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Liquid-liquid equilibria for polymer solutions and blends, including copolymers

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Abstract

A *simplified* perturbed hard-sphere-chain (PHSC) theory is applied to interpret, correlate, and (in part) predict liquid-liquid equilibria (LLE) for polymer solutions and blends, including copolymers. The PHSC equation of state uses a hard-sphere-chain reference system plus a van der Waals attractive perturbation. Three pure-component parameters are obtained from readily available thermodynamic properties. Mixture parameters are obtained using pure-component parameters, conventional combining rules, and one or two binary constants. Theoretical and experimental coexistence curves and miscibility maps show good agreement for selected blends containing polymers and copolymers. For LLE of dilute or semi-dilute solvent/polymer solutions, it is necessary to decrease the pure-component polymer chain length, probably because the mean-field approximation is not suitable for such solutions.

1. INTRODUCTION

Equations of state (EOS) provide useful tools for correlating and estimating thermodynamic properties of polymer solutions [1,2]. The EOS theory has successfully explained both lower-critical-solution-temperature (LCST) and upper-critical-solution-temperature (UCST) phenomena for polymer solutions, in contrast to the classical Flory-Huggins polymer-solution theory [3] that fails to describe LCST behavior at elevated temperatures.

Recently, we presented a perturbed hard-sphere-chain (PHSC) EOS applicable to mixtures containing solvents, polymers, and copolymers [4-9]. We first developed a hard-sphere-chain (HSC) equation of state by generalizing Chiew's result for HSC mixtures through the Carnahan-Starling radial distribution function for HSC mixtures at contact [5]. For real fluids, a van der Waals perturbation was added to the reference HSC EOS and the Song-Mason [10] method was used to scale the van der Waals covolume b and the attractive energy parameter a in terms of two pair-potential parameters. In this method, two universal functions of a reduced temperature were introduced to represent the effect of temperature on b and a [6]; they were determined from the vapor pressures and the densities of saturated liquid and vapor of argon and methane and extended to molecular fluids and polymers by using a temperature scaling factor s .

For mixtures containing polymers and copolymers, no mixing rules are required for the hard-sphere-chain contribution. Only the perturbation needs the van der Waals one-fluid ($vdW1$) mixing theory [4,7-9]. The PHSC EOS can reproduce all types of fluid phase equilibria that have been found experimentally in binary and ternary mixtures containing polymers and copolymers [7-9]. It can also quantitatively describe UCST and LCST behavior and miscibility maps in mixtures containing polymers and copolymers [4,7,9].

In this paper, we present a *simplified* version of the PHSC EOS. The scaling factor s is removed and the two universal functions are redetermined from thermodynamic properties of argon and methane over a wider range of fluid temperatures and densities. Removal of s allows use of simpler combining rules for mixtures. For pure fluids and polymers, the new PHSC EOS is still characterized by three molecular parameters: segment number per molecule r , segment size σ , and non-bonded segment-segment interaction energy ϵ ; they can be obtained from

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readily available data for thermodynamic properties such as vapor pressures, densities, and compressibilities. The new PHSC EOS is applied to LLE of binary blends containing polymers and copolymers and to binary LLE for solvent/polymer solutions.

We give attention here to LLE because representation of LLE is much more difficult than that of vapor-liquid equilibria (VLE). Several authors have shown that highly oversimplified models can represent VLE with one or two binary parameters, probably because VLE calculations require only the chemical potential of the solvent; because the polymer is not volatile, its chemical potential plays no role in VLE. However, in binary LLE chemical potentials of both components are important.

2. NEW PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

Derivation of the PHSC EOS follows a first-order statistical-mechanical perturbation theory based on a fluid of hard-sphere chains as the reference system; details are given in our previous publications [6,7]. Here we only reproduce the main equations necessary for describing the model.

