

Dipolar Solvation Dynamics in Room Temperature Ionic Liquids: An Effective Medium Calculation Using Dielectric Relaxation Data

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Solvation dynamics in four imidazolium cation based room temperature ionic liquids (RTIL) have been calculated by using the recently measured dielectric relaxation data [J. Phys. Chem. B 2008, 112, 4854] as an input in a molecular hydrodynamic theory developed earlier for studying solvation energy relaxation in polar solvents. Coumarin 153 (C153), 4-aminophthalimide (4-AP), and *trans*-4-dimethylamino-4'-cyanostilbene (DCS) have been used as probe molecules for this purpose. The medium response to a laser-excited probe molecule in an ionic liquid is approximated by that in an effective dipolar medium. The calculated decays of the solvent response function for these RTILs have been found to be biphasic and the decay time constants agree well with the available experimental and computer simulation results. Also, no probe dependence has been found for the average solvation times in these ionic liquids. In addition, dipolar solvation dynamics have been predicted for two other RTILs for which experimental results are not available yet. These predictions should be tested against experiments and/or simulation studies.

I. Introduction

The last few years have witnessed intense activity toward understanding the solvation dynamics of photoexcited dyes in room temperature ionic liquids (RTIL).^{1–37} The presence of Coulomb interactions have rendered ionic liquids several unique solvent properties, such as, low vapor pressure, considerable polarity, wide liquid range, enhanced thermal stability and miscibility with other solvents.^{38,39} These properties have made RTILs better and environment-friendly reaction media in chemical industry for synthesis, separation, catalysis and a host of other applications. Since chemical reactions usually involve charge transfer and/or redistribution, the stabilization of various intermediates and products is intimately connected to the time scale at which the surrounding solvent molecules reorganize. Understanding the time scale of solvent reorganization in such reaction media may therefore be crucially important for designing a solvent for carrying out a specific reaction for a desired product.

Solvation dynamics experiments provide the solvent reorganization time scale via monitoring the time dependent shift in the fluorescence emission spectrum of a laser-excited dye molecule.^{40–42} Subsequently, the time dependent progress of solvation is expressed in terms of solvent response function,^{40–42} $S(t) = [\nu(t) - \nu(\infty)]/[\nu(0) - \nu(\infty)]$, where $\nu(t)$ denotes some measure of the time dependent frequency (usually, peak or the first moment) of the fluorescence emission spectrum of the laser excited dye dissolved in that medium. $\nu(0)$ is the emission frequency of the time zero spectrum (at a time when the vibrational relaxation in the excited probe molecule is complete but the solvent relaxation has not begun yet) and $\nu(\infty)$ represents the emission frequency after the solvent relaxation is complete. For solvents with fast dynamics, $\nu(\infty)$ is expected to be the same as that obtained from the steady state emission spectrum of the same dye molecule in that solvent.⁴⁰ Note that $S(t)$ is normalized such that it decays from unity at $t = 0$ to zero at $t = \infty$, and a

time integration of $S(t)$ produces the average solvation time, $\langle\tau_s\rangle$. Recently, solvation dynamics in a number of RTILs have been investigated and the results from these studies can be summarized as follows:^{1–14,20–23} (i) For imidazolium and pyrrolidinium ionic liquids, $S(t)$ shows biphasic decay where a fast component with time constant in the range of 100–700 fs accounts for approximately 20% of the total decay followed by a much slower component with time constant spanning over a few picoseconds to several nanoseconds, (ii) while the fast component originates from the inertial motion of the ions, the structural relaxation in RTIL is responsible for the slow component, (iii) the slow component can be fitted either to a stretched exponential or to a biexponential functions of time, (iv) for phosphonium and several ammonium ionic liquids, the biphasic decay is absent where a stretched exponential with one time constant could sufficiently describe the full decay dynamics and (v) for a given RTIL, the average solvation time, $\langle\tau_s\rangle$, shows a considerable probe dependence.

Even-though the above results are quite general, there exist several issues pertaining to the solvation dynamics in ionic liquids which are currently under debate and discussion. For example, fluorescence upconversion measurements in two imidazolium ionic liquids²³ have indicated a smaller (~10%) fast component with a much slower time constant (600–900 fs) than those reported in earlier studies. These studies²³ have further suggested that several factors such as the internal conformational dynamics of the probe molecule and its distribution between polar and nonpolar environments in the RTIL could enhance the initial fast decay of the solvent response function as well as shorten the fast time constant. Interestingly, simulation studies of solvation dynamics in imidazolium ionic liquids predict larger amplitude of the fast component (30–75%) with a much shorter time constant (70–200 fs) than what have been observed in experiments.^{25–27,31–34} Recently, solvation dynamics in ethylammonium nitrate have been calculated using the dielectric relaxation data of the solvent and a good agreement between the calculated results and experiments found.²¹ How-

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ever, recent continuum model calculations for several imidazolium ionic liquids are found to *disagree* with the relevant experiments.⁸ Note, however, that these attempts neither included the ion–ion and ion–solute static correlations nor could use the high resolution dielectric relaxation data for imidazolium liquids which are made available only recently.⁴³ One therefore wonders whether, just like observed earlier for dipolar solvents,^{40–42} the success of such simple models for RTILs is also determined critically by the complete measurement of the dielectric relaxation and systematic inclusion of the relevant static correlations. Moreover, recent optical heterodyne-detected Raman-induced Kerr effect spectroscopic (OHD-RIKES) studies with several RTILs have revealed the presence of low frequency ($\sim 20\text{--}150\text{ cm}^{-1}$) intermolecular librational modes.^{44–48} It would therefore be also interesting to investigate whether and to what extent these librational modes couple to the solvation dynamics and influences the initial part of the polar solvation energy relaxation in ionic liquids. This question becomes relevant as the low frequency intermolecular solvent modes have been found earlier to strongly influence the solvation dynamics and ionic mobility in amides and substituted amides.^{49,50}

