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ORIGINAL PAPER

Azo-hydrazo Tautomerism and Inclusion Complexation of 1-phenylazo-2-naphthols with Various Solvents and β-cyclodextrin

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Abstract Spectral characteristics of sudan I (SDI), sudan II (SDII) and mordant violet-5 (MV5) have been studied in various solvents and β-cyclodextrin (β-CD). The inclusion complex of the above molecules with β-CD was analyzed by UV-visible, fluorometry, and DFT methods. The solvent study shows that azo-hydrazo tautomer is present in these molecules. The increase in the fluorescence intensity and a large bathochromic shift in the S_1 state indicate these molecules forms 1:1 inclusion complex with β-CD.

Keywords 1-phenyazo-2-naphthol · β-cyclodextrin · Inclusion complex · Azo-hydrazo tautomerism

Introduction

Although the tautomerism in phenyl azonaphthol is known for more than a century [1], the number of studies dealing with these compounds has risen only in the last few decades. This is not surprising, because on one hand tautomerism is an elementary processes in living systems and advanced technological application [2–4] and on the other hand it remains of substantial fundamental interest for method development in molecular spectroscopy [5, 6] and in most of these cases the individual tautomers cannot be physically separated. It is well known that the position of the tautomeric equilibrium in solutions can be shifted by changing environmental factors such as solvent properties; temperature and the corresponding spectra can be recorded but not analyzed by spectrophotometry [5, 6]. Antonov et al. studied intensively the tautomeric equilibrium and the quantitative information based on the solvents effects [7, 8] and temperature.

In addition to the solvent effects, studies on the inclusion complexation of organic molecules with CD can also provide some useful information about the geometry of guest molecules. CDs are water soluble oligosaccharides which form inclusion complexes with a large number of organic and inorganic molecules. A generally accepted reason for choosing CDs, a class of cyclic oligosaccharides with 6–8 D-glucose units linked by α-1,4-glucose bonds, as the starting materials to construct the supramolecular architectures is that the truncated cone-shaped hydrophobic cavities of CDs have a remarkable ability to include various guest molecules either in solution or in the solid state to form the functional host-guest inclusion complexes [9–12] which can be subsequently used as the building blocks of supramolecular aggregates. Among the various families of organic compounds used as guest molecules, the chromophoric guests, such as azobenzenes [13–23] are of particular importance because they can exhibit appreciable spectral changes upon complexation by inclusion with CDs in solution, and thus can be applied as the versatile spectral probes to investigate host-guest interactions. However, comparative studies on the inclusion complexation and assembly behavior of CDs with azo derivatives are still rare, to the best of our knowledge, although azo derivatives are widely focused upon because of their potential to construct photo driven molecular machines [13]. The ability of CDs to accommodate guest molecules of the appropriate size in their cavities has been utilized by many investigators to control the photochemical properties and chemical reactions of organic molecules.

The application of aromatic azo dyes for both conventional [5] and sophisticated 'high tech' [23] purposes are

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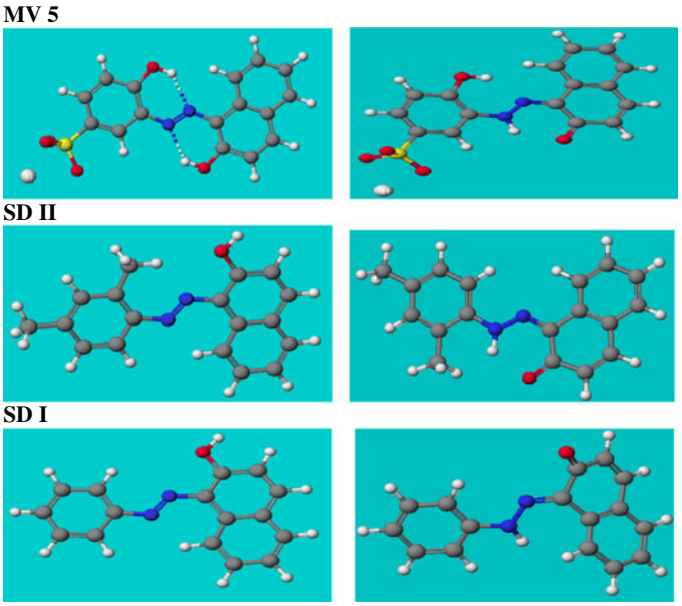
well-known. Their applications as optical sensors and for molecular memory storage due to the halo-photo and thermochromic properties attract considerable attention form both fundamental and applied point of view [24–26] and there are many reports on the inclusion complexation of cyclodextrins (CDs) with azo dyes [27, 28].

The aim of the present study is to report the spectral changes of three dyes in different solvents and β-cyclodextrin. In this work, we have examined the substituent effects on the inclusion complexation of β-CD with water soluble azo dyes (1-phenyazo-2-naphthol (SDI, Sudan I), 2, 4-dimethyl-1-phenyazo-2-naphthol (SDII, Sudan II) and mordant violet-5 (MV5, acid alizarin violet-5). The important basic structures for the dyes are given in Fig. 1.

