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A TG–DTA study of the sublimation of nicotinic acid

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Abstract

The Langmuir equation was used to construct vapor pressure curves for the sublimation phase of nicotinic acid. Three different approaches were used to calculate the pressure values. In the first, the 'k' term of the Langmuir equation was eliminated by comparing the sample with the reference compound, in the second, the actual values of the 'k' term were used and in the third approach, the 'k' term was kept constant. The vapor pressure curve constructed using the actual values of 'k' was in close agreement with the first. This indicates that the 'k' term of the Langmuir equation cannot be assumed to be constant and the systematic variation in the values of the 'k' term with temperature has to be taken into consideration.

Keywords: TG–DTA; Nicotinic acid; Langmuir equation

1. Introduction

Nicotinic acid is an essential dietary vitamin, the deficiency of which leads to Pellagra. Pellagra is characterized by signs and symptoms associated with the skin, the gastrointestinal tract and the central nervous system. The physiologically active form of nicotinic acid is nicotinamide adenine dinucleotide (NAD) or its phosphate (NADP). Both NAD and NADP function as coenzymes for a wide variety of proteins that catalyze oxidation reduction reactions essential for tissue respiration [1].

Chemically nicotinic acid is pyridine-3-carboxylic acid. It occurs as a white crystalline powder. It has a solubility of 1 in 60 in water at room temperature and is freely soluble in boiling water, alcohol, alkali hydroxides and carbonates. Nicotinic acid melts at 236.6 °C, without decomposition [2]. Nicotinic acid exhibits a reversible solid–solid transition at about 182 °C. There is no weight change associated with this transition and so it can be seen only on the DTA plot (Fig. 1) [3]. This is followed by a dual sublimation and evaporation phase.

Sublimation may be defined as the loss of mass from the solid phase to the vapor phase without any change in the chemical composition of the substance. Nicotinic acid sublimes in the range of about 220–236 °C [4]. The vapor pressure of a substance may be defined as the pressure of the vapor in equilibrium with its condensed phase at a specified temperature. A plot of pressure against temperature gives us the vapor pressure curve. TG–DTA has been used in calculating vapor pressures for a number of different compounds. This method of vapor pressure determination uses the Langmuir equation [5,7–9].

The Langmuir equation defines vaporization in vacuum as

$$\frac{\mathrm{d}m}{\mathrm{d}t} = P\alpha\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{1}$$

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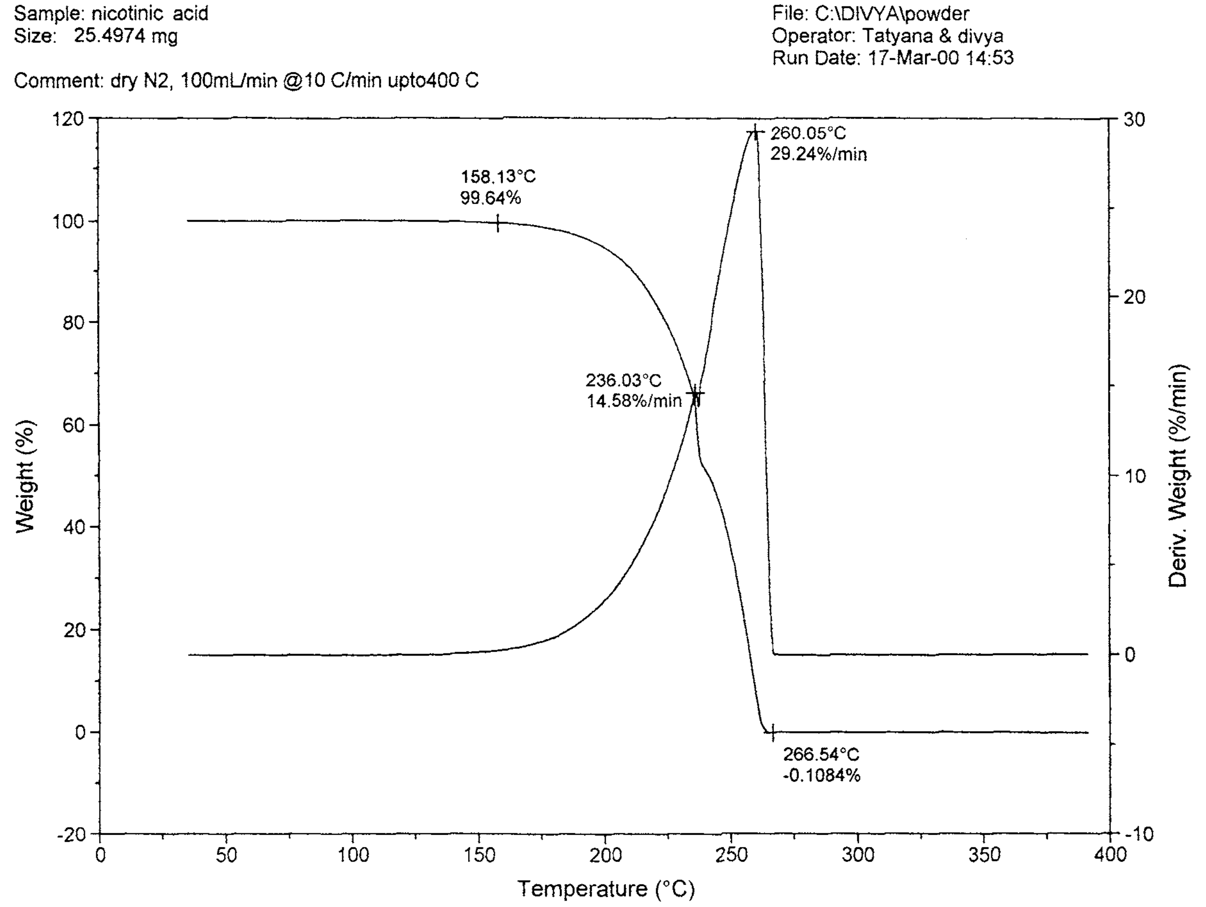

