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Microwave Dielectric Relaxation, Electrical Conductance, and Ultrasonic Relaxation of LiPF$_6$ in Poly(ethylene oxide) Dimethyl Ether-500

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Microwave dielectric complex permittivity $\epsilon^* = \epsilon' - J\epsilon''$ in the frequency range ~1−130 GHz and at temperatures of 25, 40, and 55 °C for the system LiPF$_6$ dissolved in poly(ethylene oxide) dimethyl ether of average molar mass 500 (PEO-500) are reported. The dielectric spectra are interpreted by a Cole−Davidson distribution function for both the solvent and the solutions. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the dielectric process have been determined for both solvent and solutions. Audio frequency electrical conductance of solutions of LiPF$_6$ in PEO-500, in the concentration range ~5 × 10^{-4} to 1.0 M (M = mol/dm^3) and temperatures 25, 40, and 55 °C, have been determined. The conductance data in the diluted range have been analyzed by two forms of the Fuoss-Onsager conductance theory. Despite the presence of a minimum in the conductance vs concentration functions, the presence of conducting triple ions has not been postulated, because the minimum is predicted by the functional form of the conductance theory at low solvent permittivities, for moderate ion-pair associations. Ultrasonic relaxation spectra in the frequency range ~1 to ~400 MHz and LiPF$_6$ concentration range 0.1−0.5 M at 25 °C are reported and analyzed in terms of the sum of two debye relaxation processes. The upper one centered around 150−200 MHz and common to the solvent PEO-500 is attributed to polymer-chain rearrangements, also influenced by the presence of the electrolyte. The lower relaxation process in the low megahertz frequency range is interpreted in terms of formation of dimers-ion pairs according to the process $2\text{LiPF}_6 \rightleftharpoons (\text{LiPF}_6)_2$, thus rationalizing the presence of a maximum in the static dielectric permitivity vs concentration.

Introduction

Investigation of polymer solutions of electrolytes, salts of lithium ion, to be used for the construction of batteries, has increased in recent years.[1]

Practical use of some electrolytes, such as LiClO$_4$ and LiAsF$_6$, is hindered because of safety and environmental hazards. On the other hand, LiPF$_6$ is free of the above limitations, while the octahedral structure of the PF$_6^-$ anion[2] is similar to that of AsF$_6^-$, thus perhaps mimicking the high conductivity and relatively low association of LiAsF$_6$ in solvents of low dielectric permittivity.[1] In addition to these pragmatic motivations, an investigation of the dielectric and ionic association properties of LiPF$_6$ dissolved in poly(ethylene oxide) polymer solutions appeared relevant on two grounds:

It has been noticed[3] that in highly viscous uncapped poly-(ethylene oxide) glycols (PEGs) there is no appearance of a *separate* frequency domain of dielectric relaxation attributable to the rotational relaxation of ion pairs of the electrolyte. It was of interest to investigate whether the solvent chain's rotation became the rate-determining step of the dielectric relaxation process also for electrolyte solutions of capped poly(ethylene oxide) polymers.

In low dielectric permittivity solvents, the appearance of a minimum in the conductance−concentration function is often taken as synonymous with the presence of conducting triple ions, despite several experimental proofs[4] that the dielectric permittivity increases with concentration of electrolyte, causing a redissociation effect. Also calculations[5] show the existence of activity coefficients of ion pairs being less than one, hence decreasing the apparent ionic association constant to ion pairs by increasing the concentration of electrolyte.

In the following, microwave complex dielectric permittivity $\epsilon^* = \epsilon' - J\epsilon''$ (with ϵ' and ϵ'' the coefficient of the real part and imaginary part of ϵ^*) and electrical conductance of solutions of LiPF$_6$ in PEO-500 dimethyl ether, at three temperatures, are reported and interpreted, in an effort to answer the above queries. *During this process, we have discovered that the potential appearance of a minimum in the conductance−concentration function is also predicted by the functional form of the Fuoss− Onsager conductance theory at low permittivity,*[6] an aspect previously overlooked because of the relative scarcity of data and because of the often masking effect of an overwhelming association constant term.

Ultrasonic spectra in the frequency range ~1−400 MHz have revealed, in the low megahertz frequency region, a debye contribution to the spectrum that has been interpreted as due to the relaxation of the ion-pair dimerization process: $2\text{LiPF}_6 \rightleftharpoons$

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(LiPF$_6$)$_2$. This confirms the prediction of dimerization of polar ion pairs (to apolar antiparallel dimers) deduced from the presence of a maximum in the static dielectric permittivity vs electrolyte concentration function as shown below.

Experimental Part

The equipment and procedure for the dielectric,[7,8] conductance,[9] and ultrasonic[10] measurements have been described before. The viscosities of the PEO-500 liquid polymers at 40 and 55 °C have been measured by a Brookfield rotating viscometer as described below. For the materials, LiPF$_6$ was provided by Eveready Co.; it was stored in nitrogen and redried in vacuo before use. PEO-500 was a Fluka product, dried over molecular sieves. All the weighing and solutions manipulations were carried out in a drybox filled with dry nitrogen. The dielectric and ultrasonic cells were sealed and thermostated to within ±0.1 °C. The conductance measurements were taken with solutions thermostated to within ±0.01 °C.

