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CHARACTERIZATION OF SOME ESSENTIAL OILS AND THEIR KEY COMPONENTS
Thermoanalytical techniques

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Abstract

The present study was aimed at determining the kinetics of evaporation and establishing vapor pressure curves for both single and multi-component systems by thermogravimetry (TG) and differential scanning calorimetry (DSC). Essential oils (e.g. lavender oil, orange oil, clove oil and eucalyptus oil, etc.) are typically multi-component systems consisting of various volatile pure components (e.g. linalyl acetate, limonene, cinnamaldehyde, etc.) which resemble single component systems. In this study linalyl acetate was taken as the calibration compound for TG. The vapor pressure curves for the pure substances were plotted using TG and vapor pressure plots for clove oil and eucalyptus oil were constructed using DSC. The thermodynamic and kinetic parameters of the pure compounds were compared to that of the multi-component systems to quantitatively and qualitatively measure the influence of different compounds on each other. The *k*-value from the vapor pressure data for linalyl acetate was calculated as 112006 Pa $\text{kg}^{0.5}$ $\text{mol}^{0.5}$ s^{-1} m^{-2} $\text{K}^{-0.5}$. The vapor pressure values were used to determine the Antoine constants using the SPSS 10.0 software.

Keywords: Antoine equation, DSC, essential oils, Langmuir equation, multicomponent system, TG, vapor pressure curves

Introduction

Various essential oils and their components are widely used in the field of aromatherapy and in pharmaceuticals. The essential oils are combinations of various volatile substances and, hence, represent multi-component systems, while their key components represent single component systems.

There are a few aspects of this study which should be noted. The first and foremost being to construct the vapor pressure plots for various compounds present in the essential oils using thermogravimetric analysis (TG). These substances are pure organic components and hence represent single component systems. There are several

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methods to construct the vapor pressure curves for pure components, some of which are direct while others are indirect. The methods, which have been used here, are comparatively new and can be outlined in the following manner [1]. A compound has to be taken whose Antoine constants are reported in the literature. This calibration compound has to be the same in nature as those compounds for which the vapor pressure curves need to be constructed. A specific constant has to be calculated from the vapor pressure values for the calibration compound and then must be applied to other compounds to construct their vapor pressure curves. Vapor pressure values were calculated and validated to the values given in the literature to prove the significance of this method using the pure compounds. The point to be noted is that this method can only be used for pure single component substances, which undergo a non-activated zero order evaporation process.

Another aspect of this study was to calculate Antoine constants for the compounds, which have not had values previously reported for them in the literature, using non-linear regression analysis. The method used here to calculate the Antoine constants holds true for any kind of component system.

The method for constructing vapor pressure plots using TG is only valid for a non-activated zero order process. Therefore, another aspect of this study is to determine the reaction kinetics for the essential oils and their key components by a method established in the literature as to whether they undergo a true evaporation process [3, 4].

This study tried to characterize the multicomponent systems while undergoing evaporation and to determine if the same principle applies to their evaporation pattern as it does for its major single component. After confirmation of the kinetics of the mixture, the major component of that multicomponent system was investigated and the vapor pressure plot for that compound was constructed to characterize the mixture. In most cases under investigation, the TG-DTG curves for the pure single component system resembled the multicomponent system. To quantify the differences between the single and multi-component system, each pair of substances was categorized using a specific classification. The vapor pressure curves for the multi-component systems were constructed using DSC.

The determination of the order for the reaction kinetics of evaporation is zero order. The process for determining the order of a reaction has been elaborately discussed previously in literature [3, 4]. The method mainly follows Arrhenius equation, which can be given as follows:

$$k_{\mathrm{vap}} = A\mathrm{e}^{-\mathrm{E}_{\mathrm{vap}}/\mathrm{RT}} \tag{1}$$

where E_{vap} is the activation energy of evaporation, A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature and k_{vap} is the co-efficient of evaporation.

There were several attempts in the past to demonstrate and validate methods for vapor pressure measurements. These methods included direct measurements with a manometer [5]; the use of mass spectrometry to monitor the gas phase concentration of the volatile species [6]; measuring sample volatilization by vacuum diffusion in a

Knudsen cell [7]; and the boiling point determination under reduced pressures [8]. In order to determine the vapor pressure values for the single component system, mainly two equations have been used namely the Langmuir and Antoine equations.

