

Estimation of Solubility of BTEX, Light Hydrocarbons and Sour Gases in Triethylene Glycol Using the SAFT Equation of State

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An accurate prediction of the absorption and desorption of benzene, toluene, ethylbenzene, and xylenes (BTEX) is important for the estimation of BTEX emissions from glycol units in natural gas processing plants. This work presents an approach to accurately model the solubilities of BTEX in triethylene glycol (TEG). The absorption of gases studied in this work into TEG is physical in nature, and therefore, is treated as a physisorption behavior in modeling. The Huang-Radosz version of statistical associating fluid theory (SAFT-HR) equation of state (EoS) was utilized to estimate the solubilities of BTEX in TEG. A new set of SAFT parameters for TEG, as well as a new set of binary interaction parameters between TEG and other components were obtained by fitting experimental vapor pressure and liquid density of TEG and available experimental binary VLE data, respectively. Using these parameters, solubility of multicomponent gases in TEG are accurately predicted. To have an estimation on the relative accuracy of SAFT-HR EoS, the results from Perturbed-Chain SAFT (PC-SAFT) and Peng-Robinson (PR) EoS are also reported. The overall average of root-mean-square deviations (RMSD) for the binary and ternary systems studied in this work, using SAFT-HR, PC-SAFT and PR EoS, were found to be 0.12, 0.20 and 1.56, respectively.

Keywords: Equation of state, Solubility, Absorption, Triethylene glycol, BTEX, SAFT EoS model

INTRODUCTION

Natural gas sweetening is a process of removing acid gases including carbon dioxide and sulfur compounds. After this process, the natural gas often undergoes a dehydration process, in which water is removed from the natural gas. Selection of the dehydration process is affected by some factors such as hydrate formation, corrosion in pipelines, and free water formation. The standard process of natural gas dehydration is the solvent absorption, where TEG is a common solvent [1].

The solvent used in absorption dehydration should meet several criteria such as: (1) high absorption capacity for water and low absorption capacity for hydrocarbons, (2) low volatility to minimize vaporization losses, (3) low viscosity to minimize energy required for pumping, and (4) good thermal stability to prevent decomposition at regeneration

temperatures [2]. Glycols commonly used in dehydration industry include ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetra ethylene glycol (T₄EG) and propylene glycol. Among these glycols, TEG is the common choice as an absorbent [2].

A group of the natural gas constituents, namely benzene, toluene, ethylbenzene, and xylenes (BTEX) have been attracted environmental considerations. These compounds are reported to have a significant contribution (20-40%) in the volatile organic compounds (VOC) present in the environment [3,4]. The VOCs are considered harmful environmental pollutants affecting the human health, ecosystem and atmosphere [5-9]. Benzene is considered a carcinogen compound [10,11] and stands in the 6th rank of the substance priority list reported by the Agency for Toxic Substances and Disease Registry [12]. An important source of BTEX emissions in the atmosphere is the vent gas from regenerators in sweetening and dehydration units. In the absorber, BTEX compounds present in the natural gas are

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dissolved in TEG. In the regenerator, these compounds leave TEG along with the water vapor. This led to environmental regulations on vent streams from gas processing units. Therefore, accurate estimation of solubility of BTEX compounds in TEG, is of fundamental importance in the design and optimization of natural gas dehydration units using glycols.

Several attempts have been made to estimate BTEX solubility in glycols. Li and Englezos [13] predicted VLE of systems including binary mixtures of alcohols with water and benzene, and ternary VLE for aqueous mixture of propylene glycol and EG, using SAFT EoS. Khosravanipour Mostafazadeh *et al.* [14] measured VLE data for the systems (water + TEG) and (water + TEG + toluene) at a pressure of 85 kPa. Three activity coefficient models (NRTL, UNIQUAC, and van Laar) were used for modeling and correlation of the experimental data. Fouad and Berrouk studied VLE in natural gas systems using PC-SAFT and PR EoS [15]. Vapor pressure and liquid density data were used to optimize PC-SAFT parameters of TEG and EG. The results from PR EoS were superior for the estimation of VLE of dry natural gas systems. For the systems containing water and methanol, however, PC-SAFT was more accurate than PR EoS [15]. Rodrigues *et al.* [16] measured Liquid-Liquid Equilibrium (LLE) in the systems (decane + toluene + DEG) and (decane + toluene + TEG) at two different temperatures and atmospheric pressure. The NRTL and UNIQUAC models were used to correlate experimental data.

Molecular-based equations of state are generally more complicated than cubic equations of state, and often lead to more accurate results [17-19]. The SAFT EoS is a molecular-based equation of state which is proven to have a good performance in several fields including vapor-liquid equilibrium (VLE) in fluid systems as well as gas solubility into different solvents [20-25]. In this work, the solubility of natural gas compounds, including BTEX, in TEG has been estimated using the Huang-Radosz version of SAFT (SAFT-HR) EoS [26,27]. In order to compare the accuracy of SAFT-HR EoS, results from PC-SAFT and PR EoS are presented. This article is organized as follows. Section 2 introduces the thermodynamic framework including EoS and phase equilibrium calculation algorithms used in this work. Results and discussion on pure component parameter

estimation and VLE in the systems studied are presented in Section 3, and conclusions are drawn in Section 4.

THERMODYNAMIC FRAMEWORK

SAFT EoS

SAFT EoS is based on the Wertheim's thermodynamic perturbation theory [28]. Chapman *et al.* developed the SAFT EoS on the basis of this theory [29,30]. In the SAFT framework, three parameters are required to identify a non-associating substance: the number of segments, segment volume, and the dispersion interaction energy between segments. In addition to these parameters, two parameters are needed to define association interactions in associating substances: association energy and bonding volume.

