Dynamics of Solvation and Rotational Relaxation of Coumarin 153 in Ionic Liquid Confined Nanometer-Sized Microemulsions

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The effects of confinement of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate on solvation dynamics and rotational relaxation of Coumarin 153 (C-153) in Triton X-100/cyclohexane microemulsions have been explored using steady-state and picosecond time-resolved emission spectroscopy. The steady-state and rotational relaxation data indicate that C-153 molecules are incorporated in the core of the microemulsions. The average rotational relaxation time increases with increase in *w* ([bmim][BF$_4$]/[TX-100]) values. The solvent relaxation in the core of the microemulsion occurs on two different time scales and is almost insensitive to the increase in *w* values. The solvent relaxation is retarded in the pool of the microemulsions compared to the neat solvent. Though, the retardation is very small compared to several-fold retardation of the solvation time of the conventional solvent inside the pool of the microemulsions.

1. Introduction

In recent years, room-temperature ionic liquids (ILs) have been extensively used as environment friendly "green" substitutes for the common organic solvents.[1] Their unique properties such as thermal stability, high ionic conductivity, nonflammable nature, suitable polarity, and negligible vapor pressure make them quite useful as environmentally benign solvents.[1] ILs are organic salts composed of anions and cations and remain in a liquid state at ambient temperatures. They can be extensively used for organic chemical reactions[2] and electrochemical applications.[3] Nanostructured TiO$_2$ particles have been synthesized in ILs.[4] ILs are also used to increase the thermostability of protein compared to water.[5] Many photophysical studies have been undertaken in these ILs. Aki et al.[6a] determined the polarity of the four imidazolium- and pyridinium-based ILs using UV−vis absorption and fluorescence spectroscopy. Muldoon et al.[6b] determined the polarity of the ILs using solvatochromic probes. The photoisomerization reaction[7] and intramolecular excimer formation kinetics[8] have been studied in ILs. The effects of temperature and added carbon dioxide on different fluorescent probes in ILs have been studied.[9] There are also a few reports available on time-dependent solvation in ILs.[10−13] Solvation in these ILs is mainly contributed by the ions. Solvation dynamics in these ILs is biphasic. Several theoretical studies have also been undertaken in these ILs. Structure and dynamics[14] and polarity[15] of the ILs have been investigated. Through the use of molecular dynamics simulations, the solvent responses of the ILs have been studied.[16] Sim et al.[16a] concluded that the fast component of the solvation dynamics arises due to the diffusional motion of the anion and the slower component arises due to the collective motion of the cation and anion. But in a recent paper, Kobrak et al.[16b] showed that collective cation−anion motions are responsible for the fast component of the solvation dynamics. Solvation dynamics in IL−water mixed solvents were also carried out.[17] Recent studies showed some
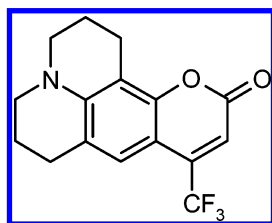
surfactants may form micelles in ILs.[18] ILs are highly polar, and their polarities are very close to those of short-chain alcohols.[6] So, ILs may be used as the polar cores of the microemulsions. In a recent work by Gao et al., 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$])/Triton X-100 (TX-100)/cyclohexane microemulsions have been prepared and characterized.[19]

Water-in-oil microemulsions are used as elegant models of biological membranes.[20] AOT (sodium dioctylsulfosuccinate) has been extensively used to form microemulsions. The solvent relaxation studies in microemulsions are quite enriched. The solvation dynamics in AOT/water microemulsions were investigated by Bhattacharyya et al.[21] and Bright et al.[22] In microemulsions, a long bimodal relaxation time was observed compared to that of pure water, and the dynamics were strongly dependent on the *w* ([water]/[surfactant]) values. The subpicosecond component in the solvation dynamics in AOT microemulsions was observed by Levinger et al.[23] To explain the bimodal relaxation in microemulsions, Bagchi et al.[24] proposed a dynamic exchange between the bound and free water molecules. Solvation dynamics in microemulsions with nonaqueous polar cores have been also extensively studied.[25−28] Levinger et al.[25] characterized various types of microemulsions in isooctane using AOT as a surfactant and formamide, methanol, acetonitrile, ethylene glycol, and *N,N*-dimethylformamide as polar solvents. Solvation dynamics using methanol,[26,27] acetonitrile,[26,27] formamide,[27,28] and DMF[28] as polar core have been investigated. Solvation dynamics in TX-100 microemulsions have been also investigated.[29] Solvation dynamics inside TX-100 microemulsions are substantially retarded compared to the solvation dynamics in bulk water.

