Determination of the liquid vapour pressure of low-volatility compounds from the Kováts retention index

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Abstract

The isothermal gas–liquid chromatographic Kováts retention index and an infinite dilution equilibrium fugacity model are combined to arrive at an expression relating the Kováts indices and the McReynolds numbers of a series of compounds to their isothermal pure liquid vapour pressures. This novel expression is the basis for ultra-low vapour pressure determination at environmentally relevant temperatures of pure organic (sub-cooled) liquids by routine gas–liquid chromatography on a non-polar stationary phase. Examples of the potential of the method are given for chlorobenzenes and chlorophenols.

1. Introduction

The vapour pressure of a compound is a physico-chemical property important for, *e.g.*, the assessment of its fate in the environment [1]. The latter demands (sub-cooled) liquid vapour pressure data at environmentally relevant temperatures, often lying below the compound's melting point. Experimental data on vapour pressures for series of compounds are required for the development of quantitative structure–activity relationships (QSARs) for vapour pressure, heat of vaporization and Henry's law constants [2].

In order to measure vapour pressure, gas saturation, effusion and gas–liquid chromatographic (GLC) methods can be used. GLC methods have several advantages over the other

methods [3]. They are not sensitive to volatile impurities, can be carried out with only small amounts of compound, are fast and require less care in obtaining accurate and reproducible results.

GLC can separate compounds with different volatilities in the liquid stationary phase. The volatility or retention of a solute depends on both its activity coefficient in the stationary phase and its vapour pressure in the pure liquid state [4]. The measurement of a single GLC retention parameter produces only one data point, which therefore is insufficient for the purpose of vapour pressure determination. In addition, the value of the activity coefficient (measured or estimated) is required.

Several attempts have been made in order to solve this fundamental problem [3,5–7]. In all instances relatively non-polar stationary phases and one or more reference compounds with known vapour pressures have been employed.

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The basic expression for most of these determinations is the Hamilton equation [7]:

$$\ln P_1 = (\Delta H_1 / \Delta H_2) \ln P_2 + C$$

where 1 refers to the compound under investigation and 2 to the reference compound, P and ΔH are the vapour pressure and heat of vaporization, respectively, and C is a constant. The ratio of specific retention volumes V_{R1}/V_{R2} is equated to the ratio of the vapour pressures P_1/P_2, which is equivalent to equating the activity coefficients of compounds 1 and 2. After substitution into the Hamilton equation, the final expression is obtained:

$$\ln (V_{R1}/V_{R2}) = (1 - \Delta H_1 / \Delta H_2) \ln P_2 - C$$

Plotting the measured specific retention volumes against known vapour pressures P_2 at different temperatures thus yields the assumed temperature-independent $\Delta H_1 / \Delta H_2$ and C and, via the Hamilton equation, also P_1 at different temperatures.

In addition, a direct correlation equation of the type

$$-\log P = B_0 + B_1 I$$

has been used to express the relationship between the vapour pressure at 25°C and the Kováts GLC retention index (I) at 200°C for a series of compounds [8]. Once the I and P values of a number of compounds in a series have been measured, B_0 and B_1 can be found through linear regression. After measurement of the I values of other members of the series, their vapour pressures at 25°C can be calculated from this correlation equation. The Kováts index used in this method expresses the specific retention time or volume of a compound i relative to two n-alkanes with z and $z + 1$ carbon atoms, eluting before and after the compound, respectively [9]:

$$I_i = 100(\log V_{Ri} - \log V_{Rz})/(\log V_{Rz+1} - \log V_{Rz})$$
$$+ 100z \qquad (1)$$

The authors [8] did not explain how the pertinent correlation equation can be derived from this definition. However, it will be shown here that a constant ratio of the activity coefficients of

i and z forms part of a larger number of necessary assumptions.

