Chapter 7. Cohesive properties and Solubility

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o Cohesive energy density , $e_{coh} \equiv \frac{E_{coh}}{V}$ (J/cm^3)

o Solubility parameter, $\delta = \left(\frac{E_{coh}}{V}\right)^{1/2}$

Hildebrand

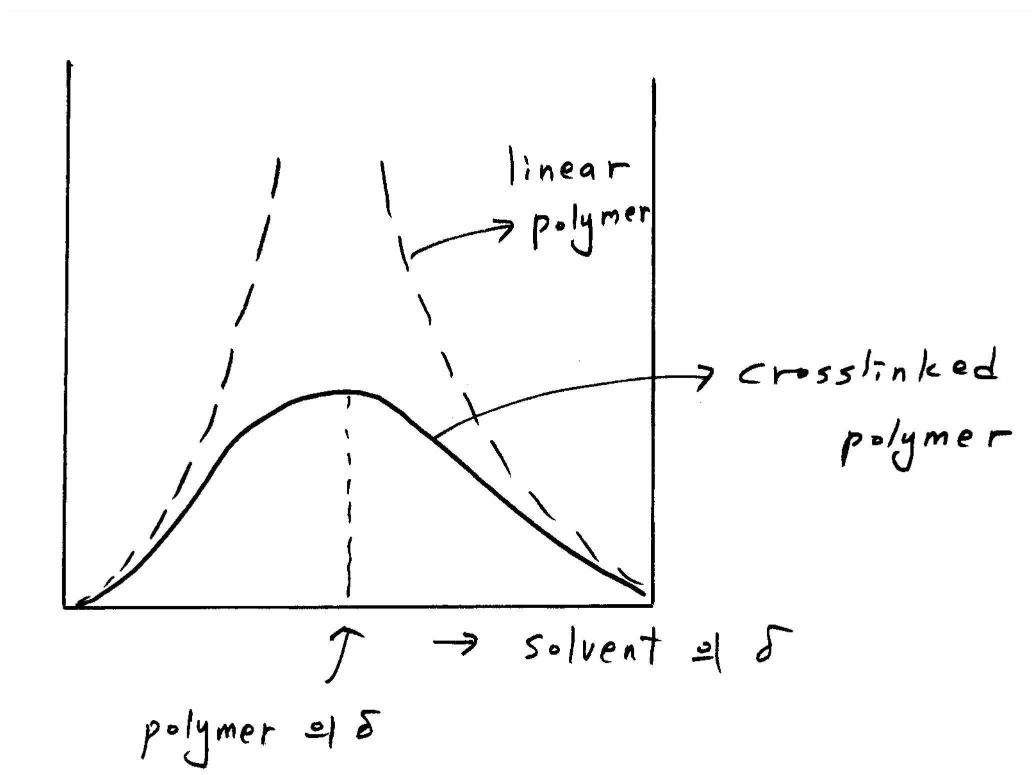
o Determination of E_{coh} :

- For liquids of low molecular weight, the cohesive energy is closely related to the molar heat of evaporation, ΔH_{vap} (at a given temp)

즉 $E_{coh} = \Delta U_{vap} = \Delta H_{vap} - P\Delta V \approx \Delta H_{vap} - RT$ (7.1)

- Polymers degrade long before reaching their vaporization temp., making it impossible to evaluate ΔE_v directly.

- The great tendency of a polymer to dissolve occurs when its solubility parameter matches that of the solvent.



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o Predition of the cohesive energy by means of additive functions.

(Method 1)
Group contribution to Ecoh (see Table 7.1)

(Method 2)
Group contribution to F (see table 7.2)
(molar attraction const), $F = [E_{coh}\ V(298)]^{1/2}$

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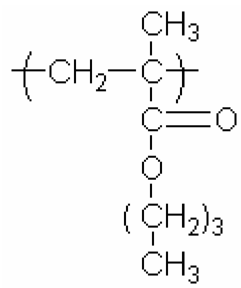
(Ex 7.1) estimate the cohesive energy of Poly(butyl methacrylate).



