Experimental determination and prediction of the gas–liquid n-hexadecane partition coefficients

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Abstract

Experimental methods based on gas-phase chromatography were tested with a view to determine the gas–liquid n-hexadecane partition coefficients, $\log L^{16}$ of non-volatile compounds at 298.2 K. It was demonstrated that reliable values of $\log L^{16}$ of compounds more volatile than n-docosane can be obtained using either capillary, or packed columns. The main limitation of both methods is the column stability at high temperatures. Here we propose a new method based on the temperature gradient mode, to obtain $\log L^{16}$ of high-boiling compounds. A group contribution model is also presented in view to predicting $\log L^{16}$ values of non-volatile compounds. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Abraham et al. [1] proposed to define the partition coefficient on n-hexadecane at 298.2 K as the solute descriptor $\log L^{16}$ representing the free energy solution process in a non-polar environment. This descriptor turned out to be very useful in characterising a wide variety of solute properties, including chromatographic retention and partition coefficient at liquid–gas and solid–gas interfaces [2–4]. Recently $\log L^{16}$ was used to estimate normal boiling temperatures and critical properties of organic compounds [5].

The $\log L^{16}$ descriptor is used in linear solvation energy relationship (LSERs) introduced by Abraham and co-workers [1,6–8] to represent a contribution related to the cavity formation and to dispersion interactions:

$$\log SP = c + rR_2 + s\pi_2^H + a\sum \alpha_2^H + b\sum \beta_2^H + l \log L^{16} \tag{1}$$

SP is a free energy related solute property. The independent variables in Eq. (1) are the solute excess molar refraction (R_2), the effective solute dipolarity/polarizability (π_2^H), the effective solute hydrogen bond acidity ($\sum \alpha_2^H$), the effective solute hydrogen bond basicity ($\sum \beta_2^H$) and, the solute gas–liquid partition coefficient on n-hexadecane at 25°C ($\log L^{16}$).

The coefficients c, r, s, a, b and l are not simply

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fitting coefficients, because they reflect complementary properties of the solvent phase. The *r*-coefficients reflect the tendency of the phase to interact with gaseous solutes through polarizability-type interactions, mostly via electron pairs. The coefficient *s* is a measure of the phase dipolarity/polarisability. The coefficient *a* represents the complementary property to solute hydrogen bond acidity and it is a measure of the hydrogen bond basicity. Likewise, the coefficient *b* is a measure of the phase hydrogen bond acidity. Finally, the coefficient *l* is a combination of the work needed to create a cavity in the phase, and the general dispersion interaction energy between solute and solvent phase.

To preserve the general character of Eq. (1), all characteristic parameters should be carefully determined and correlation between parameters should be avoided. Experimental procedures of successive determination of LSER parameters were described in the literature [1,9–12]. Log L^{16} characterises the most general interactions present in every physical system and should be determined before other parameters [11]. The original values of log L^{16} were determined from retention data on *n*-hexadecane coated packed columns at 298.2 K [1]. A number of papers proposed techniques based on the use of either capillary or packed columns in wide temperature ranges and replacing the *n*-hexadecane with other non-polar stationary phases.

The objective of this study is to test experimental methods based on gas-phase chromatography to determine the gas–liquid *n*-hexadecane partition coefficient, log L^{16} of non-volatile compounds at 298.2 K. The gas liquid partition coefficient of a solute is directly related to the experimental retention factor, *k*, by:

$$L = k \cdot \frac{V_{\mathrm{M}}}{V_{\mathrm{S}}} = \frac{k}{\Phi} \tag{2}$$

where V_{M} and V_{S} are the volumes of the mobile and stationary phases, respectively, and Φ is the phase ratio $(V_{\mathrm{S}}/V_{\mathrm{M}})$. Experimental determination of log L^{16} is often very difficult. Adsorption phenomena introduce an important error in determination of the capacity factor. Zhang et al. [9] determined log L^{16} with capillary columns coated with *n*-hexadecane and concluded that results were not influenced by

adsorption in this case. However, results of Abraham et al. [13] showed that this improvement is not general and that an interfacial adsorption still exists with capillary columns. Moreover, it is very difficult to obtain absolute retention data using this technique. Li et al. [11] and Abraham et al. [13] studied the influence of the solute support and of the stationary phase loading on adsorption phenomena. They concluded that the high loading ratio (up to 20%) of the stationary phase and the high temperature of the column allow to reduce adsorption. In this case, the knowledge of R_2, $\Sigma \alpha_2^{\mathrm{H}}$ and π_2^{H} parameters is necessary. The number and the nature of parameters needed for calculation depend on the stationary phase used.

