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The perfection of a method for the determination of the temperature/vapour-pressure function of liquids by differential scanning calorimetry

M.D. Contreras[a],*, F. Girela[b] and A. Parera[a]

[a] *Department of Pharmacy and Pharmaceutical Technology, School of Pharmacy, University of Granada, E-10871 Granada (Spain)*
[b] *Department of Applied Analytical Chemistry, Experimental Station of Zaidín, C.S.I.C. E-18008 Granada (Spain)*

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Abstract

The heating rate, the sample size and the suitability of the diameter of the orifice in the crucible lid were all investigated for vapour pressure determinations of various liquids using a Mettler TA 2000.

INTRODUCTION

Of the different techniques employed to study the temperature/vapour-pressure function, the thermal method is, in many respects, the most suitable: it requires a small amount of substance, is easy to set up and permits rapid determinations. This method is an approximation of the widely known "boiling point method".

The theory of the operation and instrumentation of differential scanning calorimetry (DSC) is sufficiently well developed and well known to enable the determination of the boiling point of a liquid to a high degree of precision and reproducibility. The boiling point of a liquid or the temperature at which the vapour pressure equals the external pressure is independent of the amount of sample and the transition may be observed as a sharp endothermic depression in the baseline.

The basis of these studies of the vapour pressure/temperature functions lies in determining the isothermal boiling point of a liquid as a function of pressure. The data are usually obtained by routine thermal techniques in the pressure interval from 10^{-1} to 10^{5} mmHg.

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* Corresponding author.

According to Seyler [1] and Barrall [2], to obtain very precise vapour pressure values it is necessary to adopt the following precautions:

Constant pressure and accurate pressure control must be maintained during boiling.

Sample quality. The presence of more than 5% of ionic impurities, such as the decomposition products of the sample, preceding or during the boiling process, invalidates the experiment. Both effects may be detected in the experimental thermograms as multiple transitions or non-isothermal boiling.

Sample mass. This should be individually selected for each apparatus and substance. For some commercial apparatus, samples of from 1 to 15 μl are advised.

Sample holder. The most suitable holder for DSC is an aluminium crucible with a small orifice in the lid, causing it to behave similarly to an effusion cell, which permits the sample to assume the same pressure as the instrument without substantial loss of liquid before boiling. The flow produced is almost perfect because there is only a few tenths of a degree difference between the liquid in the bottom of the crucible (heated dynamically) and the vapour in contact with the lid (which is cooler). When the boiling point is reached the rapid transformation of the liquid to vapour and the lack of condensation on the lid cause a sudden flow of vapour across it. This process is reflected graphically as a sharp endothermic effect.

With respect to the orifice diameter, it must be born in mind that if it is very small, the laws of effusion are not applicable. The most suitable is where the ratio of the area of the orifice to the area of the evaporation surface is 10^{-2}. For the crucible used (diameter = 6 mm), the orifice should be no larger than 0.6 mm in diameter.

The liquid should be evenly spread over the surface of the crucible. Barrall [2] recommends that a sheet of aluminium should be placed over the liquid. Moire et al. [3] add glass beads or dilute the liquid with an adsorbent substance such as carborundum powder or aluminium. The intention is to minimize the loss of mass before the boiling point is reached, and to ensure that there is direct contact between the liquid and the surface of the crucible and unhindered transmission of heat through the sample at all times.

It is recommended that high heating rates, between 10 and 20°C min^{-1}, are used so that, in addition to preventing the unnecessary loss of sample, the experiment lasts for a shorter time, and the boiling point remains unaffected.

For each liquid and apparatus, therefore, it is necessary to select the quantity of sample, the size of the crucible, and the heating rate. In this study, we investigated the influence of these factors with the aim of selecting the appropriate values for their future application in the determination of the heat of evaporation of some alcohols and lipid esters of high molecular weight, including isopropyl palmitate.

MATERIAL AND METHODS

A Mettler TA 2000 was used, calibrated with respect to the fusion temperature of indium. The furnace was connected across a safety valve to a mercury manometer (with a mmHg scale) and a vacuum pump (rotating oil pump). After eliminating air from the entrances to the furnace, the pressure in the apparatus was always maintained above 3 mmHg.

The sample containers were aluminium crucibles (6 mm in diameter and 40 μl volume), with a pinhole in the lid of 0.4 mm diameter (made by a drill bit at high velocity), in order to obtain a high ratio of surface area of effusion/surface area of evaporation.

Propylene glycol, glycerine (Q.P., Merck) and isopropyl palmitate (technical products, Glyco Ibérica) were used in the study.

RESULTS AND DISCUSSION

Sample quantity

It was established that a quantity of 4–5 μl was adequate to completely cover the surface of the aluminium crucible. With greater quantities, however, through the course of the experiment, part of the sample came out of the hole in the crucible as a consequence of the expansion of the liquid as the temperature increased. This occasionally appeared as multiple endotherms in the corresponding thermograms, hindering observation of the "real" boiling point of the liquid.

Boiling point

Because there is no recommendation for the use of any reference substance, either by Mettler or in the literature, for calibration of thermal apparatus for boiling point determinations, the apparatus was calibrated with respect to the fusion temperature of indium.

The thermal process was carried out in dynamic conditions (the furnace and sample temperature were increased in a constant linear manner). However, when the sample reached its boiling point, its temperature remained constant until all the sample had been used up.