It should be pointed out that the physical chemistry behind the Kováts index allows one to measure (sub-cooled) liquid vapour pressures at environmentally relevant temperatures on a non-polar GLC column. The McReynolds number [10] of a model compound in the GLC liquid phase is used for quantification of its activity coefficient. Vapour pressure data for liquid n-alkanes [11] are used as reference pressures. Only isothermal Kováts indices at two or more temperatures need to be measured on a non-polar GLC column. As a first validation of this method, the (sub-cooled) liquid vapour pressures of chlorobenzenes and chlorophenols were determined at 25 and 160°C, respectively. Kováts indices measured by Haken and co-workers [12,13] were applied. The specific advantages with respect to other GLC methods are discussed below.

2. Method and results

2.1. Description of the method

The method includes main assumptions on the combination of the Kováts index and an infinite dilution equilibrium fugacity model, ratios of activity coefficients of solute/n-alkane (γ_i/γ_z) and subsequent n-alkanes (γ_{z+1}/γ_z) and the temperature dependence of the Kováts index. These assumptions will be described below along with a summary of the procedure in order to obtain vapour pressures.

2.2. Kováts index and infinite dilution equilibrium fugacity

The Kováts index of a compound i is defined according to Eq. 1. By definition the term $100z$ is the Kováts index I_z of an n-alkane with z carbon atoms. Instead of the specific retention volume, one may use other retention parameters in this equation such as the net retention times $t_i - t_0$, $t_z - t_0$ and $t_{z+1} - t_0$ or the capacity factors ($t_i - t_0)/t_0$, etc., provided that a constant carrier gas

flow-rate is applied [4]; t_0 is the dead retention time of a non-sorbed compound, representing the passage of this compound through the column, including extra-column inlet and outlet spaces.

The equilibrium fugacity model states that the ratio of the mole fraction y_i and x_i in the carrier gas and stationary phase, respectively, is proportional to the activity coefficient γ_i and the vapour pressure P_i of the incompressible pure liquid compound i [4]:

$$y_i / x_i = \gamma_i P_i / P_t \qquad (2)$$

where P_t is the (mean) carrier gas pressure; $\gamma_i = 1$ for pure liquids and ideal solutions. It is assumed that the pure vapour and the vapour–carrier gas mixture both exhibit ideal behaviour or both exhibit identical non-ideal behaviour.

In order to derive an expression for the Kováts index as a function of activity coefficients and vapour pressures, we proceed as follows. It can be shown that at infinite dilution the capacity factor is inversely proportional to the ratio y_i / x_i (or volatility) of compound i in Eq. 2 [4]. The same holds true for the n-alkanes z and $z + 1$. Substitution of these relationships between volatility and capacity factor into Eq. 2 yields relationships between capacity factor and activity coefficient plus vapour pressure. After subsequent substitution of the latter relationships into Eq. 1, one ultimately arrives at

$$I_i = I_z + 100(\log \gamma_z P_z - \log \gamma_i P_i)/(\log \gamma_z P_z$$
$$- \log \gamma_{z+1} P_{z+1}) \qquad (3)$$

In Eq. 3, both the vapour pressures and the activity coefficients are temperature dependent. In addition, the activity coefficients depend on the nature of the stationary phase. Thus the Kováts index is dependent on both temperature and the nature of the stationary phase.

2.3. Ratios of activity coefficients for homologous series

Eq. 3 does not solve the fundamental problem described in the Introduction. This problem will be approached here through the assumption that

ratios between activity coefficients (γ_i / γ_z and γ_{z+1} / γ_z) are constants for (homologous) series of related compounds.

First, a simple and accurate log–linear regression relationship, $\log P_z = \log P_{H_2} + (\mathrm{d} \log P_z / \mathrm{d}z)z$, exists between the liquid vapour pressure and carbon number z of an n-alkane [H(CH$_2$)$_z$H] [13] that can be written in terms of its Kováts index:

$$\log P_z = (\mathrm{d} \log P_z / \mathrm{d}I_z)I_z + \log P_{H_2} \qquad (4)$$

where P_{H_2} is the vapour pressure of liquid hydrogen ($z = 0$). Application of Eq. 4 to both n-alkanes z and $z + 1$ yields a simple expression for $\log (P_z / P_{z+1})$. In Table 1 values of the regression coefficients and vapour pressure ratios for n-alkanes at different temperatures are given, based on Antoine constants derived from experimental vapour pressure data [11]. The lower the temperature, the larger is the decrease in vapour pressure with increase in carbon number and the higher is the vapour pressure ratio between two subsequent n-alkanes. The maximum errors in the slope and intercept of Eq. 4 amount to 1% and 0.5%, respectively.

