

Deuterium Isotope Effect on Femtosecond Solvation Dynamics in an Ionic Liquid Microemulsion: An Excitation Wavelength Dependence Study

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The deuterium isotope effect on the solvation dynamics and the anisotropy decay of coumarin 480 (C480) in a room temperature ionic liquid (RTIL) microemulsion is studied by femtosecond up-conversion. The microemulsion consists of the RTIL 1-pentyl-3-methyl-imidazolium tetra-fluoroborate ([pmim][BF₄]) in triton X-100 (TX-100)/benzene. Replacement of H₂O by D₂O in the microemulsion causes retardation of solvation dynamics. The average solvation time of C480 ($\langle\tau_s\rangle$) in RTIL microemulsion with 5 wt % D₂O is ~ 1.5 – 1.7 times slower compared to that in the H₂O containing RTIL microemulsion. This suggests that the main species in the microemulsion responsible for solvation is the water molecules. In both D₂O and H₂O containing RTIL microemulsion, the solvation dynamics exhibits marked dependence on the excitation wavelength (λ_{ex}) and becomes about 15 times faster as λ_{ex} increases from 375 to 435 nm. This is ascribed to the structural heterogeneity in the RTIL microemulsion. For $\lambda_{\text{ex}} = 375$ nm, the region near the TX-100 surfactant is probed where bound water molecules cause slow solvation dynamics. At 435 nm, the RTIL pool is selected where the water molecules are more mobile and hence gives rise to faster solvation. The average time constant of anisotropy decay shows opposite dependence on λ_{ex} and increases about 2.5-fold from 180 ps at $\lambda_{\text{ex}} = 375$ nm to 500 ps at $\lambda_{\text{ex}} = 435$ nm for D₂O containing RTIL microemulsion. The slower anisotropy decay at $\lambda_{\text{ex}} = 435$ nm is ascribed to the higher viscosity of RTIL which causes greater friction at the core.

1. Introduction

Room temperature ionic liquids (RTILs) have received a lot of recent attention as an environmentally benign (“green”) solvent and for their diverse applications.^{1–5} The heterogeneous (bicontinuous) nature of RTIL renders it a phase-transfer catalyst-like behavior and may be responsible for the unique effects of a RTIL on a chemical reaction. The polar solvation dynamics in neat RTIL have been addressed in many recent works.^{6–8} The unique properties of RTIL have inspired many theoretical studies and computer simulations.^{9,10} The simulations predict nanostructural organization with clear segregation of polar (ionic) and nonpolar (organic) domains in a neat RTIL.^{9,10} The predicted microheterogeneity is confirmed by recent small-angle X-ray scattering,^{11a} optical Kerr effect,^{11b} and Raman scattering^{11c} studies. Recently, our group^{12c} and Maroncelli and co-workers^{12d} demonstrated dynamic heterogeneity in neat RTIL by excitation wavelength (λ_{ex}) dependence of solvation dynamics. We have showed that, in neat RTIL, the average solvation time decreases 6 times from 860 to 135 ps as λ_{ex} increases from 375 to 435 nm.^{12c} It is proposed that, at a short λ_{ex} (375 nm), the fluorescent probes at the nonpolar domain (near the alkyl chains) are excited while a long λ_{ex} (435 nm) selectively excites the polar regions near the counterions. Recent computer simulations have carefully delineated the role of collective motion of the cation and the anion and polarizability in a RTIL.¹⁰

Many amphiphilic molecules self-assemble in a RTIL to form micelles.^{13–18} Several groups studied the solvation dynamics of coumarin 153 (C153) in amphiphilic ionic liquids, and their micelles in water.^{12,13,18} The magnitude of retardation (~ 2 times)

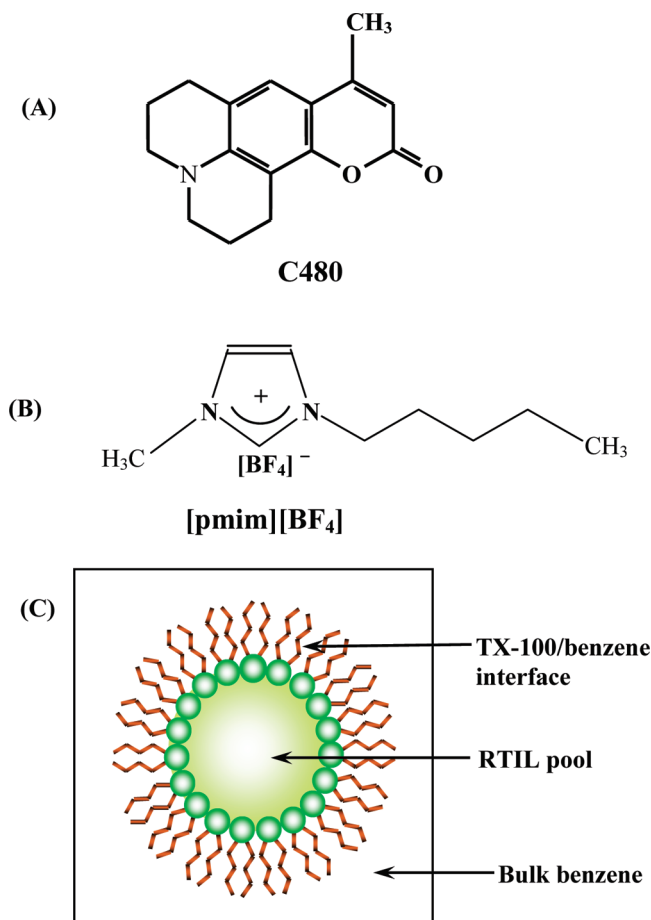
of solvation dynamics for a micelle in a RTIL compared to that in a neat RTIL is much smaller than that (100–1000 times) observed in the case of a micelle in water.^{19–23}

