

1 **Modelling of pure components high pressures densities using**
2 **CK-SAFT and PC-SAFT equations**

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

20 *Keywords:* density; modelling; non-associative compounds; SAFT; CK-SAFT;
21 PC-SAFT.

22 INTRODUCTION

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

27 Density of a compound is an essential physical property required for solving
28 the engineering problems.^{3–5} To estimate the aforementioned thermo-physical
29 property many different thermodynamic models have been proposed. In this
30 paper, we applied the equations of state (EOS) based on the statistical associating
31 fluid theory (SAFT).^{6,7} The development of SAFT EOS started with publication
32 of Chapman *et al.*⁸ They used Wertheim's theory to develop the first SAFT

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33 mathematical model.^{9–12} This thermodynamic model has been very successful for
34 predicting phase behaviour of long chains molecules.¹³ Huang and Radosz
35 upgraded the original model developed by Chapman *et al.* by replacing the ori-
36 ginal dispersion term with the dispersion term proposed by Chen and Kreg-
37 lewski,^{8,14–16} the model was entitled as CK-SAFT.¹ Later, Gross and Sadowski
38 proposed the novel definition of the dispersion term, and the new model, named
39 PC-SAFT, was disclosed.⁸

40 In the SAFT approach the thermodynamic properties of molecules are def-
41 ined as a sum of diverse contributions of Helmholtz energy, related to different
42 interactions between molecule segments. The temperature dependent hard-sphere
43 and dispersion contributions are related to so-called Lennard–Jones segment.^{14,16}
44 The chain contribution refers to chain formation between segments.^{1,2,17} In cases
45 where hydrogen-bonding interactions exist the contribution term related to these
46 interactions should be included in the model. Different versions of described
47 model have been proposed including the original SAFT or simplified SAFT, *e.g.*,
48 the CK-SAFT, the LJ-SAFT, the soft-SAFT, the SAFT-VR and the PC-
49 -SAFT.^{1,8,14,16,18–23} The main difference between them lies primarily in the dis-
50 persion contribution term, which is shown in Table SI of the Supplementary
51 material to this work.¹ The same chain and association terms are utilized in all of
52 these versions. In case of the association contribution, various SAFT models
53 assume temperature-dependent or temperature-independent diameter and radial
54 distribution function. Temperature-dependent diameter is used in original SAFT,
55 CK-SAFT, but the temperature-independent parameter is applied in other ver-
56 sions of SAFT.

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

66 THERMODYNAMIC MODELING

67 The most used thermodynamic models are defined as so-called equations of state (EOS).⁶
68 Cubic EOS are dependent on critical properties of molecules such as critical temperature, cri-
69 tical pressure, critical volume, critical compressibility factor, etc. These values are very imp-
70 portant for the determination of thermodynamic properties. However, it is often difficult to
71 determine the critical values for some complex molecules, such as polymers, so the non-cubic
72 EOS are proposed.^{8,14} Non-cubic EOS, such as SAFT-family EOS, require parameters which
73 can be determined from liquid density and vapour pressure experimental data. These experi-

74 mental data can be easily measured. In order to characterize specific molecules using the
 75 SAFT approach, the Helmholtz free energy represents starting point. It is given as a sum of
 76 molecular contributions and can be applied to calculate important thermodynamic properties
 77 such as enthalpy, heat capacity, speed of sound, etc. The Helmholtz free energy strongly
 78 depends on SAFT parameters and molecular density.

79 *SAFT concept*

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

$$85 \quad a^{\text{res}} = a^{\text{hs}} + a^{\text{disp}} + a^{\text{chain}} + a^{\text{assoc}} \quad (1)$$

86 where a denotes the Helmholtz free energy per mole and superscripts res, hs, disp, chain and
 87 assoc indicate residual, hard-sphere, dispersion reference, chain formation and association,
 88 respectively.^{1,2}

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

$$90 \quad \frac{a^{\text{hs}}}{RT} = m_i \frac{4\eta - 3\eta^2}{(1-\eta)^2} \quad (2)$$

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

$$94 \quad \eta = \tau \rho m_i v^0 \quad (3)$$

95 where $\tau = 0.74048$, ρ is the molar density and v^0 is temperature-dependent close-packed seg-
 96 ment molar volume which is described applying the temperature-independent segment volume
 97 v^∞ (the second parameter of CK-SAFT model).¹⁴

$$98 \quad v^0 = v^\infty \left[1 - 0.12 \exp \left[\frac{-3u^0}{kT} \right] \right]^3 \quad (4)$$

99 and u^0/k is a temperature-independent energy parameter which represents the third parameter
 100 of CK-SAFT model to be optimized.

