

## Comparison Between Two Versions of the SAFT EOS in the Study of PVT and VLE Phase Behavior of Pure Polymer Melts and Binary Polymer Solutions

V. Asadi Malekshah<sup>1</sup>, V. Taghikhani<sup>1,\*</sup>, A. Ramazani S.A<sup>1</sup> and M. Zarinejad<sup>2</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran.

<sup>2</sup>Department of Science and Technology, the British Council, Tehran, Iran.

### Abstract

In this work, the recently proposed SAFT-based Equation of State (EOS), the GV-SSAFT EOS, was used to study the phase behavior of associating and non-associating pure polymer melts as well as polymer-solvent mixtures at various conditions. The regressed values of the parameters for the GV-SSAFT equation of state for a wide spectrum of pure homopolymer melts were obtained using the corresponding Pressure-Volume-Temperature (PVT) experimental data available in the literature. In case of the non-associating polymers the GV-SSAFT EOS has three adjustable parameters while the number of parameters is increased to five for associating polymers. The parameters were meticulously tuned for segment number, segment molar volume, and segment-segment interaction energy, and their values for the systems studied in this work were also reported. The results obtained from the GV-SSAFT EOS were unequivocally compared with those of the Simplified version of the SAFT (SSAFT) EOS for both associating and non-associating pure polymer melts as well as polymer-solvent mixtures. The results showed that the GV-SSAFT EOS can accurately correlate the experimental data for liquid density of pure polymer melts at wide temperature ranges. In case of polymer-solvent mixtures, inferior results obtained by employing the GV-SSAFT EOS to the VLE experimental data. The results also showed that while considering the specific site-site interactions for the associating polymers makes the SAFT-based equations of state more complicated, the final results cannot be much affected by such complexity. Therefore, this kind of molecular interaction could be neglected to a good approximation. It would be worth noting that in order to do a fair comparison between the results obtained from the GV-SSAFT EOS with those of the SSAFT EOS, the same sets of experimental data and the same optimization procedure were used for both equations of state to render their regressed parameters.

**Keywords:** SAFT, equation of state, polymer solution, GV-SSAFT

### Introduction

Knowledge of phase behavior in polymer solutions is crucial to the polymer industry. Equations of state play an important role in

predicting the phase behavior of polymer solutions and hence in design and optimization of polymer processes. Numerous attempts have been made to develop and

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\* - Corresponding author: E-mail: taghikhani@sharif.edu

improve equations of state for chain molecules. As a matter of fact, equations of state for polymer solutions are either based on the lattice theory or the perturbation theory. Among the lattice-based models, the Flory–Orwoll–Vrij (FOV) EOS [1] and the Sanchez-Lacombe (SL) model [2] can be mentioned. Various models such as Perturbed Hard Chain Theory (PHCT) [3, 4], Perturbed Soft Chain Theory (PSCT) [5], Perturbed Anisotropic Chain Theory (PACT) [6, 7], and Statistical Associating Fluid Theory (SAFT) [8-10] have been developed based on the perturbation theory. SAFT was developed by Chapman et al. [8-10] based on the Wertheim first-order perturbation theory [11–16] for associating and non-associating fluids. SAFT EOS is a successful equation of state, and its different versions have been employed by many researchers to study the phase behavior of polymer solutions. Numerous applications of the SAFT equation of state to the polymer solutions have been made since the early work of Chen and Radosz [17-20]. Many attempts have been made to develop the SAFT-based equation of state in order to well describe the phase behavior of complex mixtures. Among them, the PC-SAFT [21], SAFT-VR [22], Soft-SAFT [23], Crossover SAFT [24–27], SAFT-BACK [28], SAFT-WCA [29], SAFT-MOZ [30] and the Crossover SAFT-BACK [31] can be named. The main differences between different versions of the SAFT model stem from the fact that how the segment and the chain contributions to the residual Helmholtz free energy can be estimated. It should be stated that the number of segments per molecule,  $m$ , the segment molar volume,  $v^\infty$ , and temperature independent depth of square well potential which characterizes the segment–segment interactions,  $u^0$ , are three essential adjustable parameters of the SAFT-based equations of state for pure non-associating fluids [8–10]. For associating compounds there are two additional parameters, the association energy,  $\epsilon^{AB}$ , and the association

volume,  $k^{AB}$ , characterizing specific interaction between association sites on each molecule [8–10].

In this work, two SAFT-based equations of state, the GV-SSAFT [32] and the SSAFT [33] were used to study the phase behavior of associating and non-associating polymer melts. The SAFT-based equations of state studied here were also extended to the polymer-solvent mixtures over a wide range of temperature. While the GV-SSAFT equation of state gives nearly the same results as those obtained from the SSAFT equation of state in correlating the liquid density of polymer melts, inferior results were obtained for the mixture of polymer and solvent with the GV-SSAFT equation of state.

### Theory

The SAFT-based equations of state consider at least four major contributions into the residual Helmholtz free energy of a system as follows [34-35]:

$$a^{\text{res}} = a^{\text{hs}} + a^{\text{disp}} + a^{\text{chain}} + a^{\text{assoc}} \quad (1)$$

The terms introduced in equation (1) for the simplified version of the SAFT (SSAFT) [33] are briefly expressed according to the following equations:

$$\frac{a^{\text{hs}}}{RT} = m \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (2)$$

where  $\eta$  is the reduced density and can be written as:

$$\eta = \frac{\pi N_{\text{AV}} \rho m d^3}{6} \quad (3)$$

In equation (3),  $\rho$ ,  $d$ , and  $N_{\text{AV}}$  are molar

density, temperature-dependent diameter for the segments and the Avogadro number respectively. The temperature-dependent diameter of segments,  $d$ , can be expressed according to the following relation [33]:

$$d = \left[ \frac{\sqrt{2}v^\infty}{N_{AV}} \right]^{1/3} [1 - C \exp\left[-\frac{3u^0}{kT}\right]] \quad (4)$$

The dispersion contribution takes the following form as:

$$\frac{a^{\text{disp}}}{RT} = mZ_M \text{Ln}\left(\frac{v_s}{v_s + v^* Y}\right) \quad (5)$$

with

$$Y = \exp\left(\frac{u}{2kT}\right) - 1 \quad (6)$$

where  $u$  is the depth of square well potential and can be considered to be temperature dependent as follows [33]:

$$u = u^0 \left[1 + \frac{e}{kT}\right] \quad (7)$$

In equation (7)  $e/k$  is set to be  $-10$  [33]. The chain and association contributions into the residual Helmholtz energy can be respectively expressed as:

$$\frac{a^{\text{chain}}}{RT} = (1 - m) \text{Ln}(g^{\text{hs}}(d)) \quad (8)$$

where  $g^{\text{hs}}(d)$  is the radial distribution

function (RDF) and is defined as follows:

$$g^{\text{hs}}(d) = \frac{z^{\text{hs}}}{4m\eta} \quad (9)$$

The association term in equation (1) can be written according to the following equation:

$$\frac{a^{\text{assoc}}}{RT} = \sum_A [(\text{Ln}X^A - \frac{X^A}{2})] + \frac{M}{2} \quad (10)$$

The SSAFT equation of state can be extended to the mixture of hard spheres according to the following relations for hard sphere and dispersion contributions of the residual Helmholtz free energy [33]:

$$\begin{aligned} \frac{a^{\text{hs}}}{RT} = & \frac{6}{\pi N_{AV} \rho} \left[ \frac{(\eta_2)^3 + 3\eta_1\eta_2\eta_3 - 3\eta_1\eta_2(\eta_3)^2}{\eta_3(1 - \eta_3)^2} \right. \\ & \left. - \left[ \eta_0 - \frac{(\eta_2)^3}{(\eta_3)^2} \right] \text{Ln}(1 - \eta_3) \right] \quad (11) \end{aligned}$$