Results, Calculations, and Discussion

a. Dielectric Relaxation. Figure 1AS (the S denotes Supplementary Information) reports the real part of the dielectric permittivity ϵ' and Figure 1BS reports the loss coefficient ϵ''_d (corrected by the conductance contribution, $\epsilon''_d = \epsilon'' - [(1.8 \times 10^{12})\sigma]/f$, with σ the specific conductivity), both vs the frequency f for PEO-500 at 25 °C. In the above, σ is expressed in siemens per centimeter and ϵ'' is the total loss coefficient.

Figure 1CS reports the Cole−Cole plot of ϵ''_d vs ϵ' for PEO-500 at 25 °C. The solid lines in Figure 1S were calculated by the Cole−Davidson distribution function[11] described by the equations

$$\left.\begin{array}{l} \epsilon' = (\epsilon_0 - \epsilon_\infty)\cos^\beta(\phi)\cos(\beta\phi) + \epsilon_\infty \\ \epsilon''_d = (\epsilon_0 - \epsilon_\infty)\cos^\beta(\phi)\sin(\beta\phi) \\ \phi = \tan^{-1}(f/f_R) \end{array}\right\} \quad \text{(I)}$$

with ϵ_0 and ϵ_∞ the permittivity of the solutions at frequencies low and high with respect to f_R, the average relaxation frequency. Also β is the distribution parameter.

Figure 1 reports the same quantities as in Figure 1S for a representative solution of LiPF$_6$ in PEO-500 at 25 °C. All the calculated parameters ϵ_0, ϵ_∞, f_R, and β for PEO-500 and for the LiPF$_6$ solutions in PEO-500 at the temperatures 25, 40, and 55 °C are reported in Table 1.

We have measured ϵ' and ϵ'' for the solutions (of LiPF6 in PEO-500) down to a frequency $f = 1$ GHz. At much lower frequencies, the conductance contribution $\epsilon''_\sigma = [(1.8 \times 10^{12})\sigma]/f$, to the loss coefficient ϵ'', becomes prohibitively large.

For instance, for LiPF$_6$ = 0.50 M (Table 1), at $f = 10$ MHz, one calculates $\epsilon' \approx 8.6$, $\epsilon''_d \approx 1.7 \times 10^{-2}$, but $\epsilon''_\sigma = 60$. This gives a tan $\delta = \tan(\epsilon''/\epsilon') \approx 7$, whereas our maximum measurable value of tan $\delta = 0.5$−0.7. Even if ϵ'' were measurable at $f = 10$ MHz, it would make any evaluation of $\epsilon''_d = \epsilon'' - \epsilon''_\sigma$ meaningless.

Figure 3S reports the Eyring plot of $\ln(\tau^{-1}/T)$ vs $1/T$ for PEO-500, and LiPF$_6$ 0.30, 0.50, 0.75, and 1.0 M (M = mol/dm^3) in PEO-500. In the above, τ is the average relaxation time ($\tau^{-1} = 2\pi f_R$), which according to Eyring's theory is expressible by the function

$$\tau^{-1} = \frac{kT}{h}e^{-\Delta G^\ddagger/RT} = \frac{kT}{h}e^{\Delta S^\ddagger/R}e^{-\Delta H^\ddagger/RT} \quad \text{(II)}$$
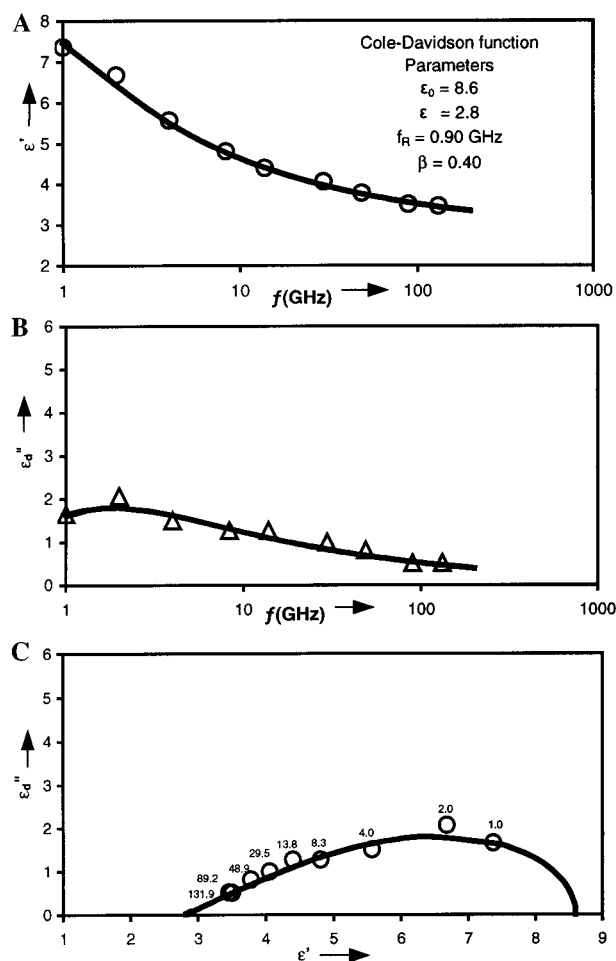
Figure 1. (A, B) Real part ϵ' and loss coefficient ϵ''_d vs the frequency f (GHz) for a representative solution of LiPF$_6$ in PEO-500 at 25 °C (c = 1 M) [$\epsilon'_d = \epsilon'' - (1.8 \times 10^{12})\sigma/f$, see text]. (**C**) Cole−Cole plot of ϵ''_d vs ϵ' for a representative solution of LiPF$_6$ in PEO-500 at 25 °C (c = 1 M).

