1

AN EXAMINATION OF DIFFUSION-INFLUENCED FLUORESCENCE QUENCHING BY NEAREST QUENCHING NEIGHBORS IN LIQUIDS

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Summary

The exclusive quenching of a potentially fluorescent species in solution by its nearest quenching neighbor imposes a finite upper integration limit to the flux equation and provides a modified version, *i.e.*

$$\frac{I_0}{I} = 1 + \frac{4\pi ND\rho k^0 \tau_0 c}{4\pi ND\rho + k^0 \{1 - (2\pi Nc)^{1/3}\rho\}}$$

of the Smoluchowski–Collins–Kimball formulation of the Stern–Volmer equation. This is applied to data reported for the fluorescence quenching of two anthraquinone derivatives by *N,N*-dimethyl-*p*-toluidine in acetonitrile solutions of different (pressure-induced) viscosities. Values of the relative fluorescence quantum yields $I_0/I(c)$ calculated from the above equation, using recovered values of the encounter diameter ρ, the intrinsic quenching rate constant k^0 and the viscosity-dependent diffusion coefficient D, agree with experimental data with an overall average deviation (2.7% for 53 data points) well within a reported experimental uncertainty of ±8%.

1. Introduction

The relative fluorescence quantum yield $I_0/I(c)$ of an electronically excited solute A^* in the absence (I_0) and presence (I) of a quenching species Q at a concentration c is generally a non-linear function of c for efficient quenching systems [1 - 6]. This behavior has recently been examined in terms of the following equation [7]:

$$\frac{I_0}{I} = 1 + \frac{4\pi ND\rho k^0 \tau_0 c}{4\pi ND\rho + k^0 \{1 - (2\pi Nc)^{1/3}\rho\}} = 1 + K_{SV}c \qquad (1)$$

where D is a coefficient of relative diffusive approach of Q and A^*, τ_0 is the electronic relaxation time of A^* in the absence of Q, k^0 is an equilibrium statistical rate constant describing the quenching of A^*–Q pairs at the encounter separation ρ and N is the Avogadro number. The development of eqn. (1) is based on the logical assumption that a potentially fluorescent solute species

of lifetime τ_0 is more likely to be quenched in a first encounter with its nearest (efficient) quenching neighbor, initially at a separation $r \lesssim (2D\tau_0)^{1/2}$, than in subsequent encounters with non-nearest neighbors. Since $(2D\tau_0)^{1/2} \approx$ 2 nm for the typical values $D = 10^{-10}$ m^2 s^{-1} and $\tau_0 = 20$ ns, the conventional boundary condition $c(r = \infty) = c > c(r < \infty)$ is an unrealistic integration limit to the time-independent flux equation to the extent that it includes "quenching" encounters of the species Q with the reference molecule A* which has already experienced nearest-neighbor quenching or undergone electronic relaxation; it also implies that $c(r) < c$ at all finite values of r. An improved description of efficient bimolecular quenching processes should therefore be provided by the imposition of a finite boundary condition $c(r \geqslant r_0 < \infty) = c > c(r < r_0)$ where r_0 is an effective separation which distinguishes nearest quenching neighbors at $r \leqslant r_0$ from non-nearest neighbors at $r > r_0$. This corresponds physically to a model in which A* acts as a sink of finite radius r_0 in a spherically symmetric distribution of nearest-neighbor quenching species, within which

$$c(r) = c \left\{ 1 - \frac{\rho}{r} \left(1 - \frac{r}{r_0} \right) \right\}$$

(for efficient quenching) and beyond which potentially quenching molecules are ineffective since $(\partial c / \partial r)_{r > r_0} = 0$.

Equation (1) is the result of assigning a sink radius r_0, equal to the most probable nearest-neighbor separation $(2\pi Nc)^{-1/3}$ [8], which is less than 3 nm (a few encounter diameters) in the range $c > 10^{-2}$ M where departures from linear Stern–Volmer behavior are usually observed for efficient quenching. The corresponding radial distribution function given by

$$g_{\mathrm{A}^*\mathrm{Q}}(r \leqslant r_0) = 1 - \frac{\rho}{r} \left\{ 1 - (2\pi Nc)^{1/3} r \right\}$$

