Hansen Solubility Parameters 50th anniversary conference, preprint 2017 PP. 22-36(2017)

Consideration of Hansen Solubility Parameters. Part 3

Donor/Acceptor interaction

HSPiP Team: Hiroshi Yamamoto, Steven Abbott, Charles M. Hansen

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. When these HSP are applied to, for example, pigment dispersion for paints, problems have been pointed out such as the inability to evaluate the difference in dispersibility between acidic and basic pigments. Many attempts have been made to divide this hydrogen bond term into Donor (Acid) and Acceptor (Base). But when we were building HSP distance equation, we could not correctly evaluate the donor/acceptor interaction. In this paper, we used Gutmann's Donor Number (DN), Acceptor Number (AN) obtained from the solvation energy of mixing via spectroscopic analysis of mixing the solvent with a probe solute. The donor/acceptor property of the whole molecule obtained here is allocated to the functional groups constituting the molecule, and an expression that can easily calculate the donor and acceptor of the molecule was developed. By introducing this donor/acceptor, a deeper analysis of solubility in water, liquid-liquid extraction, dispersibility of pigment, vapor-liquid equilibrium become possible.

Key Words: Hansen Solubility Parameter, Donor, Acceptor

1. Introduction:

1.1. The Solubility Parameter and Acid/Base

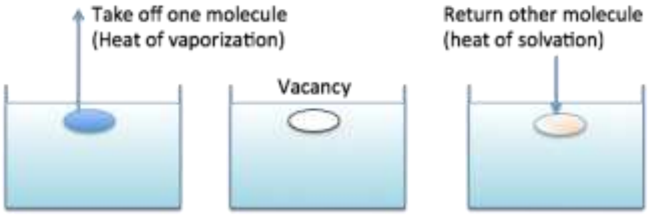


Fig.1 Solubility concept

When considering taking out one molecule from solution and returning another molecule to it, the free energy of mixing is expressed by Eq. (1).

$$\Delta G=\Delta H-\Delta TS \quad (1)$$

Mixing occurs when ΔG is zero or negative. At that time, ΔH can be written with the Eq. (2).

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

φ：volume ratio, δ：SP value

If the solubility parameter of 2 molecules are similar, ΔH becomes small, and ΔG tends to be zero or minus. With this handling, the Heat of Solvation's energy is ignored as not being large and we think only of Heat of Vaporization. However, when Acid/Base mixing is involved, the heat of solvation can not be ignored because of the large heat of neutralization.

Acid/Base has roughly two types of definition.

Brønsted-Lowry Acid/Base:

Brønsted and Lowry defined the acid as "able to emit H+" and the base as "able to receive H+". A Brønsted acid is a proton donor, and a Brønsted base is a proton acceptor. It is a definition applicable to any substance having active hydrogen. Compounds without an active hydrogen cannot be a Brønsted Acid.

Lewis Acid/Base:

In the definition Lewis submitted in 1923, an acid is any substance that receives an electron pair, and a base is any substance that donates an electron pair. The acid applicable to this definition is called Lewis acid, and the base is called Lewis base. That is, a Lewis acid is an electron pair acceptor, and a Lewis base is an electron pair donor. It is the most general and applicable definitions for substances without active hydrogen. Since it is a value defined without having active hydrogen, it is common to describe it as (Electron Pair) Donor/Acceptor instead of Acid / Base. Clearly, the division of the δ_H term must be done with this Lewis Donor/Acceptor definition.

Attempts to introduce acidity and basicity into solubility parameters have been made since many years ago.

1.2. Pioneering research of Beerbower

Beerbower, Martin, and Wu [1],[2] developed a four-component approach to the solubility of solids in polar and non-polar systems.

$\delta_T^2 = \delta_D^2 + \delta_O^2 + 2*\delta_a*\delta_b$ (3)

D:Dispersion, O:Orientation, a:Acid, b:Base

If δ_O is identified with δ_P and $\delta_H^2 = 2*\delta a*\delta b$, the three-component Hansen parameters are recovered.

$\delta_H^2 = 2*\delta a*\delta b$ (4)

For binary system i, j, free energy is determined with following scheme (5).

${}^{ij}A = ({}^i\delta_D - {}^j\delta_D)^2 + ({}^i\delta_P - {}^j\delta_p)^2 + 2({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^j\delta_b)$ (5)

The δ_p and δ_D values were based on those of Hansen and Beerbower. The value of δ_b can be determined [3] from the spectroscopic proton-accepting parameter β. δ_a can then be calculated from $(\delta_T^2 - \delta_d^2 - \delta_p^2)/ 2*\delta_b$.

1.3. HSPiP Method

We divided the δ_H term by using Abraham's Acid/Base value [4]. We have Abraham Acid/Base values for 915 compounds. The Acid value for 536 of those compounds is 0. The compounds having a significant value as Acid are carboxylic acids, alcohols, amines compounds, and halogen-containing compounds have a slight Acid value. Therefore Abraham's Acid/Base is in the sense of Brønsted-Lowry. In order to avoid confusion here, the notation of $\delta_{HAcid}/\delta_{HBase}$ is used. The used rules of division were the following three.

Rule 1: $\delta_H^2 = \delta_{Hacid}^2 + \delta_{Hbase}^2$

Rule 2: $\delta_{Hacid}:\delta_{Hbase}$ = Abraham Acid:Base

Rule 3: If we have no other way to decide, make δ_{Hacid}=0 and δ_{Hbase}=δ_H.

For example, in the case of acetone, if δ_D term and δ_P term are subtracted from the δ_T, there will remain the δ_H term. However, since it has no active hydrogen, it does not have a δ_{Hacid} term and it has only the δ_{Hbase} term.

1.4. Gutmann DN(Donor Number), AN(Acceptor Number)

The donor number (DN) of Gutmann is defined as -ΔH (in kcal/mol) for the reaction between a given Lewis base and $SbCl_5$ as the reference acid, and the numbers are evaluated in very dilute solutions of the reactants in 1,2-dichloroethane as the solvent [5]. The broad scale of donor numbers ranges from 0.1 for benzene to 61.0 for triethylamine. An extensive empirical correlations between DN values and the effects of donor solvents upon redox and ligand substitution reactions have been developed by Gutmann.

The Gutmann acceptor number (AN) values are spectral parameters derived from the ^{31}P NMR shift for triethylphosphine oxide as the reference base dissolved in single solvents or in mixed solvents [5]. However, AN-scale values are normalized shift numbers based upon an assigned value of 100 for the 1:l adduct, $SbC1_5$:Et_3P=O, in 1,2-dichloroethane and for n-hexane as zero for the reference solvent.

Gutmann's DN and AN is definitely Lewis' Acid/Base, so it is truly a Donor/Acceptor methodology.

A connective function between DN and AN has been developed [6].

1.5. Comparison of these Acid/Base values

For various solvents, we collected Gutmann's DN and AN value and compared with the parameters of Abraham, Taft and Beerbower Acid/Base.

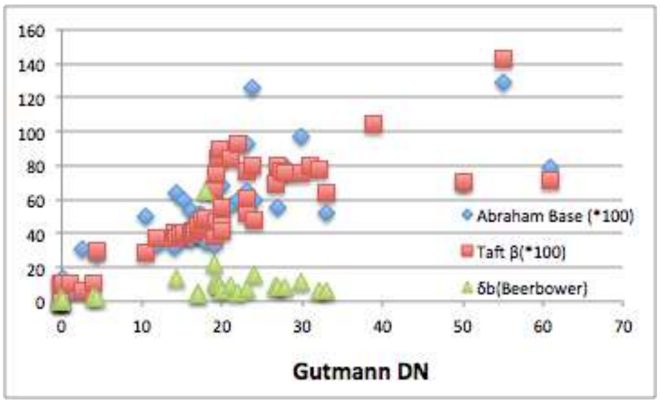


Fig. 2 Gutmann DN vs other base.

Abraham's Base is a Brønsted Base, but it is highly correlated with Gutmann's DN in the large values region. Although δ_b of Beerbower is calculated from β of Taft, the value of δ_b becomes almost constant even if β increases. That means, δ_b is neither an indicator of basicity nor acceptor properties.

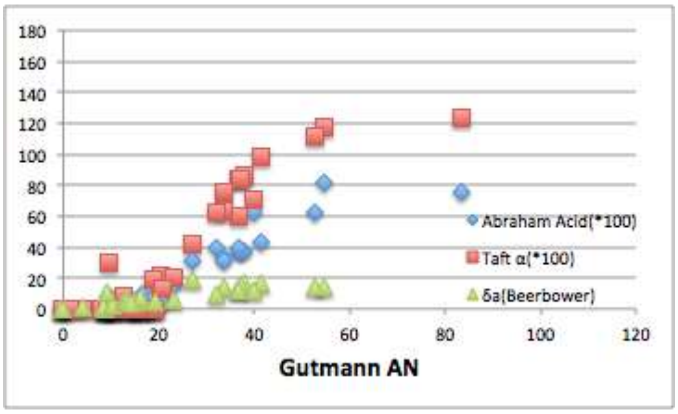


Fig. 3 Gutmann AN vs other acid

Since Gutmann's AN is calculated from the ^{31}P NMR chemical shift, it has a very high correlation with Abraham's Acid. The δ_a of Beerbower are almost constant in comparison with other parameters, so δ_a does not indicate acidity or Donor property. This is thought to come from the restriction of Equation (4).

