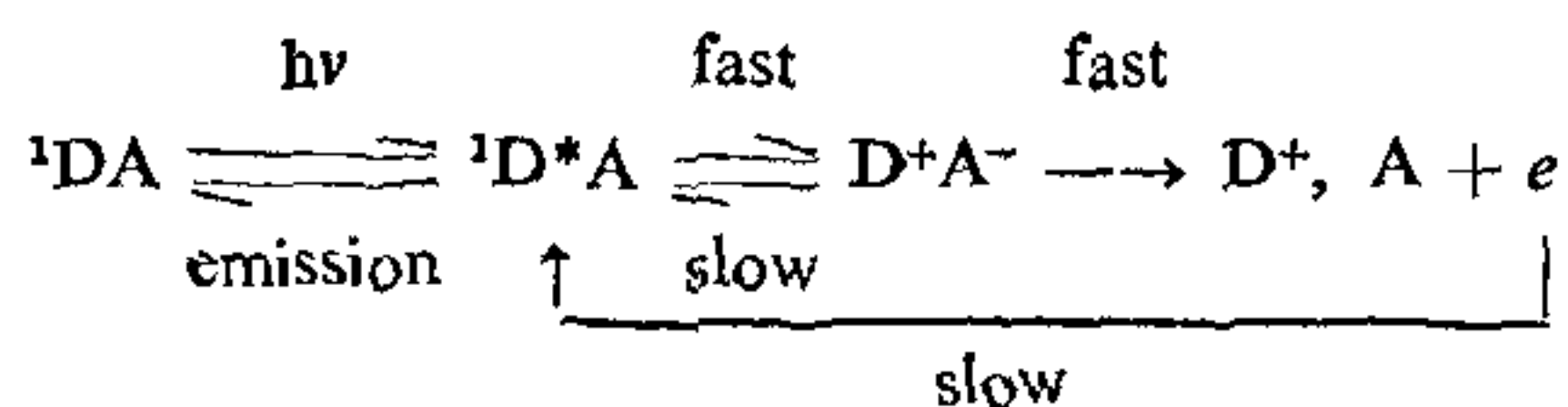# LETTERS TO THE EDITOR

## RECOMBINATION DELAYED FLUORESCENCE OF 9-AMINO ACRIDINE HYDROCHLORIDE

P. GANGOLA, N. B. JOSHI* AND D. D. PANT

Department of Physics, D.S.B. College
Kumaun University, Nainital 263 003, India

*Present address: Department of Biophysics,
Michigan State University, East Lansing, Michigan,
U.S.A.

DELAYED fluorescence (DF) of polyatomic molecules in rigid media arises due to a variety of mechanisms. The population of excited singlet state by thermal activation of triplet state is responsible for E-type DF, whereas a triplet-triplet annihilation process gives rise to p-type DF[1,2]. A third type of DF is attributed to the recombination of radical ions and matrix trapped electrons produced by the photoionization of molecules[2,3].

The photoionization of aromatic molecules in rigid glasses has been known for a long time[4], however, the first reported observation of recombination type DF was made by Lim and co-workers[5] in alcoholic glasses of acriflavine at 77 K. It was shown that a one photon ionization led to DF. In a later communication[6] the authors interpreted the phenomenon in terms of the following scheme which is due to Meyer and Albrecht[7]—

$$^{1}DA \underset{\text{emission}}{\overset{h\nu}{\rightleftharpoons}} \,^{1}D^{*}A \rightleftharpoons D^{+}A^{-} \longrightarrow D^{+},\ A + e$$

(with "fast", "fast", "slow", "slow" labels)

According to this scheme the primary photochemical process for the photoionization is the transfer of an electron from an electronically excited dye molecule $^{1}D^{*}A$ (surrounded by solvent molecules A) to the lowest vacant orbital of suitably oriented solvent molecule resulting in a charge transfer state. The CT state can revert back to the excited singlet or can dissociate to give radical ion and electron to be trapped at a more stable site. With small thermal activation, the trapped electrons and radical ions then recombine to produce an excited singlet state of dye molecule giving rise to DF. Recombination DF produced by two-photon ionisation has also been reported in some cases, the second photon being absorbed by the molecule in the lowest triplet state[3,7,8].

