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Gas chromatographic determination of vapour pressures of pheromone-like compounds IV[1]. Acetates, a reinvestigation

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Abstract

The equilibrium vapour pressures P and enthalpies of vaporization ΔH for an acetate series with carbon numbers varying from 10 to 18 were determined using a GC technique. The P and ΔH quantities at 298.15 K were calculated for more than 100 (un)saturated linear-chain compounds based on the experimental retention time measurements of the test acetates and five reference alkane standards with known vapour pressures. The advantage of utilizing several standards in the GC based vapour pressure determinations was demonstrated by comparison with previously published data. Additionally, empirical equations were developed for correlating ln P and ΔH with the number of carbon atoms (N) and double bond positions (Δ) in the chain. It was shown that with these two-parameter equations the vapour pressures of acetates can be predicted with a considerable degree of confidence. In the case of $E2$-, $E3$- and $Z4$-alkenyl acetate isomers, however, anomalies in retention time/vapour pressure–structure relationships were observed, indicating specific types of polar interactions.

Keywords: Vapour pressure; Thermodynamic parameters; Acetates; Pheromones

1. Introduction

Saturated vapour pressures belong to the most important thermochemical properties of pure fluids. The success of numerous separation techniques depends on differences in the magnitude of this property, and also theories designed to model transport rate data in the environment require vapour pressure information [1,2]. In spite of these interests, direct measurements of vapour pressures of higher boiling substances have been limited to a relatively small number of compounds and, moreover, due to experimental difficulties in the low pressure region ($P<1$ kPa), some of these measurements are of doubtful accuracy.

The potential use of gas chromatographic (GC) retention data for calculating vapour pressures has been recognized by several authors [3–5]. Two different approaches have been employed to treat the retention time/volume–vapour pressure relationship. One [6,7] uses the substance of interest as the stationary phase (inverse GC), whereas the other [8–10] makes use of normal capillary GC retention

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[1] For part III, see Ref. [16].

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behaviour of the analyte on a nonpolar phase, and a reference compound whose vapour pressure is known. The test compound's vapour pressure is determined from changes in the relative retention time with temperature and the known vapour pressure of the reference compound at the pertinent temperatures. A major advantage of this approach is that it relies on relatively simple expressions that can be used for estimating vapour pressures for large classes of compounds and requires a minute sample size. The latter technique has been successfully used for vapour pressure determinations of some herbicides, pesticides and other environmental pollutants [11–13]. In an initial study using a testing set of pheromone-like acetates we found [14] that this procedure can provide vapour pressures that differ from the literature values by about ±10%. Recently, using this approach, we have obtained vapour pressures of pheromone-like alcohols [15] and aldehydes [16].

As a part of our research program focused on the study of the vaporization process of pheromone-like compounds [14–18], determinations of the vapour pressures of pheromone-like acetates have been made in this work. The principle objective of the work was to provide vapour pressures and heats of vaporization for about 100 linear (un)saturated acetates differing in chain length, as well as in the position of (*E*)- or (*Z*)-configurated double bonds. The results should considerably extend the database for the vapour pressures of long-chain (C_{10} to C_{18}) acetates, and allow us to evaluate the effect of structural changes on the values of vapour pressures for this class of compounds. A new GC assembly with accurately adjustable temperature and gas flow parameters was used to assure a maximum precision and reproducibility of the retention time measurements. Using this new assembly, redeterminations have been carried out for some of the acetates studied previously [14].

2. Experimental

2.1. Chromatography

The retention times of acetate samples were determined using a Hewlett-Packard HP 6890 gas chromatograph equipped with a flame ionization detector (FID), electronic pneumatic control (EPC), split injection port, HP 6890 automatic injector and HP Vectra VL 2 PC with ChemStation software. Test and reference compounds were chromatographed on polydimethylsiloxane bonded-phase fused-silica capillary column (HP-1, film thickness 0.52 μm, 4 m×310 μm I.D.) in the split mode with the split ratio set at 50:1. The length of the column employed is a compromise between the need for acceptable resolution, and the need to avoid prohibitively long retention times, particularly at lower temperatures. The gas chromatograph was operated isothermally with a helium flow-rate 10.3 ml min^{-1} (EPC) at 5°C intervals in the range 40–165°C as specified. *n*-Dodecane, *n*-tetradecane, *n*-hexadecane, *n*-octadecane and *n*-eicosane were used as internal reference standards. Adjusted retention times were calculated by subtracting the retention time of methane from the retention time of the chemical. All retention times of acetates used for vapour pressure determination were the means of at least three separate runs (R.S.D.<0.035%).

2.2. Chemicals

The acetates were either obtained from the Research Institute for Plant Protection (IPO-DLO, Wageningen, Netherlands) and used as received, or synthesized from the corresponding alcohols in our laboratory. In the latter instance, the purity of the chemicals was at least 97% as determined by capillary GC. A condensed nomenclature was used for *n*-alkyl and *n*-alkenyl acetates. Any unsaturation in the main chain is indicated by the geometry *Z* or *E* followed by its position and separated from the number of carbon atoms in the chain by a hyphen; the acetate group is abbreviated Ac. For example, Z7–12:Ac denotes the (Z)-7-dodecenyl acetate.

2.3. Data treatment

Vapour pressure of an unknown acetate was calculated by the Hamilton method [4] using several alkanes as reference compounds. The calculation starts with adjusted retention time (t') measurements for the unknown (T) and reference (R) compound at ten GC temperatures. Using the equation

$$\ln\frac{t'_T}{t'_R} = (1 - \frac{\Delta H_T}{\Delta H_R}) \ln P_R + C \quad (1)$$

where ΔH is the latent heat of vaporization and C is a constant, values of $1-\Delta H_T/\Delta H_R$ and C are obtained from the regression. Then, using the relationship

$$\ln P_T = \frac{\Delta H_T}{\Delta H_R} \ln P_R + C \quad (2)$$

the vapour pressure P for the unknown can be calculated at any temperature for which a value of P for the reference is available.

For *n*-dodecane, *n*-tetradecane, *n*-hexadecane, *n*-octadecane and *n*-eicosane that were selected as reference standards in this work, the vapour pressures between the triple and normal boiling point temperatures were found [19] to fit the Cox equation

$$\ln(\frac{P}{P_0})(\text{kPa}) = (1 - \frac{T_0}{T})\exp(A_0 + A_1 T + A_2 T^2) \quad (3)$$

with parameters as follows: *n*-dodecane, $A_0 = 3.05854$, $A_1 = -2.018454 \cdot 10^{-3}$, $A_2 = 1.606849 \cdot 10^{-6}$ and $T_0 = 489.438$ K; *n*-tetradecane, $A_0 = 3.13624$, $A_1 = -2.063853 \cdot 10^{-3}$, $A_2 = 1.541507 \cdot 10^{-6}$ and $T_0 = 526.691$ K; *n*-hexadecane, $A_0 = 3.18271$, $A_1 = -2.002545 \cdot 10^{-3}$, $A_2 = 1.384476 \cdot 10^{-6}$ and $T_0 = 559.978$ K; *n*-octadecane, $A_0 = 3.24741$, $A_1 = -2.048039 \cdot 10^{-3}$, $A_2 = 1.362445 \cdot 10^{-6}$ and $T_0 = 590.023$ K; *n*-eicosane, $A_0 = 3.31181$, $A_1 = -2.102218 \cdot 10^{-3}$, $A_2 = 1.348780 \cdot 10^{-6}$ and $T_0 = 617.415$ K; for all compounds $P_0 = 101.325$ kPa. These parameters were used to interpolate vapour pressure values at the temperatures selected to develop the $P-T$ relationship. Note that the vapour pressures of *n*-octadecane and *n*-eicosane (m.p. 28.2°C and 36.8°C, respectively) at 25°C correspond to the subcooled liquid state.