$\delta_H^2 = 2*\delta_a*\delta_b$ (4)

Even if the molecule has an acidic moiety like a carboxylic acid, as the molecule becomes larger, the hydrogen bond contribution part of the whole molecule is diluted. So the δ_H term becomes smaller. However, if molecule has an acidic part, Abraham's Acid and α of Taft have almost the same value regardless of the size of the molecule. Therefore, equation (4) is not valid.

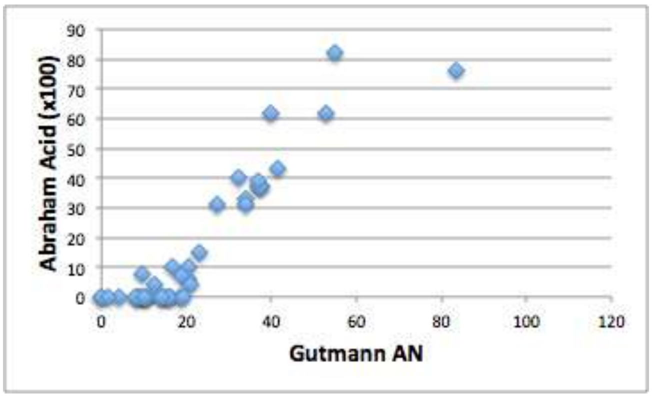


Fig. 4 Gutmann AN vs Abraham Acid

If we examined the Gutmann's AN <20 region, Abraham's Acid value becomes 0 because they are Brønsted Acid, but even for molecules having no active hydrogen, Gutmann's AN exist because they are Lewis Acids.

Lewis acid-base interactions are "unsymmetrical", involving a donor and an acceptor with different roles (rather than two equivalent participants as in dispersion interactions, which are "symmetrical"). It is apparent, therefore, that it is necessary to use two separate cohesion parameters for each partner to characterize these interactions, and this may be done in terms of a Lewis acid cohesion parameter (δ_a) and a Lewis base cohesion parameter (δ_b), in a manner analogous to that for induction interactions:

${}^{ij}A_{ab}= 2({}^{i}\delta_a - {}^{j}\delta_a)({}^{i}\delta_b - {}^{j}\delta_b)$ (6)

However, in Brønsted-Lowry Acid/Base, for example in the case of acetone, since δ_a is 0, equations (4) and (6) cannot capture the true interactions.

2. Results and Discussion

2.1. Solubility of Oleic acid

First, in order to investigate the effect of Acid/Base, the solubility of Oleic acid was investigated. Solubility in various solvents, HSP, Beabower's δa, δb Gutmann's DN, AN values are summarized in Table 1.

To evaluate the solubility of Oleic acid, we replaced the standard (1967) HSP distance with the new (2017) Distance which was explained at Part 1 of this preprint.

$\mathrm{Distance}_{1967}=\{4.0*(\delta_{D1}-\delta_{D2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2\}^{0.5}$ **(7)**

$\mathrm{Distance}_{2017} = \{(\delta_{Dvdw1}-\delta_{Dvdw2})^2+(\delta_{Dfg1}-\delta_{Dfg2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2\}^{0.5}$ (8)

2.2 Evaluation of the Beerbower's method

As δb, δa of Beerbower is Donor/Acceptor, so we introduced equation (6) into the distance equation.

$\mathrm{Distance\text{-}Beerbower} = \{(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + 2(\delta_{a1} - \delta_{a2})(\delta_{b1} - \delta_{b2})\}^{0.5}$ (9)

The solubility of oleic acid is evaluated with Distance-2017 and Distance-Beerbower as shown in Fig.5. [In the case of Diethyl ether, the Distance-Beerbower becomes negative and the square root of this scheme cannot be obtained.] The results were almost the same with the distance$_{2017}$ and showed no effect of dividing δ_H.

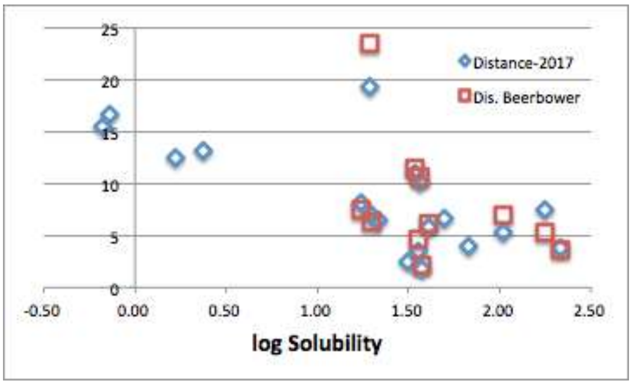
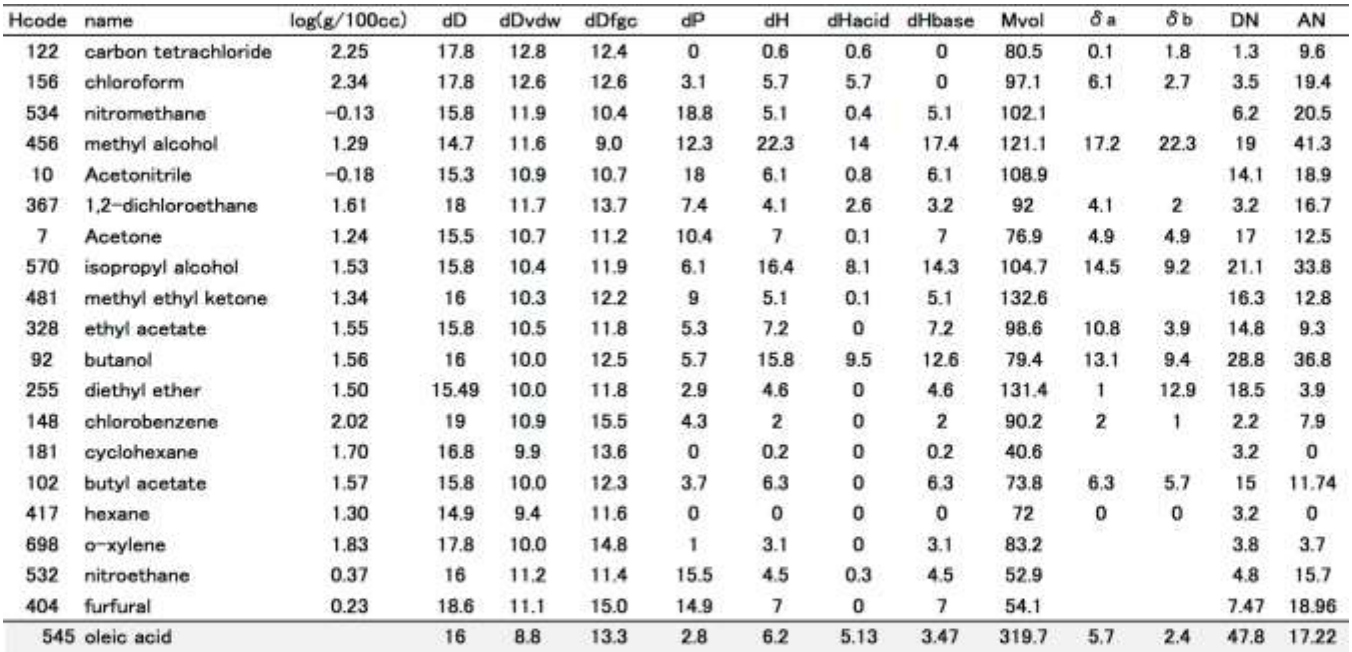


Fig.5 The solubility of Oleic Acid and Distances.

This problem suggests that the handling of equation (4) was wrong as pointed out earlier.

Table 1 The solubility of Oleic acid and HSP with Acid/Base parameters.



Hcode	name	log(g/100cc)	dD	dDvdw	dDfgc	dP	dH	dHacid	dHbase	Mvol	δ a	δ b	DN	AN
122	carbon tetrachloride	2.25	17.8	12.8	12.4	0	0.6	0.6	0	80.5	0.1	1.8	1.3	9.6
156	chloroform	2.34	17.8	12.6	12.6	3.1	5.7	5.7	0	97.1	6.1	2.7	3.5	19.4
534	nitromethane	-0.13	15.8	11.9	10.4	18.8	5.1	0.4	5.1	102.1			6.2	20.5
456	methyl alcohol	1.29	14.7	11.6	9.0	12.3	22.3	14	17.4	121.1	17.2	22.3	19	41.3
10	Acetonitrile	-0.18	15.3	10.9	10.7	18	6.1	0.8	6.1	108.9			14.1	18.9
367	1,2-dichloroethane	1.61	18	11.7	13.7	7.4	4.1	2.6	3.2	92	4.1	2	3.2	16.7
7	Acetone	1.24	15.5	10.7	11.2	10.4	7	0.1	7	76.9	4.9	4.9	17	12.5
570	isopropyl alcohol	1.53	15.8	10.4	11.9	6.1	16.4	8.1	14.3	104.7	14.5	9.2	21.1	33.8
481	methyl ethyl ketone	1.34	16	10.3	12.2	9	5.1	0.1	5.1	132.6			16.3	12.8
328	ethyl acetate	1.55	15.8	10.5	11.8	5.3	7.2	0	7.2	98.6	10.8	3.9	14.8	9.3
92	butanol	1.56	16	10.0	12.5	5.7	15.8	9.5	12.6	79.4	13.1	9.4	28.8	36.8
255	diethyl ether	1.50	15.49	10.0	11.8	2.9	4.6	0	4.6	131.4	1	12.9	18.5	3.9
148	chlorobenzene	2.02	19	10.9	15.5	4.3	2	0	2	90.2	2	1	2.2	7.9
181	cyclohexane	1.70	16.8	9.9	13.6	0	0.2	0	0.2	40.6			3.2	0
102	butyl acetate	1.57	15.8	10.0	12.3	3.7	6.3	0	6.3	73.8	6.3	5.7	15	11.74
417	hexane	1.30	14.9	9.4	11.6	0	0	0	0	72	0	0	3.2	0
698	o-xylene	1.83	17.8	10.0	14.8	1	3.1	0	3.1	83.2			3.8	3.7
532	nitroethane	0.37	16	11.2	11.4	15.5	4.5	0.3	4.5	52.9			4.8	15.7
404	furfural	0.23	18.6	11.1	15.0	14.9	7	0	7	54.1			7.47	18.96
545	oleic acid		16	8.8	13.3	2.8	6.2	5.13	3.47	319.7	5.7	2.4	47.8	17.22

2.3. Evaluation of the HSPiP's method

According to Rule 1-3, δ_{Hacid}, δ_{Hbase} are determined and plotted with the original Abraham's Acid/Base value (Fig.6, 7). There is some correlation for δ_{Hacid} / Abraham Acid. However, with regard to basicity, it is difficult to read basicity from the value of δ_{Hbase}.

