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Determination of the vapor pressure curves of adipic acid and triethanolamine using thermogravimetric analysis

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Abstract

The evaporative properties of adipic acid, triethanolamine (TEA), and glycolic acid have been studied by thermal analysis. Samples were heated in a simultaneous thermogravimetric–differential thermal analysis (TG–DTA) unit at 10 °C min^{-1} in a dry nitrogen atmosphere flowing at 100 mL min^{-1}. Benzoic acid was used to calculate a calibration constant which could then be inserted into a modified Langmuir equation to calculate vapor pressure curves for adipic acid, TEA, and glycolic acid. The results were compared to vapor pressure curves generated by use of Antoine constants, where these were available. Good correlation was obtained between the two sets of curves for adipic acid and TEA. Glycolic acid decomposed and evaporated in the same temperature range, thus, making calculations invalid.

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1. Introduction

Several studies have shown that thermogravimetry is a rapid and convenient technique for the determination of vapor pressure curves and enthalpies of sublimation and vaporization for volatile chemicals. Such studies have been used in examination of pesticides [1,2], pharmaceuticals [3], UV absorbers [4,5], antioxidants [6], and perfume components [7]. Earlier studies used the TG in an isothermal mode, but more recently a rising temperature heating program has been used which makes the acquisition of data faster (one experiment as opposed to several) and this also reduces the quantity of sample required.

Vapor pressure curves can be found using the Antoine equation, of the form:

$$\ln p = A - \frac{B}{C + T}$$

where A, B, and C are the Antoine constants which are tabulated for a range of compounds, p the vapor pressure in Pa, and T is the absolute temperature. However, there are a limited number of compounds for which this data is available, and for some of those that are available, the data covers a limited temperature range.

The theoretical basis of the TG procedure is the Langmuir equation.

$$\left(\frac{1}{a}\right)\frac{\mathrm{d}m}{\mathrm{d}t} = p\alpha\sqrt{\frac{M}{2\pi RT}}$$

where $\mathrm{d}m/\mathrm{d}t(a)$ is the rate of mass loss per unit area (kg s^{-1} m^{-2}), p the vapor pressure (Pa), M the molecular weight of the vapor of the evaporating compound (kg mol^{-1}), R the gas constant (J K^{-1} mol^{-1}), T the absolute temperature, and α is the vaporization coefficient. In vacuum, α is assumed to be 1, but in a flowing gas atmosphere as commonly found in TG experiments α assumes a significantly different value. Rearranging the Langmuir equation gives:

$$p = k\nu$$

where $k = \sqrt{2\pi R}/\alpha$, and $\nu = (1/a)(\mathrm{d}m/\mathrm{d}t)\sqrt{(T/M)}$.

The usual procedure using TG is to determine the rate of mass loss over the temperature range of interest using a compound which is known to be thermally stable, to follow ideal behavior for gas–vapor or solid–vapor transitions, and

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has known Antoine constants. Benzoic acid has been suggested as a suitable material for this role [8].

A plot of p (calculated from the Antoine constants), against ν (calculated from the TG data) should give a straight line plot with a slope of k. This calibration constant can then be used to calculate vapor pressure curves for materials for which the Antoine constants are not known.

From the Clausius–Clapeyron equation:

$$\ln p = A - \frac{\Delta H}{RT}$$

a plot of $\ln p$ against $1/T$ should give a straight line plot of slope, $\Delta H/R$. Alternatively a plot of $\ln \nu$ against $1/T$ should give a straight line plot of slope, $\Delta H/R$.

This paper reports on the determination of the vapor pressure curves and enthalpy of vaporization values for the compounds adipic acid, triethanolamine, and glycolic acid.

2. Materials and methods

Benzoic acid was obtained from Fisher Scientific Company (lot #901455), purity 99.5%+; adipic acid from J.T. Baker Chemical Company (lot #960), purity 99.5%+; triethanolamine from Professional Compounding Centers of America Inc. (lot #011983), purity NF 98%; and glycolic acid from Fluka AG (lot #242579), purity 99%.

