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SYNTHESIS AND CHARACTERIZATION OF HOST – GUEST COMPLEXES OF B – CYCLODEXTRIN WITH HYDROQUINONE

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ABSTRACT

The supramolecular structure of the inclusion complex of β – cyclodextrin (β-CD) with hydroquinone as a host – to – guest molecule was studied. The inclusion complex with 1: 1 molar ratio β – CD- hydroquinone was prepared by melting in solution and kneading methods. The inclusion complex was characterized by Fourier Transform Infrared Spectroscopy (FT – IR) and ^{1}H NMR which confirmed the formation of an inclusion complex of β – CD – hydroquinone. Complexes prepared by both methods led to the formation of inclusion complex with white powder as the final product.

Keywords: Synthesis, Characterization, Inclusion complex, β-CD, Hydroquinone.

INTRODUCTION

The term host-guest chemistry" has been used to designate a variety of processes occurring in a number of research fields, such as organic, analytical, biological and organometallic chemistry, and involving molecules and ions with different structures, dimensions and properties.

Host-guest interactions involve the establishment of multiple non-covalent bonds between a large and geometrically concave organic molecule (the host) and a simpler organic or inorganic molecule or ion (the guest). The mere formation of multiple non-covalent bonds between reactants of similar size or geometry is generally referred to as a process of supramolecular chemistry, not host-guest chemistry, because inclusion complexes are not formed. Thus, the geometrical requirements are essential to fit the definition of host-guest chemistry [1].

Supramolecular chemistry is a discipline of chemistry which has been attracting much attention, especially in the host-guest type interaction.

Macrocyclic hosts can be generally classified as types of endoreceptors in that they bind with their guests located in the interior of the host. Exoreceptors in contrast, bind to substrates on their exterior.

Supramolecules are complex and ordered molecular aggregates associated with two or more molecules, ions or coordination compounds through intermolecular interaction, which have particular functions [2]. Examples of host molecules insupramolecular chemistry include crown ethers, crypates, calixarenes, cyclodextrins (CDs), etc. [3,4].

The degradation of helical starch molecules by cyclodextringlucanotransferase from Bacillus macerans yields cyclodextrins (CDs), which consist of six or more (1-4)-linked a-D glucopyranosyl rings. The main fractions of these oligosaccharides contain six, seven, or eight residues (α, β or γ-CD).

Hydroquinone is a type of phenol with two hydroxyl groups bonded in the para positions of the benzene ring, it is stable only in a limited pH range.Stabilizers like cyclodextrins are therefore used. Due to the prevention of the oxidation of hydroquinone, the cyclodextrin complexes have a greater stability [5].

Hydroquinone and other phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides, insecticides, etc. These substances may cause environmental problems as most of these compounds are recognized as toxic carcinogens. The presence even in low concentration causes unpleasant taste and odor of drinking water and can exert negative effects on different biological processes [6].

Cyclodextrin inclusion complexes are of interest for scientific research, because they exist in aqueous solution and can be used to study the hydrophobic

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interactions which are so important in biological systems. Cyclodextrins can catalyze several chemical reactions and therefore they and their functionalized derivatives (modified cyclodextrins) provide useful enzyme models. They can be used advantageously in the production of pharmaceuticals, pesticides, foodstuffs, and toiletry articles.

The formation of CD inclusion compounds can effectively improve solubility and stability of guest molecules so they have been widely used in recognition field of model enzyme [7], molecular devices [8].

This objective of this research work was synthesize and characterize inclusion complex between β-cyclodextrin and hydroquinone using FT-IR and ^{1}H NMR, investigate the interaction between β-cyclodextrin (host) and hydroquinone (guest) and compare which method is more suitable for the preparation of inclusion complex of β-cyclodextrin and hydroquinone.

MATERIALS AND METHODS

Materials

The IR spectra were recorded on a Perkin-Elmer RX1 FT-IR spectrometer with samples prepared as KBr pellets. All the spectra were run in the range of 400-4000cm^{-1} at room temperature. The ^{1}H NMR spectra were recorded in D_2O on a Lambda JOEL 400 MHz FT-NMR spectrometer.