According to the SAFT theory, equation of state for a substance is expressed as a residual Helmholtz energy which includes three contributions from segment interaction, chain formation energy, and association [26]:

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \quad (1)$$

where a is the molar Helmholtz energy. The superscripts *res*, *seg*, *chain* and *assoc* represent the residual, segment, chain formation, and association contributions, respectively. The segment contribution includes hard sphere (*hs*) and dispersion (*disp*) contributions.

$$a^{seg} = a^{hs} + a^{disp} \quad (2)$$

SAFT-HR uses the hard sphere contribution as given by Mansoori *et al.* [31]:

$$\frac{a^{hs}}{RT} = \frac{6}{\pi\rho} \left[\frac{(\zeta_2)^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2(\zeta_3)^2}{\zeta_3(1-\zeta_3)^2} - \left[\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \right] \ln(1-\zeta_3) \right] \quad (3)$$

$$\zeta_k = \left(\frac{\pi N_{AV}}{6} \right) \rho \sum_i x_i m_i (d_i^k) \quad (4)$$

where R is the universal gas constant, ζ_k is a function of molar density, x is the molar fraction, N_{AV} is Avogadro's number, ρ is molar density, d is the temperature-dependent

segment diameter, m is the number of segments, and the index i runs over all components in the mixture.

The dispersion contribution is given by [26]:

$$\frac{a^{disp}}{RT} = \bar{m} \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \quad (5)$$

$$\bar{m} = \sum_i x_i m_i \quad (6)$$

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j m_i m_j \left[\frac{u_{ij}}{kT} \right] (v^o)_{ij}}{\sum_i \sum_j x_i x_j m_i m_j (v^o)_{ij}} \quad (7)$$

$$(v^o)_{ij} = \frac{1}{2} \left[(v^o)_i^{\frac{1}{3}} + (v^o)_j^{\frac{1}{3}} \right]^3 \quad (8)$$

$$u_{ij} = (1 - k_{ij}) (u_{ii} u_{jj})^{\frac{1}{2}} \quad (9)$$

$$\eta = \frac{\pi N_{AV}}{6} \rho m d^3 \quad (10)$$

where D_{ij} are universal constants [26], η is reduced density, v^o is temperature-dependent segment volume, k_{ij} is the binary interaction parameter between components i and j , $\tau = (\pi / 6) \sqrt{2}$ is the maximum packing fraction of spheres, and u/k is the dispersion energy between segments.

The chain contribution (a^{chain}) represents the chain formation by segments. This contribution is based on the associating fluid theory and is given by [30]:

$$\frac{a^{chain}}{RT} = \sum_i x_i (1 - m_i) \ln g_{ii}(d_{ii}) \quad (11)$$

where the radial distribution function at contact, $g_{ii}(d_{ii})$, is given by Mansoori *et al.* [31]:

$$g_{ii}(d_{ii}) = \frac{1}{(1 - \zeta_3)} + \frac{3d_{ii}}{2} \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left[\frac{d_{ii}}{2} \right]^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3} \quad (12)$$

The association contribution (a^{assoc}) is related to the association forces between chains of segments and can be

calculated from [30]:

$$\frac{a^{assoc}}{RT} = \sum_i x_i \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right] \quad (13)$$

$$X^A = \left[1 + \rho \sum_i \sum_{B_j} x_j X^{B_j} \Delta^{A,B_j} \right]^{-1} \quad (14)$$

$$\Delta^{A,B_j} = (\sigma_{ij})^3 \kappa^{A,B_j} g_{ij}(d_{ij}) \left[\exp\left(\frac{\epsilon^{A,B_j}}{kT}\right) - 1 \right] \quad (15)$$

where M indicates number of association sites, X^A is the ratio of molecules with no bond at site A to the total number of molecules, Δ^{AB} is strength of interaction between two association sites A and B , κ^{A,B_j} represents association interaction volume, ϵ is the association energy between two sites and $g_{ij}(d_{ij})$ is the radial distribution function [31]:

$$g_{ij}(d_{ij}) = \frac{1}{(1 - \zeta_3)} + \left(\frac{3d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right) \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left[\frac{d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right]^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3} \quad (16)$$

PC-SAFT EoS

Several modifications of SAFT EoS have been introduced, where the Perturbed-Chain SAFT (PC-SAFT) is one of the most successful versions [32]. The fundamental revision is that instead of making chains from segments with dispersion interactions, PC-SAFT takes chains of hard segments and adds perturbation (dispersion) to the chains. The PC-SAFT EoS can be written as [32]:

$$a^{res} = a^{hc} + a^{disp} \quad (17)$$

where a^{hc} is the hard-chain contribution given by:

$$a^{hc} = \bar{m} a^{hs} - \sum_i x_i (m_i - 1) \ln g_{ii}^{hs}(\sigma_{ii}) \quad (18)$$

where g^{hs} is the average radial distribution function, σ is segment diameter, and \bar{m} is the mean segment number given by Eq. (6).

