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PREFERENTIAL SOLVATION OF 4-CARBOXYL-2,6-DINITROPHENYL-AZOHYDROXYNAPHTHALENES IN AQUEOUS DIMETHYLFORMAMIDE AND DIMETHYLSULFOXIDE BINARY MIXTURES BY UV-VIS SPECTROSCOPY

O. E. Thomas, O. A. Adegoke[*], F. G. Adenmosun, O. J. Abiodun

University of Ibadan, Ibadan, Nigeria; e-mail: jireade@yahoo.com, ao.adegoke@mail.ui.edu.ng

The objective of this study was to evaluate the influence of partly aqueous solvent mixtures on the solubility and azohydrazone equilibrium processes for a group of phenylazohydroxynaphthalenes, AZ-01, AZ-02, AZ-03, and AZ-04, whose applications as potential color additives and chemosensors have been demonstrated in previous studies. The UV-visible spectrum was acquired between 190-900 nm at concentrations of the dyes that precluded molecular aggregation for each dye in aqueous dimethylformamide and dimethylsulfoxide binary mixtures of varying compositions. The plots of E_{12} *against mole fractions of the co-solvent showed deviation from ideality in the behaviors of the four dyes in the aqueous solvent mixtures. The solvation data were largely influenced by the structural chemistry of the dyes. In particular, AZ-01, which contains a free parahydroxyl group that can donate hydrogen to hydrogen bond acceptor solvents showed substantial bathochromic shifts in the aqueous DMF and DMSO mixtures as well as a local accumulation of the organic solvent in its solvation sphere. Conversely, the positional isomer AZ-02 with its ortho hydroxyl group being involved in intramolecular hydrazone rearrangement exhibited dielectric enrichment in both aqueous solvent mixtures. In addition, synergism through formation of the water-DMSO and water-DMF complexes was observed with all the dyes in the solvent mixtures with AZ-01 being solvated by the more polar component of the complex while AZ-02 and AZ-04 were solvated by the less polar solvent mixture component. Thus, the preferential solvation of the phenylazohydroxynaphthalene series from AZ-01 to AZ-04 in the partly aqueous DMSO and DMF solvent mixtures has been successfully studied using UV-visible spectroscopy.*

Keywords: *4-carboxyl-2,6-dinitrophenylazohydroxynaphthalenes, aqueous solvent, synergistic effect, UV-Vis spectroscopy, preferential solvation.*

ИЗУЧЕНИЕ ПРЕИМУЩЕСТВЕННОЙ СОЛЬВАТАЦИИ 4-КАРБОКСИЛ-2,6-ДИНИТРОФЕНИЛАЗОГИДРОКСИНАФТАЛИНОВ В ВОДНЫХ БИНАРНЫХ СМЕСЯХ ДИМЕТИЛФОРМАМИДА И ДИМЕТИЛСУЛЬФОКСИДА С ПОМОЩЬЮ СПЕКТРОСКОПИИ УФ-ВИДИМОГО ДИАПАЗОНА

O. E. Thomas, O. A. Adegoke[*], F. G. Adenmosun, O. J. Abiodun

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Университет Ибадана, Ибадан, Нигерия; e-mail: jireade@yahoo.com, ao.adegoke@mail.ui.edu.ng

