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Application of Chebyshev Polynomials to Calculate Density and Fugacity Using SAFT Equation of State to Predict Asphaltene Precipitation Conditions

Seyyed Alireza Tabatabaei-Nejad and Elnaz Khodapanah
Chemical Engineering Department, Sahand University of Technology, Tabriz
Iran

1. Introduction

Equations of state are the essential tools to model physical and chemical processes in which fluids are involved. The majority of PVT calculations carried out for oil and gas mixtures are based on a cubic equation of state (EoS). This type of equations dates back more than a century to the famous Van der Waals equation (Van der Waals, 1873). The cubic equations of state most commonly used in the petroleum industry today are very similar to the Van der Waals equation, but it took almost a century for the petroleum industry to accept this type of equation as a valuable engineering tool. The Redlich and Kwong EoS (Redlich & Kwong, 1949) was modified from the VdW with a different attractive term, the repulsive term being the same. Since 1949 when Redlich and Kwong (RK) formulated their two-parameter cubic EoS, many investigators have introduced various modifications to improve ability of RK-EoS. Two other well-known cubic equations are Soave-Redlich-Kwong (SRK), (Soave, 1972) and Peng-Robinson (PR) (Peng & Robinson, 1976) equations which have different formulation of the attractive term and are popular in the oil industry in the thermodynamic modeling of hydrocarbon fluids.

There are thousands of cubic equations of states, and many noncubic equations. The noncubic equations such as the Benedict-Webb-Rubin equation (Benedict et al., 1942), and its modification by Starling (Starling, 1973) have a large number of constants; they describe accurately the volumetric behavior of pure substances. But for hydrocarbon mixtures and crude oils, because of mixing rule complexities, they may not be suitable (Katz & Firoozabadi, 1978). Cubic equations with more than two constants also may not improve the volumetric behavior prediction of complex reservoir fluids. In fact, most of the cubic equations have the same accuracy for phase behavior prediction of complex hydrocarbon systems; the simpler often do better (Firoozabadi, 1999).

Hydrocarbons and other non-polar fluid vapor–liquid equilibrium properties can be satisfactorily modeled using a symmetric approach to model both, the vapor and the liquid phase fugacity with the use of a Van der Waals type equation model (Segura et al., 2008), the Soave–Redlich–Kwong or Peng–Robinson equations being the most popular ones. When

polar fluids are involved at moderate pressures, activity coefficient models are more suitable for modeling the liquid phase. When a higher pressure range is also a concern, a symmetric EoS approach with complex mixing rules including an excess Gibbs energy term from an activity coefficient model can provide good results. Unfortunately, even those approaches show limitations for complex fluids and can drastically fail near the critical region, unless a specific treatment is included (Llovell et al., 2004, 2008).

Since the early 1980's, there has been increased interest in developing an EoS for pure fluids and mixtures of large polyatomic molecules that does not rely on a lattice description of molecular configurations. A rigorous statistical-mechanical theory for large polyatomic molecules in continuous space is difficult because of their asymmetric structure, large number of internal degrees of freedom, and strong coupling between intra- and intermolecular interactions. Nevertheless, a relatively simple model represents chain-like as freely joined tangent hard spheres (Chapman et al., 1984; Song et al., 1994; Wertheim, 1984). A hard-sphere-chain (HSC) EoS can be used as the reference system in place of the hard-sphere reference used in most existing equations of state for simple fluids. Despite their simplicity, hard-sphere-chain models take into account some significant features of real fluids containing chain-like molecules including excluded volume effects and chain connectivity. To describe the properties of fluids consisting of large polyatomic molecules, it is necessary to introduce attractive forces by adding a perturbation to a HSC EoS. Assuming that the influence of attractive forces on fluid structure is week, a Van der Waals type or other mean-field term (e.g. square-well fluids) is usually used to add attractive forces to the reference hard-sphere-chain EoS (Prausnitz & Tavares, 2004).

Molecular-based equations of state, also routed in statistical mechanics, retain their interest in chemical engineering calculations as they apply to a wide spectrum of thermodynamic conditions and compounds, being computationally much less demanding than molecular simulations. Among them, the Statistical Associating Fluid Theory (SAFT) EoS has become very popular because of its capability of predicting thermodynamics properties of several complex fluids, including chain, aromatic and chlorinated hydrocarbons, esters alkanols, carboxylic acids, etc. (Huang & Radosz, 1990). SAFT was envisioned as an application of Wertheim's theory of association (Wertheim, 1984, 1986) through the use of a first-order thermodynamic perturbation theory (TPT) to formulate a physically based EoS (Chapman et al., 1990; Huang & Radosz, 1991). The ambition of making SAFT an accurate equation for engineering purposes has promoted the development of different versions that tried to overcome the limitations of the original one (Economou, 2002; Muller & Gubbins, 1995).

SAFT has a similar form to group contribution theories in that the fluid of interest is initially considered to be a mixture of unconnected groups or segments. SAFT includes a chain connectivity term to account for the bonding of various groups to form polymers and an explicit intermolecular hydrogen bonding term. A theory based in statistical mechanics offers several advantages. The first advantage is that each of the approximations made in the development of SAFT has been tested versus molecular simulation results. In this way, the range of applicability of each term in the EoS has been determined. The second advantage is that the EoS can be systematically refined. Since any weak approximations in SAFT can be identified, improvement is made upon the EoS by making better approximations or by extending the theory. Like most thermodynamic models, SAFT approaches require the evaluation of several parameters relating the model to the

experimental system. A third advantage of SAFT-type equations versus other approaches is that, as they are based on statistical mechanics, parameters have a clear physical meaning; when carefully fitted they can be used with predictive power to explore other regions of the phase diagram far from the data and operating conditions used in the parameter regression, performing better than other models for interacting compounds like activity coefficient models (Prausnitz et al., 1999). In SAFT a chain molecule is characterized by the diameter or volume of a segment, the number of segments in the chain, and the segment–segment dispersion energy. For an associating or hydrogen bonding molecule, two more physical parameters are necessary: the association energy related to the change in enthalpy of association and the bond volume related to the change in entropy on association. The SAFT equation has found some impressive engineering applications on those fluids with chain bonding and hydrogen bonding (Chapman et al., 2004).

Asphaltenes are operationally defined as the portion of crude oil insoluble in light normal alkanes (e.g., n-heptane or n-pentane), but soluble in aromatic solvents (e.g., benzene or toluene). This solubility class definition of asphaltenes suggests a broad distribution of asphaltene molecular structures that vary greatly among crude sources. In general, asphaltenes possess fused ring aromaticity, small aliphatic side chains, and polar heteroatom-containing functional groups capable of donating or accepting protons inter- and intra-molecularly. Although asphaltene fractions can be complex molecular species mixtures, they convey, as a whole, an obvious chemical similarity, irrespective of crude geographic origin (Ting, 2003). Asphaltene stability depends on a number of factors including pressure, temperature, and compositions of the fluid; the latter incorporates the addition of light gases, solvents and other oils commingled operation or charges due to contamination. During pressure depletion at constant temperature, asphaltene aggregate formation is observed within a range above and below the bubble point. As pressure drops during production from the reservoir pressure, asphaltene precipitatin can appear due to changes in the solubility of asphaltene in crude oil. The maximum asphaltene precipitation occurs at or around the bubble point pressure. Below the bubble point light gases come out of the solution increasing the asphaltene solubility again (Ting, 2003). Temperature changes also affect asphaltene precipitation, For hydrocarbons deposited in shallow structure, the wellhead flowing temperatures are typically not excessive, 110-140 ˚F. However, sea bottom temperature in deep water is cold, often near or below 40 ˚F, even in equatorial waters. Cooling of flow streams during transportation can lead to asphaltene precipitation (Huang & Radosz, 1991). Increases in temperature at constant pressure normally stabilize the asphaltene in crude oil. Depending on the composition of the oil, it is possible to find cases where precipitation first decreases and then increases with increasing temperature (Verdier et al., 2006). Also, depending on the temperature level, significant temperature effects can be observed (Buenrostro-Gonzales & Lira-Galeana, 2004). Changes in composition occur during gas injection processes employed in Enhanced Oil Recovery (EOR). Gas injection includes processes such as miscible flooding with CO_2 , N_2 or natural gas or artificial gas lifting. The dissolved gas decreases asphaltene solubility and the asphaltene becomes more unstable (Verdier et al., 2006).

The tendency of petroleum asphaltenes to associate in solution and adsorb at interfaces can cause significant problems during the production, recovery, pipeline transportation, and refining of crude oil. Therefore, it is necessary to predict the conditions where precipitation

occurs and the amount of precipitate. The approach we have taken here to model is to use the SAFT EoS, as it explicitly builds on the association interaction and the chain connectivity term to account for the bonding of various groups. Therefore, the equation is able to provide insights on the asphaltene precipitation behavior. By some algebraic manipulations on this equation, we derive a simplified form of the compressibility factor or pressure as a function of density. Due to pressure explicit form of the SAFT EoS, an approximation technique based on Chebyshev polynomials to calculate density and hence fugacity requisite to perform phase equilibrium calculations is applied. To demonstrate the ability of SAFT EoS a binary system composed of ethanol and toluene is tested. Applying Chebysheve polynomial approximation, density is calculated for the above system at different temperatures in a range of 283.15 K to 353.15 K and for pressures up to 45 MPa. Evaluating fugacity is a necessary step in phase equilibrium calculations. Hence, fugacity is derived using SAFT EoS. Then the model is used to predict phase behavior of oil-asphaltene systems.

2. Formulation of the problem

2.1 SAFT equation of state

The statistical association fluid theory (SAFT) (Chapman et al., 1990) is based on the first order perturbation theory of Wertheim (Wertheim, 1987). The essence of this theory is that the residual Helmholtz energy is given by a sum of expressions to account not only for the effects of short-range repulsions and long-range dispersion forces but also for two other effects : chemically bonded aggregation (e.g. formation of chemically stable chains) and association and/or solvation (e.g. hydrogen bonding) between different molecules (or chains). For a pure component a three step process for formation of stable aggregates (e.g. chains) and subsequent association of these aggregates is shown in figure 1. Initially, a fluid consists of equal-sized, single hard spheres. Intermolecular attractive forces are added

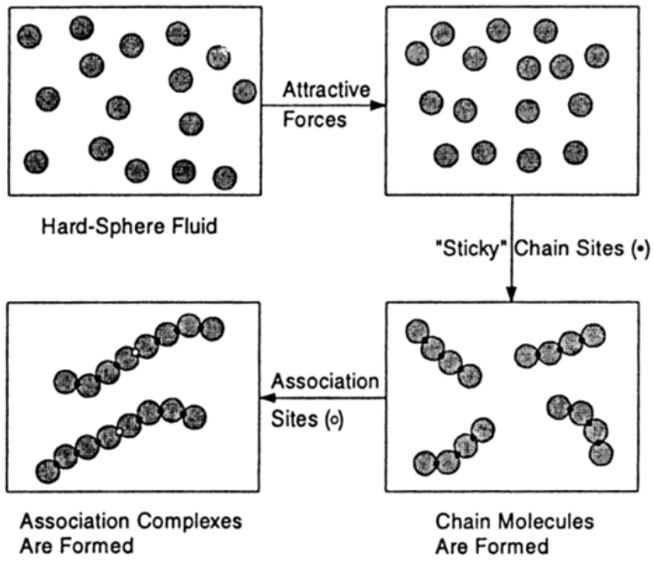


Fig. 1. Three steps to form chain molecules and association complexes from hard spheres in the SAFT model (Prausnitz et al., 1999).

which are described by an appropriate potential function, such as the square-well potential. Next, each sphere is given one, two or more "sticky spots", such that the spheres can stick together (covalent bonding) to form dimmers, trimers and higher stable aggregates as chains. Finally, specific interaction sites are introduced at some position in the chain to form association complex through some attractive interaction (e.g. hydrogen bonding). Each step provides a contribution to the Helmholtz energy.

Using SAFT EoS, the residual molar Helmholtz energy A^R contributes from formation of hard spheres, chains, dispersion (attraction), and association which would be in the form of:

$$A^R = A_{hs} + A_{ch} + A_{disp} + A_{assoc} \tag{1}$$

Here the sum of the first two terms is the hard-sphere-chain reference system accounting for molecular repulsion and chain connectivity (chemical bonding); the sum of the last two terms is the perturbation accounting for molecular attraction and for association due to specific interactions like hydrogen bonding. Application of the relation between molar Helmholtz energy, A, and the equation of state, gives the SAFT EoS for pure fluids (Prausnitz et al., 1999). We can write for compressibility factor of a real fluid:

$$Z = \frac{P}{\rho RT} = Z^{id} + Z_{hs} + Z_{ch} + Z_{disp} + Z_{Assoc} \tag{2}$$

with $Z^{id} = 1.0$ and for mixtures,

$$Z_{hs} = \frac{6}{\pi N_A \rho}\left[\frac{\xi_0\xi_3}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(3-\xi_3)\xi_2^3}{(1-\xi_3)^2}\right] \tag{3}$$

