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Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) Parameters for Propane, Ethylene, and Hydrogen under Supercritical Conditions

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***Abstract*—**Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) equation of state (EOS) is a modified SAFT EOS with three pure component specific parameters: segment number (m), diameter (σ) and energy (ε). These PC-SAFT parameters need to be determined for each component under the conditions of interest by fitting experimental data, such as vapor pressure, density or heat capacity. PC-SAFT parameters for propane, ethylene and hydrogen in supercritical region were successfully estimated by fitting experimental density data available in literature. The regressed PC-SAFT parameters were compared with the literature values by means of estimating pure component density and calculating average absolute deviation between the estimated and experimental density values. PC-SAFT parameters available in literature especially for ethylene and hydrogen estimated density in supercritical region reasonably well. However, the regressed PC-SAFT parameters performed better in supercritical region than the PC-SAFT parameters from literature.

***Keywords*—**Equation of State, Perturbed-Chain, PC-SAFT, supercritical

I. Introduction

IN a chemical process, calculation of accurate phase and chemical equilibrium and other thermophysical properties is essential for rigorous modeling of mass and energy balances. Precise estimation of these properties become even more important in the case of rate-limited chemical reactions and mass and heat transfer limited unit operations in a given process.

Two classical thermodynamic models for phase equilibrium calculations are cubic equation of state (EOS) and liquid activity coefficient models. The latter can explain mixtures with any complexity and they are versatile providing a degree of solution non-ideality into the model, but they are valid only for liquids under critical point and a cubic EOS is needed for describing the gas phase. In contrast, cubic EOS models describe fugacity, enthalpy, entropy and Gibbs free energy with relation between volume, pressure, temperature and composition in the entire fluid region, from the dilute-gas to the dense-liquid region. Therefore, cubic EOS models are not limited to incompressible liquids. Among several EOS models available in literature, Peng-Robinson and Soave-Redlich-Knowng EOS' are commonly used in petroleum and chemical industries. [1]-[3]

In addition to the activity coefficient and cubic EOS models, several more advanced models called association models have been proposed over the last few decades [1]. These models can explain the effects of hydrogen bonding in a solution between both polar and non-polar compounds, which can form hydrogen bonds. Hydrogen bonding can occur between two like-molecules (self-association) or between two unlike-molecules (cross-association) [4]. Association models are described in three different categories [1],[5]:

1- Lattice (quasi-chemical) theories are based on the number of bonds formed between segments of different molecules that occupy adjacent sites in the lattice and extent of association is determined by the number of the bonds.
2- Chemical theories assume the formation of new species that have the same molecular properties as their constituent monomers. The number of formed components determines the extent of association.
3- Perturbation theories use statistical mechanics to calculate the total energy of hydrogen bonding and hence the number of bonding site per molecule is important parameter for hydrogen bonding.

Statistical Association Fluid Theory (SAFT) is one of the most important association theories belonging to the perturbation category. It was developed based on Wertheim's contribution [6]-[9] and implemented into a useful form in several studies [10]-[14]. In SAFT approach, molecules are first formed by addition of equal size spherical segments. The formed molecules gain specific interaction sites at certain position in the chain enabling the chains to associate through some attractive interaction like hydrogen bonding (Fig. 1).

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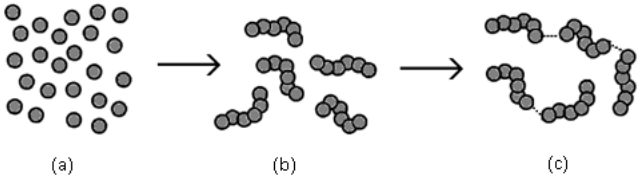


Fig. 1 Schematic representation of SAFT theory: (a): equal-sized spherical segments; (b): formed molecule chains; (c): hydrogen bonding between chains.

The Helmholtz free energy is generally used in statistical thermodynamics to express EOS since most properties of interest, such as system pressure, can be obtained by proper differentiation of it. In SAFT EOS, the residual Helmholtz energy is calculated with contribution of each step (1).

