Temperature-Dependent Magnetic Field Effect Study on Exciplex Luminescence: Probing the Triton X-100 Reverse Micelle in Cyclohexane

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The microenvironment within the reverse micelle of the nonionic surfactant Triton X-100 (TX-100) in cyclohexane has been investigated by studying the magnetic field effect (MFE) on pyrene−dimethylaniline exciplex luminescence. The nature of exciplex fluorescence and its behavior in the presence of a magnetic field have been found to vary significantly with the water content of the medium. Results are discussed in light of multiple exciplex formation within the micelle which is further supported by the fluorescence lifetime measurements. Those exciplexes emitting at longer wavelength are found to be magnetic field sensitive while those emitting toward the blue region of the spectrum are insensitive toward magnetic field. Since the exciplex's emission characteristics and magnetic field sensitivity depend on its immediate surrounding, it has been concluded that the environment within the micelle is nonuniform. With an increase in hydration level, different zones of varying polarity are created within the reverse micelle. It has been pointed out that the magnetic field sensitive components reside inside the polar core of the micelle while those located near the hydrocarbon tail are field insensitive. However it has been presumed that an interconversion between the different types of exciplexes is possible. The environment within the reverse micelle is found to be largely affected by the change in temperature, and this is reflected in the exciplex emission property and the extent of magnetic field effect. Interestingly, the variation of MFE with temperature follows different trends in the dry and the wet reverse micelle. A comparison has been drawn with the reverse micelle of the ionic surfactant to get an insight into the difference between the various types of micellar environment.

1. Introduction

Photoinduced electron transfer between excited electron acceptor and donor molecules generates radical ion pairs. The spin evolution of the radical pair in the presence of an external magnetic field has been important subject of study for the past few decades.[1−3] Radical ion pairs initially formed in the singlet spin state after electron transfer commonly have characteristics fluorescence. These radical pairs formed in close proximity, i.e., the contact ion pair (CIP) $A^{\bullet-}/D^{\bullet+}$ can diffuse out to form the solvent separated radical ion pair (SSRIP) $A^{\bullet-}(S)D^{\bullet+}$, which is also in the spin correlated singlet state. When the coupling between spin of the radicals is small, the electron−nuclear hyperfine interaction can induce transition between the singlet state (S_0) to all three degenerate triplet (T_{+1}, T_{-1}, T_0) states. In an environment of medium polarity the singlet to triplet spin evolution competes with the singlet state radical recombination and hence the luminescence process. In the presence of a magnetic field where the Zeeman splitting is large enough to exceed the hyperfine width, the intersystem crossing between the singlet to T_{+1} and T_{-1} states are suppressed. This results in increased singlet radical ion pair recombination yield, and hence the exciplex luminescence intensity increases. Thus the magnetic field effect (MFE) arises as a consequence of the competition between the spatial and spin evolution of the radical pair. MFE on inter- and intramolecular exciplex luminescence has been examined in various binary solvent mixtures.[4−7] It has been found that the dielectric constant (ϵ) and viscosity (η) of the

exciplex environment plays a major role in determining the extent of MFE. Therefore MFE on radical pairs not only provides information regarding the intermediate radical ion pair but also provides an insight into the environment where the radical pair resides.

In the present study MFE on exciplex luminescence have been monitored to study the environment inside Triton X-100 [TX-100, polyoxyethylene tetramethylbutyl phenyl ether; $CH_3C(CH_3)_2$-$CH_2C(CH_3)_2C_6H_4(OCH_2CH_2\text{-})_{9.5}OH$] reverse micelle. Reverse micelles are formed when the polar head group of the surfactant points inward to the polar solvent while the hydrophobic part remains outward. Unlike ionic reverse micelle where the polar head is charged and a well-defined water pool formation takes place, the polar head group in nonionic reverse micelle consists of long polyoxyethylene chains. These hydrophilic chains get hydrated by the water molecules, and a well distinct water pool may or may not be formed. While reverse micelles from ionic surfactants have been widely studied and have found various applications, recently micelles from nonionic surfactants have also been utilized as microreactors for nanoparticle sysnthesis.[8−10] Nonionic micelles have an advantage over ionic micelles in the sense that the complex electrostatic effects are eliminated. The phase behavior and structure of these nonionic reverse micelles have been investigated by various experimental techniques like NMR, UV-IR spectroscopy, and dynamic light scattering.[11−18] The amount of water that can be solubilized by these micelles have been found to be largely dependent on factors like the nature of the nonpolar solvent in which the surfactant is dissolved, the polyoxyethylene chain length, and also on the

