

Updated Definition of the Three Solvent Descriptors Related to the Van der Waals Forces in Solutions

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Abstract

Innovative viewpoint on the older topic of the van der Waals forces, is of interesting and significant issue to be concerned in both the fields related to the fundamental investigation and thus valuable in guiding the new physico-chemical phenomena and processes for both academic research and practical applications. The intermolecular Van der Waals forces involved in solutions have been recently deeply reconsidered as far as the solute side is concerned. More precisely, the solute descriptors (or parameters) experimentally established, have been accurately related to molecular features of a Simplified Molecular Topology. In the present study, an equivalent result is reached on the solvent side. Both experimental parameters have been obtained simultaneously in previous Gas Liquid Chromatographic studies for 121 Volatile Organic Compounds and 11 liquid stationary phases, via an original Multiplicative Matrix Analysis. In that experimental step, five groups of forces were identified, two of hydrogen bonding and three of Van der Waals: 1) dispersion (London), 2) orientation or polarity strictly speaking (Keesom), and 3) induction-polarizability (Debye). At this stage, an attempt of characterization the solvent parameters via the SMT procedure has been limited to those related to the Van der Waals forces, those related to the hydrogen bonding being for now left aside.

Keywords

Van der Waals Intermolecular Forces, Solvent Descriptors, Gas Liquid Chromatography, Chemo Informatics, Multiplicative Matrix Analysis

1. Introduction

The Kováts retention indices (RI) in Gas Liquid Chromatography (GLC) can be

expressed by a linear equation of terms, each term being a product of a solute parameter and of a solvent parameter, according to Rohrschneider in 1966 [1]. If five terms are considered, as most authors since 1976 have done so [2] [3], this equation can be written as follows:

$$RI - RI_{CH_4} = \delta D + \omega W + \varepsilon E + \alpha A + \beta B \quad (1)$$

in which RI_{CH_4} stands for the retention index of methane (always equals to 100). The lower case Greek letters stand for the solvation parameters of solutes, and the Latin upper case letters stand for the solvation parameters of stationary phases.

The first three terms correspond to the Van der Waals forces:

- δD → dispersion (London)
- ωW → orientation or polarity strictly speaking (Keesom)
- εE → polarizability-induction (Debye)

And the fourth and fifth terms correspond to the hydrogen bonding forces:

- αA → proton donor of solute and acceptor of solvent according to Brønsted
- βB → proton acceptor of solute and donor of solvent according to Brønsted

We have recently published a revisited definition, on experimental basis, of the three solute parameters or descriptors δ , ω and β , related to the Van der Waals forces in solutions, as they are involved in GLC [4]. The present study reflects a similar attempt for the solvent descriptors D, W and E. The comparison with previous results on this topic will be stated in the Discussion and Perspectives section.

2. Materials and Methods

2.1. Statistical Tools

In addition to the Microsoft Excel Windows facilities for drawing diagrams and handling data sets, the SYSTAT 12® for Windows has been applied for stepwise MLRA (Multidimensional Linear Regression Analysis).

2.2. SMT, A Simplified Molecular Topology

The principle of this tool has already been presented elsewhere [5] [6]. In the version used here, it only takes into account, for each atom of a molecule, its nature and the nature of its bonds, leaving aside the nature of its first neighbors with the exception of four cases specified hereafter. Each atom is provided with an index comprising a series of digits. Their sum is at most equal to its valence. The value of the digits define the type of bonds (1 for a single, 2 for a double bond, etc.), but the bonds with hydrogen are excluded. In the present version, the nature of atoms kept is limited to C, H, O, N, P, S, F, Cl, Br, I. In addition, the compounds which include a given atom only linked to hydrogen (e.g. CH₄, OH₂, NH₃, SH₂) are excluded. The additional topological features are:

- Chlorine linked to carbon C11
- Oxygen linked to carbon C11 (primary alcohols)
- Oxygen linked to carbon C111 (secondary alcohols)

- A connectivity parameter due to Zamora [7] called the “smallest set of smallest rings” (SSSR). According to this concept, for the naphthalene for example, which contains two individual C-6 rings and one C-10 ring embracing them, only the two six numbered rings are considered. Two six numbered rings corresponding to 12 carbon atoms, the SSSR value of naphthalene is therefore be taken as equal to 12.

Let us specify that the calculations using the SMT procedure have been made manually in this study, using 2D molecular drawings from ChemSpider [8].

2.3. Molar and Molecular Volume

The various expressions which reflect the “intrinsic molecular volume” or the “Van der Waals molecular volume”, are all additive properties (which it is not the case for the ratio molar mass/density at 20°C). We have selected among them in various studies, the values of molecular volumes (expressed in cubic angstroms) proposed by the freely interactive calculator of Molinspiration [9]. The authors of this calculator have used, in a first step, a semi-empirical quantum chemistry method to build 3D molecular geometries for a training set of about 12 000 molecules. In a second step, they have fitted the sum of fragment contributions to the supposed real volumes of the training set. We name this expression Vw (as Van der Waals volume).

We have applied in the present study, a predictive tool for Vw using the SMT procedure described in 2.2, which appears rather satisfactory as shown in **Figure 1**, and alternatively applicable to the values from Molinspiration (and easier to handle for polymers). This predictive method of the molecular volume can be considered as very similar to the one that we published in 2011 [10], but slightly refined. In this last quoted publication, it was shown that the van der Waals molecular volume appears strongly involved in the solvent properties.

