

Release Behavior of Flavor Encapsulated CD in Slurry Solution Under Boiling Conditions

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Abstract

Cyclodextrin (CD) can control flavor release rate and protect the flavor from volatilization by the formation of inclusion complex with flavor compounds. However, the flavor release rate during cooking, particularly in boiling water has hardly been understood. In this study, flavor release rate of flavor encapsulated CD in slurry or turbid solution under boiling condition was investigated. The release rate constants of methyl caproate and D-limonene depended on the CD concentration, whereas, those of phenyl ethanol hardly did. The plot of a reciprocal number of apparent release rate constant to CD concentration for D-limonene stability constant under boiling condition was obtained. Stability constants for D-limonene in α -CD and β -CD were 185 and 38 M⁻¹, respectively. These stability constants were smaller than the order of 1000 M⁻¹ at room temperature. These results suggested that the addition of CD for protection of flavors in boiling water might have small effect in comparison to that at room temperature. The behavior of flavor release in the boiling water correlated well with the first-order release rate equation, which can be described by the film theory of the interfacial mass transfer.

Introduction

Flavor release from foods is very important because it reflects consumer satisfaction. Overbosch *et al.* [1] reviewed important factors affecting flavor release. De Roos *et al.* [2] reviewed the effects of texture and microstructure on the retention of aroma compounds during processing and storage. Harrison and co-workers [3–5] investigated the dynamic release models for several systems such as macromolecules solution, food matrices, gelatin gels and liquid emulsions. Hills and Harrison [6] proposed the two-film theory of flavor release from solids for flavor release from boiled candy. Banavra *et al.* [7] investigated the flavor release from water and developed a mathematical model derived from the convective mass transfer theory. Taylor [8] reviewed flavor release from food matrices and subsequently the delivery of flavor to the olfactory and gustatory receptors. Juteau *et al.* [9] reviewed flavor release from polysaccharides gels: different approaches for determination of kinetic parameters. The release of flavor compounds from food matrices is mainly governed by two basic phenomena. The first one deals with the physico-chemical interactions which takes place between the flavor and some food ingredients. The second one

relates to the structural characteristics of food matrixes which may influence diffusion phenomena and kinetic parameters. Among various flavor release control methods, molecular inclusion of cyclodextrins (CDs) is a useful and effective technique. CD molecule can be envisioned as hollow truncated cone-shaped molecule with a hydrophobic interior cavity, with inner diameter of 5–8 Å [10]. Flavor components have been encapsulated within CDs and CD can control flavor release and protect the flavor volatilization by the formation of inclusion complex with flavor compounds. CD enhances the stability of flavors to oxygen, heat or light by including the flavor in the molecular cavity. Therefore, they are widely used in food formulations for flavor protection or flavor delivery. Yoshii *et al.* [11] and Bandari *et al.* [12] prepared the inclusion complex powder by kneading of β -CD slurry and flavors directly at low water content, suggesting that the kneading was a more efficient method than saturated solution method. Shiga *et al.* [13] investigated flavor encapsulation and release characteristics of spray-dried powder by a blended encapsulant of CD and gum arabic. Reineccius *et al.* [14] investigated the incorporation and retention on storage of a variety of flavor compounds spray-dried in α -, β -, and γ -CD. Kant *et al.* [15] investigated effect of β -CD on aroma release in model aqueous systems using static equilibrium headspace and dynamic headspace

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dilution and indicated β -CD decreased the static equilibrium headspace for some volatiles due to binding. There are few investigations of the controlled release with regard to encapsulated flavor such as emulsified spray-dried powder and CD flavor complex under cooking conditions. The flavor release rate during cooking, particularly in boiling water has hardly been understood. In this study, flavor release rate of flavor encapsulated flavor CD in slurry solution under boiling condition was investigated.

Materials and methods

Materials

Reagent grade α -, β - and γ -CD were obtained from Ensui Sugar Refining Co. (Yokohama, Japan). Methyl *n*-hexanoate, phenyl ethanol, menthol, methyl caproate, and allyl isothiocyanate (AITC) as model flavors were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). β -Limonene was from Tokyo Kasei Kogyo Co. (Tokyo, Japan).

