

Determination of structure and morphology of the cyclodextrins-iodine complexes

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Abstract

Introduction. The objective of these investigations is to study surface morphology of inclusion complexes between α - and β -cyclodextrins and molecular iodine as well as determine chemical stoichiometric ratio between these components in the formed complexes.

Materials and methods. The host-guest complexes between α - and β -cyclodextrins and iodine were synthesized according to the procedures, given in literature sources. Morphology of the surface of the samples has investigated by use of scanning electronic microscope JSM-6700F (JEOL, Japan). The platinum layer with 10 nm in depth was preliminary placed on the samples. The samples were mounted on SEM and irradiated with beam of electrons at 15 kV and probe current 0,65 nA.

Results and discussion. The scanning electronic microscopy (SEM) has been used in order to investigate morphology and structural features of the obtained complexes. This method has widely used in macromolecules analysis. It allows precise determination of elemental content in the samples. The results of iodine content in inclusion compounds with α - and β -cyclodextrins obtained from SEM and iodimetric titration methods are almost similar. It has found, that iodine content in β -CD-I₂ complex within the range 16,7-16,9 %, whereas α -CD-I₂ consisted 18,0–19,9% of active iodine. Some differences were found in respect to the iodine content in α -CD-I₂, obtained by two methods may related to the high water absorption on the complex surface result in the drop of iodine content on the surface. Experimental data of iodine content in the inclusion complexes suggested that α - and β -cyclodextrins react with KI₃ resulted in the host guest complex formation with the chemical stoichiometric ratio value of 1:1. Analysis of surface morphology of the cyclodextrin-iodine samples obtained from high resolution SEM method revealed about coarse crystalline structures formation, which is nontypical for organic polymeric compounds. Comparative studies have revealed, that cyclodextrin: iodine ratio in the obtained complexes is 1:1. It has been confirmed that one molecule of cyclodextrin bound one molecule of iodine, forming host-guest complex.

Conclusions. The complex β -cyclodextrin-I₂ was loss 9 % of active iodine at the prolonged storage during 1 year at 4 °C. It was shown, that iodine content in the α -CD-I₂ and β -CD-I₂ can be estimated with use of relatively simple and quick method of iodimetric titration, which is being important property of these complexes for their further application in food technologies.

Introduction

Cyclodextrins (CDs) are the cyclic oligosaccharides, composed from residues of α -D-glucopyranoses, made during starch transformation by specific enzymes, for example *Bacillus macerans*. Cyclodextrins belonging to ring molecules, which due to rigid glycosidic bonds between glucopyranose units have a toroidal form. The most widely used CDs are so called α -, β - and γ -cyclodextrin, which consisted six, seven and eight glucose units, respectively. Unique properties of cyclodextrins related to their ability of inclusion complexes formation in which non-polar guest molecule substitute water molecules from internal cavity of the host molecule which is leading to the complex formation [1,2]. The most common chemical stoichiometric ratio between cyclodextrins and guest molecules is 1:1 [1,3].

These complexes have been widely used in food technologies, particularly in oil-soluble compounds protection sensible to the oxygen, light and high temperatures action as well as improvement of vitamins solubility; taste and aroma stabilization of essential oils, undesirable compounds removal, lipophilic compounds solubilization, as photostabilization of light sensitive compounds, catalytic activity retention, protection from enzymatic deterioration, unnecessary taste and aroma suppression, controlled release of some food components e.t.c. CDs themselves can be recognized as non-digestible oligosaccharides and, thus, their consumption can improve beneficial microflora in gastrointestinal tract.

We have earlier synthesized host-guest complex between β -cyclodextrin and molecular iodine and applied this compounds as a food additive in boiled sausages formulation [4,5]. This compound can be considered as a promising iodophor, which able to increase iodine status of humans. According with experimental data, regular consumption of these boiled sausages by adult individuals resulted in significant improvement of their iodine status. The sensory and microbiological characteristics of the boiled sausages made with CD-I₂ inclusion and standard samples were similar so that this complex has no negative impact on quality of the boiled sausages [4,6].

X-ray analysis suggests that iodine and cyclodextrins form linear polymer chain in which one molecule of CD can bind more than one iodine molecule [7]. At the same time, however, other authors indicated that CD and iodine react with the complex formation, in which one molecule of β -cyclodextrin quench one molecule of iodine [8]. This inconsistency in iodine content of CD-iodine complexes is substantial obstacle that complicates wide application of CD-iodine complexes in food technologies and confuses rapid iodine determination

The objective of these investigations is to study surface morphology of inclusion complexes between α - and β -cyclodextrins and molecular iodine as well as determine chemical stoichiometric ratio between these components in the formed complexes.

