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Evaporation of the fragrance component, cinnamyl alcohol, using simultaneous TG–DTA

Tatyana V. Sorokina[a], David Dollimore[a,1], Kenneth S. Alexander[b,*]

[a]Department of Chemistry, College of Art and Sciences, The University of Toledo, 2801 W. Bancroft Street,
Toledo, OH 43606, USA
[b]Department of Industrial Pharmacy, College of Pharmacy, The University of Toledo,
2801 W. Bancroft Street, Toledo, OH 43606, USA

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Abstract

The thermal behavior of cinnamyl alcohol, which is used in the perfume industry to create a sweet, balsamic and hyacinth-like fragrance, was examined with a simultaneous thermogravimetric–differential thermal analysis (TG–DTA) unit. The sample was subjected to a controlled rising temperature regime under a regulated purge gas flow rate. The evaporation rates and coefficient of evaporation were calculated from TG–DTG data. From the DTG curve, it was found that the evaporation of cinnamyl alcohol is a zero-order process. The activation energy and enthalpy of vaporization for the evaporation process were determined by the use of the Arrhenius and Clausius–Clapeyron equations, respectively. The enthalpy value was calculated to be 68.10 ± 0.84 kJ, while the energy of activation was found to be 66.34 ± 0.84 kJ. The Langmuir equation was applied to the evaporation data, enabling the vapor pressure curves to be determined.

Keywords: Evaporation; Cinnamyl alcohol; Heat of evaporation; Energy of activation

1. Introduction

Calkin and Jellinek [1] described perfume as a blend of odiforous materials, which is perceived as having its own unique and aesthetically, in most cases, pleasing identity. An overall fragrance effect is achieved by releasing components over time with the term volatility referring to the speed at which a material evaporates [2]. The blended fragrance itself reaches the nose in three phases: top note; middle note; and end note [3]. The first impact, the top note, comes from components that vaporize easily, and obviously makes the first impression. The middle note comes from materials that have intermediate volatility. It is responsible for odor after the top-note components have vaporized. The end note is a residual, longer lasting scent, and comes from the least volatile materials.

Fragrances in deodorants, shampoos, or creams are important to make the product acceptable to use partly because of the smell. A concern to manufacturers is the product shelf-life, which may be limited by evaporation of fragrance components during processing, storage, and preparation. This is true for the most volatile components especially when exposed to heat. Understanding the evaporation process and the effects of

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[*] Corresponding author.
E-mail address: kalexan@utnet.utoledo.edu (K.S. Alexander).
[1] Posthumously.

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product formation as well as the properties of individual components can be very beneficial to industry.

TG is a very useful technique to study evaporation processes, product and component stability with temperature, and changes in component properties when mixed in a product formulation [4]. Such data is generally recorded as percent weight versus temperature, but if differentiated a DTG plot of the rate of mass loss (d*m*/d*t*) versus time or temperature is produced. A kinetic mechanism can often be assigned from the shape of the DTG plot. In the case of a zero-order process, the plot shows a maximum value for d*m*/d*t* at the point where the mass of material is exhausted, and thus the return of d*m*/d*t* to the base line is very abrupt [5]. In the case of evaporation from a single compound, the rate of loss of material is usually from a constant area of liquid surface. The composition of the surface and bulk remains constant and the evaporation process therefore can be classified as zero-order [4].

The coefficient of evaporation (k) at any temperature can also be obtained from the DTG plot. The energy of activation can be calculated from the relationship established from the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{1}$$

where k is the coefficient of evaporation at a specified temperature (T) in Kelvin, R the gas constant, A the corresponding pre-exponential factor, and E_a is the energy of activation. The volatility of organic compounds is usually expressed as its vapor pressure, which is the pressure of a vapor in equilibrium with its condensed phase at a specified temperature [6]. The TG data can be substituted into the Langmuir equation [8] (Eq. (2)) and a vapor pressure curve for cinnamyl alcohol constructed.

$$\frac{dm}{dt} = P\alpha\left[\frac{M}{2\pi RT}\right]^{1/2} \tag{2}$$

where d*m*/d*t* is the rate of mass loss with respect to time per unit area, P the vapor pressure, α the coefficient given the value of unity by Langmuir, and M is the molecular weight of the substance under investigation. In practice a value of $\alpha = 1$ is only true for a one component system, i.e. a liquid in equilibrium with its own vapor. Rearrangement of the Eq. (2) gives

$$P = \left[\alpha^{-1}(2\pi R)^{1/2}\left(\frac{T}{M}\right)^{1/2}\left(\frac{dm}{dt}\right)_T\right] = k'v \tag{3}$$

where $k' = \alpha^{-1}(2\pi R)^{1/2}$ and is independent of temperature and material, and $v = (T/M)^{1/2}[(dm/dt)_T]$ which is dependent upon the temperature and the material. Thus, the calculated value of k' can be used for establishing the relationship between pressure and temperature for any material of interest.