Recently, many groups reported the formation of reverse micelles and microemulsions involving RTILs.^{16,17} Gao et al.¹⁶ and Eastoe et al.^{16d} reported the formation of microemulsion with a pool of the RTIL ([bmim][BF₄]) inside a reverse micelle containing the surfactant triton-X-100 (TX-100) in a hydrocarbon. From SANS studies, Eastoe et al.^{16d} concluded that the ionic liquid pool is ellipsoidal in shape with a semiminor radius of 2.4 nm and a length of 11 nm for an equimolar ratio of [bmim][BF₄] and the surfactant TX-100. Gao et al. reported that about 6 wt % water may be encapsulated in the polar region of such a microemulsion.^{16a} We have previously studied a microemulsion consisting of the ionic liquid 1-pentyl-3-methylimidazolium tetrafluoroborate ([pmim][BF₄]), in TX-100/benzene.^{12a,c}

In a RTIL microemulsion, many species may affect solvation dynamics and anisotropy decay (molecular rotation). These include the polar head groups of the surfactant, counterions of RTIL, and water. In the present work, we attempt to examine the role of water by studying the deuterium isotope effect. We will show that replacement of H₂O by D₂O markedly affects solvation dynamics in a RTIL microemulsion while anisotropy decay remains unaffected. This shows that solvation dynamics and anisotropy decay in RTIL microemulsion originate from different sources. We also examine the red edge excitation shift (REES)^{24,25} like λ_{ex} dependence in the H₂O and D₂O containing microemulsions.

Many groups have previously studied the deuterium isotope effect on solvation dynamics in bulk water²⁶ and other

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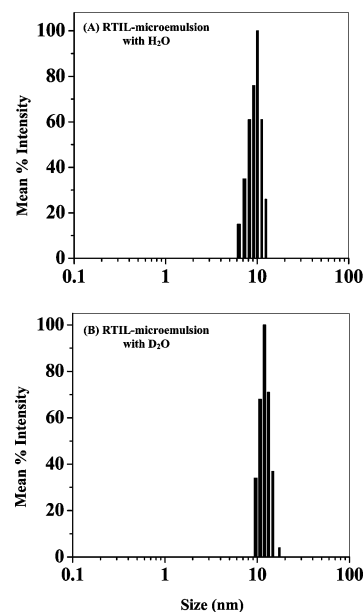
SCHEME 1: Structure of (A) Coumarin 480 (C480), (B) the Room Temperature Ionic Liquid [pmim][BF₄], and (C) Ionic Liquid Microemulsion

systems.^{27–29} In bulk, the dielectric relaxation³⁰ and solvation dynamics³¹ of D₂O is ~25% slower compared to H₂O. According to the theoretical studies, in bulk water, deuterium substitution slows down solvation dynamics by modifying the intermolecular libration frequencies.³¹ Another consequence of deuteration is slowing down of the nonradiative transitions and consequent increase in the excited state lifetime.^{31b} This may affect the long (ns) component of solvation dynamics. Recently, we have shown that, in D₂O, the average solvation time of C153 in dimethyl- β -cyclodextrin is about 1.7 times slower compared to that in water.³² For trimethyl- β -cyclodextrin in D₂O, solvation is 1.5 times slower.³² This suggests H₂O is the main species for solvation dynamics in a cyclodextrin cavity. We now examine the deuterium isotope effect on solvation dynamics and anisotropy decay in H₂O/[pmim][BF₄]/TX-100/benzene microemulsion.

2. Experimental Section

Laser grade coumarin 480 (C480, Exciton, Scheme 1A) was used as received. 1-Bromopentane (99%, Aldrich), sodium tetrafluoroborate (98%, Aldrich), and 1-methylimidazole (99%, Aldrich) were used for the synthesis of the room temperature ionic liquid (RTIL). D₂O was purchased from Sigma and used without further purification.

