

Solvent relaxation of a room-temperature ionic liquid [bmim][PF₆] confined in a ternary microemulsion

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Abstract. In this paper we have reported the solvent and rotational relaxation of 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆]) confined in tween 20/([bmim][PF₆])/water microemulsion using coumarin 153 (C-153) as probe. The most interesting feature of our experiment was that we observed an increase in solvent relaxation time with increase in R (R = tween 20-to-[bmim][PF₆] molar ratio). This is due to the fact that with increase in [bmim][PF₆] content of the microemulsions, the microviscosity of the pool of the microemulsions increases, and motion of ions of [bmim][PF₆] is hindered in the pool of microemulsions. Since motion of ions is responsible for solvation in room-temperature ionic liquids (RTILs), solvent-relaxation time increases with increase in R .

Keywords. Room-temperature ionic liquids (RTILs); [bmim][PF₆]; time-resolved emission spectrum (TRES); solvation dynamics; time-resolved anisotropy.

1. Introduction

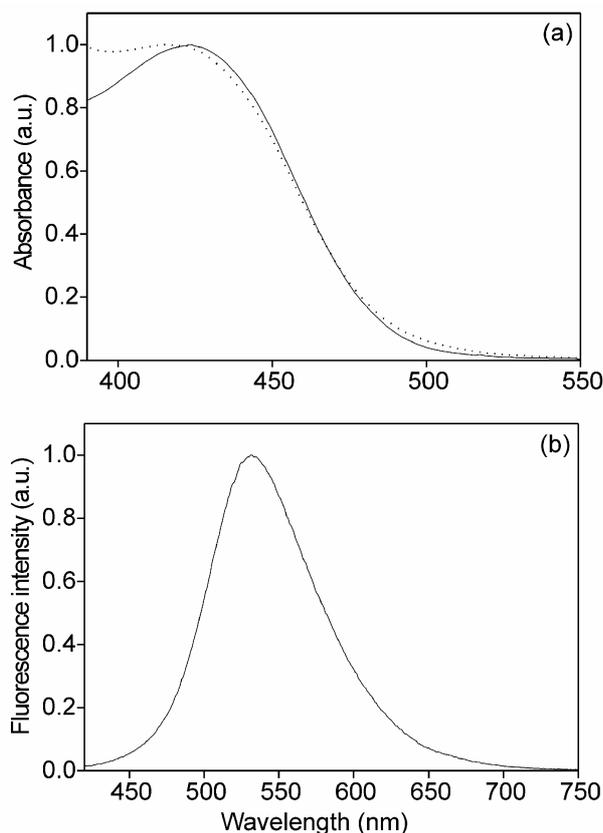
Recently, interest in room-temperature ionic liquids (RTILs) has gone up due to their unique features and diverse applications. RTILs are mainly composed of cations and anions. Different combinations of cations and anions give rise to different RTILs of the required properties. They are used as green substitutes for volatile organic solvents^{1–6} and also for industrial application.^{7–9} RTILs have some unique properties such as high conductivity, negligible vapour pressure, nonflammable nature, wide electrochemical windows, wide liquidous temperature range (–96°C to 300°C) etc. These properties make them quite useful as alternative green solvents for synthesis and industrial applications. Recently, RTILs have been extensively used in synthesis^{5,10} and also find application in analytical chemistry.^{11,12} Although RTILs are not always green,¹³ halides containing RTILs are very unstable to moisture and are hydrolysed to produce harmful, corrosive volatile HF, POF₃ etc. Baker *et al*¹⁴ showed that ionic liquid anions can be hydrolysed. In a recent paper, Earle *et al*¹⁵ showed that RTILs can be distilled at high temperature and low pressure. Nowadays, interest in RTILs is gradually increasing. Several theoretical, physical, photophysical and ultrafast spectroscopic studies were investigated in these RTILs.^{16–45} Many

