

Preferential Solvation of 4-Carboxyl-2, 6-Dinitrophenylazohydroxynaphthalenes in Mixed Hydroxylic Solvents

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A – research concept and design; B – collection and/or assembly of data; C – data analysis and interpretation; D – writing the article; E – critical revision of the article; F – final approval of article.

Abstract

Background: The applications of a group of 4-carboxyl-2,6-dinitrophenylazohydroxynaphthalenes, AZ-01 to 04, as colourants, chemosensors or synthetic intermediates have been limited by their solubility.

Aim: To investigate the effect of solvent mixture composition on the solubility, solution thermodynamics and position of equilibrium processes of the dyes.

Method: The UV-visible spectral patterns of the dyes in binary mixtures including Methanol:Water, Ethanol:Water, Methanol:Ethanol, Methanol:Propan-1-ol, Methanol:Propan-2-ol, Propan-1-ol:Water and Propan-2-ol:Water were acquired. The type and quantitative estimation of solute-solvent interactions at play were determined by fitting spectral patterns to solvent parameters using multilinear regression.

Results: Preferential solvation was detected by the non-ideality of the plots of E_{12} as against the mole fractions of co-solvent in all binary mixtures. In pure solvents, the spectral shifts of AZ-01, 03 and 04, which exist predominantly in the hydrazone form, were affected by polarity of solvent milieu while solvent basicity and acidity, in that order, were the significant parameters for AZ-02. In aqueous alcoholic mixtures, solvent polarity was contributory, although to different degrees, to the observed spectral data of the four dyes. However, solvent acidity and basicity were the primary determinants of spectral shifts observed with AZ-04 and AZ-03 respectively. Spectra-structure relationships identified the formation of the charged hydrazone tautomer which requires stabilisation by polar solvent milieu as responsible for the observed trend. In addition, interactions between new aggregated solvent-solvent species and the propionic acid substituent present in AZ-03 contributed to its spectral shifts.

Conclusion: The solvatochromic properties of the phenylazonaphthalene series in binary mixtures have been successfully studied.

Keywords: 4-carboxyl-2,6-dinitrophenylazohydroxynaphthalenes, Preferential solvation, Mixed hydroxylic solvents

INTRODUCTION

Solvents influence reaction course and rates largely in two ways viz. their effects on equilibrium properties of the reaction including the stabilization/destabilization of the products, reactants, activated complexes or activation energy and secondly their non-equilibrium or dynamic effects on reactions (Ahmad et al., 2015; Hamid and Roy, 2019). Thus, the use of solvent mixtures to achieve desired solvent properties is common for practical purposes including separation/purification procedures in organic synthesis and to dictate the rates of formation (Sasirekha et al., 2008; Gupta et al., 2017). Mixed solvent systems are also very useful in pharmaceutical

formulation science in improving the solubility of otherwise poorly soluble ingredients for the purpose of developing homogenous dosage forms (Almandoz et al., 2014). The mixing of solvents can lead to an array of effects of which one of the most important is the phenomenon called preferential solvation. When preferential solvation is operative, it is characterised by the formation of solute-solvent and solvent-solvent interactions more complex than those obtained in the pure solvents. The solvation sphere around a solute may therefore be richer in one of the components of the solvent mixture when compared with the bulk solvent (Almandoz et al., 2014). Such a solute is thus said to be preferentially solvated by the mixture

component that accumulates in its cybotactic region. Preferential solvation is not only dependent on the physicochemical properties of the solvents, the microheterogeneity in the solvent mixture e.g. self-association of components but also on the structural complexity of the solutes (Hisaindee et al., 2012). The profiling of the solvation data of new chemical entities is therefore desirable. Previous solvatochromic assessment of a group of highly functionalised azo dyes series, AZ-01 to AZ-04 revealed the presence of azo-hydrazone equilibrium and poor aqueous solubility (Adegoke and Idowu, 2010). Also having been evaluated at various times for their suitability as food/drug additives (Adegoke et al., 2012a; Adegoke et al., 2012b) and chemosensors (Adegoke et al., 2014), preferential solvation studies are required to

METHODOLOGY

Materials

All solvents used are Merck-AR-grade reagents and were used without further purification. They include Methanol, Ethanol, Propan-1-ol and Propan-2-ol. Double-distilled water was used for recordings involving water. The dye probes used were four congeneric monoazo dyes, 4-carboxyl-2, 6-dinitrophenylazohydroxynaphthalenes named AZ-01, AZ-02, AZ-03 and AZ-04 previously reported (Adegoke et al., 2008).

Instrumentation

Mettler analytical balance (Ohaus, USA), UV visible spectrophotometer 6405 (Jenway, UK)

Preparation of dye stock solutions

A 5 mg quantity of each dye was weighed separately and dissolved in 10 mL of methanol to give molar concentrations of 1.3082×10^{-3} (AZ-01 and AZ-02), 1.1013×10^{-3} (AZ-03) and 1.1060×10^{-3} M (AZ-04).

Preparation of the binary solvent mixtures

RESULTS AND DISCUSSION

Electronic Absorption spectra of azo-hydrazone tautomers in neat solvents

A cursory look at the electronic spectra of the dye probes in neat solvents yielded some useful generalizations. Azo-hydrazone tautomerism is affected by a number of factors including structure of the dye probe, presence of inter- and intra-molecular hydrogen bonding, solvent structure and properties, conjugation/aromaticity changes etc. When examined in a solvent such as methanol that can double as a proton donor and acceptor, the effect of the structural chemistry of the tautomers became highlighted. *Para*-phenylazonaphth-2-ols such as AZ-01, 03 and 04 are

understand the physical-organic reactions of these dyes which can dictate their usefulness in synthetic chemistry and chelation processes (Hisaindee et al., 2012) and in addition possible biological applications. The objective of this study was therefore to evaluate the effect of solvent mixture composition on the solubility, solution thermodynamics and position of equilibrium processes of the dye probes, AZ-01 to AZ-04. When the solvatochromic indicator is a conjugated species as is the case with the four dyes, UV-visible spectroscopy is a suitable technique for studying the solute-solvent interactions because the transition energies of the dye probes are highly dependent on the composition of their solvation shells (Umadevi et al., 2007).

A 10 mL quantity of each binary solvent mixture was prepared at volume ratios of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 relative to the other solvent component. The solvent mixtures included methanol:water, ethanol:water, methanol:ethanol, methanol:propan-1-ol, methanol:propan-2-ol, propan-1-ol:water and propan-2-ol:water.

