# FAST METHOD FOR THE EXPERIMENTAL DETERMINATION OF VAPORIZATION ENTHALPY BY DIFFERENTIAL SCANNING CALORIMETRY

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## Abstract

A simple method is proposed to estimate the vaporization enthalpy of the palmitic acid (hexadecanoic acid) at its normal boiling temperature. Differential scanning calorimetry (DSC) was the technique used to directly measure these thermodynamic properties. The advantages of this method are its speed and small amount of sample required. In order to avoid evaporation and to ensure equilibrium conditions, the experiments were carried out including α-alumina in contact with the fatty acid. The effect of the alumina concentration is discussed. The obtained experimental data ($T_{bp}$=625.4±0.5 K, $\Delta_{vap}H$=237.6±5.9 J g$^{-1}$) is compared with that obtained by using thermodynamic equations.

## Introduction

Differential scanning calorimetry (DSC) is one of the most widely used techniques for studying the thermal behavior of compounds. This technique has been employed with satisfactory results in the determination of heat capacities of fatty acids, organic compounds and for measurements of melting temperatures in vegetables and triglycerides.

Gas chromatography has been used to measure thermodynamic properties of solutions and a great number of investigators have measured vaporization enthalpies of pure materials indirectly by this technique [1]. In this method, the plot of $\ln(1/t_r)$ *vs.* $T^{-1}$, where $t_r$ is the retention time corrected for the dead volume, results in a straight line, whose slope when multiplied by the gas constant affords, $\Delta_{sol}^{g}H_m$. A modifica-

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tion of this technique was described in 1995 [2]. These modifications eliminate the need for the calorimetric measurements and generally simplify the experimental aspects of the procedure; in case where compounds are properly selected with regards to molecular structure, plotting $\Delta_{sol}^{g}H_{m}$ *vs.* the known vaporization enthalpy at temperature *T*, also affords a straight line. The equation of this line can be used to evaluate the unknown vaporization enthalpy of any structurally related material provided that the unknown is analyzed at the same time as the standards. The advantages of this method are its speed and accuracy and small samples sizes required. In addition, whereas most thermochemical measurements require purities in excess of 99%, there is no minimum purity requirement for this method.

The standard molar enthalpies of vaporization can be obtained too by microcalorimetric methods [3], using for liquids a similar technique to that described for sublimation of solids by Skinner *et al.* [4], the so called 'vacuum-sublimation drop-microcalorimetric method'. In this method, a sample of each liquid contained in a small thin glass capillary tube sealed at one end, was dropped at room temperature into the hot reaction vessel in the Calvet high microcalorimetric held at a determined temperature, and removed from the hot zone by vacuum vaporization. The thermal corrections for the glass capillary tubes were determined in separate experiments, and were reduced as far as possible by dropping tubes of nearly equal mass into each of the twin calorimeter cells.

Other way to obtain enthalpies are the transpiration studies [5, 6]. This method was performed in a heated tube containing finely powdered sample mixed with glass pellets and connected to a cooled trap; a flow of nitrogen was slowly passed through the tube. The amount of condensed product was determined by gas chromatography using an internal standard. The vapor pressure at the saturation temperature and the molar enthalpy of vaporization was calculated from the linear correlation of the logarithm of the concentration of the sample *vs.* $T^{-1}$.

Although vaporization enthalpies have been reported for a large variety of hydrocarbon derivatives, most still remain to be measured. In addition, the accuracy and reliability of numerous values reported in the literature are questionable. In these cases, the estimation methods provide some rational values in cases when experimental data are lacking and to screen the reliability of the data when such data are available [7, 8].

