How Does Water Affect the Dynamics of the Room-Temperature Ionic Liquid 1-Hexyl-3-methylimidazolium Hexafluorophosphate and the Fluorescence Spectroscopy of Coumarin-153 When Dissolved in It?

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Molecular dynamics simulations of mixtures of 1-hexyl-3-methylimidazolium hexafluorophosphate ($[HMIM^+][PF_6^-]$) and water have been performed in order to investigate how small amounts of water affect the translational and rotational dynamics of this ionic liquid (IL). We find that water is closely associated with the anions and that its presence enhances both the translational and rotational dynamics of the IL. In agreement with experiments, we find that the fluorescence spectra of Coumarin-153 is red-shifted because of the presence of water. Small amounts of water enhance the speed of relaxation of the solvent surrounding the solute probe after photoexcitation, but only at a "local environment" level. Interconversion between environments still occurs on a long time scale compared with the fluorescence lifetime of the probe. Excitation wavelength-dependent emission is observed both in the neat IL and in the IL+water mixture.

1. Introduction

Room-temperature ionic liquids (RTILs) are gaining considerable attention[1-7] because of various properties that put them in a category of their own as solvents suitable for organic reactions. One of the features of some of these systems that has almost gone unexploited is their slow heterogeneous dynamics[6-8] on a time scale compatible with photochemical reactivity. This heterogeneous dynamics can be manipulated to modify the outcome of chemical reactions and other photochemical processes. Recent experiments[9] show that the rate of processes such as photoisomerizations and intramolecular charge-transfer reactions can be adjusted by appropriately photoselecting subensembles of probe molecules within the liquid. Since the outcome of many of these processes is kinetically controlled, selecting the region in the absorption spectrum being photoexcited can lead to significantly different reaction product yields. This photoselection process is, in principle, possible in any solvent, but is not effective if the kinetics or dynamics of the solvent surrounding the excited-state probe is fast compared to the chemical or photochemical process in question. Many experiments[6,10-34] have recently been performed in order to understand the underlying dynamics of these systems. In particular, Samanta and co-workers[6,13,15] have carried out pioneering work studying the fluorescence behavior of dipolar solutes in various RTILs. In these studies it was found that, under certain circumstances, the fluorescence response of certain probes can be dependent on the excitation wavelength, a phenomenon known as the red-edge effect (REE). This break down of Kasha's rule occurs when the experiment is able to photoexcite subensembles of absorbing probes at different wavelengths, and the surrounding solvent response is slow on a time scale compatible with the lifetime of the probe. In many circumstances, this phenomenon is strongly coupled to the viscosity of the solvent.[35] Time-resolved fluorescence experiments measuring dynamic Stokes shifts[14,17,19-23,25-30,36] have

shown that relaxation after initial photoexcitation displays a very fast (picosecond or sub-picosecond) component followed by slow decay, which is sometimes fitted to multiple exponentials or stretched exponentials. Several other experiments have also shed light on the nature of the dynamical behavior of these systems by characterizing their viscosity,[37-42] dielectric relaxation,[32,33,43] and optical Kerr response.[34,44-47]

Computer simulations and theory have been powerful tools that have, in many ways, helped guide the understanding that the community has on the dynamical behavior of these liquids.[7,8,48-65] Our group has recently carried out a series of computational and theoretical studies that explain many of the features of the steady-state and time-resolved fluorescence behavior[7,8,49] of probe molecules dissolved in these systems, as well as their viscosity.[48]

An important concern when working with ILs is the effect of water contamination on their dynamics and thermodynamics. We are particularly interested in the effect that water has on spectroscopy. Experimental[28,31,66-73] and computational[53,58,65,71,74] studies have been carried out to shed light on different energetic and thermodynamic properties of mixed solvents including ILs. The addition of small amounts of water alters densities, viscosities, as well as the fluorescence spectroscopy of molecules dissolved in these liquids. The presence of water in RTILs decreases their viscosity and results in faster solvent dynamics.[68] Several infrared studies[69-72] and simulations[53,65,74] have shown that anions are mainly responsible for the interaction between ILs and water.

