ELSEVIER

Thermochimica Acta 367–368 (2001) 263–271

thermochimica acta

www.elsevier.com/locate/tca

The calculation of the vapor pressures of antioxidants over a range of temperatures using thermogravimetry

Pauline Phang*, David Dollimore†

The University of Toledo, Toledo, OH 43615, USA

Received 12 October 1999; accepted 16 May 2000

Abstract

Previous studies, as introduced by Price and Hawkins [Thermochim. Acta 315 (1998) 19], have established that it is possible to determine the vapor pressures of volatile organic compounds from data collected on a TG unit. This study involves the calculation of the partial vapor pressures of antioxidants by combining the experimental thermogravimetric data with its corresponding reference vapor pressure data obtained with Antoine constants, along with the application of the Langmuir equation for evaporation. The chosen antioxidants for this study are butylated hydroxytoluene and propenyl guaethol. Butylated hydroxytoluene was used as the calibration material from which the vapor pressure curve of propenyl guaethol is proposed. In this study, it was observed that a plot of p versus v should be sufficient to yield the constant value of k, which is needed for the construction of vapor pressure curves of other samples being studied with the same TG unit. With the aid of a plot of vapor pressure curves with various k-values and a correlation plot, it is established that the k-value as obtained by plotting p versus v yields a vapor pressure curve that is closest to a given reference vapor pressure curve. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Antioxidants; Thermogravimetry; Vapor pressure; Langmuir equation

1. Introduction

Antioxidants are generally added to food or cosmetic preparations which are high in fat or oil content [2,3]. The presence of antioxidants within formulations retard and/or inhibit the occurrence of oxidative processes that might take place within the formulation. It is these oxidative processes which cause a preparation to turn rancid. This being the case, the incorporation of antioxidants is crucial to the shelf life of a product. Therefore, the way in which antioxidants tend to vaporize is a phenomenon that is worth investigating.

Currently, there are many ways in which one can go about determining the vapor pressure values for a liquid–gas system. Some of these methods include taking manometric measurements [4] and the use of the Knudsen cell technique [5]. Consequently, it is possible to construct the vapor pressure curves for volatile organic materials from the results of these experiments.

In 1998, Price and Hawkins [1] introduced the method of the use of TG data to determine the partial vapor pressures for organic materials. Similar studies involving the determination of vapor pressures for pharmaceutical systems have also been conducted [6]. However, the focus of this study is on the method as proposed by Price and Hawkins.

---

[*] Corresponding author.
E-mail address: ddollim@aol.com (P. Phang).
[†] Deceased.

PII: S0040-6031(00)00651-1

For this study, the TG data for butylated hydroxytoluene and propenyl guaethol were collected. Butylated hydroxytoluene was selected as the calibration material. The thermogravimetric data for the butylated hydroxytoluene sample was related to its reference vapor pressure data, as obtained from given Antoine constants [7–12]. A modified form of the Langmuir equation (since, the experiments were conducted in the presence of a purge gas) was partitioned into experimentally dependent and experimentally independent variables to accommodate the collected data [13]. This modified equation is given as follows:

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

where p is the partial vapor pressure (in Pa) at any given absolute temperature, T (in K), dm/dt the rate of mass loss per unit area (in kg s^{-1} m^{-2}), α the vaporization coefficient, M the molecular weight for the vapor (in kg mol^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}). The notation v is used to represent $(\mathrm{d}m/\mathrm{d}t)(T/M)^{1/2}$, while $(2\pi R)^{1/2}/\alpha$ is denoted by k. It should be noted that v stands for the experimentally dependent term while k is the experimentally independent portion of the equation. Theoretically, the value of k is a constant by virtue of that fact that the values of π and R are established constants. The vaporization coefficient, α, may also be considered as a constant value as it is usually ascribed a value of unity for experiments which are conducted in vacuum. However, in this study, the value of α will be modified as the experiments were carried out in a nitrogen atmosphere. Various other volatile organic compounds were also investigated to confirm that a variety of materials would yield the same value of k for the instrument which was used to collect the experimental data in this study. These data will be published at a later date, but suffice to say, it was shown that the k-values were of the same magnitude. It should further be stressed that the units for all the variables in the modified Langmuir equation for evaporation were converted to SI units.

Using the above equation, the vapor pressure values for butylated hydroxytoluene at various temperatures were calculated. These values were then used to construct the vapor pressure curve for butylated hydroxytoluene. This was done in order to obtain the value of k, which is supposed to be a constant that is unique to the TG unit being used. The vapor pressure curve for the other antioxidant, propenyl guaethol, was then constructed, based upon the value of k deduced from the results from butylated hydroxytoluene calculations. It should be mentioned that there were no reference vapor pressure values available for propenyl guaethol.

