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CONTRIBUTION TO THEORETICAL STUDY OF VAPORIZATION ENTROPY

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Abstract: There are many techniques to obtain experimental thermodynamic data, including the gas chromatography method. However, to apply this approach it is necessary to consider the molecular structure to improve their thermodynamic parameters predictions. This study aims to present a non-chromatographic parameter, the vaporization entropy calculation of some terpene compounds. The vaporization entropy values are influenced by hydrogen bonding and molecular conformation.

Keywords: Terpene, vaporization entropy, thermodynamic properties, molecular structure.

INTRODUCTION

Reliable thermodynamic experimental data play a key role in the design and chemical processes and product optimization. The most used methods for measuring thermodynamic properties such as vapor pressure, vaporization enthalpy, and normal boiling point are effusion, gas saturation, calorimetric methods, and gas chromatography (Kim et al., 1984; Majer et al., 1989; Delle Site, 1997). The gas chromatography (GC) technique that uses alkanes as standards can be a good approach to obtain thermodynamic properties experimentally (Hoskoveck et al., 2005; Fonseca et al., 2020). In this method, the properties are obtained by CG correlation through the isothermal Kováts' retention indices (I_x), defined as

$$I_x = 100z + 100 \left(\frac{\ln t_{R,X} - \ln t_{R,z}}{\ln t_{R,z+1} - \ln t_{R,z}} \right) \quad (1)$$

where $t_{R,X}$ represents the retention time of solute X in the stationary phase; 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. Equation 1 can be rewritten as a function of vapor pressure (P_x)

as well as infinite dilution activity coefficient (γ_x^∞) of solute X, according to

$$I_x = 100z + 100 \frac{\ln(\gamma_z^\infty P_z / \gamma_x^\infty P_x)}{\ln(\gamma_z^\infty P_z / \gamma_{z+1}^\infty P_{z+1})} \quad (2)$$

Expressing P_x from Equation 2, considering $\gamma_x = \gamma_z^\infty = \gamma_{z+1}^\infty$, it is possible to write

$$\ln P_x = \ln P_z + \frac{(100z - I_x) \ln(P_z / P_{z+1})}{100} \quad (3)$$

Equation 3 allows the calculation of the vapor pressures at 298.15 K from accurate values of the Kováts' indices of the solute and vapor pressures of n-alkane references, once are known at this temperature (Fischer et al., 1992; Fischer and Ballschmiter, 1998). However, Hoskovec et al. (2005) demonstrated that Equation 2 was not adequate to obtain vapor pressure data at 298.15 K for many of the studied compounds, and these authors proposed a readjustment to improve the estimates based on the molecular structure. The difference in the activity coefficients logarithms of two substances (i,j) was approximated by the corresponding difference in ideal gas solubility, X^g , derived from the van't Hoff equation considering

$$\ln \gamma_i^\infty - \ln \gamma_j^\infty \approx \ln X_i^\infty - \ln X_j^\infty \cong \frac{\Delta S_{\text{vap}}^{b,i} (T_{\text{nb}}^i - T)}{RT} - \frac{\Delta S_{\text{vap}}^{b,j} (T_{\text{nb}}^j - T)}{RT} \quad (4)$$

In Equation 4, R is the universal gas constant; T is the absolute temperature and ΔS_{vap}^b is the vaporization entropy at the normal boiling point (T_{nb}^b). The vaporization entropy is proportional to the ratio of the degree of randomness in the vapor and the liquid phases. The values for a pure substance are related to molecular structure and can be estimated from the effective number of torsional bounds (τ) and the polar group number capable of

hydrogen bonding (HBN). The ΔS_{vap}^b can be calculated from specific routines as proposed by Myrdal and Yalkowsky (1997). Then, the present work aims to estimate the vaporization entropy of some terpene compounds.

MATERIAL AND METHODS

Terpenes are founded in herbal medicine, food, and cosmetics, such as the compounds presented in Figures 1 to 9, which have a variety of molecular structures and functional groups.

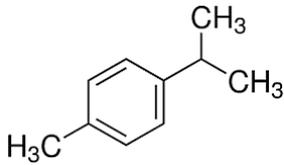


Figure 1 - Molecular structure of p-cymene.

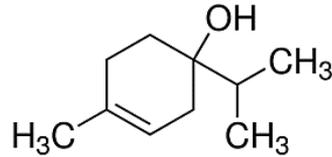


Figure 2 - Molecular structure of terpinen-4-ol.

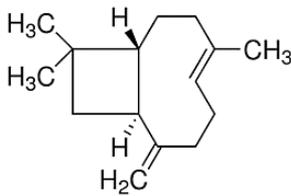


Figure 3 - Molecular structure of trans-caryophyllene.

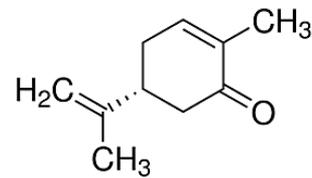


Figure 4 - Molecular structure of carvone.

