one is only an extrapolated parameter because of possible effects on non-Debye nature at $f > 100$ GHz.¹² The rather remarkable findings for the present system is the absence of a "solute" relaxation around 1-3 GHz which has been the observed behavior for alkali salts in ethereal solvents studied so far.^{13,1,2} This apparent invisibility of the dipolar pairs LiBF_4 , despite the very large K_A found by conductance, can be interpreted in two ways: either the pairs are so heavily solvated that their diffusional rotational relaxation frequency is below the range accessible to our microwave measurements, or LiBF_4 is heavily dimerized above $\sim 0.1\text{M}$ to apolar or antiparallel dimers which are practically invisible by dielectric relaxation.

Consideration of the second hypothesis, namely a sizeable dimerization, is suggested by the fact that already in DME^2 ($\epsilon = 7.0$) an ultrasonic relaxation was interpreted as due to dimerization. In DMM solvent ($\epsilon = 2.76$)⁹ simple

electrostatic considerations would suggest the quadrupole or dimer formation constant to be much larger than in DME.

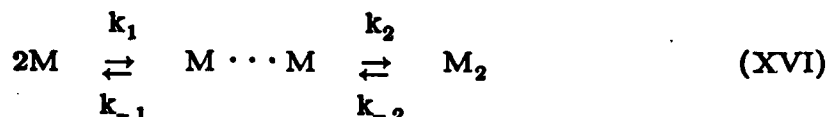
Figure 5 shows a representative plot of the excess sound absorption per wavelength $\mu = \alpha_{\text{exc}}\lambda$ plotted vs. f for LiBF_4 in DMM at 25°C . Although the data extends to about 3 decades in frequency, a single Debye process (solid line) appears adequate to represent the data according to the function

$$\mu = 2\mu_{\text{max}} \frac{f/f_r}{1+(f/f_r)^2} \quad (\text{XV})$$

where $\mu = \mu_{\text{max}}$ at the relaxation frequency $f = f_r$, $\mu = \alpha_{\text{exc}}\lambda = (\alpha - Bf^2)u/f$, and α is the sound attenuation coefficient, λ the wavelength $\lambda = u/f$, μ is the sound velocity and $B = (\alpha/f^2)_{f \gg f_r}$ the background (α/f^2) ratio for frequencies $f \gg f_r$. Table III reports the relaxation parameters μ_{max} , f_r , B and the sound velocity u for all the solutions and temperatures investigated.

From Table III it is apparent that, within experimental error, f_r is independent of concentration at 25°C , but that μ_m is not linear with concentration. This last observation negates the interpretation by a scheme $A \rightleftharpoons B$ which could represent a first order (or pseudo first order) intra-molecular process (involving the solvent).

Rather, we propose a multistep dimerization process of the type



with $M = \text{LiBF}_4$, the monomer ion-pair. This scheme leads¹⁴ to two relaxation times that for $k_1, k_{-1} \gg k_2, k_{-2}$ read

$$\tau_I^{-1} = 4k_1(M) + k_{-1}$$

$$\tau_{II}^{-1} = k_2 + k_{-2} \frac{4(M)}{4(M) + K_{-1}}, \text{ with } K_1 = (k_1/k_{-1}) = \frac{(M \cdots M)}{(M)^2} \quad (\text{XVII})$$

For $4(M) \gg K_{-1}$

$$\tau_{II}^{-1} = k_{-2} + k_2 = k_{-2}(1+K_2) \quad , \quad \text{or} \quad (XVIII)$$

$$\tau_{II}^{-1} = \frac{kT}{h} e^{+\Delta S_2^\ddagger/R} e^{-\Delta H_2^\ddagger/RT} (1+K_2)$$

with $K_2 = k_2/k_{-2}$. The above implies that a plot of $\ln(\tau_{II}^{-1}/T)$ vs. $1/T$ will have a slope¹⁵

$$\frac{d\ln(\tau_{II}^{-1}/T)}{d(1/T)} = - \frac{\Delta H_2^\ddagger}{R} - \frac{K_2}{1+K_2} \frac{\Delta H_2}{R} \quad (XIX)$$

with $K_2 = e^{-\Delta H_2/RT} e^{\Delta S_2/R}$.

Figure 6A shows a plot of $\ln(\tau_{II}^{-1}/T)$ vs. $1/T$. The solid line was calculated by linear regression giving $r^2 = 0.95$, Int = 16.01 and Slope = -466 from which $\Delta S_2^\ddagger = -15.4$ cal/K mol and

$$-466 = - \frac{\Delta H_2^\ddagger}{R} - \frac{K_2}{1+K_2} \frac{\Delta H_2}{R} \quad (XX)$$

Also, Eq. (XVIII) gives

$$5.86 \times 10^8 = \frac{kT}{h} e^{\Delta S_2^\ddagger/R} e^{-\Delta H_2^\ddagger/RT} (1+K_2) \quad , \quad \text{or} \quad (XXI)$$

$$02.12 = e^{-\Delta H_2^\ddagger/RT} (1+K_2)$$

Table III

Ultrasonic parameters μ_m , f_r , B and sound velocity u for all the concentrations of LiBF_4 in DMM and temperatures investigated.

t (°C)	c (M)	μ_m $\times 10^5$	f_r (MHz)	$B \times 10^{17}$ (cm^{-1}s^2)	$u \times 10^5$ (cm s^{-1})
25	0.35	430	85	48	1.069
25	0.24	450	90	42	1.065
25	0.168	390	80	38	1.064
25	0.093	280	80	36	1.063
15	0.25	410	80	40	1.142
5	0.25	470	75	36	1.153
-1	0.25	480	70	38	1.179

* $u \times 10^5 = 1.179 - 0.004t$, ($r^2 = 0.9$), for LiBF_4 0.25M between 25°C and -1°C, reproduces the experimental data with a % error = $\frac{|\Delta u|}{u} \% = \pm 1$