Price and Hawkins recently reported the evaporation characteristics of dyes using TG [1] and investigated such techniques for pharmaceutical solids [9, 10]. Since the use of TG is both simple and less time consuming compared to other vapor pressure measuring instruments (the method will be discussed later), there has been a plethora of data published in this field so far. The wide range of compounds that have been studied include complex organic pharmaceutical solids and cosmetic ingredients [11–15]. In a recent review article [16], Duncan Price addresses some of the issues connected to such techniques quite comprehensively. It must be pointed out, however, that this concept to date has only been applied to single component systems. For multi-component systems the standard method by ASTM [17] using pressure differential scanning calorimetry (PDSC) can be used.

Antoine equation and its application

The Antoine equation is as follows,

$$\lg P=A-B/(T+C) \tag{2}$$

where P is the vapor pressure, T is the absolute temperature and A, B and C are the Antoine constants. Here A, B and C are the empirical Antoine constants over a given temperature range, that can be obtained from the book by Stephenson and Malamowski [18] or the one by Ohe [19]. These constants have been used to define the vapor pressure curve for the reference compound linalyl acetate which was then used for calibration of the process. The exact procedure will be given in the section Experimental. There are two things one must be aware of when utilizing this equation. First, the Antoine constants are empirical and no physical significance can be associated with them to date. Second, these constants can be used to define vapor pressures only within a specified temperature range.

Langmuir equation and its applications

The Langmuir equation is as follows,

$$\mathrm{d}m/\mathrm{d}t=P\alpha(M/2\pi RT) \tag{3}$$

where ($\mathrm{d}m/\mathrm{d}t$) is the rate of mass loss per unit area, P is the vapor pressure, α is the vaporization constant and M is the molecular mass of the evaporating vapor.

The Langmuir equation can be modified to obtain/calculate the vapor pressure values of several single component substances. The following modifications are given below.

Constant (k) method

In order to suit thermogravimetric data, the Langmuir equation can be rewritten as:

$$P=\frac{\sqrt{2\pi R}}{\alpha}\frac{\sqrt{T/M}}{\mathrm{d}m/\mathrm{d}t}=k\nu \text{ or } P=k\nu \tag{4}$$

where ν can be directly obtained from the TG experimental data. If k is considered to be a constant for a given set of experiments and is independent of material used, then the plot of P *vs*. ν gives the value of k.

There have been different approaches with which one could calculate the value for k. First, an arithmetic average could be taken for all the values for k. Second, the vapor pressure values can be individually computed with different values for k which was named the 'Varying k method'. Third, this problem of choosing the correct value for k can be overcome by eliminating this factor totally from the vapor pressure calculations by using the 'comparative method'. In this study the first method has been followed in general and also the other methods have been applied where best suited. The theory behind the comparative and the varying k method is being described below.

Comparative method

Modifying Eq. (4) we can write for any compound;

$$P_{\mathrm{sam}}=\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{sam}}\sqrt{\frac{T}{M_{\mathrm{sam}}}}\,k \tag{5}$$

$$P_{\mathrm{ref}}=\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{ref}}\sqrt{\frac{T}{M_{\mathrm{ref}}}}\,k \tag{6}$$

The pressure of the sample would be the pressure for the known calibration compound and the pressure for the reference would the compound whose Antoine constants have not been reported in the literature. Combining the two equations would give

$$\frac{P_{\mathrm{sam}}}{P_{\mathrm{ref}}}=\frac{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{sam}}}{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{ref}}}\sqrt{\frac{M_{\mathrm{ref}}}{M_{\mathrm{sam}}}} \tag{7}$$

From Eq. (7), we can directly calculate the vapor pressure for the unknown substance P_{sam}, provided we have the complete vapor pressure profile for the reference at the same range of temperatures as the sample. A noticeable fact in this equation is that the unusual values for k and hence α, have been eliminated. In other words, though we are not tackling the problem directly, this might serve as a method to circumvent the problem by eliminating those values in the vapor pressure calculations. Though this method has the advantage of ignoring the k value, it would find limited use compared to the original method of keeping k as constant. In Eq. (7) the temperature term is cancelled out after assuming the fact that the temperature range for evaporation would be approximately equal for both the sample and the reference compounds.

