

Determining the vapour pressures of plant volatiles from gas chromatographic retention data

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Abstract

The frequently used vapour pressure versus Kováts retention index relationship has been evaluated in terms of its universal applicability, highlighting the problems associated with predicting the vapour pressures of structurally divergent organic compounds from experimentally measured isothermal Kováts retention indices. Two models differing in approximations adopted to express the activity coefficient ratio have been evaluated using 32 plant volatiles of different structural types as a test set. The validity of these models was established by checking their ability to reproduce 22 vapour pressures known from independent measurements. Results of the comparison demonstrated that (i) the original model, based on the assumption of equal activity coefficients for the test and reference substances, led, as expected, to a poor correlation ($r^2 = 89.1\%$ only), with significantly deviating polar compounds and (ii) the model showed significant improvement after incorporating a new empirical term related to vaporization entropy and boiling point. The addition of this term allowed more than 99% of the vapour pressure variance to be accounted for. The proposed model compares favourably with existing correlations, while having an added advantage of providing a convenient tool for vapour pressure determination of chemically divergent chemicals.

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1. Introduction

Plants emit a plethora of chemically divergent volatile organic compounds (VOCs) into the air. On a global scale, the production of plant-generated VOC species amounts to approximately 1150×10^{12} g (1150 Tg) of carbon per year [1]. Of this, about 30% derives from isoprene, 25% from other terpenoids, and the rest from non-terpenoid compounds such as methanol, hexane derivatives, etc. [2]. Because of the magnitude of their emissions as well as their photochemical reactivity compared to many other pollutants (e.g. VOCs emitted in vehicle exhaust), isoprenoids are considered to

play an important/dominant role in the chemistry of the lower troposphere and atmospheric boundary layer [3].

Since the vapour pressure, P , can be regarded as the underlying driving force leading to emissions, vapour pressure data are indispensable in the modelling of substance fate and distribution between the air, water, soil and biota [4–7].

The most commonly used methods for measuring the vapour pressures of environmentally important compounds are effusion, gas saturation and gas chromatography [8,9]. The first two methods require great care for accurate results and it is not unusual for measurements made by different methods and/or laboratories to differ by as much as one order of magnitude or more, especially for low volatility compounds [10,11]. The gas chromatographic (GC) method offers great advantages of simplicity, speed, purity, small

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sample size and reproducibility. Many modifications of the GC method including both the classical (either isothermal [8,12] or temperature-programmed [13–16] even combined with SPME [15]) and inverse chromatography [17,18] techniques have been described. In principle, all of these techniques are based on the simple concept that partitioning a solute between the gas and non-polar stationary phases is controlled mainly by vapour pressure. A great deal of work has been done by environmental chemists and chemical ecologists using the GC method to determine reasonable vapour pressures of organic pollutants and semiochemicals; several reviews have summarised the results of this research [9,19–21]. However, irrespective of the many achievements in determining P for different classes of rather specific (homologous series) compounds, the GC methods are generally linked with problems concerning the possibility of adsorption effects if polar solutes are used, and with not knowing the activity coefficients concerned [20,21]. Beside this, some additional factors influencing the accuracy of the GC methods seem to call for improvements. One of them is the selection of the best form of the function describing the temperature dependence of experimental chromatographic retention data. Such a function is necessary to know to determine the vapour pressures at 298.15 K.

Our general objective in this work is to determine the vapour pressures of 32 plant volatiles including both hydrocarbon terpenes and more polar compounds bearing a hydroxyl and/or carbonyl group using a GC method based on the Kováts retention indices as experimental input data. Our purposes are three-fold. First, we wish to check the applicability of the simple GC method on a rather heterogeneous set of environmentally important substances. Second, we hope to evaluate the performance of the Kirchhoff–Rankin-type function in relating the Kováts indices and vapour pressures to temperature. Third, we hope to draw inferences from these results about the possibilities of providing an improved, though empirical, vapour pressure versus Kováts index relationship capable of predicting the vapour pressures of diverse plant volatiles based on their Kováts indices on a non-polar column and molecular structure.

2. Theory

Isothermal Kováts retention indices (I_X) are defined as

$$I_X = 100z + 100 \frac{\ln t'_{R,x} - \ln t'_{R,x}}{\ln t'_{R,z+1} - \ln t'_{R,z}} \\ = 100z + 100 \frac{\ln(\gamma_z^\infty P_z / \gamma_X^\infty P_X)}{\ln(\gamma_z^\infty P_z / \gamma_{z+1}^\infty P_{z+1})}, \quad (1)$$

where $t'_{R,x}$, P_X and γ_X^∞ represent the adjusted retention time, vapour pressure and infinite dilution activity coefficient, respectively, of a solute X in the stationary phase, and sub-

scripts z and $z+1$ identify the reference n -alkanes with z and $z+1$ carbon atoms whose retention times encompass that of solute X .

Expressing P_X from Eq. (1), we obtain the equation

$$\ln P_X = \ln \left(\frac{P_z \gamma_z^\infty}{\gamma_X^\infty} \right) + \frac{(100z - I_X) \ln(P_z \gamma_z^\infty / P_{z+1} \gamma_{z+1}^\infty)}{100}, \quad (2)$$

which under assumption $\gamma_X^\infty = \gamma_z^\infty = \gamma_{z+1}^\infty$ gives

$$\ln P_X = \ln P_z + \frac{(100z - I_X) \ln(P_z / P_{z+1})}{100} \quad (3)$$

Eq. (3), forwarded by the Ballschmiter group in deriving the vapour pressures of many pollutants from retention data [22,23], allows direct computation of vapour pressures at 298.15 K provided that accurate values of the Kováts index of the solute and vapour pressures of n -alkane references at this temperature are known.

It is well known that partitioning organic compounds between the gas and condensed phases is strongly temperature dependent. The temperature dependence of the partition coefficient K relevant to the gas phase–stationary phase partitioning in GC was described in a general way by Castells et al. [24] and discussed in detail by González [25]. Their treatment, based on the original assumption of Clarke and Glew [26] that the enthalpy change of a given process can be expressed as a perturbation of the standard enthalpy value at some reference temperature by means of Taylor's series expansion, led to a general equation

$$\ln K(T) = a + \frac{b}{T} + c \ln T + dT + \dots \quad (4)$$

This general equation reflects the basic problem of obtaining ΔH , ΔS and ΔC_p values by fitting ΔG data (obtainable through measurements of specific retention volumes or Kováts indices, and also equilibrium constants, vapour pressures, solubilities, etc.) to a reasonable function of temperature.

As regards the Kováts retention index, I , several types of $I=f(T)$ relationships have been employed, depending on the number of terms on the right side of Eq. (4) taken into consideration. If only the first two terms are considered, Eq. (4) resembles an Antoine-type equation most frequently used in the last century. If the fourth term is added to the first two, an empirical equation utilised by Vezzani's group [27,28] in their numerical simulation of the GLC process results. Recently, a three-parameter Kirchhoff–Rankin-type Eq. (5) became popular to describe $I=f(T)$ dependence, particularly for polar compounds [29–33].

$$I(T) = C_0 + \frac{C_1}{T} + C_2 \ln T \quad (5)$$

where C_0 , C_1 , and C_2 are empirically determined constants and T is the thermodynamic temperature in Kelvins. If a sufficient amount of data is available, the constants are determined using non-linear regression techniques.