TABLE 1: Dielectric Parameters According to the Cole−Davidson Function Fit to the LiPF$_6$ in PEO-500 Data

| c, M	t, °C	ϵ_0	e.	f_R, GHz	β	σ,[a] Ω^{-1} cm^{-1}
0	25	8.0	2.6	4.0	0.70	
	40	7.6	2.7	6.0	0.70	
	55	7.6	2.5	7.0	0.65	
0.11	25	8.0	2.6	3.0	0.60	$9.6_5 \times 10^{-5}$
	40	7.5	2.7	5.5	0.70	$1.5_0 \times 10^{-4}$
0.31	25	8.5	2.5	2.0	0.50	$2.3_9 \times 10^{-4}$
	40	8.3	2.5	2.5	0.50	$3.9_8 \times 10^{-4}$
	55	8.6	2.5	3.5	0.55	6.0×10^{-4}
0.50	25	8.6	2.7	1.7	0.50	$3.3_4 \times 10^{-4}$
	40	8.6	2.5	2.5	0.50	$6.2_5 \times 10^{-4}$
	55	9.3	2.8	2.9	0.60	$9.5_6 \times 10^{-4}$
0.75	25	9.0	2.7	1.0	0.45	$3.7_5 \times 10^{-4}$
	40	9.2	2.6	1.5	0.45	$7.1_3 \times 10^{-4}$
	55	9.7	2.7	1.7	0.50	11.7×10^{-4}
1.00	25	8.6	2.8	0.90	0.40	$3.5_7 \times 10^{-4}$
	40	9.0	2.8	1.2	0.43	$7.1_0 \times 10^{-4}$
	55	9.3	2.6	1.6	0.45	11.7×10^{-4}

[a] 1 Ω^{-1} = 1 S.

which becomes

$$\ln\left(\frac{\tau^{-1}}{T}\right) = \left[\ln\left(\frac{k}{h}\right) + \frac{\Delta S^\ddagger}{R}\right] - \frac{\Delta H^\ddagger}{RT} \quad \text{(III)}$$

The solid lines in Figure 3S have been calculated by linear

TABLE 2: Results of the Analysis by the 1959 Fuoss-Onsager Theory of the Conductance Data of LiPF$_6$ in PEO-500

T	c_{max}, M	ϵ	η, P	Λ_0, S cm^2 mol^{-1}	J_1	J_2	K_A	$a_J \times 10^8$, cm
298.15	0.0260	7.98	0.2922	2.86	4944	10 573	8279	13.8
313.15	0.0282	7.53	0.162	3.20	4567	14 027	1976	8.2
328.15	0.0244	7.60	0.108	3.52	4341	13 435	281	8.9
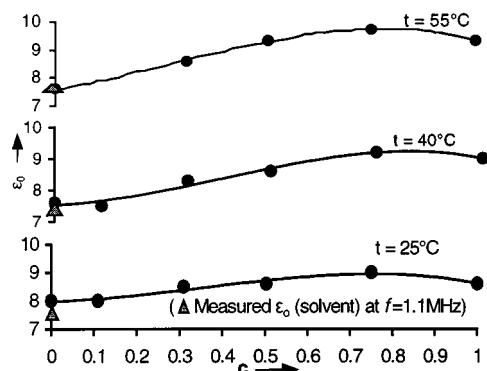
Figure 2. Calculated static permittivities ϵ_0 for PEO-500 and the solutions of LiPF$_6$ in PEO-500 vs the concentration of electrolyte at 25, 40, and 55 °C. The additional points at $c = 0$ are the dielectric resonator results for the solvent at 1.1 MHz.

Figure 3. Molar conductance Λ vs $\sqrt{c}$ for LiPF$_6$ in PEO-500 at $t = 25$ °C.

regression of the quantities $\ln(\tau^{-1}/T)$ vs. $1/T$, giving determination coefficients r^2, Intercept $= \ln(k/h) + (\Delta S^{\ddagger}/R)$ and Slope $= -\Delta H^{\ddagger}/R$.

Table 2S reports the calculated $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for the systems investigated.

Scrutiny of the results suggests that addition of LiPF$_6$ to PEO-500 slows the dielectric process mainly by increasing the entropy of activation (making it more negative). These results suggest a change in the polymer chain disorder due to the presence of the electrolyte.

