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A thermal analysis study of long chain fatty acids

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Abstract

The purpose of this study is to examine the thermal behavior of saturated fatty acids [$CH_3(CH_2)_nCOOH$], where n varies from $n = 10$ to $n = 16$, during heating. The studies were performed over a temperature range of ambient temperature to 350°C in a flowing atmosphere of nitrogen, using a SDT 2960 simultaneous TGA–DTA unit. The acids showed two endotherms due to melting at a lower temperature and vaporization at the higher temperature, which is a zero order process. The influence of flow rate and heating rate on the melting points is reported. The latent heat (ΔH_{evap}) of vaporization process is calculated by the Antoine equation and the Clausius–Clapeyron equation at different temperature ranges. The activation energy (E_{act}) was calculated from the rising temperature experiments, using the Arrhenius equation. These observations should be of use in the characterization of pharmaceutical excipients. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Zero order process; Long chain fatty acids; Heat of vaporization; Energy of activation; Antoine equation; Clausius–Clapeyron equation; Arrhenius equation

1. Introduction

The use of fatty acids is widely accepted in the pharmaceutical and food industry. Many drugs and foods contain fatty acids, and they are often subjected to thermal treatment during processing, storage and preparation. The purpose of this study is to examine the behavior of saturated fatty acids during heating, using a simultaneous TGA–DTA unit to determine the kinetics of evaporation.

Evaporation is the transition from the liquid phase to the vapor phase, without a change in chemical composition. It is a zero-order reaction [1,2]. Evaporation can be monitored by determining the rate of mass loss as the substance undergoes transition [3]. This is easily achieved with a rising temperature program, using thermogravimetry, which is a technique that measures the amount of material lost as the substance undergoes programmed heating in a controlled atmosphere [4].

The kinetic analysis of the evaporation process is usually related to the Arrhenius equation.

$$k_{\mathrm{evap}} = A\mathrm{e}^{-E_{\mathrm{act}}/RT}, \tag{1}$$

or

$$\ln k_{\mathrm{evap}} = \ln A - E_{\mathrm{act}}/RT, \tag{2}$$

where k_{evap} is the coefficient of evaporation per unit area, A the Arrhenius parameter, or pre-exponential factor, E_{act} the activation energy, and R the gas constant.

It is generally assumed that the pre-exponential factor, the order of the reaction and activation energy do not change during the course of the reaction.

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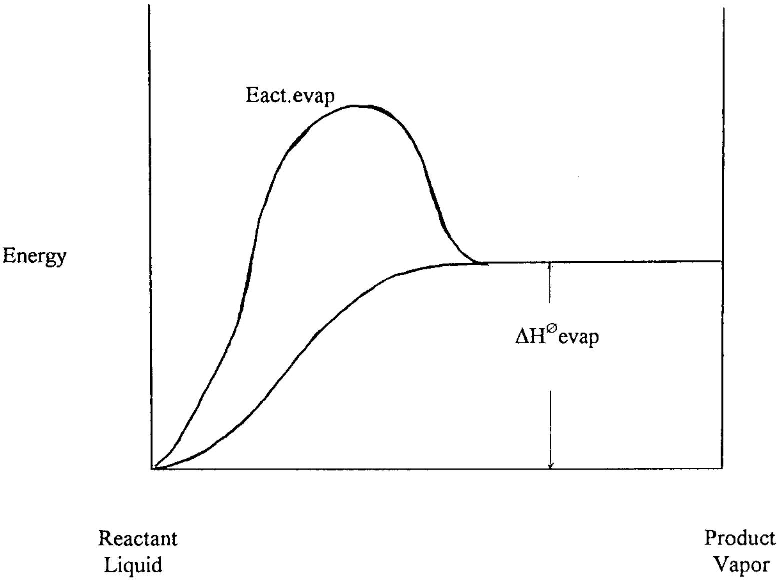

Fig. 1. Schematic diagram of reaction coordinates for the endothermic evaporation process.

Therefore, a plot of ln k_{evap} against $(1/T)$ will produce E_{act} as the slope × R. The reaction coordinates for the evaporation process can be schematically represented as seen in Fig. 1.

