

Consideration of Hansen Solubility Parameters. Part 2

δ_{Net} the parameter which hid for 50 years

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Abstract :

It was in 1967 that Dr. Hansen split the energy of evaporation into dispersion term (δ_D), polarization term (δ_P) and hydrogen bond term (δ_H). These parameters are called Hansen solubility parameters (HSP). We have treated this HSP as a three-dimensional vector and have developed an empirical formula that solvents of similar vectors are easy to dissolve solutes of similar vectors. In Part-1, this dispersion term (δ_D) was divided into δ_{Dvdw} based on the weak van der Waals interaction and δ_{Dfg} based on the polarizability of the functional group, and it was taken as the 4-dimensional solubility parameter. In this report, a new parameter δ_{Net} showing the state of association of solvents, is defined, and its influence on various thermodynamic property values is examined.

Key Words: Hansen Solubility Parameter, Network Structure

1. Introduction

In solution, various forces work between molecules. Using these intermolecular forces, it is possible to explain many dissolution phenomena such as polymer/solvent, drug/absorption, inorganic/dispersion. Classical solubility theory was developed by Hildebrand and Scott^[1], and the solubility parameter (δ_A) of molecule A was defined as being related to its evaporation energy (ΔE_A) as follows.

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

This V_A is the molar volume of molecule A, and $\Delta E_A / V_A$ is known as cohesive energy density (CED)

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

Since the energy of evaporation can be expressed by equation (2), equation (1) can be rewritten as follows.

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

Here, δ , ΔH_A , R, T are the solubility parameter, latent heat of vaporization, gas constant and absolute temperature, respectively. As a descriptor of the intermolecular force acting on the molecule on average, this solubility parameter δ is one of the important solubility indices.

Hansen divided latent heat of vaporization into three energies in 1967^[2]. The divided energy represents three intermolecular forces which dominate the dissolution phenomenon. They are three intermolecular forces of dispersion force (D), polar force (P), and hydrogen bonding force (H).

The total energy consisting of these components can be written as

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

When equation (4) is divided by molecular volume (V), equation (5) is obtained.

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

Equation (6) is obtained from equations (1) and (5).

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

These δ_D , δ_P and δ_H represent the three components of the Hansen solubility parameter (HSP), namely the dispersion term, the polar term and the hydrogen bond term. This δ_D was further divided to develop new HSP (details are reported in Part 1).

δ_T represents the total solubility parameter, which is consistent with the solubility parameter of Hildebrand. Therefore, the HSP fully incorporates the solubility parameter of Hildebrand and has extra information from the direction of vector, so it has higher accuracy with regard to solubility prediction. Incorporating the δ_H term deepened the understanding of hydrogen bonding solvents such as alcohols. However, handling of coordination binding networks based on donor / acceptor interactions has not been confirmed.

2. Results and Discussion

2.1. Consideration from latent heat of vaporization

It is generally known that there is a correlation between latent heat of vaporization at the boiling point and the boiling point (Trouton rule). Even if it is expanded to latent heat of vaporization at 25 °C, a good correlation is obtained as shown in Fig.1. Even if the molecule becomes large and the latent heat of vaporization increases, the boiling point also rises accordingly, so the value of $H_V@25^\circ\text{C}/\text{BP}$ is nearly constant and becomes 85. Similarly, for ethers, thiols, ketones compounds case, as the boiling point rises, the latent heat of vaporization also increases, so the relationship is the same. Ethers, thiols, and ketones are not Brønsted-Lowry Acid/Bases, but they do interact with Lewis donor and acceptor. However, the effect is offset by the boiling point increase.

Compounds with $H_v@25^\circ\text{C}/BP = 85$ are referred to as regular solution.

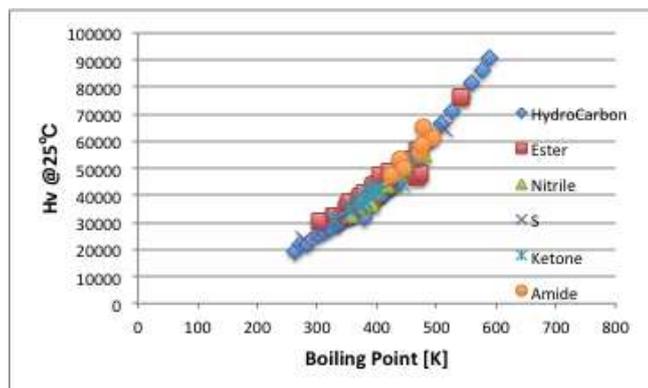


Fig.1 Relationship between boiling point and latent heat of vaporization (regular solution)

On the other hand, hydrogen-bonding alcohols and carboxylic acids are plotted as shown in Fig. 2, which is significantly different from the regular solution. Even at the same boiling point as the regular solution, more latent heat of vaporization is required. Carboxyl compounds show very specific behavior. This is because the low molecular weight carboxyl compound evaporates as a dimer, which is derived from the fact that the energy of evaporation decreases specifically. Amine compounds are close to the curve of the hydrocarbon compound, and it is closer to the regular solution, suggesting that the network structure of hydrogen bonding in amines is different from alcohols and carboxylic acids.