Thermoanalytical techniques have been employed in the measurement of many basic thermodynamic quantities [9–16]. The use of simultaneous DSC/TG is other method to the measurement of the enthalpy of vaporization. Simultaneous DSC/TG allowed for the measurement of the time or temperature dependence of both mass and energy flux. If the sample mass changes during the experiment, an additional term is added to the equation for the measured instantaneous power flux

$$\frac{dH}{dt} = m(t)C_{p}(T)\frac{dT}{dt} + \frac{dm}{dt}\Delta H_{v}(T),$$

where $dH/dt$ is the measured instantaneous power flux, $m(t)$ is the sample mass at time *t*, $dT/dt$ is the scan rate, $dm/dt$ is the differential mass (DTG) and $\Delta H_{v}(T)$ is the

enthalpy of vaporization. All variables which are a function of temperature may also be parameterized as a function of time [17–19].

The use of dynamic thermal techniques in the study of boiling processes presents a number of problems such as the equilibrium of liquid and vapor and the control of atmospheric pressure. In order to avoid evaporation and to ensure equilibrium conditions, experiments can been carried out including a solid substance in contact with the fatty acid. The use of a solid diluent serves several functions; it increases the liquid surface, reduces vaporization before boiling by retention of sample through surface tension, and acts as nucleation sites for boiling which minimizes superheating. The diluent also provides a better match of heat transfer characteristics between the sample and reference portions of a cell, especially after boiling [20]. A solid diluent allowed the use of thermogravimetric analysis to rapidly obtain data on the temperature dependence of vapor pressure and the boiling points of organic compounds [21]. The application of this method has been used too for binary mixtures of triglycerides to determine the effective heat of vaporization [22].

The present paper reports a new method of direct determination of the $T_{bp}$ and $\Delta_{vap}H$ by DSC measurements, using α-alumina as regulator for the thermal behavior of the problem sample (palmitic acid).

## Experimental

Thermogravimetric analysis (TG) were performed with a Mettler TA 4000 system, TG 50 model. A stream of nitrogen at 50 mL min$^{-1}$ flow was used as inert atmosphere, within a temperature range from 298 to 773 K (25 to 500°C), accurate to ±0.2°C and atmospheric pressure; the heating rate was set at 10°C min$^{-1}$. To check the accuracy of the TG unit, a special sample was made up for the temperature calibration; the calibration sample contained isatherm®, nickel and trafoperm®, and the temperature of Curie transition of these metals was obtained.

DSC determinations were performed with a Mettler TA 4000 system, DSC 30 model. At ambient pressure, a 50 mL min$^{-1}$ nitrogen purge flow was used as inert atmosphere. The range temperature was 298 to 773 K (25 to 500°C), with the heating rate of 10°C min$^{-1}$. Using a special pan included in the standard accessories of the Mettler equipment, the temperature and enthalpy calibration of DSC was performed; this pan contains a known, exact quantification of indium as well as lead and zinc in separate compartments. The experimental data was obtained from the melting of the three metals at 429.6, 600.4 and 692.5 K (156.5, 327.3 and 419.4°C).

The palmitic acid was supplied by Merck and had a nominal purity of 99.3 mass%; the α-alumina was supplied by Prolabo (particle size of 10–30 μm). The samples preparation was carried out homogenizing both solids in an agate mortar. The fraction of particle size less than 80 μm finally being used. The sample container used for TG and DSC was made of aluminium and the mass used was ca. 10 mg. The boiling temperature and the enthalpy of vaporization are the average of the results obtained in ten experiments.