Fig. 1. TG–DTA plot of nicotinic acid.

where dm/dt is the rate of loss of mass; P the pressure; α the vaporization constant; T the absolute temperature; R the universal gas constant; M the molecular weight of the compound (all terms are expressed in the respective SI units).

According to Langmuir, the vaporization constant (α) is independent of the substance undergoing vaporization, provided the vapor is not associated. The value of α is stipulated to be equal to 1 in vacuum. The Langmuir equation can then be rearranged to constitute a material dependent and a material independent term.

$$P = [\alpha^{-1}(2\pi R)^{1/2}]\left[\left(\frac{T}{M}\right)^{1/2}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)\right] = kv \qquad (2)$$

where $k = [\alpha^{-1}(2\pi R)^{1/2}]$ and $v = [(T/M)^{1/2}(\mathrm{d}m/\mathrm{d}t)]$

This study takes a close look at the material independent 'k' term of the Langmuir equation. The 'k' term being material independent may be 'borrowed' from a reference material for the calculation of vapor pressure for nicotinic acid. Methyl paraben was used as the reference material in this study.

Methyl paraben is the methyl ester of p-hydroxy benzoic acid. The TG–DTA analysis of methyl paraben shows that the compound evaporates following zero order kinetics. The pressure values for methyl paraben over a temperature range of 200–224 °C were calculated using the Antoine equation stated below [5].

$$\ln P = a - \frac{b}{T + c} \qquad (3)$$

The Antoine constants for methyl paraben are reported in literature [6]. The pressure values obtained from the

Table 1
Pressure values calculated for methyl paraben using the Antoine constants and for nicotinic acid using the three experimental methods

Temperature (K)	Pressure (Pa)			
	Methyl paraben	Nicotinic acid		
		Comparative	Varying	Constant
473.15	4505.106	3182.683	3139.841	2994.656
474.15	4696.238	3339.648	3294.532	3144.034
475.15	4893.884	3533.781	3485.873	3315.217
476.15	5098.206	3719.863	3669.256	3483.025
477.15	5309.367	3927.328	3873.715	3683.078
478.15	5527.535	4145.06	4088.283	3863.215
479.15	5752.879	4368.532	4308.494	4066.137
480.15	5985.569	4602.125	4538.669	4276.952
481.15	6225.779	4831.733	4764.895	4489.44
482.15	6473.683	5075.093	5004.665	4744.007
483.15	6729.46	5344.836	5270.431	4957.393

Antoine equation were used in the Langmuir equation to get the corresponding ‘k’ terms for methyl paraben. Three different approaches were used to calculate the pressure values required to construct the vapor pressure curves (Table 1).

