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Novel Improvement of the Van Der Waals Forces Characterization from Published Vaporization Enthalpies

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Abstract

Index terms—

1 I. INTRODUCTION

Acronyms used in this article are detailed at the end of the paper.

It has been published in 2020 a study on the Interest of splitting the enthalpies of vaporization in four distinct parts reflecting the Van der Waals and the hydrogen bonding forces [1]. The results can be summarized by four empirical equations as shown below. This has been optimized to obtain the best prediction of the enthalpies of vaporization values from ChemSpider [2], for a set of 445 organic compounds in liquid state at room temperature. It must be specified that these data from ChemSpider are enthalpies of vaporization at normal boiling point, also briefly called boiling enthalpies, that we will abbreviate here H BPCS : in which ? 2020, ? 2020 and ? 2020 respectively stand up-to-now for the intermolecular descriptors of dispersion, induction-polarizability and orientation or polarity strictly speaking, reflecting the forces of London, Debye and Keesom. Furthermore, Svap 2020 stands for the entropy of vaporization due to the hydrogen bonding forces. The acronyms in the first column stand for classical molecular properties widely accessible, which will be specified in the present Material and Methods section. The F values between square brackets stand for the partial statistical test F ratios in the global prediction of H BPCS , which depends on the correlation coefficient r, the number of independent variables and the number of compounds (see Abdi [3] for more details). Their values are expected to be as high as possible, and this is the case for the four equations above.

The predictive regressions of enthalpy values as the sum of equations (1)(2)(3)(4) applied to the all 445 compounds of the database under study in the previous publication and to the 116 hydrocarbons taken alone from this database are visualized in figure **??**.

Fig. **??**: Comparison of the normal boiling enthalpy prediction for two sets of VOCs (Volatile Organic Compounds) in liquid state at room temperature, expressed in kilojoules.mol -1 (from [1]). See text.

It clearly appears from figure **??** that the intermolecular forces are better characterized for the pure hydrocarbons, for which the equations 3 and 4 equal zero, than for the global set of 445 compounds. Let us however note the high partial F ratios already mentioned for the four equations involved in this case and the strong mutual independence of the four retained molecular characteristics in their 2020 version, as shown in figure 2. In another diagram reproduced hereafter (figure **??**), it has also been shown in [1] with another data set of 180 compounds including some gases and solids at room temperature, that the equations (1-4) remain relatively valid in all cases. However, the purpose of the present study is to verify and possibly refine all these recent results.

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Novel Improvement of the Van Der Waals Forces Characterization From Published Vaporization Enthalpies Fig. **??**: Prediction of the boiling enthalpy vs enthalpy published by ChemSpider [2] for 180 compounds (145 liquids, 27 solids and 8 gases), both expressed in kilojoules.mol -1 (from [1]).

3 Comment on this 2020 publication

One of the objectives of the author of this study since the beginning of his research activity in 1960, as well as of his team, has been oriented towards quantitative structure-activity relationships (QSAR) in olfaction, including in parallel measurements or calculations of molecular properties and biological properties in humans and in bees. A synthesis of the state-of-the-art in 1991 (translated into English and updated in 1994) on this subject can be read in chapter 6 of Odors and Deodorization in the Environment [4].

Without going into details, it can be said that for Corwin Hansch, considered as one of the pioneers in the more general field of QSAR in biology, the response of a biological system to a biologically active agent is mainly a function of three properties of the latter: a hydrophobic factor, a steric factor and an electronic factor [5]. Of course, the final validation of the parameters or molecular descriptors likely to be the most relevant depends on a satisfactory prediction of the biological properties. However, it turns out that biological experimental data are most often obtained with a margin of uncertainty greater than those obtained in physical chemistry, hence the approach often followed of choosing a so-called global physicochemical property based on several so-called contributing physicochemical properties. Progressively, the number of contributing factors (or descriptors) has increased to 4, then to 5 by several authors while refining. This was the case in 1973 for the author of the present study in cooperation with Andrew Dravnieks, of the IIT-Research Institute of Chicago [6]. We were left with 4 contributing descriptors for solutes and 4 for stationary phases (solvents), with the global properties assumed to be the retention (or Kováts) indices in gas-liquid chromatography (GLC). Later, our team followed the approach of Karger, Snyder and Eon [7,8] by moving to five descriptors: two for the proton donor and acceptor properties and three for the three Van der Waals forces. The rest of this pathway is detailed in the Introduction of our 2020 paper, which it does not seem necessary to repeat here in full.