Figure 2 reports the calculated static permittivities ϵ_0 for PEO-500 and for the solutions of LiPF$_6$ in PEO-500 plotted vs the concentration of electrolyte. The data show a maximum. The solid lines are the fitted function by nonlinear regressions, at the various temperatures, according to the following equations with their determination coefficients r^2:
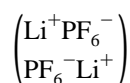
$$t = 25\ °C, \epsilon_o^{25} = 7.979 + 0.392c + 4.067c^2 - 3.827c^3; r^2 = 0.951$$

$$t = 40\ °C, \epsilon_o^{40} = 7.531 + 0.573c + 6.022c^2 - 5.126c^3; r^2 = 0.973$$

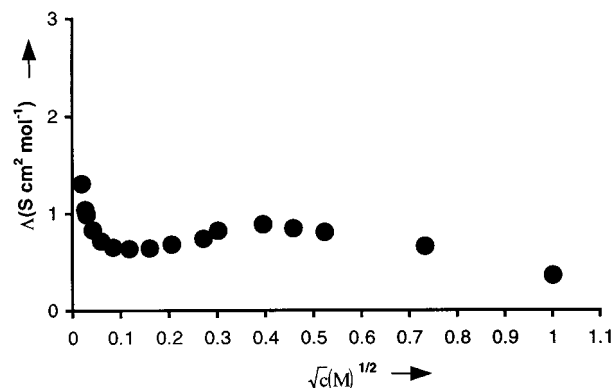$$t = 55\ °C, \epsilon_o^{55} = 7.597 + 2.468c + 4.219c^2 - 4.988c^3; r^2 = 0.999 \quad \text{(IIIa)}$$

The additional points at $c = 0$ in Figure 2 were determined by a dielectric resonance method to add credibility to the extrapolated ϵ_o's. The numerical values were $\epsilon_o = 7.80$ at 25 °C, $\epsilon_o = 7.53$ at 40 °C, and $\epsilon_o = 7.32$ at 55 °C. The data of ϵ_o at all the temperatures investigated show a maximum at ~0.7– 0.8 M LiPF$_6$.

It is possible that there is an equilibrium between ion pairs Li$^+$PF$_6^-$ and dimers (Li$^+$PF$_6^-$)$_2$ in antiparallel configuration

$$\begin{pmatrix} Li^+PF_6^- \\ PF_6^-Li^+ \end{pmatrix}$$

of apolar nature, whose formation decreases the polarization of the solution, due to the presence of polar ion pairs. As a

consequence, the permittivity of the solution would go through a maximum. Unfortunately, the conductance theory is not valid at $c \approx 0.8$ M, and, in the absence of direct evidence of the presence of apolar dimers, the above would remain a speculation. (See, however, section c below.) It is true that the molar conductance goes through a maximum with concentration. One could argue that the redissociation effect due to ion pairs is decreased when the ion pairs start dimerizing.

It is also noteworthy that for the present system, no separate frequency domain of rotational relaxation of ion pairs is observable down to ~1 GHz, the lowest frequency investigated, for LiPF$_6$ in PEO-500. It would be of interest to extend the present work to shorter chain polymers, since, in the past, separate rotational relaxation of ion pairs has been recorded, for solvent polymers of shorter chains.[1]

b. Electrical Conductance. Figure 3 reports the molar conductance Λ plotted vs $\sqrt{c}$ for LiPF$_6$ in PEO-500 at 25 °C, in the concentration range 5×10^{-4} to 1.0 M. A minimum and a maximum in Λ are clearly visible. The data at 40 and 55 °C (not shown) have, qualitatively, the same profile with concentration. As noted above, two forms of the conductance theory have been applied to the data:

1. The 1959 Conductance Theory. The first approach was to use the Fuoss-Onsager conductance theory for associated electrolytes in the 1959 version,[6] expressed by the equation for the molar conductance Λ:

$$\Lambda = \Lambda_o - S\sqrt{c\alpha} + Ec\alpha \log(c\alpha) + J_1(c\alpha) - J_2(c\alpha)^{3/2} - K_A c\alpha\Lambda f_{\pm}^2 \quad \text{(IV)}$$

In the above, α is the degree of dissociation, initially taken as $\alpha = \Lambda/\Lambda_0$. S, E, and J_1 are the coefficients of the Fuoss Onsager theory,[6] K_A is the ion pair association constant $K_A = (1 - \alpha)/\alpha^2 c f_{\pm}^2$, and $f_{\pm}$ is the average ionic activity coefficient calculable through the Debye−Huckel relations.[12] J_2, the coefficient of the $(c\alpha)^{3/2}$ term, has been treated as an empirical parameter, since Fuoss indicated[13] that other effects neglected by the theory could give rise to a $c^{3/2}$ term. A preliminary value of the limiting molar conductance Λ_o was estimated by applying Walden's rule to the result[14] $\Lambda_o = 26.31$ S cm^2 mol^{-1} for LiPF$_6$ in propylene carbonate ($\eta_{25} = 0.0251$ P) at 25 °C, yielding the initial figure

