Concept of additivity for a non-polar solute–solvent criterion log L^{16}
Non-aromatic compounds

Pavel Havelec, Jiří G.K. Ševčík*

Department of Analytical Chemistry, Charles University Albertov 2030, CZ-128 40 Prague 2, Czech Republic

Abstract

An additivity principle was formulated for functional and atom groups and their structural and interactional contributions to the log L^{16} criterion, expressing apolar solute–solvent interactions in gas–liquid chromatography. Numerical values were calculated for the contributions of 27 groups and 9 structural and 10 interactional contributions. The correlation coefficients between recalculated and measured values of log L^{16} for two sets, consisting of 336 monofunctional and 481 both mono- and polyfunctional compounds, were 0.998 and 0.997, respectively. The precision of the prediction of the log L^{16} criterion was tested on an independent data set, obtaining a correlation coefficient of 0.988.

1. Introduction

Since the early days of gas–liquid chromatography (GLC) much effort has been dedicated to obtaining a quantitative description of solute–solvent interactions (e.g., [1]). Among the criteria describing apolar interactions is log L^{16}, yielding a value of the solute partition coefficient in a gas–hexadecane system at 298 K [2]. This criterion includes both general dispersion interactions and the cavity term and has become an essential characteristic in linear solvation energy relationships (LSER) [2–7]. The importance of LSER concepts lies in the possibility of charac-

terizing solute–solvent systems and predicting retention behaviour in them.

The numerical values of log L^{16} have so far been determined experimentally on both packed [2] and capillary columns [8]. In the experimental methods, attention was paid to the contributions of gas–solid, liquid–solid and gas–liquid interfacial adsorption as a source of the differences between reported values. It was shown [8] that there is a good fit for values of log L^{16} for a remeasured set of 105 non-polar and polar solutes between both experimental methods. Still, if an experimental value of log L^{16} was not available, the LSER concept could not be applied, the retention behaviour could not be predicted and an optimization procedure, i.e., the selection of a stationary phase, could not be performed in a general manner.

The concept of additivity of partial contribu-

* Corresponding author. Present address: Analytical Laboratory Systems, GmbH, Franz-von-Buhl-Strasse 2, D-67143 Deidesheim, Germany.

tions has already been applied and verified in GLC for the prediction of some retention parameters, e.g., retention indices [9,10], but not for the calculation of the log L^{16} criterion. Abraham [11] demonstrated a calculation of the contributions of substituents (X) on the phenyl ring to log L^{16} for PhX compounds and the contribution of the carbon chain length in n-alkyl benzoate homologues, but a general approach to additivity of the log L^{16} criterion has not yet been presented.

This work was aimed at proving the validity of the principle of additivity for the calculation of log L^{16} values and demonstrating it on sets of monofunctional and polyfunctional non-aromatic compounds.

2. Results and discussion

It is assumed that the retention behaviour of compound X is the result of three contributions comprising the number of particular groups forming compound X and their structural and interactional contributions. The value of the log L^{16} criterion is then described by

$$\log(L^{16}X) = \sum_i l_i FG_i + \sum_j m_j SC_j + \sum_k n_k IC_k \tag{1}$$

where i, j, k are identification numbers of the groups (i) (see Table 1), structural contributions (j) (see Table 2) and interaction contributions (k) (see Table 3), l, m, n are the values of the regression coefficients in Eq. 1 for the contribution of a particular group (l) (see Table 1), a

structural contribution (m) (see Table 2) and an interactional contribution (n) (see Table 3) and FG, SC, IC are the numbers of particular groups (FG) forming compound X (see Table 1), structural (SC) (see Table 2) and interactional (IC) (see Table 3) contributions.

Published data on log L^{16} [3,4] were used for the analysis of the additivity hypothesis according to Eq. 1. Two data sets were formed to prove the effect of interactional contributions on the additive model of log L^{16}. The first data set (set A) contained only monofunctional compounds, a total of 336 compounds, and the second data set (set B) contained both mono- and polyfunctional compounds, a total of 481 compounds (see Appendix). For these data sets A and B, 27 types of group contributions FG (see Table 1), 9 types of structural contributions SC (see Table 2) and 10 types of interactional contributions IC (see Table 3) were specified.