The dispersion contribution, a^{disp} , is given by [32]:

$$a^{disp} = -2\pi\rho I_1(\eta, m)\overline{m^2\varepsilon\sigma^3} - \pi\rho m C_1 I_2(\eta, m)\overline{m^2\varepsilon^2\sigma^2} \quad (19)$$

where η is packing fraction, ε is the depth of pair potential, k_{ij} is the binary interaction parameter between components i and j , and I_1 and I_2 are abbreviations [32]:

$$C_i = (1 + Z^{hc} + \rho \frac{\partial Z}{\partial \rho})^{-1} = (1 + \bar{m} \frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1 - \bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^3}) \quad (20)$$

$$\overline{m^2\varepsilon\sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right) \sigma_{ij}^3 \quad (21)$$

$$\overline{m^2\varepsilon^2\sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)^2 \sigma_{ij}^3 \quad (22)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (23)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} (1 - k_{ij}) \quad (24)$$

$$I_1(\eta, \bar{m}) = \sum_{i=0}^6 a_i (\bar{m}) \eta^i \quad (25)$$

$$I_2(\eta, \bar{m}) = \sum_{i=0}^6 b_i (\bar{m}) \eta^i \quad (26)$$

$$a_i(\bar{m}) = a_{0i} + \frac{\bar{m}-1}{\bar{m}} a_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2i} \quad (27)$$

$$b_i(\bar{m}) = b_{0i} + \frac{\bar{m}-1}{\bar{m}} b_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} b_{2i} \quad (28)$$

Peng-Robinson EoS

The PR EoS can be written as [33]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v+(1-\sqrt{2})b)(v+(1+\sqrt{2})b)} \quad (29)$$

where v is molar volume, and other parameters defined are as follows:

$$a(T) = \left[0.45724 \frac{\alpha(T)R^2 T_c^2}{P_c} \right] \quad (30)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (31)$$

$$\alpha(T) = \left[(1 + 0.37464 + 1.5422\omega - 0.2699\omega^2)(1 - T_r^{0.5}) \right]^2 \quad (32)$$

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j a_{ij} \quad (33)$$

$$b = \sum_{i=1}^N x_i b_i \quad (34)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (35)$$

where the subscript C represents the critical property, ω is the acentric factor, and $T_r = T/T_c$ is the reduced temperature.

Phase Equilibrium Calculations

In this work, vapor-liquid equilibrium calculations were performed using the Flash calculations at given temperature and pressure [34]. Assuming a total amount of one mole of mixture with a given composition Z_i , the molar fraction of liquid and vapor phases can be determined from mole balance. The PT-Flash algorithm using an EoS is described in detail elsewhere [34]. It is worthwhile to mention that the solubility of gases studied in this work into TEG are assumed physical absorption, therefore no chemical reaction occurs in the liquid phase.

RESULTS AND DISCUSSION

Estimation of Pure Component Parameters

Pure component SAFT-HR parameters, for some substances is reported by Huang and Radosz [26]. In this work, the parameters of benzene, toluene, carbon dioxide, hydrogen sulfide, methane, ethane, propane, and water were adapted from Huang and Radosz [26]. The parameters of TEG required by the SAFT-HR EoS were estimated using vapor pressure and liquid density data [35]. In order to fit the parameters to the available experimental data, the following objective function, OF , was used:

$$OF = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{P_{i,cal}^{sat} - P_{i,exp}^{sat}}{P_{i,exp}^{sat}} \right)^2} + \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{\rho_{i,cal}^{sat} - \rho_{i,exp}^{sat}}{\rho_{i,exp}^{sat}} \right)^2} \quad (36)$$

Table 1. Estimated SAFT-HR Parameters of TEG from Regression ($v^\circ = 12 \text{ ml mol}^{-1}$)

| m | u/k (K) | ε/k (K) | k |
|--------|--------------|------------------------|--------|
| 6.1534 | 237.80 | 1875.8 | 0.2373 |

Table 2. Root-mean-square Deviation^a of SAFT-HR EoS Predictions of Vapor Pressure and Liquid Density of TEG from Experimental Data [35]

| RMSD p^{sat} | RMSD ρ^{sat} |
|-----------------------|--------------------------|
| 0.0633 | 0.0122 |

$$^a \text{RMSD}_p = \sqrt{\sum_{i=1}^N [(p_{i,\text{sat}}^{\text{cal}} - p_{i,\text{sat}}^{\text{exp}}) / p_{i,\text{sat}}^{\text{exp}}]^2 / (N-1)}$$

where N is the number of data points and the superscript *sat* indicates the saturated conditions.

Pure component PC-SAFT parameters for the non-associating substances including light hydrocarbons, benzene, toluene, and carbon dioxide were adapted from Gross and Sadowski [32]. Also, the parameters of TEG were used as reported by Grenner *et al.* [36].

It is a common practice to model glycol molecules using the 4C association scheme, in which a molecule contains 4 association sites, half of them having a positive attraction and the other half having a negative attraction [13,15]. For a TEG molecule having two hydroxyl groups, the association of oxygens in the hydroxyl groups is considered, while neglecting the association of oxygens in oxyethylene groups [13,15,36-38]. This leads to a total of 4 association sites on a molecule.

In order to represent the TEG as an associating substance within SAFT EoS, five pure component parameters are required: m , v° , u/k , ε/k , and k . Following the work of Huang and Radosz [26], where constant values of v° applied for alkanols and amines, in this work a value of $v^\circ = 12 \text{ ml mol}^{-1}$ was considered. The remaining four parameters were obtained by fitting experimental data of vapor pressure and liquid density [35]. The fitted parameters and the resulting deviations of SAFT-HR EoS predictions of

vapor pressure and liquid density from experimental data, are reported in Tables 1-2. In Figs. 1 and 2, the vapor pressure and liquid density predicted by SAFT-HR EoS are compared with those from available experimental data as a function of temperature.