Where

$$\eta_k = \frac{\pi N_{AV} \rho}{6} \sum_i x_i m_i (d_{ii})^k \quad k = 0, 1, 2, 3 \quad (12)$$

with

$$d_{ij} = \frac{(d_i + d_j)}{2} \quad (13)$$

$$\frac{a^{\text{disp}}}{RT} = mZ_m \text{Ln}\left(\frac{v_s}{v_s + (v^* Y)}\right) \quad (14)$$

where

$$m = \sum_i x_i m_i \quad (15)$$

$$(v^*Y) = \frac{N_{AV} \sum_i \sum_j x_i x_j m_i m_j (d_{ij}^3 / \sqrt{2}) [\exp(u_{ij} / (2kT)) - 1]}{\sum_i \sum_j x_i x_j m_i m_j} \quad (16)$$

$$u_{ij} = (1 - k_{ij}) \sqrt{u_i u_j} \quad (17)$$

$k_{ij}$  in equation (17) is the binary interaction parameter for energy parameter of square-well potential. In the same way, the binary parameter,  $l_{ij}$ , can be introduced into the segment number as follows:

$$m = \sum_i \sum_j x_i x_j m_{ij} \quad (18)$$

with

$$m_{ij} = \frac{(m_i + m_j)(1 - l_{ij})}{2} \quad (19)$$

It should be stated that  $k_{ij}$  and  $l_{ij}$  are two adjustable parameters and can be obtained by fitting the SAFT-based equations of state to the Vapor-Liquid Equilibrium (VLE) data for the polymer solutions. Also, the chain and association parts of the residual Helmholtz free energy for the mixture of hard spheres can be written as:

$$\frac{a^{\text{chain}}}{RT} = \sum_i x_i (1 - m_i) \ln(g_{ii}^{\text{hs}}(d_{ii})) \quad (20)$$

where  $g_{ii}^{\text{hs}}(d_{ii})$  is the RDF at contact value between two like segments and is given based on the following expression:

$$g_{ij}^{\text{hs}}(d_{ij}) = \frac{1}{1 - \eta_3} + \frac{3d_{ii}d_{jj}}{d_{ii} + d_{jj}} \frac{\eta_2}{(1 - \eta_3)^2} + 2 \left[ \frac{d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right]^2 \frac{\eta_2^2}{(1 - \eta_3)^3} \quad (21)$$

The association term proposed by Chapman et al. [3] is presented as follows:

$$\frac{a^{\text{assoc}}}{RT} = \sum_i x_i \left[ \sum_{A_i} \left[ \ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{M_i}{2} \right] \quad (22)$$

where  $X^{A_i}$  is a mole fraction of each association site on molecule  $i$  which is not bonded and rendered as follows:

$$X^{A_i} = [1 + N_{AV} \rho \sum_j \sum_{B_j} x_j X^{B_j} \Delta^{A_i B_j}]^{-1} \quad (23)$$

In equation (23),  $\Delta^{A_i B_j}$  is the association strength between two sites of A and B and is given as:

$$\Delta^{A_i B_j} = g_{ij}^{\text{hs}}(d_{ij}) [\exp(\epsilon^{A_i B_j} / kT) - 1] (d_{ij})^3 k^{A_i B_j} \quad (24)$$

It should be emphasized that the number of association sites should be specified for associating polymers. In fact, two associating sites are assigned on each PEG molecule when it is considered as a self-associating polymer. PEG molecule can form self-association not only through hydroxy group but also through oxygen atoms in the

polymer backbone. However, it is assumed that only the hydroxy end-group is considered as an associating factor on a PEG molecule [36]. Recently, another version of the SAFT-based equation of state, the GV-SSAFT, has been proposed by Asadi et al. [32]. In the GV-SSAFT equation of state, the hard sphere compressibility factor can be expressed according to the following relation [32]:

$$z^{\text{hs}} = m(2.9619\xi + 5.4831\xi^2 + 2.4564\xi^3 + 8.4856\xi^4 + \frac{8.9\xi^5}{1-\xi} - \frac{2.8\xi^8}{1-\xi}) \quad (25)$$

with

$$\xi = \frac{\eta}{\tau} \quad (26)$$

and

$$\tau = \frac{\pi\sqrt{2}}{6} \quad (27)$$

where  $\xi$  and  $\tau$  are the normalized and close-packed reduced densities respectively.

The hard sphere Helmholtz free energy corresponding to  $z^{\text{hs}}$  can be obtained using the following relation:

$$\frac{a^{\text{hs}}}{RT} = \int_0^{\rho} \frac{z^{\text{hs}}(\rho)}{\rho} d\rho = \int_0^{\eta} \frac{z^{\text{hs}}(\eta)}{\eta} d\eta \quad (28)$$

Therefore, using the GV-SSAFT equation of state, the hard sphere Helmholtz free energy for mixtures can be written as follows [32]:

$$a^{\text{hs}}_{\text{mix}} = m\left[\frac{1}{4}K_1(1+3Y_1) + \frac{3}{8}K_2(2Y_2 - Y_1 - 1)\right] \quad (29)$$

where  $Y_1$  and  $Y_2$  are dimensionless volume independent groups given by the following relations:

$$Y_1 = \frac{\xi_1\xi_2}{\xi_0\xi_3} \quad (30)$$

$$Y_2 = \frac{(\xi_2)^3}{\xi_0(\xi_3)^2} \quad (31)$$

In the above equations,  $\xi_i$  is the normalized form of  $\eta_i$  and presented as:

$$\xi_i = \frac{\eta_i}{\tau} \quad (32)$$

and  $K_1$  and  $K_2$  are given by the following relations:

$$K_1 = -3.14\xi_3 - .31\xi_3^2 + .45\xi_3^3 + .60\xi_3^4 + .56\xi_3^5 + .47\xi_3^6 + .40\xi_3^7 - 6.1\ln(1-\xi_3) \quad (33)$$

$$K_2 = -4.52\xi_3 - 1.16\xi_3^2 - .15\xi_3^3 + .25\xi_3^4 + .35\xi_3^5 + .35\xi_3^6 + .30\xi_3^7 + .26\xi_3^8 - 4.52\ln(1-\xi_3) \quad (34)$$

As explained before, both SSAFT and the GV-SSAFT have three adjustable parameters, i.e.  $m$ ,  $v^\infty$ , and  $u^0$ , for non-associating fluids

and two additional parameters,  $k^{AB}$ , and  $\epsilon^{AB}$  for associating fluids. These parameters can be obtained by fitting the SAFT-based equations of state to the PVT experimental data of pure polymer melts studied in this work. In order to find the regressed values for the parameters of the SAFT-based equations of state, the following objective function was used [37]:

$$\text{O.F.} = (\text{P}^{\text{cal.}} - \text{P}^{\text{exp.}})^2 \quad (35)$$

where superscripts cal and exp respectively stand for the calculated and experimental vapor pressure for the polymer systems studied in this work. It is worth mentioning that the same experimental data and the same minimization procedure were used for both equations of state studied in this work

It should be pointed out that in a polymer solution since the molecular weight of the polymer is often not known accurately it is difficult to determine the polymer mole fraction. Thus, an appropriate concentration unit such as volume fraction, weight fraction or segment fraction is commonly reported as experimental equilibrium data for polymer solutions [38]. In this study in order to obtain the values for the parameters of the SAFT-based equations of state the mole fraction concentration scale for both polymer and solvent were used. To convert the polymer weight fraction scale to that of the mole fraction scale, the following relation can be used:

$$x_1 = \frac{M_2 w_1}{(M_1 + M_2 w_1 - M_1 w_1)} \quad (36)$$

where  $x$  and  $w$  are mole and weight fractions, respectively.  $M$  is the number average of the molecular weight of polymer in a polymer-

solvent system and subscripts 1 and 2 respectively stand for solvent and polymer molecules in a polymer – solvent mixture.