Varying k method

One of the disadvantages for the original method used concerned taking the average value for *k* over the temperature range for evaporation. Understandably, for a wide temperature range, the *k* value will differ and for the purpose of making the calculations easier, averaging that value might lead to errors. It would also be interesting to note changes (if any) that might occur in the final vapor pressure curves if we do not take the mean value for *k*. Moreover, this method has the same disadvantage as that of the comparative *k* method. The temperature in which the value is being compared has to be exactly the same as that for the reference compound, in order for the method to have any realistic meaning.

Standard test methods, referred to as ASTM methods to determine the vapor pressure plots for pure liquids or melts from boiling point measurements can be made using differential thermal analysis (DTA) or DSC, which is applied at different pressures [17].

This method can be used for a temperature range of 273 to 773 K, the pressure range being from 5–2 MPa. Depending on the thermal stability of the material and the instrumentation the ranges of temperature and pressure can change. Various pressures are applied to implement this technique and that is why it requires the analyst to use high-pressure differential thermal instrumentation (HPDSC or HPDTA). The method used in this technique is given in detail in the literature [17].

Clausius–Clapeyron equation

This equation is often referred to as the classical and most widely used relationship for evaluating vapor pressure characteristics. It is used to obtain the latent heat of evaporation value. The equation can be written as follows [1]:

$$\lg\frac{p_2}{p_1}=\frac{\Delta H_{\mathrm{vap}}}{2.303R}\frac{T_2-T_1}{T_2T_1} \tag{8}$$

where p_2 and p_1 are the corresponding vapor pressures at temperatures T_2 and T_1, respectively, and R is the universal gas constant. When implementing this equation, it is observed that fitting a straight line through the data points sometimes provides anomalous results. This indicates that the ΔH_{vap}-value is not constant over higher temperature ranges. As often is the case, the change in heat capacity of a substance is not considered in higher temperature ranges. This causes an anomalous value for ΔH_{vap} to be obtained when considering the traditional Clausius–Clapeyron equation. Therefore, the heat capacity effects have to be taken into consideration [20].

Experimental

Material

The samples of Lavender Oil NF, lot # 12-00770 090978 and lemon oil, lot # 102082 were supplied by Sherman Research Lab., Toledo, OH 43602. The samples of orange oil, lot # D13472K08 and cinnamon oil, lot # F15682A23 were supplied by Ameno Drug & Chemical Co., Irvington, NJ 07111.The sample of clove oil, lot # 704200 was supplied by Fisher Scientific Co., Fair Lawn, NJ 07410. The sample of Eucalyptus Oil NF, lot # A67227128, was supplied by Gentry Corporation, Fair Lawn, NJ. The samples of linalyl; Acetate (97%), lot # 01513PU, linalyl (97%), lot # 17111TR, limonene (97%), lot # 01006CI, cinnamaldehyde (99%), lot # 08514BR, citral (95%), lot # 04515KR and cineole (99%), lot # 01627CI were supplied by Aldrich Chemical Co., Milwaukee, WI 53233. The sample of Eugenol USP XIX, lot # F>58, was supplied by Lorain Oils Inc., Lansing, MI 48910.

Instrumentation

The SDT 2960, simultaneous TG-DTA, TA instrument, with thermal analyst 2000, TA operating system version 1.0B was employed to investigate the evaporation behavior of the essential oils and their key components. An electronic flowmeter from J&W Scientific, model ADM 1000 was used to regulate the flow of nitrogen (purge gas) through the samples. Two platinum open pan crucibles supplied by TA Instruments were used for holding the samples in the thermogravimetric study of the compounds. For the statistical calculations of Antoine constants, the SPSS 10.0 for Windows software, 2000, was used. A TA Instruments 910 Differential Scanning Calorimeter with 2200 Controller was used for the DSC study of clove and eucalyptus oil. Hermetic aluminum pans with 'pinhole' lids, with pinhole sizes: 0.003–0.010" depending on pressure range were used for the DSC study. The specific pinhole lid used is indicated on each thermal curve.

Method

The methods followed in this study to construct the vapor pressure curves for single and multicomponent systems and calculation of the Antoine constants using nonlinear regression analysis are given step-by-step for clarity.

