

Solvation parameters

Part 1. Mutual improvements of several approaches and determination of two first sets of optimized values

Paul Laffort^{a,*}, Françoise Chauvin^a, Andras Dallos^b, Pascal Callegari^a, Dominique Valentin^a

^a Centre Européen des Sciences du Goût, CNRS, UMR 5170, 15 rue Hugues Picardet, F. 21000 Dijon, France

^b Department of Physical Chemistry, University of Veszprém, H-8200 Veszprém, Hungary

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Abstract

An improvement in the characterization and the determination of the solvation parameters allows, not only a better knowledge of solutions, but also of some biological phenomena. In this paper, we test several published data and approaches in the field of solubility and solvation parameters in two ways: (i) the mutual independence of the parameters and (ii) their ability to take into account recently published gas–liquid chromatographic data. From this enquiry it arises that the most suitable published values are those of Abraham concerning 314 solutes. It also arises that the parameters of dispersion and orientation of this published data set are appreciably improved using two simple equations. In addition, a new set of optimized values for 133 solutes is given, by derivation from retention indices in gas–liquid chromatography (GLC) on five selected stationary phases, published by Kováts and co-workers and in the present study. The two sets have a total of 373 defined compounds.

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1. Introduction

According to several authors, intermolecular forces similar to those involved in solutions (reflected by parameters of solutions) can, in many cases, at least partially, account for the response of a biological system to a biologically active agent. In this way, the most recent and successful results are due to Abraham et al. in domains as different as blood–brain distribution, skin permeation, eye and nose irritation [1–4]. In some way, this can be considered from the same perspective as the old strategy of quantitative structure–activity relationship (QSAR) in pharmacology of Hansch [5]. The success of this strategy, however, is generally only partial in the field of recognition of odorous substances by olfactory receptor cells, the field of interest of Laffort and co-workers [6–13], in spite of a recent remarkable exception [14]. Indeed, one of the difficulties of superimposition of odorous and physicochemical properties lies in the fact that both types of properties are often not available for the same sets of compounds. Therefore, our general purpose in this field is to

provide an accurate and simple procedure to generate parameters of solutions in order to establish them for compounds for which odorous properties are known. In the present study, two preliminary steps will be pursued, the theoretical aspects being left aside:

- (1) Testing the several sets of parameters of solutions already published and, if possible, improving them. As we will see, a selection of values results from this first step concerning 314 solutes [15], improved by using two simple equations.
- (2) Providing a set of optimized values for 133 solutes by using retention indices in gas–liquid chromatography (GLC) on five selected stationary phases.

The two sets have a total of 373 defined compounds. In order to increase the clarity of the paper, it will be divided in two sections corresponding to the two steps.

2. Mutual improvements of several approaches

A semi-theoretical approach of solutions by means of solubility parameters of solutes and solvents was elaborated by

* Corresponding author. Fax: +33 3 80 68 16 01.
E-mail address: laffort@cesg.cnrs.fr (P. Laffort).

Snyder [16] and further developed by Karger et al. [17,18]. These authors expanded the solubility parameter of Hildebrand et al. theory [19] to five partial parameters, which they called parameters of dispersion, orientation, induction, basicity and acidity. They developed from this a general model of retention, valid for several kinds of chromatography, which takes into account the partial solubility parameters of the solutes, solvents and adsorbents, and the molar volume of the solutes. They proposed an equation with five terms for gas–liquid chromatography. The number and the nature of the terms were kept by the authors that later entered this field, but not the names of the parameters and the ways to obtain them. In particular, the products of the molar volume and the partial solubility parameters of solutes according to Karger et al. [17,18] are now considered as given characteristics of solutes, forming each one a whole, which we will call *solvation* parameters, as proposed by Abraham et al. [20], in order to avoid any confusion.¹ This modification presents the additional interest to have one parameter varying with the size of the molecules (or *apolar* term): the dispersion parameter, and four parameters constant along homologous series (so-called *polar* terms): the parameters of orientation, induction-polarizability, acidity and basicity).

Several data sets of solubility and solvation parameters of solutes have been published approximately in the same period than Karger et al. [17,18] (1976–1982): Laffort and Patte [11], Patte et al. [21], Thomas and Eckert [22], whom contributions will be checked below. The suggestion of Laffort and Patte [11] to replace the former index of induction by a new one of polarizability, partially derived from the refractive index and independent of the size of the molecule should be underlined. The importance of this index in chromatography has been confirmed in 1987 [12], and it has also been shown in 1993 that this parameter is an integral part of some olfactory phenomena [14]. It was only adopted by other authors in physical chemistry of solutions in 1990, by Abraham et al. [20], who improved its definition (we will see below the arguments). In previous works of Abraham, Doherty, Kamlet, Taft and their co-workers [23–26], an oversimplified expression of the polarizability, call δ_2 , was applied: zero except for poly halogenous aliphatic compounds (=0.5) and for aromatic compounds (=1).

In order to make the pragmatic comparisons between the several approaches easier, the original names for solutes according to each author will be kept, but associated with the general identifications as follows:

DISPER: for the dispersion solvation parameters.

ORIENT: for the orientation/dipolarity solvation parameters.

POLARIZ: for the polarizability/induction solvation parameters.

ACID: for the acidity (or more correctly hydrogen bond donor) solvation parameters.

BASIC: for the basicity (or more correctly hydrogen bond acceptor) solvation parameters.

In this context, the general retention indices in gas–liquid chromatography, RI, can be written according to the following equation:

$$RI - RI_0 = D^*disp + \emptyset^*orient + P^*polariz + A^*acid + B^*basic \quad (1)$$

in which D , \emptyset , P , A and B stand for associated solvation parameters of stationary phases and RI_0 for the retention index of methane (=100, according to the definition of retention indices²)

Two thought processes have been principally applied in order to check the proposed data sets of solvation parameters:

- (1) Checking the mutual independence of the parameters, via Pearson correlation coefficients. For a given sample of solutes, the correlation coefficients between parameters must be as low as possible. Otherwise, the total information for solute-solvent affinity needs more than five terms to be carried. For example, McReynolds suggested 10 terms [28].
- (2) Optimizing the parameters by the use of the multiplicative matrix analysis (MMA) algorithm, applied in the present study with experimental solution data: a set of gas–liquid chromatography for 133 solutes and 10 stationary phases. The MMA algorithm was developed by Robin and Laffort and firstly described by Laffort and Patte [11].

2.1. Experimental and data processing

2.1.1. The experimental set of retention indices in GLC

These experimental data will be called in brief, the 133×10 Kováts data set. Part of them (see Table 1), are the retention indices obtained from GLC of 133 solutes on two apolar phases (alkanes C_{67} and C_{103}), determined in the present study, at 130°C in packed columns. These two alkanes are members of the homologous series shown in Fig. 1 (right side). Retention indices on an hypothetical C_{78} -hydrocarbon phase of the same series were calculated by interpolation, based on previous studies of Kováts and co-workers [29] where it was shown, every thing being equal, that the retention index is inversely proportional to the molecular weight of the stationary phase.

From this latter finding the relationship of the retention indices on the C_{78} hydrocarbon is given in the equation:

$$RI_{C_{78}} = 0.4035 RI_{C_{103}} + 0.5965 RI_{C_{67}} \quad (2)$$

Similarly, the indices on a hypothetical alkane of infinite molecular weight were extrapolated by using the following equation:

$$RI_{C_\infty} = 2.8611 RI_{C_{103}} - 1.8611 RI_{C_{67}} \quad (3)$$

Differences between the retention indices of the same 133 solutes on eight polar stationary phases and on the previous mentioned C_{78} hydrocarbon, also measured at 130°C in packed

¹ In previous studies of Laffort and co-workers ([11,12,21]), the concept of solvation parameters was called solubility factors.

² The retention indices in gas-liquid chromatography were defined by Kováts [27] as the real hypothetical number of carbon atoms of *n*-paraffins having the same retention time, everything being equal, than the solute under study, multiplied by 100.

Table 1
Name and structural details of the stationary phases synthesized and used by Kováts and co-workers [30–33] (***) and in the present work: (experimentally* and interpolated or extrapolated using Eqs. (2) and (3)**)

Abbreviated name	Formula	Chemical name	Functional group	Structure of C ₁₆ branches for polar phases	
C ₆₇ *	C ₆₇ H ₁₃₆	19, 19-diethyl-14, 24-ditridecylheptatricontane (67 carbon atoms)	Without		
C ₁₀₃ *	C ₁₀₃ H ₂₀₈	28, 28-diethyl-23, 33-dicosylpentapentacontane (103 carbon atoms)	Without		
C ₇₈ **	C ₇₈ H ₁₅₈	19, 24-dioctadecyldotetracontane (78 carbon atoms)	Without		
C _∞ **		(infinite carbon atoms)	Without		
POH***	C ₇₇ H ₁₅₆ O	18, 23-dioctadecyl-1-untetracontanol	Primary alcohol	X = CH ₂ OH	Y = CH ₂ CH ₃
TTF***	C ₇₈ H ₁₄₆ F ₁₁₂	19, 24-bis-(18, 18, 18-trifluorooctadecyl)-1, 1, 1, 42, 42, 42-hexafluorodotetracontane	Tetrakis(trifluoromethyl)	X = Y = CH ₂ CF ₃	
MTF***	C ₇₈ H ₁₅₅ F ₃	1, 1, 1-trifluoro-19, 24-dioctadecyldotetracontane	Monotrifluoromethyl	X = CH ₂ CF ₃	Y = CH ₂ CH ₃
PCL***	C ₇₇ H ₁₅₅ Cl	1-chloro-18, 23-dioctadecyluntetracontane	Primary chloro	X = CH ₂ Cl	Y = CH ₂ CH ₃
PBR***	C ₇₇ H ₁₅ Br	1-bromo-18, 23-dioctadecyluntetracontane	Primary bromo	X = CH ₂ Br	Y = CH ₂ CH ₃
TMO***	C ₇₄ H ₁₅₀ O	17, 22, bis-(16-methoxyhexadecyl)- 1, 38-dimethoxyoctatricontane	Tetramethoxy	X = Y = OCH ₃	
PSH***	C ₇₇ H ₁₅₆ S	18, 23-dioctadecyl-1-untetracontanethiol	Primary thiol	X = CH ₂ SH	Y = CH ₂ CH ₃
PCN***	C ₇₈ H ₁₅₅ N	1-cyano-18, 23-dioctadecyluntetracontane	Primary cyano	X = CH ₂ CN	Y = CH ₂ CH ₃

columns, were published in four papers by Kováts and co-workers [30–33]. The original retention indices for polar phases were therefore restored and listed with the apolar indices in Table A.1 of Appendix A. The set under study in the present work includes the indices on the eight polar phases and those on the two alkanes C₇₈ and C_∞.

The polar phases are all isochoric and isosteric with the C₇₈-skeleton depicted in Fig. 1 (left side). All the polar phases have 78 heavy atoms (other than hydrogen), with the heavy atoms of the polar groups substituting for methylene or methyl groups in the hydrocarbon skeleton.

The alkanes are more branched than the polar phases; hence they have a lower melting point. For example, the melting point of C₇₈ in the hydrocarbon family is around 60–70 °C, whilst that of C₇₈ hydrocarbon in the polar family is over 100 °C. Strictly speaking, the alkanes' family represented in Fig. 1 (right part), only concerns compounds with odd number of carbon atoms. The C₇₈ alkane has been derived from C₆₇ and C₁₀₃ (Eq. (2)), in order to be compared with the polar phases (left part).

