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# Absorption & Fluorescence Spectra of Phenosafranin in Aqueous Solutions in Presence of Alkylamines

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While the absorption spectra of phenosafranin (PFS) in aqueous solutions are not appreciably perturbed in the presence of alkylamines, indicating no molecular interaction between PSF and amines, the fluorescence of PSF is quenched in the presence of all the alkylamines studied. The Stern-Volmer constants ($K_{sv}$) for fluorescence quenching are correlated with the ionization potentials of the amines. The results have been interpreted in terms of charge-transfer interaction between PSF as an electron acceptor and the alkylamines as electron donors.

Photovoltage generation in systems consisting of phenosafranin (PSF) and a series of alkylamines in aqueous solution increases with decreasing ionization potentials of the amines confirming the charge-transfer (CT) interaction between PSF and amine in one of the intermediate steps[1]. One of the mechanistic steps in the photovoltage generation of PSF-EDTA system involves CT interaction between PSF (electron acceptor) and EDTA (electron donor) and this has been confirmed spectrophotometrically[2]. The CT interaction of amines as electron donors with some dyes such as methylene blue, thionine and toluidine blue has been reported[3,4]. The fluorescence quenching of acridine dye by amines in aqueous solutions[5] and of acridine orange[6] by N,N-dimethylaniline, nitrobenzene, *s*-trinitrobenzene and tetracyanoethylene has been reported and explained in terms of exciplex formation[5] and CT interaction, respectively.

To confirm the possible molecular interactions between PSF and alkylamines, presently the absorption and fluorescence spectra of PSF have been studied in aqueous solution containing different alkylamines and the results are reported here.

Phenosafranin (PSF) (Sigma Chemicals, USA) was purified chromatographically, recrystallized from ethanol-water and its purity checked. All the alkylamines used (BDH/E Merck/Fluka) were of AR grade and were fractionally distilled before use.

Absorption spectra were recorded on a Perkin-Elmer model 200 spectrophotometer with a pair of matched silica cells of 1 cm optical pathlength. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44B spectrofluorimeter (excited at 520 nm, the absorption maximum of PSF dye in aqueous solution) with automatic recorder using silica cell of 1 cm optical pathlength. The photomultiplier tube (model R 446F of Hamamatsu Corporation, Japan) was sensitive to both the red and blue regions of the visible spectrum. All measurements were done with freshly prepared solutions.

The UV-visible spectra of PSF in aqueous solution are slightly perturbed in the presence of alkylamines with a little shift in the absorption maximum. There is no specific interaction between PSF and amines as the spectrophotometric data do not yield any equilibrium between them. Therefore, the marginal change of absorption spectra of PSF in presence of amines can only be explained on the basis of medium effect, i.e, the change of refractive index of solution.

Figure 1 shows the fluorescence spectra of PSF in aqueous solution containing different concentrations of triethylamine. The fluorescence spectra of PSF in the presence of other alkylamines are similar except for the variation of fluorescence intensity quenching. By measuring the decrease in relative quantum yield of PSF (excited at 520 nm) at varying concentrations of the amines, the Stern-Volmer quenching constant, $K_{sv}$ has been calculated using the relation[7] (1).

$$\frac{\phi_f^0}{\phi_f} = 1 + K_{sv}\,[\text{Amine}] \qquad \ldots (1)$$

where $\phi_f^0$ and $\phi_f$ are the relative quantum yields of fluorescence of PSF alone and in the presence of amine respectively. The plots of $\phi_f^0/\phi_f$ against [amine] are linear in all cases with unit intercept, and from the slope, $K_{sv}$ values have been calculated. The values are: 1.88, 2.07, 2.11, 2.19, 2.67, 3.20, 3.56, 3.89 and 4-.56 $mol^{-1}dm^3$ for ethylamine, *n*-butylamine, *s*-butylamine, *t*-butylamine, dimethylamine, diethylamine, trimethylamine, triethanolamine and triethylamine respectively. According to the electron transfer mechanism for

