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Thermal behaviour and heat capacity of some high molecular weight alcohols and esters used in pharmaceutical preparations

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Abstract

The thermal behaviour and the temperature of evaporation of oleyl alcohol, 2-octyl dodecanol, isopropyl myristate, isopropyl palmitate, oleyl oleate, decyl oleate, dibutyl adipate, di(2-ethyl hexyl) adipate and propylene glycol dipelargonate, all of which are frequently used for pharmaceutical purposes, were determined by DSC and TG.

All decompose before their boiling points and evaporate at temperatures lower than this. Therefore, the heat capacity was measured as a function of temperature in high-pressure crucibles (at constant volume), in the interval between 25°C and the temperature at which they begin to decompose.

INTRODUCTION

One of the uses of the heat capacity/temperature function of a liquid is for extrapolation of the enthalpy of vaporization between two different temperatures [1]. The heat capacity of high molecular weight alcohols and esters, solvents regularly used in pharmaceutical preparations, are unknown.

In this study, the thermal behaviour at atmospheric pressure of several well known substances, oleyl alcohol, 2-octyl dodecanol, isopropyl myristate, isopropyl palmitate, oleyl oleate, decyl oleate, dibutyl adipate, di(2-ethyl hexyl) adipate and propylene glycol dipelargonate, was measured, followed by a determination of their heat capacity/temperature functions.

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METHODS AND MATERIALS

Glyco Iberica (Madrid, Spain) supplied the isopropyl myristate, isopropyl palmitate (Glyco I-309) and propylene glycol dipelargonate (Glyco PR-827); Henkel (Barcelona, Spain) supplied the oleyl alcohol (Eutanol H-D), 2-octyl dodecanol (Eutanol G), oleyl oleate (Cetiol), decyl oleate (Cetiol V) and dibutyl adipate (Cetiol B); and Aldabo-Julia (Barcelona, Spain) supplied the di(2-ethyl hexyl) adipate (Cromadol DOA). All these compounds are classified by the different companies as technical products for cosmetic use, with an impurity content of less than 4%. All were used as received.

The determinations were carried out using a Mettler differential scanning calorimeter model TA 2000 calibrated from the melting temperature of indium. The DSC curves were recorded in a static atmosphere of air with the samples varying in weight from 4.5 to 6.0 mg and at a heating rate of 10°C min^{-1}.

Mettler 500 μl high-pressure crucibles were used to study the heat capacity of the liquids; to these, a second Teflon membrane (0.25 mm thick, PIFE film (Sipem S.A., Valencia, Spain)) was attached to guarantee a perfect seal. The thermal characteristics of the membrane and the validity of this method have been described in a previous study [2].

The following conditions adopted for all the heat capacity measurements. Both crucibles (reference and sample) had a Teflon membrane of similar weight (29.5 mg ± 0.3 mg), the difference never being greater than 0.2 mg. The apparatus was maintained at an initial temperature 20°C below room temperature until a flat baseline was observed. The rate of heating was less than 2°C min^{-1}, and compatible with the data reading capacity of the DSC data processor.

In each case, the 500-μl crucibles were completely filled with sample. Each sample was weighed on a semi-microanalytical balance at 25°C before and after the assay. Three assays were carried out for each compound studied.

Thermogravimetric (TG) curves were recorded on a Mettler TA-300 system with a Mettler TG-50 thermobalance, in a dynamic atmosphere of pure air (100 $\text{cm}^3\,\text{min}^{-1}$) at a heating rate of 15°C min^{-1}, using samples varying in weight from 25 to 40 mg.

RESULTS AND DISCUSSION

Before the heat capacity of each liquid was determined, their thermal behaviour was investigated by DSC assays at atmospheric pressure and by their weight variation with temperature (TG and DTG) at equal pressure.

