Calculation of Vapor-liquid Equilibria of High Concentrated Polymer Solution by a Modified SAFT Equation of State

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Abstract

A modified SAFT (statistical associating fluid theory) equation of state is used to calculate the vapor-liquid equilibria of high concentrated polymer solutions, where the modification is focused on the reference term representing the repulsive contribution between molecules or molecular segments. The Chiew's equation of state for hard-sphere chains, based on the Percus-Yevick (PY) integral equation theory, is applied as the reference term of SAFT equation. For non-associating fluids, three parameters, chain length m, hard sphere volume υ^{00} and hard sphere interaction u^0/k, are required in the modified SAFT equation of state for the description of phase behavior of pure compounds. Parameters for normal and branched alkanes, alkenes, cyclic alkanes, aromatics, chlorinated hydrocarbons and some of polymers (PBTD, PE, PS, PIB, PDMS

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and PEO) are presented. An additional interaction parameter K_{12} is needed for the calculation of vapor-liquid equilibria of a binary mixture, which can be obtained by minimizing the average relative deviations between the experimental and calculated vapor pressure. Vapor-liquid equilibria of 29 high concentrated polymer solutions are calculated using the modified SAFT equation of state, where the weight fraction of solvent w_1 is within the interval [0.0013, 0.45]. The calculated results are compared with those calculated using the SAFT equation of state. For most of the polymer solution systems, the modified SAFT equation of state presents more accurate results than the SAFT equation of state does. Further studies on the prediction capacity show that the modified SAFT equation of state can perform vapor-liquid equilibrium predictions for some systems with good accuracy without the interaction parameters K_{12}.

Keywords

Equation of state, Vapor-liquid equilibria, Polymer solution

1 Introduction

Statistical Associating Fluid Theory (SAFT)[1,2] and Perturbed Hard-Sphere-Chain (PHSC)[3,4] equations of state, which are based on the perturbation theory and applicable over a wide range of densities and of molecular sizes, have been paid much attention in recent years. SAFT became a practical and widely used equation of state due to the framework of Chapman et al.[1] and those of Huang and Radosz[2]. SAFT equation has been successfully applied to the calculations of phase equilibria[5]. However, it encounters difficulties in some systems[6]. Since Song et al. developed a Perturbed Hard-Sphere-Chain (PHSC) equation of state[3] based on the Chiew's Hard-Sphere-Chain equation[7] with a van der Waals type perturbation term, most of the modifications

focused on the perturbation term of the PHSC type equations of state. The PHSC type equation of Hino and Prausinitz[8] is based on the analytical solution of Chang and Sandler[9] to the second-order perturbation theory of Barker and Henderson for square-well fluids of variable width. Feng and Wang[10] proposed a PHSC type equation based on the square-well coordination number model of Guo et al.[11].

In this work, a recently modified PHSC type equation by Feng et al.[12] based on the square-well fluid model of Alder et al.[13] and the Chen and Kreglewski expression[14] is applied in the calculations of vapor-liquid equilibria of high concentrated polymer solutions. The equation used in this work has similar expressions with that of SAFT equation[2], because of Chen and Kreglewski expression for attractive interaction between hard spheres and the square-well model of Alder et al. This equation could be regarded as SAFT equation with modifications on the reference term of hard-sphere-chain. The comparisons between the SAFT equation[2] and that modified by Feng et al.[12] for the calculations of vapor-liquid equilibria of high concentrated polymer solutions have been performed.

2 The equation of state

The equation of state based on the perturbation theory for non-associating fluids can be expressed as a sum of a reference term and a perturbation term, representing the contributions of the repulsion and the attraction, respectively.

$$\left(\frac{P}{\rho RT}\right)=\left(\frac{P}{\rho RT}\right)_{\mathrm{HSC}}+\left(\frac{P}{\rho RT}\right)_{\mathrm{Pert}} \tag{1}$$

where, ρ is the molar density of the fluid at temperature T and pressure P, R is the gas constant, subscripts “HSC” and “Pert” signify the hard-sphere-chain and the

perturbation term, respectively.

2.1 Hard-sphere-chain term

For modeling of the athermal freely jointed tangent hard-sphere chain fluids, Chiew[7] derived the analytical expressions of compressibility equations of state for homo-nuclear chains, hetero-nuclear chains, blends of homo- and hetero-nuclear chains, and homo-nuclear chains in a hard-sphere solvents. In the equation of Feng et al.[12], equation for homo-nuclear chain fluids by Chiew is applied as the reference term. For mixtures, the reference term can be expressed as

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

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

$$\xi_j = \frac{\pi N_{\mathrm{A}}\rho}{6}\sum_i x_i m_i d_i^j \tag{3}$$

N_{A} is the Avogadro's number, d_i is the effective temperature dependent hard-sphere diameter of component i. Chen and Kreglewski[14] presented the expression of d_i as

$$d_i = \sigma_i\left[1 - C\exp\left(-\frac{3u_i^0}{kT}\right)\right] \tag{4}$$

where, k is the Boltzmann constant, the interaction constant C is set to 0.12, (u_i^0/k) is a temperature-independent parameter representing the well depth of the square-well potential for component i, 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

$$\upsilon_i^{00} = \frac{\pi N_A}{6\tau}\sigma_i^3 \tag{5}$$

with $\tau = 0.74048$.