This method of determining the vapor pressure values of volatile organic materials (as put forth by Price and Hawkins) uses a modified form of the Langmuir equation for evaporation. The modified form of the equation must be used as there is a need to account for the presence of the purge gas which is introduced to the TG unit. In their study, Price and Hawkins obtained their k constant for their TG unit by plotting log p versus log v. However, in practice, it was observed that a plot of p versus v should also yield the constant value of k. In this study, it was shown that both the log p versus log v and p versus v plots exhibited slight curvatures in their slopes. With the aid of plotting the vapor pressure curves with various k-values and a correlation plot, it is established that the k-value as obtained by plotting p versus v yields a vapor pressure curve that is closest to a given reference vapor pressure curve.

2. Experimental

The butylated hydroxytoluene sample (CAS 128-37-0) used in this study was obtained from Sigma Chemical and it has a purity rating of 97+%, FCC. The other antioxidant, propenyl guaethol (CAS 94-86-0) was supplied by Aldrich Chemical and it also had a purity rating of 97+%, FCC. Both compounds were labeled as batches which met manufacturing standards.

The evaporation data used in this study were collected on a simultaneous TG–DTA unit, model TA SDT 2960. A pair of platinum crucibles served as the sample and reference pans. The cross-sectional surface area of the sample crucible was determined to be 0.2248 cm^2. The conditions under which the TG experiments for both antioxidants were carried out are as follows:

1. samples were subjected to a rising temperature program;
2. heating rate of 2°C/min was applied;
3. purge gas used was dry nitrogen, with a flow rate of 100 ml/min.

The reference vapor pressure values were obtained by fitting the Antoine constants to the Antoine equation, given as

$$\log p = A = \frac{B}{(C+T)} \tag{2}$$

3. Results and discussion

The TG–DTG plot for butylated hydroxytoluene is presented in Fig. 1. The plot shows that the sample undergoes total mass loss when it is subjected to heating. This event is also indicative of the complete melting and evaporation of the sample over the course of the experiment. For vapor pressure calculations, data from the linear portion of the TG–DTG curve was used. In this study, calculations were restricted to this portion of the data set because the sample maintains a constant liquid interface within this region [14]. A reference vapor pressure curve for the sample was also generated with the application of the prescribed Antoine constants for butylated hydroxytoluene to the Antoine equation.

The thermogravimetric data and reference vapor pressure data were applied to the Langmuir equation for evaporation. The spreadsheet used for these calculations is shown in Table 1. From the results of the spreadsheet calculation, various vapor pressure plots were obtained. These are presented in Figs. 2–5. It should be mentioned that for Figs. 4 and 5, the legends

