

Thermal behavior study and decomposition kinetics of linalool/ β -cyclodextrin inclusion complex

Priscila Bonetti¹ · Flávio Faria de Moraes¹ ·
Gisella Maria Zanin¹ · Rita de Cássia Bergamasco²

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Abstract Linalool is a chemical fragrance widely used globally in the cosmetic industry. However, its use has some limitations due to its poor aqueous solubility. Encapsulation of linalool in β -cyclodextrin (β -CD) can improve its solubility. Kinetic and thermodynamic parameters are helpful in understanding the reaction mechanism between a guest molecule and β -CD. In this, we paper evaluated the formation of inclusion complex of linalool in β -CD by electrospray ionization mass spectrometry (ESI–MS) and thermoanalytical methods. We determined the kinetic and thermodynamic parameters, and propose a mechanism of thermal decomposition of the linalool/ β -CD inclusion complex. The formation of the inclusion complex was confirmed using ESI–MS, differential scanning calorimetry (DSC) and thermogravimetry (TG). The activation energy of thermal decomposition of the inclusion complex was determined by Flynn–Wall–Ozawa and Starink methods to be 212.16 ± 5.06 and 211.00 ± 4.78 kJ mol⁻¹, respectively, showing there was no strong chemical interaction between linalool and β -CD. The proposed decomposition reaction mechanism was a two-dimensional diffusion model.

Keywords Linalool · β -Cyclodextrin · Thermogravimetry · Isoconversional methods · Activation energy · Thermal decomposition

✉ Rita de Cássia Bergamasco
ritabergamasco@bol.com.br; rbergamasco@uem.br

¹ Department of Chemical Engineering, State University of Maringa, Colombo Avenue, 5790, Maringá, PR CEP 87020-900, Brazil

² Department of Food Engineering, State University of Maringa, Colombo Avenue, 5790, Maringá, PR CEP 87020-900, Brazil

Introduction

Cyclodextrins (CDs) are a class of cyclic oligosaccharides that have a truncated cone shape and a hydrophobic cavity. This unique structure enables it to form inclusion complexes, trapping either the entire or part of the guest molecule within its cavity. The molecular inclusion by CDs exerts a profound effect on the physicochemical properties of the guest molecule [1]. Due to this characteristic, CDs and their inclusion complexes have been used in food, pharmaceutical, and cosmetic industries.

Linalool is a monoterpene alcohol compound present in essential oils of various aromatic plant species. It is found in cosmetics, fine fragrances and shampoos [2]. However, its use has some limitations due to its poor aqueous solubility and high volatility.

Complexation of cyclodextrins with fragrances increases their water solubility and reduces or prevents their evaporation. Additionally, it allows for the controlled release of the guest molecule. Numanoglu et al. [3] used β -cyclodextrin (β -CD) and 2-hydroxypropyl- β -cyclodextrin to increase the solubility of linalool and benzyl acetate by molecular inclusion. The formation of inclusion complexes of linalool/2-hydroxypropyl- β -cyclodextrin at a 1:1 molar ratio increased the solubility of linalool 5.9-fold. Menezes et al. [4] studied the formation of an inclusion complex of linalool/ β -cyclodextrin. The authors characterized the inclusion complex by differential scanning calorimetry, thermogravimetry, FT-IR spectroscopy, and X-ray diffractometry.

While studies on inclusion complexes of linalool and β -CD have been reported in literatures [3, 4], there is no detailed report on kinetics of thermal decomposition of inclusion complexes. This analysis is very important to understanding the interaction between linalool and β -CD as well as the reaction mechanism. The activation energy of decomposition of inclusion complex will provide an indication of the thermal stability of linalool by their encapsulation within β -CD cavity.

Thermal stability is one of the most important properties of cyclodextrins complexes [5]. Thermogravimetric analysis (TGA) is a simple technique for studying the thermal behavior of inclusion complex and kinetics of processes involving solids by following the weight loss of the samples with time. TGA provides information about the activation energy and kinetic model [6].

The present study describes the preparation and characterization of linalool/ β -CD inclusion complexes by electrospray ionization mass spectrometry (ESI-MS) and thermoanalytical methods (DSC and TG). Kinetic and thermodynamic parameters, and a mechanism of thermal decomposition of the inclusion complex were also determined.

