Photoinduced intermolecular electron transfer from aromatic amines to 9-methylanthracene in Sodium dodecyl sulfate micellar solutions

S.R.Patil*, M.S.Khot, G.B.Kolekar,

Fluorescence Spectroscopy Research Laboratory, Department of Chemistry,
Shivaji University, Kolhapur-416004 (M.S.) (INDIA)
Fax: +91-231 - 2605355
E-mail: msk_chem77@rediffmail.com

ABSTRACT

Photoinduced intermolecular electron transfer (PET) interaction between 9-Methylanthracene (a hole donor) and aromatic amine (hole acceptor) has been investigated in anionic sodium dodecyl sulfate (SDS) micellar solution using Steady State (SS) fluorescence quenching measurement and the results are compared with those observed in the homogeneous ethanol solutions. The intensity of the emission bands of 9-methylanthracene (9-MA) is quenched in presence of N,N-Dimethyl aniline (DMA) and N,N-Diethyl aniline (DEA) by electron transfer without formation of an exciplex. Steady State fluorescence quenching of the 9-MA by the amine quenchers exhibits positive deviation from linear Stern-Volmer relationship due to the localized high quencher concentrations at the micellar Stern layer. The electron donor aniline quenches the fluorescence of 9-MA without formation of exciplex. The bimolecular quenching constants (k_q^{SS}) observed in micellar solution are seen to be much smaller than those estimated in the polar homogeneous ethanol solution, indicating that the electron transfer (ET) in the micellar media is inherently inefficient. The PET occurring in present system is confirmed by electrochemical studies by Cyclic Voltammetry and used further to estimate free energy changes in the different environment. Marcus outer sphere ET theory is used to calculate the solvent reorganization energy (λ_s) and the free energy (ΔG) which enabled to propose suitable mechanism for PET at the surface of the micelle. © 2008 Trade Science Inc. - INDIA

KEYWORDS

1. INTRODUCTION

Electron transfer reactions have received a high level of attention since last many decades due to their relevance in a wide range of applications[1]. Electron-transfer events are vital to chemical, biological and technical process[2]. In most chemical systems, transfer of an electron from a ground state donor to a ground state acceptor is energetically unfavorable[3-5]. However photoexcitation of either the acceptor or the donor of-

Full Paper

ten makes the ET reactions energetically favorable and thus the reaction occurs with a reasonable rate. Numerous studies have been performed addressing the dependence of ET on different environments including liquids[6,7], micelles[8-10], vesicle[11], proteins and DNA[12]. In the last two decades such PET reactions in homogeneous solutions using polar and non-polar solvents have been investigated extensively to understand the different aspects of ET dynamics and mechanism[13-15]. Electron transfer in restricted environment[16] such as micelles, reverse micelles[17,34] and vesicles attracts a great deal of interest due to increases in the lifetime of charge transfer states and potential applications in solar cell[18]. Micelles could be a useful medium for maintaining photoinduced charge separation because of their geometry and their multiphase character[19]. Considering the important roles of microemulsion in biology, material and other related field, it is to explore the photoinduced electron transfer processes in this environment necessary and compare the results with those studied in homogeneous environment. The present paper reports photoinduced electron transfer reaction using water insoluble substituted anilines as electron donors and fluorescent aromatic organic molecule as electron acceptor in homogeneous and in micellar environment. The micellar environment not only solublised the organic molecule but also keeps donor-acceptor molecule in close contact at water-micelle interface. The 9-methylanthracene and aromatic anilines such as N,N-Dimethylaniline and N,N-Diethylaniline are donor-acceptor pairs. The results obtained in micellar microenvironment are compared with those obtained in homogenous environment in ethanol solvent.

2. EXPERIMENTAL

2.1 Apparatus

The Steady-state fluorescence spectra were recorded on PC based Spectroflurophotometer (JASCO Model-FP-750). The absorbance spectrums of solutions were recorded on UV-visible spectrophotometer Shimadzu Model UV-160A. All solutions were deareated by passing nitrogen gas before subjected to optical measurements. The oxidation and reduction potentials of the donor-acceptor pairs in SDS micellar solutions were measured by Cyclic Voltammetry (CV)

method using a Princeton applied research Perkin-Elmer Versa-Stat II model-270, Interfaced with P-III-PC. Solution of 9-MA in micellar solution containing 0.1 mol dm^{-3} potassium chloride as the supporting electrolyte were first deareated by purging high purity N$_2$ gas for about 10 minutes. CV measurements were then carried out using graphite rod as the counter electrode and silver-silver chloride {Ag / AgCl /Cl$^-$ (sat.)} as the reference electrode. The potentials thus obtained were normalized with respect to the saturated calomel electrode (SCE) and used further to estimate free energy change of ET reactions in the present system.

