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SOLVATION AND ELECTRON TRANSFER

IN IONIC LIQUIDS

A Dissertation in

Chemistry

by

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ABSTRACT

The complete solvation response of coumarin 153 (C153) in 21 neat ionic liquids (ILs) has been determined over the time range from 100 fs to 20 ns by combining broadband fluorescence upconversion (FLUPS) and time-correlated single photon counting (TCSPC) measurements. The 80 fs time resolution of FLUPS provides accurate results for the fast dynamics and the long time window (20 ns) of TCSPC enables observation of the slow portion of the dynamics. These complete solvation response functions are compared to the solvation dynamics predicted by a simple dielectric continuum model. This dielectric continuum model works well in conventional solvents. However, the dynamics predicted in most ionic liquids are systematically faster than those observed, on average by a factor of 3-5.

To bridge the knowledge gap between neat ILs and conventional solvents, the solvation dynamics of C153 in the mixture of a simple ionic liquid $[Im_{41}][BF_4]$ and the prototypical dipolar solvent acetonitrile has been studied. This mixture was chosen because it is expected to exhibit the simplest behavior without much preferential solvation is not expected to complicate interpretation due to the similar 'polarity' of acetonitrile and $[Im_{41}][BF_4]$. The solvation energies of C153 in this mixture were determined and the complete solvation dynamics of C153 were measured and compared to simple dielectric continuum predictions. In addition, the rotational dynamics of C153 in the mixtures of $[Im_{41}][BF_4]$ and acetonitrile were studied. The rotation times $<\tau_{rot}>$ of C153 vary with viscosity η in the manner $<\tau_{rot}> \propto \eta^p$ with p= 0.9.

Steady-state and picosecond time-resolved emission spectroscopy are used to monitor the bimolecular electron transfer reaction between the electron acceptor 9,10-

dicyanoanthracene in its S₁ state and the donor N,N-dimethylaniline in a variety of ionic liquids and several conventional solvents. Detailed study of this quenching reaction was undertaken in order to better understand why rates reported for similar diffusion-limited reactions in ionic liquids sometimes appear much higher than expected given the viscous nature of these liquids. Consistent with previous studies, Stern-Volmer analyses of steadystate and lifetime data provide effective quenching rate constants k_q , which are often 10 to 100-fold larger than simple predictions for diffusion-limited rate constants $k_{\rm D}$ in ionic liquids. Similar departures from k_D are also observed in conventional organic solvents having comparably high viscosities, indicating that this behavior is not unique to ionic liquids. A more complete analysis of the quenching data using a model combining approximate solution of the spherically symmetric diffusion equation with a Marcus-type description of electron transfer reveals the reasons for frequent observation of $k_q >> k_D$. The primary cause is that the high viscosities typical of ionic liquids emphasize the transient component of diffusion-limited reactions, which renders the interpretation of rate constants derived from Stern-Volmer analyses ambiguous. Using a more appropriate description of the quenching process enables satisfactory fits of data in both ionic liquid and conventional solvents using a single set of physically reasonable electron transfer parameters. Doing so requires diffusion coefficients in ionic liquids to exceed hydrodynamic predictions by significant factors, typically in the range of 3-10. Direct NMR measurements of solute diffusion confirm this enhanced diffusion in ionic liquids.

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GLOSSARY OF ACRONYMS

A	anion
ACN	acetonitrile
С	cation
C153	coumarin 153
СНХ	cyclohexane
D	donor
DCA	9,10-dicyanoanthracene
DMA	N,N-dimethylaniline
EG	ethylene glycol
F	fluorophore
FLUPS	fluorescence up-conversion spectroscopy
FWHM	full width at half maximum
G	Gaussian function
GLY	glycerol
IL	ionic liquid
IRF	instrumental response function
OD	optical density
Q	quencher
SE	Stokes-Einstein
SS	steady-state
SV	Stern-Volmer
TCSPC	time-correlated single photon counting

TR time-resolved

- vdW van der Waals
- VFT Vogel-Fulcher-Tammann

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Chapter 1. Introduction

1.1.Ionic Liquids

An ionic liquid (IL) is a salt having a freezing point below 100°C. Many ILs remain liquid even at room temperature. Room temperature ionic liquids have been known for about a century. The first observation of a room temperature ionic liquid was reported by Paul Walden in 1914,¹ but little research was performed on low melting salts until 1992 when Wilkes and Zaworotko² described the synthesis of 1-ethyl-3-methylimidazolium based ionic liquids which were both air and water stable. Figure 1.1 shows some typical cations and anions of ionic liquids.

Ionic liquids have attracted tremendous attention due to their distinctive properties, like the low volatility, intrinsic conductivity, high thermal stability and tailorability. Currently, applications of ionic liquids permeate most fields of chemistry. Among other applications, ionic liquids are being used as electrolytes in photovoltaic cells³ and supercapacitors⁴, as green solvents for synthesis and catalysis, as separation tools for mixtures, and as media for storage and transport of toxic gases⁵. For all of these emerging applications, an understanding of the basic physical chemistry of ILs and how they behave as solvent media for chemical reactions is essential.

Most chemical reactions take place in solution, which makes it very important to choose the proper solvent. The tailorability of ionic liquids makes them stand out as "designer solvents". For example, the alkyl chains of the cation, or less commonly the anion, can be easily varied to make a solvent of the desired size, viscosity and polarity.

For fundamental studies, it is thus easy to produce a series of ILs with variable properties. In addition, ionic liquids can be easily prepared through simple ion exchange reactions.



Figure 1.1: Structures of typical ionic liquids components.

Ionic liquids are often used in conjunction with conventional organic solvents as a means of increasing the fluidity and conductivity of these high-viscosity solvents. Thus, there are practical reasons for understanding solvation in mixtures of ILs with conventional solvents. Another reason for studying such mixtures is to bridge the knowledge gap between what is well known in conventional solvents and what is poorly understood about ionic liquids.

1.2.Solvation Dynamics

Solvation dynamics refers to the response of a solvent after a perturbation to a solute's charge distribution. Solvation dynamics is a key determinant of the coupling between reactions such as electron transfer and a solution environment. It is therefore important to understand this fundamental aspect of liquid state behavior.



Figure 1.2: ⁶ Diagram of solvation dynamics for a typical polar solvent. S_0 and S_1 represent the ground state and the first excitation state free energy wells of a typical probe.

Figure 1.2^6 illustrates the idea behind time-resolved emission measurements of solvation dynamics. The purple circle represents the solute molecule whose dipole moment increases after being excited from its ground state (S₀) to its excited electronic

state (S₁). The perturbation caused by the excitation of the probe disturbs the solvation equilibrium and surrounding solvent molecules rearrange to approach a new equilibrium state. One can use the frequencies time-dependent fluorescence spectra (S₁ \rightarrow S₀) to obtain information about the temporal response of the solvent to the solute excitation.

The selection of a suitable solute is very important for solvation dynamics studies. For example, one cannot observe the complete solvation response if the probe has a shorter life time than the solvation time. Coumarin 153 has a single low-lying excited state, simple solvatochromatic behavior, a relatively long lifetime (~6 ns in most ILs) and a rigid structure.⁷ All of these properties are advantages for solvation dynamics studies of ionic liquids and C153 is used exclusively in this thesis.

Solvation dynamics in conventional dipolar solvents⁸⁻¹³ including water¹⁴ has been broadly studied starting from 1980s. The results of such studies brought us a good understanding of the temporal aspects of solvation in conventional solvents. With the emergence of ionic liquids and their aforementioned potential applications, this new class of solvent has regenerated interest in solvation dynamics.^{15,16,17,18} One can study the solvation dynamics of ionic liquids either experimentally or theoretically. In this thesis, we focus on experimental observations. Other group members have recently performed molecular dynamics simulatons to study this phenomenon from a theoretical perspective.^{17,18} Experimental characterizations of solvation dynamics in ionic liquids began with the work of Karmakar and Samanta¹⁹ about a decade ago. This seminal work and many subsequent studies used time-correlated single photon counting (TCSPC). This popular technique has 20 ps time resolution in the best of cases. Early work by the Maroncelli group²⁰ showed that a significant portion, roughly half of the solvation response in common ionic liquids, is faster than what can be detected with TCSPC. A few groups have more recently used other techniques²¹⁻²⁵ with sufficient time resolution to accurately characterize the faster portions of solvation dynamics in ionic liquids. In Chapters 3 and 4, we combine the techniques of broadband femtosecond fluorescence upconversion spectroscopy (FLUPS) with 80 fs time resolution^{26,27} and TCSPC with 25 ps time resolution²⁸ but a much broader observation window. In order to cover the range 100 fs ~ 20 ns, the results of FLUPS and TCSPC were combined to capture the complete solvation response in ionic liquids and ionic liquid + polar solvent mixtures.

1.3.Bimolecular Electron Transfer

Electron transfer is a key component in many applications of ionic liquids, for example, their use in photovoltaic cells²⁹. For this reason, it is important to understand electrons transport and transfer in ionic liquids. In particular, it is important to learn the extent to which our understanding of electron transfer in conventional solvents is transferrable to ionic liquids.

Bimolecular electron transfer reactions have been previously studied in ionic liquids by several groups.³⁰⁻³⁸ These studies have shown that while the mechanisms of reaction are typically the same as in conventional solvents with the similar polarity, the high viscosities of ionic liquids often produce slower rates. The interesting result is that the slower rates in ILs are much higher than what the simple Smoluchowski model predicts. In Chapter 5, studies of bimolecular electron transfer in both ILs and conventional solvents using steady-state and picosecond time-resolved emission

techniques are discussed. The objective is to clearly understand why diffusion-limited electron transfer reactions sometimes appear to be much faster than expected based on viscosity scaling the rates observed in conventional solvents.

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Chapter 2. Experimental and Data Analysis Methods

2.1 Experimental Methods

2.1.1. Materials

The ionic liquids employed in this thesis are illustrated in Figure 2.1. The cations are ethylammonium $(N_{2,0,0,0}^+)$, *N*-alkyl-*N*-methylpyrrolidinium $(Pr_{n,1}^+)$, 1-alkyl-3- $(S(Et)_{3}^{+})$ methylimidazolium $(Im_{n.1}^{+}),$ triethylsulfonium and $(P_{14,6,6,6}^{+}).$ trihexyl(tetracdecyl)phosphonium The counter anions are bis(trifluoromethylsulfonyl)imide (Tf_2N^-), triflate (TfO^-), dicyanamide (DCA⁻), tris(pentafluoroethyl) hexafluorophosphate $(PF_{6}),$ tetrafluoroborate $(BF_{4}),$ trifluorophosphate (FAP⁻) and nitrate (NO₃⁻).



Figure 2.1: Structures of the ionic liquid components studied and their abbreviations.

The fluorophore, Coumarin 153 (C153, laser grade, **Figure 2.2**) was purchased from Exciton and used as received. C153 is applied to study the solvation dynamics of about 20 pure ionic liquids (Chapter 3) and the mixture $[Im_{41}][BF_4]$ + acetonitrile (Chapter 4). **Figure 2.2** also shows the fluorophore and the quencher studied for bimolecular electron transfer in Chapter 5. The fluorophore 9,10-dicyanoanthracene (DCA) was selected because it does not undergo a dynamic Stokes shift, which simplifies the observation of "dynamic" quenching. DCA is also chosen due to its long lifetime, 13 ns. DCA was recrystallized from pyridine/acetonitrile.¹ *N,N*-dimethylaniline (DMA, redistilled, 99.5+%) was used as received from Aldrich.



Figure 2.2: Structures of probe coumarin 153 (C153), the electron acceptor (DCA) and donor (DMA).

All of the ionic liquids studied were dried under vacuum at 45 °C overnight prior to measurement. The water contents of samples were measured using a Mettler-Toledo DL39 Karl Fischer coulometer, and were below 100 ppm by weight prior to use for most ionic liquids in this study. The viscosities of most pure ILs (Chapter 3) were measured with a Brookfield Model HBDV-III+CP cone/plate viscometer. The viscometer was calibrated using the NIST-certified viscosity standards N75 and N100. In most cases, viscosities were measured from 5 to 65 °C with an increment of 5°C. The Vogel-Fulcher-Tammann $(VFT)^2$ Equation (Eq. 2.1) was used to characterize these viscosity data.

$$\ln(\eta/cP) = A + \frac{B}{(T - T_0)/K}$$
(2.1)

In this expression, η is the liquid viscosity at temperature *T*, and *A*, *B* and *T*₀ are fitting parameters. The viscosities of the mixture $[Im_{41}][BF_4]$ + acetonitrile (Chapter 4) were measured at 20.5 °C using Cannon-Fenske Routine Viscometers (CFRV) of varying sizes from model #50 (0.8-4 cSt) to #200 (20-100 cSt). At least three values were obtained for each mixture.

2.1.2. Steady-State Measurements

Steady-state absorption spectra were measured using a Hitachi U-3000 UV/Vis spectrometer at 1 nm resolution. Most absorption spectra were measured at room temperature 21 ± 2 °C. Steady-state fluorescence spectra were recorded with a SPEX Fluorolog 212 spectrometer (2 nm resolution) at the desired temperature (\pm 0.1°C) controlled using a circulating water bath. The emission correction file of the fluorometer was made following the method described by Gardecki and Maroncelli.³ To obtain the correction file, the emission spectra of six dyes covering the range 310-840 nm were measured and the normalized spectra compared to standard emission spectra.³ Quartz cuvettes with 1 cm light path were used for the absorption and right-angle steady-state

emission measurements. The optical densities of the fluorescence samples were kept around 0.1 O.D. To reduce the effects of impurity emission, front-face geometry emission measurements were performed in ILs which had relatively high fluorescence backgrounds. Quartz cuvettes with 1 mm light path were used for the absorption and front-face steady-state emission measurements. For those measurements, the optical densities of the samples were kept around 1. The emission spectra of C153 in $[Im_{41}][BF_4]$ were measured under both right-angle and front-face conditions to check the reliability of the front-face experiment. Except for temperature-dependent measurements, all of the solvation dynamics measurements in Chapter 3 and 4 were maintained at 20.5± 0.1°C due to the limited temperature control of the fluorescence up-conversion system, while the bimolecular electron transfer in Chapter 5 was studied at 25.0±0.1°C.

2.1.3. Time- Correlated Single Photon Counting Measurements

The time-resolved fluorescence data were recorded using a home-built timecorrelated single photon counting (TCSPC) setup. **Figure 2.3** shows a schematic of the TCSPC instrument.⁴ As shown in this illustration, the fundamental laser pulse (700~1000 nm) was generated by a cavity-dumped Ti:sapphire laser, which was doubled by a BBO crystal. The frequency-doubled pulse excited the sample after travelling through a polarizer that only transmits vertical light. With the exception of anisotropy experiments, fluorescence decays were collected at the magic angle (54.7°) with respect to the excitation to eliminate the effects of solute rotation. A scattering solution was used to determine the instrumental response function. In all of the TCSPC experiments discussed here the instrument response function had a width of ~25 ps (full width at half maximum). The typical time window for data collection was about three times the fluorophore lifetime. All decays were fit to multi-exponential functions using a convolute-and-compare algorithm (see Section 2.2.2).



Figure 2.3: Time-correlated single photon counting setup. M: Mirror. BS: beam splitter. PD: photodiode. $\lambda/2$: half-wave plate. FL: focus lens. BBO: beta barium borate (β -BaB₂O₄). PL: polarizer. MCP-PMT: microchannel plate photomultiplier tube. TAC: time-to-amplitude converter. MCA: multichannel analyzer.



2.1.4. Fluorescence Up-Conversion Measurements

Figure 2.4:⁵ Schematic of the broadband Fluorescence UP-conversion Spectrometer (FLUPS). KDP II, 2-mm-thick frequency-doubling KDP crystal; Pr1, Pr2, Pr3, SF59 prisms; M1, M5, plane mirrors; M2,M3,M4,M6, spherical mirrors; L1,L2,L3,L4,L5, BK7 lenses; P1, P2, polarizers.

A broadband fluorescence upconversion spectrometer (FLUPS) with femtosecond time-resolution^{5,6} was applied to measure fast solvation dynamics by our collaborators, Xinxing Zhang and Prof. Nikolaus Ernsting from Humboldt University of Berlin. **Figure 2.4** shows a schematic of the FLUPS measurement. A Ti:sapphire laser (FEMTOLASERS *sPro*) generates 500 μ J pulses at 800 nm a 500 Hz repetition rate. This fundamental laser pulse is then split into two beams. One part was used as gating pulse which was generated by a traveling-wave optical parametric amplifier of superfluorescence (TOPAS, LIGHTCONVERSION). The other portion was frequency doubled to 400 nm pulses with 40 fs FWHM after compression and used as the optical pump. This beam was attenuated (~ 1 μ J) and focused onto the sample by a thin lens (fl = 200 mm, fused silica) to a spot diameter of 0.1 mm. The sum frequency signal was then generated by focusing the

delayed fluorescence and gating pulse into a potassium dihydrogen phosphate (KDP) crystal. The sample cell was kept in a sealed flowing argon environment consisting of a glass chamber with P_2O_5 desiccant. The water fraction could typically be maintained to lower than 200 ppm by weight using this setup. FLUPS measurements were performed at room temperature, 20.5 ± 1 °C.

2.1.5. Diffusion Measurements

Diffusion coefficients reported in Chapter 4 and 5 were measured by Anne Kaintz in the Maroncelli group. These measurements employed ¹H data measured on Bruker DRX-400 and AV-III-850 spectrometers using the longitudinal eddy current delay stimulated echo pulse sequence with bipolar gradient pulses.⁷ Diffusion coefficients Dwere then calculated according to Equation 2.2.

$$\frac{I}{I_0} = \exp\left(-D\gamma^2\delta^2 g^2 \left(\Delta + \frac{\delta}{2} + \frac{\tau}{2}\right)\right)$$
(2.2)

where I_0 is the initial peak intensity, γ the gyro-magnetic ratio of the nucleus, δ the gradient pulse duration, g the gradient amplitude, Δ the time between gradient pulse pairs, and τ the time allowed for gradient recovery before the next pulse.

2.2.Data Analysis Methods

2.2.1. Deconvolution of TCSPC Decays

To obtain the highest effective time resolution from TCSPC, deconvolution is used to partially remove the effects of the finite time resolution of the experimental setup. To do so, an appropriate instrument response function, R(t) which depends on the characteristics of both the detector and the timing electronics, is needed. We determine R(t) experimentally by the response observed from a scattering solution. The measured fluorescence decay $I_M(t)$ is a convolution of the ideal "real" decay $I_R(t)$ and the instrument response function using the following equation,⁸

$$I_M(t) = \int_0^t I_R(t-t')R(t')dt'$$
(2.3)

This convolution means that the measured emission intensity at time t is a weighted sum of all the emission between time zero and that time.

A nonlinear least squares (NLLS) data processing method is then applied to fit the ideal decay to some assumed functional form. The goal of a least square analysis is to fit the data and test whether the chosen mathematical method is consistent with the real data points. The least square analysis is applicable if the data satisfies certain assumptions. The main assumptions are that there is a sufficient number of independent data points, the uncertainties are Gaussian distributed and there is no systematic error.⁸ For TCSPC measurements of bulk samples, these requirements are usually satisfied. The next step is getting the fitting parameters from an appropriate mathematical model. The value of χ^2 ,

the goodness-of-fit parameter, is used to determine whether the mathematical model is consistent with the data or not. χ^2 is given by the following equation,⁸

$$\chi^{2} = \sum_{k=1}^{n} \frac{1}{\sigma_{k}^{2}} [I_{M}(t_{k}) - I_{C}(t_{k})]^{2}$$
(2.4)

where σ_k is the standard deviation of each data point *k*, *n* is the number of data points and $I_C(t_k)$ represents the calculated decay using the fitting parameters. For TCSPC data, it is easy to define the standard deviation, σ_k , which is the square root of the number of photon counts in a given channel *k* based on Poisson statistics.⁸ The minimization of χ^2 gives us the best fitting parameters within the chosen mathematical model. The value of χ^2 will be bigger for a larger data set, so we used the reduced χ^2 for our TCSPC data analysis,

$$\chi_R^2 = \frac{\chi^2}{n-p} \tag{2.5}$$

where *p* is the number of the variable parameters in the model. For TCSPC, the number of data points, *n*, is much larger than the number of variable parameters; therefore χ_R^2 is approximately equal to χ^2 / n . χ_R^2 is expected to be unity when there are no systematic errors present in the data and the mathematical model is appropriate.⁸ Typically, TCSPC data are fit to multi-exponential functions until the value of χ_R^2 falls in the range 0.8-1.2. **Figure 2.5** shows a typical instrumental response function (black), observed fluorescence decay (red) and the fitted fluorescence decay (blue).



Figure 2.5: Representative experimental data, instrumental response function (black), observed fluorescence decay (red) and the fitted (blue) decay.

2.2.2. Reconstruction and Fitting of Time-Resolved Spectra

To obtain time-resolved spectra from TCSPC, about twenty time-resolved emission decays were recorded at different wavelengths across the steady-state emission spectrum. The measured TCSPC emission intensity decays at specific wavelengths (λ_j) are fit to a multi-exponential function,⁸

$$I(t;\lambda_j) = I_0 \sum_i a_i(\lambda_j) \exp\left[-\frac{t}{\tau_i(\lambda_j)}\right] \qquad \text{with} \qquad \sum a_i(\lambda_j) = 1 \qquad (2.6)$$

providing $I(t;\lambda_j)$ at 20 different wavelengths, all represented by multi-exponential functions. These parameterized data are then normalized based on the steady-state fluorescence spectrum $F_{SS}(\lambda)$, using the fact that $F_{SS}(\lambda)$ at any λ is proportional to the time integral over $I(t;\lambda)$. The normalization equation used to obtain the reconstructed time-resolved spectrum is ⁹

$$F(\lambda_i;t) = \frac{I(t;\lambda_i)F_{SS}(\lambda_i)}{\int\limits_0^T I(t;\lambda_i)dt + I(T;\lambda_i)\tau_{fl}}$$
(2.7)

where τ_{fl} is the fluorescence lifetime and *T* is the time at the end of data collection window. (The second part of the denominator in Equation 2.7, is obtained by integrating $I(t;\lambda_i)$ from *T* to infinity.) Figure 2.6 shows representative time-resolved spectra obtained in this manner. Also shown is the estimated time-zero spectrum discussed in Section 2.2.3. The frequency base spectra are converted from wavelength dependent spectra in the manner $\Delta\lambda \propto -\frac{\Delta \nu}{\nu^2}$.

The spectra obtained by reconstruction are characterized by fitting the spectrum at any time to a log-normal line shape function:⁹

$$F(v;t) = h \exp\{-\ln 2\left[\frac{\ln(1+\alpha)}{\gamma}\right]^2\} \text{ (with the requirement of } \alpha > -1)$$
(2.8)

where $\alpha = \frac{2\gamma(v-v_p)}{\Delta}$, *h* the peak height, γ the asymmetry parameter, v_p the peak frequency and Δ a width parameter. The solid curves in **Figure 2.6** are from such fitting. **Figure 2.7** shows the time evolution of the fitting parameters from these spectra. In order to calculate the solvation energy in the next section, both the peak frequency $v_p(t)$ and the average (first moment) frequency $v_a(t)$ of the spectrum

$$v_a(t) = v_p(t) + \left(\frac{\Delta(t)}{2\gamma(t)}\right) \left(\exp\left(\frac{3\gamma(t)^2}{4\ln(2)}\right) - 1\right)$$
(2.9)

are applied. Besides the frequencies, the time-dependent integrated intensity I(t) and the full width at half-maximum $\Gamma(t)$ are also calculated using the following equations,

$$I(t) = \left[\frac{\pi}{4\ln(2)}\right]^{1/2} h(t)\Delta(t) \exp\left[\frac{\gamma(t)^2}{4\ln(2)}\right]$$
(2.10)

$$\Gamma(t) = \Delta(t) \left[\frac{\sinh(\gamma(t))}{\gamma(t)} \right]$$
(2.11)



Figure 2.6: The deconvoluted time-resolved spectra of C153 in $[Im_{41}][BF_4]$. Dots are the original data points at different wavelengths and the solid lines are the fitted log-normal functions. The dash line is the estimated time-zero spectrum (see Section 2.2.3).



