

Prediction of gas-hexadecane partition coefficients (L^{16}) via the solubility-parameter-based method

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Abstract

A theoretical method based on the Hildebrand–Scatchard solubility parameters of the solute and solvent are applied into a thermodynamic model for the prediction of gas-hexadecane partition coefficients ($\log L^{16}$) of different groups of polar and non-polar compounds. It is demonstrated that reliable values of $\log L^{16}$ of non-volatile compounds can be predicted. The results obtained using this thermodynamic method is in good agreement with experimental and with the results of the other existing methods. The precision of the prediction of the $\log L^{16}$ criterion was tested on an independent experimental data set, obtaining a correlation coefficient of 0.999. Five characteristic constants of solute are presented which can be used to predict any desired value of gas-hexadecane partition coefficients.

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1. Introduction

The distribution of a solute between two phases has been an important subject for theoretical and experimental studies for many years [1–8]. The ratio of the concentration of solutes distributed between two phases is called partition coefficient. There are some excellent reviews that gathered the most practical methods for determining partition coefficients [1–2]. While previous works have been devoted to distribution of solutes between two immiscible liquid phases (usually water and an immiscible organic solvent), Abraham et al. [9] have some time ago

proposed the gas-hexadecane partitioning system and measured gas-hexadecane partition coefficient, L^{16} , at 298.15 K by gas chromatography. The $\log L^{16}$ values as a descriptor have subsequently been proved to be very useful in linear solvation energy relationships (LSERs) and a general equation for the correlation and prediction of the effect of solutes on a wide variety of physicochemical and biochemical phenomena have been developed [10].

$$SP = (SP)_0 + l(\log L^{16}) + s\pi_2^* + a\alpha_2 + b\beta_2 + d\delta_2 \quad (1)$$

SP may be any chromatographic retention characteristic (e.g. gas-liquid partition coefficient K , specific retention volume V_g , adjusted retention time t_R or volume V_R) and the independent variables π_2 , α_2 , β_2 ,

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and δ_2 represent the properties of the individual solutes. The regression coefficients l, s, a, b, d and SP_0 characterize the stationary phases in gas chromatography and specify the ability of a phase to interact with a solute in a certain way. The L^{16} which is a function of Ostwald solubility coefficient [10] of a solute in *n*-hexadecane at 298.15 K represents a composite measure of the ability of a solute to interact with a solvent by dispersion forces and to some extent by induction. It also incorporates the cavity formation (to accommodate the solute molecules in the solvent) process [10]. The $\log L^{16}$ as a descriptor has been used in linear solvation energy relationship (LSERs) to represent a contribution related to the cavity formation and to dispersion interactions and turned out to be very useful in characterizing a wide variety of solute properties, including chromatographic retention and partition coefficient at liquid-gas and solid-gas interfaces and solute-solvent interactions in gas chromatography [11–18]. It has also been used to estimate normal boiling temperature and critical properties of organic compounds [19].

Serious difficulties arise when L^{16} of non-volatile compounds is to be measured [20–22]. Therefore, it would be very useful to have a method to predict the accurate gas-hexadecane partition coefficient of any solute to minimize the number of data points required for measuring $\log L^{16}$ experimentally. The motivation for the accurate determination of $\log L^{16}$ (at 25 °C) centers on the need for these values in many LSERs which is very useful for the study of chemical interactions in various solution processes [22]. Few predicting methods have been reported [23–26] which can be used to calculate $\log L^{16}$ of non-volatile compounds to overcome difficulties of measurements and also save the consumption of solvents, expensive chemicals, columns, capillaries, materials, time, etc.

A number of proposed partitioning theories have been based on the concept of cohesive energy density or the Hildebrand–Scatchard solubility parameter (δ) [27].

$$\delta = [(\Delta H^v - RT)/\bar{V}]^{1/2} \quad (2)$$

where \bar{V} , ΔH^v , R and T are the molar volume, molar heat of vaporization, universal gas constant and the absolute temperature, respectively. The solubility-parameter-

based-model enables the calculation of properties as accurate as experimental data. It should be pointed out that there are no other methods of comparable accuracy. The performance of the model has been considered to be of interest, not just for development of physicochemical theories for liquid mixing and solution, but also for application in such diverse fields as environmental chemistry, pharmaceutical chemistry, biochemistry, analytical chemistry or chemical engineering [28].