Microemulsions with an IL as the polar core dispersed in an oil-continuous phase by suitable surfactants may have some unknown properties and may have some potential applications due to the unique features of ILs and microemulsions. Moreover, the diameters of IL-containing microemulsions[19] are much larger compared to those of water or other polar liquid solubilized microemulsions.[21−23,24−28] Though solvation dynamics in neat

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SCHEME 1: Structure of Coumarin 153

Figure 1. Normalized emission spectra of C-153 in (i) cyclohexane and [bmim][BF$_4$]/TX-100/cyclohexane microemulsions at (ii) $w = 0$, (iii) $w = 0.2$, (iv) $w = 1$, and (v) $w = 1.5$.

ILs have been extensively studied,[10-13] to the best of our knowledge, there is no report regarding the solvent relaxation in the polar core of microemulsions containing ILs. In this paper, we report solvent relaxation and rotational relaxation results in [bmim][BF$_4$]/TX-100/cyclohexane microemulsions for the first time. The [bmim][BF$_4$]/TX-100/cyclohexane microemulsions have been characterized by phase behavior, conductivity measurement, dynamic light scattering, and freeze fractured electron microscopy.[19] We have used Coumarin 153 (C-153, Scheme 1) as an experimental probe because it is considered to be an ideal solvation probe.[30] The ground state of C-153 is polar with a measured dipole moment 6.55 ± 0.01 D. The S$_0$ → S$_1$ transitions lead to the S$_1$ dipole moment between 14.2 and 16.0 D.[30] The excitation of C-153 does not involve specific changes in solute−solvent interactions. The solvation time of C-153 in neat [bmim][BF$_4$] is also reported.[10a]

2. Experimental Section

C-153 (laser grade, Exciton) was used as received. [bmim][BF$_4$] was obtained from Fluka chemicals (98% purity) and purified using the literature procedure.[12] Cyclohexane (spectroscopic grade, Spectrochem, India) was used as received. The solution was prepared using the literature procedure.[19] The weight fraction of the TX-100 in the microemulsions is 0.45, and the IL/TX-100 molar ratios (w) are 0.2, 1, and 1.5 in the solvent and rotational relaxation studies. The final concentration of C-153 in all the experiments is ∼5 × 10^{-5} M.

The absorption and fluorescence spectra are measured using a Shimadzu (model no. UV1601) spectrophotometer and a Spex Fluorolog-3 (model no. FL3-11) spectrofluorimeter. The fluorescence spectra are corrected for the spectral sensitivity of the instrument. For steady-state experiments, all of the samples are excited at 410 nm. The detailed time-resolved fluorescence setup is described in our earlier publication.[29] Briefly, the samples are excited at 408 nm using a picosecond laser diode (IBH, Nanoled), and the signals are collected at magic angles (54.7°) using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is ∼90 ps. The same setup is used for anisotropy measurements. The analysis of the data is done using IBH DAS, version 6, decay analysis software. The same software is also used to analyze the anisotropy data. The temperature is kept 35 ± 0.1 °C using a Neslab RTE-7 temperature controller, because the micoemulsions are stable at 35 °C.[19]

3. Results and Discussions

3.1. Steady-State Studies. C-153 in cyclohexane shows two strong absorption peaks, one at 394 nm and another at 410 nm, though the peak at 394 nm has the maximum absorbance. After addition of TX-100 and [bmim][BF$_4$] into this solution, one strong peak is observed at ∼410 nm.

