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Fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride

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ABSTRACT

Fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride (CCl_4) was carried out in both polar and non-polar solvents at room temperature to understand the role of quenching mechanism. The negative deviation in normal Stern–Volmer (S–V) plots was observed in almost all solvents used for λ_{ex} 345 nm, 365 nm and 385 nm. The bimolecular quenching rate constant (k_q) estimated using the measured values of quenching constants and decay times were found to be dependent on the polarity of the solvent. Further, it is found that quenching efficiency increases with increasing polarity of the solvent. The negative deviations from the normal Stern–Volmer (S–V) plots shown in the fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride is interpreted in terms of the existence of different conformers of the solute in the ground-state. Fluorescence decay of the solute before quenching showed bi-exponential behavior and the analysis yielded two decay components, respectively, in the range 2.11–7.22 ns and 5.17–12 ns in all solvents except *n*-propanol and methanol. Based on the steady state and fluorescence lifetime measurements emission band I (408 nm) is assigned due to locally (LE) excited state (Trans form), band II (430 nm) due to isomer state of Cis form.

1. Introduction

Fluorescence quenching is an important technique used to obtain adequate information about the structure and dynamics of fluorescent molecules. It is a process, in which fluorescence intensity of the solute decreases by variety of molecular interactions such as excited state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collisional quenching [1–10]. Stern–Volmer plots of certain quenching reactions results upward, downward or both upward and downward curvatures. The main reason for the positive deviation (upward) is the formation of a non-fluorescent complex between the fluorophore and quencher in the ground-state (static quenching), however; the negative deviation (downward) is either due to the presence of two fluorophores with different accessibility to the quencher and/or due to the occurrence of the reverse reactions in the photochemical system [11]. Normally, the biochemical applications of quenching are due to the molecular interactions such as ground-state complex formation, exciplex formation, and energy transfer.

In general both static and dynamic quenching requires molecular contact between the fluorophore and quencher. The formation of non-fluorescent ground-state complex between the fluorophore and the quencher results in static quenching and if there is a collision between subsequent formation of a transient complex between excited state fluorophore and a ground-state quencher then dynamic quenching takes place. Thus the difference between the static and dynamic quenching is the sequence of excitation and complex formation, while the physical bases of two quenching mechanisms are the same. The fluorescence quenching of organic molecules in solution by several quenchers has been studied in depth using steady-state and transient methods and positive deviation has been observed by many researchers [12–24]. But very few reports have been appeared in the literature for downward (negative) deviations in the Stern–Volmer plot [10,11]. In the present system such downward deviations in S–V plot has been observed in bimolecular quenching reaction of anthrylvinyl acetate (solute) and CCl_4 (quencher). Therefore, a desire to get better understanding about the structure and molecular properties of anthrylvinyl acetate in the ground and excited state has motivated us to study in detail about the mechanisms involved. In the present work, the photophysical properties of anthrylvinyl acetate have been investigated in various solvents using steady state absorption and fluorescence emission as a function of concentration and excitation wavelength. Also, fluorescence lifetimes measurements were carried out to identify the emitting species. To characterize the species responsible for negative deviation the experimental results of steady state and lifetime measurements

