Carbohydrate Polymers 105 (2014) 75–80

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Study of production and pyrolysis characteristics of sweet orange flavor-β-cyclodextrin inclusion complex

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ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form 4 January 2014
Accepted 16 January 2014
Available online 28 January 2014

Keywords:
Flavor inclusion complex
Pyrolysis
Thermogravimetric
Kinetics
Thermodynamics

ABSTRACT

Flavor plays an important role and has been widely used in foods. Encapsulation can prevent the loss of volatile aromatic ingredients, provide protection and enhance the stability of the flavor. Kinetic and thermodynamic parameters are helpful in understanding the mechanism of molecular recognition between hosts and guests. This work focused on the study of production of a sweet orange flavor-β-cyclodextrin (CD) inclusion complex, and investigated the combination of flavor and β-CD by thermogravimetric analysis. Pyrolysis characteristics, kinetic and thermodynamic parameters of the flavor-β-CD inclusion complex were determined. The results showed that the flavor-β-CD inclusion complexes can form large aggregates in water. During thermal degradation of blank β-CD and flavor-β-CD inclusion complex, three main stages can be distinguished. The thermogravimetric (TG) curve of blank β-CD shows a leveling-off from room temperature to 250 °C, while the TG curve of flavor-β-CD inclusion complex is downward sloping in this temperature range.

1. Introduction

Flavor plays an important role and has been widely used in many products such as foods, beverages and cigarettes. A flavor is substance added to supplement, enhance, or modify the original tastes and/or aroma of a food, without imparting a characteristic taste or aroma of its own (Hui, 2010). It is a mixture of fragrant essential oils or aroma compounds, and solvents used to give food "pleasant scent and taste". Usually, the components of flavor are volatile liquids of which the sensory perception can be changed as a result of heating, oxidation, chemical interactions or volatilization. Microencapsulation technology is an effective method to minimize the harm of these problems and to minimize those disadvantages. Encapsulation can prevent the loss of volatile aromatic ingredients, improve shelf life of the entrapped flavor, provide protection and enhance the stability of the flavor core materials (Zhu, Xiao, & Zhou, 2012a).

Cyclodextrins are a family of compounds made up of sugar molecules bound together in a ring. β-cyclodextrin (β-CD) is a typical one which is constituted by 7 glucopyranoside units. It presents a hydrophobic inner cavity and a hydrophilic outer surface. Cyclodextrins have been widely used to prepare inclusion complexes to improve the stability and solubility, modify the release of flavor (Petrović, Stojanović, & Radulović, 2010). The inclusion complexes are defined as the result of interactions between compounds in which a smaller guest molecule fits into and is surrounded by the lattice of the other (Madene, Jacquot, & Scher, 2006). Guest molecules, with suitable dimensions to fit inside the interior, can be included into the cyclodextrin molecule to form agent-cyclodextrin complexes. Therefore, β-cyclodextrin has been used widely as wall material for flavor encapsulation. Binding energy is a useful datum to depict the interaction of flavor and β-cyclodextrin. In general, binding energy represents the mechanical work which must be done against the forces which hold an object together. Therefore, the investigation of the binding energy of flavor and β-cyclodextrin is important for a deep understanding of the interaction between flavor and β-cyclodextrin, and reaction mechanism. It can help us reveal the combination of the host and the guest. However, the binding energy of flavor and β-cyclodextrin was seldom reported.

Thermogravimetric analysis (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. Common applications of TGA are (1) materials characterization through analysis of characteristic decomposition patterns, (2) studies of degradation mechanisms and reaction kinetics, and (3) determination of organic content in a sample. TGA is a simple method and has been widely used for studies of degradation kinetics. The activation energy and the activation free energy of decomposition reaction can be obtained by TGA (Zhu, Zhu, & Xiao, 2012b, 2012c). These data can be used to evaluate the

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http://dx.doi.org/10.1016/j.carbpol.2014.01.060

binding energy of flavor and β-cyclodextrin. In this paper, TGA was employed for determination of sweet orange flavor microcapsule kinetic and thermodynamic parameters. The results of this study are very useful in helping us understand the combination of flavor and β-cyclodextrin, and understand the mechanism. The present study provided a better basis data for production of flavor microcapsule using β-cyclodextrin as wall material.