An alternative method for the generation of vapor pressure curves is the Antoine equation, which is an empirical method based on a given set of Antoine constants [7] which are defined over a specified temperature range:

$$\log P = A - \frac{B}{C + T} \tag{4}$$

where P is the vapor pressure of the substance while A, B, and C represent the Antoine constants, and T is the absolute temperature.

The Clausius–Clapeyron equation can be used to estimate the enthalpy of vaporization values, where

$$\ln P = -\frac{\Delta H_{vap}}{RT} + \text{constant} \tag{5}$$

where P is the pressure of the substance at the absolute temperature T and ΔH_{vap} is the latent heat of vaporization that can be calculated from the slope of the Clausius–Clapeyron plot. Substitution of Eq. (3) with Eq. (5) shows that value of v is proportional to the pressure. Therefore, it is possible to write

$$\ln v = -\frac{\Delta H_{vap}}{RT} + \text{constant} \tag{6}$$

as an alternative method of calculating ΔH_{vap}.

In this study, thermal analysis was applied to an investigation of the evaporation of cinnamyl alcohol. Kinetic and thermodynamic characteristics, as well as vapor pressure curves, were calculated from the mass loss curves.

2. Experimental

Cinnamyl alcohol (98%) was purchased from Aldrich (lot 306511RT).

The thermal analysis equipment consisted of a simultaneous TG–DTA unit, TA Instrument Model number 2960. The experimental data was analyzed using the TA Instruments Thermal Analyst 2000 software, TA operation system Version 2.3C. Rising temperature experiments at heating rates of 25, 10, 5 and 2 °C/min were conducted over the temperature range from ambient temperature to 350 °C in a dry nitrogen atmosphere with flow rates of 25 and 100 ml/min. Samples were placed in a 110 μl platinum crucible with a cross-section area (A) of 3.07×10^{-5} m^2. An empty crucible was used as a reference. The sample size was varied in the range of 22–43 mg. Using the data collected from the DTG curve, plots of $\ln k$ versus $1/T$ were generated. The coefficient of evaporation per unit area (k') has a unit of kg/s m^2. Vapor pressure curves were constructed empirically by using the Antoine equation and the Antoine's constants found in the literature [7], as well as from the experimental data using the Langmuir equation. Plots of $\ln v$ versus inverse temperature were constructed from the Clausius–Clapeyron equation.

3. Results and discussion

Representative TG–DTG and TG–DTA plots of cinnamyl alcohol at a heating rate of 10 °C/min are shown in Figs. 1 and 2. The first endothermic peak, which has no associated mass loss, is due to the melting of cinnamyl alcohol. The second endothermic event is much more dominant and has an associated mass loss, and can be attributed to the evaporation process. The shape of DTG plot is characteristic of a zero-order process and is typical for evaporation of a single compound.

The energy of activation and the pre-exponential factor for evaporation were calculated from the mass loss data using the Arrhenius equation. Fig. 3 represents a typical Arrhenius plot for cinnamyl alcohol, for an experiment carried out at 10 °C/min with a nitrogen