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

$$102 \quad a^{\text{hs}} = \frac{1}{\zeta_0} \left[\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right] \quad (5)$$

103 where

$$104 \quad \zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n, \quad n \in \{0, 1, 2, 3\} \quad (6)$$

105 x_i denotes mole fraction of chains, and d_i is a temperature-dependent segment diameter.¹⁴

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

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

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$$110 \quad \frac{a^{\text{chain}}}{RT} = (1 - m_i) \ln \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (7)$$

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

$$112 \quad \frac{a^{\text{assoc}}}{RT} = \sum_i x_i \left[\sum_{A_i}^{M_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{1}{2} M_i \right] \quad (8)$$

113 where M_i is the number of association sites per molecules of component i , X^{A_i} is the fraction
114 of molecules not bonded at site A and $\sum_{A_i}^{M_i}$ denotes a sum of all associating sites on the
115 molecules.¹⁴ The mole fraction is determined according to the next expression:

$$116 \quad X^{A_i} = \left[1 + \sum_j \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \quad (9)$$

117 In Eq. (9) $\Delta^{A_i B_j}$ is the association strength between two sites A and B of different
118 molecules i and j . It can be calculated as follows:

$$119 \quad \Delta^{A_i B_j} = d_{ij}^3 g_{ij}^{\text{seg}} \kappa^{A_i B_j} \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{kT} \right) - 1 \right]; d_{ij} = \frac{1}{2} (d_i + d_j) \quad (10)$$

120 where $\varepsilon^{A_i B_j}$ is the association energy, $\kappa^{A_i B_j}$ is the association volume, g_{ij}^{seg} represents the
121 radial distribution function, and d_{ij} is the average segment diameter expressed by temperature-
122 dependent diameter for pure component i and j , respectively. The association energy and
123 association volume also represent two parameters that characterize SAFT EOS, but they are
124 needed only in case the molecule is self-associating.² Small differences in the calculation of
125 radial distribution function between CK-SAFT and PC-SAFT can be found in literature.¹

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

129 The main difference between CK-SAFT and PC-SAFT is defined with the dispersion
130 term (Supplementary material to this paper, Table S-I). The dispersion term in CK-SAFT can
131 be described using the equation proposed by Alder *et al.*:²⁷

$$132 \quad \frac{a^{\text{disp}}}{RT} = \sum_i \sum_j D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j \quad (11)$$

133 where D_{ij} are universal constants found in literature and u/k is expressed as:^{15,26}

$$134 \quad \frac{u}{k} = \frac{u^0}{k} \left(1 + \frac{e}{kT} \right) \quad (12)$$

135 e/k denotes the energy parameter with the constant value equals 10 with some exceptions.¹⁴

136 In PC-SAFT the dispersion contribution can be calculated as follows:

$$137 \quad \frac{a^{\text{disp}}}{kTN} = \frac{A_1}{kTN} + \frac{A_2}{kTN} = -2\pi\rho_j m_i^2 \left(\frac{\varepsilon}{kT} \right) \sigma^3 \int_1^\infty \hat{u}(x) g^{\text{hc}}(m_i; x \frac{\sigma}{d}) x^2 dx - \quad (13)$$

$$- \pi\rho_j m_i (1 + Z^{\text{hc}} + \rho_j \frac{\partial Z^{\text{hc}}}{\partial \rho_j})^{-1} m_i^2 \sigma^2 \left(\frac{\varepsilon}{kT} \right)^2 \frac{\partial}{\partial \rho_j} \left[\rho_j \int_1^\infty \hat{u}(x)^2 g^{\text{hc}}(m_i; x \frac{\sigma}{d}) x^2 dx \right]$$

138 where σ is the temperature independent diameter of segment which is the second parameter, x
 139 is the reduced radial distance around the segment, $\hat{u}(x)$ is the reduced potential function, and d
 140 denotes the temperature dependent segment diameter. The third parameter for PC-SAFT is ε/k
 141 that denotes the temperature independent energy parameter.

142 Accordingly, the described equations for pure, non-associated molecules are charac-
 143 terized by the set of three parameters for both models, the segment number (m_i), the segment
 144 volume (v^∞), and the segment energy (u^0/k), for CK-SAFT, and for PC-SAFT the segment
 145 number (m_i), the segment diameter (σ), and the segment energy (ε/k).

146 *Calculations*

147 The idea of this work was to calculate new parameters of CK-SAFT and PC-SAFT
 148 equations from the experimental density data^{5,24} and to compare it with the deviations
 149 obtained with the literature parameters.