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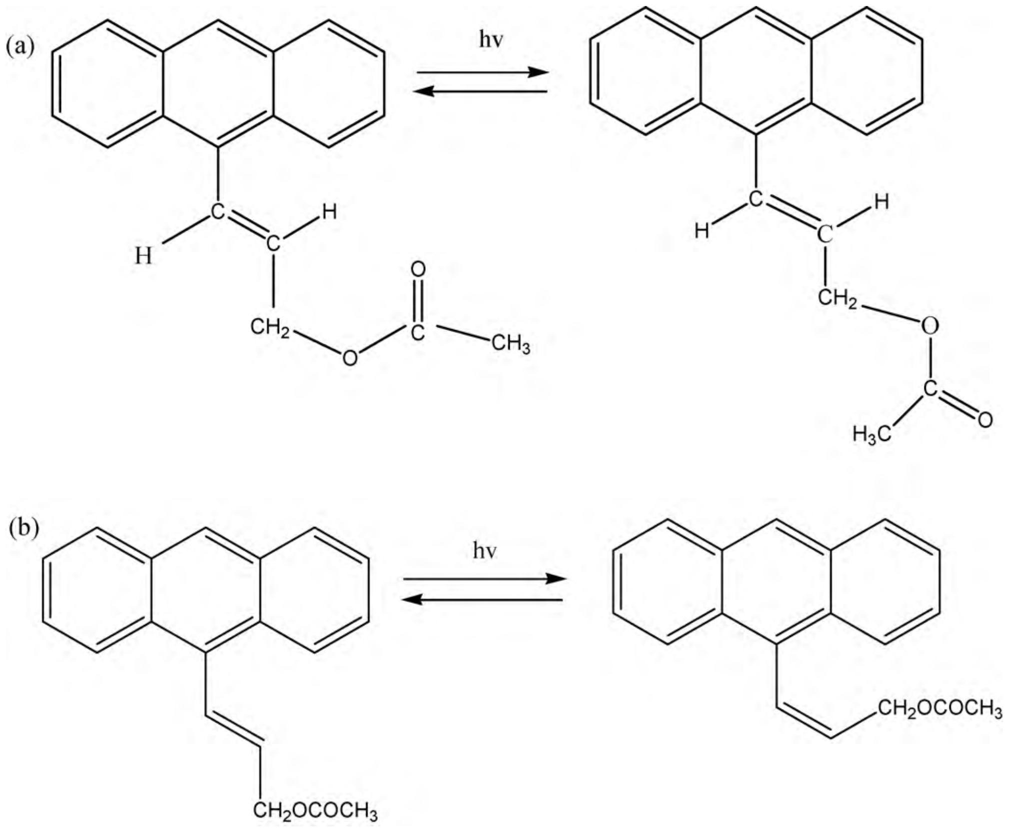

Fig. 1. (a) Ground-state conformers at room temperature (at very low energy) (orientation of the estercarbonyl group with respect to double bond is different, it can be S-Cis or it can be S-Trans). (b) Excited state geometric isomers (Cis-Trans isomers are due to rotation around double bond. This energy difference is much higher at room temperature only the more stable Trans isomers predominates).

were explained in terms of possible resonance structures of the molecule (Fig. 1).

2. Experimental

Anthrylvinyl acetate was taken from Organic division II, Indian Institute of Chemical Technology (IICT), Hyderabad [16], and was used with further purification. All solvents were of spectroscopic grade and were used as received. The absorption and fluorescence spectra were recorded using Hitachi Model U-3010/U-3310 spectrophotometer and F-7000 fluorescence spectrophotometer, respectively. The lifetime measurements were carried out using a Picosecond operated time-correlated single photon counting unit, which is described elsewhere [17]. In the present work, Nano LED (373 nm, 1.2 ns, 1 MHz) was used as the excitation light source and a TBX4 detection module (IBH) coupled with a special Hamamatsu PMT was used for fluorescence detection. In the present setup, the instrument response was ~1.2 ns (~240 ps) at FWHM. Fluorescence decays were recorded with a vertically polarized excitation beam and fluorescence was collected at magic angle 54.7° and was analyzed by a deconvolution method at room temperature.

3. Results and discussion

3.1. Steady-state measurements

The absorption spectra of anthrylvinyl acetate in various solvents at 1×10^{-5} M have three absorption peaks 345 nm, 365 nm and 385 nm in the UV region (Fig. 2). Upon the addition of quencher concentration there is no change in the absorption spectrum which indicates the non-formation of ground-state complex. Fluorescence at low concentration (1×10^{-5} M), exhibits two emission bands in all solvents, I band (408 nm) and II band (430 nm); however as the concentration is increased from10^{-5} M to 10^{-3} M, the intensity of I band goes on decreases and merges with the second band and is assigned to as Cis form of the solute. At low concentration as the excitation wavelength goes on increases the intensity of II band increases more as compared to I band in all solvents (Fig. 3). The intensity contribution of emission band I (Trans form) and II (Cis form) are 48% and 52% for λ_{ex} 345 nm, 33% and 67% for λ_{ex}