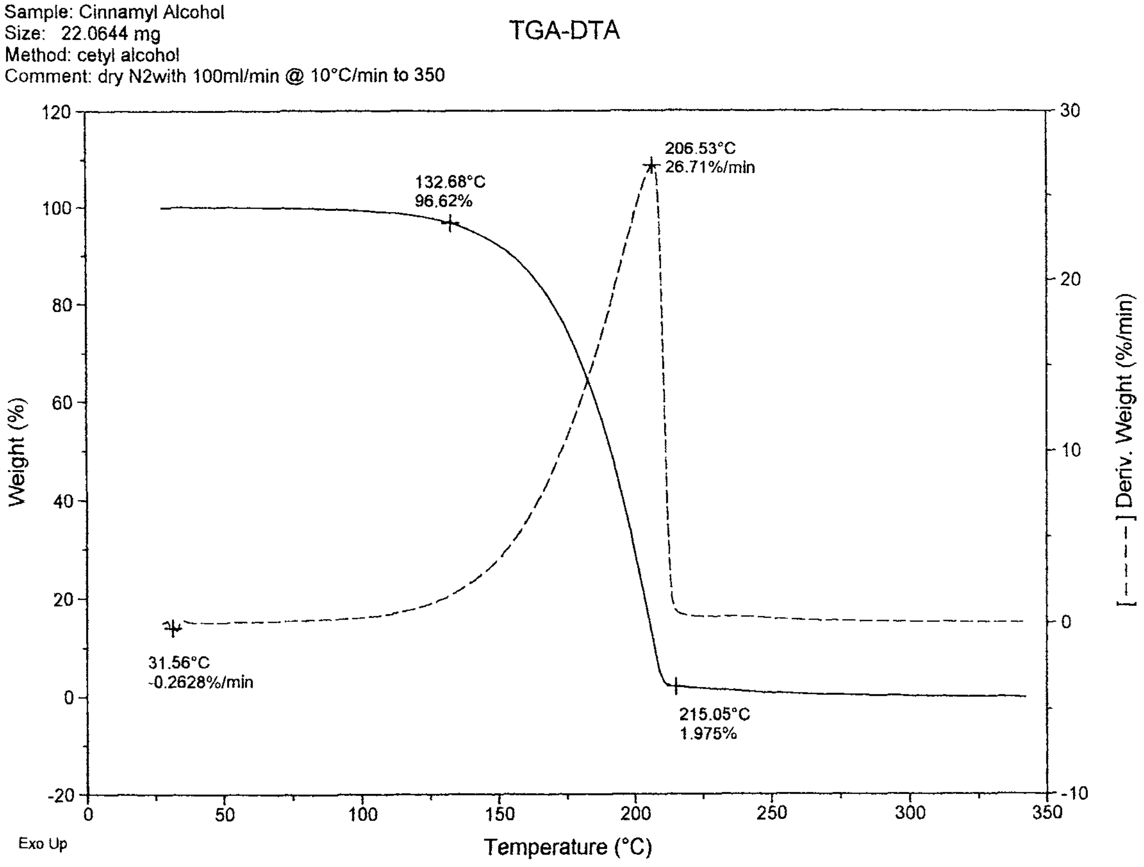

Fig. 1. Typical TG–DTG plot for cinnamyl alcohol.