The method of multi-linear correlation was applied to solve Eq. 1 by means of the matrix according to Eq. 2 for both data sets of 336 compounds (set A) and 481 compounds (set B). In Eq. 2 $FG_{x,i}$ are integral numbers of particular groups i forming compound X (see Table 1), $SC_{x,j}$ are integral numbers of particular structural contributions j in compound X (see Table 2) and $IC_{x,k}$ are integral numbers of interactional contributions k within compound X (see Table 3).

The results of the analysis of the matrix (Eq. 2) are sets of formal regression coefficients l_1 to l_{27}, m_1 to m_9 and n_1 to n_{10} such as given in Table 1 (the effect of group contributions), Table 2 (the effect of structural contributions) and Table 3 (the effect of interactional contributions).

$\log(L^{16}X)$	i	j	k	
	1 to 27	1 to 9	1 to 10	
X 1 to 336 or 1 to 481	$FG_{1,1} \cdots FG_{1,27}$ ⋮ $FG_{x,i}$ ⋮ $FG_{481,1} \cdots FG_{481,27}$	$SC_{1,1} \cdots SC_{1,9}$ ⋮ $SC_{x,j}$ ⋮ $\cdots SC_{481,1} \cdots SC_{481,9}$	$IC_{1,1} \cdots IC_{1,10}$ ⋮ $IC_{x,k}$ ⋮ $\cdots IC_{481,1} \cdots IC_{481,10}$	(2)

Table 1
Regression coefficients l_i, their standard deviations s_i and frequencies x_i for group i calculated form Eq. 1 for data sets A and B

i	Structure	Set A			Set B		
		l_i	s_i	x_i	l_i	s_i	x_i
1	CH$_3$—	0.333	0.009	620	0.358	0.009	834
2	—CH$_2$—	0.504	0.002	1256	0.499	0.002	1492
3	—CH<	0.488	0.016	129	0.437	0.017	193
4	>C<	0.456	0.029	30	0.350	0.032	46
5	H$_2$C=	0.198	0.027	13	0.280	0.020	59
6	—HC=	0.471	0.022	21	0.450	0.017	77
7	>C=	0.567	0.050	4	0.609	0.024	20
8	HC≡	0.085	0.034	11	0.063[a]	0.046	13
9	—C≡	0.595	0.035	11	0.558	0.046	13
10	F—	−0.114	0.045	4	−0.121	0.060	11
11	Cl—	0.894	0.030	9	0.786	0.020	50
12	Br—	1.293	0.027	11	1.319	0.036	13
13	I—	1.766	0.034	7	1.756	0.046	8
14	—O—	0.302	0.026	16	0.346	0.016	114
15	—CHO	0.982	0.026	13	1.014	0.030	18
16	—CO—	1.098	0.023	22	1.087	0.025	34
17	HCOO–	1.078	0.028	11	1.070	0.035	12
18	—COO—	1.108	0.019	43	1.105	0.020	65
19	—COOH	1.589	0.024	15	1.590	0.032	15
20	—CN	1.213	0.029	10	1.209	0.039	10
21	—NH$_2$	0.798	0.032	8	0.791	0.043	8
22	>NH	0.746	0.047	4	0.711	0.062	4
23	—N<	0.575	0.068	2	0.508	0.089	2
24	—NO$_2$	1.524	0.034	7	1.518	0.046	7
25	—OH	0.739	0.015	52	0.762	0.015	101
26	—SH	1.312	0.026	13	1.323	0.033	14
27	—S—	1.435	0.037	7	1.406	0.048	7

[a] Statistically not significant.

