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A comparative method for developing vapor pressure curves based on evaporation data obtained from a simultaneous TG–DTA unit

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Abstract

In the present study, a novel method for determining vapor pressure values for the construction of vapor pressure–temperature curves is introduced. These calculations are based on evaporation data, which are obtained from thermogravimetric experiments. The technique as advocated by Price and Hawkins focused on adapting the Langmuir equation for evaporation to obtain vapor pressure values for volatile organic substances. In practice, it was discovered that such calculations produce unrealistic values of the vaporization coefficient, α. Hence, a comparative method, which eliminates the need for the inclusion of this vaporization coefficient factor, is developed in the present study. This method is based on the ratio of the Langmuir equations for a reference material and the sample under investigation. The proposed method also possesses the potential for calculations that will determine the molecular weights for unknown materials.

Keywords: Evaporation; Thermogravimetry; Vapor pressure; Langmuir equation

1. Introduction

Over the years, the determination of the vapor pressures of volatile organic substances has been the subject of numerous papers [1–4]. The renewed interest in establishing an efficient means to determine vapor pressure data using a thermal balance may be attributed to the growing demand that volatile chemicals be accompanied by such data [5]. For industrial processing purposes, the determination of the exposure limit for various volatile materials may become a standard safety protocol, and the values for exposure limits can easily be established with the aid of vapor pressure data.

In 1998, Price and Hawkins published a paper entitled "Calorimetry of Two Disperse Dyes Using Thermogravimetry" which spurred the authors' interest in this subject [6]. In the past, there were also several other papers, which advocated the use of thermogravimetry to develop vapor pressure curves [7–9]. These papers were based on the application of the Langmuir equation for evaporation [10]. The Langmuir equation for evaporation is given as follows:

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

where ($\mathrm{d}m/\mathrm{d}t$) is the rate of mass loss with respect to time per unit area, P the vapor pressure, α the vaporization coefficient, M the molecular weight of material under investigation, R the gas constant and T is the absolute temperature. To facilitate the calculation

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of vapor pressure data, the above equation is often presented in the following form:

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

where v and k represent the partitioned forms of the original equation. The k term is often assumed to be independent of experimental influences. One fundamental assumption of the above equation, is that the vaporization coefficient term, α, maintains a value that is close to unity. However, it was noted that in practice, the value of α was far from ideal, as it significantly deviated from unity for experiments conducted in the present of purge gases. Hence, the question as to whether the k term is really experimentally independent is posed.

For the present study, a new method (hence, referred to as the comparative method) is proposed for calculating vapor pressure data. The purpose of this method is to address the problem of the significantly altered vaporization coefficient value, α. This method involves combining the evaporation data (as obtained from a thermal balance) with the reference vapor pressure data of a suitable reference material. The Langmuir equation for evaporation is then applied to determine the vapor pressure values of a chosen sample material. The Langmuir equations for a reference material and the sample under investigation is designated as follows:

$$\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{R}}T_1^{1/2}=\alpha M_{\mathrm{R}}\left[\frac{1}{2\pi R}\right]^{1/2}P_{\mathrm{R}} \qquad (3)$$

$$\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_{\mathrm{S}}T_1^{1/2}=\alpha M_{\mathrm{S}}\left[\frac{1}{2\pi R}\right]^{1/2}P_{\mathrm{S}} \qquad (4)$$

where the subscripts R and S refer to the reference and sample data, respectively. A ratio of Eqs. (3) and (4), and a further rearrangement of the resulting equation in terms of P_{S} would yield the comparative method equation as shown below:

$$P_{\mathrm{S}}=\left(\frac{M_{\mathrm{R}}}{M_{\mathrm{S}}}\right)^{1/2}P_{\mathrm{R}}\left[\frac{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{S}}}{(\mathrm{d}m/\mathrm{d}t)_{\mathrm{R}}}\right] \qquad (5)$$

By virtue of mathematical manipulations, the terms of $T_1^{1/2}$, α, and $(1/2\pi R)^{1/2}$ are excluded. Hence, the problem associated with the vaporization coefficient term, α, is avoided.