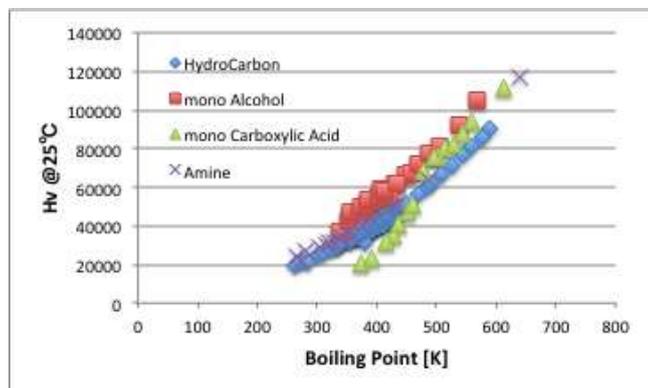


Fig.2 Relationship between boiling point and latent heat of vaporization (hydrogen bonding compound)

Since alcohols make hydrogen bonds, so boiling points will become high. Why do alcohols need more energy than the latent heat of vaporization corresponding to their boiling point?

We defined the extra energy required to destroy a three-dimensional network with equation (7).

$$E_{\text{Net}} = H_{v298} - 85 \cdot \text{Boiling point} \quad (7)$$

With equation (3) and (7), we obtained equation (8)

$$E_{\text{Net}} = \delta_1^2 \cdot \text{MVol} + 8.31 \cdot 298.15 - 85 \cdot \text{Boiling point} \quad (8)$$

$$\delta_{\text{Net}} = (E_{\text{Net}}/\text{MVol})^{0.5} \quad (9)$$

δ_{Net} is obtained by equation (9).

Equation (10) gives a new definition.

$$\delta_1^2 = \delta_{\text{Reg}}^2 + \delta_{\text{Net}}^2 \quad (10)$$

Let δ_{Reg} be the solubility parameter of the regular solution and δ_{Net} be the solubility parameter of the network.

Since δ_1 , MVol, and Boiling point were available in 1967 when HSP first appeared, this δ_{Net} has been hidden for 50 years. δ_{Net} is a parameter that existed from the beginning.

It does not mean that regular solutions have no δ_{Net} . The solubility parameter is a value obtained by taking the root of the value obtained by dividing the energy of evaporation by the molecular volume as defined scheme (3). As shown in Fig. 3, even when the horizontal axis is changed to the molecular volume, the latent heat of vaporization per unit volume of the hydrogen bonding compound becomes higher than that of the simple hydrocarbons.

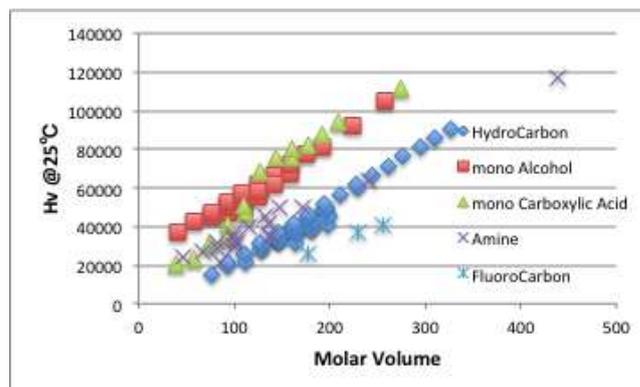


Fig.3 Relationship between molar volume and latent heat of vaporization

As shown in Fig. 4, the olefin compounds and the ether compounds have almost the same latent heat of vaporization as the hydrocarbons, and have almost no δ_{Net} . However, aromatics compounds have greater latent heat of vaporization. In handling HSP, this excess latent heat of vaporization is allocated as a large δ_D as the π - π stacking force of the aromatic ring and a weak π -Hydrogen bonding force δ_H of the aromatic ring and hydrogen attached to aromatic ring.

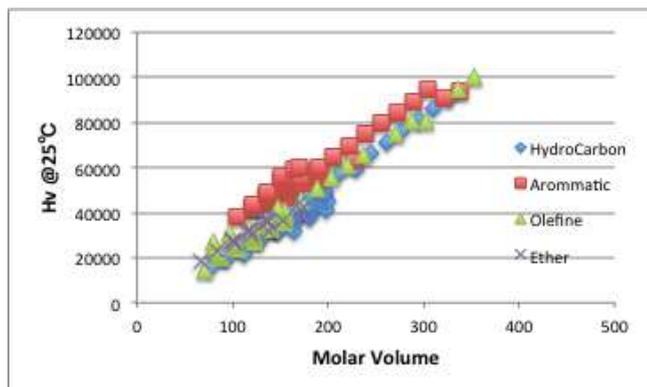


Fig.4 Relationship between molar volume and latent heat of vaporization

It is obvious from Fig. 5 that other so-called regular solutions also have large latent heat of vaporization compared to simple hydrocarbons when viewed in terms of molecular volume. Especially, the amide compound is a regular solution in consideration of the latent heat of vaporization per boiling point, but it has very high latent heat of vaporization per molecular volume. Therefore, it has a very large value of δ_{Net} .

