



Preferential Solvation of Mordant Black and Solochrome Dark Blue in Mixed Solvent Systems

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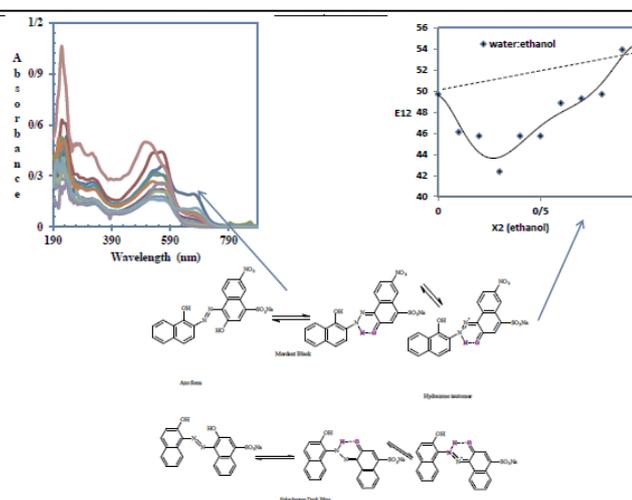
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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the preferential solvation of Mordant Black and Solochrome Dark Blue were investigated in mixed solvent systems of aqueous methanol, ethanol, propan-1-ol, propan-2-ol, methanol: ethanol, methanol:propan-1-ol, methanol:propan-2-ol, ethanol:propan-1-ol, ethanol:propan-2-ol, propan-1-ol:propan-2-ol and carbon tetrachloride: dimethylformamide. Results showed a deviation of solvation data from ideality over the majority of composition ranges in all the solvent mixtures. The type and contribution of specific and non-specific solute-solvent interactions were analyzed in the framework of the linear solvation energy relationships. Statistical analysis of single, dual, and multiparametric equations revealed that in pure solvents, spectral behaviours of MB and SDB were affected by the polarity and basicity of the solvent milieu respectively. However in aqueous alcohols, polarity of the solvent milieu was the most significant determinant of spectral patterns with α and β parameters playing secondary contributory roles in the spectral changes of MB and SDB, respectively. Multiparametric equations generally yielded the best fitted model in mixed alcohol systems with polarity remaining the largest contributor, followed by β and α of the solvent milieu in that order. Spectral-structure relationships identified ion-dipole interactions involving the charged sulphonate and hydrazone moieties as well as proton-donor-acceptor interactions of the common labile hydroxyl groups as mechanisms for the observed solvation data.

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1. Introduction

Apart from their obvious uses as media for chemical reactions and the more practical purposes of separation/purification, solvents influence the rate and direction of chemical reactions [1]. Solvents often dictate the position and intensity of absorption bands in UV-visible, IR, NMR and electron spin resonance spectroscopy [2]. However, desired solvent effects are rarely derivable from a single solvent and the use of mixed solvent systems is common in practical chemistry. Mixed solvent systems are associated with new properties and effects such as preferential solvation and solute-solvent interactions [3]. Mixed solvent systems therefore find useful applications in chromatographic separations, reaction kinetics studies, improved solubility of otherwise poorly soluble medicinal agents and improved yield of desirable products in chemical synthesis [3-6]. Studies of the influence of solvent effects on physico-chemical properties are expectedly more complex in mixed solvent systems and are usually done with solvatochromic dye probes.

Mordant Black (MB) and Solochrome Dark Blue (SDB) are monoazo dyes that have been widely employed in the qualitative detection and assays of metal ions using various techniques including titrimetry [7] and UV-visible spectrophotometry [8]. Potential applications of the dyes in phototonic and optoelectronic devices and as a post-column derivatizing reagent for rare earth metals have also been demonstrated [9, 10]. In addition, Mordant Black and Solochrome Dark Blue contain chemical features that are capable of varied solute-solvent interactions including non-specific (electrostatic, ion-dipole, and polarization) and specific interactions (hydrogen bonding) which make them potential solvatochromic dye probes. However, the possibility of these various solute-solvent interactions invariably also makes certain useful properties of the dyes such as their optical and metal coordination activities prone to solvent effects. A thorough understanding of the capable solvent interactions of the dyes will therefore be useful in process optimization and results interpretation of their applications.

The objective of this study was therefore to investigate solvent effects on the spectral patterns of Mordant Black and Solochrome Dark Blue, their preferential solvation in mixed solvent systems, predominant solute-solvent interactions and their suitability as solvatochromic dye probes.

2. Materials and Methods

2.1. Materials

Distilled water and Analar grade organic solvents were used for this study. Methanol, ethanol, carbon tetrachloride purchased from Sigma-Aldrich, St Louis USA, and propan-1-ol, propan-2-ol, N, N-dimethyl formamide (DMF) purchased from Loba Chemie, Mumbai.

2.2. Azo Dyes Utilized

Sodium 1-[1-hydroxynaphthylazo]-6-nitro-2-naphthol-4-sulphonate also known as mordant black (Aldrich, Dorset USA) and 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonic acid sodium salt also known as Solochrome Dark Blue (Aldrich, Dorset USA).

2.3. Instrumentation

A Lambda 25 digital UV-Visible spectrophotometer (Perkin Elmer model, Singapore) with 1 cm path length and matched quartz cell, Mettler analytical balance (Ohaus, USA) were the instruments used in the study.

2.4. Preparation of Dye Stock Solutions

For each dye, a 25 mg quantity was weighed separately and dissolved in some quantity of 96% ethanol before making up to 25 mL volume with the same solvent to give 2.167×10^{-3} and 2.401×10^{-3} M stock solutions of Mordant Black (MB) and Solochrome Dark Blue (SDB) respectively.

2.5. Preparation of Binary Solvent Mixtures

Binary mixtures of aqueous methanol, ethanol, propan-1-ol and propan-2-ol, methanol: ethanol, methanol: propan-1-ol, methanol: propan-2-ol, ethanol: propan-1-ol, ethanol: propan-2-ol, propan-1-ol: propan-2-ol and carbon tetrachloride: dimethylformamide were prepared by mixing in a volumetric flask appropriate pure solvents in the ratios: 0:1.0; 0.1:0.9; 0.2:0.8; 0.3:0.7; 0.4:0.6; 0.5:0.5; 0.6:0.4; 0.7:0.3; 0.8:0.2; 0.9:0.1 and 1.0:0. Adequate equilibrations were allowed before using the solvent mixtures for sample measurements.

2.6. Spectra Data Acquisition

0.1 mL quantity of the dye stock solution was separately added to 9.9 mL of each of the binary mixture in a volumetric flask which was then inverted a few times to allow for adequate equilibration before the UV-Visible spectral data, between 190-900 nm, of the resulting solutions was acquired.

