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¹SOLVATION DYNAMICS OF ION PAIRS

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Abstract

The dynamics of how a solvent responds to a solute still remains an unsolved, but critically important, scientific problem. The prospects for understanding solvation dynamics at a molecular level have increased dramatically recently with experimental refinements in ultrafast spectroscopy of liquids, as well as improvements in computational techniques for the modeling of these processes. In this project we studied the solvation dynamics associated with ion pairs in solution using the relatively new technique of femtosecond terahertz time domain transmission spectroscopy coupled with a theoretical approach based on molecular dynamics simulations. The objective of this proposal was to probe, on a molecular and intermolecular scale both experimentally and theoretically, the mechanisms and timescales involved in both the formation and dynamic behavior of ion pairs in solution. To accomplish this goal we further developed the technique of femtosecond terahertz time domain transmission spectroscopy for the study of dynamic molecular interactions in liquids, closely coupling the spectroscopic results obtained to molecular dynamics calculations. Our results validate terahertz spectroscopy as a technique for the investigation of the solvation dynamics in electrolytic solutions of technological importance.

Background and Research Objectives

Even if we know the equilibrium thermodynamics of a solvent around a solute—even if we understand the tradeoffs between solvent-solvent interactions and solute-solvent interactions and we have a complete command of all the compromises that may be necessary between local energetics and more global entropic concerns—the dynamics of how a solvent responds to a solute still remains an unsolved, but critically important, scientific problem. The sets of motions that a many-body solvent undergoes in order to make itself a more hospitable environment for a solute may still be largely mysterious: Is the motion intrinsically many-body in character or is it better to think of it in terms of individual solvent motions? Are some kinds of solvent rearrangements more efficient than others in carrying out solvation? Indeed are there even going to be universal answers to these questions or must they be continually reposed for each solute-solvent system. Recently, the prospects for understanding solvation dynamics at a molecular level have increased dramatically with experimental refinements in ultrafast spectroscopy of liquids, as well as improvements in calculational techniques for the modeling of these processes. In this project we demonstrated the ability to study the solvation dynamics associated with ion pairs in solution using the relatively new technique of femtosecond terahertz time domain transmission spectroscopy coupled with a

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theoretical approach based on molecular dynamics simulations and recently developed solvation theory.

Ion pairs, solvent-separated ion pairs and larger ion aggregates are familiar and important players in all areas of chemistry. For example, ion pairs are important intermediates in substitution reactions in which dissociation of a leaving group is the rate-limiting step (S_N1 reactions). Ion-ion interactions also become important in concentrated electrolyte solutions--indeed, classical theories of electrolytes such as the Debye-Huckel treatment become invalid as ion pairing becomes significant. The logical extreme of concentrated electrolyte solutions is molten salts, an object of extensive recent study since the discovery of molten salts which are liquid at room temperature. In 'salt-in-polymer' electrolytes, such as NaX in poly(oxyethylene), salts are dissolved in polymers which have quite low dielectric constants making the formation of ion pairs and aggregates inevitable. The improvement of the conductivity of systems with extensive ion interactions, which are of increasing importance in a range of electrochemical applications, then relies on the development of salts with ultra-low lattice energies.

A detailed understanding of ion pair interactions in solution has not yet been achieved. Theories of concentrated solutions are highly empirical and therefore lacking in a scientific understanding of the relevant phenomena. Moreover, most experimental studies invoke the formation of ion pairs and aggregates based on indirect evidence. For example, a decreasing molar conductivity with increasing salt concentration typically indicates the presence of ion pairing because a fraction of the ions are sequestered in neutral ion pairs which do not respond to the field. There are a few spectroscopic signatures of ion pairs but the existence of more extensive ion aggregates, inferred from conductivity results, is less well established. Finally, there are no direct experimental results on intermolecular dynamics of ion association/dissociation processes in solution. These processes occur on very fast timescales.

