SRI VENKATESWARA INTERNSHIP PROGRAMME FOR REASEARCH IN ACADEMICS (SRI-VIPRA)

Project Report 2022 (SVP-2237)

Spectral Studies of Azo-dyes

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SRI-VIPRA 2022

Title: "Spectral Studies of Azo-dyes"

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SRI VIPRA 2022
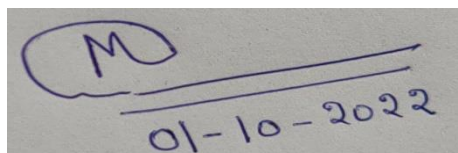
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CERTIFICATE

This serves as confirmation that the aforementioned students from Sri Venkateswara College took part in the "Spectral Studies of Azo-dyes" summer project. From July 4 to August 27, 2022, the participants worked on the research project under my direction and supervision. The work was done in offline mode and is entirely original. The references used have been declared at the end of the report.

01-10-2022

Signature of Mentor

ACKNOWLEDGEMENTS

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Abstract:

Azo dyes form an important class of dyes with widespread uses in modern-day society. Reviewing the impacts of the dye has become essential at present to help better understand the effect it may have on humans and the environment. The aforementioned is addressed by using spectrophotometry on Azo dyes: Disperse Red 1 and Direct Yellow 8 across the wavelengths of 200 nm to 700 nm. Dye solutions had been prepared with concentrations ranging from 1 µM to 100 µM across five solvents. The absorption and emission profiles were plotted and analyzed for each permutation of dye, its concentration, and its solvent. Standard formulae have been used to determine the Molar Extinction Coefficient (MEC), Oscillator Strength and Dipole Moment of the collected samples for the observed electronic transitions. MEC has been plotted against wavenumber and the maximum values have been registered for the purpose of this report. The oscillator strength and dipole moment of DY 8 in water at 10 µM was calculated as 167.61×10^{-2} $M^{-1}cm^{-2}$ and 140.27 $M^{-1/2}cm^{-1/2}$ respectively. In addition, the oscillator strength and dipole moment of Disperse Red1 was found as 84.50×10^{-2} $M^{-1}cm^{-2}$ and 9.4614 **D** respectively in the formamide at 40 µM.

1. Introduction and Literature:

Substances with the ability to absorb or emit light in the visible range are generally called colourants. Dyes are a form of colourants which have a great affinity to the material they are applied to. Aside from their obvious utility in imparting colour to matter, they find various uses in the scientific and technical industry in the form of dye lasers, liquid crystal displays, optical data storage and non-linear optics [1,2]. Dyes can be classified on the basis of their chemical structure. The dye of our concern is azo dye. Azo dyes are characterised by the functional group R−N=N−R′ where R and R' are hydrocarbyl groups [3,4]. They constitute about 60% of all dyes and 70% of the dyes used in commerce [5,6]. This extensive use in the textile, cosmetic and leather industry is due to their colour brilliancy, light stability and low cost of production [7,8]. Because of their significance, azo dyes' toxicity has been thoroughly researched. Bladder cancer rates among employees who made dyes were found to be rising as early as 1895[9]. In 2010, the International Agency for Research on Cancer (IARC) acknowledged the mutagenic and carcinogenic potential of a number of non-ionic azo dyes. Dyes can also be classified based on their method of application. Two such classes of dyes are substantive or direct dyes and disperse or dispersible dyes. Direct dyes are water soluble dyes that form electrostatic bonds with the substrate. They bind easily to cellulosic fibres like cotton and paper. Disperse dyes are water insoluble dyes that are applied in aqueous dispersions onto hydrophobic, generally synthetic, fibres like polyester [10,11]. This report is of the spectral study of two azo dyes - Direct Yellow 8 and Disperse Red 1. The photophysical parameters like molar absorption coefficient, oscillator strength and dipole moment for the two dyes corresponding to their respective absorption peaks in different solvents have been calculated.