Vapor-liquid Equilibrium in Mixtures

In this work, the solubility of benzene, toluene, carbon dioxide, methane, ethane, propane, hydrogen sulfide, and water in TEG, have been estimated using SAFT-HR, PC-SAFT, and PR EoS. For all binary systems, the binary interaction parameters were optimized using the available vapor-liquid equilibrium experimental data of binary systems. The target function used for the fitting is given by:

$$OF = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{x_{i,\text{cal}} - x_{i,\text{exp}}}{x_{i,\text{exp}}} \right)^2} + \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{y_{i,\text{cal}} - y_{i,\text{exp}}}{y_{i,\text{exp}}} \right)^2} \quad (37)$$

The results of fitting are listed in Table 3. The solubility of benzene and toluene in TEG at atmospheric pressure from experiment, SAFT-HR, PC-SAFT and PR EoS are plotted in Figs. 3 and 4, respectively. As may be appreciated, with a small binary interaction parameter, the correlations from

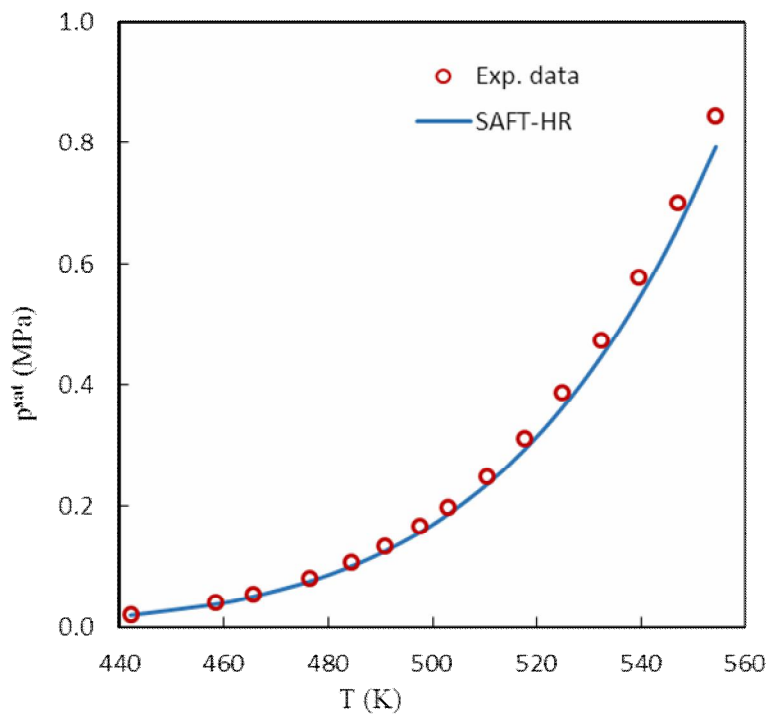


Fig. 1. Vapor pressure of TEG, experimental data (O) [35]; calculated data (—).

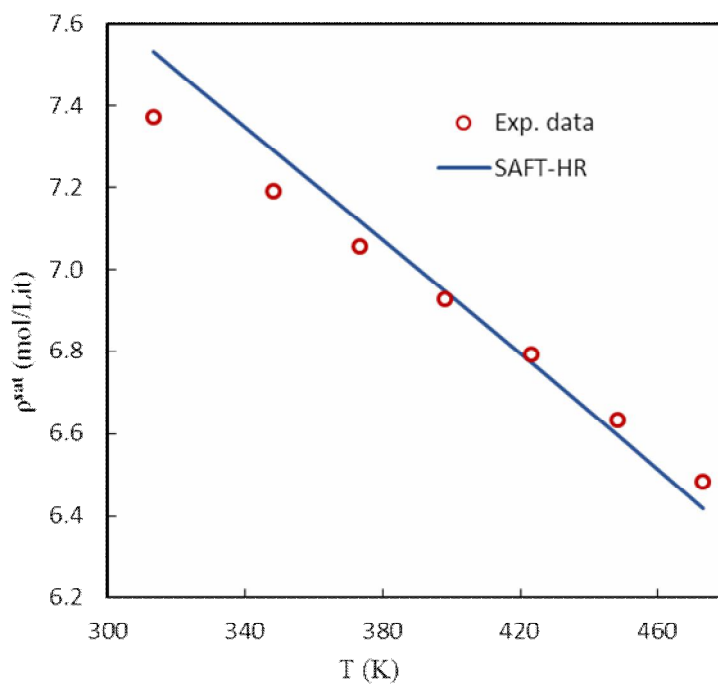


Fig. 2. Saturated liquid density of TEG, Experimental data (O) [35]; Calculated data (—).

Table 3. Fitted Binary Interaction Parameters (k_{ij})

| System | Conditions | Data | | | | Data |
|-------------------------------------|----------------------------|--------|---------|---------|--------|------|
| | | points | SAFT-HR | PC-SAFT | PR | Ref. |
| Benzene + TEG | $T = 354.60 - 428.80$ (K) | 11 | -0.010 | 0.090 | -0.440 | [39] |
| | $P = 101.325$ (kPa) | | | | | |
| Toluene + TEG | $T = 385.2 - 442.60$ (K) | 10 | -0.014 | 0.090 | -0.340 | [39] |
| | $P = 101.325$ (kPa) | | | | | |
| CH ₄ + TEG | $T = 323.15$ (K) | 51 | 0.197 | 0.251 | -0.999 | [40] |
| | $P = 0.111 - 20.200$ (MPa) | | | | | |
| C ₂ H ₆ + TEG | $T = 323.15$ (K) | 59 | 0.103 | 0.192 | -0.413 | [40] |
| | $P = 0.116 - 20.060$ (MPa) | | | | | |
| C ₃ H ₈ + TEG | $T = 298.15$ (K) | 40 | 0.081 | 0.162 | -0.989 | [40] |
| | $P = 0.016 - 6.350$ (MPa) | | | | | |
| CO ₂ + TEG | $T = 323.15$ (K) | 40 | 0.078 | 0.187 | -0.065 | [40] |
| | $P = 0.464 - 18.410$ (MPa) | | | | | |
| H ₂ S + TEG | $T = 298.15$ (K) | 40 | -0.040 | - | 0.008 | [40] |
| | $P = 0.040 - 1.958$ (MPa) | | | | | |
| Water + TEG | $T = 397.90 - 421.30$ (K) | 18 | 0.081 | - | 0.104 | [14] |
| | $P = 85.000$ (kPa) | | | | | |

SAFT-HR EoS are clearly more accurate. The deviations from experimental data are listed in Table 4.

