Additivity of vaporization properties in pheromone-like homologous series

Bohumír Koutek,[*,a] **Michal Hoskovec,**[a] **Ludvík Streinz,**[a] **Pavlína Vrkočová**[a] **and Květoslav Růžička**[b]

[a] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, CZ-16610 Praha 6, Czech Republic*
[b] *Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, CZ-16000 Praha 6, Czech Republic*

A simple method of estimating vaporization properties of normal alkyl and (*Z*)- and (*E*)-alkenyl homologous series of pheromone-like acetates, alcohols and aldehydes with 10 to 18 carbon atoms in the chain is described. The properties hold for the (subcooled) liquid state and include vapour pressure (p_{sat}) and heat of vaporization ($\Delta_{vap}H$) at 25 °C. An empirical QSPR model for ln p_{sat} and $\Delta_{vap}H$ is developed in terms of three easy-to-calculate structural descriptors related to the number of carbon atoms in the chain (*n*), the functional group characteristics (*I*) and the double bond position (Δ). The model, covering the property ranges of 2×10^{-4}–2×10^{1} Pa and 60–120 kJ mol^{-1}, explains over 99.8% of the variance in the experimental data sets containing 295 compounds, with standard errors in ln p_{sat} and $\Delta_{vap}H$ of about 0.085 ln unit and 0.62 kJ mol^{-1}, respectively. It is recommended as a useful tool in designing pheromones and in fate-modelling applications in the absence of experimental data.

Introduction

During the past 30 years there has been a rapidly expanding interest in the research of insect pheromones, at least partially in an effort to provide new pest insect control technology. Several excellent books have summarized the synthetic,[1,2] biochemical[2,3] and even practical[2,4] results of this research. However, irrespective of many achievements in selected research areas, understanding the details of processes by which pheromones are emitted and transported through the atmosphere is still limited by our lack of knowledge of their important physico-chemical properties at temperatures relevant to their practical use (~20–30 °C). Among these properties, vapour pressure (p_{sat}) and heat of vaporization ($\Delta_{vap}H$) are two of the most important.

By virtue of its definition,[5] vapour pressure will govern the distribution between the vapour and condensed phases and, in turn, often determines where and how a chemical will tend to concentrate at equilibrium. It is now generally recognized within the pheromone chemistry community that vapour pressure can be used both to correct electrophysiological activities of pheromone analogues when comparing congeners with different chain lengths and/or functional groups,[6] and to optimize existing (mostly empirical) applications of synthetic pheromone blends in insect pest control strategies.[7] If the vapour pressure is to have predictive value, the quantitative effect of temperature on this property must also be known. Assuming ideal gas behaviour in the low vapour pressure region, the vapour pressure can be recalculated from one temperature (T_1) to another (T_2) in a narrow temperature range by using a known value of $\Delta_{vap}H$ and an integrated form of the Clausius–Clapeyron equation, $\ln (p_{sat1}/p_{sat2}) = (\Delta_{vap}H/R)[(1/T_2) - (1/T_1)]$, where R is the gas constant.

The poor literature data base on vapour pressures of high-molecular-weight compounds in general and pheromone-like substances in particular is due to the experimental difficulties in directly measuring the vapour pressures of these compounds by the conventional isoteniscope, Knudsen effusion or gas saturation techniques.[8] Such direct data are available only for a limited number of substances and subject to large systematic interlaboratory errors.[9] Gas chromatography (GC) is an alternative method for indirect determination of vapour pressures. Many modifications of this method have been described,[10–12] all of them being based on the simple concept that partitioning of a solute between the gas and non-polar stationary phases is controlled mainly by vapour pressure. These methods frequently require the use of one or several reference compounds whose vapour pressures are accurately known over the whole temperature range used, which may sometimes represent a serious problem. A great deal of work has been done using the GC technique by environmental chemists in determining vapour pressures of organic pollutants,[13] and also the literature vapour pressure data of pheromones available so far are based almost exclusively on the GC-based measurements.[14–18] As in the case of vapour pressures, there are two general groups of methods for determining the heat of vaporization.[19a] The first is based on calorimetric measurements (direct methods), while the other employs calculation of $\Delta_{vap}H$ either from the vapour pressure *vs.* temperature dependence or from chromatographic data (indirect methods). Generally, the direct experimental $\Delta_{vap}H$ data are scarce for compounds with ten or more carbon atoms.

One popular approach to solve the difficulties connected with direct property measurements relies on the development of reliable estimation techniques. Many methods, differing in the amount and type of additional information required, have been developed for estimating vapour pressures. Most theoretically based equations were developed by using reduced variables such as the reduced temperature T_R ($T_R = T/T_C$) and reduced pressure P_R ($P_R = P/P_C$) and included reduced boiling points T_{BR} ($T_{BR} = T_B/T_C$). Consequently, boiling point (T_B), critical pressure (P_C) and critical temperature (T_C) must be known or estimated prior to performing the predictions. Reviews by Reid *et al.*[5] and Lyman *et al.*[20] summarize these and related approaches. In addition, molecular thermodynamic properties in general can often be estimated using quantitative structure–property relationships (QSPRs) where the property of interest is a function of molecular descriptors that can be derived in either non-empirical or empirical ways.[21] Among the non-empirical descriptors, various kinds of topological indices and surface areas have been suggested as important variables.[22] Recently, studies have also been initiated to explore neural networks as a tool to upgrade structural feature selection.[23] Examples of the empirical techniques are well-known atom-, bond- and group-additivity (GA) methods, where the property is estimated as the sum of contributions from the individual structural increments that compose the substance. Of the GA methods, the UNIFAC technique for estimating the vapour pressures is particularly worth mentioning.[24] Although this method showed some success in estimating the vapour pressures, it requires rather complicated calculations and its applicable pressure range is between 1.0 and 300 kPa.[25]

