Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 106 (2008) 50–55
Food Chemistry
www.elsevier.com/locate/foodchem

Evaluation of complex forming ability of hydroxypropyl-β-cyclodextrins

Chao Yuan, Zhengyu Jin *, Xuehong Li

School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China

Received 1 October 2006; received in revised form 19 March 2007; accepted 21 May 2007

Abstract

The complex forming ability of hydroxypropyl-β-cyclodextrins (HP-β-CDs) is highly influenced by the distribution of substituents and the average degree of substitution (DS), both the size of the cavity and the reactivity of CDs are altered when the hydroxyl groups are substituted. On the other hand, the guests themselves influence these interactions by their sizes and configurations. In the present study, 9 HP-β-CDs with different substitution patterns and DS, which have been investigated by the reductive-cleavage method and methylation analysis, were chosen. The interactions among HP-β-CDs and phenolphthalein (as a model for 'larger spheriform' guests) or *p*-methyl red (as a model for 'smaller linear' guests) were studied for determining the complex forming ability of HP-β-CDs. The results indicated that, compared with parent β-CD, HP-β-CDs have a lower ability to form inclusion complexes with the 'larger spheriform' guest molecules. With regard to the 'smaller linear' guest molecules, HP-β-CDs have a higher complex forming ability, especially the low DS value (<6.5) HP-β-CDs which have a ratio of DS (2 + 3) to DS (6) close to 1.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Hydroxypropyl-β-cyclodextrin; Substitution pattern; Inclusion complex; Phenolphthalein; *p*-Methyl red; Stability constant

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of several D-glucose units linked by α-(1,4) bonds. This cyclic configuration provides a hydrophobic internal cavity and gives the CDs a truncated cone shape. Many hydroxyl groups are situated on the edges of the ring which make the CDs both lipophilic and soluble in water. As a result, CDs are able to form inclusion complexes with a wide variety of hydrophobic compounds, and thus change the physical–chemical properties of the guest molecules (Del Valle, 2004; Dodziuk, 2002; Szejtli, 1998).

The most common parent CDs are α-, β-, γ-CD with the corresponding number of glucose units ($\alpha = 6$, $\beta = 7$, $\gamma = 8$). β-CD is the most accessible, the lowest-priced and generally the most useful, but β-CDs are not very soluble in water due to the strong hydrogen bond between HO-2 and O-3 (Saenger, 1980).

Hydroxylpropyl-β-cyclodextrin (HP-β-CD), a hydroxyalkyl derivative, is an alternative to α-, β- and γ-CD, with improved water solubility (Uekama, Hirayama, & Irie, 1998) and may be slightly more toxicologically benign (Sarah & Robert, 2005). As the first approved CD derivatives by FDA, HP-β-CDs have widely applications in food, agriculture and the pharmaceutical field (Hedges, 1998; Schneiderman & Stalcup, 2000; Singh, Sharma, & Banerjee, 2002; Szente & Szejtli, 2004). HP-β-CDs are prepared by reacting β-CD with propylene oxide in alkaline aqueous solutions. The high alkali concentration favours alkylation at O-6, while the low alkali concentration favours alkylation at O-2 (Pitha & Rao, 1990). The products are always substituted randomly when it comes to distribution among the different glucose units. In addition, the ratio of reactants, reaction time and the temperature affect the average degree of substitution (DS). It follows that the composition of the HP-β-CD samples show high variability, which is

* Corresponding author. Tel.: +86 510 85867587; fax: +86 510 85811950.
E-mail address: wheat1997@yahoo.com (Z. Jin).

0308-8146/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2007.05.045

also reflected in the chemical and physical properties (Rao, Fales, & Pitha, 1990; Szente & Szejtli, 1999).

The effect of DS on the inclusion forming ability has been studied by different authors researching this field. Müller and Brauns (1986) reported that the DS of mixtures of HP-β-CD derivatives has a large influence on the complexing abilities. A low degree of substitution is preferable, since these derivatives show the best complexing properties. Rao and Pitha (1992) found the complex forming ability of HP-β-CDs first increases and then decreases with increasing DS. A clear conclusion has not been reached due to the amorphism of HP-β-CDs. Moreover, the substitution pattern affects the stability of inclusion complexes too. It seems that both the DS and the substitution pattern influence the stereospecificity of HP-β-CDs (Buvári-Barcza & Barcza, 1999; Loukas, Vraka, & Gregoriadis, 1996). However, there are very few studies focusing on the effect of the substitution pattern of HP-β-CDs on the formation of inclusion complexes.

