Effect of Water, Methanol, and Acetonitrile on Solvent Relaxation and Rotational Relaxation of Coumarin 153 in Neat 1-Hexyl-3-methylimidazolium Hexafluorophosphate

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The dynamics of solvent relaxation in ionic liquid (IL)−water, IL−methanol, and IL−acetonitrile mixtures have been investigated using steady state and picosecond time-resolved fluorescence spectroscopy. We have used Coumarin 153 (C-153) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) as fluorescence probe and IL, respectively. The steady-state emission spectra showed that the gradual addition of cosolvents increases the polarity of the mixtures. In neat [hmim][PF_6] and all IL−cosolvent mixtures, solvation occurs in two well-separated time regimes within the time resolution of our instrument. A substantial portion of the solvation has been missed due to the limited time resolution of our instrument. The gradual addition of cosolvents decreases the viscosity of the medium and consequently solvation time also decreases. The decrease in solvation time is more pronounced on addition of acetonitrile compared to water and methanol. The rotational relaxation time of the probe is also decreasing with gradual addition of the cosolvents. The decrease in viscosity of the solution is responsible for the decrease in the rotational relaxation time of the probe molecule.

1. Introduction

In recent years ionic liquids (a class of salts that are liquid at or near room temperature) have been extensively used as “green substitutes” for volatile organic solvents.[1] Due to many unique chemical and physical properties such as thermal stability, low melting temperatures, and low vapor pressure, ionic liquids (ILs) have been used for organic synthesis,[2] separation,[3] electrochemical applications,[4] solar batteries,[5] biopolymers,[6] and many more applications. ILs are moderately to highly viscous.[7] There are lots of photophysical studies carried out in these ILs. Aki et al.[8] determined the polarity of four imidazolium and pyridinium based ILs. Bright and co-workers[9] showed the effect of temperature and added carbon dioxide on different fluorescent probes in neat 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). Femtosecond optical kerr effect measurement was used to study the low-frequency vibrational motions.[10] Intramolecular excimer formation[11] has been investigated in these ILs. There are also a few studies on time-dependent solvation in ILs.[12−15]

The biphasic solvation dynamics in these ILs is mainly contributed by the ions. In addition to experimental efforts, a few theoretical studies were carried out in these ILs to determine the structure and dynamics, polarity, and solvation properties of ILs.[16−18] Using molecular dynamics simulation Shim et al.[16] interpreted the fast component due to diffusional motion of the anion and the slower component due to collective motion of the cation and anion. But in a recent paper Kobrak et al. showed that the fast component is originating due to the collective cation and anion motions.[18a]

Recently, research has been began on IL based mixed solvents in order to expand their utility. The viscosity and density of ILs have changed due to the addition of water and other cosolvents.[19] ILs are miscible with liquids of medium to high dielectric constant and immiscible with liquids with low dielectric constant.[20] Miscibility of the dialkylimidazolium ILs with water depends on the anion.[19] $[PF_6]^-$ containing ILs are less miscible than $[BF_4]^-$. Pandey et al. investigated the effects of water,[21] ethanol,[22] aqueous ethanol,[23] and binary IL−IL[24] mixtures on solvatochromic behavior of pyrene, Reichardt’s betanine dye, 1-pyrenecarboxaldehyde, and 1,3-bis(1-pyrenyl)-propane in [bmim][PF_6]. The results show that physicochemical properties of [bmim][PF_6] could be successfully altered by the additions of the cosolvent. The binary or ternary solvent systems show nonideal behavior depending on the nature of the cosolvents or solvatochromic probe. Thus, the presence of trace amounts of cosolvent in ILs can alter the local microenvironment surrounding a probe.

There are many reports of solvation dynamics conducted in neat polar solvents[25−28] but there is a growing interest to study the solvation dynamic in mixed solvents.[29−36] Suppan et al.[29] observed that solvent mixtures of different dielectric polarities show that a process of preferential solvation, described as “dielectric enrichment”, occurs in the solvation shell of dipolar solute molecules. Cichos et al.[30] measured the solvation dynamics in binary mixtures of alcohol and alkane. They explained their results using Suppan’s preferential solvation concept.[29] Solvation dynamics of mixtures of two similar polarity solvents also have been studied.[31,32] Solvation times in the binary mixtures vary between the pure solvent limits with the composition of the solvent mixtures, and no preferential solvation occurs in this case. Castner et al.[33] investigated the anomalous behavior of aqueous 1-propanol binary solution using Coumarin 153 as a probe molecule. Solvation dynamics in acetonitrile−benzene nonassociating mixtures have been also studied.[34] Huppert and co-workers[35] investigated the solvation dynamics in hexane−propionitrile and hexane−methanol solvent mixtures. Solvation dynamics in dioxane−water solvent mixtures have also been investigated.[35c,36] Solvation dynamics in organized assemblies is also an attractive topic for investigation.[37]