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Оценено влияние частично водных смесей растворителей на растворимость и равновесные процессы в азогидразоне для группы фенилазогидроксинафталинов AZ-01, AZ-02, AZ-03 и AZ-04, используемых в качестве потенциальной цветовой добавки и хемосенсора. Спектр УФ-видимого диапазона получен в интервале 190–900 нм при концентрациях красителей, которые препятствовали агрегации молекул каждого красителя в бинарных водных смесях диметилформамида и диметилсульфоксида различного состава. Зависимости E_{12} *от мольных долей сорастворителя показывают отклонение от идеального поведения для четырех красителей в водных смесях растворителей. На данные сольватации большое влияние оказывает структурная химия красителей. В частности, AZ-01, содержащий свободную парагидроксильную группу, которая может быть донором водорода для водородных связей с акцепторными растворителями, показывает значительные батохромные сдвиги в водных смесях ДМФА и ДМСО, а также локальное накопление органического растворителя в его* *сольватной сфере. Наоборот, позиционный изомер AZ-02 с его ортогидроксильной группой, участвующей во внутримолекулярной перегруппировке гидразона, демонстрирует диэлектрическое обогащение в обеих водных смесях растворителей. Для всех красителей в смесях растворителей наблюдается синергизм за счет образования комплексов вода–ДМСО и вода–ДМФА, причем AZ-01 сольватируется более полярным компонентом комплекса, в то время как AZ-02 и AZ-04 — менее полярным компонентом смеси растворителей. С помощью УФ-видимой спектроскопии успешно изучена преимущественная сольватация фенилазогидроксинафталинового ряда от AZ-01 до AZ-04 в частично водных смесях ДМСО и ДМФА.*

Ключевые слова: *4-карбоксил-2,6-динитрофенилазогидроксинафталины, водный растворитель, синергетический эффект, спектроскопия УФ-видимого диапазона, преимущественная сольватация.*

Introduction. The behavior of a solute in mixed solvents is often more complex than in pure solvents. When investigated in solvent mixtures, the composition of a probe's solvation sphere may differ markedly from that of the bulk solvent. This is often due to the formation of new solute-solvent and solvent-solvent interactions as well as their interplay. This leads to a deviation from the ideal behavior of the probe [1]. Specific interactions, such as hydrogen bonding and/or non-specific interactions including dipole-dipole interactions, may lead to an enrichment of one of the components of the binary mixture in the solvation sphere at levels in excess of those obtainable in the bulk solvent. The solute is said to be preferentially solvated. The preferential solvation behavior of a solute is dictated by a combination of factors including its chemical structure, the microheterogeneity of the solvation sphere, as well as the physicochemical properties of the constituents of the solvent mixture. It depends also on how they differ from properties of any newly formed solvent aggregates [2]. Understanding the behavior of a molecule in pure solvent, as well as in mixed solvent systems, provides useful applications not only in small-scale laboratory procedures as chromatographic separations, optimizations of organic synthesis, and kinetic studies, but also in industrial separations and operations such as hydrometallurgy and the solubilization of otherwise poorly-soluble drug ingredients [2–4]. Mixed solvent studies are also critical in the science of the environmental disposal of a solute, when present in waste water containing various residual organic solvents arising from different industrial processes [5]. Thus, the profiling of the solvation behavior of new chemical entities is desirable. Previous studies of the new series of phenylazohydroxylnaphthalenes (tagged AZ-01, AZ-02, AZ-03, and AZ-04) in pure solvents and in equimolar binary solvent mixtures demonstrated their poor aqueous solubility, as well as the dependence of the azohydrazone equilibrium exhibited by AZ-01, AZ-03, and AZ-04 on the polarity of the mixtures [6, 7]. The objective of this study was therefore to evaluate the influence of partly aqueous solvent mixtures of varying composition on the solubility and on the azohydrazone equilibrium processes of the dyes. The study can also provide useful insight into the physical and biological properties of the azodye series which can improve their organic synthesis as well as their applications as color additives and chemosensors.

Experimental. Dimethylsulfoxide (Merck AR, Germany) and dimethylformamide (Merck AR, Germany) were used without further purification. Double-distilled water was used for the recordings involving water.

The four monoazodyes named AZ-01, AZ-02, AZ-03, and AZ-04 (Fig. 1), were synthesized as previously reported [8]. Stock solutions for the dyes were made in methanol to obtain 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).

A Mettler analytical balance (Ohaus, USA) and a Lambda 25 digital UV/VIS spectrometer (Perkin Elmer, Singapore) with 1 cm path length and matched quartz cells were used.