2. Materials and methods

2.1. Materials

β-Cyclodextrin (white crystalline powder, pharmaceutical grade) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

2.2. Preparation of sweet orange flavor

The sweet orange flavor was developed and blended in our laboratory. All the raw materials for blending sweet orange flavor were food-grade. In the experiment, sweet orange flavor was constructed from the notes of sweet orange odor. Fresh sweet orange fruit was smelled to identify the note of odor. According to the odor of sweet orange fruit, the notes of sweet orange were obtained. Proper chemical ingredients were selected to imitate the odor of sweet orange and to create a sweet orange flavor formula.

2.3. Complexation process

A precipitation method was adopted to prepare the sweet orange flavor-β-CD inclusion complex according to the references (Bhandari, D'Arcy, & Bich, 1998; Petrović et al., 2010). Approximately 2 g of β-cyclodextrin was dissolved in 50 mL of water maintained at 35 °C on a hot plate. Approximately 1.8 g of sweet orange flavor was then slowly added to the warm β-cyclodextrin solution. The mixture was continuously stirred for another 3 h at 35 °C. When its temperature decreased spontaneously to room temperature, the solution was refrigerated overnight at 5 °C. The cold precipitated material was recovered by vacuum filtration. The precipitate was washed by alcohol and dried in a convection oven at 50 °C for 24 h. The obtained complex was stored in airtight glass containers at room temperature prior to further thermogravimetric analysis.

2.4. Morphology of flavor-β-cyclodextrin inclusion complex

The morphological characteristic of the sweet orange flavor-β-cyclodextrin inclusion complex was investigated by optical microscopy (Goldroom binocular microscope GR-PL15, Shanghai, China). The inclusion complex was observed and the image was captured using a charge-coupled device (CCD) camera.

2.5. Thermogravimetric analysis

The experiments were carried out in a TGA-Q5000IR thermogravimetric analyzer (TA Instruments, USA). In the experiment, approximately 6 mg of 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.

Table 1
A typical sweet orange flavor formula.

No.	Raw material	wt%
1	Sweet orange oil	91.42
2	Lemon oil	0.62
3	Decanal	1.69
4	Linalool	0.99
5	Carvone	0.31
6	10% Ethyl maltol	0.85
7	10% Ethyl butyrate	0.85
8	Benzyl alcohol	1.27
9	Orange base	2.00
	Total	100

3. Results and discussion

3.1. Development of a sweet orange flavor formula

Sweet orange is the fruit of the citrus species in the family Rutaceae. It is one of the world's most important fruit and can be eaten as a fresh fruit, processed into juice, or added to dishes and beverages. Sweet orange flavor is a sweet and delightful fruity flavor and can be used in many products. Therefore, the development of sweet orange flavor is of great interest. Note is a distinct flavor or odor characteristic (Zhu, Xiao, & Zhou, 2013). Identification of the notes of sweet orange fruit is one important step to create sweet orange flavor. The notes of sweet orange flavor can be classified as: orange characteristic note, green note, aldehyde note, sweet note and fruity note. Based on the odor of the natural fruit, a typical sweet orange flavor formula that obtained through numerous experiments is shown in Table 1.