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \tag{1}$$

where a^{seg} is the Helmholtz energy of the segment, including both hard-sphere reference and dispersion terms, a^{chain} is the contribution from chain formation and a^{assoc} is the contribution from association. Because of separation of Helmholtz energy in three separate terms, various SAFT models were proposed. Although the chain and association terms do not change significantly in different SAFT models, the attraction (segment) term varies in various SAFT EOS models, such as simplified-SAFT, soft-SAFT and PC-SAFT. The last two terms in (1), i.e. Helmholtz energy for chain and association, are defined as:

$$\frac{a^{chain}}{RT} = \sum_i x_i (1 - m_i) \ln\left[g_{ii}(d_{ii})^{hs}\right] \tag{2}$$

$$\frac{a^{assoc}}{RT} = \sum_i x_i \left[\sum_{A_i} \ln X^{A_i} - \frac{X^{A_i}}{2}\right] + \frac{M_i}{2} \tag{3}$$

where X^{Ai} is the fraction of molecules i not bonded at site A and M_i is the number of association sites on molecule i, defined as:

$$X^{A_i} = \left[\sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j}\right]^{-1} \tag{4}$$

where ρ_j is the molar density of j and Δ^{AiBj} is the association strength between the sites A and B that belong to two different molecules i and j, which is given by:

$$\Delta^{A_i B_j} = d_{ij}^3 g_{ij}(d_{ij})^{seg} \kappa^{A_i B_j} \left[e^{\frac{\varepsilon^{A_i B_j}}{kT}} - 1\right] \tag{5}$$

In different SAFT models, small differences in the chain and association terms come from the calculation method of radial distribution function (g_{ij}) and calculation of association strength (Δ^{AiBj}). More details and various calculation methods can be found in reference [1]. The Helmholtz energy for segment term in SAFT EOS model consists of a hard-sphere reference and a dispersion contribution and it is described by:

$$a^{seg} = (a^{hs} - a^{disp}) \sum_i x_i m_i \tag{6}$$

In SAFT EOS, each component is characterized by five pure component parameters: number of segments (m), diameter of segment (σ), energy of segment (ε), volume of association (κ^{AiBj}) and energy of association (ε^{AiBj}). The last two terms, volume and energy of associations, are needed only if the molecule is self-associating. The pure component parameters can be either obtained based on group contribution methods, or in the traditional way, i.e. based on simultaneous regression of vapor pressure and liquid density data [1].

Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EOS model was developed by Gross and Sadowski [15]-[18]. In PC-SAFT EOS, the perturbation concept applies to hard sphere segments that are connected to chains rather than between disconnected segments. This is similar to considering attractive (dispersion) interactions between the connected segments (Fig. 2) instead of disconnected ones. Thus, behavior of chain molecules like hydrocarbons and polymers in solution can be captured more realistically.

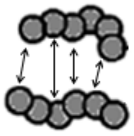


Fig. 2 Attractive interactions between the connected segments in PC-SAFT EOS

In PC-SAFT EOS, the Helmholtz energy of dispersion is expressed as a sum of two terms (first- and second-order perturbation terms):

$$\frac{a^{disp}}{kTN} = \frac{A_1}{kTN} + \frac{A_2}{kTN} \tag{7}$$

The coefficients A_1 and A_2 have a dependence on density and composition, as well as molecular size as defined in:

$$\frac{A_1}{kTN} = -2\pi\rho m^2 \left(\frac{\varepsilon}{kT}\right)\sigma^3 \int_1^\infty \tilde{u}(x) g^{hc}\left(m; x\frac{\sigma}{d}\right) x^2 dx \tag{8}$$

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$$\frac{A_2}{kTN} = -\pi\rho m\left(1+Z^{hc}+\rho\frac{\partial Z^{hc}}{\partial\rho}\right)^{-1} m^2\sigma^3 \left(\varepsilon/kT\right)^2 \frac{\partial}{\partial\rho}\left[\rho\int_1^\infty \tilde{u}(x)^2 g^{hc}\left(m;x\frac{\sigma}{d}\right)x^2dx\right] \quad (9)$$

where x is the reduced radial distance around a segment ($x = r/\sigma$), $\tilde{u}(x) = u(x)/\varepsilon$ denotes the reduced potential function, and $g^{hc}(m;x\sigma/d)$ is the average segment-segment radial distribution function of the hard-chain fluid with temperature-dependent segment diameter d(T). Following equations can be substituted in (9).

$$\left(1+Z^{hc}+\rho\left(\partial Z^{hc}\right)/\partial\rho\right) = 1+m\frac{\left(8\eta-2\eta^2\right)}{\left(1-\eta\right)^4} + (1-m)\frac{\left(20\eta-27\eta^2+12\eta^3-2\eta^4\right)}{\left[\left(1-\eta\right)\left(2-\eta\right)\right]^2} \quad (10)$$

$$I_1 = \int_1^\infty \tilde{u}(x)g^{hc}\left(m;x\frac{\sigma}{d}\right)x^2dx = \sum_{i=0}^{6} a_i\eta^i \quad (11)$$

