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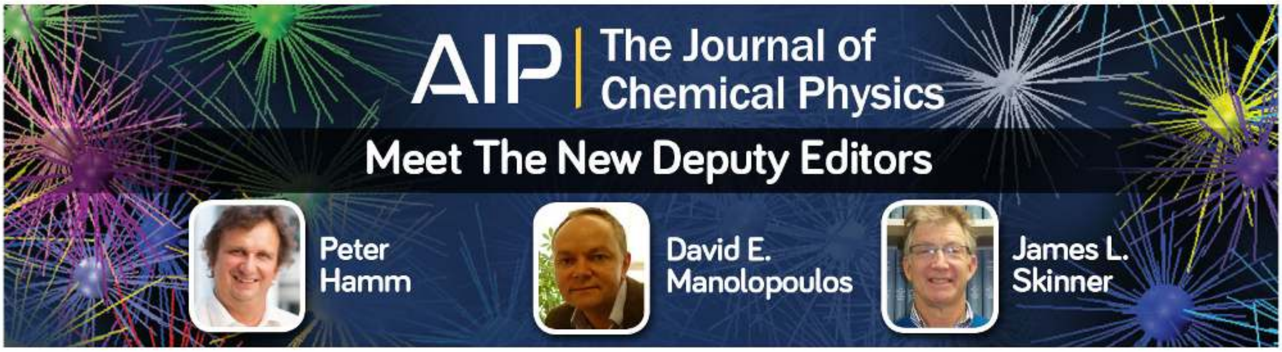

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Picosecond solvation dynamics—A potential viewer of DMSO—Water binary mixtures

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In this work, we have investigated the composition dependent anomalous behavior of dimethyl sulfoxide (DMSO)-water binary mixture by collecting the ultrafast solvent relaxation response around a well known solvation probe Coumarin 480 (C480) by using a femtosecond fluorescence up-conversion spectrometer. Recent molecular dynamics simulations have predicted two anomalous regions of DMSO-water binary mixture. Particularly, these studies encourage us to investigate the anomalies from experimental background. DMSO-water binary mixture has repeatedly given evidences of its dual anomalous nature in front of our systematic investigation through steady-state and time-resolved measurements. We have calculated average solvation times of C480 by two individual well-known methods, among them first one is spectral-reconstruction method and another one is single-wavelength measurement method. The results of both the methods roughly indicate that solvation time of C480 reaches maxima in the mole fraction of DMSO $X_D = 0.12$–0.17 and $X_D = 0.27$–0.35, respectively. Among them, the second region ($X_D = 0.27$–0.35) is very common as most of the thermodynamic properties exhibit deviation in this range. Most probably, the anomalous solvation trend in this region is fully guided by the shear viscosity of the medium. However, the first region is the most interesting one. In this region due to formation of strongly hydrogen bonded 1DMSO:2H_2O complexes, hydration around the probe C480 decreases, as a result of which solvation time increases. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4906541]

I. INTRODUCTION

Dimethyl sulfoxide (DMSO) is an important molecule due to its versatile applications in diverse fields like cell biology, cryoprotection, pharmacology, and as a commercial solvent in chemical laboratories.[1–4] As a cryoprotectant DMSO lowers the melting point of water containing biological components like protein, tissues, and stem cells and saves them from the injuries caused by freezing.[2,3] DMSO also has applications in the pharmacological purposes like membrane penetration, membrane transport, anti-inflammation, nerve blockade (analgesia), and cholinesterase inhibition.[4] Except this, aqueous DMSO solution has a crossover region near mole fraction of DMSO 0.15 ($X_D \sim 0.15$),[5–9] before which it is used as a stabilizer of protein and enhancer of enzymatic activity, and beyond this crossover, it takes an opposite action on the activity of proteins and enzymes.[10–12] Due to these versatile applications in biology, DMSO becomes more useful to the biologist than water.[13,14]

The structural aspects of DMSO are very interesting. This sulphur containing amphiphilic molecule consists of a polar S=O group and two hydrophobic -CH_3 groups.[15] Generally, polar moieties form hydrogen bonds with hydrogen bond donating solvents like water; on the other hand, methyl groups may help in cooperative aggregation of DMSO molecules through hydrophobic interaction. Not only DMSO but also dioxane,[16] ethanol,[17,18] 1-propanol,[19] and tertiary butyl alcohol (TBA)[20] form binary mixture with water and all of these exhibit composition dependent behavior. Note that all the above mentioned solutes (DMSO, dioxane, ethanol, 1-propanol, TBA) are amphiphilic in nature. Therefore, it is expected that the composition dependent behavior of these binary mixtures is somewhat related to the amphiphilic nature of the solute molecules ("Janus effect").[21]

Binary mixtures have aroused considerable attention to the scientific communities due to its non-ideal physical properties such as density,[22] viscosity,[23,24] surface tension,[25,26] adiabatic and isothermal compressibility,[27] excess mixing volume,[28] and dielectric constant.[29] Among these binary mixtures, biologically active aqueous DMSO system exhibits maximum deviation from ideal behavior at 33% mole fraction of DMSO.[26] This system has been extensively investigated by several groups using various techniques, mainly X-ray and neutron scattering[30–32] and computer simulation.[5–9,15,33–38]

DMSO-water binary mixture is an important model to study the perturbation of an intermolecular hydrogen-bonded network (water) by the hydrophobic and hydrophilic groups of DMSO. Safford *et al.*[30] studied the DMSO-water binary mixture at high and low concentration of DMSO through X-ray diffraction and inelastic neutron scattering experiments. They mentioned that at low DMSO concentration, water structure becomes rigid due to the hydrophobic hydration of methyl groups. On the other hand, in case of high DMSO content, hydrogen-bonded network of water is broken by the

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polar S═O moiety of DMSO due to formation of highly stable water-DMSO complex. They have also pointed out that ionic interactions are responsible for hydrophobic association of the DMSO molecules. Soper and Luzer performed neutron diffraction measurements in aqueous solution of DMSO at a concentration of 1DMSO:2H_2O (30% DMSO).[31] Results of neutron diffraction measurement indicate that DMSO enhances hydrogen bond network of water. Most probably, this enhanced hydrogen-bonding compared to the bulk water is due to formation of strong hydrogen bond between water and DMSO oxygen atom. Later, the same group[32] performed neutron diffraction experiment at two mole fractions of DMSO ($X_D = 0.21$ and 0.35) and concluded that hydrogen bond is shifted from "water-water" complex to "water-DMSO" complex with the addition of DMSO to water. However, the overall tetrahedral arrangement of water is not at all affected by the presence of DMSO.

