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FURTHER STUDIES ON PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER OF SUBSTITUTED BENZOATE ESTERS OF 9-ANTHRACENE METHANOL
II - SUBSTITUENT AND MEDIUM EFFECTS

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Abstract: The role of the solvent and the substituents on the chromophore are important in the efficiencies of photoinduced intramolecular electron transfer (PIET) processes. In this study esters of 9-anthracene methanol were synthesized and characterized. The fluorescence quantum yields of these esters were measured and electron transfer rates estimated. The estimated electron transfer rate constants were correlated linearly with σ values. The fluorescence quantum yields were also measured in two different micellar solutions in order to investigate the behavior of PIET in organized media. The values of the reaction constant, ρ, for the photoinduced electron transfer were calculated as 3.28 (r = 0.98), 3.42 (r = 0.96) and 2.41 (r = 0.99) in methanol, sodium dodecyl sulphate (SDS) and Triton X-100 (TX-100) respectively. This variation is explained by considering the microviscosity and micropolarity of the interior of the micelle systems.

Key Words: 9-anthracenemethyl esters, bichromophore, fluorescence, Hammett correlation, photoinduced-electron-transfer, micellar effect.

INTRODUCTION

Photoinduced intramolecular electron-transfer (PIET) is a complex phenomenon. It is strongly influenced by the molecular structure, nature and length of the chain of the molecules, solvent polarity, viscosity and temperature[1]. Several valence-linked bichromophoric systems have previously been reported to exhibit fluorescence quenching. The studies done by Pincock and De Costa[2] have shown that two chromophores connected by -CH$_2$-O-(C=O)- group shows lower fluorescence quantum yields. Recently we reported[3] the fluorescence quenching of five substituted 9-anthracene methyl benzoate esters, **2a-e**, (Figure 1). PIET explains the quenching process from the excited anthracene chromophore to the benzoate chromophore. This explanation was supported by the estimated values of free energies and solvent effects of electron transfer processes. We observed that electron-withdrawing groups attached to the benzoate chromophore enhance the electron transfer rates giving less fluorescence. On the other hand electron-donating groups give the opposite effect.

In this paper, the results of an investigation of the intramolecular electron transfer of eight more compounds is included in addition to the excited state life time of some of the compounds. The fluorescence quantum yields were also

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measured in two different micellar solutions in order to investigate the behavior of PIET in organized media. The impact of organized media on the kinetics of chemical reactions is widely recognized[4]. In particular, excited state behavior in a micellar environment has drawn much attention[5]. This is due to the compartmentalization of the excited state by the micelle in contrast to homogeneous solution. The confinement of fluorescent molecules and quenchers in small discrete aggregates, as in micellar solutions, have two important effects on the overall fluorescence decay kinetics[6]. The proximity effect makes the quenching rapid in micelles containing both an excited species and quenchers and a shielding effect hinders the quenching of excited molecules created in micelles without the quenchers. By using proper concentrations of the fluorescent probe and micelle, one can create a situation where each compartment of the micelle is singly occupied by the chromophore. This prevents the quenching process and enhances the fluorescence quantum yields. Many studies have employed fluorescence probes in order to estimate important physical parameters in micelle systems such as critical micelle concentration (cmc)[7], aggregation number (n)[8], roughness of the micelle surface[9] and degree of water molecules that penetrate into surfactant aggregates[10]. Fluorescence characteristics such as wave length for excitation and emission, fluorescence life times and polarization values and fluorescence quenching rates, etc. have been employed. However, as far as we know, PIET processes have not been used to study characteristic properties of micellar systems. In this study we have investigated sodium dodecyl sulphate (SDS) and Triton X-100 (TX-100) micellar systems.

METHODS AND MATERIALS

Absorption spectra were obtained using a Jasco V-500 UV\Visible Spectrophotometer. Infrared spectra were recorded on a Jasco FT/IR - 5300 and are given in wave numbers (cm^{-1}), ^{1}H NMR spectra were obtained on a Bruker ACF 200 instrument at 200 MHz with chemical shifts relative to TMS. Fluorescence studies were done using a RF-5000 Shimadzu Spectrofluorometer at 25° C, and spectra were corrected. Melting points were taken on a Stuart melting point apparatus.

