

Chapter 4. Polymer Solutions

4.1 Introduction

A condition for miscibility

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \quad \leftarrow \text{ necessary condition for miscibility}$$

Necessary and sufficient conditions for miscibility:

above condition + the following condition

$$\frac{\partial^2(\Delta G_{mix} / N)}{\partial x_1^2} > 0$$

N : # of moles ($N = N_1 + N_2$)

4.2 Regular solutions

: Mixtures of molecules randomly distributed,
but with different energies of interaction each other.

$$S^E = \Delta S_{mix}(\text{actual}) - \Delta S_{mix}(\text{ideal}) : \text{Excess entropy}$$

$$S^E = 0, \text{ but } H^E \neq 0 \quad (\text{Non-polar small-molecule liquid with finite mixing enthalpy})$$

↙
Excess enthalpy

No volume change on mixing

cf.) Other solutions

- *Ideal solution*: Raoult's law is obeyed.

$p_A = p_A^0 x_A$ (partial vapor p of each component in the mixture is proportional to its mole fraction)

$$\frac{\Delta S_{mix}}{N} = -R(x_1 \ln x_1 + x_2 \ln x_2) > 0 \quad \text{always}$$

$$\frac{\Delta H_{mix}}{N} = 0 \quad (\because \text{mix without change in enthalpy})$$

$$\therefore \frac{\Delta G_{mix}}{N} = RT(x_1 \ln x_1 + x_2 \ln x_2) < 0 \quad (\text{spontaneous mixing occurs})$$

- *Athermal solution*, $\Delta H = 0$ (or H^E) but $S^E \neq 0$
- *Irregular solution*, both ΔH and ΔS deviate from the ideal solutions.

- **Mixing entropy** of a binary mixture

P : The number of possible ways of arranging the mixture

$$P = \frac{n!}{n_1!n_2!}$$

n : total # of lattice positions (= # of molecules)
 $n = n_1 + n_2$

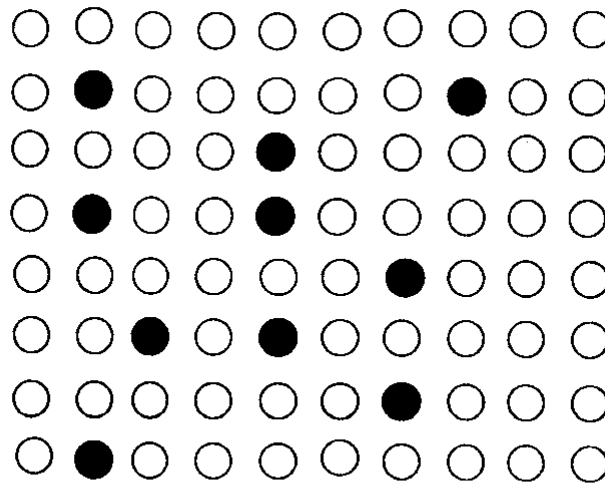


Figure 4.1 Lattice of a binary mixture of two low molar mass components.

From *statistical thermodynamics* ($S = k \ln P$)

$$\therefore \Delta S_{mix} = k(\ln n! - \ln n_1! - \ln n_2!)$$

← using *Stirling's approximation*
($\ln a! \approx a \ln a - a$)

$$\Delta S_{mix} = -k(n_1 \ln x_1 + n_2 \ln x_2) \quad x : \text{mole fraction}$$

$$\therefore \frac{\Delta S_{mix}}{N} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad N : \# \text{ of moles}$$

-Mixing enthalpy

From the interaction energies of contacting atoms

$$\frac{\Delta H_{mix}}{N} = \left(\sqrt{\Delta E_1} - \sqrt{\Delta E_2} \right)^2 x_1 x_2 = B x_1 x_2 \quad : \text{Hildebrand \& Scott}$$

$$= (\delta_1 - \delta_2)^2 x_1 x_2$$

ΔE : cohesive energy density

δ : solubility parameter

⇒ Valid for equal size molecule

- Free energy of mixing

$$\begin{aligned}\frac{\Delta G_{mix}}{N} &= \frac{\Delta H_{mix}}{N} - \frac{T\Delta S_{mix}}{N} \\ &= Bx_1x_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)\end{aligned}$$

Inflection points

$$\frac{d^2(\Delta G_{mix}/N)}{dx_1^2} = 0 \quad \rightarrow \text{spinodal points}$$

Common tangent in the plot of

ΔG_{mix} against x_1

\rightarrow binodal points

Spinodal decomposition: the process that occurs inside the spinodal region by which a homogeneous blend phase separates.

