# Stokes Shift Dynamics in (Ionic Liquid + Polar Solvent) Binary Mixtures: Composition Dependence

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S *Supporting Information*

ABSTRACT: An approximate semimolecular theory has been developed to investigate the composition dependence of Stokes shift dynamics of a fluorescent dye molecule dissolved in binary mixtures of an ionic liquid (IL) with a conventional polar solvent at different mole fractions. The theory expresses the dynamic Stokes shift as a sum of contributions from the dye–IL and the dye–polar solvent interactions and suggests substantial solute–cation dipole–dipole interaction contribution to the solvation energy relaxation. The theory, when applied to aqueous mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate ($[Bmim][PF_6]$) and tetrafluoroborate ($[Bmim][BF_4]$), and binary mixtures of ($[Bmim][BF_4]$ + acetonitrile),

predicts reduction of Stokes shift but acceleration of the dynamics upon increasing the polar solvent concentration for the most part of the mixture composition. The decrease in dynamic Stokes shift values has been found to occur due to decrease of the dye–IL interaction in the presence of the added polar solvent. For aqueous binary mixtures of IL, the predicted results are in semiquantitative agreement with the available experimental results. However, the calculated dynamics suggest much weaker composition dependence than that observed in experiments. In addition, the theory predicts a turn around for dynamic Stokes shift in its composition dependence for ($[Bmim][BF_4]$ + acetonitrile) mixtures at higher dilutions of the IL. Interestingly, effective dipolar medium calculations for Stokes shift dynamics in ($[Bmim][BF_4]$ + dichloromethane) binary mixtures predict a very weak or even nonexistent nonlinear composition dependence. These predictions should be reexamined in experiments.
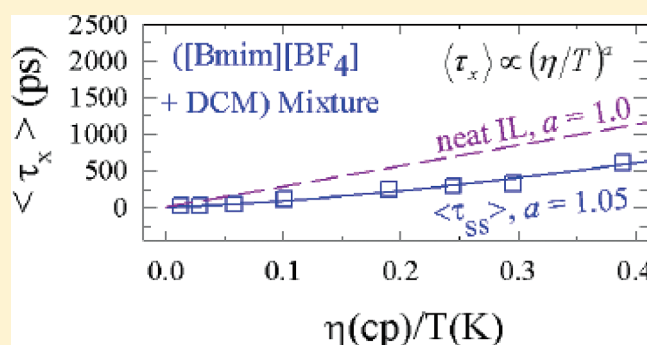
I. INTRODUCTION

Binary mixtures of ionic liquids (ILs) with dipolar solvents offer a new class of media for chemical processing because addition of cosolvents greatly expands the utility of ionic liquids as reaction media via suitably tuning their physicochemical properties. Addition of polar solvents strongly influences viscosities and electrical conductivities of the parent ILs which may make these mixtures better media for certain chemical and electrochemical applications.[1–18] Miscibility of ILs in water is a serious environmental concern as it may irreversibly damage the ecosystem by entering into the food chain. Consequently, the number of studies—both experimental[19–37] and computer simulations[38–46] investigating interactions between water and IL molecules—is much larger than those performed using binary mixtures of ILs with nonaqueous organic solvents,[47–51] supercritical fluids,[52,53] and with another IL.[54–60] Liquid solvent engineering for a desired reaction or extraction requires clear understanding of the solubility behavior[61–75] in which the medium polarity plays an important role. These studies provide crucial knowledge for the liquid–liquid extraction of reaction products and are thus very relevant to the chemical industry. Moreover, successful tailoring of a reaction requires a thorough knowledge of the medium polarity and dynamics as solvent

rearrangement often dictates the formation of a suitable reaction intermediate or a desired product through solvent stabilization.

Several spectroscopic studies in the past few years have reported local polarity around a dissolved solute for a number of (IL + dipolar solvent) binary mixtures and the issue of preferential solvation was discussed.[19–23,50–52] Nonideality in solution dynamics of (IL + dipolar solvent) and (IL + IL) binary mixtures has been explored via dielectric relaxation (DR) measurements[32,45,49,56] and time-resolved optical Kerr effect (OKE) spectroscopic techniques.[59,60] Terahertz time domain measurements of aqueous mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim][BF_4]$) have revealed moderate nonideal mixture composition dependence in relaxation parameters.[32] However, the slow IL-type time scales are missing in these experiments because of noncoverage of the dispersions occurring in the low-frequency regime. Dielectric relaxation measurements of the same mixtures in the water-rich regime covering a frequency range $0.2 \leq \nu/GHz \leq 89$ ($\omega = 2\pi\nu$) have, on the other hand, revealed a drastic reduction in the bulk static

dielectric constant (ε_0) of pure water in the presence of as low as 0.2 mole fraction of [Bmim][BF$_4$] and four different relaxation time scales ranging between approximately a nanosecond and a few picoseconds.[45] Most interestingly, computer simulation studies of aqueous mixtures of [Bmim][BF$_4$] have suggested negligible contribution to the solution ε_0 from the dipole cross correlation between imidazolium cation and water.[44] Available time-resolved fluorescence Stokes shift data for (IL + dipolar solvent) binary mixtures reveal acceleration of the average rate of solvation in presence of a cosolvent[33−36,47] over the values observed in pure ILs.[76−81] Subsequent computer simulation studies with aqueous mixtures of 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF$_6$])[43] suggest that rotational and translational motions of the ions become faster in the presence of water, which, in turn, enhances the rate of solvation. Note, however, that the existing measurements with (IL + dipolar solvent) binary mixtures[33−36,47] could not access the faster part of the solvation energy relaxation at early times due to broader time resolution employed and, therefore, the nature of the initial part of the dynamics has remained completely unknown.

Further review of the existing Stokes shift data measured with different solutes, such as coumarin 153 (C153) or 6-propionyl-2-(N,N-dimethylamino)naphthalene (PRODAN), in binary mixtures of ionic liquids with molecular solvents reveals several interesting aspects. For example, while addition of water, alcohol, or acetonitrile in any of the following ionic liquids, [Bmim][PF$_6$], [Hmim][PF$_6$], 1-ethyl-3-methylimidazolium ethyl sulfate ([Emim]-[EtSO$_4$]), and N,N,N-trimethyl-N-propylammoniumbis(trifluoromethanesulfonyl) imide ([N$_{3111}$][Tf$_2$N]), has been found to induce red shift in the steady-state fluorescence emission spectrum of a dissolved solute;[33−36,47] no such effects were observed when toluene or dioxane was added to [Bmim][PF$_6$].[48] What is even more interesting is that the time zero fluorescence emission spectrum blue-shifts upon addition of toluene or dioxane in [Bmim][PF$_6$] compared to that in the neat IL, producing a larger dynamic Stokes shift. Note that toluene and dioxane are non-dipolar solvents[82] and addition of either of them in an ionic liquid probably reduces ε_0 of the resultant mixture.[83] The decrease in ε_0 then enhances the solute−ion interaction,[83,84] leading to larger Stokes shift values in (IL + nondipolar solvent) binary mixtures. Computer simulation studies of ([Bmim][BF$_4$] + TIP3P water)[44] and ([Hmim][PF$_6$] + SPC water)[43] binary mixtures, on the other hand, suggest screening of ion−ion interactions in the presence of water molecules. One then wonders what would be the possible consequences of this screening effect on Stokes'-shift dynamics as ion−solute interactions considerably influence the Stokes shift dynamics in ionic liquids.[84−87]

In this paper, a semimolecular theory for studying the Stokes shift dynamics in binary mixtures of (IL + common dipolar solvent) has been developed where the effects of cosolvent have been incorporated via the solute−solvent interactions. As before,[84−90] we have used the classical density functional theory (DFT) to express the fluctuating solvation energy of a dissolved dipolar solute in (IL + dipolar solvent) binary mixtures. In this theory, a restriction up to the linear order in fluctuating density ($\delta\rho$) then leads to the total fluctuating solvation energy separating into contributions from the interactions between the dipolar solute and ionic liquid, and that between the dipolar solute and added cosolvent molecules. The time-dependent progress of solvation of a dipolar solute in such mixtures is followed in terms of solvation energy−energy

time correlation function. The theory is then applied to predict the Stokes shift dynamics for a few (IL + dipolar solvent) binary mixtures for which experimental results exist. Subsequently, the calculated results have been compared with those from measurements and plausible molecular level explanations offered for the experimentally observed composition dependence of the Stokes shift dynamics of a dipolar solute dissolved in such mixtures. In addition, effective medium calculations for ([Bmim][BF4] + dichloromethane) binary mixtures using the experimental solution dielectric relaxation data have been carried out in order to explore the nonideality in composition dependence of Stokes shift dynamics in such binary mixtures.

The organization of the rest of the paper is as follows. The next section contains the theoretical formulation and calculation details. Numerical results and comparison with experiments are given in section III. The paper then ends with a discussion in section IV.

II. THEORETICAL FORMULATION AND CALCULATION DETAILS

A. Derivation of Microscopic Expressions. The derivation of the microscopic expressions for the total time-dependent fluctuating solvation energy for dipolar solute in (IL + dipole solvent) binary mixtures closely follows the framework described in our earlier works.[84−87] It is first assumed that a given ionic liquid is completely dissociated in the presence of a strongly polar solvent. This assumption is perhaps justifiable for some mixtures as experimental studies have found either small or negligible ion-pair formation in binary mixtures of some ionic liquids with strongly polar solvents.[3,91] As in dynamic Stokes shift experiments, a very dilute solution of a dipolar probe in such (IL + dipolar solvent) mixture is considered for the present study. Note that such a solution is a multicomponent mixture consisting of the added dipolar solvent and the dipolar solute molecules, and the ions from the dissociated ionic liquid molecules. Moreover, either or both of the ions could be dipolar in character.[49,92−94] In such a multicomponent mixture, the Stokes shift is principally governed by the following interactions: (i) the dipolar solute−dipolar ion (dipole−dipole) interactions, (ii) the dipolar solute−ion (dipole−ion) interactions, and (iii) dipolar solute−dipolar solvent (dipole−dipole) interactions. The dynamics of Stokes shift, however, involves, in addition to the above interactions, the dipolar and ionic interactions among the ions, and the dipole−dipole interactions among the added dipolar solvent molecules. The present theory neither incorporates separately the cross interactions such as the ion−solvent and ion−ion "ion−dipole" interactions nor considers the interactions due to the presence of ion pair and higher ion aggregates.[95,96] While the ion−solvent and ion−ion ion−dipole interactions are neglected assuming that the time scales associated with the fluctuations of dipolar density and ion density are widely different and thus dynamically completely decoupled, the latter (interactions due to ion pair and higher aggregates) is ignored in order to preserve the analytical simplicity of the present theory. Note that the neglect of the cross correlations between the ion and dipole density fluctuations based on separation of time scales is purely an approximation because of the motions of the ionic and dipolar species in such mixtures are adiabatically coupled.[97−102] Dynamic Stokes shift measurements of electrolyte solutions, on the other hand, reveals that ion motions affect the dynamics at longer times.[103] It is

therefore evident from the above discussion that the present formalism provides an approximate theoretical framework for studying the Stokes shift dynamics in binary mixtures of ionic liquids with strongly polar solvents.

