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Gas chromatographic determination of vapour pressure and related thermodynamic properties of monoterpenes and biogenically related compounds

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Abstract

The (subcooled) liquid vapour pressure, heat of vapourization and gas–liquid heat capacity difference of monoterpenes and biogenically related compounds were determined by a gas–liquid chromatographic method based on Kovats retention indices. Compared to those used in previous studies using the same method, these compounds are structurally diverse and have relatively low boiling points. Despite of this and even though the difference in activity coefficients in the chromatographic column stationary phase between the test and reference compounds were ignored, results for vapour pressure compare favorably with experimental literature data. The results indicate that the method can be improved by introducing temperature dependent activity coefficients, preferably based on a physicochemical model for gas–liquid partitioning. © 2002 Published by Elsevier Science B.V.

Keywords: Vapour pressures; Thermodynamic parameters; Retention indices; Activity coefficients; Monoterpenes; Terpenes

1. Introduction

Recent developments suggest that monoterpenes and related plant constituents may be used as alternatives to chlorofluorocarbons as industrial solvents [1] and as alternative crop protectants [2]. The environmental fate of these chemicals has not been well investigated thus far. Experimental vapour pressure data, an important property in, e.g., environmental fate modeling, are scarce. Liquid vapour pressures and the thermodynamically related enthalpy and heat capacity differences can be estimated

using a gas chromatography (GC) based retention index method (GC-VAP) [3,4] which has recently been applied to several classes of compounds [3–7]. Although the GC-VAP method was not developed for the sole purpose of liquid vapour pressure determination at 25 °C, Koutek et al. [8] recently used this endpoint to compare five GC based methods and concluded that three of these, including our GC-VAP method, may serve as very useful alternatives to direct physicochemical approaches. The GC-VAP method is based on the use of Kovats retention indices determined on a nonpolar stationary phase under isothermal conditions and using liquid *n*-alkanes as reference compounds. A thermodynamic expression is derived that relates the vapour pressure

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of a compound at a certain temperature to those of the corresponding *n*-alkanes and some correction factors. In contrast to the Hamilton-based GC methods [9], the heat of vapourization of the compounds are assumed to be temperature dependent. The Hamilton assumption may lead to substantial extrapolation errors [5]. A fundamental problem in all GC based methods is the dependence of the retention time of a compound on its activity coefficient in the stationary phase. In the GC-VAP method, the ratio of activity coefficients of the substance and the nearest eluting *n*-alkane is incorporated by an expression based on McReynolds constants of model compounds [3]. Compared to previously studied compounds [3–7], those studied here represent a heterogeneous group of structures with relatively low boiling points. Considering this, two potential problems can be identified beforehand: (i) appropriate model compounds to obtain activity coefficient ratios may not be available for all of the structures studied here, and (ii) the influence of the activity coefficient on the chromatographic behavior may become unacceptably large at the lower chromatographic temperatures required for these relatively volatile compounds. Thus, this work is a new critical test of both theoretical and practical aspects of the GC-VAP method. The potential problems (i) and (ii), both related to the activity coefficients, will be studied in some detail. Chemicals for this study were selected to reflect at least some of the extreme structural diversity of monoterpenes. Most of the selected structures are potential crop protectants.

2. Retention index method (GC-VAP)

The method has been described into detail before (e.g., Refs. [3,5]). The GC method is based on the use of *n*-alkanes as reference compounds through the determination of Kovats retention indices and the equilibrium fugacity model which states that the ratio of the mole fraction y_i and x_i in the carrier gas and stationary phase, respectively, is proportional to the activity coefficient γ_i and the vapour pressure P_i of the incompressible pure liquid compound *i* [10]:

$$y_i/x_i = \gamma_i P_i / P_t \quad (1)$$

where P_t is the (mean) carrier gas pressure; $\gamma_i = 1$ for pure liquids and ideal solutions. It is assumed that the pure vapour and the vapour-carrier gas mixture both exhibit ideal behavior or both exhibit identical non-ideal behavior. The Kovats retention index of a solute *i* (I_i) is defined as follows:

$$I_i = 100 [\log (t'_{R,i}) - \log (t'_{R,z})] / [\log (t'_{R,z+1}) - \log (t'_{R,z})] + 100z \quad (2)$$

z and $z+1$ are the numbers of the carbon atoms of *n*-alkanes eluting just before and after *i*. It can be shown that at infinite dilution the capacity factor $t'_{R,i}/t_0$ is inversely proportional to the ratio y_i/x_i of compound *i* [10]; t_0 is the retention time of the unretarded component. The same holds for *n*-alkanes. Using this in Eq. (1) and by substituting the result in Eq. (2) followed by some rewriting an expression for the vapour pressure of compound *i* can be obtained:

$$\begin{aligned} \log P_i &= \log P_z \\ &+ (100z - I_i)(\log P_z - \log P_{z+1})/100 \\ &- \log (\gamma_i/\gamma_z) \end{aligned} \quad (3)$$

