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Effect of pH on the Spectral Properties of Acid Orange Seven and Plasmocorinth B Dyes in Aqueous Systems

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Abstract:

The present study investigated the effect of pH on the spectral properties of Acid Orange 7 and Plasmocorinth B azo dyes in aqueous systems. Several concentrations of each dye were prepared from a stock solution. The molar extinction coefficient (ϵ) and maximum absorption wavelength $\lambda_{\max}$ of the dyes in different pH environments were measured using a UV/Vis spectroscopy. Dye absorbance was measured between $\lambda=200$ nm-800 nm. The results indicate that the maximum absorption wavelengths $\lambda_{\max}$ of AO7 and PC-B were determined at 485 nm and 528 nm respectively. The molar extinction coefficient (ϵ) was calculated at Acid Orange 7= 20647 dm³. Mol⁻¹.cm⁻¹ and Plasmocorinth B= 19203 dm³.mol⁻¹.cm⁻¹. The finding shows that pH has no effect on the absorbance of the aqueous dye solutions indicating dye stability under different pH levels.

Keywords: Molar extinction coefficient, Maximum absorption wavelength, Plasmocorinth B, Acid Orange 7, UV/Vis Spectroscopy, pH

1. Introduction

1.1. Occurrence of Dyes

Dyes comprise of intensely coloured complex unsaturated organic substances that absorb light and give colour to the visible region. Dyes absorb part of visible spectrum (chromophore) and find wide application in the industry to colour paper, leather, textiles and other materials (Dadfarina et al., 2015; Trapaliset al., 2003; Robinson et al., 2001; Zerin, 2020). Plants have been the greatest source of dyes, notably roots, leaves, berries, barks and wood. As a result of rapid deforestation dyes sources from vegetation has not been commercialized (Silva, 2020; Chandanshive, 2018; Ayedet al., 2017). In recent times dyes have been obtained from coal and petrochemicals (Wang et al., 2017). The structures of dyes are easily modified to produce many new colours and dye types (Cernigoj, 2007). The application of dyes involves deposition from solutions onto substrate materials so that original solvents cannot remove them. Some dyes react with fibre to form covalent bonds with the material. Other dyes are initially applied as a mordant, an inorganic material that leads to the dye precipitation as an insoluble salt (Singh et al., 2015; Moreira et al., 1998; Samanta, 2011). Another dye fastening techniques vat dyeing where soluble colourless compounds is absorbed by fibre materials, oxidized to the insoluble coloured compounds making resistant to the fading effects of light, chemicals and washing (Faisal et al., 2007; Silva, 2020).

1.2. Categorization of Dyes

Dyes are generally classified into various types based on various characteristics that include:-

1.2.1. Chemical Structures

- Cationic: Cationic blue, methylene blue (MB)
- Anionic: Acid Orange 7, Plasmocorinth B, Procion B (PR) and Eosin (Cooper, 1995; Nikfar and Jaberidoost, 2014).

1.2.2. Nature of Their Chromophore

- Azo dyes based on (-N=N-) structure further divided into mono, diazo, triazo classes according to the presence of one or more azo bonds (-N=N-) and are found in various categories, i.e. acid, basic, direct, disperse, azoic and pigments (Khataee and Kajiri, 2010; Chen et al., 2016).
- Fluorescent dyes (Neutral Red, Rhodamine B, Sulfonic).
- Heteropolyaromatic (Methylene Blue)

- Acridine dyes (derivatives of acridine)
- Cyanine dyes (derivatives of phthalocyanine)
- Arylmethane dyes (based on diphenyl methane).
- Nitroso dyes (based on a -N=O nitroso functional group)
- Triarylmethane dyes (derivatives of triphenyl methane)
- Nitro dyes (based on a -NO₂ nitro functional group)
- Anthraquinone dyes (derivatives of anthraquinone and Anthraquinonic) (Ferreira, 2004; Piumettiet *al.*, 2015).

2. Literature Review

2.1. Relationship between Wavelength and Colour

Visible substances that we perceive to have colour reflect light in the visible range i.e. $\lambda=390-790$ nm. The substances that fail to absorb light in the visible region appear colourless (Ayyanppanpillai *et al.*, 2005). The colour of the substance that we are able to see is dependent on the wavelength at which the light is reflected. There is a relationship between the colour absorbed, transmitted or reflected and the wavelength of visible light (Ayyanppanpillai *et al.*, 2005). The colour is given by the fraction of light not absorbed but reflected. For the colour to be visible the substance should hold a chromophore within its structure and must be part of a conjugated system. An extended conjugated system enables the colour to change colour from light to dark resulting as a result of a bathochromic shift (Shide and Sekar, 2019). The conjugated double bonds constitute a chemical structure favorable to the absorption of light. The presence of autochromes that are ring substituents provides target colours for the substances (Burdett, 1982; Allen, 2013). The bathochromic shift is enhanced by adding a group of electron donating ability to the structure of the substance when light interacts with the substance and a fraction of light is absorbed (Rehman, 2020). Targeted groups of atoms i.e. chromophoric groups are responsible for the transformation of white light into colored light by reflection on an object from the selective absorption of energy (Freyria *et al.*, 2017).