Experimental

SDI, SDII, MV5 and β-CD were obtained from Sigma-Aldrich chemical company and used as such. The purity of the compound was checked by similar fluorescence spectra when excited with different wavelengths. Triply distilled water was used for the preparation of aqueous solutions. The solutions were prepared just before each measurement. The concentration of these compounds was of the order of



MV 5

Azo	ΔH= -121.4366 kcal/mol	μ_g =6.379		
Hydrazo	ΔH = -113.6077 kcal/mol	μ_g= 6.057		
H_7-N_2= 1.76	H_{11}-N_1= 1.76	O_2-H_{11}= 7.29	H_3-O_2= 13.13	
H_2-H_7= 7.34	O_2-N_1= 6.72	O_3-H_{11}= 7.44	H_3-O_3= 13.71	
H_2-O_1= 7.25	O_3-N_1= 7.44	O_4-H_{11}= 7.44	H_3-O_4= 13.71	
H_8-H_{11}= 4.91	O_4-N_1= 7.44	H_4-O_2= 12.48	H_4-O_3= 13.47	
H_8-O_5= 4.76	H_7-H_{11}= 4.14	H_4-O_4= 13.47	H_3-N= 13.07	
H_4-N= 12.75	H_5-O_3/O_4= 12.35			

SD II

Azo	ΔH =66.502 kcal/mol	μ_g = 1.488	
Hydrazo	ΔH =63.9856 kcal/mol	μ_g = 1.461	
H_1-H_6= 7.78	O-H_6= 7.07	H_8-H_{16}= 5.40	H_3-H_{10}= 12.35
H_{10}-H_{16}= 6.89	H_8-H_{14}= 5.40	H_3-H_{11}= 12.35	H_{11}-H_{15}= 8.49
H_8-H_{15}= 5.40	H_3-H_{12}= 12.31	H_{12}-H_{14}= 8.49	

SD I

Azo	ΔH =81.15754 kcal/mol,	μ_g = 1.831	
Hydrazo	ΔH= 84.4394 kcal/mol,	μ_g = 4.804	
H_1-H_6= 7.78	N_1-H_{10}= 6.10	H_2-H_{11}= 8.75	H_2-H_5= 6.75
N_2-H_3= 6.20	H_5-H_9= 9.55	H_3-H_{10}= 11.46	N_2-H_4= 6.40
H_4-H_{10}= 11.71	O-H_6= 7.07	O-H_{10}= 8.00	

Fig. 1 CAChe-DFT structure—MV 5, SD II and SD I

4×10^{-4} to 4×10^{-5} M. The concentration of β-CD solutions was varied from 1×10^{-3} to 1×10^{-2} M.

Absorption spectral measurements were carried out with a Hitachi Model U-2001 UV-visible spectrophotometer and fluorescence measurements were made with a Shimadzu RF 5301 spectrofluorometer. The pH values in the range 2.0–12.0 were measured on an Elico pH meter model LI-120.

Results and discussion

Effect of solvents

The absorption and fluorescence spectra of SDI, SDII and MV5 have been recorded in solvents of different polarity and hydrogen bonding tendency and the relevant data are complied in Table 1. The fluorescence spectra are shown in Fig. 2. The absorption spectral shape of the SDII resembles with SDI but the absorption maxima of SDII are red shifted than that of SDI. The large red shift and broad absorption and emission spectra in MV5 suggest intramolecular hydrogen bond (IHB) present in this molecule. The increasing order of red shift is: SDI <SDII <MV5. The above sequence indicates the position of the substituent in the aromatic ring is the key factor for the absorption and emission behavior. Increasing the polarity and proton donor capacity of solvents has no significant effect, both in the absorption and emission bands which indicate that the azo-hydrazo tautomer is present in these molecules. It is well known the solvent molecules can have dispersive interactions with the solute and also can act as proton acceptor and proton donor to the solute molecules. If π-π* transition is the lowest energy transition, the first two interactions leads to a red shift and the third leads to a blue shift in the absorption and fluorescence spectra.

The hydroxyl group can behave in two ways: The solvent molecules can have dispersive interactions with the solute and also can act as proton acceptor and proton donor to the solute molecules. If π-π* transition is the lowest energy transition, the first two interactions leads to a red shift and the third leads to a blue shift in the absorption and fluorescence spectra. Protic solvents interact with the lone pair electrons on the solute oxygen atom of hydroxyl group to form a hydrogen bond and hydrogen atom of the hydroxyl group also makes a hydrogen bond with solvents. In the former, a blue shift and in the latter, a red shift in the absorption spectra should be observed. Thus a blue shift in λ_{abs} in water suggests the formation of the H-bond with the lone pair thus inhibiting its interaction with π-cloud. The red shift in aprotic solvents is due to usual dipole-dipole effect on the π-π* transition or to the hydrogen donating character of the hydroxyl group.

The results in Table 1 and very low ε_{max} values indicate n-π* transition is present in these molecules. The observed absorption and fluorescence spectral changes are interpreted in terms of azo-hydrazo equilibrium [29]. It is evident that increasing the polarity of solvents leads to an increase in the amount of the 'hydrazo' form, whereas the opposite is not true for the 'azo' form [5–8]. Table 1 results also shows, methyl substituent hardly affect the position of the azo-hydrazo tautomeric equilibrium compared to hydroxyl substituent.

Generally solvent effects on tautomerism equilibrium can be separated into specific solute-solvent interaction (e.g. hydrogen bonding) and non-specific bulk interactions. Based on the previous investigations concerning the tautomerism of azonaphthol compounds [30–32] the solvents used can be divided into several groups depending on their type of interactions with the respective azo or hydrazo tautomer: (i) tautomer H–OH solvent interaction (via, movable proton and the oxygen of the solvent) in protic solvents; (ii) tautomer O–H solvent interaction (via the tautomeric oxygen and the proton/protons from the solvents) in solvents like $CHCl_3$, CH_2Cl_2 and CH_3CN (iii) tautomer H–O solvent interaction (via, the movable proton and the double bonded oxygen from the solvent) in solvents like DMSO, ethyl acetate.

