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Research Article

Thermodynamic Properties of Selected Bicyclic Terpenes and Related Substances by Gas Chromatography and Group Contributions

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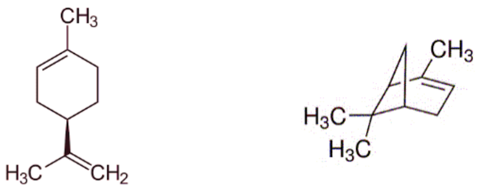
Abstract

Terpene compounds in the lower layer of the atmosphere can contribute to environmental problems through the formation of particulate material known as secondary organic aerosol (SOA). A clear understanding of the formation and composition of these particles hinges on reliable thermodynamic data. Quick estimation of these physical properties is highly desired. While experimental methods require significant resources and time, the prediction of pure-component properties through group contributions is easily applicable and straightforward. The present study compares the experimental enthalpies of vaporization at 298.15 K for bicyclic terpenes and related substances derived from the gas chromatography technique with estimated values provided by three group contribution methods. A new group contribution model specifically designed for terpene compounds is introduced. Furthermore, this study reveals previously unreported values in the literature for the enthalpy of vaporization at 298.15 K and the normal boiling temperature of Thymol methyl ether, Fenchyl alcohol, and Bicyclo [4.1.0] heptane-7-carboxylic acid.

Keywords: *Group contribution; gas chromatography; enthalpy of vaporization; bicyclic compounds.*

1. Introduction

Terpene compounds are naturally produced through secondary metabolism in a wide range of plants. These compounds are simple hydrocarbons that differ in the number of isoprene units. Hemiterpenes are formed by one isoprene unit (C5), monoterpenes by two (C10), sesquiterpenes by three (C15), diterpenes by four (C20), triterpenes by six (C30), and tetraterpenes by eight (C40). Additionally, terpenoids are defined as a modified class of terpenes with different functional groups. Terpenes can be further classified based on the degree of cyclization in the molecule, including acyclic (open chain), monocyclic, or bicyclic structures (refer to Figure 1) [1]. Compounds from this group have various applications in the chemical, pharmaceutical, and food industries, and they are also emitted into the environment in significant quantities, contributing to the diverse array of organic species found in the atmosphere [2,3].



Monocyclic: (+)-Limonene Bicyclic: α-Pinene

Figure 1. Terpene compounds molecular structures.

The significant presence of terpenes in the lower layer of the atmosphere poses environmental challenges due to their tendency to react with ozone, hydroxyl radicals, and nitrate radicals. These reactions result in the formation of particulate matter known as secondary organic aerosols (SOA) [4]. SOA can alter the radiative balance of the atmosphere by either absorbing or scattering solar radiation [5,6,7], thereby impacting air quality [8].

A comprehensive understanding of the formation and composition of these particles depends on reliable thermodynamic data for the compounds responsible for the generation of SOA. For instance, many algorithms used to predict emission rates of terpene compounds are based on physical evaporation and diffusion data [9,10,11].

The lack of such data in the existing literature emphasizes the necessity to explore robust tools capable of determining properties like vapor pressure (P_{vap}), normal boiling temperature (T_{nb}), and enthalpy of vaporization ($\Delta_{vap}H$). Typically, these thermodynamic quantities are obtained through conventional experimental techniques such as isoteniscopy, Knudsen effusion, gas saturation, and gas chromatography [12,13,14], or alternative techniques like thermogravimetry [15]. Gas chromatography, among these methods, provides an accurate means of determining the thermodynamic properties of organic compounds. Its widespread use is attributed to its high purity, small sample size requirement, and reproducibility [14,16,17].

Many experimental techniques require a substantial amount of measured data, chemically pure compounds, and high-performance equipment, which can be expensive. As the sophistication of chemicals and processes increases, along with greater societal demands for sustainability, health, safety, and economy, there is a growiand ng need to

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accurately estimate thermodynamic properties and implement property models [18]. Group contribution models are simple and accessible techniques based on molecular structural information. These models are valuable tools when measured data is unavailable and provide a diverse range of property estimates [19]. In recent work, Mann et al. [20] evaluated the prospects of group contribution models and emphasized that combining Artificial Intelligence (AI), data analysis, and models based on fundamental principles, such as classical group contribution models, with the availability of measured data holds promise in this context.

