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A thermal analysis study of methyl salicylate

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Abstract

The evaporation of methyl salicylate is studied using a simultaneous TG–DTA unit. The data are shown to be a zero order rate process. The activation energy calculated from the Kissinger and Ozawa methods as well as from the Arrhenius equations are shown to approximate the latent heat of vaporization calculated from the Clausius–Clapeyron equation. The activation energy values range from 52.5 to 60.4 kJ mol^{-1} for the Kissinger method, 52.2–63.6 kJ mol^{-1} for the Ozawa method and 47.2–50.3 kJ mol^{-1} for the Arrhenius equation. © 2001 Published by Elsevier Science B.V.

Keywords: Evaporation; Methyl salicylate; Kissinger method; Ozawa method; Arrhenius equation

1. Introduction

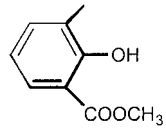
Perfumes have been widely studied using various analytical tools, such as gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) [1,2], infrared (IR) [3], and nuclear magnetic resonance (NMR) [4]. Thermal analysis [5] is an additional tool to study the aging of perfumes in which the sample is heated and the weight changes recorded as a thermogravimetric (TG) signal.

The release rate of a perfume depends on the rate of evaporation. There are several factors which can influence the rate of evaporation, such as vapor pressure, molecular weight, temperature and surface area exposed to the air. The process of evaporation therefore is of central importance to perfumery [6].

Kinetic studies are complex for most reactions involved in thermal methods, but it is important to realize that the rate of change of a specific parameter will depend on the amount of substance reacted and the temperature employed [7]. The kinetic parameters calculated using different methods may have different results. In the present study, the kinetic parameters for the evaporation of methyl salicylate are calculated using the following three methods: Arrhenius, Kissinger, and Ozawa.

2. Experimental

The material used in the present study is methyl salicylate (Lot# 106H08521) which was obtained from Sigma Chemical. The structure of methyl salicylate is shown below:



The instrument used in the present study was a simultaneous TG–DTA unit, TA Instrument model SDT 2960 and the data were analyzed using Universal

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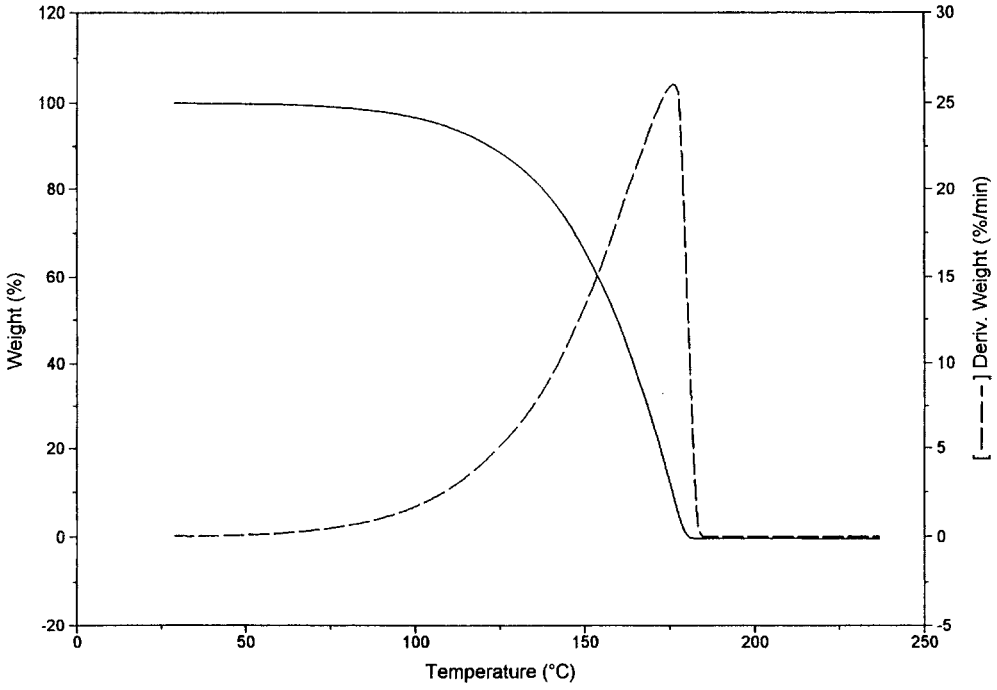

Fig. 1. A plot of TG and DTG signal for methyl salicylate at a heating rate of 10°C min^{-1} using an atmosphere of nitrogen at a flow rate of 100 ml min^{-1}.

