

FLUORESCENCE QUENCHING OF ANTHRACENE BY NITROAROMATIC COMPOUNDS

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Fluorescence quenching of anthracene by allyl 2,4-dinitrophenyl ether was studied in both nonpolar and polar solvents at room temperature. The quenching rate constants (K_{SV}) have been determined. The positive deviation from linearity in the Stern-Volmer plots has been observed in all solvents. Perrin's model was used to discuss the upward curvature of Stern-Volmer plots in all solvents excepting 1-propanol and 1-butanol where the sphere of action model was applied. During quenching process of anthracene fluorescence by dinitrophenyl ether derivative the Stern-Volmer constant did not depend on the temperature.

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1. Introduction

Polycyclic aromatic hydrocarbons exhibit intense fluorescence in solution at room temperature. They are very versatile compounds due to the availability to give derivatives with different properties such as absorption, fluorescence, oxidation potential or solubility which can be monitored by the electronic nature of their substituents [1-3]. However, the polycyclic aromatic hydrocarbons are environmental pollutants and some of them are considered to be toxic to living organisms. The toxicity can be associated with their photochemical conversion to more toxic photoproducts [4,5]. Since polycyclic aromatic hydrocarbons are usually intensely fluorescent, the fluorescence spectroscopy is especially utilized for their determination in environmental and biological samples.

Like most polycyclic aromatic hydrocarbons, anthracene and its derivatives are of major importance in obtaining luminescent materials with potential applications as materials for lasers, materials for paints, luminescent photolayers, light-emitting devices [6-9]. Anthracene and its derivatives are also used as fluorescent probes in order to investigate protein-ligand interactions by fluorescence spectroscopic techniques [10-14].

Fluorescence quenching is an important method to study the energetics of excited states. Fluorescence quenching refers to any processes by which the fluorescence intensity of the solute decreases. The decrease in the fluorescence intensity can take place by a variety of molecular interactions namely excited state reactions, energy transfer, molecular rearrangements, ground-state complex formation or collisional quenching [10,15-17]. There are mainly two types of quenching mechanisms in solution. The collisional quenching is due to collision between fluorophore and a quencher. The static quenching requires the formation of non-fluorescent ground-state complex between fluorophore and quencher. The fluorescence quenching process is described by the Stern-Volmer equation which allows the determination of quenching constants [10,15,18].

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Fluorescence quenching of anthracene in solution by several quenchers (halogenated alkanes, aliphatic amines, fullerene C₆₀, phenothiazine, aniline, maleic anhydride, etc) has been studied by steady-state and transient methods [19-24]. But there are few reports in the literature related to the fluorescence quenching of anthracene by nitroaromatic compounds [25]. In this paper we investigated the quenching behavior of anthracene by allyl 2,4-dinitrophenyl ether (DNE) using fluorescence spectra and electronic absorption spectra in order to evidence the nature of quenching mechanism.

2. Experimental

Ultraviolet-visible absorption spectra were carried out on a Specord 200 Analytik Jena spectrophotometer in 10 mm quartz cells. Fluorescence spectra were measured using a PerkinElmer LS55 luminescence spectrometer at room temperature in 10 mm quartz cells. The excitation wavelength was 360 nm, which corresponds to the highest absorption band of anthracene and the fluorescence signal was monitored at 404 nm. The quenching studies were performed in situ by recording the emission spectra of the anthracene solutions at various quencher concentrations.

Anthracene was purchased from Aldrich and used as received. The solvents were spectrophotometric grade. Allyl 2,4-dinitrophenyl ether (DNE) was obtained by the reaction of 1-chloro-2,4-dinitrobenzene and allyl alcohol in dimethyl sulfoxide under nitrogen atmosphere [26].

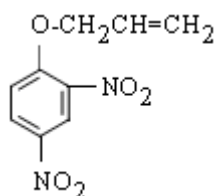


Fig. 1 Allyl 2,4-dinitrophenyl ether

3. Results and discussion

In order to establish the quenching mechanism, the fluorescence quenching data were analyzed using Stern–Volmer equation [10,15]:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} [Q] \quad (1)$$

where I_0 and I denotes the fluorescence intensity before and after the quencher (DNE) addition, respectively, k_q is the bimolecular quenching constant, τ_0 is the lifetime of the fluorophore in the absence of quencher, $[Q]$ is the quencher concentration and K_{SV} is the Stern-Volmer constant, defining the quenching efficiency.