The RTIL [pmim][Br] was prepared from 1-methylimidazole and 1-bromopentane following the sonochemical route,³³ as described in our previous work.^{12c} Pure [pmim][BF₄] (Scheme 1B) was then obtained by the metathesis of [pmim][Br] with NaBF₄ in dry acetonitrile under an argon atmosphere at room temperature.^{33a,b}

**Figure 1.** Size distribution of the RTIL/TX-100/benzene microemulsion (measured by dynamic light scattering, DLS) with (A) H₂O and (B) D₂O.

The steady-state absorption and emission spectra were recorded in a Shimadzu UV-2401 spectrophotometer and a Spex FluoroMax-3 spectrofluorimeter, respectively.

Our femtosecond up-conversion setup (FOG 100, CDP) is described in our earlier works.^{12a–c} A cross-correlation function obtained using the Raman scattering from ethanol displayed a full width at half-maximum (fwhm) of 350 fs. The femtosecond fluorescence decays were fitted using a Gaussian shape for the exciting pulse.

To fit the femtosecond data, one needs to know the long decay components. They were detected from a picosecond setup. For this purpose, the samples were excited at 375, 405, and 435 nm using picosecond diode lasers (IBH nanoleds) in an IBH Fluorocube apparatus. The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (5000U-09). The time correlated single photon counting (TCSPC) setup consists of an Ortec 9327 CFD and a Tennelec TC 863 TAC. The data is collected with a DAQ-1 card as a multichannel analyzer. The typical fwhm of the system response using a liquid scatterer is about 90 ps. The picosecond fluorescence decays were deconvoluted using IBH DAS6 software. All experiments were done at room temperature (298 K).

In order to fit the femtosecond transient, we first determined the long picosecond components by deconvolution of the picosecond decays. Then, the long picosecond components were kept fixed to fit the femtosecond data.

Fluorescence anisotropy decay was studied by the analyzer which was rotated at regular intervals to get perpendicular (I_{\perp}) and parallel (I_{\parallel}) components. Then, the anisotropy function, $r(t)$ was calculated using the formula

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} \quad (1)$$

The G value of the picosecond setup was determined using a probe whose rotational relaxation is very fast, e.g., coumarin 480 in methanol, and the G value was found to be 1.5.

The time-resolved emission spectra (TRES) were constructed using the parameters of best fit to the fluorescence decays and the steady-state emission spectrum following the procedure described by Maroncelli and Fleming.^{34a} The solvation dynamics is described by the decay of the solvent correlation function $C(t)$, defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (2)$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the emission maxima (frequencies) at time 0, t , and ∞ , respectively. Note, a portion of solvation dynamics is missed even in our femtosecond setup of time resolution 350 fs. The amount of solvation missed is calculated using the Fee–Maroncelli procedure.^{34b} The emission frequency at time zero, $\nu_{\text{em}}^{\text{p}}(0)$, may be calculated using the absorption frequency ($\nu_{\text{abs}}^{\text{p}}$) in a polar medium (i.e., C480 in [pmim][BF₄]) as

$$\nu_{\text{em}}^{\text{p}}(0) = \nu_{\text{abs}}^{\text{p}} - (\nu_{\text{abs}}^{\text{np}} - \nu_{\text{em}}^{\text{np}}) \quad (3)$$

where $\nu_{\text{em}}^{\text{np}}$ and $\nu_{\text{abs}}^{\text{np}}$ denote the steady-state frequencies of emission and absorption, respectively, of the probe (C480) in a nonpolar solvent (i.e., cyclohexane).

3. Results and Discussion

3.1. Size of RTIL/TX-100/Benzene Microemulsion with H₂O and D₂O: DLS Studies. Parts A and B of Figure 1 describe the DLS (dynamic light scattering) data on the RTIL/TX-100/benzene microemulsion with H₂O and D₂O, respectively. The average diameter in the case of D₂O (10 ± 1 nm) is found to be slightly larger than that in the RTIL/H₂O (9 ± 1 nm). The observed slightly bigger size in D₂O is consistent with previous reports of bigger micelles in D₂O.³⁵ It may be recalled that in the absence of the water (or D₂O) the size of the RTIL [pmim][BF₄]/TX-100/benzene microemulsion is much bigger (32 nm).^{12c} We will show later that the decrease in the size of the RTIL microemulsion on addition of H₂O (or D₂O) causes slower (more restricted) solvation dynamics.

3.2. Steady-State Absorption and Emission Spectra of C480 in RTIL Microemulsion with D₂O and H₂O: λ_{ex} Dependence. The emission maximum of coumarin 480 (C480) is remarkably sensitive to the polarity³⁶ of the medium and, hence, is a good indicator of the location of the probes. The emission maximum of C480 shifts from 420 nm in benzene to 435 nm in the TX-100 reverse micelle and >450 nm in RTIL/TX-100/benzene microemulsion.^{12c} The markedly red-shifted emission maximum (>450 nm) suggests formation of a microemulsion in which the probe C480 is located inside the polar domain (Scheme 1C, “pool” of the RTIL). We have shown earlier that almost all of the C480 molecules are encapsulated inside the polar pool containing the RTIL.^{12c}

On addition of H₂O (or D₂O) to the RTIL microemulsion, the emission maximum of C480 exhibits a further red shift of ~ 9 nm.^{12c} This suggests that addition of water causes an increase in the polarity of the pool. The steady-state absorption and emission spectra of the D₂O containing RTIL microemulsion are found to be the same as that containing H₂O.