The recently developed experimental technique of femtosecond terahertz time domain transmission spectroscopy[1] is well suited for the elucidation of the dynamical molecular and intermolecular interactions associated with ion pair formation. This technique uses terahertz bandwidth ($1-100\text{ cm}^{-1}$), far infrared, single-cycle pulses with subpicosecond temporal duration as a spectroscopic probe of intermolecular dynamics in liquids. Since the response of a molecule in a liquid to the absorption of electromagnetic radiation reveals the subsequent interactions and relaxation mechanisms caused by the surrounding medium which occur on the timescale corresponding to the frequency range of the radiation, our terahertz pulses are sensitive to the intermolecular spectrum of liquids corresponding to interactions which occur on timescales of 300 fs to 30 ps. Moreover, since detection of these femtosecond terahertz pulses is performed coherently, the receiver measures the temporal profile of the electric field of the terahertz pulse, rather than the pulse intensity (electric field squared) as is the case for conventional spectroscopic

techniques such as optical absorption or Fourier transform spectroscopy. The coherent measurement of transmission of the terahertz pulse through a sample directly yields both the absorption coefficient and index of refraction (or equivalently the complex permittivity) over the frequency range determined by the terahertz pulse and the bandwidth of the detector. Furthermore, since the terahertz pulse is generated by a sub-100-fs optical pulse using ultrafast optoelectronic techniques, a synchronized near infrared, visible, or ultraviolet pulse is available for femtosecond time-resolved dynamical studies. For such experiments, the visible pump pulse can induce a chemical reaction such as inter- or intramolecular electron transfer or ion pair disassociation. A series of transmission spectra of the terahertz probe propagating through the pumped region are recorded as a function of pump-probe delay, revealing the changes in the intermolecular interactions in the system as the reaction proceeds along its minimum energy pathway from reactant to product.

The association/dissociation of ions in solution is a significant chemical event that dominates the physical properties of electrolyte solutions. Lifetimes of ion pairs are estimated to be 10 ps, while the solvent motions that pry paired ions apart are expected to be even faster. A typical rotational relaxation time for a liquid water molecule is about 6 ps and chemical events such as ion pair dissociation occur even faster. Therefore, the timescales probed via terahertz spectroscopy are commensurate with the timescales needed to probe ion pair dynamics.

The objective of this proposal was to probe, on a molecular and intermolecular scale both experimentally and theoretically, the mechanisms and timescales involved in both the formation and dynamic behavior of ion pairs in solution. To accomplish this goal we further developed the technique of femtosecond terahertz time domain transmission spectroscopy for the study of dynamic molecular interactions in liquids, closely coupling the spectroscopic results obtained to molecular dynamics calculations. The project proceeded from studies on pure liquids through studies of dilute solutions of salts in the appropriate liquids, then to concentrated solutions where our data indicates the existence of aggregates of ion pairs in solution.

Importance to LANL's Science and Technology Base and National R&D Needs:

The proposed research will break ground in several new areas of importance to LANL, DOE and the nation, including advanced instrumentation, physical chemistry of concentrated electrolytes and theoretical tools for understanding concentrated electrolytes.

Femtosecond terahertz time domain transmission spectroscopy is an important technique for the study of fundamental dynamic processes in solutions. The timescale of the technique is such that it provides an experimental window into the same timescale that molecular dynamics simulations probe. Over the past few years has been used quite successfully by several groups to resolve important scientific issues relevant to molecules in the gas phase, dielectrics,

semiconductors and superconductors. Only recently have solvation processes in nonpolar and polar liquid and mixtures (e.g. $\text{CH}_3\text{Cl}/\text{CCl}_4$) been addressed using this technique [2-4]. The results of such studies, really still in their infancy, have been analyzed using empirical models such as Debye, Cole-Cole, Cole Davidson and Mori's continued fraction formalism [5-7]. Clearly the full potential of femtosecond terahertz time domain transmission spectroscopy as a tool for studying interactions in liquids will not be realized until the experimental results obtained are analyzed with more physically revealing theory. Further extension of this technique in liquids to visible pump/terahertz probe experiments is pending and its implementation for the study of ion pair dissociation and electron transfer processes should shed light on important issues in reaction chemistry. Moreover the terahertz spectroscopy techniques developed here for ion pair chemistry can ultimately be used to study other important chemical and biochemical processes in solution.