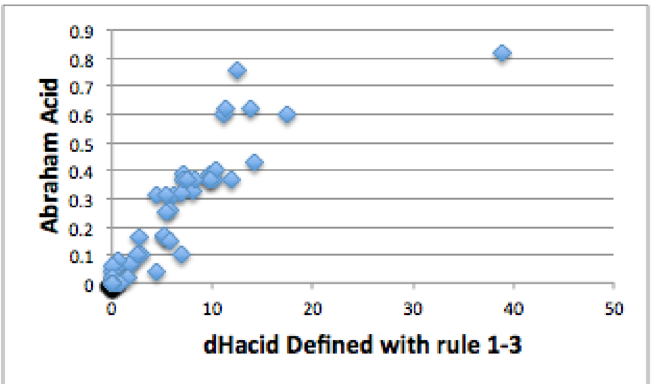


Fig. 6 δ_{Hacid} vs Abraham Acid

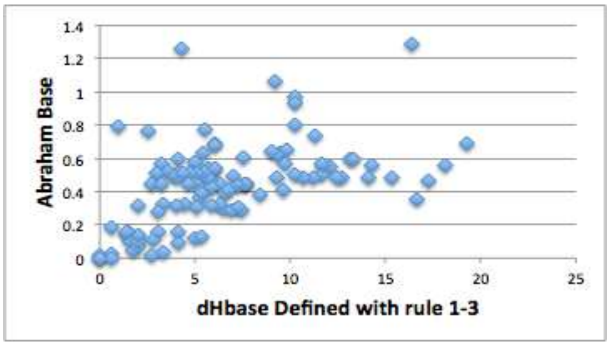


Fig. 7 δ_{Hacid} vs Abraham Base

The problem of this handling is in Rule 2.

Rule 2: δ_{Hacid}:δ_{Hbase} = Abraham Acid:Base

In Abraham's definition of Acid, what is called Acid is distributed between 0 – 1.67. But what is called Base is distributed between 0 - 96. There is no unit representing Acid, Base, and the ratio of Abraham Acid:Base has no meaning.

The carboxylic acid compounds' Abraham Acid, Base, δ_{Hacid} and δ_{Hbase} are plotted against the molar volume (Fig. 8).

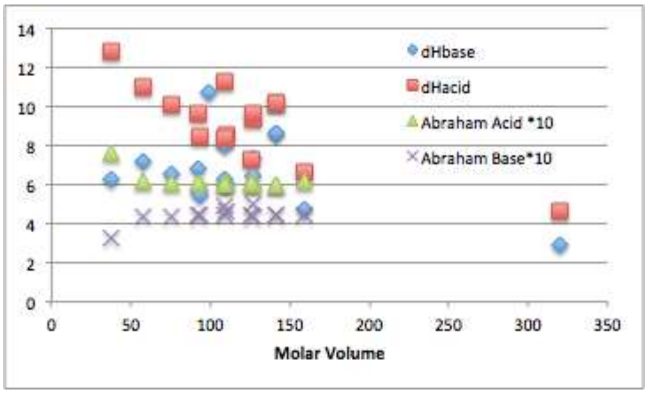


Fig.8 Molar Volume effect to Abraham Acid/Base andδ_{Hacid} / δ_{Hbase}

Abraham's Acid does not depend on molar volume so much, and they are almost constant at 0.6. That is, if the carboxyl group is attached somewhere in the molecule, the acidity is determined regardless of the molecular size. In addition, the Abraham's Base of carboxylic acids also takes almost the same value regardless of the molecular size. In contrast, δ_{Hacid}, δ_{Hbase} decreases as the molecule becomes larger. This is because the solubility parameter is based on the latent heat of evaporation and the molar volume of the molecule. So the value of the solubility parameter naturally becomes small as the volume ratio of the functional group decreases.

So the evaluation of δ_{Hacid}, δ_{Hbase} was not correct but we continued further analysis.

Distance equation using δ_{Hacid}, δ_{Hbase}

If the division of the δ_H term is done with Donor/Acceptor of Lewis, equation (3) should hold.

$$\delta_T^2 = \delta_D^2 + \delta_p^2 + 2*\delta_a*\delta_b \qquad (3)$$

However, with Brønsted's Acid/Base, for example, for a ketone compound, δ_{Hacid} is 0, and formula (3) does not hold. Therefore, here we will evaluate using a simple Euclidean distance, Eq. (10).

$$\text{Distance}_{2017}\ \text{wA/B} = \{(\delta_{Dvdw1}-\delta_{Dvdw2})^2 + (\delta_{Dfg1}-\delta_{Dfg2})^2 + (\delta_{P1}-\delta_{P2})^2 + (\delta_{Hacid1}-\delta_{Hacid2})^2 + (\delta_{Hbase1}-\delta_{Hbase2})^2\}^{0.5} \qquad (10)$$

We examined the solubility of Oleic acid with Distance$_{2017}$ which use normal δ_H and Distance$_{2017}$-wA/B which use δ_{Hacid} and δ_{Hbase}. As shown in Fig. 9, the ester solvents and alcohol solvents are greatly deviated with Distance$_{2017}$. This is because the δ_H (6.3-7.2) of the ester solvents are almost same with the δ_H (6.2) of the Oleic acid. So the difference in the δ_H term disappears in Distance$_{2017}$.

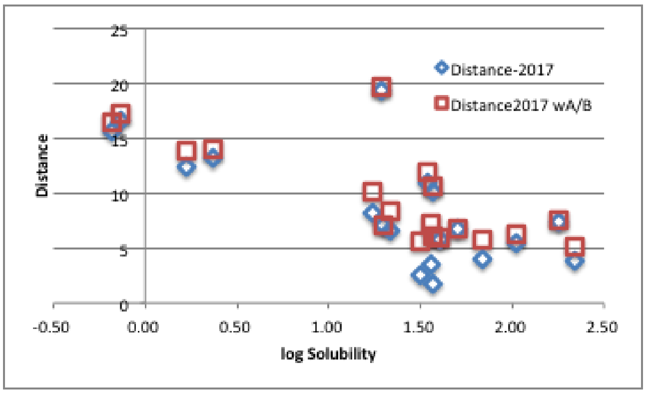


Fig. 9 The solubility of Oleic Acid and Distances.

The δ_H term of Oleic acid is divided into (δ_{Hacid}, δ_{Hbase})=(5.13, 3.47), and the δ_H term of ester solvents is assigned to δ_{Hbase} because δ_{Hacid} is 0. Therefore, when looking at Distance$_{2017}$-wA/B, the value of ($\delta_{Hacid}1$ - $\delta_{Hacid}2$) ^{2} + ($\delta_{Hbase}1$ - $\delta_{Hbase}2$) ^{2} becomes large, which is a distance corresponding to the solubility. However, even with Distance$_{2017}$-wA/B, alcohol solvents' abnormalities are not improved. This is because the stabilizing effect by recombination of hydrogen bond is not introduced.

Since the values of δ_{Hacid} and δ_{Hbase} are not correct, so absolute values are meaningless, but let's confirm the recombination effect of hydrogen bonding with Oleic acid and methanol.

Oleic acid δ_{Hacid}, δ_{Hbase} (5.13, 3.47)
Methanol δ_{Hacid}, δ_{Hbase} (14, 17.4)

$(\boldsymbol{\delta}_{\mathbf{Hacid1}}\text{-}\boldsymbol{\delta}_{\mathbf{Hacid2}})^2+(\boldsymbol{\delta}_{\mathbf{Hbase1}}\text{-}\boldsymbol{\delta}_{\mathbf{Hbase2}})^2 = 272.72$

$2({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^j\delta_b) = 2({}^i\delta_{a*}{}^i\delta_b + {}^j\delta_{a*}{}^j\delta_b) - 2({}^i\delta_{a*}{}^j\delta_b + {}^i\delta_{a*}{}^j\delta_b) = 247.12$

It can be seen that the distance becomes shorter by recombination of hydrogen bonding.

Although not perfect, when the solute clearly has a functional group showing Acid/Base, the division into δ_{Hacid}, δ_{Hbase} is superior to the conventional HSP. The effect is confirmed by the classic 88 solubility tests of polymers from Hansen, where, as in Part 1 we plot the number of "wrong" solvents.