In the derivation of Eq. (3), the ratio of the activity coefficients of *n*-alkanes (γ_z/γ_{z+1}) is approximated by 1 ($\gamma_z = \gamma_{z+1}$). For a DB-1 stationary phase at 120 °C, Spieksma et al. [3] found the value 1.113 for the ratio γ_z/γ_{z+1} by evaluating net retention data for *n*-alkanes using the relationship $(t_i - t_0)/(t_z - t_0) = (\gamma_z P_z)/(\gamma_i P_i)$ and using literature data for the *n*-alkane vapour pressures. If the approximation of γ_z/γ_{z+1} by 1 is not applied, the expression “ $(100z - I_i)[\log (\gamma_z/\gamma_{z+1})]/100$ ” would have to be added to Eq. (3), leading to a correction for $\log P_i$ at 120 °C of between -0.05 and 0.00 log units. Because both I_i and γ_z/γ_{z+1} are temperature dependent, the approximation of the ratio γ_z/γ_{z+1} by 1 results in a temperature dependent overestimation of the vapour pressure. However, the size of this overestimation is overshadowed by the similar type of correction required for the ratio (γ_i/γ_z) . In the current version of the GC-VAP model, the ratio of the activity coefficients γ_z/y_i is assumed to be constant and temperature independent. Spieksma et al. [3] calculated the $\log (\gamma_z/y_i)$ values from the ΔI values determined by McReynolds [11] for nine compounds at 120 °C.

In practice, the $\log(\gamma_z/y_i)$ value of one of the nine compounds is selected which is believed to be appropriate for the compounds under study. Uncertainties in this McReynolds approach are the selection of the model compound and the 120 °C oven temperature used. Because it was not clear which model compound from Ref. [3] is most appropriate for the compounds under study, the value of 1 was used for the ratio of the activity coefficients (γ_z/y_i).

From Eq. (3), the heat of vapourization (ΔH_{vap}) and gas–liquid heat capacity difference (ΔC_p) can be calculated by making use of their thermodynamic definitions, $\Delta H = RT^2(d \ln P/dT)$ and $\Delta C_p = d\Delta H/dT$, respectively. Note that Because γ_z/y_i is assumed to temperature independent, it does not affect the heat of vapourization and differences in heat capacity:

$$\begin{aligned} \Delta H_i(T) = & \Delta H_z + (100_z - I_i)(\Delta H_z - \Delta H_{z+1})/100 \\ & - 2.30259RT^2(\log P_z \\ & - \log P_{z+1})(dI_i/dT)/100 \end{aligned} \quad (4)$$

$$\begin{aligned} \Delta C_{p,i}(T) = & \Delta C_{p,z} \\ & + (100_z - I_i)(\Delta C_{p,z} - \Delta C_{p,z+1})/100 \\ & - [RT(\log P_z - \log P_{z+1})(dI_i/dT)/50 \\ & + (\Delta H_z - \Delta H_{z+1})(dI_i/dT)/100 \\ & + RT^2(\log P_z - \log P_{z+1})(d^2I_i/dT^2)/100] \end{aligned} \quad (5)$$

Put into practice, the first step of the GC-VAP method is the GC measurement of net retention times and I_i of Eq. (2) at several temperatures. Then the temperature dependence of I_i , including first and second order derivatives, is calculated according to:

$$I_i(T) = B_0 + B_1T^2 \quad (6)$$

B_0 and B_1 are empirical regression coefficients. The nature of this equation is not known but it generally results in accurate regression results with standard errors lower than 1%.

The next step is the calculation of $\log P_z$ of the n -alkanes by fitting T and z to experimental values of the vapour pressure, heat of vapourization, and heat

capacity differences according to the following equation:

$$\log P_z = A_z + B_z/T + C_z/T^2 \quad (7)$$

with $A_z = 4.877735 (\pm 0.014939) + 0.303157 (\pm 0.00222)z - 0.007281 (\pm 0.00007)z^2$; $B_z = 485.68961 (\pm 5.613) - 261.5436 (\pm 0.47628)z + 5.8678 (\pm 0.005539)z^2$; $C_z = -86\,487.5 (\pm 55.09) + 344.999 (\pm 14.2985)z - 874.879 (\pm 0.8257)z^2$.

The corresponding equations for the heat of vapourization and heat capacity difference for the n -alkanes can be found by using again the thermodynamic definitions for these properties given before.