Figures 5-8 show the solubility of methane, ethane, propane, and CO₂ in TEG from experimental data, SAFT-HR, and PC-SAFT EoS. Again, the SAFT-HR results are more accurate and in a good agreement with experimental data. In order to keep the figures well-arranged, the results from PR EoS were not included. Table 4 presents the deviations of EoS predictions from experimental data for these systems. Better results obtained from SAFT-HR EoS may be due to the fact that association interactions play a very important role in determination of the physical properties of the system. For the modeling of solubility of methane, ethane, and propane in TEG, there exists only the

self-association between TEG molecules. As indicated by the results, the association is very important, and ignoring it, as in PC-SAFT EoS, leads to higher deviations.

Solubility of H₂S and water in TEG were also calculated. The role of association interactions in these systems is more explicit, since these components can contribute to association. In the SAFT-HR EoS, for the systems H₂S + TEG and H₂O + TEG, the self-association of compounds, as well as the cross-association was considered. Figure 9 compares the correlated solubility of H₂S in TEG to the experimental data. In order to keep the figure well-arranged, the worst case (*i.e.* PR EoS) was not included. The deviations from experimental data are listed in Table 4. As may be appreciated, the accuracy of SAFT-HR EoS is

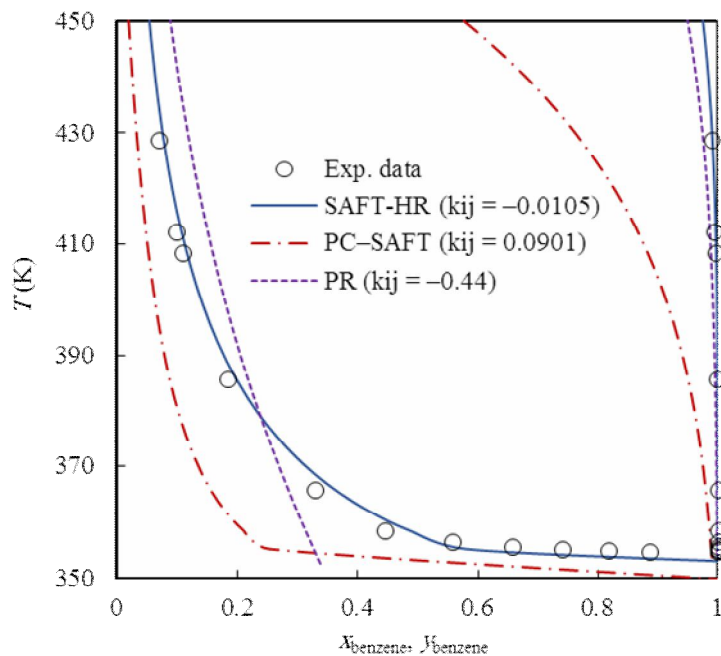


Fig. 3. VLE for benzene + TEG system at $P = 101.325$ kPa, experimental values (\circ) [39]; calculated values (lines).

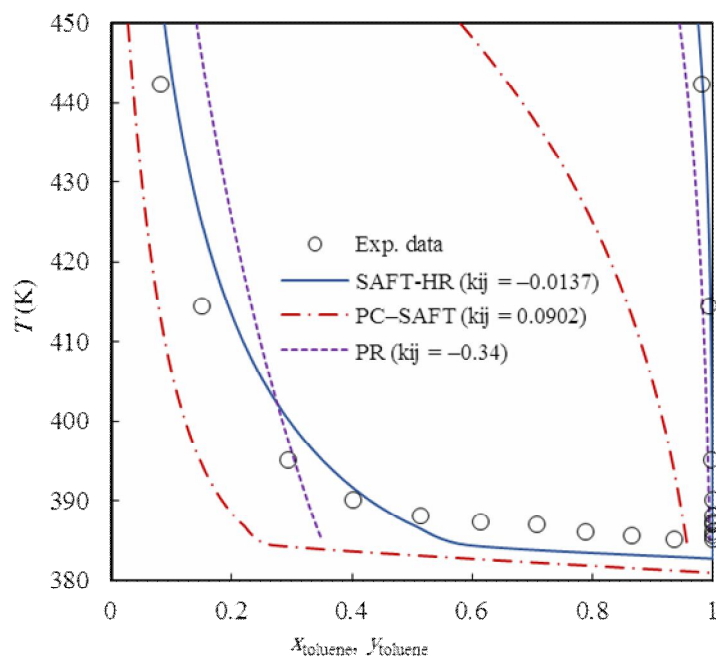


Fig. 4. VLE for toluene + TEG system at $P = 101.325$ kPa, experimental values (\circ) [39]; calculated values (lines).

