Theoretical Estimation of Partial Miscibilities by the Extended Flory-Huggins Lattice Theory

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Four types of the phase diagrams indicating the partial miscibilities in polymer-polymer or polymer-solvent systems have been explained in terms of the extended Flory-Huggins lattice theory. In this article, the term $kT\chi$ in the theory is expressed as a function of temperature. Using such a χ-parameter, the simplest forms of geometrical conditions are derived for each type of the four partial miscibilities in polymer systems. The calculated partial miscibilities are in good agreement with the experiment.

Introduction

Many theoretical approaches[1-4] have been developed in order to represent the thermodynamical properties of polymer-polymer and polymer-solvent systems. The Flory-Huggins lattice theory[1] is one of the old theories, and still widely used. In the theory, the Gibbs free energy change of mixing is composed of the combinatorial entropy change and the enthalpy change expressed in terms of the interaction parameter χ. The original form of $kT\chi$ was supposed to be independent of temperature, composition and molecular weight distribution. With respect to the temperature dependence, the Flory-Huggins lattice theory completely failed to describe the partial miscibilities in polymer systems. Koningsveld[5] mentioned the possibilities of the partial miscibilities with the temperature dependent $kT\chi$. In this work, the rigorous conditions of $kT\chi$ were derived for the four types of phase behaviors. And the experimental results were compared with the results predicted by the extended form of the Flory-Huggins lattice theory in each case.

Phase stability in terms of the Flory-Huggins lattice theory[6].

The Flory-Huggins expression for the Gibbs free energy change of mxing is

$$\frac{\Delta G_{mix}}{kT} = N_1 \ln \phi_1 + N_2 \ln \phi_2 + \chi \phi_1 \phi_2 (N_1 r_1 + N_2 r_2) \tag{1}$$

where N_i and r_i are the number of molecules and the number of lattice sites occupied by one polymer molecule of component i, respectively. In eq. (1), ϕ_i and χ, called interaction parameter, are defined as

$$\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2}, \quad i = 1,\ 2 \tag{2}$$

$$\chi = \frac{zw}{kT} \tag{3}$$

where z is the number of the nearest neighboring molecules. In eq. (3), w is defined as

$$-w = \frac{1}{2}\varepsilon_{11} + \frac{1}{2}\varepsilon_{22} - \varepsilon_{12} \tag{4}$$

where ε_{ij} is the energy of a contact between components i and j. The expressions[7] are as follows for the binodal, the boundary between the stable and the metastable states, and the spinodal, the boundary between the metastable and the unstable states.

$$\text{spinodal:} \quad \left(\frac{\partial^2 \Delta G_{mix}}{\partial \phi_1^2}\right)_{T,P} = 0 \tag{5}$$

Phase separation occurs in the unstable region where $\left(\frac{\partial^2 \Delta G_{mix}}{\partial \phi_1^2}\right)_{T,P} < 0$. From eq.(1), eq.(5) becomes

$$\frac{1}{r_1 \phi_1} + \frac{1}{r_2 \phi_2} - 2\chi = 0 \tag{6}$$

$$\text{binodal:} \quad \Delta u_i = \Delta u_i; \ i = 1,2 \tag{7}$$

where

$$\Delta \mu_i = \left(\frac{\partial \Delta G_{mix}}{\partial N_i}\right)_{T,P,N_{j\neq i}} \tag{8}$$

From eq. (1), eq. (8) becomes

$$\Delta \mu_1 = kT\{\ln \phi_1 + (1 - \frac{r_1}{r_2})\phi_2 + r_1 \chi \phi_2^2\}$$
$$\Delta \mu_2 = kT\{\ln \phi_2 + (1 - \frac{r_2}{r_1})\phi_1 + r_2 \chi \phi_1^2\} \tag{9}$$

The condition for a critical point is

$$\left(\frac{\partial^3 \Delta G_{mix}}{\partial \phi_1^3}\right)_{T,P} = 0 \tag{10}$$

From eq.'s (1) and (10) we have at the critical point

$$(\phi_1)_{critical} = \frac{1}{1 + (r_1/r_2)^{\frac{1}{2}}} \tag{11}$$

From the definition of ϕ_i, eq. (11) becomes

$$\left(\frac{N_2}{N_1}\right)_{critical} = \left(\frac{r_1}{r_2}\right)^{\frac{3}{2}} \tag{12}$$