Fluorescence quenching of anthracene by DNE was investigated in different solvents (chloroform, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol, ethanol, 1-propanol, 1-butanol) at room temperature. Fig. 2 shows the emission spectra of anthracene during quenching by DNE in ethanol solution. It can be seen that the fluorescence intensity of anthracene decreased strongly and no change in the λ_{max} of anthracene emission occurred. High value of the

quenching efficiency, defined as $\eta = \frac{I_0 - I}{I_0} \cdot 100\%$ was obtained (93%) in this case.

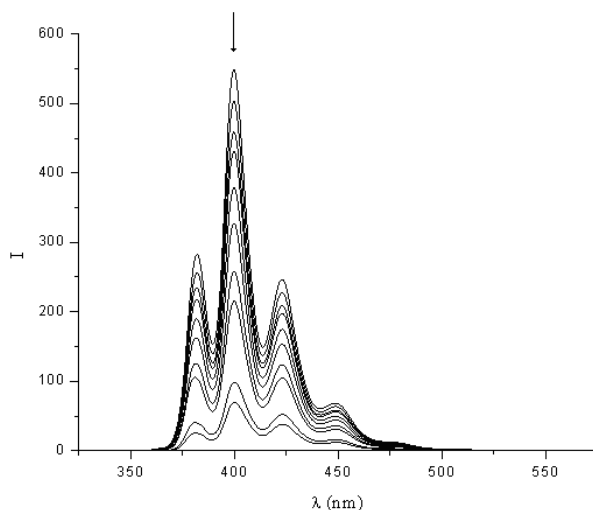


Fig. 2 Fluorescence emission spectra of anthracene in ethanol solution in presence of various DNE concentrations (0 ; $8.88 \cdot 10^{-5}$; $2.19 \cdot 10^{-4}$; $3.05 \cdot 10^{-4}$; $4.3 \cdot 10^{-4}$; $5.53 \cdot 10^{-4}$; $8.29 \cdot 10^{-4}$; $1.2 \cdot 10^{-3}$; $2.45 \cdot 10^{-3}$; $2.71 \cdot 10^{-3}$ mol/l)

Fig. 3 displays the Stern-Volmer plots of the anthracene quenching by DNE in methanol and chloroform. The Stern-Volmer plots are found to be nonlinear in all solvents under the study, showing an upward curvature toward the y-axis. Similar results for anthracene quenching were also obtained by other authors using different quenching agents [24,27].

The linearity of Stern-Volmer plot (I_0/I) versus the quencher concentration ($[Q]$) indicates generally that one type of quenching mechanism is predominating. Positive deviations from linearity of Stern-Volmer plots suggest that the quenching process simultaneously follows two mechanisms, one of which is connected with the dynamic quenching. The second mechanism is related to the static quenching by the formation of nonfluorescent complex between fluorophore and quencher in the ground state or to the presence of a quenching sphere that diminishes the fraction of fluorescing molecules [10, 28-31].

The static and dynamic quenching can be differentiated by their dependence on temperature and viscosity. With increasing temperature the quenching rate constant increase for dynamic quenching whereas the increased temperature is likely to determine lower values of the static quenching constant [10,15,32].

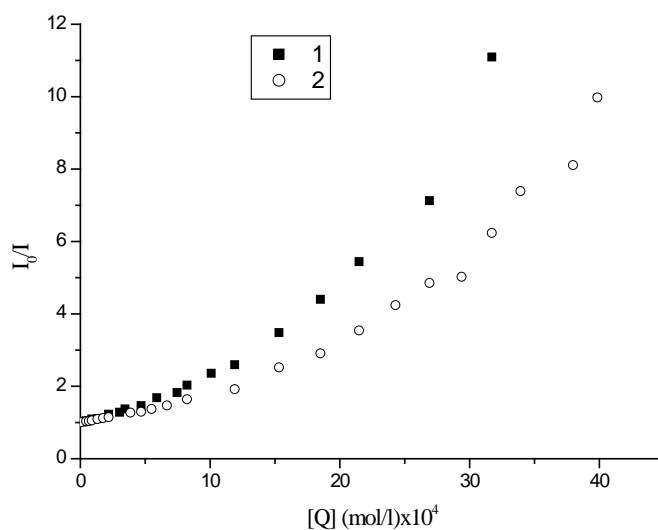


Fig. 3 Stern-Volmer plots of anthracene fluorescence quenched by DNE in (1) methanol; (2) chloroform