Serious difficulties arise when log L^{16} of non-volatile compounds is to be measured. This is due to the definition of log L^{16} itself. Indeed, direct experimental determination of log L^{16} of compounds less volatile than *n*-hexadecane is impossible. In the case of heavy compounds slightly more volatile than *n*-hexadecane the experiment is possible but difficult, especially at 298.2 K. Often it is recommended to measure retention times at higher temperatures and then extrapolate partition coefficients to the ambient temperature. In this case, the quality of results depends strongly on the extrapolation method used. The problem of the temperature dependence of retention times was often discussed in literature. A suitable extrapolation procedure was described by Defayes et al. [14]. In the case of compounds less volatile than *n*-hexadecane several authors proposed to work with columns coated with long chain branched alkanes and to establish relationships between corresponding partition coefficients and log L^{16} [10,14]. Defayes et al. [14] worked with an apolane coated stationary phase (apolane is a $C_{87}H_{176}$ branched alkane). This column can be used at temperatures up to 550 K without a mass loss of the stationary phase. Moreover, it was shown that the effect of adsorption at the liquid–gas interface is negligible in this case [14]. However, this opinion is not generally accepted and Weckwerth et al. [10] found an influence of adsorption in the case of strongly polar compounds. The same authors observed that a linear relationship exists between gas–apolane partition coefficients, log L^{87} and log L^{16} and that the data obtained with apolane can be used

to estimate the value of log L^{16}. Moreover, they demonstrated that a strong correlation between both partition coefficients exists also for log L^{87} determined at significantly higher temperatures [10]. Recently, several authors investigated the use of predictive methods to estimate log L^{16} [15–17]. This approach is particularly interesting to determine the log L^{16} of non-volatile compounds.

In this paper we propose a general strategy of determining log L^{16} of non-volatile compounds based on different techniques. For the low-volatility compounds different chromatographic techniques such as capillary and packed columns under isothermal conditions as well as the temperature gradient mode were used. In the case of non-volatile compounds log L^{16} was determined using the group contribution method.

2. Experimental

Retention times were determined using a Shimadzu GC 14 gas chromatograph equipped with a heated on-column injector and a flame ionization detector. The injector and detector temperatures were kept at 523 K during all experiments. The helium flow-rate was adjusted to obtain adequate retention times. Exit gas flow-rates were measured with a soap bubble meter. The temperature of the oven was measured with a Pt 100 probe and controlled to within 0.1 K. A personal computer directly recorded detector signals and corresponding chromatograms were obtained using Borwin 2.1 software. Deactivated fused-silica capillary columns coated with apolane-87, 15 m×0.32 mm, 0.25 μm, were from Alltech. Stationary phases used with packed columns were prepared by soaking in a 15% heavy n-alkane in cyclohexane solution. After evaporation of the cyclohexane under vacuum the support was equilibrated at 423 K during 1 h. The mass of the packing material was calculated from the mass of the packed and empty columns and was checked during experiments. The injected volumes of the sampled vapour were 0.1 μl. Non-volatile compounds were dissolved in acetone or ethyl acetate before injection. Experiments with gradient chromatography were carried out using a Megabore 15 m×0.53 mm I.D. DB-1 capillary column with a 1.5 μm bonded

methylsilicone stationary phase, purchased from J&W Scientific. This column is considered as non-polar, and can be used up to 605 K. Gradient experiments were performed between 313 K and 593 K with a heating rate of 10°C/min. n-Hexatriacontane (98%) and n-pentacontane (97%) were obtained from Aldrich. All other chemicals were obtained from commercial sources and used as received. All support materials used in the packed column studies were obtained from Supelco.

3. Determination of partition coefficients from retention data

Partition coefficients were calculated using Eq. (2). Experimental data necessary for this calculation were the dead retention time and the mass of stationary phase. In the case of the capillary and Megabore columns the retention time of methane was taken as the dead time of the column. The dead time of packed columns was determined with the retention time of the air. A direct determination of the stationary phase mass is difficult in the case of capillary or Megabore columns and the use of relative methods to determine partition coefficients from retention data is often preferred. Zhang et al. [9] proposed to calculate partition coefficients based on the well-established value of log $L_{n\text{-hexane}}$. The corresponding equation is as follows:

$$L_X = L_{n\text{-hexane}} \cdot \frac{t_{R,X} - t_m}{t_{R,n\text{-hexane}} - t_m} \tag{3}$$

where t_R and t_m are the solute retention time and the dead time of the column, respectively. Retention data of the solute X and of n-hexane should be determined at the same temperature. Available data of log $L_{n\text{-hexane}}$ on apolane were determined at 312.4 K [10]. On the other hand it was shown [10] that partition coefficients determined at two temperatures are linearly correlated:

$$\log L_T^{87} = a \log L_{T'}^{16} + b \tag{4a}$$

We propose a new relationship between the partition coefficient of the solute X at temperature T and the partition coefficient of the n-hexane at temperature T'. This relationship is based on the observation

verified with several *n*-alkane stationary phases that Eq. (4a) for one stationary phase is reduced to the following form:

$$\log L_T^{87} = \log L_{T'}^{87} + b \tag{4b}$$

Eqs. (3) and (4b) lead to a relationship between the partition coefficient at temperature T of the solute X and the partition coefficient of *n*-hexane determined at temperature T':

$$(L_X)_T = (L_{n\text{-hexane}})_T \cdot \left(\frac{t_{R,X} - t_m}{t_{R,n\text{-hexane}} - t_m} \right)_{T'} \tag{5}$$

In the case of Megabore columns used in gradient experiments partition coefficients were calculated using a new approach described in the next paragraph. The mass of the stationary phase in packed columns was determined directly as described in experimental section, and calculations of partition coefficients were carried out following the classical method. A detailed description of the latter calculations can be found in the paper of Defayes et al. [14] dealing with chromatographic determination of partition coefficients.