With

$$\xi_k = \frac{\pi N_A \rho}{6}\sum_{i=1}^{N_c} z_i r_i (d_i)^k \qquad k = 0,1,2,3 \tag{4}$$

$$d_i = \sigma_i[1 - 0.12exp(-3\varepsilon_i/kT)] \tag{5}$$

$$Z_{hs} = \frac{hs_1\rho + hs_2\rho^2 + hs_3\rho^3}{1 + hs_4\rho + hs_5\rho^2 + hs_6\rho^3} \tag{6}$$

here ρ is the total molar density, z_i, is the mole fraction of component i, r_i is the number of segments per molecule i, and d_i is the temperature dependent segment diameter. The parameters T, N_A, k, ε_i and σ_i are temperature, Avogadro's and Boltzmann's constants, segment energy and diameter, respectively. By simple algebraic manipulation on Eq. (3) , we arrive at the following simplified form of the hard sphere term:

where,

$$hs_1 = (\bar{r}S_3 + 3S_1S_2)P_{na} \tag{7}$$

$$hs_2 = (-2\bar{r}S_3^2 - 3S_1S_2S_3 + 3S_2^3)P_{na}^2 \tag{8}$$

$$hs_3 = (\bar{r}S_3^3 - S_2^3S_3)P_{na}^3 \tag{9}$$

$$hs_4 = -3S_3P_{na} \tag{10}$$

$$hs_5 = 3S_3^2P_{na}^2 \tag{11}$$

$$hs_6 = -S_3^3P_{na}^3 \tag{12}$$

The parameters used in Eqs. (7) – (12) are defined as the following:

$$\bar{r} = \sum_{i=1}^{N_c} z_i r_i \tag{13}$$

$$S_1 = \sum_{i=1}^{N_c} z_i r_i d_i \tag{14}$$

$$S_2 = \sum_{i=1}^{N_c} z_i r_i d_i^2 \tag{15}$$

$$S_3 = \sum_{i=1}^{N_c} z_i r_i \, d_i^3 \tag{16}$$

$$P_{na} = \frac{\pi N_A}{6} \tag{17}$$

The contribution accounting for the formation of chain molecules of the various components in the mixture is

$$Z_{ch} = \sum_{i=1}^{N_c} z_i(1 - r_i)L(d_i) \tag{18}$$

$$L(d_i) = \frac{2\xi_3 + 3d_i\xi_2 - 4\xi_3^2 + 2d_i^2\xi_2^2 + 2\xi_3^3 + d_i^2\xi_2^2\xi_3 - 3d_i\xi_2\xi_3^2}{(1 - \xi_3)\left(2 - 4\xi_3 + 3d_i\xi_2 + 2\xi_3^2 + d_i^2\xi_2^2 - 3d_i\xi_2\xi_3\right)} \tag{19}$$

where $\xi_k (k = 2,3)$ is given by Eq. (4). It is remarkable that no mixing rules are necessary in Eq. (3) and (18). After some arithmetic operations on Eq. (18), the following simplified density dependent equation for the chain term of SAFT EoS is presented as:

$$Z_{ch} = \sum_{i=1}^{N_c} z_i(1-r_i)\frac{ch_1(d_i)\rho + ch_2(d_i)\rho^2 + ch_3(d_i)\rho^3}{2 + ch_4(d_i)\rho + ch_5(d_i)\rho^2 + ch_6(d_i)\rho^3 + ch_7(d_i)\rho^4} \tag{20}$$

where,

$$ch_1(d_i) = [2S_3 + 3d_iS_2]P_{na} \tag{21}$$

$$ch_2(d_i) = \left[-4S_3^2 + 2d_i^2S_2^2\right]P_{na}^2 \tag{22}$$

$$ch_3(d_i) = \left[d_i^2S_2^2S_3 + 2S_3^3 - 3d_iS_2S_3^2\right]P_{na}^3 \tag{23}$$

$$ch_4(d_i) = [-6S_3 + 3d_iS_2]P_{na} \tag{24}$$

$$ch_5(d_i) = \left[6S_3^2 + d_i^2S_2^2 - 9d_iS_2S_3\right]P_{na}^2 \tag{25}$$

$$ch_6(d_i) = \left[9d_iS_2S_3^2 - 2S_3^3 - d_i^2S_2^2S_3\right]P_{na}^3 \tag{26}$$

$$ch_7(d_i) = [-3d_iS_2S_3^3]P_{na}^3 \tag{27}$$

SAFT uses the following expression for the dispersion contribution to the compressibility factor (Pedersen & Christensen, 2007):

$$Z_{disp} = -2\pi\rho\frac{\partial(\xi_3 I_1)}{\partial(\xi_3)}\overline{r^2\varepsilon\sigma^3} - \pi\rho\bar{r}\left[\mathcal{C}_1\frac{\partial(\xi_3 I_2)}{\partial(\xi_3)} + \mathcal{C}_2\xi_3 I_2\right]\overline{r^2\varepsilon^2\sigma^3} \tag{28}$$

where

$$\mathcal{C}_1 = 1 + \bar{r}\frac{8\xi_3 - 2\xi_3^2}{(1-\xi_3)^4} + (1-\bar{r})\frac{20\xi_3 - 27\xi_3^2 + 12\xi_3^3 - 2\xi_3^4}{\left[(1-\xi_3)(2-\xi_3)\right]^2} \tag{29}$$

$$\mathcal{C}_2 = -\mathcal{C}_1^2\left[\bar{r}\frac{-4\xi_3^2 + 20\xi_3 + 8}{(1-\xi_3)^5} + (1-\bar{r})\frac{2\xi_3^3 + 12\xi_3^2 - 48\xi_3 + 40}{\left[(1-\xi_3)(2-\xi_3)\right]^3}\right] \tag{30}$$

$$\overline{r^2\varepsilon\sigma^3} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c} z_iz_jr_ir_j\left(\frac{\varepsilon_{ij}}{kT}\right)\sigma_{ij}^3 \tag{31}$$

$$\overline{r^2\varepsilon^2\sigma^3} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c} z_iz_jr_ir_j\left(\frac{\varepsilon_{ij}}{kT}\right)^2\sigma_{ij}^3 \tag{32}$$

$$I_1 = \sum_{j=0}^{6} a_j(\bar{r})\,\xi_3^{\,j} \tag{33}$$

$$I_2 = \sum_{j=0}^{6} b_j(\bar{r})\,\xi_3^{\,j} \tag{34}$$

In equations (31) and (32):

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right) \tag{35}$$

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \tag{36}$$

where k_{ij} is a binary interaction parameter similar to that in the mixing rule for the a-parameter of a cubic EoS (Pedersen & Christensen, 2007). In equationa (33) and (34):

$$a_j(\bar{r}) = a_{0\mathrm{j}} + \frac{\bar{r}-1}{\bar{r}}a_{1\mathrm{j}} + \frac{\bar{r}-1}{\bar{r}}.\frac{\bar{r}-2}{\bar{r}}a_{2\mathrm{j}}\ , \quad j = 0, 1, \ldots, 6 \tag{37}$$

$$b_j(\bar{r}) = b_{0\mathrm{j}} + \frac{\bar{r}-1}{\bar{r}}b_{1\mathrm{j}} + \frac{\bar{r}-1}{\bar{r}}.\frac{\bar{r}-2}{\bar{r}}b_{2\mathrm{j}}\ , \quad j = 0, 1, \ldots, 6 \tag{38}$$

The universal constants for $a_{0\mathrm{j}}$, $a_{1\mathrm{j}}$, $a_{2\mathrm{j}}$, $b_{0\mathrm{j}}$, $b_{1\mathrm{j}}$ and $b_{2\mathrm{j}}$ are given in Table 1.

J	$\boldsymbol{a_{0j}}$	$\boldsymbol{a_{1j}}$	$\boldsymbol{a_{2j}}$	$\boldsymbol{b_{0j}}$	$\boldsymbol{b_{1j}}$	$\boldsymbol{b_{2j}}$
0	0.9105631	- 0.3084017	-0.0906148	0.7240947	0.5755498	0.0976883
1	0.6361281	0.1860531	0.4527843	2.2382792	0.6995095	-0.2557575
2	2.6861348	-2.5030047	0.5962701	-4.0025849	3.8925674	-9.1558561
3	-26.547362	21.419793	-1.7241829	-21.003577	-17.215472	20.642076
4	97.759209	-65.255885	-4.1302112	26.855641	192.67226	-38.804430
5	-159.59154	83.318680	13.776632	206.55134	-161.82646	93.626774
6	91.297774	-33.746923	-8.6728470	-355.60235	-165.20769	-29.666905

Table 1. The universal constants for $a_{0\mathrm{j}}$, $a_{1\mathrm{j}}$, $a_{2\mathrm{j}}$, $b_{0\mathrm{j}}$, $b_{1\mathrm{j}}$ and $b_{2\mathrm{j}}$ parameters used in SAFT EoS (Pedersen & Christensen, 2007).

Again, simplification of Eq. (28), would yield the following density dependent form of the dispersion term in SAFT EoS:

$$
\begin{aligned}
Z_{disp} = & \left[dI_1.\rho + dI_2.\rho^2 + dI_3.\rho^3 + dI_4.\rho^4 + dI_5.\rho^5 + dI_6.\rho^6 + dI_7.\rho^7 \right] - \left(6P_{na}\bar{r}.Adisp_2\right) \\
& .\left[\left(\frac{\rho + disp_1.\rho^2 + disp_2.\rho^3 + disp_3.\rho^4 + disp_4.\rho^5 + disp_5.\rho^6 + disp_6.\rho^7}{4 + disp_7.\rho + disp_8.\rho^2 + disp_9.\rho^3 + disp_{10}.\rho^4 + disp_{11}.\rho^5 + disp_{12}.\rho^6} \right) \right. \\
& \times \left(b_0 + dI_8.\rho + dI_9.\rho^2 + dI_{10}.\rho^3 + dI_{11}.\rho^4 + dI_{12}.\rho^5 + dI_{13}.\rho^6\right) - \left(P_{na}S_3\rho^2\right) \\
& \times \left(\frac{1 + disp_1.\rho + disp_2.\rho^2 + disp_3.\rho^3 + disp_4.\rho^4 + disp_5.\rho^5 + disp_6.\rho^6}{4 + disp_7.\rho + disp_8.\rho^2 + disp_9.\rho^3 + disp_{10}.\rho^4 + disp_{11}.\rho^5 + disp_{12}.\rho^6} \right)^2 \\
& \times \left(\frac{disp_{13} + disp_{14}.\rho + disp_{15}.\rho^2 + disp_{16}.\rho^3 + disp_{17}.\rho^4 + disp_{18}.\rho^5}{8 + disp_{19}.\rho + disp_{20}.\rho^2 + disp_{21}.\rho^3 + disp_{22}.\rho^4 + disp_{23}.\rho^5 + disp_{24}.\rho^6 + disp_{25}.\rho^7 + disp_{26}.\rho^8} \right) \\
& \left. \times \left(b_0 + Idisp_1.\rho + Idisp_2.\rho^2 + Idisp_3.\rho^3 + Idisp_4.\rho^4 + Idisp_5.\rho^5 + Idisp_6.\rho^6\right) \right]
\end{aligned} \tag{39}
$$

where the parameters used in the equation are given below,

$$disp_1 = 4(3\bar{r} - 4)S_3P_{na} \tag{40}$$

$$disp_2 = (27\bar{r} - 6)S_3^2P_{na}^2 \tag{41}$$

$$disp_3 = (82 - 70\bar{r})S_3^3P_{na}^3 \tag{42}$$

$$disp_4 = (51\bar{r} - 52)S_3^4P_{na}^4 \tag{43}$$

$$disp_5 = 16(1 - \bar{r})S_3^5P_{na}^5 \tag{44}$$

$$disp_6 = 2(\bar{r} - 1)S_3^6P_{na}^6 \tag{45}$$

$$disp_7 = -20_3S_3P_{na} \tag{46}$$

$$disp_8 = 41S_3^2P_{na}^2 \tag{47}$$

$$disp_9 = -44S_3^3P_{na}^3 \tag{48}$$

$$disp_{10} = 26S_3^4P_{na}^4 \tag{49}$$

$$disp_{11} = -8S_3^5P_{na}^5 \tag{50}$$

$$disp_{12} = S_3^6P_{na}^6 \tag{51}$$

$$disp_{13} = 40 + 24\bar{r} \tag{52}$$

$$disp_{14} = (192\bar{r} - 128)S_3P_{na} \tag{53}$$

$$disp_{15} = (148 - 372\bar{r})S_3^2P_{na}^2 \tag{54}$$

$$disp_{16} = (230\bar{r} - 70)S_3^3P_{na}^3 \tag{55}$$

$$disp_{17} = (8 - 52\bar{r})S_3^4P_{na}^4 \tag{56}$$

$$disp_{18} = (2 + 2\bar{r})S_3^5 P_{na}^5 \quad (57)$$

$$disp_{19} = -52S_3 P_{na} \quad (58)$$

$$disp_{20} = 146S_3^2 P_{na}^2 \quad (59)$$

$$disp_{21} = -231S_3^3 P_{na}^3 \quad (60)$$

$$disp_{22} = 225S_3^4 P_{na}^4 \quad (61)$$

$$disp_{23} = -138S_3^5 P_{na}^5 \quad (62)$$

$$disp_{24} = 52S_3^6 P_{na}^6 \quad (63)$$

$$disp_{25} = -11S_3^7 P_{na}^7 \quad (64)$$

$$disp_{26} = S_3^8 P_{na}^8 \quad (65)$$

$$Idisp_1 = b_1 S_3 P_{na} \quad (66)$$

$$Idisp_2 = b_2 S_3^2 P_{na}^2 \quad (67)$$

$$Idisp_3 = b_3 S_3^3 P_{na}^3 \quad (68)$$

$$Idisp_4 = b_4 S_3^4 P_{na}^4 \quad (69)$$

$$Idisp_5 = b_5 S_3^5 P_{na}^5 \quad (70)$$

$$Idisp_6 = b_6 S_3^6 P_{na}^6 \quad (71)$$

$$dIdisp_1 = 2a_1 S_3 P_{na} \quad (72)$$

$$dIdisp_2 = 3a_2 S_3^2 P_{na}^2 \quad (73)$$

$$dIdisp_3 = 4a_3 S_3^3 P_{na}^3 \quad (74)$$

$$dIdisp_4 = 5a_4 S_3^4 P_{na}^4 \quad (75)$$

$$dIdisp_5 = 6a_5 S_3^5 P_{na}^5 \quad (76)$$

$$dIdisp_6 = 7a_6 S_3^6 P_{na}^6 \quad (77)$$

$$dI_1 = -12P_{na}.Adisp_1.a_0 \quad (78)$$

$$dI_2 = -12P_{na}.Adisp_1.dIdisp_1 \quad (79)$$

$$dI_3 = -12P_{na}.Adisp_1.dIdisp_2 \quad (80)$$

$$dI_4 = -12P_{na}.Adisp_1.dIdisp_3 \quad (81)$$

$$dI_5 = -12P_{na}.Adisp_1.dIdisp_4 \quad (82)$$

$$dI_6 = -12P_{na}.Adisp_1.dIdisp_5 \tag{83}$$

$$dI_7 = -12P_{na}.Adisp_1.dIdisp_6 \tag{84}$$

$$dI_8 = 2b_1S_3P_{na} \tag{85}$$

$$dI_9 = 3b_2S_3^2P_{na}^2 \tag{86}$$

$$dI_{10} = 4b_3S_3^3P_{na}^3 \tag{87}$$

$$dI_{11} = 5b_4S_3^4P_{na}^4 \tag{88}$$

$$dI_{12} = 6b_5S_3^5P_{na}^5 \tag{89}$$

$$dI_{13} = 7b_6S_3^6P_{na}^6 \tag{90}$$

$$Adisp_1 = \overline{r^2\varepsilon\sigma^3} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c} z_iz_jr_ir_j\left(\varepsilon_{ij}/kT\right)\sigma_{ij}^3 \tag{91}$$

$$Adisp_2 = \overline{r^2\varepsilon^2\sigma^3} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c} z_iz_jr_ir_j\left(\varepsilon_{ij}/kT\right)^2\sigma_{ij}^3 \tag{92}$$

