

Consideration of Hansen solubility parameters. Part 1

Dividing the dispersion term (δ_D) and new HSP distance

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Abstract:

Dr. Hansen divided the energy of vaporization into a dispersion term (δ_D), a polar term (δ_P) and a hydrogen bond term (δ_H) in 1967. These set of parameters are called Hansen Solubility Parameters (HSP). We treat HSP as a three-dimensional vector. With respect to the method of dividing the energy of vaporization, there is no objective technique. From experimental values such as latent heat of vaporization, refractive index, dipole moment, dielectric constant, a self-consistent set of HSP have been derived. This is a big problem in applicability to new compounds especially because when the molecules becoming larger, relevant experimental data are hard to find.

Also, when calculating the similarity of HSP vectors, a coefficient of 4.0 precedes the dispersion term rather than the Euclidean distance of the vector. The factor of 4.0 found by Hansen has not been derived thermodynamically, but it continues to be used for 50 years as the factor that can substantially reproduce the solubility correctly. In this paper, we consider the implications of the dispersion term and divide it into two terms, thus creating a new HSP. When using this new HSP vector, it becomes clear that there is no need for the factor of 4.0 for calculating HSP distance. Furthermore, by assigning HSP to each functional group constituting the molecule, the HSP of a new molecule can be easily obtained.

Key Words: Hansen Solubility Parameter, Dispersion term, HSP distance

1. Introduction:

1.1. Solubility Parameter:

Various forces work between molecules. These intermolecular forces can explain many dissolution phenomena such as polymer-solvent, medicine-absorption, inorganic matter-dispersion etc. The classic solubility theory was been developed by Hildebrand and Scott^[1] who stated that the solubility parameter of a molecule A (δ_A) is related to its energy of vaporization (cohesive energy) ΔE_A as follows;

$$\delta_A = (\Delta E_A / V_A)^{0.5} \quad (1)$$

Where V_A is the molar volume of the molecule A, and $\Delta E_A / V_A$ is known as the cohesive energy density (C.E.D.).

$$\Delta E = \Delta H_A - RT \quad (2)$$

Then equation (1) can be written as:

$$\delta = ((\Delta H_A - RT) / V_A)^{0.5} \quad (3)$$

Where δ , ΔH_A , R , T are the solubility parameter, the heat of vaporization, the gas constant and the absolute temperature respectively. As a descriptor of the intermolecular forces acting on molecules on average, this solubility parameter δ is one of the important dissolution indices.

In 1967, Hansen divided the heat of vaporization energy into 3 parts^[2]. These 3 parts represent the three original molecular forces that govern the dissolving phenomena; the dispersion force (D), the polarity force (P) and the hydrogen bonding force (H). Therefore, the total cohesive energy composed of these components can be written as;

$$E = E_D + E_P + E_H \quad (4)$$

Dividing equation (4) by Volume (V) yields;

$$E/V = E_D/V + E_P/V + E_H/V \quad (5)$$

Comparing equation (1) with (5) leads to (6);

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (6)$$

Where δ_D , δ_P and δ_H represent the three components of Hansen solubility parameters; the dispersion, the polar and the hydrogen-bonding solubility parameters respectively and δ_T represents the total.

The dispersion term (δ_D) of HSP is regarded as being based on the dispersion energy. Even in systems that do not contain heteroatoms such as oxygen and nitrogen, charge distributions may be created due to movement of electrons. The electric field generated by these charge distributions create the dispersion attraction between molecules. In early studies of HSP, δ_D was determined from the so-called chart method [3]. Three types of figures were used for alkyl compounds, cyclic alkyl compounds and aromatic compounds. However, for more complex molecules this approach is less useful.

Instead of the chart method, δ_D can be determined from refractive index. The interaction energy between non-polar molecules should depend on London dispersion forces and, therefore, on the index of refraction [4].

$$\delta_D = 9.55n_D - 5.55 \quad (7)$$

We also determined our own coefficients with a more extensive and revised data set of 540 data points [5]:

$$\delta_D = (n_D - 0.784) / 0.0395 \quad (8)$$

However, it should be noted that this scheme can only be applied to the compounds that do not have significant δ_P or δ_H values. For example, in molecules such as alcohol with significant δ_P , δ_H values it is impossible to separate the refractive index term between those attributed to δ_D , and from δ_P , δ_H which cause an increase of density.

Various equations based on the group contribution method have been developed. The Van Krevelen [6], Beerbower [7], and Hansen and Beerbower [8], methods have been popular. These various developments have been summarized by Barton [9]. More recently, the Stefanis-Panayiotou [10] group contribution method and the Y-MB method [5] have become popular as they are based on a more extensive

dataset with more sophisticated treatment of multiple functional groups.

However, what we are going to do with the group contribution method is to distribute the whole δ_D term to the functional groups that make up the molecule. If the value of the original δ_D comes from an estimate that is unable to separate the effects of a polar compound on the refractive index, the coefficients of the functional groups will contain the uncertainty of that separation

1.2. Similarity of Solubility Parameters

Once the solubility parameter of the solvents had been obtained, the scheme expressing similarity of mutual solubility parameters was considered [1].

When considering removing one molecule from the solution and returning the other molecule there, the free energy of mixing is;

$$\Delta G = \Delta H - \Delta TS \quad (9)$$

And mixing occurs when ΔG is zero or negative. When we are trying to dissolve a solute 2, with a solvent 1, then ΔH can express with scheme (10).

$$\Delta H = \varphi_1 \varphi_2 V_1 (\delta_1 - \delta_2)^2 \quad (10)$$

φ : volume fraction, δ : SP value, V : molar volume

ΔH is small if the SP values are close, and ΔG tends to be zero or minus. Therefore, the principle that "like (similar SP) dissolve likes (similar SP)" was born.

Hansen expanded this formula to HSP.

$$\Delta G = \varphi_1 \varphi_2 V_1 \{ (\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \} - \Delta TS \quad (11)$$

The condition that $\Delta G < 0$ is satisfied;

$$(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 < \Delta TS / \varphi_1 \varphi_2 V \quad (12)$$

Therefore, the theory that the solvent dissolves a certain solute should be inside a sphere, radius = $(\Delta TS / \varphi_1 \varphi_2 V_1)^{0.5}$ (Hansen's dissolving sphere) is established. However, in the first paper published by Hansen in 1967, there was a coefficient of 4.0 before the dispersion term.

$$\text{Distance}_{1967} = \{4.0 * (\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2\}^{0.5} \quad (13)$$

For that reason, Hansen states as follows^[2].

”The dispersion interactions are fundamentally different from the polar and hydrogen bonding interactions, which are of a similar nature. The dispersion forces arise from atomic, induced dipole interactions, while the polar and hydrogen bonding forces are molecular in nature with the permanent dipole-permanent dipole interactions leading to the former. Thus it is not surprising that the effect of dispersion forces is not exactly the same as that of the directed, permanent polar and hydrogen bonding forces.”