The schematic represents an endothermic process where ΔH_{evap} is the latent heat of evaporation. In the limit, E_{act} would approach ΔH_{evap}. It can be easily determined by examining the data in the literature [5], using the Antoine equation as well as the Clausius–Clapeyron equation. In this present study, the thermal behavior of saturated fatty acids was characterized using a simultaneous TGA–DTA unit in an atmosphere of flowing dry nitrogen. The analysis is reviewed in the discussion of the results.

2. Experimental

2.1. Materials

The materials used in this investigation are listed in Table 1.

2.2. Thermal analysis

The thermal analysis equipment consists of a simultaneous TGA–DTA 2960 unit. The samples were placed in a platinum crucible, with an empty platinum crucible as a reference. Different heating rates of 2, 4, 6, 8, 10, 15 and 20°C/min were used during the

Table 1
The materials used in the study

Material	Company	Purity	Lot number
Lauric acid	Aldrich Chem. Co.	98%	02923 TQ
Tridecanoic acid	Sigma Chem. Co.	99%	27H 3620
Myristic acid	Aldrich Chem. Co.	99.5 + %	16626 KQ
Pentadecanoic acid	Aldrich Chem. Co.	99 + %	12502 LZ
Palmitic acid	Sigma Chem. Co.	99%	22H 00901
Margaric acid	Sigma Chem. Co.	99%	46H 2614
Stearic acid	Sigma Chem. Co.	99%	124H 8440

experiments. The samples were analyzed in dry nitrogen and the gas flow rates were 50, 100, 150, 250 and 350 ml/min.

3. Results and discussion

Fig. 2 represents the TGA, DTA and DTG plots of lauric acid at the heating rate of 8°C/min as an example. It can been seen that the evaporation process takes place after melting. The DTA signal shows two endotherms due to melting at a low temperature and the vaporization occurring at a higher temperature.

The melting points for the fatty acids were determined from the DTA peak using different heating rates as well as at different flow rate. These data are reported in Tables 2 and 3. Figs. 3 and 4 show the plots of the melting point against heating rate and flow rate for all the fatty acids investigated, respectively. The flow rate performed in this study should not significantly affect the melting points. However, the melting points increased when the heating rates increase due to a time lag effect for the material to try to catch up with the temperature sensor within the instrumentation. Unfortunately, the material looses and we inadvertently record a higher melting point. Table 4 compares the experimentally determined melting points with the reported melting points from the literature.

Fig. 5 is a plot of $\ln k_{\mathrm{evap}}$ against $(1/T)$ constructed using the data collected from the DTG plot. The values for the regression coefficients for all cases were approximately 0.998, which supported the fact that the evaporation of the fatty acids is a zero-order process. The activation energy for each fatty acid at a heating rate of 2°C/min was determined from the