The representative emission spectra of C-153 in [bmim][BF$_4$]/TX-100/cyclohexane microemulsions are shown in Figure 1. In cyclohexane, C-153 shows a strong emission peak at 452
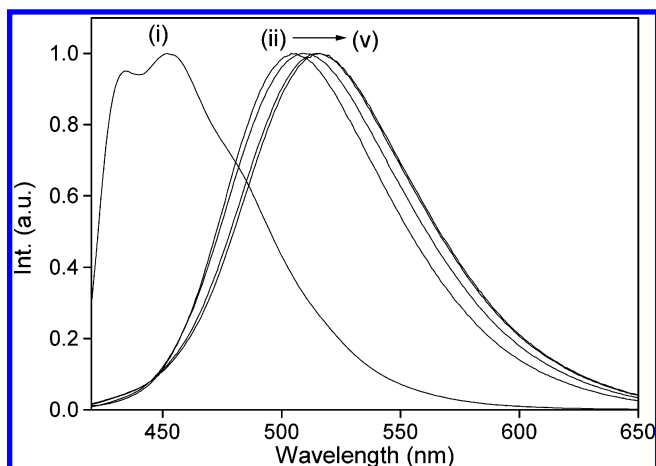
nm. With addition of TX-100 in cyclohexane, the emission spectrum is red-shifted to 505 nm. Due to the addition of [bmim]-[BF$_4$], the emission peak of C-153 has been gradually red-shifted to ∼508 and 516 nm as w increases from 0.2 to 1.5. The reported emission peak of C-153 in neat [bmim][BF$_4$] is ∼537 nm.[10a] Thus, it clearly indicates that the microenvironment surrounding the probe molecules in the microemulsions is not like that in neat [bmim][BF$_4$].

The emission spectra of C-153 in the microemulsions are markedly different from the emission spectra in cyclohexane. The red shift in emission maximum indicates C-153 molecules have experienced more polarity compared to cyclohexane. It indicates that probe molecules are gradually encapsulated in the [bmim][BF$_4$] pool of the microemulsions. TX-100 can form microemulsions in cyclohexane.[31] Due to this reason, we have observed a large red shift from cyclohexane to $w = 0$. With addition of [bmim][BF$_4$] in this system, the polarity again increases, and the emission peak becomes further red-shifted. But the observed emission peak at $w = 1.5$ (516 nm) is blue-shifted compared to the emission peak in neat [bmim][BF$_4$] (537 nm).[10a] It indicates that the polarity of the microemulsions is much lower compared to that of neat [bmim][BF$_4$].

3.2. Time-Resolved Studies. *3.2.1. Solvation Dynamics.* We have observed a dynamic Stokes' shift in the emission spectrum of C-153 in the microemulsions at different w values. The fluorescence decays of C-153 are markedly dependent on the emission wavelengths. At short wavelengths, a fast decay is observed. The growth at long wavelengths indicates that the C-153 molecule undergoes solvation in these microemulsions. Moreover, we have also observed a dynamic Stokes' shift at $w = 0$ (without addition of [bmim][BF$_4$]). A representative decay of C-153 at $w = 1$ at three different wavelengths is shown in Figure 2. The time-resolved emission spectra (TRES) has been constructed following the procedure of Fleming and Maroncelli[32] and has been described in our earlier publications.[27] To extract the time constant of solvation, we have constructed the decay of solvent response function ($C(t)$), which is defined as

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

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 at $w = 0.2$ is
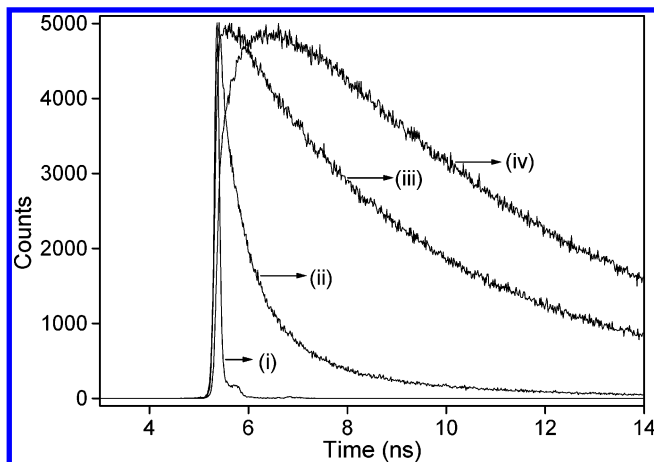
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Figure 2. Fluorescence decays of C-153 in [bmim][BF$_4$]/TX-100/ cyclohexane microemulsions at $w = 1$ at (i) instrument response function, (ii) 450, (iii) 510, and (iv) 620 nm.
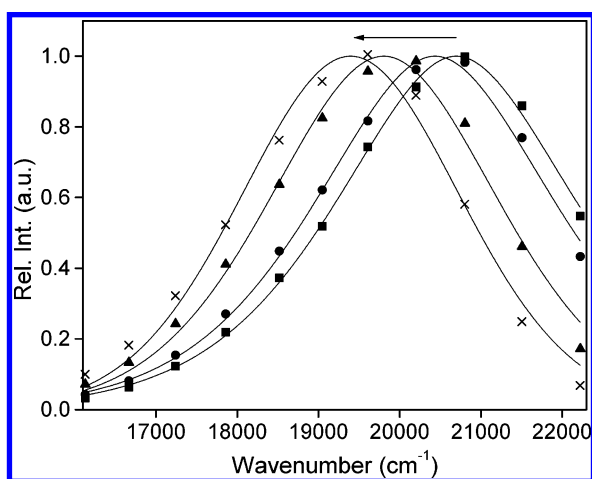