The simultaneous TG–DTA unit was manufactured by TA Instruments, model TA SDT 2960. The experimental data was analyzed with TA Instruments Universal Analysis software, V1.10B. A platinum crucible, with a measured surface area of $0.29\,\mathrm{cm}^2$, was used to hold various amounts of the samples, ranging from 5 to 10 mg. The samples were spread thinly and uniformly in the crucible completely covering the bottom surface. Each sample was heated at $10\,^{\circ}\mathrm{C\,min}^{-1}$ from ambient temperature under dry nitrogen flowing at $100\,\mathrm{mL\,min}^{-1}$. Each sample was analyzed at least three times to check reproducibility. The temperatures reported from the TG and DTA curves are the extrapolated onset and offset temperatures of the transitions.

3. Results and discussion

Benzoic acid was used as the calibrating material for the determination of k in the modified Langmuir equation. The TG plot of benzoic acid was obtained, to give $\mathrm{d}m/\mathrm{d}t$, and the vapor pressures at various temperatures calculated using the Antoine constants quoted in the temperature range 132–250 °C [9]. A plot of p against ν gave a straight line (Fig. 1) from which k was calculated to be $1.102 \times 10^5\,\mathrm{J}^{0.5}\,\mathrm{K}^{-0.5}\,\mathrm{mol}^{-0.5}$.

3.1. Adipic acid

A typical TG–DTA/DTG curve for adipic acid obtained at a heating rate of $10\,^{\circ}\mathrm{C\,min}^{-1}$ is shown in Fig. 2. The DTA plot has two endothermic events that are taking place, the first of which is due to the melting of adipic acid in the temperature range of 145–189 °C, and the second is due to the evaporation of adipic acid in the temperature range 189–301 °C. The TG curve displays a single mass loss, in the temperature range 152–268 °C. On the DTG plot, the rate of mass loss shows a rapid increase after reaching 175 °C, which is the temperature towards the end of the melting process and the beginning of the evaporation process. The rate

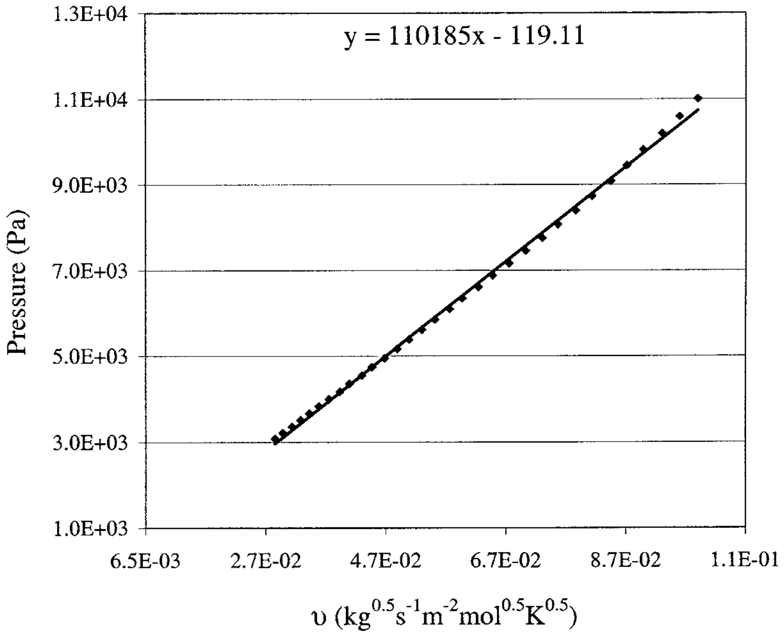

Fig. 1. Langmuir plot for the evaporation of benzoic acid.

