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Short Communication

Determination of the vapor pressure of *Lippia gracilis* Schum essential oil by thermogravimetric analysis

Carlos Eduardo Lima de Oliveira[a,*], Marco Aurélio Cremasco[b]

[a] *Chemical Engineering School, University of Campinas, 13083-852 Campinas, São Paulo, Brazil*
[b] *Chemical Engineering School, University of Campinas, 13093-970 Campinas, São Paulo, Brazil*

A R T I C L E I N F O

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A B S T R A C T

Thermogravimetric analysis was used to determine the vapor pressure of the *Lippia gracilis* S. essential oil. The calibration constant value was obtained using thymol as reference compound, due to the fact that compound represents the majority in the essential oil. To check the calibration, the vapor pressure data for carvacrol have been compared with the results reported in the literature and showed a good agreement. The method was used in the determination of the vapor pressure curve for the essential oil. From vapor curves, the Antoine constants for the essential oil were found to be: $A = 10.29230$, $B = 3116.68$ and $C = 74.23$, respectively.

1. Introduction

The species of *Lippia gracilis* (Verbenaceae family) are shrubs typical of the Northeast region of Brazil. This species is traditionally used in popular medicine [1] as well as for the treatment of influenza, cough, sinusitis, bronchitis, and nasal congestion [2–4]. This species produces an essential oil whose main component may be thymol [2,5] or carvacrol [6,7].

Thymol and carvacrol (Fig. 1) are isomers with high antimicrobial activity. There are studies that relate the biological and pharmacological activities of these phenols, such as antibacterial [8,9], antioxidant [10], fungicide [11], and acaridae activities [12]. These compounds, as well as their essential oils, are widely employed in the chemical, pharmaceutical and food industries.

Due to their wide variety of applications, essential oils have become an inexhaustible source of scientific and technological research, mostly for obtaining their major components. Because they are volatile liquids, vapor pressure data for the essential oils are not only fundamental to the design of the equipment, when one intends to concentrate the major components by distillation, but also for the understanding of the separation process [13].

The most common methods for determining the vapor pressure of a substance (isoteniscope and ebulliometer, for example) require a large amount of sample and need a very long time for carrying out the experimental tests [14]. In this case, thermogravimetric analysis (TG) has been a useful tool for determining this parameter because it is a short test and requires small samples.

There are several studies using this technique TG for vapor pressure determination. Wright et al. [15] determined the vapor pressure curves for adipic acid and triethanolamine technique using TG–DTA. Price [16] determined the vapor pressure of plasticizers by TGA. Price and Hawkins [17] used TGA to determine the vapor pressure of various dyes. Butrow and Seyler [18] demonstrated that the vapor pressure of various liquids can be determined by differential scanning calorimetry (DSC). Gomes et al. [19] used the thermogravimetric curves to determine the vapor pressure of alkaloids, warifteine and methylwarifteine.

2. Experimental

2.1. Material and equipment

Crystallized thymol (99.5% purity) was purchased from Sigma–Aldrich (Brazil), and carvacrol (purity 99.9% purity) from MP Biomedicals (Brazil). The samples of *L. gracilis* Schum essential oil were kindly provided by Laboratory of Natural Products (Federal University of Maranhão, Brazil). The chemical composition of the essential oil was identified by gas chromatography/mass

* Corresponding author. Tel.: +55 19 3521 2123; fax: +55 19 3521 3910.
E-mail addresses: carlos.ufma@gmail.com (C.E.L.d. Oliveira), cremasco@feq.unicamp.br (M.A. Cremasco).

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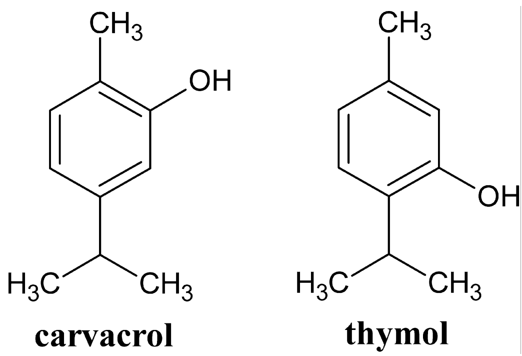

Fig. 1. Chemical structures of carvacrol and thymol.

spectrometry (GC/MS). Thymol was present as the major component at a level of approximately 82%.

The samples were analyzed in a thermogravimetric system, Shimadzu TGA-50. Rising temperature experiments were conducted at a heating rate of 10 °C min^{-1}, in nitrogen atmosphere at 50 mL min^{-1}. In order to obtain thermogravimetric curves all compounds were subjected to a temperature range of ambient up to 400 °C. At this temperature all of the material was completely evaporated. The initial samples mass ranged from 8 to 14 mg, which were placed in a platinum crucible with a cross-sectional area of 0.28 cm^2.