2.2. Relationship between Dye Colour and Wavelength

Dyes generally colour substrates e.g. fabric to which they have affinity. This characteristic of dyes is enhanced by its solubility in water. Dyes absorb light within the visible region of the electromagnetic spectrum i.e. $\lambda > 400$ nm. The light is defined by its energy, E and wavelength, λ , as illustrated in equation 1 below:-

$$E = \frac{hc}{\lambda} \quad \text{Equation 1}$$

h Planck's constant

c speed of light

E energy

Dyes differ according to the wavelength at which they absorb, transmit or reflect visible light (Freyria *et al.*, 2017). Compared to other coloured compounds, dyes exhibit smaller band gap energy. Significantly, the energy of light is inversely proportional to wavelength. Higher energy light has shorter wavelength than lower energy light that has longer wavelength (Rauf and Hisaindee, 2013; Freyria *et al.*, 2011).

2.3. Beer- Lambert Law and Molar Extinction Coefficients (E) (Molar Absorptivity)

The Beer-Lambert law defines the linear correlation between absorbance of a solution and concentration. It explain the relationship between dye concentration and absorbance. Considering normal conditions sample absorbance is directly proportional to concentration. A compound with a high molar absorptivity is efficient at absorbing light at a specified wavelength (Abel, 2012; Shinde and Sekar, 2014). The linear dependence of absorbance on concentration may not hold if there are concentration dependent effects e.g. aggregation or acid base dissociation of the solute (Shibata *et al.*, 2006). The molar extinction coefficient is a constant for a particular substance (Houet *et al.*, 2007; Ma *et al.*, 1998). The Beer's law states that absorbance of a sample depends on the molar concentration (c), light path length in centimeters (l) and molar absorptivity (ϵ) for the dissolved solute at the specific wavelength (λ). The slope of the graph (absorbance over concentration) yields the molar absorptivity coefficient $\epsilon \cdot c \cdot l$ (Mouet *et al.*, 2007).

The ideal absorbance of a dilute solution in a solvent will conform to the Beer's law i.e. $A = \epsilon \cdot c \cdot l$ where ϵ ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) is the molar absorptivity coefficient of the solute at the specific wavelength, c ($\text{mol} \cdot \text{dm}^{-3}$) is the molarity of the solute and l , is the optical path length (cm). A UV-Vis spectrophotometer is used to measure the absorbance of light at a specific wavelength by a solution (Rajeshwar, 2008; Said *et al.*, 2020; Saratale *et al.*, 2011). The absorbance values obtained can be used to determine the concentration of a chemical or biological molecule in a solution by applying the Beer-Lambert law (Mallikarjuna and Keshavayya, 2020). The light transmitted through the sample is given by T , the absorbance as A :-

$$A = -\log_{10} T$$

Equation 2

$$c = \frac{A}{\epsilon \cdot d}$$

Equation 3

Where A is absorbance measured using a spectrophotometer
 c is molarity ($\text{mol} \cdot \text{dm}^{-3}$)

ϵ is molar extinction coefficient/molar absorptivity ($\text{dm}^{-3}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)

l is the optical length (cm) (Tum, 2019)

2.4. Objectives

The main objective of the study was to determine the effect of pH on the spectral properties of Acid Orange 7 and Plasmocorinth B dyes. Experiments were done using various dye concentrations with the following specific objectives; - (i) Determine the wavelength at which Acid Orange 7 and Plasmocorinth B dyes exhibit maximum absorbance (λ_{max}) (ii) Measure the absorbance of Acid Orange 7 and Plasmocorinth B and calibrate the UV-Vis spectrophotometer and hence compute the molar extinction coefficient for each dye (iii) Evaluate the role of pH on the spectral properties of both dyes.

