Production of a transparent lavender flavour nanocapsule aqueous solution and pyrolysis characteristics of flavour nanocapsule

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Abstract Flavour plays an important role and has been widely used in many products. Usually, the components of flavour are volatile and the sensory perception can be changed as a result of volatilization, heating, oxidation and chemical interactions. Encapsulation can prevent the loss of volatile aromatic ingredients, provide protection and enhance the stability of the core materials. This work concentrated on production of a transparent lavender flavour nanocapsule aqueous solution. The results showed that a transparent lavender flavour microcapsule aqueous solution can be produced using hydroxypropyl- β -cyclodextrin (HP- β -CD) as wall material. The combination and interaction of flavour and wall materials were investigated by pyrolysis. Pyrolysis characteristics and kinetic parameters of the flavour nanocapsule were determined. During thermal degradation of blank HP- β -CD and flavour-HP- β -CD inclusion complex, three main stages can be distinguished. Due to the vaporization of lavender flavour encapsulated in HP- β -CD, the thermogravimetric (TG) curve of blank HP- β -CD shows a leveling-off from room temperature to 269 °C, while the TG curve of flavour-HP- β -CD inclusion complex is downward sloping in this temperature range. The kinetic parameters are helpful in understanding the mechanism of molecular recognition between hosts and guests.

Keywords Flavour nanocapsule · Pyrolysis · Kinetics · Thermogravimetric

Introduction

A flavour is a mixture of odorous materials derived from synthetic and natural sources. Lavender flavour has a sweet, herbaceous, slightly floral odor, and can be used in food, balms, salves, perfumes, cosmetics, and topical applications. Lavender is used with herbs and aromatherapy, and believed to soothe insect bites, burns, and headaches. Due to the inherent volatility of aromatic compounds, the lifespan of flavour is short (Vaughn et al. 2009). The sensory perception can also be changed as a result of heating, oxidation, chemical interactions or volatilization (Zhu et al. 2012a). Encapsulation can prevent the loss of volatile aromatic ingredients, improve shelf life of the entrapped flavour, provide protection and enhance the stability of the flavour core materials (Ahn et al. 2006). Cyclodextrins are a family of compounds made up of sugar molecules bound together in a ring, and can be used as wall materials. Hydroxypropyl- β -cyclodextrin (HP- β -CD) is a typical one which is constituted by 7 glucopyranoside units. It presents a hydrophobic inner cavity and a hydrophilic outer surface. Guest molecules, with suitable dimensions to fit inside the interior, can be included into the cyclodextrin molecule to form agent-cyclodextrin complexes (Chen et al. 2010). Usually, paste or powder flavour microcapsules are produced with cyclodextrins as wall materials (Petrović et al. 2010). Transparent flavour microcapsule aqueous solution is a new concept of flavour. It is stable and convenient to use. Furthermore, due to turbid problem appearing in transparent medium added flavour, the production of a transparent flavour microcapsule aqueous solution is of great interest. However, transparent flavour microcapsule aqueous solution fabrication has never been reported.

In general, binding energy represents the mechanical work which must be done against the forces which hold an object together. Therefore, the binding energy of flavour and HP- β -

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cyclodextrin is important for a deep understanding the interaction between flavour and HP- β -cyclodextrin, and reaction mechanism. It can help us revealing the combination of the host and the guest. However, the binding energy of flavour and HP- β -cyclodextrin was seldom reported. Determination of pyrolysis activation energy is an easy method to estimate the binding energy.

In this paper, a transparent lavender nanocapsule aqueous solution was produced, and the pyrolysis characteristics and kinetic parameters of the flavour-HP- β -CD inclusion complex were determined using thermogravimetric analysis.

Materials and methods

Materials

HP- β -cyclodextrin (white powder, content $\geq 98\%$) was purchased from Shandong Binzhou Zhiyuan Bio-Technology Co., Ltd. Tween-20 were purchased from Sinopharm Chemical Reagent Co. Ltd. The lavender flavour was provided by City Flower Co. Ltd.

Preparation of lavender HP- β -cyclodextrin complexation process

The complexation process adopted to prepare the lavender-HP- β -cyclodextrin complex was as follows: Approximately 25 g of HP- β -cyclodextrin was dissolved in 55 mL of deionized water maintained at 35 °C on a hot plate. About 5 g of lavender flavour was then slowly added to the warm HP- β -cyclodextrin solution. The mixture was continuously stirred for 2 h and the temperature maintained at 35 °C. A proper amount of Tween-20 was then added to the mixture. The mixture was continuously stirred for another 1 h and the temperature decreased spontaneously to room temperature at the same time.

