Accurately modeling benzene and alkylbenzenes using a group contribution based SAFT approach

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In recent work, the GC-SAFT-VR equation, which combines the SAFT equation for potentials of variable range (VR) with a group contribution (GC) approach, was proposed. Parameters for key functional groups (such as CH 2, CH 3, CH 2=CH=CH 2, C 6H 5CH 2, ether, ester, OH, NH 2, CH=O, COOH) were obtained by fitting to experimental vapor pressure and saturated liquid density data for selected low molecular weight fluids and then used to predict the phase behavior of both pure non-associating and associating fluids and their mixtures, generally without adjusting the group parameters to binary mixture data. In the GC-SAFT-VR approach the benzene ring was modeled as a single group (C 6H 6 for benzene and C 6H 5H for alkylbenzenes) however, in common with other group-contribution based SAFT approaches, this approach fails to reproduce the correct curvature seen in the experimental liquid density of alkylbenzenes. In this work, to improve upon the model adopted for ring molecules, the benzene ring is explicitly considered through the connectivity of several smaller groups to more accurately capture the n−π interactions. We demonstrate that the improved model better captures the curvature present in the experimental saturated liquid density data of pure alkylbenzenes. Additionally, mixtures of several non-associating and associating fluids with benzene and alkylbenzenes are studied.

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1. Introduction

Knowledge of the phase behavior of multi-component mixtures is essential for separation and purification techniques in the chemical process industry. Design and analysis of such operations requires the quantitative knowledge of the equilibrium composition of co-existing vapor and liquid phases. One way of catering to this need is by performing experimental measurements; however, increasingly theoretical tools that can predict phase behavior are being sought as an alternative means of generating “pseudo” experimental data. Classical equations of state (EoS), such as the Peng–Robinson and Soave–Redlich–Kwong [11] equations, and activity coefficient models [2,3], have long been used to study phase behavior; however, their role tends to be as a more correlative, rather than predictive, tool for all but the simplest of systems. Additionally, they typically rely heavily on adjustable parameters fitted to experimental data in order to obtain accurate results, thus limiting their predictive ability [4,5].

Over the past two decades significant advances have been made in the development of theoretical approaches based upon molecular-based models that can be used for the prediction of thermodynamic properties and phase behavior. The statistical associating fluid theory (SAFT) [6–8] is one such approach that has been successful in describing the phase behavior of a wide range of industrially important complex fluid systems. Based on Wertheim’s first-order perturbation theory (TPT1) [9–12], in the SAFT framework molecules are described as chains of tangentially bonded homonuclear spherical segments that can interact through short ranged dispersion and association interactions. Since the introduction of the original SAFT EoS by Gubbins and co-workers [7] many modifications have been made to the original equations and different versions of SAFT proposed (see for example, the recent review by McCabe and Galindo [13]), which has resulted in the application of SAFT to a wide range of fluid systems [14]. Typically the SAFT parameters for a pure fluid are fitted to vapor pressure and saturated liquid and vapor density data, and when mixtures are studied, cross interactions determined either from Lorentz–Berthelot combining rules or by fitting to experimental mixture data. The cross interaction parameters are generally found to be transferable in that they can be used to accurately predict phase behavior over wide ranges of temperature and pressure and to predict the phase behavior of similar systems, such as within a homologous series [15–18].
In recent works, several group-contribution based SAFT approaches have been proposed in an effort to develop predictive approaches that can be used for systems where experimental data is limited; the idea being that parameters can be developed based on functional groups, rather than molecular parameters. In the first real group-contribution based SAFT approach Tobaly et al. [19–22] proposed a group contribution scheme (GC-SAFT) that could be applied to the SAFT equation due to Huang and Radosz [8] (referred to as SAFT-0), the SAFT-VR equation [23] and the PC-SAFT equation [24]. In their approach parameters are determined for the different functional groups present in the molecule by fitting the GC-SAFT parameters to the vapor pressure and saturated liquid densities of the pure compounds. Although parameters for individual functional groups are determined, the molecular parameters are obtained by taking the geometric and arithmetic averages of the group parameters, thus converting the model into that of a homosegmented chain molecule. The approach therefore requires no modifications to the original SAFT-0, SAFT-VR or PC-SAFT expressions. The phase behavior of a wide range of pure fluids such as linear alkanes [19], alkylbenzenes [19,22], alkylocyclohexanes [19], olefins [19], alcohols [19,22], esters [25], ethers [26], aldehydes [26], ketones [26] and their various mixtures [20,27–29] have all been studied using this group contribution method.