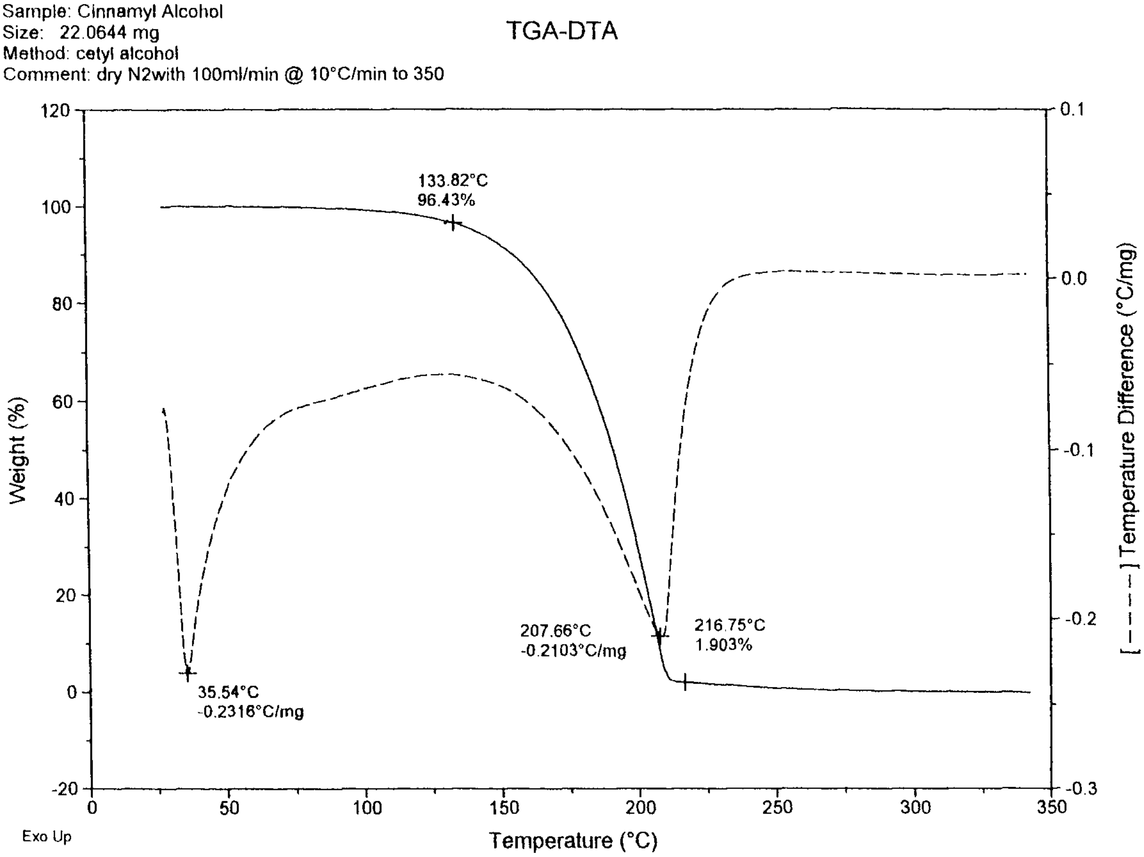

Fig. 2. Typical TG–DTA plot for cinnamyl alcohol.

flow rate of 100 ml/min and a sample mass of 30 mg. The experiments were carried out with different heating rates, gas flow rates and sample masses in order to determine the effect of changing the experimental variables on the determination of E_a and A. Table 1 shows these values for cinnamyl alcohol at different heating and flow rates in an atmosphere of dry nitrogen, and Table 2 shows the values for variation in heating rate. It is evident that the values E_a and A lie in the same range. A small decrease in the magnitude of E_a can be noticed when increasing the heating rate. This may be due to thermal lag, where the true sample temperature is at a lower value than recorded by the thermocouple.

Table 1
Kinetic data for cinnamyl alcohol samples at different heating rates and flow rates of nitrogen[a]

Flow rate (25 ml/min)			Flow rate (100 ml/min)		
Heating rate (°C/min)	E_a (kJ)	ln A	Heating rate (°C/min)	E_a (kJ)	ln A
1	62.92	10.01	1	67.64	11.53
5	67.11	11.13	5	65.76	10.88
10	63.59	10.46	10	66.81	11.14
25	64.83	10.92	25	62.06	10.28

[a] Initial sample weight: 29.0–30.15 mg, average of at least two replicate measurements.