As shown in Table 1, sweet orange oil is used for imparting orange-like odor. The orange fruity note mainly comes from sweet orange oil. Sweet orange oil is an essential oil produced by cells within the rind of an orange fruit and has a characteristic odor and taste of orange. It is a yellow to reddish-yellow liquid (Burdock, 2010; Surburg & Panten, 2006). Lemon oil is obtained by pressing peel from the fruits of *Citrus limon* (L.) Burm. It is a pale yellow liquid with a characteristic lemon peel odor. Lemon oil is employed in the sweet orange flavor to enrich the fruity note and to add the natural feeling of sweet orange flavor. Decanal is a component of many essential oils and various citrus peel oils. Decanal is a colorless liquid with strong odor, reminiscent of orange peel, which changes to a fresh citrus odor when diluted. It also has a penetrating, sweet, waxy, floral, pronounced fatty odor that develops a floral character on dilution, and fatty, citrus-like taste. In the sweet orange formula, decanal is also used to impart note of aldehyde. Linalool has a typical pleasant floral odor, reminiscent of lily of the valley, free from camphoraceous and terpenic notes. Linalool is one of the most frequently used flavor substance and is employed in the sweet orange flavor to add green note. Caravone occurs in different forms. L-Carvone exhibits odor of spearmint, while D-carvone exhibits odor reminiscent of caraway. It can provide fresh feeling and spicy note in the formula. Ethyl maltol has a very sweet, fruit-like odor of immense tenacity and sweet, fruity taste with initial bitter-tart flavor. It is used in aroma compositions with a caramel note and as a taste intensifier in fruit flavor. Ethyl butyrate has a fruity odor with pineapple undertone and sweet, analogous taste. In the sweet orange flavor formula, it can improve the juice feeling of orange fruit. Benzyl alcohol has a characteristic pleasant, fruity odor and a slightly pungent, sweet taste; the note tends to become similar to that of benzyl aldehyde on aging. It can be used in sweet orange flavor as a fixative and as a modifier. Because of its relatively weak odor, benzyl alcohol is also used in flavor as a solvent and for dilution (Burdock, 2010; Surburg & Panten, 2006).

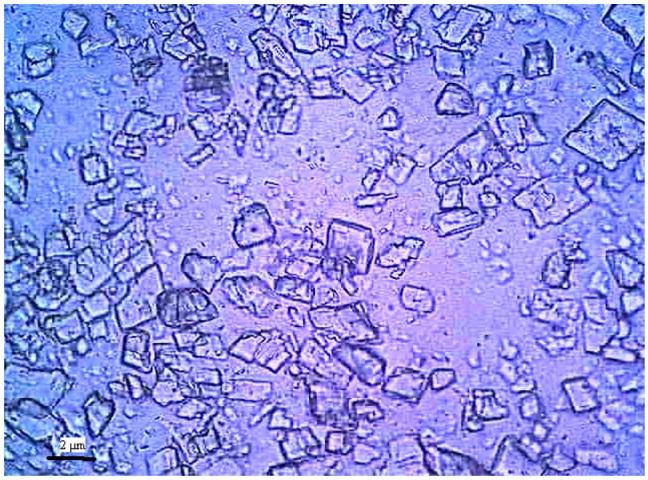

Fig. 1. The appearance and shape of flavor-β-cyclodextrin inclusion complex.

The sweet orange flavor blended according to formula as shown in Table 1 has a harmonious sweet orange odor. It has the characteristics of natural sweet orange fruit.

3.2. The appearance and shape of flavor-β-cyclodextrin inclusion complex

The relatively hydrophobic cavity of β-cyclodextrin can accommodate various kinds of guest molecules to form inclusion complexes. The inclusion complex of sweet orange flavor with β-cyclodextrin was observed by optical microscope and a selected micro-photograph is shown in Fig. 1.

In general, flavor-β-CD inclusion complexes are able to form large aggregates in water (He, Fu, & Shen, 2008). From Fig. 1, we can see that the aggregates have many geometric shapes. Some flavor-β-CD inclusion complex aggregates have regular geometric shapes. Rhombic, trapezoidal and parallelogram aggregates can be found from Fig. 1.

