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Photoinduced electron transfer from dimethyl aniline to coumarin dyes in reverse micelles

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Abstract

Photoinduced electron transfer between different coumarin dyes and *N*,*N*-dimethyl aniline has been investigated in AOT reverse micelle using steady state and time resolved fluorescence spectroscopy. We have observed a slower electron transfer rate in reverse micelle in comparison to that in the neat solvent. Moreover, we have observed retardation in the electron transfer rate in the correlation of the free energy change with the electron transfer rate. This unexpected outcome in a bimolecular electron transfer is assumed to be arising from the different diffusional rate of the reactants in the inhomogeneous AOT system.

1. Introduction

The understanding of electron transfer (ET) has been a long-standing goal in the active research area due to its important role in many chemical and biological processes [1–5]. Recent emphasis in this area has been centred on the dynamical aspect of solvent influences as well as on influences of microenvironment on this process. In recent years the photoinduced electron transfer (PET) has been found to be a well known triggering process in various physical, chemical and biological systems. Though in the past few years an extensive study on PET has been carried out in different neat solvent like aniline, dimethylaniline, etc., as well as in the homogeneous solvent like acetonitrile [6–10], the same are a few in number in the microenvironment of different organized media like micelles, reverse micelles, cyclodextrins, etc., despite these are being interesting systems. The organized media are vastly different from the homogeneous solvent in many properties like pH, viscosity, polarity, etc. As the reactants molecules are encapsulated within the small volume in organized media, they experience a different microenvironment from that in homogeneous medium. These local properties have profound influence on the structural reactivity, reaction dynamics of the local species [11,12]. It has been reported that solvation dynamics, rotational dynamics, intramolecular charge transfer, electron transfer are several times retarded in micelles, reverse micelles, cyclodextrins and various organized media than that in pure water [13,14]. Recently, many interesting results have been reported in micelles [15–20], but a systematic study of bimolecular ET in other organized media has not yet been done. Keeping this idea in mind we have chosen sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles as the system to carry out the ET investigation. We have chosen AOT reverse micelles because reverse micelles are interesting models of biological membrane. The enzymes containing reverse micelles are often used as a novel tool for biotechnology and for drug delivery through solubilization of lipophilic drugs [21,22]. Prior to the electron transfer many photophysical studies like solvation dynamics, intramolecular

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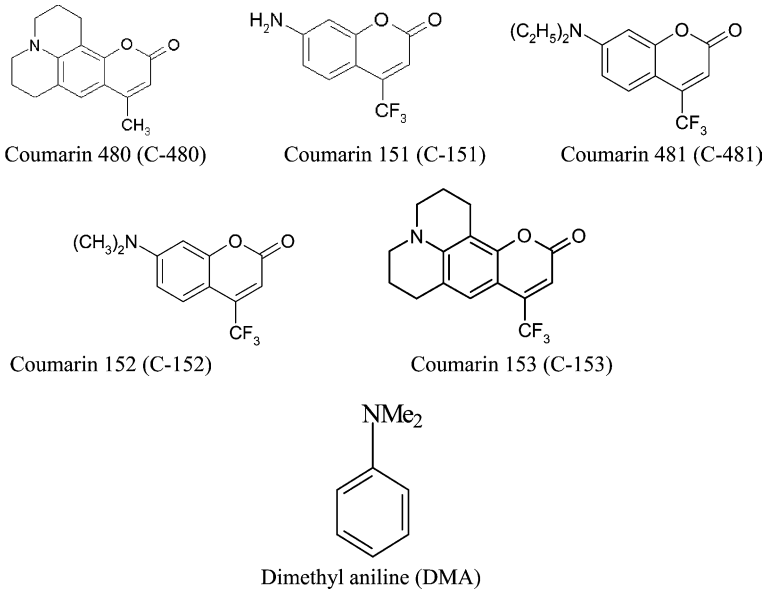
charge transfer, exciplex formation studies, etc., have been done [13,14,23–25]. Thus AOT is a well-established system and it would be interesting to carry out electron transfer in this system. In recent years, some interesting results regarding ET have appeared in micellar media. Kumbharkar et al. reported ET in SDS and TX micelles [18,19]. We have recently published a paper on ET in CTAB micellar solution [20]. In the earlier case we have ignored the role of diffusion assuming the reactants to be static in their own position. Again a free energy dependence of electron transfer process has been reported. It is well known that the bimolecular ET reaction occurs in two steps, first is the diffusion of the reactant to form the activated complex and the second is the formation of products. As in this two-steps reaction, diffusion is the slowest step, so it is obvious that it would govern the electron transfer rate. So for a bimolecular ET, it is expected that in the correlation graph of rate constant to the free energy change, no inversion should occur i.e., at higher free energy the observed rate should be independent of the free energy change. However, the reverse micelles are highly inhomogeneous systems, ET rate may not follow the same trend as described earlier. The deviation may occur due to the various reasons. In this contribution, we are going to report systematic bimolecular ET studies between the excited coumarin dyes and *N*,*N*-dimethylaniline (DMA) in AOT reverse micelles at $w_0 = 12$ using both steady state and time resolved fluorescence quenching experiments. Our main goal is to understand how ET process is affected in the microenvironment of a reverse micellar system on going from neat solvent or homogeneous solvent. We have also investigated whether or not ET depends on free energy change. We have discussed the role of diffusion in governing the ET process in reverse micelles.