A_z , B_z , and C_z in Eq. (7) have been derived from independent measurements of vapour pressures, heats of vapourization, and heat capacity differences of the n -alkanes. Thus, A_z , B_z , and C_z are empirical parameters for n -alkanes, A_z and B_z being similar to constants in the Clausius–Clapeyron equation. Heat capacity differences of the n -alkanes at 298.15 K have been used to calculate the C_z factors, which span a range of $z=3$ –14. The B_z factors have been derived from calorimetric determination of the heats of vapourization of the n -alkanes at 298.15 K, spanning a range of $z=6$ –17, and the A_z factors from 297 experimental P values in the range of $z=3$ –35, determined at 150–763 K ($\log P_z$ values between -4.56 and $+3.31$). No experimental values were omitted, even if the difference between the experimental value and the model was more than three times the standard deviation [6].

3. Experimental

3.1. Chemicals and solutions

The chemicals studied are listed in Table 1, together with their molecular formulae and CAS numbers. Chemicals were purchased from Sigma–Aldrich (Zwijndrecht, The Netherlands) and their purity was higher than 97% unless specified otherwise. They were used without further purification. To reduce the number of peaks in the chromatograms and to be able to use lower chromatographic temperatures for the more volatile compounds, three solutions were prepared in pentane (Rathburn, Walk-

Table 1

Chemicals with their molecular formula, CAS number and solution in which they were used, listed in order of gas chromatographic elution at 90 °C

Compound name	Formula	CAS No.	Solution		
			1	2	3
Myrcene	C ₁₀ H ₁₆	123-35-3	*		
Norcamphor	C ₇ H ₁₀ O	497-38-1	*		
<i>exo</i> -Norborneol	C ₇ H ₁₂ O	497-37-0	*		
(<i>R</i>)-(+)-Limonene	C ₁₀ H ₁₆	5989-27-5	*		
Cineole	C ₁₀ H ₁₈ O	470-82-6	*		
L-Adamantane	C ₁₀ H ₁₆	281-23-2	*		
α-Pinene oxide	C ₁₀ H ₁₆ O	1686-14-2	*		
α + β-Thujone ^a	C ₁₀ H ₁₆ O	546-80-5	*	*	
(+)-Limonene oxide ^b	C ₁₀ H ₁₆ O	1195-92-2		*	
(<i>R</i>)-(+)-Citronellal ^c	C ₁₀ H ₁₈ O	2385-77-5		*	
(+)-Camphor	C ₁₀ H ₁₆ O	464-49-3		*	
(+)-α-Terpineol	C ₁₀ H ₁₈ O	7785-53-7		*	
(1 <i>R</i>)-(-)-Thiocamphor	C ₁₀ H ₁₆ S	53402-10-1		*	
(<i>R</i>)-(+)-Pulegone	C ₁₀ H ₁₆ O	89-82-7		*	
Cinnamaldehyde	C ₉ H ₈ O	14371-10-9		*	*
1-Adamantanol	C ₁₀ H ₁₆ O	768-95-6		*	*
Anethole	C ₁₀ H ₁₂ O	104-46-1			*
Thymol	C ₁₀ H ₁₄ O	89-83-8			*
Carvacrol	C ₁₀ H ₁₄ O	499-75-2			*
2-Adamantanone	C ₁₀ H ₁₄ O	700-58-3			*
Eugenol	C ₁₀ H ₁₂ O ₂	97-53-0			*
Diphenylmethane (DPHM) ^d	C ₁₃ H ₁₂	101-81-5			*

^a Mixture of *cis* and *trans*, purity ~67.3%.

^b Mixture of *cis* and *trans*.

^c Purity ~90%.

^d Chem Service, West Chester, PA, USA.

erburn, UK). Table 1 shows the composition of the three solutions. To allow comparison between different solutions, some compounds were studied in two solutions. Diphenylmethane (DPHM) was included to allow comparison with previous GC-VAP studies. The *n*-alkanes C₉–C₁₂, C₁₁–C₁₃ and C₁₂–C₁₅ (Polyscience, Niles, IL, USA) were applied in solutions 1, 2 and 3, respectively.

3.2. Chromatography

A Hewlett-Packard Model 5890 series II gas chromatograph equipped with a flame ionization detector, a split–splitless injection port in the split mode and a liner with a mixing chamber was used. A 30 m×0.32 mm fused-silica column from J&W (Folsom, CA, USA) with a nonpolar DB-1 liquid

phase (film thickness 0.25 μm) was applied. As carrier gas helium was used at a constant pressure of 75 kPa. The injector and detector temperatures were 200 °C and 250 °C, respectively. At a chromatographic temperature of 100 °C, the split ratio was 1:28 (septum purge 2 ml/min, column flow 1.5 ml/min and split flow 40 ml/min). The temperature ranges applied were 50–90 °C, 60–110 °C and 70–120 °C for solutions 1, 2 and 3, respectively, with intervals of 10 °C. These temperature ranges resulted in retention times of usually less than 1 h for the last eluting compound at the lowest temperatures and baseline separation between the first eluting compound and the solvent peak at the highest temperature. The minimum temperature at which the system could be stabilized without coolant devices was 50 °C. An aliquot of 1 μl (>100 pg of compound) of the sample was manually injected. At each tempera-

ture the retention of the unretarded component was determined through injection of methane.