3. Materials and Methods

3.1. Chemicals

3.1.1. Dyes

Two anionic azo dyes were studied i.e. Acid Orange 7, which was supplied by supplied by Acros London and another mono azo dye Plasmocorinth B supplied by Sigma-Aldrich. The purity of AO 7 used in the experiments was about 95%, with the remaining 5% comprising mainly of moisture. Dye Acid Orange 7 is orange in colour and commonly applied for high temperature dyeing of wool in strong acid bath among other industrial uses (Guillardet *et al.*, 2002). It has a molecular formula $\text{HOC}_{10}\text{H}_6\text{N}=\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$ and molecular weight $350.32 \text{ g}\cdot\text{mol}^{-1}$. Its physical and chemical properties include stability at normal temperature and pressure, melting point of 164°C and its solubility in water is $116 \text{ g}\cdot\text{L}^{-1}$. Plasmocorinth B is a brown-black powder that finds various applications in the chemical industry (Cernigoj *et al.*, 2006). The purity of the dye used in the experiments is 60%. It is not clear what the remaining 40% comprised. Its molecular formula is $\text{C}_{16}\text{H}_9\text{ClN}_2\text{Na}_2\text{O}_9\text{S}_2$ and molecular weight $518.808 \text{ g}\cdot\text{mol}^{-1}$.

Figure 1: Structure - Plasmocorinth B (Guillardet *et al.*, 2002)

Figure 2: Structure Acid orange 7 (Cernigoj *et al.*, 2006)

3.2. Spectral analysis - UV-Vis Spectroscopy

3.2.1. Maximum Absorption Wavelength (λ_{max})

One quartz cuvette was cleaned and dried using distilled water and linen tissue to ensure the transparent side remained clear. UV-Vis spectrophotometer (CECIL 2041) was switched on before the cuvette (optical length 1 cm) containing distilled water (blank) was placed in the sample compartment with the transparent sides facing the light source and the sample compartment lid closed. The auto zero button was pressed to set zero absorbance. The absorbance value was then recorded for the various dye solutions after a full UV-Vis scan at $\lambda = 200\text{nm}-800\text{nm}$.

3.3. Calibration Curve and Molar Extinction Coefficient

The extinction coefficient is derived from the Lambert-Beer law when the concentration of the dye solution and the length of the cuvette used are known. To determine the extinction coefficient of Acid Orange 7 at 485 nm the following concentrations of dye solutions were prepared ($1\times 10^{-5}\text{M}$, $2.5\times 10^{-5}\text{M}$, $5\times 10^{-5}\text{M}$, $7.5\times 10^{-5}\text{M}$, $1\times 10^{-4}\text{M}$). Using a cuvette of optic length 1 cm and a spectrophotometer, absorbance was measured at wavelength 485 nm. Using the linear

extrapolation of the data obtained an experimental extinction coefficient will be calculated. To determine the extinction coefficient of the dye Plasmocorinth B at 528 nm the following concentrations of dye solutions were prepared ($1 \times 10^{-4} \text{M}$, $1 \times 10^{-5} \text{M}$, $2.5 \times 10^{-5} \text{M}$, $5 \times 10^{-5} \text{M}$, $7.5 \times 10^{-5} \text{M}$). Using a cuvette of length 1 cm and spectrophotometer absorbance was measured at wavelength 528 nm. Using the data obtained a calibration curve is plotted to calculate the molar extinction coefficient.

3.4. Effect of Ph on the Spectral Properties of Acid Orange 7 and Plasmocorinth B

The pH of distilled water used to prepare the various aqueous solutions of the dyes was 7. It is important to note that pH of distilled water used to prepare aqueous solutions of the dyes was 7, which is a neutral value. For dye Acid Orange 7, the pH of the dye solution before addition of HCl to adjust pH was 6.7, while that of dye Plasmocorinth B was 4.6. From a stock solution of dye Acid Orange 7 ($c = 1 \times 10^{-4} \text{M}$), 4 dye solutions of 100 mL were prepared and adjusted to pH = 2.98, 3.38, 4.96 and 6.73. From a stock solution of dye Plasmocorinth B ($c = 8 \times 10^{-5} \text{M}$), 6 dye solutions of 100 mL were prepared and adjusted to pH = 2.86, 3.35, 3.95, 4.27, 4.51 and 4.91. For each of the 10 dye solutions a full UV-Vis spectral scan $\lambda = 200\text{--}800 \text{ nm}$ was done using a UV-Vis spectrophotometer (CECIL 2041).

4. Results and Discussions

4.1. Maximum absorption wavelength - Acid Orange 7 and Plasmocorinth B dyes

Figure 3 below shows a UV-Vis spectra for Acid Orange 7 and Plasmocorinth B dye solutions $c = 2.5 \times 10^{-5} \text{ mol.L}^{-1}$ at $\lambda = 200\text{--}800 \text{ nm}$.