The interaction of solvents with ions is a universal problem in chemistry, impacting on reaction kinetics and mechanisms, electrolyte behavior, biomolecule function, etc. Since ion pairs are central features of a wide range of chemical systems, the basic understanding of the structure, dynamics, and energetics of formation of ion pairs and larger aggregates, which we hope to achieve through this project, will be of fundamental significance. An enhanced understanding of the role of ion-ion interactions and ion solvation in determining conduction or dissolution properties could suggest new routes to rationally designed ion conductors. The latter are important materials used in a variety of devices (e.g. batteries, fuel cells, ultracapacitors) under development at LANL. This work will also lead to a greater understanding of solvation processes in concentrated ionic solutions that are common in the processing of nuclear materials. Because of their unique chemistry and low volatility, room temperature molten salts are finding industrial applications as non-aqueous solvents. The viscosity of these ionic liquids is higher than desired for such applications. Insights from proposed studies of these systems could indicate a rational path to lower viscosity melts.

Scientific Approach and Accomplishments:

Our experimental setup is a femtosecond THz time-domain transmission spectrometer [1, P1, P2], shown in Figure 1. Briefly, the 800-nm, 100-fs output of a Ti:sapphire oscillator is split into two pulses: one pulse excites a dipole antenna with a 50- μm , low-temperature-grown GaAs (LT-GaAs) gap and the other pulse traverses a variable delay line and gates a dipole receiver which has a 10- μm , LT-GaAs gap. The THz radiation from the emitter is collimated and focused, resulting in a 1 cm spot diameter; the sample is placed at this focal spot. After traversing the sample the THz beam is focused onto the dipole receiver. The delay line in the gate

beam is scanned, yielding the temporal waveform of the electric field of the transmitted THz pulse, as shown in Figure 2. The resultant usable bandwidth of this THz spectrometer ranges from about 5 to 50 cm^{-1} . For each transmission measurement, a high purity liquid sample is loaded into 100- μm -thick crystalline quartz cell that is placed in the collimated THz beam. Immediately after the sample transmission data is obtained, the cell is emptied, flushed and dried in situ, and a reference transmission scan is taken using the empty cell. All data is taken at room temperature.

Such a coherent measurement of the transmission of the THz pulse through the sample directly yields both parts of the complex dielectric function (absorption coefficient and index of refraction) over the frequency bandwidth of the THz spectrometer in the following manner: The complex transmission function in the frequency domain, $T(\omega)$, is derived from time domain scans with a full cell and an empty cell by fast Fourier transforming each temporal scan and dividing them. An expression for $T(\omega)$ has been derived from a multi-layer dielectric model which describes the transmission and reflection at each interface for both the full and empty cell in terms of the known complex dielectric constant of the cell and the unknown dielectric constant $\epsilon(\omega)$ of the sample. This treatment includes the Fabry-Perot term describing multiple reflections in the cell gap. For each value of ω we equate this expression to the experimentally determined value for $T(\omega)$ and iteratively solve for $\epsilon(\omega)$ in the sample.

The extraction of the dynamical information from these frequency domain measurements depends heavily on the model chosen to describe the dielectric function. The most commonly used model for dielectric relaxation is the Debye model [5] which assumes that the polarization induced by applying an external electric field relaxes exponentially to equilibrium, as $\exp(-t/\tau)$ once the field is turned off. The time constant, τ , for this relaxation process is the Debye relaxation time. For a given medium, one or more Debye relaxation processes are possible. For multiple Debye-like relaxation processes the complex frequency-dependent dielectric function, $\epsilon(\omega)$, has the form:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{j=1}^n \frac{\varepsilon_j - \varepsilon_{j+1}}{\left[1 + (i\omega\tau_j)^{1-\alpha_j}\right]^{\beta_j}}$$

where ε_{∞} and ε_1 are the real dielectric constant at high frequency and the static dielectric constant (ε_s), respectively; ε_j is an intermediate value of the real dielectric constant; τ_j is the Debye relaxation time that corresponds to the j th relaxation process. For purely exponential relaxation as described by the Debye model, each term has $\alpha_j = 1$ and $\beta_j = 1$.

Before examining solutions of salts in various solvents, our first task was to verify the functioning of our experimental equipment and analysis process. This was accomplished by making measurements of pure liquids [P3] and comparing our results to those obtained previously by other researchers. Table 1 tabulates these results for water and propylene carbonate, along with the results of other researchers. It is seen that the agreement is reasonable.

