

1964). The errors involved are indicated by vertical lines. The experimental data need a further refinement before any meaning can be attached to the existing differences between the new theoretical curve ( $R + F + N$ ) and the experimental curve (E).

The authors are grateful to Prof. R. K. Asundi for his valuable suggestions and to Dr. N. A. Narasimham for the facilities provided.

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\* Communicated by Dr. S. Pancharatnam.

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## DIMER FORMATION IN ERYTHROSIN AND ROSE BENGALE

SODIUM Fluorescein and its derivatives—Eosin, Erythrosin and Rose Bengale—may exist in a solution as dianions, monoanions, neutral molecules and dimers, etc., the proportion of each variety depending upon the concentration of the dye. So it is expected that a change in the fluorescence and absorption spectra may take place with a change in the concentration of the dye. In the present investigation the fluorescence spectra in glycerin-water mixture (50–50% by volume) and the absorption spectra in aqueous solution have been recorded at various concentrations of Erythrosin and Rose Bengale and the effect of concentration has been studied. The fluorescence spectra of Erythrosin and Rose Bengale, excited by the mercury wavelength 5460 Å, were recorded with a Hilger's constant deviation spectrograph and the spectrum intensities obtained using a recording microphotometer.

Figures 1 and 2 are the microphotometer records of the fluorescence of Erythrosin and Rose Bengale respectively. The sharp lines at 5460 Å, 5769 Å, 5790 Å and 6232 Å, appearing in the microphotometer record, are the scattered mercury lines. The fluorescence spectrum intensity curves 1, 2 and 3 of Fig. 1 correspond respectively to the Erythrosin concentrations  $8.0 \times 10^{-6}$ ,  $2.0 \times 10^{-5}$  and  $7.0 \times 10^{-5}$  g./c.c. and the fluorescence spectrum intensity curves 1 and 2 of Fig. 2 correspond respectively to the Rose

Bengale concentrations  $2.0 \times 10^{-5}$  and  $6.0 \times 10^{-5}$  g./c.c. In each case an increase in the half band-width is observed at the higher concentrations. It appears that the fluorescence spectrum 3 of Fig. 1 results from the superimposition of two intensity curves, one having its maximum in the same region as the intensity curve-1 for lower concentration at  $\lambda \sim 5680$  Å and the other having its maximum at a longer wavelength at  $\lambda \sim 6000$  Å. The same appears to be the case for the intensity curve 2 of Fig. 2, the peak for lower concentration is at  $\lambda \sim 5760$  Å and another appearing at higher concentration at  $\lambda \sim 6100$  Å.