4. Results and discussion

Three methods of the $\log L^{16}$ determination were tested. The first method is based on the method described recently by Weckwerth et al. [10] and implies the use of capillary columns coated with apolane. The second method follows the traditional approach using packed columns and stationary phase coated with *n*-alkane. The third method is the temperature gradient approach performed using a Megabore DB-1 column. This latter approach is used here for the first time. A set of about 60 polar and non-polar probes was used for which the $\log L^{16}$ were published in the literature.

4.1. Capillary column coated with apolane

Apolane coated capillary columns are considered an appropriate tool to determine $\log L^{16}$ of heavy compounds. Studies of Defayes et al. [14] and Weckwerth and al. [10] provided arguments supporting this opinion. In our study we used 15 m×0.32

mm, 0.25 μm, fused-silica/apolane-87 capillary columns from Alltech. Experiments were carried out at a constant temperature $T = 373.2$ K. Non-deactivated and deactivated columns were used. Results obtained with a non-deactivated column indicate that retention times are influenced by adsorption phenomena. Indeed, polar solutes exhibited very asymmetric peaks and their retention times strongly depended on the sample size. Retention times of alcohols are longer than the literature values that may indicate the presence of active sites. As can be seen in Table 1, results obtained with a similar but deactivated column are in good agreement with the literature. Chromatographic peaks obtained with non-polar and polar compounds were symmetric. Moreover, good correlation was observed between experimental $\log L^{87}$ at 373.2 K, and literature data of $\log L^{87}$ at 312.4 K:

$$\log L_{373.2}^{87} = (0.9996 \pm 0.0026) \log L_{312.4}^{87};$$
$$n = 41, R = 0.9990, SD = 0.031 \tag{6}$$

Statistical analysis of this regression confirms the validity of the proposed method. While this method gave good results at 373.2 K, at 423.2 K the column was deactivated irreversibly within a few hours. A probable explanation of this phenomenon is that the adhesion between apolane and the deactivated silica does not assure film stability at higher temperature [11,18].

Our experience indicates that the use of commercially available apolane coated capillary columns should be limited to low temperatures. In the case of heavy compounds this implies very long retention times and imposes injection of large samples, which induces adsorption effects. Consequently, to determine $\log L^{16}$ of heavy compounds we decided to use packed columns with long chain *n*-alkane stationary phases.

4.2. Packed columns

Problems of the capillary column stability encouraged us to review the possibility of application of packed columns for determining $\log L^{16}$ of non-volatile compounds. Stationary phases used were long chain *n*-alkanes, *n*-hexatriacontane and *n*-pentacontane. They were used at temperatures up to 320 K

Table 1
Partition coefficient log L^{87} at 312.4 K obtained using experimental data determined with a deactivated apolane capillary column at 373.2 K

Compound	Log L^{87a}	Log L^{87b}	Compound	Log L^{87a}	Log L^{87b}
n-Hexane	2.176	2.176	2-Propanol	1.477	1.485
n-Pentane	1.709	1.714	1-Butanol	2.117	2.137
n-Heptane	2.626	2.628	2-Methyl-1-propanol	2.049	2.018
n-Nonane	3.519	3.529	2-Methyl-2-propanol	1.594	1.595
n-Decane	3.959	3.977	1-Pentanol	2.650	2.605
n-Undecane	4.422	4.422	1-Heptanol	3.512	3.491
n-Dodecane	4.863	4.863	1-Octanol	3.980	3.925
n-Tridecane	5.335	5.302	Phenol	3.351	3.407
n-Tetradecane	5.768	5.759	*p*-Cresol	3.799	3.761
n-Pentadecane	6.213		Benzene	2.401	2.480
n-Hexadecane	6.665		Toluene	2.885	2.926
n-Heptadecane	7.069		Ethylbenzene	3.300	3.297
1-Hexene	2.102	2.101	*o*-Xylene	3.461	3.463
Acetone	1.496	1.357	*p*-Xylene	3.359	3.372
2-Pentanone	2.331	2.356	*m*-Xylene	3.368	3.378
Ethyl acetate	1.994	1.990	1,2,3-Trimethylbenzene	3.994	
Pyridine	2.779	2.620	1,2,4-Trimethylbenzene	3.891	
2,4,6-Trimethylpyridine	3.836		1,3,5-Trimethylbenzene	3.798	
Triethylamine	2.536	2.523	1,2-Diethylbenzene	4.063	4.154
Diethylamine	2.027	2.033	Dichloromethane	1.710	1.760
Aniline	3.521	3.506	Naphthalene	4.609	4.631
Cyclohexane	2.475	2.477	1-Methylnaphthalene	5.299	
Chlorobenzene	3.184	3.218	2-Methylnaphthalene	5.083	
Bromobenzene	3.588	3.597	Fluorene	6.186	
Nitrobenzene	3.992	3.992	Indane	3.991	
Methanol	0.758	0.936	Indene	4.005	
1-Propanol	1.679	1.660	Biphenyl	5.485	

[a] Experimental values obtained in this work.
[b] Data from Weckwerth et al. [10].