In this Article, we investigate the solvation dynamics of three different probe molecules in several imidazolium ionic liquids for which the dielectric relaxation have been measured most recently by Stoppa et al.⁴³ These ionic liquids are 1-*N*-butyl-3-*N*-methylimidazolium tetrafluoroborate, [bmim][BF₄], and its hexafluorophosphate, [bmim][PF₆], and dicyanamide, [bmim][DCA], and 1-*N*-hexyl-3-*N*-methylimidazolium tetrafluoroborate, [hmim][BF₄]. The most important aspect of this dielectric relaxation study⁴³ is that these data cover the dielectric dispersion due to intermolecular librations at terahertz (THz) frequencies in ionic liquids. Subsequently, the complete dielectric relaxation data for these RTILs have been used as input in an extended molecular hydrodynamic theory (EMHT) developed earlier for studying solvation dynamics and ionic mobility in polar liquids.^{41,42} The solute parameters (such as dipole moment, diameter etc.) used in the calculation are those of the following probe molecules: coumarin 153 (C153), 4-aminophthalimide (4-AP), and *trans*-4-dimethylamino-4'-cyanostilbene (DCS). In addition, we have approximated the solvation process of a laser-excited probe molecule in RTIL as that in an effective dipolar medium, dipole moment of which is determined by the experimentally measured static dielectric constant. The static correlations (solute–solvent and solvent–solvent) are then assumed to be given by the mean spherical approximation (MSA) theory with corrections both at the short and the long wavelength limits.⁵¹ Note, however, that the inaccurate description of the static correlations at molecular length scales by the MSA theory may not vitiate the qualitative understanding of solvation dynamics in these liquids as the polar solvation energy relaxation has been found to be dominated by the collective response of the system.⁴¹ Subsequently, we have investigated the effects of cation libration^{44–48} on solvation energy relaxation in imidazolium ionic liquids by sequentially switching off the fast components in the experimentally measured⁴³ dielectric relaxation data.

The main results of this paper are as follows. For all the ionic liquids studied here, the calculated decay of the solvent response function ($S(t)$) is found to be biphasic with the slower component being nonexponential with time. It is also noticed that multi-exponential functions cannot adequately describe the calculated $S(t)$. The time constants associated with the calculated decay of $S(t)$ are found to be in the range of subpicosecond and a few hundreds of picosecond, with β (stretching exponent) values

(0.4–0.5) close to those observed in experiments. In addition, the theoretically predicted time constants are in semiquantitative agreement with those in experiments and simulation studies. The average solvation times ($\langle \tau_s \rangle$) are, however, found to be smaller by a factor of ~ 2 than those in experiments, indicating that a slower mechanism in addition to those captured in the dielectric relaxation studies might be present in the system which has not been incorporated in the present study. The freezing of the translational motion of the effective solvent dipoles does not lead to any further slowing down of the dynamics as the translational motion in these high viscous solvents is already severely restricted. The theoretical results presented here also do not reveal any probe dependence as the parameters used in the calculation for describing the different probes vary slightly from each other. The present study also reports dipolar solvation dynamics in two other room temperature ionic liquids, [bmim][DCA] and [hmim][BF₄], which should be tested against experiments.

The remaining part of the paper is arranged as follows: In section II, we give an overview of the theoretical formulation and discuss about the computational details. In section III, we present the numerical results and compare them with experimental data wherever possible. The paper then ends with concluding remarks in section IV.

II. Theoretical Formulation and Computational Details

Since we would be using the EMHT developed earlier^{41,42,52,53} for studying the solvation dynamics, only a brief discussion of the necessary expressions will be provided here. In the EMHT the time dependent solvation energy for a dipolar solute is obtained from the density functional theory.^{41,42} Although the use of the density functional theory for ionic liquids may be inappropriate and should therefore be debated, the presence of dipolar interactions (in addition to the ionic interactions) in these liquids may allow one to follow the same approach as devised for normal dipolar solvents.^{41,42} Consequently, the time dependent solvation energy for a dipolar solute in such an effectively dipolar medium becomes⁴¹

$$E_{sol}(r, \Omega, t) = -k_B T \int dr' d\Omega' c_{sd}(r, \Omega; r', \Omega') \delta\rho(r', \Omega', t) \quad (1)$$

where $E_{sol}(\mathbf{r}, \Omega, t)$ is the solvation energy of a dipolar solute located at position \mathbf{r} with orientation Ω at a time t . $c_{sd}(\mathbf{r}, \Omega; \mathbf{r}', \Omega')$ denotes the direct correlation function between the solute dipole and an effective solvent dipole at positions \mathbf{r} and \mathbf{r}' with orientations Ω and Ω' , respectively. Then, a tedious but straightforward algebra leads to the following expression for the normalized solvent response function⁵⁴

$$S(t) = \frac{\int_0^\infty dk k^2 \left\{ |c_{sd}^{10}(k)|^2 \left[1 - \frac{1}{\varepsilon_L(k)} \right] L^{-1} [z + \Sigma_{10}(k, z)]^{-1} + 2|c_{sd}^{11}(k)|^2 [\varepsilon_T(k) - 1] L^{-1} [z + \Sigma_{11}(k, z)]^{-1} \right\}}{\int_0^\infty dk k^2 \left\{ |c_{sd}^{10}(k)|^2 \left[1 - \frac{1}{\varepsilon_L(k)} \right] + 2|c_{sd}^{11}(k)|^2 [\varepsilon_T(k) - 1] \right\}} \quad (2)$$