Figure 3. Time-resolved emission spectra of C-153 in [bmim][BF$_4$]/ TX-100/cyclohexane microemulsions at $w = 0.2$ at (i) 0 ps (■), (ii) 200 ps (●), (iii) 1000 ps (▲), and (iv) 3000 ps (×).
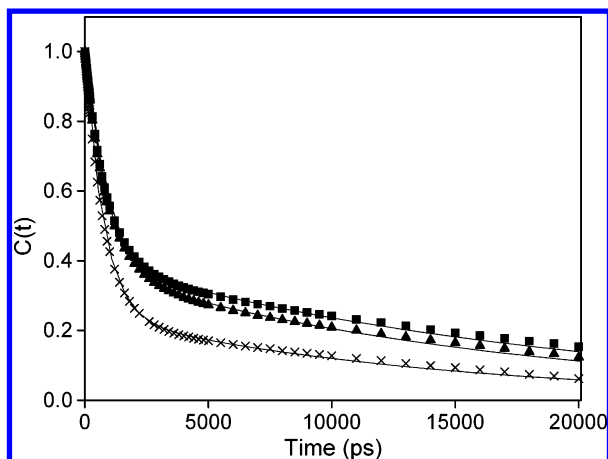

Figure 4. Decay of the solvent response function ($C(t)$) of C-153 in [bmim][BF$_4$]/TX-100/cyclohexane microemulsions at $w = 0$ (×), $w = 0.2$ (■), and $w = 1.5$ (▲).

shown in Figure 3. The decay of $C(t)$ with time (Figure 4) was fitted to a biexponental function

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

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

TABLE 1: Decay Parameters of $C(t)$ and Missing Components of C-153 in [bmim][BF$_4$]/TX-100/Cyclohexane Microemulsions at Different w Values

w	$\Delta\nu^a$ (cm^{-1})	a_1	τ_1 (ns)	a_2	τ_2 (ns)	$\langle\tau_s\rangle^b$ (ns)	missing component
0	1480	0.74	0.731	0.26	12.96	3.91	24%
0.2	2007	0.60	0.815	0.40	18.94	8.06	15%
1	1899	0.62	0.888	0.38	16.99	7.01	22%
1.5	1857	0.62	0.839	0.38	16.64	6.84	24%

$^a \Delta\nu = \nu_0 - \nu_\infty$ $^b \langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$

summarized in Table 1. We have chosen biexponential fitting for $C(t)$ in our case because in other microemulsions similar types of biexponential solvent relaxation were observed.[21−22,25−29] The solvent relaxation of IL-containing microemulsions and neat IL are occurring in the same time scales. The observed solvation time at $w = 0$ is bimodal (with time constants of 0.731 and 12.96 ns) with an average solvation time of 3.91 ns. We have observed a bimodal solvation time in all of the microemulsions, solvation time increases due to the addition of [bmim][BF$_4$], and at $w = 0.2$, the average solvation time is 8.06 ns. Further addition of [bmim][BF$_4$] decreases the average solvation time, and at $w = 1$, it becomes 7.01 ns. At $w = 1.5$ (6.84 ns), the solvation time is very close to the value at $w = 1$.