3.3. Calculations

Linear and nonlinear regression calculations were carried out using the statistical program SGPLUS (Oasis, Nieuwegein, The Netherlands). Further calculations were performed in the spreadsheet program Excel 97 for Windows (Microsoft).

4. Results and discussion

4.1. Chromatography

Compared to compound series in previous GC-VAP studies, the compounds studied here are structurally diverse. In most cases, this resulted in changes of elution order at different temperatures necessitating additional injection of standards to identify peaks. To obtain a reasonable span in retention times for all compounds, three solutions were prepared. Both these measures caused the chromatographic part of the work to be longer, thereby somewhat reducing the advantage of the GC-VAP method over several other methods. The mixture of *cis*- and *trans*-(+)-limonene oxide resulted in two peaks. The low purity of some of the chemicals did not cause any chromatographic problems, this being one of the advantages of the GC-VAP method [12].

4.2. Kovats retention indices at different temperatures

Kovats retention indices were determined in quadruplicate at the specified temperatures. Results of the regression according to Eq. (6) are summarized in Table 2. The slightly different results for *cis*- and *trans*-(+)-limonene oxide are listed separately in Table 2. Because the elution order of these isomers was not determined, the results were averaged in further calculations. As may be expected, higher B_1 coefficients generally led to better correlations. A B_1 coefficient with a low value (close to zero) indicates that the compound behaved similarly to the corresponding nearest *n*-alkane on the GC column. Un-

expectedly perhaps, generally lower B_1 coefficients were found for compounds with polar groups. In agreement with this trend, negative B_1 coefficients were observed for the hydroxyl group containing structures of *exo*-norborneol, thymol and carvacrol. A similar trend has been observed before in a series of fatty acid esters [6]. The reason for these observations is not clear at the moment. The compounds of $\alpha + \beta$ -thujone, cinnamaldehyde and 1-adamantanol were analyzed in two solutions at different temperature ranges. B_0 and B_1 coefficients obtained for these compounds at two temperature ranges are significantly different. According to Eq. (6), the B_0 values are equal to the Kovats retention index at 0 K, and are thus subject to large influences caused by the inadequacy of Eq. (6) outside the experimental temperature range. The differences between the B_1 coefficients obtained for $\alpha + \beta$ -thujone, cinnamaldehyde and 1-adamantanol at two temperature ranges are 0.043, 0.13 and 0.15, respectively. Because there is no reason to prefer one result over the other, the observed differences should be regarded as an inherent statistical uncertainty associated with the selection of temperature ranges. This implies that the observed negative B_1 coefficients may in fact not be significantly different from zero. Differences of the same order of magnitude were observed between the present and past DPHM regression results. The much higher temperatures applied in Ref. [4] compared to the temperatures used in the present study (433.15–493.15 versus 343.15–393.15 K) and the accordingly shorter retention times may explain their somewhat poorer regression results.

4.3. Thermodynamic properties

Results obtained at environmentally relevant temperatures (mostly 298.15 K) for the vapour pressure and boiling point temperatures at 760 mmHg are listed in Table 3 (1 mmHg = 133.322 Pa). Boiling point temperatures at atmospheric pressure were calculated from the liquid vapour line. Heat of vapourization and gas–liquid differences in heat capacity are listed in Table 4.

The vapour pressure values ($\log P$, mmHg) range from -1.65 for eugenol to 0.14 for myrcene at 298.15 K. These values are high compared to the $\log P$ values obtained for tetrachlorobenzyltoluenes

Table 2

GLC Kovats retention indices (I_i) as a function of temperature according to Eq. (6): regression coefficients ($B_{0,1}$), their standard errors, correlation coefficients (r^2) and the standard error of regression (SER)