Molecular dynamics simulations of mixtures of 1,3 dialkyl imidazolium IL and water have been performed to investigate the microscopic physical properties as a function of composi-

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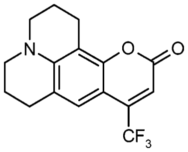
CHART 1: Structure of Coumarin 153



tion.[38] Bright et al.[39a] studied the effect of added water within [bmim][PF_6] on solvation dynamics of the PRODAN (6-propionyl-2-(*N*,*N*-dimethylamino)naphthalene). They found a 40% decrease in the average solvation time measured at the highest water concentrations. In a recent paper, we have reported the solvation dynamics in water−[bmim][PF_6] solvent mixtures using Coumarin 153 as a probe.[39b] But the effect of other cosolvents on IL in solvation dynamics is still unknown.

In this paper, we are going to report the effect of cosolvent (water, methanol, and acetonitrile) on solvent relaxation results of Coumarin 153 (C-153, Chart 1) dissolved in 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]). We have used C-153 as the experimental probe because it is considered to be an ideal solvation probe.[40] The ground state of C-153 is polar with a measured dipole moment 6.55 ± 0.01 D. The $S_0 \rightarrow S_1$ transitions leads to the S_1 dipole moment between 14.2 and 16.0 D.[40] The excitation of C-153 does not involve specific changes in solute−solvent interactions.

2. Experimental Section

C-153 (laser grade, Exciton) is used as received. [hmim][PF_6] is obtained from Acros chemicals (98% purity) and purified using literature procedure.[14] The IL is dried in vaccum for ~24 h at 70−80 °C before use. C-153 is initially dissolved in methanol and transferred to a vial. The IL is added in the vial under nitrogen atmosphere in a glovebox and stirred for 10−20 min after removing the methanol under vaccum. Then the solutions are transferred in the quartz cuvette in a glovebox and sealed with a septum and Parafilm. The final concentration of C-153 is ~5×10^{-5} M. Methanol and acetonitrile were spectroscopic grade (Spectrochem, India) and freshly distilled over calcium hydride (Spectrochem, India). The requisite amount of solvent is added to the cuvette containing IL, mixed thoroughly, and allowed to equilibrate for sufficient time before each measurement. All the experiments are performed below the saturation with the cosolvents.

Absorption and fluorescence spectra are collected using a Shimadzu (model no. UV1601) spectrophotometer and a Spex fluorolog-3 (model no. FL3-11) spectrofluorimeter. The fluorescence spectra are corrected for spectral sensitivity of the instrument. For steady-state experiment, all the samples are excited at 410 nm. The time-resolved fluorescence setup is described in detail in our earlier publication.[41] Briefly, the samples are excited at 408 nm using a picosecond diode laser (IBH) and the signals are collected at magic angles (54.7°) using a Hamamatsu MCP PMT (3809U). The instrument response function of the instrument is ~90 ps. The same setup is used for anisotropy measurements. The analysis of the data is done using IBH DAS 6 decay analysis software. The same software is also used to analyze the anisotropy data. The temperature is kept (298 ± 2 K) constant for all measurements. For viscosity measurements we have used an advanced Rheometer (TA Instrument, AR 1000).

