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Research Article

STUDY ON THE SOLID INCLUSION COMPLEX OF COUMARIN-1 WITH β-CYCLODEXTRIN

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ABSTRACT

Addition of β-Cyclodextrin to aqueous solution of Coumarin-1 results in the deaggregation of the dye to its monomer form. This is due to the association of monomeric Coumarin-1 to the cyclodextrin. The absorption and emission spectra of the aqueous dye solution have been described. This has also been proved by UV-Vis, FTIR and Scanning Eelectron Microscope (SEM). Ground state (Kg) and excited state (Ke) formation contants have been calculated and reported.

Keywords: Coumarin-1, β-Cyclodextrin, Fluorescence, FTIR.

INTRODUCTION

Rhodamine dye are extensively used as laser dyes. They have often been used to characterize novel laser system, examine the efficiency of various pump sources and obtain high-power lasers [1]. These dyes are commonly used in alcoholic solutions, even though the thermal properties of water are superiror to those of any alcohol. Specifically, the variation of the refractive index of water with temperature is much smaller than that of ethanol[2]. This characteristic is particularly important for the development of – power laser and for continuous-wave laser. The main reason for not using aqueous dye solutions is the extensive aggregation of the dye leading to the formation of dimers or higher aggregates[1,3,4]. Such aggregates quench internally the dye fluorescence and prevent effective lasing. This difficultly has been dealt with in the past by adding detergents or using solvent mixtures, leading in fact to laser action from such modified solutions. Yet, the concentrations of the additives are often in the range of 4-24%, high enough to adversely affect the superior thermal properties of the aqueous media[2]. Cyclodextrins (CD) are cyclic polysugars composed of glucose units linked by 1-4 glycoside bonds[5]. The hydrophobic cavity present in the CD structure is capable of binding organic substrates including dye molecules[6,7]. The fluorescence properties of dye are affected when associated with CD, and it has been shown that inclusion complexes exhibit considerable increase in the fluorescence quantum yields[8-10]. Either monomer or dimer emission can be enchanced depending on the size of the cavity. Recently, it has been demonstrated that dimer formation of thionine in aqueous solution is prevented in the presence of cyclodextrins[11]. This has been attributed to the association of thionine monomer to the CD cavity maintaining a low concentration of the free dye form in water, at which the monomer predominates. Absorption and fluorescence studies have been carried out by many authors[12,13].

MATERIALS AND METHODS

Materials

All the reagents used were analytical ones. Prior to their use the purity of the organic solvents (Ethanol, DMF & DMSO) was checked via fluorescence. βCyclodextrin and Cou-1 were purchased from Sigma. Double – distilled water was used throughout. Stock aqueous solutions of the βCyclodextrin (0.002M – 0.012M) were prepared daily and maintained at room temperature for use.

Stock standard solution of coumarin-1 was prepared in 5 x 10^{-5}M concentration. Working solutions were analyzed before each measurement of fluorescence, and the UV-VIS spectrum from 200 to 800nm was recorded.

Apparatus

Fluorescence spectra were recorded using a JASCO model FP∼550 spectrofluorometer, the light source of which is a 150W xenon lamp. Absorption spectra were obtained using a JASCO – UVIDEC – 650 Spectrophotometer. The IR spectra were recorded on an AVATAR – 360 Series FTIR spectrometer.The Rh6G fluorescence intensity was measured at the maximum emission wave length of 461nm, 433nm and 442nm after excitation of solutions at 382nm,372nm ,375nm in water, DMF, and in DMSO respectively. All the ^{1}H NMR experiments were performed on Bruker advanced DRX 500 MHZ super conducting NMR spectrometer. The study of Microscopic morphological structure and measurements were made with the JEOL JSM 5610 LV scanning election microscope (SEM).

Preparation of sample for SEM

Accurately weighed 0.012M βCD was added to1ml of double distilled water and stirred over an electromagnetic stirrer until it was dissolved. The βCD solution was then slowly poured into 5 x 10^{-5} M concentrated coumarin-1 solution. The above mixed solutions were continuously stirred for 48 hours at room temperature. The reaction mixture was put to dry in an oven at 150°C for 12 hours to obtain the powder product, which is the inclusion complex of coumarin-1 and βCD used in the study.