It is sometimes argued that the retention indices as defined by Kováts [27], are not directly related to thermodynamical prop-

erties [20]. In fact, from information published by Kováts and co-workers [30–33], the logarithm of the reduced retention volumes, log V_g, can be derived from all retention indices reported in Table A.1, by the simple following general equation (valid for RI ≥ 500):

$$\log V_g = \left(0.29 \frac{RI}{100}\right) - 0.4 \quad (4)$$

More details on Eq. (4) can be seen in [34] (see also the last column of Table 2).

The constancy of the multiplicative coefficient in Eq. (4) is due to the similar molecular structure of the stationary phases. Let us remember that McReynolds [28] reported values of this multiplicative coefficient, called b, varying from 0.17 to 0.30, according to the nature of the phases.

2.1.2. The multiplicative matrix analysis (MMA)

This algorithm, previously called Robin–Laffort programme, was first applied in 1972 by Dravnieks and Laffort [35]. It was presented in several circumstances, among others at the 11th International Symposium on Advances in Chromatogra-

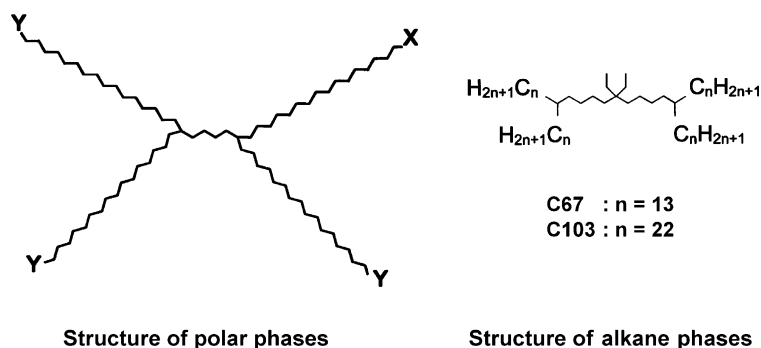


Fig. 1. Schematic representation of the stationary phases synthesized and used by Kováts and co-workers [29–33], and used in the present work. The polar phases, with X and Y representing different functional groups (see also Table 1) are indicated on the left. The structures of apolar phases are indicated on the right.

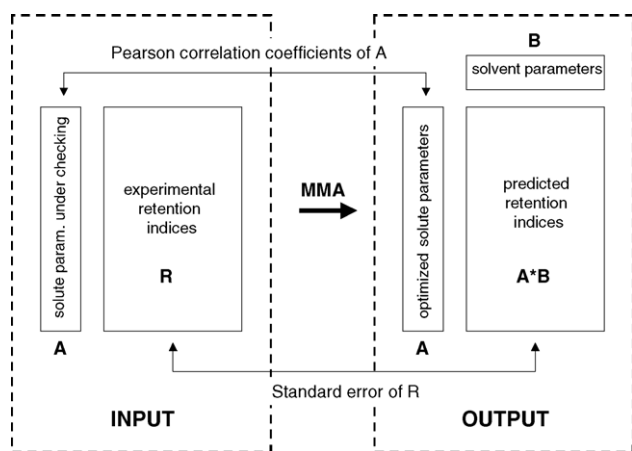


Fig. 2. Diagram of the INPUT/OUTPUT of the multiplicative matrix analysis (MMA). The correlations between input and output parameters A depend on the nature of the input parameters, for a given experimental matrix R, whereas the standard error on the reconstruction of matrix R only depends on the chosen number of parameters.

phy (Houston, 1976, [11]), at the Advanced Study Institute on Theoretical Advancement in Chromatography and Related Techniques (Ferrara, Italy, 1991 [36]), and more recently by Chauvin [34]. It is a tool to test theories on the basis of experimental data, whenever products of matrices are involved, as in Eq. (1).

The first interest of this tool, compared with more classical ones such as the step-wise multi linear regression analysis, is that it provides a test for each of the elements of the matrix, independently of their weight in the given sample of experimental data. For example, in the case of Eq. (1), each of the five solvation parameters of solutes proposed by several authors can be tested only on the criterion of its initial definition, in spite the fact that the dispersion parameter is much more involved in chromatographic phenomena than each of the four other parameters. A second interest of the MMA algorithm is that the output parameters values should be more precise than the input parameters values, on the condition that experimental data (chromatographic data in the present case) are overabundant and precise enough (see Fig. 2). This aspect will be considered in Section 4.

The formal principle of the MMA algorithm as well as its expression in MATLAB language are specified in Appendix B, whereas Fig. 2 summarizes how it works. For a given matrix of experimental data R (here the 133×10 Kováts data set of retention indices reported in Table A.1), a data set of parameters to be tested A (here, the solvation parameters of solutes, according to one or another author) is placed in INPUT. The programme runs by using successive iterations, until the reconstruction of the experimental matrix in OUTPUT is optimal. The quality of this reconstruction (R compared to $A \times B$) only depends on the number of input parameters A, not of their nature. By contrast, the output parameters A resemble to the input parameters only when the later are involved in the phenomenon under study (here the solute-solvent affinity when the molecular weight of the solvent is much greater than that of the solute). We will further verify these two points by using random data for the input matrix A.

In practice, the program starts with a classical multi linear regression, with R as independent variables and A as dependent variables. A first matrix B of solvent parameters is obtained, which in turn is considered as fixed. A first comparison between R and the product $A \times B$ is made. In a second step, a multi linear regression is applied to B and R and a second value of matrix A of solute parameters is obtained. Further, similar steps are used until two successive cycles do not provide an improvement of reconstruction of matrix R (it is experimentally observed that the system is convergent).

2.1.3. Several sets of solvation parameters of solutes

Before starting a short description of the selected INPUT data sets to be applied to the MMA algorithm, let us remember some definitions around the molar volume and the molar refraction, which are both involved in several proposed solvation parameters:

- (i) The molar volume at 20 °C:

$$V_{20} = \frac{M}{d} \quad (5)$$

in which M stands for the molar mass and d stands for the density in liquid state at 20 °C. V_{20} is not an additive property.

- (ii) An expression supposed to reflect the intrinsic molecular volume, V_x , obtained by means of molecular increments, according to Abraham and MacGowan [37].
- (iii) The molar volume at boiling point, V_b . Because at boiling point the intermolecular forces of cohesion in condensed phases are exactly equilibrated by those of thermal motion, the V_b expression has been often considered as reflecting the intrinsic molecular volume. Few experimental values are available and several expressions have been proposed to evaluate them. Chauvin and Laffort [38] proposed one by means of molecular increments, called V_b^{top} , and another one, V_b^* , supposed to be more precise:

$$V_b^* = V_{20}(1 + 0.554\delta - 0.534\delta^2 + 0.296\delta^3 - 0.066\delta^4) \quad (6)$$

in which δ is given by:

$$\delta = \frac{t - 20}{293} \quad (7)$$

with t being the boiling point in °C.

According to [38], both V_b^* and V_b^{top} fit experimental V_b values better than V_x .

- (iv) The function of index refraction:

$$\text{fn} = \frac{n^2 - 1}{n^2 + 2} \quad (8)$$

where n is the index of refraction at line D of sodium at 20 °C.

- (v) The molar refraction, according to Lorentz and Lorenz relation:

$$\text{Rm} = \text{fn} V_{20} \quad (9)$$

Rm is an additive property.

- (vi) The molar refraction, according to Abraham et al. [20]:

$$RM = fn V_x \quad (10)$$

RM is also an additive property.

- (vii) An index of polarizability, according to Laffort and Patte [11]:

$$fn \frac{V_{20}}{V_b} \quad (11)$$

This expression reflects similar information than fn , but is, in addition, constant along homologous series.

- (viii) An index of polarizability, according to Abraham et al. [20]:

$$R_2 = \frac{V_x}{100} \left(10 fn + \frac{52.553}{V_x} - 2.83195 \right) \quad (12)$$

This expression, called by the authors “an excess of molar refraction”, is also constant along homologous series.

- (ix) An index of polarizability, according to Chauvin and Laffort [38]:

$$R_{96} = \frac{V_b}{100} \left(10 fn + \frac{74.134}{V_b} - 2.8115 \right) \quad (13)$$

This expression, very similar to Eq. (12), is based on the molar volume expressed by V_b instead of V_x .

We left aside the published sets of data with less than five parameters of solutes, for example those of Hoy [39] and Hanssen and Beerbower [40] (three parameters) and those of Tijssen et al. [41] (four parameters), since there is presently a general agreement that five independent parameters are needed (this fact is verified in Section 2.2). In these conditions, five input data sets have been selected:

DISPER	$\alpha'_{82} = 0.6454Z$	+ 0.9099C	−0.5068T	−0.5504D	
ORIENT	$\omega'_{82} = 0.1551Z$	−0.3544C	+0.1993T		
POLARIZ	$\varepsilon'_{82} = -0.7228Z$	−0.6920C	+0.2771T	+0.6969P	+0.4408D
ACID	$\pi'_{82} =$	+0.8343C	−0.1663T	−0.4925P	−0.1755D
BASIC	$\beta'_{82} = 0.0959Z$	+0.0892C	−0.0312T	−0.1539P	

46 × 5 Karger data set. These values are from Karger et al. [17,18]. The original partial solubility parameters of dispersion (δ_d), orientation (δ_o), induction (δ_{in}), acidity (δ_a) and basicity (δ_b) have been multiplied by V_{20} , in order to be homogeneous to the so-called solvation parameters and to Eq. (1).

DISPER: $V_{20}\delta_d$ is homogeneous to $fn V_{20}$.

ORIENT: $V_{20}\delta_o$ is homogeneous to the dipole moment, μ , for compounds possessing a single polar functional group.

POLARIZ: $V_{20}\delta_{in}$ is homogeneous to the square of the dipole moment, μ^2 , for compounds possessing a single polar functional group.

ACID, BASIC: $V_{20}\delta_a$ and $V_{20}\delta_b$ are homogeneous to indices of acidity and basicity, constant along homologous series.

They are determined by combining the heat of hydrogen bonding for n -alcohols and the heat of hydrogen bonding between non-associated compounds and suitable solvents acceptors and donors of hydrogen bonds, respectively, via spectroscopic measurements.

144 × 5 Eckert data set. These values are from Thomas and Eckert [22]. The original partial solubility parameters of dispersion (λ), of polarity (τ), of induction (Q), of acidity (α) and of basicity (β) have also been multiplied by V_{20} . They are established by combinations, not detailed here, of several elements of structure, the dipole moment and the refractive index.

75 × 5 Laffort data set. These values are from Laffort and Patte [11]. The original solvation parameters (also called “solubility factors”) of dispersion (α as apolar), orientation (ω), polarizability (ε), acidity (π as proton donor) and basicity (β) are derived from the retention indices in GLC on five stationary phases: Zonyl E-7 (a fluorinated ester), Carbowax 1000, tricyanoethoxypropane (TCEP), polyphenyl ether-6 rings (PPE) and diethylene glycol succinate (DEGS), established by McReynolds [42].

240 × 5 Patte data set. These values are from Patte et al. [21]. The solvation parameters, similar in their expression as in the 75 × 5 Laffort data set (α , ω , ε , π , β) are derived from the retention indices in GLC measured by the authors on five similar stationary phases (with the exception of Carbowax: 1540 instead of 1000). Surprisingly, rules of derivation, not specified here, are different than in the previous set, and therefore solvation parameters values are also different for solutes. Chauvin [34] suggests a rewriting of these equations of derivation, supposed to be more appropriate, which provides a so called 240 × 5 Patte modified data set. These equations are:

where: $Z = (RI - 100)/100$ on Zonyl E7; $C = (RI - 100)/100$ on Carbowax 1540; $T = (RI - 100)/100$ on TCEP; $P = (RI - 100)/100$ on PPE 6 rings; $D = (RI - 100)/100$ on DEGS.