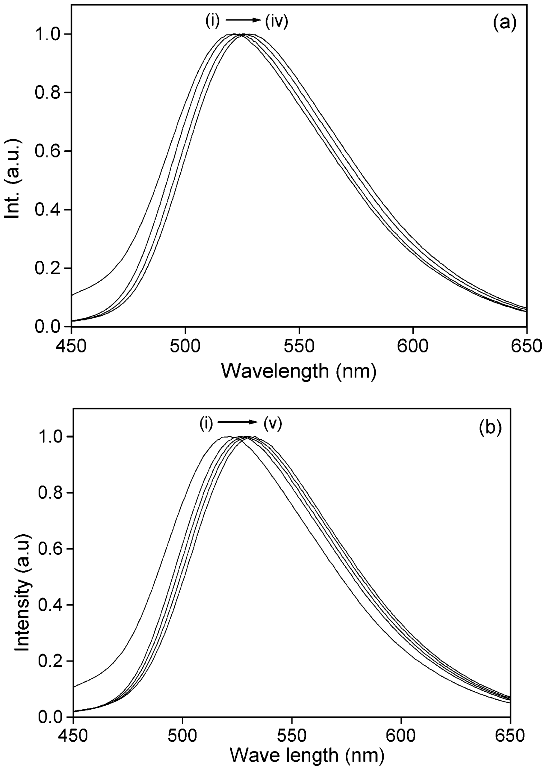


Figure 1. Normalized emission spectra of C-153 in (a) [hmim][PF_6]−water systems, (i) in neat [hmim][PF_6] and adding (ii) 0.03, (iii) 0.09, and (iv) 0.19 mol fraction of water, and (b) [hmim][PF_6]−methanol systems, (i) in neat [hmim][PF_6] and (ii) 0.10, (iii) 0.20, (iv) 0.30, and (v) 0.40 mol fraction of methanol.

3. Results and Discussion

3.1. Steady-State Studies. The representative fluorescence spectra of C-153 in [hmim][PF_6]−water and [hmim][PF_6]−methanol are shown in Figure 1 and the observed peaks are summarized in Table 1. The emission spectrum of C-153 in

TABLE 1: Emission Maxima and Decay Parameters of *C*(*t*) of C-153 Due to the Additions of Different Cosolvents in Neat [hmim][PF_6]

cosolvent	mol fraction	λ_{em}^{max} (nm)	$\Delta\nu^a$ (cm^{-1})	a_1	τ_1 (ns)	a_2	τ_2 (ns)	$\langle\tau_s\rangle^{b,c}$ (ns)	missing component (%)
		520	1075	0.70	1.181	0.30	20.46	6.96[d]	23
water	0.03	523	990	0.72	0.966	0.28	14.54	4.77	29
water	0.09	526	984	0.77	0.769	0.23	14.45	3.91	30
water	0.19	528	961	0.78	0.686	0.22	11.38	3.04	31
methanol	0.10	526	1001	0.73	0.800	0.27	14.03	4.37	28
methanol	0.20	530	968	0.79	0.617	0.21	13.43	3.31	31
methanol	0.30	530	928	0.84	0.493	0.16	10.78	2.14	34
methanol	0.40	532	899	0.86	0.416	0.14	9.71	1.72	36
acetonitrile	0.10	525	881	0.77	0.802	0.23	11.07	3.05	37
acetonitrile	0.20	525	811	0.82	0.647	0.18	9.50	2.24	42
acetonitrile	0.30	526	716	0.87	0.531	0.13	8.41	1.56	49
acetonitrile	0.40	527	602	0.90	0.441	0.10	6.07	1.00	57

[a] $\Delta\nu = \nu_0 - \nu_\infty$. [b] $\langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$. [c] Error in our measurements ±5%. [d] From ref 14.

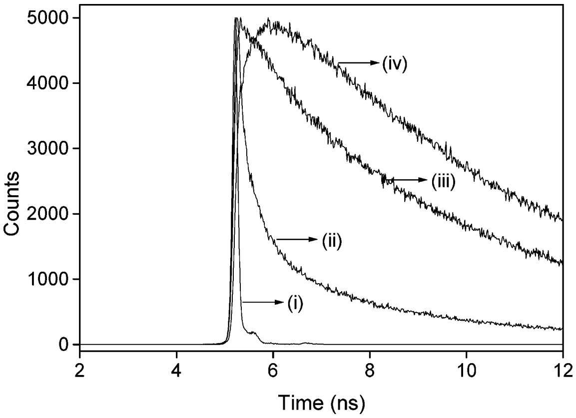


Figure 2. Fluorescence decays of C-153 in neat [hmim][PF$_6$] adding 0.20 mol fraction of acetonitrile at (i) instrument response function, (ii) 460 nm, (iii) 520 nm, and (iv) 640 nm.

