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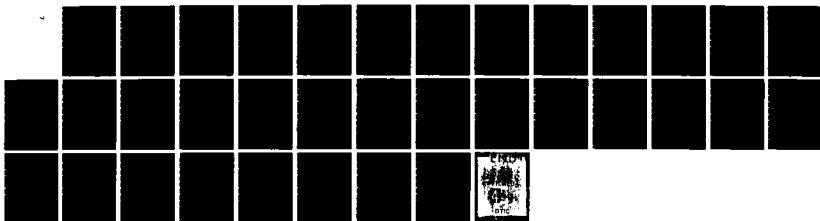
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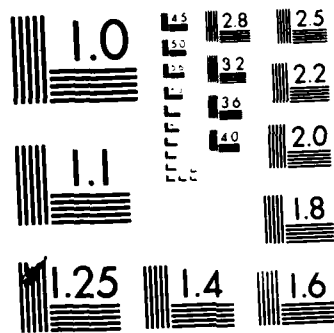
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THERMODYNAMICS OF DIMERIZATION OF LITHIUM
SALTS IN 1,2 DIMETHOXYETHANE*

by

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ABSTRACT

Electrical conductance data in the concentration range 10^{-4} to 10^{-2} for LiBF_4 in 1,2-DME are interpreted by the Fuoss-Kraus theory yielding values of the ion-pairs and triple-ions formation constants.

Complex dielectric permittivities for LiBF_4 in 1,2-DME at 25°C in the frequency range 0.9-81 GHz are reported. The data are interpreted by two Debye relaxation processes, one for the solvent and one for the solute. The latter is interpreted as due to the diffusional rotation of ion-pairs.

Ultrasonic absorption data for LiBF_4 in 1,2-DME at 25°C in the concentration range 0.28-0.55M and frequency range 10-550 MHz are reported. The data are described by a single Debye relaxation process and are interpreted as due to an ion-pair dimerization equilibrium leading to formation of quadrupoles. Theoretical expression (similar to the ones of Fuoss and Bjerrum for ion-pairs) are developed for the dimerization of ion pairs to quadrupoles. To this end, a point dipole-point dipole potential has been used. The dependence of K_F and K_B from the dipole-dipole separation distance is illustrated. Further, the thermodynamic increments ΔV_T , ΔS_o , ΔH_o and ΔV_S have been calculated. The latter quantity is compared to the corresponding parameter found during the present and previous ultrasonic research.

ΔV_T ΔS_o ΔH_o ΔV_S

ΔV_T

ΔS_o

ΔH_o

* The ultrasonic data for LiBF_4 in 1,2-DME have been already given in U. S. Army Report No. 3, dated June 30, 1983, under Grant No. DAAG-29-82-K0048. They are regiven here for the sake of logic of the present report that will be basically a paper to be submitted for publication.

INTRODUCTION

1,2 Dimethoxyethane (1,2-DME) is known to chelate lithium as well as sodium ions. LiClO_4 [1] and LiAsF_6 [2] have been investigated in this solvent by ultrasonic and dielectric relaxation and conductance methods. LiBF_4 , another electrolyte relevant to a battery construction, has now been investigated by the same methods in 1,2-DME in order to establish whether a general trend of association exists in different solvents (a sequence has already been found for the three above electrolytes in 2-Methyltetrahydrofuran [3]).

Enough systems have shown formation of quadrupoles in ethereal solvents to justify interest in theoretical expressions aimed at calculating thermodynamic parameters relevant to the ultrasonic research. To this end, using a point dipole-point dipole potential, theoretical expressions of quadrupole formation constants and thermodynamic increments as ΔS_0 , ΔH_0 , ΔV_T and ΔV_S have been obtained as shown below. In some cases already investigated, a process of dimerization consisting of two steps appeared to exist [3]. For these cases, the second step of dimerization is interpreted theoretically by the Kirkwood expression of dipole association [4].

EXPERIMENTAL

The equipment and procedure for the ultrasonic dielectric and conductance work have been described elsewhere [3]. LiBF_4 (Aldrich) was redried in vacuo (~ 1 torr) at $\sim 70^\circ\text{C}$ overnight. 1,2-DME has been purified by distillation at reduced pressure over sodium and benzophenone. Solutions were prepared just before each run. Runs performed with solutions aged 3-4 days gave results which were outside the experimental error by a systematic amount. These results were discarded.



RESULTS

Fig. 1a reports the equivalent conductance Λ vs. the concentration c in a double log plot for LiBF_4 in 1,2-DME at 25°C . In the same plot, previous results [2] for LiAsF_6 in the same solvent show that LiAsF_6 is a stronger electrolyte in this solvent. This confirms the same sequence found in 2-Methyltetrahydrofuran [3].

Fig. 2a reports the coefficients of the real part and of the imaginary part ϵ' and ϵ'' of the complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$, plotted vs. the frequency f for a representative concentration of LiBF_4 in 1,2-DME at 25°C . The solid lines are the calculated Debye functions for two relaxation processes:

$$\epsilon' = \frac{\epsilon_0 - \epsilon_{\infty 1}}{1 + (f/f_1)^2} + \frac{\epsilon_{\infty 1} - \epsilon_{\infty 2}}{1 + (f/f_2)^2} + \epsilon_{\infty 2} \quad (1)$$

$$\epsilon'' - \epsilon''_x = (\epsilon_0 - \epsilon_{\infty 1}) \frac{f/f_1}{1 + (f/f_1)^2} + (\epsilon_{\infty 1} - \epsilon_{\infty 2}) \frac{f/f_2}{1 + (f/f_2)^2} \quad (2)$$

with parameters $\epsilon_0, \epsilon_{\infty 1}, \epsilon_{\infty 2}, f_1, f_2$. ϵ''_x is the conductance contribution to the loss $\epsilon''_x = \frac{1.8 \times 10^{12} x}{f}$; x is the specific conductivity of the solution.

Table I reports all the dielectric parameters and x for the concentrations of LiBF_4 investigated at 25°C .

Fig. 3 reports a representative plot of the quantity α/f^2 vs. the frequency f for LiBF_4 in 1,2-DME at 25°C . α is the sound absorption coefficient expressed in neper cm^{-1} . The solid line is the fitted Debye function for a single relaxation process:

$$\frac{\alpha}{f^2} = \frac{A}{(1 + (f/f_r)^2)} + B \quad (3)$$

with A, B and f_r the relaxation parameters. In particular, $A (= 2\mu_{\text{max}}/f_r u)$ contains all the thermodynamic information relevant to the observed process; μ_{max} is the maximum absorption coefficient per wavelength at $f = f_r$, where

f_r is the relaxation frequency. B is the background absorption at $f \gg f_r$; namely, the value of α/f^2 at high frequency with respect to f_r , where the degrees of freedom of the observed process have been frozen (relaxed). u is the sound velocity. Table II reports the calculated parameters for the concentrations of LiBF_4 in 1,2-DME investigated at 25°C.

DISCUSSION

a. LiBF_4 in 1,2-DME

The conductance data have been treated by the Fuoss-Kraus theory of triple-ions formation [5]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_o}{\sqrt{K_p}} + \frac{\Lambda_o^T K_T}{\sqrt{K_p}} \left(1 - \frac{\Lambda}{\Lambda_o}\right) c \quad (4)$$

where $g(c)$ is a factor that lumps together all the interionic interaction terms Λ_o and Λ_o^T are the limiting equivalent conductance of $\text{Li}^+ + \text{BF}_4^-$ and of the two possible triple ions (Li_2BF_4^+ + $\text{Li}(\text{BF}_4)_2^-$), respectively. K_p and K_T are the ion pair and triple ions formation constants, respectively. The symmetrical approximation of considering the two possible formation constants of triple ions equal to each other has been retained.[5].

Fig. 1b reports the plot of $\Lambda g(c)\sqrt{c}$ vs. $c(1 - \frac{\Lambda}{\Lambda_o})$ according to Eq. (4). The solid line has been calculated by linear regression. It gives the determination coefficient $r^2 = 0.989$, intercept = 3.921×10^7 , slope = 1.3122. From a previous work [3] the value of the Walden product $\Lambda_o \eta = 0.564$ for LiBF_4 was calculated. Hence, for this electrolyte in 1,2-DME one estimates $\Lambda_o = 136.6 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$. From the above results and the arbitrary position $\Lambda_o^T = \frac{2}{3} \Lambda_o$ (consistent with previous work) [1, 2, 3] one calculates

$$K_p = 1.2 \times 10^7 \text{M}^{-1} \quad \text{and} \quad K_T = 50 \text{M}^{-1}$$

It is interesting to compare these figures with the corresponding ones [2] for LiAsF_6 in 1,2-DME $K_p = 1 \times 10^5 \text{M}^{-1}$ and $K_T = 28 \text{M}^{-1}$. One may conclude that the reason that LiAsF_6 is a stronger electrolyte in 1,2-DME with

respect to LiBF_4 is due to the difference of two orders of magnitude in the value of K_p rather than to differences in the triple ion formation constants, K_T . It is also relevant to compare the conductance results of the two electrolytes LiAsF_6 and LiBF_4 in the two solvents 1,2-DME and 2MTHF.* For the latter solvent [3], LiAsF_6 showed $K_p = 3.3 \times 10^7 \text{ M}^{-1}$, $K_T = 39 \text{ M}^{-1}$. Again, the gain in orders of magnitude of the equivalent conductances of both electrolytes, when dissolved in 1,2-DME with respect to 2MTHF, seems due to the differences in the values of K_p rather than the K_T 's. On a molecular scale it is likely that chelation of Li^+ by 1,2-DME shifts equilibrium (9) (see below) toward the left thus decreasing K_p . On the other hand, the steric hinderance caused by the presence of a $-\text{CH}_3$ group adjacent to the ethereal group of the 2MTHF may cause solvation hinderance which favors the anion as a competitor for the first coordination shell around Li^+ . This may shift equilibrium (9) toward the right increasing K_p . It is also important to realize that the major proportion of the electrolyte exists as ion-pairs with only a minor proportion as triple ions (neglecting quadrupoles which are revealed by ultrasonic relaxation as shown below). On the basis of the conductance information alone for the equilibrium [5], $\text{A} + \text{B} \xrightleftharpoons{K_p} \text{AB} + \text{B} \xrightleftharpoons{K_T} \text{AB}_2$, $(\text{AB}) = (1 - \alpha - 3\alpha_T) c \approx c$, $(\text{AB}_2) \approx \alpha_T c$, $(\text{B}) \approx \alpha c$, $\alpha \approx (\sqrt{K_p} \sqrt{c})^{-1}$, $\alpha_T = (K_T / \sqrt{K_p}) c^{1/2}$, hence $(\text{AB}_2) \approx (K_T / \sqrt{K_p}) c^{3/2}$. With the above figures $K_p = 1.2 \times 10^7 \text{ M}^{-1}$ and $K_T = 50 \text{ M}^{-1}$, at $c = 0.1$, $(\text{AB}_2) = 4.55 \times 10^{-4} \text{ M}$ or $(\text{AB}_2^- / c)\% = 0.46$.