314 × 5 Abraham data set. Abraham and co-workers started in 1990 [20] new definitions of five solvation parameters of solutes, which were improved in a series of papers and which can be considered as fixed since 1993 [15]. These parameters are defined as follows:

DISPER: Two parameters are proposed: the molar volume V_x , already cited, according to [37] and $\log L^{16}$, the Ostwald solubility coefficient of the solute on n -hexadecane at 298 K. The later should be more suitable for chromatographic purposes (not for QSAR ones).

ORIENT: The parameter π_2^H is called of dipolarity– polarizability. Initially considered as identical to the Kamlet–Taft solvatochromic parameter, π_1^* , it was further derived from chromatographic data [43].

POLARIZ: The parameter R_2 , according to Eq. (12). This expression, constant along homologous series, carries the same information than that of Laffort and Patte, $\text{fn } V_{20}/V_b$ (Eq. (11)), but we will see that it is more suitable.

ACID and BASIC: These two parameters are certainly the harder to establish, since no single *acid* can serve as unique reference of hydrogen bonding against a series of *bases* nor the reverse, and the rules to adjust results obtained with several references are not evident. Fortunately, Abraham and co-workers, using the complexation of a series of acids against a number of reference bases in dilute solution in tetrachloromethane, and reciprocally, found these rules of adjustment ([44], [45]). The authors call these two parameters, in the most recent version: $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$.

In [15], the *polar* solvation parameters are given for 340 solutes, and the complete set of parameters for 314 out of them.

In addition to these five INPUT solvation data sets, five new data sets have been established for 125 out of the 133 solutes for which retention indices are available on ten stationary phases. The values are partially found in the published sets and partially evaluated by using the rules provided by the authors or extrapolated.

2.2. Results

2.2.1. Mutual independence of the solvation parameters of solutes

Matrices of Pearson correlation coefficients have been established for the five published data sets (left side of Fig. 3) and for variations on these data (right side). To make the reading easier in Fig. 3, absolute values greater than 0.5 have been highlighted, without suggestion of significance. Several points can be noted:

- (1) The suggestion of Laffort and Patte [11], to replace $V_{20} \delta_{in}$ by $V_{20}/V_b \cdot \delta_{in}$ (i.e. R_m/V_b) noticeably improves the correlation matrix of Karger et al. [17,18]. The same phenomenon is observed for the $V_{20} Q$ parameter of Thomas and Eckert [22]. In fact, before 1990, with the exception of Laffort and co-workers' data, only four independent parameters were identified.
- (2) Another observation concerns the data of Patte et al. [21]: the multiple high values of correlation coefficients indicate that their rules of derivation from the retention indices of solutes on five GLC phases are certainly wrong, and that the modification suggested in Eq. (14) is probably suitable. However, as it can be observed in this modified matrix as well as in the Laffort and Patte matrix [11], there is a lack of independence between the acid and basic parameters, certainly due to the faint acidity character of the stationary phases Carbowax 1000 and Carbowax 1540, as pointed out by Abraham et al. [20]. These polymers are poly-ethers with

two hydroxyl functions at the extremities of the molecule, which is a very low proportion for molecules of molar mass of 1000 or 1540.

Finally, the Abraham data set [15] appears as the most satisfactory of the already published sets, but it can be slightly improved by using the following modifications of the dispersion and orientation parameters, respectively called δ_2 and ω_2 (unpublished until now):³

$$\delta_2 = \log L16 - 0.532\pi_2^H - 0.894R_2 - 0.115$$

$$\omega_2 = 1.523\pi_2^H - 0.538\Sigma\beta_2^H - 0.837R_2 \quad (15)$$

In fact, δ_2 is homogeneous to the product of the molar volume at boiling point V_b and the function of index refraction fn . The parameter ω_2 is homogeneous to the dipole moment for compounds with a sole polar group, but it has a positive value for compounds with two polar groups in an opposite side, and therefore having a dipole moment equal to zero (as, for example, the 1,4-dioxane), in a similar way than the product $V_{20}\delta_0$ according to Karger et al. [17,18].

2.2.2. Application of the MMA algorithm to the 133 × 10 Kováts data set of retention indices

This second way of checking and possibly improving the solvation parameters already published, confirms and specifies the first way.

In fact, the MMA algorithm was only applied on 125 compounds out of the 133 compounds listed in Table A.1, since input values A could not be established for three hydrocarbons and three silicon, one fluoride and one tin compounds.

We saw above that one of the characteristics of the MMA algorithm is that the quality of reconstruction of the experimental matrix R of retention indices only depends on the number of the input parameters A, not of their nature. The *standard error* is defined as follows:

$$\text{standard error} = \sqrt{\frac{(A \times B - R)^2}{N - 1}} \quad (16)$$

in which A, B and R stand for the matrices described in Fig. 2 and N stands for the number of cases.

The MMA algorithm has been applied to the 125 × 10 data set of retention indices R, according to Table A.1. The application generates, for any input matrix A (including random numbers), the diagram of standard error of retention indices versus the number of terms in Eq. (1), reported on Fig. 4.

In agreement with the several authors involved in this field for more than 30 years, the number of terms in the Eq. (1) have been fixed to five for the optimization of the input solvation

³ The expressions of δ_2 and ω_2 in Eq. (15) have been obtained using the MMA algorithm applied to the 125 × 10 Kováts data set of retention indices, as in the next paragraph, with the set $[\text{fn}V_b, \mu, R_{96}, \Sigma\alpha_2^H, \Sigma\beta_2^H]$ as input solutes parameters. Then, the output values for the dispersion and orientation parameters have been expressed as functions of the Abraham parameters using a step-wise regression analysis.

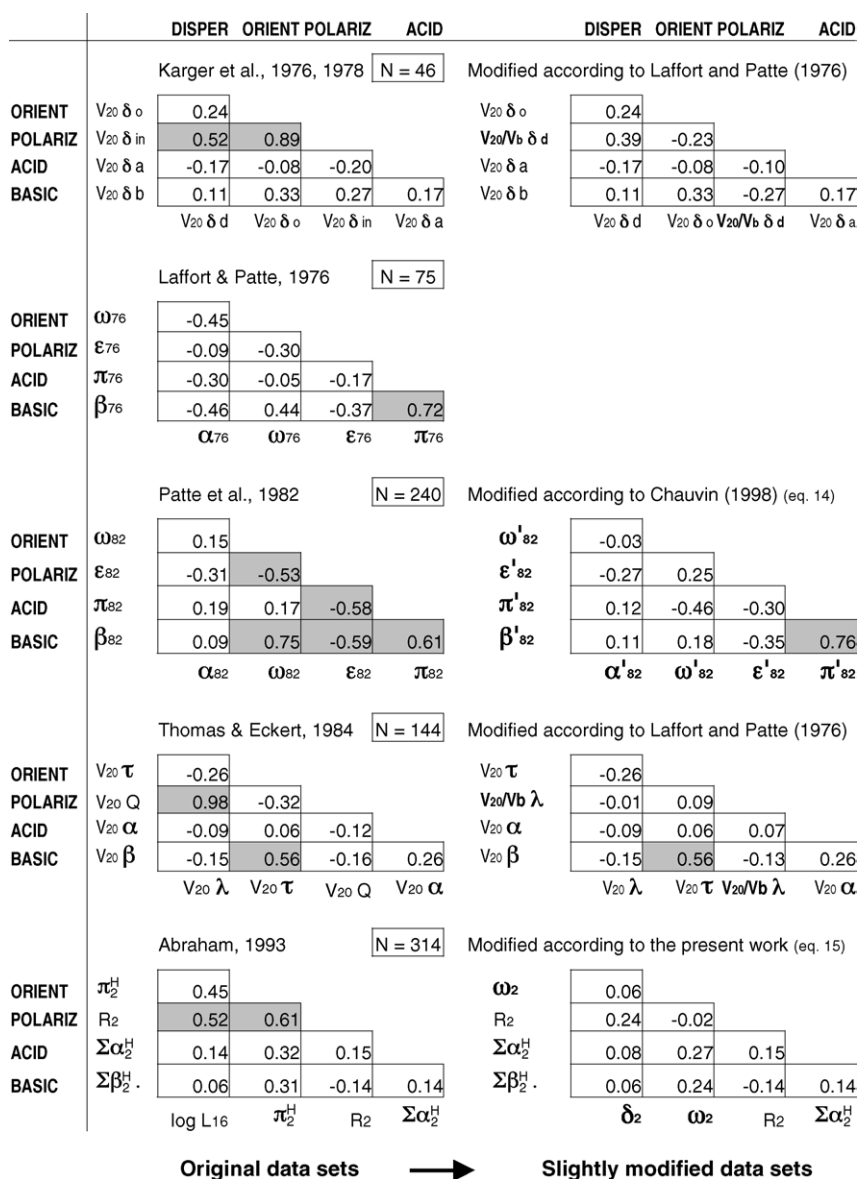


Fig. 3. Pearson correlation matrices for the solvation parameters proposed in five publications (on the left) and with some parameters slightly modified (on the right). The solvation parameters are supposed to be as mutually independent as possible, i.e. the correlation values should be low. Absolute values of correlation coefficients ≥ 0.5 are highlighted.

parameters A of solutes. This corresponds approximately to a standard error of 1 unit of retention index in the reconstruction of the matrix R of retention indices, as it can be seen in Fig. 4 (mean value in the 125×10 data set of retention indices: 797 units).

Three criteria have been used for testing the input solutes parameters in applying the MMA algorithm to the 125×5 Kováts data set of retention indices:

- (1) The mutual independence of the output parameters of solutes, in a similar way as for the values published by the authors, reported in Fig. 3. The obtained results, shown in Fig. 5 (and third column of Fig. 6), exhibit similar trends as in Fig. 3, i.e. a good mutual independence for data according to Thomas and Eckert [22] and Abraham [15], both in their

modified version. At this stage, no dramatic differences are observed between the mutual independence within these two sets and within the final set proposed in the present work.

- (2) The correlations A between the input and output parameters of solutes. They are supposed to be as high as possible, in contrast to that obtained with random data, as it can be seen in Fig. 6 (second column). To make the reading easier in this figure, values of correlation coefficients lower than 0.9 have been highlighted. At this stage, again, no significant differences are observed between the results obtained with the Abraham data and those suggested in the present work.
- (3) An absence of negative values in the output matrix B of solvent parameters, since negative values are difficult to be interpreted in terms of physicochemical meaning. When they occur, negative values probably also reflect a

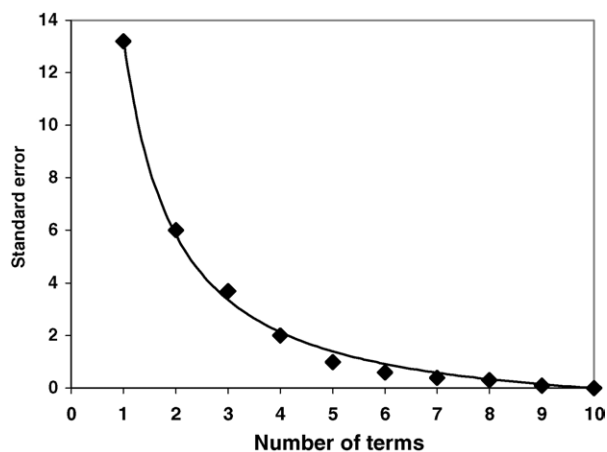


Fig. 4. Standard errors (expressed in RI units) in the reconstruction of the 125×10 Kováts matrix R of chromatographic retention indices, as a function of the number of terms in Eq. (1), by using the MMA algorithm. The results are independent of the nature of the input matrix A of solvation parameters.

lack of independence of solute parameters. At this stage, a slight better performance of the final data set proposed in the present work can be observed (fourth column of Fig. 6).

$$\begin{array}{l}
 \text{DISPER : } \delta_3 = -5.828I \quad +6.578P \quad \quad \quad -0.256F \\
 \text{ORIENT : } \omega_3 = \quad \quad \quad -0.679P \quad -0.971H \quad +1.416F \quad +0.234\emptyset \\
 \text{POLARIZ : } \varepsilon_3 = +4.207I \quad -4.080P \quad \quad \quad -0.127F \\
 \text{ACID : } \alpha_3 = -1.502I \quad +1.046P \quad \quad \quad -1.202F \quad +1.658\emptyset \\
 \text{BASIC : } \beta_3 = \quad \quad \quad -0.784P \quad +1.230H \quad -0.446\emptyset
 \end{array} \quad (17)$$

The comments on Figs. 5 and 6 will be more detailed in the Discussion section, but we can summarize the results presently reached by the assessment that the solvation parameters of Abraham [15] are the most suitable already published, on the condition to modify the dispersion and orientation parameters, according to Eq. (15). An additional improvement is obtained by replacing δ_2 by the expression of the molar refraction $\text{fn}V_b$ and the induction-polarizability parameter R_2 by R_{96} . The numerical values for $\text{fn}V_b$ and R_{96} can easily be obtained from Handbooks of physicochemical constants, by using Eqs. (6)–(8) and (13). Topological rules are also provided in [38].

