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Static studies of absorption and emission spectra of acid yellow 17-An azo dye

Neena Jaggi[1]*, Kanta Yadav[1] & Manoj Giri[2]

[1]Department of Physics, National Institute of Technology, Kurukshetra 136 119, Haryana, India

Department of Physics, Haryana College of Technology & Management, Kaithal 136 027, Haryana, India

*E-mail: neena_jaggi@rediffmail.com

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In the present paper, the absorption and emission spectra of acid yellow 17 ($C_{16}H_{10}Cl_2N_4Na_2O_7S_2$), a fluorescent azo dye, have been recorded in water at concentrations between 10^{-3} M and 10^{-6} M. This dye is used in many scientific and industrial applications. This has led to the determination of optimum concentrations to record the absorption and emission spectra of the molecule. The absorption spectrum shows three peaks at 224, 254 and 400 nm, recorded in the spectral region 200-600 nm, which have been assigned to $(\pi^* \leftarrow \pi)\ {}^1L_a \leftarrow {}^1A$ (primary), $(\pi^* \leftarrow \pi)\ {}^1L_b \leftarrow {}^1A$ (secondary) and $(\pi^* \leftarrow n)^1 W \leftarrow {}^1A$ transitions, respectively. Emission spectra of the compound show four peaks at 295, 306, 412 and 437 nm corresponding to absorption peaks at 224, 254 and 400 nm. Their corresponding Stokes shifts have also been determined.

Keywords: Dyes, Absorption, Emission, Oscillator strength, $\pi^* \leftarrow \pi$ & $(\pi^* \leftarrow n)$ transition, Stokes shift

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 industrial use in colouration of textiles, plastics, cosmetics, many scientific and technological applications such as in laser dyes, photonics, biological study and nonlinear optical devices[2-10]etc. Azo dyes are a distinct class of dyes characterized by the presence of one or more azo (−N=N−) groups[11]. The possibility of connecting an almost unlimited number of different molecules by way of the azo bridges is the reason behind the large number of representatives of this group[12]. These are the most important commercial colorants because of their wide colour range, good fastness properties, colour density, which is better than that of any other class of dyes. Azo compounds are also known for their medicinal applications and well recognized for their use as, antidiabetics, antibacterial and antitumor[13-16]. In the light of variety of diverse applications of azo dyes, it is conceivable to study such azo dyes and their derivatives in order to unfold more potential of such compounds. The steady state fluorescence analysis of azo dyes is required due to their potential applications as infrared laser dyes and photosensitive species in photographic systems. Therefore, by analyzing the importance of these dyes especially acid yellow 17, it is justified to carry out systematic spectroscopic studies for it[17-22]. In the present study, the assignment of transitions involved in the absorption peaks of this compound have been made and the corresponding extinction molar coefficient and oscillator strength have been calculated. By analyzing fluorescence spectra, the Stokes shift of the molecule has been determined The contradiction of mirror image rule is observed here and the quenching effect has also been observed in the AY 17 molecule. The molecular structure of this compound is shown in Fig. 1. It is an azo dye soluble in water to give intense yellow colour. It is used to colour all kind of natural fibres like wool, cotton and silk as well as to synthetics like polyesters, acrylic and rayon. This is also applied in paints, inks, plastics and leather.

2 Experimental Details

Analytical reagent quality acid yellow 17 was obtained from M/S Sigma Aldrich Chemical Company, Inc., USA and used without further purification. Its absorption spectra in double distilled water 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. Figure 2 shows the absorption spectrum of the compound at concentration 10^{-5} M, recorded only in the spectral region 200-600 nm. In this region,three absorption bands at 224, 254 and 400 nm are observed.

