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# THERMOGRAVIMETRY AS A SCREENING TOOL FOR THE ESTIMATION OF THE VAPOR PRESSURES OF PURE COMPOUNDS

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A simplified approach was developed to estimate the vapor pressure of pure compounds from experimental data obtained by isothermal thermogravimetric (TG) analysis. A numerical procedure was developed to estimate the Antoine parameters of the substance by the analysis of isothermal TG data. The results of the experimental validations carried out evidenced that at least a preliminary estimation of vapour pressures of pure substances by the analysis of TG data is possible. The limited time and the reduced amounts of sample required for the experimental runs make the technique attractive with respect to the conventional and more accurate techniques for vapor pressure assessment.

***Keywords:*** *diffusive evaporation, evaporation rate, thermogravimetric analysis, vapor pressure*

## Introduction

The determination of vapor pressure of pure compounds is an important problem in the pharmaceutical, chemical and process industry. Indeed, the knowledge of vapor pressure is important in several fields of application, ranging from the design of separation and purification processes to the assessment of workers exposure limits. Several static or dynamic methods are available for the assessment of the vapor pressure of a pure compound [1–15]. Although most of these methods have a high accuracy, they require rather large amounts of sample (usually some mL). Thus, an effort is currently carried out to develop rapid techniques to allow the preliminary screening of the vapor pressure using limited amounts of sample. Alternative experimental methods proposed for vapor pressure determination include gas chromatography (GC) [16], effusion [17, 18] and gas saturation methods [19–23].

The possible use of thermal analysis for the experimental measurement of vapor pressure was investigated by several authors [24–52]. With respect to the conventional techniques for vapor pressure measurement, thermogravimetry requires a more simple experimental set-up, more limited amounts of sample (usually microlitres) and short experimental times. However, an inherent limitation to the accuracy of the vapor pressure data that may be obtained by this technique is due to the open configuration of the system, as well as to the absence of sample mixing and to the presence of heat transfer and mass transfer limitations.

Several former methods proposed to use the Langmuir equation to obtain vapor pressure data from TG experimental runs. The present study focused on the exploration of the potential application of the diffusion limited evaporation theory, further developing the approach proposed by Pieterse and Focke [42] to the estimation of vapor pressure from TG experimental data. A numerical method was developed for TG data analysis, aimed to yield a correlation for the vapor pressure as a function of temperature. Isothermal mass loss data obtained at different temperatures in different crucibles were used to estimate vapor pressures. The method was validated comparing the values of the vapor pressures obtained for several sample substances to values reported in the literature.

## Experimental

A TA Q-500 thermobalance was used to perform isothermal runs on each substance in a specific temperature interval reported in the following. The choice of the upper limit of the interval derived from the need of keeping the test conditions well below the boiling point of each substance. Run duration was of 30 min. A pure nitrogen purge flow of 100 mL $\text{min}^{-1}$

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was used in experimental runs. The sample was positioned on the pan of the TG balance and then automatically inserted in the TG furnace. The temperature programme typically consisted in a rapid heating followed by an equilibration at the desired temperature. Tests were performed using different types of cylindrical crucibles. Table 1 lists the relevant characteristics of the four crucibles used. Typical sample masses ranged between 9 and 36 mg, depending on the crucible surface and the density of the compound.

The following substances were used in experimental runs: N-methyl-2-pyrrolydone [CAS 872-50-4], 1,3-propanediol [CAS 504-63-2], dibenzyl ether [CAS 103-50-4], 2-naphthol [CAS 135-19-3] and salicylic acid [CAS 69-72-7]. All the samples were provided by Aldrich (Milan, Italy).

**Table 1** Geometrical characteristics of crucibles used in isothermal TG runs

| Type | Internal diameter $d_i$/mm | Evaporating surface $A_c$/mm$^2$ | Internal height $L$/mm |
|---|---|---|---|
| A | 6.0 | 28.3 | 4.7 |
| B | 5.0 | 19.6 | 4.0 |
| C | 5.2 | 21.2 | 5.0 |
| D | 3.0 | 7.1 | 4.0 |

