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Studies on the pyrene-β-cyclodextrin and β-cyclodextrin polymer guest-host inclusion complexes by absorbance and fluorescence spectroscopy

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Abstract

Linera highly water-soluble β -CD based polymer was synthesized by controlled temperature dependent reactivity of cyanuric chlorine in alkaline medium by one pot condensation polymerization. The steady-state absorbance and fluorescence profile of pyrene has been investigated in aqueous media as a function of β -CD and β -CD polymer concentrations. The absorbance and fluorescence emission intensity of pyrene was found to be enhanced synergistically as the concentration of β -CD or β -CD polymer increases. The binding constant for the pyrene inclusion complex with β -CD/ β -CD polymer were calculated using Benesi-Hildebrand equation and it was found that the binding constant for the pyrene/ β -CD polymer inclusion complex was more than three times higher than that of the pristine β -CD/pyrene complex.

Keywords: β -cyclodextrin, β -cyclodextrin polymer, pyrene, adamantol, inclusion complex, fluorescence

1.0 Introduction

Fluorescence is widely used in microscopic imaging, dating in archaeology, medical research, forensic science, biotechnology and diagnosis [1-3]. The enhance fluorescence has attracted great attention in recent years, in terms of the quantum yield and photostability of the fluorophore [4-5]. Molecular luminescence spectrometry has become a routine technique in many analytical applications [6-7]. In many cases, molecular luminescence spectrometry can yield a lower detection limit and greater selectivity than molecular absorption spectrometry. However, although most fluorophore show strong fluorescence in non-polar solvents, the solubility and intensity of luminescence is rather weak in polar solvents [8-9]. It is available from the number of reports that cyclodextrin enhance the fluorescence property of the fuorophores due to formation of an inclusion complex. The unique torus structural conformation of the CDs protects the fluorescing singlet state or the phosphorescing triplet state of the fluorophore from external quenchers [10-14]. The effective microenvironment of the cyclodextrin nonpolar cavity is likely to be similar to that of such non-polar oxygenated solvents. The CDs solution can improve the lower detection limit for hydrophobic fluorophore in

aqueous solution by increasing their solubility or for hydrophilic fluorophore by increasing solubility of the water-insoluble fluorescent compounds into which the fluorophore are incorporated [15].

polycyclic Pyrene is a water-insoluble aromatic hydrocarbon (PAH) consisting of four fused benzene rings, resulting in a flat (planar) aromatic molecule. Pyerene is smallest peri-fused colorless solid and useful fluorescence probe for studying the microenvironment within the cyclodextrin cavity. The fluorescence intensity of pyrene is very less in polar medium. The fluorescence property of pyerene is very sensitive to solvent polarity and microenvironmental changes [16-17]. Thus, in this work, we described the systematic study of the absorbance and fluorescence enhancement of pyrene in the presence of β -CD and β -CD polymer. The study was conducted over a wide range of concentration and binding constants were calculated for pyrene inclusion complex with β -CD and β -CD polymer using Benesi-Hidebrand equation [18].

2. Experimental

2.1 Materials

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 β -Cyclodextrin was obtained from Signet Chemical Corporation, Mumbai as a gift sample and dried overnight under a vacuum oven at 60°C before use. β -Cyclodextrin based polymer was synthesized by using temperature dependent reactivity of cyanuric chloride according to our previously developed method [19].

2.1Sample preparation for Fluorescence Anaysis

The pyrene 1 x 10^{-5} M solution was prepared in absolute dry ethanol and 1% w/v β -CD and β -CD polymer solutions were separately prepared in double distilled water 7.0 pH was maintained. From the pyrene solution 1 cm³ was added to the different volumes (1-5 cm³) of β -CD or β -CD polymer solution and then total volume of the mixture was made up to 6 cm³ with double distilled water. The mixtures were stirred for 8 h and then allowed to equilibrate overnight.



Sch. 1: Reaction scheme for the inclusion complex of pyerene by β -CD and β -CD polymer

3.0 Results ans Discussion

3.1 Uv-Vis Spectra

Formation of inclusion complex between pyrene and β -CD or β -CD polymer was confirmed by UV-Vis absorbance spectra. Figure 1 shows absorbance spectra of pyrene (1.66 x 10⁻⁶M) in aqueous solutions containing various concentrations of β -CD or β -CD polymer. The absorbance maxima of pyrene in the absence of β -CD or β -CD polymer are located at 335, 319, 305, 273 and 262 nm. On addition

of β -CD or β -CD polymer the absorbance bands of pyrene were slightly shift to red shift (ca. 4 nm) with increase in oscillator strength. The absorbance intensity of pyrene increases with increasing concentration of β -CD or β -CD polymer. This phenomenon was observed due to the fact that encapsulation of pyrene and electronic properties of pyrene are favorable in presence of non-polar hydrophobic cavity of β -CD.