Subsequently Lymperiadis et al. [30] proposed the SAFT-γ approach, also based upon the SAFT-VR equation, in which the SAFT monomer fluid is defined as a collection of heteronuclear segments of different types that in turn form homonuclear chains, as in the original SAFT-VR approach. A number of functional groups [30,31] have been defined that allow the phase behavior of alkanes, alkylbenzenes, alcohols, ketones, amines, carboxylic acids and alcohols to be studied [30–32]. In similar work, the group-contribution SAFT-VR (GC-SAFT-VR) [33–35] EoS based on the SAFT-VR equation has also been proposed. In the GC-SAFT-VR approach a collection of heteronuclear segments representing the different functional groups in a given molecule are considered to form the model chain. The GC-SAFT-VR EoS therefore allows the location of functional groups and association sites within a molecule to be specified by retaining the identity of the functional groups in the hetero-segmented model chain and defining the connectivity of the segments within the chain. Using this heterosegmented approach GC-SAFT-VR parameters have been developed for a wide range of organic functional groups that allow the phase behavior of compounds such as linear and branched alkanes [33], alkenes [33], alkylbenzenes [33], ketones [33], acetates [33], esters [33], alcohols [35], aldehydes [35], amines [35], carboxylic acids [35] and polymers [34] to be studied.

While these group-contribution based SAFT approaches have been shown to be successful in predicting fluid phase behavior for most systems, all three approaches appear to struggle with the description of alkylbenzene molecules using a group contribution scheme. To model alkylbenzenes Tamouza et al. [19] introduced the (C\textsubscript{m}H\textsubscript{2m}) group to describe the benzene ring and obtained both SAFT-VR [23] and SAFT-0 [8] parameters by fitting to the vapor pressure and saturated liquid density data of ethyl to decylbenzene. While the correlated results show low deviations from the experimental results, due to the exclusion of experimental data at temperatures higher than 453 K from the correlation, this is somewhat misleading as can be seen from Fig. 1a. With the SAFT-γ approach Lymperiadis et al. [30] introduced two functional groups ACCH\textsubscript{2} and ACH (where A stands for aromatic) to model alkylbenzene molecules and also fail to predict the correct curvature seen in the experimental liquid density data of alkylbenzenes (as shown in Fig. 8 of Lymperiadis et al. [30]). In the GC-SAFT-VR approach both benzene and alkylbenzenes were studied [33] by describing, the benzene ring as a single functional group. Similar to the GC-SAFT and SAFT-γ approaches, the theory was not able to accurately correlate the alkylbenzene liquid densities as shown in Fig. 1b. While in both the GC-SAFT and SAFT-γ approaches the alkylbenzene molecule is treated as a homonuclear linear chain, the heteronuclear treatment provided by the GC-SAFT-VR approach, in which the benzene segment has different parameters from the alkyl chain, does not appear to address the problem.

Perhaps in recognition of this issue, subsequently Nguyen-Huy et al. [22] introduced a quadrupolar term into the GC-SAFT approach and defined two new functional groups ([CH]\textsubscript{fr} and (C)\textsubscript{ab} to describe the connection between the benzene ring and the alkyl chain) to model alkylbenzene molecules. Parameters for the new functional groups were obtained for use in the SAFT-0 [8], SAFT-VR [23], and PC-SAFT [24] frameworks by fitting to the experimental coexistence data for pure benzene to decylbenzene and benzene + hexadecane, benzene + toluene, and ethylbenzene + octane mixtures. The quadrupolar moments of benzene and the alkylbenzenes were included in the fitting procedure as adjustable parameters. Inclusion of polarity into the model did not improve the theory in terms of obtaining the correct curvature in the saturated liquid densities of the alkylbenzene molecules [37].

From these prior studies it is clear that a model that captures the π–π electronic interactions [38] between benzene molecules is needed in order to accurately describe the phase behavior of these molecules. In order to achieve this, we have broken the benzene ring into several smaller segments, which introduces three new functional groups, CH=(Bz) for the CH groups in benzene, CH=(aBz) for the CH groups in alkylbenzenes, and C\textsubscript{m} for the connection point in alkylbenzenes, and explicitly form a ring by considering the appropriate number of bonds amongst these.
segments. After demonstrating that a more accurate theoretical description of the phase behavior of the pure compounds can be obtained, we then extend the study to mixtures. The binary phase behavior of benzene and alklybenzene with alkanes through to strongly associating molecules, such as amines and alcohols have been studied and the results compared with experimental data.