The enthalpies of vaporization of acetates at 298.15 K (kJ mol^{-1}) were calculated from the slopes of Eq. (2) by utilizing the recommended values [19] for our reference standards (*n*-dodecane: 61.52, *n*-tetradecane: 71.73, *n*-hexadecane: 81.35, *n*-octadecane: 91.44, and *n*-eicosane: 101.81).

The statistical analyses were conducted by using Statgraphics Plus 7.0 software package (Manugistic, Rockville, MD, USA).

3. Results and discussion

Several previous investigations demonstrated that the accuracy of the GC method depends to a large extent on three factors: (i) the accuracy of the vapour pressure value for the reference compound, (ii) the proper use of a reference compound with retention characteristics differing only slightly from the substrate, and (iii) the similarity in activity coefficients of the reference standard and test compound.

Compared to our previous work concerning acetates [14], we have particularly addressed the first two points in this study to improving the GC method. The important changes were as follows: firstly, we used newly recommended accurate vapour pressure data of alkane standards [19]. These data are now available for a temperature range between the triple point and normal boiling point and they may be regarded as mutually consistent over the whole (up to $N = 20$) homologous series. Secondly, by taking advantage of this consistency, we used five alkanes as reference compounds. In doing this, we expected that the variations in activity coefficients with the length of the chain for test compounds were similar to those of standards. Thirdly, ten temperatures instead of five were used with 5°C differences to obtain relative retention vs. temperature relationships; a new Hewlett-Packard HP 6980 gas chromatographic system was used for more accurate and reproducible measurements.

Unfortunately, it was not possible to address point (iii) since the accurate vapour pressure data of acetates (which would be the best reference compounds) were not available and alkanes had to be used instead. Note that the acetates belong to only slightly polar compounds and, therefore, large differences in activity coefficients between acetates and alkanes cannot be expected. Furthermore, longer carbon chain lengths in our series ($N > 10$) might increase the nonpolar nature of the molecule and bring its γ still closer to those of the alkane standards. However the only way to check the importance of this simplification would be to com-

pare the GC-based vapour pressures with those obtained by the more elaborate methods.

3.1. Vapour pressures of saturated acetates

Since the data from direct measurements are too fragmentary to provide sole basis for reasonable comparisons, our criteria for assessing accuracy included: (i) linearity of $\ln P$ and ΔH with homologue chain length (expressed by the number of carbon atom, N, in the alkyl chain), (ii) observing whether the slopes a_1, and b_1, in Eq. (4) and Eq. (5) resemble the proposed proper slopes of about -1.06 to -1.12 ln units [20] and 4.5–5.0 kJ mol^{-1} [21,22], respectively, and (iii) ascertaining how well the data determined in this work agree with those reported in literature.

$$\ln P\,(\mathrm{Pa}) = a_0 + a_1 N \tag{4}$$

$$\Delta H\,(\mathrm{kJ\ mol^{-1}}) = b_0 + b_1 N \tag{5}$$

The adjusted mean relative retention times for the saturated acetates at temperatures ranging from 40 to 165°C are presented in Table 1, and vapour pressures P and heats of vaporization ΔH in Table 2. Included in Table 2 are also vapour pressures of acetates determined in earlier investigations. However, only three of these investigations deal with the direct measurements, using either the restricted gas flow [23] or gas saturation [24,25] techniques. The other approaches that have been utilized were (i) the GC method using a liquid crystal stationary phase [26,27], (ii) the GC method making use the substance under study as the stationary phase [6], and (iii) the estimative method based on the corresponding state equation of Lee and Kessler [17]. Since the vapour pressures determined by the approaches (i)–(iii) are of an uncertain accuracy, they are presented only for completeness. The same holds true for the data of [23] that have been measured at higher (by about 60°C) temperature ranges and had to be extrapolated to 25°C by fitting the Antoine equation. The most reliable vapour pressure data of saturated acetates up to $N=10$ are apparently those reported in [25]. Although even these data include an extrapolation, this extrapolation has been based on the Cox equation which is generally recognized to allow extrapolation to low temperatures for about 150 K with fair confidence.

A comparison between the vapour pressures determined here and those reported in [25] shows (Fig. 1) that the trend with carbon number of our data is in accord with that observed for lower acetate homologues. The correlation equation corresponding to the linear least squares curve fit for our data and [25] data taken together is:

Table 1
GC relative retention times of n-alkyl acetates

Compound	Relative retention time									
	40°C	45°C	50°C	55°C	60°C	65°C	70°C	75°C	80°C	85°C
9:Ac[a]	2.429	2.349	2.278	2.212	2.150	2.099	2.047	2.000	1.950	1.908
10:Ac[a]	5.918	5.571	5.265	4.983	4.729	4.508	4.302	4.110	3.934	3.773
	60°C	65°C	70°C	75°C	80°C	85°C	90°C	95°C	100°C	105°C
11:Ac[b]	2.142	2.087	2.035	1.987	1.941	1.899	1.859	1.827	1.793	1.758
12:Ac[b]	4.692	4.468	4.261	4.071	3.895	3.736	3.586	3.459	3.332	3.218
	80°C	85°C	90°C	95C°	100°C	105°C	110°C	115°C	120°C	125°C
13:Ac[c]	1.938	1.896	1.857	1.821	1.786	1.754	1.723	1.693	1.670	1.645
14:Ac[c]	3.871	3.714	3.569	3.435	3.308	1.194	3.084	2.984	2.898	2.812
	100°C	105°C	110°C	115°C	120°C	125°C	130°C	135°C	140°C	145°C
16:Ac[d]	3.290	3.175	3.071	2.973	2.881	2.793	2.713	2.637	2.570	2.505
	120°C	125°C	130°C	135°C	140°C	145°C	150°C	155°C	160°C	165°C
18:Ac[e]	2.857	2.773	2.694	2.621	2.551	2.485	2.423	2.363	2.312	2.260

[a] Standard n-dodecane; [b] Standard n-tetradecane; [c] Standard n-hexadecane; [d] Standard n-octadecane; [e] Standard n-eicosane.

Table 2
Vapour pressures and heats of vaporization for *n*-alkyl acetates at 25°C

Compound	P (Pa)				ΔH (kJ mol^{-1})			
	Eq. (2)	Eq. (6)	[25]	Other sources	Eq. (7)	Eq. (9)	[30,31]	Other sources
4:Ac	–	1532.8	1506.5		(42.38)[a]	–	42.24	42.71[g]
6:Ac	–	171.8	166.7	164.1[b]; 182.8[c]	(52.06)[a]	–	52.12	52.81[g]
7:Ac	–	57.5	55.4		(56.90)[a]	–	57.06	56.01[g]
8:Ac	–	(19.25)[a]	(18.52)[a]	19.03[b]; 23.83[c]	(61.74)[a]	–	62.00	
9:Ac	6.729	6.443	(6.169)[a]	5.13[d]	66.78	67.01	66.94	
10:Ac	2.531	2.157	2.06	2.27[b]; 2.89[c]; 2.18[c]; 2.26[f]	71.37	71.56	71.88	72.00[f]
11:Ac	0.686	0.722	–		76.75	77.20	76.82	
12:Ac	0.259	0.242	–	0.28[b]; 0.265[d]; 0.279[e]	81.36	81.83	81.76	
13:Ac	0.0738	0.0810	–		86.17	87.15	86.70	
14:Ac	0.0280	0.0271	–	0.0781[d]; 0.0201[e]	90.75	91.73	91.64	
16:Ac	0.00301	0.00303	–	0.0407[d]	100.63	102.33	101.52	
18:Ac	0.000332	0.000340	–		110.84	113.51	111.40	

[a] Interpolated or extrapolated values; [b] [17]; [c] [23]; [d] [24]; [e] [14]; [f] [6]; [g] [32].