We would like to report an empirical QSPR scheme that has been developed to estimate the vapour pressures and heats of vaporization of pheromone-like homologous series (a) and (b),

$$\mathrm{H{-}(CH_2)_{\mathit{n}}{-}Y} \qquad \text{(a)}$$

$$\mathrm{H{-}(CH_2)_{\mathit{p}}{-}CH\overset{\Delta}{=}CH{-}(CH_2)_{\mathit{q}}{-}Y} \qquad \text{(b)}$$

where Y denotes OH, CH=O and $OCOCH_3$, Δ indicates the double bond (*Z* or *E*) position in the chain, *n* varies from 10 to 18, and $p + q = n - 2$. These series include pheromonal components of the largest insect group, Lepidoptera,[4] and their structural features make them an attractive class of compounds for the application of QSPR studies. Since for pheromones the principal region of predictive interest is the low vapour pressure end of the scale corresponding to environmentally relevant temperatures, our method focuses on 25 °C.

The work has three major goals. The first is the presentation and correlation of coherently developed empirical models describing the vapour pressures and heats of vaporization of the series (a). Our second goal addresses the value of previous analysis in developing regression equations designed to model the properties of compounds related to the monoenic homologous series (b). To the best of our knowledge, models capable of reflecting the effect of minor structural differences in the position and configuration of the double bond on the properties of interest have not existed up to now. Finally, we hope to obtain practical correlation equations that could be used to predict values for as yet unmeasured properties of compounds. These predictions should enable pheromonal chemists and entomologists to study and model the physico-chemical behaviour of pheromones in the environment more accurately.

Methods and data

Regression equations and other statistical characteristics were obtained by options in the Statgraphic Plus for Windows 3.0 software package (Manugistic, Rockville, MD, USA).

The vapour pressures and heats of vaporization of C_{10}–C_{18} alcohols, aldehydes and acetates at 25 °C have been taken mostly from our previous GC-based measurements[16–18] and completed by available literature values from other sources. It should be noted that some of our previous data for alcohols[16] have been recalculated in this work using new vapour pressure values obtained from simultaneous correlations of vapour pressure and thermal data for our GC reference compounds (12:OH).[26] As a result, the values for decenols are slightly different from those given in our previous communication. The complementary vapour pressure data include both those determined by other authors[14–15] using GC-based techniques and those measured directly by standard methods.[27–33] The directly measured values concerned mostly the lower saturated homologous series members. To examine the accuracy of the present estimation method over the widest possible range of very low vapour pressures, some vapour pressure values were obtained by extrapolating known vapour pressures from the temperature at which they were measured to the temperature of interest. This extrapolation was carried out either by using an integrated form of the Clausius–Clapeyron equation and known $\Delta_{vap}H$ and heat capacity data (aldehydes[28]) or by using equations which are supposed to extrapolate relatively well below the experimental temperature range, *i.e.* the Cox equation (acetates[27]) and the Wagner equation (alcohols[31]). It is also to be emphasized that the GC method gives the subcooled liquid vapour pressure (defined as the liquid vapour pressure extrapolated below the melting point) for crystalline high molecular weight substances. Thus, the vapour pressure values for a few solid compounds included in this study [*e.g.* for hexadecan-1-ol (mp 56 °C) and octadecyl acetate (mp 34.5 °C)] correspond to the subcooled liquid state. The same holds true for the literature value of octadecane (mp 29–30 °C).

Interconversion of the solid ($p^{S}{}_{sat}$) and subcooled liquid ($p^{L}{}_{sat}$) vapour pressure can be done using the relationship $\ln (p^{L}{}_{sat}/p^{S}{}_{sat}) = (\Delta_{fus}S/R)(T_m - T)/T$, where $\Delta_{fus}S$ is the entropy of fusion (amounting to approximately 56.5 J deg^{-1} mol^{-1}),[34] T_m is the melting temperature and *T* is the ambient temperature. The $\Delta_{vap}H$ correlations involve supplementary data from compilations of Majer and Svoboda[19b] and other sources.[35,36] The recommended p_{sat} and $\Delta_{vap}H$ data for *n*-alkanes at 25 °C are taken from a compilation by Růžička and Majer.[9] We use a condensed nomenclature for *n*-alkyl and *n*-alkenyl compounds. Any unsaturation in the main chain is indicated by the geometry *Z* or *E* followed by its position number and separated from the number of carbon atoms in the chain by a hyphen; the functional group abbreviation (OH = alcohol, Ac = acetate and Ald = aldehyde) is separated from the rest by a colon. Thus, *e.g.* *Z*7-14:Ac denotes (*Z*)-tetradec-7-enyl acetate. For the sake of consistency, the position of the double bond (Δ) was invariably counted starting from the first carbon atom adjacent to the functional group Y. This does not necessarily agree with the usual chemical nomenclature (*e.g.* for dodec-5-en-1-ol Δ = 5 while for dodec-5-en-1-al Δ = 4). The complete datasets used in this study are available (SUPPL. NO. 57373, 8 pp.)† or as MS Excel files upon request directly to the authors.