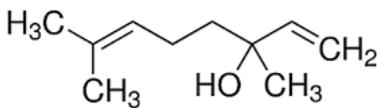


Figure 5 - Molecular structure of linalool

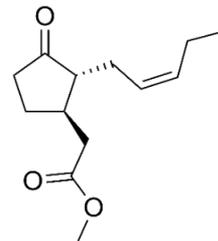


Figure 6 - Molecular structure of methyl-jasmonate.

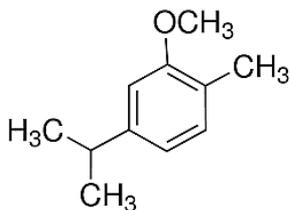


Figure 7 - Molecular structure of thymol-methyl-ether.

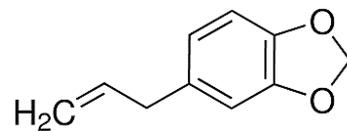


Figure 8 - Molecular structure of safrole.

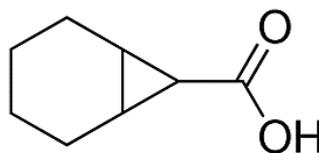


Figure 9 - Molecular structure of bicyclo[4.1.0]heptane-7-carboxylic acid.

The vaporization entropy, ΔS_{vap}^b , is influenced by the presence of hydrogen bond (HBN) that facilitates the phase change and the molecule conformation (τ) as described by (Myrdal and Yalkowsky, 1997)

$$\Delta S_{\text{vap}}^b = 86 + 0.4 \tau + 1421 \text{ HBN} \quad (5)$$

with the effective number of torsional bonds (τ), that measures the overall molecular flexibility, determined from (Myrdal and Yalkowsky, 1997)

$$\tau = \sum (\text{SP3} + 0.5 \text{ SP2} + 0.5 \text{ Ring}) - 1 \quad (6)$$

where SP3 and SP2 are non-ring and non-terminal sp^3 and sp^2 atoms; Ring indicates the number of independent ring systems found in the compound. It is important to highlight the vaporization entropy also requires the polar group number capable of hydrogen bonding (HBN). This effect is calculated by

$$\text{HBN} = \sqrt{\frac{\text{OH} + \text{COOH}}{\text{MW}}} \quad (7)$$

where OH and COOH are the number of alcohols and carboxylic acids, respectively; MW is the compound molecular weight.

RESULTS AND DISCUSSION

The selected terpene compounds presented in this work have a variety of molecular structures: open chain, cyclic, bicyclic, aromatic, and unsaturated compounds, alcohols, ketones, hydrocarbons, ethers, and carboxylic acids.

Based on the molecular structure of the analyzed compounds, the calculation of the effective number of torsional bounds (τ) and polar group number capable of hydrogen bonding (HBN) were performed, as well as the vaporization entropy at the normal boiling point (ΔS_{vap}^b) values was estimated. The results are shown in Table 1.

Analyzing the molecular structures (Figures 1 to 9) it is possible to observe that some molecules have less flexibility due to the number of unsaturation and rings, and even evaluate the propensity to phase change given the presence of hydrogen bonds, which does Equation 5 physically consistent. The parameters τ and HBN are related to molecular structure. The hydrogen bonding inhibits rotational freedom and increases the disorder magnitude that occurs with vaporization. Hence, the vaporization entropy is higher for compounds that hydrogen-bonding groups (OH and COOH) are present, as can

Compounds	τ	HBN	ΔS_{vap}^b (J K ⁻¹ mol ⁻¹)
p-cymene	0.5	0.000	86.20
terpinen-4-ol	0.5	0.006	95.41
trans-caryophyllene	0.0	0.000	86.00
carvone	0.0	0.000	86.00
linalool	3.5	0.006	96.61
methyl-jasmonate	4.0	0.000	87.60
thymol-methyl-ether	1.5	0.000	86.60
safrole	1.5	0.000	86.60
bicyclo[4.1.0]heptane-7-carboxylic acid	0.0	0.007	96.10

Table 1. Effective number of torsional bounds (τ), polar group number capable of hydrogen bonding (HBN) and vaporization entropy at the normal boiling point (ΔS_{vap}^b) of terpene analyzed in this work.

be observed for terpinene-4-ol, linalool, and bicyclo[4.1.0]heptane-7-carboxylic acid. Another significant entropy vaporization parameter is the molecular conformation, which can describe the molecular flexibility. This coefficient confirms that there is a vaporization entropy dependency on molecular conformation, whose results can be observed for linalool and methyl-jasmonate. On the other hand, carvone and trans-caryophyllene, for example, seem less flexible due to unsaturation, and their entropy vaporization values are lower than the other terpenes analyzed in this work.

CONCLUSION

This work presents the values of the effective number of torsional bounds (τ) and the vaporization entropy (ΔS_{vap}^b) for some terpene compounds. The molecular structure analysis shows the physical consistency of Myrdal and Yalkowsky's model. The vaporization entropy (ΔS_{vap}^b) values are influenced by the presence of a hydrogen bond (HBN), that facilitates the phase change and the molecular conformation (τ) which translates the molecular flexibility.

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