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Electron Transfer from Aromatic Amines to Excited Coumarin Dyes: Fluorescence Quenching and Picosecond Transient Absorption Studies

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Electron transfer (ET) from aniline, *N*-alkylanilines, *N*,*N*-dialkylanilines, and *o*-phenylenediamine to a number of excited (S_1) 4-CF_3-coumarin dyes having differently substituted 7-amino groups have been investigated in acetonitrile solutions using steady-state (SS) and time-resolved (TR) fluorescence quenching measurements. Direct evidence for the ET reactions in the present systems have been obtained by characterizing the amine cation radicals using picosecond transient absorption measurements in the visible region. The experimentally determined bimolecular quenching constants (k_q) are seen to correlate nicely with the free energy changes ($\Delta G°$) for the ET reactions, within the framework of the Marcus ET theory. The total reorganization energy (λ) estimated from such correlation indicates that the solvent reorganization (λ_s) plays the major role in governing the ET dynamics in the present systems. A comparison of the present results under diffusive conditions with those reported earlier under nondiffusive conditions indicates that the ET dynamics in the latter cases are much faster than in the former. The results are discussed considering a structural difference between the encounter complexes formed under diffusive and nondiffusive conditions.

1. Introduction

Electron transfer (ET) is ubiquitous in chemistry and biology.[1−6] In most cases, ET from a ground state donor to a ground state acceptor is not energetically favorable. However, photoexcitation of either the acceptors or the donors often makes the ET reactions occur with reasonable rates,[1−6] because the energy acquired in the photoexcitation process favorably adds to the overall energy changes for the ET reactions.[7] Photoinduced ET (PET) processes have the most important advantage that they can be initiated almost instantaneously by the use of ultrashort laser pulses, and thus the kinetics of these reactions can be investigated in real time. Such real-time measurements have made it possible to understand many details of the ET reactions, especially their dynamics, and thus to test theoretical predictions with experimental observations.[1−10]

In the past few years we have investigated the ultrafast interactions between excited (S_1) coumarin dyes and ground state aniline and substituted anilines using the latter as the solvent donors.[11−17] From femtosecond fluorescence up-conversion measurements it has been observed that when the coumarin dyes are dissolved in aniline and substituted anilines (henceforth we will call them the aniline solvents), the fluorescence lifetimes of the dyes are reduced drastically compared to those in noninteracting solvents. These drastic reductions in fluorescence lifetimes have been attributed to ultrafast intermolecular PET from the anilines to the excited coumarin dyes. It has been observed that PET in these systems often occurs with rates much faster than those predicted by conventional ET theories.[1−10] In aniline solvents, an excited acceptor (coumarin) is always within the encounter distance with a donor (anilines) molecule and thus ET occurs effectively as an unimolecular process.[11−17] In other words, the ET interactions in these systems occur under nondiffusive conditions. To the best of our knowledge, there is no report in the literature on the ET interactions of the coumarin dyes with aniline and aniline derivatives in a solution under diffusive conditions, i.e., where the donors and acceptors have to diffuse together before the ET can take place. Further, even for the interaction of the excited coumarin dyes with aniline and substituted anilines under nondifusive conditions (i.e., in aniline solvents), there is no report so far to provide direct evidence for ET in these systems, namely, by characterizing the cation radicals of the anilines or the anion radicals of the coumarin dyes. Only recently Wang et al.[18] have shown from infrared transient absorption studies that a new infrared absorption signal appears around 2150 cm^{-1} following photoexcitation of coumarin-337 (C337) in *N*,*N*-dimethylaniline (DMAN) solvent, which they attribute to the nitrile stretching mode of the C337 anion radical.

In the present work we have investigated on the interactions of a series of excited coumarin dyes with a number of aromatic amines in acetonitrile (ACN) solutions under diffusive conditions, using both steady-state (SS) and time-resolved (TR) fluorescence quenching measurements. Picosecond transient absorption measurements in the visible region have been carried out to establish the evidence for ET interaction between the aromatic amines and the excited coumarin dyes. The bimolecular quenching constants (k_q) as obtained from fluorescence measurements have been correlated with the free energy changes ($\Delta G°$) of the ET reactions using Marcus ET theory. Present results obtained under the diffusive conditions have been correlated and discussed in the light of the ET dynamics obtained for the coumarin−aniline systems under nondiffusive conditions in aniline solvents.

2. Materials and Methods

Laser grade coumarin dyes were obtained from Lambda Physik, Kodak, or Exciton and were used as received. Aniline

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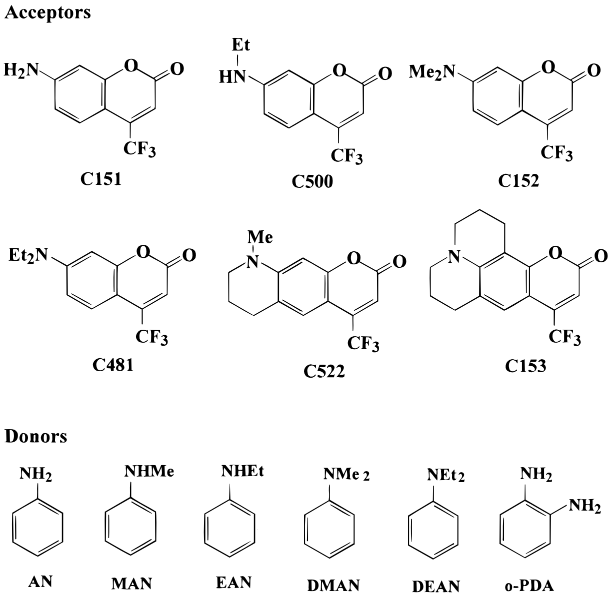


Figure 1. Chemical structures of the donors (aromatic amines) and acceptors (coumarins) used in the present study.

and its derivatives were obtained from E. Merck, Fluka, SISCO Research Laboratories (India), Spectrochem (India), or Qualigens Fine Chemicals (India). Anilines were purified by vacuum distillation just before use. *o*-Phenylenediamine (*o*-PDA) was obtained from BDH and was purified by vacuum sublimation. The chemical structures of the acceptors and the donors used in the present study are given in Figure 1, along with the abbreviations used in this article.