3. Results and Discussion

3.1. Electronic Absorption Spectra

The electronic visible absorption spectra of MB and SDB in neat solvents are presented in Figures 1 and 2, respectively.

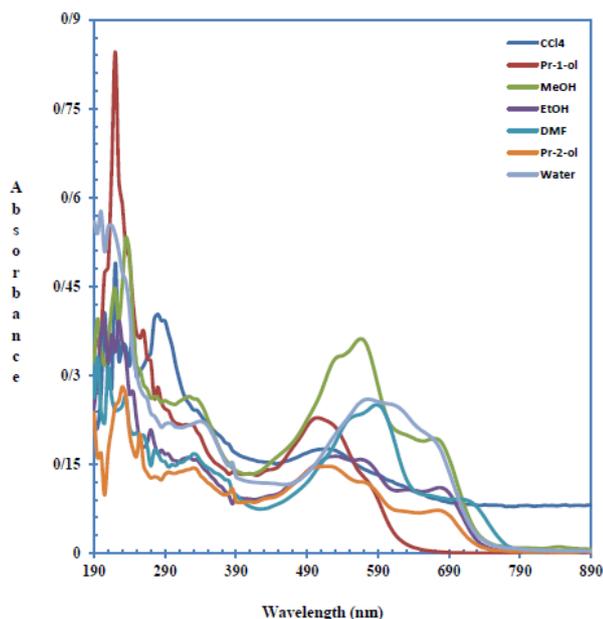


Fig. 1. Electronic absorption spectra of MB in neat solvents

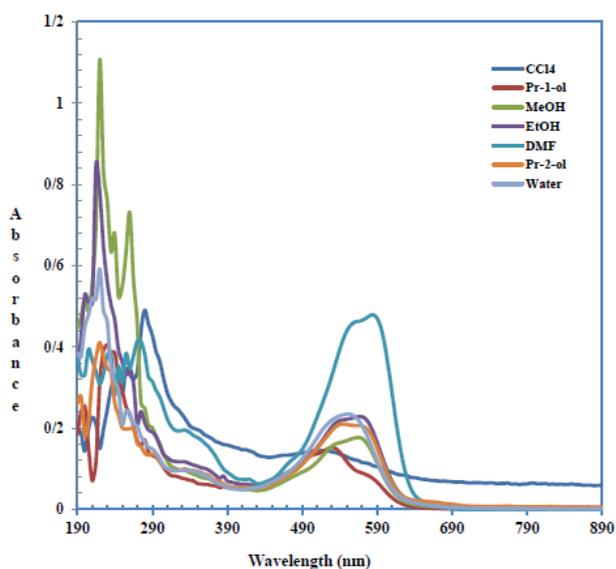


Fig. 2. Electronic absorption spectra of SDB in neat solvents

The absorption spectra of both dye probes in different solvents generally exhibited high-energy bands in the range of 200-315 nm and more pronounced low-energy bands at the range of 402-700 nm. The high-energy bands arise from the $\pi \rightarrow \pi^*$ of the naphthalene residue and owe their high absorptivity to the presence of the hydroxyl groups which act as auxochromes. On the other hand, the low-energy bands are due to $\pi \rightarrow \pi^*$ electronic transitions associated with interactions between the binaphthyl azo chromophore of the dyes and different solvents. Shifts in

the position and intensity of this band therefore offer more relevant insight into the use of solvatochromism to monitor interactions in the cybotactic region of a solute. The molar transition energy of a solute, derived from the absorption maxima, often arises from a combination of non-specific interactions (polarity and polarization effects) and specific interactions which include hydrogen bonding and other intermolecular electron transfer processes.

3.2. Solvatochromism of MB and SDB in Neat Solvents

In pure solvents, variation in the visible absorption maxima and molar transition energies of the dyes with Kamlet, Abboud and Taft (KAT) parameters were observed and are depicted in Table 1. A cursory look at the spectra of MB revealed a major peak ranging from 505 to 590 nm in the seven solvents investigated. The lowest position of the band was obtained in carbon tetrachloride ($\pi=0.28$) followed by progressive bathochromic shifts as the polarity of the solvent medium increased. Thus, with respect to carbon tetrachloride, bathochromic shifts of +10, +45 and +55 nm could be observed in the major visible band of the dye when examined in ethanol ($\pi=0.54$), methanol ($\pi=0.60$) and water ($\pi=1.09$). This red shift arises from non-specific solute-solvent interactions that stabilize the excited state of the dye better than the ground state in polar solvents. However, large bathochromic shifts observed in DMF for both dyes (λ_{max} 590 and 584 nm for MB and SDB respectively) which were much greater than those seen in water despite its higher polarity is suggestive of a secondary molecular interaction at the solute-solvent interphase. The visible spectra also revealed the presence of a second much smaller peak, often present as a shoulder, found between 565 nm and 700 nm in all the solvents except carbon tetrachloride. MB and SDB contain an azo linkage which can be involved in a hydrazone formation with one of the two ortho hydroxyl groups as shown in Scheme 1. The presence of strong intramolecular hydrogen bonding and nitro electron withdrawing group (as obtained in MB) shift the tautomerism towards the keto form. Azo compounds capable of this type of intramolecular arrangement have been reported to exhibit a single visible band often ascribable to the hydrazone tautomer in solvents [3]. This single peak arises from the unavailability of the hydroxyl group for interactions with solvents. However, MB and SDB each contain two ortho hydroxyl groups, with the involvement of one of them in hydrazone formation, making available the other for intermolecular hydrogen bond interaction with solvents and the subsequent

