Temperature dependent solvation dynamics in an ionic liquid containing microemulsions of 1-butyl-3-methylimidazolium tetrafluoroborate/Triton X–100/cyclohexane

Rajib Pramanik, Souravi Sarkar, Chiranjib Ghatak, Palash Setua, Vishal Govind Rao & Nilmoni Sarkar*
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, West Bengal, India
Email: nilmoni@chem.iitkgp.ernet.in

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A study of the temperature-dependent solvation dynamics of coumarin-480 in [bmim][BF_4]/Triton X-100/cyclohexane microemulsions at three different temperatures (299 K, 308 K and 317 K) is reported. The solvation dynamics of a room temperature ionic liquid in microemulsions becomes faster with increase in temperature. Dynamic light scattering measurements indicate a significant change in size with temperature for microemulsion systems with the hydrodynamic diameter decreasing with increase in temperature. Time-resolved fluorescence anisotropy studies reveal a decrease in the rotational restriction on the probe with increasing temperature. Wobbling-in-cone analysis of the anisotropy data also supports this finding.

Keywords: Ionic liquids, Time-resolved emission spectra, Time-resolved anisotropy, Solvation dynamics, Microemulsions

Room temperature ionic liquids (RTILs) comprise solely of ions and are liquids at temperatures below 100 °C. The low melting point of these salts is primarily due to the fact that the constituent ions are fairly large with low charge density. The most popular cationic components of the RTILs are imidazolium, pyridinium, and ammonium derivatives, while the are anions [PF_6] -, [BF_4] -, [CF_3SO_3] - , and [(CF_3SO_2)_2N] -, abbreviated as [Tf_2N] -. Since the properties of the RTILs are very much dependent on the constituent ions, various RTILs can be designed using an appropriate combination of the cationic and anionic constituents specifically for some desired properties. RTILs are receiving much attention as environmentally benign media for a wide range of applications, including organic synthesis and catalysis, inorganic synthesis, chromatography, analytical systems and biological systems, due to their unique physicochemical properties which include nonvolatility, high stability, high ionic conductivity, wide electrochemical window, and easy recyclability. RTILs are considered as green alternatives to volatile organic solvents, notably chlorinated hydrocarbons, due to their toxicity and biodegradability properties. Self-assembly of surfactants in contact with RTILs forming micelles, microemulsions, liquid crystals, gels, and vesicles has been investigated in recent years.

Microemulsions are an optically isotropic, transparent, and thermodynamically stable medium formed by two or more immiscible liquids that are stabilized by an adsorbed surfactant film at the liquid–liquid interface. The formation mechanism of RTILs-containing microemulsions stabilized by nonionic surfactants is of recent interest. It has been revealed that several common RTILs, including 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) (I), can be dispersed in some organic solvents to form the reverse IL-in-oil (IL/O) microemulsions. The swelling behavior of RTIL in microemulsions was found to be in accordance with traditional water-in-oil (W/O) microemulsions, showing that these systems...
behaved similar to common W/O microemulsions.\textsuperscript{19,20} The observed microstructure for the [bmim][BF\textsubscript{4}] in cyclohexane microemulsions was droplet shaped, which is similar to the typical spherical structure of W/O systems. Han and coworkers\textsuperscript{20} first reported that when nanosized droplets of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF\textsubscript{4}]) assembled as dispersed in cyclohexane as solvent, the RTIL microemulsions showed a regular swelling behavior similar to that in water-in-oil (W/O) microemulsions; that is, the volume of the dispersed nanodroplets is directly proportional to the amount of added RTIL. The driving force of RTIL microemulsions formation was considered to be the electrostatic interaction between the hydrophilic group of Triton X-100 (TX-100) and the imidazolium cation of [bmim][BF\textsubscript{4}].\textsuperscript{33-35} The self-aggregation behavior of RTILs in aqueous solution has recently attracted much attention\textsuperscript{36,37} due to structural similarities of RTILs with ionic surfactants. The surface activity of the long-chain imidazolium RTILs is superior to conventional ionic surfactants with the same hydrocarbon chain length.\textsuperscript{36} The major limitation of RTILs is their inability to dissolve a number of chemicals, although the properties of RTILs can be tuned. To overcome this problem, RTILs were used to form micelles or microemulsions in water, and the solute molecules can be solubilized in the dispersed water phase.\textsuperscript{19-38}