Results and discussion

The general QSPR framework which links structural features of a compound *j* with a physico-chemical property (*Q*) expresses the property Q_j as in eqn. (1), where a_0 is the *y*-intercept

$$Q_j = a_0 + \sum_{i=1}^{m} a_i x_{ij} \qquad (1)$$

of the regression line, a_i is the coefficient of the descriptor x_{ij}, and *m* is the number of descriptors in the final model. Let us propose Q_j to be equal to either $\ln p_{sat}$ or $\Delta_{vap}H$.

Applied first specifically to the homologous series (a), eqn. (1) becomes substantially simplified since the difference from member to member in this series is the addition/subtraction of one CH_2 group in the normal alkyl chain. Then, only one structural variable is needed within each series, that pertaining to the number of CH_2 groups ($x = n$), and eqn. (1) can be rewritten as eqn. (2) or (3).

$$\ln p_{sat} = a_0 + a_1 n \qquad (2)$$

$$\Delta_{vap}H = b_0 + b_1 n \qquad (3)$$

Table 1 summarizes regression parameters and statistics of eqns. (2) and (3) for the homologous series of alcohols (Y = OH), acetates (Y = $OCOCH_3$) and aldehydes (Y = CHO) of the type (a) together with the corresponding constants for the standard *n*-alkane (Y = CH_3) series. The results show that both the ln p_{sat} and $\Delta_{vap}H$ values for all compound classes

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† For details of the Supplementary Publications Scheme see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors).

Table 1 Regression parameters of eqns. (2) and (3)

		H–(CH$_2$)$_n$–Y			
Equation	Parameter	Y = CH$_3$	Y = OH	Y = OCOCH$_3$	Y = CHO
(2) ln p_{sat}	a_0	15.3302 ± 0.0343	11.1373 ± 0.2384	11.9575 ± 0.1653	13.0530 ± 0.2599
	a_1	−1.1320 ± 0.0023	−1.1023 ± 0.0186	−1.1111 ± 0.0130	−1.1184 ± 0.0192
	r^2	1.0000	0.9943	0.9989	0.9974
	SE[a]	0.0210	0.1852	0.1109	0.1365
	N[b]	10	22	10	11
(3) $\Delta_{vap}H$	b_0	6.6572 ± 0.2741	31.7828 ± 0.4615	21.5573 ± 0.5990	16.5099 ± 2.1629
	b_1	4.9946 ± 0.0186	5.0140 ± 0.0358	5.0107 ± 0.0410	4.9911 ± 0.1805
	r^2	0.9999	0.9996	0.9995	0.9935
	SE[a]	0.1684	0.2533	0.3436	0.8244
	N[b]	10	10	8	7

[a] Standard error of estimation. [b] Number of points.

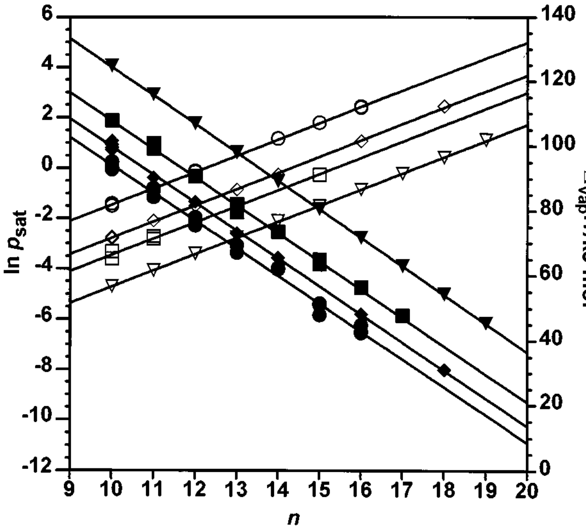

Fig. 1 Ln p_{sat} and $\Delta_{vap}H$ as a function of the number of C-atoms in the alkyl chain at 25 °C. For ln p_{sat}: (▼) *n*-alkanes, (●) *n*-alkanols, (◆) *n*-alkyl acetates, (■) *n*-alkanals; for $\Delta_{vap}H$: (▽) *n*-alkanes, (○) *n*-alkanols, (◇) *n*-alkyl acetates, (□) *n*-alkanals.

Table 2 Functional group contributions to vapour pressures and heats of vaporization at 25 °C

Functional group	I_p	$I_{\Delta H}$
-CH$_3$	0.0000	0.0000
-OH	3.3718 ± 0.0361	5.0800 ± 0.0154
-OCOCH$_3$	2.7502 ± 0.0336	3.0251 ± 0.0228
-CHO	1.8513 ± 0.0353	1.9643 ± 0.0569

investigated correlate excellently ($r^2 \geqslant 0.993$) with the numbers of methylene groups (note that r^2 gives the fraction of the variance in the data that is accounted for by the model). Straight lines representing the best fits are drawn in Fig. 1.