In order to convert the polymer segment fraction to that of the mole fraction, the following relation can be used:

$$x_1 = \frac{m_2 v_2^\infty w_1}{(m_1 v_1^\infty + m_2 v_2^\infty w_1 - m_1 v_1^\infty w_1)} \quad (37)$$

where  $m$  is the segment number and  $v^\infty$  is the close-packed molar volume of each component in a polymer-solvent mixture. Going through equation (37), it can be found out that in order to convert the polymer segment fraction to that of the mole fraction, the van der Waals volumes of hard spheres for both solvent and polymer molecules are required. This parameter can be obtained using the data reported by Bondi [39] or using the parameters obtained from the SAFT-based equations of state. The van der Waals volume for each component in solution is to be considered as  $mv^\infty$ . Therefore, without considering any additional parameter, the segment fraction is straightforwardly converted to a weight fraction using the parameters obtained from each equation of state.

### Results and discussion

Tables 1 and 2 present the values of the parameters for the SSAFT and GV-SSAFT equations of state for a number of pure polymer melts using the least square fit of the equations of state to the experimental data of the liquid densities available in the literature. It should be stated that to obtain the best values for the parameters of the SSAFT as well as the GV-SSAFT equations of state, equation (35) was globally minimized. It should also be noted that in order to do an unequivocal and fair comparison between the results obtained from two SAFT-based

equations of state, the same experimental data and minimization procedure were used. As can be seen from Tables 1 and 2, for non-associating polymer melts the values for three adjustable parameters were exclusively reported, while in case of associating pure

polymer melts, i.e. PEG, the number of adjustable parameters reported was increased to five. As mentioned before, association energy and association volume are two additional parameters for these systems.

**Table 1.** The regressed values of the segment parameters of the SSAFT equation of state obtained for a number of pure polymer melts.

polymer	m	$v^\infty$	$u^0/k$	$k^{AB}$	$\epsilon^{AB}/k$	$M_n$
HDPE	12608.40 0	3.365	97.457	-	-	52000
HMDS	32.066	4.130	70.079	-	-	162
LDPE	3823.590	5.510	105.279	-	-	25000
PDMS	107.727	3.898	71.587	-	-	594
PDMS	178.825	3.734	72.538	-	-	958
PDMS	290.378	3.618	72.903	-	-	1540
PDMS	804.709	3.476	72.661	-	-	4170
PDMS	935.462	3.694	84.594	-	-	5000
PDMS	1238.560	3.549	73.557	-	-	6560
PDMS	1437.970	3.667	73.692	-	-	7860
PDMS	7888.130	4.045	75.009	-	-	47200
PS	16820.10 0	3.601	112.249	-	-	90700
PT	7935.370	3.562	94.031	-	-	40000
PVAC	20006.10 0	2.373	83.255	-	-	84000
PIB	56074.10 0	3.209	108.445	-	-	233333.33 3
PPG	913.255	2.987	88.428	-	-	4000
PMMA	17991.00 0	3.314	117.030	-	-	100000
PVC	18720.10 0	2.652	103.167	-	-	100000
NR	25803.90 0	2.955	98.337	-	-	100000
Nylon6	24968.70 0	2.650	114.275	-	-	100000
PAR	19525.30 0	2.948	118.685	-	-	100000
PEG	1615.480	2.889	93.832	-	-	7500
PEG <sup>a</sup>	1615.080	2.889	93.881	2020.500	0.302	7500

a - Association interaction is considered in this case.

**Table 2.** The regressed values for the segment parameters of the GV-SSAFT equation of state obtained for a number of pure polymer melts.

polymer	m	$v^\infty$	$u^0/k$	$k^{AB}$	$\varepsilon^{AB}/k$	$M_n$
HDPE	12745.100	3.314	96.988	-	-	52000
HMDS	32.415	4.067	69.730	-	-	162
LDPE	3823.590	5.510	105.279	-	-	25000
PDMS	108.816	3.842	71.267	-	-	594
PDMS	180.588	3.681	72.226	-	-	958
PDMS	293.221	3.567	72.594	-	-	1540
PDMS	812.649	3.427	72.349	-	-	4170
PDMS	943.484	3.647	84.259	-	-	5000
PDMS	1250.430	3.500	73.256	-	-	6560
PDMS	1451.610	3.617	73.394	-	-	7860
PDMS	7957.510	3.995	74.708	-	-	47200
PS	16931.500	3.563	112.002	-	-	90700
PT	8002.330	3.517	93.691	-	-	40000
PVAC	20213.300	2.338	82.881	-	-	84000
PIB	56410.500	3.179	108.179	-	-	233333.3 3
PPG	921.008	2.950	88.059	-	-	4000
PMMA	17995.100	3.303	117.087	-	-	100000
PVC	18817.600	2.629	103.025	-	-	100000
NR	26003.700	2.921	97.968	-	-	100000
Nylon6	25233.200	2.611	113.658	-	-	100000
PAR	19753.700	19753.700	117.966	-	-	100000
PEG	1553.770	2.992	93.166	-	-	7500
PEG <sup>a</sup>	1513.110	3.074	92.971	2723.600	0.106	7500

a - Association interaction is considered in this case.



Table 3 gives the results of the SAFT-based equations of state, i.e., the GV-SSAFT and the SSAFT EOS along with the percent of Absolute Average Relative Deviation (AARD%) from the experimental data of liquid density over a wide range of

temperature for various pure polymer melts. As shown in Table 3, both the GV-SSAFT and the SSAFT equations of state can accurately correlate the experimental data for liquid density of pure polymer melts.

**Table 3.** The results for polymer density along with the percent of AARD from experimental data obtained using the SSAFT and the GV-SSAFT.

polymer	SSAFT (AARD) <sup>a</sup> %	GV-SSAFT (AARD) <sup>a</sup> %	T range	NO. of Data	data source
	$\rho_{liq}$	$\rho_{liq}$			
HDPE	0.406	0.407	415.25-472.85	67	40
HMDS	0.539	0.540	298.15-343.15	40	40
LDPE	0.167	0.168	398.25-471.15	42	40
PDMS	0.318	0.319	298.15-343.15	40	40
PDMS	0.262	0.262	298.15-343.15	40	40
PDMS	0.286	0.286	298.15-343.15	40	40
PDMS	0.231	0.231	298.15-343.15	40	40
PDMS	0.637	0.631	302.55-497.25	126	40
PDMS	0.229	0.229	298.15-343.15	40	40
PDMS	0.205	0.205	298.15-343.15	40	40
PDMS	0.160	0.160	298.15-343.05	64	40
PS	0.269	0.269	388.55-468.75	69	40
PT	0.150	0.148	337.17-443.98	47	40
PVAC	0.073	0.072	337.15-393.15	63	40
PIB	0.519	0.510	303.55-578.78	264	41
PPG	0.340	0.335	303.25-471.75	108	41
PMMA	0.325	0.333	413.65-503.55	176	41
PVC	0.085	0.085	355.15-370.15	18	40
NR	0.506	0.497	302.75-555.55	132	41
Nylon6	0.174	0.175	491.55-589.95	105	41
PAR	0.210	0.210	582.65-621.15	44	40
PEG	0.174	0.150	335.99-489.99	68	40
PEG <sup>a</sup>	0.173	0.146	335.99-489.99	68	40
overall error	0.336	0.332	-	-	-

