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Model-free kinetics applied to the vaporization of caprylic acid

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Abstract The evaporation of octanoic (caprylic) acid was investigated by means of thermogravimetric analysis (temperature range: 300–600 K) under a nitrogen dynamic atmosphere (heating rates: 0.16, 0.31, 0.63, 1.25, 2.5, 5 and 10 K min^{-1}). Kinetic plots for a zero-order process were constructed based on the Arrhenius equation. The activation energy for the evaporation process was calculated via both the Arrhenius plot and Vyazovkin's isoconversional model-free method.

Keywords Caprylic acid · Model-free kinetics · Vaporization

Introduction

The use of fatty acids is widely accepted in the food industry [1]. Many foods contain these acids, and they are often subjected to thermal treatment during processing, storage and preparation. The purpose of this study was to estimate the vaporization enthalpy of a saturated organic acid (octanoic acid) using dynamic thermoanalytical techniques.

One classic method for determining vaporization enthalpies is to use a Calvet-type microcalorimeter [2–4], where a liquid sample contained in a small thin glass capillary tube sealed at one end is dropped at room temperature into the hot reaction vessel in the microcalorimeter maintained at a specific temperature and removed from the hot zone by vacuum vaporization. As the experimental heat flow does not directly provide the vaporization enthalpy of the liquid, additional assays must be performed. Accordingly, thermal corrections for the glass capillary tubes are determined in separate experiments, being reduced as far as possible by dropping tubes of nearly equal mass into each of the twin calorimeter cells.

Another technique used to measure the thermodynamic properties of substances is gas chromatography [5, 6], in which the plot of ln $(1/t_r)$ versus T^{-1}, where t_r is the retention time corrected for the dead volume, results in a straight line whose slope, when multiplied by the gas constant, affords $\Delta_{\text{sol}}^{\text{g}}H_{\text{m}}$. A modification of this technique was described in 1995 [7]. These modifications eliminate the need for calorimetric measurements and generally simplify the experimental aspects of the procedure. In the case where compounds are properly selected with regards to molecular structure, plotting $\Delta_{\text{sol}}^{\text{g}}H_{\text{m}}$ against the known vaporization enthalpy at temperature T also affords a straight line. The equation of this line can be used to evaluate the unknown vaporization enthalpy of any structurally related material provided that the unknown is analyzed at the same time as the standards. The advantages of this method are its speed and accuracy and the small sample sizes required. In addition, whereas most thermochemical measurements require purities in excess of 99%, there is no minimum purity requirement for this method.

Transpiration studies are another way of obtaining enthalpies [8, 9]. This method is performed in a heated tube

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containing a finely powdered sample mixed with glass pellets and connected to a cooled trap, a flow of nitrogen being slowly passed through the tube. The amount of condensed product is determined by gas chromatography using an internal standard. The vapour pressure at the saturation temperature and the molar enthalpy of vaporization is calculated from the linear correlation of the logarithm of the concentration of the sample versus T^{-1}.

Vaporization enthalpies can also be obtained from pressure and boiling temperature data using the Clausius–Clapeyron equation,

$$\ln P = B - (A/T). \tag{1}$$

Assuming that the vapour behaves as an ideal gas, the plot of log P versus $1/T$ results in a straight line with a slope of $-\Delta H_v/2.303R$, where ΔH_v represents the enthalpy of vaporization, assumed to be constant over the measured temperature range, and R is the ideal gas constant [10].

There is a large dispersion in the data on enthalpies of vaporization, even when they are obtained by means of classical methods. Thus, the accuracy and reliability of numerous values reported in the literature are questionable. In these cases, the estimation methods provide some rational values in cases when experimental data are lacking and also screen the reliability of the data when such data are available [7, 11].

The employment of dynamic thermoanalytical techniques in the experimental determination of both melting and vaporization enthalpies has been widely reported in the literature [12–20]. These techniques are considered to be quite satisfactory and several studies are available in which the values obtained by thermoanalytical methods are compared with those obtained by classical methods in the laboratory. The use of these techniques in the study of boiling processes presents problems such as vapour-liquid equilibrium and the control of atmospheric pressure. In order to avoid evaporation and to ensure equilibrium conditions, experiments may be carried out including a solid in contact with the liquid [21]. Using this method, both vaporization enthalpy and boiling temperature were satisfactory obtained for palmitic acid using the DSC technique with addition of α-alumina in contact with the acid [22].