Table 1: Debye parameters for propylene carbonate and water

WATER	ε_{σ}	τ_1 (ps)	ε_2	τ_2 (ps)	ε_3	τ_3 (ps)	ε_{∞}
Barthel	77.97	8.32	6.18	1.02			4.59
Kindt and Schmittenmaer	78.36 (constant)	8.24 (40)	4.93 (54)	0.18 (14)			3.48 (70)
OUR DATA	78.96 (6.94)	7.87 (79)	4.80 (10)	0.18 (03)			3.42(1 8)
PROPYLENE CARBONATE							
Barthel (GHz only)	64.7	40.4	7.46	6.91			4.41
OUR DATA	64.53 (4.56)	40.0 (00)	5.71 (38)	1.40 (17)	3.40 (03)	0.22 (01)	1.87 (03)

It should be noted that although, in general, our frequency range of 5-50 cm^{-1} did not cover the main (low-frequency) relaxation for the pure solvents, we were still able to reproduce the results of others. By fitting the pure water data to two Debye relaxations we were able to match the values reported by others for all parameters, within a standard deviation. [3, 9] We used three Debye relaxations to fit the PC data [10] and were thereby able to reproduce the previous results for the main relaxation. [11]

The complex dielectric constant is often graphically displayed in a Cole-Cole plot, with the imaginary part plotted along the y-axis and the real part plotted along the x-axis, allowing the real and imaginary parts to be considered simultaneously. The Cole-Cole plot for pure propylene carbonate is shown in Figure 3.

With our understanding of THz spectroscopy for pure liquids validated, we addressed our main topic of THz spectroscopy of electrolytic solutions. Data was taken for solutions of four lithium salts in water and two lithium salts in propylene carbonate (PC) as a function of increasing salt concentration. The concentrations are as follows. In PC, concentrations of Lithium Trifluoromethanesulfonate (Li Triflate) were 0.1, 0.5, 1.0, 2.0, and 3.0 M, and concentrations of Lithium Imide (Li Imide) were 0.1, 0.5, and 1.0 M. For aqueous solutions of Li Triflate, Li Imide, and Lithium Chloride (Li Chloride), the concentrations were 0.1, 0.5, 1.0, 2.0, and 3.0 M, as well as Li Chloride at 5.0 M. For aqueous solutions of Lithium Amide (Li Amide) the concentrations were 0.1 and 1.0 M. The results were fit to a two-term Debye relaxation model for water solutions and a three-term Debye relaxation model for the PC solutions. Values for the Debye parameters resulting from these fits are given in the Tables 2 for propylene carbonate solutions and Table 3 for aqueous solutions.

According to the current understanding, for all solvent-salt combinations, ϵ_s should decrease with increasing salt concentration. This decrease is attributed to the combination of three effects:

- (1) Irrotational bonding caused by the high field strength at ionic surfaces that prevents solvent molecules in the first solvation shell from responding as freely to the applied external field.
- (2) Excluded volume effects, which refer to dilution of the solvent.
- (3) Kinetic depolarization due to relative opposing motion between solvent molecules and ions in the applied field; this motion causes friction which

increases viscosity thereby decreasing the ability of the solvent molecules to respond to an applied field.

In contrast to the behavior of the static dielectric constant, the first (main) relaxation time, τ_1 , can either decrease or increase depending on the nature of the solvent. In water τ_1 is thought to depend on the average time that an individual water molecule remains in the bulk state, that is, with three to four hydrogen bonds, before reaching a state with only one (or zero) hydrogen bond. With the addition of salts, the hydrogen-bonding structure of the liquid is interrupted and this decrease in the extent of the structure is manifested in the decrease in τ_1 . The second (fast) relaxation time is correlated with the rotation of molecules that are in the 1-hydrogen-bond state, therefore the second relaxation process is expected to be left essentially untouched by the addition of ions.

For electrolytic solutions of propylene carbonate, PC, a three-term relaxation model has been proposed [11]. There appears to be evidence that there are two rotational environments in PC, which account for the first and second relaxations; the third may indicate librational motion. For the first (main) relaxation, τ_1 is expected to increase with increasing salt concentration because, in this dipolar aprotic solvent, the addition of ions causes more interactions and clumping of the solvent molecules about the ions thereby increasing the time required for the bulk solvent to relax.

Our trends for aqueous solutions of lithium salts, as shown in Figures 4, conform to the current understanding discussed above. As expected, ϵ_s decreases with increasing concentration for all four salts; the order, from most affected ϵ_s to least, is: Li Imide > Li Amide > Li Chloride > Li Triflate. Likewise, the first relaxation time, τ_1 , also decreases with increasing concentration with the same ordering of salts. We also note that ϵ_2 increases with increasing concentration of all four salts. The value for τ_2 stays fairly constant, at the pure liquid value, with increasing concentration for all the salts, which was expected. ϵ_∞ is also fairly constant.