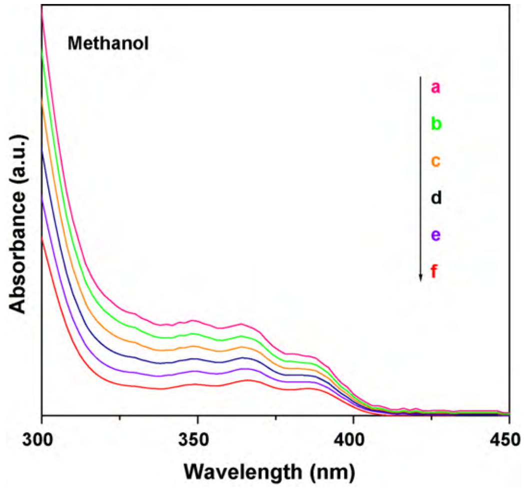

Fig. 2. Absorption spectra of anthrylvinyl acetate in methanol at fixed concentration of 1×10^{-5} M with varying quencher concentration of CCl_4: (a) 0.00 M, (b) 0.02 M, (c) 0.04 M, (d) 0.06 M, (e) 0.08 M, and (f) 0.10 M.

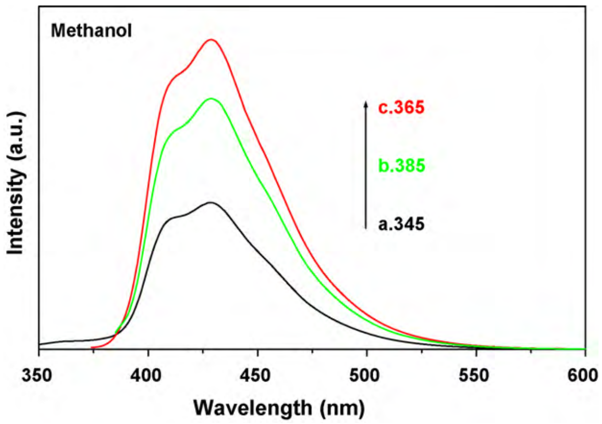

Fig. 3. Excitation wavelength dependence emission spectra in methanol solutions at concentration 1×10^{-5} M.

365 nm and 12% and 88% for λ_{ex} 385 nm and these experimental results agree well with the values of earlier reports [16]. Thus, fluorescence characteristics of the solute studied as a function of concentration and excitation wavelength reveals the existence of two emitting species. In addition the experimental results may also be explained in terms of the possible resonance structure of the molecule as shown in Fig. 1a and b. Fig. 1a, shows the ground-state conformers; at room temperature the orientation of the ester carbonyl group with respect to double bond is different, it can be S-Cis or it can be S-Trans. Fig. 1b, shows excited state geometric isomers; Cis–Trans isomers are due to rotation around double bond. It is evident from experimental observation that the energy difference between Cis–Trans isomers is much higher at room temperature therefore more stable Trans isomers predominate. However, at very low concentration and high excitation energy ($\lambda_{ex} \leq 345$ nm), the S-Cis form and S-Tans forms of the molecule are in equilibrium.

To understand the role of quenching mechanism fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride (CCl_4) was carried out in both polar and non-polar solvents for λ_{ex} 345 nm, 365 nm and 385 nm at room temperature. Infact the fluorescence of anthrylvinyl acetate in both polar and non-polar solutions is effectively quenched by the addition of CCl_4 (Fig. 4) without the alteration in the shape of the fluorescence spectra and peak position until the intensity fall below the detection limit for λ_{ex} 345 nm, 365 nm and 385 nm. Thus, no shifts in the absorption maxima and fluorescence spectra upon the addition of quencher concentration ruled out the formation of ground-state complex between the fluorophore and quencher.

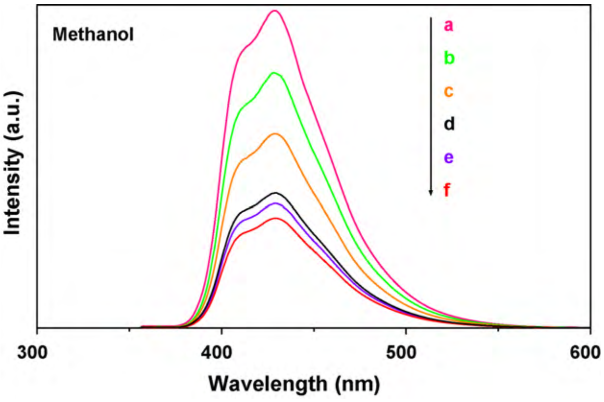

Fig. 4. Emission spectra of the solute in methanol at fixed concentration of 1×10^{-5} M with varying quencher concentration of CCl_4: (a) 0.00 M, (b) 0.02 M, (c) 0.04 M, (d) 0.06 M, (e) 0.08 M, and (f) 0.10 M.