Preparation of the binary solvent mixtures. Into each of eleven 10 mL volumetric flasks containing 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 mL of dimethylsulfoxide (DMSO), appropriate volumes of water were added to make a 10 mL quantity for each binary mixture. The binary mixtures of dimethylformamide (DMF) and water at the same volume ratios were similarly prepared. All solvent mixtures were made in closed volumetric flasks and inverted several times to ensure complete distribution and equilibration before introducing dye samples.

Measurement of UV-VIS spectrum of sample solutions. A 0.1 mL aliquot of the dye stock solution was transferred into a 5 mL volumetric flask and then made up to volume, in turn, with each of the binary mixtures prepared for DMSO and DMF as stated above. Complete mixing and equilibration were ensured by swirling the closed volumetric flasks and allowing them to stand for 1 min before the data acquisition. Using appropriate binary solvent mixtures as blank, the UV-visible spectrum from 190–900 nm of each of the resulting dye solutions at molar concentrations equivalent to 2.6164×10^{-5} M for AZ-01 and AZ-02, 2.2026×10^{-5} M for AZ-03, and 2.212×10^{-5} M for AZ-04 were determined.

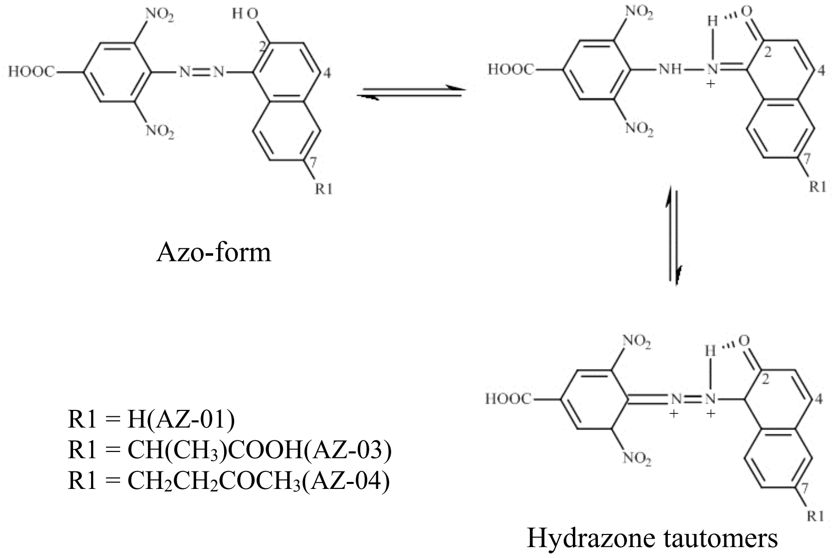

Fig. 1. Azo-hydrazone tautomeric equilibrium in AZ-01, AZ-03, and AZ-04.

Results and discussion. Three of the azo dyes (AZ-01, AZ-03, and AZ-04) investigated contain a common 2-hydroxyl group and have been previously established by NMR characterisations to exist predominantly in the hydrazone forms [8] as depicted in Fig. 1. On the other hand, AZ-02 being a positional isomer of AZ-01 with the hydroxyl group *para* to the azo linkage (i.e., position 4) is not capable of this intramolecular rearrangement. The ability or otherwise to form the hydrazone tautomer, their relative predominance, the microenvironment around the solute in each solvent mixture as well as the intrinsic characteristics (especially the basicity) of the second component of the liquid pairs are expected to dictate the solvatochromic bands of the dye probes when examined in binary solvent mixtures of water and a hydrogen bond acceptor such as DMSO or DMF.