In the first approach, which we call the comparative method, the ‘k’ term was eliminated from the Langmuir equation by comparing the expression for the sample with that for the Ref. [8]

$$\frac{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{ref}} = (P)_{\mathrm{ref}}(\alpha)_{\mathrm{ref}}(M/2\pi RT)^{1/2}_{\mathrm{ref}}}{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{sam}} = (P)_{\mathrm{sam}}(\alpha)_{\mathrm{sam}}(M/2\pi RT)^{1/2}_{\mathrm{sam}}} \tag{4}$$

This gives us,

$$(P)_{\mathrm{sam}} = \frac{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{sam}} M_{\mathrm{ref}} P_{\mathrm{ref}}}{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{ref}} M_{\mathrm{sam}}} \tag{5}$$

In the second approach, the values of the ‘k’ term for a single run of methyl paraben were used to calculate the pressure values for nicotinic acid at the corresponding temperature.

$$(P)_{\mathrm{sam}} = k_{\mathrm{ref},T\,^{\circ}\mathrm{C}}\left[\left(\frac{T}{M_{\mathrm{sam}}}\right)^{1/2}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{sam}}\right] \tag{6}$$

In the third approach, an average value of ‘k’ from three different runs of methyl paraben was used to calculate the pressure values for nicotinic acid (i.e. the value of ‘k’ was constant for the entire temperature range).

$$(P)_{\mathrm{sam}} = k_{\mathrm{ref,constant}}\left[\left(\frac{T}{M_{\mathrm{sam}}}\right)^{1/2}\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{sam}}\right] \tag{7}$$

The kinetic analysis of this rising temperature experiment was done using a differential approach. The rate of reaction can be expressed as a function of the fraction reacted.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{8}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of reaction, α the fraction reacted and is expressed as $(W_{\mathrm{i}} - W_{\mathrm{t}})/(W_{\mathrm{i}} - W_{\mathrm{f}})$ where W_{i} is the initial weight, W_{t} the weight at a specific temperature and W_{f} the final weight. ‘k’ is the reaction rate constant at a specific temperature. Using the Arrhenius equation ‘k’ can be written as

$$k = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{9}$$

Table 2
The mathematical models for the reaction mechanisms

Type	$f(\alpha)$
Order equation	
F1 first order	$(1-\alpha)$
F2 second order	$(1-\alpha)^2$
Geometric	
R2 contracting area	$2(1-\alpha)^{1/2}$
R3 contracting volume	$3(1-\alpha)^{2/3}$
Sigmoid curve	
A1.5 Avrami-Erofeev	$1.5(1-\alpha)(-\ln(1-\alpha))^{1/3}$
A2 Avrami-Erofeev	$2(1-\alpha)(-\ln(1-\alpha))^{1/2}$
A3 Avrami-Erofeev	$3(1-\alpha)(-\ln(1-\alpha))^{2/3}$
A4 Avrami-Erofeev	$4(1-\alpha)(-\ln(1-\alpha))^{3/4}$
B1 Prout-Tompkins	$\alpha(1-\alpha)$
Diffusion	
D1 1-D diffusion	$1/(2\alpha)$
D2 2-D diffusion	$-(\ln(1-\alpha))^{-1}$
D3 3-D diffusion	$1.5(1-(1-\alpha)^{1/3})^{-1}(1-\alpha))^{2/3}$
D4	$1.5(1-(1-\alpha)^{1/3})^{-1}$
Ginstling-Brounshtein	
P1 power law ($m > 1$)	$m(\alpha)^{(m-1)/m}$

where A is the pre exponential factor, E_{a} the energy of activation, R the universal gas constant and T the temperature. The equation may be expressed in the log form as

$$\ln k = \ln A - \frac{E_a}{RT} \tag{10}$$

$$\ln \frac{d\alpha/dt}{f(\alpha)} = \ln A - \frac{E_a}{RT} \tag{11}$$

using the experimental data, a plot of $\ln[(d\alpha/dt)/f(\alpha)]$ against $1/T$ using the different expressions of α gives the mechanism of the reaction (Table 2). The pre exponential factor A can be obtained from the intercept and the energy of activation from the slope of the plot.

Further, the Clausius–Clapeyron equation was applied to the sublimation phase data to calculate the enthalpy of sublimation, ΔH_{sub}. Ideally the value of the energy of activation should equal that of the enthalpy of sublimation. The slope of the plot of in P against $1/T$ gives the enthalpy of sublimation.

2. Experimental

2.1. Material

The sample of nicotinic acid was supplied by Matheson Coleman and Bell (Lot # NX375).