In the above equation (eq 2) $c_{sd}^{10}(k)$ and $c_{sd}^{11}(k)$ represent the longitudinal and transverse components of the wavenumber (k) dependent direct correlation function between the dipolar solute and an effective solvent dipole and has been calculated using mean spherical approximation (MSA) theory.⁵¹ $\varepsilon_L(k)$ and $\varepsilon_T(k)$

are the longitudinal and the transverse components of wave-number dependent dielectric constant. $\Sigma_{10}(k,z)$ and $\Sigma_{11}(k,z)$ are the longitudinal ($l = 1, m = 0$) and transverse ($l = 1, m = 1$) components of the wavenumber and frequency (z) dependent generalized rate of solvent orientational polarization density relaxation, ($\Sigma_{lm}(k,z)$).^{41,52,53} Subsequently, $\epsilon_L(k)$ is obtained by the following exact relation⁵¹

$$\left[1 - \frac{1}{\epsilon_L(k)}\right] = \frac{3Y}{1 - (\rho_0/4\pi)c(110, k)} \quad (3)$$

where the solvent orientational static correlation function, $c(110, k)$ is calculated by using the MSA model for a pure solvent with proper corrections at both $k \rightarrow 0$ and $k \rightarrow \infty$ limits and $3Y$ ($= 4\pi\mu^2\rho_0/3k_B T$, ρ_0 and μ being the effective solvent dipole density and dipole moment) is the polarity parameter.⁵¹ Finally, $\epsilon_T(k)$ is obtained from the following relation⁵¹

$$[\epsilon_T(k) - 1] = \frac{3Y}{1 + (\rho_0/4\pi)c(111, k)} \quad (4)$$

where, again, the MSA theory provides the transverse component of the solvent dipole–dipole direct correlation function $c(111, k)$.

The wavenumber and frequency dependent generalized rate of solvent polarization relaxation, $\Sigma_{lm}(k,z)$ contains two dissipative kernels—the rotational kernel ($\Gamma_R(k,z)$) and the translational kernel ($\Gamma_T(k,z)$).^{41,52,53} The translational dissipative kernel, $\Gamma_T(k,z)$, has been calculated by using the isotropic dynamic structure factor of the effective dipolar medium while the rotational kernel $\Gamma_R(k,z)$ at $k \rightarrow 0$ limit is directly related to the experimentally determined frequency dependent dielectric function, $\epsilon(z)$ of RTILs, measured recently by Stoppa et al. These authors⁴³ have performed dielectric relaxation experiment over the frequency range of 0.1 GHz–3 THz. The measured dielectric relaxation data have been expressed as follows⁴³

$$\epsilon(z) = \epsilon_\infty + \frac{S_1}{[1 + (z\tau_1)^{1-\alpha_1}\beta_1]} + \frac{S_2}{[1 + z\tau_2]} + \frac{S_3}{[1 + z\tau_3]} + \frac{S_4\Omega_4^2}{[\Omega_4^2 + z^2 + z\Gamma_4]} \quad (5)$$

where ϵ_∞ is the limiting value of $\epsilon(z)$ at high frequency and τ_j is the relaxation time for the S_j dispersion. The parameters α_1 and β_1 determine the shape of a relaxation spectrum. Ω_4 and Γ_4 denote respectively the resonance frequency and the damping constant for the contribution at the THz frequency that has been described using the damped harmonic oscillator model.⁴³ The dielectric relaxation fit parameters obtained by Stoppa et al.⁴³ are given in Table 1. Note that these data indicate that fastest modes present in the RTILs such as librations and intermolecular vibrations are responsible for dispersion amplitudes, S_3 and S_4 . Therefore, availability of the full dielectric relaxation data allows us to investigate the effects of librational motion on solvation dynamics in room temperature ionic liquids which has not been done before.

The other solute (probe) and solvent parameters necessary for the calculation are summarized in Table 2, where solvent densities and viscosities are taken from experiments,³⁸ dipole moments calculated from the experimentally measured dielectric constants and diameters from the van der Waal's space filling model.