Electronic absorption in partly aqueous solvents mixtures. The representative results of the UV-Vis spectra for AZ-02 when examined in DMF and its binary mixtures with water at various ratios are depicted in Fig. 2. The results revealed that the four dyes in all the various ratios of both aqueous DMF and aqueous DMSO mixtures exhibited well-defined high-energy UV bands occurring in the range of 226–290 nm. These highly absorbing bands have been attributed to the π–π^* transition in the aromatic skeletons [6]. The positions and absorptivities of the UV bands of the dyes in all the binary mixtures are presented in Table 1. For the four dyes in both aqueous DMSO and DMF mixtures, as the ratio of the co-solvent increased, there were initial progressive bathochromic shifts until a hypsochromic shift (although bathochromic with respect to 0 mole ratio of co-solvent) was observed. This was usually followed by further increase in the position of the bands at higher mole ratios of the co-solvents. However, a notable exception was that of AZ-02 in water:DMF. Although less generalizable, the UV spectra of AZ-02 in this solvent mixture showed consistently higher band positions and absorptivities at all co-solvent ratios when compared to those obtained with its positional isomer (AZ-01) in the same solvent mixture.

In addition, the spectra of all the four dyes revealed visible bands at wavelengths range of 458–593 nm corresponding to the π–π^* transition associated with increased conjugation between the naphthalene and benzenoid residues via the azo functional group. The formation of new solute-solvent interactions especially charge-transfer complexation between the solvents and the common hydroxyl and/or carboxylic groups on the dyes will also contribute to this band. Expectedly, the influence of the microenvironment in the solvent mixture and the chemical environment of the individual dye probes were more pronounced with the visible bands. For AZ-01, an increase in the mole fraction of the co-solvent only produced a maximum change of $\Delta\lambda = 3$ nm in the band position in the two aqueous binary mixtures. This was in sharp contrast to the UV spectra of its positional isomer (AZ-02), which revealed that an increase in the mole fraction of the co-solvent induced the transition of a shoulder at 554 nm (with almost insignificant absorptivity) to a well-defined highly absorbing peak with maximum positions of 593 and 592 nm in the aqueous DMSO and DMF solvent mixtures, respectively. These represent maximum bathochromic shifts of 35 and 34 nm, respectively. The difference in the electronic spectra patterns of the two isomers must be explainable by the position of the common hydroxyl group. When present at a position that is *para* to the azo linkage, as found in AZ-02, the hydroxyl group cannot be involved in conjugation with the azo linkage and is therefore precluded from the intramolecular hydrogen rearrangement associated with hydrazone formation. Thus, the proton can be donated to proton acceptors such as DMSO and DMF in a charge-transfer complexation. This $n \rightarrow \pi^*$ transfer is responsible for the marked hyperchromic and bathochromic shifts observable in these solvent mixtures with AZ-02. However, solvents that promote the formation of the hydrazone tautomers will induce a hypsochromic shift as their formation is associated with a distortion of the conjugated system in the naphthalene residue as shown in Fig. 1. This is probably responsible for the slight hypsochromic shifts observed with AZ-01 at higher mole fractions of DMSO (0.4–0.9) and DMF (0.5–1.0). Similar small changes in the band position and absorptivity were seen with AZ-03 and AZ-04, which are both capable of azo-hydrazone tautomerism.

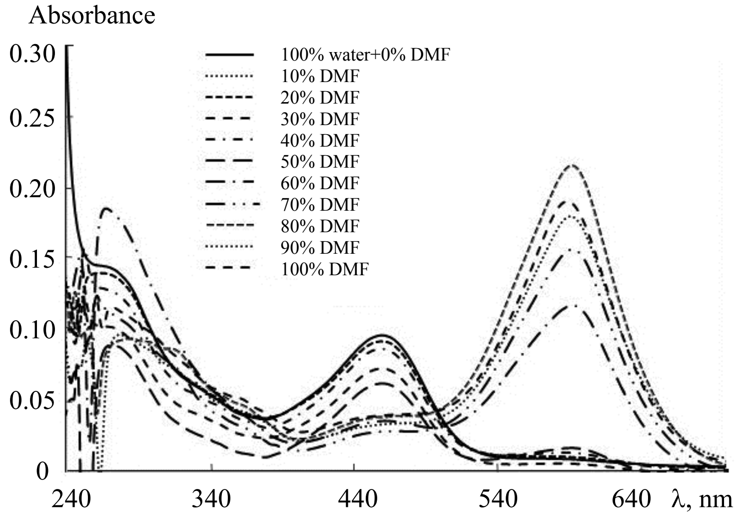

Fig. 2. Electronic absorption spectra of AZ-02 in water:DMF mixtures.