We next use the classical density functional theory (DFT) to write the expression for the interaction part of the free energy functional ($\Delta\beta F_{int}$, with $\beta = 1/k_B T$) in terms of position (r)- and orientation ($\boldsymbol{\Omega}$)-dependent densities of the dipolar ion, dipolar solute, dipolar solvent molecules, and position-dependent ion in the solution.[104−106] Then, equating the functional derivative of $\Delta\beta F_{int}$ with respect to the solute density to zero (equilibrium property) provides the expression for the average solvation energy for a dipolar solute immersed in such a mixture (see paragraph A1, Supporting Information for derivation). Subsequent extension into the time domain allows one to derive the following expression for the time (t), position- and orientation-dependent solvation energy for a mobile dipolar solute

$$\Delta E_{total}(r, \boldsymbol{\Omega}, t) =$$

$$-k_B T \rho_s(r, \boldsymbol{\Omega}, t)\Big[\int dr' \, d\boldsymbol{\Omega}' \, c_{sd}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}', \boldsymbol{\Omega}')\delta\rho_d(\mathbf{r}', \boldsymbol{\Omega}'; t)$$

$$+ \int dr' \, d\boldsymbol{\Omega}' \, c_{sp}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}', \boldsymbol{\Omega}')\delta\rho_p(\mathbf{r}', \boldsymbol{\Omega}'; t)$$

$$+ \sum_{\alpha=1}^{2} \int dr' \, c_{s\alpha}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}')\delta n_\alpha(\mathbf{r}', t)\Big] = \Delta E_{sd}(\mathbf{r}, \boldsymbol{\Omega}, t)$$

$$+ \Delta E_{sp}(\mathbf{r}, \boldsymbol{\Omega}, t) + \Delta E_{si}(\mathbf{r}, \boldsymbol{\Omega}, t) \qquad (1)$$

where $\rho_s(\mathbf{r}, \boldsymbol{\Omega}; t)$ is the position ($\mathbf{r}$)-, orientation ($\boldsymbol{\Omega}$)-, and time (t)-dependent number density of the dissolved solute. In the above equation, while $c_{sd}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}', \boldsymbol{\Omega}')$ denotes the direct correlation function (DCF) between a dipolar solute at position $\mathbf{r}$ with orientation $\boldsymbol{\Omega}$ and a dipolar ion at $\mathbf{r}'$ with $\boldsymbol{\Omega}'$, $c_{sp}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}', \boldsymbol{\Omega}')$ represents the DCF between the dipolar solute at position $\mathbf{r}$ with orientation $\boldsymbol{\Omega}$ and the dipolar solvent at $\mathbf{r}'$ with $\boldsymbol{\Omega}'$. $c_{s\alpha}(\mathbf{r}, \boldsymbol{\Omega}; \mathbf{r}')$ represents that between a dipolar solute placed at $\mathbf{r}$ with orientation $\boldsymbol{\Omega}$ and a charged species (ion) located at $\mathbf{r}'$. α denotes the type of ions (positively charged and negatively charged ions) that are interacting with the solute. The fluctuations in dipolar ion and added polar solvent densities ($\delta\rho_d$ and $\delta\rho_p$), and ion density (δn_α) from the respective equilibrium bulk values are then defined as follows: $\delta\rho_d(\mathbf{r}, \boldsymbol{\Omega}) = \rho_d(\mathbf{r}, \boldsymbol{\Omega}) - \rho_d^0/4\pi$, $\delta\rho_p(\mathbf{r}, \boldsymbol{\Omega}) = \rho_p(\mathbf{r}, \boldsymbol{\Omega}) - \rho_p^0/4\pi$, and $\delta n_\alpha(\mathbf{r}) = n_\alpha(\mathbf{r}) - n_\alpha^0$. Note that the time dependence in the fluctuating total solvation energy, $\Delta E_{total}(\mathbf{r}, \boldsymbol{\Omega}, t)$, is introduced through the temporal modulation of the fluctuating dipolar ($\delta\rho_d(\mathbf{r}, \boldsymbol{\Omega}, t)$ and $\delta\rho_p(\mathbf{r}, \boldsymbol{\Omega}, t)$) and ion ($\delta n_\alpha(\mathbf{r}, t)$) densities. Since the linear response approximation allows one to consider the fluctuation in densities either from the initial ($t = 0$) or final ($t = \infty$) state, the time-dependent fluctuating total solvation energy $\Delta E_{total}(\mathbf{r}, \boldsymbol{\Omega}, t)$ for a solute in (IL + dipolar solvent) binary mixture may be expressed as eq 1.

Note that eq 1 expresses the total fluctuating solvation energy $\Delta E_{total}(\mathbf{r}, \boldsymbol{\Omega}; t)$ as a sum of three distinct contributions: dipolar contributions from interactions of the solute with the dipolar cations ($\Delta E_{sd}(\mathbf{r}, \boldsymbol{\Omega}; t)$) and with the dipolar solvent molecules (($\Delta E_{sp}(\mathbf{r}, \boldsymbol{\Omega}; t)$), and the dipole−ion contributions from interactions of the solute with the charged species ($\Delta E_{si}(\mathbf{r}, \boldsymbol{\Omega}; t)$). Such a summation of three separate contributions arises from the linearization $\Delta\beta F_{int}$ in terms of dipolar and ionic density fluctuations ($\delta\rho_d$, $\delta\rho_p$, and δn_α). We will see later that this

approximate description of $\Delta E_{total}(\mathbf{r}, \boldsymbol{\Omega}; t)$ and the neglect of cross correlations among the ΔE_{sj} (with j = d, p, or i) terms while forming the time correlation functions lead to an expression for the total dynamic Stokes shift where these interactions contribute in a mole-fraction-weighted manner. This ideal composition-dependent description of fluctuating total solvation energy might be different from that in real solution but we consider this as an approximation in order to develop a semimolecular picture for qualitatively describing the measured Stokes shift dynamics in such complex multicomponent mixtures. Since Stokes shift dynamics in (IL + dipolar solvent) binary mixtures is expected to be governed by the long-wavelength density fluctuations, the intricate details of the solvent composition around a dissolve solute should play a minor role. This dominance of the collective solvent modes is probably the factor which nullifies inaccuracies associated with a number of approximations while developing a simple theory such as the present one and renders the ability to qualitatively describe the experimental Stokes shift dynamics of such extremely complex systems.

We next form the total (fluctuating) solvation energy autocorrelation function as follows

$$\langle\Delta E_{total}(t)\Delta E_{total}(t')\rangle = \langle\Delta E_{sd}(t)\Delta E_{sd}(t')\rangle$$
$$+ \langle\Delta E_{sp}(t)\Delta E_{sp}(t')\rangle + \langle\Delta E_{si}(t)\Delta E_{si}(t')\rangle$$
$$+ \langle\Delta E_{sd}(t)\Delta E_{si}(t')\rangle + \langle\Delta E_{si}(t)\Delta E_{sd}(t')\rangle$$
$$+ \langle\Delta E_{si}(t)\Delta E_{sp}(t')\rangle + \langle\Delta E_{sp}(t)\Delta E_{si}(t')\rangle$$
$$+ \langle\Delta E_{sd}(t)\Delta E_{sp}(t')\rangle + \langle\Delta E_{sp}(t)\Delta E_{sd}(t')\rangle$$
$$= \langle\Delta E_{sd}(t)\Delta E_{sd}(t')\rangle + \langle\Delta E_{sp}(t)\Delta E_{sp}(t')\rangle$$
$$+ \langle\Delta E_{si}(t)\Delta E_{si}(t')\rangle \qquad (2)$$

where the position and orientation dependencies of ΔE_{sj} are not shown explicitly in order to avoid crowding. The following comments are in order for the second equality in eq 2. Because of wide difference in time scales, the cross correlations between the time-dependent fluctuating dipole−dipole interaction energy (ΔE_{sd} or ΔE_{sp}) term and the dipole−ion interaction energy term (ΔE_{si}) are assumed to decouple completely from each other and thus vanish. Moreover, the simulation finding[44] of negligible contribution to solution dielectric constant from the cross correlations of fluctuating dipoles of different polar species (dipolar ion and dipolar added solvent) suggests that contributions from $\langle\Delta E_{sd}(t)\Delta E_{sp}(t')\rangle$ terms may be completely ignored. In other words, we set $\langle\Delta E_{sd}(t)\Delta E_{sp}(t')\rangle = 0 = \langle\Delta E_{sp}(t)\Delta E_{sd}(t')\rangle$, leading to the final form of eq 2.

