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Saturated vapour pressure of aroma compounds at various temperatures

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Abstract

The aim of this study was to determine experimentally the vapour pressures of aroma compounds at various temperatures, especially at negative ones. The aroma compounds were: acetone, 2-butanone, 2-hexanone, 2-octanone, ethyl acetate, ethyl butanoate, ethyl hexanoate, *n*-hexanal, *n*-hexanol and γ-hexalactone. The technique used was a static device where vapour pressure was measured at equilibrium. The temperatures of analysis varied from −40 to 25 °C. Volatility of a pure compound depends on characteristics such as length of the aliphatic chain, the functional group and temperature. Among an homologous series, volatility increases when the aliphatic chain decreases and when temperature increases. For aroma compounds which have the same number of carbon atoms in their structure, volatility depends not only on either temperature or molecular weight, but also on the functional group of the molecule. At a given temperature volatility of compounds which have the same number of carbon atoms in their structure, decreases as follows: ester > ketone > aldehyde > alcohol > lactone.

Keywords: Saturated vapour pressure; Aroma compounds; Negative temperature; Static device

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1. Introduction

Temperature affects both, kinetics (mass transfer and diffusivity) and thermodynamic equilibrium of aroma compounds in food. Formulation, storage and other processes, are some main steps in food production, where temperature has to be controlled. Since most part of food products have to be refrigerated or frozen for their preservation, the experimental values of saturated vapour pressure of aroma compounds become of main importance as a function of temperature. The concentration of a volatile compound in one or between several phases, depends on the characteristics of the pure volatile compound as well as temperature. Vapour pressure, solubility, partition coefficients (gas–liquid, liquid–liquid) and activity coefficients, are some equilibrium parameters which depend on both, temperature and physico-chemical properties of the pure volatile compound. The knowledge of either solubility or coligative properties, can be derived by related equations. Eq. (1) relates the gas–liquid partition coefficient (K_i) of a compound i at a given temperature, to both the activity coefficient of compound i at infinite dilution (γ_i^∞) and to the saturated vapour pressure (P_i^s in Pa) of i at the same given temperature,

$$K_i = \frac{P_i^s \gamma_i^\infty}{P_\mathrm{T}} \tag{1}$$

where P_T is atmospheric pressure (Pa).

Experimental data of saturated vapour pressures in literature are scarce and frequently just for volatile organic compounds of environmental importance, such as either pollutants or organic solvents (Boublik, Fried, & Hala, 1984; Delle Site, 1997) or of the oil research (Ambrose, Ellender, Gundry, Lee, & Townsend, 1981; Ambrose, Ellender, Lees, Sprake, & Townsend, 1975; Getachew, 1998; N'Guimbi, Kasehgari, Mokbel, & Jose, 1992). These authors have measured saturated

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vapour pressures of volatile organic compounds at various temperatures, in the most of cases at positive ones (20 °C and above). Indeed, there are numerous volatile organic compounds which are common for those fields and for the flavour science. In this area, few works such as those of LeThanh, Lamer, Voilley, and Jose (1993) and Espinoza-Díaz, Guetachew, Landy, Jose, and Voilley (1999) have measured saturated vapour pressures of flavour compounds. The latter authors measured saturated vapour pressures for 2-nonanone, *d*-linalool, isoamyl acetate and *d*-limonene. However, just for the last two compounds, the lowest temperature achieved in their work was −50 °C. In fact, experimental data at subzero temperatures, still has not been largely obtained.

The experimental methods to measure saturated vapour pressures of volatile organic compounds are classified in static and dynamic methods. In one hand, the static methods measure straightly the pressure induced by the vapour created by the liquid or the solid at equilibrium. On the other hand, the dynamic methods measure the saturated vapour pressure of the sample relatively to a known compound, in other words a sample of saturated vapour is removed and the concentration is determined. So, this method requires calibration with compounds of known vapour pressure, preferably of the same chemical class. Other dynamic techniques are the relative volatilization rate and the chromatographic methods. Techniques such as the manometric methods, boiling point at reduced pressures, effusion, gas saturation and partition coefficient correspond to direct experimental methods. Among these lasts, both gas saturation and effusion, are generally considered as the most accurate direct experimental methods for vapour pressures up to 1 Pa.

A well adapted method to estimate saturated vapour pressure of flavour compounds, may allow a better prediction of their behaviour in food matrix at any given temperature. Several methods have been already compared (Espinoza-Díaz et al., 1999). It was concluded that there are some methods better adapted than others; mainly depending on the physico-chemical characteristics of the pure volatile compounds, such as their chemical class and polarity of the molecule.

The aim of this work is to measure experimentally the saturated vapour pressure of aroma compounds from different chemical families (ester, ketone, alcohol, aldehyde and lactone) as a function of temperature, mainly at negative temperatures.

2. Materials and methods

2.1. Aroma compounds

All the aroma compounds were supplied by Aldrich-Sigma, Co. (Steinheim, Germany) with a minimum purity of 98%. In Table 1, their physico-chemical characteristics are presented.

Ten aroma compounds were selected to measure their saturated vapour pressure. Two homologous series of different chemical families were selected: methyl ketones (from C_3 to C_8) and ethyl esters (from C_4 to C_8) (in order to study the effect of the linear chain length on aroma's volatility). The effect of the functional group (ketone, ester, lactone, aldehyde and alcohol) was studied on molecules which have the same number of carbon atoms.

