

Concentration Depolarization, Energy Transfer and Kinetics of Concentration Quenching of Fluorescence of Anthracene Sulfonates

SEKHAR BASU, A. K. GUPTA and K. K. ROHATGI-MUKHERJEE

Physical Chemistry Laboratory, Jadavpur University, Calcutta-700 032

ANTHRACENE sulfonates are known to undergo various photochemical changes like photo-oxidation¹ and photodimerization². They have also been used as singlet oxygen sensitizer³ and as suitable probes for polarity of the medium⁴. The luminescence properties of dissolved substances depend essentially on concentration. Therefore to substantiate such studies it is necessary to evaluate various parameters relating to selfquenching, if any.

Apart from trivial radiative inner filter effect, increase in the concentration of the molecules taking part in emission processes may lead to depopulation of excited state by nonradiative processes also, causing reduction in the fluorescence quantum efficiency without any drastic alteration in the fluorescence spectrum. The absorption spectrum remains unchanged but the fluorescence lifetime is reduced. Förster⁵ has identified four types of quenching mechanisms which can be characterised by the effect of concentration on fluorescence, decay times, and viscosity and temperature dependence of fluorescence efficiency. In any one system more than one mechanism may be operative, the boundaries between them being not very strictly defined.

Basically all types of quenching involve complex formation of some kind in their ground or excited states. The ground state complex formation leads to static quenching and is not truly excited state phenomenon. The complexes formed in the excited state are termed exciplexes. One of the mechanisms suggested for concentration quenching is through the formation of excimers, the dimers formed in the excited state by collision between an excited and a ground state molecules⁶.

The phenomenon was first observed in pyrene molecules⁷. Such excimers have large radiative lifetimes and enhanced nonradiative decay probabilities. The system obeys diffusion-controlled kinetics. In the other extreme is the long range resonance energy transfer mechanism of Förster. In the long range energy transfer mechanism, the migration of energy from molecule to molecule is brought about by dipole-dipole interaction and may not lead to quenching by itself. It is necessary to have an energy sink or trap. In many systems such traps are provided by trace amounts of aggregates present in solution. This is the important mechanism in plant photosynthesis where energy absorbed by antennae chlorophyll molecules is transferred to the reaction centre which is suggested

to be a chlorophyll dimer⁸. The nonradiative resonance transfer may take place at distances greater than around 15 Å. At closer distances (< 15 Å), electron exchange mechanism may become operative⁹.

The excimers may be fluorescent or non-fluorescent. The nonfluorescent excimers cause immediate quenching whereas fluorescent excimers of aromatic hydrocarbons emit at a longer wavelength shifted by about 6000 cm⁻¹ to red from the monomer band. The excimer formation is reversible and diffusion controlled phenomenon, affected by temperature and viscosity, and requires a minimum distance of approach of the order of 3.4 Å of the two partners. Nonfluorescent excimers also require close approach and hence concentration quenching is prevented in molecules with bulky substituents such as is the case for 9,10-diphenyl anthracene^{10,12}. When the interaction is strong, photodimerisation may result¹⁰. Concentration quenching may involve either decrease in the rate constant of radiative process or increase in the rate constant of nonradiative processes or both, depending upon the system under study.

Geometrical requirement for excimer formation leading to quenching is not always clear. Anthracene excimers¹¹ are known to have two types of structures (i) sandwich structure and (ii) 55° structure. The former may lead to photodimer formation whereas the latter may just cause self quenching since the geometry is not suitable for bond formation. The 55° dimer is the more stable type (Fig. 1). In the absence of photodimer formation, the excimer may relax by dissociating into two ground state molecules or by emission of

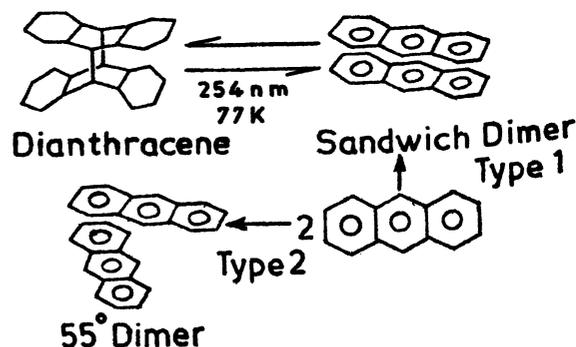


Fig. 1. Geometry of anthracene photodimer and excimer.

red shifted excimer fluorescence leading to quenching of monomer fluorescence.