Materials and methods

Materials

β -Cyclodextrin was purchased from Acros Organics. Linalool was obtained from Linax, Natural Essential Oils Industry (São Paulo, Brazil). All the chemicals used were of analytical grade.

Phase solubility studies

The phase solubility studies were performed according to Higuchi and Connors method [7]. An excess amount of linalool was added to screw-capped vials containing aqueous β -CD solutions at various concentrations (0–15 mM). The vials were sealed and shaken at 25 °C for 36 h. After equilibrium was reached, the samples were filtered through a 0.45 μ m membrane filter and analyzed for linalool by HPLC. The apparent stability constant (K_s) was calculated from the phase solubility diagram, assuming 1:1 stoichiometry, according to the following Eq. (1):

$$K_s = \frac{\text{slope}}{S_0(1 - \text{slope})} \quad (1)$$

where S_0 is the solubility of linalool in the absence of β -CD.

Determination of linalool by high-performance liquid chromatography (HPLC)

The assays for linalool determination were performed with a high-performance liquid chromatography (HPLC) system consisting of a GILSON model 321 equipped with UV/VIS-152 detector. Separation was performed using a SGE C18 (5 μ m, 250 \times 4.6 mm) column at ambient temperature. HPLC analyses were performed at a flow rate of 1 mL min⁻¹. The mobile phase composition was methanol:water (8:2, v/v). The samples were diluted in ethanol and analyzed at a wavelength of 215 nm. The retention time were observed to be 10 min. The peak areas were integrated by a computer software program (Borwin).

Preparation of inclusion complex

The inclusion complex of linalool with β -CD (1:1 molar ratio) was prepared by the co-precipitation method. β -CD was dissolved in ultra-purified water at 50 °C with stirring. The linalool solution in ethanol was added slowly to the β -CD solution. Heating was stopped and the solution was stirred for 5 h. The final solution was cooled at 4 °C for 16 h. The precipitated linalool/ β -CD inclusion complex was recovered by filtration and dried in an oven at 50 °C for 24 h. The physical mixture was prepared by simply blending linalool and β -CD (1:1 molar ratio) for 15 min with a spatula.

Electrospray ionization mass spectrometry (ESI-MS)

Complexation of linalool with β -CD was monitored by ESI-MS. The experiment was performed using a Waters Synapt HDMS QTOF Mass Spectrometer (Waters, Milford, MA, USA), equipped with an electrospray ion source, which was capable of analyzing ions in the mass range of m/z 130–1340. Inclusion complexes were prepared in distilled water, in different molar ratio of linalool: β -CD (1:1, 2:1 and 3:1). Considering linalool a guest of very small size, the possibility of a 2:1

(CD:guest) complex formation was not considered. Solutions diluted in acetonitrile and formic acid were introduced in a syringe pump at a flow rate of $40 \mu\text{L min}^{-1}$. The spray voltage was set to 4.0 kV in the positive mode, and the heated metal capillary temperature was set at 120°C .

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) curves of β -CD, the linalool/ β -CD inclusion complex, and physical mixture were analyzed in a Shimadzu DSC-50 differential scanning calorimeter at a heating rate of $10^\circ\text{C min}^{-1}$. The thermal behavior was studied by heating approximately 6 mg of the samples in aluminum crimped pans under a nitrogen atmosphere (20 mL min^{-1}) over the temperature range of 25 – 350°C .

Thermogravimetry analysis (TGA)

Thermogravimetry analysis (TGA) was performed on the samples (approximately 6 mg) using a Shimadzu thermobalance, model TGA-50 under dynamics nitrogen atmosphere (20 mL min^{-1}) and heating rate of $10^\circ\text{C min}^{-1}$ using platinum crucibles. Inclusion complex samples were analyzed at three different heating rates (10 , 15 , and $20^\circ\text{C min}^{-1}$) from 25 to 450°C .

Theoretical base of thermal decomposition kinetic

Thermal decomposition kinetics can be used to analyze the process of thermal decomposition of the linalool/ β -CD complex. According to non-isothermal kinetic theory, the thermal decomposition kinetic equation of solid-state materials is:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot f(\alpha) \quad (2)$$

where α is the degree of conversion, β is the heating rate ($^\circ\text{C min}^{-1}$), E_a is the apparent activation energy, A is the pre-exponential factor, R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and $f(\alpha)$ is the kinetic model function.