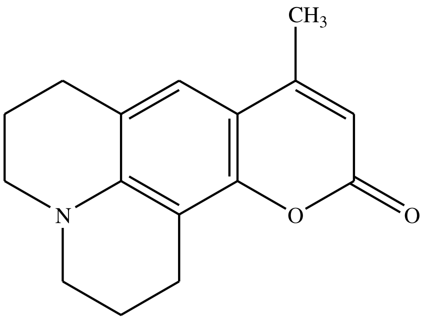
Computer simulation has a significant contribution in determining structural and dynamical characteristics of the complex formed by strong hydrogen bonding interaction between DMSO and water. Molecular dynamics simulations have repeatedly predicted two anomalous regions of aqueous DMSO binary mixture, among them the first one is at low solute concentration region ($X_D = 0.12$-0.16) and the most deviating second one is at higher solute concentration region ($X_D = 0.30$-0.40).[5–9] Earlier studies have proved the existence of 1DMSO:2H_2O complex within the aqueous solution of DMSO.[15,33] Borin and Skaf[34,35] simulated entire region of the DMSO-water binary mixture and have introduced with a new type of arrangement in agreement with the 1DMSO:2H_2O complex. According to their proposal, two DMSO molecules are interconnected to each other through a central water molecule in a same plane forming 2DMSO:1H_2O complex, which is supposed to coexist in equilibrium with 1DMSO:2H_2O complex throughout the mixture. They have also mentioned that at low DMSO concentration, the equilibrium lies in the 1DMSO:2H_2O side and vice-versa.

Bagchi and co-workers[5–9] performed molecular dynamics simulations on DMSO-water binary mixture. They have observed that at low DMSO concentration ($X_D = 0.12$-0.16), the pair hydrophobicity of the solution becomes maximum.[5] After this observation, they proposed a model "Continuum Percolation Transition." According to this model, at around 5%-10% of DMSO concentration, DMSO has a tendency to the formation of a "micromicelle"-like structure involving small aggregates of DMSO through hydrophobic interaction of methyl groups. Beyond this concentration (up to $X_D = 0.10$), DMSO has to break this "micromicelle"-like structure to form small cluster of 1DMSO:2H_2O. Further increase in DMSO concentration ($X_D = 0.12$-0.15) leads to formation of a percolating string-like network through hydrogen bonding and methyl-methyl aggregation of 1DMSO:2H_2O complexes.[6]

Solvation dynamics, which is a collective attempt of solvent molecules to stabilise the excited state of a highly polar fluorophore through the re-organization of them around the polar dipole, can provide information about the anomalous behavior of binary mixtures. Therefore, any structural transition in solvent mixtures, i.e., "pure water to DMSO-water aggregate to pure DMSO" should be clearly understood from the response of solvents. Solvation dynamics is an important tool to investigate the dynamical properties in solutions[39–45] and organized assemblies.[46–57] Recently, substantial effort is being devoted to understand the complexity of binary mixtures through the same technique. Actually, there are several factors that compete with each others during the process of solvation in binary mixtures and make it a complex and interesting one. In case of DMSO-water system, DMSO has considerably higher dipole moment than water. It also has the capability to solvate both types of charges, so it is expected that the solvation response mainly comes from the contribution of DMSO. However, due to its bulkiness it cannot solvate the small solute molecules.[36] Day[36] and Laria and Skaf[37] have given the idea about the charge specific solvation response in DMSO-water binary mixture. Martins and Skaf[38] simulated solvation response of Coumarin 153 (C153) in DMSO-water binary mixture throughout the whole region and observed sluggish response at around 33% DMSO content.

On the other hand, experimental support in favour of this anomalous behavior is not extensive.[17–20,58,59] Recently, our group have investigated anomalous behavior of DMSO-water binary mixture at low DMSO content ($X_D = 0.12$) using a fluorescence probe 2,2′-Bipyridine-3,3′-diol.[58] Very recently, Bhattacharyya *et al.*,[60] have studied the effect of DMSO-water binary mixture on the structure and conformational dynamics of lysozyme by fluorescence correlation spectroscopy (FCS). They have observed substantial fluctuation in the size of lysozyme at low DMSO concentration (0–10 mol. % DMSO). Through a series of work, Biswas *et al.*[17,18,20] have pointed out the anomalies in ethanol-water and TBA-water system. There are very few reports where solvation dynamics is used as a tool to investigate the anomalous behavior of binary mixtures. Castner and Shirota[19] showed the anomalous behavior of 1-propanol-water system at around $X_{ProH} = 0.15$-0.25 by monitoring solvation response around C153 molecule.

In this work, we have investigated the composition dependent anomalous behavior of DMSO-water binary mixtures by monitoring ultrafast solvation response around Coumarin 480 (C480) (Scheme 1) using femtosecond up-conversion technique. We have found two anomalous regions where average solvation times are abnormally high with respect to the other regions of this binary mixture. Most interestingly, the steady-state structure of the mixture predicted by Soper and Luzer[31] is in complete agreement with our femtosecond solvation dynamics result at same



SCHEME 1. Coumarin 480.

concentration region. As the water molecules are strongly hydrogen bonded to the DMSO, it is expected that the hydration decreases around the probe C480. As a result, solvation dynamics become slow at around 30% of DMSO concentration. However, to the best of our knowledge, this work is the first experimental evidence about the two anomalous regions of DMSO-water binary mixtures.

II. EXPERIMENTAL SECTION

A. Materials

Laser grade Coumarin 480 (C480) was purchased from exciton and used as received without further purification. Spectroscopic grade DMSO from Spectrochem Pvt., Ltd., India and triple distilled Milli-Q water were used to prepare all the solutions of DMSO-water binary mixtures for experimental purpose.

B. Sample preparation

We prepared two individual stock solutions of C480 in water and DMSO in two separate volumetric flasks. After keeping them for 24 h in room temperature, we measured the absorption spectra of two individual solutions. We adjusted the absorbance values (at absorption maxima) of two neat solutions near about 0.30. Then, all the binary mixtures were prepared from these two adjusted stock solutions.

C. Instruments and methods

Steady-state UV-vis absorption and fluorescence spectra were collected using a Shimadzu (model UV 2450) UV-vis spectrophotometer and a Hitachi (model no. F-7000) spectrofluorometer, respectively. For steady-state measurements, all the samples were excited at 408 nm and emissions were collected from 420 nm to 600 nm. Fluorescence quantum yields of C480 in different DMSO-water binary mixtures were calculated with respect to a secondary standard C480 in water ($\Phi = 0.66$) at 298 K.[61] Following equation was used to calculate the quantum yields:

$$\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R} \times \frac{(\mathrm{Abs})_R}{(\mathrm{Abs})_S} \times \frac{n_S^2}{n_R^2}, \tag{1}$$

where Φ represents quantum yield, A represents area under the fluorescence curve, Abs represents absorbance, and n is refractive index of the medium. The values of refractive index of DMSO-water binary mixtures were taken from a previous literature.[62] Subscripts S and R denote the corresponding parameters for the sample and reference, respectively.