Thermogravimetric analysis has been used to determine the kinetics of evaporation for different substances [23–26]. The shape of the thermogravimetric curve is a function of the reaction kinetics and can hence be used to evaluate kinetic parameters for reactions involving mass changes. Evaporation is the transition from the liquid to the vapour phase, without any change in chemical composition. Thus, in an evaporation process, the product of reaction may be assumed to be similar to the activated state. In this limit case, the activation energy (E) for the vaporization process will approach the latent heat of vaporization [27, 28]. Since an evaporation process is a zero-order reaction, kinetic analysis can be performed by applying the Arrhenius equation. However, kinetic analysis typically performed by means of thermogravimetic curves implies more complex reactions that usually include overlapped multi-step processes. In these cases, the kinetic order, which depends on the reaction mechanisms, is normally unknown. One way of solving this problem is to use kinetic analysis based on isoconversional (model-free) methods. These kinds of methods allow evaluation of the effective activation energy as a function of the process extent without assuming any predetermined reaction mechanism [29].

In this paper, the vaporization process of caprylic acid is used to prove two related assumptions: (i) isoconversional methods are also useful to study elemental thermal processes, and (ii) the vaporization enthalpy of volatile liquids by kinetic methods.

Experimental

Materials

The octanoic acid was of reagent grade (Aldrich) and was used without further purification. Thermogravimetric analyses were performed on a Mettler TA 4000 system, Model TG50. A stream of nitrogen at a flow rate of 50 mL min^{-1} was used as inert atmosphere, within a temperature range from 300 to 600 K, accurate to ±0.2 K and under atmospheric pressure. Experiments were carried out at seven different heating rates (0.16, 0.31, 0.63, 1.25, 2.5, 5 and 10 K min^{-1}). The samples of octanoic acid, with a mass of 28 ± 2 mg, were placed in open aluminum crucibles of 100 μL (ME-51119872). Each experiment was replicated five times.

Determination of kinetic parameters

The rate of heterogeneous reactions can be described by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{2}$$

where t is time, $k(T)$ is a temperature-dependent constant and $f(\alpha)$ is a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction, α. In a TG experiment, in which we obtained the variation in mass versus temperature, the extent of reaction is calculated using the following equation:

$$\alpha = \frac{(m_i - m_t)}{(m_i - m_f)} \tag{3}$$

where m_i and m_f are the initial and final masses, respectively, and m_t is the mass at the specific time t.

There are many methods for analysing kinetic data based on Eq. 1 [30]. These methods may be classified into model-fitting and isoconversional (model-free) methods in accordance with the mathematical analysis employed.

In the model-fitting method, the term $f(\alpha)$ is determined by fitting various reaction models to experimental data. Subsequently, $k(T)$ can be evaluated by the form of $f(\alpha)$ chosen. The term $f(\alpha)$ can be obtained from the tables of different mechanisms. In the present case, we studied an evaporation process that is a zero-order reaction and $f(\alpha)$ is equal to one. Hence, $k(T)$ is equal to $\mathrm{d}\alpha/\mathrm{d}t$. The rate of evaporation is represented by $\mathrm{d}m/\mathrm{d}t$. For zero-order processes, the constant $k(T)$ can be calculated by dividing $\mathrm{d}m/\mathrm{d}t$ by the cross-sectional area of the crucible used for the sample. Then, when $k(T)$ is known, the Arrhenius equation can be applied

$$k(T) = Ae^{-E/RT} \tag{4}$$

or

$$\ln k(T) = \ln A - \frac{E}{RT} \tag{5}$$

where A is the pre-exponential factor, E the activation energy, and R the gas constant. Therefore, a plot of $\ln k(T)$ versus $(1/T)$ will produce E as the slope × R.

Model-free isoconversional methods allow the activation energy to be estimated as a function of α without choosing the reaction model. The basic assumption of these methods is that the reaction rate are constant extent of conversion α depends solely on temperature [31–34]. Hence, constant E values can be expected in the case of single state decomposition (as is the case of an evaporation process), while in a multi-step process E varies with α due the variation in the relative contributions of each single step to the overall reaction rate.

Considering that the experiments are performed at a constant heating rate, the rate of the process can be described by

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} e^{-E/RT} f(\alpha). \tag{6}$$

There are several isoconversional methods that can be used. To use these methods, a series of experiments was conducted at different heating rates [35, 36].

Vyazovkin et al. developed an isoconversional method which allows both simple and complex reactions to be assessed [37]. Integrating α up to conversion, Eq. 4 gives

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} e^{-E/RT}\mathrm{d}T. \tag{7}$$

Since $E/RT \gg 1$, the temperature integral can be approximated by

$$\int_{T_0}^{T} e^{-E/RT}\mathrm{d}T \approx \frac{R}{E} T^2 e^{-E/RT}. \tag{8}$$

Substituting the temperature integral and taking the logarithm gives

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha}. \tag{9}$$

To apply the method, it is necessary to obtain at least three different heating rates (β), the respective conversion curves thus being evaluated from the measured TG curves. For each conversion (α), $\ln\left(\beta/T_\alpha^2\right)$ plotted against $1/T_\alpha$ gives a straight line with slope $-E_\alpha/R$, thus obtaining the activation energy as a function of the conversion.

