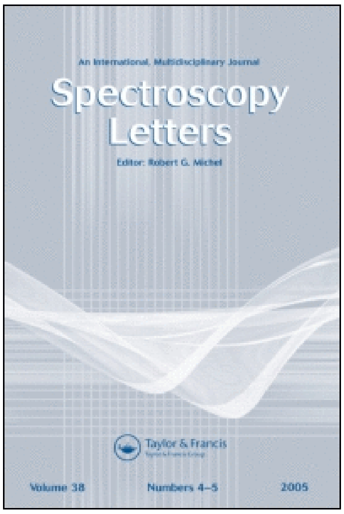

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Fluorescence Quenching of UVITEX-OB by Aniline in Alcohols and Alkanes

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Abstract: Fluorescence quenching of UVITEX-OB [2,5-thiophenediylbis(5-*tert*-butyl-1,3-benzoxazole)] by aniline in different polar and nonpolar solvents was examined at room temperature by steady-state fluorescence measurements. Positive deviations from the nonlinear Stern–Volmer plots were observed in most of the solvents indicating the extent of quenching to be large. The quencher concentration dependence data were analyzed using ground-state complex and sphere of action static quenching models in order to interpret the results. The magnitudes of the quenching rate parameters suggest that a sphere of action static quenching model is expected to describe the data most accurately. Also, the results are suggestive of both static and dynamic quenching processes being responsible for the observed positive deviation in the Stern–Volmer plot. Experimental results are described by an equation derived using the finite sink approximation model, which allows the evaluation of diffusion-limited interaction and the estimation of encounter distance and mutual diffusion coefficient independently.

Keywords: Activation energy controlled rate constant (k_a), diffusion limited (D), finite sink approximation model (FSA), fluorescence quenching (Q), quenching rate constant (k_d), static and dynamic quenching, Stern–Volmer plot, UVITEX-OB (U-OB)

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INTRODUCTION

Decrease of fluorescence intensity arising from interaction of the excited fluorophore with its surrounding solvent molecules is known as quenching. Several interactions have been proposed to account for this effect in many cases, but the mechanism of fluorescence quenching itself is still uncertain though quenching due to chemical reaction is well established. A wide variety of compounds act as quenchers of fluorescence, but the most commonly used quenchers like aniline, bromobenzene, carbon tetrachloride, halide ions, metal ions, and so forth, have been proved to be effective for investigation of quenching process.[1–9] The accessibility of fluorophores to such quenchers can be used to determine the location of probes on macromolecules to quenchers. Such studies aim at understanding the nature of bimolecular reactions taking place both under steady state and transient conditions. This leads to the importance of quenching mechanism not only in physical science but also in chemical, biological, and medical sciences.

The fluorescence quenching can be considered as a special case, an irreversible reaction between two species A and B in solution, described by

$$A^* + B \overset{k_d}{\longleftrightarrow} [A^*B] \xrightarrow{k_q} products$$

where A^* denotes an excited state fluorophore and B a quenching molecule. The rate coefficient k_d quantifies the rate of mass transport to form an encounter pair $[A^*B]$, and k_q is the intrinsic rate of the formation of products. If $k_q \gg k_d$, then the overall rate of the quenching reaction is limited by the bulk transport, and the rate equation becomes truly diffusion limited. It has been known for many years that certain quenching reactions lead to curved Stern–Volmer plots,[10,11] and both positive curvature and negative curvature have been observed.[12,13] Negative curvature involves a decrease in k_q and is associated with a change in the absorption and fluorescence spectrum of the fluorophore.[14] Deviations from the Stern–Volmer equation in such reactions have been explained by the existence of multiple fluorescing states[12] or by a compound formation.[14] On the other hand, a variety of quenching reactions have been reported to exhibit positive curvatures in Stern–Volmer plots yet show no evidence of multiple excited states or molecular association. For example, the oxygen quenching of perylene in dodecane[15] shows a large positive curvature though there is no detectable change in the absorption spectrum of perylene up to the oxygen concentrations of 1 M. If the quenching mechanism is mainly due to dynamic process, then it shall be largely due to diffusion in which case the diffusion rate parameter k_d equals the quenching rate parameter k_q ($=K_{sv}/\tau$), where K_{sv} is the slope of the linear S-V plot and τ is the lifetime of the donor fluorescence in the absence of the quencher.