# Results and discussion

Figure 1a shows the TG and DTG curves of palmitic acid. At 403 K (130°C), an early evaporation is observed, increasing with temperature. At 593 K (320°C), the phase transition has been completed. The DTG curve shows three peaks at 503, 518 and 573 K (230, 245 and 300°C). Evidently, these conditions are not adequate to determine the thermodynamic parameters associated with the boiling process of palmitic acid. The DSC data (Fig. 2) is in agreement with these considerations. The melting process is a well defined process around 340 K (67°C) [23]. However, the evaporation process takes place in a very wide temperature range. This shows the existence of an early evaporation that does not allow both the boiling temperature and the boiling enthalpy to be appropriately calculated.
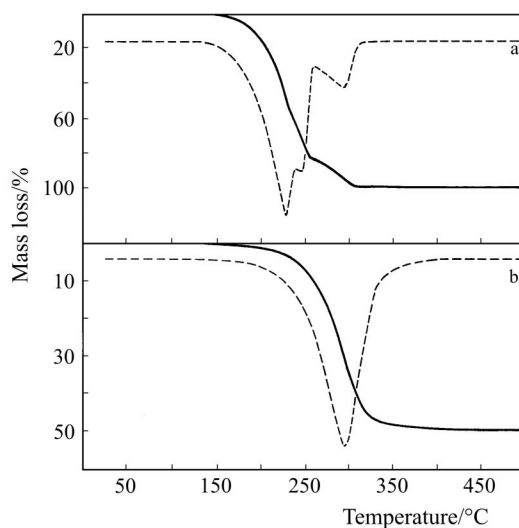


**Fig. 1** TG (—) and DTG (- - -) curves for; a – palmitic acid, and b – a mixture of palmitic acid (50 mass%) and α-alumina
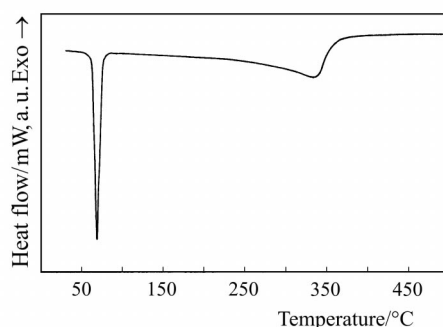


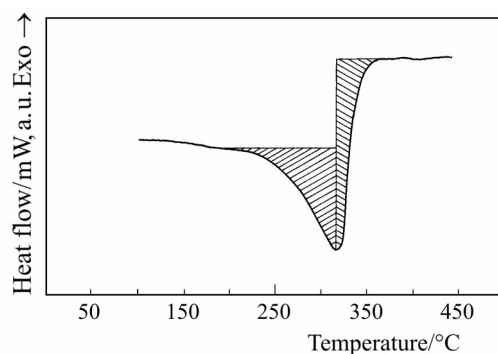**Fig. 2** DSC curve for palmitic acid

The intimate mixture of the sample with a solid material reduces the rate of vaporization, and also provides a better match of heat transfer characteristics between the sample and reference portions of a cell, especially after boiling [20]. The TG and DTG curves of the palmitic acid mixed with $\alpha$-alumina (Fig. 1b) prove the existence of a more controlled vaporization process. It is noticeable that only one peak with a minimum at 568 K (295°C) is observed in the DTG curve. Evidently, both the mass loss percentage and the DTG-minimum temperature will be a function of the concentration of $\alpha$-alumina added.

**Table 1** Temperature ($T$) and heat ($q$) data for palmitic acid as a function of the $\alpha$-alumina content in the sample (DSC data)

| $Al_2O_3$/mass% | $T$/K | $q$/J g$^{-1}$ sample | $q$/J g$^{-1}$ acid |
|---|---|---|---|
| 10.2 | 604.5±0.9 | 198.2±2.4 | 220.9±2.7 |
| 20.8 | 602.5±0.6 | 200.9±3.8 | 253.9±4.8 |
| 29.9 | 599.2±0.4 | 190.8±3.6 | 272.4±5.1 |
| 50.0 | 584.5±0.4 | 149.2±3.0 | 298.4±6.0 |
| 59.9 | 573.7±0.3 | 126.4±3.5 | 315.6±8.7 |
| 65.6 | 571.8±0.3 | 109.4±2.8 | 318.7±8.1 |
| 74.0 | 562.8±0.2 | 85.9±2.7 | 331.1±10.4 |
| 90.5 | 546.2±0.2 | 33.2±1.3 | 350.4±13.7 |