Table 4. Root-mean-square Ddeviation for Binary and Ternary Systems, Using SAFT-HR, PC-SAFT and PR EoS

| System | Conditions | Data Points | SAFT-HR | | PC-SAFT | | PR | | Ref |
|-------------------------------------|--|-------------|--------------------------------|--------------------------------|-------------------|-------------------|-------------------|-------------------|------|
| | | | RMSD _X ^a | RMSD _Y ^b | RMSD _X | RMSD _Y | RMSD _X | RMSD _Y | |
| Benzene + TEG | $T = 354.60 - 428.80$ (K) $P = 101.325$ (kPa) | 11 | 0.1471 | 0.0006 | 0.4238 | 0.0899 | 0.5217 | 0.0062 | [39] |
| Toluene + TEG | $T = 385.20 - 442.60$ (K) $P = 101.325$ (kPa) | 10 | 0.2550 | 0.0013 | 0.4872 | 0.1260 | 0.5649 | 0.0104 | [39] |
| CH ₄ + TEG | $T = 323.15$ (K) $P = 0.111 - 20.200$ (MPa) | 51 | 0.0533 | - | 0.1275 | - | 2.6611 | - | [40] |
| C ₂ H ₆ + TEG | $T = 323.15$ (K) $P = 0.116 - 20.060$ (MPa) | 59 | 0.0328 | - | 0.1128 | - | 5.5315 | - | [40] |
| C ₃ H ₈ + TEG | $T = 298.15$ (K) $P = 0.016 - 6.350$ (MPa) | 40 | 0.0333 | - | 0.1194 | - | 7.1614 | - | [40] |
| CO ₂ + TEG | $T = 323.15$ (K) $P = 0.464 - 18.410$ (MPa) | 40 | 0.0948 | - | 0.1322 | - | 0.8632 | - | [40] |
| H ₂ S + TEG | $T = 298.15$ (K) $P = 0.004 - 1.958$ (MPa) | 40 | 0.0746 | - | - | - | 0.1862 | - | [40] |
| water + TEG | $T = 397.90 - 421.30$ (K) $P = 85.000$ (kPa) | 18 | 0.4314 | 0.0064 | - | - | 0.7243 | 0.0039 | [14] |
| Toluene + water + TEG | $T = 371.20 - 400.90$ (K) $P = 85.000$ (kPa) | 17 | 0.3673 | 0.0561 | - | - | 1.8335 | 0.1744 | [14] |

$${}^a\text{RMSD}_X = \sqrt{\sum_{i=1}^N [(x_1^{\text{cal}} - x_1^{\text{exp}}) / x_1^{\text{exp}}]^2} / (N - 1). \quad {}^b\text{RMSD}_Y = \sqrt{\sum_{i=1}^N [(y_1^{\text{cal}} - y_1^{\text{exp}}) / y_1^{\text{exp}}]^2} / (N - 1)$$

higher than that in PC-SAFT and PR EoS. This could be expected since both hydrogen sulfide and water are associating compounds, while the PC-SAFT EoS considered in this work does not include association interactions. The deviations of VLE correlations in the binary systems from the experimental data, are listed in Table 4. In all the systems studied, the accuracy of SAFT-HR was higher than that in PC-SAFT and PR EoS. These results prove the importance of association interactions in the prediction of solubility of gases in TEG.

The VLE in the multicomponent systems (toluene + water + triethylene glycol), (methane + BTEX + TEG), and (methane + BTEX + water + TEG) were also correlated. The SAFT-HR EoS was used to correlate VLE in the multicomponent systems with optimized binary interaction parameters. The deviations of predictions of SAFT-HR from VLE experimental data of multi component systems are listed in Table 5. Again, the results from SAFT-HR EoS are acceptable, suggesting that accuracy of this model for

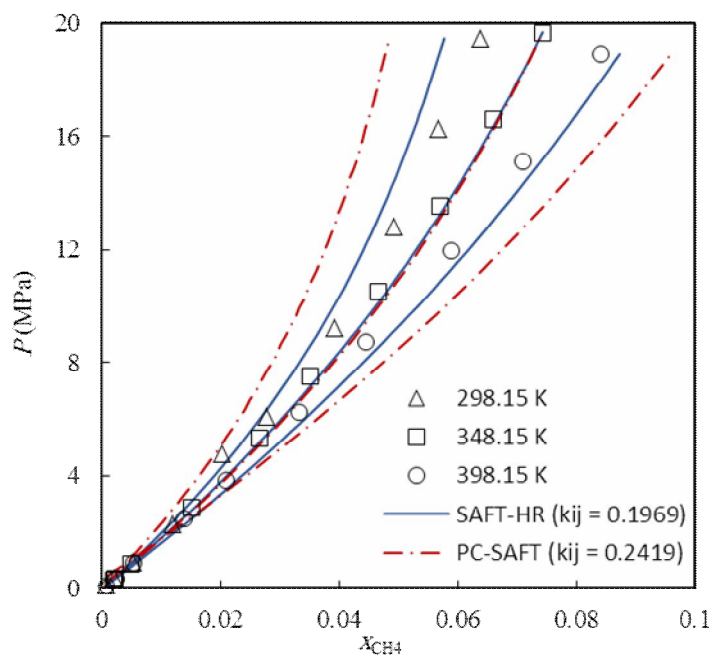


Fig. 5. VLE for $\text{CH}_4 + \text{TEG}$ system at $T = 298.15, 348.15$ and 398.15 K, experimental data (symbols) [40]; calculated data (lines).

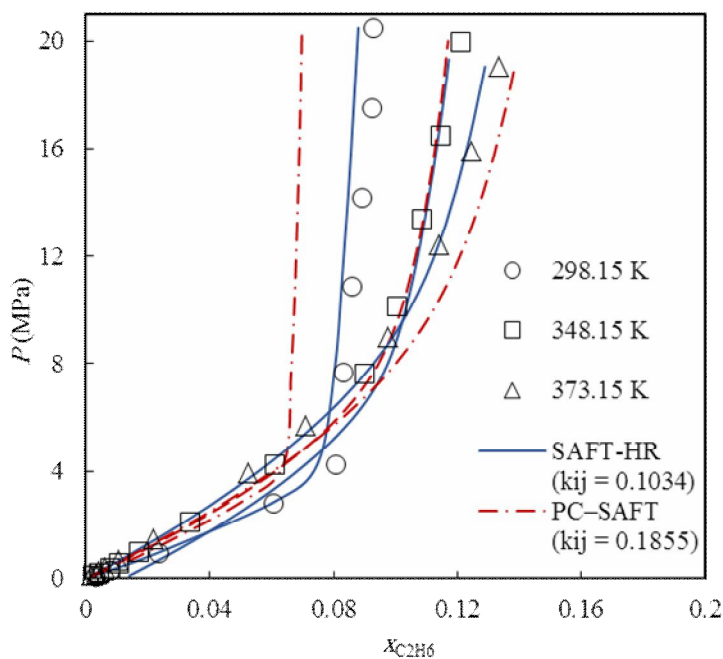


Fig. 6. VLE for $\text{C}_2\text{H}_6 + \text{TEG}$ system at $T = 298.15$ K, $T = 348.15$ K and $T = 373.15$ K., experimental data (symbols) [40]; calculated data (lines).