150 The optimization problem is defined as a search for the parameter vector k that mini-
 151 mizes $f(k)$ by scheme:²⁸

$$152 \quad f(k) = \sum_{i=1}^{N_{\text{exp}}} e_i^T Q_i e_i \quad (14)$$

153 where $k = [k_1, k_2, \dots, k_p]^T$ is the N_{exp} -dimensional vector of parameters. $e = [e_1, e_2, \dots, e_m]^T$ is
 154 the m -dimensional vector of residuals where $e_i = [\hat{y}_i - f(x_i, k)]$ and in our work $Q_i = 1 / \sigma_\varepsilon^2$
 155 is the reverse variance. The expanded uncertainty of $0.8 \text{ kg} \cdot \text{m}^{-3}$ for density measurements by
 156 Anton Paar DMA HP measuring cell was taken as variance σ_ε .²⁴ In this investigation, the initial
 157 guesses for parameters ($k^{(0)}$), were taken from the literature.^{8,14} The parameters estimation
 158 was carried out from density data taken from the literature.^{5,24} Also, the objective function was
 159 established combining the developed Eq. (1) and the standard thermodynamic relation:²⁹

$$160 \quad P - \left(\frac{\partial a^{\text{res}}}{\partial V} \right)_T = 0 \quad (15)$$

$$161 \quad \frac{\partial a^{\text{res}}}{\partial V} = f(\rho, m_i, v^\infty, u^0 / k) \text{ for CK-SAFT} \quad (16)$$

$$162 \quad \frac{\partial a^{\text{res}}}{\partial V} = f(\rho, m_i, \sigma, \varepsilon / k) \text{ for PC-SAFT} \quad (17)$$

163 The objective function is defined as:

$$164 \quad f = \sum_{i=1}^N \frac{(\rho^{\text{lit}} - \rho)^2}{\sigma_\varepsilon^2} \quad (18)$$

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

$$166 \quad \begin{aligned} \Omega_{\text{CK-SAFT}} = P - \left(\frac{\partial a^{\text{res}}}{\partial V} \right)_T = P - f(\rho, m_i, v^\infty, u^0 / k) = & \varphi_{14}(m_i, v^\infty, u^0 / k) \rho^{14} + \\ & + \varphi_{13}(m_i, v^\infty, u^0 / k) \rho^{13} + \varphi_{12}(m_i, v^\infty, u^0 / k) \rho^{12} + \varphi_{11}(m_i, v^\infty, u^0 / k) \rho^{11} + \\ & + \varphi_{10}(m_i, v^\infty, u^0 / k) \rho^{10} + \varphi_9(m_i, v^\infty, u^0 / k) \rho^9 + \varphi_8(m_i, v^\infty, u^0 / k) \rho^8 + \\ & + \varphi_7(m_i, v^\infty, u^0 / k) \rho^7 + \varphi_6(m_i, v^\infty, u^0 / k) \rho^6 + \varphi_5(m_i, v^\infty, u^0 / k) \rho^5 + \\ & + \varphi_4(m_i, v^\infty, u^0 / k) \rho^4 + \varphi_3(m_i, v^\infty, u^0 / k) \rho^3 + \varphi_2(m_i, v^\infty, u^0 / k) \rho^2 + \\ & + \varphi_1(m_i, v^\infty, u^0 / k) \rho + \varphi_0(m_i, v^\infty, u^0 / k) = 0 \end{aligned} \quad (19)$$

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

$$\begin{aligned}
 \Omega_{\text{PC-SAFT}} = P - \left(\frac{\partial a^{\text{res}}}{\partial V} \right)_T = P - f(\rho, m_i, \sigma, \varepsilon / k) = & \varphi_{24}(m_i, \sigma, \varepsilon / k) \rho^{24} + \\
 & + \varphi_{23}(m_i, \sigma, \varepsilon / k) \rho^{23} + \varphi_{22}(m_i, \sigma, \varepsilon / k) \rho^{22} + \varphi_{21}(m_i, \sigma, \varepsilon / k) \rho^{21} + \\
 & + \varphi_{20}(m_i, \sigma, \varepsilon / k) \rho^{20} + \varphi_{19}(m_i, \sigma, \varepsilon / k) \rho^{19} + \varphi_{18}(m_i, \sigma, \varepsilon / k) \rho^{18} + \\
 168 & + \varphi_{17}(m_i, \sigma, \varepsilon / k) \rho^{17} + \varphi_{16}(m_i, \sigma, \varepsilon / k) \rho^{16} + \varphi_{15}(m_i, \sigma, \varepsilon / k) \rho^{15} + \\
 & + \varphi_{14}(m_i, \sigma, \varepsilon / k) \rho^{14} + \varphi_{13}(m_i, \sigma, \varepsilon / k) \rho^{13} + \varphi_{12}(m_i, \sigma, \varepsilon / k) \rho^{12} + \varphi_{11}(m_i, \sigma, \varepsilon / k) \rho^{11} + \\
 & + \varphi_{10}(m_i, \sigma, \varepsilon / k) \rho^{10} + \varphi_9(m_i, \sigma, \varepsilon / k) \rho^9 + \varphi_8(m_i, \sigma, \varepsilon / k) \rho^8 + \varphi_7(m_i, \sigma, \varepsilon / k) \rho^7 + \\
 & + \varphi_6(m_i, \sigma, \varepsilon / k) \rho^6 + \varphi_5(m_i, \sigma, \varepsilon / k) \rho^5 + \varphi_4(m_i, \sigma, \varepsilon / k) \rho^4 + \varphi_3(m_i, \sigma, \varepsilon / k) \rho^3 + \\
 & + \varphi_2(m_i, \sigma, \varepsilon / k) \rho^2 + \varphi_1(m_i, \sigma, \varepsilon / k) \rho + \varphi_0(m_i, \sigma, \varepsilon / k) = 0
 \end{aligned} \tag{20}$$