In recent years, several physical, photophysical, ultrafast spectroscopy and theoretical studies have been investigated in RTILs, RTILs containing micelle and microemulsions.\textsuperscript{39,40} The effect of micro-molar addition of polar and nonpolar solvent on the solvation dynamics of RTILs has also been investigated.\textsuperscript{41,42} Experimental studies on solvation dynamics in neat RTILs were first reported by Samanta and coworkers\textsuperscript{43-48} and subsequently by Maroncelli and coworkers.\textsuperscript{49-53} There have been some other experiments by various groups to understand the nature of solvation in RTILs.\textsuperscript{54-70} The literature clearly suggests that solvation dynamics in RTILs is a complex phenomenon, and many of its features are not well understood.\textsuperscript{42-61} Most of these studies have indicated that the time resolvable part of the dynamics, which is biphasic or non-exponential in nature, is rather slow compared to normal solvents. Large-scale diffusional motion of the ions presumably contributes to the observable part of the solvent relaxation dynamics. Interestingly, an appreciable portion (40-50 \%) of the dynamics is found to be ultrafast and missed in most of the studies having a finite time-resolution (typically 25 ps). Another very interesting property of RTILs, i.e., static and dynamic heterogeneity, has recently been established.\textsuperscript{71-76}

In the present study, we have investigated the dynamics of the solvent and rotational relaxation of coumarin 480 (C-480) (II) in [bmim][BF\textsubscript{4}]/TX-100/cyclohexane microemulsions at varying temperature, from 26 °C to 44 °C, using TCSPC instruments with time resolution of 90 ps. Our basic interest lies in finding out how the increasing temperature influences dynamics of solvent and rotational relaxation in these reverse RTIL microemulsions. To the best of our knowledge, there are no reports on the solvation dynamics of RTIL containing microemulsions as a function of temperature, whereas there are some reports on the effect of temperature on the solvation dynamics of aqueous reverse micelle\textsuperscript{77-80} and reverse micelle systems.\textsuperscript{81} The size of the [bmim][BF\textsubscript{4}]/TX-100/cyclohexane microemulsions and solvent correlation function with increasing temperature are shown in Scheme 1.

**Materials and Methods**

C-480 (Laser grade, Exciton) was used as received. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF\textsubscript{4}]) was obtained from Kanto Chemicals (99 % purity). TX-100 was purchased from Aldrich and cyclohexane was obtained from Spectrochem (UV spectroscopy grade). [bmim][BF\textsubscript{4}] and TX-100 were dried in vacuum for 12 h at 70-80 °C before use. In the microemulsions weight ratio of TX100 and cyclohexane was (1.1:0.9). The molar ratio of RTIL/TX-100 in the microemulsions was 0.53 in the solvent and rotational relaxation studies. The final
concentrations of TX-100 and C-480 in all experiments kept at 0.8 \( M \) and \( 10^{-5} \) \( M \) respectively.