In this paper, we investigate the effect that water has on the dynamical behavior of 1-hexyl-3-methylimidazolium hexafluorophosphate ($[HMIM^+][PF_6^-]$) by analyzing the steady-state spectrum and dynamical Stokes shift of Coumarin-153 dissolved in this system. We also analyze rotational and translational correlation functions of the solvent in the presence and absence of water. Our simulations are motivated by the interesting studies recently carried out by Sarkar and co-workers.[66] The choice of IL and water concentration is based on their studies, so that

Effect of Water on [HMIM$^+$][PF$_6^-$] and Coumarin-153

J. Phys. Chem. B, Vol. 112, No. 6, 2008 **1771**
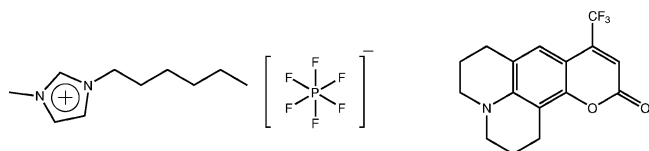
Figure 1. Cation: [HMIM+]; anion: [PF$_6^-$]; fluorescent probe: Coumarin-153.

our computational results can be closely compared to their experiments. A sketch of the IL and probe involved is depicted in Figure 1.

2. Methods

We performed molecular dynamics (MD) simulations for the system [HMIM$^+$][PF$_6^-$]. Simulations were carried out using the software GROMACS.[75,76] Potential energy parameters are those previously used in our group.[50,52] All systems were initially equilibrated using the same protocol as in our previous work.[8] In order to make sure the systems were in equilibrium, a scheme of lowering and raising the total charge of the ions was used, followed by runs at high temperature in which the temperature was slowly decreased to match experimental conditions. These runs were carried out in the NPT ensemble using the Berendsen algorithm (see GROMACS manual and citations therein). Once the systems were finally equilibrated at 300 K, production runs were carried out in the NVE ensemble with a box size of 5 nm. Cutoffs for Lennard-Jones and Coulombic interactions were set at 1.5 nm. In order to deal with long-range electrostatic interactions, the PME algorithm was used. We used the "Leapfrog" integration algorithm implemented in GROMACS. To compute the absorption and emission spectra of Coumarin-153 in neat IL and IL+water, we used an ensemble of 13 MD trajectories. Each of these trajectories consisted of a Coumarin-153 molecule and 303 pairs of [HMIM$^+$][PF$_6^-$] solvent ions. Simulations involving water have 62 extra simple point charge (SPC)[77] water molecules added to the original system. This corresponds to a concentration of 0.17 mole fraction of water.

The ground-state charges of Coumarin-153 were obtained from an ab initio ESP-fit at the Hartree Fock (HF)/6-31G* theory level using the Gaussian program.[78] The excited-state charges were estimated by computing the ground (S_0) and first singlet excited state (S_1) charge difference using the ZINDO (Zerner's intermediate neglect of differential overlap) Hamiltonian with configuration interaction.[79] These calculations were performed with the software HyperChem 7.[80] The charges in the excited-state used for our MD calculations were obtained by adding the charge difference obtained from the ZINDO calculation to the ground-state charges obtained by the HF method. The calculated ground- and excited-state dipole moments were 7.2 and 18.2 D, respectively. This methodology has already been successfully applied in the past by Maroncelli and co-workers to study the ground- and excited-state dynamics of betaine-30 and also Coumarin-153.[81,82] More calculations on the same molecule can be found in the literature.[82−88] The stretching, bending, and torsional parameters for Coumarin-153 were taken to be the same in the ground and excited electronic states. This is a reasonable approximation, given that coumarin is a fairly rigid planar molecule. These parameters were adopted from the OPLSAA force field.[89] A detailed description of the methodology we have developed in order to compute the absorption wavelength-dependent spectra of probe molecules in ILs can be found in previous publications.[8,49] Equations 1−5 are used in order to compute the time-dependent and time-independent spectra from an ensemble of trajectories in which

Coumarin-153 is initially equilibrated in its ground electronic state and then photoexcited into its first singlet excited electronic state.