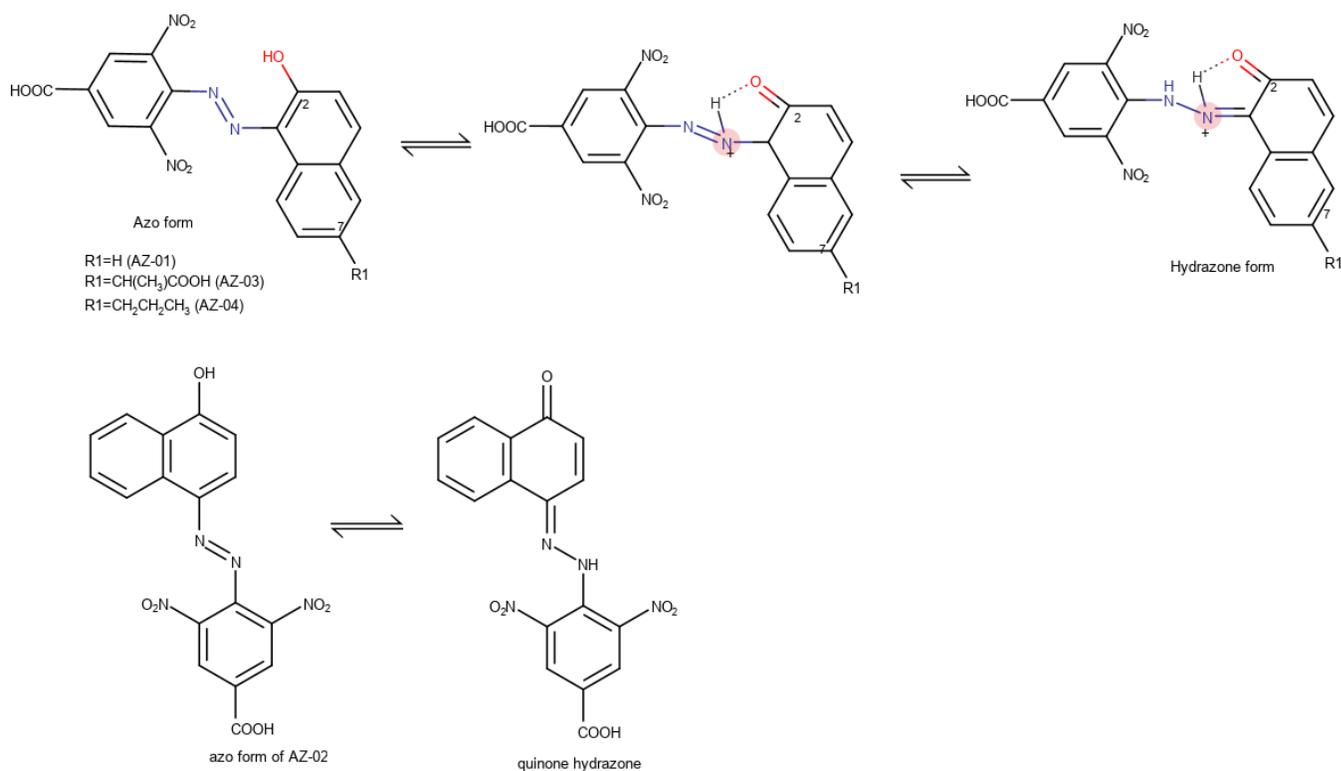
Measurement of UV-VIS spectrum of sample solutions

A 0.1 mL aliquot of the dye stock solution was added into a 5 mL volumetric flask. The solution was made up with the respective binary solvent mixtures. Thus, the molar concentrations of the dyes determined were 2.616×10^{-5} (AZ-01 and AZ-02), 2.203×10^{-5} (AZ-03) and 2.212×10^{-5} M (AZ-04). The flask was mixed by swirling and allowed to equilibrate for a minute. The absorbance of the resulting solution was then recorded from 190-900 nm after baseline correction with the corresponding solvent mixture. All the four dyes were successively treated in each of the six binary mixtures.

capable of intramolecular hydrogen bonding involving *ortho* hydroxyl and nitrogen of azo linkage as shown in Scheme 1. The presence of a strong intramolecular hydrogen bonding and electron withdrawing nitro groups shifts equilibrium towards the keto form resulting in an increase in the ring skeleton of the molecules (Richard and Welton, 2011). The predominance of the hydrazone form of AZ-01, 03 and 04 evidenced by NMR studies showing highly deshielded ketone carbon atom has been previously documented (Adegoke et al., 2008). Thus, only one visible band was observable in the electronic absorption spectra of AZ-01, 03 and 04 in methanol as

shown in Figure 1. This lone spectral peak corresponds to that of the hydrazone tautomer of each molecule. Reeves and Kaiser 1970 documented that 4-phenyl azonaphth-2-ols existed predominantly as the hydrazone in all the solvents investigated. On the other hand, similar intramolecular hydrogen bonding is not possible in 4-phenyl azonaphth-1-ols such as AZ-02 which tends to render the azo-hydrazone tautomerism of this compound more susceptible to environmental factors including solvent structure and properties. The azo-hydrazone tautomerism of AZ-02 induced by intermolecular hydrogen bonding is shown in Scheme 1. The tautomeric equilibrium is influenced by the ability of external hydrogen bonds between each

tautomer and solvents. The hydroxyl group in the azo form is capable of stronger hydrogen bonding than the imino group of the hydrazone. Thus, interaction with hydrogen bond acceptor solvents such as pyridine and alcohols will stabilise the azo form. Conversely, the imino group in the hydrazone form is basic and therefore stabilised by hydrogen bond donor solvents such as acetic acid (Richard and Welton, 2011). The electronic spectra of AZ-02 in methanol as depicted in Figure 1 therefore revealed two peaks in the visible region: the more pronounced azo form band at 451 nm and the less discernible second band at 589 nm ascribable to the hydrazone form (Nishimura et al., 1988).



Scheme 1: Azo-hydrazone tautomeric interconversion of dyes AZ-01, 02, 03 and 04

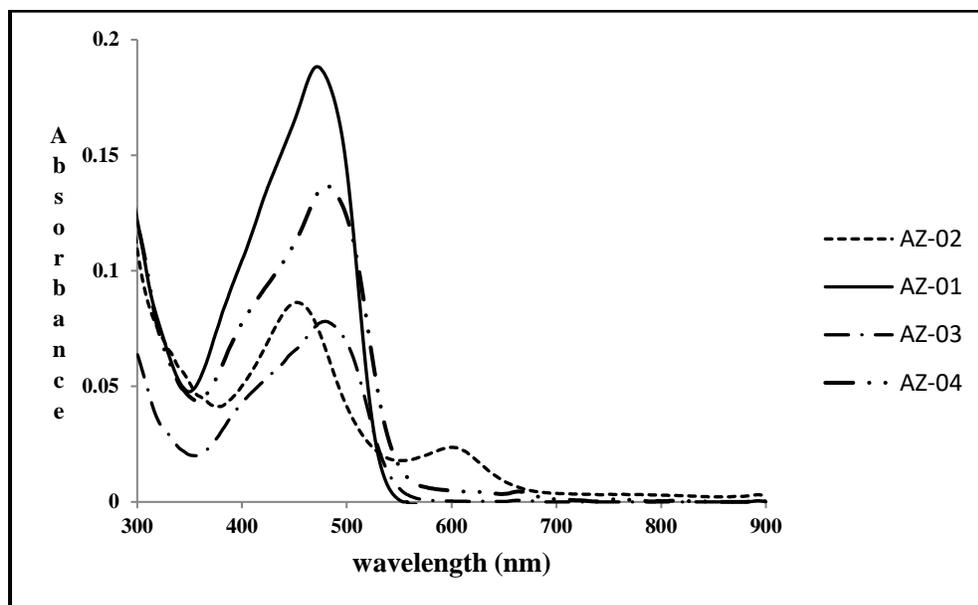


Figure 1: UV-visible spectra patterns of AZ-01 to 04 in methanol

Solvatochromism in binary mixtures

The electronic absorption spectra of the four dyes in binary solvent mixtures of different mole ratios exhibited different UV spectral patterns. The representative results of the UV-vis spectral patterns when examined in mixed alcohols and aqueous alcoholic systems are depicted by those of AZ-02 as

presented in Figure 2 and AZ-03 in Figure 3 respectively. All spectra revealed the presence of well-defined high- and low-energy bands. A secondary lower energy visible band (at around 595nm) attributed to the hydrazone form is again clearly discernible in the spectra of AZ-02 but missing in AZ-03.