The time dependence of the solvation energy relaxation is then followed in terms of the normalized solvation energy autocorrelation function

$$S_E(t) = \frac{\langle|\Delta E_{sd}(0)|^2\rangle S_{sd}(t)}{\langle|\Delta E_{sd}(0)|^2\rangle + \langle|\Delta E_{si}(0)|^2\rangle}$$
$$+ \frac{\langle|\Delta E_{sp}(0)|^2\rangle S_{sp}(t)}{\langle|\Delta E_{sp}(0)|^2\rangle + \langle|\Delta E_{si}(0)|^2\rangle} + \frac{\langle|\Delta E_{si}(0)|^2\rangle S_{si}(t)}{\langle|\Delta E_{sd}(0)|^2\rangle + \langle|\Delta E_{si}(0)|^2\rangle}$$
$$(3)$$

where S_{sd}, S_{sp}, and S_{si} are the individual normalized solvation energy autocorrelation functions due respectively to solute−dipolar ion (dipole−dipole), solute−added solvent (dipole−dipole), and solute−ion (dipole−ion) interactions. These three distinct interaction components, depending upon the average

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rate, contribute to constitute the total decay $S_E(t)$. Needless to mention, while the total decay is dominated by the fastest component, the average rate is determined by the slowest of these three separate relaxation channels.

$$S_{sd}(t) = \frac{\langle \Delta E_{sd}(t) \Delta E_{sd}(0) \rangle}{\langle |\Delta E_{sd}(0)|^2 \rangle} = \frac{A \int_0^\infty dk\, k^2 S_{solute}^{10}(k,t)|c_{sd}^{10}(k)|^2 S_{solvent}^{10}(k,t) + 2A \int_0^\infty dk\, k^2 S_{solute}^{11}(k,t)|c_{sd}^{11}(k)|^2 S_{solvent}^{11}(k,t)}{A \int_0^\infty dk\, k^2 S_{solute}^{10}(k)|c_{sd}^{10}(k)|^2 S_{solvent}^{10}(k) + 2A \int_0^\infty dk\, k^2 S_{solute}^{11}(k)|c_{sd}^{11}(k)|^2 S_{solvent}^{11}(k)} \quad (4)$$

where A is a prefactor given by $2\rho_d^0 k_B T/(2\pi)^2$. $c_{sd}^{lm}(k)$ in eq 4 denotes the Fourier transform of the (l,m) component of the static correlation function between the solute and a dipolar ion, and $S_{solvent}^{lm}(k,t)$ is the same component of the orientational dynamic structure factor of the dipolar ions. $S_{solute}^{lm}(k,t)$ denotes the (l,m) component of solute dynamic structure factor. $c_{sd}^{lm}(k)$ has been obtained by using the mean spherical approximation (MSA) theory for binary dipolar mixtures with one of the components (dipolar solute) at limiting concentration.[107,108] Note that even though the real solution is a multicomponent mixture, the use of the classical DFT and the subsequent treatment split the total solvation energy relaxation into relaxations of three distinct interaction contributions. These individual contributions then could be obtained by treating as those for binary mixtures with dipolar solute being present at infinite dilution. Note the dipole moment of the dipolar solute in its first excited state has been used while calculating $c_{sd}^{lm}(k)$ and other relevant quantities.

(i). Calculation of the Wave Vector and Time-Dependent Orientational Solvent Dynamic Structure Factor, $S_{solvent}^{lm}(k,t)$. As before,[84−88] the longitudinal ($S_{solvent}^{10}$) and transverse ($S_{solvent}^{11}$) components of the solvent (dipolar ion or added dipolar cosolvent) orientational dynamic structure factor (or, in other words, orientational dipolar dynamic structure factor) have been obtained from the experimental dielectric relaxation data. These are given by the following relations

$$S_{solvent}^{10}(k,t) = \frac{1}{4\pi 3Y}\left[1 - \frac{1}{\varepsilon_L(k)}\right] L^{-1}[z + \Sigma_{10}(k,z)]^{-1} \quad (5)$$

and

$$S_{solvent}^{11}(k,t) = \frac{1}{4\pi 3Y}[\varepsilon_T(k) - 1] L^{-1}[z + \Sigma_{11}(k,z)]^{-1} \quad (6)$$

where the polarity parameter $3Y = (4\pi/3k_B T)\mu^2 \rho_d^0$ with μ and ρ_d^0 being the dipole moment and density of the medium. $\varepsilon_L(k)$ and $\varepsilon_T(k)$ are the longitudinal and transverse components of the wavenumber-dependent dielectric function and can be obtained from the orientational static structural correlations as follows:[88,89,104] $[1 - \varepsilon_L^{-1}(k)] = 3Y f_{110}^{-1}(k)$, and $[\varepsilon_T(k) - 1] = 3Y f_{111}^{-1}(k)$ with $f_{llm}(k) = 1 - (\rho_d^0/4\pi)(-1)^m c(llm,k)$. $f_{llm}(k)$ describes the wavenumber-dependent $(1,1,0)$, $(1,1,1)$, and $(1,1,-1)$ components of the orientational static structure of the dipolar particles (dipolar ions or dipolar solvents). In the present calculations, these static structural components have been obtained from the MSA theory[104,105] for (solute + solvent) binary dipolar mixtures with solute present at limiting

B. Calculation of the Normalized Solvation Energy Autocorrelation Function Due to Solute−Dipolar Ion (Dipole−Dipole) Interaction, $S_{sd}(t)$. The normalized solvation energy autocorrelation function arising from the dipolar solute−dipolar ion interaction, $S_{sd}(t)$, is defined as follows

concentration. L^{-1} represents the Laplace inversion and z is the frequency. $\Sigma_{lm}(k,z)$ is the (l,m)th component of the generalized rate of the orientational solvent polarization density relaxation. Calculation of $\Sigma_{lm}(k,z)$ is quite nontrivial[88,106−109] and a brief outline is provided in Appendix A.

(ii). Calculation of the Solute Dynamic Structure Factor, $S_{solute}^{lm}(k,t)$. The solute dynamic structure factor is assumed to be diffusive (both rotational and translational) only and is given by[84−88]

$$S_{solute}^{lm}(k,t) = \frac{1}{4\pi}\exp[-(l(l+1)D_R^s + k^2 D_T^s)t] \quad (7)$$

The rotational (D_R^s) and translational (D_T^s) diffusion coefficients of the solute (assumed spherical) have been obtained from the medium viscosity using the *stick* boundary condition. Even though the solute motion was introduced earlier in a somewhat arbitrary manner in the expression for the time-dependent fluctuating solvation energy of a dipolar solute,[108,110] the effects of the solute motions were predicted to be quite significant for highly viscous nondipolar ionic liquids.[87] The normalizing factor, $1/4\pi$, in eq 7 arises from the time-averaging of all possible orientations for the solute dipole. This factor does not enter into the calculations of dipole−dipole contribution to the Stokes shift because the magnitude of the shift should be the same for both fixed and mobile solute cases.

Following our earlier works,[85,86,111,112] we have calculated the solute−dipolar ion interaction contribution to the total dynamic Stokes shift from the square root of the denominator of eq 4. That is, $\Delta \nu_{sd}^t = \langle |E_{sd}(0)|^2 \rangle^{1/2}$. This is because $\langle |\Delta E_{sd}(t=0)|^2 \rangle$ represents the square of the excess solvation energy due to solute−dipolar ion interactions evaluated at time zero immediately after laser excitation of a solute from its nonpolar ground state to polar excited state. The equivalence between the calculated and experimental shifts is then drawn by assuming that pure solvent structure (and dynamics) does not change in the presence of a solute (dipolar or nonpolar) or sudden alteration of polarity of it upon excitation. This is essentially the linear response approximation and each comparison between theory and experiments presented here has been performed within the purview of this approximation.

C. Calculation of the Normalized Solvation Energy Autocorrelation Function Due to Dipolar Solute-Added Dipolar Solvent (Dipole−Dipole) Interaction, $S_{sp}(t)$. The expression for the normalized solvation energy autocorrelation function due to dipolar solute−dipolar added solvent (dipole−dipole) interaction is, in fact, very similar to eq 4, and can be given by

$$S_{sp}(t) = \frac{\langle \Delta E_{sp}(t) \Delta E_{sp}(0) \rangle}{\langle |\Delta E_{sp}(0)|^2 \rangle} = \frac{A \int_0^\infty dk\, k^2 S_{solute}^{10}(k,t)|c_{sp}^{10}(k)|^2 S_p^{10}(k,t) + 2A \int_0^\infty dk\, k^2 S_{solute}^{11}(k,t)|c_{sp}^{11}(k)|^2 S_p^{11}(k,t)}{A \int_0^\infty dk\, k^2 S_{solute}^{10}(k)|c_{sp}^{10}(k)|^2 S_p^{10}(k) + 2A \int_0^\infty dk\, k^2 S_{solute}^{11}(k)|c_{sp}^{11}(k)|^2 S_p^{11}(k)} \quad (8)$$

Table 1. Comparison between the Composition-Dependent Predicted and Experimental Dynamic Stokes Shift for C153 in ([Bmim][PF₆] + Water) Binary Mixtures

mole fraction of water, x_w	density (g/cm³)	$\Delta\nu_{sd}^t$ (cm⁻¹)[a]	$\Delta\nu_{si}^t$ (cm⁻¹)[b]	$\Delta\nu_{sp}^t$ (cm⁻¹)[c]	total $\Delta\nu_{tot}^t$ (cm⁻¹)	expt (cm⁻¹)
0.00	1.368	871 (861)	877 (1219)	0	1748 (2080)	2000[d]
0.03	1.363	720 (714)	869 (1214)	9	1598 (1937)	1492[e]
0.10	1.359	684 (680)	831 (1160)	18	1533 (1858)	1494
0.18	1.355	644 (641)	785 (1098)	26	1455 (1765)	1493
0.22	1.353	625 (622)	763 (1066)	30	1418 (1718)	1506

[a] Solute−dipolar cation (dipole−dipole) interaction contribution. [b] Solute−ion (dipole−ion) interaction contribution. [c] Solute−water (dipole−dipole) interaction contribution. [d] From ref 81. [e] From ref 33.

where $c_{sp}(k)$ denote the wavenumber-dependent solute−cosolvent (added dipolar solvent) static correlations and $S_p(k,t)$ the orientational dynamic structure factor of the dipolar cosolvent added to prepare the binary mixtures. As before, $c_{sp}(k)$ has been obtained from the dipolar MSA for binary mixtures with solute at infinite dilution and $S_p(k,t)$ from the measured dielectric relaxation function of the added cosolvent. The other quantities required for the calculation of $S_{sp}(t)$ have been obtained exactly in the same manner as followed for $S_{sd}(t)$ by using eq 4. Again, the dynamic Stokes shift due to the interaction between the dipolar solute and polar cosolvent molecules are approximated as $\Delta\nu_{sp}^t = (\langle|E_{sp}(0)|^2\rangle)^{1/2}$.

