Original Research Article

Solvent and Methyl Group Effects on the Electronic Spectral Properties of Azo-2-Naphthol

ABSTRACT

The influence of solvent polarity on the absorption pattern of azo-2-naphthol dyes have been studied using a UV-Visible spectrophotometer in polar and non-polar solvents. Analysis of the spectral data obtained revealed two types of effects - the polar effect (tPE) and the non-polar effect (tNPE) - exhibited when polar and non-polar solvents are used respectively. These effects can affect differently, the direction of shift in the wavelength (λ_{max}) of electronic absorption of azo-2-naphthol dyes bathochromically or hypsochromically.

Keywords: Electronic spectra; polar effect;non-polar effect;azo dye;azo-2-naphthol.

1. INTRODUCTION

Azo compounds generally have a molecular formula of the form R-N=N-R^1, in which R and R^1 can be aromatic or aliphatic. The -N=N- group known as azo or diimide functional group is highly coloured. The colour can be intense yellow, orange, red, blue or even green depending on the exact structure of the molecules [1]. The colour is due to the azo linkage –N=N– which brings the two aromatic systems into conjugation, resulting in an extended system of delocalized π-electrons and allowing absorption in the visible region [2]. Azo compounds of 2-naphthol or its derivatives are used extensively as dye. The azo pigment forms an important class of pigments in all kinds of paints including artist paints [3-5]. The type of solvent used can affect the absorption maxima of azo dye [6]. The solvent effect on spectra, resulting from electronic transitions, is primarily dependent on the chromophore and the nature of the ($\sigma\rightarrow\sigma^*$, $n\rightarrow\sigma^*$, $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and charge transfer absorption) transition. The electronic transitions of particular interest in this respect are $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ as well as charge transfer absorptions [7]. In this paper, different solvents are investigated for their influence on the absorption pattern of azo-2-naphthol dyes. The effect of a methyl group at para position with respect to the azo phenyl ring is also studied.

2. MATERIAL AND METHODS

2.1 General

All chemicals used were of analytical grade. The IR spectra were recorded on a Shimadzu FTIR-IR Prestige (200VCE) as KBr pellets. The C, H, N data were determined using a Perkin-Elmer Instrument (200B). UV-Visible spectra were obtained on Sunny UV-7804AC UV-Visible Spectrophotometer at 27°C. The solvents used were spectroscopic grade (Merck).

2.2Synthesis of 1-(4-methylphenylazo)-2-naphthol

1-(4-methylphenylazo)-2-naphthol (MPAN) had already been synthesized and characterized elsewhere [8] and a similar procedure was followed. A solution of hydrochloric acid was prepared by diluting 2 mL of the concentrated acid in 20 mL of distilled water. 10 mmole of p-toluidine (1.074 g) was added, stirred and cooled to 0℃. 8 mL of aqueous sodium nitrite (10.88 mmole, 0.7507 g) was added in drops maintaining the temperature between 0-5 ℃. The diazonium chloride formed was consecutively coupled with 10 mmole of 2-naphthol (1.449 g) that was dissolved in 15 mL of 10% sodium hydroxide solution. The reaction mixture was stirred at 0℃ for 1 hour. The red product that precipitated was recrystallized from ethanol. Yield: 65%. IR (KBr, cm^{-1}): 3520-3380 (Ar-OH), 3060-3020 (Stretching CH), 2926 (CH3), 1632 (C=C), 1450 (N=N); Elemental Analysis Cald. for $C_{17}H_{14}N_{20}$: C 77.84, H 5.38, N 10.68; found C 77.76, H 5.23, N 10.56.