The absorption and fluorescence spectra were measured using a Shimadzu (model UV-1601) spectrophotometer and a Jobin Yvon Fluorolog 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 detailed time-resolved fluorescence setup is described in our earlier publication.\(^{82,83}\)

Briefly, the samples were excited at 408 nm using a picosecond laser diode (IBH, Nanoled), and the signals were collected at magic angles (54.7\(^\circ\)) using a Hamamatsu microchannel plate photomultiplier tube (3809 U). The instrument response function of our setup was 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 (\( I_\parallel \)) and perpendicular (\( I_\perp \)) polarizations were collected alternately until a certain peak difference between parallel (\( I_\parallel \)) and perpendicular (\( I_\perp \)) decay was reached. The peak differences depended on the tail matching of the parallel (\( I_\parallel \)) and perpendicular (\( I_\perp \)) decays. The analysis of the data was done using IBH DAS, version 6 decay analysis software. The same software was also used to analyze the anisotropy data. All the longer and shorter wavelength decays were fitted with bi-exponential and tri-exponential functions respectively because \( \chi^2 \) lies between 1 and 1.2, which indicates a good fit. For dynamic light scattering (DLS) measurements, a Malvern Nano ZS instrument employing a 4 mW He-Ne laser (\( \lambda = 632.8 \) nm) was used. Viscosity measurements were made on a Brookfield DV-II + Pro viscometer. All experiments were carried out at 299, 308 and 317 K. The temperature was maintained by circulating water through the cell holder using a Neslab thermostat (RTE7).

**Results and Discussion**

**Steady-state absorption and emission spectra**

The absorption spectra of C-480 in [bmim][BF\(_4\)]/TX-100/cyclohexane microemulsions are shown in Fig. 1a. In cyclohexane, the emission maximum of C-480 is at 415 nm. On addition of TX-100 to a solution of C-480 in cyclohexane, the emission maximum of C-480 exhibits a marked red shift to 447 nm (Fig. 1b). The marked red shift by
32 nm indicates transfer of the C-480 molecules from bulk cyclohexane to the interior of TX-100 reverse micelle. On addition of the RTIL ([bmim][BF_4]) to the TX-100/cyclohexane mixture, the emission maximum of C-480 displays a further red shift by 10 nm (at $\lambda_{ex} = 410$ nm, Fig. 1b). The red shift suggests formation of microemulsions in which the probe C-480 is located inside the polar domain (“pool” of the RTIL). The emission maximum remains unchanged on increasing temperature from 299 K – 317 K.

**Time resolved studies**

**Solvation dynamics**

To study solvent relaxation dynamics we collected the time-resolved decays monitored at different wavelengths for all the systems. The decays at the red edge of the emission spectra were preceded by a growth in fraction of nanosecond time scale while decays at the short wavelengths were fast. The wavelength-dependent behavior of temporal decays of C-480 clearly indicates that solvent relaxation is taking place in these systems. The representative decays of C-480 monitored at three different wavelengths are shown in Fig. 2. The time-resolved emission spectra (TRES) were constructed using the procedure of Fleming and Maroncelli. The TRES at a given time $t$, $S(\lambda; t)$, is obtained by the fitted decays, $D(\lambda; t)$, by relative normalization to the steady-state spectrum $S_0(\lambda)$, Eq.(1).

$$S(\lambda; t) = D(\lambda; t) \frac{S_0(\lambda)}{\int_0^\infty D(\lambda; t)dt} \quad \ldots(1)$$

Each TRES was fitted by a lognormal line shape function, which is defined by Eq. (2),

$$g(\nu) = g_0 \exp\left[-\ln(1 + \frac{2b(\nu - \nu_p)}{\Delta})^2\right] \quad \ldots(2)$$

where $g_0$, $b$, $\nu_p$, and $\Delta$ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. A representative TRES of C-480 in [bmim][BF_4]/TX-100/cyclohexane microemulsions at 317 K is shown in Fig. 3. We have obtained the peak frequency from the lognormal fitting of TRES. The solvation dynamics was monitored by the solvent response function defined by Eq. (3),

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad \ldots(3)$$

where $\nu(0)$, $\nu (t)$, and $\nu (\infty)$ are the peak frequencies at time 0, $t$, and infinity, respectively. The solvent response function, $C(t)$, was fitted to a bi-exponential decay function (Eq. 4).