D. Calculation of the Normalized Solvation Energy Autocorrelation Function Due to Dipolar Solute−Ion (Dipole−Ion) Interaction, $S_{si}(t)$. The expression for the normalized solvation energy autocorrelation function due to solute dipole−ion (dipole−ion) interaction can be written as

$$
S_{si}(t) = \frac{\langle \Delta E_{si}(t)\Delta E_{si}(0)\rangle}{\langle|\Delta E_{si}(0)|^2\rangle}
$$
$$
= \frac{B\sum_{\alpha,\beta}\sqrt{n_\alpha^0 n_\beta^0}\int_0^\infty dk\, k^2 S_{solute}^{10}(k,t)c_{s\alpha}^{10}(k)c_{s\beta}^{10}(-k)S_{\alpha\beta}^{ion}(k,t)}{B\sum_{\alpha,\beta}\sqrt{n_\alpha^0 n_\beta^0}\int_0^\infty dk\, k^2 S_{solute}^{10}(k)c_{s\alpha}^{10}(k)c_{s\beta}^{10}(-k)S_{\alpha\beta}^{ion}(k)}
$$

(9)

where $B = 2(k_B T/2\pi)^2$ and $c_{s\alpha}^{10}(k)$ denote the (1,0) component of the wavenumber-dependent static structural correlations between the dipolar solute and an ion of type α. $S_{\alpha\beta}^{ion}(k,t)$ is the partial isotropic ion dynamic structure factor. Note the derivation of eq 9 and calculation procedure of $S_{si}(t)$ have already been discussed in detail elsewhere[85,86] and thus not repeated here. For completeness, we would like to mention that a diffusive form[113] for $S_{\alpha\beta}^{ion}(k,t)$ has been used in our calculations where the diffusion coefficient of the ions (D_α) have been obtained from the medium viscosity by using the Stokes−Einstein relation with stick boundary condition. The relevant part of the isotropic ion static structure factor, $S_{\alpha\alpha}(k)$, has been approximated by the Percus−Yevick (P-Y) solution for binary mixtures[114] of singly charged hard spheres of equal radii and used the expressions derived elsewhere[115,116] for the calculation of ion static structure factor, $S_{\alpha\beta}^{ion}(k)$. The longitudinal component of the wavenumber-dependent direct correlation function between the dipolar solute and ions, $c_{s\alpha}^{10}(k)$, is taken as $c_{s\alpha}^{10}(k) = -((4\pi)/3)^{1/2}((4\pi i\mu_1 q_\alpha)/(k_B T\varepsilon_0 k))(\sin(kr_c))/(kr_c)$, where μ_1 is the excited-state dipole moment of the dipolar solute, q_α the charge of αth type ion, and r_c the distance of the closest approach between the solute dipole and the ionic species. Note that the above calculation schemes for the ion−dipole and ion−ion static

correlations do not consider at all the static heterogeneity that may be present in these mixtures. As described in our earlier works,[85,86,111,112] the ion−solute contribution to the dynamical Stokes shift is given by $\langle|\Delta E_{si}(0)|^2\rangle^{1/2}$ which can be calculated easily from the denominator of eq 9. That is, $\Delta\nu_{si}^t = \langle|E_{si}(0)|^2\rangle^{1/2}$. Subsequently, the total dynamic Stokes shift is approximated as $\Delta\nu_{tot}^t = \Delta\nu_{sd}^t + \Delta\nu_{si}^t + \Delta\nu_{sp}^t = \langle|\Delta E_{sd}(0)|^2\rangle^{1/2} + \langle|\Delta E_{si}(0)|^2\rangle^{1/2} + \langle|\Delta E_{sp}(0)|^2\rangle^{1/2}$. In addition, Stehfest algorithm[117] has been used to perform the Laplace inversion whenever required.

III. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENTS

In this section, we shall first present the theoretical predictions on dynamic Stokes shift in several (IL + polar solvent) binary mixtures and its mixture composition dependence. Next, the predicted mole fraction dependent Stokes shift dynamics for these mixtures are discussed. The solute considered in the calculations is coumarin 153 (C153) for which experimental results for a few (IL + polar solvent) binary mixtures are available. Subsequently, the calculated results have been compared with experimental data in order to test the validity of the present theory and provide molecular level explanation for the experimental observations.

A. Dynamic Stokes Shift in Binary Mixtures: Composition Dependence. *(i). Binary Mixtures of ([Bmim][PF₆] + Water).* Table 1 summarizes the predicted and measured values of the dynamic Stokes shift for ([Bmim][PF₆] + water) binary mixtures at four water mole fractions (x_w) along with that for dry [Bmim][PF₆]. Experimental densities[6] at various water concentrations shown in this table indicate decrease (small though) in solution density with successive addition of water. While the dielectric relaxation data for pure ionic liquids reported in ref 94 and for pure water in ref 118 have been used in the present work for calculations of dynamic Stokes shift, the values in parentheses have been obtained by using the dielectric relaxation data reported in ref 119. It is interesting to note that relatively smaller ε_0 value (∼12) for pure [Bmim][PF₆] reported in ref 119 significantly enhances the ion−dipole contribution to the total shift,[85,86] leading to an almost quantitative agreement between theory and experiments for the neat ionic liquid.[81] This, in fact, shows the sensitivity of the present calculation scheme to a small variation in the description of experimental dielectric relaxation data for the same liquid. However, the difference between the shift obtained for the neat ionic liquid and that in presence of water, $\Delta\Delta\nu_x^t = \Delta\nu_x^t(w=0) - \Delta\nu_x^t(w)$ (x being sd, si, or tot), remains approximately the same regardless of which dielectric relaxation data (from ref 94 or from ref 119) for [Bmim][PF₆] were used in the calculations. Interestingly, a comparison between the present calculations and experimental[33] shifts for aqueous binary mixtures of [Bmim][PF₆] reveals a close

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Table 2. Composition Dependence of the Predicted Dynamic Stokes Shift for C153 in ([Bmim] [BF$_4$] + Water) Binary Mixtures

mole fraction of water, x_w	density (g/cm^3)	$\Delta\nu_{sd}^t$ (cm^{-1})^a	$\Delta\nu_{si}^t$ (cm^{-1})^b	$\Delta\nu_{sp}^t$ (cm^{-1})^c	total $\Delta\nu_{tot}^t$ (cm^{-1})
0.0	1.182	695 (690)	1033 (1253)	0	1728 (1943)
0.1	1.179	671 (665)	970 (1177)	18	1659 (1860)
0.2	1.176	630 (625)	916 (1112)	26	1572 (1753)
0.3	1.172	583 (578)	849 (1030)	35	1467 (1643)
0.4	1.166	527 (520)	761 (924)	47	1335 (1491)
0.5	1.161	485 (480)	693 (843)	59	1237 (1382)
0.6	1.153	443 (440)	612 (745)	76	1131 (1261)
0.7	1.141	391 (381)	510 (622)	108	1009 (1111)
0.8	1.125	332 (328)	400 (488)	166	898 (982)
0.9	1.093	245 (240)	265 (335)	263	773 (838)

^{a} Solute—dipolar cation (dipole—dipole) interaction contribution. ^{b} Solute—ion (dipole—ion) interaction contribution. ^{c} Solute—water (dipole—dipole) interaction contribution.

agreement, suggesting that the interactions of the dipolar solute with the anions and dipolar cations govern the dynamic Stokes shift in this binary mixture at the water-deficient regime.

A closer inspection of Table 1 further reveals that the calculated total Stokes shift ($\Delta\nu_{tot}^t$) decreases with water concentration as both the solute—cation (diplole—dipole) and solute—ion (dipole—ion) interaction contributions decrease. The solute—water (dipole—dipole) interaction contribution to $\Delta\nu_{tot}^t$, on the other hand, increases with water concentration but remains very small ($\leq 2\%$) at this water-deficient regime. Note that, upon addition of ~ 0.22 mole fraction (1.8% w/w) of water in pure [Bmim][PF$_6$], the solute—cation dipolar interaction contribution, $\Delta\nu_{sd}^t$, decreases by ~ 250 cm^{-1} whereas the solute—ion (dipole—ion) contribution, $\Delta\nu_{si}^t$, registers a decrease[120] of approximately 100 cm^{-1}. The present calculations therefore suggest an overall decrease of ~ 350 cm^{-1} in total dynamic Stokes shift upon addition of ~ 0.22 mole fraction of water in dry [Bmim][PF$_6$]. This is somewhat different from what has been found in experiments[33] where the estimated experimental shift was found to be ~ 1500 cm^{-1} and showed no dependence on x_w. In addition, measurements described in ref 33 do not report the estimated true shift for dry [Bmim][PF$_6$], which prohibits further analyses. However, an experimental study by the same research group reported true dynamic Stokes shift of ~ 1400 and ~ 1600 cm^{-1} for C153 in dry [Hmim][PF$_6$][34] and [Emim][EtSO$_4$],[35] respectively. Interestingly, several other measurements[79,81,121] using C153 in ionic liquids containing imidazolium cations reported true estimated shift of ~ 2000 cm^{-1}. All these observations indicate that the true estimated shifts reported for C153 in ([Bmim][PF$_6$] + water) binary mixtures[33] might be $\sim 300-500$ cm^{-1} less than the expected "true" shift for this mixture. One of the most likely reasons could be imperfect drying of the ionic liquids, and the presence of additional moisture might have led to smaller shift due to reduced ion—solute interaction because of decreased ion density upon dilution. In fact, the present theory suggests that the calculated shift decreases with water concentration because of dilution effects. A more quantitative description of these dilution effects will be provided when the mixture composition dependence of dynamic Stokes shift in ([Bmim][BF$_4$] + water) binary mixtures are presented.

