



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

Victor N. Mkpene^{1*} and Emmanuel E. Essien¹

¹Department of Chemistry, University of Uyo, P.M.B. 1017, Uyo, Nigeria.

Authors' contributions

This work was carried out in collaboration between both authors. Author VNM designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors VNM managed the analyses of the study. Authors VNM and EEE managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

The influence of solvent polarity on the absorption pattern of azo-2-naphthol dyes, 1-(4-methylphenylazo)-2-naphthol (MPAN) and 1-phenylazo-2-naphthol (PAN) 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. Linear solvation energy relationships (LSER) have been used to quantify the interactions between solvents and dyes. The overall solute-solvent interaction had contributions from polarizability/dipolarity, hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities.

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

*Corresponding author: E-mail: vicmkpenie1@gmail.com;

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]. When absorption spectra are measured in solvents of different polarity, the positions, intensities, and shapes of the absorption bands are usually modified by these solvents [7]. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which tend to alter the energy difference between the ground state and excited state of the absorbing species containing the chromophore. In other words, the effects, result from the difference in solvation of the ground state and the excited state of the solute and 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 $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer absorptions [8].

The solvent effect is termed solvatochromism and is described in terms of the shifting of the peak position of the lowest energy, longest wavelength, spectral absorption peak. This can be hypsochromic (blue shift, negative solvatochromism), when the shift is to lower wavelengths, i.e., to higher energies or bathochromic (red shift, positive solvatochromism), when the shift is to longer wavelengths, i.e., to lower energies. The former effect takes place when the ground state is more dipolar than the excited state, whereas the opposite occurs when the excited state is the more dipolar one [9]. The solvent effects on absorption spectra have been determined using an empirical parameter of solvent polarity, called the $E_T(30)$ value [10] based on negatively solvatochromic pyridinium-N-phenolate betaine

dye which exhibits one of the largest solvatochromic effects ever observed. The $E_T(30)$ value for a solvent is simply defined as the transition energy measured in kilocalories per mole (kcal/mol) [11] and can be determined by Eq. (1)

$$E_T(30) = 28591.5/\lambda_{\max} \text{ (nm)} \quad (1)$$

Where λ_{\max} is the longest wavelength of $\pi \rightarrow \pi^*$ absorption band of betaine dye.

Quantitative assessment of solvents effects on electronic spectra can be achieved using Kamlet-Taft equation as given in Eq. 2 [12].

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* + b\beta + a\alpha \quad (2)$$

where π^* is an index of solvent dipolarity/polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is a measure of the solvent hydrogen-bond donor (HBD) acidity, β is a measure of the solvent hydrogen-bond acceptor (HBA) basicity, $\bar{\nu}_0$ is the regression value of the solute property in the reference solvent cyclohexane and $\bar{\nu}$ is the solute property such as wavenumber of maximum absorption in the UV/Visible spectrum. The regression coefficients s , b and a in Eq. (2) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequency) to the indicated solvent parameters. Multiparameter equations using linear combinations of existing empirical solvent parameters are known. The most successful treatment combines the $E_T(30)$ values with other solvent properties [13]. $E_T(30)$ values are sensitive to both dipolar interactions and the interaction between solute and hydrogen bond donor (HBD) solvents.

To bring all the solvent parameters to the same scale (α , β , π^*), instead of $E_T(30)$ values, the use of the normalised value, E_T^N has been recommended [14]. E_T^N values are dimensionless and can be determined according to Eq. (3).

$$E_T^N = [E_T(\text{solvent}) - 30.7] / 32.4 \quad (3)$$

In this paper, different solvents including polar and non-polar 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. The solvatochromic parameters are used to investigate the influence of solvents on other absorption bands other than the one

corresponding to the longest wavelength. The influence of solvents on other absorption bands is rarely reported to the best of our knowledge.