3.3. Pyrolysis characteristic comparison of flavor-β-CD inclusion complex to blank β-CD

TGA is an effective method to study changes in physical and chemical properties of material. The combination of flavor and β-CD can be investigated with TGA. Fig. 2(a) shows the weight loss and the rate of weight loss curve obtained during the pyrolysis of flavor-β-CD inclusion complex and blank β-CD samples under inert atmosphere at a heating rate of 10 °C/min. The curve of blank β-CD uses broken line, while the curve of flavor-β-CD inclusion complex uses real line.

As shown in Fig. 2(a), during thermal degradation of blank β-CD, three stages can be distinguished during the heating process of the sample. The first stage goes from room temperature to 285 °C; a slight weight loss in the thermogravimetric (TG) curve is observed. This could be due to the loss of water. The mass loss of this stage is 4.8% of total weight. The slight weight loss was attributed to desorption of moisture as bound water on the surface and the cavities of β-CD (Tong, 2001). The second stage goes from 285 to 375 °C. The second stage was characterized by a major weight loss, which corresponded to the main pyrolysis process. Most of β-CD was decomposed in this stage. The mass loss of the second stage is 82% of total weight. The third stage goes from 375 °C to the final temperature (500 °C) of the experiment. The solid residuals continuously decomposed at a very slow rate. A slowly continuous loss of weight was shown in the blank β-CD TG curve. The mass loss of the third stage is 3.5% of total weight. The residue yield of β-CD is 9.9%.

Compared to the pyrolysis characteristic of blank β-CD, although the TG curve of flavor-β-CD inclusion complex is similar to that of the blank β-CD (three main stages can also be distinguished from the TG curve), some new pyrolysis characteristics appear especially in the first stage. From Fig. 2(a), we can see that the TG curve of blank β-CD shows a leveling-off from room temperature to 250 °C, while the TG curve of flavor-β-CD inclusion complex is downward sloping in this temperature range. The weight losses of blank of β-CD and flavor-β-CD inclusion complex from room temperature to 250 °C are 3.4 and 13.1% respectively. The difference of the weight losses is due to the vaporization of sweet orange flavor encapsulated in β-CD. During the thermal degradation of flavor-β-CD inclusion complex, the encapsulated flavor was gradually released. Furthermore, small peaks can be observed in the derivative thermogravimetric (DTG) curve of flavor-β-CD inclusion complex. These peaks are mainly attributed to vaporization of the flavor encapsulated in the cavities of β-CD.

Flavor release mainly occurred in the first stage of the TG curve (see Fig. 2(a)). In order to make sure the combination of flavor and β-CD, It is necessary to investigate the pyrolysis characteristics of flavor-β-CD inclusion complex in the first stage of the TG curve. The small peaks in Fig. 2(a) should be explored in depth. Fig. 2(b) is a magnified image of Fig. 2(a), and shows the TG–DTG curves of flavor-β-CD inclusion complex from room temperature to 200 °C.

During the heating process of the flavor-β-CD inclusion complex from room temperature to 200 °C, three stages and three peaks can be distinguished as shown in Fig. 2(b). The first stage goes from room temperature to 66 °C, and the weight loss in this stage is 3.5%. The first peak temperature is 45.8 °C, and at this temperature the rate of weight loss attains maximum value (0.1123%/°C). The second stage goes from 66 to 107 °C, and the weight loss in this stage is 2.4%. The second peak temperature is 84.7 °C. At 84.7 °C, the rate of weight loss attains maximum value (0.0792%/°C). The third stage goes from 107 to 180 °C and the weight loss in this stage is 3.2%. The third peak temperature is 151.5 °C. At 151.5 °C, the rate of weight loss attains maximum value (0.0563%/°C). The sweet orange flavor is composed of a lot of volatile aroma compounds. The combinations of these aroma compounds and β-CD are different. This indicates that the binding energies of aroma compounds and β-CD are different. Therefore, during the heating process of the flavor-β-CD inclusion complex, three peaks in the rate of weight loss curve can be observed.