2.1. Pure fluids

The PHSC EOS for pure fluids is [6]

$$\frac{p}{\rho k_B T} = 1 + r^2 b \rho g(d^+) - (r-1)[g(d^+)-1] - \frac{r^2 a \rho}{k_B T} \quad (1)$$

where p is the pressure, $\rho = N/V$ is the number density (N is the number of molecules and V the volume), k_B is the Boltzmann constant, T is the absolute temperature, $g(d^+)$ is the radial distribution function of hard spheres at contact, and d is the effective hard-sphere diameter; $g(d^+)$ is calculated from the Carnahan-Starling equation,

$$g(d^+) = \frac{1 - \eta/2}{(1 - \eta)^3} \quad \eta = \frac{rb\rho}{4} \quad (2)$$

In Eq. (1), the first three terms represent the reference equation of state for hard-sphere chains, and the last term is a van der Waals-type perturbation to take into account attractive forces. The three segment-based parameters in Eq. (1), r , b , and a , all have a direct physical interpretation. Parameter r represents the number of effective hard spheres per molecule. Parameter b represents the second virial coefficient of hard spheres; it is an effective van der Waals covolume. Parameter a reflects the strength of attractive forces between two non-bonded segments. In the PHSC theory, both b and a are temperature-dependent according to the Song-Mason method [10]:

$$b(T) = \frac{2\pi}{3} d^3(T) = \frac{2\pi}{3} \sigma^3 F_b(k_B T/\varepsilon) \quad a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(k_B T/\varepsilon) \quad (3)$$

where ε and σ are pair-potential parameters; ε is the depth of the minimum in the pair potential and σ is the separation distance between segment centers at this minimum. In Eq. (3), $F_a(k_B T/\varepsilon)$ and $F_b(k_B T/\varepsilon)$ are two universal functions of the reduced temperature, $k_B T/\varepsilon$. Originally, these two functions were determined from fitting the vapor pressures and saturated liquid and vapor densities for argon and methane by setting $r = 1$. To apply original universal functions to molecular fluids ($r > 1$), parameter s was introduced to rescale F_a and F_b with respect to temperature such that their values remained in a consistent range for both small and large molecules; s is a function of molecular chain length only for pure fluids. However, the evaluation of s in the mixture became uncertain since the definition of molecular chain length for cross terms was not clear and the inclusion of s then led to arbitrary combining rules for mixtures.

In the present version of the PHSC EOS, scaling factor s is removed and the two universal functions F_a and F_b are redetermined from thermodynamic properties of fluid argon and methane over large ranges of temperature and density; they are accurately represented by the following empirical formulae:

$$F_a(k_B T/\varepsilon) = 1.8681 \exp[-0.0619(k_B T/\varepsilon)] + 0.6715 \exp[-1.7317(k_B T/\varepsilon)^{3/2}] \quad (4)$$

$$F_b(k_B T/\varepsilon) = 0.7303 \exp[-0.1649(k_B T/\varepsilon)^{1/2}] + 0.2697 \exp[-2.3973(k_B T/\varepsilon)^{3/2}] \quad (5)$$

Table 1 lists the new PHSC EOS parameters r , ε , σ for normal fluids. The fitting procedure is the same as that used in the previous PHSC EOS [6] except that vapor pressures and saturated liquid densities at temperatures between $0.5T_c$ and $0.9T_c$ are used, rather than temperatures between the triple point and $0.9T_c$.

2.2. Polymers

Since r is used as a measure of molecular size, for a polymer it is proportional to molecular weight M . Although both r and M are large for a polymer, the ratio r/M remains constant as M rises. Thus, for pure polymers r/M (instead r) becomes a characteristic parameter in addition to ε and σ . These three parameters for polymers can be determined from experimental pVT data. For sufficiently high-molecular-weight polymers, pVT data are usually insensitive to the molecular weight. This observation can be clearly seen by rewriting Eq. (1) as:

$$\frac{P}{\rho_r k_B T} = 1 + b\rho_r g(d^+) - (1 - 1/r)g(d^+) - \frac{a\rho_r}{k_B T} \quad (6)$$

where $\rho_r = r\rho$ is the segment density of the polymer, which is the compatible quantity to the measured mass density of the polymer. In Eq. (6), r appears explicitly only in the term $(1 - 1/r)$, which becomes essentially unity for large r . Therefore, we can obtain a simpler EOS for polymers by taking the limit of $r \rightarrow \infty$ in Eq. (6):

$$\frac{P}{\rho_r k_B T} = 1 + b\rho_r g(d^+) - g(d^+) - \frac{a\rho_r}{k_B T} \quad (7)$$

Non-linear least-squares regression is used to find a set of three molecular parameters r/M , ε and σ for each polymer by fitting Eq. (7) to pVT data. Table 2 gives parameters regressed for a number of polymers.