Solvents which do not participate in specific interactions

The present systems, which are characterized by a strong intramolecular hydrogen bond (IHB), one expects a some what different behaviour towards the solvents used. For instance, the dominating tautomer H–OH solvent interaction with alcohol in SDI, SDII and MV5 would require breaking of the IHB bond in these compounds. Thus for these molecules, a tautomer O–H solvent interaction with alcohol as well as CH_2Cl_2/CH_3CN should be energetically more favorable. Specific interactions of the tautomer H–O solvent interaction (DMSO) should hardly be possible because of unfavorable steric repulsions. Further as mentioned above, the protic and aprotic solvent values in Table 1 indicate involvement of hydrogen bonds by H-atom of the solvent and the oxygen (hydroxyl or azo) of the solute for the second type of solvent. In agreement with the results in Table 1, CH–O hydrogen bonds involving alkyl halogenides have been shown to behave very much like conventional OH–O hydrogen bonds [33]. Not surprisingly, these interactions appear to be stronger in the case of the quinine tautomer thus shifting the tautomer towards this form. Further, Antonov [5–8] et al. have already reported in phenyl azonaphthol tautomeric equilibrium shifting towards the quinone form 'hydrazo' for donor substituted derivatives with increasing solvent polarity. As can be seen there is a trend, for an increasing difference between the dipole

Table 1 Absorption, fluorescence spectral data (nm) and Stokes shifts (cm^{-1}) of Mordant Violet 5, Sudan-II and Sudan-I in selected solvents

Solvents	MV 5				SD II				SD I			
	λ_{abs}	log ε	λ_{flu}	Stokes shift	λ_{abs}	log ε	λ_{flu}	Stokes shift	λ_{abs}	log ε	λ_{flu}	Stokes shift
Cyclohexane	540–	3.41	635	2,771	516	2.36	587	2,344	502	2.29	580	2,679
	514		455		480	2.44	430		465	2.42	456	
	475		355		426	2.34	348		434	2.41	364	
	273	3.70			310	2.17			336	2.21		
	224	3.36			225	2.87			305	2.22		
									230	2.92		
Diethyl ether	535-	3.17	630	2,819	516	2.43	589	2,402	503	2.43	582	2,698
	502		455		489	2.51	355		476	2.51	350	
	483		355		426	2.40			423	2.40		
	410s	3.05			310	2.20			313	2.20		
	306	3.09			230	2.90			232	2.90		
	269	3.35										
1,4-Dioxane	536-	3.27	625	2,657	516	2.32	586	2,315	503	2.36	583	2,727
	502		455		490	2.42	355		476	2.44	365	
	484		355		426	2.27			423	2.34		
	410s	3.11			310	2.13			313	2.17		
	307	3.16			227	2.31			232	2.87		
	269	3.40										
Ethyl acetate	536-	3.15	620	2,528	516	2.36	587	2,344	503	2.43	583	2,727
	503		455		490	2.44	355		476	2.51	366	
	485		355		426	2.34			423	2.40		
	410s	3.02			310	2.17			313	2.20		
	307	3.08			227	2.87			232	2.90		
	269	3.36										
Dichloromethane	535-	4.11	620	2,563	516	2.43	587	2,344	503	2.36	585	2,786
	503		455		490	2.51	355		476	2.44	342	
	485		355		426	2.40			426	2.34		
	410s	3.05			310	2.20			315	2.17		
	307	3.09			227	2.90			228	2.87		
	269	3.28										
	226											
Acetonitrile	537-	4.22	600	1,815	516	2.43	587	2,344	503	2.36	585	2,786
	502		455		490	2.51	355		476	2.44	342	
	485		355		426	2.40			426	2.34		
	410s	3.00			310	2.20			315	2.17		
	307	3.08			227	2.90			228	2.87		
	269	3.38										
	226											
t-Butyl alcohol	538-	4.06	600	1,920	524	2.29	586	2,020	508	2.43	585	2,591
	500		344		481	2.42	356		480	2.51	344	

	410s	3.64			423	2.41			425	2.40		
	313	3.85			311	2.21			312	2.20		
	267	4.24			234	2.22			239	2.90		
	232											
2-Butanol	538-	4.29	600	1,920	524	2.36	586	2,020	508	2.36	585	2,591
	500		345		481	2.44	356		480	2.44	345	
	410s	3.93			423	2.34			425	2.34		
	314	4.09			311	2.17			312	2.17		
	266	4.50			234	2.87			239	2.87		
	228											
2-Propanol	538-	4.14	600	1,920	524	2.43	586	2,020	508	2.32	585	2,591
	505		345		481	2.51	356		480	2.42	344	
	410s	3.70			423	2.40			425	2.27		
	314	3.74			311	2.20			312	2.13		
	266	4.00			234	2.90			239	2.31		
	236											
Ethanol	539-	4.23	605	2,024	524	2.43	588	2,077	508	2.43	586	2,620
	501		345		481	2.51	356		480	2.51	340	
	410s	3.68			423	2.40			425	2.40		
	309	3.94			311	2.20			312	2.20		
	265	4.42			234	2.90			239	2.90		
	232											
Methanol	539-	4.23	605	2,024	524	2.36	588	2,077	508	2.32	587	2,649
	501		346		481	2.44	356		480	2.42	339	
	410s	3.68			423	2.34			425	2.27		
	309	3.94			311	2.17			312	2.13		
	265	4.42			234	2.87			239	2.31		
	232											
Water (pH=6.5)	539-	4.44	615	2,293	540	2.43	589	1,541	522	2.35	587	2,121
	514		347		497	2.51	406		486	2.43	455	
	410s	3.93			425	2.40	356		320	2.27	339	
	307	4.23			322	2.20			233	2.70		
	267	4.69			225	2.90						
	213											
Dipole moment	7.19		9.11		5.32		7.21		6.95		8.57	
Onsager cavity Radius (Å)	6.43				6.26				4.14			
Correlation coefficient												
$E_T(30)$ *Vs* $\Delta\overline{\nu}_{ss}$				0.8864				0.8852				0.8726
BK *Vs* $\Delta\overline{\nu}_{ss}$				0.6416				0.6358				0.6276