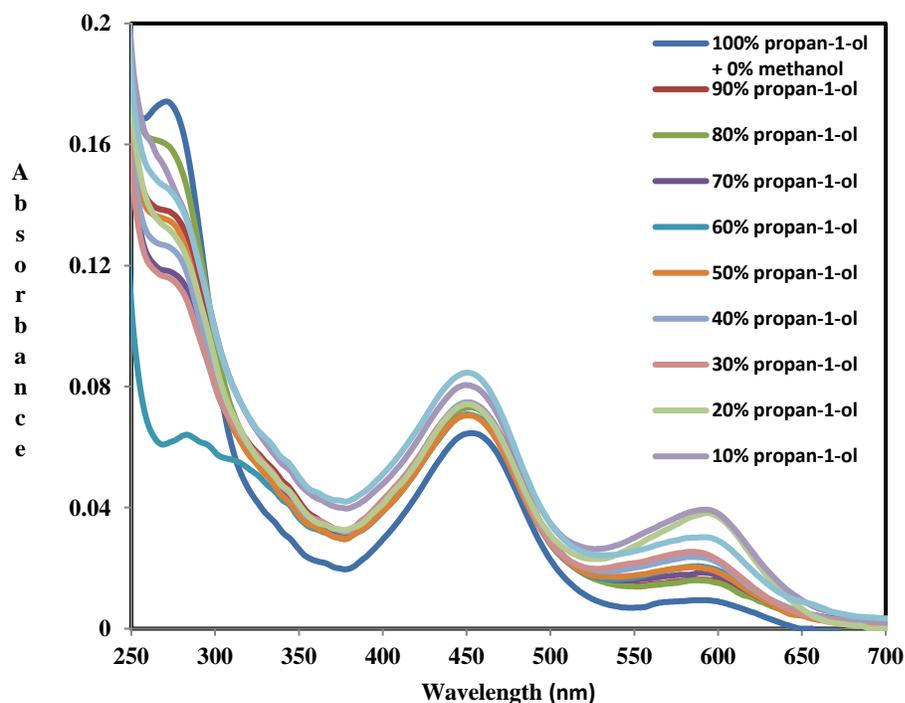


Figure 2: UV-visible spectral patterns of AZ-02 in methanol:propan-1-ol mixtures

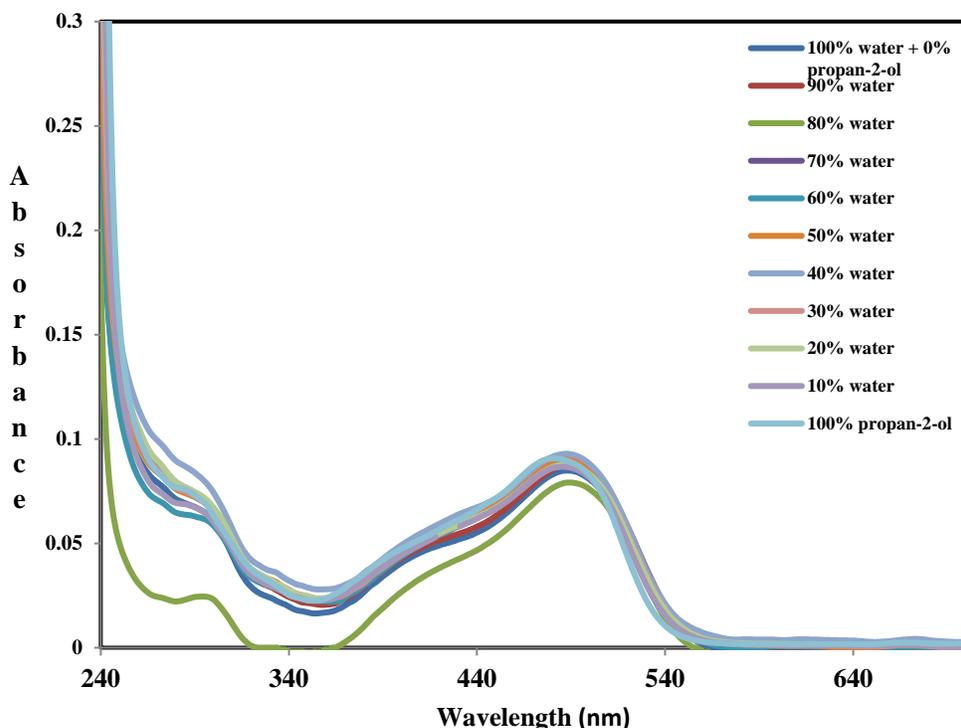


Figure 3: UV-visible spectral patterns of AZ-03 in water:propan-2-ol mixtures

Calculation of preferential solvation

Preferential solvation approach is often employed to study the solvent-solute interactions in binary mixtures. Preferential solvation takes place when in the solvation shell of a solute molecule, there is a higher concentration of one solvent than the other, when compared to the bulk composition. When a binary mixture behaves as an ideal dielectric medium the maximum absorption wavenumber of the solute is linearly additive according to equation 1.

$$\bar{\nu}_{12ideal} = \bar{\nu}_1 X_1 + \bar{\nu}_2 X_2 \text{ -----(1)}$$

Where X_1 and X_2 are the mole fractions of solvent 1 and 2 while $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_{12}$ are the values of maximum absorption wavenumber of the solute in the solvent 1, 2 and binary mixture respectively. However, in the instance that the solute is preferentially solvated in one of the solvents, the experimental data will deviate from linearity. In such a non-ideal mixture, the $\bar{\nu}_{12}$ can be given as presented in equation 2.

$$\bar{\nu}_{12} = \bar{\nu}_1 X_1^L + \bar{\nu}_2 X_2^L \text{ -----(2)}$$

Where X_1^L and X_2^L represent the mole fraction of the solvents 1 and 2 in the solvation shell respectively. This can be calculated from the experimental data using equation 3.

$$X_2^L = \frac{\bar{\nu}_{12} - \bar{\nu}_1}{\bar{\nu}_2 - \bar{\nu}_1} \text{ -----(3)}$$

The index of preferential solvation with respect to the co-solvent δ_{S2} is the difference between X_2^L and X_2 while the preferential solvation constant (K_{ps}) is derived from equation 4.

$$K_{ps} = \frac{X_2^L / X_2}{X_1^L / X_1} \text{ ----- (4)}$$

A positive value of δ_{S2} indicates a preference of the solute for solvent 2 while a negative value indicates preference for solvent 1. The preferential solvation data for the positional isomers AZ-01 and AZ-02 are depicted in Tables 1 and 2 respectively while that of AZ-03 and AZ-04 are presented in Tables 3 and 4 respectively.