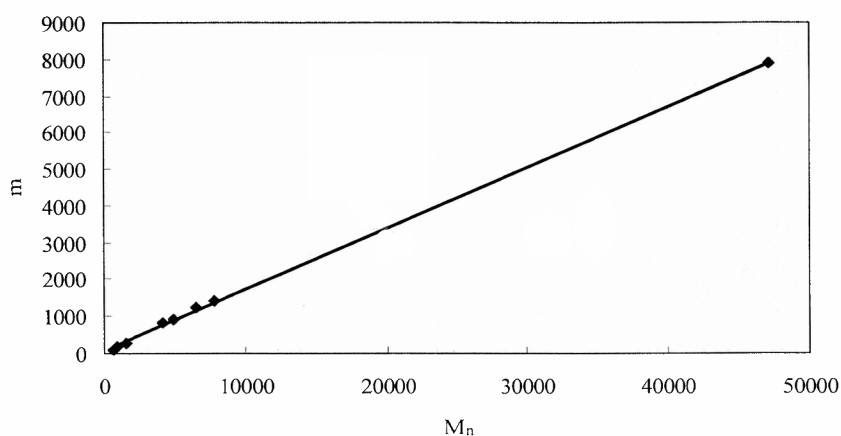
a - Association interaction is considered in this case.

$$* - \text{AARD}(\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{(\rho)^{\text{cal.}} - (\rho)^{\text{exp.}}}{(\rho)^{\text{exp.}}} \right|_i$$

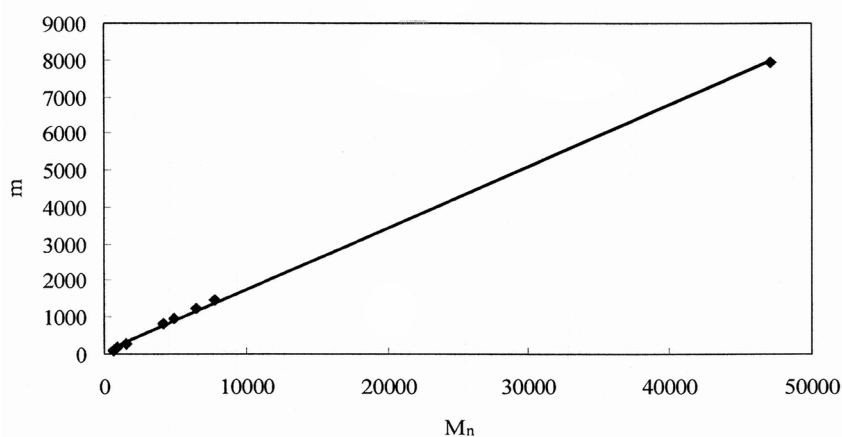
Figures 1 and 2 show the variation of the segment number of PDMS versus number average molecular weight of PDMS obtained from the SSAFT and the GV-SSAFT, respectively. As can be observed from these figures, the segment number of the polymer, PDMS, is linearly dependent upon molecular weight. Therefore, the segment number for PDMS can be found at the higher molecular

weight. The linear relationship between segment number and molecular weight obtained from the SSAFT equation of state for PDMS can be given by:

$$m=0.1659M_n+77.715 \quad (38)$$



**Figure 1.** Variation of the segment number with number average molecular weight for PDMS obtained from the SSAFT equation of state.

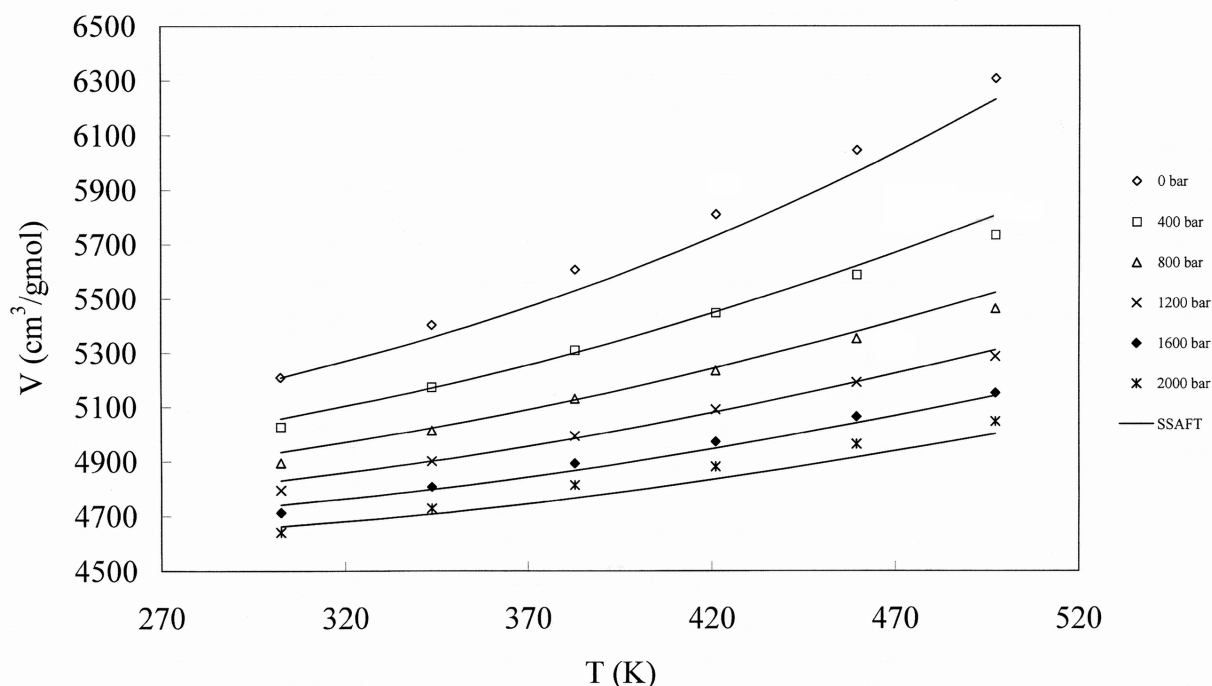


**Figure 2.** Variation of the segment number with number average molecular weight for PDMS obtained from the GV-SSAFT equation of state.

where  $m$  and  $M_n$  are segment number and number average molecular weight, respectively. In case of the GV-SSAFT the linear dependency of segment number on the number average molecular weight can be expressed according to the following relation:

$$m=0.1674M_n+78.872 \quad (39)$$

Figures 3 and 4 represent the variation of specific volume of PDMS with  $M_n=5000$  versus temperature at different pressures obtained using the SSAFT and the GV-SSAFT equations of state, respectively. Going through these two figures, the results of both equations of state are in good agreement with the corresponding experimental data.