2.2 Reagents

The 9-methylanthracene obtained from Lancaster and recrystallised from methanol and tested the purity by taking photoluminescence spectra. The production of similar spectra when excited at different wavelength confirms the purity. Sodium dodecyl sulphate was procured from Sigma and purified by repeated crystallization from water-methanol mixtures and its 5×10^{-2} mol dm^{-3} aqueous solution was prepared. The DMA and DEA were vacuum distilled and stock solutions 5×10^{-3} mol dm^{-3} were prepared in SDS solution. The calculated quantity of 9-MA required to prepare 1×10^{-5} mol dm^{-3} was solublized in SDS solution by stirring over night. The accurate concentration was obtained from optical density measurement.

2.3 Procedures

In the fluorescence quenching experiments the concentration of 9-MA was kept constant to a value 1×10^{-6} mol dm^{-3} while that of anilines varied from 1×10^{-3} to 4×10^{-3} mol dm^{-3}. The concentration of SDS was also kept constant at 50×10^{-3} mol dm^{-3}, well above its critical micelle concentration (CMC) known to be 8.1×10^{-3} mol dm^{-3}[20]. The fluorescence spectra were recorded with and without anilines at λ_{ex}.= 367 nm obtained from excitation spectra of 9-methylanthracene.

3. RESULTS AND DISCUSSION

3.1 Absorption and fluorescence spectra

From SS measurements it is observed that the fluorescence of 9-MA in SDS micellar solution is quenched in presence of aromatic amines. Typical fluorescence
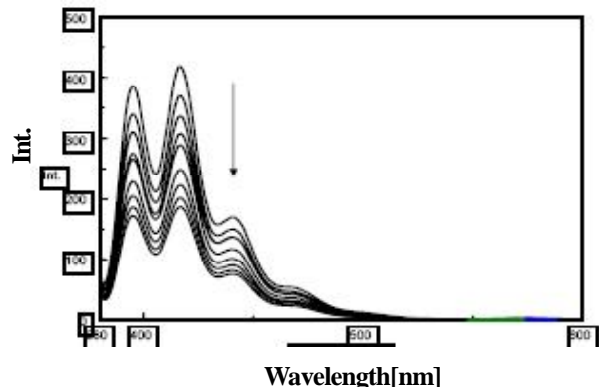
Figure 1: Steady-state fluorescence spectra of 9-MA in the presence of different effective. Concentration of DMA in SDS micellar solution. For spectra 1-9[DMA] were 0, 0.023, 0.046, 0.070, 0.096, 0.117, 0.140, 0.163 and 0.183 mol dm⁻³
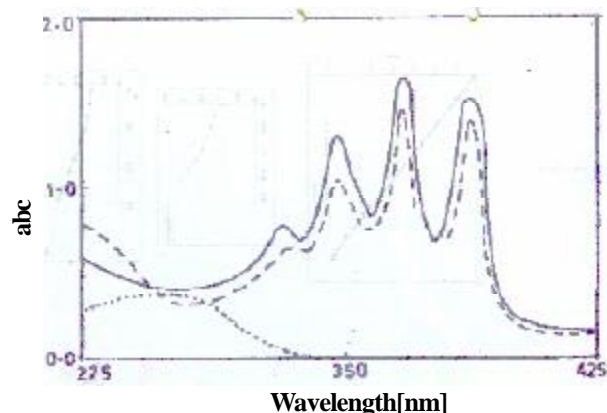

Figure 2: Typical absorption spectra of 9-MA in SDS a) in absence of DMA (___) (b) in presence of DMA (------) and (c) pure DMA(…..)