In this way, attempts to divide the energy of vaporization into multiple components have been made variously, but the specific division method differs depending on each method. As far as the dispersion term is concerned, to determine the dispersion term, it is necessary to have the molar volume at 25 °C and the Dispersion portion of latent heat of vaporization. But there is no method for unambiguously obtaining this portion.

2. Result and Discussion

2.1. Semi-empirical Molecular orbital, MOPAC (ver. 2012) calculation

We assembled about 5,800 three dimensional molecular structures and carried out molecular orbital calculation with MOPAC. We used Model Hamiltonian PM7 and keyword PRECISE and POLAR for each molecule. We obtained optimized molecular structures and several calculation results such as heat of formation, HOMO and LUMO energy level, dipole moment, COSMO volume and surface, and Polarizability.

2.2. Molar volume at 25°C

In order to obtain Hansen solubility parameters, the molar volume at 25°C is required. It is calculated from the liquid density at 25°C with the scheme;

$$\text{Molar Volume} = \text{Molecular Weight} / \text{density at } 25^\circ\text{C}. \quad (14)$$

At present, the official values of HSP are defined for ~1,200 compounds. 8.3% of them are gas at 25°C and 19.7% are solid. In the case of solids, the density needs to be measured at several degrees above melting point temperatures, then by extrapolating to the temperature at 25°C, the molar volume at 25°C can be obtained. Molar volume can not be obtained for compounds decomposing or subliming above the melting point. The compounds that are gaseous at 25°C are liquefied using liquid nitrogen or other coolant. When the temperature is returned to 25°C with high pressure, it remains as liquid and it is described as the density at 25°C in the database. However, unlike the pressure effect for gas, the liquid hardly changes in volume (density) even when pressure is applied. Therefore, the liquid density at 25°C of a gaseous compound can not be used to calculate the molar volume.

The COSMO volumes that are calculated from the MOPAC optimized structures, correspond to the volume of a molecule in vacuum. When it liquefies, the volume shrinks according to the magnitude of the intermolecular force. With this COSMO volume and the volume used in HSP, the rate of contraction by liquefaction is plotted for each molecule as shown in Figure 1.

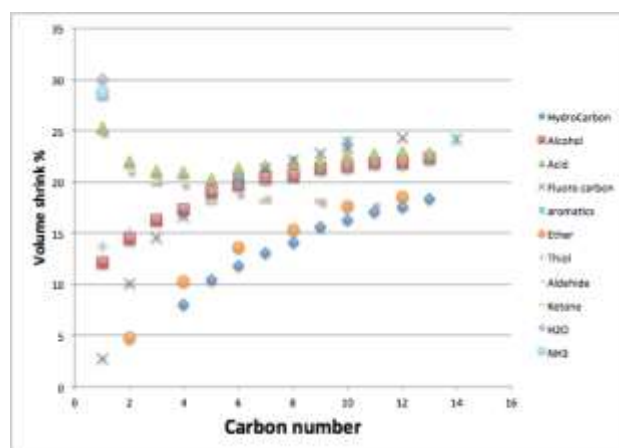


Fig. 1 The volume difference between theoretical COSMO volume and molar volume used in HSP.

For liquids such as water, ammonia and carboxylic acid, molar volume shrinks strongly due to strong hydrogen bond. Hydrocarbons and ether compounds show equivalent shrinkage, and smaller molecules shrink less. The shrinkage rate of the per-fluorinated molecules sharply increases as the number of carbon increases, which is thought to be accompanied by an increase in van der Waals force due to a very heavy fluorine atom. An interesting tendency appears for the classes of aldehydes, ketones and carboxylic acids.

When the molecule is small, it shrinks strongly, but as the molecule gets bigger the shrinkage decreases and the aldehyde and ketone curves come close to the hydrocarbon and ether curves. And the carboxylic acid shrinkage is close to that of alcohol. Such information is very important for analyzing the liquid phase structure of the real liquid. However, when attempting to calculate the volume with group contribution, the coefficient of each functional group needs to change depending on the size of the molecule. Therefore, in this study, we decided to use the COSMO volume which can neglect the change in molar volume due to molecular size and temperature effect.

By distributing this volume to the functional groups, the molecular COSMO volume can be calculated by the group contribution method.

2.2. Dispersion term at 25°C

Of the 1,200 compounds with official values of HSP, about 200 compounds are called core compounds. Before 1967, Hansen comprehensively and consistently determined from experimental values such as latent heat of vaporization, liquid density, critical constant, refractive index, dipole moment, dielectric constant, and so on. Thereafter, as the number of actual experimental values increased, about 480 compound HSPs were determined and treated as quasi core compounds. For compounds that are important as solvents (or solute) but are lacking experimental physical values, we used the results of estimation software, estimate from analogous compounds, the result from dissolution test using HSP known solvent, etc., to decide the official value.

Originally, in order to know the dispersion term δ_D of the solubility parameter, the latent heat of vaporization in scheme (3) must be divided into dispersion term, polarization term, hydrogen bond term. But more than half of official δ_D terms are obtained from estimation scheme (mainly group contribution method), refractive index, analogue, etc. You have to be careful about the “real” dispersion term.

First, we will consider compounds that do not have polarization and hydrogen bond terms. Hydrocarbon compounds and per-fluorinated compounds which do not have heteroatoms and multiple bonds do not have polarization terms nor hydrogen bond terms, so that the latent heat of vaporization of these compounds is allotted to the dispersion term.

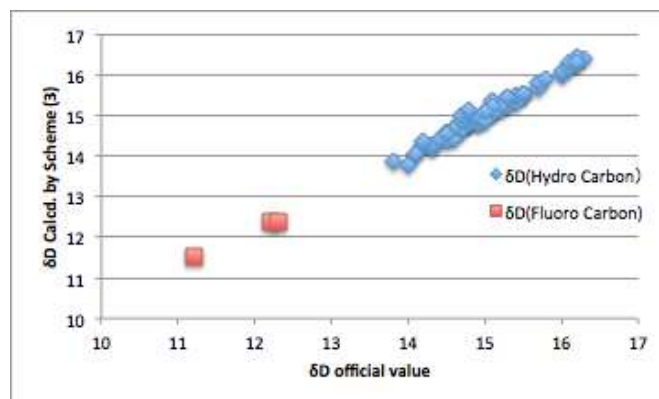


Fig. 2 Comparison of official δ_D and calculated δ_D with scheme (3)

If there is experimental latent heat of vaporization and liquid density at 25°C, it is possible to calculate the dispersion term satisfactorily as shown in Fig. 2. However, using scheme (7), calculated δ_D from the refractive index of the experimental value, it can be seen that there is a large error as shown in Fig. 3.

