

Quenching of the fluorescence of 3-carboxy-5,6-benzocoumarin by aromatic amines

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Abstract

The change of the emission properties of a coumarin derivative, 3-carboxy-5,6-benzocoumarin in the presence of five aromatic amines was studied by means of steady-state fluorescence spectroscopy. The quenching process was characterized by Stern–Volmer (SV) plots which display either the usual linear aspect (aniline, dimethyl- and diethylaniline) or an upward curvature (diphenyl- and triphenylamine). The analysis of the plots made in terms of the usual linear SV equation or of a SV modified equation including both the dynamical and static quenching allows for the estimation of the rate constant of the bimolecular quenching reaction. The use of the finite sink approximation model for the amines leading to a curve SV plot shows that the quenching was diffusion limited. The experimental data were rationalized in terms of the Marcus theory on the electron transfer reactions. The bimolecular quenching constants and the free energy change estimated by the Rehm–Weller relationship fit well the data for other coumarin–amine systems.

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1. Introduction

The fluorescence probes were widely used for obtaining information on the interactions in molecular systems, especially in drug–biopolymers ones, which play an important role in pharmacology and pharmacodynamics. Among other compounds, the coumarin derivatives were intensively studied for their wide applications as laser dyes, ionophores, fluorescence markers and probe molecules for examination of electron transfer processes and ultrafast solvation effects [1–13]. In a previous paper [14] we have shown that the photophysical properties of a new derivative in this class fulfill the conditions required for a good fluorophore. Moreover, its enhanced solubility in aqueous media makes it suitable to be used in protein study.

In order to get a deeper insight on the possible deactivation processes and especially in its implication in electron transfer reaction, the interaction of the title compound with aromatic amines was studied by steady-state fluorescence spectroscopy.

The electron transfer reaction of some coumarin derivatives with aromatic amines was previously studied in both diffusive (homogenous) and nondiffusive conditions, in all cases the S_1 excited-state of coumarins being the acceptor [9–11,15–17]. In homogeneous solutions, the photoinduced electron transfer (PET) was successfully explained using the Marcus–Rehm–Weller model, i.e. the correlation of the bimolecular quenching constants with the free energy ΔG of the reaction. It was shown that the main factor determining the electron transfer is the solvent reorganization energy.

Using the same donor–acceptor systems, but in nondiffusive condition, in neat amine solvents [10,15–17] it was shown that the electron transfer occurs faster than the solvation time and that the process can be explained only using a bidimensional model [9,15]. Between these two limits, the electron transfer reaction in micelles provide new information about the PET. The reported results show that the electron transfer process is slower than in the neat solvents and the dependence of the bimolecular quenching constants on the ΔG values presents the Marcus predicted bell-shape evidencing the so-called Marcus inverted region [18–21].

The structures of 3-carboxy-5,6-benzocoumarin (the acceptor) and the used donors are presented in Fig. 1.

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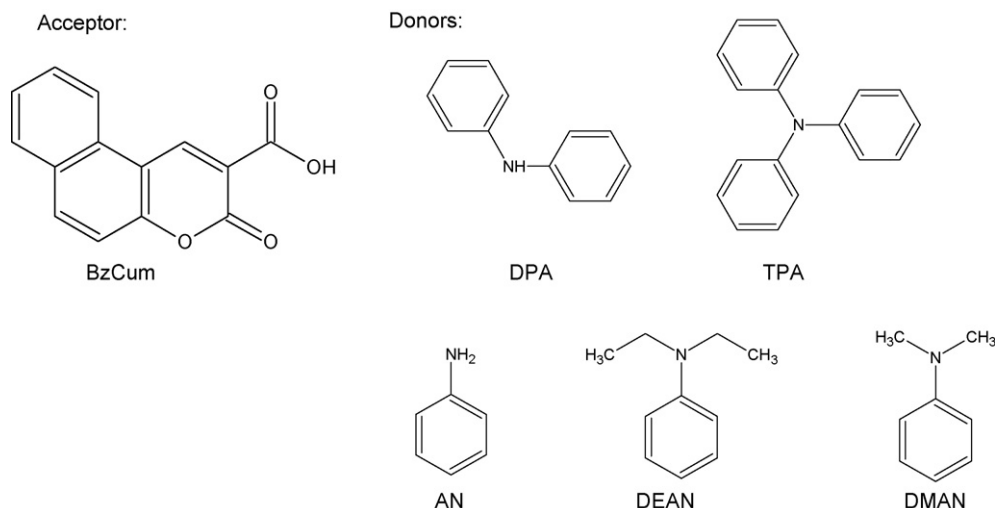


Fig. 1. Structural formula for the acceptor, BzCum and the aromatic amines used as donors.