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temperature. For example, in cyclohexane/hexanol solvent the number of water molecules that hydrate the oxyethylene chains is ~16, while in cyclohexane the number is ~5.5. The dynamical measurements within the reverse micellar interior reflect the restricted environment within the micelle.[19−21] Recently molecular dynamics simulation studies of small nonionic reverse micelles have been performed to investigate the effect of the conformation of the surfactant head group on the reverse micelle structure and water dynamics.[22,23] The TX-100 reverse micelle in cyclohexane in particular has been well characterized in the past.[15−18,24] The reverse micelles of TX-100 in cyclohexane (TX-100/cyclohexane) have been found to be nonspherical, and the size and shape of these microemulsions depend largely on the water content. Spectroscopic investigations of TX-100/cyclohexane indicate that the micellar interior is occupied by both water and cyclohexane. When the water content is increased, the cyclohexane is displaced from the micellar core. The average number of waters that hydrate the ether units has been found to be around 5.5. However, the probes previously used are ionic and short-lived. They reside and hence sense the polarity of a particular region as guided by their hydrophobic/hydrophilic interactions with the surroundings. Exciplexes on the other hand are comparatively long-lived. The lifetimes of exciplexes are further prolonged in organized media where the recombination of the ion pair by back electron transfer is restricted. The characteristics of the exciplexes depend largely on the polarity of the environment where they reside, and this is also reflected in the magnetic field behavior. MFE on radical pairs in reverse micelles and vesicles have been reported earlier.[25,26] However there are only few examples where MFE on exciplex emission has been used as a tool to probe the microenvironment of ionic reverse micelles of sodium bis(2-ethylhexyl) sulfosuccinate, commonly known as AOT.[27−29] We here extend our studies in nonionic reverse micelles. Our aim is to throw light onto the nature of the TX-100 reverse micellar environment. The results also indicate how the nonionic reverse micelle differs from its ionic counterpart. Moreover the temperature dependence of the micellar structure is reflected in the extent of the MFE. Temperature dependence of MFE on exciplex luminescence has been observed earlier in linked systems.[30,31] To the best of our knowledge such a temperature effect on MFE involving an unlinked radical ion pair system in a micellar system has not been reported previously.

2. Experimental Section

Triton X-100 was purchased from Sigma and used without further purification. Pyrene was recrystallized from an ethanol−water mixture before use. *N,N*-Dimethylaniline (DMA) was received from Aldrich and used after vacuum distillation. Spectroscopic grade cyclohexane was used as solvent. Triple-distilled water was used for all measurements. The acceptor and donor concentration was maintained constant: [pyrene]:[DMA] = 5×10^{-5} M:4×10^{-2} M. Unless indicated otherwise, the concentration of TX-100 was maintained at 0.3 M. All the solutions were deaerated by purging argon gas for 30 min.

The fluorescence spectra were measured by a Spex Fluoromax-3 spectrofluorimeter. The temperature was controlled within 25−50 °C by a Neslab thermostat using water as a heat carrier.

The magnetic field effect on exciplex luminescence was detected by employing an improved version of the phase locked detection system. The experiments were performed under a hyperfine saturating field of 300 G. The details of the setup have been discussed previously.[27,32] The setup can detect a change in luminescence in the presence of a magnetic field to a sensitivity of 1 part in 10000.
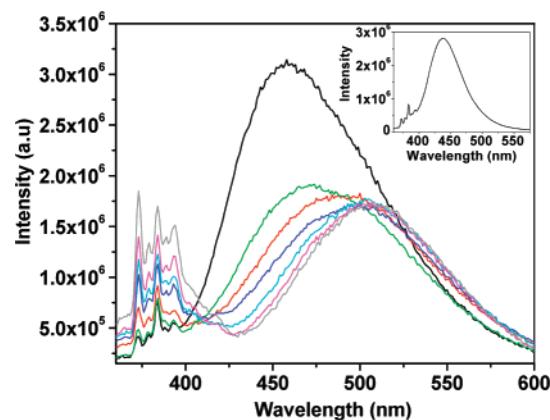

Figure 1. Fluorescence spectra of the pyrene−DMA exciplex in a dry TX-100 reverse micelle at different TX-100 concentrations (at room temperature, 27 °C): (black) 0.05 M, (green) 0.1 M, (red) 0.15 M, (blue) 0.2 M, (aqua) 0.3 M, (magenta) 0.4 M, (gray) 0.5 M. Inset: pyrene−DMA exciplex in neat cyclohexane.
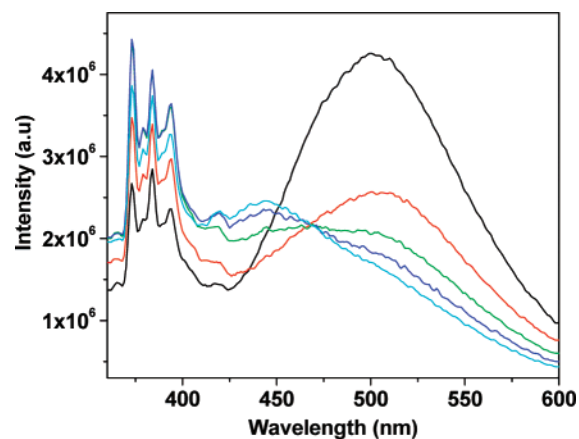

Figure 2. Fluorescence spectra of the pyrene−DMA exciplex in TX-100/cyclohexane at different water concentrations (at room temperature, 27 °C): (black) $w = 0$, (red) $w = 1$, (green) $w = 2$, (blue) $w = 3$, (aqua) $w = 4$.

The temperature variation of the MFE was performed by monitoring the temperature of the sample by a diode and heating the system in a feedback loop control.

The fluorescence lifetime measurements were measured with a Horiba Jobin Yvon sub-nanosecond spectrophotometer based on the time-correlated single-photon counting (TCSPC) technique.[33] The system has a 1 MHz repetition rate, and the half width of the instrumental response is on the order of 200 ps. The excitation wavelength was 340 nm. The decay data has been deconvoluted by inbuilt software.