2. Experimental

All the coumarin dyes were obtained from the Exciton (laser grade) and used as received. The *N*,*N*-dimethylaniline (DMA) was obtained from Aldrich chemical and distilled under reduced pressure just before use. The structure of the acceptors and donor are shown in Scheme 1. AOT (Dioctylsulfosuccinate, sodium salt, Aldrich) was purified by a standard procedure [25]. The purified AOT was dried and kept in vacuo for 12–13 h before use. *n*-Heptane was purchased from Spectrochem, India and freshly distilled over calcium hydride. The solution was prepared using procedure used by Maitra et al. [26]. The w_0 value in aqueous reverse micelle is defined as the ratio of the water to the surfactant, $w_0 = [\text{water}]/[\text{AOT}]$. The concentration of AOT was kept at 0.09 M for all the measurements. The acceptor concentration was kept 4×10^{-5} M in all the cases. The steady state absorption and emission spectra were recorded using a Shimadzu (model no: UV-1601) UV–Vis absorption spectrophotometer and a Spex Fluorolog-3 (model no: FL3-11) spectrofluorimeter. For time resolved quenching measurement we have used a nanosecond time resolved and a picosecond time resolved fluorescence spectrophotometer. The details of the picosecond time resolved fluorescence spectrophotometer was described elsewhere [20]. Briefly we have used a picosecond laser diode (IBH, UK) at 408 nm. The signal has been detected at magic angle (54.7°) polarization using Hamamatsu MCP PMT (3809U). The time resolution of our experimental setup is ~90 ps. For anisotropy measurements we have used the same setup. We do not have Picosecond diode facility to pump the probe at the very red end side of the reverse micelles. To do this, a nano LED (IBH, UK)



Scheme 1. Structure of coumarin dyes and aromatic amine.

having excitation wavelength at 460 nm and a TBX-04 detector having ~1 ns FWHM were used. The analysis of the decay and anisotropy data were performed by IBH DAS6 decay analysis software. The cyclic voltametric (CV) measurements were carried out in a CH (Model: 620 A) instrument in the acetonitrile and ethyl alcohol medium using a carbon rod as the working electrode, and Ag/AgCl/Cl^- (saturated) as reference electrode. Tetrabutylammonium perchlorate and potassium chloride were used as the supporting electrolyte. The values, obtained from this instrument were normalized with respect to saturated calomel electrode. The temperature was kept 298 ± 1 K for all the measurements.

3. Results and discussion

3.1. Steady state absorption and emission spectra

The absorption and emission spectra are taken in *n*-heptane and in AOT reverse micelles for all the coumarins are listed in Table 1. The absorption spectra show a distinct red shift on going from *n*-heptane to reverse micelle at $w_0 = 12$ for C-151. This suggests that C-151 is encapsulated in the water pool of the reverse micelles. For the other probes though after addition of 0.09 M AOT no significant shift is observed but with increasing w_0 a distinct shoulder is appearing at the red end side. This suggests that absorbance is enhanced in the red end side. Thus it may be concluded that the probe molecules undergo a migration from the bulk *n*-heptane to reverse micellar core where the polarity is higher compared to that in the bulk solvent.