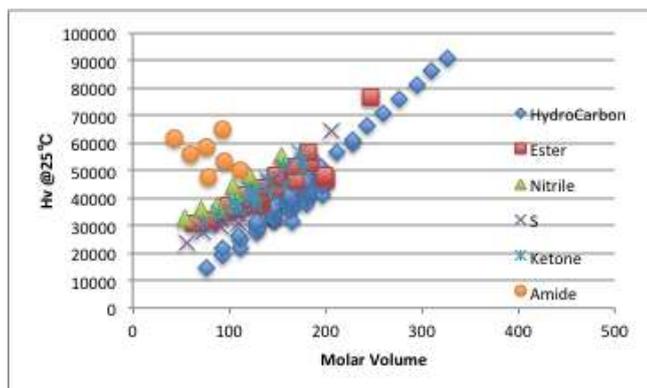


Fig.5 Relationship between molar volume and latent heat of vaporization

Also, cyclic hydrocarbons have a greater latent heat of vaporization than chain hydrocarbons. Not limited to hydrocarbon compounds, cyclic compounds have higher latent heat of vaporization and δ_{Net} . This property is considered to be, for example, the molecular orientation force of the liquid crystal. It also plays an important role in relation to the specific solubility and absorbability of drugs such as steroids.

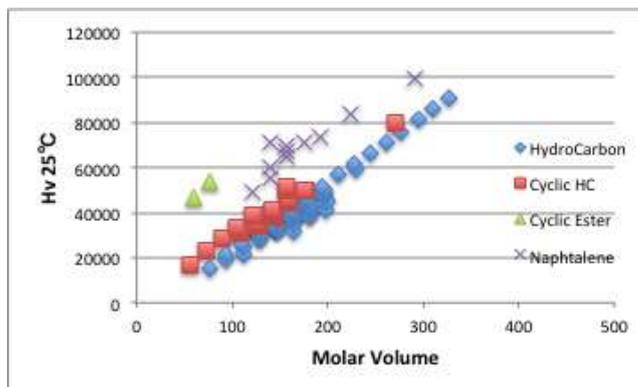


Fig.6 Relationship between molar volume and latent heat of vaporization

Furthermore, the correlation between the boiling point and the latent heat of vaporization with multifunctional alcohol is examined as shown in Fig.7. Diols having two alcohol groups have lower latent heat of vaporization than mono-alcohols. This does not match our intuition.

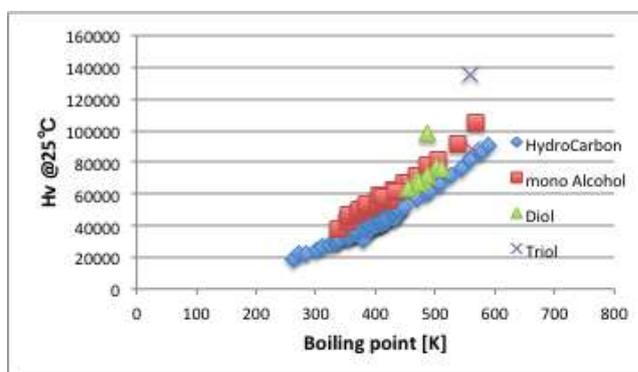


Fig.7 Relationship between boiling point and latent heat of vaporization

However, as seen in the molecular volume (Fig. 8), it is understood that diols and triols have a large latent heat of vaporization, and therefore they have large δ_{Net} values.

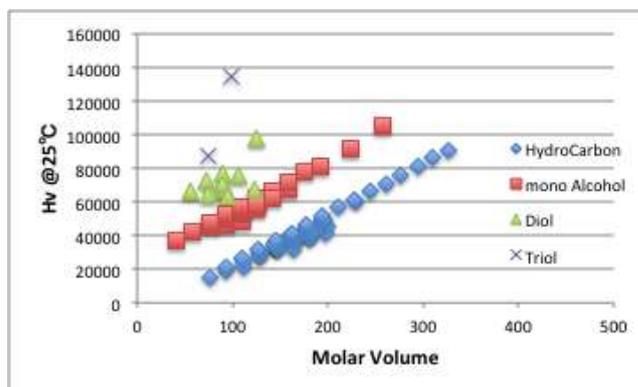


Fig.8 Relationship between molar volume and latent heat of vaporization

It seems that it is very important to consider the behavior concerning dissolution of δ_{Reg} , δ_{Net} which is easily obtained in this way. This δ_{Net} is mainly caused by a network of hydrogen bonds. Hydrogen bonds are originally formed

by hydrogen bonded to highly electronegative atoms such as oxygen or nitrogen, and correspond to Brønsted - Lowry 's acid / base. However, δ_{Net} does not require active hydrogen, for example cyclic esters have very large values. Therefore, δ_{Net} is believed to be the essence of coordination bond network formed by electron pair acceptor, (EA), electron pair donor (ED) based on Lewis Acid/Base.