$\Lambda_o = 2.26$ S cm^2 mol^{-1}. It is known that Walden's rule is only an approximation, making the value of Λ_o subject to large errors. Notice, however, that during the calculations, we have obtained new values of Λ_o, used in subsequent approximations, as pointed out below, therefore correcting for the errors due to the initial Λ_o. Equation IV, then has been rearranged in the form

$$\Lambda' = \Lambda + S\sqrt{c\alpha} - Ec\alpha \log(c\alpha) = \Lambda_0 + J_1(c\alpha) - J_2(c\alpha)^{3/2} - K_A c\alpha\Lambda f_{\pm}^2 \quad \text{(V)}$$

The calculated values of Λ' have then been subjected to multiple linear regression (ΣMLRXYZ) fitting the data to the expression

$$T = A + BX + CY + DZ \quad \text{(Va)}$$

where $T = \Lambda'$, $X = c\alpha$, $Y = (c\alpha)^{3/2}$, $Z = c\alpha\Lambda f_{\pm}^2$. The fit gives $A = \Lambda_o$, $B = J_1$, $C = -J_2$, and $D = -K_A$. In order not to have the high concentration points distort the fit with a Λ_o value out of line with the low concentration points, an initial linear regression of the low concentration values of Λ' vs $c\alpha$, where the plot is linear, gave an initial value of Λ_o. By giving 50% statistical weight to this figure, the (ΣMLRXYZ) method was applied to all the data up to $c = 0.025$ M, obtaining a new value of Λ_o. The process was repeated, recalculating the coefficients S, E, and new α's twice. The final results are collected in Table 2.

It was of interest to calculate the collision distance a_J from the determined values of J_1. To this end the J_1 values were calculated for various values of a_J and the value $a_J = 13.8 \times 10^{-8}$ cm was extracted from the obtained $J_1 = 4944$. This value of a_J is much smaller than the Bjerrum $q = e^2/2\epsilon kT = 35.08 \times 10^{-8}$ cm, where q expresses the distance where the ratio of the energy between two ions at distance q, $e^2/\epsilon q$, and kT is equal to 2. In the above, e is the electron charge, k the Boltzmann constant, and T the absolute temperature. If one were to give $a_J = 13.8 \times 10^{-8}$ cm physical significance, it would correspond to the distance between Li$^+$ and PF$_6^-$ ions in an ion pair with the ions separated by the chains of the polymer, possibly coordinated around Li$^+$ through oxygen coordination.

The calculation was repeated at 40 and at 55 °C, starting with the Walden rule Λ_o's, calculated as done above for LiPF$_6$ at 25 °C, but using viscosities $\eta = 0.162$ P at 40 °C and $\eta = 0.108$ P at 55 °C. [The viscosities at 40 and 55 °C were determined by the use of a Brookfield programmable viscometer with a coaxial cylinder rotating in a larger, water-jacketed cylindrical shell. The estimated error in the viscosities was ±0.1%.]

Table 2 reports the results of the conductance analysis at 40 and 55 °C, together with the values of J_1, a_J, and K_A. It was also of interest to relate the values of K_A; to this end, the thermodynamic relation for the free energy change of association $\Delta G° = -RT \ln K_A$ was rewritten as

$$K_A = e^{-\Delta G°/RT} = e^{\Delta S°/R}\, e^{-\Delta H°/RT}, \text{ and } \ln K_A = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \text{(VI)}$$

A plot of $\ln K_A$ vs. $1/T$ is shown in Figure 6AS. Linear regression of $\ln K_A$ vs $1/T$ gave $r^2 = 0.986$, intercept = -27.71, and slope = $10\,983$, from which the values $\Delta S° = -230$ J/K mol, $\Delta H° = -91.3$ kJ/mol, and $\Delta G° = -22.7$ kJ/mol, at $T = 298$ K, were extracted.

An important aspect of the analysis just presented should be pointed out. In the 1930s, Fuoss and Kraus[15] proposed formation of conductive triple ions, in media of low permittivity ϵ, to rationalize the appearance of a minimum in the molar

concentration vs concentration. Years later, however, it was proposed[16,17] that the concept of triple ions is often unnecessary, the increase of permittivity with the consequential redissociation of ion pairs *and* the activity coefficient of the ion pairs, (being less than one and calculable[5]) both contribute to the decrease of K_A. This decrease in the apparent association constant K_A could rationalize the appearance of a minimum in the molar conductance vs concentration profile.

In the calculations just presented, using the solvent ϵ_o, it has not been necessary, however, to use the concept of triple ions to rationalize the appearance of a minimum in the function Λ vs concentration for the system LiPF$_6$ in PEO-500. It appears that in solvents of low permittivity, ϵ_o, there may be an internal compensation between $S\sqrt{c\alpha}$, $E(c\alpha)\log(c\alpha)$ (the latter negative for $c\alpha < 1$), $J_2(c\alpha)^{3/2}$, and $K_A c\alpha\Lambda f_{\pm}^2$, all negative terms, subtracting from Λ_0, and $J_1(c\alpha)$, the latter term eventually prevailing (for moderate values of K_A) and causing the appearance of a minimum in the function Λ_o vs c.