The paper is organized as follows. The first part contains a discussion on the main properties of the acceptor and donors involved in the electron transfer reaction. The second part contains the steady-state fluorescence data, the determination of the SV and bimolecular quenching constants. The rationalization of the experimental data in terms of the Marcus theory and Rehm–Weller model is given in part 3.

2. Experimental

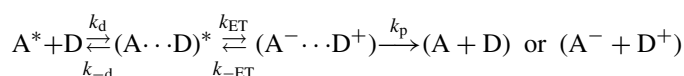
The liquid amines were distilled prior to use. The determinations were made by spectrofluorimetric titration in acetonitrile (ACN). The absorption and steady-state fluorescence spectra were recorded on a Unicam Helios UV–vis spectrophotometer and a Jasco 6300F spectrofluorimeter, respectively. The concentration of BzCum solutions was in the range of 5×10^{-6} to 5×10^{-5} M to ensure an absorption value less than 0.1. According to the absorption spectrum of BzCum, the excitation wavelength was 360 nm for all the samples. The cyclic voltammetry experiments were performed in ACN on the VOLTALAB-32 electrochemical device using a cell equipped with three electrodes, the working electrode (2 mm diameter Pt disk), the counter electrode (Pt wire), and the reference electrode (Ag wire). The potential of working electrode was corrected and the value is given relative to calomel electrode.

3. Results and discussion

The bimolecular fluorescence quenching can be due either to pure dynamic, collisional process or to both static and dynamic processes. Several mechanisms are possible like formation of ground state nonemissive complexes, electron or energy transfer. In solution, the bimolecular quenching constant, k_q is correlated to the diffusion constant, k_d , and to the energy activation rate constant, k_a [22]:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_a} \quad (1)$$

Usually, the fluorescence quenching of organic compounds by amines occurs by electron transfer in which the amines behave as donors, the following scheme being invoked [17]:



In this scheme, k_d and k_{-d} represent the diffusion constants for the formation and dissociation of the precursor complex, k_{ET} and k_{-ET} are the constants for the forward and the back electron transfer reaction and k_p is a general rate constant describing all the reactions leading to the disappearance of the ion pair ($A^- \cdots D^+$). Assuming that the back electron transfer reaction (charge recombination reaction) has a low probability and that the equilibrium constant for the diffusion process $K = k_d/k_{-d}$ is close to unity, it results the well-known formula:

$$k_q = \frac{k_d}{1 + (k_d/K \times k_{ET})} \quad (2)$$

or, by rearrangement:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{ET}} \quad (3)$$

Comparing Eqs. (1) and (3) it can be seen that k_a can be assimilated to the rate constant k_{ET} .

In the followings, the bimolecular quenching constants are obtained from the Stern–Volmer (SV) plots. In the cases for which the experimental SV plots are linear, the purely dynamic Eq. (4) will be used:

$$\frac{I_0}{I} = 1 + K_{SV} \times [Q] \quad (4)$$

in which I_0 and I represent the fluorescence intensity in the absence and the presence of the quencher, respectively, and $[Q]$ is the quencher concentration.

For the cases characterized by nonlinear SV plots we will apply both the sphere of action model and the finite sink approximation; the purpose of using this last model is to establish

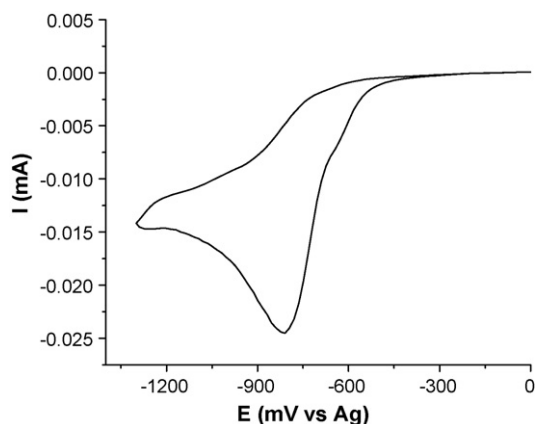


Fig. 2. Cyclic voltammogram of BzC in ACN.

which is the role of the diffusion process, whether the quenching reaction is diffusion limited or not.