III. Results and Discussion

In this section, we present numerical results on dipolar solvation dynamics of the following systems: (i) DCS in

TABLE 1: Dielectric Relaxation Parameters (from Reference 43) Used in the Calculation of Solvation Dynamics in RTILs

	[bmim][PF ₆]	[bmim][BF ₄]	[bmim][DCA]	[hmim][BF ₄]
ϵ_0	11.8	12.2	11.3	10.1
S_1	7.4	8.94	6.42	6.32
τ_1 (ps)	1406	1140	63.0	1322
α_1	0	0	0.33	0
β_1	0.37	0.21	1	0.27
S_2	0.45	0.37	0.75	0.18
τ_2 (ps)	38.8	73.1	2.09	42.6
S_3	0.81	1.15	0.94	1.46
τ_3 (ps)	1.26	0.389	0.240	0.331
S_4	1.38	0.70	1.04	0.69
$\nu_4 = \Omega_4/2\pi$ (THz)	2.77	2.85	3.68	2.4
$\gamma_4 = \Gamma_4/2\pi$ (THz)	7.77	4.85	6.37	2.47
ϵ_∞	2.10	1.06	2.13	1.47

TABLE 2: Solute and solvent parameters used in the calculation of solvation dynamics in RTILs at 298 K

RTIL	diameter (Å)	dipole moment (D) ^e	density (g/cm ³)	viscosity (P)
[bmim][PF ₆] ^a	7.78	4.4	1.37	3.1
[bmim][BF ₄]	7.20	3.8	1.208	1.54
[bmim][DCA]	7.48	3.8	1.06	0.33
[hmim][BF ₄]	7.72	3.9	1.148	2.4
DCS ^b	7.8	20		
C153 ^c	7.8	14		
4-AP ^d	6.2	6.5		

^a The value of the dipole moment for [bmim⁺] shown here (obtained from static dielectric constant) is very close to value reported in the following work: Jin, H.; O'Hare, B.; Dong, J.; Arzhantsev, S.; Baker, G. A.; Wishart, J. F.; Benesi, A. J.; Maroncelli, M. *J. Phys. Chem. B*. **2008**, *112*, 81. ^b From the work: Arzhantsev, S.; Zachariasse, K. A.; Maroncelli, M. *J. Phys. Chem. A*. **2006**, *110*, 3454. ^c From ref. ^d From the work: Wetzler, D. E.; Chesta, C.; Fernandez-Prini, R.; Aramendia, P. F. *J. Phys. Chem. A*. **2002**, *106*, 2390. ^e The values of the dipole moment of the solutes (C153, DCS, and 4-AP) are those in the excited state.

[bmim][PF₆], (ii) DCS in [bmim][BF₄], (iii) C153 in [bmim][PF₆], and (iv) 4-AP in [bmim][PF₆]. For all these probe-RTIL systems, the theoretical results have been compared with the available experimental data wherever possible. Dipolar solvation dynamics have been predicted for two other systems also, DCS in [bmim][DCA] and DCS in [hmim][BF₄], for which experimental results are not available yet. The solvent response function, $S(t)$, calculated by using the eq 2 then fitted to the following function

$$S(t) = a_1 \exp[-t/\tau_1] + a_2 \exp[-(t/\tau_2)^\beta] \quad (6)$$

where a_1 and a_2 are the amplitudes of the biphasic components constituting the total decay of normalized $S(t)$ so that $a_1 + a_2 = 1$. Analytical integration of Eq. 6 then leads to the following expression for the average solvation time, $\langle \tau_s \rangle = a_1\tau_1 + (a_2\tau_2/\beta)\Gamma(1/\beta)$.

In Figure 1 we show the decay of the solvent response function for DCS in [bmim][PF₆] calculated by using eq 2 (solid lines) and compare with the experimental results (*open circles*) of Arzhantsev and co-workers.⁶ It is evident from Figure 1 that, as observed in experiments,⁶ the calculated decay of the solvent response function is indeed biphasic with two distinctly different time constants. In the same figure we also show the results of our investigation regarding the contributions of the librational and intermolecular vibrational modes to the solvation dynamics in ionic liquids. It is clear from this figure that calculation by considering all four of the experimentally measured dielectric

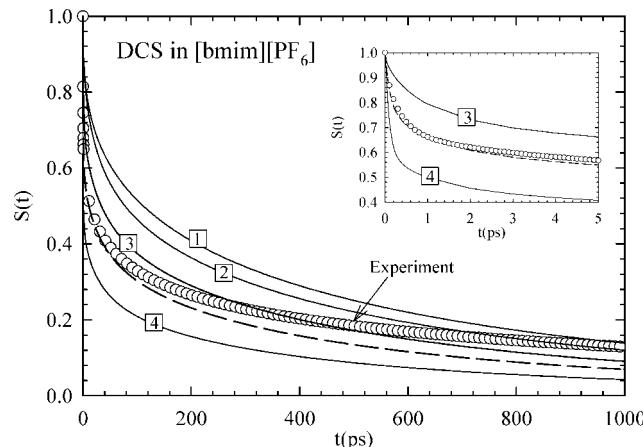


Figure 1. Comparison between the predicted decay (solid lines) of the solvent response function, $S(t)$ and that obtained from experiments (circles) for DCS in $[\text{bmim}][\text{PF}_6]$. The tags on the calculated curves represent the following: (i) “4” calculation with all the four dispersion steps reported by the experimental dielectric relaxation data by Stoppa et al.,⁴³ (ii) “3” calculation with the first three dispersion steps (the fastest step, S_4 is switched off), (iii) “2” calculation with first two dispersion steps (S_3 and S_4 are switched off), and (iv) “1” calculation with only the slowest (S_1) dispersion. The short dashed line represents the theoretical prediction when the magnitude of fastest relaxation step (S_4) in dielectric relaxation (DR) data is tuned such that $S_4 = 0.68$ and $\epsilon_\infty = 2.8$. Inset: Curves “3”, “4” and the one obtained with the tuned DR data are presented in a smaller time window in order to show the comparison with experimental results at early times. For decay fit parameters see Table 3.

dispersions in this solvent leads to the fastest decay (curve 4) of the solvent response function, whereas incorporation of only the slowest dispersion results a decay much slower (curve 1) than what has been observed in experiments.⁶ Systematic inclusion of two other dispersions in addition to the slowest one then makes the decay sequentially faster (curves 2 and 3) and closer to the experiments. This observation, therefore, indicates that, like in amide and substituted amides,^{49,50} the libration modes couple to the solvation dynamics in $[\text{bmim}][\text{PF}_6]$, and the fast component of the polar solvation energy relaxation originates from such coupling.