without significant loss of mass. The essential problem encountered with packed columns concerned adsorption effects [9,19]. In this study we used PTFE columns, inert and stable up to 330 K. Selecting an appropriate support material can reduce the adsorption on the surface of the support. Preliminary tests showed that the best results were obtained with the Chromosorb P AW DMCS and the Chromosorb W HP. Both supports were loaded with 15% of *n*-pentacontane. The fact that with Chromosorb P AW DMCS retention times depend on the sample size and chromatographic peaks are asymmetric indicates the presence of adsorption. Moreover, retention times of alcohols are longer than expected, indicating the presence of active adsorption sites on the support surface. The Chromosorb W HP support has a lower specific area and a smaller concentration of hydroxyl groups which reduces the adsorption. Results obtained are in good agreements with literature data for

most of the compounds studied and retention times depend only slightly on the sample size. However, retention times observed with polycyclic aromatic hydrocarbons are still longer than expected. Good results were obtained by deactivating the column (Tables 2 and 3) with Silyl 8, as recommended by Kersten and Poole [20]. Eq. (7) shows that correlation between log L^{16} measured with packed column coated with *n*-pentacontane at 373.2 K and experimental data at 298.2 K taken from Refs. [1,6–8,21] is satisfactory:

$$\log L^{16}_{373.2} = (1.00036 \pm 0.00062) \log L^{16}_{298.2};$$
$$n = 35, R = 0.9998, \text{SD} = 0.010 \qquad (7)$$

The use of packed columns with Chromosorb W HP coated with *n*-alkane and deactivated with Silyl 8 made it possible to obtain a homogenous set of log L^{16} values in good agreement with literature data.

Table 2
Partition coefficient log $L^{16\ exp}$ at 298.2 K obtained with a $C_{50}H_{102}$ packed column at 373.2 K

Compound	Log L^{16a}	Log $L^{16\ exp}$
n-Hexane	2.668	2.660
n-Octane	3.677	3.670
n-Nonane	4.182	4.180
n-Decane	4.685	4.686
n-Undecane	5.191	5.189
n-Dodecane	5.696	5.699
n-Tridecane	6.200	6.198
n-Tetradecane	6.705	6.701
n-Pentadecane	7.209	7.205
n-Hexadecane	7.714	7.711
Benzene	2.792	2.810
Toluene	3.325	3.331
Ethylbenzene	3.778	3.782
o-Xylene	3.939	3.943
m-Xylene	3.868	3.870
p-Xylene	3.839	3.841
1,3,5-Trimethylbenzene	4.344	4.348
1,2-Diethylbenzene	4.732	4.728
Triethylamine	3.040	2.947
1-Butanol	2.539	2.545
1-Pentanol	3.106	3.094
1-Octanol	4.569	4.556
1-Decanol	5.628	5.631
Butanone	2.287	2.274
2-Pentanone	2.755	2.758
Pyridine	3.022	3.033
Thiophene	2.819	2.809
Naphthalene	5.161	5.162
1-Methylnaphthalene	5.789	5.785
2-Methylnaphthalene	5.771	5.772
1,4-Dimethylnaphthalene	6.339	6.338
1,6-Dimethylnaphthalene	6.280	6.284
cis-Decahydronaphtalene		5.162
Indane	4.590	4.598
Phenanthrene	7.632	7.638

[a] Literature data [1,6–8,20].

4.3. Temperature gradient method

The packed column technique can be used to measure log L^{16} data of volatile organic compounds. The reasonable limit of application of this method is the retention time of n-eicosane. Experimental quantitative determination of log L^{16} of heavier compounds is difficult. To enlarge the applicability of chromatographic methods to organic compounds less volatile than n-eicosane, we used a method based on temperature gradient chromatography. Recently, Donovan [22] showed that the retention times of

Table 3
Retention times t_R and partition coefficient log $L^{16\ exp}$ at 298.2 K obtained using experimental data determined with a $C_{50}H_{102}$ packed column at 423.2 K

Compound	t_R (min)	Log $L^{16\ exp}$	Log L^{16a}
n-Nonane	1.17	4.170	4.176
n-Decane	1.87	4.682	4.686
n-Undecane	3.09	5.190	5.191
n-Dodecane	5.29	5.696	5.696
n-Tridecane	9.04	6.193	6.200
n-Tetradecane	16.28	6.711	6.705
n-Pentadecane	28.20	7.212	7.209
n-Hexadecane	48.80	7.716	7.714
n-Heptadecane	88.23	8.215	8.218
n-Octadecane	151.1	8.725	8.722
n-Nonadecane	268.1	9.236	9.226
n-Docosane	1390	10.732	10.740

[a] Experimental data taken from Refs. [6–8].