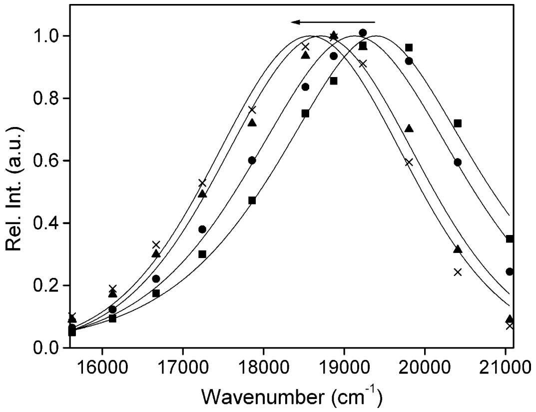


Figure 3. Time-resolved emission spectra of C-153 in [hmim][PF$_6$] adding 0.30 mol fraction of methanol at (i) 0 (■), (ii) 200 (●), (iii) 1000 (▲), and (iv) 3000 ps (×).

neat [hmim][PF$_6$] is at ~520 nm. With the gradual addition of cosolvents the emission peak is gradually red shifted. The emission peak is red shifted to ~528 nm after addition of 0.19 mol fraction of water in neat [hmim][PF$_6$]. Similarly additions of 0.4 mol fraction of methanol and acetonitrile in neat [hmim][PF$_6$] lead to the red shift of emission peaks to ~532 and ~527 nm, respectively. The observed emission peak in [hmim][PF$_6$] is very close to that of acetonitrile.[14]

3.2. Time-Resolved Studies. *3.2.1 Solvation Dynamics.* We have observed wavelength dependent Stokes' shift in the emission spectra of C-153 in all the IL containing solvent mixtures. Fluorescence decays of C-153 are markedly dependent on the emission wavelength. At short wavelength, a fast decay is observed. The growth at long wavelength indicates C-153 molecules undergo solvation in these mixed solvents. The average lifetime of C-153 (at emission peak) in neat [hmim][PF$_6$] decreases with the gradual addition of cosolvents. Representative decays of C-153 in a 0.2 mol fraction of acetonitrile−[hmim][PF$_6$] solvent mixture at three different wavelengths are shown in Figure 2. The time-resolved emission spectra (TRES) have been constructed following the procedure of Fleming and Maroncelli[42] and described in our earlier publications.[41] To extract the time constant of solvation we have constructed the decay of the solvent correlation function ($C(t)$), which is defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{1}$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the peak frequencies at time zero, t, and infinity, respectively. The peak frequencies are evaluated from the TRES. A representative TRES of C-153 in a 0.30 mol fraction of methanol−[hmim][PF$_6$] mixture is shown in Figure 3. The $C(t)$ in each case was found to be biexponential in nature within our time resolution. The decay of $C(t)$ was fitted to a biexponential decay function

$$C(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \tag{2}$$

where τ_1 and τ_2 are the two solvation times with amplitudes of a_1 and a_2, respectively. The decay parameters of $C(t)$ are summarized in Table 1 and shown in Figure 4. We have reported the average solvation time in neat [hmim][PF$_6$] as 6.96 ns in our earlier publication.[14] The average solvation time decreases with gradual additions of cosolvents. Addition of 0.19 mol fraction of water decreases the solvation time to 3.04 ns. Addition of 0.4 mol fraction of methanol in [hmim][PF$_6$] decreases the solvation time to 1.72 ns. Similarly addition of 0.4 mol fraction of acetonitrile to neat [hmim][PF$_6$] decreases the solvation time to 1.00 ns. In all the solvent mixtures, both fast and slow solvation time decreases with gradual addition of the cosolvents. The relative amplitudes of the fast components also increase.

3.2.2. Time-Resolved Anisotropy Studies. Time-resolved fluorescence anisotropy, $r(t)$, is calculated using the following equation

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} \tag{3}$$

where G is the correction factor for detector sensitivity to the polarization direction of the emission. $I_{\parallel}(t)$ and $I_{\perp}(t)$ are fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. The anisotropy results are summarized in Table 2 and representative decays of fluorescence anisotropy in neat [hmim][PF$_6$], 0.19 mol fraction of water−[hmim][PF$_6$], and 0.40 mol fraction of acetonitrile−[hmim][PF$_6$] are shown in Figure 5. The rotational relaxation data in all cases are fitted with a single-exponential function. The observed rotational relaxation time in neat [hmim][PF$_6$] is 6.71 ns.[14] The rotational relaxation time deceases to 3.53 ns due to addition of 0.19 mol fraction of water. Similarly additions of 0.40 mol fraction of methanol and acetonitrile in neat [hmim][PF$_6$] decrease the rotational relaxation time to 2.06 and 1.73 ns, respectively.