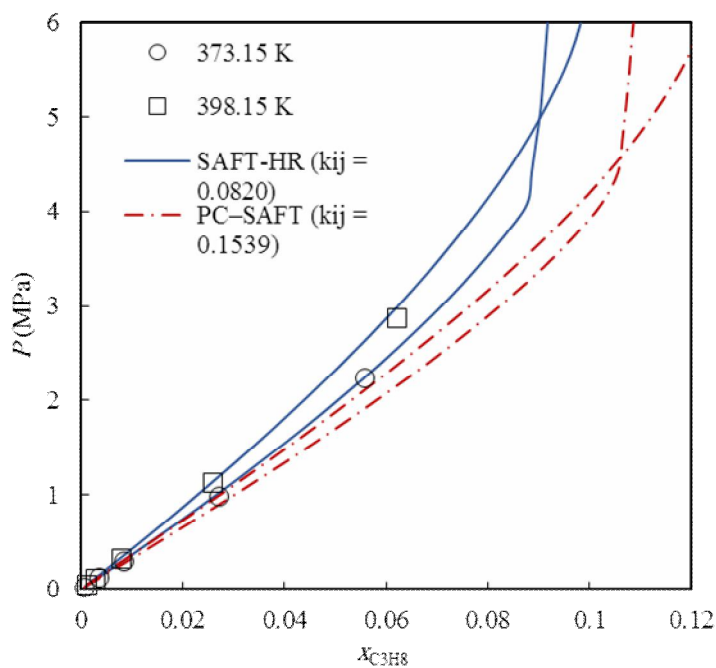


Fig. 7. VLE for $C_3H_8 + TEG$ system at $T = 373.15\text{ K}$ and 398.15 K , experimental data (symbols) [40]; calculated data (lines).

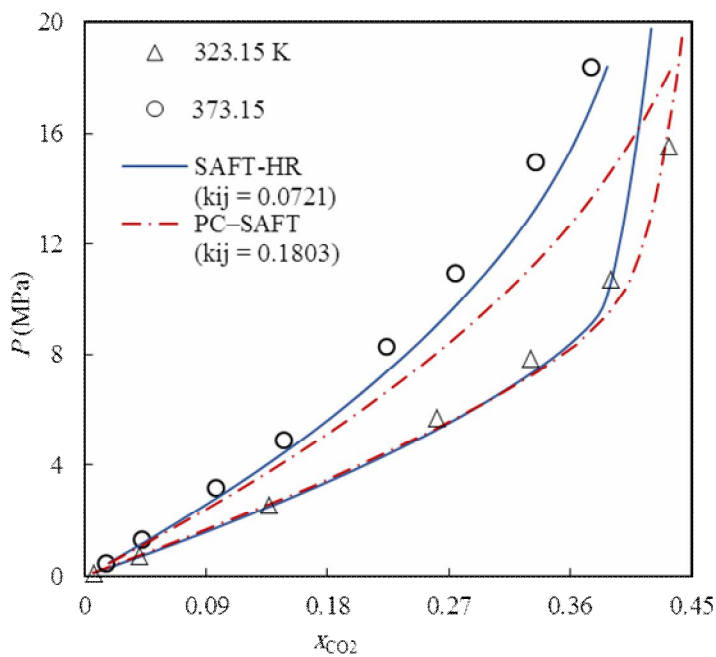


Fig. 8. VLE for $CO_2 + TEG$ system at $T = 323.15\text{ K}$ and 373.15 K , experimental data (symbols) [40]; calculated data (lines).

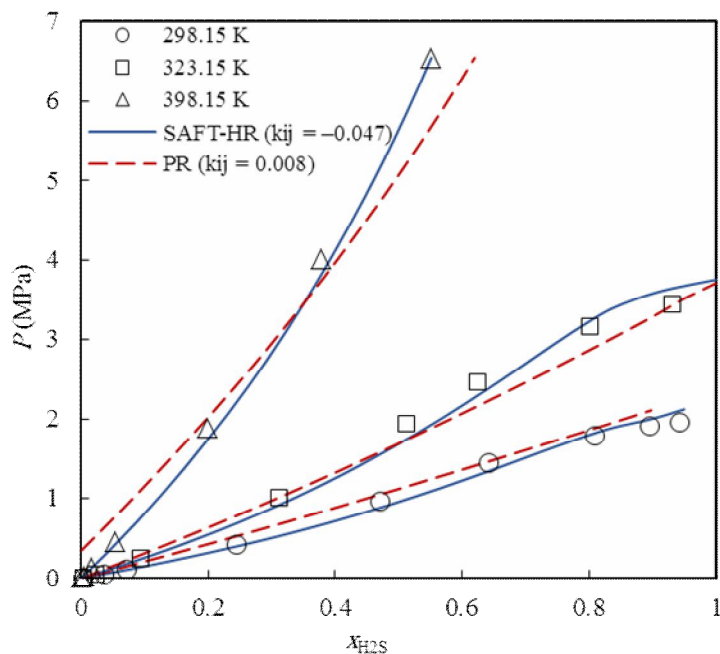


Fig. 9. VLE for H₂S + TEG system at $T = 298.15$ K, 323.15 K and 398.15 K, experimental data (symbols) [40]; calculated data (lines).

correlation of VLE in BTEX-containing systems is acceptable.