Ground state absorption measurements were made with a Shimadzu UV–vis spectrometer, Model UV-160A. Steady-state fluorescence measurements were carried out with a Hitachi spectrofluorimeter, Model F-4010. The S_1 state energies (E_{00}) of the coumarins and the amines were estimated from the intersecting wavelengths of the normalized excitation and emission spectra of the compounds in ACN.

Time-resolved fluorescence measurements were carried out using a time-domain spectrofluorimeter from Edinburgh Instruments, UK, Model 199. The instrument works on the principle of time-correlated single photon counting (TCSPC).[19] The details of this instrument are given elsewhere.[20] The fluorescence decay curves were analyzed by reconvolution procedure[19] using a proper instrument response function, obtained by substituting the sample cell with a light scatterer. The decay curves were fitted as a monoexponential function

$$I(t) = B\, exp(-t/\tau) \tag{1}$$

where τ is the fluorescence lifetime of the sample and B is the preexponential factor. The monoexponential fits thus obtained were reasonably good for all cases with chi-square (χ^2) values close to unity.

Transient optical absorption measurements were made using a picosecond laser flash photolysis setup. The details of this instrument are described elsewhere.[21] Briefly, the third harmonic output (355 nm, 7 mJ, 35 ps) of an active–passive mode-locked Nd:YAG laser (Continuum, USA, Model 501-C-10) was used for the excitation of the samples. The transients thus produced were detected as their time-resolved spectra. A white-light continuum (~400–900 nm) produced by focusing the residual fundamental (1064 nm) of the Nd:YAG laser onto a 10 cm path length quartz cell containing 50:50 (v/v) H_2O–D_2O mixture was used as the monitoring light source. The time delay between the pump and probe pulses was varied using a 1 m long delay rail at the probe end. The probe was bifurcated by using a 50:50 beam splitter to generate the reference and analyzing beams. Both the reference and analyzing beams were dispersed through a spectrograph and recorded by a dual diode array based optical multichannel analyzer system interfaced to an IBM-PC.

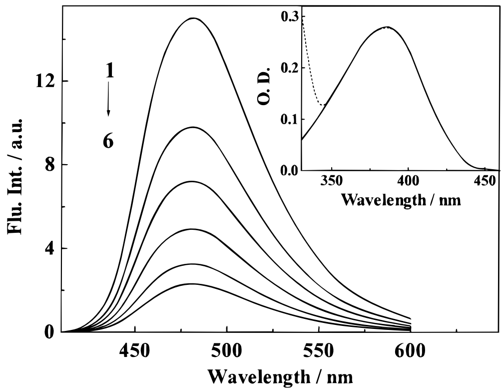


Figure 2. Steady-state fluorescence quenching of C500 by MAN in ACN. The MAN concentrations are (1) 0.0, (2) 8.6 × 10^{-3}, (3) 16.5 × 10^{-3}, (4) 30.2 × 10^{-3}, (5) 51.7 × 10^{-3}, and (6) 76.0 × 10^{-3} mol dm^{-3}. Inset: Ground-state absorption spectra of C500 in ACN in the absence (—) and in the presence (···) of 0.181 mol dm^{-3} MAN.

3. Results and Discussion

3.1. Fluorescence Quenching Studies. Fluorescence from the coumarin dyes (cf. Figure 1) in ACN is quenched by the aromatic amines (cf. Figure 1). For all the coumarin–amine systems, there is no change in the shape of the fluorescence spectra, even with the highest concentration of the amines used (~0.2 mol dm^{-3}). Thus no exciplex formation is indicated in the present systems. From the ground state absorption measurements also, there is no change in the long wavelength absorption band of the coumarin dyes, even in the presence of the highest concentrations of the amines, indicating no ground state complex formation. Typical SS fluorescence quenching results are shown in Figure 2 for C500–MAN system in ACN. Results on the ground state absorption spectra for the same system are also shown in the inset of Figure 2.

To have the estimates of the quenching dynamics, the SS fluorescence quenching results in the present systems were analyzed following Stern–Volmer (SV) relationship[22]

$$I_0/I = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \tag{2}$$

where I_0 and I are the fluorescence intensities in the absence and presence of the quenchers (Q ≡ aromatic amines), τ_0 is the fluorescence lifetime of the fluorophores (coumarins) in the absence of the quenchers, and k_q is the bimolecular quenching constant. For all the coumarin–amine systems the I_0/I vs [Q] plots were linear. Typical SV plots for some of the coumarin–amine systems are shown in Figure 3A. The k_q values for the different coumarin–amine systems were obtained from the slopes of the SV plots and are listed in Table 1.

