ELSEVIER

Thermochimica Acta 392–393 (2002) 221–229

thermochimica acta

www.elsevier.com/locate/tca

Thermal analysis of the evaporation of compounds used in aromatherapy using thermogravimetry

Anasuya Hazra, David Dollimore, Kenneth Alexander*

Department of Pharmacy Practice and Department of Chemistry, The University of Toledo, Toledo, OH 43606, USA

Received 29 December 2000; accepted 28 April 2001

Abstract

Thermogravimetric analysis is often used to evaluate the evaporation phenomenon of several substances. The present study was designed to characterize the vaporization characteristics of three essential oils; lemon oil, lavender oil and cinnamon oil and their several components. All three oils represent multi-component systems, whereas their main components represent single component systems. Linalyl acetate was used as the calibration compound and the coefficient of vaporization was obtained as 7×10^7 (SI system). The order of reaction was first determined for each of the compounds under study. Vapor pressure curves were then plotted using Langmuir and Antoine equations for the compounds, which represent single component systems, undergoing zero-order non-activated evaporation processes. The vapor pressure curves obtained were statistically quantified along with the calculations for the Antoine constants using SPSS version 10.0 software. The energies of activation for cinnamon oil, lemon oil and lavender oil were found to be 45.10, 33.2 and 33.9 kJ/mol, respectively.

Keywords: Antoine equation; Essential oils; Langmuir equation; Multicomponent system; Thermogravimetry; Vapor pressure

1. Introduction

Thermogravimetric analysis has been used to determine the kinetics of evaporation for different substances. The shape of the thermogravimetric curve is a function of the reaction kinetics and therefore, can be used to evaluate kinetic parameters for reactions involving weight changes. Many methods that had been proposed to determine the kinetic parameters of the reactions generally demand that the rate of decomposition have the following form [1]:

$$\frac{-\mathrm{d}w}{\mathrm{d}t} = A \exp\left(\frac{-\Delta E}{RT}\right) w^n \tag{1}$$

where, w is the fractional residual sample weight, T the absolute temperature, R the general gas constant; t the time; A the pre-exponential factor; ΔE the activation energy; and n is the order of reaction. The method that has been used to determine the kinetics of the reaction of evaporation in the present study treats Eq. (1) as a differential equation and the fractional weight is derived by integrating as a function of the temperature. The k-value for the Arrhenius equation is represented as:

$$k = \left(\frac{\mathrm{d}\alpha/\mathrm{d}t}{1-\alpha^n}\right) \tag{2}$$

where α can be defined as [initial weight − weight at that moment (time or temperature)]/(initial weight− final weight). For a zero-order process the equation becomes [1]

$$k = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) \tag{3}$$

* Corresponding author.
E-mail address: kalexan@utnet.utoledo.edu (K. Alexander).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00104-1

where

$$\frac{d\alpha}{dt} = \left(\frac{dwt/dt}{w_i - w_f}\right) \quad (4)$$

All the terms of Eq. (3) can be obtained directly from the TG.

The Arrhenius equation can be stated as:

$$k = A \exp\left(\frac{-\Delta E}{RT}\right) \quad (5)$$

The equation can alternatively be expressed as:

$$\ln k = \ln A + \left(\frac{-\Delta E}{RT}\right) \quad (6)$$

Therefore, for a zero-order evaporation process, plotting $\ln k$ or $\ln(d\alpha/dt)$ versus $1/T$, we obtain a straight line. The slope of this line provides the energy of activation for the evaporation process [2].

The derivative thermogravimetry (DTG) plot also plays an important role in the determination of zero-order kinetics of evaporation. The rate of mass loss of a compound reaches its maximum value at the point of exhaustion showing its highest value in the DTG plot [3]. The curve then abruptly returns to the baseline as shown by Fig. 1.

The vaporization characteristics of a compound can be depicted by the vapor pressure curve of a compound. There are several methods to determine the vapor pressure curve for a given compound. Recently, Price and Hawkins [4] reported the evaporation characteristics of certain dyes using thermogravimetry.