2.2. Measurement of saturated vapour pressure

The apparatus used for the vapour pressure measurements was a static device which belongs to the direct experimental methods of vapour pressure measurements, specifically to the manometric methods. It was set up by Sasse, Jose, and Merlin (1988) and then several improvements were carried out (Kasehgari, Mokbel, Viton, & Jose, 1993; Mokbel, Rauzy, Loiseleur, Berro, & Jose, 1995). It allows reliable measurements within a very large pressure range: 0.5–200 000 Pa. This

Table 1
Physico-chemical characteristics of the aroma compounds

Aroma compound	Molecular weight (g/mol)	Purity (%)	Melting point[a] (°C)	Boiling point[a] (°C)
n-Hexanol $C_6H_{14}O$	102.2	98	−51.6	157
n-Hexanal $C_6H_{12}O$	100.1	98	−56	128
γ-Hexalactone $C_6H_{10}O_2$	114.5	98	−18	219
Acetone C_3H_6O	58.1	99.5	−95.3	57
2-Butanone C_4H_8O	72.1	99	−85.9	78.6
2-Hexanone $C_6H_{12}O$	100.1	98	−57	127
2-Octanone $C_8H_{16}O$	128.2	98	−43.3	175
Ethyl acetate $C_4H_8O_2$	88.1	99.5	−83.4	75
Ethyl butanoate $C_6H_{12}O_2$	116.1	99	−73	121
Ethyl hexanoate $C_8H_{16}O_2$	144.2	99	−67.5	168

[a] From Fenaroli's handbook (1975).

apparatus consists basically of a cell connected to a pressure gage using high vacuum technology. The temperature was fixed and the vapour pressure was measured at equilibrium. The accuracy of measurements is 0.2% for pressures $(P) \geqslant 1000$ Pa and 1% for $P < 1000$ Pa; temperature accuracy is ±0.02 °C in a range from −70 to 190 °C.

The pure aroma compound was introduced in the stainless steel cell at room temperature. Prior to the vapour pressure determination, the sample was degassed under vacuum to eliminate the air dissolved and the volatile impurities that could be a cause of error. When degassing, the lower part of the cell was heated and the coil was traversed with ice-water so as to minimize losses of the compound during the vapour venting. The degassed sample was cooled and the vapour pressure (P_i^sexp) was measured at various temperatures, from −40 to 25 °C. The measurements were replicated at least twice. Because the experiments were carried out at slightly different temperatures around the temperatures setted up, and in order to compare the different volatile compounds at the same temperature, we used a model to describe our experimental results. The experimental vapour pressure values were used in the Antoine Eq. (2) in order to relate the saturated vapour pressure ($P_{i\,\mathrm{calc}}^s$) to temperature (K):

$$\mathrm{Log} P_i^s \mathrm{calc} = A - \frac{B}{C + T} \tag{2}$$

Constants A, B, C, were determined from experimental results for each volatile compound with the least squares adjustment. The mean percent deviation between experimental and calculated values, was obtained by Eq. (3).

$$\%\mathrm{error} = \left| \frac{P_i^s \mathrm{exp} - P_i^s \mathrm{calc}}{P_i^s \mathrm{exp}} \right|^* 100 \tag{3}$$

3. Results and discussion

3.1. Measurement of the saturated vapour pressure of aroma compounds

The experimental values obtained at nine different temperatures from −40 to 25 °C are given in Table 2. In the same table, the mean relative error for each measurement was calculated using Eq. (3) in order to test the adjustement to Antoine's equation.

The mean error shows a good agreement with Antoine's equation, being lower than 0.8%. The relatively highest variation compared with the model (1.5%) is that of *n*-hexanol. This variation might suggests, Antoine's equation might not be the best fitted method to estimate the saturated vapour pressure of organic compounds such as *n*-hexanol. Espinoza-Díaz et al. (1999) compared several different methods to estimate saturated vapour pressure of volatile compounds. They observed each method takes into account different physico-chemical parameters of molecules, resulting in methods better adapted for a certain kind of volatile compounds than others. The comparisons between the different methods show that equations such as that proposed by Gomez-Nieto and Thodos (1978) for non-polar substances are applicable for aroma compounds containing chemical groups, such as alcohol, ketone or aldehyde, able to form hydrogen bonds between the molecules.

3.2. Comparison between literature and experimental data

The values obtained in this work were compared with some results found in literature. In Table 3 the saturated vapour pressures of aroma compounds are presented at 25 °C.

Table 2
Experimental saturated vapour pressure ($P_{i\mathrm{exp.}}^s$ in Pa) of aroma compounds at different temperatures

Temperature (°C)	Acetone	2-Butanone	2-Hexanone	2-Octanone	Ethyl acetate	Ethyl butanoate	Ethyl hexanoate	*n*-Hexanol	*n*-Hexanal	γ-Hexalactone
25	30 210	11 875	1600	187	12 510	1885	215	107	1517	213
10	15 049	5559	629	62	5734	753	70	28	599	72
5	11 713	4226	449	42	4326	538	47	18	428	40
−5	6880	2355	219	18	2374	262	20	6.6	209	16
−10	5186	1724	170	11.5	1723	178	13	4	143	10
−18	3217	1015	76	5.3	1002	93	5.9	1.6	74	4.4
−25	2058	618	42	2.6	602	50	2.9	0.7	40	2.1
−30	1471	424	31	1.5	410	31	1.7	0.4	25	1.2
−40	816	218	6.8	0.5	207	13	0.5	n.d.	9.5	n.d.
Mean error (%)[a]	0.46	0.75	0.33	0.65	0.61	0.44	0.34	1.50	0.24	0.30

n.d., not determined.