2.3Synthesis of 1-phenylazo-2-naphthol

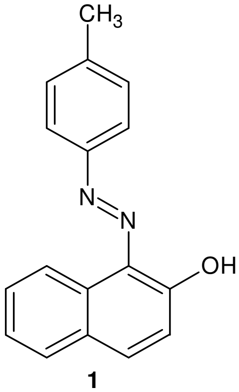
1-Phenylazo-2-naphthol (PAN) had already been synthesized and characterized elsewhere [9]. The method of preparation is similar to the one aboveexcept that aniline was used instead of p-toluidine. Yield: 68%. IR (KBr, cm^{-1}): 3320 (Ar-OH), 3050 (Stretching CH), 1600 (C=C), 1440 (N=N), 1330 (C-N); Elemental analysis Cald. for $C_{16}H_{12}N_{20}$: C 77.42, H 4.83, N 11.29; found C 77.26, H 5.78, N 11.16.

2.3UV-Visible Spectroscopic Analysis

The azo-2-naphthol (0.55 mmole) was dissolved in methanol to give the concentration of 3.5 x 10^{-5} mol/dm^3. The absorption spectra of 3 ml aliquot was taken between 200-800 nm at 50 nm wavelength interval on the UV-Visible Spectrophotometer with the cell path length of 1 cm. This was repeated for other solvents, ethanol, n-hexane and benzene.

3. RESULTS AND DISCUSSION

The structure of MPAN (**1**) and PAN (**2**) are shown.



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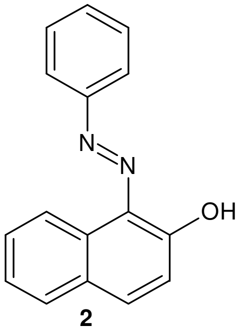

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The Uv-visible absorption spectra of MPAN and PAN were recorded using two polar protic solvents, ethanol and methanol; and two non-polar solvents, benzene and hexane. The values of the absorption maxima in the different solvents are shown in Table 1. The characteristics visible spectra band (λ_{max}) appears in the range 240-690 nm (MPAN) and 320-700 nm (PAN). The electronic spectra of MPAN and PAN are given in Figure 1-2.

Table 1. Absorption maxima of azo dyes in organic solvents at 27^{o}C

Solvent	Absorption maxima (λ_{max}) in nm					
	MPAN			PAN		
Methanol	290	470	650	350	475	700
Ethanol	240	440	640	340	460	670
Benzene	340	450	550	320	445	545
Hexane	345	460	690	325	450	650

3.1 Effects of Solvent

It is obvious that the absorption maxima of both MPAN and PAN are affected by the type of solvent used as revealed by the datain Table 1. Thus, this change in spectral position can be used as a probe to analyze various types of interactions between solute and solvent. The different absorption pattern in different solvents may be due to the change in the solvation behavior leading to the formation of a solvation complex [10]. Three absorption bands are observed for each compound (Figure 1-2). The broadness of the spectra suggests considerable charge transfer (CT) character [11-13].