Similarly, Z_{assoc} can be derived rigorously from statistical mechanics (Chapman et al., 1990). The relation is a mole fraction average of the corresponding pure-component equations:

$$Z_{assoc} = \rho\sum_{i=1}^{N_c} z_i\left[\sum_{S_i}\left(\frac{1}{X^{S_i}} - \frac{1}{2}\right)\frac{\partial X^{S_i}}{\partial\rho}\right] \tag{93}$$

where X^{S_i}, the mole fraction of component i in the mixture not bonded with other components at site S , is given by:

$$X^{S_i} = \left(1 + N_A\sum_{j=1}^{N_c}\sum_{Y_j} z_i\rho X^{Y_j}W_{ij}\right)^{-1} \tag{94}$$

with

$$W_{ij} = \left[\frac{1}{1-\xi_3} + \frac{3d_id_j}{d_i+d_j}\frac{\xi_2}{\left(1-\xi_3\right)^2} + 2\left(\frac{d_id_j}{d_i+d_j}\right)^2\frac{\xi_2^2}{\left(1-\xi_3\right)^3}\right]\left(\sigma_{ij}k^{S_iY_j}\right)\left[exp\left(\frac{\varepsilon^{S_iY_j}}{kT}\right) - 1\right] \tag{95}$$

In Eq. (94), summation $\sum_{Y_j}$ is over all specific interaction sites on molecule j and summation $\sum_j$ is over all N_c components. The association/salvation $\varepsilon^{S_iY_j}$ and the dimensionless

parameter $k^{S_iY_j}$ characterize, respectively, the association $(i=j)$ and solvation $(i\neq j)$ energy and volume for the specific interaction between sites S and Y. These parameters are adjustable. Equation (93) requires no mixing rules. As it can be seen in Eq. (94), X^{S_i}'s satisfy a non-linear system of equations which can be solved using any iterative technique such as Gauss-Seidel, Successive-Over-Relaxation (SOR) or Jacobi iterative method. The derivative of the function X^{S_i} with respect to ρ yields the following equation:

$$\left(\frac{\partial X^{S_i}}{\partial\rho}\right)=-\left(X^{S_i}\right)^2 N_A\left[\begin{array}{c}\sum_{j=1}^{N_c}\sum_{Y_j} z_j X^{Y_j} W_{ij}+\sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho X^{Y_j}\left(\frac{\partial W_{ij}}{\partial\rho}\right)\\ +\sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho W_{ij}X^{Y_j}\left(\frac{\partial X^{Y_j}}{\partial\rho}\right)\end{array}\right] \tag{96}$$

where,

$$\left(\frac{\partial W_{ij}}{\partial\rho}\right)=\left(\sigma_{ij}k^{S_iY_j}\right)\left[exp\left(\frac{\varepsilon^{S_iY_j}}{kT}\right)-1\right]$$
$$\times\left[\begin{array}{c}\left(1-\xi_3\right)^{-2}\frac{\partial\xi_3}{\partial\rho}+\frac{3d_id_j}{d_i+d_j}\left[\left(1-\xi_3\right)^{-2}\left(\frac{\partial\xi_2}{\partial\rho}\right)+2\left(1-\xi_3\right)^{-3}\xi_2\left(\frac{\partial\xi_3}{\partial\rho}\right)\right]\\ +2\left(\frac{d_id_j}{d_i+d_j}\right)^2\left[2\xi_2\left(\frac{\partial\xi_2}{\partial\rho}\right)\left(1-\xi_3\right)^{-3}+3\left(1-\xi_3\right)^{-4}\left(\frac{\partial\xi_3}{\partial\rho}\right)\xi_2^2\right]\end{array}\right] \tag{97}$$

As it can be seen from Eq. (96), $(\partial X^{S_i}/\partial\rho)$'s are solutions of a linear system of equations which can be estimated using a known technique such as Gaussian Elimination, Gauss-Jordan or Least Square method (Burden et al., 1981).

2.2 Derivation of fugacity using SAFT EoS

The fugacity of component i in terms of independent variables V and T is given by the following equation for a given phase (Danesh , 1998; Prausnitz et al., 1999; Tabatabaei-Nejad, & Khodapanah, 2009):

$$RTln\varphi_k^{\alpha}=$$
$$=RTln\frac{f_k^{\alpha}}{z_k^{\alpha}P}=\int_{V^{\alpha}}^{\infty}\left[\left(\frac{\partial P}{\partial n_k}\right)_{T,V,n_{j\neq k}}-\frac{RT}{V}\right]dV-RTlnZ^{\alpha} \tag{98}$$
$$k=1,2,\ldots,N_c\quad\alpha=L,V$$

where f_k , φ_k , n_k, V , Z and P are fugacity, fugacity coefficient and the number of moles of component k , volume, compressibility factor, and pressure, respectively. The superscript α denotes liquid (L) and vapor phases (V).

The compressibility factor is related to the volume by the following equations:

$$Z^{\alpha} = \frac{P}{\rho^{\alpha} RT} \tag{99}$$

$$\rho^{\alpha} = \frac{n^{\alpha}}{V^{\alpha}} \tag{100}$$

where n refers to the total number of moles of the known phase.

To use equation (98), we require a suitable EoS that holds for the entire range of possible mole fractions z at the system temperature and for the density range between 0 and $\left(\frac{n}{V}\right)$. Application of the SAFT EoS in Eq. (98) yields the following equation for calculating the fugacity of the components:

$$RTln\left(Z^{\alpha}\varphi_k^{\alpha}\right) = \int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{hs}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV + \int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{ch}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV$$
$$+\int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{disp}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV + \int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{assoc}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV \tag{101}$$
$$k = 1,2,\ldots,N_c$$

The following equations are derived for the first term in Eq. (101) accounting for the hard sphere contribution of SAFT:

$$IR_HS = \int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{hs}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV = \int_0^{\rho} \frac{RT}{\rho}\left[\frac{\partial\left(nZ_{hs}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} d\rho \tag{102}$$
$$k = 1,2,\ldots,N_c$$

$$\left[\frac{\partial\left(nZ_{hs}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} = \left[\left(hs_{1k} + 2hs_1\right).\rho + \left(hs_{2k} + 3hs_2\right).\rho^2 + \left(hs_{3k} + 4hs_3\right).\rho^3\right]$$
$$\times\left[1 + hs_4.\rho + hs_5.\rho^2 + hs_6.\rho^3\right]^{-1} - \left[1 + hs_4.\rho + hs_5.\rho^2 + hs_6.\rho^3\right]^{-2} \tag{103}$$
$$\times\left[\left(hs_{4k} + hs_4\right).\rho + \left(hs_{5k} + 2hs_5\right).\rho^2 + \left(hs_{6k} + 3hs_6\right).\rho^3\right]\times\left[hs_1.\rho + hs_2.\rho^2 + hs_3.\rho^3\right]$$

The parameters used in Eq. (103) are given by equations (7) – (17) and the following equations:

$$hs_{1k} = \left(\bar{r}_k S_3 + \bar{r} S_{3k} + 3S_{1k}S_2 + 3S_1 S_{2k}\right) P_{na} \tag{104}$$

$$hs_{2k} = (-2\bar{r}_k S_3^2 - 4\bar{r} S_{3k} S_3 - 3S_{1k}S_2 S_3 - 3S_{2k}S_1 S_3 - 3S_1 S_2 S_{3k} + 9S_{2k}S_2^2) P_{na}^2 \tag{105}$$

$$hs_{3k} = (\bar{r}_k S_3^3 + 3\bar{r} S_3^2 S_{3k} - 3S_2^2 S_{2k} S_3 - S_2^3 S_{3k}) P_{na}^3 \tag{106}$$

$$hs_{4k} = -3S_{3k} P_{na} \tag{107}$$

$$hs_{5k} = 6S_3S_{3k}P_{na}^2 \tag{108}$$

$$hs_{6k} = -3S_3^2S_{3k}P_{na}^3 \tag{109}$$

where,

$$\bar{r}_k = (-\bar{r} + r_k) \tag{110}$$

$$S_{1k} = -S_1 + r_k d_k \tag{111}$$

$$S_{2k} = -S_2 + r_k d_k^2 \tag{112}$$

$$\begin{gathered} S_{3k} = -S_3 + r_k d_k^3 \\ k = 1,2,\ldots,N_c \end{gathered} \tag{113}$$

The non-ideality of the mixture due to formation of chain molecules of the various components which was described using the second term in Eq. (101) is derived as the following form:

$$IR_Chain = \int_V^\infty \frac{RT}{V}\left[\frac{\partial(nZ_{ch})}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV = \int_0^\rho \frac{RT}{\rho}\left[\frac{\partial(nZ_{ch})}{\partial n_k}\right]_{T,V,n_{j\neq k}} d\rho \tag{114}$$

$$k = 1, 2, \ldots, N_c$$

$$\left[\frac{\partial\left(nZ_{ch}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}}$$

$$\times\sum_{i=1}^{N_c}\left[\begin{array}{c} \delta_{ik}.(1-r_i)\times\left[ch_{1k}(d_i).\rho + ch_{2k}(d_i).\rho^2 + ch_{3k}(d_i).\rho^3\right] \\ \times\left[2 + ch_{4k}(d_i).\rho + ch_{5k}(d_i).\rho^2 + ch_{6k}(d_i).\rho^3 + ch_{7k}(d_i).\rho^4\right]^{-1} \\ +z_i(1-r_i)\times\left[2 + ch_{4k}(d_i).\rho + ch_{5k}(d_i).\rho^2 + ch_{6k}(d_i).\rho^3 + ch_{7k}(d_i).\rho^4\right]^{-1} \\ \left[\begin{array}{c}\left(ch_{1k}(d_i) + ch_1(d_i)\right).\rho \\ +\left(ch_{2k}(d_i) + 2ch_2(d_i)\right).\rho^2 + \left(ch_{3k}(d_i) + 3ch_3(d_i)\right).\rho^3\end{array}\right] \\ -z_i(1-r_i)\times\left[ch_1(d_i).\rho + ch_2(d_i).\rho^2 + ch_3(d_i).\rho^3\right] \\ \times\left[2 + ch_4(d_i).\rho + ch_5(d_i).\rho^2 + ch_6(d_i).\rho^3 + ch_7(d_i).\rho^4\right]^{-2} \\ \left[\begin{array}{c}\left(ch_{4k}(d_i) + ch_4(d_i)\right).\rho + \left(ch_{5k}(d_i) + 2ch_5(d_i)\right).\rho^2 \\ +\left(ch_{6k}(d_i) + 3ch_6(d_i)\right).\rho^3 + \left(ch_{7k}(d_i) + 4ch_7(d_i)\right).\rho^4\end{array}\right] \end{array}\right] \tag{115}$$

$$k = 1,2,\ldots,N_c$$

where the parameters are described using equations (21) – (27) and the equations given below:

$$ch_{1k}(d_i) = (2S_{3k} + 3d_iS_{2k})P_{na} \tag{116}$$

$$ch_{2k}(d_i) = \left(-8S_3S_{3k} + 4d_i^2S_2S_{2k}\right)P_{na}^2 \tag{117}$$

$$ch_{3k}(d_i) = \left(2d_i^2S_2S_{2k}S_3 + d_i^2S_2^2S_{3k} + 6S_3^2S_{3k} - 3d_iS_{2k}S_3^2 - 6d_iS_2S_3S_{3k}\right)P_{na}^3 \tag{118}$$

$$ch_{4k}(d_i) = (-6S_{3k} + 3d_iS_{2k})P_{na} \tag{119}$$

$$ch_{5k}(d_i) = \left(12S_3S_{3k} + 2d_i^2S_2S_{2k} - 9d_iS_{2k}S_3 - 9d_iS_2S_{3k}\right)P_{na}^2 \tag{120}$$

$$ch_{6k}(d_i) = \left(9d_iS_{2k}S_3^2 + 18d_iS_2S_3S_{3k} - 6S_3^2S_{3k} - 2d_i^2S_2S_{2k}S_3 - d_i^2S_2^2S_{3k}\right)P_{na}^3 \tag{121}$$

$$ch_{7k}(d_i) = \left(-3d_iS_{2k}S_3^3 - 9d_iS_2S_3^2S_{3k}\right)P_{na}^4 \qquad k = 1,2,\ldots,N_c \tag{122}$$