In the present work we have extended the solubility-parameter-based-model [28] for derivation of five characteristic parameters ($a_i, b_i, C_{1,i,s}, C_{2,i,s}, X_{i,s}$) which can be used to predict $\log L^{16}$. Characteristic parameters derivation is based on accurate experimental values of heat of vaporization, molar liquid volume and of $\log L^{16}$. The superiority of this method over the others [29,30] is that it has all of the advantages of the solubility-parameter-based models (with respect to physicochemical basis) in addition to isomer specificity and general applicability to equilibrium partition constants. Furthermore the contribution of the heat of vaporization is combined to the vapor pressure, Henry's law constant and Kovats indices, and the exchange enthalpy (H^{ex}) contributions into an overall enthalpy contribution for a property. In the same way the entropy of contribution can be combined to the vapor pressure, Henry's law constants and Kovats indices, and the exchange entropy (S^{ex}) contributions plus the phase ratio (Φ) into an overall entropy-related contribution. Collection of the combinatorial entropy (S^{co}) contributions produces an overall contribution [28].

2. Theory and method

The following expressions based on the Raoult convention choosing the thermodynamic potentials of the pure liquid solute and solvent as reference states of solution are introduced for calculations [10,28].

$$p_i = K_H^c C_i \quad (3)$$

$$L = \frac{RT}{K_H^c} \quad (4)$$

$$\log x_i = \log (C_i \bar{V}_s / 10^6) = -\log \gamma_i \quad (5)$$

$$\begin{aligned} \log L^{16} &= -\log\left(\frac{K_H^c}{RT}\right) = -\log\left(\frac{P_i}{C_i RT}\right) \\ &= -\log\left(\frac{P_i^* \bar{V}_s}{10^6 RT}\right) - \log \gamma_i \end{aligned} \quad (6)$$

In the above equations P_i^* , P_i , C_i , R , T and K_H^c are the vapor pressure of the pure solute (i) above the solution, the concentration or the solubility (mol. Lt⁻¹) of solute (i) in solution, gas constant, temperature (K) and the Henry law constant, respectively. Also x_i , V_s , γ_i are the solubility of solute (i) in terms of mole fraction, molar volume (cm³. mol⁻¹) of the solvent (n-hexadecane) and activity coefficient of solute, respectively.

A general characteristic of solubility-parameter-based models for the activity coefficient is that they have some qualitative molecular interaction explanation, without transition into a true statistical thermodynamic theory. The mixing process of solute and solvent is modeled as an exchange of molecules in similar lattices filled with just solute or solvent molecules [31]. If solute and solvent molecules have approximately identical shapes and dimensions, only one lattice can describe solute, solvent and solution. An exchange enthalpy contribution can be understood as the result of the energy gained from the formation of solute-solvent interactions and the energy loss from breaking solute-solute and solvent-solvent interactions. An exchange entropy contribution, deviating from the random-mixing ideal-solution expression, may result especially when strong solute-solvent interactions are present, which limit the number of accessible lattice configurations. If the solute and solvent are markedly dissimilar, a combinatorial entropy contribution may arise from the extra lattice space in a lattice filled with just small molecules [28]. The activity coefficient ($\gamma_{i,s}$) of solute (i) in solvent (s) at infinite dilution is calculated [28] by:

$$\log \gamma_{i,s} = H_{i,s}^{ex} + S_{i,s}^{ex} + S_{i,s}^{co} \quad (7)$$

where

$$\begin{aligned} H_{i,s}^{ex} &= \bar{V}_i [\delta_1^2 + \delta_s^2 - 2\delta_1 \delta_s c_{1,i,s} (c_{2,i,s} \delta_s \\ &\quad + \delta_i) / (\delta_s + c_{2,i,s} \delta_i)] / RT \end{aligned} \quad (8)$$

$$S_{i,s}^{ex} = X_{i,s} \quad (9)$$

$$S_{i,s}^{co} = \log(\bar{V}_i / \bar{V}_s) - \bar{V}_i / \bar{V}_s + 1 \quad (10)$$

$$\log p_i^* = a_i - b_i \Delta H_i^v / RT \quad (11)$$

In Eq. (8), parameters $c_{1,i,s}$ and $c_{2,i,s}$ are dimensionless and are independent of temperature. They are assumed to be characteristic constants of the solute's series to which compound (i) and solvent (s) belong. In Eq. (9) the parameter $X_{i,s}$ appears, which is also considered to be characteristic constant of solute's series, i, and of solvent. By substitution of Eqs. (7-11) into Eq. (6) we obtained:

$$\begin{aligned} \log L^{16} &= -a_i + \frac{b_i \Delta H_i^v}{RT} - \log\left(\frac{\bar{V}_{16}}{10^6 RT}\right) \\ &\quad - \frac{\bar{V}_i}{RT} \left[\delta_1^2 + \delta_{16}^2 - 2\delta_1 \delta_{16} c_{1,i,s} \frac{(c_{2,i,s} \delta_{16} + \delta_i)}{(\delta_{16} + c_{2,i,s} \delta_i)} \right] \\ &\quad - X_{i,s} - \log\left(\frac{\bar{V}_i}{\bar{V}_s}\right) + \frac{\bar{V}_i}{\bar{V}_s} - 1 \end{aligned} \quad (12)$$

Experimental values of heats of vaporization (ΔH /kJ mol⁻¹) and molar volumes (\bar{V} /cm³. mol⁻¹) [calculated from liquid densities (d) and molecular weight (Mw) via $\bar{V} = Mw/d$] of variety of compounds are available [32-34]. However for many compounds experimental data (ΔH and \bar{V}) are not available and have to be estimated. On the other hand, obviously in any series of homologue compounds heat of vaporizations and molar volume are linearly related to their number of carbon atoms (n).

$$\Delta H_i^v = an + b \quad (13)$$

$$\bar{V}_i = a'n + b' \quad (14)$$

The values of a, b, a', and b' were determined by linear regression analyses of experimental values of ΔH^v and \bar{V} versus the number of carbon atoms in all series of homologue compounds (Tables 1 and 2). The values of heat of vaporizations and molar volumes of those compounds that their values are not known experimentally were then estimated and the Hildebrand-Schatchard solubility parameters were then calculated by using Eq. (2). Compound-series-phase constants ($a_i, b_i, c_{1,i,s}, c_{2,i,s}, X_{i,s}$) which are the main type of parameters have to be fitted. The values of a_i and b_i were obtained by linear regression analysis based on Eq. (11) and a numerical procedure was carried out to obtain the values of $c_{1,i,s}, c_{2,i,s}$, and $X_{i,s}$ that resulted in

Table 1
Constants appearing in Eq. 13 calculated by linear regression

No	Series	a	b	S.E.	n
1	n-Alkanes	4.967	1.756	0.174	8
2	2-Methyl alkans	5.088	-0.825	0.137	5
3	3-Methyl alkanes	4.781	1.619	0.007	3
4	n-Alk-1-enes	5.322	-1.524	0.474	8
5	n-Alk-1-yne	4.404	4.741	0.000	2
6	Chloroalkanes	4.688	14.817	0.158	7
7	Boromoalkanes	4.637	18.294	0.177	7
8	Ethers	4.394	9.651	0.090	4
9	1-Alkanals	4.153	17.178	0.000	3
10	Ket-2-ones	4.254	17.777	0.203	6
11	Ket-3-ones	3.952	18.786	0.000	2
12	Formates	4.388	19.403	0.208	4
13	Acetates	4.085	19.603	0.179	5
14	Methyl alkanoates	4.187	19.996	0.000	4
15	Ethyl alkanoates	4.187	19.423	0.000	4
16	Alkanoic acids	8.517	7.020	0.884	4
17	Nitroalkanes	2.560	35.990	0.146	3
18	Amines	4.300	19.007	0.123	6
19	n-Alkyl-1-ols	4.923	32.554	0.066	8
20	2-Methylalkyl-1-ols	5.443	29.768	0.000	3
21	3-Methylalkyl-1-ols	4.187	34.750	0.000	2
22	n-Alkyl-2-ols	4.231	32.690	0.192	4
23	2-Methylalkyl-2-ols	4.187	29.684	0.000	3
24	n-Alkan-1-thiols	4.659	17.981	0.012	3
25	Alkylbenzenes	4.328	7.739	0.162	5

S.E., Standard error; n, number of ΔH_i^v data points, ΔH_i^v (molar heat of vaporization, at 298.15 K, kJ mol^{-1}) was taken from Refs. [32] and [33]. In cases where ΔH_i^v data were not available at 298.15 they were obtained by interpolation using the available values of ΔH_i^v at other temperatures.

a least-squares fit of Eq. (12) to the experimental $\log L^{16}$ data. To do the calculation a fitting procedure has been applied by writing a non-linear fitting program. The method of calculation was applied to groups of homologous compounds that their values of $\log L^{16}$ were experimentally known. These different series of homologues display a considerable variation in polarity with dipole moments ranging from zero to several Debyes.