Time-resolved emission spectra (TRES) were recorded using a time correlated single photon counting (TCSPC) picosecond set-up. The detailed experimental setup of this TCSPC instrument has been described in our previous publication.[63] In brief, all the samples were excited using a picosecond diode laser at 408 nm (IBH, UK, Nanoled) and the signals were collected at magic angle (54.7°) using a Hamamatsu microchannel plate photomultiplier tube (3809U). The instrument response function in our setup is ~100 ps. Time-resolved fluorescence decays were analyzed using IBH DAS-6 decay analysis software.

Femtosecond fluorescence traces were collected using a fluorescence up-conversion instrument (FOG 100, CDP, Russia). The details of this experimental setup have been given in an earlier publication.[64] Briefly, all the samples were excited using the second harmonic (400 nm) of a mode-locked Ti-sapphire laser (Tsunami, Spectra physics). A nonlinear crystal (1 mm β-barium borate (BBO), $\theta = 25°$, $\phi = 90°$) was used for frequency doubling of the fundamental beam (800 nm) to generate the expected excitation source. Here, it is notable that the fluorescence emitted from the sample was not measured directly but it was up-converted in a nonlinear crystal (0.5 mm BBO, $\theta = 38°$, $\phi = 90°$) using the fundamental beam as a gate pulse. The up-converted light was then dispersed in a monochromator and detected using a photon counting electronics (Photo Multiplier Tube, PMT). The cross-correlation measured between the second harmonic and fundamental had a full-width at half-maximum (FWHM) of 300 fs.

D. Viscosity measurements

Viscosities of DMSO-water binary mixtures were measured using a Brookfield DV-II+ Pro viscometer at 298 K.

III. RESULTS AND DISCUSSION

A. Steady-state absorption and emission studies

Figure 1 shows the steady-state UV-vis absorption spectra of C480 in DMSO-water binary mixture covering the whole region ($X_D = 0.0$ to 1.0). In neat water and DMSO, the absorption maxima of C480 are centred at 392 nm and 386 nm, respectively. The overall absorption shift [Figure S1(a), supplementary material[82]] of C480 in between $X_D = 0.0$ and 1.0 can be systematically described through two stages. Initially with the addition of DMSO up to $X_D = 0.12$, a red shift (~400 cm^{-1}) in absorption maxima is observed [Figure 1(a)]. With further addition of DMSO, we have observed a pronounced blue shift up to $X_D = 1.0$ [Figure 1(b)].

Steady-state fluorescence emission spectra of C480 in DMSO-water binary mixture are depicted in Figure 2. Emission maximum of C480 in neat water is centred at 492 nm. With the addition of DMSO, it exhibits a clear blue shift (~1600 cm^{-1}) up to 456 nm in neat DMSO. We have qualitatively explained the absorption and emission shift in Subsection III B.

B. Unusual solvatochromism of C480 in DMSO—Water binary mixtures

In most of the cases, solvatochromism of a fluorescent dye in solution can be predicted on the basis of its dipole moment in the ground (μ_g) and excited state (μ_{ex}). In this study, we have used C480 as a solvation probe. It is well-known in literature that upon photo-excitation, dipole moment of C480 increases near about 6.8 D.[65] In case of DMSO-water binary

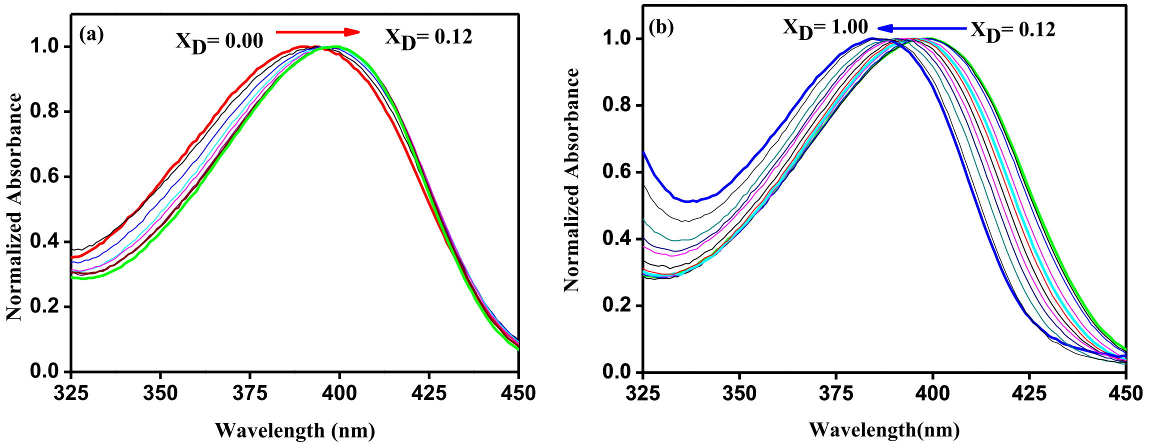


FIG. 1. Steady-state normalized absorption spectra of C480 in DMSO-water binary mixtures with increasing DMSO concentration from (a) $X_D = 0.00$ to 0.12 {$X_D = 0.00, 0.01, 0.04, 0.06, 0.08, 0.10, 0.12$} and (b) $X_D = 0.12$ to 1.00 {$X_D = 0.12, 0.20, 0.28, 0.32, 0.43, 0.50, 0.70, 1.00$}.

mixture, polarity of the medium decreases with the addition of DMSO to water.[58] Therefore, only by considering the polarity factor, it is expected that the absorption and emission maxima of C480 should shift towards the blue end from the initial addition of DMSO to water.[45] Practically, it was not found. Rather than the absorption maxima of C480 first exhibit a red shift up to $X_D = 0.12$ followed by a regular blue shift from $X_D = 0.12$ to 1.00 [Figure S1(a), supplementary material[82]]. On the other hand, emission maxima of C480 exhibit a regular blue shift throughout the whole region [Figure S1(b), supplementary material[82]]. Steady-state Stokes shift decreases with increasing DMSO content [Figure S1(c), supplementary material[82]].