3.3. Discussion. The emission peak of C-153 in [hmim][PF$_6$] is very close to that of acetonitrile. The gradual red shift of the emission peak with addition of cosolvents indicates the increase in polarity of the medium. Solubilized cosolvents in neat [hmim][PF$_6$] cause a substantial change in the cybotactic region of C-153. The microenvironment in neat [hmim][PF$_6$] is like that of acetonitrile, but in mixed solvent the microenvironment of C-153 is like that of an alcohol.

Solvation dynamics in IL are vastly different from solvation dynamics of conventional solvents. The motions of the ions are responsible for solvation in IL.[12−15] Chapman et al.[43] showed that ionic solvation is slow and dependent on the viscosity. The viscosity of [hmim][PF$_6$] is 254 cP at 25 °C. The slow solvation in IL arises due to high viscosity. Samanta and co-workers[12] ascribed the fast and slow components of solvation dynamics in ILs due to the motion of anions and collective motions of both cations and anions, respectively. According to Maroncelli et al.,[13] the fast component arises due to the translational adjustment of the ions within the solvation structure present at

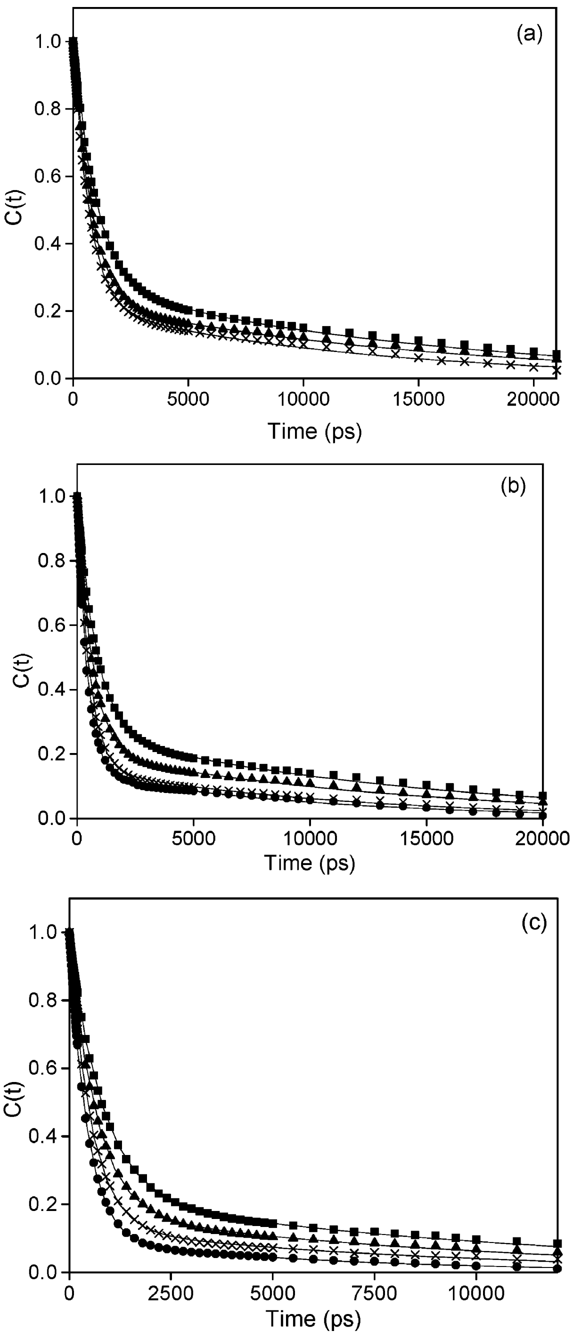


Figure 4. Decay of solvent correlation function *C*(*t*) of C-153 in [hmim][PF_6] adding (a) 0.03 (■), 0.09 (▲), and 0.19 (×) mol fraction of water, (b) 0.10 (■), 0.20 (▲), 0.30 (×), and 0.40 (●) mol fraction of methanol, and (c) 0.10 (■), 0.20 (▲), 0.30 (×), and 0.40 (●) mol fraction of acetonitrile.

the time of solute excitation. The slow component depends on the viscosity and arises due to the rearrangement of the solvation structure. Thus, the fast component arises due to the local motion of the ions and the slow component arises due to the collective diffusional motions of anions and cations.