It should be noted that several other empirical forms of $I=f(T)$ function have also been utilized to date including linear [34,35], simple quadratic [36,37], polynomial [38] and hyperbolic [39] equations.

On a capillary column the value of the dead time or column hold-up time, t_M , is significant since any error in its determination influences the calculation of parameters, such as the adjusted retention time t'_R ($t'_R = t_R - t_M$) and in turn the Kováts retention index. According to the IUPAC recommendation [40], the relationship between the retention time, t_R , and the carbon number of n -alkanes, z , is represented by the non-linear expression

$$t_{R,z} = m + \exp(n + pz^q) \quad (6)$$

where the coefficients m , n , p , and q can be determined by non-linear regression. From this expression, the hold-up time is obtained for a value of z equals zero. The coefficients of Eq. (6) can be used to calculate isothermal retention indices for compound X by [41]

$$I_X = 100 \left(\frac{[\log(t_{R,X} - m) - n]}{p} \right)^{1/q} \quad (7)$$

In this paper, we have chosen to apply Eqs. (5) and (7) in the calculation of the retention indices of plant-emitted compounds at different temperatures.

3. Experimental

3.1. Gas chromatography

The retention times of the examined compounds were determined using a HP 6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with a flame ionisation detector (FID), split/splitless injection port (230 °C) and an HP 6890 Series automatic injector. Fused-silica capillary columns (Zebron ZB-1, 100% poly(dimethylsiloxane) film thickness 0.25 μm or 1 μm) of length 30 m and I.D. 0.32 mm (Phenomenex, Torrance, CA, USA) were used in the split mode with a split ratio of 1:50. The gas chromatograph was operated isothermally with a constant helium pressure of 66 kPa) at 10 °C intervals in the 40–200 °C range as specified. n -Alkanes (C₈–C₁₆, Fluka or Aldrich) were used as reference standards. Adjusted retention times were calculated by subtracting the hold-up time from the retention time of the analyte. Retention times were recorded to three significant figures following the decimal point. The experiments were generally triplicated to ensure reproducibility; only averaged values are reported.

In fact, the ZB-1 column based on poly(dimethylsiloxane) (PDMS) stationary phase is slightly polar with the solvation parameter model system parameters [42] probably almost equal to those of DB-1. For the DB-1 column these parameters at 120 °C were determined [42] as follows: $r=b=0$, $s=0.207$, $a=0.185$. Although more non-polar stationary

phases based on poly(octymethylsiloxane) are now commercially available, such as SPB-Octyl ($a=r=b=0$, $s=0.232$), we decided to use ZB-1 in this work considering that (i) the SPB-Octyl capillary column is relatively short-lived and less familiar to many labs, and (ii) the temperature limit for SPB-Octyl is $\sim 270/280$ °C compared to ~ 360 °C for ZB-1. The high thermal stability of ZB-1 makes it possible to potentially use the same column for the analysis of both less and more volatile analytes.

3.2. Chemicals

The examined compounds (monoterpenes, sesquiterpenes and other VOCs) were acquired from Aldrich, Fluka, Symrise (Holzminden, Germany), Aroco-Aroma (Prague, Czech Republic) and our institutional terpene stock. In a typical experiment, 1 μL of the analyte solution in a standard mixture of n -alkanes in hexane was injected to gas chromatograph. The standard mixture was prepared from pure n -alkanes (C₈–C₁₆; 40 mg each of them) and 100 mL of hexane (for residual analysis, Fluka). The real sample was a solution of 1 mg of analyte in 1 mL of the previously described standard mixture.

3.3. The database

The vapour pressures of reference C₈ to C₁₅ n -alkanes at different temperatures used in this work were calculated using the Cox Eq. (8).

$$\ln \left(\frac{P}{p_0} \right) = \left(1 - \frac{T_0}{T} \right) \exp(A_0 + A_1 T + A_2 T^2) \quad (8)$$

The coefficients of this equation derived for temperatures between the triple and boiling points were taken from a critical compilation of n -alkanes data [43].

Published P values of the compounds studied at 298.15 K were obtained from several sources, namely from the CRC Handbook of Chemistry and Physics [44], from the older compilation of Dykyj and Repáš [45], from some newer sources [46–49], and from web- available databases [50,51]. In this manner, a database of P values at 298.15 K for 22 compounds was acquired. The same sources along with the commercial Fluka catalogue served to obtain the literature normal boiling point (T_b) data.

It should be noted that the literature vapour pressure data sets of plant volatiles tend to be less homogeneous than expected, probably because of the multitude of methods and investigators involved in their generation. For any given compound, there is insufficient information at this time to say which of the several values is more accurate. In view of these facts, we considered it more appropriate to use averaged values of specific literature data (designed P_L^{AVE}) instead of more or less subjectively preferred individual values in developing the P versus P_{GC} correlation.

Moreover, the experimentally inaccessible sub-cooled liquid vapour pressure of crystalline compounds has to be

derived from solid vapour pressure data. Thus, for the three solid compounds in our series (menthol, thymol, and vanillin), the original solid vapour pressure P_S values were converted to P_L values at 298.15 K according to the equation

$$\ln P_L = \ln P_S - \left(\frac{\Delta S_F}{R} \right) \left(1 - \frac{T_m}{T} \right) \quad (9)$$

where ΔS_F is the entropy of fusion at the melting point ($\text{JK}^{-1}\text{mol}^{-1}$), R is the ideal gas constant ($8.3143 \text{ JK}^{-1}\text{mol}^{-1}$) and T_m is the melting point temperature (K).

While the melting points were obtained from the standard literature, the entropy of fusion values were calculated from the enthalpy of fusion data known for thymol ($\Delta H_F = 21.3 \text{ kJmol}^{-1}$) [44] and menthol ($\Delta H_F = 11.88 \text{ kJmol}^{-1}$) [50] considering that $\Delta S_F = \Delta H_F/T_m$ or approximated using the value $\Delta S_F = 89.1 \pm 3.6 \text{ JK}^{-1}\text{mol}^{-1}$ (vanillin) originally reported for 5-chlorovanillin [52].

3.4. Data treatment

The data were subjected to statistical analyses utilizing Statgraphics 5.1 Plus (Manugistic Inc., Rockville, MD, USA). Graphic outputs were performed by Prism 3.0 (Graph-Pad Software, San Diego, CA, USA).

4. Results and discussion

Tables 1 and 2 provide a list of the 32 compounds used in this study and their Kováts retention indices at 11 or 12 temperatures. A brief inspection of the data in Table 1 reveals that, occasionally, the numerical values of I do not change regularly with increasing temperatures. Consequently, we applied Eq. (5) to evaluate the I versus T relationship for each of the compounds. A statgraphics routine for the non-linear regression (Levenberg–Marquardt algorithm) was used to determine the coefficients C_0 , C_1 and C_2 (Table 3).