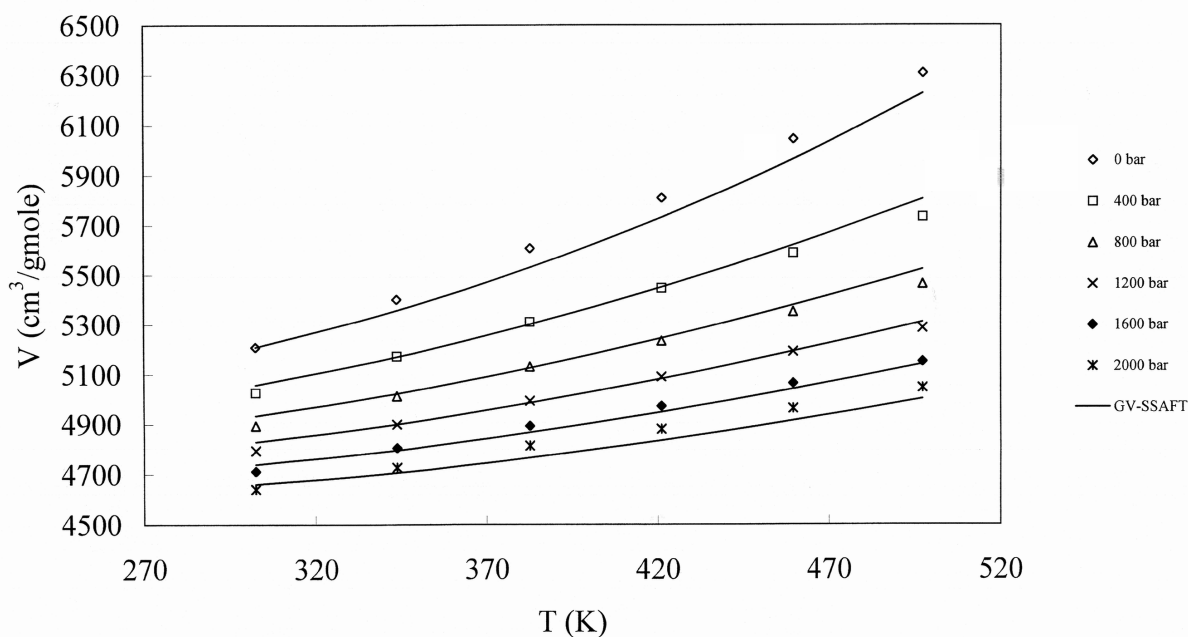
**Figure 3.** Variation of the specific volume of PDMS ( $M_n=5000$ ) versus temperature at different pressure obtained from the SSAFT equation of state

Table 4 presents the results of the VLE study for a number of associating and non-associating polymer-solvent mixtures over a wide range of temperature along with the percent of Root Mean Square Deviation (RMSD). As can be seen from Table 4, the binary interaction parameter,  $k_{ij}$ , is considered to be temperature dependent in two

SAFT-based equations of state studied in this work.

Table 5 shows the linear dependency between binary interaction parameter and temperature for two polymer-solvent mixtures under study as:

$$k_{ij}=A+BT \quad (40)$$



**Figure 4.** Variation of the specific volume of PDMS ( $M_n=5000$ ) versus temperature at different pressure obtained from the GV-SSAFT equation of state.

Such linear relationship between the binary interaction parameter and temperature cannot be observed for all systems. However, as seen for a large number of systems, the binary interaction parameters increase with temperature. Also the temperature dependent binary interaction parameter decreases as the molecular weight of the polymer increases. It can also be observed that the SSAFT EOS can more accurately correlate the vapor pressure of solvent in the polymer-solvent mixtures comparing to those obtained from the GV-SSAFT equation of state.

Table 6 gives the segment number, segment molar volume, and temperature independent depth of square well potential for a number of solvents in the polymer-solvent mixtures studied using both the SSAFT and GV-SSAFT equations of state at the specified range of temperatures. It should be stressed that the parameters reported in Table 6 were directly used in the VLE study of polymer-

solvent mixtures.

Figures 6 and 7 show the variation of the mole fraction of PEG molecules bonded at a specific site interaction with weight fraction of polymer at a different PEG number average molecular weight and at temperature of 323.15 K using the SSAFT and GV-SSAFT equations of state, respectively. From both figures 6 and 7, it can be observed that as the weight fraction of polymer in the polymer-solvent mixture increases, the mole fraction of PEG molecules bonded at specific interaction sites increases. Conversely, increase of polymer molecular weight results in a decrease in the mole fraction of PEG molecules bonded at specific interaction sites. It should be pointed out that PEG only exists in the liquid phase and hence does not self-associate in the vapor phase.

In order to significantly reduce the errors produced in application of the SAFT-based equations of state to the polymer - solvent

**Table 4.** The binary interaction parameters along with the percent of Root Mean Square Deviation (RMSD) from experimental data [41] obtained from the SSAFT and the GV-SSAFT equations of state for the polymer solutions

system	SSAFT		GV-SSAFT		T	M <sub>n</sub>	data NO.
	k <sub>ij</sub>	P RMSD*%	k <sub>ij</sub>	P RMSD*%			
PS-benzene	-0.0060000	0.954	-0.0073750	1.025	303.15	3600	8
	-0.0060625	1.355	-0.0076094	1.514	323.15	3600	11
	-0.0033359	4.782	-0.0052031	4.812	343.15	3600	13
	-0.0055938	0.445	-0.0071250	0.477	303.15	19200	11
	-0.0030938	0.931	-0.0047813	1.022	323.15	19200	8
	-0.0021250	3.636	-0.0040469	3.585	343.15	19200	11
	-0.0040625	0.167	-0.0055000	0.197	303.15	103800	10
	-0.0022813	0.103	-0.0040000	0.263	323.15	103800	7
PVAC-benzene	-0.0001875	4.019	-0.0022500	3.623	343.15	103800	11
	0.0928125	0.85	0.0908750	0.775	303.15	50500	8
	0.0930000	0.802	0.0915000	0.61	303.15	150000	8
	0.0943125	0.384	0.0920000	1.145	313.15	158000	11
PDMS-hexane	0.0971719	0.394	0.0950000	1.383	333.15	158000	10
PEG-toluene	0.0625000	0.113	0.0670000	1.728	303.08	89000	8
	0.0796953	0.343	0.0830000	0.299	323.15	200	8
	0.0909785	1.218	0.0941016	1.703	373.15	200	13
	0.0573125	0.041	0.0573750	0.118	322.75	5400	11
	0.0598750	0.162	0.0597188	0.302	342.65	5400	15
	0.0709687	0.509	0.0728750	0.411	323.15	300	9
	0.0714375	1.151	0.0725625	0.979	343.15	300	9
	0.0683125	0.077	0.0700000	0.162	323.15	400	8
	0.0703750	0.325	0.0718438	0.646	343.15	400	8
	0.0647500	0.196	0.0660625	0.076	323.15	600	9
	0.0663750	0.101	0.0674375	0.172	343.15	600	8
	0.0646250	0.227	0.0651563	0.42	343.15	1000	8
PS-nonane	0.0615625	0.153	0.0619375	0.068	323.15	1500	9
	0.0610000	0.278	0.0615000	0.225	323.15	2000	12
	-0.0603750	3.901	-0.0673750	3.471	403.15	53700	5
PS-toluene	-0.0568672	1.621	-0.0668125	7.902	423.15	53700	7
	-0.0519727	1.22	-0.0732500	13.834	448.15	53700	4
	-0.0100000	0.235	-0.0115000	0.257	303.15	232000	5
	-0.0084375	0.63	-0.0101875	0.683	323.15	232000	5
PPG-hexane	-0.0495000	0.666	-0.0520000	0.666	303.15	1260000	4
	-0.0280000	0.189	-0.0312500	0.179	323.15	1260000	4
	0.0178125	1.919	0.0181797	2.104	298.1	500	9
PMMA-toluene	0.0207812	1.828	0.0212812	1.998	312.65	500	9
	0.0225000	2.059	0.0228281	2.364	323.15	500	9
PVC-toluene	-0.0198750	0.911	-0.0218125	0.964	321.65	19770	9
NR-toluene	0.0221406	0.115	0.0203437	0.202	316.35	34000	9
overall error	0.0394531	0.991	0.0378906	2.429	303	270000	7
	-	1.053	-	1.480		-	