The dipole-dipole energy transfer is demonstrated in concentration depolarization of fluorescence whereas collisional quenching follows simple Stern-Volmer kinetics^{1,2} expressed as

$$\frac{\phi_f^0}{\phi_f} = 1 + k_q \tau [Q] \quad \dots (1)$$

$$= 1 + K_{sv} [Q]$$

where ϕ_f^0 and ϕ_f are the quantum yields of fluorescence, in absence and in presence of quencher of concentration $[Q]$ respectively, K_{sv} is the Stern-Volmer quenching constant and k_q is the rate constant measured for bimolecular quenching process.

For a diffusion controlled process^{1,3} the rate constant of a bimolecular reaction can be expressed by the Einstein-Smoluchowski^{1,3} equation based on Fick's law of diffusion

$$k_{diff} = p \frac{4\pi NDR}{1000} \left(1 + \frac{pR}{\sqrt{\pi D \tau}} \right) M^{-1} s^{-1} \quad \dots (2)$$

The factor within the bracket accounts for the transient quenching effect and is normally of the order of unity, such that the equation reduces to a simple form

$$k_{diff} = p \frac{4\pi NDR}{1000} \quad \dots (3)$$

where D is the sum of the diffusion coefficients of the two interacting partners, $R = (r_a + r_b)$ is the sum of the two interaction radii and p is the probability of quenching per encounter. For collisional quenching, interaction radii is identified with the molecular radii, r . When the effects of electrostatic interactions due to charged species are introduced^{1,4}, the equation becomes,

$$k_{diff} = p \frac{4\pi NDR}{1000} \cdot \frac{\delta}{e^{\delta} - 1} \quad \dots (4)$$

with $\delta = Z_A Z_B e^2 / \epsilon (r_a + r_b) kT$, where ϵ is the dielectric constant of the solvent, Z_A and Z_B are the numbers of charges with proper sign on the molecules A and B respectively. In the case of concentration quenching the fluorescer and the quencher are molecules of the same kind and $R = 2r$ and $D = 2D_a$; quenching involves specific interaction to dissipate the energy along nonradiative pathways.

The quantum mechanical formulation of energy transfer by Förster^{1,5} requires that the absorption spectrum of the acceptor must overlap the emission spectrum of the donor. The efficiency of intermolecular dipole-dipole transitions may be expressed in terms of a critical transfer distance, R_0 , at which probability of transfer is equal to the probability of decay of the excited molecule by all other modes as expressed by the decay constant, $\tau = (\sum k_i)^{-1}$. From the Förster equation, R_0 is expressed as follows :

$$R_0^6 = \frac{9000(\ln 10) \kappa^2 \phi_f}{128\pi^3 n^4 N} \frac{\int_0^\infty F(\tilde{\nu}) \epsilon(\tilde{\nu}) d\tilde{\nu}}{\int_0^\infty F(\tilde{\nu}) d\tilde{\nu}}$$

in which N is the Avogadro's number; n is the refractive index of the medium κ^2 is an average orientation factor resulting from the rapid rotatory Brownian motion of the donor and acceptor ($\approx 2/3$), $\int F(\tilde{\nu}) d\tilde{\nu}$ is the fluorescence emission spectrum of the donor expressed in wavenumber and normalized to unity, $\epsilon(\tilde{\nu})$ is the molar extinction coefficient of the acceptor.

The critical transfer distance for energy transfer by dipole-dipole mechanism can be experimentally obtained from the measurements of polarization degree as a function of concentration C mol l⁻¹. The expression given by Weber^{1,6} for concentration depolarization effect is

$$\left(\frac{1}{p} - \frac{1}{3} \right) = \left(\frac{1}{p_0} - \frac{1}{3} \right) \left[1 + \frac{4\pi N R_0^6 \times 10^{-8}}{15 (2r)^3} C \right] \quad \dots (6)$$

$$\text{so that, } R_0 = (2r) \left[\frac{15 S 10^8}{4\pi N \left(\frac{1}{p_0} - \frac{1}{3} \right)} \right]^{\frac{1}{3}} \quad \dots (7)$$

where S is the slope of $\left(\frac{1}{p} - \frac{1}{3} \right)$ vs C plot and $2r$ is the molecular diameter.

