New Directions in HSP Part 2 Donor/Acceptor and δ_{Net}

HSPiP

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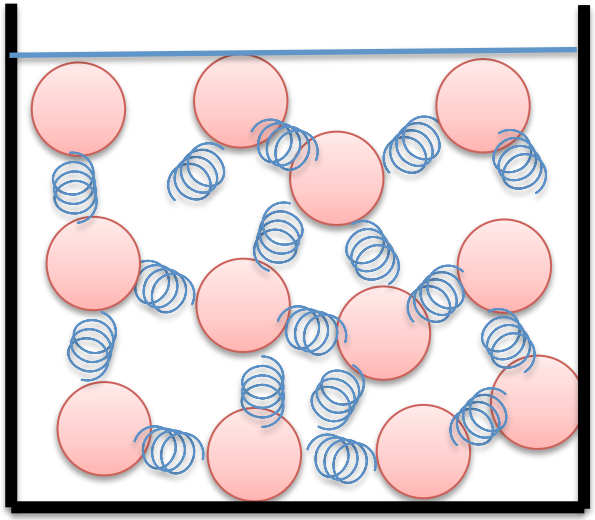
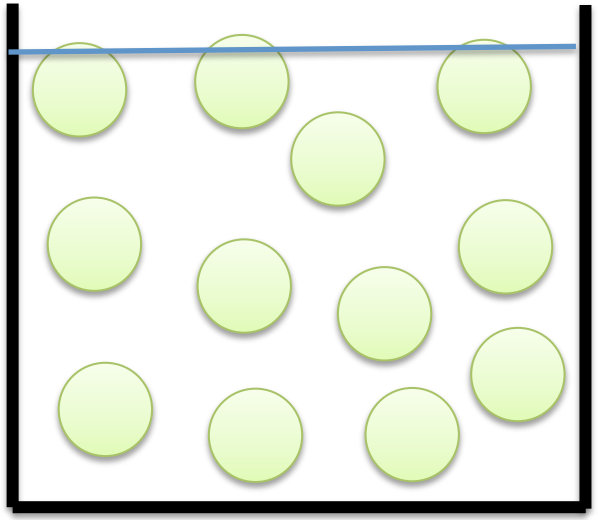
2017.4.5

Even same Molar Volume, ..



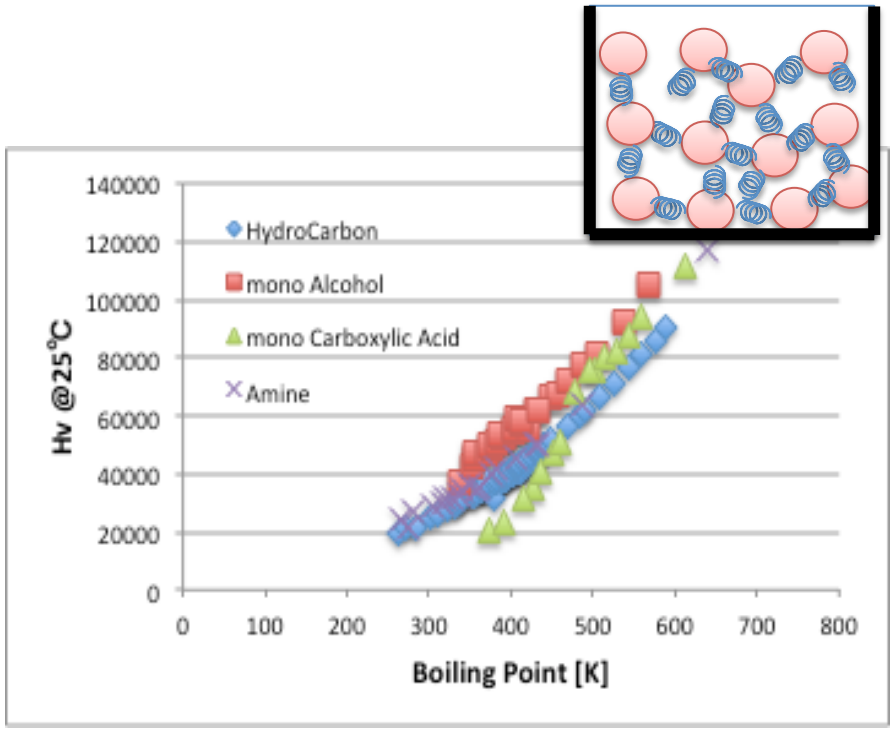
Associative liquid



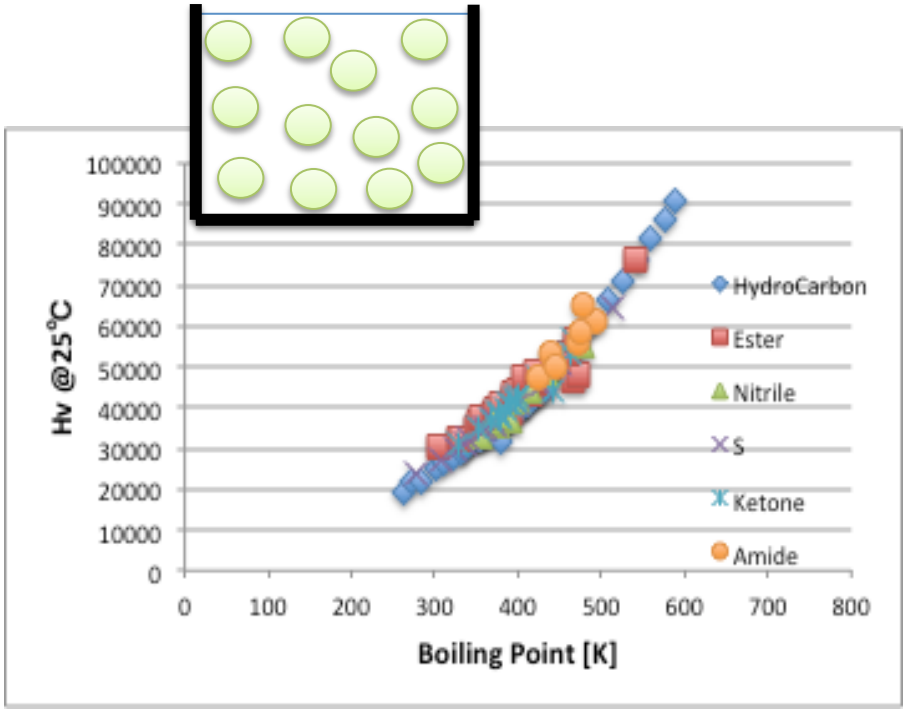
Regular Solution

Large	Hv	Small
High	Boiling Point	Low
High	Density	Low
High	Viscosity	Low

Correlation between BP and Hv



Associative liquid

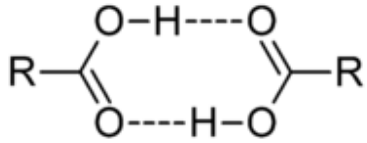


Regular Solution

H_v = 85*BP + Network Break Energy

H_v = 85*BP NBE=0 ??

Trouton Rule

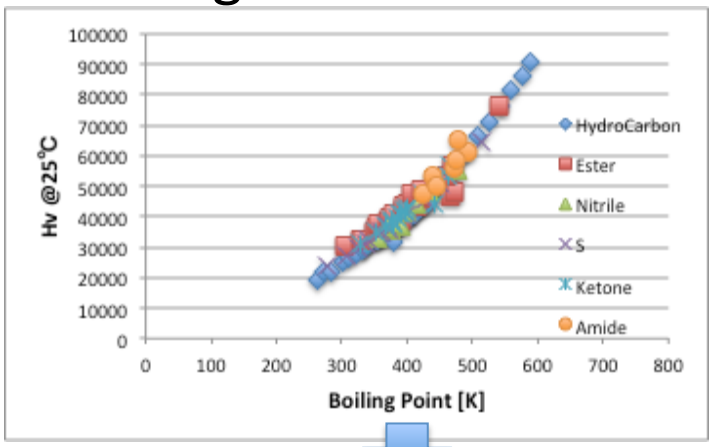


Abnormality of
Small Carboxylic Acid

Evaporate as Dimer

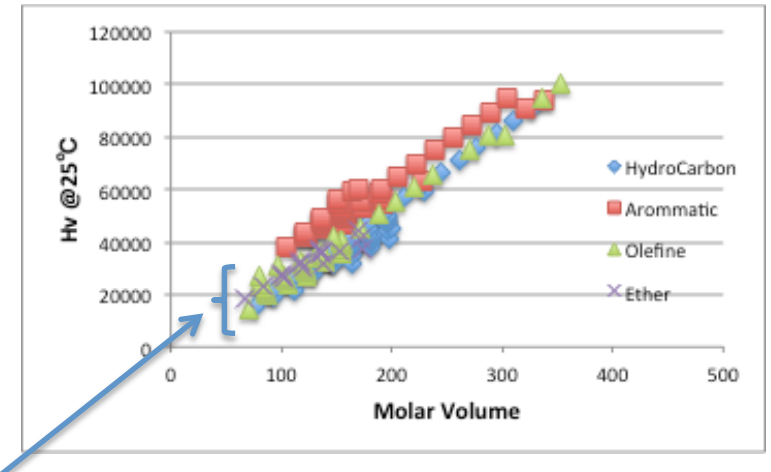
Regular Solution and the Network

Regular Solution

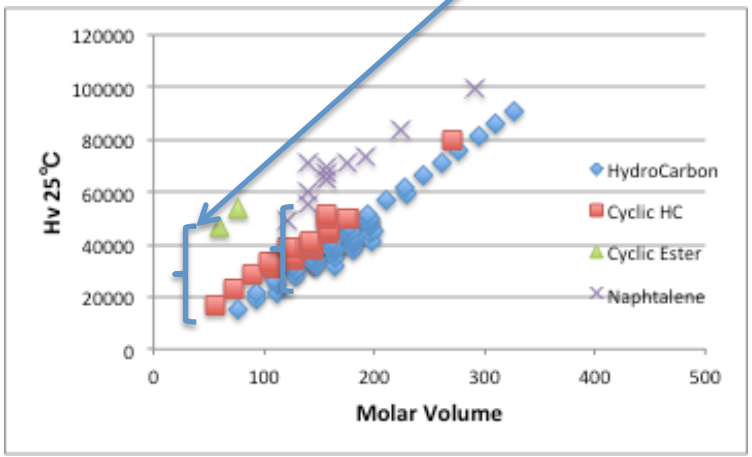


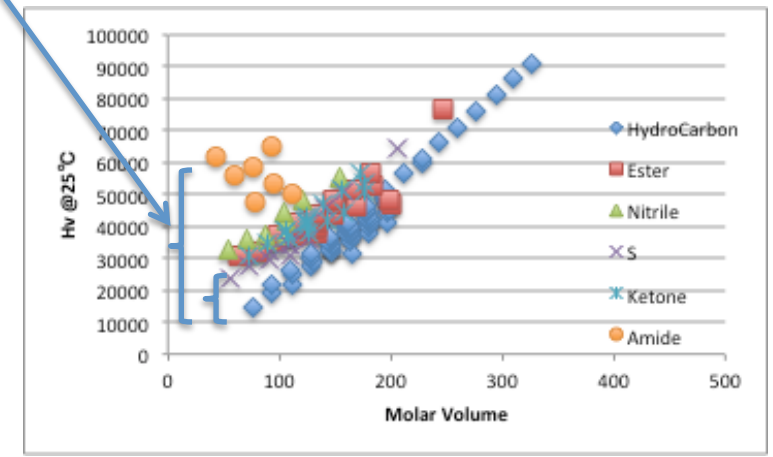
MVol

$\delta_T=((H_{v298} - RT)/MVol)^{0.5}$



Viewing from Molar Volume, even regular solution need larger Hv compare to hydrocarbons.

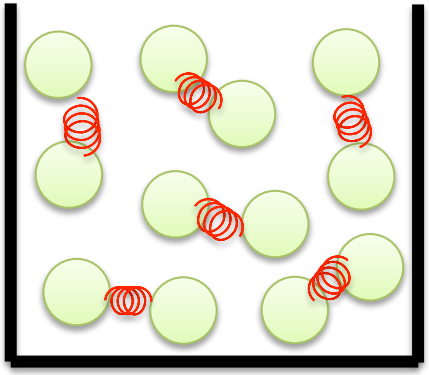




Network Energy(E_{Net}), δ_{Net} & δ_{Reg}

$$H_{v298} = 85*BP + E_{Net}$$

$$\delta_T=((H_{v298} - RT)/MVol)^{0.5}$$



Even Regular Solution have network

$$\delta_T^2= \delta_D^2 + \delta_P^2 + \delta_H^2$$

$$E_{Net} = \delta_T^2 * MVol + 8.31*298.15 - 85*BP$$

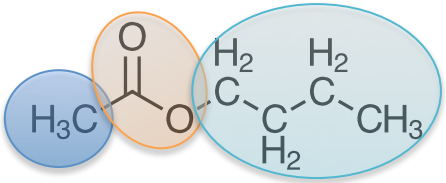
$$\delta_{Net}= (E_{Net}/MVol)^{0.5}$$

HSP
MVol
BP
} are needed to determine δ_{Net}

$$\delta_T^2 =\delta_{Reg}^2 + \delta_{Net}^2$$

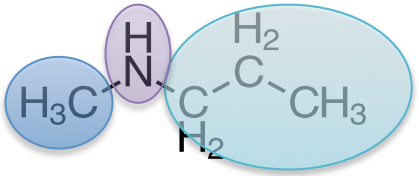
δ_{Net} is the parameter that has hidden for 50 years!