[a] % mean error: mean relative error between experimental and Antoine calculated ($P_{i\,\mathrm{calc.}}^s$)values $\left|\left(P_i^s\mathrm{exp.}-P_i^s\mathrm{calc.}\right)/\ P_i^s\mathrm{exp.}\right|^*100$.

The variation between our values and those from literature at 25 °C, was lower than 7%. Although, for 2-octanone and *n*-hexanol variation reached up to 12 and 92%, respectively. Only the vapour pressures of three aroma compounds at various temperatures (especially at negative ones) were found in literature. In Table 4 they are compared with our values down to −40 °C.

For 2-butanone, the variation between our values and those from literature was lower than 10%. Although, variation increased considerably for 2-octanone and *n*-hexanol when temperature decreased. A variation of 37% was reached for 2-octanone, whereas up to 92% was presented for *n*-hexanol. As discussed previously, the Antoine's equation was not the best fitted for organic compounds such as 2-octanone and *n*-hexanol. Further, the variation of those estimated vapour pressures increased when estimating vapour pressures with that equation at negative temperatures.

Table 3
Comparison between experimental ($P^s_{i\,\text{calc.}}$) and literature ($P^s_{i\,\text{literature}}$) values of saturated vapour pressure (Pa) of aroma compounds at 25 °C

Aroma Compound	P_i^s calc.	P_i^s literature	% ΔP
Acetone	30 210	30 806[a]	−1.9
2-Butanone	11 875	12 047[c]	−1.4
		12 079[a]	−1.7
2-Hexanone	1600	1550[a]	3.1
2-Octanone	187	164[c]	12.5
Ethyl acetate	12 510	12 925[b]	−3.3
Ethyl hexanoate	215	224[d]	−4.3
n-Hexanol	107	10[f]	91.1
n-Hexanal	1517	1420[e]	6.5

% ΔP: $[(P^s_{i\,\text{calc.}} - P^s_{i\,\text{lit.}})/P^s_{i\,\text{lit.}}] * 100$.

[a] Ambrose et al. (1975).

[b] Ambrose et al. (1981).

[c] Getachew (1998).

[d] LeThanh et al. (1993).

[e] Caccioni, Gardani, Lanciotti, and Guerzoni (1997).

[f] N'Guimbi et al. (1992).

Since the melting point of 2-butanone is much lower (−85 °C) than those of 2-octanone and *n*-hexanol (−43 and −51 °C, respectively) possibly the two last compounds started forming crystals. The purities for 2-octanone and *n*-hexanol are some of the lowest (98%) among the studied compounds. Those impurities might be nucleation cores for crystals formation. A property of *n*-hexanol is that it presents the highest capacity of hydrogen bonding among the aroma compounds studied. On the contrary, other compounds such as γ-hexalactone, poorly forms hydrogen bonds. The formation of this kind of bond is increased when temperature decreases. So, an hypothesis could be the increased formation of hydrogen bonds between *n*-hexanol molecules at low temperatures, especially near to that of freezing, resulting in the possible crystals formation. The possible presence of these crystals in the liquid sample might varied the vapour pressure values measured between the different repetitions.

3.2.1. *Effect of temperature on aroma compounds volatility*

In Fig. 1, the experimental vapour pressures obtained for the aroma compounds as a function of temperature are plotted.

Four main groups were observed: first, the most volatile compound, the acetone (C_3). Then a group of compounds of four carbon atoms was observed. These compounds were 2-butanone and ethyl acetate (the latter being more volatile than the first one for a given temperature). At −10 °C, both compounds showed the same experimental vapour pressure. Below −10 °C, 2-butanone became slightly more volatile than ethyl acetate. The third group was composed by ethyl butanoate, 2-hexanone and *n*-hexanal, in order of volatility. The three compounds have six carbon atoms in their structure, thus the difference of volatility between them is due to the functional group. The less volatile group had

Table 4
Comparison between experimental ($P^s_{i\,\text{calc.}}$) and literature ($P^s_{i\,\text{literature}}$) values of saturated vapour pressure (Pa) of aroma compounds at various temperatures

Temperature (°C)	2-Butanone			2-Octanone			*n*-Hexanol		
	$P^s_{i\,\text{calc.}}$	P_i^{sa}	% ΔP	$P^s_{i\,\text{calc.}}$	P_i^{sa}	% ΔP	$P^s_{i\,\text{calc.}}$	P_i^{sb}	% ΔP
25	11 875	12 047	−1.4	187	164	12.5	107	9.6	91.1
10	5559	5969	−7.3	62	53	14.3	28	3.9	86.3
5	4226	4273	−1.1	42	35	16.4	18	–	–
−5	2355	2356	−0.02	18	15	19.2	6.6	–	–
−10	1724	1720	0.2	11.5	10	16.2	4	0.5	87.1
−18	1015	920	9.4	5.3	3.5	34.8	1.6	0.2	90
−25	618	613	0.7	2.6	1.9	26.9	0.7	–	–
−30	424	448	−5.5	1.5	0.9	37.1	0.4	–	–
−40	218	208	4.7	0.5	–	–	n.d.	–	–

% ΔP: $[(P^s_{i\,\text{calc.}} - P^s_{i\,\text{lit.}}) / P^s_{i\,\text{lit.}}]*100$.