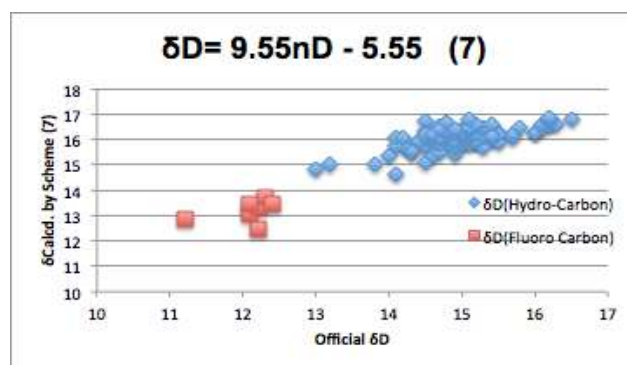


Fig. 3 Comparison of official δ_D and calculated δ_D with scheme (7)

This means that the dispersion force of London force that determines the refractive index is not the same as the dispersion force of Hansen.

2.3. Van Der Waals liquid

Dispersion force is known as weak attractive force acting between rare gas molecules. Single atoms such as He, Ne, and Ar take a closed shell electron structure and become very stable. These single atoms are a perfect spherical shape and are believed to liquefy from only very weak Van der Waals forces. When plotting the boiling point and the molecular weight of these rare gases, the curve becomes as shown in Fig. 4.

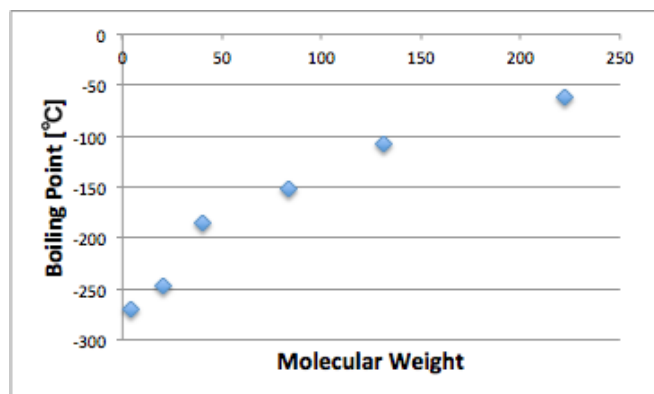


Fig. 4 The relationship between molecular weight of rare gas and its boiling point

Therefore, it can be said that at the standard boiling point of the rare gas, the van der Waals force and the kinetic energy of the molecule are balanced. Although the van der Waals force works not only with rare gas but with all molecules, and includes every kind of molecular interaction forces, we use this word in a narrow meaning. Considering interaction of rare gas, this force is thought to be very small. Here, when plotting the per-fluorinated molecules and hydrocarbon molecules with rare gases, per-fluorinated molecules' curve can be seen as almost being on the extension of the rare gas curve (Fig.5).

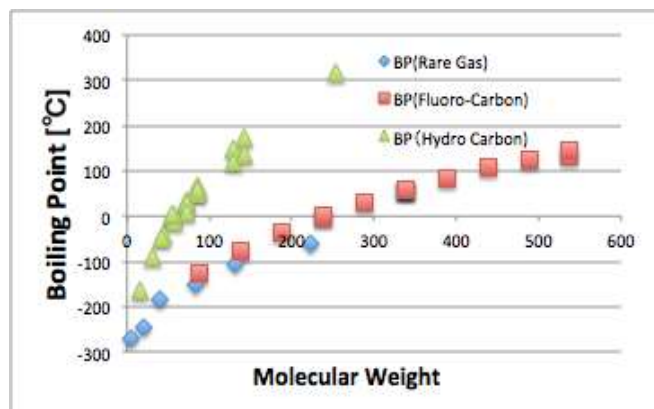


Fig. 5 The relationship between molecular weight of compounds and its boiling point

Therefore, it is suggested that the per-fluorinated molecules are liquefied with only weak van der Waals force like rare gases. If the per-fluorinated molecule and the rare gas have the same molecular weight, they have almost the same boiling point, but the hydrocarbon compounds need much higher temperature (ca. 2-300 °C) to boil even though the same molecular weight. This means that in addition to weak van der Waals interaction based on molecular weight, hydrocarbon molecules can be said to have large functional groups interactions.

Plotting the polarizability calculated by MOPAC with respect to the molecular weight (the polarizability of the rare gases are the literature values), as shown in Fig. 6, hydrocarbons have greater polarizability than per-fluorinated molecules and rare gases.

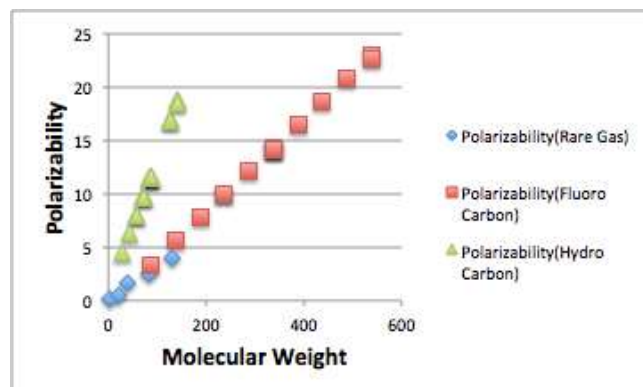


Fig. 6 Comparison of molecular weight and polarizability.

So the nature of higher boiling point of hydrocarbons is understood with the polarizability force.

This polarizability force decreases in the order of carbon > nitrogen > oxygen > fluorine. This is because the positive charge of the nucleus increases as it goes to the right of the periodic table, the restraint of electrons by the electric field of the nucleus becomes stronger, and the temporal fluctuation of the electron hardly occurs. Likewise, when going lower in the periodic table, the positive charges of the nucleus are shielded by the electrons of the inner shell, so that the electrons of the outermost shell are more susceptible to external electric field and the polarizability becomes larger. Since the polarizability of a molecule can be thought of as the sum of the polarizability of each atom, so the polarizability increases as the number of atoms increases.

This word “polarizability” is very confusing for the chemist. It is very similar to “polarity”. The polarity come from permanent dipole moment of molecule and the reason for the appearance of the dipole moment is difference of the electron negativity of atom. The electron negativity tendency is completely the reverse of polarizability.

2.4. Heat of vaporization and boiling point

It is known that there is a correlation between boiling point and latent heat of vaporization at boiling point. (Trouton rule)

In the case of latent heat of vaporization at 25 °C, although the correlation is slightly worse, the same relationship holds(Fig. 7).

