Molecular Relaxation of Lithium Arsenic Hexafluoride in One-Two-ETC(U)

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LITHIUM ARSENIC HEXAFLUORIDE
IN ONE-TWO-DIMETHOXYETHANE

TECHNICAL REPORT #1

Herman Farber, Donald Irish and
Sergio Petrucci

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Ultrasonic relaxation data are interpreted as due to the equilibrium Li⁺, S, AsF₆⁻ ⇌ LiAsF₆, S being a solvent molecule. The equilibrium appears to be heavily shifted toward the left, in accord with the information by Raman Spectra.

Microwave Dielectric Relaxation data can be interpreted as due to the diffusion rotational relaxation of ion - pairs. Estimate of the charge to charge distance in the rotating pairs reinforces the notion that the solvent resides between the cation and anion in the majority of the pairs. Mass Law appears to shift the equilibrium toward the contact pairs, by increasing the electrolyte concentrations.
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by

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Abstract

Audiofrequency electrical conductivity, Raman spectra, radiofrequency ultrasonic absorption and microwave dielectric permittivity of LiAsF$_6$ in the solvent 1-2 Dimethoxyethane (DME) are reported.

Electrical conductivity reveal the electrolyte to be associated to ion-pairs ($K_A = 1 \times 10^5$ M$^{-1}$). Raman spectra of the symmetrical stretching mode of AsF$_6^-$ suggest the ion to be "spectroscopically free", namely either unpaired or solvent separated from the cation.

Ultrasonic relaxation data are interpreted as due to the equilibrium $\text{Li}^+ + S, \text{AsF}_6^- \rightleftharpoons \text{LiAsF}_6$, $S$ being a solvent molecule. The equilibrium appears to be heavily shifted toward the left, in accord with the information by Raman spectra.

Microwave Dielectric Relaxation data can be interpreted as due to the diffusion rotational relaxation of ion-pairs.

Estimate of the charge to charge distance in the ion-pairs reinforces the notion that the solvent resides between the cation and the anion in the majority of the pairs. Mass Law appears to shift the equilibrium toward the contact pairs, by increasing the electrolyte concentrations.
Introduction

Progress in lithium batteries, using lithium electrolytes in ethereal solutions, has occurred largely in the last decade. Some battery systems have been recorded as being able to be recycled several hundred times.1, 2

Still many problems persist3 which make further studies of the molecular properties of lithium electrolytes quite relevant both on theoretical and practical grounds.

LiClO₄ as electrolyte in THF₄ was studied by us years ago by ultrasonic relaxation methods. Later we extended our study to 1-2 DME₅ because of its ability to chelate alkali - ions.

We decided then to start a research program on similar lines of the electrolyte LiAsF₆ which, in preliminary tests, appears more ionized than LiClO₄ in ethereal solvents.