The evaporation data for the reference and sample materials were obtained by taking the derivative weight with respect to time values from the thermogravimetric experiments. For the study, the temperature range for each data set spans from the point at which the material is a liquid, up to the point at which the material is almost completely evaporated from the crucible. This temperature range should also correspond to the temperature range of the reference vapor pressure data that is generated from Antoine constants for the reference material [11]. The vapor pressure values for the reference material were obtained by fitting the Antoine constants (denoted

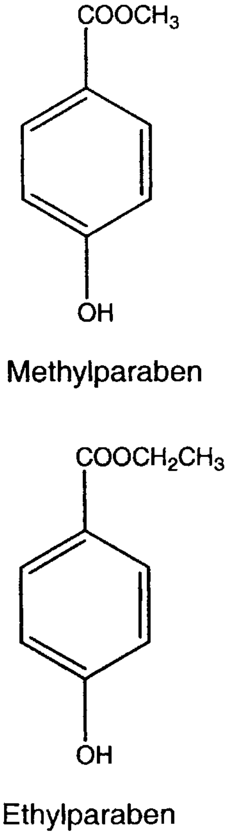

Fig. 1. A comparison of the structural similarities in methylparaben and ethylparaben.

by A, B, and C) for the material to the Antoine equation, given as

$$\log P = A - \left[\frac{B}{C+T}\right] \quad (6)$$

It would seem prudent to mention the criteria for selecting the materials involved in this study. The two main requirements imposed are, that the samples melt and evaporate within a similar temperature range, and that they exhibit structural similarities. Methylparaben (reference material) and ethylparaben (sample material) were chosen as they meet these requirements (see Fig. 1). Both compounds are preservatives that are used in the food processing industry and structurally, they differ by a –CH_2 group. They have melting points that fall within a 15 °C range and they also have comparable boiling point ranges [12].

The proposed comparative method also possesses the potential that would afford the calculation of the molecular weight for an unknown material. In addition to using the evaporation data from TG experiments, this endeavor would require the collection of experimental vapor pressure data from an apparatus for determining the boiling point of a material under reduced pressures. The equation that will be used to determine the molecular weight of the unknown material is as follows:

$$M_S = \left(\frac{P_R}{P_S}\right)^2 M_R \left[\frac{(dm/dt)_S}{(dm/dt)_R}\right]^2 \quad (7)$$

2. Experimental

The methylparaben (CAS RN 99-76-3) and ethylparaben (CAS RN 120-47-8) samples were obtained from Sigma Chemical Company, Inc., and had purity ratings of >99%, FCC. Samples were ground to a fine

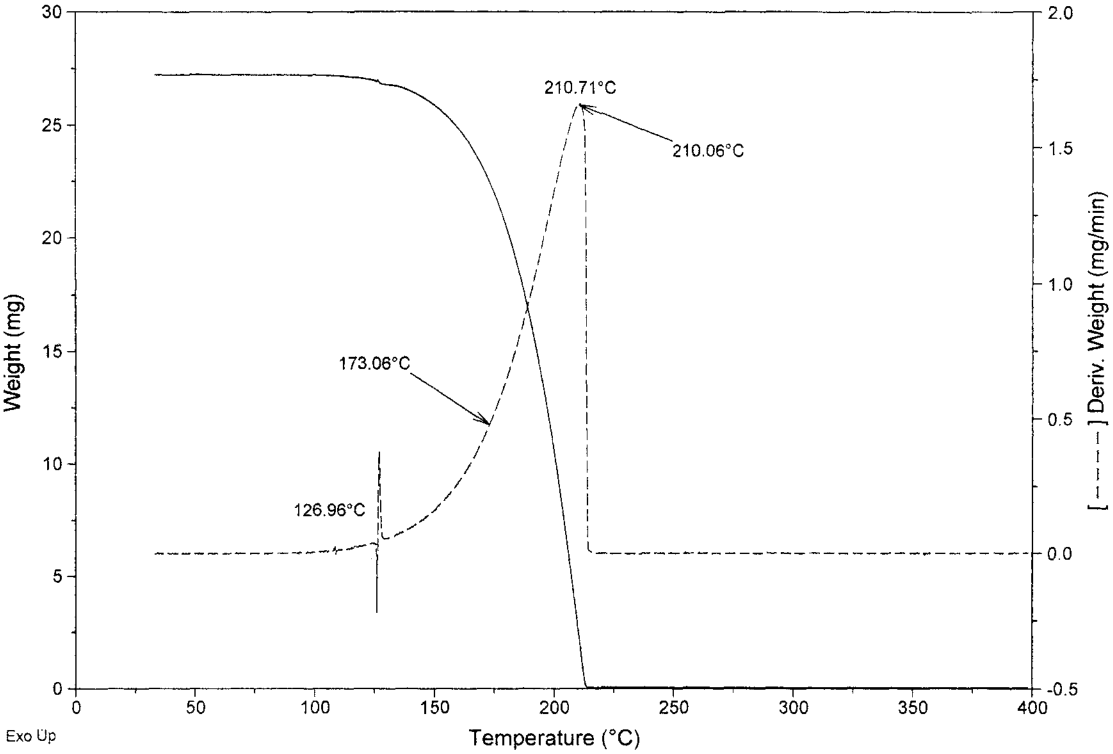

Fig. 2. The TG–DTG plot for methylparaben, with markers indicating the temperature range used for the calculation of the vapor pressure data.

