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Evaluation of vapor pressures of 5-Methylresorcinol derivatives by thermogravimetric analysis

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ABSTRACT

The present study was carried out to evaluate the vapor pressures of various 5-methylresorcinol derivatives using a thermogravimetric analyzer (TGA). In the experiments, 9–12 mg of each 5-methylresorcinol ether or ester was used, which allowed vapor pressures up to 24,500 Pa (on average) to be determined. The error in the measured vapor pressure values is estimated to be below 13.5% at vapor pressures lower than 10,000 Pa, while at values between 10,000 and 24,500 Pa it is below approximately 12%.

The quality of the vapor pressure data was evaluated with anthracene, benzoic acid, docosane, hexadecane, nonane, and resorcinol as standard compounds using different calculation methods. The results showed that vapor pressures calculated by the mass transfer equation combined with estimated binary diffusion coefficients gave the most consistent results for these compounds, with errors always smaller than 15% (average absolute deviation 6.4%). These results are also consistent with the accuracies reported in literature for non-isothermal TGA. Therefore, this method could be used for evaluation of preliminary vapor pressure data as it may give more accurate results than group contribution methods.

1. Introduction

5-Methylresorcinol is the most abundant water soluble phenol separated from Estonian Kukersite shale oil during the dephenolation process [1]. It has found widespread use in the production of cosmetic dyes, drugs, fungicides *etc*. Ethers and esters derived from 5-methylresorcinol received attention even several decades ago [2] due to the many desirable properties of these compounds. Various 5-methylresorcinol derivatives are expected to be used as lubricants in machining processes, antioxidants or plasticizers [2]. For these applications, compounds with low vapor pressures at elevated temperatures are desired. Vapor pressure is also needed for evaluating the safety and usability of chemicals. Many different methods of measuring vapor pressure exist, including the gas saturation method (10^{-5}–1000 Pa) [3], Knudsen effusion method (detection limit up to 1 Pa) [4,5], differential scanning calorimetry ($100–2 \times 10^6$ Pa) [6,7], headspace gas chromatography (higher than10^{-2} Pa) [8], optical absorbance spectroscopy in the UV–vis range (0.5–350 Pa) [9], TGA method (10 to >40,000 Pa) [10,11], just to name a few.

Often, vapor pressure data are needed in a short timeframe, and a rough vapor pressure estimation is sufficient. Of the methods mentioned, TGA stands out as a fast and simple method that requires only small amounts of sample and has a simple experimental set-up that is readily available in many laboratories.

One of the first studies that showed the use of thermogravimetry to determine vapor pressure was by Gueckel et al. [12]. Since then, many authors have used TGA to determine the vapor pressure of a wide range of substances through the rate of mass loss ($\mathrm{d}m/\mathrm{d}t$).

There are two approaches used to relate the vapor pressure to the mass loss data obtained from TGA. Firstly, the Langmuir equation of evaporation [13], and secondly, Fick's law of diffusion combined with a mass transfer equation for evaporation through a stagnant gas layer.

In 1913 Langmuir [13] proposed an equation to relate the rate of evaporation $\mathrm{d}m/\mathrm{d}t$ to the saturated vapor pressure p in a vacuum (evaporation in the molecular flow regime):

$$\frac{\mathrm{d}m}{\mathrm{d}t} = A\left(\frac{M}{2\pi RT}\right)^{1/2} p \qquad (1)$$

In this equation, A is the vaporization area, M is the molecular weight of studied material, R is the gas constant, T is the absolute

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temperature, and p is the saturated vapor pressure. To calculate the vapor pressure from the rate of evaporation to surrounding gas at finite pressure, Eq. (1) is rearranged by introducing an empirical coefficient of vaporization α ($\alpha = 1$ in vacuum), which should account for the changes in ambient pressure from vacuum to finite pressure:

$$p = \left[\frac{dm}{dt}\left(\frac{T}{M}\right)^{1/2}\right]\left[\frac{(2\pi R)^{1/2}}{\alpha A}\right] = \nu k \quad (2)$$

In Eq. (2), ν contains all the substance specific variables, and k is usually assumed to be the substance independent constant or calibration constant which is calculated by calibration with substances of known vapor pressure [14]. Eq. (2) has different modifications (for example [15]); however, only the most simple one, using only empirical α to account for the change from vacuum to finite pressure, is considered here. The value of k depends on the experimental setup and conditions and is usually taken as

- a constant value [14,16] – calibration constant (CK) method or
- a molecular weight dependent value [11] – calibration curve (CC) method.