Compound*	B_0	$B_1 \cdot 1000$	r^2	SER
Myrcene ^a	983.28±0.11	0.0860±0.0009	0.9977	0.04
Norcamphor ^a	973.8±1.9	0.230±0.016	0.9177	0.7
<i>exo</i> -Norborneol ^a	1021±3	-0.14±0.02	0.6351	1.0
Limonene ^a	974.09±0.13	0.4780±0.0011	0.9999	0.05
Cineole ^a	1036.0±1.1	0.159±0.009	0.9391	0.4
Adamantane ^a	945.3±0.3	1.120±0.003	0.9999	0.12
Pinene oxide ^a	1047.3±0.5	0.533±0.004	0.9987	0.19
Thujone ^a	1075.0±0.6	0.362±0.005	0.9959	0.2
Thujone ^b	1069.8±0.9	0.405±0.007	0.9939	0.4
Limonene oxide ^{b,e}	1114.4±1.4	0.291±0.011	0.9690	0.7
Limonene oxide ^{b,e}	1120.8±1.2	0.268±0.009	0.9732	0.6
Citronellal ^b	1147.1±0.9	0.072±0.007	0.8274	0.4
Camphor ^b	1082.6±0.9	0.607±0.007	0.9971	0.4
Terpineol ^b	1187±2	0.171±0.016	0.8238	1.0
Thiocamphor ^b	1090.83±0.19	1.1450±0.0014	1.0000	0.09
Pulegone ^b	1214.7±1.4	0.314±0.011	0.9721	0.7
Cinnamaldehyde ^b	1222±2	0.384±0.018	0.9537	1.1
Cinnamaldehyde ^c	1204.1±0.8	0.514±0.006	0.9973	0.3
Adamantanol ^b	1191±2	0.614±0.018	0.9814	1.1
Adamantanol ^c	1170.7±1.2	0.764±0.009	0.9969	0.5
Anethole ^c	1213.40±0.15	0.5290±0.0011	0.9999	0.07
Thymol ^c	1246±2	-0.229±0.015	0.9110	0.9
Carvacrol ^c	1336.8±1.9	-0.114±0.014	0.7339	0.9
Adamantanone ^c	1193.7±1.1	0.981±0.008	0.9985	0.5
Eugenol ^c	1301.0±0.5	0.443±0.004	0.9982	0.2
DPHM ^c	1293.1±0.4	0.905±0.003	0.9997	0.19
DPHM ^d	1276.9±3.6	0.777±0.017	0.998	0.76

*For complete compound names: see text and Table 1.

^a Solution 1, T range 323.15–363.15 K, $\Delta T=10$.

^b Solution 2, T range 333.15–383.15 K, $\Delta T=10$.

^c Solution 3, T range 343.15–393.15 K, $\Delta T=10$.

^d From Ref. [4], T range 433.15–493.15 K, $\Delta T=10$.

^e *cis* and *trans* isomers. Elution sequence not determined.

(-5.173 to -4.677) [5], polycyclic aromatic compounds (-4.588 to -0.599) [4], fatty acid esters (-7.17 to -1.50) [6] and chlorinated dibenzo-*p*-dioxins (-6.41 to -2.20) [7]. The log P values obtained for a series of chlorobenzenes and chlorophenols (-2.59 to 1.14) [3] cover the range of values obtained in this study.

As may be expected (see Table 2 and Section 4.2), slightly but statistically different heats of vapourization and differences in heat capacities were obtained for α + β -thujone, cinnamaldehyde and 1-adamantanol at different temperature ranges. These differences are less than 0.3 kcal/mol and 0.3 cal mol⁻¹ K⁻¹, respectively (1 cal=4.184 J). The differences

between the vapour pressures are smaller than (α + β -thujone), or similar in magnitude (cinnamaldehyde and 1-adamantanol) to the calculated standard error. These differences should be regarded as an additional statistical uncertainty associated with the selection of the temperature range. Compared to these uncertainties, somewhat larger differences were observed between the presently and previously [4] obtained vapour pressure and heat of vapourization values for DPHM. Results from Ref. [4] were obtained with an earlier version of the GC-VAP method. Since then, the parameters A_z and B_z but not C_z of Eq. (7) have been refined, probably explaining these somewhat larger differences.

Table 3

GC-VAP and experimental literature (Lit. values) for vapour pressures (log P , mmHg) at 298.15 K, unless specified otherwise, and boiling point temperature ($T_{b.p.}$, K) at 760 mmHg

Compound*, T	Log P		$T_{b.p.}$	
	GC-VAP ^a	Lit. values	GC-VAP ^a	Lit. values ⁱ
Myrcene, 297.15	0.10	0.28 ^b , 0.28 ^f	448	440
Myrcene, 298.15	0.14	0.27 ^c , 0.30 ^f		
Norcamphor	0.12		452	443
<i>exo</i> -Norborneol	0.04		446	
Limonene, 279.15	-0.61	-0.86 ^d	464	450
Limonene, 296.65	-0.05	0.18 ^d		
Limonene, 297.15	-0.03	0.30 ^b , 0.15 ^e		
Limonene, 298.15	0.00	0.20 ^c		
Cineole	-0.17		462	450
Adamantane	-0.15		491	
Pinene oxide	-0.40	-0.09 ^c	482	
Thujone ^j	-0.47		480	
Thujone ^j	-0.46	-0.40 ^f	481	
Limonene oxide	-0.65	-0.21 ^c	485	
Citronellal	-0.70	-0.57 ^f	481	480
Camphor	-0.62	-1.14 ^f , 0.22 ^g	493	477
		-0.18 ^g		
Terpineol, 279.15	-1.69	-1.88 ^{d,h} , -1.72 ^f	493	491
Terpineol, 296.65	-1.01	-1.26 ^{d,h} , -1.00 ^f		
Terpineol, 298.15	-0.95	-0.95 ^f , -1.29 ^g		
Thiocamphor	-0.91		523	502
Pulegone	-1.16	-1.63 ^f	504	497
Cinnamaldehyde ^j	-1.23	-1.58 ^f	509	524
Cinnamaldehyde ^j	-1.19		512	
Adamantanol ^j	-1.18		515	
Adamantanol ^j	-1.14		518	
Anethole	-1.25	-1.13 ^f	514	507
Thymol	-1.57	-1.19 ^f , -1.52 ^g	503	506
Carvacrol	-1.58	-1.39 ^f	506	509
Adamantanone	-1.35		534	
Eugenol	-1.65	-1.66 ^f	526	526
DPHM	-1.82	-3.96 ^f , -2.09 ^g	547	
DPHM ^k	-1.593			