HSP as Molecule



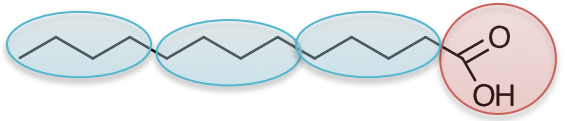
[15.8, 3.7, 6.3]
MVol=132.6,
BP=399.26K

δ_T	δ_{Reg}	δ_{Net}
17.4	15.4	8.1



[15.7, 3.9, 5.9]
MVol=102.7,
BP=336.15K

δ_T	δ_{Reg}	δ_{Net}
17.2	15.9	6.5



[16.2, 3.3, 6.4]
MVol=241.5,
BP=585.25K

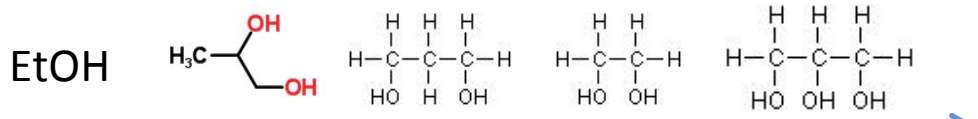
δ_T	δ_{Reg}	δ_{Net}
17.7	14.0	10.9

Effect on Solubility ?

Does Similar HSP mean
Similar Solubility ?

Similar HSP (and δ_T)

Miscibility of Solvents



Increase δ_{Net}, decrease miscibility.

δ_{Net}	15.4	21.6	23.2	23.4	24.9

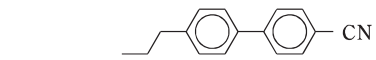
Solvents	Ethyl alcohol	1,2-propanediol	1,3-propanediol	Ethylene glycol	Glycerol	HML	LIL	δ net
4-Methyl-n-valeric acid	9.0	11.2	14.4	15.9	17.1	15.9	17.1	10.6
Diethylacetic acid	7.4	9.6	12.8	14.3	15.5	14.3	15.5	13.0
o-Cresol	8.6	10.2	13.4	14.7	15.9	15.9		13.4
3-Heptanol	8.6	10.9	14.1	15.5	16.7	15.5	16.7	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			

H.B. Solvent

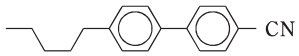
Miscible | Immiscible | Slightly missible — HSP Distance

HML : Highest Miscible Limit
LIL : Lowest Immiscible Limit

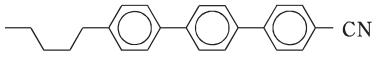
Liquid Crystal



(2) Cr66(N26)Iso

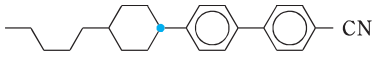


(3) Cr24N35Iso

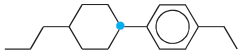


(4) Cr131N240Iso

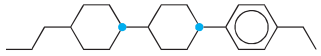
(5) Cr31N55Iso



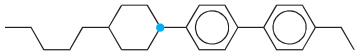
(6) Cr96N222Iso



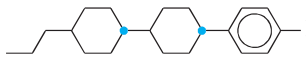
(7) Cr-1(N-70*)Iso
(*外挿値)



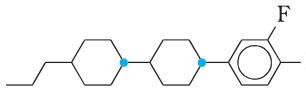
(8) Cr31Sm161N163Iso



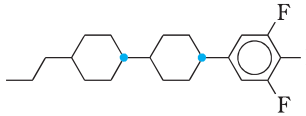
(9) Cr34SmB146N164Iso



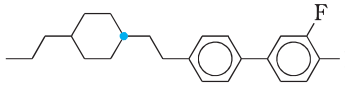
(14) Cr88N159Iso
Δε+4.8



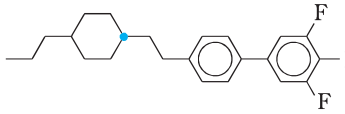
(15) Cr44N118Iso
Δε+5.3



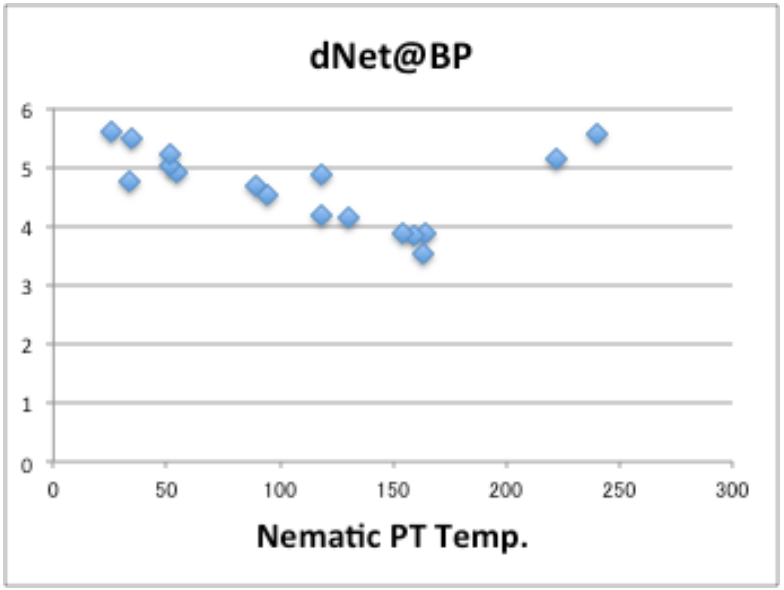
(16) Cr65N94Iso
Δε+8.3

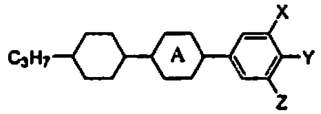


(17) Cr64N89Iso
Δε+6.3



(18) Cr48N52Iso
Δε+11.8

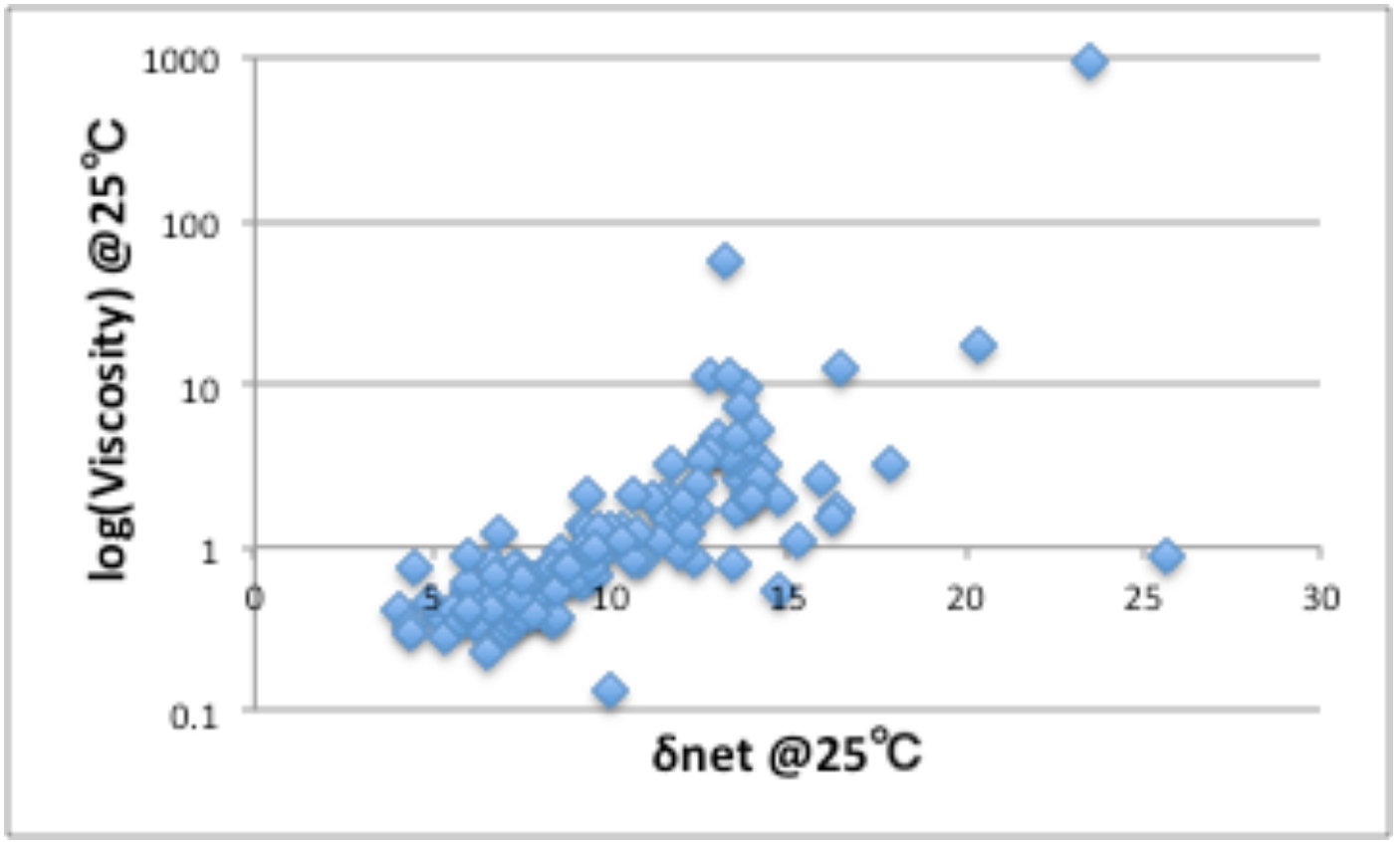




No.	X	Y	Z	A	相転移点(℃)	Δε	Δn	γ1	ref.
7	F	F	H	⬡	C 44.2 N 124.3 I	5.8	0.104	140	17)
8	F	F	F	⬡	C 64.7 N 93.7 I	8.3	0.073	171	20)
9	F	F	F	⬡	C 40.7 (N 33.2) I	12.8	0.137	143	20)
10	H	OCF_3	H	⬡	C 39B69 N154 I	6.9	0.087	142	21)
11	F	OCF_3	H	⬡	C 46 N 130I	9.0	0.089	200	21)
12	F	OCF_3	F	⬡	C 66 N 118.3 I	10.5	0.083	279	21)
13	F	F	F	⬡	C 74 (N 51.2)I	17.0	0.068	201	21)

相転移点を除き物性値はフッ素系母液晶からの外挿値

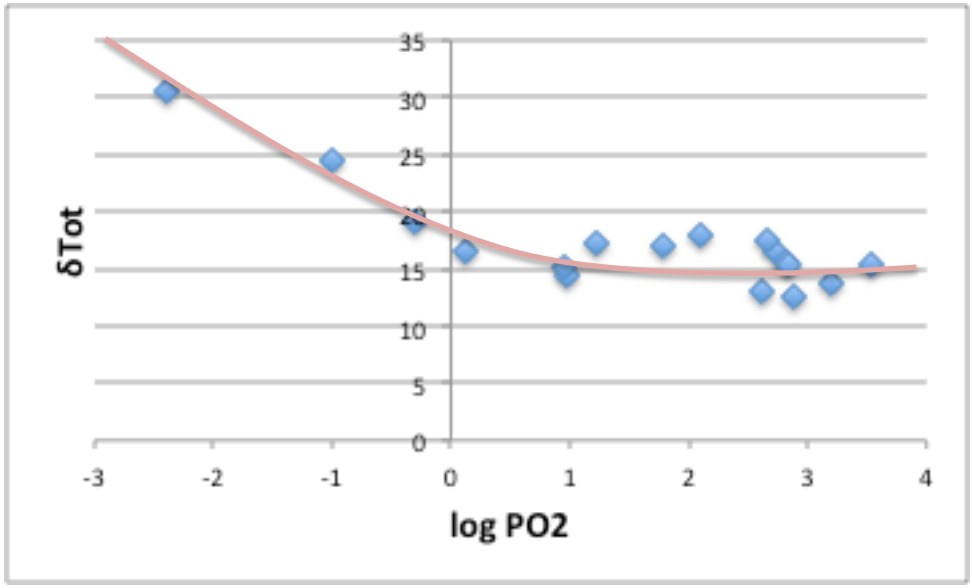
δ_{Net} and Viscosity

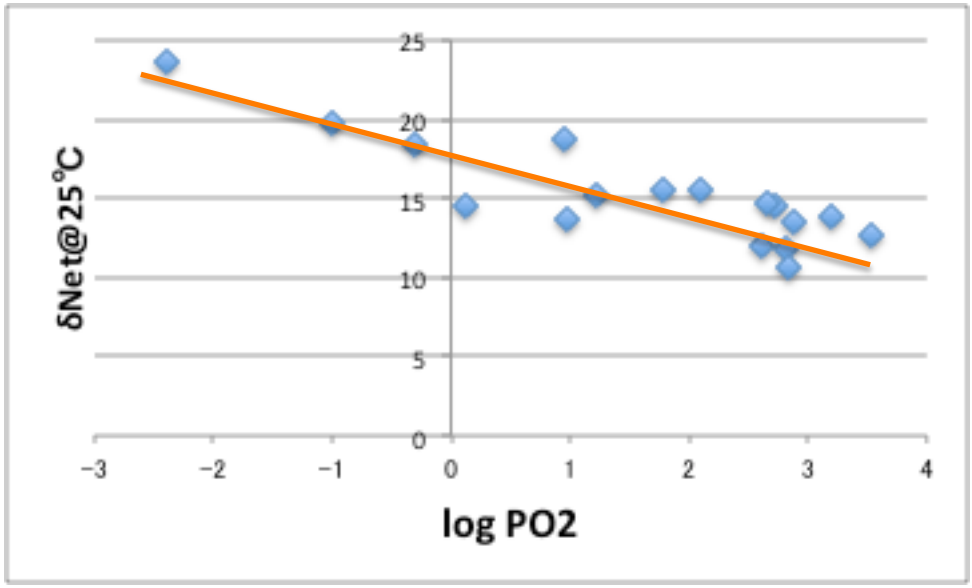


As δ_{Net} increase, log Viscosity also increase.