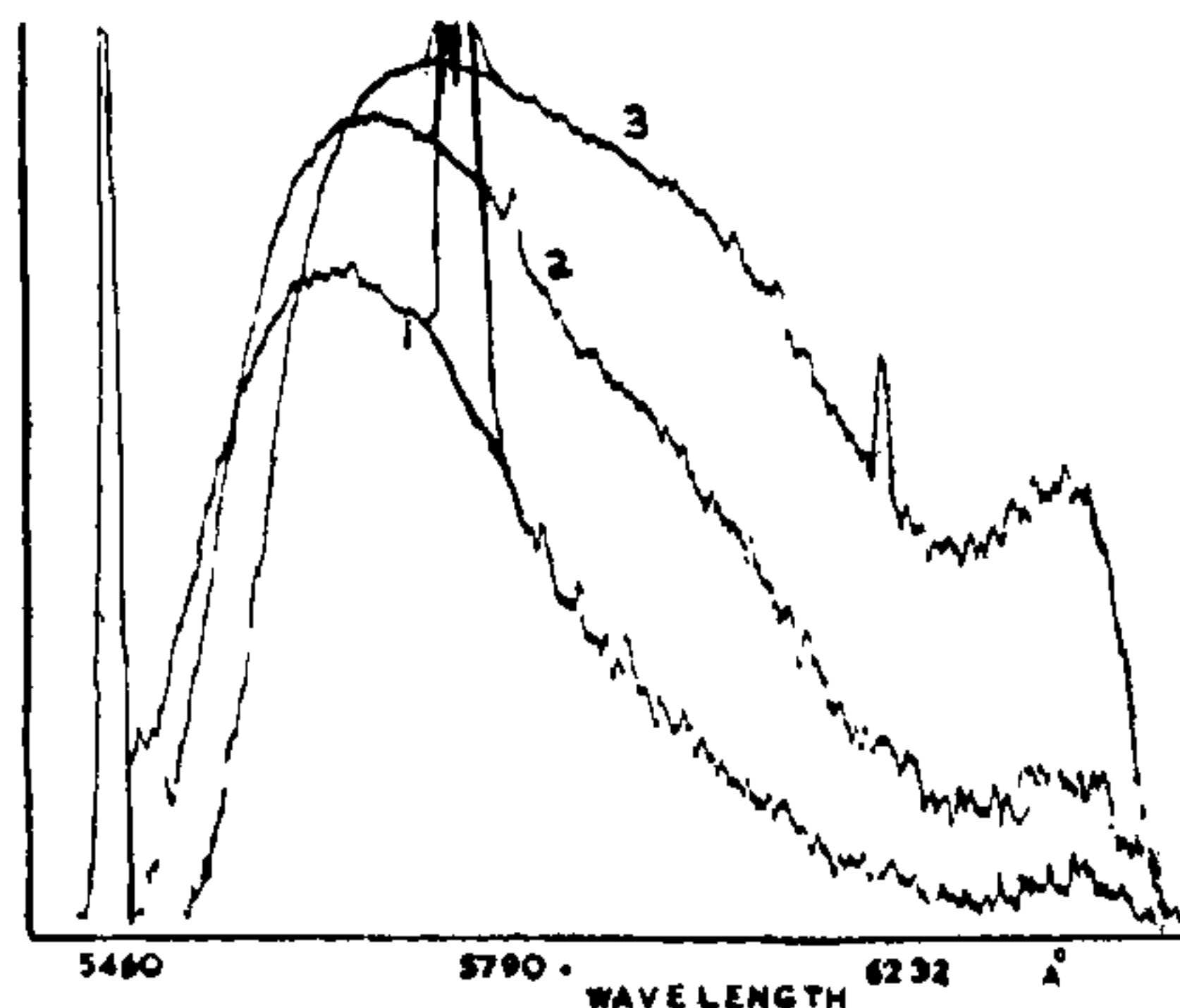


FIG. 1. Erythrosin; Microphotometer records of the fluorescence spectra at concentrations—1:  $8.0 \times 10^{-6}$  g./c.c.; 2:  $2.0 \times 10^{-5}$  g./c.c.; 3:  $7.0 \times 10^{-5}$  g./c.c.

