



Spectral Characteristics and Solvent Effects of 4-(Phenylazo) Benzoic Acid and 2-(4-Hydroxyphenylazo) Benzoic Acid on α -Cyclodextrin

KEYWORDS

4-(Phenylazo)benzoic acid, 2-(4-Hydroxyphenylazo)benzoic acid, α -cyclodextrin, inclusion complexes.

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ABSTRACT The absorption and fluorescence spectra of 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid have been recorded in different solvents of varying polarities and α -cyclodextrin (α -CD). In all solvents, the absorption and emission maxima of 2-(4-Hydroxyphenylazo)benzoic acid are red shifted than 4-(Phenylazo)benzoic acid. Studies on cyclodextrin reveal that both compounds form 1:1 inclusion complexes with α -CD. The thermodynamic parameter (ΔG) of inclusion process is also determined.

1. Introduction

In recent years, the host-guest inclusion complexes are of very much interest in various fields of Science and Technology. The naturally occurring Cyclodextrins (CDs) are well known as forming stable host-guest inclusion complexes which have the remarkable property of including organic, inorganic and biological molecules in their cavities [1-3] so long as the guest molecules have suitable polarity and dimension. α -Cyclodextrin (α -CD) is a cyclic oligosaccharide composed of six glucose units. Since α -CD is shaped like a truncated cone with a hydrophilic exterior and a hydrophobic interior cavity, it can selectively form inclusion complexes with a variety of guest molecules in solutions [4]. Usually a single guest molecule is accommodated into the α -CD cavity with the guest/host stoichiometry of 1:1. So α -CD has been often used to enhance the fluorescence intensities of several organic compounds by a process of partial encapsulation or inclusion of the organic guest molecules. When a fluorophore was included into the cavity, the fluorescence and selectivity with the outer molecules increased obviously. This led to the wide application of CDs in the fields of medicine, food, organic synthesis, environment protection and analytical chemistry etc. [5]

In the present study, two following organic compounds were selected. (i) 4-(Phenylazo)benzoic acid and (ii) 2-(4-Hydroxyphenylazo)benzoic acid. The spectral absorption and fluorescence characteristics of the two compounds have been studied in different solvents of varying polarities and α -CD concentrations both in the ground (S_0) and excited state (S_1). The objective of the study is to provide evidence that both 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid / α -CD inclusion complexes are formed in aqueous solution. 4 (Phenylazo)benzoic acid is used as "test kit" for rapid screening of functional group affinity to metal oxides in analytical chemistry. 2-(Hydroxyphenylazo)benzoic acid is used as indicator in the determination of serum albumin.

2. Experimental.

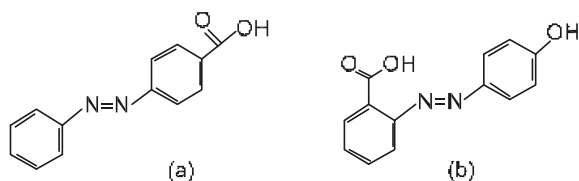
2.1. Instruments.

Absorption spectral measurements were carried out with a smart Systronics Double Beam Spectrophotometer - 2203. Fluorescence Measurements were made using JASCO Spectro Fluorometer FP - 8200.

2.2. Reagents and Materials

4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid (98% purity) and α -CD were obtained from Sigma Aldrich. All used solvents were of the highest grade. Triply distilled water was used for the preparation of aqueous solutions. The solutions were prepared just before taking measurements. The concentration of the two compound solutions were of the order (2×10^{-4} to 2×10^{-5} M). The concentration of α -CD was varied from 2×10^{-3} to 1×10^{-2} M. The experiments were carried out at room temperature (303K).

Fig.1 shows the chemical structure of (a) 4-(Phenylazo)benzoic acid and (b) 2-(4-Hydroxyphenylazo)benzoic acid.