2.3. Mixtures containing polymers

Extension of Eq. (1) to mixtures is straightforward [7]:

$$\frac{P}{\rho k_B T} = 1 + \rho \sum_{ij}^m x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^+) - \sum_i^m x_i (r_i - 1) [g_{ii}(d_{ii}^+) - 1] - \frac{\rho}{k_B T} \sum_{ij}^m x_i x_j r_i r_j a_{ij} \quad (8)$$

where $x_i = N_i/N$ is the number fraction of molecules, r_i is the number of segments (tangent hard spheres) comprising component $i = 1, 2, \dots, m$, and $g_{ij}(d_{ij}^+)$ is the ij pair radial distribution function of hard-sphere mixtures at contact. For each unlike pair of components ($i \neq j$), additional parameters, b_{ij} and a_{ij} , are needed for the mixture; b_{ij} is the second cross virial coefficient of hard-sphere mixtures and a_{ij} is the parameter reflecting attractive forces between two unlike non-bonded segments. A combining rule is not necessary for calculating b_{ij} because hard-sphere diameters are additive:

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = (b_i^{1/3} + b_j^{1/3})^3/8 \quad d_{ij}(T) = [d_i(T) + d_j(T)]/2 \quad (9)$$

However, this restriction can be relaxed when applying Eq. (9) to real mixtures; an alternate expression for b_{ij} and a_{ij} can be obtained by extending Eq. (3) to mixtures:

$$b_{ij}(T) = \frac{2\pi}{3} d_{ij}^3(T) = \frac{2\pi}{3} \sigma_{ij}^3 F_b(k_B T/\varepsilon_{ij}) \quad a_{ij}(T) = \frac{2\pi}{3} \sigma_{ij}^3 \varepsilon_{ij} F_a(k_B T/\varepsilon_{ij}) \quad (10)$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) (1 - \lambda_{ij}) \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} (1 - \kappa_{ij}) \quad (11)$$

where λ_{ij} and κ_{ij} are adjustable binary parameters. Finally, $g_{ij}(d_{ij}^+)$ is given by

$$g_{ij}(d_{ij}^+) = \frac{1}{1 - \eta} + \frac{3}{2} \frac{\xi_{ij}}{(1 - \eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1 - \eta)^3} \quad (12)$$

$$\eta = \frac{\rho}{4} \sum_i^m x_i r_i b_i \quad \xi_{ij} = \frac{\rho}{4} (b_i b_j / b_{ij})^{1/3} \sum_i^m x_i r_i b_i^{2/3} \quad (13)$$

3. EXTENSION TO COPOLYMER SYSTEMS

An important advantage of the PHSC theory is that segments (spheres) in a chain molecule need not all have the same diameter. Therefore, the PHSC EOS can be used to represent copolymers and their mixtures where different segments have different diameters.

3.1. Pure copolymers

Considering a pure copolymer system where each molecule consists of r segments but each segment has a different size, the PHSC EOS is [9]