O2 permeability through polymer

Name	logPO2
Polyethylene	3.193124598
Polypropylene	2.892094603
Poly(vinyl alcohol)	−2.397940009
Polyoxyethylene	2.722633923
Poly(vinyl fluoride)	2.621176282
Polyacrylonitrile	−1
Poly(cis−1,4−butadiene)	3.523746467
Poly(vinyl chloride)	0.977723605
Polymethacrylonitrile	−0.301029996
Poly(vinyl acetate)	1.77815125
Poly(methyl acrylate)	2.096910013
Polychloroprene	2.812913357
Poly(vinylidene chloride)	0.113943352
Polytetrafluoroethylene	2.84509804
Poly(methyl methacrylate)	1.230448921
Polystyrene	2.653212514
Poly(ethylene terephthalate)	0.954242509

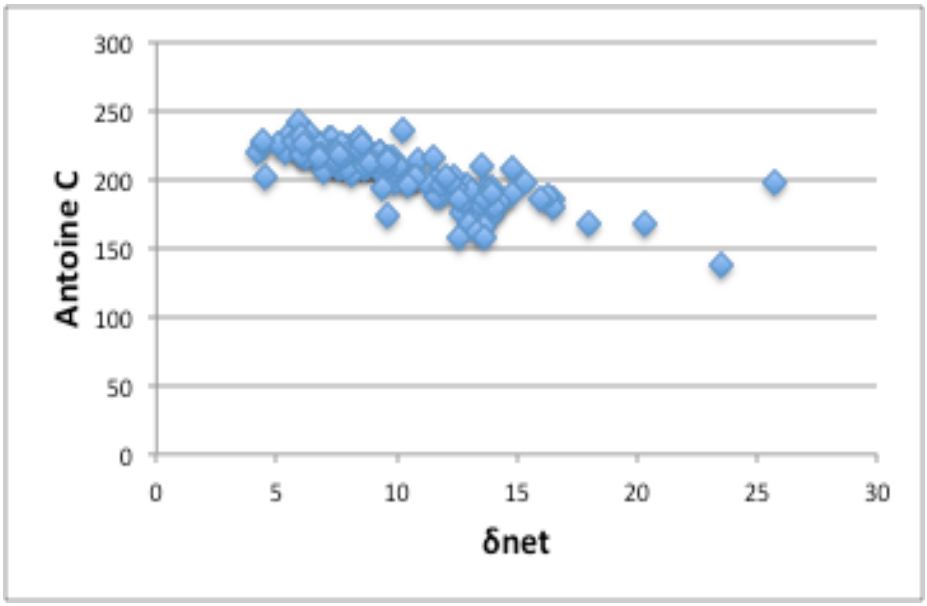


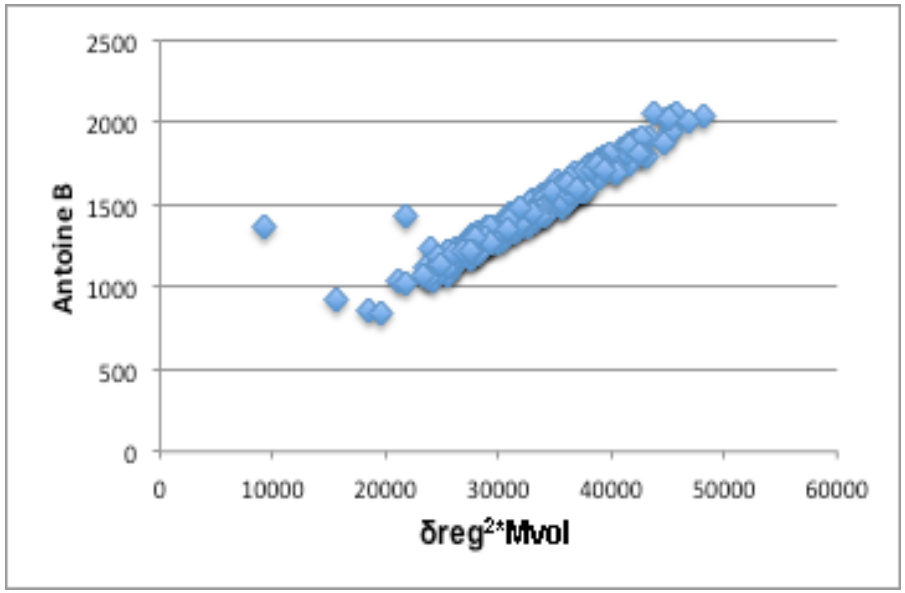


Vapor Pressure of Solvents

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

Antoine Parameters
A, B, C





δ_{Net} to Antoine C

$\delta_{Reg}{}^{2}$*Mvol to Antoine B

Extra Energy to Break Network

Increase Boiling Point with FGs

Small Antoine C means
low Vapor Pressure

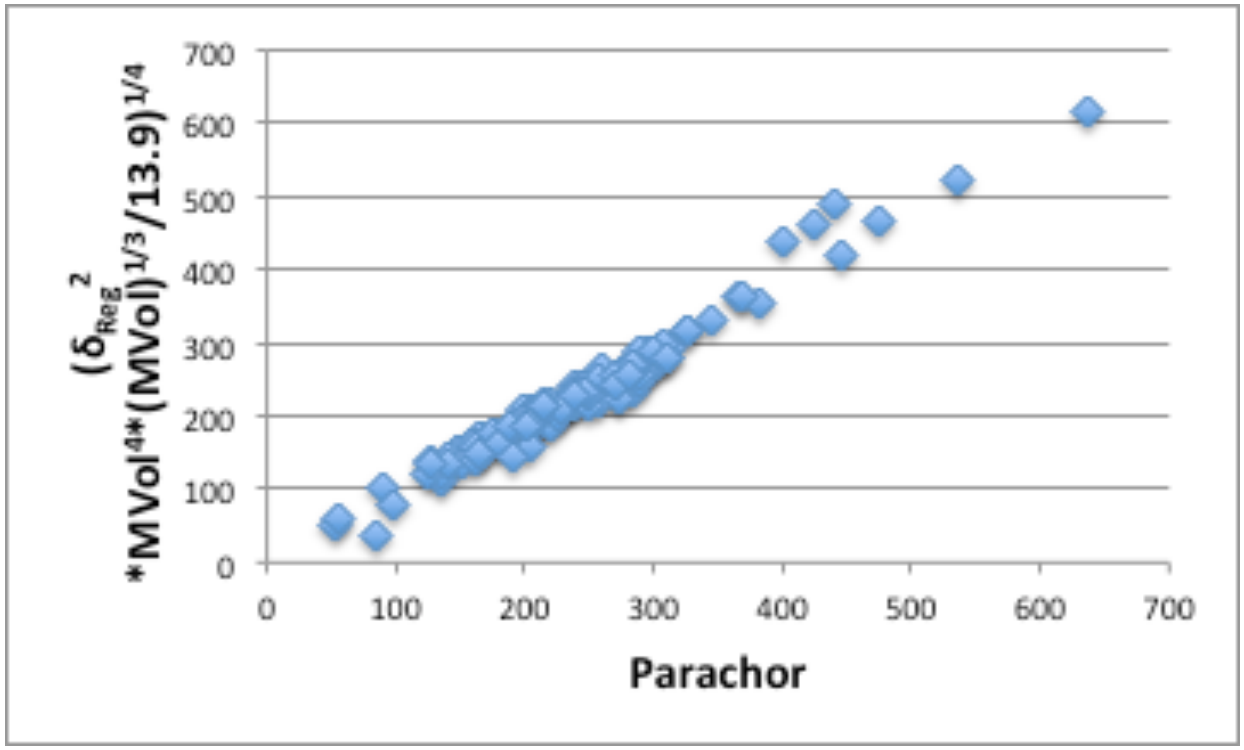
Large Antoine B means
low Vapor Pressure

Surface Tension

Macleod-Sugden method

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

P:Parachor

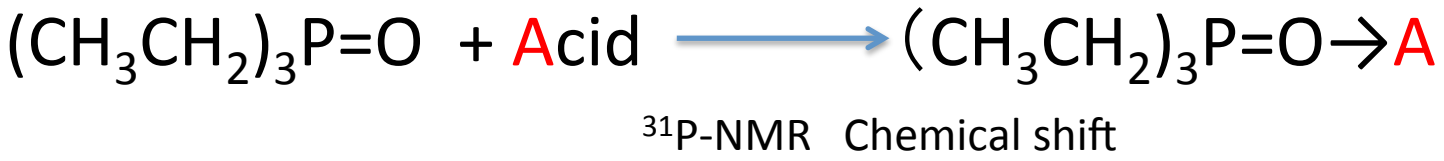


$P=(\delta_{Reg}^{2} * MVol^{13/3}/13.9)^{1/4}$

Gutmann Donor/Acceptor

Gutmann DN (Donor Number)

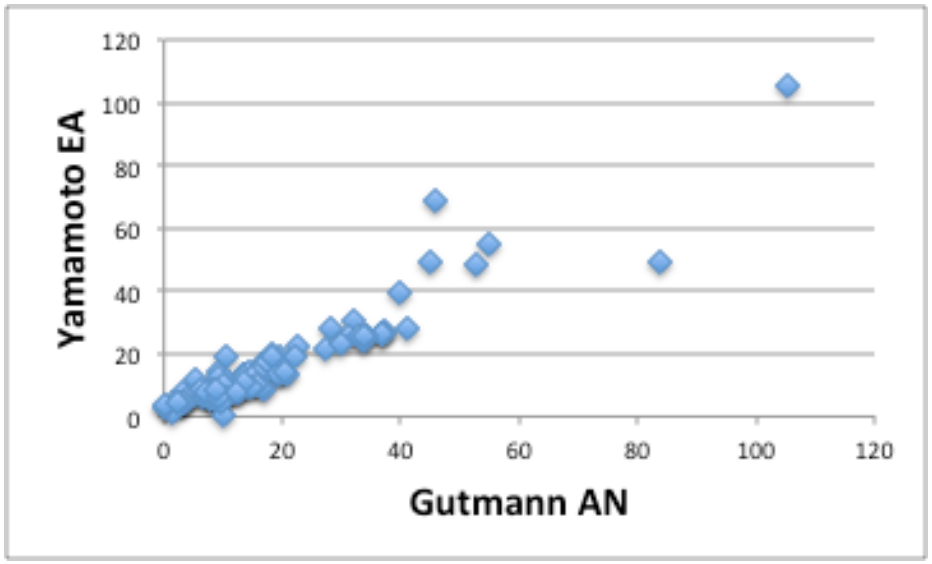
Gutmann AN (Acceptor Number)

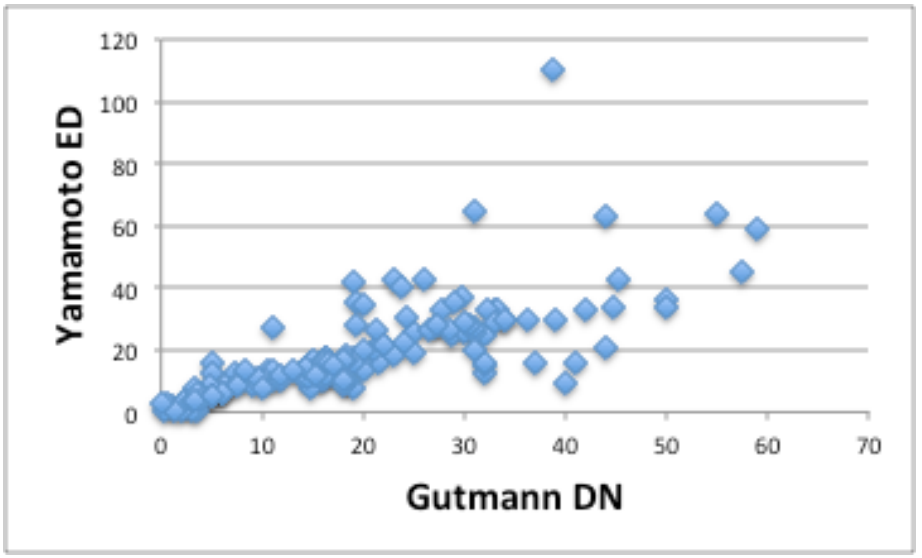


Lewis Electron Pair Donor /Electron Pair Acceptor

BASE ACID

Prediction of Lewis Electron Donor(ED) / Electron Acceptor(EA)



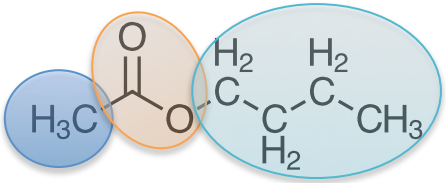


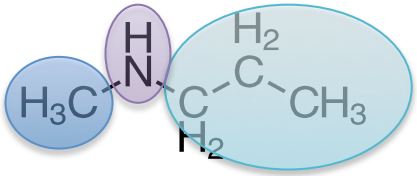
Gutmann DN, AN are measured at very dilute 1:1 complex.