Before further analyses of the data, it is instructive to examine the slopes a_1 and b_1 in Table 1. Their values vary only slightly from −1.1023 to −1.1320 ln units and from 4.9946 to 5.0140 kJ mol^{-1}. The question arises, whether the small differences observed among the slopes simply reflect an uncertainty in the experimental data (particularly for higher members of the non-alkane homologous series) or whether they are real, manifesting the dependence of the methylene group increment with respect to the functional group attached to the *n*-alkyl group. Although no final conclusion about the (non)-equivalency of methylene group contributions is possible without very accurate additional experiments, we have chosen to accept the approximate equality of the slopes and to take the parameters of alkanes as correct values. This suggestion is supported by a good correlation of alkane series data, as well as by our findings that the differences in a_1 and b_1 are generally small (<1.5% and <0.3% variance) and the values of the class-specific constants a_1 and b_1 are indistinguishable from those of the *n*-alkane series within the 95% confidence intervals. Accordingly, the addition of one methylene unit to the chain ($n \geqslant 10$) appears to reduce the vapour pressure about 3.1 times while increasing the heat of vaporization by about 4.99 kJ mol^{-1}, irrespective of the Y group character. As regards the intercepts of the respective regression lines of the alkane and alkanol series, we notice that the constant difference in $\Delta_{vap}H$ between the two series ($\Delta\Delta_{vap}H = 31.78 - 6.66 = 25.12$ kJ mol^{-1}), as follows from Table 1, represents a contribution of intermolecular H-bonds to the cohesive energy of liquid alkanols. Benson,[37] demonstrating that alkanols (up to $n = 11$) are self-associated in four-membered cyclic clusters, reported a similar value of 25.52 ± 0.42 kJ mol^{-1} for this contribution.

As is apparent from the foregoing discussion, the ln p_{sat} and $\Delta_{vap}H$ values of the *n*-alkyl derivative series should be interrelated and the properties of any non-hydrocarbon homologous series may be referred to the properties of *n*-alkanes. By broadening the definition of *n* to effective (equivalent) carbon number (ECN) with *n*-alkanes as the reference,[38] all homologous series of the type (a) can be correlated with the same regression equation parameters as the *n*-alkanes, as shown in eqns. (4) and (5), where the term ($n + I$), with I

$$\ln p_{sat} = 15.3302 - 1.1320\,(n + I_p) \qquad (4)$$

$$\Delta_{vap}H = 6.6572 + 4.9946\,(n + I_{\Delta H}) \qquad (5)$$

representing a correction increment for the given functional group, is equal to ECN.

To determine optimized values of correction increments I, the best fit to the data was determined for each series using the Statgraphics routine for a constrained non-linear Levenberg–Marquart regression. The correction increment values thus obtained (Table 2) were then incorporated into eqns. (4) and (5) and the results based on these equations were compared with the corresponding values obtained by previously developed methods.

Several group contribution schemes have been suggested for hydrocarbons,[39–41] but the only method proposed to be valid for all classes of compounds investigated here is the method of Tu.[42] In Fig. 2 our ln p_{sat} data based on eqn. (4) are compared with those computed using the Tu's group contribution technique. Considering the different database used, as well as data treatment, the agreement between both methods is surprisingly good ($N = 27$, $r^2 = 99.58\%$, SE = 0.2727) for aldehydes, alcohols and, of course, alkanes. On the other hand, the results are not in good accord for acetates, which may reflect in part the missing higher acetate data in Tu's original database. In contrast to

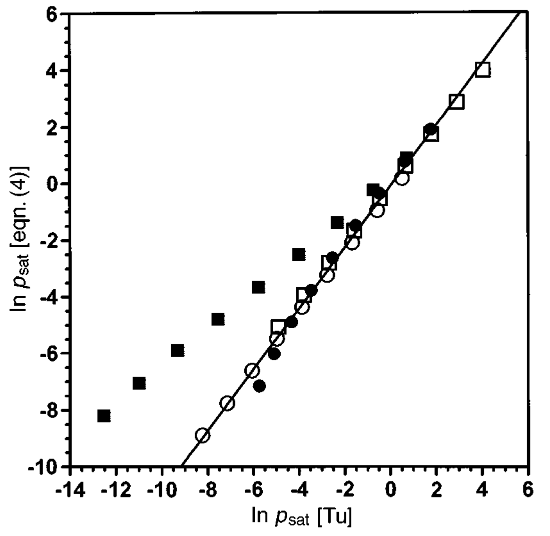

Fig. 2 A comparison of vapour pressures (25 °C) predicted by eqn. (4) with those predicted by the method of Tu.[42] The regression line is shown; (□) *n*-alkanes, (○) *n*-alkanols, (■) *n*-alkyl acetates, (●) *n*-alkanals.

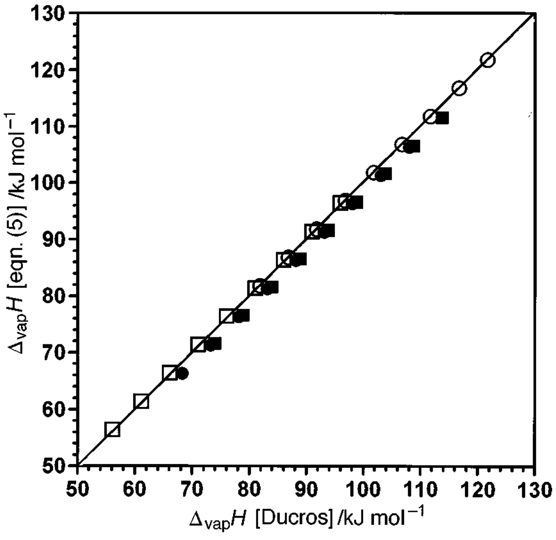

Fig. 3 A comparison of heats of vaporization (25 °C) predicted by eqn. (5) with those evaluated by the method of Ducros.[43] Solid line indicates a 1 : 1 correspondence. (□) *n*-alkanes, (○) *n*-alkanols, (■) *n*-alkyl acetates, (●) *n*-alkanals.