Similar to the absorption spectra when the molecules entrapped in the reverse micelle are excited at 408 nm, the emission spectra is found to be red shifted which indicates that a substantial amount of acceptor molecules is present in the reverse micellar core where the polarity is higher than the bulk *n*-heptane. However, no significant red shift is observed for C-153 and C-481, but a distinct shoulder appears at the red end side for these acceptors with increase in w_0 value which may be attributed for the molecules residing in the high polarity area i.e., in side the core of the reverse micelles. Again when we have excited the molecules at 460 nm, C-153, C-152 and C-481 are found to be red shifted. This may be attributed to the fact that pumping in the shoulder on red end side of the absorption spectra results to the excitation of the molecules in the high polarity area, i.e., inside the reverse micellar pool.

Table 1
Absorption and emission maxima (λ_{ex} = 408 nm) of different coumarin dyes in *n*-heptane and AOT reverse micelle at $w_0 = 12$

Compositions	λ_{abs}^{max} (nm)	λ_{emi}^{max} (nm)
C-153 + *n*-heptane	392	450
C-153 + AOT at $w_0 = 12$	392	451
C-480 + *n*-heptane	363	406
C-480 + AOT at $w_0 = 12$	363	477
C-152 + *n*-heptane	371	425
C-152 + AOT at $w_0 = 12$	371	501
C-151 + *n*-heptane	346	400
C-151 + AOT at $w_0 = 12$	378	482
C-481 + *n*-heptane	377	430
C-481 + AOT at $w_0 = 12$	377	432

3.2. Time resolved anisotropy study

The steady state absorption and emission spectra cannot give a clear picture of the location of the probe in a reverse micellar system. These studies throw an average picture. Thus to have a better insight regarding the location of the probe, we have carried out time resolved anisotropy measurement in pure *n*-heptane as well as in reverse micelles. The expression for anisotropy decay is expressed as

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

where $I_{\parallel}$ and $I_{\perp}(t)$ are the fluorescence decays polarized parallel and perpendicular to the polarization of the excitation light. The *G* factor in our case is 0.60. Here it is important to mention that since our excitation wavelength is 408 nm, so we could report the anisotropy decay in pure *n*-heptane for C-153, C-152 and C-481. For the other coumarin dyes the fluorescence emission peak in pure *n*-heptane is either lower or very close to the excitation wavelength. The anisotropy decays of these coumarin dyes in pure *n*-heptane is found to be single exponential and average rotational time is around 100 ps. Again on excitation at 408 nm a substantial amount of coumarin dyes like C-153, C-481 residing in bulk *n*-heptane are excited and these molecules have a large contribution to the observed anisotropy decay. To minimize this effect we have collected the anisotropy decays at the emission maxima by exciting the molecules at 460 nm i.e., at the red end of the absorption spectra where the molecules are entrapped in the reverse micellar water pool. Thus we collected the rotational relaxation of those molecules, which are encapsulated in the reverse micellar core. The fitted results of anisotropy decays in the AOT reverse micelles are listed in Table 2. The representative anisotropy decays of C-152 in reverse micelles at $w_0 = 12$ and in pure *n*-heptane are shown in Fig. 1a and the standard deviation for the best fitted results of anisotropy decays are shown in Fig. 1b and c respectively. From Fig. 1a it is clear that the anisotropy decay of C-152 in AOT reverse micelles is much slower compared to that in pure *n*-heptane. Thus we may conclude that in reverse micelle a substantial amount of the acceptor molecules may reside in the reverse micellar core, in the vicinity or even some molecules may be

Table 2
Initial anisotropy values (r_0) and rotational relaxation time (τ_r) of coumarin dyes in *n*-heptane and in AOT reverse micelles at $w_0 = 12$