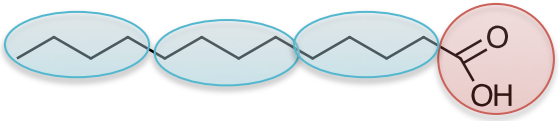
Functional Group Contribution method: Yamamoto ED, EA

Multi-Functional Group Molecule problems exist, but
we can obtain Y-ED, Y-EA from only molecular structure.

Electron Donor / Acceptor



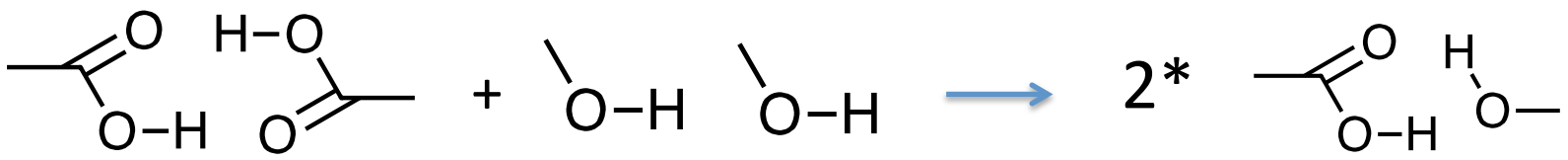




	δ_H	δ_{Net}	Y-ED	Y-EA
	6.3	8.1	15	7.3
	5.9	6.5	35.7	7.1
			Base	
				Acid
	6.4	10.9	12.6	47.4
	Volume Average		per mol	

Network re-arrangement

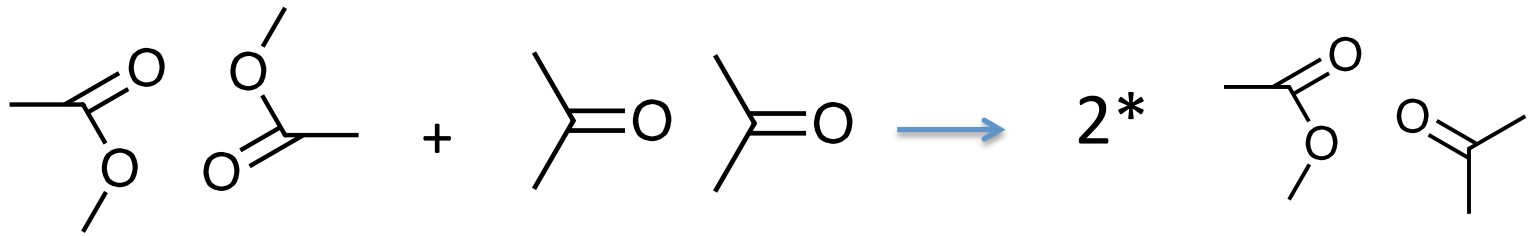
Y-ED1=11.5 Y-EA1=45.6 Y-ED2=12.7 Y-EA2=23.1



2*(Y-ED1 – Y-ED2)*(Y-EA1 – Y-EA2) =2* (11.5 – 12.7)*(45.6 – 23.1) = **-46**

Large Stabilization

Y-ED1=10.1 Y-EA1=4.4 Y-ED2=12.0 Y-EA2=5.0

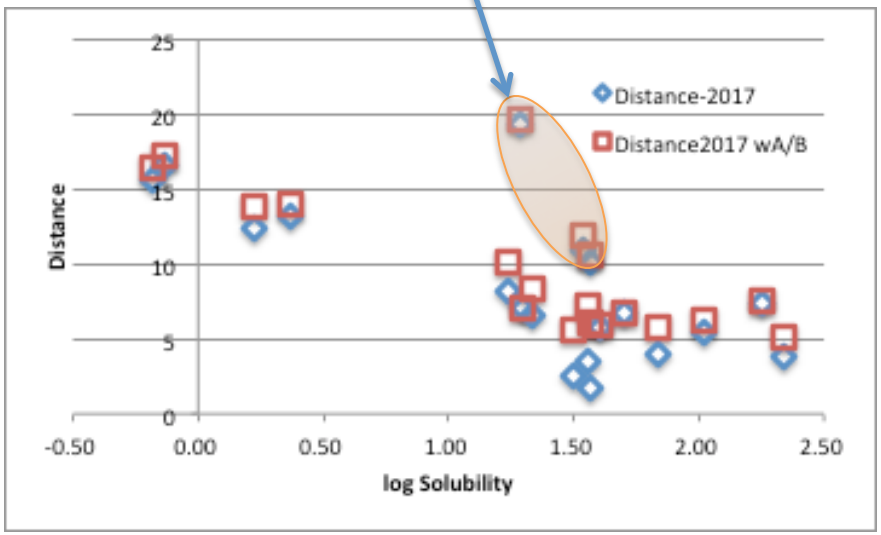


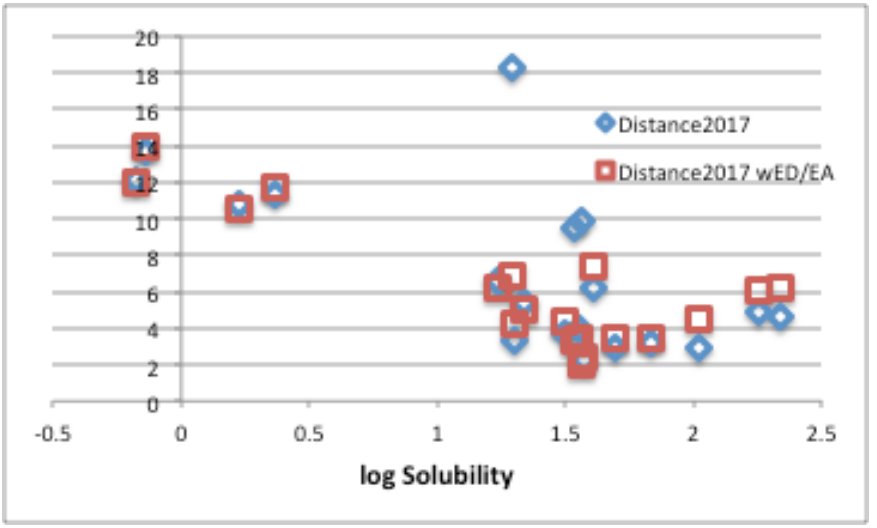
2*(Y-ED1 –Y- ED2)*(Y-EA1 – Y-EA2) = 2*(10.1 – 12)*(4.4 – 5.0) = **+2.3**

Solubility of Oleic Acid

Abnormal solubility of Alcohols

Alcohol solvents: Long HSP Distance but dissolve well.





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

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

Donor / Acceptor re-arrangement

Hexane/Water Extraction

dist-2017

Water $((\delta_{Dvdw}-13.34)^2+(\delta_{Dfg}-7.89)^2+(\delta_P-16)^2+\mathbf{Alpha})^{0.5}$

Hexane $((\delta_{Dvdw}-9.36)^2+(\delta_{Dfg}-11.68)^2+(\delta_P-2.65)^2+\mathbf{Alpha})^{0.5}$

Acid/Base(Water) $(\delta_{Hacid}-15)^2+(\delta_{Hbase}-8)^2$

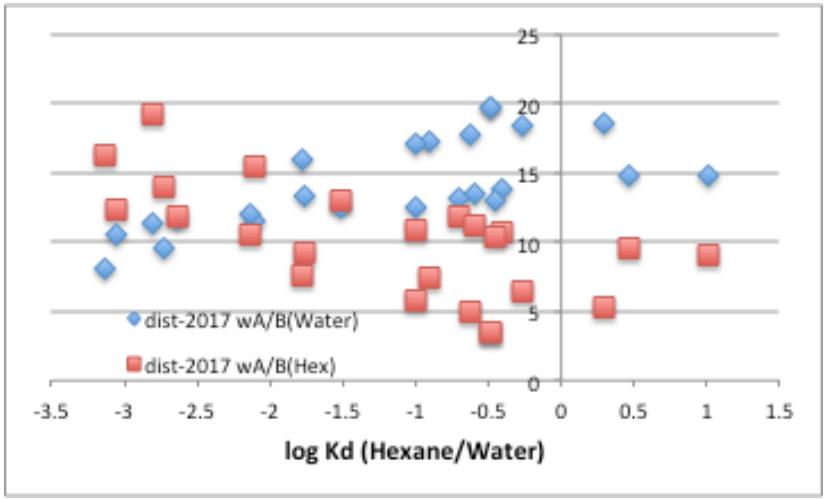
Acid/Base(Hexane) $(\delta_{Hacid}-0.6)^2+(\delta_{Hbase}-3.09)^2$

Donor / Acceptor re-arrangement

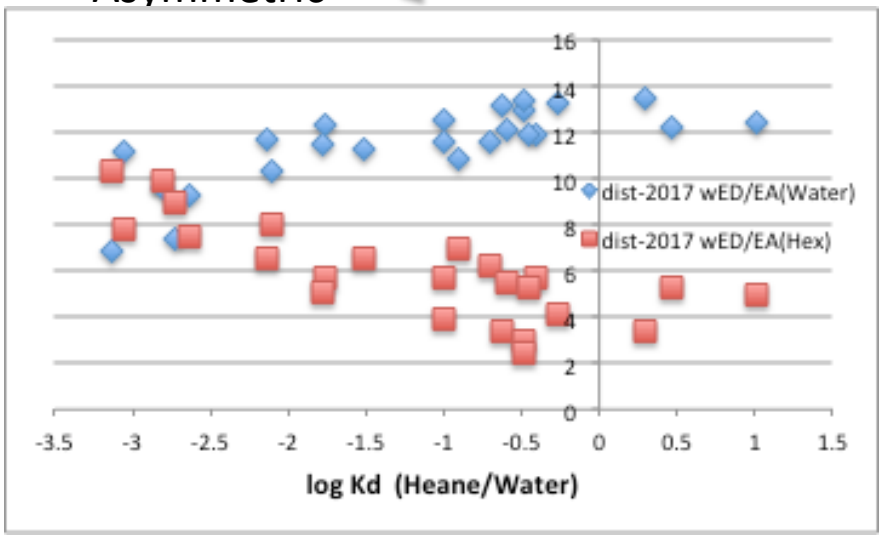
ED/EA(Water) $4.18*(Y\text{-}ED-33)*(Y\text{-}EA-54.8)/MVol$

ED/EA(Hexane) $4.18*(Y\text{-}ED-3.12)*(Y\text{-}EA-3.37)/MVol$

Symmetric



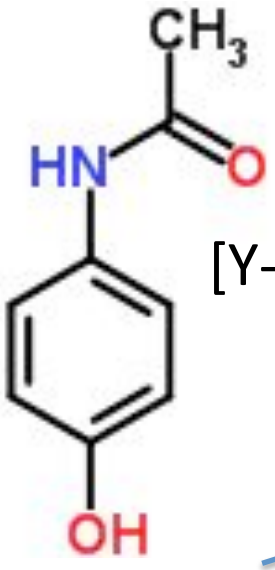
Asymmetric



Multi Functional Groups problem

Paracetamol

Donor / Acceptor re-arrangement should be taken into account one by one



S=O [35.9, 10.3]

Large Stabilization

[Y-ED, Y-EA] = [29.9, 27.4]