3.4. Pyrolysis kinetic and thermodynamic parameters of flavor-β-CD inclusion complex

3.4.1. Apparent activation energy and reaction order

In view of the fact that flavor-β-CD inclusion complex is a mixture which is composed of volatile aroma compounds, essential oil and β-CD, the decomposition of flavor-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., 2012b). The analysis of TGA graphs was used to determine the pyrolysis kinetic parameters of flavor-β-CD inclusion complex such as activation energy and reaction order. The Freemaan–Carroll method (Freeman & Carroll, 1958; Hu & Shi, 2001) was adopted to determine the pyrolysis kinetic parameters from the thermogravimetric data.

The pyrolysis reaction of the flavor-β-CD inclusion complex can be simply expressed by:

$$aS_{(s)} \rightarrow bB_{(g)} + cC_{(s)} \quad (1)$$

where S is flavor-β-CD inclusion complex in the solid state, B is volatile product, and C is other product in the condensed state.

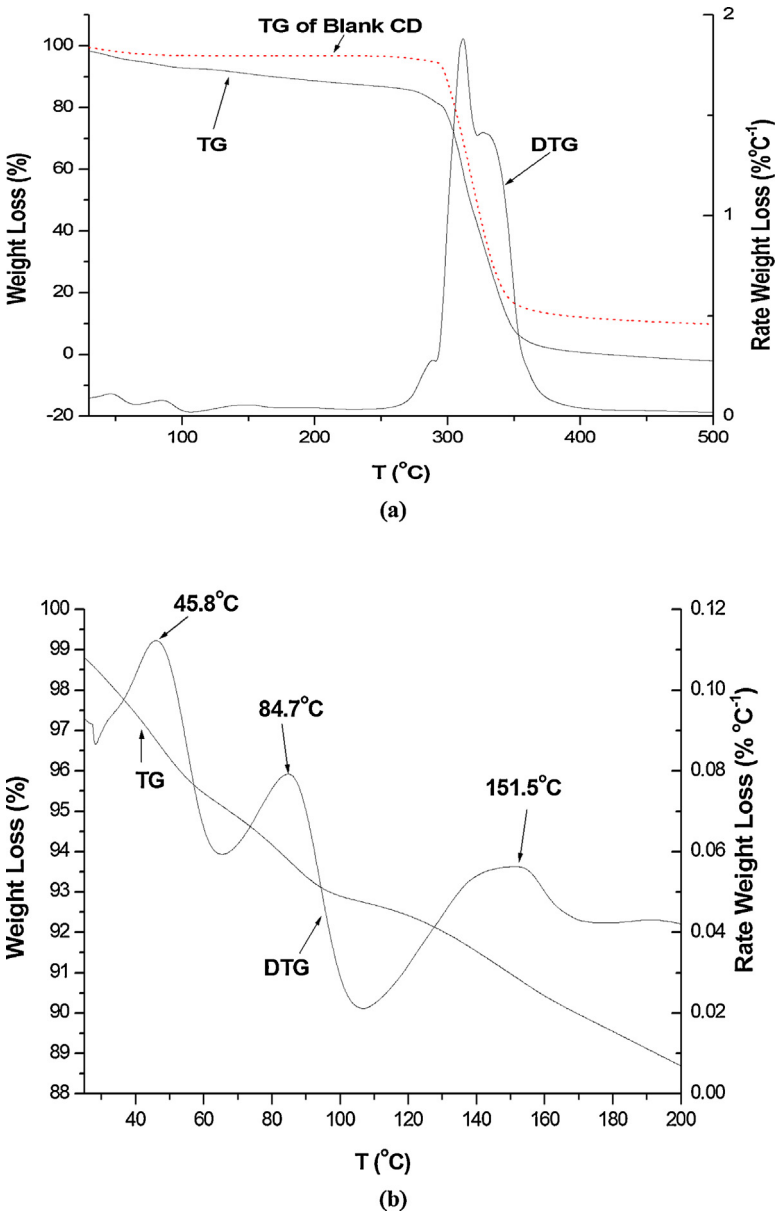

Fig. 2. (a) TG–DTG curves of blank β-CD and flavor-β-CD inclusion complex, (b) TG–DTG curves of flavor-β-CD inclusion complex from room temperature to 200 °C.

