

## Absorption, excitation and fluorescence spectra of Congo red in aqueous solutions

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**Abstract** : The absorption, excitation and fluorescence spectra of Congo red [ $C_{32}H_{22}N_6Na_2O_6S_2$ ] have been recorded in aqueous solution at concentrations between  $10^{-3}$  and  $10^{-6}$   $Ml^{-1}$ . This has led to the determination of optimum concentrations, for the absorption and fluorescence spectra of the compound. The absorption spectrum has been recorded only in the spectral region of 350–600 nm showing a peak at ~497 nm. The excitation spectrum has been recorded with  $\lambda_{em} = 600$  nm. The fluorescence spectra are recorded with  $\lambda_{ex} = 450$ –550 nm showing a peak at ~602 nm. The absorption and fluorescence transitions have been shown to correspond to each other. The absorption band has been assigned to ( $\pi^* \leftarrow n$ )  $^1W \leftarrow ^1A$  transition of the azo-biphenyl moiety of the compound.

**Keywords** : Azo-dyes, fluorescence,  $\pi^* \leftarrow n$  transition.

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### 1. Introduction

Dyes are those organic compounds which absorb in ultraviolet, visible and near infrared regions. Dyes [1] in general, constitute a very important class of fluorescent materials as they have, besides their well known commercial use in colouration of textiles, plastics, cosmetics, many scientific and technological applications such as in laser dyes [2], photonics [3], biological fluorescence probe development [4], probe of DNA protein recognition [5], nonlinear optical devices [6], watches for dial reading, sign boards etc. Also the dyes are potential candidates for use in opto- and optoelectronic devices [7]. The azo dyes are the largest class of organic dyestuffs having chromophoric azo group  $-N=N-$ . No natural dye contains this chromophore. The chromophoric azo group  $-N=N-$  is always connected on one side with an aromatic or heterocyclic nucleus, and on the other, it may be linked to an unsaturated molecule of the carbocyclic, heterocyclic or aliphatic type. The possibility of connecting an almost unlimited number of different molecules by way of the azo bridges, is the reason for the great number of

representatives of this group [8]. Azo dyes have wide industrial applications as cited above. Many of these dyes have been now recognized as non-ecofriendly as they yield upon cleavage aromatic amines which are carcinogenic. It has been reported that about 120 to 150 of the more than 2000 dyes which are currently used, are strongly suspected to cause cancer [9]. It is therefore, important to suggest sensitive and dependable quantitative analytical techniques for their identification in a routine manner. Due to an important application of azo dyes as infrared laser dye, recently a lot of interest has been developed in the study of these compounds world wide, using Laser Induced Fluorescence (LIF) technique [1]. But before making LIF or dynamic fluorescence studies of these compounds for the above purposes, a knowledge of their optimum concentration and excitation wavelength by the study of their static fluorescence is necessary [10]. To the best of our knowledge, this information is not available in literature about Congo red. In the present paper, a detailed spectroscopic study of the absorption, excitation and fluorescence spectra of Congo red has

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been given. Congo red, a bisazo dye, is found to have direct affinity for cotton probably as a result of its colloidal properties [11]. Other industrial applications include calico printing and dyeing paper [12]. Congo red with chemical formula  $[C_{32}H_{22}N_6Na_2O_6S_2]$  and molecular structure as given in Figure 1, is an azo-dye readily soluble in water to give intense red colour.

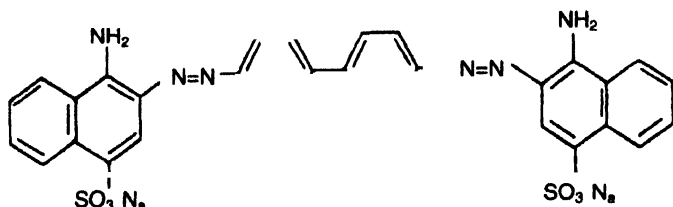


Figure 1. Molecular structure of Congo red.