Materials and methods

Materials

I₂, α - and β -cyclodextrin, DMF, KI were offered from Sigma-Aldrich. Unless specific notifications, all the chemicals were analytical reagent grade without further purification.

Synthesis of β -cyclodextrin- I_2 complex.

Synthesis of β -CD/ I_2 complex was done according to synthesis procedure, described by Wang and co-authors [8]. 3,8 g of KI and 0,38 g of I_2 (1,5 mM) were dissolved in 15 ml of distilled water during 10 minutes resulted in KI_3 formation. Further, this solution was dropped into 10 ml β -cyclodextrin solution (223 mg, 0,5 mM) in 50 ml conical flask. The mixture was stirred during 5 h at 25 °C and then retained 10 h at 4 °C in order to fully encapsulate iodine in β -CD. After storage, brown crystals of β -CD/ I_2 were filtered and washed KI solution in order to remove I_2 molecules from the filter cake and distilled water which aid to get rid from both KI and β -CD. The final product was dried at vacuum during 4 h at 40 °C. The total preparative yield was 93 %.

Iodine content in the complex was determined by iodimetric titration, described by Wang and co-authors [8]. Sample of α - or β -CD/ I_2 (0,2 g) was weighed precisely, when placed in the 10 ml flask and 4 ml of DMF was added and stirred until complete dissolution. When 140 ml of deionized water was added and titred by $Na_2S_2O_3$ standard solution (0,01 M). Titration was continued until the solution turned out light yellow and added 3 ml starch-iodine indicator and keep on titrating until solution became colorless. Titration procedure was repeated thrice. The iodine content was calculated by formula:

$$I(\%) = 0,1269 \times C(Na_2S_2O_3) \times V(Na_2S_2O_3) \times 100/m$$

The iodine content in the complex was $16,9 \pm 0,1$ %, which corresponds equimolecular ratio of β -CD and I_2 in the complex. Moreover, we determined melting point of β -CD/ I_2 in capillary tube, which was 76 °C. This value is in agreement with the data obtained by Wang and co-auth [8].

α -CD/ I_2 complex has synthesized by the same manner, taking to account that α -cyclodextrin more soluble in aqueous solution than β -CD. The total preparative yield was 94,5 %.

Methods

The scanning electronic microscopy (SEM) has been used in order to investigate morphology and structural features of the obtained complexes. This method has widely used in determination of macromolecules analysis. It allows precise determination of elemental content in the samples [9].

Morphology of the surface of the samples has investigated by use of scanning electronic microscope JSM-6700F (JEOL, Japan). The samples were applied on metal slab, and preliminary were coated with platinum layer with 10 nm in dept. The samples were mounted on SEM and irradiated with beam of electrons at 15 kV and probe current 0,65 nA.

Results and discussion

The experimental data of iodine content in the complexes, obtained by several methods was given in the table 1. According with these data molecular iodine is interacting with α - or β -CD resulted in the host-guest complex formation with the ratio 1:1.

These results are not agreed with the known X-ray diffraction assays, which indicates, that β -cyclodextrin form with iodine inclusion complex β -CD- I_7^- , whereas interaction between α -cyclodextrin and iodine resulted with complex formation with total formula α -CD- I_5^- [6]. The authors suggested that polyiodide chain consists of discrete I_7^- units, which can be formulated as $I_2 \cdot I_3^- \cdot I_2$. These units are shaped into Z-like structures. Furthermore, in

the α -CD- I_5^- complex, α -CD molecules are stacked together to form columns similar to nanotubes, and I_5^- ions are located in the columns and nearly linearly arranged in the direction of columns [10].

Table 1

Iodine content (%) in cyclodextrin-iodine complexes

Complex	SEM	Titration
α -CD- I_2	18,0 \pm 0,2	19,9 \pm 0,1
β -CD- I_2	16,82 \pm 0,4	16,9 \pm 0,1
β -CD- I_2 (1 year storage)	15,42 \pm 0,3	14,9 \pm 0,1

As it can be seen from the table 1, the results of iodine content in inclusion compounds with α - and β -cyclodextrins obtained from SEM and iodimetric titration methods are almost similar. These evidences indicates both high reproducibility of complexes synthesis procedure and precision of iodimetric titration method. However, some differences are found in respect to the iodine content in α -CD- I_2 , obtained by two methods may related to the high water absorption on the complex surface result in the drop of iodine content on the surface. Surprisingly, the data of iodine content in the samples obtained from iodimetric titration is close to the theoretically estimated on the basis of individual atomic weight. Thus, experimental data of iodine content in the inclusion complexes suggested that α - and β -cyclodextrins react with KI_3 resulted in the host guest complex formation with the chemical stoichiometric ratio value of 1:1. Interesting, that storage for 1 year at 4 °C, indicates that β -CD- I_2 inclusion complex has lost a small amount of iodine, which can be simply and accurately determined by iodimetric titration method (Table 1). Thus, the complex has remained relatively stable during prolonged storage.

