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Journal of Chromatography A, 923 (2001) 137–152

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Comparison of methods employing gas chromatography retention data to determine vapour pressures at 298 K

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Received 27 February 2001; received in revised form 8 May 2001; accepted 14 May 2001

Abstract

Validity of five models suggested for expressing the relationship between vapour pressures and GC retention times measured on a non-polar capillary column were tested on a common set of compounds [five homologous series of the type $H-(CH_2)_n-Y$, where Y denotes Cl, Br, CHO, $OCOCH_3$ and $COOCH_3$, and n varies from 6 to 14]. Standard methods of statistical analysis, as well as vapour pressure values obtained independently from direct vapour pressure measurements were used as validity criteria. For the 40-compound data set examined, the methods provided vapour pressures agreeing within 9.2–24.7% (average absolute percent error) with direct experimental data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapour pressure; Relative retention times; Retention indices; Retention times; Statistical analysis; Alkanes

1. Introduction

Representing the maximum achievable amount (or solubility) of a substance in the air, saturated vapour pressure (p^0) data are required both for assessing the likely environmental behaviour of new and existing chemicals and for estimating the exposure hazards associated with the inhalation of toxic substances [1,2]. The significance of these points is accentuated by the recent requirements that vapour pressures be reported for all new commercially important chemi-

cal entities, including pharmaceutical and plant protection products [3,4].

Vapour pressure measurements for environmentally important compounds with vapour pressures in the range 10^{-2} – 10^{-7} Pa can be made using either the direct or indirect experimental techniques [5]. While the direct techniques include all physicochemical methods that are used to measure directly the vapour pressure or another parameter related to it, the indirect techniques require a calibration with compounds of known vapour pressure. The main direct methods having official recognition to measure the vapour pressures in low-pressure range are the saturation method based on the use of a carrier gas, and two techniques based on molecular effusion

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(weighing effusion and torsion effusion methods). However, both direct methods require great care to obtain reproducible results. Due to experimental difficulties (a slight contamination of samples by lower boiling compounds or incomplete degassing can cause significant errors), the direct p^0 data are available only for a limited number of substances and subjected to relatively large systematic inter-laboratory errors [6]. Indirect experimental methods that require the use of one or several reference compounds whose vapour pressures are accurately known over the whole temperature range used are based on measuring either evaporation rates or gas chromatographic (GC) retention times. Compared to other methods, the GC technique offers particular advantages in terms of simplicity, speed, solute sample size, as well as purity and stability requirements. Although several experimental GC approaches for determination of p^0 at correlating retention data have been developed, little effort has been devoted to a comparative study of the various approaches in relation to each other. Consequently, a noticeable feature of the available literature is the lack of information concerning accuracy and/or applicability ranges of the respective GC approaches. Generally, there is very little information to guide one in determining the validity of a given model.

Virtually all GC methods known at present are, to some extent, either explicitly or implicitly based on an insight which stems from the equation:

$$V_{g,i} = 273.15 R/Mp_i^0 \gamma_i^\infty \quad (1)$$

This equation, pre-assuming the ideal gas behaviour, relates the measured specific retention volume $V_{g,i}$ of a solute i in a stationary phase, whose molecular mass is M , to its vapour pressure p_i^0 , activity coefficient at infinite dilution γ_i^∞ and the gas constant R [7,8]. Providing that a constant carrier gas flow-rate is applied, other retention parameters, e.g. adjusted retention times $t_i' = t_i - t_0$ and/or retention factors $(t_i - t_0)/t_0$ deduced from the experimental retention times (t_i) and the retention of a “non-retained” substance (the hold-up time, t_0) may be advantageously used in Eq. (1) instead of $V_{g,i}$ [9].

According to Eq. (1), adjusted retention times of two substances (a test compound 1 and a reference compound 2) measured isothermally at the same chromatographic conditions are related through:

$$\log(t_1'/t_2') = \log(p_2^0/p_1^0) + \log(\gamma_2^\infty/\gamma_1^\infty) \quad (2)$$

or in terms of the Kováts retention indices:

$$I_1 = 100 \left[z + \frac{\log(\gamma_z^\infty p_z^0/\gamma_1^\infty p_1^0)}{\log(\gamma_z^\infty p_z^0/\gamma_{z+1}^\infty p_{z+1}^0)} \right] \quad (3)$$

where p_i^0 and γ_i^∞ represent the vapour pressure and the infinite dilution activity coefficient of solute i in the stationary phase, and subscripts 1, z and $z+1$ identify the solute of interest and n -alkanes with z and $z+1$ carbon atoms whose retention volumes encompass that of solute 1.

Expressing p_1^0 from Eqs. (2) and (3), we obtain:

$$\log p_1^0 = \log p_2^0 + \log(\gamma_2^\infty/\gamma_1^\infty) - \log(t_1'/t_2') \quad (4)$$

and:

$$\log p_1^0 = \log(p_z^0 \gamma_z^\infty/\gamma_1^\infty) + \frac{(100z - I_1) \log(p_z^0 \gamma_z^\infty/p_{z+1}^0 \gamma_{z+1}^\infty)}{100} \quad (5)$$

The majority of models for GC-based determination of vapour pressures originates from Eqs. (4) or (5). Those based on Eq. (4) use the relative retention times as an experimentally measurable quantity (with no restrictions concerning the reference compound(s) thus offering certain advantages), while those based on Eq. (5) rely on measuring the more generally applicable Kováts retention indices with the pre-assumed use of linear alkanes as references. Concerning the ability of Eqs. (4) and (5) to provide reliable vapour pressures at environmentally relevant temperature 25°C, we can identify a priori two problems. The first problem is connected with the necessity to specify the variation in the value of $\gamma_i^\infty/\gamma_j^\infty$. The second problem reflects the fact that all variables appearing in Eqs. (4) and (5) are temperature-dependent. Therefore, implicit in the use of these equations is the requirement that we are able to correctly describe the temperature effects, i.e. to transform (extrapolate) the data from the temperature of GC measurement to 25°C. Both equations also have in common that considerations leading to them ignore the non-ideality of solute vapours.

Faced with these problems, several authors set out to construct more or less practical models using

approximate approaches. All these models have previously been described in detail; therefore, only a brief summary of the basic models is given below with the relevant final expressions summarized in Fig. 1.

1.1. Method A

This approach utilizes the Hamilton's method in its original version [10–20] in which the differences

in activity coefficients are completely neglected assuming that $\gamma_1^\infty \cong \gamma_2^\infty$ and, over a modest temperature range, the vapour pressure as described by Eq. (4) is related to temperature by the Clausius–Clapeyron equation. In an attempt to bring the relative activity coefficient ($\gamma_2^\infty/\gamma_1^\infty$) closer to one, later modifications of this version included the use of a reference solute that is structurally related to the test one and/or an extension of the number of reference compounds [21–23].