During the course of an investigation on the dimer and excimer emissions of 9-amino acridine hydrochloride[9], we observed that the dye also exhibits a delayed fluorescence in ethanol : methanol glass at 80 K. We wish to report here that the ion-electron recombination mechanism is operative in the present case.

Emission spectra were recorded by means of a SPM-2 Carl-Zeiss Jena monochromator and RCA 1P21 photomultiplier system. Exciting light was selected from a 125 W high pressure mercury lamp using interference and colour filters. A rotating disc phosphoroscope was used to separate delayed emission from prompt fluorescence. The decay curves were obtained by using a mechanical phosphoroscope and the intensity *versus* time display was analysed on a 502-Tektronix oscilloscope.

9-amino acridine hydrochloride (Fluka AG) was purified by repeated crystallization. The purity was checked by chromatography, emission and absorption spectra. Ethanol : methanol (1 : 1) mixture was used as solvent. The alcohols were purified as usual.

The prompt fluorescence and the long lived emission spectra of 9-amino acridine hydrochloride in ethanol : methanol glass at 80 K are shown in Fig. 1. The long lived emission consists of normal phosphorescence and delayed fluorescence having the following characteristics:

(i) The spectral distribution of DF is similar to prompt fluorescence except for an intensity shift towards low frequency vibronic bands.

(ii) The intensity of delayed fluorescence ($I_{DF}$) is found to depend on the solute concentration. Although phosphorescence intensity ($I_{p}$) enhances in concentrated solutions[‡], $I_{DF}$ diminishes and no DF is observed with concentrations exceeding $1 \times 10^{-3}$ M (Fig. 2).

(iii) $I_{DF}$ relative to $I_{p}$ is much smaller with 435 nm excitation than with more energetic 365 nm excitation (Fig. 1).

(iv) $I_{DF}$ varies linearly with the intensity of exciting light indicating a one photon process to be operative in the DF mechanism.

(v) The decay of DF at 80 K is found to be almost exponential except for the initial part, however, at 150 K DF decay is faster with more non-exponential character (Fig. 3).