In moderate pressure ranges, the Antoine equation is an excellent empirical tool that is mainly used for curve fitting purposes [5]. It can be written as:

$$\ln P = \frac{a - b}{(T + c)} \quad (7)$$

where P is the vapor pressure of a compound at absolute temperature T; $a = 2.303\ A$; $b = 2.303\ B$;

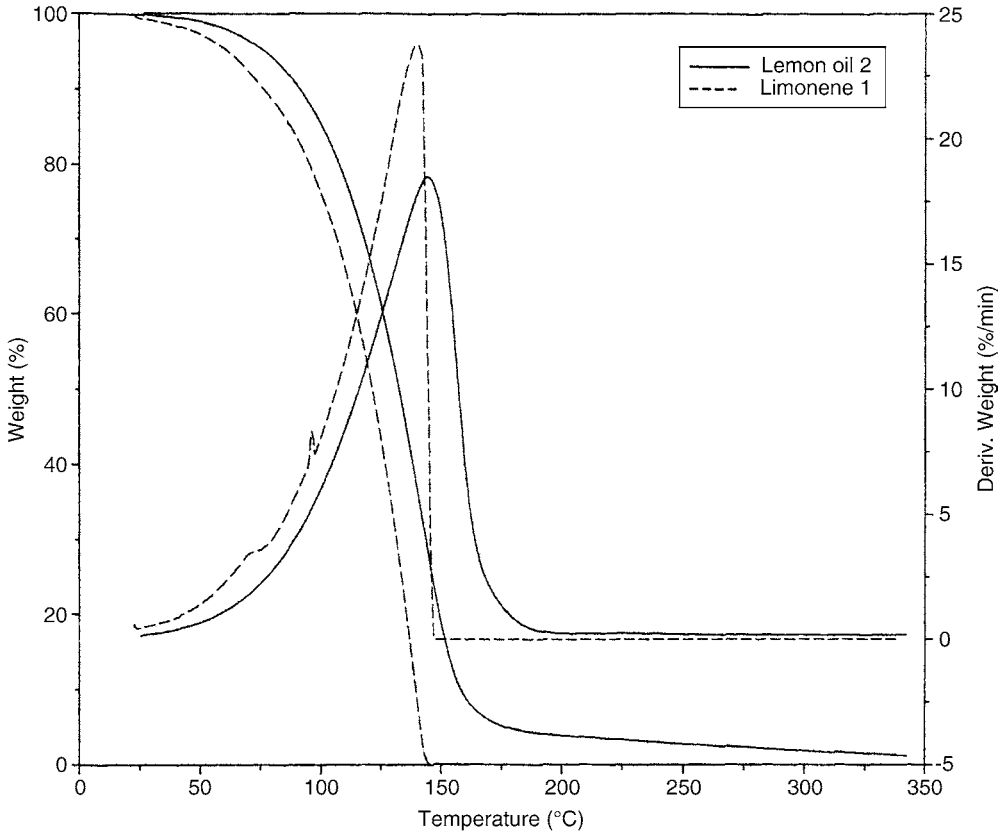

Fig. 1. TG–DTG plot for lemon oil and limonene.

and $c = C$. The A, B and C terms are the Antoine constants of that particular substance at a given temperature range, obtained from the book edited by Shuzo [6]. The Antoine constants for the calibration material (linalyl acetate) were found to be $A = 7.65402$, $B = 2093.912$ and $C = 218.352$ for a temperature range of 328.40–493 K. The P-values for linalyl acetate were obtained at each point of temperature (K) for the rising part of the DTG curve.

The Langmuir equation can explain the evaporation characteristics for a given substance

$$\frac{dm}{dt} = P\alpha\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{8}$$

Where dm/dt is the rate of mass loss per unit area, P vapor pressure of a compound at a given temperature T, α vaporization constant, M molecular weight of the compound undergoing evaporation and R is the universal gas constant. The objective is to determine the vaporization constant (i.e. α) in the presence of a purge gas [7] which is dry nitrogen for this particular study.

The Langmuir equation supposes that the substance under study evaporates from a uniform surface area and the value of α is not unity in the presence of a purge gas. It depends immensely on the experimental set up, but is independent of the vapor under study.

Eq. (8) can be rewritten as:

$$P = [\alpha^{-1}(2\pi R)^{1/2}]\left[\left(\frac{T}{M}\right)^{1/2}\left(\frac{dm}{dt}\right)\right] \tag{9}$$

$$P = kv$$

where $k = \alpha^{-1}(2\pi R)^{1/2}$ and $v = (T/M)^{1/2}(dm/dt)$.

Since k is constant for any given set of experiments then the plot of P versus v gives the value of k. Alternatively, if Eq. (9) and plot log P versus log v will obtain log k.