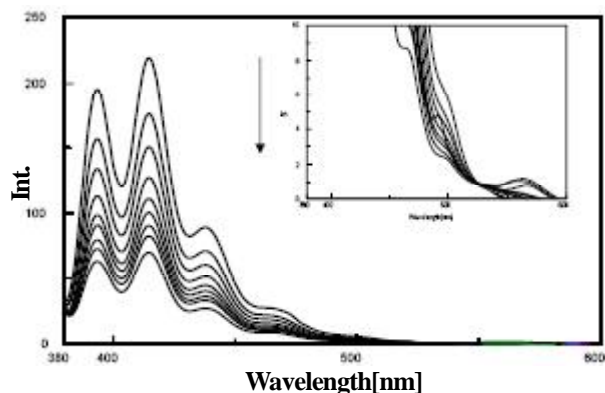**Figure 3: Steady state fluorescence spectra of 9-MA in presence of different concentrations of [DMA] in ethanol. For spectra 1-9[DMA] were 0,0.5,1, 1.5,2, 2.5,3, 3.5, and 4 × 10⁻² mol. dm⁻³. The inset of the figure shows the weak exciplex between 9-MA–DMA in ethanol**

spectra of 9-MA in the absence and presence of differ-

ent concentrations of DMA is shown in figure 1.

The careful observation of spectra indicates that the intensity of fluorescence of 9-MA is reduced substantially with concentration of DMA and DEA without any spectral modification. The expected red shifted structureless emission band of charge transfer (CT) exciplex is not seen in micellar solution even at higher concentration of DMA and DEA are used ($[Q]_{eff}$ =183 × 10^{-3}mol dm-3). The formation of ground state CT complexes was tested from the absorbance spectra. Figure 2 shows absorption spectra of 9-MA in SDS solution with and without DMA .The structured absorption spectrum of 9-MA with and without DMA are identical which indicates absence of molecular interaction in ground state to favor CT process. The fluorescence quenching studies performed for same donor-acceptor system in homogeneous polar environment obtained by using ethanol solvent is presented in figure 3, which shows quenching of fluorescence of 9-MA by DEA and weak red shifted band due to CT complex formation. The inset figure shows clearly an isoemissive point and red shifted broad emission band. An isoemissive point clearly seen in the figure is an indication of CT complex formation in the excited state between 9-MA and DEA. Similar results are obtained for 9-MA-DMA in ethanol environment.

The fluorescence quenching studies of 9MA-DMA studies in micellar solution and homogeneous alcohol medium were performed. It is observed that the spectral results of this system are all identical with that of 9MA-DEA system. The optical and quenching data of both systems are given in Table. 1. These quenching results were analyzed following the well known Stern-Volmer relationship,

$$I_0 / I = 1 + K_{sv[}Q] \tag{1}$$
$$K_{sv} = k_q \, \tau^0 \tag{2}$$

Where I_0 and I are the fluorescence intensities for the 9-MA in the absence and in presence of the quenchers[Q]respectively[21]. K_{sv} is the SV constant and[Q] is the concentration of the quenchers in the solution, k_q is a bimolecular quenching constant and τ^0 lifetime of the florophore. The plots of I_o/I Vs concentration of DEA in homogeneous and heterogeneous environment are presented in figures 4(a and b). The plot for 9-MA-DMA in ethanol is linear while that in SDS micellar solution it shows slight positive deviation from