For constant heating rate non-isothermal conditions, integration of Eq. (2) leads to:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT \quad (3)$$

Vyazovkin et al. [8] recommended that, due the mutual dependence of kinetics parameters in Eq. (2), which are, in turn, affected by the choice of the conversion model function, at least one of the kinetic triplet (E_a , A , $f(\alpha)$) elements should be computed independently from the others.

Activation energy

There are many methods for determining the activation energy from thermoanalytical data, with the most reliable being the differential or integral isoconversional methods. The integral method of Flynn–Wall–Ozawa [9], which is the most commonly used, is shown by Eq. (4):

$$\log \beta = \log \left(\frac{A \cdot E_a}{R \cdot g(\alpha)} \right) - 2.315 - 0.4567 \cdot \frac{E_a}{R \cdot T} \quad (4)$$

The integral method of Starink [10] is considered to be one of the more accurate isoconversional methods for determining activation energy, according to Vyazovkin et al. [8]. It is based on Eq. (5):

$$\ln \left(\frac{\beta}{T^{1.92}} \right) = C - 1.0008 \cdot \frac{E_a}{R \cdot T} \quad (5)$$

Compared to other methods, the advantage of the Flynn–Wall–Ozawa and Starink methods is that they do not require previous knowledge of the reaction mechanism for determining the activation energy.

Determination of the mechanism function of thermal decomposition

The Coats–Redfern method [11] is a widely used method for determining the thermal decomposition function, and uses the following equation:

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \left(\frac{A \cdot R}{\beta \cdot E_a} \right) - \frac{E_a}{R \cdot T} \quad (6)$$

If the correct $g(\alpha)$ function is used, a plot of $\ln(g(\alpha)/T^2)$ against $1/T$ should give a straight line, from which the values for activation energy and the pre-exponential factor can be calculated. There are different models available [12], and the model that gives the best linear fit is selected as the chosen model. The Coats–Redfern method has been widely and successfully used for studying the kinetics of decomposition of different solid substances when $20 < E/RT < 60$ [13].

Some thermodynamic functions, such as ΔS^\ddagger , ΔH^\ddagger , and ΔG^\ddagger , of the thermal decomposition reaction may be calculated according to Eqs. (7), (8), and (9), respectively [12]:

$$\Delta S^\ddagger = R \cdot \ln \left(\frac{A \cdot h}{e \cdot \chi \cdot k_B \cdot T_P} \right) \quad (7)$$

$$\Delta H^\ddagger = E - R \cdot T_P \quad (8)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T_P \cdot \Delta S^\ddagger \quad (9)$$

where A is the pre-exponential factor, $e = 2.7183$ (Neper number), χ is the transmission factor ($\chi = 1$ for monomolecular reactions), k_B is the Boltzmann constant

($1.381 \times 10^{-23} \text{ J K}^{-1}$), h is the Planck constant ($6.626 \times 10^{-34} \text{ J s}$), T_p is the peak temperature in the derivative thermogravimetry (DTG) curve, and E is the activation energy, which can be obtained from Eqs. (4) and (5).

Results and discussion

Phase solubility studies

The phase solubility diagram of the linalool/ β -CD system (Fig. 1) showed fragrance solubility increased linearly with increasing concentrations of β -CD. This diagram can be classified as an A_L type according to Higuchi and Connors [7]. It is related to the formation of a soluble inclusion complex.

The apparent stability constant is a very interesting parameter for the characterization of molecular interactions between a guest molecule and CD. Marques [14] reported that complexes with apparent stability constants from about 100 to 5000 M^{-1} seem to be suitable for practical applications. Very labile complexes result in premature release of the guest, while very stable complexes result in a retarded or an incomplete release of the guest. The apparent stability constant obtained for the linalool/ β -CD system was 290.03 M^{-1} , an acceptable value for the controlled release of this fragrance from the CD cavity.

Electrospray ionization mass spectrometry (ESI-MS)

ESI-MS has shown itself to be a very useful technique in describing the noncovalent interaction between β -CD and various organic molecules because of its high sensitivity, rapidity and low sample consumption [5].