Table 1
PHSC equation-of-state parameters for some normal fluids

Substance	<i>r</i>	ϵ/k_B (K)	$\sigma(\text{\AA})$	Substance	<i>r</i>	ϵ/k_B (K)	$\sigma(\text{\AA})$
normal alkanes							
ethane	1.694	206.3	3.916	aromatics			
propane	2.129	219.0	3.998	benzene	2.727	291.6	3.958
butane	2.496	231.3	4.085	toluene	3.138	287.0	4.019
pentane	3.149	226.0	3.995	ethylbenzene	3.607	279.4	4.018
hexane	3.446	235.6	4.084	propylbenzene	4.137	270.6	4.007
heptane	4.255	225.9	3.947	o-xylene	3.620	285.4	3.998
octane	5.055	219.6	3.850	m-xylene	3.721	276.4	3.977
nonane	5.748	217.3	3.804	p-xylene	3.455	287.9	4.104
decane	6.616	212.7	3.723	chlorobenzene	3.144	305.3	3.975
undecane	7.057	215.4	3.754	fluorobenzene	3.012	276.9	3.883
dodecane	7.712	214.8	3.733	styrene	3.291	304.3	4.083
tridecane	7.986	218.3	3.794				
tetradecane	9.023	213.7	3.682	acetates			
pentadecane	9.851	211.3	3.662	methyl acetate	3.804	224.8	3.338
hexadecane	10.168	214.2	3.703	ethyl acetate	4.509	213.5	3.369
heptadecane	10.834	213.7	3.680	n-propyl acetate	4.989	213.9	3.440
octadecane	11.110	216.5	3.698	i-propyl acetate	4.779	210.6	3.484
nonadecane	11.659	216.1	3.718	n-butyl acetate	5.413	216.3	3.514
eicosane	12.925	212.1	3.633	i-butyl acetate	5.574	207.4	3.461
branched & cyclic alkanes							
isobutane	2.397	226.2	4.155	t-butyl acetate	4.485	220.2	3.743
isopentane	2.777	236.7	4.182	n-pentyl acetate	6.547	206.6	3.403
neopentane	2.526	233.7	4.351	i-pentyl acetate	5.568	220.5	3.628
2,2-dimethylbutane	2.849	247.7	4.368	n-hexyl acetate	6.720	212.9	3.514
2,3-dimethylbutane	2.998	247.1	4.278	vinyl acetate	4.259	218.2	3.371
cyclopentane	2.509	277.3	4.090	ethers			
methylcyclopentane	2.902	267.2	4.153	dimethyl ether	2.519	216.6	3.553
ethylcyclopentane	3.277	269.4	4.181	diethyl ether	2.985	237.9	3.780
propylcyclopentane	3.823	262.7	4.130	ethylene oxide	2.242	277.5	3.390
cyclohexane	2.723	286.7	4.215	1,3-propylene oxide	2.381	295.4	3.729
methylcyclohexane	2.968	283.7	4.336	tetrahydrofuran	2.758	279.5	3.811
ethylcyclohexane	3.392	282.4	4.306	ketones			
propylcyclohexane	3.969	272.3	4.230	acetone	3.164	250.9	3.510
butylcyclohexane	4.580	264.5	4.151	methyl ethyl ketone	3.344	255.8	3.694
alkenes							
ethylene	1.609	196.8	3.839	diethyl ketone	3.931	245.4	3.684
propylene	2.029	221.9	3.951	2-pentanone	4.041	241.2	3.661
1-butene	2.677	218.3	3.882	2-hexanone	5.151	224.5	3.506
trans-2-butene	2.504	233.9	3.984	chlorinated hydrocarbons			
cis-2-butene	2.530	235.7	3.941	methyl chloride	2.018	256.7	3.591
1-pentene	2.828	237.1	4.087	dichloromethane	2.669	268.1	3.541
1-hexene	3.395	234.5	4.042	carbon tetrachloride	2.507	301.7	4.187
trans-decalin	3.160	333.8	4.657	chloroform	2.878	268.1	3.726
				vinyl chloride	2.175	249.7	3.773
				1,2-dichlorethane	2.994	280.9	3.691