1) Linalyl acetate, one of the components of lavender oil, was subjected to thermogravimetric runs under a variety of experimental conditions to find the optimum conditions for the study. Nitrogen was the obvious choice as the purge gas since oxygen and carbon dioxide might trigger off oxidation and other chemical processes within the compounds. Flow rates were studied at 25, 50, 80, 100 and 125 mL min^{-1}. The rates of temperature rise in the rising temperature program chosen were 2, 5, 10 and 15°C min^{-1}. The goal was to get optimum separation between the endothermic processes. This was extremely important to determine the range of temperatures over which the calculation would hold true.

2) It was experimentally verified that the best flow rate would be 100 mL min^{-1} with the temperature rising at 10°C min^{-1}. The runs were conducted over a temperature range from ambient to 350°C. An open, 110 μL platinum crucible with a cross sectional area of 0.2826 cm^2 was used to contain the sample and an empty platinum crucible of equivalent area was used as the reference. All the sample sizes were maintained from approximately 40–50 mg, which comprises approximately one-third of the crucible.

3) According to the literature in order to plot the vapor pressure curves for single component systems, a reference material had to be chosen that has its Antoine constants reported in the literature. The theory behind this method is described in Eq. (4). For the purpose of this study, linalyl acetate, the key component of lavender oil was chosen as the reference material whose Antoine constants are 7.65402(A), 2093.912(B) and 218.352(C).

4) The rate of loss of linalyl acetate due to heat (mg min^{-1}) along with the first derivative of mass loss data was obtained from the instrument. Using the Arrhenius equation, the activation energy and pre-exponential factors were calculated. With the Antoine constants reported in the literature, the theoretical vapor pressure calculations were performed and the vapor pressure curve was obtained. The k-value, from the Langmuir equation was obtained in the S.I. units, with its value being 112006 Pa $\text{kg}^{0.5}$ $\text{mol}^{0.5}$ s^{-1} m^{-2} $\text{K}^{-0.5}$. The run for linalyl acetate was repeated three times and the average calculated k-value was taken. The other compounds and the essential oils were subjected to thermogravimetric runs under the same experimental conditions. It is important that identical experimental parameters be maintained, in order to draw conclusions about any scientific outcome common to the whole class of compounds. The sample sizes for all the compounds were maintained at around 42–50 mg. Calculations for the kinetics were performed and all of the single component systems and the essential oils revealed zero order process and therefore, showed a non-activated evaporation process.

5) Using the k-value from the Langmuir equation, obtained for linalyl acetate, the vapor pressure curves for the compounds exhibiting zero order kinetics were constructed for the single component systems.

6) There have also been different approaches to calculate the vapor pressure values for the compounds other than keeping the k constant; those are [1] comparative k method and [2] varying k method which have already been described in Eq. (7). The Antoine constants for cinnamaldehyde and eugenol are reported in the literature [18, 19] and the temperature range for the endothermic part of these two compounds are same. Hence, the vapor pressure plots for eugenol were plotted by all three methods.

7) The Antoine constants over a specific temperature range had to be evaluated for the compounds. The vapor pressure curve was not linear for all the compounds studied. Also the Antoine equation could not be transformed into a linear form. Therefore, non-linear regression was the best possible measure for curve fitting purposes and statistically, the Antoine constants were obtained. The Levenberg–Marquardt algorithm was used to obtain the 'global least square fit'. The starting value for the iterations were chosen as 6, 2000 and 200 for A, B and C respectively.

8) The method of calculating the Antoine constants needed to be validated and the experimental and theoretical constants were compared with each other for linalyl acetate. They showed very close proximity which confirmed the validity of the calculated Antoine constants over a specified temperature range for each compound. It should be mentioned that the method of iterations used in SPSS 10.0 is arbitrary and if a different algorithm had been used the values for the iterations might have been different from these values.

9) For multicomponent systems, the ASTM E 1782-96, standard test method for determining vapor pressure by thermal analysis was used.

Results and discussion

Determination of the kinetic parameters

From the DTG plot, the closeness of the value for the energy of activation E_a from the Arrhenius equation and the ΔH-value from the Clausius–Clapeyron equation and the order determination by the Arrhenius equation, showed that all of the compounds under study undergo a non-activated zero-order process except lavender and lemon oil. The values for the energy of activation and the enthalpy of vaporization are reported in Table 1.