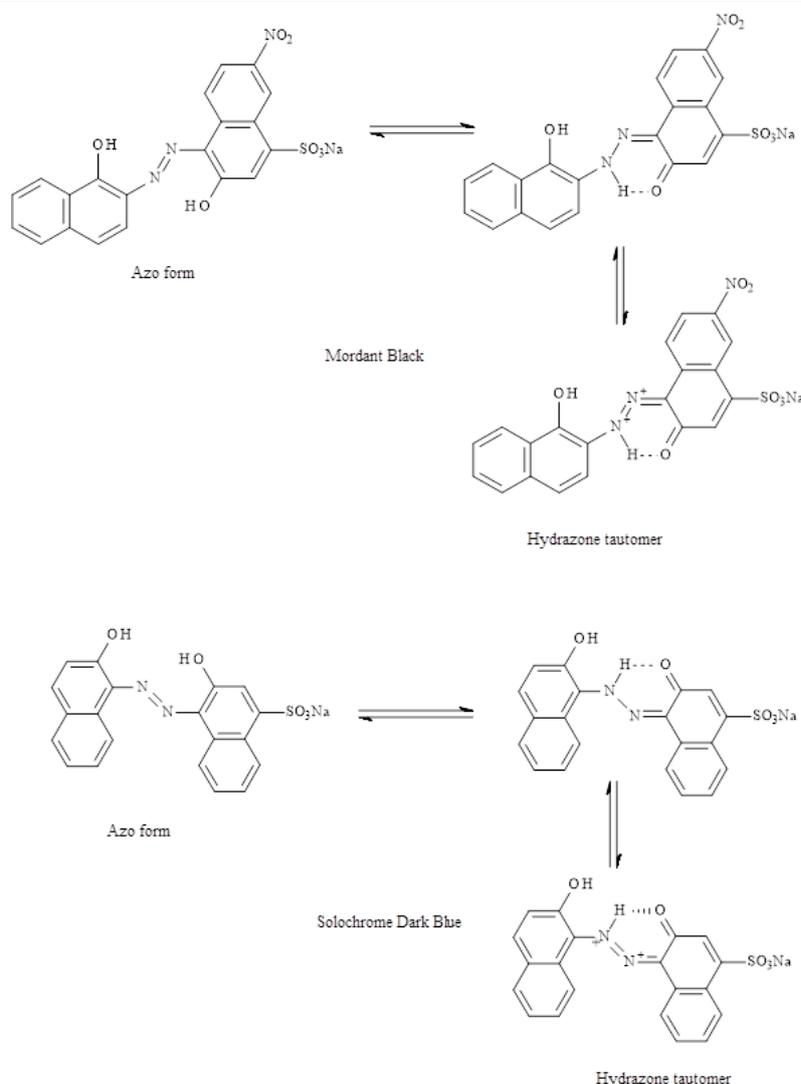
formation of a second visible band. Development and stabilization of this second peak will therefore depend largely on the hydrogen bond acceptor ability, β , of the solvent milieu. Expectedly, the presentation of the second peak in the visible spectra of MB varied markedly, ranging from its complete disappearance in carbon tetrachloride ($\beta=0.10$), as a broad shoulder in DMF ($\beta=0.69$) to distinct peaks in ethanol ($\beta=0.75$) and 2-propanol ($\beta=0.81$). With

SDB, a similar trend of increasing bathochromic shifts with increasing dipolarity of the solvents was observed. Nonetheless, the formation of a second visible band was less distinct, with the two bands appearing to be collapsed to give generally broad bands. This might be explained by lower hydrazone proportions of SDB which lack a nitro group compared to MB.

Table 1. The E_T values of dye probes and KAT parameters in neat solvents

Solvent	$\lambda(nm)$		E_T (kcal.mol ⁻¹)		Log ϵ		α	β	π^*
	MB	SDB	MB	SDB	MB	SDB			
CCl ₄	520	402	54.983	71.122	3.910	3.804	0.00	0.10	0.28
1-POH	505, 565 ⁿ	530	55.517	53.945	3.830	3.802	0.84	0.90	0.52
2-POH	515, 675	546	56.616	52.365	4.023	3.942	0.76	0.81	0.48
EtOH	530, 675	567	53.945	50.425	3.877	3.979	0.86	0.75	0.54
MeOH	565, 670	565	50.604	50.604	4.222	3.867	0.98	0.66	0.60
DMF	590, 700 ⁿ	584	48.460	48.957	4.062	4.300	0.00	0.69	0.88
Water	575, 650 ⁿ	552	49.724	51.795	4.079	3.990	1.17	0.47	1.09

n=shoulder; 1-POH= 1-propanol; 2-POH = 2-propanol



Scheme 1. Azo-hydrazone tautomeric forms of MB and SDB

3.3. Solvatochromism of MB and SDB in Binary Mixtures

MB and SDB produced different UV-Visible spectral patterns. Representative UV-Visible spectra for MB in aqueous alcoholic mixtures and mixed alcoholic systems are depicted in Figures 3 and 4, respectively. UV-Visible spectra of SDB when examined in binary mixtures of an aprotic non-polar solvent and aprotic polar solvent are depicted in Figure 5. The molar absorptivities and absorption maxima of the visible bands of the two dyes in all the binary mixtures investigated are also presented in Table 2. Useful generalizations can be drawn from these results.

In aqueous alcoholic mixtures, the low-energy bands of both dyes showed initial progressive bathochromic shifts with increasing mole ratios of the alcohol. This was then followed, in most instances, by gradual blue shifts in the alcohol-rich binary mixtures. The dyes being sulphonated compounds are water soluble. However, they also possess aromatic tetracyclic structures which are capable of solute-solvent interactions with organic solvents. The additional solute-solvent interactions between the naphthalene residues of the dyes and organic solvents (evidenced by bathochromic shifts) will increase with the organic composition of the binary mixtures up to a critical point where the primary solubilization by the sulphonic groups is compromised. Expectedly mordant black because of its aromatic nitro group which improves interaction with organic solvents exhibited a bathochromic shift of + 40 nm in water: methanol mixture as mole ratio of the co-solvent increased from 0.0 to 0.1. In contrast, only a shift of +1 nm was observed with SDB which lack the electron withdrawing group. A similar interplay between the hydrophilicity and lipophilicity properties of the dye probes was discernible in their spectra patterns when investigated in mixed alcoholic systems. Generally, as the binary mixtures became richer in the longer-chain-alcohol components, the spectra revealed either progressive blue shifts over the entire composition range or blue shifts after initial bathochromic changes.

In CCl₄: DMF mixtures, progressive large bathochromic shifts and hyperchromic changes could be observed in the visible bands of both dyes with increasing mole ratios of the co-solvent. This is attributed to the resultant charge-transfer complexation between the protons of the common hydroxyl groups and DMF. A careful observation of the spectral data will also reveal additional support for this mechanism. The increased predominance of the azo tautommer of SDB will increase the availability of its two ortho hydroxyl groups for charge transfer interaction with

DMF. Thus, maximum bathochromic shifts at much lower mole ratios of DMF ($X_2 = 0.3-0.4$) were observable in the visible spectra of SDB. Conversely, only in DMF rich regions ($X_2 = 0.9$) were similarly large bathochromic shifts observed with MB which possesses a decreased propensity for this type of charge transfer reaction due to its increased intramolecular hydrazone rearrangement of its hydroxyl groups.