2.4. Polar Surface Area (PSA)

According to Palm *et al.* [11], who have strongly promoted this molecular

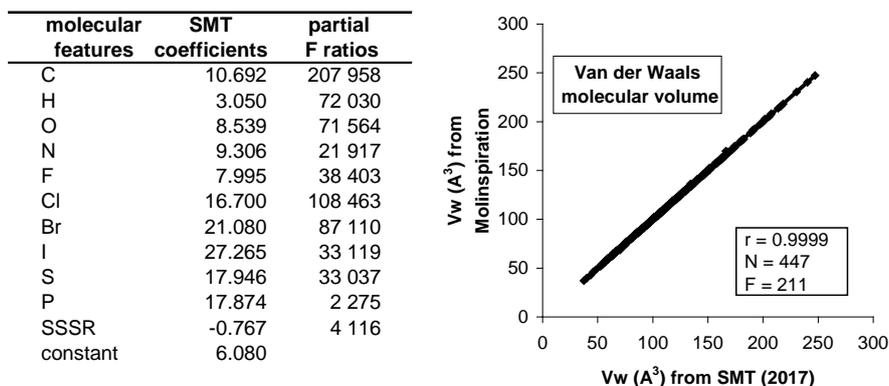


Figure 1. Correlogram between Van der Waals molecular volumes obtained using two methods. The SMT method appears more suitable for great molecules (*i.e.* polymers). The unique but scarcely noticeable visible outlier in this figure corresponds to cyclodecane.

property in pharmacology, the polar surface area can be simply and accurately defined as “the area occupied by nitrogen and oxygen atoms, and hydrogen atoms attached to these heteroatoms”. Presently, this property is considered as one of the popular molecular properties, available in various sources of chemical data banks like ChemSpider [8], Molinspiration [9] or Chemaxon [12]. However, because in some cases the values are not available, we have used in the present study a predicted method reported in **Figure 2**, which can be considered as a refined version of our 2011 publication [10].

It should be noted that out of the 447 compounds applied here for establishing the SMT model, the five outliers (clearly visible in the diagram) all correspond to 5-ring aryllic (or “aromatic”) compounds: furfural, furan, 2-methylfuran, benzofuran and pyrrole. The observed differences for these 5-ring aryllic molecules can be easily explained: two single bonds for the heteroatom in one case and two aromatic bonds in the other case. This difficulty does not appear for 6-ring molecules, where the mean adjacent bonds of heteroatoms equal 1.5 bonds in both representations. Let us emphasise that the general consistency of the SMT procedure is based on the 2D Kekulé representation.

2.5. Experimental Solvent Descriptors of the Van der Waals Forces Involved in GLC Stationary Phases

As already seen in the Introduction, the present study is similar to our 2016 study for solutes, of descriptors prediction for solvents using the SMT procedure [4]. The principal observation in this last publication for solutes, was that in order to mitigate previous disappointing published results, the optimal approach was to limit those experimental descriptors to very accurate ones, more precisely those derived from a matrix of 127 solutes \times 11 phases established by the Kováts group, using an original algorithm presently called MMA (as Multiplicative Matrix Analysis) [6] [13]. In order to follow the same strategy for stationary phases properties, are reported in **Table 1** the D, W and E values as reported in [6] for the 11 phases under study.

The first observation in view of the right columns of **Table 1** is that D descriptor is almost a constant. That is a consequence of using the Kováts retention

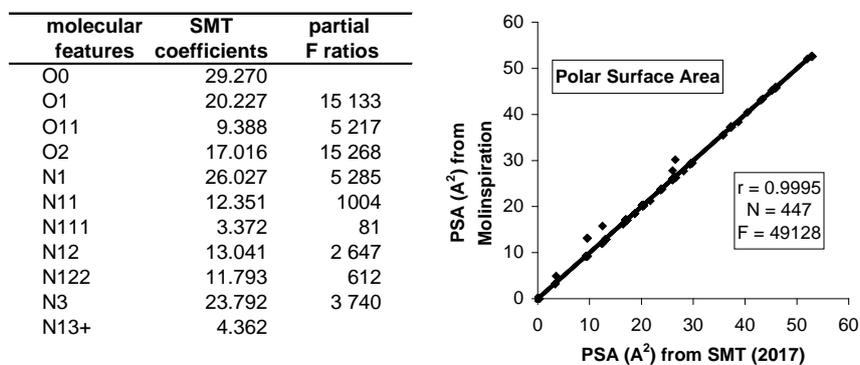


Figure 2. Correlogram between the PSA values established using two methods. The SMT method appears more suitable for great molecules (*i.e.* polymers). See text.

Table 1. Solvent descriptors D, W and E of the van der Waals forces involved in GLC, according to [6], and McReynolds b parameter according to [13] for 11 stationary phases studied by the Kováts group.