(ii). Binary Mixtures of ([Bmim][BF$_4$] + Water). Table 2 summarizes the calculated dynamic Stokes shift values for C153 in ([Bmim][BF$_4$] + water) binary mixtures at various mole fractions of water. As before, the values in parentheses have been calculated by using the dielectric relaxation data reported in ref 119 and the predicted shift for the neat [Bmim][BF$_4$] matches well with the experimental estimate (~ 1900 cm^{-1}).[79] Note here that higher solubility of water in [Bmim][BF$_4$] than in its hydrophobic counterpart [Bmim][PF$_6$] allows one to study the dynamic Stokes shift even in very dilute aqueous solution of [Bmim][BF$_4$]. Consequently, the present calculations have been extended from the neat ionic liquid to aqueous binary mixture with 0.9 mole fraction of water. Data in Table 2 indicate that except the water—solute dipolar interaction contribution ($\Delta\nu_{sp}^t$), other individual interaction contributions as well as the total calculated shift decrease upon increasing the water concentration in ([Bmim][BF$_4$] + water) binary mixture. The decrease in calculated total shift is quite large (~ 1100 cm^{-1}) for changing the water concentration from $x_w = 0$ to $x_w = 0.9$.

According to the present theory, such a substantial reduction in dynamic Stokes shift originates mainly from the following two sources. First, successive addition of water reduces the individual (anion and dipolar cation) as well as the total number densities in the mixture (see Figure S1, Supporting Information). This dilution significantly reduces the value at the collective ($k\sigma \rightarrow 0$) limit of the wavenumber-dependent solute—cation static orientational structural correlation function $[(|c_{sd}^{10}(k)|^2)^{1/2}]$. This is shown in the upper panel of Figure 1. The transverse component, $[|c_{sd}^{11}(k)|^2]^{1/2}$, on the other hand, increases with water concentration in binary mixture but the extent of increase is much smaller (lower panel, Figure 1) than the decrease in $[|c_{sd}^{10}(k)|^2]^{1/2}$. The cation—cation dipolar orientational static structural correlation function, $S_{solvent}^{lm}(k)$, also decreases with successive lowering of dipolar cation density (see Figure S2, Supporting Information). The decrease in dipolar cation density and the consequent reduction in solute—cation and cation—cation orientational static structural correlations are responsible for the lowering of the predicted value of solute—cation dipole—dipole contribution ($\Delta\nu_{sd}^t$) from 695 cm^{-1} at $x_w = 0$ to 245 cm^{-1} at $x_w = 0.9$ in ([Bmim][BF$_4$] + water) binary mixture. Second, the solute—ion dipole—ion interaction contribution, $\Delta\nu_{si}^t$, decreases by ~ 750 cm^{-1} for increasing x_w from 0 to 0.9 mainly because of the concomitant decrease in ion number densities. Note that the approximate expression used here to obtain the ion—dipole direct correlation function, $c_{s\alpha}10(k)$, does not depend on density. Moreover, the density-induced changes in the ion—ion static structural correlations, $S_{\alpha\beta}^{10}(k)$ (for both $\alpha = \beta$ and $\alpha \neq \beta$), are small (see Figure S3, Supporting Information). Therefore, the decrease in $\Delta\nu_{si}^t$ upon increasing x_w arises almost entirely from the presence of the density term as a multiplicative factor in eq 9. Note also that, at $x_w = 0.9$, the calculated value of the shift ($\Delta\nu_{sp}^t$) due to solute—water dipole—dipole interaction is only about 250 cm^{-1} which is much smaller than expected[123] for a dipolar solute like C153. This is because of using ~ 1.9 D as dipole moment for water[124] in the present calculations. However, the predicted shift becomes ~ 2000 cm^{-1} for a C153-like probe in pure water (C153 is sparingly soluble in pure water) if one uses ~ 2.5 D as water dipole moment.[125]

(iii). Binary Mixtures of ([Bmim][BF$_4$] + Acetonitrile). Next, we present the numerical results on composition-dependent dynamic Stokes shift for C153 in the ([Bmim][BF$_4$] + acetonitrile) binary mixture. This mixture is a relatively less

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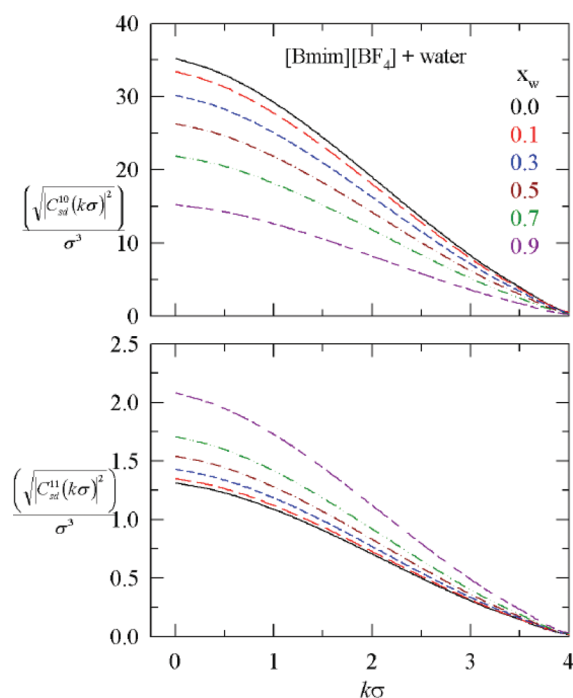
Figure 1. A plot of longitudinal (10) and transverse (11) components of the wavenumber-dependent dipolar solute–dipolar cation (dipole–dipole) static direct correlation function for aqueous mixtures of the ionic liquid $[Bmim][BF_4]$ at six different mole fractions (x_w) of water. The curves are color-coded and x_w increases from black to dark pink. The solute is C153 and the dipole moment of excited solute has been used in these calculations at $T = 298$ K.

complicated system than the corresponding aqueous mixture because of the nonassociative nature of acetonitrile. In addition, one expects a dominance of $\Delta \nu_{sp}^t$ contribution over the other two ($\Delta \nu_{sd}^t$ and $\Delta \nu_{si}^t$) at sufficiently higher concentration of acetonitrile. Since the dipole moment of acetonitrile is larger ($\sim$3.9 D)[126] than that of water, the present theory should predict larger Stokes shift values in acetonitrile than water. The calculated shift values at various mole fractions of acetonitrile (x_{AN}) are summarized in Table 3. Dielectric relaxation data necessary for the calculation of $\Delta \nu_{sp}^t$ were taken from the existing literature.[126,127] It is interesting to note here that even though the magnitudes of reduction in $\Delta \nu_{sd}^t$ and $\Delta \nu_{si}^t$ for increasing x_{AN} from zero to 0.9 in ($[Bmim][BF_4]$ + acetonitrile) binary mixture are comparable with those predicted for ($[Bmim][BF_4]$ + water) binary mixture, the decrease in total shift ($\Delta \nu_{tot}^t$) for ($[Bmim][BF_4]$ + acetonitrile) mixture is roughly one-third of that obtained for the corresponding aqueous mixture. This is because of relatively larger positive contribution of $\Delta \nu_{sp}^t$ to the total shift due to larger dipole moment of acetonitrile. In fact, $\Delta \nu_{sp}^t$ becomes larger than $\Delta \nu_{sd}^t + \Delta \nu_{si}^t$ at $x_{AN} = 0.8$ and a turnaround in composition dependence of $\Delta \nu_{tot}^t$ occurs at this acetonitrile concentration. This prediction should be tested against experiments. However, the predicted shifts at higher values of x_{AN} might be less accurate because the use of dipolar MSA for strongly polar solvents is known to produce partially incorrect solute–solvent and solvent–solvent static correlations.[104] The fact that the calculated shift for C153 in pure acetonitrile is $\sim$1500 cm^{-1}, a value $\sim$700 cm^{-1} less than what has been observed in experiments,[128] reflects this nonquantitativeness of a theory that uses static correlations as input from the MSA.

B. Composition-Dependent Stokes Shift Dynamics in (IL + Polar Solvent) Binary Mixtures.

In this subsection, theoretically predicted composition-dependent Stokes shift dynamics for C153 in three binary mixtures, ($[Bmim][PF_6]$ + water), ($[Bmim][BF_4]$ + water), and ($[Bmim][BF_4]$ + acetonitrile), will be presented. Since experimentally measured dynamics is incomplete for ($[Bmim][PF_6]$ + water) mixtures and no experimental data exist for the other two mixtures, a direct comparison of dynamics between the predicted dynamics and measurements could not be done. Therefore, experimental reexamination is necessary to test the validity of the predicted dynamics for these binary mixtures. Note our earlier works[85,86] have suggested a contribution of $\sim$10–15% to the total dynamics from the solute–ion (dipole–ion) interaction and the rest from the dipolar interaction between the solute and dipolar cations. In this work also the contribution from the solute–ion interaction (S_{si}) has been fixed to 10% and the effects of added dipolar solvent on solvation energy relaxation have been investigated via constructing the following normalized correlation function

$$S_{ss}(t) = 0.9[fS_{sd}(t) + (1-f)S_{sp}(t)] + 0.1S_{si}(t) \qquad (10)$$

where $S_{sd}(t)$, $S_{sp}(t)$, and $S_{si}(t)$ have been obtained by using eqs 4, 8, and 9, respectively. The relative contribution to the total dynamics arising from solute–cosolvent dipolar interaction can then be investigated by varying the value of f in eq 10. As usual, the average solvation time is obtained via time integration as follows: $\langle \tau_x \rangle = \int_0^\infty dt \, S_x(t)$, where x represents sd, sp, si, and ss. It is obvious then that the inclusion of a larger contribution from $S_{si}(t)$ will lead to larger value of $\langle \tau_{ss} \rangle$ as the decay of $S_{si}(t)$ is solely governed by the center-of-mass motion of the ions.