heavy organic compounds obtained in a gradient mode are linearly related to the logarithm of the vapour pressure at 298.2 K. The authors used a Megabore DB-1 column at high flow-rates of the gas phase. This method makes it possible to reduce considerably retention time. It was applied to determine the vapour pressures of pesticides and polycyclic aromatic hydrocarbons. Recently the same technique was used by Puri et al. [23] to determine the enthalpy of vaporization of heavy hydrocarbons. According to Donovan [22] two experimental data (vapour pressure or enthalpy of vaporization) are needed to establish parameters of the linear relationship between the vapour pressure and the retention time. Nevertheless, it must be noted that the precision of the results presented by Donovan is not always satisfactory. Indeed, temperature gradient experiments are carried out under non-equilibrium conditions. Moreover, the stationary phase DB-1 is slightly polar [11]. Corresponding system parameters of the poly(dimethylsiloxane) immobilized in a DB-1 column were published by Li et al. [11]. Values determined at $T = 60°C$ are as follows: $r = 0$, $s = 0.211$, $a = 0.308$ and $b = 0$. Therefore, experimental results obtained with a DB-1 column can be used to determine log L^{16} only if the LSER parameters expressing solute polarity are known; in this case log L^{16} of the solute can be calculated. No general relationship between the reduced retention time and log L^{16} valid with all organic compounds can be

obtained without the knowledge of the above parameters.

However, we hypothesize that this approach can be used to establish relationship between the reduced retention time and log L^{16} within a series of compounds. Indeed, polar parameters vary only slightly and in a regular way within a series. Moreover, as shown by Li et al. [11] certain parameters decrease strongly with rising temperature. Therefore, it can be supposed that the effect of the stationary phase polarity is nearly constant within a homologous series of moderately polar compounds. Measurements performed in a gradient mode with several homologous series confirmed this hypothesis. However, linear relationship does not afford the precision required for the log L^{16} determination. It was noticed that not only the reduced retention time t_R but also the corresponding temperature T is needed to establish the appropriate function. Function log $L^{16} = f(t_R, T)$ is linear with $R = 0.996$ that is not enough to represent the log L^{16} with the precision required. We found that the suitable function is as follows:

$$\log L^{16} = \exp\left[\frac{f(t_R)}{T}\right] \tag{8}$$

In the case of n-alkanes function $f(t_R)$ was obtained with log L^{16} literature data of n-alkanes from n-dodecane up to n-docosane. The plot of $f(t_R)$ and values of parameters determining this function are given in Fig. 1. The log L^{16} of n-alkanes up to $n = 38$ calculated with Eq. (8) using gradient mode results are presented in Table 4. As experimental data for heavy n-alkanes are not available in the literature we
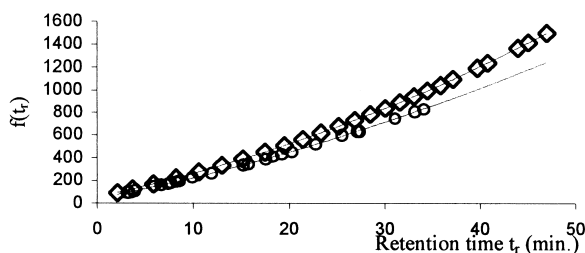
Table 4
Retention times t_R and partition coefficients log $L^{16\ \mathrm{exp}}$ of n-alkanes determined at 298.2°C using the gradient method on a DB-1 column

Compound	t_R (min)	Log $L^{16\ \mathrm{exp}}$	Log $L^{16\mathrm{a,b}}$
n-Undecane	3.70	5.221	5.191[a]
n-Dodecane	5.87	5.705	5.696[a]
n-Tridecane	8.18	6.195	6.200[a]
n-Tetradecane	10.60	6.707	6.705[a]
n-Pentadecane	12.98	7.221	7.209[a]
n-Hexadecane	15.15	7.707	7.714[a]
n-Heptadecane	17.42	8.237	8.218[a]
n-Octadecane	19.47	8.739	8.722[a]
n-Nonadecane	21.42	9.239	9.226[a]
n-Eicosane	23.30	9.743	9.731[a]
n-heinecosane	25.12	10.253	10.236[a]
n-Docosane	26.85	10.760	10.740[a]
n-Tricosane	28.48	11.259	11.252[a]
n-Tetracosane	30.05	11.759	11.758[a]
n-Pentacosane	31.57	12.262	12.244[b]
n-Hexacosane	33.07	12.779	12.744[b]
n-Heptacosane	34.47	13.280	13.244[b]
n-Octacosane	35.82	13.780	13.744[b]
n-Nonacosane	37.15	14.291	14.244[b]
n-Heinetriacontane	39.70	15.321	15.244[b]
n-Dotriacontane	40.80	15.787	15.744[b]
n-Pentatriacontane	44.00	17.223	17.244[b]
n-Hexatriacontane	45.08	17.736	17.744[b]
n-Octatriacontane	47.00	18.684	18.744[b]

[a] Literature data [6–8].
[b] Estimates calculated using the group contribution method proposed in this study.

compared our results with estimates obtained using described below group contribution method. Correlation between two series of results is given by Eq. (9):

$$\log L^{16}_{\mathrm{gradient\ method}} = (0.9995 \pm 0.0014)\log L^{16}_{298.2}$$
$$+ (0.0196 \pm 0.0169);$$
$$n = 24, R = 0.999, \mathrm{SD} = 0.023 \tag{9}$$

The statistical analysis of this regression indicate that gradient chromatography can be used to extrapolate log L^{16} in a homologous series and offers the only experimental way to determine this parameter for non-volatile compounds. Moreover, it must be noted that only 60 min are needed for determining the partition coefficient of n-octatriacontane (n-$C_{38}H_{78}$) with the gradient method while a measurement of the partition coefficient of n-docosane at

Fig. 1. Plot of $f(t_R)$ function established with temperature gradient method; aromatic and polycyclic aromatic compounds (○), n-alkanes (◊). Corresponding analytical representations are as follows: $f(t_R)_{\mathrm{alkanes}} = 0.267 t_R^2 + 18.007 t_R + 56.978$ and $f(t_R)_{\mathrm{aromatics}} = 0.2054 t_R^2 + 16.254 t_R + 41.882$.