Knowing the Antoine constants for a calibration compound we can then estimate the vapor pressure for a compound at a particular temperature within a particular range for which the Antoine constants for that particular substance holds true. Then, when plotting P versus v gives the value of k, which is theoretically constant and independent of substances for a particular set of experiments. Using this k-value for other similar types of compounds allows one to obtain the vapor pressure for a compound at a particular temperature for which the Antoine constants are not known.

The objective of the present study was to determine the kinetics of evaporation of some essential oils representing multi-component systems, using thermogravimetric analysis and to construct the vapor pressure curves for the compounds which are themselves the components of these essential oils, showing zero-order kinetics using the method described above. The challenge of the study was to eventually deal with the multi-component systems.

Lemon oil, lavender oil and cinnamon oil are widely used in aromatherapy and perfumes [8]. All of these are mixtures of different compounds and hence resemble multi-component systems.

Using thermogravimetric analysis the kinetics of evaporation for these oils have been determined and the energy of activation has been determined from the Arrhenius plot. The various components of these multi-component oils resemble single-component systems and hence, the vapor pressure plots for these compounds have been constructed using linalyl acetate as the calibration compound.

The enthalpy of vaporization (ΔH_{vap}) can be calculated using the Clausius–Clapeyron equation, which is as follows:

$$\log\left(\frac{p_2}{p_1}\right) = \left(\frac{\Delta H_{vap}}{2.303R}\right)\left(\frac{T_2 - T_1}{T_1 T_2}\right) \tag{10}$$

where p_1 and p_2 are the corresponding vapor pressures of a substance at absolute temperature T_1 and T_2, respectively and R is the universal gas constant.

Since vapor pressure curves for different volatile substances resemble non-linear patterns, therefore, for curve fitting purposes and simultaneously for the calculation of the Antoine constants for different substances the use of non-linear regression analysis holds much greater accuracy and flexibility. The empirical Antoine constants for each compound can be determined by least square curve fit method where the vapor pressure plot for each substance is fitted in to the Antoine equation, which is in turn used as the model curve fit equation for this purpose. The values of A, B and C are susceptible to changes depending on the algorithm used. But, for practical purposes, the Levenberg–Marquardt algorithm [9] was used and the ''global'' least square curve fit method was found to be consistently accurate for predicting the value of the

Antoine constants. Two parameters must be taken into consideration as follows.

1. The values of A, B and C are susceptible to changes with the particular algorithm used as stated before and therefore, the values obtained for these constants using non-linear regression must be corroborated by their original vapor pressure curves.
2. Before starting iteration, all statistical software used for non-linear regression require a starting value for each parameter. Generally the starting value can be predicted for a particular compound if the Antoine constants for any compound in that homologous series is known. For this study, starting value stipulated in ASTM methods E1719 and El 782 have been used [10].

2. Experimental

2.1. Materials

Lemon oil (Lot no. 102082), lavender oil (Lot no. 090978) were obtained from Sherman research Lab., cinnamon oil (Lot no. F15682A23) was obtained from Amend Drug and Chemical Co. Linalyl acetate (Lot no. 01627C1), limonene (Lot no. 01006C1), linalool (Lot no. 1711 1TR), cineole (Lot no.01627C1) and cinnamaldehyde (Lot no. 08514BR) were obtained from Aldrich Chemical, Milwaukee, WI.

2.2. Equipment

The SDT 2960, simultaneous TGA-DTA instrument with Thermal Analyst 2000, TA operating system