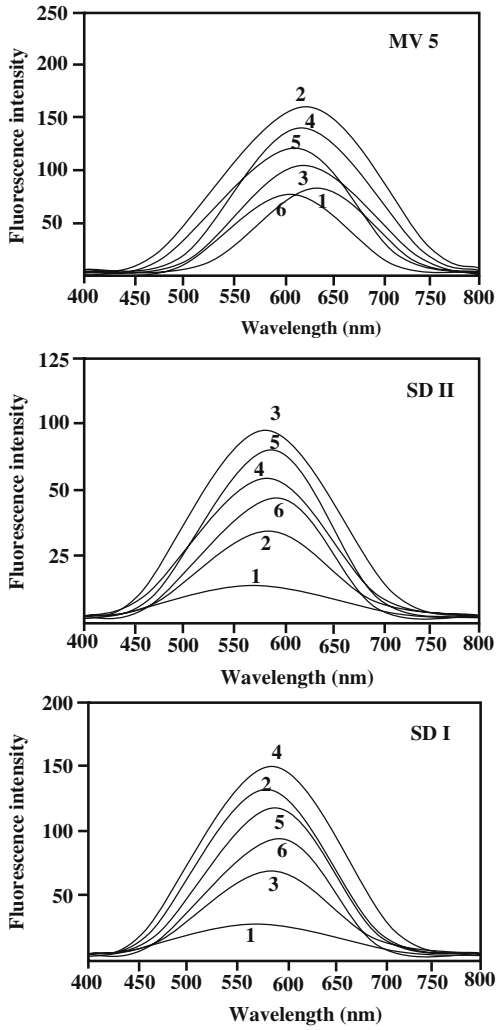


Fig. 2 Fluorescence spectra of MV 5, SD II and SD I in different solvents at 303 K: ($\lambda_{excitation}$: 420 nm): (1) cyclohexane (2) ethyl acetate (3) acetonitrile (4) 2-propanol (5) methanol and (6) water

moments of the respective tautomeric forms (i.e. hydrazo being more polar than azo form). But in the case of non planarity, the substituent cannot really affect the tautomeric fragment.

The results in Table 1 predict the donor substituent in MV5 to cause bathochromic shifts of the longest wavelength absorption bands for both tautomeric forms. A similar dependence of the UV-visible spectra has been found for the isomeric 2-hydroxy-1-naphthaldehyde [30]. However, the band positions of the UV-visible spectra are essentially independent of solvent polarity with an expected higher polarity of the hydazo tautomer and thus preferential stabilization by polar solvents. Also, negligible solvent shift of the various band maxima of the individual tautomers is observed. Therefore donor substituents apparently stabilize the hydazo tautomer, at least in polar solvents. Moreover, N–O bond distance apparently gives a good indication of IHB bond strengths, whereas the N–H lengthening due to strong H-bond formation is small. It is also evident from these data that the stronger H-bond (shorter N–O distance) is associated with the less stable tautomer [34, 35].

The tautomeric behavior of azo naphthols differs considerably from that of the corresponding azophenols [36] which exist mainly in the azo form at room temperature. Even in polar solvents such a difference could be caused by the loss of aromaticity in going from azo to hydrazo form, while in azonaphthols this effect is compensated by the transfer of aromaticity within the naphthalene fragment. In azophenols, the number of delocalized electrons in the tautomeric phenyl ring is reduced from six to four on going to the hydrazo form because of the engagement of two of those electrons in the strong C=N and C=O bonds. Thus, the phenyl ring looses much of its aromaticity. In the naphthalene compounds, this effect is compensated by the second aromatic ring [37]. The experimental (UV-Vis) absorption spectra also support this finding. At room temperature the absorption spectrum at 320–430 nm and 500 nm corresponds to azo and hydrazo forms respectively [38]. Further, the quantum yield for these compounds are fairly low, it could be explained by non-radiative decay paths to the low-lying n-π* states of the nitrogen atoms [38]. What more interest is that the excitation spectra are identical irrespective of emission wavelength, which indicates that the observed emission originates from one hydrazo tautomer only.

The Stokes shifts of SDI, SDII and MV5 measured in different solvents were correlated with the BK [39] and

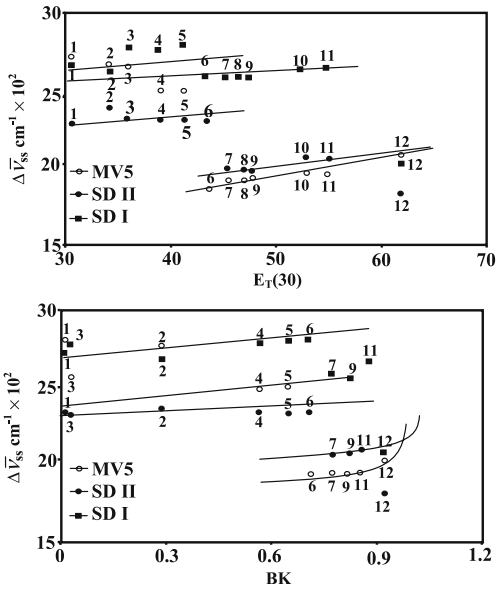


Fig. 3 Plot of Stokes shifts (cm^{-1}) of MV5, SD II and SD I vs. $E_T(30)$ and BK solvent parameters: (1) cyclohexane (2) diethyl ether (3)1,4-dioxane (4) ethylacetate (5) dichloromethane (6) acetonitirle (7) *t*-butyl alcohol (8) 2-butanol (9) 2-propanol (10) ethanol (11) methanol and (12) water