3.1. Acceptor and donors properties

The photophysical properties of isolated 3-carboxy-5,6-benzocoumarin in organic solvents and aqueous media were reported in our previous work. The significant quantities which will be used in the followings are the values determined in acetonitrile for the fluorescence quantum yield, $\Phi = 0.56$, the natural lifetime $\tau_0 = 13$ ns and the excitation energy, $E_{00} = 3.03$ eV.

The reduction potential of the acceptor, $E(A/A^-)$, was obtained by cyclic voltammetry as is described in the experimental part. The cyclic voltammogram of the coumarin derivative, is presented in Fig. 2.

It can be seen that the first reduction wave has an irreversible character, preventing the determination of the reduction potential as the average value of the reduction and oxidation peak potentials, E_{pa} and E_{pc} . Therefore, the peak potential E_{pc} value, $E_{pc} = -1.185$ V/SCE was used as the $E_{1/2}$ value for the reduction process.

The presence of an irreversible reduction process was also found for other coumarin derivatives [23,24] and the same procedure was mentioned in spite of the approximation involved. Most literature data on the acceptor character of coumarin derivatives in the electron transfer reactions refer to compounds possessing mixed substituents, alkylated amines in position 7 which enhance the donor properties and the strong acceptor CF_3 group in position 3. The values are in the range -1.5 to -1.8 V versus SCE. The presence of the methyl group instead of CF_3 determines more negative reduction potentials [15,23]. Considering the reduction potential obtained for our compound we can

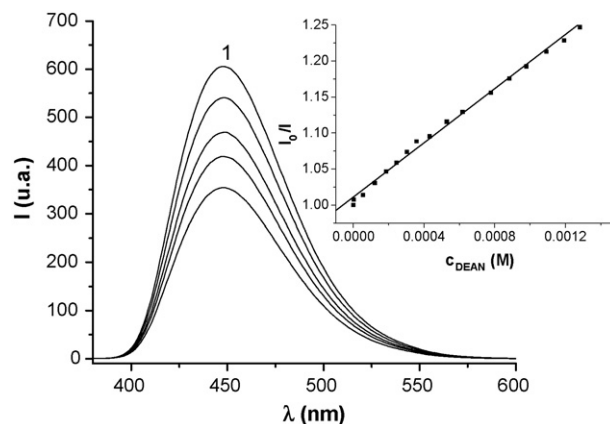


Fig. 3. Steady-state fluorescence spectra of BzCum in ACN in the absence (1) and the presence of the DEAN; $[BzCum] = 5 \times 10^{-6}$ M; $\lambda_{ex} = 360$ nm. (Inset) Linear Stern–Volmer plot, I_0/I vs. $[Q]$.

observe a better electron acceptor property than for the other investigated coumarin derivatives.

The comparison of the calculated vertical and adiabatic electron affinity for the title compound with those for C151 (7-amino-4- CF_3 -coumarin), 3.97 eV versus 3.68 eV and 4.10 eV versus 3.87 eV reflect the same trend.

The amine oxidation potentials were taken from literature data, although there is a lot of discussion about the reliability of these values and about the use of the adiabatic or vertical ionization potentials instead of them [25–27]. The used values are listed in Table 1. Also included in Table 1 are the estimated radii obtained by using the additive model of Edward [28] together with the contact acceptor–donor (A–D) distance. The estimated acceptor radius is 3.91 Å.

3.2. Steady-state fluorescence measurements

For all donors excepting low concentration solution of triphenylamine, *vide infra*, increasing their concentration results in a quenching of the acceptor emission. Depending on the amine type, the SV plots, I_0/I versus $[Q]$, the quencher concentration, present two aspects, a linear one (Case a), and a nonlinear aspect with positive curvature (Case b).

Case a. A linear aspect of the SV plot, Eq. (4) was obtained for aniline and both its alkylated derivatives, *N,N*-dimethyl- and *N,N*-diethylaniline.