The Stern-Volmer constants were evaluated from the initial linear part of the quenching curve for low quencher concentrations (Table 1). The K_{sv} constant is lower for chloroform and much higher for the other solvents, especially for DMF and DMSO which reflects higher efficiency of this quencher in polar solvents. The higher K_{sv}

Table 1 Quenching data of anthracene with DNE.

Solvent	ϵ	K_{sv} (l/mol)	K_p (l/mol)	R_s (Å)	$(R_D+R_A)-R_s$ (Å)
DMF	38.25	1409.8	913.1	7.23	0.59
DMSO	47.24	1301.4	843.7	6.94	0.89
Chloroform	4.81	766.5	570.5	6.12	1.71
Methanol	33.10	1325.8	753.8	6.76	1.07
Ethanol	25.30	1144.6	723.1	6.60	1.23
1- Propanol	20.80	1163.5			
1- Butanol	17.84	1268.7			

indicates the lower concentration of quencher is needed to quench the fluorescence [10, 33]. However, the Stern-Volmer plots of anthracene quenching by DNE in solutions at different temperatures are practically identical for DMF and chloroform (Figs. 4 and 5) and the K_{sv} constants do not depend on the temperature. It must be noticed that the quenching constants, K_{sv} in alcohols and aprotic solvents have practically closely values (Table 1), although these solvents have different polarities.

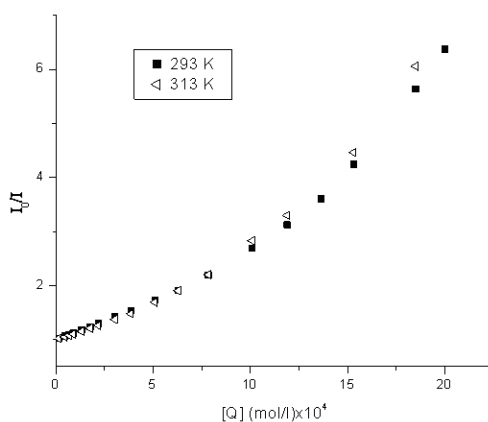


Fig. 4 Stern-Volmer plots I_0/I versus DNE concentration, $[Q]$, for anthracene in DMF at different temperatures

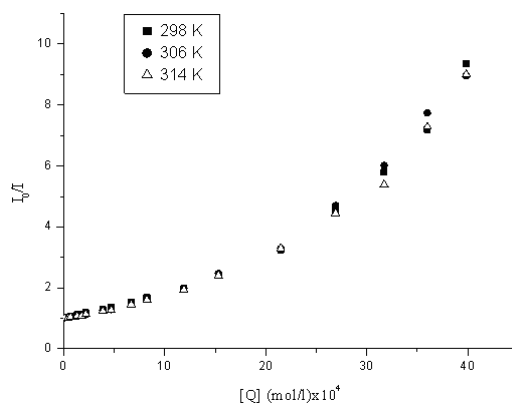


Fig. 5 Plots of I_0/I for anthracene in chloroform versus DNE concentration, $[Q]$, at different temperatures

As it seems in alcohols there are associates in which the alcohol molecules orientate so that their hydrocarbon components gather up in order to form oleophilic assemblies bounded by polar hydroxylic groups [34,35]. The hydrophobic molecules of anthracene and DNE are located in the oleophilic domains and the same quenching behavior takes place in alcohol solutions, the quenching constants having values in the closely range. The increase of temperature determines the decrease of macroviscosity of solution taking into account the weakening of bonds in polar domains and the mobility of alcoholic associates does not change with temperature increasing. In this case the quenching constants are not dependent on the temperature.

Fig. 6 shows the emission spectrum of anthracene and the UV-VIS absorption spectrum of DNE in DMSO solution. It can be seen from Fig. 6 that there is practically no overlapping between the two spectra which suggests that the energy transfer is not the way to bring about the quenching process due to the lack of the energy matching condition.