$$I_2 = \frac{\partial}{\partial\rho}\left[\rho\int_1^\infty \tilde{u}(x)^2 g^{hc}\left(m;x\frac{\sigma}{d}\right)x^2dx\right] = \sum_{i=0}^{6} b_i\eta^i \quad (12)$$

where

$$a_i = a_{0i}+\frac{m-1}{m}a_{1i}+\frac{(m-1)(m-2)}{m^2}a_{2i} \quad (13)$$

$$b_i = b_{0i}+\frac{m-1}{m}b_{1i}+\frac{(m-1)(m-2)}{m^2}b_{2i} \quad (14)$$

Lennard-Jones potential and the radial distribution function of O'Lenick et al. [19] were used to develop equations (11)-(14) for n-alkanes [1]. The constant a_{ki} and b_{ki} in equations (13) and (14) are universal and obtained by fitting thermophysical properties of pure n-alkanes. These constants are presented in Table I.

PC-SAFT EOS model applicability includes systems of small and large molecules over a wide range of temperature and pressure conditions. It is capable of accurately correlating and predicting the vapor-liquid and liquid-liquid equilibriums for mixtures of associating, non-associating components, polar and non-polar components and polymers (homo- and co-polymers) [20]. Because of its accuracy in estimating the thermophysical properties of particularly the polymeric systems, PC-SAFT EOS has nowadays found more application in modeling polymerization systems.

Application of PC-SAFT EOS model to a system requires the estimation of pure component parameters, segment number, diameter and energy. Gross and Sadowski [15] provided PC-SAFT pure component parameters for many substances and many others can be found in literature. However, these parameters are all valid for a certain temperature and pressure ranges since they are obtained by regressing experimental PVT or density data in certain range. Therefore, the PC-SAFT pure component parameters need to be validated for the temperature and pressure ranges of interest. In this study, available PC-SAFT parameters for propane, ethylene and hydrogen in literature were validated against experimental density data in supercritical region. In addition, new parameters were regressed to estimate thermophysical properties in supercritical conditions more accurately.

II. Experimental Data and Parameter Fitting

Measured pure component densities in literature for a range of temperature and pressure were collected for the regression of PC-SAFT pure component parameters. Propane density data was obtained from the work of Aalto and Liukkinen [21], and Thomas and Harrison [22]. Aalto and Liukkinen [21] measured the liquid density of pure propane and mixtures of propane and linear low density polyethylene (LLDPE) in a temperature and pressure ranges of 354-378 K and 4-7 MPa, respectively. Due to the interest of this work, only pure propane data was used in regression. In the study of Thomas and Harrison [22], the authors measured the PVT relation of pure propane in a temperature range of 240-620 K and in a pressure range of 0-40 MPa. Only the data for supercritical propane was used in the parameter fitting. For ethylene and hydrogen, the data from Younglove [23] was utilized. The range of temperature and pressure used in regression for PC-SAFT pure component parameters and critical temperature and

TABLE I
UNIVERSAL MODEL CONSTANTS FOR EQUATIONS (13) AND (14) IN PC–SAFT EOS [15]

i	a_{0i}	a_{1i}	a_{2i}	b_{0i}	b_{1i}	b_{2i}
0	0.9105631445	-0.3084016918	-0.090614835 1	0.724 0946941	-0.5755498075	0.0976883116
1	0.6361281449	0.1860531159	0.4527842806	2.2382791861	0.6995095521	-0.2557574982
2	2.6861347891	-2.5030047259	0.5962700728	-4.0025849485	3.892567339	-9.155856 153
3	-26.547362491	21.419793629	-1.7241829131	-21.003576815	-17.215471648	20.642075974
4	97.759208784	-65.25588533	-4.1302112531	26.855641363	192.67226447	-38.804430052
5	-159.59154087	83.318680481	13.77663187	206.55133841	-161.82646165	93.626774077
6	91.297774084	-33.74692293	-8.6728470368	-355.60235612	-165.20769346	-29.666905585

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pressure for propane, ethylene and hydrogen are summarizes in Table II. When fitting the pure component parameters, randomly chosen experimental data within the ranges given in Table II were used for the regression purpose and the remaining data was used in the calculation of goodness of the fit.Several authors in literature reported PC-SAFT pure component parameters for propane, ethylene and hydrogen.

TABLE II
CRITICAL POINTS, AND TEMPERATURE AND PRESSURE RANGES USED IN PARAMETER FITTING

Component	T_C (K)	P_C (MPa)	Temperature (K)	Pressure (MPa)	Ref.
Propane	369.82	4.249	370 – 400	4.5 – 7.0	[21], [22]
Ethylene	282.34	5.041	290 – 400	5.5 – 7.5	[23]
Hydrogen	33.19	1.313	200 – 400	4.0 – 10.0	[23]

These parameters were listed in Table III with references. As it can be seen, different pure component parameters for the same compound can be found in different studies. The pure component parameters in Table III were used for comparing the fitted values in this study.