Reichardt–Dimroth $E_T(30)$ [40] parameters (Table 1). It can be seen that, the plots of $\Delta\bar{\nu}_{ss}$ versus BK are non-linear, suggesting that the solute-solvent interactions are not very large and that general interactions play a major role in the spectral characteristics of these compounds. The plot of $\Delta\bar{\nu}_{ss}$ versus $E_T(30)$ are given in Fig. 3. As expected, these plots are solvent effects and hydrogen bonding effects. However, as there is no contribution from the solute-solvent charge transfer interactions to the $E_T(30)$ value, a non-linearity is observed for dioxane solvent.

Effect of β-CD

Table 2, Figs. 4 and 5 shows the absorption and emission spectra of SDI, SDII and MV5 in aqueous solutions (pH ~ 7) containing different concentrations of β-CD. The

Table 2 Absorption and fluorescence maxima (nm) of MV 5, SD II and SD I at different concentrations of β-CD

No.	Concentration of β-CD M	MV 5			SD II			SD I		
		λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}
1	Water (without β-CD)	539-502	4.26	590	559	2.05	585	536	1.92	586
		410		335	517	1.95	344	496	1.96	337
		308			329	2.25		324	1.85	
		262	3.90		270	1.98		230	2.08	
		220			221					
2	0.001	539-502	4.25	594	557	2.04	587	532	1.95	588
		410		445	516	1.96	424	499	1.96	447
		306		335	325	1.88	343	326	1.82	337
		265	4.01		256	2.10		229	2.13	
		220			221	2.39				
3	0.002	539-502	4.26	594	556	2.03	589	531	1.95	580
		410		445	514	1.93	423	499	1.96	447
		305		336	325	2.19	344	326	1.82	337
		264	4.26		256			229	2.13	
		216			221					
4	0.004	539-502	4.30	594	555	2.03	590	496	1.98	578
		410		446	514	1.94	423	316	1.89	447
		304		336	325	2.24	344	233	2.24	338
		264	4.28		260	2.38				
		216			220					
5	0.006	539-502	4.30	595	554	2.03	590	497	2.00	575
		410		446	513	1.94	423	320	1.86	447
		304		336	326	1.91	344	231	2.14	338
		262	4.33		257					
					217					
6	0.008	539-502	4.32	597	555	2.04	590	496	2.03	575
		410		446	515	1.96	423	315	1.87	447
		304		337	326	1.85	344	229	2.22	338
		262	4.42		257	2.01				
					217	2.31				
7	0.010	539-502	4.33	598	555	2.04	590	496	2.04	575
		410		447	514	1.96	424	316	1.75	447
		304		337	324	1.88	345	230	2.16	338
		261	4.46		260	2.10				
					218	2.39				
8	Excitation wavelength	320			320			320		
9	Binding constant (M^{-1})	191		429	199		333	115		324
10	ΔG KJ / mole	−13.21		−15.26	−13.33		−14.63	−11.96		−14.56

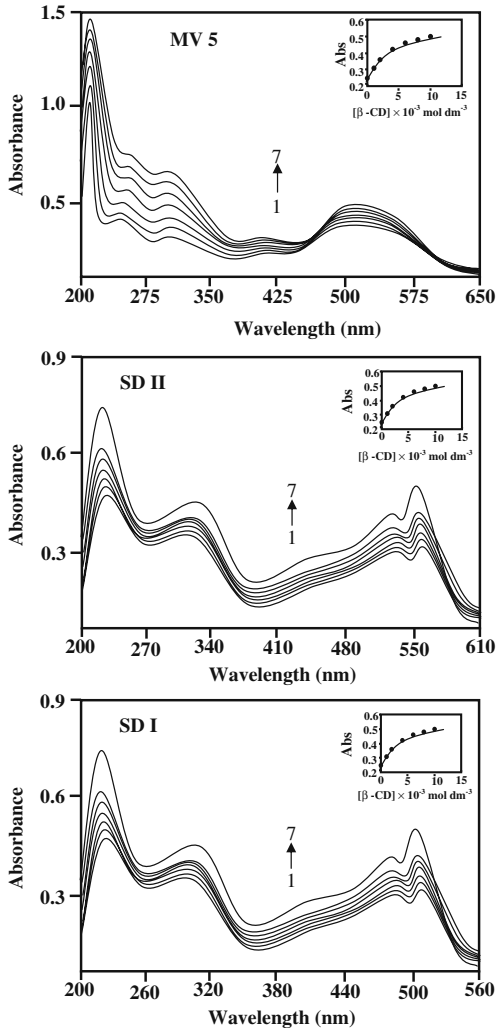


Fig. 4 Absorbance spectra of MV 5, SD II and SD I in different β-CD concentrations (M): (1) 0 (2) 0.001 (3) 0.002 (4) 0.004 (5) 0.006 (6) 0.008 and (7) 0.01

absorption spectra of these molecules in β-CD solutions show little change with those in water as observed for the solvent polarity dependence, reflecting little azo-hydrazo tautomer equilibrium in the ground state. Upon increasing the concentration of β-CD the molar extinction coefficient slightly increases at the same wavelength. The slight increase in the absorption with the addition of β-CD has been attributed to the enhanced dissolution of the guest molecule through the detergent action of β-CD [41–43].