Table

Absorption and fluorescence maxima (nm) and Stokes shift of 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid in different solvents (303 K)									
NO	Solvent	4-(Phenylazo)benzoic acid			2-(4-Hydroxyphenylazo)benzoic acid			λ_{em} (nm)	λ_{em} (nm)
		λ_{ab}	$\log \epsilon$	λ_{fl}	$\log \epsilon$	λ_{ab}	$\log \epsilon$		
1.	Ethylacetate	330	3.71	360	2025	340	4.03	375	3179
2.	Methyl ethyl ketone	332	4.54	296	2798	340	4.29	382	3230
		265.6	4.42	365		270	4.88	401	
3.	2-Propanol	336	3.43	207	4143	345	3.72	390	3344
		267.8	4.73	369		272	3.80	405	
4.	Methanol	336	4.03	378	4351	346.1	3.24	390	4051
		270	3.82	394		273	3.29	409	
5.	Water	337	3.09	370	4059	347	3.12	398	4776
		272	3.19	389		274	3.80	416	
ii.	Correlation Coefficient								
	$\Delta \log \epsilon$ vs $\log \epsilon$ (S ₀)				0.6956			0.7041	
	$\Delta \log \epsilon$ vs $\log \epsilon$ (S ₁)				0.7140			0.6891	

3. Results and discussion:

3.1. Effect of solvents

The absorption maxima, $\log \epsilon$, fluorescence maxima and Stokes shifts of 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid are compiled in table-1. In all solvents the absorption and emission maxima of

2-(4-Hydroxyphenylazo)benzoic acid are more red shifted than that of 4-(Phenylazo)benzoic acid. In polar solvents only a small spectral shift is observed in the absorption maxima of both the compounds. The greater red shift in 2-(4-Hydroxyphenylazo)benzoic acid is due to the -OH group in the 4th position of phenyl ring which is capable of forming hydrogen bonding with solvents.

Fig. 2. Shows the fluorescence spectra of both the compounds in selected solvents. The emission properties are strongly solvent dependent indicating a possibility of change in the character of the excited state. The fluorescence spectra are regularly red shifted with increase in polarity of solvents

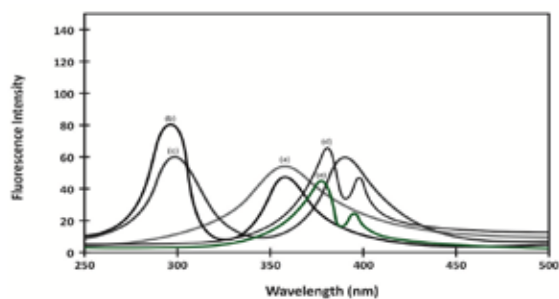


Fig.2(i)

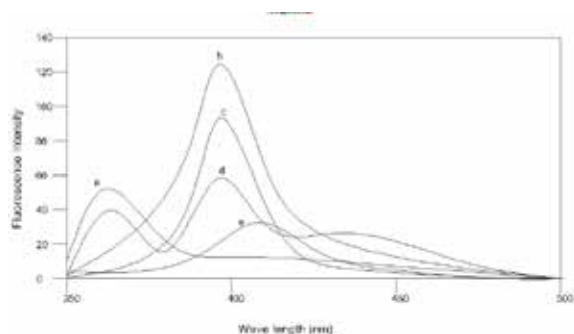


Fig.2(ii)

Fig.2 Fluorescence Spectra of (i) 4-(Phenylazo)benzoic acid and (ii) 2-(4-Hydroxyphenylazo)benzoic acid in (a) Ethylacetate (b) Methyl Ethyl Ketone (c) 2-Propanol (d) Methanol and (e) Water

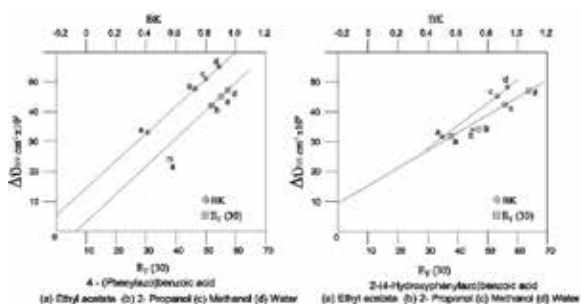


Fig. 3

In this study, the stokes shifts (Table 1 and Fig .3) of the above molecules were determined in different solvents of varying polarities are correlated with the BK [6] and $E_T(30)$ [7] parameters. Fig.3 indicates that in aprotic solvents the unspecific interactions are the key factors in shifting the fluorescence maxima towards the red for these molecules. From the slopes of the plots it is evident, these interactions are large due to the increasing dipole moment of excitation. Rigid molecules having only a limited degree

of freedom, the solvent cage changes the structure of the molecules, hence the dipole moment of the molecules changed in the excited state. This process induces a large stokes shift in polar solvents. A good correlation of stokes shift with the $E_T(30)$ Scale indicates the fact that the dielectronic solute -solvent interactions are responsible for the solvatochromic shifts in these molecules.

