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A thermal analysis study of myristic acid

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Abstract

The evaporation of myristic acid [$CH_3(CH_2)_{12}COOH$] was investigated using a simultaneous TG–DTA unit over a temperature range of ambient to 300°C, in a flowing atmosphere of nitrogen at heating rates of 2, 4, 6, 8, 10, 15 and 20°C/min. The flow rates were varied from 50 to 350 ml/min. Kinetic plots for zero-order processes were constructed based on the Arrhenius equation and the Freeman and Carroll method. The activation energy for the evaporation process calculated from two methods was reported. The relationship between the rate of mass loss and the vapor pressure for myristic acid was estimated using the Langmuir and Antoine equations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Myristic acid; Thermal analysis; Freeman and Carroll method; Vapor pressure

1. Introduction

Myristic acid is one of the saturated long chain carboxylic acids which are used in many areas of daily life and industry. Many commercial products contain fatty acids, and they are often subjected to thermal treatment during processing, storage and preparation. Therefore, the study of the thermal behavior of fatty acids is of importance [1].

Evaporation is the transition from the liquid phase to the vapor phase, without a change in chemical composition. It can be monitored by determining the rate of mass loss as the substance goes through the transition. This is easily achieved with a rising temperature program, using thermogravimetry, where the amount of material lost is monitored as the substance undergoes programmed heating in a controlled atmosphere [2].

The Arrhenius equation, Eqs. (1) and (2), can be used for the kinetic analysis of the evaporation process.

$$k_{\mathrm{evap}} = A \exp\left(\frac{-E_{\mathrm{act}}}{RT}\right) \quad (1)$$

or

$$\ln k_{\mathrm{evap}} = \ln A - \frac{E_{\mathrm{act}}}{RT} \quad (2)$$

where k_{evap} is the coefficient of evaporation per unit area, A the Arrhenius parameter, 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. Therefore, a plot of $\ln k_{\mathrm{evap}}$ against $1/T$ will produce E_{act} as the slope × R. This treatment follows from the assumption that the process is zero order. For the evaporation process:

$$k_{\mathrm{evap}} = \frac{(\mathrm{d}m/\mathrm{d}t)}{A} \quad (3)$$

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where A is the cross-sectional area of the crucible. In the present study, more than 20 points for myristic acid were collected from a printout of the DTG data, and then a plot of k_{evap} against $1/T$ was constructed. The analysis is reported in the discussion of the results.

The Freeman and Carroll method was one of the earliest and perhaps the most widely used methods to describe reaction kinetics to TG data. The equation used for kinetic analysis is [3]:

$$\frac{-(E/2.303R)\Delta(1/T)}{\Delta\log w_{\mathrm{r}}} = -n + \frac{\Delta\log(\mathrm{d}w/\mathrm{d}t)}{\Delta\log w_{\mathrm{r}}} \tag{4}$$

where w_{r} is the difference between the mass loss at the completion of the reaction and the mass loss w up to time t. The equation predicts that a plot of $[\Delta\log(\mathrm{d}w/\mathrm{d}t)/\Delta\log w_{\mathrm{r}}]$ against $[\Delta(1/T)/\Delta\log w_{\mathrm{r}}]$ would give a straight line relation of slope $-E/2.303R$ and an intercept n, which is the order of the process. The method possessed the advantage that it did not pre-identify the value of n.

Vapor pressure (p) is the force per unit area exerted by a gas that is in equilibrium with its solid or liquid. For example, vapor pressures are among the most important parameters in modeling the environmental fate of chemicals. Recently, many researchers reported vapor pressure estimation methods that used thermogravimetry [4–6]. Those methods are based on the Langmuir equation for evaporation [7]:

$$J = \frac{\mathrm{d}m}{\mathrm{d}t\,A} = p\alpha\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{5}$$

where J is the mass flux in kg s^{-1} m^{-2}, the rate of mass loss per unit area, p the vapor pressure of sample in Pa, M the molecular weight in kg mol^{-1}, R the gas constant in J K^{-1} mol^{-1}, T the absolute temperature in K, and α the evaporation coefficient, the deviation between an observed evaporation rate and the theoretical maximum rate [8].

The current paper presents a method for the estimation of relationship between the vapor pressure and the rate of mass loss that is based on the Langmuir equation and the Antoine equation. Rearranging the Eq. (5), the Langmuir equation can be expressed as the following form:

$$p = kv \tag{6}$$

where k is $(2\pi R)^{1/2}/\alpha$ and v is $(\mathrm{d}m/\mathrm{d}t\,A)(T/M)^{1/2}$. The temperature dependence of the vapor pressure can be obtained using the Antoine equation:

$$\log p = A - \frac{B}{C+T} \tag{7}$$

where A, B and C represent the Antoine constants [9]. Therefore, it is possible to estimate the value of k by plotting p against v.