4 II. MATERIALS AND METHODS

5 Statistical tools

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

6 SMT terminology

A tool named Simplified Molecular Topology (SMT) has been defined and applied in various previous studies and recently in [1]. It consists of considering, for each atom of a molecule, its nature and the nature of its bonds, leaving aside the nature of its first neighbors (with sometimes few limited exceptions). 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 defines the type of bonds (1 for a single, 2 for a double bond, etc.), but the bonds with hydrogen are excluded. The SMT has been applied to the present study for characterizing the hydroxyl term (O1), the monovalent nitrogen (N1), the pentavalent nitrogen (N122), the sulphur in thiols and sulphides (respectively S1 and S11) and the halogenated compounds (F1, Cl1, Br1 and I1).

7 Intrinsic molecular volume

The various expressions which reflect the intrinsic molecular volume or the Van der Waals molecular volume (V w), are all additive properties (which is not the case for V 20 , the ratio molar mass/density at 20?C). We have selected, among those of 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 V w (as Van der Waals volume).

A predictive tool of V w has been proposed in [10], which appears satisfactory as shown in figure 4 and alternatively applicable in some particular cases (e.g. for polymers), but we have preferred to keep the original values of Molinspiration in the present study. This GSS expression reflects in some way the molecular surface on the condition that molecules are considered as spheres. As specified in 2.5, the ratio PSA/GSS could therefore reflect a fraction of polarity without dimension.

8 Polar Surface Area (PSA)

We have considered until now three variants of PSA:

? The most classical, only including the polar atoms N and O. We have selected the values named TPSA (T as topological) established by Molinspiration [9]. We name this expression PSA1.

? The variant including the same polar atoms N and O as in TPSA, but also the divalent sulfur atoms S1 and S11 according to Ertl et al. [11]. This expression has been adopted by ChemSpider [2], without decimal. We name it PSA3.

? In 2013 [12] we have named PSA2 a third variant initially identical to PSA3, but diminished of the pentavalent nitrogen contribution according to [11]. Indeed, this molecular feature cannot be considered as polar as it is visualized in figure **??** from [12]. PSA2, as specified in the equation (9) of [12], has been selected by the MLRA processing as the most suitable variant in a QSAR (Quantitative Structure-Activity Relationship) olfactory application. Fig. **??**: Graphical representation from [12], of the four dative (or semi-polar) bonds and the four covalent bonds of nitromethane, according to the Lewis theory [13], clearly showing that the pentavalent nitrogen is not polar (absence of pairs of peripheral electrons not included in the bonding whereas each oxygen atom has two pairs).

We propose here a fourth variant named PSA4, also without nitro contributions as in PSA2, but including thiols and sulphides with different coefficients, as in addition fluorinated, chlorinated, brominated and iodinated compounds. These seven modifications, specified hereafter, have been obtained by an empirical approach that it didn't seem necessary to detail. A competition using the stepwise MLRA between the four PSA expressions divided by GSS has been applied in the present study, in order to optimize the polarity characterization.

9 The Data Sets Selected in this Study

Our previous publication on boiling enthalpy [1] was initially based on a set of 445 organic compounds in liquid state at room temperature. We keep it here under the name C445.

Also in [1] as mentioned in the Introduction at the figure **??**, we applied a second data set of 180 organic compounds including 147 liquids, 25 solids and 8 gases at room temperature to test a possible extension to solid and gaseous VOCs at room temperature of the interesting results obtained with C445. This dataset, we name A180 and already used in [12], is added in the present study.

It is also added a database for 200 compounds according to Goss and Schwarzenbach [14]. The first advantage of adding this third data set, which we call B200, is that its boiling enthalpy range covers values 20-75 kJ/mol, instead of 20-60 for A180 and 25-55 for C445. That could test a possible curvilinear inflection of the regression, suspected in figure **??** for values above 55 kJ/mol. The second advantage of considering these 200 compounds, is to test as a global molecular property, the enthalpy of vaporization at 25°C, applied by these authors, instead of the boiling enthalpy in an environment of 1 atmosphere. It should be underlined that the only difference between these three groups comes from the substances considered, as detailed above. Together, the three datasets total a database of 616 organic compounds, grouped as 616N in Appendix A as Supplementary Information.