2.2. Consideration from surface tension

Beerbower used the division of the different contributions to the C.E.D. according to Hansen in a computer analysis^[3]. For alcohol compounds, the surface tension can be calculated by the following equation.

$$\delta_d^2 + \delta_p^2 + 0.06 \delta_h^2 = 13.9 (1/Vol)^{1/3} \gamma \quad (11)$$

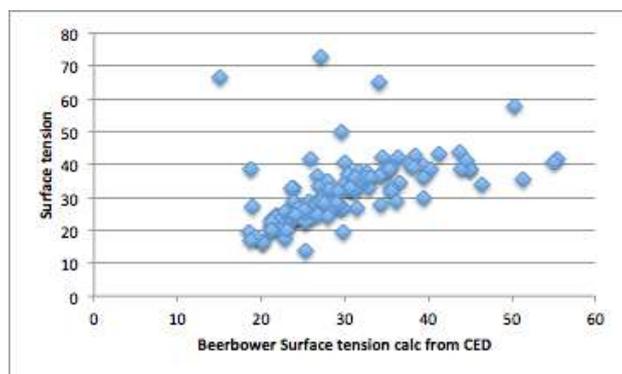


Fig.9 Surface tension calculation by scheme (11)

He concluded that the hydrogen bonding term hardly contributes to the surface tension.

Where has the energy in the hydrogen bond term gone? Among the energy of δ_T , the hydrogen bond mainly contributes to the network δ_{Net} of the coordination bond. Therefore, we evaluate scheme (13) assuming equation (12).

$$\delta_d^2 + \delta_p^2 + 0.06 \delta_h^2 = \delta_T^2 - \delta_{Net}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 - \delta_{Net}^2 = \delta_{Reg}^2 \quad (12)$$

$$\gamma = \delta_{Reg}^2 * MVol^{1/3} / 13.9 \quad (13)$$

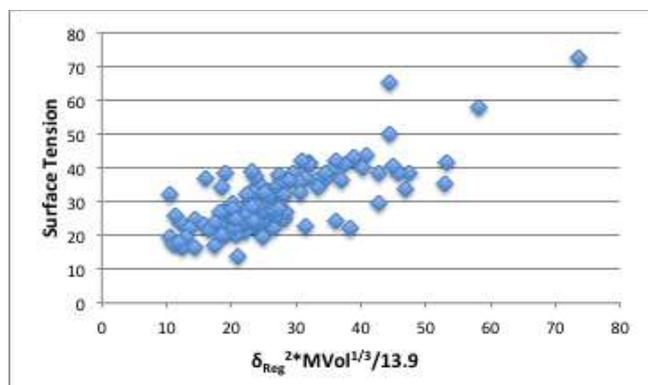


Fig.10 Surface tension calculation by scheme (13)

It can be seen that the surface tension can be estimated with considerable reproducibility including water. Such surface tension measurements are often done with the liquid in contact with very hydrophobic air. Then, on the liquid surface, the network is broken, though the network structure inside the liquid is very strong. The balance of these forces is observed as surface tension.

This has an important meaning when there are interfaces such as dissolution (or dispersion) of solids. On the surface of the liquid, the coordination network has been cut off. Therefore, on hydrophobic solid surfaces, only energy of $\delta_T^2 - \delta_{Net}^2$ can participate in solubility. However, if the surface has donor/acceptor nature, there is a possibility that solubility may be higher than expected due to rearrangement of coordination bond network. In considering adhesion of polymer, roughening the surface of the polymer with sandpaper or the like is said to effective because it increases the surface area. But it is probably not just that (and the increased area is usually very small). Even if the polymer itself has some degree of donor and acceptor nature, the surface is in contact with hydrophobic air when forming the polymer, so the network of coordination bonds goes inside the polymer. By roughening the surface, if it can come into contact with the network of internal coordination bonds the adhesion will be higher than roughening the surface. In fact, PTFE does not have high adhesion at the roughened surface.

Regarding the estimation of the surface tension, the Macleod-Sugden method is prominent.

$$\gamma^{1/4} = P (\text{Liquid Density} - \text{Gas Density}) / \text{Molecular Weight} \quad (14)$$

In many cases Gas Density is ignored as not being large. This constant P is called Parachor and is obtained for various compounds. From equation (13) and (14), Parachor can be calculated by equation (15).

$$P = (\delta_{Reg}^2 * MVol^{1/3} * (MVol)^{1/3} / 13.9)^{1/4} \quad (15)$$

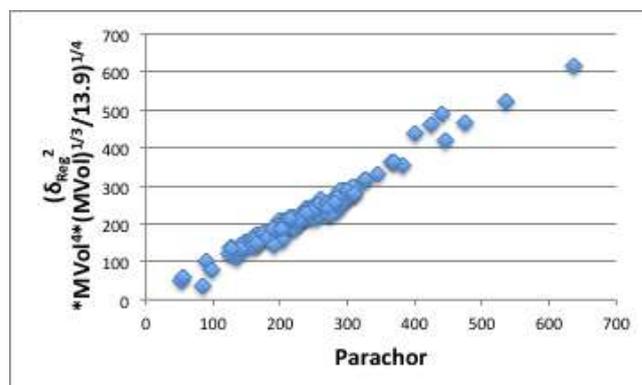


Fig.11 Evaluation of Scheme(15)

As shown in Fig. 11, the value of Parachor obtained from Equation (15) almost completely matches with experimental Parachor.

