Research paper

Observations regarding the first and second order thermodynamic derivative properties of non-polar and light polar fluids by perturbed chain-SAFT equations of state

Asma Jamali, Hassan Behnejad

Department of Physical Chemistry, School of Chemistry, University College of Science, University of Tehran, Tehran 14155, Iran

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ABSTRACT

This paper focuses on the second order derivative properties of some pure components, as the most significant challenges to develop the equations of states. For this reason, PC-SAFT equation of state has been used to predict derivative properties of n-alkanes, such as heat capacities, the speed of sound and Joule-Thomson coefficient in the wide temperature and pressure ranges up to 20 MPa. The performance of this model is evaluated against experimental data so that a good agreement with predicted properties can be observed except near the critical point and in some cases, near the coexistence phases. Furthermore, this study has tried to demonstrate the capability of polar sPC-SAFT equation of state to estimate the saturated pressure, liquid density and the speed of sound for light alcohols. Therefore, the system-dependent parameters of this model have been reassigned. The results have been compared with the available literature data and have shown a very good agreement.

1. Introduction

Today, thermodynamic models have various applications in the chemical engineering, physical sciences and biological processes. One of the main needs for the thermodynamic models is to provide not only accurate predictions on phase equilibria, but also accurate representation of derivative properties over wide temperature and pressure ranges simultaneously [1]. For example, the speed of sound as one of the derivative properties is important to connect the thermal and caloric properties in technical applications such as flow measurements. The speed of sound is also related with other thermodynamic properties such as density and heat capacities, and these properties are essential for the optimization of some industrial processes. Heat capacities are also necessary to calculate the caloric power of compounds in the chemical and oil industry. Besides the technological importance of these properties, the aim of accuracy in properties prediction without needing the experimental data for understanding the nature of molecular systems leads to their continued development and improvement of thermodynamic models. Also because of difficulty to predict and correlate some transport properties, the thermodynamic models can greatly affect the cost of process design.

One of the most important features of carbon-containing compounds, especially hydrogen-bonded systems, in chemical engineering design is dependency of their thermo-physical properties on temperature, such as density, speed of sound, viscosity and surface tension. Therefore, they have a great interest in refinery processes design. Since the second derivative properties (heat capacities, speed of sound, Joule-Thomson coefficient, etc.) can be obtained by the derivation of the first order thermodynamic properties (pressure, density, etc.) respect to the density and temperature, the second derivatives errors can be more sensitive to the accuracy in prediction of the first derivatives of thermodynamic properties. However, it has been observed that the same thermodynamic functions lead to an accuracy in predicting the first derivative properties and inaccurate result for the second derivative properties such as speed of sound [1-3]. In other words, it is not possible to describe the singularities observed in the second derivative properties such as heat capacity, isothermal compressibility, speed of sound and so on. Therefore, today, one of the most important challenges for developing equations of state (EoS) is the precise description of the second derivative thermodynamic properties [4].

Meanwhile, EoS as a mathematical model are rooted to the empirical observations, semi-empirical developments and statistical mechanics [5-8]. EoS are the analytical expressions relating the pressure to the volume and temperature used to describe the volumetric behavior, the VLE data, and the thermal properties of fluids. As it is clear, in the history of EoS, van der Waals equation of state (EoS) is the first Cubic EoS proposed to describe the quality of the thermodynamic
properties of real fluids, especially near the critical point [9]. The cubic EoS like Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) have been applied to model phase equilibrium data of a huge number of components but they cannot predict reliably the liquid density.

In recent years, besides the cubic EoS, Statistical Associating Fluid Theory (SAFT) and its variations, most remarkably and impressively, the Perturbed Chain-SAFT (PC-SAFT) EoS has been widely used in the engineering community categories [10–12]. SAFT-type EoS have terms, which take into account repulsion, attraction, chain and association forces; hence, they are more complicated to use rather than cubic EoS. SAFT parameters have a physical meaning coming from the strong theoretical background in statistical thermodynamics and they are based on accounting the size and shape of molecules. PC-SAFT EoS has already found widespread applications with great success in description of VLE and PVT data such as for alcohols and alkanes. Moreover, it presents definitely more consistent and better predictions of the density and the compressibility compared to the cubic EoS like PR or SRK, but their capability and limitation to predict the second derivative properties are more required to evaluate.

