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Effect of hydrogen bonding on intramolecular charge transfer in aqueous and non-aqueous reverse micelles

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Abstract

In this paper, we have reported the behavior of intramolecular charge transfer (ICT) state of *p*-*N*,*N*-dimethylaminobenzoic acid (DMABA) and *p*-*N*,*N*-dimethylaminobenzonitrile (DMABN) in *n*-heptane/AOT/water, *n*-heptane/AOT/methanol and *n*-heptane/AOT/acetonitrile reverse micelles. The different features of ICT emission of both the probes in water, methanol and acetonitrile reverse micelles are explained by the presence and absence of hydrogen bonded ICT state in the above-mentioned reverse micelles. Moreover, we have reported the decay characteristics of both the probes in locally excited (LE) and ICT state in these three reverse micelles.
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Keywords: Hydrogen bonding; Intramolecular charge transfer; Aqueous and non-aqueous reverse micelles

1. Introduction

The photoinduced intramolecular charge transfer (ICT) of various organic molecules containing electron donor and acceptor groups has been the burgeoning interest of recent investigation, because it is a possible mechanism for biological and chemical energy conversion [1–3]. Intramolecular charge transfer emission in which a dialkylamino group acts as an electron donor has been a subject of several recent investigations [4–19,21–30,33]. Among them, the most interesting are twisted intramolecular charge transfer (TICT) processes, which involve twisting of the dialkylamino part relative to the rest of the molecules along with the charge transfer [4–6]. The formation of excited TICT state is recognized by a phenomena of dual fluorescence exhibiting a large Stokes' shifted emission in addition to the normal emission from the local excited (LE) state. In addition to the TICT model, several other models were proposed to explain dual fluorescence of DMABN and related compounds in polar solvents. The RICT model [7] involves a rehybridized (bent) cyano group. Recently, planar intramolecular charge transfer (PICT) model [8] has been proposed as an alternative to explain the presence of dual fluorescence of DMABN and other related compounds. This model postulates a planarized structure of the emissive CT state but does not involve state interaction. However, recent theoretical [9] and experimental results obtained from the studies of *p*-*N*,*N*-dimethylaminobenzonitrile (DMABN) and ethyl *p*-*N*,*N*-diethylaminobenzoate (DEAEB) in supercritical fluids and vapor phase [10–12] support the TICT mechanism in preference to the other model. Time resolved Raman studies of DMABN also support the TICT model [13].

The ICT state of DMABN has an extremely large dipole moment (23 D) [6] and hence its energy is expected to decrease with an increase in solvent polarity. This has two consequences. Firstly, this lowering of the energy of the ICT state reduces the energy barrier between the Franck–Condon (FC) excited state and the ICT state [14,15]. Secondly, the stabilization of the ICT state decreases the energy gap between the TICT state and the FC ground state [14,15]. Since lowering torsional barrier and increasing the non-radiative rates tend to have opposite effects on the ICT emission yield, as the solvent polarity increases the ICT emission yield should first increase and then after reaching a maximum ICT emission yield should decrease. The relative yield of ICT emission increases with solvent polarity up to a $E_T(30)$ value around 46 (acetonitrile) and decreases at a higher polarity [16]. Some authors have suggested that the specific hydrogen bonding between the solvent and electron donor species also plays a major role to stabilize the twist conformer to facilitate the formation of ICT state [17,18]. Very recently, the role of hydrogen bonding of the electron acceptor with solvent in the formation of ICT state has attracted much attention [19]. Such a hydrogen bonding effect may be an

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important subject in explaining the proton coupled charge transfer phenomena often observed in biological assemblies [20].

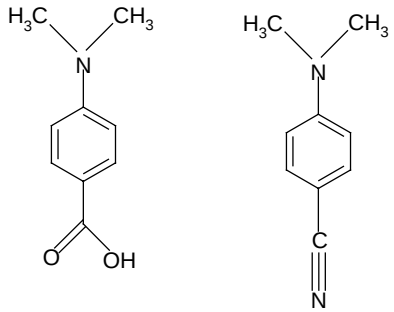
In recent years, many investigations have employed the cyclodextrin systems to control the TICT process of DMABN derivatives [21,22]. The TICT behavior is also reported within the cages of zeolites [23,24]. TICT process is also investigated in colloidal solution [25]. Many authors investigated the TICT process of DMABN derivative in micelles [26,27]. Although there are limited reports of TICT in aqueous reverse micelles [28–30], but no such reports are available in non-aqueous reverse micelles. Reverse micelles are nanometer size droplet of water or polar solvent surrounded by layer of surfactant molecules dispersed in non-polar organic solvent [31]. Depending upon the use of co-solvents (water or polar organic solvent), the reverse micelles are termed as aqueous or non-aqueous reverse micelles and the chemistry occurring in them is partly guided by these co-solvents [31]. The size of the reverse micelles is controlled by w (w = [water or polar solvent]/[surfactant]), can be increased by increasing the number of water or polar solvent molecules to that of surfactant. In order to understand the basic mechanism of ICT in biological assemblies, it is necessary to know how the ICT or TICT is affected in reverse micelle because reverse micelles is an elegant example of biological membrane. In this paper we have investigated the effect of hydrogen bonding on ICT of DMABA and DMABN in aqueous and non-aqueous reverse micelles.

