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Comparison of Perturbed Hard-Sphere-Chain Theory with Statistical Associating Fluid Theory for Square-Well Fluids

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The effect of hard-sphere-chain equations on the description of phase behavior is presented by the comparison of perturbed hard-sphere-chain (PHSC) theory with statistical associating fluid theory (SAFT) for square-well fluids. The PHSC-type equation of this work is based on the hard-sphere-chain equation of Chiew (PY-CS), the square-well fluid model of Alder et al., and the expression of Chen and Kreglewski. The PHSC-type equation has expressions similar to those of the SAFT equation. A comparison of the PHSC-type equation with the SAFT model shows that the PHSC-type equation of state presents slightly better results of pure compounds and much better vapor–liquid equilibrium results of high-concentration polymer solutions.

1. Introduction

Equations of state (EOSs) are powerful tools for the description of thermodynamic properties and phase equilibria. Recently, EOSs based on the perturbation theory have been paid much attention. The molecularly based EOSs, such as statistical associating fluid theory (SAFT),^{1,2} perturbed hard-sphere-chain (PHSC),^{3,4} hard-sphere-chain fluids (HSCF),⁵ and perturbed Lennard-Jones chain (PJLC),⁶ are derived on the basis of the perturbation theory. They are applicable over a wide range of densities and over a wide range of molecular sizes.

Chapman et al.¹ developed the framework of the SAFT equation based on the hard-sphere-chain equation of Wertheim.⁷ The work of Huang and Radosz² makes the SAFT equation a practical and widely used EOS. The SAFT equation has been successfully applied to the calculation of phase equilibria.⁸ However, it encounters difficulties in some cases.⁹

On the basis of the modification of hard-sphere-chain equation of Chiew,¹⁰ Song et al. established a PHSC EOS^{3,4} consisting of a van der Waals type perturbation term. Hino and Prausnitz's PHSC-type equation¹¹ is based on the analytical solution by Chang and Sandler¹² to the second-order perturbation theory of Barker and Henderson for square-well fluids of variable width. On the basis of the square-well coordination number model of Guo et al.,¹³ Feng and Wang¹⁴ use directly the hard-sphere-chain equation of Chiew¹⁰ to derive a PHSC-type equation.

This work aims at presenting the effect of the hard-sphere-chain equation on the description of phase equilibria. We establish the PHSC-type equation based on the hard-sphere-chain equation of Chiew (PY-CS),¹⁰ the square-well model of Alder et al.,¹⁵ and the expression of Chen and Kreglewski.¹⁶ The developed PHSC-type equation (PHSC-SW) has expressions similar to those of the SAFT equation.² For describing the pres-

sure–volume–temperature (*PVT*) relationship of pure compounds and the phase behavior of mixtures, comparison of the PHSC-SW equation with the SAFT equation has been performed. The results present the effect of hard-sphere-chain equations on the description of phase equilibria of mixtures containing polymers.

2. PHSC-Type EOS Based on the Square-Well Model

In this work, we focus on the nonassociating fluids, and the general form of the PHSC-type equation can be expressed as the sum of a reference term and a perturbation term, representing the contributions of the repulsion and attraction, respectively

$$\frac{P}{\rho RT} = \left(\frac{P}{\rho RT} \right)_{\text{hsc}} + \left(\frac{P}{\rho RT} \right)_{\text{pert}} \quad (1)$$

where ρ is the molar density of the system at temperature T and pressure P , R is the gas constant, and subscripts hsc and pert signify the hard-sphere-chain term and the perturbation term, respectively.

2.1. Hard-Sphere-Chain EOS. On the basis of the Percus–Yevick (PY) theory, for modeling of the athermal freely jointed tangent HSCF, Chiew¹⁰ derived the analytical expressions of compressibility EOSs for homonuclear chains, heteronuclear chains, blends of homonuclear and heteronuclear chains, and homonuclear chains in hard-sphere solvents. Here, Chiew's equation for homonuclear chain fluids is applied as the reference term. For mixtures, the hard-sphere-chain equation, which is referred to as the PY-CS equation by Chiew,¹⁰ can be expressed as

$$\left(\frac{P}{\rho RT} \right)_{\text{hsc}} = 1 + \frac{6}{\rho \pi} \left[\frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{\xi_2^3(3-\xi_3)}{(1-\xi_3)^3} \right] + \frac{\xi_3}{1-\xi_3} - \frac{\rho}{2(1-\xi_3)} \sum_i x_i(m_i-1) \left(2 + 3d_i \frac{\xi_2}{1-\xi_3} \right) \quad (2)$$

where x_i and m_i are the mole fraction and the chain length of component i and ξ_j ($j = 1, 2$, and 3) is defined

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as

$$\xi_j = \frac{\pi N_A \rho}{6} \sum_i x_i m_i (d_i)^j \quad (3)$$

where N_A is Avogadro's number and d_i is the effective temperature-dependent hard-sphere diameter of component i . On the basis of the work of Chen and Kreglewski,¹⁶ the equation for d_i is given by

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-\frac{3u_i^0}{\kappa T}\right) \right] \quad (4)$$

where κ is the Boltzmann constant, u_i^0/κ is a temperature-independent parameter representing the well depth of the square-well potential for component i , and σ_i is the temperature-independent hard-sphere diameter of component i . The temperature-independent hard-sphere molar volume of component i is expressed as

$$v_i^{00} = \frac{\pi N_A}{6\tau} \sigma_i^3 \quad (5)$$

where $\tau = 0.74048$.

2.2. Square-Well Fluid EOS. Like the SAFT equation of Huang and Radosz,² we apply the equation of Alder et al.¹⁵ to account for the attractive forces. The equation for mixtures can be expressed as

$$\left(\frac{P}{\rho RT}\right)_{\text{pert}} = m \sum_i \sum_j j D_{ij} \left(\frac{u}{\kappa T}\right)^i \left(\frac{\xi_3}{\tau}\right)^j \quad (6)$$

where D_{ij} are constants given by Chen and Kreglewski,¹⁶ m is the chain length of the mixture, and the mixing rule for m is

$$m = \sum_i x_i m_i \quad (7)$$

van der Waals one-fluid theory mixing rule is used for the calculation of $u/\kappa T$

$$\frac{u}{\kappa T} = \frac{\sum_i \sum_j x_i x_j m_i m_j (u_{ij}/\kappa T) v_{ij}^0}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0} \quad (8)$$

$$v_{ij}^0 = \left[\frac{(v_i^0)^{1/3} + (v_j^0)^{1/3}}{2} \right]^3 \quad (9)$$

$$u_{ij} = (u_i u_j)^{0.5} (1 - K_{ij}) \quad (10)$$

where v_i^0 is the temperature-dependent hard-sphere volume of component i , which can be expressed as

$$v_i^0 = \frac{\pi N_A}{6\tau} d_i^3 \quad (11)$$

u_i is the temperature-dependent hard-sphere energy, which is related to the temperature-independent hard-sphere energy u_i^0 as follows:¹⁶

$$u_i = u_i^0 \left(1 + \frac{e}{\kappa T} \right) \quad (12)$$

K_{ij} is the interaction parameter between components i and j . For pure compounds shown in Tables 1 and 2, e/κ is set to 1 for methane, 40 for CO₂, and 10 for the others.