In order to evaluate the capability of PC-SAFT EoS to model the second derivative properties, Gross et al. [12,13] expressed that a very good agreement between the PC-SAFT EoS and the experimental data is found for predicting the heat capacity of some hydrocarbons; for instance, isobutene, propylene and 1-octane. Lafitte et al. [14] performed a comparative test between the PC-SAFT EoS and other versions of SAFT EoS to predict the isothermal compressibility, heat capacity and speed of sound for some long chain n-alkanes in the condensed liquid phase. Calculations are performed at the selected temperature, mentioning that there is no calculation near the critical point. The results revealed that SAFT-Type EoS give a slightly better prediction than the cubic EoS. On the other hand, they argued that some SAFT versions, for example PC-SAFT, fail to predict the speed of sound and isothermal compressibility. Liang et al. [15] used two strategies to improve PC-SAFT EoS for predicting the speed of sound of n-alkanes in the wide temperature and pressure range. In the first strategy, the speed of sound was included in the objective function to estimate the pure system dependent parameters, and in the second one, the universal constants in PC-SAFT EoS were estimated with the pure system dependent parameters simultaneously. They concluded that the second strategy could not only improve the speed of sound prediction, but also keep the accuracy for estimating the phase equilibria properties. Economou et al. [16] focused on the derivative properties of six fluids related to the Carbon Capture and Sequestration (CCS). They used the pure system dependent parameters fitted to VLE data to predict the second order derivative properties. They evaluated the performance of PC-SAFT EoS in the specified temperature and pressure ranges in CCS process and concluded that the EoS is in a good agreement with the experimental data except in the critical region.

In addition to the importance of predicting the thermodynamic properties of nonpolar fluids, the influence of polar charge distribution in polar and associating fluids as a long-range interaction remains challenging in determining thermophysical properties of alcohols. Many research works focused on developing SAFT-type EoS to take into account the effect of polar interactions for polar systems with high accuracy [13], Chapman et al. [17,18] extended SAFT EoS to dipolar chains with multiple dipolar sites by adding two more adjustable parameters in addition to other parameters in SAFT EoS as the functional group dipole moment and the fraction of dipolar segments per chain. This model was performed for many compounds such as ketones, ethers and polar polymers, it was found that the model generate high quality data. Economou et al. [16] used the proposed model by Nezbeda and Pavliček [19,20] to consider the dipolar interactions. According to Economou’s model [16] the reference term of Helmholtz free energy is divided into the short range terms and perturbation term is contributed to the dispersion forces and the dipole-dipole interaction. They extended the original SAFT and PC-SAFT EoS to polar fluids such as alcohols, ketones and water, and the results showed good agreements with the experimental data.

The purpose of this work is to check the capability of PC-SAFT EoS as a theoretical approach to predict the first and second order derivative properties of n-alkane series, such as heat capacities, the speed of sound and Joule-Thomson coefficient, over the wide temperature and pressure ranges up to 20 MPa to include the critical region. On the other hand, since predicting the thermophysical behavior of light alcohols, including methanol, ethanol and 1-propanol, is crucial in oil industry as interested fuels, we have tried to consider their thermodynamic properties (the first and second order derivative properties) by performing the polar simplified PC-SAFT (polar pSC-SAFT) EoS. This equation considered the influence of dipole-dipole interactions and hydrogen bonding to capture the entire thermodynamics including physical and chemical interactions properly. The goal of this part of our work is to improve the capability of polar pSC-SAFT EoS for predicting the speed of sound by putting the speed of sound experimental data together with the vapour pressure and liquid densities into the parameters estimation process. The model proposed by Economou et al. [16] has been used to consider the dipolar interactions of alcohols and it has been tried to reassign and modify the system dependent parameters. The predictive capability of this model was evaluated thoroughly for the saturated pressure, liquid density and speed of sound.