PC-SAFT EOS pure component parameters for propane, ethylene and hydrogen were regressed using build-in regression software in Aspen Plus engineering software. Maximum likelihood principle (ML) developed by Britt and Lueke [24] was used for the regression of parameters. The ML model assumes that each measured data contains some error and therefore it requires users to define standard deviations for each measurement. The objective function (weighted sum-of-squares error) minimized in this work was defined by:

$$\text{Obj.fnc.} = \sum_{l=1}^{g} w_l \left[\sum_{i=1}^{k} \sum_{j=1}^{m} \left(\frac{x_{ij}^{est} - x_{ij}^{exp}}{\sigma_{ij}} \right)^2 \right] \quad (15)$$

where;
w = Weighting factor for a data group
l = Data group number in the regression case
g = Total number of data groups used
i = Data point number within a data group
k = Total number of points in a data group
j = Measured variable for a data point (such as temperature, pressure, or density)
m = Number of measured variables for a data point

A weighting factor of 1 was used for all the data points. The residual root-mean-square error (RRMS) was calculated by:

$$\text{RRMS} = \sqrt{\frac{\text{weighted sum of squares error}}{\text{Tot. data point in groups} - \text{Tot. parameters}}} \quad (16)$$

The average absolute deviation in percent (AAD%) was calculated by:

$$\text{ADD\%} = \frac{1}{N} \sum_{i}^{N} \left| \frac{x_i^{est} - x_i^{exp}}{x_i^{exp}} \right| \cdot 100 \quad (17)$$

where x is measured (experimental) or calculated value for temperature, pressure or density.

TABLE III
PC-SAFT EOS PURE COMPONENT PARAMETERS FOR PROPANE, ETHYLENE AND HYDROGEN AVAILABLE IN LITERATURE

Ref.	Propane			Ethylene			Hydrogen		
	m	σ (Å)	ε/k (K)	m	σ (Å)	ε/k (K)	m	σ (Å)	ε/k (K)
[1]	2.002	3.6184	208.1	1.593	3.445	176.5			
[2]	2.002	3.6184	208.1	1.593	3.445	176.5	0.8285	2.973	12.53
[3]	2.002	3.618	208.1	1.559	3.434	179.5	0.8285	2.973	12.53
[4]	2.002	3.6184	208.1	1.593	3.445	176.5			
[5]	2.002	3.6184	208.1	1.559	3.434	179.5	0.8285	2.973	12.53
[6]				1.605	3.403	176.3			
[7]	2.002	1.6184	208.1	1.593	3.445	176.5			
[8]				1.593	3.445	176.5	1.0	2.986	19.28
[9]	2.192	3.4984	197.6						

[1] J. Gross, G. Sadowski, Ind. Eng. Chem. Res., 40 (2001) 1244.
[2] Aspen Polymer Plus V7.1 Database
[3] N.P. Khare et al., Ind. Eng. Chem. Res., 43 (2004) 884.
[4] F.Garcia-Sánchez, Fluid Phase Equilib., 217 (2004) 241.
[5] Z.-H. Luo et al., Chem. Eng. J., 149 (2009) 370.
[6] Z.-H. Chen et al., J. Supercritical Fluids, 49 (2009) 143.
[7] S. Abbas et al., Chem. Eng. Proc., 43 (2004) 1449.
[8] A. Ghosh et al., Fluid Phase Equilib., 209 (2003) 229.
[9] P. Arce, J. Supercritical Fluids, 49 (2009) 135.

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III. Result and Discussion

A. Propane

Literature survey showed two different PC-SAFT parameter sets for propane (Table III). These two pure component parameter sets are given names PCS-C3_1 and PCS-C3_2 to refer later in this work (Table IV). Supercritical propane density is estimated by using the PC-SAFT parameters from Table IV and the results were compared with the experimental data in Fig. 3. Clearly, the estimation of propane density is more accurate with the PCS-C3_1 parameters than the PCS-C3_2 parameters.