The objective of this study is to determine the enthalpies of vaporization at 298.15 K and normal boiling temperatures for eight terpene compounds using gas chromatography correlation. In addition, unpublished thermodynamic data for thymol methyl ether, alcohol fenchyl, and bicyclo [4.1.0] heptane-7-carboxylic acid are provided. Three group contribution methods are employed to estimate the enthalpies of vaporization at 298.15 K for the selected terpene compounds: Chickos et al. [21] present a method that considers the molecular structure of organic compounds and includes intramolecular interactions; Joback and Reid's model [22] is a general approach that incorporates additional contributions; and a new group contribution model specifically designed for terpene compounds is introduced, addressing the gaps left by some models in the literature, with a particular focus on bicyclic terpene compounds.

2. Experimental

2.1 Chemicals

A description of the chemicals used in this work is given in Table 1. The purity of the terpene compounds analyzed by gas chromatography (> 95%) was sufficient to determine their retention times. All chemicals, including the n-alkanes standards (C_5-C_{16}), were provided by Sigma Aldrich (Holzminden, Germany).

Table 1. Sample descriptions.

Chemical name	Formula	Purity, %	M $(g.mol^{-1})$	CAS RN
(+)-Limonene	$C_{10}H_{16}$	97.0	136.23	5989-27-5
Thymol methyl (1)	$C_{11}H_{16}O$	≥ 99.0	164.24	1076-56-8
(+)-α-Pinene	$C_{10}H_{16}$	≥ 99.0	136.23	7785-70-8
(+)-β-Pinene	$C_{10}H_{16}$	≥ 99.0	136.23	19902-08-0
5-Vinyl (2)	C_9H_{12}	95.0	120.19	3048-64-4
5-Ethylidene (3)	C_9H_{12}	99.0	120.19	16219-75-3
Fenchyl alcohol	$C_{10}H_{18}O$	≥96.0	154.25	1632-73-1
Bicyclo [4.1.0] (4)	$C_8H_{12}O_2$	95.0	140.18	41894-76-2

(1) Thymol methyl ether; (2) 5-Vinyl-2-norbornene; (3) 5-Ethylidene-2-norbornene; (4) Bicyclo [4.1.0] heptane-7-carboxylic acid.

2.2 Gas Chromatography

The compounds' retention times were determined using a Perkin Elmer (Autosystem XL GC) gas chromatograph equipped with a flame ionization detector (FID). A NST 05 capillary column (60 m x 0.25 mm i.d. x 0.25 μm film thickness) was used for compound separation under isothermal conditions of column temperature (40 ºC to 200 ºC), injector temperature of 230 °C, a detector at 250 °C, and an injection volume of 1.0 μL. The carrier gas (He) flow rate was set to 1.0 mL/min. The compounds were dissolved in methanol at a concentration of 20 mg/mL. The n-alkanes (C_5 to C_{16}) were used as reference compounds. Both the studied compounds and the n-alkanes mixture were injected under the same chromatography conditions. The Kováts retention indices (I_X) were calculated using the n-alkanes with retention times encompassing each studied compound. The analyses were performed in triplicate and followed Hoskovec et al. [14] methodology. Table 2 provides the Kováts retention indices for the studied compounds at different temperature ranges.

2.3 Kováts Retention Indices

Isothermal Kováts retention indices (I_X) are defined as Eq. (1).

$$I_X = 100z + 100\left(\frac{lnt_{R,X} - lnt_{R,z}}{lnt_{R,z+1} - lnt_{R,z}}\right) = 100z + 100\frac{ln(\gamma_z^{\infty}P_z/\gamma_X^{\infty}P_X)}{ln(\gamma_z^{\infty}P_z/\gamma_{z+1}^{\infty}P_{z+1})} \qquad (1)$$

In Eq. (1), $t_{R,X}$, sonsP_X, and γ_X^{∞} represent the retention time, vapor pressure, and infinite dilution activity coefficient, respectively, of solute X in the stationary phase. The subscripts z and z+1 identify the reference n-alkanes with z and z+1 carbon atoms, whose retention times encompass that of solute X.

2.4 Thermodynamic Properties

With the requisite collection of the Kováts retention indices assembled by Eq. (1), the vapor pressures were determined from Eq. (2).

$$ln\,P_x = ln\,P_z + [(100z - I_X)\,ln(P_z/P_{z+1})/100] \qquad (2)$$

The vapor pressures of reference C_5 to C_{16} n-alkanes at different temperatures used in this work were calculated using the Cox Equation, Eq. (3).

$$ln\left(\frac{P}{P_0}\right) = \left(1 - \frac{T_0}{T}\right)exp(A_0 + A_1T + A_2T^2) \qquad (3)$$

In Eq. (3) the coefficients derived for temperatures between the triple and boiling points were taken from a critical compilation of n-alkanes data [23].