vapour pressures, numerous group additivity (GA) methods[19] have been proposed to estimate vaporization enthalpies of organic compounds at 25 °C. Since the most general (and also the most popular) techniques available are probably the methods of Ducros *et al.*,[43] Chickos *et al.*[44] and Cardozo,[45] these three GA methods were used to test the validity of eqn. (5). Statistical analysis of the relationships $\Delta\Delta_{vap}H_{(eqn.5)} = f(\Delta\Delta_{vap}H_{(GA)})$ performed independently on each GA data population reveals that rather good ($r^2 > 98.6\%$) linear correlations do exist in all cases. However, the best agreement, *viz.* $\Delta_{vap}H_{(eqn.5)} = 0.991\Delta_{vap}H_{(GA)}$ with an insignificant absolute term and a slope very close to unity ($N = 36$, $r^2 = 99.98\%$, SE = 1.175), has been found between our data and those predicted by the additivity scheme of Ducros *et al.*[43] (Fig. 3).

Since $\Delta_{vap}H$ values of alkanoates were shown[36] to be practically identical with those of acetates having an equal number of carbon atoms, these values allow an indirect validation of the present model. Accordingly, we compared our $\Delta_{vap}H$ values (kJ mol^{-1}) for 9:Ac, 11:Ac, 13:Ac, 15:Ac, 17:Ac and 19:Ac (66.75, 76.73, 86.71, 96.69, 106.67 and 116.65, respectively) based on eqn. (5) with the recently reported GC-based data[46] for methyl decanoate (66.91), methyl dodecanoate (76.81), methyl tetradecanoate (86.63), methyl hexadecanoate (96.49), methyl octadecanoate (106.30) and methyl eicosanoate (116.24). It may be seen that our values and literature values agree to within 0.36%.

Table 3 Parameters and statistics of eqns. (6) and (7)

Equation	Parameter	*Z*-isomers	*E*-isomers
(6)	a_2	1.7828 ± 0.0479	1.3324 ± 0.0466
	a_3	−1.7947 ± 0.0590	−1.3012 ± 0.0573
	r^2	0.9992	0.9992
	SE[a]	0.0848	0.0824
	MAE[b]	0.0671	0.0652
	N[c]	161	161
(7)	b_2	−11.2849 ± 0.3530	−8.4356 ± 0.3347
	b_3	11.1258 ± 0.4346	8.2183 ± 0.4121
	r^2	0.9982	0.9984
	SE[a]	0.6250	0.5927
	MAE[b]	0.4895	0.4565
	N[c]	161	161

[a] Standard error of estimation. [b] Mean absolute error. [c] Number of points.

We may now, on the basis of the preceding discussion, proceed to derive an extended model which will accommodate the ln p_{sat} and $\Delta_{vap}H$ behaviour of both the saturated (a) and unsaturated (b) homologous series. A brief examination of property Q_j changes in the class-specific *Z*- and *E*-isomer series as a function of Δ indicated that the double bond does not affect Q_j in a constant manner as anticipated by almost all GA methods. Instead, the magnitude of the Δ effect varies in passing Δ from the polar to the non-polar end of the molecule. The maximum change of ln p_{sat} and $\Delta_{vap}H$ is invariably observed upon shifting Δ to the centre of the molecule. To account for this effect, we assume that the $Q_j = f(\Delta)$ dependence, whatever its exact form, can be represented as a polynomial series. Based on our previous work concerning the alkenyl acetate series,[18] the second order terms appear to be sufficient to represent the function over the whole range of unsaturation. Consequently, we suggest the simple QSPR model given in eqns. (6) and (7). In

$$\ln p_{sat} = 15.3302 - 1.1320(n + I_p) + a_2\frac{\Delta}{n-2} + a_3\left(\frac{\Delta}{n-2}\right)^2 \qquad (6)$$

$$\Delta_{vap}H = 6.6572 + 4.9946(n + I_{\Delta H}) + b_2\frac{\Delta}{n-2} + b_3\left(\frac{\Delta}{n-2}\right)^2 \qquad (7)$$

these equations, the properties of the alkenyl position isomers are correlated as perturbations of those of the corresponding saturated compounds. The last two terms in eqns. (6) and (7) may be considered as a measure of the double bond position effect. The equations are proposed to be valid for n = 10–18 and $\Delta \leqslant n - 2$ with $\Delta \neq 1$. The latter, apparently arbitrary, selection of data can be substantiated by the fact that the isomers with $\Delta = 1$ and $\Delta = n - 1$ represent limiting molecular structures with the double bond placed at the end of the chain and they do contain information which is not well-represented by the majority of data in our study. Moreover, such isomers do not occur at significant levels in lepidopteran pheromone mixtures. For saturated compounds ($\Delta = 0$), eqns. (6) and (7) reduce to eqns. (4) and (5), respectively. A factor $1/(n - 2)$ appearing in the equations may be interpreted as a normalizing factor serving to make the term involving Δ almost independent of molecular weight for a particular isomeric change.