The value of the regression coefficient l_i describes the significance of the contribution of a particular group to the retention behaviour of compound X. The numerical values of l_i vary from −0.121 for fluorine to 1.756 for iodine, and the value of the statistical error of estimation of the regression coefficient varies from 0.002 to 0.060 for the whole data set (see Table 1). The best precision of estimation was attained for the

–CH$_2$– group (0.4%), and the worst for the HC≡ group (75%). The values of the regression coefficient l_i have been ordered according to their absolute values and it was found that there are significant differences between the groups, especially between those containing oxygen and those without oxygen atom (see Fig. 1). The results presented in Fig. 1 demonstrate the relative importance of a particular group to the

Table 2
Regression coefficients m_j, their standard deviations s_m and frequencies x_m of specified structural contributions j calculated from Eq. 1 for data sets A and B

j	Structure	Set A			Set B		
		m_j	s_m	x_m	m_j	s_m	x_m
1	3-Ring				0.117[a]	0.064	6
2	4-Ring				0.182	0.092	2
3	5-Ring	0.001[a]	0.037	8	0.060[a]	0.040	12
4	6-Ring	0.040[a]	0.033	14	0.084	0.035	18
5	7-Ring	0.169	0.042	6	0.207	0.052	6
6	8-Ring	0.299	0.090	1	0.337	0.121	1
7	*trans*	−0.090[a]	0.079	2	−0.027[a]	0.046	9
8	*cis*	0.074[a]	0.062	3	0.094[a]	0.061	5
9	Oxygen atom in ring				0.051[a]	0.030	22

[a] Statistically not significant.

Table 3
Regression coefficients n_k, their standard deviations s_n and frequencies x_n of interactional contributions k calculated from Eq. 1 for data sets A and B

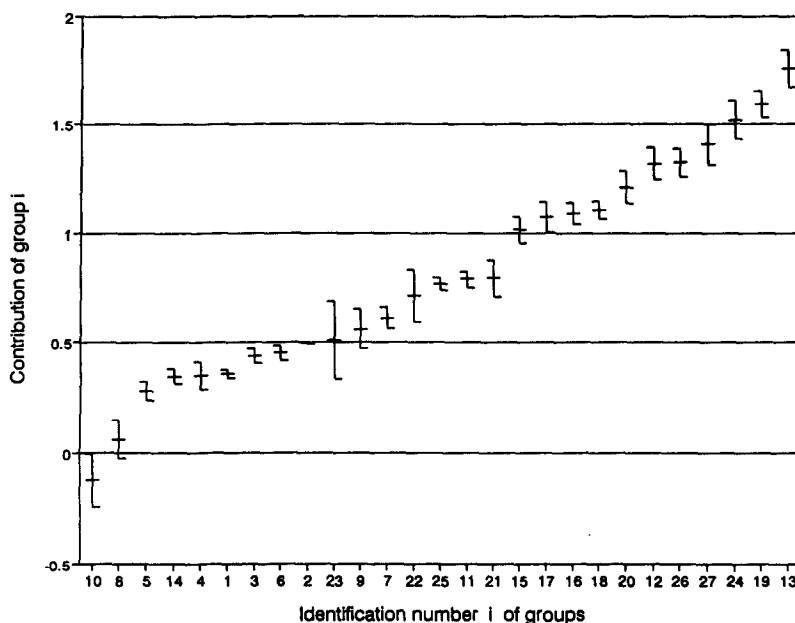| k	Structure	Set A			Set B		
		n_k	s_n	x_n	n_k	s_n	x_n
1	$\diagdown\diagup C F_2$				0.152	0.073	4
2	$\diagdown\diagup C Cl_2$				−0.117	0.025	24
3	$\diagdown\diagup C Br_2$				0.715	0.041	4
4	$\diagdown\diagup C I_2$				1.602	0.128	1
5	$\diagdown\diagup C(F,Cl)$				−0.012[a]	0.043	6
6	$=C-O-$ | O |				−0.083	0.033	31
7	—COCO—				−0.128[a]	0.088	2
8	—COCH$_2$CO—				0.471	0.122	1
9	—COOC$_n$H$_{2n}$— —OOC— (n=1—3)				1.163	0.063	4
10	$\diagdown\diagup$COHCOH$\diagup\diagdown$				0.146	0.060	5

[a] Statistically not significant.

Fig. 1. Values of regression coefficient l_i vs. magnitude of contribution of group FG_i for data set B as given in Table 1. The bar length represents the precision of estimation ($l_i \pm s_i$).

retention behaviour of compound X in a GLC system where apolar solute–solvent interactions predominate. It is of interest that the smallest value of the regression coefficient l_i was found for fluorine and the highest value for iodine. This effect could possibly be related to the polarizability of these atoms. A detailed examination of this observation will be the subject of further physico-chemical studies.