2. Experimental

DMABA and DMABN (Scheme 1) were purchased from Aldrich. DMABA was recrystallized several times from ethanol before use. DMABN was purified by vacuum sublimation and then recrystallized from ethanol. AOT (dioctylsulfosuccinate, sodium salt, Aldrich) was purified by standard procedure [34,35]. The purified AOT was dried and kept in vacuo before use. *n*-Heptane, acetonitrile and methanol of spectroscopic grade (Spectrochem, India) was freshly distilled over calcium hydride (Spectrochem, India) before use. The solution was prepared using literature procedure [34,35]. The concentration of AOT was kept at 0.09 M. The concentrations of DMABA and DMABN were 5×10^{-5} M. This concentration is low enough to avoid dimerization of both the probes [22,33]. For all measurements the probes solutions were prepared in *n*-heptane and the reverse micelle was formed by the addition of the AOT followed by the subsequent addition of co-solvents. The steady state absorption and emission spectra were measured using a Shimadzu (model no. UV-1601) UV–vis absorption spectrophotometer and Spex Fluorolog-3 (model no. FL3-11) fluorescence spectrophotometer. All the fluorescence and excitation spectra were corrected for detector sensitivity and lamp intensity fluctuations with respect to wavelength. The steady state fluorescence emission anisotropies (r) are calculated using the following relation:

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

where I_{VV} and I_{VH} represent the vertically and horizontally polarized emission intensities obtained on excitation with a vertically polarized light. G the correction factor for detection sensitivity to the polarization direction of the emission and is given by $G = I_{HV}/I_{HH}$. The experimental setup for the picosecond time correlated single photon counting (TCSPC) was described in detail in our earlier publications [34]. The full width half maximum (fwhm) of the instrument response function (IRF) is ~40 ps. The excitation wavelength for all steady state and time resolved studies were 295 nm. All the measurements are done at room temperature at 298 ± 2 K.



DMABA DMABN

Scheme 1. Structure of DMABA and DMABN.

3. Results and discussions

3.1. Absorption spectra

DMABA in *n*-heptane exhibits an absorption maximum at 307 nm. At $w = 0$, the absorption spectrum of DMABA shows a maximum at 300 nm. On addition of water/methanol/acetonitrile, the absorption maximum is slightly red shifted with the decrease in absorbance (Fig. 1a). In going from *n*-heptane to reverse micelle, the probe molecule experiences higher polarity compared to *n*-heptane and we should get a red shift in absorption spectra [34]. Thus the observed blue shift of the absorption spectra with the formation of reverse micelle is unusual. In this context, it should be mentioned that protolytic dissociation of DMABA occurs in some solvents [6]. Again, the anionic form of DMABA (in a pH 10 aqueous buffer) has an absorption maximum at 288 nm (Fig. 1a). Thus the blue shifts in absorption spectra for all the reverse micelles indicate that some DMABA molecules are ionized in the presence of AOT and encapsulated inside the reverse micelles. Though we cannot rule out the possibility of some neutral DMABA molecules are incorporated in-