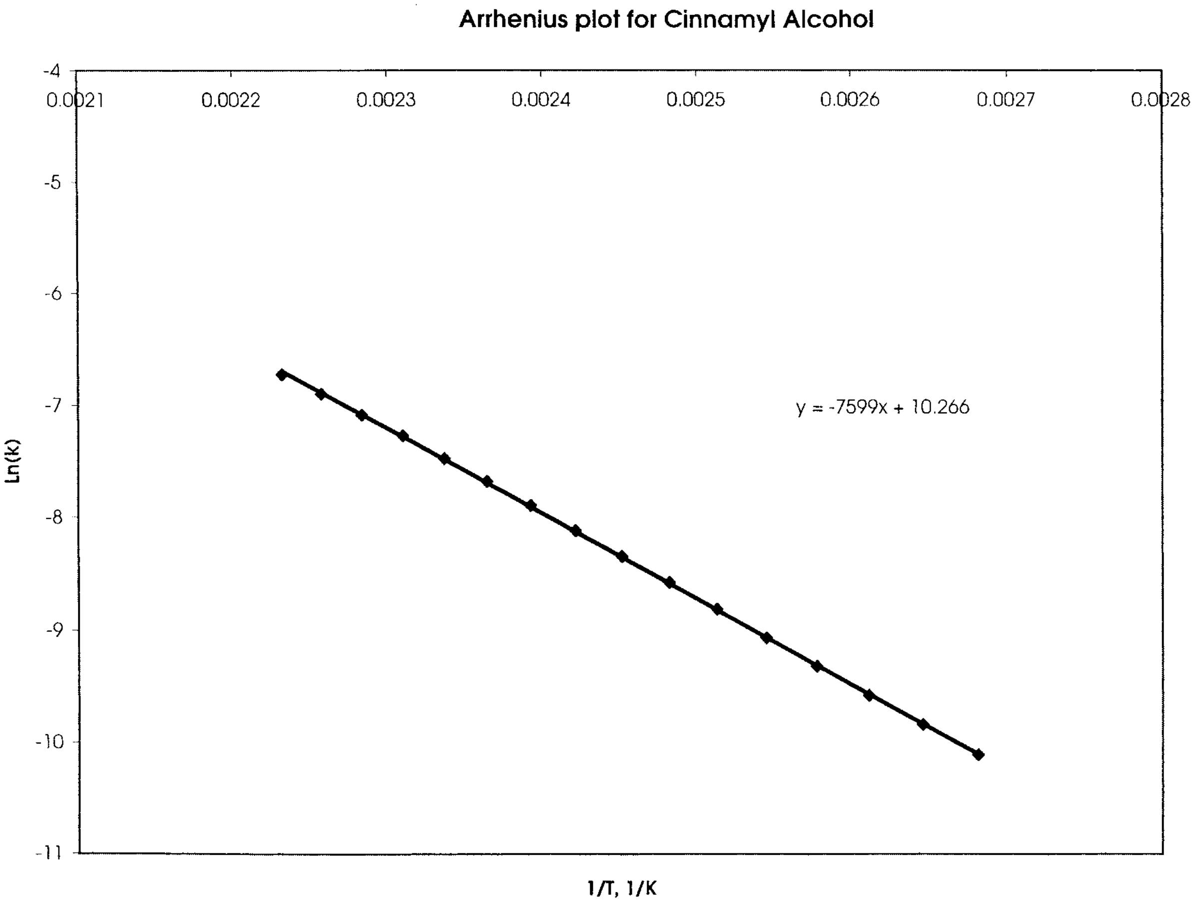

Fig. 3. Arrhenius plot for cinnamyl alcohol (heating rate: 10° C/min; sample mass: 30 mg; nitrogen flow rate: 100 ml/min).

Table 2

Energy of activation and enthalpy of vaporization for cinnamyl alcohol at different heating rates and different sample masses (nitrogen flow rate: 100 ml/min)

Heating rate (5 °C/min)			Heating rate (10 °C/min)		
Sample size (mg)	E_a (kJ)	ΔH_{vap} (kJ)	Sample size (mg)	E_a (kJ)	ΔH_{vap} (kJ)
22.93	64.72	66.41	22.18	65.88	67.59
22.15	64.13	65.84	21.64	64.52	66.23
30.21	65.10	66.80	29.24	66.59	68.33
29.24	66.43	68.13	29.05	67.04	68.74
35.14	63.03	64.73	35.07	66.41	68.16
35.60	63.51	65.19	36.74	66.99	68.70
43.30	64.29	65.94	43.35	66.72	668.43
43.56	65.24	66.90	43.95	66.89	68.60