2.2 Perturbation term

The equation of Alder et al.[13] is applied to account for the attractive forces, as it was used in the Perturbed-Hard-Chain theory of Beret and Prausnitz[15] and the SAFT equation of Huang and Radosz[2]. The perturbation term can be expressed as

$$\left(\frac{P}{\rho RT}\right)_{\text{Pert}} = m\sum_i\sum_j jD_{ij}\left(\frac{u}{kT}\right)^i\left(\frac{\xi_3}{\tau}\right)^j \tag{6}$$

where, D_{ij} are constants given by Chen and Kreglewki[14], m is the chain length of mixture following the linear mixing rule as

$$m = \sum_i x_i m_i \tag{7}$$

Van der Waals one-fluid mixing rule is applied for the calculation of (u/kT).

$$\frac{u}{kT} = \frac{\sum_i\sum_j x_i x_j m_i m_j \left(u_{ij}/kT\right)\upsilon_{ij}^0}{\sum_i\sum_j x_i x_j m_i m_j \upsilon_{ij}^0} \tag{8}$$

with

$$\upsilon_{ij}^0 = \left[\frac{\left(\upsilon_i^0\right)^{1/3} + \left(\upsilon_j^0\right)^{1/3}}{2}\right]^3 \quad \text{and} \quad u_{ij} = \sqrt{u_i u_j}\left(1 - K_{ij}\right) \tag{9}$$

where, υ_i^0 is the temperature-dependent hard sphere volume of component i

$$\upsilon_i^0 = \frac{\pi N_A}{6\tau} d_i^3 \tag{10}$$

u_i is the temperature-dependent hard sphere energy, which is related to the temperature-independent hard sphere energy u_i^0 as[14]

$$u_i = u_i^0\left(1 + e/kT\right) \tag{11}$$

K_{ij} is the interaction parameter between components i and j. For pure components, (e/k) is set to be 1 for methane, 40 for CO_2, 10 for the others.

As a summary, the equation of state used in this work can be presented as

$$\frac{P}{\rho RT}=1+\frac{6}{\rho\pi}\left[\frac{3\xi_1\xi_2}{(1-\xi_3)^2}+\frac{3\xi_2^3}{(1-\xi_3)^3}-\frac{\xi_3\xi_2^3}{(1-\xi_3)^3}\right]+\frac{\xi_3}{1-\xi_3}-$$
$$\frac{1}{2(1-\xi_3)}\rho\sum_i x_i(m_i-1)\left(2+3d_i\frac{\xi_2}{1-\xi_3}\right)+m\sum_i\sum_j D_{ij}\left(\frac{u}{kT}\right)^i\left(\frac{\xi_3}{\tau}\right)^j \tag{12}$$

For pure components, equation (12) can be rewritten as

$$\left(\frac{P}{\rho RT}\right)=1+m\frac{4\eta-2\eta^2}{(1-\eta)^3}+(1-m)\frac{2.5\eta-\eta^2}{(1-\eta)^2}+m\sum_i^4\sum_j^9 jD_{ij}\left(\frac{u}{kT}\right)^i\left(\frac{\eta}{\tau}\right)^j \tag{13}$$

where, η is equal to ξ_3, which can be expressed as

$$\eta=\tau\rho m\upsilon^{00}\left[1-0.12\exp\left(-3u^0/kT\right)\right]^3 \tag{14}$$

3 Vapor-liquid equilibria: correlations and predictions

Both the SAFT equation[2] and that modified by Feng et al.[12] require three pure component parameters, chain length m, hard-sphere interaction (u^0/k) and temperature-independent hard sphere molar volume υ^{00} for vapor-liquid equilibrium calculations. Pure component parameters of SAFT equation[2] and that modified by Feng et al.[12] used in the vapor-liquid equilibrium calculations are presented in Table 1. The parameters of modified SAFT equation by Feng et al.[12] and those of SAFT equation of 2-Methylbutane, Methyl bromide and polymers are obtained from Feng et al.[12], the others are obtained from the work of Huang and Radosz[4].