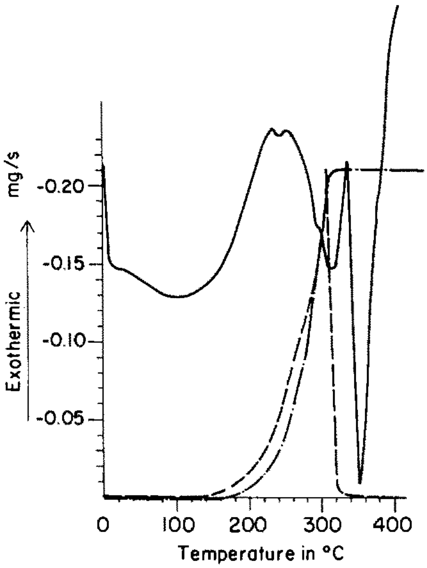

Fig. 1. DSC (——), TG (— —) and DTF (— · —) curves for oleyl alcohol.

In this way, the stability of each liquid could be determined, and thus the most suitable method for the determination of their heat capacities could be selected.

The DSC of oleyl alcohol is shown in Fig. 1 in the temperature range 0–420°C. The baseline shows an initial period of stabilization, followed by a descent to 95°C, which is followed by an exotherm identified as associated with the decomposition of oleyl alcohol; endothermic peaks were observed at 240, 320 and 360°C, probably associated with the loss of the different decomposition products. The loss of material began at 99.5°C, with a rate of evaporation at 200°C of 0.01 mg s^{-1}. At 310°C, complete evaporation occurred.

However, in the DSC curve of 2-octyl dodecanol (Fig. 2), the baseline descends steeply from 20 to 90°C, followed by stabilization until 190°C; then an exothermic effect characteristic of its decomposition occurs. As the temperature increases, an endothermic effect is observed at 370°C, probably due to the boiling of the decomposition products. Weight loss began at 113°C with a very small evaporation velocity; at 200°C, a velocity of 0.002 mg s^{-1} is reached, and at 300°C the sample is completely evaporated.

In the DSC of isopropyl myristate (Fig. 3) in the temperature range 25–400°C, a straight baseline descends slowly to 160°C, followed by an exothermic effect identified as the decomposition of the compound, after which only endothermic effects are observed due to the boiling of the decomposition compounds. For TG in the temperature range 35–400°C, the initial evaporation of the compound is observed at 66.5°C, reaching

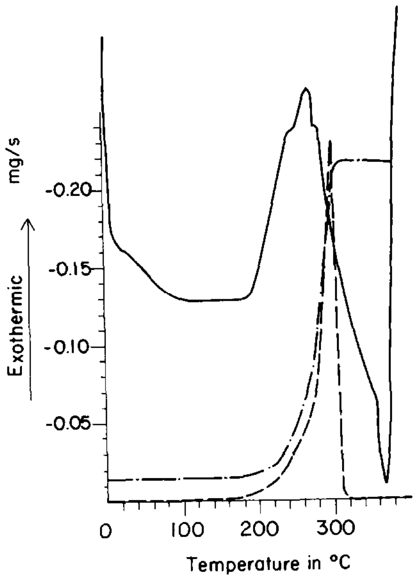

Fig. 2. DSC (——), TG (— —) and DTG (— · —) curves for 2-octyl dodecanol.

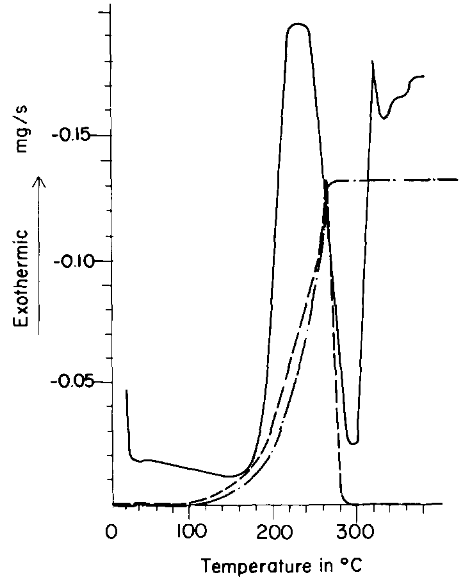

Fig. 3. DSC (——), TG (— —) and DTG (— · —) curves for isopropyl myristate.