Extended form of the Flory-Huggins lattice theory[5]. The last term of the right hand side in eq. (1) is the enthalpy change of mixing. That is

$$\Delta H_{mix} = kT\chi\phi_1\phi_2(N_1 r_1 + N_2 r_2) \tag{13}$$

Thermodynamically, ΔH_{mix} can be expressed as

$$\Delta H_{mix}(T) = \Delta H_{mix}(T_0) + \int_{T_0}^{T} \Delta C_{mix}(T)\, dT \tag{14}$$

where ΔC_{mix} is the molar heat capacity change of mixing and T_0 is a reference temperature. Relating eq. (13) to eq. (14), it is considered that $kT\chi$ is a function of temperature since the molar heat capacity is a function of temperature. Molar heat capacities are often used as a second order function of

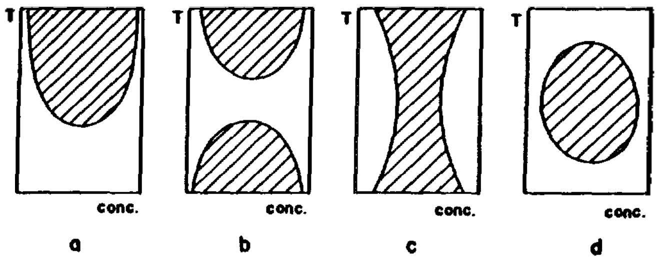

Figure 1. Schematic of liquid-liquid temperature-composition phase diagrams showing unusual partial miscibilities.

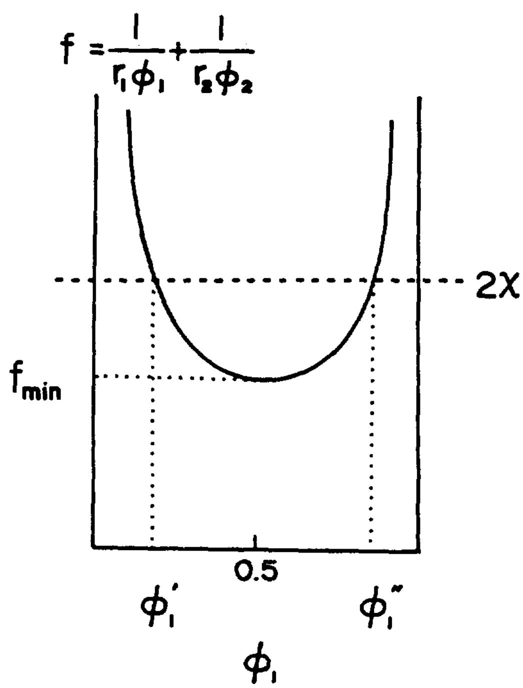

Figure 2. Schematic illustration of eq. (16). Phase separation occurs between ϕ_1' and ϕ_1'' when $2\chi > f_{min}$, where $f_{min} = (\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}})^2$.

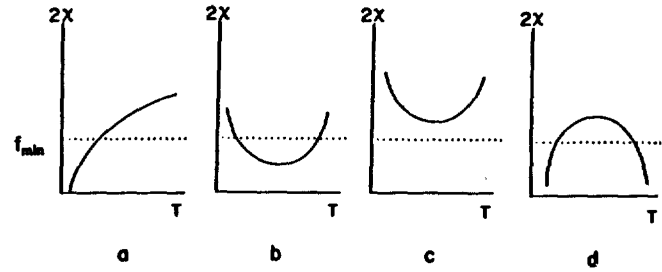

Figure 3. Temperature dependencies of 2χ corresponding to the phase behaviors in Figure 1, respectively.

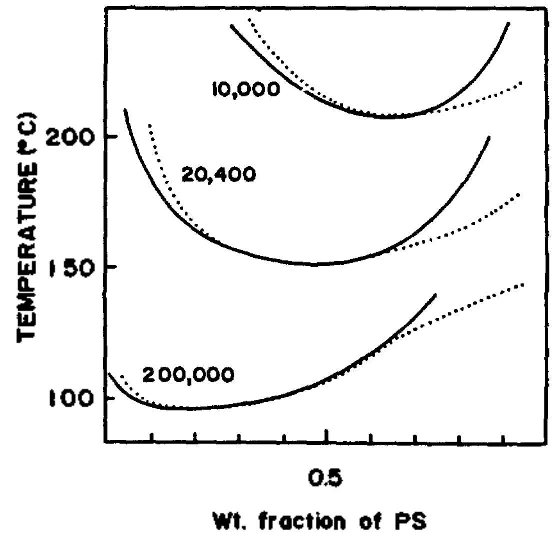

Figure 4. Phase diagrams for PS(1)-PVME(2) systems with indicated molecular weights (M.W) of PS. ·········· : experimental binodal ——— : calculated binodal.