Reagents and Solution

β- Cyclodextrin (99%) was purchased from Across (Hungary). Other reagents and chemicals were of analytical reagent grade and were used as received. Doubly distilled water was used throughout.

Methods

Preparation of β-CD-hydroquinone Inclusion Complex by Melting in Solution

Two inclusion complex of same starting material were prepared using two methods. 2g of β-CD was transferred into 20ml of water and was heated to 80 ^{0}C. The equimolar 0.194g of (hydroquinone) was added and was stirred continuously and intensively to dry. The white powder product was formed and dried in vacuum oven at 65 ^{0}C. The final product was characterized by using various instruments [9].

Preparation of β-CD- hydroquinone Inclusion Complex by Kneading

2g of β-CD was wetted with ethanol in agate mortar and kneaded to form a paste. Then equimolar of hydroquinone, 0.194g and ethanol were added. The sample was kneaded for approximately 60 minutes and dried to constant mass at 105 ^{0}C, the white precipitate obtained as final product was characterized using various instruments.

RESULTS AND DISCUSSION

Characterization of Inclusion Complexes

FTIR Analysis

Figure 1shows the FTIR spectra of β-CD, hydroquinone, β-CD-hydroquinone inclusion complex prepared by melting in solution method and β-CD-hydroquinone inclusion complex prepared by kneading method respectively while the interpretation of IR spectrum is presented in Table 1.

The FTIR spectrum of β-CD-hydroquinone prepared by kneading method is similar to that of pure β-CD, which is a major characteristic for the host-guest inclusion complex of CDs. The presence of hydroquinone in the inclusion complex is further confirmed when the most obvious band of C=C stretch is observed in the FTIR spectrum of β-CD-hydroquinone inclusion complex at 1513.46 and 1647.90cm^{-1}, respectively. This band is shifted upon inclusion complexation compared to the band of free hydroquinone [11]. The broader O-H stretching band of the inclusion complex in the range 3000-3600cm^{-1} corresponds to the multiple O-H functional groups of β-CD molecules [12]. Furthermore, FT-IR can also be used to confirm the included part of the guest molecule whereby band will be generally shifted or their intensities altered [13]. In addition, the FTIR curves in the fingerprint regions (below 1300cm^{-1}) shows that the β-CD-hydroquinone in the kneading method is different from the parent molecules, as they possess different spectroscopic signals [14].

However complex prepared by melting in solution method also shows the inclusion complex formation of β-CD-hydroquinone. An apparent differences between the spectra of a, b and d further proved the formation of β-CD-hydroquinone. Also, β-CD-hydroquinone prepared by melting in solution method showed that guest molecule is inside the β-CD cavity. For example, 1517.82cm^{-1} absorption peak of C=C decrease and shift upon formation of β-CD-hydroquinone (1510.48cm^{-1}) shown in Figure1 by using arrows. In addition, broad hydroxyl band of β-CD at 3399.94 cm^{-1} narrows in the spectrum of their β-CD-hydroquinone.

By using FTIR technique, it may be concluded that the formation of inclusion complex between β-CD and hydroquinone occurs with non-covalent interactions such as van der waals interactions, hydrophobic interactions and hydrogen bonds which will further lower the energy of the included part of hydroquinone and reduce the absorption intensities of the corresponding bonds. The spectra obtained shows clearly that both methods of preparation leads to the formation of complex between β-CD and hydroquinone.

^{1}H NMR Analysis

Information provided by ^{1}H NMR technique confirmed the formation of complex, calculation of the stoichiometry and stability constant and definition of

geometry of the complex, e.g. the orientation of the guest molecule in the CD cavity [15,16]. The method is based on observation of chemical shift differences in the presence and absence of guest molecules [17, 18].