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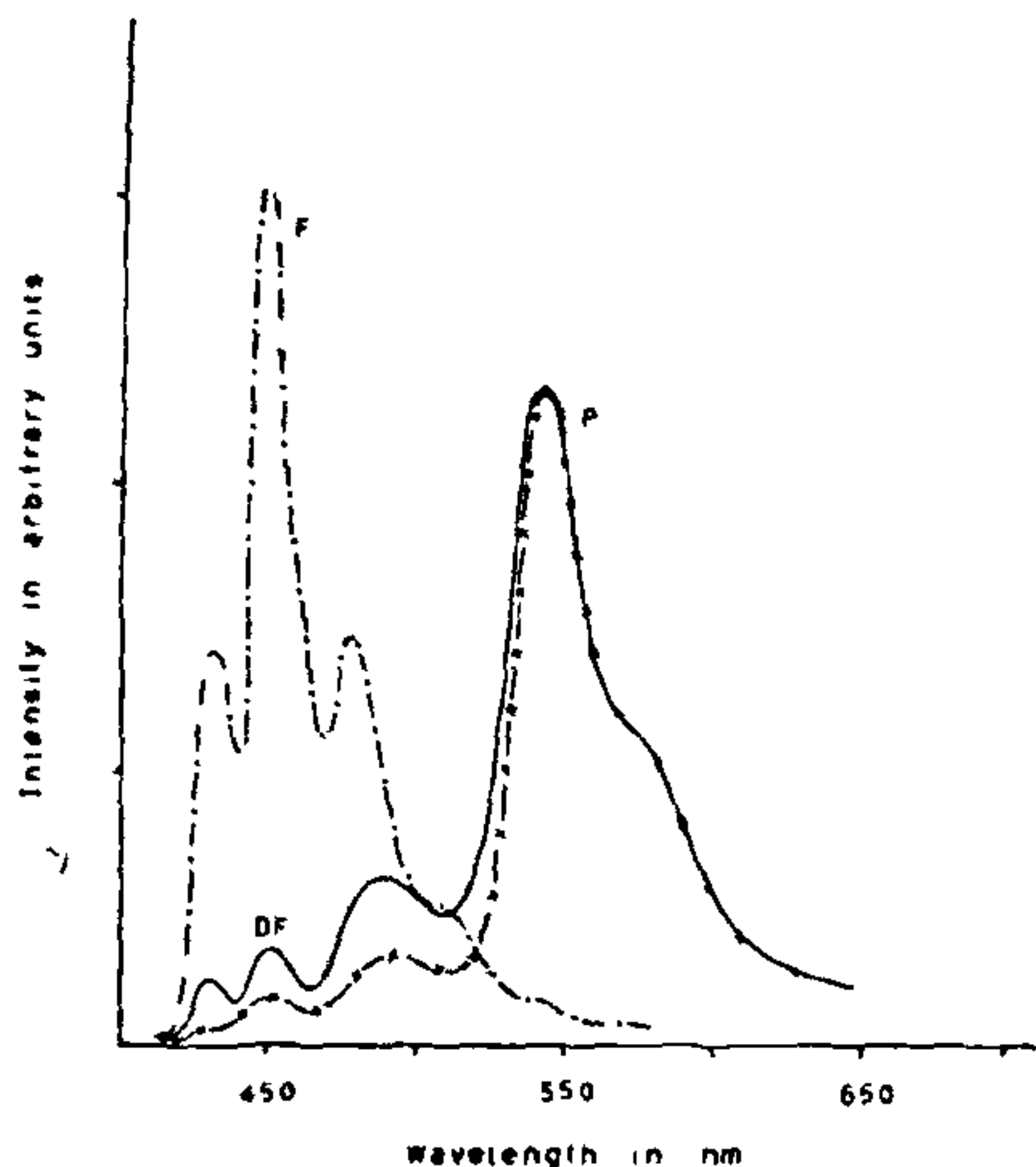‡ The red shift in phosphorescence band is due to dimer formation[9].

Fig. 1. Prompt fluorescence (F), delayed fluorescence (DF) and phosphorescence (P) of a $5 \times 10^{-5}$ M solution of 9-amino acridine hydrochloride in ethanol: methanol at 80 K.

$\lambda_{ex} = 365$ nm for (— · — · —) and (———), 435 nm for (— × — × —).



