**Modeling of pure components high pressures densities using CK-SAFT and PC-SAFT equations**

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*Abstract:* SAFT equations of state have been widely used for the determination of different thermo-physical and phase equilibria properties. In order to be used as predictive models it is necessary to calculate model parameters. In this work CK-SAFT and PC-SAFT equations of state were applied for the correlation of pure compounds densities in the wide ranges of temperature and pressure (288.15-413.15 K and 0.1-60 MPa, respectively). Calculation of densities for *n*–hexane, *n*–heptane, *n*–octane, toluene, dichloromethane and ethanol under high pressure conditions were performed with the new sets of parameters determined in this paper by CK-SAFT and PC-SAFT. Very good agreement between experimental and calculated density values was achieved, having absolute average percentage deviations lower than 0.5%.

*Keywords:* density, modeling, non-associative compounds, CK-SAFT, PC-SAFT

RUNNING TITLE: HIGH PRESSURE DENSITY MODELING

INTRODUCTION

A wide variety of molecules are exposed to harsh process conditions, and their thermodynamic properties have to be known over broad ranges of pressure and temperature.1 In chemical processes, thermo-physical and equilibrium properties are required in mathematical models related to mass and energy balances.2

Density of a compound is an essential physical property required for solving engineering problems.3-5 To estimate aforementioned thermo-physical property many different thermodynamic models have been proposed. In this paper, we applied equations of state (EOS) based on Statistical Associating Fluid Theory (SAFT) to estimate pure component density.6,7 The development of SAFT EOS started with publication of Chapman *et al*.8 They used Wertheim’s theory to develop the first SAFT mathematical model.9-12 This thermodynamic model has been very successful for predicting phase behavior of long chains molecules.13 Huang and Radosz upgraded original model developed by Chapman *et al*. by replacing original dispersion term with dispersion term proposed by Chen and Kreglewski,8,14-16 the model was entitled as CK-SAFT.1 Later, Gross and Sadowski proposed the novel definition of dispersion term, and the new model was disclosed PC-SAFT.8

In the SAFT approach thermodynamic properties of molecules are defined as a sum of diverse contributions of Helmholtz energy, related to different interactions between a molecule segments. Temperature dependent hard-sphere and dispersion contributions are related to so-called Lennard-Jones segment.14,16 Chain contribution refers to chain formation between segments.1,2,17 In cases where hydrogen-bonding interactions exist a contribution term related to these interactions should be include in model. Different versions of described model have been proposed including the original SAFT or simplified SAFT, e.g. the CK-SAFT, the LJ-SAFT, the soft-SAFT, the SAFT-VR and the PC-SAFT.1,8,14,16,18-23 The main difference between them lies primarily in the dispersion contribution term which is showed in Table SI of the Supplementary material to this work.1 The same chain and association term are utilized in all of these versions. In case of association contribution, various SAFT models assume temperature-dependent or temperature-independent diameter and radial distribution function. Temperature-dependent diameter is used in original SAFT, CK-SAFT, but the temperature-independent parameter is applied in other versions of SAFT.

In this paper, the first step was to calculate densities for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol by using parameters of CK-SAFT and PC-SAFT equations of state reported in the literature.8,14 These two versions of SAFT EOS were selected as most reliable and commonly used in the literature. In the second step, a new sets of parameters of CK-SAFT and PC-SAFT EOS were estimated using previously published values of density in the broad ranges of temperatures and pressures (288.15-413.15 K, 0.1-60 MPa, respectively).5,24,25 The new sets of parameters considerably improved density estimations.

THERMODYNAMIC MODELING

The most used thermodynamic models are defined as so-called equations of state (EOS).6 Cubic EOSs are dependent on critical properties of molecules such as critical temperature, critical pressure, critical volume, critical compressibility factor, etc. These values are very important for the determination of thermodynamic properties. However, it is often difficult to determine the critical values for some complex molecules, such as polymers, so the non-cubic EOS are proposed.8,14 Non-cubic EOS, such as SAFT-family EOS, requires parameters which can be determined from liquid density and vapor pressure experimental data. These experimental data can be easily measured. To characterize specific molecules using SAFT approach the Helmholtz free energy represents starting point. It is given as a sum of molecular contributions and can be applied to calculate important thermodynamic properties such as enthalpy, heat capacity, speed of sound, etc. The Helmholtz free energy strongly depends on SAFT parameters and density of molecule.