2. Molecular model and theory

In the proposed model of benzene and alklybenzene molecules the aromatic ring is broken down into several smaller segments (Fig. 2). In the case of benzene, the ring is divided into six CH= segments with six bonds between the segments forming a closed ring. In the case of alklybenzene molecules, the ring is modeled as a combination of CH= and C=C segments; five CH= segments in the alklybenzene molecule are connected together with four bonds, with one C=C segment bonded to two CH= segments, to form a closed ring. In the benzene molecule the six π electrons in the benzene ring occupy the lower energy bonding orbitals; this arrangement accounts for the stability of benzene. Attachment of an electron donating alkly group to the benzene ring effects the electron cloud above and below the ring (the alkly group donates electrons making the ring more electron rich [39,40]), which in turn affects the orientation of the electron cloud. To take this behavior into account, two different set of parameters for the CH= functional group have been considered for the benzene and alklybenzene molecules. The CH= groups in alklybenzene are denoted by CH=(Abz) and those associated with benzene, denoted as CH=(Bz). So, for example, if we consider ethylbenzene, as shown in Fig. 2, five CH=(Abz) groups and one C=C group form the benzyl ring and are connected to an alkly chain containing one CH2 and one CH3 functional groups.

In what follows we provide a short overview of the GC-SAFT-VR theoretical framework and refer the reader to the original work for additional details [33,35,41].

In the GC-SAFT-VR EoS, a molecule k is considered to be formed using nj functional groups within which nk functional groups are of the same kind i. Similarly, a molecule l is formed using nj functional groups within which n′j functional groups are of the same kind j. The attractive and repulsive interaction (Ukl,j) between monomer segment i of molecule k and segment j in molecule l is defined by a square-well (SW) potential of variable range λkl,ij and depth εkl,ij:

\[
U_{kl,ij}(r) = \begin{cases} 
  +\infty & \text{if } r < \sigma_{kl,ij} \\
  -\varepsilon_{kl,ij} & \text{if } \sigma_{kl,ij} \leq r \leq \lambda_{kl,ij}\sigma_{kl,ij} \\
  0 & \text{if } r > \lambda_{kl,ij}\sigma_{kl,ij} 
\end{cases} 
\]

where σkl,ij is the interaction diameter between segments i and j in molecules k and l, respectively. The cross interaction parameters between groups are determined using the Lorentz–Berthelot combining rules and the cross range parameter using the arithmetic mean as follows:

\[
\sigma_{kl,ij} = \frac{\sigma_{ki,ij} + \sigma_{lj,ij}}{2} 
\]

\[
\varepsilon_{kl,ij} = \sqrt{\varepsilon_{ki,ij}\varepsilon_{lj,ij}} 
\]

\[
\lambda_{kl,ij} = \frac{\lambda_{ki,ij}\sigma_{ki,ij} + \lambda_{lj,ij}\sigma_{lj,ij}}{\sigma_{ki,ij} + \sigma_{lj,ij}} 
\]

In the GC-SAFT-VR framework the Helmholtz free energy of a molecule can be written as:

\[
\frac{A}{N_k T} = \frac{A_{\text{ideal}}}{N_k T} + \frac{A_{\text{mono}}}{N_k T} + \frac{A_{\text{chain}}}{N_k T} + \frac{A_{\text{assoc}}}{N_k T} 
\]

where, N is the number of molecules, k the Boltzmann constant, T the temperature, and Aideal,Amono,Achain and Aassoc the contributions to the free energy due to the ideal, monomer, chain, and association interactions, respectively.

The monomer free energy term in the GC-SAFT-VR framework for a multi component mixture is given by:

\[
\frac{A_{\text{mono}}}{N_k T} = \sum_{n=1}^{N_k} \sum_{k=1}^{n} \left( x_k m_k \right) a_{\text{sw}}^{n_k,1} 
\]

where the first sum is over the number of components in the mixture and the second over the different segments in each molecule. n represents the number of functional groups of type i present in compound k, m_k represents the chain length of functional group of type i and x_k represents the mole fraction of compound k in the mixture. a_{sw} is the contribution to the free energy due to the attractive square well interactions. The monomer free energy per segment of a molecule is obtained as in the original SAFT-VR approach from a second order high temperature perturbation expansion [23]:

\[
a_{\text{sw}}^{n_k,1} = a_{\text{HS}} + \left( \frac{1}{k_B T} \right) a_1 + \left( \frac{1}{k_B T} \right)^2 a_2 
\]

where a_{\text{HS}} is the free energy contribution due to the reference hard sphere system and a_1 and a_2 are the first two perturbation terms associated with the attractive energy [23].