The dispersion contribution to the non-ideal behavior of the mixture (the third term in the right hand side of Eq. (101) is derived as the following forms:

$$IR_Disp = \int_V^{\infty} \frac{RT}{V}\left[\frac{\partial\left(nZ_{disp}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV = \int_0^{\rho} \frac{RT}{\rho}\left[\frac{\partial\left(nZ_{disp}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} d\rho \tag{123}$$

$$k = 1, 2, \ldots, N_c$$

$$\left[\frac{\partial\left(nZ_{disp}\right)}{\partial n_k}\right]_{T,V,n_{j\neq k}} = Z_{disp} + \left(Z_{disp}\right)_k \tag{124}$$

$$\left(Z_{disp}\right)_k = A_{1k} + A_{2k}A_3 + A_2A_{3k}, \quad k = 1, 2, \ldots, N_c$$

where,

$$A_1 = dI_1.\rho + dI_2.\rho^2 + dI_3.\rho^3 + dI_4.\rho^4 + dI_5.\rho^5 + dI_6.\rho^6 + dI_7.\rho^7 \tag{125}$$

$$\begin{aligned} A_{1k} = {} & \left(dI_{1k} + dI_1\right).\rho + \left(dI_{2k} + 2dI_2\right).\rho^2 + \left(dI_{3k} + 3dI_3\right).\rho^3 \\ & + \left(dI_{4k} + 4dI_4\right).\rho^4 + \left(dI_{5k} + 5dI_5\right).\rho^5 + \left(dI_{6k} + 6dI_6\right).\rho^6 + \left(dI_{7k} + 7dI_7\right).\rho^7 \end{aligned} \qquad k = 1,2,\ldots,N_c \tag{126}$$

$$A_2 = -6P_{na}\bar{r}Adisp_2 \tag{127}$$

$$A_{2k} = -6P_{na}\left[\bar{r}_k.Adisp_2 + \bar{r}.Adisp_{2k}\right] \qquad k = 1,2,\ldots,N_c \tag{128}$$

$$A_3 = \left(\frac{B_1}{B_2}\right) \cdot B_3 - \left(\frac{B_1}{\rho B_2}\right)^2 \cdot \left(\frac{B_4}{B_5}\right) \cdot B_6 \cdot B_7 \tag{129}$$

$$B_1 = 4\rho + disp_1 \cdot \rho^2 + disp_2 \cdot \rho^3 + disp_3 \cdot \rho^4 + disp_4 \cdot \rho^5 + disp_5 \cdot \rho^6 + disp_6 \cdot \rho^7 \tag{130}$$

$$\begin{gathered} B_{1k} = 4\rho + \left(d_{1k} + 2disp_1\right) \cdot \rho^2 + \left(d_{2k} + 3disp_2\right) \cdot \rho^3 + \left(d_{3k} + 4disp_3\right) \cdot \rho^4 \\ + \left(d_{4k} + 5disp_4\right) \cdot \rho^5 + \left(d_{5k} + 6disp_5\right) \cdot \rho^6 + \left(d_{6k} + 7disp_6\right) \cdot \rho^7 \\ k = 1,2,\ldots,N_c \end{gathered} \tag{131}$$

$$B_2 = 4 + disp_7 \cdot \rho + disp_8 \cdot \rho^2 + disp_9 \cdot \rho^3 + disp_{10} \cdot \rho^4 + disp_{11} \cdot \rho^5 + disp_{12} \cdot \rho^6 \tag{132}$$

$$\begin{gathered} B_{2k} = \left(d_{7k} + disp_7\right) \cdot \rho + \left(d_{8k} + 2disp_8\right) \cdot \rho^2 + \left(d_{9k} + 3disp_9\right) \cdot \rho^3 \\ + \left(d_{10k} + 4disp_{10}\right) \cdot \rho^4 + \left(d_{11k} + 5disp_{11}\right) \cdot \rho^5 + \left(d_{12k} + 6disp_{12}\right) \cdot \rho^6 \end{gathered} \tag{133}$$

$$B_3 = b_0 + dI_8 \cdot \rho + dI_9 \cdot \rho^2 + dI_{10} \cdot \rho^3 + dI_{11} \cdot \rho^4 + dI_{12} \cdot \rho^5 + dI_{13} \cdot \rho^6 \tag{134}$$

$$\begin{gathered} B_{3k} = b_{0k} + \left(dI_{8k} + dI_8\right) \cdot \rho + \left(dI_{9k} + 2dI_9\right) \cdot \rho^2 + \left(dI_{10k} + 3dI_{10}\right) \cdot \rho^3 \\ + \left(dI_{11k} + 4dI_{11}\right) \cdot \rho^4 + \left(dI_{12k} + 5dI_{12}\right) \cdot \rho^5 + \left(dI_{13k} + 6dI_{13}\right) \cdot \rho^6 \end{gathered} \tag{135}$$

$$B_4 = disp_{13} + disp_{14} \cdot \rho + disp_{15} \cdot \rho^2 + disp_{16} \cdot \rho^3 + disp_{17} \cdot \rho^4 + disp_{18} \cdot \rho^5 \tag{136}$$

$$\begin{gathered} B_{4k} = d_{13k} + \left(d_{14k} + disp_{14}\right) \cdot \rho + \left(d_{15k} + 2disp_{15}\right) \cdot \rho^2 \\ + \left(d_{16k} + 3disp_{16}\right) \cdot \rho^3 + \left(d_{17k} + 4disp_{17}\right) \cdot \rho^4 + \left(d_{18k} + 5disp_{18}\right) \cdot \rho^5 \end{gathered} \tag{137}$$

$$\begin{gathered} B_5 = 8 + disp_{19} \cdot \rho + disp_{20} \cdot \rho^2 + disp_{21} \cdot \rho^3 + disp_{22} \cdot \rho^4 + disp_{23} \cdot \rho^5 \\ + disp_{24} \cdot \rho^6 + disp_{25} \cdot \rho^7 + disp_{26} \cdot \rho^8 \end{gathered} \tag{138}$$

$$\begin{gathered} B_{5k} = \left(d_{19k} + disp_{19}\right) \cdot \rho + \left(d_{20k} + 2disp_{20}\right) \cdot \rho^2 \\ + \left(d_{21k} + 3disp_{21}\right) \cdot \rho^3 + \left(d_{22k} + 4disp_{22}\right) \cdot \rho^4 + \left(d_{23k} + 5disp_{23}\right) \cdot \rho^5 \\ + \left(d_{24k} + 6disp_{24}\right) \cdot \rho^6 + \left(d_{25k} + 7disp_{25}\right) \cdot \rho^7 + \left(d_{26k} + 8disp_{26}\right) \cdot \rho^8 \end{gathered} \tag{139}$$

$$B_6 = b_0 \cdot \rho^2 + Idisp_1 \cdot \rho^3 + Idisp_2 \cdot \rho^4 + Idisp_3 \cdot \rho^5 + Idisp_4 \cdot \rho^6 + Idisp_5 \cdot \rho^7 + Idisp_6 \cdot \rho^8 \tag{140}$$

$$\begin{gathered} B_{6k} = \left(b_{0k} + 2b_0\right) \cdot \rho^2 + \left(Idisp_{1k} + 3Idisp_1\right) \cdot \rho^3 \\ + \left(Idisp_{2k} + 4Idisp_2\right) \cdot \rho^4 + \left(Idisp_{3k} + 5Idisp_3\right) \cdot \rho^5 \\ + \left(Idisp_{4k} + 6Idisp_4\right) \cdot \rho^6 + \left(Idisp_{5k} + 7Idisp_5\right) \cdot \rho^7 + \left(Idisp_{6k} + 8Idisp_6\right) \cdot \rho^8 \end{gathered} \tag{141}$$

$$B_7 = P_{na} S_3 \tag{142}$$

$$B_{7k} = P_{na} S_{3k} \qquad k = 1,2,\ldots,N_c \tag{143}$$

The parameters used in Eqs. (125) – (143) are given through Eqs. (40) – (92) and the following equations:

$$d_{1k} = 12[\bar{r}_k S_3 + \bar{r} S_{3k}] P_{na} \tag{144}$$

$$d_{2k} = [27\bar{r}_k S_3^2 + 2(27\bar{r} - 26) S_3 S_{3k}] P_{na}^2 \tag{145}$$

$$d_{3k} = [70\bar{r}_k S_3^3 + 3S_3^2 S_{3k}(70\bar{r} + 42)] P_{na}^3 \tag{146}$$

$$d_{4k} = [51\bar{r}_k S_3^4 + 3S_3^3 S_{3k}(51\bar{r} - 27)] P_{na}^4 \tag{147}$$

$$d_{5k} = \left[-16\bar{r}_k S_3^5 + 5S_3^4 S_{3k}(8 - 16\bar{r})\right] P_{na}^5 \tag{148}$$

$$d_{6k} = \left[2\bar{r}_k S_3^6 + 6S_3^5 S_{3k}(2\bar{r} - 1)\right] P_{na}^6 \tag{149}$$

$$d_{7k} = -20 S_{3k} P_{na} \tag{150}$$

$$d_{8k} = 82 S_3 S_{3k} P_{na}^2 \tag{151}$$

$$d_{9k} = -132 S_3^2 S_{3k} P_{na}^3 \tag{152}$$

$$d_{10k} = 104 S_3^3 S_{3k} P_{na}^4 \tag{153}$$

$$d_{11k} = -40 S_3^4 S_{3k} P_{na}^5 \tag{154}$$

$$d_{12k} = 6 S_3^5 S_{3k} P_{na}^6 \tag{155}$$

$$d_{13k} = 24\bar{r}_k \tag{156}$$

$$d_{14k} = [192\bar{r}_k S_3 + (192\bar{r} - 128) S_{3k}] P_{na} \tag{157}$$

$$d_{15k} = [-372\bar{r}_k S_3^2 + 2S_3 S_{3k}(148 - 372\bar{r})] P_{na}^2 \tag{158}$$

$$d_{16k} = [230\bar{r}_k S_3^3 + 3S_3^2 S_{3k}(230\bar{r} - 70)] P_{na}^3 \tag{159}$$

$$d_{17k} = [-52\bar{r}_k S_3^4 + 4S_3^3 S_{3k}(8 - 52\bar{r})] P_{na}^4 \tag{160}$$

$$d_{18k} = \left[2\bar{r}_k S_3^5 + 10 S_3^4 S_{3k}(1 + \bar{r})\right] P_{na}^5 \tag{161}$$

$$d_{19k} = -52 S_{3k} P_{na} \tag{162}$$

$$d_{20k} = 292 S_3 S_{3k} P_{na}^2 \tag{163}$$

$$d_{21k} = -693 S_3^2 S_{3k} P_{na}^3 \tag{164}$$

$$d_{22k} = 900 S_3^3 S_{3k} P_{na}^4 \tag{165}$$

$$d_{23k} = -690 S_3^4 S_{3k} P_{na}^5 \tag{166}$$

$$d_{24k} = 312 S_3^5 S_{3k} P_{na}^6 \tag{167}$$

$$d_{25k} = -77 S_3^6 S_{3k} P_{na}^7 \tag{168}$$

$$d_{26k} = 8S_3^7 S_{3k} P_{na}^8 \qquad k = 1,2,\ldots,N_c \tag{169}$$

$$Adisp_{1k} = 2 \times \left[-\sum_{i=1}^{N_c} \sum_{j=1}^{N_c} z_i z_j r_i r_j \left(\varepsilon_{ij}/kT\right) \sigma_{ij}^3 + \sum_{i=1}^{N_c} z_i r_i r_k (\varepsilon_{ik}/kT) \sigma_{ik}^3 \right] \tag{170}$$

$$Adisp_{2k} = 2 \times \left[-\sum_{i=1}^{N_c} \sum_{j=1}^{N_c} z_i z_j r_i r_j \left(\varepsilon_{ij}/kT\right)^2 \sigma_{ij}^3 + \sum_{i=1}^{N_c} z_i r_i r_k (\varepsilon_{ik}/kT)^2 \sigma_{ik}^3 \right] \tag{171}$$

$$a_{jk}(\bar{r}) = \left[\begin{array}{c} \left[\frac{\bar{r}_k}{\bar{r}} - \frac{\bar{r}_k \cdot (\bar{r}-1)}{\bar{r}^2} \right] a_{1j} \\ + \left[\frac{\bar{r}_k \cdot (\bar{r}-2)}{\bar{r}^2} + \frac{\bar{r}_k \cdot (\bar{r}-1)}{\bar{r}^2} - 2\frac{\bar{r}_k \cdot (\bar{r}-1) \cdot (\bar{r}-2)}{\bar{r}^3} \right] a_{2j} \end{array} \right] \tag{172}$$

$$b_{jk}(\bar{r}) = \left[\begin{array}{c} \left[\frac{\bar{r}_k}{\bar{r}} - \frac{\bar{r}_k \cdot (\bar{r}-1)}{\bar{r}^2} \right] b_{1j} \\ + \left[\frac{\bar{r}_k \cdot (\bar{r}-2)}{\bar{r}^2} + \frac{\bar{r}_k \cdot (\bar{r}-1)}{\bar{r}^2} - 2\frac{\bar{r}_k \cdot (\bar{r}-1) \cdot (\bar{r}-2)}{\bar{r}^3} \right] b_{2j} \end{array} \right] \tag{173}$$

$$j = 0, 1, \ldots, 6 \qquad k = 1, 2, \ldots, N_c$$

$$Idisp_{1k} = [b_{1k} S_3 + b_1 S_{3k}] P_{na} \tag{174}$$

$$Idisp_{2k} = [b_{2k} S_3^2 + 2b_2 S_3 S_{3k}] P_{na}^2 \tag{175}$$

$$Idisp_{3k} = [b_{3k} S_3^3 + 3b_3 S_3^2 S_{3k}] P_{na}^3 \tag{176}$$

$$Idisp_{4k} = [b_{4k} S_3^4 + 4b_4 S_3^3 S_{3k}] P_{na}^4 \tag{177}$$

$$Idisp_{5k} = \left[b_{5k} S_3^5 + 5b_5 S_3^4 S_{3k}\right] P_{na}^5 \tag{178}$$

$$Idisp_{6k} = \left[b_{6k} S_3^6 + 6b_6 S_3^5 S_{3k}\right] P_{na}^6 \tag{179}$$

$$dIdisp_{7k} = 2[a_{1k} S_3 + a_1 S_{3k}] P_{na} \tag{180}$$

$$dIdisp_{2k} = 3[a_{2k} S_3^2 + 2a_2 S_3 S_{3k}] P_{na}^2 \tag{181}$$

$$dIdisp_{3k} = 4[a_{3k} S_3^3 + 3a_3 S_3^2 S_{3k}] P_{na}^3 \tag{182}$$

$$dIdisp_{4k} = 5[a_{4k} S_3^4 + 4a_4 S_3^3 S_{3k}] P_{na}^4 \tag{183}$$

$$dIdisp_{5k} = 6\left[a_{5k} S_3^5 + 5a_5 S_3^4 S_{3k}\right] P_{na}^5 \tag{184}$$

$$dIdisp_{6k} = 7\left[a_{6k} S_3^6 + 6a_6 S_3^5 S_{3k}\right] P_{na}^6 \tag{185}$$

$$dI_{1k} = -12[Adisp_{1k} \cdot a_0 + Adisp_1 \cdot a_{0k}]P_{na} \tag{186}$$

$$dI_{2k} = -12[Adisp_{1k} \cdot dIdisp_1 + Adisp_1 \cdot dIdisp_{1k}]P_{na} \tag{187}$$

$$dI_{3k} = -12[Adisp_{1k} \cdot dIdisp_2 + Adisp_1 \cdot dIdisp_{2k}]P_{na} \tag{188}$$

$$dI_{4k} = -12[Adisp_{1k} \cdot dIdisp_3 + Adisp_1 \cdot dIdisp_{3k}]P_{na} \tag{189}$$

$$dI_{5k} = -12[Adisp_{1k} \cdot dIdisp_4 + Adisp_1 \cdot dIdisp_{4k}]P_{na} \tag{190}$$

$$dI_{6k} = -12[Adisp_{1k} \cdot dIdisp_5 + Adisp_1 \cdot dIdisp_{5k}]P_{na} \tag{191}$$

$$dI_{7k} = -12[Adisp_{1k} \cdot dIdisp_6 + Adisp_1 \cdot dIdisp_{6k}]P_{na} \tag{192}$$