*SAFT concept*

CK-SAFT concept assumes that molecules are formed of hard spherical segments having equal diameter size which enables formation of chains.1 In PC-SAFT hard chain fluid is chosen as reference system rather than hard spherical molecules.6,8 All of these molecular interactions can be described by the Helmholtz free energy. The residual Helmholtz energy involves a sum of molecular contributions: 1,2,8,17

 (1)

where *a* denotes Helmholtz free energy per mole and superscripts res, hs, disp, chain, and assoc indicate residual, hard-sphere, dispersion reference, chain formation and association, respectively.1,2

In CK-SAFT the hard-sphere term was proposed by Carnahan and Starling: 25

 (2)

*mi* is a number of spherical segments and represents the first parameter of SAFT model which is the same for both, PC-SAFT and CK-SAFT, models. *η* denotes reduced density which can be described by the following equation:26

 (3)

where *τ*=0.74048, *ρj* is the molar density and *ν*0 is temperature-dependent close-packed segment molar volume which is described applying the temperature-independent segment volume *ν*∞ (the second parameter of CK-SAFT model):14

 (4)

and *u0/k* is a temperature-independent energy parameter which represents the third parameter of CK-SAFT model to be optimized.

In the PC-SAFT the hard-sphere term can be expressed as:

 (5)

where

 (6)

*xi* denotes mole fraction of chains, and *di* is a temperature-dependent segment diameter.14

The chain and association terms are essentially unchanged in almost all SAFT EOS variants.1

The contribution for chain formation from hard spheres is evaluated according to the next equation:

 (7)

The association term for pure components can be calculated by the following equation:

 (8)

where *Mi* is the number of association sites per molecules of component *i*, for the component *i*, *XAi* is the fraction of molecules not bonded at site *A* and  denotes a sum of all associating sites on the molecules.14 The mole fraction is determined according to the next expression:

 (9)

In Eq. (9) *ρj* is the molar density of component *j*, *ΔAiBj* is the association strength between two sites *A* and *B* of different molecules *i* and *j*. It can be calculated as follows:

 (10)

where *εAiBi* is association energy, *κAiBi* is association volume, *gij(dij)*seg represents radial distribution function, and *dij* is the average segment diameter expressed by temperature-dependent diameter for pure component *i* and *j*, respectively. The association energy and association volume also represent two parameters that characterize SAFT EOS, but they are needed only in case the molecule is self-associating.2 Small differences in the calculation of radial distribution function between CK-SAFT and PC-SAFT can be found in literature.1

In our work it is assumed that dichloromethane and ethanol are non-associating compounds. So, all investigated compounds were observed as pure, non-associated which further implied that associative contribution has been neglected.

The main difference between CK-SAFT and PC-SAFT is defined with the dispersion term, (Supplementary material - Table SI). As described, the reason for difference in these two versions of SAFT EOS is the reference fluid. Hard sphere and hard chains are applied as reference system for CK-SAFT and PC-SAFT, respectively. The dispersion term in CK-SAFT can be described using equation proposed by Alder *et al*.:27

 (11)

where *Dij* are universal constants found in literature and *u/k* is expressed as:15,26

 (12)

*e/k* denotes energy parameter with constant value equal 10 with some exceptions.14 In PC-SAFT the dispersion contribution can be calculated as follows:

(13)

where *σ* is the temperature independent diameter of segment which is the second parameter, *x* is the reduced radial distance around the segment, *ȗ(x)* is reduced potential function, and *d* denotes temperature dependent segment diameter. The third parameter for PC-SAFT is *ε/k* that denotes temperature independent energy parameter.

Accordingly, described equations for pure, non-associated molecules are characterized by set of three parameters for both models, segment number (*mi*), the segment volume (*v∞)*, and the segment energy (*u0/k*), for CK-SAFT, and for PC-SAFT segment number (*mi*), segment diameter (*σ*), and segment energy (*ε/k*).

CALCULATIONS

The CK-SAFT and PC-SAFT equations of state have been applied in density calculation process for selected pure, non-associated molecules. Densities were calculated using parameters reported in literature8,14 and compared with previously published values of density measured in our laboratory.24,25 In order to demonstrate accuracy of calculated densities, the absolute average percentage deviation, *AAD*, criteria has been applied.5 *AAD* obtained using CK-SAFT model were 5.42%, 6.96%, 7.61%, 5.68%, 1.63% and 23.66% while for PC-SAFT model they were 0.54%, 0.51%, 0.57%, 0.49%, 155.66% and 115.71% for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol, respectively. The results obtained by PC-SAFT equation are rather satisfying. Contrarily, the results obtained by CK-SAFT model are somewhat higher, while both models gave very poor prediction of densities for dichloromethane and ethanol. So, it was necessary to include association term in calculations.

