Dynamics of Solvent and Rotational Relaxation of Coumarin 153 in Room-Temperature Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate Confined in Brij-35 Micelles: A Picosecond Time-Resolved Fluorescence Spectroscopic Study

Anjan Chakraborty, Debabrata Seth, Debdeep Chakrabarty, Palash Setua, and Nilmoni Sarkar*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, WB, India

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The dynamics of solvent and rotational relaxation of Coumarin 153 (C-153) in ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and in the ionic liquid confined in Brij-35 micellar aggregates have been investigated using steady-state and time-resolved fluorescence spectroscopy. We observed slower dynamics in the presence of micellar aggregates as compared to the pure IL. However, the slowing down in the solvation time on going from neat IL to IL-confined micelles is much smaller compared to that on going from water to water-confined micellar aggregates. The increase in solvation and rotational time in micelles is attributed to the increase in viscosity of the medium. The slow component is assumed to be dependent on the viscosity of the solution and involves large-scale rearrangement of the anions and cations while fast component is assumed to originate from the initial response of the anions during excitation. The slow component increases due to the increase in the viscosity of the medium and increase in fast component is probably due to the hydrogen bonding between the anions and polar headgroup of the surfactant. The dynamics of solvent relaxation was affected to a small extent due to the micelle formation.

1. Introduction

In recent years considerable attention has been paid to understand the dynamical role of the solvent in liquid-state chemical and biological processes.[1−9] Attention has been centered particularly on those systems, which resemble the biological model systems. Different biologically relevant organized media like micelles,[10] mixed micelles,[11] aqueous[12] and nonaqueous reverse micelles,[13,14] cyclodextrins,[15,16] vesicles,[17] proteins,[18] proteins-surfactant complexes,[18] and amphiphilic starlike macromolecules[19] have often been chosen to study solvent relaxation process. Among these examples micelles are of particular interest since solvent relaxation has been used as a tool for microenvironment studies. Micelles are formed by aggregation of surfactant molecules in polar solvents above a certain concentration of the surfactant called the critical micellar concentration (cmc). It consists of three regions, namely the hydrocarbon core, the Stern layer, and the Gouychapman layer. The hydrocarbon core is composed of the hydrocarbon chain of the surfactant molecules. The second region is the Stern layer containing polar headgroups of the surfactant molecules, counterions, and solvent molecules. This layer is surrounded by the Gouychapman layer. In micelles solvent relaxation studies appeared to be particularly interesting. It was found that solvent relaxation is drastically retarded in micelles[4,6,10−11] as compared pure water.[1] Moreover, in micelles solvent relaxation process is biphasic consisting of a picosecond (fast) and a nanosecond (slow) component. The main candidates responsible for solvent relaxation in the micellar Stern layer are polar or ionic headgroups of surfactants, counterions, and the water molecules bound to the Stern layer. Sarkar et al.[10e,11] invoked the Nandi−Bagchi model[20] of dynamic exchange of free and bound water molecules in explaining the slow dynamics in the Stern layer of the micelles and mixed micelles.

As micelle formation occurs by the aggregation of the surfactant molecules in polar solvent, moderately polar solvents other than water such as methanol, acetonitrile, and ionic liquid (IL) may also be used for the formation of micelles.[21−23] The latter solvent is of great importance because of its unique properties such as thermal stability, high ionic conductivity, nonflammable nature, suitable polarity, low vapor pressure, etc. ILs are often used in electrochemical processes,[24] synthesis,[25] solar batteries,[26] and biopolymers.[27] ILs comprise organic salts composed of cations and anions which are in the liquid state at ambient temperature. The ILs are highly polar, and their polarity is very close to the short chain alcohols. Many interesting photophysical properties have been studied in ILs. Aki and co-workers measured the polarity of the four imidazolium- and pyridinium-based ILs using UV−vis absorption and fluorescence spectroscopy.[28] Muldoon and co-workers investigated the polarity of the ILs using solvatochromic probes.[29a] Seddon and co-workers performed polarity studies of several neat 1-alkyl-3-methylimidazolium-based ILs using the solvatochromic dye Nile red.[29b] Pyrene, Richardt's betain dye, 1-pyrenecarboxaldehyde, Nile red, and dansylamide have been used to probe the ILs adding different cosolvents.[30a−b] Viscous properties of different ILs with cosolvents were studied using various techniques.[30c−d] Photoisomerization and intramolecular eximer formation studies have also been carried out in the ILs.[31−32a] Recently, Samanta et al. investigated the optical properties of different ionic liquids and emission behavior of different molecules using absorption and fluorescence spectroscopy.[32b−d] Very recently Castner et al. investigated the ultrafast molecular dynamics of five pyrrolidinium cation room-temperature ionic liquids using femtosecond optical heterodyne-detected Raman-induced Kerr effect

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* To whom correspondence should be addressed. E-mail: nilmoni@chem.iitkgp.ernet.in. Fax: 91-3222-255303.