For a two-step dimerization process (XVI), the maximum sound absorption per wavelength μ_{II} for the slow relaxation process, is bound to the concentration of the various species by the relation¹⁴

$$\mu_{II} = \frac{\pi}{2\beta_s} \frac{\Delta V_{SII}^2}{RT} \Gamma_{II} \quad (XXII)$$

with $\beta_s = (\rho u^2)^{-1}$ the adiabatic compressibility, ρ the density, ΔV_{SII} the isoen-tropic volume change

$$\Delta V_{SII} = \Delta V_2 + \frac{1/4(M)}{1/4(M) + (M...M)} \Delta V_1$$

with ΔV_1 and ΔV_2 the isoentropic volume changes associated with the steps of process (XVI). Also, the function Γ_{II} is:¹⁴

$$\Gamma_{II} = \left[\frac{1}{(M_2)} + \frac{1}{1/4(M) + (M...M)} \right]^{-1} \quad (XXIII)$$

(the factor 1/2 instead of 1/4 in front of (M) in Eqs. (XXII) and (XXIII) reported in reference 14 was a misprint). If $(M) < (M...M)$, (M_2) , as the dielectric data seem to imply, Eq. (XXIII) can be approximated to

$$\Gamma_{II} \cong \left[\frac{1}{(M_2)} + \frac{1}{(M...M)} \right]^{-1} = \frac{K_2}{1+K_2} (M...M)$$

with $K_2 = \frac{(M_2)}{(M...M)}$. On the other hand, one can write

$$(M...M) = \frac{(M...M) + (M_2)}{1+K_2} = \frac{c^{\text{dimer}}}{1+K_2}$$

and

$$\Gamma_{II} \cong \frac{K_2}{(1+K_2)^2} c^{\text{dimer}} \quad (XXIV)$$

where $c^{\text{dimer}} = (M...M) + (M_2)$ (Notice also that ΔV_{SII} is concentration depen-dent and that indeed μ_{II} is not linear with c).

Introducing XXIV into XXII

$$\mu_{II} = \frac{\pi}{2\beta_s} \frac{(\Delta V_{SII})^2}{RT} \frac{K_2}{(1+K_2)^2} c^{\text{dimer}}$$

$$\ln(\mu_{II}T/u^2) = \ln \left[\frac{\pi \rho c^{\text{dimer}} \Delta V_{SII}^2}{2R} \right] + \ln K_2 - 2\ln(1+K_2)$$

By neglecting the temperature dependence of the quantity $\rho c^{\text{dimer}} \Delta V_{SII}^2$, the above implies that

$$\frac{d \ln(\mu_{II}T/u^2)}{d(1/T)} \cong - \frac{\Delta H_2}{R} + \frac{2K_2}{1+K_2} \frac{\Delta H_2}{R} = \frac{\Delta H_2}{R} \frac{K_2-1}{K_2+1} \quad (\text{XXVI})$$

namely, the slope of a plot of $\ln(\mu_{II}T/u^2)$ vs. $1/T$ should be expressed by Eq. (XXVI). Figure 6B shows this plot. Linear regression gives Intercept = -21.05, Slope = -526.9. Therefore,

$$-526.9 = \frac{\Delta H_2}{R} \frac{K_2-1}{K_2+1} \quad (\text{XXVII})$$

Eqs. (XX), (XXI) and (XXVII) can now be correlated. Trial and error choice¹⁵ of K_2 leads to compatibility for $K_2 = 7.8$ which leads to $\Delta H_2 = -1.45K \text{ cal/mol}$ $\Delta H_2^\ddagger = 2.2K \text{ cal/mol}$.

Table IV reports the above and the derived thermodynamic and kinetic parameters using the relations $\Delta G_2 = -RT \ln K_2 = -1.22K \text{ cal}$ at $T = 298.2K$, $\Delta S_2 = (1/T)(\Delta H_2 - \Delta G_2) = \Delta S_2^\ddagger - \Delta S_2^\ddagger$ and $\Delta H_2 = \Delta H_2^\ddagger - \Delta H_2^\ddagger$.

It would appear desirable to evaluate K_q , the overall quadrupole or dimer formation constant. From scheme (XVI) and the definitions

$$K_1 = \frac{(M \dots M)}{(M)^2}, \quad K_2 = \frac{(M_2)}{(M \dots M)}, \quad \text{and}$$

$$K_\Sigma = \frac{(M \dots M) + (M_2)}{(M)^2}, \quad \text{it results that}$$

$$K_\Sigma = K_1(1+K_2) \quad (\text{XXVIII})$$

and we have obtained $K_2 = 7.8$. K_1 could be evaluated in principle from the Maaser-Bjerrum² theoretical expression

$$K_{qBj} = K_{oq} b_q Q_q \quad (\text{XXIX})$$

with

$$K_{oq} = \frac{4\pi L a^3}{3000}, \quad b_q = \frac{\mu^2}{\epsilon a_q^3 kT} \quad \text{and}$$

$$Q_q = 0.6667 - \frac{1}{b_q} + \sum_{i=1}^{\infty} \frac{1}{(n+2)!n} (b^n - (1.5)^n) \quad , \quad (XXX)$$

for odd n's.

For $\epsilon = 2.76$ and by retaining $\mu = 16 \times 10^{-18}$ esu cm, we have calculated Q extending n to n = 17. The calculation of K_{qBj} is shown on Table V. Unfortunately, K_{qBj} appears to be too sensitive to the choice.