3. Results and discussion

Data which have been obtained by linear regression analyses of ΔH_i^v and \bar{V}_i versus the number of carbons in any series of homologue compounds are given in Tables 1 and 2 that can be

Table 2
Constants appearing in Eq. (14) calculated by linear regression

No	Series	a	b	S.E.	n
1	n-Alkanes	15.917	36.854	0.496	8
2	2-Methyl alkans	15.449	40.211	0.086	4
3	3-Methyl alkanes	16.105	33.990	0.001	2
4	n-Alk-1-enes	16.267	27.550	0.760	6
5	n-Alk-1-yne	15.222	16.548	0.836	8
6	Chloroalkanes	16.154	40.368	0.194	7
7	Boromoalkanes	16.373	42.126	0.142	7
8	Ethers	16.295	39.858	0.166	5
9	1-Alkanals	16.265	22.323	3.038	8
10	Ket-2-ones	16.595	23.563	0.353	7
11	Ket-3-ones	16.542	23.699	0.030	4
12	Formates	17.754	25.971	0.369	4
13	Acetates	16.969	30.118	0.498	6
14	Methyl alkanoates	16.500	28.929	0.000	2
15	Ethyl alkanoates	16.500	31.285	0.000	2
16	Alkanoic acids	16.865	24.039	0.649	9
17	Nitroalkanes	17.744	36.266	0.031	3
18	Amines	16.610	32.743	0.197	4
19	n-Alkyl-1-ols	16.752	24.713	0.186	8
20	2-Methylalkyl-1-ols	16.500	25.661	0.000	3
21	3-Methylalkyl-1-ols	16.500	26.72	0.000	2
22	n-Alkyl-2-ols	16.475	27.053	0.185	6
23	2-Methylalkyl-2-ols	16.500	23.371	0.000	2
24	n-Alkan-1-thiols	16.644	40.737	0.129	8
25	Alkylbenzenes	16.591	-9.758	0.170	5

S.E., Standard error; n, number of molar volume data points ($\bar{V} = \text{Mw}/d$, $\text{cm}^3 \text{mol}^{-1}$), d (density, at 298.15 K) was taken from Refs. [33,34]. In cases where molar volume data were not available at 298.15 they were obtained by interpolation using the available values at other temperatures.

used to calculate the desired values of ΔH^v and \bar{V} . The values of parameters a_i , b_i , $c_{1,i,s}$, $c_{2,i,s}$, and $X_{i,s}$ which were obtained by a non-linear regression analysis are given in Table 3. These characteristic constants of different sets of homologues were applied into Eq. (12) to predict the values of $\log L^{16}$ of desired compounds (Table 4). The agreement of the predictions presented here with the literature data of Abraham et al. [14] is of interest. There is a good agreement between present calculations and the data obtained by Abraham as demonstrated in Fig. 1. Statistical parameters of comparison between present calculations and those obtained by the other methods are also listed in Table 5. According to this table the solubility-parameter-based-model enables the calculation of gas-hexadecane partition coefficients at least as accurate as experimental data. Havelec et al. [26]

Table 3
Five characteristic constants of series of homologous (solutes) and of the solvent (n-hexadecane)

No	Solute series	a _i	b _i	C _{1,i,s}	C _{2,i,s}	X _{i,s}
1	Alkanes	7.57994	0.258467	0.981706	0.822568	-1.10623
2	Alkenes	7.57804	0.257438	0.994413	1.22098	-0.357330
3	Alkynes	9.53661	0.484331	0.888690	1.30910	-1.54372
4	Chloroalkanes	8.22351	0.301444	0.991050	1.91650	-0.706870
5	Bromoalkanes	8.57668	0.334385	0.965183	1.59722	-1.44429
6	Ethers	7.53465	0.242051	1.00189	0.875063	-0.427440
7	Aldehydes	7.79961	0.264919	1.02169	0.531873	1.45019
8	Ketones	6.85011	0.197228	1.02825	1.83386	-0.169350
9	Esters	7.58868	0.241333	1.02126	0.873898	0.828946
10	Carboxylic acids	5.31352	0.205476	1.04431	1.22615	1.86046
11	Nitroalkanes	7.69455	0.257723	0.844979	16.0527	-8.67722
12	Amines	8.51473	0.303294	0.975779	1.14106	-0.903620
13	Alcohols	8.12632	0.242926	0.996019	0.991863	-0.396720
14	Alkanethiols	7.79068	0.274197	0.992126	1.02440	-0.597680
15	Aromatics	7.79829	0.274836	0.995767	0.961424	-0.395520

have derived an additivity model for prediction of log L¹⁶ parameter of compounds.