2. Thermodynamic model

2.1. PC-SAFT equation of state

The reduced Helmholtz free energy of a fluid in SAFT-type EoS is divided into two parts: an ideal gas part ($a^{\text{id}}$) and a residual part ($a^{\text{res}}$), as a function of the independent variables temperature and density [8,21]. One of the main differences between the original SAFT EoS and PC-SAFT EoS is the perturbation sequence. On the basis of Barker and Henderson perturbation theory [22,23], in PC-SAFT version, the residual part of Helmholtz free energy is written as the sum of hard-chain, dispersion and association contributions:

$$a^{\text{res}}(\rho, T) = \frac{A^{\text{id}}(\rho, T)}{RT} = a^{\text{hc}} + a^{\text{disp}} + a^{\text{assoc}} = (a^{\text{hs}} + a^{\text{chain}}) + a^{\text{disp}} + a^{\text{assoc}},$$

(1)

where $\rho$, $T$ and $R$ are the density, temperature and ideal gas constant, respectively. $a$ is the Helmholtz free energy and the subscripts $\text{res}$, $hc$, $disp$, $assoc$, $hs$ and chain refer to the residual, hard chain, dispersion, association, hard sphere (monomer reference fluid) and chain, respectively. In the SAFT-type EoS the chain and association terms remain unchanged, while different dispersion terms are proposed in various SAFT versions.

In PC-SAFT EoS the hard chain contribution is divided into two parts based on the first order perturbation theory, the hard sphere reference and chain terms. The hard chain term is defined as:

$$a^{\text{hc}} = n a^{\text{hs}} - \sum_i x_i (m - 1) \ln[g_i^{\text{hs}}(\rho_i)],$$

(2)

where $x_i$ is the mole fraction of component $i$, and $m = \sum_i x_i m_i$ and,

$$a^{\text{hs}} = \frac{1}{\xi_0} \left[ \frac{3 \xi_2}{\xi_3} + \frac{\xi_3^2}{(1 - \xi_3)^2} \right] \ln(1 - \xi_3),$$

(3)

$$g_i^{\text{hs}} = \frac{1}{1 - \xi_3} \left( \frac{d d_i}{d d_i + d_i} \right) \frac{\xi_3^2}{(1 - \xi_3)^2} \left( \frac{d d_i}{d d_i + d_i} \right) \frac{3 \xi_3^2}{(1 - \xi_3)^3}$$

(4)

where $\xi_3 = \pi \rho_i \sum_j x_j m_j d_j^2$, $k = 0, 1, 2, 3$

(5)

and
\[ d_i = \sigma_i [1 - 0.12 \exp(-3u_i/kT)] \]  

in which \( k \) is the Boltzmann constant.

The association term is calculated from the expression:

\[ a^{\text{assoc}} = \sum A \left( \ln X^A - \frac{X^A}{2} \right) + \frac{1}{2} M, \]  

where \( M \) is the number of association sites and \( X^A \) is the mole fraction of non-bonded sites defined as:

\[ X^A = \frac{1}{1 + N_{\text{int}} \sum \alpha^A \Delta^A}, \]  

in which \( \Delta^A \) is expressed as the strength of the bond between two sides as:

\[ \Delta^A = \sqrt{2} \mu^A \exp(\varepsilon^A/kT) - 1. \]

The dispersion term is written based on the second order perturbation theory:

\[ a^{\text{disp}} = -2 \pi \sigma I_m^2 \varepsilon^3 - \pi m \left( 1 + a^A + \frac{\partial a^A}{\partial \rho} \right) I_m^2 \varepsilon^2 \sigma^3, \]  

which depends on the integral of power series of the sixth order in density:

\[ I_1(\eta, m) = \sum_{i=0}^{6} a_i(m) \eta^i, \]  

\[ I_2(\eta, m) = \sum_{i=0}^{6} b_i(m) \eta^i, \]  

in which \( \eta = \xi^A \).