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CHART 1: Structure of Brij-35

$C_{12}H_{25}(OCH_2CH_2)_{23}OH$

CHART 2: Structure of 1-Butyl-3-methylimidazolium Hexafluorophosphate

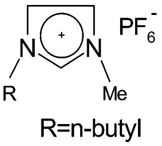
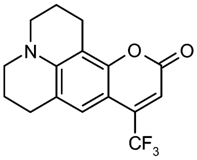


CHART 3: Structure of Coumarin 153



spectroscopy.[33] Solvent relaxation processes are particularly interesting in different ILs. Samanta et al.[34] and Maroncelli et al.[35] have reported extensively the solvent relaxation in different ionic liquids. Recently we carried out solvent and rotational relaxation studies in neat 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]), [bmim][PF_6]−water, and [hmim][PF_6]−acetonitrile mixture and also in [hmim][PF_6]−methanol mixture.[36] It was reported by various groups that in all the ILs the sovation process is biphasic and consists of a nanosecond and a picosecond component. Different suggestions have been put forward to justify these results. Shim et al. and Kobark et al. carried out molecular dynamics simulation to investigate solvent relaxation in different ILs.[37]

We mentioned earlier that the polarities of ionic liquids are very close to those of short chain alcohols.[36] Thus, ILs may be used as green substitutes for common solvents. Recently micelles were prepared in different ILs.[23] Armstrong and co-workers reported micelle formation in the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], and in 1-butyl-3-methylimidazolium chloride, [bmim][Cl], with different surfactants such as Brij-35, Brij-700, etc.[23a] Pandey and co-workers studied micelle formation of Brij-35, Brij-700, Tween-20, and Triton X-100 in the low-viscosity ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (emimTf_2N).[23b] It was found that the cmc of the surfactant in ILs is much higher than that in pure water. In pure water the cmc of Brij-35 is 0.06 mM, and it becomes ∼120 mM in [bmim][PF_6]. The hydrogen bond basicity is higher above the cmc than at the cmc or below cmc.[23a] Thus, micelle formation in ILs is quite different from micelle formation in water with respect to different physical properties. In the present case we choose Brij-35 (Chart 1) surfactant aggregates in [bmim][PF_6] (Chart 2) to study the solvent and rotational relaxation using C-153 as a probe (Chart 3).[23a] Brijs-35 is important nonionic polyoxyethylene surfactant. They are used in many fields such as cosmetics, pharmaceuticals, paints, and cleaning agents and are useful for solubilization of membrane protein such as Na/K ATPase, etc.[38,39] Recently we have studied the solvent relaxation dynamics of C-480 and C-151 in Brij-35 micellar systems in aqueous solution.[10e] These studies revealed the presence of an ultraslow component in the solvent relaxation dynamics in the micellar medium. Bhattacharyya et al. and Pal et al. investigated the effect of temperature on the solvent relaxation process in TX-100 micelle and Brij-35 micelles.[40] It was established by these groups[40] that solvent relaxation is temperature dependent in micelles. In this article, we investigated the variation of solvent and rotational relaxations in [bmim][PF_6] by the formation of micelles using Coumarin 153 as probe. We carried out the experiments at three different concentration of surfactant below the critical micellar concentration (39 mM), at the critical micellar concentration (120 mM), and above the critical micellar concentration (250 mM). We measured the solvent relaxation at 298, 313, and 333 K. The results have been analyzed with the help of existing theories and previous results reported by various groups.

2. Experimental Section

C-153 (laser grade, Exciton) was used as received. [bmim][PF_6] was obtained from Acros chemicals (98% purity) and purified using a literature procedure.[36] Brij-35 was obtained from Aldrich and used as received. IL was dried in a vacuum for ∼24 h at 70−80 °C before use. C-153 was initially dissolved in methanol and transferred to a vial. The IL was added to the vial under nitrogen atmosphere in a glovebox and stirred for 10−20 min after removing the methanol under vacuum. Then the solutions were transferred to a quartz cuvette in a glovebox and sealed with septa and Parafilm. The final concentration of C-153 was $\sim 5 \times 10^{-5}$ M. Brij-35 was used as received from Aldrich. Requisite amount of surfactant was added to the cuvette containing IL, mixed thoroughly, and allowed to equilibrate for 40−60 min to aid the dissolution of the solid surfactant at 40−60 °C.