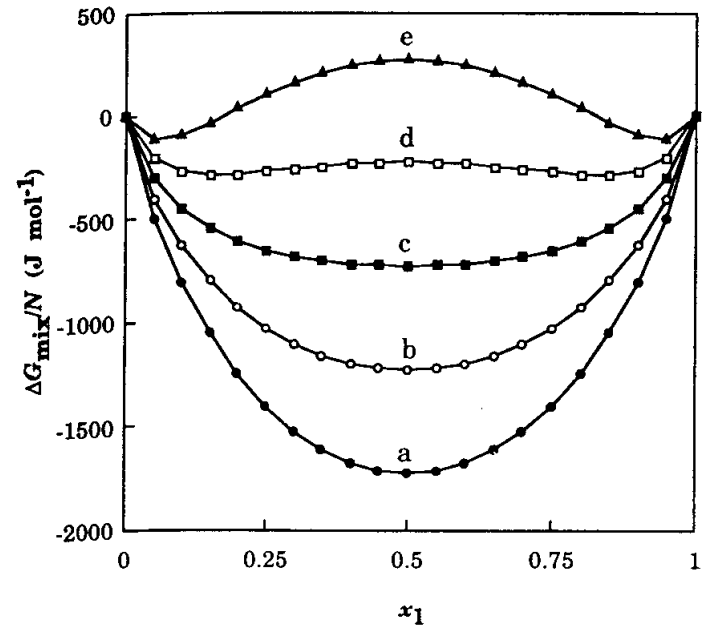
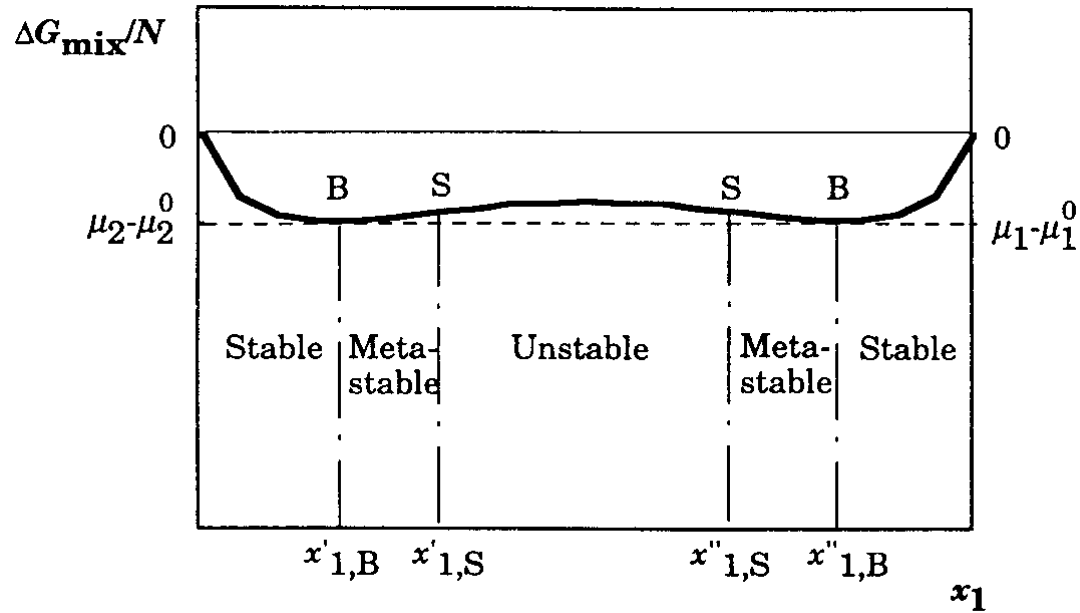


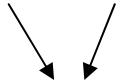
Figure 4.2 The free energy of mixing at 300 K according to eq. (4.5) for the following B values: (a) $B = 0$; (b) $B = 2000 \text{ J mol}^{-1}$; (c) $B = 4000 \text{ J mol}^{-1}$; (d) $B = 6000 \text{ J mol}^{-1}$; (e) $B = 8000 \text{ J mol}^{-1}$.