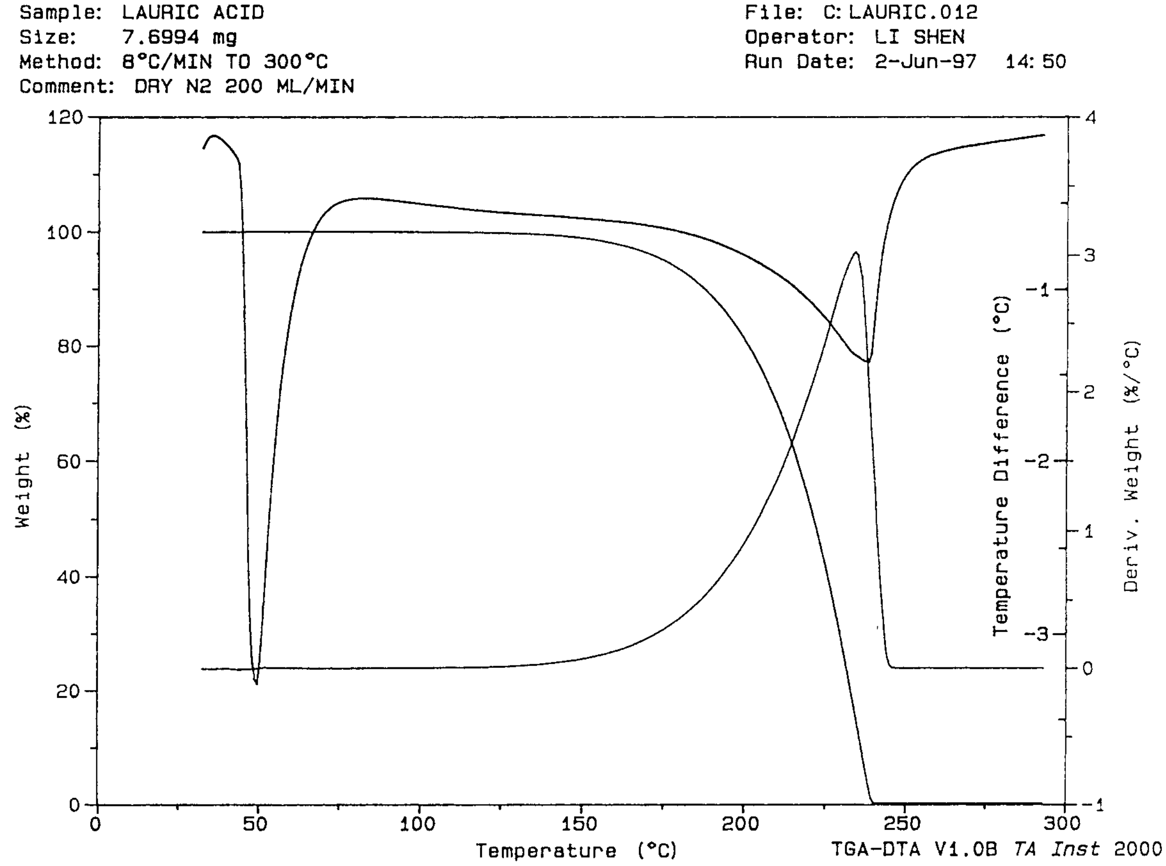

Fig. 2. TGA–DTA.

Table 2
The melting point (°C) for the fatty acids at different heating rates (°C/min)

Heating rate	Lauric acid	Tridecanoic acid	Myristic acid	Pentadecanoic acid	Palmitic acid	Margaric acid	Stearic acid
2	45.3	44.1	56.5	54.9	65.2	62.9	70.6
4	46.9	44.4	57.4	55.8	66.4	63.7	71.8
6	47.1	45.6	58.4	56.2	67.6	64.6	72.1
8	48.5	46.1	59.5	57.3	68.2	65.5	73.2
10	50.1	46.3	60.3	57.5	69.1	65.5	73.8
15	51.0	48.2	61.5	59.3	71.5	68.1	74.9
20	54.3	49.6	63.0	61.7	72.5	69.1	75.6

Table 3
The melting point (°C) for the fatty acids at different flow rates (ml/min)

Flow rate	Lauric acid	Tridecanoic acid	Myristic acid	Pentadecanoic acid	Palmitic acid	Margaric acid	Stearic acid
50	47.8	45.7	59.6	56.6	68.3	65.2	74.5
100	48.5	46.1	59.8	57.3	68.6	65.5	74.4
150	49.4	45.5	59.5	57.6	68.7	65.4	74.7
200	47.0	46.2	59.6	57.1	68.0	65.4	74.6
250	47.7	45.4	60.0	57.2	68.2	65.4	74.5
350	49.1	45.6	59.4	57.3	68.1	65.5	74.7