(i). Binary Mixtures of ($[Bmim][PF_6]$ + Water). Figure 2 displays the decay of the solvation response function, $S_{ss}(t)$, calculated at four different mole fractions of water (x_w) for a fixed value of $f = 0.9$. Composition-dependent viscosities for these mixtures are summarized in Table S4 in the Supporting Information. For comparison, the calculated decay for the neat IL is also shown in the same figure. As observed in experiments, the calculated decays are bimodal both for the neat IL[77] and its aqueous mixtures.[33] Addition of water accelerates the average decay rate over that in the neat IL, the enhancement factor between the neat IL and aqueous mixture at $x_w = 0.22$ ($\langle \tau_{ss} \rangle^{IL}/\langle \tau_{ss} \rangle^{mixture} \approx 2.2$) being roughly proportional to the change in medium viscosity[6] ($\eta^{IL}/\eta^{mixture} \approx 2.9$). The theory also predicts an insensitivity of the decay rate to x_w after the first addition of water in the neat IL for an initial period of $\sim$50 ps and then branches out, showing the effects of medium viscosity. This initial insensitivity to medium viscosity in the present theory stresses the importance of rapid angular readjustment of the dipolar particles present in the system which has been incorporated in the theory by using the experimental measured frequency-dependent dielectric function, $\varepsilon(z)$. Note that $\sim$50% of the decay is complete within this initial period, and experiments unable to capture this initial fast dynamics might lead to a different conclusion. In fact, existing measurements with limited time resolution ($\sim$85 ps)[33] report steady increase in decay rate upon addition of water in $[Bmim][PF_6]$. Interestingly, the measured average solvation time changes by a factor of $\sim$2.5 for changing x_w from $\sim$0.1 to $\sim$0.22; the calculated average times differ by a factor of $\sim$1.6 for the same variation of x_w. Since these experiments report a missing of $\sim$30–40% of the initial fast dynamics which tallies well with the prediction of half of the dynamics being complete in the first 50 ps,

Table 3. Composition Dependence of Predicted Dynamic Stokes Shift for C153 in ([Bmim][BF$_4$] + Acetonitrile) Binary Mixtures

mole fraction of acetonitrile, x_{AN}	density (g/cm^3)	$\Delta\nu^t_{sd}$ (cm^{-1})^a	$\Delta\nu^t_{si}$ (cm^{-1})^b	$\Delta\nu^t_{sp}$ (cm^{-1})^c	total $\Delta\nu^t_{tot}$ (cm^{-1})
0.0	1.182	695 (690)	1033 (1253)	0	1728 (1943)
0.1	1.160	641 (632)	972 (1180)	41	1654 (1853)
0.2	1.117	595 (592)	908 (1102)	75	1578 (1769)
0.3	1.075	537 (532)	840 (1020)	123	1500 (1675)
0.4	1.032	475 (470)	768 (933)	187	1430 (1590)
0.5	0.990	409 (401)	689 (838)	273	1371 (1512)
0.6	0.947	337 (332)	604 (735)	384	1325 (1451)
0.7	0.905	260 (254)	508 (619)	529	1297 (1402)
0.8	0.862	179 (176)	396 (484)	725	1300 (1385)
0.9	0.820	95 (90)	258 (315)	1011	1364 (1416)

^{a} Solute−dipolar cation (dipole−dipole) interaction contribution. ^{b} Solute−ion (dipole−ion) interaction contribution. ^{c} Solute−water (dipole−dipole) interaction contribution.

Table 4. Comparison between the Calculated and Experimental Solvation Response Function for C153 in Aqueous Mixture of [Bmim][PF$_6$] at $x_w = 0.1$

$S_x(t)$	f	a_1	τ_1 (ps)	α	a_2	τ_2 (ps)	β	$\langle\tau_x\rangle$ (ps)
$S_{si}(t)$		0.11	123	1	0.89	2500	1	2240
$S_{sd}(t)$		0.29	0.32	1	0.71	294	0.38	610
$S_{sp}(t)$		0.58	0.005	1	0.42	0.53	1	0.23
$S_{ss}(t)^a$	0.0	0.90	0.16	1	0.10	1972	1	194
	0.1	0.85	0.10	0.40	0.15	1667	0.67	290
	0.2	0.79	0.11	0.42	0.21	1190	0.53	354
	0.3	0.73	0.12	0.43	0.27	897	0.47	405
	0.4	0.66	0.13	0.45	0.34	720	0.44	462
	0.5	0.60	0.15	0.48	0.40	611	0.43	496
	0.6	0.49	0.20	1	0.51	427	0.35	621
	0.7	0.44	0.22	1	0.56	423	0.37	630
	0.8	0.38	0.24	1	0.62	417	0.38	680
	0.9	0.33	0.28	1	0.67	410	0.39	701
	1.0	0.27	0.31	1	0.73	404	0.40	733
expt^b		0.85	648	1	0.15	11010	1	2200

$^a =0.90[fS_{sd}(t) + (1 − f)S_{sp}(t)] + 0.10S_{si}(t)$. ^{b} From ref 33.

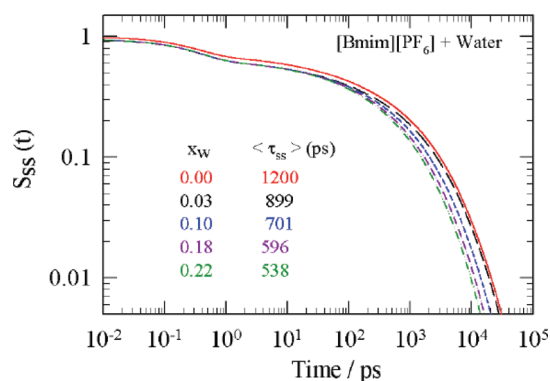**Figure 2.** Decay of the constructed solvation response function, $S_{ss}(t)$, as a function of time (log−log scale) for the laser-excited solute, C153, in binary mixtures of ([Bmim][PF$_6$] + water) at five different values of x_w at 298 K. The curves are color-coded where x_w increases from red to dark green. Note x_w values along with the corresponding average solvation times are also quoted explicitly (color-coded). Dielectric relaxation data required for the calculations have been taken from ref 94 (IL) and ref 118 (water). The dipole moment of the cation used is 4.4 D (ref 85), and radii of the cation and anion are 3.39 and 2.72 Å, respectively. The dipole moment of water used is 1.85 D and radius 1.425 Å (ref 126). The radius of C153 used is 3.9 Å (ref 128). Solution viscosity values used are those reported in ref 6.

it is likely that the experimentally observed more pronounced dependence on x_w is a reflection of incomplete detection rather than the actual composition dependence of Stokes shift dynamics in these aqueous binary mixtures.

The difference between theory and experiments becomes more prominent when one compares the amplitudes (a_i) and time constants (τ_i). Table 4 summarizes the amplitudes and time constants obtained for ([Bmim][PF$_6$] + water) binary mixture at $x_w = 0.10$ from fitting the calculated decays to the following general form: $S_{fit}(t) = a_1 \exp[−(t/\tau_1)^\alpha] + a_2 \exp[−(t/\tau_2)^\beta]$ with α and β as stretching exponents. Similar fit parameters for other values of x_w are provided in the Supporting Information (Tables S5−S7). Since the Stokes shift dynamics in water is much faster than in neat [Bmim][PF$_6$], progressive inclusion of

more contribution from the solute−cation (dipole−dipole) interaction via the factor f renders the dynamics successively slower. Note in Table 4 that the time constants associated with the measured[33] biexponential solvation response function are much larger than those obtained in the calculations at any contribution (f) of $S_{sd}(t)$. Even the predicted decay of $S_{si}(t)$, the slowest and the only biexponential among all of the components, does not produce a time constant in the range of ∼12 ns. In fact, the fastest time constant (τ_1) obtained in experiments at this x_w is much closer to the slowest (τ_2) of the calculated ones. In addition, the calculated decays of $S_{ss}(t)$ at all nonzero values of f are bimodal with a stretched exponential (for $0.1 \leq f \leq 0.5$ with $0.4 \leq \alpha \leq 0.5$) or exponential (for $f \geq 0.6$) fast component, followed by a stretched-exponential slow component with β ranging between 0.66 and 0.37. Attempt to simple exponential fit to the calculated fast component for f ranging between 0.1 and 0.5 at all water mole fractions studied here has led to inaccurate description of the relevant decays. Interestingly, average solvation time measured[33] at $x_w = 0.1$ is ∼3 ns which is approximately three times larger than even the value for neat [Bmim][PF$_6$] measured in experiments with a more sophisticated technique and/or better time resolution.[77,81] A further comparison among the data for the neat IL reported by these authors[129] and other researchers[36,130,131] strongly suggests that the measured[33] average solvation times for ([Bmim][PF$_6$] + water) binary mixtures have been uniformly overestimated by a factor of ∼3 over the "true" values. This has led us to believe that the "true" average solvation time at $x_w = 0.1$ should be less than a nanosecond. The present theory predicts such a value at $x_w = 0.1$ with $f = 0.9$ which incorporates ∼10% contribution each to the total dynamics from the water−solute (dipole−dipole) and solute−ion (dipole−ion) interactions.

The origin of the increase in average rate of solvation with water mole fraction in ([Bmim][PF$_6$] + water) binary mixtures is further explored in Figure 3 where the decays of the solute−cation dipole−dipole interaction (S_{sd}) and solute−ion dipole−ion interaction (S_{si}) components are shown as a function of time. Note the effects of medium viscosity on both S_{sd} and S_{si}
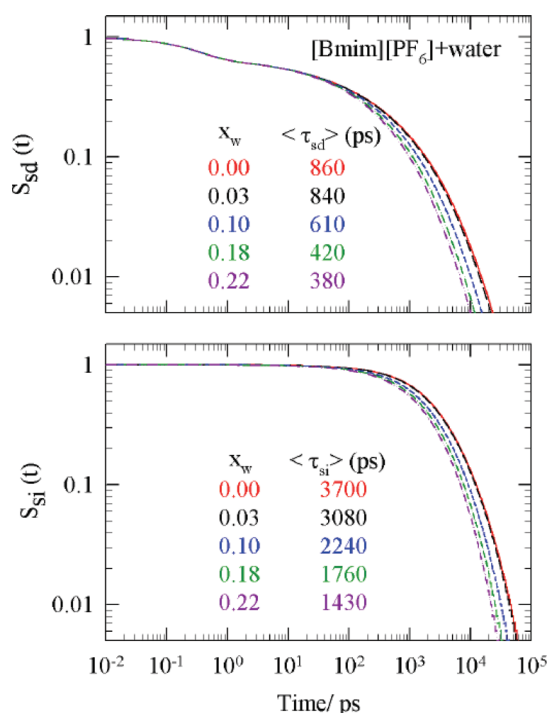
Figure 3. Decay of the calculated individual response functions at five different compositions for the binary mixture of ($[Bmim][PF_6]$ + water) at 298 K. While the upper panel shows the time-dependent decay (log−log scale) of the normalized solvation energy due to solute−cation dipole−dipole interaction, the lower panel presents that due to solute−ion dipole−ion interaction. The solute used is C153. The curves are color-coded, and both x_w values and corresponding average solvation times are clearly mentioned in these panels. Note: x_w increases from red to dark pink.