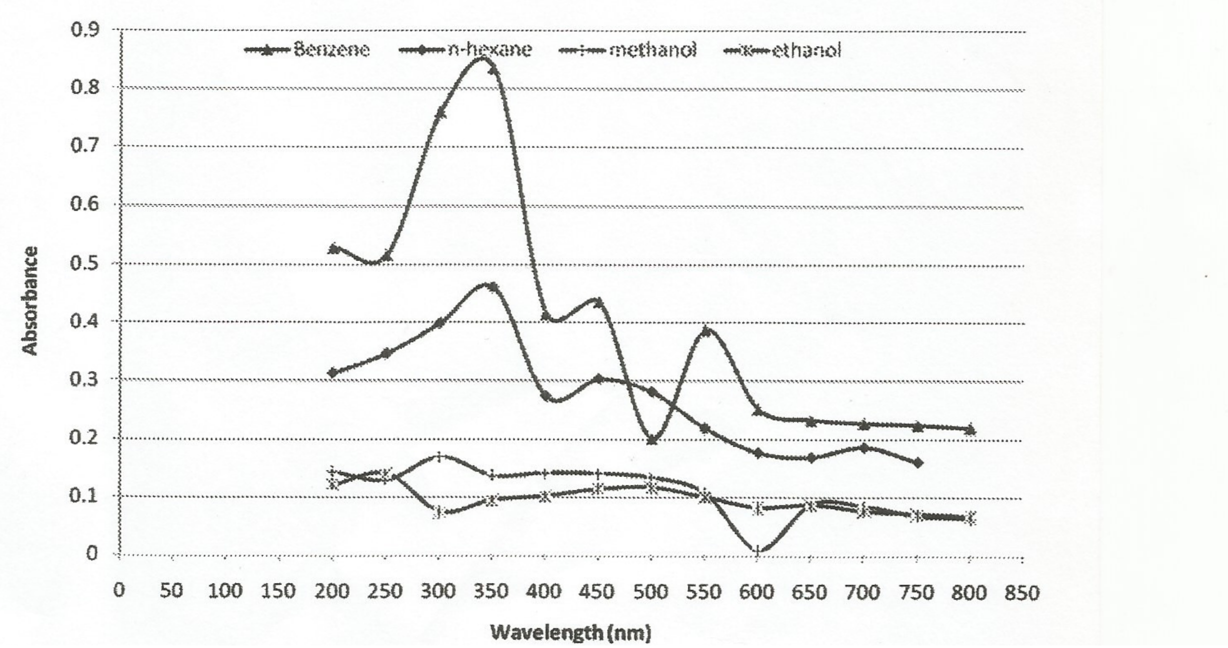


Fig. 1.UV-Visible spectra of 1-(4-methylphenylazo)-2-naphthol (MPAN)

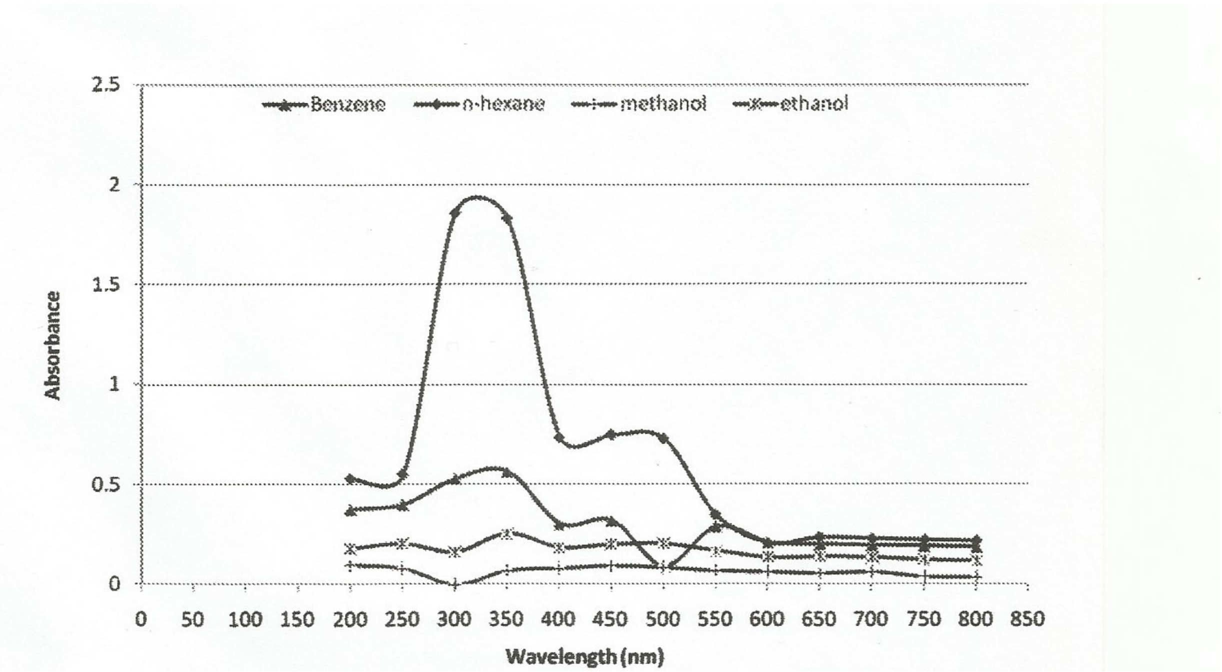
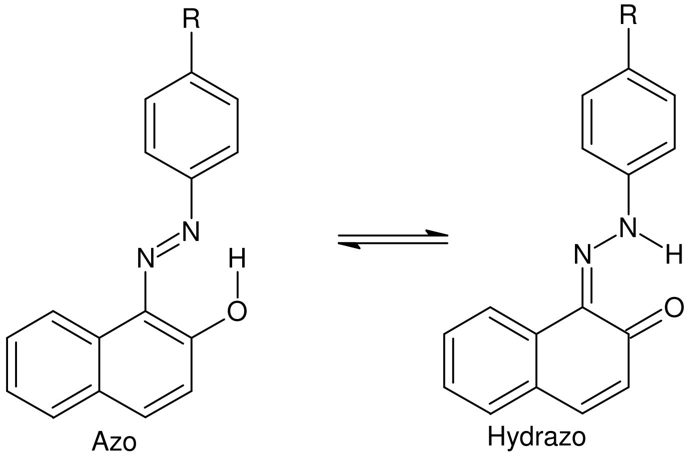