Published P values of the compounds studied at 298.15 K were obtained from literature and web-available databases [24, 25]. The same sources along with the commercial Sigma Aldrich catalogue served as a literature source for normal boiling point (T_{nb}) data.

The Antoine Equation Eq. (4) parameters A, B, and C, were determined using non-linear regression techniques and are presented in Table 3.

$$ln(P_{vap}/Pa) = A - \frac{B}{T(K) + C} \qquad (4)$$

For processing the P_{vap} versus T data, the Kirchhoff–Rankin-type Eq. (5) was used. The parameters of Eq. (5) are presented in Table 4.

$$ln(P_{vap}/Pa) = \frac{1}{R}b_0 + \frac{1}{RT}b_1 + \frac{1}{R}b_2ln(T/T_0) \qquad (5)$$

In Eq. (5) T_0 is arbitrarily equaled to 298.15 K and R=8.3145 $J.K^{-1}mol^{-1}$. The enthalpy of vaporization at temperature T may be calculated from Eq. (6).

$$\Delta_{vap}H = -b_1 + b_2T \qquad (6)$$

Table 2. Experimental data. Kováts retention indices of studied compounds at different T ranges.

	Kováts Retention Indices (I_x)							
T (K)	Monocyclic Terpenes		Bicyclic Terpenes					
	Limonene	Thymol methyl ether	(+)-α-Pinene	(+)-β-Pinene	5-vinyl (1)	5-Ethylidene (2)	Fenchyl alcohol	Bicyclo [4.1.0] (3)
313.15	-	-	926.35	965.20	-	-	-	-
323.15	1021.19	-	929.58	969.20	-	-	-	-
333.15	1023.72	-	932.52	972.80	878.20	909.84	-	-
343.15	1027.83	1228.54	936.44	978.02	880.76	911.97	-	-
353.15	1030.81	1230.54	939.51	982.15	883.20	913.99	-	-
363.17	1033.93	1233.65	943.49	986.63	885.24	915.47	-	-
373.15	1038.35	1233.11	947.91	992.24	886.95	917.07	1114.62	246.58
383.15	1039.34	1234.87	951.31	994.56	891.24	918.93	1113.78	256.62
393.15	1041.91	1238.14	954.41	998.16	891.70	918.52	1116.50	266.54
403.15	1045.54	1239.03	958.69	1002.91	893.70	920.52	1121.49	276.52
413.15	1049.26	1241.75	963.81	1007.63	894.45	921.01	1126.04	286.63
423.15	1052.04	1243.69	-	-	-	-	1131.15	296.58
433.15	-	1245.59	-	-	-	-	1134.05	246.50
443.15	-	1247.27	-	-	-	-	1136.75	-
453.15	-	-	-	-	-	-	1142.42	-
463.15	-	-	-	-	-	-	1148.00	-
473.15	-	-	-	-	-	-	1155.00	-

(1) 5-Vinyl-2-norbornene; (2) 5-Ethylidene-2-norbornene; (3) Bicyclo [4.1.0] heptane-7-carboxylic acid.

Table 3. Vapor Pressure: Antoine Equation Parameters.

Compound	A	B	C	$r^{2(a)}$
(+)-Limonene	20.92 ± 0.14	3741.14 ± 84.79	-62.53 ± 3.44	0.99998
Thymol methyl ether	20.87± 0.16	3866.04 ± 99.65	-86.93 ± 3.99	0.99997
(+)-α-Pinene	20.12 ± 0.10	3185.64 ± 56.06	-70.82 ± 2.51	0.99999
(+)-β-Pinene	20.64 ± 0.14	3597.34 ± 81.82	-57.67 ± 3.39	0.99998
5-Vinyl-2-norbornene	21.19 ± 0.24	3648.92 ± 153.90	-45.65 ± 6.82	0.99996
5-Ethylidene-2-norbornene	21.45 ± 0.19	3667.36 ± 125.39	-34.8 ± 5.71	0.99998
Fenchyl alcohol	19.33 ± 0.27	2869.94 ± 168.46	-113.19 ± 8.91	0.99985
Bicyclo [4.1.0] heptane-7-carboxylic acid	18.80 ± 0.29	2528.18 ± 144.33	-162.43 ± 6.97	0.99997

(a): correlation coefficients (r^2, %).

Table 4. Parameters of Eq. (5).