Although the explanation for positive deviations from Stern–Volmer behavior has been advanced, one most commonly used is that of a "static" quenching mechanism, which is a slight variation on the theme of molecular association. Static quenching occurs when a fraction of the quencher–fluorophore pairs are sufficiently close to each other at the time of fluorophore excitation so as to react with a rate that is limited kinetically rather than diffusionally. According to Frank and Vavilov,[11] the quenchers are treated as lying within a sphere of action of the fluorophore at the moment of excitation. However, the quenching of anthracene fluorescence by oxygen or sulfur dioxide[13] leads to a sphere of action with a radius of 30 Å, which is at odds with the fact that these quenching reactions are collisional rather than resonant.

In this paper, we present steady-state experimental data to explain the quenching of UVITEX-OB (U-OB) by aniline in a homologous series of polar (alcohols) and nonpolar (alkanes) solvents with an intention to understand the nature of quenching mechanism involved in these systems. U-OB finds various applications in the process of whitening the polymers and can give the finished products a bright bluish white glaze. It plays an important role in marking *Plutella xylostella*, a serious insect pest of cruciferous vegetables. Residues of the fluorescent tracer of U-OB were measured as part of a larger study adapting video imaging analysis to children's exposure to pesticides. Hence, photochemical and photophysical properties of such products are important to the discovery of organic and bio-organic mechanisms under solar conditions. The outline of the remainder of the paper is as follows. First, we introduce a theoretical framework that allows the calculation of quenching parameters. We then describe the experimental methods adopted. Finally, we present the results and discuss the mechanisms of quenching.

THEORETICAL BACKGROUND

The dynamical process in which quenching mechanism is due to collision is given by the linear Stern–Volmer equation

$$\frac{I_o}{I} = 1 + K_{sv}[Q] = 1 + k_q \tau [Q] \qquad (1)$$

where I_o and I are the fluorescence intensities of the solute in the absence and presence of quencher, respectively, K_{sv} $(=k_q\tau)$ is the S-V rate constant, k_q is the bimolecular quenching constant, τ is the lifetime of the fluorophore in the absence of quencher, and $[Q]$ is the concentration of quencher. Relation (1) is generally indicative of single class of fluorophores, all equally accessible to quencher. If two fluorophore populations are present, and one is not accessible to quencher, then the Stern–Volmer plot deviates from linearity, suggesting that quenching mechanism is not purely collisional due to ground-state complex formation but also to the "sphere of action static quenching model".[6] In order to see whether the ground-state complex is partly playing a role, one can use extended S-V equation[16,17] as,

$$\frac{(I_o/I) - 1}{[Q]} = (K_{sv} + k_g) + (K_{sv}k_g)\,[Q] \tag{2}$$

where k_g is the ground state association constant. From Eq. (2), the values of K_{sv} and k_g can easily be determined by linear fit to the steady-state data. The ground-state complex formation takes place if quenching constant k_q ($=K_{sv}\tau$) obtained from Eq. (2) agrees well with that obtained from the lower portions of the plot according to Eq. (1), that is, in the low concentration region where a plot of I_o/I versus $[Q]$ is linear. In this case, static quenching is very low. Apart from this, the ground-state complex formation may be noticed if there is a change in the absorption and fluorescence spectra even at higher concentrations of quencher.

In order to see the role of static quenching process, we have used the sphere of action static quenching model. According to this model, the deviation from the linear S-V plots is due to the fact that only a certain fraction W of the excited state is actually quenched by collisional mechanism. This static quenching was explained by introducing an additional factor W in the linear S-V Eq. (1).[11]

$$\frac{I_o}{I} = \frac{1 + K_{sv}[Q]}{W} \tag{3}$$

In such cases, some molecules in the excited state, the fraction of which is *(1 − W)*, are deactivated almost instantaneously after being formed, because a quencher molecule happens to be randomly positioned in the proximity at the time the molecules are excited and interacts very strongly with them. Thus, the fraction W decreases from unity in contrast with the simple S-V Eq. (1) where $W = 1$. Hence, the instantaneous or static quenching occurs if the quencher molecule is very near to or in contact with the fluorescent molecule at the moment of excitation. The factor W in the modified Eq. (3) is approximately equal to $\exp(-V[Q])$, where V is the static quenching constant and it represents an active volume element surrounding the excited solute molecule.