Figure 2.7: Example time-dependent spectral parameters obtained from the spectra in Fig 2.6. In the upper panels, the blue curves are peak frequencies and peak intensities and the red are the average frequencies and intensities.
2.2.3. Solvation Dynamics Calculation and the Time-Zero Spectrum

To characterize the time-dependence of solution, the spectral response function,

$$S_{\nu}(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$
(2.12)

is used. Equating $S_{\nu}(t)$ to the solvation response assumes that there is no significant interference from changes to vibronic structure. To determine $S_{\nu}(t)$, $\nu(0)$ and $\nu(\infty)$ are required. The following discussion describes how $\nu(0)$ can be determined based on the Fee-Maroncelli method^{10,11}. While for $\nu(t)$ and $\nu(\infty)$, the results from reconstruction of time-resolved spectra are used.

The accuracy of the experimentally determined time-zero spectrum depends strongly on the time resolution of the experimental setup. Fee and Maroncelli¹¹ have discussed the unreliability of time-zero spectra derived by the extrapolating observed spectra back to zero time and described a method for estimating the time-zero spectrum based on steady-state absorption and emission spectra. The basic idea of this method is the assumption that prior to solvent relaxation the Stokes shift of a given fluorophore in a polar solvent should be the same as its Stokes shift in a non-polar solvent. An approximate time-zero frequency v(0) can be calculated as

$$v_p(0) - v_p(abs) \approx v_{np}(em) - v_{np}(abs)$$
(2.13)

where the subscripts "p" and "np" represent the polar solvent of interest and a reference non-polar solvent, respectively. For the solvation dynamics of C153 in pure ILs (Chapter 3) and the mixture of the ionic liquid and polar solvent (Chapter 4), the absorption and emission spectra of C153 in 2-methylbutane (Fig. 2.8) are used as the non-polar references for determining the time-zero spectra.



Figure 2.8: Representative steady-state spectra. The spectra of absorption (black), emission (cyan), absorption from log-normal fitting (green dash) and the estimated time-zero (blue) spectra of C153 in $[Im_{61}][Tf_2N]$. Red dash curves are the reference emission and absorption spectra of C153 in 2-methylbutane.

Equation 2.13 is just a simple approximate way to estimate the time-zero frequency. A more accurate model of the inhomogeneous broadening in polar solvents was introduced to provide a more accurate estimate by Fee, Milsom and Maroncelli.¹⁰ Assuming that there is a single line-shape function g(v) which represents the absorption spectrum of all solutes to within some spectral shift δ , the inhomogeneously broadened absorption spectrum of the solute in a polar solvent can be described by ¹¹

$$A(v) \propto v \left[g(v-\delta)p(\delta)d\delta \right]$$
(2.14)

where A(v) represents the absorption spectrum and $p(\delta)$ is the equilibrium distribution of spectral shifts. The latter function is assumed to be Gaussian¹¹

$$p(\delta) = (2\pi\sigma^2)^{-1/2} \exp[-\frac{1}{2}(\frac{\delta - \delta_0}{\sigma})^2]$$
(2.15)

where δ_0 describes the average spectral shift from the non-polar reference solvent to the polar solvent and σ^2 represents the variance of the distribution. The time-zero emission spectrum observed with excitation v_{ex} can be described as,¹⁰

$$F_{p}(v,t=0;v_{ex}) \propto v^{3} v_{ex} \int g(v_{ex}-\delta) p(\delta) f(v-\delta) k_{rad}(\delta) d\delta$$
(2.16)

where f(v) is the emission line-shape of the solute and k_{rad} represents the radiative rate constant. To estimate the time-zero spectrum, four functions, g(v), $p(\delta)$, f(v) and $k_{rad}(\delta)$ must be specified. The line-shapes g(v) and f(v) can be obtained from the absorption $A_{np}(v)$ and emission $F_{np}(v)$ spectra of the solute in a non-polar solvent via

$$g(v) \propto v^{-1} A_{np}(v)$$
 and $f(v) \propto v^{-3} F_{np}(v)$ (2.17)

Now we need to define $k_{rad}(\delta)$ since the site distribution function $p(\delta)$ has been described in Equation 2.15. (The assumption was made that the non-radiative k_{nr} is independent of δ and all the dependence on the spectral shift δ is due to the radiative decay rate $k_{rad}(\delta)$.) Fee and coworkers^{10,11} assumed that the radiative rate only depends on the v^3 factor in the Einstein A coefficient. Thus, the radiative rate function $k_{rad}(\delta)$ is calculated as

$$k_{rad}(\delta) \propto \langle v(\delta)^3 \rangle \equiv \frac{\int f(v-\delta)v^3 dv}{\int f(v-\delta)dv}$$
(2.18)

It is worth mentioning that σ and δ are determined by fitting the absorption spectrum and these values used for the emission calculation. The value of $\sqrt{8 \ln 2}\sigma$ (also known as Γ_{inh}) describes the inhomogeneous broadening of the observed spectra. After all four functions g(v), $p(\delta)$, f(v) and $k_{rad}(\delta)$ are obtained; they can be input into the Equation 2.16 to get the time-zero spectrum of the solution in a polar solvent. Figure 2.8 shows representative time-zero estimated spectrum along with the raw absorption and emission spectra.

2.2.4. Anisotropy Analysis

The origin of emission anisotropy is the directional character of the absorption and emission of light. In an isotropic sample, fluorophore molecules are randomly oriented prior to excitation. Those molecules whose transition moments are oriented along the polarization direction (the electric vector) of the excitation pulse are preferentially excited. The decay of the fluorescence anisotropy reveals the average angular displacement of fluorophores that occurs between absorption and subsequent emission.

Figure 2.9⁸ illustrates the geometry of a typical anisotropy measurement. The orientation of the emission polarization is defined by the electric vector of the excitation pulse. I_{\parallel} represents the emission intensity observed with parallel polarization and I_{\perp} indicates the intensity of perpendicularly polarized emission. The ideal anisotropy, r(t), is then defined as,

$$r(t) = \frac{I(difference)}{I(total)} = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$
(2.19)

The difference between parallel and perpendicular emission is normalized by the total intensity, so the anisotropy is a dimensionless quantity and independent of the fluorophore concentration as well as the total emission intensity.



Figure 2.9:⁸ A diagram of the fluorescence anisotropy measurement.

The objective is to measure the anisotropy without the influence of the experimental setup. The real intensity ratio between the parallel and perpendicular emission is different from the measured intensity by a factor of G, the relative sensitivity of the detection system to these different polarizations.⁸ G varies with the emission wavelength and the band pass of the monochromator. It can be determined by

$$G = \frac{S_V}{S_H} = \frac{I_{HV}}{I_{HH}}$$
(2.20)

where S_V and S_H are the experiment sensitivity at vertical and horizontal polarization, I_{HV} is the emission intensity at vertical polarization under the horizontally polarized excitation and I_{HH} is the emission intensity at horizontal polarization with horizontal excitation. For our study, the *G* factor is calculated based on the ratio between perpendicular and parallel intensity at long times which means that the time is long enough that isotropy is reestablished in the sample. The measured anisotropy is then calculated by the following equation^{12,13},

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)}$$
(2.21)

The time-resolved anisotropy r(t) can be fit to various functions. In general, r(t) is fit to a stretched exponential function of time,

$$r(t) = r_0 \exp\left[-\left(\frac{t}{\tau_{rot}}\right)^{\beta}\right]$$
(2.22)

The average rotation time ($\langle \tau_{rot} \rangle$) is calculated as

$$<\tau_{rot}>=r_0\frac{\tau_{rot}}{\beta}\Gamma(\frac{1}{\beta})$$
(2.23)

where r_0 is the initial anisotropy which is the value in the absence of the depolarizing process. $\Gamma(x)$ is the gamma function. For some fluorescence anisotropy decays (Chapter 4), two exponential functions are used to fit the anisotropy,

$$r(t) = r_0 [a_1 \exp(-\frac{t}{\tau_1}) + a_2 \exp(-\frac{t}{\tau_2})]$$
(2.24)

The coorresponding average rotation time is

$$< au_{rot}>=a_1 au_1+a_2 au_2$$
 (2.25)

It is worth mentioning that the initial anisotropy value r_0 can be measured using a frozen sample in which the molecules do not rotate at all. Theoretically, the r_0 value should be within the range from -0.20 to 0.40 for any single-photon excitation. For this study, the r_0 value of 0.375 is applied to the C153 samples based on the Horng's measurement of C153 in a glassy solvent, propylene glycol at 200 K.¹³

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Chapter 3. Solvation Dynamics of Neat Ionic Liquids

3.1.Introduction

Studies of Ionic liquids (ILs) have been engendered by their numerous potential applications. ILs have variety outstanding properties, like the low volatility, intrinsic conductivity, and tailorabiliy. Compared to conventional organic solvents, those significant advantages make ILs good candidates for fuel cells,¹ electrolytes for batteries^{2,3} and dye-sensitized solar cells⁴. ILs are also excellent solvents for synthesis.⁵ The emergence of ionic liquids as a new type of solvent environment and the aforementioned potential applications has regenerated interest in solvation dynamics.^{6,7} Solvation dynamics, the time-dependent response of a solvent to solute perturbations, is a fundamental characteristic of liquid-phase dynamics, and it determines how fast chemical reactions like electron or proton transfer processes couple to a solvent environment.^{8,9}

What is the difference between solvation dynamics in ILs and conventional dipolar solvents? Is our understanding of conventional solvents applicable to ionic liquids? To answer these questions, the dynamic solvent response in 21 ionic liquids has been determined experimentally. To discover the extent to which our understanding of solvation in dipolar liquids is transferrable to ionic liquids, some well-known correlations in conventional solvents are examined as is the applicability of dielectric continuum models.

Early solvation dynamic studies^{10,11,12}, mostly using picoseconds techniques, showed that some part of the solvation response of ILs occurs over the time range 10⁻¹¹-

 10^{-8} s. This portion of the dynamics is now known to be directly correlated to solvent viscosity. Another important component of the response occurs at shorter times than can be detected by a time-correlated single photon counting (TCSPC) measurements which has 20-90 ps time resolution. A few groups measured solvation dynamics in ionic liquids with sufficient time resolution to observe this fast component.¹³⁻¹⁷ In the present work, the technique of broadband femtosecond fluorescence upconversion spectroscopy (FLUPS) with 80 fs time resolution^{18,19} has been introduced. The combination of both TCSPC and FLUPS can capture the complete solvation response from 10^{-13} s to 10^{-8} s.

One aspect of the present study is to test whether a simple dielectric continuum model is applicable for ionic liquid systems. Simple dielectric continuum models are known to be able to predict the solvation response of conventional dipolar solvents with good accuracy.²⁰⁻²⁴ In the fourteen ionic liquids whose dielectric data are available for comparison,²⁵⁻³² the predicted and observed solvation times are clearly related; however, the predictions are found to systematically overestimate the rate of solvation. In most cases, the predicted solvation is faster than the measured results by a factor of 2-5.

3.2.Experimental Methods

Coumarin 153 (laser grade) was obtained from Lambda Physik and Exciton and used as received. The 21 ionic liquids surveyed in this work are listed in Table 3.1. The majority of these liquids were the highest purity commercially available. Several liquids were synthesized by Gary Baker, Richard Buchner or by us, and in these cases references to the synthetic procedures are provided in the table.

#	IL	CAS RN	Chemical Name	Source	OD
21	[Im ₂₁][DCA]*	370865-89-7	1-ethyl-3-methylimidazolium dicyanamide	Iolitec (>98%)	0.48
22	[Im ₂₁][BF ₄]	143314-16-3	1-ethyl-3-methylimidazolium tetrafluoroborate	Iolitec (>98%)	0.22
24	[Im ₂₁][TfO]	145022-44-2	1-ethyl-3-methylimidazolium triflate	Merck	0.13
I2	[Im ₂₁][Tf ₂ N]	174899-82-2	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Iolitec (99%)	0.06
41	[Im ₄₁][DCA]	448245-52-1	1-butyl-3-methylimidazolium dicyanamide	Richard Buchner ³⁷	0.07
42	[Im ₄₁][BF ₄]	174501-65-6	1-butyl-3-methylimidazolium tetrafluoroborate	Iolitec (99%)	0.03
43	[Im ₄₁][PF ₆]	174501-64-5	1-butyl-3-methylimidazolium hexafluorophosphate	Iolitec (99%)	0.11
44	[Im ₄₁][TfO]*	174899-66-2	1-butyl-3-methylimidazolium trifluoromethanesulfonate	Iolitec (99%)	0.35
I4	$[Im_{41}][Tf_2N]$	174899-83-3	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Kanto Chemical	0.02
46	[Im ₄₁][FAP]*	917762-91-5	1-butyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate	EMD Chemicals (high purity)	0.41
16	[Im ₆₁][Tf ₂ N]*	382150-50-7	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Iolitec (99%)	0.38
18	[Im ₈₁][Tf ₂ N]*	178631-04-4	1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Iolitec (99%)	0.30
10	[Im _{10,1}][Tf ₂ N]*	433337-23-6	1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Iolitec (>98%)	0.11
P3	$[Pr_{31}][Tf_2N]$	223437-05-6	1-propyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.03
P4	$[Pr_{41}][Tf_2N]$	223437-11-4	1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.01
P5	$[Pr_{51}][Tf_2N]$	380497-17-6	1-pentyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.05
P6	[Pr ₆₁][Tf ₂ N]	380497-19-8	1-hexyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.01
P8	[Pr ₈₁][Tf ₂ N]	927021-43-0	1-octyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.04
P0	[Pr _{10,1}][Tf ₂ N]	1003581-49-4	1-decyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	Gary Baker ^{38,39}	0.01
M1	[N ₂₀₀₀][NO ₃]	22113-86-6	ethylammonium nitrate	this work ⁴⁰	0.17
M2	$[S_{222}][Tf_2N]$	321746-49-0	triethylsulfonium bis(trifluoromethylsulfonyl)imide	Iolitec (99%)	0.01

Table 3.1: Ionic Liquids Studied

M2 $[S_{222}][1_2N]$ S21746-49-0Internyisuitonium bis(trifidorometryisuitonyi)imideTothec (99%)# represents the ID and "IL" the structure abbreviations of ionic liquids used in this Chapter. "CAS RNs" indicate the CAS registration numbers."OD" shows the optical density of the neat ILs at 400 nm with 1 cm light path length. "*" = front-face measurement.

Apart from drying, the liquids were used as received except for $[Im_{41}][BF_4]$ and $[Im_{41}][PF_6]$ which were treated with activated carbon to remove colored impurities. All the ILs were dried in vacuum overnight at 45 °C. The water contents of most ILs were less than 100 ppm by weight prior to use.

Samples for steady-state and time-correlated single photon counting measurements were made up in vials and then transferred to either 1 cm or 1 mm sealed quartz cuvettes. Flowing solutions were used for fluorescence up-conversion. These solutions were protected from water in a Perspex box flushed with argon and pumped through a thin optical cell which can also be oscillated perpendicular to the beam direction. With this arrangement, samples typically maintained water levels of < 200 ppm over the course of an experiment (approximately 5 hours). However, in the cases of $[Im_{21}][BF_4]$ and $[Im_{41}][DCA]$ final water contents were near 1000 ppm. We do not anticipate that water even at this level will significantly alter the results reported here. This assertion is supported by experiments with $[Im_{21}][BF_4]$. For this ionic liquid we made 7 differences as a function of water content. FLUPS and absorption measurements were carried out at room temperature (20.5 ± 0.5) °C.

Steady-state and ps/ns time-resolved fluorescence measurements were performed in the same manner detailed in Ref.³⁵ The only difference was that for several of the ionic liquids having significant impurity fluorescence (denoted with asterisks in Table 3.1) 1 mm cuvettes were used and emission collected in a front-face geometry. In these cases, C153 concentrations providing ODs of near 1 were used in order to minimize the effect of impurity fluorescence. Excitation at 400 nm for TCSPC measurements was supplied by the doubled output of a cavity-dumped Ti:sapphire laser which delivers ~150 fs pulses at 800 nm and a repetition rate of 5.4 MHz. Emission was collected though an ISA H10 monochromator with a bandpass of 8 nm. The overall response time of the TCSPC instrument was 25-30 ps (FWHM), as measured using a scattering solution. Emission decays were recorded at over 20 wavelengths spanning the emission spectrum and these decays independently fit to a multi-exponential form using an iterative reconvolution algorithm in order to partially remove the effects of instrumental broadening. Reconstucted time-resolved spectra were obtained from these fitted decays according to the methods described in Ref.³⁶

Femtosecond time-resolved emission measurements were made using a homebuilt broadband fluorescence upconversion spectrograph^{18,19} which supplies emission spectra over the range 425-750 nm. The experiment is based on a Ti:sapphire laser (Femtolasers sPro) which provides 30 fs, 300 μ J pulses at 800 nm and a 500 Hz repetition rate. The output of this laser system is split into two beams with intensities in a ratio of 6:1. Pulses with 430 μ J energy drive an optical parametric amplifier (TOPAS, Light Conversion) which delivers 60 μ J, 1340 nm pulses in horizontal polarization used for optical gating. For optical pumping, the rest of the fundamental light is frequency doubled to 400 nm pulses whose polarization is set with a half wave plate plate. After passing a triple mirror on a variable delay stage, attenuated pump pulses (~ 1 μ J) are focused by a thin lens onto the sample cell, to a spot diameter of about 0.1 mm. To obtain a good optical image with the subsequent collection optics, the sample cell is made with two 0.2 mm thick windows, which are typically spaced 0.2-0.3 mm apart. Fluorescence was refocused by an off-axis Schwarzchild objective and collected by a concave mirror onto a KDP crystal for upconversion. The procedures used for spectral correction and evaluation are described in detail in Ref.¹⁹. The temporal response of the FLUPS experiment is given by the FWHM \approx 80 fs of the Gaussian fits of the time trace of pump scatter from pure methanol.

3.3.Results and Discussion

3.3.1. Solvation Energies

As in our previous work,³⁵ before examining solvation dynamics, we consider the energetics of the $S_0 \leftrightarrow S_1$ transition of C153 in different ionic liquids. The solvent contributions to the free energy difference $\Delta_{solv}G$ and the reorganization energy λ_{solv} associated with the $S_0 \leftrightarrow S_1$ transition of C153can be calculated from

$$\Delta_{sol}G = \frac{1}{2}h[v_{abs} + v(\infty)] - \Delta G_0$$
(3.1)

$$\lambda_{sol} = \frac{1}{2}h[v(0) - v(\infty)]$$
(3.2)

In these equations v_{abs} , v(0), and $v(\infty)$ represent some measure of the frequency of the absorption, "time-zero" emission, and fully equilibrated emission respectively, and ΔG_0 is the gas-phase energy difference, 296 kJ/mol.³⁵ Peak frequencies used to calculate these quantities are summarized in Table 3.2. The time-zero frequency v(0) is an approximation for the vibrationally equilibrated emission spectrum that would be

observed before any solvent relaxation. It is determined using steady-state spectra of C153 in the nonpolar reference solvent 2-methylbutane as described in Ref.⁴¹ The equilibrated emission frequency $\nu(\infty)$ is determined by extrapolating time-resolved TCSPC data using a stretched exponential fit (see below). As can be seen from the data in Table 3.2, this frequency is in all cases within 200 cm⁻¹ to the red of the steady-state emission frequency ν_{em} . Values of $\Delta_{solv}G$ and λ_{solv} in Table 3.2 were derived by combining data from peak and first moment frequencies.

#	IL	Abs Pk	SS Pk	t(0) Pk	t(∞) Pk	$-\Delta_{sol}G$	λ_{sol}
		10^{3}cm^{-1}	10^{3}cm^{-1}	10^{3}cm^{-1}	10^{3}cm^{-1}	kJ/mol ⁻¹	kJ/mol ⁻¹
21	[Im ₂₁][DCA]	23.27	18.29	20.37	18.29	47.2 ±1.1	12.7±0.9
22	[Im ₂₁][BF ₄]	23.64	18.24	20.68	18.25	45.2±1.4	14.9±1.2
24	[Im ₂₁][TfO]	23.53	18.39	20.59	18.38	45.4±1.1	13.8±0.9
I2	$[Im_{21}][Tf_2N]$	23.59	18.57	20.65	18.57	43.7±1.1	12.8±0.9
41	[Im ₄₁][DCA]	23.28	18.40	20.48	18.41	46.3±1.4	12.7±1.2
42	$[Im_{41}][BF_4]$	23.44	18.44	20.63	18.41	45.7±1.0	14.2±0.8
43	$[Im_{41}][PF_6]$	23.48	18.59	20.66	18.49	45.2±0.9	13.0±0.7
44	[Im ₄₁][TfO]	23.51	18.52	20.58	18.49	44.7±1.1	12.9±0.9
I4	$[Im_{41}][Tf_2N]$	23.51	18.65	20.68	18.62	43.7±0.8	11.7±0.6
46	[Im ₄₁][FAP]	23.56	18.85	20.62	18.80	43.5±1.1	12.1±0.9
I6	$[Im_{61}][Tf_2N]$	23.55	18.79	20.59	18.74	43.0±1.1	11.5±0.9
I8	$[Im_{81}][Tf_2N]$	23.57	18.92	20.61	18.82	42.2±1.1	11.0±0.9
I0	$[Im_{10,1}][Tf_2N]$	23.62	19.04	20.64	18.86	41.5±1.1	10.8±0.9
P3	$[Pr_{31}][Tf_2N]$	23.70	18.70	20.84	18.67	42.7±0.8	13.2±0.6
P4	$[Pr_{41}][Tf_2N]$	23.66	18.78	20.82	18.74	41.9±1.0	11.9±0.8
P5	$[Pr_{51}][Tf_2N]$	23.64	18.89	20.70	18.81	41.9±1.1	11.7±0.9
P6	$[Pr_{61}][Tf_2N]$	23.58	18.90	20.71	18.81	42.8±0.8	11.4±0.6
P8	$[Pr_{81}][Tf_2N]$	23.59	19.05	20.71	18.92	41.5±1.1	11.0±0.9
P0	$[Pr_{10,1}][Tf_2N]$	23.63	19.22	20.73	19.02	40.7±0.8	10.8±0.6
M1	[N ₂₀₀₀][NO ₃]	22.98	18.24	20.44	18.25	49.3±2.2	13.0±1.8
M2	$[S_{222}][Tf_2N]$	23.63	18.63	20.68	18.61	43.1±1.1	12.7±0.9

Table 3.2: Summary of C153 Fequencies and Energies

Notes: "Abs Pk" represents the peak frequency of the steady state absorption spectrum. "SS Pk" is the peak frequency of the steady state emission spectrum.



Figure 3.1: Solvation contribution to the free energy change and reorganization energy associated with the S₀ \leftrightarrow S₁ transition of C153 versus mean ion separation, $d = 1/V_m^{1/3}$. Filled symbols correspond to the data in Table 2 whereas open symbols are data on additional ionic liquids reported in Ref.³⁵ Blue and cyan points are data in imidazolium ionic liquids (Im⁺), light green are pyrrolidinium (Pr⁺) and dark green ammonium ionic liquids (N⁺). Red points denote ionic liquids containing the trihexyltetredecylphosphonium cation and circles denote bis(trifluoromethanesulfonyl)imide ionic liquids. Lines are fits to all data excluding the phosphonium liquids: $\Delta_{solv}G = 28.1 - 101d$ (N=30, r^2 =.80) and $\lambda_{solv} = 3.4 - 59d$ (N=29, r^2 =.59).