Results and discussion

The TG curve represents the loss of mass with respect to temperature and time. The obtained curves for the different heating rates are ordered, as expected, in accordance with the heating rate; higher heating rates thus led to vaporization occurring at higher temperatures (Fig. 1).

The activation energy of the process (E) was estimated as a function of the heating rate using both model-fitting for zero-order reactions and Vyazovkin's model-free kinetics.

Figure 2 shows the representation of $\ln k_{\mathrm{vap}}$ versus $1/T$, plotted from the data obtained from the DTG curves. The represented values correspond to the range of temperatures prior to the inflection point on the DTG curve so as to ensure a good coefficient of linear regression in the resulting straights lines ($R^2 \geq 0.995$). The activation energies $E = -(\mathrm{slope}/R)$ were then calculated from the slope of each line. Simple visual inspection indicates that

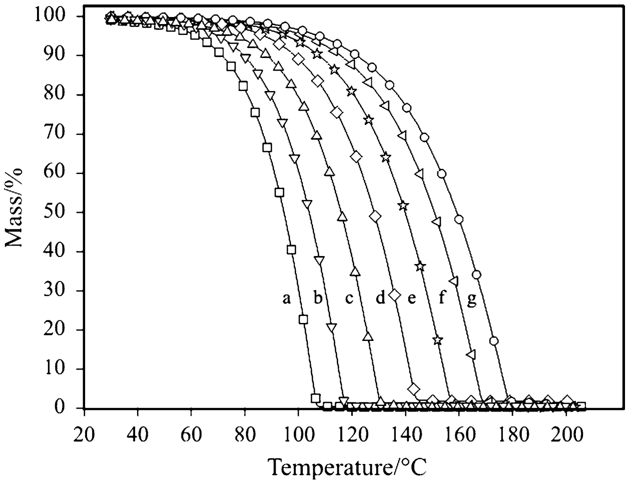

Fig. 1 TG curves obtained at different heating rates (0.16, 0.31, 0.63, 1.25, 2.5, 5 and 10 K min^{-1}) ordered from minimum (*left*) to maximum (*right*) heating rate

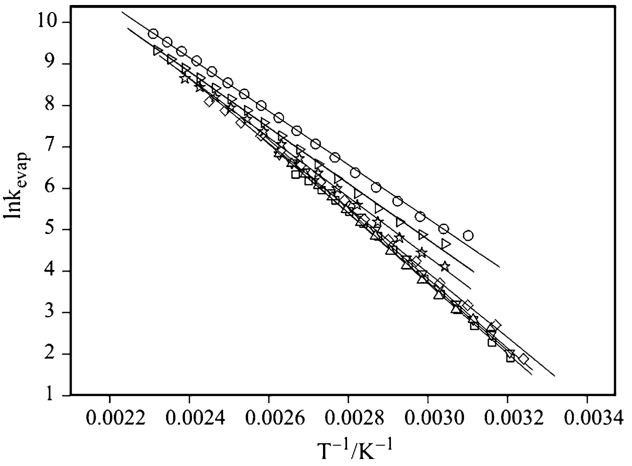

Fig. 2 The rate constant Neperian logarithm for the evaporation of octanoic acid versus the inverse of the temperature at different heating rates (for symbols, see Fig. 1)

Table 1 Activation energy (E) obtained from the Arrhenius plot using different heating rates (hr)

hr (K min^{-1})	0.16	0.31	0.63	1.25	2.5	5	10
E (kJ mol^{-1})	70.1	69.7	69.0	64.7	59.7	56.2	53.9