The SAFT equation[2] and that modified by Feng et al.[12] are applied in the calculation of the vapor-liquid equilibria of high concentration polymer solutions. The binary

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

$$F = \frac{1}{N}\sum_{i}^{N}\left|\frac{P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}}}{P_i^{\mathrm{exp}}}\right| \tag{15}$$

where, N is the number of experimental data points, P_i^{exp} and P_i^{cal} are experimental and calculated vapor pressures, respectively. The chemical potential expressed by the modified SAFT equation is presented in the Appendix of Feng et al.[12]. The correlated and predicted of vapor-liquid equilibria of 29 high concentration polymer solutions are summarized in Table 2 and Table 3.

For polystyrene+nonane systems, the binary interaction parameter of the modified SAFT equation K_{12} = 0.00341 is obtained by fitting the experimental data at 403.15K. This parameter is used in the temperature extrapolation of the vapor-liquid equilibria of polystyrene+nonane systems at 423.15K and 428.15K. This method is applicable for the extrapolation of vapor-liquid equilibria of polybutadine+ethylbenzene, poly(ethylene oxide)+benzene, polystyrene+*m*-xylene, polyethylene+ethene and polystyrene+nitrogen systems as shown in Table 2. However, this temperature extrapolation is not valid for the polystyrene+CO_2 system as shown in Table 2 and Figure 1, because of the temperature-dependent K_{12} as indicated in Table 2. For the systems presented in Table 2, the calculated results by the modified SAFT equation exhibit better agreement with the experimental data than those by the SAFT equation.

Figure 1

Good agreement between the calculated and experimental data can be obtained by the modified SAFT equation with small values of binary interaction parameters, while

relative large values of binary interaction parameters are required for the SAFT equation. An obvious example is that the values of K_{12} are 0.01336 and 0.00341 for SAFT and modified SAFT equation in vapor-liquid equilibrium calculations of polystyrene+ nonane system, respectively. As experience in this study, good accuracy can be obtained for vapor-liquid equilibrium predictions by either SAFT or modified SAFT equation with only pure component parameters when $K_{12} < 0.005$. However, most of the binary interaction parameters needed in the SAFT equation are larger than this value. Smaller values of the binary interaction parameter means that the equation has the better potential of vapor-liquid equilibrium prediction, which can be indicated by the predictions of polystyrene+nonane also shown in Figure 2, polystyrene+nitrogen also shown in Figure 3, poly(dimethylsiloxane)+hexane and poly(dimethylsiloxane)+octane systems presented in Table 3.

Figure 2

Figure 3

Vapor-liquid equilibrium predictions are performed with only pure component parameters, where the binary interaction parameter K_{12} is set to 0, in order to examine the prediction potential of the SAFT equation[2] and that modified by Feng et al.[12]. It is obvious that the modified SAFT equation shows better prediction capacity than the SAFT as indicated in Table 3. The comparisons of the prediction results of polystyrene+nonane, polystyrene+nitrogen, polyethylene+ethene and polybutadine+ cyclohexane system by SAFT and modified SAFT equation are presented in Figure 2 ~ Figure 5, respectively. In particularly, for prediction of the solubility of nitrogen in polystyrene, both equations use the same pure component parameters. The pure

component parameters of nitrogen are taken from Huang and Radosz[2] and those of polystyrene are obtained by fitting the experimental data using the SAFT equation.

Figure 4

Figure 5

4 Conclusion

Both the equations discussed in this work use the same square-well fluid model of Alder et al.[13], expression of Chen and Kreglewski[14] and mixing rule. The difference lies in the SAFT and the modified SAFT equation is that the equation of Wertheim[19] (TPT1) is used in the former as the expression of perturbation term and the hard sphere chain equation (PY-CS) of Chiew[7] in the later. For pure components, a slight difference exists between the expression of equation (16) (PY-CS) and equation (17) (TPT1)

$$\left(\frac{P}{\rho RT}\right)=1+m\frac{4\eta-2\eta^2}{(1-\eta)^3}+(1-m)\frac{2.5\eta-\eta^2}{(1-\eta)^2} \tag{16}$$

$$\left(\frac{P}{\rho RT}\right)=1+m\frac{4\eta-2\eta^2}{(1-\eta)^3}+(1-m)\frac{2.5\eta-\eta^2}{(1-\eta)(1-0.5\eta)} \tag{17}$$

where, the meaning of variables are same as those in equation (13). Actually, the comparison between the SAFT and the modified SAFT equation is equal to the comparison between the PY-CS and the TPT1 equation. Chiew performed a comparison between PY-CS and TPT1[7] based on the results of molecular simulation. The conclusions are, for chain length of 8-mer and 16-mer systems in the same range of hard sphere volume fraction, the PY-CS equation agrees well with the results of Monte Carlo simulations and superior to that of TPT1. For longer chains, TPT1 equation tends to overestimate the pressures. The performance of the modified SAFT equation is slight better than that of the SAFT equation for describing the phase behaviors of the realistic

pure compound systems[12]. However, for high concentration polymer solutions, the modified SAFT equation shows advantages in the correlation and prediction of vapor-liquid equilibria, which is consistent with those of Chiew[7].