Figure 2 shows the ^{1}H NMR spectra of (a) β-CD, (b) hydroquinone, (c) β-CD-hydroquinone prepared by both melting in solution and kneading method in D_2O. In the ^{1}HNMR spectrum of the β-CD-hydroquinone inclusion complex in both methods, the presence of hydrogen atom signals belonging to both β-CD and hydroquinone molecules strongly confirmed that the inclusion complex was formed. The β-CD proton signals in the ^{1}HNMR spectra of mixture of hydroquinone and β-CD of the kneading technique showed up field shift changes in the H-3 and H-5 proton resonances compared to pure β-CD. The up field shift of β-CD cavity proton signals can be explained in terms of ring current effect of aromatic ring penetrating the β-CD cavity, and therefore, confirming the formation of hydroquinone/ β-CD inclusion complex with respect to previous studies [12]. Other β-CD protons also showed shift changes. Table 2 shows ^{1}HNMR signal in pure β-CD, free hydroquinone and inclusion complex of β-CD-hydroquinone. ^{1}H NMR spectra confirmed strongly that the inclusion complex was formed due to the significant difference of the signal.

The changes of chemical shift of H3, H5, and H6 suggested that the hydroquinone enteredinto the hydrophobic cavity of β-CD completely. Despite the fact that H3 protons are located in the inner surface of the β-CD cavity, the upfield shift is not as high as H5. This may be due to the fact that H3 is located on the surface of a secondary hydroxyl group side and further more is a long way from the symmetrical axis of β-CD, therefore no obvious interaction observed with the included hydroquinone. Also, the upfield shift of the proton from inner surface of β-CD may result from shielding effects suggesting that the hydroquinone entered into the cavity of β-CD. The chemical shifts of H1, H2 and H4 which are located outside the cavity, were only slightly affected by the guest.

In addition, the ratio of hydroquinone to β-CD in inclusion complex was determined by their integration which confirms the inclusion complex of ratio 1:1 [6].

Also, the Ha ring proton of hydroquinone shows great upfield shift which indicates it has strong interaction with β-CD protons. The presence of hydroquinone further proves inclusion complex formation. Again based on the chemical shift of the hydroquinone, it may be that the whole molecule entered into the hydrophobic cavity of β-CD molecule. The broadening of the proton signals of hydroquinone was not observed, this indicates that hydroquinone fits loosely into β-CD cavity [19].

Fig 1. FTIR spectra of (a) β-CD-hydroquinone by kneading method, (b) hydroquinone, (c) β-CD-hydroquinone by melting in solution method (d) β-CD

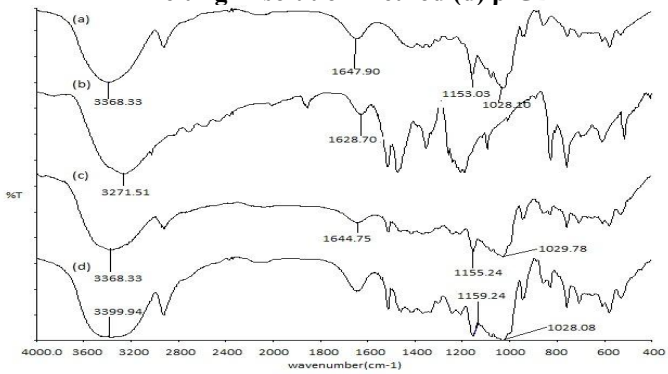
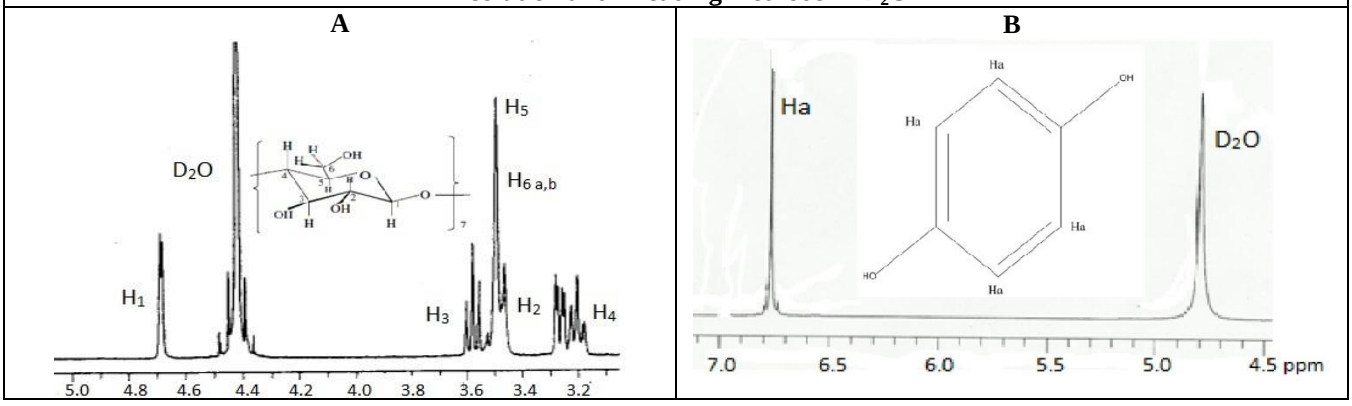


