Chap. 9 Limiting Viscosity number (Intrinsic Viscosity) and Related Properties of very dilute solutions

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$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \qquad (9.14)$$

$\eta_{sp} = \eta_{rel} - 1 = \eta/\eta_s - 1 \approx t/t_s - 1$

$[\eta] = KM^{\alpha}$ (9.15)

여기서 $[\eta]$= Intrinsic viscosity, [dL/g]

K, α = Mark-Houwink constants.

α = 0.5 (theta conditions, unperturbed state) (9.25)

α = 0.8 (good solvent)

(Ex 9.1) Extimate the limiting viscosity number of poly(methyl methacrylate) with a molecular mass $M = 2.5 \times 10^5$ in toluene.

(sol) (a) Estimation of a

$\delta_P = (E_{coh}/v)^{1/2}$, E_{coh}=31300 J/mol , V=86.5 cm^3/mol

$\delta_p = (31300/86.5)^{1/2} = 19.5\ J^{1/2}/cm^{3/2}$

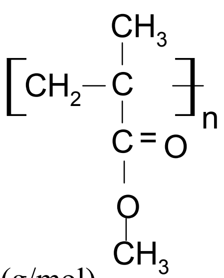
toluene 의 $\delta_s = 18.25\ J^{1/2}/cm^{3/2}$

$\delta_p - \delta_s$ = 19.05-18.25 = 0.8

식(9.35)에 의하여

a = 0.8-0.8/10 = 0.72

(b) calculation of Mcr :



M=100.1 (g/mol)

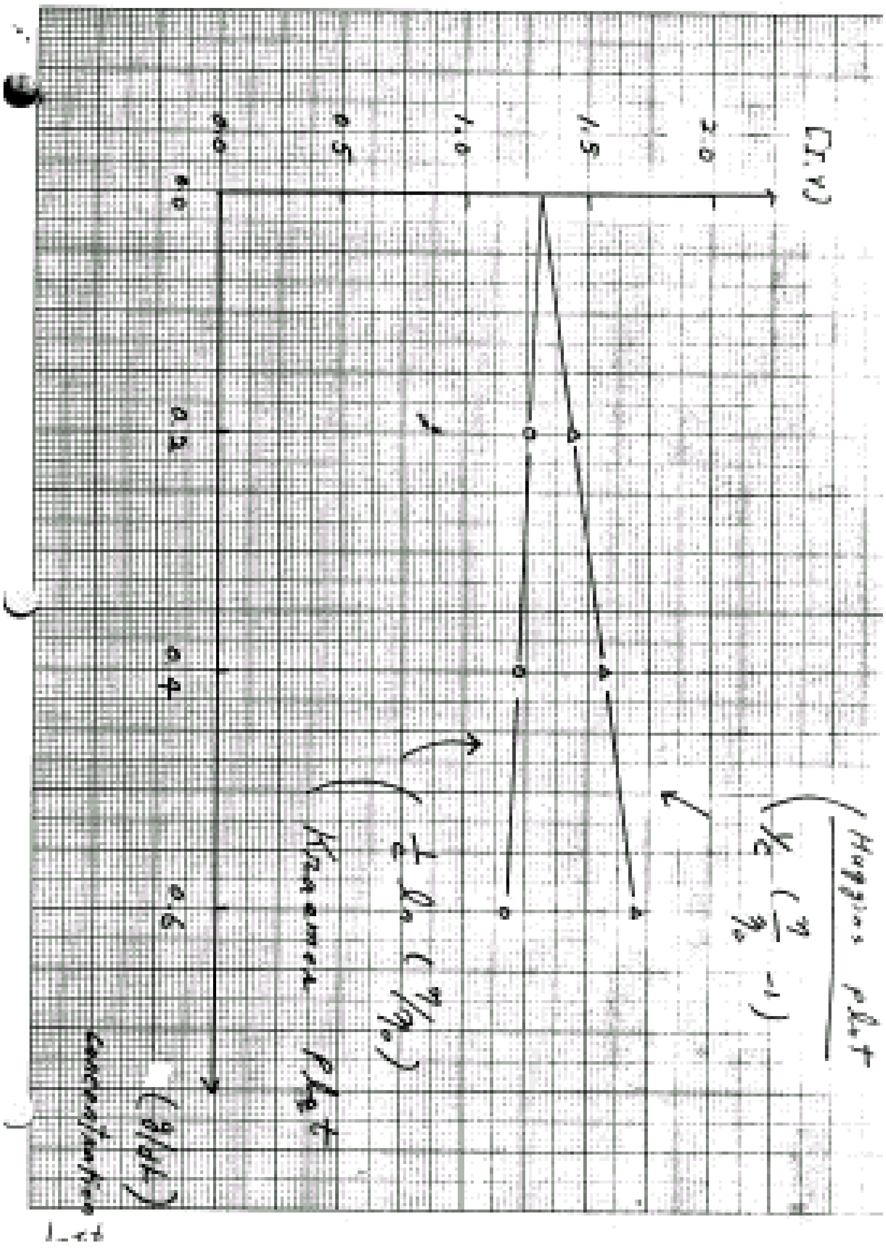
Group	Ji(molar I.V. Function)
$-CH_2-$	2.35
-C-	0
$2-CH_3$	7.1
-COOH-	6.4
	15.85

$K_\theta^{1/2} M = J + 4.2Z$ (9.34)

$K_\theta^{1/2}M = 15.85+4.2(2) = 24.25$

$K_\theta = (24.25/100.1)^2 = 0.059\ cm^3 \cdot mol^{1/2}/g^{3/2}$

식 (9.37) 에 의하여 (p.259)



$Mcr = (13/K_\theta)^2 = 4.9 \times 10^4$

(c) [η] estimation

$M/Mcr = (2.5\times10^5)/(4.9\times10^4)=5.1$

그림 9.5 (p263)에서 a=0.72 로부터

$[\eta]/[\eta]_R = 4.4$ 를 얻는다.