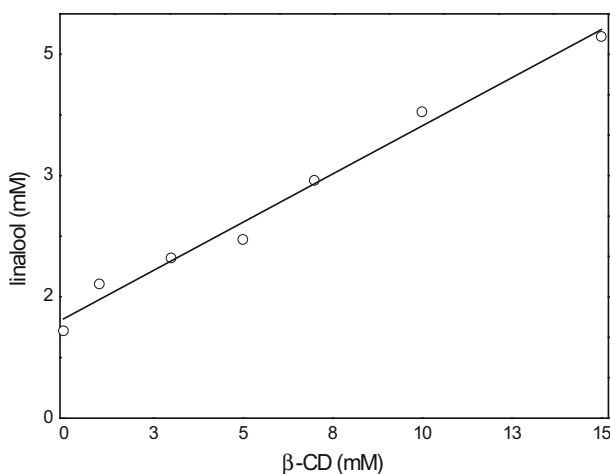


Fig. 1 Phase solubility diagram for the linalool/ β -CD system

Relative abundances and stoichiometry of the inclusion complex linalool:C- β -CD formed was determined by ESI-MS. The analysis in positive ionization mode allowed us to observe ions at m/z 1136 and 1290.0, corresponding to protonated species of β -CD and protonated species of linalool: β -CD inclusion complex, respectively (Fig. 2). This revealed that the inclusion complex was formed in a ratio 1:1; which is in agreement with the results obtained from the solubility diagrams. No signals were observed with a ratio m/z related to other complex stoichiometries.

Differential scanning calorimetry (DSC)

The DSC curves of β -CD, the physical mixture, and linalool/ β -CD inclusion complexes are shown in Fig. 3. All of the curves showed two broad endothermic peaks. The first peak, which ranged from 20 to 150 °C, was attributed to water loss of sample. The second peak, at 320 °C, corresponds to product decomposition. The first β -CD endothermic peak stabilized at 128 °C, while this peak stabilized at a higher temperature (150 °C) for inclusion complexes and the physical mixture, thus demonstrating the presence of free linalool in the sample.

The inclusion complex showed dehydration enthalpy (-22.81 J g^{-1}) lower than the β -CD (-337.03 J g^{-1}) and the physical mixture (-333.55 J g^{-1}). Del Valle [1] reported that the energy of a system is lowered when the enthalpy-rich water molecules are replaced by suitable molecules that are less polar. Meier et al. [15] observed similar behavior for inclusion complexes of capric and caprylic acids with β -CD and γ -CD.

Thermogravimetry analysis (TGA)

Thermogravimetric curves for β -CD, the physical mixture, and the linalool/ β -CD inclusion complex (Fig. 4) showed two stages of weight loss, which were