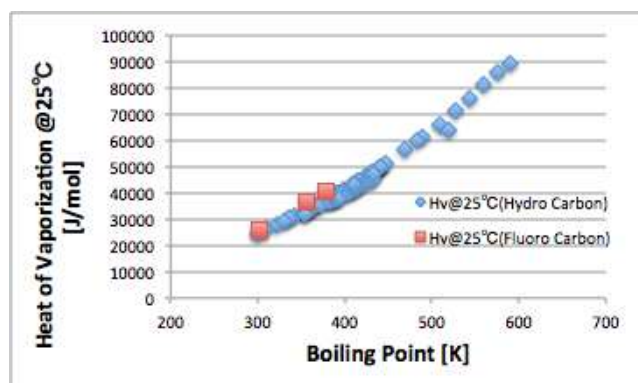


Fig. 7 The relationship between boiling point and heat of vaporization at 25°C

So heat of vaporization at 25°C is proportional to Boiling point. The boiling point and square root of molecular weight are also almost proportional as shown in Fig. 8.

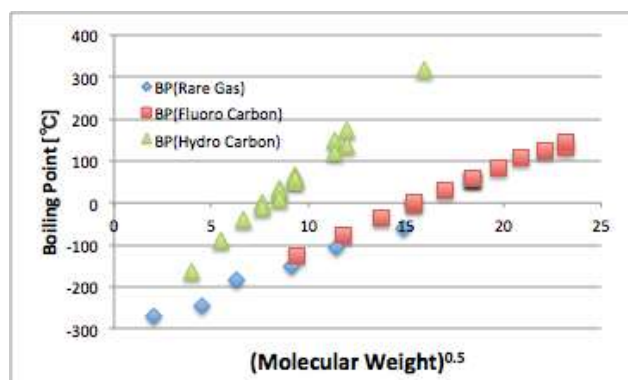


Fig. 8 The relationship between square root of molecular weight and boiling point

2.5. Dividing δ_D

There is a correlation between the boiling point and latent heat of vaporization. There is a correlation between the square root of molecular weight and boiling point. And the latent heat of vaporization has the relationship with the solubility parameter as the scheme (3). Therefore, when $\delta_D * (\text{COSMO-Volume})^{0.5}$ is plotted against the square root of molecular weight for the per-fluorinated compounds, a linear relationship is obtained (Fig. 9).

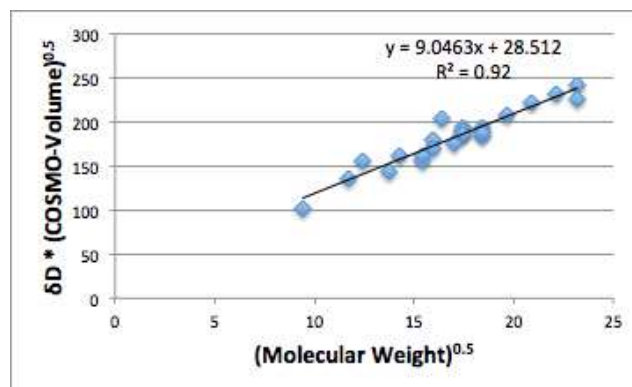


Fig. 9 The relationship between square root of molecular weight and $\delta_D * (\text{COSMO-Volume})^{0.5}$

We assumed that the per-fluorinated compounds have only the weak van der Waals interaction, so we obtained the definition of δ_{Dvdw} .

$$\delta_{Dvdw} = (9.0463 * MW^{0.5} + 28.512) / (\text{COSMO-Volume})^{0.5} \quad (14)$$

This δ_{Dvdw} is a value determined only from the molecular weight and the COSMO volume, and it can be said that all kinds of compounds have the scheme (14) force as a universal interaction force.

Hydrocarbon compounds, even with the same molecular weight as per-fluorinated compounds, have higher boiling points and higher latent heat of vaporization. It is defined as δ_{Dfg} by considering it as an interaction based on the polarizability of the functional groups.

Assuming that δ_D is obtained from latent heat of vaporization and volume at 25 °C, we can obtain δ_{Dfg} with the scheme (15).

$$\delta_{Dfg}^2 = \delta_D^2 - \delta_{Dvdw}^2 \quad (15)$$

When these forces are compared with normal alkane compounds, it becomes as shown in Fig. 10.

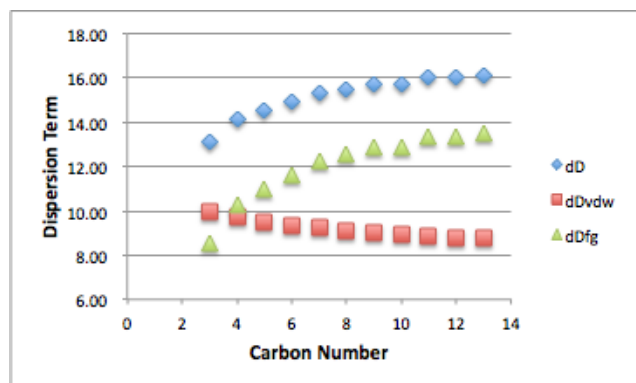


Fig. 10 The normal alkanes' δ_D , δ_{Dvdw} and δ_{Dfg} .

The δ_D gradually increases as the number of carbon increases. Conversely, δ_{Dvdw} decreases. This weak van der Waals force seems to correspond to the reduction of the surface area per unit volume as the molecule size become larger; this is because surface contact between molecules is the source of this force.

Since δ_{Dfg} depends on the polarizability of the functional groups, it increases as the molecule size increases. Up to now, these two effects have been a confusion for solubility theory. Polymers are generally denser than the monomers that make up polymer. Therefore, δ_D calculated from the functional groups constituting the polymer is increased with the increase of density. Therefore, a larger δ_D of the solvent is preferable for dissolving that polymer. When this is considered only via δ_D , a larger solvent is selected. However, as δ_D increases, δ_{Dvdw} decreases conversely. We know that some small solvents such as water have some specific solubility capabilities. We have to take into consideration both that small molecules are entropically advantageous and small molecules have large δ_{Dvdw} .

Through this division, HSP is made into four dimensions, but the value of δ_D itself does not change, Hansen space, Hansen's dissolving sphere, etc. can be handled as before. Indeed, the fact that Hansen space has been so successful in the past requires that any new theory must encompass the 3D approach. The only problems is the graphical viewing of Hansen space. In addition to the classical viewing of $[\delta_D, \delta_P, \delta_H]$, viewing with $[\delta_{Dvdw}, \delta_{Dfg}, (\delta_P^2 + \delta_H^2)^{0.5}]$ may be helpful.

2.6. New HSP Distance scheme

With the new HSP, a new HSP distance evaluation is carried out, replacing

$$\text{Distance}_{1967} = \{4.0 * (\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2\}^{0.5} \quad (13)$$

with

$$\text{Distance}_{2017} = \{(\delta_{Dvdw1} - \delta_{Dvdw2})^2 + (\delta_{Dfg1} - \delta_{Dfg2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2\}^{0.5} \quad (16)$$

Typical 19 kinds of solvents for solubility test were used for comparison.