In contrast to the weak absorbance between the SDI, SDII and MV5 (4×10^{-5} M) and β-CD, the fluorescence intensities of these molecules shows significant change with change in β-CD concentration (Fig. 5). In the β-CD free aqueous solution, three emission maxima can be seen even though the emission quantum yield of both the azo emission and the hydrazo emission (around 430 nm and 580 nm respectively) is extremely low. Upon addition of β-CD, all the emission intensities are gradually enhanced at the same wavelength and the fluorescence intensity ratio of the hydrazo to the azo tautomer (I_b/I_a) increases as the concentration of β-CD increases. The similarity in spectral changes in β-CD solutions suggest that the structural geometry of the SDI/β-CD and SDII/β-CD inclusion complexes are similar to MV5/β-CD inclusion complex in terms of the orientation of guest molecules. Thus, the polarity and viscosity variations may not play an important role in these molecules [41–43].

The presence of isosbestic point in the compounds indicates the formation of 1:1 inclusion complex. In general, the existence of an isosbestic point in the absorption spectra is an indication of the formation of well defined 1:1 complex. The formation constant of SDI is small compared with SDII/MV5 with β-CD. This is probably because, SDI molecule is not tightly encapsulated into the cavity, whereas in MV5, due to presence of naphthalene ring and ortho hydroxy group, it may tightly encapsulate in the β-CD cavity.

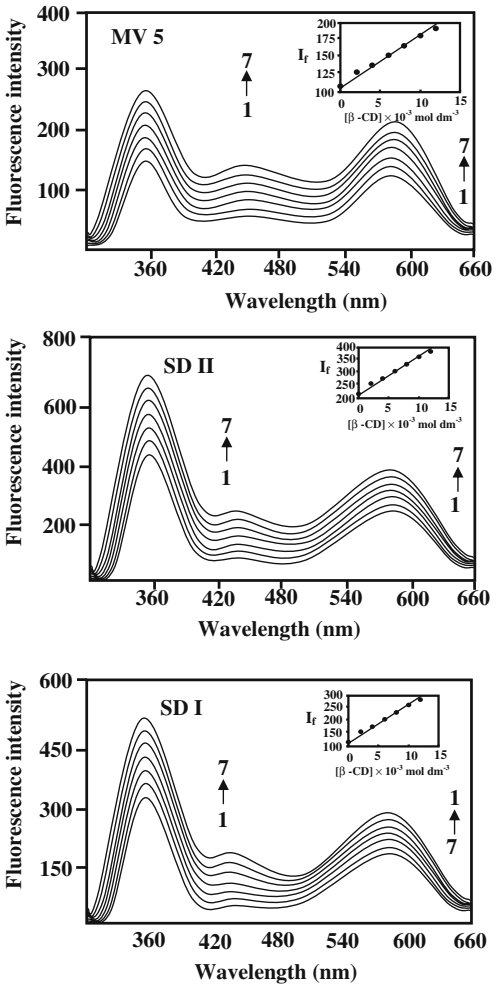


Fig. 5 Fluorescence spectra of MV 5, SD II and SD I in different β-CD concentrations (M): ($\lambda_{excitation}$: 320 nm): (1) 0 (2) 0.001 (3) 0.002 (4) 0.004 (5) 0.006 (6) 0.008 and (7) 0.01

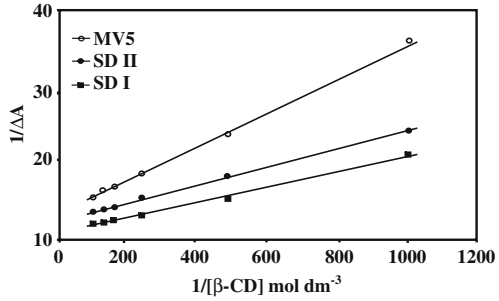


Fig. 6 Absorption spectra of Benesi–Hildebrand plot for the complexation of MV 5, SD II and SD I with β-CD (Plot of 1/ΔA vs. 1/[β-CD])

For 1:1 complex between β-CD and guest molecule the following equilibrium can be written:

$$SD + \beta - CD \rightleftharpoons SD.....\beta - CD \tag{1}$$

The formation constant 'K' and stoichiometric ratios of the inclusion complex of azonaphthol compounds were determined according to the Benesi–Hildebrand relation [44, 45] assuming the formation of a 1:1 host-guest complex:

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K(I - I_0)[\beta - CD]} \tag{2}$$

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K(I' - I_0)[\beta - CD]^2} \tag{3}$$

where $[\beta\text{-CD}]_0$ represents the initial concentration of β-CD, 'I_0' represents absorbance and fluorescence intensities in the absence of β-CD (water only), 'I' represents Absorbance and fluorescence intensities in the presence of different β-CD (0.001–0.009 M β-CD concentration and I′ represents the inclusion complex formation completed β-CD concentration (or) absorbance and emission intensity measured at the highest concentration of β-CD (0.01 M β-CD concentration). The K values were obtained from the slope and the intercept of the plots shown in Figs. 6 and 7.