10 Recapitulation of the molecular property sources used in this study

? ChemSpider [2]. This compilation of properties consists primarily of three sites: ”Experimental Data”, ”Predicted ACD/Labs”, ”Predicted EPISuite”. The second of these sites is the most complete both in number of compounds and in number of properties. Therefore, it is the one we have chosen in this study for the properties of refractive index (RI) and boiling point (BP) ? Molinspiration [9]. We used according to this calculator, the polar surface area (TPSA) and the intrinsic molecular volume (V w).

? Ertl P, Rohde B, Selzer P [11]. We used the coefficients recommended by these authors to define the polar surface areas variants PSA2 and PSA3 from PSA1, as mentioned and specified in 2.5.

? Goss, KU and Schwarzenbach, RP. [14]. We have taken their published values of enthalpy of vaporization at 25°C (H 25GS) and saturating vapor pressure at 25°C for 200 substances.

In a very few cases, these sources proved insufficient and were supplemented by the Handbook of Chemistry and Physics [15] or simple interpolations.

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11 Assistance in writing the text

The Linguee Dictionary [16] and the DeepL translator [17], both available free of charge, have been used to write this publication in English.

12 III. RESULTS

13 Testing the 2020 model for the 616N dataset

In the previous study summarized in the Introduction, the chosen global property was boiling enthalpy, which could be predicted as the sum of four molecular descriptors reflecting Van der Waals and hydrogen bonding forces for 445 organic compounds in the liquid state at room temperature.

The statistical tests r and F shown in figure **??** are high and the descriptors ? 2020 , ? 2020 , ? 2020 and S vap2020 relatively independent of each other as shown in figure 2. The pleasant surprise was, with another data set of 180 organic compounds including liquids, solids and gases, that the previous equations remain valid, with however some suspicion for boiling enthalpy values greater than 55 kJ.mol -1 , as suggested by the top of Figure **??** (for at least 1 compound). It is clear that if this curvilinear shape of boiling enthalpies vs a predicting model is confirmed for values greater than 55 kJ.mol -1 , the model cannot be considered as totally valid. And this is however the result observed with the 2020 model applied to the data set of 616 compounds, as it can be observed in figure 6.

14 compounds). See consequences in text

One possible solution to overcome this difficulty is to consider that the molecular property that reflects the sum of the four intermolecular forces is not the boiling enthalpy, but an exponential function of this boiling enthalpy.

Although this solution has been found to be partially satisfactory, it has the disadvantage that the units of the descriptors obtained can no longer be expressed in recognized thermodynamic units, in this case kilojoules.mol -1 . In addition, use of non-linear equations lead to a model less robust and readable.

In doing so, as mentioned in Material and Methods, we found it interesting to test the feasibility of considering the enthalpy of vaporization at 25°C instead of the boiling enthalpy at normal pressure, Novel Improvement of the Van Der Waals Forces Characterization From Published Vaporization Enthalpies as a global property that best reflects the four intermolecular forces under investigation in the present study. However, since experimental values of enthalpy of vaporization at 25°C are few, this option requires the prior development of a robust predictive method for this property. Subsection 3.2 describes one such method of particular relevance.

15 A first prediction of the enthalpy of vaporization at 25°C

In their study of 1999 [14], Goss and Schwarzenbach provide experimental values of enthalpy of vaporization at 25°C (H 25GS) for about 200 organic compounds of very different natures. But above all, Goss and Schwarzenbach provide an excellent QSPR (Quantitative Structure Property Relationship) between these experimental H 25GS and the saturated vapor pressures at 25°C. This result is summarized in figure 7, largely provided by the authors. Novel Improvement of the Van Der Waals Forces Characterization From Published Vaporization Enthalpies conjunction of its outlier status and the uncertainty in the following steps on its molecular volume due to the formation of stable cyclic dimmers.

The equation (**??**) has therefore been revised slightly in the equation (**??**) to consider the discarding of these two outliers:

(r = 0.991; N = 200; F = 10702) (8) where H vap25°C and svp are expressed in the same units as in equation (**??**)

We have appreciated in various previous studies (e.g. reference [18]) the expression of the saturated vapor pressure as its colog values of atmospheres at 25°C. This expression, named ICE (as Internal Cohesive Energy), has for example the advantage to be homogeneous with the molar fraction of a solute in solution in an environment of one atmosphere. The equation (9) allows the transformation of the expression of the saturated vapor pressure applied by Goss and Schwarzenbach [14] into ICE.