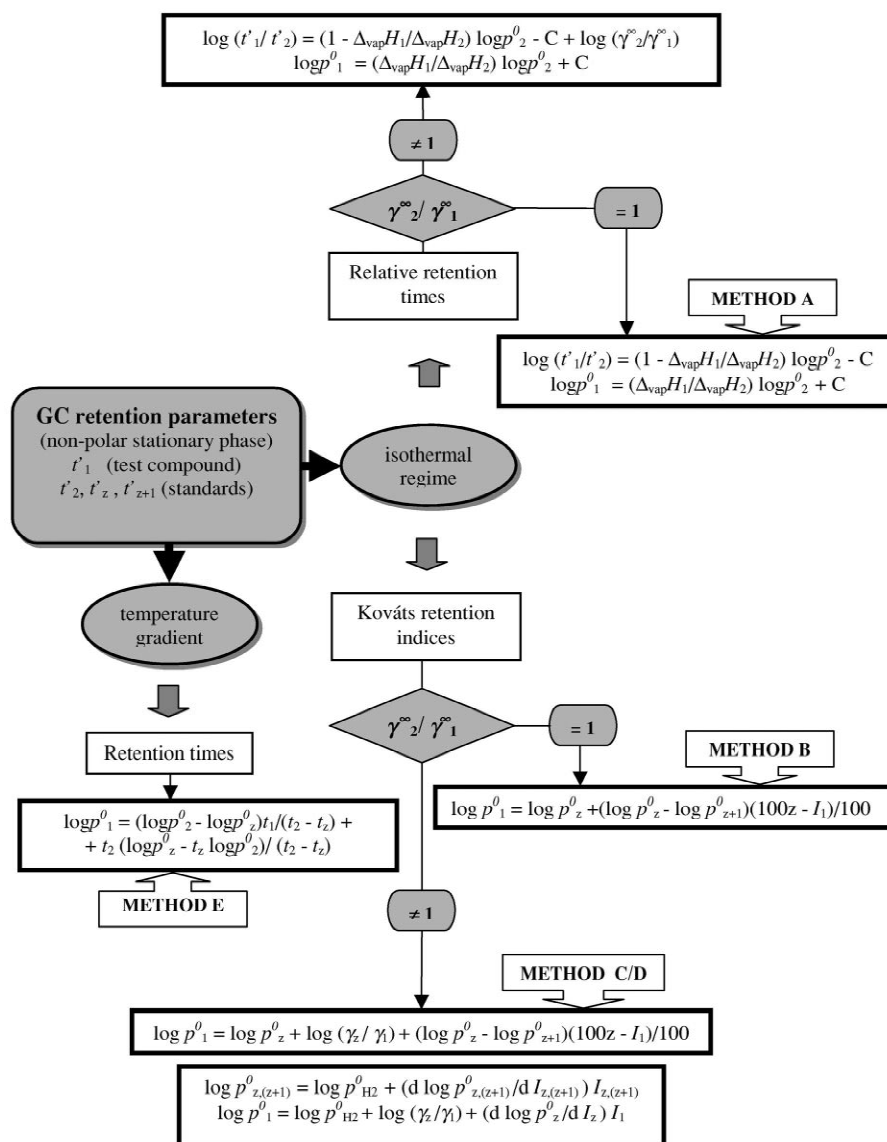


Fig. 1. Summary of expressions derived to describe the relationship between vapor pressures and GC retention times.

1.2. Method B

When compared to Method A, this approach forwarded by the Ballschmiter group [24] utilizes Kováts retention indices (see Eq. (5)) instead of relative retention times while sharing a common assumption as regards the activity coefficients, i.e. $\gamma_1^\infty \cong \gamma_z^\infty \cong \gamma_{z+1}^\infty$.

1.3. Method C

Starting from Eq. (5), Govers and his collaborators [25,26] suppose that $\gamma_1^\infty \cong \gamma_z^\infty$ while keeping $\gamma_z^\infty \cong \gamma_{z+1}^\infty$. The relative activity coefficient, $\gamma_z^\infty / \gamma_1^\infty$, is expressed by the McReynolds number of a model compound; a linear equation [27] is used to describe the $I_1 = f(T)$ dependence.

1.4. Method D

This modification of the previous method proposed by the same research group [28] is based on analogous assumptions, but differs in using a quadratic equation [29] to describe the I_1 vs. T relationship and in applying another approach to express the temperature dependence of p_z . (Note also that the sign of the third term in Eq. (2) of the original paper [28] is erroneous, probably due to the printing error).

1.5. Method E

This approach, developed by Donovan [6] differs significantly from previous methods in that it is based on a correlation between the vapour pressure and retention time measured at a temperature-programmed regime using a non-polar capillary column of standard length rather than a short one.

To complete the specification of individual models, a recent suggestion [30] to express the relative activity coefficient with help of the Wilson model of non-ideal mixing should be mentioned. Since this modification was checked only on hydrocarbons and its relative complexity seems to preclude broader practical applications, it is not considered in this work any further.

The GC methods listed above have been developed and tested using different classes of rather specific compounds. Interest in this direction at-

tracted, e.g. herbicide esters [10], organophosphorous pesticides [13], polychlorinated biphenyls [12,14,16,24], chlorinated dibenzo-*p*-dioxins and dibenzofurans [15], tetraorganostannanes [19], linear alkylbenzenes [18], chlorobenzenes, chlorophenols and chlorobenzyltoluenes [25,26], fatty acid methyl esters [28], 4,4'-disubstituted bipyridines [20], pheromone-like compounds [21–23] and alkyl dinitrates [31]. Due to the diversity in the test compound classes, as well as in reference substances and chromatographic conditions, any direct comparison of the particular methods based on the previously published data is hardly possible.

Our objective in the present paper is to report the first systematic study aimed at examining the performance of models A–E using a common set of experimental retention data. As test compounds we have chosen the members of five homologous series of the general type H-(CH₂)_{*n*}-Y, where Y denotes Cl, Br, CHO, COOCH₃ and OCOCH₃, and *n* varies from 6 to 14. For the evaluation of possible priorities among the models, vapour pressures estimated with each of the models were compared in the most objective manner possible with independently measured p^0 values reported in the literature for 25°C.

We considered the following facts in selecting the five series of mono-substituted linear alkanes as a test set of compounds. First, these compounds are of certain environmental interest and their directly measured vapour pressures, covering a significantly wide range ($\sim 2.0 \cdot 10^{-2}$ – $1.2 \cdot 10^3$ Pa), are mostly available from the literature. Second, the members of these series differ only by a number of methylene groups in the alkyl chain and, for $6 \leq n \leq 14$, we can expect a linear $\ln p^0$ vs. *n* relationship [32–34]. Third, this linearity may advantageously serve as one of the reliability criteria for the vapour pressures taken from different literature sources, as well as for those resulting from different models.

2. Experimental

2.1. Chromatography

The retention times of all samples were determined using a Hewlett-Packard HP 6890 gas chromatograph equipped with a flame ionisation

detector, electronic pneumatic control (EPC), split injection port, HP 6890 automatic injector and HP VectraVL 2PC with ChemStation software. All measurements were performed on polydimethylsiloxane bonded-phase fused-silica capillary column (HP-1, 6 m × 310 μm I.D., 0.52 μm film thickness) in split mode with a helium carrier gas. To generate sample size-independent retention times, equal (v/v) concentrations were prepared by dissolving 10 μl of the analyte in 1 ml of *n*-pentane and 1 μl of the solution was injected onto chromatographic column; symmetrical peaks indicated that infinite dilution has been attained for all the distribution processes. Isothermal measurements were performed at 90, 95, 100, 105 and 110°C with the split ratio 40:1 and the helium head pressure 25 kPa (EPC). Temperature program for gradient measurements was as follows: 2 min at 50°C followed by heating at 10°C min⁻¹ to a maximum temperature, usually 250°C. The split ratio and the helium head pressure were 35:1 and 25 kPa (EPC), respectively.

A series of *n*-alkanes ranging from *n*-heptane to *n*-heptadecane was used as reference compounds. Adjusted retention times were calculated by subtracting the retention time of methane from the retention time of the analyte. All retention times used for calculations were the means of three separate runs (mean standard deviation 0.04%).