Absorption and fluorescence spectra were collected using Shimadzu (model no. UV1601) spectrophotometer and a Spex fluorolog-3 (model no. FL3-11) spectrofluorometer. The fluorescence spectra were corrected for spectral sensitivity of the instrument. For steady-state experiments all the samples were excited at 408 nm. The time-resolved fluorescence setup was described in detail in our earlier publication.[36] Briefly, the samples were excited at 408 nm using a picosecond diode laser (IBH) and the signals were collected at the magic angles (54.7°) using a Hamamatsu MCP PMT (3809U). The instrument response function was ∼90 ps. The same setup was used for time-resolved anisotropy measurements. For the anisotropy decays we used motorized polarizer in the emission side. The emission intensity at parallel (I) and perpendicular ($I_\perp$) polarizations was collected alternatively until a certain peak difference between parallel (I) and perpendicular ($I_\perp$) decay was reached. The peak difference depends on the tail matching of the parallel (I) and perpendicular ($I_\perp$) decays. The analysis of the data was done using IBH DAS 6 decay analysis software. The different temperature was maintained using a Neslab Thermostat (RTE7). For viscosity measurement we used an advanced rheometer (TA instrument, AR 1000).

3. Results

3.1. Steady-State Studies. The emission peak of C-153 in neat [bmim][PF_6] is around 527 nm, which is very close to that in methanol. So the polarity of pure [bmim][PF_6] is close to methanol. On addition of Brij-35 to pure IL, a little blue shift is observed with a very large increase in intensity. These indicate that C-153 is partitioned in the IL and micellar interface. The emission maxima in neat [bmim][PF_6] and in the presence of Brij-35 are listed in Table 1. Figure 1 illustrates the emission spectra of C-153 in neat [bmim][PF_6] and in [bmim][PF_6]−Brij-35 micelles. The environment at the micelles or at the interface experienced by C-153 is less polar than the bulk IL.

3.2. Solvation Dynamics. To study solvent relaxation dynamics we collected the time-resolved decays monitored at

TABLE 1: Emission Maxima and Decay Parameters of C-153 in Pure IL and in IL−Brij Systems

medium	temp (K)	λ_{em}^{max} (nm)	$\Delta\nu^{a}$ (cm^{-1})	a_1	τ_1 (ns)	a_2	τ_2 (ns)	$\langle\tau_s\rangle^{a}$ (ns)
pure [bmim][PF$_6$]	298	528	915	0.81	0.8	0.19	12.49	3.02
[bmim][PF$_6$] + 39 mM Brij-35	298	527	920	0.79	0.86	0.21	12.97	3.40
[bmim][PF$_6$] + 120 mM Brij-35	298	527	954	0.75	0.89	0.25	14.00	4.16
[bmim][PF$_6$] + 250 mM Brij-35	298	526	915	0.70	0.98	0.30	15.88	5.45
pure [bmim][PF$_6$]	313	528	819	0.89	0.53	0.11	11.21	1.70
[bmim][PF$_6$] + 39 mM Brij-35	313	527	843	0.87	0.56	0.13	11.86	2.03
[bmim][PF$_6$] + 120 mM Brij-35	313	527	867	0.84	0.61	0.16	14.04	2.76
[bmim][PF$_6$] + 250 mM Brij-35	313	526	836	0.79	0.74	0.21	15.18	3.77
pure [bmim][PF$_6$]	333	528	728	0.66	0.22	0.34	0.69	0.38
[bmim][PF$_6$] + 39 mM Brij-35	333	527	733	0.76	0.28	0.24	0.97	0.44
[bmim][PF$_6$] + 120 mM Brij-35	333	527	743	0.93	0.38	0.07	6.50	0.81
[bmim][PF$_6$] + 250 mM Brij-35	333	526	783	0.89	0.49	0.11	9.25	1.45

[a] Experimental error within ±5%.