In the RTIL microemulsion (both with and without water), there is a marked red shift of the emission maximum of C480 with an increase in λ_{ex} (Figure 2). The emission maximum of C480 in the RTIL microemulsion without H₂O or D₂O shifts from 451 nm ($\lambda_{\text{ex}} = 375$ nm) to 457 nm ($\lambda_{\text{ex}} = 435$ nm). The

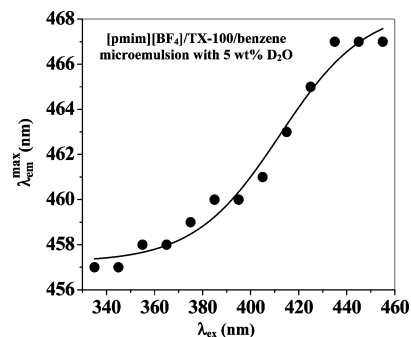


Figure 2. Plot of emission maxima of C480 in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % D₂O as a function of excitation wavelength.

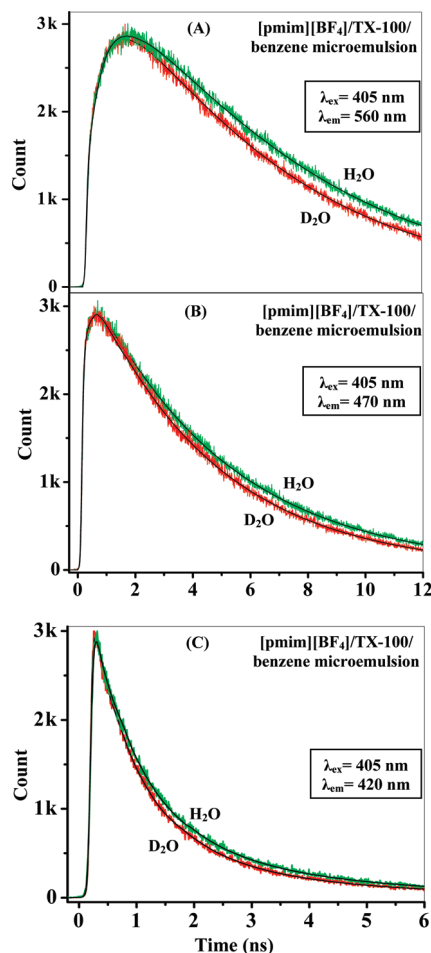


Figure 3. Picosecond decays of the C480 in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % H₂O (green) and 5 wt % D₂O (red) at (A) $\lambda_{\text{ex}} = 405$ nm, $\lambda_{\text{em}} = 560$ nm; (B) $\lambda_{\text{ex}} = 405$ nm, $\lambda_{\text{em}} = 470$ nm; and (C) $\lambda_{\text{ex}} = 405$ nm, $\lambda_{\text{em}} = 420$ nm along with their fitted line (black).

6 nm REES (i.e., red edge excitation shift) suggests that C480 molecules are distributed over a variety of locations inside the microemulsion. The variation of the emission maxima with excitation wavelength is shown in Figure 2. Excitation at a short wavelength (“blue edge”) selects the probe in the relatively less polar region near the surfactant (TX-100), and excitation at a red end selects the probe molecules in a polar region inside the core of the pool containing RTIL.

3.3. Solvation Dynamics of C480 in [pmim][BF₄]/TX-100/Benzene Microemulsion with D₂O: λ_{ex} Dependence. The solvation dynamics of C480 in the RTIL microemulsion with

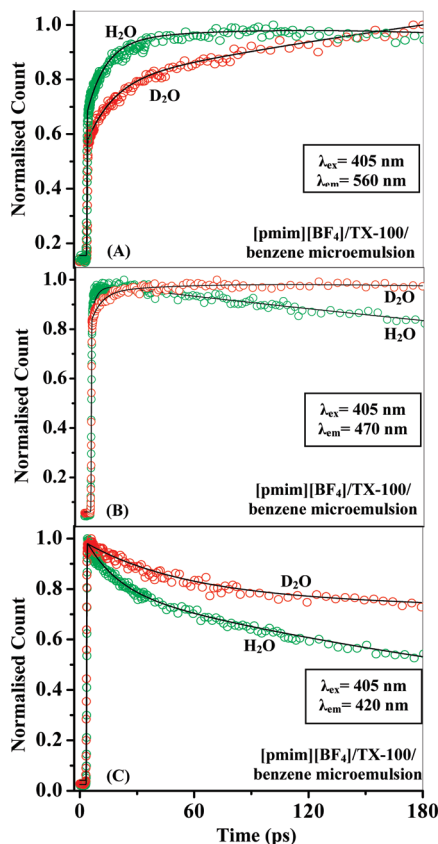


Figure 4. Femtosecond transients of the C480 in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % H₂O (green) and 5 wt % D₂O (red) at (A) $\lambda_{\text{ex}} = 405 \text{ nm}$, $\lambda_{\text{em}} = 560 \text{ nm}$; (B) $\lambda_{\text{ex}} = 405 \text{ nm}$, $\lambda_{\text{em}} = 470 \text{ nm}$; and (C) $\lambda_{\text{ex}} = 405 \text{ nm}$, $\lambda_{\text{em}} = 420 \text{ nm}$ along with their fitted line (black).