Figure 3.1 shows these energies plotted versus the inverse of the mean ion separation $d = V_m^{1/3}$ where V_m is the molar volume. We use 1/d here as a coarse measure of the strength of electrostatic interactions. This choice is based on the facts that the lattice energy of the neat ionic liquid should scale with d^{-1} and also that the solvation energy of ionic and dipolar solutes are inversely related to an effective cavity size, $a = R_{solute} + R_{ions} \sim R_{solute} + d/2$. As illustrated in Fig. 3.1, variations in both $\Delta_{solv}G$ and λ_{solv} with ionic liquid appear to be reasonably correlated to this mean ion separation. This observation and comparisons to conventional solvents were already discussed in our previous work.³⁵ The present study expands the original data set to 35 distinct ionic liquids. As previously noted, ionic liquids based on the highly alkylated phosphonium cation tetradecyltrihexylphoshonium ($P_{14,666}^+$) do not follow the same correlation as established by the remaining ionic liquids (lines). The reorganization energy of protic ionic liquid ethylammonium nitrate ("M1") comprised of the smallest ions also seems to deviate from the general trend. We also explored correlations of these energies which incorporated the refractive index in an attempt to account for electronic polarizability, which is expected to be relevant to $\Delta_{solv}G$. But the refractive indices of the liquids studied span a small range $(1.43\pm.03)$ and no improvement in the correlations was found. The same can be said of the relative permittivities, ε_r . Except for ethylammonium nitrate $(\varepsilon_r = 28.3 \pm 0.5^{42})$, the relative permittivities available for 15 of the 21 liquids listed in Table 3.2 all fall in a range characteristic of moderately polar conventional solvents ε_r = 16±2.



Figure 3.2: Time-resolved emission spectra of C153 in $[Pr_{51}][Tf_2N]$. The top panel show FLUPS data (100 fs to 650 ps) and the middle panel spectra reconstructed from TCSPC decays (10 ps to 20 ns). The spike near 24,000 cm⁻¹ is due to Raman scattering. The smooth curves in both panels are fits of the data to log-normal lineshape functions. The bottom panels compare the TCSPC and FLUPS spectra at two times.

Figure 3.2 shows representative time-resolved emission spectra in $[Pr_{51}][Tf_2N]$. In the top panel are broad-band spectra recorded using the FLUPS technique. In the middle panel are spectra reconstructed from TCSPC decays (points). Both types of data were fit with log-normal lineshape functions (smooth curves in both panels) in order to parameterize the time evolution of the spectra.³⁶ The bottom panel of Fig. 3.2 shows the level of agreement typically observed between spectra obtained with FLUPS and TCSPC over the time range where both spectra are expected to be reliable.

Figure 3.3 displays the behavior of two log-normal parameters derived from the spectra in Fig. 3.2, the width $\Gamma(t)$ and the peak frequency $v_{pk}(t)$. As illustrated in the top panel of Fig. 3.3, we typically observe a substantial (~1000 cm⁻¹) decrease in the width of the spectrum at times of less than 100 ps. Recent work in conventional solvents demonstrates that this width change is due primarily to vibrational cooling subsequent to excitation with excess energy (~3000 cm⁻¹).⁴³ As has been done in past work, we will ignore this effect and focus on the evolution of the peak frequency to monitor the solvation response. Specifically, we will extract the spectral response function,

$$S_{\nu}(t) = \frac{\nu_{pk}(t) - \nu_{pk}(\infty)}{\nu_{pk}(0) - \nu_{pk}(\infty)}$$
(3.3)

and equate this frequency response to the solvation response, i.e. the normalized function describing relaxation of the solute-solvent interaction energy. The solvation response functions obtained in this manner will be contaminated to some degree by the vibrational effect, but we anticipate that the distortions will not be greater than other sources of uncertainty in the data.



Figure 3.3: Illustration of the combination of FLUPS and TCSPC. Time evolution of the spectral width (FWHM; $\Gamma(t)$) and peak frequency $\nu_{pk}(t)$ obtained from log-normal fits of the FLUPS and TCSPC spectra in Fig. 3.2. (See text.)

As shown in the bottom panel of Fig. 3.3, the peak frequencies measured in the FLUPS and TCSPC experiments are not in perfect agreement. In the case illustrated here, there is a 230 cm⁻¹ difference between the two frequencies over the time range, 100-600 ps, where we expect both methods to be reliable. These data are representative in that the average absolute discrepancy is 270 cm⁻¹ for the 21 data sets reported here. The sign of the deviation is random (the signed average is 30 cm⁻¹) and we attribute it to the variability in the spectrum of the gating light used in the FLUPS experiments. Because the TCSPC data are referenced to calibrated steady-state spectra we take the TCSPC frequencies as being correct and shift the FLUPS spectra to best match over the 100-600 ps range. To smoothly splice together the two sets of data, we take a weighted average of the shifted FLUPS and TCSPC frequencies such that the FLUPS data are given 100% weight at 100 ps and the TCSPC data 100% weight at 600 ps, as shown in Fig. 3.3.

Composite $v_{pk}(t)$ data generated in this fashion are shown in Fig. 3.4 for the homologous series of ionic liquids $[Im_{n1}][Tf_2N]$ and $[Pr_{n1}][Tf_2N]$. Given that one expects systematic behavior as a function of alkyl chain length *n* in such series, these data provide some indication of the uncertainties in the $v_{pk}(t)$ data. At times greater than 10 ps systematic behavior is observed in both series. There is an orderly progression of the limiting frequencies $v_{pk}(\infty)$ and between 100 ps – 1 ns the $v_{pk}(t)$ parallel one another to better than 100 cm⁻¹. (As will be seen shortly this parallelism indicates a common stretched-exponential time dependence throughout these series.) At times below 1 ps the data are not as orderly and below 300 fs the various curves cross in unexpected ways.



Figure 3.4: Time evolution of the peak frequencies $v_{pk}(t)$ of C153 in the imidazolium $[Im_{n1}][Tf_2N]$ and pyrrolidinium $[Pr_{n1}][Tf_2N]$ series of ionic liquids.

In the case of the $[Im_{n1}][Tf_2N]$ series it is only the *n*=4 data that appears to misbehave whereas in the $[Pr_{n1}][Tf_2N]$ series the data are randomly ordered at 100 fs. We interpret these observations as indicating uncertainties in the $v_{pk}(t)$ data to be roughly ±100 cm⁻¹ at times greater than 1 ps and as large as ±400 cm⁻¹ at 100 fs. With Stokes shift magnitudes of ~2000 cm⁻¹ these uncertainties translate into uncertainties in $S_1(t)$ of ±5% at most times and up to ±20% at sub-picosecond times. Due to the large uncertainty in some early time data, for converting $v_p(t)$ data to spectral response functions, we used the values of $v_{pk}(0)$ obtained from steady-state estimates as described in Section 2.2.3. In the majority of the data sets (16/21 cases) the mean absolute deviation of $v_{pk}(t=50 \text{ fs})$ from the estimated $v_{pk}(0)$ was 170 cm⁻¹ (8% of the predicted Stokes shift). In most of these cases the observed frequency was slightly less than that predicted, as would be expected based on the finite time resolution of the experiment. However in the [Pr_{n1}][Tf₂N] series for *n*>3 (5 data sets) the observed frequencies at early time exceeded the time-zero estimates by an average of nearly 600 cm⁻¹ (29%). The reasons for the large discrepancies in these particular solvents are not known.

Representative spectral/solvation response functions $S_v(t)$ are provided in Fig. 3.5. As is clear from this figure and from the previous $v_{pk}(t)$ plots, the solvation response is strongly bimodal, consisting of a sub-picosecond component followed by another component that extends from a few picoseconds out to nanosecond times. A convenient way of characterizing these two components of the response is through fits of the $S_v(t)$ data to a Gaussian + stretched exponential form

$$S_{\nu}(t) = f_{G} \exp\{-\frac{1}{2}\omega_{G}^{2}t^{2}\} + (1 - f_{G})\exp\{-(t/\tau)^{\beta}\}$$
(3.4)



Figure 3.5: Representative spectral response functions (points) and fits to Eq. 3.4 (solid curves).

Example fits are shown as the smooth curves in Fig. 3.5. In all cases, this simple functional form suffices to represent the observed data to within anticipated uncertainties.⁴⁴ Table 3.3 summarizes the fit parameters for all of the ionic liquids studied here. Also listed in Table 3.3 under the heading "Q" is a rough assessment of the relative quality of the data sets based on the frequency shift required to match the FLUPS an TCSPC data, the similarity of the data in the splicing region, and the level of agreement between observed and predicted time-zero frequencies. Q=1 represents the most reliable data.

#	IL	Q	$f_{ m G}$	ω _G	<\tau>G	τ	β	<\alpha>_str
				ps ⁻¹	ps	ns		ns
21	[Im ₂₁][DCA]	1	0.18±0.08	14±2.8	0.09	0.01	0.34	0.051±0.010
22	$[Im_{21}][BF_4]$	1	0.45 ± 0.08	6.7±1.3	0.19	0.05	0.40	0.16±0.03
24	[Im ₂₁][TfO]	1	0.39±0.08	7.8±1.6	0.16	0.20	0.41	0.61±0.12
I2	$[Im_{21}][Tf_2N]$	2	0.25±0.08	6.2±1.2	0.20	0.06	0.44	0.15±0.04
41	[Im ₄₁][DCA]	1	0.27±0.08	12±2.5	0.10	0.04	0.40	0.12±0.02
42	[Im ₄₁][BF ₄]	2	0.34±0.08	7.0±1.4	0.18	0.17	0.48	0.37±0.11
43	$[Im_{41}][PF_6]$	1	0.33 ± 0.08	5.8±1.2	0.22	0.45	0.50	0.90±0.18
44	[Im ₄₁][TfO]	2	0.37 ± 0.08	6.7±1.3	0.19	0.24	0.50	0.48±0.14
I4	$[Im_{41}][Tf_2N]$	3	0.39±0.15	4.1±1.6	0.31	0.19	0.60	0.29±0.12
46	[Im ₄₁][FAP]	1	0.21±0.08	2.8±0.6	0.44	0.23	0.51	0.44±0.09
I6	$[Im_{61}][Tf_2N]$	3	0.22 ± 0.08	4.7±0.9	0.27	0.25	0.55	0.41±0.17
I8	$[Im_{81}][Tf_2N]$	2	0.13±0.11	3.1±0.9	0.41	0.40	0.52	0.76±0.23
IO	$[Im_{10,1}][Tf_2N]$	1	0.11±0.08	3.4±0.7	0.37	0.55	0.49	1.13±0.23
P3	$[Pr_{31}][Tf_2N]$	1	0.32 ± 0.08	3.9±0.8	0.32	0.14	0.49	0.29±0.06
P4	$[Pr_{41}][Tf_2N]$	2	0.33±0.11	3.3±1.0	0.38	0.21	0.54	0.37±0.11
P5	$[Pr_{51}][Tf_2N]$	2	0.29±0.15	2.3±0.9	0.55	0.31	0.56	0.51±0.15
P6	$[Pr_{61}][Tf_2N]$	2	0.32±0.15	2.8±1.1	0.45	0.42	0.58	0.66±0.20
P8	$[Pr_{81}][Tf_2N]$	3	0.22±0.15	3.4±1.4	0.37	0.59	0.56	0.98±0.39
P0	$[Pr_{10,1}][Tf_2N]$	3	0.16±0.15	1.1±0.4	1.16	0.82	0.53	1.49±0.60
M1	[N ₂₀₀₀][NO ₃]	1	0.39±0.08	8.1±1.6	0.16	0.03	0.45	0.062±0.012
M2	$[S_{222}][Tf_2N]$	2	0.28±0.11	3.0±0.9	0.42	0.07	0.54	0.13±0.04

Table 3.3: Parameterization of Spectral Response Data

Notes: "Q" represents the quality of the experimental results. 1=very good, 2=good, 3=poor. Fitting parameters for $S_v(t)$ are from the Gaussian + stretched exponential form Eq. 3.4.

Before discussing the fit parameters some comment is necessary concerning the values of ω_G obtained here. We have not attempted to deconvolute the FLUPS data in order to try to eliminate the effects of the 80 fs (FWHM) instrumental response function (IRF). This IRF width corresponds to a Gaussian frequency of $\omega_{IRF} = 8.7 \text{ ps}^{-1}$ and one might anticipate that observed values of ω_G near to ω_{IRF} would be significantly reduced from their true values by instrumental broadening. Assuming both the fast response and

the IRF to be Gaussian functions of time, one would expect $\omega_{obs}^{-2} = \omega_{true}^{-2} + \omega_{IRF}^{-2}$ so that values of $\omega_G > \omega_{IRF}$ would not be observed. But, as seen from Table 3.3, we do find $\omega_G > \omega_{IRF}$ in a number of cases. The reason is that we use an independent means of establishing $v_{pk}(0)$, which forces the fit of $S_v(t)$ to account in approximate way for the shortfalls in $v_{pk}(t\rightarrow 0)$ caused by instrumental broadening. This approach appears to provide the best means of extracting short-time information from the current data and we believe that the fitted values of ω_G reported in Table 3.3 should provide reasonable estimates even for $\omega_G > \omega_{IRF}$. Comparison to data with much higher time resolution discussed later supports this claim.

We examined the extent to which the parameters f_G , ω_G , $t_G^{(1/e)}t_{eG}$, β , and $\langle \tau \rangle_{str}$ correlate with various properties of the ions or bulk liquids. The times t_{eG} and $\langle \tau \rangle_{str}$ are respectively the 1/e time associated with the Gaussian component and the integral time of by $t_G^{(1/e)} = (2e^{-1})^{1/2} / \omega_G$ the stretched exponential component, given and $\langle \tau \rangle_{str} = \tau \Gamma(\beta^{-1})/\beta$. The ion properties examine included the cation (C) an anion (A) masses and van der Waals radii, R_C and R_A , the reduced mass of a C+A pair, μ , and the "inertial factor" $(R_C + R_A)^{3/2} \mu^{1/2}$ introduced in Ref.¹⁴ Bulk liquid properties tested were the molar volume and viscosity.⁴⁵ Only weak correlations were found between f_G and these quantities. Given the fact that estimated uncertainties in f_G (± 0.1-.15) are a large fraction of its range this result is not surprising. It is clear, however, that f_G decreases with increasing alkyl chain length n in the two series $[Im_{n1}][Tf_2N]$ and $[Pr_{n1}][Tf_2N]$. The timescale of the subpicosecond component of the response, characterized by ω_G or $\langle \tau \rangle_G$ is most strongly correlated to the C+A reduced mass, anion mass, and the inertia factor.



Figure 3.6: Correlation of the Gaussian frequency ωG with the inverse of the reduced cation+anion reduced mass. Circles indicate ionic liquids with the Tf₂N⁻ anion, other shapes are other anions. Red and green symbols are the $[Im_{n1}][Tf_2N]$ and $[Pr_{n1}][Tf_2N]$ series, respectively, blue symbols are liquids with Im_{n1}^+ cations and dark red symbols M1 and M2. Numbers indicate ionic liquids as listed in Table 3.1. The line is a linear fit to all of the data except M1 ($[N_{2000}][NO_3]$), 20 points correlation coefficient = 0.92.

As noted in previous work,^{14,46} without pointing to any particular solvation mechanism, such correlations confirm the inertial character of this ultrafast component, as predicted by numerous simulation studies.⁴⁷ Figure 3.6 illustrates the best of these correlations, between ω_G and μ^{-1} . The dashed line labeled "IRF" in this figure is a reminder of the 80 fs instrumental response time of the FLUPS experiment. With the exception of the data in ethylammonium nitrate (M1) which is excluded from the fit shown here, the correlation is quite good. This correlation would predict a much higher Gaussian frequency for ethylammonium nitrate than what is observed. It is worth mentioning that the predicted magnitude of the Stokes shift (or reorganization energy, Fig. 3.1) observed in this ionic liquid (M1) is also much smaller than expected relative to other ILs. These two deviations are likely to be related and warrant further study.



Figure 3.7: Correlation of the integral time associated with the stretched exponential component with solvent viscosity. Circles indicate ionic liquids with the Tf₂N⁻ anion, other symbols are other anions. Red and green symbols are the $[Im_{n1}][Tf_2N]$ and $[Pr_{n1}][Tf_2N]$ series, respectively, blue symbols are liquids with Im_{n1}^+ cations and dark red symbols M1 and M2. Numbers indicate ionic liquids as listed in Table 3.1. The line is the correlation $<\tau>_{str}$ / ps = $1.8(\eta/cP)^{1.2}$.

The slow component of the solvation response, measured by $\langle \tau \rangle_{str}$, is most strongly correlated to the solvent viscosity η . Figure 3.7 displays this correlation, which can be represented by a power law, $\langle \tau \rangle_{str} \propto \eta^p$ with $p=1.2\pm0.2$. This type of near proportionality of the integral solvation time to viscosity in a single ionic liquid versus temperature and within collections of ionic liquids has been reported numerous times previously.^{13,35} In the present case it appears to hold to within uncertainties for the two homologous series $[Im_{n1}][Tf_2N]$ and $[Pr_{n1}][Tf_2N]$ but with a number of outliers, most notably $[Im_{21}][TfO]$ ("24") and ethylammonium nitrate ("M1"). This relationship between the time of the slow solvation component and viscosity presumably reflects the fact that solvation is associated with structural relaxation of the solvent as found in computer simulations.⁴⁸ One additional relationship, not previously noted, can be found in the data in Table 3.3. There is a fairly good correlation (*R*=-0.84) is observed between the dispersity of the slow solvation component, represented by the stretching exponent β , and the Gaussian frequency ω_G . It is unclear whether there is any physical meaning to this correlation or not.

3.3.3. Comparisons to Dielectric Continuum Predictions

We now examine to what extent one can use the dielectric dispersion data recently collected on neat ionic liquids (see Table 3.4) as input to simple continuum descriptions of solvation to predict the solvation response measured here with C153. The model we employ assumes the solute to be a point dipole centered in a spherical cavity of dielectric constant $\varepsilon_u=2$, representing the solute polarizability, surrounded by a solvent having the generalized dielectric response function $\hat{\eta}(v)$. The calculations are essentially the same as those described in Ref.¹⁴ and previous work.²⁰ Normalized response functions are determined using the expressions

$$S_{dc}(t) = \frac{L_p^{-1}\{[\hat{\chi}(\infty) - \hat{\chi}(p)]/p\}}{\hat{\chi}(\infty) - \hat{\chi}(0)}$$
(3.4)

$$\hat{\chi}(p) = \frac{\hat{\eta}(p) - 1}{\hat{\eta}(p) + \frac{1}{2}\varepsilon_u}$$
(3.5)

where L_p^{-1} denotes an inverse Laplace transform with respect to the variable $p = 2\pi i v$. In contrast to Ref.¹⁴ where the contribution of conductivity was erroneously neglected, the dielectric function used here is the generalized function,⁴⁹

$$\hat{\eta}(\nu) = \hat{\varepsilon}(\nu) + \frac{2i\sigma_0}{\nu}$$
(3.6)

This function describes the frequency dependence actually observed in dielectric measurements, whereas $\hat{\varepsilon}(v)$, the remainder after the diverging conductivity contribution is removed, is what is typically reported.^{29,50}

#	IL	Freq. Range	60	$(\infty)_3$	n _D	$\epsilon(\infty)-n_D^2$	cond	Label	Diel. Ref.	n _D ref	Cond Ref
							S/m				
21	[Im ₂₁][DCA]	100 MHz - 10 THz +OKE	11.0	2.5	1.510	0.2		В	30	51	52
22	$[Im_{21}][BF_4]$	100 MHz - 10 THz +OKE	15.9	1.94	1.411	-0.1	1.55	В	30	53	54
22	$[Im_{21}][BF_4]$	1 MHz - 20 GHz	13.6	6.7	1.411	4.7	1.52	Ν	31	31	31
24	[Im ₂₁][TfO]	500 MHz - 10 THz	17.7	2.12	1.432	0.1	0.98	В	55	53	52
I2	$[Im_{21}][Tf_2N]$	90 GHz	12.9	3.18	1.423	1.2	0.90	В	63	56	57
I2	$[Im_{21}][Tf_2N]$	1 MHz - 20 GHz	12.3	4.7	1.421	2.7	0.95	Ν	31	31	31
I2	$[Im_{21}][Tf_2N]$	20 GHz	12.3	3.23	1.423	1.2	0.83	W	25	56	25
41	[Im ₄₁][DCA]	100 MHz - 3 THz	11.3	2.13	1.509	-0.1	1.052	B1	29	58	54
41	[Im ₄₁][DCA]	100 MHz - 10 THz + OKE	12.3	2.36	1.509	0.1	1.052	B2	30	58	54
42	[Im ₄₁][BF ₄]	100 MHz - 3 THz	12.2	1.06	1.422	-1.0	0.35	В	29	47	54
42	$[Im_{41}][BF_4]$	1 MHz - 20 GHz	14.1	5.45	1.421	3.4	0.44	Ν	31	31	31
42	$[Im_{41}][BF_4]$	200 MHz-20 GHz	11.0	4.08	1.422	2.1	0.30	W	26	47	26
43	[Im ₄₁][PF ₆]	100 MHz - 3 THz	11.8	2.1	1.410	0.1	0.15	В	29	47	54
43	$[Im_{41}][PF_6]$	1 MHz - 20 GHz	14.1	4.8	1.407	2.8	0.165	N	31	31	31
43	$[Im_{41}][PF_6]$	40 MHz - 40 GHz	12.4	3.26	1.410	1.3	0.16	Y	32	47	32
44	[Im ₄₁][TfO]	100 MHz - 90 GHz	15.6	1.82	1.438	-0.2	0.29	В	63	59	54
I4	$[Im_{41}][Tf_2N]$	100 MHz - 90 GHz	12.9	2.23	1.427	0.2	0.39	В	63	56	57
I4	$[Im_{41}][Tf_2N]$	1 MHz - 20 GHz	13.7	4.25	1.426	2.2	0.42	Ν	31	31	31
I4	$[Im_{41}][Tf_2N]$	200 MHz-20 GHz	11.5	3.03	1.427	1.0	0.37	W	25	56	25
I4	$[Im_{41}][Tf_2N]$	40 MHz - 40 GHz	12.7	2.7	1.427	0.7	0.37	Y	32	56	25
I6	$[Im_{61}][Tf_2N]$	200 MHz - 89 GHz	12.7	2.58	1.430	0.5	0.22	В	60	56	57

 Table 3.4:
 Dielectric Dispersion Data Used

I6	$[Im_{61}][Tf_2N]$	1 MHz - 20 GHz	14.1	4.8	1.430	2.8	0.226	Ν	31	31	31
18	$[Im_{81}][Tf_2N]$	1 MHz - 20 GHz	16.8	3.72	1.432	1.7	0.14	Ν	31	31	31
P4	$[Pr_{41}][Tf_2N]$	200 MHz - 10 THz	12.1	2.33	1.423	0.3	0.26	В	63	39	27
P4	$[Pr_{41}][Tf_2N]$	200 MHz-20 GHz	11.7	2.42	1.423	0.4	0.26	W	27	39	27
M1	[N ₂₀₀₀][NO ₃]	500 MHz - 12 THz	28.5	2.52	1.452	0.4	2.50	В	61	62	28
M1	[N ₂₀₀₀][NO ₃]	10 MHz - 1 THz (wet)	26.4	3.2	1.452	1.1	2.50	Κ	28	62	28
M2	[S ₂₂₂][Tf ₂ N]	100 MHz - 3 THz	14.7	2.2	1.426	0.2	0.512	В	63	Min 2012	²⁷ (measured)
M2	$[S_{222}][Tf_2N]$	200 MHz-20 GHz	13.2	1.83	1.426	-0.2	0.711	W	27	Min 2012	²⁷ (fit)

Dielectric relaxation data are currently available for 14 of the 21 ionic liquids studied here. The data are primarily from the groups of Buchner^{29,30,55,60,61} and Weingärtner,²⁵⁻²⁸ as summarized in Table 3.4. Listed in this table are frequency ranges over which data were collected. The upper limit of this range has a significant impact on the quality of the solvation dynamics predictions possible. To capture the majority of the intramolecular nuclear dynamics of relevance to solvation, characterization of $\hat{\eta}(\nu)$ should extend to the terahertz range. For only 9 of the solvents are such extended frequency data available. As shown by the column labeled $\Delta \varepsilon = \varepsilon_{\infty} - n_D^2$ in Table 3.4, in the remaining cases, some portion of the dielectric spectrum is missed. Although the fraction missed, $(\varepsilon_{\infty} - n_D^2)/(\varepsilon_0 - n_D^2)$, is typically <25%, this missing fraction has a large impact on the short-time response and, if not accounted for, can also affect the long time behavior of S(t).