The value of the regression coefficient m_j describes the role of the structural arrangement, especially the size of the ring in compound X. The numerical values of coefficient m_j are smaller then those of l_i and thus the role of the structural, cyclic arrangement is less important for the retention behaviour than the role of the group contributions. The precision of the estimated regression coefficients m_j was significantly poorer (around 50%) than that for group contribution l_i and it could only be speculated that either an insufficient number of input data were used or that the selected structural contributions specified in Table 2 were of limited significance.

The value of the regression coefficient n_k

describes the role of interactional contributions between neighbouring groups bonded to a common carbon atom. The values of the coefficient n_k are both positive and negative, as can be expected from general theories of interactions. The numerical value of n_k varies over a broad range (see Table 3), similar to the range of coefficient l_i, and it can be interpreted as an indication that interactional contributions are highly important for the description of additivity of the $\log L^{16}$ criterion. Based on the differences between the calculated and measured values of $\log L^{16}$ for polyfunctional compounds, it can be assumed that there are some cross-linked interactions over the carbon chain length. This effect was not proved by the data sets used and it would be a subject of further studies.

A test of the significance of the differences in the regression coefficients l_i and m_j between data set A and data set B was used to assess the importance of the individual contributions. Only monofunctional compounds were selected for data set A, whereas data set B consisted of both mono- and polyfunctional compounds. Hence if

Table 4
Test of statistical significance of differences in regression
coefficients l_i and m_j for data sets A and B

Coefficient	Structure	Result of σ-test[a]	Significance level (%)
l_1	CH_3—	1.919	94.5
l_2	—CH_2—	1.831	93.3
l_3	—CH<	2.257	97.6
l_4	>C<	2.445	98.6
l_5	H_2C=	2.466	98.6
l_6	—HC=	0.725	53.2
l_7	>C=	0.740	54.1
l_8	HC≡	0.384	29.9
l_9	—C≡	0.644	48.0
l_{10}	F—	0.093	7.4
l_{11}	Cl—	2.995	99.7
l_{12}	Br—	0.570	43.2
l_{13}	I—	0.176	14.0
l_{14}	—O—	1.408	84.1
l_{15}	—CHO	0.813	58.4
l_{16}	—CO—	0.342	26.8
l_{17}	HCOO—	0.167	13.3
l_{18}	—COO—	0.080	6.4
l_{19}	—COOH	0.027	2.2
l_{20}	—CN	0.070	5.6
l_{21}	—NH_2	0.145	11.5
l_{22}	>NH	0.455	35.1
l_{23}	—N<	0.603	45.3
l_{24}	—NO_2	0.115	9.2
l_{25}	—OH	1.055	70.9
l_{26}	—SH	0.266	21.0
l_{27}	—S—	0.482	37.0
m_3	5-Ring	1.071	71.6
m_4	6-Ring	0.910	63.7
m_5	7-Ring	0.568	43.0
m_6	8-Ring	0.253	19.9
m_7	*trans*	0.686	50.8
m_8	*cis*	0.239	18.9

[a] The σ-test was carried out according to the following expressions:

$$\sigma = \frac{|l_i(A) - l_i(B)|}{[s_l(A)^2 + s_l(B)^2]^{0.5}}$$

or

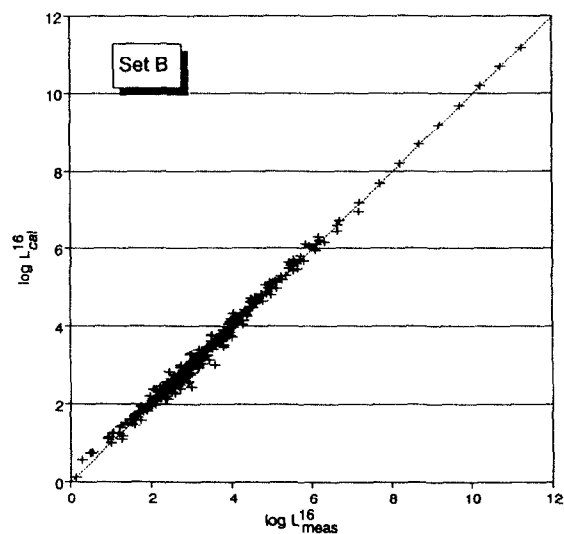$$\sigma = \frac{|m_j(A) - m_j(B)|}{[s_m(A)^2 + s_m(B)^2]^{0.5}} .$$