Table IV

Thermodynamic and kinetic parameters for the slow relaxation dimerization process for $LiBF_4$ in DMM

K_2	7.8
ΔG_2	-1.22 K cal/mol
ΔH_2	-1.45 K cal/mol
ΔS_2	-0.8 cal/ K, mol
$\Delta H_{-2}^{\ddagger}$	2.2 K cal/mol
$\Delta S_{-2}^{\ddagger}$	-15.4 cal/K, mol
$\Delta H_2^{\ddagger}$	0.76 K cal/K mol
$\Delta S_2^{\ddagger}$	-16.2 cal/K, mol
k_2	$5 \times 10^8 s^{-1}$

of the parameter a_q , the minimum dipole-dipole separation distance to make an assignment of $K_{qBj} = K_1$ short of being an arbitrary assumption.

Table V

Calculated values of K_{qBj} according to the expression $K_{qBj} = K_{oq} b Q_q$ as a function of a_q the dipole-dipole minimum separation distance for $\mu = 16 \times 10^{-18}$ cm esu the dipole moment of the pairs, $T = 298.2$, $\epsilon = 2.76$ and $b_q = \mu^2 / \epsilon a_q^3 kT$. $K_{qBj} = 0$ for a separation distance $q = \left(\frac{2}{3} \frac{\mu^2}{\epsilon kT} \right)^{1/3} = 11.4_5 \times 10^{-8}$ cm, for the above parameters.

a_q	b_q	K_{oq}	Q_q	K_{qBj}
5	18.035	0.3152	5507	3.1×10^4
6	10.437	0.5447	23.34	132.7
7	6.572	0.8649	2.913	16.57
8	4.403	1.291	1.231	7.00
9	3.092	1.839	0.6935	3.94
10	2.254	2.522	0.3734	2.12
11	1.694	3.356	0.1129	0.642

Conclusion

The Fuoss-Kraus triple ion conductance theory allows for the determination of $K_A = 6 \times 10^{16} \text{M}^{-1}$ and $K_T = 826 \text{M}^{-1}$, pending the validity of the Walden rule and the assumption $\Lambda_o^T = \frac{2}{3} \Lambda_o$. The Fuoss-Jagodzinski association relation for K_A gives $d = 5.1 \times 10^{-8} \text{cm}$ for the charge separation of the ion-pair. The theoretical expression XII derived above for K_T gives $a = 8.0 \times 10^{-8} \text{cm}$ for the minimum separation ion distance between the ion and the dipole, close to the axion $a = 1.5d = 7.7 \times 10^{-8} \text{cm}$. The dielectric data shows absence of a dielectric relaxation for the solute in all the frequency ranges investigated. This could be rationalized by either the dipole pairs relaxing below 1 GHz, or, more likely, by the electrolyte being dimerized to apolar dimers.

An ultrasonic relaxation of Debye type is interpreted as due to the second step of a coupled two-step dimerization process. Kinetic and thermodynamic parameters have been extracted from the data. In particular, the formation constant for the second step of dimerization $K_2 = 7.8$. The constant for the first step K_1 cannot be determined without a reliable knowledge of a_q the pair to pair minimum separation distance.

Acknowledgement

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ADDENDUM

After the completion of the present work we have performed static permittivity measurements at $f = 3.5$ MHz with a Bontoon resonator and a cell of capacity $C_0 = 5.0_7 \pm 0.0_7$ p Farad of a solution 0.09_3 M LiBF_4 in DMM at 25°C . The average of two experiments gave $\epsilon_0 = 2.8_2 \pm 0.0_1$, a value close to the figure extrapolated from the microwave range $\epsilon_0 = 2.78$ as reported above. This confirms the hypothesis advanced above that the electrolyte is heavily associated to apolar dimers.