2.2. Equipment

The SDT 2960 simultaneous TG–DTA from TA Instruments with Universal Analysis for Windows 95/NT Ver. 2.3C, was used to carry out the thermal analysis of nicotinic acid. An electronic flow meter

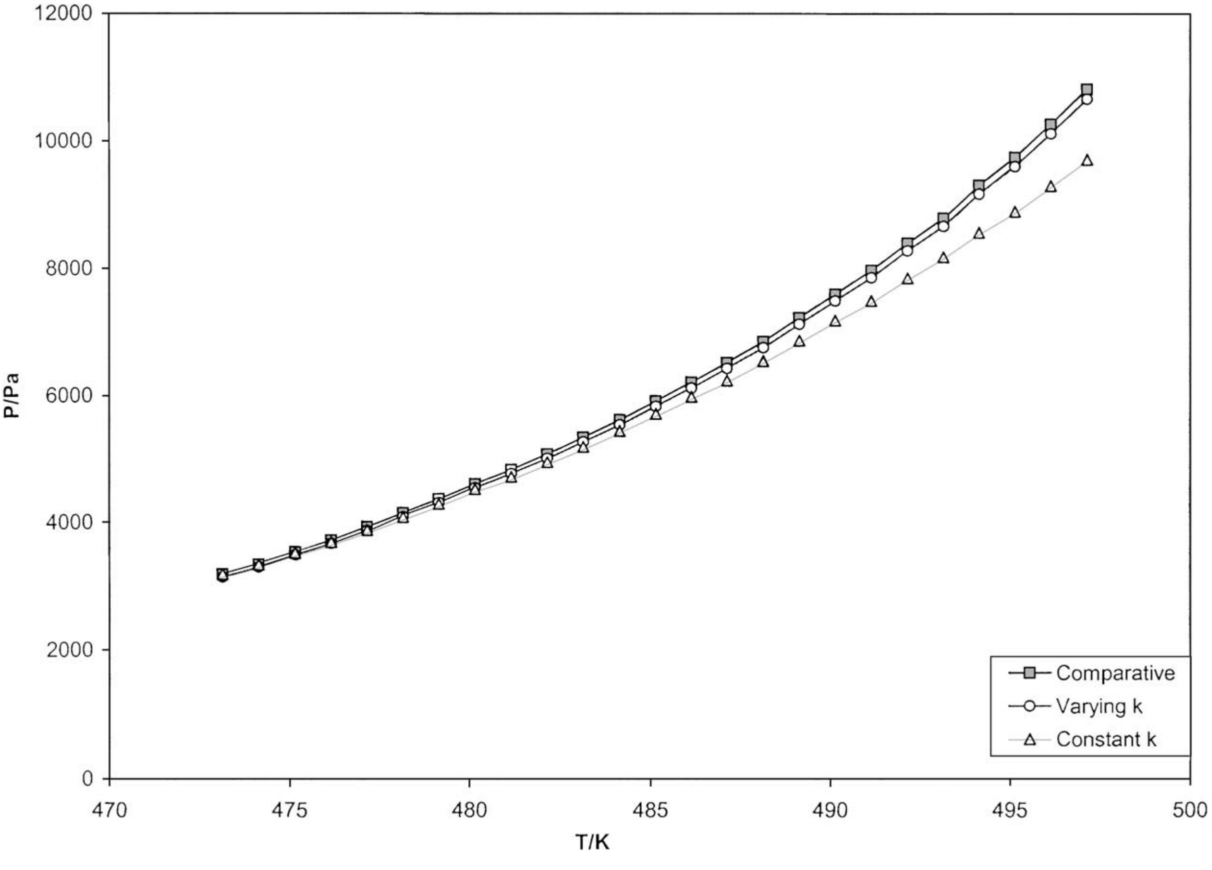

Fig. 2. Vapor pressure curves for the sublimation phase of nicotinic acid.

from J&W Scientific, Model ADM 1000, was used to monitor the flow of nitrogen, the purge gas.

2.3. Procedure

The sample was analyzed in an atmosphere of dry nitrogen set to a flow rate of 100 ml/min, subject to a temperature program of a 100 °C/min ramp to 400 °C. The 'v' term of the Langmuir equation was calculated using the slope of the DTG signal. Vapor pressure curves for the sublimation phase were constructed using the methods described earlier.

3. Result and discussion

3.1. Vapor pressure curves

The vapor pressure curve obtained by using the actual values of the 'k' term was found to be very close to the one constructed by the comparative method (Fig. 2). The 'k' values for methyl paraben show a systematic increase with an increase in temperature. This has to be taken into consideration. If the values are averaged out and used, a considerable deviation from the first curve is seen. It would seem that more attention has to be diverted to the actual use of the Langmuir equation to construct vapor pressure curves. It is not enough to simply calculate an average value of 'k' and construct a vapor pressure curve on the basis that 'k' is a constant.

3.2. Kinetic analysis

Sublimation of nicotinic acid was found to follow zero order kinetics. This is typical of sublimation processes with a constant surface area. From the plot of $\ln k$ against $1/T$, the energy of activation was found to be 87.29 kJ mol^{-1}. The enthalpy of sublimation was found to be 89.33 kJ mol^{-1}. This indicates that the process of sublimation in nicotinic acid is a spontaneous process.

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