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

Compound	E_{act}/kJ mol^{-1}	ΔH_{vap}/kJ mol^{-1}
Linalyl acetate	40.44	45.68
Citral	43.71	48.72
Cinnamaldehyde	47.94	50.50
Eugenol	50.42	49.77
Cineole	38.17	34.56
Limonene	41.60	36.38
Linalool	46.12	39.67
Clove oil	36.74	49.15
Eucalyptus oil	31.19	39.92
Lavender oil	39.04	NA
Lemon oil	35.55	NA
Orange oil	38.86	NA
Cinnamon Oil	51.05	NA

Vapor pressure curves using various methods

One of the aims of this study was to validate an established method for vapor pressure curve construction, (i.e. keeping the *k*-value constant), under different experimental conditions and in the presence of nitrogen. The vapor pressure values for eugenol from the literature were taken. From the vapor pressure curves, it was observed that the ‘comparative method’ and the ‘varying *k* method’ resemble the original vapor pressure curves with the former being the better fit. Therefore, the vapor pressure curves were plotted using the comparative method for all of those single component systems for which reference materials are present in the literature.

Similarity of single and multi-components TG and VP curves

From the TG-DTG and DTA plots for clove oil and eugenol (Fig. 1), it is observed that they are similar and when the vapor pressure curves (Fig. 2) were compared they also were similar. Therefore, the nature of the vapor pressure curves for a multi-component system might be predicted using TG and vice versa, if a major component of that oil comprises above 90% of that system. Eucalyptus oil and its major component cineole also show similar types of TG-DTG (Fig. 3) and DTA curves. Therefore, the vapor pressure curve (Fig. 4) for cineole can be predicted from the vapor pressure curve of eucalyptus oil as their TG-DTG plots are also similar.

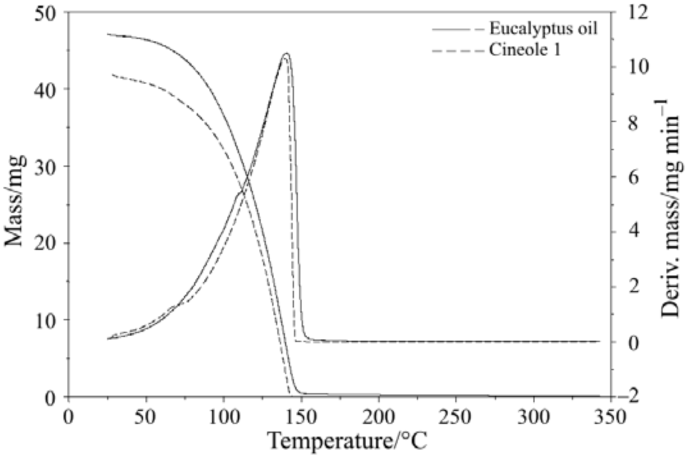

Fig. 1 TG-DTG plot for eucalyptus oil and cineole as a function of mass (TG), derivative mass with respect to time (DTG)