Composition	r_0	a_{1r}	τ_{1r} (ns)	a_{2r}	τ_{2r} (ns)
C-153 + *n*-heptane	0.4	0.4	0.080		
C-152 + *n*-heptane	0.25	0.25	0.090		
C-481 + *n*-heptane	0.38	0.38	0.116		
C-153 + AOT at $w_0 = 12$	0.37	0.31	0.130	0.06	1.052
C-480 + AOT at $w_0 = 12$	0.40	0.26	0.314	0.14	1.623
C-152 + AOT at $w_0 = 12$	0.34	0.20	0.218	0.14	1.00
C-481 + AOT at $w_0 = 12$	0.40	0.15	0.738	0.25	1.662
C-151 + AOT at $w_0 = 12$	0.40	0.24	0.252	0.16	1.239

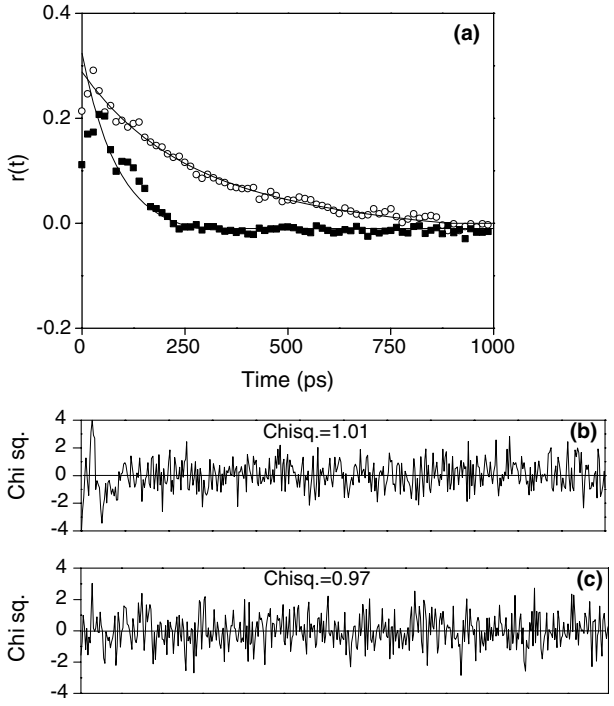


Fig. 1. (a) Decays of fluorescence anisotropy ($r(t)$) of C-152 in pure *n*-heptane and water reverse micelle at $w_0 = 12$. For pure *n*-heptane. (■) and for AOT reverse micelle at $w_0 = 12$ (O). (b) Standard deviation for the best-fitted result of anisotropy in *n*-heptane. (c) Standard deviation for the best-fitted result of anisotropy in AOT reverse micelles at $w_0 = 12$.

entangled with the AOT surfactant chain. These molecules are responsible for the slow component in the anisotropy decay.

3.3. Quenching study using steady state and time resolved fluorescence measurements

The steady state and time resolved fluorescence quenching measurements were performed by exciting the molecules at 408 and 460 nm, respectively. The representative steady state fluorescence quenching spectra of C-153 excited at 408 nm in presence of different concentration of DMA are shown Fig. 2. The location of DMA in reverse micellar solution is very important.

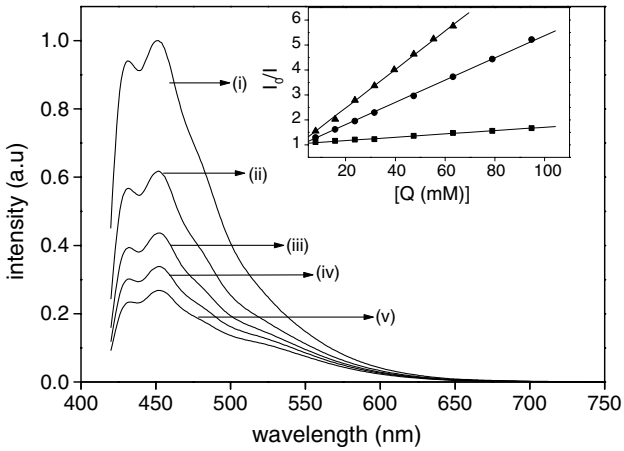


Fig. 2. Steady state quenching of C-153 molecules in AOT reverse micelle, excitation wavelength at 408 nm in presence of DMA concentration (i) 0 mM, (ii) 15.8 mM, (iii) 31.6 mM, (iv) 47.4 mM, (v) 63.2 mM. In the inset: the I_0/I vs. [Q] plot for C-152 (■), C-153 (●) and for C-481 (▲).