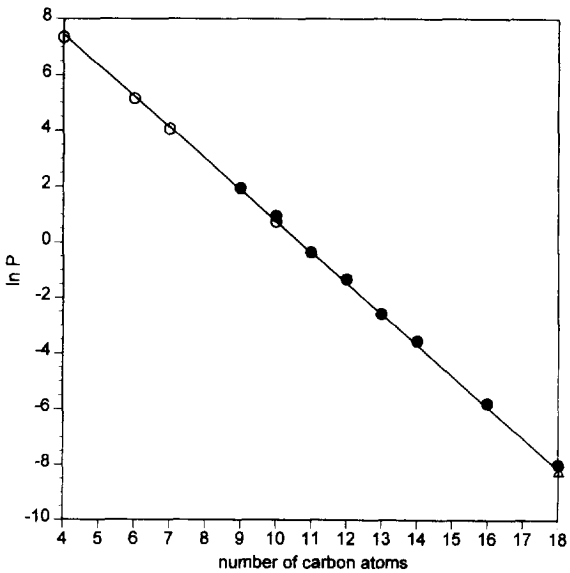

Fig. 1. Scatter plot of the present GC-based (Eq. (2)) and literature [25] gas-saturation vapour pressures of alkyl acetates at 25°C. [(●) present work; (○) Ref. [25]; (△) solid vapour pressure of octadecyl acetate (m.p. = 34.5°C) based on the fugacity ratio correction (see Ref. [15])]. The line corresponds to Eq. (6).

$$\ln P\ (\mathrm{Pa}) = (11.7125 \pm 0.0600) - (1.0944 \pm 0.0052)N \quad (6)$$

with $n = 12$, $r = 0.9998$ and the standard error of the estimate SE = 0.0706. According to Eq. (6), the addition of one methylene unit reduces the vapour pressure 2.987 times. This factor is similar to the factor 2.8 previously estimated for lower acetate homologues up to pentyl acetate [28].

Taken separately, our data and Ref. [25] data afford a similarly close correlation ($r > 0.999$) with intercepts, (11.8707±0.1251) vs. (11.7115±0.0058), as well as slopes (1.1054±0.0090) vs. (1.0991±0.0008), varying only slightly (by max. 1.35%) around the corresponding values given in Eq. (6). It is noticeable that the vapour pressure predicted by Eq. (6) for 4:Ac (1532.8 Pa) compared favourably (within 1.7%) with the value 1506.5 Pa obtained [25] for this compound from the independent measurements.

The enthalpies of vaporization obtained from the slopes of Eq. (2) (Table 2) can be represented by the equation

$$\Delta H\ (\mathrm{kJ\ mol^{-1}}) = (23.022 \pm 0.357) + (4.840 \pm 0.027)N \quad (7)$$

with $n = 8$, $r = 0.9998$ and the standard error of the estimate SE = 0.218.

The slope can be identified with the methylene group contribution to the molar enthalpy of vaporization, and the intercept with the enthalpy of vaporization of the parent compound. The identification of the intercept with the enthalpy of vaporization of our parent compound, i.e., acetic acid ($\Delta H = 23.36$ kJ mol^{-1} [29]), seems to be very nearly justified. Also, considering that the homologous series of alkanes exhibit the largest -CH_2- contribution of ca. 5.0 kJ mol^{-1}, our methylene group contribution of 4.84 kJ mol^{-1} appears to be acceptable taking into account the presence of an electronegative oxygen atom attached to the carbon chain (cf. [22]). As can be also seen from Table 2, the ΔH values determined in this work are in excellent agreement (within 1.0%) with those based on a group contribution method which consists of adding the contributions of the methyl (4.71), methylene (4.94), and ester (18.0) groups [30,31].

Table 3
Parameters of the Antoine equation for *n*-alkyl acetates

Compound	ln P (Pa) = $A - B/(C + T(\mathrm{K}))$			r^2	Validity range (°C)
	A	B	C		
9:Ac	22.892±0.044	4857.4±23.0	−66.690±0.613	1.000000	25–85
10:Ac	23.357±0.049	5191.8±25.7	−66.677±0.631	1.000000	25–85
11:Ac	23.313±0.045	5372.8±23.6	−71.355±0.572	0.999999	25–105
12:Ac	23.764±0.047	5697.3±24.8	−71.308±0.568	0.999999	25–105
13:Ac	23.684±0.096	5861.9±51.2	−75.182±1.141	0.999998	25–125
14:Ac	24.148±0.045	6192.8±24.0	−74.778±0.507	1.000000	25–125
16:Ac	24.407±0.047	6592.8±25.2	−79.941±0.500	1.000000	25–145
18:Ac	24.624±0.048	6947.3±26.1	−85.469±0.491	1.000000	25–165

For each compound, our GC vapour pressures were fitted with Antoine equation:

$$\ln P\,(\mathrm{Pa}) = A + B/(T + C) \quad (8)$$

A Statgraphic routine for the non-linear Marquart regression was used to determine the coefficients A, B and C (Table 3). From the constants B and C the temperature dependence of the vaporization enthalpy of each compound was calculated according to the equation

$$\Delta H\ (\mathrm{kJ\ mol^{-1}}) = (BR/1000)[T/(T + C)]^2 \quad (9)$$

where R is the gas constant (8.31441 J $\mathrm{mol^{-1}\ K^{-1}}$)

The enthalpy values so obtained for $T = 298.15$ K are also reported in Table 2.

3.2. Vapour pressures of unsaturated acetates

The relative retention times measured for C_{10}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16} and C_{18} monoenic acetates at ten temperatures are listed in Tables 4–10 along with the corresponding vapour pressures and heats of vaporization calculated for 25°C. When analyzing the tabulated results with respect to the vapour pressures, it may be observed that, as expected, they reflect the position of the double bond, the geometrical arrangement and the length of the carbon chain. Several trends are apparent.

3.2.1. Effects of double bond position

The position of the double bond affects the vapour pressures of alkenyl acetates in a similar manner as found in alcohols [15] and aldehydes [16]. Its position relative to both the polar (Δ-unsaturation) and nonpolar (ω-unsaturation, $\omega = N - \Delta$) end of the molecule is significant. Almost all alkenyl acetates exhibit greater vapour pressures than their saturated equivalents. The ω-2 unsaturated compounds (e.g., 8-10:Ac, 10-12:Ac and 12-14:Ac) behave anomalously, exhibiting either nearly the same (E-isomers) or lower (Z-isomers) vapour pressures than saturated compounds. In an effort to better understand the controlling force(s) behind the influence of Δ on P, we tried to describe the dependence more quantitatively using a series $P(\Delta) = a + b(\Delta) + c(\Delta)^2 + \ldots$, where the expansion is about an operating unsaturation, Δ. We assumed that second order terms are sufficient to represent the function over the experimental range of double bond positions. That is, we proposed a relationship of the form

$$\ln P = c_0 + c_1(\Delta) + c_2(\Delta)^2 \quad (10)$$

The agreement between the experimental and the calculated (solid lines) values based on Eq. (10) is illustrated in Figs. 2 and 3 for (Z/E)Δ-12:Ac and (Z/E)Δ-14:Ac. Although the juxtaposition of data points and calculated lines attest to a reasonable correlation (Table 11) in all acetate series, the regularity of these dependencies is significantly disrupted for E2-, E3- and Z4-isomers. While for E3- and Z4-isomers the experimental vapour pressures are greater than predicted by Eq. (10), the opposite behaviour is observed for the E2-isomers. In each series, the Z4-alkenyl acetates have the highest vapour pressures of all positional and geometrical isomers investigated. Note that the same effect as illustrated in Figs. 2 and 3 for C_{12} and C_{14}-alkenyl acetates may be invariably observed for the remaining subseries with all curves closely resembling those shown in the figures. On insertion of ΔH as a dependent variable into Eq. (10), analogous results were obtained in assessments of the dependence of ΔH on Δ. The curves, however, become shaped reversely. This effect appears to be characteristic for all alkenyl acetate subseries.