Can't Add

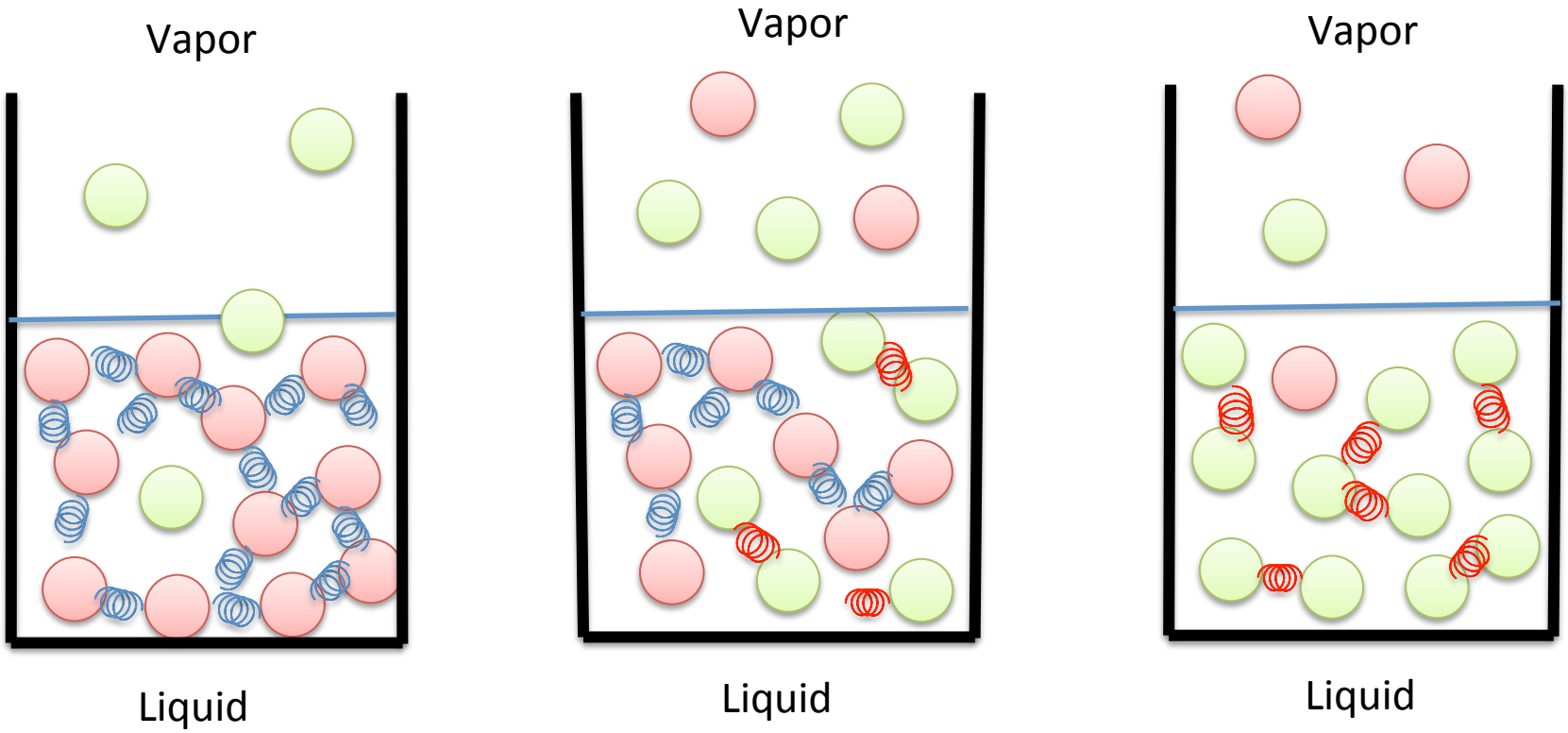
X [35.5, 66.2]

[Y-ED, Y-EA] = [5.6, 38.8]

Large Stabilization

NH [32.4, 4.2]

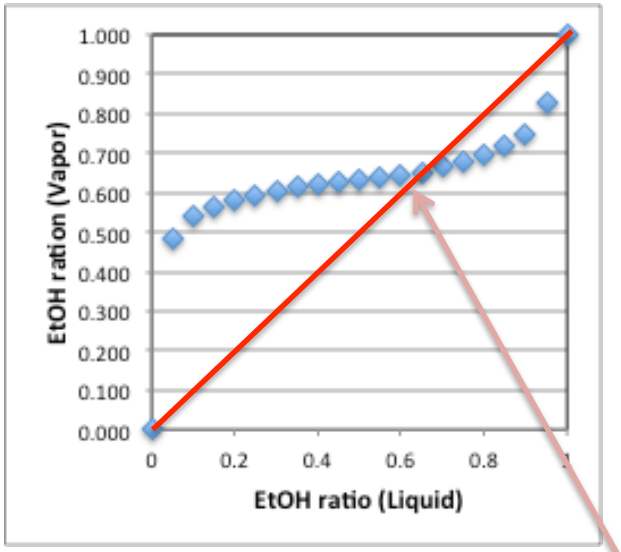
Vapor-Liquid Equilibrium (VLE)



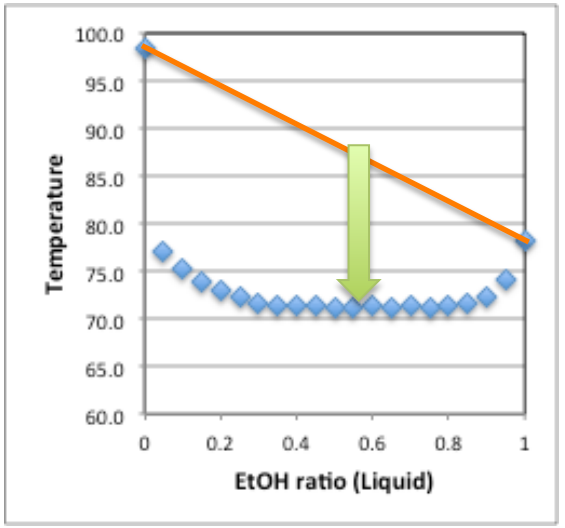
Liquid composition ≠ Vapor Composition

Real VLE

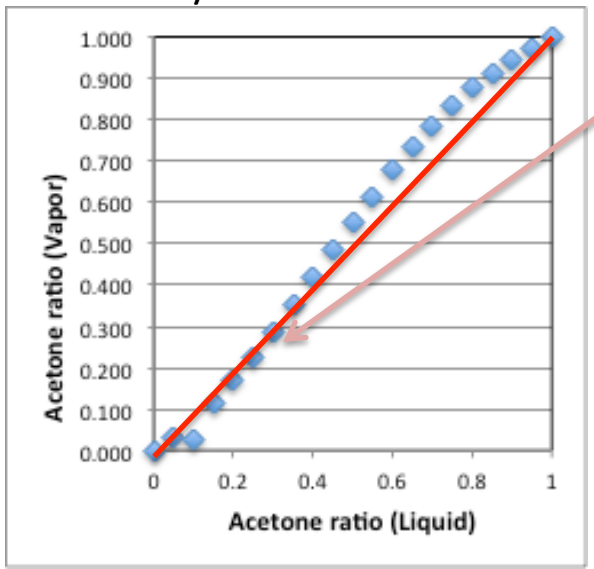
Ethanol / n-Heptane



Minimum Azeotrope



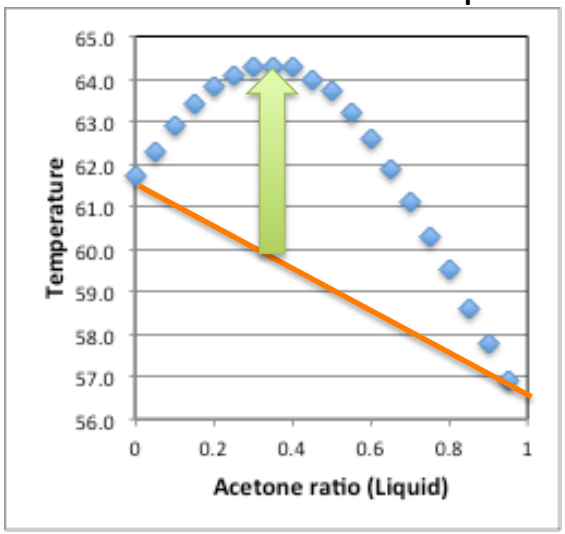
Acetone / Chloroform



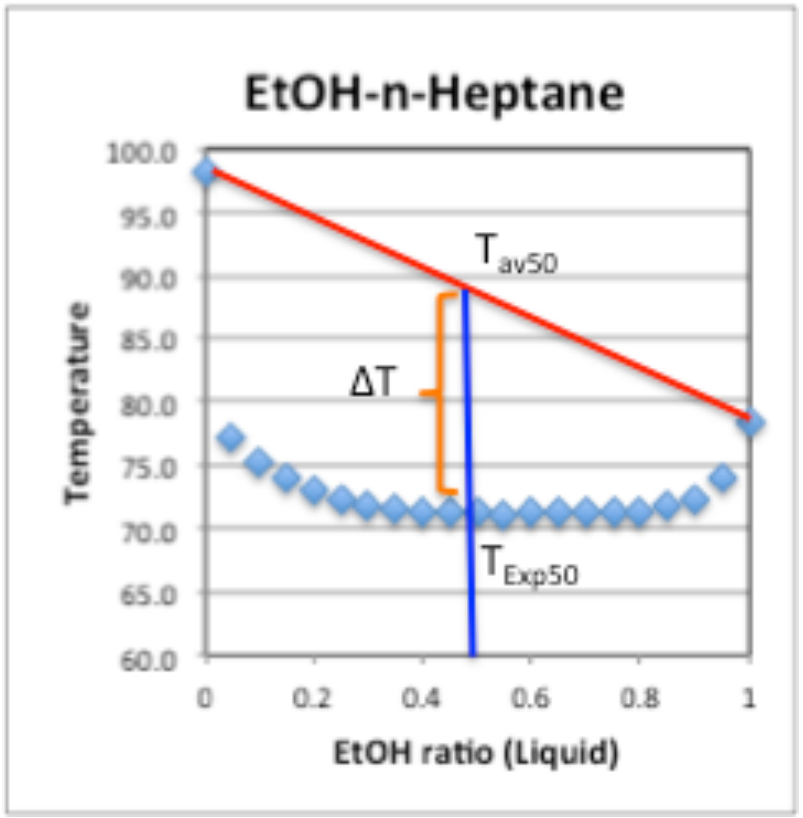
Azeotrope Point

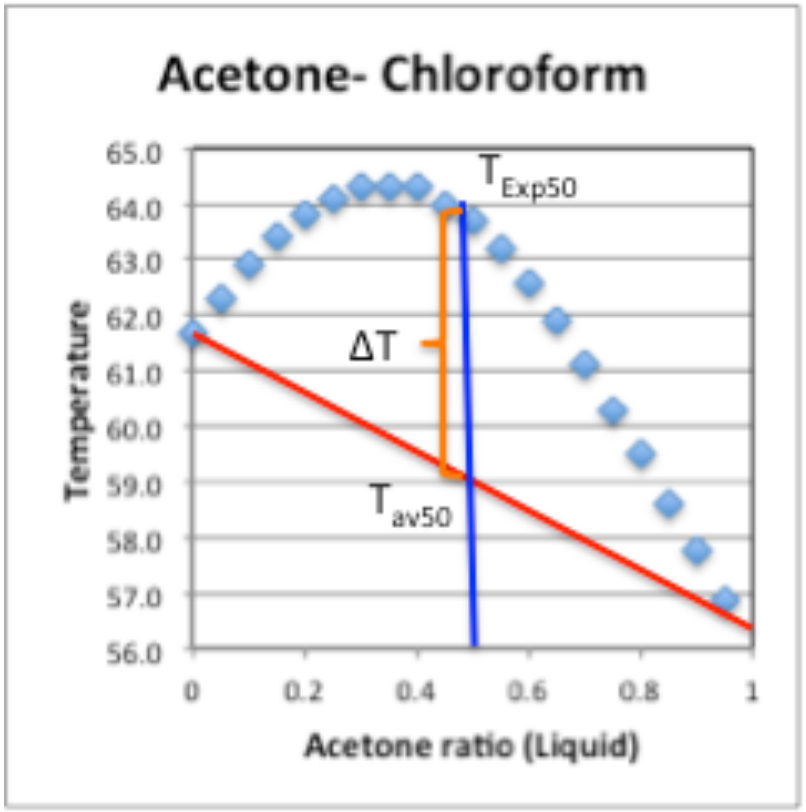
Composition of Liquid phase equal to that of Vapor phase.