2.2. Chemicals

The chloroalkanes, bromoalkanes, alcohols and methyl esters were mostly the commercial products from Applied Science Labs. (USA), Aldrich (USA), Sigma (USA) or Merck (Germany) in a purity at least 97% and used as received. Some odd carbon atom halogen derivatives, as well as all aldehydes and acetates were synthesized in our laboratory from corresponding alcohols using the standard phosphorus halogenide-based halogenation, PCC-based oxidation (aldehydes) and esterification (acetates) procedures. *n*-Pentane for organic trace analysis, Suprasolv (Merck) was used as a common solvent.

2.3. Data treatment

Recently, the literature vapour pressures of alkanes between the triple and normal boiling point

temperatures have been critically evaluated [35] and found to fit the Cox equation:

$$\ln\left(\frac{p}{p_0}\right) = \left(1 - \frac{T_0}{T}\right) \exp(A_0 + A_1T + A_2T^2) \quad (6)$$

The parameters of Eq. (6) given in the original paper [35] were used throughout this work to obtain interpolated vapour pressure values of reference alkanes at the temperatures selected to develop the *p*-*T* relationship.

The basic equation relevant to Method E (Fig. 1) may be theoretically applied to any two reference compounds whose vapour pressures at 25°C are known, thus allowing the slope and intercept of the linear log *p* vs. *t* relationship to be determined [6]. In this work, the vapour pressures of eleven C₈ to C₁₈ alkane standards at 25°C provided by Eq. (6) were related to retention times measured under temperature gradient. The correlation equation corresponding to the linear least squares curve fit of these data was:

$$\log p \text{ [Pa]} = -(0.3566 \pm 0.0064)t + (3.6830 \pm 0.060) \quad (7)$$

with *R*² = 99.67% and the standard error of estimate SE = 0.094. The coefficients of Eq. (7) were then used to estimate vapour pressures according to Method E instead of originally proposed [6] two-point-based values.

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

3. Results and discussion

The study consists of four parts, namely: (1) measurement of adjusted retention times and Kováts retention indices for all test compounds either isothermally at five temperatures or using a temperature gradient, (2) generation of the reliable reference vapour pressure data base, (3) elaboration of (approximate) rules for selection of appropriate *n*-alkanes to be used as standards in expressing the relative retention times, and (4) comparison of Methods A–E as to their capability to correctly

Table 1
Adjusted retention times of alkane standards H-(CH₂)_n-CH₃

n	t' (min)				
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K
6	0.079	0.068	0.060	0.051	0.046
7	0.164	0.140	0.121	0.104	0.091
8	0.329	0.277	0.237	0.201	0.174
9	0.653	0.541	0.455	0.382	0.325
10	1.284	1.047	0.865	0.715	0.599
11	2.499	2.011	1.636	1.329	1.095
12	4.827	3.808	3.049	2.447	1.993
13	9.332	7.220	5.673	4.471	3.577
14	18.034	13.691	10.557	8.174	6.430
15	34.726	25.871	19.607	14.919	11.540
16	66.859	48.921	36.394	27.224	20.698

reproduce the vapour pressure values determined by direct physicochemical methods.

3.1. Measurement of adjusted retention times and Kováts retention indices

Tables 1–6 summarize the results of our isothermal GC retention time measurements for standard alkanes and test compounds presented as means of three replicate experiments. The last two columns in Tables 2–6 include the values of Kováts indices related to 25°C (I_{25}). These extrapolated values were estimated using either the linear ($I = c_0 + c_1T$ [25,26]) or simple quadratic ($I = d_0 + d_1T^2$ [28])

Table 2
GC retention data of homologous chlorides H-(CH₂)_n-Cl

n	t' (min) ^a					I ^b 298.15 K	I ^c 298.15 K
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K		
6	0.230	0.197	0.171	0.147	0.128	836.7	840.9
7	0.453	0.382	0.325	0.276	0.236	940.8	943.9
8	0.889	0.736	0.615	0.515	0.453	1039.8	1042.9
9	1.742	1.418	1.163	0.958	0.795	1139.2	1143.4
10	3.411	2.725	2.195	1.776	1.449	1240.9	1244.7
11	6.644	5.211	4.121	3.283	2.637	1340.4	1344.6
12	12.922	9.945	7.723	6.048	4.777	1440.8	1445.1
13	25.004	18.895	14.415	11.096	8.621	1540.8	1545.2
14	48.434	35.924	26.914	20.355	15.553	1642.2	1646.4

^a Adjusted retention times.

^b Kováts retention indices extrapolated to 298.15 K using the function $I = c_0 + c_1T$.

^c Kováts retention indices extrapolated to 298.15 K using the function $I = d_0 + d_1T^2$.

Table 3
GC retention data of homologous bromides H-(CH₂)_n-Br

n	t' (min) ^a					I ^b , 298.15 K	I ^c , 298.15 K
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K		
6	0.386	0.326	0.281	0.241	0.209	920.6	921.4
7	0.763	0.633	0.534	0.451	0.382	1023.4	1023.9
8	1.498	1.220	1.011	0.841	0.701	1120.8	1122.7
9	2.946	2.352	1.913	1.559	1.284	1220.5	1223.0
10	5.749	4.503	3.596	2.890	2.337	1320.9	1323.5
11	11.192	8.602	6.743	5.328	4.235	1420.9	1423.8
12	21.760	16.396	12.624	9.810	7.662	1521.9	1524.7
13	41.991	31.106	23.529	17.966	13.807	1621.2	1624.3

^{a,b,c} See notes in Table 2.

Table 4
GC retention data of homologous aldehydes H-(CH₂)_n-CHO

n	t' (min) ^a					I ^b , 298.15 K	I ^c , 298.15 K
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K		
8	1.146	0.935	0.777	0.646	0.544	1079.1	1080.7
9	2.244	1.809	1.476	1.207	1.002	1179.3	1181.2
10	4.349	3.438	2.763	2.235	1.833	1277.5	1280.2
11	8.435	6.534	5.162	4.096	3.300	1379.0	1381.3
12	16.365	12.443	9.651	7.515	5.949	1479.9	1482.1
13	31.651	23.608	18.004	13.779	10.710	1580.5	1582.7

^{a,b,c} See notes in Table 2.

Table 5
GC retention data of homologous methyl esters H-(CH₂)_n-COOCH₃

n	t' (min) ^a					I ^b , 298.15 K	I ^c , 298.15 K
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K		
5	0.339	0.283	0.237	0.207	0.177	908.3	907.0
6	0.673	0.556	0.457	0.395	0.334	1007.9	1006.8
7	1.331	1.082	0.882	0.743	0.618	1108.8	1107.7
8	2.598	2.083	1.673	1.383	1.133	1207.1	1206.9
9	5.040	3.961	3.135	2.515	2.065	1312.6	1310.2
10	9.772	7.533	5.853	4.676	3.717	1409.7	1408.7
11	18.927	14.320	10.927	8.572	6.697	1509.9	1509.0
12	36.542	27.141	20.346	15.684	12.049	1610.2	1609.3

^{a,b,c} See notes in Table 2.

relationships following original procedures of the authors of Methods C and D, respectively. For the temperature range investigated, both the linear and quadratic functions were found to fit the data excellently ($r \geq 0.9998$). The linear temperature-programmed (LTP) retention times required for Method E are listed in Table 7.