The largest vapour pressure of Z4-10:Ac out of the Δ-10:Ac series isomers has also been reported by Olsson et al. [6]. On the basis of models generated by a computer, the authors argued that Z4-10:Ac (folded form) is the most symmetrical compound of all Δ-10:Ac with respect to the double bond position. Accordingly, it should possess the smallest effective size and consequently a higher vapour pressure than the other decenyl acetate isomers which are effectively larger. The present data (Figs. 2 and 3) do not justify such an interpretation based on a symmetry, since the increasingly asymmetrical Z4-12:Ac, Z4-14:Ac and Z4-16:Ac isomers show the same behaviour as Z4-10:Ac.

Regardless of the ultimate explanation, the dependencies shown in Figs. 2 and 3 raise a fundamental question whether some kind of specific interactions typical for E2-, E3- and Z4- isomers may be the prerequisite of this behaviour. Two types of specific interactions are imaginable: (i) the intermolecular

Table 4
GC data and vapour pressures (25°C) of decenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	40°C	45°C	50°C	55°C	60°C	65°C	70°C	75°C	80°C	85°C	Intercept	Slope	r^2(%)		
*Z*3-10:Ac	4.6647	4.4450	4.2487	4.0535	3.8862	3.7424	3.6020	3.4665	3.3723	3.2347	2.0640	−0.12946	99.94	3.327	69.49
*E*3-10:Ac	4.9075	4.6557	4.4334	4.2269	4.0356	3.8762	3.7203	3.5720	3.4438	3.3194	2.1538	−0.13911	99.98	3.127	70.08
*Z*4-10:Ac	4.4347	4.2399	4.0622	3.8987	3.7424	3.6132	3.4873	3.3645	3.2599	3.1536	1.9812	−0.12129	99.99	3.530	68.98
*E*4-10:Ac	5.0018	4.7459	4.5182	4.3063	4.1156	3.9505	3.7920	3.6400	3.5099	3.3843	2.1727	−0.13907	99.98	3.068	70.08
*Z*5-10:Ac	4.9540	4.7322	4.5116	4.3107	4.1177	3.9550	3.8044	3.6609	3.5359	3.4192	2.1424	−0.13333	99.97	3.110	69.72
*E*5-10:Ac	5.1675	4.8892	4.6378	4.4098	4.2017	4.0253	3.8558	3.6979	3.5530	3.4222	2.2357	−0.14671	99.98	2.945	70.55
*Z*6-10:Ac	5.0935	4.8330	4.6000	4.3809	4.1852	4.0172	3.8574	3.7035	3.5665	3.4402	2.1936	−0.13973	99.98	3.011	70.12
*E*6-10:Ac	5.2603	4.9743	4.7196	4.4891	4.2781	4.0929	3.9213	3.7606	3.6170	3.4793	2.2546	−0.14699	99.98	2.892	70.56
*Z*7-10:Ac	5.5010	5.2004	4.9301	4.6849	4.4588	4.2674	4.1247	3.9137	3.7608	3.6161	2.3066	−0.14868	99.94	2.759	70.67
*E*7-10:Ac	5.5661	5.2450	4.9619	4.7054	4.4691	4.2727	4.0761	3.9003	3.7439	3.5937	2.3457	−0.15559	99.98	2.707	71.09
*Z*8-10:Ac	6.5657	6.0191	5.6814	5.3721	5.0944	4.8514	4.6226	4.4146	4.2212	4.0437	2.5146	−0.16288	99.99	2.335	71.54
*E*8-10:Ac	5.9869	5.6320	5.3160	5.0278	4.7677	4.5465	4.3318	4.1384	3.9623	3.7974	2.4450	−0.16199	99.98	2.497	71.49

[a] Standard *n*-dodecane.

Table 5
GC data and vapour pressures (25°C) of dodecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	60°C	65°C	70°C	75°C	80°C	85°C	90°C	95°C	100°C	105°C	Intercept	Slope	r^2(%)		
*Z*2-12:Ac	3.9183	3.7622	3.6181	3.4846	3.3600	3.2435	3.1326	3.0421	2.9498	2.8648	1.7606	−0.11158	99.99	0.3313	79.73
*E*2-12:Ac	4.4612	4.2576	4.0686	3.8948	3.7345	3.5887	3.4491	3.3301	3.2144	3.1077	1.9512	−0.12875	99.99	0.2766	80.97
*Z*3-12:Ac	3.7025	3.5631	3.4357	3.3146	3.2049	3.0989	2.9995	2.9168	2.8345	2.7563	1.6811	−0.10509	99.99	0.3573	79.27
*E*3-12:Ac	3.8950	3.7364	3.5906	3.4546	3.3325	3.2149	3.1055	3.0122	2.9209	2.8337	1.7596	−0.11308	99.99	0.3319	79.84
*Z*4-12:Ac	3.4874	3.3669	3.2570	3.1536	3.0580	2.9660	2.8783	2.8060	2.7346	2.6644	1.5881	−0.09574	99.99	0.3900	78.60
*E*4-12:Ac	3.9192	3.7651	3.6116	3.4765	3.3526	3.2378	3.1279	3.0363	2.9452	2.8589	1.7629	−0.11231	99.98	0.3307	79.79
*Z*5-12:Ac	3.7107	3.5716	3.4450	3.4242	3.2140	3.1077	3.0066	2.9248	2.8521	2.7777	1.6775	−0.13068	99.95	0.3583	79.17
*E*5-12:Ac	3.9506	3.7845	3.6358	3.4947	3.3673	3.2483	3.1355	3.0410	2.9465	2.8589	1.7800	−0.11498	99.98	0.3256	79.98
*Z*6-12:Ac	3.7262	3.5859	3.4570	3.3356	3.2225	3.1160	3.0180	2.9343	2.8513	2.7767	1.6869	−0.10503	99.98	0.3552	79.26
*E*6-12:Ac	3.9924	3.8273	3.6781	3.5360	3.4052	3.2845	3.1706	3.0751	2.9782	2.8907	1.7914	−0.11503	99.99	0.3219	79.98
*Z*7-12:Ac	3.9340	3.7758	3.6318	3.4980	3.3723	3.2559	3.1456	3.0549	2.9622	2.8770	1.7637	−0.11140	99.99	0.3302	79.72
*E*7-12:Ac	4.0846	3.9116	3.7525	3.6035	3.4672	3.3399	3.2203	3.1204	3.0192	2.9272	1.8272	−0.11867	99.99	0.3113	80.24
*Z*8-12:Ac	4.1609	3.9817	3.8223	3.6712	3.5335	3.4041	3.2823	3.1812	3.0819	2.9877	1.8421	−0.11785	99.98	0.3065	80.18
*E*8-12:Ac	4.1841	3.9992	3.8324	3.6766	3.5340	3.4005	3.2748	3.1697	3.0663	2.9711	1.8623	−0.12193	99.98	0.3011	80.48
*Z*9-12:Ac	4.3980	4.2017	4.0220	3.8548	3.7022	3.5587	3.4264	3.3166	3.2031	3.1010	1.9210	−0.12438	99.98	0.2843	80.65
*E*9-12:Ac	4.4204	4.2152	4.0279	3.8538	3.6951	3.5475	3.4105	3.2934	3.1793	3.0748	1.9434	−0.12931	99.98	0.2788	81.01
Z10-12:Ac	5.0725	4.8229	4.5999	4.3902	4.2015	4.0251	3.8585	3.7208	3.6007	3.4767	2.0993	−0.13482	99.95	0.2394	81.40
*E*10-12:Ac	4.7539	4.5209	4.3110	4.1144	3.9371	3.7713	3.6177	3.4880	3.3605	3.2428	2.0403	−0.13615	99.99	0.2541	81.50

[a] Standard *n*-tetradecane.