3. Results

3.1. Steady-State Fluorescence Measurements. The fluorescence spectra of pyrene−DMA exciplex in the TX-100 reverse micelle at different surfactant concentrations are shown in Figure 1. The exciplex emission peak has been found to shift to longer wavelengths with an increase in surfactant concentration. While in neat cyclohexane the exciplex fluorescence maximum appears at 440 nm, in dry reverse micelle of 0.3 M TX-100 the fluorescence peak is very red-shifted and appears at ~500 nm. The present result thus indicates that in dry TX-100 micellar medium the pyrene−DMA exciplex senses a higher polarity than that of neat cyclohexane. Figure 2 shows the fluorescence spectra of pyrene−DMA exciplex in TX-100/cyclohexane at different molar ratios of water to TX-100 ($w =$
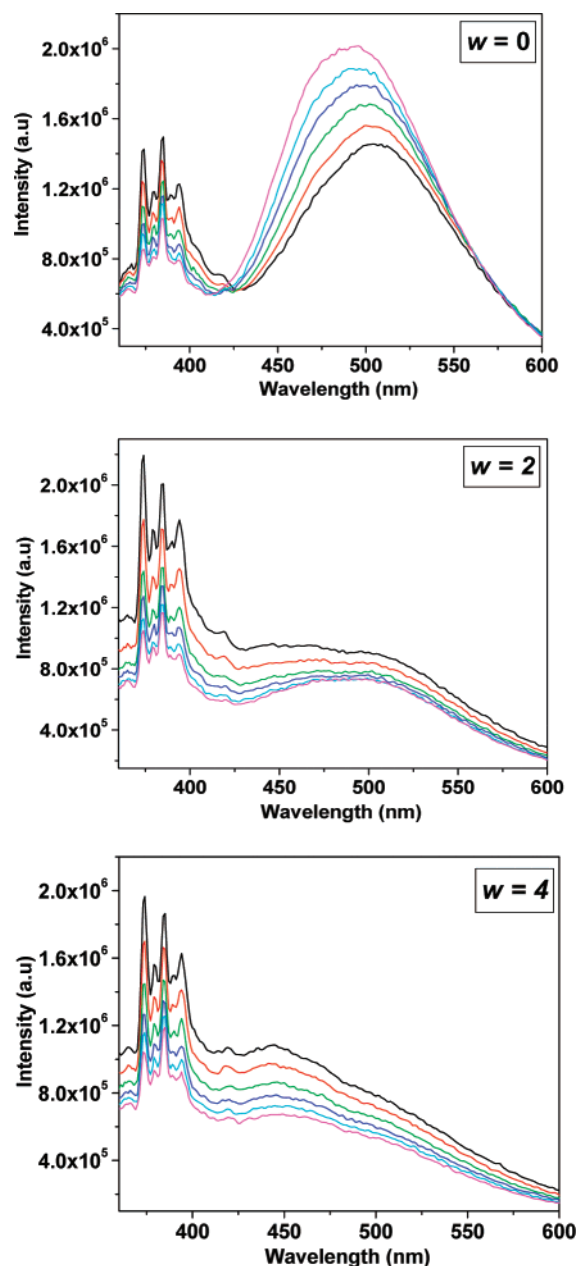
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Figure 3. Fluorescence spectra of pyrene−DMA exciplex in TX-100/cyclohexane at different temperatures: (black) 25 °C, (red) 30 °C, (green) 35 °C, (blue) 40 °C, (aqua) 45 °C, (magenta) 50 °C.

Figure 4. $\Delta\Phi/\Phi$ vs w curve in TX-100/cyclohexane at different emission wavelengths (at room temperature, 27 °C): (■) 425 nm, (△) 450 nm, (▼) 500 nm, (●) 560 nm, (★) 600 nm.

[H₂O]/[TX-100]). On gradual addition of water the fluorescence intensity at 500 nm is found to decrease, quenching being rapid at lower w values. The emission intensity at 440 nm is observed to increase at higher w values. The increase in surfactant concentration and the water content of the medium also alters the ratio of intensity of the first to that of third peak of pyrene monomer (I_1/I_3). It is important to mention that previous studies on pyrene−DMA exciplex in the AOT/*n*-heptane reverse micelle have shown that the exciplex fluorescence peak appears at 470 nm.[27] Thus in TX-100/cyclohexane the exciplex emission is very red-shifted compared to that in AOT/*n*-heptane which indicates that the exciplex resides in a region of higher polarity in TX-100 compared to AOT reverse micellar medium.

The temperature dependence of the fluorescence spectra has been recorded at different w values and presented in Figure 3. The exciplex emission characteristics are found to change differently at lower and higher water content. In dry reverse micelle at $w = 0$, the emission peak shows a blue shift with
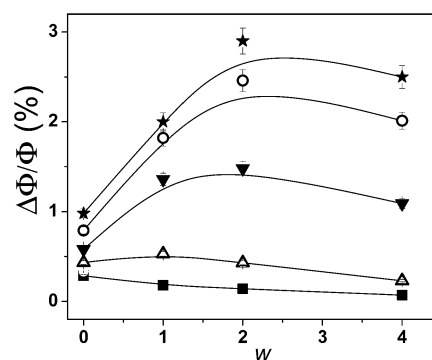
increase in temperature which suggests that the polarity of the medium decreases. At higher water content, the exciplex emission gets quenched with a rise in temperature. The emission at the blue end (∼440 nm) is found to decrease prominently compared to that in the longer wavelength.