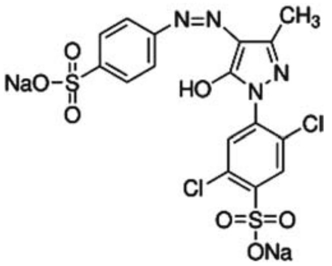

Fig. 1— Molecular structure of acid yellow 17 azo dye

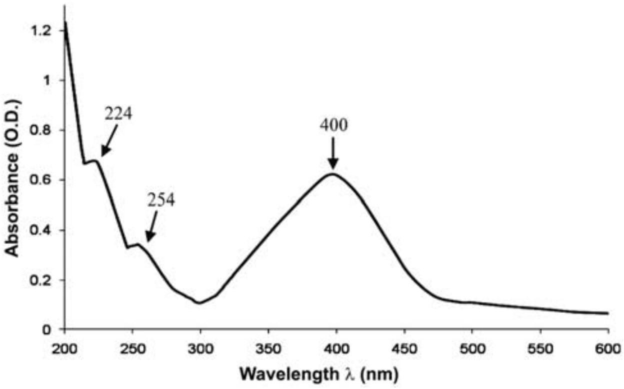

Fig. 2—Absorption spectrum of acid yellow 17 at concentration 10^{-5} M in water

The wavelength of the maximum absorbance is a characteristic value, designated as $\lambda_{max.}$ Different molecules have very different absorption maxima and absorbance. From the analysis of absorption spectrum of AY 17, the compound shows maximum absorbance at 400 nm (λ_{max}). This observed value is confirmed as we compare the curve as shown in (Fig. 2) with the reported curve which[23] also shows λ_{max} at the same wavelength. Excitation and emission spectra of the compound in distilled water for all the above mentioned concentrations were recorded on Shimadzu photoluminescence spectrophotometer utilizing xenon flash lamp. The excitation slit width and emission slit width were kept at 10 nm during the experiment so as to get an optimum intensity in excitation and emission spectra.

3 Analysis and Discussion

Although absorption spectra of the compound were recorded at four concentrations between 10^{-3} and 10^{-6} M in the range 200-600 nm, those at only two concentrations i.e. 10^{-4} and 10^{-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 three absorption peaks at about the same wavelengths viz 224, 254 and 400 nm (Fig. 2). In case of ultraviolet and visible spectroscopy, the transitions which occur in the absorption, are transitions between electronic energy levels. The position and intensity are the main features of an absorption peak. The position relates to the wavelength of radiation whose energy is equal to that required for an electronic transition. The intensity of absorption mainly depends on two factors: (i) probability of interaction between radiation and electronic system to raise the molecule from ground level to an excited level and (ii) polarity of the excited state. This probability of electronic transition is proportional to the square of the transition moment. This transition moment is also known as dipole moment of transition is proportional to the change in the electronic charge distribution occurring during excitation. An intense absorption peak occurs when a transition takes place by a great change in the transition moment. The low probability transitions are forbidden transitions[24]. In the present study, λ_{max} is observed at 400 nm. A plot of optical density for these observed bands against wave number ν (cm^{-1}) for the concentration 10^{-5} M is shown in Fig. 3 From this plot, the value of maximum molar extinction coefficient (ε_{max}) for the absorption bands I, II and III at frequencies 4.46×10^4 cm^{-1}, 3.93×10^4 cm^{-1} and 2.50×10^4 cm^{-1} have been calculated as 67.0×10^3, 34.0×10^3 and 62.0×10^3 (M^{-1} cm^{-1}), respectively. The oscillator strength[25], $f = 4.315\times10^{-9} \int \varepsilon \, d\nu$, for these bands have also been calculated as 22.4×10^{-2}, 19.8×10^{-2} and 47.4×10^{-2} (M^{-1} cm^{-2}), respectively. Acid yellow 17 consists of chloro-substituted sodium salt of benzene sulphonic acid which is connected

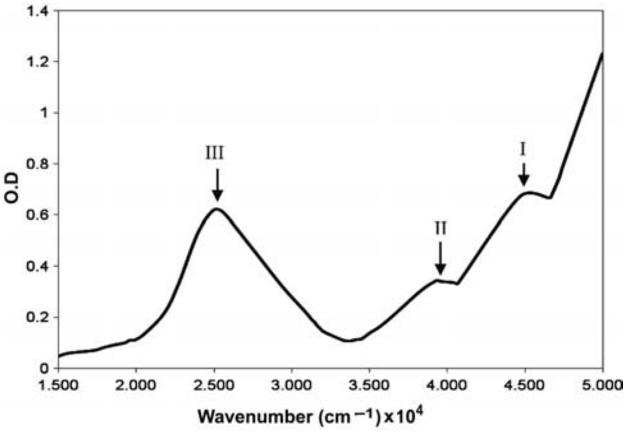

Fig. 3—Variation of optical density against wave number of acid yellow 17 at concentration 10^{-5} M in water