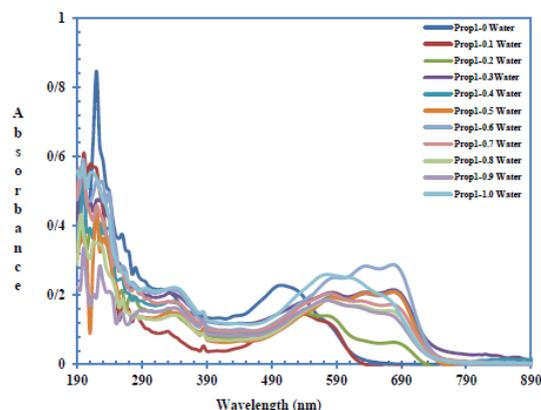


Fig. 3. Electronic absorption spectra of MB in water: propan-1-ol mixtures

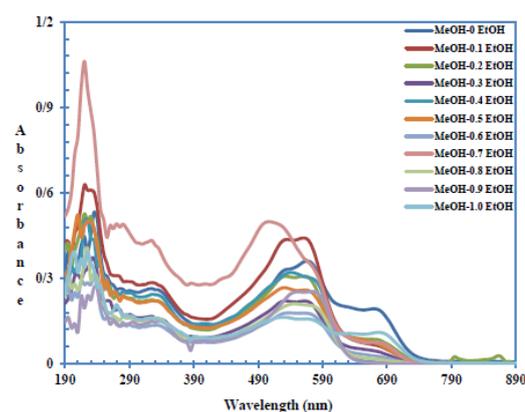


Fig. 4. Electronic absorption spectra of MB in methanol: ethanol mixtures

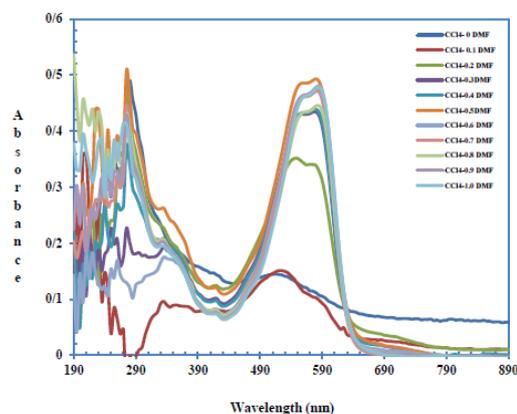


Fig. 5. Electronic absorption spectra of SDB in carbon tetrachloride: dimethylformamide mixtures

Table 2. Low-energy Electronic Absorption spectral data of the dyes in binary solvent mixtures

Dyes	$\lambda_{max}(\log \epsilon_{max})$									
	Mole ratio (X_2)									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
H₂O:Methanol										
MB	615(4.133)	620(4.190)	625(4.176)	625(4.151)	630(4.310)	670(4.259)	630(4.152)	635(4.039)	565(3.964)	565(4.222)
SDB	553(4.002)	554(3.952)	555(3.999)	555(4.010)	558(3.960)	556(4.001)	555(3.977)	558(4.020)	558(4.031)	565(3.867)
H₂O:Ethanol										
MB	620(3.967)	625(4.009)	675(4.037)	625(3.966)	625(4.074)	585(3.843)	580(3.838)	575(3.772)	530(3.958)	530(3.877)
SDB	597(4.204)	597(4.198)	598(4.246)	600(4.215)	599(4.256)	558(4.141)	558(4.149)	558(4.212)	558(4.132)	567(3.979)
H₂O:Propan-1-ol										
MB	575(3.932)	580(3.932)	580(3.975)	680(4.123)	680(3.986)	680(3.983)	680(3.998)	540(3.836)	535(3.830)	505(4.023)
SDB	551(4.274)	554(4.316)	557(4.279)	555(4.319)	558(4.274)	558(4.300)	558(4.335)	558(4.264)	546(4.279)	530(3.802)
H₂O:Propan-2-ol										
MB	585(3.962)	630(3.995)	675(4.063)	675(4.113)	680(3.980)	680(4.058)	680(4.021)	580(3.929)	515(3.861)	515(3.830)
SDB	551(4.207)	555(4.235)	557(4.222)	558(4.209)	558(4.224)	558(4.253)	558(4.197)	558(4.237)	546(4.164)	546(3.942)
Methanol:Ethanol										
MB	560(4.309)	560(4.153)	530(4.008)	540(4.170)	530(4.091)	535(3.917)	505(4.362)	545(3.988)	575(4.068)	530(3.877)
SDB	522(3.830)	561(3.949)	563(3.943)	565(3.933)	565(3.935)	564(3.924)	565(3.917)	566(3.942)	567(4.098)	567(3.979)
Methanol:Propan-1-ol										
MB	530(4.064)	540(4.215)	520(4.011)	530(4.066)	510(4.071)	505(4.058)	505(4.077)	505(4.077)	505(4.098)	505(4.023)
SDB	566(3.980)	567(3.901)	567(3.780)	569(3.887)	567(3.868)	540(3.813)	538(3.846)	535(3.940)	531(3.917)	530(3.802)
Methanol:Propan-2-ol										
MB	565(4.078)	530(4.001)	565(3.877)	530(4.014)	530(3.930)	525(3.930)	525(3.985)	520(3.952)	505(4.027)	515(3.830)
SDB	558(4.085)	558(4.162)	554(3.974)	563(4.013)	556(4.003)	553(4.000)	571(3.871)	546(3.994)	547(3.999)	546(3.942)
Ethanol:Propan-1-ol										
MB	505(4.065)	505(4.105)	505(3.785)	510(4.080)	505(3.791)	505(3.959)	500(3.974)	505(4.175)	500(3.827)	505(4.023)
SDB	559(4.286)	558(4.328)	559(4.292)	541(4.271)	538(4.175)	535(4.181)	524(4.209)	520(4.190)	517(4.124)	530(3.802)
Ethanol:propan-2-ol										
MB	520(4.046)	520(4.004)	505(3.951)	505(4.129)	505(3.965)	505(3.981)	505(4.073)	505(4.035)	530(4.061)	515(3.830)
SDB	548(3.874)	545(4.029)	546(3.978)	544(4.010)	545(4.000)	546(3.973)	545(4.095)	546(4.090)	566(4.144)	546(3.942)
Propan-1-ol:Propan-2-ol										
MB	500(3.676)	500(4.006)	500(3.930)	500(3.682)	500(3.773)	500(3.865)	500(3.893)	500(3.942)	500(3.915)	515(3.830)
SDB	558(4.315)	564(4.300)	543(4.282)	565(4.197)	545(4.316)	545(4.244)	565(4.278)	566(4.348)	566(4.464)	546(3.942)
Carbon tetrachloride:Dimethyl formamide										
MB	510(3.954)	515(3.958)	520(3.935)	520(3.880)	530(3.886)	535(3.852)	540(3.891)	545(3.917)	585(3.956)	590(4.062)
SDB	524(3.799)	549(4.166)	578(4.258)	580(4.262)	580(4.312)	582(4.295)	582(4.293)	584(4.269)	582(4.301)	584(4.300)

3.4. Preferential Solvation of MB and SDB in Binary Mixtures

When present in a mixture of solvents that form an ideal dielectric medium, the behavior of a solute such as its wavenumber follows the lineal additive model governed by equation 1:

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

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 maxima absorption wavenumber of the solute in solvent 1, 2 and binary mixture, respectively. However, it is well known that the behaviour of solutes in solvent mixtures often deviate from ideality such that the composition of the cybotactic region of a solute may differ markedly from the bulk composition. Solute-solvent and solvent-solvent

interactions might result in the formation of new solvent entities in the solvation shell of the solute. When there is a preferential accumulation of one of the components of a solvent mixture in the solvation shell of a solute, the phenomenon is referred to as preferential solvation. In such non-ideal mixtures, the wavenumber of the solute is governed by Equation 2.

$$\bar{\nu}_{12} = \bar{\nu}_1 X_1^L + \bar{\nu}_2 X_2^L \tag{2}$$

Where X_1^L and X_2^L are the mole fractions of solvents 1 and 2 in the cytotactic region. The mole fractions can be derived from the experimental data using Equation 3.