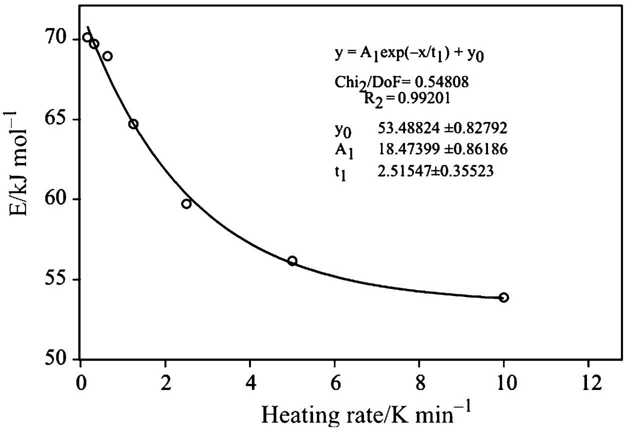

Fig. 3 Activation energy (obtained from Fig. 2) versus heating rate

Table 2 Vaporization enthalpy (ΔH_v) data for octanoic acid

ΔH_v (kJ mol^{-1})	Procedure	Reference
81.0 ± 0.6	Transpiration	[38]
82.9 ± 1.0	Effusion and torsion	[39]
81.2	Gas chromatography	[7]
85.3	Vapor pressure data	[40]
79.8 ± 0.6	Transpiration	[38]
66.6	Calculated from the vapor pressure data reported by the method of least squares	[41]
74.4	Ebulliometry and calculated from the vapor pressure data reported by the method of least squares	[40]
80	Ebulliometry and calculated from the vapor pressure data reported by the method of least squares	[42]
70	Isoteniscope	[43]

Table 3 Activation energy (E) at half-conversion, obtained from Vyazovkin's isoconversional method using a variable number of different heating rates (nhr)

nhr	3	4	5	6	7
E (kJ mol^{-1})	74 ± 11	73 ± 7	73 ± 4	74 ± 3	74 ± 1

these straight lines are not parallel; evidently, the calculated activation energy values are influenced by the experimental heating rate used in their estimation (Table 1). This finding is not surprising, as the application of the Arrhenius equation implies that the system is at thermodynamic equilibrium, which is truer at slow heating rates. Figure 3 shows the obtained variation in E values versus the heating rate. As can be seen, this curve can be fitted to an exponential decay ($R^2 = 0.992$). Extrapolating this curve to zero, we obtained a value of 72 kJ mol^{-1} (corresponding to a zero heating rate). This datum is in good agreement with the caprylic acid vaporization enthalpy (determined by ebulliometry) compiled in the "Handbook of the Thermodynamics of Organic Compounds" [40], although a great dispersion exists depending on the method used for their determination (see Table 2).

Vyazovkin's model-free kinetics, on the other hand, requires at least three dynamic curves with different heating rates. In the present study, the TG curves were obtained employing seven different heating rates (see Fig. 1). The experimental TG curves were then used to construct the respective conversion curves, which were employed to calculate the apparent activation energy of the process following Vyazovkin's method. This calculation was performed using all the experimental data grouped at three, four, five, six or seven different heating rates. Table 3 shows the E-values obtained at half-conversion (50%). Their value is almost independent of how many experimental TG-curves are used in the analysis; only the dispersion of the results improves if more curves are used. Figure 4 shows the activation energy as a function of the degree of vaporization (all the experimental data are used). This curve has a decerelatory shape especially at low conversions when the temperature of evaporation is not stabilised, as should be expected for nonisothermal processes where the enthalpies of vaporization are inversely related to temperature [44]. The apparent value of activation energy of the process of vaporization of octanoic acid decreases as the reaction extent increases, reaching a value

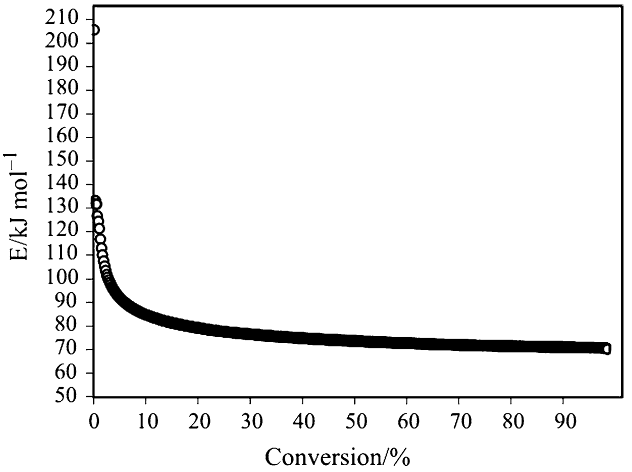

Fig. 4 Vyazovkin's method: activation energy (obtained from all seven experimental TG curves) versus conversion

of 74 ± 1 kJ mol^{-1} for half-conversion, a similar datum to the average value in the lineal variation zone (73 kJ mol^{-1}, 35–95% conversion).

Conclusions

The activation energy of a vaporization process provides an approximation of the latent heat of vaporization. The present study indicates that the activation energy obtained by direct application of the Arrhenius equation in the kinetic analysis for a zero-order process (as is the evaporation of caprylic acid) depends on the heating rate. However, the application of Vyazovkin's model-free method affords the activation energy directly. We propose kinetic model-free methods as a useful tool for studying dynamic processes involved in vaporization in complex volatile liquids.

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