3.2. Generation of the reference vapour pressure database

One of the basic requirements for evaluating the Methods A–E is an accurate representation of reference vapour pressures at 25°C (p_{ref}^0). In this work, the recommended p_{ref}^0 data for *n*-alkanes were taken

Table 6
GC retention data of homologous acetates H-(CH₂)_n-OCOCH₃

n	t' (min) ^a					I ^b , 298.15 K	I ^c , 298.15 K
	363.15 K	368.15 K	373.15 K	378.15 K	383.15 K		
6	0.619	0.510	0.426	0.356	0.319	979.2	984.6
7	1.223	0.991	0.814	0.669	0.586	1086.1	1088.8
8	2.391	1.912	1.542	1.248	1.069	1188.7	1190.4
9	4.650	3.652	2.906	2.318	1.956	1287.7	1290.0
10	9.005	6.946	5.431	4.258	3.527	1387.5	1389.9
11	17.522	13.265	10.210	7.850	6.365	1490.7	1492.2
12	33.790	25.124	18.989	14.363	11.425	1590.4	1592.2
13	64.848	47.358	35.100	26.144	20.642	1688.2	1690.4
14	124.609	89.367	65.080	47.648	36.918	1790.0	1791.6

^{a,b,c} See notes in Table 2.

Table 7
Retention times of the H-(CH₂)_n-Y homologues measured under temperature programmed conditions

<i>n</i>	<i>t</i> (min) ^a				
	Y=Cl	Y=Br	Y=CHO	Y=COOCH ₃	Y=OCOCH ₃
6	1.098	–	–	2.360	3.827
7	2.527	3.512	–	3.976	5.457
8	3.983	5.183	6.455	5.615	7.009
9	5.621	6.763	8.287	7.154	8.465
10	7.153	8.239	9.245	8.600	9.825
11	8.592	9.621	10.497	9.959	11.124
12	9.938	10.921	11.718	11.242	12.336
13	11.205	12.161	12.883	12.456	13.483
14	12.412	–	–	–	14.585

^a Temperature program: 50°C (2 min)–10°C/min–250°C (2 min).

from a critically reviewed compilation by Růžička and Majer [35]. For other compounds, reliable p_{ref}^0 values, particularly of higher homologous series members, have been rather difficult to obtain. Consequently, three types of directly measured vapour pressure data reported in the literature had to be considered. First, experimental vapour pressures quoted directly for 25°C [36]. Second, interpolated data from different literature sources based on originally suggested forms of the $\ln p^0 = f(T)$ equation. Third, extrapolated data; the extrapolation was carried out by using equations which are supposed to extrapolate well below the experimental temperature range (cf. Ref. [37]), e.g. the Cox equation, Wagner

equation or Chebychev-type polynomial in x of degree 3.

Vapour pressure values reported in the literature were collected, and the values obtained by different researchers for a substance were statistically examined for outliers. Any significant outliers were eliminated from the set and the remaining values for each homologous series were then checked up for internal consistency by examining the $\ln p^0$ against the carbon number (n) plots giving equal weight to each reported value. The values corresponding to the best fits were then used as “best” reference vapour pressures. The reference p_{ref}^0 data of the compounds covered by this study are summarized in Table 8,

Table 8
Reference vapor pressures of homologues H-(CH₂)_n-Y at 298.15 K

<i>n</i>	p_{ref}^0 (Pa)				
	Y=Cl	Y=Br	Y=CHO	Y=COOCH ₃	Y=OCOCH ₃
5	–	–	–	407.8	–
6	1269	533.6	–	134.3	188.3
7	403.4	164.2	–	44.25	62.36
8	128.2	50.56	55.72	14.57	20.65
9	40.76	15.56	18.33	4.801	6.835
10	12.95	4.791	6.031	1.581	2.263
11	4.118	1.475	1.984	0.5208	0.7492
12	1.309	0.4540	0.6528	0.1716	0.2480
13	0.4161	0.1398	0.2148	–	0.08213
14	0.1323	–	–	–	0.02719
Sources of data	[36,38–40]	[38,39]	[36,41,42]	[41]	[36,41,43–45]

along with the literature sources. Since the reported vapour pressures of dodecyl- and tetradecyl aldehydes (m.p. 44.5 and 30°C, respectively) correspond to crystalline solids (p_S^0), inter-conversion $p_S^0 \Rightarrow p_L^0$ was made using Eq. (8):

$$p_S^0/p_L^0 = \exp[-\Delta_{\text{fus}}S (T_m/T - 1)/R] \quad (8)$$

where subscripts S and L refer to solid and (sub-cooled) liquid states, T_m is the melting point (K) and $\Delta_{\text{fus}}S$ is the entropy of fusion; an averaged value of $\Delta_{\text{fus}}S \cong 56.5$ J/mol K commonly accepted [12,16] for intermediate size organic molecules was used in converting the data.

3.3. Selection of appropriate *n*-alkane standards

While the selection of *n*-alkane standards for Methods B, C and D is directed by the definition of Kováts retention indices and any two (or more) *n*-alkane standards may be theoretically used for Method E, the correct selection of *n*-alkane standards for Method A meets with a serious uncertainty. Several authors [12,15] have observed that vapour pressures determined by Method A using a common standard for test compounds with significant differences in their molecular mass are underestimated and overestimated at the high- and low-volatility ends of the scale. To improve the accuracy of the GC calculation method, the use of standards of “similar

structure and polarity” [20] and/or those that “would chromatograph in a manner similar to the test compounds” [15] has been recommended. This kind of selection, however, remains somewhat subjective and standardized choices concerning the *n*-alkane standards to be used for Method A would be highly desirable. For this reason, an extensive series of tests was run using the framework of method A and alkanes with *n* varying from 6 to 16 as reference standards for every members of the testing set.

The results expressed as relative percent errors, δ , ($\delta[\%] = 100(p_{\text{GC}}^0 - p_{\text{ref}}^0)/p_{\text{ref}}^0$, with p_{ref}^0 listed in Table 8) are exemplified for Y=Cl in Table 9. Inspection of Table 9 and equivalent tables (not shown) that were constructed for remaining Y groups (Br, CHO, COOCH₃ and OCOCH₃) reveals that the magnitude and sign of δ depend on the number of methylene groups present both in the test compounds, $n(\text{Y})$, and in reference alkanes, $n(\text{A})$. Furthermore, it is observed that $|\delta|_{\text{min}}$ shows a regular trend getting invariably around a diagonal in $n(\text{A}) \times n(\text{Y})$ matrices for each homologous series. This indicates that for a given homologous series characterized by $n(\text{Y})$ there can be found a single value of $q = n(\text{A}) - n(\text{Y})$ applicable to all members of the series. Attempting to quantify this effect, we fitted the percent errors δ by the least squares method into equations with $n(\text{Y})$ and $n(\text{A})$ predictor variables utilizing standard methods of linear, as well as non-linear regression analysis. While several combina-

Table 9

Variation of the δ (%) value as functions of the number of carbon atoms in homologous series of alkyl chlorides and *n*-alkanes

<i>n</i> (Cl) ^a	<i>n</i> (A) ^b										
	6	7	8	9	10	11	12	13	14	15	16
6	42.1	4.6 ^c	-18.9	-34.0	-45.0	-53.1	-61.0	-67.0	-72.0	-75.6	-79.3
7	70.1	24.9	-3.3	-21.4	-34.5	-44.2	-53.7	-60.7	-66.7	-71.0	-75.4
8	107.0	51.8	17.3	-4.7	-20.7	-32.4	-43.9	-52.5	-59.7	-64.9	-70.2
9	144.6	78.8	38.0	12.1	-6.8	-20.6	-34.2	-44.2	-52.7	-58.8	-65.1
10	186.8	109.2	61.2	30.8	8.7	-7.5	-23.3	-35.1	-45.0	-52.0	-59.3
11	243.9	150.3	92.5	56.2	29.6	10.3	-8.7	-22.6	-34.4	-42.8	-51.5
12	307.5	195.9	127.2	84.2	52.6	29.9	7.5	-9.0	-22.9	-32.6	-43.0
13	387.8	253.3	170.9	119.5	81.7	54.5	27.8	8.2	-8.3	-19.9	-32.2
14	479.6	318.8	220.5	159.7	114.6	82.5	50.9	27.7	8.2	-5.4	-20.0

^a The number of carbon atoms in the test series H-(CH₂)_{*n*}-Cl.