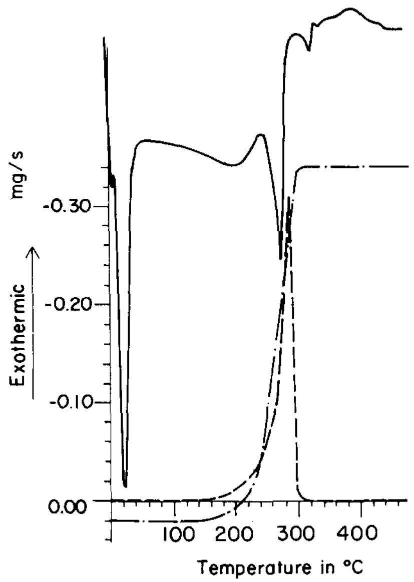

Fig. 4. DSC (——), TG (— —) and DTG (— · —) curves for isopropyl palmitate.

evaporation velocities of 0.005 mg s^{-1} at 140°C and 0.034 mg s^{-1} at 265°C, above which there is practically complete loss of sample.

For isopropyl palmitate (Fig. 4) in the temperature range between −5 and 474°C for DSC, an endothermic peak is observed at 14°C (the melting temperature of the compound) followed by the recovery of a straight baseline and then a descent until 200°C, where the decomposition of the compound begins. At 82°C, the compound begins to evaporate and evaporation is complete at 290°C.

In the temperature range 25–490°C, similar thermal behaviour is observed for di(2-ethyl hexyl) adipate and dibutyl adipate. For di(2-ethyl hexyl) adipate (Fig. 5), the decomposition takes place at 170°C, with another endothermic process being observed at 320°C, probably associated with the boiling of the decomposition products. For dibutyl adipate (Fig. 6), the thermogram shows a descending baseline to 198°C, followed by an exothermic effect identified as the decomposition of the product. However, the evaporation of di(2-ethyl hexyl) adipate begins at 103°C, with an evaporation rate of 0.010 mg s^{-1} at 100°C and 0.4 mg s^{-1} at 165°C, where there is total loss of the sample. For dibutyl adipate, loss of mass occurs at a lower temperature (80°C), and the maximum rate of evaporation is at 270°C (0.148 mg s^{-1}), by which temperature practically all the substance has evaporated.

The DSC of decyl oleate (Fig. 7) in the temperature range from 0 to 400°C indicates an endothermic peak (melting) at 20°C followed by a straight baseline up to approximately 175°C where a large endothermic

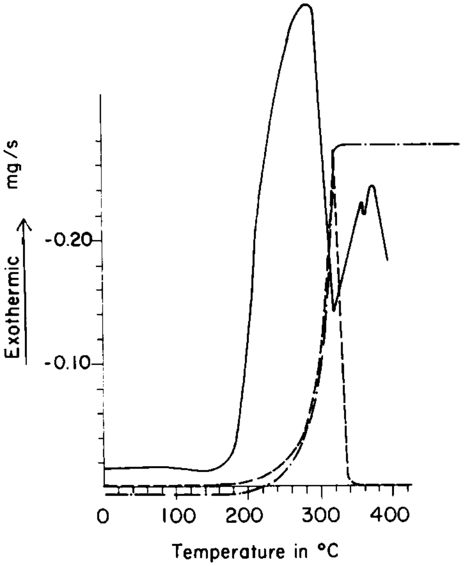

Fig. 5. DSC (——), TG (— —) and DTG (— · —) curves for di(2-ethyl hexyl) adipate.

reaction takes place, probably due to the rapid decomposition and evaporation of the products; another sharp endotherm is seen at 320°C. A slight loss of material is observed from 150°C, with a rate of evaporation of 0.008 mg s^{-1} at 200°C, 0.04 mg s^{-1} at 300°C and 0.20 mg s^{-1} at 320°C.