As a result, the final expression of the PHSC-type equation based on the square-well model¹⁵ (PHSC-SW) for mixtures is

$$\begin{aligned} \frac{P}{\rho RT} = 1 + \frac{6}{\rho \pi} & \left[\frac{3\xi_1 \xi_2}{(1 - \xi_3)^2} + \frac{3\xi_2^3}{(1 - \xi_3)^3} - \frac{\xi_3 \xi_2^3}{(1 - \xi_3)^3} \right] + \\ & \frac{\xi_3}{1 - \xi_3} - \frac{1}{2(1 - \xi_3)} \rho \sum_i x_i (m_i - 1) \left(2 + 3d_i \frac{\xi_2}{1 - \xi_3} \right) + \\ & m \sum_i \sum_j D_{ij} \left(\frac{u}{\kappa T} \right)^i \left(\frac{\xi_3}{\tau} \right)^j \end{aligned} \quad (13)$$

For pure compounds, eq 13 can be rewritten as

$$\begin{aligned} \frac{P}{\rho RT} = 1 + m \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + (1 - m) \frac{2.5\eta - \eta^2}{(1 - \eta)^2} + \\ m \sum_i \sum_j j D_{ij} \left(\frac{u}{\kappa T} \right)^i \left(\frac{\eta}{\tau} \right)^j \end{aligned} \quad (14)$$

where η is equal to ξ_3 for pure compounds and can be expressed as

$$\eta = \tau \rho m v^{00} \left[1 - 0.12 \exp\left(-\frac{3u^0}{\kappa T}\right) \right]^3 \quad (15)$$

3. Results and Discussion

3.1. Nonassociating Fluids. Both the PHSC-SW and the SAFT equations need three parameters, chain length m , hard-sphere interaction u^0/κ , and temperature-independent hard-sphere molar volume v^{00} , to describe the PVT relationship of pure compounds. The three parameters are determined by minimizing the objective function

$$F = \sum_i^N \left[\frac{\rho_i^{\text{cal}}(T_i) - \rho_i^{\text{exp}}(T_i)}{\rho_i^{\text{exp}}(T_i)} \right]^2 + \sum_i^N \left[\frac{P_i^{\text{cal}}(T_i) - P_i^{\text{exp}}(T_i)}{P_i^{\text{exp}}(T_i)} \right]^2 \quad (16)$$

where N is the number of data points, $\rho_i^{\text{exp}}(T_i)$ and $P_i^{\text{cal}}(T_i)$ are experimental and calculated liquid densities, and $P_i^{\text{exp}}(T_i)$ and $P_i^{\text{cal}}(T_i)$ are experimental and calculated vapor pressures at temperature T_i , respectively.

The calculated results of 54 normal fluids are shown in Table 1, including the parameters determined by the PHSC-SW equation and comparison of the PHSC-SW equation with the SAFT model for relative deviations of saturated liquid densities and vapor pressures.

Figures 1 and 2 show the results obtained by the PHSC-SW equation. Figure 1 shows that the chain lengths of n -alkanes, aromatics, ketones, and alkenes have a good linear relationship with molecular weight. The molar mass of molecules increases linearly with the number of hard-spheres. The results prove the hypothesis that the molecules are made of homonuclear diameter hard spheres. Figure 2 presents the relationship between the hard-sphere energy u^0/κ and the

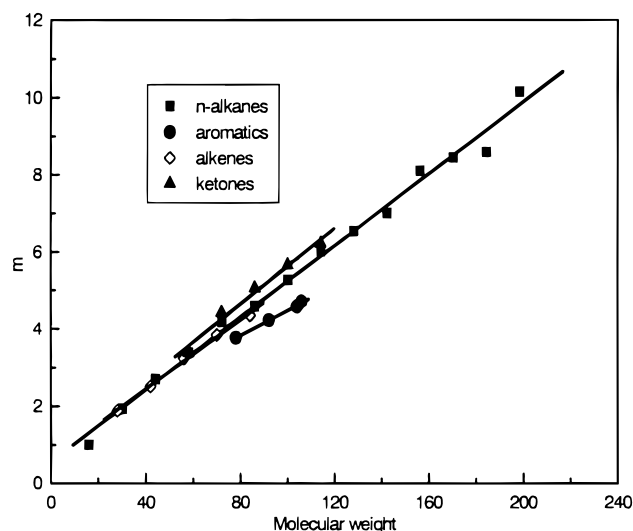
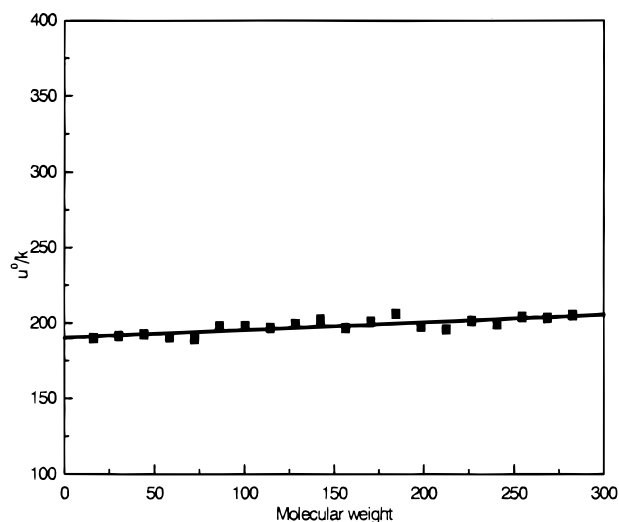
Table 1. PHSC–SW EOS Parameters for Nonassociating Fluids^a