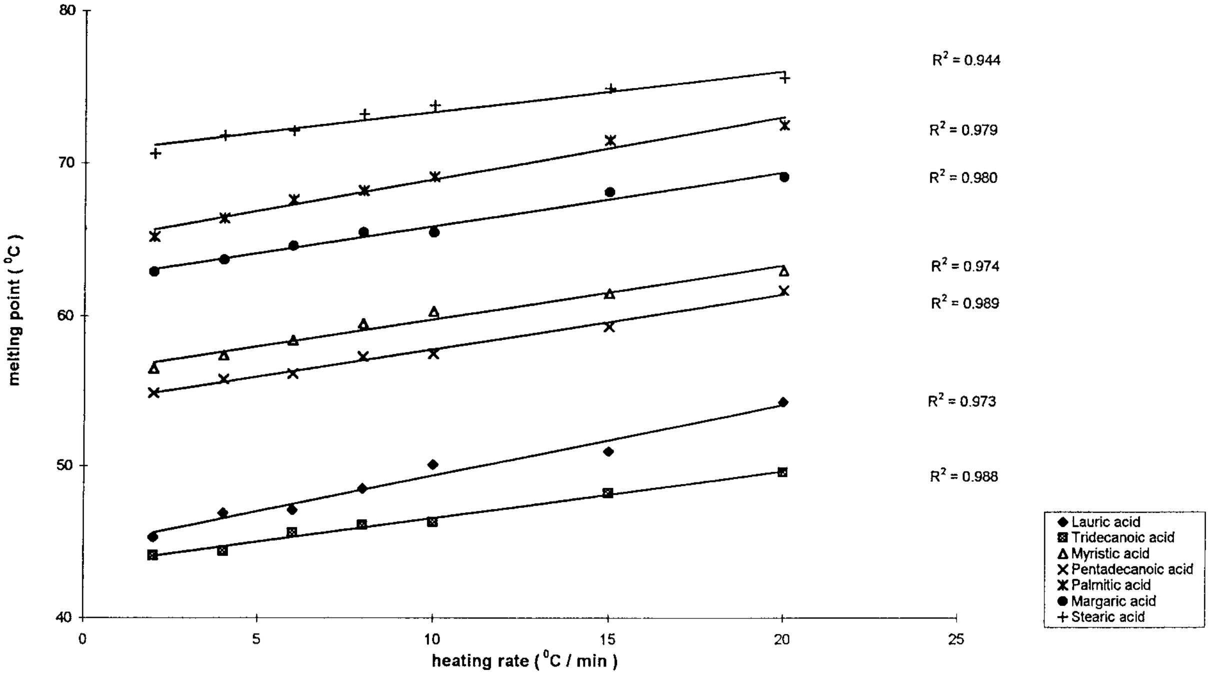

Fig. 3. The effect of heating rate on m.p. of fatty acid at flow rate 100 ml/min N_2.