$$I_{ab}(\Delta E_{ex}) = \sum_l I_{ab}^l(\Delta E_{ex}) \tag{1}$$

$$I_{em}^l(\Delta E_{em}) = \int_0^\infty \delta(\Delta E(t) - \Delta E_{em}) \times e^{-(t/\tau_f)}dt \tag{2}$$

$$I_{em}^l(\Delta E_{em},t) = \int_{t-\Delta t}^{t+\Delta t} \delta(\Delta E(\tau) - \Delta E_{em}) \times e^{-\tau/\tau_f}d\tau \tag{3}$$

$$I_{em}(\Delta E_{ex},\Delta E_{em}) = \sum_l I_{em}^l(\Delta E_{em})I_{ab}^l(\Delta E_{ex}) \tag{4}$$

$$I_{em}(\Delta E_{ex},\Delta E_{em},t) = \sum_l I_{em}^l(\Delta E_{em},t)I_{ab}^l(\Delta E_{ex}) \tag{5}$$

Here $I_{ab}^l(\Delta E_{ex})$ is the probability distribution of absorption energy gaps ΔE_{ex} in trajectory l. $I_{ab}(\Delta E_{ex})$ denotes the total probability distribution at vertical transition excitation energy ΔE_{ex} computed as a sum over all trajectories. $I_{em}^l(\Delta E_{em})$ is the corresponding steady-state probability distribution of emission energy gaps ΔE_{em} weighted by an exponential decay corresponding to the lifetime (τ_f) of the probe (assumed to be 4.85 ns in neat [HMIM$^+$][PF$_6^-$] and 4.11 ns in the water mixtures[66,90]) for trajectory l. $I_{em}^l(\Delta E_{em},t)$ is the time-dependent intensity of emission computed from trajectory l after initial photoexcitation. $I_{em}(\Delta E_{ex},\Delta E_{em})$ denotes the intensity or joint probability distribution of emission energy ΔE_{em} when the excitation energy is ΔE_{ex}. Correspondingly, $I_{em}(\Delta E_{ex},\Delta E_{em},t)$ stands for the time-dependent emission spectrum. It should be noted here that these are purely classical simulations.

In our simulations, the gap between ground and excited states is the sum of two contributions $\Delta E(g)$ and ΔE_{sol}. The component $\Delta E(g)$ is the gas-phase excitation energy, which is independent of the solvent. The value that we use for $\Delta E(g)$, 356 nm, was obtained from our ZINDO calculations. The reported experimental value is 368 nm.[91] In our simulations, $\Delta E(g)$ is simply taken as a constant that shifts the overall position of the spectra but is totally independent of the dynamics in solution. ΔE_{sol} is obtained from the difference in interaction energies between the solvent with the ground and excited states of the probe molecule. We have made no attempt to take into account Frank−Condon factors or other quantum selection rules. Emission spectra in this article are always reported as area normalized.

3. Results

3.1. Structure. Structural properties derived from our parametrization of the neat IL chosen for this study have previously been reported.[50] Water−anion and water−cation radial distribution functions are shown in Figure 2. It is clear that the first peak of $g(r)$ is much more prominent in the case of the anion. We only show results for C3 in the case of the cation (this is the carbon atom in between the two nitrogens), but results are similar if the center of mass of the cation ring or any of the other ring atoms are chosen instead. Our result indicating close hydrogen bonding interactions between water and the anions is in agreement with recent experiments[69] of attenuated total reflectance infrared spectroscopy for IL−water systems based on the 1-alkyl-3-methylimidazolium cation involving various different anions. The strength of the H-bonding between water molecules and different anions appears from these experiments to increase in the order [PF$_6$]$^-$ < [S$_b$F$_6$]$^-$ < [BF$_4$]$^-$ < [(CF$_3$SO$_2$)$_2$N]$^-$ < [ClO$_4$]$^-$ < [CF$_3$SO$_3$]$^-$ < [NO$_3$]$^-$ < [CF$_3$CO$_2$]$^-$.
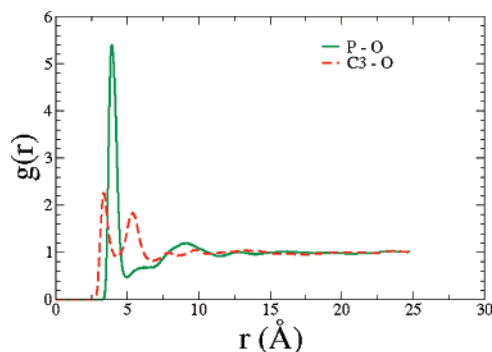
Figure 2. Radial distribution function $g(r)$ (green) between the P atom in the anion and the oxygen atom in water, and (red) between C3 in the cation and the oxygen atom of water.
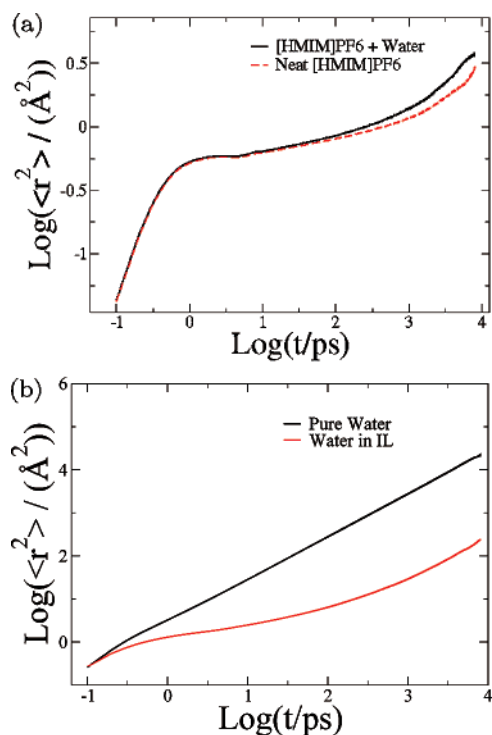
Figure 3. MSD as a function of time for (a) PF6 in neat IL (red) and IL+water (black) and (b) water in IL (red) and pure water (black).