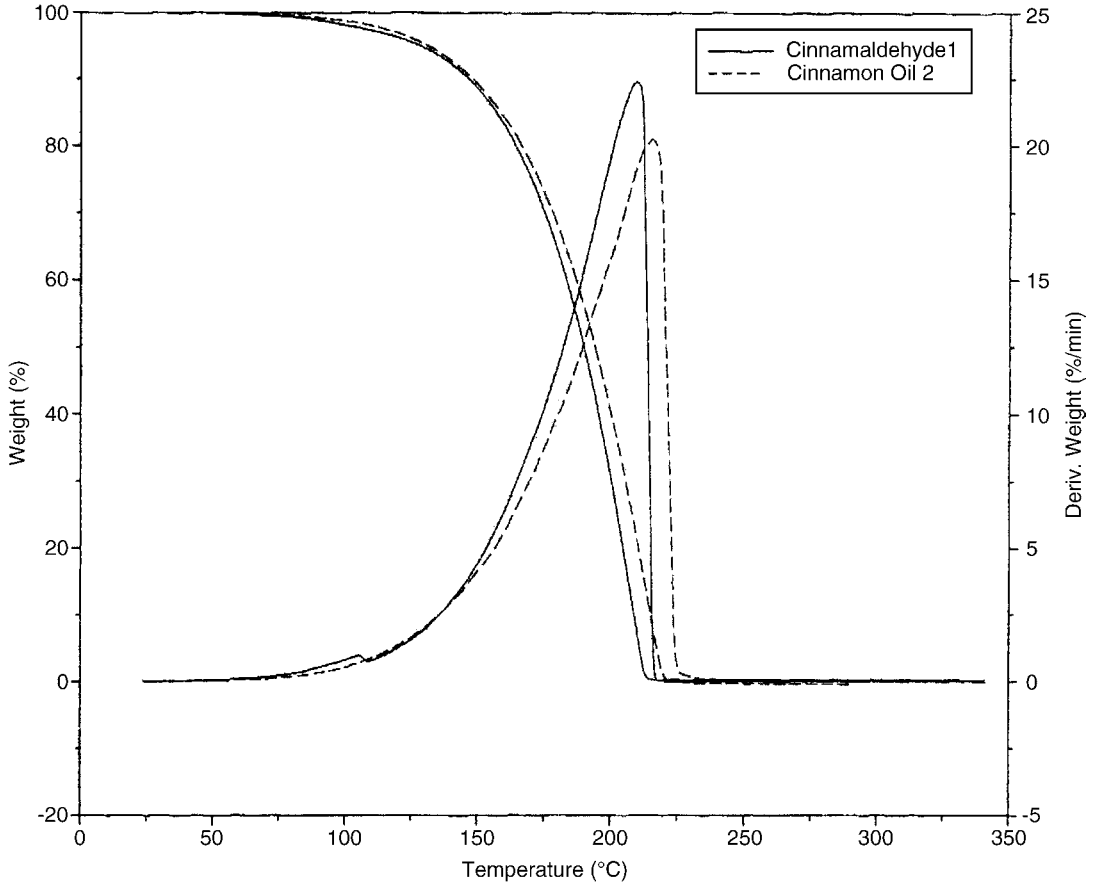

Fig. 2. TG–DTG plots for cinnamaldehyde and cinnamon oil.

version 1.0 B was used. An electrical flow meter from J & W Scientific model ADM 1000 was used to regulate the flow of the purge gas dry nitrogen. Two platinum crucibles from TA Instruments were used to hold the sample. The SPSS version 10.0 software was used for the statistical analysis.

2.3. Procedure

Rising temperature programs were applied to the samples under study and readings were taken every 1 °C interval. The rising temperature runs were performed on the TG to 350 °C at a rate of 10 °C/min. The dry nitrogen purge gas was used at a rate of 100 ml/min. An open 110 μl platinum crucible with a cross-sectional area of 0.2826 cm^2 was used to hold the sample and an empty crucible with the same cross-sectional area was used as the reference. The choice of sample size was dependent on the amount of area covered by the substance since it is always required for the substance to cover the cross-sectional surface of the crucible to ensure uniform evaporation.

The data obtained from the Universal Analysis software was used to construct the Arrhenius plot in order to determine the energy of activation for the evaporation process as well as to determine the reaction kinetics for the oils and their components. Cinnamon oil and lemon oil showed zero-order kinetics (Fig. 2), whereas lavender oil deviated somewhat from zero-order kinetics (Fig. 3). All of the other compounds showed zero-order kinetics. The Clausius–Clapeyron equation was used to calculate the enthalpy of vaporization. The Antoine and the Langmuir equations were then used to construct the vapor pressure plots for limonene, cineole, cinnamaldehyde and linalool.