## 2. Experimental details

Analytical reagent quality Congo red was obtained from M/s Tokyo Kasei Kogyo Co. Ltd., Japan and used without further purification. Its absorption spectra in triple distilled water at concentrations between  $10^{-3}$  and  $10^{-6}$   $Ml^{-1}$  were recorded on a JASCO model V-550 spectrophotometer using a Hellma fluorimeter quartz cell of path length 10 mm. Figure 2 shows the absorption spectrum having  $\lambda_{max}$  at  $\sim 497$  nm at the concentration  $10^{-5}$   $Ml^{-1}$  of the compound. This band along with three more absorption

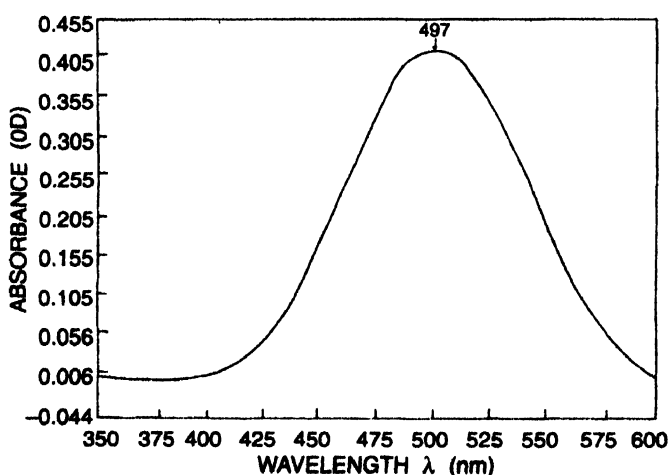


Figure 2. Absorption spectrum of Congo red at concentration  $10^{-5}$   $Ml^{-1}$  in water.

peaks at lower wavelengths have been reported for the Sigma Aldrich product [12] earlier. This confirmed the purity of the compound procured by us. Excitation and fluorescence spectra of the compound in triple distilled water at four concentrations in the range mentioned above, were recorded on a JASCO, model FP-777 spectrofluorometer. The wavelength of excitation source was varied between 450–550 nm to obtain intensity variation of the excitation spectra at fluorescence wavelengths ( $\lambda_{em}$ )

between 575 and 625 nm. The intensity variation in the excitation spectrum at  $\lambda_{em} = 600$  nm and the conc.  $10^{-5}$   $Ml^{-1}$  of the sample in water has been shown in Figure 3

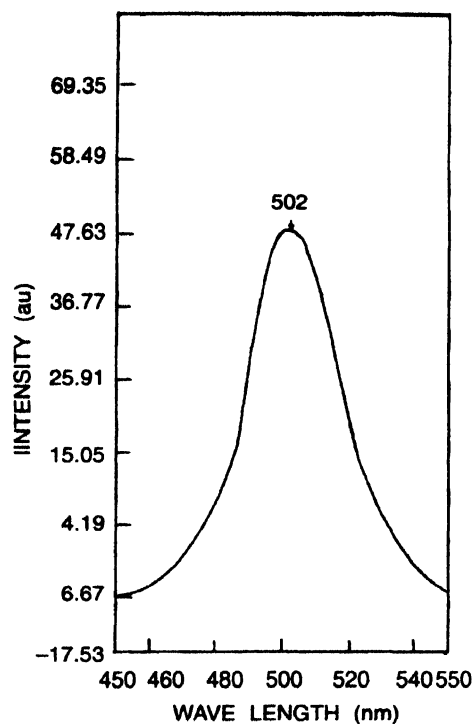


Figure 3. Excitation spectrum of Congo red at concentration  $10^{-5}$   $Ml^{-1}$  in water with  $\lambda_{em} = 600$  nm.

This is more or less a reproduction of the absorption spectrum of the compound at the same concentration (Figure 2). Fluorescence spectra of the compound were recorded by choosing different excitation wavelengths ( $\lambda_{ex}$ ) of the source between 450–550 nm. Figures 4 and 5