169 In this paper two optimization approaches were applied, the unconstrained least squares
 170 trust region (LSQR) and the constrained sequential quadratic programming (SQP).³⁰ They
 171 were used to minimize the objective function, Eq. (18), by adjusting the values of parameters.
 172 Both methods gave results in a good agreement with selected literature density values^{5,24} but
 173 the results obtained applying LSQR method were slightly better, so they were presented in
 174 Tables I and II.

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

$$180 \quad A = \sum_{i=1}^N \left(\frac{\partial f}{\partial k} \right)^T \frac{1}{\sigma_\varepsilon^2} \left(\frac{\partial f}{\partial k} \right) \tag{21}$$

181 where A is $N_{\text{exp}} \times N_{\text{exp}}$ dimensional matrix, A^* is matrix A evaluated at k^* which denotes the
 182 optimal values of estimated parameters.

183 The joint confidence region $(1-\alpha) \times 100$ % for the parameter vector k is defined and
 184 described by next equation:²⁸

$$185 \quad [k - k^*]^T [A^*]^{-1} [k - k^*] = \frac{pf(k^*)}{Nm - p} F_{p, Nm-p}^\alpha \tag{22}$$

186 α is the probability level in Fisher's F -distribution and $F_{p, Nm-p}^\alpha$ is obtained from the F -dis-
 187 tribution tables. Further, the corresponding $(1-\alpha) \times 100$ % marginal confidence interval for all
 188 parameter leads to the following term:

$$189 \quad k_i^* - t_{0.5\alpha}^V \hat{\sigma}_{ki} \leq k_i \leq k_i^* + t_{0.5\alpha}^V \hat{\sigma}_{ki} \tag{23}$$

190 $t_{0.5\alpha}^V$ is obtained from tables of Student's T-distribution. In order to obtain the standard error
 191 ($\hat{\sigma}_{ki}$) of parameter k_i the next relation has been applied:²⁸

$$192 \quad \hat{\sigma}_{ki} = \hat{\sigma}_\varepsilon \sqrt{\left\{ [A^*]^{-1} \right\}_{ii}} \tag{24}$$

193 Densities of n -hexane, n -heptane, n -octane, toluene, dichloromethane and ethanol were cal-
 194 culated, in wide ranges of temperature between 288.15–413.15 K and pressures up to 60

195 MPa.^{5,24} The tests started from the literature density values and the previously determined
 196 parameters.^{2,13} All of these compounds in our investigation were treated as non-associated.

197 The following equations for the absolute average percentage deviation (*AAD*), the per-
 198 centage maximum deviation (*MD*), the average percentage deviation (*Bias*), and standard
 199 deviation (*sdev*) are used in order to compare the obtained densities with values that were
 200 found in the literature:^{5,24}

$$201 \quad AAD = \frac{100}{N} \sum_{i=1}^N \left| \frac{\rho_i^{\text{lit}} - \rho_i}{\rho_i^{\text{lit}}} \right| \quad (25)$$

$$202 \quad MD = \max \left(100 \left| \frac{\rho_i^{\text{lit}} - \rho_i}{\rho_i^{\text{lit}}} \right| \right), i = 1, \dots, N \quad (26)$$

$$203 \quad Bias = \frac{100}{N} \sum_{i=1}^N \frac{\rho_i^{\text{lit}} - \rho_i}{\rho_i^{\text{lit}}} \quad (27)$$

$$204 \quad sdev = \sqrt{\frac{\sum_{i=1}^N (\rho_i^{\text{lit}} - \rho_i)^2}{N - m}} \quad (28)$$

205 where ρ_i^{lit} is the density found in literature, ρ_i is the calculation value obtained with the new
 206 sets of parameters by CK-SAFT and PC-SAFT, N is a number of experimental data, and m
 207 denotes the number of parameters.