All the chemicals except 9-anthracene aldehyde (from Aldrich) were purchased from Fluka. All the solvents used in spectroscopic measurements are either of Analar grade or general purpose grade (purified by distillation). The surfactant sodium dodecyl sulfate, SDS (BDH) was purified before use and Triton X - 100 (TX - 100, Aldrich) was used as supplied.
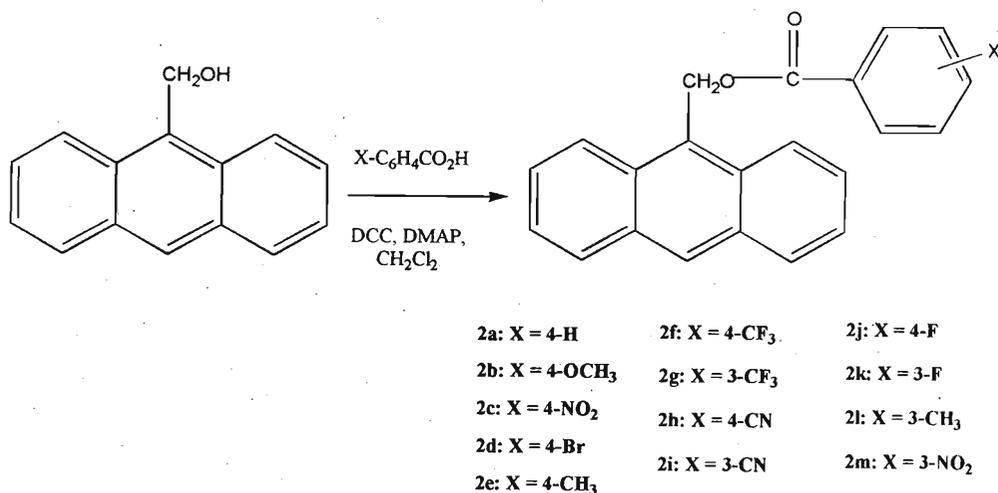
Absorption spectra: The absorption spectra of 1×10^{-5} solutions of the esters **1** and **2a-m** in methanol were recorded at 25°C. Nitrogen gas was bubbled through the solution for 20 min, prior to recording the spectra.

Fluorescence studies: The emission spectra of esters in the above solutions were recorded. The samples were purged with nitrogen for 20 min before measurements were taken.

Fluorescence life time measurements: Fluorescence life time was measured using a PRA single photon counting apparatus with a hydrogen flash lamp of pulse width about 1 ns.

Fluorescence measurements in micellar media: The micellar solutions were prepared by injecting a methanol solution of the substrate into the micellar solution (Methanol concentration < 1%). All solutions were prepared using deoxygenated solvents.

General method for preparation of esters: In our previous work[3] we prepared the esters, **2a-e** by the reaction between 9-anthracene methanol and the corresponding acid chloride in benzene in the presence of pyridine. However, we found that the yields could be tremendously increased by the following method as shown in Figure 1. The esters **2f-m** were prepared by this new method.

2a: X = 4-H	**2f:** X = 4-CF$_3$	**2j:** X = 4-F
2b: X = 4-OCH$_3$	**2g:** X = 3-CF$_3$	**2k:** X = 3-F
2c: X = 4-NO$_2$	**2h:** X = 4-CN	**2l:** X = 3-CH$_3$
2d: X = 4-Br	**2i:** X = 3-CN	**2m:** X = 3-NO$_2$
2e: X = 4-CH$_3$		

Figure 1 : Scheme for preparation of esters 2a-m

The method of preparation of esters **2a-e** was given in the previous paper[3]

To a solution of alcohol (10 mmol), acid (10 mmol) and 4-dimethylamino pyridine (2 mmol) in 10 ml of CH_2Cl_2, DCC (11 mmol) were added. After stirring for 1 h, the mixture was filtered. The filtrate was washed with 10 ml of 5% acetic acid followed by 10 ml of water and the organic layer was separated. This layer was dried and evaporated to give a solid. This crude product was chromatographed on silica gel with 2% ethylacetate: hexane as eluent.

9-Anthracenemethyl -4- trifluoro benzoate (2f):

Mp= 103-105°C, ^1H nmr (CDCl$_3$) δ : 6.4 (s, 2H), 7.45-7.61 (m, 6H), 8.06 (m, 4H, J=9Hz), 8.40 (d, 2H, J=9Hz), 8.52 (s, 1H), IR (CCl$_4$) cm^{-1} :1715, 1325, 1273, 1136, 775.