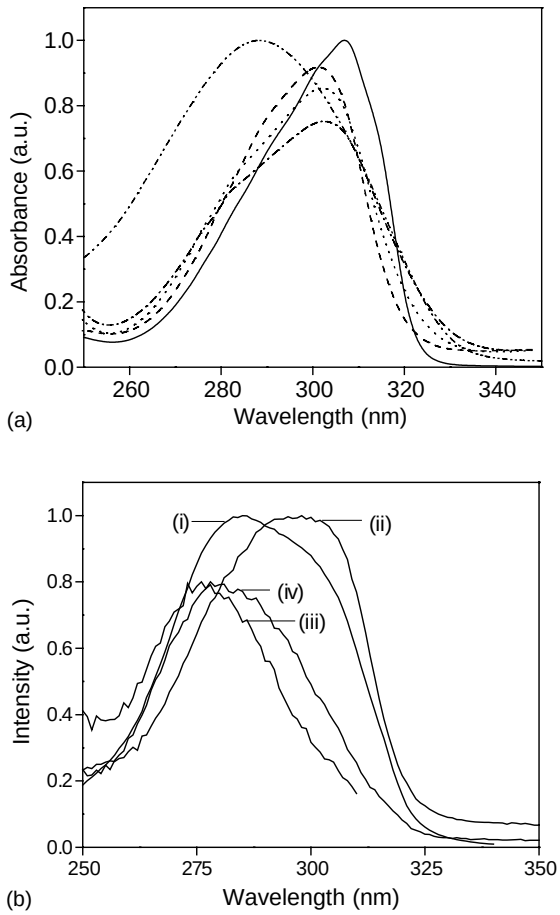


Fig. 1. (a) Absorption spectra of DMABA in *n*-heptane/AOT/water reverse micelles. Solid lines for pure *n*-heptane, dashed lines for $w = 0$, dotted lines for $w = 4$ and dash-dotted lines for $w = 32$. Dash-dot-dotted lines for DMABA in pH 10 aqueous buffer solution. (b) Excitation spectra of DMABA and DMABN in *n*-heptane/AOT/methanol reverse micelles. The excitation spectra of DMABA in $w = 6$ methanol reverse micelles, monitored at (i) 350 nm and (ii) 450 nm. (iii) and (iv) are the excitation spectra of DMABN in $w = 6$ methanol reverse micelles monitored at (iii) 320 nm and (iv) 440 nm.

side the reverse micelles. Jiang and Jin [28] also reported that inside the aqueous reverse micelles both neutral and anionic forms co-exist. We have estimated the partition coefficient (using conventional UV–vis absorption spectroscopy [35] and DMABA as a probe) in two-phase model systems, namely, *n*-heptane/water, *n*-heptane/methanol and *n*-heptane/acetonitrile to get a quantitative idea of probe partition in different phases. The partition coefficients (K_I = [non-polar]/[polar]) for *n*-heptane/acetonitrile, *n*-heptane/methanol, and *n*-heptane/water are 0.016, 0.041 and 0.044, respectively. It suggests that the solubility of the probe (DMABA) in the polar solvents (water, methanol, acetonitrile) is quite high. For all the reverse micelles, the excitation spectra monitored at the blue and red end of the emission spectra are different. The difference in excitation spectra at the blue end and red end of the emission spectra indicates that there are broadly two kinds of probe molecules portioned in all the reverse micelles. Representative excitation spectra in case of methanol reverse micelles are shown in Fig. 1b.

In *n*-heptane DMABN shows absorption maximum at 281 nm. On addition of AOT and co-solvents (water/methanol/acetonitrile) no remarkable peak shifts are observed for water, methanol and acetonitrile reverse micelles. It suggests that a substantial amount of DMABN may reside in bulk *n*-heptane. To get a quantitative idea of the probe partition in different phases, we have also estimated the partition coefficient of DMABN in two-phase model systems using UV–vis absorption spectroscopy. The partition coefficients (K_I = [non-polar]/[polar]) for *n*-heptane/acetonitrile, *n*-heptane/methanol, and *n*-heptane/water are 0.045, 0.111, and 24.0, respectively. It suggests that the solubility of the probe DMABN in the polar solvents (methanol and acetonitrile) is quite high. But in case of *n*-heptane/water system, the high value of partition coefficient suggests very little solubility of the probe in the water. But on addition of surfactant (0.056 M AOT) the partition coefficient is reduced to 4.85. This indicates that in the presence of AOT there is a finite probability of the probe to enter into the water. For all these reverse micelles, a tail appears in the red end side of absorption spectrum (data not shown), indicating the probe molecules are incorporated in the reverse micelles [34,35]. Though the probe molecules are definitely transferring inside the reverse micelles, but a substantial amount of probe molecules remain in the bulk *n*-heptane. The excitation spectra monitored at two different emission wavelengths are different, suggesting the distribution of probe molecules between *n*-heptane and inside the reverse micelles (Fig. 1b). It is very difficult to predict the location and orientation of the probe inside the reverse micelles. The most probable location for DMABN inside the reverse micelles is at the interface, since neutral probe molecules reside at the interface of the reverse micelles [30,34,35].

3.2. Steady state fluorescence anisotropy

In order to determine the location of the probe in AOT reverse micelles, we have measured the steady state fluorescence anisotropy (r) as a function of w. The high value of fluorescence anisotropy at $w = 0$ compared to *n*-heptane indicates that the probe molecules strongly interacts with the surfactant molecules. However, a high value of fluorescence anisotropy in water, methanol and acetonitrile reverse micelles compared to pure *n*-heptane (Table 1) indicates that rotational motion of DMABA is more restricted in the above mentioned three reverse micelles. This fact confirms that the probe molecules are residing inside the reverse micelles. Moreover, the fluorescence anisotropy value of the probe decreases with the increase in water/methanol/acetonitrile content of the reverse micelles (Table 1). It seems that probe molecule faces initial restriction in small pool size, which decreases with bigger pool size. But it is very difficult to point out the solubilization region of DMABA in AOT reverse micelle. It may reside either at the interfacial region