Detailed expressions of individual terms in Eqs. (1)–(12) can be found in referred literatures \[12,24\]. According to this thermodynamic model, and depending on non-associating or associating compound, three or five pure system-dependent parameters, respectively, are required to describe the phase behavior of each component. These parameters include \[25\]:

1. \( m \): the number of segments,
2. \( \sigma \): the diameter of each segment,
3. \( u/k \): the interaction between segments,
4. \( \varepsilon^A \): the association energy,
5. \( \kappa^A \): the effective association volume.

The last two parameters are required to describe an associating compound.

The other attractive force namely dipole-dipole interaction has not been considered originally in the SAFT-type EoS. Since the SAFT EoS is nothing more than a perturbation theory, this feature makes it possible to include intermolecular interactions in terms of the Helmholtz free energy in a straightforward manner. Therefore, the dipole-dipole interaction could be incorporated as a perturbation term to improve the predictive capability of SAFT EoS \[26\]. Consequently, to account the dipole-dipole interactions in polar systems, an additional perturbation term \( a^{\text{polar}} \) is added to Eq. (1) which is written in the Padé approximation form \[17,18,27\]:

\[ a^{\text{polar}} = \frac{\alpha^{\text{polar}}}{1 - \alpha^{\text{polar}}/\alpha^{\text{polar}}}, \]  

The dipolar terms of this simple model are suggested by Nezbeda and Pavlček \[19,20\], corresponding to:

\[ \alpha^{\text{polar}} = -\frac{4}{3} \left( \frac{\mu}{K T} \right)^2 \bar{\mu}^2 F_2, \]  

\[ F_2 = \frac{\eta^2}{K T}, \]  

where \( K = \sigma^0/\alpha \) is a short range cutoff introduced for the dipolar interactions \( \alpha_2 = \left[ \left( \frac{6 \xi}{\pi N_m} \right)^{1/3} \right] \). By adding Eq. (13) to Eq. (1), a new parameter will be required as the segment volume of dipole–dipole interactions \( \nu_{\text{dd}} \) to satisfy the description of dipolar interactions. The schematic description of polar PC-SAFT EoS has been shown in Fig. 1.

In turn, conversion of PC-SAFT EoS to the simplified version makes the computation of the derivatives in phase equilibria simpler and less
computational intensive for the hard sphere chain and the association terms. Hence, the modifications are presented as:

\[ \delta^h(\eta) = \frac{1 - \eta/2}{(1 - \eta)^2}, \]

\[ d^{hi} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2}. \]

\[ (19) \]

\[ (20) \]

2.2. The second derivative thermodynamic properties

The analytical expressions of the second order thermodynamic derivative properties can be implemented as derivatives of Helmholtz free energy with respect to density, \( \rho \), and temperature, \( T \), as the following equations [1,2,28,29]:

(a) Isochoric heat capacity:

\[ C_v(T, \rho) = C^{\text{ideal}}_v(T) + C^{\text{ex}}_v(T, \rho) = C^{\text{ideal}}_v(T) - T \left( \frac{\delta^2 a^{\text{ex}}(T, \rho)}{\delta T^2} \right)_\rho, \]

\[ (21) \]

(b) Isobaric heat capacity:

\[ C_p(\rho, T) = C^{\text{ideal}}_p(T) + C^{\text{ex}}_p(\rho, T), \]

\[ (22) \]

\[ C_p^{\text{ex}}(\rho, T) = C_v^{\text{ex}}(\rho, T) - \frac{T}{\rho^2} \left( \frac{\delta^2 P}{\delta T^2} \right)_\rho + R, \]

\[ (23) \]