theoretical methods were used to study the gas phase ion-pair structure of different RTILs.^{16–19} Theoretical study of the nature of solvation in these RTILs was also studied.^{20–23} Polarities of neat RTILs are also determined.^{24–26} Various groups, including ours, also reported experimental studies of the nature of solvation dynamics in neat RTILs.^{27–38} Solvation dynamics in RTIL–polar solvent mixtures were also investigated.^{39–41} Red-edge effect was also established, both experimentally and theoretically in neat RTILs. We know that water from micelles and reverse micelles and other less polar solvents like methanol, acetonitrile, formamide etc. forms reverse micelles with suitable surfactant molecules. Since polarities of RTILs are close to methanol or acetonitrile, we can expect to form micelles or microemulsions using RTILs. Recently, use of RTILs to form micelles or microemulsions has gained much attention. Several groups prepared and characterized RTILs containing micelles and microemulsions.^{46–52} Gao *et al*⁵² recently prepared and characterized 1-butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆])/tween 20/water containing microemulsion. We are interested in systematically studying solvent relaxation and rotational relaxation of RTILs in solutions containing micelles or microemulsions. In this paper, we are going to report solvent and rotational relaxation of [bmim][PF₆] in [bmim][PF₆]/tween 20/water ternary microemulsions using coumarin 153 (C-153) as probe molecule. Re-

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Table 1. Composition of the tween 20/[bmim][PF₆]/water containing microemulsions at different I values (I = [bmim][PF₆]-to-tween 20 weight ratio).

I	Tween 20 (wt %)	Water (wt %)	[bmim][PF ₆] (wt %)	R^a
0.05	14	85.3	0.7	0.216
0.18	11	87	2	0.785
0.25	10	87.5	2.5	1.08

^a R = [bmim][PF₆]-to-tween 20 molar ratio**Figure 1.** (a) Absorption spectra of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at $R = 0.216$ (dotted line) and $R = 1.08$ (solid line). (b) Fluorescence spectra of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at $R = 1.08$.

cently, we have also reported solvent relaxation of RTILs in RTILs containing micelles and microemulsions.^{53–55} In these ternary microemulsions three types of microstructures are present in the microemulsions: water-in-[bmim][PF₆], bicontinuous and [bmim][PF₆]-in-water. In this paper, we are interested only in the [bmim][PF₆]-in-water microstructure of the microemulsion. In this the microemulsion, micelles swell with gradual increase in amount of [bmim][PF₆].

2. Experimental

Coumarin 153 (C-153) (laser grade, exciton) was used as received. 1-Butyl-3-methyl-imidazolium hexafluorophosphate ([bmim][PF₆]) was obtained from Acros Chemicals (98% purity). The RTIL was dried in vacuum for ~24 h at 70–80°C before use. Tween 20 (Aldrich) was used as received. The solution were prepared at three different [bmim][PF₆]-to-tween 20 weight ratios (I) value with $I = 0.05$, 0.18 and 0.25 respectively.⁵² The molar ratios of [bmim][PF₆]-to-tween 20 (R) are listed in table 1. The specific amounts of water, tween 20 and [bmim][PF₆] taken to prepare microemulsions are also listed in table 1.

Absorption and fluorescence spectra were measured using a Shimadzu (model no: UV-1601) spectrophotometer and a Spex-Fluorolog-3 (model no. FL3-11) spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the instrument. For steady-state experiments, all samples were excited at 408 nm. The time-resolved fluorescence setup was described in detail in our earlier publication.⁵⁶ Briefly, the samples were excited at 408 nm using a picosecond diode laser (IBH), and the signals were collected at magic angle (54.7°) polarization using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function of our setup is ~90 ps. The same setup was used for anisotropy measurements. For the anisotropy decays, we used a motorized polarizer in the emission side. The emission intensities at parallel ($I_{||}$) and perpendicular (I_{\perp}) polarizations were collected alternatively until a certain peak difference between parallel ($I_{||}$) and perpendicular (I_{\perp}) decays were reached. The peak differences depended on the tail matching of the parallel ($I_{||}$) and perpendicular (I_{\perp}) decays. The analysis of the time resolved data was done using IBH DAS, version 6, decay analysis software. The same software was also used to analyse the anisotropy data. All experiments were carried out at 303 K.

Table 2. Absorption and emission maxima of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at different I values ($I = [\text{bmim}][\text{PF}_6]$ -to-tween 20 weight ratio) and in tween 20/water mixture.