RESULTS AND DISCUSSION

Effect of Solvents

The absorption and fluorescence spectra of coumarin-1 were studied in different solvents and the experimental results have been compiled and presented in Table 1.

The absorption spectra of coumarin-1 in all solvents consist of absorption bands of longer wavelengths. H-O transition may account for the display by the compound of a broad visible band of considerable charge transfer (CT) on emission.

The absorption spectrum of coumarin-1 in water is largely blue-shifted than in other solvents DMF and DMSO but their spectra do not exhibit marked changes in their shape.

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

Solvents	λ_{abs} (nm)	log ε ($M^{-1}cm^{-1}$)	λ_{flu} (nm)	stokes shift (cm^{-1})
Water	382	6.883	461	4486
DMF	372	6.871	433	3787
DMSO	375	6.875	442	4042

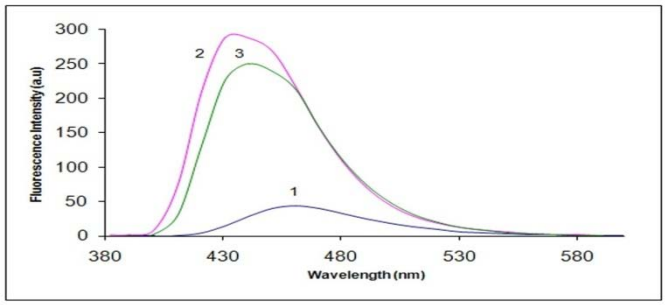

Fig. 1: Fluorescence spectra of Coumarin-1 in different solvents 1.Water, 2. DMF, 3. DMSO

Fig. 1. depicts the fluorescence spectra of coumarin-1 in water and solvents DMF and DMSO and the compiled relevant data have been presented in Table 1.

The large red shift in fluorescence when the width of the band is maximum and of increased polarity.

[DMF (6.4) < DMSO (7.2) < water (9)]

It is evidence of the hydrogen bonding tendency of the solvents. With different solvents a large Stokes- shift emission band was observed and the sensitivity of the band to change in solvent polarity leads to the inference that greater charge transfer takes place.

Absorption and Fluorescence Spectral Studies

Fig. 2 shows the absorption spectra of coumarin-1 in the absence and presence of different concentrations of cyclodextrin with absorption maxima at 382nm in water [535.50nm in DMF and 540nm in DMSO respectively]. A red shift observed in the presence of βCD leads the inference βCD is interacting with coumarin-1.

The effect of βCD on the fluorescence spectra of coumarin-1 is more pronounced than its effect in absorption spectra. Only the maximum intensity of fluorescence increases and no shift (Red or blue) was observed. There is an increase in the intensity of fluorescence with the addition of βCD up to a concentration of 12 x 10^{-3} mol dm^{-3}. Fluorescence intensity of Cou-1 is higher in DMSO (664 A.U) than in solutions of Water (520A.U) and DMF (468A.U). Enhancement of fluorescence intensity suggests the formation of the inclusion complex of coumarin-1 and βCD. An increase in the fluorescence intensity on the formation of an inclusion complex was observed earlier [14-16]

Data present in Table 1 depict the absorption and emission maxima of coumarin-1, in βCD solutions. Absorption peak was observed at 382nm.

It can be seen that fluorescence characteristics of coumarin-1 in the solvents water, DMF and DMSO undergo drastic changes in the presence of βCD (Fig. 3).