Fig. 2. Functional dependence of criterion $\log L_{cal}^{16}$ vs. $\log L_{meas}^{16}$ for data set B (see Appendix). Total number of analysed compounds $X = 481$; slope = 1; correlation coefficient $r = 0.997$.

there is a statistically significant difference $[(l_i)_{set\ A} < > (l_i)_{set\ B}]$, the interactional contributions n_k will be of importance, in addition to the group and structural contributions. The results of the test are given in Table 4. It was found that

Table 5
Summarized data of linear regression analysis of calculated and measured values of the criterion $\log L^{16}$ for monofunctional (set A) and mono- and polyfunctional (set B) compounds according to Eq. 3

Characterization of sets	Set A	Set B
No. of compounds	336	481
Degrees of freedom	303	435
$\log L_{min}^{16}$	0.15	0.15
$\log L_{max}^{16}$	11.25	11.25
$\log L_{mean}^{16}$ ($\bar{x}_{set}$)	3.57	3.40
No. of functional groups	27	27
No. of structural contributions	6	9
No. of interaction contributions	0	10
Correlation coefficient (r)	0.998	0.997
Standard deviation (s)	0.089	0.120
Maximum error (me)	0.309	0.573
Mean statistical error (v, %)	2.491	3.518

$$me = \max|\log L_{estimated}^{16} - \log L_{measured}^{16}| .$$

$$v = 100 \cdot \frac{s_{set\ A\ (B)}}{\bar{x}_{set\ A\ (B)}} .$$

the regression coefficient l_i differs between data sets A and B at different statistical levels, and a significance higher than 95% was found for groups such as —CH$\diagdown$, $\diagup$C$\diagdown$, H_2C= and Cl, i.e., groups providing a large numbers of different interactional contributions. Hence the description of additivity principle of log L^{16} according to Eq. 1, consisting of three types of contribution, group, structural and interactional, is correct.

Based on the calculated values of the regression coefficients l_i, m_j and n_k (see Tables 1, 2 and 3, respectively), the values of log L_{cal}^{16} were calculated for the original sets of input com-

pounds and the significance of their fit to the measured data was estimated from linear regression analysis: see Eq. 3a for set A, Eq. 3b for set B and Eq. 3c for set C.

$$\log L_{cal(A)}^{16} = 1.000(\pm 0.001)\log L_{meas(A)}^{16} \quad (3a)$$

$$\log L_{cal(B)}^{16} = 0.999(\pm 0.001)\log L_{meas(B)}^{16} \quad (3b)$$

$$\log L_{cal(C)}^{16} = 0.993(\pm 0.006)\log L_{meas(C)}^{16} \quad (3c)$$

The difference between the slope values found with Eqs. 3a, 3b and 3c and the predefined value of 1.00 are statistically not significant and further

Table 6
Examples of prediction of log L_{pred}^{16} values and their comparison with the measured values

Compound[a]	Log L_{meas}^{16}	Contribution		Log L_{pred}^{16}	
		Type	Amount	Partial	Total
Adamantane		$l2$	6	$6 \cdot 0.499$	
		$l3$	4	$4 \cdot 0.437$	
		$m4$	4	$4 \cdot 0.084$	
	5.095				5.078
Methoxyflurane		$l1$	1	$1 \cdot 0.358$	
		$l3$	1	$1 \cdot 0.437$	
		$l4$	1	$1 \cdot 0.350$	
		$l10$	2	$2 \cdot (-0.121)$	
		$l11$	2	$2 \cdot 0.786$	
		$l14$	1	$1 \cdot 0.346$	
		$n1$	1	$1 \cdot 0.152$	
		$n2$	1	$1 \cdot (-0.117)$	
	2.864				2.856
3,4-Dihydropyran		$l2$	3	$3 \cdot 0.499$	
		$l6$	2	$2 \cdot 0.450$	
		$l14$	1	$1 \cdot 0.346$	
		$m4$	1	$1 \cdot 0.084$	
		$m9$	1	$1 \cdot 0.051$	
	2.910				2.876

