

# Using temperature gradient gas chromatography to determine or predict vapor pressures and linear solvation energy relationship parameters of highly boiling organic compounds

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## Abstract

An isothermal chromatographic method allowing determination of  $\Sigma\beta_2^H$  and  $\Sigma\alpha_2^H$  descriptors of the linear solvation energy relationship (LSER) was tested and results obtained are presented. This method is based on the use of four stationary phases of various polarity. On the other hand, it was demonstrated that the temperature gradient chromatography may be successfully used to determine LSER descriptors. Results of  $\pi_2^H$ ,  $\Sigma\beta_2^H$  and  $\log L^{16}$  determination are reported. This approach opens new possibilities of precise and rapid determination of LSER descriptors of high boiling compounds using a small number of phases. It was demonstrated that the  $\log L^{16}$  descriptor may be used to estimate vapor pressures of high boiling organic compounds with a better accuracy than those usually obtained with chromatographic methods.

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## 1. Introduction

Important progress has been made over the last years in understanding the relationships between various properties of organic compounds and their chemical structures. Numerous predictive models were developed that aim to predict mixture thermodynamic properties from parameters that quantify the structure of a pure component. Such models are called quantitative structure–activity relationships

(QSARs). Among the most significant achievements of QSARs is the linear solvation energy relationship (LSER) of Kamlet et al. [1] that has the form:

$$\begin{aligned} \text{Property} = & \text{bulk/cavity} + \text{dispersive forces} \\ & + \text{dipolarity/polarizability} \\ & + \text{hydrogen bonding acidity} \\ & + \text{hydrogen bonding basicity} \end{aligned} \quad (1)$$

Each of these descriptors characterizing corresponding terms in Eq. (1), were derived empirically; the cavity term was usually the molar volume while

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the other three terms were determined from UV–Vis spectral shifts [2–4]. Abraham et al. proposed to reformulate Eq. (1) in terms of parameters drawn from chromatographic results. They suggested using the solute gas–liquid partition coefficient on *n*-hexadecane at 25 °C,  $\log L^{16}$ , to describe dispersion interactions and the cavity formation process [5]. Thus,  $\log L^{16}$ , dipolarity/polarizability and polarizability are correlated. Indeed, dispersion interactions are strongly dependent on the solute polarizability and the cavity formation process is dependent on the solute volume and consequently on the molar refraction. Accordingly, in the LSER model, the first three terms of Eq. (1) can be described as a function of  $\log L^{16}$  and of descriptors characterizing dipolarity/polarizability and polarizability. Inherent correlation of these parameters makes their experimental determination difficult. While the first three terms of Eq. (1) do not model any single specific type of interaction, the last two are well defined and successfully model the capacity to form hydrogen bonding.

The LSER model proposed by Abraham and co-workers [5–8] to express a given property SP is as follows:

$$\log \text{SP} = c + rR_2 + s\pi_2^{\text{H}} + a\sum\alpha_2^{\text{H}} + b\sum\beta_2^{\text{H}} + l \log L^{16} \quad (2)$$

In this equation, the property SP is expressed in terms of five LSER descriptors.

$\log L^{16}$  is the partition coefficient of the solute between *n*-hexadecane and the perfect gas at 298.15 K. The solute excess molar refraction ( $R_2$ ) is the difference between the refraction of the compound and the refraction of a hypothetical *n*-alkane of the same volume [6].

The effective solute hydrogen bond acidity ( $\sum\alpha_2^{\text{H}}$ ) and the effective solute hydrogen bond basicity ( $\sum\beta_2^{\text{H}}$ ) are defined as proposed by Abraham [7]. The author established scales of solute hydrogen bond acidity  $\alpha_2^{\text{H}}$  and solute hydrogen basicity  $\beta_2^{\text{H}}$  using 1:1 complexation constants in tetrachloromethane. In order to take into account all kind of complexation of the solute with any surrounding solvent molecules he used scales defined as the “summation” hydrogen bond acidity  $\sum\alpha_2^{\text{H}}$  and the “summation” hydrogen

bond basicity  $\sum\beta_2^{\text{H}}$  [7]. This new scale was set up with gas–liquid chromatography data that made it possible to enlarge considerably the number of the compounds included. The descriptor  $\pi_2^{\text{H}}$  corresponds to the effective dipolarity/polarizability of the solute.

Coefficients *c*, *r*, *s*, *a*, *b* and *l* reflect properties of the solvent phase. *r*, *s*, *a*, *b*, and *l* are complementary properties of  $R_2$ ,  $\pi_2^{\text{H}}$ ,  $\sum\alpha_2^{\text{H}}$ ,  $\sum\beta_2^{\text{H}}$  and  $\log L^{16}$ , respectively.

The descriptors  $\pi_2^{\text{H}}$ ,  $\sum\alpha_2^{\text{H}}$ ,  $\sum\beta_2^{\text{H}}$  and  $\log L^{16}$  are usually determined using gas–liquid chromatography. The main problem of their experimental determination is to avoid the correlation between descriptors. Therefore, descriptors published in the literature were usually obtained using numerous chromatographic stationary phases [8–11]. These phases were selected in a way to cover a large interval of *r*, *s*, *a*, *b*, and *l* descriptors. Today, one can find in the open literature descriptors of more than 2000 organic compounds. These data may be used to check and to scale new experimental results obtained with a view of determining LSER descriptors. The use of literature data allows to reducing the number of stationary phases that are necessary to obtain non-correlated results. In the present work  $\pi_2^{\text{H}}$ ,  $\sum\alpha_2^{\text{H}}$  and  $\sum\beta_2^{\text{H}}$  descriptors were established using this approach.