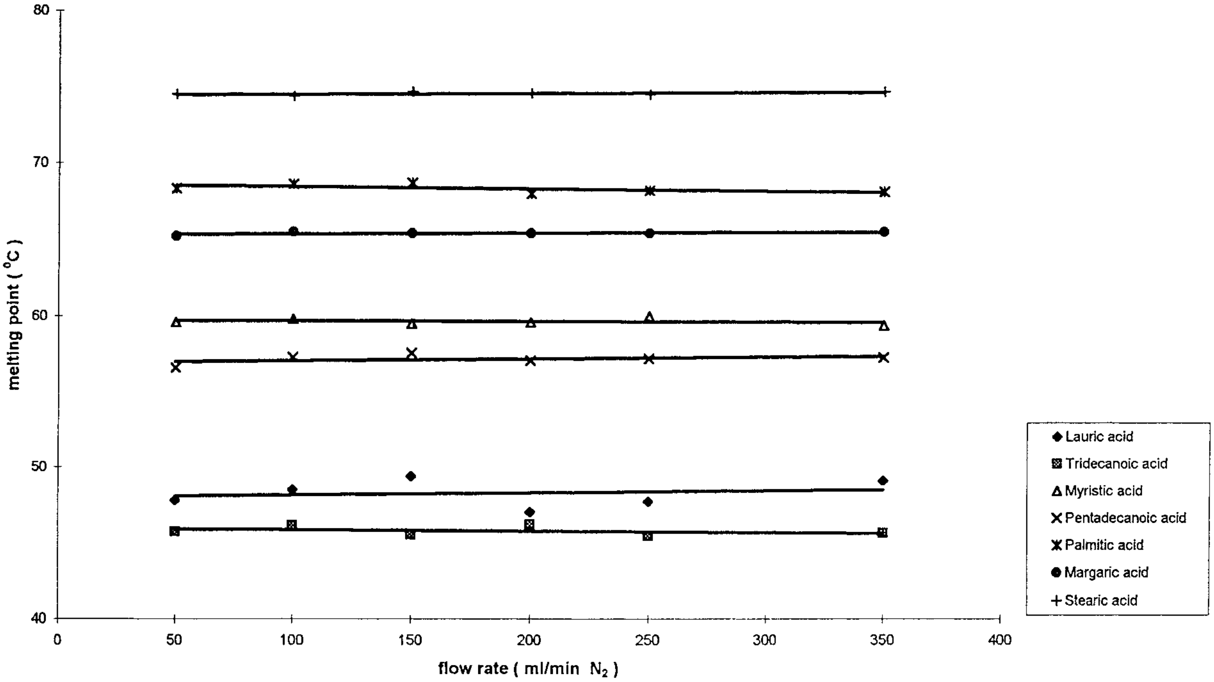

Fig. 4. The influence of flow rate on m.p. of fatty acid at heating rate 8°C/min.

Table 4
The extrapolated melting points compared with the literature values for the fatty acids at the flow rate of 100 ml/min nitrogen

	Lauric acid	Tridecanoic acid	Myristic acid	Pentadecanoic acid	Palmitic acid	Margaric acid	Stearic acid
Lit. m.p. (°C)	44	44–45	58	53–54	63	62–63	71.2
Ext. m.p. (°C)	44.7	48.5	56.2	54.2	64.8	62.4	70.6

Table 5
Activation energy and pre-exponential factor for the fatty acids at the heating rate of 2°C/min, 100 ml/min nitrogen

	Lauric acid	Tridecanoic acid	Myristic acid	Pentadecanoic acid	Palmitic acid	Margaric acid	Stearic acid
E_{act} (KJ mol^{-1})	81.98	83.89	87.60	88.67	91.65	92.82	94.83
$A/10^9$	5.29	5.40	10.9	8.39	11.2	9.45	9.55

slope of this plot. The results are provided in Table 5. Fig. 6 shows the plot of E_{act} against the number of carbons for all the fatty acids investigated. The E_{act} for the material increases as the number of carbons in the fatty acid increases.

The ΔH_{evap} can be calculated from the Clausius–Clapeyron equation:

$$\ln p = C - \left(\frac{\Delta H_{\mathrm{evap}}}{RT}\right), \tag{3}$$

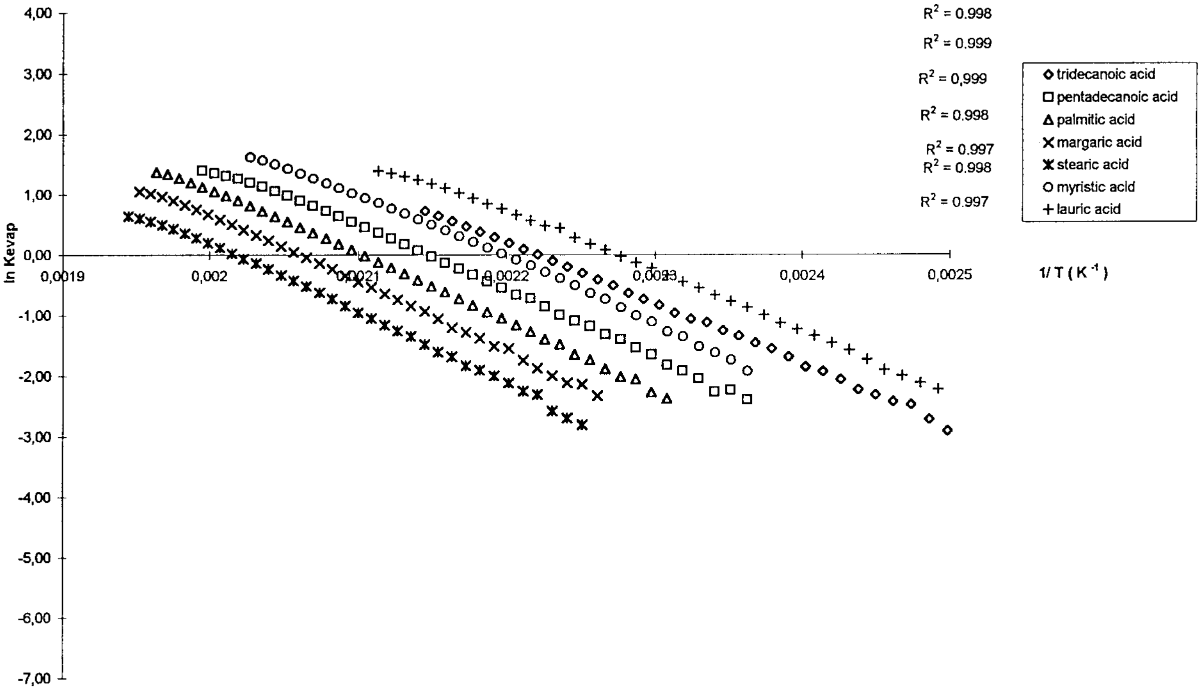

Fig. 5. A plot of the natural log of the rate constant for the evaporation of fatty acids vs the inverse of the temperature in kelvin (heating rate 2°C/min, flow rate 100 ml/min N_2).

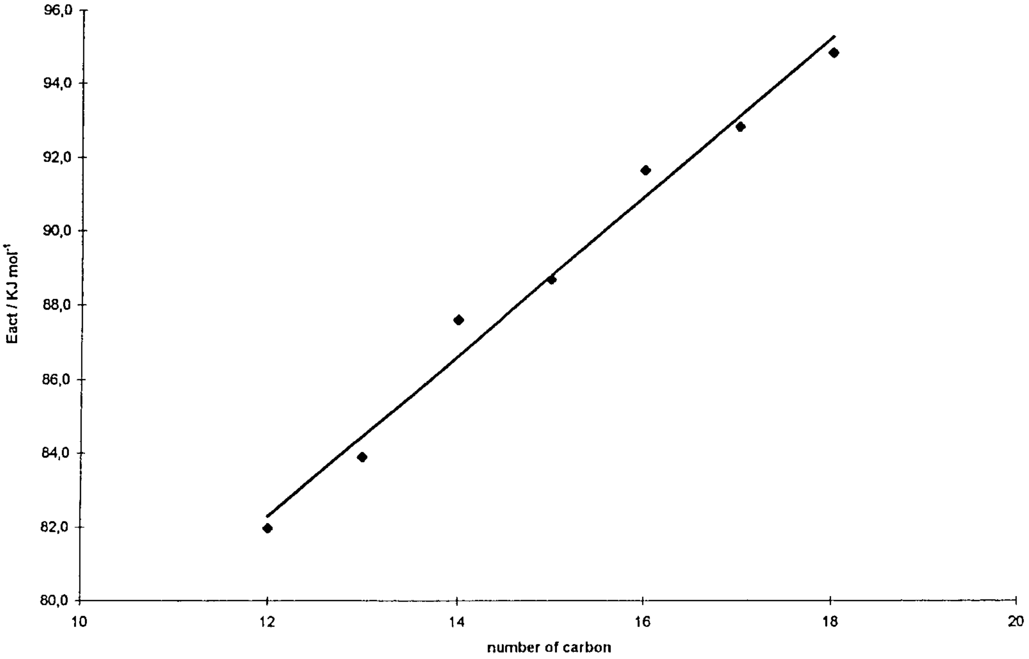

Fig. 6. A plot of activation energy for the evaporation of fatty acids vs the number of carbon with $R^2 = 0.9836$.

Table 6
The latent heat of evaporation and Antoine constants for the fatty acids over the calculated temperature range

	Lauric acid	Tridecanoic acid	Myristic acid	Pentadecanoic acid	Palmitic acid	Margaric acid	Stearic acid
ΔH_{evap} (KJ mol^{-1})	82.92	86.25	86.97	90.19	92.02	95.45	96.62
a	6.393	6.198	6.116	5.928	5.854	5.730	5.852
b	1847	1768	1751	1676	1650	1596	1717
c	−150.3	−163.9	−172.7	−185.2	−195.7	−208.0	−201.8
T range (K)	393–573	409–585	423–599	431–613	440–625	449–537	457–649

where p is the vapor pressure and T the temperature in degree Kelvin.