여기서 $[\eta]_R = 13.0\ cm^3/g$ (p.260)

$[\eta] = 57(cm^3/g)$

(d) Estimate of K

식 (9.43)에서

$\log K=\log K_\theta -(a-1/2)\log Mcr+\log a^3_{h,cr}$ ….(i)

여기서 a=0.72 과 그림 9.4 에서

$\log a^3_{h,cr} = 0.13,\quad K_\theta = 0.059$

식(i)에서부터 $\log K = -2.13$ $K=0.0074$

식 (9.36)에서 approximate value 는

$\log K = -2.04$ $K = 0.0091$

· Polymer Handbook 의 literature 값과 비교하며 25ºC, toluene 에서 PMMA 의 [η] 는

$[\eta] = 0.0071\ M^{0.73}$

$M=2.5\times10^5,\quad [\eta] = 61.9(cm^3/g)$

(Ex) Estimate the Intrinsic Viscosity of polystyrene with a molecular mass $M=5\times10^5$ in toluene.

(a) a Estimation

(b) Mcr Estimation

(c) [η] Estimation

(d) K Estimation

(Ex) Estimate the intrinsic viscosity of polystylene with a molecular mass $\overline{M_w} = 5\times10^5$ in toluene

(sol) **(a)** Estimation of a

$$\delta_p = \left(\frac{E_{coh}}{V}\right)^{1/2}$$ Ecoh=38,300 (J/mol)

$$= \left(\frac{38{,}300}{98}\right)^{1/2}$$ V=98.0(cm^3/mol)

$= 19.77\ (J^{1/2}/cm^{3/2})$

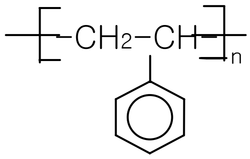
toluene 의 $\delta_s = 18.25$

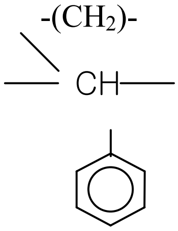
$\delta_p - \delta_s = 19.77 - 18.25 = 1.52$

식(9.35)에 의하여

a=0.8-0.1(1.52)=<u>0.64</u>

(b) calulation of M_{cr} :



GROUP	Ji (Table 9.2)
-(CH_2)-	2.35
	1.15
	18.25
	21.75

(Molar I.V. Function)

$K_\Theta^{/12} M = J + 4.2Z$ (9.34)

$K_\Theta^{1/2} M = 21.75 + 4.2\ (2) = 30.15$

$$\therefore \quad K_\Theta = \left(\frac{30.15}{104.1}\right)^2 = 0.084\ (cm^3 mol^{1/2}/g^{3/2})$$ (p.252, Table 9.3)

식(9.37)에 의하여 (P.259)

$$M_{cr} = (13/\ K_\Theta)^2 = (13/\ 0.084)^2 = 2.4\times10^4$$

(c) [η] estimation.

$$\frac{M}{M_{cr}} = \frac{5\times10^5}{2.4\times10^4} = 20.83$$

그림 9.5 (p.262)에서 $\log\frac{M}{M_{cr}} = 1.32$ 와 a=0.64 로부터

$$\log\frac{[\eta]}{[\eta]_k} = 1.0$$

$\therefore \quad \frac{[\eta]}{[\eta]_k} = 10.0$

여기서 $[\eta]_R = 13$ (cm^3/g)

$\therefore [\eta] = 10 \times 13 =$ 130 (cm^3/g)

(d) Estimation of K

식 (9.4.3)에서

$\log K = \log K_\Theta - (a-1/2)\log Mcr + \log a^3_{h,cr}$ (9.43)

여기서 a=0.64 와 그림 9.4 에서 (P.261)

$\log a^3_{h,cr} = 0.04$, $K_\Theta = 0.084$

식(9.43) 에서 $\log K = \log 0.084 - (0.64-0.5)4.38 + 0.0$

$= -1.6489$

$\therefore$ K=0.0224

식 (9.36)에서 approximate value 는 (ㅔ.254)

$\log k = \log K_\Theta - C(a-1/2)$

$= \log(0.084) - 3.7(0.64-0.5)$

$= -1.0757 - 0.518$

$= -1.5937$

$\therefore$ K=0.0255

p.278 **C. Interrelationships of “Limiting”Diffusive Transport Quantities**.

Diffusivity, (D)

$$D = \frac{\partial C / \partial t}{\partial^2 C / \partial x^2} \quad (\text{cm}^2/\text{s})$$

$$= \frac{\textit{the rate of change of concentration}}{\textit{the rate of the conc. gradient}}$$

as a function of the distance of transport

- The diffusivity is a function of the polymer conc., the molecular weight, and the temp. (pressure : 약간)

- temp dependence,

$$\frac{D(T)}{D(298)} = \frac{\eta_s(298)}{\eta_s(T)} \times \frac{T}{298} \qquad (9.61)$$

- molecular weight dependence,

$$\underline{D_0 = K_D M^{-d}} \qquad (9.62)$$

(see Table 9.5)