In the present study using the TCSPC setup, we are missing the fast component of the solvation dynamics ($<$90 ps). We can apply the method of Fee and Maroncelli[33] to calculate the missing component. We have calculated a "time zero spectrum" using the above procedure. This indicates a total Stokes' shift of $\sim$2372 cm^{-1} at $w = 0.2$. But we have observed 2007 cm^{-1} as the total Stokes' shift. Thus, we have missed $\sim$15% of the total spectral shift. The missing components for all of the w values are tabulated in Table 1. From Table 1, it is clear that the missing components are increasing with an increase in the w values. Samanta et al.[10a] reported that more than 50% of the total solvent response in neat [bmim][BF$_4$] occurs in subpicosecond time scales. Petrich and co-workers[13] also observed that half or more than half of the solvent response was completed within 100 ps. So, the percentage of the missing component decreases in microemulsions compared to that of neat [bmim][BF$_4$]. It suggests that the solvent relaxation of IL is much slower in microemulsions compared to that of neat IL.

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

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

where G is the correction factor for detector sensitivity to the polarization direction of the emission and $I_\parallel(t)$ and $I_\perp(t)$ are the fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. The representative anisotropy decays of C-153 at $w = 0$ and at $w = 1.5$ are shown in Figure 5. The decay parameters are listed in Table 2. The initial anisotropy values (r_0) are also listed in Table 2. The rotational relaxation of C-153 in cyclohexane is fitted with a single exponential function, and the rotational relxation time is 135 ps. But in microemulsions, all of the rotational relaxation decays are fitted with a biexponential function. For example, at $w = 0.2$, the observed rotational relaxation time is bimodal, having components of 0.348 and 2.15 ns, respectively. The average rotational relaxation time can be roughly used to
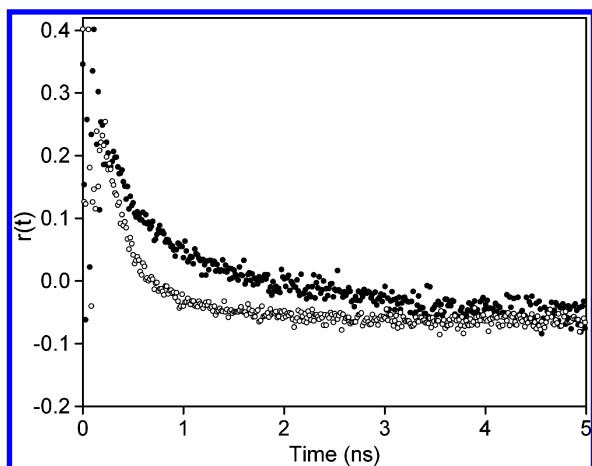
Figure 5. Decay of the fluorescence anisotropy ($r(t)$) of C-153 in [bmim][BF$_4$]/TX-100/cyclohexane microemulsions at $w = 0$ (○) and at $w = 1.5$ (●).

TABLE 2: Rotational Relaxation Time of C-153 in [bmim][BF$_4$]/TX-100/Cyclohexane Microemulsions at Different w Values

w	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$\langle \tau_r \rangle^a$ (ns)
0	0.40	0.95	0.310	0.05	5.01	0.545
0.2	0.40	0.87	0.348	0.13	2.15	0.582
1	0.37	0.70	0.421	0.30	2.36	1.00
1.5	0.39	0.64	0.396	0.36	2.64	1.20

$^a \langle \tau_r \rangle = a_{1r}\tau_{1r} + a_{2r}\tau_{2r}$

compare the anisotropy decays. The average rotational relaxation time of C-153 increases from cyclohexane to the microemulsions. Again, average rotational relaxation time increases with an increase in w values.

3.3. Discussion. To comprehend the solvation dynamics results, a thorough understanding of the microemulsion structure and location of the probe within the microemulsions are necessary. Schelly et al.[32] characterized the water/TX-100/ cyclohexane microemulsions. According to them, TX-100 forms nonspherical microemulsions in cyclohexane, with cyclohexane penetrating the polar interior of the aggregates. Gao et al.[19] have showed that with addition of [bmim][BF$_4$] in TX-100/cyclohexane the size of the droplets increases with w values, similar to other microemulsions with water domains. Dynamic light scattering experiments show that the structure of the microemulsions is spherical and that the hydrodynamic diameter increases from 10 to 94 nm as w varies from 0.2 to 1.5.