approaches the Smoluchowski limit as $c \to 0$ ($r_0 \to \infty$) and increases with c, as required, to its random distribution value of unity at $r = r_0$ [9]. The quenching rate constant $k_{\mathrm{Q}} = K_{\mathrm{SV}}/\tau_0$ (eqn. (1)) has the correct limit $k_{\mathrm{Q}} \to k^0$ both for reaction-controlled quenching ($k^0 \ll 4\pi ND\rho$) and for all quenching processes in a pure quenching solvent where $\rho = r_0$ and diffusion is not a quenching prerequisite. Moreover, in the diffusion limit of efficient quenching ($k^0 \gg 4\pi ND\rho$), $k_{\mathrm{Q}} \approx 4\pi ND\rho / \{1 - (2\pi Nc)^{1/3}\rho\}$ and increases with c in quantitative agreement with observation [7]. Thus, linear least-squares regressions of K_{SV}^{-1} on $c^{1/3}$, with correlation coefficients generally in the acceptable range, provide the characteristic quenching parameters

$$K_{\mathrm{SV}}^0 = \frac{4\pi ND\rho k^0 \tau_0}{4\pi ND\rho + k^0} = 4\pi ND\rho' \tau_0 \tag{2}$$

$$c_0^{1/3} = \frac{2(2\pi N)^{2/3} D\tau_0}{K_{\mathrm{SV}}^0} = \frac{1}{(2\pi N)^{1/3}\rho'} \tag{3}$$

which have been shown [7] to reproduce the experimental data $I_0/I(c)$ for 12 efficient quenching systems (111 data points) with an overall average deviation of about 2%. Moreover, relative diffusion coefficients D recovered directly from eqn. (3) are of the correct magnitude, as are those of $\rho = \rho'$ where the effective quenching diameter ρ' is demonstrably independent of D or of solvent viscosity, and $k^0 \gg 4\pi ND\rho$ (eqn. (2)).

We examine here the application of eqn. (1) to data reported [10] for the fluorescence quenching of 1,4-dihydroxyanthraquinone (DHAQ) and of 1-aminoanthraquinone (AAQ) by N,N-dimethyl-p-toluidine (DMPT) in acetonitrile, where solvent viscosity is increased by the application of pressure and quencher concentrations are compensated for solvent compressibility. Kawenoki *et al.* [10] conclude that the quenching process is not diffusion limited ($k^0 \not\gg 4\pi ND\rho$) in these systems, from an analysis of the data in terms of eqn. (4), which essentially combines an exponential "static" quenching term with an infinite upper limit of integration to the flux equation for a time-dependent concentration gradient, specifically

$$\frac{I_0}{I} = \frac{\exp(NVc)(1 + K'_{SV}c)}{\int_0^\infty \exp(-\mu - \lambda\mu^{1/2})\,d\mu} \tag{4}$$

where μ is a variable related to reaction time. λ, V, K'_{SV} are given by

$$\lambda = \frac{2\sigma}{(\pi D\tau_0)^{1/2}} \frac{K'_{SV}k^0c}{4\pi ND\sigma + k^0}(1 + K'_{SV}c)^{-1/2}$$

$$V = \frac{4\pi\sigma^3 K'_{SV}k^0}{(4\pi ND\sigma + k^0)^2\tau_0}\left\{\frac{1}{3}\left(1 - \frac{\rho^3}{\sigma^3}\right)\left(1 + \frac{k^0}{4\pi ND\sigma}\right) - 1\right\}$$

$$K'_{SV} = \frac{4\pi ND\sigma k^0\tau_0}{4\pi ND\sigma + k^0}$$

and σ (greater than ρ) is a "chemical reaction distance".

2. Procedure

Quenching constants K_{SV}^0 and $c_0^{1/3}$ are obtained from linear least-squares regressions of K_{SV}^{-1} on $c^{1/3}$. Since $I_0/I(c)$ at low c cannot be accurately retrieved from Figs. 1 and 2 of ref. 10, and the error in the dependent variable K_{SV} exceeds that of the measured quantity $I_0/I(c)$ by a factor of $I_0/(I_0 - I)$, the regressions are limited to experimental data reported for the ranges $I_0/I(c) > 3$ and $c \geqslant 0.1$ mol dm^{-3}. The diffusional quenching parameters