Figure 3: UV-Vis spectra – Plasmocorinth B and Acid Orange 7 dyes $c = 2.5 \times 10^{-5} \text{ mol.L}^{-1}$

The results observed in Figure 3 indicate that dye Acid Orange 7 has maximum absorbance at $\lambda = 485 \text{ nm}$, while dye Plasmocorinth B has its highest absorbance at $\lambda = 529 \text{ nm}$. The two cationic dyes absorb light across the UV-Vis spectrum of light $\lambda = 200\text{--}800 \text{ nm}$. Acid Orange dye does not absorb visible light between $\lambda = 550\text{--}800 \text{ nm}$. Plasmocorinth B dye does not absorb visible light between $\lambda = 640\text{--}800 \text{ nm}$. Acid Orange 7 dye is observed to absorb UV light in better proportions compared to Plasmocorinth B in the UV region. Plasmocorinth B dye absorbs greater proportions of visible light compared to Acid Orange.

4.2. Molar Extinction Coefficient (ϵ) - Calibration Curve

4.2.1. Acid Orange 7

Figure 4 below shows a calibration curve for Acid Orange 7 using dye solutions of varying concentrations.

Figure 4: Calibration curve Acid Orange 7

Figure 4 shows a calibration curve for Acid Orange 7 obtained from measuring the absorbance of dye solutions as described in (section 3.3). Absorbance values were determined for each dye solution. Using the data obtained a calibration curve was plotted as illustrated in figure 4.2. Using the linear extrapolation of the data obtained an experimental extinction coefficient value of $20647 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ was calculated. This value indicates that Acid Orange 7 dye absorbs light efficiently at $\lambda = 485 \text{ nm}$, which lies in the UV region of the electromagnetic spectrum.

4.2.2. Plasmocorinth B

Figure 5 below shows the calibration curve for Plasmocorinth B.

Figure 5: Calibration Curve for Plasmocorinth B

The molar extinction coefficient for Plasmocorinth B was determined by preparing dye solutions outlined in (section 3.3). Using the data obtained a calibration curve was plotted as shown in in Figure 5 Using the linear extrapolation of the data obtained an experimental extinction coefficient of $19203 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ was calculated. This high value of the coefficient of molar absorptivity indicates that dye Plasmocorinth B absorbs light very well at $\lambda = 528 \text{ nm}$, which lies in the visible spectrum of light.

4.3. Effect of pH on the Spectral Properties of dye Acid Orange 7 and Plasmocorinth B

4.3.1. Acid Orange 7

The UV/Vis spectra in Figure 6 below shows the effect of pH on the spectral properties of Acid Orange 7 dye.

Figure 6: The effect of pH on Spectral Properties of Dye Acid Orange 7 of $c = 1 \times 10^{-4} \text{ M}$

The pH of dye Acid Orange 7 solution before addition of HCl to adjust pH was 6.7. This initial pH value shows that dye is slightly acidic. The UV/Vis spectra for Acid Orange 7 dye solutions of $c(1 \times 10^{-4} \text{ M})$ adjusted to various pH levels as shown in Figure 6 indicate dye stability. The findings show that Acid Orange 7 dye maintains stable spectral properties despite variations in pH. The UV/Vis patterns in Figure 6 are consistent with the results observed in Figure 3.

4.3.2. Plasmocorinth B

Figure 7 below shows the effect of pH on the spectral properties of Plasmocorinth B dye under varying pH environments.

Figure 7: The Effect of pH on Spectral Properties of dye Plasmocorinth B $c=8 \times 10^{-5} M$.

The pH of the initial stock solution of dye Plasmocorinth B was determined to be 4.6 before adjusting with HCl to various pH values. The pH values show that dye Plasmocorinth B is acidic. From Figure 7 we observe that pH has no effect on the absorbance of the aqueous solutions of Plasmocorinth B dye. The results show that the dye is stable under different pH conditions and accurate dye concentrations can be determined despite changes in pH. The spectral stability observed in Figure 7 can be compared to the spectra in Figure 3 showing that spectral properties remain constant despite variations in pH.

5. Conclusion

Acid Orange 7 and Plasmocorinth B dyes remain stable under different pH environments i.e. change in pH has no effect on the spectral properties of the dyes. Acid Orange 7 dye effectively absorbs electromagnetic radiation in the form of UV light at $\lambda=485$ nm while dye Plasmocorinth B efficiently absorbs visible light at $\lambda=529$ nm.

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