Table 1: Preferential solvation data for AZ-01 dye in mixed hydroxylic solvents

| X ₂ | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} |
|----------------|-----------------------------|---------------|-----------------|-----------------------------|---------------|-----------------|------------------------------------|---------------|-----------------|------------------------------------|---------------|-----------------|
| | H₂O: MeOH | | | H₂O: EtOH | | | H₂O: Propan-1-ol | | | H₂O: Propan-2-ol | | |
| 0.1 | 0.000 | -0.100 | 0.188± 0.04 | -0.245 | -0.345 | 0.172± 0.03 | -0.197 | -0.297 | -0.425± 0.14 | 0.000 | -0.100 | 0.296± 0.09 |
| 0.2 | 0.000 | -0.200 | | -0.245 | -0.445 | | -0.197 | -0.397 | | -0.164 | -0.364 | |
| 0.3 | -0.123 | -0.423 | | -0.245 | -0.545 | | 0.000 | -0.300 | | 0.000 | -0.300 | |
| 0.4 | 0.000 | -0.400 | | 0.123 | -0.277 | | 0.198 | -0.202 | | 0.165 | -0.235 | |
| 0.5 | 0.123 | -0.377 | | 0.123 | -0.377 | | 0.397 | -0.103 | | 0.000 | -0.500 | |
| 0.6 | 0.247 | -0.353 | | 0.247 | -0.353 | | 0.397 | -0.203 | | 0.497 | -0.103 | |
| 0.7 | 0.371 | -0.329 | | 0.247 | -0.453 | | 0.397 | -0.303 | | 0.497 | -0.203 | |
| 0.8 | 0.371 | -0.429 | | 0.371 | -0.429 | | 0.597 | -0.203 | | 0.497 | -0.303 | |
| 0.9 | 0.621 | -0.279 | | 0.496 | -0.404 | | 0.597 | -0.303 | | 0.664 | -0.236 | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | |
| | MeOH:EtOH | | | MeOH:Propan-1-ol | | | MeOH:Propan-2-ol | | | | | |
| 0.1 | -2.006 | -2.106 | -1.809± 0.76 | 0.0 | -0.100 | -0.45± 0.23 | 0.00 | -0.100 | 0.460± 0.29 | | | |
| 0.2 | -2.006 | -2.206 | | 0.00 | -0.200 | | 0.00 | -0.200 | | | | |
| 0.3 | -2.006 | -2.306 | | 0.00 | -0.300 | | 0.00 | -0.300 | | | | |
| 0.4 | -4.021 | -4.421 | | 0.335 | -0.065 | | 0.501 | 0.101 | | | | |
| 0.5 | -2.006 | -2.506 | | 0.335 | -0.165 | | 0.00 | -0.500 | | | | |
| 0.6 | 0.000 | -0.600 | | 0.335 | -0.265 | | 0.501 | -0.099 | | | | |
| 0.7 | 0.000 | -0.700 | | 0.335 | -0.365 | | 0.00 | -0.700 | | | | |
| 0.8 | 0.000 | -0.800 | | 0.335 | -0.465 | | 0.501 | -0.299 | | | | |
| 0.9 | 1.998 | 1.098 | | 0.335 | -0.565 | | 0.00 | -0.900 | | | | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.00 | | 1.00 | 0.00 | | | | |

Table 2: Preferential solvation data for AZ-02 dye in mixed hydroxylic solvents

| X ₂ | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} | $x_{\frac{L}{2}}$ | δ_{s2} | K _{ps} |
|----------------|-----------------------------|---------------|-----------------|-----------------------------|---------------|-----------------|------------------------------------|---------------|-----------------|------------------------------------|---------------|-----------------|
| | H₂O: MeOH | | | H₂O: EtOH | | | H₂O: Propan-1-ol | | | H₂O: Propan-2-ol | | |
| 0.1 | -0.123 | -0.223 | 0.461± 0.182 | -0.493 | -0.100 | 2.478± 0.70 | 0.145 | 0.045 | 2.524± 0.01 | -0.330 | -0.430 | 2.980± 0.01 |
| 0.2 | 0.000 | -0.200 | | 0.000 | -0.200 | | 1.833 | 1.633 | | -0.330 | -0.530 | |
| 0.3 | 0.123 | -0.177 | | 0.000 | -0.300 | | 1.558 | 1.258 | | 0.665 | 0.365 | |
| 0.4 | 0.247 | -0.153 | | 1.000 | 0.600 | | 1.419 | 1.019 | | 2.013 | 1.613 | |
| 0.5 | 0.247 | -0.253 | | 0.748 | 0.248 | | 1.558 | 1.058 | | 1.000 | 0.500 | |
| 0.6 | 0.371 | -0.229 | | 0.748 | 0.148 | | 1.419 | 0.819 | | 0.665 | 0.065 | |
| 0.7 | 0.496 | -0.204 | | 1.000 | 0.300 | | 1.280 | 0.580 | | 1.336 | 0.636 | |
| 0.8 | 0.747 | -0.053 | | 1.000 | 0.200 | | 1.419 | 0.619 | | 1.336 | 0.536 | |
| 0.9 | 0.873 | -0.027 | | 1.000 | 0.100 | | 1.140 | 0.240 | | 1.336 | 0.436 | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | |
| | MeOH:EtOH | | | MeOH:Propan-1-ol | | | MeOH:Propan-2-ol | | | | | |
| 0.1 | 0.335 | 0.235 | 3.791± 0.844 | 0.000 | -0.100 | 1.593± 0.484 | -1.004 | -1.104 | 1.002± 0.01 | | | |
| 0.2 | 0.668 | 0.468 | | 0.335 | 0.135 | | 0.000 | -0.200 | | | | |
| 0.3 | -0.674 | -0.974 | | 0.335 | 0.035 | | 0.000 | -0.300 | | | | |
| 0.4 | 0.668 | 0.268 | | 0.000 | -0.400 | | -1.004 | -1.404 | | | | |
| 0.5 | 0.668 | 0.168 | | 0.668 | 0.168 | | 0.501 | 0.001 | | | | |
| 0.6 | 0.668 | 0.068 | | 0.335 | -0.265 | | 1.996 | 1.396 | | | | |
| 0.7 | 0.668 | -0.032 | | 0.668 | -0.032 | | 1.000 | 0.300 | | | | |
| 0.8 | 1.330 | 0.530 | | 1.000 | 0.200 | | 2.987 | 2.187 | | | | |
| 0.9 | 1.330 | 0.430 | | 1.000 | 0.100 | | 1.996 | 1.096 | | | | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | | | |

Table 3: Preferential solvation data for AZ-03 dye in mixed hydroxylic solvents

| X ₂ | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} |
|-----------------------------|-----------------|---------------|-----------------------------|-----------------|---------------|-------------------------------------|-----------------|---------------|------------------------------------|-----------------|---------------|-----------------|
| H₂O: MeOH | | | H₂O: EtOH | | | H₂O: Propan-1- ol | | | H₂O: Propan-2-ol | | | |
| 0.1 | -0.109 | -0.209 | 0.179± 0.038 | -0.331 | -0.431 | 1.584± 0.456 | 0.165 | 0.065 | 0.670± 0.249 | 0.000 | -0.100 | 0.409± 0.115 |
| 0.2 | -0.109 | -0.309 | | -0.660 | -0.860 | | 0.000 | -0.200 | | 0.000 | -0.200 | |
| 0.3 | 0.000 | -0.300 | | -0.660 | -0.960 | | 0.497 | 0.197 | | 0.000 | -0.300 | |
| 0.4 | 0.000 | -0.400 | | -0.331 | -0.731 | | 0.664 | 0.264 | | 0.247 | -0.153 | |
| 0.5 | 0.109 | -0.391 | | -0.331 | -0.831 | | 0.497 | -0.003 | | 0.247 | -0.253 | |
| 0.6 | 0.219 | -0.381 | | -0.331 | -0.931 | | 0.664 | 0.064 | | 0.123 | -0.477 | |
| 0.7 | 0.329 | -0.371 | | 0.000 | -0.700 | | 0.664 | -0.036 | | 0.247 | -0.453 | |
| 0.8 | 0.440 | -0.360 | | 0.332 | -0.468 | | 0.664 | -0.136 | | 0.247 | -0.553 | |
| 0.9 | 0.662 | -0.238 | | 0.332 | -0.568 | | 0.664 | -0.236 | | 0.371 | -0.529 | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | |
| MeOH:EtOH | | | MeOH:Propan-1-ol | | | MeOH:Propan-2-ol | | | | | | |
| 0.1 | 0.752 | 0.652 | 3.865± 0.356 | 0.000 | -0.100 | 0.311± 0.093 | 0.335 | 0.235 | 0.295± 0.163 | | | |
| 0.2 | 0.502 | 0.302 | | 0.252 | 0.052 | | 0.000 | -0.200 | | | | |
| 0.3 | 0.752 | 0.452 | | 0.252 | -0.048 | | 1.000 | 0.700 | | | | |
| 0.4 | 0.752 | 0.352 | | 0.000 | -0.400 | | 0.668 | 0.268 | | | | |
| 0.5 | 0.752 | 0.252 | | -0.253 | -0.753 | | 0.335 | -0.165 | | | | |
| 0.6 | 1.000 | 0.400 | | 0.252 | -0.348 | | 0.335 | -0.265 | | | | |
| 0.7 | 0.752 | 0.052 | | 0.502 | -0.198 | | 0.335 | -0.365 | | | | |
| 0.8 | 1.000 | 0.200 | | 0.502 | -0.298 | | 0.335 | -0.465 | | | | |
| 0.9 | 1.000 | 0.100 | | 0.752 | -0.148 | | 0.335 | -0.565 | | | | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | | | |

Table 4: Preferential solvation data for AZ-04 dye in mixed hydroxylic solvents

| X ₂ | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} | $x \frac{L}{2}$ | δ_{s2} | K _{ps} |
|-----------------------------|-----------------|---------------|-----------------------------|-----------------|---------------|-------------------------------------|-----------------|---------------|------------------------------------|-----------------|---------------|-----------------|
| H₂O: MeOH | | | H₂O: EtOH | | | H₂O: Propan-1- ol | | | H₂O: Propan-2-ol | | | |
| 0.1 | -1.009 | -1.109 | -1.335± 0.823 | 0.877 | 0.777 | 0.927± 0.285 | -1.485 | -1.585 | -1.162± 0.542 | 0.000 | -0.100 | 2.479± 0.701 |
| 0.2 | 0.000 | -0.200 | | 1.123 | 0.923 | | -1.975 | -2.175 | | 0.000 | -0.200 | |
| 0.3 | -4.609 | -4.909 | | 1.123 | 0.823 | | -0.992 | -1.292 | | 0.000 | -0.300 | |
| 0.4 | 1.000 | 0.600 | | 0.877 | 0.477 | | -0.992 | -1.392 | | 0.748 | 0.348 | |
| 0.5 | -3.052 | -3.552 | | 0.753 | 0.253 | | 0.000 | -0.500 | | 0.748 | 0.248 | |
| 0.6 | 1.000 | 0.400 | | 0.629 | 0.029 | | 0.000 | -0.600 | | 0.748 | 0.148 | |
| 0.7 | -2.026 | -2.726 | | 0.629 | -0.071 | | 0.000 | -0.700 | | 1.000 | 0.300 | |
| 0.8 | 0.000 | -0.800 | | 0.379 | -0.421 | | -0.497 | -1.297 | | 1.506 | 0.706 | |
| 0.9 | 1.000 | 0.100 | | 0.379 | -0.521 | | 0.000 | -0.900 | | 0.748 | -0.152 | |
| 1.0 | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | | 1.000 | 0.000 | |
| MeOH:EtOH | | | MeOH:Propan-1-ol | | | MeOH:Propan-2-ol | | | | | | |
| 0.1 | 2.004 | 1.904 | -2.813± 1.059 | 1.000 | 0.900 | -0.273± 0.084 | -1.004 | -1.104 | -1.656± 0.741 | | | |
| 0.2 | 2.004 | 1.804 | | 0.000 | -0.200 | | 0.000 | -0.200 | | | | |
| 0.3 | 0.000 | -0.300 | | 0.000 | -0.300 | | -2.013 | -2.313 | | | | |
| 0.4 | 3.013 | 2.613 | | 0.000 | -0.400 | | 0.000 | -0.400 | | | | |
| 0.5 | 1.000 | 0.500 | | 0.000 | -0.500 | | 0.000 | -0.500 | | | | |
| 0.6 | 0.000 | -0.600 | | -0.996 | -1.596 | | -1.004 | -1.604 | | | | |
| 0.7 | 2.004 | 1.304 | | -0.996 | -1.696 | | 0.000 | -0.700 | | | | |
| 0.8 | 1.000 | 0.200 | | 0.000 | -0.800 | | 0.000 | -0.800 | | | | |
| 0.9 | 3.013 | 2.113 | | 1.000 | 0.100 | | 1.996 | 1.096 | | | | |
| 1.0 | 2.004 | 1.004 | | 1.000 | 0.000 | | 1.000 | 0.000 | | | | |

The plots of the molar transition energy in the binary mixture E_{12} vs the mole fraction of the co-solvent when examined in water-alcohol and mixed alcohol solvent binary systems are represented by those of AZ-01 in water:methanol and AZ-03 in methanol:ethanol

as shown in Figures 4 and 5 respectively. Over the majority of the composition range, the plots showed deviation from linearity thus indicative of preferential solvation.