$$C(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \quad \ldots(4)$$

The bi-exponential fitting parameters of solvent response function, $C(t)$, are tabulated in Table 1 and are shown in Fig. 4.
Time-resolved anisotropy studies

The time-resolved anisotropy ($r(t)$) was calculated using the following equation (Eq. 5),

$$r(t) = \frac{I_{||}(t) - GI_{\perp}(t)}{I_{||}(t) + 2GI_{\perp}(t)} \quad \ldots(5)$$

where $G$ is the correction factor for detector sensitivity to the polarization direction of the emission and $I_{||}(t)$ and $I_{\perp}(t)$ the fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light, respectively. The $G$ factor in the present setup is 0.6. The anisotropy results are summarized in Table 2 and representative decays of fluorescence anisotropy in [bmim][BF$_4$]-containing microemulsions are shown in Fig. 5b. The rotational relaxation data in all cases are fitted with a bi-exponential function.

Viscosity measurements

We have measured the viscosity of neat [bmim][BF$_4$] and [bmim][BF$_4$]-containing microemulsions with varying temperature from 299–317 K. With increasing temperature in microemulsions, the bulk viscosity of [bmim][BF$_4$]-containing microemulsions decreases. The bulk viscosities of [bmim][BF$_4$]-containing microemulsions at different temperatures are listed in Table 2.

Dynamics light scattering studies

Dynamic light scattering (DLS) is used to obtain the hydrodynamic diameter ($D_h$) of the [bmim][BF$_4$] containing microemulsions with varying temperature. Figure 6 shows that the hydrodynamic diameter of the microemulsions decreases with increasing temperature. The hydrodynamic diameter ($D_h$) of the [bmim][BF$_4$]-containing microemulsions with varying temperature are listed in Table 1.

At first we are going to discuss the important features of solvation dynamics in pure room temperature ionic liquids. It should be noted that solvation dynamics in RTILs are vastly different from that in the isopolar conventional solvents such as methanol, acetonitrile, etc. Solvation in RTILs 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.

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Table 1 — Decay parameters of solvent correlation function $C(t)$ of C-480 and hydrodynamic diameter of TX-100[bmim][BF$_4$]/cylohexane microemulsions at different temperatures

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\alpha_1$</th>
<th>$\tau_1$</th>
<th>$\alpha_2$</th>
<th>$\tau_2$</th>
<th>$&lt;\tau_{ei}&gt;$</th>
<th>$\Delta\nu$ (cm$^{-1}$)</th>
<th>Missing component (%)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.64</td>
<td>0.46</td>
<td>0.36</td>
<td>7.83</td>
<td>3.11</td>
<td>1708</td>
<td>23</td>
<td>22.8</td>
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<tr>
<td>35</td>
<td>0.69</td>
<td>0.43</td>
<td>0.31</td>
<td>7.69</td>
<td>2.68</td>
<td>1617</td>
<td>24</td>
<td>15.2</td>
</tr>
<tr>
<td>44</td>
<td>0.70</td>
<td>0.31</td>
<td>0.30</td>
<td>5.77</td>
<td>1.95</td>
<td>1552</td>
<td>25</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 2 — Anisotropy decay parameters $r(t)$ of C-480 and bulk viscosity of [bmim][BF$_4$] containing microemulsions at different temperatures

<table>
<thead>
<tr>
<th>Systems</th>
<th>Temp. (°C)</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$\alpha_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$&lt;\tau_{ei}&gt;$ (ns)</th>
<th>$R_0$</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX100[cyclohexane/[bmim][BF$_4$]C-480</td>
<td>26</td>
<td>0.31</td>
<td>0.41</td>
<td>0.69</td>
<td>2.47</td>
<td>1.83</td>
<td>0.35</td>
<td>36</td>
</tr>
<tr>
<td>TX100[cyclohexane/[bmim][BF$_4$]C-480</td>
<td>35</td>
<td>0.29</td>
<td>0.19</td>
<td>0.71</td>
<td>1.39</td>
<td>1.04</td>
<td>0.35</td>
<td>25</td>
</tr>
<tr>
<td>TX100[cyclohexane/[bmim][BF$_4$]C-480</td>
<td>44</td>
<td>0.22</td>
<td>0.11</td>
<td>0.78</td>
<td>0.84</td>
<td>0.68</td>
<td>0.32</td>
<td>17</td>
</tr>
<tr>
<td>TX100/CyclohexaneC-480</td>
<td>26</td>
<td>1</td>
<td>0.63</td>
<td>0.63</td>
<td>0.32</td>
<td>3.42</td>
<td>0.30</td>
<td>98</td>
</tr>
</tbody>
</table>