Fig. 1: Uv-Vis absorbance spectra of pyrene (1.66 x 10^{-6} M) in aqueous solution of (A) β -CD and (B) β -CD-polymer at different concentrations: (a) 0.00 %, (b) 0.166 %, (c) 0.333 %, (d) 0.500 %, (e) 0.666 %, (f) 0.833 %

3.2 Fluorescence Emission Spectra

The photoluminescence emission spectra (excited at 340 nm) of the pyrene in aqueous solution containing various concentration of β -CD or β -CD polymer are shown in Figure 2. The fluorescence emission intensity was enhanced upon the addition of β -CD or β -CD polymer to a solution of pyrene (1.66 x 10⁻⁶M) in the range of 370 to 410 nm fluorescence band is attributed to the formation of pyrene monomer in non-polar cavity. Also there was no broadening of peak was observed after 410 nm which ascribed there was no pyrene dimer formation in the cavity. The molecular sizes of pyrene and β -CD cavity (internal diameter = 7.8°A) is capable of including only one pyrene

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molecule within the inner cavity. This phenomenon was observed due to the formation of inclusion complex which afford the rotation of the pyerene molecule is hindered, and the relaxation of the solvent molecules is considerably decreased. Both of these effects can result in a decrease in the vibrational deactivation. The non-polar cavity of β -CD protects the quenching of the pyrene emission by water molecule. The CDs cavity behaves similarly to the organic solvent which gives non-polar surrounding for the included molecule. This altered microenvironment can provide favorable polarity for enhanced quantum efficiencies and hence the intensities of fluorescence increase.



Fig. 2: Fluorescence spectra (excited at 340 nm) of pyrene (1.66 x 10^{-6} M) in aqueous solution of (A) β -CD and (B) β -CD-polymer at different concentrations: (a) 0.00 %, (b) 0.166 %, (c) 0.333 %, (d) 0.500 %, (e) 0.666 %, (f) 0.833 %

It was reported that while pyrene molecule is fluorescent in aprotic medium, the fluorescence yield drops rapidly due to hydrogen bond donating solvents [20]. Thus the enhancement of the fluorescence of the pyrene on the addition of β -CD or β -CD polymer is a reflection of the passage molecule into the non-polar host cavity. On comparing the effect of β -CD and β -CD polymer, for the same concentration the fluorescence enhancement is higher for β -CD polymer due to the higher order of inclusion

ability. These are shown in Scheme 1. Higher enhancement in β -CD polymer in aqueous solution indicates that encapsulation is more favored in this case owing to each β -CD unit in of the β -CD polymer include pyrene molecule. Using the Benesi-Hildebrand equation binding constants were also calculated from the fluorescence data on the basis of 1:1 association between pyrene and β -CD as shown below.

Benesi-Hildebrand Equation

$$\frac{[Py]}{I} = \frac{1}{K_b \varepsilon} \frac{1}{[CD]} + \frac{1}{\varepsilon}$$

Where, $[Py] = Concentration of Pyrene, I = Fluorescence Intensity, K_b = Binding Constant and <math>\varepsilon$ = Extinction Coefficient.

The plot of [Py]/I Vs $1/[\beta-CD]$ and $/[\beta-CD]$ polymer] gave a straight line with a slope and intercept are shown in Figure 3. A good linear fit to the experiment data obtained for all the inclusion complexes, indicating that a 1:1 inclusion complex is formed. The spectral maximum is observed at around 374 nm wavelength was used for the calculation. The extinction coefficient at 374 nm for the free pyrene, β -CD encapsulated-pyrene and β-CD polymer encapsulatedpyrene are $1.579 \times 10^7 \text{ cm}^{-1}\text{M}^{-1}$, $8.514 \times 10^7 \text{ cm}^{-1}\text{M}^{-1}$ and $10.297 \text{ x } 10^7 \text{ cm}^{-1}\text{M}^{-1}$, respectively. The binding constant K_b calculated from the emission spectra for the β -CD polymer is 2000 M⁻¹ which is higher than the value of the β -CD which is 600 M⁻¹ (Table 1). Thus the qualitative comparison of the binding constants of the two complexes suggests that β -CD polymer provide a better fit for the pyrene guest molecule.



Fig. 3: Benesi-Hildebrand plot of [Py]/I Vs $1/[\beta$ -CD] and [Py]/I Vs $[1/[\beta$ -CD Polymer]

Table 1

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Inclusion Complex	Binding Constant K_b
Pyrene-β-CD	$6.0 \times 10^2 \mathrm{M}^{-1}$
Pyrene-β-CD polymer	$2.0 \times 10^3 \text{ M}^{-1}$

4.0 CONCLUSION

The steady state absorbance and fluorescence spectra of pyrene inclusion complex with pristine β -CD and polymeric β -CD in mixed aqueous medium were studied effectively to increase the fluorescence intensity of pyrene in aqueous medium. The binding constant obtained from the Benesi-Hildebrand equation for the pyrene- β -CD polymer inclusion complex was more than three time greater than the pyrene- β -CD inclusion complex due to the more inclusion ability of β -CD polymer.

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