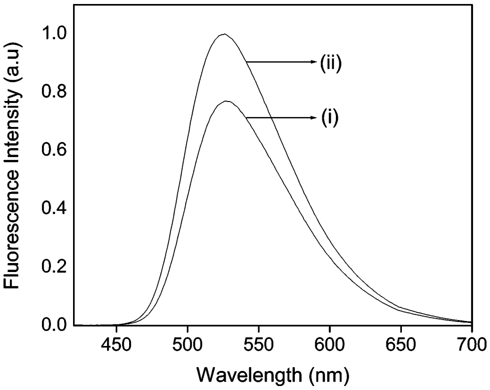


Figure 1. Emission spectra of C-153 in (i) neat [bmim][PF$_6$] and (ii) adding 120 mM Brij-35 in [bmim][PF$_6$] at 298 K.

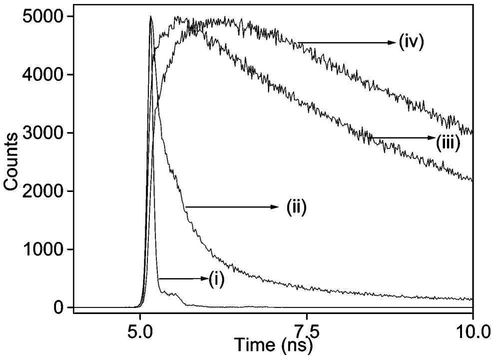


Figure 2. Fluorescence decays of C-153 in neat [bmim][PF$_6$] after addition of 39 mM of Brij-35 at 298 K: (i) instrument response function; (ii) 460 nm; (iii) 530 nm; (iv) 640 nm.

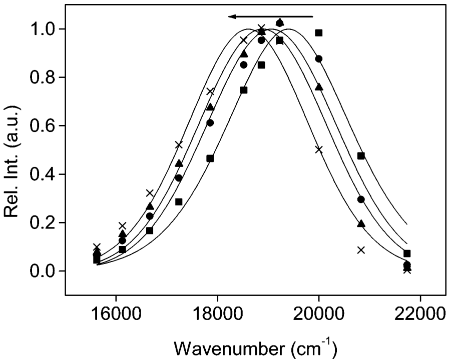


Figure 3. Time-resolved emission spectra of C-153 in [bmim][PF$_6$] after addition of 39 mM of Brij-35 at 298 K at (i) 0 ps (■), (ii) 500 ps (●), (iii) 1000 ps (▲), and (iv) 5000 ps (×).

different wavelengths for all the systems. The decays at the red edge of the emission spectra were preceded by a growth in nanosecond time scale while decays at the short wavelengths are fast. The wavelength-dependent behavior of temporal decays of C-153 clearly indicates that solvent relaxation is taking place in these systems. The representative decays of C-153 monitoring at three different wavelengths are shown in Figure 2. The time-resolved emission spectra (TRES) were constructed by following the procedure of Fleming and Maroncelli[41] as described in our earlier publication.[36] The solvation dynamics was monitored by the solvent response function 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 0, t, and infinity, respectively. The peak frequencies were evaluated from the TRES. The representative TRES of C-153 in [bmim][PF$_6$] in the presence of 39 mM Brij-35 at 298 K are shown in Figure 3. The solvent response function ($C(t)$) 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 relaxation times with amplitude a_1 and a_2 respectively. It is important to mention here that Maroncelli and co-workers[35] used stretched exponential to describe the nonexponential nature of the solvation dynamics in different ILs. However, we did not obtain a good fit to a stretched exponential function. In our case the best fitting was observed by using the biexponential function as eq 2. To improve the quality of biexponential fitting we used a stretched factor β as Huppert et al. did in case of molten salt.[42] But in this case also the fittings were not improved on varying β value from 0.5 to 0.9. Samanta and co workers[34] earlier reported the similar observation. The solvent relaxation times thus obtained from the solvent correlation function ($C(t)$) are summarized in Table 1. The representative decays of $C(t)$ are shown in Figure 4. From Table 1 we obtained average solvation time of C-153 in neat [bmim][PF$_6$] of ~3 ns consisting of a fast component around 800 ps (81% in amplitude) and a slow component around 12.5 ns (19% in amplitude). The average solvation time in the present case is comparatively smaller than our previous report.[36a]