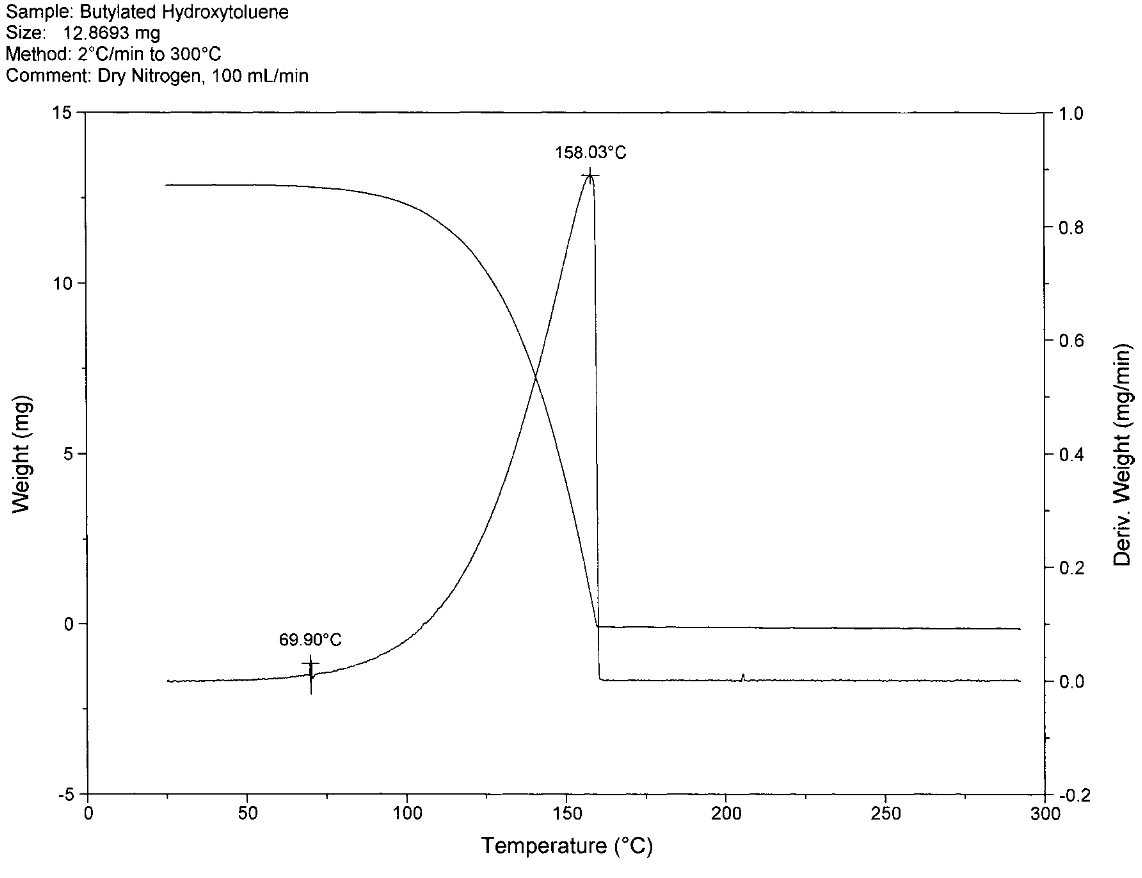

Fig. 1. TG–DTG plot of butylated hydroxytoluene.

Table 1
Spreadsheet showing vapor pressure calculations for butylated hydroxytoluene

T	$(\mathrm{d}m/\mathrm{d}t)/A$	T/M	$(T/M)^{1/2}$	$\log p$	p	v	k	α
390.15	1.339E-04	1770.59	42.078	−0.1410	722.76	0.0056	128283	5.642E-05
392.15	1.481E-04	1779.67	42.186	−0.0995	795.24	0.0062	127257	5.687E-05
394.15	1.633E-04	1788.75	42.294	−0.0585	874.04	0.0069	126529	5.720E-05
396.15	1.808E-04	1797.82	42.401	−0.0179	959.63	0.0077	125160	5.783E-05
398.15	1.990E-04	1806.90	42.508	0.0222	1052.50	0.0085	124429	5.817E-05
400.15	2.197E-04	1815.97	42.614	0.0619	1153.17	0.0094	123184	5.875E-05
402.15	2.406E-04	1825.05	42.721	0.1011	1262.20	0.0103	122807	5.893E-05
404.15	2.628E-04	1834.13	42.827	0.1399	1380.16	0.0113	122616	5.903E-05
406.15	2.869E-04	1843.20	42.933	0.1783	1507.67	0.0123	122393	5.913E-05
408.15	3.139E-04	1852.28	43.038	0.2163	1645.39	0.0135	121790	5.943E-05
410.15	3.420E-04	1861.36	43.143	0.2538	1793.98	0.0148	121581	5.953E-05
412.15	3.711E-04	1870.43	43.249	0.2910	1954.17	0.0160	121769	5.944E-05
414.15	4.020E-04	1879.51	43.353	0.3277	2126.73	0.0174	122033	5.931E-05
416.15	4.331E-04	1888.59	43.458	0.3641	2312.43	0.0188	122853	5.891E-05
418.15	4.658E-04	1897.66	43.562	0.4000	2512.12	0.020	123798	5.846E-05
420.15	5.005E-04	1906.74	43.666	0.4356	2726.68	0.022	124758	5.801E-05
422.15	5.354E-04	1915.82	43.770	0.4709	2957.02	0.023	126191	5.735E-05