On the other hand, the stability of inclusion complexes is also influenced by the sizes and configurations of the guests. Different guest molecules have different abilities to fit into the CD cavity. A recent evaluation found the stability constant value of 38 drugs/HP-β-CD complexes to vary considerably from $34\ M^{-1}$ to $150{,}000\ M^{-1}$ (Loftsson, Hreinsdóttir, & Másson, 2005). Therefore the appropriate model guests have to be chosen to study the issue. Phenolphthalein (PP) and *p*-methyl red (MR) may be the ideal choices (Fig. 1) since they are aromatic compounds, which are typical guests for inclusion, and the changes in absorbance make it easy to calculate the quantity. PP was chosen for modelling the 'large spheriform' guest, as only a part of its molecule is included during the complex formation (Buvári, Barcza, & Kajtár, 1988). MR served as a suitable 'small linear' molecule model since it can enter the CD cavity rather easily and the fitting is loose (Tawarah & Khouri, 1993; Tawarah & Khouri, 2000).

Preparations of HP-β-CD with low DS value (<8) were found to have optimal solubilisation properties for guests and these preparations could also be transformed into non-hygroscopic powders (Pitha, Milecki, Fales, Pannell, & Uekama, 1986). The HP-β-CDs used in this study had been investigated by the reductive-cleavage method and methylation analysis, the DS value of the HP-β-CD samples were well distributed between 0 and 9. The formation and stability of inclusion complexes formed between HP-β-CDs and PP or MR were investigated using two spectrophotometric methods. Comparing the trends in the stability constants for different hosts and guests, some new and more general conclusions were drawn.

2. Materials and methods

2.1. Materials

HP-β-CD samples were prepared in our laboratory by reacting β-CD with propylene oxide under two different base concentrations [group A (samples 1–4) under 18%; group B (samples 5–8) under 5%], except one (sample 9) which was purchased from Wako Pure Chemical Industries, Ltd. (Chuoku, Osaka, Japan). The substitution pattern and DS of the HP-β-CD samples had been investigated by a reductive-cleavage method and methylation analysis (Ciucanu & Kerek, 1984), Table 1 shows the result. All other materials were of analytical grade and used without future purification. The water used was deionized.

2.2. Determination of stability constant

The stability constants of CD–PP inclusions were determined by spectrophotometry using a UV1201 instrument (Rayleigh, Chaoyang, Beijing, China). Stock solutions of an average molar concentration of about 1.2×10^{-3} were prepared from β-CD and each HP-β-CD sample, a solution of PP (0.375 mM, 2.5 mL) was added to each stock solution (2 mL), sodium carbonate (0.04 M, 2.5 mL) was then added and the volume brought to 25 mL by addition of water. The obtained mixtures were stirred (500 rpm) at constant temperature (30 °C) until equilibrium (72 h). The absorbance was scanned from 200 nm to 850 nm to determine the formation of an inclusion complex and the characteristic absorption wavelength. At the characteristic absorption wavelength, absorbance was measured to determine the amount of PP in solutions since the complexed form is colourless (Buvári et al., 1988). With known concentrations of PP ([PP]) and the total concentrations (c_{PP} and c_{CD}), the stability constants can be calculated from the given Eqs. (1)–(3)

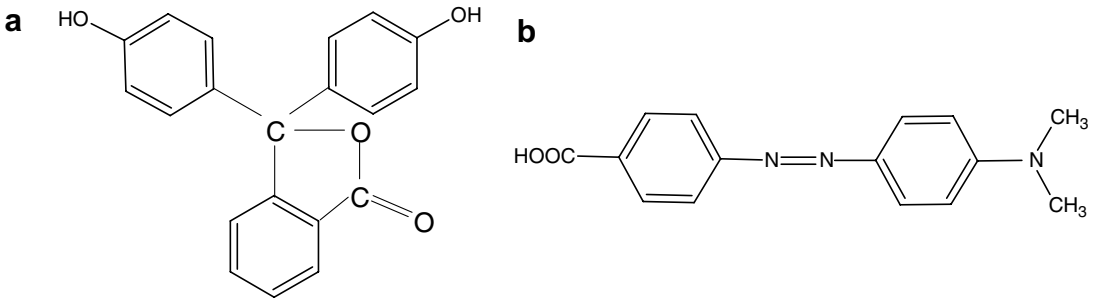

Fig. 1. Structural formulas of phenolphthalein (a) and *p*-methyl red (b).

Download English Version:

https://daneshyari.com/en/article/1189086

Download Persian Version:

https://daneshyari.com/article/1189086

Daneshyari.com