both H₂O and D₂O exhibit strong λ_{ex} dependence and the deuterium isotope effect. Figures 3 and 4 show the picosecond and femtosecond fluorescence transients of C480 in [pmim][BF₄]/TX-100/benzene microemulsion with H₂O and D₂O. It is evident from the femtosecond transients that there is a substantial deuterium isotope effect on solvation dynamics of the RTIL microemulsion. The decays of $C(t)$ for the microemulsion at different λ_{ex} are shown in Figure 5, and the decay parameters are summarized in Table 1. Figure 6 shows the time-resolved emission spectra (TRES) at $\lambda_{\text{ex}} = 405 \text{ nm}$. Solvation dynamics in [pmim][BF₄]/TX-100/benzene microemulsion (i.e., decay of $C(t)$) with both D₂O and H₂O becomes faster with a rise in λ_{ex} from 375 to 435 nm.

It may be noted that, on addition of H₂O (or D₂O) to the RTIL microemulsion, the solvation dynamics becomes slower and $\langle \tau_s \rangle$ increases. The retardation of solvation dynamics may be assigned to the smaller size ($\sim 9 \text{ nm}$) of the water-containing microemulsion compared to that ($\sim 32 \text{ nm}$) in the absence of H₂O. At $\lambda_{\text{ex}} = 375 \text{ nm}$, $\langle \tau_s \rangle$ increases from 1480 ps in the absence of H₂O to 1750 ps on addition of H₂O and to 2940 ps on addition of D₂O (Table 1).

The average solvation time exhibits a 1.5–1.7-fold increase for all λ_{ex} (375–435 nm) in D₂O containing RTIL/TX-100/benzene microemulsion compared to those in H₂O containing microemulsion (Table 1). The ultrafast component of solvation dynamics displays a relatively weak deuterium isotope effect (2 ps in H₂O containing RTIL microemulsion and 3 ps in D₂O containing RTIL microemulsion), while the two slower time components show a more pronounced deuterium isotope effect (from ~ 250 and 2200 ps in H₂O containing RTIL microemul-

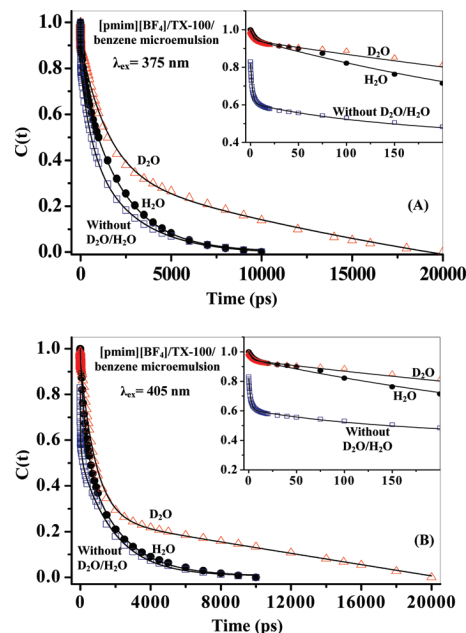


Figure 5. Decay of the solvent response function, $C(t)$, of C480 in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % D₂O (Δ , red) and 5 wt % H₂O (\bullet , black) and without D₂O/H₂O (\square , blue). The points denote the actual values of $C(t)$, and the solid lines (black) denote the best fit. Initial points of the decays are shown in the insets.

sion to 500 ps and $\sim 3600 \text{ ps}$ in D₂O containing RTIL microemulsion). The deuterium effect suggests that water plays a greater role in solvation than other species (BF₄[−] or imidazolium ion).