The various reports in this regard have already confirmed that the absorption and emission spectra of DMA in AOT reverse micelle are vastly different from that in pure *n*-heptane [23,24]. The spectra are found to be red shifted in presence of AOT reverse micelles. Thus it is clear that DMA is encapsulated in the reverse micellar core. The shape of the emission spectra remains unaltered in presence of maximum concentration of DMA, consequently it rules out the possibility of any exciplex formation. Similarly the possibility of ground state complexation is also ruled out by the fact that the absorption spectra do not change even in presence of maximum quencher concentration.

The quenching constant was estimated by using the following equation

$$\frac{I_0}{I} = 1 + K_{SV}[Q], \tag{2}$$

where I_0 and I are the intensities of coumarin dye in reverse micelle in absence of quencher and in presence of quencher, K_{SV} is the Stern–Volmer constant and [Q] is the concentration of DMA.

The I_0/I vs. [Q] plots for different probes exciting at 408 nm are shown in Fig. 2 (in the inset). The slope of the plot gives the estimation of Stern–Volmer constant. The quenching constant k_q for the steady state measurement is then obtained by dividing the Stern–Volmer constant with the lifetime of the acceptor in absence of quencher. The k_q values thus obtained are listed in Table 3.

Similar to the steady state fluorescence quenching measurements, we have also performed time resolved quenching measurements to have a better understanding of ET processes in these systems. It is seen from Fig. 3a that the lifetime of corresponding decay of the molecules becomes shorter as the concentration of amine increases.

Table 3
Lifetime and quenching constants for different coumarin-amine systems in AOT reverse micelles at $w_0 = 12$ as obtained from steady state (SS) and time resolved (TR) fluorescence quenching studies

Coumarin	τ_0 (ns)[a]	Amine	SS $k_q/10^9$ mM^{-1} s^{-1} (λ_{ex} = 408 nm)	TR $k_q/10^9$ mM^{-1} s^{-1} (λ_{ex} = 408 nm)	TR $k_q/10^9$ mM^{-1} s^{-1} (λ_{ex} = 460 nm)
C-153	2.99	DMA	0.01260	0.01630	0.00184
C-152	1.38	DMA	0.00460	0.00263	0.00160
C-480	4.45	DMA	0.00083	0.00053	0.000774
C-481	2.63	DMA	0.02900	0.0341	0.00230
C-151	5.18	DMA	0.00147	0.00180	0.00311

[a] The lifetime obtained exciting the molecules at 408 nm.