temperature fitted with experimental values within a given temperature range. Thus, χ can be simply expressed as the following temperature dependent form.

$$\chi = \frac{\alpha}{T} + \beta + \gamma T \tag{15}$$

where α, β and γ are constants.

This expression is the extended form of the interaction parameter in the Flory-Huggins lattice theory.

Phase behavior predicted by the extended Flory-Huggins Latice theory. The simplest phase behavior is an upper critical solution temperature (UCST) behavior. Many of liquid-liquid mixtures show UCST behavior. However, phase behavior as shown in Figure 1 have been observed, especially, in polymer-polymer or polymer-polvent systems. It will be shown in the following that the unusual behavior can be predicted by the extended Flory-Huggins lattice theory. From eq. (6), phase separation occurs in the region.

$$\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} < 2\chi \tag{16}$$

This is illustrated in Figure 2. That is, phase separation occurs in the region between ϕ_1' and ϕ'' when 2χ is larger than f_{min}, and no phase separation occurs when 2χ is less than f_{min}. In Figures 2 and 3, the point, at which 2χ is equal to f_{min}, is the critical temperature. It is seen from Figures 1 and 2 that the temperature dependent forms of χ for the phase behaviors in Figure 1a,b,c, and d correspond to Figure 3a,b,c, and d, respectively. In each case, the simple forms of eq. (15) for the χ's from the geometrical conditons are as follows.

(i) Case of Figure 3a

$$2\chi = \frac{\alpha}{T} + \beta \tag{17}$$

where $\alpha<0$, and $\beta>f_{min}$

(ii) Case of Figure 3b

$$2\chi = \frac{\alpha}{T} + \beta + \gamma T \tag{18}$$

where $\alpha>0$, $r>0$ and $2\sqrt{\alpha\gamma} + \beta<f_{min}$

(iii) Case of Figure 3c

$$2\chi = \frac{\alpha}{T} + \beta + \gamma T \tag{19}$$

where $\alpha>0$, $\gamma>0$, and $2\sqrt{\alpha\gamma} + \beta>f_{min}$

(iv) Case of Figure 3d

$$2\chi = \frac{\alpha}{T} + \beta + \gamma T \tag{20}$$

where $\alpha<0$, $\gamma<0$, and $2\sqrt{\alpha\gamma} + \beta>f_{min}$.

Results and Discussion

The extended Flory-Huggins lattice theory was applied to polystyrene (PS)-polyvinylmethylether (PVME),[8]

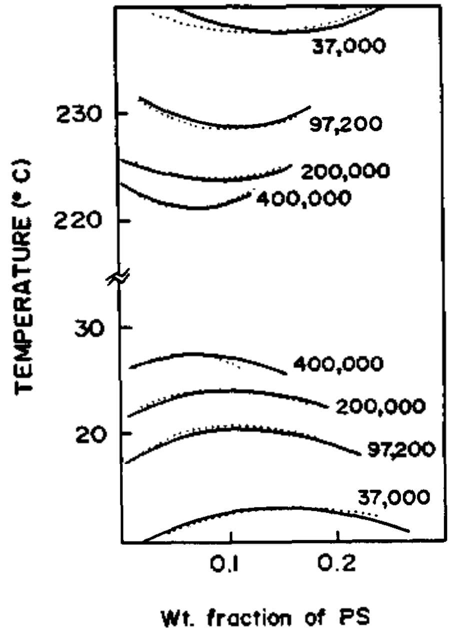

Figure 5. Phase diagrmas for PS(1)-cyclohexane(2) systems with indicated M.W.'s of PS. ...., ———: the same notations as in Figure 4.