CONCLUSIONS

The SAFT-HR equation of state was used to predict VLE and solubility of several compounds in systems containing TEG at different temperatures and pressures. The pure component SAFT parameters for TEG were regressed in this work using vapor pressure and liquid density data. The binary interaction parameters for all binary systems, were optimized by fitting the vapor-liquid equilibrium experimental data. In order to have an estimation on the relative accuracy of SAFT-HR EoS, a comparison between SAFT-HR, PC-SAFT and PR equations of state was made. The PR EoS was selected as a representative of cubic EoS, and the PC-SAFT EoS was selected as a representative molecular-based EoS without considering association. Both of these EoSs are widely used in VLE calculations. Based on the results presented in Table 4, the overall average of root-mean-square deviations (RMSD) from available experimental data for binary and ternary systems studied in

this work, using SAFT-HR, PC-SAFT and PR EoS, were found to be 0.12, 0.20 and 1.56, respectively. According to the results obtained in this work, the accuracy of SAFT-HR EoS is higher, which is a result of considering association interactions. This indicates the important role of association interactions in determining the properties of TEG-containing systems.

NOMENCLATURE

Greek Symbols

Δ^{AB} : Strength of interaction between the sites A and B

ε : Depth of pair potential (J)

$\frac{\varepsilon}{k}$: Association energy between the sites A and B (K)

ε^{AB} : Association energy between sites A and B (J)

ζ_n : Abbreviation

η : Packing fraction

κ : Bonding volume

ρ : Molar density (M)

σ : Segment diameter (Å)

Table 5. Root Mean Square Deviations of Predictions for BTEX Equilibrium Compositions in VLE of Multicomponent Systems, Using SAFT-HR and PC-SAFT EoS, Using the Fitted Binary Interaction Parameters from Table 3

| System | Conditions | Data points | SAFT-HR | | PC-SAFT | | Ref |
|-----------------------|--|-------------|--------------------------------|--------------------------------|-------------------|-------------------|------|
| | | | RMSD _X ^a | RMSD _Y ^b | RMSD _X | RMSD _Y | |
| CH ₄ (1) + | | | | | | | |
| Benzene (2) + | <i>T</i> = 298.15 - 477.55 (K) <i>P</i> = 138 - 6895 (kPa) | 8 | 0.1998 | 0.2648 | 0.8021 | 0.7545 | [41] |
| Toluene (3) + | | | 0.2657 | 0.4431 | 1.0823 | 0.8649 | |
| Ethylbenzene (4) + | | | 0.2270 | 0.3613 | 1.0940 | 0.8674 | |
| Xylenes (5) + | | | 0.0995 | 0.1966 | 0.9816 | 0.8646 | |
| TEG (6) | | | | | | | |
| CH ₄ (1) + | | | | | | | |
| Benzene (2) + | <i>T</i> = 298.15 - 398.15 (K) <i>P</i> = 689 - 6895 (kPa) | 6 | 0.0062 | 0.1895 | | | [41] |
| Toluene (3) + | | | 0.0060 | 0.2754 | | | |
| Ethylbenzene (4) + | | | 0.0038 | 0.2500 | | | |
| Xylenes (5) + | | | 0.0021 | 0.1854 | | | |
| Water (6) (1 wt%) | | | | | | | |
| + | | | | | | | |
| TEG (7) | | | | | | | |
| CH ₄ (1) + | | | | | | | |
| Benzene (2) + | <i>T</i> = 298.15 - 477.15 (K) <i>P</i> = 150 - 6895 (kPa) | 6 | 0.1413 | 0.0871 | | | [41] |
| toluene (3) + | | | 0.2239 | 0.0963 | | | |
| Ethylbenzene (4) + | | | 0.1871 | 0.1016 | | | |
| Xylenes (5) + | | | 0.1144 | 0.1109 | | | |
| Water (6) (5 wt%) | | | | | | | |
| + | | | | | | | |
| TEG (7) | | | | | | | |

^aRMSD_X: Root mean square deviation for molar fraction of components in liquid phase. ^bRMSD_Y: Root mean square deviation for molar fraction of components in vapor phase.

Letters

d: Temperature-dependent segment diameter (Å)

D_{ij}: Universal constant

*I*₁, *I*₂: Abbreviations

k_{ij}: Binary interaction coefficient

m: Number of segments

M: Number of association sites on the molecules

N: Total number of molecules

N_{AV} : Avogadro's number (mole^{-1})
 p : Pressure (MPa)
 p_c : Critical pressure (MPa)
 p^{sat} : Saturated vapor pressure (MPa)
 R : Ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
 T : Temperature (K)
 T_c : Critical temperature (K)
 $\frac{u}{k}$: Temperature-dependent dispersion energy of interactions between segments (K)
 v : Molar volume (ml mol^{-1})
 v^o : Temperature-dependent segment volume (ml mol^{-1})
 x : Mole fraction in liquid phase
 X^A : Mole fraction of molecules not bounded at site A
 y : Mole fraction in vapor phase
 Z : Compressibility factor
 Z_i : Total mole fraction of component i

Subscripts

C : Critical property
 cal : calculated value
 exp : experimental data
 i, j : Summation index
 r : Reduced property
 sat : Saturated property

Superscripts

$assoc$: association
 $disp$: dispersion
 hc : hard chain
 hs : hard sphere
 res : residual
 seg : segment

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