Actually, most of the aqueous-binary mixtures exhibit this type of peculiar behavior. Biswas *et al.*[17] also found this type of behavior in the UV-visible absorption maxima of C153 in ethanol–water and TBA–water binary mixture. According to them with the addition of alcohol to water, alcohol clusters are formed which enhance the hydrogen bonding network between all the species. Particularly at low alcohol concentration, alkyl groups of alcohol cluster enter into the cavity formed by the hydrogen bonding network of water and thus reduce the compressibility of the solution. This reduced compressibility creates a more compact solvation environment around the probe molecules. As a result, energy levels of the probe molecules gradually become stable resulting in an initial red shift of the absorption maxima of C153. On the other hand, as the alcoholic clusters are very short lived (20–30 ps) with respect to the average lifetime of the probe molecule (>1 ns), environmental fluctuations faced by the photo-excited probe molecules do not affect the emission maxima at low alcohol content. As a result, emission transition energy becomes completely dependent on the polarity of the medium resulting in a blue shift from the very beginning (addition of alcohol to water). However, the absorption transition energy is affected by some factor other than the polarity. In correlation with their results, we have found the similar observation. Except this, we have tried to give an additional possible explanation on the basis of a model discussed by Hynes *et al.*[66]

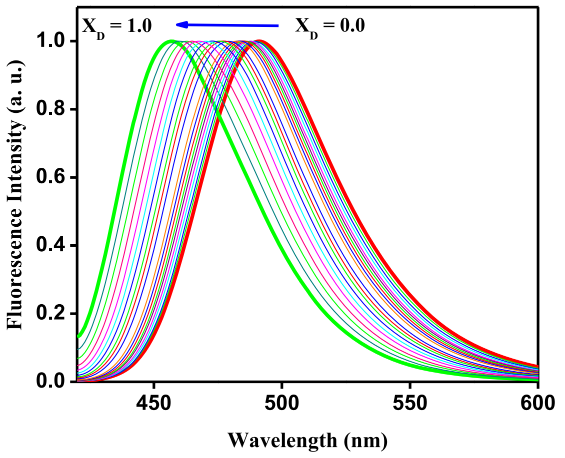


FIG. 2. Steady-state normalized fluorescence emission spectra of C480 in DMSO-water binary mixtures with increasing DMSO concentration from $X_D = 0.00$ to 1.00.

In 2003, Hynes *et al.*[66] proposed a theoretical formalism to explain the anomalous solvatochromic behavior of charged push-pull polyenes (CPPP). Hemicyanine dyes are the member of CPPP family. Their dipole moments in the excited-state are in the range of 5–15 D and the difference in dipole moment between the ground and excited state remains within 1–7 D.[67] In case of C480, these two factors (excited state dipole moment and the difference in dipole moment between ground and excited-state) are almost similar to that of hemicyanine dyes. As a result of this, we have used the model proposed by Hynes *et al.* in case of C480 to explain its UV-vis absorption behavior in DMSO-water binary mixture. According to their model, absorption transition energy (E_{abs}) and emission transition energy (E_{em}) can be obtained from the following equations:

$$E_{abs} = V_{eq}{}^{adia} + \Lambda_s{}^{ex} \qquad E_{em} = V_{eq}{}^{adia} - \Lambda_s{}^{g}, \tag{2}$$

where, $V_{eq}{}^{adia}$ is the equilibrated energy gap between adiabatic ground and excited states. $\Lambda_s{}^{g}$ and $\Lambda_s{}^{ex}$ are the adiabatic solvent reorganization energies in the ground and excited state, respectively. As the highly polar excited state dipole of C480 becomes more and more unstable on going from neat water to neat DMSO, the factor $V_{eq}{}^{adia}$ increases. On the other hand, $\Lambda_s{}^{g}$ and $\Lambda_s{}^{ex}$ decrease with the decrease in polarity of the medium. Therefore, it is possible that after addition of a certain

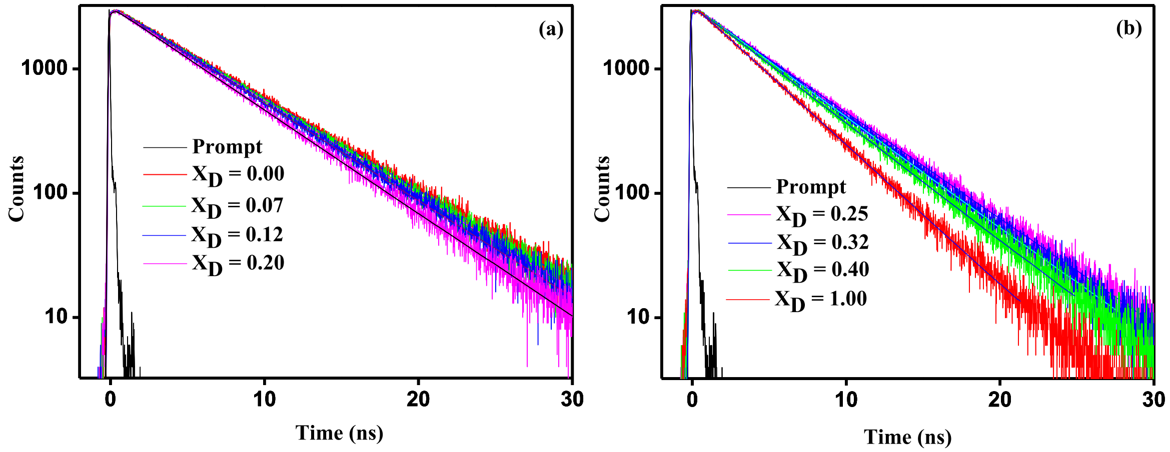


FIG. 3. (a) and (b) Fluorescence decays of C480 (λ_{ex} = 408 nm) in DMSO-water binary mixtures with increasing DMSO content.

amount of DMSO to neat water, V_{eq}^{adia} factor dominates over Λ_s^{g} and Λ_s^{ex}. As a result, after a particular region ($X_D = 0.12$), absorption and emission transition energy may be completely depend on V_{eq}^{adia} factor. As the V_{eq}^{adia} factor increases with increasing DMSO content, absorption and emission maxima of C480 shift towards the blue end after $X_D = 0.12$. Before this region ($X_D = 0.12$), Λ_s^{g} and Λ_s^{ex} have significant contributions on E_{em} and E_{abs}, respectively. In between $X_D = 0.0$ and 0.12, the rate of decrease of Λ_s^{ex} is much faster than Λ_s^{g}. As a result, the sum, i.e., ($V_{eq}^{adia} + \Lambda_s^{ex}$) decreases very slowly in between the regions. Therefore, the absorption maxima of C480 exhibit a bathochromic shift on going from $X_D = 0.00$ to $X_D = 0.12$. On the other hand, the factor ($V_{eq}^{adia} - \Lambda_s^{g}$) slowly increases in this region. As a consequence, the emission maxima of C480 shift towards the blue end throughout the whole range of DMSO-water binary mixture. Recently, our group reported the same type of behavior in the dioxane-water mixture using a hemicyanine dye (LDS-698).[16]

C. Time-resolved fluorescence studies

In this section, we want to focus on the long decay components of C480 in DMSO-water binary mixture. Time-resolved fluorescence decays of C480 in neat water, neat DMSO, and in DMSO-water binary mixtures were collected at their emission maxima [Figure 3]. In neat water and in DMSO, C480 exhibits a single decay component, corresponds to ~5.90 ns and ~3.98 ns.[61,68] In case of binary mixture, the decays were nicely fitted by a single exponential function. Note that with increasing DMSO content, the lifetime value of this long decay component is decreased. Interestingly, there is no such anomaly present in the long decay components of C480 in DMSO-water binary mixture. Most probably, the effect of DMSO-water binary mixture is limited to the ultrafast component of C480 within a very short time window. As a consequence, the long decay component which is far away from that of the ultrafast time window has not affected at all.