3.2. Fluorescence Lifetime Measurements. The fluorescence lifetime of the exciplex has been measured at different wavelengths over the exciplex emission band. The data has been presented in Table 1. In the region 440 nm, the decay is triexponential with a fast growth on the order of 2 ns, and two decays have ∼10 ns and ∼44 ns lifetimes. The fast growth and the 10 ns decay remain more or less unchanged with an increase in w whereas the slow decay becomes faster at higher w. At 500 nm, the decay is biexponential; the fast growth and a long decay, similar to that at 440 nm, is present. However the decay of 10 ns is absent. At 540 nm, the lifetime measurement shows the presence of a slow growth on the order of 7 ns along with a slow decay of 50 ns. The slow decay is almost identical to that obtained at 440 and 500 nm, and it becomes faster with an increase in w. The wavelength dependence of the exciplex lifetime indicates the presence of more than one type of component in the medium. The lifetime of pyrene−DMA exciplexes in neat cyclohexane has been measured. At 440 nm, a decay of 100 ns and a growth of 2 ns have been obtained. The growth matches with the 2.5 ns decay of pyrene monomer at 384 nm. A long decay due to the tail end of the exciplex emission band has also been noted at 384 nm. The absence of a slow decaying component of 100 ns in the TX-100/cyclohexane reverse micelle suggests that the exciplex resides within the micellar zone rather than in the bulk cyclohexane.

The lifetime has been monitored at the monomer band at 384 nm in TX-100/cyclohexane containing pyrene−DMA exciplex. It consists of a strong fast decay on order of 50 ps along with two components on the order of 3 and 10 ns. The contribution of the 50 ps component increases with an increase in w. However this signature is also present in the bare TX-100/cyclohexane system in the absence of pyrene−DMA (Table 2). The TX-100/cyclohexane system on excitation at 340 nm is found to emit in the region of 360−400 nm, and thus the lifetime data at the monomer band is contaminated by the emission from TX-100. Therefore, the assignment of the pyrene monomer lifetime in the reverse micelle becomes difficult due to the overlap of the emission from the surfactant itself.

3.3. Magnetic Field Effect on Exciplex Luminescence. The relative enhanced exciplex luminescence in the presence of the magnetic field, i.e., $\Delta\Phi/\Phi$ value, of the pyrene−DMA exciplex in the TX-100 reverse micelle has been measured at different water concentrations in the TX-100 reverse micelle. The $\Delta\Phi/\Phi$ values at varying w have been monitored at different wave-

TABLE 1: Lifetime Values of Pyrene−DMA (5×10^{-5} M:4×10^{-2} M) Exciplex in TX-100/Cyclohexane at Different w Values (at Room Temperature, 27 °C)[a]

	384 nm	440 nm	500 nm	540 nm
$w = 0$	48.2 ps [0.391]	2.09 ns [−0.039]	3.03 ns [−0.117]	6.74 ns [−0.146]
	3.08 ns [0.013]	9.88 ns [0.138]	51.97 ns [0.147]	55.91 ns [0.166]
	8.89 ns [0.012]	44.93 ns [0.022]	$\chi^2 = 1.1257$	$\chi^2 = 1.0683$
	$\chi^2 = 1.0919$	$\chi^2 = 1.0751$		
$w = 2$	19.21 ps [2.612]	3.73 ns [−0.052]	4.758 ns [−0.117]	8.11 ns [−0.222]
	4.09 ns [0.0064]	12.55 ns [0.136]	33.65 ns [0.1633]	35.09 ns [0.223]
	12.78 ns [0.0047]	36.99 ns [0.038]	$\chi^2 = 1.2611$	$\chi^2 = 1.0194$
	$\chi^2 = 1.0614$	$\chi^2 = 1.1507$		
$w = 4$	9.28 ps [15.564]	2.863 ns [−0.050]	4.560 ns [−0.123]	7.575 ns [−0.226]
	3.73 ns [0.0048]	11.65 ns [0.115]	28.42 ns [0.179]	27.32 ns [0.248]
	12.27 ns [0.0036]	31.41 ns [0.045]	$\chi^2 = 1.3062$	$\chi^2 = 1.0215$
	$\chi^2 = 1.0237$	$\chi^2 = 1.0100$		
pyrene−DMA in cyclohexane	2.557 ns [0.032]	2.150 ns [−0.106]		
	100.3 ns [0.004]	106.3 ns [0.1218]		
	$\chi^2 = 1.1097$	$\chi^2 = 1.0272$		

[a] Positive or negative values signify decay or growth, respectively. Magnitudes within brackets signify pre-exponential factors.