Table 6
GC data and vapour pressures (25°C) of tridecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	70°C	75°C	80°C	85°C	90°C	95°C	100°C	105°C	110°C	115°C	Intercept	Slope	r^2(%)		
*Z*7-13:Ac	3.4433	3.3244	3.214	3.1107	3.0148	2.9229	2.8384	2.7641	2.6906	2.6219	1.5642	−0.09737	99.99	0.1142	84.25
*E*7-13:Ac	3.6078	3.4724	3.3489	3.2323	3.1246	3.0229	2.9272	2.8445	2.7638	2.6870	1.6372	−0.10524	99.99	0.1057	84.85
*Z*9-13:Ac	3.7912	3.6437	3.5094	3.3849	3.2677	3.1585	3.0569	2.9678	2.8804	2.7987	1.6969	−0.10834	99.99	0.09943	85.09
*E*9-13:Ac	3.8374	3.6833	3.5412	3.4088	3.2864	3.1716	3.0646	2.9722	2.8821	2.7969	1.7248	−0.11301	99.99	0.09645	85.45
*Z*11-13:Ac	4.5522	4.3473	4.1608	3.9893	3.8292	3.6823	3.5449	3.4249	3.3099	3.2002	1.9381	−0.12573	99.99	0.07737	86.42
*E*11-13:Ac	4.2878	4.0958	3.9224	3.7594	3.6097	3.4709	3.3408	3.2284	3.1183	3.0181	1.8778	−0.12552	99.99	0.08219	86.41

[a] Standard *n*-pentadecane.

Table 7
GC data and vapour pressures (25°C) of tetradecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	80°C	85°C	90°C	95°C	100°C	105°C	110°C	115°C	120°C	125°C	Intercept	Slope	r^2(%)		
*Z*2-14:Ac	3.2960	3.1767	3.0753	2.9810	2.8912	2.8086	2.7304	2.6571	2.5937	2.5297	1.4990	−0.09500	99.98	0.0365	89.08
*E*2-14:Ac	3.6778	3.5348	3.4045	3.2821	3.1699	3.0637	2.9679	2.8743	2.7954	2.7126	1.6574	−0.10956	99.99	0.0304	90.26
*Z*3-14:Ac	3.1103	3.0146	2.9249	2.8415	2.7621	2.6879	2.6185	2.5518	2.4954	2.4378	1.4205	−0.08801	99.99	0.0399	88.51
*E*3-14:Ac	3.2535	3.1424	3.0435	2.9493	2.8604	2.7764	2.6966	2.6230	2.5596	2.4958	1.4909	−0.09583	99.98	0.0367	89.15
*Z*4-14:Ac	2.9225	2.8434	2.7676	2.6959	2.6294	2.5648	2.5038	2.4451	2.3977	2.3474	1.3304	−0.07931	99.98	0.0443	87.80
*E*4-14:Ac	3.2488	3.1432	3.0437	2.9518	2.8647	2.7829	2.7054	2.6307	2.5707	2.5062	1.4830	−0.09376	99.99	0.0371	88.98
*Z*5-14:Ac	3.0350	2.9447	2.8607	2.7814	2.7064	2.6365	2.5690	2.5055	2.4532	2.3984	1.3867	−0.08513	99.99	0.0415	88.28
*E*5-14:Ac	3.2299	3.1233	3.0233	2.9310	2.8431	2.7612	2.6835	2.6099	2.5476	2.4857	1.4801	−0.09474	99.99	0.0372	89.06
*Z*6-14:Ac	2.9886	2.9013	2.8208	2.7446	2.6729	2.6059	2.5412	2.4789	2.4280	2.3753	1.3644	−0.08300	99.99	0.0425	88.10
*E*6-14:Ac	3.2272	3.1228	3.0258	2.9346	2.8486	2.7683	2.6904	2.6179	2.5575	2.4964	1.4737	−0.09296	99.99	0.0375	88.91
*Z*7-14:Ac	3.0733	2.9822	2.8945	2.8139	2.7368	2.6649	2.5966	2.5310	2.4774	2.4212	1.4032	−0.08629	99.99	0.0407	88.37
*E*7-14:Ac	3.2515	3.1439	3.0451	2.9509	2.8649	2.7812	2.7030	2.6287	2.5674	2.5045	1.4857	−0.09440	99.99	0.0370	89.03
*Z*8-14:Ac	3.1732	3.0723	2.9789	2.8946	2.8091	2.7319	2.6579	2.5887	2.5316	2.4707	1.4484	−0.09042	99.99	0.0386	88.71
*E*8-14:Ac	3.3013	3.1901	3.0852	2.9886	2.8976	2.8127	2.7319	2.6555	2.5917	2.5268	1.5081	−0.09666	99.99	0.0360	89.21
*Z*9-14:Ac	3.3092	3.1992	3.0967	3.0017	2.9119	2.8281	2.7487	2.6736	2.6106	2.5461	1.5040	−0.09471	99.99	0.0363	89.05
*E*9-14:Ac	3.4249	3.3031	3.1896	3.0849	2.9870	2.8956	2.8086	2.7260	2.6569	2.5862	1.5601	−0.10138	99.99	0.0339	89.60
*Z*10-14:Ac	3.4923	3.3704	3.2555	3.1477	3.0475	2.9554	2.8662	2.7831	2.7136	2.6433	1.5778	−0.10080	99.99	0.0334	89.55
*E*10-14:Ac	3.5071	3.3792	3.2571	3.1468	3.0432	2.9478	2.8560	2.7705	2.6970	2.6239	1.5946	−0.10477	99.99	0.0326	89.87
*Z*11-14:Ac	3.6614	3.5251	3.3987	3.2793	3.1709	3.0676	2.9708	2.8797	2.8048	2.7262	1.6436	−0.10657	99.99	0.0309	90.02
*E*11-14:Ac	3.6559	3.5124	3.3817	3.2600	3.1452	3.0400	2.9416	2.8485	2.7701	2.6890	1.6555	−0.11079	99.99	0.0304	90.36
*Z*12-14:Ac	4.1523	3.9822	3.8246	3.6789	3.5427	3.4167	3.2988	3.1881	3.0944	2.9990	1.8050	−0.11749	99.99	0.0259	90.91
*E*12-14:Ac	3.9150	3.7540	3.6067	3.4687	3.3426	3.2249	3.1136	3.0073	2.9215	2.8321	1.7429	−0.11670	99.99	0.0276	90.84

[a] Standard *n*-hexadecane.

Table 8
GC data and vapour pressures (25°C) of pentadecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	90°C	95°C	100°C	105°C	110°C	115°C	120°C	125°C	130°C	135°C	Intercept	Slope	r^2(%)		
*Z*9-15:Ac	2.9443	2.8600	2.7811	2.7074	2.6374	2.5703	2.5112	2.4479	2.3964	2.3452	1.3419	−0.08292	99.99	0.0128	93.64
*E*9-15:Ac	3.0818	2.9857	2.8988	2.8110	2.7316	2.6566	2.5881	2.5202	2.4635	2.4048	1.4113	−0.09045	99.99	0.0116	94.29
*Z*10-15:Ac	3.0739	2.9808	2.8932	2.8122	2.7335	2.6608	2.5914	2.5291	2.4713	2.4149	1.4007	−0.08796	99.99	0.0119	94.08
*E*10-15:Ac	3.1541	3.0513	2.9559	2.8670	2.7828	2.7044	2.6293	2.5593	2.4997	2.4375	1.4448	−0.09383	99.99	0.0112	94.58
*Z*11-15:Ac	3.2262	3.1220	3.0245	2.9327	2.8473	2.7676	2.6922	2.6189	2.5563	2.4940	1.4675	−0.09377	100.00	0.0109	94.58
*E*11-15:Ac	3.2447	3.1341	3.0326	2.9367	2.8483	2.7637	2.6865	2.6121	2.5470	2.4826	1.4843	−0.09743	99.99	0.0106	94.90
*Z*12-15:Ac	3.3890	3.2716	3.1631	3.0616	2.9660	2.8773	2.7943	2.7144	2.6475	2.5790	1.5344	−0.09951	99.99	0.0100	95.07
*E*12-15:Ac	3.3704	3.2500	3.1374	3.0329	2.9356	2.8438	2.7576	2.6763	2.6087	2.5396	1.5407	−0.10326	99.99	0.00988	95.40
*Z*13-15:Ac	3.8032	3.6606	3.5263	3.4024	3.2863	3.1784	3.0770	2.9799	2.8994	2.8185	1.6810	−0.10936	99.99	0.00844	95.93
*E*13-15:Ac	3.5888	3.5888	3.3270	3.2108	3.1017	2.9994	2.9040	2.8142	2.7379	2.6609	1.6218	−0.10905	99.99	0.00896	95.90

[a] Standard *n*-heptadecane.