Radiative (k_r) and non-radiative (k_{nr}) decay rate constants are the two important parameters to characterize the excited state behavior of C480 in DMSO-water binary mixture. For this purpose, we have determined k_r and k_{nr} values of C480 from the average fluorescence lifetime and fluorescence quantum yield values using the following equations:

$$k_r = \frac{\Phi_f}{\langle\tau\rangle_f}, \tag{3}$$

$$k_{nr} = \frac{1}{\langle\tau\rangle_f} - k_r. \tag{4}$$

Looking at the results given in Table S1 (supplementary material[82]), it can be stated that the non-radiative decay rate constants of C480 decrease with increasing DMSO content up to $X_D = 0.17$. After this region, K_{nr} value increases up to $X_D = 0.24$ then again decreases on going from $X_D = 0.24$ to 0.27. This result clearly indicates that non-radiative decay rate constants are significantly affected by the presence of DMSO-water binary mixture in spite of having no direct influences on the long decay components of C480.

D. Study of ultrafast solvation dynamics in DMSO-water binary mixture

There are several reports of solvation dynamics in binary solvent mixtures.[69–71] In order to follow the ultrafast solvation dynamics in DMSO-water binary system, we have collected time-resolved decays of C480 at different wavelengths covering the entire region of steady-state emission spectra. Fluorescence up-conversion traces at the red end of emission spectra consist of a growth (rise) component which is an indication of solvation dynamics. To fit the femtosecond transients [Figure 4], we have determined the long decay components of C480 from the proper fitting of TCSPC data. Then, the long components were kept constant to determine the ultra short components.

Solvation dynamics is defined by a solvent correlation function C(t) which is denoted as

$$C(t) = \frac{\upsilon(t) - \upsilon(\infty)}{\upsilon(0) - \upsilon(\infty)}, \tag{5}$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ are the peak frequency at time zero, intermediate time, and infinity, respectively. The decays of C(t) are fitted by a bi-exponential function

$$C(t) = a_1 \exp^{-t/\tau_1} + a_2 \exp^{-t/\tau_2}, \tag{6}$$

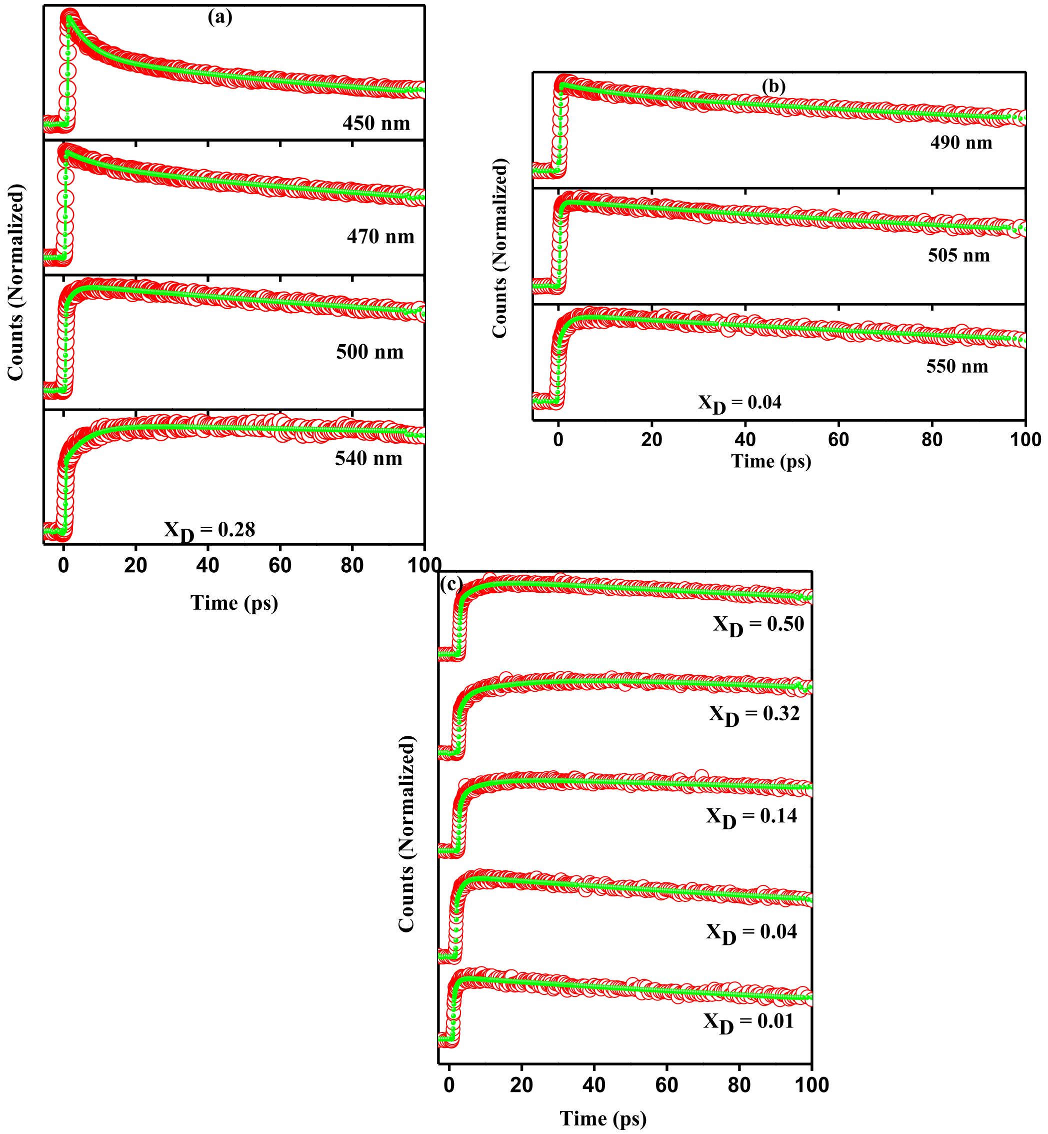


FIG. 4. Normalized femtosecond fluorescence up-conversion traces (λ_{ex} = 400 nm) of C480 in DMSO-water binary mixtures (a) X_D = 0.28, (b) X_D = 0.04, and (c) at 550 nm with various mole fraction of DMSO. Time-resolved traces at the red end (at 540 nm, 500 nm for X_D = 0.28 and 550 nm, 505 nm for X_D = 0.04 and all the traces in (c)) show a growth component, which signifies solvation dynamics.