TABLE 2: Lifetime Values of Neat TX-100/Cyclohexane at 384 nm at Different w Values (at Room Temperature, 27 °C)[a]

$w = 0$	$w = 2$	$w = 4$
52.67 ps [0.380]	27.70 ps [1.490]	29.60 ps [1.279]
2.803 ns [0.018]	3.57 ns [0.005]	3.07 ns [0.0071]
7.58 ns [0.0062]	10.09 ns [0.00083]	7.91 ns [0.0026]
$\chi^2 = 1.13384$	$\chi^2 = 1.150522$	$\chi^2 = 1.067697$

[a] Positive or negative values signify decay or growth, respectively. Magnitudes within brackets signify pre-exponential factors.

lengths and are presented in Figure 4. It has been found that the variation in $\Delta\Phi/\Phi$ with water content follows different trends at different emission wavelengths. $\Delta\Phi/\Phi$, when monitored at shorter wavelengths, is found to decrease with increasing w, while at longer wavelengths the $\Delta\Phi/\Phi$ value increases with increasing water content of the micellar medium and passes through a maxima at $w \approx 2$. Interestingly MFE have been found to be significantly higher than that obtained in aqueous and nonaqueous AOT/n-heptane reverse micelles.[25,27] In order to characterize the magnetic field sensitivity of different species present within the micellar medium, as indicated by the fluorescence lifetime studies, the $\Delta\Phi$ has been monitored at different emission wavelengths. The result is presented in Figure 5. Similar experiments have been previously reported to isolate the emission of the field sensitive component from that of the insensitive component.[34] The maxima of the $\Delta\Phi$ vs wavelength plots appear at around 515 nm, which indicates that the magnetic field sensitive component is centered on this particular region. It is to be noted that the maxima of $\Delta\Phi$ vs wavelength curves are close to the steady-state fluorescence maxima. At higher w, the peak of the $\Delta\Phi$ vs wavelength curve is slightly red-shifted and appears at 525 nm. At higher w though the exciplex emission is largely quenched, and the maxima of $\Delta\Phi$ vs wavelength curves appears at ~525 nm which indicates that the magnetic field sensitive component emits exclusively at longer wavelength.

$\Delta\Phi/\Phi$ at different w values have been measured at 560 nm by varying the temperature of the solution. The results show that the extent of MFE is sensitive toward the temperature of the medium. However, the variation of $\Delta\Phi/\Phi$ with temperature is different in the case of dry and wet reverse micelles. At $w = 0$, $\Delta\Phi/\Phi$ values decrease with a rise in temperature, whereas at higher w values MFE has been found to increase with temperature. The results suggest that the micellar behavior is distinctly different in dry and wet conditions. The $\Delta\Phi/\Phi$ values at different temperatures are presented in Figure 6.

4. Discussion

The above experimental results clearly indicate that the environment of the nonionic reverse micelle of TX-100/cyclohexane differs with addition of water as well as with variation in temperature. Both pyrene and DMA are soluble in cyclohexane and give a strong exciplex luminescence in neat cyclohexane at ~440 nm (inset of Figure 1). However in reverse micelle the ratio of the I_1/I_3 of pyrene monomer is found to vary with the surfactant concentration as well as with the water content of the medium. Such variation of the pyrene monomer fluorescence is only possible if pyrene is incorporated inside the micellar core where the water molecules reside. In fact the increase in the I_1/I_3 ratio of pyrene monomer indicates that the effective polarity of the medium increases.[35] The red-shifted emission of the exciplex in TX-100 reverse micelle compared to that in cyclohexane (Figure 1) also indicates that the exciplex is located inside the micelle, and with increasing surfactant concentration they effectively sense a higher local polarity. On gradual addition of water to dry TX-100, the intensity of the exciplex band at 500 nm quenches rapidly. Such a decrease in the emission can be interpreted as the fast relaxation of the exciplex residing in micellar core due to the increase in the surrounding polarity with w. As w increases, the water molecules become more free which causes the dynamical quenching of the exciplex. The different states of the solubilized water molecules in reverse micelles of polyoxyethylated nonylphenyl ethers in cyclohexane have been determined by NMR, ESR, and NIR studies.[36] Three states of water have been characterized for these surfactants. Water added initially hydrates the oxyethylene chain of TX-100 and forms the primary hydration shell. On further addition of water the secondary hydration shell and the free water are formed which results in the increased mobility of the probe molecules. However, the relative amount of water forming the pool varies with the surfactant chain length. Investigation of the polar core of TX-100 using methyl orange probe also indicated the existence of dispersed water molecules within the surfactant chains of TX-100 rather than formation of water pool.[15] Once the primary hydration shell is formed, the added water bridges the adjacent oxyethylene chains. The solvation dynamics study in TX-100/cyclohexane has shown that on increasing the hydration level the dynamics inside the reverse micelle gets faster which has been interpreted in terms
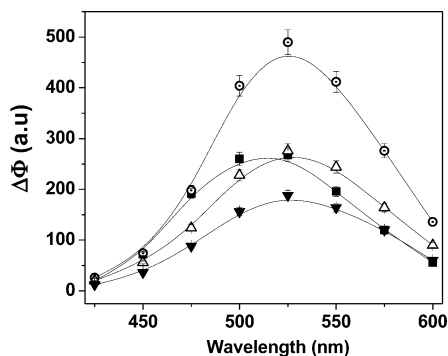
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Figure 5. $\Delta\Phi$ vs wavelength (λ) curve in TX-100/cyclohexane at different water contents (at room temperature, 27 °C): (■) $w = 0$, (⊙) $w = 2$, (△) $w = 4$, (▼) $w = 4.5$.
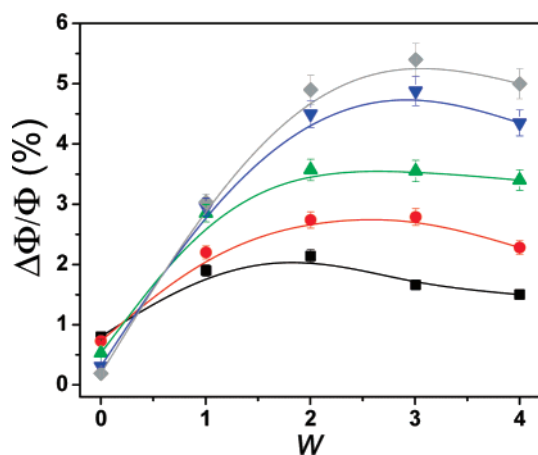