Direct Yellow 8

Direct Yellow 8 is a green light yellow azo dye. It is water soluble and has some solubility in other organic solvents. Its molecular formula is $C_{24}H_{19}N_4NaO_5S_2$ and IUPAC name is sodium; 2-[4-[(1-anilino-3-hydroxy-1-oxobut-2-en-2-yl) diazenyl] phenyl]-6-methyl-1,3-benzothiazole-7-sulfonate [12]. The molecular weight of the dye is 530.55. Applications of the dye include cotton and viscose fabric dyeing and printing [13]. Figure 1(a) and 1(b) show the 2-D and 3-D chemical structure of the dye respectively.
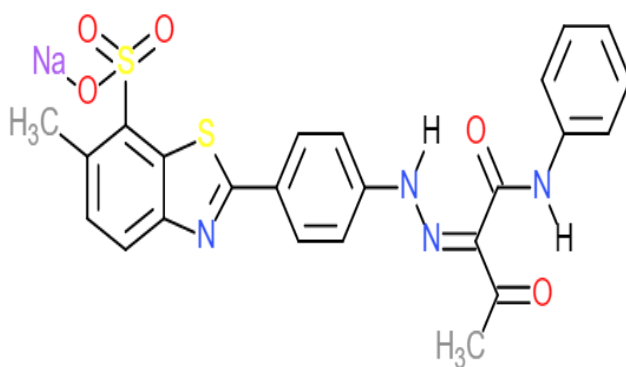
Fig. 1(a) 2D Structure of Direct Yellow 8
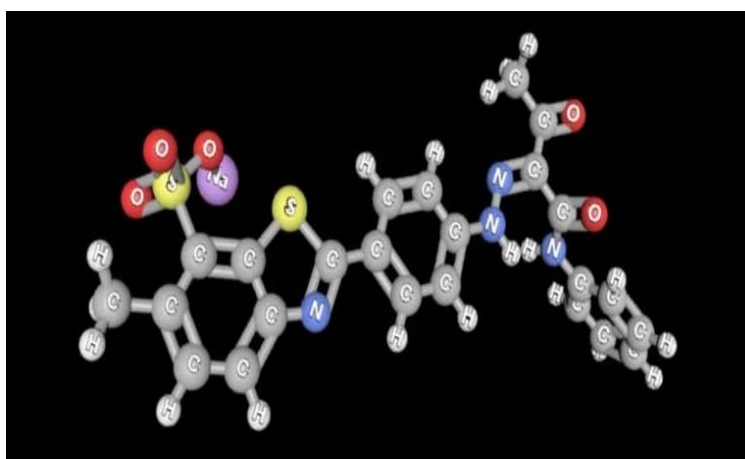
Fig. 1(b) 3D Structure of Direct Yellow 8

Disperse Red 1

Disperse Red 1 is an azo dye commercially sold as a dark red powder. It is water insoluble but soluble in ethanol and benzene. It is mainly used for polyester dyeing and printing [14]. It is a carbocyclic monoazo [15]. compound with molecular formula $C_{16}H_{18}N_4O_3$ and IUPAC name 2-[N-ethyl-4-[(4-nitrophenyl) diazenyl] anilino] ethanol. The molecular weight for this compound is 314.34. It is an allergen [16]. The figures 1(c) and 1(d) show the 2-D and 3-D molecular structures of the dye.

Fig. 1(c) 2D Structure of Disperse Red 1

Fig. 1(d) 3D Structure of Disperse Red 1

2. Apparatus and Experimental Detail:

Spectrophotometry

Spectrophotometry is a subfield of electromagnetic spectroscopy that deals with the quantitative measurement of a material's reflection or transmission qualities as a function of wavelength [17]. It is a result of the d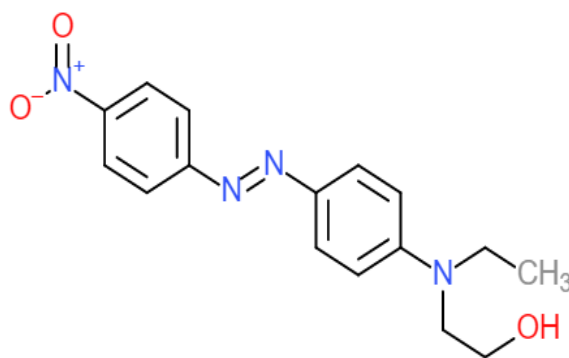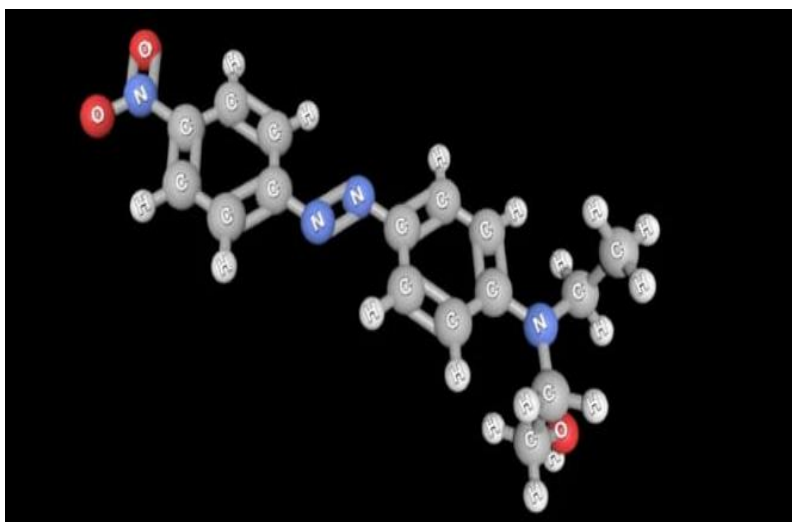iscrete interactions between electromagnetic radiations and atoms and molecules which result in recognizable absorption and emission profiles [18]. Spectrophotometry makes use of devices called spectrophotometers that gauge a light beam's intensity at various wavelengths. Modern day spectrophotometers can analyze a large portion of the electromagnetic spectrum however this report is limited to UV and visible regions (200-700 nm).