Analysis Software, V2.3C. The flow rate was regulated by a J & W Scientific Intelligent Flowmeter, model ADM 1000. The experiments used an atmosphere of nitrogen for various heating and flow rates. The heating rate was varied from 2, 4, 6, 8 and 10°C min^{-1}. The flow rate was varied from 50, 100, 150, 200 and 250 ml min^{-1}.

3. Results and discussion

From the TG and DTG curve, an evaporation process was observed which can be seen in Fig. 1. The evaporation peak temperature at different flow rates and different heating rates is reported in Table 1. From these values, it can be seen that when the heating rate increases, the peak temperature also increased. However, the peak temperature was not influenced by the flow rate. A plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ was used to construct the Kissinger plot which takes the form

$$\frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{0.4567}{R}E(\%) \quad (1)$$

where β is the heating rate, T_p the peak temperature, E the activation energy, and R the gas constant. A plot of

Table 1
Values of peak temperature (T_p) at different flow rates and different heating rates

Heating rate (°C min^{-1})	T_p (°C) at flow rate				
	50 ml min^{-1}	100 ml min^{-1}	150 ml min^{-1}	200 ml min^{-1}	250 ml min^{-1}
2	141.6	139.2	139.7	138.9	137.5
4	156.8	154.9	155.9	155.8	153.1
6	166.5	165.9	165.5	164.3	164.2
8	172.8	171.7	171.3	171.7	172.6
10	178.8	175.9	178.3	177.3	176.9