Figure 6. $\Delta\Phi/\Phi$ vs w curve in TX-100/cyclohexane at different temperatures (at $\lambda = 560$ nm): (■) 25 °C, (●) 30 °C, (▲) 40 °C, (▼) 50 °C, (◆) 60 °C. (At $\lambda = 560$ nm)

of the increase in solvent mobility.[20] The decrease in the exciplex lifetime values with increasing w in TX-100 (Table 1) also reflects the dynamic quenching by water due to the increased mobility of the environment. At higher w, the increase in the emission intensity at the blue end (~445 nm) suggests that the surrounding environment of the fluorescent exciplex is not uniform throughout the micellar interior at various levels of water content. The possibility of exciplex residing in the bulk cyclohexane has been ruled out since the lifetime values of the exciplex at 440 nm in TX-100/cyclohexane is quite different from that in neat cyclohexane. Studies concerning the characterization of the microenvironment of TX-100/cyclohexane at different w values indicated that the hydrophilic region of dry TX-100 reverse micelle is occupied by both cyclohexane and water.[15,16] On addition of water the cyclohexane molecules within the polar region are displaced outward. The experiments revealed that while in the dry reverse micelle the molar ratio of [cyclohexane]/[TX-100] in the micellar interior is around 4.5 the ratio becomes 3.0 at $w = 2.5$ and consequently the polarity of the micellar interior increases with increasing w. The pyrene−DMA exciplex being bipolar can reside over the entire hydrophilic region of the micelle, and the emission characteristics of the exciplex depend on the local polarity. Thus the gradual appearance of the peak at 440 nm in the fluorescence spectra at higher w values suggests that regions with varying polarity coexist within the micellar interior at higher water concentration. Such a difference in the dielectric constant may arise from the different extent of hydration of the polyoxyethylene chains as

more water is added. As water is added to the dry reverse micelle, cyclohexane residing inside the micelle is pushed outward and the oxyethylene chains get hydrated by the water molecules. At lower w values both water and cyclohexane compete for the hydrophilic part, and the hydration is uniform. However at higher w the water molecules get attached to the OH group of the oxyethylene chain at the micellar interior. The oil is displaced toward the outer peripheral oxyethylene groups close to the alkyl chain resulting in the enhanced concentration of the cyclohexane in this zone. Thus the exciplexes located at the outer region of the surfactant chains experience a lower dielectric constant and emit toward shorter wavelengths. These exciplexes increase in number at higher w values. Such a nonuniform distribution of the water in the micellar core of TX-100 reverse micelles has been previously proposed on the basis of the studies with fluorescent and spin probes.[24] It was also suggested that segregation of water in the polar core increases with an increase in the w values. Thus with increasing water content the structure of the micellar interior gradually changes which is reflected in the spectral properties of the exciplexes. A close look at Table 1 shows high resemblance of the lifetime data of the pyrene−DMA exciplex system in the TX-100 reverse micelle with that in the aqueous and nonaqueous AOT reverse micelles.[28,29] The wavelength-dependent variation of the lifetime suggests that at least two types of subensembles of exciplex are possible, one with the emission centered around 440−500 nm (Ex$_{440}$) and the other emitting at a longer wavelength (Ex$_{540}$). Since the fluorescence lifetime is a measure of the environment where the probe resides, the existence of an exciplex having a different lifetime thus points to the heterogeneity within the micellar core. Ex$_{440}$, which has a fast growth (~2 ns), is essentially an unrelaxed Frank−Condon state which occurs at a specific region of the reverse micelle where the mobility is restricted.[28] The decay of 9 ns at 440 nm closely matches the growth at 540 nm which is on the order of 7 ns. In light of our earlier work we presume that Ex$_{540}$ is generated from Ex$_{440}$. The long decay of 50 ns is observed throughout the exciplex emission band that has been attributed to Ex$_{540}$ which we call the relaxed exciplex. These relaxed exciplexes reside in a region of higher dielectric constant. It is interesting to note that the pre-exponential factor of this component increases toward the red end of the exciplex emission band (0.02 at 440 nm, 0.16 at 540 nm for $w = 0$; 0.044 at 440 nm, 0.25 at 540 nm for $w = 4$). It is further noticeable that as w is increased the long decay gets shortened (at 540 nm for $w = 0$ it is 55 ns whereas for $w = 4$ it is 27 ns). This happens because as w is increased the central polar core becomes more mobile with an increase in effective dielectric constant and the relaxed exciplexes become more solvated resulting in the quenching in the exciplex emission. It is to be noted that each subensemble does not consist of identical pyrene−DMA exciplexes; rather there are large number of states, each differing in their microenvironment and having a different lifetime. We think that the distribution of these microdomains within the polar core of the TX-100 micelle is broad and fuzzy. Thus in the TX-100 reverse micelle the exciplex emission bands are broad and overlap with each other. Around 500 nm, the fast decay (~9 ns) of the unrelaxed exciplex merges with the growth (~7 ns) of the relaxed exciplex, and we only observe the fast growth (~2 ns) of the unrelaxed exciplex and the slow decay (~50 ns) of the relaxed one. As discussed earlier our attempt to correlate the lifetime of the monomer fluorescence band with exciplex ones failed because of the contamination of the lifetime data from the emission of TX-100/cyclohexane itself.