It should be noted that, unlike the majority of equations proposed in this study, equation (9) is not the result of a regression, but of a strict equivalence between two expressions of the same property: the saturation vapor pressure. ICE = 5.005717 -0.4342945 ln p iL * (Pa, 25 °C)

Therefore, the equation (**??**0) is an alternative expression of the equation (**??**) with the saturated vapor pressure expressed in ICE:

(r = 0.991; N = 200; F = 10702) (10)

The satisfactory result described here is not fundamentally surprising in terms of substance, since it appears in several equations derived from Emile Clapeyron's general and simplified formulas published in 1834 [19] and recovered by Rudolf Clausius in 1850 [20]. The nice surprise is the high degree of correlation observed here for 200 substances of very different natures. We have however to underline that the application of equations 8 or 10 based on saturated vapor pressure of a given component is not always easily and accurately accessible. Indeed, it can be obtained on required temperature using formulas such as Antoine equation based on various empirical parameters but only for some ranges of value. Therefore, an alternative prediction is described in the subsection 3.3.

16 An alternative prediction of the enthalpy of vaporization at 25°C

Equation (11) below is the best performing one we have obtained in a first stage, using a purely empirical approach based on multiple linear regression analysis (MLRA) applied to 199 out of the initial B200 dataset, squalane having been excluded because of its strong outlier behavior, as can be seen in Figure 8. This compound is a highly branched substance, unlike all others in the present study, and this molecular characteristic could perhaps account for the observed exception. where: BP CS stand for boiling point in °C from ChemSpider (ACD/Labs) M stand for molecular weight T BPCS stand for boiling point in kelvin O1 stand for oxhydric molecular element N1 stand for primary amine element

The proportionality coefficients of O1 and N1, initially separated and unexpectedly found to be identical, were brought together. Furthermore, these two molecular characteristics being considered as the main ones involved in hydrogen bonding, we propose to call provisionally HB 2023 (as Hydrogen Bonding) the third term of equation 11. Whatever the case of equation 11, which at the present stage of the inquiry appears to be the most efficient for representing a general estimate of the enthalpy of vaporization at 25 °C, let us recall that the main goal of this study is the characterization of each of the four molecular descriptors reflecting the three Van der Waals forces and the hydrogen bonding forces of compounds in a condensed phase at 25 °C. Therefore, a first important step remains to be performed now: the splitting H25 pred eq11 2023 in four suitable descriptors for 616 organic compounds, similarly to those published in 2020 for 445 compounds on the basis of the boiling enthalpy in the environment of one atmosphere, as recalled in the present Introduction (equations 1-4).

Of course, a second step is also needed to be performed: the verification that the molecular descriptors remain constant when the size and nature of the component samples vary.

These two topics are the subject of subsection 3.4. in which ? 2023, ? 2023 and ? 2023 , similarly to equations 1-4, respectively stand for the update molecular descriptors values reflecting the forces of London, Debye and Keesom. Furthermore, HB 2023 stands for the descriptor reflecting the hydrogen bonding forces involved in pure organic compounds in condensed phases at 25°C. The acronyms in the first column stand for the classical molecular properties widely accessible, which have been specified in the present Material and Methods section. The F values between square brackets stand for the partial statistical tests F ratios.

? The descriptor of Dispersion ? 2023 , as in our previous papers on GLC since 2005 [18] and in that of 2020 using boiling enthalpy, is based on the product fn*Vw.

? The descriptor of Induction-Polarizability ? 2023 is also based as previously on a bilinear regression of fnVw and Vw, but slightly modified, characterized by negative values for fluorinated and branching compounds and by strongly positive values for polycyclic compounds and compounds with multiple bonds. Most of normal paraffines have values near of zero. (Let us underline that the initial data set of 200 substances do not include fluorinated compounds).

? The descriptor of orientation or polarity strictly speaking ? 2023 is similar to that of 2020, but including an expression of polar surface area in its version of PSA4, as selected by the MLRA processing. This is not surprising since is not easy to understand, from a strictly physicochemical point of view, a definition of a polarity not including values for divalent sulfur compounds and halogenated compounds.