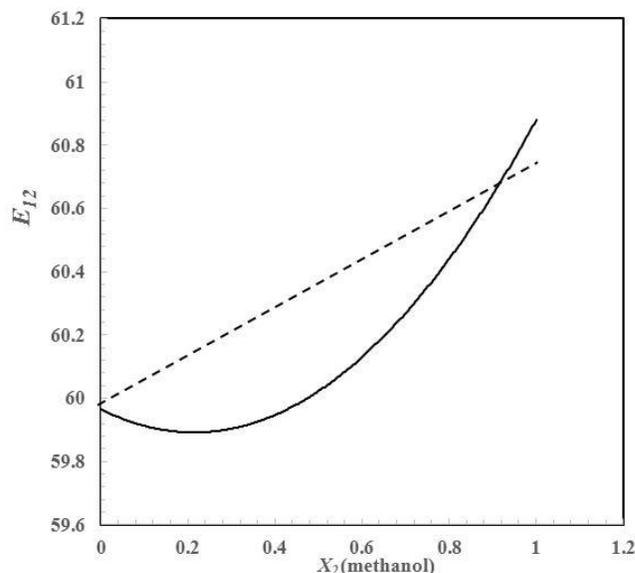


Figure 4: Variation in E_{12} of AZ-01 in water:methanol mixtures of different composition

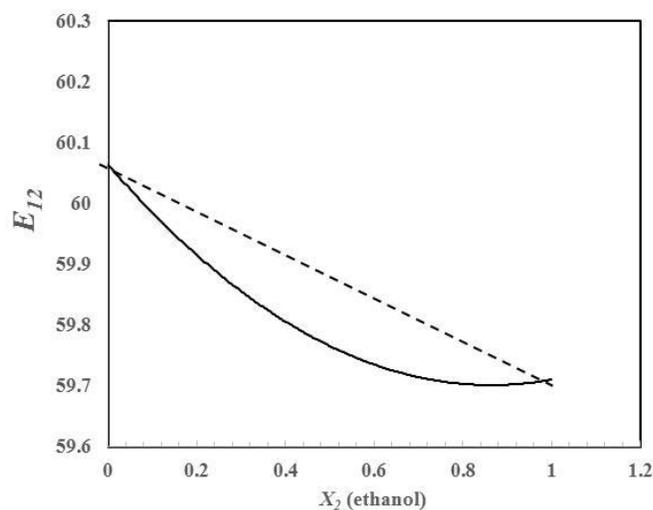


Figure 5: Variation in E_{12} of AZ-03 in methanol:ethanol with increasing mole fraction of co-solvent

Mixed hydroxylic solvents mixture with water as co-solvent

In water:methanol binary mixtures, the spectra data of the four dyes showed a preferential accumulation of water in the cytochromic region of the solute. However, the solvation data in the other aqueous alcoholic mixtures provided patterns that could be better attributed to the difference in chemical structure of the dyes. Thus, solvation data indicated that over the

majority of the composition range, dyes AZ-01 and 03 were preferentially solvated by water molecules as evidenced by the negative values of index of preferential solvation, δ_{s2} , and the small mole fractions of the organic solvent in their solvation shell compared to the bulk solvent. Conversely, AZ-02 and to a lesser degree AZ-04 (as evidenced by its solvation data in ethanol at $X_2=0.1-0.6$ and in propan-2-ol at $X_2=0.4-0.8$) showed preferential solvation by the

organic component of the binary mixtures. In all instances, the plots of the E_{12} against the mole fraction of the co-solvent showed a deviation from ideality. Although the dyes are largely hydrophobic and are thus expected to show higher affinity for organic solvents, the dye molecules all contain groups in varying number and capacities to impart hydrophilicity. The preferential solvation of a molecule in organic-water mixed solvents systems is often a reflection of the balance of the hydrophobic and hydrophilic properties of the molecule (Mabesoone et al., 2020). It is also well reported that at higher composition, water molecules self-associate *via* hydrogen bonding thus causing a preferential accumulation of the organic component in the solvation shell of a solute (Fayed and Etaiw, 1998; Sasirekha et al., 2008). Thus, a molecule as exemplified by AZ-04 in water:ethanol mixtures, might be preferentially solvated by the organic solvent in the water rich regions (positive δ_{s2} values at $X_2 = 0.1$ to 0.6) while it is more solvated by water molecules at higher mole fractions of ethanol. At higher composition, the polar protic alcohol is capable of disrupting the self-association of water molecules following new solvent-solvent interaction *via* hydrogen bonding to form aggregated water-ethanol species that reduces the preferential solvation of the solute by ethanol (Almandoz et al., 2014).

Dyes AZ-01 and 02 are positional isomers which differ only in the relative position of the free hydroxyl group to the azo linkage. The observed trends in their solvation data should therefore be explainable by this structural difference. While the *ortho*-hydroxyl AZ-01 showed a preference for water over ethanol, 1-

propanol or 2-propanol, AZ-02 which contain a *para* hydroxyl group showed a preference for the same organic solvents over water. The tautomeric conversion of AZ-01 from the azo to the predominant hydrazone form as shown in Scheme 1 is associated with the development of an overall positive charge on the molecule which can facilitate ion-dipole or some other charge-mediated interactions with water (Adegoke et al., 2008). Although AZ-03 and 04 also exist predominantly in the hydrazone form, the presence of an additional hydrocarbon chain at position 7 is expected to impact on the lipophilicity-hydrophilicity balance of these molecules and thereby prevent a complete and comprehensive generalization of the effects of self-associated water molecules on their solvation.

Thus, AZ-03, that contains propionic acid substituent, which is capable of some form of polar interactions including hydrogen bonding, exhibited preferential accumulation of water in its solvation shell when the co-solvent is methanol, ethanol, 2-propanol and to a substantial extent 1-propanol ($X_2 = 0.7-1.0$). Expectedly, AZ-04 with a butanone substituent, is more lipophilic and shows preferential solvation in the alcohols (except 1-propanol) compared to water over majority of the composition range. The observed effect for AZ-04 in Figure 6 showed a reduction in molar transition energies as solvent composition approached 100% ethanol. In addition, a careful examination of the solvatochromic shifts in Figure 6 revealed values of AZ-03 in ethanol-water mixtures ($X_2 = 0.1 - 0.9$) that are lower than the pure solvents.