powder before they were subjected to heating. A pair of platinum crucibles served as the reference and sample pans. The thermogravimetric data for both samples were obtained with a simultaneous TG–DTA unit, *TA Instruments* model number 2960. Rising temperature experiments were conducted in an atmosphere of dry air, at a flow rate of 100 ml min^{-1}. The heating rate was set at 20 °C min^{-1}, and the temperature values ranged from ambient to an end temperature of 400 °C.

3. Results and discussion

Thermogravimetric experimental data were collected for methylparaben and ethylparaben samples. In this particular study, methylparaben served as the reference calibration material. As shown in Fig. 2, the TG–DTG plot for methylparaben exhibits a distinct melting point at 126.96 °C There is no sample material left in the crucible beyond 210.71 °C, as observed by the sharp decrease on the DTG curve at this peak temperature. This is indicative that the sample undergoes melting and complete evaporation upon thermal treatment. In Fig. 2, the working temperature range for the subsequent vapor pressure calculations is clearly marked. This temperature range (173–210 °C) was selected to ensure that the data used to represent the evaporation process is occurring from a constant liquid interface.

In order to calculate the vapor pressure values for ethylparaben, the evaporation data for methylparaben was combined with the appropriate reference vapor pressure data for methylparaben. The reference vapor pressure values were generated with the appropriate Antoine constant values for methylparaben. These values are presented in Table 1. A spreadsheet as presented in Table 2, shows by example how these calculations were achieved. Using the calculated vapor pressure values, a plot of P versus T yields the vapor pressure curve for ethylparaben (see Fig. 3).

As outlined in the introduction, it is possible to use a modified form of the equation for the comparative method to determine the molecular weight of an unknown material. For the purpose of illustrating this point, a non-existent material (nebaraplyhtem) is designated as the unknown sample. Table 3 provides a representative spreadsheet that would be used for such calculations.

The aim of the proposed comparative method, is to address the problem of the non-ideal vaporization coefficient term, α. To illustrate the extent of the deviation of this term from unity, a sample spreadsheet involving the determination of these values are

Table 1
Reference vapor pressure data for methylparaben that were generated from the appropriate Antoine constants

T (K)	P (kPa)	T (K)	P (kPa)
446	1.2768	482	6.4737
447	1.3450	483	6.7295
448	1.4162	484	6.9933
449	1.4905	485	7.2654
450	1.5680	486	7.5458
451	1.6488	487	7.8349
452	1.7331	488	8.1328
453	1.8208	489	8.4397
454	1.9122	490	8.7557
455	2.0074	491	9.0811
456	2.1064	492	9.4161
457	2.2094	493	9.7608
458	2.3165	494	10.1155
459	2.4278	495	10.4804
460	2.5435	496	10.8557
461	2.6637	497	11.2415
462	2.7885	498	11.6381
463	2.9180	499	12.0457
464	3.0524	500	12.4645
465	3.1918	501	12.8948
466	3.3364	502	13.3367
467	3.4863	503	13.7904
468	3.6416	504	14.2563
469	3.8026	505	14.7344
470	3.9692	506	15.2250
471	4.1417	507	15.7284
472	4.3203	508	16.2448
473	4.5051	509	16.7744
474	4.6962	510	17.3174
475	4.8939	511	17.8741
476	5.0982	512	18.4446
477	5.3094	513	19.0293
478	5.5275	514	19.6284
479	5.7529	515	20.2420
480	5.9856	516	20.8705
481	6.2258	517	21.5141

Methylparaben—Formula: $C_6H_8O_3$; M_W: 152.14 g mol^{-1}; mp: 131 °C (404 K); bp: 270–280 °C (543–553 K); CA: 99-76-3; Antoine constants (for liquid): $A = 5.23662$, $B = 1159.34$, $C = -220.03$; $\log P = A - [B/(C+T)]$; range: 446–517 K; S.D.:1.0.