? Concerning the descriptor reflecting the hydrogen bonds HB 2023 , its definition is very different of that in the 2020 paper, but its consideration in the present one seems to be pragmatically acceptable. In this respect, one can note the very strong resemblance of the coefficient of the third term of equation 11 (9.391) with that of equation 15 (9.437). One could very well separate, as soon as equation 11 was obtained, the third term of this equation as the definitive definition of HB 2023 (instead of provisional) and called the sum of the other terms ”Global Property reflecting the Van der Waals forces” (GWP). Not only could this be done, but we did it, and the resulting values of ? 2023 , ? 2023 and ? 2023 turned out to be practically identical to those in equations 12-15. The reason we did not keep this procedure as a pathway is in order to keep the reference to the H25 enthalpy all the way through.

17 Novel Improvement of the Van Der Waals Forces Characterization From Published Vaporization Enthalpies

In order to base the reference values of the three descriptors reflecting the Van der Waals forces on the largest number of compounds studied so far, the 616N dataset has of course been chosen. The results given by equations 12, 13, 14 and 15 are applied in figure **??**.

18 Fig 9:

Application of the four equations 12-15 to the 616N dataset, showing a good proximity between equation 11 (without squalane) on one side and the equations 12-15 on another side, as both validated predicting tools of H25. The second option presenting the additional interest to be reflect the four molecular intermolecular forces, has been selected to be kept for both purposes.

It now remains to test that the four molecular descriptors defined by equations 12-15 remain valid in their nature when the sample of substances to be studied is changed. Figure 10 is directly deduced from Figure **??** in which only the initial 200 substances were retained. There is a clear improvement in the correlation observed in this figure 10 compared to figure 8, which reinforces the aforementioned choice in favor of the predictive model of H25 via equations 12-15, rather than via equation 11. There is also a more Gaussian distribution of points in figure 10 in a comparison of figures 8 and 9 , making the high value of the correlation coefficient more convincing. To complete the comparisons between the 2020 study and the present one, the correlation matrix in Figure 11 shows that for the 616 selected compounds, the relative independence of the molecular descriptors reflecting the four intermolecular forces is comparable to that observed in Figure 2.

19 Supplementary Information

An abridged version of the dataset for the 616 VOCs used in the present study is reproduced in Appendix A. This database is limited to organic compounds including C, H, O, N, S, P, F, Cl, Br, I. Therefore, compounds including Se, Pb or Si, for example, are excluded.

The main information reported in this Appendix are the values of the four contributing molecular descriptors defined in equations 12, 13, 14, and 15, as well as their sum characterizing the predicted values of enthalpy of vaporization at 25°C (H25). All these data are expressed in kilojoules/mol.

20 IV. DISCUSSION AND COMMENTS

Generally speaking, the present publication represents the most recent step of a long investigation of our team in Physical Chemistry, pursued since the 1970’s in parallel with other less risky themes and more centered on the olfactory physiology in Man and in Honeybee. This physicochemical thematic initially privileged the Kováts retention indices in gas-liquid chromatography (GLC), associated with a data processing that we now call MMA (Multiplicative Matrix Analysis). This MMA algorithm seems to have been poorly understood in the publications involved in this subject. However, it allowed us to characterize since 1976 [21], a polarizability parameter reflecting the Debye forces in a relatively satisfactory way, with an optimization in 2005 still valid today [18]. In this 2005 paper, we also refined the characterization of dispersion or London forces. In fact, the content of this 2005 publication was already present in Françoise Chauvin's 1998 thesis [22], of which chapter 2 is a translation into French of a multi-author manuscript submitted to a well-known Chromatography journal and twice rejected (see page 26 of this thesis for the presentation of the chapter in question)...

There remained the polarity, whose characterization turned out to be different according to the GLC-MMA tandem and according to a SMT molecular topology procedure [23]. A first solution, suggested by a QSAR publication in olfaction in 2013 [12], was obtained in our 2020 publication by using normal boiling enthalpy as a global property in place of GLC retention indices, as well as the PSA1/GSS fraction to characterize a polarity independent of the polarizability. The latter approach has been refined in the present study with the PSA4/GSS fraction. an important advance. The PSA4/GSS fraction that we propose remains to be verified and possibly improved, for example with an evaluation of the molecular surface more in line with a general reality than GSS, and less complicated than those proposed so far in the literature.