Table 2

Oxygen content (%) in cyclodextrin-iodine complexes

Complex	Experimental	Theoretical
α -CD- I_2	30,9 \pm 0,5	36,3
β -CD- I_2	39,52 \pm 0,6	38,1
β -CD- I_2 (1 year storage)	38,7 \pm 0,5	38,1

The oxygen content in the samples of CDs and their complexes with iodine was derived with the help of SEM method. As it can be seen from the table 2, these data close to those theoretically calculated taking to account masses of the individual atoms constituting the bonds in the molecules (table 2). It is known, that SEM method usually is not able to give reliable data for mass content of atoms with relatively low atomic weight, like oxygen or carbon. This was observed for the carbon content in the samples, whereas SEM method provides good result for oxygen content in the samples. These findings are also indicated

that iodine with the α - or β -CD will form 1:1 complex. Potassium is also present in the complexes, mainly due to KI application at the complexes synthesis. The potassium content in the samples varies within the range 0,8-1,48 % which is also confirmed stoichiometric ratio of the complexes.

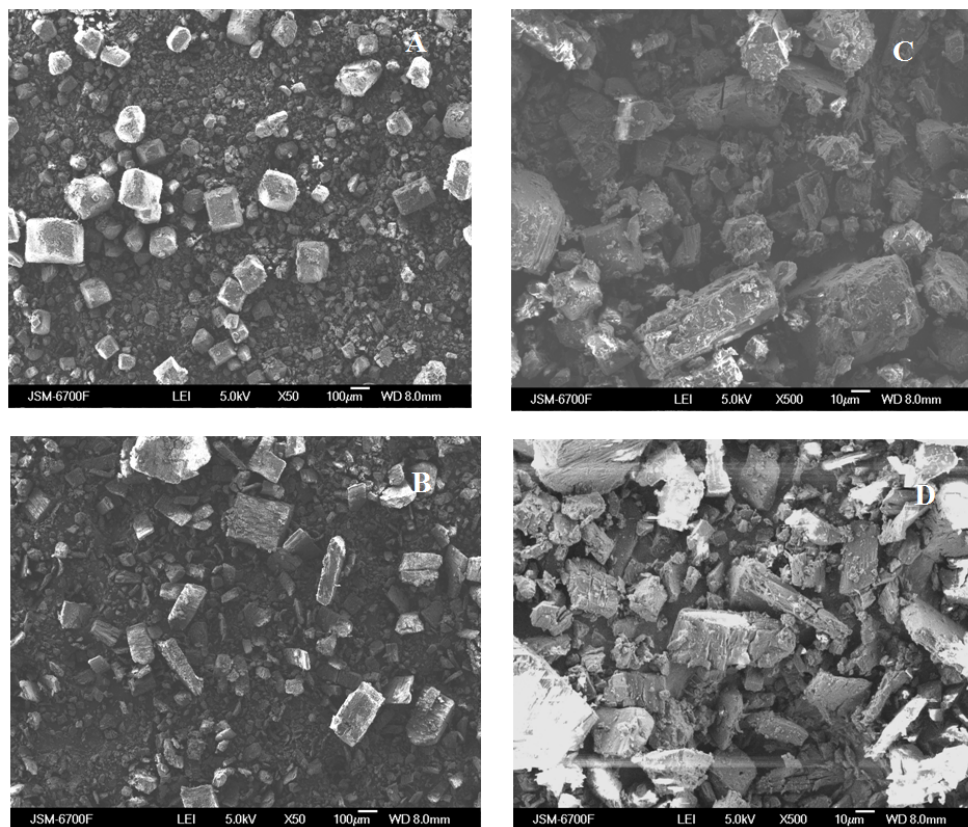


Figure 1. Scanning electronic microphotographs of the surfaces of α -CD (A) and β -CD (B) Left, 50×magnification; α -CD (C) and β -CD (D) Right, 500×magnification

The changes in particle morphology that occurred during CDs synthesis are indicated in the SEM study. The SEM microphotographs of α - and β -CD shown in Figure 1. These images observation indicates the presence of some not fully transformed starch granules in a very small amount. It is confirmed high level of starch transformation into CDs. As illustrated in Figure2, CDs complexes with iodine existed in needle like crystals, whereas α - and β -CD was observed as irregular “shrunked” crystals.