## Modeling of evaporation rate during TG runs

Evaporation rates of low-volatility compounds in TG analyzers are controlled by the vapor diffusion rate through the steady gas film that is formed inside the TG crucible [42]. A monodimensional analysis based on Fick's law [53] may thus be applied to model the evaporation rate if convective phenomena may be neglected, as reasonable at the low purge gas rates used in TG runs. Thus, the evaporation of a liquid during a TG isothermal run may be schematized as shown in Fig. 1. The simplified scheme reported in the figure may be used as the starting point for a simplified screening of vapor pressure, based on the evaporation rates measured in isothermal TG experimental runs. Following the conventional approach to the modeling of diffusive evaporation processes, some assumptions were introduced in the analysis of the experimental data [53]. In particular, the system was considered isothermal and a quasi-steady-state condition was assumed to calculate the gas-phase concentrations and the liquid level in the crucible. The latter assumption is verified for low values of the vapor pressure and allows a steady-state analysis of the gas-phase diffusion process. Since by this assumption the liquid level at a generic time $t$ may be considered constant, this parameter may be easily estimated by the sample mass measured in the TG analyzer, the liquid density and the crucible geometrical data reported in Table 1. Since atmospheric pressure is present in conventional TG devices, an ideal behaviour may be considered for the gas phase. Thus, the partial pressure of the vapor may be calculated from the total pressure of the system and from the molar fraction of the vapor in the gas phase. The values of the partial pressure of the vapor may thus be estimated in two significant positions: the liquid surface and the crucible edge. If the evaporation rate is low, allowing the liquid to be considered isothermal, the partial pressure of the evaporating compound at the liquid surface may be assumed equal to the vapour pressure of the substance at the temperature recorded by the TG analyzer. At the crucible edge, the partial pressure of the evaporating compound may be approximated to zero, assuming that a sufficient purge flow is supplied.

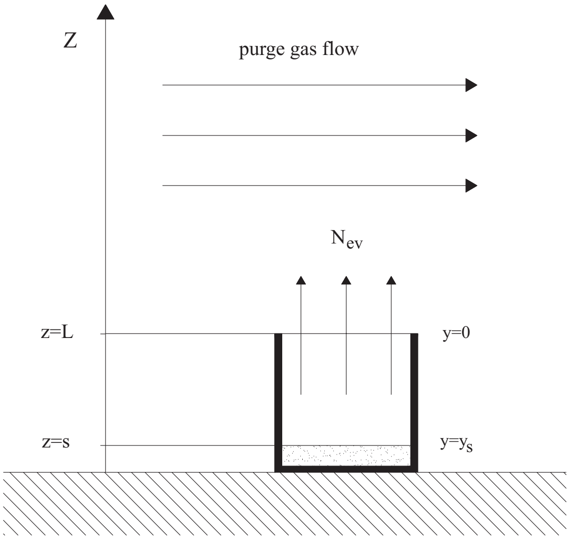

**Fig. 1** Schematization of the mass transfer process during the evaporation

A differential molar balance on the $z$-axis (Fig. 1) may thus be derived from the application of Fick's law on the basis of the above assumptions:

$$N_{\mathrm{ev}} = -A_{\mathrm{c}} \frac{DP}{RT} \frac{\mathrm{d}y}{\mathrm{d}z} + yN_{\mathrm{b}} \tag{1}$$

where $N_{ev}$ is the molar flow of the compound of interest due to the evaporation process, $A_c$ is the surface available for mass transfer, $D$ is the diffusivity of the compound in the gas mixture at the temperature of the experimental run, $P$ is the total pressure, $y$ is the molar fraction of the compound of interest, $R$ is the gas constant, $T$ is the temperature and $N_b$ is the overall molar bulk flow. In the absence of thermal degradation, the overall bulk flow $N_b$ equals the evaporative flow $N_{ev}$. Rearranging and integrating Eq. (1) between the evaporating surface of the liquid and the crucible edge (($y_s$; $s$) and (0; $L$), as shown in Fig. 1) results in the following expression for $N_{ev}$:

$$N_{ev} = -A_c \frac{DP}{RT(L-s)} \ln(1-y_s) \qquad (2)$$

where $L$ is the height of the crucible, $s$ is the height of the liquid and $y_s$ is the value of the molar fraction in the gas phase at the liquid surface (Fig. 1). The driving force in Eq. (2) may as well be directly expressed as a function of the vapor pressure $P_{sat}$:

$$N_{ev} = -A_c \frac{DP}{RT(L-s)} \ln\left(1-\frac{P_{sat}}{P}\right) \qquad (3)$$

The above expression may be used to correlate the vapor pressure to the experimental TG data. The overall molar evaporation rate may thus be directly calculated dividing the experimental mass loss rate of the sample by the molecular mass of the evaporating substance. Temperature, pressure and crucible geometrical data are known during experimental runs, and have constant values if isothermal experiments are carried out. The height of the liquid, $s$, may be calculated from the sample mass, obtained by the TG data as discussed above.