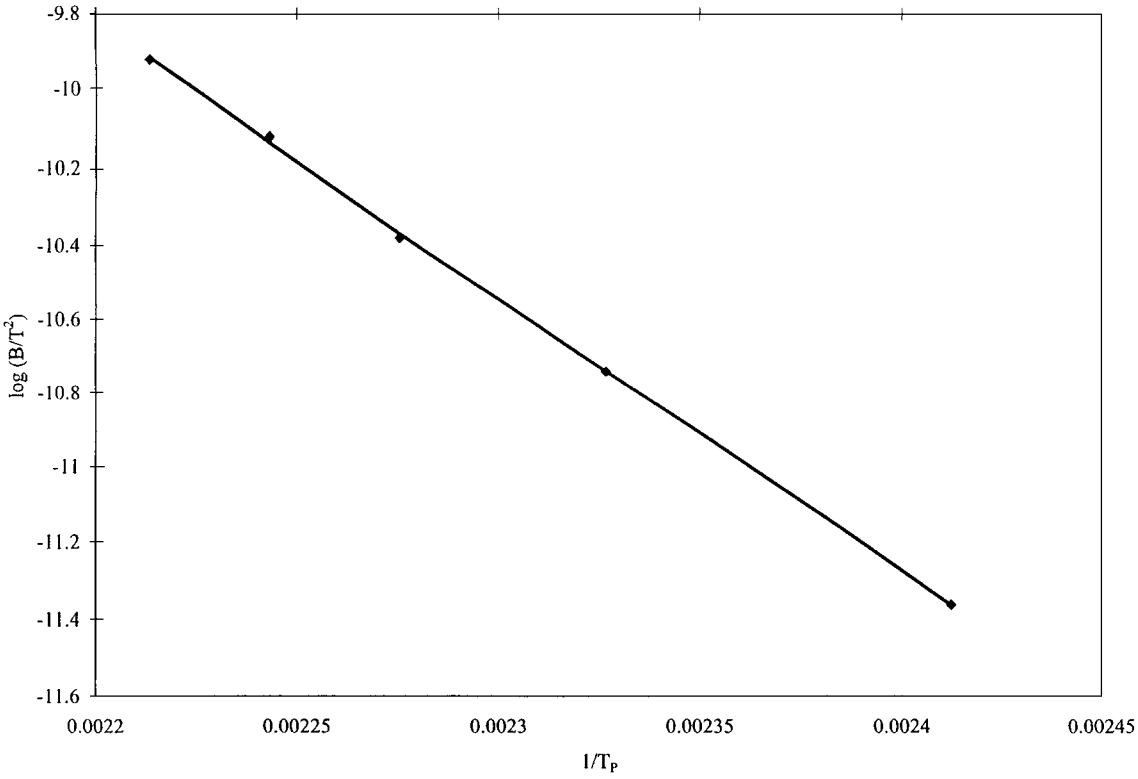

Fig. 2. A Kissinger plot for methyl salicylate using an atmosphere of nitrogen at a flow rate of 100 ml min^{-1}, where $R^2 = 0.9952$, slope $= -7081.3$ and an intercept of 5.8159.

$\ln(\beta/T_p^2)$ versus $1/T_p$ should yield a line whose slope is E/R. A typical Kissinger plot for methyl salicylate is shown in Fig. 2. From the slope, the activation energy at various flow rates can be calculated and the values are reported in Table 2. The results showed that the activation energy at lower flow rates of nitrogen have a greater value than at higher flow rates. The activation energy values range from 52.5 to 60.4 kJ mol^{-1}.

Table 2
Values for E and R^2 obtained from the kissinger method using various flow rates

Flow rate (ml min^{-1})	E (kJ mol^{-1})	R^2
50	60.4	0.9997
100	58.9	0.9952
150	58.3	0.9982
200	57.9	0.9985
250	52.5	0.9984

A plot of $\ln\beta$ versus $1/T$ is used to construct the Ozawa plot which takes the form

$$\frac{d(\ln\beta)}{d(1/T)} = -\frac{E}{R} \quad (2)$$

where β is the heating rate, T the temperature from the various heating rates at the same mass loss, E the activation energy, and R the gas constant. A plot of $\ln\beta$ versus $1/T$ should yield a line with a slope E/R. A typical Ozawa plot for methyl salicylate is shown in Fig. 3. From the slope, the activation energy at various flow rates can be calculated and the values are reported in Table 3. The results showed that the activation energy at a lower flow rate of nitrogen has a greater value than at a higher flow rate. The activation energy values range from 52.2 to 63.6 kJ mol^{-1}. These results are compared to values obtained by the Kissinger method.