Determination of the particle size distribution

The average diameter and the size distribution of the encapsulated lavender flavour nanocapsule in three replicates were determined by Zetasizer Nano ZS (Malvern Instruments Ltd, UK). The size distribution was evaluated for all samples according to the polymer dispersibility index (PDI). PDI is an indicator of the nanocapsule size distribution in the range 0–1. PDI values of < 0.2 indicate a monodisperse emulsion, whereas values > 0.5 show larger distributions.

Transmission electron microscopy (TEM) measurement

TEM measurement was conducted using a FEI Tecnai electron microscopy at an acceleration voltage of 200 kv to

investigate the morphology of the lavender flavour microcapsule. The transparent lavender flavour microcapsule aqueous solution was dripped onto a 300 mesh copper grid coated carbon film. The sample was dried before viewing on the transmission electron microscopy.

Thermogravimetric analysis (TGA)

The experiments were carried out in a TGA-Q5000IR thermogravimetric analyzer (TA Instruments, USA). In the experiment, approximately 6 mg of dried sample was spread uniformly on the bottom of the ceramic crucible of the thermal analyzer. The pyrolysis experiment was performed at a heating rate of 10 °C/min in a dynamic high purity nitrogen flow of 20 ml/min. The temperature of the furnace was programmed to rise from room temperature to 500 °C.

Results and discussion

The appearance of flavour-HP- β -cyclodextrin inclusion complex

The relatively hydrophobic cavity of HP- β -cyclodextrin can accommodate various kinds of guest molecules to form inclusion complexes. A transparent lavender flavour nanocapsule aqueous solution was produced according to above method. The inclusion complex of lavender flavour with HP- β -cyclodextrin is shown in Fig. 1. The flavour-HP- β -cyclodextrin inclusion complex aqueous solution is a clear transparent pale yellow liquid. It is convenient to use in transparent medium.

Diameter and the size distribution

The average diameter and the size distribution of the encapsulated lavender flavour microcapsule were determined by Zetasizer Nano ZS. The results showed that the average

Fig. 1 Transparent lavender flavour nanocapsule aqueous solution

Fig. 2 TEM image of the transparent lavender flavour nanocapsule

diameter and the PDI of the encapsulated lavender flavour microcapsules were about 15 nm and 0.3 respectively.

Morphology of the lavender flavour-HP- β -cyclodextrin inclusion complex

The TEM image of the transparent lavender flavour nanocapsule is shown in Fig. 2. Figure 2 demonstrates those lavender flavour inclusion complexes are nano spherical particles. The diameter of the capsules dispersed evenly (about 15 nm). The size of the lavender flavour nanocapsule conforms to the result that obtained by Zetasizer Nano ZS. The flavour-HP- β -cyclodextrin inclusion complexes are nanocapsules. Owing to the large surface area to volume ratio

and high surface energy, the nanocapsules have good affinity for cotton fabrics, leathers and papers. These aromatic products with sustained flavour release may be produced via this flavour nanocapsule.

Pyrolysis characteristic comparison of flavour-HP- β -CD inclusion complex to blank-HP- β -CD

In order to investigate the mechanism of the combination of flavour and HP- β -CD, and to evaluate the binding energy, TGA was employed in the experiment. TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature, or as a function of time. The activation energy of decomposition reaction can be obtained by TGA (Zhu et al. 2012c, 2014). Binding energy, which can be evaluated by pyrolysis activation energy, is useful data to understand the interaction of flavour and HP- β -cyclodextrin.

Figure 3 shows the weight loss and the rate of weight loss curve obtained during the pyrolysis of blank HP- β -CD and flavour-HP- β -CD inclusion complex samples under inert atmosphere at a heating rate of 10 °C/min. As shown in Fig. 3, during thermal degradation, three main stages can be distinguished from the TG curves of both blank HP- β -CD and encapsulated samples. The first stage goes from room temperature to 269 °C; a slight weight loss in the thermogravimetric (TG) curve is observed. The second stage goes from 269 to 410 °C, and is characterized by a major weight loss, which corresponded to the main pyrolysis process of HP- β -CD. Most of HP- β -CD was decomposed in this stage. Two strong peaks appeared at 336.6 °C in the DTG curves of both blank

Fig. 3 TG-DTG curves of blank HP- β -CD (broken line) and flavour-HP- β -CD inclusion complex (real line)

Table 1 Results of flavour-HP- β -CD inclusion complex pyrolysis activation energy and reaction order

Peak temperature (°C)	Temperature range (°C)	Apparent activation energy (kJ/mol)	Reaction order	R
93.1	29.2–176.4	24.6	1	−0.9988
256.8	176.4–270	86.4	0.04	−0.9866

HP- β -CD and encapsulated samples, and were due to the decomposition of HP- β -CD. At this temperature, the rate of weight loss attained the maximum value. The third stage goes from 410 °C to the final temperature (500 °C) of the experiment. The solid residuals continuously decomposed at a very slow rate in the third stage.