A typical example is given in Fig. 3 for DEAN. The Stern–Volmer constants and the correlation coefficient for the plots are given in Table 2.

It can be seen similar values for the three amines.

Table 1

Oxidation potentials, E_{D/D^+} , and molecular radii, r_D , of the amines and the contact D–A distance (acceptor radii, $r_A = 3.91$ Å)

	AN	DMAN	DEAN	DPA	TPA
E_{D/D^+} (eV)	0.930 [15]	0.756 [15]	0.720 [10]	0.780 [10]	0.870 [10]
r_D (Å)	3.098	3.367	3.589	3.780	4.278
$r_A + r_D$ (Å)	7.008	7.277	7.499	7.690	8.188

Table 2
Stern–Volmer constants, K_{SV} (M^{-1}) and the correlation coefficients (r^2) for the amines leading to linear SV plots

Donor	AN	DMAN	DEAN
K_{SV}	204 ± 4	221 ± 9	188 ± 4
r^2	0.960	0.981	0.992

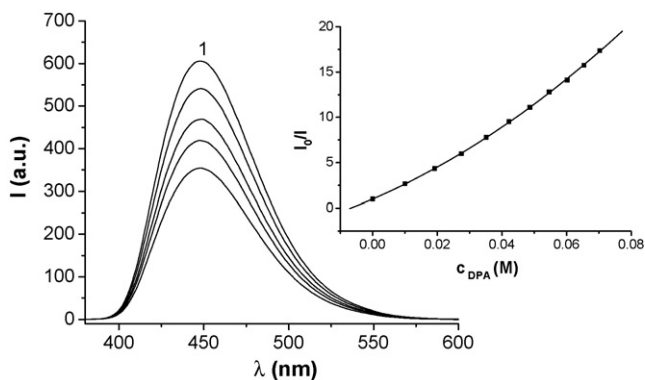


Fig. 4. Steady-state fluorescence spectra of BzCum in ACN in the absence (1) and the presence of the DPA; $[BzCum] = 5 \times 10^{-5} M$; $\lambda_{ex} = 360 nm$. (Inset) The nonlinear fitting curve using Eq. (5).

Case b. An upward curvature, reflecting the fact that the quenching is not purely collisional and may be due to other processes, was found for diphenylamine and triphenylamine. The fluorescence spectra are presented in Fig. 4 for diphenylamine.

The process observed in the presence of triphenylamine deserves a special discussion. At the usual acceptor concentration, $5.17 \times 10^{-6} M$, the fluorescence of the compound decreases quickly in the presence of increased donor concentrations and a new fluorescence band with a maximum at 420 nm is apparent. As this band belongs to triphenylamine, which is also excited at the excitation wavelength, we considered that at this low acceptor concentration the quenching appeared immediately. Therefore all the data for this donor were obtained at a concentration of $5.17 \times 10^{-5} M$.

The experimental points were fitted using Eq. (5) [29] and Eq. (6) [30,31]. In these equations, V represents the volume of

the sphere of action, and W is the fraction of the excited-state quenched by the collisional mechanism. W is correlated to V by Eq. (7):

$$\frac{I_0}{I} = \{1 + K_{SV} \times [Q]\} \exp(V \times [Q]) \quad (5)$$

$$\frac{1 - (I/I_0)}{[Q]} = K_{SV} \times \frac{I}{I_0} + \frac{1 - W}{[Q]} \quad (6)$$

$$W = \exp(-V \times [Q]) \quad (7)$$

Considering Eq. (5) a nonlinear regression procedure was used, leading to the SV constants and $V(Q)$ values (Fig. 4).

According to Eq. (6), $(1 - I/I_0)/[Q]$ was plotted against I/I_0 and the SV quenching constant, K_{SV} was obtained by the least-square fit method determining the slope. The intercept of the plot was used to calculate the W values for each quencher concentration $[Q]$. From the W values, the static quencher constant V was obtained using Eq. (7). Both procedures are illustrated in Fig. 5(a) and (b). From the V values the effective quenching radii were estimated. The results are reported in Table 3. It can be seen that for DPA both procedures led to the same values of the Stern–Volmer constant, whereas some differences were obtained in the case of TPA. In the followings both values of K_{SV} will be considered for this amine.