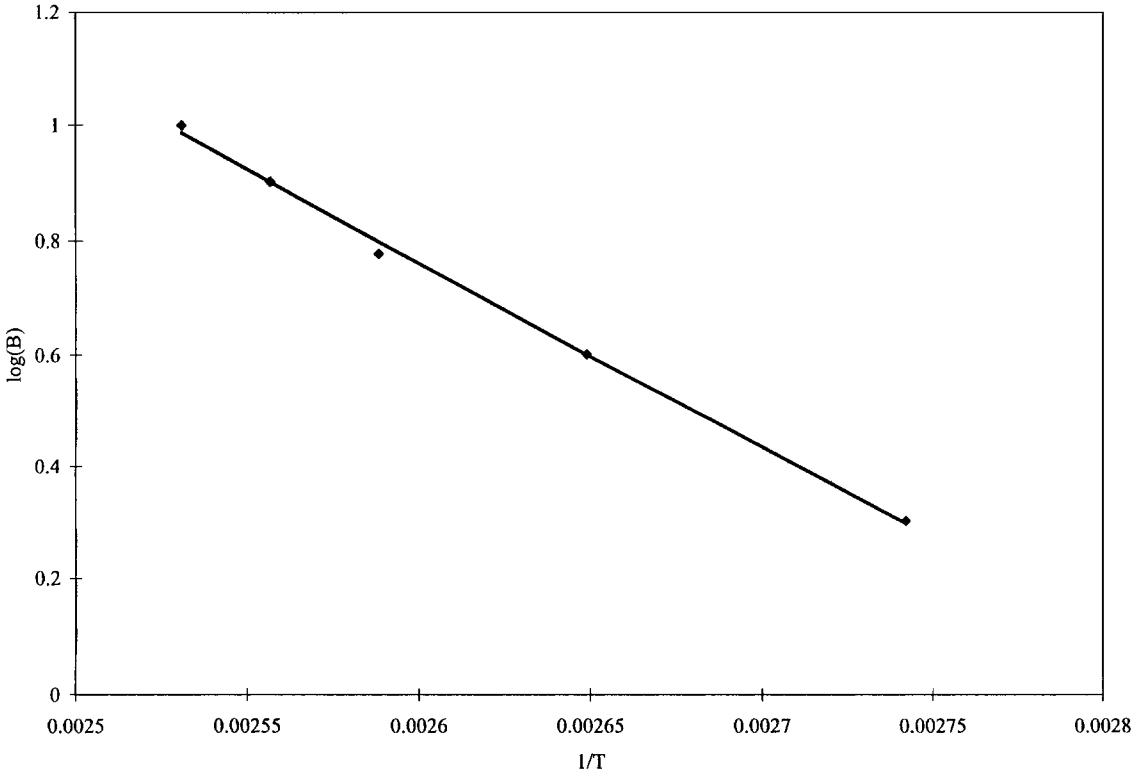

Fig. 3. An Ozawa plot for methyl salicylate using an atmosphere of nitrogen at a flow rate of 100 ml min^{-1}, where $R^2 = 0.9976$, slope = −3316.3 and an intercept of 8.8826.

A plot of $\ln k$ versus $1/T$ is used to construct the Arrhenius plot and takes the form

$$\ln k = \ln A - \frac{E}{RT} \quad (3)$$

where k is the coefficient of evaporation at a specified temperature in milligrams per minute per square-centimeter and T the temperature in Kelvin. A plot of $\ln k$ versus $1/T$ for methyl salicylate can be seen in Fig. 4. From this plot, the Arrhenius parameters, namely the pre-exponential factor (A) and activation energy (E), can be calculated. The values for the activation energy calculated from the Arrhenius equation at different flow rates and different heating rates is reported in Table 4. The activation energy values range from 47.2 to 50.3 kJ mol^{-1}.

The Clausius–Clapeyron equation [8] gave a value of 52.3 kJ mol^{-1} for the latent heat of vaporization

Table 3
Values for the activation energy calculated from the Ozawa method using different flow rates and different heating rates

Flow rate (ml min^{-1})	E (kJ mol^{-1})								
	$T_{0.9}$	$T_{0.8}$	$T_{0.7}$	$T_{0.6}$	$T_{0.5}$	$T_{0.4}$	$T_{0.3}$	$T_{0.2}$	$T_{0.1}$
50	62.9	62.6	62.8	62.9	63.2	63.4	63.5	63.6	63.6
100	59.6	60.0	60.4	60.9	61.3	61.7	62.1	62.3	62.6
150	52.2	58.2	59.2	59.9	60.4	60.9	61.3	61.6	61.9
200	57.0	57.8	58.5	59.1	59.6	60.1	60.4	60.8	63.6
250	53.1	55.2	56.2	56.9	57.2	57.7	57.9	58.2	58.4