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

A measure of the preference of the solute for the co-solvent called the index of preferential solvation, δ_{s2} , can therefore be estimated from the difference between the mole fraction of the co-solvent in the cybotactic region

(X_2^L) and its bulk composition (X_2). An accumulation of the co-solvent in the solvation shell will yield positive δ_{s2} values while negative figures are indicative of a preference for solvent 1.

A preferential solvation constant (K_{ps}) can also be derived using equation 4.

$$K_{ps} = \frac{X_2^L/X_2}{X_1^L/X_1} \tag{4}$$

The preferential solvation data for MB and SDB in the various binary mixtures are presented in Table 3 and 4 respectively. Representative plots of the molar transition energy $E_{1/2}$ of MB and SDB in various binary mixtures as against the mole fractions of the co-solvent are also presented in Figure 6 and 7 respectively. The plots revealed a deviation from linearity in all the binary mixtures investigated with the preferential solvation data also offering some useful generalizations.

Table 3. Preferential solvation data for MB in binary mixtures

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	-3.675	-3.775	-0.854± 0.63	-0.855	-0.955	-0.702± 0.58	0	-0.100	-0.301± 0.34	-0.147	-0.247	-0.668± 0.46
0.2	-4.101	-4.301		-0.942	-1.142		-0.062	-0.262		-0.749	-0.949	
0.3	-4.520	-4.820		-1.745	-2.045		-0.062	-0.362		-1.272	-1.572	
0.4	-4.520	-4.920		-0.942	-1.342		-1.114	-1.514		-1.272	-1.672	
0.5	-4.933	-5.433		-0.942	-1.442		-1.114	-1.614		-1.325	-1.825	
0.6	-8.011	-8.611		-0.201	-0.801		-1.114	-1.714		-1.325	-1.925	
0.7	-4.933	-5.633		-0.102	-0.802		-1.114	-1.814		-1.325	-2.025	
0.8	-5.339	-6.139		0.000	-0.800		0.468	-0.332		-0.074	-0.874	
0.9	1.000	0.100		1.000	0.100		0.539	-0.361		1.000	0.100	
1.0	1.000	0.000		1	0		1	0.000		1.000	0.000	
MeOH:EtOH				MeOH:Propan-1-ol			MeOH:Propan-2-ol			Ethanol:Propan-1-ol		
0.1	0.135	0.035	2.247± 1.66	0.556	0.456	5.129± 3.67	0.000	-0.100	1.894± 1.07	1.000	0.900	1.633± 0.77
0.2	0.135	-0.065		0.390	0.190		0.680	0.480		1.000	0.800	
0.3	1.000	0.700		0.728	0.428		0.000	-0.300		1.000	0.700	
0.4	0.701	0.301		0.556	0.156		0.680	0.280		0.792	0.392	
0.5	1.000	0.500		0.908	0.408		0.680	0.180		1.000	0.500	
0.6	0.849	0.249		1.000	0.400		0.785	0.185		1.000	0.400	
0.7	1.799	1.099		1.000	0.300		0.785	0.085		1.212	0.512	
0.8	0.556	-0.244		1.000	0.200		0.891	0.091		1.000	0.200	
0.9	-0.263	-1.163		1.000	0.100		1.224	0.324		1.212	0.312	
1.0	1.000	0.000		1.000	0.000		1.000	0.000		1.000	0.000	
Ethanol:Propan-2-ol				Propan-1-ol:Propan-2-ol			Carbon tetrachloride:DMF					

0.1	0.660	0.560	1.281± 7.68	-0.515	-0.615	-0.350± 0.26	-0.165	-0.265	-0.134± 0.59
0.2	0.660	0.460		-0.515	-0.715		-0.082	-0.282	
0.3	1.700	1.400		-0.515	-0.815		0.000	-0.300	
0.4	1.700	1.300		-0.515	-0.915		0.000	-0.400	
0.5	1.700	1.200		-0.515	-1.015		0.159	-0.341	
0.6	1.700	1.100		-0.515	-1.115		0.236	-0.364	
0.7	1.700	1.000		-0.515	-1.215		0.312	-0.388	
0.8	1.700	0.900		-0.515	-1.315		0.387	-0.413	
0.9	0.000	-0.900		-0.515	-1.415		0.937	0.037	
1.0	1.000	0.000		1.000	0.000		1.000	0.000	