*Error in experimental data of ±5%.
around an excited dye. Chapman and Maroncelli\textsuperscript{89} showed that ionic solvation is slower as compared to the pure solvent and is dependent on the viscosity of the medium. They ascribed the fast component to the translation adjustment of the ions within the solvation structure present at the time of solute excitation.\textsuperscript{48-50} According to Samanta \textit{et al.}\textsuperscript{43,44} the fast component to the motion of the anions, and the slow component is ascribed to the collective motions of cations and anions, respectively. Kobrak \textit{et al.}\textsuperscript{90} also showed that collective cation-anion motions are responsible for the fast component. According to Shim \textit{et al.}\textsuperscript{68} the fast sub-picosecond component is mainly from inertial ion translation and that the slow component is due to ion transport. Thus in RTILs, local motions of the ions are responsible for the fast component, and collective diffusive motions are responsible for the slow component.

In this work, the weight ratio of cyclohexane/TX-100/[bmim][BF\textsubscript{4}] is 0.9:1.1:0.2 ([bmim][BF\textsubscript{4}]/[TX-100] molar ratio, \(R = 0.53\)) for the cyclohexane-based microemulsions. Figure 6 shows the temperature-dependence of the microemulsions size through DLS study. It can be seen that the average microemulsions droplets are mono-dispersed and the diameter decreases from 22.8 to 9.4 nm as temperature is raised from 26 to 44 °C (Table 1). In [bmim][BF\textsubscript{4}]/TX-100/cyclohexane microemulsions, the observed dynamics is bimodal. The average solvation time of C-480 in microemulsions at 299 K is 3.11 ns with components 0.46 ns and 7.83 ns and the relative contribution of the components are 64 % and 36 % respectively. In [bmim][BF\textsubscript{4}]/TX-100/cyclohexane microemulsions a portion of ions of [bmim][BF\textsubscript{4}] reside at the interfacial region and the rest of the portion of ionic liquid reside in the core of microemulsions. The interfacial region ionic liquids are restricted and their motion consequently decreases the diffusional motion of the
constituent ions of [bmim][BF$_4$]. Generally with decreasing size of the RTIL containing microemulsions the motion of ions of RTILs in microemulsions core are more restricted and slow down the solvent relaxation dynamics. Also the decrease in solvation time with increasing size of the microemulsions (i.e. increasing ionic liquid content) is due to decrease in the proportion of ionic liquid in the interfacial regions. This leads to increase in the diffusional motion of the ions and decreases the slow component values of the solvation dynamics. On the other hand, with increasing temperature the motion of ions of RTILs in microemulsions core is less restricted, leading to faster solvent relaxation dynamics. On increasing the temperature of [bmim][BF$_4$]/TX-100/cyclohexane microemulsions, there are two factors operating in solvent relaxation dynamics in the core of the microemulsions. Firstly, there is a size decrease which slows down solvent relaxation. Secondly, increase in temperature leads to faster solvent relaxation dynamics. On increasing temperature from 26 °C to 44 °C, we observed a gradual decrease average solvation time from 3.11 ns (fast and slow components are 0.46 ns (64 %) and 7.83 ns (36 %) respectively) to 1.95 ns (fast and slow components are 0.31 ns (70 %) and 5.77 ns (30 %) respectively). Thus, temperature effect is more prominent than the size effect. This is due to the fact that with an increase in temperature, the micro viscosity of microemulsions gradually decreases which increases the motions of ions of RTILs and decreases the average solvation time (shown in Fig. 4 and Scheme 1).