Frank and Vavilov[11] have suggested that the instantaneous quenching results at the time instances in a randomly distributed system, when a quencher happens to reside within a sphere of action with a volume of V/N'

$$\frac{V}{N'} = (4\pi r^3)/3 \tag{4}$$

and radius r (kinetic distance) surrounding a solute molecule at the time of excitation.

As W depends on the quencher concentration $[Q]$, the S-V plots for a quencher with high quenching ability generally deviate from linearity. Thus it is worth rewriting Eq. (3) as

$$[1-(I/I_o)]/[Q] = K_{sv}(I/I_o) + (1-W)\ [Q] \tag{5}$$

From Eq. (5), one can easily calculate K_{sv} and the values of W by least squares fit method. According to Andre et al. and Zeng et al.,[17,18] if the distance between the quencher molecule and the excited molecule lies between the encounter distance and the kinetic distance, the static effect takes place especially in the case of steady-state measurements irrespective of the ground-state complex formation provided reactions are limited by diffusion. In order to find whether the reactions are diffusion limited, one can invoke the finite sink approximation model.

Finite Sink Approximation Model (FSA)

Keizer[19–21] has proposed a nonequilibrium statistical modification of the Smoluchowski–Collins–Kimball (SCK) expression to fit the I_o/I ratio in the fluorescence quenching.

In case of SCK model, time-dependent rate coefficient *k(t)* for diffusion-limited reactions is given by[18,22,23]

$$k(t) = a + b\ \exp(c^2 t)\ \mathrm{erfc}(ct^{1/2}) \tag{6}$$

where

$$a = k_a\left[1 + \frac{k_a}{4\pi N'RD}\right]^{-1} \tag{7}$$

$$b = k_a\left[1 + \frac{4\pi N'RD}{k_a}\right]^{-1} \tag{8}$$

$$c = \left[1 + \frac{k_a}{4\pi N'RD}\right]\frac{D^{1/2}}{R} \tag{9}$$

Integration of Eq. (6) between the limits $[Q]\ [R]$ at $r \to \infty$ and $[Q]\ [R]$ at $r = R$ provides the well-known expression

$$1/k_d = (1/k_q) + (1/k_a) \tag{10}$$

where $k_d = 4\pi N'DR$, k_a is the activation energy controlled rate constant describing the reaction of encountered pairs at a reactive distance R, and D is the sum of the diffusion coefficient of the solute and quencher molecules. Following this expression, k_q is independent of $[Q]$, whereas for efficient quenching process in liquids, k_q is often observed to increase with increasing $[Q]$. This might be attributed as discussed above to static fluorescence quenching of solute molecule, in the vicinity of $[Q]$, transient effects arising from an initial time dependence of the concentration gradient, or combination of these.[18]

But assuming only the first encounter is of interest in the case of efficient fluorescence quenching, an initial average separation distance, r_o, can be defined (sink radius) so that the diffusive region of interest for a first encounter is in the range $R \leq r \leq r_o$ such that all subsequent encounters are eliminated. Integration of the flux equation between the limits $[Q](r_o)$ at r_o and $[Q](R)$ at R leads to modification of expression (10) as

$$\frac{1}{k_q} = \frac{1 - (R/r_o)}{k_d} + \frac{1}{k_a} \tag{11}$$

This equation reduces to the reaction limited from the $(k_q = k_a)$ both for inefficient quenching $(k_a \ll k_d)$ and for quenching in pure quenching solvents where $R = r_o$. In the diffusion-controlled limit $(k_a \gg k_d)$, Eq. (11) reduces to