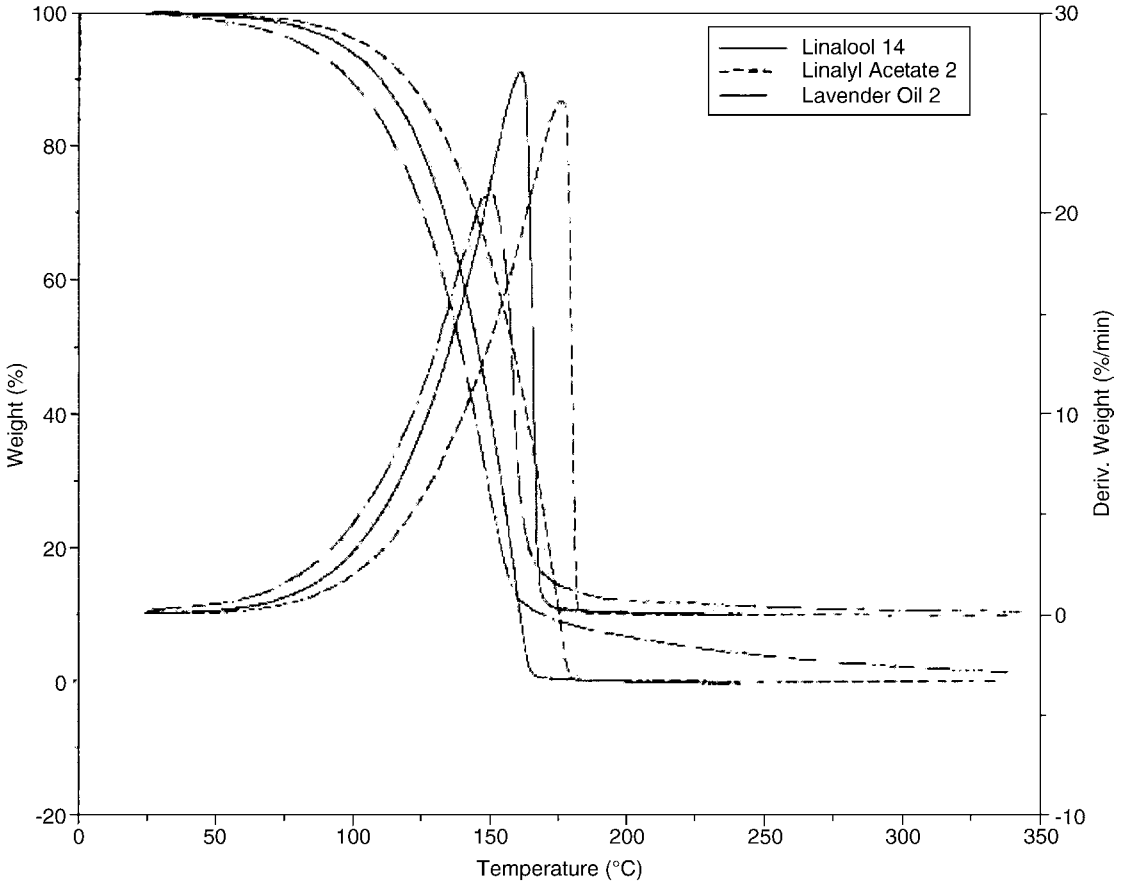

Fig. 3. TG–DTG plot for linalool, linalyl acetate and lavender oil.