Spectrophotometers

A spectrophotometer is a device that quantifies the intensity of electromagnetic energy at each wavelength of light in a specified region of the electromagnetic spectrum [19]. In this device, a prism or grating monochromator divides the measurement light into its individual wavelengths. By using a deuterium lamp for the UV region and a tungsten lamp for the visible region, a continuous variation of wavelength over the spectral region for the subsequent measurements is provided [20]. The liquid sample is held in a cell called cuvette. Cuvettes used in UV-Visible spectrophotometry are made of glass or quartz. As the absorbance of the sample depends on the light intensity, a series of detectors and monitors are used to convert the light intensity to an electrical signal which can be further analyzed [21].

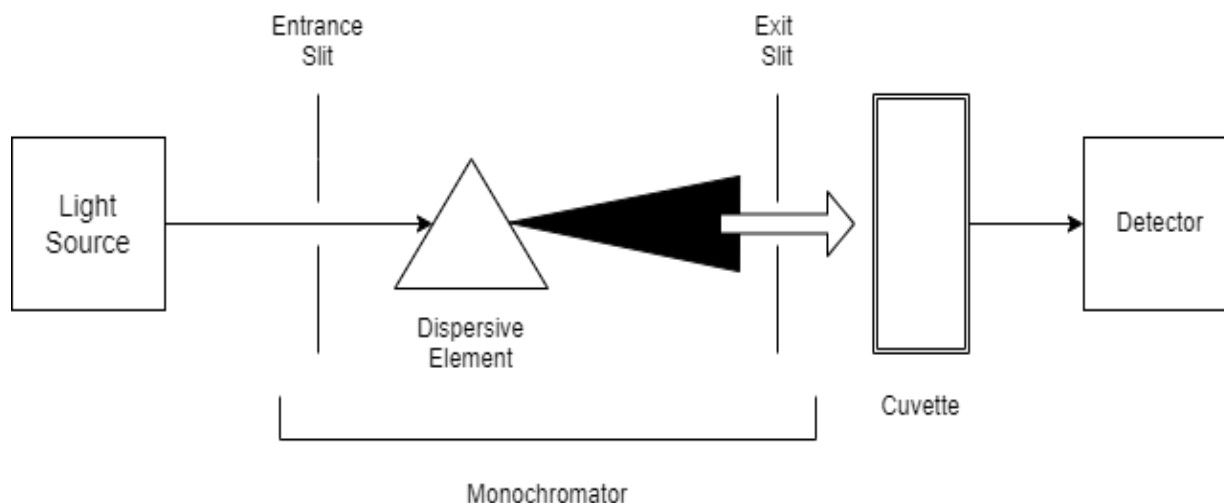The following figure shows a basic diagrammatic representation of a spectrophotometer.

Fig. 2 Spectrophotometer

Data Collection

The samples for different concentrations (ranging from 1µM to 100µM) of Direct Yellow 8 and Disperse Red 1 in various solvents were made and their absorption spectrum was measured by the Beckman Coulter DU 730 UV/Vis Spectrophotometer [22] with a quartz cuvette of path length 10 mm. Disperse Red 1 was procured from M/s Sigma Aldrich Chemical Company, Inc., USA and Direct Yellow 8 from M/s Tokyo Kasei Kogyo Co. Ltd., Japan.

3. Data Analysis and Discussion:

Photophysical parameters calculation

Standard formulae are used to derive the major photophysical parameters based on the obtained absorption spectra. For each value of λ_{max}, i.e. the wavelength of the peak optical density in the absorption spectra, a corresponding value of ν_{max} is observed. A plot of wavenumber (ν) versus molar extinction coefficient (ε) is plotted where ε is calculated using the Beer-Lambert Law: [23]

$$\varepsilon = \frac{A}{C \times l}$$

where

- ε is the molar extinction coefficient (M^{-1}cm^{-1})
- A is the absorbance of the sample
- C is the concentration of the sample (in M)
- l is the path length of the incident light through the sample (in cm)

The maximum value of the molar extinction coefficient ε_{max} for the absorption bands can then be worked out from the plot and be used for further calculations. The oscillator strength for the bands can be calculated using the relation

$$f = \frac{4.315 \times 10^{-9} \int \varepsilon \, dv}{n}$$

where f is the oscillator strength (M^{-1}cm^{-2}) and n is the refractive index of the solvent.

The dipole moment (M$^{-1/2}$cm$^{-1/2}$) for the transition can be calculated using

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} \times v_{max}}$$

where v_{max} is the wavenumber corresponding to the maximum absorption energy and f is the oscillator strength for the respective peak [24].

Direct Yellow 8 in Water

The graph in figure 3(a) shows the absorption spectra of Direct Yellow 8 in distilled water ($n=1.33$) for concentrations 1µM and 10µM recorded in the spectral range 300-600 nm. An absorption peak is observed for the solution at around 395 nm.

Fig. 3(a) Absorption Spectra for Direct Yellow 8 in Water

A sharper peak can be observed for the 10µM aqueous solution so further analysis is done on the said concentration. The highest value of absorbance equal to 1.056 was found at $\lambda_{max} = 395$ nm. The variation of the molar extinction coefficient and wavenumber is shown in figure 3(b) below where $\varepsilon_{max} = 105600$ M^{-1}cm^{-1} was calculated for the corresponding $\nu_{max} = 25316.4557$ cm^{-1}.