The comparison of the radius of the sphere of action, R_q , the “kinetic” distance, with the encounter distance (the sum of the acceptor and donor radii) shows a larger value for the first one. In this case, according to Andre et al. [32] and Zeng and Durocher [33] the static effect takes place irrespective of the ground state complex formation if the reaction is limited by diffusion.

In order to verify whether the reaction is diffusion limited the finite sink approximation was used, considering the modified Stern–Volmer relationship in which K_{SV}^{-1} is linear dependent on $[Q]^{1/3}$ [33–36]:

$$K_{SV}^{-1} = (K_{SV}^0)^{-1} - \frac{(2\pi N)^{1/3}}{4\pi N D \tau_F^0} [Q]^{1/3} \quad (8)$$

In Eq. (8), K_{SV} is calculated from the experimental data as $((I_0/I) - 1)/[Q]$. The intercept of the linear plot $(K_{SV})^{-1}$ against $[Q]^{1/3}$ gives the value of $(K_{SV}^0)^{-1}$ and the slope allows for the

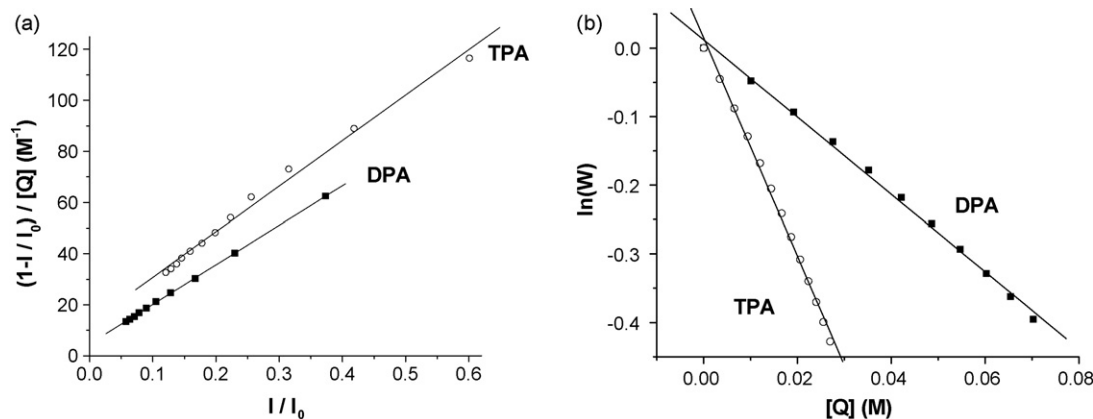


Fig. 5. SV plots considering (a) $(1 - I/I_0)/[Q]$ vs. I/I_0 , Eq. (6) and (b) $\ln(W)$ vs. $[Q]$, Eq. (7).

Table 3

Stern–Volmer constants, K_{SV} , the volumes V_q , the radii, R_q , of the effective sphere of quenching and the correlation coefficients of the fit for the donors belonging to class b

Quencher	Eq. (5)				Eqs. (6) and (7)			
	K_{SV} (M^{-1})	V_q (M^{-1})	R_q (\AA)	r^2	K_{SV} (M^{-1})	V_q (M^{-1})	R_q (\AA)	r^2
DPA	154 ± 2	5.39 ± 0.21	12.88	0.999	155 ± 1	5.63 ± 0.10	13.07	0.999
TPA	196 ± 4	9.22 ± 0.80	15.41	0.999	178 ± 5	15.91 ± 0.30	18.48	0.993

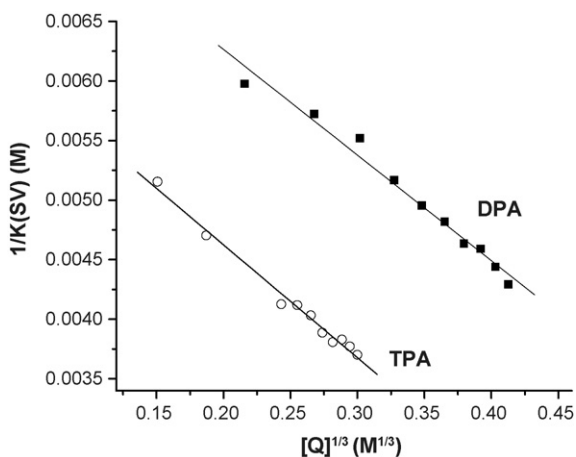


Fig. 6. Modified SV plots considering the sink approximation, $1/K_{SV}$ vs. $[Q]^{1/3}$, Eq. (8).

estimation of the diffusion coefficient, D . The plots for DPA and TPA are given in Fig. 6 and the results in Table 4.