Formation of complex powder between CD and flavor with kneading method

The inclusion complexes of flavors with CDs were prepared using kneading method. Thirty grams of CD powder was weighed and mixed with 1.5 times molar quantity of flavor, followed by the addition of distilled water to moisture content of 50% on a dry basis. The mixture was then kneaded in a twin-screw kneader (KRC-S1, Kurimoto Steel Ltd., Osaka, Japan) at 20 °C for 30 min. The kneaded wet slurry was vacuum dried at 40 °C for 3 h, and 70 °C for 10 h. The dried powder was ground and sieved into 80–100 mesh and freeze-dried at –30 °C. The flavor content in the powder was measured using FID gas chromatography. The extraction procedure was the same as reported elsewhere [16]. Molar ratios of encapsulated flavors to CDs are as shown in Table 1.

Flavor release behavior of flavor-encapsulated CD in slurry solution under boiling conditions

The flavor release behavior in boiling water was investigated by weighing about 0.1 g of kneaded powder into a glass tube (13 mm diameter×100 mm height) and then pouring in 4 ml of distilled water. The tube was dipped in boiling water for a fixed time. The tube was then opened, and a small amount of water was evaporated. After the prescribed time, the tube was removed from the boiling water and chilled in ice-cooled water. The remaining amount of flavor in the samples was quantified by FID gas chromatography as follows. One milliliter of chloroform was added to the solution in the tube, followed by vigorous mixing with a vortex mixer for 1 min. To extract the flavor into chloroform, the

Table 1. Encapsulation molar ratio of flavor to CDs

Flavor	α -CD	β -CD	γ -CD
Phenyl ethanol	0.81	0.90	1.32
β -Limonene	0.40	0.83	1.40
Menthol	0.48	0.81	1.10
Methyl caproate	0.82	0.77	1.20
AITC	0.64	0.71	0.95

The added molar ratio of flavor to CD was 1.5 in kneading operation.

mixture was heated in a heating block with intermittent shaking. The extraction time and temperature were 20 min and 80 °C, respectively. The extracted mixture was then centrifuged at 3000 rpm for 10 min to separate chloroform from the water. Two micro liters of chloroform was injected twice for each sample into the gas chromatograph (GC-14B, Shimadzu Corporation, Kyoto, Japan) equipped with a PEG-20M packed column (2 m×3.2 mm). The chromatographic conditions were as follows: flame ionization detector (FID) at 220 °C for phenyl ethanol or 150 °C for AITC, β -limonene, menthol and methyl caproate with N₂ as the carrier gas. The column temperature was controlled at constant values of 100, 100, 140, 170 and 190 °C for β -limonene, methyl caproate, AITC, menthol, and phenyl ethanol, respectively. The external standard method was used to calculate the flavor quantity. Two bottles of the standard of each flavor in hexane were prepared. Two micro liters of the standard was injected into the gas chromatograph twice for each bottle of standard.

Flavor release was analyzed with the first-order release rate equation. The retention of flavors during heating was defined as the ratio of the flavor content in the solution to the initial flavor content.

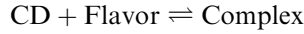
Flavor release model with volumetric mass transfer coefficient

The flavor encapsulated CD in the tube was turbid solution under boiling condition.

The mass balance of flavor at gas–liquid surface in the tube is given by

$$-\frac{dC_{\text{Flavor(Total)}}}{dt} = (k_L a)C_{\text{Flavor(free)}} \quad (1)$$

where $C_{\text{Flavor(Total)}}$ is total flavor concentration in the solution and $C_{\text{Flavor(free)}}$ is non-encapsulated flavor in the solution. ($k_L a$) is apparent volumetric mass transfer coefficient, a is a specific gas–liquid surface area. This model assumes that flavor transport across the gas–liquid interface can be described by the film theory of the interfacial mass transfer. Flavor and CD have equilibrium in the solution. The assumption is the encapsulation reaction between flavor and CD concludes following equilibrium equation, (2).



$$K = \frac{C_{\text{complex}}}{\text{CD}_{(\text{free})} C_{\text{Flavor}(\text{free})}} \quad (2)$$

C_{complex} is the complex concentration of flavor and CD, and $\text{CD}_{(\text{free})}$ is the concentration of free CD. K is the stability constant. Eq. (2) can change to Eq. (3) and Eq. (4) to free flavor concentration.

$$\begin{aligned} C_{\text{Flavor}(\text{Total})} &= C_{\text{Flavor}(\text{free})} + C_{\text{complex}} \\ &= C_{\text{Flavor}(\text{free})} + K \text{CD}_{(\text{free})} C_{\text{Flavor}(\text{free})} \quad (3) \\ &= C_{\text{Flavor}(\text{free})} (1 + K \text{CD}_{(\text{free})}) \end{aligned}$$

$$C_{\text{Flavor}(\text{free})} = \frac{C_{\text{Flavor}(\text{Total})}}{(1 + K \text{CD}_{(\text{free})})} \quad (4)$$