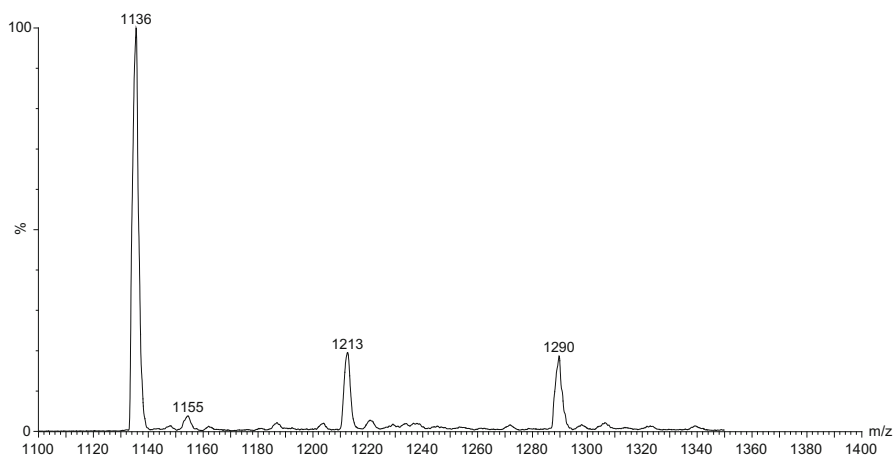


Fig. 2 Mass spectra of linalool: β -CD inclusion complex, in a 2:1 molar ratio

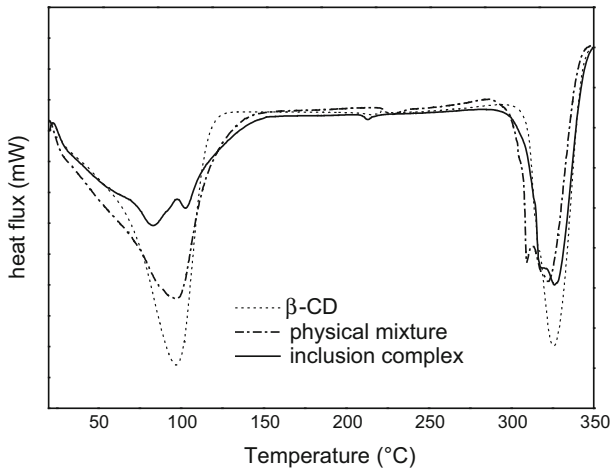


Fig. 3 DSC curves of β -CD, the physical mixture, and linalool/ β -CD inclusion complexes

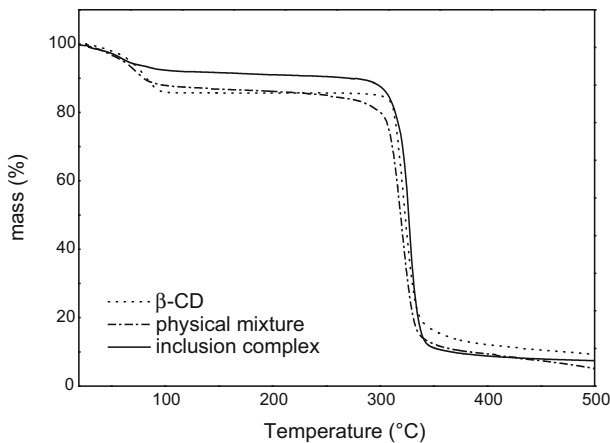


Fig. 4 Thermogravimetric curves of β -CD, the physical mixture, and linalool/ β -CD inclusion complexes

associated with the dehydration and decomposition of the samples. In the temperature range of 102–280 °C, the physical mixture and inclusion complex lost 4.43 and 2.48 % of their masses, respectively, while β -CD lost no mass. This fact is related to the presence of free linalool in the sample. The loss was greater for the physical mixture because this sample had more free linalool than the inclusion complex.

β -CD and the physical mixture lost 70 and 75 % of their masses, respectively, in the temperature range of 140–355 °C, while the inclusion complex lost 81 %. This greater weight loss of the inclusion complex in this temperature range is related to linalool being released of the CD cavity.

Non-isothermal TGA

The dissociation of the linalool/ β -CD inclusion complex can be described by two major steps:

1. Linalool $\cdot\beta$ -CD_(s) \rightarrow β -CD_(s) + linalool_(s).
2. Decomposition of β -CD_(s).

The purpose of this study was to identify the kinetic mechanism of the first stage, when the decomposition of the linalool/ β -CD inclusion complex occurs.

Xu et al. [16] reported that guest molecules generally have molecular masses below 400, and the percent of the total mass of the guest in its inclusion complex of β -CD would be less than 30 %. The authors also reported that after the inclusion complex exceeded 30 % weight loss, only β -CD can remain in the residue in a specific state. In the current study, weight loss versus temperature data were collected in the range of 10–40 % of weight loss.

The activation energy of the thermal decomposition process was obtained by the Flynn–Wall–Ozawa and Starink isoconversional methods at different degrees of conversion. In Fig. 5, the trends of activation energy against the degree of conversion from the mentioned isoconversional methods are compared. The calculated average values of activation energy for Flynn–Wall–Ozawa and Starink methods were in good agreement (Fig. 4). Equations (4) and (5) were derived assuming a constant activation energy, and this is correct for $0.3 \leq \alpha \leq 1.0$, for which the relative error of the activation energy is lower than 10 %. Since activation energies are independent of the degree of conversion, the decomposition process is dominated by a single reaction step [8]. The average activation energy values calculated within the interval of $0.3 \leq \alpha \leq 1.0$ using the Starink and Flynn–Wall–Ozawa methods were