9-Anthracenemethyl -3- trifluoro benzoate (2g):

Mp= 121-123°C, ^1H nmr (CDCl$_3$) δ : 6.4 (s, 2H), 7.46-7.46 (m, 3H), 7.76 (d, 2H, J=9Hz), 8.07 (d, 2H, J=9Hz), 8.16 (d, 2H, J=6Hz), 8.27 (s, 1H), 8.43 (d, 2H, 9Hz), 8.56 (s, 1H), IR (CCl$_4$) cm^{-1} : 1713, 1333, 1217, 1136, 777.

9-Anthracenemethyl -4- cyanobenzoate (2h):

Mp= 170-172°C, ^1H nmr (CDCl$_3$) δ : 6.4 (s, 2H), 7.46-7.64 (m, 6H), 8.04 (d, 4H, J=10.3Hz, 2Hz), 8.39 (d, 2H, J=9Hz), 8.52 (s, 1H), IR (CCl$_4$) cm^{-1}: 2234, 1721, 1271, 1105, 737.

9-Anthracenemethyl -3- cyanobenzoate (2i):

Mp= 126-128°C, ^1H nmr (CDCl$_3$) δ : 6.4 s, 2H), 7.35-7.71 (m, 7H), 8.0 (d, 2H, J=8Hz), 8.15 (d, 1H, J=9Hz, 2Hz), 8.37 (d, 2H, J=7Hz), 8.48 (s, 1H), IR (CCl$_4$) cm^{-1} : 2236, 1721, 1275, 1184, 777.

9-Anthracenemethyl -4- fluorobenzoate (2j):

Mp= 126-128°C, ^1H nmr (CDCl$_3$) δ : 6.35 δ s, 1H), 6.86-7.10 (m, 2H), 7.42-7.6 (m, 4H), 7.87-8.01 (m, 4H), 7.87-8.01 (m, 4H), 8.4 (d, 2H, J=9Hz), 8.46 (s, 1H), IR (CCl$_4$) cm^{-1} :1713, 1269, 1240, 1109, 752.

9-Anthracenemethyl -3- fluorobenzoate (2k):

Mp= 117-119°C, ^1H nmr (CDCl$_3$) δ : 6.35 (s, 1H), 7.03-7.24 (m, 2H), 7.40-7.67 (m, 6H),7.88 (d, 2H, J=8Hz), 8.29 (d, 2H, J=9Hz), 8.41 (s, 1H), IR (CCl$_4$) cm^{-1}: 1717, 1275, 1202, 1094, 787.

9-Anthracenemethyl -3- methylbenzoate (2l):

Mp= 110-112°C, ^{1}H nmr (CDCl$_3$) δ : 2.25 (s, 3H), 6.35 (s, 2H), 7.07-7.21 (m, 2H), 7.42-7.49 (m, 4H), 7.89 (d, 2H, J= 9Hz), 8.04 (d, 2H, J= 9Hz), 8.42 (s, 1H), IR (CCl$_4$) cm^{-1} : 1711, 1275, 1198, 1107, 735.

9-Anthracenemethyl -3- nitrobenzoate (2m):

Mp= 138-140°C, ^{1}H nmr (CDCl$_3$) δ : 6.30 (s, 2H), 7.29-7.58 (m, 6H), 7.93 (d, 2H, J= 8Hz), 8.10-8.19 (m, 2H), 8.32 (s, 1H), 8.37 (d, 2H, J=4Hz), IR (CCl$_4$) cm^{-1} : 1723, 1535, 1260, 1130, 723.

RESULTS

Determination of Quantum Yields

In our previous report[3] the quantum yield of fluorescence for the esters **2a-e** were estimated by taking the anthracene as the reference compound. This method does not give the accurate absolute values due to the long excited state lifetime of anthracene. In this report we have used quinine sulphate in 1M H$_2$SO$_4$ as the reference compound (Φ_f = 1.0). The fluorescence quantum yields of esters **1** and **2a-m** in methanol are given in Table 1. Fluorescence quantum yields of **1** were determined in various concentrations of aqueous SDS and TX -100 solutions and the data presented in Table 2. The fluorescence quantum yields of **1** and **2** were measured in 20 mM of SDS and 5 mM of TX-100 and the data presented in Tables 3 and 4.

Determination of Electron transfer rates

Reaction Scheme which was proposed in our previous report[3] can be used to explain the variation of fluorescence quantum yields with substituent for the esters **2f-m**. The following relationship which we derived in the earlier report has been used:

$$\Phi_{et} = 1 - \frac{\Phi_f^B}{\Phi_f^A} \qquad \dots\dots\dots (1)$$

(Φ_f^B and Φ_f^A are quantum yields of fluorescence for benzoate, **2** and acetate, **1** respectively. k$_{et}$ and Φ_{et} are respectively the rate constant and quantum yield of electron transfer process. τ is the life time of the acetate, **1** ester.