Table 4. Preferential solvation data for SDB in binary mixtures

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		
			3.297± 2.86			-1.057± 2.12			-0.139± 0.29			-0.312± 0.94
0.1	0.079	-0.021		2.849	2.749		0.044	-0.056		0.165	0.065	
0.2	0.157	-0.043		2.849	2.649		-0.087	-0.287		-0.492	-0.692	
0.3	0.235	-0.065		2.908	2.608		-0.216	-0.516		-0.817	-1.117	
0.4	0.235	-0.165		3.024	2.624		-0.130	-0.530		-0.978	-1.378	
0.5	0.467	-0.033		2.966	2.466		-0.259	-0.759		-0.978	-1.478	
0.6	0.313	-0.287		0.406	-0.194		-0.259	-0.859		-0.978	-1.578	
0.7	0.235	-0.465		0.406	-0.294		-0.259	-0.959		-0.978	-1.678	
0.8	0.467	-0.333		0.406	-0.394		-0.259	-1.059		-0.978	-1.778	
0.9	0.467	-0.433		0.406	-0.494		0.265	-0.635		1.000	0.100	
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			Ethanol:Propan-1-ol		
			-1.923± 1.06			0.791± 0.07			2.096± 1.44			3.253± 0.69
0.1	-23.353	-23.453		-0.027	-0.127		0.360	0.260		0.205	0.105	
0.2	-2.021	-2.221		-0.053	-0.253		0.360	0.160		0.231	0.031	
0.3	-1.007	-1.307		-0.053	-0.353		0.571	0.271		0.205	-0.095	
0.4	0.000	-0.400		-0.106	-0.506		0.102	-0.298		0.688	0.288	
0.5	0.000	-0.500		-0.053	-0.553		0.465	-0.035		0.772	0.272	
0.6	-0.503	-1.103		0.701	0.101		0.624	0.024		0.857	0.257	
0.7	0.000	-0.700		0.760	0.060		-0.302	-1.002		1.175	0.475	
0.8	0.501	-0.299		0.849	0.049		1.000	0.200		1.295	0.495	
0.9	1.000	0.100		0.970	0.070		0.946	0.046		1.385	0.485	
1.0	1.000	0.000		1.000	0.000		1.000	0.000		1.000	0.000	
	Ethanol:Propan-2-ol			Propan-1-ol:Propan-2-ol			Carbon tetrachloride:DMF					
			-9.857± 0.59			12.057± 2.94						80.849± 19.51
0.1	0.901	0.801		1.712	1.612		0.747	0.647				
0.2	1.050	0.850		2.057	1.857		0.859	0.659				
0.3	1.000	0.700		0.817	0.517		0.977	0.677				
0.4	1.099	0.699		2.114	1.714		0.985	0.585				
0.5	1.050	0.550		0.939	0.439		0.985	0.485				
0.6	1.000	0.400		0.939	0.339		0.992	0.392				
0.7	1.050	0.350		2.114	1.414		0.992	0.292				
0.8	1.000	0.200		2.170	1.370		1.000	0.200				
0.9	0.046	-0.854		2.170	1.270		0.992	0.092				
1.0	1.000	0.000		1.000	0.000		1.000	0.000				

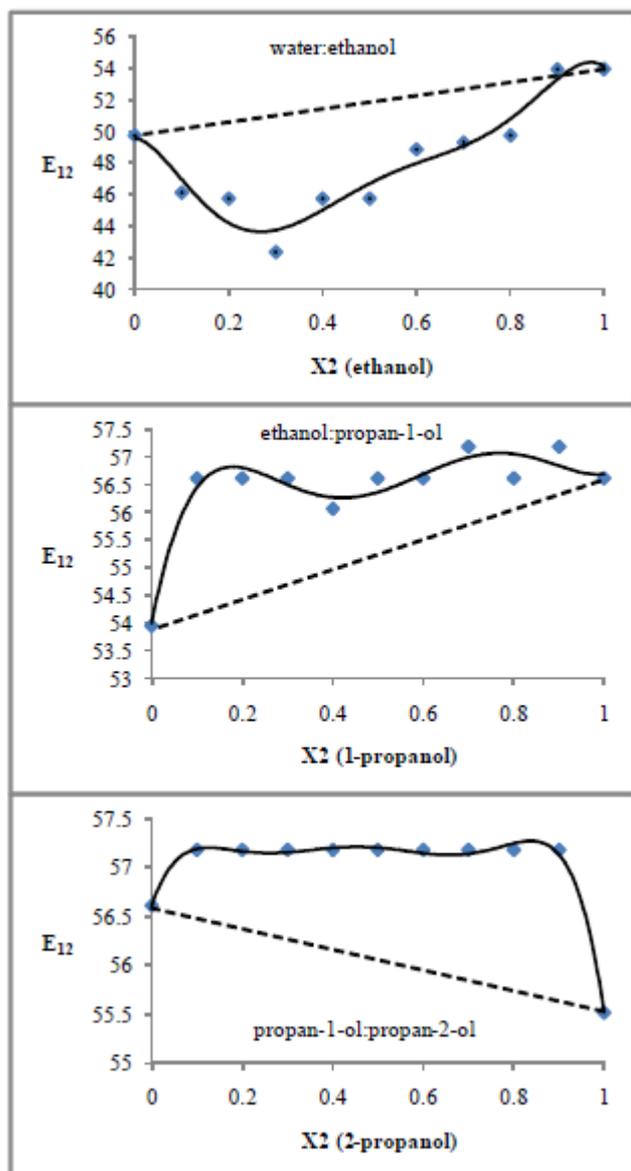


Fig.6. Variation of the molar transition energies of MB with mole fractions of binary mixtures

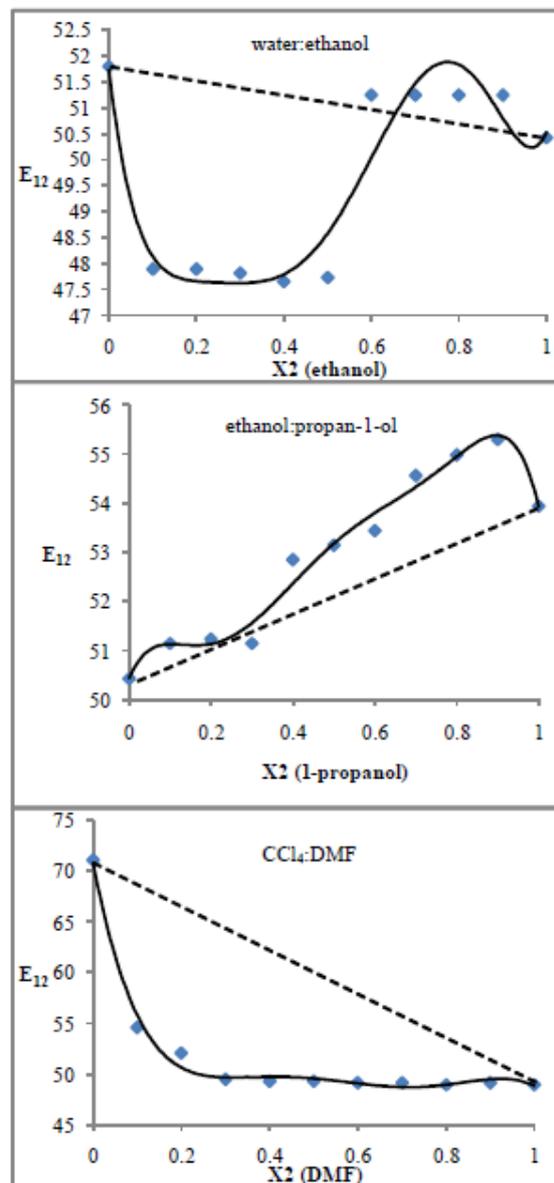


Fig. 7. Variation of the molar transition energies of SDB with mole fractions of binary mixtures