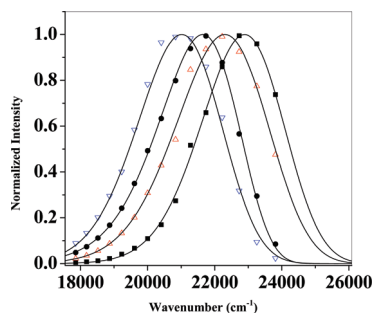
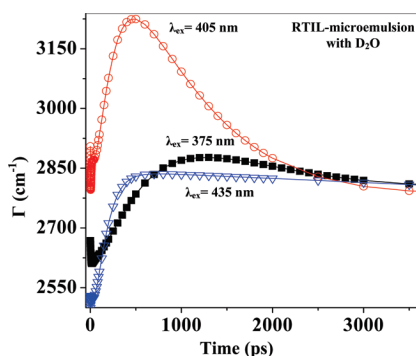
The solvation dynamics display an appreciable excitation wavelength dependence and becomes about 15-fold faster as λ_{ex} increases from 375 to 435 nm. In the case of H₂O containing microemulsion, the average solvation time decreases from 1725 ps at $\lambda_{\text{ex}} = 375 \text{ nm}$ to 120 ps at $\lambda_{\text{ex}} = 435 \text{ nm}$. For D₂O, the average solvation time decreases from 2940 to 180 ps. The excitation wavelength dependence may be ascribed to the location dependence of solvation dynamics. At the core of the pool, the contribution of the “free” water molecules is substantially increased. Such excitation wavelength dependence has been detected earlier for solvation dynamics^{12c} and FRET^{12a} in H₂O/RTIL/TX-100/benzene microemulsions.

For excitation at 375 nm, C480 molecules near the TX-100 are probed. In the palisade layer of TX-100, there are a lot of “bound” water molecules which are bound by hydrogen bonds to the polar head groups of TX-100. Such slow and bound water molecules in reverse micelles has been suggested earlier in simulations^{37,38} and observed by photon-echo experiments.^{39d} The bound water molecules are partially immobilized and give rise to slow solvation. At the RTIL pool (for $\lambda_{\text{ex}} = 435 \text{ nm}$), solvation in this region is dominated by the relatively free water molecules and also by the small BF₄[−] ions. This causes faster solvation at $\lambda_{\text{ex}} = 435 \text{ nm}$ compared to that at $\lambda_{\text{ex}} = 375 \text{ nm}$.

It is readily seen that there is a marked deuterium isotope effect on solvation time ($\langle \tau_s \rangle$). The deuterium effect suggests that water plays a greater role in solvation than other species (BF₄[−] or imidazolium ion). The very long component of solvation dynamics (e.g., 2200 or 3800 ps at $\lambda_{\text{ex}} = 375 \text{ nm}$) may arise from self-diffusion of C480 from the nonpolar to polar region following excitation of the probe. Such a self-diffusion in microheterogeneous or nanoconfined systems has been predicted in computer simulations^{38,40} and was proposed in

TABLE 1: Decay Parameters of $C(t)$ of C480 in [pmim][BF₄]/TX-100/Benzene Microemulsions in the Absence and Presence of 5 wt % H₂O and D₂O at Different λ_{ex}

system	λ_{ex} (nm)	$\Delta\nu_{\text{obs}}$ ($\nu_0(\text{expt})$) (cm ⁻¹)	$\tau_i(a_i)$ (ps)	$\langle\tau_s\rangle$ (ps)
RTIL microemulsion without H ₂ O/D ₂ O	375	1255 (23083)	2 (19%), 200 (15%), 2200 (66%)	1480
	405	1025 (22825)	≤ 0.3 (17%), ^a 2 (22%), 200 (12%), 2200 (49%)	1100
	435	235 (22154)	≤ 0.3 (79%), ^a 2 (5%), 200 (16%)	30
RTIL microemulsion with 5 wt % H ₂ O	375	1670 (22986)	2 (10%), 250 (13%), 2200 (77%)	1725
	405	1490 (22858)	≤ 0.3 (3%), ^a 2 (4%), 250 (35%), 2200 (58%)	1360
	435	500 (21990)	≤ 0.3 (65%), ^a 2 (7%), 250 (12%), 500 (16%)	120
RTIL microemulsion with 5 wt % D ₂ O	375	2263 (23168)	3 (8%), 500 (17%), 3800 (75%)	2940
	405	1700 (22890)	≤ 0.3 (1%), ^a 3 (4%), 500 (43%), 3500 (52%)	2040
	435	840 (22120)	≤ 0.3 (51%), ^a 3 (12%), 300 (21%), 800 (16%)	180

^a Calculated using the Fee–Maroncelli method.^{34b}**Figure 6.** Time-resolved emission spectra (TRES) of C480 in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % D₂O at 0 ps (■, black), 500 ps (△, red), 2500 ps (●, black), and 28000 ps (▽, blue).**Figure 7.** Plot of fwhm (Γ) of the time-resolved emission spectra with time (t) for C480 in RTIL microemulsion with D₂O at (i) $\lambda_{\text{ex}} = 375$ nm (■, black), (ii) $\lambda_{\text{ex}} = 405$ nm (○, red), and (iii) $\lambda_{\text{ex}} = 435$ nm (▽, blue). The points denote the actual value of Γ .

previous experimental studies.⁴¹ The slow component may also arise from collective motion of the surfactant chains (“cooperative chain melting”) along with bound water and polar head groups.