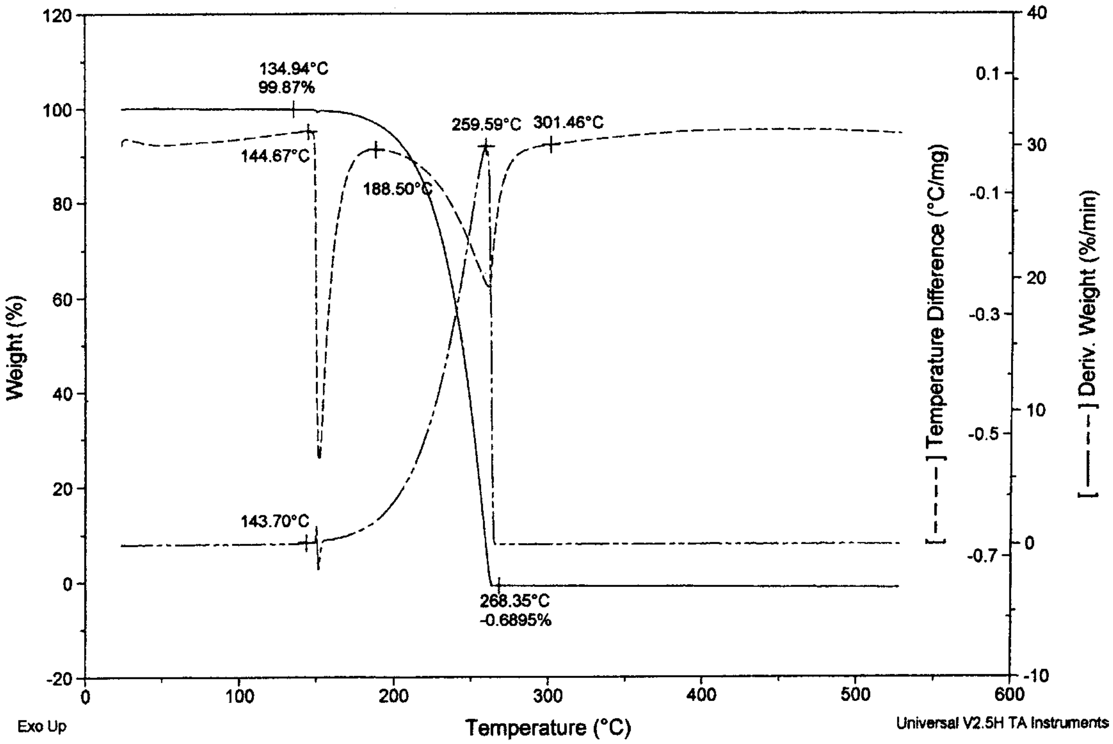

Fig. 2. TG–DTA/DTG plot of adipic acid (10 °C min^{-1}, 100 mL min^{-1}, N_2).

of mass loss continues to increase as the sample evaporates reaching the maximum rate at the DTG peak temperature of 260 °C. With an empty sample crucible and a total mass loss of 100% upon completion of the TA experiment, it is concluded that adipic acid has completely evaporated.

Using the Antoine constants for the evaporation of adipic acid quoted in the temperature range 159–338 °C [9], the vapor pressure values within the evaporation temperature range of 188–258 °C were calculated and plotted. The vapor pressure values were also calculated using the k-value (1.102×10^5 J$^{0.5}$ K$^{-0.5}$ mol$^{-0.5}$) obtained from the evaporation data of benzoic acid. Both vapor pressure curves are shown in Fig. 3, and show very good agreement between the plots obtained from the two different approaches. Once the value of ν was found using the TG data, a plot of ln ν against $1/T$ gave a straight line (Fig. 4), and from the slope the enthalpy of evaporation was found to be 88.9 ± 0.48 kJ mol^{-1}. The standard deviation was calculated from six determinations carried out under identical experimental conditions. The effect of heating rate on the ΔH_{vap} value of was examined, and the values calculated from data obtained at heating rates of 2, 5, 10, 15, and 20 °C min^{-1} at a constant nitrogen flow rate of 100 mL min^{-1} are given in Table 1. Here the mean value was 89.2 ± 0.66 kJ mol^{-1}. Similar experiments were conducted at a constant heating rate of 5 °C min^{-1} but with variation in the nitrogen flow rate of 50, 100, 150,

