

Effect of α-Cyclodextrin on 4-Nitro Benzoic Acid And 3, 5 -Dinitro Benzoic Acid

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Abstract

The absorption fluorescence FT-IR and SEM charcecteristics of 4- nitro benzoic acid (4–NBA) and *3,5-dinitrobenzoic acid (3,5–DNBA)* have been investigated for different concentration of α -Cyclodextrin (α -CD). The inclusion processes are discussed based on absorption, emission, FT-IR spectroscopy and SEM studies. The absorption and emission studies show that carbonyl group is deeply entrapped in the α -Cyclodextrin cavity and NO₂ group is entrapped in the upper rim of the α -Cyclodextrin. The higher formation constant value for 4-NBA proves that 4-NBA included deeply in the α -Cyclodextrin cavity than 3. 5-DNBA . Lower formation constant value suggest that Intramolecular hydrogen bonding and steric hindrance are present in 3, 5-DNBA. Change in the IR frequency shows that both 4-NBA and 3, 5-DNBA are included in the cavity. Benesi – Hildebrand 1:1 α -Cyclodextrin plot confirmed that stoichiometric ratio was present in the inclusion complex. SEM study cleared shows the morphological difference in the inclusion complex.

Key words: α-Cyclodextrin, 4-nitro benzoic acid, 3,5-dinitro benzoic acid, Formation constant, Morphological features, Absorption, Emission.

Introduction:

Cyclodextrins have the property of forming inclusion complex with various guest molecules with suitable polarity and dimension because of their special molecular structure, hydrophobic internal cavity and hydrophilic external surface¹. The majority of all these reactions are of host - guest type. Cavity allows the cyclodextrins to include different guest molecules with different stoichiometry depending on the size of the guest molecule. Terekhova have studied the encapsulation of para aminobenzoicacid in alpha cyclodextrin in aqueous solution². Cyclodextrins are indispensible function material in the pharmaceutical design and formulation in pharmaceutical science³.

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Materials and Methods:

Absorption spectral measurements were carried out with a Double beam spectrophotometer smart 2203 and Fluorescence spectral measurements were carried out with a Fluorimetry Elico SL 170 spectro fluorometer. ∞ -Cyclodextrin (∞ -CD), 4-nitrobenzoic acid (4-NBA),

3, 5-initrobenzonic acid (3,5-DNBA) and methanol were obtained from E.Merck. Double distilled water was used for the preparation of aqueous solutions. All solvents used were of the highest grade commercially available. The solutions were prepared just before taking the measurements.

∞- Cyclodextrin solution preparation:

The solutions of stock 4-NBA, 3,5-DNBA was transferred into 10 ml volumetric flasks containing 0.002, 0.004, 0.006, 0.008, 0.01 mol dm⁻³ \propto -cyclodextrin solution. The mixed solution was diluted to 10 ml with doubly distilled water and shaken thoroughly. The absorption and fluorescence spectra were recorded.

Solid inclusion complex preparation:

4-NBA, ∞ -CD in the ratio 1:2 was taken and 3,5-DNBA, ∞ -CD in the ratio 1:2 taken and Stirred for about 48 hours at room temperature. The precipitate was was filtered using G4 sand filter paper. White solid inclusion complex was dried for 12 hour in a hot oven at 60° C. The yield was 60%

Results And Discussion:

Table (1) and fig (1)(2) shows the absorption and fluorescence maxima and spectra of 4-nitrobenzoic acid solutions containing various concentrations of α -cyclodextrin. The absorption maxima of 4-nitrobenzoic acid appear at 213.3 nm. Upon increasing the concentration of α -CD the absorption maxima is blue shifted from 213.3 nm to 203.3 nm

TABLE - 1 Absorption And Fluorescence Maxima Of 4 -nitrobenzoic acid at different

α-CD concentration	λ_{max}	1/[α-CD]	Loge	λ _{flu} nm
0	213.3		3.78	-
0.002	210.5	500	3.75	430
0.004	208.6	250	3.66	432
0.006	207.0	166.66	3.73	435
0.008	205.0	125	3.74	438
0.01	203.3	100	3.78	452

concentration of α -cyclodextrin

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Figure 1 Absorption spectra of 4 - NBA in different α -CD concentration



Figure 2. The fluorescence spectra of 4-NBA in different ∞-CD concentration

It is well known fact that, deprotonation of - COOH group gives blue shifted maxima^{4, 5}. There is no clear spectral wavelength for the fluorescence spectra. But by the addition of α -cyclodextrin the fluorescence spectra appears at 430 nm. As the concentration of α -cyclodextrin increases the fluorescence spectra is red shifted. This result indicates that 4-nitrobenzoic acid molecule is entrapped in the α -cyclodextrin to form 4-NBA : α -CD inclusion complex.

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Ft-Ir Spectral Studies:

Fig 3, 4, depicts the FT-IR α -cyclodextrin, and 5 spectra of 4-nitrobenzoic acid and its inclusion complex. On comparison with α -cyclodextrin 4nitrobenzoic acid and its complex, the aliphatic stretch at 2950 cm⁻¹ is seen in α -cyclodextrin and is lost in 4-nitrobenzoic acid and its complex. The aromatic CH stretching at 3194 cm⁻¹ is shifted in the complex to 3191 cm⁻¹. The OH stretching frequency appeared at 3317 in α -cyclodextrin, but in the complex it is shifted to 3315 cm⁻¹. The C-N frequency appears at 1344 cm⁻¹ in 4-nitrobenzoic acid is also shifted to 1342 cm⁻¹ in the complex. The NO₂ shift in 4-nitrobenzoic acid appears at 1683 cm⁻¹ is present as such in the complex. The C-O stretching mode at 1268 cm⁻¹ is moved to 1278 cm⁻¹ in the complex.