Full Paper

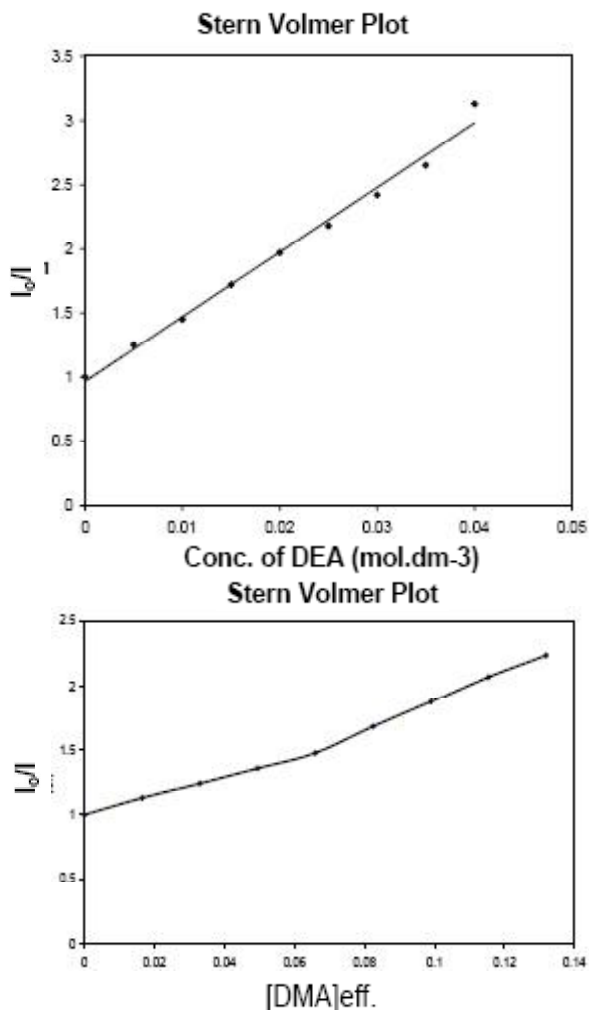## Stern Volmer Plot

Stern Volmer Plot

Figure 4: (a) Stern-Volmer (SV) plot for the steady-state fluorescence quenching of 9-MA in ethanol by DEA; (b) Stern-Volmer (SV) plot for the steady-state fluorescence quenching of 9-MA in SDS micellar solution by DEA

TABLE 1: Absorption maxima (λ_{abs}), Fluorescence emission maxima (λ_{em}), Lifetime (ns) and Bimolecular quenching constant (k_q) in polar homogeneous and micellar media.

Medium	Lifetime (ns)	Amines	λ_{abs} (nm)	λ_{em} (nm)	$k_q^{ss}/10^9$ dm^3 mol^{-1} sec^{-1}
SDS	4.9	DMA	367	417	1.9252
		DEA	368	418	1.8533
Ethanol	5.2	DMA	364	416	10.56
		DEA	369	412	9.69

linearity. It is evident from figure 4a. that for present systems, the linearity in the SV plots can be considered only for very low amine concentrations. The bimolecular quenching rate constant (k_q) were calculated from the initial slopes of the plots and the lifetimes of 9- MA in the respective micellar environment and values are given in TABLE 1. The quenching rate constant in mi-

celle solution are lower than those observed in ethanol solution for the similar donor-acceptor system. It is shown that the total concentration of the solute in micelle and actual available concentration are different, hence the effective concentration of the amine$[Q]_{eff}$ is much higher than the total quencher concentration$[Q]_t$ used in the solution. In the present systems, since the solubility of fluorophor (9-MA) and quenchers are very low in aqueous media, it is expected that both the reactants mainly resides at the micellar Stern Layer. The effective concentration was calculated by using the relation[22],

$$[Q]_{eff} = \frac{N_{egg}x[Q]_t}{44.75\{[SDS]_t - CMC\}} \tag{3}$$
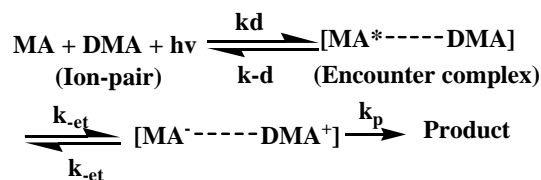
Where N_{agg} is the average aggregation number for SDS micelle ($N_{agg} \approx 62)$[23], $[SDS]_t$ is the total SDS concentration used (5×10^{-2} mol dm^{-3}), CMC is the critical micellar concentration of SDS micelle ($\approx 8\times10^{-3}$ mol.dm^{-3}) and$[Q]_t$ is the total amine concentration used in the solution. The effective micelle concentration is also estimated by using the relation,

$$[M] = \frac{[S] - CMC}{N_{agg}} \tag{4}$$

Where [S] denotes the surfactant concentration[24,25] and found to be 4.77×10^{-4} mol dm^3.

3.2 Kinetics of fluorescence quenching

The Bimolecular florescence quenching of 9- MA by DMA and DEA may be due to either energy transfer or electron transfer. The mechanism of energy transfer from singlet excited 9-MA to aniline is easily ruled out because the excitation energy of singlet state (E_s) of 9-MA (2.7 eV) is lower than that of DMA (3.81 eV) and DEA (3.77 eV)[26,27]. Hence the probable mechanism should be electron transfer. To understand the nature of interaction, the bimolecular quenching constants are correlated with the oxidation potential of the amines {E (D/D$^+$)} and the reduction potentials of the 9-MA {E (A/A$^-$)}. The probable mechanism proposed for in the 9-MA-DMA system consisting electron transfer from aniline is as given below.