We have also studied the variation of the full width at half-maximum (Γ , fwhm) with time, and it has been shown in Figure 7. The width of the spectra mainly arises from the fluctuation or the heterogeneity of the local environment of the fluorescent probe. This shows that at $\lambda_{\text{ex}} = 375$ and 435 nm the change of Γ with time (t) is negligible but at $\lambda_{\text{ex}} = 405$ nm the change is quite significant. The variation of Γ for the predominantly uniform nonpolar ($\lambda_{\text{ex}} = 375$ nm) and polar ($\lambda_{\text{ex}} = 435$ nm) environment is much less than the heterogeneous environment probed at $\lambda_{\text{ex}} = 405$ nm.

3.4. Fluorescence Anisotropy Decay of C480 in [pmim][BF₄]/TX-100/Benzene Microemulsion in D₂O and H₂O: λ_{ex} Dependence. The anisotropy decay of C480 is single exponential with a time constant of 110 ± 30 ps in H₂O and 150 ± 30 ps

in D₂O. The slower anisotropy decay (rotational dynamics) in D₂O may be attributed to the $\sim 25\%$ higher viscosity of D₂O.⁴² A similar deuterium isotope effect is observed for water/RTIL/TX-100/benzene microemulsion at $\lambda_{\text{ex}} = 435$ nm (400 ps in H₂O and 500 ps in D₂O). However, the deuterium isotope effect on anisotropy decay is negligible at 375 and 405 nm. This suggests that, at these two λ_{ex} values, the friction arises from surfactant chains and not from bound or trapped water.

The anisotropy decay of C480 in both H₂O/RTIL/TX-100/benzene and D₂O/RTIL/TX-100/benzene microemulsion (Table 2) is found to be much slower than that in bulk water and may be fitted to a biexponential function

$$r(t) = r_0[\beta \exp(-t/\tau_{\text{slow}}) + (1 - \beta) \exp(-t/\tau_{\text{fast}})] \quad (4)$$

Table 2 summarizes the average rotational time ($\langle\tau_{\text{rot}}\rangle = a_{1R}\tau_{1R} + a_{2R}\tau_{2R}$). For $\lambda_{\text{ex}} = 375$ nm, the average rotational time ($\langle\tau_{\text{rot}}\rangle$) is 180 ps both in D₂O and H₂O containing microemulsion. This is much slower than the rotational time (~ 100 ps) of C480 in bulk water. For $\lambda_{\text{ex}} = 405$ nm, $\langle\tau_{\text{rot}}\rangle = 240$ ps in both D₂O and H₂O containing microemulsion. For $\lambda_{\text{ex}} = 435$ nm, $\langle\tau_{\text{rot}}\rangle = 500$ ps in D₂O containing microemulsion and $\langle\tau_{\text{rot}}\rangle = 400$ ps for H₂O containing microemulsion. From these results, it is clear that the deuterium isotope effect on anisotropy decay in the RTIL microemulsion is rather weak for $\lambda_{\text{ex}} = 375$ and 405 nm (Table 2).

The λ_{ex} dependence of anisotropy decay in the [pmim][BF₄]/TX-100/benzene microemulsion (Figure 8) may be explained as follows. For $\lambda_{\text{ex}} = 375$ nm, i.e., in the TX-100 interface region, during rotation, C480 molecules experience friction from the alkyl chains of the surfactant. In the absence of RTIL, the average rotational time of C480 in TX-100 reverse micelle without RTIL or water is 180 ps.^{12c} On addition of RTIL, a new slow component of ~ 700 ps emerges.^{12c} The 700 ps component is attributed to the RTIL pool region where the rotation is greatly hindered by the big imidazolium ion. Note, in neat [pmim][BF₄], the rotational time of C480 is 3800 ps.^{12c} The rotational time of C480 decreases to 700 ps in the RTIL microemulsion and to 800 ps on addition of water. This suggests that the nearest neighbors of the C480 molecules in the RTIL pool are not only the RTIL molecules but also water and even surfactant chain and the friction in the RTIL pool is very different from that in neat RTIL.

In summary, the friction in the RTIL pool ($\langle\tau_{\text{rot}}\rangle = 800$ ps) is greater than that at the TX-100 interface ($\langle\tau_{\text{rot}}\rangle = 180$ ps). For $\lambda_{\text{ex}} = 435$ nm, at the RTIL pool, contribution (43%) of the 800 ps component is more than that (30%) of the 180 ps

TABLE 2: λ_{ex} Dependence of Anisotropy Decay of C480 in [pmim][BF₄]/TX-100/Benzene Microemulsion in the Absence and Presence of 5 wt % H₂O and D₂O

system	λ_{ex} (nm)	r_0	decay parameters of $r(t)$		$\langle\tau_{\text{rot}}\rangle^a$ (ps)
			τ_{1R} (ps) (a_{1R})	τ_{2R} (ps) (a_{2R})	
RTIL microemulsion without H ₂ O/D ₂ O	375	0.28	180 (61%)	700 (10%)	180
	405	0.33	180 (53%)	700 (30%)	300
	435	0.34	180 (32%)	700 (50%)	400
RTIL microemulsion with 5 wt % H ₂ O	375	0.30	180 (69%)	800 (7%)	180
	405	0.27	180 (49%)	800 (19%)	240
	435	0.29	180 (30%)	800 (43%)	400
RTIL microemulsion with 5 wt % D ₂ O	375	0.25	180 (55%)	800 (10%)	180
	405	0.23	180 (44%)	800 (20%)	240
	435	0.35	180 (33%)	800 (55%)	500