Compound	b_0	b_1	b_2	$r^{2(a)}$
(+)-Limonene	256.2 ± 3.9	-63822 ± 1168	-50.5 ± 3.2	0.99998
Thymol methyl ether	298.1 ± 5.5	-82189 ± 1705	-73.9 ± 4.3	0.99997
(+)-α-Pinene	257.5 ± 3.1	-61608 ± 922	-56.8 ± 2.6	0.99998
(+)-β-Pinene	244.7 ± 4.0	-58834 ± 1205	-45.4 ± 3.4	0.99997
5-Vinyl-2-norbornene	225.4 ± 6.4	-50452 ± 1954	-29.6 ± 5.3	0.99996
5-Ethylidene-2-norbornene	229.5 ± 4.6	-52642 ± 1398	-30.2 ± 3.8	0.99998
Fenchyl alcohol	295.40 ± 12.0	-77914 ± 3736	-78.6 ± 8.9	0.99984
Bicyclo [4.1.0] heptane-7-carboxylic acid	464.10 ± 17.4	-136073 ± 5412	-190.9 ± 13.3	0.99997

(a): correlation coefficients (r^2, %).

Eqs. (5) and (6) were implemented to predict $\Delta_{vap}H$ values at 298.15 K for the studied compounds. In addition, since it is known that the normal boiling temperature T_{nb} of a substance in the liquid phase is the temperature at which its vapor pressure equals atmospheric pressure (1 atm), it is possible to define P in Eq. (5) as 1 atm to obtain the T_{nb} data. Table 5 summarizes the enthalpy of vaporization ($\Delta_{vap}H$) at 298.15 K and the normal boiling temperature (T_{nb}) of studied terpene compounds.

3. Group Contribution Methods

The group contribution methods are based on the principle that a function of structurally dependent parameters defines the property values. These values are determined by.

Table 5. $\Delta_{vap}H$ and T_{nb}: Literature and Experimental data obtained in this work at 298.15 K and 101.325 kPa.

Compound	$T_{nb}^{lit\ (a)}$ (K)	$T_{nb}^{exp\ (b)}$ (K)	RD$^{(c)}$ %	$\Delta_{vap}H^{lit(a)}$ (kJ mol^{-1})	Method$^{(d)}$	$\Delta_{vap}H^{exp\ (b)}$ (kJ mol^{-1})	RD$^{(c)}$ %
(+)-Limonene	451.15$^{(e)}$	461.44	2.28	49.60$^{(g)}$	GC	48.77	1.67
Thymol methyl ether	-	501.77	-	-	GC	60.16	-
(+)-α-Pinene	429.35$^{(e)}$	442.44	3.05	44.84$^{(g)}$	GC	44.67	0.40
(+)-β-Pinene	439.15$^{(e)}$	453.01	3.16	46.19$^{(g)}$	GC	45.30	1.93
5-Vinyl-2-norbornene	414.2$^{(f)}$	423.12	2.15	42.29$^{(h)}$		41.64	1.33
5-Ethylidene-2-norbornene	419.2$^{(f)}$	429.15	2.37	44.30$^{(i)}$	EB	43.63	1.51
Fenchyl alcohol	-	481.30	-	-	GC	54.47	-
Bicyclo [4.1.0] heptane-7-carboxylic acid	-	516.95	-	-	GC	79.15	-

[(a)] T_{nb}^{lit} and $\Delta_{vap}H^{lit}$: literature normal boiling temperature and enthalpy of vaporization at 298.15 K.

[(b)] T_{nb}^{exp} and $\Delta_{vap}H^{exp}$: experimental normal boiling temperature and enthalpy of vaporization at 298.15 K obtained in this work.

[(c)] RD: absolute relative deviation.

[(d)] Gas Chromatography (GC), Ebulliometry (EB).

[(e)][24]. [(f)][25]. [(g)][14]. [(h)][26]. [(i)][27].

summing the frequency of each group occurring in the molecule multiplied by its contribution. These methods provide quick estimates without requiring substantial computational resources. The representation of molecular structures through functional groups provides these methods with a predictive quality regarding the range of molecular structures that can be handled. Methods based on the group contribution approach has been developed for a wide range of properties and are routinely used when measured data for properties are not available [19].

To ensure consistency in the results, terpene compounds with available enthalpies of vaporization in the literature [14,26,27] were selected. Enthalpies of vaporization at 298.15 K were predicted using the methods proposed by Chickos et al. [21], Joback and Reid [22], and a new group contribution method was introduced in this work. Each of these methods employs specific fragmentation schemes and interactions between groups

3.1 Proposed Model

This newly developed group contribution method is designed to estimate the enthalpy of vaporization of pure organic compounds. It introduces a specific fragmentation scheme adapted for essential oil compounds, which primarily consist of monoterpene hydrocarbons, sesquiterpene hydrocarbons, and oxygenated derivatives. The selection of compounds for the database followed specific criteria, including saturated and unsaturated hydrocarbons with open-chain and branched structures ranging from C_7 to C_{15} carbon atoms. It also encompassed bicyclic hydrocarbons and oxygenated derivatives. Due to their low occurrence in essential oils, compounds containing sulfur, nitrogen, and alkynes hydrocarbons were excluded from the database. The proposed method is based on first-order groups. The fragmentation scheme considers molecular characteristics, such as distinguishing between open-chain, cyclic, aromatic groups, and bicyclic structures. A total of 26 groups were defined. Table 6 presents all the groups utilized in the regression and their respective contributions to the prediction of enthalpy of vaporization.