TABLE 1. High and Low-Energy Electronic Absorption Spectral Data λ_{max} ($\log\varepsilon_{max}$) of the Dyes in Partly Aqueous Solvents

Dyes	Mole ratio (X_2)									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	H_2O:Dimethylsulphoxide									
AZ-01	240(4.29) 478(4.11)	242(4.46) 479(4.11)	250(4.28) 478(4.13)	246(4.13) 479(3.98)	249(4.26) 478(4.15)	250(4.28) 477(4.07)	253(4.17) 476(4.01)	254(4.23) 474(4.10)	268(4.22) 474(4.07)	266(4.31) 474(4.09)
AZ-02	227(5.03) 458(3.45) 578(2.89)	226(3.82) 458(3.51) 578(3.10)	241(3.98) 459(3.41) 584(3.24)	244(3.81) 461(3.21) 584(3.33)	245(3.87) 461(3.22) 588(3.46)	257(3.64) 592(3.69)	253(3.40) 593(3.69)	254(3.86) 593(3.78)	257(3.81) 591(3.76)	247(3.81) 590(3.54)
AZ-03	239(4.13) *290(3.57) 487(3.63)	242(3.85) 488(3.61)	244(4.02) 487(3.64)	246(3.87) 488(3.69)	248(3.96) 487(3.65)	250(3.83) 487(3.65)	265(3.56) 485(3.56)	253(3.79) 486(3.64)	237(3.61) 487(3.61)	258(3.69) 485(3.63)
AZ-04	239(4.34) 488(3.75)	242(3.96) 490(3.76)	245(3.84) 490(3.74)	245(4.08) 490(3.76)	248(3.97) 490(3.81)	249(4.08) 490(3.73)	251(4.29) 490(3.81)	248(3.58) 490(3.70)	257(3.81) 491(3.76)	262(3.80) 490(3.90)
	H_2O:Dimethylformamide									
AZ-01	248(4.23) 479(4.07)	251(4.22) 479(4.05)	254(4.05) 479(4.00)	255(4.04) 478(4.00)	263(4.14) 478(4.00)	259(4.04) 477(4.05)	261(4.09) 477(4.05)	262(4.08) 476(4.03)	272(4.13) 476(4.07)	270(4.37) 474(4.03)
AZ-02	*263(3.73) 458(3.55) *558(2.62)	*263(3.73) 458(3.55) 558(2.63)	*267(3.59) 459(3.44) 582(2.36)	*264(3.69) 459(3.52) 584(2.72)	271(3.53) 459(3.52) 589(2.81)	267(3.85) 592(3.65)	261(3.68) 591(3.78)	284(3.55) 591(3.92)	277(3.57) 590(3.84)	*272(3.73) 588(3.86)
AZ-03	247(4.27) *291(3.39) 489(3.56)	250(3.90) *291(3.59) 489(3.66)	252(3.83) *282(3.44) 490(3.57)	257(3.50) 490(3.59)	257(3.54) 489(3.58)	257(4.10) 489(3.53)	260(4.49) 488(3.54)	262(3.67) 487(3.56)	256(3.49) 486(3.55)	248(3.71) 487(3.53)
AZ-04	247(4.20) 489(3.89)	250(4.11) 489(3.88)	252(4.03) 490(3.88)	254(4.00) 489(3.91)	255(4.10) 488(3.91)	258(3.92) 488(3.89)	299(3.39) 487(3.89)	264(3.88) 487(3.89)	263(4.27) 487(3.90)	266(4.14) 489(3.95)

*Shoulder.