where τ_1 and τ_2 are the solvation times with amplitudes of a_1 and a_2, respectively. The C(t) versus time (t) plots of C480 in DMSO-water binary mixture are represented in Figure 5. Then, the average solvation time $\langle \tau_s \rangle$ is calculated using the following equation:

$$\langle \tau_s \rangle = a_1\tau_1 + a_2\tau_2. \tag{7}$$

Solvation time determined in this procedure is called "spectral-reconstruction method."

TRES were constructed following the procedure of Fleming and Maroncelli.[72] The TRES at a given time t, $S(\lambda;t)$, is obtained by the fitted decays, $D(t;\lambda)$, by relative normalization to the steady-state spectrum, $S_0(\lambda)$, as follows:

$$S(\lambda;t) = D(\lambda;t)\frac{S_0(\lambda)}{\int_0^\infty D(\lambda;t)dt}. \tag{8}$$

Each TRES was fitted by a "log-normal line shape function," which is defined as

$$g(\upsilon) = g_0 \exp\left[(-\ln 2)\left(\frac{\ln[1+2b(\upsilon-\upsilon_p)/\Delta]}{b}\right)^2\right], \tag{9}$$

where g_0, b, ν_p, and Δ are the peak height, asymmetric parameter, peak frequency, and width parameter, respectively. The TRES plot of C480 in DMSO-water binary mixture at $X_D = 0.28$ is shown in Figure S2 of the supplementary material.[82]

The spectral changes in time-resolved emission are a mixture of the solvent response and solute–solvent interactions. However, we are much more interested in solvent response in our solvation dynamics study. Ladanyi and Nugent[73] have shown the effect of solute-solvent interaction on solvation dynamics in supercritical carbon dioxide (CO_2). Their study indicates that the long time scale of solvation dynamics is associated with the increased solute-solvent electrostatic attraction in the S1 state of solute. Therefore, by considering this aspect, we have measured the solvation time ($\langle \tau_s \rangle$) of C480 in DMSO-water binary mixture by the

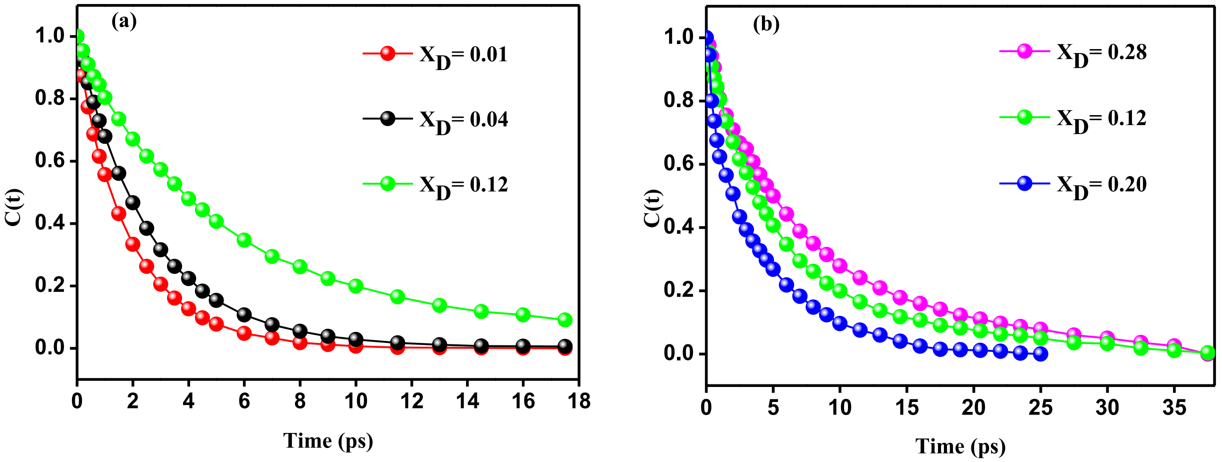


FIG. 5. Decay plots of solvent correlation function C(t) of C480 in DMSO-water binary mixtures (a) $X_D = 0.01$ (red line), 0.04 (black line), 0.12 (green line) and (b) $X_D = 0.12$ (green line), 0.20 (blue line), 0.28 (magenta line).

single-wavelength measurement method, in which solvation time has been calculated from the growth components (solely arise from the solvent response) and their relative contributions of a particular femtosecond upconversion trace. This method was developed by Barbara and co-workers.[74,75] First, for determination of the optimal wavelength, a quantity called spectral density at different wavelengths is plotted as a function of frequency corresponds to the emission maxima in various solvents for a particular fluorophore. The optimal wavelength is that one, where the spectral density is linearly dependent with the emission frequency. Therefore, C(t) can be calculated by collecting the emission transients at that particular wavelength. The same group has shown that the optimal wavelength for C480 is 420 nm which is in the blue end of the emission spectrum. On the other hand, Maroncelli and Gardecki[76] have shown that in case of C153, measurements can be done at two wavelengths, i.e., at 476 nm (blue side of the fluorescence spectrum) and 556 nm (red side of the fluorescence spectrum). However, they have found that 556 nm is the optimal wavelength for C153. Using this wavelength (560 nm), Shirota and Castner[19] studied solvation dynamics of C153 in aqueous 1-propanol binary solution. In our system, single-wavelength measurement at 420 nm is not possible due to the very low fluorescence intensity of C480 at this wavelength. By considering C153 as reference, we have chosen a wavelength (550 nm) which is in the red side of the fluorescence spectrum of C480. Fluorescence transients at 550 nm with various X_D are shown in Figure 4(c). The time constants of solvation dynamics along with their relative contributions are listed in the Table S2 [supplementary material[82]].