ID	GLC Stationary Phases	Formula	McR b	D	W	E
Kov_01	19, 24-dioctadecyldotetracontan (C78)	C78 H158	0.293	204.0	66.2	283.2
Kov_02	infinite carbon atoms (Cinf)	Cinf Hinf	0.288	204.2	68.3	306.6
Kov_03	18, 23-dioctadecyl-1-untetracontanol (POH)	C77 H156 O	0.291	204.1	86.8	291.5
Kov_04	19, 24-bis-(18, 18, 18-trifluorooctadecyl)-1, 1, 1, 42, 42, 42-hexafluorodotetracontane (TTF)	C78 H146 F12	0.288	204.2	141.4	284.8
Kov_05	1, 1, 1-trifluoro-19, 24-dioctadecyldotetracontane (MTF)	C78 H155 F3	0.291	204.1	88.1	283.0
Kov_06	1-chloro-18, 23-dioctadecyluntetracontane (PCI)	C77 H155 Cl	0.293	204.2	85.0	290.1
Kov_07	1-bromo-18, 23-dioctadecyluntetracontane (PBr)	C77 H155 Br	0.291	204.2	83.9	291.5
Kov_08	17, 22, bis-(16-methoxyhexadecyl)-1, 38-dimethoxyoctatricontane (TMO)	C74 H150 O	0.291	204.2	122.7	305.8
Kov_09	18, 23-dioctadecyl-1-untetracontanethiol (PSH)	C77 H156 S	0.286	204.1	81.4	293.5
Kov_10	1-cyano-18, 23-dioctadecyluntetracontane (PCN)	C78 H155 N	0.291	203.9	124.6	301.2
Kov_11	18, 23-dioctadecyl-7-hentetracontanol (SOH)	C77 H156 O	0.290	204.1	87.2	289.1
	Mean value		0.290	204.0		
	Standard deviation		0.002	0.1		

indices, which are relative expressions to n-alkanes of affinities of given solutes to given solvents, rather than absolute expressions.

Before going further, a few words of explanation on the column of **Table 1** on McReynolds b parameter (or shortly McR b) are needed. In its study of 1970 [14], this author published various expressions of the polarity for 226 GLC columns (207 phases). This b descriptor or parameter allows for a quick transforming Kováts retention indices into absolute retention indices directed related to the solute/solvent affinity, according to West [15]:

$$RSL = \frac{McRb}{McRb_{reference}} \quad (2)$$

in which RSL stands for relative slope (the reference phase being squalane in most cases)

$$\text{and } RI_{abs} = RI \times RSL \quad (3)$$

in which RI and RI_{abs} respectively stand for Kováts retention index strictly speaking and absolute retention index.

Unfortunately, in the particular case shown in **Table 1**, the McR b values are also constant and consequently a possible predicting model of McR b, and then of D_{abs} , has to be established using another experimental data set. We have selected for that the pooled McR b values from **Table 1** and from McReynolds in 1970 [14], both reported in **Table 2**.

3. Results

In our last publication devoted to the solvent properties of GLC stationary

Table 2. Experimental McReynolds b descriptors values for 86 GLC identified stationary columns (75 phases) from McReynolds [14] and from the Kováts group as reported above in **Table 1**. Highlighted columns correspond to duplicated phases from different suppliers.

ID ₂₀₁₇	Rank McR	Col McR	Liquid Stationary phase Phase	M	CAS	ChemSpid	McR b
1	1	2000	Squalane (reference)	422.8	111-01-3	7798	0.2891
2	2	2015	Squalane	422.8	111-01-3	7798	0.2890
3	3	2226	Hexatriacontane	507.0	630-06-8	11906	0.2899
4	38	2186	Butyl Stearate	340.6	123-95-5	29018	0.2917
5	44	2171	2-Butoxyethyl Stearate	384.6	109-38-6	59448	0.2897
6	49	2179	Dinonyl Sebacate (DNS)	454.7	4121-16-8	18914	0.2832
7	51	2052	Diocetyl Sebacate	426.7	219-411-3	68042	0.2862
8	52	2178	Di (2-Ethylhexyl) Sebacate	426.7	122-62-3	28959	0.2829
9	56	2056	Diisodecyl Adipate (DIDA)	426.7	27178-16-1	31101	0.2843
10	58	2169	Ditridecyl Phthalate	530.8	119-06-2	8076	0.2811
11	59	2149	Bis (2-ethylhexyl) 3, 4, 5, 6-tetrachlorophthalate	528.3	34832-88-7	105622	0.2874
12	60	2310	Diethylene Glycol Stearate	372.6	106-11-6	7500	0.2817
13	61	2313	n-Octyl Decyl Adipate	398.6	110-29-2	7752	0.2835
14	62	2250	Dilauryl Phthalate	502.8	2432-90-8	16167	0.2811
15	63	2170	Diisooctyl Adipate [Di (2-Ethylhexyl) Adipate] (DEHA) (FMC Corporation)	370.6	103-23-1	7358	0.2822
16	64	2024	Trimethylolpropane Tripelargonate	554.9	88426-26-0	29084	0.2804
17	65	2057	Diisooctyl Adipate	370.6	103-23-1	7358	0.2848
18	66	2187	Diisodecyl Phthalate (DIDP)	446.7	26761-40-0	30996	0.2812
19	68	2070	Dinonyl Phthalate	418.6	84-76-4	6529	0.2804
20	70	2168	Tris (2-ethylhexyl) Phosphate	434.6	78-42-2	6289	0.2809
21	73	2060	Di n-Octyl Phthalate (DNOP)	390.6	117-84-0	8043	0.2792
22	74	2115	Di-2-Ethylhexyl Phthalate (DEHP)	390.6	117-81-7	21106505	0.2789
23	75	2011	Di n-Octyl Phthalate (DNOP)	390.6	117-84-0	8043	0.2807
24	76	2103	N, N-Dimethyloctadecanamide (Hallcomid M-18)	311.6	3886-90-6	18617	0.2860
25	77	2116	Diisooctyl Phthalate (DIOP)	390.6	27554-26-3	31280	0.2799
26	78	2172	Butyl Octyl Phthalate	334.5	84-78-6	59911	0.2782
27	80	2114	N, N-Dimethyloleamide (Hallcomid M18 OL)	309.5	2664-42-8	4512466	0.2844
28	81	2022	Flexol plasticizer 8N8	483.7	61461-77-6	no	0.2733
29	83	2291	Span 60 (Sorbitan monostearate)	430.6	1338-41-6	16736467	0.2728
30	90	2069	Span 80 (Sorbitan monooleate)	428.6	1338-43-8	21171844	0.2719

