

LETTERS TO THE EDITOR

POLARIZATION OF FLUORESCENCE OF  
TETRABROMO-SODIUM FLUORESCEIN

THE fluorescence emission from tetrabromo-sodium fluorescein consists of a broad band extending from ~ 540 nm to ~ 600 nm which corresponds to a  $\pi \leftrightarrow \pi^*$  transition. There are several excitation bands, corresponding to different excited states, viz., the first singlet excited state  $S_1 [^1(\pi\pi^*)]$ , the second singlet excited state  $S_2 [^1(\pi\pi^*)]$ , etc., which give rise to the same fluorescence emission. In order to get information about these excited states, the polarization spectrum is investigated for different exciting wavelengths. The polarization spectrum is measured with Aminco Bowman spectrophoto-fluorometer at ~ 39° C for a concentration of ~ 10<sup>-4</sup> g/cc of tetrabromo-sodium fluorescein in glycerol. Polarization of the emission band was measured for those excitation wavelengths for which the intensity of fluorescence emission was maximum. The effect of scattering was checked by using pure glycerol in the cell. In general, the error in the measurement of polarization is ± 1.5% but the accuracy is better in the region of the maximum emission. The results obtained are given in Table I.

TABLE I

$\lambda_{em}$ nm	Percentage polarization		
	$\lambda_{ex} \sim 554$ nm	$\lambda_{ex} \sim 462$ nm	$\lambda_{ex} \sim 352$ nm
540	..	15.2	-16.1
550	..	22.4	-23.2
568	26.3	28.8	-4.0
580	25.1	25.5	-6.4
590	24.9	26.5	-4.8
600	25.0	22.4	-4.1

The observations indicate that there are three values of  $\lambda_{ex}$ , viz., 352 nm, 462 nm and 554 nm. The last two long wavelengths of excitation correspond to  $\lambda_{nb}$ , 480 nm and 510 nm reported earlier by Rathi *et al.*<sup>1</sup>, as due to  $\pi\pi^*$  and  $\eta\pi^*$  transitions. The fluorescence band 540 nm to 600 nm with the maximum intensity of emission at  $\lambda_{em} \sim 568$  nm corresponds to  $\pi\pi^*$  transition. The  $\eta\pi^*$  state possibly degrades through internal conversion to  $\pi\pi^*$  state and gives rise to the same emission band. It can be seen from the observations

(Table I) that the polarization is positive in both the cases of  $\pi\pi^*$  and  $\eta\pi^*$  excitation indicating the transition moment direction for these levels as almost parallel. However, when exciting wavelength 352 nm is used, the fluorescence is negatively polarized. It appears that with this excitation, the dye molecule is excited to the second excited singlet state  $S_2 [^1(\pi\pi^*)]$  which by internal conversion gets down to the first excited singlet state  $S_1 [^1(\pi\pi^*)]$  and then the molecule returns to the ground state by fluorescence emission<sup>3-5</sup>.

These transitions agree with the suggested<sup>2</sup> energy levels for the molecule under consideration. The negative polarization for  $\lambda_{ex} \sim 352$  nm further suggests that the transition moment directions of the first and second  $^1(\pi\pi^*)$  states are somewhat normal to each other. During the time, the higher level drops to the lower with electron reorientation, the depolarization takes place and hence the magnitude of observed polarization should be less. This is in conformity with the observation, because it can be seen from Table I, that the average value of polarization for  $\lambda_{ex} \sim 554$  nm is ~ 25% but for  $\lambda_{ex} \sim 352$  nm it is far less ~ -5%, for the emission band 568 nm to 600 nm.

It may also be noted that the polarization for emission wavelengths from ~ 560 nm to ~ 600 nm is almost constant, within experimental errors, for all the three excitation wavelengths. In a classical sense this corresponds to one type of emission oscillator which could mean that for this concentration (~ 10<sup>-4</sup> g/cc) the dye exists in solution, only in one molecular form.

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