Large uncertainties caused by adsorption may appear during chromatographic determination of the capacity factor of high boiling compounds. Li et al. [12] and Abraham et al. [13] studied the influence of the support and of the stationary phase loading on adsorption phenomena. They concluded that the high loading ratio of the stationary phase and the high temperature of the column allow to reduce adsorption. According to findings of these authors, the loading ratio used in this work was of 15% with all packed columns. That allowed considerable reduction of adsorption.

Very long retention times that are observed with high boiling compounds limit the application domain of isothermal mode chromatography. It was demonstrated [10] that gradient temperature mode chromatography (GTC) considerably reduces retention times and may be successfully used to determine LSER descriptors within a homologous series of compounds. This finding agrees with results of Martos et al. [14]. They showed that the logarithm of dis-

tribution coefficient ( $\log K$ ) and linear temperature-programmed retention index (LTPRI) are linearly correlated within a homologous series. According to this result, it is possible to establish distribution coefficient corresponding to every peak in a chromatogram provided that its LTPRI (published or experimentally determined) is known:

$$\log(K) = a + b \cdot \text{LTPRI} \quad (3)$$

The LTPRI has been used [15] to establish a new scale of retention index similar to that introduced by Kovats [16]. In this case, retention index (LTPRI) may be established within a homologous series in the following way:

$$\text{LTPRI} = 100 \cdot \left( \frac{t_{R(A)} - t_{R(n)}}{t_{R(n+1)} - t_{R(n)}} \right) + 100n \quad (4)$$

where  $t_{R(A)}$  is the solute retention time,  $t_{R(n)}$  is the retention time of the  $n$ -alkane eluting directly before  $t_{R(A)}$ ,  $t_{R(n+1)}$  is the retention time of the  $n$ -alkane eluting directly after  $t_{R(A)}$ , and  $n$  is the number of carbon atoms for  $t_{R(n)}$ . It must be pointed out that Eq. (4) is established with retention times and not with logarithms of retention times as in the case of Kovats index [16]. Consequently,  $\log(K)$  may be directly related to the solute retention time  $t_{R(A)}$  using Eqs. (3) and (4). On the other hand, the molar free energy of transfer between the mobile phase and the stationary is related to  $\log(K)$  and to the retention time  $t_R$  measured in the temperature gradient mode, as given by Eq. (5):

$$\Delta G^0 = RT \log K = f(t_R) \quad (5)$$

In this case, the LSER equation proposed by Abraham must be rewritten as follows:

$$t_R = c' + r'R_2 + s'\pi_2^H + a'\sum\alpha_2^H + b'\sum\beta_2^H + l'\log L^{16} \quad (6)$$

As TGC data can be used to establishing LSER parameters within a homologous series only, they do not allow to characterize the stationary phase. Thus,  $c'$ ,  $r'$ ,  $l'$ ,  $s'$ ,  $a'$  and  $b'$  coefficients obtained with TGC data have not the same meaning and values as  $c$ ,  $r$ ,  $l$ ,  $s$ ,  $a$  and  $b$  obtained with isothermal conditions. Nevertheless, it is still possible to relate

retention times to  $R_2$ ,  $\pi_2^H$ ,  $\sum\alpha_2^H$ ,  $\sum\beta_2^H$  and  $\log L^{16}$  descriptors.

In the present work, we developed a new and fast method to establish LSER descriptors in terms of TGC retention times and we determined values of descriptors  $\pi_2^H$ ,  $\sum\beta_2^H$  and  $\log L^{16}$  of a series of organic compounds. Moreover, we showed that the descriptor  $\log L^{16}$  may be used to estimate vapor pressures of high boiling organic compounds with a better accuracy than those usually obtained with chromatographic methods.

## 2. Experimental

Both isothermal mode chromatography (IC) and GTC experiments were carried out 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. 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. Packed columns used in ion chromatography (IC) were prepared with Carbowax 20M, Apiezon L, OV 17 and OV 210 purchased from Supelco, USA. Stationary phases used with packed columns were prepared by soaking chromatographic silica WHP 60–80 mesh from Supelco, in 15% stationary phase/appropriate solvent solution. After evaporation of the solvent under vacuum the support was equilibrated at 423 K during 4 h. The mass of the packing material was calculated from the mass of the packed and empty column and was checked during experiments.

The dead time of packed columns was determined with the retention time of the air. Experiments with the gradient chromatography were carried out using a Megabore 15 m×0.53 mm I.D. DB-1 capillary column with a 1.5  $\mu\text{m}$  bonded methyl silicone stationary phase purchased from J&W Scientific, USA. This column is considered as non-polar, and can be used up to 605 K. The injected volumes of the sampled vapor were 0.1  $\mu\text{l}$ . Nonvolatile com-

pounds were dissolved in acetone or ethyl acetate before injection. GTC experiments were performed between 313 and 593 K with a heating rate of 10 °C/min. 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. Results and discussion

Below results concerning determination of LSER descriptors  $\pi_2^H$ ,  $\Sigma\alpha_2^H$ ,  $\Sigma\beta_2^H$  and  $\log L^{16}$  using IC and GTC modes are reported.