Fig. 4 depicts the quantity $\left[(\epsilon_o - \epsilon_{\infty 1}) \frac{2\epsilon_o + 1}{3\epsilon_o} \right]$ vs. c according to the Böttcher function [6]:

$$(\epsilon_o - \epsilon_{\infty 1}) = \frac{4\pi L x c \times 10^{-3}}{(1 - \alpha f)^2} \frac{\mu^2}{3kT} \frac{3\epsilon_o}{2\epsilon_o + 1} \quad (5)$$

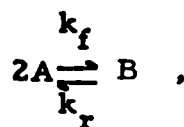
where the polarizability α , reactor field factor f term $(1 - \alpha f)^2$ generally of the order of 0.9 has been equated to 1. In the above μ is the apparent dipole moment of the rotating polar entity which increases the polarization of the solution and makes $\epsilon_o > \epsilon_{\infty}$. The solid line in Fig. 4 has been calculated by linear regression (50% stat. weight to the origin) giving $r^2 = 0.98$, $\text{int} = 0.031 \pm 0.16$, $\text{slope} = 15,255 \pm 2743$ from which $\mu = (15.8 \pm 1.4) \times 10^{-18}$ e.s.u. cm. By taking a rigid dipole moment $\mu = ae$ where e is the

* 2MTHF = 2-Methyltetrahydrofuran.

electron charge $a = 3.3 \pm 0.3 \times 10^{-8}$ cm. This figure, when compared to the one obtained for LiAsF_6 in the same solvent from a previous work [2] $a = (3.8 \pm 0.04) \times 10^{-8}$ cm, suggests a smaller charge to charge separation of the rotating entity for LiBF_4 with respect to LiAsF_6 . This may simply reflect the molecular dimensions of the two anions. On the other hand, LiClO_4 in 1,2-DME gave [1] $\mu = 14.7 \times 10^{-18}$ esu cm and $a = 3.1 \times 10^{-8}$ cm. The following sequence for the apparent dipole moments and charge separation seems to appear $\text{LiAsF}_6 > \text{LiBF}_4 \geq \text{LiClO}_4$. As the crystallographic radius of ClO_4^- is larger than BF_4^- , it appears that other factors i.e., solvation and the different ability of the anions to penetrate the solvation shell of Li^+ , play a role in the found sequence of the a_μ 's. It is also noteworthy that for all the above electrolytes in 1,2-DME $f_r \approx 2.0$ GHz, hence the decay time of the polarization is constant. Neglecting differences between this latter quantity and the molecular relaxation time τ and retaining the Debye expression [7] for a spherical dipole

$\tau = \frac{4\pi a^3}{kT} \eta$, it results that $a_\tau = 4.0 \times 10^{-8}$ cm expressing the average solvated radius of the rotating entity.

The ultrasonic data will now be discussed. Linear dependence of f_r on c and nonlinear concave-up dependence of μ_{max} on c suggest [1] a dimerization process of the type:



with A symbolizing the LiBF_4 ion-pairs and B the dimers $(\text{LiBF}_4)_2$. The following expressions are valid for this process [1]:

$$\tau^{-1} = 2\pi f_r = 4k_f(A) + k_r \quad (6)$$

$$\mu_m = \frac{\pi}{2\beta_s} \frac{(\Delta V_s)^2}{RT} \frac{K_q(A)^2}{1 + 4K_q(A)} \quad (7)$$

where k_f and k_r are the rate constants, ΔV_s is the isoentropic volume change for the process, $\beta_s = (\rho u^2)^{-1}$ is the adiabatic compressibility of

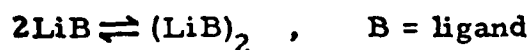
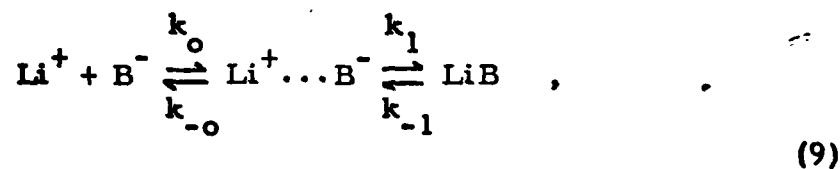
the liquid, ρ the density and $K_q = k_f/k_r$ the equilibrium constant of dimerization.

To a first approximation if K_q is not large ($\sim 1 - 3M^{-1}$) one may approximate $(A) \approx c$ taken as the concentration of ion pairs, the major species present in a solvent of this permittivity ($\epsilon \approx 7$). A plot of τ^{-1} vs. c is depicted in Fig. 5a. Linear regressions give slope = 9.68×10^8 , intercept = 2.95×10^8 , determination coefficient $r^2 = 0.84$ (r is the correlation coefficient). Then, $k_f = 2.4 \times 10^8 M^{-1}S^{-1}$, $k_r = 2.95 \times 10^8 S^{-1}$ and $K_q = 0.8 M^{-1}$. Equation (7) can be transformed to the Farber's function [1]:

$$\frac{\pi c^2}{2\beta_s \mu_m RT} = \frac{1}{K_q (\Delta V_s)^2} + \frac{4}{(\Delta V_s)^2} c \quad (8)$$

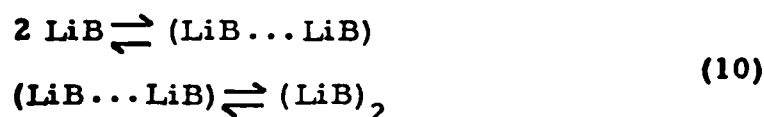
The Farber plot is shown in Fig. 5b. It gives: slope = 8.65×10^{-2} , intercept = 0.90×10^{-5} , $r^2 = 0.81$ from which one calculates $\Delta V_s = 6.8 \text{ cm}^3/\text{mol}$ and $K_q = 2.4 M^{-1}$, of the same order of magnitude of the figure $K_q = 0.8 M^{-1}$ obtained above. Fig. 5c and Table II report the calculated and the experimental μ_m 's testing the internal consistency of the calculated parameters ΔV_s and $K_q = 2.4 M^{-1}$.

Comparing the above ultrasonic results with the ones obtained for LiAsF_6 and LiClO_4 in DME, one has to conclude that ultrasonic relaxation seems able to detect one of the following equilibria, depending on the system:



namely, one of the steps leading to the contact ion pair LiB or to the dimer (or quadrupole $(\text{LiB})_2$). Generally, in media of low permittivity the first step of the scheme above is not detectable because of the small concentration of the free ones. It appears that for LiAsF_6 in 1,2-DME the step

$\text{Li}^+ \dots \text{B}^- \rightleftharpoons \text{LiB}$ was detected [2], whereas for both LiBF_4 and LiClO_4 [1] only the dimerization is visible. This could reflect the extent of association of the different electrolytes, LiAsF_6 being associated only to the form LiB , dimers being in a minor quantity. Similarly in a poorer solvent as 2-Methyltetrahydrofuran, LiAsF_6 shows formation of quadrupoles by a single step [3], LiBF_4 by a double step [3] and LiClO_4 only by a first order process [8] according to the sequence



This would show that LiClO_4 is mainly in the form of quadrupoles of the outer sphere to inner sphere type [8] and the sequence of association $\text{LiAsF}_6 \approx \text{LiBF}_4 < \text{LiClO}_4$ is confirmed. At this point of the research it was felt that enough systems had shown presence of quadrupoles and enough parameters as K_q and ΔV_s had been determined to justify interest in calculating the order of magnitude of these quantities on a theoretical ground. This shall be attempted in the sections to follow.

b. Calculation of the Quadrupole Formation Constant for Dipole-Dipole Interaction

We shall start our calculation with a Fuoss-like expression for dipole-dipole interaction. As already shown by Saar et. al. [9], one can paraphrase the Fuoss expression for the association constant of simple ions [5] to a dipole-ion pair to the one of dipoles to a quadrupole by writing

$$K_F = \frac{4\pi L r^3}{3000} \exp\left(-\frac{U}{kT}\right) \quad (11)$$

Where r is now the separation distance between the centers of the two dipoles of moment μ and U is the dipole-dipole potential $U = -\mu^2/\epsilon r^3$, with ϵ the permittivity. One then writes

$$K_F = \frac{4\pi L r^3}{3000} \exp\left(\frac{\mu^2}{\epsilon r^3 kT}\right) = K_o e^b \quad (12)$$

with $K_o = 4\pi Lr^3/3000$ and $b = \mu^2/\epsilon r^3 kT$.

Refinements to this equation could be added as done by Jagodzinski [10] for the association of ions to ion-pairs. One can consider the change in the number of degrees of freedom in going from two dipoles to a quadrupole. By using the classical equipartition principle (and reasoning that each ion pair will have 3-translational, 2-rotational, and 1-vibrational degree of freedom) one writes for the non-electrostatic internal energy [10] of the two ion pairs

$$2U_{nel} = 2\left[\frac{3}{2}RT + RT + RT\right] = \frac{14}{2}RT$$

The quadrupole, on the other hand, taken as a nonlinear* molecule, namely, a "±" entity, will have 3-translational, 3-rotational, and (3N-6) = 6 vibrational degrees of freedom. Then

$$U_{nel} = \frac{3}{2}RT + \frac{3}{2}RT + 6RT = \frac{18}{2}RT$$

The net result of the formation of a quadrupole from two dipoles will be a change in non-electrostatic internal energy per mole of $\Delta U_{ne} = 2RT$, whereas the total energy change per mole will be

$$\Delta U = \Delta U_{ne} + U_{el} = 2RT - \frac{\mu^2}{\epsilon r^3} L \quad (13)$$

with L the Avogadro's number. Then

$$K_F^* = \frac{4\pi Lr^3}{3000} e^{-2} e^{\mu^2/\epsilon r^3 kT} = K_o^* e^b \quad (14)$$

with

$$K_o^* = \frac{4\pi Lr^3}{3000} e^{-2} \quad \text{and} \quad b = \frac{\mu^2}{\epsilon r^3 kT}$$

* Although ultrasonic relaxation has detected quadrupoles, dielectric relaxation for Li^+ salts in the same solution has never detected these species. Hence they must have a zero or negligible dipole moment.