The Helmholtz free energy contribution due to the formation of a chain containing heterogeneous SW segments is given by:

\[
\frac{A_{\text{chain}}}{N_k T} = \sum_{k=1}^{N_k} \sum_{j=1}^{n_k} \ln y_{w,k,j}(\sigma_{ki,ij}) 
\]

where, the first sum is over all compounds in the mixture and the second sum considers the chain formation and connectivity between the segments of type i and j within a molecule of compound k. The background correlation function y_{w,k,j}(\sigma_{ki,ij}) is in turn given by:

\[
y_{w,k,j}(\sigma_{ki,ij}) = \exp \left( \frac{-\varepsilon_{ki,ij}}{k_B T} \right) a_{\text{sw}}^{n_k,1}(\sigma_{ki,ij}) 
\]

where a_{\text{sw}}^{n_k,1}(\sigma_{ki,ij}) is the radial distribution function for the SW monomers evaluated at the contact distance \sigma_{ki,ij} and is approximated by a first-order high-temperature perturbation expansion [42]. The exact form of Eq. (8) depends upon the number of monomer segments and the connectivity between them. For example for a pure benzene molecule where six CH= (Bz) segments are bonded with six bonds between them the equation reduces to:

\[
\frac{A_{\text{chain}}}{N_k T} = -6n_{\text{CH=}}(\text{Bz}) \ln y_{w,k,j}(\sigma_{ki,ij}) 
\]

where, n_{\text{CH=}}(\text{Bz}) is the number of CH= segments in Bz.
In case of alkylbenzenes, such as ethylbenzene, where we have five CH\textsubscript{1}(=aBz) segments, one C\textsubscript{6} segment and CH\textsubscript{2} and CH\textsubscript{3} segments the expression becomes:

\[
A_{\text{chain}}^{\text{moc}} = - \left[ 5m_{\text{CH}(=aBz)} \cdot m_{C(=C)} - m_{C(=C)} \cdot m_{C(=C)} \right] \ln y_{\text{w}}^{\text{CH}(=aBz),CH(=aBz)} \left( \sigma_{\text{CH}(=aBz),CH(=aBz)} \right) \]

\[+ (m_{C(=C)} - 1) \ln y_{\text{vCH},C(=C)}^{\text{w}} \left( \sigma_{\text{C(=C),C(=C)}} \right) + 2 \ln y_{\text{CH}(=aBz),C(=C)}^{\text{w}} \left( \sigma_{\text{CH}(=aBz),C(=C)} \right) + (m_{CH_{2}} - 1) \ln y_{\text{CH}_{2},CH_{2}}^{\text{w}} \left( \sigma_{\text{CH}_{2},CH_{2}} \right) + \ln y_{\text{CH}_{2},2}^{\text{w}} \left( \sigma_{\text{CH}_{2},CH_{2}} \right) \]

\[+ (m_{CH_{3}} - 1) \ln y_{\text{CH}_{3},CH_{3}}^{\text{w}} \left( \sigma_{\text{CH}_{3},CH_{3}} \right) + \ln y_{\text{CH}_{3},2}^{\text{w}} \left( \sigma_{\text{CH}_{3},CH_{2}} \right) \]

(11)

In Eq. (11), the first term represents the four bonds between the five CH\textsubscript{1}(=aBz) segments, the second term describes the contribution from the single C\textsubscript{6} segment in the molecule, and the two bonds between C\textsubscript{6} and the CH\textsubscript{1}(=aBz) segments are represented by the third term. The remaining terms describe the bonding between the C\textsubscript{6}, CH\textsubscript{2} and CH\textsubscript{3} groups in an analogous way.