Fig. 3. Temperature dependence of DF decay of $5 \times 10^{-5}$ M solution excited at 365 nm. (a) 80 K, (b) 150 K.
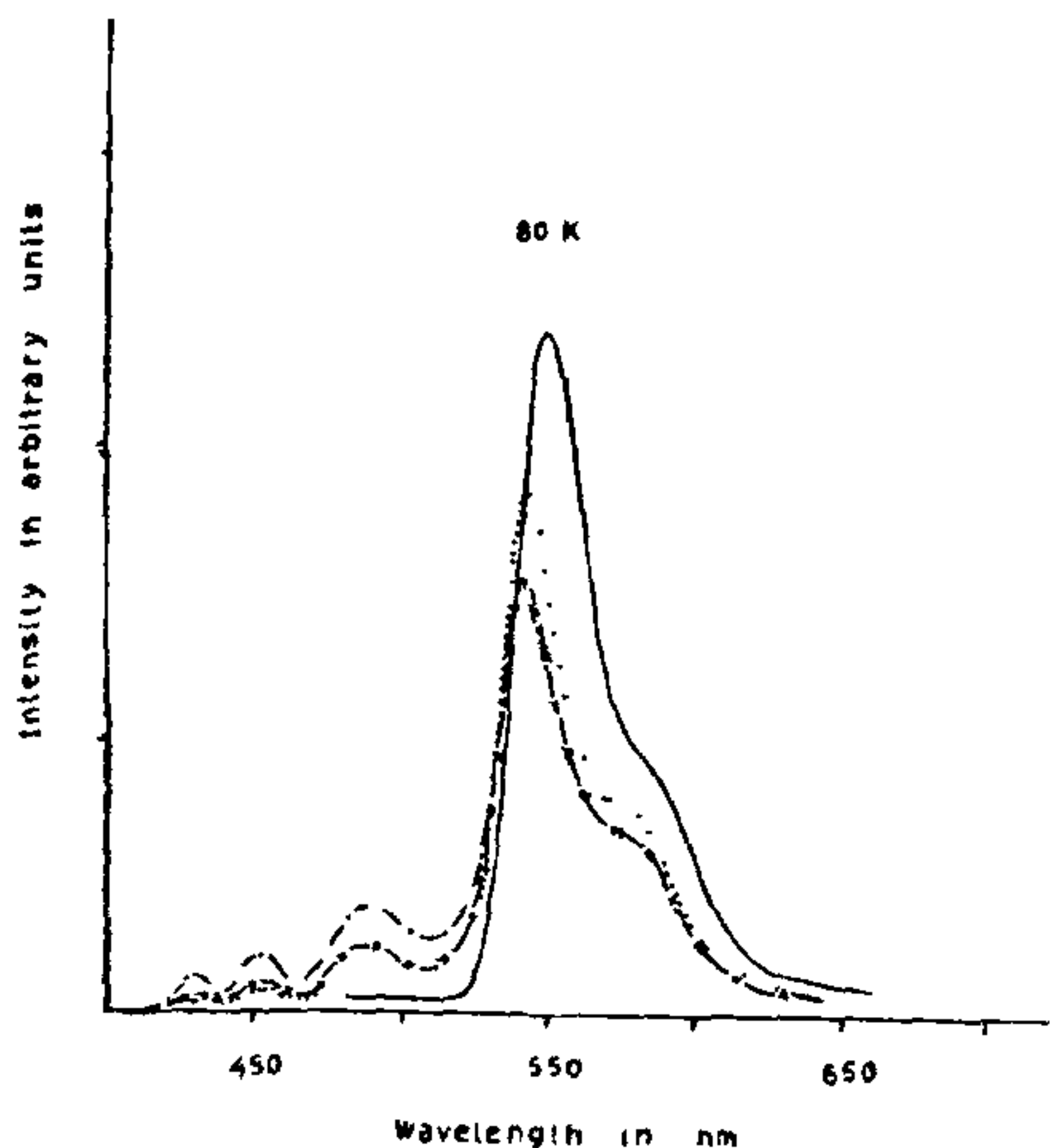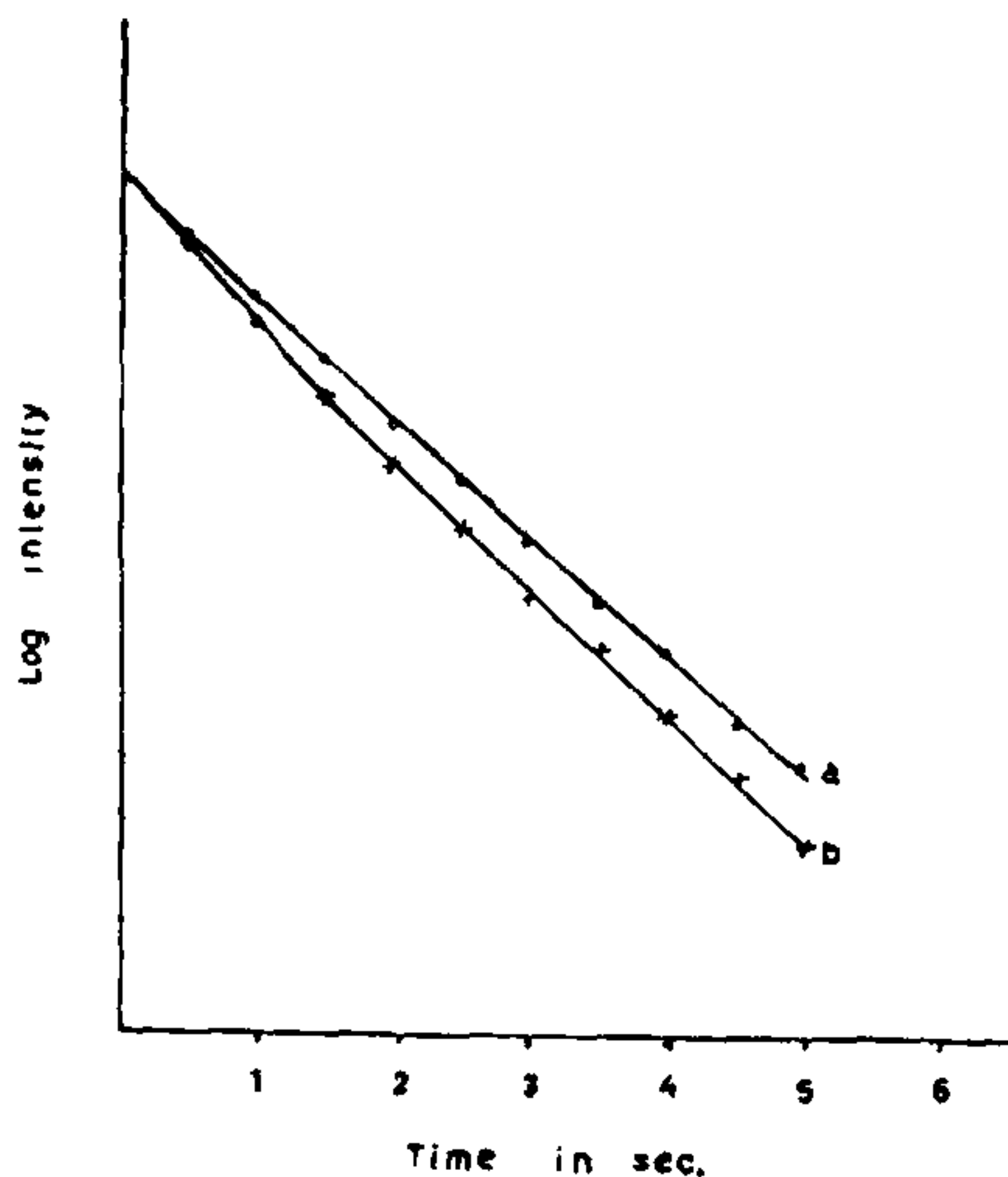