The remaining problem to solve is how to obtain easily data for new substances. The answer in the present study will be limited to the method of gas–liquid chromatography applied to the 133 compounds of Table A.1.

3. A suitable determination of solvation parameters for 133 solutes by using gas–liquid chromatography

The two methods applied in Section 2 to reconsider the already published solvation parameters of solutes, converge in similar results:

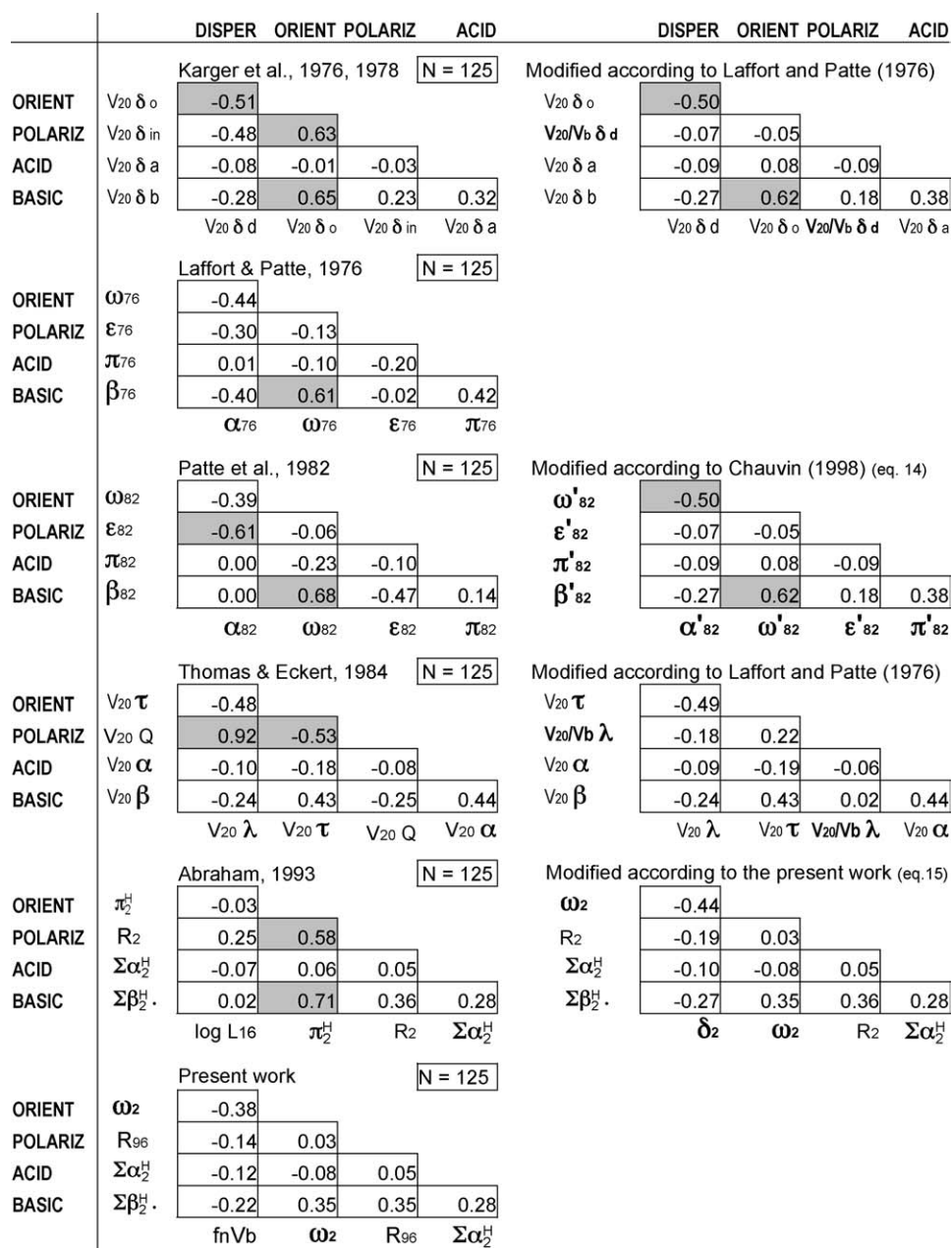
- (1) The most suitable published data are those of Abraham [15], concerning 314 defined compounds.
- (2) Two equations (Eq. (15)) allow to appreciably improve them by simple internal reorganization.
- (3) An additional improvement of two of these published parameters, those of dispersion and induction/polarizability, can easily be obtained by using Eqs. (6)–(8) and (13) applied to information available in Chauvin and Laffort [38] and in the Handbook of Chemistry and Physics [46].

The remaining challenge is the easy determination of solvation parameters for new compounds. The aim of Section 3 is to start this purpose on the basis of the results obtained in Section 2.

A multiple linear regression analysis of the output parameters of solutes versus the retention indices reported in Table A.1 for 125 solutes, clearly shows that five stationary phases (solvents) are sufficient to account for the entire phenomenon (range of correlation coefficients: 0.99–1.00). The rules to establish the final parameters of solutes proposed in the present work, from the retention indices on five stationary phases, are given by Eq. (17). The correspondent solubility parameters for the 133 solutes of Table A.1, are presented in Table C.1 of Appendix C.

in which I , P , H , F and \emptyset are (RI standing for retention indices): $I = (\text{RI} - 100)/100$ on the paraffin phase in C_∞ (infinite); $P = (\text{RI} - 100)/100$ on the paraffin phase in C_{78} ; $H = (\text{RI} - 100)/100$ on the primary alcohol phase; $F = (\text{RI} - 100)/100$ on the tetrakis(trifluoromethyl) phase; $\emptyset = (\text{RI} - 100)/100$ on the tetramethoxy phase.

As can be seen in Figs. 3, 5 and 6, one of the difficulties with simplified notations of the solute parameters, is that each author has his own (some authors have several! ...). One of the results of the present study is that the first parameter, which we called α as apolar in previous works, seems to be rather related to the molar refraction than to the molar volume. Therefore, the name δ as dispersion seems appropriate. The letters α and β are the most used by several authors to refer to acidity and basicity; we therefore keep them. The letter π has been used to call too different properties (proton donor ability, polarity, polarizability); we therefore discard it, and keep, for the orientation/polarity parameter, the letter ω . For the polarizability-induction parameter, we keep the letter ε , chosen by us since 1972 [35], as reminiscent of electron donor ability: this parameter exhibits high values for molecules with multiple bonds, with pi electrons (halogens, oxygen, sulfur) and with high connectivity (cycles). The subscript 3 is added to avoid confusion with other definitions.



Output matrices A, from input matrices according to authors



Output matrices A, from input matrices slightly modified

Fig. 5. Pearson correlation matrices for the output matrices A of solutes parameters obtained by using the MMA algorithm applied to the 125×10 Kováts matrix of retention indices R, with several hypothesis of input matrices A. Input data are partially original, partially calculated according to the indications of the authors and partially extrapolated. As in Fig. 3, the correlation values should be low. Absolute values of correlation coefficients ≥ 0.5 are highlighted.

It should be noted that, as in previous studies [11,21], values of parameters have been fixed such as the following relation is verified:

$$ICE = \alpha_3 + \omega_3 + \epsilon_3 + \alpha_3 + \beta_3 - 1.867 \quad (18)$$

where internal cohesive energy (ICE) is equal to the negative decimal logarithm of the saturated vapor pressure at 25°C , expressed in atmospheres, for liquids and solids, and calculated

by using the Eq. (19) for gases.⁴ For the 133 solutes under study, the correlation coefficient obtained with the relation 18 is 0.99 (therefore, Eq. (18) can be an additional tool to estimate one of the parameters when it is missing, if the ICE value and the other parameters are available).

⁴ $ICE_{25} = ((T_b/402.8) + 0.6168)^3 - 2.45$ (for $t_b \leq 25^\circ\text{C}$), where t_b and T_b being, respectively, the temperature at boiling point in $^\circ\text{C}$ and K.

MODELS	INPUT/OUTPUT correlations A					Number of $ r \geq 0.5$ in fig. 5	Number of neg. values in matrix B
	DISPER	ORIENT	POLARIZ	ACID	BASIC		
random numbers	0.04	0.10	0.00	0.12	0.07	3	zero
	0.13	0.15	0.10	0.06	0.17	2	zero
	0.02	0.13	0.15	0.00	0.06	5	zero
Karger et al. (original)	$V_{20} \delta d$ 0.97	$V_{20} \delta o$ 0.80	$V_{20} \delta in$ 0.86	$V_{20} \delta a$ 0.95	$V_{20} \delta b$ 0.85	3	(param. 3) 6
Karger et al., (modified)	$V_{20} \delta d$ 0.98	$V_{20} \delta o$ 0.91	$V_{20} V_b \delta d$ 0.82	$V_{20} \delta a$ 0.96	$V_{20} \delta b$ 0.93	2	zero
Laffort & Patte (original)	α_{76} 0.98	ω_{76} 0.99	ϵ_{76} 0.94	π_{76} 0.99	β_{76} 0.95	1	(param. 4) 10
Patte et al. (original)	α_{82} 0.88	ω_{82} 0.99	ϵ_{82} 0.62	π_{82} 0.98	β_{82} 0.83	2	(param. 4) 8
Patte et al. (modified)	α'_{82} 0.96	ω'_{82} 0.98	ϵ'_{82} 0.94	π'_{82} 0.96	β'_{82} 0.95	2	(param. 5) 9
Thomas & Eckert (original)	$V_{20} \lambda$ 0.98	$V_{20} \tau$ 0.94	$V_{20} Q$ 0.94	$V_{20} \alpha$ 0.95	$V_{20} \beta$ 0.94	2	(param. 3) 10
Thomas & Eckert (modified)	$V_{20} \lambda$ 0.98	$V_{20} \tau$ 0.94	$V_{20} V_b \lambda$ 0.80	$V_{20} \alpha$ 0.95	$V_{20} \beta$ 0.94	zero	zero
Abraham (original)	$\log L_{16}$ 1.00	π_2^H 0.99	R_2 0.91	$\Sigma \alpha_2^H$ 0.98	$\Sigma \beta_2^H$ 0.98	2	(param. 4 & 5) 15
Abraham (modified)	δ_2 0.99	ω_2 0.97	R_2 0.91	$\Sigma \alpha_2^H$ 0.98	$\Sigma \beta_2^H$ 0.98	zero	(param. 4) 6
Present work	fnV_b 0.98	ω_2 0.97	R_{96} 0.92	$\Sigma \alpha_2^H$ 0.98	$\Sigma \beta_2^H$ 0.98	zero	zero

Fig. 6. Three criteria for testing the input solute parameters by applying the MMA algorithm to the 125 × 5 Kováts data set of retention indices: the input/output correlations A, the mutual independence of the output solutes parameters (a summary of the Fig. 5 plus analogous results with random data) and an absence of negative values in the matrix B. Unfavorable results are highlighted.