We considered two salts, Li Triflate and Li Imide, in PC. Figure 3 reveals the Cole-Cole plot of Li Triflate as a function of concentration. The trends of the Debye parameters as a function of concentration are plotted in Figure 5 for both salts. As expected, for both salts, ϵ_s decreased with increasing concentration, while τ_1 increased. Li Imide induced the greater decrease

in ϵ_s and the larger increase in τ_1 , as compare to Li Triflate. Though ϵ_∞ shows increasing behavior as a function of concentration, all of the other intermediate ϵ 's and τ 's show a plateau-like behavior out to 1 M; the parameter values for concentrations greater than or equal to 2 M (for Li Triflate) show a distinct drop-off. Interpretation of this drop-off, based on our preliminary results, must include a discussion of the ratio of solvent molecules to Li ions. At lower concentrations (0.1 to 1.0 M) the ratio of cations to solvent molecules ranges from approximately 1:100 to 1:10; by contrast, the ratios for the 2 and 3 M solutions are 1:6 and 1:4, respectively. Further investigations of solutions with concentrations between 1 and 2 M will elucidate the transitional behavior of the drop-off.

Our understanding of the behavior of salts in aprotic solvents would lead us to expect the opposite ordering of the salts in PC as compared to water. Our data fulfills this expectation: the order of most affected ϵ_s and τ_1 is Li Imide > Li Triflate in water, and Li Triflate > Li Imide in PC. In water, we postulate that Li Triflate has more ion pairing than Li Imide, and because more free cations must be solvated for Li Imide, more disruption occurs in the hydrogen-bonding structure of the solvent. In PC, more ion pairing is expected than in water because fewer large PC molecules can be packed around the cation than small water molecules (PC molecules are a factor of 5 larger in radius than water molecules). PC molecules associated with ion pairs respond more slowly to applied external fields, and since Li Triflate appears to show more ion pairing than Li Imide, we would expect Li Triflate to show a greater affect in PC than Li Imide. These expectations are supported by the data.

We developed the equilibrium solvation theory necessary to address ion pairing, resulting in the ability to predict activated complex geometries and activation free energies for chemically realistic molecular models. We now understand the role of solvent molecules in establishing transition state properties, including the reaction path for decomposition of the complex. Thus we now possess the necessary theoretical and experimental tools to unravel the solvation dynamics associated with ion pairs in solution [P4-P6]. Preliminary molecular dynamics simulations were also be carried out for the solvents studied and the results used to interpret the permittivity data.

In conclusion, we studied the solvation dynamics associated with ion pairs in solution using the technique of femtosecond terahertz time domain transmission spectroscopy. The objective

of this proposal was to probe, on a molecular and intermolecular scale both experimentally and theoretically, the mechanisms and timescales involved in both the formation and dynamic behavior of ion pairs in solution. To accomplish this goal we further developed the technique of femtosecond terahertz time domain transmission spectroscopy for the study of dynamic molecular interactions in liquids. Our results validate terahertz spectroscopy as a technique for the investigation of the solvation dynamics in electrolytic solutions of technological importance.

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Figure Captions:

1. Femtosecond terahertz time domain spectrometer.
2. Representative terahertz waveforms transmitted through the cell with and without liquid sample.
3. Cole-Cole plot for pure propylene carbonate and solutions of Li Triflate in PC. The small amplitude oscillations observed in the data are artifacts due to a slight lack of parallelism in the two cell walls.
4. Debye fit parameters for lithium salts in water as a function of concentration.
5. Debye fit parameters for lithium salts in propylene carbonate as a function of concentration.

Table Captions

- 1) Debye fit parameters for propylene carbonate and water.
- 2) Debye fit parameters for lithium salts in propylene carbonate.
- 3) Debye fit parameters for lithium salts in water.

THz Setup: generation and detection

Figure 1

Figure 2: Example waveforms for cell with liquid sample and empty

Figure 3: Cole-Cole plot for pure PC and solutions of Li Triflate in PC. The small amplitude oscillations apparent in the data are due to a slight lack of parallelism in the two cell walls.