Fig. 3(b) Variation of ε with wavenumber for given concentration of Direct Yellow 8

The oscillator strength f has been calculated as 1.676101737 $M^{-1}cm^{-2}$ and the dipole moment μ_{12} as 11.8436 $M^{-1/2}cm^{-1/2}$ for the peak using the above previously mentioned formulae.

Direct Yellow 8 in Methanol

The graph in figure 3(c) shows the absorption spectra of Direct Yellow 8 in Methanol ($n=1.327$) for concentrations 1μM, 10μM, 20μM and 40μM recorded in the spectral range 300-600 nm. An absorption peak is observed for the solution at around 400 nm.
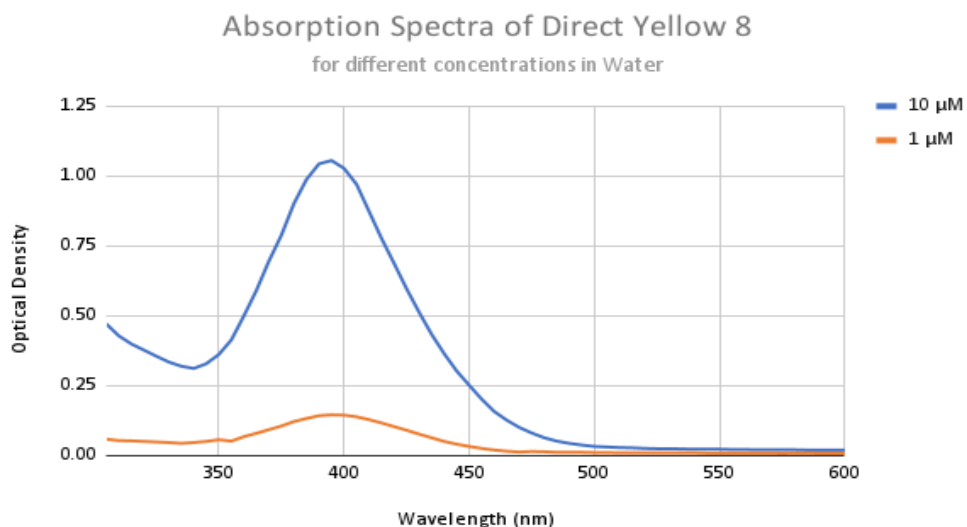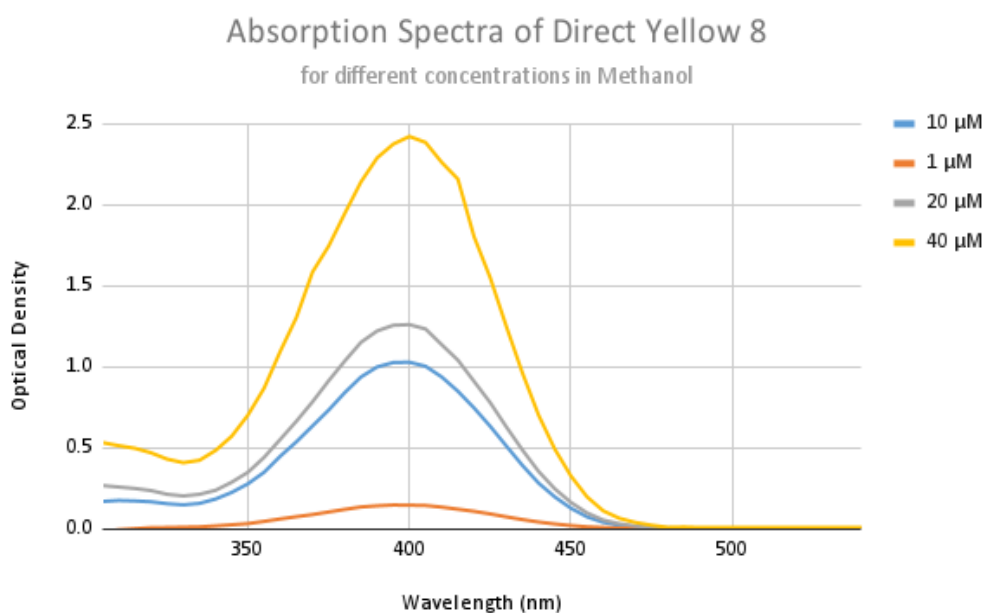

Fig. 3(c) Absorption Spectra for Direct Yellow 8 in Methanol

A sharper peak can be observed for the 40μM solution so further analysis is done on the said concentration. The highest value of absorbance equal to 2.423 was found at λ_{max} = 400 nm. The variation of the molar extinction coefficient and wavenumber is shown in figure 3(d) below where ε_{max} = 60575 $M^{-1}cm^{-1}$ was calculated for the corresponding v_{max} = 25000 cm^{-1}.