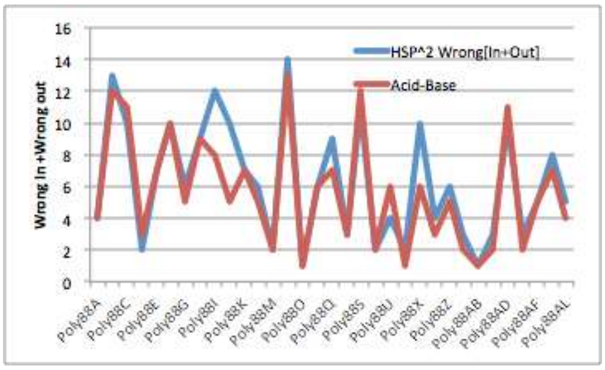


Fig.10 The result of solubility test of polymer

Polymer88-I Plastopal H-urea formaldehyde resin, Badische Anilin- und Soda Fabrik.

Polymer88-J H Sec. Nitrocellulose-H 23, A. Hagedorn and Co.

Polymer88-X Lutanol IC/I23-poly (isobutylene), Badische Anilin- und Soda Fabrik.

These three systems greatly reduced false recognition of Wrong In+Wrong Out. It can be said that the effect of introducing δ_{Hacid} and δ_{Hbase} is large in a polymer having a hydrogen bonding functional group.

Even in other polymer systems, by introducing δ_{Hacid} and δ_{Hbase}, the number of false assignments was reduced a little in many cases.

The merit of this method is that although it does not take into consideration the stabilizing effect by rearrangement of hydrogen bonds it is able to search Hansen's dissolving spheres even if we do not know what kind of polarity the solute has.

2.4. Evaluation of Gutmann DN(Donor Number), AN(Acceptor Number) Method

Since DN of Gutmann is defined by the calorific value at the time of making a complex with $SbCl_5$, $-\Delta H$ (in kcal / mol), compatibility with the solubility parameter will be good because solubility parameter is based on ΔH of evaporation.

In the case of general complex formation [7], ΔH is calculated from following scheme.
$\Delta H = DN*AN / 100$

It is thought that this 100 indicates the approximate molar volume. As the molar volume of the solvent increases, the donor point and the acceptor point that react are reduced, so the amount of heat generation also decreases, so here we use molar volume instead of 100.

Because of this definition, Gutmann’s DN, AN is Lewis' Donor, Acceptor, and has a unit of kcal/mol, so it is easy to compare. And we can use equations (3) and (5) proposed by Beerbower.

$\delta_T^2 = \delta_d^2 + \delta_p^2 + 2*\delta_a*\delta_b$ (3)

${}^{ij}A = ({}^i\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + 2({}^i\delta_a - {}^j\delta_a)({}^i\delta_b - {}^j\delta_b)$ (5)

As tentative DN and AN value for Oleic acid, we used (17.22, 47.8).

$Distance_{2017}$ wD/A = $\{(\delta_{Dvdw1}-\delta_{Dvdw2})^2 + (\delta_{Dfg1}-\delta_{Dfg2})^2 + (\delta_{P1}-\delta_{P2})^2 + 4.18*(DN1 - DN2)(AN1 - AN2)/MVol\}^{0.5}$ (11)

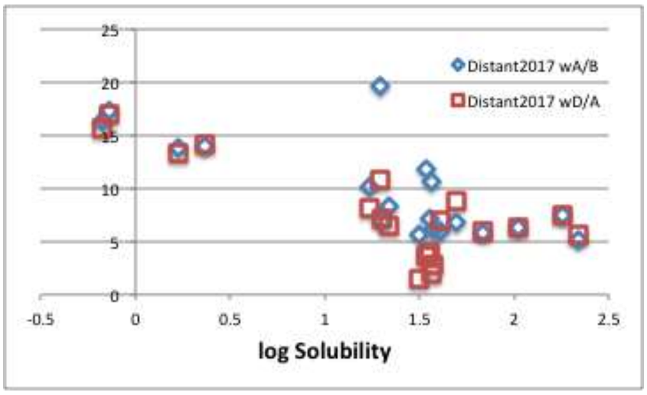


Fig. 11 The solubility of Oleic Acid and Distances.

Compared with the introduction of δ_{Hacid}-δ_{Hbase}, there was no significant divergence of alcohols. This is probably because the rearrangement of hydrogen bonding was correctly evaluated.

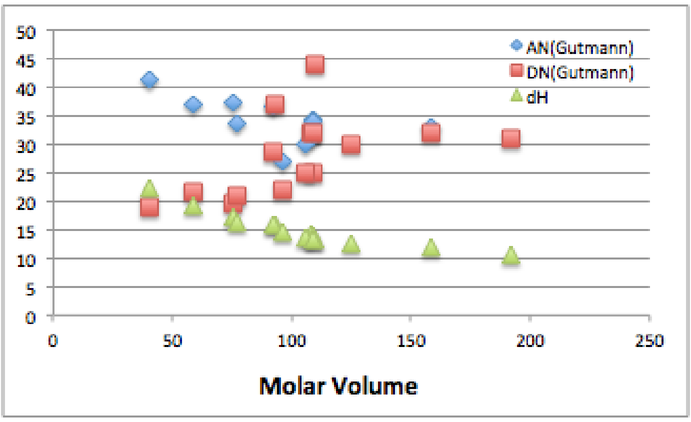


Fig. 12 Molar Volume effect to Gutmann DN/AN and δ_H

The Gutmann's DN, AN, and Hansen's δ_H against the molar volume of alcohols are plotted(Fig. 12). Gutmann's DN shows coordination heat per mole, so it does not depend much on the molecular size. However, Hansen's δ_H decreases with increasing molar volume.
Therefore, Beerbower assumed equation (4) is not satisfied as shown in Fig.13.

$\delta_H^2 = 2*\delta a*\delta b$ (4)

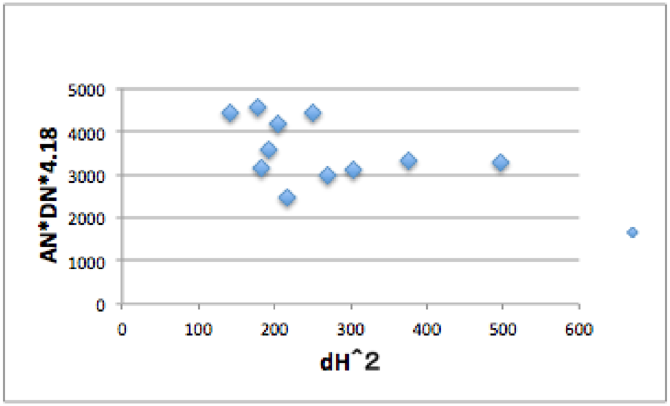


Fig. 13 Evaluation of scheme (4)

2.5. Consideration from latent heat of vaporization

We have defined the energy (E_{Net}) required to destroy a three-dimensional network as reported in detail in preprint Part 2.

$E_{Net} = \delta_T{}^2 * MVol + 8.31*298.15 - 85*\text{Boiling point}$ (12)

$\delta_{Net} = (E_{Net} / MVol)^{0.5}$ (13)

δ_{Net} is obtained by equation (13).

Gutmann defined heat of coordination due to donor and acceptor interaction as $\Delta H = DN*AN/100$ kcal/mol. So we compared E_{Net} with $(DN*AN/100)*4.18*1000$ J/mol.

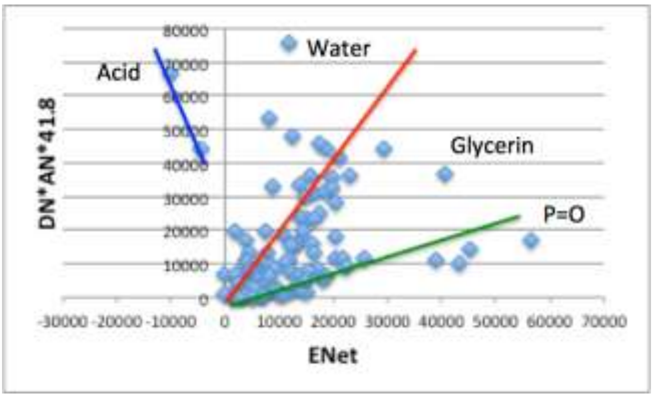


Fig.14 The correlation of E_{Net} to heat of coordination.

There are many exceptions, but as indicated by the red line, about half of the donor and acceptor interaction energy is used to construct the network. The remaining half is considered to be used to boost the boiling point itself.

In the carboxylic acids, the value of E_{Net} is negative. This is due to the fact that the low molecular weight carboxylic acids evaporate in the form of a dimer and their latent heats of vaporization are small. Although carboxylic acids have very strong coordination bond the network stops at two molecules. It can be said that they formed closed network. On the other hand, water and alcohols form open networks involving multiple molecules and this increases E_{Net}.

It is thought that the effect of polyfunctionalization is mixed in the reason that the phosphorus compound behaves in a specific way because it has oxygen and nitrogen bonded to P.

Since (DN, AN) is almost unchanged in Glycerin (19, 48), Ethylene Glycol (19.2, 44.9) and Ethanol (21.5, 37.1), so DN*AN has almost the same value. But the difference of hydroxyl group number make E_{Net} changes greatly. Mono-functional Ethanol rides on the red line. In addition, DN * AN greatly changes from 1059.84 (n-butanol) to 593.49 (t-butanol) depending on the environment surrounding the functional group, whether the alcohol is primary or tertiary.