If the quenching of the fluorescence intensity of the coumarin dyes by the amines was due to dynamic interactions, the fluorescence lifetimes of the dyes are also expected to become reduced in the presence of the quenchers. Thus the effect of the added amines to the fluorescence lifetimes (τ) of the coumarins has also been investigated using TR fluorescence measurements. It is seen that τ becomes reduced with the amine concentrations, following the SV linear relationship.[22]

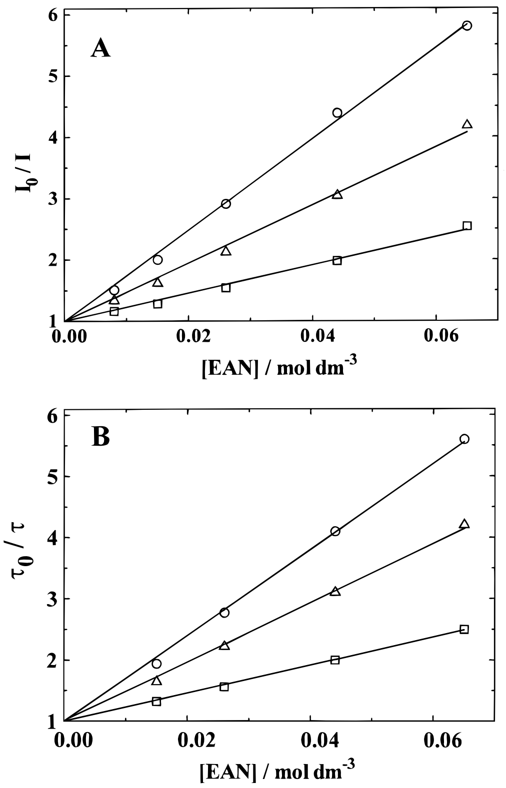


Figure 3. Steady-state (A) and time-resolved (B) Stern−Volmer plots for C151-EAN (○), C152-EAN (□), and C522-EAN (△) systems in ACN.

$$\tau_0/\tau = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \qquad (3)$$

Typical SV plots for some of the coumarin−amine systems as obtained in the TR measurements are shown in Figure 3B. The k_q values thus obtained from the slopes of such plots are listed in Table 1. It is seen from this table that, for any particular coumarin−amine system, the k_q values from SS and TR measurements are the same within the experimental error. These results thus indicate that the quenching of the S_1 state of the coumarins by the amines takes place without involving any intermediates such as exciplexes, and thus the quenching is collisional in nature.

TABLE 1: Bimolecular Quenching Constant (k_q) of the Coumarin−Amine Systems in ACN

				$k_q/10^9$ dm^3 mol^{-1} s^{-1}	
donor	acceptor	τ_0/ns[a]	$\Delta G°$/eV	SS	TR
AN	C151	5.18	−0.548	11.9	10.9
	C500	5.28	−0.373	11.8	10.3
	C152	1.96	−0.259	9.73	9.1
	C481	0.71	−0.217	7.22	6.5
	C522	5.48	−0.170	4.97	5.3
	C153	5.54	−0.058	2.26	2.3
MAN	C151		−0.665	15.6	14.9
	C500		−0.491	13.3	12.8
	C152		−0.377	12.9	12.9
	C481		−0.335	12.0	12.0
	C522		−0.289	9.65	9.8
	C153		−0.177	6.92	6.7
EAN	C151		−0.674	13.9	13.5
	C500		−0.500	11.2	11.0
	C152		−0.386	10.8	10.8
	C481		−0.344	13.1	13.0
	C522		−0.298	9.0	8.6
	C153		−0.186	7.3	7.3
DMAN	C151		−0.718	15.6	14.0
	C500		−0.544	15.1	13.9
	C152		−0.430	13.3	11.9
	C481		−0.388	11.4	11.0
	C522		−0.342	9.3	8.8
	C153		−0.230	7.4	7.2
DEAN	C151		−0.753	13.7	12.0
	C500		−0.579	13.7	13.4
	C152		−0.464	11.6	11.6
	C481		−0.423	12.9	11.9
	C522		−0.377	10.0	9.5
	C153		−0.265	7.4	7.4
o-PDA	C151		−1.026	17.8	17.0
	C500		−0.852	15.8	15.3
	C152		−0.737	16.9	15.9
	C481		−0.696	15.8	15.3
	C522		−0.649	15.8	15.5
	C153		−0.537	17.7	16.8

[a] Fluorescence lifetime of the coumarin dyes in ACN solutions.

TABLE 2: Redox Potentials (vs SCE) and E_{00} Energies of the Acceptors and Donors in ACN

acceptor			donor		
compound	E_{00}/eV	$E(A/A^-)$/V	compound	E_{00}/eV	$E(D/D^+)$/V
C151	2.98	−1.565	AN	3.91	0.93
C500	2.85	−1.607	MAN	3.87	0.81
C152	2.76	−1.626	EAN	3.85	0.80
C481	2.75	−1.66	DMAN	3.81	0.76
C522	2.70	−1.653	DEAN	3.77	0.72
C153	2.62	−1.685	*o*-PDA	3.86	0.45