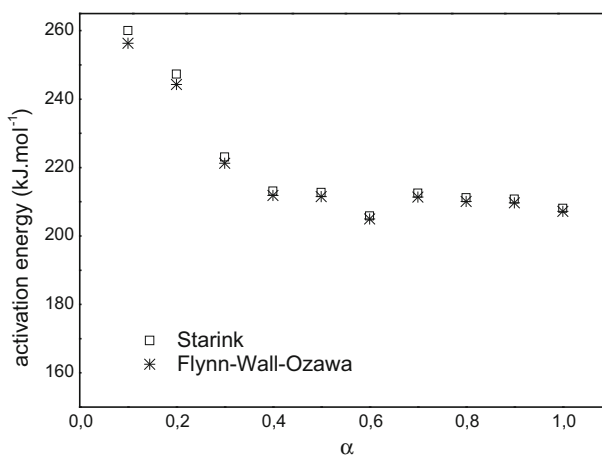


Fig. 5 Activation energy versus degree of conversion calculated from the Flynn–Wall–Ozawa and Starink methods

212.16 ± 5.06 and 211.00 ± 4.78 kJ mol^{-1} , respectively. This average activation energy value obtained for the thermal decomposition of the linalool/ β -CD inclusion complex shows that there was no strong chemical interaction between linalool and β -CD. This result is in agreement with studies of inclusion complexes of β -CD and weakly polar guest molecules, from which it has been confirmed that the stable energy of inclusion complexes consists mainly of Van der Waals energy, and the escape of guest molecules from β -CD cavity is easy [17].

The Coats–Redfern method was used to determine the most probable mechanism function. Different kinetics models were tested [12], and the most probable mechanism function was assumed to be the one for which the value of the correlation coefficient was higher and the activation energies calculated by the Coats–Redfern method were close to the value obtained by the Flynn–Wall–Ozawa and Starink methods. Therefore, for the thermal decomposition of the linalool/ β -CD inclusion complex, the integral form of the reaction mechanism function is $g(\alpha) = (1 - (1 - \alpha)^{1/2})^{1/2}$, which corresponds to a two-dimensional diffusion model.

The activation energies and pre-exponential factor, calculated by Coats–Redfern method, for the three heating rates studied are shown in Table 1.

Some studies have suggested using diffusion models to represent the thermal decomposition of inclusion complex of CDs. Li et al. [18] evaluated the thermal decomposition of the anisaldehyde/ β -CD inclusion complex and obtained values of 139.23 kJ mol^{-1} and 1.0394×10^{12} min^{-1} for the activation energy and pre-exponential factor, respectively, for a thermal decomposition dominated by a two-dimensional diffusion process. Li et al. [17] calculated values for the activation energy and pre-exponential factor of 160 kJ mol^{-1} and 5.8×10^{14} min^{-1} , respectively, for a thermal decomposition of a cinnamic aldehyde/ β -CD inclusion complex, which is a decomposition dominated by a one-dimensional process. Zhang et al. [19] showed that the thermal decomposition of the ethyl benzoate/ β -CD inclusion complex is dominated by a three-dimensional diffusion process, and had an activation energy value of 116.19 kJ mol^{-1} and pre-exponential factor of 6.5358×10^9 min^{-1} . Cruickshank et al. [20] reported that diffusion models could be applied to a diffusion-limited reaction that takes place at a phase interface that forms between the product (guest molecule) and the reactant (inclusion complex). During the decomposition process, the guest molecules diffuse towards the crystal surface and finally desorb from the surface.

As shown in Table 1, the average activation energy obtained by the Coats–Redfern method was 198.36 kJ mol^{-1} , which is in good agreement with the value

Table 1 Kinetics parameters of the Coats–Redfern equation (Eq. 6)

β ($^{\circ}\text{C min}^{-1}$)	E_a (kJ mol^{-1})	A (min^{-1})	R^2
10	219.54	9.97×10^{18}	0.9938
15	193.65	5.28×10^{16}	0.9966
20	181.89	4.32×10^{15}	0.9928
Mean	198.36	3.34×10^{18}	–

calculated using the Flynn–Wall–Ozawa and Starink methods (relative error $E_a \leq 10\%$).