(c) Speed of sound:

\[ \gamma = \sqrt{\frac{\rho}{M \cdot W}} \left( \frac{\partial P}{\partial \rho} \right)_T, \quad (\gamma = \frac{C_p}{C_v} \text{ and } M \cdot W = \text{Molecular Weight}) \]

\[ (24) \]

(d) Joule-Thomson coefficient:

\[ \mu_{JT} = T \left( \frac{\partial P}{\partial T} \right)_\rho - \rho \left( \frac{\partial P}{\partial \rho} \right)_T. \]

\[ (25) \]

Regarding the dependency of ideal terms on temperature, it affects calculating the isochoric and isobaric heat capacity directly and the speed of sound indirectly. Therefore, their ideal contributions were obtained from a complete data library [30].

3. Application to fluids

In this work, PC-SAFT EoS and polar sPC-PSAFT EoS are applied to numerous pure fluids, to non-associating and polar fluids including n-alkanes and light alcohols, respectively.

In the following, more detailed analysis of the model performance and the assessed parameter values will be mentioned for each of the studied fluids.
3.1. Pure n-Alkanes

In the present work, the predictive capability of PC-SAFT EoS on the estimation of the thermodynamic derivative properties for pure n-alkanes has been checked in the wide temperature ranges and pressures up to 20 MPa. We use Gross et al. [12] PC-SAFT parameters (m, σ, and u) as pure component parameters for alkanes given in Table 1. In Table 2, the results of PC-SAFT EoS analysis are provided for n-alkanes by reporting the Average Absolute Deviation (AAD%) of the second order derivative properties. The accuracy of PC-SAFT EoS results in predicting the isochoric and isobaric heat capacities and speed of sounds at subcritical and the supercritical conditions depicted by presenting contour plots of AAD% in Figs. 2–4. The accuracy in predicting the thermodynamic properties has been decreased by approaching the critical point, due to the basis of PC-SAFT EoS on the mean field theory, in which the critical fluctuations are neglected. Whereas by getting away from the critical region agreement between calculations and data taken from NIST [24] has been improved. However, the capability of PC-SAFT EoS in prediction of the second order derivative properties of light alkanes is stronger than the long chain hydrocarbons. It is inferred from Figs. 2–4 that the capability of PC-SAFT EoS decreased in the subcritical condition by increasing the number of carbons in hydrocarbon chains except for \( C_P \); although, the results are still reliable in comparison to the critical region.

The ideal heat capacity contribution of the fluids is determined from the Ref. [24] and the residual part is obtained from Eqs. (21)–(23). According to the Eq. (21), \( C_{im}^{res} \) is a function of temperature, and by approaching the critical point the deviation of predicting \( C_{im}^{res} \) increases, because the trend of PC-SAFT EoS is in the opposite of available correlated data, taken from NIST Chemistry Web Book in this region. The \( C_P \) is well described by PC-SAFT EoS and the relative \( C_P \) errors are less than 4% for all examined cases.

To further test the PC-SAFT EoS, we turned our attention to the speed of sound. As it can be seen in Table 2, the deviation of PC-SAFT EoS from experimental data to predict the speed of sound is at most 9.9% for Ethane. From Eq. (24), the accuracy of predicting the speed of sound depends on three portions: \( C_P, C_V \) and \( \frac{\partial P}{\partial V} \). By \( \gamma = C_P/C_V \) ratio, some errors will be canceled; hence, the errors of speed of sound is mainly controlled by the error in \( \frac{\partial P}{\partial V} \). Joule-Thomson coefficient is the last property examined here and presented in Fig. 5. While the pressure increases, the Joule-Thomson coefficient changes from positive to negative values and its deviation decreased. The higher deviations are at the lower pressures and close to the phase change. From Eq. (25) this fact has been deduced that this property depends on two partial derivatives, so the errors are probably additive, especially near the coexistence phases.