The Eq. (20) give the rules to estimate the values of the version of solute parameters here presented, from already published properties used as input of the MMA algorithm in the previous section. To avoid any confusion, the parameters in the Eq. (20) are marked with an asterisk superscript:

$$\begin{array}{llll}
 \text{DISPER} & \delta_3^* = 7.88fnV_b/100 - 0.092 & (\text{Eqs. 6, 8}) & (r = 0.98, N = 125) \\
 \text{ORIENT} & \omega_3^* = \omega_2 & (\text{Eq. 15}) & (r = 0.97, N = 125) \\
 \text{POLARIZ} & \epsilon_3^* = 0.729R_{96} & (\text{Eqs. 6, 8, 13}) & (r = 0.93, N = 125) \\
 \text{ACID} & \alpha_3^* = 2.825 \sum \alpha_2^H & [\text{Ref. 15}] & (r = 0.98, N = 125) \\
 \text{BASIC} & \beta_3^* = 0.728 \sum \beta_2^H & [\text{Ref. 15}] & (r = 0.98, N = 125)
 \end{array}$$

Similarly, the rules to establish the final parameters of solvents D_3 , W_3 , E_3 , A_3 and B_3 proposed in the present work, from the retention indices on five selected solutes, are given by Eq. (21) (Latin upper-case characters for solvents correspond to Greek lower-case characters used for solutes, in the

(20)

Table 2
Solvents parameters D_3 , W_3 , E_3 , A_3 and B_3 of the ten stationary phases under study, according to Eq. (20)

Phases	D_3	W_3	E_3	A_3	B_3	b
C_∞	202.7	75.4	287.0	15.2	21.8	0.288
C_{78}	202.7	76.9	308.8	12.8	26.4	0.293
POH	202.7	96.21	299.4	39.9	114.8	0.291
TTF	202.7	147.1	289.4	18.3	83.6	0.288
MTF	202.7	94.7	287.2	19.3	43.9	0.291
PCL	202.7	94.4	293.9	19.3	38.8	0.293
PBr	202.7	92.8	298.8	17.6	38.7	0.291
TMO	202.7	137.5	312.4	78.4	59.1	0.291
PSH	202.7	90.6	295.6	21.6	38.2	0.286
PCN	202.7	137.9	306.9	45.4	61.3	0.291

Also the slopes b of $\log V_g$ vs. number of carbon atoms for *n*-paraffins are presented. As already seen in Eq. (4), they are almost equal to 0.29. Values in bold suggests the most appropriate phases to be selected.

adapted Eq. (1):

$$\begin{aligned}
 D_3 &= +0.2896\emptyset \\
 W_3 &= -0.3368\emptyset + 0.9446N - 0.3515Y \\
 E_3 &= +0.5625\emptyset + 1.1602N - 2.5926H - 0.3403L + 1.6754Y \\
 A_3 &= -0.0852\emptyset + 1.0657L - 0.7235Y \\
 B_3 &= -1.6092\emptyset - 2.0605N + 3.3425H + 0.4051L
 \end{aligned} \tag{21}$$

where: $\emptyset = RI - 100$ of octane; $N = RI - 100$ of nitropropane; $H = RI - 100$ of 2-hexanone; $L = RI - 100$ of 1-butanol; $Y = RI - 100$ of pyridine.

The correspondent solubility parameters for the 10 solvents of Table 1, are presented in Table 2.

Eq. (17) and Table 2 are of limited interest for the reader, since these stationary phases have been synthesized in small quantity for internal use and are not commercially available. They clearly show, however, that the best set of commercial phases for further determinations of solute parameters from gas–liquid chromatography, should include two non-polar phases of very different molecular weight and three polar phases: a strongly fluorinated, a classical polyether and an alcoholic (as, for example, diglycerol).

The immediately applicable results of the second section in the present study are the Table C.1 and the Eq. (20). In addition, Eqs. (21) could be useful in the future, for checking and selecting further sets of stationary phases commercially available.

4. General discussion

4.1. Comparisons of several studies

The purpose of the present study is not at all a competition game. It is quite logical to observe, as it is summarized in Figs. 3, 5 and 6, that older studies are less suitable than more recent ones, but the latter are based on the former and the merit of the various contributions cannot be compared. The main purpose is to refine more and more the determination of the data values, but mentioning the successive principal contributions since the pioneers. In order to avoid any confusion,

the following comments are referred, as in the other sections of the present study, to the *solvation parameters*, i.e. the product of the *solubility parameters* strictly speaking and the molar volume.

4.2. The number of parameters

The initial concept of the solubility parameter of Hildebrand et al. [19] has first been specified in three partial parameters (dispersion, orientation and hydrogen bonding) by Hoy [39] and Hansen and Beerbower [40]. Tijssen et al. [41] extended the hydrogen bonding parameter by separating the proton donor and proton acceptor contributions. In Section 2 we detailed that since 1976, the number and the nature of the partial parameters is in principle fixed to five by everybody, but that in practice the independence of values has been achieved only in the present study. It should be noted that in olfactory studies of Laffort and

co-workers previous to 1976, a similar evolution is observed: three molecular parameters in 1969–1973 [6,7], four parameters in 1972–1976 [9,10,35] and finally five parameters since 1976 [11].

4.3. The dispersion parameter

In our previous works, this *apolar* term was identified to the molar volume at boiling point V_b . For some authors, it was the molar polarizability defined by the product fnV_{20} and for others, the Ostwald solubility coefficient of the solute on *n*-hexadecane L^{16} . We found more consistent results in the present study with the molar polarizability expressed by the product fnV_b (the competitions between V_b , V_{20} , V_x , fnV_{20} and fnV_b have not been detailed in Figs. 3, 5 and 6; by contrast, the advantage of δ_2 , homogeneous to fnV_b , over L^{16} proposed by Abraham [15], appears very clearly in Figs. 3 and 6).

4.4. The orientation parameter

It can be considered as the most ancient to have been separated from the global entity of free enthalpy of vaporization. It corresponds to the expression of *polarity* used by chromatographers. The orientation parameter has been often refined by many authors, not all cited here. The more recently published values, due to Abraham [15] and expressed as π_2^H , exhibit a lack of independence with the basicity and the polarizability-induction parameters, as it can be seen in Figs. 3 and 5. The

alternative expressions ω_2 and ω_3 , proposed here, appear more suitable.

4.5. The acidity and basicity parameters

As already underlined above, these two parameters have certainly been the hardest to establish, since no single acid can serve as unique reference of hydrogen bonding against a series of bases nor the reverse. It is the merit of the pioneers Tijssen, Billiet, Schoenmakers [41], Karger, Synder, Eon [17,18], and more recently of Abraham and co-workers [44,45], to have overcome this difficulty. The more recent values, published by Abraham [15], do not need any improvement, according to Figs. 3, 5 and 6.

4.6. The polarizability-induction parameter

Because this parameter is strongly involved in olfactory properties, Laffort and co-workers have proposed several successive definitions since 1969 [6]. By contrast, probably because its role in solutions is smaller, this parameter has been ignored a long time or incorrectly expressed in the physicochemical literature, as it has been seen in the present study (periods with three and four solubility parameters, oversimplified characterization of the fifth parameter). Between 1976 [11] and 1997 [38] Laffort and co-workers defined this parameter as the ratio between the molar polarizability and the molar volume (Eq. (11)). It can clearly be observed in Figs. 3 and 5, that this expression appreciably improves the expressions of Karger et al. [17,18] as well as those of Thomas and Eckert [22]. However, the bilinear expression of molar polarizability and molar volume (instead of their ratio) proposed by Abraham et al. [20], called R_2 (Eq. (12)), provides better results (see Fig. 6). The expression R_{96} (Eq. (13)), which we prefer, is just an improvement of R_2 ([38] and the present study).

4.7. Meaning of the solvents parameters

In the general case, the retention indices must be previously transformed into logarithm of the reduced retention volumes $\log V_g$, when the slopes b of $\log V_g$ versus the number of carbon atoms for n -paraffins are not constant, before trying to understand the meaning of the solvents parameters as reported in Table 2. This amounts to the same thing as multiplying the parameters of Table 2 by the slopes b . We saw, however, that in the present study a constancy of these slopes b is observed (Eq. (4) and last column of Table 2); the solvent parameters of Table 2 can therefore be left as they are. The comparison of the structure of the phases described in Table 1 and the solvent parameters reported in Table 2, clearly shows that A_3 is identified to a basicity character, B_3 to acidity and W_3 to polarity, similarly to the solute parameters β_3 , α_3 , and ω_3 . The product D_3^*b being a constant in the present study, no relation with the molecular structure can be suggested from the data reported here. The E_3 parameter is also clearly related to a molecular property inversely proportional to the molecular weight, everything being equal, as already shown in some way by Martire [47] and

by Kováts and co-workers [48,29].⁵ Claverie [49] and Laffort and co-workers [12,36] suggested and partially demonstrated that this property inversely proportional to the molecular weight could be “the density at a given temperature, which reflects the relative absence of holes of the solvent, or in other words its compactability”.

4.8. Meaning of some negative values of solutes parameters

In the Appendix C, few negative values are observed for the four polar parameters: strongly for the polarizability-induction parameter, slightly for the basicity parameter and in between for the two other ones. Since the solute parameters are defined with methane as reference, the general explanation should be that such negative value for a given compound means that the corresponding property is lower than that for methane. Some small negative values, however, could be interpreted as included within the confidence intervals for parameter values equal to zero. This question will be re-open in a further study.

4.9. Application of the present study to a classification of GLC stationary phases

Several classification methods have been proposed in literature, the most popular being that of McReynolds [27], which proposed ten terms. More recent attempts of classification of stationary phases for open-tubular columns [51,52] are based on the Abraham approach, which is, as we saw, not completely satisfactory for the dispersion and orientation parameters. In other respects, sets of phases covering the five solvation parameters were not found in these recent publications of Santiuste and García-Domínguez [51] and Poole et al. [52]: none of the selected stationary phases are hydrogen-bond acids, and deficiencies are noted for the solvent parameter associated with the polarizability-induction solute parameter. This last deficiency could be overcome using two apolar phases of very different molecular weight. In all cases, Eq. (21) provides an alternative method, perhaps simpler and clearer than those proposed by these authors, to characterize the up-dated solvation solvent factors.

4.10. Comparison between the two data sets of solute parameters

The search for a mutual independence of published solute solvation parameters as well as the comparison between input and output parameters using the MMA algorithm, allowed us to optimize in Section 2, the parameters for a set of 314 solutes (from Abraham and co-workers studies). This search also allowed us to propose in Section 3, a new method of parameters' determination for 133 solutes (derived from Kováts and co-workers GC measurements). Both sets can be considered as valuable and

⁵ In fact, if Martire [47] was apparently the first to observe in 1974 a so-called polarity of hydrocarbon phases of high molecular weight, he did not identify the corresponding solute property, i.e. as we saw, the polarizability-induction parameter ϵ . This was done by Laffort in 1977 [50].

they together make up a solid basis for further derivations of parameters from the molecular structure. The question remains, for further experimental determinations (always more reliable than predicted from the structure), which approach is the most suitable. The entirely chromatographic method could perhaps be easier, using a pentacolumn device similar to that we used in 1982 [21], but up-dated: Columns in parallel rather than in series, open tubular columns rather than packed (if possible), better panel of stationary phases, and including an high level of automation. However, some solutes of very low volatility are difficult to study using GLC and, therefore, both methods could perhaps be developed in parallel.