	M_W	T_{range} (K)	m	v^{00} (cm ³ /mol)	U^0/κ (K)	AAD % ^b			
						SAFT		PHSC–SW ^c	
						P^{sat}	ρ^{liq}	P^{sat}	ρ^{liq}
carbon dioxide ¹	44.010	218–293	1.422	13.783	212.460	3.45	1.59	3.48 (16)	2.00 (16)
<i>n</i> -Alkanes									
methane	16.043	91–187	1.000	21.499	190.051	1.59	0.86	1.59 (22)	0.86 (22)
ethane	30.070	163–304	1.933	14.791	191.233	2.40	3.48	2.69 (16)	3.89 (16)
propane	44.096	274–363	2.709	13.149	192.437	0.57	1.31	0.49 (15)	1.22 (15)
butane	58.124	217–386	3.380	13.607	190.543	1.51	2.80	0.94 (14)	2.03 (14)
pentane	72.150	291–454	4.187	12.742	189.508	1.34	2.55	0.89 (23)	1.75 (23)
hexane	86.117	252–494	4.586	13.758	197.566	3.24	3.71	2.85 (25)	2.71 (25)
heptane	100.203	264–523	5.274	13.421	197.726	2.28	4.40	1.34 (17)	3.29 (17)
octane	114.230	296–552	6.026	13.019	196.702	2.09	4.24	1.19 (17)	3.05 (17)
nonane	128.257	344–424	6.547	13.587	199.247	0.26	1.36	0.15 (15)	1.03 (15)
decane ¹	142.285	260–550	7.012	13.831	202.202	6.07	4.27	4.66 (30)	3.24 (30)
undecane ¹	156.312	248–607	8.110	12.798	196.799	2.71	5.87	2.12 (37)	4.59 (37)
dodecane ¹	170.338	264–554	8.456	13.523	200.694	2.82	4.44	1.19 (30)	3.45 (30)
tridecane ¹	184.365	268–658	8.602	14.231	205.928	6.52	4.74	4.33 (40)	3.41 (40)
tetradecane ¹	198.392	279–669	10.162	12.344	197.679	3.24	7.76	3.35 (40)	6.35 (40)
pentadecane ¹	212.419	384–673	11.058	12.216	195.717	3.24	6.78	4.03 (40)	5.38 (40)
hexadecane ¹	226.446	292–681	11.044	13.163	201.323	3.83	5.85	2.43 (40)	4.51 (40)
heptadecane ¹	240.473	336–686	12.038	12.510	199.088	4.27	6.37	5.42 (36)	5.00 (36)
octadecane ¹	254.500	302–692	12.013	13.265	204.019	2.25	7.33	1.27 (40)	6.01 (40)
nonadecane ¹	268.527	306–696	12.641	13.437	203.401	2.28	6.22	2.02 (40)	4.92 (40)
eicosane ¹	282.553	310–740	13.155	13.457	205.254	7.22	6.56	4.36 (44)	5.13 (44)
Aromatics									
benzene	78.113	284–550	3.759	12.079	239.639	1.75	2.89	1.43 (22)	2.05 (22)
toluene	92.140	282–546	4.220	12.971	240.028	2.07	3.34	1.23 (16)	2.38 (16)
styrene	104.151	289–418	4.576	13.532	249.341	1.86	1.23	1.61 (12)	0.86 (12)
ethylbenzene	106.167	277–467	4.731	13.561	237.345	1.00	2.45	0.43 (19)	1.86 (19)
<i>m</i> -xylene	106.167	276–582	4.850	12.984	235.882	3.14	3.98	2.01 (19)	2.93 (19)
<i>o</i> -xylene	106.167	277–595	4.739	13.247	242.776	3.03	3.96	1.85 (15)	2.96 (15)
<i>p</i> -xylene	106.167	288–491	4.702	13.722	239.418	1.54	2.61	0.89 (10)	1.95 (10)
propylbenzene	120.194	271–428	5.175	14.467	236.220	0.45	1.01	0.21 (10)	0.79 (10)
Ketones									
acetone	58.08	275–493	3.380	13.607	190.543	2.39	2.17	1.81 (16)	1.96 (16)
2-butanone	72.107	272–319	4.418	10.424	216.484	0.18	0.56	0.11 (7)	0.40 (7)
2-pentanone	86.133	282–353	5.056	10.806	210.612	0.15	0.88	0.06 (11)	0.63 (11)
2-hexanone	100.160	299–332	5.662	11.243	209.349	0.05	0.48	0.03 (11)	0.37 (11)
2-heptanone	114.187	290–424	6.221	11.530	209.406	0.65	1.95	0.25 (12)	1.47 (12)
Branched and Cyclic Alkanes									
cyclopropane	42.080	203–386	2.54	12.155	208.202	1.77	2.70	1.21 (20)	2.17 (20)
cyclobutane	56.107	199–285	2.476	16.811	251.038	0.59	0.17	0.48 (19)	0.22 (19)
2-methylbutane	72.150	266–447	3.851	13.934	193.208	2.14	3.53	1.54 (14)	2.56 (14)
cyclohexane	84.161	279–541	3.842	14.177	232.294	1.83	3.27	1.01 (16)	2.27 (16)
cycloheptane	98.188	290–575	4.163	14.820	244.699	2.67	4.62	1.74 (15)	3.54 (15)
cyclooctane	112.214	288–466	4.489	15.949	252.131	0.77	2.23	0.21 (13)	1.74 (13)
Ethers									
benzyl ethyl ether ¹	136.194	278–618	5.967	12.239	232.601	6.32	5.06	4.92 (35)	3.99 (35)
diethyl ether ¹	74.1228	157–447	4.558	10.717	180.856	2.06	4.77	1.31 (30)	3.80 (30)
dimethyl ether ¹	46.069	132–382	2.683	12.007	206.896	9.18	1.83	7.87 (26)	1.50 (26)
Alkenes									
ethene	28.050	132–281	1.884	14.024	174.415	2.78	3.03	2.50 (20)	3.30 (20)
propene	42.080	138–364	2.514	14.262	191.132	6.09	5.08	5.37 (14)	5.28 (14)
1-butene	56.107	215–388	3.233	13.390	192.470	2.06	2.21	1.48 (13)	1.40 (13)
1-pentene	70.134	194–443	3.841	13.511	195.671	2.67	3.60	1.48 (14)	2.61 (14)
1-hexene	84.161	283–334	4.353	14.153	200.834	0.15	0.87	0.09 (12)	0.66 (12)
Chlorinated Hydrocarbons									
methyl bromide	94.939	205–275	2.215	13.261	271.471	0.55	0.33	0.48 (12)	0.30 (12)
chloromethane	50.488	193–393	2.649	9.731	214.814	2.52	1.37	1.88 (20)	0.95 (20)
dichloromethane	84.933	212–406	3.161	10.310	242.558	3.82	2.26	5.13 (16)	1.89 (16)
trichloromethane	119.378	252–431	3.645	11.201	231.906	2.10	2.44	1.57 (14)	1.84 (14)
tetrachloromethane	153.823	253–543	3.514	14.105	245.088	1.90	3.04	1.05 (22)	2.17 (22)
chloroethane	64.515	250–383	3.017	11.354	223.473	1.10	3.33	0.79 (13)	2.95 (13)
Polymers									
PB ^{d,2}	250000	277–328	12969.51	12.0	244.403		1.28		0.96 (86)
PE ³	190000	413–473	10202.54	12.0	210.280		2.30		1.37 (42)
PIB ³	52000	325–383	2637.145	12.0	206.24		1.93		1.34 (70)
PDMS ³	166000	298–340	7878.205	12.0	204.632		0.59		0.19 (60)
PS ⁴	279000	388–469	12007.01	12.0	210.00		4.07		2.88 (64)
PEO ⁵	100000	361–497	4172.825	12.0	220.00		2.19		1.36 (100)

^a Superscripts 1–5 signify the data source as follows: (1) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*; Data Compilation; Hemisphere Publishing Corp.: New York, 1989. (2) Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 238. (3) Beret, S.; Prausnitz, J. M. *Macromolecules* **1975**, *8*, 536. (4) Quach, A.; Simha, R. *J. Appl. Phys.* **1971**, *42*, 4592. (5) Jain, R. K.; Simha, R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1929. Experimental data of other systems are taken from Simha and Sirvastava.¹⁷ ^b AAD %: $(1/N) \sum_i |(P_i^{\text{cal}} - P_i^{\text{exp}})/P_i^{\text{exp}}| \times 100$ for the relative deviation of vapor pressure. $(1/N) \sum_i |(\rho_i^{\text{cal}} - \rho_i^{\text{exp}})/\rho_i^{\text{exp}}| \times 100$ for the relative deviation of liquid density. ^c Numbers in parentheses indicate the number of data points used in the correlation. ^d Abbreviations: PB, polybutadiene; PE, polyethylene; PS, polystyrene; PIB, polyisobutylene; PDMS, poly(dimethylsiloxane); PEO, poly(ethylene oxide).