Seyler [1], Barrall [2], and other authors have suggested taking the boiling point as the temperature obtained by extrapolation of the isotherm to the baseline. They proposed that the maximum on the thermogram

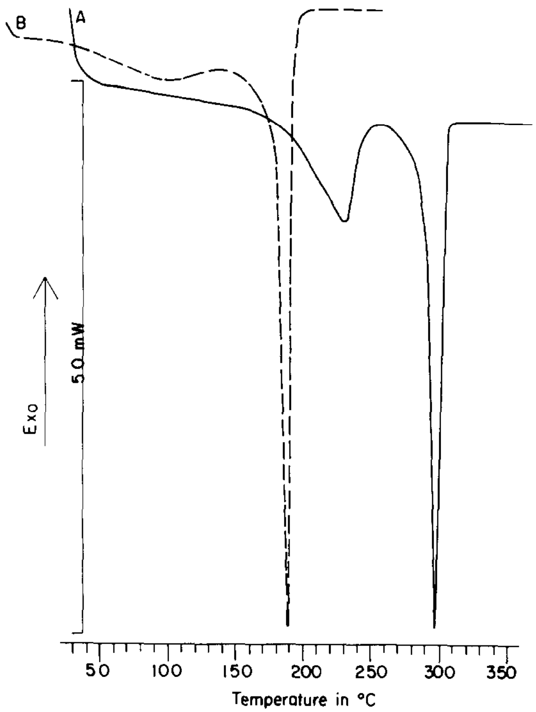

Fig. 1. DSC of glycerine (curve A) and propylene glycol (curve B) at atmospheric pressure. Boiling point of both substances.

represents the moment at which the sample is completely evaporated, and that the boiling point is several degrees lower.

In order to determine the difference between these values (the boiling point and the maximum on the thermogram), the boiling points of samples of two liquids (glycerine and propylene glycol, 5 mg each) were determined in the same crucibles to be used later (aluminium with an orifice of 0.4 mm diameter). It may be observed (Fig. 1) that in both cases the maximum temperature on the thermogram corresponds to the boiling point, 292°C for glycerine and 189°C for propylene glycol, confirmed in reference 4.

Therefore, for the apparatus calibrated with indium and samples weighing approximately 5 mg, the maximum endothermic point corresponds to the boiling point of the liquid.

Orifice diameter

In spite of our attempts to rule out the influence of the size of the orifice in the lid on the maximum boiling point by applying identical methods of manufacturing the pinhole, we observed differences of approximately two degrees in the maximum boiling point of isopropyl palmitate when samples were heated in different crucibles and when all other influencing factors (heating rate and sample weight) were the same. However, when this test was carried out repeatedly in the same crucible, a difference of only a few tenths of a degree was observed. To achieve this, the liquid was introduced through the orifice in the lid using a microsyringe with a specially adapted needle having a diameter of less than 0.4 mm. The use of this microsyringe allowed the controlled introduction of a specific volume of liquid into the crucible.

Heating rate

Once the sample quantity was decided upon, the most suitable heating rate could be determined. To do this a series of tests was carried out in which the boiling points of one of the liquids studied, isopropyl palmitate, were determined at different pressures and different heating rates, 5, 10 and 150°C min^{-1}. In order to make the tests of similar duration, thus minimizing its influence on the results, the determinations began at 100°C for a heating rate 5°C min^{-1}, at 75°C for 10°C min^{-1}, and at 25°C for 15°C min^{-1}.

The results given in Table 1 indicate that when working with the lowest heating rate (5°C min^{-1}) at different pressures, the boiling points obtained differ by approximately 10°C from those obtained at higher rates (10 or

TABLE 1

Variation in boiling point (θ_b) of isopropyl palmitate with pressure (p) and heating rate (rate)

p/mmHg	Rate/(°C min^{-1})	Weight/mg	θ_b/°C
5	15	4.86	193.4
	10	5.57	191.0
	5	5.06	182.3
10	15	5.46	204.8
	10	5.38	202.9
	5	5.15	193.8
15	15	4.99	213.3
	10	5.14	210.7
	5	5.07	201.4
20	15	4.80	218.6
	10	4.45	215.2
	5	4.90	205.1
24.25	15	5.42	223.4
	10	4.55	221.1
	5	5.03	208.3

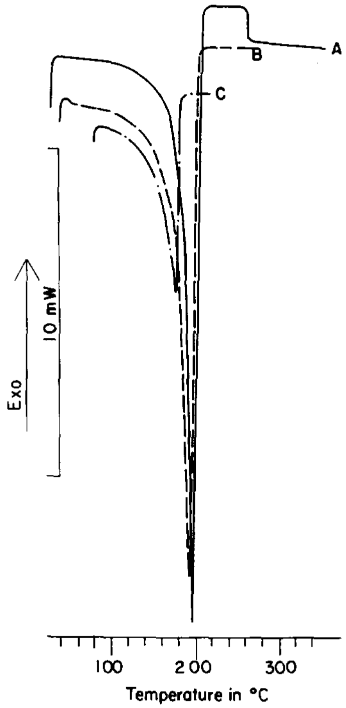

Fig. 2. DSC of isopropyl palmitate at 5 mmHg pressure. Boiling point at 15°C min^{-1} (curve A), at 10°C min^{-1} (curve B), and at 5°C min^{-1} (curve C).

15°C min^{-1}). In addition, in the low-heating-rate thermogram (Fig. 2, curve C), there is no clear endothermic peak at boiling which suggests that there is an insufficient amount of sample to obtain a boiling point. This is due to the prolonged exposure of this sample to high temperatures.

For high heating rates, the thermograms (Fig. 2, curves A and B) show sharp boiling endotherms, separated by 2–3°C.

The results show us that 40 μl aluminium crucibles with a pinhole of 0.4 mm diameter in the lid, samples of 5 ± 0.5 mg and heating rates of 10 or 15°C min^{-1} are suitable for determinations of boiling points and the vapour pressure/temperature function of liquids similar to isopropyl palmitate.

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