The proposed model comprises a dataset of 1,719 different organic substances, with a total of 3,591 data points for enthalpy of vaporization. Considering that some terpenes in the dataset have multiple values for enthalpy of vaporization, the division was based on the number of compounds. The cross-validation technique was chosen for parameter selection as it enhances the model's generalization capacity [28]. The training and validation phases utilized 80% of the database, while the remaining 20% was allocated for testing. Parameter optimization was performed using gradient descent, which is widely used in training machine learning models, such as linear regression. It provides an efficient way to find optimal parameter values that minimize the cost function, allowing the models to better fit the training data and make accurate predictions on new, unseen data.

Regarding the contribution values, some considerations are necessary. Groups containing carbonyl (C=O) and hydroxyl (-OH) exhibit the highest contributions, which aligns with their polar nature and strong intermolecular dipole-dipole forces. Additionally, groups containing hydroxyl, such as alcohols, phenols, and carboxylic acids, also demonstrate significant contributions due to hydrogen bonding. Descriptors for bicyclic compounds and cis-trans isomerism display negative values, reflecting the stereoisomeric positions in these compound types. Moreover, groups associated with aliphatic compounds or segments of molecules, such as $-CH_3$ and $-CH_2-$, show lower contributions, likely attributed to the branching that diminishes intermolecular attraction and influences thermodynamic properties such as normal boiling temperature and enthalpy of vaporization.

The Eq. 7 performs the prediction by the proposed model.

$$\Delta_{vap}H = 19.55 + \sum_i N_i C_i \tag{7}$$

In Eq. (7), N_i represents the occurrence of each group in the structure, and C_i denotes the contribution to the enthalpy of vaporization from each group. The application of this method is shown in Table 7.

The relative deviation (RD) for each method is defined in Eq. (8).

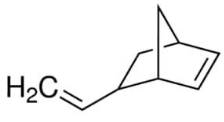
$$RD\% = 100.abs\left[\frac{\Delta_{vap}H^{exp} - \Delta_{vap}H^{est}}{\Delta_{vap}H^{exp}}\right] \tag{8}$$

In Eq. (8), $\Delta_{vap}H^{exp}$ and $\Delta_{vap}H^{est}$ represent the experimental and estimated enthalpies of vaporization, respectively.

Table 6. Proposed model group contribution fragments.

Nº	Group	Contribution
0	h_0	19.548
1	$-CH_3$	0.475
2	$-CH_2-$	3.900
3	$>CH-$	4.172
4	$>C<$	4.380
5	$=CH_2$	-1.196
6	$=CH-$	4.525
7	$=C<$	5.008
8	$-CH_2-$ (cyclic)	2.793
9	$>CH-$ (cyclic)	3.197
10	$>C<$ (cyclic)	4.535
11	$=CH-$ (cyclic)	3.048
12	$=C<$ (cyclic)	4.862
13	$=CH$ (aromatic)	2.808
14	$=C<$ (aromatic)	5.610
15	OH (alcohol)	17.421
16	-O-	2.255
17	O-C=O	12.162
18	C=O	6.301
19	OH (phenol)	7.979
20	-O- (cyclic)	4.307
21	C=O (cyclic)	10.589
22	bicyclic (correction)	-2.053
23	HC=O	8.912
24	OHC=O	30.201
25	*cis* correction	0.983
26	*trans* correction	1.338

Table 7. Estimated enthalpy of vaporization ($\Delta_{vap}H^{est}$) of 5-Vinyl-2-norbornene using this work proposed model at constant temperature (298.15 K). Experimental literature data [26]: $\Delta_{vap}H^{exp}$ (298.15 K) = 42.29 kJ/mol.