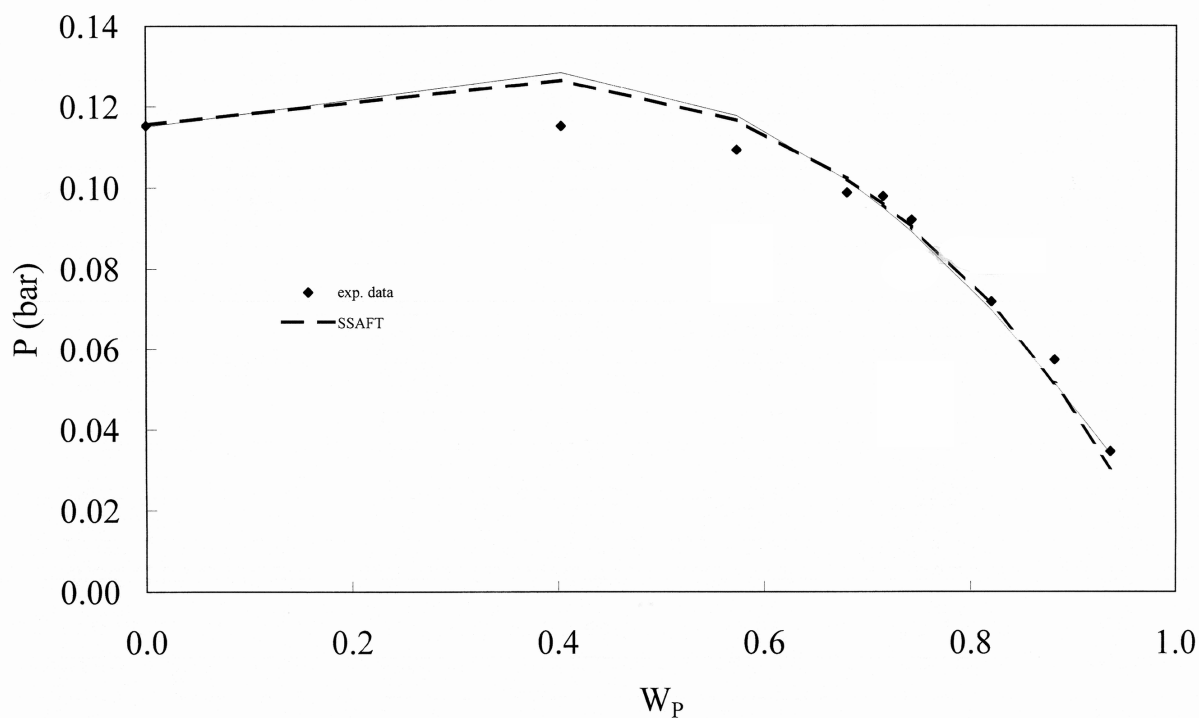
$$*_- \text{RMSD}(\%) = 100 \sqrt{\frac{\sum_{i=1}^N (P_i^{\text{exp.}} - P_i^{\text{cal.}})^2}{N}}$$

**Table 5.** Regressed values for the parameters used in equation (40) for the systems studied in this work and obtained from both the SSAFT and the GV-SSAFT equations of state.

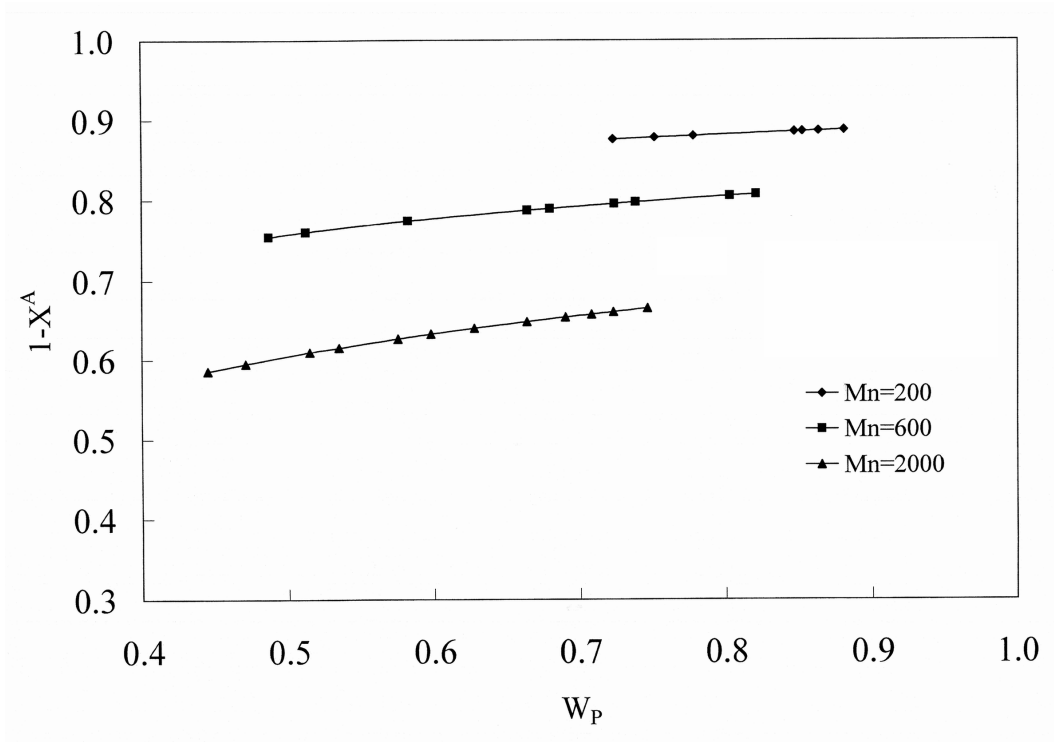
model	system	A	B
SSAFT	PS-benzene	0.0001	-0.0335
	PPG-c6	0.0002	-0.0382
GV-SSAFT	PS-benzene	0.0002	-0.0375
	PPG-c6	0.00008	-0.0302

**Table 6.** Parameters of the SSAFT and the GV-SSAFT equations of state for a number of solvents studied in this work [32].

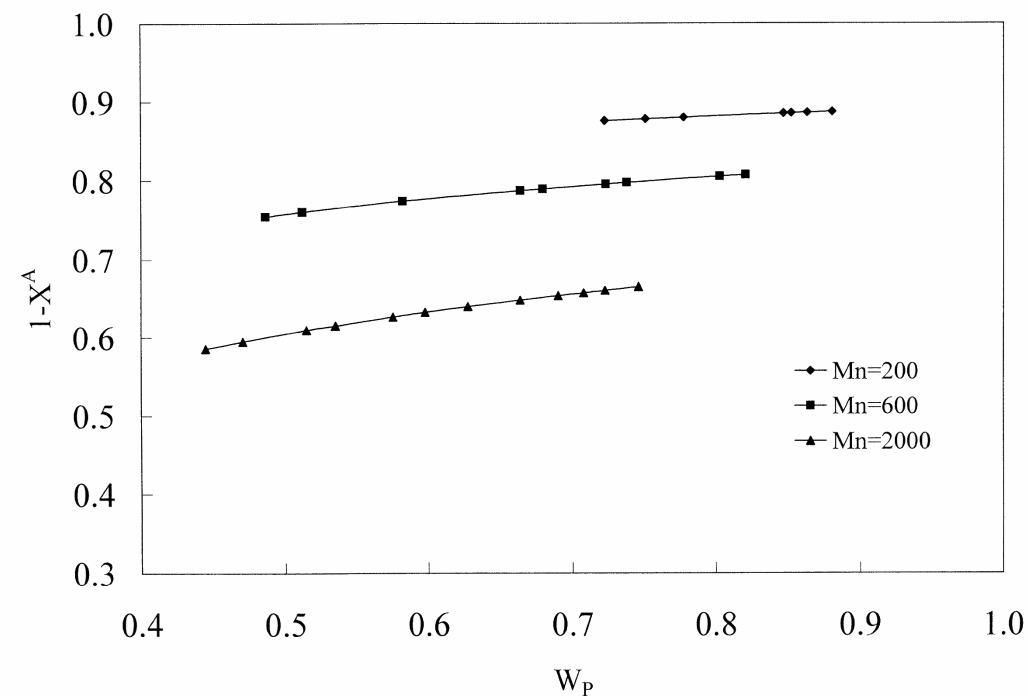
Comp.	SSAFT			GV-SSAFT			$T_r$
	m	$v^\infty$	$u^0/k$	m	$v^\infty$	$u^0/k$	
hexane	4.338	18.505	102.222	4.402	18.145	101.481	0.467-0.969
nonane	6.704	17.104	99.594	6.813	16.740	98.818	0.505-0.975
benzene	3.269	17.722	127.895	3.319	17.375	126.936	0.534-0.961
toluene	3.574	19.532	130.420	3.621	19.188	129.580	0.461-0.923