#### 3.1. IC determination of $\pi_2^H$ and $\Sigma\alpha_2^H$ using packed columns with four stationary phases

Determination of  $\pi_2^H$  and  $\Sigma\alpha_2^H$  descriptors was carried out using four stationary phases of varying polarity; Carbowax 20M, Apiezon L, OV 17 and OV 210. Coefficients  $c$ ,  $r$ ,  $s$ ,  $a$  and  $b$  of these stationary phases were determined at 403.2 K using 26 probes (Table 1), selected to cover a wide range of LSER descriptors. This set of probes included structurally diversified solute molecules, which were chosen in order to minimize the correlation between the five descriptors  $R_2$ ,  $\pi_2^H$ ,  $\Sigma\alpha_2^H$ ,  $\Sigma\beta_2^H$  and  $\log L^{16}$ . The correlation matrix is listed in Table 2. Excepting a significant correlation between  $R_2$  and  $\pi_2^H$  and between  $R_2$  and  $\log L^{16}$  that is due to the LSER model characteristic properties, the correlation between parameters is rather low. Coefficients of four phases were calculated with solute retention data using multiple linear regression analysis (MLRA). In this case,  $c$ ,  $r$ ,  $s$ ,  $a$ ,  $b$  and  $l$  coefficients were calculated using Minitab software. Results reported in Table 3 are in good agreement with the literature data [5–11]. While coefficient  $b$  characterizing the hydrogen bond acidity is zero with four stationary phases studied, Eq. (2) reduces to Eq. (7):

$$\log t'_R = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + l\log L^{16} \quad (7)$$

Four stationary phases were used to determine  $\pi_2^H$  and  $\Sigma\alpha_2^H$  descriptors. Calculations were carried out using literature data of  $\log L^{16}$  and  $R_2$  descriptors. Retention times of 73 compounds on four stationary

Table 1  
LSER descriptors of the 26 solute probes

Compound	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\log L^{16}$
<i>n</i> -Hexane	0.000	0.00	0.00	0.00	2.668
<i>n</i> -Octane	0.000	0.00	0.00	0.00	3.677
<i>n</i> -Nonane	0.000	0.00	0.00	0.00	4.182
Cyclohexane	0.305	0.1	0.00	0.00	2.964
1-Hexene	0.078	0.08	0.00	0.07	2.572
Benzene	0.61	0.52	0.00	0.14	2.768
Toluene	0.601	0.52	0.00	0.14	3.325
Ethylbenzene	0.613	0.51	0.00	0.15	3.778
Dichloromethane	0.387	0.57	0.10	0.05	2.019
Trichloromethane	0.425	0.49	0.15	0.02	2.48
Tetrachloromethane	0.458	0.38	0.00	0.00	2.833
1-Butanol	0.224	0.42	0.37	0.48	2.601
2-Propanol	0.212	0.36	0.33	0.56	1.764
2-Pentanone	0.143	0.68	0.00	0.51	2.755
Butanone	0.166	0.7	0.00	0.51	2.287
Triethylamine	0.101	0.15	0.00	0.79	3.04
Pyridine	0.631	0.84	0.00	0.52	3.022
Thiophene	0.687	0.57	0.00	0.15	2.819
Nitropropane	0.242	0.95	0.00	0.31	2.894
2,2,2-Trifluoroethanol	0.015	0.6	0.57	0.25	1.224
Diethylether	0.041	0.25	0.00	0.45	2.015
Hexafluoroisopropanol	-0.24	0.55	0.77	0.1	1.392
1,4-Dioxane	0.329	0.75	0.00	0.64	2.892
Trifluoroethanol	0.015	0.6	0.57	0.25	1.224
2-Fluorophenol	0.66	0.69	0.61	0.26	3.453
3-Fluorophenol	0.667	0.98	0.68	0.17	3.842

phases were measured and used together with the corresponding literature data [5–11] of  $R_2$  and  $\log L^{16}$  to determine  $\pi_2^H$  and  $\Sigma\alpha_2^H$ . Calculations were carried out applying MLRA to Eq. (7). The Descfit SIMPLEX procedure [17] was used to estimate  $\pi_2^H$  and  $\Sigma\alpha_2^H$  descriptors. Comparison with literature data led to standard deviations of  $\pi_2^H$  and  $\Sigma\alpha_2^H$  of, respectively, 0.05 and 0.01. Calculated descriptors of 47 probes that were not included in the training set are reported in Table 4. A good agreement with the literature data confirms the validity of the present

Table 2  
Correlation matrix of the five descriptors obtained with 26 probes

	$R_2$	$\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\log L^{16}$
$R_2$	1				
$\pi_2^H$	0.475	1			
$\Sigma\alpha_2^H$	-0.134	0.345	1		
$\Sigma\beta_2^H$	-0.055	0.317	0.023	1	
$\log L^{16}$	0.465	0.107	0.385	-0.169	1

Table 3  
LSER coefficients of four stationary phases at  $T=403.2$  K

Stationary phase	$c$	$r$	$s$	$a$	$b$	$l$	$F$	SD	$\rho$
OV 17	-2.340 ( $\pm 0.03$ )	0.104 ( $\pm 0.03$ )	0.591 ( $\pm 0.03$ )	0.000	0.000	0.510 ( $\pm 0.01$ )	1125	0.03	0.992
Apiezon L	-2.250 ( $\pm 0.04$ )	0.204 ( $\pm 0.05$ )	0.110 ( $\pm 0.03$ )	0.086 ( $\pm 0.03$ )	0.000	0.567 ( $\pm 0.02$ )	581	0.05	0.971
OV 210	-2.430 ( $\pm 0.08$ )	-0.307 ( $\pm 0.07$ )	1.060 ( $\pm 0.07$ )	0.000	0.000	0.469 ( $\pm 0.02$ )	812	0.05	0.980
Carbowax 20M	-2.800 ( $\pm 0.06$ )	0.247 ( $\pm 0.05$ )	1.240 ( $\pm 0.06$ )	1.790 ( $\pm 0.03$ )	0.000	0.457 ( $\pm 0.02$ )	744	0.04	0.976

$F$ : Fischer  $F$ -statistic.

SD: Standard deviation of the regression.

$\rho$ : Correlation coefficient between observed and calculated  $\log t_R$  values.

method. Significant deviations observed with acids and certain polar compounds are probably due to the fact that in the case of these compounds adsorption phenomena strongly influence determination of  $\pi_2^H$  and  $\Sigma\alpha_2^H$  descriptors despite the high loading ratio of the stationary phases.