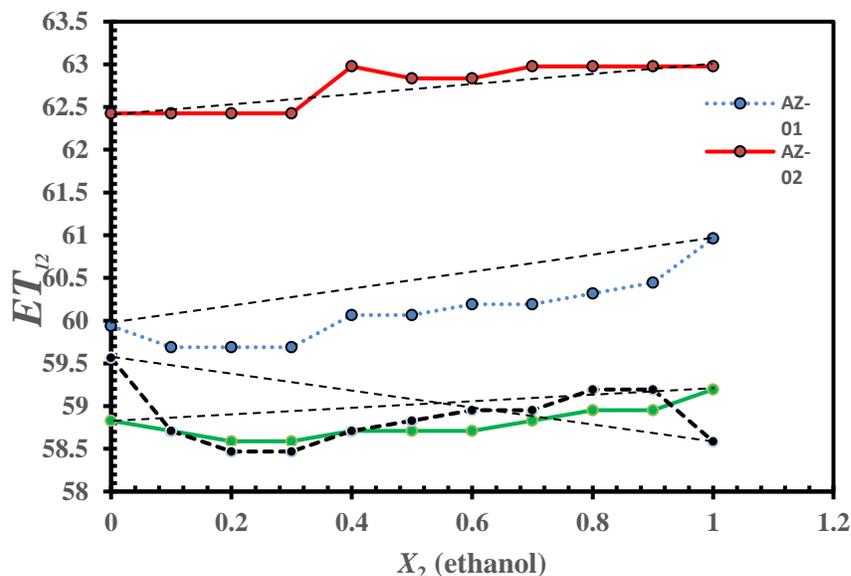


Figure 6: Solvatochromic shifts in the E_{T12} values of the four dyes as a function of the mole fraction of the co-solvent in water:ethanol mixture

This is probably due to synergistic behaviour arising from interactions between the components of the mixture to form aggregated species that are more polar than the individual solvents (Gupta et al., 2016). In a study to examine the relative strength of hydrogen bond interaction in alcohol-water mixtures, it was reported that ethanol-water co-solvents can exist in two heterodimeric forms, RH...H₂O where alcohol is a proton acceptor or a proton donor, ROH...OH₂ (Fileti et al., 2004). The presence of propionic substituents which can also serve as both proton donor and acceptor in AZ-03 may therefore enhance interaction with these heterodimeric forms and solvation in aqueous ethanolic systems. Interestingly, similar lowering of E_{12} values was present in both AZ-01 and AZ-04 ($X_2 = 0.1 - 0.3$ and $0.2 - 0.3$ respectively) while no such effect was seen with AZ-02, but rather a new plateau was obtained within this mole ratio ranges.

Mixed alcoholic systems

The behaviour of the four dyes in mixed binary systems containing methanol with another higher molecular weight alcohol serving as co-solvent was also investigated. In mixed alcoholic systems, it is anticipated that the hydrogen bonding ability and dipolar interactions in the studied composition range will dictate the observed trends. Thus, methanol with a stronger hydrogen bonding ability than ethanol, 1-propanol or 2-propanol will preferentially accumulate in the solvation shell of a solute capable of some form of polar interactions. This explains the general preferential solvation of AZ-01 and 03 in methanol at various mole fractions of the different co-solvents. On the contrary, the more neutral AZ-04 (due to modulating effect of butanone residue) generally showed preference for the more hydrophobic component in methanol:ethanol and methanol:propan-1-ol binary mixtures. In methanol-ethanol mixtures, AZ-01 showed preference for methanol over a wide composition range up to 0.8 of the co-solvent while AZ-03 showed preference for ethanol in methanol-rich regions. The preference of AZ-03 for ethanol at high mole fractions of methanol can be attributed to the fact that methanol molecules can self-associate to form hydrogen-bonded network which cannot be readily disrupted by the ethanol molecules. Thus, isolated

ethanol molecules can interact with the solute *via* hydrogen bonding leading to its preferential solvation by ethanol (Fayed et al., 1998). With increased mole fraction of ethanol molecules ($X_2 = 0.7 - 1.0$), there is increased interaction between the alcohols leading to a decrease in preferential solvation of the solute in ethanol as evidenced by smaller values.

Correlation studies

Preferential solvation arises from the interplay of specific (hydrogen bonding) and non-specific (dielectric effects) interactions between the components of the solvent mixtures and the solute. Deciphering the predominant mode of interaction is often done using correlation studies. The observed trends of the dye probes in the different binary mixtures can be explained in terms of the Kamlet and Taft parameters of the solvents (π^* , α , β) which form the basis of linear solvation energy relationships model (Sancho et al., 2011). The index of solvent dipolarity/polarizability (π^*), measures the ability of a solvent to stabilise a charge or dipole. The α scale or solvents acidity scale is a measure of the hydrogen bond donor ability of solvent while β is a measure of the basicity of the solvent i.e., its ability to serve as an electron pair donor in a solvent-solute hydrogen bond interaction.

In non-chlorinated solvents, the contribution of specific and non-specific interactions to the total solvation energy is given by equation 5

$$E_T = A_0 + \alpha\alpha + b\beta + p\pi^* \quad \text{-----(5)}$$

Where A_0 refers to the intercept of the regression equation while α , b and p are coefficients that measure the contribution of solvent acidity, basicity and polarity to total solvation energy. The values of the KAT parameters for pure solvents and solvent mixtures were obtained from literature (Marcus, 1994; Roses et al, 1995). Regression equations containing all possible combinations of the KAT parameters were generated and analysed to determine the KAT equation that best fitted the spectral data of the dyes in each of the solvent mixtures (Naderi et al., 2014).

The most significant regression equations describing the relationship between the E_{12} of the dyes and the solvent parameters are given in Table 5.

Table 5: Multiple linear regression analysis of KAT parameters for the E₁₂ values of the dyes