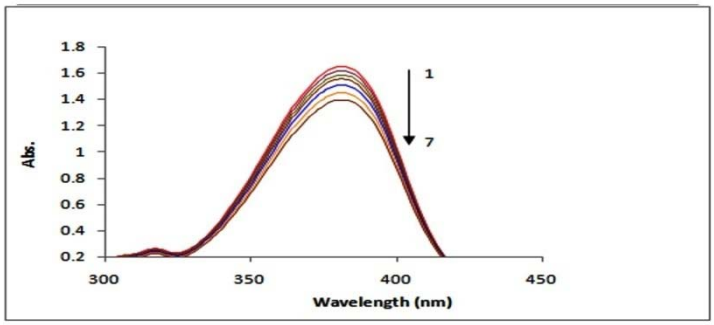

Fig. 2: Absorption spectra of in Coumarin-1 different βCD concentrations (mol dm^{-3}) in water (1) 0, (2). 0.002, (3). 0.004, (4). 0.006, (5). 0.008, (6). 0.010, (7). 0.012.

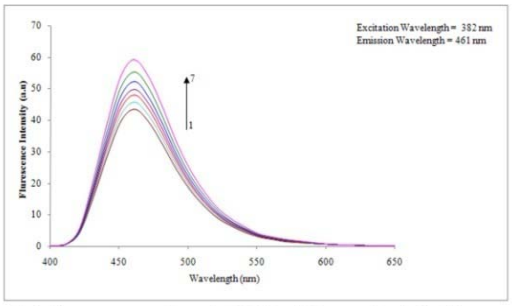

Fig. 3a. Fluorescence spectra of Coumarin - 1 in different βCD concentrations (mol dm-3) in water. (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

Fig. 3a: Fluorescence spectra of Coumarin-1 in different βCD concentrations (mol dm^{-3}) in water (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012.

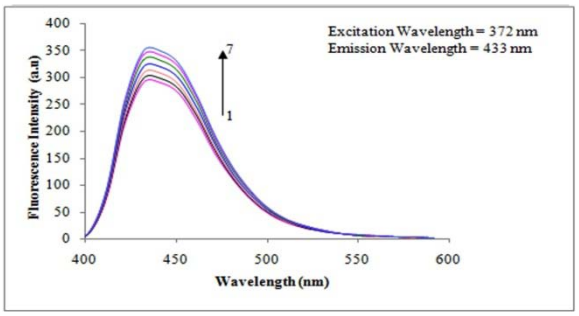

Fig. 3b. Fluorescence spectra of Coumarin - 1 in different βCD concentrations (mol dm^{-3}) in DMF. (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

Fig. 3b: Fluorescence spectra of Coumarin-1 in different βCD concentrations (mol dm^{-3}) in DMF (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

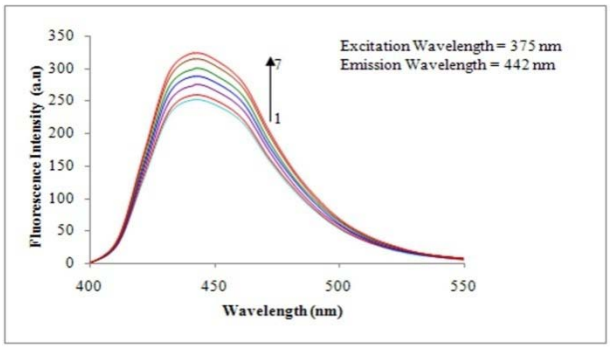

Fig. 3c: Fluorescence spectra of Coumarin-1 in different βCD concentrations (mol dm^{-3}) in DMSO (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

The formation constant of the βCD: coumarin-1 complex was determined analyzing changes in the maximum of the intensity of absorption and fluorescence with different concentrations of βCD. Using Benesi – Hildebrand relation[17]the formation constant of the complex (K) was determined; it indicates the formation of 1:1 complex of coumarin-1 and βCD; the equilibrium can be written as,

$$\text{cou-1} + \beta\text{CD} \overset{K}{\rightleftharpoons} \text{Cou-1: } \beta\text{CD}$$[18]

Where cou-1, βCD and cou-1: βCD represent, coumarin-1, beta cyclodextrin and the 1:1 inclusion complex of βCD and Cou-1 respectively.

Plotting $\left(\frac{1}{\text{Ao} - \text{A}}\right)$ and $\left(\frac{1}{\beta - CD}\right)$ will result in a straight line as in Fig. 4.