^b The number of carbon atoms in the reference alkane series H-(CH₂)_{*n*}-CH₃.

^c The low(est) $|\delta|$ values are italicized.

tions and data transformations of the variables were tested for statistical significance, acceptable results were achieved with an empirical equation:

$$\delta[\%] = a_0 + a_1/(a_2 + q) \quad (9)$$

with $q = n(A) - n(Y)$.

To determine optimised values of the coefficients a_0 to a_2 of Eq. (9), the best fit to the data was determined for each series using the Statgraphics routine for a non-linear Levenberg–Marquart regression. The regression coefficients and their asymptotic standard errors obtained for at least 66 data points in each series are shown in Table 10. To visualize the descriptor effects, plots were generated of the fitted response surfaces of Eq. (9) along with the contour plots for each homologous series. Fig. 2 exemplifies these plots for chloride and methyl ester series. Inspection of Fig. 2a reveals that changes in the chain length of n -alkane references dramatically influence the relative error. It can easily be seen that the use of “short” n -alkanes as references for relatively “long” test compounds [$n(A) \ll n(Y)$] causes invariably errors reaching several hundreds percent. Interestingly, the reverse situation [$n(A) \gg n(Y)$] does not affect the error so dramatically.

Based on the R -squared statistics, the model explains about 92.6–99.3% of the variance in the data, implying that the fitted surface of the model is worthy of interpretation. Consequently, we can find out an optimal (hypothetical) reference alkane for each series by setting δ in Eq. (9) equal to zero and

expressing $n(A)$ as a function of $n(Y)$. From the values of q thus obtained (see the bottom row in Table 10) an hypothetical reference alkane of the type $H-(CH_2)_{n+q}-CH_3$ can be selected for each of the members of each of the series $H-(CH_2)_n-Y$ (see Fig. 2b for illustrative examples). With the values of q thus predetermined, our further efforts have been focused on identifying a parameter whose value would be approximately identical for the $-CH_2Y$ and $-(CH_2)_q-CH_2CH_3$ groups. The use of vaporization enthalpy increments of Ducros [46,47] $\Delta_{vap}H_i$ ($-CH_2Y$) and $\Delta_{vap}H_i$ (A) [$A = -(CH_2)_q-CH_2CH_3$] to relate functional groups in the non-alkane and alkane homologous series led to empirical equations:

$$\Delta_{vap}H_i(A) = 103.215 - 1.411\Delta_{vap}H_i(Y) - 1064.63/\Delta_{vap}H_i(Y) \quad (10)$$

or (by setting $\Delta_{vap}H_i(A) = 10.63 + 4.98q$):

$$q = 18.591 - 0.2833\Delta_{vap}H_i(Y) - 213.782/\Delta_{vap}H_i(Y) \quad (11)$$

Since the enthalpy of vaporization certainly influences the partitioning of a solute between chromatographic phases and its close relation to vapour pressures is well known [48], the use of $\Delta_{vap}H_i$ to characterize end-groups of homologues seems to be justified. The correlation represented by Eqs. (10) and (11) is surprisingly good ($R^2 = 99.5\%$, $SE = 0.0615$) for chlorides, bromides, aldehydes, methyl

Table 10
Regression parameters of Eq. (9) for the particular series $H-(CH_2)_n-Y$

Parameter ^a	Y=Cl	Y=Br	Y=CHO	Y=COOCH ₃	Y=OCOCH ₃
a_0	-223.25 (9.96)	-227.41 (6.43)	-307.39 (32.50)	-269.01 (22.83)	-267.20 (23.34)
a_1	2902.79 (187.69)	3132.23 (132.75)	4625.65 (648.97)	3988.97 (462.19)	3994.50 (444.59)
a_2	12.06 (0.27)	11.91 (0.20)	12.05 (0.65)	11.77 (0.53)	11.96 (0.46)
R^2 [%]	97.76	99.33	95.52	95.04	92.59
MAE ^b	10.14	6.09	20.44	18.88	26.50
N ^c	99	88	66	88	108
$n(A)_{opt}$	$n(Y) + 0.945$	$n(Y) + 1.856$	$n(Y) + 2.997$	$n(Y) + 2.993$	$n(Y) + 3.061$

^a Asymptotic standard errors are given in parentheses.

^b Mean absolute error.

^c Number of points.