Preferential interaction in partly aqueous solvents mixtures. In the absence of preferential solvation, the behavior of a probe molecule is given by the equation $\nu_{12\text{ideal}} = \nu_1 X_1 + \nu_2 X_2$, where X_1 and X_2 are mole fractions of the solvent 1 and 2, and ν_1, ν_2, and ν_{12} are the values of maximum absorption wavenumber of the solute in the solvents 1, 2, and binary mixture, respectively. However, most often there is an uneven distribution of one of the components of the solvent mixture between the solvation sphere and the bulk solvent. The local excess of that solvent component over the bulk composition is used to describe preferential solvation in which case $\nu_{12} = \nu_1 X_1^L + \nu_2 X_2^L$, where X_1^L and X_2^L represent the mole fractions of the solvents 1 and 2 in the solvation shell, respectively. The mole fraction of the solvent in the cybotactic region can be calculated experimentally using the equation

$$X_2^L = (\nu_{12} - \nu_1)/(\nu_2 - \nu_1). \tag{1}$$

The difference in the mole fractions of the co-solvent in the solvation sphere (X_2^L) and the bulk mixture (X_2) is the index of preferential solvation (δ_{s2}). A positive value of δ_{s2} indicates preference of the solute for the co-solvent while a negative value indicates preference for the solvent 1. The preferential solvation constant (K_{ps}) is derived from the indices of solvation and mole fractions and is presented in the equation

$$K_{ps} = \frac{X_2^L / X_2}{X_1^L / X_1}. \tag{2}$$

The plots of the E_T of the four dyes with the composition of the binary mixtures showed some generalizations. As shown in Fig. 3, the E_T value of AZ-03 and 04 varied in a non-linear fashion with the mole fractions of the co-solvent in the aqueous DMF mixtures.

The dashed line represents the ideal behavior in which instance the bulk composition is the same as that of the solvation sphere of the probe. As seen in the plot depicted in Fig. 3b, there is a clear deviation from linearity over the majority of the mole fractions of the co-solvent indicative of preferential solvation by one of the components of the solvent mixtures. At 0.1 to 0.7 mole fractions of the co-solvent, the deviation from linearity is negative, which implies that AZ-04 is preferentially solvated by DMF, which has E_T values lower than that of water. On the other hand, a positive deviation from linearity and a preference of the dye for water were observed at higher mole fractions (0.8–0.9) of DMF. Thus, the extent of preferential solvation decreased in the DMF-rich regions with the probe's behavior closest to linearity at the mole fractions of 0.7–0.9. Conversely, while the plots for all four dyes showed the deviation from linearity, preferential solvation of AZ-02 increased in the DMF-rich regions. Therefore, to study this in greater detail, the extent of preferential solvation for the dyes were calculated from the variation of E_T with mole fractions of the co-solvent in various solvent mixtures and the results are presented in Table 2.