[a] Structures of the compounds are as follows:
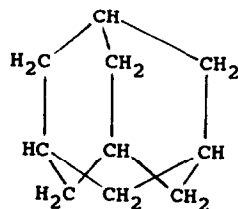
adamantane   methoxyflurane   3,4-dihydropyran

CH_3—O—CF_2—$CHCl_2$
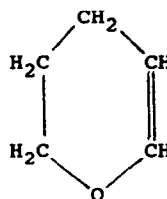
Table 7
List of compounds in data set C and their evaluation

Compound	Log L_{meas}^{16} [a]	Log L_{pred}^{16} [b]	Difference
Ethylcyclohexane	3.877	3.873	0.004
Cyclohexylcyclohexane	6.434	6.032	0.402
Adamantane	5.095	5.076	0.019
cis-2-Methyldecaline	5.550	5.329	0.221
2-Methyl-2-butene	2.226	2.132	0.094
2-Methyl-2-pentene	2.588	2.631	−0.043
3-Methylcyclohexene	3.379	3.276	0.103
4-Methylcyclohexene	3.372	3.276	0.096
Cyclooctene	4.119	4.232	−0.113
1,3-Cyclohexadiene	2.917	2.884	0.033
1,4-Cyclohexadiene	3.132	2.884	0.284
1,3-Cycloheptadiene	3.607	3.506	0.101
1,5-Cyclooctadiene	4.300	4.135	0.165
1,3,5-Cycloheptatriene	3.442	3.408	0.034
1,3,5,7-Cyclooctatetraene	3.884	3.940	−0.056
α-Pinene	4.200	4.620	−0.420
Dicyclopentadiene	4.651	4.726	−0.075
Fluorocyclohexane	3.215	2.894	0.321
Iodocyclohexane	4.785	4.772	0.013
1-Chlorocyclohexene	3.990	3.925	0.065
1-Bromocyclohexene	4.350	4.458	−0.108
1-Bromo-4-methylcyclohexene	4.669	4.753	−0.084
1-Iodocyclohexene	4.838	4.895	−0.057
Fluorotrichloromethane	1.995	2.200	−0.205
Methyl cyclohexyl ether	3.861	3.719	0.142
1,2-Dimethoxyethane	2.565	2.405	0.160
trans-2-Hexen-1-al	3.400	3.244	0.156
trans-2-Hepten-1-al	3.897	3.743	0.154
Carvone	5.330	5.269	0.061
Ethyl trimethylacetate	3.481	3.386	0.095
Cyanocyclohexane	4.333	4.225	0.108
Isopentylamine	3.058	2.941	0.117
Cyclohexylamine	3.796	3.806	−0.010
3-Methylcyclohexylamine	4.125	4.102	0.023
Diisobutylamine	3.901	4.014	−0.113
Tripropylamine	4.229	4.576	−0.347
Nitrocyclohexane	4.826	4.533	0.293
3,4-Dihydropyran	2.910[c]	2.878	0.032
Cyclooctanone	4.981[c]	4.917	0.064
Allylamine	2.268[c]	2.021	0.247
Cyclopropylcarbinol	2.675[c]	2.813	−0.138
Diallyl sulphide	3.750[c]	3.866	−0.116
1,1,1,2-Tetrachloroethane	3.641[d]	3.641	0.000
Isopentyl isopentanoate	4.580[e]	4.907	−0.327
Methyl heptanoate	4.356[f]	4.316	0.040
Methyl octanoate	4.838[f]	4.815	0.023
Methyl nonanoate	5.321[f]	5.314	0.007
Methyl decanoate	5.803[f]	5.813	−0.010
Methyl undecanoate	6.285[f]	6.312	−0.027

[a] Measured values of log L_{meas}^{16} are from [11], except where indicated otherwise.
[b] Predicted values of log L_{pred}^{16} were calculated from sets of regression coefficients l_i (Table 1), m_j (Table 2) and n_k (Table 3).
[c] From [3].
[d] From [12].
[e] From [5].
[f] From [13].

statistical evaluations, such as given in Tables 5 and 8, were carried out under this assumption.