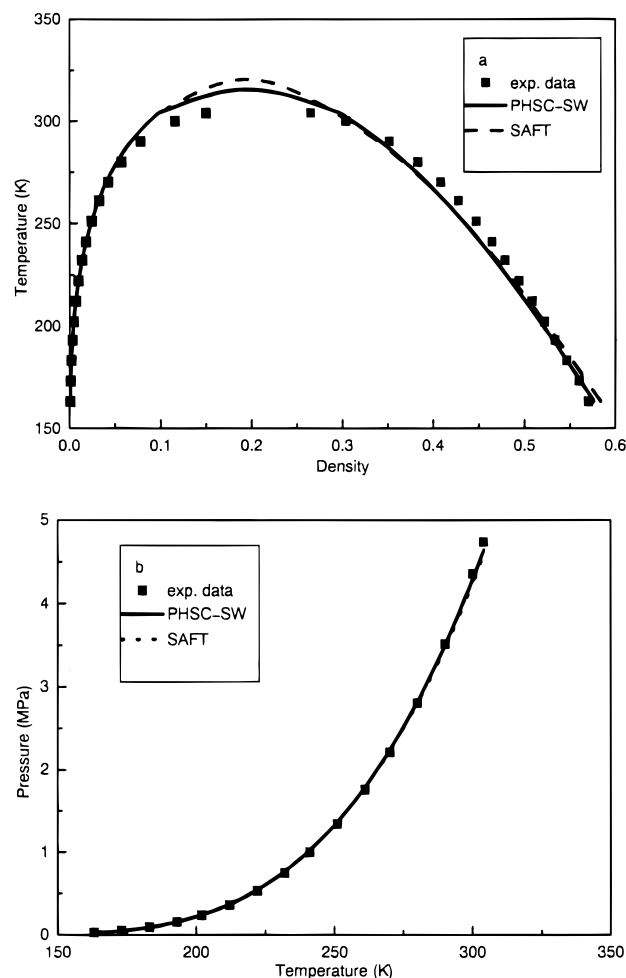
Table 2. SAFT Equation Parameters Used in the Phase Equilibrium Calculation of Mixtures

	M_W	m	v^{00} (cm ³ /mol)	u^0/k (K)
methyl bromide	94.939	2.000	14.626	298.283
2-methylbutane	72.15	3.872	13.154	200.690
polybutadiene	250000	12969.51	12.0	244.403
polyisobutylene	1000000	47714.47	12.0	206.240
polyethylene	248700	12658.83	12.0	216.150
polystyrene	247000	9934.532	12.0	210.000
poly(dimethylsiloxane)	89000	3986.649	12.0	204.632
poly(ethylene oxide)	100000	3884.593	12.0	220.000

**Figure 1.** Chain length m for n -alkanes, aromatics, ketones, and alkenes as a function of molar mass.**Figure 2.** Hard-sphere energies u^0/k for n -alkanes as a function of molecular weight.

molecular weight for n -alkanes. The hard-sphere energies u^0/k , playing an important role in the phase equilibrium calculations, are in the range of 190–205 K for n -alkanes.

Figures 3 and 4 present a comparison of the calculated and experimental data for ethane and hexane, where the experimental data are taken from Simth and Srivastava.¹⁷ The solid and dashed lines correspond to the results calculated by the PHSC-SW and SAFT equations, respectively.

**Figure 3.** Comparison of the calculated results with the experimental results for ethane: (a) coexistence curves; (b) vapor pressure versus temperature. Solid lines indicate the PHSC-SW equation and dashed lines the SAFT equation.

For 54 pure compounds listed in Table 1, the calculated results of the PHSC-SW equation are slightly better than those of the SAFT equation.

3.2. Polymers. Polymer liquid PVT experimental data are required for determining the three parameters, chain length m , hard-sphere interaction u^0/k , and temperature-independent hard-sphere molar volume v^{00} . Both the PHSC-SW equation and the SAFT equation² determine the three parameters by minimizing the objective function

$$F = \sum_i^N \left[\frac{\rho_i^{\text{cal}}(T_i) - \rho_i^{\text{exp}}(T_i)}{\rho_i^{\text{exp}}(T_i)} \right]^2 \quad (17)$$

In eq 17, N is the number of data points and $\rho_i^{\text{exp}}(T_i)$ and $\rho_i^{\text{cal}}(T_i)$ are experimental and calculated liquid densities.

The calculated results of six polymers are listed in Tables 1 and 2. Table 1 lists the parameters obtained by the PHSC-SW equation and relative deviations of liquid densities. Table 2 lists the parameters obtained by the SAFT equation.

3.3. Binary Mixtures. Both equations are applied to describe vapor-liquid equilibria (VLE) of high-concentration polymer solutions. In polymer solutions, polymer is regarded as a nonvolatile component, only

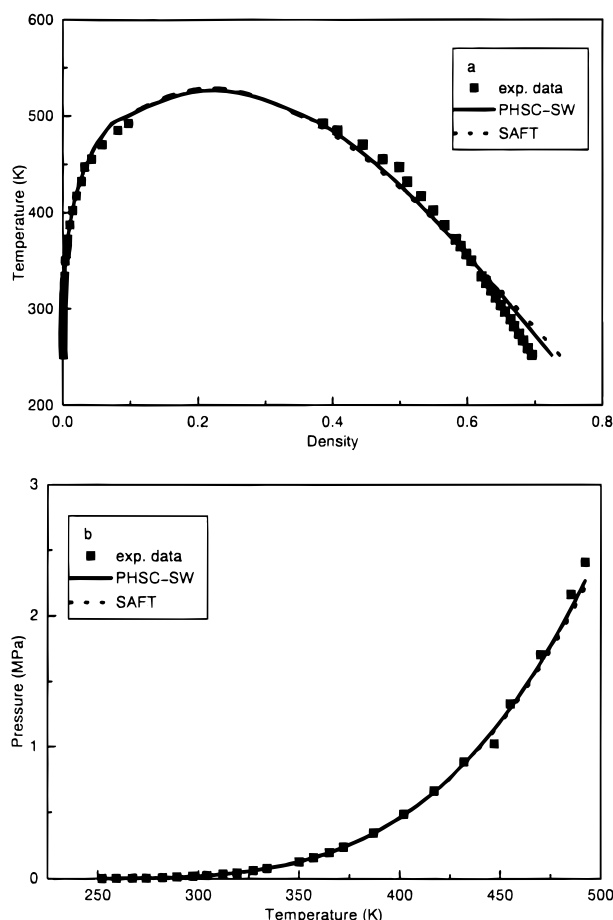


Figure 4. Comparison of the calculated results with the experimental results for hexane: (a) coexistence curves; (b) vapor pressure versus temperature. Solid lines indicate the PHSC–SW equation and dashed lines the SAFT equation.