Our aim is to try to give, by a diversified study by classical and modern methods, a molecular picture of the particular behavior of a given electrolyte as LiAsF₆ in a given ether. Hopefully this would give a molecular rationale for the choice of a given electrolyte in battery construction. Empiricism on the contrary and phenomenological information (low internal resistance) has been the criteria so far in the majority of the cases.
Experimental Part
The experiment and procedure for the conductivity, ultrasonic and
dielectric measurements have been described elsewhere.\textsuperscript{5,6}
Raman spectra were collected at the University of Waterloo, Ontario
Canada from a Jarrel-Ash 100 Raman spectrometer equipped with an
argon-ion laser source tuned at 514.5 nm and interfaced to a Commodore
microcomputer.
1-2 Dimethoxyethane was purified as described before.\textsuperscript{5} LiAsF\textsubscript{6} (Alfa
Division, Andover Mass.) was redried in vacuum at 60°C for one day.
The original product was found, by weight loss, to contain about 1% of
moisture. Raman spectra of solutions prepared using the original
product, revealed a faint OH stretch band at about 3500 cm\textsuperscript{-1}, the same
position 3520 cm\textsuperscript{-1} shown by a 0.4 M aqueous solution in 1-2 DME
prepared and used for comparison's sake. The distilled solvent had no
water band in the same wavelength region. Solutions at comparable
concentrations of the dried LiAsF\textsubscript{6} in 1-2 DME showed no water band by Raman spectra.
Repetitive attempts to dry LiAsF\textsubscript{6} in vacuum at 100 - 115°C resulted in
the same weight loss as above. However when the dried product was
dissolved in 1-2 DME, some opalescence and small amounts of precipitate
occurred, suggesting some thermal decomposition of the electrolyte,
upon drying at 100 - 115°C. Solutions were prepared by weight for the
conductance runs, converting the molalities to molarities by the use
of densities. Other solutions were prepared weighing the electrolyte
directly in volumetric flasks and diluting to mark with the distilled
solvent. All the solutions were used shortly after preparations and
kept sealed in large dessicators over Mg(ClO\textsubscript{4})\textsubscript{2}. Contact with the
open air in transferring the solutions to the cells or capillaries was kept within 30 - 60 seconds.
Results and Calculations
(Fig. 1A) Fig. 1A shows the equivalent conductance data \( \Lambda (\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}) \) plotted vs. the concentration \( c \) (mole/liter = M) in a log-log plot, for \( \text{LiAsF}_6 \) in 1-2 DME at \( t = 25.00^\circ C \). In the same plot the corresponding data for \( \text{LiClO}_4 \) are reported. One may see that there is a dramatic increase of almost one order of magnitude in the equivalent conductance of the \( \text{LiAsF}_6 \) with respect to the one of \( \text{LiClO}_4 \) in 1-2 DME. Fig. 1B shows the Fuoss-Kraus plot of \( \Lambda \sqrt{c} \) vs. \( c \) according to the simplified version of the triple-ion theory, neglecting long range ionic interactions. A curvature appears in the plot as already noticed for \( \text{LiClO}_4 \) in 1-2 DME. By applying linear regressions one obtains determination coefficient \( r^2 = 0.983 \); Intercept = 0.558; Slope = 65.5. This simplified theory leads to:

\[
\Lambda \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_A}} + \frac{K_T \Lambda_0^T}{\sqrt{K_A}} \ c,
\]  

with \( K_A \) and \( K_T \) the ion-pair and triple ion formation constants [using the symmetrical approximations \( K_{T1} = K_{T2} \) for the two possible triple ions \( \text{Li(AsF}_6^\text{2} \) and \( \text{Li}_2(\text{AsF}_6^\text{2}^+) \)]. Further \( \Lambda_0 \) is the triple ion conductance set equal to \( 2/3 \Lambda_0 \). We have evaluated \( \Lambda_0 \) from Walden's rule and the figure \( \Lambda_0(\text{LiAsF}_6) = 178.2 \ \Omega^{-1} \ \text{cm}^2 \ \text{eq}^{-1} \) in CH\textsubscript{3}CN at 25°C. The viscosity of acetonitrile at 25°C is \( \eta = 0.003449 \) poise. Therefore from Walden's rule we calculate \( \Lambda_0(\text{LiAsF}_6) = 149 \ \Omega^{-1} \ \text{cm}^2 \ \text{eq}^{-1} \) in 1-2 DME at 25°C. From the above data one then calculates \( K_A = 0.71 \times 10^5 \text{ M}^{-1} \) and \( K_T = 177 \text{ M}^{-1} \). Presence of the curvature and suspect of large systematic errors involved in neglecting interionic terms led us to
the use of the full version of the Fuoss – Kraus theory. This gives:

\[ \Lambda g(c) \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_A}} + \frac{\Lambda_T K_T}{\sqrt{K_A}} c \left(1 - \frac{\Lambda}{\Lambda_0}\right), \]

(II)

with \( g(c) = \exp \left( - \frac{\beta'}{\sqrt{\Lambda_0}} \right) \left(1 - \frac{S}{\Lambda_0^{3/2} \sqrt{c \Lambda}} \right)^{1/2} \cdot \frac{1/2}{1 - \frac{\Lambda}{\Lambda_0} \sqrt{c \Lambda}} \) \) .

(III)

\( \beta' \) is the Debye – Hückel activity coefficient and \( S \) the Onsager conductance coefficient.