Thus, Eq. (3) relates the experimental mass loss rate to the vapor pressure and the gas-phase diffusivity of the vapor in the purge gas (pure nitrogen was used in all the experimental runs performed). Vapor pressure at a given temperature, $T$, may be calculated using the Antoine relation [5, 54–56]. The values of vapor diffusivity in nitrogen as a function of temperature are usually unknown, but several models are available for their estimate (e.g. [53, 54] and references cited therein). Gas-phase diffusivity is known to vary with temperature following a power law, with an exponent between 1.5 and 1.75 [53, 57]. In the following, vapor diffusivities in nitrogen were approximated as a constant (depending on substance properties) multiplied by the 1.5 power of the absolute temperature ($k_0T^{1.5}$).

## Results and discussion

Isothermal TG runs at different temperatures were carried out on the substances listed in experimental section using all the crucibles described in Table 1. After the initial transient, the sample and furnace temperatures are maintained constant for all the duration of the test.

The results of isothermal TG runs performed in crucible B on 1,3-propanediol at temperatures between 80 and 110°C are shown in Fig. 2a. As evident in the figure, the evaporation rate, and thus the mass loss rate given by the slope of the curves reported, increases with temperature. The mass loss rate at a given temperature may be considered almost constant in the temperature range explored, although a slight decrease in the slope of the mass loss curves and thus in the evaporation rate is actually present. Figure 2b reports mass loss rate data obtained in isothermal TG runs on 1,3-propanediol at 90°C using different crucibles. Table 1 reports the relevant characteristics of the crucibles used. Figure 2b evidences that a higher value of the ratio of the crucible open surface, $A_c$, over the crucible height, $L$, results in a higher evaporation rate. Qualitatively similar results were obtained for all the other substances investigated. Thus, the results obtained confirm that the evaporation rate at a given temperature is influenced by the sample surface available for the evaporation.

The approach discussed in the previous section to the analysis of diffusive evaporation during a TG run was applied to estimate the vapor pressures of the samples on the basis of the TG data obtained. The experimental TG data on the evaporation rate, $N_{ev}$, were used to calculate the Antoine parameters. The relation between the measured evaporation rate, the geometrical constraints and the Antoine parame-

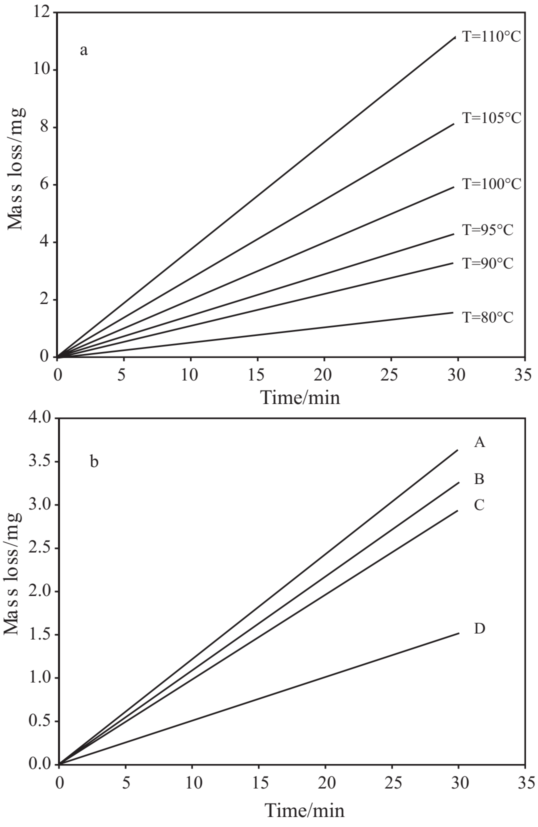

**Fig. 2** Results of isothermal TG runs carried out on 1,3-propanediol samples. a – Mass loss in TG runs at temperatures between 80 and 110°C in type B crucible; b – mass loss in TG runs at 90°C in different crucible types