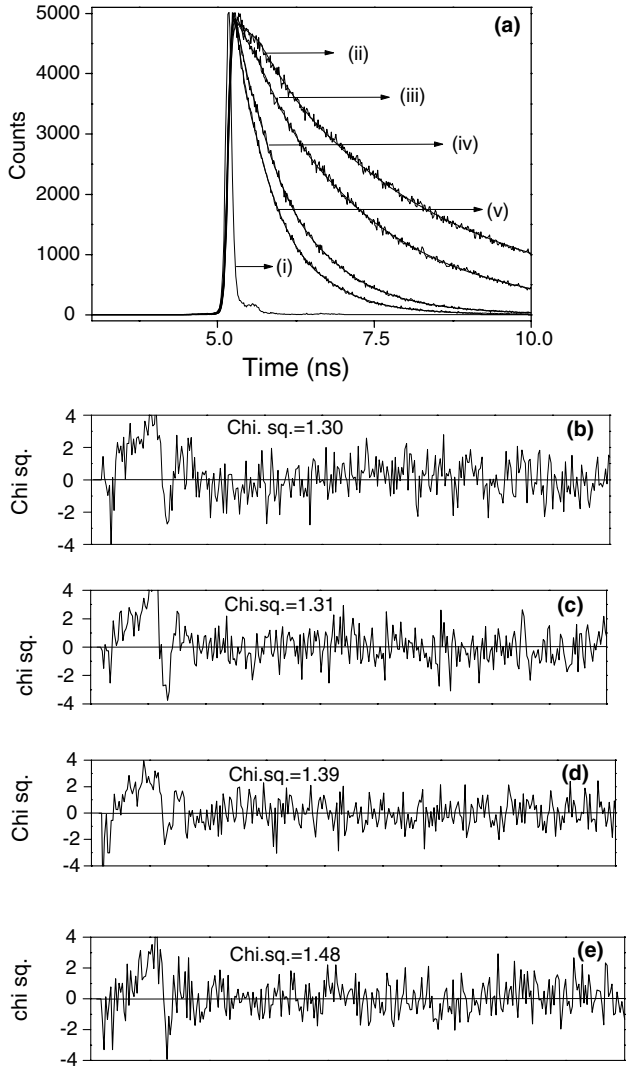


Fig. 3. (a) Time resolved fluorescence decays of C-481 in AOT reverse micelle at $w_0 = 12$ on excitation at 408 nm in presence of DMA concentration (i) lamp profile, (ii) 0 mM (iii) 7.9 mM, (iv) 31.6 mM, (v) 47.4 mM. (b)–(e) are the best fitted results of the corresponding decays.

The standard deviation in the measurement of these decays is shown in Fig. 3b–e. As AOT reverse micelles is an inhomogeneous system, so the acceptor coumarin molecules experience more than one type of the environment. In the Section 3.2, we have mentioned that the probe molecules might reside in the different portion of AOT reverse micelles. Some molecules may reside inside the water pool, or in the interface while the remaining are in the bulk heptane. Thus a multi-exponential decay is expected. In the present case we have fitted the decays using biexponential functions. Again it is found that both the fast and the slow components decrease with addition of quencher. Thus to estimate the ET parameters we have taken the average lifetime of the corresponding decays. The quenching constant is determined from the following equation

$$\frac{\tau}{\tau_0} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]. \quad (3)$$

The typical plot for τ_0/τ vs. $[Q]$ is shown in Fig. 4. The results of time resolved quenching constants on exciting the molecules at 408 and 460 nm are listed in Table 3. It is important to compare the ET rate in reverse micelle to that in homogeneous solvents and neat solvents. In the last case the acceptor molecules are always in contact with the donor molecules and there is no question of diffusion arising. The ET in these systems has widely been studied by Yoshihara's group and they took the help of two dimensional electron transfer (2DET) model to rationalize the phenomenon [6,7,9]. Pal et al. [17] recently explored the ET using Oxazine dye as donor

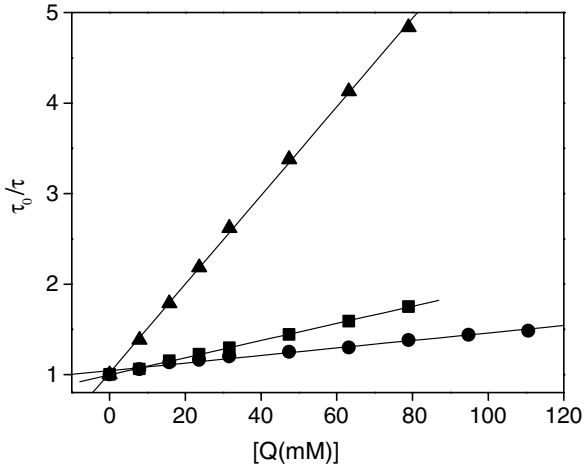


Fig. 4. The plot of τ_0/τ vs. $[Q]$ for C-151 (■), C-152 (●), and for C-153 (▲) at the same excitation wavelength.

and DMA as acceptor in SDS and TX-100 micelles. According to Marcus theory the ET rate is markedly dependent on the coupling strength between donor and the acceptor molecules. The coupling strength related to the distance R as $e^{-\beta R}$ where $\beta = 1$ Å^{-1}. Thus with increase in R the coupling strength decreases several times. Therefore we may conclude that lower ET rate in reverse micelle compared to that in neat solvent is caused by the reduction in the electron coupling matrix element. However we cannot ignore the role of viscosity in retarding the ET rate in this context. The higher viscosity in the reverse micelles compared to the homogeneous solution provides a more confined geometry causing significant reduction in the electron transfer rate.