Table 3. Relationship of Chain Length with Molecular Weight for Polymers

polymer	SAFT equation	PHSC–SW equation
polyisobutylene	$m = 0.04771M_W$	$m = 0.05071M_W$
polyethylene	$m = 0.05090M_W$	$m = 0.05366M_W$
polystyrene	$m = 0.04022M_W$	$m = 0.04305M_W$
poly(dimethylsiloxane)	$m = 0.04479M_W$	$m = 0.04745M_W$
poly(ethylene oxide)	$m = 0.03885M_W$	$m = 0.04713M_W$

pure solvent exists in the vapor phase. Pure compound parameters needed for calculation of VLE are listed in Tables 1 and 2. For the SAFT equation, except the parameters of pure compounds listed in Table 2, others are obtained from the paper of Huang and Radosz.² According to the relationship between the chain length and the molecular weight presented in Table 3, we can obtain the parameters of polymers with different molecular weights.

The binary interaction parameter K_{12} is determined by minimizing the objective function

$$F = 1/N \sum_i |(P_i^{\text{cal}} - P_i^{\text{exp}})/P_i^{\text{exp}}| \quad (18)$$

where N is the number of experimental data points and P_i^{exp} and P_i^{cal} are experimental and calculated vapor pressures, respectively. The chemical potential expressed by the PHSC–SW equation, which is needed in the phase equilibrium calculations, is given in the Appendix.

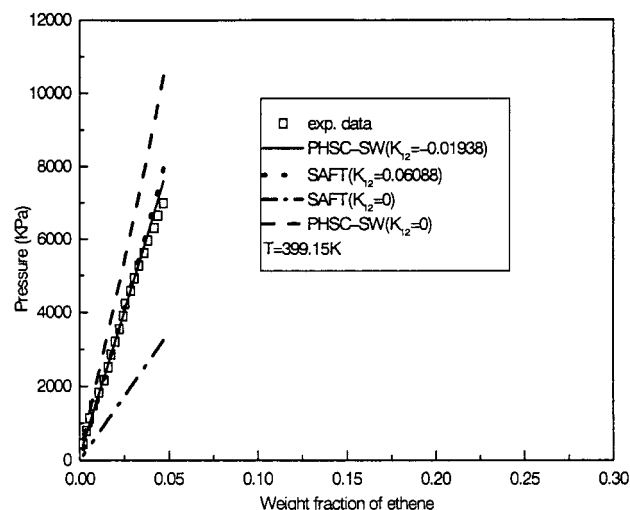


Figure 5. Solubility of ethene in polyethylene at 399.15 K.

For VLE of 29 high-concentration polymer solutions, the calculated and predicted results are presented in Tables 4 and 5.

(1) For polystyrene + nonane systems, the binary interaction parameter $K_{12} = 0.00341$ for the PHSC–SW equation is obtained by fitting experimental data at 403.15 K. This binary interaction parameter is applied to predict VLE of polystyrene + nonane systems at 423.15 and 428.15 K. A similar method is used for the calculations of polystyrene + *m*-xylene, polyethylene + ethene, polystyrene + nitrogen, poly(ethylene oxide) + benzene, and polybutadiene + ethylbenzene systems. However, for the polystyrene + CO₂ system, the solubility of CO₂ in polystyrene cannot be calculated by using the above method. The results indicate that the binary parameter K_{12} is temperature-dependent. For the systems listed in Table 4, the results calculated by the PHSC–SW equation exhibit a better agreement with the experimental data than those calculated by the SAFT model.

(2) Good agreement between the calculated results and experimental data can be obtained by the PHSC–SW equation with small values of the binary interaction parameter, such as $K_{12} = 0.00341$ for the polystyrene + nonane system, while relatively large values of the binary interaction parameter are needed for the SAFT equation, such as $K_{12} = 0.01336$ for the polystyrene + nonane system. Good accuracy can be obtained for VLE prediction by both the PHSC–SW and the SAFT equations using only pure compound parameters when $K_{12} < 0.005$. However, most binary interaction parameters needed in the SAFT equation are larger than 0.005. A smaller value of the binary interaction parameter means that the equation has a better potential of VLE prediction, which can be indicated by the predicted results of polystyrene + nonane, polystyrene + nitrogen, poly(dimethylsiloxane) + hexane, and poly(dimethylsiloxane) + octane presented in Table 5.

(3) Only pure compound parameters are used in the prediction of VLE (the binary interaction parameter K_{12} is set to 0) in order to examine the prediction potential of VLE. Table 5 indicates that the PHSC–SW equation can present good predicted results. In contrast, the SAFT equation fails to predict VLE for most systems listed in Table 5.

Table 4. Comparison of the PHSC–SW Equation with the SAFT Equation for Mixtures

polymer	solvent	T(K)	X_1 range ^a	SAFT		PHSC–SW		data source ^c
				K_{12} ^a	AAD % ^b	K_{12} ^a	AAD % ^b	
PS ^d	nonane	403.15	0.026–0.12	0.01336	4.160	0.003412	0.700	1
		423.15	0.024–0.07		2.640		4.771	1
		448.15	0.015–0.03		9.036		2.968	1
	<i>m</i> -xylene	403.15	0.044–0.17	0.04479	4.802	0.034500	2.938	1
		423.15	0.035–0.13		4.049		2.812	1
		448.15	0.023–0.12		32.45		9.880	2
	carbon dioxide	373.20	0.023–0.12	0.1170	9.922	0.1091	7.169	2
		413.20	0.035–0.10		9.268		4.760	2
		453.20	0.009–0.07		17.75		1.987	2
	nitrogen	373.20	0.038–0.07	0.08818	7.890	0.0006	4.398	2
		413.20	0.033–0.09		10.08		5.830	2
		453.20	0.039–0.10		13.49	–0.01938	4.177	1
PE	ethene	399.15	0.0018–0.05	0.06088	17.01		7.327	1
		413.15	0.0015–0.04		24.19		14.17	1
		428.15	0.0013–0.04		13.47	0.00885	5.700	1
PEO	hexane	273.15	0.013–0.07	0.01356	8.461		6.287	1
		273.15	0.011–0.12		28.34		16.12	1
		343.15	0.060–0.45		5.528	0.02505	2.601	1
PDMS	benzene	375.15	0.021–0.12	–0.02460	6.238		5.034	1
		303.04	0.005–0.09		1.352		5.363	1
		303.00	0.009–0.095		4.778	–0.00134	5.157	1
PB	octane	313.15	0.028–0.454	0.01035	15.79		14.05	1
		353.15	0.044–0.35		4.993		2.978	1
		373.15	0.039–0.39		2.131	–0.03752	7.734	1
PIB	ethylbenzene	403.15	0.023–0.17	–0.04533	11.99		5.774	1
		373.15	0.023–0.25		2.053	–0.00023	0.978	1
		333.15	0.082–0.34		22.99		13.13	1
		298.15	0.128–0.57		3.898		4.807	1
		298.15	0.015–0.044		2.617		4.229	3