Table 5
Partition coefficients log $L^{16\ \text{exp}}$ of aromatic and polycyclic aromatic compounds at 298.2°C determined with the gradient method on a DB-1 column

Compound	t_R(min)	Log $L^{16\ \text{exp}}$	Log L^{16a}
p-Xylene	3.33	3.822	3.839
Ethylbenzene	3.14	3.780	3.778
1,3,5-Trimethylbenzene	5.92	4.319	4.344
1,2,3-Trimethylbenzene	7.38	4.574	4.565
1,2,4-Trimethylbenzene	6.64	4.451	4.441
1,4-Diethylbenzene	8.56	4.764	4.732
1,2-Diethylbenzene	8.22	4.710	4.732
Indane	7.66	4.620	4.590
Acenaphtene	20.27	6.539	
Naphthalene	11.92	5.277	5.161
1-Methylnaphthalene	15.66	5.835	5.789
2-Methylnaphthalene	15.23	5.771	5.771
1,5-Dimethylnaphthalene	19.19	6.371	6.447
2,6-Dimethylnaphthalene	18.30	6.234	6.226
Biphenyl	17.56	6.122	6.014
Fluorene	22.77	6.936	
Phenanthrene	27.16	7.670	7.632
Anthracene	27.45	7.721	7.568
9-Methylanthracene	31.10	8.377	
Pyrene	34.10	8.949	
Fluoranthene	33.15	8.764	

[a] Literature data [6–8,20].

$T = 373.2$ K takes more than 24 h. It is reasonable to suppose that partition coefficients of heavy *n*-alkanes up to approximately $C_{45}H_{92}$ can be obtained with the gradient method. In Table 5, results obtained with aromatic and polycyclic aromatic hydrocarbons are reported. Standard deviations are greater in this case (SD = 0.044). This can be explained by the fact that the two families of compounds considered should be dealt with two separate reference functions $f(t_R)$.

It should be pointed out that the present approach based on gradient mode chromatography can be used only to determine log L^{16} within a homologous series of moderately polar compounds. The use of the present method with less polar stationary phase (recently, Li et al. [11] have shown that in the case of poly(methyloctylsiloxane) columns $r = 0$, $a = 0$, $b = 0$) can facilitate the study of polar compounds and perhaps obtain more general results.

5. Group contribution method for calculation of the partition coefficient log L^{16}

Predictive methods allow to calculate these physico–chemical parameters which are inaccessible via direct experiment. This alternative is particularly interesting in the case of log L^{16} of non-volatile compounds. We consider that the methods described in the preceeding paragraph are useful for the determination of log L^{16} of volatile and moderately non-volatile compounds. The gradient method allows one to move experimental limits towards molecules as non-volatile as *n*-octatriacontane. The thermal stability of stationary phases and different compounds defines ultimate limits of chromatographic methods. Therefore, the large data bank of log L^{16} values already available in the literature can be used to establish group additivity rules and to predict log L^{16} of less volatile compounds. Havelec and Sevcik [15,16] presented a general group contribution method making it possible to calculate accurate estimates of log L^{16} of about 2000 organic compounds. The number of groups necessary to obtain good estimates of log L^{16} depends on the complexity of the molecular structure and rises in the case of polyfunctional molecules. This explains the high number of adjustable parameters used in the model of Havelec and Sevcik [15,16]. For instance, log L^{16} of non-aromatic hydrocarbons is established with 33 parameters and nine structural contributions. The total number of all group parameters, interactional parameters and structural contributions is 131. The contribution of a given group is represented by Havelec and Sevcik with three parameters related to the structure of the molecule and to its interactions with the stationary phase [15,16]. As log L^{16} is dependent on the solute vapour pressure and on the infinite dilution activity coefficient this approach is basically correct. However, molecular interactions are always related to *n*-hexadecane and certain parameters can be correlated. Platts et al. [17] recently proposed a new predictive method based on a careful analysis of contributions of various functional groups to establish log L^{16} and other LSER parameters. Therefore, molecular segments were defined in view to obtain good estimates of each. The log L^{16} of hydrocarbons is calculated with nine parameters only. This method was established with 81 parameters, using a databank of 1908 compounds. We propose a new model to calculating log L^{16} for non-volatile organic compounds with special attention paid to heavy hydrocarbons. Data for 550 organic compounds containing mainly hydrocarbons and members of homologous

series were used in regression. Basic heteroatom segments were taken into account but the polyfunctional organic compounds were not dealt with. Values of $\log L^{16}$ were taken from the literature [1,6–8,21]. To elaborate the group contribution method a simple and efficient approach proposed by Joback [24] was used. Accordingly, $\log L^{16}$ of the compound X was calculated with the following expression:

$$\log L_{X}^{16} = \sum_{i} n_i c_i \tag{10}$$

where c_i is the contribution of the group "i" and n_i is the number of groups "i" in the compound X. Values of 33 parameters c_i were calculated using multi-linear regression and are given in Table 6. The standard deviation obtained with this regression was SD = 0.122. Two structural increments were introduced for molecules containing two or three aromatic rings. Increments corresponding to four and more ring structures could not be established due to the lack of experimental data. An increment for long chain *n*-alkanes with $n > 20$ was necessary to represent experimental data published in literature [1,6–8,21] well. This was established with $\log L^{16}$ data of *n*-alkanes with $20 < n < 24$. Table 7 presents esti-

mates of $\log L^{16}$ of 39 compounds that were not included in the regression data set. These estimates are compared with those given by models proposed by Havelec and Sevcik [15,16], and by the model of Platts et al. [17]. Results obtained with *n*-alkanes reproduce well literature data up to *n*-tetracosane. Results for *n*-alkanes with $24 < n < 29$ are in agreement with experimental results obtained using a gradient method. The latter data were not included in the data set used in regression. Deviations observed with aromatic and polycyclic compounds are generally of the order of the experimental uncertainty. Important deviations observed with certain polyfunctional isomers can be explained by the proximity effect that was not taken into account in the presented model. Table 8 shows that standard deviations obtained using four methods considered are of the same order. Slightly worse results obtained with Platts's model [17] can be explained by a smaller number of characteristic hydrocarbon parameters. On the other hand $\log L^{16}$ of hydrocarbons is estimated with the same standard deviation by Havelec and Sevcik models [15,16] using 32 parameters, and by the present model with 12 parameters only. We believe that the present model can afford trustful

Table 6
Group contribution approach to calculating $\log L^{16}$ at 298.2 K

Molecular segment	c_i	Molecular segment	c_i
Non-ring increments:		Halogen increments:	
CH_3-	0.370	$-F$	0.085
$-CH_2-$	0.498	$-Cl$	0.747
$-CH\langle$	0.452	$-Br$	1.242
$\rangle C\langle$	0.299	Oxygen increments:	
$CH_2=$	0.210	$-OH$ (alcohol)	0.611
$-CH=$	0.472	$-OH$ (phenol)	0.702
$CH\equiv$	0.075	$-O-$ (non-ring)	0.354
$-C\equiv$	0.572	$-O-$ (ring)	-0.089
Ring increments:		$\rangle C=O$ (nonring)	1.035
$-CH_2-$	0.529	$O=CH-$ (aldehyde)	0.996
$\rangle C\langle$	0.196	$-COOH$ (acids)	1.464
$-CH\langle$	0.385	$-COO-$ (esters)	1.083
$-CH=$	0.480	Sulfur increments:	
$=C\langle$	0.613	$-SH$	1.305
Nitrogen increments:		$-S-$ (non-ring)	1.492
$-NH_2$	0.779	$-S-$ (ring)	1.023
$\rangle NH$ (nonring)	0.659	Three-rings	0.346
$\rangle NK$ (ring)	0.659	Four-rings	0.600
$\rangle N-$	0.436	Long chain increment:	
$-CN$	1.612	For *n*-alkanes with $n > 20$	$0.002 \times n$
$-NO_2$	1.528		

Values of group increments defined according to Eq. (6).