The third and final suggestion for possible improvement of this study concerns the polarizability descriptor that we have called ? 2023 . As we saw in subsection 3.4 and as can be verified in Appendix A, this descriptor is characterized by negative values for fluorinated compounds as well as for squalane, the substance that caused us some difficulties mentioned in the Results section. The hypothesis that this singularity characterizes a highly branched molecular structure seems to be confirmed, but our present definition of ? 2023 proves to be inadequate to account for partial branching. However, it is possible that a more general branching index established by molecular topology, such as the one proposed by Randic [32], would allow an improvement of the definition of ? 2023 . Unfortunately, we did not succeed in applying this Randic index, which seemed to us rather complex. This is not the case for a similar topological index such as the one proposed by Zamora in 1976 under the name of SSSR (Smallest Set of Smallest Rings) **??**33] to characterize the connectivity of polycyclic substances.

We have used it successfully on several occasions, but in the present study it was not necessary as the fn and Vw properties proved sufficient.

21 Estimates in the literature of the energies of the diverse intermolecular forces

Although they are not always an agreement among colleagues in this scientific discipline, figure 12 reflects quite well a certain consensus, namely that the Van der Waals forces are relatively clustered and distinct from the hydrogen bonding forces, and that among the former the London forces are the most important and the Debye forces the weakest. One may note that this last observation is reminiscent of the order of the F ratios in equations 12-15. Finally, the intramolecular covalent forces are really very far from all the intermolecular forces (up to 1100 kJ.mol -1).

Fig. 12: Order of magnitude of the energies usually encountered, expressed in kJ.mol -1 , in the intermolecular forces of VOC compared to the intramolecular covalent forces.

22 Other alternatives for getting predicted values of enthalpies of vaporization at 25°C (H25)

Several equations for predicting the enthalpy of vaporization at a given temperature are proposed in the physicochemical literature. One of the simplest and most popular is the one proposed by Watson in 1943 [34], reproduced below in the particular case of 25°C :

Novel Improvement of the Van Der Waals Forces Characterization From Published Vaporization Enthalpies Where H BP stands for the enthalpy at boiling point T BP stands for the boiling point expressed in kelvins Tc stands for the critical temperature expressed in kelvins Although relatively simplified, this equation has the disadvantage of depending on the critical temperature Tc, which is not well represented in the physicochemical property banks. As an example, out of the 616 substances studied in this study, we could obtain Tc values from the Handbook of Chemistry and Physics (1995) **??**28] for only 206 of them. The second drawback is that the exponent of 0.38 is totally empirical, valid in many cases, but must be modulated for some compounds (for the 206 compounds tested, methanol and ethanol). All this does not correspond to the objective we had set ourselves, namely to provide the reader with a simple and generalizable tool.

23 Can Van der Waals forces be relevant for odorant recognition by olfactory receptors?

This has been the hypothesis that has guided us for many years, but we have to recognize that it is very little shared. Before debating it and trying to demonstrate it, let us make a small but general incursion into the animal world on individual recognition, without which many observed behaviors could not occur. For example, the recognition of the leader of a deer herd won in a yearly fight, or a perennial couple life in whales. The principal sensory modality for this can be song coupled with hearing, as for example in whales for their pair life, but also in many species of diurnal birds for the duration of a nest. However, undoubtedly the most widespread individual recognition in the animal world is done via olfaction, vision remaining the prerogative of the human species and of some other Primates. Let us take the example of vision which is familiar to us. Without underestimating the richness of the visual information brought by color, stereoscopic vision and the appreciation of movement, individual recognition can be using only a two-dimensional black and white photography. In other words, using only three physical properties: X and Y coordinates and luminance. Only three physical properties, but a very large number of points (let us call them pixels) that differ from each other in their modulation of these three properties. This is only possible if these points are very numerous and if we have a powerful information processing system, which is indeed the case with the voluminous human visual cortex located in the occipital part of the brain. Why would it not be the same with olfaction, with, for example, the three Van der Waals forces? This does not exclude additional refinements such as, for example, those due to the individuals themselves using memory, and those due to additional molecular details such as optical isomerism.

In 1993 **??**35], a planar representation was published showing a fairly good superposition, on one hand of odorant clusters obtained experimentally using electrophysiological responses from frog olfactory mucosa by the group of André Holley in Lyon, and on the other hand of their X and Y coordinates equal to expressions of the molecular descriptors that we now call ? (dispersion) and ? (polarizability). A satisfactory characterization of the descriptor ? (orientation-polarity) has been long to obtain in order to complete this three-dimensional space, but it has been curiously suggested by a publication of QSAR in olfaction [12]. Let us note, however, that this publication [12] was not about olfactory quality (and thus about recognition of odorants by olfactory receptors), but about a relationship between threshold values and odorant intensities perceived at the supraliminal level.