In the present study using the time-correlated single photon counting (TCSPC) setup, the fast component of the solvation dynamics (<90 ps) was missing. The method of Fee and Maroncelli$^{91}$ can be applied to calculate the missing component. We calculated a time zero spectrum using the Fee and Maroncelli$^{91}$ procedure. The time zero frequency can be estimated using the following relationship from absorption and fluorescence spectra Eq. (6),

$$v_p(t = 0) = v_p(\text{abs}) - \left[ v_{np}(\text{abs}) - v_{np}(\text{em}) \right] \quad \ldots (6)$$

where the subscripts p and np refer to the polar and nonpolar spectrum, respectively. The percentage of missing component is $$(V_{\text{cal}(0)} - V(0))/(V_{\text{cal}(0)} - V(\infty))$$. In the present study using C-480 as the experimental probe, using the previous procedure,$^{55}$ we calculated a total Stokes’ shift of 2241 cm$^{-1}$ at 26 °C. However, we observed a total Stokes’ shift of 819 cm$^{-1}$. Thus, we observed 77 % of the solvent relaxation dynamics and the rest 23 % of the dynamics was missing. With increasing temperature, the percentage of missing dynamics remains almost unaltered. The percentages of missing components are 24 % and 25 % at 35 °C and 44 °C respectively.

To comprehend the solvation dynamics results, a thorough understanding of the microemulsions structure and location of the probe within the microemulsions is necessary. In bulk cyclohexane, the time constant of fluorescence anisotropy decay of C-480 is 70 ps.$^{91}$ The anisotropy decay of C-480 in TX-100/cyclohexane is found to be quite fast with a time constant of 0.63 ns at 26 °C. On addition of the ionic liquid [bmim][BF$_4$] to the TX-100/cyclohexane reverse micelle, the anisotropy decay of C-480 slows down markedly with the emergence of an additional slow (2.5 ns) component (Fig. 5a, and Table 2). This suggests that within the RTIL containing microemulsions, there are two broadly different regions: a fast region near the head group of TX-100 of rotational relaxation time 0.60 ns and a slow region of rotational relaxation time 2.5 ns at the pool of the RTIL. The average rotational time is found to be 1.83 ns with fast and slow components as 0.41 ns (31 %) and 2.47 ns (69 %) respectively. The markedly slow anisotropy decay of C-480 in microemulsions strongly suggests that the major fraction probe molecules are residing in the core of the microemulsions. In neat bmimBF$_4$, C-480 exhibits a very slow rotational dynamics (Fig. 5a) with an exponential decay of time constant of 3.42 ns. The slow anisotropy decay in neat ionic liquid is due to the high viscosity of [bmim][BF$_4$] (98 cP). It is interesting to note that both the components of rotational relaxation are faster in the RTIL containing microemulsions than in neat [bmim][BF$_4$]. Recently Sasmal et al.$^{92}$ explored the origin of fast and slow components in anisotropy decay of C-480 in RTILs microemulsions through excitation wavelength dependence study. Their results suggest that the nearest neighbors of the C-480 molecules in the RTIL pool are not only the RTIL molecules but also surfactant chain and the friction in the RTIL pool is very different from that in neat RTIL.

The rotational relaxation times in microemulsions are slower compared to those in cyclohexane. In microemulsions, the rotational relaxation time is bimodal in nature. Previous studies show that the
rotational relaxation time in RTILs containing microemulsions is independent of the size of the microemulsions if the amounts of RTILs are constants and rotational relaxation is guided by the viscosity of the systems.  