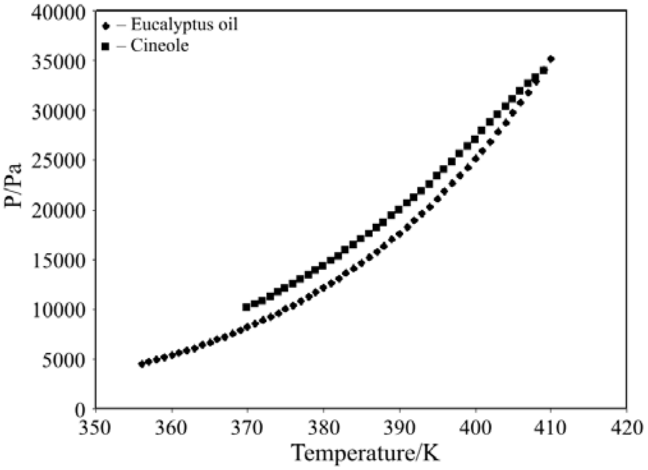

Fig. 2 Vapor pressure plots for eucalyptus oil and cineole

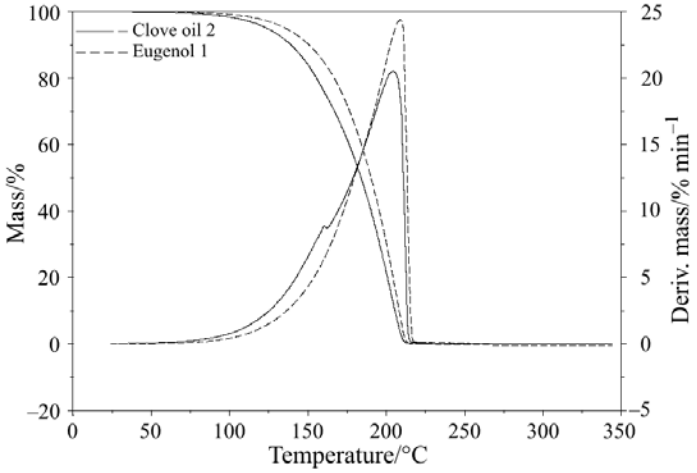

Fig. 3 TG-DTG plot for clove oil and eugenol

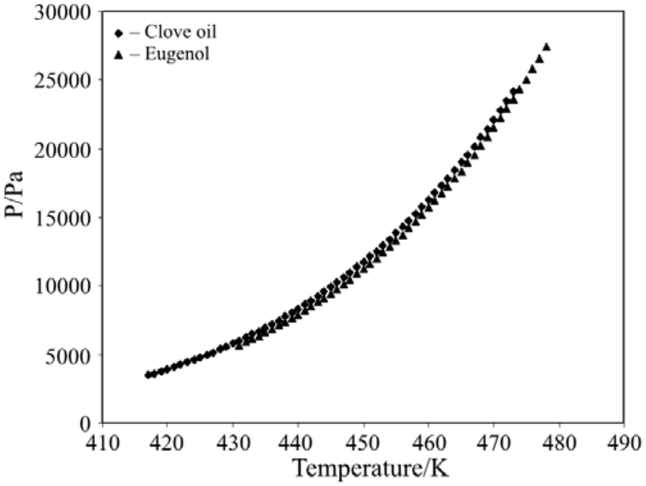

Fig. 4 Vapor pressure plots for clove oil and eugenol

Depending on the pattern of evaporation and the temperature at the maximum rate of volatilization (i.e. the peak of the endotherm in the DTG, the essential oils and their key components), the materials have been divided into three categories. It has been seen that though the substances evaporate in different ranges of temperatures, their maximum rate of mass loss are almost the same at the peak. The standard deviations are 1.58 for the single component systems and 2.23 for the multi-component systems. Details are given in Table 2. The description and examples for the various categories are given below.

Table 2 Material characterization of essential oils by thermal analytical techniques

Oil systems	Thermal analytical techniques				Category
	DTA		DTG		
	T_0 [1]	T_p [2]	T_p	mass% min^{-1} [3]	
			Single component		
Cinnamaldehyde	163	215	212	22	1
Eugenol	162	209	206	24	1
Cineole	101	146	144	23	2
Limonene	98	148	144	25	2
Linalyl acetate	134	187	186	24	3
Citral	139	177	176	24	3
Linalool	124	162	160	27	3
Standard deviation				1.57	
			Multi-component		
Cinnamon oil	156	210	206	22	1
Clove oil	146	204	201	20	1
Eucalyptus oil	82	139	138	22	2
Lemon oil	87	142	141	19	2
Lavender oil	103	152	152	18	2
Orange oil	82	134	130	24	2/3
Standard deviation				2.23	

[1] T_0 is the onset temperature for DTG and DTA, [2] T_p is the peak temperature for DTG and DTA, [3] mass% min^{-1} is the maximum rate of evaporation of the material

Category 1: Those oils and their key components for which the difference between the peak temperatures for their DTG is 5°C or less can be categorized under this group (for example, cinnamon oil and cinnamaldehyde). The vapor pressure values calculated by TG and DSC are compared with the literature values and the relative error is given in Table 3. It is seen that the DSC gives more precise results than TG. This might be due to the use of vacuum and the use of a closed pan in DSC as opposed to the open pan in TG. The difference in the vapor pressure values between the essential oils and their key components are also the least in the case of Category 1.

Category 2: Those oils and their key components for which the difference between the peak temperatures for their DTG is more than 5 but less than 15°C can be categorized under Category 2, (for example, eucalyptus oil and cineole or eucalyptol). The difference between the vapor pressure values for the essential oils and their key components is more than the materials under Category 1, but less than the materials under Category 3. The details are given in Tables 2 and 3.

Category 3: Those oils and their key components for which the difference between the peak temperatures for their DTG is more than 15°C can be categorized under this group (for example, lavender oil and linalyl acetate). For this group, since the difference between the endotherm for the essential oil and the key component was noticeable, therefore, a comparison was not done with the literature value and between the TG and DSC data. The details are given in Tables 2 and 3.