The rate expression for the disappearance of reactant S from the mixture may be expressed by:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

where α is the fraction of S decomposed at time t, which is defined as $(w_0 - w)/(w_0 - w_\infty)$, n is the order of reaction, w_0 is the mass of initial sample, w is the mass of actual sample at time t, w_∞ is the mass of residue at the end of the reaction, and k is the rate constant, which is also defined by the Arrhenius equation:

$$k = A \quad \exp\left(\frac{-E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

For a linear heating rate of, say, β K min^{-1}:

$$\beta = \frac{dT}{dt} \tag{4}$$

By combining Eqs. (2)–(4), the reaction rate can be written in the form:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{5}$$

The logarithmic form of Eq. (5) can be written in the form:

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} + n\ln(1-\alpha) \tag{6}$$

Differentiating Eq. (6) gives Eq. (7)

$$d\ln\left(\frac{d\alpha}{dT}\right) = -\frac{E}{R}d\left(\frac{1}{T}\right) + n(d\ln(1-\alpha)) \tag{7}$$

Integrating the Eq. (7) gives Eq. (8)

$$\Delta\ln\left(\frac{d\alpha}{dT}\right) = -\frac{E}{R}\Delta\left(\frac{1}{T}\right) + n(\Delta\ln(1-\alpha)) \tag{8}$$

Table 2
The values of apparent activation energy and reaction order.

Peak temperature (°C)	Temperature range (°C)	Apparent activation energy (kJ/mol)	Reaction order	R
45.8	28.3–66	80.0	0.46	−0.9945
84.7	66–107	98.3	0.42	−0.9958
151.5	107–180	104.5	1.04	−0.9960

Dividing Eq. (8) by $\Delta \ln(1-\alpha)$, one obtains Eq. (9)

$$\frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1-\alpha)} = -\frac{E}{R}\left(\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)}\right) + n \quad (9)$$

From Eq. (9), it is apparent that plots of $\Delta(1/T)/\Delta \ln(1-\alpha)$ vs. $\Delta \ln(d\alpha/dT)/\Delta \ln(1-\alpha)$ 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 order respectively. These plots resulted in straight lines as shown in Fig. 3. There are three peaks in the rate of weight loss curve as shown in Fig. 2(b). These peaks divide the TG curve of flavor-β-CD inclusion complex into three stages, and indicate that three kinds of binding modes of aroma compounds and β-CD. As shown in Fig. 3, three straight lines obtained by fitting method correspond to the three peaks respectively. There is a good linear relationship between $\Delta(1/T)/\Delta \ln(1-\alpha)$ and $\Delta \ln(d\alpha/dT)/\Delta \ln(1-\alpha)$. The values of apparent activation energy and reaction order calculated by Freemaan–Carroll method are given in Table 2. All the plots has a high linear correlation coefficients greater than 0.99, which demonstrated that Freemaan–Carroll method is suitable to investigate the pyrolysis kinetics of the flavor-β-CD inclusion complex. From Table 2 we can see that the apparent activation energy at 45.8 °C is relatively small. The apparent activation energy tends to increase as the temperature increases. The smaller the apparent activation energy is, the more easily the reaction carries out. Small activation energy indicates that aroma compounds easily release from the inclusion complex, while high activation energy implies that aroma compounds are bound to β-CD firmly. The flavor inclusion complex pyrolysis reaction is not an integer. This means that aroma compound release reaction is not an elementary reaction, but is controlled by many elementary reactions (Zhou, Xiao, & Chen, 2008).