Hence, although on increasing the temperature the size of the microemulsions decreases, the bulk viscosity of the medium decreases from 36 cP to 17 cP. Consequently, rotational relaxation time decreases from 1.83 ns to 0.68 ns on increasing temperature from 299 K to 317 K. The bi-exponential anisotropy decays in these microemulsions can be explained with the help of a two-step model and wobbling-in-a-cone model. The two-step model shows that the observed slow rotational relaxation ($\tau_s$) is a convolution of the relaxation time corresponding to the overall rotation of the micelles ($\tau_m$) and lateral diffusion of the probe ($\tau_0$). The wobbling-in-a-cone model describes the internal motion of the probe ($\tau_e$) in terms of a cone angle ($\theta_0$) and wobbling diffusion coefficient ($D_w$). The $\tau_m$, $\tau_0$, $\tau_e$, $\theta_0$, and $D_w$ values are calculated from the relevant equations defined by Quitevis et al. as follows (Eqs 7 and 8),

\[
\frac{1}{\tau_2} = \frac{1}{\tau_D} + \frac{1}{\tau_m} \quad \text{...}(7)
\]

\[
\frac{1}{\tau_1} = \frac{1}{\tau_e} + \frac{1}{\tau_2} \quad \text{...}(8)
\]

where $\tau_1$ and $\tau_2$ 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 relationship, Eq. (9),

\[
\tau_m = \frac{4\pi\eta r_h^3}{3kT} \quad \text{...}(9)
\]

where $\eta$ 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 $\tau_m$ values are in the range of several nanoseconds. It could be noted that the $\tau_m$ values are an order of magnitude higher than the $\tau_1$ and $\tau_2$ values. Therefore, overall rotation does not contribute to the anisotropy decays. Thus, slow components are arising due to the lateral diffusion of the probe. This is because the reorientation time for the overall rotation of the reverse micelle becomes very long and consequently the fluorescence depolarization due to this process becomes negligible. 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 $S^2 = a_2$.

The magnitude of the $S$ is a measure of spatial restriction and has values from zero (unrestricted motion) to 1 (completely restricted motions). 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 $\theta_0$ and wobbling diffusion coefficient from Eqs 10 and 11,

\[
\theta_0 = \cos^{-1}\left(\frac{1}{2}\left(1 + 8S^2\right)^{\frac{1}{2}} - 1\right) \quad \text{...}(10)
\]

\[
D_w = \frac{7\theta_0^2}{24\tau_e} \quad \text{...}(11)
\]

where $\theta_0$ is cone angle in radians. The $D_w$ value of C-480 increases with increasing temperature. This indicates that the micro-viscosity experienced by the probe decreases with an increase in temperature. With an increase in temperature, the internal motions of ions of [bmim][BF$_4$] increases in the core of the microemulsions. Hence, the micro-viscosity also decreases, and the value of $D_w$ increases.

**Conclusions**

This work reports the temperature dependence of the solvation dynamics and anisotropy decay in [bmim][BF$_4$] containing microemulsions. The nature of temperature-dependent structural changes of the microemulsions with various sizes has also been explored by DLS studies. Both the solvent and rotational relaxation of C-480 in microemulsions is faster on increasing the temperature. The effect of temperature on the change in solvent relaxation of C-480 in microemulsions is less prominent as compared to rotational relaxation.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\tau_e$ (ns)</th>
<th>$\tau_m$ (ns)</th>
<th>$\tau_0$ (ns)</th>
<th>$D_w \times 10^8$ (s$^{-1}$)</th>
<th>$\theta_0$ (deg.)</th>
<th>$S$</th>
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<tbody>
<tr>
<td>26</td>
<td>0.49</td>
<td>17</td>
<td>2.89</td>
<td>44.6</td>
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<td>98.8</td>
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<td>44</td>
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<td>2.57</td>
<td>1.25</td>
<td>120.7</td>
<td>23</td>
<td>0.88</td>
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*Error in experimental data of ±5 %.*
References


