Absorption and fluorescence spectra of disperse red 19-An azo dye

Neena Jaggi1*, Manoj Giri2 & Kanta Yadav1
1Department of Physics, National Institute of Technology, Kurukshetra 136 119, Haryana, India
2Department of Physics, Haryana College of Technology & Management, Kaithal136 027, Haryana, India
*E-mail: neena_jaggi@rediffmail.com
Received 1 November 2012; revised 25 April 2013; accepted 7 August 2013

The absorption and fluorescence spectra of disperse red 19 (C16H18N4O4), a fluorescent azo dye have been recorded in ethanol at concentrations between 10⁻³ M and 10⁻⁶ M. This dye finds use in many scientific and industrial applications. This has led to the determination of optimum concentrations to record the absorption and fluorescence spectra of the molecule. The absorption spectrum shows two absorption peaks at 285 and 495 nm, recorded in the spectral region 200-700 nm, which have been assigned to (π*←π)¹G, (π*←A)¹B, and (π*←n)¹W←¹A transitions, respectively. Fluorescence spectra of the compound have shown two fluorescence peaks at 324 and 640 nm at different concentrations giving Stokes shift of the order of 39 and 145 nm, respectively.

Keywords: Azo dyes, Absorption, Fluorescence, Oscillator strength, (π*←n) transition, Stokes shift

1 Introduction

Dyes1 are defined as those organic substances which are designed to be absorbed or adsorbed by, made to react with, or deposited within a substrate in order to impart colour to that substrate with some degree of permanence. They have many scientific and technological applications such as in laser dyes, photonics, biological fluorescence probe development, probe of DNA protein recognition, non-linear optical devices etc.2-12 Azo dyes are characterized by the presence of at least one R₁−N=N−R₂ functional group. The azo group often helps to stabilize the dyes and forms a conjugated system which very often absorbs visible light13. Among the varieties of dyes demanded by the various industries, azo dyes constitute up to 60% of the demand14. 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 group15. The steady state fluorescence study of azo dyes is needed due to their potential applications as infrared laser dyes, for further laser induced fluorescence (LIF) or dynamic fluorescence studies. Therefore, by analyzing the importance of these dyes especially disperse red 19 in textile and scientific industries, it is logical to carry out systematic spectroscopic studies for it16-20. The molecular structure of disperse red 19 compound is shown in Fig. 1. It is an azo dye soluble in ethanol, acetone and benzene to give intense red colour. It is used to dye nylon, polyester, sheepskins, furs etc. In the present study, an assignment of transitions involved in the absorption peaks of this compound has been made and the corresponding extinction molar coefficient and oscillator strength have been calculated. By analyzing fluorescence spectra, we have determined the Stokes shift of the molecule.

2 Experimental Details

Analytical reagent quality disperse red 19 was obtained from M/s Sigma Aldrich Chemical Company, Inc., USA and used without further purification. Its absorption spectra in 50% ethanol at concentrations between 10⁻³ and 10⁻⁶ M are recorded on a CAMSPEC-M550, UV-Visible spectrophotometer using quartz cell of path length 10 mm. Fig. 2 shows the absorption spectrum of the compound at concentration 10⁻⁵ M, recorded only in the spectral region 200-700 nm. In this region, two absorption bands at 285 and 495 nm are observed. It has been reported in literature that this compound shows

![Fig. 1 — Molecular structure of disperse red 19 azo dye](image-url)
two absorption bands\textsuperscript{21} at about the same wavelengths. Fluorescence spectra of the compound in ethanol at the above mentioned concentrations were recorded on a FluroMax-4 Fluorescence Spectrofluorometer.

3 Analysis and Discussion

Although absorption spectra of the compound were recorded at four concentrations between 10\textsuperscript{-3} and 10\textsuperscript{-6} M in the range 200-700 nm, those at only two concentrations i.e. 10\textsuperscript{-4} and 10\textsuperscript{-5} M were found to be regular in form and with enough absorbance or optical density (O D). The absorption spectra at both these concentrations showed two absorption peaks at about the same wavelengths viz 285 and 495 nm (Fig. 2). The band observed at 285 nm has an asymmetrical broad shape due to various transitions involved in this band. In the present study, \( \lambda_{\text{max}} \) is observed at 495 nm, which has also been reported in literature\textsuperscript{22} at about the same wavelength. A plot of optical density for these observed bands against wave number \( \nu \) (cm\textsuperscript{-1}) for the concentration 10\textsuperscript{-4} M is shown in (Fig. 3).