Fig. 2. Effect of concentration on delayed fluorescence and phosphorescence excited by 365 nm radiation. (— · — · —) $5 \times 10^{-5}$ M, (— × — × —) $1 \times 10^{-4}$ M, (......) $1 \times 10^{-3}$ M, (———) $5 \times 10^{-2}$ M.
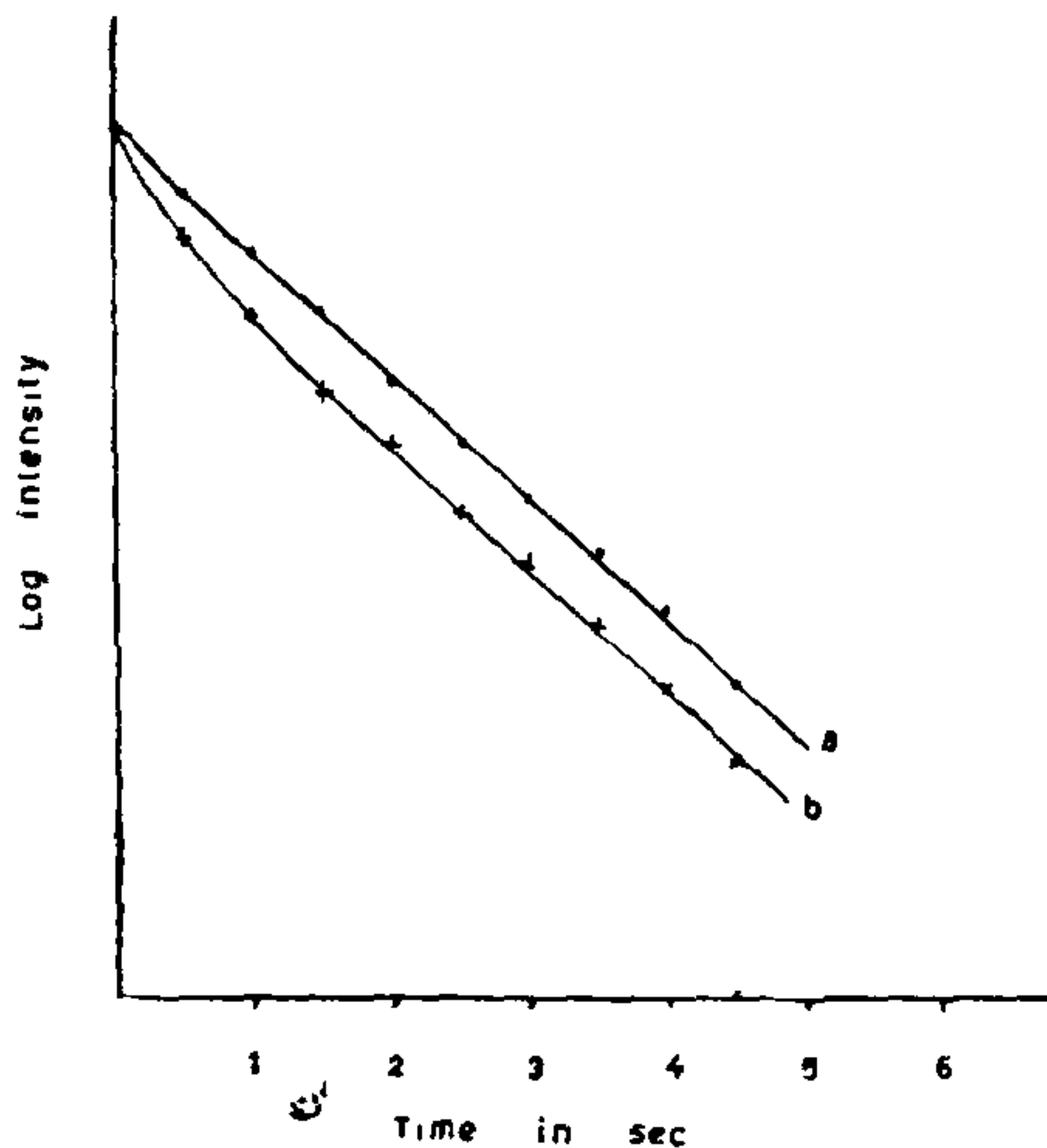