Based on the r -squared statistics, the $I=f(T)$ model represented by Eq. (5) explains more than 99.8% of the variance in the data for all compounds, implying it provides a highly significant description of the retention data. Additionally, for the compounds investigated in this work and the temperature ranges used, the model seems to show a high flexibility resulting in three distinct types of $I=f(T)$ behaviour (for illustrative examples see Fig. 1): (i) the first type is characterised by a linear or almost linear dependence of I on T which is typical for α -pinene (Fig. 1a) and most of the other hydrocarbon terpenes, (ii) the second type, while characterised by a striking non-linearity, does not exhibit an extreme in the experimental temperature range; this type can be exemplified by linalool (Fig. 1b) and other compounds such as geranial, neral, *cis*-

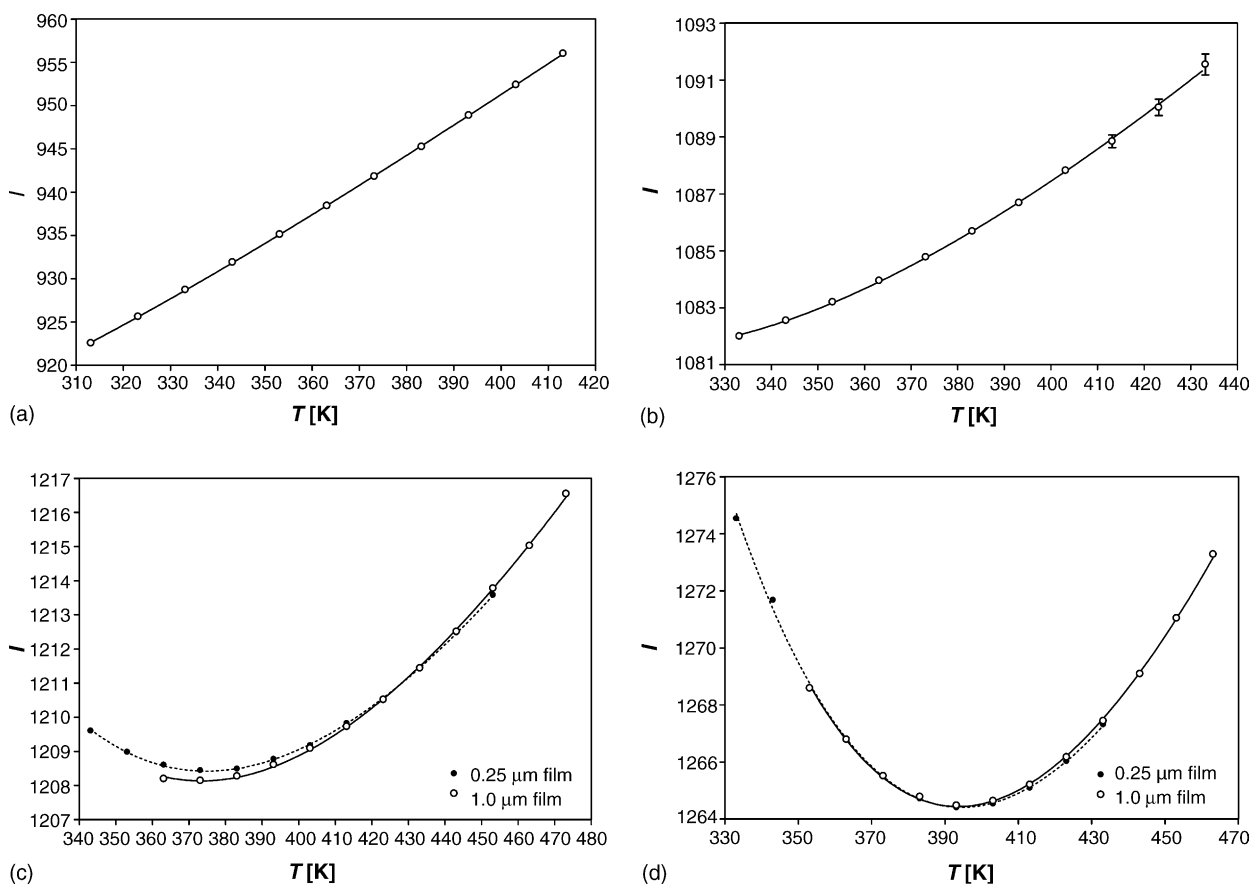


Fig. 1. Dependence of Kováts retention index I on temperature T for α -pinene (a), linalool (b), citronellol (c) and thymol (d).

Table 1
Retention indices of compounds 1–32 (0.25 μm stationary phase film)