The percentage of fluorescence quenching = $1 - \frac{\Phi_f^B}{\Phi_f^A} \times 100 \qquad \dots\dots\dots (2)$

The percentage of fluorescence quenching was plotted against the substituent constant σ⁻ as given in Figure 1 for methanol, SDS and TX-100 respectively.

Table 1 : The emission properties of compounds 1-2k in methanol

Compound	Quantum yield of fluorescence (a)	(k^X_{et}/k^H_{et}) (b)	$\log(k^X_{et}/k^H_{et})$	σ (d)	% of fluorescence quenching by electron transfer (c)	Singlet state life time/ns
1	0.195	-	-	-	-	7.3
2a: X=H	0.182	1.00	0.00	0.00	6.0	6.8
2b:X=4-OCH$_3$	0.190	0.39	-0.41	-0.29	2.7	7.0
2c:X=4-NO$_2$	0.018	136	2.14	1.23	91	ND
2d:X=4-CH$_3$	0.187	0.64	-0.19	-0.17	4.3	7.1
2e:X=4-Br	0.176	1.56	0.19	0.21	10	ND
2f:X=4-CK$_3$	0.011	234	2.37	0.65	94	ND
2g:X=3-CF$_3$	0.029	80	1.90	0.46	85	3.2
2h:X=4-CN	0.002	1352	3.13	0.99	99	ND
2i:X=3-CN	0.029	80	1.90	0.62	85	ND
2j:X=4-F	0.180	1.20	0.68	0.15	7.7	4.2
2k:X=3-F	0.080	20	1.30	0.34	59	3.8
2l:X=3-CH$_3$	0.191	0.29	-0.54	-0.06	2.0	7.0
2m:X=3-NO$_2$	0.065	28	1.45	0.71	67	ND

(a) Quantum values were measured using quinine sulphate in H_2SO_4. These values for **2a-e** are different from previously reported values[2].

(b) Estimated values using the equation (4) in the text.

(c) Estimated values using the equation (3) in the text.

(d) Values taken from reference (14)

Taking the electron transfer rates for unsubstituted and substituted benzoates as k_{et}^H and k_{et}^X respectively and using the Hammett linear free energy relationship (LFER),

$$\log\left[\frac{k_{et}^X}{k_{et}^H}\right] = \rho\sigma \qquad\qquad ....(3)$$

where ρ and σ are the reaction constant and the substituent constant respectively. The values for the above equation are given in Tables 1, 3, and 4 for methanol, SDS and TX-100 respectively. The photoinduced electron transfer rates of **2a-2k** were determined in methanol, SDS and TX-100 and $\log(k_{et}^X/k_{et}^H)$ were plotted against the σ values as given in Figure 3. From the slope, the values of the reaction constant, ρ, for the photoinduced electron transfer were calculated as 3.42 ($R^2 = 0.96$) and 2.41 ($R^2 = 0.99$) in SDS and TX-100, respectively excluding the points corresponding to **2c, 2e** and **2m**. Linear plots were obtained as given in Figure 2.

Table 2 : Variation of Fluorescence Quantum Yields of Ester 1 in SDS and TX-100.

[SDS]/mM	Φ_f	[TX-100]/mM	Φ_f
4	0.12	0.200	0.12
6	0.24	0.225	0.20
8	0.29	0.250	0.28
10	0.31	0.500	0.32
20	0.32	0.750	0.33
30	0.32	1.000	0.35
40	0.33	2.000	0.35
50	0.34	5.000	0.35
80	0.34	10.00	0.35