The idea of this work was to calculate new parameters of CK-SAFT and PC-SAFT equations from experimental density data and to compare it with the *AAD* values obtained with literature parameters.

The idea of this work was to calculate new parameters of CK-SAFT and PC-SAFT equations from experimental density data5,24 and to compare it with the deviations obtained with literature parameters.

The optimization problem is defined as a search for parameter vector *k* that minimizes f(*k*) by scheme:28

 (14)

where  is the Nexp-dimensional vector of parameters.  is the m-dimensional vector of residuals where  and in our work  is reverse variance with value of 0.8 kg·m-3. The expanded uncertainty (k=2) of 0.8 kg·m-3 for density measurements by Anton Paar DMA HP measuring cell was taken as variance *σ*ε.24 In this investigation, initial guesses for parameters, *k(0)*, were taken from the literature.8,14 Parameters estimation was carried out from density data taken from the literature.5,24,25 Also, the objective function was established combining developed Eq. (1) and standard thermodynamic relation:29

 (15)

 for CK-SAFT (16)

 for PC-SAFT (17)

Objective function is defined as:

 (18)

The density using CK-SAFT EOS was estimated by the following expression:

(19)

The density using PC-SAFT EOS was estimated by the following expression:

(20)

In this paper two optimization approaches were applied, unconstrained least squares trust region (LSQR) and constrained sequential quadratic programming (SQP).30 They were used to minimize objective function, Eq. (18), by adjusting values of parameters. Minimization of the objective function was carried out by adjusting values of parameters. Selected methods were chosen because they allowed setting low and up boundaries to constrain parameter values to physical meaning values. Unconstrained method required solving polynomial expressed by Eq. (19). Polynomial is the fourteenth and twenty fourth degrees for CK-SAFT and PC-SAFT, respectively, so, there were 14 or 24 equations solutions depending on model EOS. LSQR optimization method chooses solutions which have the closest experimental values of density. Eq. (19) is defined as nonlinear constrained according unconstrained optimization method. So, SQP method can determine values of density. However, constrained method applying analytical derivatives was faster than unconstrained method. Both methods gave results in good agreement with examined density values.24,25

Based on the chosen optimization method, the described objective function is minimized applying multi start in order to achieve efficient parameters estimation. Iterative procedure continues until convergence to the optimal parameter values is achieved. Both methods gave results in a good agreement with selected literature density values5,24 but results obtained applying LSQR method were slightly better, so they were presented in Tables I and II.

Once the unknown sets of parameters are evaluated, it is very important to carry out some additional calculations to establish estimates of the standard error in the parameters.28 Applying the described method to search the best parameter values, the model equations are linearized. So, our parameters data have linear least squares characteristics. In case of linear least squares, parameters are independent of initial assumed data.

 (21)

where *A* is Nex*pxNexp* dimensional matrix, *A\** is matrix *A* evaluated at *k*\* which denotes optimal values of estimated parameters.

The joint confidence region (1-*α*)·100% for the parameter vector *k* is defined and described by next equation:28

 (22)

*α* is the probability level in Fisher’s F-distribution and  is obtained from the F-distribution tables. Further, the corresponding (1-*α*)·100%marginal confidence interval for all parameter leads to following term:

 (23)

 is obtained from tables of Student’s T-distribution. In order to obtain the standard error  of parameter *ki* next relation has been applied:28

 (24)

In our approach there are a lot of data points, so we can take as the 95% confidence interval twice the standard error.

Densities of *n*–hexane, *n*–heptane, *n*–octane, toluene, dichloromethane and ethanol were calculated, in wide ranges of temperature between 288.15-413.15 K and pressure up to 60 MPa.5,24,25 Tests started from literature density values and the previously determined parameters.2,13 All of these compounds in our investigation were treated as non-associated..