The thermal behaviour of oleyl oleate (Fig. 8) is different from those of

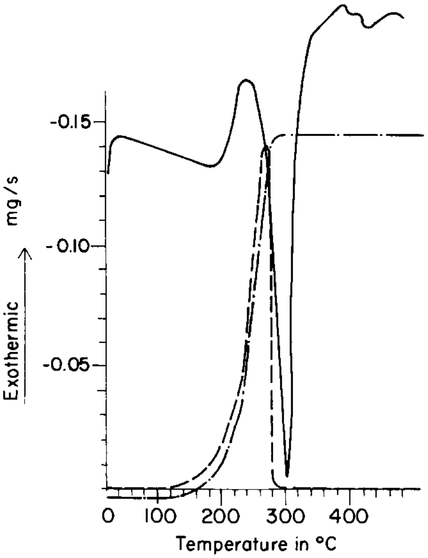

Fig. 6. DSC (——), TG (– –) and DTG (— · —) curves for dibutyl adipate.

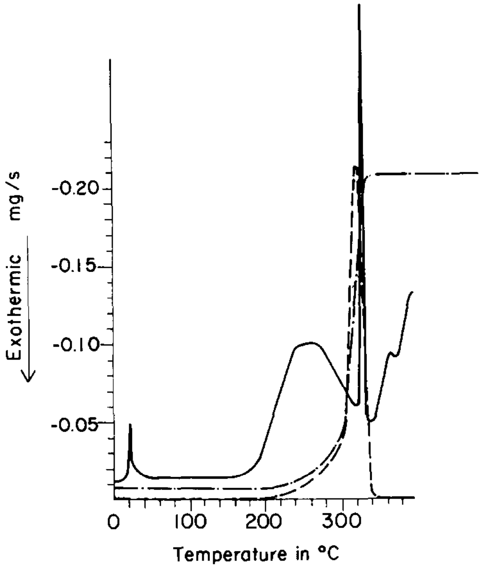

Fig. 7. DSC (——), TG (– –) and DTG (– · –) curves for decyl oleate.

compounds previously described. In the range 25–480°C, a straight baseline is observed descending to 198°C, where an exothermic reaction suddenly begins (decomposition of the compound). Then three endothermic reactions are observed, at 250 and 338°C, and one very pronounced reaction at 438°C, all of which are probably due to the boiling of the different

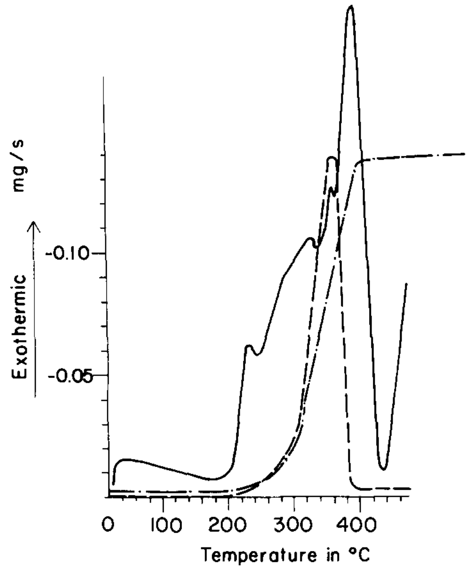

Fig. 8. DSC (——), TG (– –) and DTG (— · —) curves for oleyl oleate.