No.	Compound	Retention index ($^{\circ}\text{C}$)																
		40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
1	(–)- α -Pinene	922.57	925.64	928.73	931.91	935.13	938.44	941.85	945.26	948.88	952.43	956.02						
2	(+)- β -Pinene	958.28	961.96	965.76	969.63	973.60	977.62	981.73	985.97	990.18	995.018	1000.00						
3	Camphene	932.53	936.31	940.16	944.09	948.10	952.21	956.38	960.64	964.96	969.38	973.81	978.46					
4	(+)-2-Carene	985.96	988.45	991.06	993.75	996.47	999.01	1002.04	1005.20	1008.36	1011.43	1014.46						
5	(+)-3-Carene	994.21	996.99	1000.00	1002.83	1005.88	1008.96	1012.09	1015.29	1018.60	1021.88	1025.31						
6	(+)-Limonene	1011.10	1013.66	1016.32	1018.99	1021.74	1024.53	1027.41	1030.32	1033.31	1036.39	1039.52						
7	γ -Terpinene	1040.00	1042.21	1044.39	1046.63	1048.89	1051.17	1053.46	1055.82	1058.25	1060.70	1063.13						
8	Sabinene	957.68	960.31	962.99	965.75	968.57	971.45	974.38	977.34	980.41	983.56	986.74						
9	α -Thujene	922.45	925.48	928.57	931.72	934.99	938.26	941.65	945.05	948.55	952.29	955.68						
10	(–)- α -Phellandrene	986.95	989.59	992.30	995.05	997.86	1000.00	1003.67	1006.67	1009.74	1012.78	1015.83	1019.04					
11	<i>p</i> -Cymene			1007.14	1009.71	1012.30	1014.92	1017.61	1020.31	1023.06	1025.90	1028.75	1031.56	1034.50	1037.54			
12	1,8-Cineol	1006.89	1010.01	1013.30	1016.72	1020.25	1023.90	1027.66	1031.53	1035.51	1039.66	1043.79						
13	(–)-Myrtenal		1147.35	1151.46	1155.93	1160.56	1165.32	1170.25	1175.32	1180.54	1185.89	1191.36	1196.22					
14	(+)-Carvon		1194.54	1197.94	1201.12	1205.05	1208.89	1212.83	1216.93	1221.14	1225.42	1229.89	1234.47	1239.00				
15	(+)-Pulegon					1203.81	1208.00	1212.29	1216.66	1221.11	1225.70	1230.35	1235.16	1239.97	1244.84	1250.14		
16	Geranial				1236.27	1237.57	1238.99	1240.57	1242.28	1244.09	1246.03	1248.08	1250.29	1252.56	1254.86	1257.34		
17	Neral				1207.12	1209.05	1211.09	1213.25	1215.50	1217.84	1220.26	1222.79	1225.45	1228.09	1230.89	1233.68		
18	Linalool			1082.00	1082.56	1083.20	1083.95	1084.78	1085.69	1086.69	1087.83	1088.85	1090.04	1091.55				
19	Terpinen-4-ol		1143.97	1147.52	1151.16	1154.87	1158.69	1162.62	1166.67	1170.83	1175.01	1179.37	1183.77	1188.31				
20	(+)- <i>cis</i> -Verbenol		1111.03	1113.76	1116.73	1119.91	1123.29	1126.88	1130.67	1134.65	1138.83	1143.13	1147.55	1152.35				
21	(+)- <i>trans</i> -Verbenol		1114.12	1117.03	1120.01	1123.20	1126.58	1130.16	1133.96	1137.97	1142.04	1146.35	1150.76	1155.37				
22	Citronellol				1209.60	1208.98	1208.60	1208.44	1208.49	1208.77	1209.17	1209.82	1210.54	1211.43	1212.46	1213.56		
23	(–)-Menthol		1143.95	1146.99	1149.57	1152.38	1155.38	1158.58	1161.95	1165.41	1169.10	1172.79	1176.76	1180.78				
24	Thymol			1274.53	1271.67	1268.62	1266.78	1265.51	1264.72	1264.40	1264.54	1265.09	1266.02	1267.31				
25	(<i>E</i>)- β -Farnesene						1441.80	1442.98	1444.19	1445.07	1446.33	1447.60	1448.81	1450.11	1451.40	1452.77	1454.09	1455.44
26	β -Caryophyllene						1392.14	1400.00	1407.76	1412.51	1419.57	1426.69	1433.93	1441.31	1449.01	1456.63	1464.50	
27	Anisole						889.68	891.69	893.73	895.86	897.86	900.00	902.32	904.91	907.48	909.99	912.78	
28	Methyl salicylate			1154.15	1157.80	1161.55	1165.41	1169.35	1173.30	1177.24	1181.56	1185.90	1190.36	1195.52				
29	Methyl phenyl acetate			1139.02	1140.48	1142.07	1143.76	1145.60	1147.51	1149.57	1151.74	1154.04	1156.39	1158.70				
30	Ethyl phenyl acetate			1205.65	1207.01	1208.64	1210.19	1211.83	1213.64	1215.50	1217.58	1219.66	1221.84	1224.16	1226.48			
31	2-Phenyl ethanol	1073.43	1074.60	1076.16	1078.09	1080.29	1082.78	1085.50	1088.47	1091.65	1095.04	1100.00						
32	Vanillin					1333.89	1337.52	1340.83	1344.69	1348.80	1353.19	1357.77	1362.62	1367.56	1372.86	1378.46	1384.33	

Table 2
Retention indices of compounds 1, 11, 20, 22 and 24 (1.0 μm stationary phase film)

No.	Compound	Retention index (°C)																		
		40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200		
1	(-)-α-Pinene	928.69	931.87	935.08	938.37	941.76	945.19	948.69	952.30	955.94	959.63	963.45	967.39							
11	<i>p</i> -Cymene	1007.14	1009.71	1012.30	1014.92	1017.61	1020.31	1023.06	1025.90	1028.75	1031.56	1034.50	1037.54							
20	(+)- <i>cis</i> -Verbenol		1116.45	1119.53	1122.95	1126.57	1130.41	1134.42	1138.60	1143.00	1147.53	1152.23	1157.08							
22	Citronellol				1208.2	1208.15	1208.27	1208.61	1209.09	1209.73	1210.52	1211.44	1212.51	1213.78	1215.02	1216.54				
24	Thymol			1268.59	1266.79	1265.51	1264.78	1264.48	1264.64	1265.21	1265.21	1266.17	1267.44	1269.09	1271.04	1271.04				

or *trans*-verbenol, 2-phenyl ethanol and vanillin, and (iii) the last type is represented by only two compounds, viz. citronellol (Fig. 1c) and thymol (Fig. 1d) and is characterised by a well-defined minimum at 374.7 and 394.6 K, respectively. Note that derivation of Eq. (5) provides the minimum of the I versus T curve ($T_{\min} = C_1/C_2$).

Noticeably, Eq. (5) shows a better fitting of the data for citronellol and thymol ($r^2 = 99.98\%$ and 99.85% , respectively) than previously used equations no matter whether linear or hyperbolic in form. On stationary phases with polarities similar to our ZB-1, Hennig and Engewald [53] (HP-5), as well as Tudor and Moldovan [54] (SE-30) invariably found a worse fitting of the data. For the linear regression, r^2 values found by these authors were 0.858 and 0.898 (citronellol) and 0.500 and 0.616 (thymol), while slightly better correlation coefficients ($r^2 = 0.971$ and 0.905) for citronellol and thymol, respectively, were calculated from the hyperbolic equation. The effects of interfacial adsorption have been suggested as a cause of this non-linearity in the $I = f(T)$ dependence of alcohols and phenols chromatographed on non-polar stationary phases.

Since insight into the importance of adsorption as a retention mechanism may be obtained by comparing experimental retention data on columns with stationary phases of different film thickness, we measured additional I values for citronellol and thymol and some other compounds on a Zebron ZB-1 column with 1 μm film thickness (Table 2). The differences in extrapolated I values at 298.15 K for citronellol and thymol obtained using the coefficients C_0 – C_2 [Nos. 22a, 22b, 24a, 24b in Table 3] valid for columns with film thickness of 0.25 and 1 μm were not found to be significant, reaching only 0.64 and 0.37 index units. The very small difference in experimental retention data when comparing the columns with 0.25 μm versus 1 μm film thickness suggests that adsorption at the interface is not the dominant cause of retention.

With the requisite collection of Kováts indices at 298.15 K (I_X^{298}) assembled by using Eq. (5) and coefficients listed in Table 3, we proceeded to determine the vapour pressures at 298.15 K by making use of Eq. (3). To obtain additional information concerning our GC approach, we also examined the temperature dependence of P_{GC} values. For processing the P_{GC} versus T data, we used again the Kirchhoff–Rankin-type Eq. (10) [55]

$$\ln P_{GC} = \frac{B_0}{R} + \frac{B_1}{RT} + \frac{B_2}{R} \ln \left(\frac{T}{T_0} \right) \quad (10)$$

where T_0 is arbitrary equalled to 298.15 K and $R = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$.