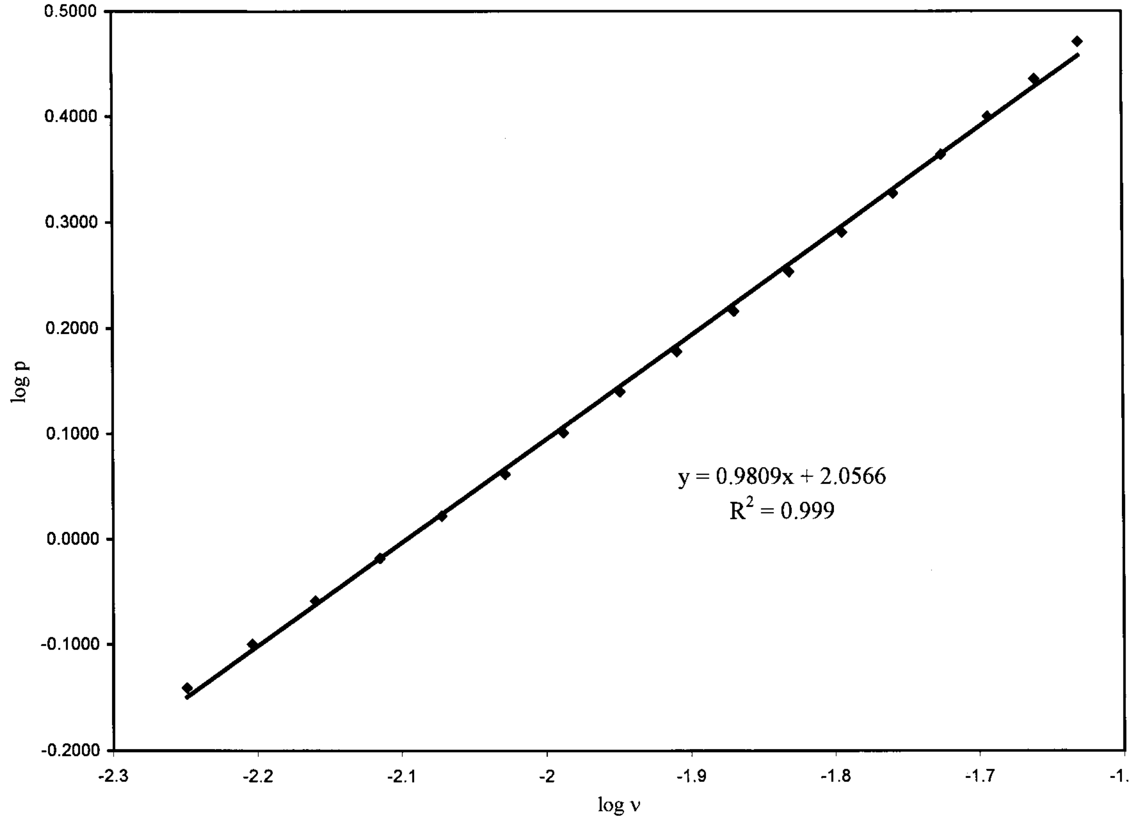

Fig. 2. Plot of log p versus log v for butylated hydroxytoluene.