List of symbols

d: effective temperature dependent hard-sphere diameter

D: constants in perturbation term

F: objective function

k: Boltzmann constant

K: binary interaction parameter in equation (9)

m: chain length

N: number of experimental data points

N_A: Avogadro's number

P: vapor pressure

R: gas constant

T: temperature

u: temperature-dependent hard sphere energy

u^0: temperature-independent hard sphere energy

x: mole fraction

Greek letters

η: quantity defined by equation (14)

ρ: molar density of the fluid

σ: temperature-independent hard sphere diameter

τ: quantity equals to 0.74048

υ^0: temperature-dependent hard sphere volume

υ^{00}: temperature-independent hard sphere molar volume

ξ_j (j = 1, 2, 3): quantities defined by equation (3)

Subscripts

i, j: counter for constants in equation (6) and for components

HSC: hard-sphere-chain

Pert: perturbation

Superscripts

cal: calculated

exp: experimental

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Table 1. Pure component parameters used in the vapor-liquid equilibrium calculations

Compound	M_W	SAFT/This work			
		T range, K	m	υ^{00}, cm^3/mol	u^0/k, K
Carbon dioxide	44.010	218–288/218–293	1.417/1.422	13.578/13.783	216.08/212.46
Notrogen	28.013	–/–	1.000/1.000	13.457/13.457	123.53/123.53
Pentane	72.150	233–450/291–454	4.091/4.187	12.533/12.742	200.02/189.51
Hexane	86.178	243–493/252–494	4.724/4.586	12.475/13.758	202.72/197.57
Octane	114.230	303–543/296–552	6.045/6.026	12.234/13.019	206.03/196.70
Nonane	128.257	303–503/344–424	6.883/6.547	12.240/13.587	203.56/199.25
2-Methylbutane	72.150	266–447	3.872/3.851	13.154/13.934	200.69/193.21
Cyclohexane	84.161	283–513/279–541	3.970/3.842	13.502/14.177	236.41/232.29
Ethene	28.050	133–263/132–281	1.464/1.884	18.157/14.024	212.06/174.42
Benzene	78.113	300–540/284–550	3.749/3.759	11.421/12.079	250.19/239.64
Ethylbenzene	106.167	293–573/277–467	4.719/4.731	12.681/13.561	248.79/237.34

Table 1. Continued

Compound	M_W	SAFT／This work			
		T range, K	m	υ^{00}, cm^3/mol	u^0/k, K
m-Xylene	106.167	309–573／276–582	4.886／4.850	12.184／12.984	245.88／235.88
Methyl bromide	94.939	205–275	2.000／2.215	14.626／13.261	298.28／271.47
PBTD	2.50×10^5	277–328	12970／12970	12.0／12.0	244.40／244.40
PDMS	$0.89-1.66\times10^5$	298–340	$0.0448M_W$／$0.0474M_W$	12.0／12.0	204.63／204.63
PE	$1.90-2.487\times10^5$	413–473	$0.0509M_W$／$0.0537M_W$	12.0／12.0	216.15／210.28
PEO	1.00×10^5	361–497	$0.0388M_W$／$0.0471M_W$	12.0／12.0	220.00／220.00
PIB	$0.52-10.0\times10^5$	325–383	$0.0477M_W$／$0.0507M_W$	12.0／12.0	206.24／206.24
PS	$2.47-2.79\times10^5$	388–469	$0.0402M_W$／$0.0430M_W$	12.0／12.0	210.00／210.00

Abbreviations: PBTD: polybutadiene; PDMS: poly(dimethylsiloxane); PE: polyethylene; PEO: poly(ethylene oxide); PIB: polyisobutylene; PS: polystyrene.

Table 2. Comparison of vapor-liquid equilibrium calculations by SAFT and modified SAFT equation

				SAFT		This work		
Polymer	Solvent	T, K	w_1 range	K_{12}	ADD	K_{12}	ADD	Data
PS	Nonane	403.15	0.026–0.12	0.01336	4.16	0.00341	0.70	16
		423.15	0.024–0.07		2.64		4.77	16
		448.15	0.015–0.03		9.04		2.97	16
	m-Xylene	403.15	0.044–0.17	0.04479	4.80	0.03450	2.94	16
		423.15	0.035–0.13		4.05		2.81	16
	CO_2	373.20	0.023–0.12	0.1170	32.45	0.1091	9.88	17
		413.20	0.035–0.10	0.1429	9.92	0.1172	7.17	17
		453.20	0.009–0.07	0.1661	9.27	0.1329	4.76	17
	Nitrogen	373.20	0.038–0.07	0.08818	17.75	0.0006	1.99	17
		413.20	0.033–0.09		7.89		4.40	17
		453.20	0.039–0.10		10.08		5.83	17