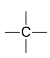
M= 142.2
ρ_a= 1.045
V_a =136 (cm^3/mol)

(a) Group contribution (by van krevelen)
From Table 7.1

(b) According to Small's method, from Table 7.2.

(sol)

Groups	$\sum Ei(J/mol)$	$\sum Fi$
4 (CH_2-)	4(4190)=16760	272×4= 1088
2 (-CH_3)	2(9640)=19280	876
1(CH_4)	-5580	-190
1(-COO-)	13410	634
	Ecoh = 43870	F = 2408



(a) Ecoh = 43,870 (J/mol)

(b) Ecoh $= \frac{F^2}{V} = \frac{(2408)^2}{136}$ = 42,700 (J/mol)

B.Solubility

- According to Hildebrand, the entalpy of mixing can be calculated by

$$\Delta H_m = \phi_1\phi_2 (\delta_1 - \delta_2)^2 \qquad (7.3)$$

여기서 ΔH_m= entalpy of mixing per unit volume,

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

-two substance are mutually soluble if ΔG_m is negative
-the requirement of mutual solubility :
$(\delta_P - \delta_S)^2$ has to be small ;

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- By burrell, mutual solubility only occurs
  if the degree of hydrogen bonding is about equal.

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- Burrell 은 solvent 의 hydrogen bonding 을 poorly, moderately, 그리고
  strongly 한것으로 나누었다.(Table 7.6)

p204
o Refinements of the solubility parameter concept.

- In Eq (7.3), $\Delta H_m = \phi_1\phi_2 (\delta_1 - \delta_2)^2$,
only dispersion forces have been taken into account.

- Cohesive energy is also dependent on the interaction between <u>polar groups</u> and on <u>hydrogen bonding.</u>

- Three type of interaction forces,

$$E_{coh} = E_d + E_p + E_h \qquad (7.4)$$

$$\delta^2 = \delta d^2 + \delta p^2 + \delta h^2 \qquad (7.5)$$

- by hansen, the value of δ_d of a given solvent was assumed
  to be equal to that of a non-polar substance.

$$\delta p^2 + \delta h^2 = \delta^2 - \delta d^2 (= \delta a^2)$$

o solvent 의 δ_d, $\delta_{d,}$ δ_h are shown in pages <u>776 – 789</u>

o Polymer 의 δ 는 Table 7.5
δ_d, $\delta_{p,}$ δ_h 는 Table 7.7

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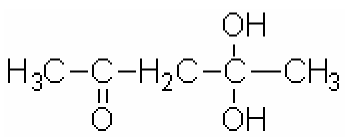
o Predition of the solubility parameter components of diacetone alcohol.

(Ex7.2) Estomate the solubility parameter components of diacetone alcohol,



(sol) v= 123.8 (cm^3/mol)
table 7.8 과 Eq. (7.10), (7.11), (7.12)로부터,

$$\delta_d = \frac{\sum F_{di}}{V} = \frac{1960}{123.8} = 15.8 \ (J^{1/2}/cm^{3/2})$$

$$\delta_p = \frac{\sqrt{\sum Fpi^{\ 2}}}{V} = \frac{\sqrt{84300}}{123.8} = 7.4 \ (J^{1/2}/cm^{3/2})$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} = \sqrt{\frac{22000}{123.8}} \ 13.3 \ (J^{1/2}/cm^{3/2})$$

문헌치 (literature value)는 각각
$\delta_d = 15.7$, $\delta_p = 8.2$, $\delta_h = 10.9$

$$\therefore \delta = \sqrt{\delta d^2 + \delta p^2 + \delta h^2} = 21.9 \ (J^{1/2} / cm^{3/2}) \quad \text{or} \quad (J/cm^3)^{1/2}$$

$$\delta_{exp} = 18.8 - 20.8 \ (J/cm^3)^{1/2}$$