[a] Getachew (1998).

[b] N'Guimbi et al. (1992).

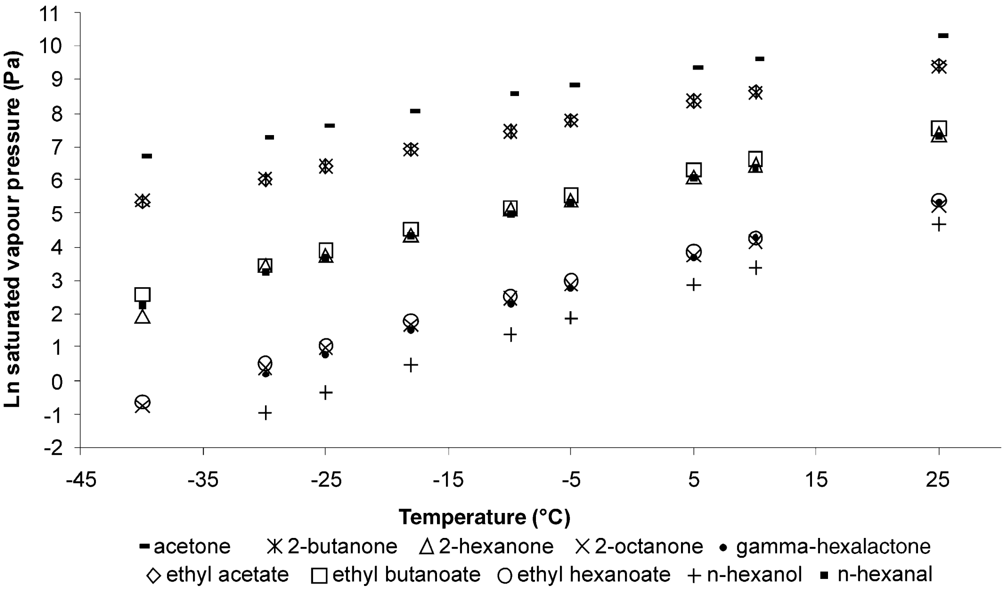

Fig. 1. Saturated vapour pressure of aroma compounds at various temperatures.

compounds of both six and eight carbon atoms: ethyl hexanoate, γ-hexalactone, 2-octanone and *n*-hexanol (in volatility order); the first two had similar volatility in the range from −5 to 25 °C. Below −5 °C, volatility of γ-hexalactone decreased more than that of ethyl hexanoate. Finally, 2-octanone (C_8) and *n*-hexanol (C_6) remained the less volatile compounds of all studied. From our results, volatilities of aroma compounds which have the same carbon number in their aliphatic chain (C_6) decreased as follows: ester > ketone > aldehyde > lactone > alcohol.

For all the studied compounds, no discontinuity of the values of saturated vapour pressures was observed between positive and negative temperatures. Saturated vapour pressure presented an exponential dependence on temperature. Correlation coefficients (R^2) were greater than 0.99 in the range from −40 to 25 °C. Ambrose et al., 1975 measured experimentally the saturated vapour pressures of methyl ketones in a temperature range from 25 to at least 90 °C obtaining as well exponential correlations ($R^2 > 0.99$). An Arrhenius representation of the saturated vapour pressures measured in this work is presented in Fig. 2.

A linear dependence of Ln P on the inverse of temperature and correlations greater than 0.999 were obtained. From this plot, apparent activation energies of vapourization for the pure aroma compounds were calculated. Using Ambrose's results, the apparent activation energies of vapourization for the range from −40 to 90 °C were calculated and are presented in Table 5.

Among an homologous series, activation energy increased when aliphatic chain increased, obtaining very similar energies for the two series analysed. When comparing compounds with six carbon atoms in their structure, apparent activation energy as a function of temperature increased as follows: ester < aldehyde < ketone < lactone < alcohol. It can be noticed that apparent activation energies are not only valid for the range from −40 to 25 °C, but at least until 90 °C since there is practically no difference between the energies calculated.

3.2.2. Effect of both aliphatic length and chemical group on aroma compounds volatility

Volatilities of the two homologous series (methyl ketones and ethyl esters) are shown in Figs. 3 and 4, respectively.

In both figures, it is observed volatility of a pure aroma compound decreases when the number of the carbon atoms in the aliphatic chain increases. As well, when temperature decreases, volatility does.

Vapour pressure for ethyl esters was higher than that of methyl ketones, at any given temperature. At negative temperatures, from −25 to −40 °C, vapour pressures for ethyl butanoate and ethyl hexanoate became similar. Although, for ethyl acetate volatility remained considerably higher than those of the other two esters. In order to compare the functional group effect on compounds volatility, in Fig. 5, the vapour pressure of aroma compounds which have six carbon atoms in the aliphatic chain is plotted.

For compounds which have six carbon atoms, the more the carbonyl group is reduced, the less the compound's volatility. In Fig. 5, two groups are observed; in the first one, volatility decreased as follows: ethyl butanoate, 2-hexanone and *n*-hexanal, at any given temperature. Even though, their values were of the same order of magnitude. The second group was constituted by γ-hexalactone and *n*-hexanol, in order of volatility, being the less volatile compounds among all studied.