$$k_q = \frac{k_d}{1 - (R/r_o)} \tag{12}$$

and k_q depends on the quenching concentration through r_o. Because the sink radius (r_o) is identified with the most probable nearest neighbor initial separation, the appropriate distribution requires that $r_o = (2\pi N'\ [Q])^{-1/3}$.[20a,b] Replacing r_o by this value in Eq. (11) and k_d by its value $(4\pi N'DR)$ and dividing throughout by the fluorescence lifetime of solute in the absence of quencher (τ), one obtains the modified S-V relationship[17] as

$$K_{sv}^{-1} = (K_{sv}^{o}) - \frac{(2\pi N')^{1/3}}{4\pi N' D\tau}[Q]^{1/3} \tag{13}$$

A plot of $K_{sv}^{-1} = (4\pi N'DR\tau k_a/4\pi N'DR + k_a)$ against $[Q]^{1/3}$ becomes linear with negative slope. Mutual diffusion coefficient D becomes directly accessible from the slope of the graph exemplified in Eq. (13), and K_{sv} is obtained at $[Q] = 0$ regardless of the relative magnitudes of k_a and k_d $(=4\pi N'DR)$, irrespective of whether quenching is diffusion limited or not. From K_{sv}, we only have access to R', which is a composite of R and k_a through Eq. (14)

$$K_{sv} = 4\pi N' D R' \tau \tag{14}$$

where R' is the distance parameter and has the same meaning as in the long-time SCK model[17,22] and is given as

$$R' = R[1 + 4\pi RDN'/k_a] \tag{15}$$

Then according to the theory discussed above, if k_a is greater than k_d [i.e., Eq. (10)], then the reaction is said to be diffusion limited (i.e., for $R' < R$). But for $R' > R$, the bimolecular reactions of fluorescence quenching are said to be diffusion limited[22] if the values of k_q determined from Eq. (5) are greater than $4\pi N'R'D$.

MATERIALS AND METHODS

U-OB obtained from Ceba Specialty Chemicals Inc., Switzerland was used without further purification. The quencher aniline and all the other solvents used were of spectroscopic grade. The steady-state fluorescence spectra were recorded using fluorescence spectrophotometer (Hitachi F-2000, Japan) at a fixed solute concentration of 5×10^{-6} M in order to avoid self-absorption effects, and the quencher concentration was in the range 0.02–0.1 M for all the solvents. The sample solution contained in a quartz cell of 1 cm path length was excited by 375 nm radiation, and the fluorescence was detected in perpendicular geometry. The peak positions of fluorescence spectra of solutions were 422 nm in alkanes and 434 nm in alcohols. However, the lifetime of U-OB in each solvent is found to be independent of the polarity. The fluorescence lifetime of U-OB was measured in alcohols and alkanes using TCSPC technique.

RESULTS AND DISCUSSION

Figure 1 shows the plot of I_o/I versus $[Q]$ in different solvents. As can be seen, plots are nonlinear exhibiting positive deviation in all the solvents. Similar results have been reported by others.[2,23] The positive deviation observed is not purely due to collision, but may be due to the formation of either ground-state complex or static quenching process.[2,9,16,18]