Second, an evaluation of the ratio γ_z / γ_{z+1} at 120°C reveals that this ratio can be approximated by 1 ($\gamma_z = \gamma_{z+1}$) within an overestimation error of 2–18% depending on the nature of the stationary phase. The results of this evaluation are given in Table 2. They were obtained by evaluating net retention data for n-alkanes at 120°C [10] using the relationship $(t_i - t_0)/(t_z - t_0) = (\gamma_z P_z)/(\gamma_i P_i)$

Table 1
Calculated regression coefficients of Eq. 4 and vapour pressure ratios of n-alkanes at different temperatures (T) using Antoine constants [11] with 95% confidence limits in parentheses

T (°C)	$\mathrm{d} \log P_z / \mathrm{d}I_z \cdot 10^{-3}$	$\log P_{H_2}$ [a]	z	P_z / P_{z+1}
180	−2.257 (0.021)	5.181 (0.016)	10–18	1.681
160	−2.454 (0.023)	5.151 (0.018)	10–18	1.759
140	−2.684 (0.027)	5.129 (0.021)	10–18	1.855
120	−2.985 (0.035)	5.119 (0.027)	10–18	1.976
25	−5.213 (0.009)	5.315 (0.008)	5–14	3.322

[a] Log P values based on P in Torr (1 Torr = 133.322 Pa).

Table 2
Ratios of experimental net retention times taken from the literature [10] and ratios of activity coefficients of subsequent *n*-alkanes on different stationary phases at 120°C, calculated from these and from the vapour pressure ratios in Table 1 (see text)

Stationary phase	$(t_{z+1} - t_0)/(t_z - t_0)$	γ_z/γ_{z+1}
Squalane	1.945	1.016
SE-30, DB1	1.776	1.113
OV-101	1.771	1.116
OV-3, DB5	1.797	1.100
OV-17	1.799	1.098
Carbowax 20M	1.673	1.181

also used in the derivation of Eq. 3 and applying the vapour pressure ratios in Table 1.

After insertion of Eq. 4 and $\gamma_z = \gamma_{z+1}$ into Eq. 3 and some rearrangements, the isothermal pure liquid vapour pressure P_i can be written as a function of the isothermal Kováts index I_i of component *i*:

$$\log P_i = (\text{d} \log P_z/\text{d}I_z)I_i + \log P_{H_2} + \log(\gamma_z/\gamma_i)$$
(5)

Finally, an assumption has to be introduced regarding the ratio γ_z/γ_i in Eq. 5. This can be

expressed in the ΔI values of McReynolds [10]. ΔI of a compound on a stationary phase is its shift in Kováts index compared with the most non-polar stationary phase squalane (Sq). It follows from Eq. 5, with $\Delta I = I_i - I_i(\text{Sq})$, written explicitly in terms of the ratio of the activity coefficients, that

$$\log (\gamma_z/\gamma_i) = \log [\gamma_z(\text{Sq})/\gamma_i(\text{Sq})]$$
$$- (\text{d} \log P_z/\text{d}I_z) \Delta I$$
(6)

The activity coefficient ratios at 120°C of compounds containing typical functional groups can be evaluated using data from McReynolds [10] and Eqs. 5 and 6 (see Table 3). McReynolds measured the Kováts indices of 68 compounds on 25 liquid phases and selected the ten most characteristic compounds to give the best prediction of the Kováts index on different stationary phases. For these ten compounds the Kováts index was measured on more than 200 liquid phases. For chlorinated compounds (*e.g.*, chlorobenzenes) 1-iodobutane is the best compound to predict Kováts indices, whereas for alcohols (*e.g.*, phenols) 2-methyl-2-pentanol is the better predictor [9]. In addition, ΔI and γ_z/γ_i values are considered to be temperature independent. As