Continued

31	92	2096	Tri-12-Hydroxystearin (Castorwax)	939.5	38264-86-7	23447	0.2684
32	96	2317	Polypropylene Glycol (PPG) 2000	1992.8	25322-69-4	no	0.2616
33	102	2182	Bis (2-butoxyethyl) Adipate	346.5	141-18-4	8505	0.2704
34	104	2160	Acetyl Tributyl Citrate	402.5	77-90-7	6259	0.2653
35	105	2173	Di-2-Ethylhexyl Phthalate (DEHP)	390.6	117-81-7	21106505	0.2715
36	106	2177	Didecyl Phthalate	446.7	84-77-5	6530	0.2714
37	108	2167	Dicyclohexyl Phthalate	330.4	84-61-7	6519	0.2722
38	111	2068	Polyphenyl ether 5 rings (OS 124)	446.5	2455-71-2	68090	0.2660
39	112	2111	Tributyl Citrate (Citroflex 4)	360.5	77-94-1	6261	0.2666
40	114	2017	Polyphenyl ether 6 rings (OS 138)	538.6	3705-62-2	69716	0.2623
41	115	2147	Bis (2-Ethoxyethyl) Sebacate	346.5	624-10-2	66585	0.2677
42	116	2048	Bis (2-butoxyethyl) Phthalate	366.5	117-83-9	8042	0.2656
43	117	2174	Bis (2-butoxyethyl) Phthalate	366.5	117-83-9	8042	0.2636
44	118	2188	Tri (Butoxyethyl) Phosphate (TBEP)	398.5	78-51-3	6292	0.2658
45	121	2132	Squalene	410.7	111-02-4	553635	0.2638
46	124	2047	Tricresyl Phosphate	368.4	1330-78-5	6281	0.2630
47	125	2085	Sucrose Acetate Hexaisobutyrate (SAIB)	846.9	126-13-6	29072	0.2489
48	143	2183	Cresyl Diphenyl Phosphate	340.3	26444-49-5	136815	0.2573
49	153	2146	Bis (2-Ethoxyethyl) Phthalate	310.3	605-54-9	62281	0.2504
50	160	2185	Bis (Ethoxyethoxyethyl) Phthalate	398.5	117-85-1	60383	0.2460
51	175	2090	N, N, N', N'-Tetrakis-(2-hydroxypropyl)-ethylenediamine (Quadrol)	292.4	102-60-3	7333	0.2353
52	181	2028	Polyethylene Glycol (PEG) 20M	20018.5	25322-68-3	no	0.2235
53	182	2095	Polyethylene Glycol (PEG) 20M-TPA	20018.5	25322-68-3	no	0.2237
54	184	2029	Polyethylene Glycol (PEG) 6000	6009.4	25322-68-3	no	0.2239
55	186	2315	Polyethylene Glycol (PEG) 4000	3980.9	25322-68-3	no	0.2238
56	189	2133	Sorbitol Hexaacetate	434.4	7208-47-1	7978713	0.2094
57	192	2026	Polyethylene Glycol (PEG) 1000	987.2	25322-68-3	no	0.2174
58	193	2196	Sucrose Octaacetate	678.6	126-14-7	29073	0.2047
59	195	2119	Polyethylene Glycol (PEG) 600	590.7	25322-68-3	no	0.2180
60	196	2208	1, 4-Butanediol Succinate (Supelco Inc)	190.2	110-63-4	no	0.2106