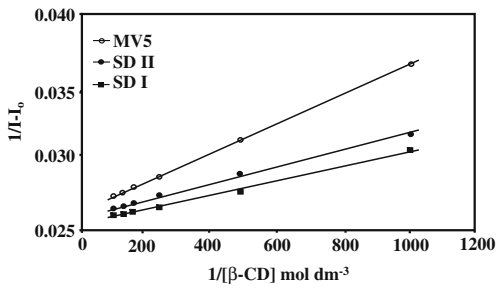


Fig. 7 Fluorescence spectra of Benesi–Hildebrand plot for the complexation of MV 5, SD II and SD I with β-CD (Plot of $1/I\text{-}I_0$ vs. 1/[β-CD])

According to the above equations, a plot of $1/I\text{-}I_0$ versus $1/[\beta\text{-CD}]^2$ (both absorption and fluorescence) gives an upward curves (this figure is not given). However a plot of $1/\Delta A$ versus 1/[β-CD] and $1/I\text{-}I_0$ versus 1/[β-CD] reveals a linear relationship as shown in Figs. 6 and 7. This analysis reflects the formation of 1:1 inclusion complex between these compounds and β-CD.

The free energy change of these complex were calculated from the following equation

$$\Delta G = -RT \ln K \tag{4}$$

As can be seen from Table 2, ΔG is negative which suggests that the inclusion process proceeded simultaneously at 303 K. The negative values in the experimental temperature indicate the inclusion process is an exothermic and enthalpy controlled process. The hydrophobic interaction between the internal wall of β-CD and guest molecules is an important factor for the stability of inclusion complexes. In MV5, SDI and SDII, it may safely be considered that the difference in the magnitude of the hydrophobic interaction is related to that of the contact area of the guest molecule for the internal wall of β-CD.

Several driving forces have been postulated for the inclusion complexation of CD with guest compounds [46]: (1) van der Waals forces, (2) hydrophobic interactions, (3) hydrogen bonding, (4) release of distortional energy of CD by binding guest and (5) extrusion of 'high energy water' from the cavity of CD upon inclusion complex formation. Tabushi [47] proposed a thermodynamic model for the process of CD inclusion complex formation. Based on the thermodynamic parameter (ΔG) calculated for the inclusion complexes, we conclude that the hydrogen bonding interaction, van der Waals interaction, and breaking of the water cluster around the polar compounds are mainly dominate the driving force for the inclusion complex formation.

It is well known that the strength of interaction is also dependent on the size of the CD cavity and size of the substituent in the inclusion complex [48]. This means that the interaction is more sensitive to the size of substituents and the CD in the complexation. The CDs are truncated, right-cylindrical, cone-shaped molecules, 7.8 Å heights with a central cavity. The diameters of the narrower and wider rim of the cavity for β-CD are 5.8 Å and 6.5 Å, respectively [49]. It is well known that the van der Waals force including the dipole-induced dipole interactions are proportional to the distance between the SDI, SDII, MV5 and the wall of the CD cavity and to the polarizabilities of these components. It is thus a short range interaction. Therefore, the neutral SDI, SDII and MV5 may embed deeper in the β-CD cavity than its anion. The phenyl moiety may achieve a maximum contact area [50] with the internal surface of the cavity of the β-CD; hence, the

interaction of the phenyl ring with β-CD would play an important role.

In general, the inclusion of CDs with guest compounds is also affected by hydrophobic and electronic interactions [51]. Since CDs have a permanent dipole [52], the primary hydroxyl end is positive and the secondary hydroxyl end is negative in the glucose units of CDs. The stability of binding by hydrophobic interaction is partly the result of van der Waals force but is mainly due to the effects of entropy produced on the water molecules [53]. In aqueous solution, a hydrophobic guest compound is restricted by the water shell formed by the hydrogen bonding network [54]. It has a strong tendency to break down the water cluster and penetrate the non-polar cavity of CD. This process is an exothermic due to entropic gain [55]. The association constants for the inclusion of β-CD with guest compounds were observed to be proportional to the substituent hydrophobic constant of the guest.

However, in the molecules the hydrogen bonding interactions play major roles in the inclusion complexation with β-CD. The 'K' value is a reasonable measure of hydrogen bonding and the change in hydrogen bonding of SDI, SDII and MV5 are caused only by the hydrogen ion concentrations. Since the hydroxyl substituent locates near the wider rim of the CD cavity and carboxyl group locates narrower range of the CD cavity, the 'K' values are proportional to the hydrogen bonding interactions. The difference in the slope in Figs. 6 and 7 for these molecules and β-CD complexes indicates that the interactions of hydrogen atoms, especially MV5 with β-CD is much stronger than SDI and SDII. This is because of MV5 interaction is approximate to the hydrogen bonding contact but in SDI and SDII they are somewhat weak, since the hydroxyl group is far from the internal surface of the β-CD cavity in the inclusion complexes. Thus for MV5, the association constant with β-CD is greater than with SDI and SDII (Table 2).