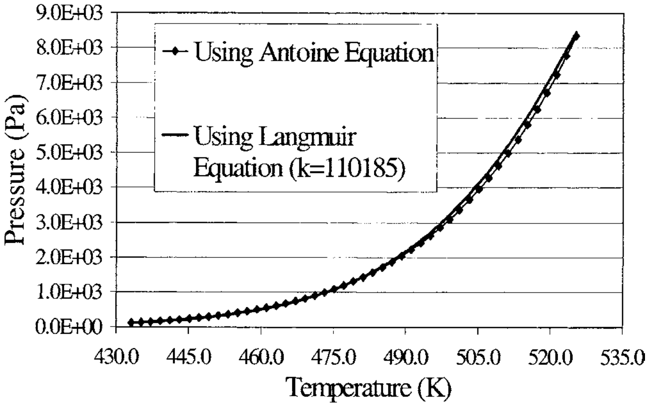

Fig. 3. Comparison of vapor pressure curves calculated from the Langmuir and the Antoine equations for adipic acid.

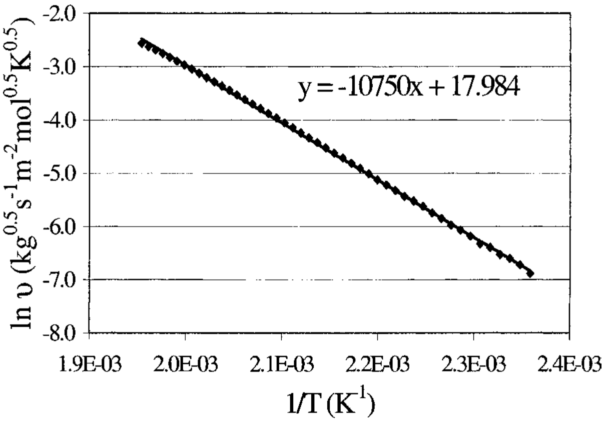

Fig. 4. Clausius–Clapeyron plot for adipic acid.

Table 1
Enthalpies of vaporization for adipic acid at various heating rates with a constant flow rate of 100 mL min^{-1} of dry N_2

β (°C min^{-1})	ΔH_{vap} (kJ mol^{-1})
2	89.8
5	89.7
10	89.4
15	88.5
20	88.4

Table 2
Enthalpies of vaporization for adipic acid at various flow rates of dry N_2 with a constant heating rate of 5 °C min^{-1}

Flow rate (mL min^{-1})	ΔH_{vap} (kJ mol^{-1})
50	90.3
100	89.7
150	89.1
200	88.4
300	88.5

200, and 300 mL min^{-1}. The values of ΔH_{vap} calculated from this data are given in Table 2, with a mean value of 89.2 ± 0.81 kJ mol^{-1}. Hence, although the values of ΔH_{vap} are very close for all three sets of data, there was a small increase in the standard deviation as the experimental conditions changed, with the change in gas flow rate having the greatest effect. The values compare well with a value of 87.5 kJ mol^{-1} calculated from the graph of vapor pressure against temperature obtained from the Antoine constants.

3.2. Triethanolamine

A typical TG–DTA/DTG curve of TEA heated at 10 °C min^{-1} in nitrogen flowing at 100 mL min^{-1} is shown in Fig. 5. The DTA plot reveals an endothermic peak in the temperature range of 204–314 °C, associated with a single mass loss beginning at 50 °C and ending at 304 °C. Both events are caused by the evaporation and/or decomposition of TEA. On the DTG plot, the rate of mass loss is shown to accelerate to the maximum rate at the peak temperature of 271 °C. A black carbon residue of about 2% of the total mass loss remained in the sample crucible at the end of the experiment, indicating that a minor amount of pyrolytic decomposition of TEA had occurred, and evaporation was not the only process taking place in this temperature range.