The regression coefficients of eqns. (6) and (7) and their asymptotic standard errors are shown in Table 3 separately for *Z*- and *E*-isomers for a total of 134 unsaturated and 27 saturated compounds in each isomer series. Since all the three

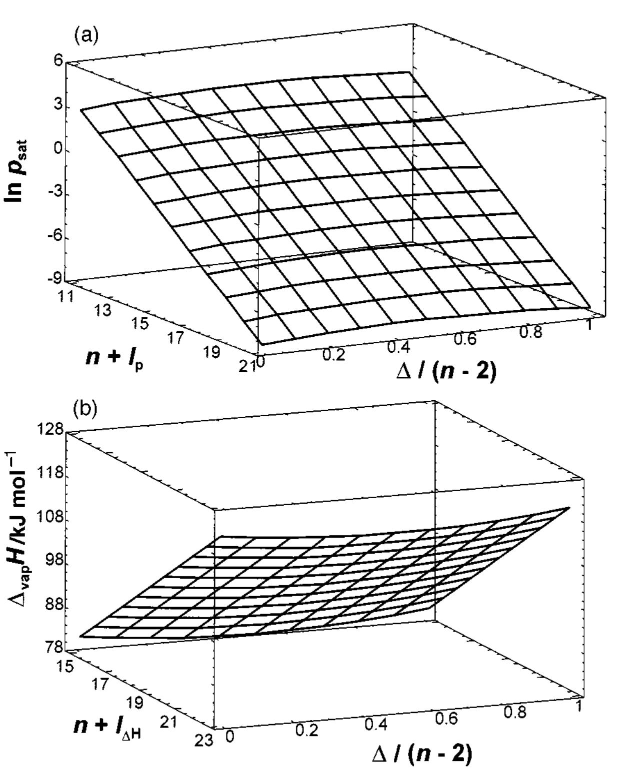

Fig. 4 Fitted polynomial response surface representing (a) eqn. (6) (*Z*-isomer series); (b) eqn. (7) (*Z*-isomer series)

independent variables were found to be significant at the $p < 0.001$ significance level, the fitted surface of the models is worthy of interpretation. Prior to accepting these results, eqns. (6) and (7) were subjected to an additional statistical validation, *i.e.* all coefficients of these equations including those of the *n*-alkane series were kept variable and were optimized by a multiple linear regression procedure. The fact that neither the quality of the model nor its coefficients changed significantly (within the 95% confidence interval) strongly supports our QSPR model given by eqns. (6) and (7) and the rationale behind its development. To visualize the descriptor effects, the fitted polynomial response surfaces for the *Z*-isomer series are illustrated in Fig. 4(a) and (b) (similar plots can be drawn for the *E*-isomer series). The linear effect of $(n + I)$ on $\ln p_{sat}$ and $\Delta_{vap}H$ is shown by the slope in the direction of chain length increase. In contrast, the non-linear effect of Δ is demonstrated by a parabolic dependence with the extreme at about $\Delta/(n - 2) \cong 0.5$.

Inspection of Table 3 reveals that for vapour pressures [eqn. (6)] the standard error of the estimate is 0.085 (*Z*-isomer series) and 0.082 (*E*-isomer series) ln units. Consequently, the vapour pressure p_{sat} can be estimated to within an accuracy of a factor of about $e^{0.085}$ or 1.09. Of a total 295 compounds correlated in both isomer series, 5 compounds exhibited deviations between 20–27% of the experimental vapour pressure value, 65 compounds had deviations between 10–20% while the remainder showed deviations of <10%. While we hesitate to draw conclusions concerning outlier trends since most of the substantial differences seem to develop rather suddenly along the series, it was interesting to note that at very low pressures, in some cases our model slightly underestimates the reported or extrapolated experimental vapour pressures; however, these data points are not as accurate as higher pressure values. A certain disparity between the results of the model and the experimental data also occurs for some Δ-3 alcohols (*e.g. E*3-14:OH, *E*3-16:OH, *E*3-18:OH), as the calculated vapour pressure values are too small. Until more detailed treatments of this effect become available, we tentatively assume that intramolecular interactions between the double bond and the OH function might be responsible for this behaviour. Taking into account that (i) the error in the experimental vapour pressure measurement is at best 6% but may be much larger for low vapour pressure compounds[47] (for example, the estimated repeatability of the gas saturation method is 10–30%[10]), and (ii) reports in the literature indicate that a factor error of 1.6 for GA estimation methods is still considered acceptable,[40] the assessment of the overall value of the present results shows the model to be highly viable.

For heats of vaporization [eqn. (7)], the standard error of estimate amounts to 0.62 (*Z*-isomers) and 0.59 (*E*-isomers) kJ mol^{-1}. The mean absolute deviation of the 295 compounds used in the correlation was 0.51%, with 38 compounds exhibiting deviations 1–1.8% and the remainder <1%.