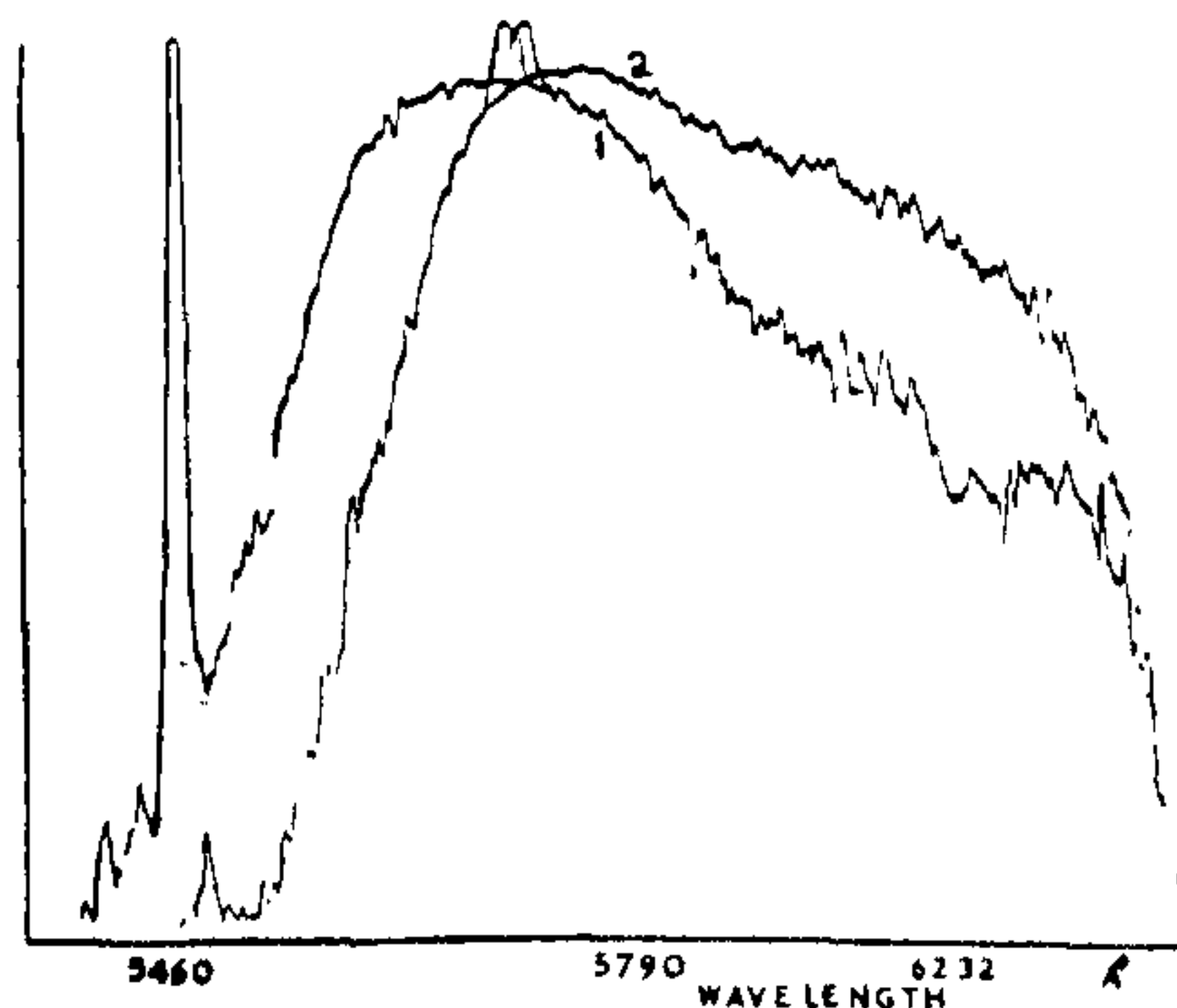


FIG. 2. Rose Bengale; Microphotometer records of the fluorescence spectra at concentrations—1:  $2.0 \times 10^{-5}$  g./c.c.; 2:  $6.0 \times 10^{-5}$  g./c.c.

Figures 3 and 4 are the absorption spectra of Rose Bengale and Erythrosin respectively. Absorption curves 1, 2 and 3 of Fig. 4 correspond to the Erythrosin concentrations  $1.25 \times 10^{-5}$ ,  $2.50 \times 10^{-5}$  and  $5.0 \times 10^{-5}$  g./c.c. respec-

tively, and the absorption curves 1, 2 and 3 of Fig. 3 correspond to the Rose Bengale concentrations  $2.0 \times 10^{-5}$ ,  $5.0 \times 10^{-5}$  and  $7.0 \times 10^{-5}$  g./c.c. respectively. In each case at higher concentrations of the dye a new peak appears in addition to the peak which is present at lower concentration of the dye. In all the cases this

