

Effect of Solvents on the Absorption Spectra of Ten Synthesized Azo Dyes

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Abstract

Azo dyes are among the most profoundly explored classes of organic compounds both from theoretical and practical viewpoints because of their wide spread applications in many areas of dye stuff industries, pharmacy and dosimetry due to the presence of Azo (N=N) linkage. Ten Azo dyes were synthesised by the methods of diazotization and coupling with the aim of studying the effect of solvents on the absorption spectra of these dyes in organic solvent of different characters. The structures of these dyes were confirmed by UV-VIS spectroscopic technique. The effects of solvent polarity and solvent/solute hydrogen bonding interactions were analysed. The result showed that most of the synthesised Azo dyes exhibited positive solvatochromism so that the absorption bands of the dye moved towards longer wavelengths as the polarity of the solvent increase. It was observed that dye 3 exhibited the greatest bathochromic shift of +84nm in ethanol relative to hexane. Dye 8 displayed negative solvatochromism with increasing solvent polarity as it shifted hypsochromically with -32nm in ethanol relative to hexane. Spectra data for the various substituted Azo dyes showed that there is a general tendency for the visible absorption to move bathochromically in accordance with the electron donor-acceptor groups in the diazo and coupling components.

Key words: Azo Dyes. UV-VIS Spectroscopic. Solvatochromism. Hypsochromism. Bathochromism

I. Introduction

Dyes are coloured organic compounds that are used to impart colour to various substrate including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials (Bassam, 2009). Dyes have maintained their status as one of the most prevalent and widely spread examples of applied chemical technology (Hudson, 1992). Out of different classes of dyes, Azo dyes constitute the largest group of colourants used in industries. Azo dyes do not occur in nature and are produced only through chemical synthesis (Maynard, 1983). There are many advantages of Azo dyes which includes wide colour ranges available, ability to bind to a wide variety of fabrics, the cheap production cost and the fact that the environmental impact is favourable because water is the primary solvent used in most synthesis and reactions. In the modern world, the impact of Azo dyes can be seen everywhere (Cardon, 2007).

Azo dyes have been applied as acid/base indicators, biological stains, textiles dyes, plastic/polymer colourants and in high-tech industries (Heaton, 2010). For example, blue Azo dyes are often used to produce the recording layer of most DVD and CD disk in the market today (Catino and Farns, 1985), one of the most popular uses of Azo dyes is in the laboratory as pH indicators. Three common Azo dyes used as pH indicators in many laboratories are methyl orange, para red and methyl red. The biological stain seen in almost every cell biology laboratory such as trypan blue, is a diazo dye. Trypan blue is commonly used to stain dead cells in order to count them (Christle, 2001). Another important use of Azo dyes is in the textile industry, typically Azo dyes have been used to dye common fabrics such as silk, cotton, wool etc. (Hudson, 1992)

Azo dye are also used in the manufacturing industry to test for flaws or cracks in the surface of castings, forging and wells. Specifically, the Azo dye 1 Red 164 is used in non-destructive testing of many metals. This Azo compound is commonly used because of the bright red colour and the ease with which it will point out the flaws. Azo dyes are also used in paper and ink. Many coloured ink jet printer cartridges contain polyazo dyes. Azo dyes are versatile class of coloured organic dyes accounting for 60-70% of all synthetic dye used to date and have received a large amount of attention in the literature, as a consequence of their exciting biological

properties and their application in various fields such as textile, paper, leathers, additives, cosmetics and organic synthesis (Zollinger, 2003). This class of dyes was established as an alternative to more expensive anthraquinone dyes for both environmental and economic reasons (Klaus, 2003). In recent years, the use of heterocyclic intermediates in the synthesis of Azo disperse dyes is well established and the resultant dyes exhibit good factorial strength and excellent brightness (Zollinger, 2003).

The growing interest in heterocyclic Azo dye chemistry is focused on designing new synthetic approaches to these materials, theoretical calculations and applications in various industrial fields. Besides having important applications as textile colourants, they find increasing accessibility in photo-responsive (NLO) biomaterials, optical sensing of metal ions, non-linear optics and photo electronics. The importance of Azo dyes and pigments depends on their donating and attracting effects which leads to their existence in several tautomeric form connected with different types of hydrogen bonds. The existence of Azo-hydra zone tautomerism affects the basic characteristics (colour tone, photostability) of Azo dyes which can be used for the design of compounds having required colour properties.