$$dI_{8k} = 2[b_{1k}S_3 + b_1S_{3k}]P_{na} \tag{193}$$

$$dI_{9k} = 3[b_{2k}S_3^2 + 2b_2S_3S_{3k}]P_{na}^2 \tag{194}$$

$$dI_{10k} = 4[b_{3k}S_3^3 + 3b_3S_3^2S_{3k}]P_{na}^3 \tag{195}$$

$$dI_{11k} = 5[b_{4k}S_3^4 + 4b_4S_3^3S_{3k}]P_{na}^4 \tag{196}$$

$$dI_{12k} = 6\left[b_{5k}S_3^5 + 5b_5S_3^4S_{3k}\right]P_{na}^5 \tag{197}$$

$$dI_{13k} = 7\left[b_{6k}S_3^6 + 6b_6S_3^5S_{3k}\right]P_{na}^6 \tag{198}$$

The association contribution to the non-ideal behavior of mixtures containing associating compounds (the last term given by the right hand side of Eq. (101) is derived as the following forms:

$$IR_Assoc = \int_V^\infty \frac{RT}{V}\left[\frac{\partial(nZ_{assoc})}{\partial n_k}\right]_{T,V,n_{j\neq k}} dV = \int_0^\rho \frac{RT}{\rho}\left[\frac{\partial(nZ_{assoc})}{\partial n_k}\right]_{T,V,n_{j\neq k}} d\rho \tag{199}$$

$$k = 1, 2, \ldots, N_c$$

$$\left[\frac{\partial(nZ_{assoc})}{\partial n_k}\right]_{T,V,n_{j\neq k}} = Z_{assoc} + \rho(A_k) + \rho^2 \sum_{i=1}^{N_c} z_i \left(\frac{\partial A_i}{\partial n_k}\right)_{T,V,n_{j\neq k}} \tag{200}$$

$$k = 1, 2, \ldots, N_c$$

where,

$$\left(\frac{\partial A_i}{\partial n_k}\right)_{T,V,n_{j\neq k}} = \sum_{S_i} -\frac{1}{(X^{S_i})^2}\left(\frac{\partial X^{S_i}}{\partial n_k}\right)_{T,V,n_{j\neq k}} \cdot \left(\frac{\partial X^{S_i}}{\partial \rho}\right) + \left(\frac{1}{X^{S_i}} - \frac{1}{2}\right)\left[\frac{\partial}{\partial n_k}\left(\frac{\partial X^{S_i}}{\partial \rho}\right)\right]_{T,V,n_{j\neq k}} \tag{201}$$

$$k = 1, 2, \ldots, N_c$$

$$A_i = \sum_{S_i} \left(\frac{1}{X^{S_i}} - \frac{1}{2}\right)\left(\frac{\partial X^{S_i}}{\partial \rho}\right) \tag{202}$$

where $(\partial X^{S_i}/\partial\rho)$ is given by Eq. (96), other derivatives of X^{S_i} used in Eq. (202) are given below:

$$\left(\frac{\partial X^{S_i}}{\partial n_k}\right)_{T,V,n_j\neq k} = -(X^{S_i})^2 N_A \left[\begin{array}{c} \sum_{j=1}^{N_c}\sum_{Y_j}\frac{1}{V}\delta_{jk}X^{Y_j}W_{ij} + \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho X^{Y_j}\left(\frac{\partial W_{ij}}{\partial n_k}\right)_{T,V,n_j\neq k} + \\ \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho W_{ij}\left(\frac{\partial\, X^{Y_j}}{\partial n_k}\right)_{T,V,n_j\neq k} \end{array}\right] \tag{203}$$

$$k = 1, 2, \ldots, N_c$$

$$\left[\frac{\partial}{\partial n_k}\left(\frac{\partial X^{S_i}}{\partial \rho}\right)\right]_{T,V,n_j\neq k} = 2\left(X^{S_i}\right)^{-1}\left(\frac{\partial X^{S_i}}{\partial n_k}\right)_{T,V,n_{j\neq k}} \cdot \left(\frac{\partial X^{S_i}}{\partial \rho}\right)$$

$$-\left(X^{S_i}\right)^2 N_A \left[\begin{array}{c} \sum_{j=1}^{N_c}\sum_{Y_j}\frac{\delta_{jk}-z_j}{n}X^{Y_j}W_{ij} + \sum_{j=1}^{N_c}\sum_{Y_j} z_j W_{ij}\left(\frac{\partial X^{Y_j}}{\partial n_k}\right)_{T,V,n_{j\neq k}} + \sum_{j=1}^{N_c}\sum_{Y_j} z_j X^{Y_j}\left(\frac{\partial W_{ij}}{\partial n_k}\right)_{T,V,n_{j\neq k}} \\ + \sum_{j=1}^{N_c}\sum_{Y_j}\frac{\delta_{jk}}{V}X^{Y_j}\left(\frac{\partial W_{ij}}{\partial \rho}\right) + \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho\left(\frac{\partial X^{Y_j}}{\partial n_k}\right)_{T,V,n_{j\neq k}} \cdot \left(\frac{\partial W_{ij}}{\partial \rho}\right) \\ + \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho X^{Y_j}\left(\frac{\partial}{\partial n_k}\left(\frac{\partial W_{ij}}{\partial \rho}\right)\right)_{T,V,n_{j\neq k}} + \sum_{j=1}^{N_c}\sum_{Y_j}\frac{\delta_{jk}}{V}W_{ij}\left(\frac{\partial X^{Y_j}}{\partial \rho}\right) \\ + \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho\left(\frac{\partial W_{ij}}{\partial n_k}\right)_{T,V,n_{j\neq k}} \cdot \left(\frac{\partial X^{Y_j}}{\partial \rho}\right) + \sum_{j=1}^{N_c}\sum_{Y_j} z_j\rho W_{ij}\left(\frac{\partial}{\partial n_k}\left(\frac{\partial X^{Y_j}}{\partial \rho}\right)\right)_{T,V,n_{j\neq k}} \end{array}\right] \tag{204}$$

where $\left(\partial W_{ij}/\partial\rho\right)$ is given by Eq. (97), other derivatives of W_{ij} are given as the following:

$$\left(\frac{\partial W_{ij}}{\partial n_k}\right)_{T,V,n_{j\neq k}} = \left(\sigma_{ij}k^{S_iY_j}\right)\left[exp\left(\frac{\varepsilon^{S_iY_j}}{kT}\right)-1\right]$$

$$\times\left[\begin{array}{c} \left(1-\xi_3\right)^{-2}\frac{\partial\xi_3}{\partial n_k} + 3\frac{d_i d_j}{d_i+d_j}\left[\left(1-\xi_3\right)^{-2}\left(\frac{\partial\xi_2}{\partial n_k}\right) + 2\left(1-\xi_3\right)^{-3}\xi_2\left(\frac{\partial\xi_3}{\partial n_k}\right)\right] \\ +2\left(\frac{d_i d_j}{d_i+d_j}\right)^2\left[2\left(1-\xi_3\right)^{-3}\xi_2\left(\frac{\partial\xi_2}{\partial n_k}\right) + 3\left(1-\xi_3\right)^{-4}\left(\frac{\partial\xi_3}{\partial n_k}\right)\xi_2^2\right] \end{array}\right] \tag{205}$$

$$k = 1,2,\ldots,N_c$$

$$\left(\frac{\partial}{\partial n_k}\left(\frac{\partial W_{ij}}{\partial \rho}\right)\right)_{T,V,n_{j\neq k}}$$
$$= \left(\sigma_{ij} k^{S_i Y_j}\right)\left[exp\left(\frac{\varepsilon^{S_i Y_j}}{kT}\right) - 1\right]$$
$$\times \left[\begin{array}{l} 2\left(1-\xi_3\right)^{-3}\left(\frac{\partial \xi_3}{\partial n_k}\right)\left(\frac{\partial \xi_3}{\partial \rho}\right) + \left(1-\xi_3\right)^{-2}\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_3}{\partial \rho}\right) \\ +\frac{3d_i d_j}{d_i+d_j}\left[\begin{array}{c} 2\left(1-\xi_3\right)^{-3}\left(\frac{\partial \xi_3}{\partial n_k}\right)\left(\frac{\partial \xi_2}{\partial \rho}\right) + \left(1-\xi_3\right)^{-2}\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_2}{\partial \rho}\right) \\ +6\left(1-\xi_3\right)^{-4}\left(\frac{\partial \xi_3}{\partial n_k}\right)\xi_2\left(\frac{\partial \xi_3}{\partial \rho}\right) + 2\left(1-\xi_3\right)^{-3}\left(\frac{\partial \xi_2}{\partial n_k}\right)\left(\frac{\partial \xi_3}{\partial \rho}\right) \\ +2\left(1-\xi_3\right)^{-3}\xi_2\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_3}{\partial \rho}\right) \end{array}\right] \\ +2\left(\frac{d_i d_j}{d_i+d_j}\right)^2\left[\begin{array}{c} 2\left(1-\xi_3\right)^{-3}\left(\frac{\partial \xi_2}{\partial n_k}\right)\left(\frac{\partial \xi_2}{\partial \rho}\right) + 2\xi_2\left(1-\xi_3\right)^{-3}\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_2}{\partial \rho}\right) \\ +6\left(1-\xi_3\right)^{-4}\left(\frac{\partial \xi_3}{\partial n_k}\right)\xi_2\left(\frac{\partial \xi_2}{\partial \rho}\right) + 12\left(1-\xi_3\right)^{-5}\left(\frac{\partial \xi_3}{\partial n_k}\right)\left(\frac{\partial \xi_3}{\partial \rho}\right)\xi_2^2 \\ +3\left(1-\xi_3\right)^{-4}\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_3}{\partial \rho}\right)\xi_2^2 + 6\left(1-\xi_3\right)^{-4}\left(\frac{\partial \xi_2}{\partial n_k}\right)\xi_2\left(\frac{\partial \xi_3}{\partial \rho}\right) \end{array}\right] \end{array}\right] \quad (206)$$

$$k = 1, 2, \ldots, N_c$$

here,

$$\frac{\partial \xi_2}{\partial \rho} = P_{na} S_2 \quad (207)$$

$$\frac{\partial \xi_3}{\partial \rho} = P_{na} S_3 \quad (208)$$

$$\left(\frac{\partial \xi_2}{\partial n_k}\right)_{T,V,n_{j\neq k}} = \frac{1}{V} P_{na} r_k d_k^2 \quad (209)$$

$$\left(\frac{\partial \xi_3}{\partial n_k}\right)_{T,V,n_{j\neq k}} = \frac{1}{V} P_{na} r_k d_k^3 \quad (210)$$

$$\left(\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_2}{\partial \rho}\right)\right)_{T,V,n_{j\neq k}} = P_{na}.\sum_{i=1}^{N_c}\left(\frac{\delta_{ik} - z_i}{n}\right) r_i d_i^2 = \frac{1}{V}.P_{na}.\frac{1}{\rho}\left[r_k d_k^2 - S_2\right] \quad (211)$$

$$\left(\frac{\partial}{\partial n_k}\left(\frac{\partial \xi_3}{\partial \rho}\right)\right)_{T,V,n_{j\neq k}} = P_{na}.\sum_{i=1}^{N_c}\left(\frac{\delta_{ik}-z_i}{n}\right) r_i d_i^3 = \frac{1}{V}.P_{na}.\frac{1}{\rho}\left[r_k d_k^3 - S_3\right] \tag{212}$$

$$kk = 1, 2, \ldots, N_{c_c}$$

In the above equations , δ_{jk} refers to dirac delta function which is defined as following:

$$\delta_{jk}\delta_{ik} = \begin{cases} 0 & j \neq k \\ 1 & j = k \end{cases} \tag{213}$$

3. Application of Chebyshev polynomials to calculate density

The integration of the terms used in equations (102), (114), (123) and (119) for calculating the fugacity coefficients are performed numerically using Gaussian quadrature method. We found that five point quadrature method leads to a result with acceptable accuracy. As it can be seen from Eq. (101) the fugacity coefficient is a function of temperature, pressure, composition and the properties of the components. In order to calculate the fugacity coefficient of each component, we should first calculate the density of mixture at a given pressure, temperature and composition using Eq. (2). As it can be seen, from the mentioned equation, the density as function of the pressure is not known explicitly. Therefore, the estimation of the density at a given pressure should be performed using an iterative procedure, starting from initial guesses because of the multiplicity of the solution. A solution which is obtained by an iterative technique depends on the choice of the initial guess. Therefore, iterative procedures can not cover all acceptable roots unless the number of roots and the approximate values of the solutions (i.e. initial guesses) had already been known. Hence, an alternative, robust, fast and accurate technique that can predict all acceptable solutions is proposed. The proposed method is based on a numerical interpolation using Chebyshev polynomials in a finite interval (Burden et al., 1981).

It should be pointed out that Chebyshev series provide high accuracy and can be transformed to power series which are suitable for root finding procedure. More general accounts of root finding through Chebyshev approximations are given in (Boyd, 2006). The aforementioned method enables us to calculate all possible solutions and select among them those which are physically interpretable.

It should be considered that using Chebyshev polynomials to approximate a given function will become more efficient when it has non-zero values at both end points of the interval. It can be shown that the pressure vs. density function in SAFT EoS linearly goes to zero for negligible values of the density. In order to avoid this problem, P/ρ vs. density using Chebyshev polynomials was interpolated.

Another advantage of using Chebyshev polynomials for approximating a function is that for a specific number of basic functions, it always leads to a well-conditioned matrix during the calculation of the unknown coefficients of the basis functions, which is more accurate than the other interpolation techniques.

Figure 2 shows the interpolation error using Chebyshev polynomials of degree 15 for approximating pressure vs. density of a binary mixture of ethanol and toluene containing 37.5 mole% ethanol. Figure 3 shows the error in interpolation for another system (oil sample) for which the composition is given in Table 2 (Jamaluddin et al., 2000).

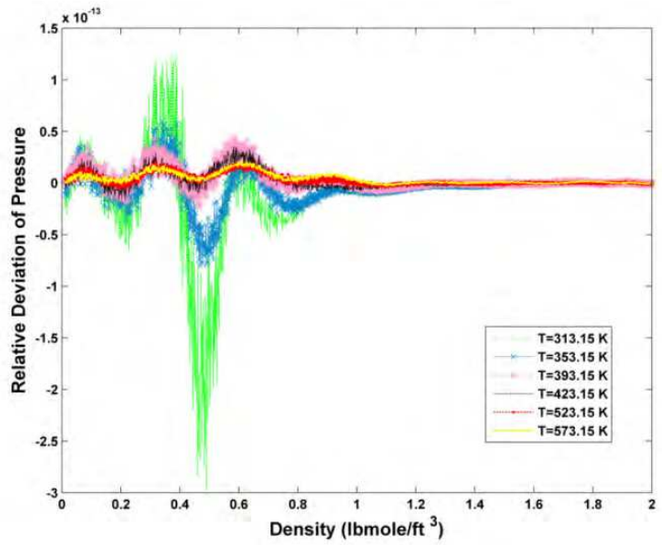


Fig. 2. Interpolation error using Chebyshev polynomials for approximating preesure vs. density of a binary mixture of ethanol and toluene containing 37.5 mole% of ethanol at different temperatures.

