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PHYSICS

STUDY ON THE INTERACTION OF COUMARIN WITH β – CYCLODEXTRIN BY ABSORPTION AND FLUORESCENCE SPECTROSCOPY

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Abstract
The ability of β-cyclodextrin (β-CD), to break the aggregate of the coumarin and to form 1:1 inclusion complexes has been studied by absorption and fluorescence spectroscopy. Experimental conditions including concentrations of β-cyclodextrin were investigated for the inclusion formation in detail. The formation constants are calculated by using steady – state fluorimetry. The infrared spectroscopy and scanning electron microscopy were studied to conform the inclusion complex.

Keywords: Coumarin; βCD; Fluorescence; absorption

Introduction
Cyclodextrins as host molecules have been the subject of numerous investigations because of their abilities to bind various organic compounds into their cavities in aqueous solution [1]. The binding forces between host and guest have been attributed to weak interactions such as hydrogen bonding, vander walls and hydrophobic interactions. On this basis, modified CDs with appropriate functional groups can act as enzyme mimiccatalysts or receptors [2,3]. Meanwhile, several modified cyclodextrins bearing a fluorescence probe have been synthesized and their complexation behaviours have been investigated [4,5].

CDs are torus – shaped cyclic oligosaccharides composed of six, seven, or eight D- glucopyranose units (α, β, γ – CD, respectively). A variety of organic compounds can be included in their central cavities in aqueous solution [6]. It was reported that β-CD formed inclusion complexes with coumarin derivatives [7] as well as with naphthalene [8] and dansyl [9] derivatives. In this report, we describe the spectroscopic analysis of the β-CD inclusion complex with Coumarin.

Experimental
Reagents
Coumarin was of analytical reagent grade. (Sigma Aldrich, Banglore). It's stock solution of 5 x 10^{-4} mol/l was prepared by directly dissolving its crystal into water. β-CD (Sigma Aldrich, Banglore) was recrystalized twice from double – distilled water before use. All other reagents were analytical – reagent and used without further purification. Double distilled water was used throughout.

Apparatus
The absorption and fluorescence measurements were performed with a JASCO– UVIDEC. – 650 spectrophotometer and a JASCO model FP ~ 550 spectro fluorometer respectively. The IR spectra were recoreded on AVATAR – 360 series FTIR spectrometer and microscopic morphological structure measurements were performed with JEOL JSM 5610 LV scanning electron microsope (SEM).

Results and Discussion
Fluorescence spectra of coumarin in β-CD solution
Coumarin itself could emit the fluorescence spectra in the absence of βCD at 362 nm and 352 in DMF and DMSO respectively. Addition of different βCD, an enhanced florescence emission of coumarin was observed. These changes were due to the interaction between coumarin and βCD implying the formation of coumarin – βCD, inclusion complexes. The increase of fluorescence intensity resulted from the increase of fluorescence quantum yield, which came from the increase of electronic density after coumarin molecule entered hydrophobic cavity of βCD. The absorption and fluorescence spectra of coumarin were studied in DMSO and DMF and the experimental results have been compiled and presented in Table 1.

Table 1. Absorption, log ε fluorescence spectral data (nm) and stoke's shift (cm^{-1}) of coumarin in different solvents

Solvents	λ_{abs} (nm)	log ε x 10^5	λ_{flu} (nm)	Stoke's shift (cm^{-1})
DMF	291.5	2.4646	362	6681
DMSO	292	2.465	352	5837

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Absorption spectra of coumarin and determination of Kg value

A plot of $\left(\frac{1}{A_0 - A}\right)$ versus $\left(\frac{1}{\beta - CD}\right)$ yields as a straight line as shown in fig.1. from the slope values of this plot, Kg is evaluated and presented in Table.2. The formation constant in DMF is considerably greater than that in DMSO.

Fig. 1 Plot of $\left(\frac{1}{A_o - A}\right)$ versus $\left(\frac{1}{\beta - CD}\right)$ for coumarin

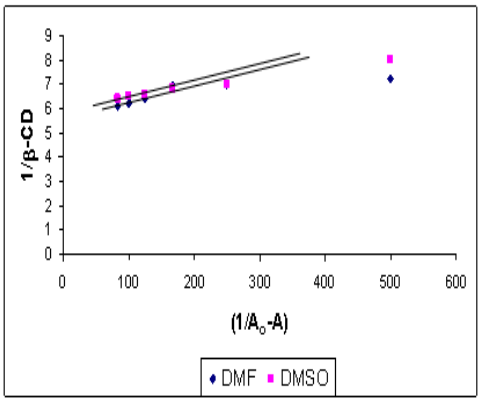


Table 2. Formation constant K (m^{-1}) and free energy ΔG (KJ mol^{-1}) of coumarin with βCD

Solvents	βCD			
	Kg (m^{-1})	Ke (M^{-1})	ΔG_g	ΔG_e
DMF	0.012	0.00035	11.141	20.046
DMSO	0.009	0.0336	11.866	8.548

Inclusion complexation of coumarin with β-cyclodextrin

Coumarin itself existed absorption at 291nm and 312nm in DMF and 292nm and 312nm in DMSO. In the presence of β-CD the original absorption maximum of coumarin were observed.