Solvent effects on organic reactivity and on absorption spectra have been studied for more than a century. It is well known that the photo-physical behaviour of a dissolved dye depends on the nature of its environment i.e. the intensity, shape and maximum absorption wavelength of the absorption band of dye in solution depends strongly on the solvent-solute interactions and solvent nature (Karci & Karci, 2008). This effect is closely related to the nature and degree of dye-solvent interaction. The solvent dependent spectra shift can arise from either non-specific (dielectric enrichment) or specific (hydrogen-bonding) solute-solvent interactions. The solvent effect can be determined by solvent polarity scale or solvate chromic parameters (Reichardt, 2004). Recently, the use of heterocycles in dye synthesis is gaining wide popularity among researchers because the heterocycles are being contemplated to eventually replace benzenes in dye synthesis. The synthesis of heterocycle dyes, spectroscopic properties and economic value remains to be seen.

II. Objectives of the study

The objectives of this work are:

1. To synthesize and purify Azo dyes.
2. To determine the effect of different solvents on the absorption bands of the synthesized Azo dyes.

III. Experimental

Materials : All the chemical used for the synthesis of Azo dyes (table 1) were of commercial grade. All solvents (Table 2) used were either of analytical grade or redistilled commercial grade.

Synthesis and purification of dye stuffs : Synthesis of Azo dyes (1-10) (Table 2) were done according to literature methods which involve the diazotization of primary aromatic amines followed by coupling with aromatic amines or with phenols and naphthols. The Azo dyes were purified by re-crystallisation method and the melting points of these dyes were also determined.

Absorption spectroscopy : Double beam shimadzu UV-2450 scan UV-visible spectrophotometer combined with a cell temperature controller was used to record the absorption spectra over a wavelength range 200-800nm. Quartz cuvettes were used for the measurements in solution via $l=1\text{cm}$.

Table 1. Physical Properties of the Solvents Used

Solvent	Dielectric constant (ϵ_r)	Dipole moment (D)
Hexane ⁿ	1.9	0.00 D
Toluene ⁿ	2.3	0.36 D
Diethylether ⁿ	4.3	1.15 D
Chloroform ^{sp}	4.8	1.04 D
Ethanol ^p	25	1.70 D

n-non-polar solvent, p-polar solvent, sp-slightly polar solvent (*Knovel Critical Tables 2nd Edition*)

IV. Results and discussion

The electronic absorption spectra of the dyes were studied in organic solvents of different polarities viz; hexane, toluene, chloroform diethylether and ethanol. This was done with the intention of investigating the solvatochromic behaviour of the synthesized Azo dye compounds. The solvatochromic behaviour of a dye is the shift of absorption wavelength due to the interaction with solvents of different polarities. The electronic data shows that the UV bands ($\pi-\pi^*$ and $n-\pi^*$) experienced solvent shift a behaviour which is characteristic of these types of electronic transition. These shifts are due to the solvent stabilization of the excited or ground electronic states, thus resulting in a change in the energy gap between the energy levels involved in the transition. The essential physical properties of the solvents used such as dielectric constant and dipole moment are shown in table 1, while the electronic data of Azo dyes 1-10 obtained in some selected solvents at room temperature were given in table 2

Table 2. UV/ Vis visible spectra data of Azo dyes 1-10 in various solvents at 25⁰C

Dye No	IUPAC Name of Dyes	Hexane λ_{max} (nm)	Toluene λ_{max} (nm)	Diethylether λ_{max} (nm)	Chloroform λ_{max} (nm)	Ethanol λ_{max} (nm)	$\Delta\lambda^a$ (nm)
1	sodium salt of 1-(4-sulphophenylazo)-2-naphthol	328	334	334	340	370	+42
2	1-(4-nitrophenylazo)-2-naphthol	324	334	352	334	370	+46
3	1-phenylazo-1-naphthol	384	386	416	462	468	+84
4	1-(4-methylphenylazo)phenol	322	340	354	360	368	+46
5	p-hydroxyazobenzene	320	354	362	368	360	+40
6	1-phenylazo-2-naphthol	402	460	474	480	482	+80
7	1-(4-sulphophenylazo)-2-hydroxybenzoic acid	320	340	320	350	390	+70
8	1-(4-sulphophenylazo)-2-hydroxy-5-sulphobenzoic acid	334	330	378	380	302	-32
9	1-(4-nitrophenylazo)-1-naphthol	320	328	322	340	366	+46
10	1-(4-nitrophenylazo)-2-hydroxybenzoic acid	364	340	386	382	366	+2

^aDifference in λ_{max} between the most polar solvent (Ethanol) and least polar solvent (Hexane) It was found that the absorption maxima of all dyes are strongly solvent dependent and vary with solvent polarity in the order Ethanol > Chloroform > diethylether > toluene > hexane. The solvent dielectric constant (i.e. the relative permisivity (ϵ) is often predicted to serve as a quantitative measure of solvent polarity. Positive solvachromism corresponding to bathochromic shift (red) was recorded for most of the dyes. The same trend of absorption shift in various solvent used were observed for the entire series of dyes shown in table 2 except for dyes 5, 8, and 10 which showed irregular pattern of absorption maxima with increasing solvent polarity. The absorption maxima (λ_{max}) of all the dyes obtained in hexane; the (reference solvent) to which the absorption maxima obtained in the remaining solvents are compared. The absorption spectra of the dyes (except dyes 5, 8 and 10) in ethanol solution are most bathochromic (Red shifted) as compared to the dye spectra in other solutions indicating relatively strong guest-host interaction between the dye molecules and the ethanol environment.