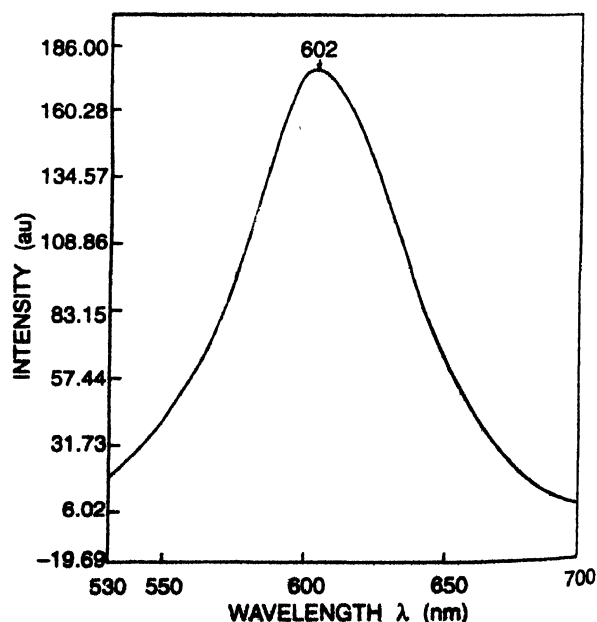


Figure 4. Fluorescence spectrum of Congo red at concentration  $10^{-4}$   $Ml^{-1}$  in water with  $\lambda_{ex} = 550$  nm.

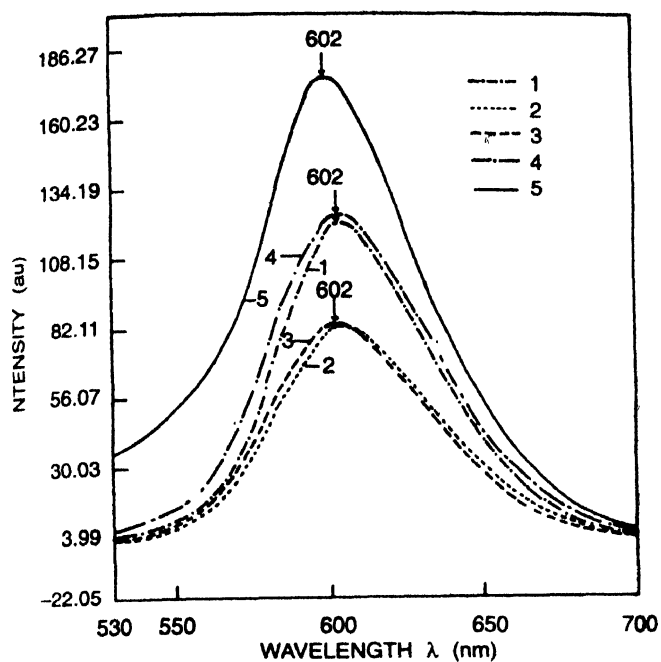


Figure 5. Fluorescence spectra of Congo red at concentration  $10^{-4} \text{ Ml}^{-1}$  in water with  $\lambda_{\text{ex}} = (1) 450, (2) 475, (3) 500, (4) 525$  and  $(5) 550 \text{ nm}$ .

show the emission spectra of the compound at the concentration  $10^{-4} \text{ Ml}^{-1}$  with  $\lambda_{\text{ex}} = 450, 475, 500, 525$  and  $550 \text{ nm}$ , in the range of  $530$  to  $700 \text{ nm}$ .

### 3. Results and discussion

Although absorption spectra of the compound were recorded at four concentrations between  $10^{-3}$  and  $10^{-6} \text{ Ml}^{-1}$  in the range of  $450$ – $550 \text{ nm}$ , those at only two concentrations *i.e.*  $10^{-4}$  and  $10^{-5} \text{ Ml}^{-1}$  were found to be regular in form and with enough absorbance or optical density (OD). The absorption spectra at both these concentrations showed maximum absorption peak at about the same wavelength  $497 \text{ nm}$  (Figure 2). A plot of optical density for this band against wave number  $\nu$  ( $\text{cm}^{-1}$ ) for the concentration  $10^{-5} \text{ Ml}^{-1}$  is shown in Figure 6. From this plot, the value of maximum molar extinction

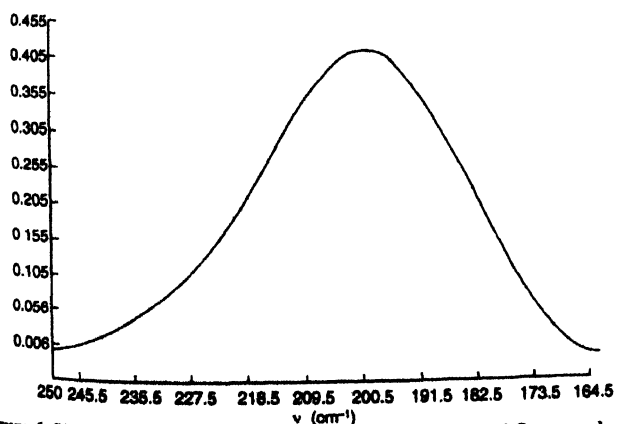


Figure 6. Variation of optical density against wave number of Congo red at concentration  $10^{-5} \text{ Ml}^{-1}$  in water.