As the calculated solvent response function is very sensitive to the quality of the dielectric relaxation data, the present theory provides an opportunity to investigate the effects of uncertainty associated with the estimates of various dispersion amplitudes⁴³ obtained through fit to the experimental dielectric relaxation data. The results of one such calculation for $[\text{bmim}][\text{PF}_6]$ is also presented in the same figure (dashed line) where all the four dispersions have been considered with the following variation in the fastest relaxation: $S_4 = 0.68$ and $\epsilon_\infty = 2.1 + 0.7 = 2.8$. In the inset we show the decay of the solvent response function up to 5 ps where the calculated initial fast component of the solvation energy relaxation appears to agree quantitatively with that in experiments.⁶ The parameters required to fit the calculated decays by using eq 6 are summarized in Table 3 and typical fits to the calculated decay are provided in the Supporting Information (Figure S1). An inspection to the data in Table 3 reveal that modification of ϵ_∞ and leaving out of the fastest dispersion leads not only the fast and slow time constants (τ_1 and τ_2 , respectively) but the stretching exponent (β) also to a good agreement with those obtained from experimental studies.⁶ However, the calculated τ_1 is moderately faster (212 fs) with slightly larger amplitude (24%) than those in experiments (330 fs and 19%).⁶ These parameters along with $\sim 30\%$ larger β value (0.41 versus 0.31) give rise to average solvation time ($\langle \tau_s \rangle$) 300

ps, a value approximately 3 times less than that (1000 ps) in experiments.⁶ This disagreement is not unexpected given the fact that no attempt has been made in the present calculation to include the structural heterogeneity of the medium. Note also that the calculated τ_1 is agreeing well with that found in recent simulation studies of solvation dynamics in this ionic liquid.²⁵

Another feature to be noted in the theoretical study of solvation dynamics of DCS in $[\text{bmim}][\text{PF}_6]$ is that calculations with any number of dispersions leads to nonexponential and biphasic decay of the solvent response function with time constants lying between ~ 100 –900 fs and ~ 100 –300 ps with β values in the range of 0.38–0.41. Interestingly, an initial fast time scale of 600–900 fs with $\sim 10\%$ amplitude, which are comparable to those reported in a recent fluorescence up-conversion study of C153 in two other imidazolium based ionic liquids,²³ is obtained only after switching off the two higher frequency librational contributions in $[\text{bmim}][\text{PF}_6]$. Even though this switching off leads to higher values for β , the calculated values are still at least 1.5 times smaller than those reported in the above up-conversion experiments.²³ It is, however, to be recognized here that the side chains attached to the imidazolium unit and the counterions are different in the ionic liquids used in the up-conversion study²³ and hence in the absence of complete dielectric relaxation data the present calculation cannot suggest anything about the degree of correctness of the up-conversion data in these ionic liquids.²³

In Figure 2, we show the numerical results on solvation dynamics of DCS in another RTIL, $[\text{bmim}][\text{BF}_4]$ and compared with the relevant experimental data.⁶ While the solid lines represent the theoretically predicted solvent response functions obtained after sequential addition of dielectric dispersion steps, the circles represent the experimental results of Arzhantsev and co-workers.⁶ As observed in $[\text{bmim}][\text{PF}_6]$, the calculated solvent response function with any number of dispersions exhibits biphasic decay, even though the time constants become increasingly slower as the fast components in the dielectric relaxation data are switched off systematically (see Table 3). Note in Figure 2 that, unlike in $[\text{bmim}][\text{PF}_6]$, solvation dynamics in $[\text{bmim}][\text{BF}_4]$ appears not to couple to the fast modes of the solvent. Moreover, use of only the slowest dispersion step in the dielectric relaxation data does not make the decay of the solvent response function as slow as that observed in experiments. The fit parameters summarized in Table 3 indicate that calculation even with only the slowest dispersion gives rise to the fast and slow time constants respectively four times and twice as small as those found in experiments, although the calculated amplitudes are comparable. On the other hand, the total magnitude of spectral shift measured in the time-resolved experiments⁶ does not indicate missing of any component faster than what has been detected. Then, the observed discrepancy between the theory and experiments could be due to either the enhanced heterogeneity in $[\text{bmim}][\text{BF}_4]$, or, a small overestimation of the dispersion amplitudes in the dielectric relaxation data of $[\text{bmim}][\text{BF}_4]$.⁴³ Interestingly, the β_1 values reported by the dielectric relaxation experiments⁴³ seem to suggest that $[\text{bmim}][\text{BF}_4]$ is more heterogeneous than $[\text{bmim}][\text{PF}_6]$, which is, however, opposite to the trend found in solvation dynamics experiments in these two liquids.⁶