The accuracy of SAFT-type EoS for the prediction of the second derivative properties of pure fluids has been studied by many researchers such as Llovell and Vega (soft-SAFT EoS) [1], Kontogeorgis and co-workers (sPC-SAFT EoS) [24]. Nevertheless, due to the difference in fluids and conditions (i.e. temperature and pressure range) direct numerical comparing is not possible. Generally, PC-SAFT has been verified by the present work in predicting the second order derivative properties of pure fluids.
applied with the reasonably high accuracy in the wide temperature and pressure range for all the properties, except for the Joule-Thomson coefficient.

3.2. Pure light alcohols

Due to the importance of alcohols in the industrial chemical process as the organic solvents, accuracy in calculating their thermodynamic properties is very essential to process design. Since alcohols are a molecule containing an –OH group, with a hydrogen and two lone pairs of electron as requirements of hydrogen bond, two association scheme can be considered for this compounds-type, namely, 2B (one association site on oxygen and one site on hydrogen) and 3B (two association site on oxygen and one site on hydrogen). In this work, 2B scheme has been selected to evaluate the associating interactions in alcohols.

The intermolecular model parameters of these interest compounds-type have been determined with the performance of polar sPC-SAFT EoS for the speed of sound by fitting procedure to simultaneously available vapor-liquid and speed of sound experimental data. Therefore, in this work the following objective function is proposed to find the optimum value of six pure component parameters ($\mu_k$, $\nu^0$, $\varepsilon^{AB}$, $\chi^{AB}$ and $\nu^{dA}$).

\[
\text{Objective Function} = \sum_{i} \left( \frac{p^{\text{exp}}_{i} - p^{\text{calc}}_{i}}{p^{\text{calc}}_{i}} \right)^2 + \sum_{i} \left( \frac{\rho^{\text{exp}}_{i} - \rho^{\text{calc}}_{i}}{\rho^{\text{calc}}_{i}} \right)^2 + \sum_{i} \left( \frac{V^{\text{exp}}_{S,i} - V^{\text{calc}}_{S,i}}{V^{\text{calc}}_{S,i}} \right)^2
\]

where $P$, $\rho$, and $V_S$ are vapor pressure, liquid density, and speed of sound, respectively, and $N_p$ is total experimental points. The saturated
pressure and liquid density have been determined by DIPPR correlations [31]. As it is clear, equal weights for mentioned properties are used in this study. There are two challenges to estimate the parameters value, one of which is due to the multiplicity of parameters and the other one is because of the convergence of some parameters to unrealistic (with no physical meaning) values. The multiplicity in parameter sets leads to find several local minima and a unique solution may be obtained by a global optimization method. In the case of parameter estimation, the parameter values that are finally selected should satisfy their physical meaning. As it is clear, the resulting values to determine the values of the parameters depend on a priori conditions, and we need to estimate quantities.

The details of estimated parameters, temperature and pressure ranges for methanol, ethanol and propanol can be found in Table 3. To reduce the number of adjusted parameters, the \( \mu \) value is selected as the same value used by Economou et al. [16]. An optimum value of \( \nu_{dd} \) as a dipole-dipole interaction volume for ethanol was found completely different value in compare to the Economou et al. [16] to find better description for speed of sound. AAD\% between the available correlated data, taken from NIST Chemistry Web Book and polar sPC-SAFT EoS reported in Table 4. The speed of sound and saturated pressure diagrams of methanol and the counter plots of speed of sound for ethanol in the specified temperature and pressure range have been depicted in Figs. 6 and 7. In general, the more excellent agreement between the polar sPC-SAFT EoS predictions and data taken from NIST has been observed. The results showed that the association and polar terms play an important role to predict the speed of sound for light alcohols. However, the calculated speed of sound without considering it in objective function is not in high divergence but by improving the objective function the better coincidence with calculated speed of sound and correlated data of NIST can be observed. It is taken from the results in Table 4 that, AAD\% of saturated pressure and liquid density may be partially increased, but these results are comparable to those calculated by Economou et al. [16].