(Fig.1C) A plot of eq. II is shown in Fig. 1C. The curvature is largely disappeared. Linear regressions give: \( r^2 = 0.973; \) Intercept \( = 0.464; \) Slope \( = 8.545 \). From this \( K_A = 1.0 \times 10^5 \text{ M}^{-1} \) and \( K_T = 28 \text{ M}^{-1} \). As in previous cases, some change in \( K_A \) but a huge variation in \( K_T \) are noticed. We believe the latter figure \( K_T = 28 \text{ M}^{-1} \) to be more reliable.

Notice that for LiClO\(_4\) in 1-2 DME at 25°C we calculated \( K_A = 4.1 \times 10^6 \text{ M}^{-1} \) and \( K_T = 20.3 \text{ M}^{-1} \). This indicates that the increase in conductivity of LiAsF\(_6\) with respect to LiClO\(_4\) is mainly due to a decrease of ion – pair association by one order of magnitude. Fig. 2 shows the Raman spectra of LiAsF\(_6\) 0.4 M and 0.2 M corresponding to the symmetrical stretch of AsF\(_6^–\) ion. No asymmetry of the spectrum is visible.

This suggests that AsF\(_6^–\) is spectroscopically free, namely not in contact with Li\(^+\). Because of the above conductance information (\( K_T = 10^5 \text{ M}^{-1} \)), the logical conclusion is that Li\(^+\) must seat in the majority of the cases around AsF\(_6^–\) but separated by one or more solvent molecules. It appears therefore that a preponderant portion of the ion – pairs exists as solvent separated pairs.
Fig. 3A and 3B shows the ultrasonic spectrum of LiAsF₆ in 1-2 DME at various concentrations and temperatures in the form of \( \alpha/\nu^2 \) vs. \( \nu \), where \( \alpha \) is the absorption coefficient of sound (neper cm\(^{-1}\)) and \( \nu \) the frequency. The solid fitted lines are the Debye function for a single relaxation function:

\[
\frac{\alpha}{\nu^2} = \frac{A}{1 + (\nu/\nu_r)^2} + B, \tag{IV}
\]

where \( A \) is a relaxation parameter, \( \nu_r \) is the relaxation frequency and \( B \) the background sound absorption at \( \nu \gg \nu_r \). The results for \( A, \nu_r \) and \( B \) together with the sound velocities \( U \) (cm s\(^{-1}\)) and the calculated maximum excess sound absorption per wavelength (Table I) \( \mu_m = \frac{1}{2} A \nu_r U \) are collected in table I.

From table I it is apparent that at 25°C \( \nu_r \) is independent of concentration within experimental error (±5%). Further \( \mu_m \) is linear with \( c \) (see below). These observations suggest a first order or pseudo-first order process of the type \( A \rightarrow B \). From the information above we advance the hypothesis that the process of ionic association between Li\(^+\) and AsF\(_6^-\) follows the Eigen-type mechanisms:

\[
\text{Li}^+ + \text{AsF}_6^- \xrightarrow{k_0} \text{LiAsF}_6 \xrightarrow{k_1} \text{LiAsF}_6 \tag{V}
\]

followed by further steps leading to triple ions. However we are disregarding these further steps for the treatment of the ultrasonic process. Formation of triple ions would require at least a second order process and a concentration dependent relaxation frequency contrary to what
observed here.

Because of the value of $K_A = 1 \times 10^5 \text{ M}^{-1}$, we suggest that at the concentrations of the ultrasonic work the first step of scheme V is irrelevant, too few free ions existing. The process then may be written as:

$$
\text{LiSAsF}_6 \xrightleftharpoons{\kappa_1}{\kappa_{-1}} \text{LiAsF}_6
$$

(VI)

We will denote the free ion concentrations by $c_1$ and the ones of the two complex species by $c_2$ and $c_3$ respectively, with the condition $c = c_1 + c_2 + c_3$ (neglecting other species).