Compound	Proposed model	
	Group Contribution	
 5-Vinyl-2-norbornene	h_0	19.548
	$-CH_2-_{(ring)}$	2.792
	$=CH-_{(ring)}$	3.048
	$>CH-_{(ring)}$	3.197
	$=CH-$	4.525
	$=CH_2$	-1.196
	Bicyclic correction	-2.053
	$\Delta_{vap}H^{est}$ (kJ.mol^{-1})	42.10
	$\Delta_{vap}H^{exp}$(kJ.mol^{-1}) [(a)]	42.29
	RD (%)	0.45

[(a)][26].

3.2 Chickos et al. (1998)

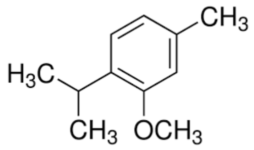
In this method [21], the evaluation of the nature and location of functional groups is performed. The steric environment of the functional groups is identified using characteristics such as hybridization and substitution.

Estimation is further enhanced by accounting for intramolecular hydrogen bonding.

$$\Delta_{vap}H = 4.69\left(N_C - N_Q\right) + 1.3N_Q + 3.0 + \sum_i n_i F_i b_i + C \qquad (9)$$

Eq. (9) defines the parameters N_C and N_Q as the total number of carbons and the total number of quaternary sp³ hybridized carbon atoms, respectively. The product $F_i.b_i$ depends on the nature (b) and location (F) of the functional group, while C represents a correction parameter associated with intramolecular interactions. The application of this method is presented in Table 8.

Table 8. Estimated enthalpy of vaporization ($\Delta_{vap}H^{est}$) of Thymol methyl ether at 298.15 K using the method proposed by Chickos et al. [21]. Experimental data from this study: $\Delta_{vap}H^{exp}$ (298.15 K) = 60.16 kJ/mol.

Compound	Chickos et al.'s [21]	
	Group contribution	
 Thymol methyl ether	N_C	11
	N_Q	0
	Functional group class	b_i
	$> O$	5.0
	Substitution Factor	F_i
	Single substitution on a primary sp^3 atom	1.62
	Single substitution on a quaternary sp^2 atom	0.85
	Correction	C
	Ortho and vicinal alkyl branching cyclic sulfides on sp^2 and sp^3 carbons on 5 and 6-membered rings	-2
	$\Delta_{vap}H^{est}$ (kJ.mol^{-1})	62.69
	$\Delta_{vap}H^{exp}$(kJ.mol^{-1}) [(a)]	60.16
	RD (%)	4.21

[(a)]Experimental enthalpy of vaporization at 298.15 K obtained in this work.

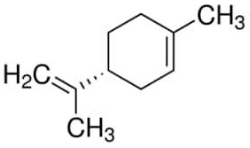
3.3 Joback and Reid (1987)

The method proposed by Joback and Reid [22] predicts eleven important and commonly thermodynamic properties of pure components from molecular structure only. This method assumes that there are no interactions between the groups and therefore only uses additive contributions.

$$\Delta_{vap}H = 15.30 + \sum_i N_i h_{v,i} \qquad (10)$$

In Eq. (10), Ni represents the occurrence of each group in the structure, and $h_{v,i}$ denotes the contribution to the enthalpy of vaporization from each group. The application of this method is summarized in Table 9.

Table 9. Estimated enthalpy of vaporization ($\Delta_{vap}H^{est}$) of (+)-Limonene at 298.15 K using the method proposed by Joback and Reid [22]. Experimental literature data [14]: $\Delta_{vap}H^{exp}$ (298.15 K) = 49.60 kJ/mol.

Compound	Joback and Reid's method [22]	
	Group Contribution	
 (+)-Limonene	h_0	15.30
	CH_3	2.373
	$=CH_2$	1.724
	$=C<$	2.138
	$CH_{(ring)}$	1.942
	$=CH_{(ring)}$	2.544
	$=C<_{(ring)}$	3.059
	$CH_{2(ring)}$	2.398
	$\Delta_{vap}H^{est}$ (kJ.mol^{-1})	38.55
	$\Delta_{vap}H^{exp}$(kJ.mol^{-1}) [(a)]	49.60
	RD (%)	22.28

[(a)][14].

4. Results and Discussion

New experimental data were obtained for terpene compounds, including (+)-Limonene, Thymol methyl ether, (+)-α-Pinene, (+)-β-Pinene, 5-Vinyl-2-norbornene, 5-Ethylidene-2-norbornene, Fenchyl alcohol and Bicyclo [4.1.0] heptane-7-carboxilic acid at 298.15 K using gas chromatography correlation.

Table 2 presents the Kováts retention index values for the monocyclic and bicyclic terpenes evaluated in this study. From the I_x data of each compound within their respective temperature range, the dependence of vapor pressure on temperature was evaluated using Eq. (2). The resulting vapor pressure curves for the analyzed bicyclic and monocyclic terpenes are displayed in Figure 2 and Figure 3, respectively.