Table III reports the values of K_F and K_F^* vs. the interaction distance r for two dipoles of moment $\mu = 14.7 \times 10^{-18}$ esu cm immersed in a medium of permittivity $\epsilon = 7$ at $T = 298.2K$. It may be seen that both functions go through a minimum by increasing r . This is self evident by observing that K_F or K_F^* depends on the product $r^3 e^{1/r^3}$, namely, the product of the two functions, one increasing and one decreasing with r^3 . The position of the minimum can be found by maximizing Eqs. 12 or 14. Then in the case of Eq. 14:

$$\frac{\partial K_F^*}{\partial r} = K_0^* \frac{\partial}{\partial r} [r^3 e^{\mu^2/\epsilon r^3 kT}] = 0$$

which gives the distance at the minimum of K_F^*

$$r_m = \left(\frac{\mu^2}{\epsilon kT} \right)^{1/3} = 9.1 \times 10^{-8} \text{ cm} \quad (15)$$

It may be useful to recall [11] that K_0 is a measure of the excluded volume due to the presence of neutral dipoles or, in other words, the probability of association increasing with the volume occupied by neutral dipoles.

Some researchers [12] in the past have expressed preference for the Bjerrum theory of ion-pair association over the Fuoss one based on the fact that the former seems to follow the data for the formation constant with ϵ more closely than the latter one. It appears natural then, at this point, to develop a Bjerrum-like theory for quadrupole formation and compare it with Eqs. 12 and 14.

Following Bjerrum [13], the probability of finding a dipole at a distance r from a given one will be given by the radial distribution function:

$$dP = \frac{Lc}{1000} 4\pi r^2 dr e^{-U/kT} \quad (16)$$

where $Lc/1000$ is the concentration of dipoles expressed as molecule cm^{-3} , $4\pi r^2 dr$ is the spherical volume element of radius r and thickness dr , U is the dipole-dipole potential $U = -\mu^2/\epsilon r^3$. Then,

$$dP = \frac{Lc}{1000} \left[\exp\left(\frac{\mu^2}{\epsilon r^3 kT}\right) \right] 4\pi r^2 dr \quad (17)$$

The probability function will have a minimum with r as it depends on the product $e^{1/r^3} \times r^2$. Therefore

$$\frac{dP}{dr} = \Delta r \frac{Lc}{1000} 4\pi \frac{\partial}{\partial r} \left[\left(\exp \frac{\mu^2}{\epsilon r^3 kT} \right) r^2 \right] = 0$$

which leads to the condition

$$q = r_m = \left[\frac{3}{2} \frac{\mu^2}{\epsilon kT} \right]^{1/3} \quad (18)$$

Notice that the minimum in the distribution function corresponds to the position $\mu^2/\epsilon q^3 = 2/3 kT$, namely, to the ratio of the dipole-dipole energy to kT equal to $2/3$. Following Bjerrum [13], we shall limit the definition of associated dipoles to the distances r in the range from a to q , with a the minimum approach distance of two dipoles of moment μ . The probability that two dipoles are associated, namely, the degree of association $1-\sigma$ will be given by

$$1-\sigma = \frac{4\pi Lc}{1000} \int_a^q \left(e^{\mu^2/\epsilon r^3 kT} \right) r^2 dr$$

Call the quantity $Y = \mu^2/\epsilon r^3 kT$ and $b = \mu^2/\epsilon a^3 kT$. Then, $3r^2 dr = -(\mu^2/\epsilon kT) Y^{-2} dY$ and

$$1-\sigma = -\frac{4\pi Lc}{1000} \frac{\mu^2}{3\epsilon kT} \int_b^{2/3} e^Y Y^{-2} dY$$

since for $r=a$, $Y=b$ and for $r=q$, $Y=2/3$. Then the equilibrium constant expressed, in dilute solutions, after Bjerrum [13], as $K_{Bj} = 1-\sigma/c$, will be given by

$$K_{Bj} = \frac{4\pi L}{1000} \left(\frac{\mu^2}{3\epsilon kT} \right) \int_{2/3}^b e^Y Y^{-2} dY \quad (19)$$

or

$$K_{Bj} = \frac{4\pi La^3}{3000} b \int_{2/3}^b e^Y Y^{-2} dY \quad (20)$$

The integral $Q = \int_{2/3}^b e^Y Y^{-2} dY$ can be solved by expanding in a convergent series e^Y , namely $e^Y = 1 + Y + \frac{Y^2}{2!} + \frac{Y^3}{3!} + \frac{Y^4}{4!} \dots$. Then,

$$Q = \int_{0.67}^b \left[\frac{1}{Y^2} + \frac{1}{Y} + \frac{1}{2!} + \frac{Y}{3!} + \frac{Y^2}{4!} \dots \right] dY$$

or

$$Q = \left[-\frac{1}{Y} + \ln Y + \frac{1}{2!} Y + \frac{1}{3!} \frac{1}{2} Y^2 + \frac{1}{4!} \frac{1}{3} Y^3 + \dots + \frac{1}{(n+1)!} \frac{1}{n} Y^n \right]_{0.67}^b \quad (21)$$

Eq. 21 can be written in a more compact way as

$$Q = 1.8930 + \ln b - \frac{1}{b} + \sum_{1}^{\infty} \frac{1}{(n+1)!n} \left[b^n - (0.67)^n \right] \quad (22)$$

It appears that in a medium of permittivity $\epsilon = 7$, for dipoles of moment $\mu = 14.7 \times 10^{-18}$ esu cm at $T = 298.2$ K, a sufficiently approximate value of Q can be obtained for $a > 5 \times 10^{-8}$ cm by limiting n in Eq. 12 to $n = 10$.

Table III gives K_{Bj} as a function of $r = a$ and Fig. 6 compares Eq. 20 with Eqs. 12 and 14 (although the comparison with Eq. 14 is not consistent, the evaluation of $\Delta U_{\text{nonelect}}$ having been omitted in the evaluation of K_{Bj}). Equation 20 predicts obviously $K_{Bj} = 0$ for $b = 0.67$, which corresponds to $a = q$. At this point the same refinement to K_F , namely, the introduction of a non-electrostatic potential change U_{nonelect} can be applied to K_{Bj} . The matter reduces to write the total potential change per molecule of dimer

$$U = 2kT - \frac{\mu^2}{\epsilon r^3}$$

giving

$$1-\sigma = \frac{4\pi Lc}{1000} e^{-2} \int_a^q (e^{\mu^2/\epsilon r^3 kT}) r^2 dr$$

which becomes

$$K_{Bj}^* = \frac{4\pi Lc}{3000} e^{-2} \int_{2/3}^b e^Y Y^{-2} dY \quad (23)$$

The above expression can be written in the form

$$K_{Bj}^* = K_o^* b Q$$

Table III gives the values of K_{Bj}^* for various values of r . The same quantities are depicted in Fig. 6.

c. Calculation of the Thermodynamic Parameters

We shall now proceed to calculate the thermodynamic parameters relevant to the ultrasonic work namely the isoentropic ΔV_S of the chemical process of ion-pair dimerization to form quadrupoles. As the ΔV_S is related to the ΔV_T , the isothermal volume change of the process by the relation

$$\Delta V_S = \Delta V_T - \frac{\theta}{\rho c_p} \Delta H^0 \quad (24)$$

it will be necessary to calculate ΔH^0 as well. In the above $\theta = \partial \ln V / \partial T$ is the expansivity, ρ and c_p the density and specific heat of the liquid, respectively.

The calculation for ΔV_T will follow analogous lines of the estimation of ΔV_T for the formation of ion-pairs from free ions after Hemmes [14]. The expression for the formation constant of quadrupoles to be bound to the ΔV_T has to be expressed in molality

$$\left(\frac{d \ln K_m}{dp} \right)_T = - \frac{\Delta V_T}{RT}$$

and K_m is related to the equilibrium constant expressed in molarities by the relation

$$\ln K_m = \ln K + \ln p$$

Therefore

$$\left(\frac{d \ln K}{dp}\right)_T = -\frac{\Delta V_T}{RT} - \left(\frac{d \ln p}{dp}\right)_T = -\frac{\Delta V_T}{RT} - \beta_T$$

with

$$-\left(\frac{d \ln p}{dp}\right)_T = \left(\frac{d \ln V}{dp}\right)_T = -\beta_T = \frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

where β_T is the isothermal compressibility of the liquid. We shall use for K , Eq. 14

$$\ln K_F^* = \ln \frac{4\pi L r^3}{3000} - 2 + \frac{\mu^2}{\epsilon r^3 kT}$$

$$\left(\frac{d \ln K_F^*}{dp}\right)_T = \frac{\mu^2}{r^3 kT} \frac{d\epsilon^{-1}}{d\epsilon} \frac{d\epsilon}{dp} = \frac{\mu^2}{r^3 kT} (-\epsilon^{-2}) \frac{d\epsilon}{dp}$$

$$\left(\frac{d \ln K_F^*}{dp}\right)_T = -\frac{\mu^2}{r^3 \epsilon kT} \left(\frac{d \ln \epsilon}{dp}\right)_T$$

Let us call after Fuoss $r = a$ as the contact distance of collision between two dipoles when they are defined as associated. Then by calling

$$b = \frac{\mu^2}{a^3 \epsilon kT}$$

$$\left(\frac{d \ln K_F^*}{dp}\right)_T = -b \left(\frac{d \ln \epsilon}{dp}\right)_T$$

and

$$-\frac{\Delta V_T}{RT} = -b \left(\frac{d \ln \epsilon}{dp}\right)_T + \beta_T$$

or

$$\Delta V_T = RT \left[b \left(\frac{d \ln \epsilon}{dp}\right)_T - \beta_T \right] \quad (25)$$

In order to have an evaluation of ΔV_T in 1,2-DME the following approximate calculation will be performed. At 25°C for 1,2-DME the density $\rho = 0.8614 \text{ gr/cm}^3$ [15] and the sound velocity $u = 1.18 \times 10^5 \text{ cm/sec}$. The isentropic compressibility $\beta_S = (\rho u^2)^{-1} = 83.37 \times 10^{-12} \text{ gr}^{-1} \text{ cm sec}^2$. We shall approximate $\beta_S \approx \beta_T$. Also, for toluene Fuoss et al. [16] reported $\epsilon^{30}(1 \text{ at m}) = 2.375$ and $\epsilon^{30}(5808 \text{ at m}) = 2.775$, hence $(d \ln \epsilon / dp)_{30} = 2.7 \times 10^{-5} \text{ at m}^{-1}$. By retaining this value for 1,2-DME, the figure of Table IV for ΔV_T as a function of the distance a have been collected.