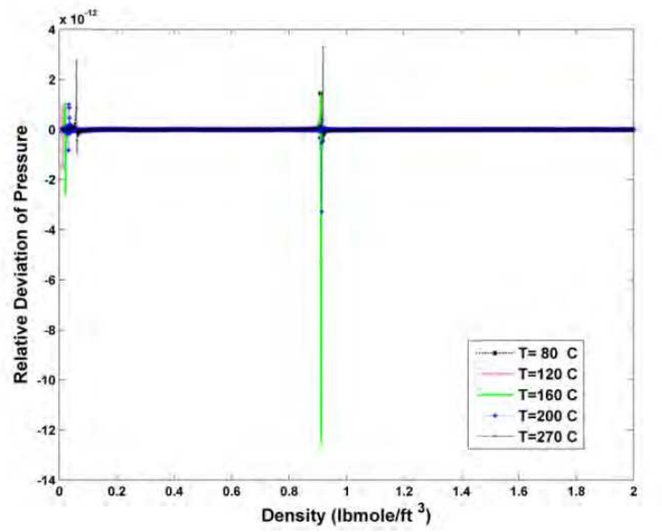


Fig. 3. Interpolation error using Chebyshev polynomials for approximating preesure vs. density at different temperatures for an oil sample of the composition given in Table 2.

After approximating the $P(\rho)$ function using Chebyshev polynomials, it is necessary to find solutions for density values at the given pressure(s) and select those which are physically interpretable. In doing so, the complex and negative solutions and those which make $\partial P/\partial \rho$

Component and Properties	Oil
N_2	0.49
CO_2	11.37
H_2S	3.22
C_1	27.36
C_2	9.41
C_3	6.70
iC_4	0.81
nC_4	3.17
iC_5	1.22
nC_5	1.98
C_6	2.49
C_{7+}	31.79
C_{7+} molecular weight	248.3
C_{7+} density (g/cm^3)	0.877

Table 2. Composition (mole%) and properties of the oil sample used to investigate the effect of temperature and pressure on asphaltene precipitation (Jamaluddin et al., 2000).

negative, are discarded because they have no physical meaning. Figure 4 shows a typical plot of pressure versus density for SAFT EoS in the positive region of density. As it can be seen in Figure 4, the derivative of pressure with respect to density ($\partial P/\partial \rho$) has two zeros in this region for different values of the shown temperatures. For pressures between the maximum and minimum of the $P(\rho)$ function (e.g. the pressure region between two parallel lines passing through the maximum and minimum of the middle curve), the system has three zeros one of which is not acceptable. The smaller root corresponds to the vapor phase density and the larger root corresponds to the liquid phase density. At pressures below the minimum of $P(\rho)$, the function has only a single root which is identified as the vapor phase density. At pressures above the maximum of $P(\rho)$, only a single zero is detected for the function which is identified as the liquid phase density. By increasing the temperature (Figure 5), the roots of $\partial P/\partial \rho$ approaches to each other. At some temperature they coincide above which $\partial P/\partial \rho$ has not any zero. At these temperatures the system has only a single root for any value of the pressure which is identified as the vapor phase density. Therefore, the procedure for finding roots of the SAFT EoS at the given pressure can be summarized as the following:

1. The pressure versus density of SAFT EoS is approximated using Chebyshev polynomials.
2. The derivative of pressure with respect to density is calculated to find zeros of $\partial P/\partial \rho$. The complex and negative zeros are eliminated.
3. The roots of the fitting polynomial are estimated at the given pressure using a proper root finding algorithm for polynomials. The negative and complex roots and those which make $\partial P/\partial \rho$ negative are eliminated.

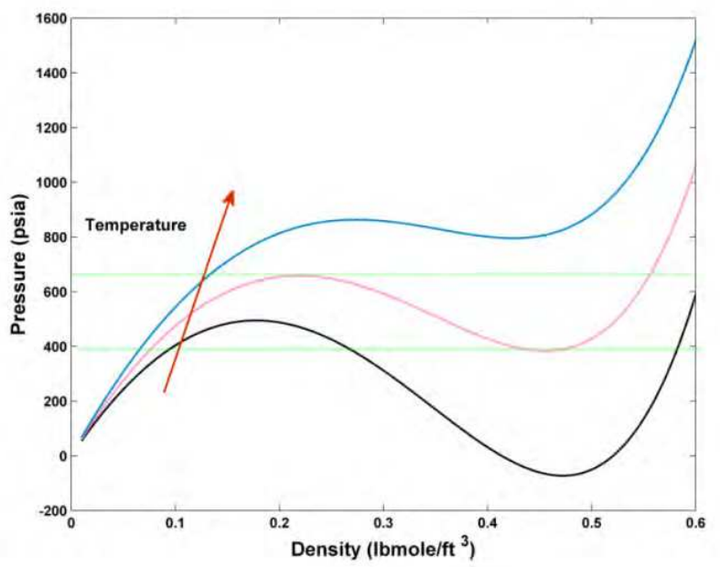


Fig. 4. A typical plot of pressure versus density of SAFT EoS at different temperatures.

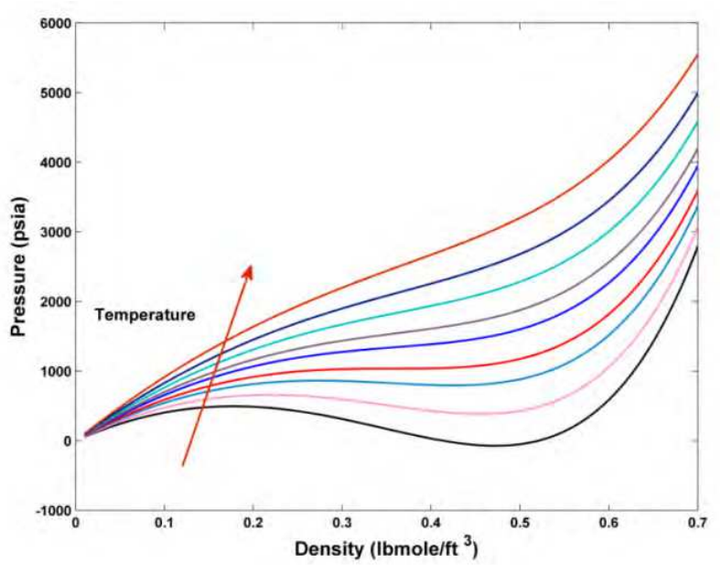


Fig. 5. A typical plot of pressure versus density of SAFT EoS at different temperatures.

4. If two physically meaning roots are obtained at the given pressure, the smaller root corresponds to vapor phase density and the larger one corresponds to the liquid phase density.
5. If the system has only a single root at the given pressure and $\partial P/\partial \rho$ has two zeros, if the obtained root is larger than the larger root of $\partial P/\partial \rho$, it is identified as the liquid phase density, otherwise, if the estimated root is smaller than the smaller root of $\partial P/\partial \rho$, it corresponds to the vapor phase density.
6. If the system has only a single root at the given pressure and $\partial P/\partial \rho$ has not any zero, the calculated root is identified as the vapor phase density.

4. Results and discussion

4.1 Density calculation for binary systems of ethanol and toluene

The SAFT EoS was first applied to calculate densities of the asymmetrical binary systems composed of ethanol and toluene. Experimental liquid densities for ethanol (1) and toluene (2) and seven of their binary mixtures in the temperature range 283.15-353.15 K at each 10 K and for pressures up to 45 MPa in steps of 5 MPa are given in (Zeberg-Mikkelsen et al., 2005). No density measurements were performed at 353.15 K and 0.1 MPa for ethanol as well as for mixtures containing more than 25 mole% ethanol, since ethanol and all mixtures with a composition higher than 25 mole% ethanol is either located in the two phase region or the gaseous phase (Zeberg-Mikkelsen et al., 2005). A comparison of the experimental density values of the aforementioned binary mixtures and pure compounds with the values calculated using SAFT EoS has been performed in this work. Figure 6 shows plots of the compressibility factor (Z-factor) of ethanol for different pressures of 0.1, 25 and 45 MPa using the SAFT EoS. As can be seen in this figure the contribution from the hard chain term ($Z_{hc} = Z_{hs} + Z_{ch}$), the dispersion term (Z_{disp}), and the association term (Z_{assoc}) are shown at different pressures versus density. Each point on a constant pressure curve corresponds to a certain temperature. Increasing the temperature, the liquid density decreases. A comparison between experimental and calculated densities using SAFT equation are presented in figures 7-10 versus pressure for different temperatures. The average absolute values of the relative deviations (AAD) found between experimental and calculated densities for different compositions of the binary mixtures of ethanol and toluene at different pressures and temperatures is 0.143%. Figure 11 represents relative deviations for different mixtures of ethanol and toluene on a 3D diagram.

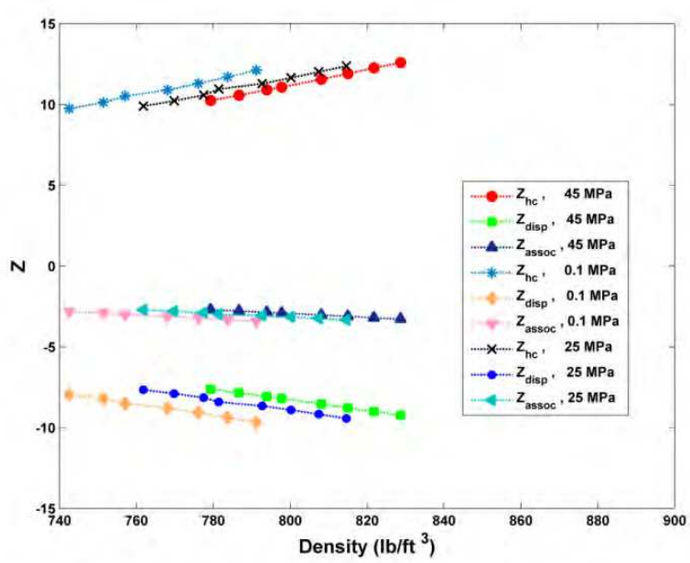


Fig. 6. Contributions to Z-factor of ethanol at different pressures and temperatures according to SAFT EoS.

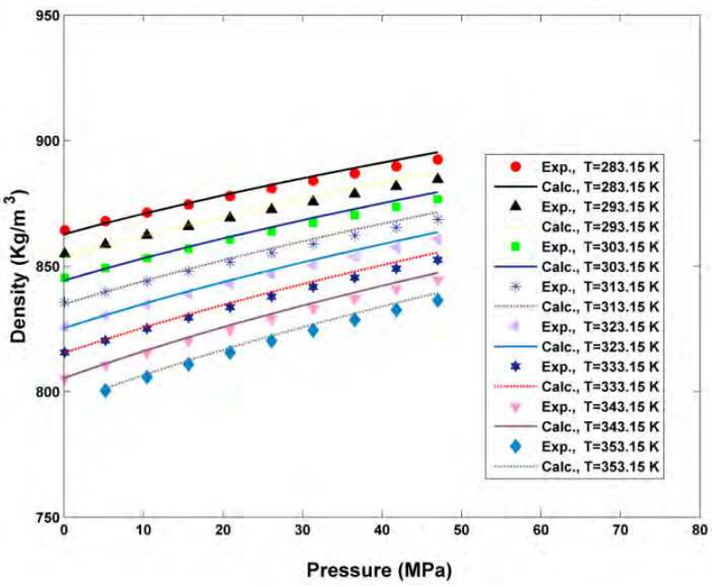


Fig. 7. Experimental and calculated densities versus pressure at different temperatures using SAFT EoS for binary system composed of ethanol and toluene at 25.0 mole% of ethanol.

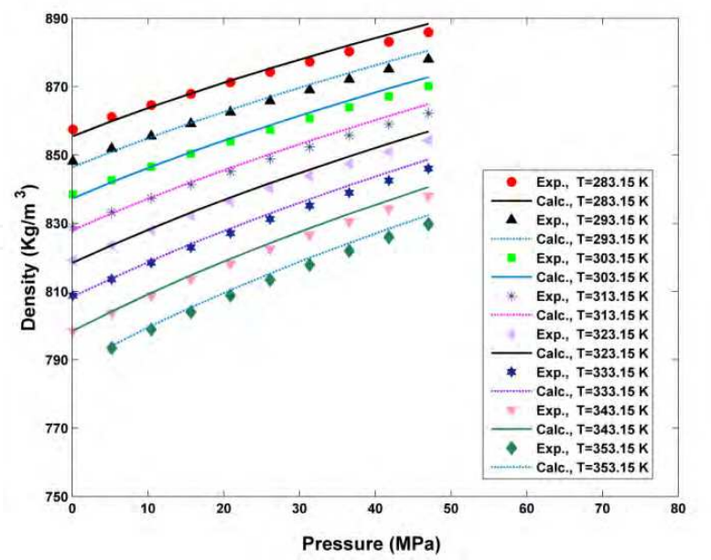


Fig. 8. Experimental and calculated densities versus pressure at different temperatures using SAFT EoS for binary system composed of ethanol and toluene at 37.5 mole% of ethanol.

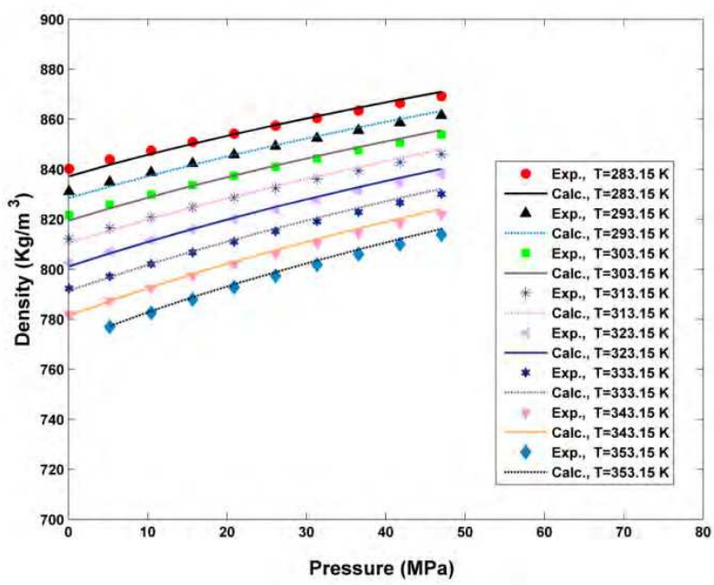


Fig. 9. Experimental and calculated densities versus pressure at different temperatures using SAFT EoS for binary system composed of ethanol and toluene at 62.5 mole% of ethanol.