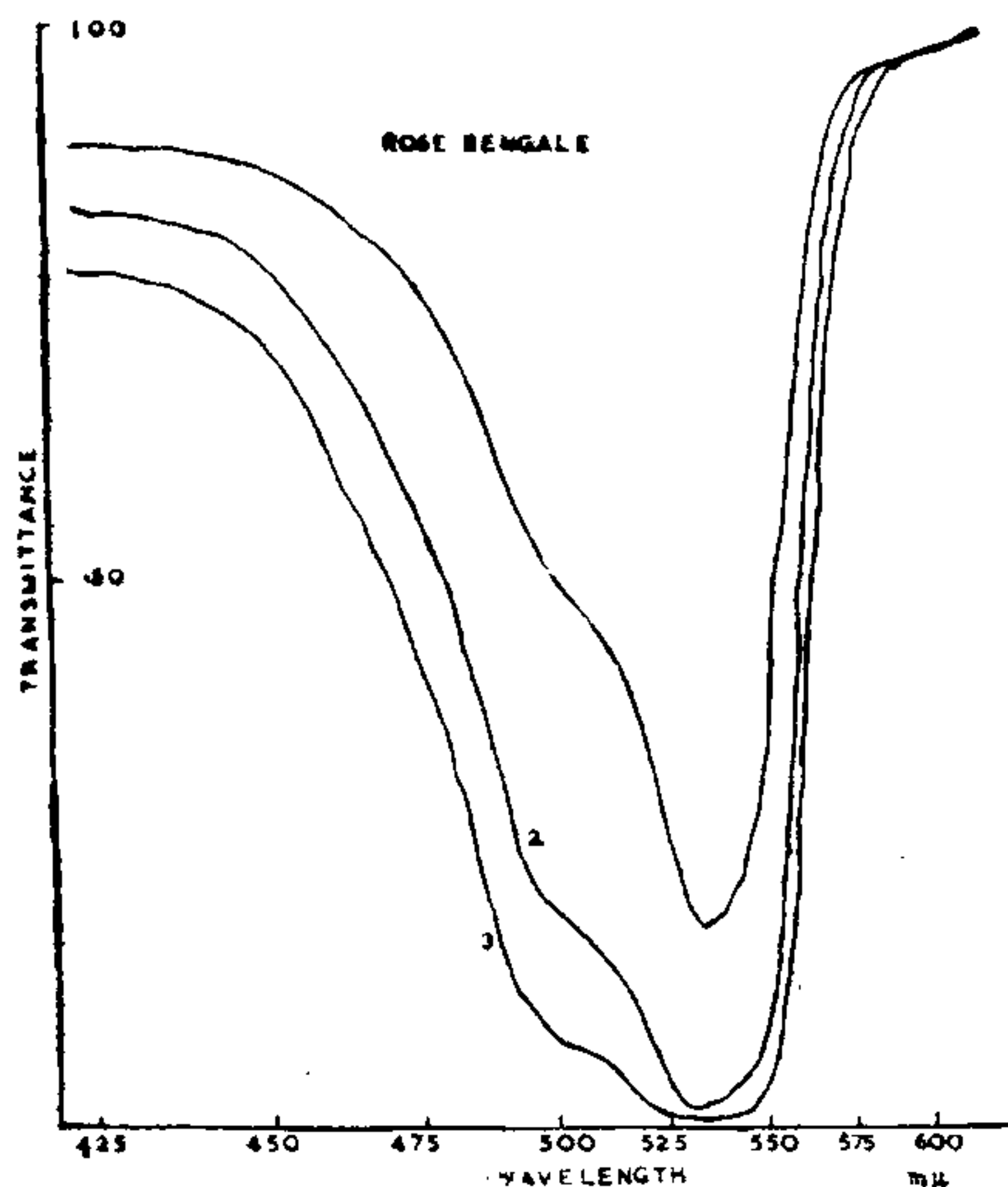


FIG. 3. Rose Bengale: Absorption spectra at concentrations—1:  $2.0 \times 10^{-5}$  g./c.c.; 2:  $5.0 \times 10^{-5}$  g./c.c.; and 3:  $7.0 \times 10^{-5}$  g./c.c.