* For complete compound names: see text and Table 1.

^a This work. Standard errors amount to 0.04 log units (log P) and 4 K ($T_{b.p.}$).^b Ref. [15]. Experimental method unknown.^c Ref. [13]. Air flow method. Uncertainty less than 0.1 log units (95% level).^d Ref. [1]. Static method.^e Ref. [14]. Static method.^f Extrapolated data from Ref. [16] using the equation $\log P = A - B/(T + C)$. Experimental method unknown.^g Interpolated data from Ref. [17] using the equation $\log P = A - B/T$. Effusion method(s).^h Solid vapour pressure converted to liquid vapour pressures. See text.ⁱ $T_{b.p.}$ was taken from Ref. [19] or supplier catalogues.^j Compounds used in two solutions: see text and Table 1.^k Result from previous GC-VAP study [4].

Table 4
Heat of vapourization (ΔH , cal/mol) and gas–liquid heat capacity difference (ΔC_p , cal mol⁻¹ K⁻¹) at 298.15 K

Compound*	ΔH^a	ΔH^b	ΔH^c	ΔH^d	ΔC_p^a	ΔC_p^e
Myrcene	12 087		11 189	11 350	-17.295	-16.69
Norcamphor	11 960			11 474	-17.170	-16.03
<i>exo</i> -Norborneol	12 557				-17.901	-16.62
Limonene	11 937	11 692		11 765	-17.231	-15.47
Cineole	12 706			11 765	-18.277	-19.75
Adamantane	11 529				-16.896	-17.60
Pinene oxide	12 806				-18.614	-18.95
Thujone ^f	13 150		12 681		-19.070	-22.24
Thujone ^f	13 084				-18.987	
Limonene oxide	13 667				-19.895	-18.08
Citronellal	14 033		13 076	13 034	-20.403	-23.71
Camphor	13 217		19 930	12 805	-19.293	-20.87
Terpineol	14 500		15 017	13 508	-21.262	-19.86
Thiocamphor	13 265			13 987	-19.628	
Pulegone	14 818		24 535	13 769	-21.947	-20.55
Cinnamaldehyde ^f	14 906		14 896	14 960	-22.158	-22.45
Cinnamaldehyde ^f	14 679				-21.823	
Adamantanol ^f	14 516				-21.549	-23.49
Adamantanol ^f	14 257				-21.192	
Anethole	14 788		14 035	14 207	-22.039	-22.58
Thymol	16 408		14 116	14 163	-24.606	-24.33
Carvacrol	16 295		14 718	14 295	-24.469	-24.33
Adamantanone	14 512				-21.759	-23.97
Eugenol	15 839		15 296	15 050	-23.983	-28.40
DPHM	15 708		36 190	15 544	-24.014	-24.68
DPHM ^g	15 084				-23.98	

* For complete compound names: see text and Table 1.

^a This work. Standard errors amount to 34–46 cal/mol (ΔH) and 0.008–0.016 cal mol⁻¹ K⁻¹ (ΔC_p).

^b Ref. [21]. Calorimetric method. Standard error approximately 20 cal/mol.

^c Calculated by applying $\Delta H = RT^2(\ln P/dT)$ to Antoine's equation and taking the values for *A*, *B* and *C* from Ref. [16].

^d Calculated from the boiling point temperature ($T_{b,p}$ /K) according to the Hildebrand rule [22]: ΔH (cal/mol) = $-2950 + 23.7T_{b,p} + 0.02T_{b,p}^2$. $T_{b,p}$ was taken from Ref. [19] or supplier catalogues.

^e Ref. [23]. Calculated as $C_p(\text{gas})$ (procedure Rihani–Doraiswamy) – $C_p(\text{liquid})$ (procedure Chueh and Swanson or Johnson and Huang).

^f Compounds used in two solutions: see text and Table 1.

^g Result from previous GC-VAP study [4].