**Figure 5.** Pressure-weight fraction phase diagram for system of PMMA-toluene at 321.65 K and  $M_n=19770$ .



**Figure 6.** Variation of mole fraction of PEG bonded at site A with weight fraction of PEG at different molecular weights of PEG and at 323.15 K in PEG-toluene system using the SSAFT equation of state.



**Figure 7.** Variation of mole fraction of PEG bonded at site A with weight fraction of PEG at different molecular weights of PEG and at 323.15 K in PEG-toluene system using the GV-SSAFT equation of state.

mixtures, one more binary interaction parameter was added to the segment number of polymer and solvent molecules. This parameter, in fact, considers a dependency for hard sphere segment number on different types of molecular interactions in a polymer-solvent mixture. The results are presented in Table 7 for a number of polymer-solvent mixtures. As can be inferred from Table 7, by adding an adjustable binary interaction parameter, the results obtained from two SAFT based equations of state are much more improved.

Table 8 represents the results of saturation pressure for the system of PEG, with different molecular weight, and toluene at 323.15 K obtained from two SAFT-based equations of state studied in this work. A careful study of Table 8 indicates that

considering the specific association site-site interaction for PEG molecule as an associating compound cannot improve the results to a large extent. Therefore, these kind of interactions can be ignored remarkably. Such assumption dramatically reduces the complexity of the model. It is worth stating that the polymer molecules studied in this work were considered to be monodisperse and the effect of polydispersity on the VLE phase behavior of the polymer-solvent mixtures were neglected. As a matter of fact, the polymer polydispersity cannot significantly affect the vapor-liquid equilibrium of polymer solutions. However, in the case of liquid-liquid equilibrium for polymer solutions the polydispersity effect is of central importance [40].

**Table 7.** The binary interaction parameters along with the percent of Root Mean Square Deviation (RMSD) from experimental data [41] obtained from the SSAFT and the GV-SSAFT equations of state for the polymer solutions.

system	SSAFT			GV-SSAFT			T(K)	M <sub>n</sub>	data No.
	k <sub>ij</sub>	l <sub>ij</sub>	P RMSD*%	k <sub>ij</sub>	l <sub>ij</sub>	P RMSD*%			
PS-benzene	0.0065746	0.0022044	2.782	0.0050298	0.0032044	3.106	343.15	3600	13
	0.0083281	-	3.831	0.0067109	-	3.776			
PS-c9	-0.0470016	0.0014851	1.008	-0.0508883	-0.0026276	1.008	403.15	53700	5
	-0.0458125	-	3.551	-0.0526406	-	3.264			
	-0.0429792	0.0003786	0.648	-0.0482235	-0.0044097	0.648	423.15	53700	7
	-0.0425000	-	1.441	-0.0521328	-	7.428			
	-0.0383619	0.0001455	0.289	-0.0481145	-0.0031051	0.289	448.15	53700	4
	-0.0376563	-	1.13	-0.0582500	-	12.819			
PPG-c6	0.0147125	0.0023680	0.226	0.0347405	-0.0082011	0.226	298.1	500	9
	0.0219687	-	1.837	0.0224375	-	1.974			
	0.0189362	0.0015792	0.388	0.0326281	-0.0057246	0.388	312.65	500	9
	0.0246406	-	1.748	0.0252188	-	1.868			
	0.0217703	0.0013369	0.455	0.0336336	-0.0050930	0.401	323.15	500	9
	0.0261875	-	1.908	0.0266250	-	2.128			

$$* - \text{RMSD}(\%) = 100 \sqrt{\frac{\sum_{i=1}^N (P_i^{\text{exp.}} - P_i^{\text{cal.}})^2}{N}}$$



**Table 8.** The effect of the association site-site interaction for PEG molecule on the vapor pressure obtained from both the SSAFT and the GV-SSAFT equations of state

system	associating				non-associating				T(K)	M <sub>n</sub>	data No.
	SSAFT		GV-SSAFT		SSAFT		GV-SSAFT				
	k <sub>ij</sub>	P RMSD%	k <sub>ij</sub>	P RMSD%	k <sub>ij</sub>	P RMSD%	k <sub>ij</sub>	P RMSD%			
PEG-toluene	0.0728750	0.317	0.0747500	0.407	0.0829219	0.353	0.0847500	0.301	323.15	200	8
	0.0661250	0.363	0.0668125	0.251	0.0738125	0.528	0.0745000	0.424	323.15	300	9
	0.06531250	0.183	0.0658750	0.374	0.0709844	0.102	0.0715625	0.141	323.15	400	8
	0.0635000	0.107	0.0639375	0.118	0.0671875	0.229	0.0676250	0.089	323.15	600	9
	0.0623750	0.151	0.0619375	0.059	0.0640000	0.192	0.0635000	0.083	323.15	1500	9
	0.0621250	0.284	0.0618125	0.222	0.0632500	0.304	0.0629375	0.233	323.15	2000	12

## Conclusion

In this work, the GV-SSAFT EOS was used to study the phase behavior of associating and non-associating pure polymer as well as polymer-solvent mixtures at various conditions. The regressed values of the parameters for the SSAFT and GV-SSAFT equations of state for a large variety of pure homopolymer melts were obtained using the PVT experimental data. In the case of non-associating polymers the GV-SSAFT EOS has three adjustable parameters while the number of parameters is increased to five for associating polymers. The parameters were adjusted for segment number, segment molar volume, and segment-segment interaction energy. The results obtained from the GV-SSAFT EOS were favorably compared with those of the SSAFT EOS for both associating and non-associating pure polymer melts and polymer-solvent mixtures. It was shown that the GV-SSAFT EOS can accurately correlate the experimental data for liquid density of pure polymer melts at wide temperature ranges. Inferior results were obtained using the GV-SSAFT EOS to the VLE experimental data of polymer-solvent mixtures. It was also shown that while considering the specific site-site interactions for the associating polymers makes the SAFT-based equations

of state more complicated, the results cannot be much influenced by such complexity. The results showed that the GV-SSAFT EOS similar to the SSAFT can be used to study the phase behavior of associating and non-associating mixtures. Since the performance of the GV-SSAFT is only as good as that of the original SSAFT, the added value for practical applications may not be sufficient to justify the greater algebraic and computational complexity.

## References

1. Flory, P. J., Orwoll, R. A., Vrij, A., Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons. *J. Am. Chem. Soc.* **86**, 3570 (1964).
2. Sanchez, I. C., Lacombe, R. H., Elementary Molecular Theory of Classical Fluids-Pure Fluids. *J. Phys. Chem.* **80**, 2352 (1976).
3. Beret, S., Prausnitz, J. M., Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules. *AIChE J.* **26**, 1123 (1975).
4. Donohue, M. D., Prausnitz, J. M., Perturbed Hard-Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology. *AIChE J.* **24**, 849 (1978).