$$\text{MA + DMA + h}\nu \xrightleftharpoons[\text{k-d}]{\text{kd}} [\text{MA*-----DMA}]$$
$$\text{(Ion-pair)} \qquad \text{(Encounter complex)}$$

$$\xrightleftharpoons[\text{k-et}]{\text{k-et}} [\text{MA}^-\text{-----DMA}^+] \xrightarrow{\text{k}_p} \text{Product}$$

SCHEME 1

It is believed that the donor (DMA) and the acceptor (excited MA*) molecules diffuse together to form an encounter complex (MA*—DMA), which then undergoes reorganization to reach the transient state, where ET takes place from the donor to the acceptor to give the ion - pair (MA$^-$—DMA$^+$). The parameters k_d and k_{-d} are the diffusion controlled rate constants for the formation and dissociation of (MA*—DMA), k_{et} and k_{-et} are the forward and reverse ET rate constants and k_p is the sum of all rate constants causing the disappearance of the (MA$^-$—DMA$^+$) state. The two most important processes in k_p would be charge recombination (k_{CR}) to produce the ground states of the acceptor and donor (MA and DMA) and ion dissociation (k_{ID}) to give the solvent separated ions (MA$^-$ and DMA$^+$).
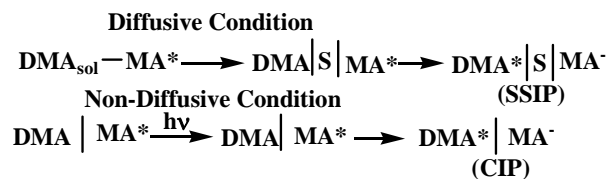
The diffusional rate constant is higher ($k_d > k_q$) than that of quenching rate constant. The diffusional rate constant k_d is calculated by using the relation

$$k_d = \frac{RT}{3000\eta} \qquad (5)$$

Where η is the dynamic viscosity of the medium at the room temperature[28]. The diffusional rate constant k_d and k_{-d} are believed to be nearly same and are greater than the quenching rate constants. It is hoped that in micellar medium the electron transfer occurs by diffusive processes as indicated in SCHEME 2. The electron transfer rate were estimated by using the following relation,

$$k_{et} = \frac{k_d x k_q}{K(k_d - k_q)} \qquad (6)$$

Assuming $K = k_d / k_q = 1$ dm^3 mol^{-1} the values of k_{et} under diffusive condition $k_{et.d}$ were estimated for the system where $k_d > k_q$ and are listed in TABLE 2. The electron transfer rate constants in ethanol environment are more than those observed in micellar environment. It is concluded that the electron transfer process from aniline to excited 9-MA is less efficient than in ethanol solvent. The results are in agreement with the literature reports on similar types of system in micellar environment[19,22]. The micellar core is highly nonpolar ($\varepsilon = 2.4$) while the bulk water is highly polar ($\varepsilon = 78.6$), therefore the excited 9-MA seems to resides in the stern layer of micro environment of SDS micelle. The present results thus indicate that only the mutual diffusion of the reactants might not play significant role in determining the rate constants. It is believed that the observed quenching kinetics is due to this spatial distribution of the do-

Diffusive Condition

$$\text{DMA}_{sol} - \text{MA*} \longrightarrow \text{DMA}|S|\text{MA*} \longrightarrow \text{DMA*}|S|\text{MA}^-$$
$$\text{(SSIP)}$$

Non-Diffusive Condition

$$\text{DMA}\ |\ \text{MA*} \xrightarrow{\ h\nu\ } \text{DMA}|\ \text{MA*} \longrightarrow \text{DMA*}|\ \text{MA}^-$$
$$\text{(CIP)}$$

SCHEME 2

nor molecules around the excited 9-MA in micellar environment as shown in SCHEME 2.

3.3 Energetic of electron transfer reactions

Electron transfer reaction involves the crossing of the free energy surface of the reactant to the product at Transition State similar to the dark reactions[29-30]. Feasibility of PET from ground state donor (amine) to an excited state acceptor (9-MA) mainly depends upon free energy change (ΔG^0) for the ET reaction. For the present system, the (ΔG^0) values were calculated using the following Rehm-Weller relation[31],

$$\Delta G^0 = E(D/D^+) - E(A/A^-) - E_s - e^2/\varepsilon_s r_0 \qquad (7)$$

where, $E(D/D^+)$ and $E(A/A^-)$ are the oxidation and reduction potentials of amines and 9-MA respectively, E_s is the singlet excited energy of the 9-MA in the S_1 state, e is the charge on electron, $_s$ is the static dielectric constant of reaction medium and r_0 is chemical separation between interacting 9-MA and amine molecules as are given in TABLE 2.