### 3.2. TGC determination of $\log L^{16}$ using the DB-1 capillary column

Recently [10], we have demonstrated that retention times of a homologous series can be related to  $\log L^{16}$ . This result was obtained with alkanes and aromatic hydrocarbons using a Megabore, 15 m  $\times$  0.53 mm I.D., DB-1 capillary column that is considered to be nearly non-polar. However, when the polarity of the DB-1 stationary phase was neglected, a strongly non-linear relationship between the reduced retention time and  $\log L^{16}$  was obtained for every one of two homologous series. When a small polarity of DB-1 is included in the correlation, Eq. (8), the relationship becomes linear and is valid for aliphatic and aromatic hydrocarbons:

$$t_R = -18.4677(\pm 0.489) + 1.6504(\pm 0.175) \cdot R_2 + 5.46918(\pm 0.072) \cdot \log L^{16} \quad (8)$$

$r=0.998$ ,  $SD=0.05$ ,  $F=2520$ ,  $n=15$ ; where  $r$  is the correlation coefficient between observed and calculated  $t_R$  values,  $SD$  is the standard deviation of the regression,  $F$  is the Fisher  $F$ -statistic and  $n$  is the number of data points.

The training test used to determine these parameters included  $n$ -alkanes from  $n$ -nonane to  $n$ -hexadecane, 1,3,5-trimethylbenzene, 1,2,3-trimethylben-

zene,  $m$ -xylene,  $cis$ -decalin, naphthalene, 1,5-dimethylnaphthalene and biphenyl. Values of  $R_2$  were either taken from the literature [5–11] or calculated using predictive method proposed by Platts et al. [18].

In the present case, values of  $r'$  and  $l'$  for the DB-1 stationary phase as given in Eq. (8) agree with literature data obtained using the IC method [19]. However, this agreement is rather an exception than the rule. Results of  $\log L^{16}$  calculated with 36 aliphatic and aromatic hydrocarbons are presented in the Table 5. Average standard deviation of about 0.05 units was observed between TGC results and the literature data of  $\log L^{16}$ . This result is satisfactory and confirms the validity of TGC to determine  $\log L^{16}$  of high boiling compounds. Estimates of  $\log L^{16}$  of four polar organic compounds are also included in Table 5. Surprisingly, results agree with the literature data. Once more, the agreement cannot be considered as generally valid with others polar compounds. Data of  $\log L^{16}$  of 10 polyaromatic hydrocarbons not published in the literature are presented in Table 6. In order to check the validity of our approach, results are compared with  $\log L^{16}$  calculated using two group contribution methods [18,20]. A good agreement is observed with values calculated using the method proposed by Platts et al. [18]. The main advantage of the TGC method is its rapidity. While, 60 min is needed to determining the retention time of  $n$ -octatriacontane ( $n$ -C<sub>38</sub>H<sub>78</sub>) using TGC, the IC method necessitates more than 24 h to establish the retention time of  $n$ -docosane at  $T=373.2$  K. The analysis of our results indicates that TGC may be used to determine  $\log L^{16}$  of compounds boiling as high as  $n$ -pentatetracontane (C<sub>45</sub>H<sub>92</sub>).

Table 4  
 $\pi_2^H$  and  $\Sigma\alpha_2^H$  descriptors obtained at  $T=403.2$  K using packed columns with four stationary phases (Table 1)

Compound	$\pi_2^{H \text{ lit}}$	$\pi_2^H$	$\Sigma\alpha_2^{H \text{ lit}}$	$\Sigma\alpha_2^H$
Cyclohexene	0.2	0.23	0.00	0.02
<i>n</i> -Decane	0.00	0.00	0.00	0.00
<i>n</i> -Undecane	0.00	0.00	0.00	0.00
<i>n</i> -Dodecane	0.00	0.00	0.00	0.00
<i>p</i> -Xylene	0.52	0.47	0.00	0.00
<i>m</i> -Xylene	0.52	0.46	0.00	0.00
<i>o</i> -Xylene	0.56	0.54	0.00	0.00
1,2,3-Trimethylbenzene	0.61	0.55	0.00	0.00
1,2,4-Trimethylbenzene	0.56	0.49	0.00	0.00
1,3,5-Trimethylbenzene	0.52	0.44	0.00	0.00
Naphthalene	0.92	0.92	0.00	0.00
1-Methylnaphthalene	0.92	0.90	0.00	0.00
<i>cis</i> -Decahydronaphthalene	0.25	0.24	0.00	0.00
1,2,3,4-Tetrahydronaphthalene	0.65	0.59	0.00	0.00
Biphenyl	0.99	0.90	0.00	0.00
Indane	0.62	0.59	0.00	0.00
Indene	0.77	0.73	0.00	0.00
2,4-Dimethylphenol	0.80	0.78	0.53	0.54
<i>p</i> -Cresol	0.87	0.86	0.57	0.58
2-Methyl-1,3-butadiene	0.23	0.23	0.00	0.05
Chlorobutane	0.40	0.43	0.00	0.01
2-Nitrotoluene	1.11	1.13	0.00	0.00
2,4,6-Trimethylpyridine	0.69	0.59	0.00	0.06
2-Nonanone	0.68	0.71	0.00	0.00
2-Hexanone	0.68	0.67	0.00	0.00
Hexanoic acid	0.60	0.90	0.60	0.54
Heptanoic acid	0.60	0.87	0.60	0.56
4-Ethyl toluene		0.46		0.00
Hexanal	0.65	0.65	0.00	0.00
Benzaldehyde	1.00	1.00	0.00	0.03
1-Heptanal	0.65	0.63	0.00	0.00
1-Hexanol	0.42	0.56	0.37	0.26
1-Heptanol	0.42	0.49	0.37	0.37
2-Heptanol	0.40	0.45	0.33	0.3
1-Octanol	0.42	0.47	0.37	0.38
1-Nonanol	0.42	0.52	0.37	0.30
1-Decanol	0.42	0.45	0.37	0.33
Butylamine	0.35	0.42	0.16	0.08
1-Pentanethiol	0.35	0.40	0.00	0.02
1-Hexanethiol	0.35	0.40	0.00	0.04
Quinoline	0.97	1.00	0.00	0.03
2,4-Dimethylpyridine	0.76	0.72	0.00	0.01
Aniline	0.96	1.02	0.26	0.27
<i>N,N</i> -Diethylaniline	0.80	0.80	0.00	0.00
2-Chloroaniline	0.92	1.06	0.25	0.21
3-Chloroanisidine		1.22		0.37