Direct Yellow 8 in Methanol (40 µM)

Wavenumber v/s Molar Extinction Coefficient

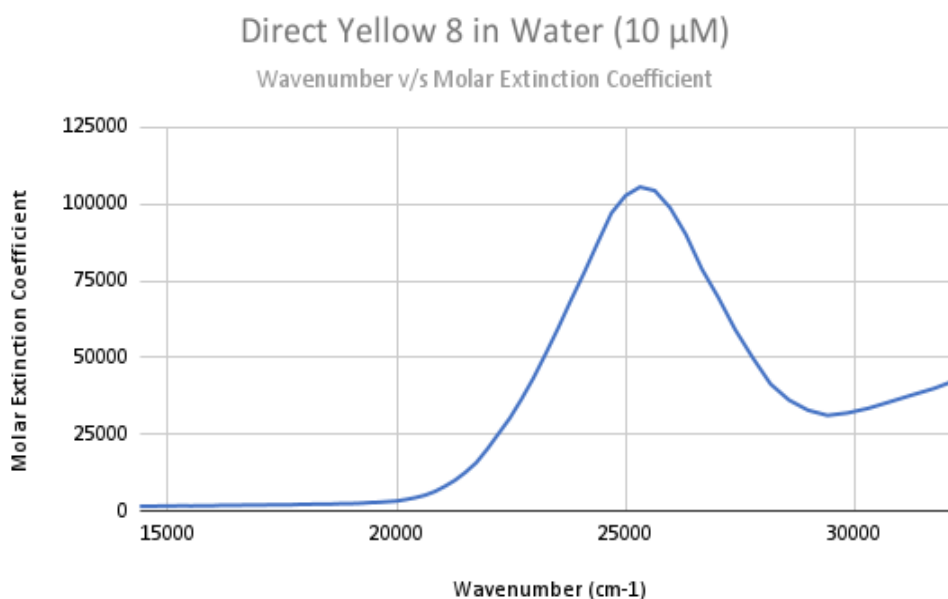*Fig. 3(d) Variation of ε with wavenumber for given concentration of Direct Yellow 8*

The oscillator strength f has been calculated as 0.8920131307 $M^{-1}cm^{-2}$ and the dipole moment μ_{12} as 8.6945 $M^{-1/2}cm^{-1/2}$ for the peak using the previously mentioned formulae.

Disperse Red 1 in Acetone

The graph in figure 3(e) shows the absorption spectra of Disperse Red 1 in Acetone ($n=1.3586$) for concentrations 10µM and 20µM recorded in the spectral range 350-650 nm. An absorption peak is observed for the solution at around 485 nm.

Absorption Spectra of Disperse Red 1

for different concentrations in Acetone

Fig. 3(e) Absorption Spectra for Disperse Red 1 in Acetone

A clearer peak can be observed for the 20μM solution so further analysis is done on the said concentration. The highest value of absorbance equal to 0.942 was found at λ_{max} = 485 nm. The variation of the molar extinction coefficient and wavenumber is shown in figure 3(f) below where ε_{max} = 47100 $M^{-1}cm^{-1}$ was calculated for the corresponding ν_{max} = 20618.56 cm^{-1}.
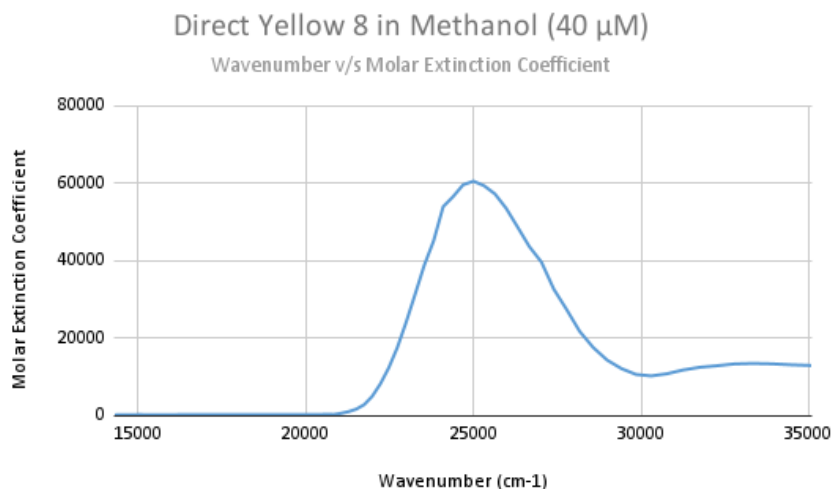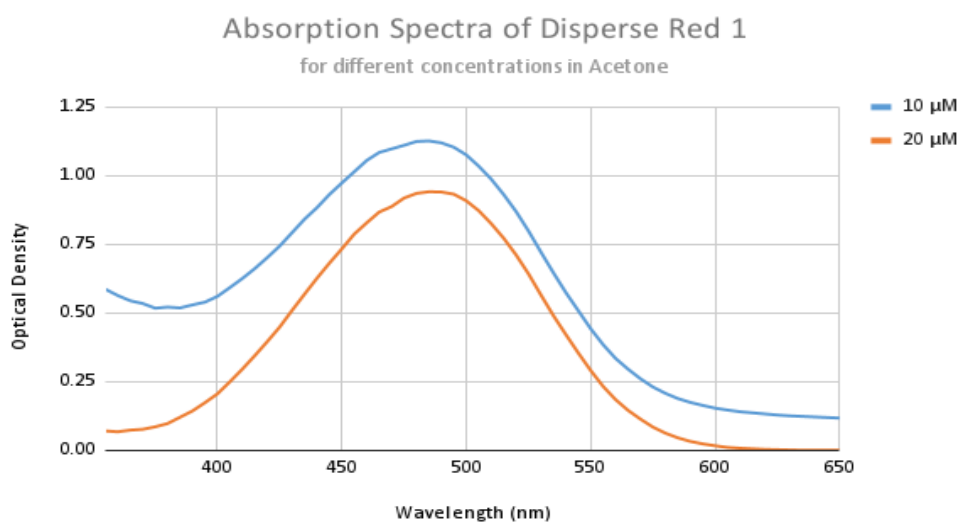