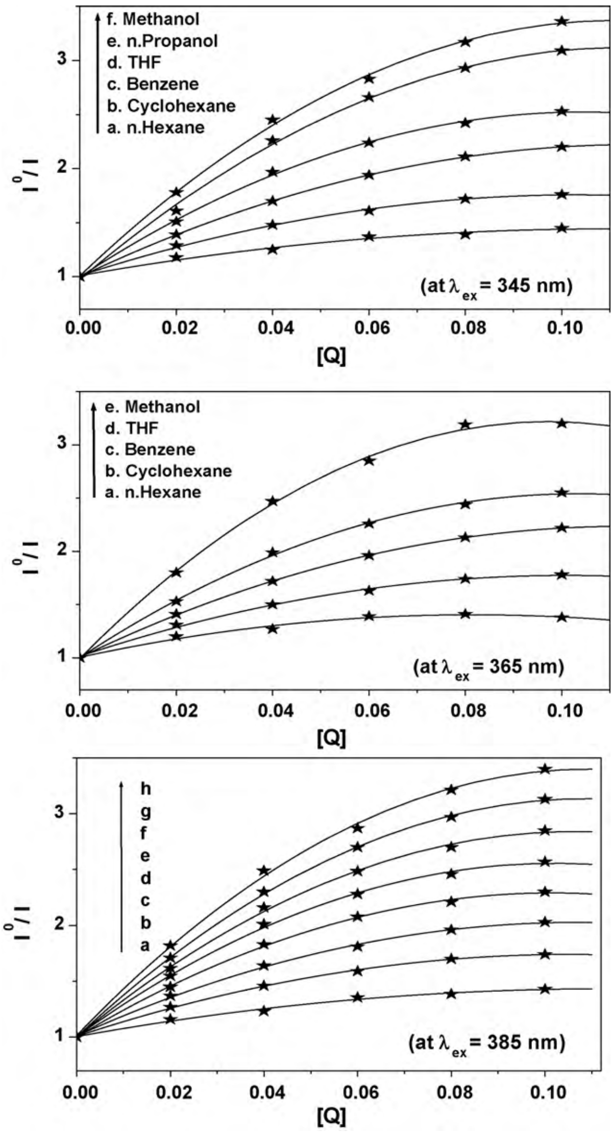

Fig. 5. Stern–Volmer plots of I^0/I versus [Q] exhibiting negative deviation in different solvents with varying polarities: (a) *n*-hexane, (b) cyclohexane, (c) benzene, (d) toluene, (e) tetrahydrofuran (THF), (f) butanol-1, (g) *n*-propanol and (h) methanol for λ_{ex} (A) 345 nm, (B) 365 nm and (C) 385 nm.

In the present system, among the several models normal Stern–Volmer relation and the modified Stern–Volmer or Lehrar relations was used to understand the quenching process. A normal Stern–Volmer equation used to understand the quenching mechanisms is given by the relation [25]

$$\frac{I^0}{I} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q] \quad (1)$$

where I^0 and I are the fluorescence intensity in the absence and presence of quencher. τ_0 is the lifetime value in the absence of the quencher, k_q is the bimolecular quenching rate constant and K_{SV} is the slope of the plot of I^0/I versus quencher concentration. Fig. 5 shows the plots of I^0/I versus quencher concentration and is non-linear exhibiting negative deviation with the intercept equal to unity. When I^0/I at λ_{em} 420 nm were plotted against quencher concentration (Fig. 5), the S–V plot appear linear at lower concentration (0.00–0.04 M) and is ascribed to diffusion-limited dynamic quenching. Whereas at higher quencher concentrations (0.04–0.1 M) a significant downward deviation from the linearity is observed for λ_{ex} 345 nm, 365 nm and 385 nm. This could be due