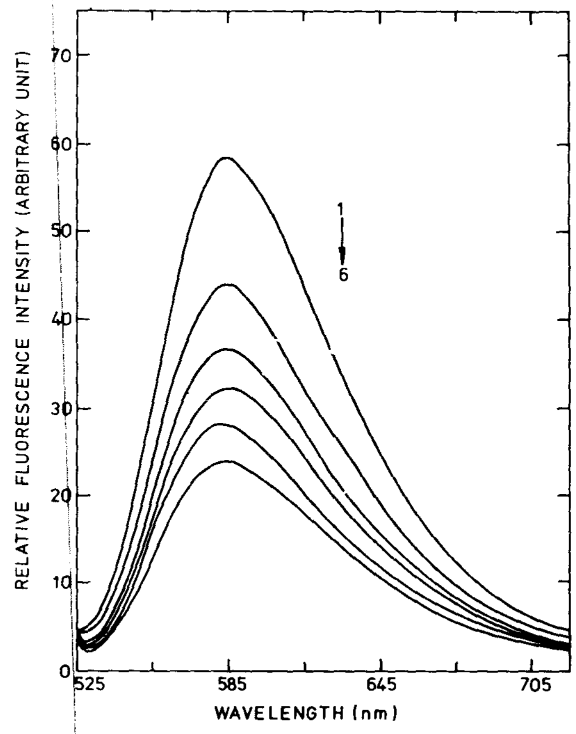

Fig. 1—Fluorescence spectra of PSF in aqueous solution containing different concentrations of triethylamine at 25°C. [PSF] = ($1.17 \times 10^{-5}$ mol dm$^{-3}$); and [Triethylamine] (mol dm$^{-3}$); (1) 0.00, (2) $1.0 \times 10^{-1}$, (3) $2.0 \times 10^{-1}$, (4) $3.0 \times 10^{-1}$, (5) $4.0 \times 10^{-1}$, and (6) $5.0 \times 10^{-1}$).

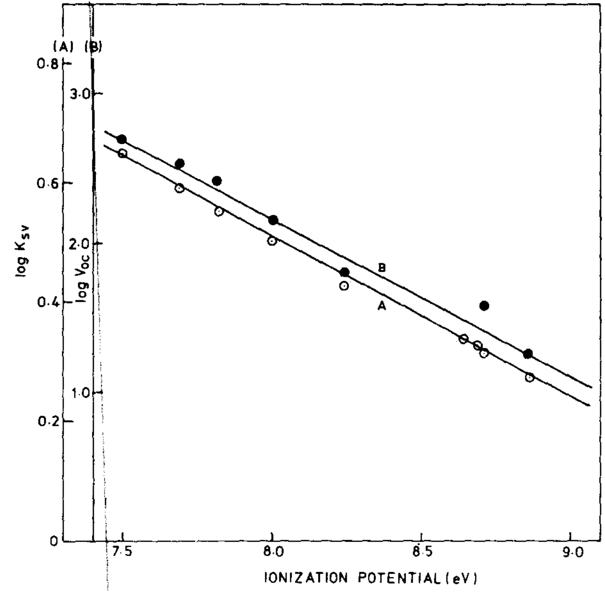

Fig. 2—(A) Plot of log $K_{sv}$ versus ionization potentials of the amines and (B) plot of log $V_{oc}$ versus ionization potentials of the amines ($V_{0c}$ values taken from literature[1]).

quenching[8] we should expect that a fluorescer which is an electron acceptor, is quenched by an electron donor or vice versa and that the quenching constant should increase with decreasing ionization potential of the electron donating quencher when a same fluorescer is quenched by different electron donor quenchers. The results presented herein are consistent with this electron transfer or CT mechanism of quenching. A good correlation between log $K_{sv}$ versus ionization potentials of the amines is shown in Fig. 2 (IP of amine were taken from literature[19]).

The generation of photovoltage in PSF-amine systems also supports the CT interaction between excited PSF and amine molecule[2] as an intermediate step before photochemical change occurs for photovoltage generation. Hence open-circuit photovoltage ($V_{oc}$) of these systems is expected to increase with decrease in ionization potential of the amine ($V_{oc}$ values were taken from literature[1]). This is found to be so (Fig. 2). The possible mechanism for the quenching of PSF by amine in aqueous solution may be represented as shown in Scheme 1.

$$D + h\nu \rightarrow D^*$$

$$D^* \rightarrow D + h\nu_f$$

$$D^* \rightarrow D + \text{heat}$$

$$D^* + NR_3 \rightleftharpoons (D...NR_3^+) \rightleftharpoons (D^-...\overset{+}{N}R_3) \rightarrow D + NR_3$$

Scheme 1

where D represents PSF dye, R represents alkyl or hydrogen and ($D^-...NR_3^+$) represents exciplex (CT complex in excited state). The $K_{sv}$ values have been measured at comparatively higher concentrations of amines and no curvature is obtained in the Stern-Volmer plots, thus ruling out ground state complex formation[10] in these systems, which is further verified by absorption spectra. Thus, the present spectral studies of PSF-amine systems show a good correlation with the photogalvanic effects of these systems in photoelectrochemical cells[1].

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