The enthalpy of vaporization at temperature T may be calculated from Eq. (11)

$$\Delta_1^g H_m^0(T) = -B_1 + B_2 T \quad (11)$$

Eqs. (10) and (11) were thus implemented to predict $\Delta_1^g H_m^0$ values at 298.15 K for all 32 compounds. Table 4

Table 3

Kováts retention indices as a function of temperature according to the Kirchoff–Rankin-type Eq. (5)

No.	Compound	Coefficient ^a			r^2	SEE
		C_0	C_1	C_2		
1a	(-)- α -Pinene	-1216.6 \pm 37.7	75339 \pm 1966	330.4 \pm 5.5	99.99	0.0616
1b	(-)- α -Pinene	-1540.9 \pm 49.2	92848 \pm 2713	377.2 \pm 7.1	99.99	0.0486
2	(+)- β -Pinene	-1988.5 \pm 152.5	108959 \pm 7951	452.3 \pm 22.1	99.97	0.2490
3	Camphene	-1717.2 \pm 46.4	93398 \pm 2445	409.2 \pm 6.7	99.99	0.0920
4	(+)-2-Carene	-1063.1 \pm 79.9	75911 \pm 4168	314.4 \pm 11.6	99.98	0.1305
5	(+)-3-Carene	-989.0 \pm 43.2	69791 \pm 2252	306.3 \pm 6.3	99.99	0.0705
6	(+)-Limonene	-825.9 \pm 39.0	65090 \pm 2036	283.5 \pm 5.7	99.99	0.0637
7	γ -Terpinene	-309.0 \pm 31.8	45357 \pm 1659	209.6 \pm 4.6	99.99	0.0520
8	Sabinene	-915.1 \pm 36.6	66244 \pm 1908	289.1 \pm 5.3	99.99	0.0597
9	α -Thujene	-1189.5 \pm 45.8	74082 \pm 2388	326.4 \pm 6.7	99.99	0.0748
10	(-)- α -Phellandrene	-955.7 \pm 116.2	69986 \pm 6117	299.2 \pm 16.8	99.96	0.2302
11a	<i>p</i> -Cymene	-623.9 \pm 38.9	56267 \pm 2026	251.7 \pm 5.6	99.99	0.0634
11b	<i>p</i> -Cymene	-779.6 \pm 34.6	64483 \pm 1910	274.3 \pm 5.0	99.99	0.0405
12	1,8-Cineol	-1710.9 \pm 41.6	101743 \pm 2169	416.4 \pm 6.0	99.99	0.0679
13	(-)-Myrtenal	-2394.9 \pm 92.0	132573 \pm 4912	542.0 \pm 13.3	99.99	0.1416
14	(+)-Carvon	-1995.3 \pm 49.1	124493 \pm 2650	485.4 \pm 7.1	99.99	0.0919
15	(+)-Pulegon	-2295.0 \pm 86.2	137782 \pm 4924	529.9 \pm 12.3	99.99	0.1122
16	Geranial	-1002.0 \pm 31.1	101249 \pm 1755	332.9 \pm 4.5	99.99	0.0520
17	Neral	-976.3 \pm 31.6	91676 \pm 1765	328.2 \pm 4.5	99.99	0.0434
18	Linalool	-215.2 \pm 54.1	59456.7 \pm 2955	192.6 \pm 7.8	99.95	0.0786
19	Terpinen-4-ol	-1741.0 \pm 51.5	108421 \pm 2774	441.3 \pm 7.4	99.99	0.0962
20a	(+)- <i>cis</i> -Verbenol	-2552.2 \pm 65.7	153580 \pm 3545	551.8 \pm 9.5	99.99	0.1229
20b	(+)- <i>cis</i> -Verbenol	-2931.2 \pm 39.9	174240 \pm 2228	606.4 \pm 5.7	99.99	0.0503
21	(+)- <i>trans</i> -Verbenol	-2431.2 \pm 59.0	147321 \pm 3184	534.7 \pm 8.5	99.99	0.1104
22a	Citronellol	-895.5 \pm 15.6	113847 \pm 880	303.8 \pm 2.2	99.98	0.0261
22b	Citronellol	-1016.1 \pm 37.3	119972 \pm 2199	321.2 \pm 5.3	99.99	0.0353
23	(-)-Menthol	-1838.4 \pm 100.3	121903 \pm 5410	450.9 \pm 14.5	99.98	0.1876
24a	Thymol	-3472.6 \pm 95.6	267870 \pm 5223	678.9 \pm 13.8	99.85	0.1389
24b	Thymol	-3598.0 \pm 47.3	274379 \pm 2725	697.1 \pm 6.8	99.99	0.0295
25	(<i>E</i>)- β -Farnesene	410.2 \pm 49.2	42884 \pm 2898	155.0 \pm 7.0	99.98	0.0740
26	β -Caryophyllene	-4003.1 \pm 618.6	214138 \pm 36100	815.4 \pm 88.1	99.92	0.7636
27	Anisole	-965.9 \pm 90.0	71957 \pm 4691	282.9 \pm 13.1	99.97	0.1469
28	Methyl salicylate	-2032.7 \pm 173.7	124663 \pm 9492	484.3 \pm 25.0	99.97	0.2525
29	Methyl phenyl acetate	-911.8 \pm 31.1	88151 \pm 1699	307.5 \pm 4.5	99.99	0.0452
30	Ethyl phenyl acetate	-736.0 \pm 50.3	83725 \pm 2777	291.0 \pm 7.2	99.99	0.0889
31	2-Phenyl ethanol	-2845.0 \pm 226.3	176204 \pm 11800	584.0 \pm 32.9	99.86	0.3695
32	Vanillin	-3869.0 \pm 133.3	237330 \pm 7688	772.3 \pm 19.0	99.99	0.2112

a—measured on column with film 0.25 μ m thickness; b—measured on column with film 1 μ m thickness.^a The best-fit coefficients of Eq. (5) presented with their standard errors, correlation coefficients (r^2 , %) and the standard error of estimation (SEE).

provides information by which the performance of the model can be assessed. Two trends are evident: first, our $\Delta_1^g H_m^0$ values at 298.15 K compare reasonably well with those reported for α -pinene (46.6 kJmol⁻¹ [56]), β -pinene (43.5 kJmol⁻¹ [56]), (+)-limonene (48.9 kJmol⁻¹ [57]), 2-carene (47.8 kJmol⁻¹ [50]), 3-carene (48.3 kJmol⁻¹ [50]) and anisole (46.8 kJmol⁻¹ [44]) resulting in relative percent errors, δ , ($\delta(\%) = 100(\Delta_1^g H_{GC} - \Delta_1^g H_{lit})/\Delta_1^g H_{lit}$) of 3.8%, 6.2%, 1.4%, 0.4% and 5.4%, respectively; errors of similar order are observed between our results and $\Delta_1^g H_m^0$ values estimated using the Hildebrand rule (not shown). Second, a comparison of our boiling point temperatures at atmospheric pressure calculated from Eq. (10) by extrapolating our P_{GC} data to 101.325 kPa (using an iteration procedure in the standard Excel programme) with lit-

erature data results in an average percent error, $\delta_\phi(\%) = 100 \sum |(T_{b,GC} - T_b)/T_b|/N$, of 1.8% with the two largest differences between $T_{b,GC}$ and literature T_b found for β -caryophyllene (20.65 K) and vanillin (18.55 K). It is not known whether these exceptionally large errors in predicting T_b are due to a deficiency of the method or due to the inaccuracy of the reported T_b values. Despite this, the overall agreement may be considered as surprisingly good, taking into account the uncertainties related both to the relatively long-range extrapolation via Eq. (10) and generally low accuracy of the boiling points for higher boiling substances. The results indicate that such an extrapolation might be useful in cases of compounds with unknown normal boiling point temperatures.