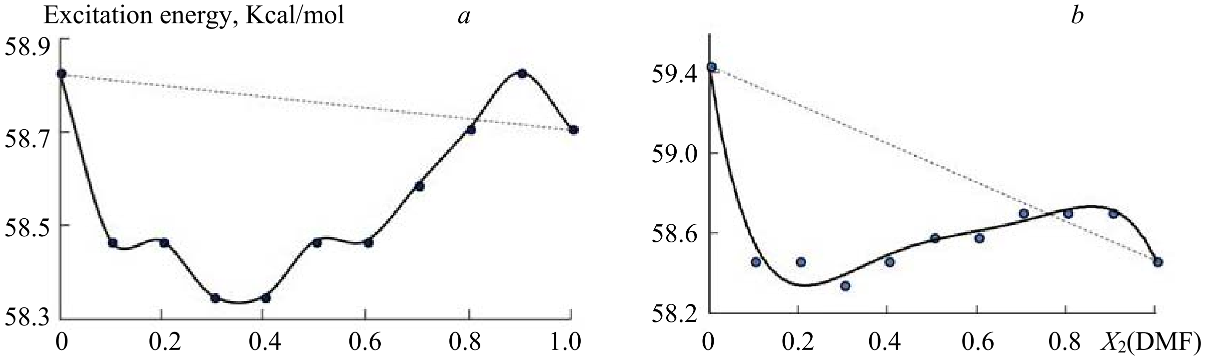

Fig. 3. Variation of E_{12} of AZ-03 (a) and AZ-04 (b) with mole fraction of DMF.

The dyes possess largely hydrophobic aromatic skeletons and would be expected to be more soluble in organic solvents than water. However, the presence, type and position of extra substituents on the skeletons, especially polar functional groups such as hydroxyl and carboxylic acid, would modulate the hydrophilic-lipophilic balance of each molecule and its resultant solubility in solvents. Thus, over the majority of the composition range in both aqueous mixtures, AZ-04, which contains a butanone substituent at position 7 and is the most neutral among the four dyes, showed a preferential accumulation of DMSO and DMF in its solvation sphere. On the other hand, although similar preferential solvation of AZ-03 (which contains the more

TABLE 2. Preferential Solvation Data for the Dyes in Partly Aqueous Solvents

X_2	X_2^L	δ_{s2}	K_{ps}	X_2^L	δ_{s2}	K_{ps}	X_2^L	δ_{s2}	K_{ps}	X_2^L	δ_{s2}	K_{ps}
	AZ-01			AZ-02			AZ-03			AZ-04		
	Water:Dimethylsulphoxide											
0.1	–0.331	–0.431	–1.913±0.45	–0.01	–0.11	61.539±3.02	–0.996	–1.096	–1.608±0.12	0.502	0.402	9.074±0.01
0.2	–0.660	–0.860		–0.01	–0.21		–1.988	–2.188		1.0	0.80	
0.3	–0.331	–0.631		0.0	–0.30		–0.996	–1.296		1.0	0.70	
0.4	–0.660	–1.060		0.964	0.564		–1.988	–2.388		1.0	0.60	
0.5	–0.331	–0.831		0.988	0.488		–0.996	–1.496		1.0	0.50	
0.6	0.0	–0.600		1.012	0.412		–0.996	–1.596		1.0	0.40	
0.7	0.332	–0.368		1.018	0.318		1.000	0.300		1.0	0.30	
0.8	1.0	0.20		1.018	0.218		0.0	–0.80		1.0	0.20	
0.9	1.0	0.10		1.006	0.106		–0.996	–1.896		1.247	0.347	
1.0	1.0	0.0		1.0	0.0		1.0	0.0		1.0	0.0	
	Water:Dimethylformamide											
0.1	–0.660	–0.760	–1.259±0.46	–0.010	–0.110	26.27±2.99	2.988	2.888	1.504±0.51	1.0	0.90	4.389±2.43
0.2	–0.660	–0.860		–0.010	–0.210		2.988	2.788		1.0	0.80	
0.3	–0.660	–0.960		0.0	–0.300		3.976	3.676		1.123	0.823	
0.4	–0.331	–0.731		0.0	–0.40		3.976	3.576		1.0	0.60	
0.5	–0.331	–0.831		0.0	–0.50		2.988	2.488		0.877	0.377	
0.6	0.0	–0.60		1.024	0.424		2.988	2.388		0.877	0.277	
0.7	0.0	–0.70		1.018	0.318		1.996	1.296		0.753	0.053	
0.8	0.332	–0.468		1.018	0.218		1.0	0.20		0.753	–0.047	
0.9	0.332	–0.568		1.012	0.112		0.0	–0.90		0.753	–0.147	
1.0	1.0	0.0		1.0	0.0		1.0	0.0		1.0	0.0	