Compared to the pyrolysis characteristic of blank HP- β -CD, although the TG curve of flavour-HP- β -CD inclusion complex is similar to that of the blank HP- β -CD, some new pyrolysis characteristics appear especially in the first stage. From Fig. 3, we can see that the TG curve of blank HP- β -CD shows a leveling-off from room temperature to 269 °C, while the TG curve of flavour-HP- β -CD inclusion complex is downward sloping in this temperature range. The weight losses of blank of HP- β -CD and flavour-HP- β -CD inclusion complex from room temperature to 269 °C are 3.6 % and 9.3 % respectively. The components of lavender flavour include linalool, linalyl acetate, α -pinene, limonene, 1,8-cineole, *cis*- and *trans*-ocimene, 3-octanone, camphor, and terpinen-4-ol. The primary components of lavender flavour are linalool (51 %) and linalyl acetate (35 %) (Prashar et al. 2004). The difference of the weight losses is mainly due to the vaporization of linalool and linalyl acetate encapsulated in HP- β -CD. From the difference of the two values of weight loss, flavour loading capacity can be estimated. The lavender flavour loading capacity is about 5.7 %. During the thermal degradation of flavour-HP- β -CD inclusion complex, the encapsulated flavour was gradually released. Furthermore, small peaks can be observed in the derivative thermogravimetric (DTG) curve of flavour-HP- β -CD inclusion complex. These peaks are mainly attributed to vaporization of the linalool and linalyl acetate. Flavour release mainly happened in the first stage of the TG curve as shown in Fig. 3. In order to make sure the combination of flavour and HP- β -CD, It is necessary to investigate the pyrolysis characteristics of flavour-HP- β -CD inclusion complex in the first stage of the TG curve. The small peaks in Fig. 3 should be explored in depth. During the heating process of the flavour-HP- β -CD inclusion complex from room temperature to 269 °C, two stages and two peaks can be distinguished as shown in Fig. 3. The first stage goes from room temperature to 176.4 °C, and the weight loss in this stage is 3.1 %. The first peak temperature is 93.1 °C, and at this temperature the rate of weight loss attains maximum value (0.0617 %/°C). The second stage goes from 176.4 to 269 °C, and the weight loss in this stage is 6.2 %. The second peak temperature is 256.8 °C. At 256.8 °C, the rate of weight loss

attains maximum value (0.1178 %/°C). The peaks at 93.1 and 256.8 °C are possibly due to vaporization of linalyl acetate and linalool respectively. The lavender flavour is composed of a lot of volatile aroma compounds. The binding energies of aroma compounds and HP- β -CD are different. Linalool and linalyl acetate are two primary components. Therefore, during the heating process of the flavour-HP- β -CD inclusion complex, two peaks in the rate of weight loss curve can be observed.

Pyrolysis kinetic parameters of flavour-HP- β -CD inclusion complex

In view of the fact that flavour-HP- β -CD inclusion complex is a mixture which is composed of volatile aroma compounds and HP- β -CD, the decomposition of flavour-HP- β -CD inclusion complex comprises a large number of reactions in parallel and in series, whereas DTG measures the overall weight loss rate. Therefore, DTG provides general information on the overall kinetics rather than individual reactions (Zhu et al. 2012c, 2014). The analysis of TGA graphs was used to determine the pyrolysis kinetic parameters of flavour-HP- β -CD inclusion complex such as activation energy and reaction order. According to the Freeman-Carroll method, the relationships used to relate activation energy to weight loss can be expressed as Eq. (1) (Freeman and Carroll 1958).

$$\frac{\Delta \ln \left(\frac{dw}{dt} \right)}{\Delta \ln W_r} = -\frac{E}{R} \left(\frac{\Delta \frac{1}{T}}{\Delta \ln W_r} \right) + n \quad (1)$$

where E is the activation energy, R is the gas constant, T is the absolute temperature, t is time, n is reaction order, w is total weight loss up to time t , W_r is $w_c - w$, w_c is weight loss at completion of reaction.