System	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{flu}}$ (nm)
C-153 in microemulsions at $I = 0.05$	415	531
C-153 in microemulsions at $I = 0.18$	423	533
C-153 in microemulsions at $I = 0.25$	423	533
C-153 in tween 20/water binary mixture	423	531

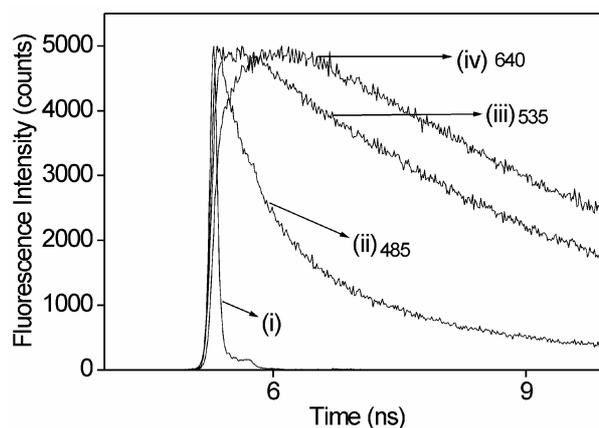
3. Results

3.1 Steady-state studies

The absorption peak of C-153 in water is at 434 nm. In tween 20-water binary mixture the absorption peak is blue-shifted to 423 nm. With addition of small amounts of [bmim][PF₆] ($I = 0.05$) the absorption peak is further blue-shifted to 415 nm, which clearly shows the change in microenvironment of C-153 molecules and also shows structural change of the medium from micelle to microemulsion. With further addition of [bmim][PF₆] absorption peak is red-shifted to 423 nm. So from absorption spectra we have observed a clear change in microenvironment around probe molecules. The emission peak of C-153 in water is at 549 nm. The emission peak of C-153 in tween 20-water binary mixture is at 531 nm. With addition of [bmim][PF₆] we have observed only a small change in emission maximum.

3.2 Time-resolved studies

3.2a Solvation dynamics: In all microemulsions we have observed a dynamics Stokes' shift in the emission spectra of C-153. In all microemulsions fluorescence decay of C-153 is markedly dependent on emission wavelength. At the red edge of the emission spectra we have observed decay profiles consisting of clear rise followed by usual decay, and at the short wavelength a fast decay is observed. Typical decay of C-153 in microemulsion at different wavelengths is shown in figure 2. The time-resolved emission spectrum (TRES) has been constructed following the procedure of Fleming and Maroncelli⁵⁷ and described in our earlier publication.⁵⁸ In all microemulsions we have observed a shift in TRES with time. The relative shift in TRES ($\Delta\nu$) for all system is listed in table 2. Each TRES was fitted by a log-normal function to extract the peak frequencies. These peak frequencies were then used to calculate the decay of solvent correlation function ($C(t)$), which is defined as

**Figure 2.** Fluorescence decays of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at $R = 0.785$ at (i) instrument response function, (ii) 485, (iii) 535, (iv) 640 nm.

$$C(t) = (\nu(t) - \nu(\infty)) / (\nu(0) - \nu(\infty)), \quad (1)$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the peak frequencies at time zero, t , and infinity, respectively. The representative TRES of C-153 in microemulsions is shown in figure 3. The decay of $C(t)$ was best fitted by bi-exponential 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 of $C(t)$ in microemulsions is shown in figure 4. The decay parameters of $C(t)$ are summarized in table 3.

3.2b Time resolved anisotropy studies: Time-resolved fluorescence anisotropy ($r(t)$) is calculated using the following equation

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

where G is the correction factor for detector sensitivity to the polarization direction of the emission

Table 3. Decay parameter of C(t) for C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at different *I* values (*I* = [bmim][PF₆]-to-tween 20 weight ratio).