Koddermann et al.[71] combined Fourier transform infrared spectroscopy and density functional calculations and also found that water molecules are mainly H-bonded to the anions. Similar conclusions have previously been reached in the MD studies of water−dimethylimidazolium chloride mixtures by Lynden-Bell and co-workers,[65,74] and in the case of water and 1-octyl-3-methylimidazolium nitrate by Voth and co-workers.[53]

3.2. Dynamics. In order to elucidate the effect of water on the dynamics of [HMIM$^+$][PF$_6^-$], we show in Figure 3a the mean square displacement (MSD) of [PF$_6^-$] at 300 K in the presence and absence of water. We do not show results for the cations, since as it has been demonstrated before[8] that the results closely follow those for the anions. Figure 3a clearly shows the existence of three different regimes. At short times, we have subpicosecond ballistic behavior, followed by a very long (tens of nanoseconds) sub-diffusive cage regime. This time scale is where non-Gaussian dynamics[8] is predominant and is also the typical time scale on which most relevant chemical and photochemically induced electronic processes take place in the liquid. Gaussian diffusion, where the slope in Figure 3 is 1, is only established after tens to hundreds of nanoseconds in the
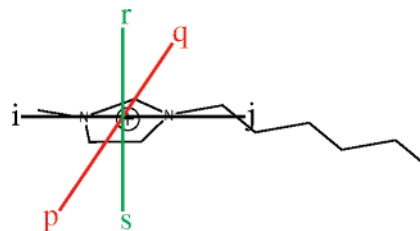
**Figure 4.** Body-fixed vectors used to compute rotational correlation functions.

neat IL. It is important to emphasize that not all ILs are the same. Imidazolium-based ILs with shorter alkyl tails display faster dynamics.[29,92] The size of the anion also plays an important role in determining the time scale on which these systems show non-Gaussian dynamics. From Figure 3a we can see that the transition form ballistic to the intermediate cage regime is very similar in the presence and absence of water; however, the diffusive regime is achieved faster when water is present. It is fair to say that water enhances or lubricates the translational motion of this IL. Figure 3b shows a logarithmic plot of the MSD as a function of time for pure SPC water at 300 K and SPC water in the IL. Clearly, the behavior of water in the IL is very different from that in bulk water at 300 K and is similar instead to that found in the supercooled regime.