Using the K_{SV}^0 and D values obtained from the plots in Fig. 6 the R' values, can be calculated accordingly to the formula:

$$K_{SV}^0 = 4\pi DN'R'\tau_F^0 \quad (9)$$

where R' represents the distance parameter. Both D and R' allow for the calculation of the activation energy controlled rate constant for the electron transfer:

$$k_a = \frac{4\pi N'DR}{(R/R')-1} \quad (10)$$

k_a can be calculated only when $R > R'$, that means in our case only for DPA, the value being $1.24 \times 10^{11} M^{-1} s^{-1}$, practically an order of magnitude larger than k_q , attesting the diffusion limitation. For the second donor, TPA, as $k_q > 4\pi N'DR'$ we can also admit according to Joshi [37], that the bimolecular quenching reaction is diffusion limited. Starting from the Stern–Volmer constants, the rate constants for the bimolecular quenching reaction were obtained using Eq. (11) and the previously determined fluorescence quantum yield and the natural lifetime of the accep-

tor in acetonitrile [14]:

$$k_q = \frac{K_{SV}}{\tau} \quad (11)$$

3.3. Electron transfer mechanism

Although it is known that the fluorescence quenching of coumarinic compounds by amines is due to electron transfer, in order to rationalize the experimental data several hypothesis were considered too. As no new bands were evidenced in the absorption spectra, the hypothesis of the formation of a complex in the ground state was ruled out.

Moreover, it can be observed from Table 3, the large differences between the K_{SV} and V values explaining the absence of changes in the absorption spectra on addition of the quenchers.

Similarly, as a careful examination of the emission spectrum of BzCum and the absorption spectra of the amines shows that there is no overlap between them (for instance $E_{em}(BzCum) = 2.73$ eV and $E_{abs}(TPA) = 3.73$ eV) we ruled out also the possibility of a deactivation process by energy transfer.

Assuming an electron transfer mechanism, according to the Marcus theory [38], the rate constant for the electron transfer reaction is given by Eqs. (12) and (13):

$$k_{et} = \nu \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (12)$$

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4 \times \lambda} \quad (13)$$

In these equations ν is the frequency factor, ΔG^* and ΔG^0 represent the free energy of activation and the free energy change for the ET reaction, respectively, and λ stands for the total reorganization energy, given by the sum of the internal reorganization energy, λ_{in} and the solvent reorganization energy, λ_s :

$$\lambda = \lambda_{in} + \lambda_s \quad (14)$$

Table 4

Parameters of the sink approximation model, the Stern–Volmer constant at $[Q] = 0$, K_{SV}^0 , the diffusion coefficient, D , the distance parameter R' , the encounter distance R and the diffusion constant, $4\pi N'R'D$, for DPA and TPA

	K_{SV}^0 (M^{-1})	D ($\times 10^5$ $cm^2 s^{-1}$)	R' (\AA)	R (\AA)	$4\pi N'R'D$ ($\times 10^{10}$ $M^{-1} s^{-1}$)
DPA	125	1.79	7.10	7.71	1.04
TPA	153	1.77	9.33	8.21	1.20

Table 5

Rate constant for the bimolecular quenching reaction (k_q , $M^{-1} s^{-1}$) and the free energy change for the electron transfer reaction (ΔG^0 , eV)

	AN	DMAN	DEAN	DPA	TPA
$k_q (\times 10^{10})$	1.57	1.70	1.45	1.18	1.51 ^a , 1.37 ^b
ΔG^0	-0.960	-1.132	-1.167	-1.105	-1.012

^a Value obtained using K_{SV} from Eq. (5).

^b Value obtained using K_{SV} from Eq. (6).