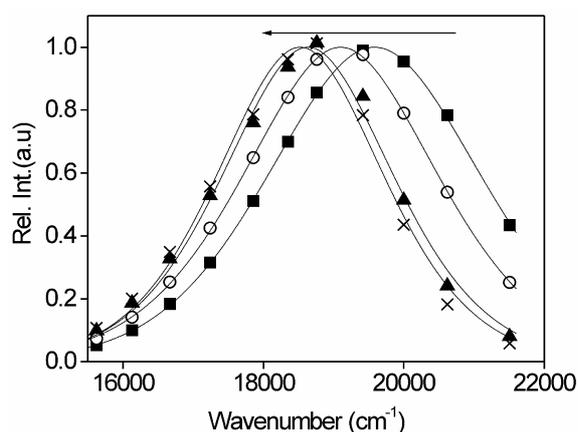
System	$\Delta\nu^a$ (cm ⁻¹)	a_1	a_2	τ_1 (ns)	τ_2 (ns)	$\langle\tau_s\rangle^b$ (ns)
C-153 in microemulsions at <i>I</i> = 0.05	1060	0.94	0.06	0.80	7.2	1.18
C-153 in microemulsions at <i>I</i> = 0.18	1170	0.86	0.14	0.77	14.7	2.72
C-153 in microemulsions at <i>I</i> = 0.25	1180	0.84	0.16	0.76	14.5	2.96
C-153 in tween 20/water binary mixture	1050	0.92	0.08	0.73	8.4	1.34

^a $\Delta\nu = \nu_0 - \nu_\infty$; ^berror in experimental data of $\pm 5\%$

Table 4. Rotational relaxation parameters of C-153 in microemulsions and tween 20/water mixture.

System	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)	$\langle\tau_r\rangle^{a,b}$ (ns)
C-153 in microemulsions at <i>I</i> = 0.05	0.39	0.52	0.27	0.48	1.56	0.89
C-153 in microemulsions at <i>I</i> = 0.18	0.39	0.51	0.30	0.49	1.56	0.92
C-153 in microemulsions at <i>I</i> = 0.25	0.39	0.49	0.26	0.51	1.55	0.92
C-153 in tween 20/water binary mixture	0.39	0.55	0.29	0.45	1.43	0.80

^a $\langle\tau_r\rangle = a_{1r}\tau_{1r} + a_{2r}\tau_{2r}$. ^berror in experimental data of $\pm 5\%$

**Figure 3.** Time-resolved emission spectra (TRES) of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at *R* = 0.785 at (i) 0 (■), (ii) 500 (○), (iii) 2000 (▲), (iv) 6000 (×) ps.

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 *G* factor for our setup is 0.6. The rotational relaxation time of C-153 in all microemulsions is fitted to a biexponential function. In all microemulsions rotational relaxation time remain more or less the same (figure 5). The anisotropy decay parameter is listed in table 4.

4. Discussion

From steady-state results it is observed that C-153 is located in a position in the microemulsions, where

the polarity sense by the C-153 molecule is less than that by bulk water. The average solvent-relaxation time of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at *R* = 0.216 is 1.18 ns. With gradual increase in amount of [bmim][PF₆] i.e. with increase in *R*, solvent-relaxation time gradually increases. The solvent-relaxation time of C-153 at *R* = 1.08 is 2.96 ns. That is, a 2.5 times increase in solvent-relaxation time on going from *R* = 0.216 to *R* = 1.08. We also observed the solvent relaxation time of C-153 in tween 20/water mixture, which is 1.34 ns. In common reverse micelles or microemulsions with increase in *w* ([polar solvent]/[surfactant]) solvent relaxation time generally decreases.^{58–60} It is due to the fact with increase in *w* value the dye molecules migrate towards the polar solvent pool of the microemulsions and the size of the microemulsions also increases, so that mobility of the solvent in the microemulsion pool increases, which leads to decrease in solvent-relaxation time. In some cases where the probe molecule resides at the surface of the microemulsion, solvent-relaxation time is practically unaltered with change in *w* value.^{61,62} This result, i.e. with increase in *R* solvent-relaxation time increases is the somewhat opposite trend that is observed in common microemulsions.