From Table 1 we have made several interesting observations. The average solvation time decreases ~85% due to the addition of 0.4 mol fraction of acetonitrile. But addition of the same amount of methanol decreases the average solvation time to ~75%. Addition of 0.19 mol fraction of water decreases the solvation time to ~55%. Both the fast and the slow components gradually decrease due to gradual addition of cosolvents. The relative amplitudes of the fast component also increase.

TABLE 2: Rotational Relaxation Parameters of C-153 Due to the Additions of Different Cosolvents in Neat [hmim][PF_6] and Viscosity of Different IL−Solvent Mixtures

cosolvents	mol fraction	viscosity (cP)[a]	r_0	τ_r (ns)[a]
		254	0.25	6.71[b]
water	0.03		0.25	5.45
water	0.09	163	0.27	4.28
water	0.19	109	0.26	3.53
methanol	0.10	180	0.27	5.13
methanol	0.20		0.28	3.55
methanol	0.30		0.28	2.95
methanol	0.40	55	0.30	2.06
acetonitrile	0.10	136	0.26	4.91
acetonitrile	0.20		0.28	3.74
acetonitrile	0.30		0.28	2.65
acetonitrile	0.40	38	0.28	1.73

[a] Error in our experiments ±5%. [b] From ref 14.

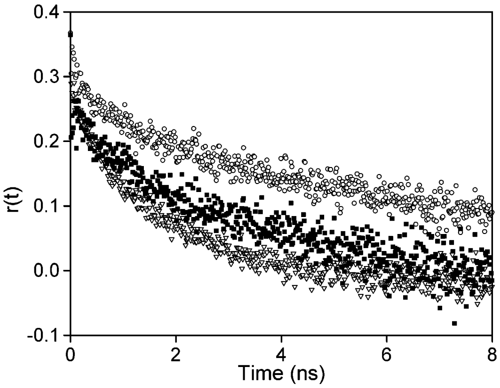


Figure 5. Decay of fluorescence anisotropy (*r*(*t*)) of C-153 in neat [hmim][PF_6] (○) and adding 0.19 mol fraction of water (■) and 0.40 mol fraction of acetonitrile (▽).

Seddon et al.[19] showed that the viscosity of the neat IL decreases due to the addition of the cosolvents. The presence of cosolvent reduces the electrostatic attraction between the ions, and decreases the overall cohesive energy resulting in a decrease in viscosity. So, gradual addition of the cosolvents decreases the viscosity of the solvent mixtures. The slow solvation in IL arises due to the high viscosity. The decrease in viscosity leads to the decrease in the solvation time. Due to the decrease in the viscosity, the motions of the ions become faster. The local motions of the ions are responsible for the fast component of the solvation time. Thus the time constant of the fast component also decreases due to the gradual addition of the cosolvents. Decrease in viscosity also leads to the faster collective diffusive motions (responsible for the slow component of the solvation dynamics) of the ions. Thus the slow component of the solvation dynamics also decreases with gradual addition of the cosolvents.

We have compared the effect of addition of the same mole fraction of cosolvents on solvation time. The decrease in the average solvation time is more prominent (Table 1) due to the addition of the acetonitrile. But for methanol and water the changes are almost the same. The decrease of the viscosity of IL due to the addition of cosolvents follows a different pattern depending on the nature of the cosolvent, possibly due to differences in polarities. Cammarata et al. showed that water and methanol can form hydrogen bonds with the anion of the IL.[44] But acetonitrile is not a hydrogen bonded solvent. So interaction of the acetonitrile with IL is different from that of water or methanol. Here local motions of the ions are responsible for the solvation in these systems. As the anion can be hydrogen bonded with the water or methanol molecules, this bond must be broken for the anion to reorient. But in acetonitrile−IL

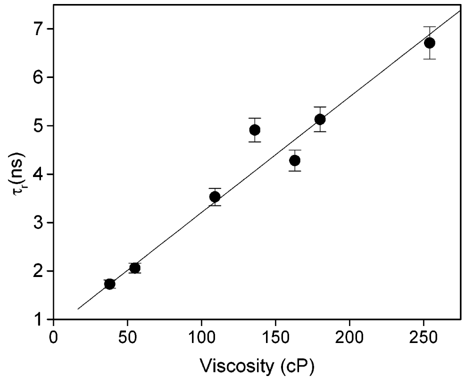


Figure 6. Variation of rotational relaxation time with viscosity in different IL−solvent mixtures.

mixtures anions can simply reorient after excitation. So motions of the anions are somewhat hindered in water or methanol containing mixed solvent. So, we have observed the maximum decrease in solvation time due to the addition of acetonitrile.