Table 2

Comparative method spreadsheet showing the calculations used to determine the vapor pressure data for ethylparaben

T_1 (K)	M_R (kg mol^{-1})	M_S (kg mol^{-1})	A: $(M_R/M_S)^{1/2}$	B: P_R (Pa)	$(dm/dt)_S$ (mg min^{-1})	$(dm/dt)_R$ (mg min^{-1})	C: $[(dm/dt)_S/(dm/dt)_R]$	$(A \times B \times C)$: P_X (Pa)
446	0.15214	0.16617	0.95685	1276.780	0.3617	0.4759	0.7600	928.5262
447	0.15214	0.16617	0.95685	1344.994	0.3785	0.4988	0.7588	976.5739
448	0.15214	0.16617	0.95685	1416.206	0.3942	0.5213	0.7562	1024.7091
449	0.15214	0.16617	0.95685	1490.516	0.4139	0.5436	0.7614	1085.9204
450	0.15214	0.16617	0.95685	1568.028	0.4291	0.5686	0.7547	1132.2721
451	0.15214	0.16617	0.95685	1648.847	0.4490	0.5929	0.7573	1194.7871
452	0.15214	0.16617	0.95685	1733.080	0.4694	0.6191	0.7582	1257.3212
453	0.15214	0.16617	0.95685	1820.837	0.4902	0.6475	0.7571	1319.0159
454	0.15214	0.16617	0.95685	1912.231	0.5105	0.6727	0.7589	1388.5451
455	0.15214	0.16617	0.95685	2007.375	0.5332	0.7010	0.7606	1460.9856
456	0.15214	0.16617	0.95685	2106.385	0.5529	0.7295	0.7579	1527.5820
457	0.15214	0.16617	0.95685	2209.382	0.5769	0.7606	0.7585	1603.4683
458	0.15214	0.16617	0.95685	2316.485	0.6021	0.7893	0.7628	1690.8355
459	0.15214	0.16617	0.95685	2427.818	0.6258	0.8213	0.7620	1770.0894
460	0.15214	0.16617	0.95685	2543.506	0.6499	0.8528	0.7621	1854.7164
461	0.15214	0.16617	0.95685	2663.678	0.6762	0.8854	0.7637	1946.5373
462	0.15214	0.16617	0.95685	2788.463	0.7020	0.9196	0.7634	2036.8002
463	0.15214	0.16617	0.95685	2917.994	0.7279	0.9540	0.7630	2130.3608
464	0.15214	0.16617	0.95685	3052.406	0.7549	0.9896	0.7628	2228.0115
465	0.15214	0.16617	0.95685	3191.835	0.7803	1.0280	0.7590	2318.2186
466	0.15214	0.16617	0.95685	3336.422	0.8076	1.0650	0.7583	2420.8789
467	0.15214	0.16617	0.95685	3486.307	0.8361	1.1020	0.7587	2530.9739
468	0.15214	0.16617	0.95685	3641.635	0.8643	1.1450	0.7548	2630.2728
469	0.15214	0.16617	0.95685	3802.551	0.8942	1.1800	0.7578	2757.2306
470	0.15214	0.16617	0.95685	3969.204	0.9209	1.2210	0.7542	2864.4791
471	0.15214	0.16617	0.95685	4141.746	0.9501	1.2600	0.7540	2988.3233
472	0.15214	0.16617	0.95685	4320.328	0.9798	1.3000	0.7537	3115.7039
473	0.15214	0.16617	0.95685	4505.106	1.0130	1.3430	0.7543	3251.5008

Reference material: methylparaben; sample material: ethylparaben.

presented (refer to Table 4). The method used to calculate the various parameters displayed in the spreadsheet, has previously been reported. While the deviation in these α values may appear to be negligible, the resultant effect of these small variations on the calculated k values is rather significant. Hence, by excluding the need for the determination of these α, and subsequently the k terms, the errors associated with the use of these values in the calculation of vapor pressure values should be minimized.

Table 3

A sample spreadsheet illustrating the calculations used to determine the molecular weight of a non-existent unknown material, nebaraplyhtem

T_1 (K)	P_R (Pa)	P_S (Pa)	A: $(P_R/P_S)^2$	B: M_R (kg mol^{-1})	$(dm/dt)_S$ (mg min^{-1})	$(dm/dt)_R$ (mg min^{-1})	C: $[(dm/dt)_S/(dm/dt)_R]^2$	$(A \times B \times C)$: M_S (kg mol^{-1})
446	961	974	0.97348	0.15214	0.3617	0.4759	0.5777	0.0856
447	971	983	0.97573	0.15214	0.3785	0.4988	0.5758	0.0855
448	981	992	097795	0.15214	03942	0.5213	0.5718	0.0851

Reference material: methylparaben; sample material: nebaraplyhtem.