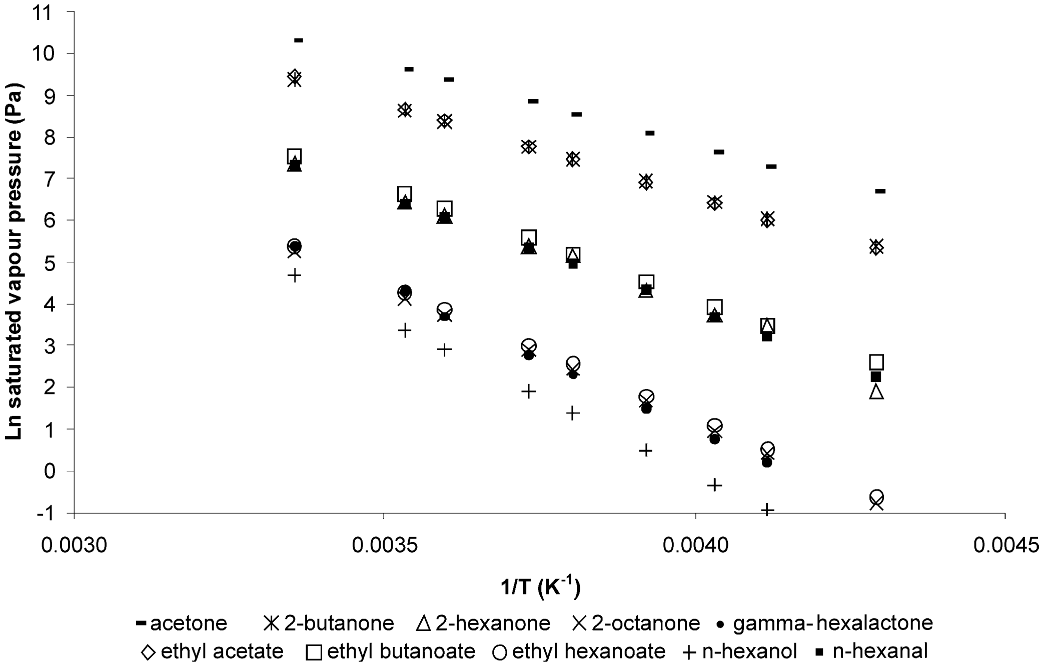

Fig. 2. Arrhenius representation of aroma compounds saturated vapour pressure.

Table 5
Activation energy of vaporization ($Ea_{vap.}$) for pure aroma compounds

Aroma compound	$Ea_{vap.}$–40 to +25 °C (kJ/mol)	$Ea_{vap.}$–40 to +90 °C[a] (kJ/mol)
Acetone	32.5	–
2-Butanone	36	35.2
2-Hexanone	46.7	42
2-Octanone	53.2	–
Ethyl acetate	36.9	35.9
Ethyl butanoate	44.5	–
Ethyl hexanoate	53.3	–
n-Hexanol	61.6	–
n-Hexanal	45	–
γ-Hexalactone	57.2	–

[a] Results of this work with those of Ambrose et al. (1975).

Compounds such as *n*-hexanol and γ-hexalactone, have facility to form intermolecular bonding: in the case of *n*-hexanol, hydrogen bonds can be formed between molecules whereas hydrophobic interactions are created between the aliphatic rings of γ-hexalactone molecules. Hydrophobic interactions are attractive forces between molecules which are greater when either the molecule's aliphatic chain (and thus molecule's size) or shape increase. Boiling point of molecules is as well influenced by these interactions, resulting in higher boiling temperatures as either size or interactions between molecules increase (Loudon, 1988).

In the case of aroma compounds which have four (ethyl acetate and 2-butanone) and eight (ethyl hexanoate and 2-octanone) carbon atoms, volatility order was the same as that observed for compounds of six carbon atoms. The relation between the saturated vapour pressure of methyl ketones and ethyl esters at 25 °C and the carbon atom number in their aliphatic chain (expressed as hydrophobicity: partition coefficient between *n*-octanol/water), is compared in Table 6.

Table 6
Hydrophobicity (log *P*) and saturated vapour pressure ($P^{s}_{i\exp.}$) of methyl ketones and ethyl esters at 25 °C

Number of carbon atoms in the molecule	Methyl ketones		Ethyl esters	
	log P[a]	$P^{s}_{i\exp.}$ (Pa)	log P[a]	$P^{s}_{i\exp.}$ (Pa)
3	−0.26	30 209	–	–
4	0.35	11 874	0.67	12 510
6	1.41	1599	1.73	1885
8	2.46	187	2.8	215

[a] Estimated by using the molecular modelling pro software [revision 3.25 ChemSW(R) NorGwyn Montgomery Software Inc., 1999–2000].

It is observed that, ethyl esters have higher hydrophobicity values, (thus less polarity of the molecules) than methyl ketones. When plotting vapour pressure against the carbon number in the molecule (log *P*), an exponential decrease of vapour pressure was found with a $R^2 > 0.99$ for ethyl esters and a $R^2 > 0.999$ for methyl ketones; saturated vapour pressure of ethyl esters was more important than that of methyl ketones.

This suggests both attractive intermolecular forces such as hydrogen and hydrophobic bonds between molecules (cohesion force) and molecule's size play a very important role in pure molecule's volatility.