Maximum Azeotrope



Yamamoto-T_{ij50} Parameter





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

Tb_{mix} change, Hv_{mix} also change

I have determined 5000+ pair of $Y\text{-}T_{ij50}$

List of $Y\text{-}T_{ij50}$

Large $Y\text{-}T_{ij50}$ pair Acid – Base Pair

Compound-A	Compound-B	Y-Tij50
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

$$HSPmix = \frac{HSP1*\phi1 + HSP2*\phi2}{\phi1 + \phi2}$$

ϕ: Volume Fraction

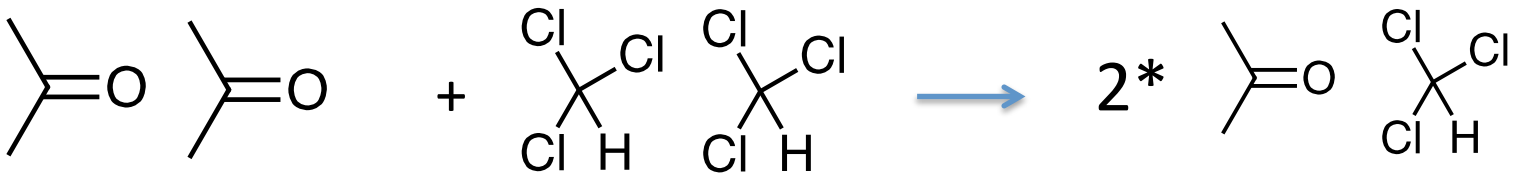
Small $Y\text{-}T_{ij50}$ pair

Compound-A	Compound-B	Y-Tij50
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

Polar – non Polar pair

Network re-arrangement

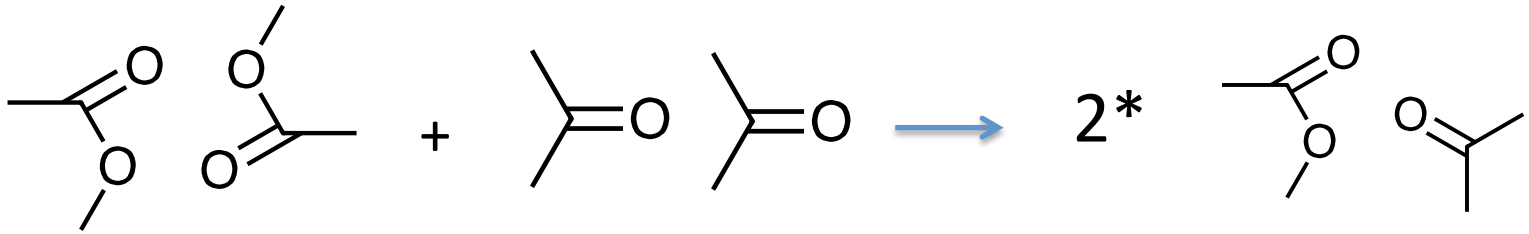
Y-ED1=12.0 Y-EA1=5.0 Y-ED2=3.5 Y-EA2=19.4



2*(Y-ED1 – Y-ED2)*(Y-EA1 –Y- EA2) =2* (12.0 – 3.5)*(5 – 19.4) = **-244.8**

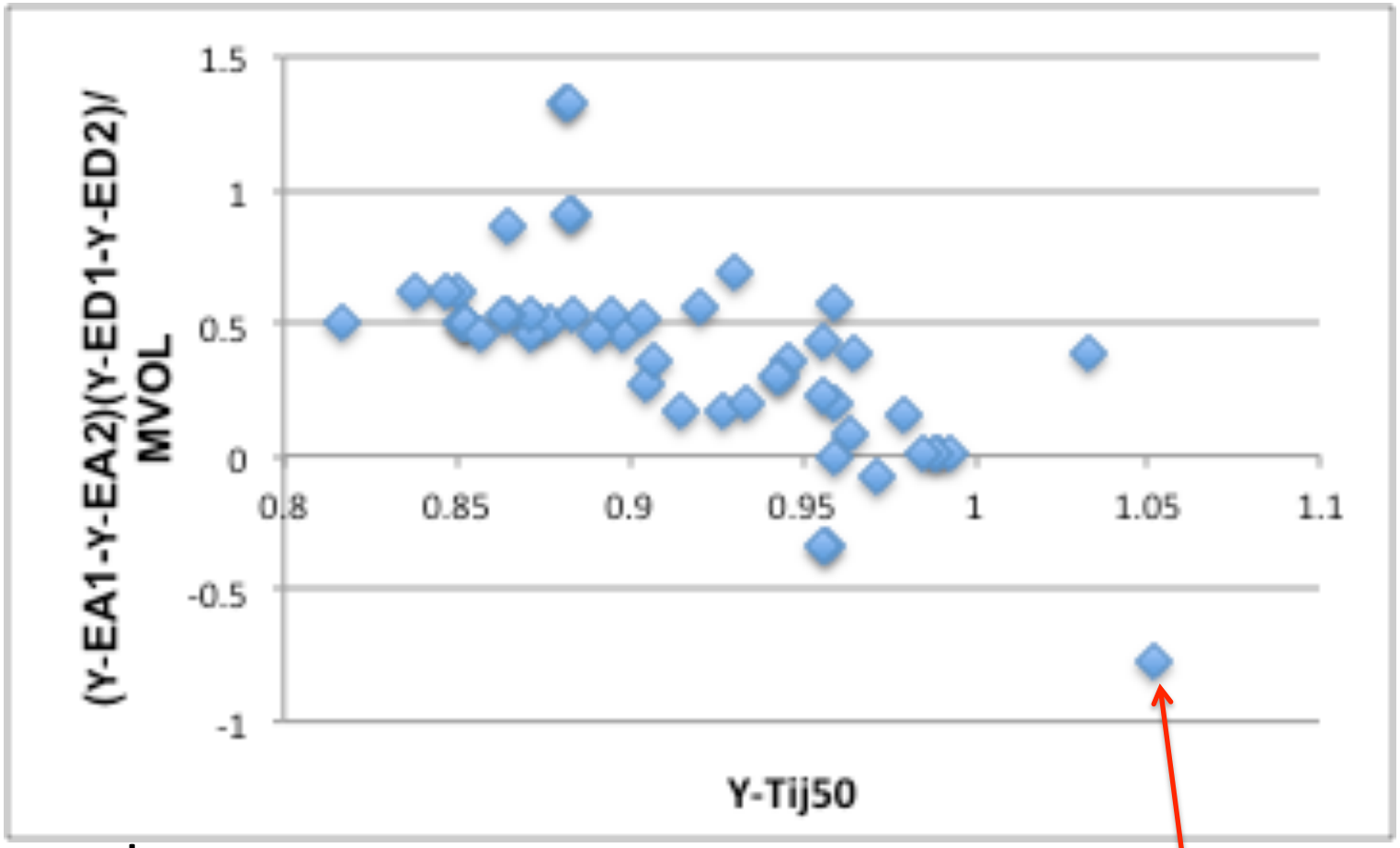
Large Stabilization

Y-ED1=10.1 Y-EA1=4.4 Y-ED2=12.0 Y-EA2=5.0



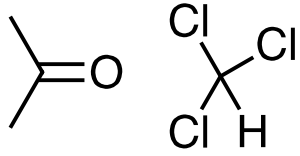
2*(Y-ED1 – Y-ED2)*(Y-EA1 – Y-EA2) = 2*(10.1 – 12)*(4.4 – 5.0) = **+2.3**

Y-T_{ij50} Parameter for Acetone

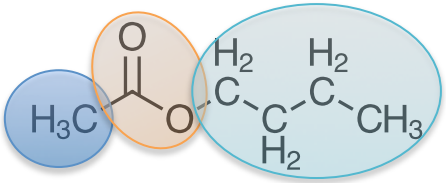


Network rearrangement energy.

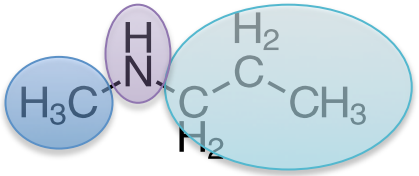
(Y-ED1 – Y-ED2)*(Y-EA1 – Y-EA2) /MVol



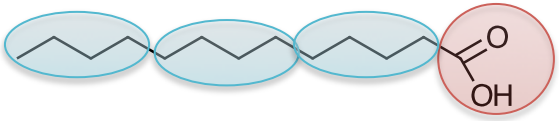
δ_H Electron Pair Donor / Acceptor



δ_H	Y-ED	Y-EA	δ_{Hedo}	δ_{Heac}
6.3	15	7.3	5.23	2.95



5.9	35.7	7.1	5.98	1.17



6.4	12.6	47.4	1.69	6.35
	per mol		per Volume	

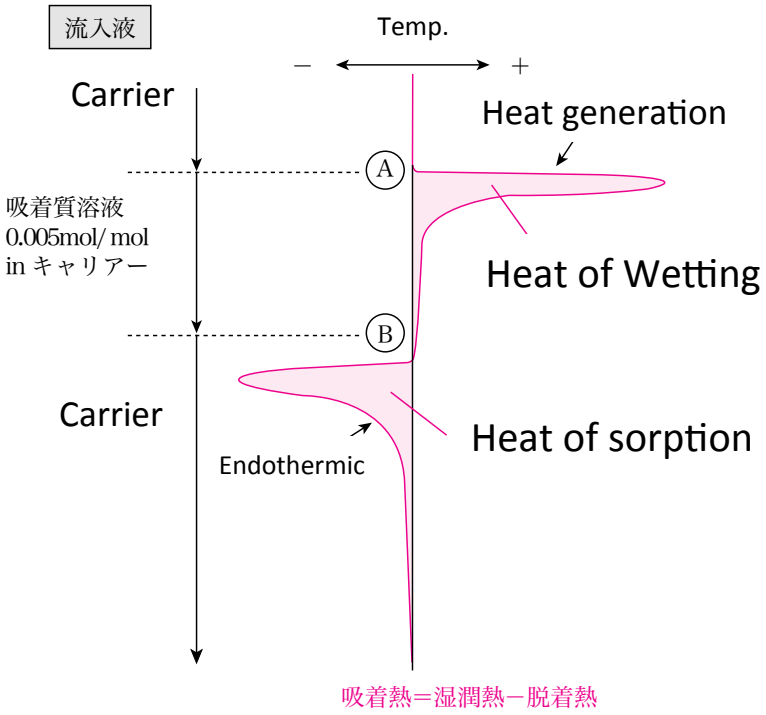
$$\delta_{Hedo} : \delta_{Heac} = \text{Y-ED} : \text{Y-EA}$$

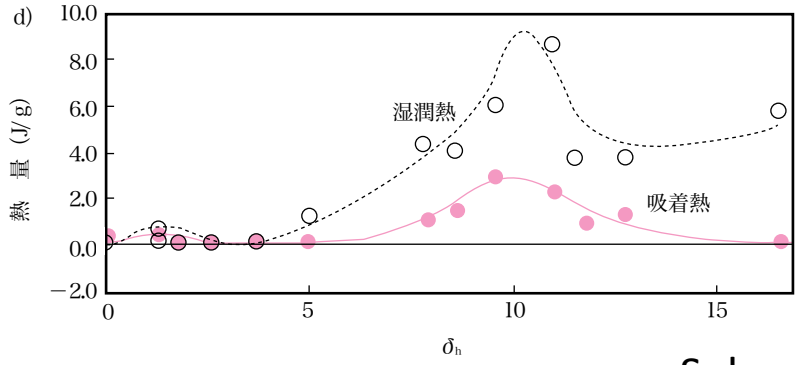
$$\delta_H^2 = 2 * \delta_{Hedo} * \delta_{Heac}$$

Heat of Sorption, Wetting

Study on solutions adsorption behavior of pigments by measuring heat of wetting

Flow Micro Calorimeter (FMC)





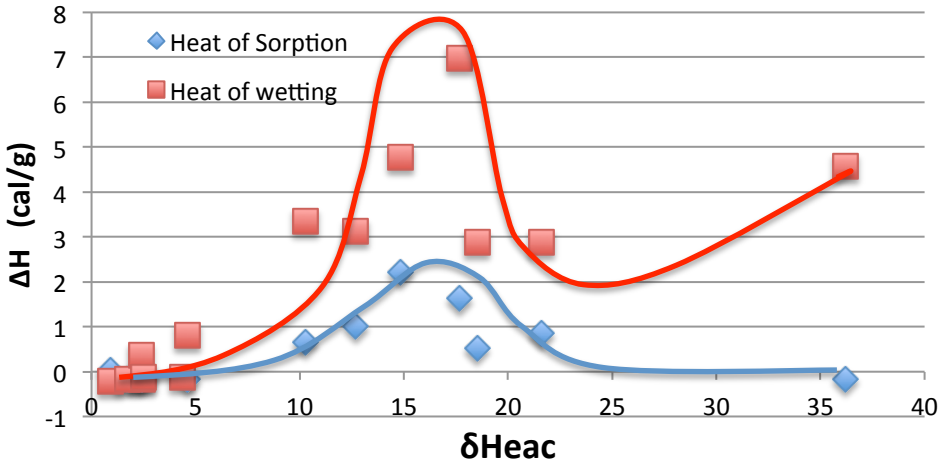
TiO_2 Pigments

Lewis Base

Solvent

Lewis Acid

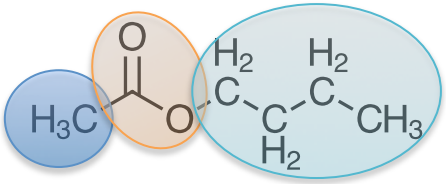
δ_{Heac}



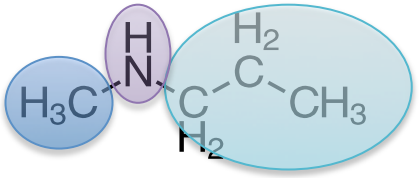
Kansai Paint:

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

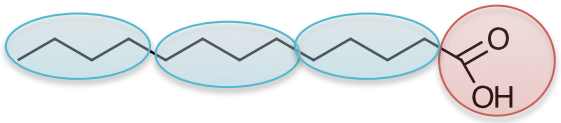
Electron Donor / Acceptor for δ_{Net}



Y-ED	Y-EA	δ_{Net}	δ_{NetED}	δ_{NetEA}
15	7.3	8.1	8.46	4.77



35.7	7.1	6.5	8.67	1.7



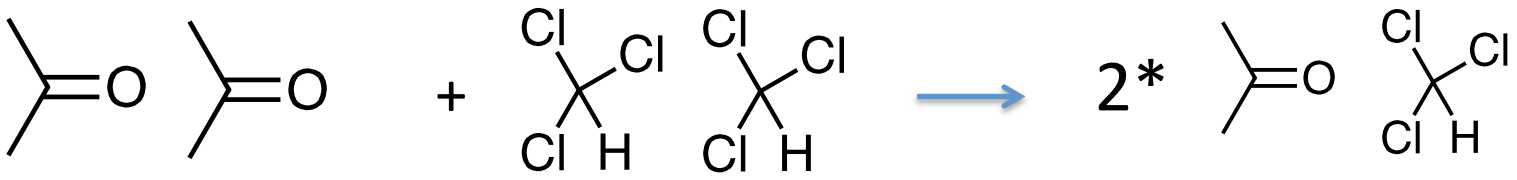
12.6	47.4	10.9	4.56	17.17

$$\delta_{NetED} : \delta_{NetEA} = \text{Y-ED} : \text{Y-EA}$$

$$\delta_{NET}^{2} = 2 * \delta_{NetED} * \delta_{NetEA}$$

Network re-arrangement

Y-ED1=12.0 Y-EA1=5.0 Y-ED2=3.5 Y-EA2=19.4



2*(Y-ED1 – Y-ED2)*(Y-EA1 –Y- EA2) =2* (12.0 – 3.5)*(5 – 19.4) = **-244.8**

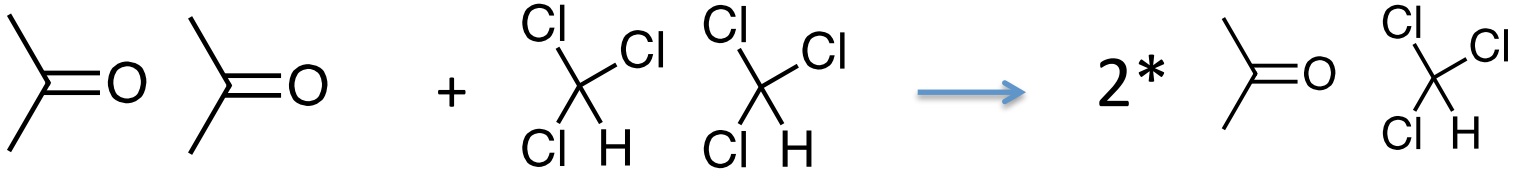
Large Stabilization

d_{Net}ED1=4.48

d_{Net}EA1=2.62

d_{Net}ED2=1.29

d_{Net}EA2=29.78



2*(d_{Net}ED1 – d_{Net}ED2)*(d_{Net}EA1 – d_{Net}EA2)

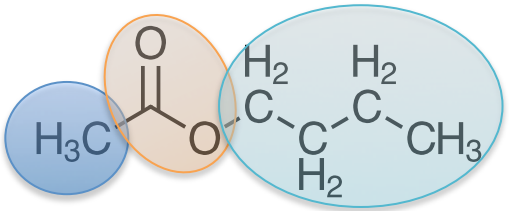
= 2*(4.48 – 1.29)*(2.62 – 29.78) = **-173.3**

HSP_{1967} to HSP^2_{2017}

HSP_{1967} $[\delta D, \delta P, \delta H] = [15.8, 3.7, 6.3]$ $\delta_T = 17.4$

MVol=132.6,

BP=399.26K



HSP^2_{2017} $\delta_T = 17.4$ (Y-ED, Y-EA)=(12.9, 7.1)

$\delta_D = 15.9$

$(\delta_{Dvdw}, \delta_{Dfg}) = (10.0, 12.3)$

$\delta_P = 4.5$

$(\delta_{Pedo}, \delta_{Peac}) = (4.2, 2.4)$

$\delta_H = 6.0$

$(\delta_{Hedo}, \delta_{Heac}) = (5.7, 3.2)$

$(\delta_{HAcid}, \delta_{HBase}) = (0.5, 6.1)$

$(\delta_{Reg}, \delta_{Net}) = (15.1, 9.0)$

$(\delta_{NetED}, \delta_{NetEA}) = (8.5, 4.8)$

Once pair is determined,

Network re-arrangement

$Y\text{-}T_{ij50}$

Conclusion

$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$

$\delta_T^2 = \delta_{Reg}^2 + \delta_{Net}^2$ Alternative Breakup

Great help to understand Thermo-Chemical Properties

Yamamoto Electron Donor /Electron Acceptor ⇨ δ_{Net}

δ_{Net} Hydrogen Bond Network
Coordination Bond Network } Hard to Assign to δ_H, δ_P

Donor / Acceptor re-arrangement

(Y-ED1 – Y-ED2)*(Y-EA1 – Y-EA2)

New breakup of δ_H, δ_P, δ_{Net} $\delta_H^2 = 2*\delta_{Hedo}*\delta_{Heac}$ so on

The new name?

Please think of new name of HSP!

In Japan, I used HSP^2

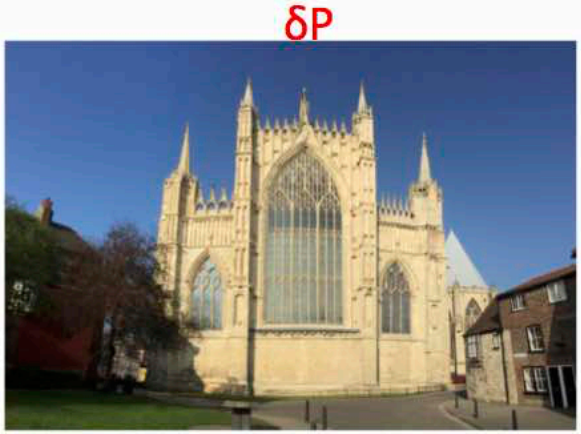
Hansen-Hiroshi-Steven Solubility Parameters for Prediction

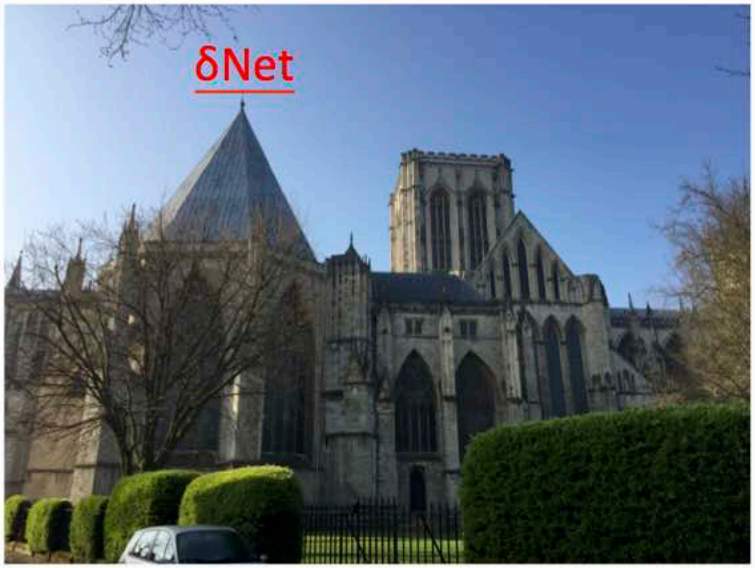
Keep brand identity of “HSP”
Network searchable.
Image of new and powerfulness.

Expanded HSP

EHSP: English for High School Preparation, Enhanced High Speed Processor
Equine Health Studies Program

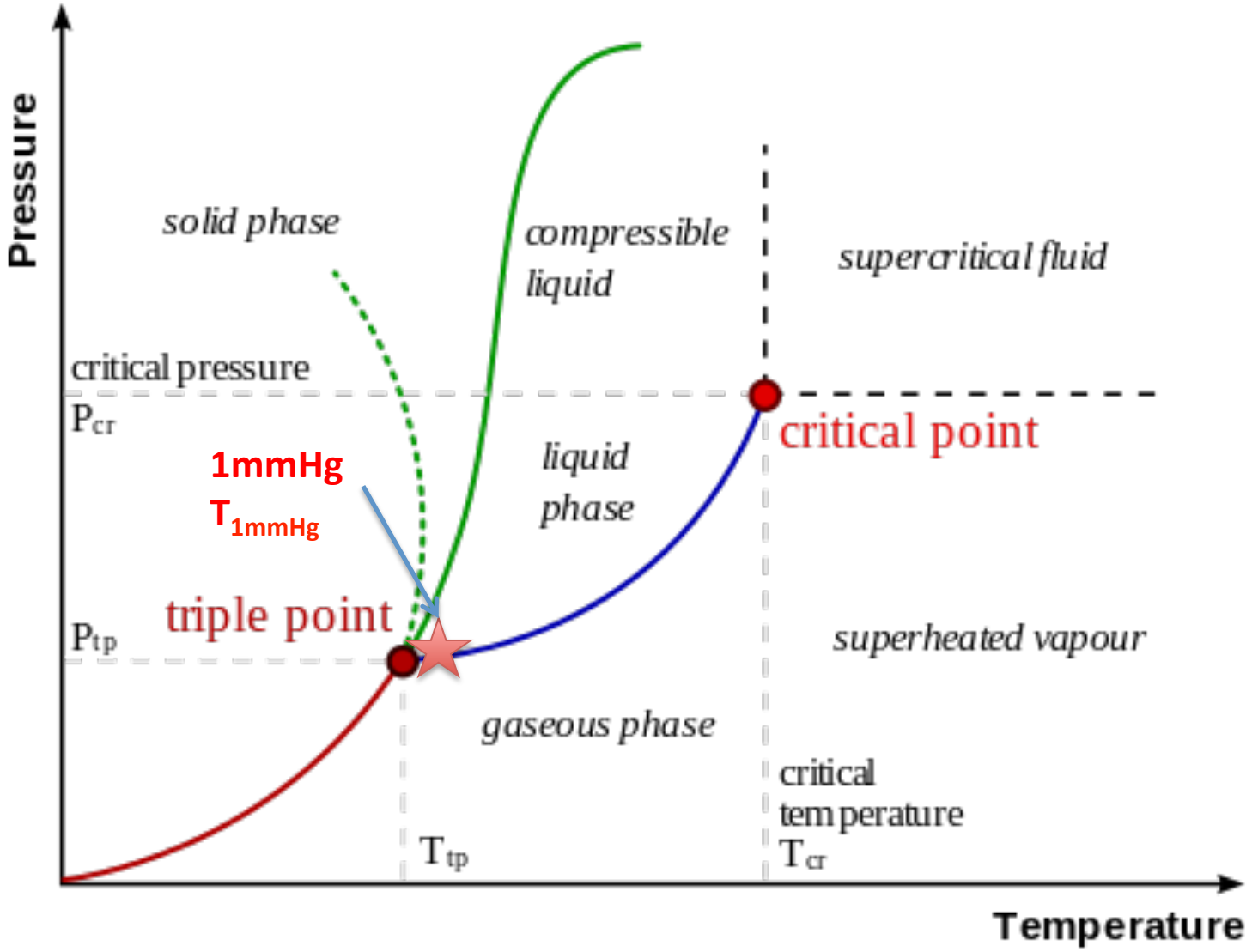
From where you want to view of molecule





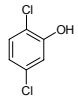
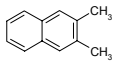
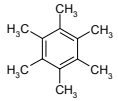
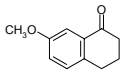
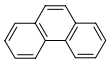
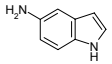
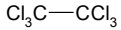
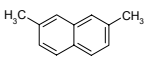
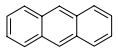
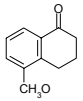
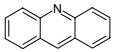
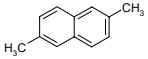
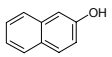
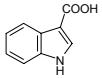
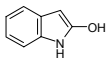
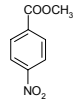
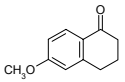
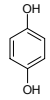
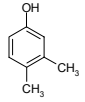
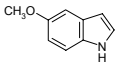
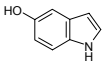
The “Front” is depend on each Researcher!