The fluorescence quenching of a fluorophore by a quencher can be due to a number of possible reaction mechanisms, namely, ET, energy transfer, proton transfer, hydrogen bonding, etc. To understand the nature of interaction in the present systems, we have correlated the bimolecular quenching constants with the oxidation potential of the amines $\{E(D/D^+)\}$ and the reduction potential of the coumarins $\{E(A/A^-)\}$. Table 2 lists the $E(D/D^+)$ and $E(A/A^-)$ values in ACN for different amines and coumarins investigated in the present work.[11−14] Comparing Tables 1 and 2, it is seen that for a particular coumarin the k_q value gradually increases as the $E(D/D^+)$ of the amines is decreased. Similarly for a particular amine, the k_q value gradually increases as the $E(A/A^-)$ of the coumarins becomes less negative. These observations indicate that ET from the amines to the excited coumarin dyes might be the mechanism responsible for the fluorescence quenching in the present systems. An alternative mechanism like the singlet−singlet energy transfer is easily ruled out because the E_{00} energies of the amines are much higher than those of the coumarins (cf. Table 2). A mechanism involving the hydrogen bonding interaction between the excited coumarins and the ground state amines is also excluded on the basis of the following arguments. (i) If the amino group hydrogens of the amines were to form hydrogen bonds with the coumarins, the tertiary amines should not have given any quenching. (ii) If the amines were acting as the hydrogen bond acceptors, except C151 and C500 all other coumarins should not have shown any quenching interaction. From Table 1 it is seen that the experimental observations do not agree with these expectations.

3.2. Picosecond Transient Absorption Studies. To obtain direct evidence for the ET reactions in the present systems, we carried out the transient absorption measurements using picosecond laser flash photolysis (LFP) technique. The transient absorption measurements were made for different coumarin−amine systems in ACN solutions and also using anilines directly as the solvent donors (nondiffusive conditions).

In ACN solutions the picosecond transient absorption measurements were carried out for the coumarin−DMAN and coumarin−DEAN systems. Since almost all the coumarin dyes

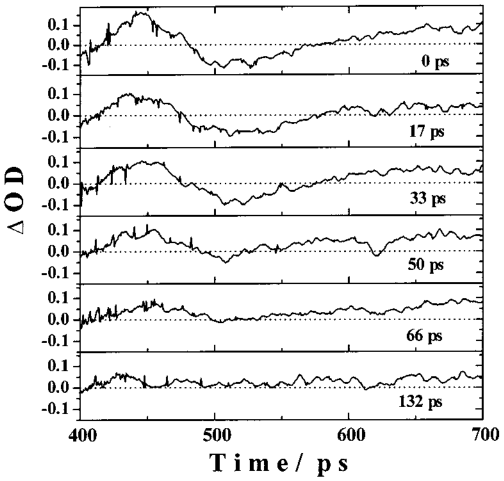


Figure 4. Picosecond time-resolved transient absorption spectra for the C152−DEAN system in ACN. The DEAN concentration used was 1 mol dm^{-3}. Time delays between the pump and probe pulses are indicated in the figure.

(except C152 and C481) are strongly fluorescent in ACN,[23−25] the contributions from the stimulated emissions in the transient absorption spectra are always very large. Thus, to minimize the effect of the stimulated emissions, we had to use quite high concentrations of the amines to quench the S_1 state of the coumarins to a large extent and thus to observe the absorption signals of the transients produced following ET reactions unambiguously. The amine concentrations were thus used in the range of about 1 mol dm^{-3} in ACN solutions. Even with these high amine concentrations, the transient absorption signals, especially those of the amine cation radicals, could be observed undoubtedly only for a limited number of coumarin−amine systems, namely, C152−DMAN, C152−DEAN, C481−DMAN, and C481−DEAN. For the rest of the coumarin−amine systems, the transient absorption spectra were an interplay of the stimulated emissions, depletion of the ground state coumarins, and the absorption signals of the transients. Thus the absorption signals for the transients produced following ET reactions could not be characterized definitely for these coumarin−amine systems.

Typical picosecond time-resolved transient absorption spectra as obtained for C152−DEAN system in ACN with an amine concentration of about 1 mol dm^{-3} are shown in Figure 4. As are seen from this figure, an absorption band with a peak around 450 nm appears immediately after the excitation pulse. This absorption band is attributed to the DEAN cation radical.[26−29] The negative absorption signals observed in the 500−550 nm region at the early time scales are attributed to the stimulated emission from the excited C152, as this is the spectral region which overlaps with the fluorescence spectra of the coumarin dye.[23−25] In the transient absorption spectra, there is also a broad absorption band without any definite peak in the spectral region above about 600 nm. This we attribute to the coumarin anion radicals.[30] To the best of our knowledge, the absorption spectra of the coumarin anion radicals are not reported in the literature. For C152, the ground state absorption spectra appears below about 420 nm and thus the contribution of the ground state coumarin depletion on the transient absorption spectra is not that strong for the present system. Since we used very high concentrations of the amines in the picosecond experiments, the appearance of the absorption signal for DEAN cation radicals immediately after the 35 ps excitation pulse indicates that this is due to the ion-pair state produced following ET reaction. The results obtained in the picosecond transient absorption studies for C152−DMAN, C481−DMAN, and C481−DEAN systems in ACN are qualitatively similar to those observed for C152−DEAN system. Thus the picosecond transient absorption measurements provide direct evidence for the ET interactions between the excited coumarin dyes and the ground state of the aromatic amines in ACN solutions.

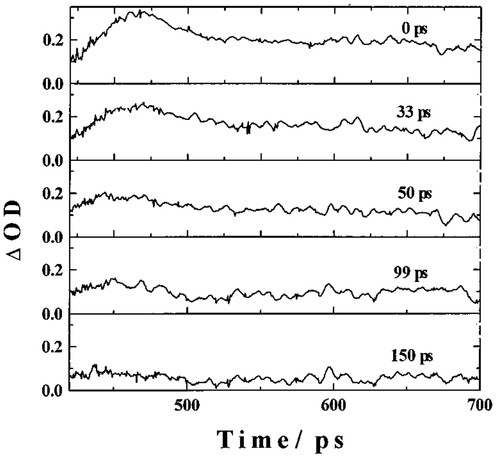


Figure 5. Picosecond time-resolved transient absorption spectra for C152 in neat DEAN. Time delays between the pump and probe pulses are indicated in the figure.