The following equations for the absolute average percentage deviation, *AAD*, the percentage maximum deviation, *MD*, the average percentage deviation, *Bias*, and standard deviation, *sdev*, are used in order to compare obtained densities with values that were found in the literature:5,24

 (25)

 (26)

 (27)

 (28)

where *ρi*lit is density found in literature, *ρi* is calculation value obtained with new sets of parameters by CK-SAFT and PC-SAFT, *N* is a number of experimental data, and *m* denotes the number of parameters.5

RESULTS AND DISCUSSIONS

Densities of *n*–hexane, *n*–heptane, *n*–octane, toluene, dichloromethane and ethanol were calculated using parameters reported in literature8,14 in CK-SAFT and PC-SAFT equations of state and compared with previously published values of density measured in our laboratory5,24 showing not so good agreement. *AAD* obtained using CK-SAFT model with literature parameters14 were 5.42%, 6.96%, 7.61%, 5.68%, 1.63% and 23.66% while for PC-SAFT model using previously published parameters8,14 they were 0.54%, 0.51%, 0.57%, 0.49%, 155.66% and 115.71% for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol, respectively. The results obtained by PC-SAFT equation are rather satisfying, while the deviations obtained by CK-SAFT model are somewhat higher. The largest deviations are occurred predicting density at pressure around atmospheric, while both models gave very poor prediction of densities for dichloromethane and ethanol at whole studied temperature and pressure ranges.

The densities used in CK-SAFT and PC-SAFT models parameters optimization were measured under high pressure conditions using Anton Paar DMA HP measuring cell. The expanded uncertainty (k=2) of 0.8 kg·m-3 for density measurements in the temperature interval 288.15-363.15 K and 1.7 kg·m-3 at temperatures 373.15-413.15 K, was reported.24,31 The new sets of parameters for both models were evaluated by applying LSQR and SQP methods.

The initial values of CK-SAFT parameters are specified by Radosz for all components.14 However, PC-SAFT initial parameters values for *n*–hexane, *n*–heptane, *n*–octane and toluene are used from Gross and Sadowski.8 Segment numbers for dichloromethane and ethanol are taken from CK-SAFT model, because those values could not be found in literature. Based on derived values from CK-SAFT, the second two parameters were assumed and expressed by the following expressions:

 (29)

 (30)

Also, it is needed to obtain the inference regions for determined parameters using the Gauss-Newton method for linear approximation.

Results for CK-SAFT and PC-SAFT parameters and its marginal confidence intervals are listed in Tables I and II, respectively. Obtained values of parameters do not depend on initial assumptions.8,14 The marginal confidence intervals, *ci*, of parameters confirms good fit quality agreement with assumed values.

TABLE I: Parameters of CK-SAFT equation for pure substances

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Calculated values | | | | | | Literature values14 | | |
| Component | *mi* | *cimi* | *v∞*  / cm-3mol-1 | *civ∞*  /cm-3mol-1 | *u0k-1*  /K | *ciu0k-1*  /K | *mi* | *v∞*  / cm-3mol-1 | *u0k-1*  /K |
| *n*-hexane | 3.951 | ±0.064 | 17.455 | ±0.306 | 265.503 | ±1.914 | 4.724 | 12.475 | 202.720 |
| *n*-heptane | 4.415 | ±0.055 | 17.955 | ±0.238 | 278.237 | ±1.540 | 5.391 | 12.282 | 204.610 |
| *n*-octane | 4.894 | ±0.125 | 18.288 | ±0.517 | 287.493 | ±3.271 | 6.045 | 12.234 | 206.030 |
| Toluene | 3.358 | ±0.031 | 18.006 | ±0.183 | 340.456 | ±1.573 | 4.373 | 11.789 | 245.270 |
| Dichloro-  methane | 2.542 | ±0.014 | 13.489 | ±0.078 | 305.261 | ±0.851 | 3.114 | 10.341 | 253.030 |
| Ethanol | 1.341 | ±0.010 | 24.909 | ±0.181 | 453.894 | ±1.719 | 2.457 | 12.000 | 213.480 |

TABLE II: Parameters of PC-SAFT equation for pure substances

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | Calculated values | | | | | | Literature values10,14 | | |
| Component | | *mi* | | *cimi* | *σ*  / Ǻ | *ciσ*  / Ǻ | *εik-1*  /K | *ciεik-1*  / K | *mi* | *σ*  / Ǻ | *εik-1*  /K |
| *n*-hexane | 1.736 | | | ±0.023 | 3.886 | ±0.018 | 305.764 | ±2.115 | 3.05810 | 3.79810 | 236.77010 |
| *n*-heptane | 2.184 | | | ±0.032 | 3.755 | ±0.019 | 290.088 | ±2.153 | 3.48310 | 3.80510 | 238.40010 |
| *n*-octane | 2.583 | | | ±0.038 | 3.692 | ±0.019 | 282.321 | ±2.096 | 3.81810 | 3.83710 | 242.78010 |
| Toluene | 1.673 | | | ±0.017 | 3.731 | ±0.013 | 356.789 | ±1.822 | 2.81510 | 3.71710 | 285.69010 |
| Dichloro-methane | 1.000 | | | ±0.073 | 3.717 | ±0.099 | 389.312 | ±10.861 | 3.11414 | 2.17914 | 253.03014 |
| Ethanol | 1.000 | | | ±0.291 | 3.617 | ±0.385 | 416.042 | ±44.864 | 2.45714 | 2.28914 | 213.48014 |