coefficient ( $\epsilon_{\text{max}}$ ) for this absorption band at frequency  $\approx 2.00 \times 10^4 \text{ cm}^{-1}$ , has been calculated as  $41.4 \times 10^3 (\text{Ml}^{-1} \text{ cm}^{-1})$ . The oscillator strength  $f = 4.315 \times 10^{-9} \int \epsilon \nu$  for this band has also been calculated as  $\sim 75.66 \times 10^{-2} \text{ Ml}^{-1} \text{ cm}^{-2}$  [13]. The chromophoric groups present in Congo red are the two naphthalene, two diazo ( $-\text{N}=\text{N}-$ ) and one-biphenyl groups. The biphenyl group attaches one azo group on each side in para position and each of the azo groups is linked with a naphthalene group in position 2 (Figure 1). A comparison of the absorption bands of these moieties with that observed for Congo red may be useful in determining the transition involved in this band. Solution spectra of naphthalene in ethanol shows three peaks in the accessible UV region at  $312, 289$  and  $220 \text{ nm}$  with increasing order of absorbance. While first of these has been shown to correspond to  ${}^1L_b \leftarrow {}^1A$  ( $\epsilon_{\text{max}} < 10^3$ ), second to  ${}^1L_a \leftarrow {}^1A$  ( $\epsilon_{\text{max}} \sim 10^4$ ) and third to  ${}^1B_b \leftarrow {}^1A$  ( $\epsilon_{\text{max}} \sim 10^5$ ) transitions [13]. When one amino group is attached with naphthalene [14] in  $\alpha$  position, it has been found that the  ${}^1L_a$  and  ${}^1L_b$  bands fuse probably because of the large bathochromic displacement of the  ${}^1L_a$  band [13]. However, in the present study, bands in the region lower than  $400 \text{ nm}$  have not been recorded for Congo red. Biphenyl displays only a single absorption band in the readily accessible UV region at  $251.5 \text{ nm}$  with  $\epsilon_{\text{max}} \sim 10^4$ . This band may be considered to correspond to the benzene transition  ${}^1L_a \leftarrow {}^1A$  at  $204 \text{ nm}$ . This assignment is consistent with the expectation that conjugation of the two-phenyl rings results in a bathochromic shift [13]. However, an  $\pi^* \leftarrow n$  transition has been observed at  $420 \text{ nm}$  in azo benzene. As such due to substitution of azo group in biphenyl moiety we may expect a corresponding transition in the present compound at a higher wavelength. So the absorption band at  $\lambda \sim 497 \text{ nm}$  in Congo red is assigned to the  $\pi^* \leftarrow n$  ( ${}^1W \leftarrow {}^1A$ ) transition.

The fluorescence spectrum of the compound recorded with  $\lambda_{\text{ex}} = 550 \text{ nm}$  in the emission range of  $530$  to  $700 \text{ nm}$ , shows only one peak at  $\sim 602 \text{ nm}$  of low intensity (Figure 4). It is also clear from (Figure 5) that the intensity of the fluorescence band at  $602 \text{ nm}$  varies as  $\lambda_{\text{ex}}$  is changed from  $450$  to  $550 \text{ nm}$ . These observations clearly show that  $\lambda_{\text{ex}} = 550 \text{ nm}$  is most suitable for this fluorescence which corresponds to the absorption band at  $497 \text{ nm}$ , giving Stoke's shift of  $\sim 105 \text{ nm}$ .

### 4. Conclusions

The aqueous solution absorption spectrum of Congored with  $\lambda_{\text{max}}$  at  $\sim 497 \text{ nm}$  observed in the present study has

been shown to correspond to the  $\pi^* \leftarrow n$  ( ${}^1W \leftarrow {}^1A$ ) transition of azo-biphenyl group. It has also been concluded that the other absorption bands of this compound in the wavelength region of 340–195 nm, correspond to the naphthalene moiety of the compound.

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