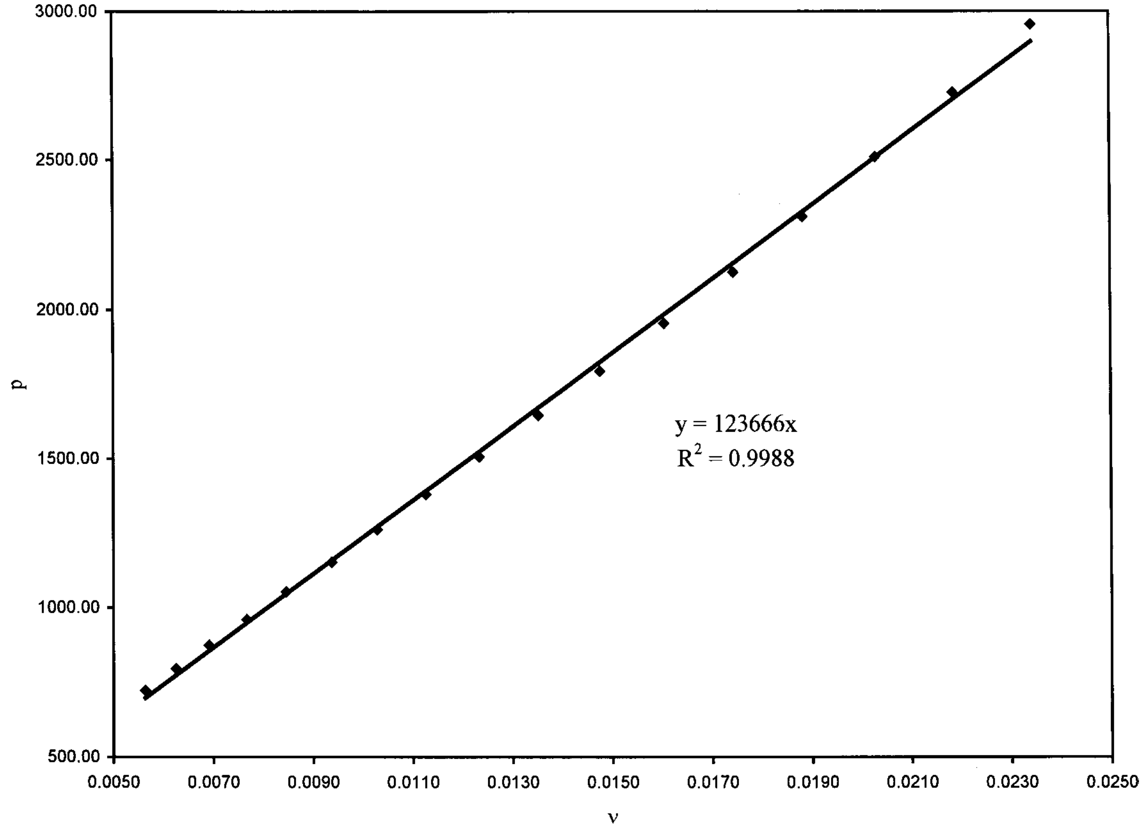

Fig. 3. Plot of p against log v for butylated hydroxytoluene.

"Average" refers to the vapor pressure curve constructed with the calculated k average value, "Ours" refers to the curve constructed with the k-value obtained from a plot of p against v, and "Price–Hawkins" refers to the curve constructed with the k-value obtained from a plot of $\log p$ versus log v.

Fig. 2 represents the results of a $\log p$ versus log v plot. This plot was constructed in the manner as proposed by Price and Hawkins' paper [1]. The k-value is obtained from the intercept value of this plot. In Fig. 3, a p versus v plot is shown. For this case, the k-value simply corresponds to the slope of the curve. It should be noted that there exists a slight, systematic curvature in the data points for both plots (refer to Figs. 2 and 3).

In order to explore the validity of the various k-values (as established by both plots and the average k-value) vapor pressure plots using all three k-values were constructed and compared with the applicable reference vapor pressure curve. The result of this endeavor is depicted in Fig. 4. From Fig. 4, it may be observed that the k-value as obtained from a plot of p versus v yields a vapor pressure curve which is closest to the reference vapor pressure curve. The average value of k produced a vapor pressure curve that is least ideal.

It should also be cautioned that this noticeable variation in vapor pressure curves was seen over a relatively small range of temperature. This would seem to indicate that the method would not be feasible for studies involving a wider temperature range. Complications would arise if a wider range of temperature was studied, because the interface of the sample would no longer be consistent (due to a marked decrease in sample material) as it undergoes heating at elevated temperatures.

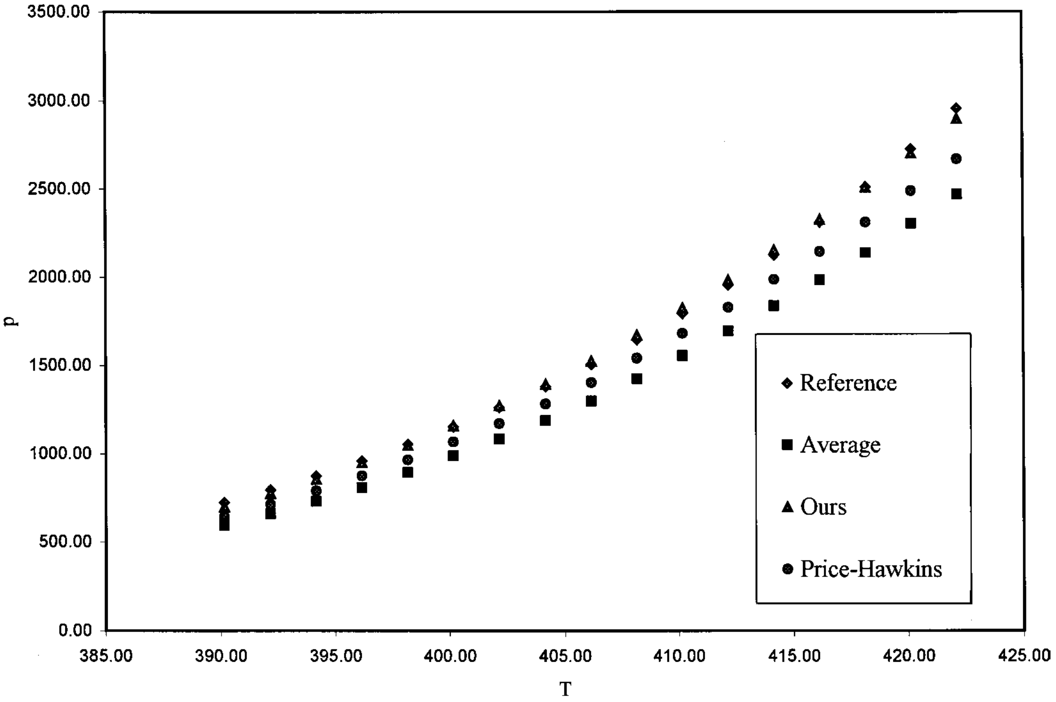

Fig. 4. Vapor pressure curves using various *k*-values.