As seen from Figure 4, the absorption signals for the DEAN cation radicals, the negative absorptions due to stimulated emissions, and the broad absorptions beyond 600 nm due to coumarin anion radicals gradually reduce as the delay between the pump and probe pulses is increased. Similar observations are also made for the other coumarin−amine systems. Assuming that the transient absorption signals in the 450 nm region is due to the amine cation radicals in the ion-pair states, the lifetime of these states (τ_{IP}) could be estimated following the decay of these signals. However, since the signal strengths are low and also the signals are quite noisy, we could not estimate the τ_{IP} values accurately in ACN solutions. Qualitatively, however, it is indicated from the picosecond results that the τ_{IP} values for these coumarin−amine systems in ACN are less than about 100 ps.

As already mentioned, using anilines as the solvent donors, the fluorescence lifetimes of the coumarin dyes are drastically reduced in comparison to those observed in noninteracting solvents, like ACN.[11−17] We attributed these results to ultrafast intermolecular ET from anilines to excited coumarin dyes.[11−17] Direct evidence for the ET reactions between anilines and coumarin dyes in aniline solvents, however, is not provided in our earlier work.[11−17] Thus, in the present work, the picosecond transient absorption studies have also been carried out for the coumarin dyes using DMAN and DEAN directly as the solvent donors. Figure 5 shows the picosecond time-resolved transient absorption spectra for C152 in DEAN solvent. The results are qualitatively very similar to the results obtained for C152−DEAN system in ACN (cf. Figure 4), except that in the present case there is no signal for the stimulated emission of the coumarins, as the fluorescence is strongly quenched under the present experimental conditions. As seen from Figure 5, the DEAN cation radical absorption around the 450 nm region is clearly indicated in the transient absorption spectra obtained following the photoexcitation of C152. A broad absorption band without any distinct peak is also seen in the transient absorption spectra at the longer wavelength region (above about 500 nm), which are due to the coumarin anion radicals.[30] As the time delay between the pump and probe pulses increases, both the

TABLE 3: Lifetimes of the Ion-Pair States (τ_{IP}) for Different Coumarin−Amine Systems in Aniline Solvents

system		
coumarin	amine	τ_{IP}/ps
C151	DMAN	180 ± 40
	DEAN	120 ± 40
C152	DMAN	160 ± 40
	DEAN	110 ± 40
C481	DMAN	180 ± 40
	DEAN	100 ± 40

amine cation radical and the coumarin anion radical absorptions gradually reduce. Exactly the same results have also been obtained with C151 and C481 in DEAN and C151, C152, and C481 in DMAN solvents. These picosecond results in DMAN and DEAN solvents thus clearly indicate that the excited coumarin dyes interact with the anilines via ET mechanism. For other coumarins in DMAN and DEAN solvents, the transient absorption spectra were not very clear to distinctly characterize the transient intermediates. One of the reasons for this is probably the ground state absorption of the coumarins, which appears in the 400−500 nm region and thus suppresses the absorption signals for the DMAN and DEAN cation radicals. However, drawing an analogy with the picosecond results obtained for C151, C152, and C481 in DMAN and DEAN solvents, it is inferred that for all the coumarin−amine systems ET is the mechanism responsible for the drastic reduction in the fluorescence lifetime of the dyes in aniline solvents.

The lifetime of the ion-pair states (τ_{IP}) for the coumarins in DMAN and DEAN solvents have been estimated from the decay of the 450 nm transient absorption band and are listed in Table 3. It is indicated from this table that the ion-pair states in DMAN and DEAN solvents are only marginally longer lived than those in ACN solutions. Further, the τ_{IP} values for the systems listed in Table 3 are seen to be in almost the same range. With the limited number of data points, however, we are not in a position to comment further about the back electron transfer dynamics and their correlation with ET theory.

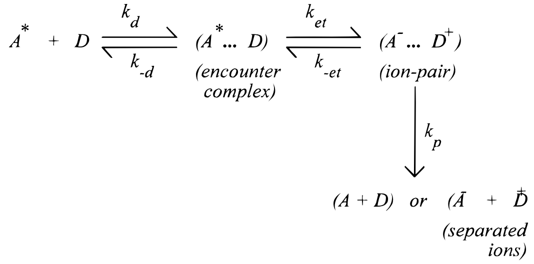
3.3. Correlation of the Quenching Constants with Marcus ET Theory. The feasibility of photoinduced ET from a ground state donor (amines) to an excited state acceptor (coumarins) is dictated by the standard free energy change, $\Delta G°$, for the ET reaction. The $\Delta G°$ for a PET reaction in a polar solvent like ACN can be expressed as[7]

$$\Delta G° = E(\mathrm{D/D^+}) - E(\mathrm{A/A^-}) - E_{00} - e^2/\epsilon r_{\mathrm{DA}} \qquad (4)$$

where e is the charge of an electron, ϵ is the dielectric constant of the medium, and r_{DA} is the separation between the donor and acceptor at the encounter. Since the exact estimation of r_{DA} is not practically possible, we assumed it to be equal to the sum of the radii of the donors and acceptors for the present systems. The sizes of the acceptors and donors were estimated using Edward's volume addition method,[31] assuming the molecules to be effective spheres. The $\Delta G°$ values thus estimated for different donor−acceptor pairs in ACN are listed in Table 1.