A common way to overcome the molecular weight dependence is to use a substance for calibration that has similar properties (binary diffusion coefficients in the surrounding gas) to the measured compound [17] and to assure that the conditions are identical to those used for calibration. A plot of ν *versus* p for the calibration compound is built, and a k value is found as the slope of the line and used as is for the compound being studied. In the CC method, standard compounds with different molecular weights are analyzed in the same way as with the CK method, and a calibration curve is obtained by plotting molecular weight *versus* k [11]. Based on the molecular weight of the analyte, a value of k can be obtained from the calibration curve.

The modified Langmuir equation (Eq. (2)) is extensively used because of its simplicity, and the fact that only molecular weight is needed to calculate the vapor pressure from the mass loss data [10,18–20]. However, as stated in several articles [20–22], Eq. (2) can mostly be used for estimation of the magnitude of the vapor pressure as the quality of the obtained data is often referred to as having good, but not precise, agreement with the reference data. Of course, if calibration compounds are selected appropriately, accurate experimental values in a narrow temperature range may be obtained.

The second approach for vapor pressure calculation from TGA mass loss data – Fick's law of diffusion combined with a mass transfer equation for evaporation through a stagnant gas layer (hereby designated as MT method) – assumes that vaporization (diffusion) takes place from a vessel with a constant diffusion area through the stagnant gas layer at steady state conditions into the surrounding environment. Considering the simplifying assumptions that are listed by Pieterse and Focke [24] Eq. (3) is obtained:

$$p = \frac{hRT}{ADM}\frac{dm}{dt}. \quad (3)$$

Here, D is binary diffusion coefficient of the substance in the carrier gas, h is the length of the diffusion path. Other quantities are as previously defined (Eq. (1)).

Eq. (3) may be used to measure the binary diffusion coefficients of compounds for which vapor pressure is known [23,25]. However, to calculate vapor pressure the binary diffusion coefficient must be known, measured, or estimated.

Ideally, vapor pressure measurements by TGA should be conducted isothermally to meet the assumption of steady state conditions. However, as shown by Pieterse and Focke [24], temperature equilibrium in TGA experiments is reached fast, and continuous heating can be used instead of step-by-step isothermal heating. Therefore, heating rates around 1–20 °C/min are generally used [14].

To meet the assumption that the partial pressure of the evaporating substance above the sample pan is zero, a purge gas is used to remove the sample from the TGA. The optimal purge gas flow rate is setup and device specific. In different studies, it can be as low as 25 ml/min [25], or it can be 100 ml/min [14,24] and even higher [15,26].

Eq. (2) is often used because it is a convenient, easy and fast method for calculating vapor pressures of unknown substances. [14,21,22,27,28]. However, as already mentioned, k depends on the substance. References [11] and [25] have shown that the slope k is related to the molecular weight, and using a calibration curve instead of a calibration constant can improve the accuracy of the results. This is not surprising since comparing Eqs. (2) and (3) show that the vaporization coefficient not only accounts for the non-equilibrium pressure above the liquid surface, but also depends on the binary diffusion coefficient [21]:

$$\alpha = \frac{D}{h}\left(\frac{2\pi M}{RT}\right)^{1/2}. \quad (4)$$

The TGA method has previously been used for the measurement of vapor pressures of both plasticizers [14,21] and lubricants [29]. The purpose of this study was to estimate the vapor pressures, enthalpies and entropies of vaporization of synthesized, oil shale based 5-methylresorcinol esters and ethers, which is necessary for evaluating their usability and for material safety data sheets. The TGA method as well as different approaches for calculating vapor pressure from TGA data was evaluated to find the best results using standard compounds. The vapor pressure data obtained for 5-methylresorcinol derivatives were compared to the values calculated by the group contribution (GC) method of Rarey and co-workers [30].

2. Experimental

2.1. Materials

The TGA method was applied to the compounds shown in Table 1 and in Fig. 1 to estimate the temperature dependence of

Table 1
Names, R-groups, molecular weights and purities of the studied compounds.

IUPAC name	R-group	Abbreviation	Molecular weight (g/mol)	Puritiy (%)
1-Methyl-3,5-bis(2-methylpropoxy) benzene	2-Methylpropyl	2MP	236.35	99.7
1-Methyl-3,5-bis(2-phenylethoxy) benzene	2-Phenylethyl	2PE	332.44	99.8
1-Methyl-3,5-bis(propan-2-yloxy) benzene	Propan-2-yl	P2Y	208.30	97.0
3-Methyl-5-(pentanoyloxy) phenyl pentanoate	Pentanoyl	Pent	292.37	98.9
3-[(2,2-Dimethylpropanoyl) oxy]-5-methylphenyl 2,2-dimethylpropanoate	2,2-Dimethylpropanoyl	22DMP	292.37	99.5
1,3-Dibutoxy-5-methylbenzene	Butyl	But	236.35	99.5