Subsequently, we have performed a test calculation by using only the slowest dispersion with its amplitude decreased by 1.4, leaving the relaxation time unchanged. That is, $\epsilon_s(12.2) \rightarrow \epsilon_1(4.66)$ with the Cole–Davidson relaxation time, $\tau_{CD} = 1140$ ps and the shape parameter, $\beta_1 = 0.21$.⁴³ The solvent response function thus calculated is shown by the dashed line in Figure

TABLE 3: Fit Parameters Required To Describe the Calculated and Experimental $S(t)$

system	type of study	a_1	τ_1 (ps)	a_2	τ_2 (ps)	β	$\langle \tau_s \rangle$ (ns)
DCS in [bmim][PF ₆]	theory						
	1	0.09	0.78	0.91	308	0.52	0.51
	2	0.07	0.90	0.93	224	0.47	0.47
	3	0.21	0.82	0.79	197	0.46	0.4
	4	0.40	0.13	0.60	87	0.38	0.2
	tuned DR data with 4 dispersion steps	0.24	0.21	0.76	126	0.41	0.3
	4 dispersion steps but only $k\sigma \rightarrow 0$ mode	0.31	0.19	0.69	32	0.33	0.13
	experiment (ref 6)	0.19	0.33	0.81	140	0.31	1.0
	theory						
	1	0.17	0.09	0.83	56	0.38	0.18
DCS in [bmim][BF ₄]	2	0.15	0.08	0.85	43	0.37	0.16
	3	0.35	0.13	0.65	23	0.33	0.1
	4	0.51	0.07	0.49	16	0.31	0.06
	tuned DR data with the slowest dispersion step	0.15	0.10	0.85	92	0.41	0.23
	experiment (ref 6)	0.19	0.32	0.81	130	0.41	0.34
	theory						
	1	0.10	0.79	0.90	310	0.52	0.52
	2	0.07	0.94	0.93	224	0.46	0.49
	3	0.21	0.83	0.79	195	0.46	0.37
	4	0.39	0.13	0.61	101	0.39	0.22
C153 in [bmim][PF ₆]	experiment (ref 4)						
	theory						
	1	0.11	0.81	0.89	312	0.52	0.52
	2	0.07	0.91	0.93	225	0.47	0.47
	3	0.22	0.81	0.78	193	0.46	0.35
	4	0.39	0.13	0.61	96	0.39	0.20
	experiment (ref 3)						
	theory						
	1	0.33	24.6	0.67	81	0.45	0.14
	2	0.27	11.6	0.73	49	0.41	0.11
4AP in [bmim][PF ₆]	3	0.15	0.61	0.85	20	0.35	0.08
	4	0.31	0.08	0.69	11	0.32	0.05
	theory						
	1	0.13	0.22	0.87	142	0.45	0.30
	2	0.11	0.19	0.89	119	0.43	0.29
	3	0.44	0.18	0.56	88	0.42	0.15
	4	0.58	0.09	0.42	66	0.39	0.1
	Experiment						

2, which is agreeing semiquantitatively with the experiments.⁶ In order to show the agreement at the initial time, we compare the results in a smaller time window (up to 5 ps) in the *inset*.

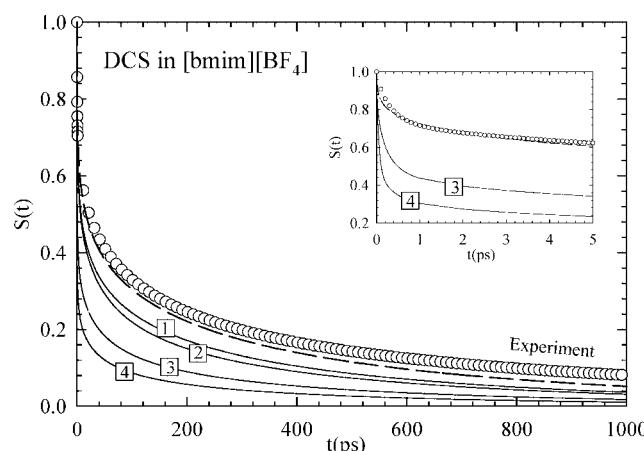


Figure 2. Comparison between the predicted decay (solid lines) of the solvent response function, $S(t)$, and that obtained from experiments (circles) for DCS in [bmim][BF₄]. The tags on the calculated curves represent the same protocol of the calculations as described in Figure 1. The dashed line represents the calculation by considering only the slowest step (S_1) of the DR data but with a tuning to make $\varepsilon_1 = \varepsilon_\infty = 4.66$. Here again the *inset* shows the comparison between the theory and experiments at early times. The representations remain the same as in Figure 1. The decay fit parameters are summarized in Table 3.

These results and the fit parameters given in Table 3 therefore suggests that a little tuning in the dielectric dispersion data is probably warranted for the agreement between theory and experiments on solvation dynamics in [[bmim][BF₄]. We of course mention that the observed decoupling of the calculated solvation dynamics from the librational and intermolecular vibrational modes in ionic liquids may originate from the fact that the present theory completely neglects the structural heterogeneity that characterizes these media. Therefore, the observed agreement upon tuning the dielectric relaxation data may not reveal the totally correct mechanism of the solvation dynamics in these room temperature ionic liquids.