The cmc values obtained from a plot between fluorescence quantum yield and micellar concentrations (Figures 4 and 5) are 8.2 and 0.27 mmol dm^{-3} for SDS and TX-100 respectively. These two values are very close to the literature values[12] of 8 and 0.25 mmol dm^{-3} for micelle system SDS and TX-100 respectively.
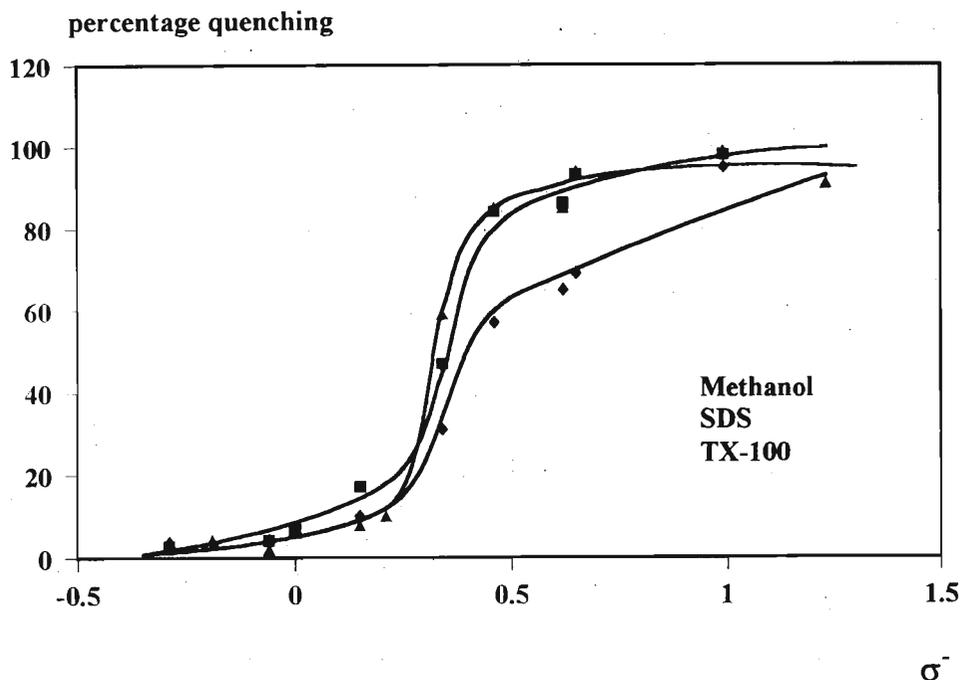
percentage quenching

Figure 2 : Relationship between percentage quenching and σ in methanol, SDS and TX -100.

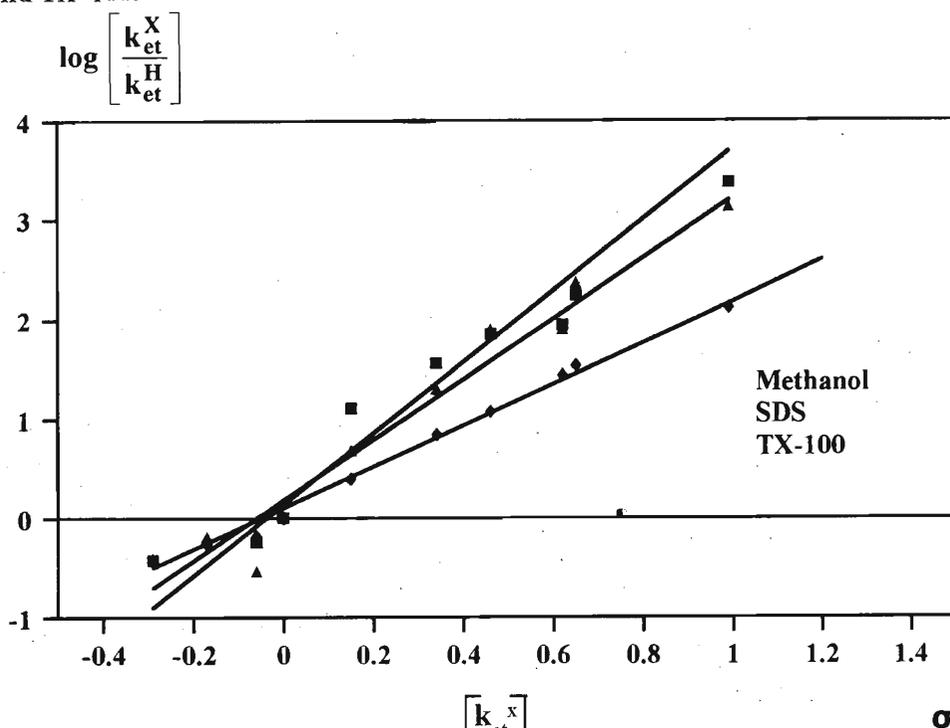$$\log\left[\frac{k_{et}^{X}}{k_{et}^{H}}\right]$$