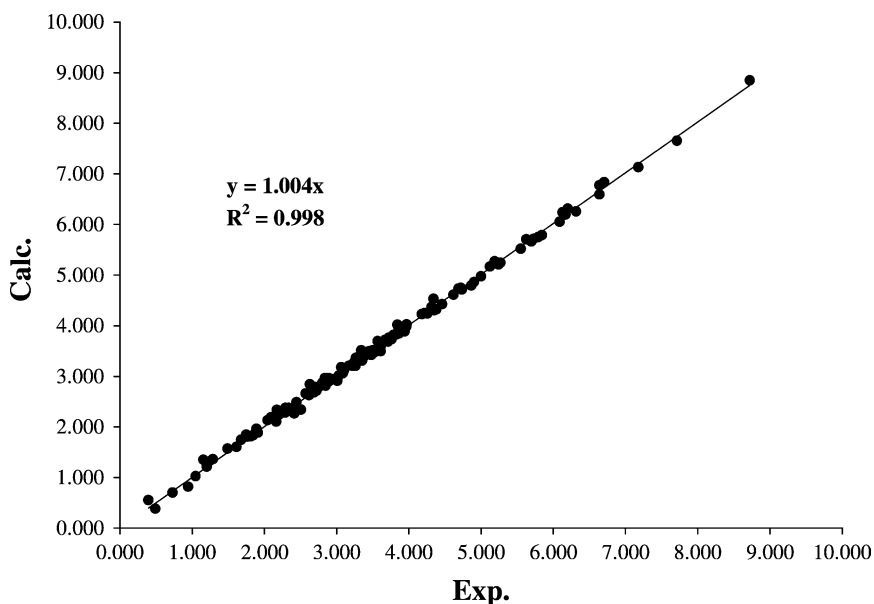
$$\log(L^{16}(X)) = \sum_i l_i \times FG_i + \sum_j m_j \times SC_j + \sum_k n_k \times IC_k \quad (15)$$

where FG, SC, IC are the number of particular groups (FG) forming compound X, structural contributions (SC), interactional contributions (IC), respectively. i, j, k are the identification number of group (i), of a structural contribution (j), of an

Table 4
Series of homologous (solutes) for which log L¹⁶ were calculated by using Eqs. (12), (16) and (17)

No	Solute series	Range of solutes	#
1	Alkanes	Ethane—n-Eihexacontane, 2-Methylpropane—2-Methylpentadecane, 3-Methylpentane—3-Methyleicosane	88
2	Alkenes	Ethene—Hexadec-1-ene	15
3	Alkynes	Ethyne—Heinecos-1-yne	20
4	Chloroalkanes	1-Chloromethane—1-Chloroeicosane	20
5	Bromoalkanes	1-Bromoethane—1-Bromoeicosane	20
6	Ethers	Dimethyl ether—Dieicosyl ether	20
7	Aldehydes	Formaldehyde—1-Eicosanal	20
8	Ketones	Acetone—Docosan-2-one, Pentan-3-one—Nonaadeca-3-one	40
9	Esters	Methyle formate—Eicosyl formate, Methyl acetate—Eicosyl acetate, Methyl propanoate—Methyl eicosanoate, Ethyl propanoate—Ethyl eicosanoate	76
10	Carboxylic acids	Formic acid—Eitriacontanoic acid	30
11	Nitroalkanes	Nitromethane—1-Nitroeicosane	20
12	Amines	Methylamine—Eicosylamine	20
13	Alcohols	Methanol—Eitriacontan-1-ol, 2-Mthylpropan-1-ol— 2-Methyldocosan-1-ol, 3-Methylbutan-1-ol—3-Methyltricosan-1-ol, Propan-2-ol—Docosan-2-ol, 2-Methylpropan-2-ol—2-Methyldocosan-2-ol	110
14	Alkanethiols	Ethanthiol—n-Heinetriacontan-1-thiol, 2-Methylpropan-1-thiol	31
15	Aromatics	Benzene, Methylbenzene—Pentadecylbenzene, o-xylene, p-xylene, m-xylene, 1,3,5-Trimethylbenzene	20

Number of solutes.