3.3. Time-Resolved Anisotropy Studies. Time-resolved anisotropy were recorded at the emission maxima of steady-state spectra. Time-resolved fluorescence anisotropy, $r(t)$, was estimated using the following equation:

$$r(t) = \frac{I(t) - GI_{||}(t)}{I(t) + 2GI_{||}(t)} \tag{3}$$

Here G is the correction factor for detector sensitivity to the

TABLE 2: Rotational Relaxation Parameters of C-153 in IL−Brij Systems

medium	temp (K)	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$\langle\tau_r\rangle^a$ (ns)
pure [bmim][PF_6]	298	0.27			1	4.70	4.70
[bmim][PF_6] + 39 mM Brij-35	298	0.32	0.17	0.73	0.83	7.25	6.14
[bmim][PF_6] + 120 mM Brij-35	298	0.30	0.12	0.80	0.88	8.17	7.28
[bmim][PF_6] + 250 mM Brij-35	298	0.34	0.19	1.00	0.81	11.09	9.17
pure [bmim][PF_6]	313	0.30			1	3.91	3.91
[bmim][PF_6] + 39 mM Brij-35	313	0.34	0.14	0.60	0.86	4.81	4.22
[bmim][PF_6] + 120 mM Brij-35	313	0.34	0.20	0.86	0.80	5.28	4.40
[bmim][PF_6] + 250 mM Brij-35	313	0.32	0.18	0.91	0.82	6.71	5.66
pure [bmim][PF_6]	333	0.32			1	2.10	2.10
[bmim][PF_6] + 39 mM Brij-35	333	0.34	0.13	0.35	0.87	2.45	2.18
[bmim][PF_6] + 120 mM Brij-35	333	0.33	0.18	0.51	0.82	2.69	2.30
[bmim][PF_6] + 250 mM Brij-35	333	0.32	0.18	0.50	0.82	3.32	2.81

[a] Experimental error within ±5%.

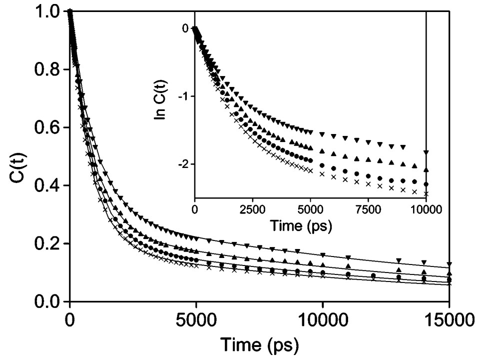


Figure 4. Decay of solvent response function $C(t)$ of C-153 at 298 K in [bmim][PF_6] (×) and after addition of 39 mM Brij-35 (●), 120 mM Brij-35 (▲), and 250 mM Brij-35 (▼). In the inset is ln $C(t)$ vs time plot for of C-153 at 298 K in [bmim][PF_6] (×) and after addition of 39 mM Brij-35 (●), 120 mM Brij-35 (▲), and 250 mM Brij-35 (▼)

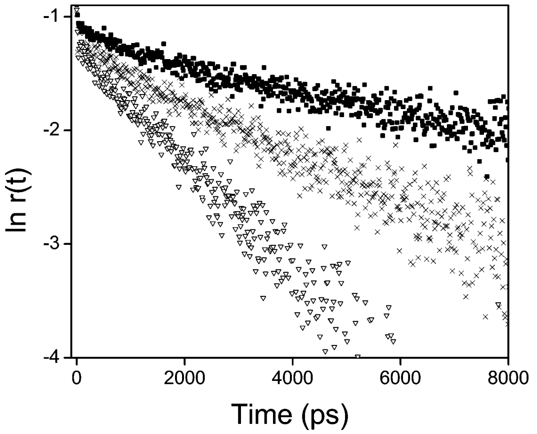


Figure 5. Anisotropy decays of C-153 in [bmim]PF_6 adding 250 mM Brij-35 at 298 K (■), at 313 K (×), and at 333 K (▽).

polarization direction of the emission. $I_{\parallel}(t)$ and $I_{\perp}(t)$ are fluorescence decays parallel and perpendicular to the polarization of the excitation light, respectively. It is important to note that the anisotropy decays in pure [bmim][PF_6] were fitted with single-exponential functions. On the other hand, in the presence of surfactant the anisotropy decays were fitted with the biexponential functions. The anisotropy decay parameters are listed in Table 2. The representative decays of anisotropy are shown in Figure 5.