Before describing solvent-relaxation results in these microemulsions we discuss first some distinct features of solvation dynamics in neat RTILs and water or other polar solvents. Nature of solvation in neat RTILs is totally different from other polar solvents. In polar solvent such as water, alcohols etc. the sol-

vent molecules reorient themselves around the photoexcited solute molecules, whereas in neat RTILs the motions of cations and anions around excited dye molecules are responsible for solvation. Kobark *et al*²¹ showed that collective cation and anion motions are responsible for the fast component. According to Shim *et al*²⁰, the fast subpicosecond component arises due to translational motion of the anion and slow dynamics due to collective diffusional motion of cations and anions. Chapman *et al*⁶³ showed that ionic solvation is slower compared to other polar solvents⁶⁴⁻⁶⁶ and dependent on the viscosity of the medium. Bart *et al*⁶⁷ also showed that ionic solvation is slow and biphasic in nature, which is in contrast to the mono-

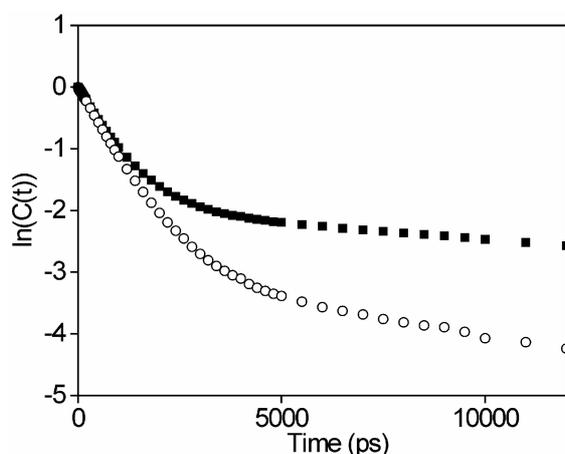


Figure 4. $\ln(C(t))$ vs time plot for C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at $R = 0.216$ (O), and $R = 1.08$ (■).

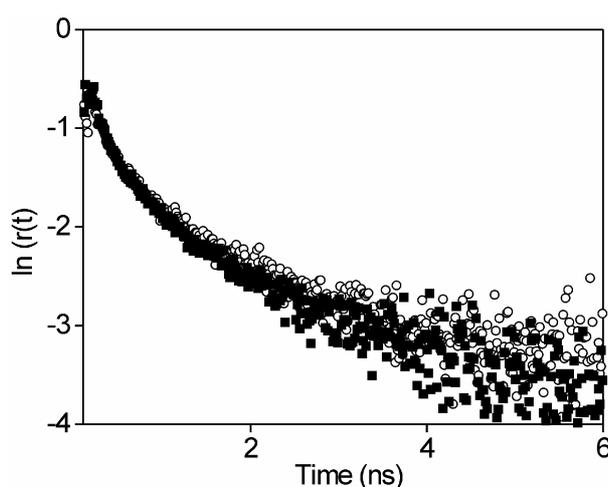


Figure 5. Fluorescence anisotropy decays (in logarithm scale) at the emission maximum of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions at $R = 0.216$ (■), and $R = 1.08$ (O).

phasic nature in some polar solvents. They also showed that solvent relaxation in molten salt depends on the solute. Due to different sizes of cations and anions of RTILs, mobility of cation is different from anion so we have observed biphasic dynamics compare to monophasic dynamics observed in some polar solvent. Maroncelli *et al*³²⁻³⁵ postulated that the fast component arises due to the translational adjustment of the ions within the solvation structure present at the time of solute excitation. The slow component is viscosity-dependent and involves large-scale rearrangement of the solvent structure. Samanta *et al*²⁷⁻³¹ ascribed that the fast component arises due to the anions, and the slow component due to the collective motions of both cations and anions. Thus in neat RTILs, motions of ions are responsible for fast dynamics and the collective diffusional motions are responsible for slow dynamics, whereas solvent relaxation time in pure water is very fast. It is reported by Jimenez *et al*⁶⁴ that solvent relaxation of C-343 in water consists of an initial decay of 55 fs (50%), attributed to the librational motion. Solvent relaxation of C-102 in water is bimodal with time constants of <50 ps (26%) and 310 fs (74%).^{64,65} The fast intermolecular vibrational and librational motions of water are responsible for very fast solvent relaxation of water. In water containing micelles, solvent-relaxation time is retarded several times as compared to pure water. The extended hydrogen bonding between water and surfactant molecules, counterions, and the micellar headgroups are responsible for slowing down solvent relaxation compared to neat water. Recent computer simulations studies⁶⁸⁻⁷¹ showed that the hydrogen bonding between water molecules and surfactant is much stronger than the hydrogen bond between two water molecules. These two types of water molecules are responsible for the slow and fast components of solvation relaxation in water containing micelles.