Fig. 1. Correlation between experimental and calculated values of $\log L^{16}$ at 298.15 K.

interactional contribution (k), respectively. l, m, n are the regression coefficients for the contributions of particular groups (l), structural contributions (m), interactional contributions (n), respectively. Based on the Carr's hypothesis [35] (a selective methylene group contribution as a function of the type of the homologous series) Havelec has

developed an equation

$$\log(L^{16}(X_i)) = A' \times n_{\text{CH}_2}(X_i) + B' \quad (16)$$

and has only reported the values of A' . Where n_{CH_2} is the number of CH_2 groups in the compound. To apply Eq. (16) a starting value of $\log L^{16}$ as a reference is needed and the value of B' has to be

Table 5

Statistical parameters of comparison between present results (Eq. (12)) and experimental values (literature values + those obtained by Eq. (17))

No	Series	X variable	Intercept	Ad. R ²	S.E.	Mean d	Sd	t-Test	t-Test ^a (95%)	n
1	Alkanes	1.010	-0.051	1.000	0.062	0.070	0.106	-0.726	1.96	88
2	n-Alk-1-enes	1.000	0.001	1.000	0.029	0.000	0.095	0.000	2.14	15
3	n-Alk-1-yne	1.000	0.000	1.000	0.062	0.000	0.060	0.000	2.09	20
4	Chloroalkanes	0.995	0.039	0.999	0.078	0.011	0.077	0.595	2.09	20
5	Bromoalkanes	1.000	0.000	1.000	0.049	0.000	0.048	-0.007	2.09	20
6	Ethers	1.002	-0.013	1.000	0.080	0.006	0.078	0.357	2.09	20
7	Aldehydes	1.000	0.000	1.000	0.035	0.000	0.034	-0.001	2.09	20
8	Ketones	1.000	0.000	1.000	0.024	0.000	0.024	0.003	2.02	40
9	Esters	0.995	0.031	0.994	0.219	-0.002	0.218	-0.060	1.96	76
10	Carboxylic acids	1.000	0.000	1.000	0.049	0.000	0.048	0.009	2.04	30
11	Nitroalkanes	1.000	0.000	1.000	0.043	0.000	0.042	0.000	2.09	20
12	Amines	0.998	0.012	0.997	0.198	0.000	0.197	0.004	2.09	20
13	Alcohols	0.998	0.012	0.997	0.198	0.000	0.197	0.004	1.96	110
14	Alkanethiols	1.000	0.000	1.000	0.026	0.000	0.025	0.077	2.04	31
15	Aromatics	1.000	0.000	1.000	0.055	0.000	0.054	0.038	2.09	20

Ad. R², Adjusted R square; S.E., Standard error; Mean d, Mean deviation; Sd, Standard deviation; n, number of data points.

^a Ref. [36].

Table 6
Statistical parameters of linear regression analyses of Eqs. (16) and (17)

No	series	n	A (Eq. (17))	B (Eq. (17))	A' (Eq. (16))	B' (Eq. (16))	Ad.R ² (Eq. (17))	Ad.R ² (Eq. (16))	S. E. (Eq. (17))	S.E. (Eq. (16))
1	n-Alkanes	13	0.511	-0.437	0.506	-0.409	0.9996	0.9996	0.040	0.040
2	n-Alk-1-enes	7	0.541	0.709	0.496	-0.493	0.9977	0.9977	0.056	0.052
3	Chloroalkanes	5	0.509	0.672	0.517	0.637	0.9997	0.9997	0.014	0.014
4	Ethers	6	0.469	0.217	0.488	0.020	0.9967	0.9967	0.100	0.105
5	1-Alkanals	8	0.523	0.209	0.523	0.207	0.9995	0.9995	0.027	0.027
6	Ket-2-ones	9	0.495	0.275	0.485	0.364	0.9998	0.9998	0.020	0.019
7	Esters (formate)	6	0.536	0.784	0.531	0.850	0.9985	0.9985	0.039	0.038
8	Acetates	7	0.499	1.356	0.506	1.301	0.9989	0.9989	0.035	0.035
9	Carboxylic acids	11	0.543	0.660	0.543	0.657	1	1	0.004	0.003
10	n-Alkyl-1-ols	12	0.514	0.496	0.512	0.545	0.9997	0.9997	0.031	0.031
11	n-Alkyl-2-ols	6	0.512	0.264	0.500	0.338	0.9993	0.9993	0.025	0.025
12	Alkanethiols	9	0.516	1.143	0.520	1.124	0.9998	0.9998	0.021	0.021

n, number of observation; Ad. R², adjusted R square; S.E., standard error.