- Morris, W. O., Vimalchand, P., Donohue, M. D., The Perturbed-Soft-Chain Theory: An Equation of State Based on The Lennard-Jones Potential. *Fluid Phase Equilib.* **32**, 103 (1987).
- Vimalchand, P., Donohue, M. D., Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic Chain Theory. *Ind. Eng. Chem. Fundamentals.* **24**, 246 (1985).
- Vimalchand, P., Celmins, I., Donohue, M. D., VLE Calculations for Mixtures Containing Multipolar Compounds Using the Perturbed Anisotropic Chain Theory. *AIChE J.* **32**, 1735 (1986).
- Chapman, W. G., Jackson, G., Gubbins, K. E., Phase Equilibria of Associating Fluids Chain Molecules with Multiple Bonding Sites. *Mol. Phys.* **65**, 1057 (1988).
- Chapman, W. G., Gubbins, K. E., Jackson, G., Radosz, M., SAFT Equation of State Solution Model for Associating Fluids. *Fluid Phase Equilib.* **52**, 31 (1989).
- Chapman, W. G., Gubbins, K. E., Jackson, G., Radosz, M., New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* **29**, 1709 (1990).
- Wertheim, M. S., Fluids with Highly Directional Attractive Forces. 1. Statistical Thermodynamics. *J. Stat. Phys.* **35**, 19 (1984).
- Wertheim, M. S., Fluids with Highly Directional Attractive Forces. 2. Thermodynamic Perturbation Theory and Integral Equations. *J. Stat. Phys.* **35**, 35 (1984).
- Wertheim, M. S., Fluids with Highly Directional Attractive Forces. 3. Multiple Attraction Sites. *J. Stat. Phys.* **42**, 459 (1986).
- Wertheim, M. S., Fluids with Highly Directional Attractive Forces. *J. Stat. Phys.* **42**, 477 (1986).
- Wertheim, M. S., Fluids of Dimerizing Hard Spheres, and Fluid Mixtures of Hard Spheres and Dispheres. *J. Chem. Phys.* **85**, 2929 (1986).
- Wertheim, M. S., Thermodynamic Perturbation Theory of Polymerization. *J. Chem. Phys.* **87**, 7323 (1987).
- Chen, S.-J., Radosz, M., Density-Tuned Polyolefin Phase Equilibria. 1. Binary Solutions of Alternating Poly (ethylene-propylene) in Subcritical and Supercritical Propylene, 1-Butene, and 1-Hexene. Experimental and Flory-Patterson Model. *Macromolecules*, **25**, 3089 (1992).
- Bokis, C. P., Orbey, H., Chen, C.-C., Properly Model Polymer Processes. *Chem. Eng. Prog.* **95**, 39 (1999).
- Kirby, C. F., McHugh, M. A., Phase Behavior of Polymers in Supercritical Fluid Solvents. *Chem. Rev.* **99**, 565 (1999).
- Lambert, S. M., Song, Y., Prausnitz, J. M., Equations of State for Polymer Systems, in: Sengers, J. V., Kayser, R. F., Peters, C.J., White Jr (Eds.), H.J., *Equations of State for Fluids and Fluid Mixtures*, Elsevier, Amsterdam, (2000).
- J. Gross, G. Sadowski, Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* 2001, **40**, 1244.
- A. Gill-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, Statistical Associating Fluid Theory for Chain Molecules with Attractive Potentials of Variable Range. *J. Chem. Phys.* 1997, **106**, 4168–4186.
- Blas, F. J., Vega, L. F., Thermodynamic Behavior of Homonuclear and Heteronuclear Lennard-Jones Chains with Association Sites from simulation and Theory. *Mol. Phys.* **92**, 135 (1997).
- Kiselev, S.B., Ely, J.F., Crossover SAFT Equation of State: Application for Normal Alkanes. *Ind. Eng. Chem. Res.* **38**, 4993 (1999).
- Kiselev, S.B., Ely, J. F., Simplified Crossover SAFT Equation of State. *Fluid Phase Equilib.* **174**, 93 (2000).
- Kiselev, S. B., Ely, J. F., Adidharma, H., Radosz, M., A Crossover Equation of State for Associating Fluids. *Fluid Phase Equilib.*

- 183, 53 (2001).
27. Kiselev, S. B., Ely, J.F., Abdulagatov, I.M., Magge, J.W., Crossover SAFT Equation of State and Thermodynamic Properties of Propan-1-ol. *Int. J. Thermophys.* **21**, 1373 (2000).
  28. Zhang, Z.-Y., Yang, J.-C., Li, Y.-G., The Use of Statistical Associating Fluid Theory to Improve The BACK Equation of State. *Fluid Phase Equilib.* **172**, 111 (2000).
  29. Ndiaye, P. M., Dariva, C., Vladimir, J., Oliveira, F.W., Improving SAFT Equation of State By Using an Effective WCA Segment Diameter. *Fluid Phase Equilib.* **194**, 531 (2000).
  30. Min Sun Yeom, Jaeon Chang, Hwayong Kim, Equation of State Based on The Thermodynamic Perturbation Theory of Supercritical Polymerization for Associating Molecules and Polymers. *Fluid Phase Equilib.* **194**, 579 (2002).
  31. Hu, Z.-Q., Yang, J.-C., Li, Y.-G., Crossover SAFT-BACK Equation of State for Pure CO<sub>2</sub> and H<sub>2</sub>O. *Fluid Phase Equilib.* **205**, 25 (2003).
  32. Malekshah, V. A., Taghikhani, V., Ramazani S.A., A., Ghotbi, C., Application of a New Simplified SAFT to VLE Study of Associating and Non-Associating Fluids. *Fluid Phase Equilib.* **233**, 110 (2005).
  33. Fu, Y. H., Sandler, S. I., A Simplified SAFT Equation of State for Associating Compounds and Mixtures. *Ind. Eng. Chem. Res.* **34**, 1897 (1995).
  34. Huang, S. H., Radosz, M., Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* **29**, 2284 (1990).
  35. Huang, S., Radosz, M., Equation of State for Small, Large, Polydisperse, and Associating Molecules-Extension to Fluid Mixtures. *Ind. Eng. Chem. Res.* **30**, 1994 (1991).
  36. Wiesmet, V., Weidner, E., Behme, S., Sadowski, G., Arlt, W., Measurement and Modeling of High Pressure Phase Equilibria in The Systems Polyethylene-glycol (PEG)-Propane, PEG-Nitrogen and PEG-Carbon Dioxide. *J. Supercritical Fluids*, **17**, 1 (2000).
  37. Rodgers, P. A., Pressure-Volume-Temperature Relationships for Polymeric Liquids: A Review of Equations of State and Their Characteristic Parameters for 56 Polymers. *J. Appl. Polym. Sci.* **48**, 1061 (1993).
  38. Wolfarth, C., *Vapor-Liquid Equilibrium Data of Binary Polymer Solutions*, Elsevier Publishing Company, (1994).
  39. Bondi, J., *Physical Properties of Molecular Crystals, Liquids and Glasses*, J. Wiley & Sons, New York, (1968).
  40. Danner, I.P., High, M.S., *Handbook of Polymer Solution Thermodynamics*. Department of Chemical Engineering; The Pennsylvania State University; University Park, PA 16802, (1993).
  41. Zoller, P., Walsh, D., *Standard Pressure-Volume-Temperature Data for Polymers*. Technomic Publishing Company, Inc. (1995).