Continued

61	200	2139	1, 4-Butanediol Succinate (Wilkins instrument and Research Inc)	190.2	110-63-4	no	0.2110
62	204	2209	Diethylene Glycol Adipate	234.2	58984-19-3	91180	0.2105
63	205	2027	Polyethylene Glycol (PEG) 1540	1559.9	25322-68-3	no	0.2137
64	209	2339	Hyprose SP-80 (UNII:0LQ049BKK3)	806.9	no	70928	0.2007
65	212	2107	Diethylene Glycol Succinate (Supelco 1045)	206.2	9050-18-4	74256	0.1992
66	214	2325	Diethylene Glycol Succinate (Chemical Research Services)	206.2	9050-18-4	74256	0.1925
67	216	2210	Diethylene Glycol Succinate (Supelco 1303)	206.2	9050-18-4	74256	0.1906
68	217	2303	Diethylene Glycol Succinate (PolyScience Corp.)	206.2	9050-18-4	74256	0.1900
69	219	2329	Glycol Succinate (Chemical Research Services)	162.1	21583-38-0	80267	0.1844
70	220	2110	N, N, N', N'-Tetrakis-(2-hydroxyethyl) -ethylenediamine (THEED)	236.3	140-07-8	60653	0.1906
71	221	2097	Tetracyanoethylated Pentaerythritol	348.4	2465-91-0	226976	0.1887
72	223	2035	1, 2, 3-Tris (2-cyanoethoxy) Propane (TCEP)	251.3	2465-93-2	68097	0.1789
73	224	2232	1, 2, 3-Tris (2-cyanoethoxy) Propane (TCEP)	251.3	2465-93-2	68097	0.1778
74	225	2099	Cyanoethyl Sucrose	766.8	18304-13-7	14455857	0.1653
75	226	2117	N, N-bis-(2-Cyanoethyl) Formamide (BCEF)	151.2	3445-84-9	69430	0.1951
76	Kov_01		19, 24-dioctadecyltetracontan (C78)	1096.1	no	24593508	0.2930
77	Kov_02		infinite carbon atoms (Cinf)	inf	no	no	0.2880
78	Kov_03		18, 23-dioctadecyl-1-untetracontanol (POH)	1098.1	no	no	0.2910
79	Kov_04		19, 24-bis-(18, 18, 18-trifluorooctadecyl)-1, 1, 1, 42, 42, 42-hexafluorodotetracontane (TTF)	1312.0	no	no	0.2880
80	Kov_05		1, 1, 1-trifluoro-19, 24-dioctadecyltetracontane (MTF)	1150.1	no	no	0.2910
81	Kov_06		1-chloro-18, 23-dioctadecyluntetracontane (PCl)	1116.5	no	no	0.2930
82	Kov_07		1-bromo-18, 23-dioctadecyluntetracontane (PBr)	1161.0	no	no	0.2910
83	Kov_08		17, 22, bis-(16-methoxyhexadecyl)-1, 38-dimethoxyoctatetracontane (TMO)	1104.0	no	no	0.2910
84	Kov_09		18, 23-dioctadecyl-1-untetracontanethiol (PSH)	1114.2	no	no	0.2860
85	Kov_10		1-cyano-18, 23-dioctadecyluntetracontane (PCN)	1107.1	no	no	0.2910
86	Kov_11		18, 23-dioctadecyl-7-hentetracontanol (SOH)	1098.1	136841-68-4	28682246	0.2900

phases [10], a number of general trends were observed:

- the descriptors McR b, W and E appeared related to PSA, in addition to other molecular features.
- each molecular feature concerned, including PSA, appeared to be involved in a ratio of this feature to the molecular volume, V_w , contrary to the observations for solute descriptors. In other words, the various types of solvent polarities appeared in some way as densities of polarity.
- the predicting equation for E, even not excellent ($r = 0.85$ for 11 phases), implied a confirmation of the previous observation of the Kováts group [16] [17] [18] [19] that the alkanes, in order to be completely apolar phases, should be of infinite carbon atom numbers.
- the predicting equation for McR b, relatively acceptable ($r = 0.91$ for 66 phases), was seemingly the first one proposed reflecting its physicochemical meaning. It also confirmed the observation pointed out in various studies, of an abnormal chromatographic behaviour of diglycerol [20] [21] [22] [23].

As outlined in the Introduction, the following presented Results aim to confirm the results above, and where possible improve on them.

3.1. McReynolds b Descriptor

Let us firstly recall the model proposed in 2011 [10]:

$$\text{McRb}_{2011} = 0.29 - 0.26 \frac{\text{PSA}}{V} + \frac{6.22}{V} \quad (4)$$

with: $r = 0.908$; $N = 74$ columns (66 phases); $F = 166$.

After observing that with the slightly extended experimental data set in **Table 2**, both r and F values appear slightly improved with this 2011 model, finally an optimal model is presently shown in **Figure 3**.

It should be noted that using only two molecular features (PSA/ V and O2/ V), we obtained a very similar correlogram ($r = 0.956$, but $F = 443$). That can be interpreted as follows: the coefficients for O1/ V , O11/ V and N3/ V are directly proportional in the PSA/ V prediction and in the McR b prediction. In contrast,

molecular features	SMT coefficients	partial F ratios
O1/ V	-5.046	263
O11/ V	-2.890	281
O2/ V	-1.587	29
N3/ V	-6.665	282
constant	0.297	

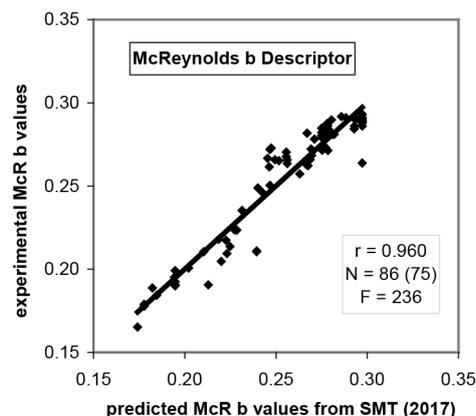


Figure 3. Optimal prediction to date of the McReynolds b descriptor using the experimental values from **Table 2** and the SMT procedure.