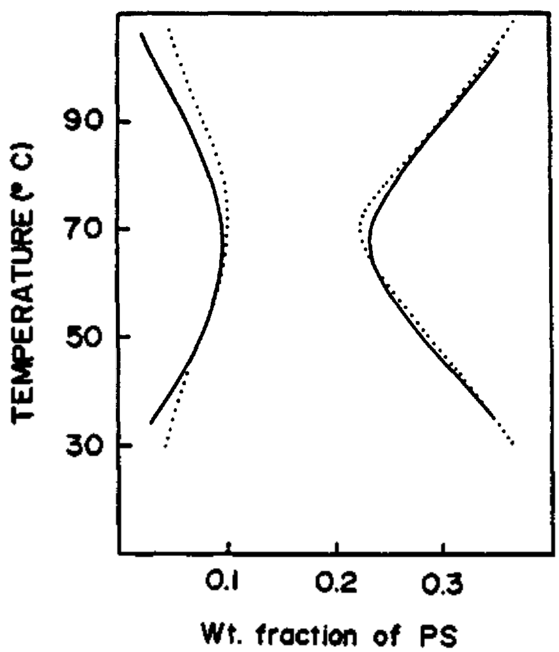

Figure 6. Phase diagram for PS(1)-acetone(2) system M.W. of PS is 19,800. ...., ———: the same notations as in Figure 4.

polystyrene-cyclohexane,[9] polystyrene-acetone,[10] and polyvinylalcohol (PVA)-water[11] systems.

In the calculations, the volume ratios of two components are often used as r_1/r_2 ratios, but in many cases it is not appropriate to real chain molecules, which are different from ideal chain molecules treated in the Flory-Huggins lattice theory. In this work, the ratios of r_1/r_2 were used as the calculated values using eq. (12) from the experimental critical compositions. Semi-empirical predictions using eq.'s (7) to (9), were compared with the experimental cloud point curves in Figures 4 to 7. The input parameters for Figures 4 to 7 are listed in Tables 1 to 4. The figures show good agreement between the theory and the experiment. The χ-parameters used for the systems in Tables

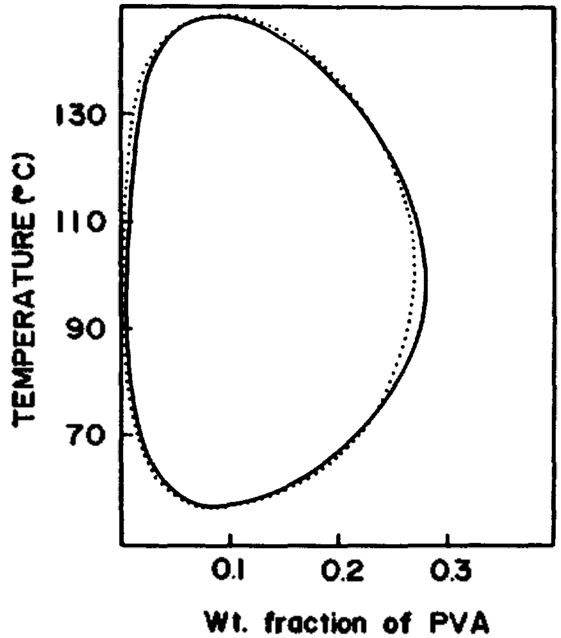

Figure 7. Phase diagram for PVA(1)-water(2) system M.W. of PVA is 140,000. ...., ———: the same notations as in Figure 4.

TABLE 1: Parameters for PS(1)-PVME(2) System having Various Molecular Weights of PS with Molecular Weight 5,150 of PVME

M.W.	r_1/r_2	$2\chi r_1$
10,000	0.9805	$-\frac{6006.2}{T}+16.519$
20,400	2.862	$-\frac{3960.0}{T}+11.832$
200,000	33.00	$-\frac{2958.7}{T}+9.3705$

M.W. : molecular weight.

TABLE 2: Parameters for PS(1)-cyclohexane(2) System having Various Molecular Weights of PS

M.W.	r_1/r_2	$2\chi r_1$
37,000	201.63	$\frac{2498.7}{T}-12.485+0.01711\,T$
97,200	476.9	$\frac{1930.7}{T}-9.3321+0.01311\,T$
200,000	881.9	$\frac{2083.1}{T}-10.136+0.01411\,T$
400,000	1837.7	$\frac{2098.1}{T}-10.180+0.01413\,T$

1 to 4 satisfy the conditions of eq.'s (13) to (16). That is, the χ-parameters have the same temperature dependence as in Figure 3. This behavior agrees well with thermodynamic stability that the larger $\Delta H_{mix}/(N_1r_1+N_2r_2)kT\,(=\chi\phi_1\phi_2)$ of some state, the more unstable it is, which means that phase separation occurs more likely. Tables 1 and 2 show that r_1/r_2 ratio increases as the molecular weight of component 1 increases. This is expected since the number of lattice sites, r_i, occupied by one molecule increase with increasing the chain length of the molecule proportional to the molecular weight.