The Antoine constants for TEA are only available for a limited temperature range of 250–306 °C [9]. Using the constants, the vapor pressure in this range is plotted in Fig. 6. Again, the k-value (1.102×10^5 J$^{0.5}$ K$^{-0.5}$ mol$^{-0.5}$) from the benzoic acid calculations was used to calculate the vapor pressure values for TEA, and this curve is also plotted in Fig. 6. These plots show good correlation with each other. However, the advantage of using the TG data to construct the vapor pressure curve is obvious, as the complete temperature range of evaporation is covered. The value of ν was determined from the mass loss data, and a plot of $\ln \nu$ versus $1/T$ was constructed (Fig. 7). The linear nature of this curve allowed for the enthalpy of vaporization to be calculated from the slope, and was found to be 82.0 ± 2.0 kJ mol^{-1}. If we take this as the average value in the temperature range

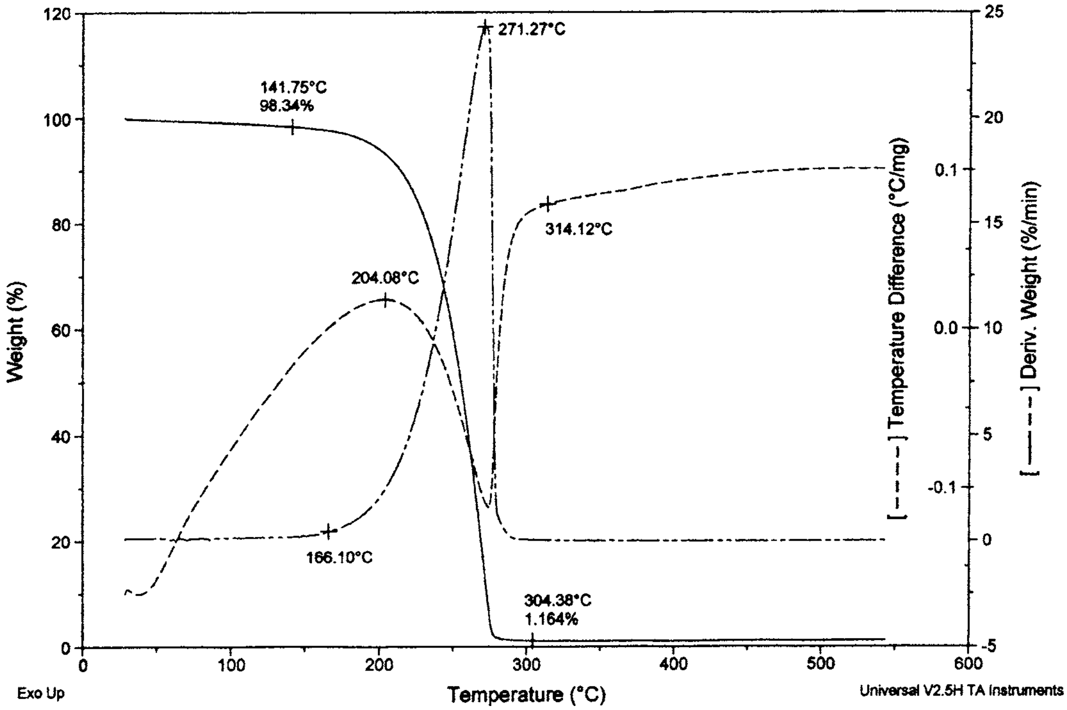

Fig. 5. TG–DTA/DTG plot of triethanolamine (10 °C min^{-1}, 100 mL min^{-1}, N_2).