**Table 2** Comparison among literature [5] and calculated values for the Antoine parameters

| Antoine parameters | N-methyl-2-pyrrolidone | 1,3-Propanediol | Dibenzylether | 2-Naphthol | Salicylic acid |
|---|---|---|---|---|---|
| Literature | | | | | |
| *A* | 7.4038 | 8.34759 | 6.84322 | 7.2293 | 5.53812 |
| *B*/K | 2570.3 | 3149.87 | 2507.3 | 2827.5 | 1049.95 |
| *C*/K | 0 | 9.1444 | –43.15 | –19.868 | –228.144 |
| Calculated | | | | | |
| *A* | 4.92 | 9.63 | 4.01 | 3.05 | 1.43 |
| *B*/K | 946.3 | 2994.9 | 750.5 | 467.4 | 35.6 |
| *C*/K | –153.8 | –56.8 | –222.2 | –257.6 | –397.8 |

ters is given by the following expression, obtained substituting the Antoine relation in Eq. (3):

$$N_{\mathrm{ev}} = -A_{\mathrm{c}} k_0 \frac{PT^{1/2}}{R(L-s)} \ln\left[1-\frac{1}{P}10^{\left(\mathrm{A}-\frac{\mathrm{B}}{\mathrm{T+C}}\right)}\right] \qquad (4)$$

A non-linear least-squares best fit procedure was used to estimate the Antoine parameters and the diffusivity constant, $k_0$. The relevant number of unknown parameters (4) that need to be estimated from experimental runs suggests to carry out the analysis on a sufficiently extended experimental data set, as that shown in Fig. 3 for N-methyl-2-pyrrolidone.

The values estimated by the above procedure for the Antoine parameters of the substances considered in the present study are shown in Table 2. The geometrical characteristics of the crucibles used in the experimental runs used for data analysis are reported in Table 1.

The numerical values of the best fit Antoine parameters are quite different from the literature values, also reported in Table 2. However, similar values of the vapor pressure are obtained by both sets of parameters, as shown in Figs 4 and 5. A further validation of the results was obtained comparing the experimental evaporation rates to those calculated by Eq. (3) on the basis of the best fit parameters reported in Table 2. The results obtained for 2-naphthol are shown in Fig. 6. Similar results were obtained for the other substances considered in the present study and were not reported for the sake of brevity. The figure evidences that limited differences are present between the calculated evaporation rates and the experimental

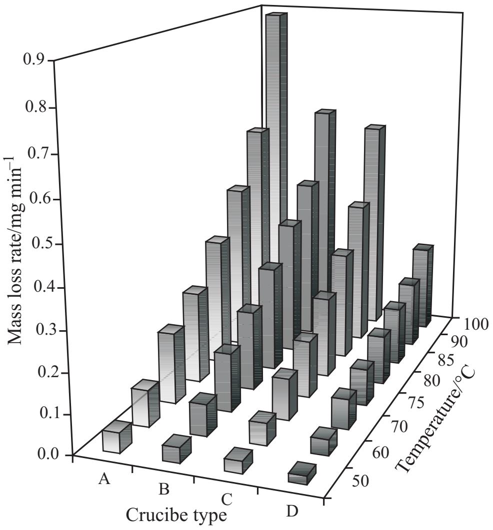

**Fig. 3** Experimental mass loss rate due to evaporation in isothermal TG runs carried out on N-methyl-2-pyrrolidone using different crucibles (Table 1)

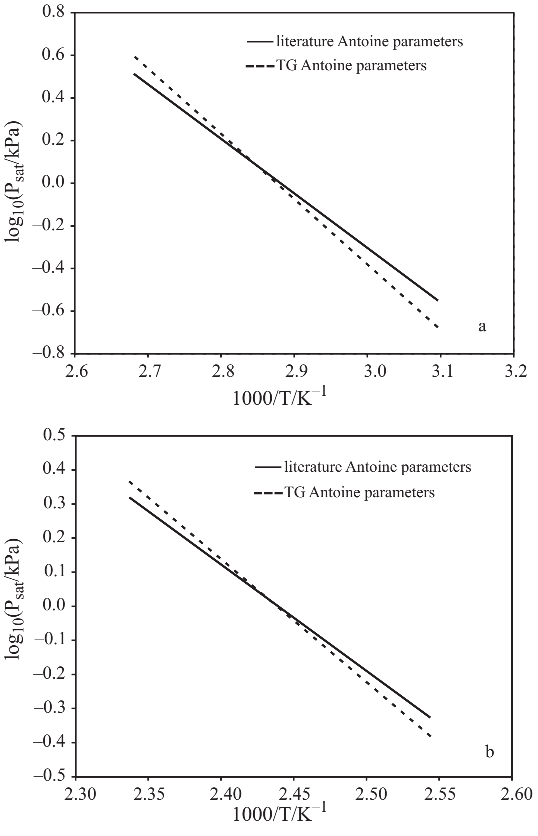

**Fig. 4** Comparison of vapor pressure values estimated from experimental TG data and using literature values for the Antoine parameters. a – N-methyl-2-pyrrolidone, b – dibenzyl ether