Table 3
Calculated activity coefficient ratios at 120°C of compounds with different functional groups on SE-30 and Carbowax 20M (CW-20) stationary phases, calculated with Eqs. 5 and 6, and auxiliary data from the literature

Compound	$I_i(\text{Sq})$ [a]	P_i [b] (Torr)	Log $\gamma_z/\gamma_i(\text{Sq})$ [c]	ΔI [a]		Log (γ_z/γ_i) [d]	
				SE-30	CW-20	SE-30	CW-20
Benzene	653	2297	0.191	15	322	0.236	1.153
1-Butanol	590	823	−0.442	53	536	−0.284	1.158
2-Pentanone	627	1260	−0.147	44	368	−0.016	0.952
Nitropropane	652	546	−0.436	64	572	−0.245	1.272
Pyridine	699	871	−0.093	41	510	0.030	1.430
2-Methyl-2-pentanol	690	739	−0.191	31	387	−0.098	0.964
1-Iodobutane	818	575 [e]	0.083	3	282	0.092	0.924
2-Octyne	841	466 [e]	0.060	22	221	0.126	0.720
1,4-Dioxane	654	1310	−0.049	44	434	0.082	1.246

[a] Data from ref. 9.
[b] Data from ref. 11.
[c] Calculated using Eq. 5.
[d] Calculated using Eq. 6.
[e] Using the Clausius–Clapeyron equation and the enthalpies of vaporization and boiling points from ref. 16.

far as γ_z/γ_i is concerned, the same assumption is made in the well known Flory–Huggins athermal approximation for polymer solutions [4].

2.4. Kováts index and temperature

From Eq. 3, it follows that the Kováts index will be a complicated function of temperature. However, a simple linear relationship was given by Kováts [9]:

$$I_i = (dI_i/dT)T + I_{i0} \tag{7}$$

In Eq. 7, the intercept I_{i0} is the Kováts index at $T = 0°C$. In Table 4, Eq. 7 is evaluated using Kováts indices for chlorobenzenes at 140, 160 and 180°C on non-polar SE-30 and polar Carbowax 20M stationary phases.

The difference in temperature dependence of the Kováts index (i.e., the difference in the slope dI_i/dT; see Table 4) on two stationary phases can only originate from different temperature dependences of the activity coefficients in Eqs. 3 and 5. The Kováts index on the non-polar SE-30 stationary phase shows the best linear behaviour (lowest errors in slope and intercept).

According to Kováts [9], an inversion of the elution sequence of compounds when extrapolating from $I_i(T)$ to I_{i0} normally does not occur.

Table 4
Regression coefficients of Eq. 7 on SE-30 and Carbowax 20M stationary phases using Kováts indices at 140, 160 and 180°C [12] with 95% confidence limits in parentheses

Chlorobenzene congener	SE-30		Carbowax 20M	
	I_{i0}	dI_i/dT $(°C^{-1})$	I_{i0}	dI_i/dT $(°C^{-1})$
Mono-	815 (1)	0.15 (0.03)	1144 (2)	0.80 (0.09)
1,2-Di-	972 (2)	0.48 (0.07)	1000 (2)	3.20 (0.09)
1,3-Di-	985 (1)	0.20 (0.03)	1077 (23)	2.35 (0.81)
1,4-Di-	993 (3)	0.15 (0.06)	1155 (10)	2.28 (0.36)
1,2,3-Tri-	1111 (3)	0.75 (0.12)	1458 (4)	1.75 (0.14)
1,2,4-Tri-	1098 (2)	0.60 (0.06)	1388 (9)	1.70 (0.32)
1,3,5-Tri-	1091 (1)	0.38 (0.04)	1250 (6)	1.88 (0.22)
1,2,3,4-Tetra-	1209 (1)	1.13 (0.04)	1627 (2)	1.75 (0.06)
1,2,3,5-Tetra-	1195 (3)	0.95 (0.12)	1532 (2)	1.75 (0.09)
1,2,4,5-Tetra-	1195 (3)	0.95 (0.12)	1508 (3)	1.65 (0.12)
Penta-	1339 (3)	1.18 (0.10)	1710 (6)	1.78 (0.22)
Hexa-	1497 (2)	1.25 (0.09)	1849 11)	2.00 (0.40)