Table 2
PHSC equation-of-state parameters for common polymers

Polymer	<i>r/M</i>	ϵ/k_B (K)	$\sigma(\text{\AA})$	Polymer	<i>r/M</i>	ϵ/k_B (K)	$\sigma(\text{\AA})$
high density polyethylene	0.04938	324.1	3.825	poly(vinyl acetate)	0.05166	292.6	3.346
low density polyethylene	0.05854	306.0	3.603	poly(methyl methacrylate)	0.04222	373.5	3.608
<i>i</i> -poly(propylene)	0.02831	392.1	4.705	<i>i</i> -poly(methyl methacrylate)	0.05071	347.6	3.367
<i>i</i> -poly(1-butene)	0.04024	353.2	4.120	poly(butyl methacrylate)	0.04764	323.4	3.604
poly(isobutene)	0.04963	331.9	3.725	poly(cyclohexyl methacrylate)	0.03742	379.3	3.856
poly(4-methyl-1-pentene)	0.02890	381.7	4.685	poly(ethylene terephthalate)	0.04777	363.5	3.320
poly(styrene)	0.03834	385.4	3.899	poly(carbonate)	0.03885	393.0	3.707
poly(<i>o</i> -methyl styrene)	0.03925	393.5	3.893	poly(ether ether ketone)	0.04424	375.0	3.429
cis-1,4-poly(butadiene)	0.07049	276.8	3.301	poly(sulphone)	0.03720	425.7	3.721
poly(vinyl chloride)	0.03672	365.1	3.590	poly(tetrafluoroethylene)	0.02705	215.9	3.244
poly(ethylene glycol)	0.04778	316.6	3.532	poly(tetrahydrofuran)	0.04277	327.6	3.833

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{\alpha=1}^r \sum_{\beta=1}^r b_{\alpha\beta} g_{\alpha\beta} - \sum_{\alpha=1}^{r-1} [g_{\alpha,\alpha+1} - 1] - \frac{\rho}{k_B T} \sum_{\alpha=1}^r \sum_{\beta=1}^r a_{\alpha\beta} \quad (14)$$

where subscripts α and β denote the α th and β th segments (effective hard spheres) in a copolymer molecule, $b_{\alpha\beta}$ is the van der Waals covolume between two segments, $g_{\alpha\beta}$ is the radial distribution function of hard spheres when the α th and β th segments are at contact, and $a_{\alpha\beta}$ is the parameter reflecting attractive forces between non-bonded segments α and β . Parameters $b_{\alpha\beta}$, $g_{\alpha\beta}$ and $a_{\alpha\beta}$ are given by

$$b_{\alpha}(T) = \frac{2\pi}{3} \sigma_{\alpha}^3 F_b(k_B T / \varepsilon_{\alpha\alpha}) \quad b_{\alpha\beta}(T) = \frac{1}{8} (b_{\alpha}^{1/3} + b_{\beta}^{1/3})^3 \quad (15)$$

$$g_{\alpha\beta} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{\alpha\beta}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{\alpha\beta}^2}{(1-\eta)^3} \quad (16)$$

$$\eta = \frac{\rho}{4} \sum_{\alpha=1}^r b_{\alpha} \quad \xi_{\alpha\beta} = \frac{\rho}{4} (b_{\alpha} b_{\beta} / b_{\alpha\beta})^{1/3} \sum_{\gamma=1}^r b_{\gamma}^{2/3} \quad (17)$$

$$a_{\alpha\beta}(T) = \frac{2\pi}{3} \sigma_{\alpha\beta}^3 \varepsilon_{\alpha\beta} F_a(k_B T / \varepsilon_{\alpha\beta}) \quad \varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta})^{1/2} (1 - \kappa_{\alpha\beta}) \quad (18)$$

where $\kappa_{\alpha\beta}$ is an adjustable parameter.