From the above results, we notice some interesting points: (i) the 'K' value for MV5 and SDII is higher than that of SDI which may be attributed to the more

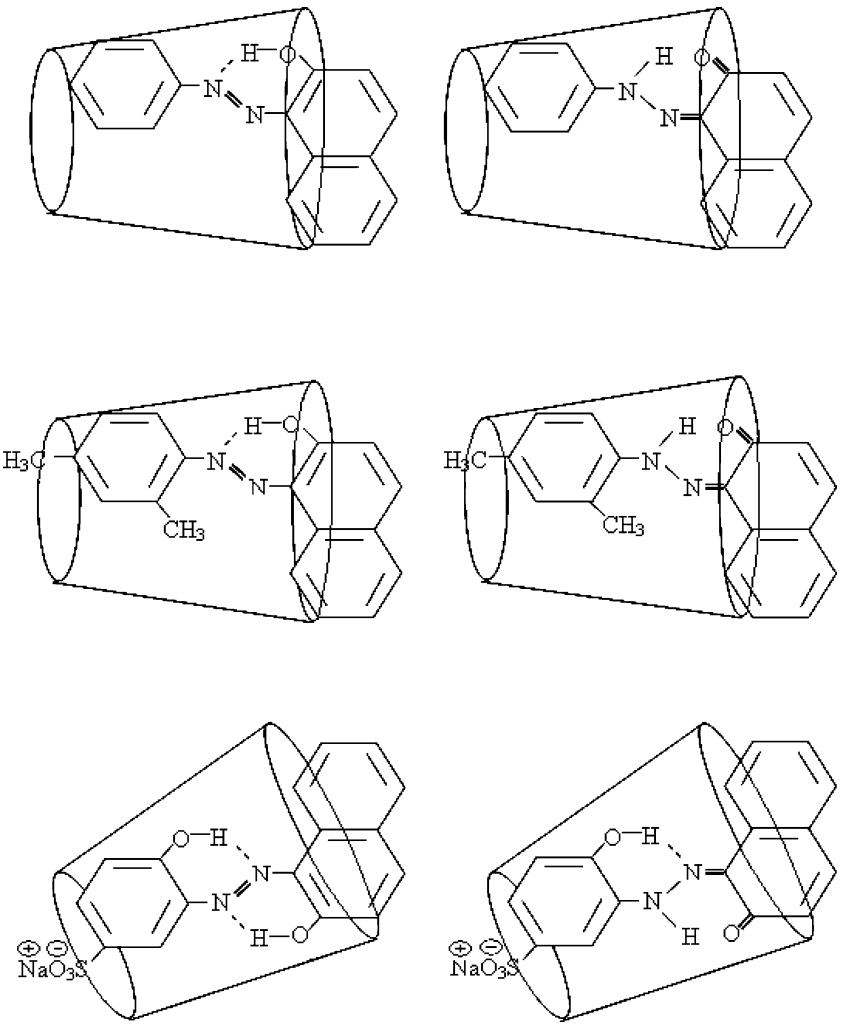


Fig. 8 Proposed inclusion complex structure of MV 5, SD II and SD I

hydrophobic interaction between the naphthalene ring and the internal wall of β-CD; (ii) the small binding constant for SDI implies that the phenyl ring is not more tightly embedded in the β-CD cavity; (iii) in MV5, the large blue shifted absorption and emission spectra suggests one of the hydroxy group is present in the interior part of the β-CD cavity. The results in Table 2 conforms the molecular disposition of MV5 in the inclusion complex is similar to that of SDI and SDII. Further it is a well known fact that hydrophobicity is the driving force to the formation of inclusion complexes. Since phenyl group is more hydrophobic than naphthol part hence phenyl ring may include in the β-CD cavity. It is also recognized that the naphthol group is located outside the β-CD cavity (i.e. in hydrophilic environments) [41–43].

Considering the above results, three different types of inclusion complex formation between these molecules and β-CD are possible: (i) with the phenyl ring captured, (ii) with naphthol ring captured and (iii) 1:2 inclusion complex. Since these molecules are neutral and have large size compared to β-CD they can be included in either of the two directions in the neutral β-CD cavity and may also be responsible for the formation of third type of inclusion complexes in the β-CD solution as demonstrated in Fig. 8. The fluorescence spectra of these molecules are same in the presence of high concentration of β-CD. As the intensity of hydrazo maxima have increased with increasing β-CD concentration, it seems that the naphthalene ring protrude into the bulk phase. This is reasonable because naphthol-quinone ring is more polar and can form H-bonds with either of the hydroxyl groups of the β-CD cavity rim or bulk water molecules or both. It should be preferable for the naphthol quinone group to protrude in to the polar aqueous phase. Even though both azo group and hydrazo group can be hydrogen bonded with water, the orientations of these groups can be different with regard to water molecule by forming different patterns of β-CD inclusion complexes. Moreover, because of tautomerization process, protonation may take place in the azo nitrogen atom; hence interaction with β-CD hydroxyl group is not possible; thus azo part can easily get entrapped in the β-CD cavity.

Further, the inclusion patterns of SDI/β-CD, SDII/β-CD and MV5/β-CD could be explained in terms of internal diameter of the β-CD cavities as well as the dimensions of these compounds. To determine the dimension of the above molecules, the ground state geometry of the above molecules were optimized by using the DFT methods (Fig. 1). This calculation reveals that the lengths of these molecules are bigger than that of the CD cavity (7.8 Å). Therefore these molecules can only partially get entrapped in the β-CD cavity. Even though the diameter of the naphthalene ring is higher than that of phenyl ring, this group easily gets entrapped in the β-CD cavity with the naphthalene ring exposed to the bulk phase as shown in Fig. 8. The emission intensities of the molecules are increased with increasing β-CD concentration at the same wavelength supporting this implication. The absorption and fluorescence spectral changes are also supporting the formation of a 1:1 inclusion complex between these molecules and β-CD.

Conclusions

The following conclusions can be drawn from the above studies:(i) in all solvents, SDI, SDII and MV5 molecules exhibit azo-hydrazo tautomers, (ii) large red shift is noticed for MV5 in all solvents and β-CD solutions indicating IHB is also present in this molecule and (iii) In β-CD solutions, the increase in the fluorescence intensity and a large bathchromic shift in S_1 state indicates the above molecules forms 1:1 inclusion complex with β-CD.

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