dI_i/dT values are small for most compounds and constant over a wide range of temperatures. Errors resulting from extrapolation over 100°C amount to a few I units at the maximum. From Fig. 1, it can be inferred that inversion occurs only for 1,2-dichlorobenzene with respect to the 1,3-plus 1,4-isomers.

2.5. Determination of pure liquid vapour pressure using the Kováts index

On the basis of Eq. 5, a general procedure can be described for the determination of the vapour pressure of compound i (P_i) or of a series of related compounds at a particular temperature (T').
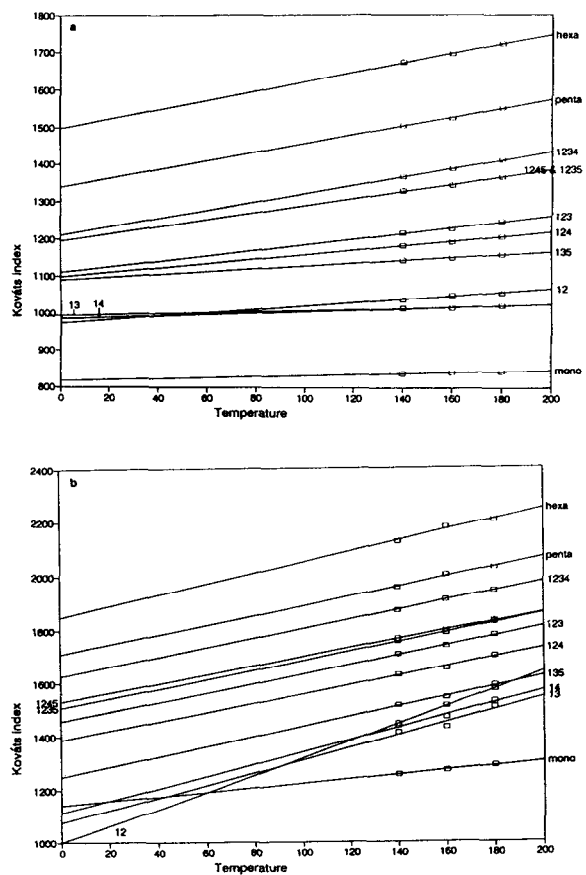

Fig. 1. Kováts indices (I) of chlorobenzenes on (a) non-polar SE-30 and (b) polar Carbowax 20M GLC stationary phases as a function of temperature $(T, °C)$.

The first step is the routine measurement of the isothermal Kováts index (I_t) of compound i at two or more temperatures on a non-polar column (*e.g.*, SE-30 or DB1). These temperatures have to be as close as possible to T' in order to minimize extrapolation errors.

The second step is the calculation of I_i at T' with the help of Eq. 7 by extrapolation from the experimental temperatures to T'.

The third step is the calculation of the regression coefficients d log P_z/dI_z and log P_{H_2} at T' using data from Ohé [11] for liquid *n*-alkanes in Eq. 4. Table 1 already provides regression coefficients at some specified temperatures.

The fourth step is the calculation of log γ_z/γ_i from Eq. 6, using ΔI values from McReynolds [10] for the pertinent stationary phase and the compound with the proper functional group or using data from Table 3.

The final step is the calculation of the vapour pressure at the desired temperature inserting I_i, log P_{H_2}, d log P_z/dI_z and log (γ_i/γ_z) in Eq. 5.