Next we present the results on solvation dynamics in [bmim][PF₆] using two different probes, C153 and 4-AP. The calculated decays of the solvent response function with these two probe molecules in this ionic liquid are shown in Figures 3 and 4 and compared with the relevant experimental results.^{3,4} It is evident from these figures that in both the cases the experimental decay^{3,4} is much slower than the theory even when the calculation is performed using only the slowest dispersion. Experimental studies with C153 have indicated that ~30% of the initial fast dynamics is missed due to the limited time resolution employed in the experiments.⁴ For 4-AP, the missing component is even larger,³ which is ~60%. It is seen that when experiments are able to capture the complete solvation dynamics,⁶ a fast time constant of ~300 fs with ~20% amplitude is obtained and the rest is carried by a component with a time constant of 100–150 ps. The

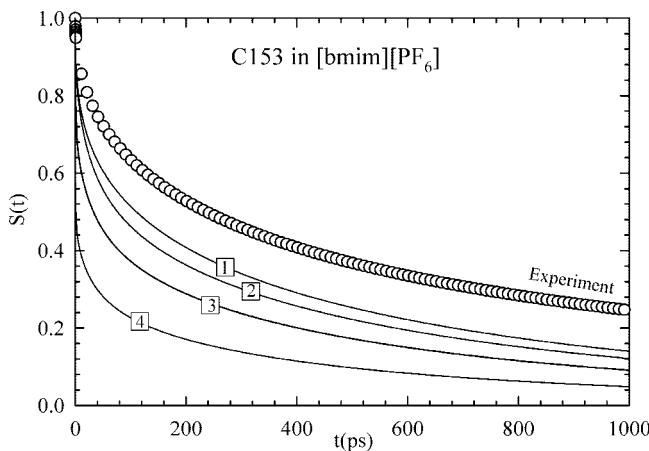


Figure 3. Comparison between the calculated and experimentally obtained decays of the solvent response function for C153 in [bmim][PF₆]. The representations remain the same in Figure 1. Note here that a substantial fraction of the early dynamics has been missed in the experiment. Fit parameters are provided in Table 3.

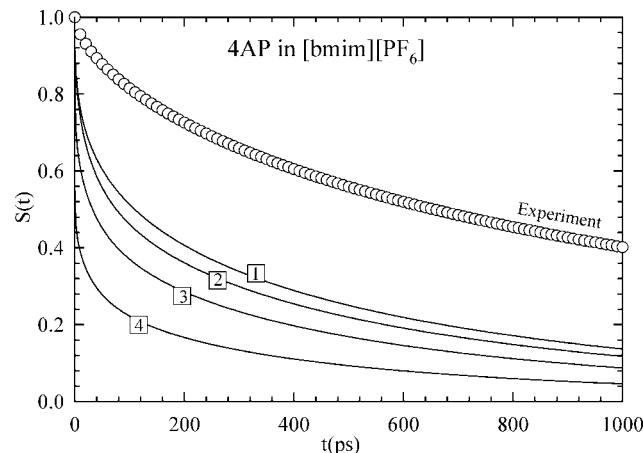


Figure 4. Solvation dynamics of 4-AP in [bmim][PF₆]. The representations remain the same as in Figure 1. Note that ~60% of the total decay has been missed in the experiment. The fit parameters are given in Table 3. For discussion, see text.

present calculation also reveals similar time scales in this ionic liquid, *albeit* with a little tuning in the dielectric relaxation data. Also, simulation studies²⁵ of C153 in [bmim][PF₆] suggests the presence of a fast component of amplitude $\sim 10\text{--}20\%$ with a time constant of ~ 200 fs. Furthermore, consideration of only the collective ($k\sigma \rightarrow 0$) mode of the solvent polarization relaxation obtained after using the tuned (as described in Figure 1) dielectric relaxation data⁴³ can generate the biphasic decay with two time constants, one in the range of ~ 200 fs and the other ~ 50 ps, and a β value of 0.33 (see Table 3 and Figure S2, Supporting Information). Therefore, the existence of a fast component of amplitude $\sim 10\text{--}20\%$ with time constant in the range of 200–300 fs associated with the solvation dynamics of dipolar probes in imidazolium ionic liquids is well supported by the present calculations.

Next we turn our attention to the probe dependence of solvation dynamics in ionic liquids. Experimental studies of solvation dynamics in [bmim][PF₆] with different probe molecules such as DCS, C153 and 4-AP have revealed that the average solvation time varies by approximately a factor of 2 among these probes, a result obtained from experimental data where a significant portion of the early dynamics has been

missed.⁴ The present theory does not predict such a probe dependence for [bmim][PF₆] as the average solvation times calculated with a given number of dispersion steps (see Table 3) remain largely *insensitive* to the identity of these probes. As the amplitudes and time constants associated with the biphasic decay of the calculated solvent response function are not too different due to small variations in the probe parameters (Table 2), the average solvation time exhibits almost complete independence from the nature of the probe used in this study. Similar probe dependence has also been predicted for solvation dynamics in dipolar solvents at ambient condition because of the dominance of the collective ($k\sigma \rightarrow 0$) mode of the solvent polarization relaxation.⁴¹