TABLE IV
PC-SAFT PURE COMPONENT PARAMETERS FOR PROPANE FROM LITERATURE (SEE TABLE III FOR REFERENCES)

Parameter	PCS-C3_1	PCS-C3_2
m	2.002	2.192
ε/k (K)	208.11	197.61
σ (Å)	3.6184	3.4987

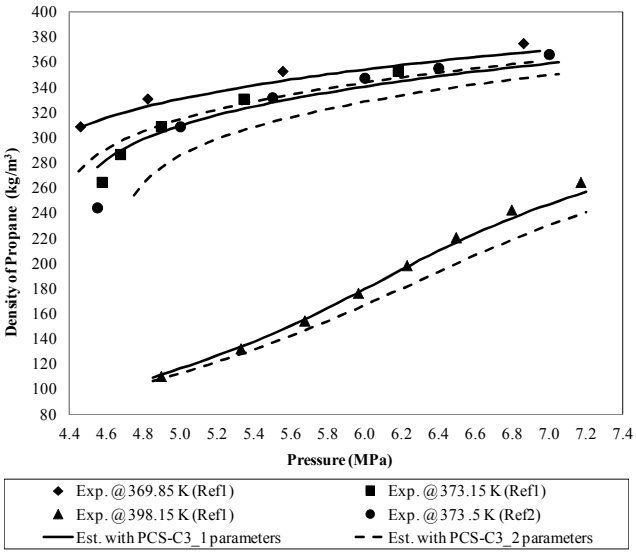


Fig. 3 Supercritical propane experimental and estimated density with PC-SAFT EOS as a function of pressure (Ref1:M.A. Aalto, S.S. Liukkonen, J. Chem. Eng. Dat., 43 (1998) 29, and Ref2:R.H.P. Thomas and R.H. Harrison, J. Chem. Eng. Dat., 27 (1982) 1)

The regression of PC-SAFT parameters with the supercritical propane experimental data resulted in the parameters in Table V. Estimated propane densities as a function of pressure and temperature with the regressed pure component parameters were compared against experimental data in Fig. 4 and Fig. 5, respectively. For comparison, estimated densities with PCS-C3_1 parameters and calculated AAD% values were shown in the figures. Both figures illustrate a better fit with the regressed parameters and the calculated AAD% values verify the best estimate with the regressed parameters. The AAD% values were always calculated more than 1.0 with the PC-SAFT parameters from literature whereas the same calculation with regressed parameters yielded AAD% values of less than 1.0 (Fig. 4 and Fig. 5).

TABLE V
REGRESSED PC-SAFT PURE COMPONENT PARAMETERS FOR SUPERCRITICAL PROPANE

Parameter	Value	Standard deviation
m	1.62913209	0.07705062
ε/k (K)	230.884554	5.42962087
σ (Å)	3.86692695	0.06317573
RRMS	1.44761381	

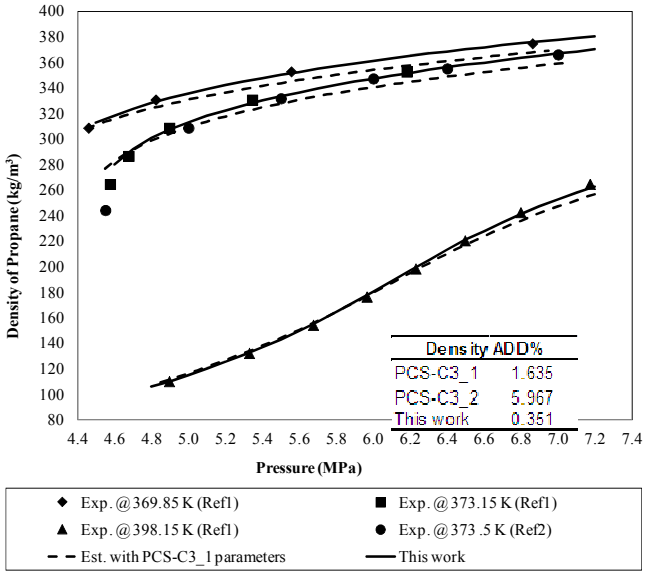


Fig. 4 Supercritical propane experimental and estimated density with regressed PC-SAFT parameters (see Table IV for PCS-C3_1 and PCS-C3_2 values; Ref1: M.A. Aalto, S.S. Liukkonen, J. Chem. Eng. Dat., 43 (1998) 29; Ref2: R.H.P. Thomas and R.H. Harrison, J. Chem. Eng. Dat., 27 (1982) 1)

B. Ethylene

Three different sets of PC-SAFT pure component parameters for ethylene were found in literature and these parameters are called PCS-C2_1, PCS-C2_2 and PCS-C2_3 (Table VI). Estimated supercritical ethylene density with these PC-SAFT parameters as a function of temperature was plotted against experimental data in Fig. 6. As a matter of fact, all of these PC-SAFT parameters for ethylene seem to estimate the ethylene density at supercritical region quite well. Particularly, the estimation improves and become indistinguishable with all

TABLE VI
PC-SAFT PURE COMPONENT PARAMETERS FOR ETHYLENE FROM LITERATURE (SEE TABLE III FOR REFERENCES)

Parameter	PCS-C2_1	PCS-C2_2	PCS-C2_3
m	1.593	1.559	1.605
ε/k (K)	176.5	179.5	176.3
σ (Å)	3.445	3.434	3.403

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three PC-SAFT parameter sets as the temperature increases (going away from the critical point).