$$D\tau_0 = \frac{K_{SV}^0 c_0^{1/3}}{2(2\pi N)^{2/3}} \tag{5}$$

$$\rho' = \frac{\rho k^0}{4\pi ND\rho + k^0} = (2\pi Nc_0)^{-1/3} \tag{6}$$

recovered from the quenching constants K_{SV}^0 and $c_0^{1/3}$ using the forms (eqns. (5) and (6)) of eqn. (3), provide direct access to (a) the relative diffusion coefficient D if τ_0 is independently accessible, (b) $\rho = \rho'$ if ρ' is independent of D or solvent viscosity and $k^0 \geqslant 4\pi ND\rho$ (eqn. (6)), as in the case of 1,2-benzanthracene quenched by CBr_4 in both propanediol and mineral oil at three different temperatures [3, 7] and (c) ρ and k^0 if ρ' varies with D or solvent viscosity according to eqn. (2) in the form

$$\frac{1}{K_{SV}^0} = \frac{1}{k^0\tau_0} + \frac{1}{(2\pi Nc_0)^{1/3}\rho K_{SV}^0} \tag{7}$$

For the systems under examination, the experimental data $I_0/I(c)$ are compared with values calculated from eqn. (1) using the recovered parameters ρ, D and k^0 and with those estimated from the reduced form (eqn. (8)) of eqn. (1):

$$\frac{I_0}{I} = 1 + \frac{4\pi ND\rho\tau_0 c}{1 - (2\pi Nc)^{1/3}\rho} \tag{8}$$

This equation is appropriate to a diffusion-limited quenching process ($k^0 \geqslant 4\pi ND\rho$) with $\rho = \langle\rho'\rangle$, the average value of ρ' for solutions of different viscosity.

3. Results

3.1. AAQ fluorescence quenching by DMPT in acetonitrile

Table 1 lists the quenching constants and derived parameters D and ρ' for five solutions of the viscosity indicated, using a reported value of $\tau_0 = 0.9$ ns [11]. Values of $\rho \approx 695$ pm and $k^0 = 6.8 \times 10^{10}$ dm^3 mol^{-1} s^{-1} from a least-squares linear regression of $1/K_{SV}^0$ on $1/c_0^{1/3}K_{SV}^0$ (eqn. (7), $R = 0.99894$) are virtually identical with those ($\rho = 700$ pm; $k^0 = 7 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) used to obtain a best fit of eqn. (4) to the data with $\sigma = 990$ pm [10]. Calculated quotients $I_0/I(c)$ from eqn. (1) using the recovered values of ρ, k^0 and the appropriate diffusion coefficient (Table 1), and from eqn. (8) with $\langle\rho'\rangle = 560$ pm are respectively compared with the experimental data in Figs. 1(a) and 1(b). The average percentage deviations of calculated from experimental data are given in Table 1.

3.2. DMPT quenching of DHAQ fluorescence in acetonitrile

Quenching constants and derived parameters, using a reported value of $\tau_0 = 2.8$ ns [11], are listed for this system in Table 2. Equation (7) yields the values $\rho = 808$ pm and $k^0 = 1.15 \times 10^{11}$ dm^3 mol^{-1} s^{-1} ($R = 0.99866$), of the order of those used ($\rho = 700$ pm, $k^0 = 1.5 \times 10^{11}$ dm^3 mol^{-1} s^{-1}) to obtain a best fit of the data to eqn. (4) with $\sigma = 995$ pm [10]. A comparison of the

TABLE 1

Quenching constants and derived parameters for AAQ fluorescence quenching by DMPT in acetonitrile[a]

Viscosity ($\times 10^3$ kg m^{-1} s^{-1})	K_{SV}^0 (dm^3 mol^{-1})	$c_0^{1/3}$ (mol$^{1/3}$ dm^{-1})	$D \times 10^9$ (m^2 s^{-1})	ρ' (pm)	R[b]	Δ[c] (%)		k^{0}[d]$/$ $4\pi ND\rho$
						Equation (1)[d]	Equation (8)[e]	
0.36	14.0	1.179	3.77	544	−0.99919	1.5	5.6	3.4
0.415	13.4	1.181	3.61	544	−0.99947	1.5	5.3	3.6
0.51	12.5	1.160	3.32	553	−0.99966	3.0	5.8	3.8
0.70	10.9	1.109	2.76	579	−0.99971	2.2	6.1	4.7
0.89	10.05	1.110	2.55	578	−0.99925	1.5	6.1	5.0

[a]τ_0 = 0.9 ns [11].
[b]Correlation coefficient for least-squares linear regression of K_{SV}^{-1} on $c^{1/3}$.
[c]Average percentage deviation of calculated from experimental values of $I_0/I(c)$.
[d]With k^0 = 6.77 $\times 10^{10}$ dm^3 mol^{-1} s^{-1} and ρ = 695 pm from eqn. (7).
[e]With $\langle \rho' \rangle$ = 560 pm.