Table 1
Steady state fluorescence anisotropy (r) of DMABA in *n*-heptane, aqueous and non-aqueous reverse micelles

Medium	w	λ_{em} (nm)	r
n-Heptane	–	340	0.034
n-Heptane + 0.09 M AOT	0	340	0.194
Water reverse micelle	4	345	0.136
Water reverse micelle	32	345	0.095
Methanol reverse micelle	2	350	0.250
Methanol reverse micelle	6	350	0.125
Acetonitrile reverse micelle	2	350	0.060
Acetonitrile reverse micelle	4	350	0.045

or in the solvent pool of the reverse micelle or spreading in both regions. In analogy to what has been assigned for DMABA in an AOT reverse micelle [28] and DMABA in CTAB/1-heptanol/water reverse micelle [29], we can assume that the DMABA molecules are inserted at the interface inside these three (water, methanol and acetonitrile) reverse micelles. As the change in steady state fluorescence anisotropy of DMABN from *n*-heptane to reverse micelles is very small and it is within error limits, hence we have not reported the results. Thus we cannot draw any definite conclusion from these results.

3.3. Steady state fluorescence spectra

The variations of fluorescence spectra of DMABA in all the three reverse micelles as a function of w value are shown in Fig. 2. On excitation, DMABA in *n*-heptane shows a strong peak at ~340 nm (Fig. 2), which is assigned to be arising from the locally excited state, called LE emission [6]. With the addition of 0.09 M of AOT to this solution, the LE emission peak is more or less unaffected but the intensity decreases (Fig. 2). With further addition of water/methanol/acetonitrile, the intensity of LE emission decreases but the peak position of LE remains unchanged (Fig. 2). The intensity of LE emission decreases from *n*-heptane to reverse micelles due to the enhanced rate of transition from LE to ICT state as the energy barrier between LE and ICT state decreases with the increase in polarity [14,15]. In *n*-heptane DMABA does not show any ICT emission due to the lower polarity of the solvent. At low polarity, ICT state exists in higher energy level compared to LE state [14,15]. We have not observed any ICT peak at the red end side of the emission spectra in addition to the LE peak in water reverse micelle (Fig. 2a); whereas in methanol reverse micelle ICT peak appears as a shoulder (Fig. 2b), but in acetonitrile reverse micelle we have observed a clear ICT peak at around ~440 nm which is assigned to be arising from ICT state, called ICT emission (Fig. 2c).

Fig. 3 shows the fluorescence spectra of DMABN in water, methanol and acetonitrile reverse micelles. Like DMABA, the LE emission intensity gradually decreases from *n*-heptane to the reverse micelles (Fig. 3). In this context, it should be mentioned that the observed emission from LE state of DMABN in reverse micelles is the convolution of the emission of DMABN present inside the reverse micelles and in bulk heptane, because a reasonable amount of probes remain in bulk *n*-heptane. On addition of AOT and co-solvents to *n*-heptane, the energy gap decreases between