For the mono-functional compounds, the following formula (14) is roughly established.

$\delta_T{}^2 * MVol + 8.31*298.15 - 85*\text{Boiling point} = E_{Net} = 0.5*(41.8*DN*AN)$ (14)

$\delta_{Net} = (0.5*(41.8*DN*AN)/MVol)^{0.5}$ (15)

The increasing of latent heat of vaporization can be understood as the energy required to cut off the donor/acceptor coordination network. Well then, you may think that δ_{Net} can be subtracted from δ_H, but unfortunately it can not be done. Ethylene Carbonate has a very large δ_P [δ_D, δ_P, δ_H] = [18, 21.7, 5.1], but δ_H is only 5.1. δ_{Net} calculated by equation (13) is 13.6, which is larger than δ_H. Also in equation (15), $\delta_{Net} = (0.5 * (41.8 * 16.4 * 22.2) / 66)^{0.5} = 10.7$, so it is larger than δ_H. Obviously δ_{Net} is a coordination network, it is not a network with only hydrogen bonding, so it cannot be calculated from δ_H alone.

Therefore, there is no way to reasonably assign δ_{Net} to δ_H and δ_P at present, but the value itself can be easily obtained from HSP, boiling point and molar volume.

In addition, this coordination network is meaningful only after the solute's DN and AN have been determined. When solubility testing of polymers of unknown structure is carried out, only Distance_{2017}-wA/B can be used. If the solubility test shows large $\delta_{Hacid}/\delta_{Hbase}$ values, the effect due to the interaction of DN and AN may be considered afterwards. When the structure is clear in, for example a pharma molecule, the DN/AN approach can be applied from the start.

2.6. Solubility in water

In the past, HSP has been regarded as difficult to apply to the solubility of compounds in water. Because water has too complicated structure.

Ethylene Carbonate [δ_D, δ_P, δ_H] = [18, 21.7, 5.1] is a 100% water-soluble compound. Considering from [δ_D, δ_P, δ_H] of water = [15.5, 16, 42.3], Distance-1967 is 37.96, which is unlikely to be mutually soluble.

Gutmann's [DN, AN] is Ethylene Carbonate [16.4, 22.2], and water [33, 54.8].

It is still an incomplete scheme, but $Distance_{2017}$ wD/A becomes 8.9, and it can be predicted that the solubility will increase by rearrangement of coordination bonds.

N, N-dimethylacetamide [DN, AN] is [27.8, 13.6]. This compound is also a 100% water-soluble compound.
(DN1 - DN2) (AN1 - AN2) is calculated by the combination of water, Ethylene Carbonate and N, N - dimethylacetamide.
water/Ethylene Carbonate 541.16
water/N,N-dimethylacetamide 214.24
Ethylene Carbonate/N,N-dimethylacetamide -98.04

Therefore, when a polyamide resin is added to a carbonate/water mixture, it is suggested that the carbonate forms a coordination bond network with the amide resin and gets further stabilizes.

As described above, considering the network of coordination bonds, it becomes possible to consider the solubility in water more deeply.

2.7. Donor/Acceptor Estimation from structure

When saying donor character, the meaning is reversed from proton donor and electron donor. The acid of Brønsted-Lowry is a proton donor, and the DN of Gutmann is an electron donor. Also, originally Gutmann's DN is the coordination heat when making a 1: 1 complex with $SbCl_5$, so when predicting the network structure made by a poly-functional alcohol, it is necessary to multiply the number of functional groups. Therefore, in order to distinguish clearly from Gutmann's DN, AN, it is written as Yamamoto's ED, EA (Y-ED, Y-EA).

At present, 147 compounds have known Gutmann's DN, and 119 compounds of which AN is known. Since the number of known compounds is rather small it is not possible to create a valid functional group contribution scheme. Therefore, we tentatively estimated Gutmann's DN and AN for a data set containing all necessary functional groups.

For that purpose, we use several assumptions.

Gutmann's DN/AN and Abraham's Base/Acid have an approximate correlation (Fig. 2, 3).

Gutmann's DN has a high correlation with LUMOs obtained from semi-empirical molecular orbital calculations.

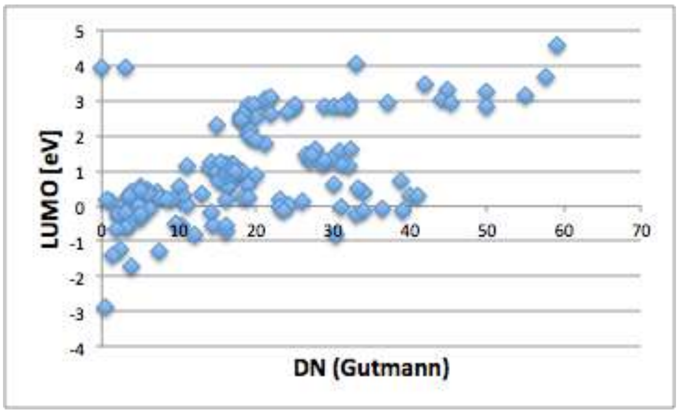


Fig.15 Gutmann DN vs LUMO

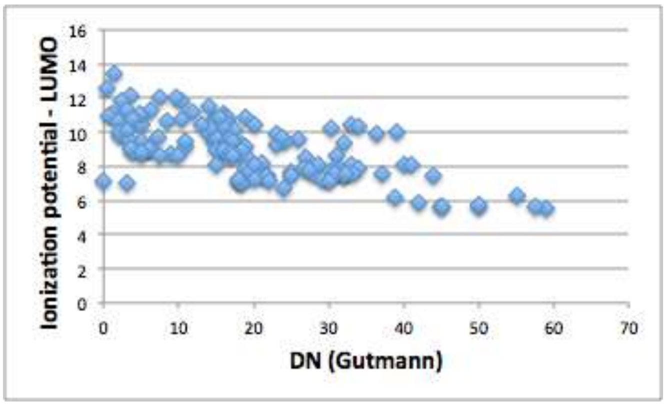


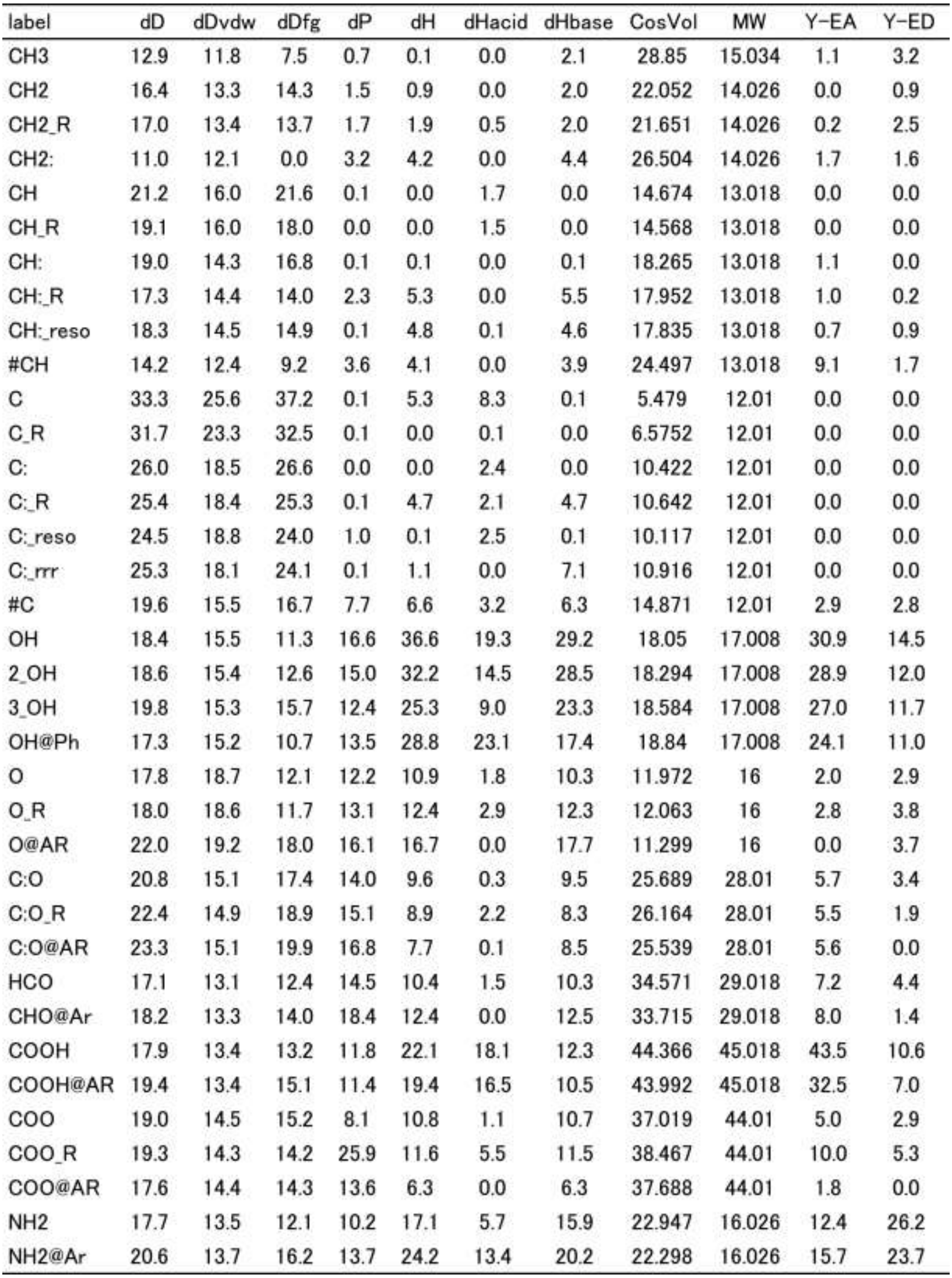
Fig. 16 Gutmann DN vs Ionization Potential-LUMO

Furthermore, the value obtained by subtracting the LUMO from Ionization Potential is more highly correlated as shown Fig. 16.