TABLE 2

Quenching constants and derived parameters for DHAQ fluorescence quenching by DMPT in acetonitrile[a]

Viscosity ($\times 10^3$ kg m^{-1} s^{-1})	K_{SV}^0 (dm^3 mol^{-1})	$c_0^{1/3}$ (mol$^{1/3}$ dm^{-1})	$D \times 10^9$ (m^2 s^{-1})	ρ' (pm)	R[b]	Δ[c] (%)		k^{0}[d]$/$ $4\pi ND\rho$
						Equation (1)[d]	Equation (8)[e]	
0.34	41.0	0.910	2.74	705	−0.99008	2.2	11.6	6.9
0.415	37.8	0.916	2.55	700	−0.99257	3.7	13.9	7.4
0.51	30.1	0.858	1.90	748	−0.97685	4.7	2.9	9.9
0.605	28.1	0.861	1.78	745	−0.97581	3.0	3.4	10.6
0.80	25.5	0.872	1.64	736	−0.99386	3.2	2.1	11.5
0.89	22.5	0.853	1.41	753	−0.98693	3.4	6.5	13.3
0.94	21.7	0.856	1.38	749	−0.99116	3.4	4.7	13.6

[a]τ_0 = 2.8 ns [11].
[b]Correlation coefficient for least-squares linear regression of K_{SV}^{-1} on $c^{1/3}$.
[c]Average percentage deviation of calculated from experimental values of $I_0/I(c)$.
[d]With k^0 = 1.15 $\times 10^{11}$ dm^3 mol^{-1} s^{-1} and ρ = 808 pm from eqn. (7).
[e]With $\langle \rho' \rangle$ = 730 pm.

experimental data with $I_0/I(c)$ estimated from eqn. (1) with recovered values of ρ, k^0 and D, and from eqn. (8) with $\langle \rho' \rangle$ = 730 pm, provides the average percentage deviations indicated (Table 2).

4. Discussion

The following points are noted with reference to Fig. 1 and the tabulated data.
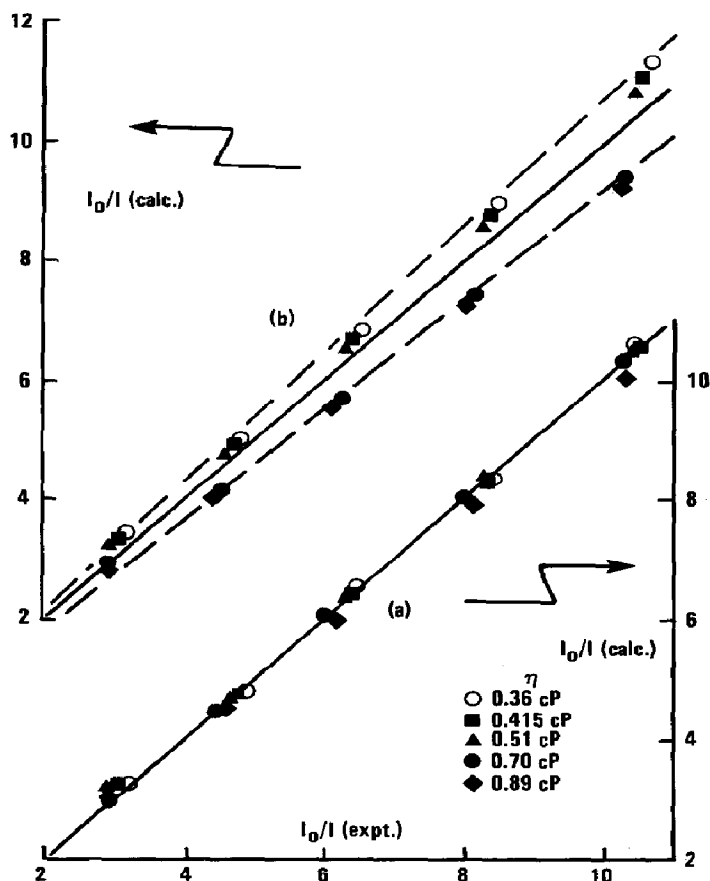
Fig. 1. Comparison of calculated with experimental values of $I_0/I(c)$ for the AAQ–DMPT system in acetonitrile solutions of indicated viscosity: (a) from eqn. (1) with $\rho = 695$ pm, $k^0 = 6.8 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and tabulated values of D; (b) from eqn. (8) with $\rho = \langle\rho'\rangle = 560$ pm and same values of D. Solid lines are drawn through the origin with unit slope; broken lines indicate reported error limits ($\pm 8\%$) in the experimental data [10]. (1 cP unit of viscosity (η) equals 1×10^{-3} kg m^{-1} s^{-1}.)

