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Manuscript title: “Modeling of pure components high pressures densities using CK-SAFT and PC-SAFT equations”

We wish to thank the Reviewers for their valuable comments that have helped us to improve our paper. We have carefully taken into account all of their comments.

Our point-by-point response to the reviewers is given below. The comments made by the reviewers are quoted in italics.

Response to reviewer’s comments:

**Reviewer A**

**Comment #1:**

*Line 69: Ref. 25 does not contain density experimental data of tested substances (probably ref. 5)*

**Response #1:** We would like to thank the reviewer for pointing out on this error. Due to the changes made in the Manuscript relating to the answer on Reviewers' comments, the order of reference list has been changed but the reference numbered 24 from the previous version of the Manuscript remained unchanged.

We made a change:

Old: In the second step, a new set of parameters of CK-SAFT and PC-SAFT EOS was estimated using previously published values of density in the broad range of temperatures and pressures (288.15-413.15 K, 0.1-60 MPa, respectively).24,25

New: In the second step, new sets of parameters of CK-SAFT and PC-SAFT EOS were estimated using previously published values of density in the broad ranges of temperature and pressure (288.15-413.15 K, 0.1-60 MPa, respectively).5,24

**Comment #2:**

*Lines 123-125, 155-156, 217: Three times was pointed out that ethanol and dichloromethane were treated as non-associating compounds even though they are not. Why?*

**Response #2:** The goal was to explore how CK-SAFT and PC-SAFT models behave when association term is not included into the model. Therefore, we are pointing out that these compounds are treated as non-associating, to explain the failure of model to accurate estimate components densities.

**Comment #3:**

*Line 149: Wrong ref. 25, probably ref. 5*

**Response #3:** We would like to thank the reviewer for pointing out on this error.

We made a change:

Old: Densities were calculated using parameters reported in literature8,14 and compared with previously published values of density measured in our laboratory.24,25

New: 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.

**Comment #4:**

*Line 150: Instead of ref. 5, probably equation (26)*

**Response #4:** We would like to thank reviewer for the suggested comment. However, in order to avoid equations citation prior to their introducing in the text, in the new version of the manuscript text that was previously given at the beginning of Calculation Section is moved to Results and discussions.

**Comment #5:**

*Line 220: Ref. 24 should be added, probably*

**Response #5:** To address reviewer’s very valid comment, Ref. 24 has been added.

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

New: 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

**Comment #6**:

*Line 228: Unnecessary citation (ref. 5)*

**Response #6:** To address reviewer’s very valid comment, Ref. 5 has been omitted from the mentioned sentence.

**Comment #7:**

*Line 252: Table II is not well-arranged*

**Response #7:** We would like to thank the reviewer for pointing out on this error. We changed Table II

**Comment #8:**

*Lines 256-257: It is not necessary to give calculated densities in Table SII and SIII, because the quality of estimations is presented in Table III*

**Response #8:** We would like to thank the reviewer for their constructive comment and Tables SII and SIII have been omitted from the Supplementary material.

**Comment #9:**

*REPORT: Calculated density data should be compared with calculated data using some empirical model such as Tobler (Ind.Eng.Chem.Res. 37,2565 (1998)) or TRIDEN (Ind.Eng.Chem.Res. 40,4470 (2001)) and underline EOS advantages relative to empirical models.*

**Response #9:** We are thankful for reviewer’s advice but correlation of density data using empirical model for studied compounds has been already done with modified Tammann-Tait equation in our previous papers, and our intention was to correlate the data by more theoretical procedure, using equations of state. This is clarified in the Results and discussions section:

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. 24,31 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 equation24,31, *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.

**Reviewer B:**

**Comment #1:**

*Line 98,99 The meaning of j is confusing. If j is component then should be ηj, or equation should be η=τρmiν0?*

**Response #1:** We would like to thank the reviewer for the constructive comment. We agree with above comment, the equation has been revised and corrected accordingly.

**Comment #2:**

*Line 93-105 Calculation of hard sphere term in PC-SAFT is undefined, only CK-SAFT is defined?*

**Response #2:** We would like to thank reviewer for comment. To address reviewer comment in Manuscript has been added the equation for hard-sphere term in PC-SAFT:

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

**Comment #3:**

*Line 109-110 Association term for pure components is calculated from In Equation 6. For mixtures (index i)?*

**Response #3:** The aim of our work was to investigate non-associating pure compounds. Dichloromethane and ethanol were treated as non-associative. So, mentioned equation was not use in our calculations. Equation was shown in order to explain the Helmholtz free energy and their contributions.

**Comment #4:**

*Line 111-113 “XAi is the fraction of molecules not bonded at site A and ΣAi denotes a sum of all associating sites on the molecules.”*

*Should be:*

*“for the component i, XAi is the fraction of molecules not bonded at site A and ∑Ai^Mi (upper bound Mi) denotes a sum of all associating sites on the molecules”?*

**Response #4:** To address reviewer’s very valid comment, the mentioned sentence has been changed as suggested.

**Comment #5:**

*Line 118-119 In Equation 8. explanation of dii and djj is missing?*

**Response #5:** To address reviewer’s very valid comment, the explanation for di and dj has been added into the text of the manuscript. In order to better understanding we made a change in index: dii to di, and djj to dj.

**Comment #6:**

*Line 136, Equation 11. ȗ (x) should be fixed.*

**Response #6:** We would like to thank the reviewer for pointing out on this error. We made a change according to instruction.

**Comment #7:**

*Line 162 Equation is confusing, upper bound for i is N, for k is p, and for e is m? Also the values of Qi and σε are 0.8 kg/m3, and Qi=1/σε^2?*

**Response #7:** We would like to thank reviewer for very valid comments. We agreed with above comment, so the upper bound of *i* is *Nexp*, for *k* is *p* and for *e* is *m*. Also the value of variance was 0.8kg/m3, but Qi=1/σε^2=1/0.8^2.

**Comment #8:**

*Line 200 In Equation 22., i=1 to N, and in text A is pxp dimensional matrix?*

**Response #8:** To address reviewer’s valid comment, in the following text has been changed error: A is a Nexp x Nexp dimensional matrix.

**Comment #9:**

*Line 217 At the end of line is “non-associated..” , should be “non-associated.”*

**Response #9:** We would like to thank the reviewer for pointing out on this error. We made a change.

**Comment #10:**

*Line 235-237 “The initial values for CK-SAFT are specified by Radosz for all components. However, PC-SAFT parameters values for n–hexane, n–heptane, n–octane and toluene are used from Gross and Sadowski.”*

*Should be:*

*“The initial parameters values for CK-SAFT are specified by Radosz for all components. However, PC-SAFT initial parameters values for n–hexane, n–heptane, n–octane and toluene are used from Gross and Sadowski.”*

**Response #10:** To address reviewer’s very valid comment, the pointed sentence has been changed as suggested.

**Comment #11:** *Line 252, Table Literature value for σ of dichloromethane should be 2.179 (σ=∛(v∞ ))*

**Response #11**: We would like to thank the reviewer for pointing out on this error. We made a change of table literature value for σ of dichloromethane.