O2/V is out of this proportionality. It also should be specified that the compounds including F, Cl, Br, S, N111, present in **Table 2**, have not been kept by the MLRA program. In contrast, various other molecular features of N, present in the prediction of PSA, are absent in **Table 2**. For this reason we prefer to consider as temporarily valid the model shown in **Figure 3**, rather than the alternative one including PSA.

3.2. W and E Descriptors

The results obtained on the basis of **Table 1** for the W and E descriptors are summarized in **Figure 4** and **Figure 5**.

Apart from the spectacular (and unexpected) match of experimental points to the models in **Figure 4** and **Figure 5** compared to similar attempts in 2011, let us firstly emphasise the important role played by the reverse of the molecular volume in **Figure 5** (and its absence in **Figure 3** and **Figure 4**). That confirms our observation in 2011, and above all the already mentioned previous observation of the Kováts group [16] [17] [18] [19], that the alkanes, in order to be completely “non polar” in the chromatographic sense, should be of infinite carbon atom numbers. That is not the case for squalane, generally chosen as a reference stationary phase.

molecular features	SMT coefficients	partial F ratios
1000 O1/V	25.30	285
1000 O11/V	17.71	1403
1000 N3/V	75.22	1599
1000 S1/V	18.06	92
1000 F1/V	8.51	2533
1000 Cl1/V	22.78	147
1000 Br1/V	21.43	130
constant	67.72	

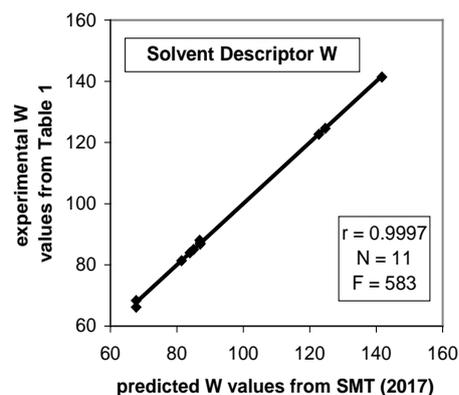


Figure 4. Predictive model of the W solvent descriptor, based on **Table 1** and the SMT procedure.

molecular features	SMT coefficients	partial F ratios
1000 (O1 lk C11)/V	11.05	208
1000 (O1 lk C111)/V	7.89	106
1000 O11/V	7.47	1159
1000 N3/V	23.70	947
1000 S1/V	13.54	309
1000 Cl1/V	9.14	141
1000 Br1/V	10.93	301
1000/V	-30.93	1572
constant	306.65	

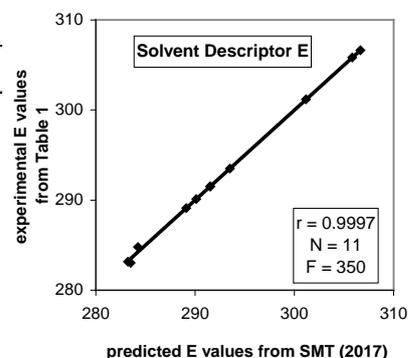


Figure 5. Predictive model of the E solvent descriptor, based on **Table 1** and the SMT procedure.

Another observation is the important role played by the fluorine compounds in the W descriptor, and its total absence in the other two. It is also worth highlighting the important difference of coefficients for primary and secondary alcohols in the E descriptor, and the absence of difference for the other two descriptors.

4. Discussion and Perspectives

The publication of McReynolds in 1970 [14] principally includes two types of experimental chromatographic data: 1) a matrix of retention indices of 10 solutes on 226 columns (207 phases), 2) the McR b descriptors for the same 226 columns. The first cited data set has been applied by number of authors in a purpose of classification the stationary phases, e.g.: [10] [21] [22] [23] [24], but, as above mentioned, the polar descriptor McR b has only previously studied in a QSPR prospect in our study of 2011 [10] and have been refined in the present one.

Compared with the results here presented using the experimental data from the Kováts group, those obtained from the 226×10 matrix of McReynolds can be considered as less satisfactory, whatever the authors are. In contrast, of course, the variety of the molecular structures on which the Kováts data are based is narrowed.

On the other hand and more generally speaking as already underlined [4], all the studies based on the so called Abraham molecular descriptors are difficult to be compared with those based on mutually independent solute descriptors, as we are proposing since 2005 [13].

It is not easy to foresee the fruitful development of the results here presented. The author has been along all his activity time, interested by the olfaction in a broadest sense of the term, and involved in parallel in physicochemical and physiological aspects. The reason is that he is convinced that the recognition of the odorants by the olfactory receptors is not at all similar to the internal chemoreception, which is based on very specific key and cue mechanisms of recognition. The olfactory recognition, in contrast, is very probably based on a great amount of weakly specific receptors and a powerful system of information processing. The implicated labile intermolecular forces could be the Van der Waals forces ... Some few results have been obtained in this sense, the last one in 2013 [25].