Finally, the contribution to the Helmholtz free energy due to the short ranged association interactions between association sites on specified functional groups is given by:

\[
A_{\text{moc}}^{\text{moc}} = \frac{1}{k_{B} T} \sum_{k=1}^{n_{a}} \sum_{i=1}^{n_{i}} \sum_{i=1}^{n_{i}} \left( \ln x_{\text{ka}} + \frac{1 - x_{\text{ka}}}{2} \right)
\]

where the first sum is over the number of components present in the multi component mixture; the second sum is over the number of different type of functional groups \(n_{a}\) present in the molecule. \(v_{ik}\) is the number of functional group of type \(i\) present in the molecule \(k\). The third sum corresponds to the number of type of sites \(n_{i}\) present in a functional group \(i\) and \(n_{a}\) is the number of associating sites of type \(a\) in that functional group. \(x_{\text{ka}}\) is the fraction of component \(k\) not bonded at site \(a\) of the functional group \(i\).

### Table 1

<table>
<thead>
<tr>
<th>Group</th>
<th>(\sigma_{\text{BA}}) (Å)</th>
<th>(m_{\text{k}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{1}(=Bz)</td>
<td>3.028</td>
<td>0.619</td>
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<tr>
<td>CH\textsubscript{1}(=aBz)</td>
<td>3.828</td>
<td>0.350</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>2.112</td>
<td>0.382</td>
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</table>

### 3. Results and discussion

#### 3.1. Pure compounds

Three new functional groups, CH\textsubscript{1}(=aBz), CH\textsubscript{1}(=Bz), and C\textsubscript{6}, have been defined in this work to model the benzene and alkylbenzene molecules in conjunction with the CH\textsubscript{2} and CH\textsubscript{3} segments developed in earlier work [33]. The GC-SAFT-VR parameters for the CH\textsubscript{1}(=Bz) group in benzene were obtained by fitting to experimental vapor pressure and saturated liquid density data for pure benzene [36] using a simulated annealing (SA) technique [43,44]. Experimental data close to the critical region (around 10%) were excluded from the fitting procedure, as GC-SAFT-VR like other analytical EoS exhibits classical critical behavior and over predicts the critical point. Additionally data points near the triple point have also been excluded since it has been shown that inclusion of the experimental data close to triple point can distort the results [45,46].

In the same manner parameters for the CH\textsubscript{1}(=aBz) and C\textsubscript{6} groups in alkylbenzenes were obtained by fitting to the saturated liquid density and vapor pressure data for toluene and decylbenzene [36]. In Tables 1–3 the GC-SAFT-VR parameters \(\sigma_{\text{BA}}\), \(\lambda_{\text{BA}}\), \(\epsilon_{\text{BA}}\), \(\chi_{\text{BA}}\), \(m_{\text{k}}\) are reported for the new functional groups obtained using the SA optimization procedure. The use of SA is intended to find the global optimum parameters; the values reported in Tables 1–3 are the optimal parameters found from multiple applications of the SA method using different initial guesses. Tables 2 and 3 also provide the molecular parameters that describe the interactions between and with the new functional groups studied herein. In all cases Lorentz–Berthelot combining rules have been used to determine the cross interactions between the functional groups.

### Table 2

<table>
<thead>
<tr>
<th>Group</th>
<th>(\sigma_{\text{BA}}) (K)</th>
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<tr>
<td>CH\textsubscript{1}</td>
<td>234.25</td>
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<tr>
<td>CH\textsubscript{1}</td>
<td>234.74</td>
</tr>
<tr>
<td>OCH\textsubscript{3}(ether)</td>
<td>205.49</td>
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<tr>
<td>OCH\textsubscript{3}(ether)</td>
<td>205.49</td>
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<tr>
<td>NH\textsubscript{2}</td>
<td>239.09</td>
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<tr>
<td>OH\textsubscript{Linear}</td>
<td>353.95</td>
</tr>
<tr>
<td>CH\textsubscript{1}(=Bz)</td>
<td>185.24</td>
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<tr>
<td>CH\textsubscript{1}(=aBz)</td>
<td>293.44</td>
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<tr>
<td>C\textsubscript{6}</td>
<td>153.86</td>
</tr>
</tbody>
</table>

### Table 3

<table>
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<th>Group</th>
<th>(\lambda_{\text{BA}}) (K)</th>
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<tbody>
<tr>
<td>CH\textsubscript{1}</td>
<td>1.49209</td>
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<tr>
<td>CH\textsubscript{1}</td>
<td>1.58292</td>
</tr>
<tr>
<td>OCH\textsubscript{3}(ether)</td>
<td>1.58282</td>
</tr>
<tr>
<td>OCH\textsubscript{3}(ether)</td>
<td>1.58282</td>
</tr>
<tr>
<td>NH\textsubscript{2}</td>
<td>1.51868</td>
</tr>
<tr>
<td>OH\textsubscript{Linear}</td>
<td>1.59089</td>
</tr>
<tr>
<td>CH\textsubscript{1}(=Bz)</td>
<td>1.58042</td>
</tr>
<tr>
<td>CH\textsubscript{1}(=aBz)</td>
<td>1.58042</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>1.49048</td>
</tr>
</tbody>
</table>