Fig. 3(f) Variation of ε with wavenumber for given concentration of Disperse Red 1

The oscillator strength *f* has been calculated as 0.7609173706 $M^{-1}cm^{-2}$ and the dipole moment μ_{12} as 8.8424 $M^{-1/2}cm^{-1/2}$ for the peak using the previously mentioned formulae.

Disperse Red 1 in Dimethyl Formamide

The graph in figure 3(g) shows the absorption spectra of Disperse Red 1 in Dimethyl Formamide (*n=1.4305*) for concentrations 10μM, 20μM and 40μM

recorded in the spectral range 200-700 nm. An absorption peak is observed for the solution at around 500 nm.

Absorption Spectra of Disperse Red 1
for different concentrations in Formamide

Fig. 3(g) Absorption Spectra for Disperse Red 1 in Formamide

A clearer peak can be observed for the 40µM solution so further analysis is done on the said concentration. The highest value of absorbance equal to 2.259 was found at $\lambda_{max} = 500$ nm. The variation of the molar extinction coefficient and wavenumber is shown in figure 3(h) below where $\varepsilon_{max} = 56475$ M^{-1}cm^{-1} was calculated for the corresponding $\nu_{max} = 20000$ cm^{-1}.

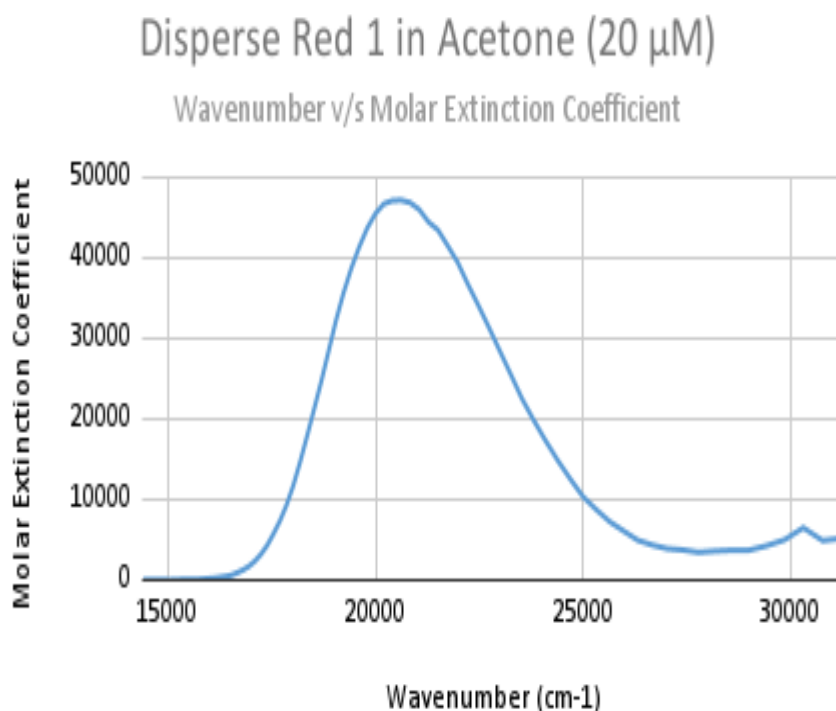**Fig. 3(h) Variation of ε with wavenumber for given concentration of Disperse Red 1**

The oscillator strength f has been calculated as 0.8450433982 $M^{-1}cm^{-2}$ and the dipole moment μ_{12} as 9.4614 $M^{-1/2}cm^{-1/2}$ for the peak using the previously mentioned formulae.

Disperse Red 1 in Dimethyl Sulphoxide (DMSO)

The graph in figure 3(i) shows the absorption spectra of Disperse Red 1 in DMSO ($n=1.4793$) for concentrations 1µM, 10µM, 20µM and 40µM recorded in the spectral range 200-700 nm. An absorption peak is observed for the solution at around 510 nm.