polar propionic acid substituent at the same position 7) was observed in the aqueous DMF mixtures at all mole fractions of the co-solvent except at $X_2 = 0.9$; the same solute in the aqueous DMSO mixtures showed consistent preferential solvation by water over the majority of the composition of the solvent mixtures. The solvation data of the two positional isomers AZ-01 and 02 also revealed contrasting patterns, which can be attributed to the difference in the position of the common hydroxyl group. When present at a position *para* to the azo linkage as found in AZ-02, the proton is not involved in hydrazone formation and is thus available for donation to proton acceptors such as DMSO and DMF in a charge-transfer complexation process. Thus, preferential accumulation of the co-solvent can be observed in the solvation shell of AZ-02 in the DMSO- and DMF-rich regions. In contrast, *ortho*-hydroxyl AZ-01, which exists predominantly in the positively charged hydrazone form, showed preferential solvation by water over the majority of the composition ranges in both solvent mixtures. The preferential accumulation of water over DMSO or DMF in the solvation sphere of the dye is as a result of the greater ability of water (as evidenced by the solvent dipolarity index 1.09) to stabilize the charge on the hydrazone compared to either DMF or DMSO with $\pi^* = 0.88$ and 1.0 respectively. This enrichment of the cybotactic region of the dye with the solvent with the highest relative permittivity through dye/solvent dipole-dipole interactions is known as dielectric enrichment and can also be observed in the solvation behavior of AZ-03, which is equally capable of hydrazone tautomerism in the aqueous DMSO mixtures. The hydrogen bond interaction between the propionic acid substituent in AZ-03 and DMF in all probability contributes to the preferential accumulation of the co-solvent in the dye's solvation sphere, as evidenced by positive δ_{s2} values at $X_2 = 0.1–0.8$. In addition, as can be observed from the representative plots presented in Fig. 3, all the dyes showed a strong synergistic effect in both aqueous solvent mixtures with E_T values that are lower than those of the pure solvents. Synergism occurs through the formation of 1:1 complex arising from hydrogen bond interaction between a hydrogen bond donor (HBD) solvent and a hydrogen bond acceptor (HBA) solvent, yielding the S_{12} species. These complexes when present have been demonstrated to be capable of solvating a solute in diverse ways and can therefore be differentiated by structurally different probes [9]. Thus, while Reichardt's betaine dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, was solvated by the more polar component of the complex, pyrene, 4-[4(dimethylamino)styryl]-1-methylpyridinium iodide was solvated by the less polar solvent partner [2, 10]. The solvation data revealed that AZ-01 was solvated by the more polar component (water) of the complex, while AZ-02 and AZ-04 were solvated by the less polar solvent mixture component. Similarly, AZ-03 was solvated by water and the co-solvent in the aqueous DMSO and DMF mixtures respectively. The synergistic effect observed in the aqueous mixtures is due to the fact that highly polar and water-miscible solvents such as

DMSO and DMF interact so strongly with water that the mole fraction of the resultant hydrogen bond mediated DMSO-water or DMF-water complexes is greater than the mole fractions of either the free water or self-associated water molecules [11]. A combination of the high hydrogen bond acceptor capability of DMSO ($\beta = 0.76$) and DMF ($\beta = 0.69$) with the high hydrogen donor capability of water ($\alpha = 1.17$) will result in the formation of strongly associated complexes via hydrogen bonding, which are responsible for the preferential solvation of the dyes. Thus, the microenvironment of the dyes will be enriched by the DMSO-HOH or DMF-HOH complexes that are oriented with their methyl groups towards the hydrophobic dye molecules.

Conclusion. The preferential solvation of the phenylazohydroxynaphthalene series AZ-01 to 04 in partly aqueous DMSO and DMF solvent mixtures has been successfully studied using UV-visible spectroscopy. The four dyes showed varying extents of synergistic effects in both aqueous solvent mixtures.

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