Using these parameters independent of functional groups, we provisionally determined Gutmann's DN, AN for about 3800 compounds and assigning them to each functional group. Y-EA, Y-ED will clearly be values revised very frequently and are therefore provisional values. If you want to calculate Y-EA, Y-ED of a molecule, you just make a summation of number of the number of functional groups times each coefficient.

Regarding how to adopt Y-EA, Y-ED, it is not yet definite. If you want to use Gutmann's DN, AN, you will only select one functional group with the largest Y-ED, Y-EA in the table. Care must be taken when calculating molecules composed of multiple large Y-EDs and Y-EAs. For example, in the case of ethylene glycol having two primary hydroxyl groups, if the calculation is made as Y-ED = 14.5 * 2, Y-EA = 30.9 * 2, the result may be greatly overestimated. For example, the interaction between carboxylic acid and alcohol is evaluated by (ED1 - ED2) (EA1 - EA2). For acetic acid / ethanol, (10.6-14.5) * (43.5-30.9) = - 49.14, the minus value means largely stabilized by rearrangement. But for acetic acid / ethylene glycol (10.6-14.5 * 2) * (43.5-30.9 * 2) = 336.72. It is thought that interaction should be integrated for each functional group one by one.

Table 2 Contribution coefficient of each functional group



label	dD	dDvdw	dDfg	dP	dH	dHacid	dHbase	CosVol	MW	Y-EA	Y-ED
CH3	12.9	11.8	7.5	0.7	0.1	0.0	2.1	28.85	15.034	1.1	3.2
CH2	16.4	13.3	14.3	1.5	0.9	0.0	2.0	22.052	14.026	0.0	0.9
CH2_R	17.0	13.4	13.7	1.7	1.9	0.5	2.0	21.651	14.026	0.2	2.5
CH2:	11.0	12.1	0.0	3.2	4.2	0.0	4.4	26.504	14.026	1.7	1.6
CH	21.2	16.0	21.6	0.1	0.0	1.7	0.0	14.674	13.018	0.0	0.0
CH_R	19.1	16.0	18.0	0.0	0.0	1.5	0.0	14.568	13.018	0.0	0.0
CH:	19.0	14.3	16.8	0.1	0.1	0.0	0.1	18.265	13.018	1.1	0.0
CH:_R	17.3	14.4	14.0	2.3	5.3	0.0	5.5	17.952	13.018	1.0	0.2
CH:_reso	18.3	14.5	14.9	0.1	4.8	0.1	4.6	17.835	13.018	0.7	0.9
#CH	14.2	12.4	9.2	3.6	4.1	0.0	3.9	24.497	13.018	9.1	1.7
C	33.3	25.6	37.2	0.1	5.3	8.3	0.1	5.479	12.01	0.0	0.0
C_R	31.7	23.3	32.5	0.1	0.0	0.1	0.0	6.5752	12.01	0.0	0.0
C:	26.0	18.5	26.6	0.0	0.0	2.4	0.0	10.422	12.01	0.0	0.0
C:_R	25.4	18.4	25.3	0.1	4.7	2.1	4.7	10.642	12.01	0.0	0.0
C:_reso	24.5	18.8	24.0	1.0	0.1	2.5	0.1	10.117	12.01	0.0	0.0
C:_rrr	25.3	18.1	24.1	0.1	1.1	0.0	7.1	10.916	12.01	0.0	0.0
#C	19.6	15.5	16.7	7.7	6.6	3.2	6.3	14.871	12.01	2.9	2.8
OH	18.4	15.5	11.3	16.6	36.6	19.3	29.2	18.05	17.008	30.9	14.5
2_OH	18.6	15.4	12.6	15.0	32.2	14.5	28.5	18.294	17.008	28.9	12.0
3_OH	19.8	15.3	15.7	12.4	25.3	9.0	23.3	18.584	17.008	27.0	11.7
OH@Ph	17.3	15.2	10.7	13.5	28.8	23.1	17.4	18.84	17.008	24.1	11.0
O	17.8	18.7	12.1	12.2	10.9	1.8	10.3	11.972	16	2.0	2.9
O_R	18.0	18.6	11.7	13.1	12.4	2.9	12.3	12.063	16	2.8	3.8
O@AR	22.0	19.2	18.0	16.1	16.7	0.0	17.7	11.299	16	0.0	3.7
C:O	20.8	15.1	17.4	14.0	9.6	0.3	9.5	25.689	28.01	5.7	3.4
C:O_R	22.4	14.9	18.9	15.1	8.9	2.2	8.3	26.164	28.01	5.5	1.9
C:O@AR	23.3	15.1	19.9	16.8	7.7	0.1	8.5	25.539	28.01	5.6	0.0
HCO	17.1	13.1	12.4	14.5	10.4	1.5	10.3	34.571	29.018	7.2	4.4
CHO@Ar	18.2	13.3	14.0	18.4	12.4	0.0	12.5	33.715	29.018	8.0	1.4
COOH	17.9	13.4	13.2	11.8	22.1	18.1	12.3	44.366	45.018	43.5	10.6
COOH@AR	19.4	13.4	15.1	11.4	19.4	16.5	10.5	43.992	45.018	32.5	7.0
COO	19.0	14.5	15.2	8.1	10.8	1.1	10.7	37.019	44.01	5.0	2.9
COO_R	19.3	14.3	14.2	25.9	11.6	5.5	11.5	38.467	44.01	10.0	5.3
COO@AR	17.6	14.4	14.3	13.6	6.3	0.0	6.3	37.688	44.01	1.8	0.0
NH2	17.7	13.5	12.1	10.2	17.1	5.7	15.9	22.947	16.026	12.4	26.2
NH2@Ar	20.6	13.7	16.2	13.7	24.2	13.4	20.2	22.298	16.026	15.7	23.7

Table 2 continued.

label	dD	dDvdw	dDfg	dP	dH	dHacid	dHbase	CosVol	MW	Y-EA	Y-ED
NH	20.7	15.6	17.8	9.7	14.9	0.0	14.9	16.526	15.018	3.8	27.9
NH_R	19.0	15.7	15.5	14.1	18.3	5.2	17.6	16.412	15.018	7.0	23.3
NH@AR	30.7	16.4	28.7	16.6	23.6	9.1	21.0	15.081	15.018	17.9	18.8
N	25.2	19.5	24.7	9.3	11.9	4.4	11.9	10.27	14.01	0.0	19.6
N_R	25.0	20.5	22.2	7.6	19.5	0.0	20.3	9.258	14.01	0.0	10.0
N@AR	30.3	18.0	31.3	0.0	16.4	7.5	14.5	12.071	14.01	0.0	15.6
C#N	17.0	12.8	12.5	21.8	9.6	2.5	9.3	34.123	26.02	12.8	8.8
C#N@AR	18.9	12.8	14.8	20.8	4.4	0.0	4.8	33.996	26.02	5.6	6.7
NO2	17.9	14.2	12.4	20.6	6.9	0.0	7.3	40.261	46.01	11.4	8.3
NO2@AR	19.3	14.4	14.0	15.7	7.6	2.1	7.1	38.781	46.01	6.1	6.2
SH	19.1	13.3	15.0	9.0	9.7	1.7	9.7	36.401	33.078	2.8	8.9
SH@AR	22.6	13.2	19.0	3.1	9.1	7.4	4.9	37.174	33.078	9.5	12.5
S	23.4	15.0	20.6	7.0	6.9	2.8	6.8	28.329	32.07	0.0	12.0
S_R	23.1	15.0	19.2	11.4	11.6	0.7	12.0	28.146	32.07	2.9	12.4
S@AR	27.2	15.0	24.9	9.7	0.0	0.0	0.0	28.204	32.07	0.0	13.1
S:O	23.8	14.6	20.5	21.0	9.4	2.8	9.2	38.825	48.07	1.3	23.2
NHCO	21.3	13.5	17.2	23.1	17.5	10.4	13.8	42.127	43.028	29.4	22.0
NHCO_R	23.7	13.4	20.6	24.0	13.1	2.0	13.1	42.673	43.028	23.0	14.1
NCO	24.4	14.8	21.8	22.3	13.6	3.7	13.5	34.892	42.02	1.0	15.4
NCO_R	22.6	14.5	19.7	19.2	12.5	0.4	12.8	36.302	42.02	10.3	13.3
OCOO	17.6	14.3	13.5	10.9	9.6	3.4	9.1	47.854	60.01	7.4	0.2
OCOO_R	19.5	13.9	14.5	29.0	10.3	0.0	10.3	50.201	60.01	13.3	5.5
CF3	10.7	14.3	0.0	1.8	0.0	0.0	0.0	52.733	69.01	4.5	0.0
CCl3	17.9	13.1	13.2	0.0	0.0	0.3	0.0	94.365	118.36	6.5	0.0
CF2	13.4	15.4	3.5	0.0	1.1	1.5	0.0	36.238	50.01	0.1	0.2
CCl2	18.8	14.0	13.6	6.6	4.3	2.5	3.2	62.755	82.91	3.6	0.0
CF	15.9	17.1	7.8	0.0	0.0	2.1	0.1	21.274	31.01	0.0	0.0
CCl	20.6	14.9	18.2	6.7	3.9	4.9	0.0	36.981	47.46	0.0	0.0
F	0.1	17.6	0.1	0.0	4.6	0.1	0.1	14.84	19	2.7	0.3
Cl	16.4	15.7	8.7	0.0	0.0	0.0	2.4	27.463	35.45	3.4	0.1
Br	19.8	18.1	10.2	7.1	6.3	1.5	6.2	36.43	79.9	5.6	0.1
I	21.0	19.0	11.4	5.6	5.2	2.0	5.0	47.221	126.9	3.3	1.7
Si	10.7	14.0	11.3	0.0	0.0	1.7	0.0	29.985	28.09	0.0	0.0
P	17.7	14.3	13.7	6.5	0.0	4.5	0.0	30.305	30.97	11.5	10.2
B	20.5	15.9	18.8	0.1	0.0	5.3	0.0	13.342	10.81	0.0	37.0

2.8. Hexane / water distribution ratio

Table 3 Hexane/Water log Partition coefficients.