24 V. CONCLUSION

We can presently state that the results presented above represent a clear improvement of those presented in 2020. Firstly by an improvement of the correlation between a global molecular property and the sum of four contributing molecular descriptors, from 0.95 to 0.99 in round numbers, and moreover based on a more numerous and more diversified sample of substances, for which the 2020 model proved to be insufficient and partially deficient (outside the window of r = 0.95).

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One can certainly object that in 2020 the chosen global property, the enthalpy of vaporization at the boiling point in a pressure environment of 1 atmosphere, is a widely published and accessible physicochemical property, and that this is not the case for the enthalpy of vaporization at 25°C (H25) in a constant volume and variable pressure environment (the saturation vapor pressure). We therefore had to go through an intermediate step of predicting H25 via equation 11.

We can already add, however, that the four contributing molecular descriptors defined in equations 12, 13, 14 and 15 follow a long progressive improvement in gas-liquid chromatography (GLC) from 1976 to 2018, as well as on the basis of the boiling enthalpy of vaporization in 2020. The small changes to the 2020 version have already been specified in Section 3.4, after their actual definitions.

The important difference of our approaches compared to those reported in the very interesting Poole review of 2002, is that the descriptors reflecting the Debye and Keesom forces can very well be separated according to us, contrary to what is claimed by many authors.

In spite of a possible improvement in the future, highlighted in 4.2, of the polarizability index ? 2023 , the author of the present study, started in 2020, cannot help but feel enthusiastic about the results reported in subsections 3.3 and 3.4 and summarized in figures 8, 9 and 10, which are better than those initially expected. Perhaps, the future will tell, they close a long investigation in physical chemistry of our team, pursued since the 1970s. The optimum we thought possible regarding the characterization of molecular parameters reflecting the three Van der Waals forces for solutes in solutions using GLC was published in 2016, the approach using the normal boiling enthalpy of pure organic compounds developed in 2020 performed better, and finally the present study via the enthalpy of vaporization at 25°C together with the modified characterization of the polar surface area seems to result in a clear improvement. As for using it, readers now have here all the details for establish the corresponding values of ? 2023 , ? 2023 and ? 2023 and try to apply them to olfaction or to other pharmacological properties. The author will also try to work in this direction.

25 ACKNOWLEDGEMENTS

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26 Summary of the Acronyms Applied in Equations

? ?, ? and ? stand for the molecular descriptors reflecting the Van der Waals forces (? for dispersion, ? for orientation or polarity strictly speaking and ? as reminiscent of electronic for polarizability) ? O1 stands for an oxygen atom in a hydroxyl group ? N122 stands for a nitrogen in nitrates ? S VAP stands for the boiling entropy due to the hydrogen bonding forces involved in pure organic compounds in condensed phases (2020 version).

? HB stands for the same meaning in the 2023 version ? H BPCS stands for normal Boiling Enthalpy from ChemSpider [2] ? V w stands for Van der Waals molecular volume according to Molinspiration [4] ? GSS stands for Global Spherical Surface ? T BP stands for boiling point expressed in kelvins

27 Some column headings explanations:

? A stand for data used in figure **??** for 180 VOCs in liquid, solid and gaseous phases at room temperature and involved in olfactory studies [1, **??**6, **??**7] ? B stand for data from Goss KU and Schwarzenbach RP [9] for 200VOCs in liquid, solid and gaseous phases at room temperature ? C stand for data from 445 VOCs in liquid phase at room temperature applied in our 2020 study on boiling enthalpy [1] ? 616N stand for the global ranking of the 616 VOCs applied in the present study and resulting of the union of A + B + C ? ID ChSpd stand for the identification number of ChemSpider [2] ? d 2023 , e 2023 , w 2023 and HB 2023 stand respectively for the molecular descriptors reflecting the intermolecular forces, expressed in kJ/mol,of London, Debye, Keesom and of hydrogen bonding, according to equations 12, 13, 14 and 15 of the present study. [1] [2] [3] [4] [5] [6] [7] [8] [9] [10] [11]

Figure 1:

2

Figure 2: Fig. 2 :?