3.5. Aqueous Alcoholic Mixtures

In aqueous alcoholic mixtures, both MB and SDB showed preferential accumulation of water in their solvation shells for the majority of the composition range. This can be attributed to the combination of the high solubilizing power of the sulphonic group, its ion-dipole interaction with water and the overall positive charge on the hydrazone forms of the dyes as shown in [Scheme 1](#) which can also drive ion-dipole interactions with water. The data showed an increase in preferential solvation by water up to a critical point after which a steady decline was observed as the behaviour tends towards linearity at

very high alcohol fractions ($X_2 = 0.9$ to 1). This is consistent with the explanation that small increments in alcohol composition lead to an initial increase in overall solute-solvent interactions until the ion-dipole interactions are compromised in an extremely non-polar environment. The magnitude of preferential solvation of MB by water was also in the order: aqueous methanol (-8.611 at $X_2 = 0.6$) > aqueous ethanol (-2.045 at $X_2 = 0.3$) > aqueous propan-2-ol (-2.025 at $X_2 = 0.7$) > aqueous propan-1-ol (-1.814 at $X_2 = 0.7$). It can thus be deduced that increase in the alkyl chain of the alcohol co-solvent generally limited preferential solvation of the dyes by water. The notable exception to this general behavior in

aqueous alcoholic mixtures was the biphasic curve obtained with plot of the molar transition energy of SDB with increasing ethanol mole ratios. As shown in Figure 7, an initial preferential solvation by ethanol ($X_2= 0.1$ to 0.5) was prevalent before a sharp transition to preferential solvation by water in alcohol-rich regions. In aqueous alcohol mixtures, water molecules tend to form relatively strong network of self-associated molecules which precludes interaction with the alcohol. This will lead to formation of isolated pockets of ethanol molecules which can interact with the dye using hydrogen bonding and consequently accumulate in its solvation sphere. Increasing amounts of the ethanol co-solvent will eventually lead to a disruption of the water-water network, the subsequent formation of new water-ethanol aggregates and a reduction of preferential solvation by ethanol. Thus, a sharp disruption of the preferential solvation by ethanol and subsequent increasing accumulation of water molecules in the cytotactic region of solute will be anticipated as seen in its solvation data. It is also noteworthy that synergistic interactions existing at these mole ratios ($X_2= 0.1$ to 0.5) as can be seen in the plot would contribute significantly to the observed trend. Synergism which refers to the interaction of two components of a mixture to form aggregated species which are more polar than either of the two pure components is particularly common in water: ethanol mixtures. This is because ethanol-water co-solvents can exist in two heterodimeric forms, $R^+OH_2...HO^-$ where alcohol is a proton acceptor or a proton donor, $RO^-...^+OH_2$ thereby increasing the possibility of interactions with varying functionalities such as the hydroxyl group of SDB [11]. Synergistic effects was also seen in the solvation data plots of SDB in aqueous 1-propanol, aqueous 2-propanol and with MB in all the aqueous alcohol mixtures.

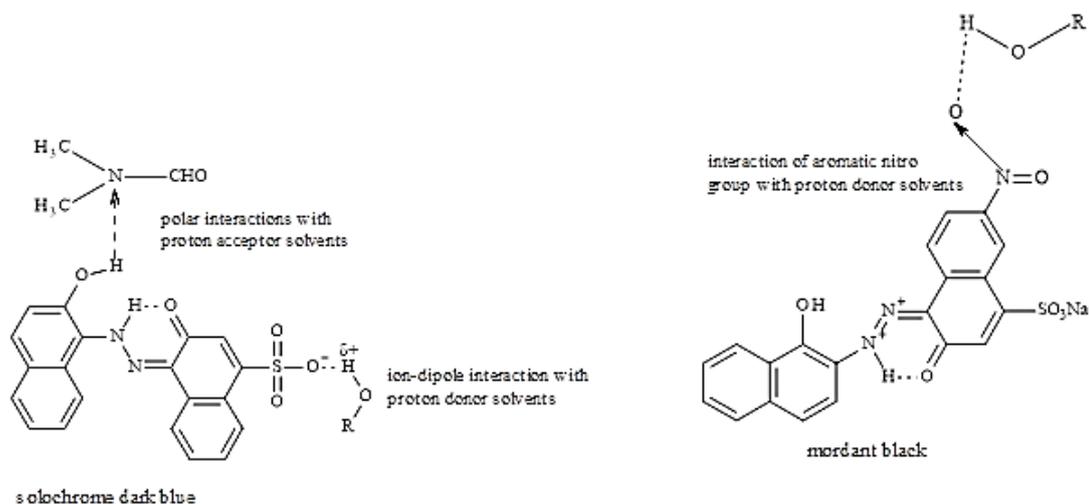
3.6. Mixed Alcoholic Systems

In mixed alcoholic systems MB and SDB, because of their bi-naphthyl skeletons, expectedly showed preferential solvation by the more hydrophobic alcohol over the majority of the composition ranges. A notable exception however, was the preferential solvation of SDB by the more polar alcohol component over the majority of composition ranges when examined in methanol: ethanol

and methanol: propan-1-ol mixtures. This contrast in solvation data may be due to the modulating influence of the nitro group which is present only in MB. In a study to determine the hydration number of nitro groups and cyano groups with high polarities due to their high dipole moments, results showed that nitro functional groups do not form strong hydrogen bonds with proton donors but rather exhibit hydrophilicities intermediate between those of hydrophilic and hydrophobic molecules [12]. Aromatic nitro group, when present, may therefore decrease hydrogen bonding between the dyes and alcohols especially those involving proton donor solvents and acceptor sites such as oxygen of the hydroxyl group on the dye probes as shown in Scheme 2. Hydrogen bond donor solvents are also good solvators of anions including sulphonic groups present in both dyes [3]. The absence of the disruptive influence of aromatic nitro group in SDB may therefore alternatively enhance its interaction via hydrogen bonding and some other polar interactions. It is noteworthy that this deviation was only seen with methanol which has the greatest proton donation capability.

3.7. Binary Mixture of Carbon Tetrachloride and Aprotic Proton Acceptor

Solvation data revealed a preferential solvation of MB by carbon tetrachloride for the majority of the composition ($X_2=0.1-0.8$) before tendency towards linearity. Conversely, SDB exhibited a preferential accumulation of DMF in its solvation sphere over the entire composition range of the mixture. The differences in solvation data can be attributed to the substituent effect of nitro group which is present only on the azonaphthalene residue of MB. Firstly the hydrophobic nitro group confers an increase in solubility in non-polar solvents such as carbon tetrachloride. In addition, the electron withdrawing effect of the group favours the intramolecular rearrangement involving the azo group and one of its two ortho hydroxyl groups, thereby reducing its availability for intermolecular hydrogen bonding with DMF. On the other hand, the reduced predominance of hydrazone tautomer of SDB makes the hydroxyl group available for proton donation to DMF as shown in Scheme 2.