From this plot, the value of maximum molar extinction coefficient (\( \varepsilon_{\text{max}} \)) for the absorption bands I and II at frequencies 3.50x10\textsuperscript{4} cm\textsuperscript{-1} and 2.02x10\textsuperscript{4} cm\textsuperscript{-1} have been calculated as 9.3x10\textsuperscript{3} and 23.0x10\textsuperscript{3} (M\textsuperscript{-1}cm\textsuperscript{-1}), respectively. The oscillator strength, \( f = 4.315\times10^{-9} \) fdey, for these bands have also been calculated as 32.9x10\textsuperscript{-2} and 48.5x10\textsuperscript{-2} (M\textsuperscript{-1}cm\textsuperscript{-2}) respectively\textsuperscript{23}. The chromophoric groups present in disperse red 19 are two phenyl and one azo group. The two benzene rings are connected to each other through azo-bridge (Fig. 1). The NO\textsubscript{2} and OH additional groups are linked with these phenyl rings. The molecular structure of disperse red 19 is exactly the same as that of azobenzene, besides some additional chromophoric groups. The comparison of the absorption bands of azobenzene with those observed for disperse red 19 may be useful in deciding the transitions involved in the observed absorption peaks of the compound. The absorption spectra of azobenzene in 15% ethanol shows four absorption peaks at 223, 258, 314 and 420 nm which have been assigned to \( ^1\text{C} \leftarrow ^1\text{A} \), \( ^1\text{G} \leftarrow ^1\text{A} \), \( ^1\text{B} \leftarrow ^1\text{A} \) and \( ^1\text{W} \leftarrow ^1\text{A} \) transitions. The band reported at 420 nm for azobenzene is expected to show a bathochromic shift (red shift) on adding some additional groups like NO\textsubscript{2} because of resonance effect. So the band observed at 495 nm in disperse red 19 can be correlated to (\pi*\leftarrow\pi)\textsuperscript{1}W \leftarrow ^1\text{A} transition and band observed at 285 nm with asymmetrical shape to (\pi*\leftarrow\pi)\textsuperscript{1}G,\textsuperscript{1}B\leftarrow ^1\text{A} transitions due to overlapping of absorption bands of azobenzene reported at 258 and 314 nm.

Fluorescence spectra of the dye under study were recorded by selecting different excitation wavelengths (\( \lambda_{\text{ex}} \)) of the source, because an excitation spectrum is the dependence of emission intensity at a single wavelength (\( \lambda_{\text{em}} \)), upon various excitation wavelengths. In other words, it gives the intensity contribution to the observed emission at a given wavelength by different excitation wavelengths for which the sample is exposed. The fluorescence spectra show two
fluorescence peaks clearly at 324 and 640 nm at concentrations $10^{-4}$ M and $10^{-5}$ M when excited with excitation wavelength $\lambda_{ex} = 250$ nm in desired wavelength regions (Figs 4 and 5). With so much high degree of intensity of fluorescence, it is assumed that this sample is highly fluorescent material. The observed fluorescence peak at 324 nm is related to absorption band observed at 285 nm giving Stokes shift of the order of 39 nm. The emission peak at 640 nm obviously corresponds to absorption peak at 495 nm leading to Stokes shift of the order of 145 nm. This observed phenomenon of absorption and fluorescence verify mirror image rule$^{24}$.

Fig. 4 — Fluorescence spectrum of disperse red 19 at concentration $10^{-4}$ M in ethanol with $\lambda_{ex}= 250$ nm

Fig. 5 — Fluorescence spectrum of disperse red 19 at concentration $10^{-5}$ M in ethanol with $\lambda_{ex}= 250$ nm

4 Conclusions

The absorption spectrum of the compound recorded at the concentration $10^{-4}$ M shows two absorption bands at 285 and 495 nm in the spectral region 200-700 nm. These peaks have been assigned to $(\pi^* \leftarrow \pi)^1 G, (\beta \leftarrow \pi)^1 A$ and $(\pi^* \leftarrow n)^1 W \leftarrow 1 A$ transitions, respectively. The extinction coefficient and oscillator strength of these bands have also been determined. The fluorescence spectra of the compound show two fluorescence peaks at 324 and 640 nm corresponding to absorption peaks at 285 and 495 nm, giving Stokes shift of the order of 39 and 145 nm, respectively. It is observed that $10^{-4}$ M and $10^{-5}$ M concentrations are optimum for the spectroscopic study of the compound.

Acknowledgement

Thanks are due to Dr Maya S Nayar, Assistant Professor at Department of Biotechnology, Indian Institute of Technology (IIT) Roorkee and her research scholar Padmapriya K for their help in recording fluorescence spectra of the sample.

References