We shall now proceed to the calculation of ΔH^0 . From the expression $K_F = K_o^* e^b$

$$\Delta G_o = -RT \ln K_F = -RT \ln K_o^* - RTb$$

and

$$\Delta S_o = - \left(\frac{\partial \Delta G_o}{\partial T} \right)_p = R \ln K_o^* + Rb + RT \frac{\partial b}{\partial T}$$

but

$$\frac{\partial b}{\partial T} = \frac{\mu^2}{a^3 k} \frac{\partial}{\partial T} (\epsilon^{-1} T^{-1}) = \frac{\mu^2}{a^3 k} \left[T^{-1} \frac{\partial \epsilon^{-1}}{\partial \epsilon} \frac{\partial \epsilon}{\partial T} + \epsilon^{-1} \frac{\partial T^{-1}}{\partial T} \right]$$

$$\frac{\partial b}{\partial T} = \frac{\mu^2}{a^3 k} \left[-\frac{1}{T} \epsilon^{-2} \frac{\partial \epsilon}{\partial T} - \frac{1}{\epsilon} T^{-2} \right] = -\frac{\mu^2}{a^3 \epsilon k T} \left[\frac{\partial \ln \epsilon}{\partial T} + \frac{1}{T} \right]$$

$$\frac{\partial b}{\partial T} = -b \left[\frac{\partial \ln \epsilon}{\partial T} + \frac{1}{T} \right]$$

Then,

$$\Delta S_o = R \ln K_o^* + Rb - RTb \left[\frac{\partial \ln \epsilon}{\partial T} + \frac{1}{T} \right]$$

$$\Delta S_o = R \ln K_o^* - RTb \frac{\partial \ln \epsilon}{\partial T} \quad (26)$$

also

$$\Delta H_o = \Delta G_o + T\Delta S_o = -RT \ln K_o^* - RTb + RT \ln K_o^* - RT^2 b \frac{\partial \ln \epsilon}{\partial T}$$

$$\Delta H_o = -RTb \left[1 + \frac{\partial \ln \epsilon}{\partial \ln T} \right] \quad (27)$$

In Table IV the calculated ΔH_o 's are reported. The parameters used were $\epsilon = 7$, $\mu = 14.7 \times 10^{-18}$ esucm, while the value of $d \ln \epsilon / dT = 5 \times 10^{-3}$ has been taken from the data of Jagodzinski [10] for THF, assuming a similar temperature dependence of ϵ for 1,2-DME. This leads to $(d \ln \epsilon / d \ln T) = 1.491$. The above calculation is admittedly approximate, but as we are looking for an order of magnitude of ΔV_s it appears adequate for the purpose.

The calculation proceeds with the estimation of θ , the expansivity. From the densities of THF with temperature of Jagodzinski [10], one obtains

$$\theta = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{\partial \ln V}{\partial T} = - \frac{\partial \ln \rho}{\partial T} = 1.18 \times 10^{-3} \text{K}^{-1}$$

between 25 and -15°C . The specific heat of diethyl-ether [17] $C_p(30^\circ\text{C}) = 2.30$ Joule/K, gr. Then the quantity

$$\frac{\theta}{\rho c_p} = \frac{1.18 \times 10^{-3}}{0.88 \times 2.30} = 5.817 \times 10^{-4} \frac{\text{cm}^3}{\text{Joule}}$$

or

$$5.817 \times 10^{-11} \text{cm}^3/\text{ergs}$$

The term $(\theta / \rho c_p) \Delta H_o$ expressed in cm^3/mole is then reported in Table IV together with the calculated ΔV_s 's according to Eq. 27.

So far for LiBF_4 in 1,2-DME and for LiClO_4 in 1,2-DME the values found for the ΔV_s 's were of the order of $7-10 \text{cm}^3/\text{mole}$. Judging from Table IV, one would estimate a collision distance between the two dipoles of the order of $6-7 \times 10^{-8} \text{cm}$, a very reasonable range of figures for any model envisaging two dipoles of charge separation $2.5 - 3 \times 10^{-8}$ colliding to form a quadrupole. In addition, the experimental value of K_q the quadrupole formation constant has been found to be in the range of $1-3 \text{M}^{-1}$. Judging from Table III, equating $K_q = K_F^*$ would again lead toward $a = 6-7 \times 10^{-8} \text{cm}$.

It appears proper at this point to repeat the above sequence of calculations with the Bjerrum-like function Q of quadrupole formation constant.

$$K_{Bj} = K_o b Q = \frac{4\pi L a^3}{3000} \frac{u^2}{e a^3 kT} \int_0^b e^Y Y^{-2} dY$$

Given the relation

$$\frac{d \ln K_{Bj}}{dp} = - \frac{\Delta V_T}{RT} - \beta_T$$

$$\ln K_{Bj} = \ln K_o + \ln b + \ln Q$$

$$\frac{d \ln K_{Bj}}{dp} = \frac{d \ln b}{db} \frac{db}{dp} + \frac{d \ln Q}{dQ} \frac{dQ}{db} \frac{db}{dp}$$

Also

$$\frac{dQ}{db} = e^b b^{-2} \quad (28)$$

and

$$\frac{db}{dp} = \frac{u^2}{a^3 kT} \frac{d\epsilon^{-1}}{d\epsilon} \frac{d\epsilon}{dp} = -b \frac{d \ln \epsilon}{dp}$$

Therefore

$$\frac{d \ln K_{Bj}}{dp} = - \left[\frac{1}{b} + \frac{1}{Q} e^b \frac{1}{b^2} \right] b \frac{d \ln \epsilon}{dp}$$

$$\frac{d \ln K_{Bj}}{dp} = - \left[1 + \frac{1}{Q} \frac{e^b}{b} \right] \frac{d \ln \epsilon}{dp}$$

and

$$\Delta V_T = RT \left\{ \left[1 + \frac{1}{Q} \frac{e^b}{b} \right] \frac{d \ln \epsilon}{dp} - \beta_T \right\} \quad (29)$$

As done above, in order to calculate ΔV_S one needs an estimation of ΔH_o .
Then:

$$\Delta G_o = -RT \ln K_{Bj}$$

$$\Delta S_o = -\frac{\partial \Delta G_o}{\partial T} = R \ln K_{Bj} + RT \left[\frac{d \ln b}{db} + \frac{d \ln Q}{dQ} \frac{dQ}{db} \right] \frac{db}{dT}$$

as found above

$$\frac{db}{dT} = -b \left[\frac{1}{T} + \frac{d \ln \epsilon}{dT} \right]$$

$$\Delta S_o = R \ln K_{Bj} - RTb \left[\frac{1}{b} + \frac{1}{Q} \frac{e^b}{b^2} \right] \left[\frac{1}{T} + \frac{d \ln \epsilon}{dT} \right]$$

$$\Delta S_o = R \ln K_{Bj} - R \left[1 + \frac{1}{Q} \frac{e^b}{b} \right] \left[1 + \frac{d \ln \epsilon}{d \ln T} \right] \quad (30)$$

and $\Delta H_o = \Delta G_o + T \Delta S_o$ gives

$$\Delta H_o = -RT \left[1 + \frac{1}{Q} \frac{e^b}{b} \right] \left[1 + \frac{d \ln \epsilon}{d \ln T} \right] \quad (31)$$

Eqs. 30 and 31 have been evaluated by using the following parameters (as done above): $d \ln \epsilon / dp = 2.7 \times 10^{-5}$ at $m^{-1} = 2.65 \times 10^{-11}$ dyne⁻¹ cm²; $\beta_T \approx \beta_S = 83.4 \times 10^{-12}$ dyne⁻¹ cm²; $\epsilon = 7.0$; $\mu = 14.7 \times 10^{-18}$ esu cm; $d \ln \epsilon / dT = 5 \times 10^{-3}$ K⁻¹, $\theta / \rho c_p = 5.817 \times 10^{-11}$ cm³/erg. The results for ΔV_T and ΔV_S are reported in Table V for various collision distances a . Notice that usage of K_{Bj}^* rather than K_{Bj} affects ΔG_o and ΔS_o , but does not affect ΔV_T , ΔH_o and hence ΔV_S as reported in Table V. Comparing the results of Tables IV and V one may see that the results, especially because of the ΔH_o term, differ widely. The values of the ΔV_S , however, seem roughly comparable around $a = 6-8 \times 10^{-8}$ cm. They also are of the same order of magnitude as the experimental ΔV_S 's. It would appear therefore that both theories suggest $6-8 \times 10^{-8}$ cm as the average separation distance of the quadrupoles in solution of 1,2-DME. Given for $LiClO_4$ the separation distance of the charges with dipole is $a_d = 3 \times 10^{-8}$ cm ($\mu/\epsilon = 14.7 \times 10^{-18} / 4.8 \times 10^{-10}$) the above would imply a "solvated"

quadrupole. The situation may be different for LiBF_4 in 2MTHF given $a_d \approx 2.5 \times 10^{-8}$ cm and because two steps of association to quadrupoles have been detected by ultrasonic relaxation techniques [3].