4. Discussion

4.1. Solvation Dynamics in Pure [bmim][PF_6]. At first we will discuss the important features of solvation dynamics in pure ionic liquids. It should be noted that solvation dynamics in ILs are vastly different from that in the isopolar conventional solvents such as methanol, acetonitrile, etc.[2,3] Solvation in ILs takes place due to the motion of the ions around an excited dye, while in water, methanol, and acetonitrile, i.e., in polar solvents, solvation takes place as the solvent molecules reorient themselves around an excited dye. Chapman and Maroncelli[43] showed that ionic solvation is slower compared to the pure solvent and dependent on the viscosity of the medium. Samanta and co-workers observed biphasic solvation dynamics in different ILs.[34] They ascribed the fast component to the motion of the anions, and the slow component is ascribed to the collective motions of the both cations and anions, respectively. However, Maroncelli et al.[35] postulated that the fast component arises due to the translation adjustment of the ions with in the solvation structure present at the time of solute excitation. According to them the slow component is viscosity dependent and involves large-scale rearrangement of the solvent structure. Thus, the fast component of solvation dynamics in ILs originates from local motion of the ions and the slow component comes from the diffusional motion of both cations and anions and is related to viscosity.

From Table 1 we obtained that the average solvent relaxation time of C-153 in neat [bmim][PF_6] is ∼3 ns with a fast component of 800 ps (80% in amplitude) and a slow component of 12.5 ns (20% in amplitude). This value is comparatively smaller than our previous report where we estimated the average solvation time in pure [bmim][PF_6] around 3.3 ns. We suspect that the discrepancy between our present results and the previous one arises due to the presence of small amount of water in IL. It was reported by Seddon[44] et al. that viscosity of neat ILs decreases due to the addition of cosolvents. The present of cosolvents reduces the cohesive energy resulting in a decrease in the visocosity. The smaller solvation time in the present case thus may be due to the decrease in viscosity of the medium. Recently we reported that solvation dynamics in neat ILs becomes faster on addition of cosolvents such as water, methanol, acetonitrile, etc.[36b,c] It was found in those reports that average solvation time is linearly correlated to the viscosity of the medium.

In this context we may compare the present value of average solvation time with those measured by other groups. Maroncelli et al. reported that average solvation time in [bmim][PF_6] around 1.8 ns using 4- aminophthalimide and 1.0 ns using C-153 as the probes.[35a,35c] Samanta et al. reported average solvation time in [bmim][PF_6] around 1.0 ns using Nile red as the probe.[34d] The solvation times reported by other the groups are smaller than our result.[45] This is due to the fact that the quality of the ionic liquid used by different groups is vastly different and the presence of a small amount of impurity like chloride ions has great influence on the viscosity of ILs as well as on the dynamics. In a recent study Chowdhury and co-workers[45] reported that a small amount of impurity present in IL might affect the solvation time severely. Recently Maroncelli and co-workers[35d] pointed out that discrepancy might arise due to the different methods adopted by different groups to represent data. The lifetime of the probes measured in a different setup has a great influence on the slow component of response function. Maroncelli and co-workers[35] preferred to fit the $\nu(t)$ data to a stretch exponential function while the other groups[34,36] fit the data to a multiexponential function. According to Maroncelii et al. $\nu(t)$ data often contains a component slower than the lifetime of the probe, and when this is fitted to a multiexponential function, the tails fit to a small amplitude component with higher time constant than solute lifetime. This may be a plausible explanation for obtaining the higher average solvation time in our case.

4.2. Solvation Dynamics in [bmim][PF$_6$]−Brij-35 Micelles. While average solvation time increases by two times in the IL−Brij-35 micellar system compared to pure IL, several thousand times increase in solvation time is observed in water−Brij-35 micelles[10e] compared to pure water.[1] Let us first summarize the salient features of solvation dynamics in pure water and in water−Brij-35 micelles. Then we will discuss the factors causing solvation dynamics in the IL−Brij-35 micellar system. In pure water solvent relaxation occurs on the femtosecond time scale. Jimenez et al.[1] observed that solvent relaxation of C-343 in water consists of an initial decay of 55 fs (50%), attributed to the librational motions. Solvent relaxation dynamics of C-480 in water is bimodal with time constants of $<$50 ps (26%) and 310 fs (74%).[1,2] The very fast solvent relaxation in water is attributed to the intermolecular vibrational and librational motions. These processes require very small activation energy. In micelles the solvent relaxation dynamics is slowing down several times as compared to pure water. Recently, we[10e] investigated the solvent and rotational relaxation in Brij micellar systems in aqueous solution using C-480 as a probe. It was found that in this system the relaxation dynamics is retarded severely compared to pure water. The average solvent relaxation time in the Brij-35 micelles is around 1 ns with a fast component of 490 ps (87%) and a slow component of 4.02 ns (13%). The main effect explaining the fast component in water−Brij-35 micelles is likely the presence of water molecules attached to the palisade layer. The slow component may be arising from the small amplitude motion of the polar headgroups of the surfactant molecules in the vicinity of the probe. The reorientation of the strongly hydrogen bonded water molecules located between the two surfactant molecules may be responsible for slowing down the relaxation process. Thus, in the water−micellar system the relaxation is likely to be significantly slowed compared to that in pure water. However, average solvation time increases only 2−3-fold on going from pure IL to the IL−micellar system. In pure [bmim][PF$_6$] at 298 K the solvent relaxation time is approximately 3 ns with a fast component of 0.80 ns (80%) and a slow component of 12.5 ns (20%). In the presence of 250 mM Brij-35 we obtained the maximum solvent relaxation time of 5.45 ns with a fast component of 0.98 ns (70%) and a slow component of 15.90 ns (30%). Thus, the 2−3-fold increase in solvation time after micelle formation in IL is obviously due to the very high viscosity of neat IL.