### Table 4

<table>
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<th>Group</th>
<th>(\chi_{\text{BA}}) (K)</th>
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</tr>
<tr>
<td>CH\textsubscript{1}</td>
<td>1.58292</td>
</tr>
<tr>
<td>OCH\textsubscript{3}(ether)</td>
<td>1.58292</td>
</tr>
<tr>
<td>OCH\textsubscript{3}(ether)</td>
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<tr>
<td>NH\textsubscript{2}</td>
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<td>OH\textsubscript{Linear}</td>
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<td>CH\textsubscript{1}(=Bz)</td>
<td>1.58042</td>
</tr>
<tr>
<td>CH\textsubscript{1}(=aBz)</td>
<td>1.58042</td>
</tr>
<tr>
<td>C\textsubscript{6}</td>
<td>1.49048</td>
</tr>
</tbody>
</table>

The percent average absolute deviation in vapor pressure (\%AAD\textsubscript{p}) and saturated liquid density (\%AAD\textsubscript{\rho\textsubscript{lq}}) from the experimental data for
benzene and the alkylbenzene molecules is reported in Table A.1 of Appendix A. In Fig. 3, we present the pure phase behavior of benzene and alkylbenzenes from toluene through to octylbenzene. Although these are correlated systems and so we would expect good agreement between the theory and the experimental saturated liquid density and vapor pressure data, from the figure we can clearly see that the theory is now able to capture the correct trend in the curve of the alkylbenzene saturated liquid densities, which is a significant improvement over prior group-contribution descriptions of these molecules [19,30,33]. For the GC-SAFT-VR approach this is also reflected in the lower % average absolute deviation (AAD) in the saturated liquid densities (1.82 compared to 3.53 obtained in previous work) [33].

After determining the optimal parameters for the newly defined functional groups, the phase behavior of higher members of the homogeneous series were then predicted as a means of testing and validating the new parameters. The percentage average absolute deviations from the experimental data are again reported in Table A.1. We note that the GC-SAFT-VR equation is accurately predicting the saturated liquid density for the alkylbenzenes studied, though higher deviations are seen for the vapor pressures, which is typical from a group contribution method as the vapor pressure is a more sensitive property. Remembering that the main focus of the work was to obtain a more accurate model for the saturated liquid density of the alkylbenzenes, we can consider the model to be in good agreement with the experimental data and examine the influence of the more accurate model in the study of the phase behavior of mixtures of benzene and alkylbenzenes. Here, we focus primarily on presenting results for new binary mixtures and only reconsider systems previously studied when differences are observed in the predicted results with the new ring based model compared to the earlier work [34,35].

3.2. Binary mixtures

3.2.1. Benzene/alkylbenzenes + n-alkanes

Initially we consider binary mixtures of benzene and alkylbenzenes with linear alkanes. In Fig. 4 results for binary mixtures of benzene and toluene (methylbenzene) with alkanes from n-hexane to n-decane at a temperature of 313.15 K are presented. As stated earlier, for these binary systems three functional groups are used to represent the toluene molecule (CH3, CH=CH2 and C=), two functional groups are used to represent the alkane molecules (CH3 and CH2) and only one type of group CH=CH2 is used to describe benzene. As can be seen from the figure, the theoretical predictions for the constant temperature P-x-y slices of the phase diagrams are in good agreement with the experimental data, except for the case of the benzene + n-hexane and + n-heptane binary mixtures where significant deviations from experiment are observed. Although the use of a fitted cross interaction parameter between the CH=CH2 group of the benzene ring and the CH3 group in the alkane chain could significantly reduce this deviation, we are focusing here on the predictive capability of the theory using only Lorentz–Berthelot combining rules. In Fig. 4b, we also note that the theory accurately captures the changes in phase behavior with the increase in the number of CH2 groups in the linear alkane.

3.2.2. Benzene + alkylbenzene mixtures

We now consider constant temperature and pressure slices of the phase diagrams for binary mixtures of benzene with}

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**Fig. 3.** Comparison between theoretical results from the GC-SAFT-VR equation and experimental data for (a) vapor pressures and (b) saturated liquid densities for benzene to octylbenzene (from left to right). Symbols and solid lines represent the experimental data [36] and theoretical results, respectively.