$$C(t) = \langle \vec{ij}(0) \cdot \vec{ij}(t) \rangle \qquad (6)$$

Further evidence of the lubricating action of water can be obtained by analyzing the rotational motion of the [HMIM$^+$] cation. Rotational diffusion is intimately related to viscosity. We have computed rotational correlation functions $C(t)$ for the [HMIM$^+$] cation along three different body-fixed directions depicted in Figure 4 (see eq 6 for a definition of $C(t)$). As is to be expected, rotation of the $i−j$ axis is slowest since it requires reorientation along the longest molecular axis. Figure 5a shows plots of these rotational correlation functions in the case of the neat IL. It is really important to recognize that very little loss of correlation occurs on a 4 ns time scale. In other words, on the time scale on which spectroscopy of typical fluorescent probes occur, not much happens in terms of rotational dynamics in this particular IL. The effect of water on this correlation function is noticeable and compatible with what we have observed in terms of translational diffusion. Figure 5b−d compares rotational correlation functions in the presence and absence of water. In all cases, we observe a decay of correlations that is faster when water is present. It is clear now that the experimentally observed decrease in viscosity is a consequence of the faster translational and rotational dynamics caused by the presence of water. This phenomenon is non-negligible, even though the volume or mass fraction of water is quite small (62 water molecules in a system of 303 [HMIM$^+$][PF$_6^-$] ions). Both anions and cations are much larger than a single water molecule.

A simple explanation is in place for this set of observations. Figure 6 displays a distribution of the Coulombic interactions between cations and anions in the presence and absence of water. These results are averages over 13 trajectories. It is obvious that these interactions are stronger in the absence of water. The screening effect is reflected in the higher translational and rotational mobility of the IL. This lubricating effect of water is ultimately responsible for the decrease in viscosity observed experimentally in references 31, 37, 66, and 68 and in computer simulations.[58]

3.3. Coumarin-153 Spectroscopy in the Presence and Absence of Water. It is now well established from experimental
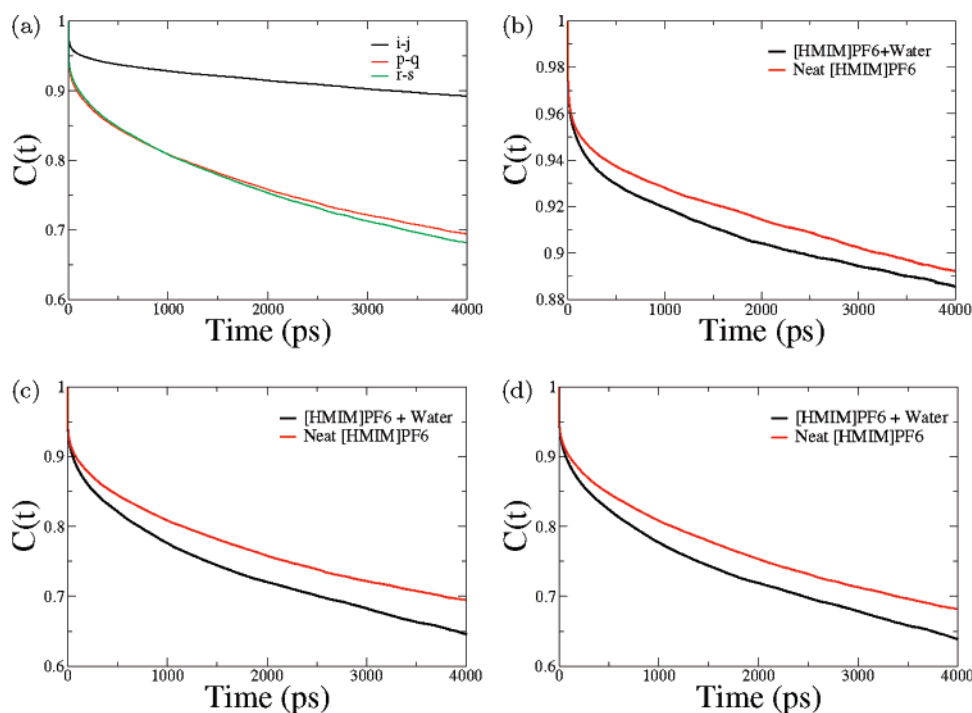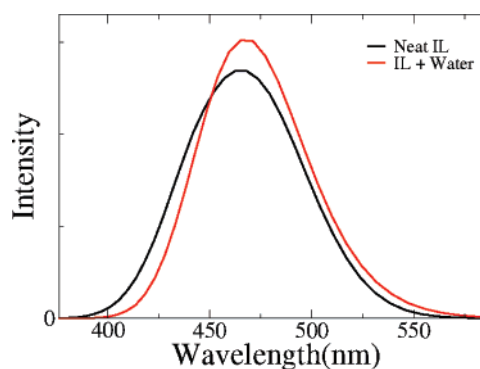
Figure 5. Rotational correlation functions for the [HMIM$^+$] cation along the three directions defined in Figure 4: (a) neat IL, (b) *ij* axis, (c) *pq* axis, and (d) *rs* axis.
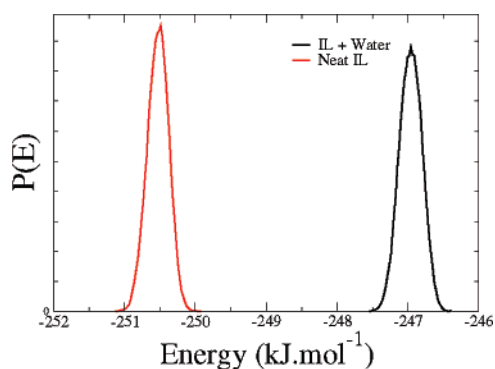
Figure 6. Cation−anion Coulombic interaction energies per ion pair averaged over 13 trajectories.
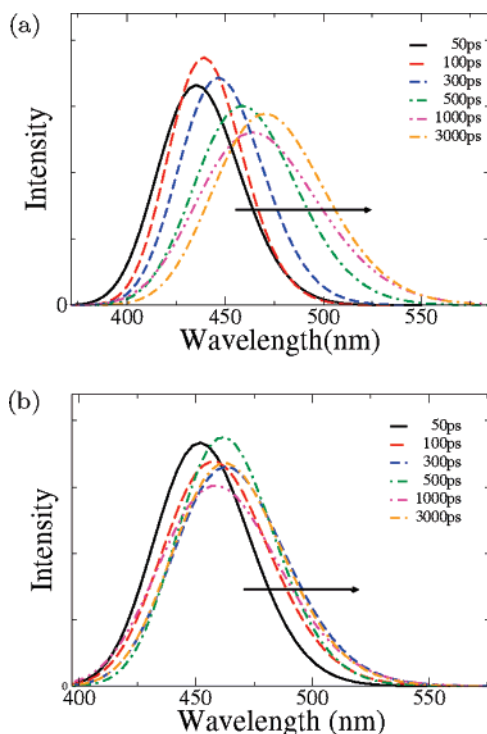