It is interesting to notice that *n*-hexanol and *n*-hexanal, have relatively the same molecular weight, the same number of carbon atoms and also, the same hydrophobicity values (log *P*) 1.88 and 1.89, respectively. Although vapour pressures for *n*-hexanal are at least 14 times more important than those of *n*-hexanol. This shows the important role of chemical groups in volatility of molecules.

In the case of methyl ketones, *n*-hexanol and *n*-hexanal, functional groups are present in the extreme of the linear molecules. In order to study if the position of the chemical group in the linear molecule influences volatility, in Fig. 6 are presented the vapour pressures of

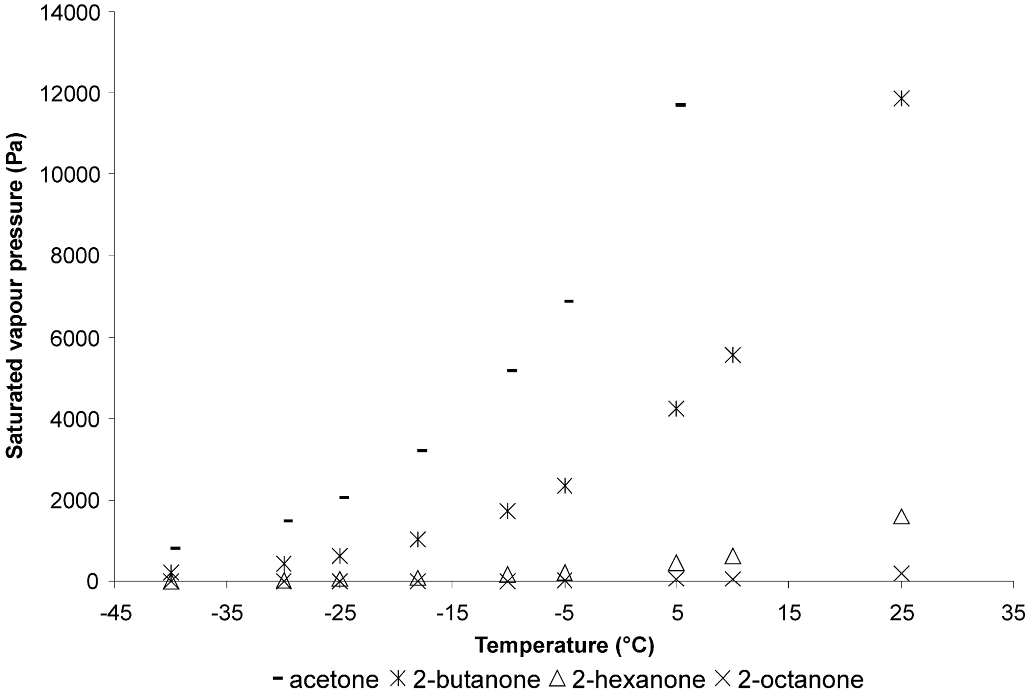

Fig. 3. Saturated vapour pressure of an homologous series of methyl ketones.

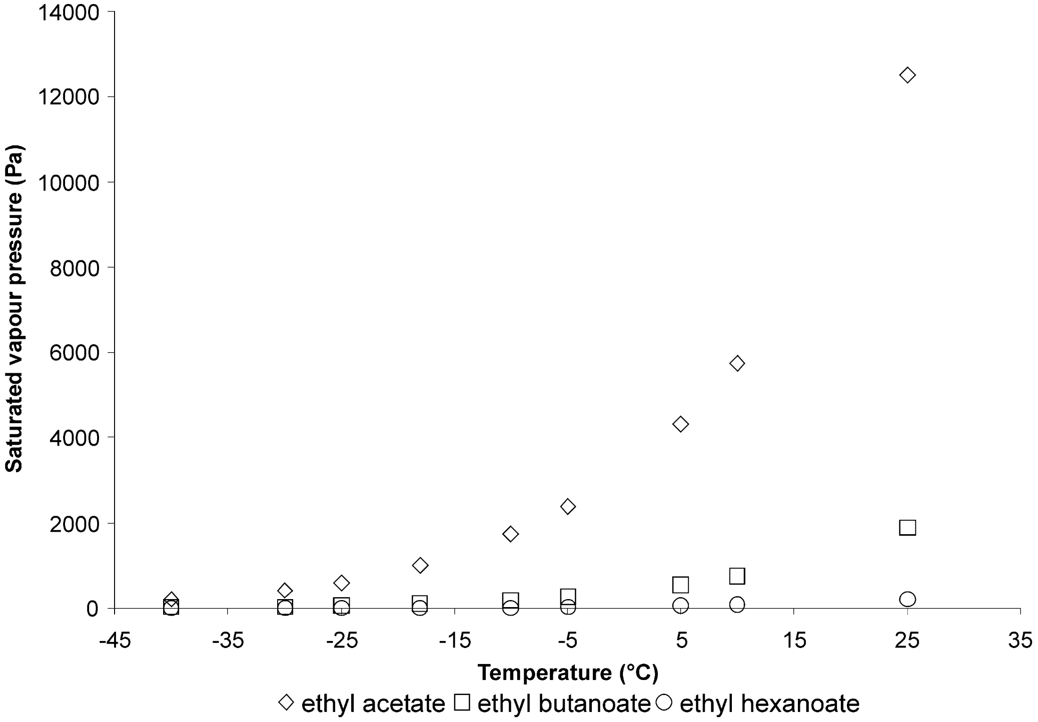

Fig. 4. Saturated vapour pressure of an homologous series of ethyl esters.

ketones with functional group in two different positions in the aliphatic chain (each methyl ketone has the same log *P* value as that of the ethyl ketones).