2.3. Consideration from vapor Pressure

The simplest formula to provide a good fit to the change of vapor pressure with temperature is the Antoine equation (16) with 3 constants.

$$\log P = A - B/(T^{\circ}\text{C} + C) \quad (16)$$

The C of Antoine means the efficiency of temperature effect. The $B / (T^{\circ}\text{C} + C)$ increases when C is small, so the vapor pressure decreases. The C parameter is an index showing how effectively the temperature is reflected in the vapor pressure. As shown in Fig. 12, when δ_{Net} becomes larger, the network of coordination bond becomes stronger and the temperature is not effectively converted to vapor pressure. Therefore, Antoine C becomes small with increasing δ_{Net} .

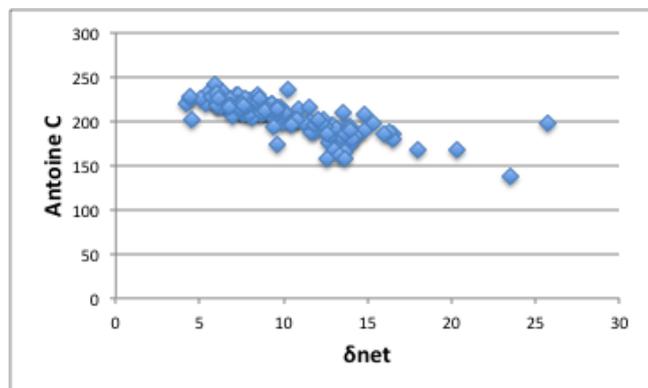


Fig.12 The correlation of δ_{Net} to Antoine C

B of Antoine is known to correlate with latent heat of vaporization. This coincides with the cohesive energy of δ_{Reg} as shown in Fig.13.

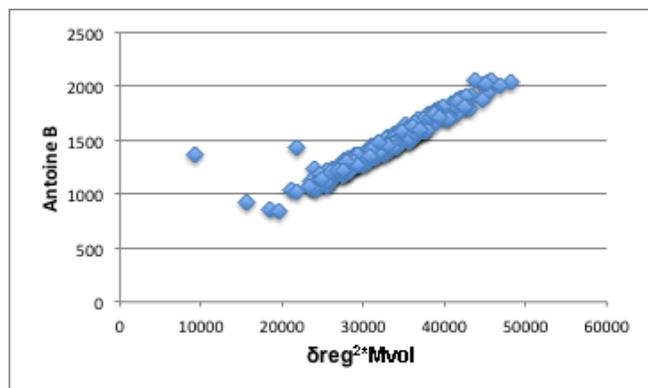


Fig.13 Relationship between δ_{Reg} and Antoine B

Substituting the temperature at which the vapor pressure becomes 1 mmHg into the equation (16) results in the equation (17).

$$\log(1) = 0 = A - B / (T_{1\text{mmHg}} - 273.15 + C) \quad (17)$$

$T_{1\text{mmHg}}$ can be calculated by the equation (18).

$$T_{1\text{mmHg}} = B/A + 273.15 - C \quad (18)$$

Originally it should be treated with melting point (T_m), but melting point is susceptible to symmetry such as ease of packing of molecules, and the accuracy of estimation is low. $T_{1\text{mmHg}}$ which can be conveniently calculated only from the Antoine constant is an important temperature index.

$$\theta_b = (298.15 - T_{1\text{mmHg}}) / (T_b - T_{1\text{mmHg}}) \quad (19)$$

$(T_b - T_{1\text{mmHg}})$ means a temperature range that is liquid. Therefore, θ_b is an index indicating where in the liquid phase region room temperature (25°C) is located.

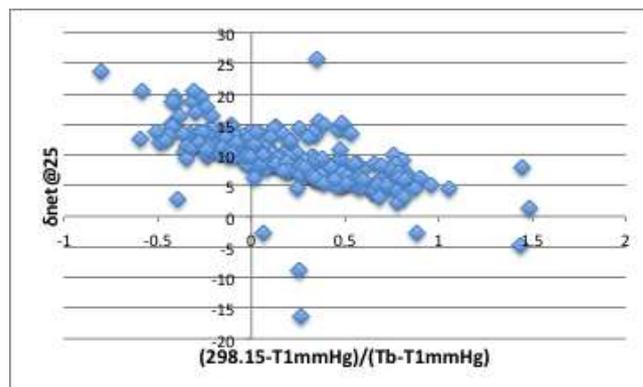


Fig.14 The correlation of θ_b to δ_{Net}

This θ_b correlates with δ_{Net} as shown in Fig.14.

We already built temperature dependent properties estimation scheme for, Molar Volume, δ_D , δ_P , so on. We can calculate properties at the temperature $T_{1\text{mmHg}}$ and T_b .