For the case observed for LiBF_4 in 2MTHF, the formation of quadrupoles ought to be written according to the scheme [3]



where B = ligand and $\text{LiB} \dots \text{LiB}$ is a solvent separated dimer. For LiBF_4 in 2MTH the formation constant for the second step of the above scheme has been estimated to be $K_2 = 0.4$. The calculation of ΔV_2 , the volume change associated with the second step will follow the same lines suggested by Hemmes [14], based on the Kirkwood's expression [4] for the free energy of a dipole in solution

$$G_L = -\frac{\mu_i^2}{3r_i} \frac{\epsilon-1}{2\epsilon+1}$$

For the process $\text{LiB} \dots \text{LiB} \rightleftharpoons (\text{LiB})_2 + \text{S}$, where S is a solvent molecule, one would then write

$$\Delta G_2^0 = -\left[\frac{\mu_{is}^2}{3r_{is}} + \frac{\mu_s^2}{3r_s} - \frac{\mu_{os}^2}{3r_{os}} \right] \frac{\epsilon-1}{2\epsilon+1} = -RT \ln K_2 \quad (32)$$

where the subscript "is", "os" and "s" stand for inner-sphere, outer-sphere, and solvent, respectively

$$\Delta V_{2,T} = \frac{\partial \Delta G_2}{\partial p} = -\left[\frac{\mu_{is}^2}{3r_{is}} + \frac{\mu_s^2}{3r_s} - \frac{\mu_{os}^2}{3r_{os}} \right] \frac{d}{d\epsilon} \left(\frac{\epsilon-1}{2\epsilon+1} \right) \frac{d\epsilon}{dp}$$

giving

$$\Delta V_{2,T} = -\left[\frac{\mu_{is}^2}{3r_{is}} + \frac{\mu_s^2}{3r_s} - \frac{\mu_{os}^2}{3r_{os}} \right] \frac{\epsilon-1}{(2\epsilon+1)} \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d\ln\epsilon}{dp}$$

$$\Delta V_{2,T} = -RT \ln K_2 \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d\ln\epsilon}{dp} \quad (33)$$

In order to perform the calculation of $\Delta V_{2,T}$, the following figures have been retained: $K_2 = 0.4$, $\epsilon = 7$, $d \ln \epsilon / dp = 3 \times 10^{-5} \text{ atm}^{-1}$. This gives $\Delta V_{2,T} = 0.16 \text{ cm}^3/\text{mole}$. The same sequence as above will now be followed for the calculation of $\Delta V_{2,S}$

$$\Delta S_2^0 = - \frac{\partial \Delta G_2^0}{\partial T} = \left[\frac{\mu_{is}^2}{r_{is}^3} + \frac{\mu_s^2}{r_s^3} - \frac{\mu_{os}^2}{r_{os}^3} \right] \frac{d}{d\epsilon} \frac{(\epsilon-1)}{2\epsilon+1} \frac{d\epsilon}{dT}$$

giving

$$\Delta S_2^0 = \left[\frac{\mu_{is}^2}{r_{is}^3} + \frac{\mu_s^2}{r_s^3} - \frac{\mu_{os}^2}{r_{os}^3} \right] \frac{\epsilon-1}{(2\epsilon+1)} \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d \ln \epsilon}{dT}$$

$$\Delta S_2^0 = RT \ln K_2 \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d \ln \epsilon}{dT} \quad (34)$$

Then

$$\Delta H_2^0 = \Delta C_2^0 + T \Delta S_2^0 = -RT \ln K_2 + RT^2 \ln K_2 \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d \ln \epsilon}{dT}$$

$$\Delta H_2^0 = -RT \ln K_2 \left[1 - \frac{3\epsilon}{(2\epsilon+1)(\epsilon-1)} \frac{d \ln \epsilon}{d \ln T} \right] \quad (35)$$

The calculations of ΔH_2^0 with the same parameters as above, namely, $K_2 = 0.4$, $\epsilon = 7$, $d \ln \epsilon / dT = 5 \times 10^{-3}$, gives $\Delta H_2^0 = 1.48 \times 10^{10} \text{ ergs/mole} = 1.48 \text{ KJ/mole}$. Then, given $\theta / \rho c_p \approx 5.8 \times 10^{-11} \text{ cm}^3/\text{erg}$, it gives $\Delta H_2 \theta / \rho c_p = 0.86 \text{ cm}^3/\text{mole}$ and

$$\Delta V_{2,S} = \Delta V_{2,T} - \frac{\theta}{\rho c_p} \Delta H_2 = 0.16 - 0.86 = -0.70 \text{ cm}^3/\text{mole}$$

This figure appears to be smaller than the one calculated for a one-step process for $a = 6-8 \times 10^{-8} \text{ cm}$. The same conclusion was reached by Hemmes [14] for the analogous case of a two-step association to ion-pairs starting from free ions.

Table I

Dielectric relaxation parameters ϵ_0 , $\epsilon_{\infty 1}$, $\epsilon_{\infty 2}$, f_1 , f_2 and specific conductivity κ for LiBF_4 in 1,2-DME at the concentrations investigated and $t = 25^\circ\text{C}$.

c (M)	ϵ_0	$\epsilon_{\infty 1}$	$\epsilon_{\infty 2}$	f_1 (GHz)	f_2 (GHz)	κ ($\Omega^{-1}\text{cm}^{-1}$)
0.092	9.0	7.0	2.6	2.5	35	6.0×10^{-5}
0.05	8.4	7.1	2.7	2.0	35	2.7×10^{-5}
0.035	8.0	7.0	2.6	2.0	40	1.75×10^{-5}
0.075	8.5	7.0	2.7	2.5	40	4.6×10^{-5}

Table II

Relaxation parameters A, B and fr, maximum excess sound absorption per wavelength μ_m ($=\frac{1}{2}Afr u$) and sound velocity u for LiBF_4 in 1,2-DME at the concentrations investigated at $t = 25^\circ\text{C}$. Calculated μ_m 's using Eqs. 7 and the parameters $\Delta V_s = 6.8 \text{ cm}^3/\text{mole}$ and $K_q = 2.4 \text{ M}^{-1}$.

c (M)	$A \times 10^{17}$ ($\text{cm}^{-1} \text{s}^2$)	$B \times 10^{17}$ ($\text{cm}^{-1} \text{s}^2$)	fr (MHz)	$\mu_m \times 10^5$	$u \times 10^{-5}$ (cm s^{-1})	$\mu_m \times 10^5$
0.55	51	45	140	428	1.198	421
0.50	55	50	115	379	1.197	376
0.46	53	47	120	382	1.202	341
0.41 ₅	42	52	110	277	1.198	302
0.38	40	51	100	238	1.192	271
0.28	36	44	95	203	1.190	186

Table III

Values of b , K_O , K_F , K_O^* , K_F^* , Q , K_{BJ} and K_{BJ}^* as functions of the parameter r for dipole-dipole interaction, where $\mu = 14.7 \times 10^{-18}$ esucm, $\epsilon = 7.0$, $T = 298K$.

$r \times 10^8$ cm	b	K_O M^{-1}	K_F M^{-1}	K_O^* M^{-1}	K_F^* M^{-1}	Q	K_{BJ}^a M^{-1}	K_{BJ}^* M^{-1}
12	0.4343	4.357	6.73	0.590	0.910			
11	0.5637	3.356	5.90	0.454	0.798			
10	0.7503	2.522	5.34	0.341	0.723	0.3234	0.61	0.082
9	1.029	1.838	5.14	0.249	0.696	1.1933	2.26	0.306
8	1.465	1.291	5.59	0.175	0.756	2.1828	4.13	0.559
7	2.187	0.865	7.71	0.117	1.044	3.5448	6.71	0.908
6	3.474	0.545	17.6	0.0737	2.377	6.3303	11.98	1.62
5	6.002	0.315	127.4	0.0427	17.27	20.597	38.97	5.27

a

Notice that following Eq. 20 $K_{BJ} = K_O b Q$, Q has been calculated with the series expansion up to $n=10$. Also $q = 10.40 \times 10^{-8}$ cm in this case.

Table IV

Calculated ΔV_T , ΔH_0 and ΔV_S for a dimerization of dipoles in 1,2-DME at $T = 298.2K$ according to Eqs. 14, 25 and 27.						
$a \times 10^8$ (cm)	$RTb \frac{d \ln \epsilon}{dp}$ $cm^3/mole$	$RT\beta$ $cm^3/mole$	ΔV_T $cm^3/mole$	ΔH_0^a KJ/mole	$(\theta/\rho c) \Delta H_0$ $cm^3/mole$	ΔV_S^b $cm^3/mole$
12	0.28	2.07	-1.79	-2.68	-1.56	-0.23
11	0.37	2.07	-1.70	-3.48	-2.02	0.32
10	0.49	2.07	-1.58	-4.63	-2.69	1.11
9	0.67	2.07	-1.40	-6.35	-3.70	2.30
8	0.96	2.07	-1.11	-9.05	-5.26	4.15
7	1.43	2.07	-0.64	-13.5	-7.86	7.22
6	2.26	2.07	0.19	-21.5	-12.5	12.7
5	3.91	2.07	1.84	-37.1	-21.6	23.4
4	7.64	2.07	5.57	-72.4	-42.1	47.7

$$^a \Delta H_0 = -2.68 \text{ KJ/mole} = -2.68 \times 10^{10} \text{ ergs/mole, etc.}$$

$$^b \Delta V_S = \Delta V_T - \frac{\theta}{\rho c} \Delta H_0.$$

Table V

Evaluated ΔV_T , ΔH_O and ΔV_S for a dimerization of dipoles in 1,2-DME at $T = 298.2K$ according to Eqs. 29 and 31.				
$a \times 10^8$ (cm)	ΔV_T cm^3/mole	ΔH_O^a ergs/mole	$(\theta/\rho c_p)\Delta H_O$ cm^3/mole	ΔV_S^b cm^3/mole
10	4.32	-6.00×10^{11}	-34.90	39.2
9	0.09	-2.02×10^{11}	-11.77	11.9
8	-0.52	-1.45×10^{11}	- 8.45	7.93
7	-0.65	-1.33×10^{11}	- 7.74	7.09
6	-0.45	-1.52×10^{11}	- 8.84	8.39
5	+0.74	-2.64×10^{11}	-15.35	16.1

$$^a \Delta H_O = -6.00 \times 10^{11} \text{ ergs/mole} = -60.0 \text{ KJ/mole etc.}$$