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Appendix A

See Table A.1.

Table A.1

GLC retention indices for 133 solutes on 12 stationary phases at 130 °C, according to [30–33] (polar phases) and the present study (apolar phases)

		C67	C103	C78	Cinf	OH	TTF	MTF	PCL	PBR	TMO	PSH	PCN
1	1-Butanol	591.0	594.9	592.6	602.2	658.9	633.6	608.5	609.7	609.9	690.4	611.6	657.4
2	2-Methyl-2-propanol	467.8	471.2	469.2	477.5	528.8	511.4	484.2	482.1	482.5	543.4	481.2	519.0
3	1-Pentanol	696.1	699.8	697.6	706.7	765.5	739.3	712.9	714.3	714.8	797.2	715.9	764.1
4	2-Methyl-2-butanol	596.3	598.2	597.1	601.7	652.9	637.0	610.2	610.5	610.5	669.4	609.8	646.3
5	1-Hexanol	798.4	801.7	799.7	807.8	868.3	841.5	814.6	816.4	817.7	901.0	818.0	867.2
6	Cyclohexanol	848.7	854.0	850.8	863.9	916.6	887.1	864.1	867.9	869.6	940.4	869.8	912.7
7	2-Methyl-2-pentanol	689.2	691.2	690.0	694.9	745.2	730.7	703.1	703.3	703.3	762.1	703.1	739.3
8	1-Heptanol	900.2	903.1	901.4	908.5	971.3	943.7	916.6	918.5	919.9	1003.7	919.8	969.0
9	2-Methyl-2-hexanol	785.5	786.2	785.8	787.5	841.9	827.2	799.6	799.0	799.4	858.5	798.5	835.4
10	2-Butanol	543.9	546.2	544.8	550.5	603.7	585.0	559.6	559.7	560.1	626.7	560.3	599.1
11	2-Pentanol	643.1	645.5	644.1	650.0	704.4	685.8	659.5	658.9	659.5	727.1	659.4	699.4
12	2-Hexanol	743.8	746.0	744.7	750.1	805.5	786.7	759.9	759.6	760.3	829.0	760.2	801.0
13	2-Heptanol	843.8	845.9	844.6	849.8	906.2	886.7	859.5	859.6	860.3	929.9	860.3	901.5
14	2-Phenylethanol	1050.6	1058.3	1053.7	1072.6	1135.2	1114.3	1073.2	1078.4	1080.6	1188.6	1081.2	1145.4
15	Benzyl alcohol	969.9	978.3	973.3	993.9	1059.6	1024.8	992.7	999.6	1001.4	1125.6	1003.3	1072.7
16	Pentanal	644.7	647.7	645.9	653.3	687.8	709.8	664.7	663.9	664.7	695.1	661.6	696.4
17	Hexanal	747.1	749.5	748.1	754.0	790.9	812.6	766.8	766.2	766.8	798.4	764.3	800.0
18	2-Butanone	533.1	536.8	534.6	543.7	580.7	607.3	557.5	553.8	553.4	587.2	552.2	591.3
19	2-Pentanone	627.3	628.9	627.9	631.9	674.6	700.1	649.6	647.4	646.8	680.0	644.5	684.0
20	Cyclopentanone	737.8	742.8	739.8	752.1	800.2	817.3	763.1	763.2	764.4	802.6	760.4	807.4
21	2-Hexanone	728.8	730.9	729.6	734.8	777.5	802.8	751.0	749.5	749.0	782.4	746.5	786.7
22	Cyclohexanone	851.2	856.7	853.4	866.9	915.1	931.9	877.0	877.6	878.5	915.0	875.1	921.8
23	2-Heptanone	829.7	831.2	830.3	834.0	879.2	904.2	851.8	850.2	850.5	883.6	847.4	887.9
24	Dipropylether	655.3	655.5	655.4	655.9	671.7	671.5	659.9	660.1	660.4	670.5	659.5	668.3
25	Dibutyl ether	854.0	853.6	853.8	852.9	870.0	870.3	858.3	858.1	858.8	868.6	857.8	866.4
26	Tetrahydrofuran	607.7	612.3	609.6	620.9	648.0	646.4	621.6	622.2	623.3	640.8	622.0	641.9
27	1,4-Dioxane	667.3	672.1	669.2	681.0	716.5	717.7	683.3	683.7	684.6	716.6	683.4	709.9
28	Methyl phenyl ether (anisole)	905.3	912.8	908.3	926.8	935.0	953.8	921.1	924.0	924.7	956.4	936.2	951.2
29	Phenetole	974.7	981.0	977.2	992.7	1004.7	1021.1	990.3	991.5	992.2	1022.3	1000.2	1017.3
30	Nitroethane	563.5	568.0	565.3	576.4	612.6	665.1	593.2	593.0	592.5	657.7	590.3	655.5
31	1-Nitropropane	659.6	662.9	660.9	669.0	706.5	757.7	688.0	688.3	687.6	747.7	684.1	747.1
32	1-Nitrobutane	763.1	766.3	764.4	772.3	809.5	860.0	791.8	791.4	791.2	849.3	787.4	849.6
33	1-Nitropentane	864.8	868.2	866.2	874.5	911.8	961.8	893.7	893.2	893.2	950.7	889.0	950.6
34	1-Nitrobenzene	1045.2	1054.6	1049.0	1072.1	1095.3	1140.0	1081.5	1077.2	1077.8	1136.2	1073.8	1130.7
35	1-Cyanoethane	484.3	489.3	486.3	498.6	543.5	592.2	521.9	514.9	514.2	571.5	514.3	575.9
36	1-Cyanopropane (Butyronitrile)	584.3	587.8	585.7	594.3	641.6	688.3	617.5	614.2	614.2	668.1	609.6	674.2
37	1-Cyanobutane (valeronitrile)	691.6	694.4	692.7	699.6	749.6	795.3	724.2	721.8	721.9	774.5	716.9	781.6
38	1-Cyanopentane	793.6	796.3	794.7	801.3	852.5	897.5	826.2	824.3	824.3	877.0	819.3	884.4

Table A.1 (Continued)

		C67	C103	C78	Cinf	OH	TTF	MTF	PCL	PBR	TMO	PSH	PCN
39	Pyridine	719.3	726.4	722.2	739.6	785.6	778.2	739.9	741.6	744.3	778.8	741.3	775.9
40	2-Picoline	798.7	805.1	801.3	817.0	866.1	850.5	816.3	817.6	820.5	849.6	817.8	848.1
41	3-Picoline	840.4	847.6	843.3	861.0	915.6	905.3	863.1	863.1	866.7	899.7	863.4	900.4
42	4-Picoline	838.5	846.4	841.7	861.1	916.4	905.4	861.3	863.3	865.9	898.7	861.7	900.5
43	2,3-Lutidine	930.6	938.2	933.7	952.3	1003.6	988.6	949.5	951.6	953.5	982.6	951.9	984.3
44	2,4-Lutidine	915.4	922.4	918.2	935.4	991.0	975.6	933.3	937.1	938.7	966.3	935.4	968.4
45	2,5-Lutidine	915.4	922.6	918.3	936.0	988.5	972.1	934.2	935.9	937.8	964.5	934.1	966.2
46	2,6-Lutidine	869.2	875.0	871.5	885.8	934.9	915.7	887.0	885.2	887.7	913.8	887.8	912.0
47	3,4-Lutidine	981.0	989.5	984.4	1005.3	1070.5	1057.3	1004.9	1005.7	1008.6	1044.9	1008.2	1050.4
48	3,5-Lutidine	959.6	967.5	962.8	982.2	1043.2	1030.9	982.7	984.3	986.0	1019.3	985.2	1023.9
49	3-Chloropyridine	881.0	888.9	884.2	903.6	930.7	927.9	896.6	901.1	902.7	941.8	901.3	932.8
50	1-Acetoxypropane	635.9	636.6	636.2	637.9	678.1	696.1	654.3	650.8	649.5	682.1	647.9	677.4
51	1-Acetoxybutane (butyl acetate)	738.2	738.7	738.4	739.6	781.3	798.6	756.3	753.0	752.3	784.4	749.9	780.1
52	1-Acetoxybutane (pentyl acetate)	839.2	839.0	839.1	838.6	882.2	899.0	856.9	853.6	853.0	885.4	850.3	881.2
53	1,1,1-Trifluorooctane	726.5	721.8	724.6	713.1	735.5	781.4	742.4	732.3	730.9	754.1	727.5	750.8
54	Fluorobenzene	663.9	668.2	665.6	676.2	683.4	701.5	675.4	676.6	676.8	705.5	675.5	696.5
55	Hexafluorobenzene	549.9	549.3	549.7	548.2	558.3	610.8	566.6	557.2	554.7	586.6	551.8	580.8
56	Trifluoromethylbenzene	656.8	658.0	657.3	660.2	674.7	714.8	673.0	669.1	667.6	704.2	664.7	695.3
57	Dichloromethane	497.0	505.5	500.4	521.3	524.7	528.2	511.3	513.7	514.9	559.7	513.5	543.2
58	Trichloromethane	601.6	608.2	604.3	620.5	630.0	621.4	611.9	615.1	616.4	669.5	616.6	644.6
59	Tetrachloromethane	675.2	680.8	677.5	691.2	683.8	679.1	676.6	682.3	683.2	697.2	683.2	687.8
60	1-Chlorobutane	638.3	641.7	639.7	648.0	654.7	667.4	647.2	649.6	650.1	669.8	648.5	666.7
61	1-Chloropentane	740.8	744.3	742.2	750.8	758.2	770.8	750.2	751.9	752.4	772.0	751.1	769.1
62	1-Chlorohexane	842.4	845.6	843.7	851.6	860.1	872.8	852.0	853.4	853.9	873.8	852.7	870.8
63	Chlorobenzene	861.4	869.0	864.5	883.1	884.5	893.8	872.0	876.3	877.7	905.1	876.8	897.1
64	1-Bromopropane	626.5	630.7	628.2	638.5	645.4	652.6	636.1	638.7	639.6	659.8	639.4	656.5
65	1-Bromobutane	729.8	734.4	731.7	743.0	749.2	756.6	739.9	742.1	743.1	762.5	742.5	759.6
66	1-Bromopentane	832.4	836.4	834.0	843.8	851.7	859.7	841.8	844.4	845.5	864.9	844.8	862.0
67	Bromobenzene	955.9	964.7	959.5	981.1	981.7	986.0	965.5	972.4	974.0	1002.4	974.2	994.5
68	1-Butanethiol	714.8	718.7	716.4	726.0	733.0	729.2	720.8	726.8	728.1	746.5	726.8	742.0
69	1-Pentanethiol	817.2	821.0	818.7	828.1	836.0	832.2	822.6	828.8	830.3	848.9	830.1	845.0
70	n-Hexanethiol	918.9	922.6	920.4	929.5	939.0	935.3	924.5	930.9	931.9	950.9	932.1	946.9
71	Thiophene	680.2	687.5	683.1	701.1	702.8	706.5	691.2	694.2	695.6	721.6	694.2	710.9
72	1-Hexene	584.4	585.4	584.8	587.3	587.4	589.5	585.6	586.9	587.3	592.2	587.0	588.8
73	Cyclohexene	704.2	706.8	705.2	711.6	712.3	703.7	704.7	708.8	710.1	714.8	709.6	712.1
74	1,4-Cyclohexadiene	722.5	728.2	724.8	738.8	736.2	731.1	726.3	731.3	732.6	743.6	732.4	739.5
75	1,3-Cyclohexadiene	687.8	691.8	689.4	699.2	701.0	697.9	692.6	695.6	696.4	707.8	695.9	703.9
76	1-Heptene	684.8	684.9	684.8	685.1	688.2	690.4	686.4	687.4	687.8	693.0	687.4	689.6
77	1-Octene	783.9	784.7	784.2	786.2	787.6	789.7	785.4	786.2	786.7	792.0	786.4	788.9
78	1-Nonene	884.6	885.1	884.8	886.0	888.5	890.8	886.3	886.9	887.7	892.6	887.5	889.8
79	1-Decene	984.4	985.0	984.6	986.1	988.2	990.4	985.9	986.7	987.2	992.3	987.0	989.2
80	1-Pentyne	481.6	481.6	484.4	488.5	498.2	503.7	491.7	491.5	491.9	514.9	491.0	503.5
81	1-Hexyne	586.7	588.5	587.4	591.8	601.3	606.7	593.8	594.8	594.8	618.6	594.6	607.3
82	2-Hexyne	643.4	642.7	643.1	641.4	656.9	656.6	646.9	649.4	649.7	666.1	649.3	659.2
83	3-Hexyne	620.3	620.2	620.3	620.0	632.8	628.0	623.1	625.8	626.4	642.0	626.0	634.3
84	1-Heptyne	687.8	688.6	688.1	690.1	702.9	708.0	694.7	696.0	695.9	720.2	695.6	708.7
85	1-Octyne	787.4	788.3	787.8	790.0	802.5	808.0	794.1	795.3	795.0	819.6	795.2	808.3
86	4-Octyne	810.2	809.7	810.0	808.8	821.5	819.9	812.5	814.7	815.6	829.8	815.0	822.9
87	1-Nonyne	887.7	888.6	888.1	890.3	902.9	908.7	894.5	895.7	896.1	920.0	895.6	908.7
88	1-Decyne	987.7	988.8	988.1	990.8	1003.0	1008.6	994.5	995.9	995.9	1019.9	995.5	1008.9
89	Benzene	673.5	679.3	675.8	690.1	692.8	701.3	683.4	685.3	686.2	704.7	685.5	700.4
90	Toluene	782.0	788.3	784.5	800.0	801.4	812.0	792.0	794.0	795.2	812.4	794.2	808.9
91	Ethylbenzene	872.0	877.9	874.4	888.9	890.8	899.8	881.3	883.8	884.8	901.9	884.3	898.2
92	Naphthalene	1208.2	1221.1	1213.4	1245.1	1248.1	1257.4	1224.8	1231.5	1231.3	1262.0	1232.7	1257.0
93	Azulene	1319.9	1334.6	1325.8	1362.0	1361.7	1365.5	1334.6	1344.1	1346.3	1382.4	1347.4	1380.6
94	Pentane	500.0	500.0	500.0	500.0	500.0	500.0	500.0	500.0	500.0	500.0	500.0	500.0
95	Cyclopentane	587.9	588.5	588.1	589.6	590.2	581.5	586.1	589.5	590.6	591.1	590.8	590.2
96	2,2-Dimethylbutane	541.1	540.7	540.9	540.0	541.2	544.7	542.3	541.0	540.6	541.9	539.4	540.9
97	2,3-Dimethylbutane	572.6	573.0	572.8	573.7	573.4	575.6	573.5	573.5	573.4	574.0	571.2	572.8
98	Hexane	600.0	600.0	600.0	600.0	600.0	600.0	600.0	600.0	600.0	600.0	600.0	600.0
99	Cyclohexane	693.1	694.6	693.7	697.4	696.4	687.6	692.1	695.0	696.5	696.4	696.3	695.4
100	2,2-Dimethylpentane	628.4	627.6	628.1	626.1	628.0	632.8	629.6	628.2	627.6	628.8	626.9	628.0
101	2,3-Dimethylpentane	679.3	679.3	679.3	679.3	679.8	681.6	680.2	679.9	679.8	680.2	678.9	679.4