3.2. Mixtures containing copolymers

Equation (14) is readily extended to mixtures containing copolymers:

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{ij}^m x_i x_j \left[\sum_{\alpha=1}^r \sum_{\beta=1}^r b_{ij,\alpha\beta} g_{ij,\alpha\beta} \right] - \sum_i^m x_i \sum_{\alpha=1}^r [g_{ii,\alpha,\alpha+1} - 1] - \frac{\rho}{k_B T} \sum_{ij}^m x_i x_j \left[\sum_{\alpha=1}^r \sum_{\beta=1}^r a_{ij,\alpha\beta} \right] \quad (19)$$

where indices i and j denote components in the mixture; they should not be confused with indices α and β labeling segments in a molecule. The physical significances of $b_{ij,\alpha\beta}$, $g_{ij,\alpha\beta}$ and $a_{ij,\alpha\beta}$ are the same as those for pure fluids in Eq. (14). We again have two choices for calculating $b_{ij,\alpha\beta}$; one follows from hard-sphere additivity:

$$b_{ij,\alpha\beta}(T) = \frac{2\pi}{3} d_{ij,\alpha\beta}^3(T) = \frac{1}{8} (b_{i,\alpha}^{1/3} + b_{j,\beta}^{1/3})^3 \quad d_{ij,\alpha\beta}(T) = [d_{i,\alpha}(T) + d_{j,\beta}(T)]/2 \quad (20)$$

Another method for $b_{ij,\alpha\beta}$ and $a_{ij,\alpha\beta}$ can be obtained by extending Eq. (10) to copolymer mixtures:

$$b_{ij,\alpha\beta}(T) = \frac{2\pi}{3} d_{ij,\alpha\beta}^3(T) = \frac{2\pi}{3} \sigma_{ij,\alpha\beta}^3 F_b(k_B T / \varepsilon_{ij,\alpha\beta}) \quad a_{ij,\alpha\beta}(T) = \frac{2\pi}{3} \sigma_{ij,\alpha\beta}^3 \varepsilon_{ij,\alpha\beta} F_a(k_B T / \varepsilon_{ij,\alpha\beta}) \quad (21)$$

$$\sigma_{ij,\alpha\beta} = \frac{1}{2} (\sigma_{i,\alpha} + \sigma_{j,\beta}) (1 - \lambda_{ij,\alpha\beta}) \quad \varepsilon_{ij,\alpha\beta} = (\varepsilon_{ii,\alpha\alpha} \varepsilon_{jj,\beta\beta})^{1/2} (1 - \kappa_{ij,\alpha\beta}) \quad (22)$$

where $\lambda_{ij,\alpha\beta}$ and $\kappa_{ij,\alpha\beta}$ are adjustable parameters. Finally, $g_{ij,\alpha\beta}$ is given by

$$g_{ij,\alpha\beta} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij,\alpha\beta}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij,\alpha\beta}^2}{(1-\eta)^3} \quad (23)$$

$$\eta = \frac{\rho}{4} \sum_i^m x_i \left[\sum_{\alpha=1}^r b_{i,\alpha} \right] \quad \xi_{ij,\alpha\beta} = \frac{\rho}{4} (b_{i,\alpha} b_{j,\beta} / b_{ij,\alpha\beta})^{1/3} \sum_k^m x_k \left[\sum_{\gamma=1}^r b_{k,\gamma}^{2/3} \right] \quad (24)$$

4. COMPARISON WITH EXPERIMENT

To correlate experimental LLE, it is necessary to use Eqs. (10) and (11) to calculate b_{ij} ($i \neq j$) and a_{ij} ($i \neq j$) for mixtures containing polymers and to use Eqs. (21) and (22) to calculate $b_{ij,\alpha\beta}$ ($i \neq j$) and $a_{ij,\alpha\beta}$ ($i \neq j$) for mixtures containing copolymers. To illustrate, Figure 1 compares theoretical coexistence curves with experimental data [11] for poly(α -methyl styrene)(PMS)/polystyrene(PS) mixtures which exhibit UCST behavior. The EOS parameters for poly(α -methyl styrene) are those for poly(α -methyl styrene) (see Table 2). Binary parameters λ_{12} (0.0000924) and κ_{12} (-0.0000585) are determined such that theory agrees with experiment for both PMS62/PS58 and PMS56/PS49 (where PMS62, e.g., denotes PMS at the weight-average molecular weight 62000). Agreement is good but sensitive to the choice of binary parameters. The semibroken line is the glass-transition temperature T_g of the mixture, calculated from this equation: $1/T_g(K) = w_{PS}/373 + (1-w_{PS})/444$ where w_{PS} is the weight fraction of

polystyrene. The PHSC theory predicts that the coexistence curve of PMS44/PS37 lies below the glass-transition temperature of the mixture, consistent with experimental observation [11].