Figure 3

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The phenyl ring stretching 740 cm⁻¹ is also moved to 730 cm⁻¹ and its intensities are decreased in the inclusion complex. The hydrogen bonded OH stretch 3780 cm⁻¹ is shifted to 3793 cm⁻¹. Moreover the ratio of the intensities between the pure and the inclusion complex are largely varied to confirm 4-nitrobenzoicacid forms inclusion complex with α -cyclodextrin. In 4nitrobenzoic acid there is no significant frequency changes. The C-N stretching vibrations is also blue shifted in the complex substantiate the formation of inclusion complex.

Table (2) and fig (6), (7) shows the absorption spectra of 3,5-dinitrobenzoic acid in different concentration of α -cyclodextrin the absorption maxima of 3,5-dinitrobenzoic acid decreases from 243nm to 238 nm.



Figure 4

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The increase in the absorbance is due to the encapsulation of 3,5-dinitrobenzoic acid into the α -cyclodextrin cavity⁶. The emission spectrum is blue shifted from 361 nm to 302 nm. This large blue shift is due to the presence of two electrons with drawing nitro groups. The molecule is also entrapped in the α -cyclodextrin to form 3,5-DNBA : α -CD inclusion complex⁷.



Figure 5

The association constant (k) for the formation of an inclusion complex has been determined by analysing the changes in the intensities of absorption and fluorescence maxima with the α cyclodextrin concentration. The association constant and stoichiometric ratios of the inclusion complex of 4-nitrobenzoic acid with α -cyclodextrin can be determined by using the Benesi-Hilde-brand relation⁸.

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TABLE – 2 Absorption and fluorescence maxima of 3,5 -dinitrobenzoic acid at different concentration of α -cyclodextrin:

α-CD concentration	λ _{max} nm	1/[α-CD]	Loge	λ _{flu} nm
0	243.0		3.44	361
0.002	241.2	500	3.48	312
0.004	238.8	250	3.64	310
0.006	240.4	166.66	3.49	307
0.008	240.4	125	3.90	306
0.01	238.0	100	3.84	302



Fig-6 Absorption spectra of 3, 5-DNBA in different ∞ -CD concentration:



Figure 7 The fluorescence spectra of 3,5-NBA in different ∞ -CD concentration:

The equations for 1:1 complexes are given below,

Absorption	$1/A-A_o$	=	$1/\dot{A} - A_0 + 1/K (\dot{A} - A_0) [\alpha - CD]$
Fluorscence	1/I-Io	=	$1/\dot{I} - I_{o} + 1/K (\dot{I} - I_{o}) [\alpha - CD]$

In the above equation, A_o/I_o is the intensity of absorbance / fluorescence of 4nitrobenzoic acid and 3,5-Dinitrobenzoic acid without α -cyclodextrin.

A/I is the absorbance / fluorescence intensity with a particular concentration of α -cyclodextrin.

A'/I' of α - cyclodextrin used and K is the association constant. Linearity is obtained in the plot of $1/A-A_0$ or $1/I-I_0$ verses $1/[\alpha-CD]$ for 1:1 complex.

The association constant K was calculated from the slope of Benesi - Hilde - Brand plot using the equation.

 $K = 1/slope (A'-A_o)$ for absorption

K = 1/slope ($I' - I_o$) for fluorescence.



Upperline:3,5 DNBA

Lower line: 4-NBA

Fig – 8 Benesi - Hilde brand plot of $1/A-A_o$ versus $1/[\alpha-CD]$ for the complexation of 4-NBA and 3, 5-DNBA with $1/[\alpha-CD]$:

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Upper line:3, 5-DNBA

Lower line:4-NBA

Fig- 9 Benesi – Hilde brand p lot of $1/I-I_o$ versus $1/[\alpha-CD]$ 4-NBA and 3,5-DNBA with $1/[\alpha$ -CD]: for the complexation of

SEM studies:

The powered form of α -CD (a), 3,5-DNBA (b), and inclusion complexes (c) are observed by scanning Electron Microscope (Fig.10). The pictures clearly elucidate the difference of α-CD, 3,5-DNBA and inclusion complex. As seen from the SEM figures α -CD shows sheeted structure 3,5-DNBA shows some what plated structure and the complex structure is different from α -CD and 3.5DNBA. Modification of crystals and powder can be assumed as a proof of the formation of new inclusion complex.



(b)







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Reference

- 1]. J.Szejtli, *Cyclodextrin technology*, Dordrecht, The Netherland, Kluwer Acacemic publishers, 1988, 81-83
- 2]. I.V.Terekhova ,N.A Obukhova ., Solution chem., 2007.36;1167-1169
- 3]. K.Uekama, "Pharmaceutical application of cyclodextrins as multi functional drug carriers", Yakugaku Zasshi.,2004.124;909-935
- 4]. Gaitaino.G, J.Phy.chem, 2004, 108, 392-394
- 5]. J.Premakumari, G. Allen Gnana Raj,N. Rajendiran, "Study on the spectral characteristics of 4hydroxy
- 6]. 3-methoxybenzoicacid in different pH and α CD", 2009.86; 53-57
- 7]. M.S.Matos, M.H.Gehlen, Spectrochim Acta, 2004.60A;1421-1424
- 8]. J.Premakumari., G.Allen Gnana Raj, A. Antony Muthu Prabhu , G.Venkatesh., V.K.Subramanian , N. Rajendiran , J. Physics and chemistry of liquids, 2010, 1 -25
- 9]. H.A.Benesi, J.H. Hildibrand , J.Am chem. Soc, 1949,7; 2703-2705

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