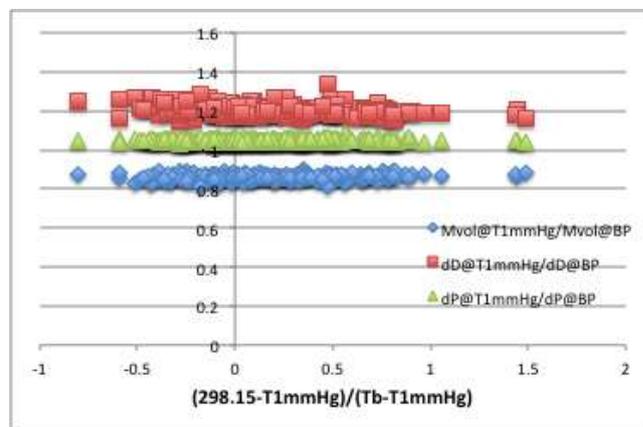


Fig.15 Reduced Volume, Reduced δ_D and Reduced δ_P

The actual $T_{1\text{mmHg}}$ and T_b are dependent on solvents, though the properties@ $T_{1\text{mmHg}}$ / properties@ T_b become identical as shown Fig.15. This is another interpretation method of the Corresponding State Theory.

The intermolecular force has disappeared at the critical point. Various physical properties are estimated based on how far the temperature and the pressure are apart from critical point. In that case, the critical point (T_c , P_c , V_c) and the boiling point (BP, 760 mmHg, V_b) are often taken as reference points. However, it is in the gas state during BP -

T_c. It is often convenient to predict the physical properties of liquids based on the liquid phase up to T_m - BP. In the corresponding state theory, triple points are used in many cases other than the critical point. However, it is difficult to experimentally obtain the triple point. So, it is very interesting that the point of [T_{1mmHg}, 1mmHg, MVol@1mmHg] works as reference of temperature-dependent properties.

2.4. Consideration from Critical Point

As shown in Fig.16, the critical pressure is highly correlated with δ_{Reg} . At the critical point, the intermolecular force forming the network disappears.

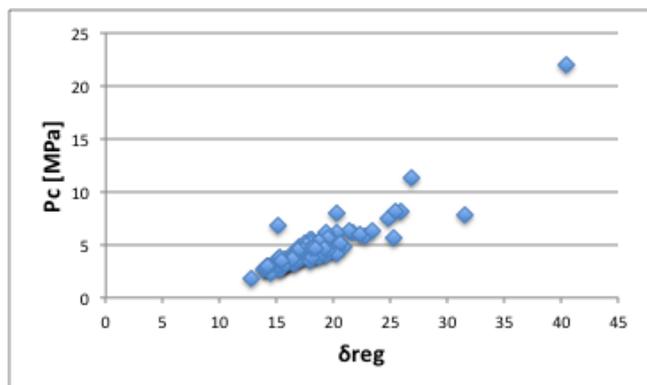


Fig.16 Relationship between δ_{Reg} and critical pressure

Conversely, it can be said that the kinetic energy necessary for eliminating the network is given at the critical temperature of T_c.

Also, as shown in Fig. 17, the critical volume has a very high correlation with the value of Parachor described in the section on surface tension. As Parachor itself depends on δ_{Reg} and molecular volume as shown in Equation (15), the critical volume at the critical temperature T_c expands by an amount corresponding to δ_{Reg} .

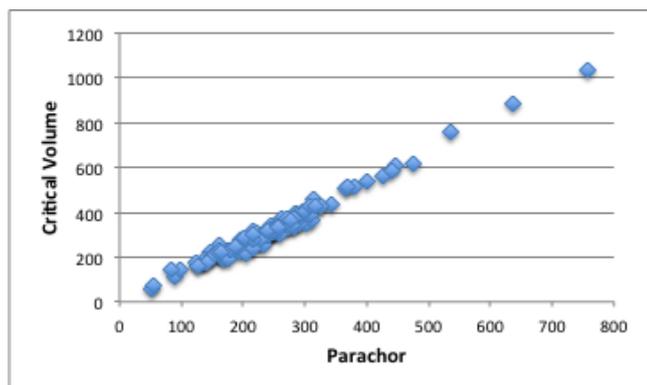


Fig.17 Relationship between Parachor and critical volume

2.5. Consideration from Viscosity

Needless to explain, viscosity increases as the network of coordination bonds becomes stronger. In the dispersion of inorganic materials and the like, the sedimentation rate may

be taken as dispersion stability, but care should be taken because the viscosity greatly affects this sedimentation rate.

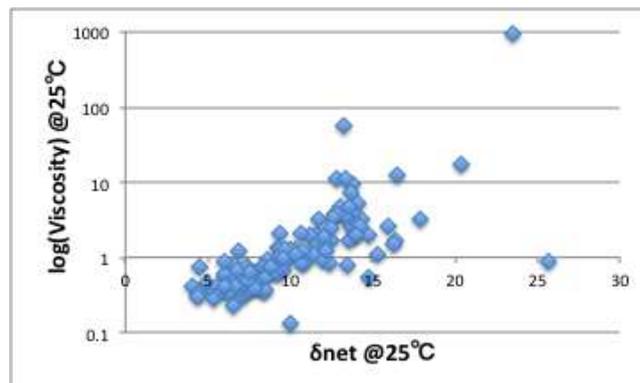


Fig.18 Relationship between δ_{Net} and viscosity

2.6. Consideration from Dielectric constant

The dielectric constant of the organic solvent is a parameter necessary for calculating the δ_p term of HSP and is a very important physical property value.