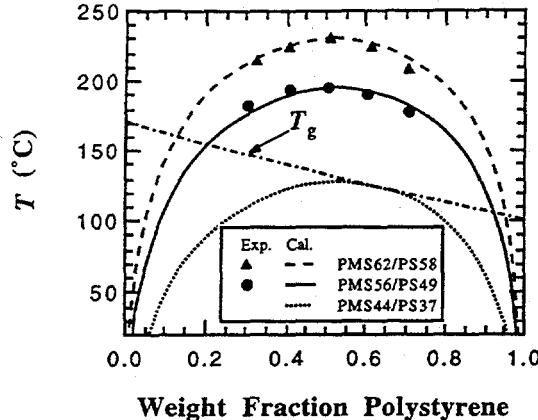


Fig.1. Coexistence curve for PMS/PS mixtures

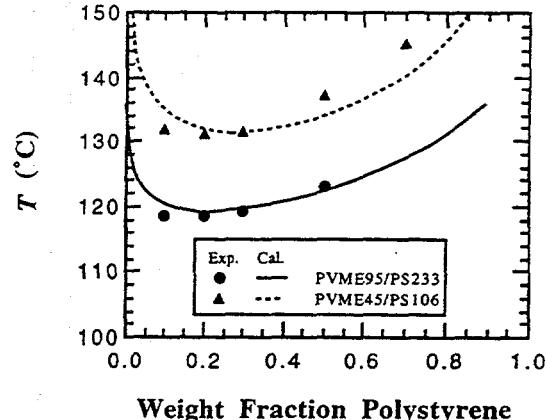


Fig.2. Coexistence Curve for PVME/PS mixtures

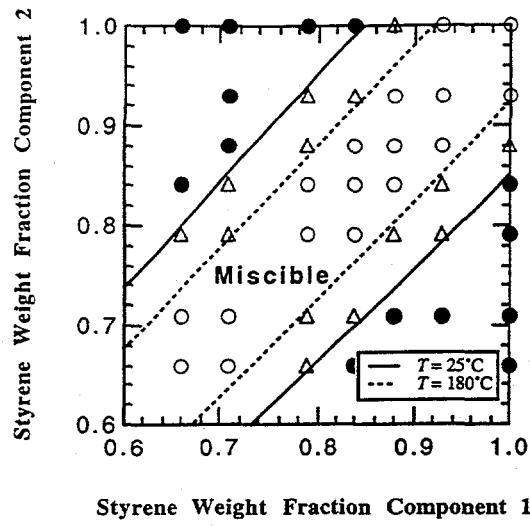
Figure 2 compares theoretical coexistence curves with experiment for poly(vinyl methyl ether)(PVME)/polystyrene mixtures which exhibit LCST behavior. Experimental data are from Walsh *et al.* [12]. Binary parameters λ_{12} (0.000152) and κ_{12} (0.000720) are determined as in Figure 1. Agreement is good although the PHSC theory slightly overestimates the critical weight fraction of polystyrene.

Figure 3 compares a theoretical miscibility map with experiment for binary mixtures of poly(styrene-*co*-methyl methacrylate) (S-*co*-MMA) random copolymers differing in copolymer compositions [13]. The weight-average molecular weight of copolymer sample is 150000 and parameters $\lambda_{S\text{-MMA}}$ (-0.013) and $\kappa_{S\text{-MMA}}$ (0.01626) are determined by fitting to experimental data. In this mixture, the only difference between components 1 and 2 is in copolymer composition; the mixture becomes more miscible as the difference in copolymer composition declines. Therefore, the miscibility map shown in Figure 3 has a miscible region around the diagonal line. The miscible area decreases with temperature because the miscible pair of copolymers eventually exhibits phase separation at elevated temperature due to LCST behavior. Although it is difficult to identify the miscibility-immiscibility boundary from experimental data, theory and experiment appears to be in fair agreement.