2.6. Determination of the vapour pressures of chlorobenzenes and chlorophenols

Validation of the method

The procedure described in the previous section can be validated by comparison of vapour pressure values obtained in this way with vapour pressure data obtained independently via other methods. Especially the fourth step in our procedure is associated with several uncertainties with respect to the choice of the proper model chemical and the availability of data at only one temperature (120°C). Experimental vapour pressure data suitable for this purpose are available for chlorobenzenes and chlorophenols [14]. For these compounds we can use Kováts indices already available in the literature [12,13] in order to obtain vapour pressure values determined via our method.

Vapour pressure and heat of vaporization of chlorobenzenes at 25°C

The vapour pressures of (sub-cooled) liquid chlorobenzenes at 25°C were determined accord-

ing to our method with the help of Eq. 5. Experimental Kováts indices on an SE-30 stationary phase [12] were extrapolated to 25°C using the data in Table 4. (Mean) values of the regression coefficients d log P_z/dI_z and log P_{H_2} at 25°C were available from Table 1. The log (γ_z/γ_i) value of 1-iodobutane at 120°C on SE-30 from Table 3 was used. With the help of the same data and additional calculations of the regression coefficients of Eq. 4, the vapour pressures at 0, 5, 10, 15 and 20°C were calculated and from these, using the Clausius–Clapeyron equation, the heats of vaporization (ΔH) in the temperature range 0–25°C. The results are given in Table 5. Deviations from current data are considered to be acceptable in view of the known errors of other methods. However, it remains uncertain to what extent the results are sufficiently accurate in order to determine the differences between isomeric compounds in the proper way. Inversion of the retention sequence might have been caused by the large extrapolation step from Kováts indices at 140–180°C to 25°C, in addition to the uncertainties in the log (γ_z/γ_i) value from Table 3.

Vapour pressure of chlorophenols at 160°C

The (sub-cooled) liquid vapour pressures of phenol and nine chlorophenols at 160°C were determined according to our method with the help of Eq. 5. Experimental Kováts indices on SE-30 stationary phase at 160°C were available in the literature [13] and no extrapolation was required or possible. Values of the regression coefficients d log P_z/dI_z and log P_{H_2} at 160°C were taken from Table 1. The log (γ_z/γ_i) value of 2-methyl-2-pentanol at 120°C on SE-30 from Table 3 was used. The results are given in Table 6. With respect to isomer sequences, the results are better than those for the chlorobenzenes. The reason is probably the smaller extent to which temperature effects are present. Apparently the ΔI and γ_z/γ_i values are temperature independent. Except for the inversion for phenol and 2-monochlorophenol, and to a lesser extent also for the two trichlorophenols, the isomer values show a sequence similar to that of the literature data.

Table 5
Comparison of vapour pressure (P_i, in Pa) and heat of vaporization (ΔH, in kJ/mol) data for chlorobenzenes at ca. 25°C derived from Kováts indices on SE-30 using Eq. 5 and using other methods

Chlorobenzene congener	P_i [a]	P_i [b]	ΔH [a] (0–25°C)	ΔH [c] (25°C)
Mono-	1828	1560	43.91	41.55 (40.97)[d]
1,2-Di-	252	185	50.90	49.87
1,3-Di-	236	299	53.89	48.55
1,4-Di-	216	257	54.83	48.74
1,2,3-Tri-	44.1	56.9	57.16	56.64
1,2,4-Tri-	53.4	60.1	57.62	55.74
1,3,5-Tri-	62.4	74.9	59.00	54.82
1,2,3,4-Tetra-	12.1	8.0	60.14	63.19
1,2,3,5-Tetra-	15.1	16.3	60.69	61.69
1,2,4,5-Tetra-	15.1	12.5	60.69	61.42
Penta-	2.49	2.19[e]	67.74	67.54
Hexa-	0.367	0.344[e]	76.80	73.82

[a] Derived using Eq. 5.
[b] Data from ref. 14.
[c] Values calculated from experimental boiling point data according to the Hildebrand rule [2].
[d] Ref. 16.
[e] Extrapolated value from ref. 15.