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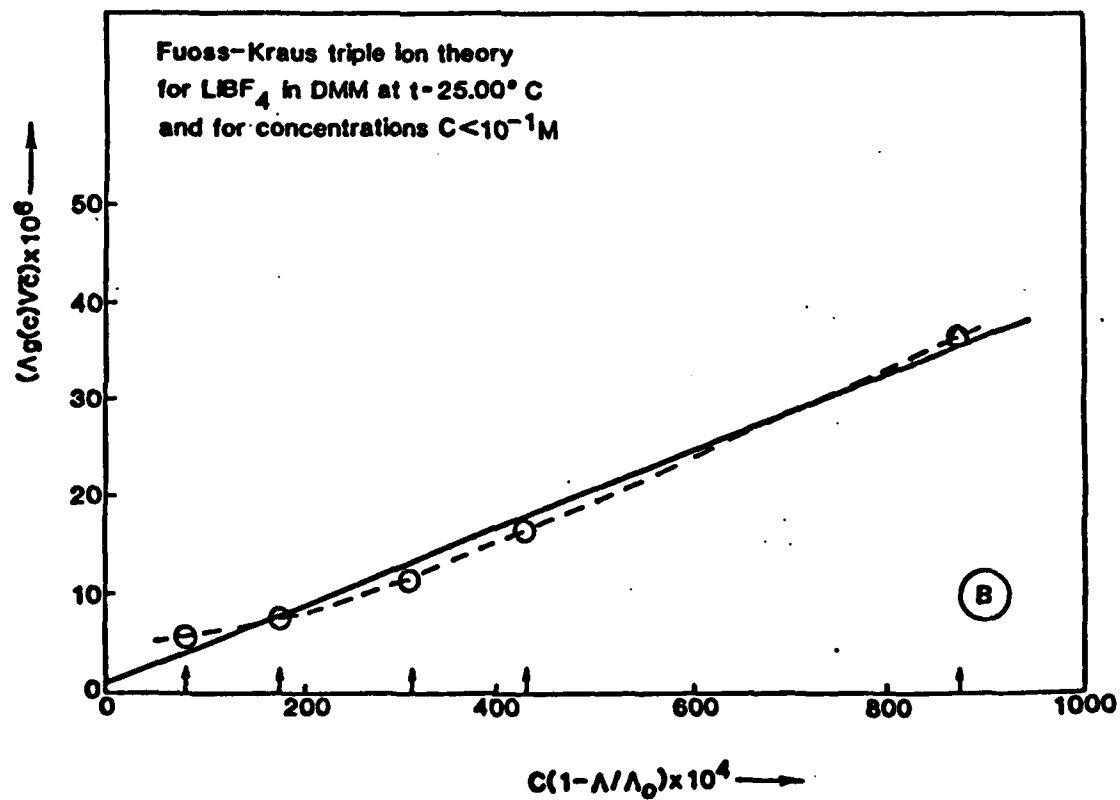
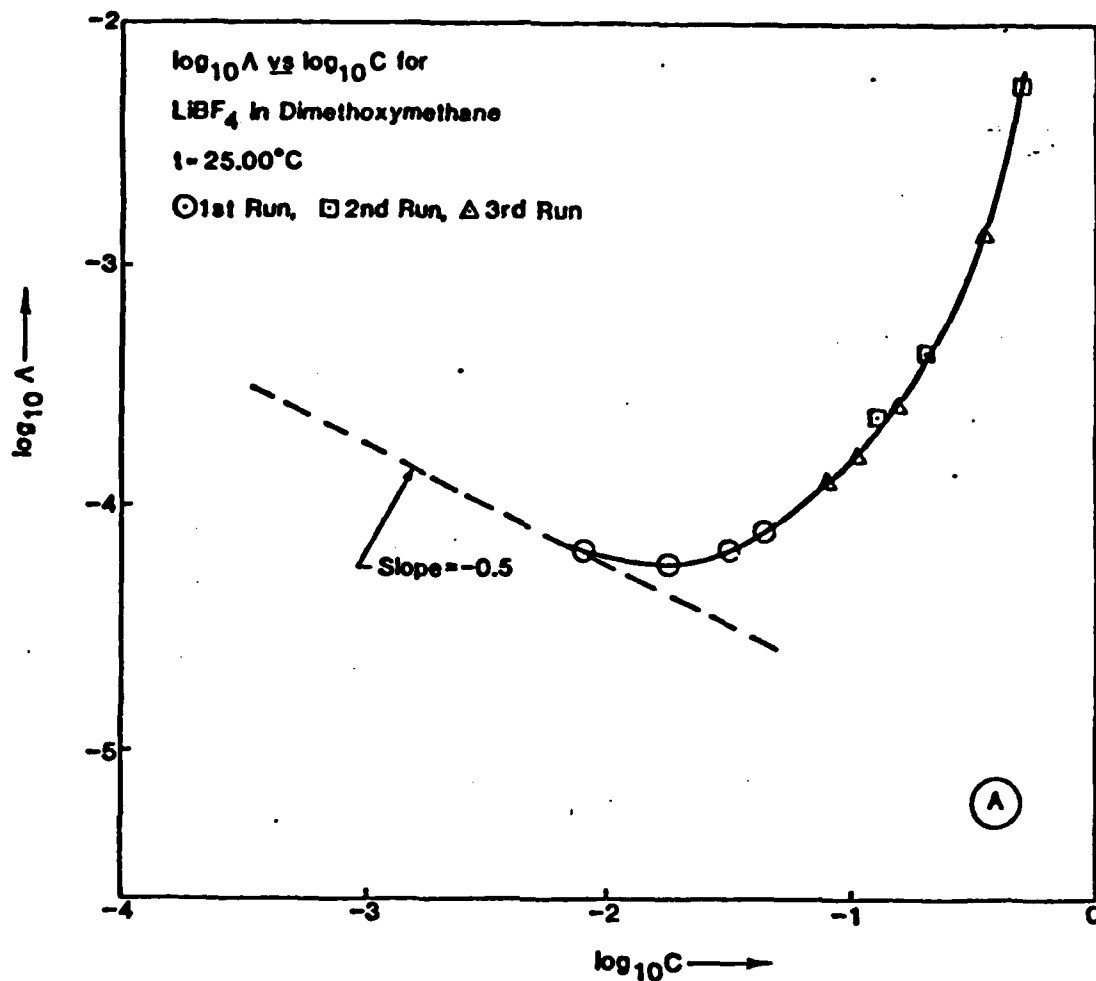
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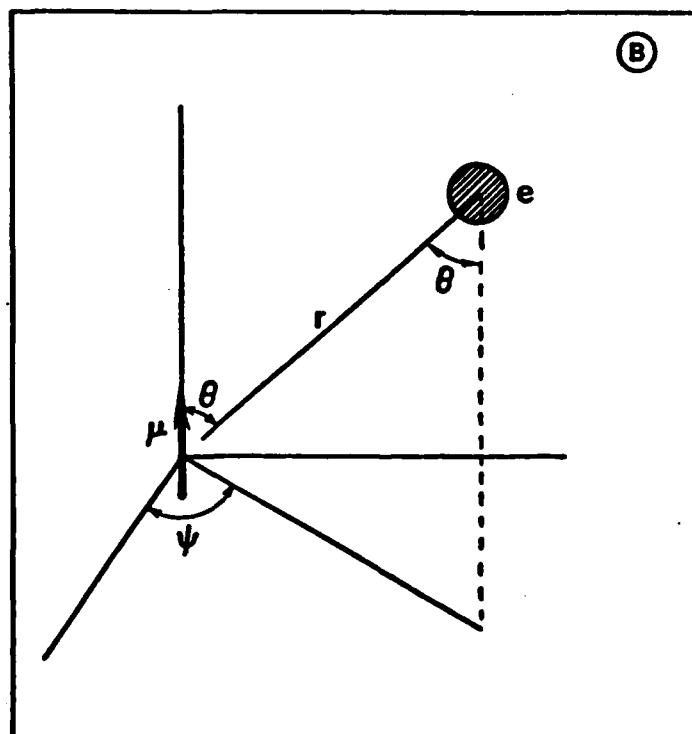
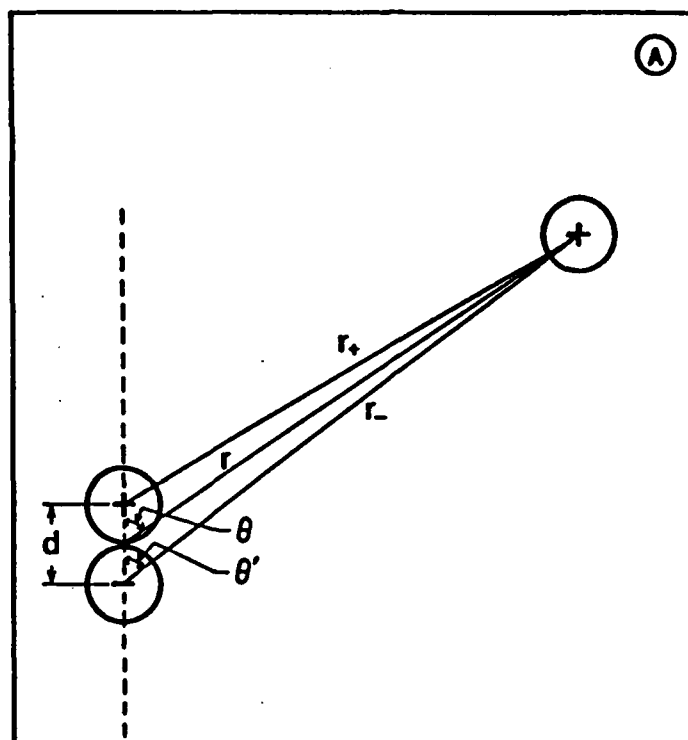