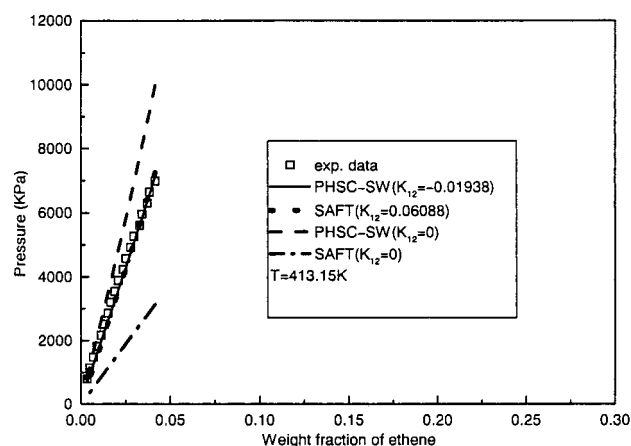
^a X_1 is the weight fraction of solvent, and K_{12} is the binary interaction parameter. ^b AAD % = $(1/N) \sum_i |(P_i^{\text{cal}} - P_i^{\text{exp}})/P_i^{\text{exp}}| \times 100$. ^c (1) Wen, H.; Elbro, H. S.; Alessi, P. Polymer Solution Data Collection. Part 1: Vapor–Liquid equilibrium. *DECHEMA Deutsche Gesellschaft für Chemisches Apparatewesen, Chemische Technik und Biotechnologie E.V.*; DECHEMA: Frankfurt/Main, Germany, 1992. (2) Sato, Y.; Yurugi, M.; Fujiwara, K.; Takishima, S.; Masuoka, H. *Fluid Phase Equilib.* **1996**, *125*, 129. (3) Gupta, R. B.; Prausnitz, J. M. *J. Chem. Eng. Data* **1995**, *40*, 784. ^d Abbreviations: PS, polystyrene; PE, polyethylene; PEO, poly(ethylene oxide); PDMS, poly(dimethylsiloxane); PB, polybutadiene; PIB, polyisobutylene.

Table 5. Predicted Results of VLE by the SAFT and PHSC–SW Models with $K_{12} = 0$

polymer	solvent	T(K)	AAD % ^a	
			SAFT	PHSC–SW
polystyrene	nonane	403.15	43.11	13.95
		423.15	40.65	9.931
		448.15	45.06	11.25
	nitrogen	373.20	49.17	1.905
		413.20	48.88	4.243
polyethylene	ethene	453.20	46.94	5.557
		399.15	58.81	33.71
		413.15	60.72	25.32
		428.15	63.03	14.37
poly(dimethylsiloxane)	hexane	303.00	20.67	27.69
polybutadiene	octane	313.15	30.36	7.708
		353.15	44.42	38.44
		373.15	30.10	23.80
polyisobutylene	cyclohexane	403.15	30.76	22.24
		333.15	21.35	1.187
		298.15	8.754	20.06

^a AAD % = $(1/N) \sum_i |(P_i^{\text{cal}} - P_i^{\text{exp}})/P_i^{\text{exp}}| \times 100$.

(4) The predicted results of polyethylene + ethene (Figures 5–7), polystyrene + nitrogen (Figures 8–10), polystyrene + CO₂ (Figure 11), polybutadiene + cyclohexane (Figure 12), poly(dimethylsiloxane) + octane (Figure 13), and polystyrene + nonane (Figure 14) systems are obtained by the PHSC–SW and SAFT equations. In all of the predictions, only the parameters of pure compounds are used, without using any binary interaction parameters. In particular, for predicting the solubility of nitrogen in polystyrene, both equations use the same pure compound parameters.

**Figure 6.** Solubility of ethene in polyethylene at 413.15 K.

The parameters of pure nitrogen are obtained from the paper of Huang and Radosz,² and the parameters of polystyrene are obtained by fitting the experimental data using the SAFT equation. It is evident that the PHSC–SW equation shows a much more powerful prediction potential than the SAFT equation does for high-concentration polymer solutions.

4. Conclusions

Both the PHSC–SW and SAFT equations use the square-well fluid model of Alder et al.,¹⁴ the expression of Chen and Kreglewski,¹⁶ and the van der Waals one-fluid theory mixing rule for mixtures. The difference lies in the fact that the PHSC–SW equation is based on

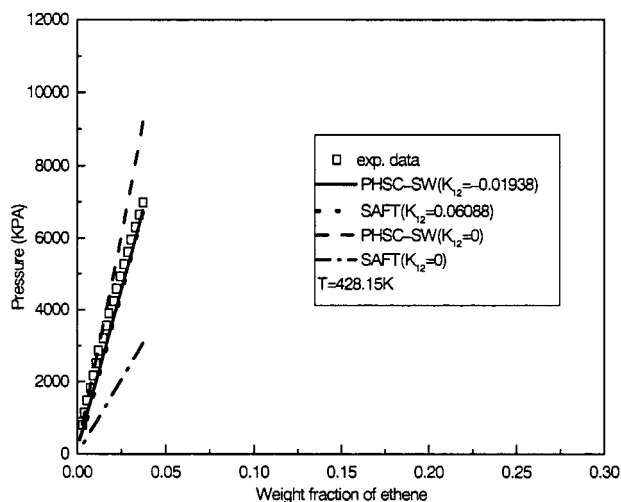


Figure 7. Solubility of ethene in polyethylene at 428.15 K.

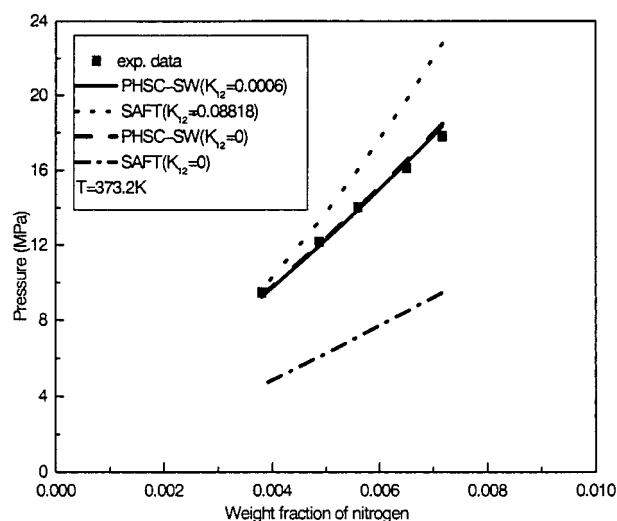


Figure 8. Solubility of nitrogen in polystyrene at 373.2 K.