**Fig. 4.** Vapor–liquid equilibria for binary mixtures of (a) benzene and (b) toluene with Hexane (○), Heptane (□), Octane (△), Decane (●) at 313.15 K. The solid lines represent the theoretical predictions and the symbols represent the experimental results [47].
methylbenzene, ethylbenzene and propylbenzene. These systems being chosen as experimental data is available in the literature for comparison. In Fig. 5 constant temperature P-x-y slices of the benzene + toluene [48] and benzene + ethylbenzene [49] phase diagrams are presented. As can be seen from the figures, the proposed model is able to capture the changes in phase behavior as a function of temperature without fitting cross interactions to the experimental mixture data, though we observe some deviation for the toluene + benzene mixture (due to the over prediction of the vapor pressure of pure toluene (Table A.1)).

In Fig. 6, a constant pressure T-x-y slice of the benzene + propylbenzene phase diagram is presented at 1.01325 bar for which excellent agreement with the experimental data is obtained. Unfortunately additional experimental data against which we can compare the theory to is, to the best of our knowledge, unavailable for benzene + alkylbenzene systems.

3.2.3. Benzene, alkylbenzene + ether mixtures

Ethers are slightly polar molecules due to the presence of a lone pair of electrons on the oxygen atom that can interact with the delocalized electrons in the benzene ring and so represent a good test of the new functional groups in terms of capturing the unlike interactions. In Fig. 7, the binary phase behavior of dimethylether and dibutylether with benzene is presented. Here two functional groups (OCH3(ether) and CH3) are used to form the dimethylether molecule and three functional groups (OCH2(ether), CH3 and CH2) are used to form dibutylether, the parameters for which are all taken from earlier work [33,34]. As discussed in the introduction, in previous work [34] benzene was described as a single C6H6 group in the GC-SAFT-VR approach; using this model benzene + ether phase behavior was studied and a cross-interaction parameter between the C6H6 group and the OCH2(ether) group was used to capture the non-ideal nature of the mixtures. Here we find that using the new ring based model for benzene, the GC-SAFT-VR approach can predict the correct phase behavior for the binary benzene + ether mixtures using Lorentz–Berthelot combining rules. In contrast to earlier work [34] we therefore do not use a fitted cross-interaction parameter between the OCH2(ether) and CH2=CH group. In this regard, it appears that the explicit modeling of the benzene ring improves the predictive capability of the EOS, though we again note that there is limited experimental data against which to test the broader applicability of the theoretical approach.

In Fig. 8a the phase behavior of methylbenzene + diethyl ether has been studied at a constant pressure of 1.01325 bar and in Fig. 8b constant P-x-y slices of the ethylbenzene + dipropylether binary mixture is presented. Again we do not use any fitted cross-interaction parameters between the CH2=CH2 and OCH2 group and so the results presented are true predictions. Although at higher pressures, and close to the pure limit of ethylbenzene, the theory under predicts the pressure due to the fact that we under predict the vapor pressure of pure dipropylether, a good description of the equilibrium phase composition is obtained [53].

3.2.4. Benzene, alkylbenzene + associating fluids

In Fig. 9 we consider mixtures of benzene and alkylbenzenes with ethanol and 1-butanol. It is interesting to study mixtures of strongly associating fluids with compounds containing a benzene ring to test whether the theory can capture the complex interactions between the lone pair of electrons present on the alcohol oxygen atom and the π electrons of the benzene ring. 1-butanol is formed from the CH3, CH2 and OH (terminal) functional groups, and the hydrogen bonding interactions are described by three association sites on the OH (terminal) group, the parameters for which are taken from previous studies [33,35]. From Fig. 9a, we find that the theory shows good agreement with experimental results [55] at 308 K, with the prediction being more accurate for toluene than benzene. We also note that the GC-SAFT-VR approach correctly predicts the azeotropic nature of the mixtures studied, again without fitting any binary interaction parameters. Though one could argue that a cross-interaction parameter between the CH2=CH2 and OH (terminal) group could be warranted due to the non-ideal nature of the mixture. In Fig. 9b, we present the phase behavior of ethanol and toluene at two different temperatures 303.15 K and 328.15 K. It can again be observed that the
Fig. 7. Vapor–liquid equilibria for binary mixtures of (a) benzene + dimethylether at 323.15 K (○) and (b) benzene + dibutylether at 308.15 K (○). The solid lines represent the theoretical predictions and the symbols represent the experimental results [51,52].