Thus, optimized parameters were used in the process of density calculation. Densities of investigated pure substances were determined in broad ranges of temperature and pressure between 288.15-413.15 K and 0.1-60 MPa, respectively. These calculated values are shown in Tables SII and SIII for CK-SAFT and PC-SAFT model, respectively.

Comparisons of calculated data with literature values5,24 are presented by *AAD*, *MD*, *Bias* and *σ* in Table III showing very good agreement between these two data sets. The largest deviations are obtained predicting density at pressure around atmospheric and the worst agreement was observed for dichloromethane and ethanol. Furthermore, the largest deviations are reached for dichloromethane and ethanol. The reason for this is initial assumption that both components are non-associated so, therefore, the association contribution term to Helmholtz energy should be included to improve density prediction quality for these components. Therefore, for these components association contribution term to Helmholtz energy should be included to improve density prediction quality.

TABLE III: Comparison of obtained deviations (*AAD*, *MD*, *Bias*, *σ*) in the temperature range 288.15-413.15 K and pressure range 0.1-60 MPa

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | CK-SAFT | | | |  | PC-SAFT | | | |
| Component | *AA*D  /% | *MD*  /% | *Bias*  /% | *sdev*  /kgˑm-3 |  | *AAD*  /% | *MD*  /% | *Bias*  /% | *sdev*  /kgˑm-3 |
| *n*-hexane | 0.185 | 2.207 | -0.001 | 0.002 |  | 0.068 | 0.339 | 0.000 | 0.001 |
| *n*-heptane | 0.155 | 1.389 | -0.001 | 0.001 |  | 0.075 | 0.324 | 0.000 | 0.001 |
| *n*-octane | 0.143 | 1.145 | 0.000 | 0.001 |  | 0.076 | 0.295 | 0.001 | 0.001 |
| Toluene | 0.078 | 0.736 | 0.000 | 0.001 |  | 0.037 | 0.186 | 0.000 | 0.000 |
| Dichloromethane | 0.104 | 1.099 | 0.001 | 0.002 |  | 0.179 | 1.171 | 0.001 | 0.003 |
| Ethanol | 0.203 | 0.554 | 0.007 | 0.002 |  | 0.574 | 1.452 | 0.015 | 0.005 |

The estimated densities for *n*-hexane, *n*-heptane and *n*-octane at temperature 288.15 K for both models are presented graphically in Fig 1. PC-SAFT model shows slightly better agreement with experimental values than CK-SAFT what is also evident by the deviations given in Table III. On the other hand, CK-SAFT was more successful in predicting densities of both dichloromethane and ethanol (see Fig 2).



Fig 1. The comparison of calculated density data for (,, ––) *n*-hexane, (,, ---) *n*-heptane, (,, ···) *n*-octane and (▼, ∇, -·-) toluene for CK-SAFT, PC-SAFT models with experimental values at 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT, PC-SAFT and experimental values, respectively.



Fig 2. The comparison of calculated density data for (,, ––) dichloromethane and (,, --- ) ethanol for CK-SAFT, PC-SAFT models with experimental values at temperature of 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT, PC-SAFT and experimental values, respectively.

The abovementioned deviations between densities calculated using CK-SAFT and PC-SAFT model including literature parameters8,14 and literature density data5,24 are significantly higher than those obtained using CK-SAFT and PC-SAFT parameters optimized and presented here (Table III). This justifies the optimization of the new parameters of CK-SAFT and PC-SAFT models for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol performed in this paper.

Densities of the examined compounds were fitted to the modified Tammann-Tait equation, an empirical equation widely used for high pressure density correlation, and obtained comparison criteria were somewhat lower that those presented here, as expected.5,24 Although the densities calculated using CK-SAFT and PC-SAFT models with here optimized parameters deviate more from literature data5,24 than those obtained from the modified Tammann-Tait equation5,24, *AAD* values given in Table III are still acceptably low. However, bearing in mind physical meaning of parameters used in CK-SAFT and PC-SAFT models, they are preferable to empirical ones. Additionally, the advantage of SAFT models over the modified Tammann-Tait equation is lower number of required parameters, e. g. the modified Tammann-Tait equation requires nine parameters to estimate toluene density, while the CK-SAFT and PC-SAFT models require only three parameters.