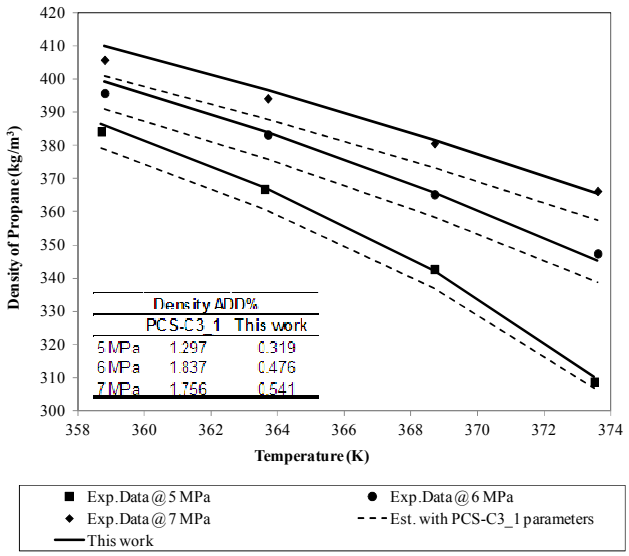


Fig. 5 Supercritical propane experimental versus estimated density with regressed PC-SAFT pure component parameters (see Table IV for PCS-C3_1 values; exp. data: M.A. Aalto, S.S. Liukkonen, J. Chem. Eng. Dat., 43 (1998) 29)

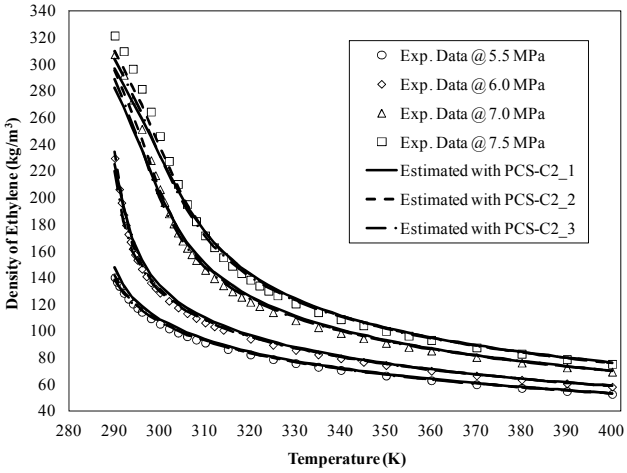


Fig. 6 Supercritical ethylene experimental versus estimated density with PC-SAFT as a function of temperature (Exp. Data: B.A.Younglove, J. Phys. Chem. Ref. Dat., 11 (1982) 1)

In spite of the good estimate of the ethylene density with the PC-SAFT parameters from literature, experimental data was regressed to obtain new PC-SAFT parameters. The regressed PC-SAFT parameters for ethylene and statistical data of the regression can be seen in Table VII. Estimated supercritical ethylene density with regressed PC-SAFT parameters were plotted against experimental data in Fig. 7. The estimated densities with the regressed parameters fit as good as those estimated with the PC-SAFT parameters from literature at higher temperatures. However, comparison of Fig. 6 and Fig. 7 shows that regressed PC-SAFT parameters seem to estimate the density more accurately at high pressures and low temperatures (close to the critical temperature) than PC-SAFT parameters available in literature. For a better judgment on the goodness of the fit, the calculated density AAD% values were compared in Table 8. Density ADD% values were calculated for each pressure and for combined pressure data. The results point to a smaller ADD% value with the regressed PC-SAFT parameters than with the PC-SAFT parameters from literature. This clearly indicates that the supercritical ethylene density is estimated with the regressed PC-SAFT parameters better than with the PC-SAFT parameters from literature.