(a) Equation (1) describes the appropriate functional dependence of I_0/I on the quencher concentration over the range examined for these systems.

(b) Recovered values of the parameters ρ and k^0 from eqn. (7) are similar to those used by Kawenoki *et al.* to obtain a best fit of eqn. (4) to the experimental data and the range of quotients $k^0/4\pi ND\rho$ for AAQ–DMPT (3.4 - 5.0) and DHAQ–DMPT (6.9 - 13.6) collected in Tables 1 and 2 include the respective values of 5 and 10 used by these researchers [10].

(c) Tabulated diffusion coefficients recovered from eqn. (5) are of the expected magnitude insofar as Stokes–Einstein estimates range from (3.6 - 1.3) $\times 10^{-9}$ m^2 s^{-1} over the viscosity range (3.4 - 9.0) $\times 10^{-4}$ kg m^{-1} s^{-1} at ambient temperature if the diffusing species each has a diffusion radius of $\rho/2 \approx 350$ pm; the higher values of D retrieved for the AAQ–DMPT pair, relative to those for the DHAQ–DMPT system, are qualitatively consistent

with the smaller encounter diameter for AAQ–DMPT but may also reflect relative uncertainties in the values of τ_0 used to extract D from the recovered parameter $D\tau_0$.

(d) The use of eqn. (1) with the recovered values of the parameters ρ, k^0 and D cited provides a satisfactory description of the data reported [10] for both systems with an overall average deviation of calculated from observed quotients I_0/I of 2.7% and none exceeding the reported experimental error limits of $\pm 8\%$. However, an overall average deviation of 6.1% is introduced by eqn. (8) with values exceeding 8% for 18 of the 53 data points. We therefore conclude, in agreement with previous findings [10], that quenching is diffusion influenced rather than diffusion limited for both systems.

Equations (1) and (4) both provide acceptable descriptions of the data examined here. This is illustrated for the DHAQ–DMPT system in Fig. 2 where $I_0/I(c)$ values calculated from eqn. (1) using parameters recovered from the theoretical curves of eqn. (4) (Fig. 1(a) of ref. 10) are compared with data interpolated from the same theoretical curves. Since eqns. (1) and (4) describe formally different functional dependences of I_0/I on c, their apparently equivalent descriptions of these data probably originate in the presence of the additional (adjustable) parameter σ of eqn. (4). However, until experimental values of the parameters ρ, k^0 and D (for electronically excited species) become available independently, we believe that the use of eqn. (1) is advantageous in that it permits direct parameterization from experimental data, the recovered values of these parameters are of a realistic magnitude and it reduces to the expected (static quenching) limit for pure quenching solvents.
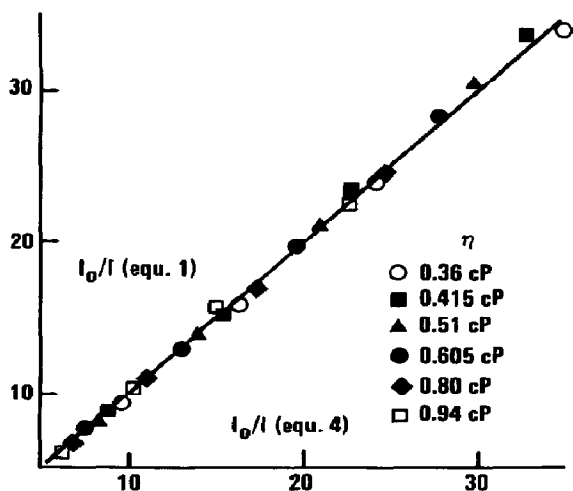

Fig. 2. Comparison of $I_0/I(c)$ calculated from eqns. (1) and (4) for the DHAQ–DMPT system. The parameters used in eqn. (1) are those recovered from the theoretical curves provided by eqn. (4) ($\rho = 790$ pm; $k^0 = 1.26 \times 10^{11}$ dm^3 mol^{-1} s^{-1}). The solid line is drawn through the origin with unit slope.

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