From Table 1 we see that with addition of maximum concentration (250 mM) Brij-35 to IL the fast component increases only by 200 ps, while the slow component increases by 2 ns to 3 ns. Again average solvation time in pure IL is ∼3 ns, and on addition of 250 mM Brij-35 to this solution average solvation time increases up to 5.45 ns at 298 K**.** It seems to us that with the addition of surfactant to IL the viscosity increases and consequently the solvent relaxation time increases. The increase in the slow component directly depends on the viscosity of the medium and involves large-scale rearrangement of the cations and anions together with the small amplitude motion of the surfactant polar headgroups. The viscosity suppresses the collective diffusive motion of the ions, and consequently, the solvent relaxation time increases. To establish this fact we plotted average solvation with viscosity (Table 3). The linear relationship in Figure 6 between average solvation time and viscosity indicates that solvation time is directly proportional to the observed viscosity of the medium. A large amplitude motion associated with the poly(oxyethylene) (POE) chain is ruled out since the motion of the polar headgroups of the surfactant is very much restricted and chain dynamics occurs on a much larger time scale (100 ns).[46]

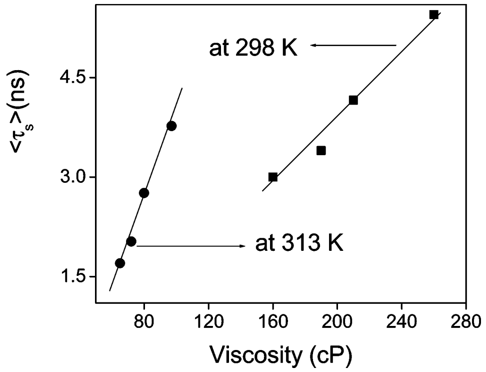


Figure 6. Plot of average solvation time vs viscosity at 298 and 313 K.

TABLE 3: Viscosity of IL−Brij-35 Systems at Two Different Temperatures

medium	temp (K)	viscosity (cP)
pure [bmim][PF$_6$]	298	160
[bmim][PF$_6$] + 39 mM Brij-35	298	190
[bmim][PF$_6$] + 120 mM Brij-35	298	210
[bmim][PF$_6$] + 250 mM Brij-35	298	260
pure [bmim][PF$_6$]	313	65
[bmim][PF$_6$] + 39 mM Brij-35	313	72
[bmim][PF$_6$] + 120 mM Brij-35	313	80
[bmim][PF$_6$] + 250 mM Brij-35	313	97

However, in the present case the small increase in the fast component (200 ps) perhaps is not related to the increased viscosity of the solvent. Samanta and co-workers[34] assumed that the fast component arises due to the initial response of the anion. If we consider their explanation, then it is obviously that increase in the fast component of the average solvation time is due to the strong hydrogen bonding between the anions of IL, i.e., $[PF_6]^-$ and the −OH group of the surfactant molecules. It was reported in the literature[47] that $[PF_6]^-$ is capable of hydrogen bonding with the −OH group of water molecules. Recently Bright et al.[48] and Chakrabarty et al.[36b] reported solvent relaxation dynamics in neat [bmim][PF$_6$], [hmim][PF$_6$], and [bmim][PF$_6$]−water and [hmim][PF$_6$]−water mixtures. In those studies it was found that the hydrogen-bonding ability of the anion with water has a great influences on the observed solvent relaxation dynamics. We mentioned earlier that water molecules may be present as an impurity in the IL. If it is so, the increase in the fast component may also be attributed to the hydrogen bonding between the water molecules and the −OH group of the surfactant.