calculated. In this work we have calculated the value of B' (Table 6) and have then predicted the values of log L¹⁶ for all series of homologous compounds listed in Table 4. Moreover, within any

series of homologous compounds the experimental values of log L¹⁶ are linearly related to their number of carbons (n_c).

$$\log L^{16} = A(n_c) + B \quad (17)$$

Table 7
Experimental and predicted values of log L¹⁶ of alkylbenzenes at 298.15 K

No	Compound	log L ^{16a} (exp.)	log L ^{16b} (cal.)	log L ^{16c} (cal.)	log L ^{16d} (cal.)	Dev.%
1	Benzene	2.803	2.819	2.855	2.866	-2.245
2	Toluene	3.344	3.312	3.344	3.339	0.144
3	Ethylbenzene	3.789	3.805	3.833	3.811	-0.571
4	Propylbenzene		4.298	4.322	4.261	
5	Butylbenzene		4.791	4.810	4.818	
6	Pentylbenzene		5.284	5.300	5.274	
7	Hexylbenzene		5.777	5.789	5.764	
8	Heptylbenzene		6.270	6.277	6.255	
9	Octylbenzene		6.763	6.767	6.749	
10	Nonylbenzene		7.256	7.256	7.243	
11	Decylbenzene		7.749	7.744	7.739	
12	Undecylbenzene		8.242	8.234	8.237	
13	Dodecylbenzene		8.735	8.722	8.735	
14	Tridecylbenzene		9.228	9.211	9.234	
15	Tetradecylbenzene		9.721	9.701	9.734	
16	Pentadecylbenzene		10.214	10.189	10.235	
17	o-Xylene	3.942			3.886	1.420
18	m-Xylene	3.864			3.847	0.447
19	p-Xylene	3.836			3.827	0.223
20	1,3,5-Trimethylbenzene	4.316			4.367	-1.182

^a Experimental values (Ref. 14).

^b From Eq. (17)

^c Eq. (16).

^d This work

$$\text{Dev. \%} = \frac{(L_{\text{Calcd.}}^{16} - L_{\text{Exp.}}^{16})}{L_{\text{Exp.}}^{16}} \times 100$$

In this work we have used the values of log L¹⁶ that have been reported by Abraham et al. [14] to obtain the values of A and B. While the values of A and B were known (Table 6), values of log L¹⁶ of any related compound were predicted. In addition to this, these estimated values of log L¹⁶ were considered to be as interpolated and extrapolated values of experimental values of log L¹⁶, and in order to obtain the most accurate and comprehensive constants, these values were then added to the experimental values of log L¹⁶ to have more data points which resulted in the best fit of Eq. (12). Table 7 shows results that have been obtained by different methods, typically.

Statistical parameters in Table 5 illustrate that the solubility-parameter-based-model enables the calculation of gas-hexadecane partition coefficients at least as accurate as experimental data. This must also be pointed out that Abraham et al. [14] have measured the values of log L¹⁶ for 137 compounds, while in the present work we have predicted the values of log L¹⁶ for 413 extra compounds for which experimental data were not available. The most advantages of this model (Eq. (12)) over Eqs. (16) and (17) are that values of log L¹⁶ indeed may be analyzed in terms of enthalpy, entropy and activity coefficient. One can also calculate the effect of these contributions to isomer or compound resolution. Eq. (12) is a general and comprehensive model. Application of characteristic constants given in Table 3 will give the values of log L¹⁶ of any desired compound including isomers (Table 7).

4. Conclusion

Statistical parameters of linear regression analyses of calculated values versus the experimental values of log L¹⁶ indicate that the solubility-parameter-based-model enables the calculation of gas-hexadecane partition coefficients at least as accurate as experimental data. The log L¹⁶ (at 25 °C) which is very useful for the study of chemical interactions in various solution processes for 413 different compounds (mostly nonvolatile) have been predicted to overcome difficulties of measurements. Five characteristic constants have been obtained which can be applied

into the model to predict any desired value of log L¹⁶ provided that the compound belongs to each of 15 series of compounds that have been studied in this work.

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