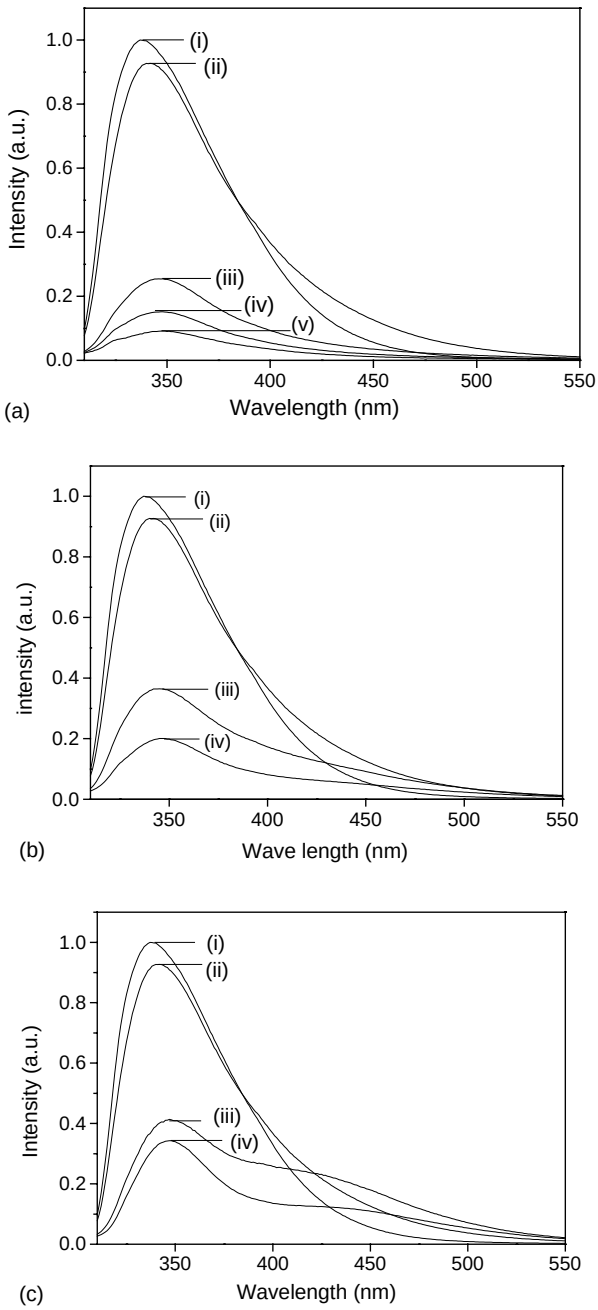


Fig. 2. (a) Emission spectra of DMABA in *n*-heptane/AOT/water reverse micelles: (i) in pure *n*-heptane, (ii) $w = 0$, (iii) $w = 4$, (iv) $w = 16$, and (v) $w = 32$ of water reverse micelle. (b) Emission spectra of DMABA in *n*-heptane/AOT/methanol reverse micelles: (i) in pure *n*-heptane, (ii) $w = 0$, (iii) $w = 2$, and (iv) $w = 6$ of methanol reverse micelle. (c) Emission spectra of DMABA in *n*-heptane/AOT/acetonitrile reverse micelles: (i) in pure *n*-heptane, (ii) $w = 0$, (iii) $w = 2$, and (iv) $w = 4$ of acetonitrile reverse micelle.

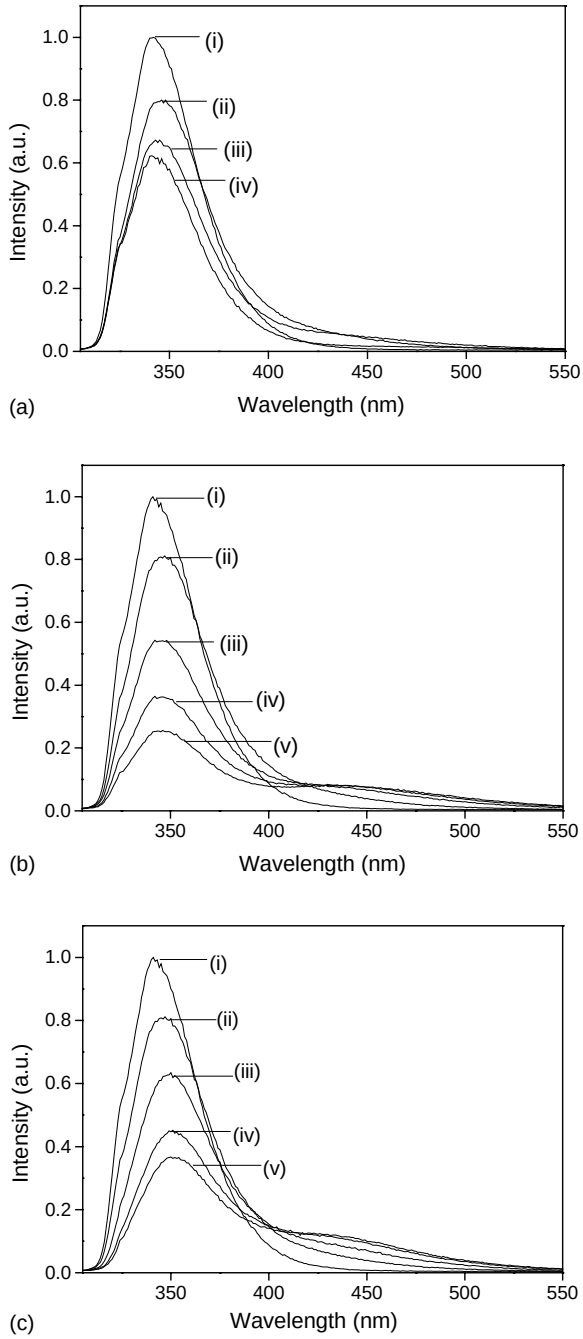


Fig. 3. (a) Emission spectra of DMABN in *n*-heptane/AOT/water reverse micelles: (i) in pure *n*-heptane, (ii) $w = 0$, (iii) $w = 2$, (iv) $w = 16$ of water reverse micelle. (b) Emission spectra of DMABN in *n*-heptane/AOT/methanol reverse micelles: (i) in pure *n*-heptane, (ii) AOT, $w = 0$, (iii) $w = 2$, (iv) $w = 4$, and (v) $w = 6$ of methanol reverse micelle. (c) Emission spectra of DMABN in *n*-heptane/AOT/acetonitrile reverse micelles: (i) in pure *n*-heptane, (ii) $w = 0$, (iii) $w = 2$, (iv) $w = 4$ and (v) $w = 5$ of acetonitrile reverse micelle.