Scheme 2. Amphiprotic interactions of dye probes with solvents

3.8. Multiparametric Correlation Studies

For quantitative representation of the specific and non-specific interactions between the solute and solvents, the multiple regression analysis approach was used based on the linear solvation energy relationships established by Kamlet, Abboud and Taft [13]. In non-chlorinated solvents, the contribution of specific and non-specific interactions to the total solvation energy is given by Equation 5.

$$E_T = A^\circ + a\alpha + b\beta + p\pi^* \quad (5)$$

where α , β and π are the KAT parameters corresponding to the electron donor acceptor capability, proton acceptor capability and dipolarity/polarizability of solvent milieu respectively. The A° , a , b , and p are regression functionalities; A° refers to the intercept of the equation while a , b and p are coefficients that measures the magnitude of contribution of solvent acidity, basicity and polarizability respectively to the total solvation energy. The KAT parameters for the pure solvents and

binary mixtures are obtainable from literature with the exception of aqueous propan-1-ol and propan-1-ol:propan-2-ol mixtures[14-17]. Regression for all possible combinations of the solvent parameters (α , β , π^*) was carried out in the neat solvents (excluding carbon tetrachloride) and the binary mixtures; three cases including only one of the three parameters, another three cases involving two parameters only and a single case involving all three.

Statistical analysis of the single, dual and multiparametric equations was employed to determine the best fitted model for the spectral patterns obtained in each of the solvent systems [18]. The KAT equation with the highest F-statistics contains the Kamlet-Taft parameters that are most fitting in describing the solvatochromism observed with the dye probes. The Kamlet-Taft parameters with the highest contribution to the solute-solvent interactions in all the solvent systems are depicted in Table 5.

Table 5. Multiple linear regression analysis of the KAT equation for the E_T values of MB and SDB

Solvents	Dye probe	A°	a	b	p	F	r^2
Neat solvents	MB	60.030			-11.023	7.524	0.70
	SDB	27.694	4.576	20.155	8.411	6.210	0.903
Water:methanol	MB	8208.441	10850.97		-3349.56	3.00	0.43
	SDB	50.138			1.404	19.410	0.70
Water:ethanol	MB	89.951		-34.824	-23.180	8.167	0.70
	SDB	50.403			1.186	16.291	0.65
Water:propan-2-ol	MB	55.927	-10.146			0.50	0.10
	SDB	65.593	-8.560	-8.967		0.504	0.112
Methanol:ethanol	MB	72.251			-35.191	1.391	0.134
	SDB	34.623			29.483	2.725	0.232
Methanol:propan-1-ol	MB	306.396	-47.835	-115.303	-189.204	46.080	0.951
	SDB	66.816	-17.056			30.947	0.80
Methanol:propan-2-ol	MB	81.391			-49.615	21.254	0.703
	SDB	47.934		4.750		6.107	0.404
Ethanol:propan-2-ol	MB	288.973	-60.730	-137.154	-141.268	5.416	0.70
	SDB	183.309	-35.790	-78.902	-74.472	1.691	0.42

In pure solvents, a single parametric equation produced the best fit to the spectral patterns of MB. Thus, the spectral changes of MB are mainly driven by changes in polarity of the solvent milieu. Expectedly, the sign of the coefficient is negative indicative of the inverse relationship between the electronic transition energy of MB and polarity of solvents. On the other hand, the highest contributors to the observed spectral patterns of SDB are the hydrogen bond acceptor ability and polarity of the solvent environment. This is consistent with the explanation that the reduced predominance of the hydrazone form of SDB molecule will increase its propensity to donate proton from its hydroxyl group to suitable proton acceptor solvents.

Generally, in aqueous alcoholic mixtures a dual parametric model was observed with both dyes. This might explain the biphasic relationship observed in the spectral patterns of the dyes. Thus with MB in water: methanol, the predominant solute-solvent interactions are hydrogen bond donor capability and polarity of solvent mixture. The negative sign of the polarity coefficient is possibly responsible for the initial bathochromic shifts which were then followed by progressive hypochromic shifts as a result of the positive contribution of the coefficient of hydrogen bonding interactions. Similarly, when investigated in water: ethanol mixtures, the dual parameters of hydrogen bond acceptor capability and polarity of solvent system defined the spectral patterns of MB. On the other hand, the behavior of SDB was best explained by polarity in the two aqueous alcoholic mixtures but fitted a dual parametric model in water: propan-2-ol.

In methanol: propan-1-ol and ethanol: propan-2-ol mixtures, a multiparametric equation showed the best fit for MB data. Thus solvent effects on spectral shifts of MB can be explained by a combination of α , β and π^* properties of the binary mixtures. The contribution of the parameters to solute-solvent interactions in both mixed alcoholic systems was in the order: $\pi^* > \beta > \alpha$. An inverse relationship between the molar transition energy of the dyes and each of the solvent parameters can also be observed in both solvent systems. In methanol:propan-2-ol, single parametric equation fitted the data of both dyes with polarity and hydrogen bond donor capability of solvents being the major contributors to the spectral shifts of MB and SDB respectively. The multiple effects seen in mixed alcoholic systems are expected. They arise from the simultaneous dual hydrogen bonding effects in amphiprotic solvents such as alcohols which can donate proton to nitro group (as well as oxygen of the common

hydroxyl groups) of the dyes as well as accept protons from the probe's hydroxyl groups as shown in Scheme 2. Although in both instances, hydrogen bonding lead to a decrease in electronic transition energies, the predominant solvatochromic effects can often be deduced from the order of the observed bathochromic shifts [13]. When solvent effects are due to hydrogen bonding type in which alcohol acts as a proton donor, the extent of observed bathochromic shift increases with hydrogen bond donor capability and vice-versa. Consequently, the trend observed in Table 5 in which the coefficient of the α parameter in regression equations for MB was consistently higher than those of SDB in all solvent systems is anticipated as hydrogen bond donor capacity of solvents will play more significant roles in solvatochromism of MB which contain an additional proton acceptor site, aromatic nitro group, compared to SDB.

4. Conclusion

The solvatochromic properties of two monoazo dyes, mordant black and solochrome dark blue were successfully investigated with UV-visible spectroscopy. Linear solvation energy relationship was employed to decipher predominant solute-solvent interactions, using the Kamlet and Taft solvent parameters. In pure solvents, the spectral effects of MB and SDB were mostly affected by the polarity and basicity of the solvent milieu respectively. In binary mixtures of aqueous alcohols, polarity of the solvent milieu was the most significant determinant of spectral patterns with α and β parameters playing secondary contributory roles in the observed spectral changes of MB and SDB respectively. Properties of solvents played more pronounced effect in spectral effects of both dyes when investigated in mixed alcoholic system than in other binary mixtures. However, polarity was still the largest contributor, followed by β and α parameters of the solvent milieu.

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Conflict of interest

The authors declare that they have no competing interests.

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