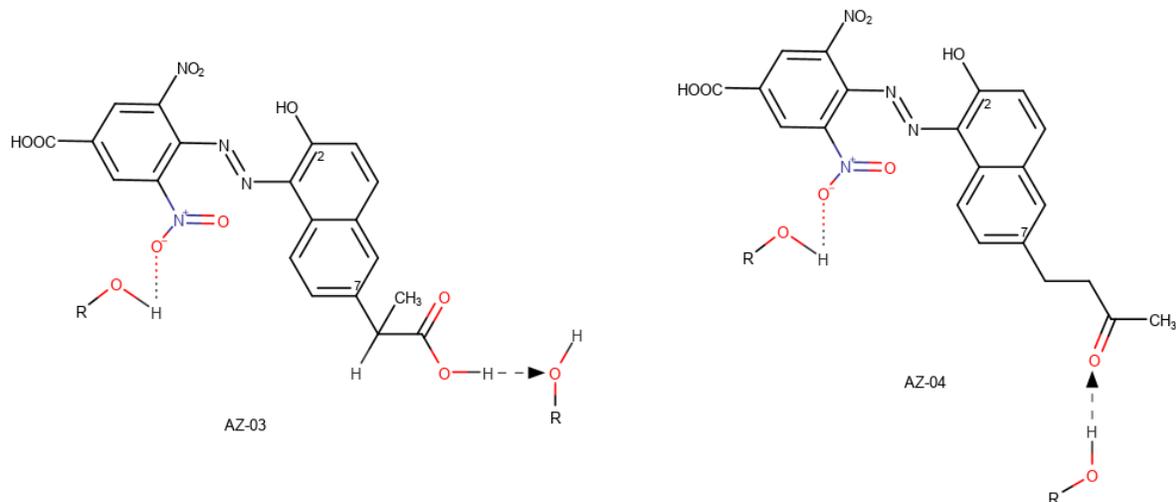
| Solvents | Dye | A ₀ | a | b | p | F | r ² |
|----------------------|-------|----------------|--------|--------|---------|---------|----------------|
| Neat solvents | AZ-01 | 61.245 | | | -1.010 | 9.210 | 0.650 |
| | AZ-02 | 32.150 | 17.609 | 20.630 | | 109.761 | 0.982 |
| | AZ-03 | 60.209 | | | -1.298 | 7.636 | 0.604 |
| | AZ-04 | 57.538 | 2.908 | | 1.892 | 5.194 | 0.722 |
| Water-methanol | AZ-01 | 61.665 | | | -1.651 | 44.732 | 0.833 |
| | AZ-02 | 64.773 | | | -2.167 | 340.411 | 0.974 |
| | AZ-03 | 60.830 | | | -1.939 | 74.999 | 0.893 |
| | AZ-04 | 54.992 | 4.932 | | -1.308 | 4.680 | 0.540 |
| Water-ethanol | AZ-01 | 61.423 | | | -1.560 | 35.002 | 0.80 |
| | AZ-02 | 63.669 | | | -1.093 | 42.989 | 0.827 |
| | AZ-03 | 60.663 | | -1.517 | -1.080 | 9.300 | 0.700 |
| | AZ-04 | 54.768 | 5.934 | | -2.034 | 9.507 | 0.704 |
| Water-propan-2-ol | AZ-01 | 61.118 | | | -1.256 | 21.676 | 0.707 |
| | AZ-02 | 63.682 | | | -1.219 | 10.536 | 0.540 |
| | AZ-03 | 72.351 | -5.089 | -9.203 | -3.248 | 14.321 | 0.860 |
| | AZ-04 | 59.717 | | | -1.104 | 18.774 | 0.676 |
| Methanol-ethanol | AZ-01 | 61.978 | 5.943 | | -12.939 | 6.868 | 0.631 |
| | AZ-02 | 60.244 | 3.165 | | | 10.296 | 0.534 |
| | AZ-03 | 56.470 | | | 6.021 | 20.791 | 0.698 |
| | AZ-04 | 60.634 | | | -2.046 | 0.903 | 0.09 |
| Methanol-propan-1-ol | AZ-01 | 61.879 | | -1.637 | | 19.142 | 0.680 |
| | AZ-02 | 61.823 | 1.874 | | | 42.282 | 0.824 |
| | AZ-03 | 61.557 | | -2.506 | | 13.329 | 0.597 |
| | AZ-04 | 52.207 | 3.731 | 5.627 | | 0.862 | 0.178 |
| Methanol-propan-2-ol | AZ-01 | 60.394 | 0.412 | | | 6.046 | 0.402 |
| | AZ-02 | 61.342 | | | 3.745 | 10.778 | 0.545 |
| | AZ-03 | 53.658 | 3.321 | 4.005 | | 2.396 | 0.375 |
| | AZ-04 | 67.644 | | -4.066 | -9.289 | 6.525 | 0.620 |

In neat solvents, a single parametric equation best described the spectral behavior of AZ-01 and 03 with solvent polarity being the highest contributor. In both instances, an inverse relationship between the molar electronic transition energies and polarity was observed. In contrast, the spectral patterns of the *para*-hydroxyl positional isomer best fitted dual parametric modelling with predominantly the hydrogen bond donor capability of AZ-02 (and to a lesser extent solvent acidity) responsible for more than 98% of the observed behavior. This difference between the two isomers further emphasizes the role of the common hydroxyl group which is involved in hydrazone formation in AZ-01 and thus cannot be involved in hydrogen bonding with solvent milieu unlike the labile hydroxyl group in AZ-02. Acidity of solvent milieu and solvent polarity in that order were the largest contributors to the spectral data of AZ-04.

In aqueous alcoholic mixtures, a general trend can be observed. Solvent polarity was contributory, although to different degrees, to the observed spectral data of the four dyes. This is anticipated as all four dyes can form hydrazones, albeit of two different types, which

are more dipolar than the azo forms and thus will be better stabilized in more polar solvent microenvironment. Expectedly, there is an inverse relationship between the molar transition energies of the four dyes and polarity of the aqueous alcoholic mixtures. In addition to the general solvent polarity effects, specific solute-solvent interactions can also be deciphered from the modelling. In water:ethanol mixtures, the primary contributor to the spectral changes of AZ-03 was basicity of the solvent milieu while a multiparametric equation best fitted the spectral data of the dye in water:propan-2-ol mixtures. Thus, the solvent effects on spectral shifts of AZ-03 when examined in aqueous propan-2-ol can be attributed to a combination of the polarity, acidity and basicity properties of the binary mixtures with the order of contribution being: $\beta > \alpha > \pi$. Multiple effects, such as these, are common in mixtures of amphiprotic solvents including water and alcohols as these solvents can act as both proton donors and acceptors (Thomas et., al 2019; Kamlet and Taft, 1976). Amphiprotic solvents can therefore donate protons to the oxygen atoms of the common aromatic

nitro and carboxylic acid groups of the dye. On the other hand, these solvents can also serve as proton acceptors in interactions with C-7 propionic acid substituent and the carboxylic acid residue in AZ-03 as shown in Scheme 2. For AZ-04, the primary contributor to its spectral changes in aqueous methanol



Scheme 2: Solute-solvent interactions in amphiprotic solvents

The polarity of methanol:ethanol systems predominantly influenced the spectral changes of the dyes with the sole exception of AZ-02 whose spectral data fitted a single parametric equation involving solvent electron pair acceptor capability. Conversely, electron pair donor capability was the most consistent contributor to the spectral shift of the dyes when examined in methanol:propan-1-ol and methanol:propan-2-ol binary mixtures. This property was the sole or largest determinant of spectral behaviours of AZ-01, 03, 04 in methanol:propan-1-ol and AZ-03 in methanol:propan-2-ol. Solvent basicity

CONCLUSION

The solvatochromic properties of the phenylazonaphthalene series, AZ-01 to 04 in binary mixtures of varying composition have been successfully studied using UV-visible spectroscopy. Spectra-structure relationships identified the formation of the charged hydrazone tautomer which

and ethanol binary mixtures was the hydrogen bond donor capability of the mixtures. This is in all probability being mediated by the polar interactions between the solvents, the C-7 butanone residue and the common nitro group.

also played secondary contributory role in the solvation data of AZ-04 in methanol:propan-2-ol. The more pronounced contribution of solvent basicity when the dyes were examined in mixtures containing 1- or 2-propanol is anticipated as they are more basic than corresponding methanol or ethanol mixtures. Basicity of solvent was the single most consistent contributor to the spectral changes of AZ-03 in all the solvent mixtures. This in all probability is due to the hydrogen bond interaction between the solvent and the C-7 propionic acid moiety that is unique to this dye probe.

requires stabilisation by polar solvent milieu as responsible for the observed trend. In addition, interactions between new aggregated solvent-solvent species, that were somewhat more polar than the pure solvents, and the propionic acid substituent present in AZ-03 contributed to its spectral shifts.

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