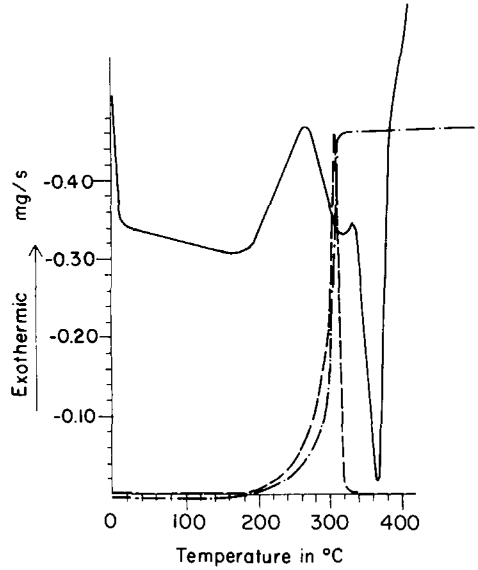

Fig. 9. DSC (——), TG (– – –) and DTG (— · —) curves for propylene glycol dipelargonate.

decomposition products formed. The loss of mass due to evaporation begins at 175°C, and at 350°C the material is completely evaporated.

For propylene glycol dipelargonate (Fig. 9) in the range 0–420°C, there is a straight baseline up to 180°C, where an exothermic effect (decomposition) begins; the two endothermic reactions at 310 and 370°C are probably due to the boiling of the different decomposition products. Loss of material begins at 144°C.

In agreement with the previous TG investigations, evaporation was slow but constant for all the liquids studied, before reaching the decomposition temperature. This makes the accurate determination of heat capacity in open crucibles at constant pressure impossible over a wide temperature range, because of the loss of initial sample. It is therefore necessary to use special high-pressure crucibles which prevent evaporation of the liquid and subsequent sample loss.

The heat capacity of the different liquids was therefore determined at constant volume $(C_l)_V$, in the range between 25°C and a maximum above which the compound begins its decomposition, previously determined by DSC and variable depending on the substance, but always greater than 100°C.

Three different tests were carried out on each of the liquids in the temperature range from 25°C to boiling point. The heat capacity values were measured at 1°C intervals. The relative standard deviation of the heat capacity values was never greater than 4%.

The best correlation between the average heat capacity values for each liquid and its temperature was determined by applying the least-squares

TABLE 1

The heat capacity temperature dependence. Heat capacity: $C_V = A + BT + CT^2$ with C_V in cal mol^{-1} K^{-1} and T in K

Compound	T [a]	°C min^{-1} [b]	A	B	C	N	r^2	$s(\times 10^{-2})$
Oleyl alcohol	299.15–370.15	1.3	3.093	-9.686×10^{-3}	2.135×10^{-5}	73	0.8941	0.3407
2-Octyl dodecanol	299.15–441.15	2	−4.670	3.498×10^{-2}	-4.210×10^{-5}	143	0.9307	4.7814
Isopropyl myristate	298.15–426.15	1.8	1.434	1.492×10^{-3}	1.343×10^{-6}	128	0.9453	2.1288
Isopropyl palmitate	334.15–471.15	2	−0.782	9.201×10^{-3}	-8.522×10^{-6}	137	0.9604	2.1956
Dibutyl adipate	299.15–435.15	1.8	0.170	7.325×10^{-3}	-6.604×10^{-6}	136	0.9668	1.8424
Di(2-ethyl hexyl) adipate	297.15–426.15	1.8	0.625	5.386×10^{-4}	4.009×10^{-6}	129	0.9479	2.1065
Oleyl oleate	298.15–438.15	2	−5.058	3.635×10^{-2}	-4.648×10^{-5}	141	0.4389	12.650
Decyl oleate	297.15–426.15	1.8	1.450	2.723×10^{-4}	4.009×10^{-6}	129	0.9447	2.8979
Propylene glycol dipelargonate	298.15–428.15	1.9	−0.125	7.569×10^{-3}	-6.331×10^{-6}	123	0.7974	5.4888

[a] Temperature range. [b] Rate of heating.

method. In each case, second-degree polynomial equations with coefficients of determination (r^2) greater than 0.79 (except for oleyl oleate) were obtained (Table 1).

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