The observed rotational relaxation time of C-153 in cyclohexane is 135 ps. In microemulsions, the rotational relaxation time is bimodal in nature. The biexpoential nature of rotational relaxation in TX-100/water microemulsions has been reported.[34] Both rotational relaxation times in microemulsions are slower compared to those in cyclohexane. It strongly suggests that the probe molecules are residing in the cores of the microemulsions. The biexponential anisotropy decays in these microemulsions can be explained with the help of a two-step model and wobbling-in-a-cone model.[35] The two-step model describes that observed slow rotational relaxation (τ_2) is a convolution of the relaxation time corresponding to the overall rotation motion of the micelles (τ_m) and lateral diffusion of the probe (τ_D). The wobbling-in-a-cone model describes the internal motion of the probe (τ_e) in terms of a cone angle (θ_0) and wobbling diffusion coefficient (D_w). The τ_m, τ_D, τ_e, θ_0, and D_w values are calculated from the relevant equations defined by Quitevis et al.[35a] as follows

$$\frac{1}{\tau_2} = \frac{1}{\tau_D} + \frac{1}{\tau_m} \tag{4}$$

$$\frac{1}{\tau_1} = \frac{1}{\tau_e} + \frac{1}{\tau_2} \tag{5}$$

where τ_1 and τ_2 are the observed fast and slow components. The results are summarized in Table 3. Overall rotation of the micelles can be estimated using the Stokes−Einstein−Debye relation[35]

$$\tau_m = \frac{4\pi\eta r_h^3}{3kT} \tag{6}$$

where η is the viscosity of the cyclohexane, r_h is the hydrodynamic radius of the microemulsions, and k and T are Boltzmann's constant and the absolute temperature, respectively. From Table 3, it is inferred that τ_m values are in the range of a several microseconds. Thus, overall rotation does not contribute to the anisotropy decays. Thus, slow components are solely arising due to the lateral diffusion of the probe. We have also calculated the order parameter (S) to get a clear idea about the location of the probe. The value of S is obtained from the relative amplitude of the slow component as

$$S^2 = a_{2r} \tag{7}$$

The magnitude of the S is a measure of spatial restriction and has values from zero (unrestricted motion) to 1 (completely restricted motions). The value of S ranges between 0.36 and 0.60 in the microemulsions. The high value of the order parameter indicates that probe molecules are experiencing restricted motions, which is possible if they are located in the core of the microemulsions. We can calculate the cone angle θ_0 and wobbling diffusion coefficient as follows

$$\theta_0 = \cos^{-1}\left[\frac{1}{2}((1 + 8S)^{1/2} - 1)\right] \tag{8}$$

$$D_w = \frac{7\theta^2}{24\tau_e} \tag{9}$$

where θ is cone angle in radians. The D_w value of C-153 decreases with an increase in the w values. This indicates that the microviscosity experienced by the probe increases with an increase in the w values. With an increase in the w value, the number of [bmim][BF$_4$] molecules increases in the core of the microemulsions; thus, microviscosity also increases, and the value of D_w decreases. The average rotational relaxation time also increases due to the addition of highly viscous [bmim]-[BF$_4$], consequently increasing the viscosity of the cores of the microemulsions. From the above discussion, it is clear that C-153 is located in the core of the [bmim][BF$_4$]/ TX-100 microemulsions.

The striking observation of this experiment is that we have observed slow solvation at $w = 0$ also. The observed solvation is bimodal with 3.91 ns as an average solvation time. Schelly et al.[31] suggested that at $w = 0$ TX-100 forms microemulsions in cyclohexane, with cyclohexane penetrating the polar region. The observed slow solvation at $w = 0$ is possible due to the polymer motion. The cooperative motions arising from the local dynamics of the ethylene oxide parts of TX-100 may be responsible for the slow dynamics. The reorientation of entire oligomeric molecules may also be responsible for the slow

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TABLE 3: Analytical Parameters Obtained from the Anisotropy Decays of C-153 in [bmim][BF$_4$]/TX-100/Cyclohexane Microemulsions at Different w Values

w	τ_e (ps)	τ_m (μs)	τ_D (ns)	$D_w \times 10^{-8}$ (s^{-1})	θ_0 (deg)	S
0.2	0.415	0.110	2.19	7.89	61	0.36
1	0.512	11.43	2.36	4.11	48.5	0.55
1.5	0.466	91.4	2.64	3.88	45.2	0.60

dynamics. Shirota et al. observed a similar type of slow dynamics in different liquid poly(ethylene glycol)s.[36]