The Perrin model describes the static quenching between randomly distributed fluorophores and quenchers that are located in the proximity. In this model, one assumes that there is instantaneous quenching of an excited donor by quencher molecule, if the quencher is located inside a sphere of volume V_q around the fluorophore and there is no quenching when the quencher is outside of this quenching sphere [15,24,36].

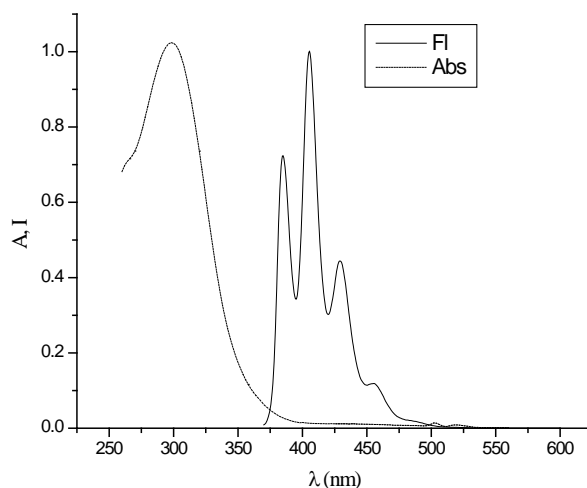


Fig. 6 Absorption of DNE and emission spectra of anthracene in DMSO

The Perrin static quenching model is described by the following equation:

$$\ln \frac{I_0}{I} = Kp \cdot [Q] \quad (2)$$

$$Kp = Vq \cdot N_A = \frac{4}{3} \pi R_s^3 N_A \quad (3)$$

where N_A is Avogadro number, I is the fluorescence intensity in the presence of quencher, I_0 is the fluorescence intensity when $[Q]=0$, R_s is the radius of the quenching sphere.

The fitting curves of the experimental data according to relation (2) are presented for different solvents in Fig. 7. The quenching constants Kp are given in Table 1. The Perrin radius was obtained from the slope of $\ln(I_0/I)$ versus $[Q]$ plots (Table 1). Also, it is noticed that the radius of the sphere of action, R_s is lower than the encounter distance $R=R_A+R_D$ (the sum of the acceptor and donor radii) in all solvents. However, the linear dependence of $\ln(I_0/I)$ on $[Q]$ was not observed in 1-propanol and 1-butanol solutions, when a deviation from linearity appeared even at beginning of quenching process.

The positive deviation from linearity of the Stern-Volmer plots can be explained by the sphere of action static quenching model [10,37-39]. According to this model, static quenching

takes place if the quencher molecule is positioned very near to or in contact with fluorophore just at the moment of its excitation and only a certain fraction W of excited state is quenched by the collisions. The remaining molecules in excited state (fraction $(1-W)$) are deactivated practically instantaneously after being excited since quencher molecule is situated in the proximity of the excited molecules and interacts with them. The probability of the quencher to be found in the sphere of action with a volume V depends on the volume V and on the quencher concentration.

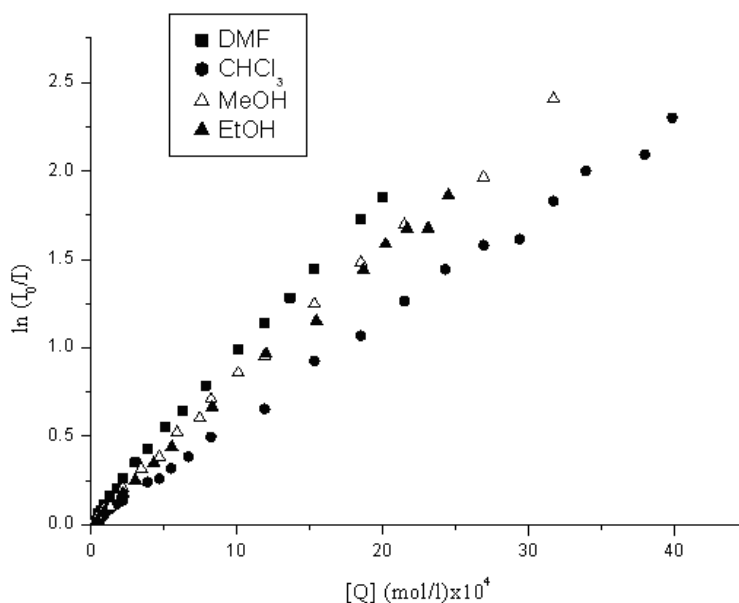


Fig. 7 Plots of $\ln(I_0/I)$ as a function of DNE concentration, $[Q]$, for anthracene solutions in different solvents