We have also studied solvation dynamics of DCS in two other RTILs, [bmim][DCA] and [hmim][BF₄] for which experimental results are not available yet. The calculated decays of the solvent response function for these two ionic liquids are shown in Figures S3 and S4 of the Supporting Information and the decay fit parameters are also summarized in Table 3. These parameters indicate that solvation dynamics in these ionic liquids is also biphasic in nature. The calculated dynamics in [bmim][DCA] is predicted to be 4–5 times faster than its hexafluorophosphate analogue and twice as fast as that in [hmim][BF₄]. However, the solvation dynamics in [bmim][BF₄] is found to be comparable with that in [bmim][DCA]. It is to be noted that [bmim][DCA] is different from the other three ionic liquids in the sense that it possesses the lowest density, smallest viscosity and fastest rotational relaxation times, along with a nonzero value for α_1 and the highest value for β_1 . Therefore, the time scale of solvation dynamics in [bmim][DCA] is expected to be different, and this is also reflected in the present calculation. However, the calculated average solvation times in these RTILs do not scale linearly with the solvent viscosity which probably a manifestation of the strong structural heterogeneity that exists in these ionic liquids. Another interesting point that emerges from the predicted solvation dynamics in all these four ionic liquid is that the value of β (the stretching exponent in eq 6) becomes successively smaller as the fast components in the dielectric relaxation data are sequentially incorporated in the calculation (Table 3). This is in corroboration with the observations of Arzhantsev and co-workers⁶ who found that complete detection of faster dynamics led to the reduction in β values obtained earlier⁴ with broader time resolution.

IV. Conclusion

Solvation dynamics of different dipolar probes in four imidazolium cation based ionic liquids have been studied using a molecular hydrodynamic theory where the most recent dielectric relaxation data⁴³ have been used as input. The present theory models these ionic liquids as effective dipolar media whose dipole moments are obtained from the experimentally measured static dielectric constants. While the static probe–solvent and solvent–solvent correlations required for the calculation have been obtained from the MSA with corrections at both the short and long wavelength limits, the present theory does not include the structural heterogeneity that originates from the relatively longer-ranged ion–ion interactions in these liquids. The solution heterogeneity is also reflected in several studies^{36,37,48,55} that report formation of polar and nonpolar regions through tail aggregation. In heterogeneous systems, the molecular correlation is known to extend over longer ranges⁵⁶ (beyond a couple of molecular diameters) which, in turn, makes the structural relaxation sluggish. The use of dipolar MSA in such systems would

always underestimate the static correlations because such simple models are useful for homogeneous liquids. Since solute–solvent and solvent–solvent static correlations are important inputs in the present theory, any underestimation of these correlations would make the polar solvation energy relaxation faster than what should be in the presence of proper enhanced correlations. This is probably one of the reasons that the theoretically predicted solvent response functions are uniformly faster than those observed in experiments. Nonetheless, it is interesting to see that even with a simplified model, the present theory can predict the experimentally observed biphasic dynamics where the calculated time scales are in semiquantitative agreement with those from experiments and simulation studies. The reason for this success of this effective medium calculation is probably due to the dominance of the long wavelength ($k\sigma \rightarrow 0$) polarization fluctuation and the use of the complete experimental dielectric relaxation data. The success of the present molecular theory in predicting solvation dynamics and ionic mobility in polar solvents have also been traced earlier to the above factors. Hence, we believe and also predicted already by Petrich and co-workers²⁵ that the use of complete dielectric relaxation data can lead to the understanding of the essential features of the polar solvation dynamics in ionic liquids. We have also presented theoretical results on solvation dynamics in two ionic liquids for which experimental data are not available yet. These predictions should be tested against experiments.

We would like to mention here that the discrepancy between theory and experiment can also come from the inaccuracy⁵⁷ in the dielectric data of Stoppa et al.⁴³ For instance, when a Cole–Davidson relaxation is used for the slowest mode, one obtains an unexpected increase of static permittivity with temperature.⁵⁷ If a Cole–Cole relaxation is used, the expected decrease of static permittivity with increasing temperature is found. Therefore, the use of these models in fitting the dielectric relaxation data of these liquids requires further work as the experimental accuracy below 1 GHz is too limited (here the dominating conductivity contribution swamps the “dielectric” signal).⁵⁷

The present calculations also show that the solvent fast modes such as libration and intermolecular vibrations may or may not couple completely to the polar solvation dynamics in the room temperature ionic liquids studied here. We would also like to mention here that the present theory will not be able to predict the solvation dynamics in ionic liquids where the frequency dependent dielectric function, $\varepsilon(z)$ would be close to $\varepsilon(\infty)$ for all frequencies. In such systems, the solvation dynamics would be closer to nonpolar solvation dynamics where the translational motions, rather than the ion rotations, would account for the relaxation time scales.^{58,59} One therefore requires two different theories, where the different interactions would be consistently incorporated while properly calculating the static correlations in order to investigate the solvation dynamics in these inherently heterogeneous systems. That would definitely be a challenging task.

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Supporting Information Available: Figures showing typical fits of the calculated decays to eq 6 of the text and predicted

decays of the solvent response function obtained by using the complete dielectric relaxation data⁴³ for DCS in (i) [bmim][PF₆] after considering only the $k\sigma \rightarrow 0$ mode of the solvent polarization relaxation, (ii) [bmim][DCA], and (iii) [hmim][BF₄]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (54) Eq. 2 is obtained by using the following expression for the normalized solvation energy correlation function: $S_E(t) = \langle E_{sol}(t)E_{sol}(0) \rangle / \langle |E_{sol}(0)|^2 \rangle$. Note that while $S_E(t)$ is an equilibrium correlation function, $S(t)$ constructed from the frequency of time resolved fluorescence emission spectra is a non-equilibrium correlation function. Within the linear response regime, $S(t)$ is assumed to be the equivalent of $S_E(t)$. See the relevant discussions in refs 41 and 42.
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