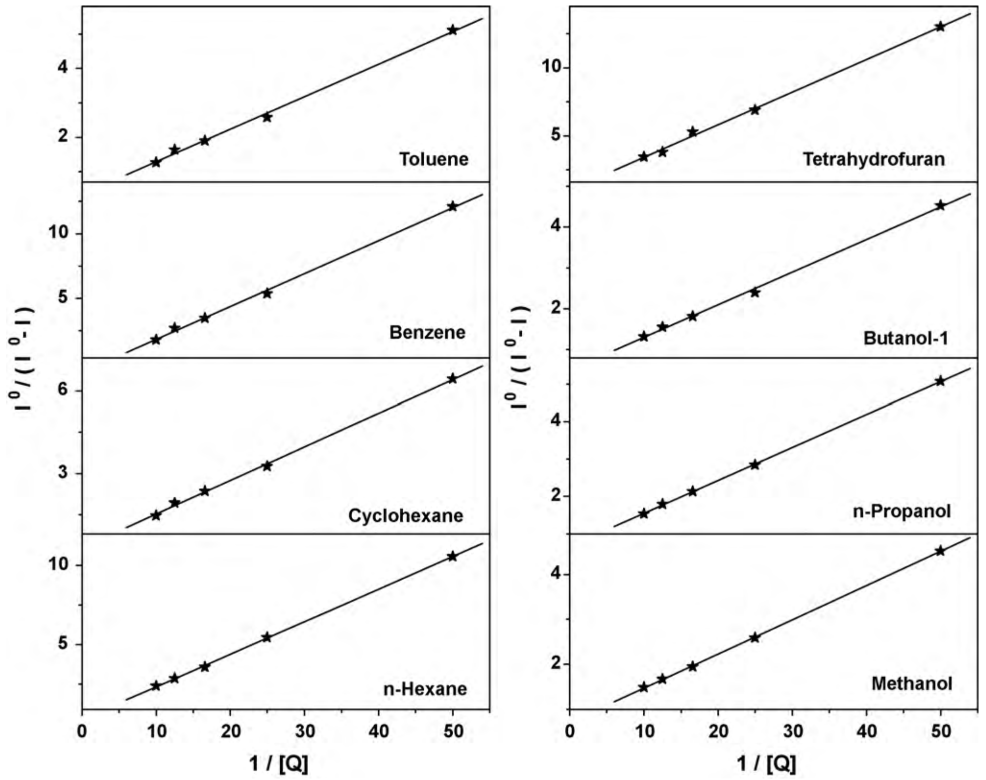

Fig. 6. Modified linear Stern–Volmer plots of $I^0/(I^0-I)$ versus 1/[Q] in different solvents with varying polarities.

to either the presence of two fluorophores with different accessibility to quencher (CCl_4) or the occurrence of a reverse reaction in the photochemical process [18]. The negative deviations (downward curvature from linearity) in the Stern–Volmer plot may be due to the existence of different conformers of anthrylvinyl acetate [10] and in the limit, a fraction of the fluorophores may be completely segregated from the quencher [1].

Further, the modified Stern–Volmer or Lehrar equation is given by [1]

$$I = (1-f)I^0 + \frac{f\,I^0}{1+K_{SV}[Q]} \tag{2}$$

where I intensity of fluorescence in the presence of quencher, I^0 total fluorescence in the absence of quencher, (1–f) I^0 is the fluorescence intensity of not quenchable fluorophore and 'f' is the quenchable fraction of the fluorophores, which lies between 0 and 1 ($0 \le f \le 1$) and it indicates that two conformers are accessible to the quencher for which an estimate of Stern–Volmer constant (K_{SV}) varies between 1 M^{-1} and 10 M^{-1} implying that 0.06 M of quencher concentration is required to quench one half of the fluorescence intensity of anthrylvinyl acetate. Infact the quenching of the rest of the fluorophores, the quenchable fraction will obey the Stern–Volmer equation in the absence of static quenching mechanism [1]. The usual form of the modified Stern–Volmer (Lehrar) equation can also be obtained with the rearrangement of Eq. (2) and is given by

$$\frac{I^0}{I^0-I} = \frac{I^0}{\Delta I} = \frac{1}{f} + \frac{1}{f\,K_{SV}}\frac{1}{[Q]} \tag{3}$$

The plot of $I^0/\Delta I$ versus 1/[Q] (Fig. 6) will yield a straight line with slope $1/(f\,K_{sv})$ and intercept $1/f$, with K_{SV} = intercept/slope.