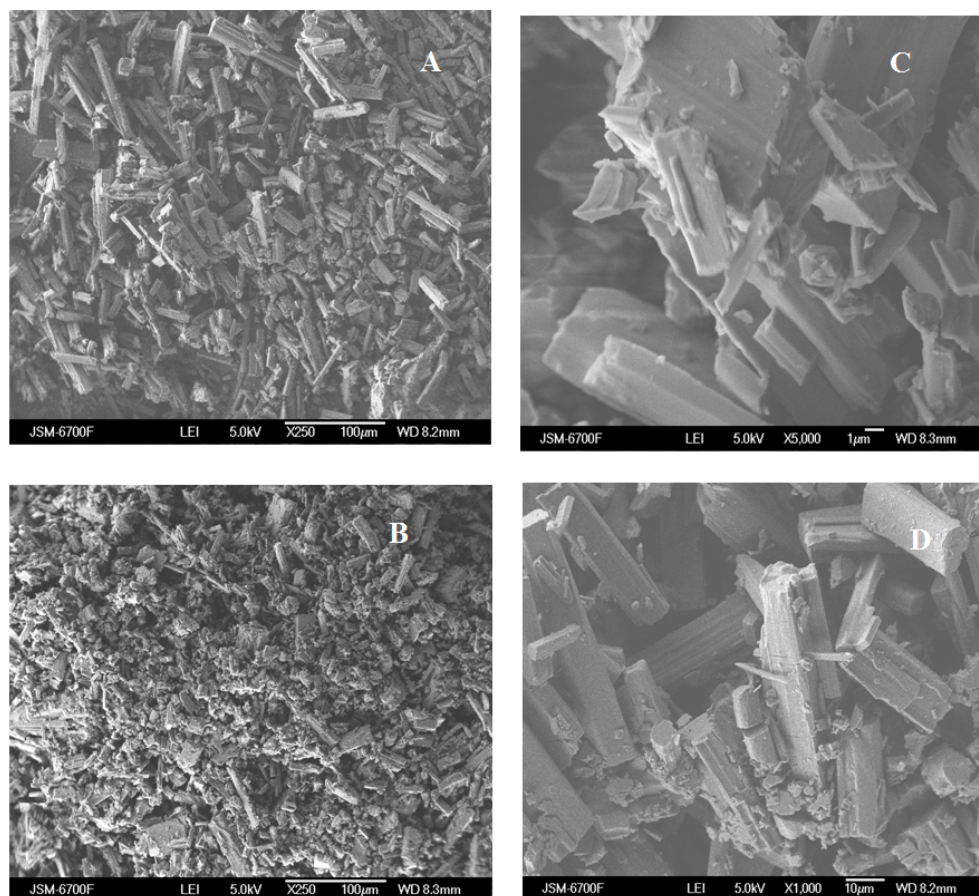


Figure 2. Scanning electronic microphotographs of the surfaces of α -CD-I₂ (A) and β -CD-I₂ (B) Left, 250×magnification; α -CD-I₂ (C) and β -CD-I₂ (D) Right, 5000×magnification

The changes in particle morphology that occurred during CDs synthesis are indicated in the SEM study (Figures 1 and 2). The SEM microphotographs of α - and β -CD complexes with iodine are almost similar as shown in Figure 2. It is appeared, that during synthesis, original morphology of CDs almost fully disappeared and needle shaped crystals with regular size were present.

The SEM microphotographs of CDs are similar to those obtained by Ikotun and coauth [11]. Analysis of surface morphology of the cyclodextrin-iodine samples obtained from high resolution SEM method revealed about coarse crystalline structures formation, which is nontypical for organic polymeric compounds.

The mentioned above disparity between literature data and our experimental results related to the iodine content in CD-I₂ inclusion complexes can be explained by intense washing of synthesized crystals by KI aqueous solution. This is obviously resulted in polyiodide chain disruption and incapsulated extrinsic molecular iodine washing out. In the

other words, one molecule of α - or β -CD was binding a one molecule of iodine during synthesis.

Probably, at the initial stage of complex formation, iodine molecule bind to the molecule of cyclodextrin give rise to inclusion complex formation with stoichiometric ratio 1:1. Further, additional complexation may occur as a result of iodine interaction with the 1:1 complex.

Conclusions

Thus, comparative studies have revealed, that cyclodextrin: iodine ratio in the obtained complexes is 1:1. Reproducibility of procedure of CD-I₂ synthesis has confirmed. These complexes remain stable during storage for 1 year and lost approximately only 9 % of iodine. It has shown, that iodine content in the α -CD-I₂ and β -CD-I₂ can be estimated with use of relatively simple and quick method of iodimetric titration, which is being important property of these complexes for their further application in food technologies.

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