To assist in achieving an adequate boiling process, variable quantities of $\alpha$-alumina were added to palmitic acid (10–90 mass%). In all the cases, the TG-DTG curves have a similar profile to that shown in Fig. 1b. Independently of the amount of palmitic acid, the vaporization process takes place at higher temperatures than that observed in the absence of $\alpha$-alumina. Figure 3 shows a DSC-curve characteristic of the fatty acid and $\alpha$-alumina mixture. Table 1 presents the temperature data obtained from the minimum DSC peaks as a function of the percentage of $\alpha$-alumina. Plotting the $T$-values as a function of the percentage of $\alpha$-alumina (Fig. 4a), a straight line ($r=0.996$) is obtained when the $\alpha$-alumina mass percentage is greater than 30%. The extrapolation of this straight line to zero allows the boiling temperature of palmitic acid to be obtained. The value obtained in this study, 625.4±0.5 K (352.3±0.5°C), converges with those previously published (Table 2).

The determination of the heat involved in the vaporization process implies the integration of the DSC-curves. A discontinuity in the base line is observed due to a change in the heat capacity of the system before and after vaporization of the palmitic acid. This sudden change in the base line complicates the integration process, which has been carried out as shown in Fig. 3. Table 1 presents the heat data obtained from the DSC measurements as a function of the percentage of $\alpha$-alumina. If the $\alpha$-alumina mass percentage is lower than 30%, the presence of this material does not adequately control the vaporization process. When the values obtained from DSC are plotted as a function of the

**Fig. 3** DSC curve for a mixture of palmitic acid (50 mass%) and α-alumina showing the integration method

percentage of α-alumina (Fig. 4b), a straight line is obtained ($r$=0.997). The extrapolation to zero allows the enthalpy of vaporization, $\Delta_{vap}H$, of palmitic acid to be obtained. The value of 237.6±5.9 J g$^{-1}$ obtained in this study is comparable to that obtained using thermodynamic methods of estimation (Table 2).

**Table 2** Estimation of the vaporization enthalpy values ($\Delta_{vap}H$) for palmitic acid obtained from a number of theoretical methods [16]

| Method | $T_{bp}$/K | | | |
| | Gunstone | Bailey Markley | Prieto | This study |
| | 627.0 | 624.7 | 625.2 | 625.4 |
| | $\Delta_{vap}H$/J g$^{-1}$ acid | | | |
|---|---|---|---|---|
| Riedel | 247.9 | 242.3 | 243.7 | 244.0 |
| Giacalone | 247.4 | 243.3 | 244.3 | 244.5 |
| Chen | 232.4 | 228.4 | 229.4 | 229.6 |
| Veterene | 230.6 | 226.6 | 227.6 | 227.8 |
| Hsiun and Ping | 235.4 | 236.4 | 236.2 | 236.1 |
| Pitzer | 209.5 | 210.7 | 210.4 | 210.3 |
| Riedel-Planck | 233.7 | 233.0 | 233.2 | 233.2 |
| Lereder | 233.2 | 234.4 | 234.1 | 234.1 |
| Watson | 247.9 | 242.3 | 243.7 | 244.0 |

In conclusion, from our point of view the experimental procedure described in this paper is highly adequate for the determination of temperature and boiling heat of fatty acids and related compounds, since it is rapid, needs only a small amount of sample and provides substantial information.
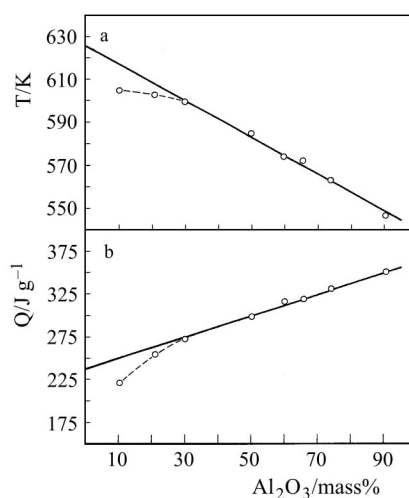
**Fig. 4** Influence of the α-alumina mass percentage in the DSC data of mixed samples;
a – temperature and  b – heat

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