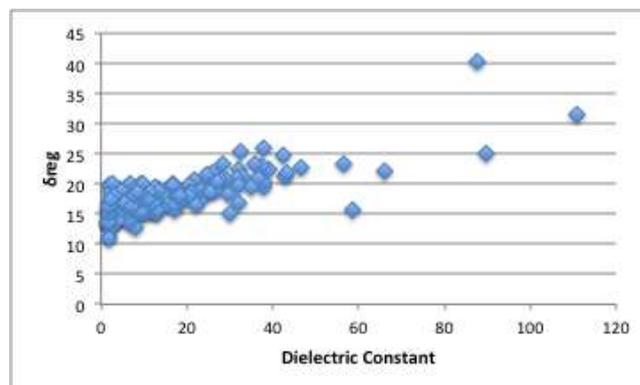


Fig.19 Relationship between dielectric constant and δ_{Reg}

Generally, the higher the polarity of the solvent, the higher the dielectric constant, but there are few methods to estimate the dielectric constant from the molecular structure. However, when plotting the value of dielectric constant as δ_{Reg} , it is found that there is a rough correlation as shown in Fig.19.

Until now, latent heat of vaporization, refractive index, dipole moment and dielectric constant were necessary to determine HSP. From now on, the HSP can be verified also from vapor pressure, surface tension, Critical properties, Parachor, molar refraction, Antoine constant etc.

3. Further insight

We analyzed the effect of the network structure from data on mutual miscibility between solvents [4].

From the reference literature, the mutual miscibility of various solvents for alcohols was taken out and the HSP distances calculated using formula (19) shown in Table 1. The above three groups are acids, alcohols, amines and hydrogen bonding compounds. Below that is a compound

that creates coordination bond networks other than hydrogen bonds.

$$Distance_{2017} = \{(\delta_{Dvdw1} - \delta_{Dvdw2})^2 + (\delta_{Dfg1} - \delta_{Dfg2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2\}^{0.5} \quad (19)$$

Ethyl alcohol is miscible with all other solvents, though, HSP distance is a very wide range of 8.6 to 19.2. For 1,3-Propandiol, Ethylene glycol, Glycerol as the number of hydroxyl groups increases, the number of solvents that do not mix increases. 1,2-Propandiol, 1,3-Propandiol have the same number of hydroxyl groups, but 1,3-propandiol does not mix with more solvents. This trend is consistent with the trend of δ_{Net} of alcohols. As a general rule, solvents with large δ_{Net} can be said to be less miscible because the network must be destroyed. When looking at the row of the table,

except for one exception (Di-n-amylamine / Ethylene glycol), the HSP distance increases as going to the right. However, when looking at the table vertically, there are many inconsistencies between the HSP distance and miscibility. For example, as in the case of Glycerol, it does not mix with Salicylaldehyde (Distance:15.3) but dissolves with Diisopropylamine (Distance:25.8). Therefore it is not possible to predict miscibility of non-cognate solvents at HSP distances. We have discussed solubility in HSP distance no matter what the subject is. In doing so, it has been recommended to avoid solvents of homologues and to evaluate with as much solvent as possible. And this result is contradictory. It remains to be seen whether adding the size ratio factor (common in miscibility theories) helps improve the predictability.

Table 1 Miscibility of alcohols to solvents

Solvents	Ethyl alcohol	1,2-propanediol	1,3-propanediol	Ethylene glycol	Glycerol	HML	LIL	δ_{net}
4-Methyl-n-valeric acid	9.0	11.2	14.4	15.9	17.1	15.9	17.1	10.6
Diethylacetic acid	7.4	9.6	12.8	14.3	15.5	14.3	15.5	13.0
o-Cresol	8.6	10.2	13.4	14.7	15.9	15.9		13.4
3-Heptanol	8.6	10.9	14.1	15.5	16.7	15.5	16.7	13.3
Tetradecanol	11.9	14.1	17.4	18.6	19.8	14.1	17.4	13.6
Pyridine	14.2	15.7	18.1	20.3	21.5	21.5		21.8
Di-n-amylamine	16.0	18.3	21.4	20.7	24.1	21.4	20.7	16.9
Diisopropylamine	17.5	19.9	23.1	24.5	25.8	25.8		15.3
Salicylaldehyde	8.7	9.6	11.9	14.1	15.3	9.6	11.9	16.2
Diethyl formamide	10.7	12.2	14.2	16.9	18.1	18.1		12.9
Methyl isopropyl ketone	15.1	17.3	19.9	22.1	23.3	19.9	22.1	6.7
Acetone	12.5	14.4	16.6	19.2	20.4	19.2	20.4	7.2
Diisobutyl ketone	16.3	18.5	21.5	23.2	24.4	16.3	18.5	9.4
Isoamyl acetate	13.7	16.1	19.3	20.7	22.0	16.1	19.3	8.6
n-Heptyl acetate	15.2	17.5	20.7	22.1	23.4	15.2	17.5	9.2
Ethyl chloroacetate	12.3	14.2	16.6	18.9	20.2	14.2	16.6	10.2
Ethyl phenylacetate	14.6	16.6	19.4	21.2	22.4	14.6	16.6	11.2
Ethyl ether	16.0	18.4	21.5	23.0	24.2	16.0	18.4	6.6
Benzyl ether	16.2	18.0	21.0	22.4	23.6	16.2	18.0	13.6
Chloroform	15.0	17.3	20.5	21.9	23.1	20.5	21.9	6.1
n-Amyl cyanide	15.1	16.8	19.1	21.6	22.8	16.8	19.1	9.4
Tri-n-butyl phosphate	15.5	17.5	20.3	22.3	23.5	20.3	22.3	12.6
Benzene	19.2	21.3	24.4	25.9	27.1	19.2	21.3	6.1
δ_{net}	15.4	21.6	23.2	23.4	24.9	HML: Highest Miscible Limit LIL: Lowest Immiscible Limit		
	Miscible	Immiscible	Slightly miscible					