The vapor pressure for each of the fatty acids in this study was calculated using the Antoine equation:

$$\ln p = a - \frac{b}{T + c}, \tag{4}$$

where a, b and c are the Antoine constants at a given temperature range [5]. Table 6 records ΔH_{evap}, a, b, and c at a given temperature range. Fig. 7 is a plot of ΔH_{evap} vs the number of carbons in the fatty acid. The higher the number of carbons, the greater the ΔH_{evap}. It should be noted that there is a difference between odd and even numbered fatty acids, as seen in Figs. 6 and 7. This is characteristic for many homologous series of organic straight chain compounds undergoing solid state transitions. What is being measured within the zero-order kinetic process is the internal energy, or escaping energy, for vaporization. It is generally related to the enthalpy by the addition of a work term which is about 1 kJ at 100°C.

4. Conclusion

This study indicates that a zero-order process describes the TGA plots for the fatty acids investi-

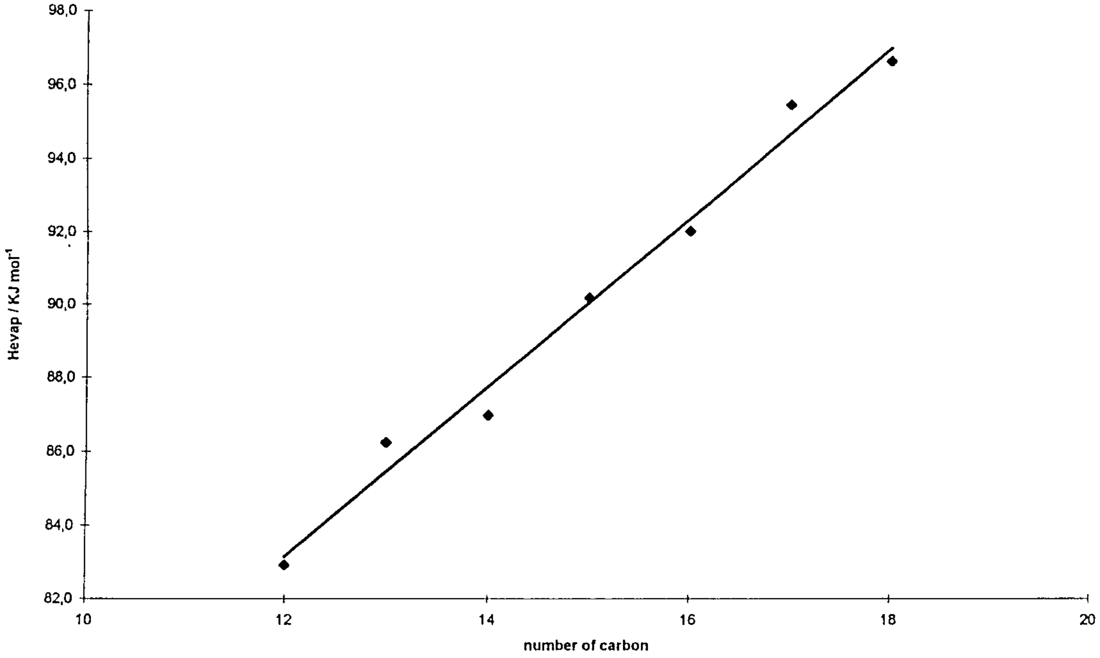

Fig. 7. A plot of latent heat for the evaporation of fatty acids vs the number of carbon with $R^2 = 0.9856$.

gated. The rate of evaporation was determined from the points on the DTG plot, thus providing a simple tool for their investigation. The melting points for the fatty acids are independent of the heating rate employed, however one must be careful that the material being studied has the capacity to keep up with the instrumented heating rate. The E_{act} and ΔH_{evap} calculated in this study are in good agreement and increases as the number of carbons in the fatty acid increases.

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