Considering ET to be responsible for the fluorescence quenching in the present systems, as is established from the picosecond transient absorption results, Scheme 1 is presented to explain the observed fluorescence quenching results.[1−6] According to this scheme, the excited acceptor (A^*) and the ground state donor (D) molecules diffuse together to form an encounter complex, ($A^*\cdots D$). The ($A^*\cdots D$) then undergoes a reorganization to reach the transition state (TS), where ET takes place from the donor to the acceptor to give the ion-pair state, ($A^-\cdots D^+$). The parameters, k_d and k_{-d} are the diffusion-controlled rate constants for the formation and dissociation of ($A^*\cdots D$), k_{et} and k_{-et} are the forward and reverse ET rate constants, and k_p is the sum of all the rate constants causing the disappearance of the ($A^-\cdots D^+$) 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 (A and D), and ion dissociation (k_{ID}) to give the solvent separated ions (A^- and D^+).

SCHEME 1



From energetic considerations, the reverse ET (k_{-et}) is usually an unlikely process.[1−6] Thus it can be assumed that $k_p \gg k_{-et}$. Following this assumption and applying the steady-state conditions in Scheme 1 one can derive the following expression (eq 5)[1−6] for the observed bimolecular quenching constant, k_q.

$$k_q = \frac{k_d}{1 + (k_d/Kk_{et})} \qquad (5)$$

where K ($=k_d/k_{-d}$) is the diffusional equilibrium constant for the encounter complex formation and can be expressed as[32,33]

$$K = \frac{4\pi N r_{\mathrm{DA}}^2\, \delta r}{1000} \exp\left(-\frac{w_c}{RT}\right) \qquad (6)$$

In eq 6, N is Avogadro's number, r_{DA} is the separation between donor and acceptor in the encounter complex, r_{DA} and ($r_{\mathrm{DA}} + \delta r$) are the center-to-center distances over which the ET can take place, and w_c is work required to bring the donor and acceptor to the encounter distance. For neutral molecules diffusing freely in solution, w_c is assumed to be zero. In general a value of about 2 Å is considered for δr in the ET reactions.[32,33] Thus following eq 6, an approximate estimate for K is about 1 mol^{-1} dm^3 for two reactants diffusing freely in solution.

In its simplified form, the activation-controlled ET rate constant (k_{et}) can be expressed as

$$k_{et} = \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad (7)$$

where ν is the frequency factor and ΔG^* is the free energy of activation for the ET process. The value of ν can range from 10^{12} to 10^{14} s^{-1} depending on the systems.[34−36] While a variety of forms have been proposed for ΔG^*, the quadratic relation (eq 8) derived by Marcus[1−10] has extensively been used for a variety of ET reactions.

$$\Delta G^* = \frac{(\Delta G° + \lambda)^2}{4\lambda} \qquad (8)$$

$\Delta G°$ is the free energy change for the ET reaction and λ is the total reorganization energy, given as

$$\lambda = \lambda_{\mathrm{in}} + \lambda_{\mathrm{s}} \qquad (9)$$

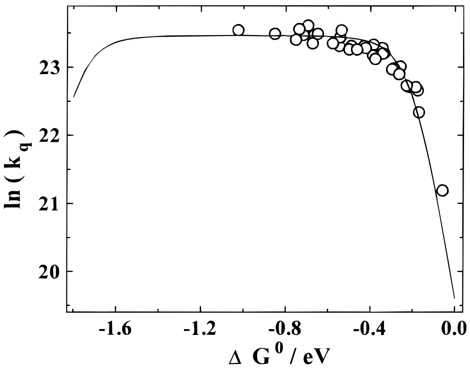


Figure 6. $\ln(k_q)$ vs $\Delta G°$ plot for the different coumarin−amine pairs in ACN. Experimental points are presented by the circles, and the caculated k_q values using Marcus ET theory are presented by the continuous curve.

where λ_{in} is the contribution arising due to the intramolecular bond length and bond angle changes in the donor and acceptor during ET and the λ_s is the contribution arising due to the solvent reorganization. From the consideration of the nonequilibrium polarization of the medium and employing the dielectric continuum model for the solvent, Marcus derived[1−6] the following expression for λ_s.

$$\lambda_s = (e^2)\left\{\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{2r_{DA}}\right\}\left\{\frac{1}{n^2} - \frac{1}{\epsilon}\right\} \qquad (10)$$

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 is the dielectric constant of the solvent. Average values of r_D (=3.05 Å) and r_A (=3.68 Å) were estimated using the sizes of the donors and acceptors as obtained using Edward's volume addition method.[31] Similarly the r_{DA} (=6.73 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 differences 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 to be about 1.1 eV using eq 10.