Table 9
GC data and vapour pressures (25°C) of hexadecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	100°C	105°C	110°C	115°C	120°C	125°C	130°C	135°C	140°C	145°C	Intercept	Slope	r^2(%)		
*Z*3-16:Ac	2.7651	2.6925	2.6238	2.5581	2.4981	2.4392	2.3837	2.3311	2.2863	2.2404	1.2585	−0.07768	99.99	0.00421	98.54
*E*3-16:Ac	2.8213	2.7421	2.6656	2.5950	2.5285	2.4652	2.4070	2.3492	2.3011	2.2500	1.2960	−0.08333	99.99	0.00396	99.06
*Z*4-16:Ac	2.5616	2.5043	2.4475	2.3951	2.3449	2.2963	2.2510	2.2071	2.1702	2.1308	1.1524	−0.06799	99.99	0.00486	97.66
*E*4-16:Ac	2.8094	2.7324	2.6605	2.5913	2.5269	2.4651	2.4065	2.3511	2.3035	2.2548	1.2854	−0.08116	99.99	0.00404	98.86
*Z*5-16:Ac	2.6120	2.5488	2.4891	2.4328	2.5136	2.3284	2.2797	2.2346	2.1945	2.1535	1.1812	−0.07115	99.99	0.00466	97.95
*E*5-16:Ac	2.7676	2.6933	2.6235	2.5551	2.4916	2.4309	2.3745	2.3196	2.2741	2.2266	1.2683	−0.08042	99.99	0.00412	98.79
*Z*6-16:Ac	2.5721	2.5127	2.4554	2.4010	2.3489	2.3013	2.2529	2.2079	2.1694	2.1322	1.1611	−0.06951	99.99	0.00479	97.80
*E*6-16:Ac	2.7611	2.6883	2.6180	2.5550	2.4929	2.4344	2.3797	2.3269	2.2805	2.2341	1.2582	−0.07804	100.00	0.00420	98.58
*Z*7-16:Ac	2.5820	2.5225	2.4658	2.4110	2.3593	2.3102	2.2632	2.2180	2.1791	2.1414	1.1644	−0.06929	99.99	0.00478	97.78
*E*7-16:Ac	2.7416	26700	2.6016	2.5382	2.4776	2.4196	2.3646	2.3114	2.2673	2.2215	1.2502	−0.07767	99.99	0.00424	98.54
*Z*8-16:Ac	2.6137	2.5508	2.4915	2.4380	2.3829	2.3316	2.2830	2.2373	2.1971	2.1564	1.1817	−0.07098	99.99	0.00466	97.93
*E*8-16:Ac	2.7552	2.6828	2.6138	2.5475	2.4869	2.4286	2.3728	2.3198	2.2747	2.2275	1.2574	−0.07841	100.00	0.00420	98.61
*Z*9-16:Ac	2.6699	2.6038	2.5415	2.4815	2.4252	2.3718	2.3205	2.2717	2.2303	2.1876	1.2110	−0.07358	99.99	0.00448	98.17
*E*9-16:Ac	2.8180	2.7409	2.6682	2.5989	2.5338	2.4716	2.4122	2.3562	2.3085	2.2610	1.2895	−0.08146	99.99	0.00402	98.89
*Z*10-16:Ac	2.7661	2.6937	2.6244	2.5596	2.4990	2.4402	2.3849	2.3319	2.2870	2.2413	1.2589	−0.07769	99.99	0.00421	98.54
*E*10-16:Ac	2.8640	2.7827	2.7060	2.6328	2.5652	2.4997	2.4394	2.3813	2.3308	2.2802	1.3137	−0.08412	100.00	0.00388	99.13
*Z*11-16:Ac	2.8735	2.7931	2.7175	2.6451	2.5789	2.5150	2.4559	2.3987	2.3496	2.2993	1.3106	−0.08216	99.99	0.00392	98.95
*E*11-16:Ac	2.9512	2.8637	2.7800	2.7021	2.6290	2.5595	2.4945	2.4327	2.3795	2.3253	1.3553	−0.08794	99.99	0.00367	99.48
*Z*12-16:Ac	3.0204	2.9295	2.8451	2.7659	2.6905	2.6196	2.5539	2.4898	2.4359	2.3793	1.3782	−0.08785	99.99	0.00359	99.47
*E*12-16:Ac	3.0243	2.9305	2.8420	2.7586	2.6809	2.6074	2.5383	2.4735	2.4163	2.3609	1.3906	−0.09147	99.99	0.00349	99.80
*Z*13-16:Ac	3.1499	3.0504	2.9566	2.8693	2.7859	2.7080	2.6350	2.5669	2.5072	2.4487	1.4362	−0.09305	99.99	0.00332	99.95
*E*13-16:Ac	3.1263	3.0231	2.9265	2.8369	2.7519	2.6724	2.5978	2.5280	2.4653	2.4063	1.4397	−0.09665	99.99	0.00326	100.28

[a] Standard *n*-octadecane.

Table 10
GC data and vapour pressures (25°C) of octadecenyl acetates

Acetate	Relative retention time[a]										Eq. (1)			P (Pa)	ΔH_v (kJ mol^{-1})
	120°C	125°C	130°C	135°C	140°C	145°C	150°C	155°C	160°C	165°C	Intercept	Slope	r^2(%)		
Z3-18:Ac	2.4280	2.3741	2.3235	2.2749	2.2282	2.1845	2.1419	2.1024	2.0672	2.0311	1.0961	−0.06761	100.00	0.000460	108.69
E3-18:Ac	2.5051	2.4452	2.3882	2.3341	2.2818	2.2329	2.1860	2.1409	2.1028	2.0648	1.1456	−0.07349	99.99	0.000423	109.29
Z9-18:Ac	2.2913	2.2474	2.2058	2.1655	2.1267	2.0898	2.0543	2.0206	1.9910	1.9612	1.0120	−0.05907	99.99	0.000528	107.82
E9-18:Ac	2.4293	2.3763	2.3251	2.2767	2.2313	2.1870	2.1444	2.1035	2.0686	2.0327	1.0969	−0.06759	99.99	0.000460	108.69
Z11-18:Ac	2.3870	2.3366	2.2892	2.2432	2.2005	2.1587	2.1189	2.0816	2.0474	2.0152	1.0688	−0.06428	100.00	0.000483	108.35
E11-18:Ac	2.5014	2.4426	2.3871	2.3334	2.2840	2.2359	2.1899	2.1460	2.1083	2.0704	1.1387	−0.07175	99.99	0.000430	109.11
Z13-18:Ac	2.4298	2.3755	2.3244	2.2760	2.2297	2.1855	2.1426	2.1032	2.0680	2.0342	1.0963	−0.06752	99.99	0.000461	108.68
E13-18:Ac	2.6090	2.5419	2.4791	2.4189	2.3628	2.3085	2.2568	2.2081	2.1668	2.1246	1.1997	−0.07795	99.99	0.000389	109.75
Z15-18:Ac	2.7719	2.6963	2.6250	2.5577	2.4942	2.4347	2.3773	2.3237	2.2769	2.2315	1.2735	−0.08234	99.99	0.000352	110.19
E15-18:Ac	2.7392	2.6612	2.5873	2.5188	2.4545	2.3931	2.3366	2.2809	2.2336	2.1867	1.2706	−0.08535	99.99	0.000347	110.50

[a] Standard *n*-eicosane.