Figure 4. Composition dependence of the constructed solvation response function for C153 in binary mixtures of ($[Bmim][BF_4]$ + water) at 298 K. Time-dependent decays at five different water mole fractions (x_w) are shown using a color code where x_w increases from red to dark green. Numerical values for the x_w considered and the corresponding average solvation times are also shown. The cation and anion radii used are (in Å) 3.39 and 2.29, respectively, and the cation dipole moment 3.7 D (ref 85). Dielectric relaxation data required for the calculations have been taken from ref 94 (IL). Solution viscosity values used are taken from ref 6.

have been incorporated via the translational kernel ($\Gamma_T(k,z)$, see eq A2) only. As expected,[89] larger translational diffusion coefficient at higher water concentration (that is, lower viscosity[6]) facilitates the decay of $S_{sd}(t)$ at longer times, and the decay of $S_{si}(t)$ becomes faster uniformly over the entire time range. Consequently, the ratio between the average solvation times at $x_w = 0$ and 0.22 calculated from the decay of $S_{si}(t)$ is somewhat closer ($\langle\tau_{si}(x_w=0)\rangle/\langle\tau_{si}(x_w=0.22)\rangle \approx 2.6$) to the corresponding viscosity ratio ($\langle\eta(x_w=0)\rangle/\langle\eta(x_w=0.22)\rangle \approx 2.9$) than that ($\approx2.3$) for the average times obtained from $S_{sd}(t)$. The effects of change in solution viscosity are more pronounced for $S_{si}(t)$ because the relevant relaxation occurs only via the translational diffusion of the ionic particles.

(ii). Binary Mixtures of ($[Bmim][BF_4]$ + Water). Calculated decays of the solvation response function ($S_{ss}(t)$) for C153 in aqueous solution of $[Bmim][BF_4]$ for five different water mole fractions (x_w) are presented in Figure 4. Note that, for $x_w \neq 0$, calculations have been performed with $f = 0.9$. Dielectric relaxation data used in these calculations are those reported in ref 94. As observed for ($[Bmim][PF_6]$ + water) binary mixtures, here too the decay becomes increasingly faster upon successive addition of water in $[Bmim][BF_4]$. The fit parameters for the calculated decays at various values of x_w are summarized in Table S8 (Supporting Information). Following the trend of mixture composition-dependent viscosity presented in Table S4 (Supporting Information), all measures of the average solvation time ($\langle\tau_{si}\rangle$, $\langle\tau_{sd}\rangle$, and $\langle\tau_{ss}\rangle$) show a decrease upon increasing

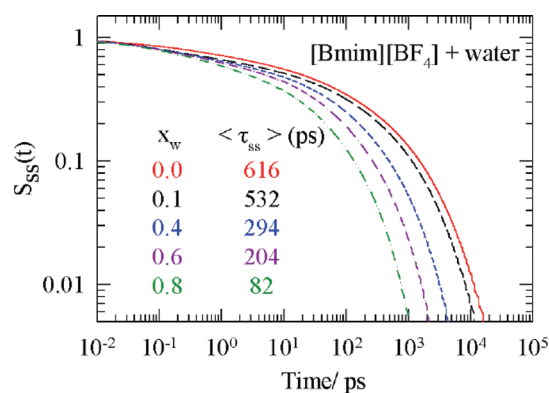x_w in the mixture. Data in this table (Table S8) reveal that $\langle\tau_{ss}(x_w=0)\rangle/\langle\tau_{ss}(x_w=0.8)\rangle$ is much smaller (≈7.8) than the corresponding viscosity ratio, $\langle\eta(x_w=0)\rangle/\langle\eta(x_w=0.8)\rangle \approx 20$). Such a relatively weaker viscosity dependence originates in the calculations from the weaker coupling of the $S_{sd}(t)$ to medium viscosity which produces $\langle\tau_{sd}(x_w=0)\rangle/\langle\tau_{sd}(x_w=0.8)\rangle \approx 6.3$. This is approximately three times smaller than the corresponding viscosity ratio. The coupling for $S_{si}(t)$ is stronger, producing $\langle\tau_{si}(x_w=0)\rangle/\langle\tau_{si}(x_w = 0.8)\rangle \approx 12.4$. The fact that $\langle\tau_{ss}(x_w=0)\rangle/\langle\tau_{ss}(x_w=0.8)\rangle$ is closer to $\langle\tau_{sd}(x_w=0)\rangle/\langle\tau_{sd}(x_w=0.8)\rangle$ than to $\langle\tau_{si}(x_w=0)\rangle/\langle\tau_{si}(x_w=0.8)\rangle$ indicates dominance of the solute−cation dipole−dipole interaction contribution in the solvation energy relaxation of a laser-excited polar dye in these binary mixtures. Experimental studies with ($[Bmim][BF_4]$ + water) binary mixtures should be carried out to test whether such a decoupling between average solvation time and viscosity exists for this mixture.

(iii). Binary Mixtures of ($[Bmim][BF_4]$ + Acetonitrile). Calculated decays of $S_{ss}(t)$ for C153 in a binary mixture of ($[Bmim][BF_4]$ + acetonitrile) for five different acetonitrile mole fractions (x_{AN}) are shown in Figure 5. As before, calculations have been performed with $f = 0.9$ for mixtures at $x_{an} \neq 0$. Decays shown in this figure are clearly bimodal and indicate progressive enhancement of average solvation rate upon successive addition of acetonitrile in this ionic liquid. Time constants and amplitudes obtained from the fit of these decays and a few others are provided in Table S9 (Supporting Information). As these data indicate, average solvation times obtained from the individual (S_{sd} and S_{si}) and the constructed (S_{ss}) decays decrease steadily upon successive addition of acetonitrile in $[Bmim][BF_4]$. In fact, $\langle\tau_{ss}\rangle$ decreases so much upon addition of water or acetonitrile in $[Bmim][BF_4]$ that it becomes comparable to the measured average solvation times in 1-butanol or 1-pentanol[128] at 0.8 mole fraction of added dipolar solvent. As seen in the ($[Bmim][BF_4]$ + water) binary mixture, the ratio of average solvation times at the lowest and highest acetonitrile concentrations, $\langle\tau_{ss}(x_{an}=0)\rangle/\langle\tau_{ss}(x_{an}=0.8)\rangle$, is approximately 10 and much smaller than the

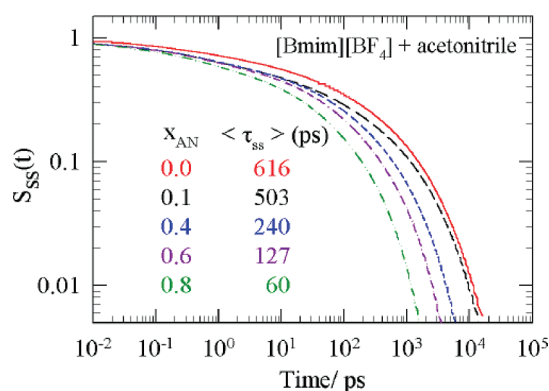**Figure 5.** Acetonitrile mole fraction (x_{AN}) dependence of the constructed solvation response function, $S_{ss}(t)$, for binary mixtures of ($[Bmim][BF_4]$ + acetonitrile) at 298 K. As before, curves are color-coded where (x_{AN}) increases from red to dark green. Average solvation times calculated at these acetonitrile mole fractions are also mentioned (color coded). Dielectric relaxation data for acetonitrile used in the calculations are those from refs 126 and 127. Radius of acetonitrile used is 2.24 Å (ref 88).

corresponding viscosity ratio, $\langle \eta_{ss}(x_{an}=0)\rangle/\langle \eta(x_{an}=0.8)\rangle \approx 31$. Interestingly, $\langle \tau_{sd}(x_{an}=0)\rangle/\langle \tau_{sd}(x_{sd}=0.8)\rangle \approx 7.6$ and $\langle \tau_{si}(x_{an}=0)\rangle/\langle \tau_{si}(x_{an}=0.8)\rangle \approx 11$, which again suggests substantial decoupling of the average solvation rate from medium viscosity and a minor role for the structural relaxation via ion translation.

IV. DISCUSSION

The theory developed here is a generalized semimolecular theory for studying Stokes shift dynamics in binary mixtures of ionic liquid with a conventional polar solvent. This theory can also be suitably extended to investigate the fluorescence dynamics in binary mixture of ionic liquids, provided suitable dielectric relaxation data are available. It is to be mentioned that the present treatment incorporates neither the effects of medium heterogeneity nor the shape of the ions while calculating the static correlations. Moreover, a linearized statistical mechanical prescription, such as the MSA, has been used to calculate the spatial correlations between solute−ion, ion−ion, and solvent−solvent particles. These approximations definitely make the theory a less quantitative one because the real mixture is composed of neither spherical particles (ions or solvent molecules) nor completely free of heterogeneity.[131−137] However, this becomes a minor issue as the measured polar solvation response in these systems via fluorescence Stokes shift experiments is primarily a collective response where details of the spatial arrangement assume secondary importance. A more important issue is, however, the systematic incorporation in the theory of the nonideal composition dependence observed in experiments[20−22] with several (ionic liquid + polar solvent) binary mixtures. Unfortunately, the nonideality in spatial correlations (that is, solution structure) cannot be incorporated in the theory described here in its present form.