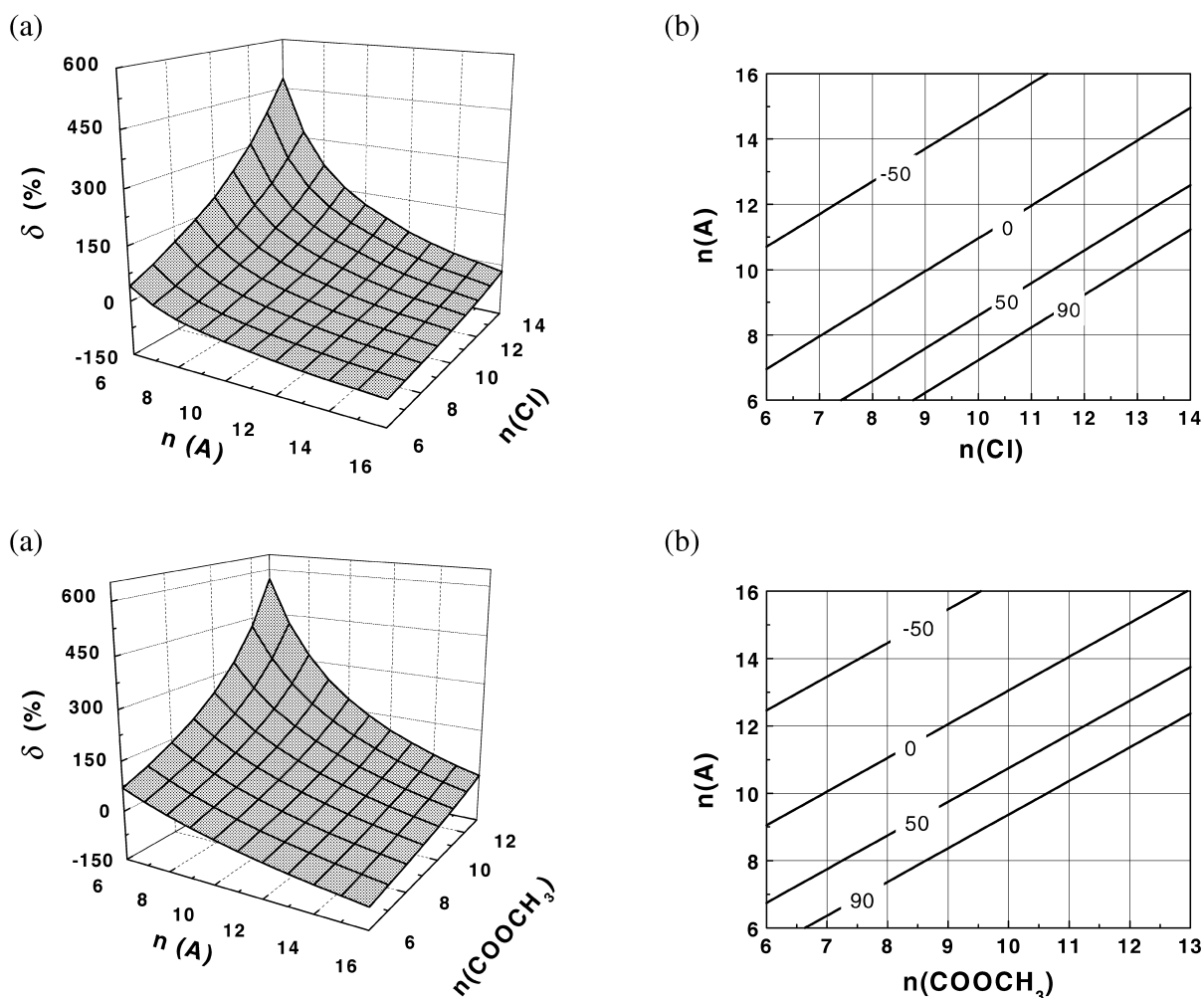


Fig. 2. Fitted response surfaces (a) and contour plots (b) representing Eq. (9) for homologous n -alkyl chlorides and methyl esters.

esters and acetates, predicting practically the same values of q [$q=0.976$ ($Y=\text{Cl}$), 2.056 ($Y=\text{Br}$), 2.941 ($Y=\text{CHO}$), 3.017 ($Y=\text{COOCH}_3$) and 3.009 ($Y=\text{OCOCH}_3$)] as did Eq. (9) for $\delta=0$ (cf. Table 10). The closest (within the standard error) integers that would correspond to real alkanes are thus 1, 2, 3, 3 and 3, respectively. The relationship expressed by Eq. (11) suggests an easy implementation and the capability to predict appropriate reference alkanes across varied structural classes of $\text{H}-(\text{CH}_2)_n-\text{Y}$ homologues ($6 \leq n \leq 16$), whose vaporization enthalpy contribution increment ΔH_i (Y) is known and tabulated. We have utilized q -values predicted by Eq. (11) to select appropriate n -alkane references within

a given compound class when dealing with Method A.

In an attempt to understand the physical significance of the optimized $q=n(\text{A})-n(\text{Y})$ values, we have checked the possibility that the q -values might accommodate the effect of minimized differences between the combinatorial (entropic) contributions $\gamma_i^\infty(\text{comb})$ to γ_i^∞ and γ_2^∞ . The combinatorial part of γ_i^∞ accounts for differences in size and shape between the molecules in solution and, according to Flory–Huggins [49] is described by the equation:

$$\ln \gamma_i^\infty(\text{comb}) = \ln(V_i/V) + 1 - (V_i/V) \quad (12)$$

where V_i and V represent the solute and the stationary

phase molar volumes. For two similar solutes 1 and 2 it holds that $(V_1 - V_2) \ll V$ and Eq. (12) simplifies to:

$$\gamma_1^\infty(\text{comb})/\gamma_2^\infty(\text{comb}) = V_1/V_2 \quad (13)$$

Assuming that the volume ratio term can be approximately expressed using the Van der Waals molecular volumes, we may in terms of the Van der Waals group contributions [50,51] equate $n(\text{A}) = (V_{\text{T}}^{\text{AW}} - 13.67 - 3.44)/10.23$ and $n(\text{Y}) = (V_{\text{T}}^{\text{YW}} - V^{\text{YW}} - 3.44)/10.23$ with V_{T}^{AW} , V_{T}^{YW} and V^{YW} representing the total molecular volumes of an optimal alkane, corresponding Y-substituted derivative and the van der Waals volume contribution of the functional group Y. The optimized difference $n(\text{A}) - n(\text{Y})$ is then given by:

$$n(\text{A}) - n(\text{Y}) = [(V_{\text{T}}^{\text{AW}} - V_{\text{T}}^{\text{YW}}) - (13.67 - V^{\text{YW}})] = q \quad (14)$$

where q values corresponding to each homologous series are given in Table 10. Hence, we can write:

$$V_{\text{T}}^{\text{AW}} - V_{\text{T}}^{\text{YW}} = q + (13.67 - V^{\text{YW}}) = C^{\text{Y}} \quad (15)$$

and, combining Eqs. (13) and (15):

$$\frac{V_{\text{T}}^{\text{AW}}}{V_{\text{T}}^{\text{YW}}} = \frac{\gamma_{\text{A}}^\infty(\text{comb})}{\gamma_{\text{Y}}^\infty(\text{comb})} = 1 + \frac{C^{\text{Y}}}{V_{\text{T}}^{\text{YW}}} \quad (16)$$

where C^{Y} is a constant characteristic for each homologous series. The values of C^{Y} are listed in Table 11 together with estimated maximum values of the second term on the right side of Eq. (16). The results demonstrate that, along our series of test compounds, the magnitude of $C^{\text{Y}}/(V_{\text{T}}^{\text{YW}})_{\text{min}}$ varies in the range 0.15–0.37. Consequently, the optimized

Table 11
Parameters of Eq. (16)

Y	C^{Y} (ml/mol)	$(V_{\text{T}}^{\text{YW}})_{\text{min}}$ (ml/mol) ^a	$\frac{C^{\text{Y}}}{(V_{\text{T}}^{\text{YW}})_{\text{min}}}$
Cl	11.717	76.44	0.15
Br	18.257	79.22	0.23
CHO	29.629	79.52	0.37
COOCH ₃	15.917	94.95	0.16
OCOCH ₃	15.824	94.95	0.15

^a Van der Waals volumes of the lowest series members ($n=6$).

choices of reference alkanes as described in this section correspond to the activity coefficient ratios differing from 1 by 15–37% at the most. Although this difference is not negligible, we feel that further elaboration would be untimely, since some of the assumptions made in establishing Eq. (16) are such that even larger departures can be expected.

3.4. A comparison of vapour pressures estimated by retention models A–E

Once a selection criterion for reference alkanes to be used in model A had been found, retention data provided in Tables 1–7 were fitted to functions corresponding to the particular models (Fig. 1) to evaluate their performances in estimating vapour pressures for all forty compounds investigated.

When determining the vapour pressures at 25°C from GC retention data, it is a common practice [12,21] to correct the p_{GC}^0 values for systematic errors by using a linear correlation of the form:

$$\ln p_{\text{ref}}^0 = b_0 + b_1 \ln p_{\text{GC}}^0 \quad (17)$$

where p_{ref}^0 denotes the relevant literature vapour pressure data. Considering that in an ideal case the constants b_0 and b_1 should approach 0 and 1 respectively, Eq. (17) was used as a first criterion to compare the results provided by the particular models.