4.4. Literature data

Experimental literature vapour pressure data and when known, the experimental methods used and the claimed statistical uncertainties, are listed in Table 3. The experimental methods include an air flow method [13], static methods [1,14] and in one case the method was not specified [15]. These experimental methods are generally referred to as “direct methods” because they are based on the direct measurement of the vapour pressure or another parameter related to it. In addition, vapour pressures at 298.15 K were calculated by inter- (myrcene) or extrapolations on the liquid vapour line using the *A*, *B* and *C*

parameters taken from Ohe [16] in Antoine's equation $\log P = A - B/(T + C)$. The resulting low vapour pressures for (+)-camphor and DPHM compared to other experimental literature data may be explained by the large extrapolations (approximately 150 and 200 K, respectively) according to the Antoine equations outside their experimental temperature region. Applying the Clausius–Clapeyron equation to the data collected by Ohe [16] results in a much higher vapour pressure for DPHM at 298.15 K ($\log P$, mmHg = -1.212) [5]. Uncertainties related to extrapolations to 298.15 K via the Antoine equation have been observed before [4,5]. For other compounds than (+)-camphor and DPHM, the differ-

ences between experimental temperature range at which Antoine's parameters were determined and 298.15 K are less than 60 K.

Finally, (sublimation) vapour pressures were calculated by interpolations on the solid vapour line using the A and B parameters taken from Jones [17] in the equation $\log P = B - A/T$. The solid-phase (sublimation) vapour pressures (P_S) of terpineol [1], and the vapour pressures taken from Jones [17] were converted to liquid vapour pressures (P_L) by using the melting point temperature in the equation $\ln(P_S/P_L) = -6.8(T_{m.p.}/T - 1)$ taken from Ref. [18]. $T_{m.p.}$ was taken from Ref. [19] or supplier catalogues. The constant 6.8 in this equation is equal to $\Delta S_f/R$, in which ΔS_f is the entropy of fusion and R is the gas constant (1.987 cal/mol·K). ΔS_f has been shown to be remarkably constant at 13.5 cal mol⁻¹ K⁻¹ for many organic molecules [20]. (+)-Camphor, however, has a substantially lower ΔS_f value of 3.61 cal mol⁻¹ K⁻¹ [21]. For (+)-camphor, therefore, the constant of 6.8 was replaced by 1.82 (=3.61/1.987).

For the heat of vaporization at ambient temperatures, one result of a calorimetric measurement was found in the literature {11 692 cal/mol for *R*-(+)-limonene [21]}. Heats of vaporization at 298.15 K calculated from the boiling point temperature by the Hildebrand rule (see Ref. [22]) and by applying the thermodynamic definition of the heat of vaporization [$\Delta H = RT^2(d \ln P/dT)$] to Antoine's equation are included in Table 4. Boiling point temperatures were obtained from supplier catalogues and Ref. [19]. Again, values for camphor and DPHM obtained via the Antoine equation may be unreliable due to extrapolation errors.

Experimental literature data for differences in heat capacity could not be found. In principle, heat capacity differences, being related to the second order derivatives to temperature, can be calculated from Antoine's equation. However, due to the uncertainties associated with use of Antoine parameters outside the temperature region of their measurement, especially for the calculation of heat capacity differences, it was decided to calculate gas-liquid heat capacity differences at 298.15 K from molecular structure according to the procedures of Rihani-Doraiswamy and Chueh and Swanson given by Lyman et al. [23] for gas and liquid heat capacities,

respectively (Table 4). For cinnamaldehyde and DPHM, the group contribution method of Johnson and Huang for the liquid heat capacity, also given by Lyman et al. [23], was used.

4.5. Comparison with experimental and calculated literature data

In all cases, experimental temperature ranges are within 298.15 K and the boiling points. Excluding the vapour pressure ($\log P$) values for (+)-camphor and DPHM calculated from Antoine parameters far outside the temperature region of their measurement, the differences between the experimental literature vapour pressures and the GC-VAP results are within ± 0.4 log units. Mostly these are underestimations which, as may be expected, generally result in overestimation of the boiling point temperatures of 20 K at a maximum.

The one experimental value for the enthalpy of vaporization found for *R*-(+)-limonene [21] is about 245 cal/mol lower than the GC-VAP value. This difference is significant only when the contribution of the selection of the experimental temperature range to the overall standard error is ignored. Again excluding the results for (+)-camphor and DPHM, the heats of vaporization values at 298.15 K obtained with the GC-VAP method are within 2 kcal/mol (carvacrol and thymol) or within 1 kcal/mol from the values calculated using the Antoine parameters. Including (+)-camphor and DPHM, differences of similar order were observed between the GC-VAP results and the heats of vaporization estimated using the Hildebrand rule. Although the statistical uncertainties of both the heats of vaporization calculated from the Antoine parameters and the Hildebrand rule are unknown, the observed differences are not likely to be statistically significant. Moderate (<4.5 cal/mol) and often surprisingly small differences (<1 cal mol⁻¹ K⁻¹) were observed between the heat capacity differences obtained with the GC-VAP method and values calculated from molecular structure [23].