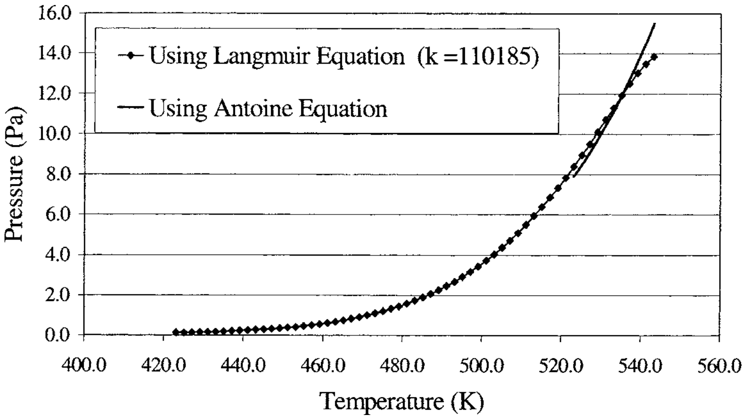

Fig. 6. Comparison of vapor pressure curves calculated from the Langmuir and the Antoine equations for triethanolamine.

147–257 °C, then this gives the value of 82.0 kJ mol^{-1} at the mid-temperature range of 202 °C. This compares well with a value of 85.5 kJ mol^{-1} at 200 °C, taken from a plot of enthalpy of evaporation against temperature given in the manufacturer's product literature [10]. One group measured the vapor pressure of TEA at three different temperatures in the range 50–70 °C, and from the straight line plot of enthalpy of vaporization against temperature extrapolated to give a value of 105.9 ± 2.2 kJ mol^{-1} at 25 °C [11]. If the plot is extrapolated to 200 °C the value is approximately 50 kJ mol^{-1}. If the Antoine constant data is used, the value calculated from the graph was 79.24 kJ mol^{-1}. This variation in values may be due to the reported decomposition of TEA above 170 °C [12], and self-sustained decomposition above 250 °C [10]. The presence of 2% carbon in the pan at the end of the TG experiment was an indication that other relatively minor reactions were taking place in this temperature range. However, since the TG data was calculated from 147 to 257 °C, and since decomposition is likely to be much slower at the lower temperatures, the TG data is probably more valid than that obtained from the Antoine data.

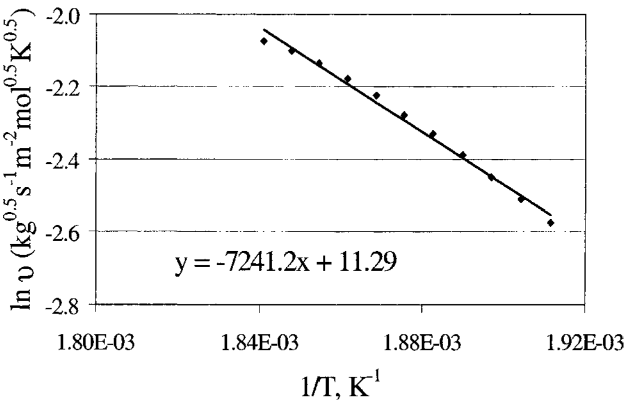

Fig. 7. Clausius–Clapeyron plot for triethanolamine.

3.3. Glycolic acid

Samples of glycolic acid were heated in the TG–DTA apparatus under the same experimental conditions used for the other compounds. However, the TG curve displayed a two stage mass loss, the first beginning at 100 °C and slowing down at 258 °C, and then accelerating again at 280 °C and ending at 375 °C. The DTA curve showed an endothermic peak between 62 and 112 °C corresponding to the melting of the glycolic acid, and then two further endothermic peaks between 112–262 and 323–382 °C corresponding to the mass losses. It is evident that glycolic acid is simultaneously undergoing evaporation and significant decomposition, as indicated by the 40% mass remaining at the end of the first mass loss. Hence, it was not possible to determine the vapor pressure characteristics of this material.

4. Conclusions

For two of the compounds examined, adipic acid and TEA, the TG results gave vapor pressure curves which were in close agreement with those generated from the Antoine constants. In addition, the vapor pressure curve from the TG data for TEA covered a much larger temperature range than available from the Antoine constants. For glycolic acid, the sample decomposed in the same temperature range as evaporation, and so calculations were rendered invalid. This, however, is another advantage of the use of TG–DTA for these kinds of measurements, as the formation of the intermediate product was obvious on the TG–DTA curves.

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