In the 1930s,[15] as only the Onsager $S\sqrt{c\alpha}$ term was known, the above possible internal compensation of terms could not have been predicted. In the late 1950s, Fuoss in his monograph[6] suggested dropping, at low permittivities, all the terms with the exception of $S\sqrt{c\alpha}$, as the $K_A c\alpha f_{\pm}^2$ term would swamp all of the other ones. In fact, for moderate values of K_A, it may occur that a minimum in Λ appears, because of internal compensation of terms. In this case, postulating the presence of triple ions seems unnecessary, even without using the dielectric permittivity of the solution or an ion pair activity coefficient less than one. This concept can be illustrated by plotting the quantity $\Delta\Lambda$ vs concentration where
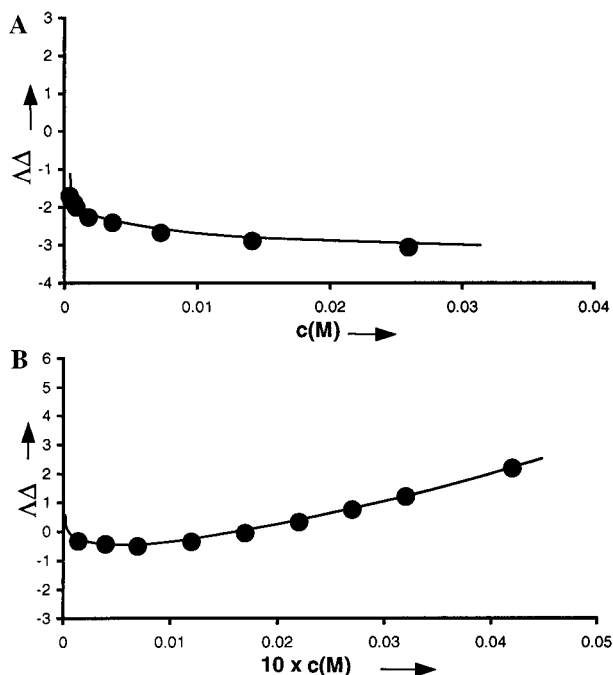
$$\Delta\Lambda = [-S\sqrt{c\alpha} + E(c\alpha)\log(c\alpha) - J_2(c\alpha)^{3/2} - K_A c\alpha\Lambda f_{\pm}^2] + J_1 c\alpha \quad \text{(VII)}$$

namely, $\Delta\Lambda$ is the algebraic sum of all the terms subtracted from Λ_o and confined to the squared parenthesis of eq VII, above, and $J_1(c\alpha)$. For $\Lambda = \Lambda_o + \Delta\Lambda$ to show a minimum, the quantity $\Delta\Lambda$ has to go through a (negative) maximum.

In Figure 4A the quantity $\Delta\Lambda$ is plotted vs the concentration c, showing $\Delta\Lambda$ increasing toward a maximum. Unfortunately, the conductance theory ceases to be operative before $\Delta\Lambda$ reaches a maximum. However, the concept can be paraphrased in another way. Let us consider a hypothetical unassociated electrolyte ($\alpha = 1$) with otherwise the same parameter as for LiPF$_6$ in PEO-500 at 25 °C, namely, $\Lambda_0 = 2.86$ S cm^2 mol^{-1}, $\epsilon_0 = 7.98$, $\eta = 0.2922$ P (the dielectric permittivity and viscosity of the solvent). Further retain $J_1 = 4944$ and $J_2 = 10\,753$, the coefficients found for LiPF$_6$ in PEO-500 at 25 °C. Figure 7B shows $\Delta\Lambda$ first being negative, going through a maximum and then becoming positive by increasing the concentration c.

2. Justice Approach and the Permittivity of the Solutions. In the next stage of the calculations, the dielectric permittivity of the solutions has been calculated from eqs IIIa above. Further, following Justice's proposal,[18] the positions $J_1 = J_1(q)$ and $J_2 = J_2(q)$ have been retained in the calculations. Fuoss[19] pointed out that, in solvents of low relative permittivity ϵ_o, the quantity q becomes too large (in PEO-500, at 25 °C, $q \cong 35 \times 10^{-8}$ cm) to assume that the radial component of the hydrodynamic velocity of two colliding ions would go to zero when their mutual decreasing distance reaches q (much larger than atomic dimensions). Nevertheless, many researchers have since used the theory with two distances q and a_K, the latter calculated from K_A set equal to Bjerrum's association constant,[6] using $J_1(q)$ and $J_2(q)$ in eq IV. The results of the present data at 25 °C,

Figure 4. (A) $\Delta\Lambda = [-S\sqrt{c\alpha} + Ec\alpha \log c\alpha - J_2(c\alpha)^{3/2} - K_A c\alpha\Lambda f_{\pm}^2] + J_1 c\alpha$ plotted vs c for LiPF$_6$ in PEO-500 at $t = 25$ °C. **(B)** $\Delta\Lambda$ vs c for a hypothetical unassociated electrolyte ($\alpha = 1$) with the same parameter as for LiPF$_6$ in PEO-500 at 25 °C.

using $J_1(q)$, $J_2(q)$, and the permittivity of the solutions, up to $c = 36.7 \times 10^{-4}$ M, gives a decreasing value of K_A expressible as ln K_A vs the concentration of the ion pairs $c_p = (1 - \alpha)c$ by the function ln $K_A = 9.401 - 221.1[c(1 - \alpha)]$, with $r^2 = 0.89$ as shown in Figure 8S. From the intercept, one calculates $K_A = 12.1 \times 10^3$.