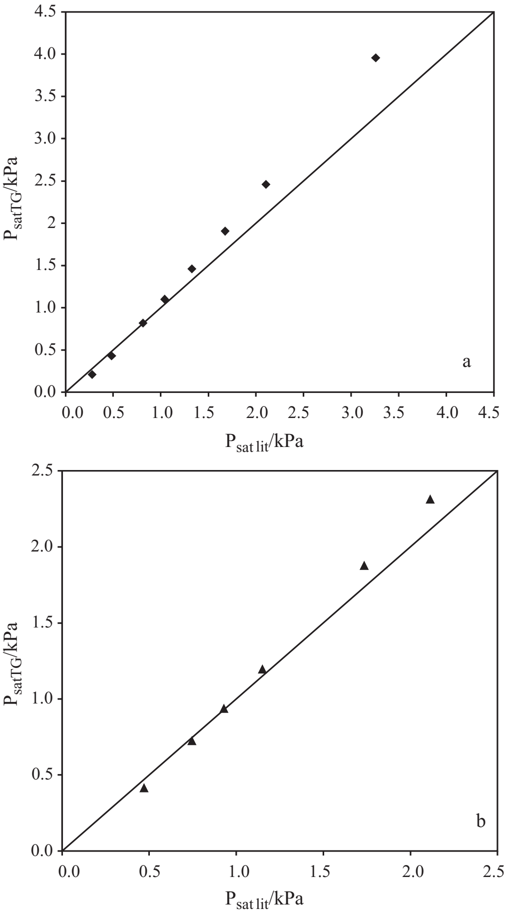

**Fig. 5** Parity plot of the values of vapor pressure calculated from TG experimental data and from the literature for a – N-methyl-2-pyrrolidone and b – dibenzyl ether

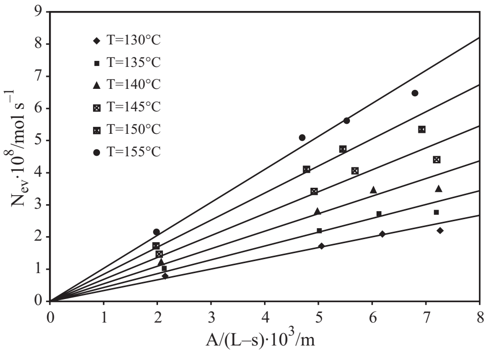

**Fig. 6** Comparison between experimental TG (dots) and calculated (lines) data for the evaporation rate of 2-naphthol at different temperatures

data, thus confirming the validity of the approach applied to the analysis of the evaporation rate.

The data analysis thus evidences a sufficiently good agreement among experimental and literature data. Limited discordance is present between the vapor pressure values calculated by both sets of coefficients, at least in the temperature range where the experimental runs were carried out. For all the substances considered the mean relative error present among the literature values of the vapor pressure and those calculated from the TG data obtained in the present approach is always below 20% and usually of about 5% for most of the substances considered in the present study.

## Conclusions

An approach to the assessment of the apparent values of the vapor pressure of pure substances from TG data was developed. The methodology allows the estimation of the Antoine parameters through a numerical procedure based on a non-linear least square algorithm. The procedure was validated by an extended data set, comparing the estimated values of vapor pressure to literature data. As expected, the accuracy of vapor pressure estimation by TG data resulted far lower than that of the conventional techniques used for vapor pressure measurement. However, the results obtained confirmed that the TG technique has a sufficient accuracy to be used at least for a preliminary screening of the volatility of a pure compound, also due to the very limited amount of substance (few microlitres) required to carry out the experimental runs.

## Nomenclature

| | |
|---|---|
| $A$ | Antoine parameter |
| $A_c$ | surface available for mass transfer, m$^2$ |
| $B$ | Antoine parameter, K |
| $C$ | Antoine parameter, K |
| $D$ | diffusivity, m$^2$ s$^{-1}$ |
| $k_0$ | diffusivity constant, m$^2$ s$^{-1}$ K$^{-1.5}$ |
| $L$ | crucible height, m |
| $N_b$ | overall molar bulk flow, mol s$^{-1}$ |
| $N_{ev}$ | evaporation rate, mol s$^{-1}$ |
| $P$ | total pressure, Pa |
| $P_{sat}$ | vapor pressure, Pa |
| $R$ | universal gas constant, J mol$^{-1}$ K$^{-1}$ |
| $s$ | sample height, m |
| $T$ | temperature, K |
| $y$ | molar fraction |
| $y_s$ | molar fraction in the gas phase at sample surface (Fig. 1) |
| $z$ | position on the $z$-axis in Fig. 1, m |

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