150

Quenching of Fluorescence of Pyronine-G by Halide Ion in Water & Methanol

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Quenching of the fluorescence of pyronine-G by I^- has been studied in water and methanol. It is found that no ground state complex is formed between the dye and anion. The increased quenching in methanol in comparison to that in water is attributed to the low viscosity of the former.

HALIDE ions[1-3] have long been known to quench the fluorescence of several acceptors and dyes. In connection with our studies on photopolymerization of vinyl monomers sensitized by dyes[4], we have studied the quenching of fluorescence of pyronine-G by I^- in aqueous and non-aqueous media and the results are reported in this paper.

The solvents employed (BDH, Analar) were further purified by distillation and the middle fractions of the distillate were used. Pyronine-G was microscopically pure and was used as such. The fluorescence measurements were made on a Carl-Zeiss ZFM4 spectrofluorometer connected to mains by a voltage stabilizer. The wavelengths were isolated using suitable filters. Absorption measurements were also made with the same instrument.

The fluorescence spectra of pyronine-G in methanol and water are shown in Fig. 1. The absorbance spectra of the dye and potassium iodide are shown in Fig. 2. Fig. 2 shows that the formation of ground state complex between the dye and iodide ion is minimal. Quenching of fluorescence of the dye by potassium iodide fits into linear Stern-Volmer equation

$$F_0/F = 1 + k_q \tau \times [I^-]$$

where F_0 and F refer to the fluorescence intensity in the absence and presence of quencher respectively.
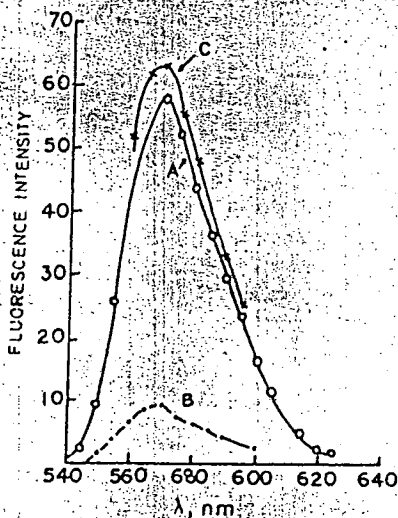

Fig. 1 — Fluorescence emission spectrum of pyronine-G ($5 \times 10^{-5} M$) in water at excitation wavelengths [(A) 365 nm; (B) 405 nm and (C) 546 nm]
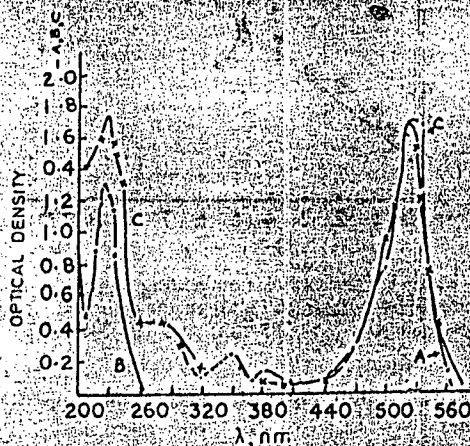

Fig. 2 — Absorption spectrum of (A) pyronine-G ($5 \times 10^{-5} M$); (B) potassium iodide ($1 \times 10^{-4} M$) and (C) pyronine-G ($5 \times 10^{-5} M$) + potassium iodide ($1 \times 10^{-4} M$)
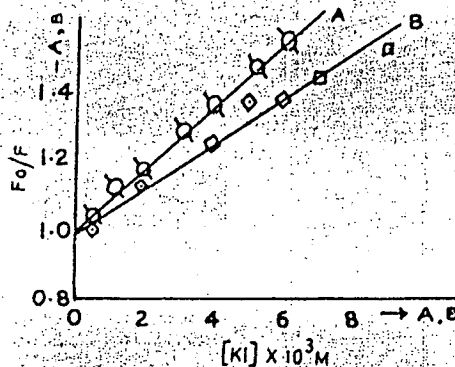

Fig. 3 — Stern-Volmer plot for quenching of the fluorescence of pyronine-G by potassium iodide in water at excitation wavelengths [(A) 365 nm and (B) 546 nm]

The quenching constants ($k_q \tau$) were evaluated from the slopes of the Stern-Volmer plots for quenching in methanol and water respectively (Figs. 3 and 4). These constants have values of 8·50 and 1·50 (at 365 nm) and 6·0 and 1·50 (at 546 nm) in water and methanol respectively. It was found that methanol or isopropanol by itself has no quenching action. The quenching action of the alcohol was studied by varying the solvent composition. Lewis and Ware[5] have observed a wavelength dependence of the quenching of fluorescence of anthracene by carbon tetrachloride which was attributed to the existence of ground state complex. But the above values of the quenching constants indicate that there is no wavelength effect on the quenching of fluorescence. From these observations, it appears that the ground state complex formation between the dye and I^- is minimal. The high quenching in methanol is understandable if one applies the theoretical Eq. (1) to calculate the quenching constant.

$$k_q = \frac{8RT}{2000 \, \eta} \qquad \ldots(1)$$
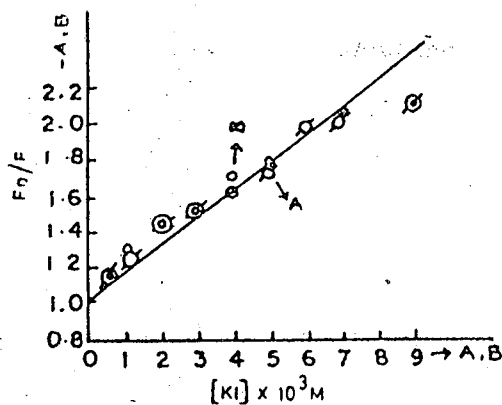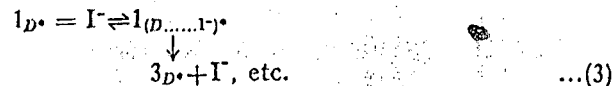
where k_q = quenching constant, R = gas constant,

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Fig. 4 — Stern-Volmer plot for quenching of the fluorescence of pyronine-G by potassium iodide in methanol at excitation wavelengths [(A) 365 nm; and (B) 546 nm]

T = absolute temperature, and η = viscosity in centipoise.

It is probable that the quenching process may take place by exciplex formation mechanism. The same view has been expressed by Beer et al.[1] and Davidson and Lewis[3] in their studies on the fluores-cence of hydrocarbons quenched by anions. The quenching process may be described by Eqs. (2) and (3).

$$D \rightarrow 1_{D^*} \qquad \qquad ...(2)$$

$$1_{D^*} = I^- \rightleftharpoons 1_{(D......I^-)^*}$$
$$\downarrow$$
$$3_{D^*} + I^-, \text{ etc.} \qquad \qquad ...(3)$$

The actual quenching in different solvents is controlled by the various processes.

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