5. Conclusion

Taking into account the presently available experimental and accurate descriptors values for solvents, the results here presented appear rather satisfactory. They could be summarized as:

- the confirmation of some broad trends previously published, as the role played by the molecular volume taken alone in the descriptor E, and the involvement of all the other molecular features expressed as ratios to the mo-

lecular volume;

- the involvement of PSA has also be partially confirmed, but alternative regressive equations only based on SMT procedure presently provide much more better fitting with experimental values;
- the results obtained for the McR b descriptor are obviously not so good than for W and E, but the explanation could be due to experimental material established in 1970 for McR b, and at the end of the nineties for W and E. Indeed, the chromatographic technology has greatly progressed in the time interval.

The challenge remains to know if, as they are, these results can be applied in purely physical chemistry and in other fields such as pharmacology or sensory physiology.

6. Supporting Information

Supporting information associated with this article is freely available by contacting the author at: <paul.laffort@sfr.fr>.

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The eight latter publications we have signed or co-signed, including the present one, have been all based on an important collective work of the Kováts group in Lausanne and Veszprém [26]-[31], and also on fruitful exchanges and discussions with Ervin Kováts himself during many years. The author should like to reiterate his heartfelt gratitude to him and honour his memory for these contributions.

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References

- [1] Rohrschneider, L. (1966) Eine Methode zur Charakterisierung von Gaschromatographischen Trennflüssigkeiten. *Journal of Chromatography A*, **22**, 6-22. [https://doi.org/10.1016/S0021-9673\(01\)97064-5](https://doi.org/10.1016/S0021-9673(01)97064-5)
- [2] Karger, B.L., Snyder, L.R. and Eon, C. (1976) An Expanded Solubility Parameter Treatment for Classification and Use of Chromatographic Solvents and Adsorbents: Parameters for Dispersion, Dipole and Hydrogen Bonding Interactions. *Journal of Chromatography A*, **125**, 71-88. [https://doi.org/10.1016/S0021-9673\(00\)93812-3](https://doi.org/10.1016/S0021-9673(00)93812-3)
- [3] Laffort, P. and Patte, F. (1976) Solubility Factors in Gas-Liquid Chromatography: Comparison between Two Approaches and Application to Some Biological Studies. *Journal of Chromatography A*, **126**, 625-639. [https://doi.org/10.1016/S0021-9673\(01\)84107-8](https://doi.org/10.1016/S0021-9673(01)84107-8)
- [4] Laffort, P. (2016) A Revisited Definition of the Three Solute Descriptors Related to the Van der Waals Forces in Solutions. *Open Journal of Physical Chemistry*, **6**, 86-100. <https://doi.org/10.4236/ojpc.2016.64009>

- [5] Laffort, P. and Héricourt, P. (2006) Solvation Parameters. 2. A Simplified Molecular Topology to Generate Easily Optimized Values. *Journal of Chemical Information and Modeling*, **46**, 1723-1734. <https://doi.org/10.1021/ci0600152>
- [6] Laffort, P. and Héricourt, P. (2009) Solvation Parameters. Part 4: What Is the Impact of Recent Chromatographic Data Update? *The Open Applied Informatics Journal*, **3**, 12-21. <https://doi.org/10.2174/1874136300903010012>
- [7] Zamora, A. (1976) An Algorithm for Finding the Smallest Set of Smallest Rings. *Journal of Chemical Information and Computer Sciences*, **16**, 40-43. <https://doi.org/10.1021/ci60005a013>
- [8] ChemSpider, Search and Share Chemistry. (2017) <http://www.chemspider.com/Search.aspx>
- [9] Molinspiration, Calculation of Molecular Properties and Bioactivity Score. (2017) <http://www.molinspiration.com/cgi-bin/properties>
- [10] Laffort, P. (2011) Solvation Parameters. Part 5: Physico-Chemical Interpretation of Experimental Solvent Values for Stationary Phases of Gas-Liquid Chromatography. *Journal of Chromatography A*, **1218**, 4025-4033. <https://doi.org/10.1016/j.chroma.2011.04.068>
- [11] Palm, K., Luthman, K., Ungell, A.L., Strandlund, G. and Artursson, P. (1996) Correlation of Drug Absorption with Molecule Surface Properties. *Journal of Pharmaceutical Sciences*, **85**, 32-39. <https://doi.org/10.1021/js950285r>
- [12] ChemAxon Ltd. (2017) <https://www.chemaxon.com/>
- [13] Laffort, P., Chauvin, F., Dallos, A., Callegari, P. and Valentin, D. (2005) Solvation Parameters: Part 1. Mutual Improvements of Several Approaches and Determination of Two First Sets of Optimized Values. *Journal of Chromatography A*, **1100**, 90-107. <https://doi.org/10.1016/j.chroma.2005.09.022>
- [14] McReynolds, W.O. (1970) Characterization of Some Liquid Phases. *Journal of Chromatographic Sciences*, **8**, 685-691. <https://doi.org/10.1093/chromsci/8.12.685>
- [15] West, S.D. (1989) Correlation of Retention Indices with Resolution and Selectivity in Reversed-Phase HPLC and GC. *Journal of Chromatographic Sciences*, **27**, 2-12. <https://doi.org/10.1093/chromsci/27.1.2>
- [16] Huber, G.A. and sz. Kováts, E. (1973) Standard Stationary Phases. *Analytical Chemistry*, **45**, 1155-1163. <https://doi.org/10.1021/ac60329a013>
- [17] Fritz, D.F. and sz. Kováts, E. (1973) Activity Coefficient for Gas Chromatography. Influence of the Molecular Weight of the Stationary Phase on Gas Chromatographic Data. *Analytical Chemistry*, **45**, 1175-1179. <https://doi.org/10.1021/ac60329a021>
- [18] Défayes, G., Fritz, D.F., Görner, T., Huber, G., De Reyff, C. and sz. Kováts, E. (1990) Organic Solutes in Paraffin Solvents. Influence of the Size of the Solvent Molecule on Solution Data. *Journal of Chromatography A*, **500**, 139-184. [https://doi.org/10.1016/S0021-9673\(00\)96067-9](https://doi.org/10.1016/S0021-9673(00)96067-9)
- [19] Reddy, K.S. and sz. Kováts, E. (1990) Dependence of Solution Data at Ideal Dilution on Solvent Molecular Size. *Chromatographia*, **30**, 493-499. <https://doi.org/10.1007/BF02269794>
- [20] SUPELCO, Bellefonte, PA, USA (2017) Bulletin 880. Online Catalog. <https://www.sigmaaldrich.com/Graphics/Supelco/objects/7800/7741.pdf>
- [21] Li, J., Zhang, Y. and Carr, P.W. (1992) Novel Triangle Scheme for Classification of Gas Chromatographic Phases Based on Solvatochromic Linear Solvation Energy Relationships. *Analytical Chemistry*, **64**, 210-218. <https://doi.org/10.1021/ac00026a022>