Our discussion thus far has dealt with the general performance of Eq. (10). In the next step, the vapour pressures at

Table 4
Parameters of Eq. (10) and derived physico-chemical quantities

No.	Compound	Coefficient ^a			r^2	ΔH^b (kJmol ⁻¹)	T_b^{GC} (K)	T_b^{lit} (K)	$\delta\%$
		B_0	B_1	B_2					
1	(-)- α -Pinene	258.9 \pm 1.6	-61945 \pm 442	-57.4 \pm 1.2	99.99	44.84 (46.61)	440.1	429.35	2.50
2	(+)- β -Pinene	265.7 \pm 1.7	-64970 \pm 496	-63.0 \pm 1.4	99.99	46.19 (43.47)	452.5	438.15	3.27
3	Camphene	255.7 \pm 1.5	-61254 \pm 463	-55.7 \pm 1.3	99.99	44.65	445.2	433.15	2.78
4	(+)-2-Carene	272.7 \pm 1.6	-67894 \pm 479	-65.2 \pm 1.4	99.99	48.45 (47.78)	454.6	440.15	3.28
5	(+)-3-Carene	269.8 \pm 1.3	-67268 \pm 392	-62.9 \pm 1.1	99.99	48.51 (48.30)	457.3	446.15	2.50
6	(+)-Limonene	274.2 \pm 1.2	-69075 \pm 372	-65.3 \pm 1.1	99.99	49.60 (48.92)	460.5	451.15	2.07
7	γ -Terpinene	279.4 \pm 1.1	-71462 \pm 334	-67.4 \pm 0.9	99.99	51.38	465.3	456.15	2.00
8	Sabinene	266.0 \pm 1.4	-65094 \pm 406	-61.0 \pm 1.2	99.99	46.91	447.6	436.7	2.49
9	α -Thujene	258.7 \pm 1.5	-61889 \pm 450	-57.2 \pm 1.3	99.99	44.80	440.0		
10	(-)- α -Phellandrene	269.2 \pm 1.7	-66867 \pm 516	-62.2 \pm 1.4	99.99	48.32	454.6	448.05	1.63
11	<i>p</i> -Cymene	272.2 \pm 1.2	-68218 \pm 346	-63.6 \pm 1.0	99.99	49.24	457.5	450.15	1.46
12	1,8-Cineol	274.9 \pm 1.6	-69134 \pm 469	-67.7 \pm 1.3	99.99	48.95	463.2	449.55	3.03
13	(-)-Myrtenal	293.6 \pm 2.2	-78599 \pm 679	-79.0 \pm 1.9	99.99	55.05	501.5	493.7	1.58
14	(+)-Carvon	305.1 \pm 2.2	-83421 \pm 664	-84.5 \pm 1.8	99.99	58.24	507.9	502.15	1.14
15	(+)-Pulegon	300.7 \pm 2.0	-82080 \pm 608	-81.0 \pm 1.6	99.99	57.93	507.2	497.15	2.02
16	Geranial	325.2 \pm 2.3	-90762 \pm 684	-94.7 \pm 1.8	99.99	62.54	506.2	502.15	0.81
17	Neral	312.3 \pm 2.0	-85960 \pm 607	-86.5 \pm 1.6	99.99	60.18	501.2	502.15	0.20
18	Linalool	302.1 \pm 1.8	-79516 \pm 556	-81.4 \pm 1.5	99.99	55.25	469.8	470.15	0.07
19	Terpinen-4-ol	293.4 \pm 1.9	-78620 \pm 585	-77.5 \pm 1.6	99.99	55.52	495.6	482.15	2.79
20	(+)- <i>cis</i> -Verbenol	303.6 \pm 2.6	-80668 \pm 791	-86.3 \pm 2.2	99.99	54.94	488.4		
21	(+)- <i>trans</i> -Verbenol	302.5 \pm 2.5	-80426 \pm 767	-85.3 \pm 2.1	99.99	55.00	488.9		
22	Citronellol	340.7 \pm 2.7	-84891 \pm 829	-105.3 \pm 2.2	99.99	63.50	496.1	497.65	0.31
23	(-)-Menthol	304.4 \pm 2.3	-81856 \pm 678	-84.9 \pm 1.9	99.99	56.56	493.8	489.6	0.86
24	Thymol	409.8 \pm 5.0	-117662 \pm 1513	-157.0 \pm 4.1	99.99	70.85	517.5	505.65	2.34
25	(<i>E</i>)- β -Farnesene	345.8 \pm 1.6	-102680 \pm 488	-101.2 \pm 1.3	99.99	72.50	541.8		
26	β -Caryophyllene	322.6 \pm 2.9	-93616 \pm 884	-94.2 \pm 2.4	99.99	65.54	557.8	537.15	3.85
27	Anisole	262.8 \pm 1.6	-62194 \pm 489	-60.0 \pm 1.4	99.99	44.31 (46.84)	428.3	426.86	0.34
28	Methyl salicylate	299.5 \pm 2.1	-80523 \pm 646	-81.7 \pm 1.8	99.99	56.17	497.8	495.2	0.52
29	Methyl phenyl acetate	308.7 \pm 2.1	-83049 \pm 620	-86.2 \pm 1.7	99.99	57.36	486.5	489.3	0.57
30	Ethyl phenyl acetate	316.8 \pm 2.0	-87364 \pm 618	-89.6 \pm 1.7	99.99	60.66	500.3	502.2	0.38
31	2-Phenyl ethanol	317.5 \pm 2.8	-83866 \pm 833	-98.3 \pm 2.4	99.99	54.55	479.0	493.15	2.87
32	Vanillin	349.5 \pm 3.4	-100665 \pm 1028	-113.2 \pm 2.7	99.99	66.92	539.6	558.15	3.32

^a The best-fit coefficients of Eq. (10) presented with their standard errors and correlation coefficients (r^2 , %).

^b $\Delta_1^g H_m^0$ at 298.15 K according to Eq. (11) with available literature values in parentheses.

298.15 K determined using Eq. (3) (designated P_{GC}) were compared to those available in the literature (P_L^{AVE}) for 22 compounds.

It was found that P_{GC} values were not equal to P_L^{AVE} over the entire vapour pressure range. Positive or negative systematic errors were observed. Thus, P_{GC} underestimated or overestimated P_L^{AVE} at the high- and low-volatility ends of the scale. The regression equation obtained by a least-squares treatment in an attempt to reduce systematic errors in P_{GC} values caused by inequalities of the test and reference compound activity in the stationary phase, is

$$\ln P_L^{AVE} = (-1.5065 \pm 0.4067) + (1.2626 \pm 0.0949) \ln P_{GC} \quad (12)$$

with $N=22$, $r^2=89.11\%$, and the standard error of the estimate standard error of estimation, $SEE=0.623$. Provided that the hydroxyl group containing outliers (vanillin, citronellol, menthol, methyl salicylate, 2-phenyl ethanol and linalool), as well as anisole are excluded from the regression

(Fig. 2a) the regression, while significantly improved ($N=15$, $r^2=98.37\%$, $SEE=0.211$) still deviates from the ideal 1:1 relationship. The slope of the regression is 1.1731 instead of unity, and the intercept is -0.8013 rather than zero.