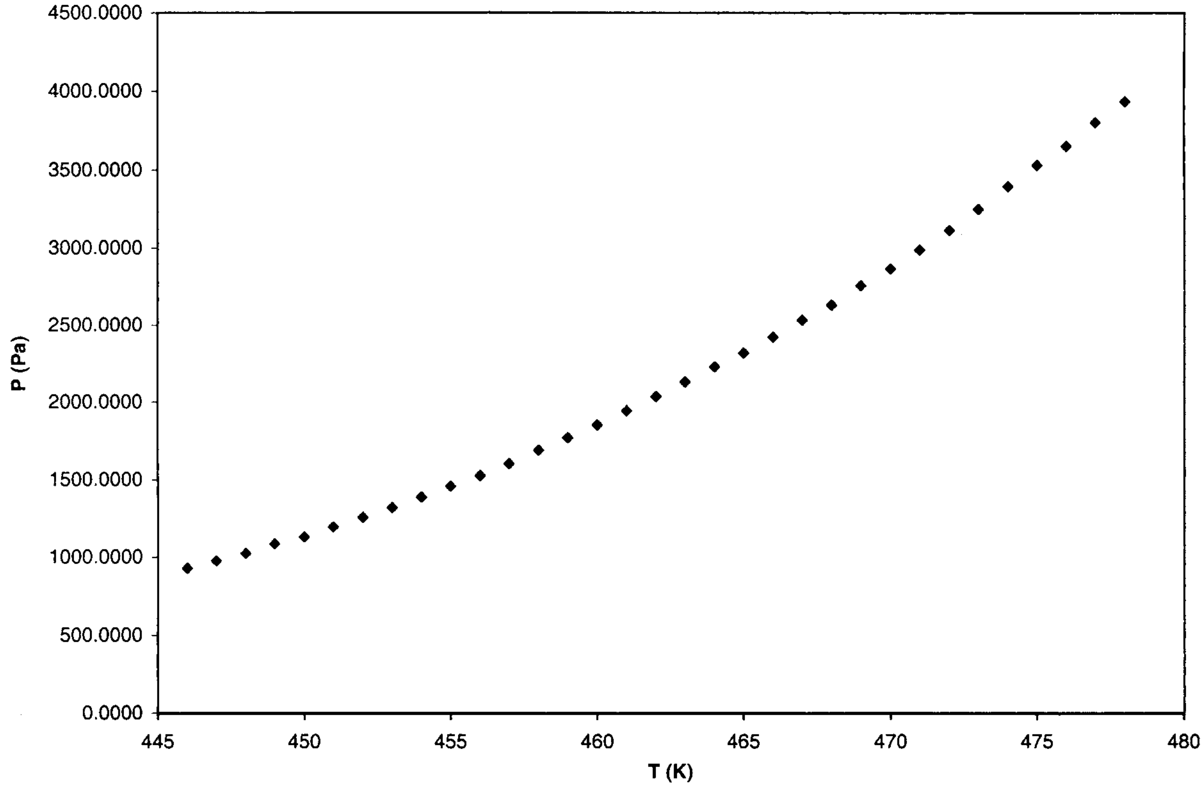

Fig. 3. A plot of P vs. T, which yields the vapor pressure curve for ethylparaben.

Table 4
A spreadsheet for vapor pressure calculations for butylated hydroxytoluene (BHT), displaying the deviations in the calculated and k values

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	5.91 3E−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	1954.18	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	0.0200	122798	5.846E−05
420.15	5.005E−04	1906.74	43.666	0.4356	2726.68	0.0220	124758	5.801E−05
422.15	5.354E−04	1915.82	43.770	0.4709	2957.02	0.0230	126191	5.735E−05

$M_{\mathrm{W}} = 220.35$ g mol^{-1} or 0.22035 kg mol^{-1}; area of pan, $A = 0.2248$ cm^2 or 2.248E−05 m^2.

4. Conclusions

The results from this study show that the comparative method is a suitable approach for determining the vapor pressure data of materials, as used in conjunction with thermogravimetric data from a thermal balance. It gives good vapor curves and is especially well suited for analyzing small amounts of materials (e.g. pharmaceutical samples). A modified form of the equation used in the comparative method may also be applied to give the molecular weight of an unknown material.

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