Chiew's hard-sphere-chain equation (PY-CS)¹⁰ and that the SAFT equation is based on the equation of Wertheim⁷ (TPT1). The comparison of the PHSC-SW equation with the SAFT equation is actually the comparison of the PY-CS equation with the TPT1 equation. For pure compounds, there is a slight difference between eq 19 (PY-CS) and eq 20 (TPT1)

$$\frac{P}{\rho RT} = 1 + m \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + (1 - m) \frac{2.5\eta - \eta^2}{(1 - \eta)^2} \quad (19)$$

$$\frac{P}{\rho RT} = 1 + m \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + (1 - m) \frac{2.5\eta - \eta^2}{(1 - \eta)(1 - 0.5\eta)} \quad (20)$$

where the meanings of the variables are same as those of eq 14. On the basis of the results of molecular simulation, Chiew¹⁰ performed a comparison of eq 19 (PY-CS) with eq 20 (TPT1). The conclusions are that, in the same range of hard-sphere volume fraction and for chain lengths of 8- and 16-mer systems, the PY-CS equation agrees well with the Monte Carlo simulations and is superior to that of TPT1; for longer chains, the TPT1 equation tends to overestimate the pressures. Compared with the SAFT equation, for describing the PVT relationship of pure compounds, the PHSC-SW

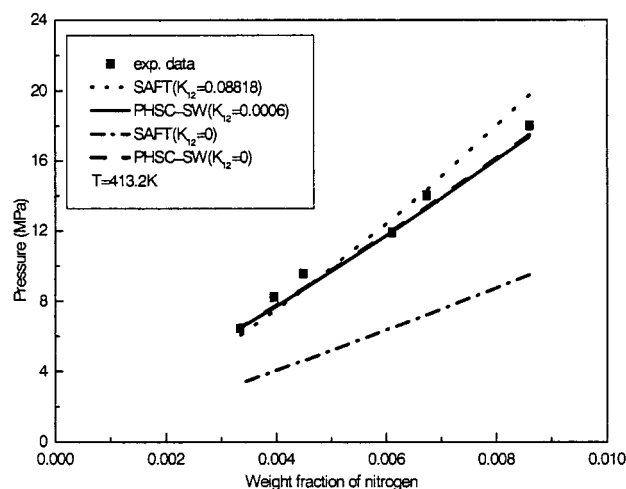


Figure 9. Solubility of nitrogen in polystyrene at 413.2 K.

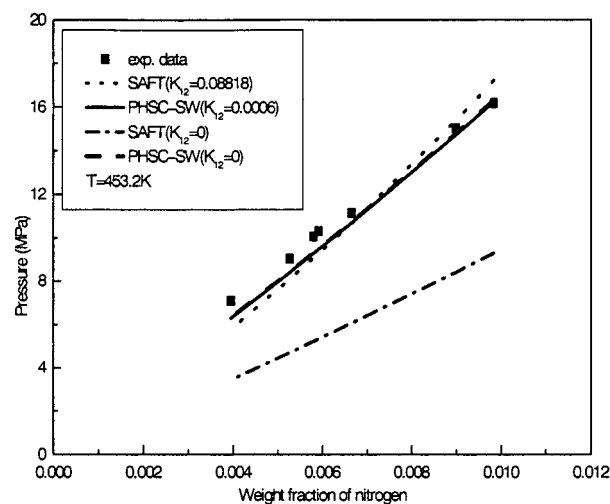


Figure 10. Solubility of nitrogen in polystyrene at 453.2 K.

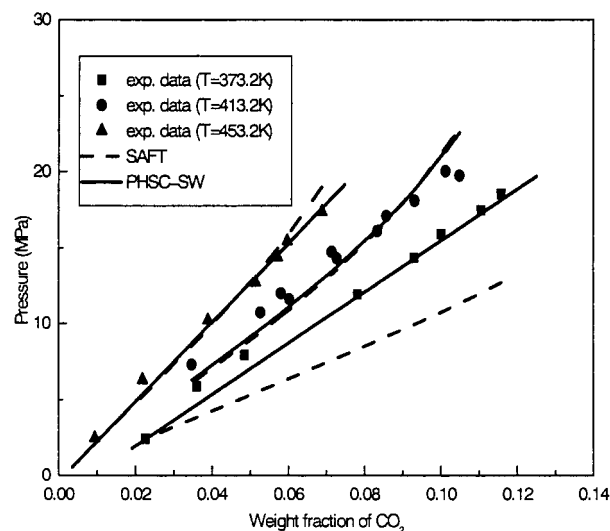


Figure 11. Solubility of carbon dioxide in polystyrene.

equation presents slightly better results. For mixtures of high-concentration polymer solutions, the PHSC-SW equation shows the advantage in the calculations and predictions of VLE phase behavior. The results of this work present the effect of hard-sphere chain equations on the description of phase equilibria of mixtures containing polymers.

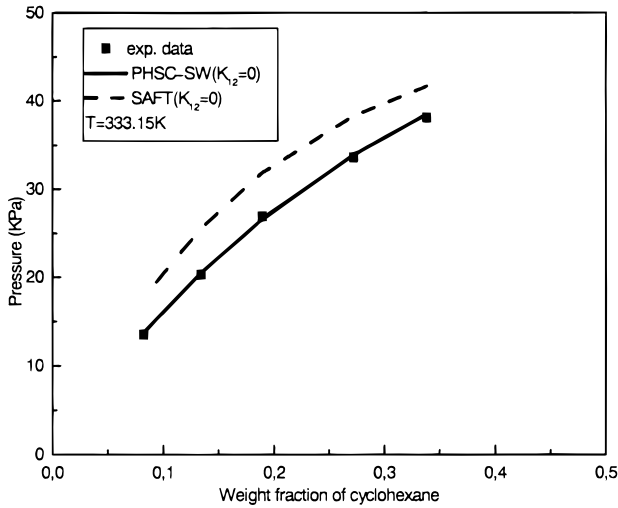


Figure 12. VLE of polybutadiene + cyclohexane.

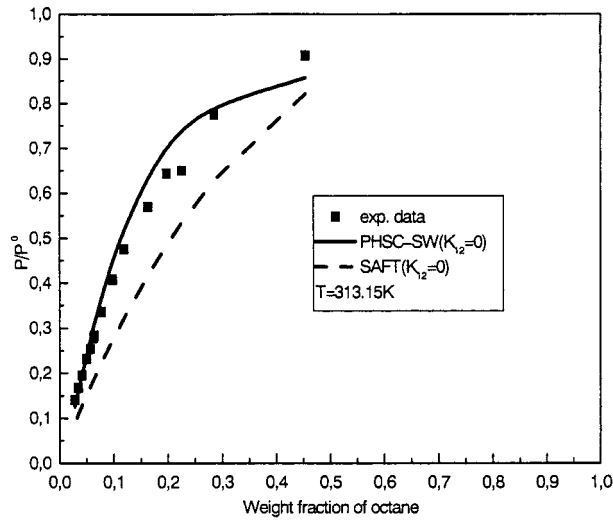


Figure 13. VLE of poly(dimethylsiloxane) + octane.