Table 2. Continued

Polymer	Solvent	T, K	w_1 range	SAFT		This work		Data
				K_{12}	ADD	K_{12}	ADD	
PE	Ethene	399.15	0.0018–0.05	0.06088	13.49	–0.01938	4.18	16
		413.15	0.0015–0.04		17.01		7.33	16
		428.15	0.0013–0.04		24.19		14.17	16
	Hexane	273.15	0.013–0.07	0.01356	13.47	0.00885	5.70	16
	Methyl bromide	273.15	0.011–0.12	0.13460	8.46	0.11470	6.29	16
PEO	Benzene	343.15	0.060–0.45	0.03799	28.34	0.02505	16.12	16
		375.15	0.021–0.12		5.53		2.60	16
PDMS	Pentane	303.04	0.005–0.09	–0.02460	6.24	–0.04188	5.03	16
	Hexane	303.00	0.009–0.095	0.00546	1.35	–0.00550	5.36	16
	Octane	313.15	0.028–0.454	0.01035	4.78	–0.00134	5.16	16
PBTD	Ethylbenzene	353.15	0.044–0.35	0.01136	15.79	0.00852	14.05	16

Table 2. Continued

Polymer	Solvent	T, K	w_1 range	SAFT		This work		Data
				K_{12}	ADD	K_{12}	ADD	
		373.15	0.039–0.39		4.99		2.98	16
		403.15	0.023–0.17		2.13		7.73	16
	Nonane	373.15	0.023–0.25	–0.04533	11.99	–0.03752	5.77	16
	Cyclohexane	333.15	0.082–0.34	–0.00631	2.05	–0.00023	0.98	16
PIB	Cyclohexane	298.15	0.128–0.57	0.03870	22.99	0.03139	13.13	16
	2-methylbutane	298.15	0.015–0.044	0.00809	3.90	–0.00814	4.81	16
	Hexane	298.15	0.074–0.34	0.00282	2.62	–0.00591	4.23	18

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}}}{P_i^{\mathrm{exp}}}\right| \times 100$$

Abbreviations: PBTD: polybutadiene; PDMS: poly(dimethylsiloxane); PE: polyethylene; PEO: poly(ethylene oxide); PIB: polyisobutylene; PS: polystyrene.

Table 3. Vapor-liquid equilibrium predictions with K_{12} = 0

Polymer	Solvent	T, K	AAD	
			SAFT	This work
PS	Nonane	403.15	43.11	13.95
		423.15	40.65	9.93
		448.15	45.06	11.25
	Nitrogen	373.20	49.17	1.90
		413.20	48.88	4.243
		453.20	46.94	5.557
PE	Ethene	399.15	58.81	33.71
		413.15	60.72	25.32
		428.15	63.03	14.37
PDMS	Hexane	303.00	20.67	27.69
	Octane	313.15	30.36	7.708
PBTD	Ethylbenzene	353.15	44.42	38.44
		373.15	30.10	23.80
		403.15	30.76	22.24
	Cyclohexane	333.15	21.35	1.187
PIB	Hexane	298.15	8.754	20.06

$$\mathrm{AAD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}}}{P_i^{\mathrm{exp}}}\right| \times 100$$

Abbreviations: PBTD: polybutadiene; PDMS: poly(dimethylsiloxane); PE: polyethylene; PIB: polyisobutylene; PS: polystyrene.