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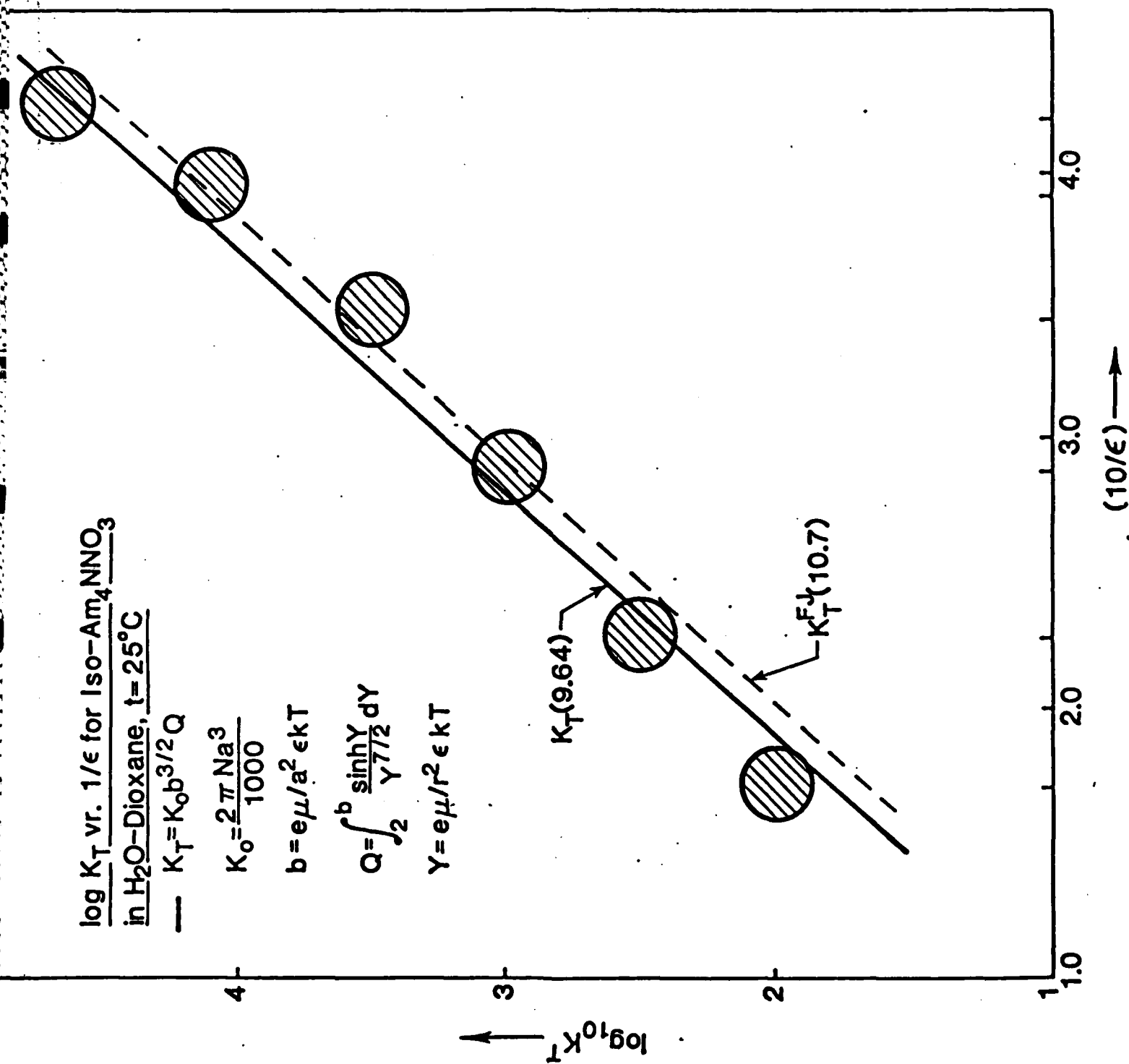
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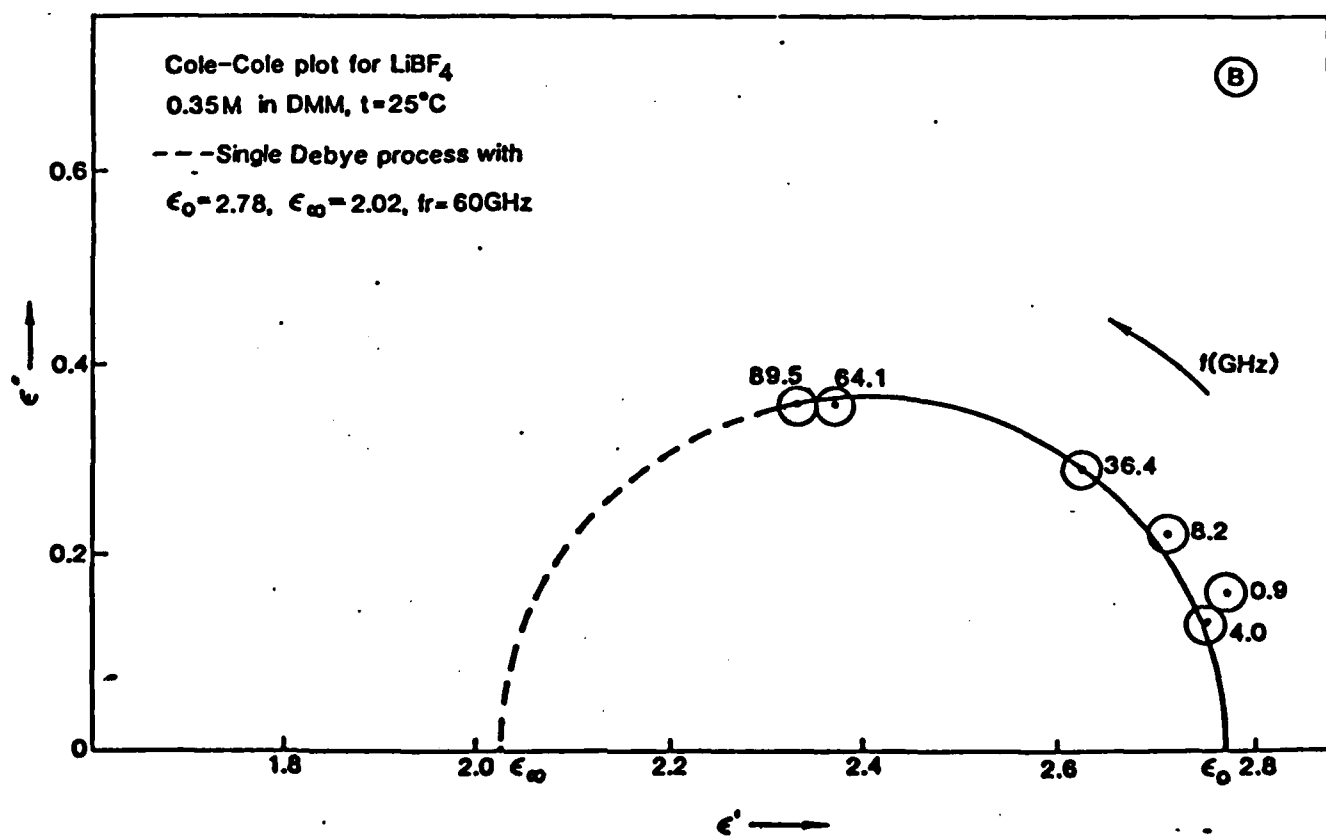
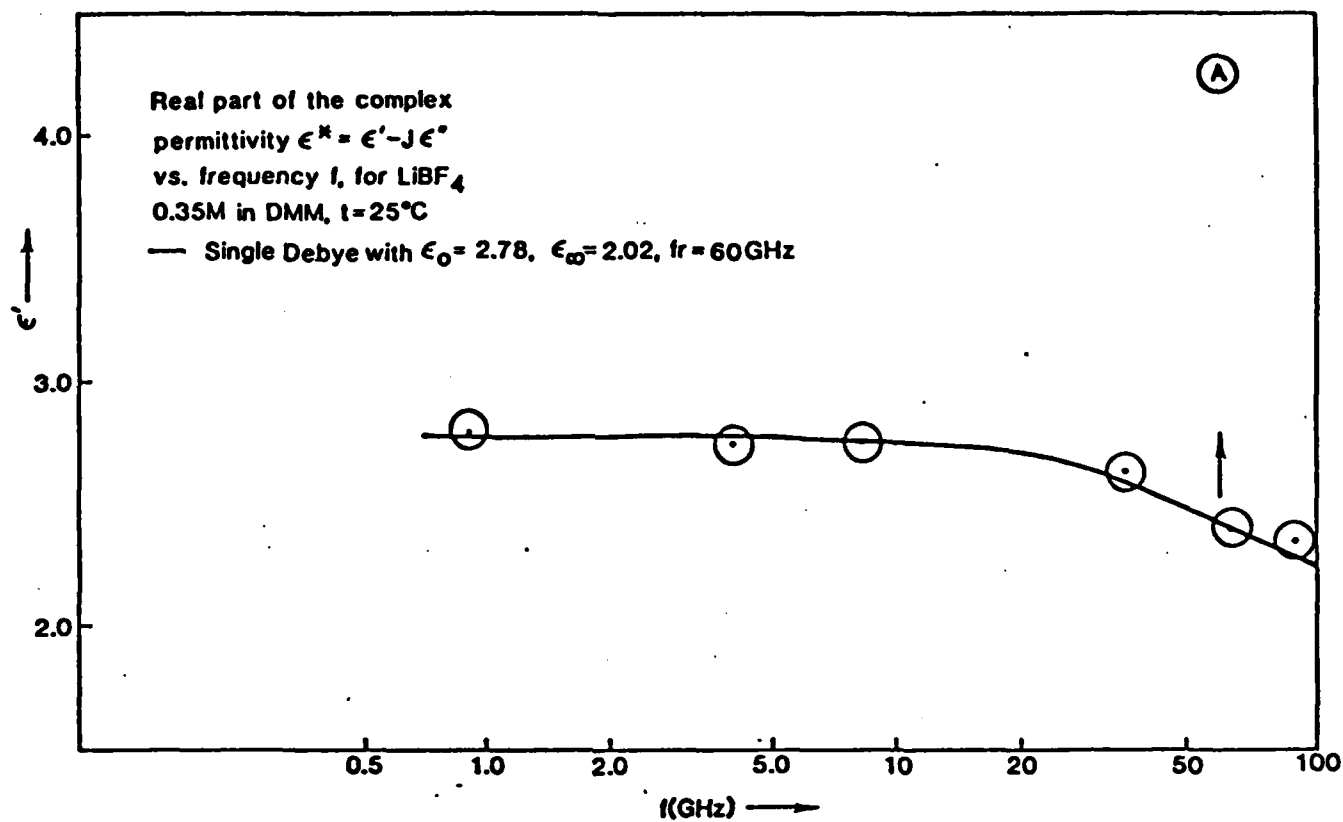
- Fig. 1A $\log_{10}\Lambda$ vs. $\log_{10}c$ for LiBF_4 in DMM at 25°C .
- Fig. 1B $\Lambda g(c)\sqrt{c}$ vs. $(1 - \frac{\Lambda}{\Lambda_0})c$ for LiBF_4 in DMM at 25°C according to the Fuoss-Kraus theory.
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- Fig. 2B Polar coordinate representation of the dipole μ (taken as the origin of the Cartesian coordinate) and of an ion of charge e .
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- Fig. 6A Eyring plot for LiBF_4 0.25M in DMM.
- Fig. 6B Lamb plot for LiBF_4 0.25M in DMM.