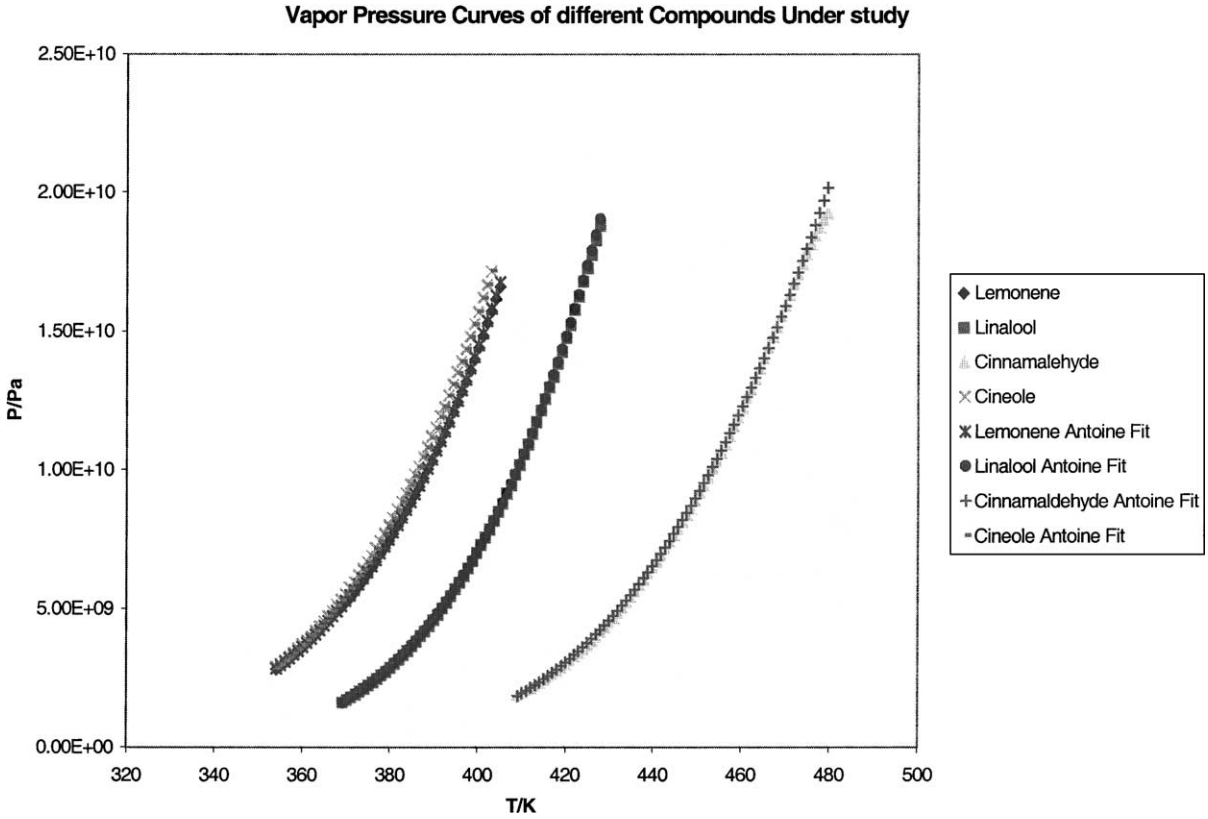

Fig. 4. Vapor pressure plots for cinnamaldehyde, cineole, limonene and linalool.

The compound linalyl acetate was used as the calibration compound since the Antoine constants of which were reported in the literature over a certain temperature range, especially from 328.40 to 493 K as $A = 7.65402$, $B = 2093.912$ and $C = 218.352$. The vapor pressure curves for linalool, limonene, cinnamaldehyde and cineole were generated using the k-value obtained from linalyl acetate (Fig. 4).

3. Results and discussion

3.1. Evaporation kinetics

In order, for a reaction to be stated as evaporation, it is imperative that the loss of weight with respect to time or temperature should be a zero-order process. The DTG curve for the zero-order kinetics is generally characterized by a sharp, vertical decline of the curve from the maximum value to the baseline. The use of the Arrhenius equation for the determination of the zero-order reaction further strengthens the determination of the kinetics for the reaction. All the oils showed a zero-order process and can, therefore, be considered as evaporation. The activation energies for these oils and the activation energies for linalool, limonene, cineole and cinnamaldehyde are listed in Table 1.

Table 1
Summary of the values for E_{act} and H_{vap} for the compounds studied

Compound	E_{act} (kJ mol^{-1})	H_{vap} (kJ mol^{-1})
Cinnamon oil	45.10	–
Lemon oil	33.20	–
Lavender oil	33.90	–
Cinnamaldehyde	50.79	52.63
Cineole	39.64	41.22
Limonene	37.87	39.44
Linalool	65.64	52.12

The DTG plots for different oils and their components are given together for the comparison between single component and multi-component systems. The enthalpy of vaporization for the components of the oils showing a zero-order process are also listed in Table 1. These values are close to the energy of activation values showing zero-order kinetics.

3.2. Vapor pressure curves

Linalyl acetate was taken as the calibration material since its Antoine constants were reported in the literature. A plot of log P versus log v was used to obtain the value for the vaporization coefficient (i.e. k) which was found to be 7×10^7 in SI units. This k-value is different from the value reported in [11]. The value of k might vary depending on the various experimental parameter sets (e.g. the change in flow of the nitrogen; the heating rate; or due to the change in the α-value in the Langmuir equation). However, these factors were not investigated in this study. The k-value also changes depending on the types of compounds investigated. Since these compounds under study are quite volatile and the rates of exhaustion are very high as compared to less volatile compounds, then the possibility exists that these compounds have a different k-value as reported in the literature (Figs. 5 and 6).