The magnetic field effect on the exciplexes luminescence in TX-100 reverse micelle at varying water content and emission wavelength suggests that the environment plays a crucial role in determining the exciplex behavior. An external magnetic field affects the spin of the radical pair only when the radicals diffuse out to a distance where the exchange interaction is negligible. For a charged radical pair the diffusion dynamics depend largely on the potential energy surface which in turn depends on the electrostatic solvent interaction. In a solvent of low dielectric constant the contact ion pairs are formed. With an increase in solvent polarity the probability for the CIP to diffuse out to form an SSRIP increases. Though SSRIPs are not themselves luminescent, they control the population of the luminescent CIP. In moderately polar solvent the potential energy surface is such that diffusional excursion of the radical pair occurs to such an extent that the singlet to triplet interconversion is possible. On application of an external magnetic field the degeneracy between singlet and triplet states is lifted which results in reduction of ISC rate. This in turn increases the population of the singlet CIP. Thus dielectric constant and viscosity of the solvent modify the diffusional dynamics, and as a consequence the extent of MFE is found to depend on the surrounding solvent nature. MFE in alcoholic and nonalcoholic homogeneous medium has been found to maximize at an optimum dielectric constant and gets reduced at a lower or higher dielectric constant.[4-6] In alcoholic mixture the MFE peaks at $\epsilon = 26$ while for nonalcoholic solvent the maximum appears at $\epsilon = 16$. Thus it is expected that the magnetic field sensitive component resides in an environment of medium dielectric constant. The peak of $\Delta\Phi$ vs wavelength curve (Figure 5) which appeared near 515 nm at $w = 0$ is slightly red-shifted compared to that of the fluorescence curve. The result indicates that the field sensitive component resides in a relatively polar environment and thus emits at higher wavelength. The red shift of the maxima to 525 nm on addition of water suggests that the magnetic field component resides in a region which is occupied by the water molecules, i.e., in the polar core of the reverse micelle. Thus the relaxed type of exciplex (Ex_{540}) emitting at the red end is found to be magnetic field sensitive. The dielectric constant surrounding these exciplexes is thus adequate for the CIP to SSRIP conversion. The unrelaxed type, i.e., fast decaying components which are located toward the hydrocarbon tail of the surfactant, is insensitive toward magnetic field. The results in Figure 4 show that, for a given value of w, $\Delta\Phi/\Phi$ increases at longer wavelength. This obviously indicates that the emission at longer wavelength arises mostly from the magnetic field sensitive component. It should be mentioned that, because the micellar interior is heterogeneous, the field sensitive component actually denotes an ensemble of species residing within the oxyethylene chains of the surfactant, which are sensitive toward the magnetic field. Their characteristics differ from each other depending on their immediate locality. The different trends in the variation of the $\Delta\Phi/\Phi$ value with increasing w reflect the occurrence of various types of exciplexes. At shorter wavelength, ∼440 nm, the $\Delta\Phi/\Phi$ value has been found to decrease with addition of water. Such results can be explained due to the formation of the cyclohexane-rich zone toward the outer periphery of the surfactant chain. As more and more cyclohexane is pushed outward on increasing w, the region becomes nonpolar. The exciplexes residing in this zone are magnetic field insensitive, and their population increases with w resulting in the diminution of effective MFE. $\Delta\Phi/\Phi$, when monitored at longer wavelength, is found to pass through a maximum. It can be inferred that at $w = 0$ the surfactant chain is mostly occupied by cyclohexane and the environment is such

that the diffusion of the CIP to form the SSRIP is hindered which results in the small extent of MFE. As water is added, the polarity as well as the mobility of the solvent within the micelle increases, which favors the condition for MFE. The resemblance between the $\Delta\Phi/\Phi$ vs w curve in the TX-100 reverse micelle at 500 nm and above with the $\Delta\Phi/\Phi$ vs dielectric constant curve in the homogeneous alcoholic solvent mixture[4-6] indicates that the MFE in the reverse micelle is guided by the polarity of the medium. Comparisons between the two curves give an estimation of the polarity within the reverse micelle, which is roughly equal to that of alcohol. Moreover, the maxima of the $\Delta\Phi$ vs wavelength curves (Figure 5), ∼515 nm, match with those of the pyrene−DMA exciplex in alcohol, indicating that the field sensitive component resides in a region where the effective polarity is alcohol-like. Earlier, spectroscopic investigations revealed that the polarity within the micelle lies in between isopropanol and methanol.[12]