These findings demonstrate that Eq. (3), in general, does not provide an adequate means of predicting the vapour pressures from GC retention data, and are consistent with a previously published view [21] that “in some cases, errors as high as three-fold are possible” if the differences in activity coefficients at infinite dilution between the reference and test compounds are neglected in the GC vapour pressure model. Certainly, several approaches would be possible to solve this fundamental problem. In the GC-VAP method developed by Govers and co-workers [34–37], the ratio of activity coefficients of the substance and the nearest eluting *n*-alkane was incorporated by an expression based on McReynolds constants of model compounds. The problems associated with this method (such as the appropriate selection of the model compound and the single temperature 120 °C) have been discussed before [37]. Semiempirical models such as UNI-

Table 5
Parameters of Eq. (14) and vapour pressures derived from Eq. (3) and Eq. (14)

No.	Compound	I_X^{298}	P_L (Pa)	P_L^{AVE} (Pa)	ΔS (JK ⁻¹ mol ⁻¹)	$\ln(X_Z/X_X)$	$P_L^{[Eq. (3)]}$ (Pa)	$\delta\%$	$P_L^{[Eq. (14)]}$ (Pa)	$\delta\%$
1	(-)- α -Pinene	918.5	588.5 ^a , 529 ^b , 544 ^c , 582.1 ^d	560.9	86	-0.06	468.5	-16.5	514.5	-8.3
2	(+)- β -Pinene	953.8	391.3 ^a , 391.0 ^d	391.1	86	-0.37	311.1	-20.5	340.5	-12.9
3	Camphene	927.6			86	-0.2	421.8		438.7	
4	(+)-2-Carene	982.8	312.02 ^d	312.02	86	-0.44	222.2	-28.8	290.9	-6.8
5	(+)-3-Carene	990.4			86	-0.65	203.3		230.8	
6	(+)-Limonene	1007.7	192.2 ^d , 213 ^b , 202 ^c , 200 ^e , (133.3) ⁱ	201.8	86	0.03	166.4	-17.6	183.4	-9.1
7	γ -Terpinene	1037.1	103 ^c , 145.32 ^f	124.16	86.2	-0.15	118.3	-4.8	137.2	10.5
8	Sabinene	954.2			86.4	-0.34	309.6		349.7	
9	α -Thujene	918.4			86.4	-0.46	469.1		347.5	
10	(-)- α -Phellandrene	983.6	195.2 ^d	195.2	86.2	-0.61	220.1	12.7	245.3	25.7
11	<i>p</i> -Cymene	999.1	192.1 ^d , 194.65 ^f	193.37	86.2	0.06	183.9	-4.9	193.4	0
12	1,8-Cineol	1002.9	260.0 ^d , 253.31 ^f , (90.14) ⁱ	256.65	86	0.09	176	-31.4	197.2	-23.2
13	(-)-Myrtenal	1138.0			86.2	-0.65	36.8		25.7	
14	(+)-Carvon	1187.8	14.63 ^d , 21.33 ^f , 13.3 ^h	14.5	86	-0.93	20.7	43	16.1	10.8
15	(+)-Pulegon	1186.2	16.40 ^f , (9.224) ⁱ	16.4	86	-0.75	21.1	28.8	19.2	17.2
16	Geranial	1234.1	12.17 ^f	12.17	87.4	-0.28	12.2	-0.1	11.8	-3
17	Neral	1201.3	7.74 ^d , 12.17 ^f	9.96	87.4	-0.28	17.8	78.3	13.6	36.4
18	Linalool	1081.6	27 ^e , 21.33 ^f , 26.6 ^h	27.98	96.61	-1.36	70.4	182	35.0	40.0
19	Terpinen-4-ol	1136.7			95.41	-0.93	37.3		19.5	
20	(+)- <i>cis</i> -verbenol	1106.6			95.33	-1.16	52.7		17.3	
21	(+)- <i>trans</i> -verbenol	1110.1			95.33	-1.18	51		16.8	
22	Citronellol	1217.0	6.42 ^g , 5.88 ^f	6.147	97.09	-0.9	14.8	141	6.8	11
23	(-)-Menthol	1139.6	18.15 ^{g-j} , 11.16 ^{f-j}	14.66	95.29	-1.21	36.1	146.1	14.6	-0.5
24	Thymol	1293.7	4.33 ^{d-j} , 4.03 ^k (3.59) ⁱ	4.178	95.66	-1.09	6.1	46.3	4.0	-3.1
25	(<i>E</i>)- β -Farnesene	1437.1			88.4	-0.35	1.2		1.1	
26	β -Caryophyllene	1360.9			86	-1.37	2.8		1.1	
27	Anisol	887.5	472 ^l	472	86.2	-0.97	672.2	42.4	567.5	20.2
28	Methyl salicylate	1144.5	15.0 ^l , 16.96 ^d , 4.573 ^f	12.17	95.34	-1.43	34.1	180.1	11.5	-5.5
29	Methyl phenyl acetate	1136.0	21.87 ^f	21.87	87.2	-0.57	37.6	72	27.9	27.7
30	Ethyl phenyl acetate	1202.9	16.11 ^d , 8.32 ^f	12.21	87.6	-0.3	17.4	42.7	13.2	8.5
31	2-Phenyl ethanol	1073.3	12.66 ^g , 11.57 ^f , 7.11 ^d	10.45	98.03	-2.37	77.6	642.5	13.1	25.7
32	Vanillin	1327.4	0.381 ^{d,j}	0.381	95.94	-2.42	4.1	989.1	0.446	17

^a Ref. [55].

^b Ref. [46].

^c Ref. [49].

^d Ref. [45].

^e Ref. [48].

^f Ref. [51].

^g Ref. [50].

^h Ref. [47].

ⁱ GC-VAP [37].

^j Recalculated to liquid vapour pressure according to Eq. (9).

^k Ref. [58].

^l Ref. [44].

FAC and others are presently available for estimating infinite dilution activity coefficients. In spite of its great success in many applications, the UNIFAC model has been continuously revised and extended and its correct use appears to require specialists in the area. Also important, some laboratories may not have appropriate computational routines immediately available. UNIFAC does not distinguish between isomers and its predictive accuracy for solvent-polymer systems is considered "less than satisfactory" [59].

In this work, instead of using any of the previously described models, correlations based on a new empirical approach were developed. We propose that the difference in

logarithms of activity coefficients at infinite dilution between the compounds *i* and *j*, whatever its exact form, might be approximated by the corresponding difference in ideal gas solubility, X_i^g , originally derived [60] from the van't Hoff equation

$$\ln \gamma_i^\infty - \ln \gamma_j^\infty \approx \ln X_i^g - \ln X_j^g$$

$$\cong \frac{\Delta S_{b,i}^v(T_b^i - T)}{RT} - \frac{\Delta S_{b,j}^v(T_b^j - T)}{RT} \quad (13)$$

where ΔS_b^v is the entropy of vaporization at the normal boiling point T_b .