2.2. Procedure

Thymol was chosen as the reference material for two reasons. First, it is the major component in *L. gracilis* S. essential oil. Second, it has its Antoine constants reported in the literature (NIST) [21]. The Antoine and Langmuir equations were used to determine the value of the calibration constant (γ), from the vapor pressure curve obtained. The Antoine equation [20] is presented as:

$$\log(p/\text{Pa}) = A - \frac{B}{T + C} \tag{1}$$

where p is the vapor pressure; T is the absolute temperature; A, B, and C are the Antoine constants of that particular substance at a given temperature range. Antoine constants for thymol are: $A = 5.29395$, $B = 2522.332$ and $C = -28.575$, valid from 337.5 up to 505 K [21].

The Langmuir equation [19] often used to determine the vapor pressure of various substances is presented as:

$$\frac{1}{a} k_{vap} = \frac{\beta}{(m_i - m_f)} . p . \sqrt{\frac{M}{2\pi RT}} \tag{2}$$

where a is the area of the container (crucible); M is molar mass of the substance; β is the vaporization coefficient, usually constant with a value equal to 1 [16], but in the presence of a carrier gas the value of this constant tends to be different from unity [22]; R is the universal gas constant. The evaporation coefficient (k_{vap}) for a zero-order evaporation process, is given by the rate of mass loss (dm/dt), and it is obtained from thermogravimetry [23,24]. The following modification is described [19]:

$$p = \left[\frac{1}{\beta a}\sqrt{2\pi R}\right] \left[k_{vap}(m_i - m_f)\sqrt{\frac{T}{M}}\right] = \gamma \, . \, Y_{vap} \tag{3}$$

where $\gamma = 1/(\beta \cdot a)\sqrt{2\pi R}$ and $Y_{vap} = k_{vap}(m_i - m_f)\sqrt{T/M}$. The variables m_i and m_f are the initial and final masses in milligrams, respectively [25]. It is important to mention that (β) and (a) values are implicit in the γ-value.

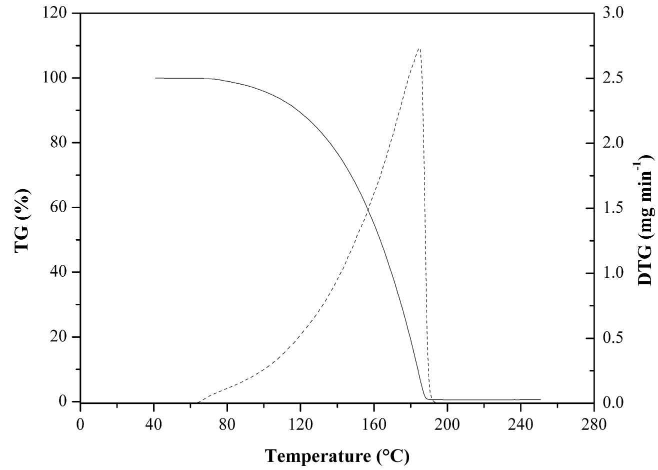

Fig. 2. Thermogravimetric and derivative thermogravimetric (TG–DTG) curves of thymol.

The Y_{vap}-value can be obtained experimentally by thermogravimetry, and it depends only on the molar mass of the compound under study. Thus, the plot of (p) versus (Y_{vap}) gives the γ-value. The value of (γ) was used to determine the vapor pressure curves, first, carvacrol and, after validation in the literature, it was determined the vapor pressure curve of the oil.

3. Results and discussion

Phang and Dollimore [26], as well as Chatterjee et al. [27] used a compound whose Antoine constants are known, and they applied this method to compare the vapor pressure curves found in the literature with those from thermogravimetry. In this work the thymol was chosen as the calibration compound.

The thermogravimetric and derivative thermogravimetric (TG–DTG) curves for thymol can be seen in Fig. 2. Derivative thermogravimetry curves (DTG) are fundamental to determining the reaction order [28,29]. Fig. 2 shows that thymol exhibits one simple stage of evaporation that can be observed through an increased rate of mass loss to a maximum value which decreases abruptly to the baseline. This indicates that thymol was undergoing a zero-order process [27]. The essential oil and carvacrol also exhibit a zero-order kinetics process which can be attributed to the evaporation (Fig. 3).

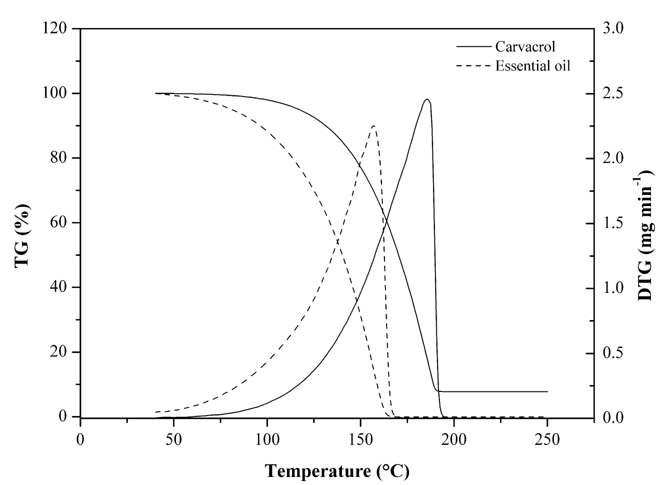

Fig. 3. Thermogravimetric and derivative thermogravimetric (TG–DTG) curves of carvacrol and essential oil.