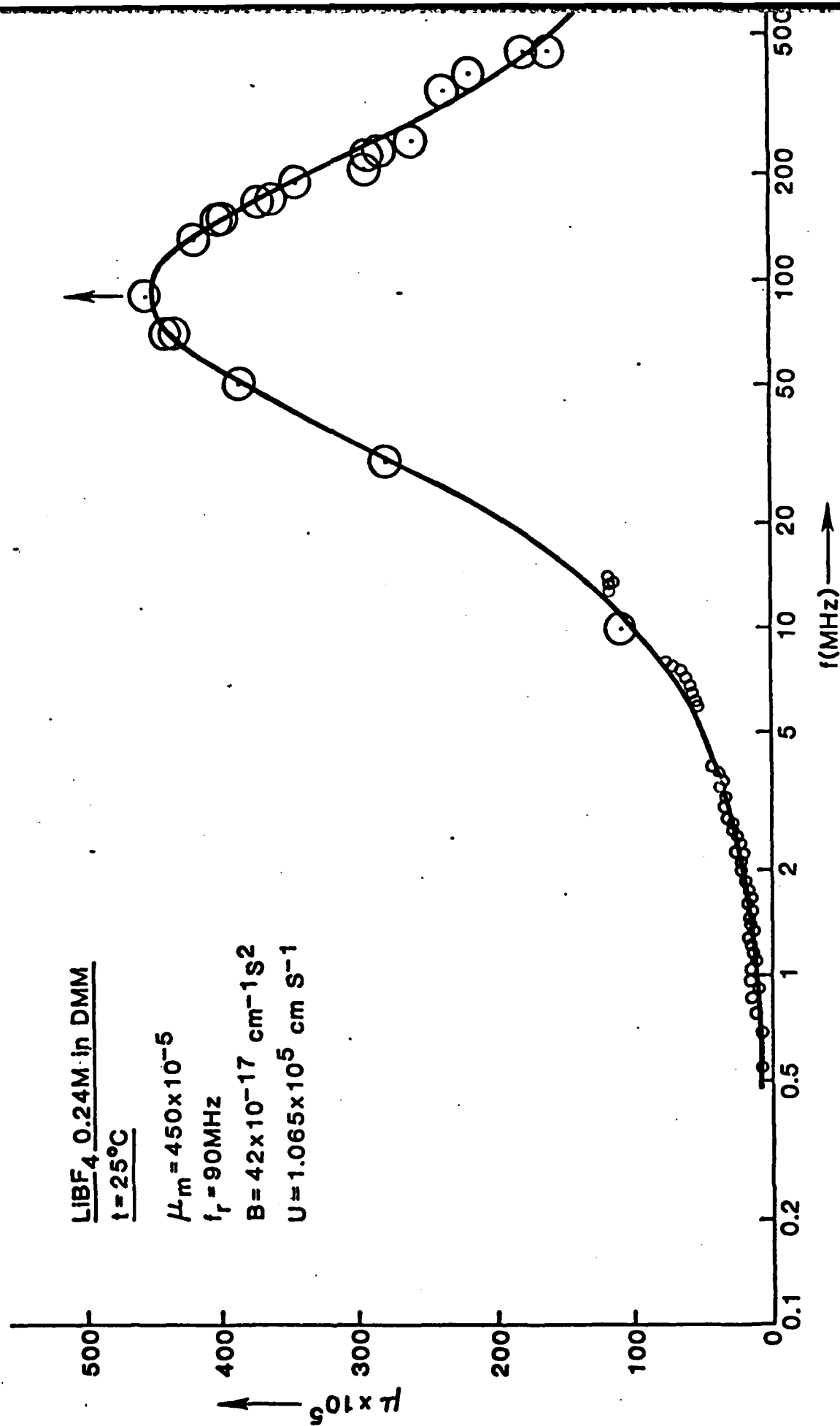
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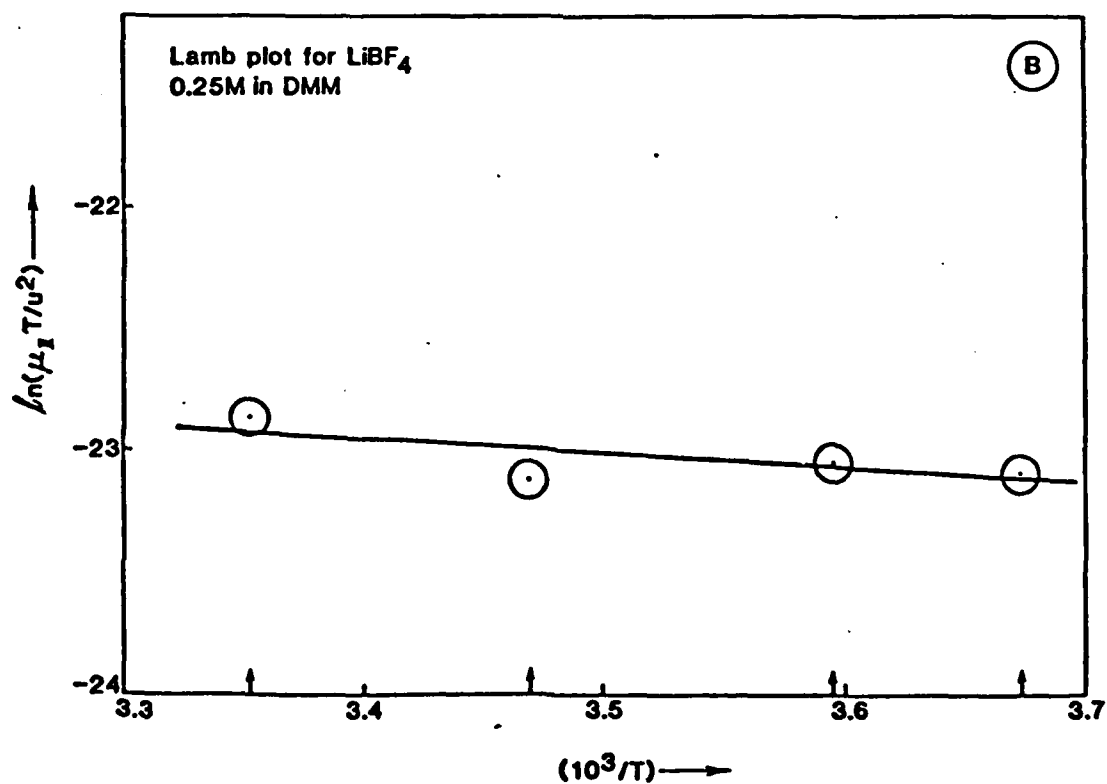
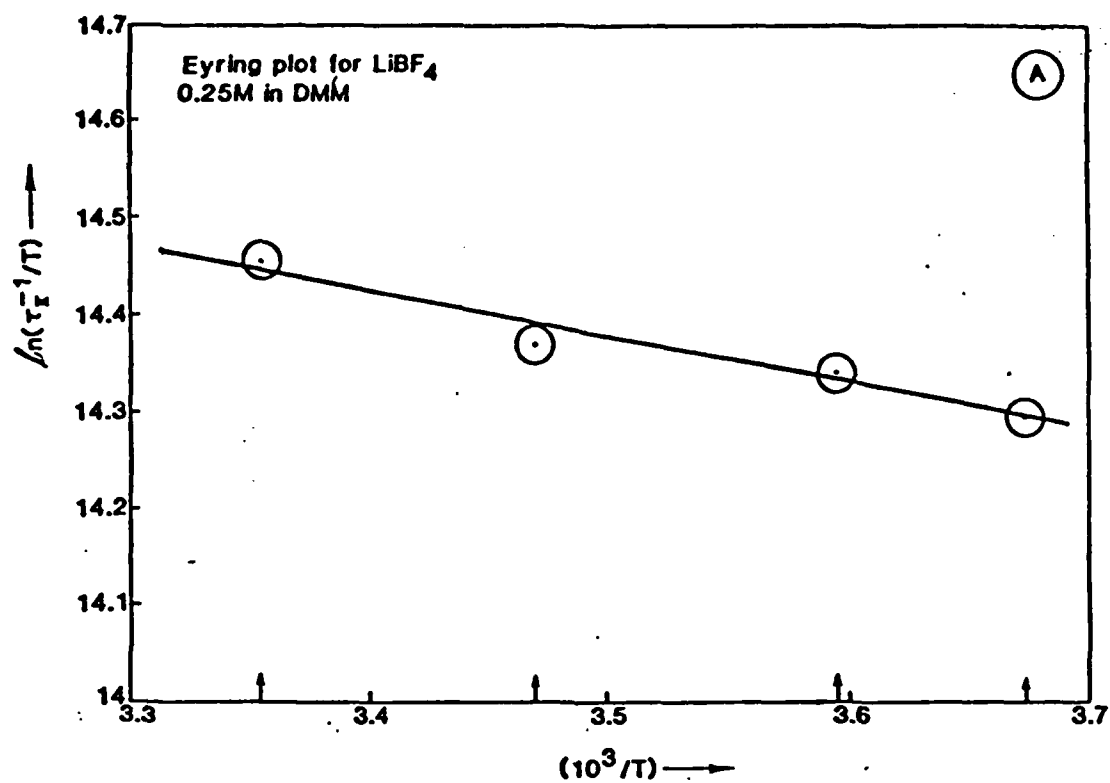












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