Materials and method :

Anthracene 1- and 2-monosulfonates and 1,5- and 1,8-disulfonates, abbreviated as 1-AS, 2-AS, 1,5-AS and 1,8-AS, were prepared from corresponding quinones by the method described earlier¹. Glycerol (B.D.H.) was distilled twice under reduced pressure and emission impurities were checked.

Absorption spectra were measured manually by Perkin-Elmer spectrophotometer, Model Hitachi 200. The fluorescence spectra were recorded with a Perkin Elmer MPF 44 B spectrofluorimeter.

The fluorescence intensity at different concentrations of anthracene sulfonates were measured at an angle 90° to the direction of incidence in a Brice Phoenix Universal Light Scattering instrument model 1000 series, with suitable primary and secondary filters. A HP Hg-discharge lamp (85 watts), type AH-3, was used as the excitation source. 365 nm line of mercury was selected for excitation. The solutions were taken in 1 cm all side clear silica cell. The cell was covered with black paper on two adjacent sides leaving only a small opening (0.3 cm width, 0.4 cm height) in the direction of excitation as well as in the direction of observation. The edge of the cell at the joint portion was also covered with black paper to avoid scattered and reflected light. In effect, the total fluorescence was measured from the solution of volume 0.3 × 0.3 × 0.4 ml.

Such arrangement is expected to minimise error due to re-absorption and re-emission and to also diminish the area of incomplete illumination within the area of observation at high concentrations of fluorescer. As the overlap integrals of the absorption and emission spectra of these sulfonates are small, specific correction for re-absorption and re-emission

suggested by Rohatgi and Singhal¹⁷ was not applied. An interference filter (413 nm) was placed before the photomultiplier to cut off the overlap region of the emission spectrum to further minimise the re-absorption and re-emission errors in the measurement of fluorescence.

Fluorescence polarization intensities were measured in the same instrument at right angles to the direction of propagation of the incident light. The solutions in glycerol (90%) were excited by both vertically and horizontally plane polarized light of wavelength 365 nm, obtained by using polarizer supplied with the instrument. Both, horizontal and vertical components of the fluorescence light were measured by using the analyzer.

The degree of polarization (P) was determined by using the refined expression proposed by Azumi and McGlynn¹⁸.

$$P = \frac{I_{EE} - I_{EB} (I_{BE}/I_{BB})}{I_{EE} + I_{EB} (I_{BE}/I_{BB})}$$

where E represents the polarization direction with electric vector perpendicular to the plane formed by the excitation beam and the observation beam: B represents polarization direction with electric vector in the plane formed by the excitation beam and the observation beam.

Results and Discussion

The Stern-Volmer plots ϕ_0/ϕ_f vs C, for anthracene 1- and 2-mono sulfonates and 1,5- and 1,8-disulfonates in water are given in Fig. 2. For the

measurement of ϕ_f , $10^{-5}M$ solution of each anthracene sulfonate in the corresponding solvent was taken as standard. Corrections for re-absorption, re-emission, refraction and the geometry of the experimental set up was taken into consideration.

In aqueous solution the concentration quenching of all these anthracene sulfonates obeys the Stern-Volmer equation. But in glycerol solution no measurable amount of quenching was observed and the slope of the S-V plot was negligible. S-V quenching constant, K_{sv} , for concentration quenching was measured directly from the slope and the experimental rate constants for concentration quenching (k_q^{esp}) were obtained from the equation

$$k_q^{esp} = \frac{K_{sv}}{\tau} \quad \dots (8)$$

where τ is the lifetime obtained by single-photon counting technique reported earlier¹⁹. The rate constant for concentration quenching, k_q^{esp} , in aqueous solution so obtained experimentally for all the anthracene sulfonates are given in Table 1, column 5. They are of the same order as that for anthracene 9.3×10^9 , 9.7×10^9 and $11.7 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$ in benzene, chloroform and kerosene respectively obtained by Bowen *et al*¹². The low value of K_{sv} but high value of rate constant (15×10^9) for 1,8-AS is expected because of its very low lifetime ($\tau = 145 \text{ ns}$) and quantum yield ($\phi_f^0 = 0.16$) as compared to anthracene and other sulfonates. Similar observation was made by Bowen¹² for 1,5-