- **Chemical potentials of the components**

← by the intercept method



The conditions of miscibility in a binary system :

$$\Delta\mu_i' = \Delta\mu_i'' \quad i = 1, 2 \quad (\Delta\mu_i = \mu_i^0)$$


different phases (“ ’ ” and “ ” ” phases)

Chemical potential

$$\mu_i \equiv \left(\frac{dG}{dn_i} \right)_{T,p,n_j} \quad \leftarrow \text{At equil., equal for both components in both phases}$$

At binodal points (equilibrium points),

$$\begin{aligned} \mu_1' - \mu_1^0 &= \mu_1'' - \mu_1^0 \\ \& \mu_2' - \mu_2^0 &= \mu_2'' - \mu_2^0 \end{aligned}$$

$$\begin{aligned}\therefore \frac{\Delta G_{mix}}{N} &= (\mu_2 - \mu_2^0) + x_1 \{(\mu_1 - \mu_1^0) - (\mu_2 - \mu_2^0)\} \\ &= x_1(\mu_1 - \mu_1^0) + x_2(\mu_2 - \mu_2^0)\end{aligned}$$

Gibbs-Duhem relationship:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

을 적용하여 정리하면

$$\begin{aligned}\mu_1 - \mu_1^0 (= \Delta\mu_1) &= \frac{\Delta G_{mix}}{N} + x_2 \frac{d(\Delta G_{mix} / N)}{dx_1} \\ \mu_2 - \mu_2^0 (= \Delta\mu_2) &= \frac{\Delta G_{mix}}{N} + x_1 \frac{d(\Delta G_{mix} / N)}{dx_2}\end{aligned}$$

의 관계식을 얻을 수 있다.

- *Binodal curve*

: the equilibrium curve differentiating stable one-phase systems from heterogeneous systems

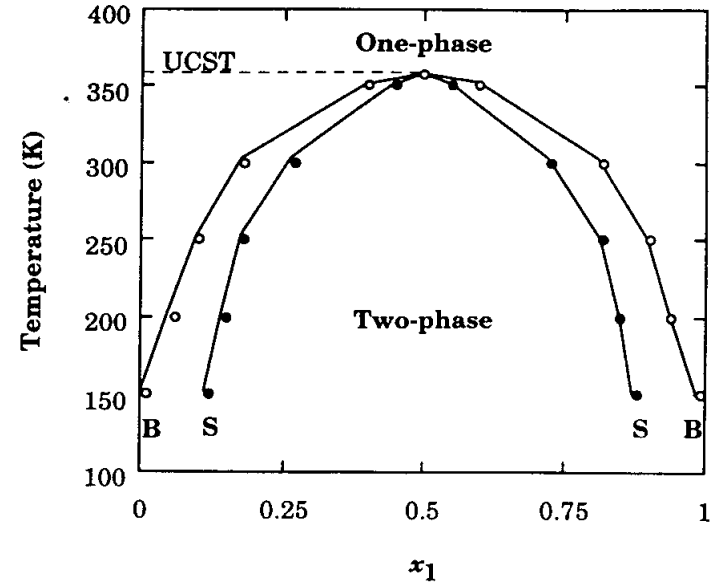
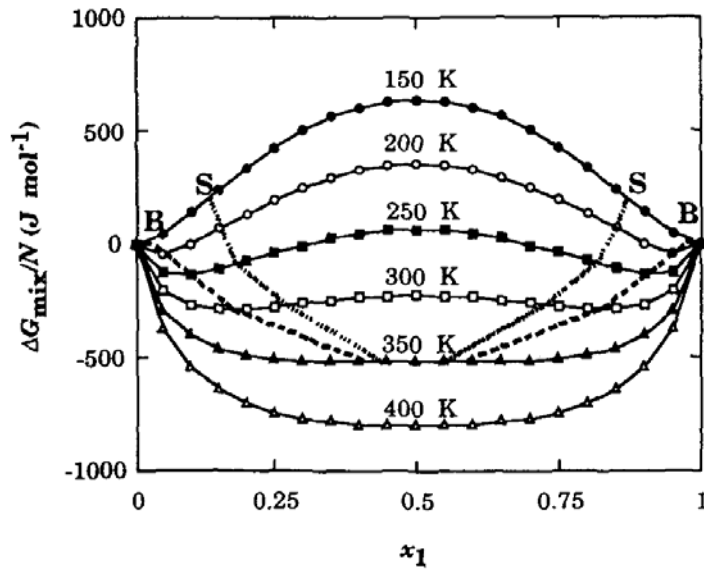
In the concentration range between binodal & spinodal points

→ free energy curvature > 0

→ solution : metastable

→ nucleation & growth

* Temperature variation with constant enthalpy ($\therefore B$ const.)



- Upper critical solution temperature (UCST)

→ spinodal and binodal curves meet.

$T > \text{UCST}$: miscible at entire compositions

$$\frac{d^3(\Delta G_{mix} / N)}{dx_1^3} = 0$$



즉 2계 미분한 자취가 극점을 갖는 조건