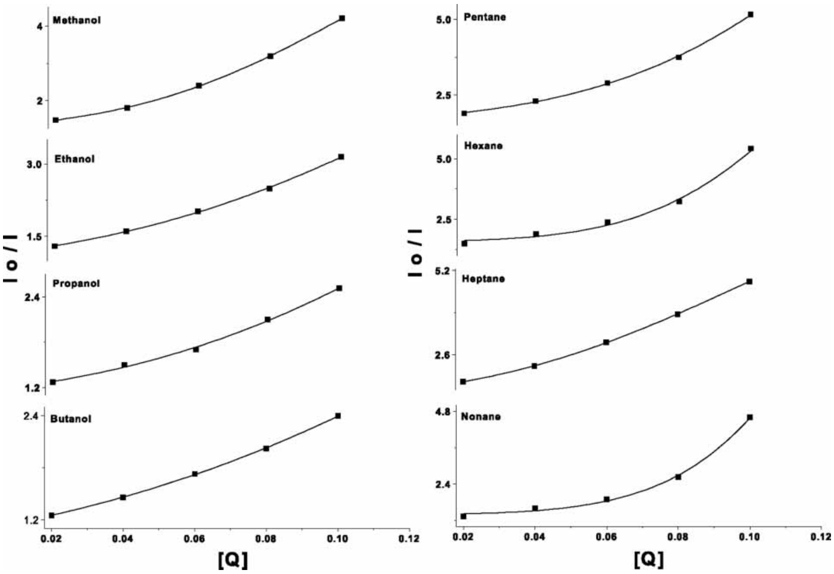

Figure 1. Stern–Volmer plots of I_o/I against $[Q]$ in alcohols and alkanes.

It is noted that the nonlinearity observed is identical in most of the solvents indicating that the quenching is independent of the polarity of the solvents in case of U-OB. A close examination of Table 1 reveals that the experimentally determined K_{sv} [from Eq. (2)] values in all the alcohol and alkane solvents are found to be imaginary and as such one can rule out the possibility of ground-state complex formation.[2,16,24] This is also confirmed by the fact that there is no shift in the peak position in the emission spectrum with different quencher concentrations as shown in Fig. 2 for U-OB in methanol and *n*-hexane. Thus, the analysis of the data was carried out by employing the sphere of action static quenching model. Therefore, a plot of $1-(I/I_o)/[Q]$ versus I/I_o (Fig. 3) for UVITEX-OB with aniline as quencher was used for analysis of the data in all the solvents.

The bimolecular quenching rate parameters k_q were determined from the experimentally measured values of K_{sv} and τ using the relation $k_q = K_{sv}/\tau$ (Table 1). The higher values of k_q suggest the efficient quenching of fluorescence. The magnitudes of the static quenching constant V and radii r of the sphere of action (kinetic distance) were determined for sphere of action model in order to support static and dynamic effects. The values of V and r are determined by the least squares fit method in all the solvents using Eqs. (4) and (5) and are collected in Table 1. These values agree fairly well with those reported in literature.[25,26] According to the models described for static quenching, V can be thought of as an association constant or as surrounding

Table 1. The values of Stern–Volmer constant K_{sv}, lifetime τ_f, bimolecular quenching rate parameter k_q, static quenching constant V and kinetic distance r for different solvents

Solvent	K_{sv} (M^{-1})	τ_f (ns)	$k_q \times 10^{-10}$ ($M^{-1}\,s^{-1}$)	V ($mol^{-1}\,dm^3$)	r (Å)
Methanol	17.86	1.31	13.63	3.36	11.00
Ethanol	10.29	1.52	6.77	4.29	11.94
Propanol	11.48	1.57	7.31	1.20	7.81
Butanol	10.47	1.53	6.84	1.28	7.97
Pentanol	10.57	1.50	7.05	2.26	9.64
Hexanol	7.34	1.50	4.89	3.58	11.24
Octanol	6.92	1.48	4.68	1.09	7.56
Pentane	23.87	1.20	19.89	4.12	11.78
Hexane	16.85	1.04	16.20	5.07	12.62
Heptane	24.57	1.04	23.62	3.47	11.12
Nonane	7.76	1.26	6.16	7.69	14.50
Decane	18.22	1.33	13.70	1.32	8.05
Dodecane	9.92	1.27	7.81	4.39	12.03
Hexadecane	7.15	1.07	6.68	4.79	12.38

$R(R_Y + R_Q) = 7.44$ Å.