One can, however, partially account for the solution nonideality via using the experimental dielectric relaxation data of the binary mixture, assuming the mixture an effective dipolar medium where the solution ε_0 determines the dipole moment of the "fictitious" effective dipolar species.[84] The ions are then assumed to be dispersed in effective dipolar medium. Dynamic Stokes shift in such an effective medium can then be described
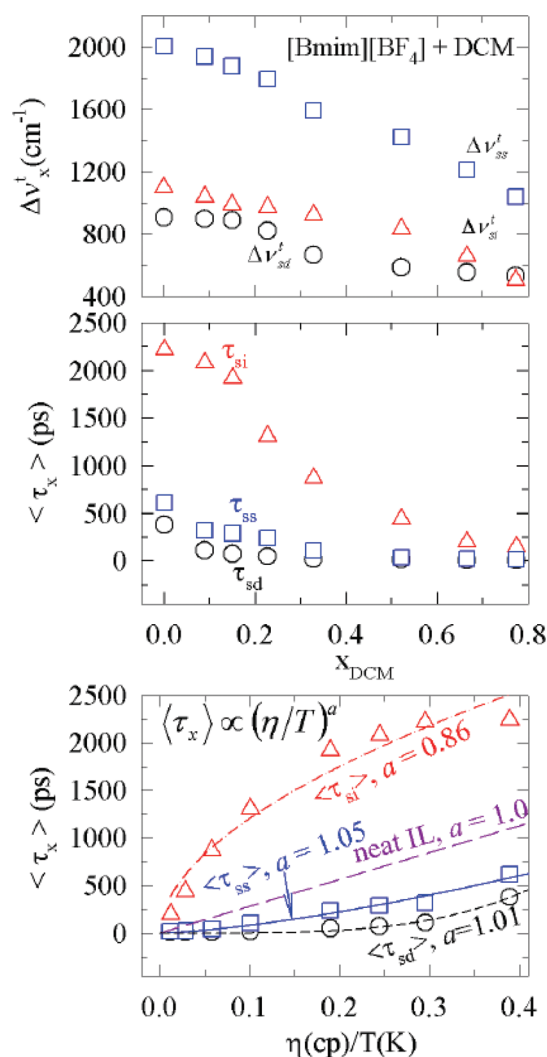

Figure 6. Composition dependence of dynamic Stokes shift and average solvation times, and solution viscosity dependence of average solvation times, in a binary mixture of ($[Bmim][BF_4]$ + dichloromethane) at 298 K. The calculated values are shown either as a function of dichloromethane mole fraction (x_{DCM}) or temperature-reduced solution viscosity (η/T). The solute is C153. As discussed in the text, calculations have been performed assuming the binary mixture as an effective dipolar medium where the required dielectric relaxation data were supplied by ref 91. Mixture composition dependent viscosity values are taken from ref 6. The radius of a DCM molecule is 2.35 Å (ref 140). Squares, circles, and triangles in all these panels denote calculated results for total shift, dipole−dipole, and dipole−ion interaction contributions. The lines going through the symbols in the bottom panel represent fits to a general form, $\langle \tau_x \rangle = B(\eta/T)^a$. The values for a are already indicated. B values for $\langle \tau_{si}\rangle$, $\langle \tau_{sd}\rangle$, and $\langle \tau_{ss}\rangle$ are (in proper units) 4168, 13 838, and 2256, respectively. The dark pink broken line ($B = 3559$) denotes the fit through the experimentally measured average solvation times (data not shown to avoid clutter) for a number of neat ILs at various temperatures reported in ref 139.

as composed of contributions from dipolar solute−dipolar medium(effective) interaction and dipolar solute−ion (dipole−ion) interaction. Subsequently, one calculates Stokes shift and dynamics as before by using eqs 4 and 9. Accordingly, the dynamic Stokes shift may be expressed as $\Delta\nu^t_{tot,eff} = \Delta\nu^t_{sd,eff} + \Delta\nu^t_{si,eff}$, and the dynamics as $S_{ss,eff}(t) = 0.9S_{sd,eff}(t) + 0.1S_{si}(t)$.

We have already carried out such calculations for binary mixtures of $[Bmim][BF_4]$ and dichloromethane (DCM) for which composition-dependent dielectric relaxation data measured over a broad frequency range[91] are available. Mixture composition-dependent effective dipole moment is obtained from solution ε_0 by using Cavell's equation.[91,138] The calculated dynamic Stokes shifts and average solvation times are shown as a function of DCM mole fraction (x_{DCM}) in the first two panels of Figure 6. The bottom panel shows the solution viscosity dependence of calculated average solvation times for ($[Bmim][BF_4]$ + DCM) binary mixtures where the same (viscosity dependence) for experimentally measured solvation times in several pure ionic liquids at different temperatures are also presented. The results are shown for DCM mole fraction up to 0.8 in order to avoid inaccuracy in the calculations due to the presence of complex ionic species in the real mixtures at further higher dilutions of the ionic liquid.[91] Interestingly, the calculated total shift decreases almost *linearly* with increasing x_{DCM} and does not reflect the nonlinear composition dependence observed in experiments for ε_0 (Figure S10, Supporting Information). The individual (dipole—dipole and dipole—ion) interaction contributions, also decreasing with increasing x_{DCM}, exhibit a slight nonideality with opposite trends which cancel each other to produce a linear dependence of the total shift on mixture composition. The dipole—dipole interaction contribution, $\Delta\nu_{sd}^t$, decreases because of reduction in both the effective dipole moment (4.49 D at $x_{DCM} = 0$ to 2.7 D at $x_{DCM} \approx 0.8$) and the dipole density. Note here that the dipole—ion contribution to the shift, $\Delta\nu_{si}^t$, decreases with decreasing static dielectric constant even though it was argued earlier[85] that $\Delta\nu_{si}^t$ should increase in such a scenario. The steady decrease in ion density upon successive addition of DCM in the mixture which is shown in the second panel of Figure S10 is responsible for the decrease of $\Delta\nu_{si}^t$ with DCM mole fraction. The calculated average solvation times also show a weak nonideal mixture composition dependence because of the weak to moderate nonlinear composition dependence of the dielectric relaxation times and solution viscosity (see, respectively, the third and the fourth panels, Figure S10). The lower panel of Figure 6 suggests that the composition-dependent $\langle\tau_{ss}\rangle$ exhibits a power-law dependence on solution viscosity ($\langle\tau_{ss}\rangle \propto (\eta/T)^a$) with $a = 1.05$. Note that this value of power (a) indicates validity of hydrodynamic description ($a = 1$) of motions for solvating particles and resembles the results for neat ionic liquids ($a = 1$).[139] The individual average solvation times ($\langle\tau_{sd,eff}\rangle$ and $\langle\tau_{si}\rangle$), however, show nonlinear composition dependence but with opposite trends. A relatively smaller weight of $\langle\tau_{si}\rangle$ in $\langle\tau_{ss}\rangle$ and subsequent mutual cancellation of composition dependence trends produces the linear dependence on solution viscosity for $\langle\tau_{ss}\rangle$. This prediction should be reexamined in experiments.

■ APPENDIX A: CALCULATION DETAILS OF THE GENERALIZED RATE, $\Sigma_{LM}(K,Z)$

The (l,m)th component of the generalized rate of orientational solvent polarization density relaxation has been shown to be given by[88,106—109]

$$\Sigma_{lm}(k,z) = \frac{k_B T k^2 f_{llm}(k)}{M\sigma^2[z + \Gamma_T(k,z)]} + \frac{k_B T l(l+1) f_{llm}(k)}{I[z + \Gamma_R(k,z)]} \quad \text{(A1)}$$

where σ, M, and I denote, respectively, the diameter, mass, and average moment of inertia of the solvent molecule. $\Gamma_T(k,z)$ and

$\Gamma_R(k,z)$ are respectively the wavenumber- and frequency-dependent translational and rotational dissipative kernels.

The translational dissipative kernel, $\Gamma_T(k,z)$, is related to the isotropic liquid dynamic structure factor, $S(k,z)$.[88] If one considers only the diffusive dynamics for the relaxation of the isotropic dynamic structure factor, then in time plane one can write $S(k,t) = S(k) \exp[-D_T k^2 t/S(k)]$ which leads to the following relation for $\Gamma_T(k,z)$:

$$\frac{k_B T}{M\sigma^2[z + \Gamma_T(k,z)]} = \frac{D_T}{\sigma^2} \quad \text{(A2)}$$

The translational diffusion coefficient, D_T ($=2k_B T/C\eta\sigma$) can be obtained from hydrodynamics by using effective diameter of a given ionic liquid molecule and experimentally measured medium viscosity (η). The calculation of the rotational kernel ($\Gamma_R(k,z)$), on the other hand, is somewhat involved and has already been discussed in detail in many of our earlier works.[84—88,106—109] In short, $\Gamma_R(k,z)$ was first approximated by its long-wavelength limit ($\Gamma_R(k,z) \approx \Gamma_R(k=0,z)$) and then connected to the experimentally measured frequency-dependent dielectric function $\varepsilon(z)$ as follows

$$\frac{2k_B T}{I[z + \Gamma_R(k,z)]} = \frac{z\varepsilon_0[\varepsilon(z) - \varepsilon_\infty]}{f_{110}(k = 0)\varepsilon_\infty[\varepsilon_0 - \varepsilon(z)]} \quad \text{(A3)}$$

where ε_∞ is the optical frequency dielectric constant of the pure medium. Since eq 2 expresses the total solvation energy as a sum total of contributions from pure components, $\varepsilon(z)$ used in the calculations are those measured for pure systems. Subsequently, we have calculated $\Sigma_{11}(k,z)$ by multiplying eq A3 with $f_{111}(k)$.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Derivation of the total fluctuating solvation energy for a mobile dipolar solute in a binary mixture of (ionic liquid + polar solvent); figures showing composition-dependent densities, dipole—dipole and ion—ion static structural correlations; tables summarizing composition-dependent viscosity coefficients; parameters from fit to solvation response functions for (IL + polar solvent) binary mixtures; and figures showing composition dependence of experimental dielectric relaxation parameters, viscosity coefficients, and densities for ($[Bmim][BF_4]$ + dichloromethane) binary mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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