This approximation may be justified as follows: Given the scheme:

$$
A + B \xrightleftharpoons{\kappa_2}{\kappa_1} AB + B \xrightleftharpoons{\kappa_3}{\kappa_2} A_2B
$$

$$(AB) = (1 - \alpha - 3\alpha_T)c \equiv c; \quad (A) = (B) = \alpha c; \quad (AB_2) = (A_2B) = \alpha_T c
$$

Then:

$$
K_A = \frac{1-\alpha}{\alpha c} \frac{1}{c} ; \quad \alpha = \frac{1}{\sqrt{K_A} c},
$$

$$
K_T = \frac{\alpha_T}{\alpha (1 - \alpha - 3\alpha_T)} = \frac{\alpha_T}{\alpha_c} ; \quad \alpha_T = \frac{K_T}{\sqrt{K_A} c}.
$$

If $K_T = 28 \text{ M}^{-1}$ and $K_A = 1 \times 10^5$ at $c = 0.1 \text{ M}, \alpha_T = 0.03, \alpha_T C = (AB_2) = (A_2B) = 3 \times 10^{-3} \text{ M}$. Further $\alpha = 0.01$ and single ions account only for a few percent of the total concentration of electrolyte (neglecting other species).

The collected data of Table I applied to scheme VI lead to the following treatment.

From the relation: $^{14}$
\[ \tau^{-1} = k_1 + k_{-1} = k_{-1}(1 + K_1) = \frac{kT}{h} e^\frac{\Delta S^\ddagger_1}{R} e^\frac{-\Delta H^\ddagger_1}{RT} (1 + K_1), \quad (VII) \]

A plot of ln(\((\tau^{-1}/T)\)) vs. \((1/T)\) should be linear with slope and intercept:

\[ \text{Slope} = \frac{\Delta \ln(\tau^{-1}/T)}{d(1/T)} = -\frac{\Delta H^\ddagger_1}{R} - \frac{K_1}{1+K_1} \frac{\Delta H_1}{R}, \quad (VIII) \]

\[ \text{Intercept} = \left( \ln \left( \frac{k}{h} \right) + \frac{\Delta S^\ddagger_1}{R} \right). \quad (IX) \]

(Fig. 4A) The results are shown in Fig. 4A. The solid line has been calculated by linear regressions. The results are: \( r^2 = 0.995 \), Intercept = 22.74, and Slope = -2510. From the intercept one calculates \( \Delta S^\ddagger_1 = -2.0 \) e.u.

Scheme VI leads also to the relation:

\[ \mu_m = \frac{\pi}{2} \frac{(\Delta V_s)^2}{RT} \frac{K_1}{(1 + K_1)^2 c}, \quad (X) \]

Where the isentropic compressibility \( \beta_s = \frac{1}{\rho U^2} \) and \( \Delta V_s = \Delta V_T - \frac{\theta}{\rho c_p} \Delta H_1 \), with \( \theta \) the expansivity \( \rho \) the density, \( c_p \) the specific heat of the liquid.

Eq. X implies that a plot of ln(\((\mu_m T/U^2)\)) vs. \(1/T\) should give a straight line with slope:

\[ \frac{d \ln(\mu_m T/U^2)}{d(1/T)} = \frac{K_1 - 1}{K_1 + 1} \frac{\Delta H_1}{R} \quad (XI) \]

(neglecting the temp. dependence of \( \rho \) and \( c_p \)).

(Fig. 4B) The results are shown in Fig. 4B. Linear regressions applied to these
data give: \( r^2 = 0.991 \), Intercept = -14.82, and Slope = -2517.

We are now able to write the system of three equations:

\[
\begin{align*}
\frac{d \ln(\tau^{-1}/T)}{d(1/T)} &= -2510 = -\frac{\Delta H_{-1}^f}{R} - \frac{K_1}{1 + K_1} \frac{\Delta H_1}{R}, \\
\frac{d \ln(\nu m T / U^2)}{d(1/T)} &= -2517 = \frac{K_1 - 1}{K_1 + 1} \frac{\Delta H_1}{R}, \\
\tau^{-1} &= \frac{kT}{h} e^{\Delta S_{-1}^f / R} e^{-\Delta H_{-1}^f / RT} (1 + K_1),
\end{align*}
\]

with the unknown parameters \( K_1, \Delta H_1, \Delta H_{-1}^f \).

Trial and errors by changing \( K_1 \) lead to compatible solutions with \( K_1 \approx 0.01 \) (\( K_1 \) much smaller than \( 10^{-2} \) gives still compatible solutions but it is unreasonable. No ultrasonic relaxation would be observable if the concentration of one of the two species is too small).