Figure 1. Solubility of carbon dioxide in polystyrene

Figure 2. Vapor-liquid equilibria of polystyrene+nonane

Figure 3. Solubility of nitrogen in polystyrene

Figure 4. Solubility of ethene in polyethylene

Figure 5. Vapor-liquid equilibria of polybutadiene+cyclohexane

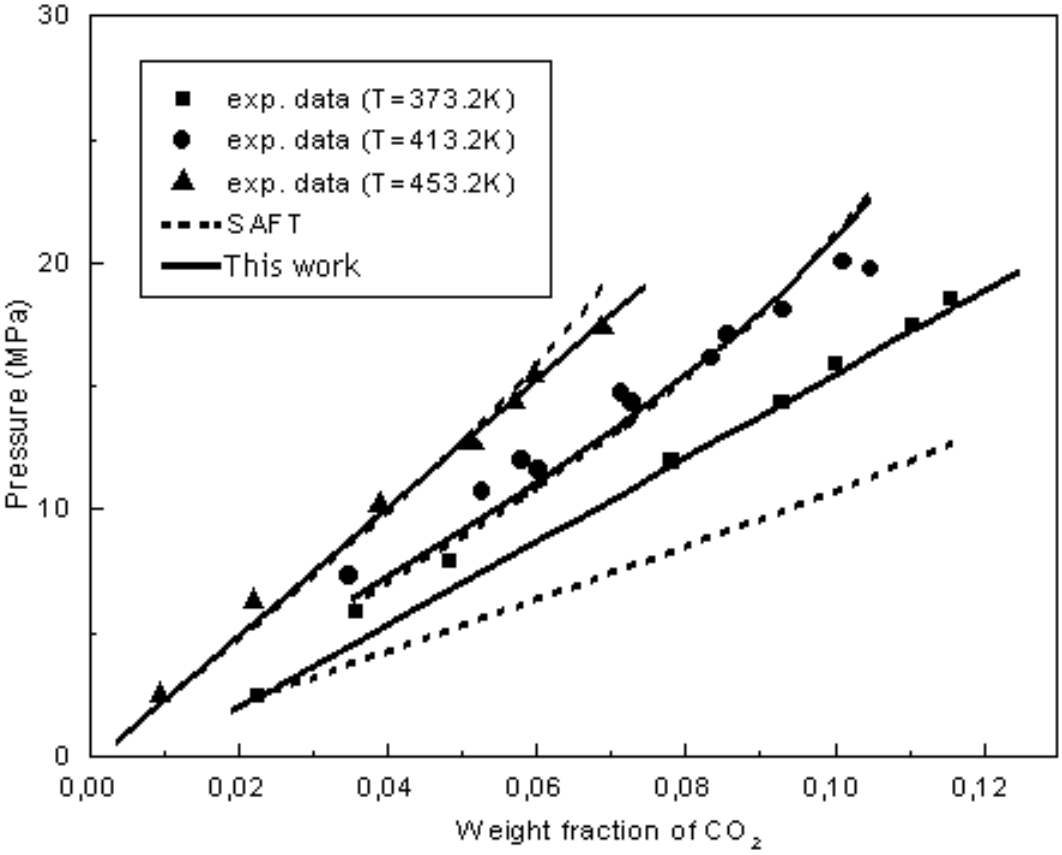
30
20
10
0
Pressure (MPa)
0,00
0,02
0,04
0,06
0,08
0,10
0,12
Weight fraction of CO2
exp. data (T=373.2K)
exp. data (T=413.2K)
exp. data (T=453.2K)
SAFT
This work

Figure 1

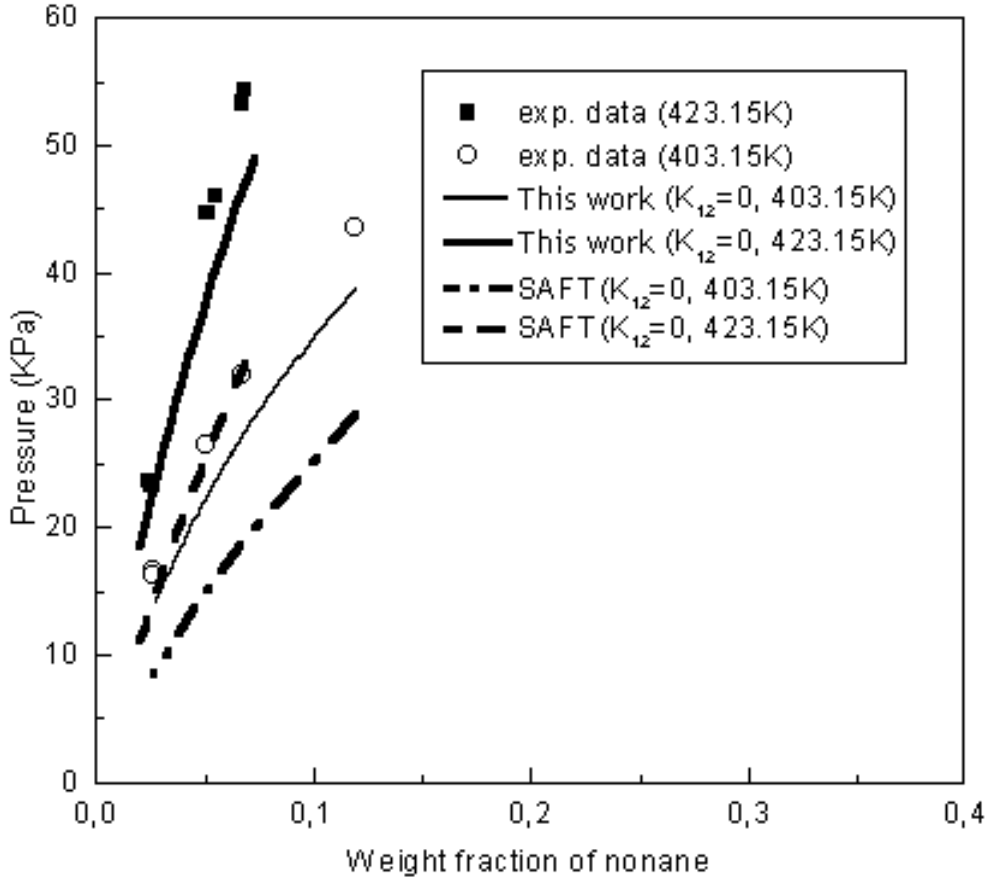
60
50
40
30
20
10
0
Pressure (KPa)
0,0
0,1
0,2
0,3
0,4
Weight fraction of nonane
exp. data (423.15K)
exp. data (403.15K)
This work (K12=0, 403.15K)
This work (K12=0, 423.15K)
SAFT (K12=0, 403.15K)
SAFT (K12=0, 423.15K)