It is to be noted that for the proper interpretation of the quenching data and the determination of K_{SV} requires the identification of the particular mechanism through which quenching occurs. A significant downward deviation from linearity displayed at higher concentrations (from 0.04 M to 0.1 M) of CCl_4 (quencher) could be due to either the presence of two fluorophores with different accessibility to quencher or the occurrence of reverse reaction in the photochemical process [18]. However, the interpretation of the results becomes very difficult if the static quenching contributes to the total quenching process or when the fluorophore population is heterogeneous [26]. But the static quenching is due to the presence of quencher in the vicinity of the solute at the moment of excitation and is expected to be very weak because the ground-state asso-

Table 1
Fluorescence lifetimes (τ_{av}), Stern–Volmer constant (K_{SV}), bimolecular quenching rate parameter (k_q) and diffusion-limited rate constant (K_0).

Solvent	Dielectric constant	η (cP)	τ_1 (ns)	τ_2 (ns)	τ_{av} (ns)	χ^2	K_{SV} (M^{-1})	$k_q \times 10^{-9}$ ($M^{-1}S^{-1}$)	$K_0 \times 10^{-10}$ ($M^{-1}S^{-1}$)
n-Hexane	1.880	0.294	2.29 [4.74]	5.17 [95.26]	5.03	1.16	1.26	0.251	3.924
Cyclohexane	2.010	0.894	3.59 [8.02]	6.74 [91.98]	6.49	1.15	2.42	0.372	1.340
Benzene	2.284	0.604	2.53 [6.77]	6.53 [93.23]	6.26	1.09	2.90	0.464	1.949
Toluene	2.379	0.560	2.11 [4.15]	6.41 [95.85]	6.23	1.22	3.62	0.581	2.094
THF	7.580	0.456	3.01 [5.05]	7.08 [94.95]	6.87	1.11	4.25	0.619	2.542
Butanol-1	17.510	2.544	7.22 [94.27]	11.93 [5.73]	7.49	1.13	6.18	0.825	0.499
n-Propanol	20.210	2.250	7.02 [100]	–	7.02	1.24	7.55	1.076	0.562
Methanol	32.630	0.544	6.41 [100]	–	6.41	1.13	9.32	1.454	2.152

ciation constant (K_S) calculated from the linear fit of I^0/I against [Q] is almost relatively small as compared to dynamic quenching constant (K_{SV}) in all the solvents used which supports the non-involvement of static quenching in the total quenching process involved.

The increase of Stern–Volmer constant (K_{SV}) with increasing the polarity of the solvents (Table 1) does not indicate the involvement of electron or charge transfer as possible quenching mechanism, still then some electron or charge transfer processes might have occurred between the fluorophore and quencher molecule at the excited state [27]. In general, quenching in non-polar media is thought to proceed via charge transfer mechanism and in polar medium through electron transfer mechanism [28]. Usually, the efficiency of quenching can be affected by two important solvent parameters, namely, solvent polarity and solvent viscosity [29]. Thus from the experimental observation, it may be inferred that quenching is mediated by charge transfer conformers formation and the major deactivation pathways for the conformers could be due to the factors like enhanced intersystem crossing [30]. As the conformers are having charge transfer character therefore the increase in quenching efficiency is expected with the increase in polarity of the solvents.

The bimolecular quenching rate parameters k_q was determined using the relation $k_q = K_{SV}/\tau_{av}$ with the substitution of the experimentally measured values of K_{SV} and τ_{av} (Table 1). The higher values of k_q suggest the efficient quenching of fluorescence and the gradual increase in k_q with increase of solvent polarity indicates the increase of quenching efficiency with increase of solvent polarity.

However, in case of efficient quenching mechanism quenching may take place before the complete formation of an exciplex/conformer and the diffusion limited quenching is expected to increase with decreasing solvent viscosity. In order to understand the effect of solvent viscosity (η), the diffusion-limited rate constant K_0 is estimated using the following equation [8]:

$$K_0 = \frac{4\pi N D R}{1000}\{1 + R(2D\tau_{av})^{-1/2}\} \quad (4)$$

where N is the Avogadro's number, $D = D_S + D_Q$ and $D = R_S + R_Q$ represents the sum of the diffusion coefficients and sum of the molecular radii of the solute and the quencher, respectively.