Another interesting observation is that at all the temperatures (except at 333 K) with increase in surfactant concentration the

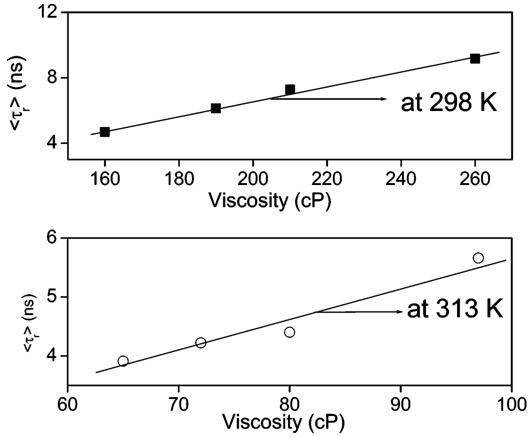


Figure 7. Plot of average rotational time vs viscosity at 298 and 313 K.

relative magnitude of the fast component decreases. It is because of the fact that C-153 partitions inside the micelles or at the micellar interface. Since these environments are less polar than bulk solvent, they would tend to contribute less to the Stokes' shift on polarization. Since these would represent the local rapid response, the decrease in the relative magnitude of the rapid component of Stokes' shift could simply be due to a partition of C-153 in the micelles or at its interface.

Though we observed a slow solvent relaxation component in the present case, a substantial part of the fast (<90 ps) solvent relaxation component is missed due to the limited time resolution of our setup. We applied the method of Fee and Maroncelli[49] to calculate the missing component in the solvent relaxation dynamics. The time zero spectrum was estimated using this process. The predicted Stokes' shift in the neat IL is approximately 1480 cm^{-1} for [bmim][PF_6] at 298 K. The observed Stokes' shift is approximately 900 cm^{-1}. Thus, we missed at least 40% of the total solvent relaxation dynamics. However, addition of the Brij-35 surfactant led to the decrease in the missing component. At maximum concentration of the surfactant (250 mM) the missing component is observed to be 35% at 298 K. As the temperature rises up, the missing component increases. In pure [bmim][PF_6] at 333 K the missing component is ∼49%, and it decreases to ∼40% when maximum concentration of surfactant is added. In all the cases there is an increase in the value of $\nu(\infty)$ at higher temperature. The magnitude of the Stokes shift decreases with the increase in temperature. The missing components which occur rapidly without the rearrangement of the neighboring molecules in <5 ps remain unobserved in the present case is due to the low time resolution of our instrument.

4.3. Rotational Relaxation Study. From Table 2 it is seen that with increase in the surfactant concentration the rotational time increases. Both the fast and slow component increases with addition of the surfactant molecules. At 298 K the rotational relaxation time of C-153 in pure IL is 4.70 ns, while in the presence of 250 mM Brij-35 it becomes 9.17 ns. It is seen from Table 2 that fast component increases by 200−300 ps while the slow component increases by 3−5 ns. It seems that the increased viscosity of the medium is responsible for the increase in the average rotational relaxation time. We plotted rotational relaxation time as a function of viscosity of the solvent (Figure 7). The linear corelationship between the viscosity of the medium and the rotational time confirms that viscosity is responsible for increase in the rotational relaxation time, and it supports the hydrodynamic theory.

The other possible reason is that C-153 may be hydrogen bonded with the polar −OH headgroups of the surfactant hence slowing down the average rotational relaxation time.

5. Conclusion

The solvent relaxation dynamics is estimated in neat [bmim][PF_6] and in [bmim][PF_6]−Brij micelles. Solvation is found to occur in two well-separated time regimes. The solvent relaxation dynamics is slower in [bmim][PF_6]−Brij micelles as compared to [bmim][PF_6]. The steady increase in the solvent relaxation time with addition of the surfactant is ascribed to increase in viscosity of the solution. However, the slowing down in the solvation time on going from neat IL to IL confined micelles is much smaller compared to that on going from water to water confinded micellar aggregates. The fast component originates from the translational motion of the anions and does not depend on viscosity. The magnitude of the fast component increases due to the hydrogen bonding between the −OH group of the surfactant and the $[PF_6]^-$ ions. At higher temperature the viscosity decreases, the motions of ions become faster hence the solvent relaxation time decreases. The same trend is observed in the rotational relaxation dynamics. The increase in the rotational relaxation time of the probe after formation of the micelles in [bmim][PF_6] is significantly smaller than the increase in aqueous micelle. The higher rotational relaxation time in the IL−surfactant mixture is attributed to the increase in the viscosity of the solution.

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