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Modelling 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 use these equations as predictive models it is necessary to calculate the 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). The calculations 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; modelling; non-associative compounds; SAFT; CK-SAFT; PC-SAFT.

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 the engineering problems.^{3–5} To estimate the aforementioned thermo-physical property many different thermodynamic models have been proposed. In this paper, we applied the equations of state (EOS) based on the statistical associating fluid theory (SAFT).^{6,7} The development of SAFT EOS started with publication

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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 behaviour of long chains molecules.¹³ Huang and Radosz upgraded the original model developed by Chapman *et al.* by replacing the original dispersion term with the 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 the dispersion term, and the new model, named PC-SAFT, was disclosed.⁸

In the SAFT approach the thermodynamic properties of molecules are defined as a sum of diverse contributions of Helmholtz energy, related to different interactions between molecule segments. The temperature dependent hard-sphere and dispersion contributions are related to so-called Lennard–Jones segment.^{14,16} The chain contribution refers to chain formation between segments.^{1,2,17} In cases where hydrogen-bonding interactions exist the contribution term related to these interactions should be included in the 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 shown in Table SI of the Supplementary material to this work.¹ The same chain and association terms are utilized in all of these versions. In case of the 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 the most reliable and commonly used in the literature. In the second step, new sets of parameters of CK-SAFT and PC-SAFT EOS were estimated using the previously published values of density in the broad ranges of temperature and pressure (288.15–413.15 K and 0.1–60 MPa, respectively).^{5,24} The new sets of parameters considerably improved the density estimations.

THERMODYNAMIC MODELING

The most used thermodynamic models are defined as so-called equations of state (EOS).⁶ Cubic EOS 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, require parameters which

can be determined from liquid density and vapour pressure experimental data. These experimental data can be easily measured. In order to characterize specific molecules using the SAFT approach, the Helmholtz 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 energy strongly depends on SAFT parameters and molecular density.

SAFT concept

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

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

where a denotes the Helmholtz 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

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

m_i 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 and η denotes the reduced density. η can be described by the following equation:²⁶

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

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

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

and u^0/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:

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

where

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

x_i denotes mole fraction of chains, and d_i 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:

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

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

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

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

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

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

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

where $\varepsilon^{A_i B_j}$ is the association energy, $\kappa^{A_i B_j}$ is the association volume, $g_{ij}(d_{ij})^{\text{seg}}$ represents the radial distribution function, and d_{ij} 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 the investigated compounds were observed as pure, non-associated, which further implied that the associative contribution has been neglected.

The main difference between CK-SAFT and PC-SAFT is defined with the dispersion term (Supplementary material to this paper, Table S-1). The dispersion term in CK-SAFT can be described using the equation proposed by Alder *et al.*:²⁷

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

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

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

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

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

$$\begin{aligned} \frac{a^{\text{disp}}}{kTN} = \frac{A_1}{kTN} + \frac{A_2}{kTN} = & -2\pi\rho_j m_i^2 \left(\frac{\varepsilon}{kT}\right) \sigma^3 \int_1^\infty \tilde{u}(x) g^{\text{hc}}(m_i; x \frac{\sigma}{d}) x^2 dx - \\ & -\pi\rho_j m_i (1 + Z^{\text{hc}} + \rho_j \frac{\partial Z^{\text{hc}}}{\partial \rho_j})^{-1} m_i^2 \sigma^2 \left(\frac{\varepsilon}{kT}\right)^2 \frac{\partial}{\partial \rho_j} \left[\rho_j \int_1^\infty \tilde{u}(x)^2 g^{\text{hc}}(m_i; x \frac{\sigma}{d}) x^2 dx \right] \end{aligned} \quad (13)$$

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

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

Calculations

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

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

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

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

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

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

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

The objective function is defined as:

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

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

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

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

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

In this paper two optimization approaches were applied, the unconstrained least squares trust region (LSQR) and the constrained sequential quadratic programming (SQP).³⁰ They were used to minimize the objective function, Eq. (18), by adjusting the values of parameters. Both methods gave results in a good agreement with selected literature density values^{5,24} but the 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 the estimates of the standard error in the parameters.²⁸ Applying the described method to search for the best parameter values, the model equations are linearized, so our parameters data have linear least squares characteristics. In the case of linear least squares, parameters are independent of the initial assumed data:

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

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

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

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

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

$$k_i^* - t_{0,5\alpha}^V \hat{\sigma}_{ki} \leq k_i \leq k_i^* + t_{0,5\alpha}^V \hat{\sigma}_{ki} \quad (23)$$

$t_{0,5\alpha}^V$ is obtained from tables of Student's T -distribution. In order to obtain the standard error ($\hat{\sigma}_{ki}$) of parameter k_i the next relation has been applied:²⁸

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

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 pressures up to 60

MPa.^{5,24} The tests started from the 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 the obtained densities with values that were found in the literature:^{5,24}

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

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

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

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

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

RESULTS AND DISCUSSIONS

The densities of *n*-hexane, *n*-heptane, *n*-octane, toluene, dichloromethane and ethanol were calculated using the parameters reported in literature^{8,14} in CK-SAFT and PC-SAFT equations of state and compared with the previously published values of density measured in our laboratory^{5,24} showing not such a good agreement. *AAD* obtained using CK-SAFT model with the literature parameters¹⁴ were 5.42, 6.96, 7.61, 5.68, 1.63 and 23.66 % while for PC-SAFT model using the previously published parameters^{8,14} 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 occurred predicting the 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 $0.8 \text{ kg}\cdot\text{m}^{-3}$ for density measurements in the temperature interval 288.15–363.15 K and $1.7 \text{ kg}\cdot\text{m}^{-3}$ at temperatures 373.15–413.15 K, was reported.^{5,24} 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 the 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 the derived values from CK-SAFT, the second two parameters were assumed and expressed by the following expressions:

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

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

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

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 |

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 |

Thus, the optimized parameters were used in the process of density calculation. The 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. The comparisons of calculated data with the literature values^{5,24} are

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

TABLE III. Comparison of obtained deviations (*AAD*, *MD*, *Bias* and *sdev*) in the temperature 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 |

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

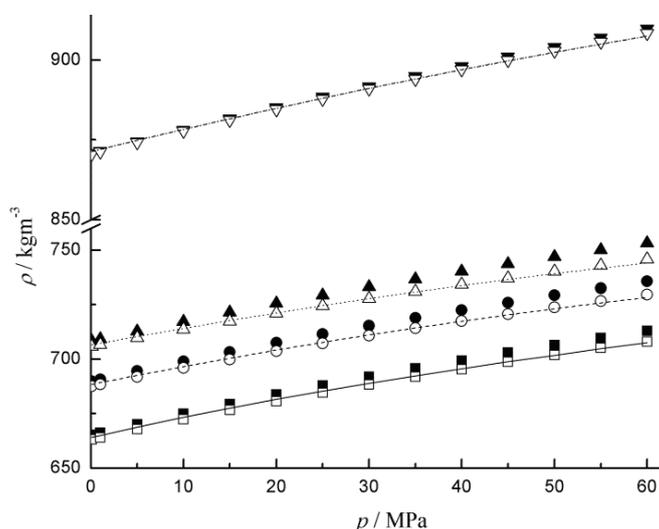


Fig. 1. The comparison of calculated density data for (■, □, —) *n*-hexane, (●, ○, ---) *n*-heptane, (▲, △, ···) *n*-octane and (▼, ▽, -.-) toluene for CK-SAFT, PC-SAFT models with experimental values at 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT, PC-SAFT and experimental values,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

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).

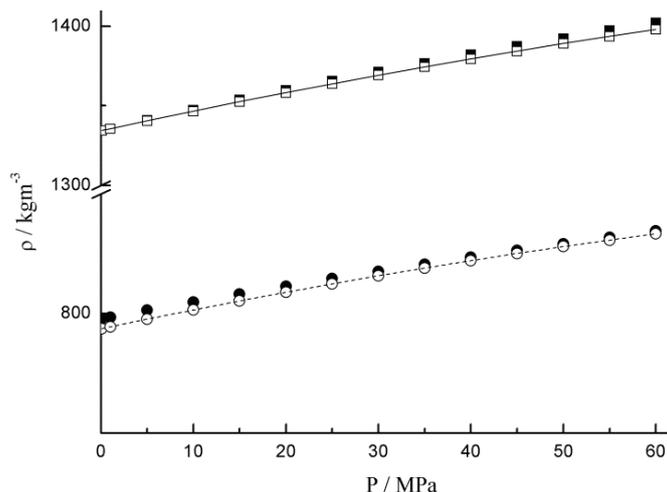


Fig. 2. The comparison of calculated density data for (●, ○, —) dichloromethane and (■, □, ---) ethanol using CK-SAFT and PC-SAFT models with experimental values at temperature of 288.15 K. Full symbols, empty symbols and lines denote CK-SAFT, PC-SAFT and experimental values, respectively.

The abovementioned deviations between densities calculated using CK-SAFT and PC-SAFT models including the literature parameters^{8,14} and literature density data^{5,24} 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.

The densities of the examined compounds were fitted to the modified Tammann–Tait equation, an empirical equation widely used for high pressure density correlation, and the obtained comparison criteria were somewhat lower than those presented here, as expected.^{24,31} Although the densities calculated using CK-SAFT and PC-SAFT models, with parameters optimized here, deviate more from the literature data^{5,24} than those obtained from the modified Tammann–Tait equation,^{24,31} *AAD* values given in Table III are still acceptably low. However, bearing in mind the 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 a 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 the density modelling 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. 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 the absolute average percentage deviations for dichloromethane and ethanol were higher probably because of 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

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

a – molar Helmholtz energy, J/mol

ci – marginal confidence intervals

d – temperature-dependent segment diameter, Å

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

k^* – optimal values of estimated parameters

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

M – molar mass, g/mol

m_i – number of spherical segments

N – total number of molecules

P – pressure, MPa

Q_i – reverse variance, m^3/kg

R – gas constant, J/(mol K)

r – radial distance between two segments, Å

$sdev$ – standard deviation, kg/m^3

T – temperature, K

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

u – temperature-dependent energy parameter, K

V – molar volume, m^3/mol

x_i – mole fraction of chains

Greek letters

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

η – reduced density

v^0 – temperature-dependent segment volume, cm^3/mol

v^∞ – temperature-independent segment volume, cm^3/mol

ρ – calculated density, kg/m^3

ρ^{lit} – literature density, kg/m^3

σ – temperature-independent segment diameter, Å
 σ_e – variance

SUPPLEMENTARY MATERIAL

SAFT equations are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

МОДЕЛОВАЊЕ ГУСТИНА ЧИСТИХ КОМПОНЕНАТА НА ВИСОКИМ ПРИТИСЦИМА ПРИМЕНОМ СК-SAFT И РС-SAFT ЈЕДНАЧИНА СТАЊА

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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 предвиђању термодинамичких величина неопходно је претходно одредити параметре модела. У овом раду су коришћене СК-SAFT и РС-SAFT једначине стања за одређивање густина чистих компонената у широком опсегу температура и притисака (288,15–413,15 К, односно 0,1–60 МПа). 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 СК-SAFT и РС-SAFT модела. Коришћењем добијених параметара постигнути су веома добри резултати са апсолутним средњим процентуалним грешкама мањим од 0,5 %.

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