Figure 3.8 illustrates the problem and our method of approximating this missing contribution. In Fig. 3.8 we show dielectric data reported by four laboratories for the ionic liquid $[Im_{41}][Tf_2N]$.^{25,31,32,63} Panel (a) shows the functions as reported. Panel (b) shows these same functions modified by the addition of a damped harmonic oscillator of amplitude $\Delta \varepsilon = \varepsilon_{\infty} - n_D^2$, which is used to account for unobserved high-frequency components of $\hat{\varepsilon}(v)$. The data of Buchner *et al.*⁶³ is not modified in this fashion because $\Delta \varepsilon = 0$. We note that the data of Buchner *et al.*⁶³ ("B", blue), Nakamura and Shikata³¹ ("N", red) and Daguenet *et al.*²⁵ ("W", green) are in good agreement over their region of overlap, whereas the data of Mizoshiri *et al.*³² ("Y", purple) is rather different between

100 MHz – 20 GHz. Of these four data sets, only the data of Buchner *et al.*⁶³ extend to the THz range necessary to reduce $\varepsilon'(\nu)$ to close to its value n_D^2 at optical frequencies.



Figure 3.8: Dielectric relaxation and calculated solvation response functions of $[Im_{41}][Tf_2N]$. (a)&(b): Dielectric permittivity ($\varepsilon'(\nu)$, upper curves) and loss ($\varepsilon''(\nu)$, lower curves) functions calculated from the parameterizations provided in Refs.^{25,31,32,63} (The legend refers to references as coded in Table 3.4.) (c)&(d): Solvation response functions calculated on the basis of the dielectric data in panel (a) and (b). The inset tables show the average time (tav) in ps required to reach certain values of S(t), 0.7, 0.5, 0.3 and 0.1. The values labeled "x" shows the spread in values which is obtained using the different dielectric data as the ratio of maximum value over minimum value excluding the "Y" values (dashed curves).

Figure 3.8 panel (c) shows the solvation response functions directly calculated from aforementioned four dielectric parameterizations. Equations 3.4 and 3.5 predict the short-time (t < 10 ps) dynamics differ significantly as clearly shown in Figure 3.8 panel (a). To account for the difference between ε_{∞} and n_D^2 , an effective high-frequency component is included in Equation 3.7, in the form of a damped harmonic oscillator,

$$\Delta \hat{\varepsilon}(p) = (\varepsilon_{\infty} - n_D^2) \frac{v_0^2}{v_0^2 + p(p+\gamma)}, \qquad (3.7)$$

In Figure 3.8 panel (c) the dielectric functions as parameterized are used and in panel (d) these functions are modified by the addition of this damped harmonic oscillator (Eq. 3.7). The inset shows the average times required to reach certain value of S(t). τ_{av} is the average time of the three solvation response ("B", "N" and "W"). "x", the ratio of the maximum value over the minimum value among those three predictions, represents the spread in values. Obviously, the panel (d) has much better agreement. Therefore, the effective high-frequency contribution is included for all the dielectric continuum predictions.

Figure 3.9 illustrates six representative comparisons between the experimental solvation response functions and the S(t) predicted by the dielectric continuum model. The black curves are the measured solvation response functions and colored curves are from the dielectric continuum predictions. The labels "B", "N", "W" and "Y" represent the dielectric data sources defined in Table 3.4. In most cases the dielectric continuum predictions are similar in shape to the observed S(t) functions, especially in the ps~ns time range. [Im₂₁][TfO] is an extreme case where the predicted response is much faster than the observed solvation response for reasons which are presently unclear.



Figure 3.9: Comparison of measured C153 spectra response functions (black curves) with dielectric continuum model predictions (colored curves). The legend with color to each plot indicates the source of the dielectric data (see Table 3.4.).
Figure 3.10 shows the comparisons of times when the S(t) functions reach certain values. For 14 ionic liquids which we have dielectric data (Table 3.4), the times required for S(t) predicted and observed to relax to four different values, 0.7, 0.5, 0.3, and 0.1 as well the integral time $\langle \tau \rangle$ are plotted. In general, the fast solvation dynamics are indicated by the times when S(t) reaches levels of 0.7 and 0.5, while the 0.3 and 0.1 times characterize the slower components of the solvation response. As illustrated in Fig. 3.10, the predicted solvation response is faster than the observed response roughly by a factor between 2 and 10.



Figure 3.10: Comparison of the times required for predicted and observed S(t) at certain values of 0.7, 0.5, 0.3 and 0.1. The inset illustrates the meaning of the times when S(t) reaches certain values along with the color coding. The solid cyan symbols are the integral response times. The symbols with the diamond shape represent ILs with the Im_{n1}^+ cation and M1. The circle symbols are ILs with the Tf_2N^- anion.

3.4.Summary and Conclusions

The complete solvation response of coumarin 153 in 21 room-temperature ionic liquids has been measured by combining broadband fluorescence upconversion and time-correlated single photon counting. The combination of these two techniques provides temporal coverage over times of 100 fs to 20 ns, which enables the observation of the complete solvation response in a variety of ionic liquids. The fast solvation dynamics of ionic liquids are correlated to the reduced mass of an ion pair. Such correlations confirm the inertial character of this ultrafast component, as predicted by simulation results. The slow solvation dynamics are correlated to the bulk viscosity, as has been observed previously³⁵. The measured solvation dynamics are then used to test the applicability of simple dielectric continuum models to ionic liquids systems. The simple dielectric continuum models to ionic liquids systems. The simple dielectric continuum models a good starting point for predicting solvation dynamics in ionic liquids, but the predicted dynamics are systematically faster than experiment.

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Chapter 4. Solvation and Rotational Dynamics in a Prototypical Ionic Liquid + Dipolar Solvent Mixture: Coumarin 153 in 1-Butyl-3-Methylimidazolium Tetrafluoroborate + Acetonitrile

4.1. Introduction

Ionic liquids (ILs) are often mixed with conventional organic solvents as a means of increasing the fluidity and conductivity of these high-viscosity liquids. Thus, it is important to study the nature of solvation in mixtures of ionic liquids and conventional solvents. Another reason for studying such mixtures is to bridge the knowledge gap between what is well known in conventional solvents and what remains mysterious about ionic liquids. One can certainly learn more about ionic liquids through the mixtures if a given phenomenon is well understood in conventional solvents but not in ILs.

The binary mixture $[Im_{41}][BF_4]$ and acetonitrile was chosen for further study for the following reasons. $[Im_{41}][BF_4]$ is completely miscible with acetonitrile at room temperature. $[Im_{41}][BF_4]$ is a simple prototypical ionic liquid while acetonitrile is a prototypical high-polarity solvent. One does not expect much preferential solvation of solutes in this system due to the similar 'polarity' of acetonitrile and $[Im_{41}][BF_4]$. Instead, we expect this mixture to exhibit the simplest possible behavior. A number of ionic liquids + actonitrile mixtures have already been studied.¹⁻⁶ In 2007, Mellein reported representative solvatochromic data in the mixture $[Im_{61}][Tf_2N]$ + acetonitrile.⁷ They studied preferential solvation using Reichardt's dye 30 (betaine-30) and concluded that this probe is preferentially solvated by $[Im_{61}][Tf_2N]$ by plotting the relative solvatochromic shift versus mole fraction of the ionic liquid.⁷ Chakrabarty et al. reported the solvation dynamics of C153 in mixtures of $[Im_{61}][PF_6]$ + acetonitrile.⁶ In this study, the fast dynamics (<10 ps) could not be characterized due to their limited experimental time resolution.

As we discussed in Chapter 3, there are two phases to solvation dynamics in ionic liquids. The slow dynamics is correlated to the bulk solvent viscosity and the fast portion of dynamics is related to inertial dynamics. With the introduction of the conventional solvent acetonitrile, which has a smaller viscosity, the transition from the slow dynamics of the neat ionic liquid to the ultrafast dynamics in acetonitrile can be observed. Similarly to Chapter 3, two independent experimental techniques, florescence up-conversion spectroscopy (FLUPS) and time-correlated single photon counting (TCSPC) combined together to observe the complete solvation response of C153 over the time window from 100 fs to 20 ns. We used similar techniques and methodology as in our previous work in Chapter 3 to examine the energetic and dynamics of solvation of C153 in the mixture of $[Im_{41}][BF_4]$ + acetonitrile. As in Chapter 3, we compare the observed dynamics to the predictions of a dielectric continuum model. Here we also measure the rotational dynamics of C153 in these mixtures and its relation to solvent viscosity. In addition, self diffusion coefficients of the cation $[Im_{41}^+]$ and acetonitrile are obtained using NMR methods and compare them to recent simulations of Chaban and Prezhdo³.

4.2. Experimental Methods

Coumarin 153 was purchased from Exciton and used without further purification. 1-Butyl-3-methylimidazolium tetrafluoroborate $[Im_{41}][BF_4]$ was obtained from Iolitec and dried under vacuum at 45 °C overnight prior to sample preparation. Acetonitrile (anhydrous, spectrophotometric grade) was used as received from Sigma-Aldrich. The mixtures were prepared by weight inside a nitrogen-purged glove box. The water contents of the mixtures were measured using a Mettler-Toledo DL39 Karl Fischer coulometer and were below 100 ppm by weight in all cases.

A Hitachi U-3000 UV/Vis spectrometer was used to measure the absorption spectra of C153 in the mixtures. Corrected⁹ fluorescence spectra were measured using a SPEX Fluorolog 212 spectrometer exciting at 400 nm. A water bath was connected to the emission sample holder to maintain the temperature at 20.5 °C \pm 0.1 °C. A stock solution of the fluorophore C153 in methanol was used to prepare the sample for solvation dynamics measurements. The methanol was fully vaporized prior to addition of the solvent mixture. Optical densities were maintained near to 0.1 in 1 cm quartz cuvettes for emission measurements and 1 for absorption measurements.

Refractive indices were measured using a Reichert Abbe Mark II Refractometer at 25 °C. Diffusion coefficients of the mixtures were obtained from NMR ¹H data measured on Bruker DRX-400 and AV-III-850 spectrometers using the longitudinal eddy current delay stimulated echo pulse sequence.¹⁰

The viscosities of all mixtures were measured at 20.5 °C ± 0.1 °C using Cannon-Fenske glass viscometers of varying sizes. At least three measurements were recorded for each mixture. The Cannon-Fenske viscometers measure the kinematic viscosity (cm²/s) which must be converted to dynamic viscosity (Pa·s) using the density. The densities used for this purpose were those reported by Huo et al.¹¹ Several of the highest viscosity mixtures ($x_{IL} = 0.6$, 0.9 and 1) were also measured with a Brookfield Model HBDV-III+CP cone/plate Rheometer between 5 and 65 °C. Calibration was made using the NIST-certified viscosity standards N75 and N100 (Cannon Instruments). The latter temperature-dependent viscosities from the rheometer were fit to the Vogel-Fulcher-Tammann¹² equation and compared to measured values at 20.5 °C from the glass viscometer measurements. They agree with each other within uncertainties.

Time-resolved fluorescence data were recorded using a home-built timecorrelated single photon counting (TCSPC) setup at Penn State University and florescence up-conversion spectroscopy (FLUPS) at Humboldt University of Berlin. For TCSPC, excitation was the doubled output of a cavity-dumped Ti:sapphire laser (Coherent Mira 900F/APE PulseSwitch) operating at 800 nm and a repetition rate of 3 MHz. The full-width of the instrumental response of this system was 25 ps as measured using a scattering solution. Emission transients were measured with magic angle polarization through a monochromator (ISA H10) with an emission band-pass of 4 nm after a UV filter to cut off the excitation pulse. About 20 decays were collected across the steady-state emission spectrum. Each decay was fit to a multi-exponential form with an iterative reconvolution algorithm and time-resolved spectra reconstructed from these fits.^{13,14} All TCSPC data were recorded at 20.5 \pm 0.1 °C.

A broadband fluorescence upconversion spectrometer with femtosecond timeresolution^{15,16} was applied to measure fast portion of the solvation dynamics. A Ti:sapphire laser (FEMTOLASERS *sPro*) generates 500 μ J pulses at 800 nm and a 500 Hz repetition rate. This fundamental laser pulse is then split into two beams in a 6:1 ratio. The stronger beam was sent to a traveling-wave optical parametric amplifier of superfluorescence (TOPAS, LIGHTCONVERSION) which generated the gating pulse at 1340 nm. The weaker beam was frequency doubled to 400 nm pulses with 40 fs FWHM after compression and used as the optical pump. This beam was attenuated (~ 1 μ J) and focused onto the sample by a thin lens (fl = 200 mm, fused silica) to a spot diameter of 0.1 mm. The upconverted signal was then generated by focusing the delayed fluorescence and the gating pulse onto a potassium dihydrogen phosphate (KDP) crystal. The sample cell was kept in a sealed flowing argon environment consisting of a glass chamber with P₂O₅ desiccant. The water content could be kept to less than 200 ppm by weight using this setup. These experiments were performed at room temperature, 20.5 ± 1 °C.

The time-resolved spectra were obtained by combining FLUPS and TCSPC experimental data as described in Chapter 3. The solvation response function is calculated as the Equation 4.1.

$$S(t) = \frac{v(t) - v(\infty)}{v(0 - v(\infty))}$$
(4.1)

where $\nu(0)$ is estimated from steady-state spectra¹³ and $\nu(\infty)$ is extrapolated from TCSPC data at long times.

To measure the rotation time of coumarin 153, TCSPC transients were recorded at parallel, perpendicular and magic angles with respect to the excitation polarization. For every mixture, three sets of rotation data at three different emission wavelengths were collected and fit independently. One wavelength was at the peak and the other two at the half intensity points of the steady-state spectrum. The parallel, perpendicular and magic decays were simultaneously fit by a convolute-and-compare algorithm in order to obtain the anisotropy decay, r(t), assumed to be a bi-exponential function of time. The average of the three data sets at different wavelengths was used as the final rotation time. The

initial anisotropy r_0 is fixed during the two exponential fitting with value of 0.375 from Horng's paper¹⁷.

4.3. Results and Discussion

4.3.1. Physical Properties of the Mixtures

Viscosities measured at 20.5 °C are summarized in Table 4.1 and plotted in Figure 4.1 (a). The dark green dots in Figure 4.1(a) represent the measured viscosities and the green smooth line is the fit $\ln(\eta/cP) = 5.98x_{IL}^{0.77} - 1.08$. Viscosities obtained from literature souces^{18,19,4} at 25 °C are also plotted in Figure 4.1 (b). The blue curve is a fit of the data from Zhu et al.¹⁸ and Wang et al.⁴ with the equation of $\ln(\eta/cP) = 5.84x_{IL}^{0.77} - 1.11$. The data from Li et al.¹⁹ are not included in this fit because they appear to be systematically too high (green squares in Figure 4.1(b)).



Figure 4.1: Measured and literature viscosity values of the mixtures. (a) The measured viscosities at 20.5 °C (symbols) plotted vs. the ionic liquid mole fraction. The dark green curve is the fit of these data (see text). The dashed blue curve reproduces the fit to the 25 °C data in panel (b) for comparison.

(b). Literature viscosity data at 25 °C. Black circles, red triangles and green squares represent data from Zhu et al.¹⁸, Wang et al.⁴ and Li et al.¹⁹, respectively. The blue curve is a fit of the data of Zhu et al. ¹⁸ and Wang et al.⁴

X _{IL}	Φ _{IL}	$\rho*/g ml^{-1}$	n _D	<i>f</i> (n _D ²)	η /cP	D(ACN)/ 10 ⁻¹¹ m ² s ⁻¹	<i>D</i> (Im ₄₁ ⁺)/ 10 ⁻¹¹ m ² s ⁻¹
0.00	0.000	0.788	1.3414	0.210	0.35	485	
0.10	0.285	0.911	1.3705	0.226	0.87		
0.20	0.473	0.990	1.3879	0.236	1.84	144.2	50.6
0.30	0.606	1.046	1.3975	0.241	3.72		
0.40	0.705	1.086	1.4037	0.244	6.58	58.9	20.2
0.50	0.782	1.117	1.4088	0.247	11.85		
0.60	0.843	1.140	1.4125	0.249	18.78	23.4	6.4
0.80	0.935	1.173	1.4182	0.252	53.27	12.1	2.9
0.90	0.970	1.185	1.4202	0.253	84.17	8.3	2
1.00	1.000	1.194	1.4212	0.254	130.13		1.6

Table 4.1: Mixtures studied and some of their properties.

Note: All data are at 25 °C except for viscosities which were measured at 20.5 °C. The uncertainty of the refractive index (n_D) is ± 0.0004 and the viscosity (η) data has $\pm 1\%$ uncertainty. x_{IL} represents the mole fraction and Φ_{IL} is the volume fraction. D(ACN) and D(Im_{41}^+) represent the diffusion coefficient of acetonitrile and cation of the ionic liquids, respectively. * The density data is from literature Huo et al 2007.¹¹

Refractive indices (n_D, Table 4.1) were measured for use in considering the solvatochromism of C153 in the following section. Most relevant to this use is the reaction field factor $f(n_D^2)$, plotted in Figure 4.2.

$$f(n_D^2) = \frac{n_D^2 - 1}{n_D^2 + 2} \tag{4.2}$$

These data are conveniently fit to a function $f(n_D^2) = a\Phi_{IL}^3 + b\Phi_{IL}^2 + c\Phi_{IL} + d$. where Φ_{IL} is the volume fraction of the ionic liquid, a=0.0057, b=-0.0271, c=0.0649 and d=0.2103.

The green line is the function $f(n_D^2) = \Phi_{IL} f(n_{D,IL}^2) + (1 - \Phi_{IL}) f(n_{D,ACN}^2)$, expected for "ideal" mixtures.



Figure 4.2: Plots of reaction field factor $f(n_D^2)$ vs. the mole fraction x_{IL} (black circles) and the volume fraction Φ_{IL} (blue squares). The blue curve is the fitting $f(n_D^2) = a\Phi_{IL}^3 + b\Phi_{IL}^2 + c\Phi_{IL} + d$. (see text). The green line is linear behavior of a ideal mixture.²⁰

As mentioned in the Experimental section, the self-diffusion coefficients of the cation and acetonitrile components at some mixture compositions were obtained from NMR measurement. The results are provided in Table 4.1. There are some simulation data for this mixture from Chaban and Prezhdo³ who simulated the diffusion rates using a new force field model. Figure 4.3 shows the plots of the diffusion rates of cation Im_{41}^{+} and the acetonitrile versus the $[Im_{41}][BF_4]$ mole fraction. The black circles represent the

simulation data from Chaban and Prezhdo³ and the red triangles are the NMR results. The red lines are the fitting functions from the experimental data, $D(\text{Im}_{41}^+) = 131.4 \exp(-4.8x_{IL})$ and $D(ACN) = 191.4 \exp(-12.8x_{IL}) + 293.6 \exp(-4.1x_{IL})$. There is reasonable agreement between the simulated and measured diffusion rates.



Figure 4.3: Measured and simulated diffusion coefficients of the mixtures. (a) Diffusion rates of the cation [Im41+] from simulation data of Chaban and Prezhdo³ (black circle), the NMR measurement (red triangle) and the fitting for experimental results (red line, see text). (b) diffusion rates of acetonitrile.

The diffusion coefficients (D_{SE}) are also calculated from Stokes-Einstein equation with stick boundary condition.

$$D_i = \frac{k_B T}{6\pi\eta R_i} \tag{4.3}$$

Where k_B represents Plank's constant, η viscosity and *R* the diffusor's radius. The van der Waals volumes of Im₄₁⁺, BF₄⁻ and acetonitrile are 163.5, 50.5 and 47.1 Å³ respectively. The calculated radii are 3.4 Å (Im₄₁⁺), 2.3 Å (BF₄⁻) and 2.2 Å (ACN). The molecular volume ratio V_u/V_v is the molecular volume of the diffusion target molecule over the mixture solvent molecular volume which is the weighted volume of all three species. Figure 4.4 (a) is the plot of the measured diffusion coefficients versus the reciprocal of the solvent viscosities. The ratios of predicted and measured diffusion rate are plotted vs. the molecular volume ratio V_u/V_v in Figure 4.4 (b). The dark green curve is the fitting function from the literature values of measured ionic liquid diffusion coefficients.²¹ The ratios are correlated to V_u/V_v in roughly the same manner as are solutes in neat ILs. The weak conclusion is that there is not anything obviously unusual about the diffusion coefficients in these mixtures.



Figure 4.4: Observed and Stokes-Einstein predicted diffusion coefficients. (a): correlation between the measured diffusion rates and the reciprocal of the viscosity. The fitting functions are $\ln(D_{ACN}) = 0.77 \times \ln(1/\eta) - 19.92$ and $\ln(D_{Im41BF4}) = 0.86 \times \ln(1/\eta) - 20.90$.

(b): Ratios of the Stokes-Einstein predicted and observed diffusion coefficients vs. the molecular volume ratio V_u/V_v. The dark green curve is the correlating equation $\frac{D_{SE}}{D_{obs}} = \left| 1 + a \left(\frac{V_u}{V_v} \right) \right|$

4.3.2. C153 Spectra and Energies

Normalized absorption and steady-state emission spectra of C153 in acetonitrile (red dashed curves) and $[Im_{41}][BF_4]$ (blue curves) are shown in Figure 4.5. For comparison we also include spectra of the ionic liquid $[Im_{41}][BF_4]$ plotted relative to the C153/ $[Im_{41}][BF_4]$ spectra. The absorption and emission spectra of C153 in the two neat solvents are similar and differ primarily in a small shift. The fluorescence of unavoidable impurities in the $[Im_{41}][BF_4]$ was not a concern relative to the much stronger emission from the solute C153.



Figure 4.5: Steady state absorption and emission spectra of C153 in pure acetonitrile (red, short dash) and in pure [Im₄₁][BF₄] (blue, solid). Spectra of pure [Im₄₁][BF₄] (dark green, dash-dot),

$x_{\rm IL}$	<i>v</i> (0)	$v(\infty)$	f_{G}	ω _G	a_1	a ₂	a ₃	τ_1	τ_2	τ_3	<τ _G >	$<\tau_{exp}>$	$<\tau_{sol}>$
				ps⁻¹				ps	ps	ps	ps	ps	ps
0	20.89	18.91	0.544	7.85	1.00			0.33			0.16	0.33	0.24
0.20	20.62	18.52	0.539	5.39	0.70	0.14	0.16	1.40	14	118	0.23	22	10
0.30	20.62	18.46	0.418	7.13	0.55	0.27	0.17	0.76	9	90	0.18	19	11
0.40	20.55	18.46	0.600	5.38	0.43	0.39	0.17	2.00	37	237	0.23	56	23
0.50	20.55	18.45	0.189	9.70	0.56	0.24	0.20	0.41	16	161	0.13	37	30
0.60	20.52	18.40	0.423	8.50	0.38	0.30	0.32	0.55	71	287	0.15	112	65
0.80	20.51	18.39	0.341	8.40	0.35	0.44	0.21	0.65	86	779	0.15	198	131
0.90	20.51	18.36	0.082	11.87	0.49	0.23	0.28	0.26	39	648	0.11	193	177
1	20.53	18.37	0.307	6.98	0.19	0.40	0.41	1.76	64	790	0.18	350	243

 Table 4.2:
 Summary of limiting frequencies and parameters of fits of S(t) data to Eq. 4.10.