3.4.2. Pre-exponential factors and reaction rate constants

According to literatures (Coats & Redfern, 1964; Zhu et al., 2012b, 2012c), the relationship among pre-exponential factor, activation energy, temperature, and the fraction of substrate decomposed can be expressed by Eq. (10).

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (\text{for} \quad n \neq 1) \quad (10)$$

Eq. (10) is based on the Coats–Redfern method (Coats & Redfern, 1964). Pre-exponentials factors, A, can be calculated according to Eq. (10).

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. (3).

The pre-exponential factors and reaction rate constants are shown in Table 3.

3.4.3. Free energy of activation ($\Delta G^{\neq}$), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$)

Entropy is a measure of the number of specific ways in which a system may be arranged, often taken to be a measure of disorder, confusion, and disorganization. Following the second law of thermodynamics, entropy of an isolated system always increases.

The relationship among entropy of activation, temperature, and pre-exponential factor can be expressed as Eq. (11) (Hu & Shi, 2001).

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \quad (11)$$

where h is Plank constant, k_B is Boltzmann constant.

Changing Eq. (11) gives Eq. (12)

$$\Delta S^{\neq} = R \ln\left(\frac{Ah}{k_B T}\right) \quad (12)$$

$\Delta S^{\neq}$ can be obtained by solving Eq. (12).

Enthalpy is a measure of the total energy of a thermodynamic system. It includes the system's internal energy of thermodynamic potential, as well as its volume and pressure. The enthalpy is the preferred expression of system energy changes in many chemical and physical measurements, because it simplifies certain

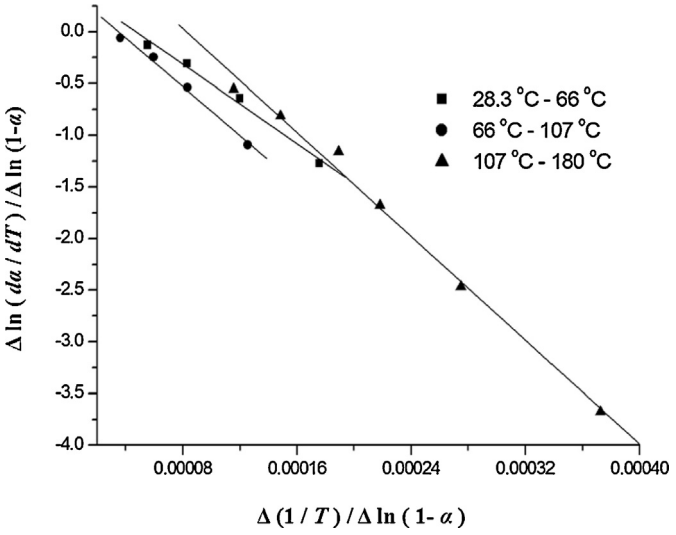

Fig. 3. Plots of $\Delta(1/T)/\Delta \ln(1-\alpha)$ vs. $\Delta \ln(d\alpha/dT)/\Delta \ln(1-\alpha)$.

Table 3
The pre-exponential factors and reaction rate constants calculated at various temperatures.

Temperature (°C)	Pre-exponential factor	Reaction rate constant
30	2.89×10^{12}	0.046
40	7.83×10^{12}	0.347
45.8 (peak)	7.23×10^{12}	0.562
50	6.42×10^{12}	0.737
60	4.09×10^{12}	1.144
70	1.02×10^{14}	0.112
80	1.43×10^{14}	0.418
84.7 (peak)	1.31×10^{14}	0.590
90	1.11×10^{14}	0.816
140	5.71×10^{12}	0.354
150	4.50×10^{12}	0.572
151.5 (peak)	4.32×10^{12}	0.609
160	3.51×10^{12}	0.884

Table 4
Values of free energy of activation, entropy of activation, enthalpy of activation.

Temperature (°C)	$\Delta S^{\neq}$ (J/K)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)
151.5	205	104.5	17.6

descriptions of energy transfer. Enthalpy change accounts for energy transferred to the environment.