It is observed that, position of carbonyl group in the aliphatic chain, seems not to influence in an important way the volatility of the molecules. However, a slight increase of vapour pressure is observed for ketones with carbonyl group in the third carbon of the chain.

Either the chemical nature or the structure of volatile organic compounds influence the physico-chemical properties of the pure molecules, such as melting and boiling points and volatility. Moreover, physical parameters such as temperature influence the behaviour of those molecules either at the pure state or in the presence of other substances. The presence of these other substances in the same media as that of volatile organic

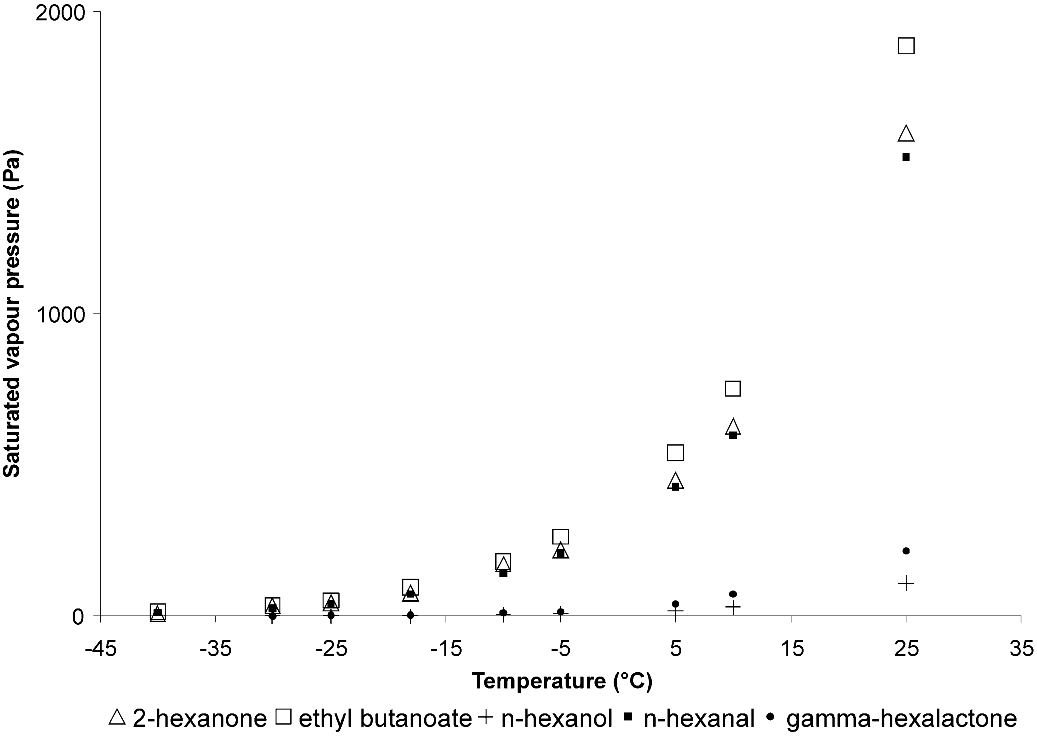

Fig. 5. Saturated vapour pressure of volatile compounds with six carbon atoms in their aliphatic chain.

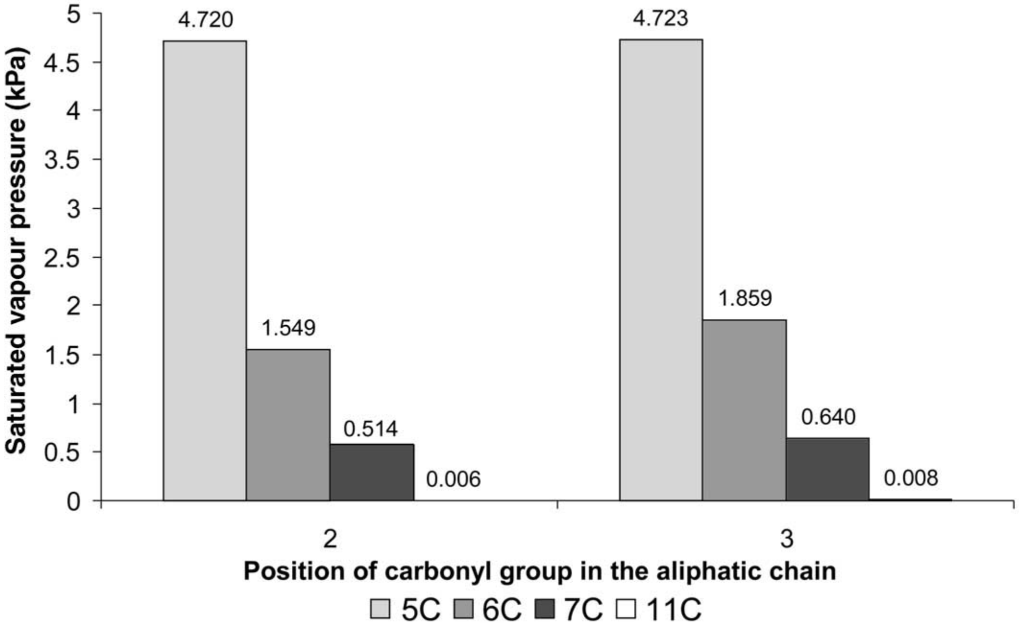

Fig. 6. Saturated vapour pressure of ketones with functional group in two different positions in the aliphatic chain (Ambrose et al., 1975).

compounds, results in physico-chemical interactions between molecules. Thermodynamic equilibrium such as partition coefficients, activity coefficients and solubility of compounds, are related by the saturated vapor pressure and influenced by temperature.