Note: $\nu(0)$ is estimated from steady-state spectra¹³ and $\nu(\infty)$ is extrapolated from TCSPC data at long times.

The average times are from Equations 4.11- 4.13.

Frequency data are summarized in Table 4.2. The emission peak frequencies of C153 in the mixtures at time-zero are estimates as described in Section 2.2.3. Frequencies at time infinity are from the deconvoluted TCSPC data. The fitting parameters of solvation response function and the solvation correlation time are also provided in Table 4.2.



Figure 4.6: Peak frequencies of the absorption and emission spectra. (a). The steady-state absorption peak frequency vs. mole fraction of the ionic liquid; (b). The emission peak frequency (open circle) and emission peak frequency at time infinity (filled circle) vs. mole fraction of the ionic liquid.

(c) & (d). Peak frequencies vs. reaction field factor $f(n_D^2)$.

In Figure 4.6, the peak frequencies of the emission and absorption spectra are plotted versus mole fraction of the ionic liquid (a, b) and the reaction field factor

$$f(n_D^2) = \frac{n_D^2 - 1}{n_D^2 + 2}$$
 (c, d). The peak frequencies at time infinity are also plotted in figure 4

to compare to the steady state frequency shift. The time infinity spectra are obtained from TCSPC setup using 20 ns time window. The frequency trend is similar to the one from steady state results. The peak frequencies of steady-state and at infinity time are nearly equal when $\tau_{sol} < \tau_{fluor}$ (here in the mixtures with x_{IL} closes to 0.). One could interpret the nonlinearity versus x_{IL} as being a result of preferential solvation but the $f(n_D^2)$ results say otherwise. Figure 4.6 (c) and (d) indicate that the peak frequencies are approximately linearly related to the reaction field factor very well, which means that there is no preferential solvation.

The solvation free energy difference $(\Delta_{sol}G)$ of C153 between the ground state and the excited state, and the reorganization energy λ_{sol} were also calculated based on the following equations: ²²

$$\Delta_{sol}G = \frac{1}{2}h[v_{abs} + v(\infty)] - \Delta G_0$$
(4.4)

$$\lambda_{sol} = \frac{1}{2} h[v(0) - v(\infty)]$$
(4.5)

where v_{abs} is the peak frequency of the absorption spectrum, *h* is the Planck's constant, ΔG_0 is the gas phase value estimated from a dielectric extrapolation in conventional solvents. Here 295.9 kJ/mol is used as the value of ΔG_0 which is taken from the literature.²²



Figure 4.7: The solvation free energy and reorganization energy. (a). The correlation between the solvation free energies and the reaction field factor $f(n_D^2)$. $\Delta G = -13.10 - 129.45 f(n_D)$ (b). The reorganization energies are fitted to a function corresponding to the mole fraction of ionic liquid. $\lambda = 12.27 + 0.93\{1 - \exp(-14.47x_{IL})\}$

The solvation energy is calculated from Equation 4.4 and plotted in Figure 4.7 (a). The reorganization energy is also plotted in Figure 4.7 (b). The solvation free energies and reorganization energies are plotted versus the reaction field factor and the mole fraction of the ionic liquid, respectively. The solvation free energies is close to a linear function of $f(n_D^2)$ suggesting that the main source of the variation with composition is the difference in electronic polarizabilities of acetonitrile and $[Im_{41}][BF_4]$. The reorganization energies are fit to a smooth curve to see the trend. Our original assumption was that one would expect to see a constant value of λ_{sol} due to the similar polarity of acetonitrile and $[Im_{41}][BF_4]$, but the data shows a different story. Obviously, the reorganization energy of pure acetonitrile is lower than the mixtures and pure ionic liquid by 7%.

4.3.3. C153 Rotational Dynamics

Fluorescence anisotropy data were fit to the function

$$r(t) = r_0 \left[a_1 \exp(-\frac{t}{\tau_1}) + a_2 \exp(-\frac{t}{\tau_2}) \right]$$
(4.6)

Fit parameters are summarized in Table 4.2. In these fits the initial anisotropy r_0 is fixed at the value of 0.375, derived from the frozen-solvent data reported in Ref.¹⁷ The rotational correlation time is then obtained by the following equation,

$$< au_{rot} >= a_1 au_1 + a_2 au_2$$
 (4.7)

x _{IL}	0.2	0.3	0.4	0.5	0.6	0.8	0.9	1
a1	0.30	0.31	0.31	0.43	0.24	0.20	0.18	0.21
τ 1 / ps	13	49	72	200	118	172	154	67
a2	0.70	0.69	0.69	0.57	0.76	0.80	0.82	0.79
τ 2 / n s	0.15	0.27	0.41	0.94	1.23	2.71	3.74	5.24
<\u03c0_rot	0.11	0.20	0.31	0.62	0.97	2.21	3.10	4.18
Unc */ns	0.01	0.02	0.07	0.09	0.10	0.17	0.19	0.45

Table 4.3: Parameters of Biexponential Fits to Fluorescence Anisotropy Data

Note: * The uncertainty is obtained from the 95% confidence limit for three measurements.

Figure 4.8 shows the correlation between rotation time and viscosity. The line shows the fit $\ln \langle \tau_{rot} \rangle = 4.1 + 0.9 \ln(\eta/cP)$. The relation $\tau \propto \eta^{0.9}$ is close to hydrodynamic expectations.¹⁷ The inset in Figure 4.8 is the rotational coupling constant (C_{rot}) versus x_{IL} where C_{rot} is given by

$$C_{rot} = \frac{\zeta_{obs}}{\zeta_{stick}} = \frac{\langle \tau_{obs} \rangle}{\langle \tau_{stick} \rangle}$$
(4.8)

The hydrodynamic prediction using stick boundary condition is

$$\left\langle \tau_{stick}^{(L)} \right\rangle = \frac{6Vf\eta}{L(L+1)k_BT} \tag{4.9}$$

where *L* is the rank of the orientational correlation function (L=2 here),¹⁷ *V* the molecular volume (246 Å³), and *f* the shape factor (1.71).¹⁷ From the results of Horng et al.¹⁷, for dipolar solvents, $C_{rot} = 0.57 \pm 0.09$. In these mixtures we find that C_{rot} decreases from 0.6 to 0.3 with the increase of mole fraction of the ionic liquid (inset of Figure 4.8). The observed rotation time is faster with the increase of mole fraction of $[\text{Im}_{41}][\text{BF}_4]$ compared to the stick hydrodynamic prediction, which may be caused by the preferential solvation of C153. Horng et al¹⁷ point out that the rotation time of C153 depends on solvent size from a molecular perspective. The solvent size increases with the increase of the ionic liquid mole fraction. The rotational coupling constant is decreasing with x_{IL} increasing.



Figure 4.8: Plot of the rotation times vs. viscosities. The black line is the fitting function $\ln \langle \tau \rangle_{rot} = 4.12 + 0.90 \ln(\eta/cP)$. The inset figure is a plot of rotational coupling constant vs. x_{IL} . The rotation time of C153 in neat acetonitrile is from Horng et al¹⁷.

4.3.4. Solvation Dynamics

Representative time-resolved spectra (x_{IL} =0.50) are plotted in Figure 4.9. The blue curves are from FLUPS measurement at early times (100 fs – 20 ps) and the green points and lognormal fits are TCSPC data at longer times (50 ps – 20 ns). The dash line is the estimated time zero spectrum (see Sec. 2.2.3). The sharp rise on the blue edge of the spectrum at 0.1 ps is due to Raman scattering. The early spectra are fit over a region that avoids the interference from the Raman (Sec. 3.2). Apart from the need for a

small frequency correction of the FLUPS data, we generally find good agreement between the spectra obtained using the two techniques. The spectra narrow somewhat in time but the primary feature of these spectra is a frequency shift of $\sim 200 \text{ cm}^{-1}$.



Figure 4.9: Representative time-resolved spectra of C153 in the X_{IL} = 0.5 mixture. The blue curves are from FLUPS measurement at times of 0.1, 0.3, 0.5, 1, 2, 5, 10 and 20 ps. Green points are TCSPC data at times of 0.05, 0.1, 0.2, 1, 5 and 20 ns and the smooth green curves are lognormal fits to these data. The black dashed curve shows the estimated time-zero spectrum.

Peak frequency data from the FLUPS and TCSPC experiments were combined as described in Sec. 3.2 and used to calculate the spectral response function $S_v(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}$. To summarize the $S_v(t)$ data they were fit to a function consisting

of one Gaussian and three exponential components,

$$S(t) = f_G \times \exp[-\frac{1}{2}(\omega_G \times t)^2] + (1 - f_G) \times [a_1 \times \exp(-\frac{t}{\tau_1}) + a_2 \times \exp(-\frac{t}{\tau_2}) + (1 - a_1 - a_2) \times \exp(-\frac{t}{\tau_3})]$$
(4.10)

The Gaussian function represents the fast inertial component of the response and the remainder represents the slower diffusive components. The integral time of the Gaussian portion is given by

$$< au_G>=\int_{0}^{\infty}\exp(-\frac{\omega_G^2 t^2}{2})dt = \left(\frac{\pi}{2}\right)^{1/2}\omega_G^{-1} = \frac{1.2533}{\omega_G}$$
(4.11)

and that of the remainder by

$$< \tau_{exp} >= a_1 \times \tau_1 + a_2 \times \tau_2 + (1 - a_1 - a_2) \times \tau_3$$
(4.12)

The total solvation time is then calculated as

$$\langle \tau_{sol} \rangle = f_G \times \langle \tau_G \rangle + (1 - f_G) \times \langle \tau_{exp} \rangle$$
(4.13)

The fit parameters and solvation time of all mixtures are tabulated in Table 4.2. Figure 4.10 shows the quality of the fits of some representative response functions. Figure 4.10(a) shows the solvation response of mixtures with the ionic liquid mole fraction of 0.3, 0.5 and 0.8. Figure 4.10 (b) represents the spectral response from experimental results of all mixtures.



Figure 4.10: Observed solvation response functions. (a). Three solvation response functions (dots) and fits to Eq. 4.10 (solid line): x_{IL} =0.3 (blue), x_{IL} =0.5 (red) and x_{IL} =0.8 (green). (b). S(t) summary plot of experimental data.

The solvation times of the mixtures are plotted versus solvent viscosities in Figure 4.11. The red triangles represent the fast solvation time $\langle \tau_G \rangle$. The blue squares are the slow solvation component $\langle \tau_{exp} \rangle$ and black circles are the integral solvation times $\langle \tau_{sol} \rangle$. The colored lines are fits excluding the neat acetonitrile data. The fast solvation time component $\langle \tau_G \rangle$ is basically the same for all the mixtures. The slow solvation time $\langle \tau_{exp} \rangle$ is fit by $\ln \langle \tau_{exp} \rangle = 2.41 + 0.69 \ln(\eta/cP)$. The integral solvation time $\langle \tau_{sol} \rangle = 1.59 + 0.81 \ln(\eta/cP)$.



Figure 4.11: Solvation times vs solvent viscosity, fast solvation time $\langle \tau_G \rangle$ (red triangle), slow solvation $\langle \tau_{exp} \rangle$ (blue square) and the integral solvation time $\langle \tau_{sol} \rangle$ (black circle). The colored lines are fits without the neat acetonitrile data.



Figure 4.12: Some representative measured and predicted S(t). The black dots represent experimental data and dielectric calculation results are labeled with solid lines: X_{IL} =0.3 (blue), X_{IL} =0.5 (red) and X_{IL} =0.8 (green).

To compare to the experimental results, a simple dielectric continuum model is applied to predict the solvation dynamics of the mixtures. The details of this calculation can be found in Chapter 3. And the dielectric data are from Buchner's preliminary results. The solvation response functions predicted by the simple dielectric continuum model are compared to the observed solvation response in Fig. 4.12. The black dots are the experimental results and the colored solid lines represent the dielectric continuum predictions. For smaller ionic liquid mole fractions, the calculated solvation response function matches the experimental results very well for t > 1 ps. But for the higher mole fraction ionic liquid mixtures, the observed *S*(t) shows difference with the calculated data at time range from 1 ps to 1 ns. As we know, the dielectric continuum model predicts the solvation response very well for conventional solvents but not very well for ionic liquids (Chapter 3). This may be the reason that we see bigger deviation for higher mole fraction of the ionic liquid.



Figure 4.13: Comparison of the solvation response times of measured and predicted response functions at certain S(t) values, 0.1(black), 0.3(red), 0.5(green) and 0.7(blue). The inset plot shows the meaning of these times.

As a means of assessing the level of agreement between the observed and calculated response functions we compare the times required for S(t) to reach values of 0.1, 0.3, 0.5 and 0.7. This comparison is provided in Figure 4.13. For example, for the 0.5 ionic liquid mole fraction mixture, the observed time for S(t) reaches 0.3 is 4.1 ps

and the predicted time at 0.3 of S(t) is 3.3 ps. The point plotted in Figure 13 is then (3.33, 4.12). The outstanding green square is the S(t)=0.5 point of C153 in the pure ionic liquid. Except for this point, the observed solvation times are highly correlated to the predicted times, even though the measured and calculated solvation dynamics differ systematically at long times.

4.4. Summary and Conclusions

Solvation dynamics of the acetontrile and 1-butyl-3-methylimidazolium tetrafluoroborate were measured using the standard probe coumarin 153. Combing the FLUPS technique which has 80 fs time resolution with TCSPC, the entire solvation response is captured. The validity of the simple dielectric continuum model is tested against these mixture data. The measured solvation response functions are matched well with the calculated results. The rotation times of C153 in all the mixtures are measured and correlated well to the viscosity. The diffusion coefficient measured NMR experiments are matched well with the simulated diffusion coefficients.

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Chapter 5. Experimental Bimolecular Electron Transfer Between the 9,10-dicyanoanthracene and *N*,*N*-dimethylaniline in Ionic Liquids

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Other People's contributions:

Anne Kaintz measured the diffusion coefficients. Gary Baker made all pyrrolidinium ionic liquids.

5.1.Introduction

Among the myriad uses for which ionic liquids are currently being investigated, numerous applications fall within the area of energy generation and storage.¹ For example, the low volatility, intrinsic conductivity, and tailorabiliy of ionic liquids afford significant advantages over conventional organic solvents in devices such as fuel cells, supercapacitors and batteries, and dye-sensitized solar cells.^{2,3} Electron transfer is a key component of many such applications and for this reason it is important to achieve a sound understanding of the nature of electron transfer processes in ionic liquids. In particular, it is important to learn to what extent the theoretical approaches developed for treating electron transfer in conventional solvents are also applicable to ionic liquids. Toward this end many electrochemical studies of heterogeneous electron transfer have been performed.^{4,5} These studies have shown that while the mechanisms of reaction are typically the same as in high-polarity conventional solvents, the high viscosities of ionic liquids often produce much slower rates. Some interesting attempts have been made to relate heterogeneous reaction kinetics to fundamental theories of electron transfer,⁶ but the largely unknown and apparently complex structure of ionic liquid - electrode interfaces⁷ renders comparison to theory difficulty. In the case of homogeneous electron transfer, simulations⁸⁻¹¹ and recent experimental studies of photo-induced intramolecular processes¹² suggest that electron transfer is comparable in ionic liquids and high-polarity conventional solvents. The primary difference found in ionic liquids is a marked decrease in rates caused by the much slower and highly dispersed solvation dynamics characteristic of these solvents.^{13,14}

#	Reaction ^(a)	Ionic Liquids ^(b)	η/c P ^(c)	[Q]/M ^(c)	$\tau_0/\mathrm{ns}^{(\mathrm{c})}$	$k_q/k_D^{(c)}$	Technique ^(d)	Ref.
1	$C15n^* + DMA \rightarrow C15n^- + DMA^+$	[Im ₅₁][BF ₄]	135	.5-1.5	1-4	100-170	ps FL	23
2	$C15n^* + DMA \rightarrow C15n^- + DMA^+$	$[Im_{21}][Tf_2N]$	31	.0525	1-3	5-8	ps FL	21
3	$C15n^* + DMA \rightarrow C15n^- + DMA^+$	DAF	75	.0108	1-3	33-35 130-150	ps FL SS FL	20
4	$BPH^* + CCl_4 \rightarrow BPH^+ + CCl_4^-$	$[Im_{41}][Tf_2N]$	49	.0112	5	16	ns TA	22
5	$DCA^* + D \rightarrow DCA^- + D^+$	$[Im_{n1}][PF_6] n=4,8$	350, 570	0.4-1.1	12, 13	85, 150	SS FL	19
6	$Py^* + DMA \rightarrow Py^- + DMA^+$	4 Im ILs	34-330	.0106	300	2-4	ns FL & TA	81
7	$BuPy^{\bullet} + DQ \rightarrow BuPy^{+} + DQ^{\bullet}$	5 N ⪻ ILs	80-700	< .004	$\sim 5 \times 10^{4}$	5-14	radiolysis	17
8	$^{3}\text{Bp}^{*}$ + Naph \rightarrow Bp + 3 Naph *	5 Im ILs	50-700	< .003	>2000	3-12	ns TA	16
9	$\frac{\text{Ru(bpy)}_{3}^{*2+} + \text{MV}^{2+} \rightarrow \text{Ru(bpy)}_{3}^{*3+} + \text{MV}^{+}}{\text{MV}^{+}}$	[Im ₄₁][PF ₆]	260	< .015	~2000	1.1	ns TA	15
10	$I_2^- + I_2^- \rightarrow I_3^- + I^-$	6 assorted ILs	55-300	(<10 ⁻⁵)		1.0-1.8	ns TA	82
11	$MV^+ + MV^{2+} \rightarrow MV^{2+} + MV^+$	3 Im ILs	10-12	(5×10 ⁻⁴)		.3234	ESR lineshape	18

Table 5.1: Diffusion-Limited Bimolecular Reactions in ILs

(a) C15n = various coumarin dyes (151, 152, ...), DMA = *N*,*N*-dimethylaniline, BPH = ketyl radical, DCA = 9,10-dicyanoanthracene, D = various amine donors, Py = pyrene, MV = methylviologen, BuPy = n-butylpyridine, DQ = duraquinone, Bp = benzophenone, Naph = naphthalene, Ru(bpy)₃ = ruthenium tris-bipyridine

(b) Im_{n1} designates a methylimidazolium cation with a C_nH_{2n+1} substituent, DAF = *N*,*N*-dimethylethlyammoniumformate, and Im, N, and Pr respectively denote imidazolium, ammonium, and pyrrolidinium ionic liquids.

(c) η denotes solvent viscosity, [Q] the "quencher" (abundant reactant) concentration, τ_0 the "fluorophore" (rare reactant) lifetime in the absence of quencher, k_q the observed bimolecular rate constant, and k_D the rate constant calculated from $k_D = 8k_BT/3\eta$.

(d) FL = fluorescence, SS = steady state, TA = transient absorption

Bimolecular electron transfer reactions, the subject of the present work, have been previously studied by several groups.¹⁵⁻²³ In a number of cases, the rates of reactions known to be diffusion limited in conventional solvents show what on first glance appear to be anomalously high rates in ionic liquids. Table 5.1 documents some of the results currently available. In one of the earliest studies (#8 in Table 5.1) McLean et al. measured the electron transfer quenching of triplet benzophenone in five ionic liquids and two conventional solvents as a function of temperature.¹⁶ Whereas the rates observed in the solvents acetonitrile and toluene were close to expectations for a diffusion-limited process, $k_D = 8k_BT/3\eta$, McLean *et al.* noted that the rates in ionic liquids were up to an order of magnitude larger. (k_B is Boltzmann's constant, T the temperature, and η the solution viscosity.) Similar observations were made in another early study by Skrzypczak and Neta¹⁷ (#7) who measured rates of electron transfer between the butylpyridinyl radical and duraquinoneto be 5-14 times larger than expected based on viscosity-scaling rates observed in conventional solvents. Skrzypczak and Neta proposed that these high rates were the result of reactants diffusing more rapidly than would be expected based on the high bulk viscosities of ionic liquids. But enhanced diffusion is unlikely to account for some of the very high values of k_a/k_D shown in Table 5.1. For example, using a Stern-Volmer analysis of steady-state fluorescence data on the electron transfer quenching of S₁ 9,10-dicyanoanthracene by amine donors, Viera and Falvey reported values of $k_a/k_D > 50$ in two high-viscosity ionic liquids.¹⁹ Similarly high values were reported in independent studies of the fluorescence quenching of excited coumarin dyes by the groups of Sarkar(#3) and Bhattacharyya (#1). But there are also several cases (#2 and #6) in which neutral solutes show only modest rate enhancements compared to

expectations. In addition, in one study (#3), Stern-Volmer analysis of steady-state and time-resolved fluorescence data produced very different bimolecular rate constants. To date, no explanation for these varied results has been offered, and it is far from clear what it is about the ionic liquid environment that sometimes produces unexpectedly high bimolecular electron transfer rates.

In the present study we take a closer look at these issues and attempt to explain some of the apparently anomalous behavior observed. We report steady-state and timeresolved emission measurements of the electron transfer quenching of S_1 9,10dicyanonanthracene (DCA) by N,N-dimethylaniline (DMA) in ionic liquids and conventional solvents. The DCA + DMA system was chosen in part because of the extreme values of (k_a/k_D) reported by Viera and Falvey¹⁹ for strong electron donors like DMA. The long lifetime (~13 ns) of DCA and the fact that this solute shows only a very small dynamic Stokes shift also prove useful in the present work. The sort of data we collect in ionic liquids is qualitatively similar to what has been reported in previous studies. One distinction from prior work is that in addition to measuring the reaction in low viscosity conventional solvents, we also make measurements in mixtures of ethylene glycol + glycerol, which have viscosities (and polarities) comparable to those of ionic liquids. These data show that the "anomalies" reported in ionic liquid solvents are in large part due to their high viscosities and are not a special aspect of electron transfer in ionic media. We also for the first time measure diffusion rates of one of the species involved in the reaction (DMA) using NMR techniques. These measurements (and more extensive work on other solutes²⁴) show that diffusion of neutral solutes of moderate size

in ionic liquids is typically faster than hydrodynamic predictions, but usually only by factors of 3-5.

The main way in which the present work differs from other ionic liquid studies to date is that we attempt a much more detailed analysis of the bimolecular electron transfer reaction. Instead of simply applying Stern-Volmer analyses²⁵ to determine guenching rate constants for comparison to the "diffusion limit" k_D , we fit time-resolved emission decays to a complete model which couples a classical Marcus description of the distance dependent electron transfer process²⁶ to a Smoluchoski-type spherical diffusion + reaction approach^{27,28} to model the overall population kinetics. This sort of modeling has been applied previously by the groups of Tachiya,²⁹⁻³² Fayer,³³⁻³⁵ and most recently Grampp³⁶⁻³⁸ to understand bimolecular electron transfer in conventional solvents. Rather than solving the reaction-diffusion equations numerically as done by these other groups, we employ the convenient analytical approximations derived recently by Dudko and Szabo.³⁹ To our knowledge this is the first time that this method has been employed to model experimental data. We find that it is possible to satisfactorily model all of the experimental quenching collected in high polarity conventional solvents and ionic liquids using a single set of physically sensible parameters. This modeling makes it clear that theories developed to treat electron transfer and diffusion-limited reaction in conventional solvents apply equally well in ionic liquids. Once the much higher viscosities and the poorer approximation provided by hydrodynamic predictions for diffusion are accounted for, the rates of bimolecular electron transfer reactions in ionic liquids do not appear anomalous or distinctive.