2. Experimental

The myristic acid samples used in the present study were acquired from Aldrich (99.5+%). The data for the kinetic analysis of myristic acid were obtained using a simultaneous TGA–DTA 2960. The samples were placed in a platinum crucible with the cross-section area of 0.104 cm^2. An empty platinum crucible of the equivalent size was used as a reference. Rising temperature programs were performed on myristic acid at various heating rates, which were 2, 4, 6, 8, 10, 15 and 20°C/min. 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

Based on the TG–DTG data obtained, the study consists of three parts:

1. Determination of the activation energy of evaporation process for myristic acid using the Arrhenius equation.
2. Determination of the activation energy and the order of evaporation process for myristic acid using the Freeman and Carroll method.
3. Estimation of the relationship between the rate of mass loss and the vapor pressure for myristic acid using the Langmuir equation and the Antoine equation.

The overall picture for myristic acid investigated is its evaporation. Fig. 1 represents the TG and DTA plots for myristic acid at a heating rate of 8°C/min as an example. The TG data shows that all materials were lost and there is no remaining residue. The two

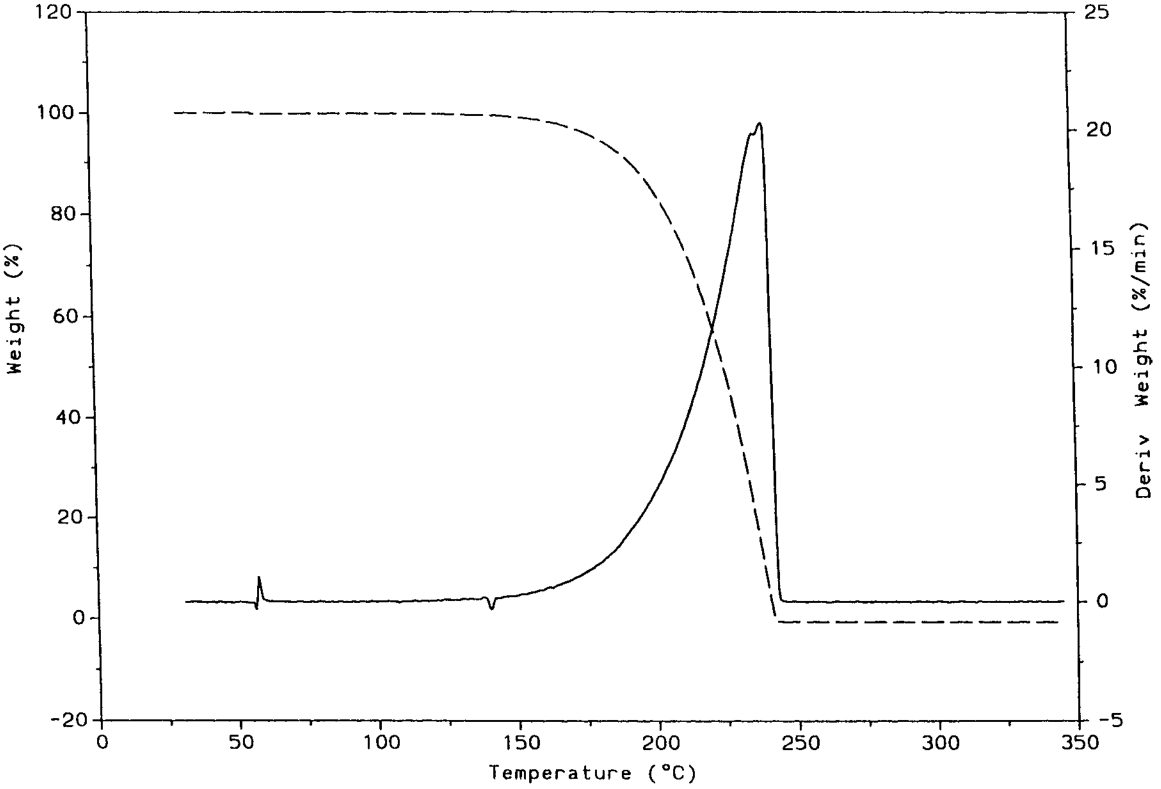

Fig. 1. TG and DTG curves for myristic acid at a heating rate of 8°C/min under an atmosphere of nitrogen (100 ml/min).

processes of melting at a lower temperature and evaporation at a higher temperature can be seen on the DTA plot as endothermic processes for myristic acid in this study.