ET rates in SDS micellar solution are much slower than those observed in homogeneous ethanol solution due to diffusive condition. In the absence of diffusion of the reactants, the observed ET rates may be because of effective distribution of the amines quencher around the excited 9-MA in the micellar stern layer. It is also believed that reactant molecules will increase the average donor-acceptor separation in comparison to those in homogeneous solution. Hence the observed ET rates in micellar solution are lower than in homogeneous ethanol solution. The λ is the total reorganization energy given as,

$$\lambda = (\lambda_s + \lambda_i) \qquad (8)$$

λ_s being the solvent reorganization energy arising due to the polarization and orientation of the solvent molecule around the reactant (MA*+DMA) and the product (MA$^-$ + DMA$^+$) states, λ_i being the intramolecular reorganization energy arising due to the intramolecular bond length and bond angle changes in the donor (DMA) and acceptor (MA) molecule undergoing ET. If the solvent system is considered to be a dielec-

Full Paper

TABLE 2: Redox potential, Electronic excitation energy (E_s), Standard free energy (ΔG^0), Solvent reorganization energy (λ_s) and Electron transfer rate (k_{et}) for 9-MA-Amine systems in polar homogeneous and micellar media

Medium	ε	E(A/A⁻)/V (vs SCE)	E_S /(eV)	Amines	E(D/D⁺)V(vs SCE)	ΔG^0/(eV)	λ_s/ eV	$k_{et}/10^{10}$ S⁻¹
SDS	32	-1.603	2.722	DMA	0.2982	-1.1788	1.21	0.2540
		-1.593	2.716	DEA	0.3185	-1.1525	1.10	0.2316
Ethanol	24.55	-1.421	2.729	DMA	0.7831	-0.9059	0.44	2.357
		-1.432	2.735	DEA	0.7482	-0.9718	0.40	2.163

tric continuum model for the SDS, Marcus derived the following expression for λ_s [32],

$$\lambda s = \left(e^2\right)\left\{\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{2r_{DA}}\right\}\left\{\frac{1}{n^2} - \frac{1}{\varepsilon}\right\} \qquad (9)$$

Where r_D and r_A are the radius of the donor and acceptor respectively, r_{DA} is the separation between the donor and acceptor in the encounter complex, n is the refractive index and ε dielectric constant of the solvent. Average values of r_D (3.94 Å) and r_A (3.36 Å) were estimated using the sizes of the donors and acceptors as obtained using Edwards's volume addition method[33]. Similarly the r_{DA} (7.3 Å) is considered to be equal to the sum of the average r_D and r_A values. We used the average values of r_D, r_A and r_{DA} for the calculation of λ_s because small difference in the radii of the donors and acceptors do not make any significant variations in the estimated λ_s values. The λ_s for the present systems thus estimated are listed in TABLE 2.

4. CONCLUSION

The present result indicates a strong interaction between aromatic molecule 9-MA and tertiary amines but excludes the possibility of formation of emissive charge transfer complex (CT) as the intermediate. The observed quenching arise due to the presence high local concentration of the amines in the micellar stern layer. This situation keeps the excited 9-MA in the micelle in physical contact with the amines. The fluorescence quenching rate constant seen to depend upon the electron donating methyl and ethyl group in aniline donor in both the homogeneous and micellar media. The presence of bulky ethyl group in DEA decreases the quenching rate constant of 9-MA .The Bimolecular fluorescence quenching constant(k_q^{ss}) in the present system are seen to correlate nicely with free energy changes (ΔG^0) of the ET reaction within the frame work of Marcus ET. The smaller ΔG^0 values observed for 9-MA and substituted aniline system indicated faster rate of ET in both

media. Under diffusive condition the solvent reorganization energy appears to play the major role in governing the ET dynamics.

5. REFERENCES

[1] H.L.Tavernier, M.M.Kalashnikov, M.D.Fayer; J. Chem.Phys., 113, 10191 (2000).