We have also applied the Fuoss-Onsager theory with the positions $J_1 = J_1(q)$, $J_2 = J_2(q)$, and $\epsilon = \epsilon(c)$ (eq IIIa) to the conductance data of LiPF$_6$ in PEO-500 at 40 and 55 °C, obtaining the values of K_A extrapolated at zero concentration $K_{A°} = 3677$ at 40 °C and $K_{A°} = 1119$ at 55 °C. The same thermodynamic analysis (eq VI) applied to the above data of K_A at 25, 40, and 55 °C give the results illustrated in Figure 6BS. Linear regression of ln K_A vs $1/T$ (solid line in Figure 6BS) gives $r^2 = 0.999$, intercept $= \Delta S°/R = -17.32$, and slope $= \Delta H°/R = 7760$, from which $\Delta S° = -138.1$ kJ/mol, $\Delta H° = -64.5$ kJ/mol, and $\Delta G° = -23.3$ kJ/mol.

The K_A values, although different from the ones given above, from the use of the 1959 Fuoss-Onsager theory, are of comparable order of magnitude with the K_A results obtained in Table 3 by the 1959 theory. The main reasons for the differences are probably the use of $J_1(q)$ and $J_2(q)$, forcing the $[K_A c\alpha\Lambda f_{\pm}^2]$ term to change in order to absorb the differences in calculating Λ at each concentration. The use of the permittivity of the solutions, changing with concentration, also has some role in producing the above differences.

c. Ultrasonic Relaxation Kinetics. Figure 5A reports a plot of the excess sound absorption coefficient α_{exc} times the wavelength λ, namely, $\mu = \alpha_{exc} \lambda$, plotted vs the frequency f for a representative concentration of LiPF$_6$ dissolved in PEO-500 at 25 °C. The solid line in Figure 5A corresponds to the sum of two Debye processes according to the function

$$\mu = 2\mu_I \frac{f/f_I}{1 + (f/f_I)^2} + 2\mu_{II} \frac{f/f_{II}}{1 + (f/f_{II})^2} \qquad \text{(VIII)}$$
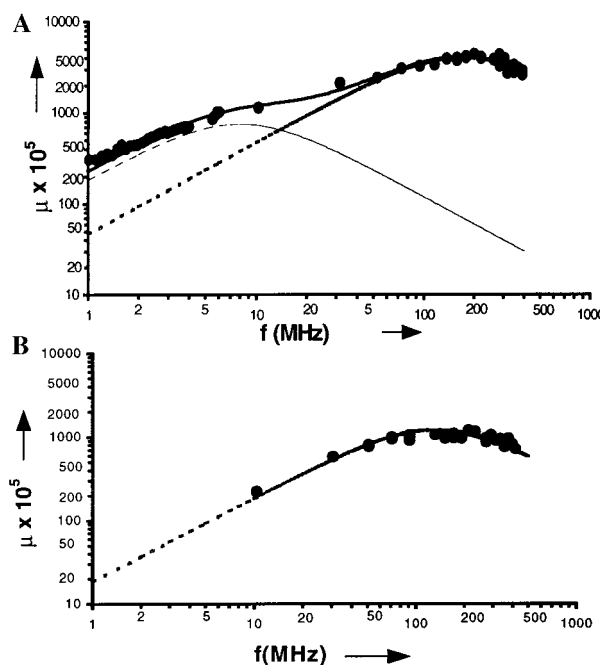
Figure 5. (A) $\mu = \alpha_{exc}\lambda$ (the excess sound absorption coefficient α_{exc} times the wavelength λ) vs the frequency f for a representative concentration of LiPF$_6$ dissolved in PEO-500 at 25 °C. The solid line corresponds to the sum of two debye processes, characterized by the parameters μ_I, f_I, μ_{II}, and f_{II}, according to eq VIII. **(B)** μ vs f for the solvent PO-500 at $t = 25$ °C. The solid line corresponds to a debye process characterized by the parameters μ_I and f_I, with $\mu = 2\mu_I(f/f_I)/(1 + (f/f_I)^2)$.