Eq. (4) was substituted for Eq. (1).

$$\begin{aligned} -\frac{dC_{\text{Flavor}(\text{Total})}}{dt} &= \frac{(k_L a)}{(1 + K \text{CD}_{(\text{free})})} C_{\text{Flavor}(\text{Total})} \quad (5) \\ &= k_1 C_{\text{Flavor}(\text{Total})} \end{aligned}$$

k_1 is an apparent first-order flavor release rate constant. Integration of Eq. (5) becomes the following Eq. (6).

$$-\ln \frac{C_{\text{Flavor}(\text{Total}),t=t}}{C_{\text{Flavor}(\text{Total}),t=0}} = \frac{(k_L a)}{(1 + K \text{CD}_{(\text{free})})} t \quad (6)$$

The flavor release behavior could be correlated with the first-order release equation as shown in Eq. (6).

The apparent release rate constant, k_1 is shown in the following Eq. (7).

$$k_1 = \frac{(k_L a)}{(1 + K \text{CD}_{(\text{free})})} \quad (7)$$

The reverse equation of Eq. (7) is Eq. (8).

$$\frac{1}{k_1} = \frac{K}{(k_L a)} \text{CD}_{(\text{free})} + \frac{1}{(k_L a)} \quad (8)$$

This estimation model of stability constant was applied to the flavor release of the encapsulated flavor CD in boiling solution.

Results and discussion

Figure 1 shows flavor release behavior of flavor encapsulated α -CD (α -CD=25 mM) in boiling water at 373 K. Flavor retentions in boiling water decreased monotonously with time. In Figure 1, the solid lines were correlated by Eq. (6). In solution and the slurry solution system, the flavor release mechanism can be described by the gas desorption rate in the limiting step of the mass transfer at the gas-liquid interface. Therefore, the flavor release rate might be the first-order release reaction as shown in Eq. (6). Table 2 shows the apparent release rate constant, k_1 (first-order release rate

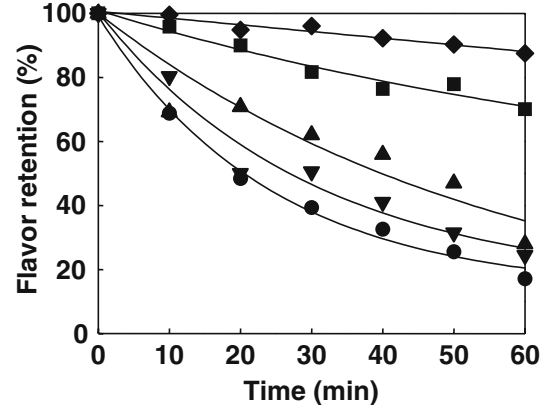


Figure 1. Flavor release behavior of flavor encapsulated α -CD in boiling water. \blacklozenge , phenyl ethanol; \blacksquare , D-limonene; \blacktriangle , L-menthol; \blacktriangledown , methyl caproate; \bullet , AITC. Incubation temperature was 100 °C. α -CD concentration was 25 mM. Solid lines were correlated with the first-order release rate equation, Eq. (1).

constant), [10^{-4} /s] for various flavors and CDs. Flavor retentions depended on the guest flavor. The values of k_1 for phenyl ethanol were 0.350×10^{-4} 1/s for α -CD, 0.383×10^{-4} 1/s for β -CD and 0.317×10^{-4} 1/s for γ -CD, respectively. Apart from phenyl ethanol and menthol, the release rate constants of α -CD became smaller in comparison with β and γ -CD. In α -CD or β -CD, the flavor release rate decreased in the order of phenyl ethanol > D-limonene > menthol > methyl caproate > AITC. The apparent release rate constants of phenyl ethanol were smaller about 13 to 14 times for α -CD and β -CD, and 28 times for γ -CD in comparison with the apparent release rate constant of AITC.

Figure 2 shows the flavor release behavior of encapsulated phenyl ethanol and encapsulated AITC in α -CD, β -CD and γ -CD in 25, 22 and 19 mM complex powder concentration, respectively. The release rates of phenyl ethanol were almost the same for α -CD, β -CD and γ -CD. On the other hand, the release behaviors for AITC were dependent on the kinds of CD.

Effect of concentration (1–25 mM) of CD encapsulated flavor powder in boiling water was investigated in regards to the release rate. Figure 3 shows the effect of the amount of D-limonene encapsulated α -CD on the release rate of D-limonene in boiling water. The release rate constant decreased with concentration of the powder. The release rate constants of methyl caproate and D-limonene depended on the CD concentration, whereas, those of phenyl ethanol hardly depended.