The analysis results in correlation coefficients of 0.998 for data set A and 0.997 for data set B. These data demonstrate that the functional dependence is statistically significant and thus lead to confirmation of the hypothesis of additivity of partial contributions for calculation of the criterion log L^{16}. Fig. 2 demonstrates this dependence and Table 5 lists the data for the regression analysis according to Eqs. 3. It should be pointed out that the errors of estimation of the log L^{16}_{cal} values are small (about 3%) and can probably be further minimized by using additional data sets and describing the particular contributions to the log L^{16} criterion is more detail.

The predictive power of the additivity concept of the criterion log L^{16} and the precision of prediction were tested on an independent data set C for compounds that were not used for the calculation of the regression coefficients (the compounds were not included in either data set A or B). The compounds in set C were split into elementary contributions of groups, structural and interactional contributions (see Tables 1, 2 and 3, respectively) and their values of log L^{16}_{pred} were calculated (examples are given in Table 6). The predicted values of log L^{16}_{pred} were compared with the measured log L^{16}_{meas} values for data set C by means of linear regression according to Eq. 3c. A list of the compounds in data set C and the measured and predicted values of log L^{16} are

Table 8
Summarized data of regression analysis of functional dependence of log L^{16}_{pred} vs. log L^{16}_{meas} according to Eq. 3 for data set C (see Table 7)

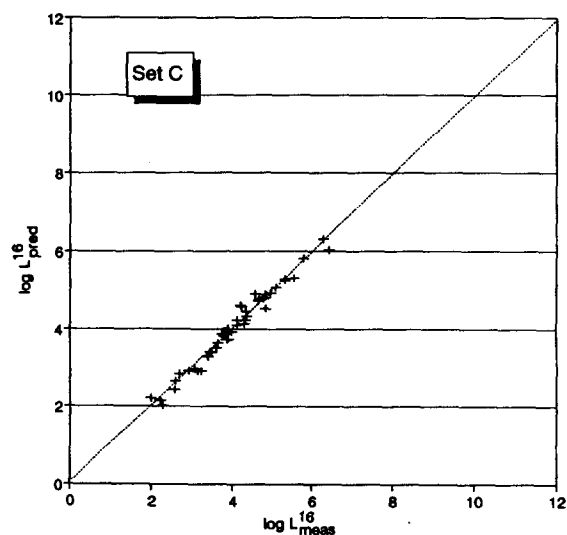| Characterization of set	Set C
No. of compounds	49
Log L^{16}_{min}	1.995
Log L^{16}_{max}	6.434
Log L^{16}_{mean} ($\bar{x}_{set}$)	4.017
Correlation coefficient (r)	0.988
Standard deviation (s)	0.163
Maximum error (me)	0.402
Mean statistical error (v, %)	4.05

For definitions of me and v, see Table 5.

Fig. 3. Functional dependence of criterion log L^{16}_{pred} vs. log L^{16}_{meas} for data set C (see Table 7). Total number of predicted values of log $L^{16}_{pred} = 49$; slope = 1; correlation coefficient $r = 0.988$.

given in Table 7 and summarized data of the regression analysis in Table 8 and Fig. 3. It can be seen that the prediction based on Eq. 1 yields good results for a whole set of complex compounds exhibiting all kinds of contributions. A correlation coefficient of 0.987 was found for the function log $L^{16}_{pred} = \log L^{16}_{meas\ c}$ and thus applicability of the additivity principle to the prediction of the values of the criterion log L^{16} was verified. Comparing the correlation coefficients for functional dependences log $L^{16}_{cal} = \log L^{16}_{meas}$ ($r = 0.997$) and log $L^{16}_{pred} = \log L^{16}_{meas}$ ($r = 0.988$), it can be seen that both data sets B and C could be merged and used for confirmation of predictability of the criterion log L^{16} on the principle of additivity of partial contributions.

3. Conclusions

The results of the analysis of data sets containing 336 and 481 compounds confirm the hypothesis of additivity of partial contributions for calculation of the log L^{16} criterion, as a measure of apolar solute–solvent interactions in GLC. It was shown that, in addition to the

contribution of groups, there are important structural and interactional contributions. The significant correlation between the calculated and measured values of log L^{16} (a correlation coefficient of 0.997) demonstrates that the proposed additivity form according to Eq. 1 is correct.