Table 1 The typical 19 kinds of solvents

Code	name	dD	dP	dH	dDvdw	dDfg
7	acetone	15.5	10.4	7	10.63	11.28
92	butanol 1-Butanol, Butyl Alcohol	16	5.7	15.8	10.00	12.49
115	gamma-butyrolactone	16	16.6	7.4	11.11	14.16
148	chlorobenzene	19	4.3	2	10.95	15.53
255	diethyl ether	15.49	2.9	4.6	10.06	11.78
306	1,4-dioxane	17.5	1.8	9	10.90	13.69
326	monoethanolamine	16.8	6.8	20	10.79	12.87
375	2-butoxyethanol butyl cellosolve	16	5.1	12.3	9.83	12.63
491	4-methyl-2-pentanone MIBK	15.3	6.1	4.1	9.88	11.85
531	nitrobenzene	20	10.6	3.1	10.98	16.72
532	nitroethene	16	15.5	4.5	11.26	11.36
584	Propylene Carbonate	20	18	4.1	11.21	16.56
637	toluene	18	1.4	2	10.13	14.88
649	trichloroethylene	18	3.1	5.3	12.16	13.27
368	ethylene glycol	17	11	28	11.19	12.80
521	N-methyl-2-pyrrolidone NMP	18	12.3	7.2	10.40	14.69
599	2-pyrrolidone	18.2	12	9	10.83	14.63
612	1,1,2,2-tetrabromoethane	20.2	7	8.2	15.01	13.52
297	N,N-dimethylformamide DMF	17.4	13.7	11.3	10.54	13.84

For all combinations of solvents, both HSP distances are calculated and plotted (Fig. 11).

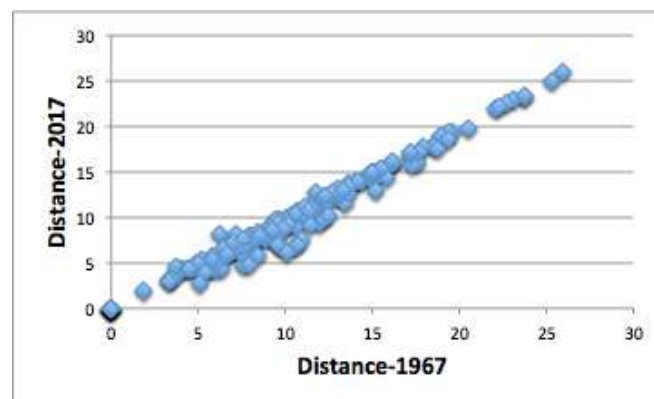


Fig. 11 Comparison Distance₁₉₆₇ and Distance₂₀₁₇

1,1,2,2-Tetrabromoethane, Nitrobenzene, Propylene carbonate and other compounds with $\delta_D > 19$ have large errors but Distance₂₀₁₇ has almost the same distance with Distance₁₉₆₇ even without the use of the number 4.

Generally, as the number of dimensions increases, the distance between vectors also increase. Let's examine this effect with Ethanol and Nitromethane.

Where Ethanol $\delta_T = 26.5$ and Nitromethane $\delta_T = 25.1$, in the one-dimensional SP value, the difference in SP value is only 1.4.

However, in terms of three dimensions [$\delta_D, \delta_P, \delta_H$], ethanol = [15.8, 8.8, 19.4], nitromethane = [15.8, 18.8, 5.1], then the Euclidian distance become 17.4. (Fig. 12, purple line).

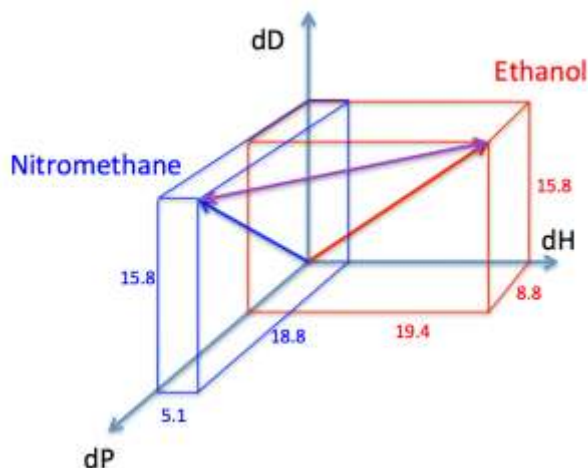


Fig. 12 3-dimensional view of HSP.

We had thought that δ_D originated only from one force. Then, Hansen's solubility region does not become a sphere when displayed in a three-dimensional graphic. So Hansen expanded δ_D axis twice to make Hansen Space, and the solubility region becomes a sphere. Not only for the graphical view problem but also for the actual dissolution test, double expansion of δ_D has been necessary. So, for 50 years the number of 4 has been, rightly, used.

However, the new distance equation shows the same distance as the classic distance by dividing δ_D to δ_{Dvdw} and δ_{Dfg} .

$$(\delta_{D1}-\delta_{D2})^2 < (\delta_{Dvdw1}-\delta_{Dvdw2})^2 + (\delta_{Dfg1}-\delta_{Dfg2})^2 \quad (17)$$

When the left side is multiplied by 4, it is almost equal to the right side.

2.7. Validation of new HSP distance

In order to investigate the validity of this new distance scheme, we applied it to the solubility of the polymer. Hansen examined the solubility of 33 kinds of polymers using 88 kinds of solvents in 1967. These results are summarized in HSPiP software as examples. We used these examples. We apply the classic distance

to solubility data using HSPiP software to determine Hansen's dissolving sphere. The sphere center is assigned as the polymer's HSP, and the radius of sphere is assigned as interaction radius. In almost all cases there are several exceptions noted as "Wrong in" or "Wrong out".

"Wrong in" means that a certain solvent is located inside the Hansen's dissolving sphere but actually does not dissolve the polymer. This may be due to the fact that the solvent size is too large and can not penetrate inside the polymer. On the contrary, "Wrong out" should not dissolve from the point of HSP but it in fact does dissolve the polymer, perhaps due to entropic effects because the molecular size is small.

The solubility of these polymers was similarly studied using the newly developed HSP and the new distance scheme. The algorithm for finding the center and radius of the sphere is to make the total sum of "Wrong in" and "Wrong out" as small as possible and to search for a smaller radius of the dissolving sphere. So the algorithm of fitting is different, and can not be compared exactly, but the results are shown in Fig. 13.