The maximum absorption of these dyes shifted in the order:
Ethanol > chloroform > diethylether > toluene > hexane

In ethanol, the trend in absorption maxima is in the order Dye 6 (482nm) > dye 3 (468nm) > dye 7 (390nm) > dye 8 (302nm). Dye 3 showed the highest bathochromic shift of +84nm relative to its λ_{max} in hexane i.e (λ_{max} is 384nm in hexane and 468nm in ethanol). Also, dye 6 has a bathochromic shift of +80nm in ethanol relative to its absorption maxima in hexane and 4nm shorter relative to dye 3. Similarly, the bathochromic shifts of +70nm, +46nm, +42nm and +2nm were recorded for dyes 7, 2, 4, 1 and dye 10 respectively in ethanol relative to

hexane. However, dye 8 shifted hypsochromically(-32nm) in ethanol relative to hexane. It is evident from the table 2, that there is a progressive increase in absorption maxima of most of these dyes as the solvent polarity increases Ethanol > chloroform > diethylether > toluene > hexane. These bathochromic shifts so observed can be attributed to $\pi \rightarrow \pi^*$ transitions involving the π -electronic system of these compounds. The $\pi \rightarrow \pi^*$ band shifts to longer wavelength or lower energy in a more polar solvent because the $\pi \rightarrow \pi^*$ transitions have a polar excited state which would naturally be stabilized by hydrogen bonding in more polar solvents. This lowers the energy gap between π and π^* , and consequently increase the wavelength of $\pi \rightarrow \pi^*$ band. Therefore, the interaction of a solvent with a dye molecule is greater in polar solvents (ethanol in this case), which possess strong permanent dipole, and is most pronounced with solute molecule that contains a permanent dipole.

Dyes 5, 8 and 10 exhibited irregular pattern of absorption maxima with change in polarity of the organic solvents. This anomalous trend can be considered to correspond to the net of several solvent effects such as polarity, basicity, and Hydrogen bond and electron accepting ability. Other competing factors such as substituent effects or steric inhibition of resonance might be contributive.

Dye 8 showed hypsochromic shift (-32nm) in ethanol relative to hexane and blue shift of -78nm relative to chloroform. The negative solvatochromic behaviour of this dye in ethanol and chloroform can be assigned to the $n \rightarrow \pi^*$ transitions due to the abundance of non-bonded electrons in the auxochromic groups on the Azo coupler ring i.e. COOH, SO₃H. In $n \rightarrow \pi^*$ transitions, as solvent polarity increases the ground state molecule is better stabilized. Since in polar and hydroxylic solvents (e.g. ethanol), the n-electrons are expected to be blocked by the solvent H⁺ ions through intermolecular H-bonds and consequently the excitation of n-electrons is difficult, i.e. an $n \rightarrow \pi^*$ band will appear as an ill-defined band in polar solvents. The net result of the solvation is that the energy of $n \rightarrow \pi^*$ becomes higher (blue shift).

Apart from this, another factor that may be contributive to this negative solvatochromism exhibited by Dye 8 is steric inhibition of resonance. The UV spectra are very sensitive to distortion of the chromophores and consequently the steric repulsions which oppose the coplanarity of the conjugated π -electron system. The bulky substituents attached to the Azo coupler ring may distort the chromophore leading to a blue shift. Dyes 4 and 5 have similar structure except for the methyl group attached to dye 5 in para – position to the Azo group. The λ_{\max} for dye 4 and 5 in ethanol are 365nm and 360 nm respectively. The presence of methyl group (-CH₃) in the former provides additional charge delocalization leading to smaller energy increments from transition to excited states. The added opportunity for stabilization of the excited state π^* brings the lowest excited state closer to the highest ground state and thus permits a lower energy (longer wavelength for transition).

V. Conclusion

These results show that most of the synthesised dyes exhibited positive solvatochromism such that the absorption of the dyes moved towards longer wavelength according to the polarity of the solvent. Since the polarities of ground and excited states of a chromophore are different, a change in solvent polarity will lead to different stabilization of the ground and excited states and thus a change in the energy gap between the electronic states. Consequently, variations in the position, intensity and the shape of the absorption spectra can be direct measures of the specific interactions between the solute & solvent molecules.

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