2. MATERIALS 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).

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

1-(4-methylphenylazo)-2-naphthol (MPAN) was synthesized by well-known procedure given in the literature [15]. 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°C. 8 mL of aqueous sodium nitrite (10.88 mmole, 0.7507 g) was added in drops maintaining the temperature between 0-5°C. 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°C 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 (CH_3), 1632 (C=C), 1450 (N=N); Elemental Analysis Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$: C 77.84, H 5.38, N 10.68; found C 77.76, H 5.23, N 10.56.

2.3 Synthesis of 1-phenylazo-2-naphthol

Synthesis of 1-phenylazo-2-naphthol (PAN) had been reported elsewhere [16]. The method of preparation is similar to the one above except 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 Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$: C 77.42, H 4.83, N 11.29; found C 77.26, H 5.78, N 11.16.

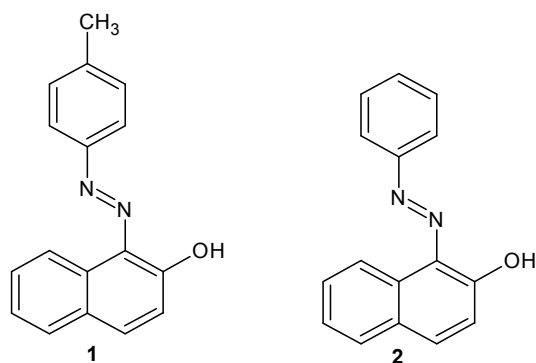
2.4 UV-Visible Spectroscopic Analysis

The azo-2-naphthol (0.55 mmole) was dissolved in methanol to give the concentration of 3.5×10^{-5}

mol/dm^3 . The absorption spectra of 3 ml aliquot were taken between 200-800 nm wavelengths 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.



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. Three absorption bands were observed for both MPAN and PAN in all the solvents. They include: absorption maxima in the range 290-350 nm (peak 1) due to $\pi \rightarrow \pi^*$ transition, absorption maxima in the range 450-474 nm (peak 2) which may be attributed to $n \rightarrow \pi^*$ transition and absorption maxima in the range 650-700 nm (peak 3) due to $\pi \rightarrow \pi^*$ transition. The electronic spectra of MPAN and PAN are given in Figs. 1-2.

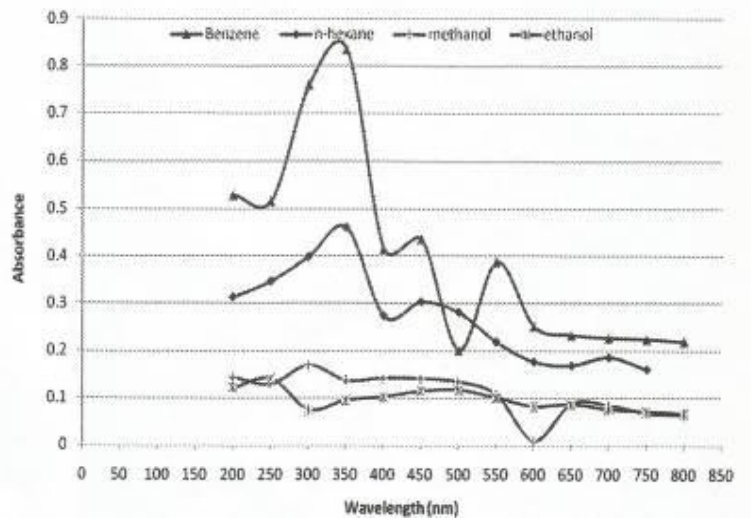
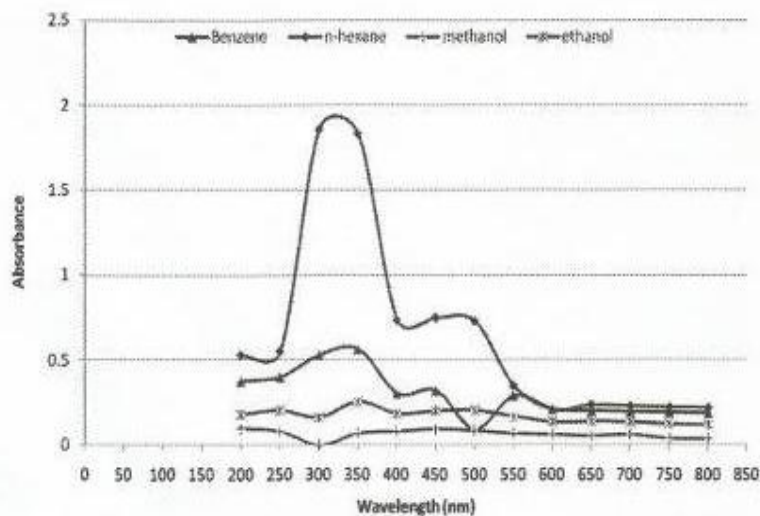
3.1 Effects of Solvent