Let us discuss our present result of solvent-relaxation time in microemulsions. It is unusual that with increase in R solvent relaxation time increases, but, we have observed it in our experiment. It may be possible that with addition of [bmim][PF₆] microscopic viscosity sense by the C-153 molecules increases. From steady state spectral feature, and rotational relaxation time of C-153 in microemulsions, it is expected that location of C-153 may be in the interface of the microemulsions. With addition of [bmim][PF₆], weightage of fast component gradually decreases and time constant of fast component remain almost the same. Similarly, with addition of

[bmim][PF₆] the time constant of slow component and their amplitude gradually increases. With addition of R , number of [bmim][PF₆] molecules in the core as well as in the surface of the microemulsions increases, i.e. more [bmim][PF₆] molecules interact with the C-153 molecule. The solvent-relaxation time of C-153 in neat [bmim][PF₆] is ≈ 3 ns^{38,54}. So with increase in [bmim][PF₆] solvent relaxation time of C-153 in microemulsions shows feature of neat [bmim][PF₆] in the microenvironment of the microemulsions, since the motion of ions is responsible for solvation in neat RTILs. So with increase in [bmim][PF₆] concentration, the motion ions is hindered. Moreover, it is expected that with increase in [bmim][PF₆] concentration, microviscosity in the pool of the microemulsions increases. Since the slow component of solvent relaxation in RTILs is viscosity dependent, we have observed increase in the time constant of the slow component of solvent relaxation in micremulsions with increase in R .

We have also measured the rotational relaxation time ($r(t)$) of C-153 in microemulsions at different R -values. It is observed that with increase in R , i.e. with addition of [bmim][PF₆], change in rotational relaxation time of C-153 is very small. The average rotational relaxation time of C-153 in tween 20/water mixture is 0.80 ns, whereas the average rotational relaxation time of C-153 in microemulsions at $R = 1.08$ is 0.92 ns. This 120 ps increase in $r(t)$ is due to addition of [bmim][PF₆].

In the present study using the TCSPC setup, we miss the fast component of the solvation dynamics (<90 ps). We can apply the method of Fee and Maroncelli⁷² to calculate the missing component. We have calculated a "time zero spectrum" using the above procedure. The time zero frequency can be estimated using the following relation from absorption and fluorescence spectra,

$$\nu_p(t=0) \approx \nu_p(\text{abs}) - [\nu_{np}(\text{abs}) - \nu_{np}(\text{em})], \quad (4)$$

where the subscripts p and np refer to the polar and non-polar spectrum respectively. $\nu_p(t=0)$ is the calculated frequency at time zero. $\nu_p(\text{abs})$ and $\nu_{np}(\text{abs})$ are the absorption frequencies of the probe molecule in polar and nonpolar medium respectively. $\nu_{np}(\text{em})$ is the emission frequency of the probe molecule in polar medium. The percentage of missing component is $((\nu_{\text{cal}}(0) - \nu(0))/(\nu_{\text{cal}}(0) - \nu(\infty)))$. Using the above procedure we have observed that at $R = 0.216$ we miss about 54% of the solvent-relaxation dynamics. With increase in R the missing component decreases.

At $R = 1.08$ we miss 41% of the solvent-relaxation dynamics. Hence, the missing component data also show a similar feature that with increase in R the solvent relaxation of C-153 becomes more hindered.

5. Conclusions

The solvent-relaxation time of C-153 in tween 20/[bmim][PF₆]/water containing microemulsions shows an unusual feature. With increase in R ($R = [\text{bmim}][\text{PF}_6]$ -to-tween 20 molar ratio) solvent relaxation time gradually increases. Steady-state results and rotational relaxation time of C-153 in different microemulsions show that C-153 is located at the surface of the microemulsions. With increase in [bmim][PF₆] content in the microemulsions microviscosity sense by the C-153 molecules in the core of the microemulsions increases and also the motions of ions of [bmim][PF₆] become hindered. Thus we observe increase in solvent-relaxation time of C-153 with increase in R .

Acknowledgment

NS thanks the Council of Scientific and Industrial Research (CSIR), Government of India for a research grant. DS, PS and AC are thank the CSIR for fellowships.

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