Literature data of  $\pi_2^{H \text{ lit}}$  and  $\Sigma\alpha_2^{H \text{ lit}}$  were taken from Refs. [5–11].

Table 5  
 $\log L^{16}$  of hydrocarbons determined using TGC with DB-1 capillary column

Compound	$R_2$	$\log L_{\text{lit}}^{16}$	$\log L^{16}$
<i>n</i> -Nonane	0	4.182	4.088
<i>n</i> -Decane	0	4.686	4.689
<i>n</i> -Undecane	0	5.191	5.244
<i>n</i> -Dodecane	0	5.696	5.796
<i>n</i> -Tridecane	0	6.2	6.331
<i>n</i> -Tetradecane	0	6.705	6.840
<i>n</i> -Pentadecane	0	7.209	7.321
<i>n</i> -Hexadecane	0	7.714	7.778
<i>n</i> -Heptadecane	0	8.218	8.209
<i>n</i> -Octadecane	0	8.722	8.619
<i>n</i> -Nonadecane	0	9.226	9.210
<i>n</i> -Docosane	0		10.720
<i>n</i> -Tetracosane	0	11.758	11.770
Ethylbenzene	0.613	3.778	3.766
<i>m</i> -Xylene	0.623	3.839	3.799
<i>o</i> -Xylene	0.663	3.939	3.892
<i>p</i> -Xylene	0.613	3.839	3.801
1,3,5-Trimethylbenzene	0.649	4.344	4.263
1,2,3-Trimethylbenzene	0.677	4.441	4.522
1,2,4-Trimethylbenzene	0.728	4.565	4.371
1,4-Diethylbenzene	0.645	4.732	4.747
1,2-Diethylbenzene	0.688	4.732	4.672
Naphthalene	1.34	5.161	5.152
1-Methylnaphthalene	1.344	5.789	5.834
2-Methylnaphthalene	1.304	5.771	5.768
1,5-Dimethylnaphthalene	1.369	6.447	6.472
2,6-Dimethylnaphthalene	1.329	6.226	6.322
Indane	0.829	4.59	4.527
Fluorene	1.588	6.922	7.061
Biphenyl	1.36	6.014	6.177
Anthracene	2.29	7.568	7.598
9-Methylanthracene	2.29	8.438	8.372
Phenanthrene	2.055	7.632	7.723
Pyrene	2.808	8.833	8.764
Fluoranthene	2.377	8.827	8.721
<i>cis</i> -Decaline	0.544	5.156	5.017
2,4,6-Trimethylpyridine	0.634	4.324	4.326
Quinoline	1.268	5.457	5.422
Chlorobenzene	0.718	3.657	3.663
Bromobenzene	0.882	4.041	3.952

Comparison with literature data,  $\log L_{\text{lit}}^{16}$  taken from Refs. [5–11].

### 3.3. TGC determination of $\pi_2^H$ and $\Sigma\beta_2^H$ using Apiezon L and Carbowax 20M packed columns

$\pi_2^H$  and  $\Sigma\beta_2^H$  descriptors were determined using two columns packed, respectively, with Apiezon L or Carbowax 20M stationary phases. In the case of

Table 6

Comparison of  $\log L^{16}$  of polyaromatics determined using TGC with DB-1 capillary column with  $\log L^{16}$  calculated using group contribution methods [18,20]

Compound	Log $L^{16}$		
	This work	Havelec and Sevcik [20]	Platts et al. [18]
Chrysene	10.494	10.092	10.345
Perylene	12.000	11.580	11.692
Dibenz[ <i>ah</i> ]anthracene	12.996	12.518	12.728
Benzo[ <i>a</i> ]pyrene	12.000	11.580	11.698
9-Methylanthracene	8.475	8.262	8.367
Dibenz[ <i>ac</i> ]anthracene	12.996	12.518	12.870
Benz[ <i>a</i> ]anthracene	10.494	10.092	10.296
Triphenylene	10.494	10.092	10.340
Coronene	15.012	14.556	13.944
Naphthacene	10.494	10.092	10.573

TGC measurements, the validity of  $c'$ ,  $r'$ ,  $l'$ ,  $s'$  and  $b'$  coefficients of Eq. (6) is limited to probes of similar polarity. Therefore, alcohols and aromatics were dealt with separately. Coefficients  $c'$ ,  $r'$ ,  $l'$ ,  $s'$  and  $b'$  of both homologous series do not have the same values as those obtained under isothermal conditions. As was previously mentioned, these coefficients have not the same physical meanings.