Fig. 2.UV-Visible spectra of 1-phenylazo-2-naphthol (PAN)

The effects of solvent, based on the pattern observed can be divided into two: The polar effect (tPE), and the non-polar effect (tNPE), The tPE and tNPE can be considered as specific interaction when azo dyes are dissolved in polar and non-polar solvents respectively. It is necessary to discuss these effects based on the type of solvent (polar or non-polar) since they absorption pattern is different for each solvent group. Considering MPAN, tPE tends to support shift in absorption maxima to longer wavelength (bathochromic) as the polarity of the solvent increases whereas tNPE tends to support shift of absorption maxima to shorter wavelength (hypsochromic) as the solvent polarity increases. PAN also exhibit similar shift in the absorption maxima according to tPE and tNPE. This difference in absorption pattern of azo-2-naphthols based on the type of solvent may indicate differential solvation pattern based on the solvent group (polar or non-polar) or solvent-solute interaction based on the chromophore and nature of the transitions involved in the dye.

PAN and its derivatives have been shown to exist as tautomers [14] and these two forms (azo and hydrazo) exist in equilibrium (**3**). These tautomers will therefore exhibit different solvation pattern due to structural differences. Thus, it appears that the azo form is stabilized more in polar solvent while the hydrazo form is stabilized more in non-polar solvent, hence the difference in absorption pattern giving rise to tPE and tNPE. Absorption bands of hydrazo form may arise from n-π* transition since such transitions suffer hypochromic shifts on increasing solvent polarity while that of azo form may arise from π-π* transitions since such transitions are shifted bathochromically [15].



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3.2Effect of Methyl Group

Comparing PAN and MPAN, the structural difference is the presence a methyl group (CH_3). Methyl group is an electron donating group. The tPE and tNPE is also observed in the absorption pattern for each solvent group. The presence of a methyl group is observed to cause a shift in the absorption maxima towards longer wavelength in non-polar solvents as the polarity increases. An electron releasing substituent is known to increase the polarizability leading to a decrease in the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) resulting in a bathochromic shift [16]. In polar solvents, the pattern is different. The absorption maxima are shifted to shorter wavelength as the solvent polarity increases.

4. CONCLUSION

Electronic absorption pattern of azo-2-naphthol dyes are dependent on solvent polarity. The trend in the absorption pattern does not generally depend on the increase in the polarity of the solvents, but on the solvent type. These trends have been discussed in terms of polar effect and non-polar effect. The polar and non-polar effects affect the solvation pattern giving rise to different spectral properties of azo-2-naphthol dye. The presence of an electron releasing substituent, methyl group, causes a shift in the absorption maxima towards longer wavelength in non-polar solvents as the polarity increases. In polar solvents, the absorption maxima are shifted to shorter wavelength as the solvent polarity increases

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