The final results then are:

\[
\begin{align*}
K_1 &\approx 10^{-2} \text{ i.e. } k_1 \gg k_1, \\
\tau^{-1} &\approx k_1 = 5.0 \times 10^8 \text{ s}^{-1}, \\
\Delta H_{-1}^f &= 4.9 \text{ Kcal/mole}, \\
\Delta S_{-1}^f &= -2.0 \text{ e.u.}, \\
\Delta H_1 &= 5.1 \text{ Kcal/mole}, \\
\Delta H_{-1}^f &= 10.0 \text{ Kcal/mole},
\end{align*}
\]

Further information can be obtained as follows:

If \( K_1 = 10^{-2} \), \( \Delta G_1 = -RT \ln K_1 = 2.73 \text{ Kcal/mole} \), and \( \Delta S_1 = \frac{1}{T} (\Delta H_1 - \Delta G_1) = 8.0 \text{ e.u.} \)

Then: \( \Delta S_1^f = \Delta S_1 + \Delta S_{-1}^f = 6.0 \text{ e.u.} \) and \( k_1 = 6 \times 10^6 \).
Finally, combination of ultrasonic and conductance results lead to the correlation:

\[ K_A = 1.0 \times 10^5 = K_0 (1 + K_1) \approx K_0 \quad \text{as} \quad \frac{c_3}{c_2} = 0.01. \]

This implies that \( c_3 \ll c_2 \) and that the contact species are in much smaller concentrations than the solvent separated species. Notice that calling \( \frac{c_3}{c_2} = 0.01 \) would imply the converse condition at variance with the indication by Raman spectra.

The ultrasonic relaxation method cannot indicate for a first order process the direction of the molecular process which must be deduced from collateral information.

If the above is correct, it would imply that we are looking for the observed process \( r^{-1} = k_1 \), to the transformation \( c_3 \rightarrow c_2 \), or \( \text{LiAsF}_6 \rightarrow \text{LiSAsF}_6 \). A final parameter can be calculated.

From eq. X one would expect linearity between \( \mu_m \) and \( c \). This is shown (Fig. 4C) in Fig. 4C. Linear regressions, forcing the intercept through the origin, (50% statistical weight to the origin), gives: \( r^2 = 0.986 \), Slope = 12.0, by expressing \( c \) in mole/cm\(^3\). Then since \( K_i \ll 1 \):

\[ \Delta V_s = \left[ \frac{2 \rho_s RT}{\pi K_1} \frac{\mu_m}{c} \right]^{1/2} = 40.4 \ \text{cm}^3/\text{mole}. \]

(Fig. 5A) Fig. 5A shows \( c' \) and \( (\epsilon'' - \epsilon''')x \), the coefficients of the real and imaginary parts of the complex permittivity \( \epsilon^* = \epsilon' - J(\epsilon'' - \epsilon''') \) plotted vs. the frequency \( f \) (GHz) for a representative concentration of \( \text{LiAsF}_6 \) in 1-2 DME. The frequency covered is \( \sim 1 - 90 \) GHz. The solid lines are the sum of two single Debye processes according to the functions:
\[ \varepsilon' = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + (f/f_{r1})^2} + \frac{(\varepsilon_\infty - \varepsilon_\infty)}{1 + (f/f_{r2})^2} + \varepsilon_3; \quad \text{(XII)} \]

and:

\[ \varepsilon'' - \varepsilon''_x = (\varepsilon_0 - \varepsilon_\infty) \frac{f/f_{r1}}{1 + (f/f_{r1})^2} + (\varepsilon_\infty - \varepsilon_\infty) \frac{f/f_{r2}}{1 + (f/f_{r2})^2}, \quad \text{(XIII)} \]

where \( \varepsilon''_x = \frac{1.8 \times 10^{12}}{x} \) is the specific conductance contribution to the dielectric loss; \( x \) is the specific conductance and \( \varepsilon_0 \) is the static permittivity of the solution. The quantities \( \varepsilon_0, \varepsilon_\infty, f_{r1} \) are due to the presence of the solute whereas the parameters \( \varepsilon_\infty, f_{r2} \) are relaxation parameters of the solvent in the solution. In other words the pure solvent would have similar values of \( \varepsilon_0 \text{ solvent} = \varepsilon_\infty, \varepsilon_\infty \) and \( f_{r2} \) as for the solutes, at least in dilute solutions.