208 RESULTS AND DISCUSSIONS

209 The densities of *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane
 210 and ethanol were calculated using the parameters reported in literature^{8,14} in CK-
 211 SAFT and PC-SAFT equations of state and compared with the previously pub-
 212 lished values of density measured in our laboratory^{5,24} showing not such a good
 213 agreement. *AAD* obtained using CK-SAFT model with the literature parameters¹⁴
 214 were 5.42, 6.96, 7.61, 5.68, 1.63 and 23.66 % while for PC-SAFT model using
 215 the previously published parameters^{8,14} they were 0.54, 0.51, 0.57, 0.49, 155.66
 216 and 115.71 % for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and
 217 ethanol, respectively. The results obtained by PC-SAFT equation are rather satis-
 218 fying, while the deviations obtained by CK-SAFT model are somewhat higher.
 219 The largest deviations occurred predicting the density at pressure around atmo-
 220 spheric, while both models gave very poor prediction of densities for dichloro-
 221 methane and ethanol at whole studied temperature and pressure ranges.

222 The densities used in CK-SAFT and PC-SAFT models parameters opti-
 223 mization were measured under high pressure conditions using Anton Paar DMA
 224 HP measuring cell. The expanded uncertainty ($k = 2$) of $0.8 \text{ kg} \cdot \text{m}^{-3}$ for density
 225 measurements in the temperature interval 288.15–363.15 K and $1.7 \text{ kg} \cdot \text{m}^{-3}$ at
 226 temperatures 373.15–413.15 K, was reported.^{5,24} The new sets of parameters for
 227 both models were evaluated by applying LSQR and SQP methods.

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

$$235 \quad \sigma = \sqrt[3]{v^\infty} \quad (29)$$

$$236 \quad \varepsilon_i/k = u^0/k \quad (30)$$

237 The results for CK-SAFT and PC-SAFT parameters and its marginal confi-
 238 dence intervals are listed in Tables I and II, respectively. The obtained values of
 239 parameters do not depend on initial assumptions.^{8,14} The marginal confidence
 240 intervals (*ci*) of parameters confirm good agreement with the assumed values.

241 TABLE I. Parameters of CK-SAFT equation for pure substances

| Component | Calculated values | | | | | Literature values ¹⁴ | | | |
|----------------------|-------------------|-----------|---|--|--------------|---------------------------------|-------|---|--------------|
| | m_i | ci_{mi} | v^∞ cm ³ mol ⁻¹ | ci_{v^∞} cm ³ mol ⁻¹ | u^0/k K | $ci_{u^0/k}$ K | m_i | v^∞ cm ³ mol ⁻¹ | u^0/k K |
| <i>n</i> -Hexane | 3.951 ±0.064 | | 17.455 | ±0.306 | 265.503 | ±1.914 | 4.724 | 12.475 | 202.720 |
| <i>n</i> -Heptane | 4.415 ±0.055 | | 17.955 | ±0.238 | 278.237 | ±1.540 | 5.391 | 12.282 | 204.610 |
| <i>n</i> -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 |

242 TABLE II. Parameters of PC-SAFT equation for pure substances

| Component | Calculated values | | | | | Literature values ^{8,14} | | | |
|----------------------|-------------------|-----------|---------------|------------------|------------------------|-----------------------------------|---------------------|---------------------|------------------------|
| | m_i | ci_{mi} | σ Å | ci_σ Å | ε_i/k K | $ci_{\varepsilon_i/k}$ K | m_i | σ Å | ε_i/k K |
| <i>n</i> -Hexane | 1.736 ±0.023 | | 3.886 ±0.018 | | 305.764 | ±2.115 | 3.058 ⁸ | 3.798 ⁸ | 236.770 ⁸ |
| <i>n</i> -Heptane | 2.184 ±0.032 | | 3.755 ±0.019 | | 290.088 | ±2.153 | 3.483 ⁸ | 3.805 ⁸ | 238.400 ⁸ |
| <i>n</i> -Hectane | 2.583 ±0.038 | | 3.692 ±0.019 | | 282.321 | ±2.096 | 3.818 ⁸ | 3.837 ⁸ | 242.780 ⁸ |
| Toluene | 1.673 ±0.017 | | 3.731 ±0.013 | | 356.789 | ±1.822 | 2.815 ⁸ | 3.717 ⁸ | 285.690 ⁸ |
| Dichloro- methane | 1.000 ±0.073 | | 3.717 ±0.099 | | 389.312 | ±10.861 | 3.114 ¹⁴ | 2.179 ¹⁴ | 253.030 ¹⁴ |
| Ethanol | 1.000 ±0.291 | | 3.617 ±0.385 | | 416.042 | ±44.864 | 2.457 ¹⁴ | 2.289 ¹⁴ | 213.480 ¹⁴ |