The formation constants in DMSO are considerably higher in value than similar constants in water and DMF solvents. This is due to the dipole moment values of the solvents.The dipole moment of water is 1.85D,DMF is 3.82D and DMSO is 3.96D.

With increasing concentration of βCD the resulting straight line plotted with $\left(\frac{1}{\text{I} - \text{Io}}\right)$ and $\left(\frac{1}{\beta - \text{CD}}\right)$ changes with the intensity of fluorescence (Fig. 5).

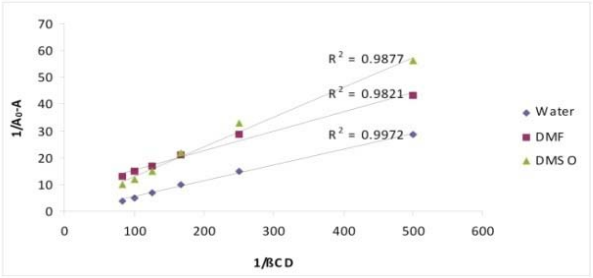

Fig. 4: Plot of $\left(\frac{1}{A_0 - A}\right)$ versus $\left(\frac{1}{\beta - CD}\right)$ for Coumarin-1

The ground state formation constant (Kg) has been evaluated from the slope values of this graph, and been tabulated and presented in Table 2.

Table 2: Formation constant k (M^{-1}) and free energy ΔG (kJmol^{-1}) of coumarin-1 with βCD

Solvent	βCD			
	Kg (M^{-1})	Ke (M^{-1})	ΔGg	ΔGe
Water	0.08	0.0012	6.362	16.942
DMF	0.09	0.0002	5.877	21.456
DMSO	0.12	0.0001	5.178	22.541

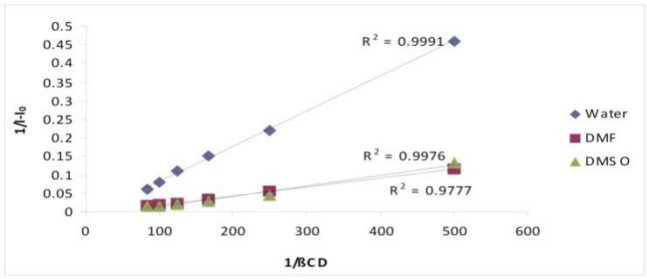

Fig. 5: Plot of $\left(\frac{1}{I - I_0}\right)$ versus $\left(\frac{1}{\beta - CD}\right)$ for Coumarin-1

The excited state formation constant (Ke) has been evaluated from the slope values.

Free energy change can be calculated from the formation constant 'K' with the equation

$\Delta G = - RT \ln K$

The change in free energy ΔG, (ΔGg -ground state, ΔGe-excited state) increases according to the increase of the dielectric constant of the solvents.The values have been presented in Table 2.

The formation constant of the absorption spectrum of the dimer of coumarin-1 was evaluated and the geometric structure of the aggregate was determined using exciton theory[19]. Deaggregation in concentrated solutions and variable complex formation in dilute solutions were proposed to account for the β-cyclodextrin induced effects[20].

The large red shifted emission maxima in all solvents would indicate a dipolar interaction between the molecules of the solute and solvent. The nature of emission is not always easy to ascertain, since it can be the result of a variety of causes including dimer formation (or other kinds of aggregates) in the ground state excimer emission or charge transfer processes[14,17]. In the case of coumarin-1, there may be the possibility of the formation of dimers. Change in the free energy of the complex is higher in its excited state than in its ground state in all the three solvents viz., water, DMF and DMSO, which indicates the more strong inclusion complex was formed in excited state than in ground state. It can be seen that the difference in change in free energy between its ground and excitation states of the complexes in the three different solvents is in the following order:

DMSO > DMF >Water.