The mean statistical relative errors of the estimation of log L_{cal}^{16} for data sets A and B (see Appendix) were 2.49% and 3.52%, respectively. In other words, the error of calculation is of about the same order of magnitude as the experimental errors [11].

The prediction power of the present concept was tested on an independent data set and a correlation coefficient of 0.988 between the predicted and measured values of log L^{16} was found. We are convinced that it is an unequivocal advantage to have an access to one of the general criteria of solute–solvent interactions by means of calculation, especially from the point of view of optimization procedures carried out by GLC expert systems.

Appendix

A list of compound types and their abundance in data sets A and B used for testing of additivity character of the log L^{16} criterion is given below

Type of compound	Set A	Set B
Alkanes	41	41
Cycloalkanes	11	11
Alkenes	13	13
Cycloalkenes	6	6
Alkadienes		3
Alkynes	11	11
Monofluoroalknes	4	4
Monochloroalkanes	8	8
Chlorocycloalkanes	1	1
Polychloroalkanes		8
Polychloroalkenes		4
Monobromoalkanes	10	10
Bromocycloalkanes	1	1
Polybromoalkanes		2
Monoiodoalkanes	7	7

Type of compound	Set A	Set B
Polyiodoalkanes		1
Dialkyl ethers	16	17
Cycloalkyl ethers		12
Alkyl alkyl diethers		23
Cycloalkyl diethers		2
Alkyl alkyl triethers		2
Cycloalkyl triethers		2
Alkyl alkenyl ethers		4
Dialkenyl ethers		1
Alkyl alkenyl diethers		1
Difluorotetrachloroalkanes		2
Alkanals	13	13
Alkenals		4
Alkadienals		1
Alkanones	19	19
Cycloalkanones	3	3
Alkenones		4
Alkadiones		3
Alkyl formates	11	11
Alkyl acetates	19	20
Cycloalkyl acetates	1	1
Alkyl propanoates	10	10
Alkyl butanoates	10	10
Alkyl isobutanoates	3	3
Alkyl acrylates		6
Alkenyl carboxylates		8
Alkoxy carboxylates		4
Alkylenedicarboxylates		4
Cyanoalkanes	10	10
Alkylamines	8	8
Dialkylamines	4	4
Trialkylamines	2	2
Nitroalkanes	7	7
Carboxylic acids	15	15
Alkanols	48	48
Cycloalkanols	4	4
Alkanediols		8
Alkenols		12
Alkynols		2
Chloroalkanols		1
Alkoxyalkanols		11
Alkenoxyalkanols		1
Hydroxyalkanones		5
Trifluoroalkanols		1
Alkanethiols	13	13
Alkenethiols		1
Dialkyl sulphides	7	7

References

[1] L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.

[2] M.H. Abraham, P.L. Grellier and R.A. McGill, *J. Chem. Soc., Perkin Trans.* 2, (1987) 797.

[3] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 213.

[4] M.H. Abraham, *Chem. Soc. Rev.*, 110 (1993) 73.

[5] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chem. Soc., Perkin Trans. 2*, (1990) 1451.

[6] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chem. Soc. Perkin Trans. 2*, (1990) 1851.

[7] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 518 (1990) 329.

[8] Y. Zhang, A.J. Dallas and P.W. Carr, *J. Chromatogr.*, 638 (1993) 43.

[9] V. Tekler, G. Tarjan and J.M. Takacs, *J. Chromatogr.*, 406 (1987) 131.

[10] P.H. Weiner and D.G. Howery, *Anal. Chem.*, 44 (1972) 1189.

[11] M.H. Abraham, *J. Chromatogr.*, 644 (1993) 95.

[12] M.H. Abraham, G.S. Whiting, R.M. Doherty and W.J. Shuely, *J. Chromatogr.*, 587 (1991) 229.

[13] M.H. Abraham, J. Andonian-Haftvan, I. Hamerton, C.F. Poole and T.O. Kollie, *J. Chromatogr.*, 646 (1993) 351.