The dashed lines in Fig. 5A are the single Debye contributions to \( \varepsilon'' - \varepsilon''_x \).

(Fig. 5B) Fig. 5B reports the Cole-Cole plot \( \varepsilon'' - \varepsilon''_x \) vs. \( \varepsilon' \) for the same solution of LiAsF\(_6\) in 1-2 DME. The solid line is the sum of the two individual Debye contributors indicated in Fig. 5B by the dashed semicircles. The parameters \( \varepsilon_0, \varepsilon_\infty, f_{r1} \) and \( f_{r2} \), together with the conductance of the solutions studied, is reported in Table II.
Discussion

Conductance, Raman spectra and ultrasonic relaxation all concur to suggest that the majority of LiAsF$_6$ exists as an outer-sphere or solvent-separated ion pair.

Fig. 6 shows the relaxation strength $(\varepsilon_0 - \varepsilon_\infty)$ plotted vs. the concentration $c = c_2$ for LiAsF$_6$ in 1-2 DME.

According to the Böttcher equations:

$$\varepsilon_0 - \varepsilon_\infty = \frac{4\pi L c x 10^{-3}}{(1 - \alpha f)^2} \frac{\mu}{3kT} \frac{3\varepsilon_0}{2\varepsilon_0 + 1} c.$$  \hspace{1cm} (XIV)

By neglecting the polarizability-reaction field factor $(1 - \alpha f)^2$ (generally of the order of 0.9), one can calculate $\mu$. Linear regression analysis applied to the data of Fig. 6, forcing the intercept through the origin gives:

$$r^2 = 0.999, \quad \text{Slope} = 19.8 \times 10^3$$

where $c$ has been expressed in mole/cm$^3$.

It results $\mu = 1.8.0 \times 10^{-18}$ e.s.u. cm. By taking a rigid sphere model it results $\mu = ea$, where $e$ is the charge of the electron. Then $a = 3.8 \times 10^{-8}$ cm the apparent charge to charge separation of the Li$^+$ and AsF$_6^-$ in the rotating dipole.

Notice that, from conductance $K_1 = K_0 = 1 \times 10^5$ M$^{-1}$. By equating $K_0$ to the Fuoss-Jagodzinski equation:

$$K_0 = K_F = \frac{4\pi L a^3}{3000} e^{-1/2} e^b,$$  \hspace{1cm} (XV)

with $b = \frac{e^2}{a\kappa kT}$.
on can evaluate $a \approx 6.3 \times 10^{-8}$ cm, a figure larger than the value estimated above from the dielectric data. This might be due to the mass effect and to the higher concentration used in the dielectric work, forcing more contact species to be present. This would lower the average distance between the ions in the pairs.
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   (1979) 8,147


    (1980) 16,263


13.


TABLE I

Ultrasonic relaxation parameters $A$, $B$, and $f_r$, sound velocity $U$ and maximum excess absorption per wavelength $\mu_m$ for LiAsF$_6$ in 1-2 DME at the concentrations $c$ and temperatures investigated.

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>$c$ (M)</th>
<th>$A \times 10^{17}$ (cm$^{-1}$ s$^2$)</th>
<th>$B \times 10^{17}$ (cm$^{-1}$ s$^2$)</th>
<th>$f_r$ (MHz)</th>
<th>$U \times 10^{-5}$ (cms$^{-1}$)</th>
<th>$\mu_m \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>102</td>
<td>60</td>
<td>35</td>
<td>1.286</td>
<td>230</td>
</tr>
<tr>
<td>10.0</td>
<td>0.29</td>
<td>95</td>
<td>55</td>
<td>48</td>
<td>1.248</td>
<td>285</td>
</tr>
<tr>
<td>15.0</td>
<td>0.30</td>
<td>88</td>
<td>55</td>
<td>55</td>
<td>1.233</td>
<td>299</td>
</tr>
<tr>
<td>25.0</td>
<td>0.40</td>
<td>95</td>
<td>55</td>
<td>80</td>
<td>1.209</td>
<td>459</td>
</tr>
<tr>
<td>25.0</td>
<td>0.30</td>
<td>80</td>
<td>51</td>
<td>80</td>
<td>1.181</td>
<td>378</td>
</tr>
<tr>
<td>25.0</td>
<td>0.20</td>
<td>64</td>
<td>48</td>
<td>80</td>
<td>1.123</td>
<td>287</td>
</tr>
<tr>
<td>25.0</td>
<td>1.10</td>
<td>35</td>
<td>43</td>
<td>80</td>
<td>1.130</td>
<td>158</td>
</tr>
</tbody>
</table>
TABLE II