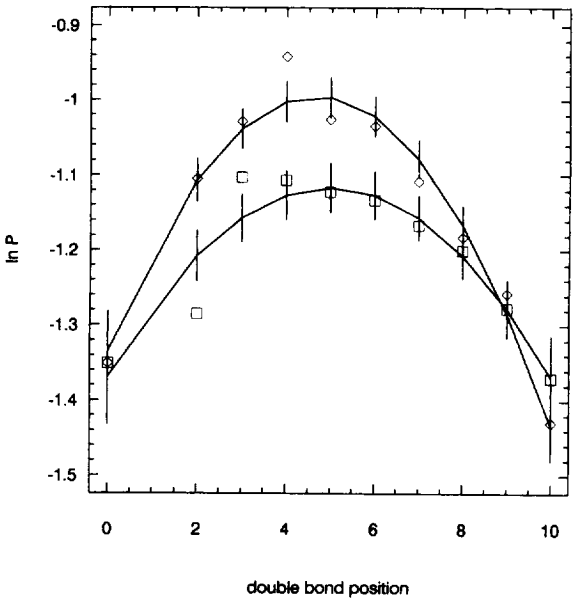

Fig. 2. Graphical representation of the nonlinear variation of vapour pressures upon successively changing the double bond position (△) in *Z*- and *E*-dodecenyl acetates (◇=*ZΔ*-12:Ac; □=*EΔ*-12:Ac). Error bars indicate 95% confidence interval.

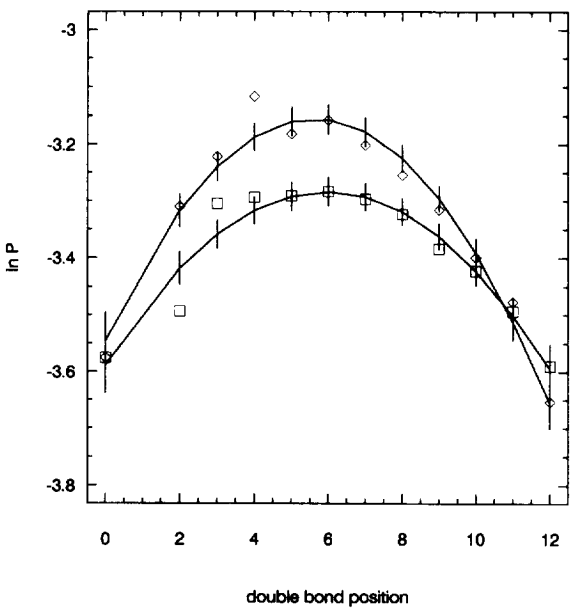

Fig. 3. Graphical representation of the nonlinear variation of vapour pressures upon successively changing the double bond position (*Δ*) in *Z*- and *E*-tetradecenyl acetates (◇=*ZΔ*-14:Ac; □=*EΔ*-14:Ac). Error bars indicate 95% confidence interval.

(solute–solvent) interactions between the compound and stationary phase and, more likely, (ii) the intramolecular interactions between the double bond and acetate function itself. Although this phenomenon is open to more detailed studies, it is worth emphasizing in this context that the so-called propyl effect was analogously to (ii) confirmed for *E*4-alkenes as a leading cause disturbing the regularity of all correlations between structure and retention [33] within the alkene series.

3.2.2. Effects of chain length and double bond configuration

As was shown above, the vapour pressures of olefinic compounds depend on the position of the double bond. Strict additivity should only be expected for a series of homologues in which the double bond is at a constant position relative to the nonpolar end of the molecule and is faraway enough from the polar end so as to eliminate the mutual interaction. Indeed, the *ω*-2 to *ω*-9 homologous series showed a constant incremental thermodynamic change between adjacent members. Despite the good linear correlation of the type $\ln P = a_0 - a_1 N$ achieved for all the *ω*-subseries investigated ($r^2 > 0.99$), difficulty was experienced in evaluating a statistical significance of differences among the subseries. All the values of intercepts a_0 and slopes a_1, vary only slightly (by $< \pm 2.3\%$) around mean values of 12.010 and 1.1120, respectively, thus not allowing discrimination among the individual subseries coefficients at the 95% confidence limits. As expected, the value of the mean slope a_1, is also similar to the slope of Eq. (6) (1.0944 ± 0.0153), suggesting nearly the same methylene group contributions for both the monounsaturated and saturated homologous series. On the other hand, the value of the mean intercept a_0 differs significantly from that of Eq. (6) (11.7125 ± 0.060). Given the approximately constant slope for all types of acetates investigated, the vapour pressure difference between an unsaturated acetate and its saturated counterpart is for each type of unsaturation generally independent of the carbon number and its average magnitude arises almost entirely from the magnitude of the intercept. Hence, it approximately holds $\ln P_{UNSAT} - \ln P_{SAT} = 0.2975$, or $P_{UNSAT} = 1.346\ P_{SAT}$. The ad-

Table 11
Regression coefficients and statistics of Eq. (10)

Series[a]	c_0	$-c_1$	$-c_2$	r^{2a}	SE[a]	F^a
ZΔ-10:Ac	0.9325	0.1513	0.0202	0.9439	0.035	51.4
EΔ-10:Ac	0.9357	0.0964	0.0125	0.9529	0.019	61.7
ZΔ-12:Ac	−1.3355	0.1454	0.0155	0.9596	0.031	107.8
EΔ-12:Ac	−1.3695	0.1010	0.0101	0.8632	0.037	29.4
ZΔ-14:Ac	−3.5454	0.1388	0.0123	0.9623	0.033	141.6
EΔ-14:Ac	−3.5884	0.1019	0.0085	0.9183	0.033	62.9
ZΔ-16:Ac	−5.7787	0.1336	0.0101	0.9583	0.032	127.3
EΔ-16:Ac	−5.7873	0.0956	0.0071	0.9782	0.016	248.3

[a] No attempts were made to improve the correlations by rejecting outliers.

vantage of these approximate expressions is that they can be used to predict vapour pressures of unsaturated acetates by using a reasonable vapour pressure value of the corresponding saturated compound.

Within each alkenyl subseries, *Z*-isomers mostly have greater vapour pressures than their *E*-counterparts. A reverse behaviour may be invariably observed for ω-2 alkenyl acetates.

To broaden the scope of our model inference, Eqs. (4,10) were combined and expressed as a single correlation

$$\ln P = d_0 + d_1 N + d_2(\Delta) + d_3(\Delta)^2 \qquad (11)$$

The regression coefficients and their 95% confidence intervals are shown in Table 12 separately for *Z* and *E* isomers. Although the magnitude of the double bond position effect as compared with the chain length effect is relatively small, the overall *F*-ratios associated with the complete second degree Eq. (11) are for *Z* and *E*-compounds 10 365 and 25 496, respectively, i.e., more than 1000 times larger than the tabulated critical values at $P=0.001$ significance level. This, together with excellent coefficients of determination ($r^2=0.9982$ and 0.9993), imply that the models are worthy of interpretation, explaining more than 99% of the variance in vapour pressure data. The extrapolated vapour pressures of 4:Ac (1320 Pa and 1490 Pa) resulting from the use of equations detailed in Table 12 (by setting $\Delta=0$, $N=4$) provides an additional check on the validity of these equations. Considering that all available data (including the deviating *E*2-, *E*3- and *Z*4- isomers) were included into the correlations, the agreement between the extrapolated and actual vapour pressure of 4:Ac (1506 Pa [25]) is very good. The correlation based on the *E*-isomer series yields the extrapolated vapour pressure of 4:Ac within ±1%. Predicted vapour pressures for the complete (57 compounds) *E*-isomer acetate series using this correlation are compared with the experimental data in Fig. 4.