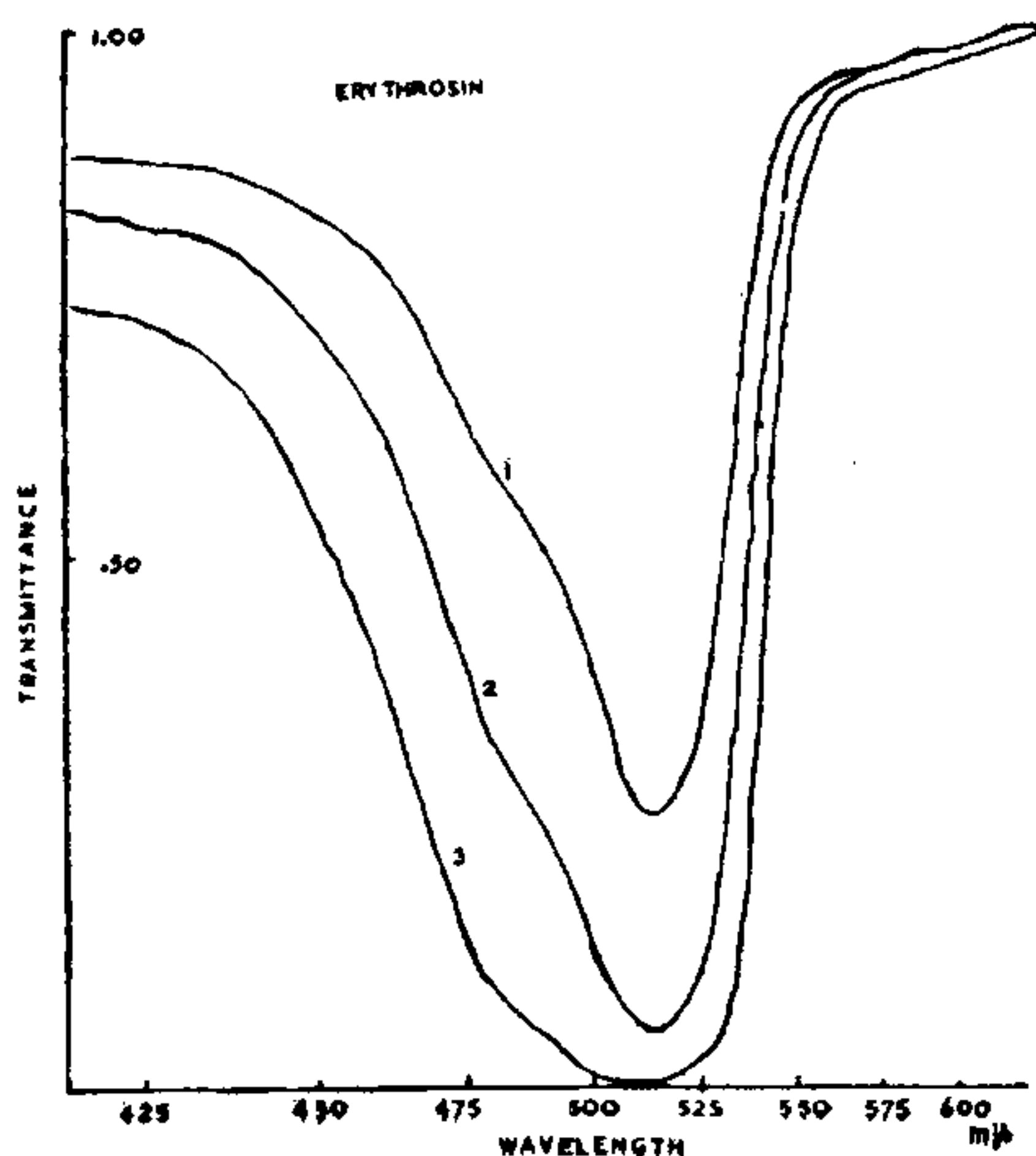


FIG. 4. Erythrosin: Absorption spectra at concentrations—1:  $1.25 \times 10^{-5}$  g./c.c.; 2:  $2.50 \times 10^{-5}$  g./c.c.; and 3:  $5.0 \times 10^{-5}$  g./c.c.

additional peak at higher concentration lies on the shorter wavelength side. In Erythrosin the two peaks are at  $\lambda \sim 5130 \text{ Å}$  and  $\lambda \sim 4800 \text{ Å}$  and in Rose Bengale at  $\lambda \sim 5320 \text{ Å}$  and  $\lambda \sim 4970 \text{ Å}$ .

The fluorescence peak at  $\lambda \sim 5680 \text{ Å}$  and the absorption peak at  $\lambda \sim 5130 \text{ Å}$ , in case of Erythrosin, correspond to the dianions of Erythrosin as shown by their appearance at lower concentrations where the dye is known to exist in doubly ionised form.<sup>1</sup> Similarly the fluorescence peak at  $\lambda \sim 5760 \text{ Å}$  and the absorption peak at  $\lambda \sim 5320 \text{ Å}$ , in case of Rose Bengale, correspond to its dianions.<sup>1</sup> In case of Erythrosin the observed fluorescence peak at shorter wavelength  $\lambda \sim 5680 \text{ Å}$  lies in the same region as the single peak reported by earlier workers<sup>1</sup> at  $\lambda \sim 5600 \text{ Å}$ . The difference in location of the peak may be due to different solvents. But in case of Rose Bengale the fluorescence peak has been reported in [1] to be at  $5900 \text{ Å}$  which does not coincide with any of the peaks at  $\lambda \sim 5760 \text{ Å}$  and  $\lambda \sim 6100 \text{ Å}$  as observed by us. Probably, in [1] the fluorescence spectrum of Rose Bengale has been recorded at a higher concentration of the dye which will show a mean maximum in the reported region of [1]. The peaks at higher concentrations in the absorption and fluorescence spectra, in each case, seem to be due to some common cause as shown by their appearance at the concentrations of the same order and may be attributed to the dimers of these dyes which will be in greater abundance at higher concentrations.

Similar results have also been obtained by us for fluorescein and eosin indicating dimer formation in those cases.<sup>2</sup>

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#### COMPLEXES OF NICKEL PERCHLORATE WITH $\gamma$ -PICOLINE

EARLIER we reported<sup>1</sup> some four and six-co-ordinated paramagnetic nickel (II) complexes obtained by reacting nickel chloride, thiocyanate and perchlorate with 4-vinyl pyridine. In this communication, we report two more complexes obtained by reacting nickel perchlorate with  $\gamma$ -picoline. These compounds are interesting specially because we obtained both six-co-ordinated paramagnetic and tetra-co-ordinated