In upconversion measurement, the main difficulty is to the collect the decay too near to the excitation wavelength as discussed by Shirota and Castner.[19] We have faced the same problem while calculating C(t) by spectral-reconstruction method especially in the DMSO rich regions. Except this, it is a lengthy procedure containing several steps. Each and every step contains some error. Therefore, it is expected that a huge error or artifact is propagated throughout the calculation procedure. However, in case of single-wavelength measurement method, only one upconversion trace is needed to calculate the solvation time. In addition, the ultrafast event within the instrument response can be directly captured through this method, whereas, spectral-reconstruction never allows for the shortest time data to be included directly. Therefore, this procedure is much easier than the other one. In this method, upconversion traces of C480 at 550 nm in DMSO-water binary mixture are analyzed by a tri-exponential function (Eq. (10)), where the longest decay component is kept constant at the fluorescence lifetime of C480

$$I_{550}(t) = a_{fl}\exp(-t/\tau_{fl}) + \sum_{i=1}^{2} a_{si}\exp(-t/\tau_{si}), \qquad (10)$$

$$\sum_{i=1}^{2} a_{si} = 1, \qquad (11)$$

where, $I_{550}(t)$ is the time-dependent fluorescence intensity of C480 at 550 nm, a_{si} are the amplitudes of the solvation contribution, τ_{si} are the solvation time constants, and a_{fl} is the contribution of the fluorescence lifetime. The relative amplitudes of the two solvation components are normalized to be unity.

Average solvation times ($\langle\tau_s\rangle$) are calculated by using the following equation:

$$\langle\tau_s\rangle = \int_0^\infty C(t)dt = \sum_{i=1}^{2} a_{si}\tau_{si}. \qquad (12)$$

We have detected two anomalous regions of DMSO-water binary mixture by monitoring solvent relaxation response around C480 using two different methods, among them first one is spectral-reconstruction method and another one is single-wavelength measurement method. C480 is extensively used as a solvation probe due to the dramatic increase in dipole moment upon photoexcitation ($\Delta\mu \approx 7$ D).[65] Additionally, due to its rigid structure, the other nonradiative pathway like intramolecular charge transfer (ICT) is inhibited compared to its other analogues.[77] Although the prediction of both the methods is similar in case of first anomalous region ($X_D = 0.12$–0.17) of DMSO-water binary mixture, deviation is observed in case of second anomalous region ($X_D = 0.28$–0.35). Shirota and Castner[19] discussed the advantages

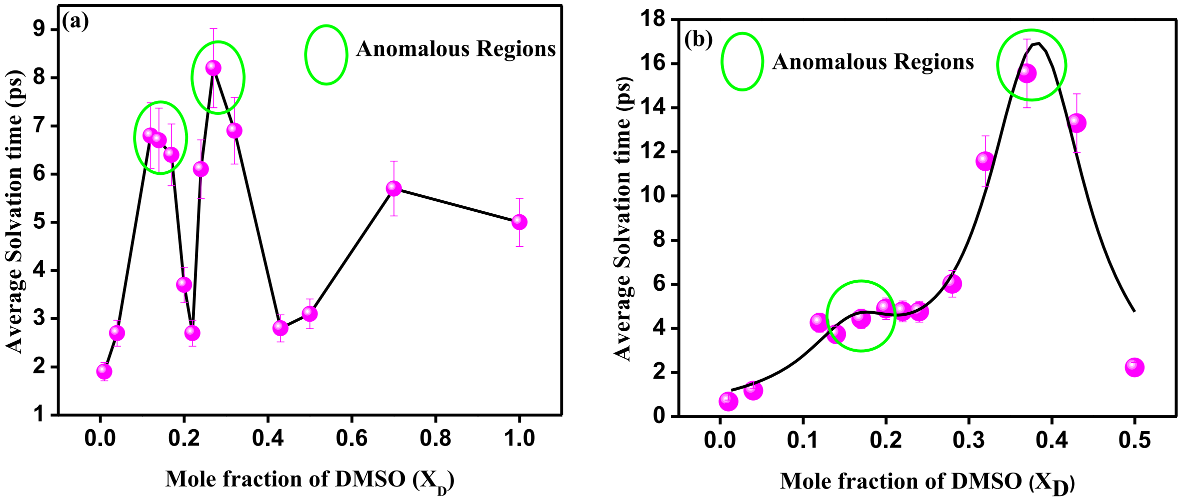


FIG. 6. Variation of average solvation time of C480 as a function of increasing mole fraction of DMSO (X_D) in DMSO-water binary mixtures (a) using spectral-reconstruction method and (b) single-wavelength measurement method (at 550 nm) [anomalous regions are marked by circles].

and disadvantages of single-wavelength measurement method in comparison to the spectral-reconstruction method. They told that the results of single-wavelength measurement method do not agree perfectly with those from the spectral-reconstruction method. Maroncelli and Gardecki[76] compared two methods for determining the solvation-response function. They concluded that (i) spectral-reconstruction method should be the choice of interest for accurate determination of the solvation-response function. (ii) Single-wavelength measurement method can provide a useful check on the results of spectral-reconstruction procedure. (iii) Single-wavelength measurement method is appropriate for those systems where solvation dynamics is measured in a series of related solvent conditions, i.e., binary solvent mixture as a function of composition. In such cases, better precision is expected from the single-wavelength estimates compared to those of spectral-reconstruction. (iv) Although, the ultimate accuracy is less than that obtained from spectral-reconstruction method.

Considering all the points, we have first analyzed the solvation response of C480 in DMSO-water binary mixture using spectral-reconstruction method. After that we have verified the result through single-wavelength measurement method. Plot of solvation time ($\langle\tau_s\rangle$) versus X_D [Figure 6 and Figure S3, supplementary material[82]] has indicated two anomalous maxima, i.e., from $X_D = 0.12$ to 0.17 and $X_D = 0.27$ to 0.35 where the average solvation times are abnormally high with respect to the other regions of this binary mixture. The necessary information regarding the solvation dynamics, i.e., decay time constants of C(t) with corresponding amplitudes are tabulated in Table I (spectral-reconstruction method).

Very often, solvation time (especially the slow component of solvent correlation function) is discussed with respect to the viscosity of the medium.[78,79] To correlate our result, we have measured the shear viscosity of DMSO-water binary mixture at different mole fractions of DMSO [S4, supplementary material[82]]. We have found that initially with the addition of DMSO, shear viscosity of the medium increases. After reaching a maximum in between 30% and 40% mole fraction of DMSO, it decreases up to the neat DMSO. Our results are in good agreement with a previous literature report.[26] Figure S5(a) indicates that slow decay component of C(t) follows the same trend as we have found in case of shear viscosity (except the region $X_D = 0.12$-0.17). We have also plotted other fluorescence data (Stokes shift and average lifetime of C480) as a function of viscosity of the medium [Figures S5(b) and S5(c)]. However, no such behavior like Figure S5(a) is found at low DMSO content. Castner *et al.*[80] studied the aqueous DMSO solution by optical heterodyne-detected Raman-induced Kerr effect spectroscopy. Their result indicates that longer diffusive relaxation time constant (τ_2), which has been assigned to DMSO reorientation, is loosely correlated with the viscosity of the medium. τ_2 increases with increase in viscosity up to $X_D \sim 0.30$. However, they do not find any anomalous behavior in τ_2 at low mole fraction of DMSO ($X_D = 0.12$-0.17), which is an indication about the viscosity guided reorientational time constant of DMSO. This result along with our result (Figure S5) indicates that between two

TABLE I. Decay parameters of C(t) of C480 in DMSO-water binary mixtures at different DMSO contents.