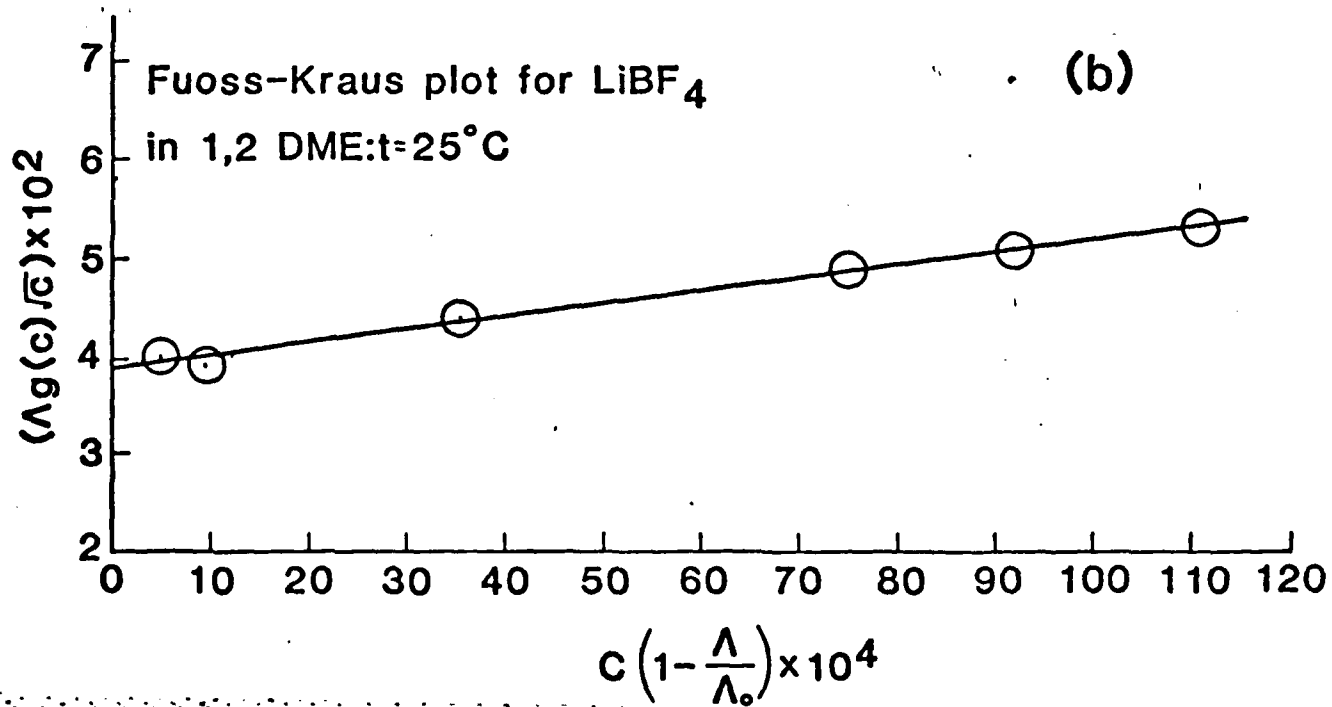
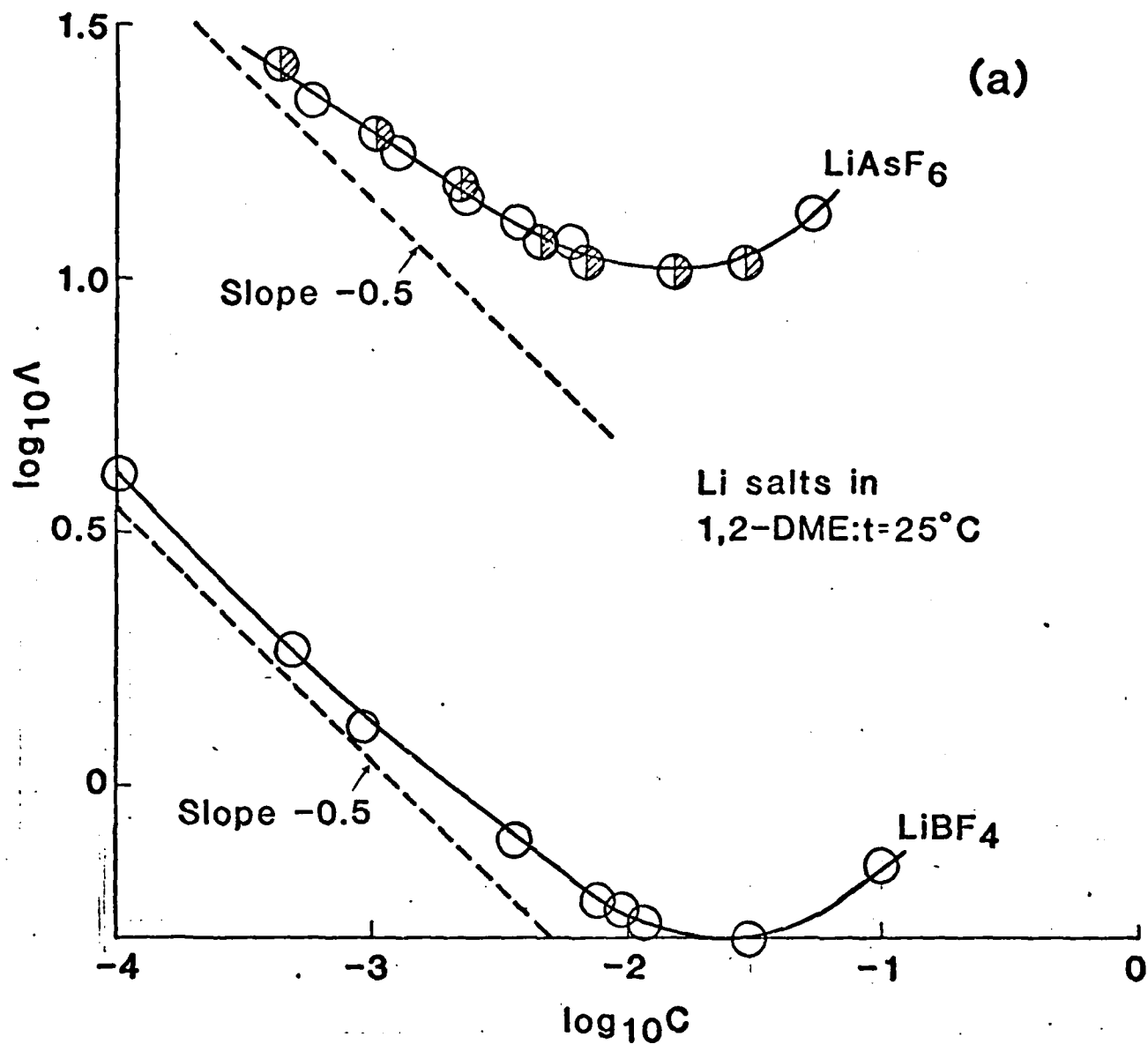
$$^b \Delta V_S = \Delta V_T - \frac{\theta}{\rho c_p} \Delta H_O$$