3.3. Curve fitting using antoine equations

The method of non-linear regression was used to calculate the Antoine constants for linalool, limonene, cineole and cinnamaldehyde. The Antoine equation cannot be linearized unless some bold assumptions have been made which might not be true over a certain temperature range and hence, the use of non-linear regression was deemed to be the best for this calculation. The SPSS version 10.0 software was used and the Levenberg–Marquardt algorithm for the global fit method was applied. The parameter specifications were performed according to ASTM methods E1719 and E1782 and for A, B and C they are 9.3, 2000 and -37, respectively, when the pressure is in Pascal and the temperature is in Kelvin [9]. The values for the Antoine constants obtained using non-linear regression were corroborated comparing the vapor pressure curves for those compounds generated by the Langmuir equation and proved to be the best curve

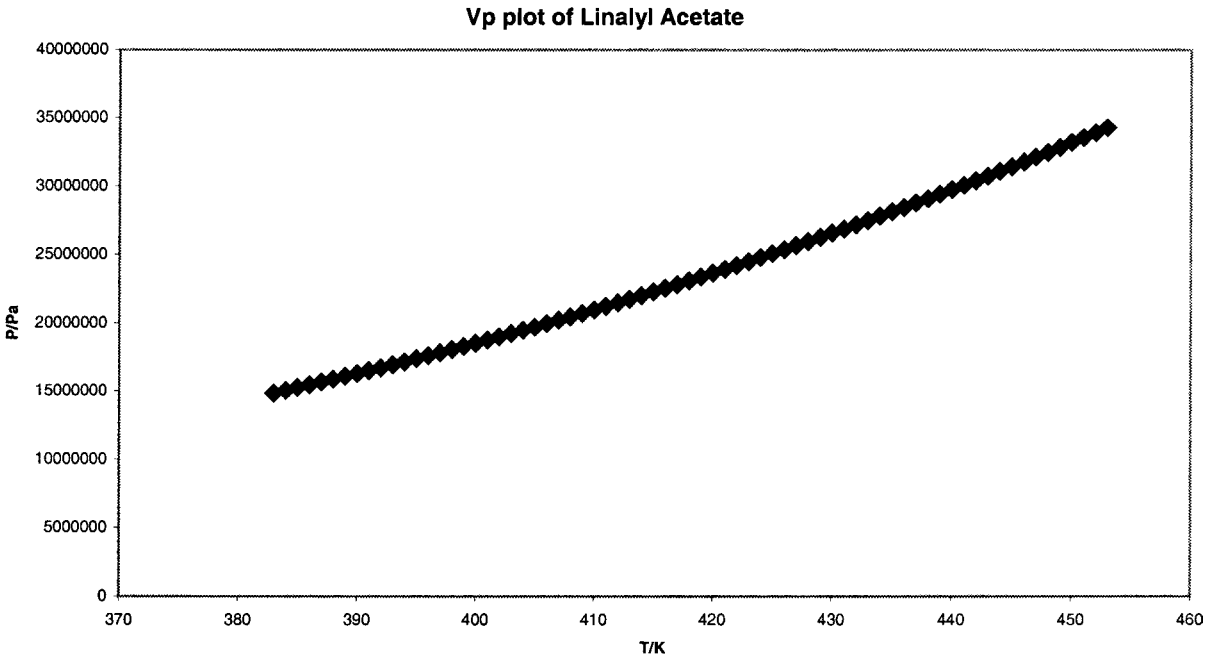

Fig. 5. Vapor pressure plot for linalyl acetate with its Antoine constants reported in the literature.