Stern-Volmer equation (1) becomes [32,40]:

$$\left(1 - \frac{I}{I_0}\right) \frac{1}{[Q]} = K_{sv}' \frac{I}{I_0} + (1-W) \frac{1}{[Q]} \quad (4)$$

$$\text{and } W = e^{-V[Q]} \quad (5)$$

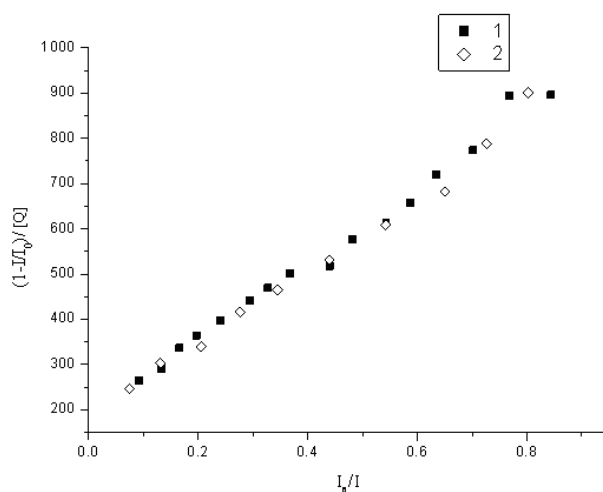


Fig. 8 Plots of $\left(1 - \frac{I}{I_0}\right) \frac{1}{[Q]}$ against $\frac{I}{I_0}$ for anthracene quenching by DNE in: (1) 1-propanol; (2) 1-butanol;

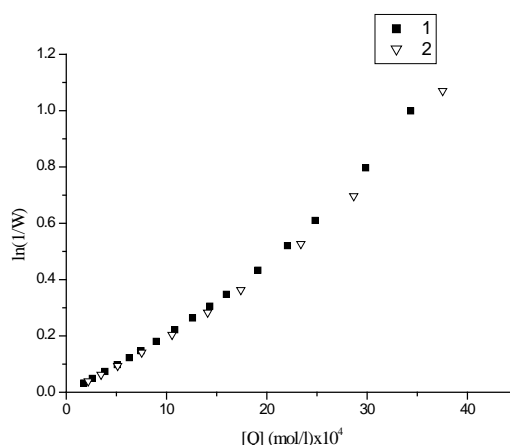


Fig. 9 Plots of $\ln(1/W)$ versus $[Q]$, eq. (5), in: (1) 1-propanol; (2) 1-butanol;

From equation (4) one can estimate K'_{SV} and values of W . V denotes the volume of the sphere of action.

Stern-Volmer plots $(1 - \frac{I}{I_0}) \frac{1}{[Q]}$ versus $\frac{I}{I_0}$ were drawn in Fig. 8 and were found to be

linear in 1-propanol and 1-butanol. The Stern-Volmer quenching constant (K'_{SV}) was evaluated by least square fit procedure using equation (4) and the values for 1-propanol and 1-butanol were 950.8 and 791.7 l/mol. From the intercepts of plot from Fig. 8, W values can be calculated for each quencher concentration. Then, from the W values, the constant V can be estimated using eq. (5), taking into account the plot $\ln(1/W)$ versus quencher concentration (Fig. 9). But in this case the plot is not a straight line. It results that the V values can not be calculated and this model can not be applied to anthracene quenching by DNE in 1-propanol and 1-butanol.

4. Conclusions

The fluorescence quenching of anthracene by a nitroderivative in different solvents was investigated by using dynamic, static and simultaneous dynamic and static quenching model. Various rate constants for the quenching process have been determined by Perrin's model (static quenching model) and depend on the solvent polarity. The nonlinearities in the Stern-Volmer plots are interpreted in term of the sphere of action defined in the static quenching model.

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