[(a)] 5-Vinyl-2-norbornene; [(b)] 5-Ethylidene-2-norbornene; [(c)] Bicyclo [4.1.0] heptane-7-carboxylic acid.

Figure 2. Temperature dependence of the vapor pressure for the bicyclic terpenes studied in this work.

By analyzing the temperature-dependent vapor pressure, the constants of the Antoine equation Eq. (3) were determined. As shown in Table 3, all the compounds exhibited correlation coefficients (r^2) above 0.999, indicating a strong fit to the model.

Figure 3. Temperature dependence of the vapor pressure for the monocyclic terpenes studied in this work.

The enthalpy of vaporization, which is directly related to vapor pressure, was calculated using Eq. (5) based on the obtained vapor pressure curves (Figures 2 and 3). The parameter values for Eq. (5) were obtained through nonlinear regression analysis performed using Origin 8.1 (Origin Lab, Northampton, Massachusetts, USA), and are presented in Table 4. The normal boiling temperature (T_{nb}) was calculated by extrapolating the data to 101.325 kPa using an iteration procedure in Excel. The calculated values for $\Delta_{vap}H$ in this work were compared with literature data, and the absolute relative deviation demonstrated agreement with results reported in the literature, as shown in Table 5. Furthermore, a comparison of our boiling point temperatures with literature values revealed a low relative deviation in predicting T_{nb}^{exp}, indicating that gas chromatography using n-alkanes as standards can be a reliable method for obtaining these thermodynamic properties experimentally.

The absolute relative deviation (RD) is defined as Eq. (11).

$$RD\% = 100.abs(TP^{lit} - TP^{exp}/TP^{lit}) \qquad (11)$$

In Eq. (11), TP^{lit} and TP^{exp} referred to the thermodynamic properties of the literature and that obtained experimentally in this work. The TP parameter is substituted by the enthalpy of vaporization or normal boiling temperature depending on the analyzed property.

Experimental data for enthalpy of vaporization from the literature and determined in this work were compared with data provided from estimation methods at constant temperature (298.15 K) developed by Chickos et al. [21], Joback and Reid [22] and a new group contribution method proposed in this work. The performance of the studied methods was examined and discussed. The results are presented in Table 10.

The mean relative deviation (MRD) for each method is defined in Equation (12):

$$MRD\ (\%) = \frac{100}{n} abs\left[\frac{\Delta_{vap}H^{exp,i} - \Delta_{vap}H^{est,i}}{\Delta_{vap}H^{exp,i}}\right] \qquad (12)$$

In Eq. (12), n is the number of compounds, and i represents each compound.

The method proposed by Chickos et al. [21] demonstrates reasonable estimates for most of the studied monocyclic and bicyclic terpenes, with a mean relative deviation of 9.51%. Although this model incorporates contributions for functional groups, types of carbon bonding and hybridization, as well as correction terms for intramolecular interactions, its database is limited in terms of the number of compounds representing each functional group and molecular structure. Moreover, it does not distinguish the contributions of isomers, as observed in the cases of (+)-α-Pinene and (+)-β-Pinene, as well as 5-Vinyl-2-norbornene and 5-Ethylidene-2-norbornene, respectively.

Joback and Reid [22] proposed a classical group contribution method that utilizes additive contributions and does not consider intramolecular interactions. However, it demonstrated the highest mean relative deviation of 20.00% among the examined models. This method assumes no interactions between groups and relies solely on additive contributions. Additionally, it does not differentiate between aromatic and non-aromatic rings, which significantly impacts the performance of this group contribution method.

The proposed model encompasses terpene compounds and integrates group contributions for bicyclic compounds. In this method, the most significant deviation of 11.69% was observed for (+)-Limonene and Thymol methyl ether, while the smallest deviation was found for bicyclic compounds. This model includes groups that describe the studied molecules, specifically terpene compounds, with the addition of bicyclic structures and isomers. However, it lacks a correction for interactions between carbons in cyclic or aromatic structures, resulting in a mean relative deviation of 8.00%

Table 10. The enthalpy of vaporization at 298.15 K: experimental ($\Delta_{vap}H^{exp}$) and estimated ($\Delta_{vap}H^{est}$) data.