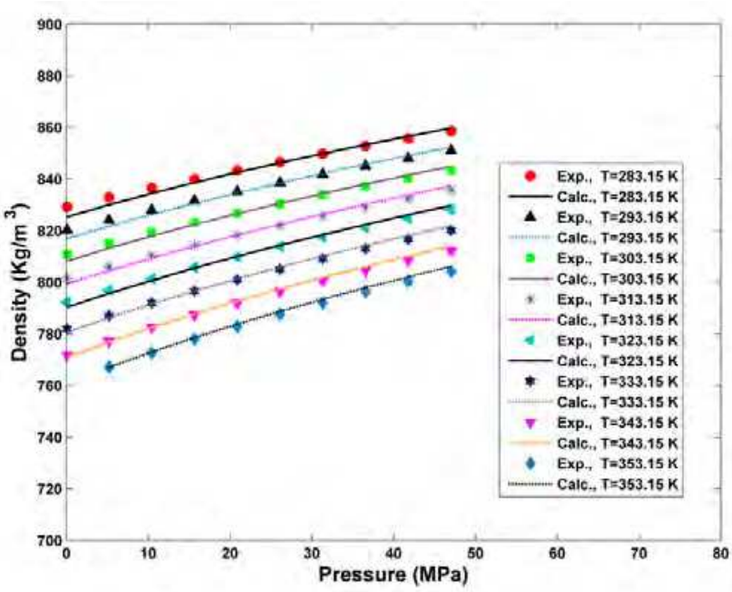


Fig. 10. Experimental and calculated densities versus pressure at different temperatures using SAFT EoS for binary system composed of ethanol and toluene at 75.0 mole% of ethanol.

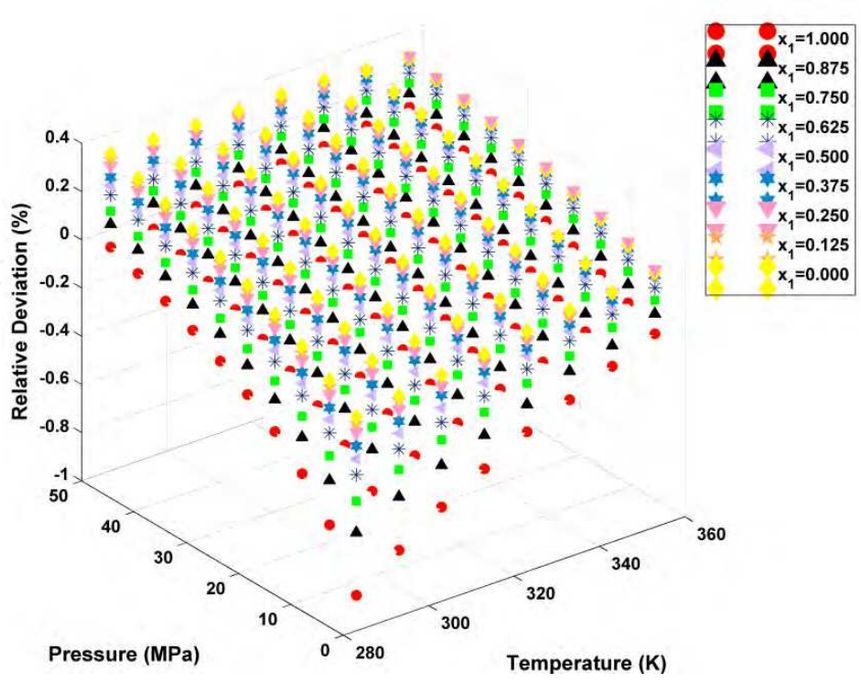


Fig. 11. Percent relative deviation of the calculated densities using SAFT EoS for different compositions of ethanol.

4.2 Phase equilibrium calculations for asphaltene-oil systems

Given a pressure, P, a temperature, T, and a mixture with global composition $z_i (i = 1, \dots, n_c)$, flash calculations determine the phase molar fraction and composition by solving equations (214) and (215),

$$f_i^V = f_i^L \qquad i = 1, \dots, N_c \tag{214}$$

$$f_{N_c}^L = f_{N_c}^S \tag{215}$$

f_i^V, f_i^L are the fugacity of component i in the vapor and liquid phase, respectively. $f_{N_c}^L$ and $f_{N_c}^S$ represent the fugacity of the asphaltene component in the liquid and solid phases respectively. The fugacity of the components in the vapor and liquid phases are calculated using the SAFT model as mentioned previously. In order to calculate the fugacity of the asphaltene component in the solid phase an experimental value of the asphaltene precipitation amount at a given temperature and pressure is required. Then, the thermodynamic equality of the fugacities at equilibrium conditions is used to calculate the reference value of the fugacity of the asphaltene component. The Quasi Newton Successive Substitution (QNSS) method, is used to solve the equilibrium equations. In conjunction with the above equations, the following material balance equations can be derived:

$$\sum_{i=1}^{N_c} \frac{\left(K_i^{VL} - 1\right) z_i}{1 + V\left(K_i^{VL} - 1\right) + S\left(K_i^{SL} - 1\right)} = 0 \qquad i = 1, \dots, N_c \tag{216}$$

$$\sum_{i=1}^{N_c} \frac{\left(K_i^{SL}-1\right)z_i}{1+V\left(K_i^{VL}-1\right)+S\left(K_i^{SL}-1\right)} = 0 \qquad i = 1, \ldots, N_c \tag{217}$$

where, V and S are the mole fraction of the gas and solid phases, respectively. K_i^{VL} and K_i^{SL} are the equilibrium ratios of the vapor-liquid and liquid-solid phase equilibrium, respectively. In order to find the values of V and S using the above system of equations, we used the Newton-Raphson method. The complexity of multiphase flash calculations is due to the fact that the number of phases in equilibrium is not known a priori. The stability test for performing multiphase flash calculations has been performed using the stage-wise method developed by Michelsen (Michelsen, 1982a, 1982b). The parameters of the SAFT EoS including r, σ and ε have been given by Gross and Sadowski (2001) for N_2, CO_2 and hydrocarbons from C_1 to C_{20}. The values of these parameters for heavier and lumped component, also the volume and energy parameters used in association term have been estimated using a tuning approach. The thermodynamic model was applied to predict the precipitation behavior of petroleum fluids. The SAFT model has been used to describe the oil and gas phases. Table 3 presents the composition of an oil sample and a solvent from Burke et al. (1990). The oil sample was mixed with various amounts of solvent. Table 4 shows the precipitation and saturation pressure data for different concentrations of solvent in the oil sample for which the compositions are given in Table 3. The weight percent corresponds to the percentages with respect to the original mass of the oil. The last column in Table 4 shows the total amount of precipitates. To estimate the fugacity of pure asphaltene phase at a reference state, data at 0 mole% of solvent and $P^* = 3014.7$ psia and $T = 218$ °F was used. The amount of precipitate, 0.14 weight%, was removed from the feed. The fugacity of the asphaltene component in the remaining mixture was then calculated using SAFT equation of state and equated to f_s^* (reference state fugacity of the asphaltene). The amounts of asphaltene precipitation and saturation pressures are also calculated using WinProp (CMG software) in which the fluid phases are described with a cubic equation of state and the fugacities of components in the solid phase are predicted using the solid model desribed in (Nghiem & Heidemann, 1982). In this work the Peng-Robinson equation of state has been used to describe the fluid phases non-ideality. Figures 12-13 represent a comparison between experimental and calculated asphaltene precipitation amounts and saturation pressures at different concentrations of solvent in the oil sample using SAFT EoS and WinProp software. As it can be seen in Figure 12 and Table 4, for solvent concentration above 78 mole%, the measured values show a substantial decrease in the precipitate. For this case, WinProp does not show a drop in the amount of precipitate. Howevere, it shows that the amount of precipitate levels off at high concentration of the solvent. Burke et al. (1990), and Chaback (1991) attributed the decrease in the precipitate at high solvent concentration to the switching of the mixture from bubble point fluid to a dew point fluid. WinProp does not show a decrease in the precipitate, while SAFT EoS based on the developed method for the calculation of densities and fugacities shows a very good agreement with measured data. The saturation pressures calculated using the proposed model at solvent concentrations above 78 mole % correspond to the upper dew point pressures while those calculated using WinProp are the buuble point pressues (Figure 13). The average relative deviations of saturation pressure and asphaltene precipitation amount using SAFT EoS are 4.6% and 3.8%, respectively. The values of AAD obtained using WinProp are higher than 17% for both parameters.

Component and Properties	Oil	Solvent
N_2	0.51	3.17
CO_2	1.42	17.76
C_1	6.04	30.33
C_2	7.00	26.92
C_3	6.86	13.09
iC_4	0.83	1.26
nC_4	3.35	4.66
iC_5	0.70	0.77
nC_5	3.46	1.26
C_6	3.16	0.78
C_{7+}	66.68	
C_{7+} molecular weight	281	
C_{7+} specific gravity	0.9020	
Oil molecular weight	202.4	
API gravity of stock tank oil	24.0	
Reservoir temperature, °F	218	
Saturation pressure, psia	600	

Table 3. Composition (mole%) and properties of oil ad solvent from Burke et al. (1990).

Solvent (mol%)	Mixture Saturation Pressure (psia)		Test Pressure (psia)	Precipitates from oil (wt%)		Total Precipitaes (wt%)
	Exp.	Calc.		Exp.	Calc.	
0	600	596.14	3014.7	0.14	0.1578	8.97
20	1050	1053.3	3014.7	0.27	0.2667	7.83
50	2310	2142	3014.7	1.46	1.4700	6.96
70	3750	3467	4214.7	1.65	1.6503	4.34
78	4510	4565	5014.7	3.21	3.4025	7.84
85	5000	5395	5014.7	1.29	1.2714	8.02
90	4250	4578	5014.7	1.10	1.0428	7.17

Table 4. Experimental and calculated values of the amount of asphaltene precipitation and saturation pressure for different mixtures of the oil sample and solvent given in Table 3.

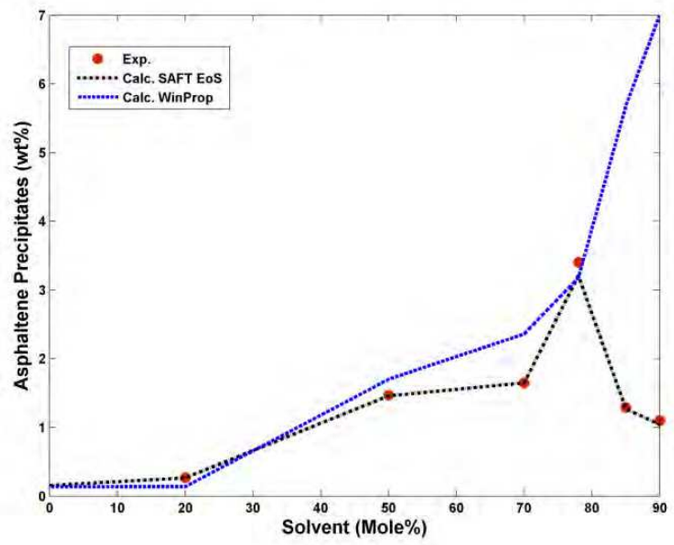


Fig. 12. Comparison between experimental and calculated values of the amount of asphaltene precipitation for different mixtures of the oil sample and solvent given in Table 3 using SAFT EoS and WinProp.

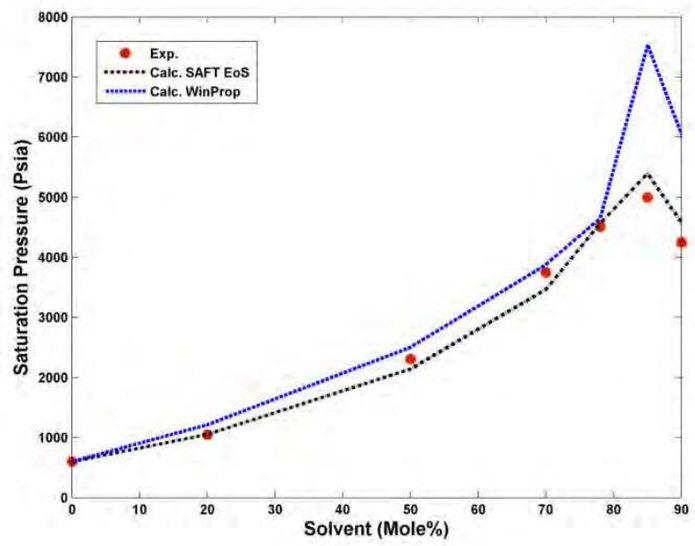


Fig. 13. Comparison between experimental and calculated values of the saturation pressure for different mixtures of the oil sample and solvent given Table 3 using SAFT EoS and WinProp.