ΔG^0 was calculated by the Rehm–Weller formula [39], Eq. (15):

$$\Delta G^0 = E \left(\frac{D}{D^+} \right) - E \left(\frac{A}{A^-} \right) - E_{00} - \frac{e^2}{\epsilon \times (r_D + r_A)} \quad (15)$$

The k_q and ΔG^0 values are listed in Table 5.

As the plot $\ln k_q - \Delta G^0$ for only five points is not conclusive for the behavior of the benzocoumarinic acid, we have plotted our values together with literature results on other coumarin derivatives (C151, C500, C152, C481, C522, C153) and eight aromatic amines (aniline, methylaniline, ethylaniline, dimethylaniline, diethylaniline, *o*-phenylenediamine, diphenylamine and triphenylamine) [10,11] (Fig. 7).

Although our values (filled squares) correspond to more negative ΔG^0 values than those of the other coumarins (open circles), they can still be found on the plateau of the Marcus plot and show no evidence for an inverted region, reflecting that the quenching constants level off at the diffusion control limit. Our points fit well the curve obtained for related systems. The best fit, considering all the points was obtained for $k_d = 1.34 \times 10^{10} M^{-1} s^{-1}$, $\nu = 1.53 \times 10^{12} s^{-1}$ and $\lambda = 0.79$ eV values close to those previously reported [10,11]. A direct estimation of the solvent reorganization energy in terms of Eq. (16), considering an averaged value for the amine radius, $r_D = 3.05$ Å and $r_A = 3.91$ Å led

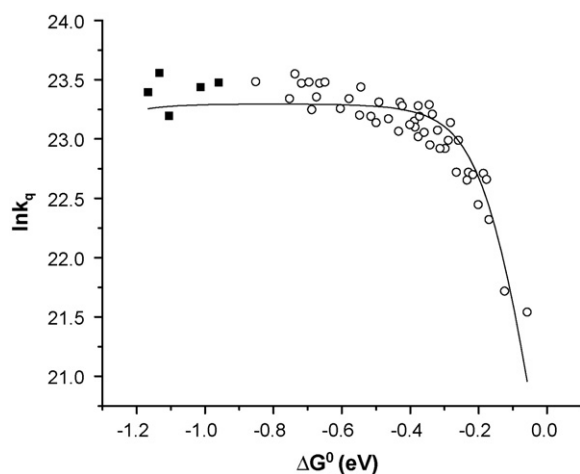


Fig. 7. Marcus plot, $\ln k_q$ vs. ΔG , considering both our values (filled squares) and literature data (open dots) [10,11] for other coumarin derivatives. The curve represents the best fit of the experimental points and is characterized by the parameters, $\lambda = 0.79$ eV, $\nu = 1.53 \times 10^{12} s^{-1}$ and $k_d = 1.34 \times 10^{10} M^{-1} s^{-1}$.

to $\lambda = 1.12$ eV:

$$\lambda_S = e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right) \times \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (16)$$

Considering the definition of λ , Eq. (14), it can be seen that the internal reorganization energy has an insignificant contribution, an expectable fact in diffusion conditions. In the same time, taking into account the approximation in the donor radii, we consider that there is a satisfactory agreement between the fitted value and the estimated λ_S .

4. Conclusions

The results attest that the fluorescence quenching of 3-carboxy-5,6-benzocoumarin by some aromatic amines is due to an electron transfer from the amines to the excited-state of the acceptor, the coumarin derivative. Aniline and two alkyl anilines, DMAN and DEAN produce linear Stern–Volmer plots, pointing to a collisional process. In the case of DPA and TPA curved SV plots were obtained reflecting and upward, positive curvature. The treatment of the experimental data by the sphere of action and sink models shows the presence of a static quenching, but insignificant in respect to the dynamic one. For both these cases it was found that the quenching process is diffusion limited. Inclusion of our data in a Marcus–Rehm–Weller plot containing other coumarin–amine systems allows for the estimation of the frequency factor, the diffusion constant and the solvent reorganization energy. The present data, in addition to our previous results on the photophysical properties of this compound, show that it fulfills the conditions to be suitable as a fluorescence probe for proteins. Its sensitivity to the presence of electron donors will allow for the characterization of the binding sites. Our findings are in agreement with several recent literature data showing that the presence of COOH and OH groups confers good binding properties to both bovine and human albumins, the major protein transporter of endogenous and exogenous compounds [40–48].

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