Figure 7. Emission spectra of Coumarin-153 at 386 nm in neat IL and in the IL+water system. In the presence of water, the emission spectrum is red-shifted.

and theoretical perspectives that this and other similar ILs display relaxation dynamics following the photoexcitation of certain fluorescent probes that can induce absorption wavelength-dependent fluorescence spectra. This phenomenon can be exploited as a selectivity tool since the yield of photochemical reactions can be manipulated by adjusting the excitation wavelength. It is clear from our previous work[7,8,49] and from the results of this study on Coumarin-153 that, after fast initial energy relaxation upon photoexcitation, further relaxation of the solvent is very slow, and full local environment interconversions often do not occur on a time scale that we are able to probe using computer simulations. This can be clearly seen from the fact that the solute−solvent energies after photoexcitation do not converge to a common average value if one analyzes trajectories with different initial conditions but with otherwise the same number of particles, average pressure, and temperature.[7]

Following the interesting work of Sarkar and co-workers[66] we have studied the effect of water on the fluorescence spectra of Coumarin-153 in [HMIM$^+$][PF$_6$$^-$]. Figure 7 shows our ensemble-averaged emission spectra for Coumarin-153 both in the neat IL and in the IL+water mixture, corresponding to our maximum in absorption. It is clear that the emission spectrum

is red-shifted in the presence of water. Our results show the same trend experimentally observed by Sarkar and co-workers in reference 66, which is consistent with previous observations in other similar IL systems.[28] Analyzing our simulations, we find that the red-shift in the steady-state emission spectrum appears to have two different origins. First, the ensemble-averaged ground- to excited-state energy difference at time zero is smaller in the presence of water. Second, the relaxation of the solvent surrounding the probe onto local energy minima is faster in the presence of water. This faster relaxation is clear from the time evolution of the emission spectra computed using eq 5 in the presence and absence of water. In Figure 8(a) we see that the emission spectrum for Coumarin-153 in the neat IL significantly shifts with time until at least 3000 ps, whereas we do not see such slow relaxation in Figure 8b. Figure 8b, which displays the time dependence of the emission spectrum in the presence of water, does not appear to significantly change after 300 ps.