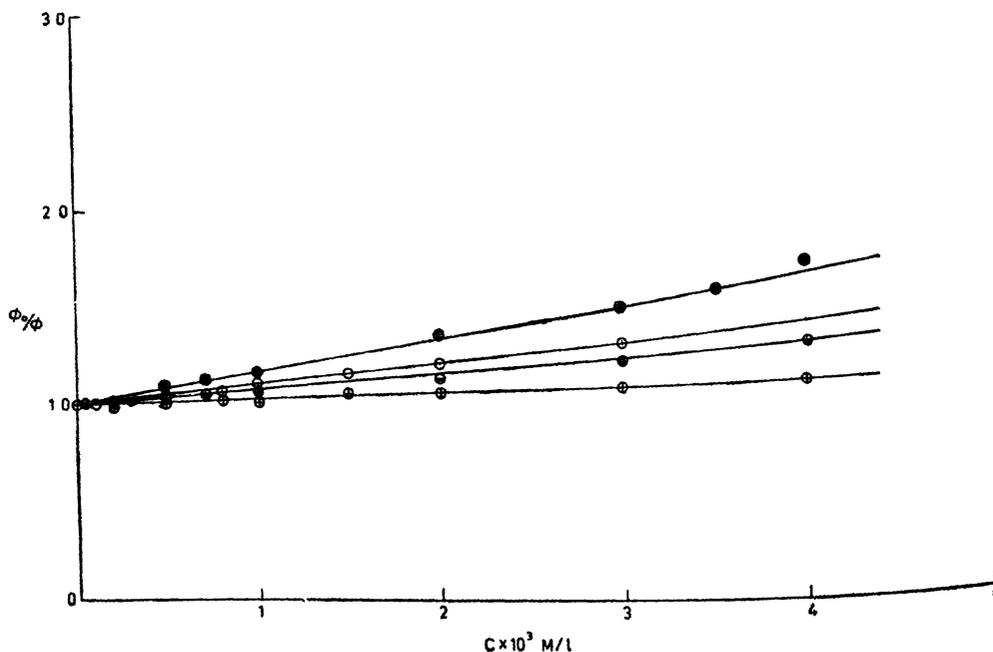


Fig. 2. Stern-Volmer plots: ϕ_0/ϕ_f vs C for different anthracene sulfonates in water at 30°.

- → 1-AS
- → 2-AS
- → 1,5-AS
- ⊗ → 1,8-AS

dichloro anthracene whose K_{sv} was found to be small ($K_{sv}=11$) mainly because of small value of fluorescence efficiency. On the other hand, K_{sv} for coronene ($K_{sv}=650$) is large because of its long lifetime in the excited state. The K_{sv} values of a number of anthracene derivatives in solvents like benzene, chloroform and kerosene are observed¹² to lie between 10 to 100 which supports the value of our experimentally determined S-V quenching constant of anthracene sulfonates. The systems under study were not deoxygenated.

For anthracene sulphonates, charge and solvent dielectric properties are also important. The quenching of 1,5- and 1,8-disulfonates is less efficient than that for 1- and 2-monosulfonates in water evidently due to two units of negative charge and consequently greater electrostatic repulsion. For 1,8-AS such repulsion is expected to be greater than 1,5-AS due to two negative charged groups at the same side of the ring. Consequently, its slope for concentration quenching is very small. Assuming concentration quenching of fluorescence of anthracene sulphonates to occur by diffusion controlled process only, a theoretical value of the rate constant can be calculated for each system using eqn. (4). The k_q^{theo} values are presented in column 6 of Table 1 for two different solvents water and glycerol. Experimental K_{sv} and k_q^{exp} obtained in water are reported in columns 4 and 5 respectively.

values. The anomaly is likely to be due to pR values which may be much larger than the assumed collision radii with $p=1$. This indicates that long range dipole-dipole mechanism of Förster type is also involved in concentration quenching. Very low calculated values of k_q^{theo} in glycerol are understandable since the probability of diffusion-controlled encounter formation will be very small in such viscous solvents.