LE state and ICT state [14,15] of DMABN and favors the formation of ICT state from LE state. The most interesting results observed in these reverse micelles are as follows. Firstly, the ICT peak of the probe appears as a shoulder at the red end side of the emission spectra in addition to the LE peak at low w value of water reverse micelle (Fig. 3). Secondly, we have observed a clear ICT peak at ∼440 nm in methanol and acetonitrile reverse micelles in addition to the LE peak (Fig. 3).

Both DMABA and DMABN are structurally very similar; DMABN has –CN group (as an acceptor) in place of –COOH group of DMABA. So, the different ICT behavior of the two probes in water, methanol reverse micelles arises due to the presence of different acceptor group. Among the three co-solvents used in these reverse micelles, acetonitrile is polar aprotic solvent, whereas water and methanol are polar protic solvents. So, hydrogen bonding between the probe and hydroxylated solvents may take a major role for the observed anomalous results in water and methanol reverse micelles. The deactivation via internal conversion (IC) resulting from the hydrogen bonding has been proposed to account for the fluorescence quenching of many molecules having ICT state [32]. Very recently, Kwok et al. [19] showed that IC deexcitation rate of HICT (hydrogen bonded ICT) state is much larger than that of ICT state and is mainly responsible for the reduced quantum yield of DMABN in methanol. Thus, the deactivation rate (via IC) from the hydrogen bonded ICT (HICT) state which arises due to the hydrogen bond formation between the –COOH/–COO^- group of DMABA and water/methanol may be responsible for the observed anomalous results in water and methanol reverse micelles. The internal conversion rate from the HICT state is not so high in case of DMABN because the hydrogen bond strength between –CN group and water/methanol is low enough. Hence, we can see a weak ICT emission in case of DMABN at low w value of water reverse micelles. Moreover, the relative strength of the hydrogen bond between the –COOH/–COO^- group and water/methanol is high compared to the same between –COOH/–COO^- group and acetonitrile. As a result, we have observed a clear ICT peak of DMABA in case of acetonitrile reverse micelles. In summary, hydrogen bonded ICT state of DMABA is responsible for the anomalous results in case of water and methanol reverse micelles.

In order to understand the hydrogen bonding effect, we have studied the effect of addition of water/methanol in the emission spectra of DMABA and DMABN in acetonitrile solvent. Acetonitrile is a polar aprotic solvent, so hydrogen bond formation between the solute and solvent is not possible. With the addition of water/methanol in acetonitrile, hydrogen bond formation between the solute and added water/methanol molecule is possible. The emission spectra of both DMABA (Fig. 4a) and DMABN (Fig. 4b) show sharp decrease in ICT emission intensity with the increase in water concentration. The effect of ICT emission intensity on addition of water to acetonitrile is more severe for DMABA in comparison to DMABN. Moreover, using the same probe the effect is more pronounced in case of water compared to methanol. It again confirms that hydrogen bonded ICT state of DMABA is responsible for the anomalous results in case of water and methanol reverse micelles.