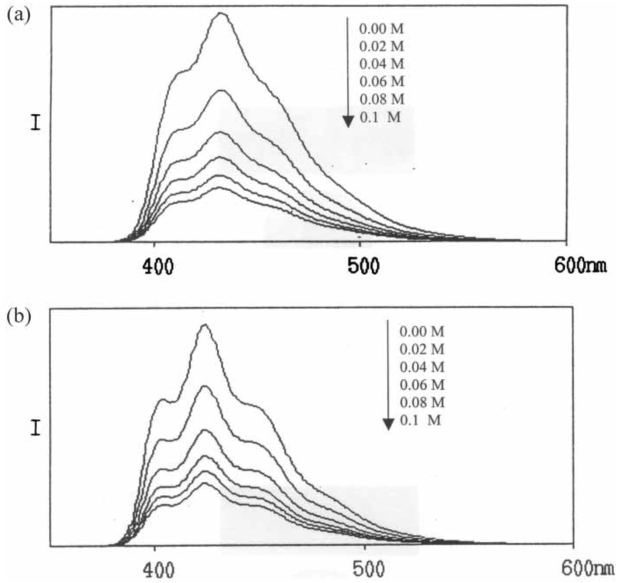

Figure 2. (a) Emission spectra of UVITEX-OB in methanol (5×10^{-6} M fixed) with different quencher concentrations of aniline. (b) Emission spectra of UVITEX-OB in n-hexane (5×10^{-6} M fixed) with different quencher concentrations of aniline.

volume element having a radius r. As can be seen from Table 1, the magnitude of V does not depend greatly on the polarity, temperature, or composition of the solution. For these reasons, it seems most reasonable in case of U-OB to discuss the static quenching phenomena in terms of sphere of action.

The radii R_Y and R_Q of the solute and the quencher molecules were determined by adding the atomic volumes of all the atoms constituting the molecules as suggested by Edward[27] (shown at the bottom of the Table 1). The value of R ($=R_Y + R_Q$) referred to as encounter distance is compared with the values of r to check whether the reaction is due to sphere of action model. According to Andre et al.[17] and Zeng et al.,[18] if the distance between the quencher molecule and excited molecule lies between the encounter distance R and kinetic distance r, the static effect predominates especially in the case of steady-state experiments irrespective of ground-state complex formations provided the reactions are limited by diffusion. From Table 1, we see that the values of r are greater than the values of encounter distance R in all the solvents indicating that the sphere of action model holds good in our case also.[6,28] It may also be noted that the positive deviation in S-V plot is expected when both static and dynamic quenching occur simultaneously.[16]

Further, to find out whether the reactions are diffusion limited or not, we invoke the finite sink approximation model for steady state, which helps

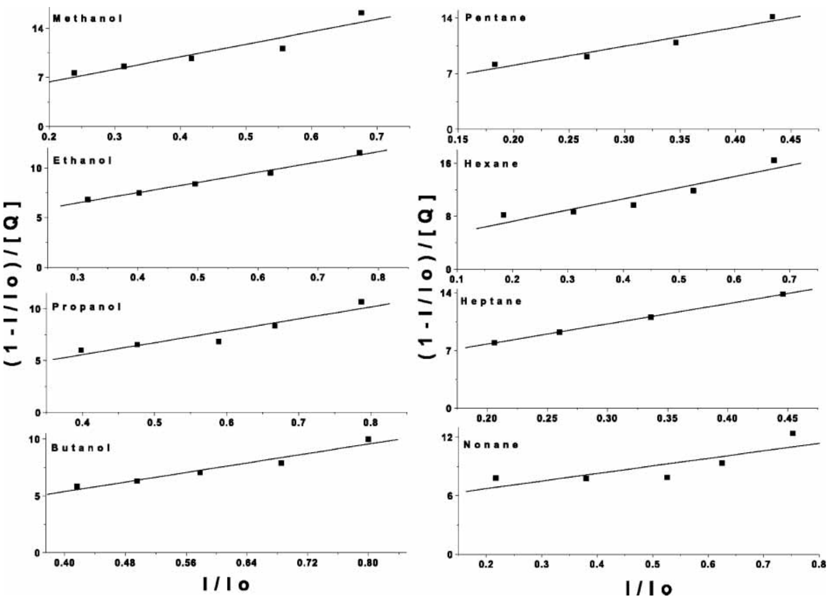

Figure 3. Plots of $[1 - (I/I_o)]/[Q]$ against I/I_o in alcohols and alkanes.