Theoretical formalism for diffusion-controlled reaction is under scrutiny by Ware *et al*²⁰. The models have been developed²¹ which allow calculation of rate constants for systems which follow partly diffusion controlled kinetics. For the systems with excited state lifetimes shorter than 100 ns and in conventional solvents, nonstationary processes also become important which require apparent rate constants to become time dependent. The classical expression for apparent rate constant $k(t)$ is then expressed as

$$k(t) = p4\pi D\sigma N^2 \left[1 + \frac{\sigma}{(\pi Dt)^{1/2}} \right] \quad \dots (9)$$

where σ = encounter distance and $D = D_a + D_b$. The term within the bracket, which corrects for the transient quenching, will become important for times shorter than σ^2/D or near this value. At times much longer than this, $k(t)$ is approximately equal to $4\pi N\sigma D$, and steady state diffusion takes place.

TABLE 1

Compound	$\phi_f^{(a)}$	τ ns Single photon method	$K_{sv}^{(b)}$ l mol ⁻¹	$k_q^{exp} \times 10^{-9} (c)$ l mol ⁻¹ s ⁻¹	$k_q^{theo} \times 10^{-9} (d)$ l mol ⁻¹ s ⁻¹
(1)	(2)	(3)	(4)	(5)	(6)
1-AS	0.25	7.30	80(W)	10.9(W)	2.6 (W) 0.0044 (G)
2-AS	0.40	4.50	50(W)	11.1(W)	2.6 (W) 0.0044 (G)
1,5-AS	0.26	3.22	27(W)	8.3(W)	1.24 (W) 0.0002 (G)
1,8-AS	0.16	1.46	22(W)	15.0(W)	1.24 (W) 0.0002 (G)

(a) A. K. Gupta and K. K. Rohatgi-Mukherjee, Ref. 3.

G - glycerol, W - water

(b) Calculated from equation (1), (c) Calculated from equation (8),

(d) Calculated from equation (4), using r (1-AS and 2-AS) = 4.27 Å and r (1,5-AS and 1,8-AS) = 4.63 Å; D (1-AS and 2-AS) = 6.4×10^{-9} cm²/sec in water and 8.1×10^{-9} cm²/sec in glycerol and D (1,5-AS and 1,8-AS) = 5.9×10^{-9} cm²/sec in water and 7.50×10^{-9} cm²/sec in glycerol.

The experimental values of rate constant for anthracene sulfonates are higher than the theoretical values measured for the diffusion controlled limiting expression including charge effect as shown in Table 1. These differences may be expected due to the value of ' r ' which may still need some correction as solvation effect has not been taken into consideration. The value of diffusion co-efficient calculated from r value obtained by density data also introduce some error. There may be some error due to re-absorption re-emission phenomenon.

These corrections, however, cannot explain the large differences in theoretical and experimental

The instantaneous rate constant is then time independent. For 1-AS

$$\tau_0 = \frac{\sigma^2}{2D_a} = \frac{(8.54)^2 \times 10^{-16} \text{cm}^2}{2 \times 0.64 \times 10^{-9} \text{cm}^2 \text{s}^{-1}} = 5.7 \times 10^{-10} \text{s} \quad \dots (10)$$

The lifetime of 1-AS, $\tau = 7.4 \times 10^{-9}$, is greater than this critical time τ_0 by an order of magnitude. The transient term may not contribute much to the overall rate constant. If at all, the transient term may have some contribution to make for 1,5-AS and 1,8-AS whose lifetimes are 3.22 and 1.46 ns, respectively. The values of $\left(1 + \frac{p\sigma}{\sqrt{\pi D\tau}}\right)$, assuming $p=1$,

$\sigma=2r$ and $D=2D_a$, are 1.16, 1.20, 1.30 and 1.45 for 1-AS, 2-AS, 1,5-AS and 1,8-AS respectively.