The pre-exponential factor was $3.34 \times 10^{18} \text{ min}^{-1}$. Turmanova et al. [21] reported that the pre-exponential factors for solid-phase reactions are expected to be in a wide range (six or seven orders of magnitude), even after the effect of surface area is corrected. Low factors often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a ‘tight’ complex. High factors usually indicate a ‘loose’ complex. Based on these reasons, the thermal decomposition of linalool/ β -CD inclusion complexes may be interpreted as a ‘loose’ complex.

Figure 6 proves the validity of kinetic mechanism for the thermal decomposition of linalool/ β -CD for all of the heating rates studied. The result shows that the model-predicted plots agree with the experimental plots, indicating that the two-dimensional diffusion model is suitable for the thermal decomposition of the linalool/ β -CD inclusion complex.

The thermodynamic parameters were calculated from Eqs. (7)–(9). The average values of the parameters are as follows: $\Delta H^\ddagger = 193.38 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 68.72 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta G^\ddagger = 152.22 \text{ kJ mol}^{-1}$. The enthalpy change showed the energy difference between the reagent and activated complex. If this difference was small, the formation of the activated complex was favored because the potential energy barrier was slow. The change in Gibbs free energy reveals the total energy increase of the system at the approach of the reagents and the formation of the activated [13]. The positive ΔH^\ddagger and ΔG^\ddagger values revealed that it was connected with the introduction of heat and was a nonspontaneous process [6].

The change in entropy for the formation of activated complex from the reagent reflects how close the system was to its own thermodynamic equilibrium. Lower entropy means that the material has just passed through some kind of physical or

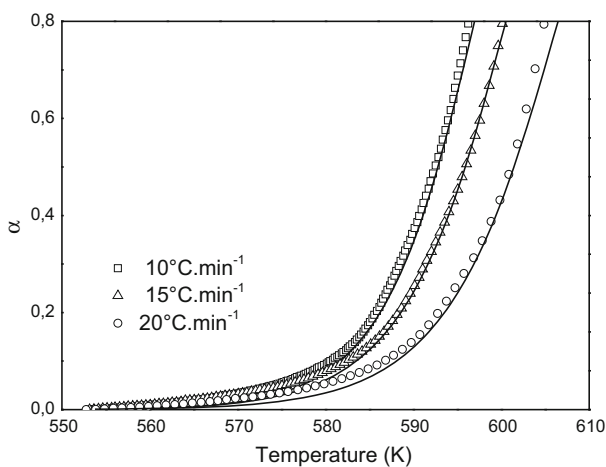


Fig. 6 Comparison of predicted data (*solid line*) and experimental data (*symbol line*) of the thermal decomposition of the linalool/ β -CD inclusion complex at the three heating rates studied

chemical rearrangement of the initial structure, bringing it to a state close to its own thermodynamic equilibrium. In this situation, the material shows little reactivity, increasing the time necessary to form the activated complex. The positive value of activated entropy indicates that the corresponding activated complex has a lower degree of arrangement (i.e., the activated complex is a “less organized” structure when compared to the initial substance) [13]. In the terms of the activated complex theory (transition theory), this positive ΔS^\ddagger value for the thermal decomposition of linalool/ β -CD may be interpreted as a “fast” stage.

Conclusion

The results of this study showed that linalool could be complexed with β -CD by a co-precipitation method. The aqueous solubility of linalool was significantly increased by inclusion in β -CD. The results of the thermoanalytical techniques and ESI-MS demonstrated that the linalool/ β -CD inclusion complex had different physicochemical characteristics from the physical mixture of linalool and β -CD. Kinetic of thermal decomposition of the linalool/ β -CD inclusion complex showed that the process was dominated by a two-dimensional diffusion reaction, with the integral form $g(\alpha) = (1 - (1 - \alpha)^{1/2})^{1/2}$. The activation energies, obtained by Flynn-Wall-Ozawa and Starink isoconversional methods, were 212.16 ± 5.06 and 211.00 ± 4.78 kJ.mol⁻¹, respectively. The pre-exponential factor, calculated by Coats-Redfern method, was 3.34×10^{18} min⁻¹. This result showed that there was no strong chemical interaction between linalool and β -CD. The thermodynamic parameters (ΔS^\ddagger , ΔH^\ddagger , and ΔG^\ddagger) of the activated complex were also calculated, and the positive ΔH^\ddagger and ΔG^\ddagger values revealed that it was connected with the introduction of heat and was a nonspontaneous process.

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