Hcode	Name	Hexane/water
5	acetic acid	-3.06
7	acetone	-0.91
92	butanol	-0.70
105	butylamine	-0.62
114	butyric acid	-1.76
129	chloroacetic acid	-3.14
252	diethylamine	-0.48
325	ethyl alcohol	-2.10
328	ethyl acetate	0.29
331	ethylamine	-1.77
431	isobutanol	-0.60
930	1-hexanol	0.46
456	methyl alcohol	-2.80
464	methyl acetate	-0.26
552	1-pentanol	-0.40
569	propyl alcohol	-1.52
576	propanoic acid	-2.14
580	propylamine	-1.00
665	trimethylamine	-0.48
861	Trichloroacetic Acid	-2.63
931	1-heptanol	1.01
945	dichloroacetic acid	-2.72
1022	hexanoic acid	-0.46
1023	pentanoic acid	-1.00

The HSP distance to partition coefficient for hexane/water was plotted. When Disatnce_{2017} wA/B is plotted against water and hexane, it becomes as shown in Fig.17. Solutes are mainly acids, amines, alcohols, but the HSP distance varies greatly depending on the solute and it is difficult to compare.

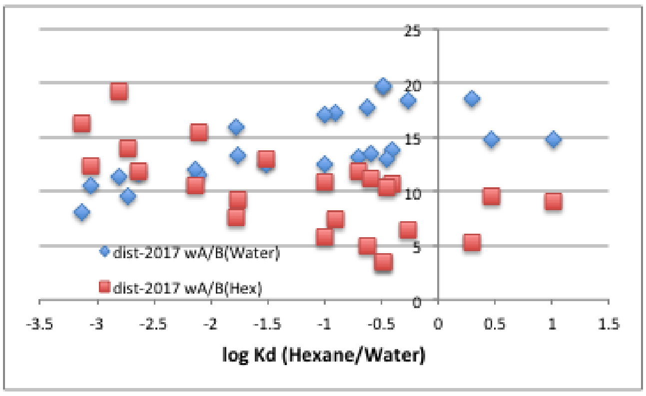


Fig.17 Hexane / water partition coefficient and HSP distance (Acid/Base)

On the other hand, as shown in Fig. 18, it was revealed that HSP distance clearly separated from hexane and water with Distance_{2017} wED/EA. For this calculation, we used newly developed Y-ED/Y-EA.

$$\text{Distance}_{2017}\ \text{wED/EA} = \{(\delta_{Dvdw1}-\delta_{Dvdw2})^2 + (\delta_{Dfg1}-\delta_{Dfg2})^2 + (\delta_{P1}-\delta_{P2})^2 + 4.18*(\text{Y-ED1}-\text{Y-ED2})(\text{Y-EA1}-\text{Y-EA2})/\text{MVol}\}^{0.5} \quad (16)$$

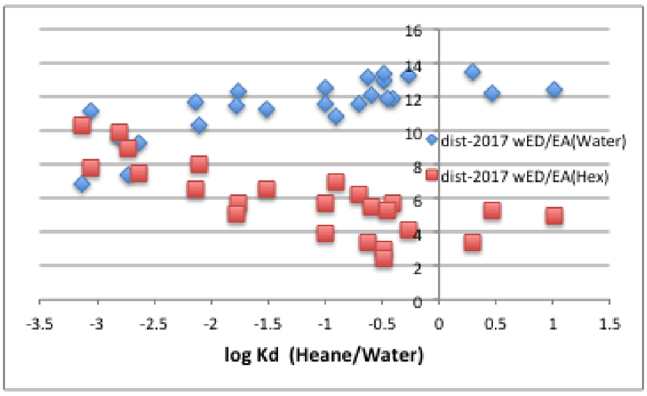


Fig.18 Hexane/water partition coefficient and HSP distance (Donor/Acceptor)

This result also indicated that Y-ED and Y-EA must be taken into consideration when analyzing water and hydrogen bonding compounds with HSP.

2.9. Solubility of oleic acid again

The solubility of oleic acid was investigated using the estimated values of the newly developed Y-ED/Y-EA.

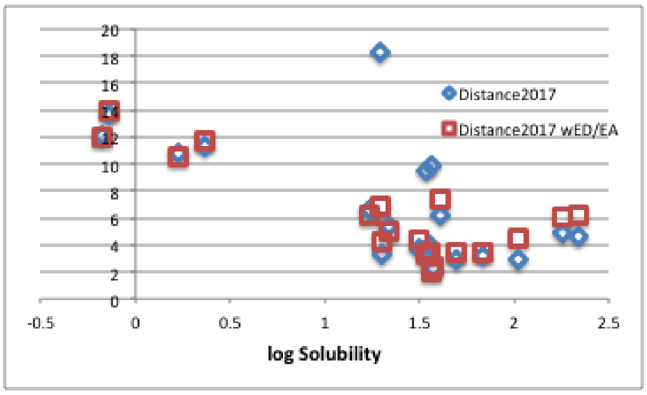


Fig.19 Solubility of oleic acid and HSP distance

As shown in Fig. 19, even using values obtained by functional group contribution method, a good correlation was obtained between the solubility of oleic acid and Distance_{2017} wED/EA. Compounds whose log (solubility) exceeds 2 are solubility of more than 100g/100ml. Practically, it can be said that equation (16) has sufficient accuracy.

2.10. Dispersibility of pigment

In order to know the interaction between the pigment and the solvent, the calorific value and heat of adsorption when the solvent is wetted by the pigment are measured [10]. It is known that this calorific value is related to δ_H. In the case where the pigment is titanium oxide, since titanium oxide is a basic pigment, it is considered that the acid component of Lewis in δ_H is involved in heat generation. When Y-ED, Y-EA become estimable from the molecular structure, δ_H can be divided into donor/acceptor. For the division, we used following rules.

$$\delta_{Hedo} : \delta_{Heac} = \text{Y-ED:Y-EA}$$

$$\delta_H^2 = 2 * \delta_{Hedo} * \delta_{Heac}$$

The electron pair donating property of δ_H is δ_{Hedo} and the electron pair accepting property is δ_{Heac}. The thermal measurement results of titanium oxide with respect to δ_{Heac} of various solvents are plotted as shown in Fig. 20.

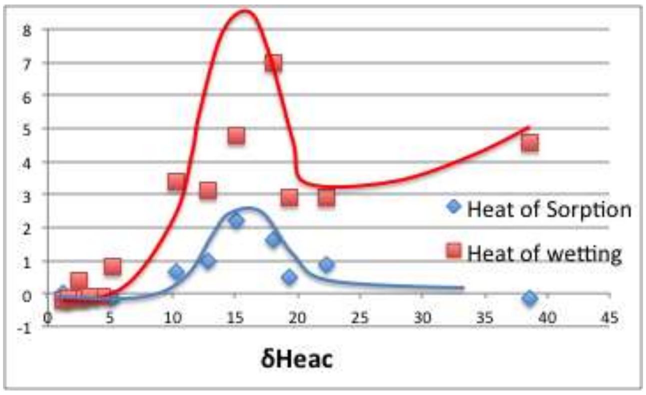


Fig.20 Heat of wetting and heat of sorption for titanium oxide

What is important here is that δ_{Heac} exists which maximizes both heat of wetting and heat of sorption. Presumably this is due to a maximum (negative) value in an equation such as $(yEA_{TiO2}\text{-}yEA_{Solvent})(yED_{TiO2}\text{-}yED_{Solvent})$

3. Further insight

The liquid/vapor phase ratio at the boiling point and the vapor-liquid equilibrium at the boiling temperature are measured in various systems by changing the mixing ratio of the two kinds of liquids. If two kinds of liquids are similar liquids like benzene/toluene, they act as ideal solutions. In the case of an ideal solution, the liquid phase composition and the vapor phase composition are in agreement, and the boiling point is determined by the composition ratio of the boiling points of the respective liquids. The boiling point of the actual mixed liquid changes greatly depending on the system. The boiling point (T_{Exp}50) of the experimental value when the composition weight ratio is 50: 50 is often lower than the average value (T_{av}50) of the boiling points of the respective liquids. Here, the point of the mass weight ratio of 50:50 is taken because the value of Y-T_{ij50} does not change even if the combination order of solvents is reversed.

$$\text{Y-}T_{ij50} = 1-(T_{av50} - T_{Exp50})/100 \quad (17)$$

In many systems, Y-T_{ij50} is less than 1 as in the ethanol/heptane system shown in Fig.21.