Figure 4: Debye fit parameters of Lithium salts in water as functions of concentration

Figure 5: Debye fit parameters of Lithium salts in PC as functions of concentration

Table 2(a)

Lithium Triflate in Propylene Carbonate: Debye Fits

	Pure PC	0.1 M Li Triflate	0.5 M Li Triflate	1.0 M Li Triflate	2.0 M Li Triflate	3.0 M Li Triflate
ϵ_s	64.79 (3.16)	61.23 (2.97)	54.56 (2.48)	52.31 (1.53)	40.25 (5.33)	31.17 (53)
τ_1	40.26 ps (1.42)	40.56 ps (1.59)	45.05 ps (2.44)	47.87 ps (1.62)	56.92 ps (6.77)	53.57 ps (2.91)
ϵ_2	5.74 (22)	5.65 (13)	5.86 (21)	5.58 (13)	4.83 (07)	4.48 (06)
τ_2	1.39 ps (10)	1.37 ps (04)	1.33 ps (09)	1.30 ps (07)	0.69 ps (06)	0.64 ps (07)
ϵ_3	3.34 (05)	3.39 (02)	3.37 (05)	3.42 (03)	3.09 (13)	3.04 (15)
τ_3	0.21 ps (01)	0.19 ps (00)	0.21 ps (01)	0.21 ps (01)	0.14 ps (03)	0.18 ps (03)
ϵ_∞	1.83 (04)	1.83 (02)	1.96 (03)	1.97 (03)	1.87 (12)	2.10 (04)
χ^2	0.118	0.0607	0.0963	0.0604	0.107	0.0655

Table 2(b)

Lithium Imide in Propylene Carbonate: Debye Fits

	Pure PC	0.1 M Li Imide	0.5 M Li Imide	1.0 M Li Imide
ϵ_s	64.79 (3.16)	65.16 (1.22)	58.82 (1.47)	49.35 (1.95)
τ_1	40.26 ps (1.42)	42.07 ps (84)	41.21 ps (81)	46.82 ps (1.93)
ϵ_2	5.74 (22)	5.79 (09)	5.69 (11)	5.60 (16)
τ_2	1.39 ps (10)	1.33 ps (04)	1.35 ps (06)	1.36 ps (07)
ϵ_3	3.34 (05)	3.32 (02)	3.54 (03)	3.48 (02)
τ_3	0.21 ps (01)	0.20 ps (01)	0.22 ps (01)	0.21 ps (01)
ϵ_∞	1.83 (04)	1.88 (02)	1.99 (02)	1.93 (02)
χ^2	0.118	0.0986	0.0683	0.0398

Table 3(a)

Lithium Triflate in Water: Debye Fits

	Pure Water	0.1 M Li Triflate	0.5 M Li Triflate	1.0 M Li Triflate	2.0 M Li Triflate	3.0 M Li Triflate
ϵ_s	78.96 (6.94)	74.56 (58)	70.51 (40)	66.56 (32)	52.49 (32)	47.46 (26)
τ_1	7.87 ps (79)	7.50 ps (06)	7.47 ps (00)	7.29 ps (00)	6.59 ps (05)	6.53 ps (03)
ϵ_2	4.80 (10)	4.84 (03)	4.88 (05)	5.01 (00)	5.45 (03)	5.55 (03)
τ_2	0.18 ps (03)	0.12 ps (01)	0.16 ps (02)	0.15 ps (01)	0.29 ps (00)	0.29 ps (01)
ϵ_∞	3.24 (18)	2.51 (22)	2.95 (22)	2.69 (15)	3.41 (02)	3.48 (03)
χ^2	1.25	1.33	1.76	1.53	1.04	0.56

Table 3(b)

Lithium Imide in Water: Debye Fits

	Pure Water	0.1 M Li Imide	0.5 M Li Imide	1.0 M Li Imide	2.0 M Li Imide	3.0 M Li Imide
ϵ_s	78.96 (6.94)	68.60 (88)	57.50 (63)	47.20 (35)	32.97 (49)	25.59 (25)
τ_1	7.87 ps (79)	6.98 ps (09)	6.51 ps (01)	5.65 ps (00)	5.21 ps (10)	4.69 ps (00)
ϵ_2	4.80 (10)	4.76 (06)	4.89 (08)	4.75 (04)	5.26 (04)	5.23 (05)
τ_2	0.18 ps (03)	0.14 ps (02)	0.17 ps (02)	0.16 ps (01)	0.29 ps (01)	0.29 ps (01)
ϵ_∞	3.24 (18)	2.47 (24)	2.77 (16)	2.45 (13)	3.22 (03)	3.08 (04)
χ^2	1.25	3.56	3.23	2.40	0.914	0.877