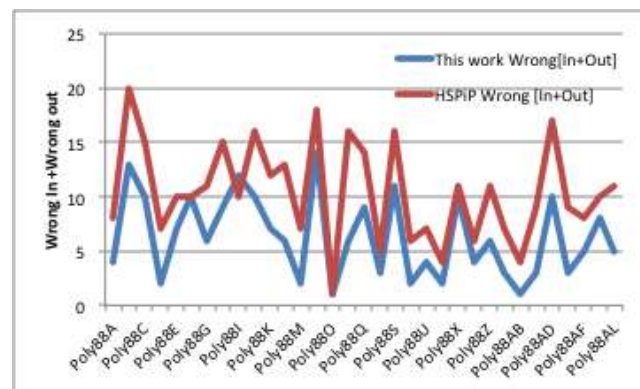


Fig. 13 False fit numbers.

With one exception, the number of "Wrong" solvents has decreased greatly.

Also, the radius of the dissolving sphere of each polymer is plotted as shown in Fig. 14.

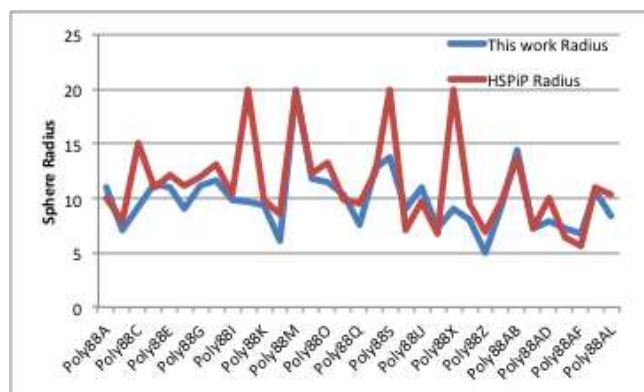


Fig. 14 The radius of Hansen's dissolving sphere

In many cases, the radius of the dissolving sphere is found to be smaller.

Compounds which greatly differ between Distance₁₉₆₇ and Distance₂₀₁₇ are compounds having $\delta_D > 19$. Among the 88 solvents in which the solubility of the polymer was investigated, there are 10 kinds of solvents having $\delta_D > 19$. The misperception rate of these solvents was examined. In Distance₁₉₆₇, the misperception rate was 7.4%, but in Distance₂₀₁₇ it was 4.5%. It is thought that this is due to the fact that the coefficient of 4.0 is too large for these cases.

$$4.0 * (\delta_{D1} - \delta_{D2})^2 = (\delta_{Dvdw1} - \delta_{Dvdw2})^2 + (\delta_{Dfg1} - \delta_{Dfg2})^2 \quad (17)$$

Suppose, Solvent1 $\delta_D(\delta_{Dvdw}, \delta_{Dfg}) = 20(20^{0.5}, 20^{0.5})$ and Solute2 $\delta_D(\delta_{Dvdw}, \delta_{Dfg}) = 16(16^{0.5}, 16^{0.5})$ are put into scheme (17).

$4 * (20 - 16)^2 = 64 \gg 0.446 = (20^{0.5} - 16^{0.5})^2 + (20^{0.5} - 16^{0.5})^2$.
As the result, when having large δ_D , Distance₁₉₆₇ over estimate the distance. So, we can conclude that using the new distance instead of the classic distance is advantageous.

2.8. Reproduction of new HSP by group contribution method

Many physical properties such as critical constants, boiling point, refractive index, molar volume are estimated using the group contribution method. It should be noted here that there are two types of physical properties, boiling point type and density type. The boiling point type of physical properties are approximately doubled if the number of functional

groups constituting the compound is doubled. Physical properties of this type can be estimated by the group contribution method. However, even if the number of groups is doubled, the density type of properties do not become doubled. In that case, the relationship of density = molecular weight / molar volume is used. The molar volume and molecular weight show boiling point type properties, and they are estimated by using the group contribution method and converted to density. So, which property type is the solubility parameter?

From the fundamental solubility parameter scheme (3), we obtained scheme (18).

$$\delta^2 * V_A + RT = \Delta H_v \quad (18)$$

The right side of equation, ΔH_v is a boiling point type of property, so we can estimate both side by using group contribution method.

This concept is common to the method for estimating the solubility parameter. For the example of polymers, the solubility parameter is calculated as the square root of the cohesive energy density (C.E.D) divided by unit volume. C.E.D and unit volume are calculated by group contribution method. The Fedors method and the Van Krevelen method have been popular.

Let's build an estimation scheme for hydrocarbon and per-fluorinated compounds. There are 169 compounds whose δ_D were determined. Then these compounds were divided into functional groups. The necessary functional groups are seven, **CH₃**, **CH₂**, **CH**, **C**, **CF₃**, **CF₂** and **CF**. Here, we used the COSMO volume as molar volume. The R is gas constant and T is 298.15K, so we have the left side of equation (18) and functional groups set. We determined each group contribution coefficients.

$$\begin{aligned} \delta^2 * V_A + RT &= \Delta H_v \\ &= 4895.853 * \mathbf{CH_3} + 6233.337 * \mathbf{CH_2} + 5985.316 * \mathbf{CH} + 5089 \\ &\quad .445 * \mathbf{C} + 11482.367 * \mathbf{CF_3} + 3990.937 * \mathbf{CF_2} - \\ &\quad 4460.700 * \mathbf{CF} \quad (19) \end{aligned}$$

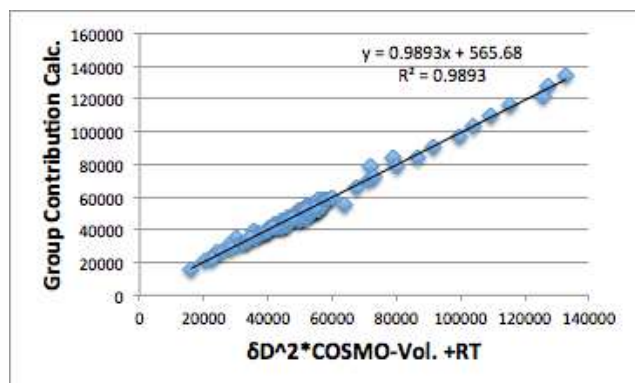


Fig. 15 The group contribution calculation result.

It is obvious from scheme (18), that if the groups are all 0, the answer is 0.

If the accuracy of estimation is insufficient, we identify compounds that lower the estimation accuracy and introduce new groups that characterize the compounds. In many cases, a larger group such as a tertiary butyl group is added. But for simplicity here we proceed with this result.

Since V_A and RT are known, δ_D is calculated and compared with the original δ_D .

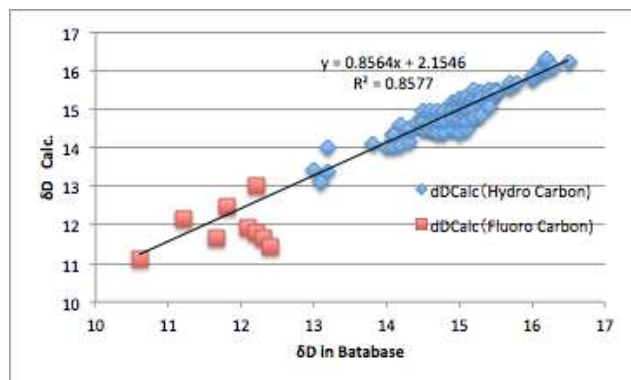


Fig. 16 reproducibility of the δ_D

Then it turns out that the accuracy of the calculation is very low. (Fig. 16) The first problem in this

relationship is that the slope of the formula is not 1, the intercept is not 0.