Table 3 Classification of the natural oils by TG-DTG and DSC

Category	Natural oils	Step one	Step two: Vapor pressure	
		DTG/DTA	Relative error[*] between observed and literature values/%	
		ΔT_p [1]	TG based	DSC based
1	Clove[2] Cinnamon	≤5°C	2 to 3	1
2	Eucalyptus[2] Lemon Orange	5–15°C	8	3
3	Lavender Orange (citral)	15–30°C	NA	NA

[*]Sampling: n=50, [1]ΔT_p: Variation in peak temperature, [2] Data evaluated by both high pressure DSC and TG

Application of non-linear regression to calculate the Antoine constant

After performing non-linear regression on the literature values for the vapor pressure of eugenol, linalyl acetate and cinnamaldehyde the calculated values for the Antoine constants were the same as the literature values and, therefore, this method was used to calculate the Antoine constants for the others. The Antoine constants for various oils and their key components are given in Table 4.

Table 4 List of Antoine constants for compounds undergoing evaporation

Compound	Antoine constants			Temperature range/K
	A	*B*	*C*	
Linalyl acetate[**]	7.654	2093.912	218.352	328–493
Cinnamaldehyde[**]	8.326	2676.568	245.334	349–519
Eugenol[**]	7.964	2463.351	230.924	351–526
Citral	6.182	1074.499	103.251	409–457
Limonene	1.839	1975.993	150.58	409–438
Eucalyptus oil	8.279	2402.808	273.15	356–410
Clove oil	7.142	1864.451	181.716	417–473

[**]Antoine constants reported in the literature

Conclusions

TG and PDSC can be effectively used to determine the vapor pressure values for various components. PDSC is the direct and TG the indirect method for calculating the vapor pressure values. TG can readily provide the kinetic data for the sample.

The determination of vapor pressure by TG can be considered as a rapid method for constructing vapor pressure curves, the only requirement being the use of the TG instrument. The other advantage for the method is that a minute sample is required. If the instrument is optimized with a small amount of sample, then this is quite a practical method when expensive samples are utilized. It was seen that DSC curves are quite reproducible if the masses taken are approximately the same. This attribute actually helped to set the methodology for the experiment.

Apart from the general thermal characterization, determination of vapor pressure and enthalpy of vaporization are very important aspects in the determination of solubility parameters for any liquid. Therefore, this rapid method for vapor pressure determination would be useful in the pharmaceutical characterization of any liquid.

The method of vapor pressure determination using TG can only be used in the case of single component systems, since the Langmuir equation requires the knowledge of the molecular mass for a substance. Therefore, if the exact composition and the molecular masses for the components of a mixture are known, then TG can be used to determine the vapor pressure values provided the average molecular mass of the mixture could be determined.

If the average molecular masses of a mixture are not known, (for example, the natural essential oils) DSC can be considered as a good method for vapor pressure determination of multi-component systems.

The k value calculated from the TG data for linalyl acetate is 112545 which is different from the value reported in the literature [9, 15] and therefore, it can be concluded that the use of the 'constant k method' is not applicable for all systems and temperature ranges and therefore, use of the 'varying k method' and 'comparative method' are better suited for these substances.

The unit system used for vapor pressure and temperature is an important factor which has to be taken into consideration when adopting values from the literature. Any exception to this fact might create a significant error in the results reported.

The Clausius–Clapeyron equation, in its present form cannot be applied to higher temperature ranges and, thus, a straight line may not always be obtained while plotting $\ln P$ *vs*. $1/T$. Therefore, the Antoine equation is a better equation for curve-fitting purposes.

The maintenance of optimum conditions throughout the experimental procedure is very important. This is especially true for the maintenance of the mass of the sample, since excess material causes broadening of the curve (DTG and DTA) and causes the data to be less precise.

Though the value of α in the Langmuir equation was considered to be unity, in a vacuum, in this study the value is very small which will require further extensive research concerning the effects of the purge gas and other factors on the coefficient of vaporization (α) value.

Since the vapor pressure curves for various materials are not linear over a broad temperature range, therefore, non-linear regression and the Antoine equation can be effectively used to determine the Antoine constants for substances after determining their vapor pressure values. The methods in this study have been validated using substances for which the Antoine constants are already reported in the literature.

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