The effect of temperature and pressure on the solid model prediction results has also been investigated. To do so, different hydrocarbon mixtures have been used. Figure 14 shows a comparison between the calculated and experimental values of the bubble point pressure and upper asphaltene onset pressure (AOP) for an oil sample (Jamaluddin et al., 2002). As it can be seen in this figure, excellent agreement is observed between experimental and predicted values of the upper AOP using SAFT EoS. The average values of the relative

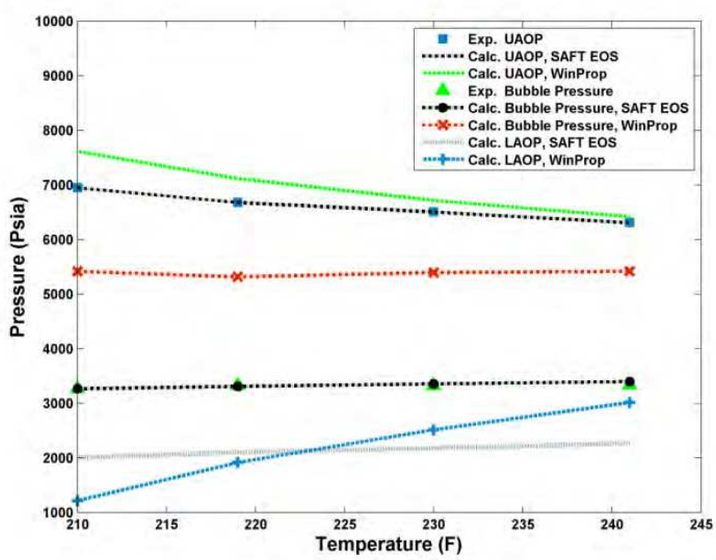


Fig. 14. Comparison between experimental and calculated values of the saturation pressure, upper and lower AOP's for the oil sample given in (Jamaluddin et al., 2002) using SAFT EoS and WinProp.

deviation in calculating the upper AOP using SAFT EoS and WinProp are 0.002% and 5.26%, respectively. Also, shown in Figure 14 are the calculated values of the lower AOP at different temperatures. The amounts of asphaltene precipitation vs. pressure at different temperatures is presented in Figure 15 for SAFT EoS. As it shown (Fig. 15) the maximum values of the asphaltene precipitation occures at the bubble point pressure of the mixture above which the amount of precipitaes decreases by increasing pressure up to upper AOP. In the pressure range below the bubble point pressure, decreasing pressure leads to a decrease in the amount of asphaltene precipitation and becomes infinitesimal at lower AOP. The effect of the injection gas on the asphaltene precipitation conditions has also been investigated for an oil sample given in (Rydahl et al., 1997) (Figures 16-17). Figure 17 shows that by increasing the amount of the injection gas added to the initial oil, the pressure interval of the asphaltene precipitation increases and shifts to the right side of the figure. Also, the amount of asphaltene precipitation increases by increasing the amount of the injection gas. A similar scenario happens when using WinProp.

The amount of asphalltene precipitation at different dilution ratios of normal heptane (nC_7) and stock tank conditions, are also calculated using both models for two Iranian oil samples, Sarvak oil A and Fahliyan oil (Bagheri et al., 2009). Figures 18-19 shows a comparison between experimental and calculated amount of asphaltene precipitation vs. dilution ration of nC_7 using SAFT EoS and WinProp. Again an excellent agreement has been observed using SAFT EoS with the experimental data. As it can be seen in these figues using WinProp, the amount of precipitaes increases rapidly at low dilution ratios after which the slope of the curve does not change considerably. The results show that SAFT EoS with average relative deviations of 2.32% and 1.73% for Sarvak oil A and Fahliyan oil, agrees well with the experimental data in comparison with the results obtained using WinProp (10.26% and 13.19%).

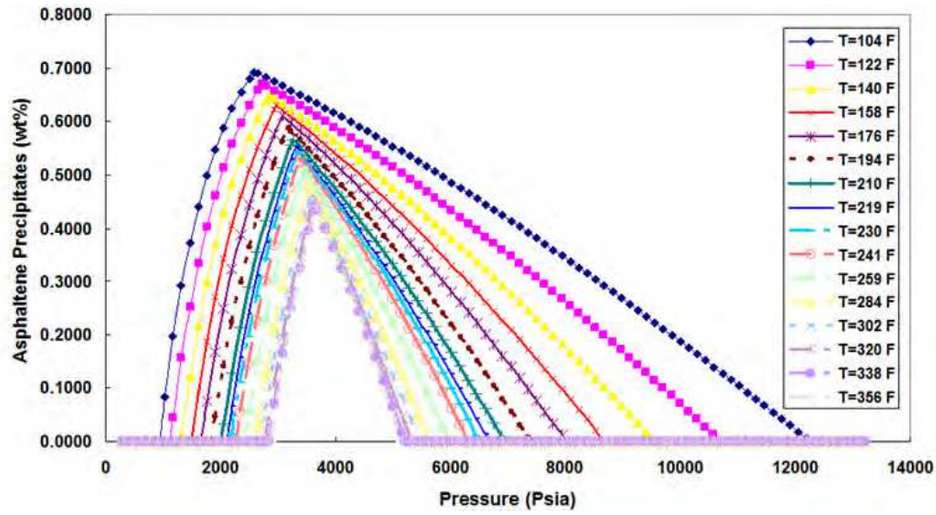


Fig. 15. The amount of asphaltene precipitation vs. pressure at different temperatures for the oil sample given in (Jamaluddin et al., 2002) using SAFT EoS.

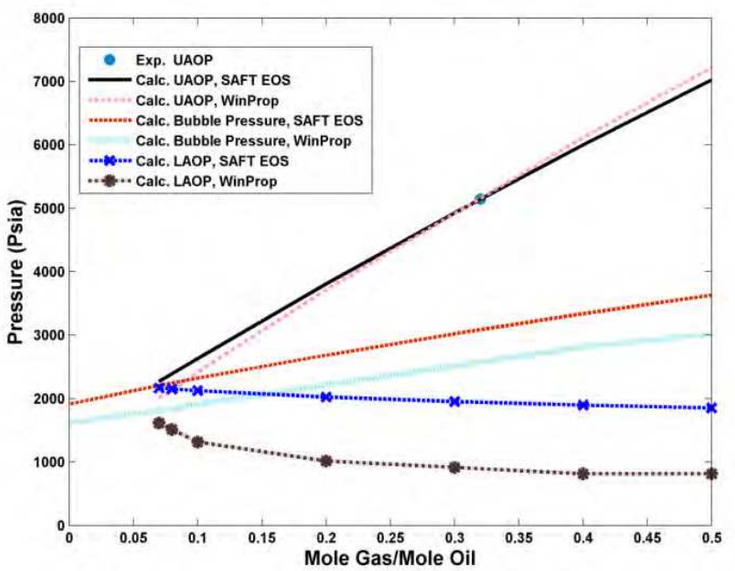
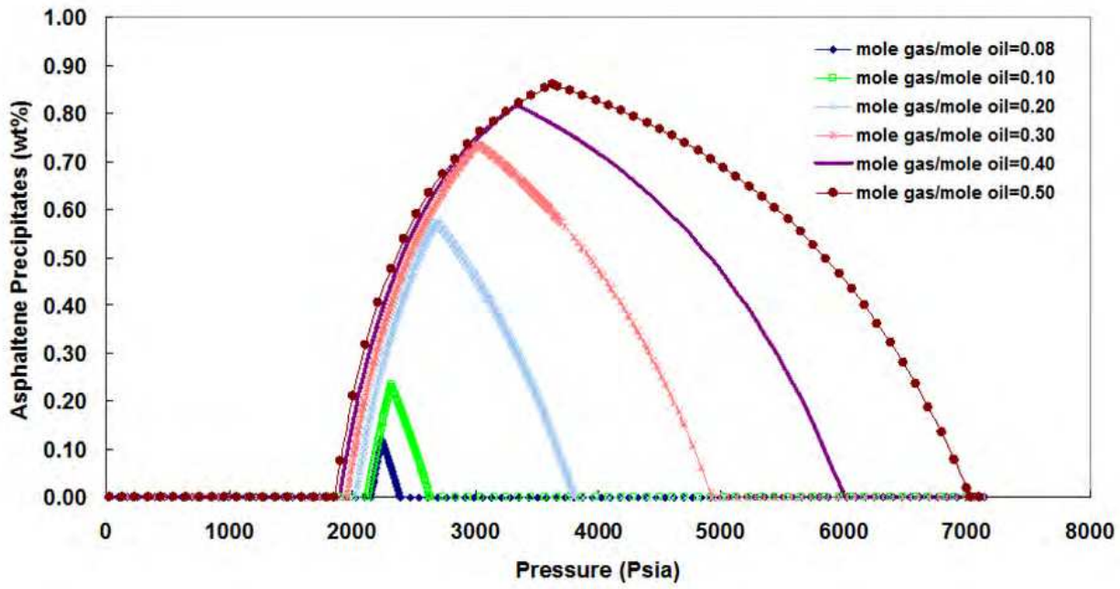
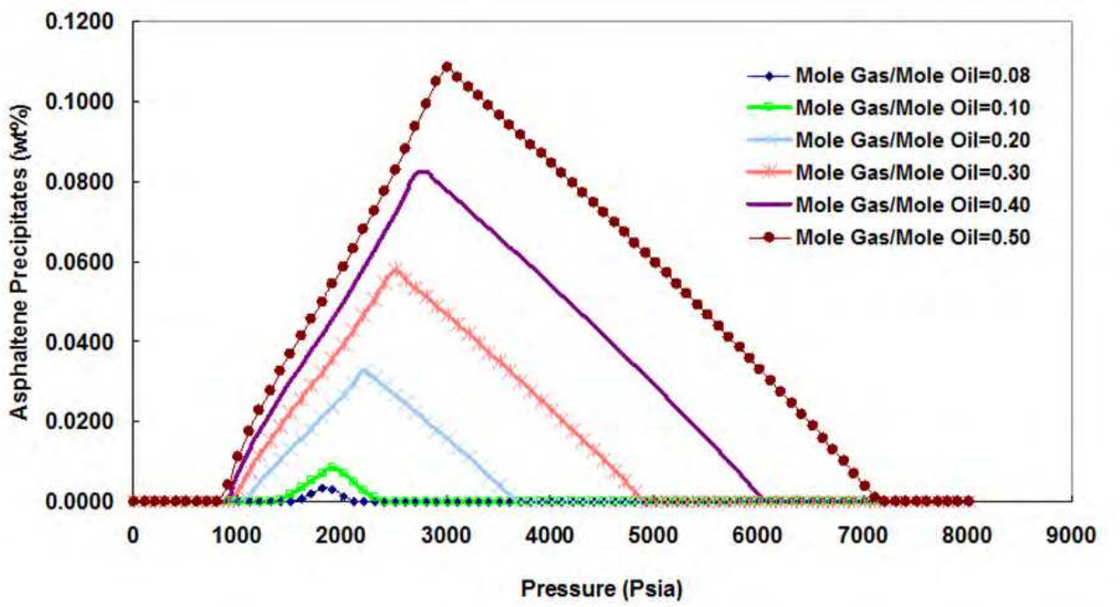


Fig. 16. Calculated values of the saturation pressure, upper and lower asphaltene AOP's vs. the amount of injection gas for the oil sample given in (Rydahl et al., 1997) using SAFT EoS and WinProp.



(a)



(b)

Fig. 17. The amount of asphaltene precipitation vs. pressure at different values of the injection gas for the oil and gas samples given in (Rydahl et al., 1997) using (a) SAFT EoS and (b) WinProp.

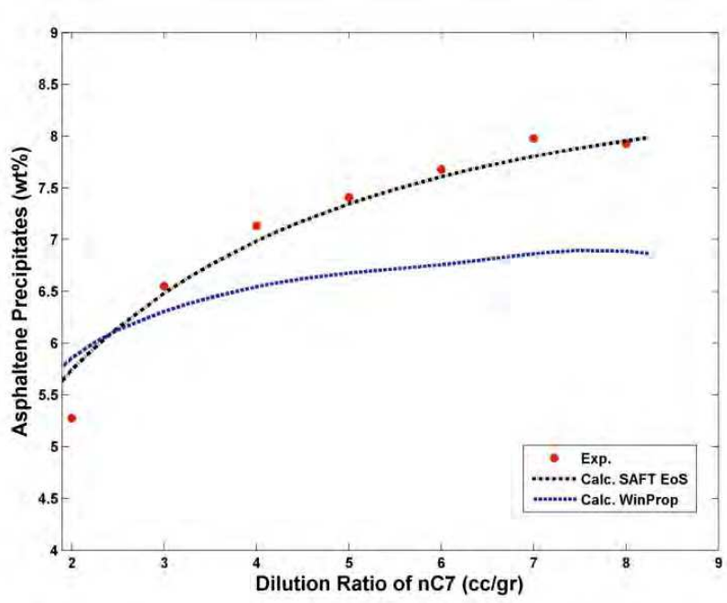


Fig. 18. Comparison between experimental and calculated values of the amount of asphaltene precipitation vs. dilution ration of nC_7 for Sarvak Oil A (Bagheri et al., 2009) using SAFT EoS and WinProp.

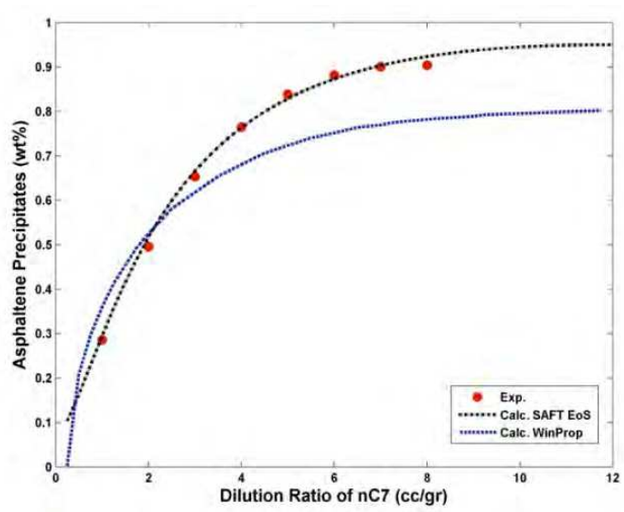


Fig. 19. Comparison between experimental and calculated values of the amount of asphaltene precipitation vs. dilution ration of nC_7 for Fahliyan Oil (Bagheri et al., 2009) using SAFT EoS and WinProp.

5. Conclusion

In this study a model based on statistical association fluid theory (SAFT) has been developed to predict phase behavior of hydrocarbon systems containing asphaltene and associating components. A robust, fast and accurate method based on Chebyshev polynomial approximation was proposed to find density using SAFT EoS which plays an important role in the calculation of the fugacity coefficients. The model was first evaluated using binary systems of ethanol and toluene. A good agreement between experimental and calculated liquid densities at different pressures, temperatures and compositions was obtained. The proposed model was then used to investigate the effect of solvent addition on the amount of asphaltene precipitate. The results showed a good agreement between experimental and calculated values of the amount of precipitate for different solvent–oil mixtures. In addition, the effect of temperature on the onset pressure of asphaltene precipitation and bubble point pressure was investigated. An excellent agreement was observed between experimental and predicted values of the asphaltene onset pressure at different temperatures.

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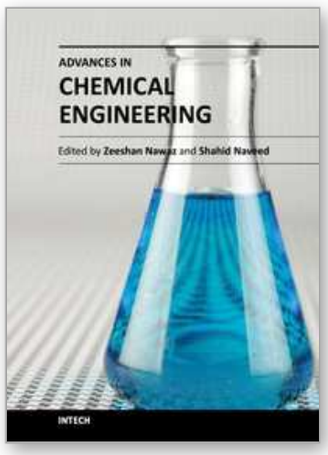
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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the sate of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided in to two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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