In the extreme case, if the original δ_D is 0, the calculated value δ_D will be 2.15.

Let's see Fig. 10 again.

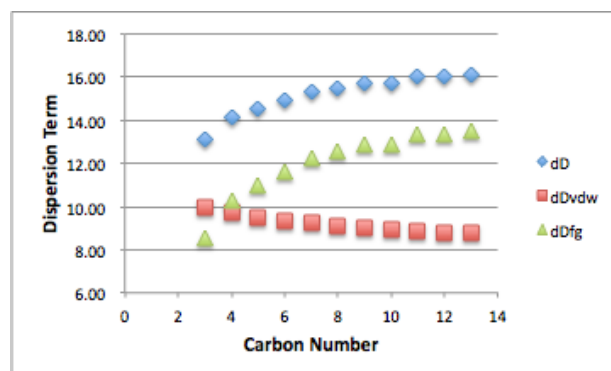


Fig. 10 The normal alkanes' δ_D , δ_{Dvdw} and δ_{Dfg} .

Originally, it is the term of δ_{Dfg} that can be estimated by the group contribution method. The term of δ_{Dvdw} is a term that decreases as the number of group increases. The δ_D term combining these two terms can not be estimated adequately by the group contribution method. Therefore, because per-fluorinated compounds have almost no δ_{Dfg} term, but have only a δ_{Dvdw} term, the predicted δ_D values show large errors.

Since δ_{Dvdw} is a value calculated from molecular weight and COSMO volume, it is strictly determined for each compound. Therefore, we build a group contribution scheme for δ_{Dfg} , δ_P , δ_H and COSMO volume. We summarized the result in Table 2. By using this table, new HSP can be easily obtained. We explain how to use butyl acetate as an example. (The contribution of δ_D is given as a reference value.)

Table 2 The coefficient list of standard Functional Groups

Label	dD	dDfg	dP	dH	CosVol	MW	Label	dD	dDfg	dP	dH	CosVol	MW
CH3	12.9	7.5	0.7	0.1	28.85	15.034	NH	20.7	17.8	9.7	14.9	16.53	15.018
CH2	16.4	14.3	1.5	0.9	22.05	14.026	NH_R	19.0	15.5	14.1	18.3	16.41	15.018
CH2_R	17.0	13.7	1.7	1.9	21.65	14.026	NH@Ar	30.7	28.7	16.6	23.6	15.08	15.018
CH2:	11.0	0.0	3.2	4.2	26.50	14.026	N	25.2	24.7	9.3	11.9	10.27	14.01
CH	21.2	21.6	0.1	0.0	14.67	13.018	N_R	25.0	22.2	7.6	19.5	9.26	14.01
CH_R	19.1	18.0	0.0	0.0	14.57	13.018	N@Ar	30.3	31.3	0.0	16.4	12.07	14.01
CH:	19.0	16.8	0.1	0.1	18.26	13.018	C#N	17.0	12.5	21.8	9.6	34.12	26.02
CH:_R	17.3	14.0	2.3	5.3	17.95	13.018	C#N@Ar	18.9	14.8	20.8	4.4	34.00	26.02
CH:reso	18.3	14.9	0.1	4.8	17.84	13.018	NO2	17.9	12.4	20.6	6.9	40.26	46.01
#CH	14.2	9.2	3.6	4.1	24.50	13.018	NO2@Ar	19.3	14.0	15.7	7.6	38.78	46.01
C	33.3	37.2	0.1	5.3	5.48	12.01	SH	19.1	15.0	9.0	9.7	36.40	33.078
C_R	31.7	32.5	0.1	0.0	6.58	12.01	SH@Ar	22.6	19.0	3.1	9.1	37.17	33.078
C:	26.0	26.6	0.0	0.0	10.42	12.01	S	23.4	20.6	7.0	6.9	28.33	32.07
C:_R	25.4	25.3	0.1	4.7	10.64	12.01	S_R	23.1	19.2	11.4	11.6	28.15	32.07
C:reso	24.5	24.0	1.0	0.1	10.12	12.01	S@Ar	27.2	24.9	9.7	0.0	28.20	32.07
C:rrr	25.3	24.1	0.1	1.1	10.92	12.01	S:O	23.8	20.5	21.0	9.4	38.82	48.07
#C	19.6	16.7	7.7	6.6	14.87	12.01	NHCO	21.3	17.2	23.1	17.5	42.13	43.028
OH	18.4	11.3	16.6	36.6	18.05	17.008	NHCO_R	23.7	20.6	24.0	13.1	42.67	43.028
2_OH	18.6	12.6	15.0	32.2	18.29	17.008	NCO	24.4	21.8	22.3	13.6	34.89	42.02
3_OH	19.8	15.7	12.4	25.3	18.58	17.008	NCO_R	22.6	19.7	19.2	12.5	36.30	42.02
OH@Ar	17.3	10.7	13.5	28.8	18.84	17.008	OCOO	17.6	13.5	10.9	9.6	47.85	60.01
O	17.8	12.1	12.2	10.9	11.97	16	OCOO_R	19.5	14.5	29.0	10.3	50.20	60.01
O_R	18.0	11.7	13.1	12.4	12.06	16	CF3	10.7	0.0	1.8	0.0	52.73	69.01
O@Ar	22.0	18.0	16.1	16.7	11.30	16	CCI3	17.9	13.2	0.0	0.0	94.36	118.36
C:O	20.8	17.4	14.0	9.6	25.69	28.01	CF2	13.4	3.5	0.0	1.1	36.24	50.01
C:O_R	22.4	18.9	15.1	8.9	26.16	28.01	CCI2	18.8	13.6	6.6	4.3	62.76	82.91
C:O@Ar	23.3	19.9	16.8	7.7	25.54	28.01	CF	15.9	7.8	0.0	0.0	21.27	31.01
HCO	17.1	12.4	14.5	10.4	34.57	29.018	CCI	20.6	18.2	6.7	3.9	36.98	47.46
CHO@Ar	18.2	14.0	18.4	12.4	33.72	29.018	F	0.1	0.1	0.0	4.6	14.84	19
COOH	17.9	13.2	11.8	22.1	44.37	45.018	Cl	16.4	8.7	0.0	0.0	27.46	35.45
COOH@A	19.4	15.1	11.4	19.4	43.99	45.018	Br	19.8	10.2	7.1	6.3	36.43	79.9
COO	19.0	15.2	8.1	10.8	37.02	44.01	I	21.0	11.4	5.6	5.2	47.22	126.9
COO_R	19.3	14.2	25.9	11.6	38.47	44.01	Si	10.7	11.3	0.0	0.0	29.98	28.09
COO@Ar	17.6	14.3	13.6	6.3	37.69	44.01	P	17.7	13.7	6.5	0.0	30.30	30.97
NH2	17.7	12.1	10.2	17.1	22.95	16.026	B	20.5	18.8	0.1	0.0	13.34	10.81
NH2@Ar	20.6	16.2	13.7	24.2	22.30	16.026							