Life Time Spectral Study

The steady-state fluorescence and absorption measurement is not sufficient enough o have a clear picture of the formation of inclusion complex of cou-1 and βCD derivatives. Thus to have a better knowledge of the formation of inclusion complex, time resolved fluorescence experiments were performed for cou-1 and also for inclusion complexes. [Cou-1+ βCD]. Fig. 6 gives the fluorescence decay curves of (i) Cou-1 and (ii) the inclusion complex of Cou-1 and βCD.

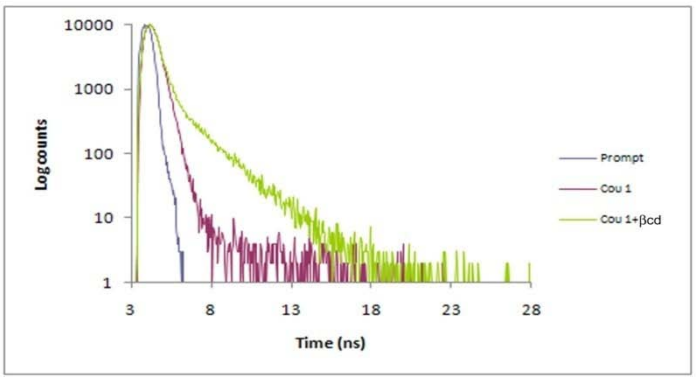

Fig. 6: Fluorescence decay curves of coumarin-1 and the inclusion complex of coumarin-1 with βCD

The Lifetimes and amplitudes of Cou-1 with and without βCD derivatives are given Table. 3.

Table 3: Fluorescence lifetime and amplitude of Coumarin-1 with βCD

Sample	Life time (Sec.) τ	Relative amplitude	χ^2	Standard deviation
Coumarin-1	3.69×10^{-10}	100	1.43	6.57×10^{-4}
Coumarin-1 + βCD	3.63×10^{-10}	78.15	1.02	7.60×10^{-4}
	1.91×10^{-9}	21.85		9.88×10^{-5}

The time – resolved fluorescence of Cou-1 with βCD derivatives shows bi-exponential decay indicating the equilibrium between free and complexed forms. The χ^2 values for the single bi-exponential fitting are less than 1.5.

FTIR Spectral Study

The FTIR spectra of coumarin-1 and the solid inclusion complex are shown in Figs.7a and 7b respectively and the values have been presented in Table 4.

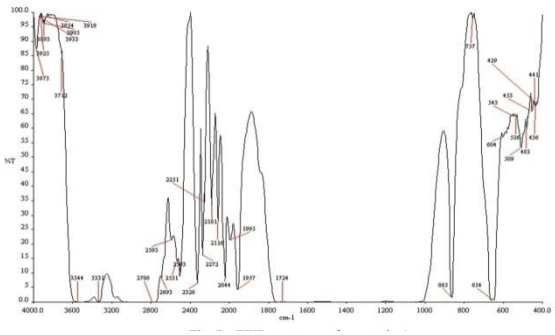

Fig. 7a: FTIR spectrum of Coumarin-1

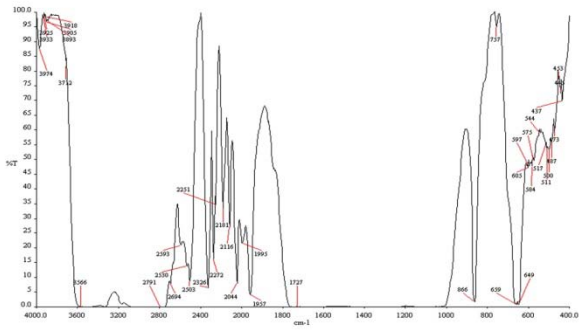

Fig. 7b: FTIR spectrum of (Coumarin-1 + βCD) complex

Table 4: **Difference in FTIR absorption Peak intensities of coumarin-1 before and after the formation of inclusion complex**

Tentative assignment	Courmain-1 (cm^{-1})	Inclusion complex (βCD) (cm^{-1})	Difference in intensitises prior to and after (%)
Hydroxy stretching	2693	2694	1
S – H stretching	2593	2593	1
S – H stretching	2531	2530	1
S – H stretching	2503	2502	1
C = N stretching	2326	2326	1
C = N stretching	2272	2272	2
C = N stretching	2251	2251	3
N = C = N antisym stretching	2181	2181	2

The comparison of coumarin-1 with rhodamine 123 non-radiative rate constants indicated a relative decrease, suggesting that C-H and other lower frequency modes of vibrational energy transfer to solvent modes are less efficient than N-H stretching modes[21,22].