Figure 2

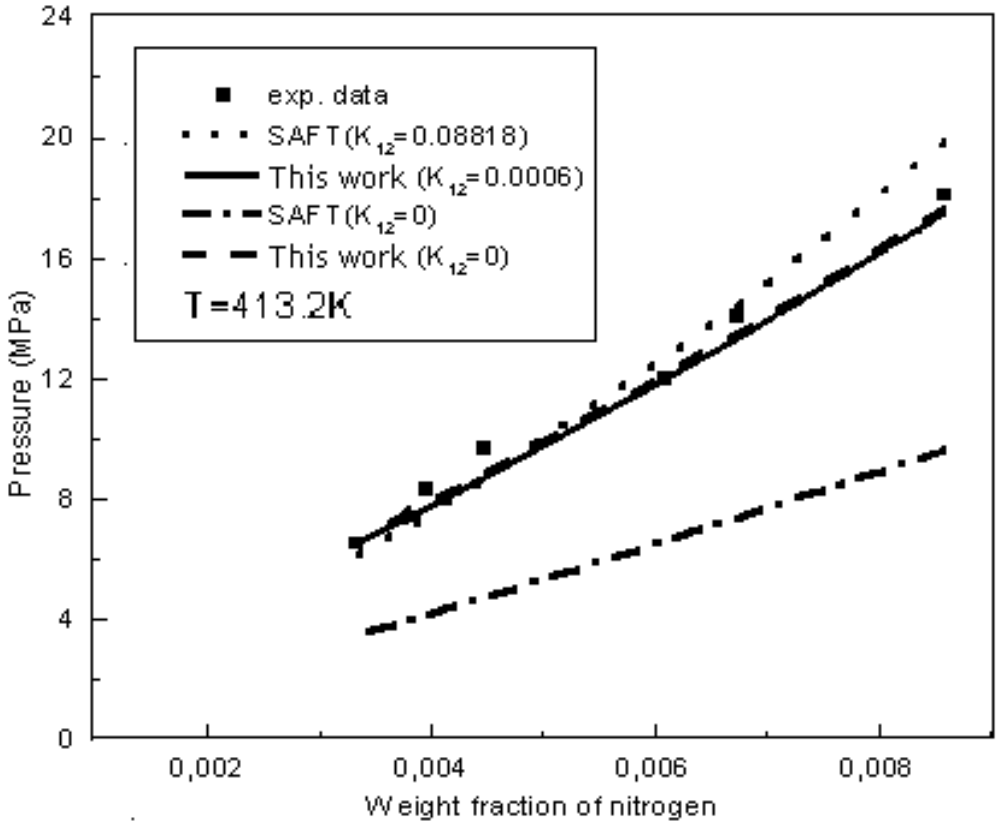
exp. data
SAFT(K12=0.08818)
This work (K12=0.0006)
SAFT(K12=0)
This work (K12=0)
T=413.2K
Pressure (MPa)
Weight fraction of nitrogen
0
4
8
12
16
20
24
0,002
0,004
0,006
0,008