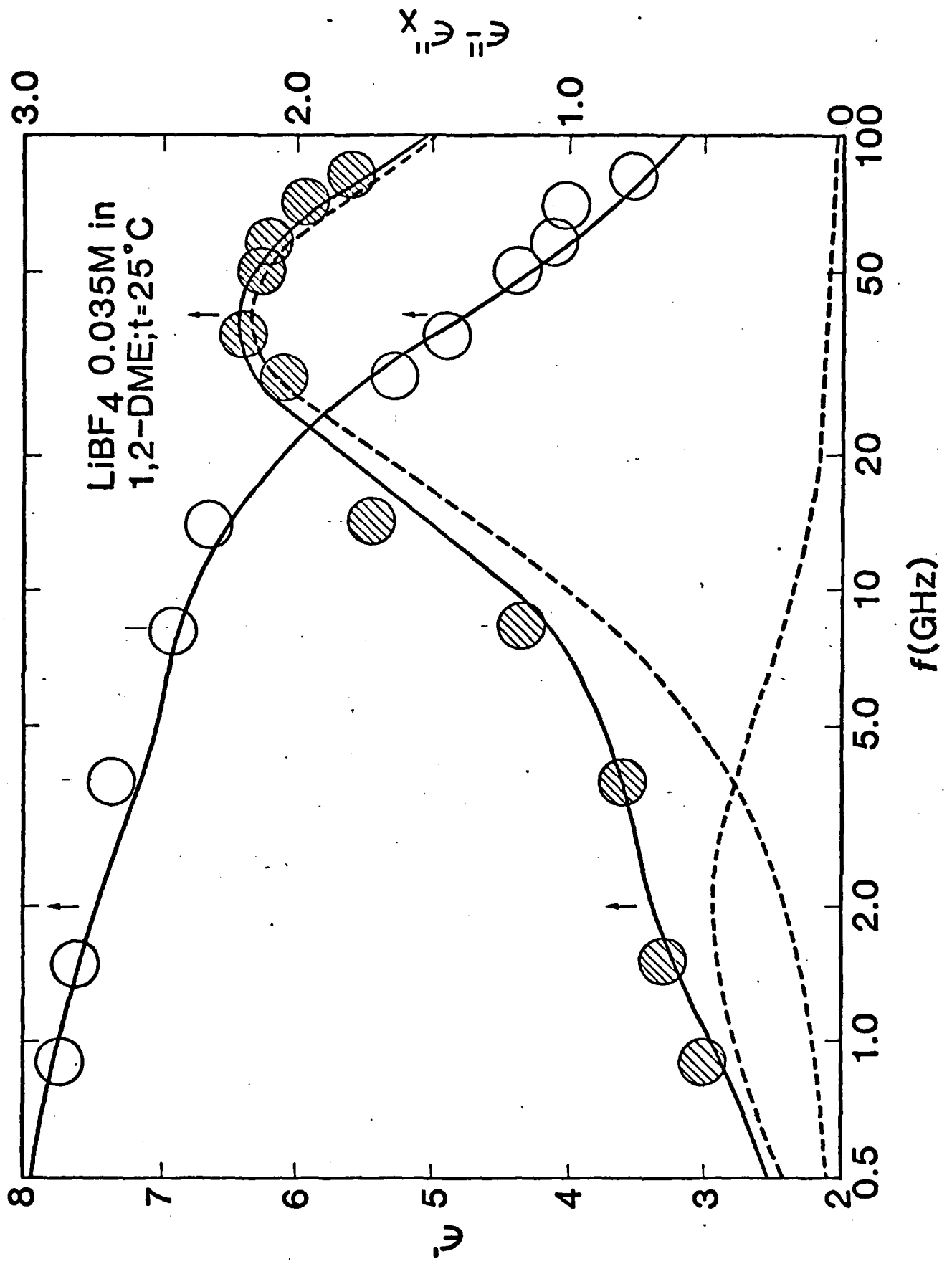
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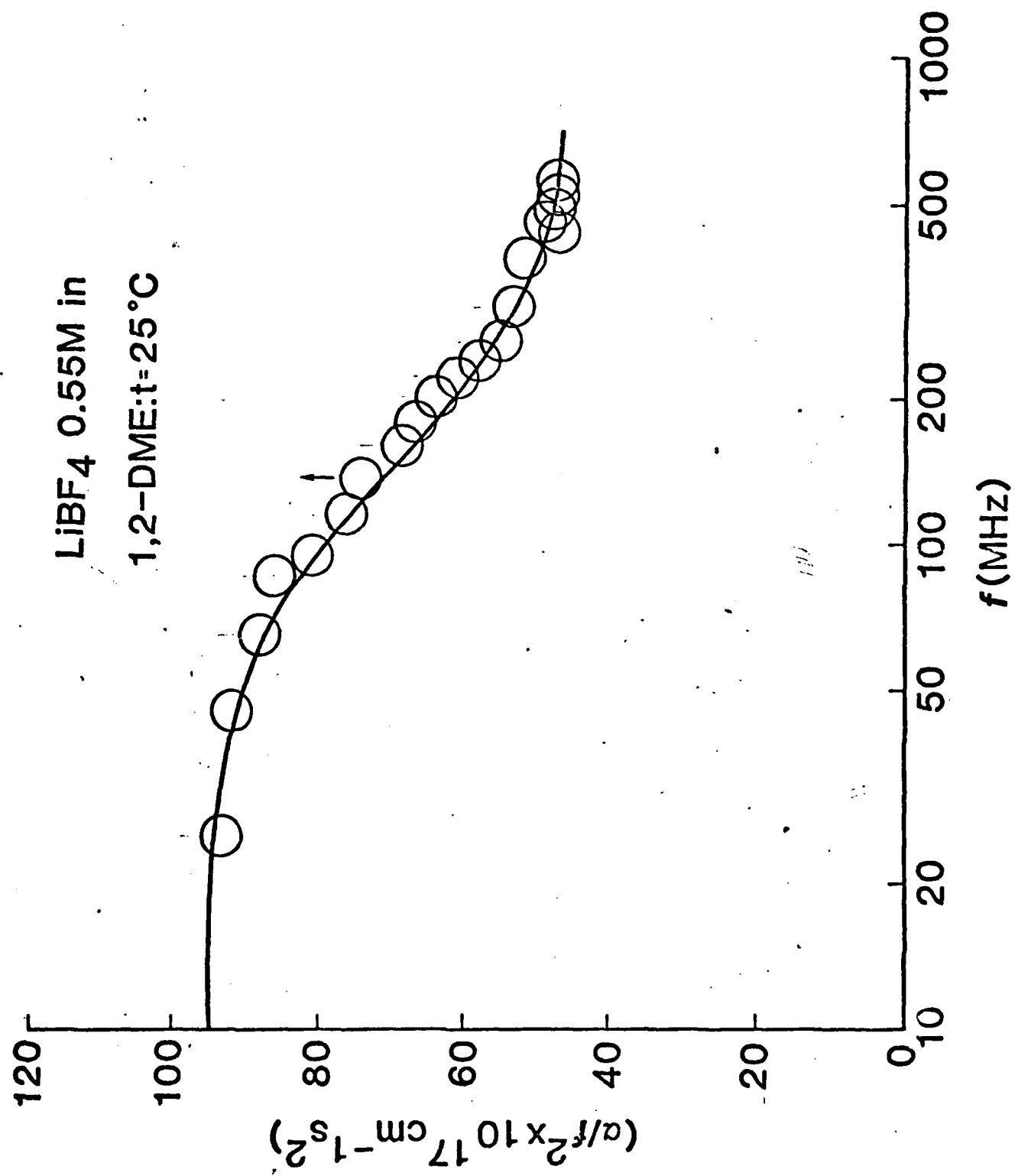
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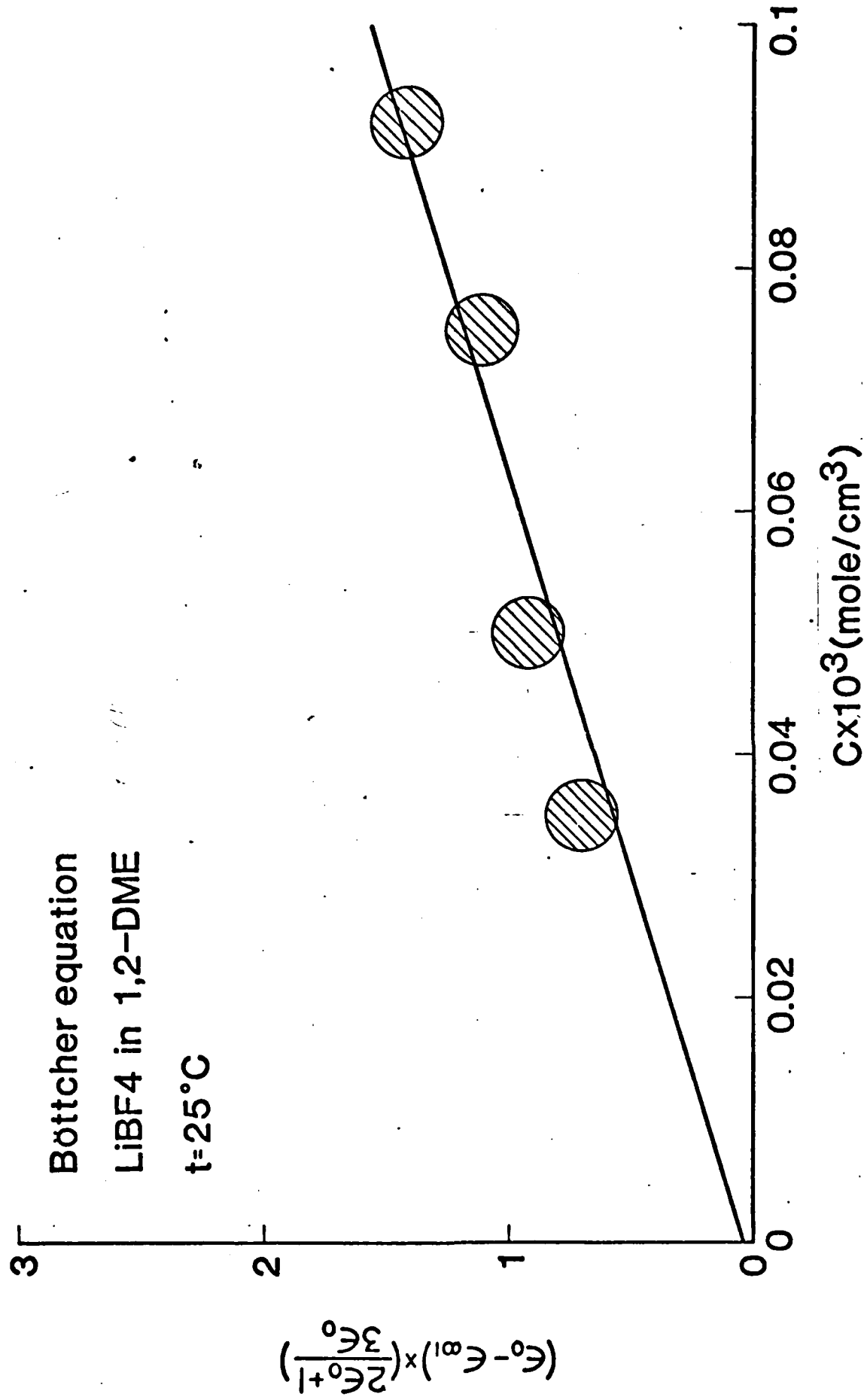
Figure Captions