243 Thus, the optimized parameters were used in the process of density cal-
 244 culation. The densities of investigated pure substances were determined in broad
 245 ranges of temperature and pressure between 288.15–413.15 K and 0.1–60 MPa,
 246 respectively. The comparisons of calculated data with the literature values^{5,24} are

247 presented by *AAD*, *MD*, *Bias* and *sdev* in Table III showing very good agreement
 248 between these two data sets. The largest deviations are obtained predicting the
 249 density at pressure around atmospheric and the worst agreement was observed
 250 for dichloromethane and ethanol. The reason for this is the initial assumption that
 251 both components are non-associated so, therefore, the association contribution
 252 term to Helmholtz energy should be included to improve the density prediction
 253 quality for these components.

254 TABLE III. Comparison of obtained deviations (*AAD*, *MD*, *Bias* and *sdev*) in the temperature
 255 range 288.15–413.15 K and pressure range 0.1–60 MPa

| Component | CK-SAFT | | | | PC-SAFT | | | |
|-------------------|-----------------|----------------|------------------|-----------------------------------|-----------------|----------------|------------------|-----------------------------------|
| | <i>AAD</i> % | <i>MD</i> % | <i>Bias</i> % | <i>sdev</i> kg m ⁻³ | <i>AAD</i> % | <i>MD</i> % | <i>Bias</i> % | <i>sdev</i> kg m ⁻³ |
| <i>n</i> -Hexane | 0.185 | 2.207 | -0.001 | 0.002 | 0.068 | 0.339 | 0.000 | 0.001 |
| <i>n</i> -Heptane | 0.155 | 1.389 | -0.001 | 0.001 | 0.075 | 0.324 | 0.000 | 0.001 |
| <i>n</i> -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 |

256 The estimated densities for *n*-hexane, *n*-heptane and *n*-octane at temperature
 257 288.15 K for both models are presented graphically in Fig. 1. PC-SAFT model
 258 shows slightly better agreement with the experimental values than CK-SAFT

Comment [N2]: and toluene?

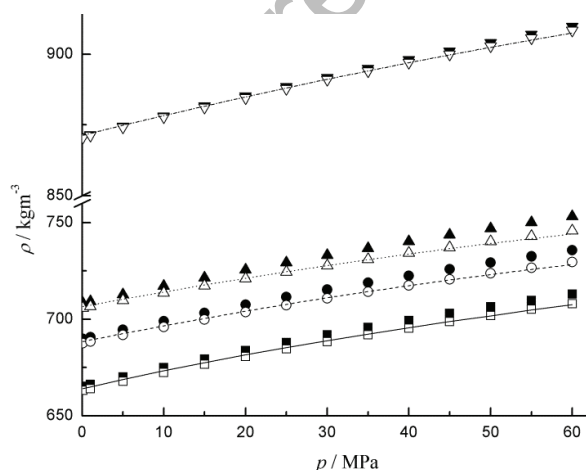
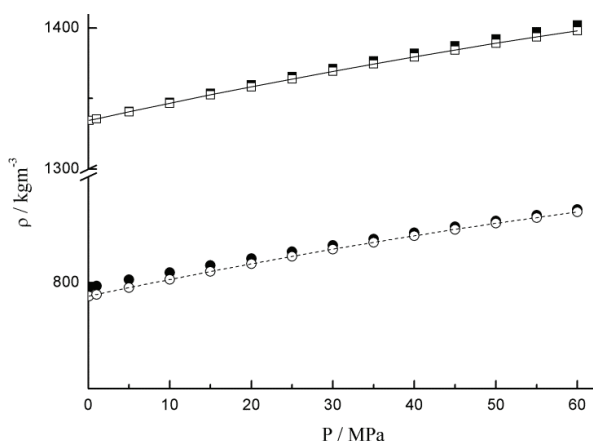


Fig. 1. The comparison of calculated density data for (■, □, —) *n*-hexane, (●, ○, ---) *n*-heptane, (▲, △, ···) *n*-octane and (▼, ▽, ···) toluene for CK-SAFT, PC-SAFT models with experimental values at 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT, PC-SAFT and experimental values, respectively.