Fluorescence spectra of coumarin in β-CD solution

Coumarin itself could emit the fluorescence spectra in the absence of βCD at 362 nm and 352 in DMF and DMSO respectively. Addition of different βCD, an enhanced florescence emission of coumarin was observed. These changes were due to the interaction between coumarin and βCD implying the formation of coumarin – βCD, inclusion complexes. The increase of fluorescence intensity resulted from the increase of fluorescence quantum yield, which came from the increase of electronic density after coumarin molecule entered hydrophobic cavity of βCD. The absorption and fluorescence spectra of coumarin were studied in DMSO and DMF and the experimental results have been compiled and presented in Table 1.

Effect of βCD concentration

Coumarin concentration was held constant at 5.0 x 10-4 mol/l, while βCD was varied from 0.002 mol/l to 0.012 m/l. The fluorescence intensity of the coumarin was gradually enhanced with an increases of βCD. Concentration until the stable inclusion complex was formed.

Formation constants of coumarin – βCD complex

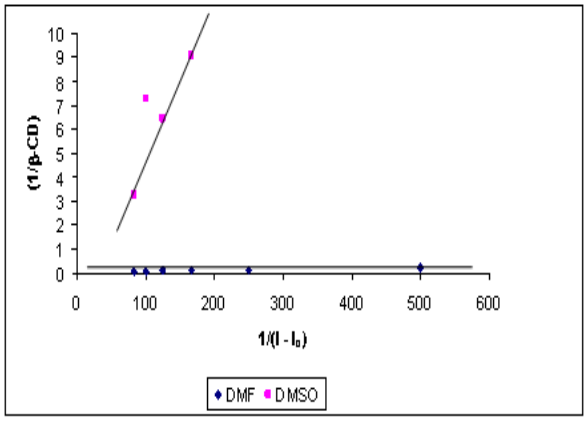
Inclusion formation constant (Ke) was a measure for complexing capacity of **β**CD. The formation constant for the excited state of coumarin with βCD in DMSO and DMF were evaluated assuming a 1:1 (βCD: coumarin) inclusion model. The inclusion process is as follows.

$$\beta CD + Cou \rightleftharpoons \beta CD - Cou.$$

Where the symbols βCD, cou and βCD – Cou represent beta cyclodextrin, coumarin and the inclusion complex respectively.

Fig.2 shows the plot of $\left(\frac{1}{I-I_0}\right)$ versus $\left(\frac{1}{\beta-CD}\right)$. The formation constant of the coumarin -βCD complexes were listed in Table 2. The formation constants (K_e) followed the order Kg in DMSO > Kg in DMF. The free energy change is calculated from the formation constant and these values have been presented in Table 2.

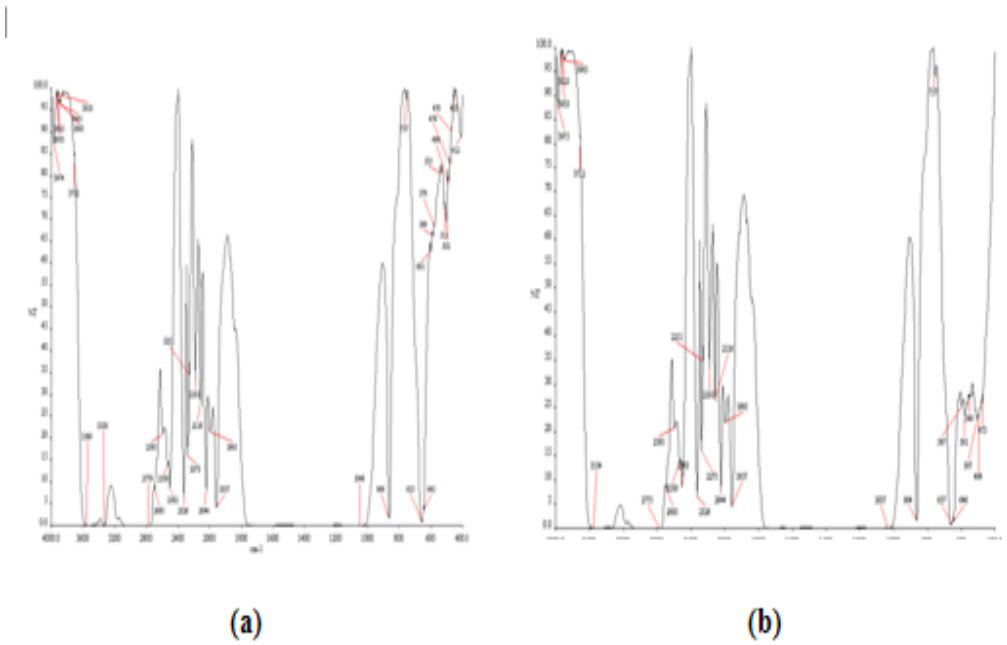
Fig. 2 Plot of $\left(\frac{1}{I-I_o}\right)$ versus $\left(\frac{1}{\beta-CD}\right)$ for coumarin