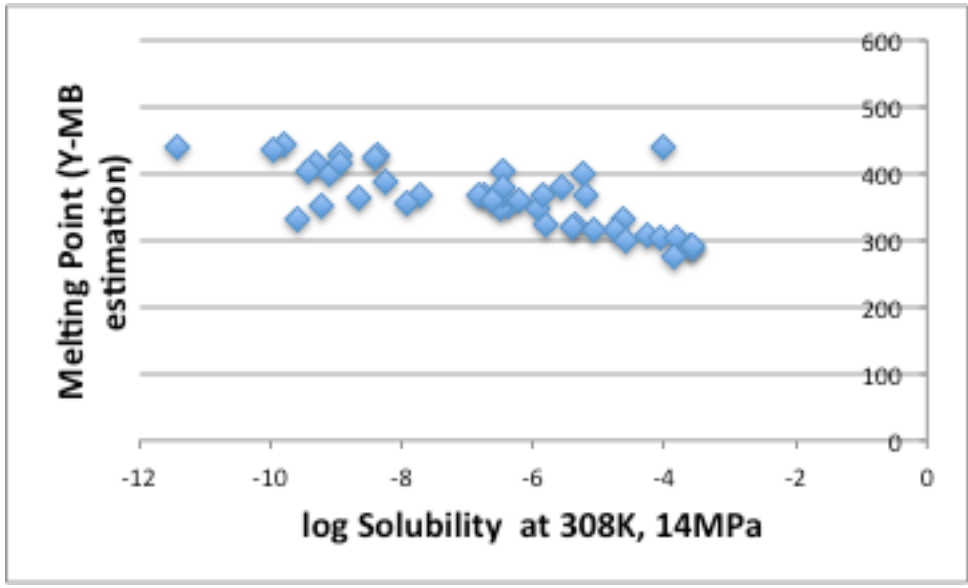
CST base point

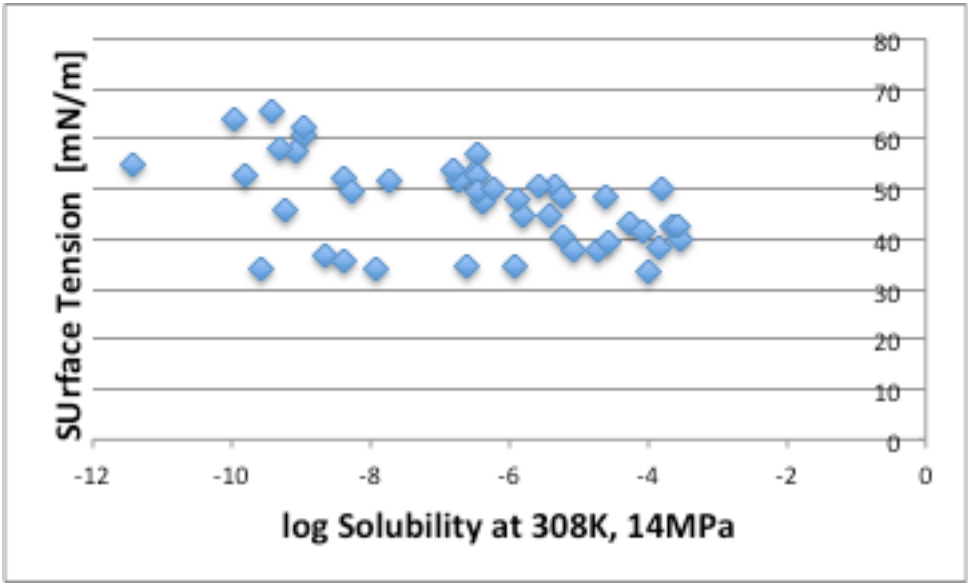


Super Critical CO2 Solubility

Table 1 Structure formula of organic compounds.

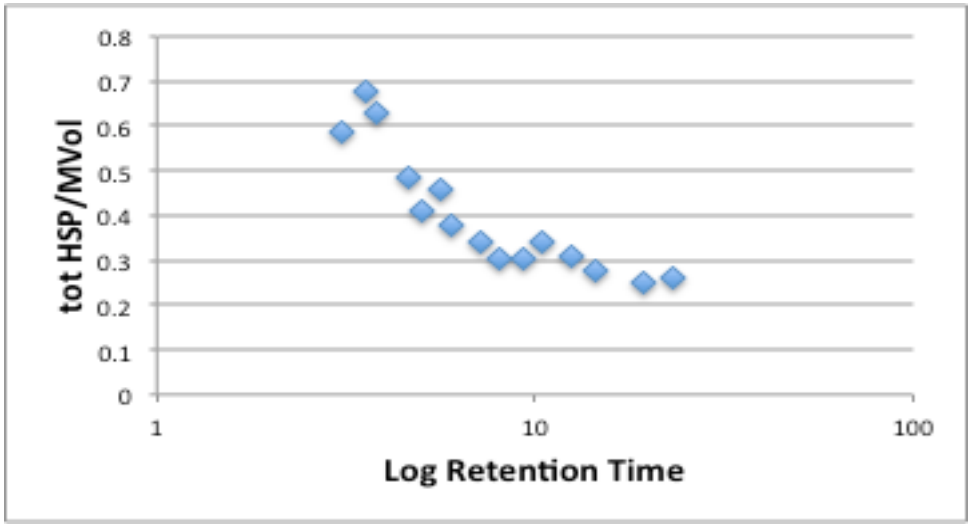
No	Structure	No	Structure	No	Structure	No	Structure
1	 2,5-dichlorophenol	10	 2,3-dimethylnaphthalene	19	 hexamethyl benzene	28	 2-aminobenzoic acid
2	 7-methoxy-1-tetralone	11	 indole	20	 phenanthrene	29	 5-aminoindole
3	 hexachloroethane	12	 2,7-dimethylnaphthalene	21	 1-naphthol	30	 anthracene
4	 *p*-chlorophenol	13	 5-methoxy-1-tetralone	22	 acridine	31	 indole-3-aldehyde
5	 phenol	14	 2,6-dimethylnaphthalene	23	 2-naphthol	32	 indole-3-carboxylic acid
6	 naphthalene	15	 3-methylindole	24	 2-hydroxyindole		
7	 methyl *p*-nitrobenzoate	16	 benzoic acid	25	 *o*-hydroxybenzoic acid		
8	 6-methoxy-1-tetralone	17	 phthalic anhydride	26	 hydroquinone		
9	 3,4-dimethylphenol	18	 5-methoxyindole	27	 5-hydroxyindole		

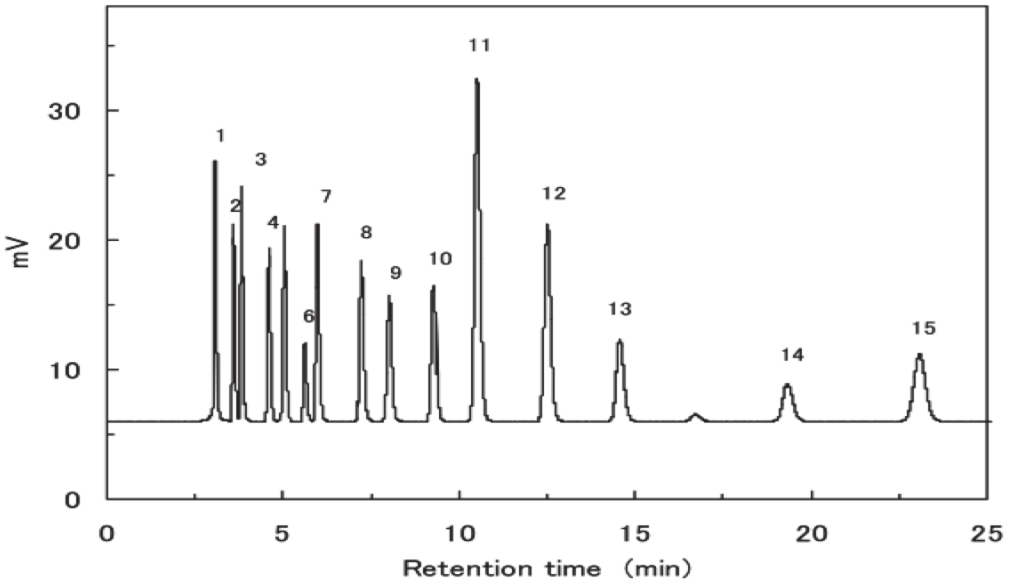




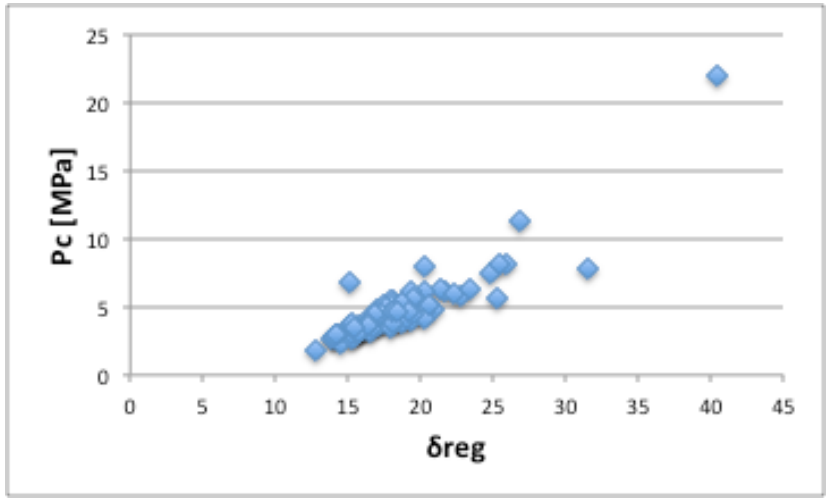
HPLC retention time

Name	RT
oxalic acid	3.068
L-tartaric acid	3.579
formic acid	3.831
L-malic acid	4.597
L-ascorbic acid	5.002
lactic acid	5.622
acetic acid	5.967
maleic acid	7.191
citric acid	8.008
succinic acid	9.279
fumaric acid	10.475
acrylic acid	12.471
propionic acid	14.53
glutaric acid	19.278
itaconic acid	23.037





Critical Point



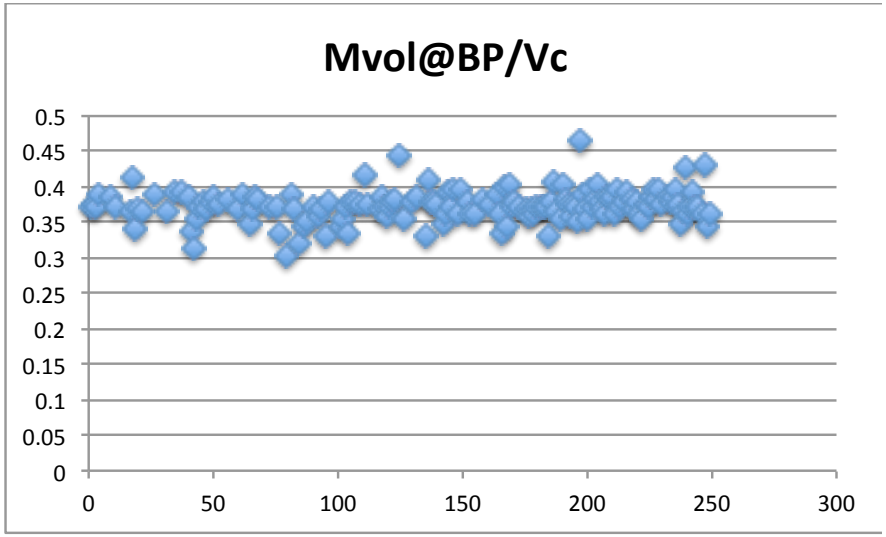
All the Network Energy disappear at T_C

At Critical Point (Tc, Pc, Vc)

Heat of Vaporization = 0

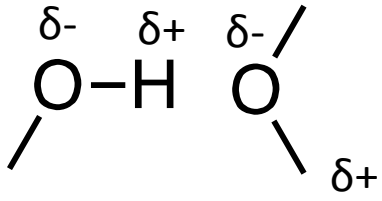
All HSP are 0

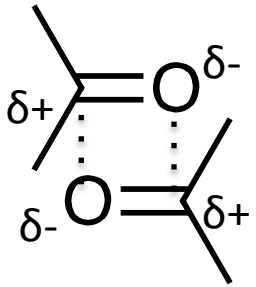
MVol@BP/Vc = 0.373



Network Energy

Permanent Charge





Classic ~~Hydrogen Bond~~

This type interaction should be assign to δP(water=16).

Coordination bond Network

Quantum Resonance Hydrogen Bond