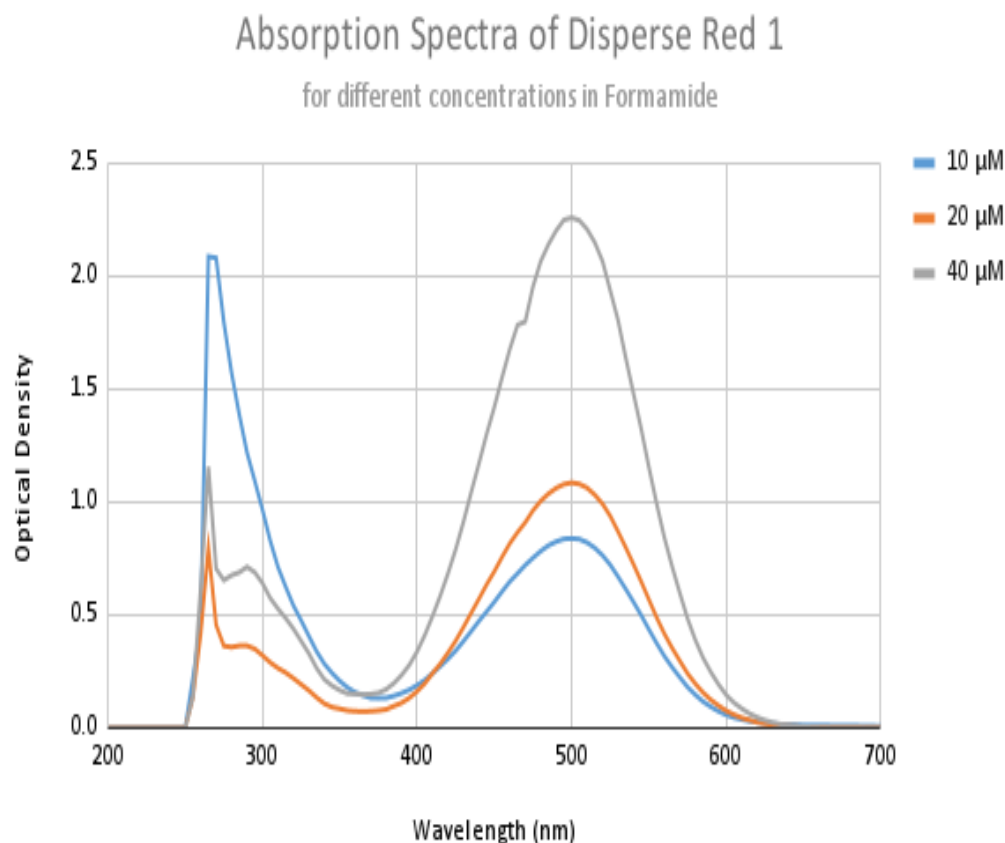**Fig. 3(i) Absorption Spectra for Disperse Red 1 in DMSO**

A clearer peak can be observed for the 40μM solution so further analysis is done on the said concentration. The highest value of absorbance equal to 1.873 was found at $\lambda_{max} = 510$ nm. The variation of the molar extinction coefficient and wavenumber is shown in figure 3(j) below where $\varepsilon_{max} = 46825$ $M^{-1}cm^{-1}$ was calculated for the corresponding $\nu_{max} = 19607.84$ cm^{-1}.

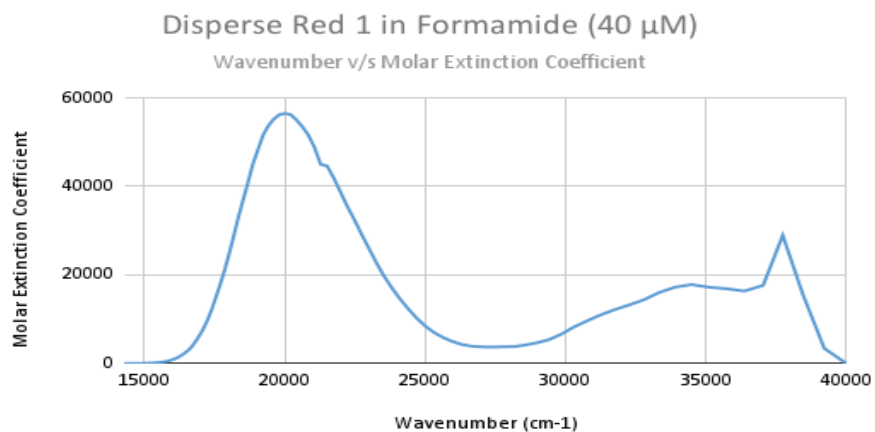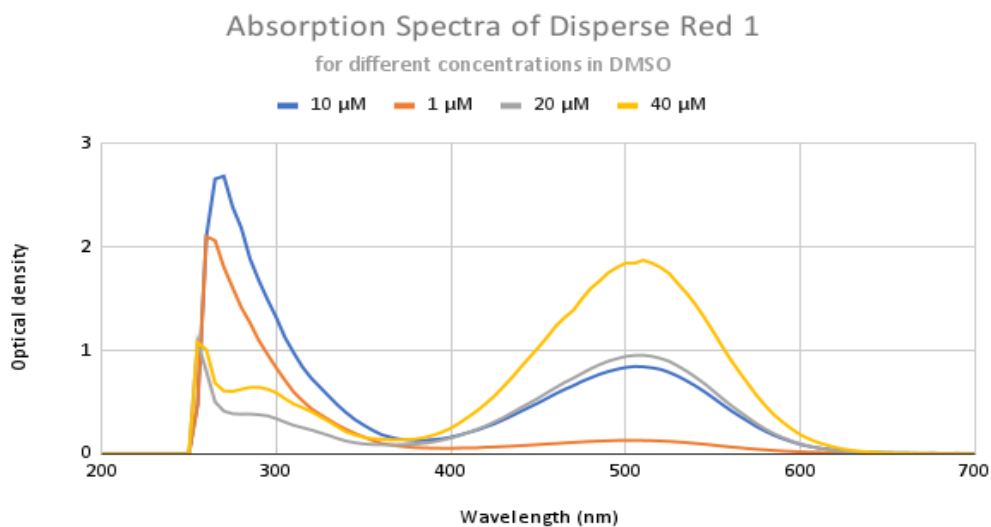**Disperse Red 1 in DMSO (40 μM)**