Absorption and fluorescence maxima (λ_{max}) of 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid at different concentrations of α -CD (30:1)

NO.	Concentration of α -CD(M)	4-(Phenylazo)benzoic acid			2-(4-Hydroxyphenylazo)benzoic acid		
		λ_{abs}	λ_{em}	λ_{exc}	λ_{abs}	λ_{em}	λ_{exc}
1.	Water	329	4.03	385	343.4	3.74	398
		237.5	3.82	369	246.2	3.24	374
2.	0.002	328.5	3.99	383	343	3.78	401
		237.2	3.75	370	246	3.38	374
3.	0.004	328.8	4.02	400	342.5	3.82	409
		235.4	3.75	369	244.6	3.43	373
4.	0.006	325.4	4.01	399	342.1	3.87	399
		235	3.75	369	242.6	3.53	372
5.	0.008	325.3	4.04	398	342	3.82	397.5
		234.2	3.85	368.7	241.7	3.54	371.5
6.	0.010	325	4.02	397	340.7	3.61	397.3
		234	3.8	367	241	3.57	370
7.	Excitation Wave Length		320	340			
8.	Binding Constant (M^{-1})		589.7	1295	317.46	999.7	
	Molar Extinction		-14.81	-18.49	-18.29	-18.23	

Effects of α -CD

The absorption and emission maxima and spectra of 4-(Phenylazo)benzoic acid and 2-(4-Hydroxyphenylazo)benzoic acid are shown in Table 2 and fig.4, fig.5, fig.6 and fig.7. The absorption and emission maxima of both the molecules are blue shifted with gradual increase in the molar extinction coefficient. The increase in the absorbance and fluorescence intensity is due to the encapsulation of these molecules in α -CD cavity and it is attributed to detergent action of α -CD. [8]. These results indicate that both the compounds are entrapped in the α -CD to form inclusion complexes.

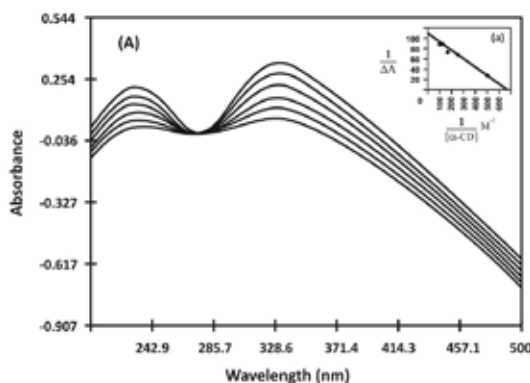


Fig.4

(A) – Absorption Spectra of 4-(Phenylazo)benzoic acid, (a) Benesi - Hildebrand Plot for 1:1 Complex with α -CD

The presence of isosbestic point in the absorption spectra suggests both the molecules formed 1:1 complexes with α -CD. In order to determine the stoichiometry of the inclusion complex, the absorbance and fluorescence dependence behaviours of the molecules on α -CD

were analysed using the Benesi - Hildebrand equation [9] for 1:1 Complex as shown below.

$$\frac{1}{A - A_0} = \frac{1}{A' - A_0} + \frac{1}{K[A - A_0][\alpha - CD]} \quad \text{--- (1)}$$

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K[I - I_0][\alpha - CD]} \quad \text{--- (2)}$$

Where K is the formation constant, A_0/I_0 is the initial absorption/ fluorescence intensity of the molecules, A'/I' is the absorption / fluorescence intensity of α -CD inclusion complexes and A/I is the observed absorption/ fluorescence intensity. According to equation (1) and (2) a plot of $1/A - A_0$ / $1/I - I_0$ Vs $1/[\alpha - CD]$ gives a linear line as shown in fig 4,5,6 and 7. This analysis reflects both the molecules form 1:1 inclusion complexes with α -CD.