5.2.Experimental Methods

9,10-dicyanoanthracene (DCA) was obtained from TCI-America (97%) and was recrystallized from a mixture of pyridine + acetonitrile prior to use. N,N-dimethylaniline (DMA; 99.5+%), cyclohexane and acetonitrile (HPLC grade), ethylene glycol (99.8%), and glycerol (99.5%) were obtained from Sigma-Aldrich and were used as received. The series of *N*-alkyl-*N*-methylpyrrolidinium*bis*(trifluoromethylsulfonyl)imides, $[Pr_{n1}][Tf_2N]$ with n = 3, 4, 6, 8, 10, were prepared as Ref.⁴⁰ described in Propyltrimethylammoniumbis(trifluoromethylsulfonyl)imide, $[N_{3111}][T_2fN],$ was obtained from Kanto Chemical and 1-butyl-3-methylimidazolium hexafluorophostphate, [Im₄₁][PF₆], from Iolitec (99%) and were used as received except for drying. Decyltrimethylammoniumbis(perfluoroethanesulfonyl)imide, [N_{10,111}][Beti], was obtained by metathesis of the bromide salt (TCI America 99+%) and [Li][Beti].⁴¹ Finally, tributyltetradecylphosphonium*bis*(trifluoromethylsulfonyl)imide $([P_{14,666}][Tf_2N])$ was prepared as described in Ref.¹² All of the ionic liquids were dried under vacuum at 45 °C overnight prior to measurement. The water contents were measured using a Mettler-Toledo DL39 Karl Fischer coulometer and were below 100 ppm by weight. Mixtures of ethylene glycol + glycerol were made by weight and had water contents of <250 ppm.

Samples for optical spectroscopy were prepared in a nitrogen-purged glove box using a stock solution of the fluorophore DCA in cyclohexane. The cyclohexane was removed by evacuation prior to adding solvent. The optical densities of these samples were maintained near 0.1 in 1 cm quartz cuvettes. Aliquots of the quencher DMA were added directly to the cuvette samples using a micropipette. Estimated uncertainties in the DMA concentration are between 16-6% over the range 0.05-0.3 M. All optical measurements were maintained at constant temperature, usually 298 K.

Steady-state absorption spectra were measured using a Hitachi U-3000 UV/Vis spectrometer at 1 nm resolution and steady-state fluorescence spectra recorded with a SPEX Fluorolog 212 spectrometer (2 nm). The emission spectra were corrected for detector sensitivity using a method based on a series of dye standards.⁴² Time-resolved fluorescence data were recorded using a home-built time-correlated single photon counting (TCSPC) setup.⁴³ The excitation source (420 nm) was the doubled output of a cavity-dumped Ti:sapphire laser (Coherent Mira 900F + APE PulseSwitch) operating at a repetition rate of 3MHz. Fluorescence was collected at magic angle with respect to the excitation polarization through a monochromator (ISA H10) with an emission bandpass of 4 nm. The instrumental response of this setup was 25-30 ps (FWHM) as judged by the signal from a scattering solution. Fluorescence decays having greater than 5000 peak counts were collected over time windows of between 8-45 ns (4096 channels) depending on sample lifetime. Decays were fit to multi-exponential functions using a convolute-and-compare algorithm. Three decays were typically measured for each sample and an averaged multi-exponential description used for analysis as described later.

The viscosities of the ionic liquid solutions and ethylene glycol + glycerol mixtures were measured with a Brookfield Model HBDV-III+CP cone/plate viscometer. The viscometer was calibrated using the NIST-certified viscosity standards N75 and N100. In most cases, viscosities were measured from 5 to 65 °C with an increment of 5°C and fit to the Vogel-Fulcher-Tammann equation used to characterize these data.

Diffusion coefficients of DMA were determined from ¹H data measured on Bruker DRX-400 and AV-III-850 spectrometers using the longitudinal eddy current delay stimulated echo pulse sequence with bipolargradient pulses.⁴⁴ In the case of the $[Pr_{n1}][Tf_2N]$ series of ionic liquids, diffusion measurements were made on DMA solutions at a series of concentrations between 0 – 0.3 M and diffusion coefficients extrapolated to infinite dilution. In this manner it was found that diffusion coefficients measured with 50 mM DMA are within uncertainties (~8%) of the limiting values. Diffusion coefficients of DMA in other solvents were therefore determined only at [DMA] = 50 mM.

5.3. Modeling the Time-Dependent Quenching Process

5.3.1. The Formalism



Scheme 1

We assume quenching (Scheme 1) to be the result of irreversible electron transfer between an excited fluorophore F^* (DCA^{*} here) and a quencher Q (DMA) as depicted in

Scheme 1. Measured fluorescence decays I(t) are assumed to be related to the timedependent reaction rate coefficient k(t) via

$$\frac{I(t)}{I(0)} = \frac{[F^*(t)]}{[F^*(0)]} = \exp\left\{-k_0 t - [Q]\int_0^t k(t')dt'\right\}$$
(5.1)

where [*Q*] indicates the concentration of quencher and k_0 is the fluorescence decay rate constant in the absence of quencher. k(t) is determined from the spherically symmetric reaction – diffusion equation for the F^* - *Q* pair distribution p(r,t):^{27,28,36}

$$\frac{\partial p(r,t)}{\partial t} = \left\{ D \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \exp[-\beta w(r)] \frac{\partial}{\partial r} \exp[+\beta w(r)] - \kappa(r) \right\} p(r,t)$$
(5.2)

where *D* is the relative diffusion coefficient of F^* and *Q*, assumed to be given by the sum of the individual diffusion coefficients $D = D_{F^*} + D_Q$, w(r) is the potential of mean force between F^* and *Q*, $\beta = (k_B T)^{-1}$ with k_B being Boltzmann's constant and *T* the temperature, and $\kappa(r)$ describes how the reaction rate varies with F^* - Q separation *r*. Finally, p(r,t) and k(t) are related by

$$k(t) = 4\pi \int_{0}^{\infty} r^{2} p(r,t) dr$$
(5.3)

Exact solution of Eq. 5.2 for k(t) is only possible in a few simple cases,⁴⁵which do not include situations in which $\kappa(r)$ includes non-contact reactions appropriate to electron transfer quenching. Before discussing solution of Eq. 5.2, we digress briefly to discuss one case in which Eq. 5.2 is analytically solvable because the results are important for the later discussion.

In the absence of significant F - Q interactions and when $\kappa(r)$ is such that reaction occurs instantaneously at some contact distance σ but not elsewhere, solution of Eq. 5.2 provides the prediction first obtained by Smoluchowski⁴⁶

$$k(t) = k_D \left\{ 1 + \sqrt{\frac{\sigma^2}{\pi D t}} \right\}$$
(5.4)

and

$$\frac{I(t)}{I(0)} = \exp\{-k_0 t - [Q](k_D t + 8\sigma^2 \sqrt{\pi D t})\}$$
(5.5)

with $k_D = 4\pi \alpha D$. If one can ignore the \sqrt{t} or "transient term" in Eq. 5. 5, exponential emission decays are predicted, and Stern-Volmer type of analysis²⁵ of either steady-state emission intensities or emission lifetimes as a function of quencher concentration yields bimolecular rate constant equal to k_D . For systems of the sort studied here, the value of k_D can be evaluated with moderate accuracy using the Stokes-Einstein predictions for diffusion coefficients, $D = k_B T / 6\pi \eta R$ where η is the solvent viscosity and R the radius of the diffusing molecule. Denoting the radii of F^* and Q by R_F and R_Q and assuming $\sigma = R_F + R_Q$, one obtains what we will refer to as the simple Smoluchowski prediction for the diffusion-limited rate constant:^{47,48}

$$k_{D} = \frac{8k_{B}T}{3\eta} \left(\frac{(R_{F} + R_{Q})^{2}}{4R_{F}R_{Q}} \right)$$
(5.6)

For comparably sized F and Q the term in parenthesis in Eq. 5. 6 is close to unity and one has the remarkably simple prediction $k_D = 8k_BT/3\eta$ used in Table 5.1. Like mentioned in the experimental part, the viscosities were measured from 5 to 65 °C with an increment of 5°C and fit to the Vogel-Fulcher-Tammann equation (5.7) and the fitted results were applied to get k_D values.

$$\ln(\eta / cP) = A + \frac{B}{(T - T_0) / K}$$
(5.7)

Returning now to the more general case, to solve Eq. 5.2 for k(t) we rely on the approximate solution proposed by Dudko and Szabo.³⁹ These authors showed that k(t) can be approximately expressed.

$$k(t) = k(\infty)[1 + \alpha_1 e^{\gamma_1^2 t} erfc(\sqrt{\gamma_1^2 t}) + \alpha_2 e^{\gamma_2^2 t} erfc(\sqrt{\gamma_2^2 t})]$$
(5.8)

where the long-time limiting rate constant $k(\infty)$

$$k^{-1}(\infty) = \left\langle \kappa \right\rangle^{-1} + k_{DC}^{-1}(\infty) \tag{5.9}$$

is a composite of the reaction-limited rate constant $<\kappa>$, given by

$$\left\langle \kappa^{n} \right\rangle = \int_{0}^{\infty} 4\pi r^{2} e^{-\beta w(r)} \kappa^{n}(r) dr$$
(5.10)

with n=1, and the long-time diffusion-controlled ("DC") rate constant

$$k_{DC}(\infty) = \frac{\frac{D}{4\pi} \langle \kappa \rangle^2}{\int_0^\infty \frac{e^{+\beta w(r)}}{r^2} \left(\int_0^r x^2 \kappa(x) e^{-\beta w(x)} dx\right)^2 dr}$$
(5.11)

The time-dependent portion of k(t) is written in terms of the parameters⁴⁹

$$\gamma_{1,2} = (\mu \mp \lambda) \frac{\langle \kappa^2 \rangle}{\langle \kappa \rangle^2} \quad \text{and} \quad \alpha_{1,2} = \frac{\langle \kappa \rangle}{2k_{DC}(\infty)} \left(1 \pm \frac{\mu}{\lambda}\right)$$
 (5.12)

where
$$\mu = \frac{k_{DC}^2(\infty)}{8\pi D^{3/2}}$$
 and $\lambda^2 = \mu^2 - [\langle \kappa \rangle + k_{DC}(\infty)] \frac{\langle \kappa \rangle^2}{\langle \kappa^2 \rangle}$ (5.13)

Dudko and Szabo tested these expressions against numerical solutions of Eq. 5.2.⁴⁵ In the case of contact reactions (reaction only at $r=\sigma$ as described above) they found this approximation to be within a few percent of numerical solution of Eq. 5.2 for a wide range of system parameters. In cases with significant distance dependence to reaction they found more modest accuracies in the range 10-15%. Given that the distance dependence of electron transfer can only be predicted semi-quantitatively, we view this level of accuracy appropriate to our purposes.

To model the distance dependence of the quenching reaction we employ the semiclassical form of the Marcus expression for non-adiabatic electron transfer:^{26,50,51}

$$\kappa = \frac{V_{el}^2}{h} \left(\frac{1}{4\pi\lambda k_B T}\right)^{1/2} \exp\left\{-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right\}$$
(5.14)

where V_{el} is the electronic coupling, λ the reorganization energy, and ΔG the driving force for reaction. All three of these quantities are expected to depend upon the separation between $F^* - Q$, and we represent these dependences as follows. The electronic coupling is expected to decrease exponentially with distance as

$$V_{el}^{2}(r) = V_{0}^{2} \exp\{-\beta_{el}(r - r_{0})\}$$
(5.15)

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Where $r_0 = R_F + R_Q$ and V_0 is the electronic coupling at r_0 . The reorganization energy consists of an intramolecular contribution and a solvent contribution $\lambda(r) = \lambda_{intra} + \lambda_{solv}(r)$. For the solvent contribution we use the 2-sphere dielectric continuum expression of Marcus:^{52,53}

$$\lambda_{sol}(r) = \frac{e^2}{(4\pi\varepsilon_0)} \left\{ \frac{1}{2R_F} + \frac{1}{2R_Q} - \frac{1}{r} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\varepsilon_r} \right\}$$
(5.16)

where ε_0 is the permittivity of free space, *n* the refractive index and ε_r the relative permittivity of the solvent. For the distance dependence of the driving force we adopt the Rehm-Weller expression including the free energy of reaction ΔG_0^{54}

$$\Delta G(r) = \Delta G_0 - \frac{e^2}{(4\pi\varepsilon_0)\varepsilon_r} \frac{1}{r}$$
(5.17)

5.3.2. The Specification of Model Parameters

Application of the model just described requires specification of a number of parameters characterizing the reactants, the electron transfer process, and the solvent. For convenience these parameters are summarized in Table 5.2. How values of these parameters were chosen is discussed below.

Parameter	Value	Use in Fits
R_F – fluorophore radius	3.66 Å	fixed
R_Q – quencher radius	3.12 Å	fixed
λ_{intra} – intramolecular reorganization energy	0.4 eV	fixed
V_0 - electronic coupling at $r=R_F+R_Q$	100 cm ⁻¹	initially varied
β_{el} – coupling length scale parameter	1.5 Å ⁻¹	fixed
\mathcal{E}_r – relative permittivity	39 (or 2.0) ^a	fixed
<i>n</i> – refractive index	1.42	fixed
ΔG_0 – free energy change	-1.2 (or+0.8)ªeV	varied
τ_0 – unquenched lifetime	10-14 ns	fixed at [Q]=0 value
σ_{FQ} – size parameter of $U(r)$	R _F +R _Q	fixed
\mathcal{E}_{FQ} – energy parameter of $U(r)$	~2.5 kJ/mol	varied
R_h – effective hydrodynamic radius	~1.7 Å	varied

Table 5.2: Summary of Model Parameters used in Fitting Quenching Data

(a) Values in parenthesis are used only in the case of cyclohexane solvent.

The fluorophore and quencher radii R_F and R_Q are determined assuming spherical shapes and the van der Waals volumes⁵⁵ of DCA and DMA. The intramolecular reorganization energy is set at $\lambda_{intra} = 0.4$ eV based upon values obtained from gas-phase calculations at the B3LYP/6-31G(d) and MP2/6-31G(d,p) levels. The value of V_0 , the electronic coupling at the "contact" distance R_F+R_Q , is a poorly defined quantity, as this coupling is strongly dependent upon the relative orientations of the F-Q pair in addition to the their separation,⁵⁶⁻⁵⁸ Computational studies⁵⁶⁻⁵⁸ and analyses of experimental data on similar systems^{29,36,37} suggest V_0 to be on the order of 100 cm⁻¹ (12 meV). We examined the effect that varying this parameter had on fits to the observed quenching kinetics and ultimately fixed the value at 100 cm⁻¹. Experimental and computational work suggests that the decay constant β_{el} should lie within the range $1.0 \le \beta_{el} \le 2.0 \text{Å}^{-1}$ for most solvents.^{56,59-61} We adopt a fixed value of $\beta_{el} = 1.5 \text{ Å}^{-1}$ for all solvents studied here.

The reaction free energy can be estimated using the measured oxidation potential $E(Q/Q^+)$ of the donor Q and the reduction potential $E(F/F^-)$ and 0-0 transition frequency of the acceptor $F(E_{00})$ via the relation:⁵⁴

$$\Delta G_0 = E(Q/Q^+) - E(F/F^-) - E_{00}$$
(5.18)

Averages over reported literature values⁶²⁻⁶⁴ are E(F/F) = -0.95 eV (vs. SCE) and $E_{00} = 2.89$ eV for DCA in acetonitrile. The oxidation potential of DMA is $E(Q/Q^+) = 0.74$ eV (vs SCE),⁶⁴⁻⁶⁷ which together provide the value $\Delta G_0 = -1.20\pm0.10$ eV in acetonitrile. ΔG_0 has not been measured in other solvents but we anticipate that it will be close to -1.2 eV in all of the solvents studied here except for cyclohexane where +0.8 eV is obtained.

The solvent dependence of ΔG_0 is due to differences in the solvation energies of the separated reactants and products. It can be estimated by assuming negligible differences for the neutral species and using the Born equation for the solvation free energies of the ions

$$\Delta_{solv}G_i = -\frac{e^2}{4\pi\varepsilon_0} \left(1 - \frac{1}{\varepsilon_r}\right) \frac{1}{2R_i}$$
(5.19)

The difference between the driving force in a solvent x compared to the reference solvent (acetonitrile) is then

$$\Delta G_0^x - \Delta G_0^{ref} = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{\varepsilon_r^x} - \frac{1}{\varepsilon_r^{ref}} \right) \left(\frac{1}{R_F} + \frac{1}{R_Q} \right)$$
(5.20)

At 298 K the dielectric constants of the conventional solvents examined here are $\varepsilon_r =$ 35.9, 37.7, 42.5, and 2.02 for acetonitrile, ethylene glycol, glycerol, and cyclohexane. Equation 5.20 predicts negligible (.02 eV) differences between the three polar solvents but a value of $\Delta G_0 = +0.8$ eV in cyclohexane.

The relative permittivities of only two of the ionic liquids examined here have been reported to date: $\varepsilon_r = 14.7$ and 14.0 (at 298K) for $[Pr_{41}][Tf_2N]$ and $[Im_{41}][PF_6]$, respectively.⁶⁸ The values of most of the other ionic liquids are expected to be similar and to fall in the range $10 \le \varepsilon_r \le 15$. Use of such values in Eq. 5.20 would predict ΔG_0 to be 0.2-0.3 eV less negative in ionic liquids compared to acetonitrile. But it is not appropriate to use these permittivities in Eq. 5.20 or in Eqs. 5.16 and 5.17 to estimate solvation energies.⁶⁹ A variety of experiments⁷⁰⁻⁷³ and simulations^{8,9,74} have shown that electrostatic solvation energies in ionic liquids are typically close to those in high-polarity conventional solvents like acetonitrile. (Rather than $\varepsilon_r \sim 14, \varepsilon_r = \infty$ would be more appropriate to use for these conducting solvents.⁷⁵) In addition, Castner and coworkers⁷⁶ have measured ΔG_0 for reactions between DCA and two variants of DMA in acetonitrile and the ionic liquid [Pr₄₁][Tf₂N]. They find nearly identical values, $-1.2 \le G_0 \le -1.1$ eV,⁷⁶ which are within uncertainties of our estimates for the DCA + DMA reaction in acetonitrile. For these reasons we expect ΔG_0 to be close to -1.2 eV in all of the ionic liquid solvents as well as the conventional polar solvents examined here.We therefore use $\Delta G_0 = -1.2$ eV as a starting point for all solvents except cyclohexane for which we adopt the value $\Delta G_0 = +0.8$ eV.

For determining the distance dependent reorganization energies (Eq. 5.16) and driving forces (Eq. 5.17), the same problem arises with respect to use of measured values of ε_r for ionic liquids. For calculating $\lambda_{solv}(r)$ and $\Delta G(r)$ we assume that these quantities are nearly the same in all of the high-polarity solvents studied and for simplicity we represent these quantities using an average set of dielectric parameters $\varepsilon_r = 39$ and n =1.42 for all solvents, except for cyclohexane(where we use $\varepsilon_r = 2.02$). We recognize the fact that λ_{solv} and ΔG are not likely to be strictly constant in the dipolar and ionic liquids studied here. Based on measurements of the solvation energies associated with the S₀-S₁ transition of coumarin 153⁷³ we expect that solvation free energies will vary by 5-10% and reorganization energies by ~20% across this collection of solvents. But, in the absence of a more accurate way to assign these quantities, we use Eqs. 5.16 and 5.17 with ε_r and *n* values as reasonable first approximations and allow for some variation of ΔG_0 if needed.

The potential of mean force, w(r) in Eq. 5.2, is related to the radial distribution function $g_{FQ}(r) = \exp\{-w(r)/k_BT\}$ which describes the non-uniform distribution of Fand Q prior to initiation of the reaction. In the case of spherical solutes and solvents, radial distribution functions exhibit a characteristic peak in relative probability near to the contact distance followed by a tail which oscillates periodically about unity. For polyatomic solvents and solutes of arbitrary shape, radial distribution functions based on center-of-mass distances are much less coherently structured. A significant but broadened first peak in $g_{FQ}(r)$ is still found near some average contact distance but the oscillations at larger separations tend to be averaged out by the many relative orientations of *F* and *Q* molecules. We represent the expected behavior of $g_{FQ}(r)$ for the types of solutes and solvents studied here using a Lennard-Jones form for w(r):

$$w(r) = 4\varepsilon_{FQ} \left\{ \left(\frac{\sigma_{FQ}}{r} \right)^{12} - \left(\frac{\sigma_{FQ}}{r} \right)^{6} \right\}$$
(5.21)

Simulations of a few nonpolar solutes in an idealized model ionic liquid⁷⁷ suggest that $g_{FQ}(r)$ can be reasonably represented using values of σ between 0.8-1 times the sum of radii defined by the van der Waals volumes of the solutes and values of $\varepsilon \sim k_B T$. For simplicity we use $\sigma_{FQ} = R_F + R_Q$ and allow ε_{FQ} to vary when fitting the quenching data.

The final parameter that needs to be specified is the relative diffusion coefficient D. We adopt a hydrodynamic description and relate D to the solution viscosity η an effective hydrodynamic radius R_h via the Stokes-Einstein relation:

$$D = \frac{k_B T}{6\pi\eta R_h} \tag{5.22}$$

Quenching data are fit using R_h as an adjustable parameter using measured values of η . If a hydrodynamic description is correct one expects $R_h = (R_F^{-1} + R_Q^{-1})^{-1} = 1.68$ Å here.

5.4.Results and Discussion

5.4.1. General Features of the Quenching Data

Steady state absorption and emission spectra of DCA in the ionic liquid $[N_{3111}][Tf_2N]$ are shown in Figure 5.1. Also shown for reference is the absorption of neat DMA. Two features of the DCA fluorophore make it more convenient than several other solutes we examined for these experiments. First, the S₁ absorption band of DCA lies sufficiently in the visible region of the spectrum that it is possible to excite the fluorophore (420 nm) where absorption of the DMA quencher is negligible at the concentrations employed. Second, as shown in the bottom panel of Fig. 5.1, DCA undergoes only a very small solvation-induced dynamic Stokes shift. Lack of a significant dynamic Stokes shift means that, in contrast to the more popular coumarin dyes, the emission decays of DCA are very close to single exponential functions of time in the absence of the quencher. This feature, as well as the long lifetime of DCA (~13 ns), enables more definitive measurement of the time-dependent quenching process. As indicated by the arrows labeled "obs" in Fig. 5.1, we measured emission decays at 2-4 wavelengths near the peak of the second vibronic feature in the emission band and used averages over these decays for the quenching analysis.



Figure 5.1: Steady-state (top) and timeresolved (bottom) spectra of DCA in $[N_{3111}][Tf_2N]$ at 298 K. The dashed curve in the top panel is the absorption of the DMA quencher. (Other spectra are normalized but the DMA absorption is the OD observed for neat DMA in a 1 cm cuvette.) "exc" and "obs" illustrate the excitation and observation wavelengths typically used in these experiments. The bottom panel shows time-resolved spectra obtained via spectral reconstruction (points) and fits to these data (smooth curves) assuming the time-dependent spectra to be shifted versions of the steady-state spectrum. The inset shows the frequency shift from the steady-state spectrum versus time based on such fits.

Figure 5.2 shows representative steady-state spectra and time-resolved decays of DCA + DMA in $[Pr_{41}][Tf_2N]$ at 298 K. Parameters extracted from these data are summarized in Table 5.3. As shown here, we typically collected data at quencher concentrations near to 0, 0.05, 0.1, 0.15, and 0.2 M and used such data sets for the fits described in the following section. As illustrated in Fig. 5.2(a) the shape of the steadystate emission is invariant to quencher concentration. This invariance was observed for both emission and absorption in all polar solvents studied, at least up to 0.3 M DMA. In cyclohexane, addition of DMA induced a slight red-shift of the absorption spectrum consistent with what would be expected for nonspecific solvation. As a measure of the relative intensity I of the steady-state emission we use the integral over the range shown (430-550 nm) except for CHX which is integrated between 440 and 460. And this quantity is listed in the Stern-Volmer format I_0/I in Table 5.3. Decays in the presence of quencher were collected over time windows where the intensity dropped by roughly 100fold relative to the initial intensity in order to focus attention on the most important part of the quenching kinetics and to avoid the potential influence of impurity fluorescence from the ionic liquid solvents. Parameters of multi-exponential representations of these data, derived from iterative reconvolution fitting, are provided in Table 5.3. As shown there, even at 50 mM quencher concentrations, the observed decays are non-exponential. For concentrations above 0.15 M at least three exponentials are typically required to represent such data. This non-exponentiality, which is observed in all cases studied, signals the fact that much of the observed quenching takes place in the "transient" portion of the overall reaction, prior to the establishment of any well-defined reaction rate constant.