The regression coefficients and the statistical analysis of Eq. (17) are shown in Table 12. Results of the regression indicate that all five models are able to predict vapour pressures correlating very well with reference literature data. Diagnostic statistics associated with the best two models D and A were: $R^2=99.87$ and 99.87% with corresponding MAE=0.079 and 0.067. The correlation is getting slightly poorer for models B and C, amounting $R^2=98.60\%$ and MAE=0.227 for model E. Notably, three models (A, B and D) produce intercepts of lower statistical significance ($P=0.01$ – 0.7) along with slopes very close to 1 while models C and E do not satisfy this requirement.

A comparison of relative errors (δ) produced by models A–E is shown in Fig. 3 using the same set of data that were involved in Eq. (17). It may be quickly gathered from Fig. 3 that of the models

Table 12
Regression parameters of Eq. (12)

Model	b_0^a	b_1^a	R^2 (%)	MAE ^b	F ^c
A	0.0610 (0.0385)	0.9890 (0.0055)	99.87	0.067	30910.9
B	0.0396 (0.0250)	0.9922 (0.0076)	99.77	0.115	16966.6
C	0.2756 (0.0202)	0.9339 (0.0060)	99.84	0.088	24089.4
D	-0.0056 (0.0191)	0.9789 (0.0057)	99.87	0.079	29542.0
E	0.3024 (0.0581)	0.9585 (0.0185)	98.60	0.227	2671.2

^a Standard error is given in parentheses.

^b Mean absolute error.

^c Fisher *F*-test.

based on measuring the Kováts' retention indices (models B, C and D), the models B and D provide rather similar results. The course of $\delta = f(n)$ dependence for particular classes of compounds, as well as the maximum error (δ_{\max}) limits, are surprisingly similar for both models. Additionally, both models show a tendency to overestimate p^0 of all aldehydes and lower ($n < 9$) methyl esters while a tendency to underestimate p^0 is observed for higher ($n > 8$) acetates. Unlike the B and D cases, the C model appears to rather generally underestimate p^0 values for all homologous series members with $n = 10$. It can be concluded from these findings that models C and D do not offer a significant improvement over model B, despite their more sophisticated features. The problems associated with the use of McReynolds constants have been discussed before [30].

The controlled selection of reference alkanes appears to bring an important improvement for relative retention-based model A, making it at least competitive to other apparently more complete models. Regardless of its most commonly voiced deficiency, which revolves around the assumptions $\gamma_2^\infty/\gamma_1^\infty = 1$ and $\Delta_{\text{vap}}H_{\text{rel}} = \text{const.}$ over a modest temperature range, the modified model A was found to reproduce the experimental data well, the highest differences being found for acetates ($\delta_{\max} = 22.7\%$ for undecyl acetate).

In order to form an opinion on the capability of

each of the models to estimate vapour pressures for substances corresponding to their respective classification, the results expressed as average absolute percent errors, $\delta_\phi[\%]$:

$$\delta_\phi[\%] = (1/N)\sum|\delta| \quad (18)$$

where N is the number of experimental data, have been summarized in Table 13. This table presents the gross average errors associated with different classes of compounds and thus assists in a broad sense to assess the capability of each model to estimate p^0 for each class of compounds.

A cursory review of the errors presented in Table 13 indicates that for certain classes of compounds (acetates) all models yield relatively high (more than about 12%) δ_ϕ , while for other compound classes the magnitude of δ_ϕ is found to be model-dependent. However, the highest errors along all classes of compounds are invariably associated with the use of model E. In general, the models considered in this study yield average absolute percent errors that range between 9.2% (model A) to 24.7% (model E).

4. Conclusions

To compare the performance of the five models suggested for extracting saturated vapour pressure

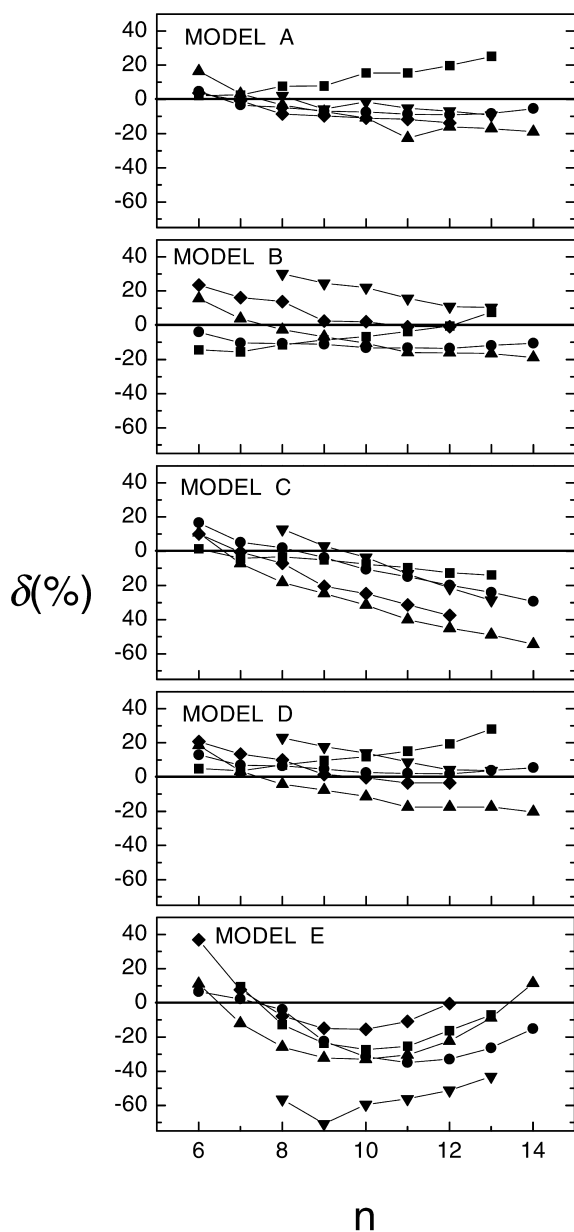


Fig. 3. Summary of relative percent errors (δ) according to applied models (● = chlorides, ■ = bromides, ▼ = aldehydes, ◆ = methyl esters, ▲ = acetates).

data from gas chromatographic retention, a common comparison set of forty chemicals for which independently measured vapour pressure data have

been reported was assembled. These chemicals cover a range of five homologous series and span a wide range (about five orders of magnitude) of pressures. The following conclusions can be made on the basis of the preceding comparison results: (a) The average absolute percent error, δ_{ϕ} , associated with the use of models A–E increases in the order A ($\delta_{\phi}=9.2\%$) < D ($\delta_{\phi}=10.4\%$) < B ($\delta_{\phi}=11.9\%$) < C ($\delta_{\phi}=17.5\%$) < E ($\delta_{\phi}=24.7\%$). Hence, of all models under consideration, only three (A, B, and D) are able to reproduce directly measured vapour pressure data with δ_{ϕ} under 12%. Given the rather small differences in δ_{ϕ} among models A, B, and D, as well as paucity of really accurate direct experimental p_{ref}^0 data, it seems not meaningful to prefer any of these models.

(b) It appears that model A, despite its simplicity, is capable of producing good results, provided that an appropriate alkane is selected as a reference compound. An empirical selection criterion, requiring only the knowledge of $\Delta_{\text{vap}}H_i$ increments to characterize the functional groups of the respective test series, has been suggested.

(c) Considering that the error in direct vapour pressure measurement “.. is at best 6%, but may be much larger, a factor of 2–3..” [52], the present results support a view that the GC-based methodology represented by models A, B, and D may serve as a very useful alternative to direct physicochemical approaches.