The diffusion coefficients of solute D_S and quencher D_Q can be calculated using Stokes–Einstein equation.

$$D = \frac{kT}{a\pi\eta R} \quad (5)$$

where k is the Boltzmann's constant, T is the absolute temperature, η is the viscosity of the solvent, R is the radius of the solvent or quencher as the case may be and 'a' is a Stokes–Einstein number. In the present case, the radius of the solute molecule is larger than the solvent molecule, and that of the quencher molecule is close to the solvent molecule. Therefore, based on this reasoning, the values of radius a, for solute and quencher is taken as 6 and 3 and molecular radii are $R_S = 3.86$ Å and $R_Q = 2.80$ Å, respectively [31–33].

Further from the plot of K_0/k_q versus inverse of viscosity η^{-1} (P^{-1}) of the solvents (Fig. 7) it is observed that the diffusion-limited rate constant K_0 increases with decrease in viscosity of the solvents where as the bimolecular quenching rate parameter k_q does not depend on the viscosity of the solvent. Hence it is inferred that the quenching phenomenon is not solely controlled by material diffusion [32]. The bimolecular quenching constant k_q was found to be sensitive to polar nature of the solvent, it increases with increasing polarity of the solvent (Fig. 8) and therefore this molecule may act as a probe for identifying polar nature of the solvents.

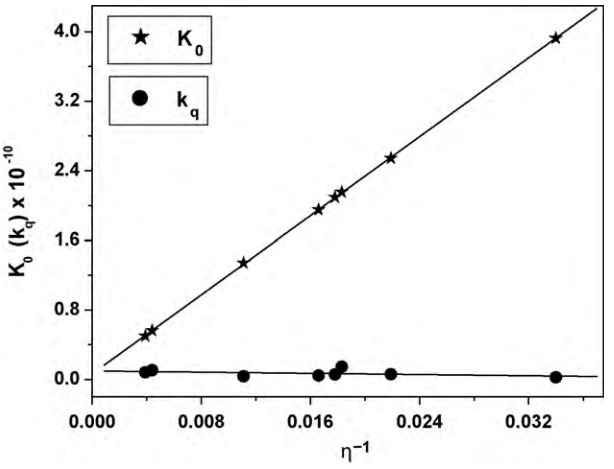

Fig. 7. Variation of K_0 and k_q (M^{-1} S^{-1}) as a function of inverse viscosity η^{-1} (P^{-1}) of the solvents.

3.2. Fluorescence decays

The fluorescence decays of the solute at 420 nm emission in various solvents without quencher at 373 nm excitation were fitted to bi-exponential function.

$$I(t) = a_1 \exp\left(\frac{-t}{\tau_1}\right) + a_2 \exp\left(\frac{-t}{\tau 2}\right) \quad (6)$$

where τ_1 and τ_2 are the lifetimes of the two decay components and a_1 and a_2 are their respective amplitudes with $a_1 + a_2 = 1$. A typical fluorescence decay profile of the solute in methanol solutions without quencher is represented in Fig. 9 and the parameters of bi-exponential fits are listed in Table 1. From the table it is to be noted that the lifetime (τ_1) and amplitudes (a_1) of the first component of the solute in all solvents used without quencher is less than the second components ($\tau_1 < \tau_2$) and ($a_1 < a_2$) however; in butanol the lifetime (τ_1) of the first component is less than τ_2 ($\tau_1 < \tau_2$) with a_1 greater than a_2 ($a_1 > a_2$) i.e., the relative contribution is reversed. The experimental observation of large difference between two decay components may indicate the presence of two emitting species or a single species from two different excited states. In dilute solutions, the average separation of solute molecules is too large to allow an appreciable proportion of the excited molecules to encounter a second solute molecule within the lifetime of the excited state. Thus formation of conformers/charge transfer state in dilute solutions is small, however as concentration increases; the average separation between solute molecules becomes too small to allow the interaction between solute/solvent molecules