On expanding the equation (9), we obtain

$$k=4\pi N'D(p\sigma) + \frac{4\pi N'D}{\sqrt{\pi D\tau}}(p\sigma)^2$$

which when multiplied throughout by the lifetime τ becomes

$$k\tau=4\pi N'D(p\sigma)\tau + \frac{4\pi N'D}{\sqrt{\pi D\tau}}(p\sigma)^2\tau$$

$$K_{sv}=4\pi N'D\tau(p\sigma)+4N'\sqrt{\pi D\tau}(p\sigma)^2$$

On rearranging and introducing the charge factor

$B\left(\frac{\delta}{e^{\delta}-1}\right)$ a quadratic equation is obtained:

$$4N'\sqrt{\pi D\tau} B(p\sigma)^2+4\pi N'D\tau B(p\sigma)-K_{sv}=0$$

which is of the form

$$ax^2+bx+c=0 \text{ where } x=p\sigma \text{ and is given by}$$

$$x=\frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

and $a=4N'B\sqrt{\pi D\tau}$, $b=4\pi N'D\tau B$, $c=-K_{sv}$

The values of $p\sigma$ so calculated are reported in Table 4, column 2. The values 7.43 Å, 13.5 Å, 32.2 Å and 40.7 Å for 1-AS, 2-AS, 1,5-AS and 1,8-AS are far different from kinetic collision radii.

On the other hand, the critical transfer distance R_0 between molecules fixed in position in viscous medium can be calculated from spectroscopic data using Förster equation¹⁵. Assuming $\langle \kappa^2 \rangle = 2/3$ which implies that the rotational lifetime for the solute molecules is much smaller than the actual radiative lifetime τ , the values of R_0 in Å and critical concentration C_0 in mol per litre are given in Table 2. C_0 values were calculated from the relationship

$$C_0 = \frac{1}{V_0} = \frac{3000}{4\pi R_0^3 N_0}$$

TABLE 2

Compound	$J(\nu) \times 10^{15}$ $M^{-1} cm^2$	R_0 Å	$C_0 \times 10^3$ M/l
1-AS	13.56	19	5.7
2-AS	14.63	20	4.9
1,5-AS	15.61	19	5.7
1,8-AS	7.35	17	8.0

assuming R_0 to be the radius of a sphere with the excited molecule in the centre and only one quencher molecule within the sphere. The overlap integral was calculated graphically with the help of planimeter (Fig. 3).

R_0 values were also calculated from the data of concentration depolarization of anthracene sulphonates in glycerol solution. The plot of $(1/p_0-1/3)$ vs C according to Weber's equation (7) is shown in Fig. 4. The slope S of the straight line and R_0 values derived therefrom are given in Table 3.

TABLE 3

	1-AS	2-AS	1,5-AS	1,8-AS
$(1/p_0-1/3)$	32	24	15	7
$S \times 10^{-4}$	20.06	19.01	5.83	3.05
R_0 (Å)	45	46	43	44

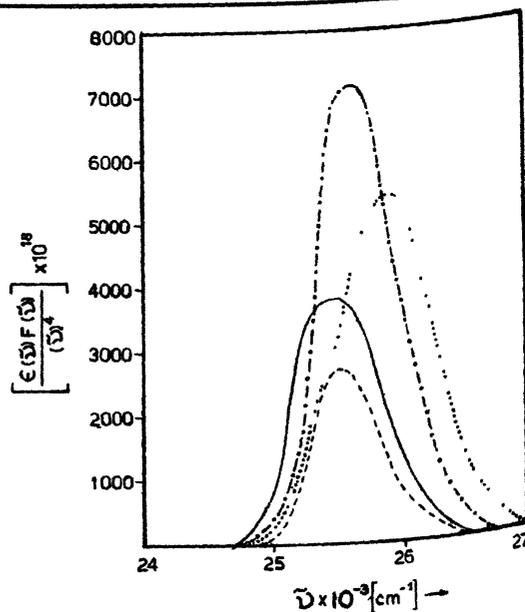


Fig. 3. Plots of $\epsilon(\tilde{\nu})F(\tilde{\nu})/\tilde{\nu}^4$ vs $\tilde{\nu}$ for different anthracene sulphonates. $\epsilon(\tilde{\nu})$ is the molar extinction coefficient at wave number $\tilde{\nu} \text{ cm}^{-1}$ and $F(\tilde{\nu})$ is the relative fluorescence quantum intensity at wave number $\tilde{\nu} \text{ cm}^{-1}$.