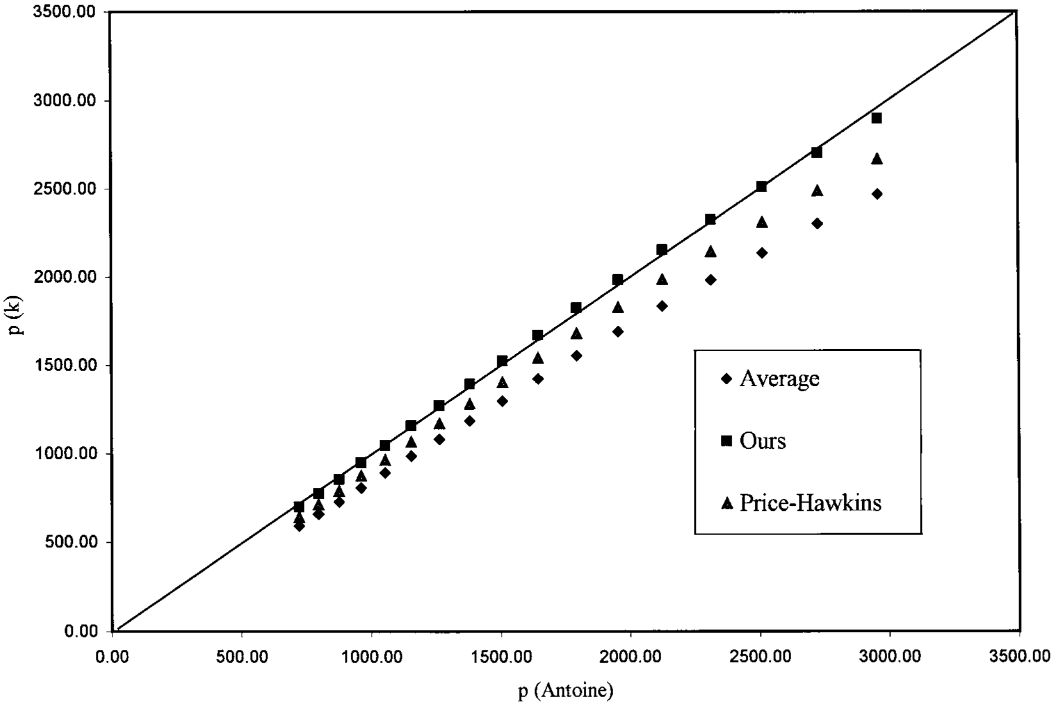

Fig. 5. Correlation plot of vapor pressure values.