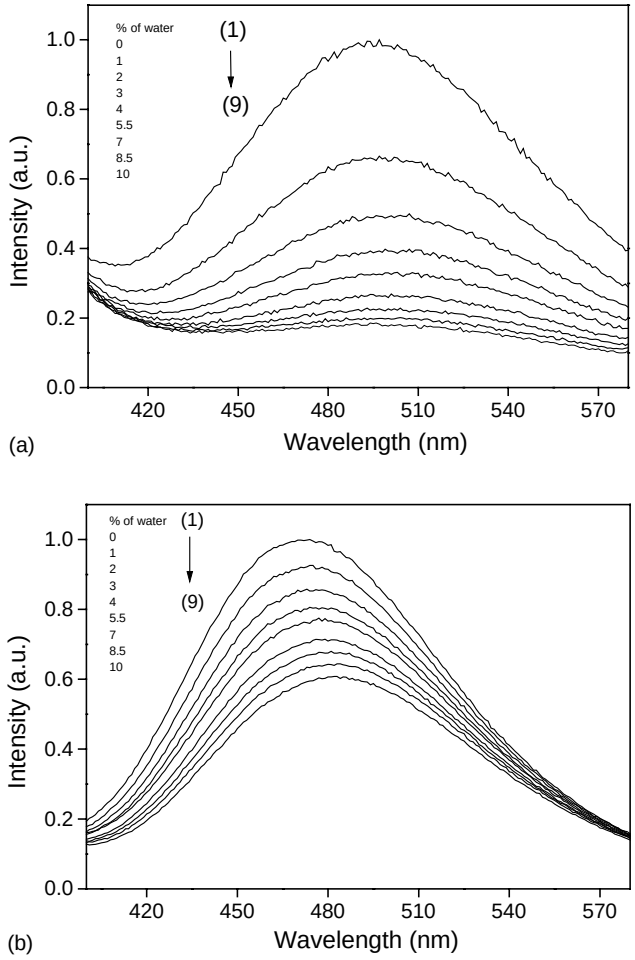
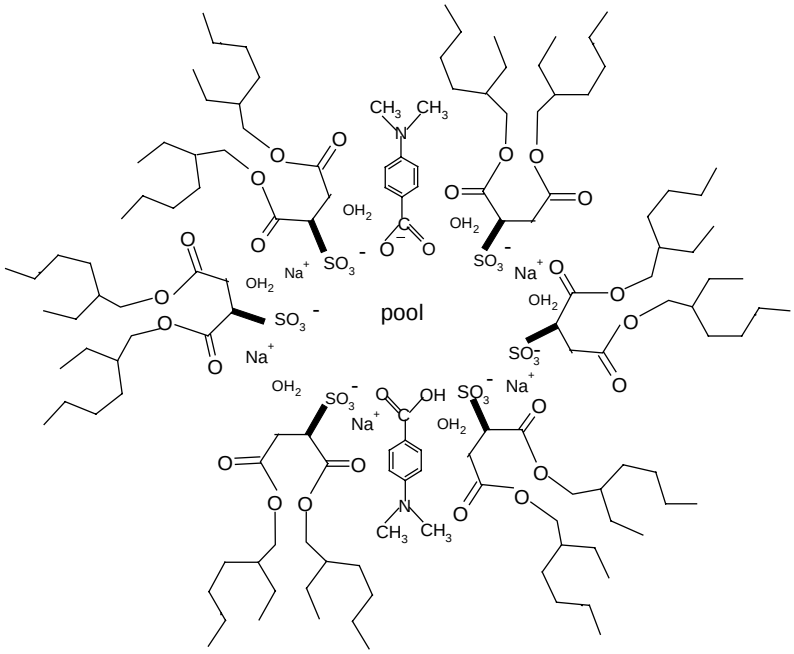


Fig. 4. Variation of emission spectra of (a) DMABA and (b) DMABN in acetonitrile with the increase in water concentration.

We have already predicted the probe molecules are located at the interface of the reverse micelles from the absorption and steady state anisotropy results. On the basis of the hydrogen bonding between the acceptor groups of the probe molecules (DMABA and DMABN) and co-solvents for the observed ICT behavior in water, methanol and acetonitrile reverse micelles, we can predict that the probe molecules are oriented at the interface of these three reverse micelles with its acceptor group (–COOH or $–COO^-$ group for DMABA and –CN group for DMABN) towards the water/methanol/acetonitrile pool, while $–NMe_2$ group remains buried at the interface (Scheme 2).

3.4. Time resolved studies

To understand the decay kinetics of dual emission of DMABA and DMABN, we have measured the fluorescence lifetime of both LE and ICT band. The results are shown in Tables 2 and 3. The representative fluorescence decays of DMABN at $w = 2$ of methanol reverse micelle are shown in Fig. 5. The lifetime of LE and ICT state of both the probes in reverse micelles is bi-exponential or tri-exponential in nature. This arises due to the heterogeneity of medium as well as distribution of probe molecules between *n*-heptane and inside the reverse micelles. The lifetime of LE state of each probe decreases from *n*-heptane to reverse micelles. In going from *n*-heptane to reverse micelles, the polarity increases, which favors the enhanced rate of conversion from LE to ICT [14,15]. The lifetime of ICT state also decreases from low w value to high w value of reverse micelles. With the increase in w value, the polarity of the reverse micelles increases and hence the energy gap between ICT state and



Scheme 2.

Table 2
Fluorescence decay times of DMABA at LE and ICT states in aqueous and non-aqueous reverse micelles

Medium	w	λ_{flu} (nm)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)
n-Heptane	–	340	1	1.50	0	0	0	0
n-Heptane + 0.09 M AOT	0	340	0.20	0.131	0.63	1.36	0.17	3.15
Water reverse micelle	4	345	0.79	0.383	0.21	2.81	0	0
Water reverse micelle	16	345	0.65	0.075	0.21	1.10	0.14	3.64
Methanol reverse micelle	2	350	0.70	0.680	0.30	2.55	0	0
		450	0.90	2.07	0.10	4.79	0	0
Methanol reverse micelle	6	350	0.75	0.503	0.25	2.65	0	0
		450	0.62	0.872	0.34	2.06	0.04	6.11
Acetonitrile reverse micelle	2	350	0.51	0.171	0.33	1.06	0.16	3.45
		440	0.37	1.49	0.63	3.82	0	0
Acetonitrile reverse micelle	4	350	0.57	0.105	0.27	1.07	0.16	3.37
		440	0.42	0.872	0.58	3.49	0	0