with pyrazole linked with sodium benzene sulphonic through azo group (Fig. 1). The comparison of the absorption bands of moieties involved in this molecule may be useful in deciding the transitions involved in the observed absorption peaks of the compound. An $\pi^* \leftarrow n$ transition has been observed at 387 nm in azomethane[25]. As such due to the substitution of azo group with pyrazole, it is expected to change this transition in to visible region in the present molecule at a higher wavelength due to resonance effect. Therefore, we say here that the –N=N– group gives the molecule ($\pi^* \leftarrow n$) $^1W \leftarrow {}^1A$ transition, which is involved in the absorption peak observed at 400 nm. The bands observed at 224 and 254 nm for acid yellow 17 may be correlated to transitions of benzene ring associated with additional group, because benzene ring[25] shows two absorption transitions in this region one at 204 (primary $\pi^* \leftarrow \pi$) $^1L_a \leftarrow {}^1A$ and another weak at 254 nm (secondary $\pi^* \leftarrow \pi$) $^1L_b \leftarrow {}^1A$. So, the bands observed in the present molecule at 224 nm (having high absorbance) and 254 nm (having less absorbance) may be correlated to primary and secondary ($\pi^* \leftarrow \pi$) transitions of phenyl ring. The absorption spectrum of pyrazole shows absorption at 210 nm and on substitution it indicates a red shift. A possible masking of the band present in case of pyrazole at 210 nm may be due to through these two transitions of phenyl ring. Emission spectra of the compound under study were recorded by choosing different excitation wavelengths (λ_{ex}) of the source. Because an excitation spectrum is dependent on emission intensity at a single wavelength (λ_{em}), upon various excitation wavelengths. In other words, it gives the intensity contribution to the observed emission at a given wavelength by different excitations wavelengths for which the sample is exposed. The excitation spectrum of acid yellow 17 shows two excitation peaks at 250 and 360 nm at concentration 10^{-4} M in water with λ_{em}= 400 nm as shown in Fig. 4. The purpose of the excitation spectrum is to know about the suitable excitation wavelengths by which we excite the sample to get the maximum emission. At another concentration, it shows the same peaks as observed.

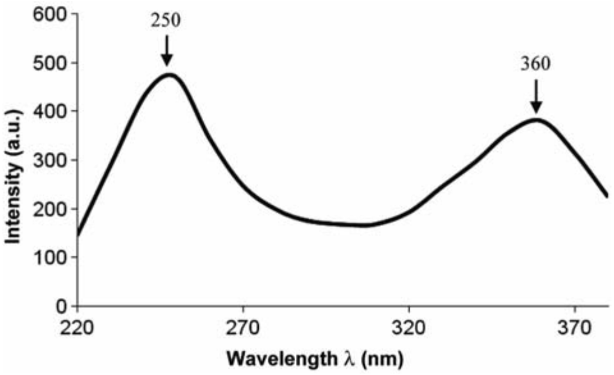

Fig. 4— Excitation spectrum of acid yellow 17 at concentration 10^{-4} M in water with λ_{em}= 400 nm

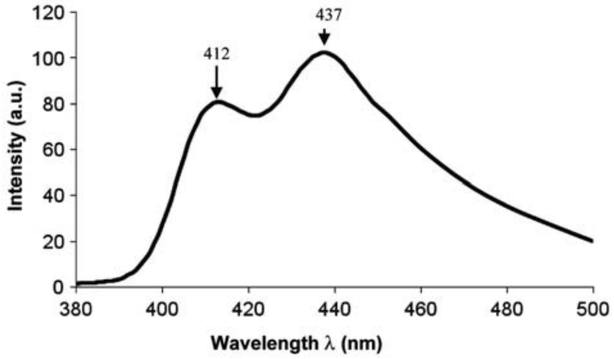

Fig. 5— Emission spectrum of acid yellow 17 at concentration 10^{-4} M in water with λ_{ex}= 360 nm

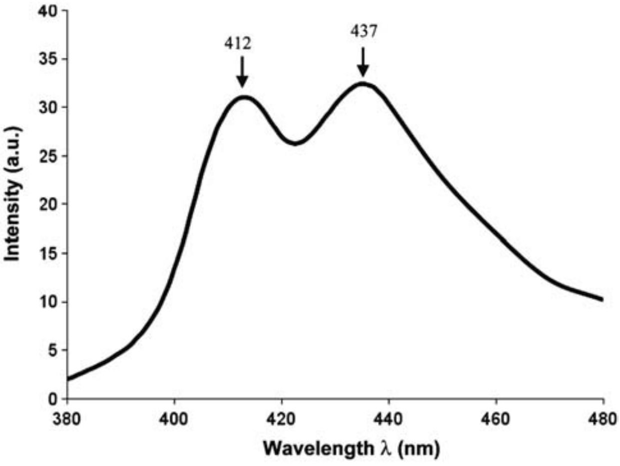

Fig. 6— Emission spectrum of acid yellow 17 at concentration 10^{-5} M in water with λ_{ex}= 360 nm