From Eq. (1), it is apparent that plots of $\Delta(1/T)/\Delta \ln W_r$ vs. $\Delta \ln(dw/dt)/\Delta \ln W_r$ should result in straight lines with slope of $-E/R$ and intercept of n . From the slope and the intercept of the line, we can estimate apparent activation energy and reaction

Table 2 Values of pre-exponential factors and reaction rate constants

Temperature (°C)	Pre-exponential factor	Rate constant
93.1	6.6×10^2	0.21
256.8	1.0×10^8	0.31

order respectively. There are two peaks in the rate of weight loss curve of the flavour-HP- β -CD inclusion complex from room temperature to 269 °C as shown in Fig. 3. These peaks divide the TG curve of flavour-HP- β -CD inclusion complex into two stages, and indicate that two kinds of binding modes of aroma compounds and HP- β -CD. The values of apparent activation energy and reaction order calculated according to Eq. (1) are given in Table 1.

All the linear correlation coefficients are greater than 0.98, so using Freeman–Carroll method to investigate the pyrolysis kinetics of the flavour-HP- β -CD inclusion complex is feasible. From Table 1, we can see that the apparent activation energy at 93.1 °C is relatively small compared with that at 256.8 °C. Different apparent activation energy means different reactions. A low activation energy means a fast reaction and a high activation energy means a slow reaction according to the Arrhenius equation. Small activation energy indicates that aroma compounds easily release from the inclusion complex, while high activation energy implies that aroma compounds are bound to HP- β -CD firmly. Therefore, linalool is bound to HP- β -CD more firmly than linalyl acetate.

According to literatures (Coats and Redfern 1964; Zhu et al. 2012b), the relationship among pre-exponential factor, activation energy, temperature, and the fraction of substrate decomposed can be expressed by Eq. (2) and Eq. (3).

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (\text{for } n \neq 1) \quad (2)$$

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (\text{for } n = 1) \quad (3)$$

where A is the pre-exponential factor, R is the gas constant, β is the heating rate and α is the converted rate of reaction.

Equations (2) and (3) are based on the Coats–Redfern method (Coats and Redfern 1964). Pre-exponentials factors, A , can be calculated according to Eqs. (2) and (3).

The Arrhenius equation is a simple, but remarkably accurate, formula for the temperature dependence of the reaction rate constant, and therefore, rate of a chemical reaction. The Arrhenius equation gives “the dependence of the rate constant of chemical reactions on the temperature and activation energy”. So, the reaction rate constant can be obtained by solving the Arrhenius equation as Eq. (4).

$$k = A \exp \left(\frac{-E}{RT} \right) \quad (4)$$

The pre-exponential factors and reaction rate constants obtained are shown in Table 2. As indicated in Table 2, the

pre-exponential factor and reaction rate constant of linalool release at 256.8 °C are higher than those of linalyl acetate release at 93.1 °C.

Conclusion

The paper deals with production of a lavender flavour-HP- β -CD inclusion complex, and investigation of pyrolysis characteristics and kinetics of the flavour-HP- β -CD inclusion complex using thermogravimetric analysis. A transparent lavender flavour nanocapsule aqueous solution was obtained. The lavender flavour inclusion complexes obtained are nano spherical particles. The average diameter of the encapsulated lavender flavour nanocapsules is about 15 nm. The transparent lavender flavour nanocapsule aqueous solution is stable and convenient to use. Furthermore, it can solve the turbid problem appearing in transparent medium.

The results of pyrolysis of blank HP- β -CD and lavender flavour-HP- β -CD inclusion complex showed that three main stages can be distinguished during thermal degradation. Flavour release mainly happened in the first stage (from room temperature to 269 °C) of the TG curve. Pyrolysis kinetic parameters of the flavour nanocapsule were determined. The values of apparent activation energy are 24.6 kJ/mol and 86.4 kJ/mol, reaction order is 1 and 0.04, pre-exponential factors are 6.6×10^2 and 1.0×10^8 , and reaction rate constants are 0.21 and 0.31 at 93.1 °C and 256.8 °C respectively. The study of pyrolysis characteristics and kinetic parameters was hoped to provide an approach to investigate the combination of flavour and HP- β -CD. Determination of pyrolysis activation energy is an easy method to estimate the binding energy. Furthermore, it is helpful in understanding the mechanism of molecular recognition between hosts and guests.

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