In the case of alcohols, coefficients  $c'$ ,  $r'$ ,  $l'$ ,  $s'$  and  $b'$  of both stationary phases were calculated using retention times of 10 compounds indicated in Table 7. It turned out that parameters  $a'$  and  $b'$  of

Apiezon L and  $a'$  and  $s'$  of Carbowax 20M are zero. The resulting equations are as follows:

$$t_{R \text{ Apiezon L}} = -10.3(\pm 1.472) - 15.3(\pm 12.96) \cdot R_2 + 18.3(\pm 7.516) \cdot \pi_2^H + 3.09(\pm 0.1802) \log L^{16} \quad (9)$$

$r=0.996$ ,  $SD=0.01$ ,  $F=574$ ,  $n=10$  and:

$$t_{R \text{ Carbowax 20M}} = -9.47(\pm 1.132) \cdot \sum \beta_2^H + 2.68(\pm 0.132) \cdot \log L^{16} \quad (10)$$

$F=820$ ,  $r=0.997$ ,  $SD=0.04$ ,  $n=10$ .

Table 7

$\pi_2^H$  and  $\sum \beta_2^H$  descriptors of alcohols determined using Apiezon L and Carbowax 20M packed columns equations

Compound	$\pi_2^H$ estimated	$\pi_2^H$ lit.	$\sum \beta_2^H$ estimated	$\sum \beta_2^H$ lit.
1-Pentanol	0.41	0.42	0.50	0.48
2-Pentanol	0.40	0.41		
3-Pentanol	0.41	0.40		
2-Methyl-1-butanol	0.39	0.39	0.61	0.48
3-Methyl-1-butanol*	0.37	0.39	0.61	0.48
2-Methyl-1-pentanol	0.39	0.40	0.55	0.48
3-Methyl-1-pentanol*		0.44		0.47
4-Methyl-2-pentanol*	0.34	0.33	0.69	0.56
1-Octanol	0.45	0.42	0.45	0.48
1-Nonanol	0.40	0.39	0.47	0.48
1-Hexanol	0.44	0.42	0.48	0.48
1-Decanol	0.43	0.42	0.47	0.48
1-Heptanol	0.42	0.42	0.47	0.48
2-Heptanol*	0.35	0.36	0.58	0.56
1-Undecanol*	0.40	0.42	0.47	0.48
1-Dodecanol*	0.40	0.42	0.51	0.48

Literature data of  $\pi_2^H$  lit. and  $\sum \beta_2^H$  lit. were taken from Refs. [5–11].

Comparison of  $\pi_2^H$  and  $\Sigma\beta_2^H$  obtained using TGC with the literature data yields standard deviations of 0.01 and 0.04, respectively. Results are reported in Table 7. Six compounds marked with a star were not included in the training set used to determine coefficients of Eqs. (9) and (10).

In the case of aromatic hydrocarbons, retention data of toluene, ethylbenzene, 1,2,3-trimethylbenzene, *o*-xylene, 1,2-diethylbenzene were used to establish coefficients of Eqs. (11) and (12):

$$t_{R \text{ Apiezon L}} = -11.7(\pm 0.017) + 4.41(\pm 0.032) \cdot \pi_2^H + 3.98(\pm 0.002) \cdot \log L^{16} \quad (11)$$

$F = 120\,000$ ,  $r = 0.999$ ,  $SD = 0.02$ ,  $n = 5$  and:

$$t_{R \text{ Carbowax 20M}} = -17.2(\pm 0.539) + 13.5(\pm 2.443) \cdot R_2 - 14.8(\pm 9.633) \cdot \Sigma\beta_2^H + 3.69(\pm 0.1512) \cdot \log L^{16} \quad (12)$$

$F = 6229$ ,  $r = 0.999$ ,  $SD = 0.01$ ,  $n = 5$ .

Comparison of  $\pi_2^H$  and  $\Sigma\beta_2^H$  obtained using TGC with literature data yields standard deviations of 0.02 and 0.01, respectively. Results are reported in Table 8. Fifteen compounds listed at the bottom of Table 8

were not included in the training set used to determine coefficients of Eqs. (11) and (12). Estimates are in good agreement with the literature data [8–11].

### 3.4. Estimation of vapor pressure data of high boiling compounds using the $\log L^{16}$ descriptor

Gas chromatography was often used to determine vapor pressures of non-polar and moderately polar compounds [21–24]. This method was recently extended to high boiling compounds by Donovan [21]. Donovan showed that TGC retention times are linearly related to the logarithm of the vapor pressure at 298.2 K. This method was applied to determine vapor pressures of pesticides and polyaromatic hydrocarbons, but the accuracy of results was not always satisfactory. We observed that better results are obtained using a relationship between vapor pressures and  $\log L^{16}$ . Moreover, the stationary phase DB-1 is slightly polar [12]. Corresponding system parameters of the poly(dimethylsiloxane) immobilized in DB-1 column were published by Li et al. [12]. Values determined at  $t = 60^\circ\text{C}$  are as follows:  $r = 0$ ,  $s = 0.211$ ,  $a = 0.308$  and  $b = 0$ . There-

Table 8  
 $\pi_2^H$  and  $\Sigma\beta_2^H$  descriptors of aromatics determined using Apiezon L and Carbowax 20M packed columns