To have a quantitative understanding on ET, it is necessary to estimate the change in free energy (ΔG^0) for each coumarin–amine systems. This is because of the fact that rate of ET depends on change in free energy. The usual expression to calculate ΔG^0 is given by the famous Rehm–Weller equation, which we have discussed in our earlier publication [20]

$$\Delta G^0 = E(D/D^+) - E(A/A^-) - E_{00}, \quad (4)$$

where E_{00} is the energy required for the transition of coumarin dyes from ground state (S_0) to first excited electronic state (S_1). This is obtained from the intersection point of normalized absorption and emission spectra. For this purpose we have excited the acceptor molecules at 360 nm as to get the effective overlap between the absorption and emission spectra. Here $E(D/D^+)$ and $E(A/A^-)$ denote the oxidation potential of the donor and reduction potential of the acceptor. Since the polarity of the reverse micelle is close to ethyl alcohol, so all the measurements of the reduction and oxidation potential have been carried out in ethyl alcohol using CV measurement. We have omitted the coulomb energy due to very negligible value. The results thus obtained are summarized in Table 4. The calculated values of ΔG^0 are listed in Table 4.

The most interesting observation of this work comes out when we plot the rate const k_q with the free energy change. The Fig. 5a in which $\ln k_q$ has been plotted against the free energy change at $w_0 = 0$ (data are not shown) represents basically graph of scattered points. We cannot reach any conclusion from this graph. However Fig. 5b and c are most interesting. These two plots ($\ln k_q$ vs. free energy change (ΔG^0)) at $w_0 = 12$ reveal the same feature. In these two figures initially ET rate increases with change in the free energy, reaches a

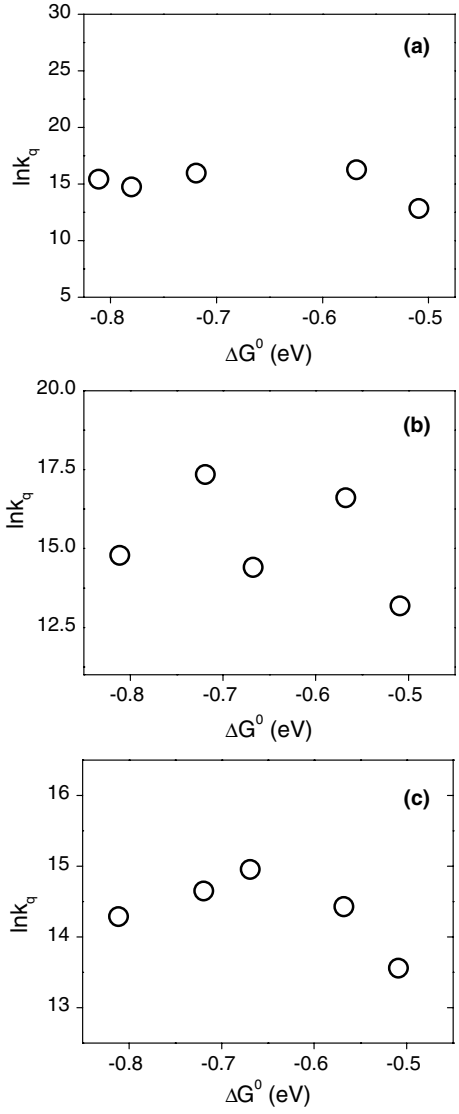


Fig. 5. (a) The plot of $\ln k_q$ vs. ΔG^0 for Coumarin-DMA system at $w_0 = 0$, (k_q values are obtained at excitation 408 nm). (b) The plot of $\ln k_q$ vs. ΔG^0 for Coumarin-DMA system at $w_0 = 12$ (k_q values are obtained at excitation 408 nm). (c) The plot of $\ln k_q$ vs. ΔG^0 for Coumarin-DMA system at $w_0 = 12$ (k_q values are obtained at excitation 460 nm).