At different w values of the TX-100 microemulsions, we have observed slow bimodal solvation dynamics. The average solvation time varies from 8.06 to 6.84 ns as w is increasing from 0.2 to 1.5. Thus, the observed slow dynamics is not due to the polymer motion as observed at $w = 0$ rather it reflects the dynamics of the IL in the interior of the microemulsions. The diameters of the [bmim][BF$_4$] pools of the microemulsions are 10, 47, and 94 nm at $w = 0.2$, 1, and 1.5, respectively. So the solvation times in the [bmim][BF$_4$] pools of the microemulsions are almost independent of the [bmim][BF$_4$] content or the size of the microemulsions. The situation is completely different from AOT/water or TX-100/water reverse micelles, where solvation time decreases with an increase in the w values.[21−23,29] The average solvation time of C-153 in neat [bmim][BF$_4$] is 2.13 ns.[10a] So solvation dynamics is hindered in the pool of the microemulsions compared to that in neat [bmim][BF$_4$]. But retardation is very small (only 4 times) compared to the several-fold retardation of solvation dynamics of conventional solvents inside the cores of the microemulsions.[21−23,28] Recently, Petrich and co-workers[13] have observed that half or more of the solvation is completed within 100 ps in [bmim][BF$_4$] using fluorescence up-conversion measurement. In comparison to this result, solvent relaxation is much slower in the cores of the IL-containing microemulsions.

Solvation in neat ILs is possible due to the motions of the ions. It was verified earlier that ionic solvation is slow.[37] Samanta et al.[10] ascribed the fast solvation due to the anions and the long components due to the collective motions of both anion and cation. According to Maroncelli et al.,[11] the fast component arises due to the translational adjustment of the ions within the solvent structure present at the time of solute excitation. The slow component is linked to the viscosity and involves large scale rearrangement. Kobrak et al.[16b] also showed that collective cation−anion motions are responsible for the fast component. Thus, in neat ILs, local motions of the ions are responsible for the fast component, and collective diffusive motions are responsible for the slow component. In microemulsions, the motions of the ions are also responsible for the slow solvation. Moreover, IL feels a restricted environment in the cores of the microemulsions, and both the local motion and the collective diffusive motions are slower compared to those of neat ILs. Hence, solvation dynamics become retarded in the pools of the microemulsions compared to those of the neat ILs.

The increase in [bmim][BF$_4$] contents (due to the increase in the w values) increases the sizes of the microemulsions. Thus, the local ion concentration remains almost constant near C-153. Thus, the solvation time remains almost constant with an increase in the w value. The slight decrease in solvation time with an increase in the w value is due to the increase in the sizes of the microemulsions. The increase in size leads to the increase in the free motions of the ions and decreases the solvation time.

4. Conclusions

Steady-state and time-resolved fluorescence spectroscopy have been used to investigate the [bmim][BF$_4$]/TX-100/cyclohexane microemulsions at different w values. The gradual red shift in emission spectra of C-153 with the increase in the [bmim][BF$_4$] content indicates that C-153 molecules may reside in the core of the microemulsions. The bimodal rotational relaxation time also supports this conjecture. The average rotational relaxation time increases with an increase in the w values due to the addition of highly viscous [bmim][BF$_4$]. The bimodal rotational relaxation time arises due to the wobbling motion and lateral diffusion of the probe. We have also observed slow solvation dynamics at $w = 0$ (3.91 ns). The observed slow dynamics may be due to the polymer motions and the segmental dynamics of ethylene oxide chain. The observed solvation time varies from 8.06 to 6.84 ns as w is increasing from 0.2 to 1.5. The solvation time inside the cores of the microemulsions is retarded (~4 times) compared to the solvation time in neat [bmim][BF$_4$]. However, the retardation is very small compared to the several-fold retardation of solvation time in conventional solvents inside microemulsions. Ionic motions are also responsible for solvation inside microemulsions as in neat ILs. The microemulsions impose restrictions in the ionic motions and retarded the solvation time.

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