The relationship among enthalpy of activation, entropy of activation, temperature, and pre-exponential factor can be expressed as Eq. (13) (Hu & Shi, 2001).

$$A \exp\left(\frac{-E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \quad (13)$$

This equation is only correct for a first order reaction, for which the rate constant has the dimension reciprocal time. At 151.5 °C, the reaction order is 1.04, which can be seen as a first order reaction. Therefore, the Eq. (13) can be used to calculate thermodynamic parameters. By combining Eq. (3) and (13), Eq. (14) can be obtained.

$$\ln\left(\frac{kh}{k_B T}\right) = \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \quad (14)$$

Changing Eq. (14) gives Eq. (15)

$$\Delta H^{\neq} = RT\left(\frac{\Delta S^{\neq}}{R} - \ln\left(\frac{kh}{k_B T}\right)\right) \quad (15)$$

$\Delta H^{\neq}$ can be obtained by solving Eq. (15).

In thermodynamics, the free energy is a thermodynamic potential that measures the "usefulness" or process-initiating work obtainable from a thermodynamic system at a constant temperature and pressure. The free energy is also the chemical potential that is minimized when a system reaches equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, it is a convenient criterion of spontaneity for processes with constant pressure and temperature.

Eq. (16) gives the relationship of free energy of activation, entropy of activation, enthalpy of activation.

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (16)$$

$\Delta G^{\neq}$ can be obtained by solving Eq. (16).

According to the theoretical studies discussed above, the values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ have been calculated as shown in Table 4.

From Table 3 we can see that, during the heating process of the flavor-β-CD inclusion complex, the value of $\Delta S^{\neq}$ increases. In this process, the aroma compounds of sweet orange flavor were gradually released. The enthalpy of activation, $\Delta H^{\neq}$, is 104.5 kJ/mol, which is approximately equal to the activation energy. The free energy of activation, $\Delta G^{\neq}$, is 17.6 kJ/mol. This indicates that the driving force of the formation of flavor-β-CD inclusion complex comes from non-covalent interactions such as van der Waals forces, electronic effects, hydrophobic interactions, and steric factors. This result is similar to that of Rekharsky and Inoue (Rekharsky & Inoue, 1998).

4. Conclusion

The paper deals with production of a sweet orange flavor-β-cyclodextrin (CD) inclusion complex, and investigation of pyrolysis characteristics, kinetic and thermodynamic parameters of the flavor-β-CD inclusion complex using thermogravimetric analysis. It was found that the flavor-β-CD inclusion complexes were able to form large aggregates in water. These aggregates usually have regular geometric shapes. Pyrolysis characteristics of blank β-CD and flavor-β-CD inclusion complex were obtained. During thermal degradation of blank β-CD and flavor-β-CD inclusion complex, three main stages can be distinguished. Due to the vaporization of sweet orange flavor encapsulated in β-CD, the thermogravimetric (TG) curve of blank β-CD shows a leveling-off from room temperature to 250 °C, while the TG curve of flavor-β-CD inclusion complex is downward sloping in this temperature range. Kinetic and thermodynamic parameters in terms of apparent activation energy, reaction order, and reaction rate constant, pre-exponential factor, free energy of activation, entropy of activation and enthalpy of activation were determined. The free energy of activation indicates that the driving force of the formation of flavor-β-CD inclusion complex comes from non-covalent interactions such as van der Waals forces, electronic effects, hydrophobic interactions, and steric factors. The study of pyrolysis characteristics, kinetic and thermodynamic parameters was hoped to provide an approach to investigate the combination of flavor and β-CD. Furthermore, it is helpful in understanding the mechanism of molecular recognition between hosts and guests.

Acknowledgments

This work was financially supported by the National Natural Science Fund of China (21276157), International Cooperation Project of Shanghai "Mountaineering Plan" (11290707600), and Project of Shanghai Institute of Technology (YJ2012-30) for financial support.

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