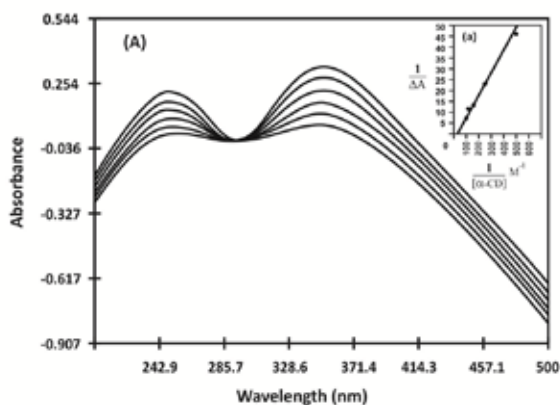


Fig.5

(A) – Absorption Spectra of 2 – (4-(Hydroxyphenylazo)benzoic acid, (a) Benesi - Hildebrand Plot for 1:1 Complex with α -CD

The free energy was calculated from the formation constant (K)

$$\Delta G = -RT \ln K \quad \text{--- (3)}$$

From the table 2, the value of thermodynamic parameter ΔG for the formation of the guest molecule to α -CD is -ve, which suggests that the inclusion process proceeded simultaneously at 303 K. The experimental results indicate that the inclusion reactions of the α -CD with the molecule are exothermic process.

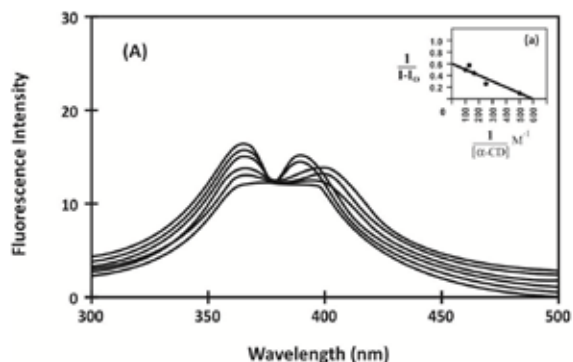


Fig.6

(A) – Fluorescence Spectra of 4 –(Phenylazo)benzoic acid , (a) Benesi - Hildebrand plot for 1:1 Complex with α -CD

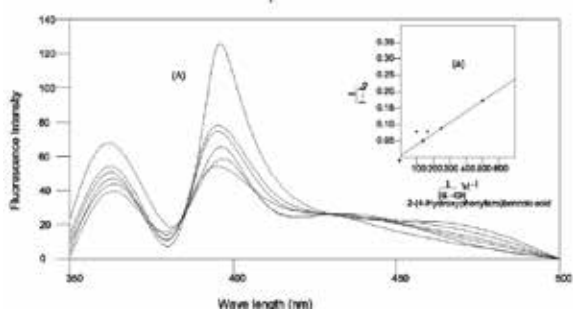


Fig.7

(A) – Fluorescence Spectra of 2 –(4-(Hydroxyphenylazo)benzoic acid , (a) Benesi - Hildebrand plot for 1:1 Complex with α -CD

Several driving forces have been postulated for the inclusion complexation of CD with guest compounds [10]. Tabushi [11] Proposed a thermodynamic model for the process of CD -Inclusion complex formation. Based on the thermodynamic parameter (ΔG) calculated for the inclusion of complexes we conclude that the hydrogen bonding interaction, van der Waals interaction and breaking of the water cluster around the polar guest compound mainly dominated the driving force for the inclusion complex formation.

Conclusion

The following conclusions can be drawn from the above studies. Solvent studies show that the absorption and emission maxima of 2-(4-(Hydroxyphenylazo)benzoic acid are red shifted than 4-(Phenylazo)benzoic acid. α -CD studies reveal that both the molecules form 1:1 complexes with α -CD. This study also confirms that inclusion process is spontaneous and van der Waals interaction forces and hydrophobic interactions are the driving forces for the formation of inclusion complexes.

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