Table A.1 (Continued)

		C67	C103	C78	Cinf	OH	TTF	MTF	PCL	PBR	TMO	PSH	PCN
102	2,4-Dimethylpentane	628.4	628.9	628.6	629.8	628.1	632.6	629.9	628.6	628.5	628.8	627.4	627.9
103	2,2,3-Trimethylbutane	650.4	652.3	651.2	655.8	653.2	658.3	654.6	651.6	651.0	652.5	650.0	651.6
104	Heptane	700.0	700.0	700.0	700.0	700.0	700.0	700.0	700.0	700.0	700.0	700.0	700.0
105	Cycloheptane	835.8	839.4	837.3	846.1	841.4	830.0	835.4	838.8	840.2	840.3	841.2	839.7
106	Methylcyclohexane	757.6	759.4	758.3	762.7	761.2	755.0	757.8	759.3	760.0	760.6	759.5	759.4
107	2,3-Dimethylhexane	765.8	765.4	765.6	764.7	765.9	768.2	766.3	766.1	765.8	766.5	765.3	766.0
108	2,4-Dimethylhexane	733.2	733.0	733.1	732.6	732.9	737.1	734.6	732.8	732.8	733.0	731.9	732.8
109	3,4-Dimethylhexane	779.3	781.1	780.0	784.4	780.6	782.1	780.9	780.3	780.1	781.0	780.0	780.6
110	2,2,4-Trimethylpentane	696.5	694.2	695.6	689.9	695.8	702.6	698.4	695.5	694.9	695.6	694.1	694.9
111	2,3,4-Trimethylpentane	765.8	765.4	765.6	764.7	766.9	769.0	766.8	766.0	765.5	766.9	765.5	766.2
112	<i>cis</i> -1,2-Dimethylcyclohexane	866.5	869.9	867.9	876.2	871.8	865.5	868.3	869.3	870.7	870.7	870.7	870.2
113	<i>trans</i> -1,2 Dimethylcyclohexane	836.7	839.1	837.7	843.6	840.9	836.7	837.7	838.6	839.3	839.9	839.4	839.3
114	<i>cis</i> -1,4-Dimethylcyclohexane	836.4	839.4	837.6	845.0	840.5	836.0	837.7	839.0	839.6	840.2	839.7	839.6
115	<i>trans</i> -1,4 Dimethylcyclohexane	814.8	817.9	816.1	823.7	818.6	815.9	816.9	817.1	817.4	818.5	817.7	817.5
116	Octane	800.0	800.0	800.0	800.0	800.0	800.0	800.0	800.0	800.0	800.0	800.0	800.0
117	Cyclooctane	963.0	968.4	965.2	978.4	970.5	957.7	961.9	967.0	968.5	969.2	969.1	968.2
118	Nonane	900.0	900.0	900.0	900.0	900.0	900.0	900.0	900.0	900.0	900.0	900.0	900.0
119	Decane	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0	1000.0
120	Cyclodecane	1177.3	1184.3	1180.1	1197.3	1185.6	1172.0	1175.3	1183.4	1182.1	1185.7	1183.4	1183.9
121	<i>cis</i> -Hydrindane	1032.0	1038.5	1034.6	1050.6	1041.1	1027.7	1033.8	1038.1	1039.6	1040.2	1039.2	1038.9
122	<i>trans</i> -Hydrindane	999.1	1004.7	1001.4	1015.1	1005.3	994.8	1001.0	1003.9	1003.9	1005.6	1003.1	1003.5
123	<i>cis</i> -Decalin	1150.5	1157.9	1153.5	1171.7	1159.3	1146.0	1154.0	1157.2	1156.3	1158.4	1156.8	1157.3
124	<i>trans</i> -Decalin	1109.1	1115.8	1111.8	1128.3	1118.0	1106.4	1112.3	1114.1	1115.3	1116.5	1115.2	1115.1
125	Adamantane	1133.6	1140.9	1136.5	1154.5	1147.9	1126.1	1133.4	1139.8	1140.4	1142.6	1142.7	1140.6
126	Undecane	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0	1100.0
127	Dodecane	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0	1200.0
128	Tridecane	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0
129	Tetradecane	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0	1400.0
130	Tetramethylsilane	425.5	422.1	424.1	415.8	427.3	430.9	433.0	430.0	428.5	432.6	428.4	430.7
131	Hexamethyldisilane	688.1	681.6	685.5	669.5	685.0	697.0	690.7	686.2	685.9	688.0	683.7	687.1
132	Hexamethyldisiloxane	599.5	590.1	595.7	572.6	595.4	611.7	602.9	595.2	593.5	600.6	591.1	596.1
133	Tetramethylthi	602.6	600.4	601.7	596.3	605.3	607.8	604.8	604.3	604.5	608.4	602.5	607.5

See the Table 1 for identification of phases. From experimental indices on C₆₇ and C₁₀₃, indices on C₇₈ and C_∞ are derived, according to Eqs. (2) and (3). Indices on C₇₈ and C_∞ and on polar phases are called in brief, in the present study, the 133 × 10 Kováts data set, and also the matrix R.

Appendix B

B.1. Theoretical basis of the multiplicative matrix analysis (MMA)

The system to be solved does not correspond to a square matrix, and cannot be treated with classical numerical methods.

Let:

A : matrix containing the solute factors

B : matrix containing the solvent factors

R : matrix containing the experimental retention indices

Matrices A and B are unknown while R is known (experimentally determined). Moreover, A is initialized with values taking into account the phenomenon under study (here the intermolecular forces involved in solutions). According to Eq. (1), we have:

$$A \times B = R$$

Now, matrix A is not square, therefore cannot be inverted. Thence, the necessity to transform the above relation:

$$A^t \times A \times B = A^t \times R$$

where A^t is the transposed form of A.

Finally, in order to determine B, one should reverse the square non-singular matrix A^t × A with dimension n × n (while the square matrix with dimension m × m resulting from A × A^t is singular). When this matrix can be inverted, the problem is solved. Experiment and the hypotheses cited confirm that it could not be otherwise. Therefore, we have:

$$B = (A^t \times A)^{-1} \times A^t \times R$$

By applying a system of shuttles, one determines alternately the values of the matrices A and B (method of successive approximations, it is assumed that the system converges). Therefore, the final equation is:

$$A \times B = R$$

$$A \times B \times B^t = R \times B^t$$

$$A = R \times B^t \times (B \times B^t)^{-1}$$

B.2. Programme in MATLAB language

```

function [A, B, count, corrA, errB]=mma(R, A, epsilon);
%usage [A, B, count,corrA,errB ]=mma(R, A, epsilon);

Aold=A;          % keeps the initial value of A

[nlr,ncr]=size(R); %dimension matrix R
[nla,nca]=size(A); %dimension matrix A
N=nlr*ncr;       %number of elements of R

B=rand(nca,ncr); %initialize B

test=1;          %initialize test

count=0;         %initialize count

while sum(sum(abs(test) > epsilon)),
    AB=A*B;
    count=count+1
    B=pinv(A)*R;
    A=R*pinv(B);
    test=(A*B)-AB;
    SSD= sum(sum( (R - A*B) .^ 2 )); %sum of squares of differences between AB and R
    errB(count)= sqrt( SSD / (N-1)); %standard error

end;

corrA=corr_mat(A, Aold);          %correlation A predicted and A experimental

save Acalc.txt A /ascii
save Bcalc.txt B /ascii
save corrA.txt corrA /ascii
save errB.txt errB /ascii

```


Appendix C

See Table C.1.