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[1] Volume 23 | Issue 8 | Compilation 1.0 © 2023 Great Britain Journal Press

[2] ©

[3] ©

[4] ©

[5] ©

[6] ©

[7] ©

[8] ©

[9] ©

[10] ©

[11] ©

Figure 3:

4

Figure 4: Fig. 4 :

6

Figure 5: Fig. 6 :

7

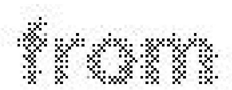
Figure 6: Fig 7 :

8

Figure 7: Fig 8 :

10

Figure 8: Figure 10 :



from

11

Figure 9: Fig. 11 :

[202]	[264]	[81]

Figure 10:

obtained using MLRA :
H25 pred eqs 12-15/2023 =
0.9353 fn Vw [F = 20110] (? 2023) (12)
+ 0.3192 fn Vw -0.08917 Vw + 1.70 [F = 159] (? 2023) (13)
+ 31.86 PSA4/GSS [F = 1011] (? 2023) (14)
+ 9.437 (O1 +N1) [F = 724] (HB 2023) (15)
+ 7.949

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Figure 11:

Figure 12: ?

		C013	13		2-Hexanol	11794	51.678	28.282	0.562	5.448	9.437
		C014	14		2-Methyl-1-pentanol	7459	51.680	28.285	0.562	5.447	9.437
		C015	15		2-Methyl-2-pentanol	11056	51.647	28.209	0.588	5.465	9.437
		C016	16		4-Methyl-2-pentanol	7622	51.474	28.111	0.523	5.454	9.437
A075		C017	17		1-Heptanol	7837	55.771	32.806	0.588	4.990	9.437
		C018	18		2-Heptanol	10511	55.634	32.686	0.567	4.995	9.437
		C019	19		3-Heptanol	11036	55.634	32.686	0.567	4.995	9.437
		C020	20		2-Methyl-2-hexanol	11739	55.610	32.621	0.594	5.009	9.437
A125	B195	C021	21		1-Octanol	932	59.874	37.257	0.609	4.622	9.437
		C022	22		1-Nonanol	8574	63.943	41.636	0.605	4.315	9.437
		C023	23		2-Nonanol	11861	64.232	41.834	0.693	4.319	9.437
		C024	24		1-Decanol	7882	68.022	45.988	0.593	4.055	9.437
		C025	25		1-Undecanol	7892	72.202	50.389	0.596	3.831	9.437
A039		C026	26		Cyclopentanol	7026	51.033	25.246	1.947	6.454	9.437
A035	B150	C027	27		Cyclohexanol	7678	54.294	29.295	1.831	5.783	9.437
		C028	28		Cycloheptanol	9970	57.674	33.319	1.706	5.263	9.437
A159		C029	29		2-Propen-1-ol (allylalcohol)	13872989	41.414	14.846	0.954	8.228	9.437
		C030	30		trans-2-Buten-1-ol	13871721	45.362	19.714	1.167	7.094	9.437
		C031	31		2-Propyn-1-ol (Propargylalcohol)	21106466	41.836	14.427	1.299	8.724	9.437
	B160	C032	32		m-Cresol	21105871	58.402	32.169	2.993	5.854	9.437
		C033	33		Benzylalcohol(?-Hydroxytoluene)	13860335	58.468	32.240	2.996	5.846	9.437
A146		C034	34		2-Phenylethanol (phenethylalcohol)	5830	62.351	36.651	3.002	5.312	9.437
A059	B128	C035	35		Acetaldehyde	172	25.665	8.812	0.411	8.493	0.000
	B129	C036	36		Propionaldehyde	512	28.262	13.010	0.346	6.958	0.000

A	B	C		61 6N	Compounds	ID ChSpd	2023 H25 pred	? 2023	? 2023	? 2023	HB 2023
		C001		1	Methanol	864	36.748	6.726	0.678	11.958	9.437
A063	B190	C002		2	Ethanol	682	38.327	10.983	0.631	9.327	9.437
		C003		3	1,2-Ethanediol	13835235	59.788	14.800	1.198	16.967	18.874
A154	B191	C004		4	1-Propanol	1004	41.136	15.343	0.621	7.786	9.437
A155		C005		5	2-Propanol (isopropylalcohol)	3644	40.916	15.152	0.576	7.802	9.437
A017	B192	C006		6	1-Butanol	258	44.440	19.691	0.607	6.756	9.437
A018		C007		7	2-Butanol (sec.butylalcohol)	6320	44.228	19.510	0.565	6.767	9.437
							38.851	26.195	1.069	3.638	0.000
A136	B193	C008	179	8	1-Pentanol	6040	48.032	24.041	0.594	6.010	9.437

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