Compound	$\Sigma\beta_2^H \text{ lit.}$	$\Sigma\beta_2^H \text{ Carbowax 20M}$	$\Delta\Sigma\beta_2^H$	$\pi_2^H \text{ lit.}$	$\pi_2^H \text{ Apiezon L}$	$\Delta\pi_2^H$
Benzene	0.14	0.05	0.09	0.52	0.59	0.07
Toluene	0.14	0.13	0.01	0.52	0.51	0.01
Ethylbenzene	0.15	0.15	0.00	0.51	0.50	0.01
<i>p</i> -Xylene	0.16	0.18	0.02	0.52	0.53	0.01
<i>m</i> -Xylene	0.16	0.19	0.03	0.52	0.53	0.01
<i>o</i> -Xylene	0.16	0.15	0.01	0.56	0.55	0.01
<i>n</i> -Propylbenzene	0.15	0.14	0.01	0.50	0.51	0.01
1,2,3-Trimethylbenzene	0.19	0.18	0.01	0.61	0.61	0.00
1,2,4-Trimethylbenzene	0.19	0.17	0.02	0.56	0.59	0.03
1,3,5-Trimethylbenzene	0.19	0.18	0.01	0.52	0.57	0.05
Isobutylbenzene	0.15	0.15	0.00	0.47	0.51	0.04
<i>sec</i> -Butylbenzene	0.16	0.16	0.00	0.48	0.51	0.03
<i>n</i> -Butylbenzene	0.15	0.14	0.01	0.51	0.51	0.00
1,2-Diethylbenzene		0.19		0.54	0.53	0.01
1,4-Diethylbenzene		0.18		0.50	0.54	0.04
1,3-Diisopropylbenzene	0.20	0.19	0.01	0.46	0.42	0.04
1,4-Diisopropylbenzene	0.20	0.20	0.00	0.47	0.47	0.00
<i>n</i> -Pentylbenzene	0.15	0.15	0.00	0.51	0.52	0.00
<i>n</i> -Hexylbenzene	0.15	0.16	0.01	0.50	0.50	0.00
<i>n</i> -Decylbenzene	0.15	0.16	0.01	0.47	0.48	0.00

Literature data of  $\pi_2^H \text{ lit.}$  and  $\Sigma\beta_2^H \text{ lit.}$  were taken from Refs. [5–11].



Table 9  
Vapor pressure of *n*-alkanes at 422.15 K estimated using Eq. (13)

Compound	$P_{\text{lit.}}$ (bar)	Log $P$	$P_{\text{estimated}}$ (bar)	$\Delta P$ (%)
<i>n</i> -Nonane	0.96844	-0.0139	0.88047	9.99
<i>n</i> -Decane	0.49460	-0.3057	0.48696	1.57
<i>n</i> -Undecane	0.27282	-0.5641	0.26901	1.42
<i>n</i> -Dodecane	0.14730	-0.8318	0.14861	0.88
<i>n</i> -Tridecane	0.08012	-1.0963	0.08219	2.52
<i>n</i> -Tetradecane	0.04314	-1.3651	0.04540	4.98
<i>n</i> -Pentadecane	0.02393	-1.6210	0.02511	4.68
<i>n</i> -Hexadecane	0.01309	-1.8831	0.01387	5.63
<i>n</i> -Heptadecane	0.00736	-2.1330	0.00767	4.04
<i>n</i> -Octadecane	0.00424	-2.3724	0.00424	0.02
<i>n</i> -Nonadecane	0.00238	-2.6240	0.00235	1.28
<i>n</i> -Docosane	0.00042	-3.3812	0.00040	4.95
<i>n</i> -Tetracosane	0.00013	-3.8733	0.00012	11.81
<i>n</i> -Octacosane	0.00001	-4.9088	0.00001	11.14

Literature data ( $P_{\text{lit.}}$ ) were taken from Ref. [25].

fore, experimental results obtained with a DB-1 column can be used to determine  $\log L^{16}$  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. [12] certain param-

eters decrease strongly with rising temperature. Predictive Eq. (13) relating the vapor pressures of *n*-alkanes with their  $\log L^{16}$  is as follows:

$$\log P = 2.07903(\pm 0.0285) - 0.510357(\pm 0.0037) \cdot \log L^{16} \quad (13)$$

$$F = 18\,672, r = 0.999, SD = 0.008, n = 10.$$

Parameters of Eq. (13) were determined using data of *n*-alkanes from *n*-nonane to *n*-octadecane. Estimates of vapor pressures of *n*-alkanes heavier than *n*-octadecane (non-included in the training set) were calculated with Eq. (13) and are in good agreement with the literature data [25], as shown in Table 9.

In the case aromatic hydrocarbons, Eq. (14) was obtained using  $\log L^{16}$  data of 12 compounds listed in the upper part of Table 10:

$$\log P = 2.62360(\pm 0.049) - 0.649561(\pm 0.0087) \cdot \log L^{16} \quad (14)$$

$$F = 18\,672, r = 0.999, SD = 0.008, n = 12.$$

Estimates of vapor pressures of 11 aromatic hydrocarbons not used in the training are presented

Table 10  
Vapor pressure of aromatics at 422.15 K estimated using Eq. (14)

Compound	$P_{\text{lit.}}$ (bar)	Log $P$	$P_{\text{estimated}}$ (bar)	$\Delta P$ (%)
1,3,5-Trimethylbenzene	0.65746	-0.1821	0.71507	8.06
1,2,3-Trimethylbenzene	0.48903	-0.3107	0.48577	0.67
1,2,4-Trimethylbenzene	0.58722	-0.2312	0.60858	3.51
Indane	0.46914	-0.3287	0.48192	2.65
Fluorene		-1.8641	0.01089	
Biphenyl	0.04504	-1.3464	0.04086	10.24
Naphthalene	0.15341	-0.8142	0.18932	18.97
Acenaphthene	0.02595	-1.5858	0.02174	19.39
1-Methylnaphthalene	0.07077	-1.1502	0.06820	3.76
2-Methylnaphthalene	0.07874	-1.1038	0.07534	4.52
Phenanthrene	0.00402	-2.3953	0.00405	0.60
<i>p</i> -Xylene	1.33550	0.1256	1.42856	6.51
Ethylbenzene	1.41174	0.1498	1.50475	6.18
1,5-Dimethylnaphthalene		-1.4851	0.02627	
2,6-Dimethylnaphthalene	0.03700	-1.3953	0.03291	12.44
1,4-Diethylbenzene	0.35140	-0.4542	0.34675	1.34
1,2-Diethylbenzene	0.39905	-0.3990	0.38799	2.85
Pyrene	0.00076	-3.1213	0.00085	11.29
9-Methylanthracene	0.00154	-2.8111	0.00153	0.80
Fluoranthene	0.00082	-3.0878	0.00091	10.21
Chlorobenzene	1.60546	0.2056	1.75535	8.54
<i>m</i> -Xylene	1.31380	0.1185	1.43110	8.20
<i>o</i> -Xylene	1.14093	0.0573	1.24685	8.49

Literature data ( $P_{\text{lit.}}$ ) were taken from Ref. [25].

in the lower part of Table 10. A good agreement is observed with the literature data [25]. Deviations are usually lower than 10%. Vapor pressures calculated using Eqs. (13) and (14) are mostly more accurate than estimates yielded by TGC methods described in the literature [21–24]. More general correlation established with several families of compounds yield less satisfactory results.