Table 12
Parameters of Eq. (11)

	Alkenyl acetates	
	Z	*E*
d_0	11.4791±0.1009	11.6515±0.0648
d_1	−1.0734±0.0069	−1.0862±0.0044
d_2	0.10066±0.01222	0.07715±0.00784
d_3	−0.00847±0.00092	−0.00615±0.00059
N	57	57
r^2	0.9982	0.9993
SE	0.1099	0.0705
MAE	0.0802	0.0520
F	10 365	25 496

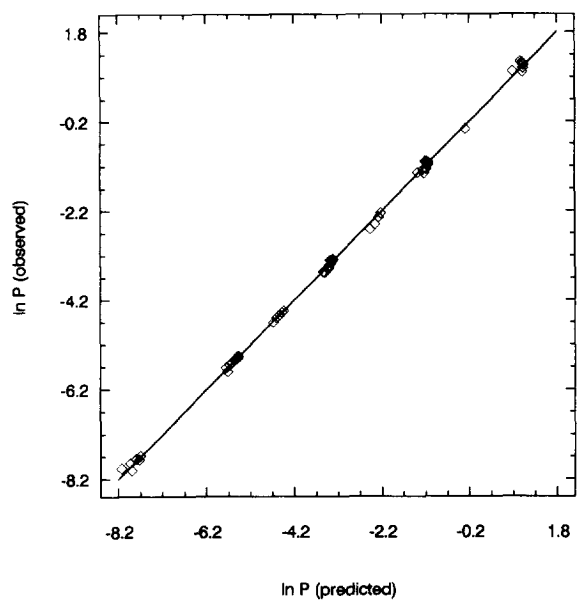

Fig. 4. Correlation between the observed and predicted (Eq. (11)) vapour pressures of 57 acetates (saturated compounds and *E*-isomers). For statistics see Table 12.

3.3. Comparison of present vapour pressures with literature data

The difficulty with this comparison is that (i) no vapour pressure data of unsaturated acetates based on direct measurements are available (ii) all earlier vapour-pressure determinations of unsaturated acetates have been based exclusively on GC techniques and limited to a relatively small number of compounds [6,26,27], and (iii) most of the published data [26,27] refer to a single but not exactly defined room temperature of ca. 30°C; the vapour pressures reported in our previous work [14] belong to the same category, since they have been corrected for column specificity using the earlier GC based data as the true values. In spite of this difficulty, some qualitative trends are apparent from Table 13 summarizing the earlier and present data converted to 30°C by using the enthalpies of vaporization listed in Tables 2–10.

It may be observed that the new and old data sets cross in the point corresponding approximately to $N=12$. Fig. 5 shows a log–log plot of this comparison with the regression line and the $y=x$ line. Although the results are well correlated ($r^2=0.9991$), the slope of the regression line is 1.0916 ± 0.0091, which indicates that the short chain congeners show greater vapour pressures by the present GC method than determined previously while the opposite is true for the long chain members.

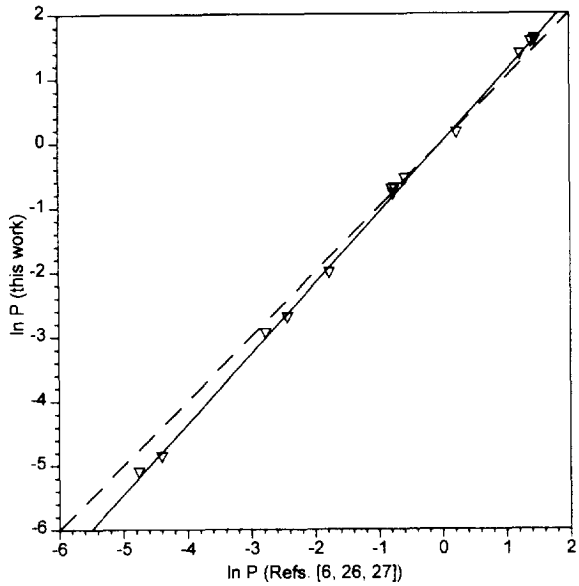

Fig. 5. Log–log plot of GC vapour pressures (30°C) from this work vs. literature [6,26,27] data. The regression line (solid) and the $y=x$ line (dashed) are shown.

When fitting the new and old data separately by Eq. (11), two statistically distinguishable straight lines are obtained. Again, the correlation derived from the new data appears to extrapolate rather well even for compounds with N far below the experimental N range on which the equation is based. Thus, for 4:Ac (with P at 30°C equal 2016 Pa [25]) it predicts 2099 Pa. Taking into account the long extrapolation required (over six carbon atoms), the deviation of ca. 4% may be regarded as quite a good agreement. On the other hand, the corresponding extrapolated value resulting from the old data (1172 ± 500 Pa) underestimates the actual vapour pressure by more than 40%.

Recalling that our present vapour pressure for 10:Ac at 30°C (3.888 Pa) agrees to within ±10% with that determined by a gas saturation method (3.561 Pa [25]) and the extrapolation ability of our GC vapour pressure data to lower N is of even better accuracy (see above), it appears that the methodology developed in this work is capable of yielding more reliable vapour pressure data than any of the earlier

Table 13
Vapour pressures of some alkyl and alkenyl acetates at 30°C

Compound	P (Pa)				
	This work	[26,27]	Other sources		
10:Ac	3.888	3.42	3.66[a],	3.438[b],	3.632[c]
11:Ac	1.143	1.26	1.306[c]		
12:Ac	0.445	0.4633	0.470[b],	0.463[c]	
13:Ac	0.1314	0.1700	0.173[c]		
14:Ac	0.0514	0.0624	0.0534[b],	0.0635[c]	
16:Ac	0.00592	0.0086	0.0088[c]		
Z5-10:Ac	4.945	–	4.29[a],	4.132[b]	
E5-10:Ac	4.709	–	4.07[a],	4.000[b]	
Z6-10:Ac	4.800	–	4.29[a]		
Z7-12:Ac	0.561	0.559	0.532[a],	0.579[b],	0.518[c]
Z9-12:Ac	0.486	0.472	0.493[b]		
E9-12:Ac	0.478	0.453	0.483[b]		
Z9-14:Ac	0.0656	0.0877	0.090[a],	0.0803[b],	0.0697[c]
Z11-16:Ac	0.00757	0.0123	0.0143[b],	0.00970[c]	

[a] [6].
[b] [14].
[c] [17].

GC based methods. The estimated accuracy is ±10%.

4. Conclusions

It has been demonstrated that the GC method presented in this paper yields reasonable vapour pressures for both the saturated and unsaturated acetates at 25°C provided that several alkanes are used as the reference standards. The results cover a wider range of compounds than has been studied before for any homologous series, and they provide a good framework for correlation of vapour pressures of acetates. A correlation scheme which reproduces the general properties of acetates, i.e., the number of carbon atoms (N) and position of the double bond (Δ) in the chain, has been developed. The low standard errors, high correlation coefficients, and large F-ratios indicate that the equations presented here are good representations of the experimental vapour pressure data summarized in Table 2 Tables 4–10. An indirect indication of the reliability of our vapour pressure data base is afforded by the quality of extrapolated data to lower carbon number homologues (i.e., to higher vapour pressure region) where reliable data from independent measurements are available. We believe that the Eqs. (3–11) provide as reliable a means for interpolation and extrapolation between $N=4$ and $N=20$ as is possible at present. The finding that $E2$-, $E3$-, and $Z4$-isomers behave anomalously does not weaken the predictive capabilities of these equations; on the contrary, it may help in a more general understanding of double bond dependent phenomena in acetates.

Although this investigation has been limited to acetates, the results of this study offer a strong inference that the general forms of the vapour pressure relationships should be applicable to other homologous series of compounds.

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