^a $\langle\tau_{\text{rot}}\rangle = a_{1R}\tau_{1R} + a_{2R}\tau_{2R}$; note, we took into account the fast component of anisotropy decay (<100 ps) which leads to an r_0 value less than 0.4.

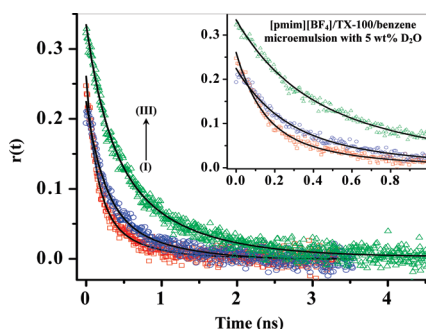


Figure 8. Fluorescence anisotropy decay of C480 along with a fitted curve (black) in [pmim][BF₄]/TX-100/benzene microemulsion with 5 wt % D₂O at (I) $\lambda_{\text{ex}} = 375$ nm and $\lambda_{\text{em}} = 450$ nm (\square , red), (II) $\lambda_{\text{ex}} = 405$ nm and $\lambda_{\text{em}} = 450$ nm (\circ , blue), and (III) $\lambda_{\text{ex}} = 435$ nm and $\lambda_{\text{em}} = 450$ nm (Δ , green). Initial parts of the decays are shown in the inset.

component (Table 2). For $\lambda_{\text{ex}} = 375$ nm, 180 ps contributes more (69%) than the 800 ps component (7%) (Table 2).

It is apparent that for $\lambda_{\text{ex}} = 375$ and 405 nm $\langle\tau_{\text{rot}}\rangle$ for H₂O and D₂O are very similar but at $\lambda_{\text{ex}} = 435$ nm the anisotropy decay for D₂O is 20% slower. It is evident that the deuterium isotope effect on the rotational relaxation time (Table 2) is much less than that on solvation time. This suggests that the main source of friction in the microemulsion is the RTIL molecules. Note, during rotational motion, the probe (C480) sweeps a large volume equal to that of the probe (~ 1 nm) and experiences friction from both water and RTIL molecules. The predominant role of the RTIL molecule toward friction is responsible for the almost total absence of deuterium isotope effect for $\lambda_{\text{ex}} = 375$ and 405 nm. This seems to be the reason for the lack of deuterium isotope effect on the anisotropy decay.

The contrasting deuterium isotope effect on solvation dynamics and anisotropy decay reiterates that these two processes are governed by different kinds of motions. Solvation is controlled by motion of water molecules and controlled mainly by one or two layers of water molecules of ~ 0.24 nm thickness. On the other hand, anisotropy decay arises from rotation of the solute probe (C480) and, in this case, friction and the high viscosity of RTIL play a dominant role.⁴³

Finally, it is interesting to note that on increase of λ_{ex} , while the solvation dynamics becomes faster, the rotational dynamics becomes slower. In bulk liquids (including RTIL), there is a near-proportionality between the time constant for solvation and rotational relaxation.^{7,44} It seems that this relation breaks down in a highly heterogeneous RTIL microemulsion where multiple species are involved (e.g., water, BF₄[−], and imidazolium ions).

It may be recalled that a similar opposite trend of variation of solvation and anisotropy decay with λ_{ex} has been reported earlier in the case of bile salt aggregates.⁴¹ In bile salt micelles at $\lambda_{\text{ex}} = 375$, i.e., in the buried location, solvation is slower (because of bound water) than that in an exposed site ($\lambda_{\text{ex}} = 435$ nm).⁴¹ In the buried site (375 nm), however, rotation is faster (than that at $\lambda_{\text{ex}} = 435$ nm) because of the presence of “voids” created by the nonplanar bile salt.⁴¹

4. Conclusion. This work demonstrates that the local structure of microemulsion varies rapidly from the nonpolar surfactant chains to the polar domain (“pool”) and this seems to be the major source of acceleration of solvation dynamics with increase in λ_{ex} . The deuterium isotope effect on solvation dynamics suggests that the water molecules (rather than BF₄[−] or imidazolium ions) play a major role in solvation dynamics. The very long component of solvation dynamics has been attributed to self-diffusion and cooperative motion of the surfactant chains along with associated water molecules. Opposite λ_{ex} variation (slower rotation at longer λ_{ex}) is attributed to the higher viscosity of the RTIL pool (though it is different from neat RTIL).

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References and Notes

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