— 1-AS
 2-AS
 - - - - 1,5-AS
 - - - - 1,8-AS

According to dipole-dipole mechanism, the critical transfer distance R_0 in a solution is calculated on the assumption that the solute molecules are statistically distributed and fixed in a medium of infinite viscosity, so that energy transfer is a much faster process than mass transfer and rotational randomisation is complete. The spectra were measured in aqueous solution and the R_0 values were defined for 50% transfer efficiency. On the other hand, the R_0 values calculated from concentration depolarization data are much higher than those calculated from spectroscopic data. Such discrepancy has been observed previously also and has been discussed by Kawski²². Concentration depolarization arises due to hopping of excitational energy over molecules of different orientations before finally impinging on the photomultiplier detector. In the process, original orientation is lost leading to depolarisation. The effect increases with concentration. If rotational depolarization is superimposed on concentration depolarization, observed depolarization degree will be much higher. At the same time concentration quenching will reduce the radiative lifetime and decrease the depolarization degree. A large value

of R_0 will also be obtained when diffusion occurs along with energy transfer, i.e., the molecule is free to diffuse and transfer energy. The influence of diffusion on dipole-dipole transfer from anthracene to anthranilic acid in alcohols of various η have been studied by Elkana *et al.*²³. In the most viscous solvent (glycerol) they found an unexpected discrepancy between the values of R_0 , 27 Å obtained from energy transfer data and 22.4 Å obtained from spectroscopic data. They have shown that there is a variation of intermolecular distance between donor and acceptor, as a result of Brownian motion, during lifetime of the excited state. Theoretical approach to the problem of diffusional energy transfer is a field of active research^{20, 21, 24}.

The diffusion length $\sqrt{2D\tau}$, based on random walk model²⁴ for these molecules in aqueous solution and in glycerol are given in Table 4, column 5. The diffusion lengths in glycerol lie within 1.0 Å to 0.4 Å only i.e., the molecules are virtually fixed in position although Brownian movement of rotation is complete. In aqueous solutions $\sqrt{2D\tau} > R_0$, diffusional motion is considerable. All the data are collected in Table 4.

TABLE 4

	n_0 in Å	R_0 (Förster) in Å	R_0 depolariza- tion in Å	$\sqrt{2D\tau}$ in Å	$\sigma + \sqrt{2D\tau}$ in Å
1-AS	7.43	19	45	30	37.4
2-AS	13.50	20	46	24	37.5
1,5-AS	32.20	19	43	19	51.2
1,8-AS	40.70	17	44	13	53.7

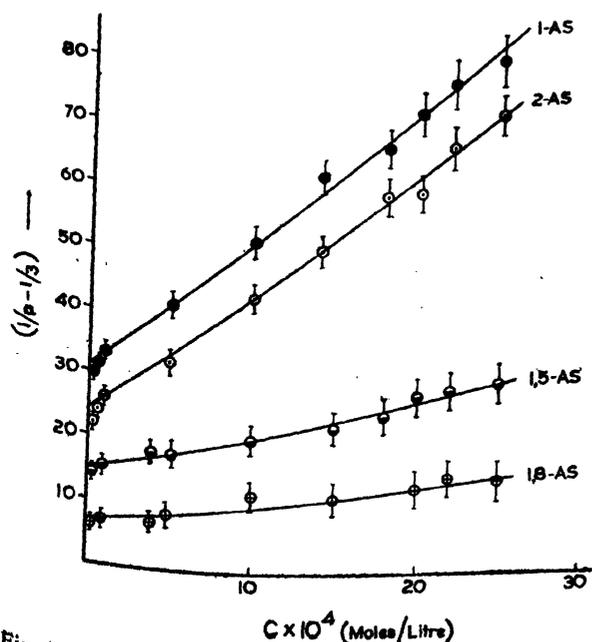


Fig. 4. Plots of $(1/p - 1/3)$ vs C for different anthracene sulphonates in 80% glycerol-water mixture at 30°.