Table 3(c)

Lithium Amide in Water: Debye Fits

	Pure Water	0.1 M Li Amide	1.0 M Li Amide
ϵ_s	78.96 (6.94)	72.22 (80)	54.55 (24)
τ_1	7.87 ps (79)	7.60 ps (00)	6.15 ps (03)
ϵ_2	4.80 (10)	4.93 (05)	5.06 (03)
τ_2	0.18 ps (03)	0.20 ps (02)	0.19 ps (01)
ϵ_∞	3.24 (18)	3.04 (11)	3.22 (06)
χ^2	1.25	1.33	0.71

Table 3(d)

Lithium Chloride in Water: Debye Fits

	Pure Water	0.1 M Li Chloride	0.5 M Li Chloride	1.0 M Li Chloride	2.0 M Li Chloride	3.0 M Li Chloride	5.0 M Li Chloride
ϵ_s	78.96 (6.94)	70.22 (47)	68.21 (40)	62.07 (3.25)	58.75 (14)	56.37 (42)	46.63 (30)
τ_1	7.87 ps (79)	7.15 ps (05)	6.97 ps (04)	6.34 ps (40)	5.80 ps (00)	5.73 ps (05)	5.20 ps (04)
ϵ_2	4.80 (10)	4.93 (03)	5.12 (03)	5.21 (07)	5.50 (00)	5.62 (05)	6.06 (04)
τ_2	0.18 ps (03)	0.20 ps (01)	0.22 ps (01)	0.17 ps (02)	0.23 ps (00)	0.23 ps (02)	0.25 ps (01)
ϵ_∞	3.24 (18)	3.18 (17)	3.31 (01)	2.99 (15)	3.51 (04)	3.60 (17)	3.66 (17)
χ^2	1.25	0.61	0.70	0.56	0.43	1.08	0.68

Figure 4: Debye fit parameters of Lithium salts in water as functions of concentration

Figure 5: Debye fit parameters of Lithium salts in PC as functions of concentration

Table 2(a)

Lithium Triflate in Propylene Carbonate: Debye Fits

	Pure PC	0.1 M Li Triflate	0.5 M Li Triflate	1.0 M Li Triflate	2.0 M Li Triflate	3.0 M Li Triflate
ϵ_s	64.79 (3.16)	61.23 (2.97)	54.56 (2.48)	52.31 (1.53)	40.25 (5.33)	31.17 (53)
τ_1	40.26 ps (1.42)	40.56 ps (1.59)	45.05 ps (2.44)	47.87 ps (1.62)	56.92 ps (6.77)	53.57 ps (2.91)
ϵ_2	5.74 (22)	5.65 (13)	5.86 (21)	5.58 (13)	4.83 (07)	4.48 (06)
τ_2	1.39 ps (10)	1.37 ps (04)	1.33 ps (09)	1.30 ps (07)	0.69 ps (06)	0.64 ps (07)
ϵ_3	3.34 (05)	3.39 (02)	3.37 (05)	3.42 (03)	3.09 (13)	3.04 (15)
τ_3	0.21 ps (01)	0.19 ps (00)	0.21 ps (01)	0.21 ps (01)	0.14 ps (03)	0.18 ps (03)
ϵ_∞	1.83 (04)	1.83 (02)	1.96 (03)	1.97 (03)	1.87 (12)	2.10 (04)
χ^2	0.118	0.0607	0.0963	0.0604	0.107	0.0655

Table 2(b)

Lithium Imide in Propylene Carbonate: Debye Fits

	Pure PC	0.1 M Li Imide	0.5 M Li Imide	1.0 M Li Imide
ϵ_s	64.79 (3.16)	65.16 (1.22)	58.82 (1.47)	49.35 (1.95)
τ_1	40.26 ps (1.42)	42.07 ps (84)	41.21 ps (81)	46.82 ps (1.93)
ϵ_2	5.74 (22)	5.79 (09)	5.69 (11)	5.60 (16)
τ_2	1.39 ps (10)	1.33 ps (04)	1.35 ps (06)	1.36 ps (07)
ϵ_3	3.34 (05)	3.32 (02)	3.54 (03)	3.48 (02)
τ_3	0.21 ps (01)	0.20 ps (01)	0.22 ps (01)	0.21 ps (01)
ϵ_∞	1.83 (04)	1.88 (02)	1.99 (02)	1.93 (02)
χ^2	0.118	0.0986	0.0683	0.0398