Table 2. Apparent release rate constant, [10^{-4} /s] for various flavor

Flavor	α -CD	β -CD	γ -CD
Phenyl ethanol	0.350	0.383	0.317
D-Limonene	0.967	1.37	1.60
Menthol	2.97	1.70	1.50
Methyl caproate	3.93	4.08	5.47
AITC	4.85	5.15	8.88

The concentration of CD complex is 25 mg/ml.

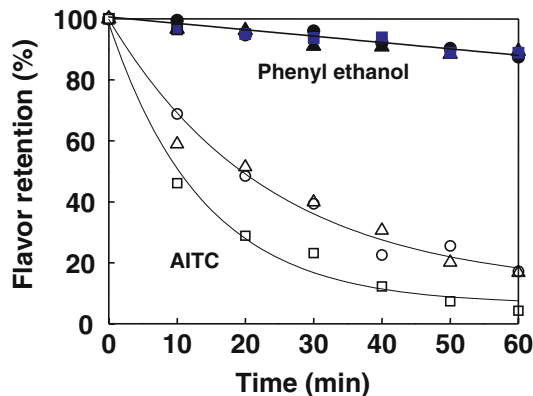


Figure 2. Flavor release behavior of flavor encapsulated CD in boiling water. ●, ○: α -CD (25 mM); ▲, △: β -CD (22 mM); ■, □: γ -CD (19 mM). Closed keys indicate the data of phenyl ethanol. Open keys indicate the data of AITC. Solid lines were correlated with the first-order release rate equation, Eq. (1).

Figure 4 shows the plot of the reciprocal number of apparent release rate constant vs. α -, and β -CD concentration to obtain D-limonene stability constants under boiling condition by using Eq. (8). The stability constant, K is a useful value to estimate the equilibrium between guest, CD and the complex. The reciprocal values of the apparent release rate constants correlated well with straight lines for α -, and β -CD, respectively. The K was calculated from the slope of the straight line by Eq. (8). Stability constants for D-limonene in α -CD and β -CD were 185 and 38 M^{-1} , respectively. These stability constants were smaller than the order of 1000 M^{-1} at room temperature [10]. These results suggest that the addition of CD for protecting of flavors in boiling water might have small effect in comparison to that at room temperature. The behavior of flavor release

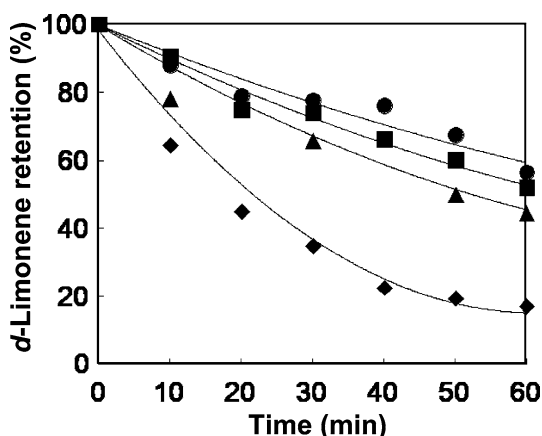


Figure 3. Effect of addition amount of D-limonene encapsulated α -CD in boiling water on the release behavior. ●, 25 mM; ■, 13 mM; ▲, 5 mM; ◆, 1 mM. Solid lines were correlated with the first-order release rate equation, Eq. (1).

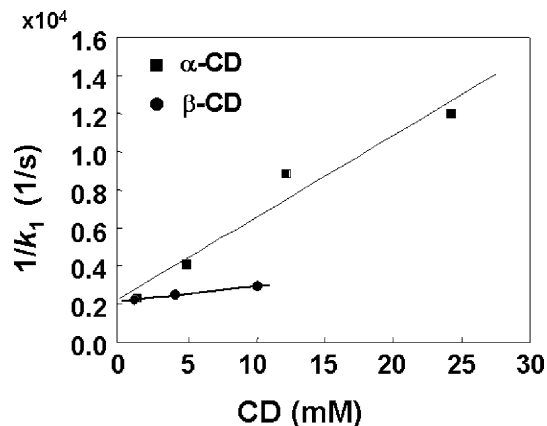


Figure 4. Plot of a reciprocal number of apparent release rate constant to α -, or β -CD concentration. ■, α -CD; ●, β -CD. Solid straight lines were correlated with Eq. (8).

in the boiling water correlated well with the first-order release rate equation.

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