FT – IR spectral Studies

The FTIR spectra of coumarin and (coumarin + βCD) inclusion complex are shown in Fig. 3) respectively. The tentative assignments are given in Table 3. The results confirms the inclusion complex formation of coumarin and βCD.

Fig. 3 FTIR Spectra of Coumarin a. Coumarin, b. Coumarin + βCD complex



(a) (b)

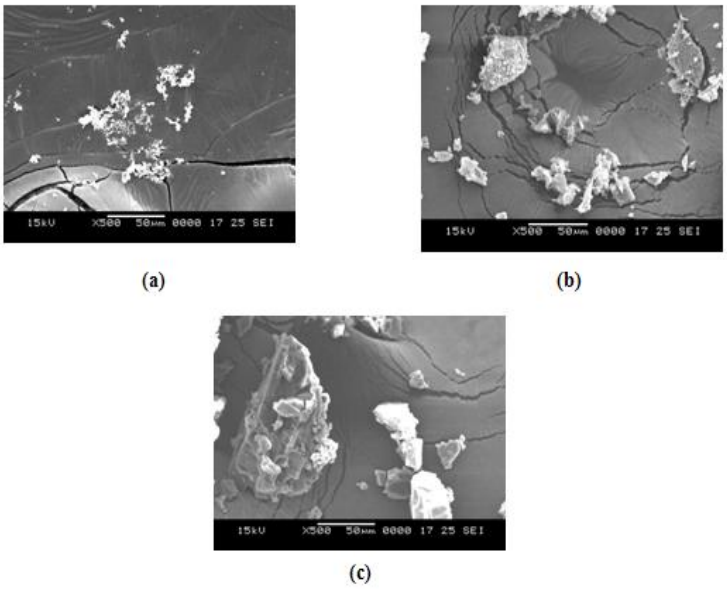
Table 3. Tentative assignments for coumarin behave and after the formation of inclusion complex

FTIR frequency (Cm-1)			
Coumarin	Inclusion	Intensity	Tentative assignment
2779	2775	W	C-H Stretching
2693	2693	W	Hydroxyl stretching
2593	2593	W	S-H stretching
2530	2530	W	S-H stretching
2502	2503	W	S-H stretching
2326	2326	M	C = N stretching
2272	2273	M	C = N stretching
2251	2251	M	C = N stretching
2181	2181	VS	C = N stretching
2116	2116	VS	N = C = N antisym stretch
2044	2044	-	-
1995	1995	-	-
1957	1957	-	-
1048	1037	VS	C-O stretch
866	864	VS	CH2 out of plane wage
757	757	VS	CH out of plane bending
655	657	VS	C-C-CHO bending
645	646	S	C-C-CHO bending
601	597	S	O-C = O bending
589	581	S	C = C – H bending
578	-	M	C – C – CN bend
535	549	S	C = O out of plane bending
515	507	M-S	C – C = O bend
502	499	M	C – C out of plane bending
490	-	-	-
479	473	VW	C – C out of plane bending
470	-	S	C – C =) bend
453	-	S	= CH_2 + wisting
412	-	W	C – OH bending

Microscopic morphological observation

First, we observed powdered form of coumarin and βCD separately by scanning electron microscope, then we also observed powdered form of inclusion complex Fig.4. Pictures clearly elucidated the difference of powder of each other. It can be assumed as a proof of the formation of new inclusion complex.

Fig. 4 Scanning electron microscope photograph of (a) Coumarin, (b) β-CD (c) Coumarin + β-CD



Conclusion

β-Cyclodextrin breaking the aggregate of the coumarin and forming 1 : 1 inclusion complexes have been studied by absorption and fluorescence spectroscopy and conformed by FTIR and SEM analysis. There will be potential applications in medical and biological applications.

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