Figure 5.2: Representative steady-state emission spectra (a) and time-resolved decays (b; 460 nm) of DCA + DMA in $[Pr_{41}][Tf_2N]$ at 298 K. DMA concentrations are 0, 0.05, 0.1, 0.15, 0.2 M. Emission spectra are shown on a logarithmic intensity scale in order to display their constant shape. These spectra are truncated slightly on the blue edge to avoid the 420 nm excitation light. The decay data are shown normalized for easy comparison; they are collected to ~5000 counts in the peak channel. Points are the actual data and the solid black curves are multi-exponential fits to these data.

[DMA]	I_0/I	<i>I</i> (0)	a_1	a_2	a_3	$ au_1$	$ au_2$	$ au_3$	< 7>	$\tau_0 / < \tau >$
0	1.0	5077	1	0	0	13.1			13.1	1.00
0.05	2.1	4994	0.776	0.224	0	9.00	2.64		7.58	1.73
0.11	4.7	5903	0.662	0.338	0	6.46	1.67		4.84	2.71
0.16	8.2	6110	0.397	0.362	0.240	5.52	2.48	0.61	3.09	4.25
0.21	13.8	6327	0.301	0.384	0.315	4.62	2.12	0.53	2.21	5.95

Table 5.3: Representative Quenching Data in [Pr₄₁][Tf₂N] at 298 K

[DMA] is the concentration of quencher and I_0/I the factor by which the steady-state emission intensity decreases compared to that in the absence of quencher. I(0) and the a_i and τ_i are parameters of multi-exponential fits of the time-resolved decays to

 $I(t)/I(0) = \sum_{i} a_{i} \exp(-t/\tau_{i})$, and $\langle \tau \rangle = \sum_{i} a_{i}\tau_{i}$ and τ_{0} is the lifetime in the absence of quencher. All times are in units of ns.



Figure 5.3: Stern-Volmer plots of quenching efficiencies in $[Pr_{41}][Tf_2N]$ based on (a) integral intensities from steady-state spectra and (b) integral decay times from time-resolved decays. Points are data at the indicated temperatures and solid curves are fits to Eq. 5.23.

Although this non-stationary character of the kinetics suggests that Stern-Volmer analysis might be misleading, to summarize the quenching data and for purposes of comparing to previous studies, we first employed a Stern-Volmer type of analysis.²⁵ Figure 5.3 shows representative Stern-Volmer plots of I_0/I and $\tau_0/\langle \tau \rangle$ versus quencher concentration in [Pr₄₁][Tf₂N] at four temperatures. The $\langle \tau \rangle$ here are the integral decay timesof the non-exponential decays and τ_0 is the time constant in the absence of quencher. In keeping with the non-stationary kinetics observed these plots are nearly always nonlinear.⁷⁸ As can be deduced from the different vertical scales in Fig. 5.3, the steady state I_0/I data tend to lie above the $\tau_0/\langle \tau \rangle$ data and are usually more strongly curved. Both types of data can be accurately represented by quadratic functions of concentration,

$$I_0 / I = a_2 [DMA]^2 + a_1 [DMA] + 1$$
 (5.23a)

$$\tau_0 / \langle \tau \rangle = b_2 [\text{DMA}]^2 + b_1 [\text{DMA}] + 1$$
(5.23b)

Table 5.4 summarizes all of the data we have collected in both ionic liquids and conventional solvents in terms of such quadratic Stern-Volmer fits. Also listed in this table are values of solvent viscosity and the simple Smoluchowski predictions for the diffusion-limited rate constant k_D . If one ignores the nonlinearity of the Stern-Volmer data and simply calculates a quenching rate "constant" k_q from the value of $r_{SV} = I_0/I$ or $\tau_0/\langle \tau \rangle$ at some concentration to estimate a quenching rate constant via $k_q \approx (r_{SV} - 1)/[Q]\tau_0$ the rates so obtained are typically greater and often much greater than k_D . The columns labeled $(k_q/k_D)^{(x)}$ with x = I or τ list the apparent enhancements

over the diffusion controlled limit based on the steady-state and time-resolved data at a quencher concentration of 0.1 M. (Comparable values of this ratio are also obtained if one ignores the quadratic terms in Eq. 5.23.) In ionic liquids, the values of (k_q/k_D) we observe are similar to the values tabulated for a number of the other reactions in Table 5.1.⁷⁹ In contrast, in the low-viscosity conventional solvent acetonitrile (k_q/k_D) ~2. As discussed in the Introduction, this difference with low-viscosity conventional solvents has lead previous authors to conclude that diffusion-limited electron transfer reactions are much more rapid than expected in ionic liquids, probably as a result of anomalously rapid solute diffusion. But it can be seen from Table 5.4 that large values of (k_q/k_D) are not unique to ionic liquids. Conventional solvents possessing viscosities comparable to those of ionic liquids show comparable values of (k_q/k_D) . Moreover, as illustrated in Fig. 5.4, there is a correlation between the value of (k_q/k_D) and solvent viscosity.

There is, in fact, nothing anomalous about the rates of reaction in the ionic liquids or other high-viscosity solvents. The higher and apparently anomalous rates in ionic liquids reflect the combined effect of multiple shortcomings of the simple Smoluchowski approach for predicting effective k_q values derived from Stern-Volmer data in the case of electron transfer reactions in high-viscosity media. As shown in the following section, a more complete analysis which recognizes the importance of the transient component of the reaction and uses a reasonable description of the distance dependence of electron transfer, accounts for the quenching behavior observed in all solvents.

				SS Results		TR Results			Comparisons at 0.1 M			
Solvent	Т /К	[Q] _{max} /M	η_0 mPa s	k_D /10 ⁸ M ⁻¹ s ⁻¹	a_2 /M ⁻²	a_1 /M ⁻¹	τ ₀ /ns	<i>b</i> ₂ /M ⁻²	b_1 /M ⁻¹	$\left(\frac{k_q}{k_D}\right)^{(I)}$	$\left(\frac{k_q}{k_D}\right)^{(\tau)}$	f_{obs}
acetonitrile	298	0.30	0.34	194	2574	309	12.8	409	355	2.3	1.6	0.99
ethylene glycol	298	0.30	16	4.1	447	15.8	13.6	53	20.9	11	4.7	0.87
EGG; x_{EG} =0.8	298	0.20	29	2.3	216	11.7	13.5	32	13.1	11	5.2	0.85
EGG; x_{EG} =0.7	298	0.15	51	1.3	322	11.8	13.4	0	17.6	26	10.2	0.82
EGG; x_{EG} =0.5	298	0.20	135	0.49	86	7.22	13.2	0	7.8	24	12.0	0.83
$[Pr_{31}][Tf_2N]$	298	0.17	60	1.1	348	9.18	13.1	74	16.2	31	16	0.89
$[Pr_{41}][Tf_2N]$	283	0.21	153	0.41	159	8.16	13.0	31	7.9	45	21	0.82
$[Pr_{41}][Tf_2N]$	298	0.21	74	0.89	242	7.69	13.1	48	11.6	27	14	0.86
$[Pr_{41}][Tf_2N]$	313	0.21	41	1.7	320	13.6	13.2	68	17.1	20	11	0.88
$[Pr_{41}][Tf_2N]$	333	0.21	21	3.5	486	24.6	13.4	104	28.3	15	8.2	0.91
$[Pr_{61}][Tf_2N]$	298	0.20	104	0.63	176	11.4	13.0	53	10.2	35	19	0.86
$[Pr_{81}][Tf_2N]$	298	0.30	139	0.48	173	9.19	12.9	51	16.5	43	35	0.96
$[Pr_{10,1}][Tf_2N]$	298	0.30	183	0.36	194	4.23	13.0	44	11.6	50	34	0.91
[N ₃₁₁₁][Tf ₂ N]	298	0.15	76	0.88	407	16.0	13.9	0	34.6	47	29	0.93
[N _{10,111}][Beti]	318	0.20	254	0.28	241	8.33	13.2	112	10.5	89	59	0.92
[Im ₄₁][PF ₆]	293	0.30	262	0.25	104	0.65	12.8	19	6.4	35	26	0.93
[P _{14,666}][Tf ₂ N]	298	0.20	346	0.19	357	43.7	12.6	56	30.7	329	151	0.90
cyclohexane	298	0.30	0.90	74	3604	113	10.6	419	210	6.1	3.2	0.98

Table 5.4: Stern-Volmer Characterization of Steady-State and Time-Resolved Quenching Data

 $[Q]_{max}$ is the maximum concentration of quencher examined, η_0 is the viscosity of the solvent (in the absence of quencher), and k_D is the diffusionlimited rate constant from Eq. 5.6. a_1 and a_2 and b_1 and b_2 are the parameters of Eq. 5. 23 describing the steady-state and time-resolved Stern-Volmer plots and τ_0 is the DCA lifetime in the absence of quencher. $(k_q/k_D)^{(x)}$ are ratios of effective quenching rate constants to k_D based on steady-state (x=I) and time-resolved ($x=\tau$) data and f_{obs} is the fraction of the reaction observed from the present time-resolved experiments.



Figure 5.4: Correlation between the ratio of quenching rate constants k_q obtained from Stern-Volmer plots at 0.1 M DMA to diffusion-controlled rate constant k_D . Filled and open symbols denote data in conventional solvents and ionic liquids respectively. Circles are data from steady-state intensity measurements (I_0/I) and diamonds are data from integral decay times ($\tau_0/\langle \tau \rangle$).

Before discussing this analysis it is useful to consider the meaning of the differences in the Stern-Volmer plots obtained from steady-state versus time-resolved measurements. As already noted, the extent of quenching reported by steady-state measurements is generally larger, which indicates that some portion of the quenching is missed by the time-resolved experiments, presumably due to insufficient time resolution of the TCSPC experiment. As shown in Fig. 5.3 the difference between I_0/I and $\tau_0/\langle \tau \rangle$ is greater than a factor of 2 at the higher concentrations of quencher. Such large differences might be interpreted to mean that a substantial fraction of the reaction is too fast to be observed in the present experiments. But this is not the case. The two experiments report the fraction of molecules that are quenched prior to emission as

$$f_q^{(I)} = 1 - \frac{I}{I_0}$$
 and $f_q^{(\tau)} = 1 - \frac{\langle \tau \rangle}{\tau_0}$ (5.24)

The fraction of the molecules initially excited but not observed in the time-resolved experiments (the so-called "static" quenching component²⁵) is the difference $f_{static} = f_q^{(I)} - f_q^{(\tau)}$. The fraction of excited molecules that *are* observed is thus

$$f_{obs} = 1 + \frac{I}{I_0} - \frac{\langle \tau \rangle}{\tau_0}$$
(5.25)

This fraction is listed in the last column of Table 5.4. The f_{obs} values listed correspond to 0.1 M quencher but values are similar at other concentrations. In case is $f_{obs} < 0.8$; it averages 0.91 over the data set examined here. The ~25 ps resolution of the TCSPC technique does not preclude accurately fitting the quenching data obtained here as long as this missing fraction is accounted for.

5.4.2. Fitting to the Reaction Model

Rather than directly fitting the observed time-resolved decays to the reaction model, we instead used the multi-exponential representations of the decay data such as those shown in Table 5.3. Data sets for each solvent and temperature were fit separately, with most sets consisting of five quencher concentrations of approximately 0, 0.05, 0.1, 0.15, 0.2 M. The multi-exponential parameterizations of these data were used to create samples of 200 points equally spaced between 100 ps and the time at which the fluorescence dropped to 1% of its initial intensity (1-50 ns) for each quencher concentration. The starting time of 100 ps was chosen as the point where the effects of instrumental broadening were expected to be negligible after multi-exponential fitting. To account for the fact that some of the early decay was missed due to limited time resolution, each sampled decay was normalized using the value of f_{obs} determined from the differences between I_0/I and $\tau_0/\langle \tau \rangle$ as described in the previous section. In addition to the decay data, figure 5.5 shows how the viscosity data are interpolated. Figure 5.5a shows some representative plots. All the ionic liquids and other solvents studied here are treated in the same way as these plots. The estimation of the solution viscosities as functions of composition were supplied as what is shown in figure 5.5b. The data in Table 5.5 shows that at 0.3 M concentration DMA induces a decrease of $\sim 24\%$ in the viscosities of the ionic liquids studied. In the highest viscosity conventional solvent used for quenching experiments, 50 mole percent ethylene glycol + glycerol, the change is only 5% and it is expected to be smaller in the conventional solvents of lower viscosity.



Figure 5.5: VFT fitting (eq. 5.7). (a): The mixtures of ethylene glycol and glycerol. Points are measured data and smooth curves the VFT fits. (b): Viscosities of $[Pr_{41}][Tf_2N]$ and a 50 mole percent mixture of ethylene glycol + glycerol mixture without (filled symbols) and with (open symbols) 0.3 M DMA added.

Neat Solvents												
Solvent	Range/K	A	В	<i>T</i> ₀ /K	<i>Т/</i> К	η(T)						
[Pr ₃₁][Tf ₂ N]	278-338	-1.90	839	158	298	60						
[Pr ₄₁][Tf ₂ N]	Pr ₄₁][Tf ₂ N] 278-338		1266	128	298	74						
[Pr ₆₁][Tf ₂ N]	278-338	-1.92	875	166	298	109						
[Pr ₈₁][Tf ₂ N]	278-338	-1.91	887	168	298	139						
[Pr _{10,1}][Tf ₂ N]	278-338	-2.34	1028	162	298	183						
[N ₃₁₁₁][Tf ₂ N]	293-333	-0.78	563	190	298	82						
[N _{10,111}][Beti]	308-343	-2.58	988	197	318	254						
[Im ₄₁][PF ₆]	283-337	-1.88	879	177	293	300						
[P _{14,666}][Tf ₂ N]	288-338	-3.10	1389	143	298	346						
EGG; <i>x_{EG}</i> =0.8	293-338	-3.27	815	175	298	29						
EGG; <i>x_{EG}</i> =0.7	308-338	-3.05	781	185	298	46						
EGG; <i>x_{EG}</i> =0.5	293-338	-6.85	2293	103	298	137						
EGG; <i>x_{EG}</i> =0.3	293-333	-4.96	1620	146	298	288						
glycerol	293-338	-4.09	1346	176	298	982						
	With	h Addea	I DMA									
Solvent	[DMA]	A	В	<i>Т</i> ₀/К	η(T)	%Δ						
[Pr ₃₁][Tf ₂ N]	0.30	-2.44	925	153	50	-17%						
[Pr ₄₁][Tf ₂ N]	0.30	-0.72	516	192	62	-17%						
[Pr ₆₁][Tf ₂ N]	0.30	-2.88	1029	154	70	-36%						
[Pr ₈₁][Tf ₂ N]	0.30	-2.58	979	162	102	-26%						
[Pr _{10,1}][Tf ₂ N]	0.30	-3.09	1145	154	126	-31%						

 Table 5.5:
 Summary of Temperature-Dependent Fits to Viscosity Data

[N ₃₁₁₁][Tf ₂ N]	0.29	-2.40	983	150	68	-17%
[Im ₄₁][PF ₆]	1.12	-2.57	983	167	181	-40%
$[P_{14,666}][Tf_2N]$	0.20	-4.10	1635	129	270	-22%
EGG; <i>x_{EG}</i> =0.5	0.19	-4.16	1298	154	130	-5%

Notes: "Range" specifies the temperature range of the data, A, B, and T₀ are parameters in Eq.5.7 $\ln(\eta/cP) = A + \frac{B}{(T - T_0)/K}$, *T* is the temperature at which quenching experiments were conducted, $\eta(T)$ the fitted viscosity at that temperature and $\theta(A)$ the percent changes in viscosity equations.

that temperature and $\%\Delta$ the percent change in viscosity caused by the added DMA.

Fits were performed using programs written in Matlab using the nonlinear optimization routine "Isqnonlin" provided with this software.⁸⁰ The sum of the squared residuals (r^2) in the fitted and normalized data sets was used as the fit criterion for minimization. For fitting purposes, most of the twelve model parameters summarized in Table 5.2 were fixed at the known or assumed values as described in Sec. 5.3.2. The five parameters V_0 , β_{el} , ΔG_0 , ε_{FQ} , and R_h were considered for fitting the model to the experimental data. The electron transfer parameters V_0 , β_{el} , and ΔG_0 are strongly coupled and are not sufficiently constrained by the data to be independently varied. As already discussed, β_{el} was fixed at the estimate of 1.5 Å⁻¹, despite the fact that it could depend upon solvent. V_0 represents an orientationally-averaged value which cannot be predicted with any certainty, but it is reasonably assumed to be solvent independent. Fixing ΔG_0 to -1.2 eV and allowing V_0 to vary led to best-fit values in the range $40 \leq V_0 \leq 200$ cm⁻¹ and we chose an average value of $V_0=100$ cm⁻¹ for all solvents. With these two parameters fixed, variation of ΔG_0 primarily changes the overall rate of the electron transfer reaction.

The interplay between the electron transfer rate and the rate of diffusion, represented by the second variable parameter R_h , is the main determinant of the shapes of the fluorescence decays. The final variable parameter ε_{FQ} , which describes the F-Q potential of mean force, determines the relative concentration of quencher near to the fluorophore at time zero. It enables some adjustment of the relative rates of reaction at short and long times. To fit a given set of data we began with $V_0 = 100 \text{ cm}^{-1}$, $\beta_{el} = 1.5 \text{ Å}^{-1}$, $\Delta G_0 = -1.2 \text{ eV}$ (or +0.8 eV for cyclohexane), and $\varepsilon_{FQ} = 2.5 \text{ kJ/mol}$, and varied only R_h . Then, separate and simultaneous variations of ε_{FQ} and ΔG_0 were attempted. If the value of r^2 didn't decrease by more than 25% by optimizing one of these latter parameters, the constrained value was adopted.

	Т /К	η ₀ /mPa s	ΔG_0 /eV	<i>€_{FQ}</i> /kJ mol ⁻¹	R_h /Å	r^2 /10 ⁻ 5	$\frac{D_{\rm DMA}}{10^{-11}}$ m ² s ⁻	D_{obs}/D_{SE}	R_{est}/R_h
acetonitrile	298	0.34	-1.2	4.7	0.65	0.4	323	1.6	2.6
ethylene glycol	298	16	-1.2	1.3	0.74	3.5	8.2	1.9	2.3
EGG; x_{EG} =0.8	298	29	-1.2	2.5	0.97	3.6	3.9	1.6	1.7
EGG; $x_{EG}=0.7^{(a)}$	298	51	-1.2	3.8	0.67	1.9	2.7	2.0	2.5
EGG; $x_{EG}=0.5^{(a)}$	298	135	-1.2	5.1	0.79	2.1	1.3	2.5	2.1
[Pr ₃₁][Tf ₂ N]	298	60	-1.2	1.4	0.46	3.7	1.7	3.2	3.7
$[Pr_{41}][Tf_2N]$	283	153	-1.2	2.9	0.31	3.8		3.0	5.5 ^(b)
$[Pr_{41}][Tf_2N]$	298	74	-1.2	2.2	0.37	1.9	1.4	3.4	4.6
$[Pr_{41}][Tf_2N]$	313	41	-1.2	1.5	0.37	1.7		3.7	4.5 ^(b)
$[Pr_{41}][Tf_2N]$	333	21	-1.2	1.0	0.37	1.4		4.2	4.5 ^(b)
$[Pr_{61}][Tf_2N]$	298	104	-0.97	4.0	0.36	2.0	1.0	5.3	4.7
			-1.2	2.5	0.29	2.6			
$[Pr_{10,1}][Tf_2N]$	298	183	-0.97	3.9	0.24	2.9	0.57	6.3	7.0
			-1.2	2.5	0.20	3.3			
$[N_{3111}][Tf_2N]$	298	76	-0.87	5.8	0.23	2.7			7.2
			-1.2	3.1	0.18	3.9			
[N _{10,111}][Beti]	318	254	-0.87	6.5	0.17	0.2	2.9	14	9.7
	• • • •		-1.2	4.0	0.11	2.6			
$[Im_{41}][PF_6]$	293	262	-0.89	5.0	0.37	2.5	1.4	5.2	4.5
	200	246	-1.2	3.5	0.27	4.3	2.0	1.5	
$[P_{14,666}][It_2N]$	298	346	-0.96	5.4	0.070	2.9	3.0	15	24
			-1.2	3.7	0.055	4.6			
cyclohexane	298	0.90	0.80	6.5	0.67	13	163	2.1	2.5
			0.80	6.6	1.13	4.2			

Table 5.6: Summary of Fit Results

 V_0 , β_{el} , ΔG_0 , ε_{FQ} , and R_h are the model parameters described in Sec. 3 and Table 1. Values in parenthesis indicate values held constant in the fitting (in addition to V_0 and β_{el} .) r^2 is the mean squared residual of the fit, $r^2 = \sum_{i=1}^{N} (y_i^{obs} - y_i^{fit})^2 / N$. D_{obs}/D_{SE} is the ratio of the measured diffusion coefficient of DMA to the Stokes-Einstein prediction $D = k_B T / 6\pi R \eta$. R_{est}/R_h is the corresponding ratio of the estimated effective diffusion radius $R_{est} = (R_F^{-1} + R_Q^{-1})^{-1} = 1.68$ Å and the value R_h determined from fitting the quenching data (Eq. 5. 22). (a) The data for the $x_{EG} = 0.7$ and 0.5 mixtures only extend to 0.15 M in DMA due to its limited solubility. (b) values estimated from temperature-dependent diffusion data on solutes other than DMA.

Representative fits to the model of Sec. 5.3 are shown in Figs. 5.6 and 5.7, and a summary of resulting model parameters is provided in Table 5.6. The two data sets in Fig. 5.6 illustrate the quality of the fits achieved for ionic liquid solvents. According to the values of the goodness of fit metric (r^2 , Table 5.6) these two limiting temperatures of the [Pr₄₁][Tf₂N] series represent the best (333 K) and worst (283 K) fits achieved. The first thing to be noted is that even in the best cases, the fits do not capture the deconvoluted and sampled experimental data to within uncertainties. (We estimate a value $r^2 \le 3 \times 10^{-6}$ would indicate such a fit.) Some of this imperfect fit can be ascribed to inaccuracies in the measured quencher concentrations and in estimates of f_{obs} , both of which have an important impact on the value of r^2 . This problem can be seen in the 333 K data in Fig. 5.6 where the fit of one particular decay ([DMA] = 0.05 M) appears to be incorrect by a small factor. For this decay the measured value of f_{obs} is 0.91. Changing this value to 0.95 i.e. rescaling the experimental data at this particular quencher concentration by 4%, produces good agreement between all of the model and observed decays and reduces r^2 by a factor of four, without causing an appreciable change in the fit parameters. Given that uncertainties in f_{obs} are expected to be on the order of a few percent, it is clear that some deviations between the model fits and the experimental data can be attributed to inaccuracies in the estimates of f_{obs} . But it is also clear that the model does not provide a perfect representation of the experimental data. For example, in Table 5.6 one sees that the value of r^2 increases systematically with decreasing temperature in the $[Pr_{41}][Tf_2N]$ series. Lowering temperature slows diffusion and the overall rate of the quenching reaction and increases the non-exponentiality of the fluorescence decays. As illustrated by the 283 K data, the increasing non-exponentiality of the emission decays
with increasing quencher concentration is captured by the model, but deviations from experiment are larger than expected uncertainties even if one considers concentration uncertainties allows for some rescaling of the decays to account for f_{obs} inaccuracies.