us to estimate independently the mutual diffusion coefficient D and distance parameter R'. Hence, we have determined the values of K_{sv}^{-1} and $[Q]^{1/3}$ by an equation using finite sink model, where $K_{sv} = [(I_o/I) - 1]/[Q]$, and $[Q]$ is the quencher concentration ranging from 0.02 M to 0.1 M. It is observed that K_{sv} increases with increasing $[Q]$ in all the solvents. The plot of K_{sv}^{-1} versus $[Q]^{1/3}$ shown in Fig. 4 are almost linear in all the solvents, and small deviations observed may be attributed to experimental uncertainties. The intercept of this plot gives Stern–Volmer constant, K_{sv}^{o} (at $Q = 0$), and the slope leads to the mutual diffusion coefficient D according to Eq. (13). The distance parameter R' was determined from Eq. (14) using K_{sv}^{o} and D values (Table 2). It may be noted that the values k_q [determined from Eq. (5)] are greater than $4\pi N'R'D$. The bimolecular reactions are said to be diffusion limited if $k_q > 4\pi N'R'D$, which is an expected result for diffusion-limited reaction.[22] The activation energy controlled rate constant $k_a[=4\pi N'DR/(R/R' - 1)]$ was estimated by considering the values of distance parameter R' and encounter distance R. k_a can be determined only when $R' < R$. According to Zeng et al.,[18] if k_a is greater than $k_d[=4\pi N'RD]$, then the reactions are said to be diffusion limited. Here, the values of both k_a and k_d are expressed in terms of D (mutual diffusion coefficient, determined by Stokes–Einstein relation) because D is the same in both cases, and the values of k_d are shown at the bottom of Table 2. It is observed that k_a is greater than k_d in most of the alcohols and

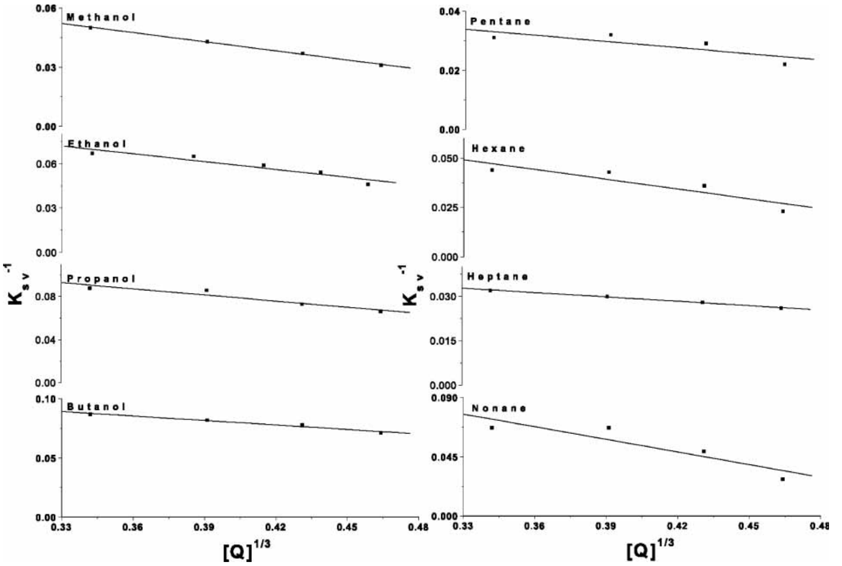

Figure 4. Plots of K_{sv}^{-1} versus $[Q]^{1/3}$ in alcohols and alkanes.

alkanes shown in Table 2, which suggests that the activation process is more predominant in the quenching mechanism than the diffusion process.[22]

It is important to note that when an attempt was made to correlate the experimentally determined values of D and R' using FSA model with the corresponding values of D^a and R calculated from Stokes–Einstein and Edward's empirical relation for U-OB-aniline system in all the solvents, it was found that, in case of ethanol, propanol, butanol, hexanol, octanol (alcohols) and dodecane, hexadecane (alkanes), the values of D and R' (or R) determined from the two methods are quite comparable. But we see that the correlation is poor in the rest of the solvents (Tables 2 and 3). Similar discrepancies also observed by other workers in some bimolecular quenching reactions[17,22] were ascribed to uncertainties in the value of adjustable parameter a in Stokes–Einstein relation and the approximation made in the value of atomic volume in the Edward's relation. Hence, we conclude that finite sink approximation model is valid in recovering the parameters D and R' (or R). Also, it is important to note here that the experimentally obtained values of D and D^a calculated using Stokes–Einstein and Edward's empirical relation are greater in alkanes compared with alcohols.