Although this investigation has been limited to only five homologous series, the results offer a strong inference that the general conclusions should be applicable to other non-polar and/or moderately polar series of homologues. The extension beyond this class of compounds deserves further consideration and treatment.

Acknowledgements

This work was done in the framework of the research project Z4 055 905. We also wish to thank the Grant Agency of the Czech Republic for financial support (Grant No 203/00/0219).

Table 13

Summary of average percent errors δ_{ϕ} , according to the functional groups in homologous series H-(CH₂)_n-Y

Y	Number of substances	δ_{ϕ} (%)				
		Model A	Model B	Model C	Model D	Model E
Cl	9	6.5	10.9	14.0	5.2	19.6
Br	8	12.0	8.5	7.2	12.5	15.3
CHO	6	5.1	19.0	13.9	12.0	56.2
COOCH ₃	8	8.1	11.2	19.0	9.9	20.6
OCOCH ₃	9	12.9	11.9	31.2	13.1	20.8
Overall	40	9.2	11.9	17.5	10.4	24.7

References

- [1] H.F. Hemond, E.J. Fechner, *Chemical Fate and Transport in the Environment*, Academic Press, New York, 1994, Chapter 1.
- [2] B. Choy, D.D. Reibe, *Diffusion Models of Environmental Transport*, Lewis Publishers, Boca Raton, FL, 2000, Chapter 1.
- [3] M. Tesconi, S.H. Yalkowsky, *J. Pharm. Sci.* 87 (1998) 1512.
- [4] T. Kröhl, R. Kästel, W. König, H. Ziegler, H. Köhle, A. Parg, *Pestic. Sci.* 53 (1998) 300.
- [5] A.D. Site, *J. Phys. Chem. Ref. Data* 26 (1997) 157.
- [6] S.F. Donovan, *J. Chromatogr. A* 749 (1996) 123.
- [7] H. Purnell, *Gas Chromatography*, Wiley, New York, 1962, p. 206.
- [8] C.B. Castells, R.C. Castells, *J. Chromatogr. A* 755 (1996) 49.
- [9] J. Novak, in: J.A. Jonsson (Ed.), *Chromatographic Theory and Basic Principles*, Marcel Dekker, New York, 1987, p. 103.
- [10] D.J. Hamilton, *J. Chromatogr.* 195 (1980) 75.
- [11] J.W. Westcott, T.F. Bidleman, *J. Chromatogr.* 210 (1981) 331.
- [12] T.F. Bidleman, *Anal. Chem.* 56 (1984) 2490.
- [13] Y.-H. Kim, J.E. Woodrow, J.N. Seiber, *J. Chromatogr.* 314 (1984) 37.
- [14] W.T. Foreman, T.F. Bidleman, *J. Chromatogr.* 330 (1985) 203.
- [15] B.D. Eitzer, R.A. Hites, *Environ. Sci. Technol.* 22 (1988) 1362.
- [16] D.W. Hawker, *Environ. Sci. Technol.* 23 (1989) 1250.
- [17] D.A. Hinckley, T.F. Bidleman, W.T. Foreman, J.R. Tusshall, *J. Chem. Eng. Data* 35 (1990) 232.
- [18] P.M. Sherblom, P.M. Gschwend, R.P. Eganhouse, *J. Chem. Eng. Data* 37 (1992) 394.
- [19] D.W. Hawker, *Chemosphere* 25 (1992) 427.
- [20] H.-W. Kuo, J.-D. Wang, J.-M. Lin, *Chemosphere* 24 (1992) 1679.
- [21] B. Koutek, M. Hoskovec, P. Vrkočová, K. Konečný, L. Feltl, *J. Chromatogr. A* 679 (1994) 307.
- [22] B. Koutek, M. Hoskovec, P. Vrkočová, K. Konečný, L. Feltl, J. Vrkoč, *J. Chromatogr. A* 719 (1996) 391.
- [23] B. Koutek, M. Hoskovec, P. Vrkočová, L. Feltl, *J. Chromatogr. A* 759 (1997) 93.
- [24] R.C. Fischer, R. Wittlinger, K. Ballschmiter, *Fresenius J. Anal. Chem.* 342 (1992) 421.
- [25] W. Spieksma, R. Luijk, H.A.J. Govers, *J. Chromatogr. A* 672 (1994) 141.
- [26] A.G. van Haelst, F.W.M. van der Wielen, H.A.J. Govers, *J. Chromatogr. A* 727 (1996) 265.
- [27] E. Tudor, *J. Chromatogr. A* 779 (1997) 287.
- [28] H.B. Krop, M.J.M. van Velzen, J.R. Parsons, H.A.J. Govers, *J. Am. Oil Chem. Soc.* 74 (1997) 309.
- [29] E. Tudor, *J. Chromatogr. A* 858 (1999) 65.
- [30] W. Spieksma, *J. High Resolut. Chromatogr.* 22 (1999) 565.
- [31] R.G. Fischer, K. Ballschmiter, *Fresenius J. Anal. Chem.* 360 (1998) 769.
- [32] T.C. Gerbino, G. Castello, *J. Chromatogr.* 537 (1991) 305.
- [33] B. Koutek, M. Hoskovec, L. Streinz, P. Vrkočová, K. Růžička, *J. Chem. Soc. Perkin Trans. 2* (6) (1998) 1351.
- [34] J.S. Chickos, S. Hosseini, J.F. Liebman, *J. Org. Chem.* 58 (1993) 5345.
- [35] K. Růžička, V. Majer, *J. Phys. Chem. Ref. Data* 23 (1994) 1.
- [36] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, 77th ed., CRC Press, Boca Raton, 1996–1997.
- [37] K. Růžička, V. Majer, *AIChE J.* 42 (1996) 1723.
- [38] J.C.M. Li, F.D. Rossini, *J. Chem. Eng. Data* 6 (1961) 268.
- [39] R.R. Dreisbach, *Physical Properties of Chemical Compounds*, Vol. III, ACS, Washington, 1961.
- [40] H.R. Kremme, S.I. Kreps, *J. Chem. Eng. Data* 14 (1969) 98.
- [41] J. Dykyj, M. Repáš, J. Svoboda, *Tlak nasýtenej pary organických zlúčenín*, Veda, Bratislava, Vol. I, 1979; Vol. II, 1984.
- [42] G.N. Djakova, G.L. Korichev, A.D. Korkhov, T.F. Vasiljeva, *Zh. Prikl. Khim.* 54 (1981) 1644.
- [43] E.F. Meyer, M.J. Awe, R.E. Wagner, *J. Chem. Eng. Data* 25 (1980) 371.
- [44] J.W. Shigley, C.W. Bonhorst, C.C. Liang, P.M. Althouse, H.O. Triebold, *J. Am. Oil Chem. Soc.* 32 (1955) 213.
- [45] Y. Hirooka, M. Suwanai, *Appl. Entomol. Zool.* 13 (1978) 38.
- [46] M. Ducros, J.F. Greison, H. Sannier, I. Velasco, *Thermochim. Acta* 44 (1981) 134.
- [47] V. Majer, V. Svoboda, V. Pick, J. Pick, *Heats of Vaporization of Fluids*, Academia, Prague, 1989, p. 161.

- [48] K.I. Goss, R.P. Schwarzenbach, *Environ. Sci. Technol.* 33 (1999) 3390.
- [49] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [50] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [51] T. Hanai, *J. High Resolut. Chromatogr.* 13 (1990) 178.
- [52] N.N. Nirmalakhandan, R.E. Speece, *Environ. Sci. Technol.* 22 (1988) 1349.