We have observed bimodal slow dynamics in all the solvent mixtures. But a part of the solvent response may be too fast to be detected using our instrument setup (<90 ps). We can calculate the missing component using the Fee and Maroncelli procedure.[45] Using the "time zero spectrum", the total Stokes' shift is ~1400 cm^{-1} for [hmim][PF$_6$]. But the observed Stokes' shift is less than the calculated Stokes' shift. The observed missing component for pure [hmim][PF$_6$] is ~23%.[14] The calculated missing components are shown in Table 1. In all cases the missing component increases due to the addition of the cosolvents. The increase is more prominent in the case of acetonitrile. Recent computer simulation studies[10,17,39] reveal libration, vibration, ion ballistic motion, ion local basin exploration, and ion basin hoping are responsible for the missing component. The solvation time of pure methanol and acetonitrile is 5 ps and 260 fs, respectively.[40] Solvation of pure water also occurs in the ultrafast time scale.[46] So, ultrafast relaxation of the cosolvents is also responsible for the missing components. Thus percentage of missing component increases with an increase in cosolvent concentration.

The observed rotational relaxation time of C-153 in [hmim][PF$_6$] is 6.71 ns.[14] The high rotational relaxation time of C-153 in [hmim][PF$_6$] is ascribed due to the high solvent viscosity (254 cP). With the addition of the cosolvent the rotational relaxation time of the probe decreases in all cases. The rotational relaxation time of C-153 decreases 75% and 69% due to the additions of 0.40 mol fraction of acetonitrile and methanol, respectively. The rotational relaxation time of the probe decreases 47% due to the addition of 0.19 mol fraction of water. Addition of cosolvents to the IL decreases the viscosity of the solution. This decrease in solution viscosity causes the observed decrease in rotational relaxation time of the probe. We have measured the viscosity of different IL−cosolvent mixtures. The viscosities are reported in Table 2. According to hydrodynamic theory the rotational relaxation time of the probe is proportional to viscosity and inversely proportional to temperature (Debye−Stokes−Einestein equation). We have plotted the measured viscosity of different IL−solvent mixtures with the observed rotational relaxation time of the probe (Figure 6). The plot is almost linear and it confirms that rotational relaxation of C-153 in different IL−solvent mixtures follows the simple hydrodynamic theory. Thus we may conclude that the viscosity is the main guiding factor to determine the rotational relaxation time of the probe molecule in all these IL−solvent mixtures.

4. Conclusion

The variation of solvation dynamics of C-153 in neat [hmim][PF$_6$] has been investigated with the addition of different cosolvents (water, methanol, acetonitrile). The steady-state spectra showed that the microenvironment in different [hmim][PF$_6$]−cosolvents mixtures is different from that of the neat IL. In neat IL and all other mixed solvents solvation occurs in two well-separated time regimes within our instrumental time resolution. A substantial amount of solvation is too fast to be detected in our instrument. Local motions of the ions and diffusional motions of the ions are responsible for the fast and slow component of solvation in neat IL, respectively. The solvation time decreases due to the addition of cosovents. The addition of cosolvent decreases the electrostatic attractions between the ions and decreases the viscosity. Hence both local motions and diffusional motions of the ions become faster and consequently solvation time decreases. Addition of the same amount of acetonitrile has a more pronounced effect on solvation time than water or methanol. Water or methanol can form hydrogen bonds with the anions. So this bond must be broken before reorientations of the anion. But acetonitrile is not a hydrogen bonded solvent. It cannot form such hydrogen bonds with the anion of the IL. So, a decrease in solvation time is more prominent due to the addition of acetonitrile. Rotational relaxation time also decreases due to the addition of cosolvents. The variations of rotational relaxation time of the probe follow hydrodynamic theory and decrease with a decrease in viscosity. Thus viscosity is the main guiding factor to determine the rotational relaxation time of the probe in these solvent mixtures.

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