Figure 3 : Relationship between $\log\left[\frac{k_{et}^{X}}{k_{et}^{H}}\right]$ and σ in methanol, SDS and TX -100.
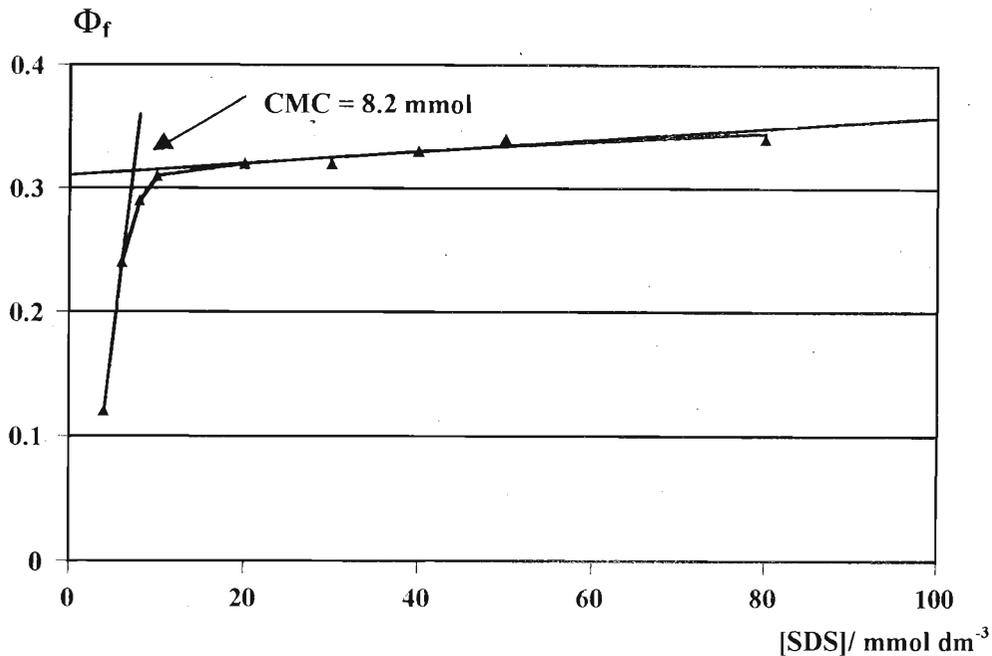
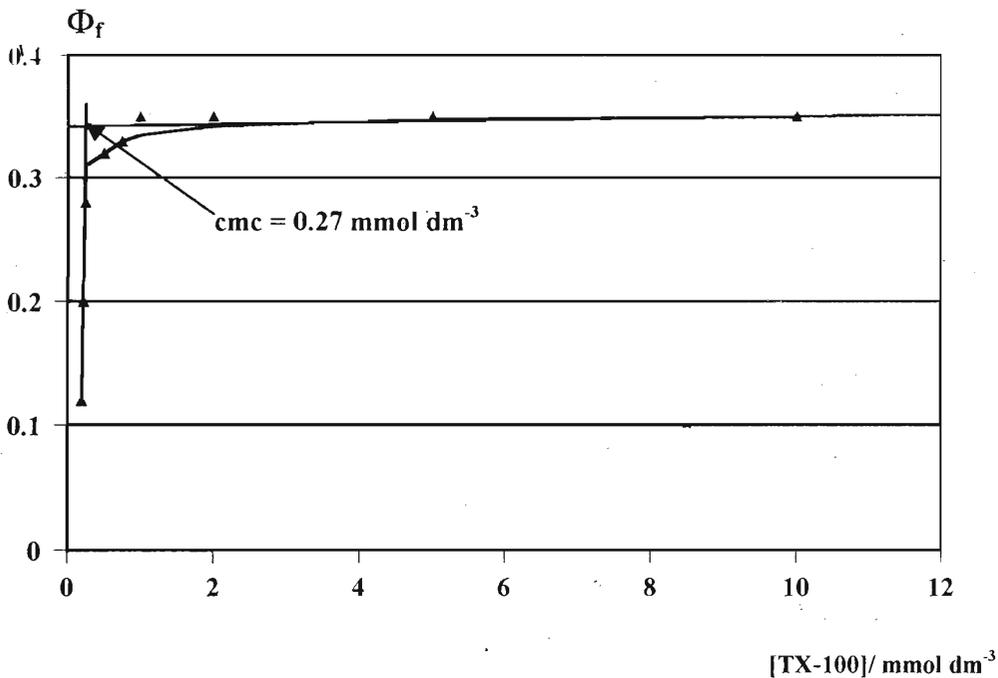Figure 4 : Relationship between fluorescence quantum yield and (SDS).