Fig. 2 shows the plot of $\ln k_{\mathrm{evap}}$ against $1/T$ for myristic acid studied. It can be seen that the Arrhenius plot constructed from the DTG values yields a straight line, in which E_{act} can be calculated from the slope and

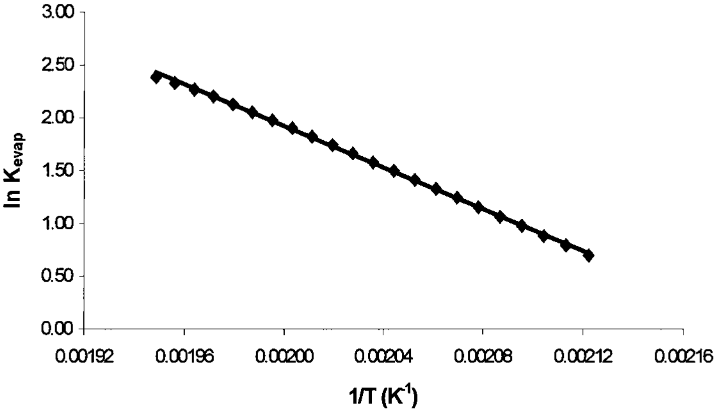

Fig. 2. Plot of the natural log of the rate constant for the evaporation of myristic acid versus the inverse of the temperature in K (heating rate 8°C/min, flow rate 100 ml/min N_2).

Table 1
E_{act}, $\ln A$ and R^2 obtained from the Arrhenius plot using different heating rates (β) for myristic acid under an atmosphere of 100 ml/min N_2

β (°C/min)	E_{act} (kJ mol^{-1})	$\ln A$	R^2
2	80.5	21.2	0.997
4	80.7	21.2	0.997
6	80.8	21.3	0.998
8	80.2	21.2	0.997
10	79.4	20.9	0.997
15	79.3	21.0	0.997
20	79.7	21.1	0.996

Table 2
E_{act}, $\ln A$ and R^2 obtained from the Arrhenius plot using different flow rates of dry N_2 and a heating rate of 8°C/min for myristic acid

Flow rate (ml/min)	E_{act} (kJ mol^{-1})	$\ln A$	R^2
50	81.2	21.5	0.998
100	80.1	21.1	0.999
150	78.4	20.8	0.997
200	79.5	21.1	0.998
250	78.4	20.9	0.998
350	78.6	20.8	0.997

Table 3
E_{act}, n and R^2 obtained from the Freeman and Carroll method using different heating rates (β) for myristic acid under an atmosphere of 100 ml/min N_2

β (°C/min)	E_{act} (kJ mol^{-1})	n	R^2
2	87.7	0.11	0.998
4	86.1	0.09	0.998
6	85.1	0.07	0.998
8	86.6	0.10	0.999
10	85.5	0.11	0.999
15	86.0	0.11	0.999
20	86.8	0.11	0.999

Table 4
E_{act}, n and R^2 obtained from the Freeman and Carroll method using different flow rates of dry N_2 and a heating rate of 8°C/min for myristic acid

Flow rate (ml/min)	E_{act} (kJ mol^{-1})	n	R^2
50	87.0	0.09	0.999
100	85.3	0.15	0.997
150	84.8	0.10	0.999
200	84.7	0.08	0.999
250	86.7	0.13	0.999
350	86.5	0.12	0.997

$\ln A$ is equal to the intercept. The E_{act}, $\ln A$ and R^2 at different heating rates and flow rates are listed in Tables 1 and 2. Fig. 3 is a plot of $[\Delta\ln(\mathrm{d}w/\mathrm{d}t)/\Delta\ln w_r]$ against $[\Delta(1/T)/\Delta\ln w_r]$. The plot based on Freeman and Carroll's mathematical analysis also yields a straight line for myristic acid, in which E_{act} can be obtained from the slope and the order of reaction is equal to the intercept. The E_{act}, n and R^2 are reported in Tables 3 and 4. It is found that the heating rate and flow rate performed in this study do not seem to

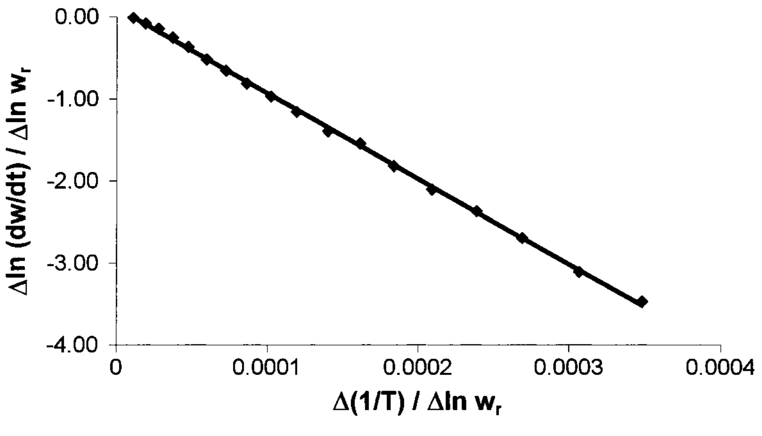

Fig. 3. Freeman and Carroll's mathematical analysis of TG and DTG data for the evaporation of myristic acid (heating rate 8°C/min, flow rate 100 ml/min N_2).

