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# Study of the cyclodextrin and its complexation with 2,4-dinitrobenzoic acid through photophysical properties and 2D NMR spectroscopy

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## HIGHLIGHTS

- Photophysical and electrochemical studies plays a major role in the host–guest inclusion complex process.
- Solid complex characterized by $^1$H NMR, 2D NMR, FT-IR, XRD and SEM techniques.
- The structure of inclusion complex proposed by molecular docking study.

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## ABSTRACT

The host–guest inclusion complex formation of 2,4-dinitrobenzoic acid (2,4-DNB) with nano-hydrophobic cavity of β-cyclodextrin (β-CD) in solution phase were studied by UV–visible spectrophotometer and electrochemical method (cyclic voltammetry, CV). The prototropic behaviors of 2,4-DNB with and without β-CD and the ground state acidity constant (p*K*a) of host-guest inclusion complex (2,4-DNB-β-CD) was studied. The binding constant of the inclusion complex at 303 K was calculated using Benesi–Hildebrand plot. The solid inclusion complex formation between β-CD and 2,4-DNB was confirmed by $^1$H NMR, 2D $^1$H NMR (ROESY), FT-IR, XRD and SEM analysis. A schematic representation of this inclusion process is proposed by molecular docking studies using the patch dock server.

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## 1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6, 7, and 8 units of 1,4-linked glucose units, and are named alpha (α), beta (β) and gamma (γ)-Cyclodextrins, respectively (Scheme 1). These macromolecules, which can be spatially represented as a torus with wide and narrow openings corresponding to secondary and primary hydroxyl groups respectively, can encapsulate a large variety of compounds due to the hydrophobic character of their internal cavity [1]. Although the depth of the cavities for the three CDs is the same (~0.78 nm), their cavity diameters are ~0.57, 0.78 and 0.95 nm respectively (Scheme 1). Due to the unique chemical structure of CD molecules, the inner side of the cavity is hydrophobic and the outer side is hydrophilic. The hydrophobic nature of the CD cavities facilitates the ability of CDs to act as host for both non-polar and polar guests, which include small molecules as well as polymers [1–4]. Once the inclusion compound is formed, the stability of the guest molecules increases due to the binding forces (van der Waals attractions, hydrogen bonding, hydrophobic attractions, etc.) between the host (CDs) and guest molecules [5,6]. The CDs also have several advantages in other areas, such as the food, cosmetics industries and agro chemistry [7–9], especially owing to their capacity to protect the guest molecules against oxidation, light-induced reaction and loss by evaporation. Additionally, they usually enhance the aqueous solubility of poorly soluble or even insoluble compounds [10].

2,4-Dinitrobenzoic acid (2,4-DNB) belong to major organic pollutants that have been analysed in the environment. 2,4-DNB used as an anticorrosion protection of metals and or coated with a Cr-laminated glass support when mixed with cross linkable buthylmetacrylate and then heated under defined conditions. Aqueous emulsions of some dinitrobenzoic acids were used in order to render steel sheet and strip C-smut free after batch annealing [11]. 2,4-DNB are listed as priority pollutions by the US Environmental Protection Agency [12]. They have great potential toxicities of carcinogenesis, teratogenesis, and mutagenesis [13,14]. It's released into the air, water and soil. It may also be released into the environment from landfill leaks and accidental spills. Consequently, due to the harmful effects of these organic compounds, the

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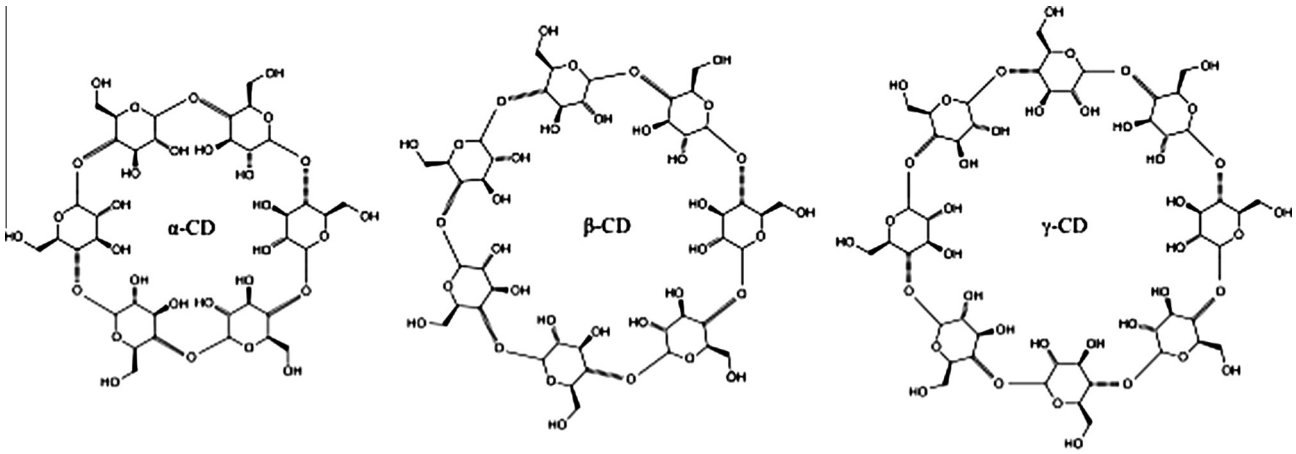


**Scheme 1.** 3D view of chemical structures of α-CD, β-CD and γ-CD.

wastewaters containing them must be treated before being discharged to receiving water bodies. In order to assess the fate of 2,4-DNB in wastewater and to control their mobility and reactivity during remediation processes, the sorption behavior of these toxic contaminants must be understood and revealed.