CONCLUSION

CK-SAFT and PC-SAFT EOS were used for density modeling of six pure compounds over the temperature range from 288.15-413.15 K and pressure range from 0.1-60 MPa. New parameters of CK-SAFT and PC-SAFT models were calculated for *n*–hexane, *n*–heptane, *n*–octane, toluene, dichloromethane and ethanol using LSQR and SQP methods. In order to obtain more accurate values of parameters, the Gauss-Newton method for solving nonlinear least squares problem has been used. All compounds were treated as non-associating compounds.

The absolute average percentage deviations obtained by both applied models for hydrocarbon systems were excellent. On the other hand absolute average percentage deviations for dichloromethane and ethanol were higher, i.e. 0.104% and 0.203% for CK-SAFT model and 0.179% and 0.574% for PC-SAFT model, respectively. Higher deviations are probably caused by the assumption that dichloromethane and ethanol are non-associating compounds although they are capable to form homoassociates. The obtained model parameters are of practical importance for process industry, because they could be used to determine various thermodynamic properties.

Abbreviations

*A1, A2-Helmholtz free energy of first and second-order perturbation term, J*

*a-molar Helmholtz energy per mole of molecules, J/mol*

*ci-marginal confidence intervals*

*d-temperature-dependent segment diameter, Å*

*k-Boltzmann’s constant≈1.381·10-23 J/K*

*ki\*- optimal values of estimated parameters*

*ki-p dimensional vector of parameters, i=1,…p*

*M-molar mass, g/mol*

*mi- number of spherical segments*

*N-total number of molecules*

*P-pressure, MPa*

*Qi-reverse variance, m3/kg*

*R-gas constant, J/molK*

*r-radial distance between two segments, Å*

*sdev-standard deviation, kg/m3*

*T-temperature, K*

*u0/k-temperature-independent energy for CK-SAFT, K*

*u-temperature-dependent energy parameter, K*

*V-molar volume, m3/mol*

*xi-mole fraction of chains*

*- Greek letters*

*ε/k-temperature-independent energy parameter for PC-SAFT, K*

*η-reduced density*

*ν0-temperature-dependent segment volume, cm3/mol*

*ν∞- temperature-independent segment volume, cm3/mol*

*ρ-calculated density, kg/m3*

*ρj-molar density, mol/cm3*

*ρlit-literature density, kg/m3*

*σi-temperature-independent segment diameter, Å*

*σ-standard deviation, kg/m3*

*σε-variance=0.8 kg/m3*

SUPPLEMENTARY MATERIAL

SAFT equations and calculated density data for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol, applying CK-SAFT and PC-SAFT equations of state at temperatures 288.15-413.15 K and pressures up to 60 MPa, are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/.

*Acknowledgments:* This work is supported by Ministry of Education, Science, and Technological Development of the Republic of Serbia, under project OI 172063.

ИЗВОД

МОДЕЛОВАЊЕ ГУСТИНА ЧИСТИХ КОМПОНЕНАТА НА ВИСОКОМ ПРИТИСКУ ПРИМЕНОМ *CK-SAFT* И *PC-SAFT* ЈЕДНАЧИНА СТАЊА

ЈОВАНА М. ИЛИЋ ПАЈИЋ1, МИРКО З. СТИЈЕПОВИЋ2, ГОРИЦА Р. ИВАНИШ2, ИВОНА Р. РАДОВИЋ2, ЈАСНА Т. СТАЈИЋ-ТРОШИЋ1 И МИРЈАНА Љ. КИЈЕВЧАНИН2

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SAFT једначине стања се веома често користе за одређивање различитих термофизичких својстава, као и у описивању различитих равнотежа фаза. Да би се ови модели могли користити у циљу предвиђања термодинамичких величина неопходно је претходно одредити параметре модела.У овом раду су CK-SAFT и PC-SAFT једначине стања коришћене за одређивање густина чистих компонената у широком опсегу температура и притисака (288,15-413,15 K, односно 0,1-60 MPa). Прорачун густина *n*-хексана, *n*-хептана, *n*-октана, толуена, дихлорметана и етанола је извршен на високим притисцима са сетовима параметара одређених у овом раду помоћу наведених CK-SAFT и PC-SAFT модела. Коришћењем добијених параметара постигнути су веома добри резултати са средњим процентуалним грешкама мањим од 0,5%.

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