Table 3 Calculation of Butyl acetate's new HSP

Group	δ_D	δ_{Dfg}	δ_P	δ_H	Vol	MW	No
CH3	12.9	7.5	0.7	0.1	28.85	15.034	2
CH2	16.4	14.3	1.5	0.9	22.05	14.026	3
COO	19	15.2	8.1	10.8	37.02	44.01	1
Total					160.88	116.16	

You need to select the necessary functional groups from the table and decide the number of atomic groups constituting the molecule. Molar volume and molecular weight are determined immediately. The sum of δ allocated to each functional group uses an equation for calculating the mixed solvent's HSP.

$$\delta_{\text{mix}} = (\delta_1 * \text{Vol}_1 + \delta_2 * \text{Vol}_2) / (\text{Vol}_1 + \text{Vol}_2) \quad (20)$$

Each term is calculated as follow:

$$\delta_D = (12.9 * 28.85 * 2 + 16.4 * 22.05 * 3 +$$

$$19.0 * 37.02 * 1) / 160.88 = 15.76 \text{ (Just reference)}$$

$$\delta_{Dfg} = (7.5*28.85*2 + 14.3*22.05*3 + 1.5*37.02*1)/160.88 = 12.03$$

$$\delta_P = (0.7*28.85*2 + 1.5*22.05*3 + 8.1*37.02*1)/160.88 = 2.75$$

$$\delta_H = (0.1*28.85*2 + 0.9*22.05*3 + 10.8*37.02*1)/160.88 = 2.86$$

From definition (Scheme 14)

$$\delta_{Dvdw} = (9.0463*MW^{0.5} + 28.512)/(COSMO-Volume)^{0.5} = 9.93$$

$$\delta_D = (\delta_{Dvdw}^2 + \delta_{Dfg}^2)^{0.5} = (9.93^2 + 12.03^2)^{0.5} = 15.6$$

The calculation result of group contribution become;

$$[\delta_D(\delta_{Dvdw}, \delta_{Dfg}), \delta_P, \delta_H] = [15.6(9.93, 12.03), 2.75, 2.86]$$

The official Butyl acetate's HSP is;

$$[\delta_D, \delta_P, \delta_H] = [15.8, 3.7, 6.3]$$

So the dispersion term estimation can be said to be good enough.

As for the polarization term, the calculated value is a little too small. Although this is originally a value calculated from the dipole moment (and dielectric constant) of a molecule, since the group contribution method divides the molecule into functional groups, information on where in the molecule the ester group was introduced is lost. Therefore, it is computed as an average value and is slightly smaller. To solve this we need to define larger groups. In the HSPiP software, since the butyl group is defined, it is closer to the official value.

Regarding the hydrogen bond term, it is much smaller than the official value. This comes from the uncertainty of how to obtain the hydrogen bond term of Hansen's solubility parameter. δ_T is determined from latent heat of vaporization of solvent and molar volume. Then, δ_P is determined from dipole moment (and dielectric constant), δ_D is determined from the refractive index. Then, δ_H is calculated from the following equation.

$$\delta_H^2 = \delta_T^2 - \delta_D^2 - \delta_P^2 \quad (21)$$

All the remaining forces are put in δ_H .

Since ester compounds originally do not have active hydrogen, there is no hydrogen bonding term similar to hydroxyl group. However, when calculating the group contribution of the δ_H term, the force evaluated as a hydrogen bond term appears statistically.

2.9. Further insight

When solvents are defined by the set of new HSP, new insights about solubility can be obtained. For example, if you search a database for a solvent with HSP [$\delta_D, \delta_P, \delta_H$] equivalent to butyl acetate, you will find;

$$\text{Butyl acetate} = [15.8, 3.7, 6.3]$$

$$\text{Methyl propyl amine} = [15.7, 3.9, 5.9]$$

$$\text{Tridecanoic acid} = [16.2, 3.3, 6.4]$$

We calculated these solvents by using the group contribution method and obtained HSP [$\delta_D(\delta_{Dvdw}, \delta_{Dfg}), \delta_P, \delta_H$].

$$\text{Butyl acetate} = [15.6(9.93, 12.03), 2.75, 2.86]$$

$$\text{Methyl propyl amine} = [15.0(9.73, 11.43), 2.27, 2.44]$$

$$\text{Tridecanoic acid} = [16.3(9.06, 13.49), 2.89, 3.78]$$

Comparing with δ_D , the largest difference is only 1.3, but it is 0.87 for δ_{Dvdw} and 2.06 for δ_{Dfg} . For example, when compared with small molecules such as water [15.5(13.34, 7.89), 16, 42.3], the largest difference in δ_D is 0.8, but it appears as a very large difference (7.0) using $\delta_{Dvdw}, \delta_{Dfg}$.

So the calculated new HSP are also very similar even though the δ_{Dvdw} values reflects the size of the molecule.

Then would they show the same solubility if the new HSP were almost the same?

A characteristic group part of HSP [$\delta_D(\delta_{Dvdw}, \delta_{Dfg}), \delta_P, \delta_H$] is extracted as follows.

$$\text{Ester} = [18.98(14.55, 15.19), 8.14, 10.77] \text{ Vol.} = 37.02$$

$$\text{NH} = [20.67(15.64, 17.79), 9.69, 14.93] \text{ Vol.} = 16.53$$

$$\text{COOH} = [17.9(13.4, 13.2), 11.8, 22.1] \text{ Vol.} = 44.37$$

It is obvious that these are located very far away in the 4-dimensional space. Whether it is 3D or 4D, the HSP

of the solvent is expressed as an average value of the molecule. Even if the partial HSP is greatly different, depending on the type, number of other groups and volume, the average value may become similar.

It seems that this is the cause of less than 100% predictability of polymer solubility even using new HSP.

3. Conclusion

The dispersion term (δ_D) of the HSP was divided into the $\delta_{D_{vdw}}$ term based on the weak van der Waals force and the $\delta_{D_{fg}}$ term based on the functional group interaction.

The HSP distance using this new HSP was the Euclidean distance of a simple vector.

We have developed an group contribution method to conveniently calculate new HSP.

MOPAC polarizability calculation may help obtaining theoretical δ_D but need further considerations.

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