Table 4
Redox potential, E_{00} values, and ΔG^0 values for the coumarin–amine systems studied in reverse micellar medium at $w_0 = 12$

Coumarins	$E(A/A^-)/V$ vs. SCE	E_{00}/eV	Amines	$E(D/D^+)/V$ vs. SCE	ΔG^0/eV
C-153	−1.66	2.94	DMA	0.711	−0.569
C-480	−2.00	3.22	DMA		−0.509
C-152	−1.58	3.10	DMA		−0.81
C-151	−1.53	2.906	DMA		−0.665
C-481	−1.635	3.064	DMA		−0.719

maximum and then falls off. One may be tempted here to conclude that the observed retardation in the electron transfer rate at relatively higher free energy change looks similar to the so-called Marcus inverted region. In the earlier work Kumbhakar et al. as well as our group have reported the similar observation in SDS, CTAB and TX-100 micelle, respectively [18–20]. It is important to note here that in homogeneous acetonitrile medium the same experiment were carried out by Nad et al. But they did not find any inversion in ET rate [10]. The reaction in acetonitrile medium was found to fall in the normal Marcus region. There are a very few examples of bimolecular ET reaction in which Marcus inverted region has been undoubtedly established [27,28]. In most of the cases Marcus inverted region was found to be true for the intramolecular ET reaction, charge recombination reaction [29–32]. Recently Gopidas and co-workers have reported the driving force dependence of electron transfer in a series of hydrogen bonded donor and acceptor systems [33,34]. When the donors and acceptors are bonded through hydrogen bonding interactions, diffusion is prevented in intramolecular ET, and the Marcus behavior is observed. On the other hand when diffusion is allowed in intermolecular ET, Rehm–Weller behavior is observed. It is a well-known fact that rate of a bimolecular reaction is composed of two components; the first arises from the molecular diffusion and the second arises due to the rate of electron transfer in the encounter pair. If the rate of molecular diffusion controls the over all reaction, hence the electron transfer rate becomes independent of the identity of the molecules.

In the present case, the observed retardation in the ET rate may not be considered as a Marcus inverted region. Here the ET has been carried out in a highly inhomogeneous medium. As the AOT reverse micellar medium is not a rigid system, so there is a finite possibility of molecular diffusion in this system. Again due to the heterogeneity of the system the diffusion of the different molecules should not be the same due to the different strength in the binding of the acceptor coumarin molecules to the heterogeneous AOT system. Hence even if the rate-limiting step is the diffusion process, the rate will be different for different acceptors, which is reflected in Fig. 5b and c. This might have been nicely interpreted if we could show different mobility of the acceptor molecules due to the diffusional effect to the same donor. Recently we have started some works on this aspect in micellar media where the translational diffusion coefficient has been ascribed to the observed effect. Thus the observed phenomenon in the present case is explained on the basis of the molecular diffusion of the acceptor molecules in AOT reverse micelle. Worral et al., found a similar type of observation in the experiment of electron transfer reaction of Anthracene adsorbed on silica gel [35].

The other explanation is that due to heterogeneous distribution, the accessibility of acceptor molecules to the donor partner is different which impose a steric restriction on the encounter pair, hence the observed rate becomes dependent on ease with which the coumarin and DMA can interact in a favorable orientation.

4. Conclusion

In the present case we have studied the bimolecular ET study from aromatic amine to different coumarin dyes using time resolved and steady state fluorescence quenching measurements. The time resolved fluorescence anisotropy measurement was performed to justify the location of the probe. It is revealed that a substantial amount of probe was residing in the reverse micellar core. The steady state absorption and emission spectra supported the above conjecture. The observed ET has been found to be slower than that in neat solvent and homogeneous medium. The correlation between driving force and quenching rate constant revealed retardation in the electron transfer rate. The observed retardation in the ET rate at higher free energy region was attributed to the different ability of diffusion of the acceptor molecules due to the binding in the heterogeneous AOT medium. Moreover, the different accessibility of the acceptors to the donor molecules due to heterogeneous distribution may also be responsible for the observed effect.

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