As a final validation of our model, the results based on eqns. (6) and (7) should be compared with independent experimental data that were not used in the generation of the model. For unsaturated compounds in the range of $10 < n < 18$, however, the only suitable p_{sat} and $\Delta_{vap}H$ data we could locate in the literature were those for *Z*7-12:Ac (0.326 Pa, 77.5 kJ mol^{-1}) and *Z*9-14:Ac (0.0490 Pa, 90.00 kJ mol^{-1}).[14] Compared to our predictions based on eqns. (6) and (7), *i.e.* 0.368 Pa and 79.25 kJ mol^{-1} for *Z*7-12:Ac, and 0.0368 Pa and 89.94 kJ mol^{-1} for *Z*9-14:Ac, the agreement is quite impressive, perhaps with the exception of the vapour pressure values for *Z*9-14:Ac where the deviation reaches about 24.8%. An independent GC-based value of $\Delta_{vap}H$ (106.82 ± 1.0 kJ mol^{-1}) was also found in the literature[48] for methyl (*Z*)-octadec-9-enoate. This value agrees to within 2.7% with our $\Delta_{vap}H$ value for the corresponding *Z*8-17:Ac (103.82 kJ mol^{-1}).

Conclusions

This work establishes the first successful modelling of the vaporization properties of diverse *n*-alkenyl compounds. A model has been developed for predicting the vapour pressures and heats of vaporization of (un)saturated C_{10}–C_{18} aldehydes, alcohols and acetates at 25 °C. Besides the ECN number characterizing the functional group, the model requires only the number of carbon atoms and the position of the double bond in the chain to be known. Although there are several approximations inherent in the model [*e.g.* an assumption of the constant methylene group contribution to the property for differently functionalised series, or representation of the true $Q_j = f(\Delta)$ function by a polynomial], the correlations obtained with this model enable the calculation of properties with an acceptable accuracy. Overall, with the three empirical descriptors, the model explains over 99.8% of the variance in the data, with the mean absolute deviations for vapour pressures and heats of vaporization of 6.6 and 0.51%, respectively. Considering the accuracy and reproducibility of other methods, as well as the fact that the correlations were applied over a range of vapour pressures that covers over five orders of magnitude, the errors in results provided by the model appear to be close to experimental uncertainty. Although this investigation has been limited to only three classes of compounds, the results strongly suggest that the general forms of eqns. (6) and (7) should be applicable to other homologous series and types of compounds.

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References

1 K. Mori, *The Total Synthesis of Natural Products*, ed. J. W. ApSimon, Wiley, New York, 1992, vol. 9.
2 *Insect Pheromone Research. New Directions*, eds. R. T. Cardé and A. K. Minks, Chapman & Hall, New York, 1997.
3 *Pheromone Biochemistry*, eds. G. D. Prestwich and G. J. Blomquist, Academic Press, New York, 1987.

4 (*a*) *Behavior-Modifying Chemicals for Insect Management. Applications of Pheromones and Other Attractants*, eds. R. L. Ridgway, R. M. Silverstein and M. N. Inscoe, Marcel Dekker, New York, 1990; M. S. Mayer and J. R. McLaughlin, *Handbook of Insect Pheromones and Sex Attractants*, CRC Press, Boca Raton, 1991.

5 R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 4th edn., 1987.

6 T. Liljefors, B. Thelin, J. N. C. Van der Pers and C. Lofstedt, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1957; M. Bengtsson, T. Liljefors, B. S. Hansson, C. Lofstedt and S. V. Copaja, *J. Chem. Ecol.*, 1990, **16**, 667; M. Hoskovec, B. Kalinová, K. Konečný, B. Koutek and J. Vrkoč, *J. Chem. Ecol.*, 1993, **19**, 735; M. Hoskovec, O. Hovorka, B. Kalinová, B. Koutek, L. Streinz, A. Svatoš, P. Šebek, D. Šaman and J. Vrkoč, *Bioorg. Med. Chem.*, 1996, **4**, 479.

7 Y. Hirooka and M. Suwanai, *Appl. Entomol. Zool.*, 1978, **13**, 38; R. R. Heath, P. E. A. Teal, J. H. Tumlinson and L. J. Mengelkoch, *J. Chem. Ecol.*, 1986, **12**, 2133.

8 W. F. Spencer and M. M. Cliath, *Residue Rev.*, 1983, **85**, 57.

9 (*a*) K. Růžička and V. Majer, *J. Phys. Chem. Ref. Data*, 1994, **23**, 1; (*b*) K. Růžička and V. Majer, *AIChE J.*, 1996, **42**, 1723.

10 S. F. Donovan, *J. Chromatogr. A*, 1996, **749**, 123.

11 T. F. Bidleman, *Anal. Chem.*, 1984, **56**, 2490; D. A. Hinckley, T. F. Bidleman, W. T. Foreman and J. R. Tuschall, *J. Chem. Eng. Data*, 1990, **35**, 232; W. Spieksma, R. Luijk and H. A. J. Govers, *J. Chromatogr. A*, 1994, **672**, 141.

12 Y.-H. Kim, J. E. Woodrow and J. N. Seiber, *J. Chromatogr.*, 1984, **314**, 37; B. D. Eitzer and R. A. Hites, *Environ. Sci. Technol.*, 1988, **22**, 1362; D. W. Hawker, *Chemosphere*, 1992, **25**, 427; H.-W. Kuo, J.-D. Wang and J.-M. Lin, *Chemosphere*, 1992, **24**, 1679; P. M. Sherblom, P. M. Gschwend and R. P. Eganhouse, *J. Chem. Eng. Data*, 1992, **37**, 394; R. C. Fischer, R. Wittlinger and K. Ballschmiter, *Fresenius' J. Anal. Chem.*, 1992, **342**, 421; A. G. Van Haelst, F. W. M. Vanderwielen and H. A. J. Govers, *J. Chromatogr. A*, 1996, **727**, 265.