Figure 5 : Relationship between fluorescence quantum yield and (TX-100)

Table 3 : The emission properties of compounds 1-2k in SDS (20 mM)

Compound	Quantum yield of Fluorescence	k_{et}^x / k_{et}^H (a)	$\log(k_{et}^x / k_{et}^H)$	σ (c)	% of fluorescence quenching by electron transfer (b)
1	0.341				
2a:X=H	0.318	1.00	0.00	0.00	6.7
2b:X=4-OCH$_3$	0.332	0.37	-0.43	-0.29	2.6
2f:X=4-CK$_3$	0.0047	174	2.24	0.65	93
2g:X=3-CF$_3$	0.099	70	1.85	0.46	84
2h:X=4-CN	0.002	2343	3.37	0.99	98
2i:X=3-CN	0.049	87	1.94	0.62	86
2j:X=4-F	0.142	12	1.10	0.15	17
2k:X=3-F	0.094	36	1.56	0.34	47
2l:X=3-CH$_3$	0.328	0.56	-0.25	-0.06	4.1
2m:X=3-NO$_2$	0.042	98	1.99	0.71	87

(a) Estimated values using the equation (4) in the text
(b) Estimated values using the equation (3) in the text
(c) Values taken from reference (14)

Table 4 : The emission properties of compounds 1-2k in TX-100 (5 mM)

Compound	Quantum yield of Fluorescence	(K_{et}^X/k_{et}^H) (a)	$\log (k_{et}^X/k_{et}^H)$	σ (c)	% of fluorescence quenching by electron transfer (b)
1	0.349				
2a:X=H	0.326	1.00	0.00	0.00	6.6
2b:X=4-OCH$_3$	0.336	0.55	-0.26	-0.12	3.7
2c:X=4-NO$_2$	0.035	127	2.29	1.23	90
2f:X=4-CK$_3$	0.107	32	1.54	0.65	69
2g:X=3-CF$_3$	0.198	11	1.07	0.46	57
2h:X=4-CN	0.019	246	2.12	0.99	95
2i:X=3-CN	0.122	26	1.44	0.62	65
2j:X=4-F	0.316	1.48	0.39	0.15	10
2k:X=3-F	0.242	6.27	0.84	0.34	31
2l:X=3-CH$_3$	0.334	0.64	-0.18	-0.06	4.3
2m:3-NO$_2$	0.137	22	1.34	0.71	61

(a) Estimated values using the equation (4) in the text.
(b) Estimated values using the equation (3) in the text.
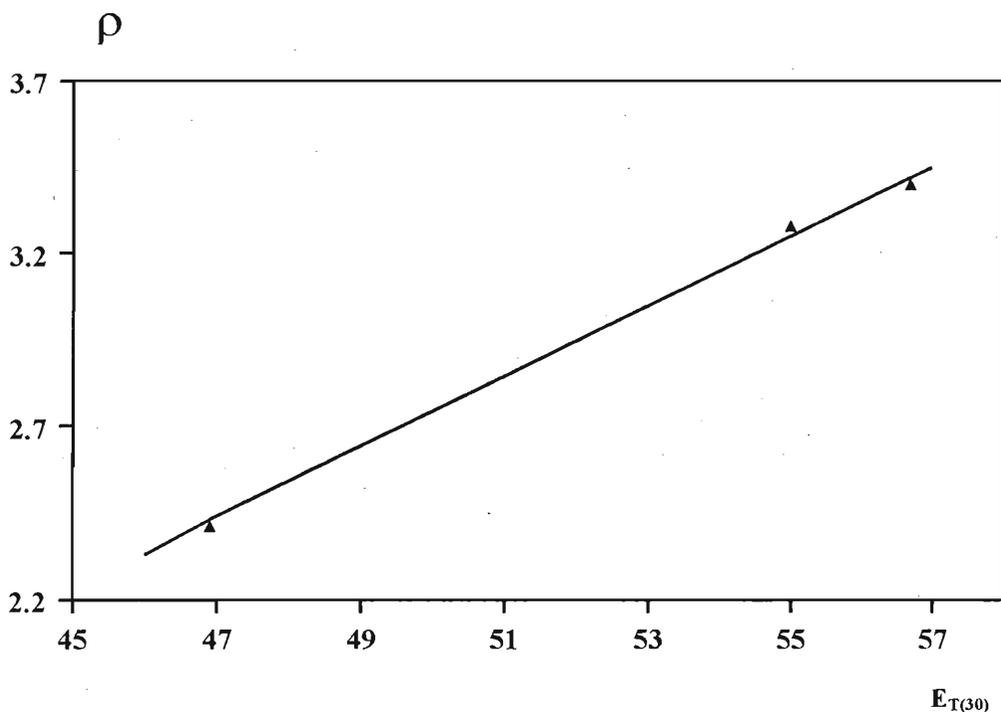(c) Values taken from reference (14).