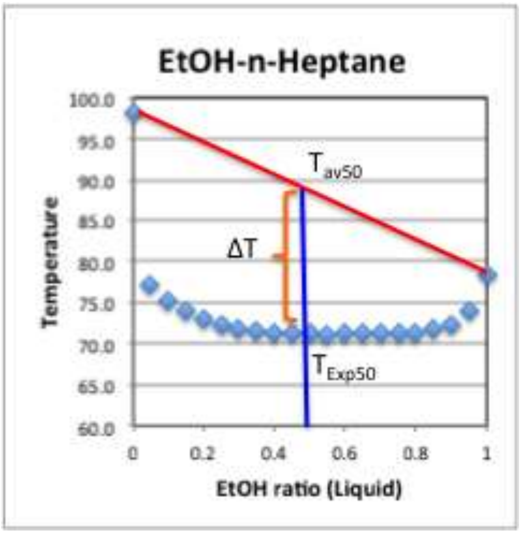


Fig.21 Ethanol/heptane X-T Chart

However, there are systems such as acetone/chloroform system shown in Fig. 22 where Y-T_{ij50} is 1 or more. Such a system requires a higher temperature to boil because the two kinds of liquid interact strongly. When such a system causes an azeotropic phenomenon, the maximum azeotrope is obtained.

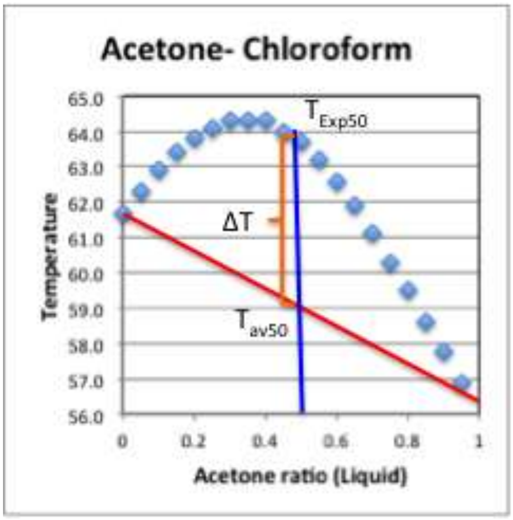


Fig.22 Acetone/chloroform X-T Chart

Therefore, Y-T_{ij50} defined by equation (17) means a bimolecular interaction parameter in vapor-liquid equilibrium.

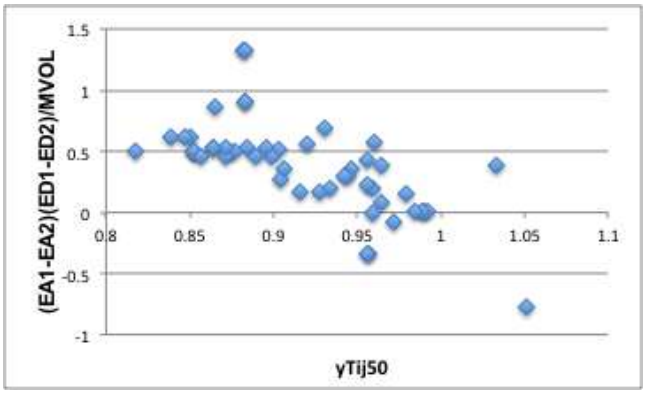


Fig.23 Relationship between Y-T_{ij50} and equation (18)

As shown in Fig. 23, Y-T_{ij50} in the case where acetone is the first component has a high correlation with the energy formula (18) of the rearrangement of coordination bonds.

(Y-ED1-Y-ED2)(Y-EA1-Y-EA2)/MVol (18)

We set Y-T_{ij50} for about 5000 compound pairs. As shown in Table 4, most of the compound pairs with large Y-T_{ij50} were acid/base pairs.

Table 4 Compound pair with large Y-T_{ij50}

Compound-A	Compound-B	Y-T_{ij50}
2-Methylpyridine	Formic acid	1.40
Acetic Acid	Pyridine	1.22
Acetic Acid	2-Methylpyridine	1.21
Acetic acid	4-Methylpyridine	1.21
Acetic Acid	N,N'-dimethylacetamide	1.21
Acetic acid	3-Methylpyridine	1.20
acetonitrile	3-methylbutyl butanoate	1.24
acetonitrile	phenetole	1.21
acetonitrile	isobutyl isopentanoate	1.21
Phenol	2,4-Dimethylpyridine	1.21
Phenol	4-Methylpyridine	1.21
Triethyl amine	Acetic acid	1.42
trimethylamine	Formic acid	1.25

Approximately 10% of compound pairs resulted in Y-T_{ij50} of 1 or more. In such a system, heat of neutralization of acid / base is generated, and analysis of solubility phenomenon using HSP has been often inappropriate.

On the contrary, as shown in Table 5, the combination of polar compounds and nonpolar compounds is the reason why Y-T_{ij50} is small, which is considered to be a combination which is considered to have almost no mutual solubility.

Table 5 Compound pair with small Y-T_{ij50}

Compound-A	Compound-B	Y-T_{ij50}
Acetamide	octane	0.53
Acetamide	1-Iodo-2-Methylpropane	0.50
Acetamide	tetrachloroethylene	0.49
alpha-pinene	Methanol	0.56
Ethylene glycol	Toluene	0.56
Ethylene Glycol	Dibenzyl Ether	0.56
Ethylene Glycol	1-Bromonaphthalene	0.55
Ethylene Glycol	1,2-Diphenylethane	0.55
Ethylene Glycol	Benzyl Phenyl Ether	0.54
Ethylene Glycol	Fluorene	0.49
Ethylene Glycol	Stilbene	0.45
Glycerol	Toluene	0.56
Glycerol	gamma-terpinene	0.47
Glycerol	Indene	0.46
Methanol	2-Pinene (dl)	0.55
Methanol	Camphene	0.54

These polar compounds are solvents that create a very large hydrogen bond (coordination bond) network and must be destroyed for mutual dissolution. Even if it can be mixed, it is considered that the calculation method based on the conventional volume fraction can not be used for the HSP value of the mixed solvent.

When Y-T_{ij50} can be estimated with a pair of arbitrary solvents, it is considered to be a very useful index in vapor-liquid equilibrium, mutual solubility of solvents, calculation of mixed HSP value of mixed solvent, and the like.

4. Conclusion

In order to incorporate Heat of Solvation as a solubility index, it was confirmed that it is reasonable to base it on Gutmann's DN, AN. However, DN and AN are values determined for the functional group having the largest value among the functional groups in the molecule, and in the case of a compound having a plurality of functional groups, it is necessary to add each functional group contribution. It was shown that the size of the network of the coordination bond

(δ_{Net}) itself can be calculated from HSP and boiling point, molar volume, and is clearly closely related to various other thermodynamic property values. Although δ_{Net} is mainly a network of hydrogen bonds, assigning it to δ_H and δ_P is not easy because some compounds with a small δ_H and large δ_P (such as ethylene carbonate and acetonitrile) possess a coordination bond network. Future work is planned to gradually clarify the relationship between the thermodynamic properties of pure substances and their effects within mixtures, starting with vapor-liquid equilibria as a key source of insightful data. Whilst it is now feasible to apply DN/AN and δ_{Net} ideas in some specific cases, it is envisaged that a more robust approach will emerge that combines the ease of HSP calculations with the extra capabilities enabled by these factors.

Finally, it is worth emphasising that the investigations into both the splitting of δ_D (Part 1) and the issues of donor/acceptor and δ_{Net} (Part 2) have confirmed what we have always known from experience – that HSP provide a robust tool in a large variety of circumstances and that the new features are welcome refinements, not replacements for a technique that has stood the test of time.

Literature

[1] Beerbower, A., Wu, P. L., and Martin, A., Expanded solubility parameter approach. I. Naphthalene and benzoic acid in individual solvents, J. Pharm. Sci.. 73, 179, 1984.

[2] Marti_n, A_., Wu, P. L., and Beerbower, A., Expanded solubility parameter approach. II. p-Hydroxy- benzoic acid and p-hydroxybenzoate in individual solvents, J. Pharm. Sci., 73, 188, 1984.

[3] Kamlet, M. J., Abboud, J. L. M., and Taft, R. W., An examination of linear solvation energy relationships, in Progress in Physical Organic Chemistry, Vol. 13, Taft, R. W., Ed., John Wiley & Sons, New York, 1981, 485.

[4] HSPiP e-Book ver. 4.0

[5] V. Gutmann, Chem. Tech., 7, 255 (1977).

[6] U.Mayer,V.Gutmann,and W.Gerger,Monatsh. Chem.,106,1275(1975).

[7] Gutmann, V, Electrochem. Actc 21, 661 (1976)

[8] A.Beerbower, J.colloid Interface Sci. , 35, 126 (1971).

[9] Koenhen, D.N. and Smolders, C.A., The determination of solubility parameters of solvents and polymers by means of correlation with other physical quantities, J. Appl. Polym. Sci., 19, 1163–1179, 1975.

[10] Atsunao Hiwara and Toshihide Fujitani, Research of Paint No.132 Apr. 1999