Using eqs 5, 7, and 8, the bimolecular quenching constants (k_q) were calculated for different $\Delta G°$ values. The equilibrium constant K for the encounter complex formation was assumed to be 1 dm^3 mol^{-1} for the present systems. Different combinations of k_d, ν, and λ values were tried to get a good correlation between the calculated and the experimental k_q values. The best correlation thus obtained with $k_d = 1.55 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $\nu = 5 \times 10^{12}$ s^{-1}, and $\lambda = 1.0$ eV, is shown in Figure 6, where the circles are the experimental points and the continuous curve is the calculated k_q values for different $\Delta G°$. From Figure 6 it is indicated that the k_q value initially increases steeply as $\Delta G°$ gradually becomes more negative and then ultimately the k_q value levels off at the diffusion-controlled limit at highly negative $\Delta G°$ values. Thus it is indicated that the majority of the coumarin−amine systems investigated in the present work seem to fall in the normal Marcus region. Further, the nature of correlation we observe in Figure 6 indicates that the present systems under diffusive conditions behave in exactly the same way as are generally seen in most of the ET reactions under similar conditions.[7,34−40]

One more interesting point to be noted from Figure 6 is that the λ value of 1.0 eV, as obtained from the correlation of the experimental and the calculated k_q values (cf. Figure 6), is quite close to the λ_s value estimated using eq 10. Since the estimations of r_D, r_A, and r_{DA} are quite approximate, such an agreement between the two values seems to be quite satisfactory. The present results thus indicate that the solvent contribution is the only reorganization required for the ET to take place under the diffusive conditions.

3.4. Comparison of the ET Rates under Diffusive and Nondiffusive Conditions. In our earlier work on ultrafast (femtosecond) PET from aniline solvents to excited coumarin dyes (under nondiffusive conditions), it was observed that ET often occurs with rates much faster than the solvent reorganization rates. Conventional ET theories[1−6] could not explain the ultrafast ET rates, faster than the solvation rates, and thus were not applicable to these systems under the nondiffusive conditions.[11−17] On the contrary, in the present experimental conditions, where donors and acceptors have to diffuse together before ET can take place, it appears that the observed reaction dynamics are well correlated within the framework of the Marcus outer sphere ET theory.[1−6] Present systems under diffusive conditions thus seem to behave very normally, similar to the observations made by many authors in the ET studies under similar conditions.[7,34−40]

As the present results indicate, under diffusive conditions, the solvent reorganization appears to play the major role in governing the ET dynamics. The contribution from the intramolecular reorganizations seems to be negligible under the present experimental conditions. On the contrary, under the nondiffusive conditions, it was seen that there is about 0.3 eV of intramolecular reorganization from the low frequency vibrational modes required for ET to take place in the coumarin−aniline systems.[12,15] Similarly there is about 0.2 eV of reorganization energy involved from the high frequency vibrational modes of the reactants.[12,15] Though for most of the donor−acceptor pairs investigated in the present work the observed quenching rate constants are leveled off to the diffusion-controlled rate constant, apparently it is indicated from the correlation in Figure 6 that the intramolecular reorganizations must have a very negligible contribution in determining the ET dynamics under the diffusive conditions. Thus there must be a fundamental difference in the ET mechanism under diffusive and nondiffusive conditions for coumarin−aniline systems.

For the donor−acceptor pairs, for which the bimolecular quenching constants are less than the diffusion-controlled rate constants, the absolute rate constant for the ET reaction (k_{et}) can be obtained using eq 6. Thus rearranging eq 6, the k_{et} can be expressed as

$$k_{et} = \frac{k_d k_q}{K(k_d - k_q)} \qquad (11)$$

Assuming $K = 1$ dm^3 mol^{-1}, the values of k_{et} under diffusive conditions ($k_{et,d}$) were estimated for the systems where $k_q < k_d$. The $k_{et,d}$ values thus obtained for different systems are listed in Table 4. Table 4 also lists the average ET rate constants $\langle k_{et}\rangle_{nd}$ obtained for these systems under nondiffusive conditions in aniline solvents.[11,12,15] We consider only the average ET rate constants under the nondiffusive conditions, because under this experimental condition the ET dynamics were found to be non single exponential.[11−17] A comparison of the $\langle k_{et}\rangle_{nd}$ and $k_{et,d}$ values in Table 4 for the different coumarin−aniline systems indicateds that the former is always much higher than the latter value. It is thus indicated that the ET reaction under nondiffusive conditions occur with much faster rates than those under diffusive conditions. Though for the coumarin−amine pairs for which $k_q \approx k_d$ it is difficult to comment on the absolute ET

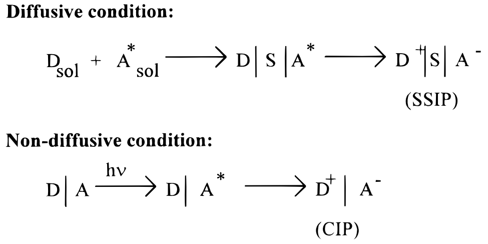
TABLE 4: Electron-Transfer Rate Constants under Diffusive ($k_{et,d}$) and Nondiffusive ($\langle k_{et}\rangle_{nd}$) Conditions for Different Coumarin−Amine Systems

donor	acceptor	$k_{et,d}/10^{10}$ s^{-1}	$\langle k_{et}\rangle_{nd}/10^{10}$ s^{-1}
AN	C151	5.12	63.3
	C500	4.94	34.6
	C152	2.61	13.7
	C481	1.35	9.80
	C522	0.73	3.86
	C153	0.27	1.27
MAN	C522	2.50	22.5
	C153	1.25	6.70
EAN	C522	2.15	20.1
	C153	1.38	6.13
DMAN	C522	2.33	55.9
	C153	1.42	5.38
DEAN	C522	2.82	20.8
	C153	1.38	2.45

rates, drawing analogy to the systems given in Table 4 it may be assumed that $\langle k_{et}\rangle_{nd}$ is always higher than $k_{et,d}$ for the coumarin−amine systems. Thus, from the comparison of $\langle k_{et}\rangle_{nd}$ and $k_{et,d}$ it is indicated that there must be a fundamental difference in the ET mechanism under diffusive and nondiffusive conditions.