Figure 6: Relationship between ρ and $E_{T(30)}$

DISCUSSION

The points corresponding to **2c, 2d** and **2m** (X = 4-NO$_2$ and 4-Br, 3-NO$_2$, respectively) have been excluded in the plot between $\log(k_{et}^X/k_{et}^H)$ and σ- , (Figure 2). The unusual singlet excited state behavior of chromophores has been reported when they are substituted with nitro and bromo groups[11]. Therefore **2c, 2d** and **2m** could have different behavior compared to the rest of the compounds. The linear plot is strong evidence for the validity of the proposed mechanism for the PIET.

As mentioned in the introduction, fluorescence is normally enhanced in organized media. The increase in fluorescence quantum yields with increasing concentration of micelle can be explained by the lower penetration of water molecules to the interior of the micelle. As the concentration of surfactant increases the polarity of the interior of the micelle decreases. Many researchers have shown[12] that fluorescence quantum yields of poly aromatic compounds are significantly enhanced in micelles. The main cause of the enhancement is its isolation from quenchers as well as increased microviscosity of the environment[13]. The higher fluorescence quantum yield of 1 in TX-100 compared to that of SDS can be attributed to the higher microviscosity of the TX-100 micelle. The higher microviscosity restricts the mobility of the enclosed molecule in the micelle, thus enhancing the fluorescence.

Using the cmc, aggregate number, n, and the substrate concentration (10^{-5} M) the minimum concentration of the micellar solutions required to achieve the mono occupancy can be estimated as 8.008 and 0.26 mmol dm^{-3} in SDS and TX-100, respectively. In our study, the fluorescence quantum yields of **1** and **2a-k** were measured in solutions with concentrations of 20 mmol dm^{-3} for SDS and 5 mmol dm^{-3} for TX-100. Use of these concentrations allows us to make the reasonable assumption that each substrate molecule is singly occupied in the micelle system. The micelle interior is a liquid phase less fluid than hydrocarbon solvents of similar chain length. There is some porosity near the micelle-water interface where water molecules can penetrate[15] deeply. Therefore both microviscosity and micropolarity of the environment of a molecule associated with a micelle may differ substantially from those of the bulk aqueous phase. These factors are responsible for the common properties of micellar systems. The higher microviscosity of the interior of the micelle restrict the dynamic behavior of the solubilized molecules and enhance the fluorescence quantum yields. This explains the higher fluorescence quantum yield of the substrate in micelle compared to that of the same molecule in methanol, i.e., the fluorescence quantum yield of 1 in methanol is 0.195 compared to 0.318 in SDS and 0.349 in TX-100.

Dielectric constant and $E_{T(30)}$ values are commonly used in quantification of polarity of the solvents. Higher values for dielectric constant and $E_{T(30)}$ have been observed for more polar solvents whereas non polar solvents give lower values. The dielectric constant for methanol is 32.7 whereas for micelle-water interface of SDS and TX-100 are 45 and 15 respectively. The $E_{T(30)}$ values for methanol, SDS and TX-100 are 55.0, 56.7 and 46.9, respectively. The magnitude of $E_{T(30)}$ in micellar systems suggest that the polarity of the solubilization site of the micelle is mainly determined by the amount of water molecules that penetrate into the interior. This is greater in SDS than TX-100 and therefore gives a higher $E_{T(30)}$ value for SDS. The order of the $E_{T(30)}$ values is SDS > methanol > TX-100. This indicates that the polarity of the solubilized site of SDS is higher than that of methanol while polarity of the solubilized site of TX-100 is lower than that of methanol.

The values of the reaction constant for SDS, methanol and TX-100 are 3.40, 3.28 and 2.41 respectively. This variation is parallel to the variation of $E_{T(30)}$. The plot between reaction constant, ρ and $E_{T(30)}$ is given in Figure 6. Although this plot has only three points, it is in agreement with our explanation of the medium effect on the electron transfer process. Both these effects namely the substituent and the solvent effect agreed with our explanation for the quenching of fluorescence by electron transfer.

In conclusion, the substituent on the benzoate chromophore with electron accepting capabilities enhance the electron transfer rate by making the process thermodynamically more favorable. On the other hand medium with lower polarity

reduces the electron transfer rates. Therefore both substituent and solvent effects play a significant role in the photoinduced intramolecular electron transfer processes.

Acknowledgement

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