Table 3
Fluorescence decay times of DMABN at LE and ICT state in aqueous and non-aqueous reverse micelles

Medium	w	λ_{flu} (nm)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)
n-Heptane	–	340	1	2.30	0	0	0	0
n-Heptane + 0.09 M AOT	0	345	0.56	1.66	0.44	2.79	0	0
Water reverse micelle	4	340	0.40	1.22	0.60	2.37	0	0
Water reverse micelle	16	340	0.30	1.11	0.70	2.36	0	0
Methanol reverse micelle	2	350	0.70	1.21	0.30	2.50	0	0
		445	−0.87	0.745	1.87	3.26	0	0
Methanol reverse micelle	6	350	0.85	0.708	0.15	2.55	0	0
		445	−0.78	0.310	1.78	2.50	0	0
Acetonitrile reverse micelle	2	350	0.42	0.832	0.58	2.36	0	0
		445	0.79	0.318	1.79	3.34	0	0
Acetonitrile reverse micelle	4	350	0.56	0.488	0.44	2.33	0	0
		445	−1.05	0.242	1.51	2.66	0.54	3.92

Franck–Condon excited state decreases. This leads to the increased rate of non-radiative transition from ICT state. The long lifetime of ICT state of DMABA in methanol and acetonitrile reverse micelles compared to *n*-heptane indicates the formation of stabilized ICT state by polar solvents in reverse micelles. According to two-state model [14–16], the decay time of LE state should be equal to the rise time of ICT state, because ICT state is formed from LE state. But the observed long rise time at ICT state of DMABN in methanol and acetonitrile reverse micelles is not equal to the decay time of the same in methanol and acetonitrile reverse micelles. This is attributed to the heterogeneity of the medium as well as distribution of DMABN between *n*-heptane and within the reverse micelles. The long rise time (τ_1) of ICT state at ~450 nm also implies the formation of stabilized ICT state at the expense of LE state and these two states are reaching equilibrium. We have not detected any rise time of DMABA in methanol and acetonitrile reverse micelles. This may arise due to the

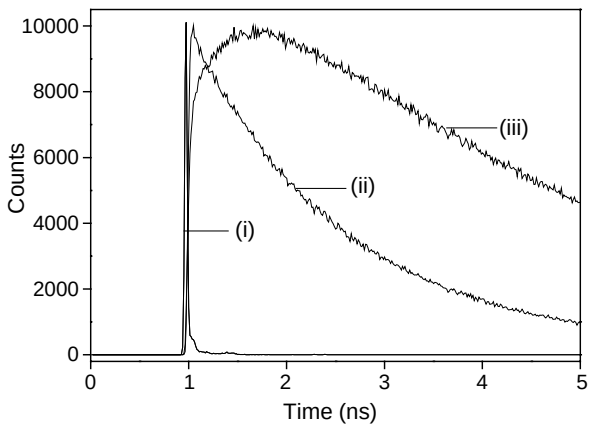


Fig. 5. Fluorescence decays of DMABN in *n*-heptane/AOT/methanol reverse micelle in $w = 2$ at (i) instrument response function (IRF), (ii) 350 nm and (iii) 445 nm.

fact that rise time of ICT states of DMABA in the mentioned systems is too fast (<40 ps) to be detected in our systems.

4. Conclusion

In this paper, we have investigated the ICT behavior of DMABA and DMABN in aqueous and non-aqueous reverse micelles of AOT. In acetonitrile reverse micelle, both the probes exhibit a strong ICT peak along with LE emission. In methanol reverse micelle, a strong ICT emission peak of DMABN is observed at the red end side of the emission spectra. But for DMABA, the same appears as a shoulder at the red end side of the emission spectra in methanol reverse micelle. The ICT state of DMABA in water reverse micelle is not observed, whereas the same for DMABN appears as a shoulder in water reverse micelle. The IC rate from the hydrogen bonded ICT state which arises due to the hydrogen bond formation between the –COOH/–COO^- group of DMABA and water/methanol in case of water/methanol reverse micelles is responsible for the observed anomalous results in water and methanol reverse micelles. The long lifetime at ICT state implies that the polar solvent stabilizes the ICT state. Moreover, a high rise time of DMABN in methanol and acetonitrile reverse micelles indicates that the formation of stabilized ICT state at the expense of LE state and these two states are reaching equilibrium.

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