Fig 2. 400-MHz ^{1}H NMR spectra of (a) β-CD (b) hydroquinone and (c) β-CD- hydroquinone prepared by melting in solution and kneading methods in D_2O



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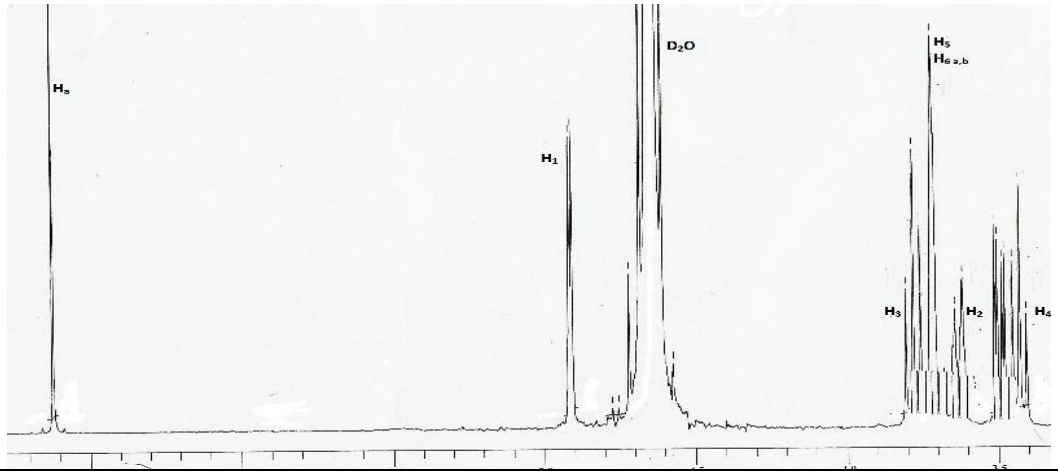

Table 1. FT-IR interpretation of inclusion complex formed

Functional Group	B-CD (cm^{-1})	Hydroquinone (cm^{-1})	IR shift in IC by melting in solution (cm^{-1})	IR shift in IC by kneading (cm^{-1})
O-H	3399.94	3271.51	3368.33	3368.33
C=C	_	1628.70	1644.75	1647.90
C-O	1159.24	_	1155.24	1153.03
C-O-C	1028.08	_	1029.78	1028.10

Table 2. The chemical shifts (δ) of β- cyclodextrin, hydroquinone and β-CD-HQ

	β-CD	Hydroquinone	β-CD- HQ	
	δ	Δ	Δ	Δδ
H_1	4.9258	-	4.9191	-0.0067
H_2	3.5266	-	3.5144	-0.0122
H_3	3.8262	-	3.7835	-0.0427
H_4	3.4674	-	3.4558	-0.0116
H_5	3.7384	-	3.6816	-0.0568
H_6	3.7701	-	3.7609	-0.0092
Ha	-	6.7673	6.6252	-0.1421

CONCLUSION

The inclusion complex with host – to – guest ratio 1: 1 was prepared successfully with β – CD and hydroquinone. The results obtained by Fourier Transform Infrared Spectroscopy (FT –IR) and ^{1}H NMR Spectroscopic technique indicated that both kneading and melting in solution methods of the complex led to the formation of complex between β – CD and hydroquinone. Also, the characterization by various techniques supported the formation of inclusion complex in which the rings of the guest were encapsulated within the β – CD cavities.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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