- [22] Zenkevich, I.G. and Makarov, A.A. (2005) A New Application of McReynolds Constants to the Characterization of the Chromatographic Properties of Stationary Phases. *Journal of Analytical Chemistry*, **60**, 845-850.
<https://doi.org/10.1007/s10809-005-0193-8>
- [23] Hoffmann, E.A., Fekete, Z.A., Rajkó, R., Pálkó, I. and Körtvélyesi, T. (2009) Theoretical Characterization of Gas-Liquid Chromatographic Stationary Phases with Quantum Chemical Descriptors. *Journal of Chromatography A*, **1216**, 2540-2547. <https://doi.org/10.1016/j.chroma.2009.01.026>
- [24] Hoffmann, E.A., Rajkó, R., Fekete, Z.A. and Körtvélyesi, T. (2009) Quantum Chemical Characterization of Abraham Solvation Parameters for Gas-Liquid Chromatographic Stationary Phases. *Journal of Chromatography A*, **1216**, 8535-8544. <https://doi.org/10.1016/j.chroma.2009.09.074>
- [25] Laffort, P. (2013) A Slightly Modified Expression of the Polar Surface Area Applied to an Olfactory Study. *Open Journal of Physical Chemistry*, **3**, 150-156.
<https://doi.org/10.4236/ojpc.2013.34018>
- [26] Reddy, K.S., Dutoit, J.C. and sz. Kováts, E. (1992) Pair-Wise Interactions by Gas Chromatography: Part I. Interaction Free Enthalpies of Solutes with Non Associated Primary Alcohol Groups. *Journal of Chromatography A*, **609**, 229-259.
[https://doi.org/10.1016/0021-9673\(92\)80167-S](https://doi.org/10.1016/0021-9673(92)80167-S)
- [27] Cloux, R., Défayes, G., Fóti, K., Dutoit, J.C. and sz. Kováts, E. (1993) Pair-Wise Interactions by Gas Chromatography: Part III. Synthesis of Isosteric Stationary Phases for Gas-Chromatography. *Synthesis*, **09**, 909-919.
- [28] Reddy, K.S., Cloux, R. and sz. Kováts, E. (1994) Pair-Wise Interactions by Gas Chromatography: Part IV. Interaction Free Enthalpies of Solutes with Trifluoromethyl-Substituted Alkanes. *Journal of Chromatography A*, **673**, 181-209.
[https://doi.org/10.1016/0021-9673\(94\)85037-2](https://doi.org/10.1016/0021-9673(94)85037-2)
- [29] Défayes, G., Reddy, K.S., Dallos, A. and sz. Kováts, E. (1995) Pair-Wise Interactions by Gas Chromatography: Part V. Interaction Free Enthalpies of Solutes with Primary Chloro- and Bromo-Alkanes. *Journal of Chromatography A*, **699**, 131-154.
[https://doi.org/10.1016/0021-9673\(95\)00023-G](https://doi.org/10.1016/0021-9673(95)00023-G)
- [30] Reddy, K.S., Cloux, R. and sz. Kováts, E. (1995) Pair-Wise Interactions by Gas Chromatography: Part VI. Interaction Free Enthalpies of Solutes with Primary Methoxyalkane, Cyanoalkane, and Alkanethiol Groups. *Journal of Chromatography A*, **704**, 387-436. [https://doi.org/10.1016/0021-9673\(95\)93206-B](https://doi.org/10.1016/0021-9673(95)93206-B)
- [31] Dallos, A., Sisak, A., Kulcsár, Z. and sz. Kováts, E. (2000) Pair-Wise Interactions by Gas Chromatography: VII. Interaction Free Enthalpies of Solutes with Secondary Alcohol Groups. *Journal of Chromatography A*, **904**, 211-242.
[https://doi.org/10.1016/S0021-9673\(00\)00908-0](https://doi.org/10.1016/S0021-9673(00)00908-0)