[2] J.R.Balton, N.Mataga, G.L.McLendon; 'Electron Transfer in Inorganic, Organic and Biological Systems', American Chemical Society, Washington, (1991).

[3] P.F.Barbara, W.Jarzeba; Adv.Photochem., 1, 15 (1990).

[4] Spectral Issue on Electron Transfer, Chem., 92, 365 (1992).

[5] T.Tang, K.Peneva, K.Mullen, S.Webber, J.Phys. Chem.A, 111, 10609 (2007).

[6] S.F.Swallen, K.Weidemaier, H.L.Tavernier, M.D. Fayer; J.Phys.Chem.A, 101, 1887 (1997).

[7] M.Hui, W.Ware; J.American Chemical Society, 98, 16 (1976).

[8] H.L.Tavernier, A.V.Barzykin, M.Tachiya, M.D. Fayer; J.Phys.Chem.B, 102, 6028 (1998).

[9] C.Jan, T.Kwak; Langmuir, 12, 269-275 (1996).

[10] S.Pal, D.Mandal, D.Sukul, K.Bhattacharya; J.Chem.Phys., 249, 63-67 (1999).

[11] L.Hammarstrom, T.Norrby, G.Stenhagen, J. Martensson, B.Akermark, M.Almgren; J.Phys. Chem.B, 101, 7494 (1997).

[12] H.L.Tavernier, M.D.Fayer; J.Phy.Chem.B, 104, 1154 (2000).

[13] M.D.Newton, N.Sutin; Ann.Rev.Phy.Chem., 35, 437 (1984).

[14] B.Wenzhange, Y.Cao, J.Weibai, J.Rongchan; J. Photochemistry and Photobiology A Chemistry, 106, 169-175 (1997).

[15] G.P.Zanini, A.Hernan, A.Montejano, J.Cosa, M. Previtali; J.Photochemistry and Photobiology A: Chem., 109, 9-14 (1997).

[16] H.Avota, S.Araki, V.Morishima, M.kamachi; Macromolecules, 30, 4090 (1997).

Full Paper

[17] X.Zhang, K.Chan; Chem.Mater., **15**, 451 **(2003)**.

[18] L.Hammarstrom, H.Berglund, M.Almagren; J.Phys.Chem., **98**, 9588 **(1994)**.

[19] M.Kumbhakar, S.Nath, T.Mukherjee, H.Pal; J. Chem.Phys., **122**, 84512 **(2005)**.

[20] P.H.Elworthy, A.T.Florence, C.B.Macfarlane; 'Solubilization by surface-active agents', Chapman and Hall Ltd, 11New Fetter Lane, London, EC4.

[21] K.K.Rohatgi, Mukherjee; 'Fundamentals of Photo-chemistry', New Age Int., New Delhi, India, **(1986)**.

[22] M.Kumbhakar, S.Nath, H.Pal, A.V.Sapre; J.Chem.Phys., **1**, 119 **(2003)**.

[23] K.Kalyansundara; 'Photochemistry in Microhetero geneous Systems', Academic, Orlando, **(1987)**.

[24] 'Experimental Phy.Chemstry : Laboratory Text Book', 2nd edition Prentice Hall, **(1997)**.

[25] S.K.Ghosh, P.K.Khatua, S.C.Bhattacharya; Int.J. Mol.Sci., **4**, 562 **(2003)**.

[26] S.Nad, H.Pal; J.Phys.Chem.A, **104**, 673-680 **(2000)**.

[27] S.R.Patil, S.B.Patwari; J.of Luminscence, **82**, 115-119 **(1999)**.

[28] R.B.Cundall, A.Gillbert; 'Photochemistry, Applied Century Crafts', Educational Division, New York.

[29] J.M.Chen, T.I.Ho, C.Y.Mou; J.Phys.Chem., **94**, 2889-2896 **(1990)**.

[30] B.Legros, P.Vandereecken, J.ph.Soumillin; J.Phys. Chem., **95**, 4752-4761 **(1991)**.

[31] D.Rehm, A.Weller; Isr.J.Chem., **8**, 259 **(1970)**.

[32] R.A.Marcus; J.Chem.Phys., **24**, 966 **(1956)**.

[33] J.T.Edward; J.Chem.Education, **47**, 261 **(1970)**.

[34] D.Das, D.Nath, P.Parui, M.Chowdhury; Chemical Physics Letters, **424**, 300-306 **(2006)**.