Table 7
Group contribution approach to calculating log L^{16} at 298.2 K

Compound	Log $L^{16\,exp}$	Log L^{16a}	Log L^{16b}	Log L^{16c}	Log L^{16d}	MSD[a]	MSD[b]	MSD[c]	MSD[d]
Ethylcyclohexane	3.877	3.898	3.873	3.918	3.814	0.021	0.004	0.041	0.063
Benzofuran	4.355	4.460	4.459	4.621	4.421	0.105	0.104	0.266	0.066
2-Chlorostyrene	4.785	4.575	4.965	4.798	4.506	0.21	0.18	0.013	0.279
2-Ethoxyethanol	2.815	2.829	2.886	2.883	2.850	0.014	0.071	0.068	0.035
1-Methoxy-2-propanol	2.655	2.655	2.699	2.644	2.622	0.000	0.044	0.011	0.033
Methyl butanoate	2.893	2.819	2.819	2.755	2.901	0.074	0.074	0.138	0.008
Pentyl butanoate	4.764	4.811	4.815	4.763	4.897	0.047	0.051	0.001	0.133
Ethyl hexanoate	4.251	4.313	4.316	4.261	4.398	0.062	0.065	0.010	0.147
Methyl nonanoate	5.321	5.309	5.314	5.265	5.396	0.012	0.007	0.056	0.075
2-Chloroaniline	4.674	4.672	4.750	4.927	4.574	0.002	0.076	0.253	0.100
3-Chloroaniline	4.909	4.672	4.750	4.927	4.574	0.237	0.159	0.018	0.335
3,4-Dimethylaniline	5.089	5.002	4.618	5.105	4.870	0.087	0.471	0.016	0.219
2-Methoxyaniline	4.818	4.777	4.451	4.974	4.754	0.041	0.367	0.156	0.064
Hexylthiol	4.133	4.165	4.165	4.148	4.074	0.032	0.032	0.015	0.059
Heptylthiol	4.635	4.663	4.669	4.650	4.573	0.028	0.034	0.015	0.062
Fluorocyclohexane	3.215	3.115	2.894	3.094	2.801	0.100	0.321	0.121	0.414
Cyclooctene	4.119	4.134	4.232	4.164	3.992	0.015	0.113	0.045	0.127
2-Methyl-2-butene	2.226	2.225	2.132	2.182	2.056	0.001	0.094	0.044	0.170
2-Methyl-2-pentene	2.588	2.723	2.631	2.684	2.555	0.135	0.043	0.096	0.033
1,3-Cyclohexadiene	2.917	2.884	2.884	3.008	2.874	0.033	0.033	0.091	0.043
1,4-Cyclohexadiene	3.132	2.884	2.884	3.008	2.874	0.248	0.248	0.124	0.258
Isopentylamine	3.058	2.967	2.941	3.010	2.870	0.091	0.117	0.048	0.188
9-Methylanthracene	8.377	8.101		8.475	8.262	0.276		0.098	0.115
Pyrene	8.949	9.078		9.498	9.154	0.129		0.549	0.205
1,5-Dimethylnaphthalene	6.447	6.072		6.456	6.432	0.375		0.009	0.015
2,6-Dimethylnaphthalene	6.226	6.072		6.456	6.432	0.154		0.230	0.206
Fluorene	6.936	6.821		7.303	6.747	0.115		0.367	0.189
Fluoranthene	8.764	8.824		8.323	8.434	0.060		0.441	0.330
n-Heinetriacontane	15.321	15.244	15.282	15.238	15.113	0.077	0.039	0.083	0.208
n-Dotriacontane	15.787	15.744	15.786	15.74	15.612	0.043	0.001	0.047	0.175
n-Pentatriacontane	17.223	17.244	17.298	17.246	17.109	0.021	0.075	0.023	0.114
n-Hexatriacontane	17.736	17.744	17.802	17.748	17.608	0.008	0.066	0.012	0.128
n-Octatriacontane	18.684	18.744	18.810	18.752	18.606	0.060	0.126	0.068	0.078
Undecanoic acid	6.640	6.316	6.458	6.450	6.354	0.324	0.182	0.190	0.286
Dodecanoic acid	7.180	6.814	6.962	6.952	6.853	0.366	0.218	0.228	0.327
Heptyl acetate	4.865	4.811	4.798	4.763	4.856	0.054	0.067	0.102	0.009
3,4-Dihydropyran	2.910	2.901	2.876	2.993	2.794	0.009	0.034	0.083	0.116
Methoxyflurane	2.864	3.139	2.856	2.813	2.625	0.275	0.008	0.051	0.239

[a,b,c,d]Log $L^{16\,exp}$: experimental data (this work, [1,6–8,20]). [a,b,c,d]Log L^{16} estimates and corresponding MSDs obtained with the group contribution method proposed by: [a]Mutelet and Rogalski, this work; [b]Havelec and Sevcik [15]; [c]Havelec and Sevcik [16]; [d]Platts et al. [17]. MSD is the mean square deviation between experimental and calculated data.

estimates of the log L^{16} of non-volatile organic compounds, excluding polyfunctional molecules.

6. Conclusion

In this study we used several chromatographic methods in view of determining the gas–liquid *n*-hexadecane partition coefficient, log L^{16}, of non-

volatile compounds at 298.2 K. Log L^{16} values of moderately non-volatile compounds were determined using capillary columns coated with apolane. This technique was successfully applied at temperatures up to 373.2 K. At this temperature, log L^{16} of compounds boiling as high as 580 K can be determined. Packed columns coated with *n*-hexatriacontane or *n*-pentacontane were used with still heavier compounds with boiling temperatures up to

Table 8
Results of linear correlation between experimental and estimated $\log L^{16}$ data

Group contribution method	n	SD	R^2
This work	38	0.1040	0.9990
Havelec and Sevcik [15]	32	0.1100	0.9991
Havelec and Sevcik [16]	38	0.1110	0.9986
Platts et al. [17]	38	0.1500	0.9989

Statistic parameters were obtained with the training test detailed in Table 7.

650 K. It was demonstrated that the use of PTFE columns packed with *n*-alkane coated Chromosorb W HP and deactivated with Silyl 8 allows one to obtain a homogenous set of $\log L^{16}$. For the first time, an experimental approach based on the gradient temperature mode was proposed to determining $\log L^{16}$ of compounds with boiling points exceeding 650 K. The method offers a unique experimental way to determine $\log L^{16}$ values of non-volatile compounds. The retention time observed with *n*-octatriacontane, the heaviest *n*-alkane studied, was 60 min, which indicates that this method can be used to determine $\log L^{16}$ of compounds even less volatile.

On the other hand, a simple and general group contribution method was elaborated with a large literature data base to estimate $\log L^{16}$ values of non-volatile hydrocarbons and monofunctional organic compounds.

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