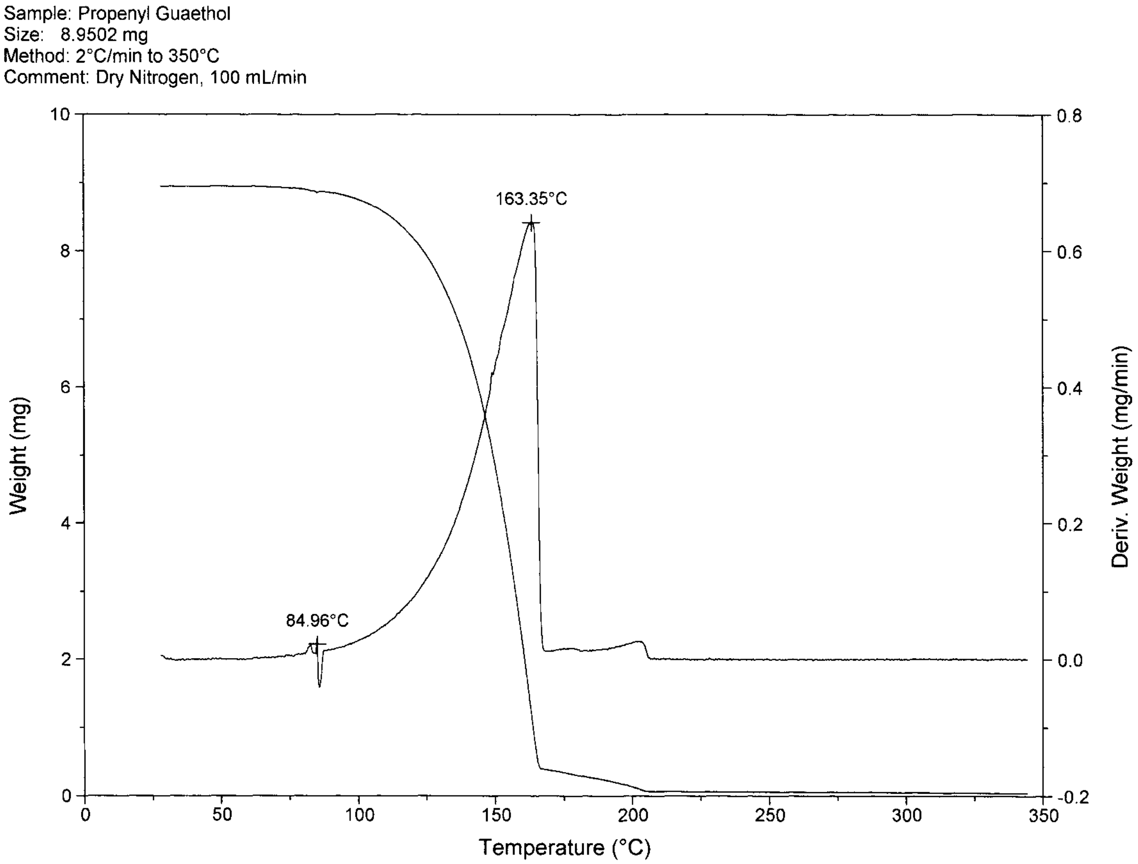

Fig. 6. TG–DTG plot of propenyl guaethol.

To further illustrate the legitimacy of the claim that p versus v yields the better k-value (as compared to the other two methods), a correlation plot (as shown in Fig. 5) was constructed. The function of a correlation plot is to demonstrate the relationship between two variables. If there is a strong correlation, the two variables should exhibit a 45° angle correlation between the two data sets. As seen in Fig. 5, the vapor pressure curve plotted with the k-value obtained from a p versus v plot, shows the strongest correlation to the reference vapor pressure curve.

For propenyl guaethol, the TG–DTG plot shows a two-step mass loss (refer to Fig. 6). The first major step is indicative of the sample undergoing melting and evaporation, while a secondary minor step accounts for the minute residue that is left in the sample pan after the sample is subjected to heating. There is no reference vapor pressure data made available for this material. This makes it an ideal compound

Table 2
Spreadsheet showing vapor pressure calculations for propenyl guaethol

T	$(\mathrm{d}m/\mathrm{d}t)/A$	T/M	$(T/M)^{1/2}$	v	p
390.15	5.750E-05	2190.87	46.807	0.0027	332.83
392.15	6.398E-05	2202.10	46.927	0.0030	371.29
394.15	7.153E-05	2213.33	47.046	0.0034	416.16
396.15	7.970E-05	2224.56	47.165	0.0038	464.87
398.15	8.852E-0s	2235.79	47.284	0.0042	517.62
400.15	9.831E-05	2247.02	47.403	0.0047	576.30
402.15	1.091E-04	2258.25	47.521	0.0052	641.15
404.15	1.204E-04	2269.49	47.639	0.0057	709.32
406.15	1.331E-04	2280.72	47.757	0.0064	786.08
408.15	1.478E-04	2291.95	47.874	0.0071	875.04
410.15	1.641E-04	2303.18	47.991	0.0079	973.92
412.15	1.823E-04	2314.41	48.108	0.0088	1084.57
414.15	2.025E-04	2325.64	48.225	0.0098	1207.67
416.15	2.248E-04	2336.87	48.341	0.0109	1343.89
418.15	2.493E-04	2348.10	48.457	0.012	1493.93
420.15	2.767E-04	2359.33	48.573	0.013	1662.09
422.15	3.125E-04	2370.56	48.688	0.015	1881.60