Fig. 4. Concentration dependence of DF decay at 80 K. (a) $5 \times 10^{-5}$ M, (b) $1 \times 10^{-3}$ M solutions excited by 365 nm radiation.

(vi) In concentrated solutions also the decay rate is faster and non-exponential (Fig. 4).

(vii) The decay curve for phosphorescence is completely exponential even though a faster rate is observed in concentrated frozen glass.

(viii) The DF decay time is greater than the phosphorescence decay time of the same sample (for a $5 \times 10^{-5}$ M solution $\tau_{DF} = 2 \cdot 6$ sec, $\tau_P = 2 \cdot 2$ sec).

E-type DF which represents a thermal activation of triplets to the lowest excited singlet state cannot be involved since the DF is observed at 80 K at which temperature thermal activation is energetically not probable.

If the triplet-triplet annihilation process was involved, DF would show a biphotonic nature with $I_{DF} \alpha I_p^2$ and $\tau_{DF} = \frac{1}{2} \tau_P$. As mentioned earlier in a series of experiments with increasing solute concentration, the phosphorescence intensity increases whereas DF shows a decrease. This observation along with $\tau_{DF} > \tau_P$ and monophotonic nature of DF rules out the triplet-triplet annihilation as well as any other mechanism which includes the participation of triplet state.

The results obtained here, however, suggest that the excited singlet state giving rise to DF is generated by the recombination of radical ions and trapped electrons originally produced by the one photon ionization of the dye, as also observed in some other acridine dyes[5,6,10]. This recombination will give rise to a simple exponential decay as observed. The initial faster decay is due to the reversal of the CT state.

The decrease in intensity and decay time of DF with increasing concentration can be explained to be due to increase in columbic attraction between the charged cation and the trapped electron, which abbreviates the storage time of the electrons in the traps. Similarly, with increasing temperature the thermal motion decreases the storage time of electrons and a faster decay is observed. The increase in $I_{DF}$ with 365 nm excitation is obviously due to enhanced photoionization of the molecule with more energetic radiation.

The slight anomaly in the intensity distribution of DF cannot be explained in a normal way. It is possible that the molecule formed on recombination in the excited state may slightly be perturbed, compared to a relaxed molecule emitting prompt fluorescence.

*May 1, 1981.*

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## PHOTOELECTROCHEMICAL CONVERSION OF LIGHT USING ELECTRODES COATED WITH POLYMER FILM CONTAINING THIAZINE DYE

R. Tamilarasan and P. Natarajan

Department of Chemistry, University of Madras
Autonomous Post-Graduate Centre
Tiruchirapalli 620 020, India

THIONINE condensed with poly(N-methylolacrylamide) produces a water insoluble film which can be coated on to a platinum electrode. Irradiation of the coated platinum electrode using a tungsten lamp produces an open circuit photopotential of 32 mV and short circuit current of $3 \cdot 7 \mu A$. The direction of current flow in this type of cell is reversed compared with the well-known thionine-Fe(II) photogalvanic cell which shows that the irradiated platinum electrode functions as a photocathode. The cathode reaction is suggested to be

$$[\text{Semithionine} - \text{Fe}]^{++} + e \rightarrow \text{Semithionine} + \text{Fe}^{2+}$$
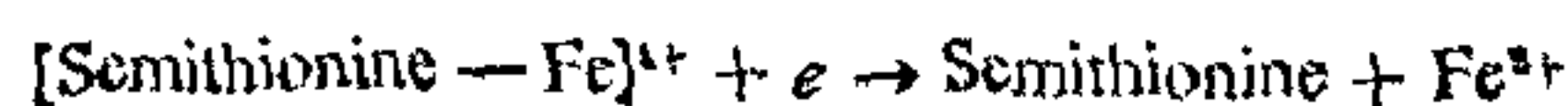
$Fe^{2+}$ ions produced at the anode combines with semithionine to give thionine and ferrous ion back.

The power output of the cell is comparable to that of the Totally Illuminated Thin Layer cell using $SnO_2$ as the anode. The advantage in this cell is that light is absorbed by the film only without any thionine in the solution. The coating procedure is simple with no need for electro-deposition or vacuum coating.

*Introduction*

The photoredox property of Iron(II)-Thionine (TH) system is widely studied due to its utilization in photo-