#### 4. Conclusion

Recent improvements of LSER method allow for excellent correlation and accurate predictions for many important chemical systems [26–28]. This method has been widely used, in a variety of the quantitative structure–property/activity relationship (QSPR/QSAR) studies. In chemical engineering LSER was applied to develop methods for selecting solvents for liquid extraction processes or to predict pure compound characteristic properties. Recently, predictive method using LSER descriptors were proposed to estimate physical properties of organic compounds [29] and their mixtures [30]. The still growing number of LSER applications increases the need of LSER descriptors. The values of descriptors for over 2000 compounds exist in the open literature but this data bank is often insufficient. Therefore, rapid and trustful experimental methods to determine LSER descriptors are requested. In this study we present a simple and accurate chromatographic methods to determine LSER descriptors of organic compounds. TGC method has been used for the first time to determine  $\pi_2^H$  and  $\Sigma\beta_2^H$  descriptors. This approach opens new possibilities of precise and rapid determination of LSER descriptors with a small number of stationary phases. The same approach can be used to measure vapor pressures of high boiling compounds.

#### References

- [1] M.J. Kamlet, R.W. Taft, J.-L.M. Abboud, *J. Am. Chem. Soc.* 825 (1977) 91.
- [2] R.W. Taft, M.J. Kamlet, *J. Am. Chem. Soc.* 98 (1976) 2886.
- [3] M.J. Kamlet, R.W. Taft, *J. Am. Chem. Soc.* 98 (1976) 377.
- [4] M.J. Kamlet, J.L. Abboud, R.W. Taft, *J. Am. Chem. Soc.* 99 (1977) 6027.
- [5] M.H. Abraham, P.L. Grellier, R.A. McGill, *J. Chem. Soc., Perkin Trans. 2* (1987) 797.
- [6] M.H. Abraham, G.S. Whiting, *J. Chem. Soc., Perkin Trans. 2* (1990) 1451.
- [7] M.H. Abraham, *Chem. Soc. Rev.* 110 (1993) 73.
- [8] M.H. Abraham, G.S. Whiting, R.M. Doherty, W.J. Shuely, *J. Chromatogr.* 587 (1991) 213.
- [9] J.D. Weckwerth, M.F. Vita, P.W. Carr, *Fluid Phase Equilibria* 183 (2001) 143.
- [10] F. Mutelet, M. Rogalski, *J. Chromatogr. A* 923 (2001) 153.
- [11] M.H. Abraham, G.S. Whiting, *J. Chromatogr.* 594 (1992) 229.
- [12] Q. Li, C.F. Poole, W. Kiridena, W.W. Koziol, *Analyst* 125 (2000) 2180.
- [13] M.H. Abraham, J. Andonian-Haften, C. My Du, J.P. Osei-Owusu, P. Sakellariou, W.J. Shuely, C.F. Poole, S.K. Poole, *J. Chromatogr. A* 688 (1994) 125.
- [14] P.A. Martos, A. Saraullo, J. Pawliszyn, *Anal. Chem.* 69 (1997) 402.
- [15] M. Chai, J. Pawliszyn, *Environ. Sci. Technol.* 29 (1995) 693.
- [16] E. Kovats, *Helv. Chim. Acta* 41 (1958) 1915.
- [17] A.M. Zissimos, M.H. Abraham, M.C. Barker, K.J. Box, K.Y. Tam, *J. Chem. Soc., Perkin Trans. 2* (2002) 470.
- [18] J.A. Platts, D. Butina, M.H. Abraham, A. Hersey, *J. Chem. Inf. Comput. Sci.* 39 (1999) 835.
- [19] J. Li, *J. Chromatogr. A* 927 (2001) 19.
- [20] P. Havelec, J.G.K. Sevcik, *J. Phys. Chem. Ref. Data* 25 (1996) 1483.
- [21] S.F. Donovan, *J. Chromatogr. A* 749 (1996) 123.
- [22] T.F. Bidleman, *Anal. Chem.* 56 (1984) 2490.
- [23] D.A. Hinckley, T.F. Bidleman, W.T. Foreman, J.R. Tuschall, *J. Chem. Eng. Data* 35 (1990) 232.
- [24] B. Koutek, J. Cvacka, L. Streinz, P. Vrkocová, J. Doubský, H. Simonová, L. Felt, V. Svoboda, *J. Chromatogr. A* 923 (2001) 137.
- [25] Thermodynamics Research Center, Texas Engineering Experiment Station, The Texas A&M University System, College Station, TX, April 1987.
- [26] C.J. Cramer, G.R. Famini, A.H. Lowrey, *Acc. Chem. Res.* 26 (1993) 599.
- [27] J. Dai, L. Jin, S. Yao, L. Wang, *Chemosphere* 42 (2001) 899.
- [28] M.D. Trone, M.G. Khaledi, *J. Chromatogr. A* 886 (2000) 245.
- [29] F. Mutelet, M. Rogalski, *Phys. Chem. Chem. Phys.* 3 (2001) 432.
- [30] F. Mutelet, M. Rogalski, *Rec. Prog. Genie Proc.* 15 (2001) 145.