Similar observations can be made of all of the other quenching data in polar solvents. The ethylene glycol data in Fig. 5.7 provides another typical example. Thus, we find that the model presented in Sec. 3 provides a good albeit imperfect description of the quenching data in high polarity solvents. The same is not true of the cyclohexane data. As shown in Fig. 5.7, in this solvent the concentration dependence of the decays is poorly reproduced. We note that simply by adjusting the concentration of the 0.2 M data by \sim 20% leads to an acceptable fit (data in parenthesis in Table 5.6) suggesting that DMA association in this nonpolar solvent might be important. But more study is necessary to determine the real cause of this deviation.



Figure 5.6: Fits of time-resolved DCA decays in $[Pr_{41}][Tf_2N]$ with different [DMA] at 283 K (left panels) and 333 K (right panels). Sampled data are shown as crosses and the fits (Table 4) solid curves. These two data sets represent some of the worst (283 K; $r^2=4\times10^{-5}$) and best (333 K; $r^2=1\times10^{-5}$) fits among the ionic liquids studied.



Figure 5.7: Fits of DCA quenching data with different [DMA] in cyclohexane (left panels) and ethylene glycol (right panels) at 25 °C. Sampled data are shown as crosses and the fits (Table 5.4) solid curves.

We now consider whether the model parameters derived from these fits (Table 5.6) are physically reasonable, restricting attention to the polar solvent results. As shown in Table 5.6, reasonable fits are achieved in most cases using the estimated value ΔG_0 = -

1.2 eV accompanied by values of ε_{FQ} which average 2.9 kJ/mol. The latter values are near to k_BT as anticipated. We note that in the series of ethylene glycol + glycerol mixtures and in the [Pr₄₁][Tf₂N] temperature series the value of ε_{FQ} increases systematically with increasing viscosity. Rather than indicating a real change in the F-Q potential of mean force, this systematic variation probably reflects some shortcoming of the model. In addition, the quenching data in a number of the ionic liquid solvents are better fit with a smaller value of ΔG_0 near -0.9 eV with concomitantly higher values of ε_{FQ} . (ΔG_0 and ε_{FQ} are strongly correlated in these fits.) Variation of ΔG_0 by 0.3 eV is larger than expected for these ionic liquids and these better fits coupled to unrealistically high values of ε_{FQ} , are also likely due to imperfections in the description of the quenching reaction. The final parameter R_h , which is well determined by the fits, fixes the relationship between the solution viscosity and the relative F-Q diffusion coefficient. Fitted values of R_h are all smaller than the value estimated from the radii of F and Q, R_{est} =1.68 Å. There is also a clear distinction between the values of R_h in conventional and ionic liquid solvents. In conventional solvents the ratio $R_{est}/R_h \sim 2$ (final column of Table 5.6) whereas in ionic liquids this ratio is typically between 4-7 with some values, such as that in $[P_{14,666}]$ [Tf₂N], being much larger.

To explore whether the latter differences are actually related to differences in solute diffusion or are simply fitting artifacts, we have measured tracer diffusion coefficients of DMA in all of these solvents. The results are also provided in Table 5.6 along with the values of D_{obs}/D_{SE} , the ratios of the measured DMA diffusion coefficients to those estimated from the Stokes-Einstein (SE) equation, $D_{SE} = k_B T / 6\pi \eta R$. As shown in Table 5.6 the ratios D_{obs}/D_{SE} and R_{est}/R_h parallel one another in the different solvent

types; in conventional solvents $D_{obs}/D_{SE} \sim 2$ whereas larger values are found in ionic liquids. Overall we find $R_{est}/R_h = (1.2\pm0.3)D_{obs}/D_{SE}$ independent of solvent type. Thus, the variations in R_h obtained by fitting the quenching data do appear to reflect the relative F-Q diffusion coefficients in different solvents and the fact that $R_h \neq R_{est}$ is primarily a result of the inaccuracy of the SE equation. In a related study of solute diffusion²⁴ we show that D_{obs}/D_{SE} increases as a function of the solvent-to-solute size ratio. The fact that values of R_{est}/R_h and D_{obs}/D_{SE} are larger in ionic liquids than in conventional solvents can thus be attributed to fact that ionic liquid ions are typically larger than molecules of many conventional organic solvents. Although we didn't measure diffusion coefficients of the fluorophore here, measurements of similar molecules show that similar ratios of D_{obs}/D_{SE} should pertain to DCA as well as DMA.

The foregoing discussion indicates that the model employed here provides a sound, albeit imperfect, description of the quenching of DCA by DMA. In most cases the concentration-dependent shapes of the decay curves are reasonably reproduced in both conventional and ionic liquid solvents using a consistent and reasonable set of electron transfer parameters. In addition, the relative diffusion coefficients derived from these fits, as embodied in the effective hydrodynamic radius R_h , are consistent with independently measured solute diffusion coefficients. It is the case that deviations between the observed and fitted decays are often larger than experimental uncertainties, even after accounting for the effect of uncertainties in f_{obs} . It seems likely that better agreement with experiment could be achieved through refinement of the model, for example by considering more sophisticated theories of the electron transfer process, an improved description of the F-Q distribution function, or inclusion of a distance-

dependent diffusion coefficient to account for hydrodynamic interactions between F and Q. Evaluation of such improvements, which would benefit from measurements able to capture the early dynamics (<100 ps) not monitored here, are reserved for future studies. For now, we are satisfied that the present model is sufficiently realistic provide insight into the nature of the DCA+DMA reaction and help explain the "anomalous" kinetics exhibited by this and similar reactions in ionic liquids.

5.4.3. Interpretation of the DCA+DMA Reaction

Figure 5.8 shows the distance dependence of the electron transfer parameters ΔG , λ , V_{el} , exp{-($\Delta G + \lambda$)²/4 $\lambda k_B T$ } (labeled " E_a ") and the total electron transfer rate constant κ . Solid curves correspond to the model as applied to polar solvents and dashed curves to cyclohexane. As a result of the way in which the relative permittivity enters Eq. 5.17, the reaction free energy ΔG depends little upon reactant separation in polar solvents whereas it is strongly dependent on r in cyclohexane (Fig. 5.8a). Just the opposite behavior occurs for the reorganization energy λ , which has zero solvent contribution in the case of cyclohexane. In both cases $\Delta G + \lambda > 0$ at all accessible values of r, meaning that electron transfer always occurs in the normal regime. Because of the much smaller value of λ in cyclohexane, the activation energy term $\exp{-(\Delta G + \lambda)^2/4\lambda k_B T}$ exhibits a much steeper distance dependence than in polar solvents and is nearly equal in importance to the coupling term V_{el}^2 (Fig. 5.8b). As a result, the net distance dependence of the electron transfer rate constant $\kappa(r)$ is considerably steeper in the case of cyclohexane. $\kappa(r)$ decreases approximately

exponentially with decay constants of 1.9 and 3.0 Å⁻¹ in polar solvents and cyclohexane respectively (Fig. 5.8c). For both types of solvent κ is predicted to achieve a rate constant of ~1 ps⁻¹ near contact. Finally, Fig. 5.8d illustrates F-Q distributions spanning the range of values of ε_{FQ} obtained from the fits. We note that for values of ε_{FQ} as large as 5 kJ/mol (~2 k_BT here at 298K) the enhanced probability of finding an F-Q pair near contact (g_{FQ} ~8) seems unrealistic. Such values, which are obtained in several of the fits in Table 5.6 probably, reflect some error in the model representation at early times.



Figure 5.8: Some features of the electron transfer model applied here: (a) $\Delta G(r)$ and $\lambda(r)$ (Eqs. 5.16, 5.17); (b) the normalized exponential terms associated with the activation energy (" E_a ", eq. 5.14) and the electronic coupling (" V_{el}^{2n} , Eq. 5.15); (c) complete electron transfer rate constant. Solid curves show the model as applied to polar solvents and dashed curves the model for cyclohexane using the parameters specified in Table 2. (d) F-Q radial distribution functions (Eq. 5.21) of the model with values of the energy parameter $\varepsilon_{FQ} = 1.2$, 2.5, and 5 kJ/mol at 298 K.

Finally, Fig. 5.9 uses "standard parameters" for polar solvents as listed in Table 5.2 to illustrate the effect of changing viscosity on the time-dependent reaction rate coefficient k(t) and the fluorescence decay profiles I(t)/I(0). The latter are shown for a quencher concentration of 0.1 M. At times sufficiently short that no reactant motion has

occurred, the rate coefficient is given by $k(t=0) = \langle \kappa \rangle$. As can be seen from Eq. 5.9, the initial rate constant is dictated solely by $\kappa(r)$ and the F-Q distribution. In the present reaction we find $k(0) \sim 2 \times 10^{10} \text{ s}^{-1}$. For sufficiently rapid diffusion, represented by $\eta = 0.1$ cP in Fig. 5.9, the equilibrium spatial distribution of F-Q distances is not perturbed by the reaction. In this reaction-limited regime, k(t) remains equal to k(0) for all times, the overall quenching process has the well-defined rate constant $k_q = \langle \kappa \rangle$, and I(t) decays exponentially with the rate constant $k = k_0 + k_q[Q]$. For higher viscosities (slower diffusion), the initial spatial distribution can no longer be maintained. Population is depleted at small r and k(t) decreases with time until the spatial distribution becomes stationary, whereupon k(t) achieves its limiting value $k(\infty)$ (Eq. 5.8). Values of $k(\infty)$ for different viscosities are listed in the inset table in Fig. 5.9. For sufficiently slow diffusion, the "diffusion-controlled" regime, in which $k(\infty) = k_{DC}(\infty) \propto D \propto \eta^{-1}$, is reached. For the DCA+DMA reaction in polar solvents this regime is achieved for $\eta > 10$ cP. It is important to recognize that, except in the reaction-controlled regime, k(t) significantly time dependent and there is therefore no unique rate constant k_q that can be associated with the reaction. For purposes of discussion we can define an integral rate parameter,

$$\bar{k}_q = \frac{1}{t_{obs}} \int_0^{t_{obs}} k(t) dt$$
(5.26)

where t_{obs} represents some time window over which the reaction is effectively monitored (see below). This parameter is plotted in the middle panel of Fig. 5.9. We use it to examine why the values of " k_q " obtained from Stern-Volmer type analyses of electron

transfer reactions are often much larger than the simple Smoluchowski prediction $k_D = 8k_BT/3\eta$ in ionic liquids.

The model of the DCA+DMA reaction developed here indicates that there are multiple contributions which conspire to cause the large values of k_q/k_D shown in Table 5.4. As a representative example, we consider $[Pr_{61}][Tf_2N]$, which has a viscosity of ~100 cP at 298 K. As listed in Table 5.4, Stern-Volmer analysis of the steady-state quenching data yields the value $k_q/k_D = 35$ at 0.1 M DMA for this case. The first contribution to this underestimation of k_q relates to the fact that the reaction model assumed in the simple Smoluchowski prediction for k_D differs from the reaction model adopted here. The simple Smoluchowski approach assumes negligible F-Q interactions, i.e. w(r) = 0 for $r > R_F + R_Q$, and also assumes infinitely rapid reaction at contact but no reaction elsewhere. Inclusion of a non-zero w(r) and a finite, distance-dependent $\kappa(r)$ in the more complete model used here leads to the differences between $k(\infty)$ and k_D shown in the inset table in Fig. 5.9. In the diffusion-controlled regime, which pertains to $[Pr_{61}]$ [Tf₂N], these differences in reaction model only increase $k(\infty)$ over k_D by a modest 34%. A second, and more important source of error in k_D is the inaccuracy of the Stokes-Einstein equation for predicting diffusion coefficients in ionic liquids. The value of $D_{obs}/D_{SE} = 5.3$ (Table 5.6) indicates that use of this hydrodynamic approximation results in a value of k_D which is about 5-fold smaller than what would be obtained using measured diffusion coefficients. (As mentioned previously, the large size of ionic liquid constituents makes this contribution to k_q/k_D much larger in ionic liquids than in many conventional solvents.) A final source of error lies in the fact that k_D is only an estimate for the long-time limiting rate constant pertaining after the F-Q distribution has become

stationary. By comparing Stern-Volmer quenching data to k_D one implicitly assumes that little or no quenching occurs during the "transient" portion of the reaction. Such an assumption is typically incorrect. In the present systems a substantial portion of the quenching occurs before a stationary distribution has been established. When k(0) and $k(\infty)$ differ substantially, as they do here for viscosities greater than 10 cP (Fig. 5.9), nonexponential decays and net quenching efficiencies much greater than predicted from k_D or $k(\infty)$ are expected. For example, the effective quenching rate "constants" k_q used in compiling $(k_q/k_D)^{(I)}$ values in Table 5.4 are defined by $k_q = (\frac{I_0}{I} - 1)/(\tau_0[Q])$. Such k_q values, determined from model I(t)/I(0) decays for a quencher concentration of 0.1 M, are listed in the inset table to Fig. 5.9. At a viscosity of 100 cP, which pertains to the $[Pr_{61}][Tf_2N]$ case, $k_q/k(\infty) = 4.6$. Thus, in this example, the error in the simple Smoluchowski prediction for the extent of reaction k_q/k_{D} ~ 35, can be thought of as resulting from a product of three factors: (i) a modest factor of ~ 1.3 due to neglect of a non-uniform initial F-Q distribution and the distance dependence of reaction (ii) a factor of ~5 error due to inaccuracy of the SE prediction of diffusion coefficients, and (iii) another factor of ~5 error due to the fact that much of the reaction occurs during the nonstationary regime.



Figure 5.9: Model calculations illustrating the dependence of the quenching reaction upon solution viscosity (values in mPa·s). k(t) is the time-dependent rate constant (Eq. 5.7), $\overline{k}_q(t)$ is the cumulative average of k(t) defined in Eq. 5.26, and I(t)/I(0) is the normalized fluorescence decay (Eq. 5.1). Parameter values are those appropriate to polar solvents listed in Table 2 with [Q]=0.1 M and $\tau_0 = 13$ ns. The crosses in the middle panel indicate effective observation windows defined by $\overline{k}_q(t_{obs}) = (1/\langle \tau \rangle - 1/\tau_0)/[Q]$ with $\langle \tau \rangle = \int_0^{\infty} I(t) dt / I(0)$. The curve labeled τ_0 is the decay in the absence of quencher. The inset table compares values of the limiting rate constant at infinite time ($k(\infty)$; Eq. 5.8), the diffusion-limited rate constant k_D given by Eq. 5.6, and the effective quenching rate constant $k_q \equiv (1/\langle \tau \rangle - 1/\tau_0)/[Q]$.

We finally ask how viscosity and other experimental variables influence the last of these three sources of deviation in k_q/k_D and thereby offer some insight into the literature data collected in Table 5.1. To do so it is helpful to define an effective time window t_{obs} over which quenching experiments monitor reaction. We define this time by $\bar{k}_q(t_{obs}) \equiv (1/\langle \tau \rangle - 1/\tau_0)/[Q]$. Such times for [Q]=0.1 M are marked as crosses in the middle panel of Fig. 5.9. From this figure one finds that with decreasing viscosity the reaction becomes faster and t_{obs} becomes shorter. With this truncation of the observation window k_q approaches k(0) and one might therefore expect k_q to be even farther from the diffusion-controlled limit $k(\infty)$. But, because the difference between k(0) and $k(\infty)$ lessens with decreasing viscosity, the net effect is to cause $k_q/k(\infty)$ to decrease relative to

middle panel of Fig. 5.9. From this figure one finds that with decreasing viscosity the reaction becomes faster and t_{obs} becomes shorter. With this truncation of the observation window k_q approaches k(0) and one might therefore expect k_q to be even farther from the diffusion-controlled limit $k(\infty)$. But, because the difference between k(0) and $k(\infty)$ lessens with decreasing viscosity, the net effect is to cause $k_a/k(\infty)$ to decrease relative to its value at high viscosities. For this reason, equating k_q to $k(\infty)$ as is done in the simple Smoluckowski approach, often appears to be a good approximation in low viscosity solvents, it becomes progressively worse as viscosity increases. This effect is the primary reason for the variation of k_q/k_D with η as shown in Fig. 5.4. Quencher concentration and fluorophore lifetime τ_0 also affect the observation window and thus how much k_q departs from $k(\infty)$. For $\eta=100$ cP and [Q]=0.1M one finds that $t_{obs} \sim \tau_0$, i.e. it is the fluorophore lifetime that mainly limits the extent of reaction. For $\tau_0 = 1, 10, 100$ ns values of $k_q/k(\infty) = 19$, 5, and 2. Thus, other things being equal, a longer-lived fluorophore achieves effective quenching rates closer to the diffusion limit. If the quencher concentration is increased beyond 0.1 M at $\eta = 100$ cP, the reaction limits the observation window. For example, changing [Q] from 0.1 M to 1 M causes the observation window to decreases from ~11 ns to ~1 ns and $k_a/k(\infty)$ increases from 4.6 to 16.

These observations provide some insight into the wide range of values of k_q/k_D listed in Table 5.1. First we note that for reactions measured in multiple ionic liquids having widely differing viscosities (#5, 6, 7, 8, 10) values of k_a/k_D increase with increasing viscosity similarly to what is shown in Fig. 5.4. Presumably the interpretation of this behavior is the same as just described for the DCA+DMA reaction. For a number of reactions examined in high viscosity ionic liquids (#6-10) values of k_a/k_D were found to be modest, less than 10 in most cases. Common to these cases is the fact that observations were made at low reactant concentrations and with reactants whose lifetimes were relatively long. Under these conditions the observation window is not limited to short times and the measurements do not tend to emphasize the transient portion of the reaction. In contrast, extreme values of $k_q/k_D(\#1, 3, 5)$ are limited to high-viscosity systems in which solute lifetimes and/or high concentrations tend to emphasize the shorttime portions of k(t) occurring well before stationary conditions apply. These observations are also consistent with what would be expected based on the foregoing analysis. One aspect of the data in Table 5.1 that seems contrary to expectations is the difference between k_q/k_D in systems 2 and 3. These data are for quenching of coumarins C151 and C152 by DMA in two different ionic liquids. These data were recorded by a single research group using the same methods.^{20,21} It is difficult to rationalize why large values of k_a/k_D should be observed in the moderate viscosity liquid (DAF) at relatively low quencher concentrations when much more modest values are observe in [Im₂₁][Tf₂N]. For example, using the model parameters in Table 5.2 with $\eta = 100$ cP, τ_0 = 1 ns, and [Q] = 1 M and assuming $D_{obs}/D_{SE} \sim 5$ one finds $k_q/k_D \sim 200$, comparable to the most extreme values in Table 5.1. Thus, it seems reasonable to expect that detailed

analyses of the sort described here, taking into account the specifics of the electron transfer processes involved as well as the underestimation of diffusion coefficients by Stokes-Einstein predictions, would provide satisfactory explanations for what appear to be widely variable and sometimes unexpectedly high reaction rates reported for diffusion-limited reactions in ionic liquids.

5.5. Summary and Conclusions

We have studied the electron transfer reaction between S_1 DCA and DMA using steady-state and picosecond time-resolved emission techniques in ionic liquids and conventional solvents. Our primary interest was to better understand why diffusionlimited electron transfer reactions sometimes appear to be much faster than expected based on viscosity scaling the rates observed in conventional solvents.

For the quencher concentrations examined here (0.05-0.3 M) emission decays were typically found to be significantly non-exponential and Stern-Volmer plots of steady-state intensities and (integral) lifetimes far from linear in ionic liquid solvents. These features indicate that reaction does not involve a simple kinetic process. Application of the usual Stern-Volmer(SV) analysis to such data provided results qualitatively similar to what was reported by Vieira and Falvey¹⁹ for this particular reaction and by others for other similar reactions. Even at concentrations of 0.1 M in DMA, effective quenching rate "constants" k_q were found to be much larger than the simple Smoluchowski prediction for diffusion-limited reactions, $k_D = 8k_BT/3\eta$. Values of k_q/k_D greater than 10 are typical with values greater than 100 observed in some cases. But such large departures from the k_D prediction are not a unique feature of ionic liquids. We also observed $k_q >> k_D$ in conventional solvents having viscosities comparable to those of ionic liquids. Moreover, a general correlation between k_q/k_D and viscosity was noted. The origin of these departures from k_D predictions and, indeed, even the meaning of the k_q values obtained in this manner, is unclear without further analysis.

We therefore also considered a more complete description of the quenching process, using a model that combines solution of a spherical diffusion equation coupled to a Marcus-type description of the electron transfer reaction. Such modeling has been applied to reactions in conventional solvents^{29,30,31-38} but had not yet been considered in ionic liquids. Using this approach we were able to obtain satisfactory fits of the concentration-dependent fluorescence decay profiles observed in both ionic liquids and conventional solvents using a consistent set of physically reasonable parameters. The model developed for the DCA+DMA reaction showed that there are two main reasons why the k_q values obtained from SV analysis are often much greater than k_D in ionic liquids and other high viscosity media. First, conditions of high viscosity (slow diffusion) emphasize the "transient" portions of reaction, i.e. those portions occurring prior to establishment of steady-state conditions where the rate coefficient k(t) is timedependent. The rate constant k_D is only a prediction for the limiting time constant $k(t \to \infty)$, which is smaller than k(t) at any earlier time. Stern-Volmer analysis provides an effective rate constant k_q which can be viewed as an average of k(t) over some time window set by a combination of the net quenching rate and fluorophore lifetime. k_q is therefore necessarily larger than $k(\infty)$ whose estimate is k_D . In high viscosity ($\eta > 100$ cP) solvents and for the conditions employed here we estimate that $k_q/k(\infty)$ is in the range of 5-10. Even larger values are expected for experiments conducted with higher quencher concentrations and/or shorter fluorophore lifetimes. These considerations are the same for ionic liquids and conventional solvents.

The second important contributor to large values of k_q/k_D is the fact that the Stokes-Einstein relationship, $D_{SE} = k_B T / 6\pi \eta R$, used in deriving the simple Smoluchowski prediction for k_D , significantly underestimates diffusion coefficients in ionic liquids. This effect was suggested by the small effective hydrodynamic radii required to fit the quenching data to the model and also confirmed by direct measurements of the diffusion coefficients of DMA in all of the solvents studied. Ratios of D_{obs}/D_{SE} in all solvents are in part a function of the relative sizes of solute and solvent molecules. The fact that ionic liquid cations and anions are often larger than the molecules of many conventional solvents makes such ratios larger in ionic liquids. Values of 3-5 are typical in ionic liquids but values of D_{obs}/D_{SE} larger than 10 are observed for ionic liquids comprised of the largest cations studied. These diffusion factors multiply the factors of $k_q/k(\infty)$ caused by transient effects so that together quite large values of k_q/k_D are obtained.

We have only considered one particular reaction in this study and have applied what can be viewed as a minimally realistic model for treating bimolecular electron transfer reactions. Nevertheless, it seems likely that foregoing interpretations suffice to account for other cases in which surprisingly large values of k_q (i.e. $k_q \gg k_D$) have been reported. No special character of electron transfer need be postulated to explain such observations. Furthermore, while solute diffusion is faster than what Stokes-Einstein estimates in ionic liquids, values of D_{obs}/D_{SE} are likely to be much smaller than the extreme values of k_q/k_D observed. We therefore conclude that none of the studies published to date offer clear evidence for bimolecular electron transfer rates being anomalously high in ionic liquids.

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found highly non-exponential Stern-Volmer plots. The reason for this discrepancy is not known.

- 79. Our value of $(k_q/k_D) = 35$ for the DCA+DMA reaction in $[Im_{41}][PF_6]$ at 0.1 M DMA differs significantly from $(k_q/k_D) = 85$ calculated from the value of k_q reported by Vieira and Falvey¹⁹ for this identical system. However, the latter authors measured quenching at higher DMA concentrations where the non-linearity of the Stern-Volmer plots makes the effective rate "constant" k_q much larger.
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- 2. Zhang, XX.; Liang, M.; Ernsting, N.; Maroncelli, M., The Complete Solvation Response of Coumarin 153 in Ionic Liquids. 2012. (manuscript in preparation)
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