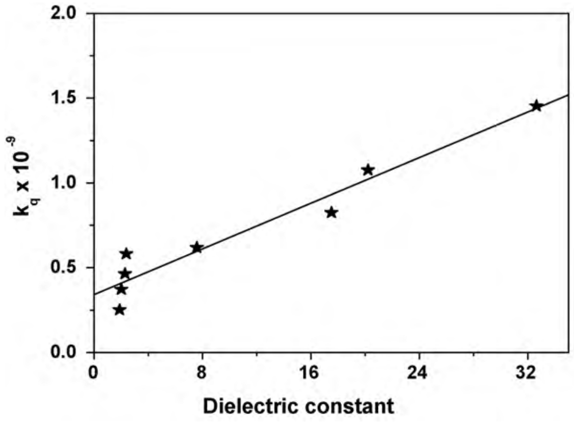

Fig. 8. Variation of k_q (M^{-1} S^{-1}) as a function of dielectric constant (ε) of the solvents.

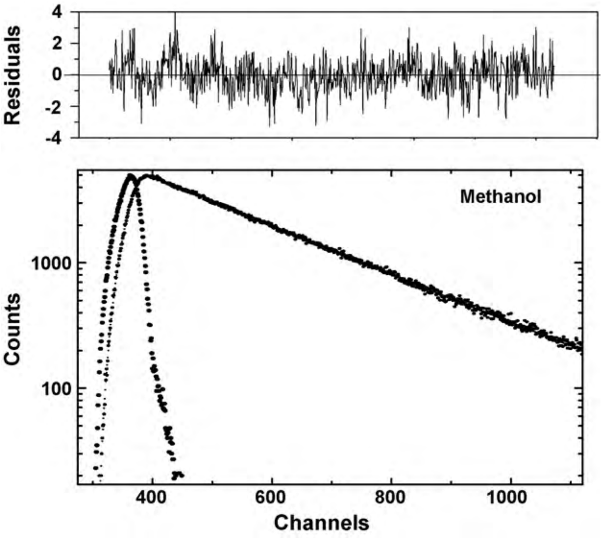

Fig. 9. Fluorescence decay of anthrylvinyl acetate in methanol without quencher.

leading to the formation of charge transfer state. The positive amplitude obtained within the spectral region investigated indicates that both the emissions corresponding to these species decay independently. Fluorescence decay of the solute before quenching showed bi-exponential behavior and the analysis yielded two decay components, respectively in the range 2.11–7.22 ns and 5.17–12 ns in all solvents except *n*-propanol and methanol. Based on the steady state measurements and resonance structure of the molecule the lifetime values in the range 2.11–7.22 ns and 5.17–12 ns are assigned to Trans form (band I at 408 nm) and Cis form (band II at 430 nm) of the molecule. However, single exponential decay observed with decay times 7.02 ns and 6.41 ns, respectively, in *n*-propanol and methanol solvents may due to the overlapping of the states or may be due to equilibrating forms of both S-Trans and S-Cis in these solvents. Thus bi-exponential decay parameters with a_1 is less than a_2 ($a_1 < a_2$) in all other solvents in the absence of quencher is in agreement with the conclusion that the negative deviations from the normal Stern–Volmer (S–V) plots shown in the fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride is due to the existence of different conformers of the solute in the ground-state.

4. Conclusion

Fluorescence quenching of anthrylvinyl acetate by carbon tetrachloride (CCl_4) was carried out in both polar and non-polar solvents at room temperature to understand the role of quenching mechanism. From the steady-state measurements negative deviations in normal Stern–Volmer (S–V) plots were observed in almost all solvents used for λ_{ex} 345 nm, 365 nm and 385 nm. The negative deviation of the quenching from the Stern–Volmer relationship indicates the existence of two ground-state conformers in aqueous solutions. Thus negative deviation (downward) is either due to the presence of two fluorophores with different accessibility to the quencher and/or due to the occurrence of the reverse reactions in the photochemical system (Fig. 1). From the study of fluorescence quenching parameters in various solvents downward curvature is ascribed to diffusion-limited dynamic quenching and the existence of two ground-state conformers However, based on the concentration, excitation wavelength dependence fluorescence measurements and lifetime measurements in all solvents (without quencher) band I (408 nm) is assigned due to locally (LE) excited state (Trans form), band II (430 nm) due to isomer state of Cis form. Further to differentiate and bring out the relative importance of solvent polarity and viscosity, fluorescence quenching studies in mixed solvent system of acetonitrile: benzene are under taken.

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