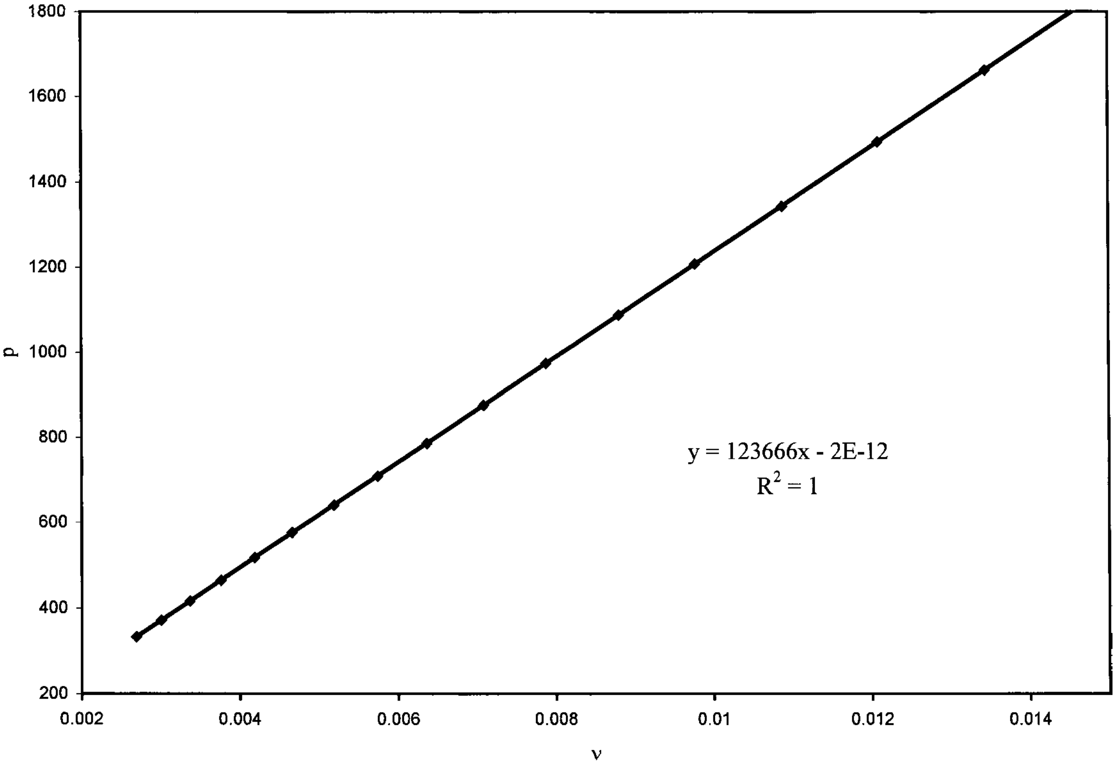

Fig. 7. Proposed vapor pressure curve for propenyl guaethol.

for a proposed vapor pressure curve, using the *k*-value obtained from the calibration material. The spreadsheet used for the calculations is similar to that used for butylated hydroxytoluene and it is presented in Table 2. Fig. 7 shows the proposed vapor pressure curve for propenyl guaethol.

4. Conclusions

In this study, it was established that the *k*-value which is unique to a TG unit, is best determined from a *p* versus *v* plot. A single calibration material is sufficient to produce the value of *k*, and this value may be extended for use to determine the vapor pressure values of other materials, which are in the same temperature range. It is further recommended that this method of determining vapor pressure values for volatile organic materials be restricted for use over a small range of temperatures.

References

[1] D.M. Price, M. Hawkins, Thermochim. Acta 315 (1998) 19.

[2] A. Levy, Cosmetics and Toiletries 104 (1989) 43.

[3] E. Kronhausen, P. Kronhausen, H.B. Demopoulos, Formula for Life: The Antioxidant, Free-radical, Detoxification Program, New York, 1989.

[4] C.G. deKruif, T. Kuipers, J.C. van Miltenburg, R.C.F. Schaake, G. Stevens, J. Chem. Thermodyn. 13 (1981) 1081.

[5] J. Pfefferhorn, H.G. Wiedermann, Prog. Vac. Microbal. Tech. 2 (1973) 221.

[6] J.P. Elder, J. Thermal. Anal. 44 (1996) 1251.

[7] T. Boublik, V. Fried, E. Hala, The Vapour Pressures of Pure Substances, Elsevier, Amsterdam, 1973.

[8] J.R. Cunningham, O.K. Jones, Experimental results for phase equilibria and pure component properties, DIPPR Data Series, American Institute of Chemical Engineers, New York, 1991.

[9] C.L. Yaws, Handbook of Vapor Pressure, Gulf Publishing Company, Texas, 1994.

[10] R.R. Dreisbach, Pressure–volume–temperature relationship of organic compounds, Handbook of Publishers, Ohio, 1952.

[11] S. Ohe, Computer Aided Data Book of Vapor Pressure, Data Book Publishing Company, Tokyo, Japan, 1976.

[12] R.M. Stephenson, S. Malanowski, Handbook of the Thermodynamics of Organic Compounds, Elsevier, New York, 1987.

[13] I. Langmuir, Phenomena, Atoms and Molecules, Philosophical Library, New York, 1950.

[14] P. Phang, D. Dollimore, Thermochim. Acta 27 (1999) 67.