TABLE 3: Ultrasonic Relaxation Parameters μ_I, f_I, μ_{II}, f_{II}, and B According to Equation VIII and Sound Velocity u for LiPF$_6$ Dissolved in PEO-500 at 25 °C

| C, M	$\mu_I \times 10^5$	f_I, MHz	$\mu_{II} \times 10^5$	f_{II}, MHz	$B \times 10^{17}$, cm^{-1} s^2	$u \times 10^5$, cm s^{-1}
0	1200	130			140	1.495
0.11	1800	140	200	5.5	150	1.510
0.20	2100	140	350	6.0	160	1.510
0.30	3200	160	370	7.0	140	1.522
0.40	4000	150	500	7.5	160	1.533
0.50	4000	170	750	8.0	180	1.541

In the above, f_I and f_{II} are the relaxation frequencies of the two Debye processes having maximum sound absorption times wavelength μ_I and μ_{II} (centered at f_I and f_{II}, respectively). [Equation VIII could be expressed in the form

$$\frac{\alpha}{f^2} = A_I \frac{1}{1 + (f/f_I)^2} + A_{II} \frac{1}{1 + (f/f_{II})^2} + B \qquad \text{(IX)}$$

with $A_I = 2\mu_I/uf_I$, $A_{II} = 2\mu_{II}/uf_{II}$, where u is the sound velocity. Also B (the value of α/f^2 at frequencies $f \gg f_I, f_{II}$) is related to μ by the expression $\alpha/f_2 = \mu/uf + B$.][20] Table 3 reports the relaxation parameters μ_I, f_I, μ_{II}, f_{II}, and B and the sound velocity u for the concentrations of LiPF$_6$ in PEO-500 at 25 °C, investigated.

The relaxation process at higher frequency is common with the one for the pure solvent PEO-500 (Figure 9B). The effect of the presence of the electrolyte is to increase its amplitude μ_I and to shift its relaxation frequency f_I to somewhat higher values. We attribute it to polymer chain rearrangements affected by the presence of LiPF$_6$ ion pairs, Li$^+$ being the center of coordination of chains, enhancing chains entanglements. The relaxation process at lower frequency is due to the presence of the electrolyte LiPF$_6$. Notice, in fact, that the data in Figure 5A

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below 10 MHz have been obtained by using the resonator technique that uses the solvent polymer as reference, obtaining directly ($\alpha_{exc}\lambda$) of the solution. This ensures that the process noticed in Figure 5A at lower frequencies than 10 MHz is due to the presence of the electrolyte solute despite the absence of points below 10 MHz in Figure 5B for the pure solvent. For this latter case the pulse technique has been used, which is not of practical use at frequencies below ~10 MHz unless the absorption coefficient α is abnormally high. At the concentrations studied, the concentrations of both Li$^+$ and PF$_6^-$ are very small as compared to [LiPF$_6$], due to ion pair association, which cannot therefore be invoked as the source of the observed relaxation process. We advance the hypothesis that the observed process is due to dimerization of ion pairs, according to the process:

$$2\mathrm{LiPF}_6 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (\mathrm{LiPF}_6)_2.$$
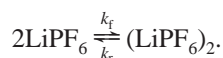
The concentrations [LiPF$_6$] = c_p and [LiPF$_6$]$_2$ = c_d are related to the relaxation time $\tau = (2\pi f_{II})^{-1}$ of the process, by the relation[20]

$$\tau^{-1} = 4k_f\, c_p + k_r \qquad\qquad (X)$$

Equation X has been applied to the present data, starting with the approximation $c \approx c_p$. Linear regression of τ^{-1} vs c gave determination coefficient $r^2 = 0.979$, intercept $= 3.0 \times 10^7$, and slope $= 4.1 \times 10^7$, from which $k_r = 3.0 \times 10^7\mathrm{s}^{-1}$, $k_f = 1.0 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, and $K_d = 0.33$ were extracted. We then combined $K_d = c_d/c_p^2$ with the conservation equation $c = c_p + 2c_d = c_p + 2K_d c_p^2$, to calculate c_p for each c. The cycle was repeated 4 times, with the results for $K_d = 0.49$, 0.54, 0.57, and 0.57 being the converged value. The final results of the final plot shown in Figure 10S, were $k_f = 1.6 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_r = 2.8 \times 10^7\ \mathrm{s}^{-1}$, and $K_d = 0.57$. As quoted above, the presence of dimers, now confirmed by ultrasonic relaxation kinetics, was predicted by the presence of a maximum in the static permittivity vs concentration of electrolytes. The maximum was presumably due to the apolar, antiparallel structure of the dimers, decreasing the polarization of the solution.

Conclusion

The conductance analysis reveals the electrolyte LiPF6 to be heavily associated to ion pairs, when dissolved in PEO-500. These dipole ion pairs increase the permittivity of the solution and contribute to the presence of a minimum in the conductance data, by increasing concentration, around ~0.01 M. At much higher concentration, appearance of dimer ion pairs, of apolar nature, decreases the polarization of the solution. Consequently the static permittivity and the electrical conductance of the solution both go through a maximum. Thus, it appears that ion pairs and dimers suffice, through their effect on the dielectric permittivity of the solution, to rationalize the conductance behavior of the electrolyte.

Supporting Information Available: Supporting Information. Table II of dielectric and activation parameters for LiPF$_6$ in PEO-500 and Figures 1S, 3S, 6S, 8S, and 10S. This material is avaliable free of charge via the Internet at http://pubs.acs.org.

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