It is obvious that the absorption maxima of both MPAN and PAN are affected by the type of solvent used as revealed by the data in 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 [17].

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

Table 1. Absorption maxima of azo dyes in organic solvents at 27°C

Solvent	Absorption bands λ (nm)					
	MPAN			PAN		
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
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

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

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 the

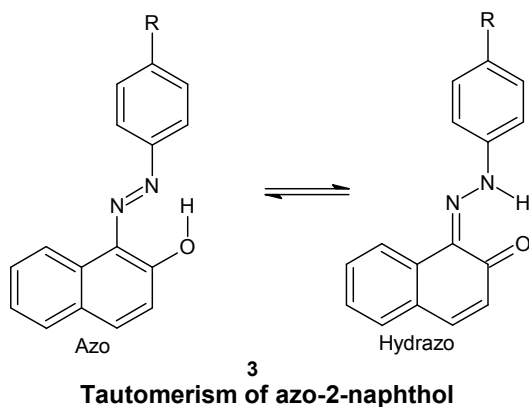
absorption pattern is different for each solvent group. Considering MPAN, tPE tends to support shift in absorption maxima to longer wavelength (bathochromic) as the polarity of the solvent increases whereas tNPE tends to support shift of

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 [18] 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.

3.2 Effect of Methyl Group

Comparing PAN and MPAN, the structural difference is the presence a methyl group (CH₃). 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. Electron donating substituents were observed to increase the electron density at the anilide nitrogen giving rise to bathochromic shift of the long wavelength of absorption maximum [19]. In polar solvents, the pattern is different. The absorption maxima are shifted to shorter wavelength as the solvent polarity increases.



3.3 Correlation of Solvent Parameters

To get further insight on the solvatochromic behavior of MPAN and PAN, spectroscopic

properties were correlated with relevant solvent polarity scales. For this purpose, the absorption data were converted to corresponding transition energies using Eq. (1) and the data are given in Table 2.

The $E_T(30)$ values have been reported to correlate satisfactorily with solvatochromic parameters using the linear solvation energy relationship (LSER). A multiple regression model for the evaluation of solute-solvent interaction permit the quantitative assessment of the contribution of various solvents parameters to the overall solvent effects. For compatibility of solvent parameters, the $E_T(\text{dye})$ were normalized to $E_T^N(\text{dye})$ using Eq. (4), a modified form of equation Eq. (3) and the normalized values are presented in Table 3.

$$E_T^N(\text{dye}) = [E_T(\text{dye}) - 30.7] / 32.4 \quad (4)$$

The different solvent parameters used for regression analysis were obtained from literature [9] and are given in Table 4.

The solvents parameters were subjected to regression analysis using LSER (Eq. 5) where the regression coefficients, α , β and s measure the sensitivities of the concerned parameters toward the solute property E_T^N . The different absorption maxima (peaks 1-3) were correlated with the solvent parameters to investigate which of the absorption peak (band) is more sensitive to the solvent parameters.

$$E_T^N = E_{T0}^N + s\pi^* + \alpha\alpha + \beta\beta \quad (5)$$

It was found that the absorption data for investigated azo-2-naphthol dyes in polar protic and non-polar solvents show satisfactory correlation with α , β and π^* parameters. The results of the multiple regressions are presented in Table 5.