Figure 9a,b shows the excitation wavelength-dependent emission spectra for Coumarin-153 in the presence and absence of water. In both figures we can clearly see that Coumarin-153 excited at different wavelengths gives rise to different emission

Figure 8. Time evolution of the emission spectrum of Coumarin-153 in (a) neat IL and (b) in the IL+water system.
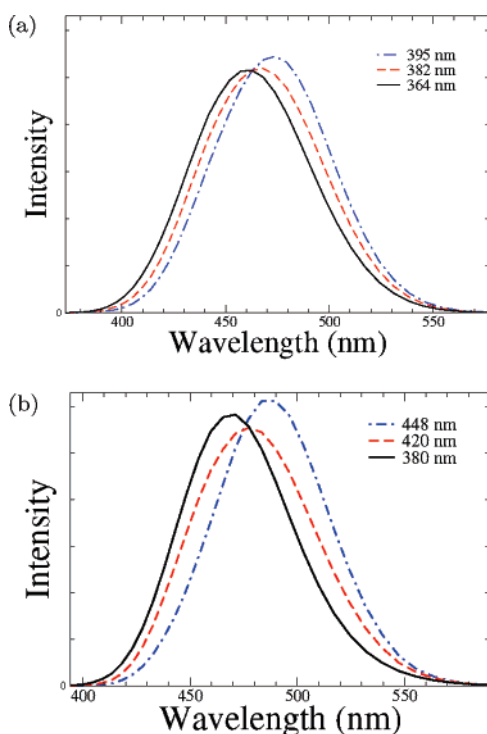

Figure 9. Emission spectra at different excitation energies: (a) neat IL and (b) IL+water.

spectra, which are red-shifted as the excitation wavelength is increased. The same phenomenon is observed in the experiments of Sarkar and co-workers[66] and in a very similar system in reference 28. This wavelength-dependent emission spectra is common in ILs when the lifetime of the probe is shorter or of comparable magnitude to the time scale for solvent reorganization around the excited-state probe.[7,8,48]

One very important observation stemming from our results is that even though the solvent relaxation at the local environ-
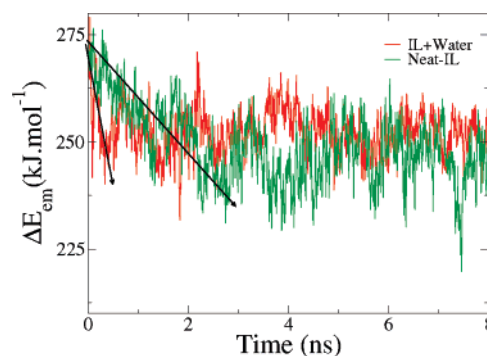
Figure 10. ΔE_{em} as a function of time for two arbitrarily chosen trajectories (IL+water = red, and neat IL = green).
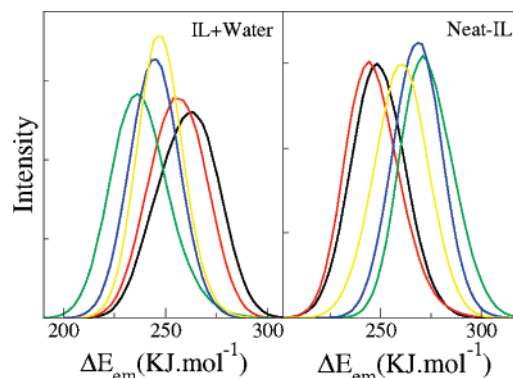
Figure 11. Emission spectra for five independent trajectories of IL+water (left) and neat IL (right).

ments level appears to be faster in the case when water is present, emission is still absorption wavelength dependent. This indicates that the fast relaxation observed is only partial and leads to local minima on a time scale compatible with the lifetime of Coumarin-153. Global solvent reorganization takes much more time at least longer than 10 ns. This is consistent with the dynamic Stokes shifts observations in references 28, 29, and 66.