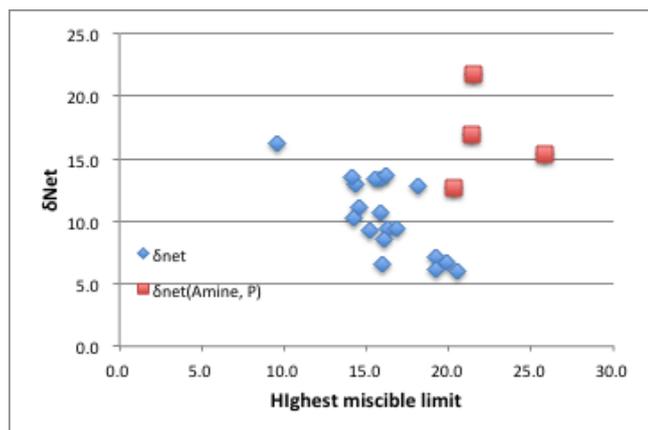


Fig.20 Relationship between HML and solvent's δ_{Net}

Fig. 20 shows the Highest Miscible Limit (HML) of the HSP distance that mixed with solvents to the δ_{Net} of solvents. Fig. 21 shows a plot of the Lowest Miscible Limit (LIL) of the unmixed HSP distance to the δ_{Net} of solvents.

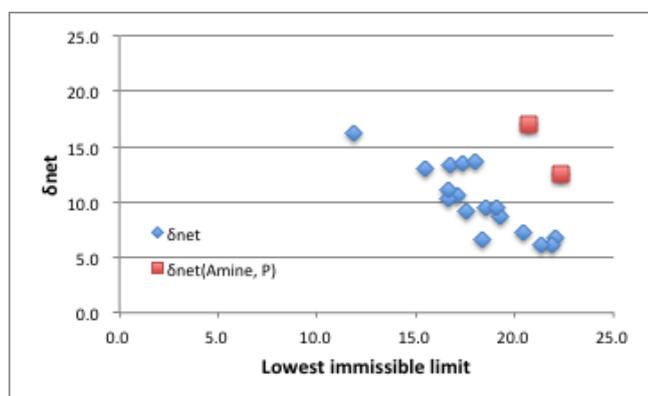


Fig.21 Relationship between LIL and solvent's δ_{Net}

Amines and Phosphate are exceptions, but these HML and LML have good correlation with δ_{Net} of solvents. The meaning of Fig. 21 is that there are solvents that do not mix even though HSP distance is short, and they tend to have a large δ_{Net} . Such a situation is thought to occur when the network of coordination bonds made by solvents and the network of hydrogen bonds of alcohols are incompatible. On the contrary, Fig. 20 shows that there are miscible pairs such as amines that have a long HSP distance. This is thought to be stabilized by a combination of hydrogen bonds of the alcohol and hydrogen bonds of the amine and to mix them despite the long HSP distance. Since cleavage of the network of hydrogen bonds or coordination bonds becomes

conspicuous by mixing of solvents between low molecules, it seems that they did not affect the dissolution of polymers and the like so far. However, it seems to be very important in the design of mixed solvents. In addition, polyhydroxy polymers such as cellulose are considered to have a very high δ_{Net} above Glycerol, and in order to dissolve them, select a solvent in which network relocation works effectively, or select alkali that change the hydroxyl group to a negative ion and repel.

4. Conclusion

It is shown that the size of the coordination bond network itself is δ_{Net} calculated from HSP, boiling point and molar volume. And that δ_{Net} is clearly closely related to various other thermodynamic properties. Although this δ_{Net} is mainly a network of hydrogen bonds, as discussed in Part 3 even a compound having a large δ_p exists as a coordination bond network. It is suggested that the stabilization by rearrangement between hydrogen bond and coordination bond is low, perhaps analogous to hard/soft acid/base where hard-hard (δ_H) and soft-soft (δ_P) can be strong while hard/soft is weak. In almost all systems exceptions are low molecular carboxylic acids. It is necessary to incorporate whether it is a closed network in which the network ends with two molecule pairs or an open network spreading in three dimensions.

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