The emission spectra show two nearby emission peaks clearly at 412 nm and 437 nm at concentrations 10^{-4} M and 10^{-5} M, when dye is exposed with excitation wavelength λ_{ex} = 360 nm in desired wavelength regions (Figs 5 and 6). The intensity of the emission peaks is shown to be increased at concentration 10^{-4} M as compared to 10^{-5} M. These observed emission peaks are related to broad absorption band observed at 400 nm giving stokes shift of 12 and 37 nm, respectively. This observed phenomenon of absorption and emission is

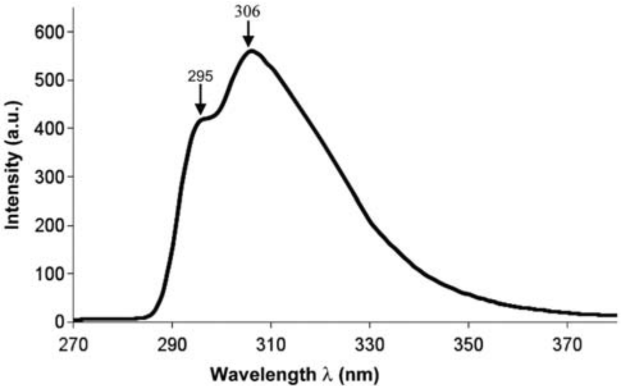

Fig. 7 — Emission spectrum of acid yellow 17 at concentration 10^{-4} M in water with λ_{ex}= 250 nm

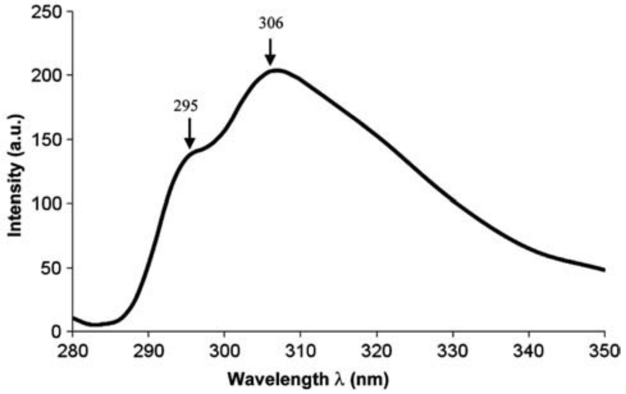

Fig. 8 — Emission spectrum of acid yellow 17 at concentration 10^{-5} M in water with λ_{ex}= 250 nm

contradicting mirror image rule due to change in its vibrational structures of ground and excited[26]. Using the excitation wavelength at λ_{ex} = 250 nm, the emission spectra show a peak at 306 nm with a prominent shoulder at 295 nm for both the concentration 10^{-4} M and 10^{-5} M (Figs 7 and 8).

The emission peak at 306 nm is related to absorption band at 254 nm giving Stokes shift of 52 nm. The shoulder emission band observed at 295 nm is related to absorption band at 224 nm resulting in Stokes shift of 71 nm. The sample at concentration 10^{-3} M shows no emission indicating the quenching effect at high concentration because the molecule shows no clear peak at any wavelength when exposed to λ_{ex} = 360 and 250 nm. Also the intensity of the fluorescence spectra is larger at 10^{-4} M as compared to 10^{-5} M concentration with same excitation and emission slit width showing that 10^{-4} M concentration is the optimum concentration of the sample in distilled water for recording emission spectra.

4 Conclusions

The absorption spectrum of the compound recorded at the concentration 10^{-5} M shows three absorption bands at 224, 254 and 400 nm in the spectral region 200-600 nm. These peaks have been assigned to $\pi^*\leftarrow\pi$ (primary) $^1L_a \leftarrow {}^1A$, $\pi^*\leftarrow\pi$ (secondary) $^1L_b \leftarrow {}^1A$ and ($\pi^*\leftarrow$ n) $^1W \leftarrow {}^1A$ transitions, respectively. The extinction coefficient and oscillator strength of these bands have also been determined. The emission spectra of the compound show four emission peaks at 295, 306, 412 and 437 nm corresponding to absorption peaks at 224, 254 and 400 nm. Their relatively Stokes shifts have been calculated. It is observed that 10^{-4} M is the optimum concentrations for the spectroscopic study of the compound. Mirror image rule is not verified for absorption bands III and its related emission bands at 412 and 437 nm.

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