The results of the current investigation are summarized as follows: The fluorescence quenching behavior of UVITEX-OB with quencher aniline has been investigated in alcohols and alkanes. The S-V plots show positive deviation with high bimolecular rate ($k_q \sim 14 \times 10^9$ for alcohol solvents and $24 \times 10^9\ M^{-1}\ s^{-1}$ for alkanes), which indicate high quenching efficiency. Both static constant V and kinetic distance r are in good agreement with those

Table 2. The values of K_{sv}^{o} (steady state quenching constant at $[Q] = 0$), mutual diffusion co-efficient D, distance parameter R', $4\pi NR'D$, quenching rate parameter k_q and activation energy controlled rate constant k_a

Solvent	K_{sv}^{o} (mol^{-1} dm^{3})	$D^{a} \times 10^{5}$ (cm^{2} s^{-1})	R' (Å)	$4\pi NR'D \times 10^{-10}$ (M^{-1} s^{-1})	$k_q \times 10^{-10}$ (M^{-1} s^{-1})	$k_aD \times 10^{15}$ M^{-1} s^{-1}
Methanol	9.70	1.02	9.59	0.76	13.63	—
Ethanol	10.16	1.28	6.90	0.67	6.77	7.19
Propanol	6.42	0.69	7.83	0.41	7.31	—
Butanol	7.64	1.07	6.17	0.50	6.84	2.74
Pentanol	9.90	1.73	5.04	0.66	7.05	1.18
Hexanol	7.50	0.99	6.67	0.50	4.89	4.88
Octanol	4.52	0.56	7.21	0.31	4.68	17.65
Pentane	17.62	2.47	7.86	1.47	19.89	—
Hexane	9.64	1.20	10.21	0.93	16.20	—
Heptane	20.45	4.05	6.42	1.97	23.62	3.54
Nonane	5.47	0.51	11.25	0.43	6.16	—
Decane	20.22	4.95	4.06	1.52	13.70	0.68
Dodecane	9.87	1.49	6.89	0.78	7.81	7.05
Hexadecane	3.71	0.53	8.64	0.35	6.68	—

Quenching rate constant for diffusion controlled reaction $k_d = 0.563D \times 10^{15}$ M^{-1} s^{-1}.

Table 3. Values of mutual diffusion co-efficient D^a and D^b and distance parameter R'

Solvents	$D^a \times 10^5$ cm^2 s^{-1}	$D^b \times 10^5$ cm^2 s^{-1}	R' (Å)
Methanol	3.70	1.02	9.59
Ethanol	1.88	1.28	6.90
Propanol	1.04	0.69	7.83
Butanol	0.78	1.07	6.17
Pentanol	0.58	1.73	5.04
Hexanol	0.45	0.99	6.67
Octanol	0.27	0.56	7.21
Pentane	9.51	2.47	7.86
Hexane	7.01	1.20	10.21
Heptane	5.22	4.05	6.42
Nonane	3.04	0.51	11.25
Decane	2.42	4.95	4.06
Dodecane	1.47	1.49	6.89
Hexadecane	0.67	0.53	8.64

Viscosity data from alcohols Ref. [G. B. Dutt & Sumati Ramam, *J. Chem. Phys.*, **2001**, *114*, 6702–6713].

reported in literature and it is seen that $k_q > 4\pi N'DR'$ in most of the solvents (Table 2). The quality of agreement between experimentally obtained and the calculated mutual diffusion coefficient from finite sink approximation model and diffusion coefficient from Stokes–Einstein relation is quite good in most of the solvents used. Therefore, the above facts suggest that quenching reaction is diffusion limited and that both static and dynamic quenching processes partly play a role in these two systems.

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