TABLE VII
REGRESSED PC-SAFT PURE COMPONENT PARAMETERS FOR SUPERCRITICAL ETHYLENE

Parameter	Value	Standard deviation
m	2.467115	1.857421
ε/k (K)	144.9669	50.97402
σ (Å)	2.856809	0.843797
RRMS	330.71	

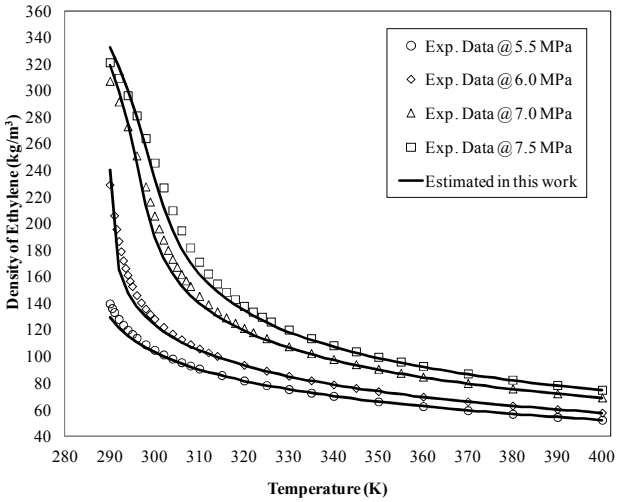


Fig. 7 Supercritical ethylene experimental versus estimated density with regressed PC-SAFT pure component parameters (Exp. Data: B.A.Younglove, J Phys. Chem. Ref. Dat., 11 (1982) 1)

C. Hydrogen

The literature survey revealed two different PC-SAFT parameter sets for hydrogen as seen in Table IX. The estimated density of hydrogen in supercritical region with these PC-SAFT parameters was compared with the experimental data as a function of temperature in Fig. 8. Both parameter sets, i.e. PCS-H2_1 and PCS-H2_2, explained the measured density quite well.

TABLE VIII
CALCULATED ETHYLENE DENSITY AAD% VALUES FOR EACH AND COMBINED PRESSURE DATA SETS

	Density AAD%			
Pressure	PCS-C2_1	PCS-C2_2	PCS-C2_3	This work
5.5 MPa	2.372	1.387	1.141	1.010
6.0 MPa	2.373	1.684	1.448	1.281
7.0 MPa	3.151	2.161	2.136	1.539
7.5 MPa	3.067	2.160	2.259	1.742
Combined	2.741	1.848	1.746	1.393

TABLE IX
PC-SAFT PURE COMPONENT PARAMETERS FOR HYDROGEN AVAILABLE IN LITERATURE (SEE TABLE III FOR REFERENCES)

Parameter	PCS-H2_1	PCS-H2_2
m	0.8285	1.0
ε/k (K)	12.53	19.28
σ (Å)	2.973	2.986

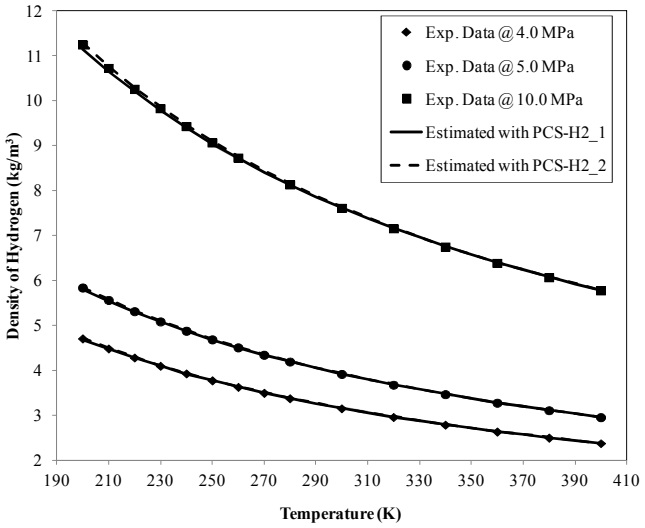


Fig. 8 Supercritical hydrogen experimental versus estimated density with PC-SAFT EOS as a function of temperature (Exp. Data: B.A.Younglove, J. Phys. Chem. Ref. Dat., 11 (1982) 1)

Table X shows the estimated PC-SAFT parameters and their standard deviation for hydrogen by using supercritical density data. The estimated density for supercritical hydrogen with the regressed PC-SAFT parameters was plotted against experimental density data for 4, 5 and 10 bar as a function of temperature in Fig. 9. The estimated density explained the experimental data quite well. However, the good fit also with the PC-SAFT parameters from literature (Fig. 8) makes difficult to conclude on the performance of the regressed parameters. On the other hand, the calculated density AAD% values (Table XI) clearly indicates better fit of estimated density with the regressed PC-SAFT parameters to the experimental data than with the literature values. The regressed PC-SAFT parameters generally yield a smaller AAD% value than those from literature. It is also visible in Table XI that PCS-H2_1 parameters estimate hydrogen density in supercritical region more accurately that PCS-H2_2 parameters.