The absorption intensity of the inclusion complex is significantly weaker than that of the intensity of coumarin-1. The inclusion complex IR peaks in the range 2000 cm^{-1}--3000 cm^{-1} and is 1-3% weaker than that of the coumarin-1 molecule. As there is no change in the wavelength other than the change in absorption intensities, it can be concluded that 1-3% weaker inclusion complex was formed of coumarin-1 and βCD.

^{1}H NMR Spectral Studies

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy has proved to be a useful tool in the study of β-CD inclusion complexes[23,24]. ^{1}H NMR spectroscopy provides an effective means of assessing the dynamic interaction site β-CD with that of the guest molecules. The basis of information gained from NMR spectroscopy is located in the shifts, loss of resolution and broadning of signals observed for the host and guest protons.Although, only limited information can be obtained from the ^{1}H NMR data, the observation of slight up field shifts of the guest protons in the presence of β-CD is consistent with the inclusion of each guest in to the cavity.

The H-3 and H-4 proton are located in the interior of the β-CD cavity and it is therefore likely that the interaction of the host with the β-CD inside the cavity will affect the chemical shifts of the H3 and H4 protons. In order to obtain evidence in support of the structure of the β-CD inclusion complex with coumarin-1 we measured ^{1}H NMR spectra of these Cou-1 molecules with and without β-CD. These are shown in figs 8a,8b &8c.