Dielectric Relaxation Parameters $\varepsilon_0$, $\varepsilon_{\infty 1}$, $\varepsilon_{\infty 2}$, $f_{r1}$, $f_{r2}$ and specific conductance $\chi$ of LiAsF$_6$ in 1-2 DME at the concentrations investigated at $t = 25^\circ$C.

<table>
<thead>
<tr>
<th>$c$ (M)</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_{\infty 1}$</th>
<th>$\varepsilon_{\infty 2}$</th>
<th>$f_{r1}$ (MHz)</th>
<th>$f_{r2}$ (MHz)</th>
<th>$\chi$ $\Omega^{-1} \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>9.8</td>
<td>7.0</td>
<td>2.7</td>
<td>2.0</td>
<td>35</td>
<td>1.4$\times 10^{-3}$</td>
</tr>
<tr>
<td>0.05</td>
<td>8.7</td>
<td>7.2</td>
<td>2.9</td>
<td>2.0</td>
<td>30</td>
<td>7.3$\times 10^{-4}$</td>
</tr>
<tr>
<td>0.028</td>
<td>8.0</td>
<td>7.2</td>
<td>3.0</td>
<td>2.0</td>
<td>35</td>
<td>3.5$\times 10^{-4}$</td>
</tr>
</tbody>
</table>
Captions for the figures

Fig. 1  
A  logA vs. log c for LiAsF₆ and LiClO₄ in 1-2 DME at t = 25°C  
B  A√c vs. c for LiAsF₆ in 1-2 DME;  t = 25°C  
C  A g(c)√c vs. c(1 - \frac{A}{A_0}) for LiAsF₆ in 1-2 DME;  t = 25°C

Fig. 2  
Raman Spectrum of LiAsF₆ 0.2 M and 0.4 M in 1-2 DME in the symmetrical stretch region of AsF₆⁻

Fig. 3  
A - C  \(\alpha f^2\) vs. frequency f for LiAsF₆ in 1-2 DME at various concentrations at t = 25°C  
B  \(\alpha f^2\) vs. frequency f for LiAsF₆ 0.3 M in 1-2 DME at t = 10°C

Fig. 4  
A  Eyring plot: ln(τ^{-1}/T) vs. 1/T for LiAsF₆ 0.3 M in 1-2 DME  
B  Lamb plot: ln(\mu m T/U²) vs. 1/T for LiAsF₆ 0.3 M in 1-2 DME  
C  \(\mu m\) vs. concentration for LiAsF₆ in 1-2 DME;  t = 25°C

Fig. 5  
A  \(\varepsilon'\) and (\(\varepsilon'' - \varepsilon_x'\)) vs. frequency f for LiAsF₆ 0.05 M in 1-2 DME at t = 25°C  
B  (\(\varepsilon_0 - \varepsilon_{\infty}\)) vs. concentration c for LiAsF₆ in 1-2 DME at t = 25°C

Fig. 6  
Böttcher equation for LiAsF₆ in 1-2 DME
Solvent: 1-2 Dimethoxyethane

$T = 25^\circ C$

1st Run

2nd Run

LiAsF$_6$

LiClO$_4$


A

LiAsF$_6$ in 1-2 DME

$T = 25^\circ C$

B

Fuoss-Kraus triple-ions theory

LiAsF$_6$ in 1-2 DME

$T = 25^\circ C$

C
Figure A: Cole-Cole plot for LiAsF$_6$ 0.05M in 1-2 DME; $t=25^\circ$C

Figure B: Cole-Cole plot for LiAsF$_6$ 0.05M in 1-2 DME; $t=25^\circ$C
Böttcher's equation:

\[(e_0 - e_{\infty})(2e_0 + 1/3e_0)\]

vs concentration for

LiAsF6 in 1-2 DME

t = 25°C
DATE

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