4. Conclusions

Saturated vapour pressure dependence on temperature follows an Arrhenius behaviour from −40 to at least up to 90 °C. No discontinuity of the values was observed between positive and negative temperatures. The chemical structure of the pure molecules influences volatility due to the effect of both, functional group and hydrophobicity of the compounds. The saturated vapour pressure of two homologous series, methyl ketones and ethyl esters, decreases when either the aliphatic chain increases or temperature decreases. For aroma compounds which have the same carbon atoms number in their structure, volatility decreases as follows: ester > ketone > aldehyde > lactone > alcohol. Thermodynamic parameters, such as partition coefficients (vapour–liquid, liquid–liquid), activity coefficients, solubility, depend on saturated vapour pressure. Experimental values of the latter measured in this work, contribute to the little data in literature especially at negative temperatures. The knowledge of these values will allow to calculate, with accuracy and taking into account the chemical characteristics of molecules, other thermodynamic parameters at negative temperatures. Subzero temperature is an important physical parameter which influences physico-chemical equilibria and kinetics of volatile organic compounds not only in food systems, but as well in other biological and environmental systems.

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References

Ambrose, D., Ellender, J. H., Lees, E. B., Sprake, C. H. S., & Townsend, R. (1975). Thermodynamic properties of organic oxygen compounds XXXVIII. Vapour pressures of some aliphatic ketones. *Journal of Chemical Thermodynamics*, *7*, 453–472.

Ambrose, D., Ellender, J. H., Gundry, H. A., Lee, D. A., & Townsend, R. (1981). Thermodynamic properties of organic oxygen compounds LI. The vapour pressures of some esters and fatty acids. *Journal of Chemical Thermodynamics*, *13*, 795–802.

Boublik, T., Fried, V., & Hala, E. (1984). *The vapour pressures of pure substances. 2nd edition.* In: *Physical sciences data series* (No. 17). Amsterdam, The Netherlands: Elsevier Science.

Caccioni, D. R. L., Gardani, F., Lanciotti, R., & Guerzoni, M. E. (1997). Antifungal activity of natural volatile compounds in relation to their vapour pressure. *Sciences des Aliments*, *17*, 21–34.

Delle Site, A. (1997). The vapor pressure of environmentally significant organic chemicals: A review of methods and data at ambient temperature. *Journal of Physical Chemistry Reference Data*, *26*, 157–193.

Espinoza-Díaz, M. A., Guetachew, T., Landy, P., Jose, J., & Voilley, A. (1999). Experimental and estimated saturated vapour pressures of aroma compounds. *Fluid Phase Equilibria*, *157*, 257–270.

Fenaroli, G. (1975). In T. E., Furia, & N., Bellanca (Eds.), *Handbook of flavour ingredients. 2nd edition.* Cleveland, OH: The Chemical Rubber Company.

Getachew, T. (1998). *Etude de systèmes biphasiques d'intérêt pétrolier: hydrocarbures peu volatils, mélanges eau-méthanol et eau-méthanol-chlorure de sodium.* PhD thesis, University Claude Bernard- Lyon I, Villeurbanne, France.

Gomez-Nieto, M., & Thodos, G. (1978). Generalized vapor pressure equation for nonpolar substances. *Industrial and Engineering Chemistry Research Fundamentals*, *17*, 45–51.

Kasehgari, H., Mokbel, I., Viton, C., & Jose, J. (1993). *Fluid Phase Equilibria*, *108*, 103.

LeThanh, M., Lamer, T., Voilley, A., & Jose, J. (1993). Détermination des coefficients de partage vapeur-liquide et d'activité de composés d'arôme à partir de leurs caractéristiques physico-chimiques. *Journal de Chimie Physique*, *90*, 545–560.

Loudon, M. G. (1988). *Organic chemistry. 2nd edition.* California: The Benajamin Cummings Publishing Company.

Mokbel, I., Rauzy, E., Loiseleur, H., Berro, C., & Jose, J. (1995). Vapor pressures of 12 alkylcyclohexanes, cyclopentane, butylcyclopentane and trans-decahydronaphthalene down to 0.5 Pa. Experimental results, correlation and prediction by an equation of state. *Fluid Phase Equilibria*, *108*, 103–120.

N'Guimbi, J., Kasehgari, H., Mokbel, I., & Jose, J. (1992). Tensions de vapeur d'alcools primaires dans le domaine 0.3 Pa à 1.5 kPa. *Thermochimica Acta*, *196*, 367–377.

Sasse, K., Jose, J., & Merlin, J. C. (1988). A static apparatus for measurement of low vapor pressures. Experimental results on high molecular-weight hydrocarbons. *Fluid Phase Equilibria*, *42*, 287–304.