Appendix

The PHSC-SW equation of state for mixtures is expressed as

$$\frac{P}{\rho RT} = 1 + \frac{6}{\rho \pi} \left[\frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} - \frac{\xi_3\xi_2^3}{(1-\xi_3)^3} \right] + \frac{\xi_3}{1-\xi_3} - \frac{1}{2(1-\xi_3)} \rho \sum_i x_i (m_i - 1) \left(2 + 3d_i \frac{\xi_2}{1-\xi_3} \right) + m \sum_i \sum_j D_{ij} \left(\frac{u}{\kappa T} \right)^i \left[\frac{\xi_3}{\tau} \right]^j \quad (\text{A1})$$

The equation for calculating the Helmholtz energy A in terms of T , p , and x_i is

$$\frac{A}{nRT} = \frac{\sum A_i^0(T)}{nRT} + \int_0^p \left(\frac{P}{\rho RT} - 1 \right) \frac{d\rho}{\rho} + \sum_i x_i \ln(x_i \rho RT) \quad (\text{A2})$$

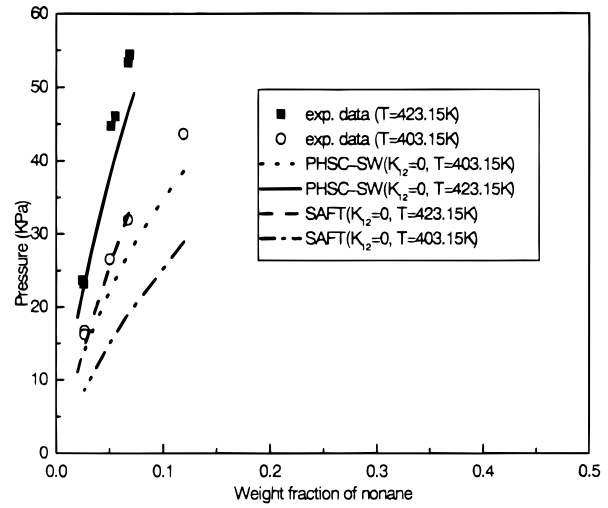


Figure 14. VLE of polystyrene + nonane.

When eqs A1 and A2 are combined, the residual Helmholtz energy is obtained as

$$\frac{a^{\text{res}}}{RT} = \frac{\frac{3BC}{D}\xi_3 - \frac{C^3}{D^2}}{1 - \xi_3} + \frac{\frac{C^3}{D^2}}{(1 - \xi_3)^2} + \left(\frac{C^3}{D^2} - 1 \right) \ln(1 - \xi_3) + F + E \sum_i \sum_j D_{ij} G^j \left(\frac{\xi_3}{\tau} \right)^j \quad (\text{A3})$$

where

$$B = \sum_i x_i m_i d_i \quad \xi_1 = \frac{\pi N_A}{6} \rho B \quad (\text{A4})$$

$$C = \sum_i x_i m_i (d_i)^2 \quad \xi_2 = \frac{\pi N_A}{6} \rho C \quad (\text{A5})$$

$$D = \sum_i x_i m_i (d_i)^3 \quad \xi_3 = \frac{\pi N_A}{6} \rho D \quad (\text{A6})$$

$$E = m = \sum_i x_i m_i \quad (\text{A7})$$

$$F = \frac{3}{2} \sum_i x_i (1 - m_i) d_i \frac{\xi_2}{1 - \xi_3} \quad (\text{A8})$$

$$G = \frac{u}{\kappa T} = \frac{\sum_i \sum_j x_i x_j m_i m_j (u_{ij}/\kappa T) v_{ij}^0}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0} \quad (\text{A9})$$

Then the chemical potential can be obtained by eq A10.

$$\frac{\mu^{\text{res}}}{RT} = \left[\frac{\partial(Na^{\text{res}}/RT)}{\partial N_i} \right]_{T, V, N_j} = \frac{a^{\text{res}}}{RT} + \left[\frac{\partial(a^{\text{res}}/RT)}{\partial x_i} \right]_{T, V, x_j} - \sum_j x_j \left[\frac{\partial(a^{\text{res}}/RT)}{\partial x_j} \right]_{T, V, x_i} + Z - 1 \quad (\text{A10})$$

The derivatives of the residual Helmholtz energy with respect to B – G are as follows:

$$\left(\frac{a^{\text{res}}}{RT}\right)_B = \frac{3\frac{C}{D}\xi_3}{1 - \xi_3} \quad (\text{A11})$$

$$\left(\frac{a^{\text{res}}}{RT}\right)_C = \frac{3\frac{B}{D}\xi_3 - 3\frac{C^2}{D^2}}{1 - \xi_3} + \frac{3\frac{C^2}{D^2}}{(1 - \xi_3)^2} + 3\frac{C^2}{D^2}\ln(1 - \xi_3) \quad (\text{A12})$$

$$\begin{aligned} \left(\frac{a^{\text{res}}}{RT}\right)_D &= \frac{\frac{1}{D}\xi_3 + \frac{C^3}{D^3}(2 - \xi_3)}{1 - \xi_3} + \frac{3\frac{BC}{D^2}\xi_3^2 - \frac{C^3}{D^3}(2 + \xi_3)}{(1 - \xi_3)^2} + \\ &\quad \frac{2\frac{C^3}{D^3}\xi_3}{(1 - \xi_3)^3} - 2\frac{C^3}{D^3}\ln(1 - \xi_3) + \frac{\pi\rho}{6\tau}E\sum_i\sum_j jD_{ij}G^i\left[\frac{\xi_3}{\tau}\right]^{j-1} \end{aligned} \quad (\text{A13})$$

$$\left(\frac{a^{\text{res}}}{RT}\right)_E = \sum_i\sum_j D_{ij}G^j\left(\frac{\xi_3}{\tau}\right)^j \quad (\text{A14})$$

$$\left(\frac{a^{\text{res}}}{RT}\right)_F = 1 \quad (\text{A15})$$

$$\left(\frac{a^{\text{res}}}{RT}\right)_G = E\sum_i\sum_j iD_{ij}G^{i-1}\left(\frac{\xi_3}{\tau}\right)^j \quad (\text{A16})$$

The derivatives of B – G with respect to mole fraction x_k are obtained by

$$(B)_{x_k} = m_k d_k \quad (\text{A17})$$

$$(C)_{x_k} = m_k (d_k)^2 \quad (\text{A18})$$

$$(D)_{x_k} = m_k (d_k)^3 \quad (\text{A19})$$

$$(E)_{x_k} = m_k \quad (\text{A20})$$

$$\begin{aligned} (F)_{x_k} &= \frac{3}{2}(1 - m_k)d_k\frac{\xi_2}{1 - \xi_3} + \\ &\quad \frac{\pi}{4}\rho\sum_i x_i(1 - m_i)d_i\left(\frac{m_k d_k^2}{1 - \xi_3} + \frac{m_k d_k^3 \xi_2}{(1 - \xi_3)^2}\right) \end{aligned} \quad (\text{A21})$$

$$(G)_{x_k} = \frac{2\sum_j x_j m_k m_j \left(\frac{u_{kj}}{\kappa T}\right) v_{kj}^0 - G(2\sum_j x_j m_k m_j v_{kj}^0)}{\sum_i \sum_j x_i x_j m_i m_j v_{ij}^0} \quad (\text{A22})$$

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