### Table 3

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( m )</th>
<th>( \nu^{\text{m}} ) (mol/ml)</th>
<th>( \nu/k ) (K)</th>
<th>( \varepsilon_{\text{AB}} ) (K)</th>
<th>( \kappa_{\text{AB}} )</th>
<th>( \mu ) (D)</th>
<th>( \nu_{dd} ) (mol/ml)</th>
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<tr>
<td>Methanol</td>
<td>1.743</td>
<td>12.5</td>
<td>180.45</td>
<td>2766.50</td>
<td>0.0499</td>
<td>1.70</td>
<td>44.2</td>
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<tr>
<td>In this work</td>
<td>1.4707</td>
<td>15.401</td>
<td>197.5</td>
<td>2976.712</td>
<td>0.02602</td>
<td>1.70</td>
<td>60.2</td>
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<tr>
<td>Ethanol</td>
<td>2.549</td>
<td>12.5</td>
<td>188.06</td>
<td>2635.77</td>
<td>0.0419</td>
<td>1.69</td>
<td>44.2</td>
</tr>
<tr>
<td>In this work</td>
<td>1.533</td>
<td>23.27</td>
<td>162.55</td>
<td>1574.80</td>
<td>0.0908</td>
<td>1.69</td>
<td>1.61</td>
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<tr>
<td>1-Propanol</td>
<td>3.442</td>
<td>12.5</td>
<td>224.75</td>
<td>2128.00</td>
<td>0.0171</td>
<td>1.68</td>
<td>44.2</td>
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<tr>
<td>In this work</td>
<td>2.855</td>
<td>15.034</td>
<td>248.07</td>
<td>1495.40</td>
<td>0.0065</td>
<td>1.68</td>
<td>45.79</td>
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### Table 4

<table>
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<th>Component</th>
<th>( P_{\text{sat}} )</th>
<th>( \rho_{\text{liq}} )</th>
<th>( T ) range (K)</th>
<th>( V_S )</th>
<th>( T ) range (K)</th>
<th>( P ) range (MPa)</th>
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<tr>
<td>Methanol</td>
<td>30.32</td>
<td>0.850</td>
<td>256–456</td>
<td>1.342</td>
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<td>0.1–50</td>
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<td>Ethanol</td>
<td>33,34</td>
<td>1.873</td>
<td>333–503</td>
<td>2.980</td>
<td>193.4–333.01</td>
<td>0.1–275.93</td>
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<tr>
<td>Propanol</td>
<td>35</td>
<td>1.423</td>
<td>427.75–536.83</td>
<td>3.82</td>
<td>2173.15–323.15</td>
<td>27.58–96.53</td>
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</table>

Fig. 6. (a) Saturated pressure (b) the speed of sound diagrams of Methanol, Solid lines are predictions in this work, dashed lines predictions by Economou et al. [16] predictions, and points are experimental data [30–32].

4. Conclusion

This study follows two goals, in the first one the performance of PC-
SAFT EoS is evaluated for the second derivative properties of fluids, such as heat capacities and speed of sound. In the next, it is tried to investigate the ability of polar sPC-SAFT EoS to predict the saturated pressure, liquid density and speed of sound of light alcohols by improving the objective function. The results reveal that the functional form of the PC-SAFT EoS is greatly important for developing an approach to predict the second derivative properties. Therefore, the inclusion of heat capacities and speed of sound data into the definition of the objective function for the pure component the polar sPC-SAFT could give satisfactory results.

Since alcohols contain a hydroxyl group for hydrogen bond formation, two additional terms have been considered in Helmholtz free energy, association term and dipolar term, in order to complete describing the interactions in the alcohols. Finally, the results of investigating methanol, ethanol and propanol indicates that by adding the speed of sound into the definition of the objective function for the pure component the polar sPC-SAFT could give satisfactory results.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cryogenics.2019.03.002.

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