TABLE 3: Parameters for PS(1)-acetone(2) System Having Molecular weights 19,800 of PS

r_1/r_2	$2\chi r_2$
146.1	$\frac{1329.4}{T} - 6.6527 + 0.01153T$

TABLE 4: Parameters for PVA(1)-water(2) System having Various Molecular Weights 140,000 of PVA

r_1/r_2	$2\chi r_2$
3035.3	$\frac{-392.83}{T} + 3.1598 - 2.8256 \times 10^{-3}T$

Conclusion

The partial miscibilities in polymer-polymer or polymer-solvent systems have been explained in terms of the extended form of the Flory-Huggins lattice theory. Mathematical conditions for the four partial miscibilities were derived, and the results were in good aggreement with the experimental results of PS-PVME, PS-cyclohexane, PS-acetone, and PVA-water systems.

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Synthesis and Stereochemistry of the Complexes of Cobalt(III) with New Tetradentate Ligands. Cobalt(III) Complexs of Ethylenediamine-N,N'-*di*-α-butyric Acid

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A new flexible N_2O_2-type tetradentate ligand, ethylene-diamine-N,N'-di-α-butyric acid (eddb), has been synthesized, and a series of cobalt (III) complexes of eddb, $[Co(eddb)L]^{n+}$ (L = Cl_2, $(H_2O)_2$, Cl H_2O, and CO_3^{2-}), have been prepared. Only s-*cis* isomers have been yielded during the preparation of complexes. Ring strain is cited as the primary cause for the preference for the s-*cis* geometric configuration.

A linear flexible edda-type ligand (edda = ethylenediamine-diacetic acid, $HOOCCH_2NHCH_2CH_2NHCH_2COOH$) can occupy four coordination sites with three geometric isomers possible : *trans*, s-*cis* (symmetric *cis*), and uns-*cis* (unsymmetric *cis*)

Mori *et al*[1] were the first to report the synthesis of cobalt (III) complexes of edda. They prepared the carbonato, diaqua and dinitro complexes, and postulated the s-*cis* configuration from a comparative analysis of absorption spectra. Legg and Cooke[2] prepared $[Co(edda)(am)]^+$, (am = en, $2NH_3$) and Co (III) complexes of N-alkyl substituted analgoue of edda. They isolated the s-*cis* and uns-*cis* isomers for the edda complex although the latter isomers were obtained in trace quantities only. Kuroda[3-5] prepared a group of edda cobalt (III) complexes with ammonia, en, pyridine, 2,2'-bipyridyl, and observed that the coordination mode of edda depended upon the temperature. Later, Legg[6-7] and others[8-11] prepared and characterized uns-*cis* isomers of $[Co(edda)(L)]^{n+}$ (L = en, S-alanine, R-propylenediamine).

The first C-alkyl-substituted analogue of edda was ethylenediamine-N,N'-dis-α-propionate, $HOOCCH(CH_3)NHCH_2CH_2NHCH(CH_3)COOH$, (SS-eddp) prepared by Liu and coworkers.[12] Both s-*cis* and uns-*cis* isomers of $[Co(SS\text{-}eddp)(L)]^+$ (L = en, R-Pn) were isolated. Recently, two other C-alkyl-substituted edda ligands have been reported. One is S-stilbenediamine-N,N'-diacetate (S-sdda)[13] whose cobalt (III) complexes, $[Co(S\text{-}sdda)(L)]^+$, (L = en, S-stilbenediamine) has yielded only s-*cis* isomer, and the other ethylenediamine-N,N'-di-S-α-isovalerate(ven)[14,15]. The $[Co(ven)(H_2O)NO_3]$ complex existed only as the s-*cis* isomer, while in the case of $[Co(ven)(H_2O)_2]^+$ and $[Co(ven)(en)]^+$ complexes both s-*cis* and uns-*cis* were found to exist. Woon and O'Connor,[16] and strasak and Bachraty[17] have independently prepared 2s, 2's-1, 1'-(ethane-1, 2-diyl)