Table 3(a)

Lithium Triflate in Water: Debye Fits

	Pure Water	0.1 M Li Triflate	0.5 M Li Triflate	1.0 M Li Triflate	2.0 M Li Triflate	3.0 M Li Triflate
ϵ_s	78.96 (6.94)	74.56 (58)	70.51 (40)	66.56 (32)	52.49 (32)	47.46 (26)
τ_1	7.87 ps (79)	7.50 ps (06)	7.47 ps (00)	7.29 ps (00)	6.59 ps (05)	6.53 ps (03)
ϵ_2	4.80 (10)	4.84 (03)	4.88 (05)	5.01 (00)	5.45 (03)	5.55 (03)
τ_2	0.18 ps (03)	0.12 ps (01)	0.16 ps (02)	0.15 ps (01)	0.29 ps (00)	0.29 ps (01)
ϵ_∞	3.24 (18)	2.51 (22)	2.95 (22)	2.69 (15)	3.41 (02)	3.48 (03)
X^2	1.25	1.33	1.76	1.53	1.04	0.56

Table 3(b)

Lithium Imide in Water: Debye Fits

	Pure Water	0.1 M Li Imide	0.5 M Li Imide	1.0 M Li Imide	2.0 M Li Imide	3.0 M Li Imide
ϵ_s	78.96 (6.94)	68.60 (88)	57.50 (63)	47.20 (35)	32.97 (49)	25.59 (25)
τ_1	7.87 ps (79)	6.98 ps (09)	6.51 ps (01)	5.65 ps (00)	5.21 ps (10)	4.69 ps (00)
ϵ_2	4.80 (10)	4.76 (06)	4.89 (08)	4.75 (04)	5.26 (04)	5.23 (05)
τ_2	0.18 ps (03)	0.14 ps (02)	0.17 ps (02)	0.16 ps (01)	0.29 ps (01)	0.29 ps (01)
ϵ_∞	3.24 (18)	2.47 (24)	2.77 (16)	2.45 (13)	3.22 (03)	3.08 (04)
X^2	1.25	3.56	3.23	2.40	0.914	0.877

Table 3(c)

Lithium Amide in Water: Debye Fits

	Pure Water	0.1 M Li Amide		1.0 M Li Amide		
ϵ_s	78.96 (6.94)	72.22 (80)		54.55 (24)		
τ_1	7.87 ps (79)	7.60 ps (00)		6.15 ps (03)		
ϵ_2	4.80 (10)	4.93 (05)		5.06 (03)		
τ_2	0.18 ps (03)	0.20 ps (02)		0.19 ps (01)		
ϵ_∞	3.24 (18)	3.04 (11)		3.22 (06)		
X^2	1.25	1.33		0.71		

Table 3(d)

Lithium Chloride in Water: Debye Fits

	Pure Water	0.1 M Li Chloride	0.5 M Li Chloride	1.0 M Li Chloride	2.0 M Li Chloride	3.0 M Li Chloride	5.0 M Li Chloride
ϵ_s	78.96 (6.94)	70.22 (47)	68.21 (40)	62.07 (3.25)	58.75 (14)	56.37 (42)	46.63 (30)
τ_1	7.87 ps (79)	7.15 ps (05)	6.97 ps (04)	6.34 ps (40)	5.80 ps (00)	5.73 ps (05)	5.20 ps (04)
ϵ_2	4.80 (10)	4.93 (03)	5.12 (03)	5.21 (07)	5.50 (00)	5.62 (05)	6.06 (04)
τ_2	0.18 ps (03)	0.20 ps (01)	0.22 ps (01)	0.17 ps (02)	0.23 ps (00)	0.23 ps (02)	0.25 ps (01)
ϵ_∞	3.24 (18)	3.18 (17)	3.31 (01)	2.99 (15)	3.51 (04)	3.60 (17)	3.66 (17)
X^2	1.25	0.61	0.70	0.56	0.43	1.08	0.68