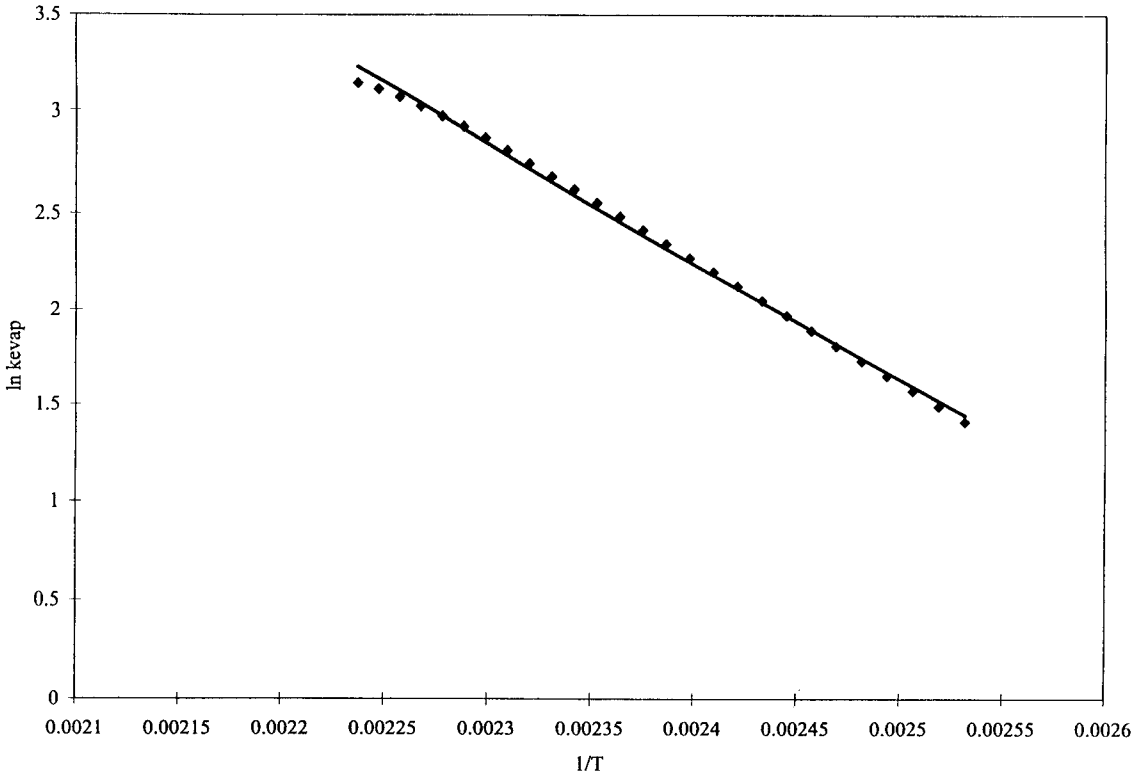

Fig. 4. A plot of $\ln k$ versus $1/T$ at a heating rate of 10°C min^{-1} using an atmosphere of nitrogen at a flow rate of 100 ml min^{-1}, where $R^2 = 0.9971$, slope $= -6053.5$ and an intercept of 16.767.

Table 4
Values for the activation energy calculated from the Arrhenius equation using different flow rates and different heating rates

Heating rate (°C min^{-1})	E (kJ mol^{-1}) at flow rate				
	50 ml min^{-1}	100 ml min^{-1}	150 ml min^{-1}	200 ml min^{-1}	250 ml min^{-1}
2	49.8	48.5	47.7	47.5	47.2
4	49.2	49.5	49.2	48.2	48.3
6	49.6	49.4	49.4	48.4	48.3
8	50.0	49.7	48.6	49.6	47.7
10	49.3	50.3	48.7	49.8	48.3

(ΔH_{vap}). Thus, the activation energy approaches the latent heat of vaporization.

4. Conclusions

The rates of evaporation for methyl salicylate were calculated from the Kissinger and Ozawa method as well as from the Arrhenius equation. The Kissinger and Ozawa methods seem to be very simple because the kinetic data can be obtained from a single point along the curve. The results from the Kissinger and Ozawa methods show that the activation energy at lower nitrogen flow rates has a greater value than at higher flow rates. The evaporation process for methyl salicylate is a non-activated kinetic process and the system is in equilibrium at all stages of evaporation.

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