259 what is also evident by the deviations given in Table III. On the other hand, CK-
 260 -SAFT was more successful in predicting densities of both dichloromethane and
 261 ethanol (see Fig. 2).



262
 263 Fig. 2. The comparison of calculated density data for (●, ○, —) dichloromethane and
 264 (■, □, ---) ethanol using CK-SAFT and PC-SAFT models with experimental values at
 265 temperature of 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT,
 266 PC-SAFT and experimental values, respectively.

267 The abovementioned deviations between densities calculated using CK-
 268 -SAFT and PC-SAFT models including the literature parameters^{8,14} and literature
 269 density data^{5,24} are significantly higher than those obtained using CK-SAFT and
 270 PC-SAFT parameters, optimized and presented here (Table III). This justifies the
 271 optimization of the new parameters of CK-SAFT and PC-SAFT models for
 272 *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol performed
 273 in this paper.

274 The densities of the examined compounds were fitted to the modified Tam-
 275 mann–Tait equation, an empirical equation widely used for high pressure density
 276 correlation, and the obtained comparison criteria were somewhat lower than those
 277 presented here, as expected.^{24,31} Although the densities calculated using CK-
 278 -SAFT and PC-SAFT models, with parameters optimized here, deviate more
 279 from the literature data^{5,24} than those obtained from the modified Tammann–Tait
 280 equation,^{24,31} *AAD* values given in Table III are still acceptably low. However,
 281 bearing in mind the physical meaning of parameters used in CK-SAFT and PC-
 282 -SAFT models, they are preferable to empirical ones. Additionally, the advantage
 283 of SAFT models over the modified Tammann–Tait equation is a lower number of
 284 required parameters, *e.g.*, the modified Tammann–Tait equation requires nine

285 parameters to estimate toluene density, while the CK-SAFT and PC-SAFT
286 models require only three parameters.

287 CONCLUSION

288 CK-SAFT and PC-SAFT EOS were used for the density modelling of six
289 pure compounds over the temperature range from 288.15–413.15 K and pressure
290 range from 0.1–60 MPa. New parameters of CK-SAFT and PC-SAFT models
291 were calculated for *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and
292 ethanol. All compounds were treated as non-associating compounds.

293 The absolute average percentage deviations, obtained by both applied
294 models for hydrocarbon systems, were excellent. On the other hand the absolute
295 average percentage deviations for dichloromethane and ethanol were higher
296 probably because of the assumption that dichloromethane and ethanol are non-
297 associating compounds, although they are capable to form homoassociates. The
298 obtained model parameters are of practical importance for process industry,
299 because they could be used to determine various thermodynamic properties.

300 ABBREVIATIONS

301 A_1, A_2 – Helmholtz free energy of first and second-order perturbation term, J

302 a – molar Helmholtz energy per mole of molecules, J/mol

303 ci – marginal confidence intervals

304 d – temperature-dependent segment diameter, Å

305 k – Boltzmann's constant $\approx 1.381 \times 10^{-23}$ J/K

306 k^* – optimal values of estimated parameters

307 k_i – p dimensional vector of parameters, $i = 1, \dots, p$

308 M – molar mass, g/mol

309 m_i – number of spherical segments

310 N – total number of molecules

311 P – pressure, MPa

312 Q_i – reverse variance, m³/kg

313 R – gas constant, J/(mol K)

314 r – radial distance between two segments, Å

315 $sdev$ – standard deviation, kg/m³

316 T – temperature, K

317 u^0/k – temperature-independent energy for CK-SAFT, K

318 u – temperature-dependent energy parameter, K

319 V – molar volume, m³/mol

320 x_i – mole fraction of chains

321 *Greek letters*

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

323 η – reduced density

324 v^0 – temperature-dependent segment volume, cm³/mol

325 v^∞ – temperature-independent segment volume, cm³/mol

326 ρ – calculated density, kg/m³

327 ρ^{lit} – literature density, kg/m³

Comment [N3]: Check please.

Comment [N4]: Check please.

328 σ – temperature-independent segment diameter, Å
 329 σ_c – variance

330 SUPPLEMENTARY MATERIAL

331 SAFT equations are available electronically at the pages of journal website: [http://](http://www.shd.org.rs/JSCS/)
 332 www.shd.org.rs/JSCS/, or from the corresponding author on request.

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 334 nological Development of the Republic of Serbia, under project OI 172063.