Table C.1
Solvation parameters values for 133 solutes, according to Eq. (17)

Compounds	δ_3	ω_3	ε_3	α_3	β_3	ICE
Alcohols						
1-Butanol	1.77	0.17	0.35	0.98	0.38	2.07
2-Methyl-2-propanol	1.23	0.19	0.30	0.60	0.40	1.28
1-Pentanol	2.32	0.16	0.33	1.01	0.39	2.54
2-Methyl-2-butanol	2.09	0.19	0.14	0.65	0.36	1.66
1-Hexanol	2.88	0.16	0.29	1.06	0.39	2.86
Cyclohexanol	2.85	0.08	0.51	0.85	0.41	2.66
2-Methyl-2-pentanol	2.52	0.21	0.15	0.63	0.36	1.97
1-Heptanol	3.44	0.16	0.24	1.08	0.40	3.30
2-Methyl-2-hexanol	3.18	0.21	0.02	0.68	0.37	2.45
2-Butanol	1.76	0.19	0.19	0.79	0.36	1.63
2-Pentanol	2.24	0.20	0.20	0.79	0.37	2.10
2-Hexanol	2.76	0.20	0.17	0.81	0.37	2.48
2-Heptanol	3.27	0.20	0.17	0.83	0.38	2.99
2-Phenylethanol	3.45	0.38	0.72	1.22	0.40	3.99
Benzyl alcohol	2.98	0.25	0.80	1.60	0.38	4.38
Aldehydes						
Pentanal	2.10	0.61	0.23	-0.06	0.30	1.35
Hexanal	2.69	0.62	0.17	-0.03	0.30	1.87
Ketones						
2-Butanone	1.43	0.70	0.29	-0.14	0.33	0.92
2-Pentanone	2.19	0.69	0.08	-0.06	0.34	1.33
Cyclopentanone	2.25	0.66	0.42	-0.08	0.46	1.82
2-Hexanone	2.62	0.69	0.13	-0.08	0.35	1.77
Cyclohexanone	2.73	0.66	0.47	-0.13	0.48	2.21
2-Heptanone	3.20	0.70	0.06	-0.06	0.36	2.29
Ethers						
Dipropylether	2.67	0.11	0.00	0.05	0.13	1.03
Dibutylether	3.73	0.11	-0.06	0.06	0.13	1.94
Tetrahydrofuran	1.76	0.22	0.43	-0.09	0.33	0.67
1,4-Dioxane	2.00	0.34	0.43	0.03	0.37	1.28
Anisole	2.80	0.50	0.72	-0.03	0.11	2.31
Phenetole	3.32	0.46	0.60	-0.01	0.14	2.66
Nitrogen compounds						
Nitroethane	1.40	1.17	0.34	0.17	0.17	1.57
1-Nitropropane	2.05	1.13	0.22	0.15	0.17	1.88
1-Nitrobutane	2.58	1.11	0.21	0.14	0.18	2.34
1-Nitropentane	3.06	1.11	0.23	0.13	0.18	2.80
1-Nitrobenzene	3.11	1.04	0.86	0.00	0.18	3.43
1-Cyanoethane	0.92	1.14	0.38	-0.05	0.32	1.24
1-Cyanopropane	1.64	1.10	0.23	0.00	0.32	1.61
1-Cyanobutane	2.26	1.09	0.16	0.02	0.34	2.00
1-Cyanopentane	2.78	1.09	0.15	0.03	0.34	2.43
Pyridine	1.92	0.31	0.66	0.00	0.53	1.57
2-Picoline	2.42	0.18	0.60	-0.03	0.58	1.82
3-Picoline	2.48	0.31	0.67	-0.08	0.64	2.09
4-Picoline	2.37	0.31	0.74	-0.11	0.66	2.09
2,3-Lutidine	2.89	0.21	0.71	-0.13	0.64	2.44
2,4-Lutidine	2.89	0.22	0.65	-0.15	0.68	2.39
2,5-Lutidine	2.87	0.19	0.68	-0.15	0.66	2.36
2,6-Lutidine	2.86	0.11	0.55	-0.04	0.59	2.13
3,4-Lutidine	2.96	0.34	0.79	-0.19	0.79	2.80
3,5-Lutidine	2.96	0.32	0.73	-0.17	0.74	2.65
3-Chloropyridine	2.63	0.30	0.76	0.14	0.32	2.11

Table C.1 (Continued)

Compounds	δ_3	ω_3	ε_3	α_3	β_3	ICE
Esters						
1-Acetoxypropane	2.40	0.55	0.00	0.02	0.31	1.38
1-Acetoxybutane	2.93	0.54	-0.03	0.02	0.32	1.85
1-Acetoxybutane	3.53	0.54	-0.10	0.06	0.32	2.27
Halogen compounds						
1,1,1-Trifluorooctane	3.61	0.77	-0.56	-0.02	0.00	1.70
Fluorobenzene	2.08	0.43	0.40	0.07	0.04	0.99
Hexafluorobenzene	2.15	0.87	-0.14	-0.10	-0.06	0.95
Trifluoromethylbenzene	2.44	0.75	0.05	0.04	0.00	1.29
Dichloromethane	0.69	0.30	0.84	0.34	0.03	0.26
Trichloromethane	1.50	0.15	0.66	0.63	0.03	0.59
Tetrachloromethane	2.05	0.01	0.57	0.10	-0.01	0.84
1-Chlorobutane	2.11	0.32	0.31	0.04	0.05	0.86
1-Chloropentane	2.60	0.32	0.33	0.02	0.06	1.39
1-Chlorohexane	3.14	0.32	0.30	0.03	0.07	2.10
Chlorobenzene	2.62	0.32	0.75	0.04	0.06	1.81
1-Bromopropane	1.95	0.25	0.40	0.08	0.07	0.74
1-Bromobutane	2.40	0.25	0.44	0.04	0.08	1.28
1-Bromopentane	2.99	0.26	0.38	0.06	0.08	1.81
Bromobenzene	2.92	0.26	0.88	0.07	0.08	2.23
Sulfur compounds						
1-Butanethiol	2.45	0.09	0.39	0.20	0.07	1.23
1-Pentanethiol	2.97	0.09	0.38	0.20	0.08	1.72
n-Hexanethiol	3.48	0.10	0.36	0.19	0.09	2.31
Thiophene	1.77	0.23	0.73	0.09	0.07	0.98
Hydrocarbons						
1-Hexene	2.24	0.06	0.10	0.03	0.00	0.61
Cyclohexene	2.62	-0.07	0.27	0.08	0.04	0.93
1,4-Cyclohexadiene	2.25	0.02	0.58	0.03	0.06	0.89
1,3-Cyclohexadiene	2.32	0.05	0.40	0.06	0.06	0.88
1-Heptene	2.86	0.07	0.01	0.06	0.01	1.13
1-Octene	3.25	0.06	0.08	0.03	0.01	1.64
1-Nonene	3.79	0.07	0.04	0.04	0.01	2.13
1-Decene	4.27	0.07	0.06	0.04	0.01	2.59
1-Pentyne	1.61	0.21	0.15	0.21	0.03	0.30
1-Hexyne	2.10	0.21	0.16	0.22	0.03	0.76
2-Hexyne	2.75	0.11	-0.09	0.24	0.07	1.37
3-Hexyne	2.57	0.04	-0.02	0.27	0.06	0.90
1-Heptyne	2.74	0.21	0.06	0.26	0.04	1.37
1-Octyne	3.22	0.22	0.07	0.25	0.04	2.15
4-Octyne	3.55	0.07	-0.06	0.23	0.05	1.75
1-Nonyne	3.71	0.22	0.07	0.25	0.04	2.40
1-Decyne	4.18	0.22	0.09	0.24	0.04	2.76
Benzene	1.95	0.26	0.57	-0.04	0.08	0.90
Toluene	2.41	0.29	0.62	-0.10	0.08	1.43
Ethylbenzene	2.92	0.26	0.58	-0.07	0.08	1.90
Naphthalene	3.54	0.40	1.28	-0.20	0.21	3.44
Azulene	3.84	0.35	1.47	-0.08	0.19	3.89
Pentane	1.98	0.00	0.00	0.00	0.00	0.18
Cyclopentane	2.34	-0.11	0.07	0.11	0.01	0.38
2,2-Dimethylbutane	2.22	0.05	-0.04	-0.02	0.00	0.38
2,3-Dimethylbutane	2.28	0.04	0.03	-0.03	0.00	0.51
Hexane	2.47	0.00	0.00	0.00	0.00	0.70
Cyclohexane	2.73	-0.11	0.16	0.06	0.02	0.89
2,2-Dimethylpentane	2.71	0.07	-0.09	-0.01	0.00	0.86
2,3-Dimethylpentane	2.86	0.03	0.00	-0.01	0.00	1.04
2,4-Dimethylpentane	2.53	0.06	0.05	-0.06	-0.01	0.89
2,2,3-Trimethylbutane	2.44	0.08	0.18	-0.13	0.02	0.87
Heptane	2.96	0.00	0.00	0.00	0.00	1.22
Cycloheptane	3.15	-0.14	0.38	0.01	0.04	1.53
Methylcyclohexane	3.00	-0.07	0.19	0.01	0.03	1.22

Table C.1 (Continued)

Compounds	δ_3	ω_3	ϵ_3	α_3	β_3	ICE
2,3-Dimethylhexane	3.33	0.04	-0.04	0.00	0.00	1.51
2,4-Dimethylhexane	3.15	0.06	-0.03	-0.04	0.00	1.40
3,4-Dimethylhexane	3.10	0.03	0.18	-0.07	0.00	1.55
2,2,4-Trimethylpentane	3.26	0.10	-0.25	0.00	0.00	1.19
2,3,4-Trimethylpentane	3.33	0.04	-0.04	-0.01	0.01	1.45
<i>cis</i> -1,2-Dimethylcyclohexane	3.32	-0.07	0.35	-0.05	0.04	1.66
<i>trans</i> -1,2-Dimethylcyclohexane	3.30	-0.04	0.25	-0.04	0.03	1.56
<i>cis</i> -1,4-Dimethylcyclohexane	3.22	-0.04	0.31	-0.05	0.02	1.57
<i>trans</i> -1,4-Dimethylcyclohexane	3.10	-0.02	0.32	-0.07	0.02	1.53
Octane	3.46	0.00	0.00	0.00	0.00	1.73
Cyclooctane	3.52	-0.15	0.56	-0.04	0.05	2.09
Nonane	3.95	0.00	0.00	0.00	0.00	2.25
Decane	4.45	0.00	0.00	0.00	0.00	2.67
Cyclodecane	4.35	-0.15	0.73	-0.07	0.04	3.09
<i>cis</i> -Hydrindane	3.70	-0.15	0.68	-0.06	0.05	2.65
<i>trans</i> -Hydrindane	3.67	-0.12	0.58	-0.06	0.03	2.34
<i>cis</i> -Decalin	4.16	-0.15	0.78	-0.10	0.05	2.81
<i>trans</i> -Decalin	4.05	-0.13	0.70	-0.10	0.06	2.30
Adamantane	4.10	-0.24	0.77	-0.04	0.11	3.50
Undecane	4.94	0.00	0.00	0.00	0.00	3.09
Dodecane	5.43	0.00	0.00	0.00	0.00	3.67
Tridecane	5.93	0.00	0.00	0.00	0.00	4.16
Tetradecane	6.42	0.00	0.00	0.00	0.00	4.66
Silicon compounds						
Tetramethylsilane	2.07	0.09	-0.36	0.18	0.00	0.05
Hexamethyldisilane	3.80	0.17	-0.69	0.14	-0.02	1.42
Hexamethyldisiloxane	3.75	0.24	-0.99	0.24	-0.03	1.32
Miscellaneous						
Tetramethylthi	2.78	0.07	-0.23	0.12	0.01	0.84

The parameters are of: dispersion (δ_3), orientation (ω_3), polarizability-induction (ϵ_3), acidity (α_3) and basicity (β_3). Also shown are ICE values (as internal cohesive energy): negative decimal logarithm of saturated vapour pressure at 25 °C, expressed in atmospheres.

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