3. Discussion and conclusions

A method was developed for the determination of the (sub-cooled) liquid vapour pressures of low-volatility compounds or series of compounds at environmentally relevant tem-

Table 6
Comparison of vapour pressure (P_i, in Pa) data for chlorophenols at 160°C derived from Kováts indices on SE-30 using Eq. 5 and using other methods

Chlorophenol congener	P_i [a]	P_i [b]
Phenol	79	53
2-Mono-	56	70
3-Mono-	22	18
4-Mono-	22	18
2,4-Di-	20	22
2,6-Di-	17	16
2,4,5-Tri-	7.1	7.3
2,4,6-Tri-	7.5	7.1
2,3,4,6-Tetra-	2.5	2.6
Penta-	0.91	0.72

[a] Derived using Eq. 5.
[b] Data from ref. 14.

peratures. The results obtained for chlorobenzenes and chlorophenols according to this method are within 3–51% of values obtained by other methods with an average deviation of only 19%. These deviations are considered to be acceptable in view of the available data on the accuracy and reproducibility of other methods [3,15]. Remaining uncertainties are associated with the extrapolation of Kováts indices from the temperature region of their measurement to environmentally relevant temperatures and with the selection of McReynolds model compounds for log (γ_z/γ_i) values at suitable temperatures. The method can be improved with respect to these uncertainties. After these improvements it will probably be sufficiently accurate to distinguish between isomers in a completely reliable way.

The uncertainties associated with the current method are present in other GLC methods to an even greater extent. In GLC methods based on the Hamilton equation [3,5–7] (see Introduction), C and $(1 - \Delta H_1/\Delta H_2)$ values are obtained at the temperatures of measurement of the relative retention times. Only if these values

are assumed to be temperature independent and if a value of the vapour pressure of the reference compound is available at the environmentally relevant temperature can vapour pressures at the latter temperature be found. In addition, the Hamilton equation assumes a constant value of 1 for the ratio γ_1/γ_2 of the activity coefficients of compound 1 and its reference compound 2. The reference compound may have a retention time differing considerably from that of the compound. This assumption has not yet been validated and is only treated implicitly in this method. In the present method a constant value, different from 1, is assumed for the ratio γ_i/γ_z of the activity coefficient of compound i and the reference n-alkane z, eluting close to compound i. Moreover, this value is treated explicitly and therefore is open to improvement. It is interesting to note an example of the use of the Hamilton method with two reference n-alkanes (octadecane and eicosane) [3]. The present method, using an extensive series of n-alkanes, can be considered as a further development of this idea.

Finally, the present method can be compared with the use of a direct correlation equation relating the Kováts index at 200°C to the vapour pressure at 25°C as mentioned in the Introduction [8]. One may ask which further assumptions have to be introduced into Eq. 5 in order to arrive at a simple direct correlation equation. After application of Eq. 5 at 25°C and substitution of Eq. 7 [$I_i(25°C) = I_i(200°C) - (\mathrm{d}I_i/\mathrm{d}T)$ $(200 - 25)$], it follows that in addition to the independence of d log $P_z/\mathrm{d}I_z$ of z and γ_i/γ_z of z and i, $\mathrm{d}I_i/\mathrm{d}T$ also has to be independent of i. The first two requirements are also included in our method, whereas the last is not. From Table 4, it can be seen that large differences between $\mathrm{d}I_i/\mathrm{d}T$ values for different congeners exist and that, as a consequence, this requirement cannot be fulfilled. This may lead to erroneous predictions if isomer sequences of vapour pressures in the case of inversion of $I_i(T)$ values within the pertinent temperature range. Non-linear correla-

tion equations are currently in use that apply much less drastic assumptions [2]. In addition, the direct correlation equation can be used only when several vapour pressure values of compounds belonging to the series are already known.

Acknowledgement

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