335 И З В О Д
 336 МОДЕЛОВАЊЕ ГУСТИНА ЧИСТИХ КОМПОНЕНАТА НА ВИСОКИМ ПРИТИСЦИМА
 337 ПРИМЕНОМ СК-SAFT И РС-SAFT ЈЕДНАЧИНА СТАЊА

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 339 ЈАСНА Т. СТАЈИЋ-ТРОШИЋ¹ И МИРЈАНА Љ. КИЈЕВЧАНИН²

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343 SAFT једначине стања се веома често користе за одређивање различитих термофи-
 344 зичких својстава, као и у описивању различитих равнотежа фаза. Да би се ови модели
 345 могли користити у предвиђању термодинамичких величина неопходно је претходно
 346 одредити параметре модела. У овом раду су коришћене СК-SAFT и РС-SAFT једначине
 347 стања за одређивање густина чистих компонената у широком опсегу температура и при-
 348 тисака (288,15–413,15 К, односно 0,1–60 МПа). Прорачун густина *n*-хексана, *n*-хептана,
 349 *n*-октана, толуена, дихлорметана и етанола је извршен на високим притисцима са сето-
 350 вима параметара одређених у овом раду помоћу наведених СК-SAFT и РС-SAFT модела.
 351 Коришћењем добијених параметара постигнути су веома добри резултати са апсолут-
 352 ним средњим процентуалним грешкама мањим од 0,5 %.

353 (Примљено 13. јуна, ревидирано 4. августа, прихваћено 7. августа 2017)

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Supplementary material

399

SUPPLEMENTARY MATERIAL TO

400

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

401

402

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407

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408

TABLE S-I. Equations for the dispersion term (a^{disp}) used in different SAFT equations

| Original SAFT | |
|--|--|
| $a_0^{\text{disp}} = \frac{\varepsilon R}{k} (a_{01}^{\text{disp}} + \frac{a_{02}^{\text{disp}}}{T_R}); T_R = kT / \varepsilon; \rho_R = [6 / (2^{0.5} \pi)] \eta$ | |
| $a_{01}^{\text{disp}} = \rho_R [-0.85959 - 4.5424 \rho_R - 2.1268 \rho_R^2 + 10.285 \rho_R^3]$ | |
| $a_{02}^{\text{disp}} = \rho_R [-1.9075 + 9.9724 \rho_R - 22.216 \rho_R^2 + 15.904 \rho_R^3]$ | |
| CK-SAFT | |
| $\frac{a_0^{\text{disp}}}{RT} = \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j$ | |
| $u = u^0 (1 + e / kT); e / k = 10; \tau = 0.74048$ | |

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409 TABLE S-I. Continued

| SAFT-VR | |
|---|--|
| $a^{disp} = \frac{a_1}{kT} + \frac{a_2}{(kT)^2}$ | |
| $a_1 = -\rho_s \sum_i \sum_j x_{s,i} x_{s,j} \alpha_{ij}^{VDW} g^{HS}[\sigma_x; \zeta_x^{eff}]$ | |
| $a_2 = \sum_{i=1}^n \sum_{j=1}^n x_{s,i} x_{s,j} \frac{1}{2} K_{HS} \varepsilon_{ij} \rho_s \frac{\partial a_1}{\partial \rho_s}$ | |
| $\alpha_{ij}^{VDW} = 2\pi \varepsilon_{ij} \sigma_{ij}^3 (\lambda_{ij}^3 - 1) / 3; \zeta_x^{eff} = c_1 \zeta_x + c_2 \zeta_x^2 + c_3 \zeta_x^3$ | |
| $\sigma_x^3 = \sum_i \sum_j x_{s,i} x_{s,j} \sigma_{ij}^3; \zeta_x = \frac{\pi}{6} \rho_s \sigma_x^3$ | |
| $K_{HS} = \frac{\zeta_0 (1 - \zeta_3)^4}{\zeta_0 (1 - \zeta_3)^2 + 6 \zeta_1 \zeta_2 (1 - \zeta_3) + 9 \zeta_2^3}$ | |
| PC-SAFT | |
| $\frac{a^{disp}}{kTN} = \frac{A_1}{kTN} + \frac{A_2}{kTN}$ | |
| $\frac{A_1}{kTN} = -2\pi \rho m^2 \left(\frac{\varepsilon}{kT}\right) \sigma^3 \int_1^\infty \tilde{u}(x) g^{hc}(m; x\sigma / d) x^2 dx$ | |
| $\frac{A_2}{kTN} = -\pi \rho m (1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho})^{-1} m^2 \left(\frac{\varepsilon}{kT}\right)^2 \sigma^3 \cdot$ | |
| $\cdot \frac{\partial}{\partial \rho} \left[\rho \int_1^\infty \tilde{u}(x)^2 g^{hc}(m; x\sigma / d) x^2 dx \right]$ | |
| $x = r / \sigma; \tilde{u}(x) = u(x) / \varepsilon$ | |