For the coumarins in aniline solvents, it has been established[11−17] that the conventional ET model, where the reaction is viewed in a one-dimensional reaction coordinate, cannot explain the ultrafast nature of the ET dynamics. Thus one had to consider a two-dimensional ET (2DET) model,[41−43] where it is assumed that the intramolecular and the solvent modes participate in a noncoupled manner to assist the reactants to reach the TS. In this 2DET model, the reorganizations along the intramolecular modes occur much faster than the solvent modes. Thus the reactants can reach the TS for ET via the involvement of these intramolecular modes even when the solvent modes are frozen altogether. Under this situation, the ET rates can thus become faster than the solvation rates, as were observed in our earlier studies for coumarins in aniline solvents.[11−17] Under diffusive conditions, as the present results indicate, the ET rates are much slower than those under nondiffusive conditions. Further, the ET rates or more specifically the bimolecular quenching constants under diffusive conditions are well correlated within the framework of conventional Marcus ET theory,[1−6] assuming the reorganizations of solvent modes as the only governing factor for the ET dynamics. Comparing the present results with those obtained in aniline solvents,[11−17] it is thus indicated that in the two experimental conditions there is a fundamental difference in the ET step itself. When a ground state donor and an excited state acceptor diffuse toward each other in a solution, each of the reactants is expected to move with its respective solvation shells (cf. D_{sol} and A^*_{sol}). It is thus likely that the encounter complex formed between these two reactants must have a structure where the donor and the acceptor are separated by a solvent layer (D/S/A*). Similarly the ion-pair state produced following ET in these encounter complexes must have a solvent layer between the two ions ($D^+/S/A^-$) and thus it must be a solvent-separated ion-pair (SSIP) state.[22,44] On the contrary, under the nondiffusive conditions, it is expected that the donor and acceptor must be in physical contact (D/A) prior to the photoexcitation. Further, under nondiffusive conditions, the donor and acceptor are most likely to be in a preferred face-to-face configuration (sandwich structure) in the encounter complex. Thus the encounter complex (D/A*) under this condition is structurally different than that in the diffusive condition. The ion-pair state produced following ET in a nondiffusive condition (D^+/A^-) is thus expected to be a contact ion pair (CIP) rather than the SSIP.[22,44] Scheme 2 shows the conceptual presentation of the above two situations.

SCHEME 2



From the above discussions, it is thus expected that under diffusive conditions the mixing of the reactant state (D/S/A*) with the product state ($D^+/S/A^-$) will be much weaker than that between (D/A*) and (D^+/A^-) states under nondiffusive conditions. The net result will thus be slower ET rates in the former than in the latter cases. Further, it is expected that intervention of solvent between D and A in the encounter complex under diffusive conditions will make the ET reactions highly sensitive to the solvent reorganizations but less sensitive to the intramolecular reorganizations. Under nondiffusive conditions, the situation becomes just opposite and the ET reactions are mostly controlled by the intramolecular reorganizations of the reactants.

Recently Tachiya and co-workers[45] have shown some similar observations in the fluorescence quenching dynamics of 9-cyanoanthracene and 9,10-dicyanoanthracene by DMAN in noninteracting solvents. It has been shown by these authors[45] that in the lower concentration range of the quenchers ($<$0.15 mol dm^{-3}), where the diffusion of the reactants is a prerequisite for the reaction to take place, the quenching dynamics are nicely explained using the conventional Marcus ET theory. At higher amine concentrations, where there is expected to be a good contribution from the static quenching (nondiffusive condition), the fluorescence decays of the cyanoanthracenes are always seen to have an ultrafast component in the quenching dynamics. This ultrafast component of the ET dynamics cannot be accounted for on the basis of the conventional Marcus ET theory and thus demands a separate mechanistic model for the ET reactions under the nondiffusive conditions. Tachiya and co-workers assumed the involvement of a charge-transfer (CT) interaction between the cyanoanthracenes and the amines to explain the ultrafast component in the quenching dynamics for these systems.[45] For the coumarins in aniline solvents,[11−17] however, no indications for such CT interactions were observed, though the quenching dynamics showed the ultrafast nature of the ET processes, which could not be explained using conventional Marcus ET theory. Since in the present study we used a reasonably lower concentration range of the quenchers ($<$0.1 mol dm^{-3}), the diffusion of the reactants is the prerequisite for ET to take place. Under this situation, the Marcus ET theory is seen to correlate the experimental results quite successfully.

4. Conclusions

Fluorescence of the 4-CF_3-coumarins having differently substituted 7-amino groups is quenched by aromatic amines in ACN. The quenching mechanism has been attributed to ET from the ground state amines to the excited (S_1) coumarin dyes. Direct evidence for the ET reactions in the present systems has been obtained from the picosecond transient absorption studies in the visible region. The bimolecular fluorescence quenching constants (k_q) in the present systems are seen to correlate nicely with the free energy changes ($\Delta G°$) of the ET reactions within the framework of Marcus ET theory. A comparison of the present results under diffusive conditions with those obtained under nondiffusive conditions in aniline solvents, indicates that ET dynamics are much faster in the latter cases than in the former. Further, under diffusive conditions, the solvent reorganization appears to be the most dominating factor in governing ET dynamics and the contribution of the intramolecular reorganizations appears to be negligible. The results are discussed in terms of the structural difference in the encounter complexes formed under diffusive and nondiffusive conditions.

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