The effect of temperature on the solubilization of water in ternary (surfactant/oil/water) systems comprising ampiphiles containing hydrophilic polyoxyethylene chains has been studied.[37,38] It has been found that the interactions of oil and water molecules with the oxyethylene moiety of the surfactant play an important role in determining the aggregation and phase behavior. The rise in the temperature of the nonionic surfactant solution causes breaking of the hydrogen bonding between surfactant head groups and those between the surfactant chains and water. The lipophilic interactions are more profoundly affected compared to the cyclohexane−surfactant interaction.[39] It has been found that increases in temperature enhances the solubility of water in nonionic reverse micelle solution.[17,18,40] Our fluorescence measurements of the pyrene−DMA exciplex at $w = 0$ shows a blue shift with increasing temperature. The results indicate that the polarity of the micellar core decreases with a rise in temperature. A possibility is the penetration of cyclohexane within the micellar core which results in lowering of the polarity surrounding the exciplex. In other words, such an enhanced cyclohexane concentration within the micellar core forces the aggregates to dissociate into the monomer as has been suggested previously by Schelly et. al.[16] They have proposed a temperature induced decrease in core polarity resulting from cyclohexane penetration. The decrease in MFE with increasing temperature at $w = 0$ suggests that increasing cyclohexane concentration within the micelle results in the decrease in the local polarity that restricts the diffusion of the CIP to the SSRIP which in turn causes a decrease in the extent of MFE. The fluorescence data at higher w shows that with a rise in temperature the exciplex emission intensity at the blue region decreases to a greater extent than that toward the longer wavelength. The rise in temperature increases the mobility of the encapsulated water which in turn results in enhanced solvation of the exciplex thus favoring the formation of SSRIP and quenches the overall fluorescence from the CIP. The increase in temperature effectively distributes the water molecules evenly within the micellar core. The water molecules move toward the outer periphery of the micelle and hence increase the local dielectric constant and quench the unrelaxed exciplex. Since the extent of the change in the local environment with the rise in temperature is more toward the periphery than in the micellar core, the emission at the blue end is rapidly quenched compared to that of the longer wavelength. Most importantly, at higher w values the extent of MFE on exciplex luminescence is found to increase with rise in temperature. This indicates that the contribution from the magnetic field sensitive components becomes relatively greater at higher temperature.

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The results can be explained on the basis of the activation barrier between the unrelaxed exciplex and relaxed exciplex. As temperature is increased, the barrier crossing rate is increased, and more relaxed exciplexes are formed. The relaxed exciplexes being magnetic field sensitive results in the increase of MFE with rise in temperature The above results is also supported by the multiple state model proposed by Mataga et. al. which supposes the formation of various kinds of exciplex that differ in the solvent configuration around them.[41] These exciplexes can undergo interconversion among themselves.

Comparison of the results in TX-100 reverse micelle with that obtained previously in aqueous AOT reverse micelle in *n*-heptane reveals that the water molecules in the micellar interior are significantly different in nature in two cases. The red-shifted exciplex emission in the TX-100 compared to that in the AOT reverse micelle indicates a higher polarity in the former case. The interfacial water molecules in the AOT reverse micelle are perturbed by the high surface potential. The water molecules remain strongly hydrogen bonded to the polar head groups and are immobilized. In the case of TX-100, there is a high demand for hydrated water molecules. Thus most of the water molecules get dispersed within the long hydrophilic chains which results in the absence of tightly bound water molecules. Investigation of the photophysical behavior of dye molecules have pointed to differences in the structural and dynamical properties of the water in AOT reverse micelle and TX-100 reverse micelle.[42] The labile nature of the solvent molecules in TX-100 favors the necessary condition for MFE, i.e., the diffusion of CIP to form the SSRIP. This is evident from the larger extent of MFE in nonionic reverse micelle compared to that in ionic micelle.

5. Conclusion

In the present work the microenvironment of the TX-100 reverse micelle in cyclohexane has been investigated by studying the MFE on pyrene−DMA exciplex luminescence. The effect of temperature on the exciplex fluorescence and MFE in TX-100/cyclohexane has been investigated at varying water contents. The results have been explained on the basis of the competition between water and cyclohexane molecules for accessing the oxyethylene chain of TX-100. In the dry reverse micelle both cyclohexane and water reside within the hydrophilic core of the micelle whereas at higher *w* water molecules hydrate the oxyethylene chains and push the cyclohexane toward the outer hydrophobic periphery. The exciplexes residing in the outer cyclohexane-rich periphery have the identical emission signature as those in bulk cyclohexane (440 nm); however, the local environment is very different as indicated by the lifetime of the exciplex. As temperature is increased the water molecules residing at the central region and bridging the adjacent oxy-ethylene chains move outward and cause quenching of emission from exciplexes in the cyclohexane-rich boundary. The pyrene−DMA exciplex system is broadly classified in two subensembles. One is the unrelaxed exciplex which resides at the less mobile cyclohexane-rich zone of the reverse micelle and is magnetic field insensitive, while that residing in the mobile zone within the micellar polar core is magnetic field sensitive. The unrelaxed exciplexes lying in energetically higher states decay to the relaxed form, and this conversion is facilitated by the rise in temperature.

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