Molar Extinction Coefficient v/s Wavenumber
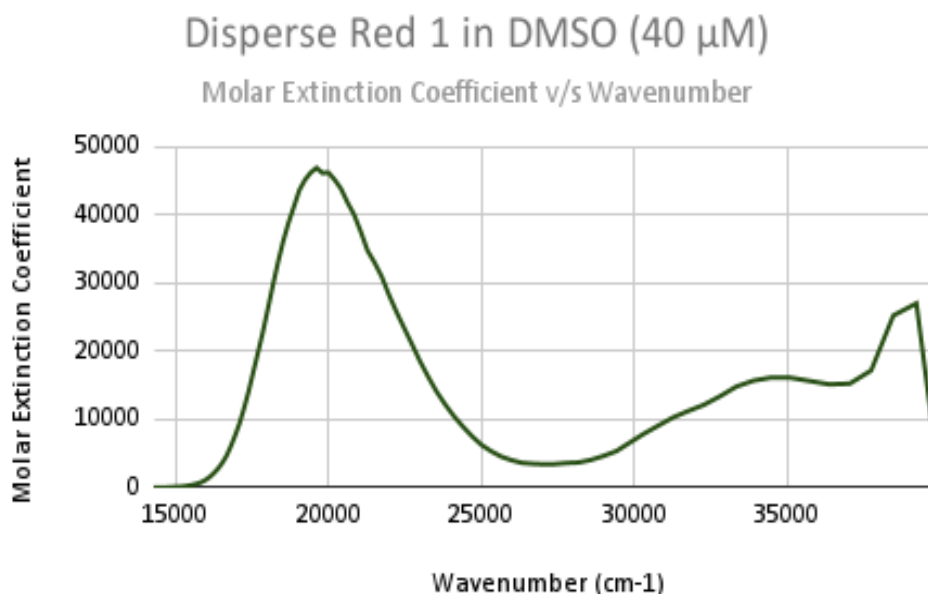
Fig. 3(j) Variation of ε with wavenumber for given concentration of Disperse Red 1

The oscillator strength f has been calculated as 0.6554973478 $M^{-1}cm^{-2}$ and the dipole moment μ_{12} as 8.4159 $M^{-1/2}cm^{-1/2}$ for the peak using the previously mentioned formulae.

4. Conclusions:

Upon analysis of the optical absorbance of the azo dyes Direct Yellow 8 and Disperse Red 1, dissolved in different solvents, in the UV-Visible region (200-700nm), we observed absorption maxima corresponding to their electronic transitions. The maximum optical density (A_{max}) and molar extinction coefficient (ε_{max}) corresponding to the peak wavenumber (ν_{max}) for the two dyes in their different

solutions is determined. Alongside is the oscillator frequency (f) and the square of the dipole moment (μ_{12}^2) of the transition which is proportional to the probability of the electronic transition. Various photophysical parameters of scientific importance have been calculated and shown in the Table 1.

Dye and Solvent	A_{max}	ε_{max} (M⁻¹cm⁻¹)	f (M⁻¹cm⁻²)	μ_{12}^2 (M⁻¹ᐟ²cm⁻¹ᐟ²)
Direct Yellow 8 in Water (10µM)	1.056	105.6×10^3	167.61×10^{-2}	140.27
Direct Yellow 8 in Methanol (40µM)	2.423	60.575×10^3	89.20×10^{-2}	75.59
Disperse Red 1 in Acetone (20µM)	0.942	47.1×10^3	76.09×10^{-2}	78.19
Disperse Red 1 in Formamide (40µM)	2.259	56.47×10^3	84.50×10^{-2}	89.52
Disperse Red 1 in DMSO (40µM)	1.873	46.8×10^3	65.55×10^{-2}	70.83

Table 1- Photophysical parameters of Direct Yellow 8 and Disperse Red 1

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