The vapour pressure values in Table 3 have not been corrected for the differences in activity coefficients between test compound and *n*-alkane. For this, one of the nine model compounds available from Spieksma et al. [3] has to be selected which

most resembles the structures under study. The activity coefficient ratios [$\log(\gamma_z/\gamma_i)$] at 393.15 K, calculated for these model compounds by Spieksma et al. [3] using McReynolds data, range from -0.284 to 0.236 for 1-butanol and benzene, respectively. In most cases, corrections of this order are sufficient to obtain agreement with the experimental vapour pressure data. Comparing the molecular structures of the monoterpenes with the available model compounds, appropriate selections seem the model compounds octyne [$\log(\gamma_z/\gamma_i)=0.126$] for myrcene, benzene [$\log(\gamma_z/\gamma_i)=0.236$] or octyne for (*R*)-(+)-limonene and pentanone [$\log \gamma_z/\gamma_i = -0.016$] for (*R*)-(+)-citronellal, improving the GC-VAP results compared to the experimental literature values. In most cases, however, selection of a model compound is not straightforward. For example, thymol and carvacrol are structures containing both a phenyl and a hydroxy group, suggesting both benzene [$\log \gamma_z/\gamma_i=0.236$] and 1-butanol [$\log(\gamma_z/\gamma_i)=-0.284$] as model compounds. This illustrates that the structural diversity in the presently available model compounds from Spieksma et al. [3] is not sufficient for the monoterpenes studied here.

The activity coefficient ratios (γ_z/γ_i) are calculated by Spieksma et al. [3] at 393.15 K and, in further use, are assumed to be temperature independent. The possible necessity for a temperature dependent γ_z/γ_i is discussed here by comparing the GC-VAP vapour pressures for myrcene with the data collected by Ohe [16]. Based on the favorable comparison of the data for myrcene taken from Ohe [16] with reliable experimental literature data at 298.15 K from Ref. [13], the data for myrcene from Ohe [16] are assumed to be reliable over the entire experimental literature temperature range of 287.65 to 446.65 K. Compared to the data taken from Ohe [16], the GC-VAP method underestimates the vapour pressures ($\log P$) for myrcene at 446.65, 393.15, 298.15 and 287.65 K by 0.03, 0.05, 0.17 and 0.19 log units, respectively. These results show that the γ_z/γ_i of model compound octyne [$\log \gamma_z/\gamma_i=0.126$] improves the GC-VAP data at 298.15 K with respect to the data taken from Ohe [16]. However, at 393.15 K, the temperature at which the γ_z/γ_i values of model compounds were actually determined [3], the correction is not an improvement. The temperature dependent deviation between the GC-VAP vapour pressures

and the data taken from Ohe [16] for myrcene, amounts to 0.16 log units (0.19–0.03) over the experimental literature temperature range ($\Delta T=159$ K). Taking into account a systematic correction, a correction of ± 0.08 log units, being equal to about ± 2 times the standard error in the GC-VAP method, would be necessary in the temperature range of 287.65 to 446.65 K. The results of a similar analysis on the other data taken from Ohe [16], suggested temperature dependent corrections, ranging from ± 0 to ± 3 times the standard error in the GC-VAP vapour pressures over the experimental temperature ranges reported by Ohe (ΔT between 157 and 175 K).

The results indicate that, when model compounds for the γ_z/γ_i corrections are available, GC-VAP vapour pressures at ambient temperatures can be significantly improved with respect to experimental literature data. Unfortunately, the group of available model compounds is limited. For this group to be of practical use, especially in case of structurally diverse group of compounds such as monoterpenes, many additional model compounds would have to be included. In addition, the results indicate that different corrections are needed at 393.15 K, the temperature at which the γ_z/γ_i values for the model compounds was determined [3], and 298.15 K, the temperature of interest for most environmental studies. Over temperature intervals ranging from 157 to 175 K, being realistic values considering the extrapolations generally required in GC based vapour pressure determinations, non systematic differences of up to ± 3 times the standard deviation of the GC-VAP vapour pressures have been observed between GC-VAP and experimental literature data. For these reasons, we suggest that further improvement of the GC-VAP method should not be attempted by including more model compounds for the γ_z/γ_i correction, but by incorporating this correction in the model in a temperature dependent way. This would best be achieved by returning to the physicochemical mechanism of GC retention. A consequence of any attempt in this area would be that additional physicochemical data relevant to gas–liquid partitioning has to be known from experiment or estimation. For example, Spieksma [24] derived an expression for the temperature dependent γ_z/γ_i in which temperature dependent molar volumes and heats of vaporization can be found. Especially for environmen-

tally relevant chemicals, these data may be hard to find.

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