The multiple correlation coefficient (R) indicates that E_T^N of dye can be predicted with high accuracy. The coefficient of determination (R^2) shows that 100% of the investigated absorption properties can be explained by the solvent parameters. R^2 given as 1.00 for both MPAN and PAN and for all the absorption peaks of the two dyes shows a best fit for the regression model. From Table 5, it is clear that for MPAN, hydrogen bond acceptor ability (β) has a major influence on absorption peaks 1 and 2 whereas peak 3 is insensitive to HBA. Contributions from polarizability/dipolarity (π^*) and hydrogen bond

Table 2. Observed E_T of azo dye in organic solvents at 27°C

Solvent	μ	D	$E_T(30)$	$E_T(\text{Dye})$ in kcal/mole					
				MPAN			PAN		
				Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
Methanol	2.87	32.66	55.4	98.6	60.2	44.0	81.7	60.2	40.8
Ethanol	1.66	24.55	51.9	119.1	65.0	44.7	84.1	62.2	42.7
Benzene	0	2.27	32.3	84.1	63.5	52.0	89.3	64.2	52.5
Hexane	0.09	1.88	31	82.9	62.2	41.4	88.0	63.5	44.0

μ : dipole moment; D: dielectric constant; $E_T(30)$: transition energy of reference dye

Table 3. Normalised E_T of azo dye in organic solvents at 27°C

Solvent	E_T^N	$E_T^N(\text{Dye})$					
		MPAN			PAN		
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
Methanol	0.76	2.10	0.91	0.41	1.57	0.91	0.31
Ethanol	0.65	2.73	1.06	0.43	1.65	0.97	0.37
Benzene	0.11	1.65	1.01	0.66	1.80	1.03	0.67
Hexane	0.01	1.61	0.97	0.33	1.76	1.01	0.41

Table 4. Solvent parameters

Solvent	α	β	π^*
Methanol	0.98	0.66	0.60
Ethanol	0.86	0.75	0.54
Benzene	0.00	0.10	0.55
Hexane	0.00	0	-0.11

Table 5. Regression fits to solvatochromic parameters

Dye/Absorption band	E_{T0}^N	s	a	b	R	R^2
MPAN						
Peak 1	1.548	-0.565	-1.871	4.129	1.00	1.00
Peak 2	0.963	-0.675	-0.582	0.846	1.00	1.00
Peak 3	0.383	0.485	-0.336	0.098	1.00	1.00
PAN						
Peak 1	1.761	0.011	-0.424	0.330	1.00	1.00
Peak 2	1.009	-0.012	-0.283	0.282	1.00	1.00
Peak 3	0.450	0.360	-0.513	0.223	1.00	1.00

R: Correlation coefficient; R^2 : Coefficient of determination; E_{T0}^N : Regression intercept

donor (α ,) ability are equally important for all the peaks. For PAN, the major contribution comes from HBA for all the peaks. Peaks 1 and 2 were insensitive to dipolarity/polarizability and for peak 3, all the solvent parameters contribute significantly. This shows that the absorption bands in the dyes respond differently to the various solvent parameters which include non-specific interaction (π^*) and specific interaction (HBD and HBA). The percentage contributions of solvatochromic parameters of azo-2-naphthol dyes are given in Table 6.

Table 6. Percentage contribution of solvatochromic parameters

Dye/Absorption band	$P_{\pi^*}(\%)$	$P_{\alpha}(\%)$	$P_{\beta}(\%)$
MPAN			
Peak 1	9	28	63
Peak 2	32	28	40
Peak 3	53	37	10
PAN			
Peak 1	2	55	43
Peak 2	2	49	49
Peak 3	33	47	20

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 also on the solvent group (polar or non-polar). These trends have been discussed in terms of polar effect (TPE) and non-polar effect (tNPE). 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. The spectral properties have been satisfactorily correlated with solvatochromic parameters, α , β and π^* using linear solvation energy relation (LSER). The various absorption bands making up the spectra of the dyes responds differently to the solvent parameters. The spectral properties of the dyes were influenced by dipolarity/polarizability, hydrogen bond donicity and hydrogen bond acceptor ability.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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