The two situations, the reactions controlled by diffusion and the reactions controlled by resonance energy transfer, are examples of two extreme conditions: (i) the diffusional mixing is complete and the system obeys S-V kinetics and (ii) the molecules are fixed in position and energy transfer occurs by resonance interaction, Förster kinetics is valid. It is observed that concentration quenching is negligible in glycerol solution, the slope of S-V plot is nearly zero. This observation goes against the hypothesis of quenching by energy transfer. Normally one does not expect quenching when energy migrates from one molecule to another of the same kind. The concentration quenching in chlorophyll, which also shows much higher rate constant for quenching than that predicted by diffusion controlled mechanism, has been recently explained by Beddard and Porter^{25, 26} assuming quenching by energy transfer to those statistical pairs which are approximately 10 Å apart at the instant of excitation. The quenching occurs through excimer formation within such statistical pairs. Anthracene and their derivatives are known to form dimers and excimers¹⁰. Various substituted anthracene sulphonates also form photodimers although with low efficiency in deaerated solutions⁹. The low efficiency of photodimerization is likely to arise because of steric hindrance to sandwich configuration due to bulky SO_3^- groups but quenching may occur in nonsandwich configurations. If this mechanism is valid, there should be quenching in glycerol solution also. The life of such statistical pairs should be greater in viscous solvent as compared to a solvent of low viscosity. That energy transfer does occur between anthracene sulphonates is definitely established by concentration depolarization studies. These studies predict large critical transfer distances.

Concentration depolarization studies do not differentiate between transfer by single step or by a number of steps. The transfer distance from spectroscopic data using Förster equation is based on one step transfer. When $\tau_D^* > \tau_{ET}$ energy migration by excitation hopping creates a statis-

tical distribution of excited centres $A^* + A \xrightarrow{k_{ET}} A + A^*$, with k_{ET} as the energy migration rate constant, Stern-Volmer kinetics can still be applied²⁷. Since the experimental S-V plots are good-linear straight lines in all the systems, the interpretation of the data should be based on combined effect of diffusional quenching and excitation hopping. The non-radiative traps for quenching by energy transfer is likely to be ground state dimers which may be present in very trace amounts and hence not detectable spectroscopically. Yuen *et al.*²⁸ has proposed a revised mechanism of concentration quenching in chlorophyll using the dimers as the energy traps. The existence of dimers and higher aggregates was established by very sensitive difference spectroscopy. The absence of quenching in glycerol solution is then due to inhibition of diffusional quenching due to high viscosity and

inhibition of quenching by energy transfer due to nonformation of aggregates. The flat anthracene moieties with hydrophilic substituent $-\text{SO}_3$ can form aggregates. Specially for 1,5-AS which has highest solubility amongst the sulfonates under study the observation is that for concentration variation between 10^{-3} – 10^{-2} M, the fluorescence spectra remain unaltered in intensity and shape presumably due to aggregate formation². Aggregate formation in naphthalene sulphonate has been established by light scattering studies²⁹.

On examining the experimental value of $p\sigma$ derived from concentration quenching data, (Table 4, column 2), the values for monosulphonates are less than 15 Å. Assuming $p=1$, the interaction radii, $p\sigma$, is 7.5 Å for 1-AS and 13 Å for 2-AS, suggesting short range quenching by exchange mechanism. The energy dissipation within the encounter complex can be brought about through perturbation of energy levels of colliding partners which can promote forbidden transitions, hidden under the allowed energy state, by vibronic coupling. But for disulphonates, the large values of $p\sigma$ envisage long range energy transfer. Since the lifetimes of the molecules τ_D^* are small, a hopping mechanism may be assumed before being trapped by a ground state dimer. Answer to the question as to why should monosulphonates and disulphonates should differ in the quenching step is not apparent immediately. Another interesting observation is that the experimental values of $p\sigma$ and diffusion-lengths $\sqrt{2D\tau}$ add up to constant values which is 37.5 Å for monosulphonates and 52.5 Å for disulphonates. An explanation for this is also not available. In disulphonates, two units of negative charge present an electrostatic barrier to close approach recommending long range interactions, whereas monosulphonates can manage to come close together with specific orientation. The ground state dimers may be mere stacked species held together by π - π^* interaction or hydrogen bonded through $-\text{SO}_3$ groups and water molecules. Quenching by 55° dimers is also a possibility. Furthermore, in concentrated solutions the average orientation factor κ^2 may not be completely randomised³⁰ specially so in cases of the charged species.

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