Theoretical LLE for solvent/polymer systems (where molecules are significantly different in size) show deviations from experiment; the PHSC EOS overestimates the EOS effect which causes the LCST at elevated temperature[14]. As a result, the PHSC EOS predicts a LCST lower than experiment when pure-component parameters of polymers are used. To improve agreement, we introduce an adjustable parameter that, in effect, decreases densities of pure polymers [14]; here we present only a brief summary and give an example.

Consider a binary solvent/polymer system where components 1 and 2 represent solvent and polymer, respectively. In Eq. (8), the term $r_i r_j \rho_{ij}$ in the perturbation term represents the attractive force between components i and j . The density of a polymer can be decreased by decreasing the magnitude of $r_2 r_2 a_{22}$ in the perturbation term. Therefore, we correct the overestimated EOS effect in dilute polymer solutions by multiplying r_2 by a factor ζ smaller than unity in the perturbation term [14]. By introducing adjustable parameter ζ , we require that hard-sphere diameters of unlike segments are additive; *i.e.*, b_{12} is given by Eq. (9). As a result, we use only two adjustable parameters ζ and κ_{12} for binary mixtures.

Figure 4 shows the effect of molecular weight on LCST and UCST for *n*-pentyl acetate(*n*-CH₃CO₂C₅H₁₁)/polyethylene(PE) mixtures [15]. Here $r=r_2/r_1$ and the molecular-weight range of polyethylene is $M_\eta=13600-175000$ where M_η is the viscosity-average molecular weight. Two adjustable parameters are: $\zeta=0.824$ and $\kappa_{12}=0.01777$. The mixture is miscible in all proportions at temperatures between LCST and UCST. The PHSC EOS is able to represent simultaneous occurrence of an UCST and a LCST in this solvent/polymer system.



Styrene Weight Fraction Component 1

Fig.3. Miscibility Map for P(S-co-MMA) Copolymer Mixtures

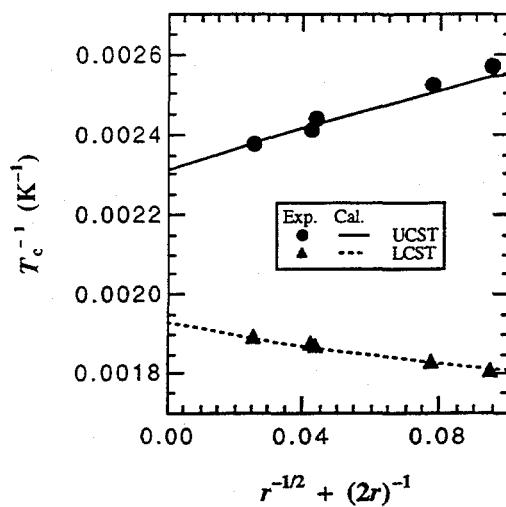


Fig.4. Molecular-Weight Dependence of LCST
UCST for $n\text{-CH}_3\text{CO}_2\text{C}_5\text{H}_{11}/\text{PE}$ mixtures

5. CONCLUSION

A simplified PHSC EOS is presented and applied to LLE of binary mixtures containing solvents, polymers, and copolymers. The PHSC EOS is able to represent UCST behavior as well as LCST behavior in polymer blends including copolymer mixtures. Theoretical and experimental coexistence curves and miscibility maps show good agreement for mixtures containing poly(α -methyl styrene), poly(styrene), poly(vinyl methyl ether), and poly(styrene-*co*-methyl methacrylate). To correct the overestimated EOS effect in solvent/polymer systems, an empirical correction is introduced into the perturbation term of the PHSC EOS to reduce the polymer's chain length. This correction is probably necessary to compensate for failure of the mean-field assumption for dilute and semi-dilute polymer solutions. The modified PHSC EOS can quantitatively represent simultaneous occurrence of UCST and LCST in selected solvent/polymer systems, including molecular-weight dependence of both critical solution temperatures.

6. ACKNOWLEDGMENT

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