Compounds	$\Delta_{vap}H^{exp}$ (kJ.mol^{-1})	Estimated enthalpy of vaporization (kJ.mol^{-1})					
		Chickos et al.'s method [21]		Proposed model		Joback and Reid's method [22]	
		$\Delta_{vap}H^{est}$	RD%	$\Delta_{vap}H^{est}$	RD%	$\Delta_{vap}H^{est}$	RD%
Monocyclic terpene							
(+)-Limonene	49.60 $^{(a)}$	49.90	0.60	43.80	11.69	38.55	22.28
Thymol methyl ether	60.16 $^{(b)}$	62.69	4.21	53.13	11.69	45.72	24.00
Bicyclic terpene							
(+)-α-Pinene	44.84 $^{(a)}$	46.51	3.72	43.35	3.32	37.36	16.68
(+)-β-Pinene	46.19 $^{(a)}$	46.51	0.69	41.42	10.33	36.56	20.85
5-Vinyl-2-norbornene	42.29 $^{(c)}$	45.21	6.90	42.10	0.45	34.95	17.36
5-Ethylidene-2-norbornene	44.30 $^{(d)}$	45.21	2.05	45.43	2.55	36.72	17.11
Fenchyl alcohol	54.47 $^{(b)}$	83.75	53.75	60.18	10.48	51.63	5.21
Bicyclo [4.1.0] *	79.15 $^{(b)}$	82.42	4.13	68.46	13.51	50.26	36.50
MRD (%)			9.51		8.00		20.00

* Bicyclo [4.1.0] heptane-7-carboxilic acid.
Experimental data from literature: $^{(a)}$[14], $^{(c)}$ [26], $^{(d)}$[27].
$^{(b)}$ Experimental data obtained in this work.

Figure 4 illustrates the distribution of the three group contributions to estimated vaporization enthalpies in relation to the experimental data.

Figure 4. Enthalpies of vaporization distribution: estimated ($\Delta_{vap}H^{est}$) and experimental ($\Delta_{vap}H^{exp}$) data.

Comparing the results obtained by the studied models and analyzing Figure 4, it can be observed that the proposed model achieved a correlation coefficient (r^2) value of 0.8398, indicating a high level of accuracy in fitting the utilized data. In contrast, Chickos et al. [21] and Joback and Reid [22] proposed models had r^2 values of 0.6693 and 0.6666, respectively, suggesting a comparatively less precise fit. Consequently, the proposed model demonstrated superior performance when compared to the other evaluated models.

5. Conclusion

This paper compares three group contribution methods, including a new model specifically designed for terpene compounds, with different fragmentation schemes. These methods were evaluated against experimental enthalpies of vaporization obtained through gas chromatography correlation. Reliable experimental thermodynamic data are crucial for understanding chemical processes like secondary organic aerosol (SOA) formation and for building the database used in the development of group contribution models. However, experimental techniques often require significant effort. Group contribution methods are valuable in this regard as they only require knowledge of the chemical structure to estimate physical properties.

The enthalpy of vaporization ($\Delta_{vap}H$) at 298.15 K and the normal boiling temperature (T_{nb}) of (+)-Limonene, (+)-α-Pinene, (+)-β-Pinene, 5-Vinyl-2-norbornene, 5-Ethylidene - 2-norbornene, Thymol methyl ether, Fenchyl alcohol, and Bicyclo [4.1.0] heptane-7-carboxilic acid were determined by gas chromatography technique using n-alkanes as standards, yielding good results. The referenced thermodynamic parameters of the last three compounds were previously unpublished in the literature and are being presented for the first time in this study.

The comparison of the three studied group contributions highlights that a reliable database and the fragmentation scheme are crucial for an accurate group contribution method. Among the studied models, the proposed model demonstrated better performance for the analyzed compounds ($r^2 = 0.8398$). It is a first-order group model. The accuracy of the group contribution-simple (based on first-order groups) is qualitatively acceptable, but a more precise prediction is obtained through the addition of second and third-order group contributions [29]. The proposed model fills a gap in predictive methods specific to the physical properties of terpene compounds and can be further enhanced by incorporating second and third-order contributions.

Nomenclature

$\Delta_{vap}H$	Enthalpy of vaporization (kJ.mol^{-1})
exp	The superscript symbol "exp" means experimental
est	The superscript symbol "est" means estimated
lit	The superscript symbol "lit" means literature
GC	Gas chromatography
I_X	Kováts retention index
MRD	Mean relative deviation
P_{vap}	Vapor pressure (Pa)
RD	Relative deviation
R	universal gas constant (J.K^{-1}mol^{-1})
r^2	Correlation coefficient
T	Temperature (K)
T_0	Reference temperature (K)
T_{nb}	Normal boiling temperature (K)
TP	Thermodynamic property
t_R	Retention time (s)
X	Solute, analyzed compound
γ^{∞}	Infinite dilution activity coefficient
z	Carbon number

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