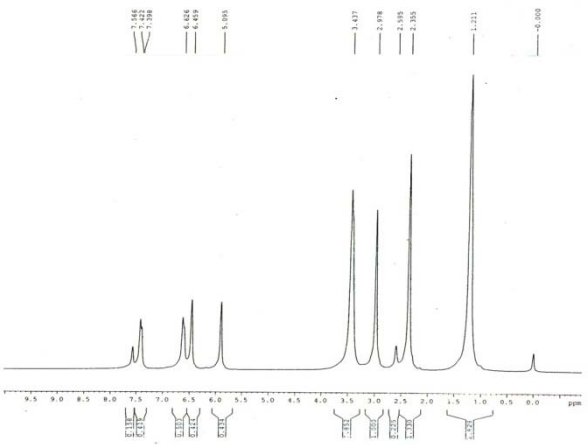

Fig. 8a : ^{1}H NMR spectrum of Coumarin-1

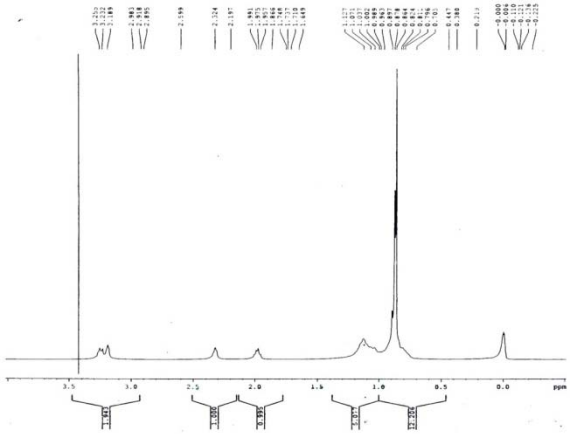

Fig. 8b : ^{1}H NMR spectrum of βCD

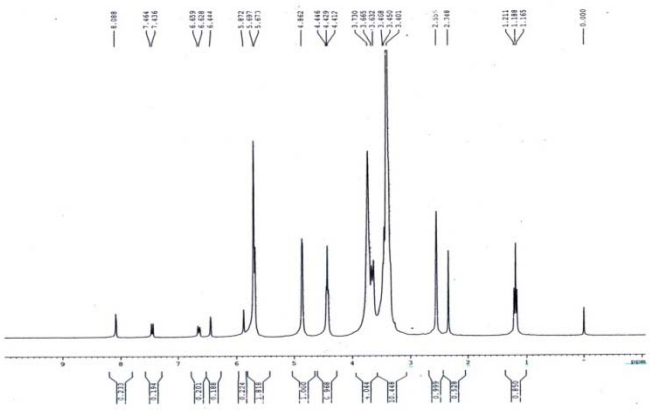

Fig. 8c : ^{1}H NMR spectrum of (Coumarin-1 + βCD) complex

The addition of coumarin-1 to the solution of β-CD results in a up field shift for the Cou-1 protons (Table 5).

Table 5: ^{1}H NMR Chemical shift data of coumarin-1inclusion complex

Proton	Coumarin-1	βCD	Complex	Δδ coumarin-1 & complex
H-1	2.9	2.3	4.8	1.9
H-2	3.4	3.3	5.6	2.2

Scanning Electron Microscopic Studies

The powdered form of coumarin-1, βCD and the powdered form of the inclusion complex were observed through the scanning electron microscope and what was observed has been given in figs.9a,9b and 9c .It could be seen that the structure of the inclusion complex is different from that of the coumarin-1 and βCD which is enough proof of the formation of a new inclusion complex.

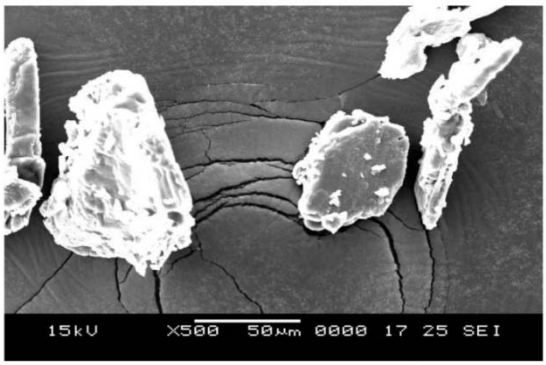

Fig. 9a: Scanning electron microscope photograph of Coumarin-1

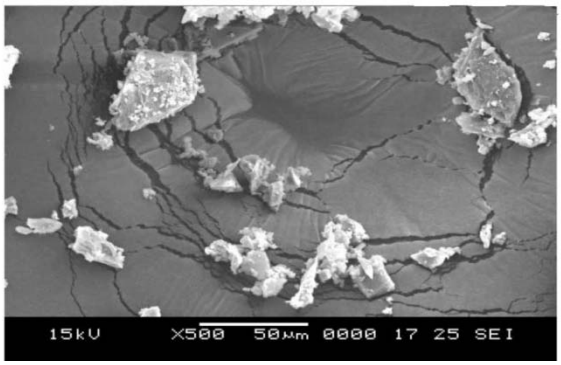

Fig. 9b: Scanning electron microscope photograph of βCD

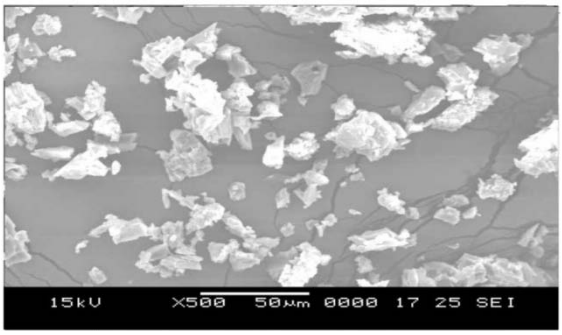

Fig. 9c: Scanning electron microscope photograph of (Coumarin-1+ βCD) complex.

CONCLUSION

The study demonstrates the effects of βCD on the photophysical properties of coumarin-1 in water , DMF and DMSO. Association of monomer coumarin-1 to the hydrophopic cavity of β-Cyclodextrin induces the dissociation of dimers to the monomer dye forms. FTIR,and SEM results suggest. coumarin-1formed a solid inclusion complex with βCD.

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