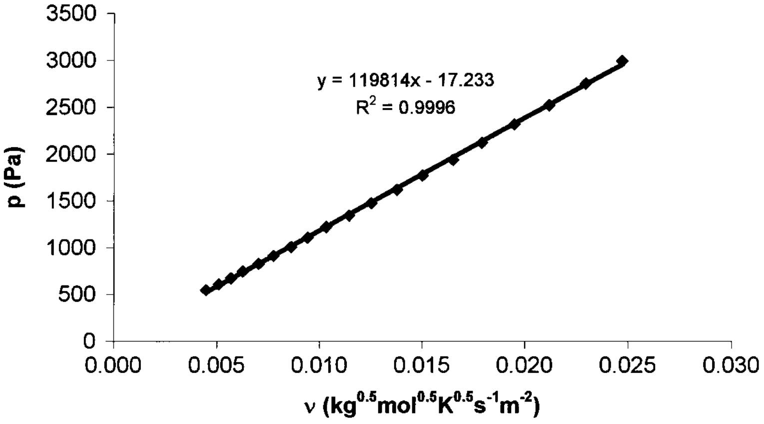

Fig. 4. Relationship between vapor pressure (p) and v for myristic acid.

significantly effect the activation energy of evaporation process for myristic acid, and the evaporation process is considered as a zero-order process.

Evaporation rates are determined from the rate of sample mass loss per unit cross-section area at various temperatures. Vapor pressures corresponding to various temperatures are calculated using the Antoine equation with $A = 6.78583$, $B = 2143.4$, and $C = -143.27$. A plot of vapor pressure (p) against v for myristic acid is then constructed as shown in Fig. 4. It is apparent from the plot that the relationship between the vapor pressure (p) and v is linear, which gives $p = 1.20 \times 10^5 v$ with $R^2 = 0.9996$.

With this relation of p and v we can estimate the latent heat (ΔH_{evap}) of evaporation process using thermogravimetric data by combining Eq. (6) with the Clausius–Clapeyron equation:

$$\ln p = c - \frac{\Delta H_{\text{evap}}}{RT} \tag{8}$$

which gives:

$$\ln v = c' - \frac{\Delta H_{\text{evap}}}{RT} \tag{9}$$

Within a certain temperature range, ΔH_{evap} may be a constant and can be found from the slope by plotting $\ln v$ against $1/T$. Fig. 5 is such a plot with $R^2 = 0.998$ for myristic acid at the heating rate of 2°C/min under an atmosphere of 100 ml/min N_2. The latent heat of evaporation process (ΔH_{evap}) obtained from the slope

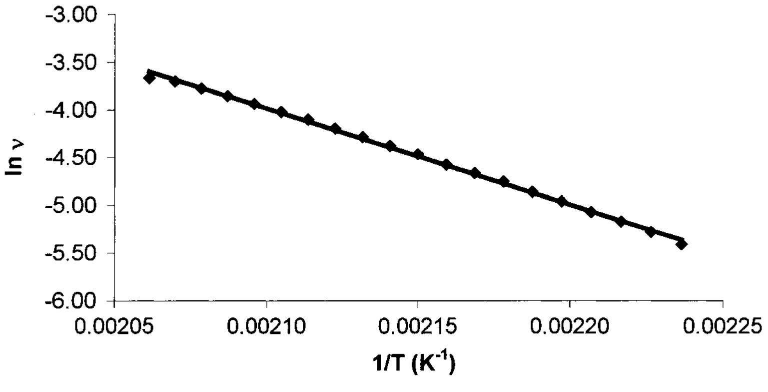

Fig. 5. Plot of the natural log of v for the evaporation of myristic acid versus the inverse of the temperature in K.

of the plot is equal to 83.77 kJ/mol, which is in good agreement with the literature value of 84.77 kJ/mol calculated from the vapor pressure data [9].

4. Conclusion

This study indicates that a zero-order process describes the TG plots for myristic acid. The Freeman and Carroll method is being used as an approach for calculating the kinetic parameters for the evaporation process and has been proven to be a practical and reliable method. It is possible to estimate the relationship between vapor pressure and evaporation rate from thermogravimetric methods. Moreover, this method for determining the latent heat of evaporation process via the evaporation rate yields good results. Both of these techniques may be also applied to other long chain acids.

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