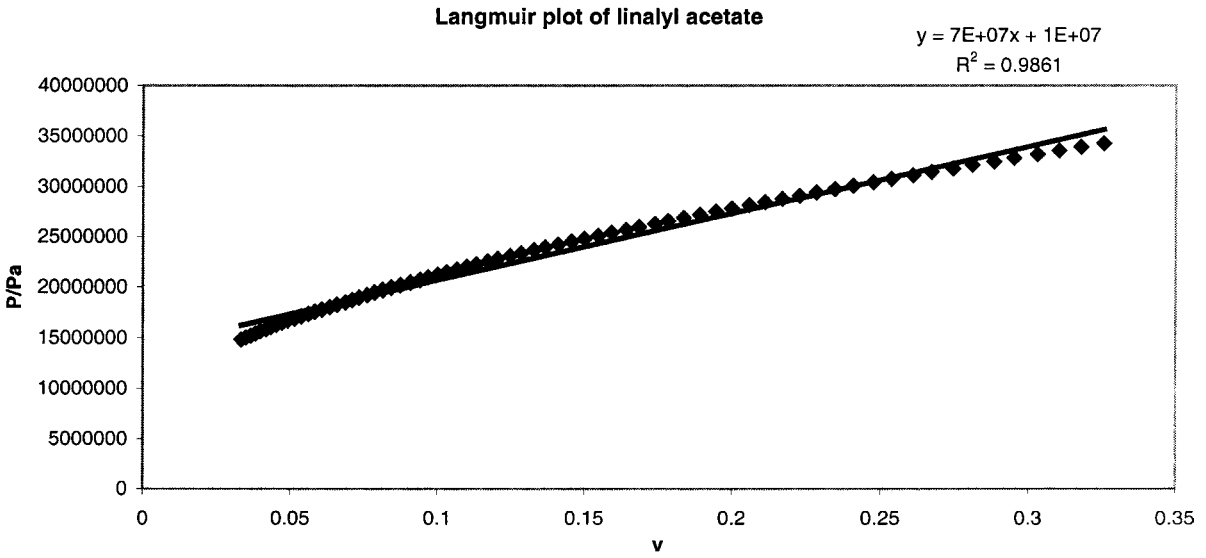

Fig. 6. Calculation for the coefficient of evaporation (k); plot of $\log p$ vs. $\log v$.

Table 2
List of Antoine constants for compounds undergoing evaporation

Compound	Calculated Antoine constants			Temperature range (K)
	A	*B*	*C*	
Cineole	14.09	1171.43	−98.84	353–403
Cinnamaldehyde	12.61	540.96	−245.24	408–480
Limonene	14.66	1592.66	−45.66	353–405
Linalool	10.49	785.22	−183.21	368–428

fit. The values of the Antoine constants for various compounds under study are given in Table 2.

3.4. Conclusions

All the single-component systems under study showed evaporation and hence resemble zero-order kinetics. Thermogravimetry has been found to be a good and simple method to plot the vapor pressure curves for different single component systems under study. The method used here to construct the vapor pressure plots for single component systems can be extrapolated to plot the vapor pressure curves for multi-component systems provided the exact composition and the amount of each constituent of the multi-component system or the average molecular weight of the multi-component system is known. SPSS version 10.0 was effectively used to calculate the Antoine constants of various compounds using non-linear regression.

References

[1] G.M. Barrow, Physical Chemistry, 5th edition. McGraw-Hill Book Company, New York, 1988.
[2] D. Dollimore, T.A. Evans, Y.F. Lee, F.W. Wilburn, Correlation between the shape of a TG/DTG curve and the form of the kinetic mechanism which is applying, Thermochim. Acta 198 (2) (1992) 249–257.
[3] S.L. Alexander, S. Kenneth, A thermal analysis study of long chain fatty acids, Thermochim. Acta 340/341 (1999) 271–278.
[4] M.P. Duncan, M. Hawkins, Calorimetry of two disperse dyes using thermogravimetry, Thermochim. Acta 315 (1998) 19.
[5] Majer, V. Svoboda, J. Pick, Heats of vaporization of fluids, Elsevier, Amsterdam, 1989, p. 27.
[6] O. Shuzo, Eng. Computer Aided Data Book of Vapor Pressure, Tokyo, Japan, 1976.
[7] I. Langmuir, Phenomena, Atoms and Molecules, Philosophical Library Inc., New York, 1950.
[8] Guenther, Ernest. The Essential Oils, Vol. 1–4, D. Van Nostrand Co., New York, 1948.
[9] W.G. Bardsley, N.A.J. Bukhari, M.W.J. Ferguson, J.A. Cachaza, F.J. Burguillo, Evaluation of model discrimination, parameter estimation and goodness of fit in nonlinear regression problems by test statistics distributions, Comput. Chem. 19 (2) (1995) 75–84.

[10] Standard test method for vapor pressure of liquids by ebulliometry, Annual Book of ASTM Standards, Designation: E 1719-97, 1997, No. 11.01. Copyright 2000 American Society for Testing and Materials, West Conshohocken, PA.

[11] D. Dollimore, P. Tong, K.S. Alexander, The kinetic interpretation of the decomposition of calcium carbonate by use of relationships other than the Arrhenius equation, Thermochim. Acta 282/283 (1996) 13–27.