The author studied the host-guest inclusion complex mechanism between 2,4-DNB and β-CD in different techniques. In this study, we report for the spectral and electrochemical behaviors of 2,4-DNB in different pH with β-cyclodextrin. With respect to the formation of host-guest inclusion complex of 2,4-DNB with β-CD in solution phase was studied by UV–Visible spectroscopy (UV–Vis) and cyclic voltammetric technique (CV). The solid complex was prepared and characterized by $^1$H NMR, 2D $^1$H NMR (ROESY), FT-IR, XRD, and SEM techniques. The schematic representation of this inclusion process is proposed by molecular docking studies using the patch dock server.

## 2. Experimental

### 2.1. Instruments

The UV–Vis spectra (absorption spectral measurements) were carried out with Shimadzu UV-2401PC double-beam spectrophotometer (range 1100–200 nm) with scan speed of 400 nm min$^{-1}$, the pH values in the range 1.0–12.0 were measured on Elico pH meter LI-120; Electrochemical studies were carried out using Auto lab electrochemical analyzer (GPES software), A conventional three electrode cell assembly was used for the electrochemical measurements. Cyclic Voltammetry measurements at a glassy carbon electrode (diameter: 1 mm) were carried out at an applied potential of −0.9 V to 0.4 V for each concentration of β-cyclodextrin at single cycle only. Reference electrode was saturated calomel electrode (SCE) and platinum wire as counter electrode. All experiments were carried out at 30 ± 1 °C. The working electrode was polished to a mirror with 0.05 μm alumina aqueous slurry, and rinsed with triply distilled water before each experiment. The supporting electrolyte was pH∼1 (0.1 M $H_2SO_4$ + 0.1 M $Na_2SO_4$) and pH∼7 (0.1 M $KH_2PO_4$ + 0.1 M NaOH). FT-IR was recorded using Nicolet 380 Thermo Electron Corporation Spectrophotometer using KBr pellets and scan between 4000 and 400 cm$^{-1}$. The sample solutions for $^1$H NMR were prepared by dissolving the dinitro compounds and their complexes in $D_2O$ solvent to obtain the final concentration of 20 mM. Two-dimensional rotating-frame Overhauser effect spectroscopy (ROESY) experiments were performed using BRUKER-NMR 400 MHz instrument operating at 300 K and the standard Bruker program was used, DMSO-$d_6$ was used as a solvent, relaxation delay of 1 s and mixing time 300 ms under the spin lock conditions. Powder X-ray diffraction spectra were taken by XPert PRO PANalytical diffractometer (2Theta:0.001; Minimum step size Omega:0.001). The surface morphology was taken by Hitachi S 3000 H SEM.

### 2.2. Molecular docking study

The most probable structure of the 2,4-DNB:β-CD inclusion complex was determined also by molecular docking studies using the Patch Dock server [15]. The 3D structural data on β-CD was obtained from HIC-Up database (http://xray.bmc.uu.se/hicup) using the search interface. The 3D structures of 2,4-DNB were obtained by translating the SMILES formula of 2,4-DNB using CORINA server (http://www.molecular-networks.com/ online_demos/corina_demo).The guest molecule (2,4-DNB) was docked into the host molecule (β-CD) cavity using PatchDock server by submitting the 3D coordinate data of 2,4-DNB and β-CD molecules. Docking was performed with complex type configuration settings. PatchDock server follows a geometry-based molecular docking algorithm to find the docking transformations with good molecular shape complementary. PatchDock algorithm separates the Connolly dot surface representation [16] of the molecules into concave, convex and flat patches. These divided complementary patches are matched in order to generate candidate transformations and evaluated by geometric fit and atomic desolvation energy scoring [17] function. RMSD (root mean square deviation) clustering is applied to the docked solutions to select the non-redundant results and to discard redundant docking structures.

### 2.3. Reagents

β-Cyclodextrin {(β-CD), were obtained from the Sd fine chemical company} and used without further purification. 2,4-Dinitrobenzoic acid (2,4-DNB) purchased from Alfa Aesar company and used without further purification. Triply distilled water was used to prepare all solutions. Solutions in the pH range 2.0–12.0 were prepared by adding the appropriate amount of NaOH and $H_3PO_4$. Yagil basicity scale ($H_-$) [18] for solutions above pH∼12 (using a NaOH–$H_2O$ mixture) and a modified Hammett's acidity scale ($H_0$) [19] for the solutions below pH∼2 (using a $H_2SO_4$–$H_2O$ mixture) was employed. The solutions were prepared just before taking measurements. The concentrations of the solutions were of the order ($10^{-4}$ to $10^{-5}$ mol dm$^{-3}$). The stock solution of 2,4-DNB and β-CD preparation for spectral and electrochemical studies was

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