System	τ_f (a_f) (ps)	τ_s (a_s) (ps)	$\langle\tau_s\rangle$ (ps)[a]
$X_D = 0.01$	0.4 (0.11)	2.1 (0.89)	1.9
$X_D = 0.04$	2.4 (0.82)	4.1 (0.18)	2.7
$X_D = 0.12$	3.8 (0.65)	12.5 (0.35)	6.8
$X_D = 0.14$	3.7 (0.79)	17.8 (0.21)	6.7
$X_D = 0.17$	1.9 (0.29)	8.2 (0.71)	6.4
$X_D = 0.20$	0.6 (0.30)	5.1 (0.70)	3.7
$X_D = 0.22$	0.8 (0.67)	6.7 (0.33)	2.7
$X_D = 0.24$	1.1 (0.13)	6.8 (0.87)	6.1
$X_D = 0.28$	1.4 (0.19)	9.8 (0.81)	8.2
$X_D = 0.32$	1.7 (0.36)	9.8 (0.64)	6.9
$X_D = 0.43$	0.7 (0.36)	4.0 (0.64)	2.8
$X_D = 0.50$	2.3 (0.82)	6.8 (0.18)	3.1
$X_D = 0.70$	0.3 (0.07)	6.1 (0.93)	5.7
$X_D = 1.00$	...	5.0 (1.00)	5.0

[a] Error in experimental measurements ±10%.

anomalous regions (as mentioned above), the slow solvation dynamics in the region $X_D = 0.27$-0.35 is possibly attributed to the higher shear viscosity of the medium. However, the other region, i.e., $X_D = 0.12$–0.17 is not at all related to the viscosity of the medium.

Actually, solvation dynamics in pure water is completely different from that of binary mixtures. It is generally expected that with increasing water content, solvation time becomes gradually faster in case of an aqueous binary mixture. However, on going from pure DMSO to pure water, we have noticed two regions where average solvation times are abnormally high. Among them, the second one ($X_D = 0.27$-0.35) is already explained in terms of the higher shear viscosity of the medium. To interpret the anomalous slowdown in solvation response in $X_D = 0.12$-0.17, we have taken the help of recent molecular dynamics simulation performed by Bagchi and Roy.[9] According to their studies even at 5% of DMSO concentration, the dynamics of this binary mixture become slow due to formation of "micromicelle" type structure which is surrounded by a huge amount of water. Probably due to this type of interaction between DMSO and water, average solvation time increases on going from $X_D = 0.01$ to 0.04. If we go towards the higher DMSO content, i.e., beyond $X_D = 0.10$, we have to face a region where the average solvation times are not at all dependent on the concentration of DMSO. As mentioned earlier, a cluster type network is formed by repeating the structural unit 1DMSO:2H_2O in between the regions $X_D = 0.12$ and 0.17. Possibly due to presence of this type of clusters which are invariant throughout this region, average solvation time remains as it is with increasing DMSO content. After passing this region, average solvation time slowly approaches toward its maximum value (~8.2 ps) in between the regions $X_D = 0.27$ and 0.35 due to the higher shear viscosity of the medium. Further increase in DMSO concentration leads to decrease in solvation time due to the segregation of cluster networks. Some group noticed the clustering even at higher DMSO content.[34,35] In correlation with their results, we have found a rise in average solvation time at around $X_D = 0.60$–0.70. In neat DMSO, average solvation time reaches ~5.0 ps.

In binary mixtures, one of the most interesting phenomena is the preferential solvation of solute molecules. Bagno *et al.*[81] studied the preferential solvation of phenol in DMSO-water binary mixture by ^{1}H Nuclear Overhauser effect spectroscopy NMR spectroscopy. Their study indicates that phenol molecules are preferentially solvated by DMSO molecules at low DMSO content. From Table I, it is cleared that the relative contribution of long decay component of C(t) [assigned to DMSO-water clusters] exhibits a sudden increase in the mole fraction region $X_D = 0.12$–0.17 and near about $X_D = 0.30$. It is an indication about the depletion of free water molecules by the large DMSO-water clusters from the immediate vicinity of C480 molecules. This is further corroborated by the drop in steady-state anisotropy (r_0) of C480 particularly in these two regions [Figure S6, supplementary material[82]]. As the preferential solvation in this system is entirely depends on the individual solute–solvent interactions, it is expected that only DMSO molecules have very least capability to solvate the solute molecules. Therefore, the summary is that DMSO molecules first form DMSO-water clusters to take part in preferential solvation by replacing free water molecules.

IV. CONCLUSION

In conclusion, we have studied the anomalous behavior of DMSO-water binary mixture by collecting solvent relaxation response around a well-known solvation probe C480 using a femtosecond fluorescence up-conversion spectrometer. The overall observation is that every steady-state and time-resolved measurements are connected through a nonlinear relationship with the mole fraction of DMSO (X_D). We have calculated average solvation time of C480 by two methods, among them first one is spectral-reconstruction method and another one is single-wavelength measurement method. Each of which exhibits abnormal rise in solvation time in between the regions $X_D = 0.12$–0.17 and $X_D = 0.27$–0.35 as predicted from molecular dynamics simulation.[9] Although the first region ($X_D = 0.12$–0.17) is quite consistent with the simulation, some deviation is observed in case of second region ($X_D = 0.27$–0.35). This second anomalous region ($X_D = 0.27$–0.35) is probably due to the higher shear viscosity of the medium. First region is the most interesting one. In this region due to formation of strongly hydrogen bonded 1DMSO:2H_2O complexes, hydration around the probe C480 decreases, as a result of which solvation time increases. Additionally, we have found another rise in average solvation time at around $X_D = 0.60$–0.70. We are still working on this binary system (also with the alcohol-water binary mixture). Most probably, we will discuss in details about this region in our next contribution. We think that this slow-down in solvation time at different regions of this binary mixture is an indication of structural heterogeneity at the molecular level, which arises from the intermolecular aggregation between DMSO and water molecules.

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