13 A. D. Sitte, *J. Phys. Chem. Ref. Data*, 1997, **26**, 157.

14 A. M. Olsson, J. A. Jonson, B. Thelin and T. Liljefors, *J. Chem. Ecol.*, 1983, **9**, 375.

15 R. R. Heath and J. H. Tumlinson, *J. Chem. Ecol.*, 1986, **12**, 2081.

16 B. Koutek, M. Hoskovec, P. Vrkočová, K. Konečný and L. Feltl, *J. Chromatogr. A*, 1994, **679**, 307.

17 B. Koutek, M. Hoskovec, P. Vrkočová, K. Konečný and L. Feltl, *J. Chromatogr. A*, 1996, **719**, 391.

18 B. Koutek, M. Hoskovec, P. Vrkočová and L. Feltl, *J. Chromatogr. A*, 1997, **759**, 93.

19 (*a*) V. Majer, V. Svoboda and J. Pick, *Heats of Vaporization of Fluids*, Academia, Praha, 1989; (*b*) V. Majer and V. Svoboda, *Enthalpies of Vaporization of Organic Compounds*, Blackwell, Boston, 1985.

20 *Handbook of Chemical Property Estimation Methods*, eds. W. J. Lyman, W. F. Reehl and D. H. Rosenblatt, American Chemical Society, Washington, DC, 1990.

21 A. R. Katritzky, V. S. Lobanov and M. Karelson, *Chem. Soc. Rev.*, 1995, 279.

22 M. Chastrette, D. Cretin and F. Tiyal, *C.R. Acad. Sci. Paris*, *Ser. II*, 1995, **318**, 1059; S. C. Basak, B. D. Gute and G. D. Grunwald, *J. Chem. Inf. Comput. Sci.*, 1997, **37**, 651.

23 R. Kühne, R. U. Ebert and G. Schüürmann, *Chemosphere*, 1997, **34**, 671.

24 T. Jensen, A. Fredenslund and P. Rasmussen, *Ind. Eng. Chem. Fundam.*, 1981, **20**, 239; J. Gmehling, D. Tiegs and U. Knipp, *Fluid Phase Equilib.*, 1990, **54**, 147.

25 B. Willman and A. S. Teja, *Ind. Eng. Chem. Process Des. Dev.*, 1985, **24**, 1033.

26 K. Růžička, unpublished results, see also ref. 9*b*.

27 E. F. Meyer, M. J. Awe and R. E. Wagner, *J. Chem. Eng. Data*, 1980, **25**, 371.

28 G. N. Djakova, G. L. Korichev, A. D. Korkhov, T. F. Vasiljeva and I. A. Vasiljev, *Zh. Prikl. Khim.*, 1981, **54**, 1644.

29 D. Ambrose, J. H. Ellender and C. H. S. Sprake, *J. Chem. Thermodyn.*, 1974, **6**, 909.

30 J. N'Guimbi, H. Kaseghari, I. Mokbel and J. Jose, *Thermochim. Acta*, 1992, **196**, 367.

31 D. Ambrose and J. Walton, *Pure Appl. Chem.*, 1989, **61**, 1395.

32 J. W. Shigley, C. W. Bonhorst, C. C. Liang, P. M. Althouse and H. O. Triebold, *J. Am. Oil Chem. Soc.*, 1955, **32**, 213.

33 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, 77th edn., 1996–1997.

34 D. Mackay, A. Bobra, D. W. Chan and W. Y. Shin, *Environ. Sci. Technol.*, 1982, **16**, 645.

35 M. Mansson, P. Sellers, G. Stridh and S. Sunner, *J. Chem. Thermodyn.*, 1977, **9**, 91.

36 C. H. Fisher, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1101.

37 S. W. Benson, *J. Am. Chem. Soc.*, 1996, **118**, 10 645.

38 J. D. Chase, *Chem. Eng. Prog.*, 1984, **80**, 63.

39 S. E. Stein, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1457.

40 J. S. Chickos, S. Hosseini and J. F. Liebman, *J. Org. Chem.*, 1993, **58**, 5345.

41 K. Nass, D. Lenoir and A. Kettrup, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1735.

42 C.-H. Tu, *Fluid Phase Equilib.*, 1994, **99**, 105.

43 M. Ducros, J. F. Greison, H. Sannier and I. Velasco, *Thermochim. Acta*, 1981, **44**, 134.

44 J. S. Chickos, D. G. Hesse, J. F. Liebman and S. Panshin, *J. Org. Chem.*, 1988, **53**, 3424.

45 R. L. Cardozo, *AIChE J.*, 1991, **37**, 290.

46 H. B. Krop, M. J. M. van Velzen, J. R. Parsons and H. A. J. Govers, *J. Am. Oil Chem. Soc.*, 1997, **74**, 309.

47 N. N. Nirmalkhandan and R. E. Speece, *Environ. Sci. Technol.*, 1988, **22**, 1349.

48 R. Fuchs and L. A. Peacock, *Can. J. Chem.*, 1980, **58**, 2796.

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