Figure 3

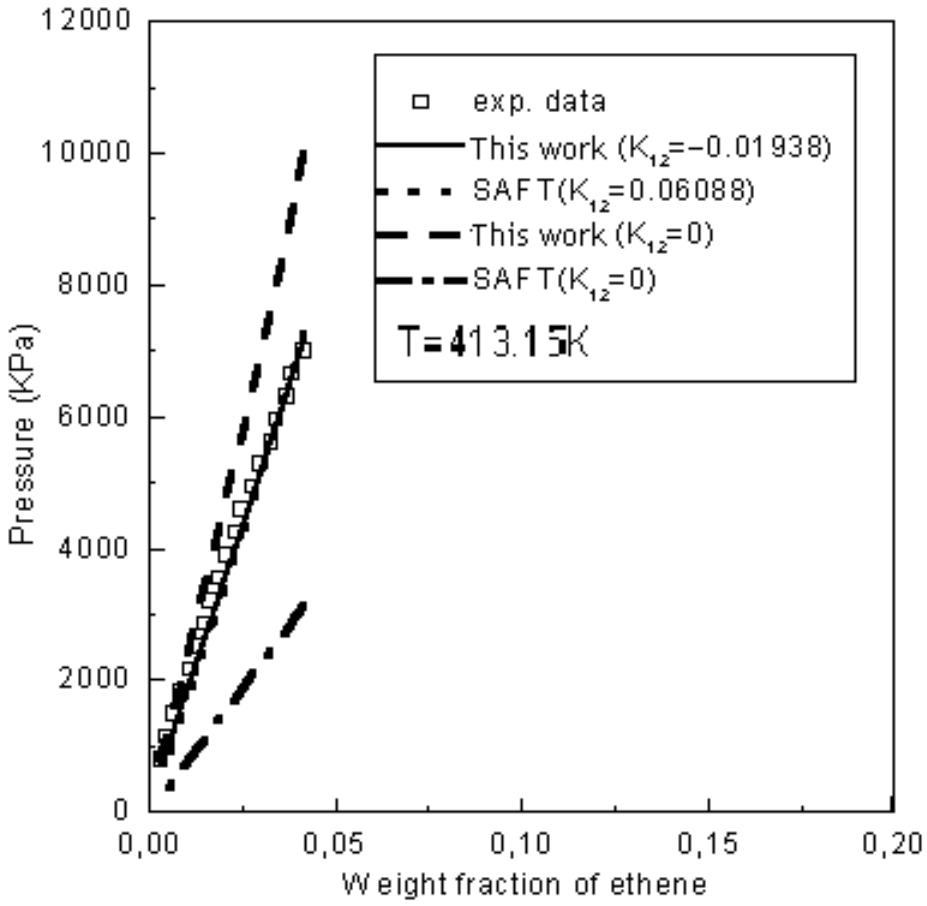
12000
10000
8000
6000
4000
2000
0
Pressure (KPa)
0,00
0,05
0,10
0,15
0,20
Weight fraction of ethene
exp. data
This work (K12=-0.01938)
SAFT(K12=0.06088)
This work (K12=0)
SAFT(K12=0)
T=413.15K

Figure 4

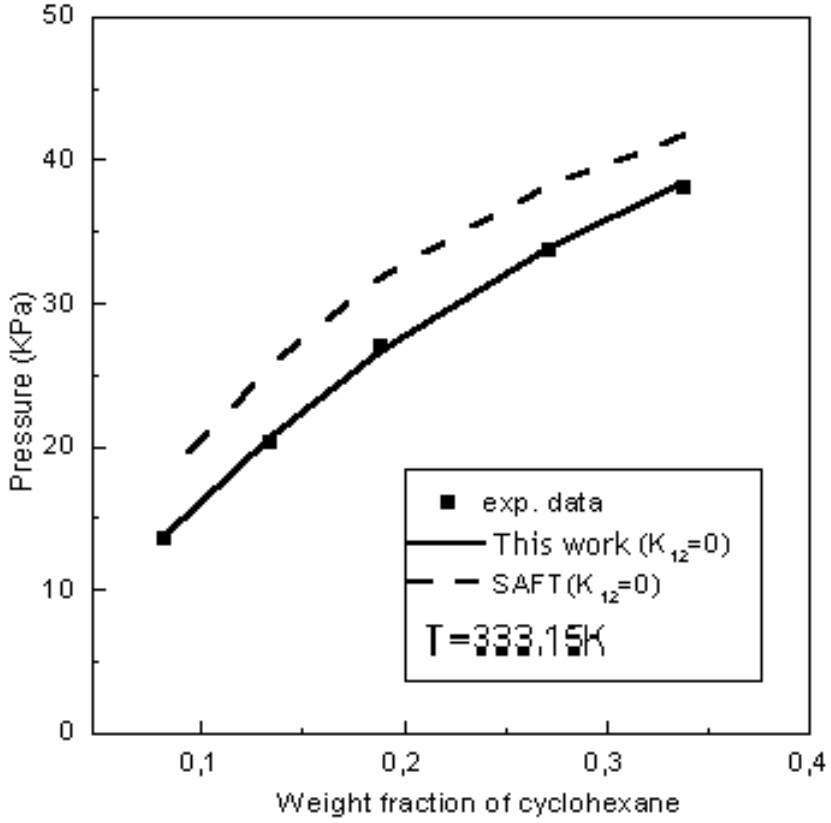
50
40
30
20
10
0
Pressure (KPa)
0,1
0,2
0,3
0,4
Weight fraction of cyclohexane
exp. data
This work (K12=0)
SAFT(K12=0)
T=333.15K

Figure 5