TABLE X
REGRESSED PC-SAFT PURE COMPONENT PARAMETERS FOR SUPERCRITICAL HYDROGEN

Parameter	Value	Standard deviation
m	0.935864	0.329673
ε/k (K)	25.62934	4.650316
σ (Å)	2.912599	0.461407
RRMS	0.01027	

TABLE XI
CALCULATED HYDROGEN DENSITY AAD% VALUES FOR EACH AND COMBINED PRESSURE DATA SETS

	Density AAD%		
Pressure	PCS-H2_1	PCS-H2_2	This work
4.0 MPa	0.181	0.624	0.060515
5.0 MPa	0.218	0.772	0.073955
10.0 MPa	0.321	1.422	0.172259
Combined	0.238	0.928	0.10065

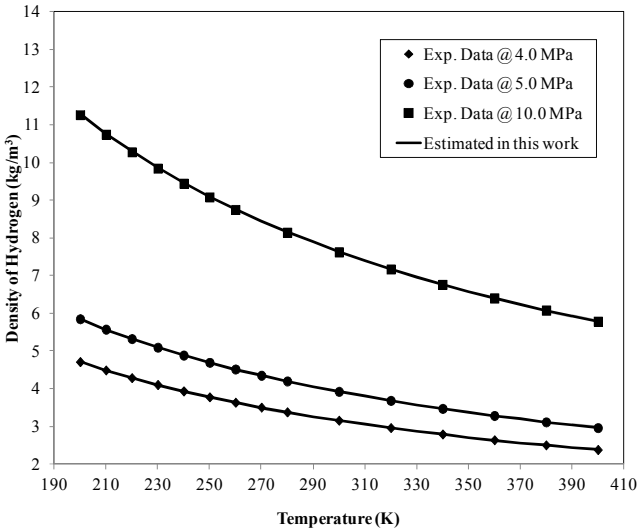


Fig. 9 Supercritical hydrogen experimental versus estimated density with regressed PC-SAFT pure component parameters (Exp. Data: B.A.Younglove, J Phys. Chem. Ref. Dat., 11 (1982) 1)

IV. Conclusions

PC-SAFT pure component parameters, segment number, diameter and energy, for propane, ethylene and hydrogen available in literature were used to estimate the pure component density in supercritical region. Few different PC-SAFT parameter sets were found for each component in literature. Although these parameters sets were obtained by regressing experimental data in subcritical region, some of the parameter sets estimated the density in supercritical region sufficiently well, especially for ethylene and hydrogen. However, the experimental density data at supercritical

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conditions were used to fit new PC-SAFT parameters. The results were compared with those from literature. The regressed PC-SAFT parameters enabled better estimation of the density in supercritical region than the PC-SAFT parameters available in literature.

APPENDIX

a^{assoc}	Helmholtz energy due to associative bonding (J/mol)
a^{chain}	Helmholtz energy due to repulsion (J/mol)
a^{res}	Total residual Helmholtz energy (J/mol)
a^{seg}	Helmholtz energy due to attraction forces (J/mol)
d	Temperature-dependent diameter
g	Radial distribution function
k	Boltzmann's constant (J/K)
M_i	Number of association sites on molecule i
m	Segment number
N	Total number of molecules or number of measurements
P	Pressure (MPa)
R	Universal gas constant (bar l/mol/K)
r	radial distance (A^o)
T	Temperature (K)
u	Temperature dependent energy parameter
ũ	Reduced intermolecular potential
w	Weighting factor for a data group in equation (15)
X^{Ai}	Fraction of A-sites of molecule i that are not bonded
x	Reduced radial distance or measured (experimental)/calculated value in equation (15)
x_i	Liquid mole fraction of component i or measured/calculated value in equation (17)
Z	Compressibility factor

Greek letters

Δ	Association strength
ε/k	Segment energy (temperature in K)
η	Volume fraction
κ	Association volume of PC–SAFT
σ	Segment diameter (A^o) or standard deviation in equation (15)
ρ	Molar density (mol/l)

Subscripts and superscripts

A_i	Site A in molecule i
A_iB_j	Site A in molecule i with site B in molecule j
B_j	Site B in molecule j
c	Critical point
assoc	Association
chain	Chain
disp	Dispersion
est	Estimated data
exp	Experimental (measured) data
hs	hard sphere
i, j	Component indexes or data point number within a data group in equation (15)
o	Non-associated segment
res	Residual
seg	Segment

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