A different way to show that local relaxation is faster in the presence of small amounts of water is through the actual time history of the ground to excited-state energy gaps after photo-excitation. Figure 10 shows a plot of ΔE_{em}, the energy difference between ground and excited states after photoexcitation for a typical trajectory with and without water. Consistent with Figure 8a,b, we clearly see that initial relaxation is faster when water is present. However, we emphasize that this is only local relaxation since the left panel in Figure 11 shows that five arbitrarily chosen trajectories in which water is present have completely different steady-state emission spectra. This can be compared with five trajectories in the absence of water Figure 11 (right panel) in which the same phenomenon is observed. It is clear, that if the solvent was able to visit all possible configurations that could solvate the excited-state probe on the time scale of emission, then all trajectories would yield identical emission spectra. We have shown this to be the case in a previous article.[8] Water indeed facilitates the mobility of the IL through a screening effect, but the dynamics leading to full relaxation of the solvent is still on a much longer time scale than the lifetime of the probe, even in the presence of small amounts of water.

Not all ILs are the same. Samanta and co-workers[6,15] found that the phenomenon of excitation wavelength-dependent emission is highly dependent on the probe molecule and the RTIL. In particular, they did not observed a REE for Coumarin-153

Effect of Water on [HMIM$^+$][PF$_6^-$] and Coumarin-153

J. Phys. Chem. B, Vol. 112, No. 6, 2008 **1775**

in [BMIM$^+$][PF$_6^-$], [EMIM$^+$][BF$_4^-$], and [BMIM$^+$][BF$_4^-$]. On the other hand, both our simulations and the experiments in references 28, 29, and 66 indicate the presence of an absorption wavelength-dependent emission spectrum and Stokes shift in the case of the same probe in a slower IL. Maroncelli and co-workers' recent results[9] also show a modest absorption wavelength dependence in the emission spectrum of Coumarin-153 in a much less viscous solvent than the one we are using in our study. It is now well understood that two conditions must be satisfied for the observation of such phenomenon:[6−8,35] inhomogeneous broadening must be present in the absorption spectrum (quite common in many solvents), and the solvation time scale must be slower than the fluorescence lifetime of the probe species. According to the second condition, only ILs with solvation times that are rather long (the lifetime of Coumarin-153 is 4.85 ns in neat [HMIM$^+$][PF$_6^-$][66]) will show a considerable REE. Since the solvation times of [BMIM$^+$][PF$_6^-$], [EMIM$^+$][BF$_4^-$], and [BMIM$^+$][BF$_4^-$] estimated from dynamic Stokes shift experiments are usually less than 2 ns,[6,19] it is obvious that, if present at all, the importance of the REE will be small in such liquids.

4. Conclusions

In this article we analyzed the role that water plays at small concentrations in the dynamics of [HMIM$^+$][PF$_6^-$] as well as in the fluorescence spectroscopy of Coumarin-153 dissolved in this IL. We find that water screens the direct Coulombic interactions between cations and anions and that it facilitates rotational and translational motion. Consistent with these observations, we also find that relaxation of solvent environments to local minima is considerably faster in the presence of small amounts of water.

Absorption wavelength-dependent emission spectra are observed both in the presence and in the absence of water. Steady-state emission spectra derived from different MD trajectories are trajectory dependent, indicating that fast relaxation is onto a local state, but full solvent averaging around the solute probe does not occur on a time compatible with the lifetime of the probe. A question that deserves some thought arises from our results and recent experiments. How much of a driving force (as compared with the ion−ion interactions in the liquid) still exists after initial relaxation following photoexcitation? If this driving force that would force all excited-state probes to exist in a similar solvent environment is very small, then relaxation after photoexcitation will simply be dominated by the very slow intrinsic cage dynamics of the solvent, will last for as long as the liquid is non-diffusive, and will be almost probe independent. A clear-cut experimental answer to these question is difficult since the emission signal is convoluted with the lifetime of the probe, and two probes with similar lifetimes do not necessarily have the same ground and excited-state dipole moments or volumes.

The fact that one can choose ILs such that the dynamics or kinetics of relaxation of the solvent can be controlled (selected) by adjusting the absorption frequency of a probe is not just an odd property of these solvents, but actually is a fundamental tool that has not yet been fully taken advantage of. Maroncelli and co-workers[9] have been able to tune the yield of different photoprocesses by taking advantage of this break down of Kasha's rule. In conventional solvents, reorganization around an excited-state molecule occurs very fast, and there is no opportunity to use the slow dynamics of the solvent as an instrument for selectivity. One of the most commonly used terms to describe ILs, i.e., designer solvents, is appropriate in this

case. It is important to emphasize that not all ILs, no matter how similar in structure they may be, will show the same selectivity properties. A delicate interplay between the solvation times and probe lifetimes has to be considered before any prediction can be made.

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