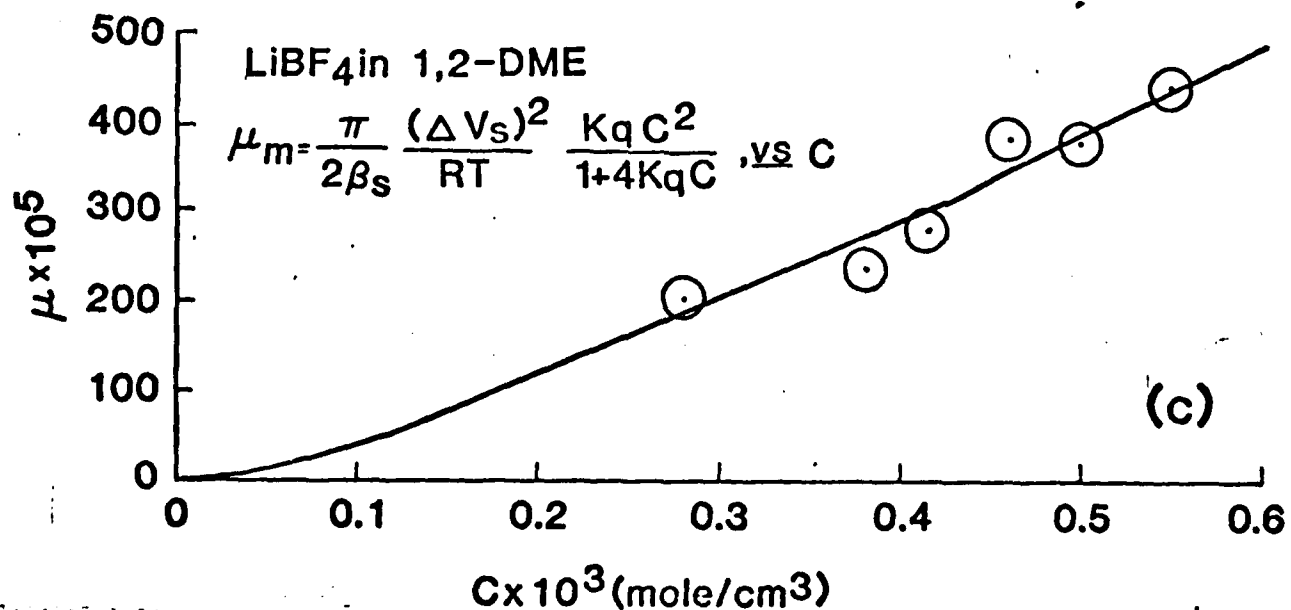
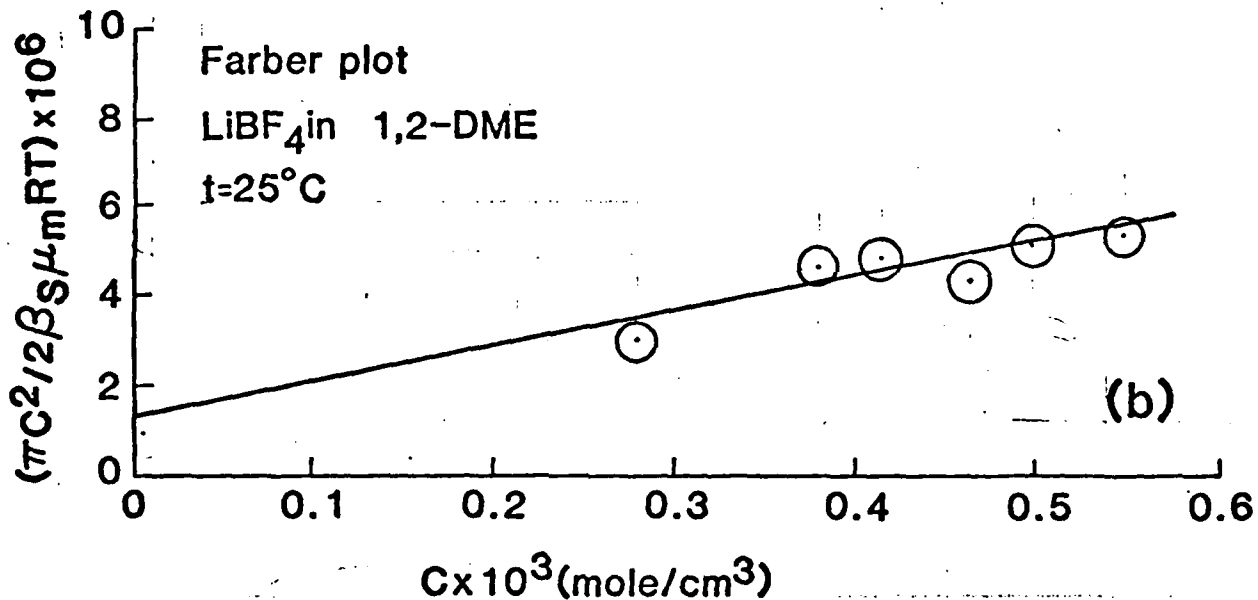
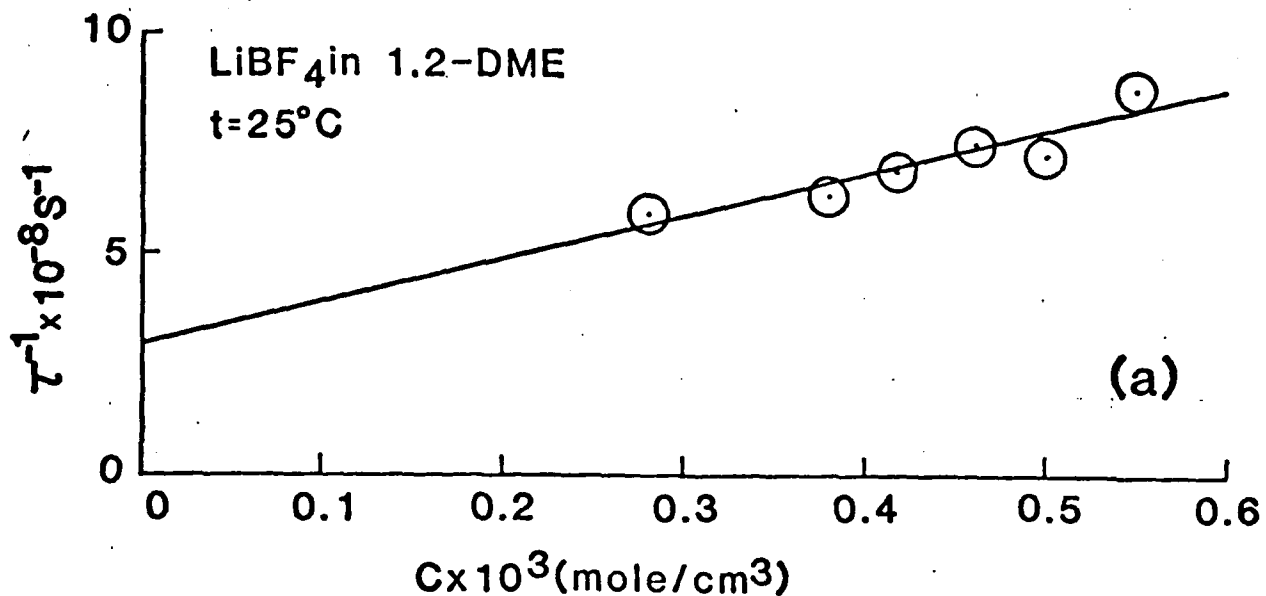
- Fig. 1 a. $\log_{10} \Lambda$ vs. $\log_{10} c$ for LiBF_4 in 1,2-DME at 25°C .
b. $\Lambda g(c) \sqrt{c}$ vs. $c(1 - \frac{\Lambda}{\Lambda_0})$ for LiBF_4 in 1,2-DME at 25°C .
- Fig. 2 Representative plot of ϵ' and ϵ'' vs. f for LiBF_4 in 1,2-DME at $t = 25^\circ\text{C}$.
- Fig. 3. Representative plot of the quantity α/f^2 vs. the frequency f for LiBF_4 in 1,2-DME at 25°C .
- Fig. 4 Böttcher plot for LiBF_4 in 1,2-DME at $t = 25^\circ\text{C}$.
- Fig. 5 a. τ^{-1} vs. c for LiBF_4 in 1,2-DME, $t = 25^\circ\text{C}$.
b. $(\pi c^2 / 2\beta_s \mu_m RT)$ vs. c for LiBF_4 in 1,2-DME at 25°C .
c. Calculated (solid line) and experimental values of μ_m vs. c for LiBF_4 in 1,2-DME at $t = 25^\circ\text{C}$.
- Fig. 6 Plot of the functions K_F , K_F^* , K_{Bj} and K_{Bj}^* vs. the dipole-dipole separation distance in a medium of permittivity $\epsilon = 7$ for dipoles of moment $\mu = 14.7 \times 10^{-18}$ esu cm at $T = 298.2\text{K}$.



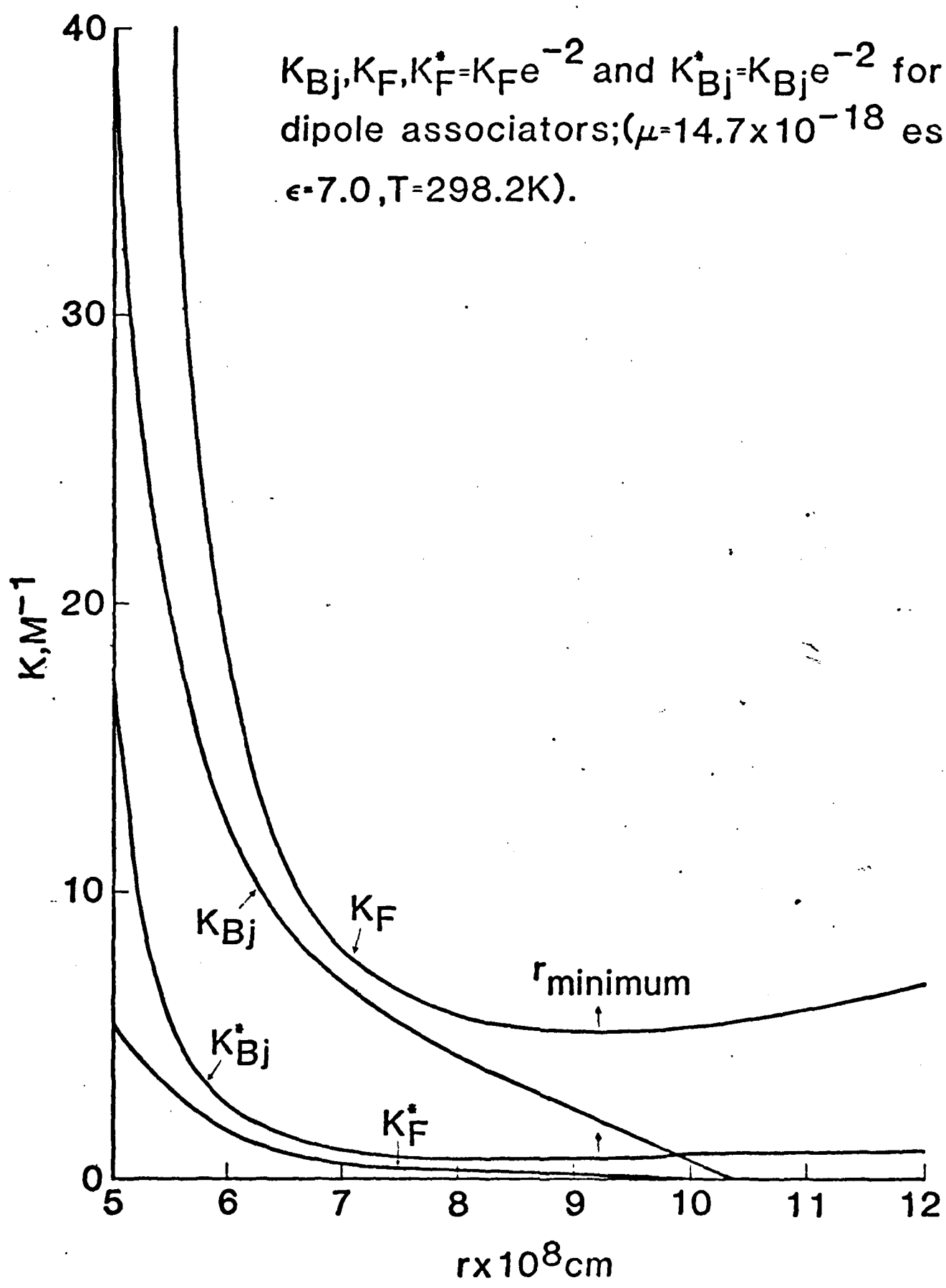








$K_{Bj}, K_F, K_F^* = K_F e^{-2}$ and $K_{Bj}^* = K_{Bj} e^{-2}$ for dipole associators; ($\mu = 14.7 \times 10^{-18}$ esu cm, $\epsilon = 7.0, T = 298.2$ K).



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