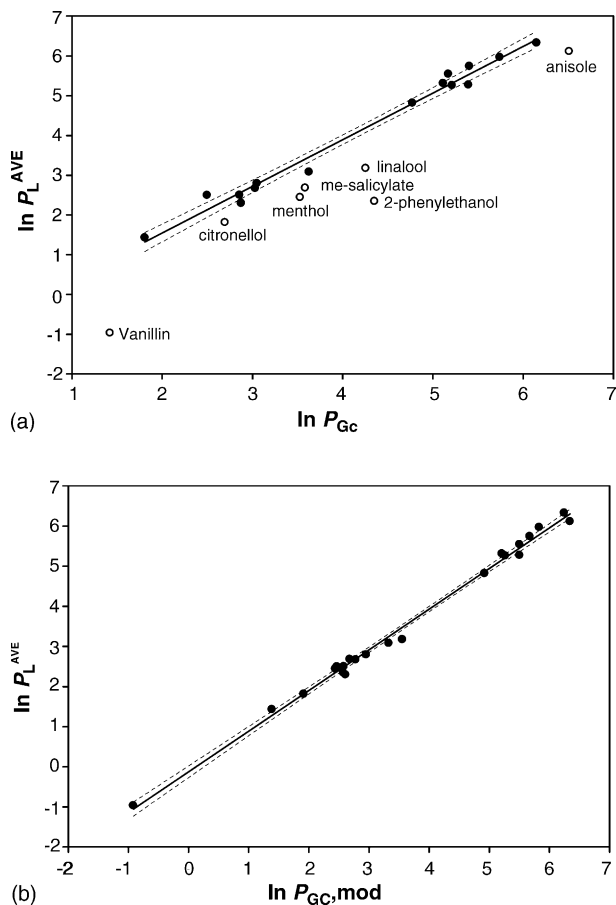


Fig. 2. Calculated vs. literature experimental values of vapour pressures at 298.15 K. The dashed lines signify a confidence interval (99%). (a) From Eq. (3); (b) from Eq. (14).

Accordingly, the ratio of activity coefficients can be represented using only two non-chromatographic parameters, T_b and ΔS_b^v . While T_b data for many compounds are available from standard sources, ΔS_b^v estimates can be easily deduced from structural information such as the torsional bond number (i.e. an estimate of molecular flexibility) and number of polar groups capable of hydrogen bonding. The procedure described in detail by Myrdal et al. [61] was followed to obtain ΔS_b^v values from the numerical representations of the molecular structures.

After inserting Eq. (13) into Eq. (3), the vapour pressure P_X can be written as a function of the Kováts index I_X of the component X and some easily accessible non-chromatographic, physicochemical quantities

$$\ln P_X = \ln P_z + (\ln X_z^g - \ln X_X^g) + \frac{(100z - I_X)[\ln(P_z/P_{z+1}) + (\ln X_z^g - \ln X_{z+1}^g)]}{100} \quad (14)$$

If all compounds with P_L^{AVE} values at 298.15 known from the literature are taken into account to validate our hypothesis, the new GC method based on Eq. (14) turns out to produce

an excellent correlation for all 22 compounds (Fig. 2b), viz.

$$\ln P_L^{AVE} = (-0.1224 \pm 0.0673) + (1.0141 \pm 0.01639) \ln P_{GC,mod} \quad (15)$$

with $N=22$, $r^2=99.4\%$, and $SEE=0.141$. Hence, the new model explains over 99% of the variance in the data, leaving only 1% for inadequacy of the model and the experimental errors in the data. The absence of a prediction bias demonstrated by an insignificant absolute term and a slope very close to unity in Eq. (15) is an additional advantage of the modified GC method.

The vapour pressure results based on Eq. (14) and their comparison with those based on Eq. (3) are shown in Table 5. Inspection of Table 5 reveals that (i) the average percent error δ_ϕ reduces from 126% to 15% on going from Eq. (3) to (14), (ii) the numerical values of $(\ln X_i^g - \ln X_j^g)$ terms for $i=z$ and $j=X$ vary significantly as the test series of compounds is traversed; on the other hand, only a slight ($\pm 16\%$) variation around the mean value of -0.79 was observed (not shown) for $i=z$ and $j=z+1$ along the reference n -alkane series used, and (iii) the errors produced by Eq. (3) and Eq. (14) are almost comparable for hydrocarbon terpenes while large error differences emerge for the remaining plant volatiles. It is apparent that, in contrast to Eq. (3) and (14) based on the simultaneous use of Kováts indices and estimated ideal gas solubility data agrees well with all available literature P_L values, with a maximum error under 40%. Of a total of 22 compounds correlated, 7 compounds exhibited relative percent errors between 20% and 40% of the literature vapour pressure value, 6 compounds had errors of 10%–20% while the remainder showed errors of $<10\%$. Encouraged by these results, we continued to use Eq. (14) to predict the vapour pressures of those 10 compounds in our set lacking P_L literature data. The needed T_b values were either taken from literature (if available), or estimated by extrapolating our vapour pressure data (Table 4). Prediction results for compounds not included in the development of Eqs. (12) and (15) are also presented in Table 5. Certainly, for a substance lacking any experimental T_b information, the calculated vapour pressures may be associated with more propagated errors.

It should be also noted that aside from the approach described above, i.e. the primary extrapolation of experimental I_X data to 298.15 K with subsequent fitting of these data to Eq. (14), another approach could include determination of vapour pressures at experimental temperatures by applying Eq. (14) directly to experimental I_X values, an extension of this $\ln P=f(T)$ series by including the literature normal boiling point value, and the subsequent use of Eq. (10) to obtain the vapour pressure at 298.15 by extrapolation. Interestingly, similar results to those reported in Table 5 (in some cases with even slightly lower errors) were achieved when this alternative approach was applied.

The results of our evaluation suggest that while sufficient evidence has been presented in support of the correlative capability of our model, the limited database used

makes a generalization preliminary in nature. An expanded compilation of precise experimental vapour pressure data to include various chemical structures is required for more generalized predictions. Similarly, we hesitate to draw conclusions concerning the accuracy of this method considering the uncertainty of literature vapour pressure data and additional uncertainty introduced by the $P_S \rightarrow P_L$ conversion, which in the case of compounds with a high melting point can lead to substantial errors. Despite this potential for problems, it appears that the proposed model compares favourably to existing correlations, while having the added advantages of covering structurally very diverse compounds with different degrees of acentricity and polarity.

5. Conclusion

The vapour pressures of 32 diverse plant volatiles at 298.15 K were determined using a modified gas chromatographic method applicable to solutes chromatographed on low-polarity stationary phases. The characteristic feature of our method is that Kováts retention indices at 298.15 K are combined with an empirical (entropy and boiling point related) term approximately substituting the activity coefficient ratio. The vapour pressure values resulting from this new framework are in good agreement with those based on direct experimental measurements showing an average percent error under 15%. Although this approach is essentially empirical, the results obtained suggest an underlying physical significance for the model and show the potential for a systematic progression from a correlative model to a predictive one. Work is in progress to test the new model using other compounds, particularly those with known accurate vapour pressures, such as some homologous series of polar compounds.

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