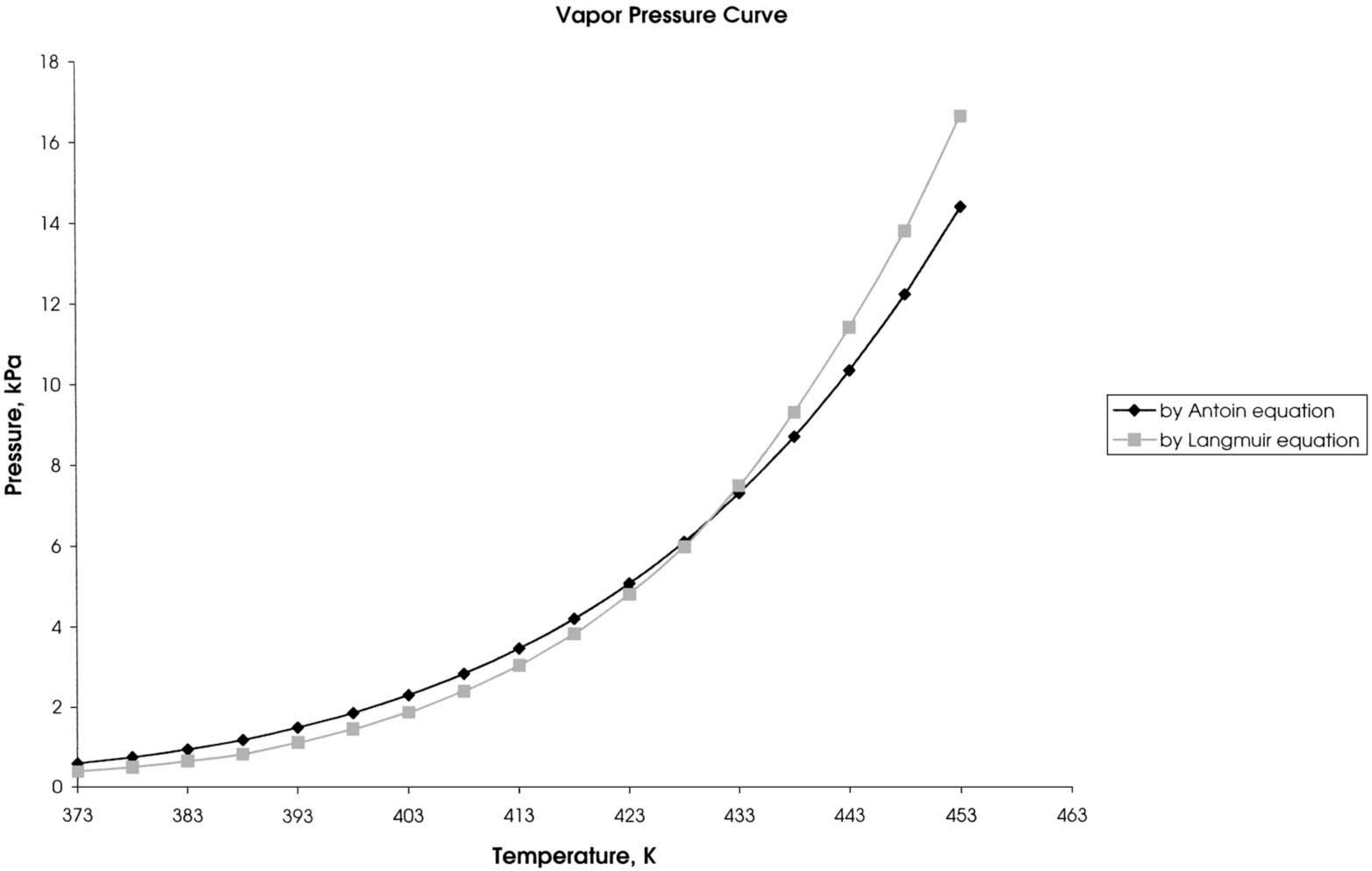

Fig. 4. Vapor pressure curves for cinnamyl alcohol constructed from the Langmuir equation and the Antoine equation TG data collected at a heating rate of 10 °C/min, sample mass 30 mg, nitrogen flow rate 100 ml/min.

Table 3
Variation of the k' value with temperature and the sample size

Temperature (°C)	Sample size (mg)			
	22.06	29.17	43.50	51.95
	$k' \times 10^5$			
100	2.855	3.145	2.530	2.240
130	2.442	2.302	1.977	1.735
160	1.827	1.705	1.459	1.365
200	1.571	1.418	1.241	1.131

The enthalpy of vaporization for cinnamyl alcohol was calculated for samples with various masses and at different heating rates. This data is shown in the Table 2, together with values for E_a. It is noticeable that the energy of activation values are close to the enthalpy of vaporization, thus indicating a non-activated kinetic process.

The coefficient of vaporization (k') for cinnamyl alcohol was calculated from the mass loss data and the values presented in Table 3. The data shows that k' varies with temperature within the single run, and with sample size alterations. Since k' is proportional to α^{-1}, it follows that α is much less than unity and alters with temperature. This is because the Langmuir equation was derived for single component systems under vacuum, whereas this study was carried out at atmospheric pressure with dry nitrogen as the purged gas. Therefore, the ideal conditions for the Langmuir equation are no longer valid.

For the generation of vapor pressure curves, the average magnitude of the mean values for a heating rate of 10 °C/min, and a nitrogen flow rate of 100 ml/min, was used. Obtained results indicated a good correlation between vapor pressure values calculated by the Langmuir and Antoine methods (Fig. 4) for experiments with alteration of the heating rate in the range 1–25 °C/min and gas flow rate in the range 25–100 ml/min.

4. Conclusions

Cinnamyl alcohol was examined with TG and DTA, and showed melting and evaporation transitions during analysis. Results of the thermal analysis were used to calculate the coefficient of evaporation, activation energy and pre-exponential factor, and enthalpy of evaporation. The DTG analysis data was also used to construct vapor pressure curves using the Langmuir equation, providing a fast method for establishing the relationship between vapor pressure of the analyte and temperature as an alternative to the Antoine method.

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