Fig. 8. Vapor–liquid equilibria for binary mixtures of (a) toluene + diethylether at constant pressure of 1.01325 bar (○) and (b) ethylbenzene + dipropylether at 323.15 K (●), 333.15 K (▲), 343.15 K (♦). The solid lines represent the theoretical predictions and the symbols represent the experimental results [53,54].

GC-SAFT-VR approach is able to successfully predict the isotropic phase behavior observed in the alcohol + alkylbenzene systems. We note that higher deviations are seen for ethanol due to the fact that smaller members of a family of chemical compounds typically fail to exhibit group additivity and hence show higher pure component deviations [35].

Finally, we consider the mixture of benzene and alkylbenzenes with amines, which are also associating fluids. In Fig. 10, we present results for the binary mixture of benzene, toluene and ethylbenzene with n-butylamine. n-butylamine is described using the CH₃, CH₂ and NH₂ functional groups determined in earlier work [35]. As can be seen from the figure, using these group parameters and without fitting to mixture experimental data we can accurately capture the phase behavior of the binary mixtures of alkylbenzenes with amines at 298.15 K [57,58]. We also note that the theory correctly predicts the transformation from a non-azeotropic phase behavior for alkylbenzene+amine binary mixtures to an azeotropic system for mixtures containing benzene. Compared to earlier work by dos Ramos et al. (Fig. 7a) [35] in which the alkylbenzene and benzene rings were modeled as a single group, we note...

Fig. 9. Vapor–liquid equilibria for binary mixtures of (a) 1-butanol + benzene (○), toluene (●) at 308.15 K and (b) ethanol + toluene at 303.15 K (●) and 328.15 K (●). The solid lines represent the theoretical predictions and the symbols represent the experimental results [55,56].
a definite improvement in the predictive ability of the theory for amine + alkylbenzene systems. In particular, at lower temperatures (below 325 K) the new ring based model improves the saturated liquid densities of pure alkylbenzenes which results in better agreement between experimental and predicted phase behavior for alkylbenzene + amine systems. However for the benzene + amine system studied the azotropic pressure maximum is overpredicted compared to dos Ramos et al., which can be attributed to the fact that when benzene is treated as a single group the predicted pure component vapor pressure is lower than that reported in this study.

4. Conclusion

The correct curvature in the experimental saturated liquid densities of pure alkylbenzenes has been captured in a group-contribution SAFT based approach by explicit consideration of the benzene ring in the theoretical framework. Typically alkylbenzenes are described in group contribution SAFT approaches as linear chain molecules and fail to describe the correct trend in the curvature of the saturated liquid densities that is seen experimentally for alkylbenzenes. To our knowledge this is the first time ring molecules have been explicitly described in a group contribution SAFT approach. In this work we propose three new functional groups CH≡(Bz), CH≡(aBz), C= to describe benzene and the alkylbenzene family. The parameters for these groups were obtained by fitting to experimental vapor pressure and saturated liquid density data for benzene and the lower members of the alkylbenzene (methylbenzene to decylbenzene) family. These parameters were then used to predict the phase behavior of longer members of the alkylbenzene family and study the phase behavior of binary mixtures of benzene and alkylbenzenes with alkanes, ethers, amines and alcohols. If we draw a comparison between the earlier heteronuclear chain model for alkylbenzenes with the current ring based model we find improvement in the theoretical representation of the saturated liquid densities, particularly at lower temperatures. For mixture systems, the results obtained from the two models are generally comparable, though we do obtain better predictive ability for the mixture of alkylbenzene (toluene/ethylbenzene) and n-butylamine. Additionally by more accurately capturing the intermolecular forces between unlike groups using the ring based model we are able to predict the correct phase behavior using simple Lorentz–Berthelot combining rules.

Acknowledgment

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Appendix A.

In A1, we present the deviation of the theoretical correlations and predictions for the vapor pressure and saturated liquid density from the experimental data for the benzene and alkylbenzenes [36].

The average absolute deviations in pressure and liquid density expressed using AAD P (%) and AAD ρliq (%) are given by following equations:

\[
AAD P(\%) = \frac{1}{Npt} \sum_{i=1}^{Npt} \left| \frac{P_{\text{theo}} - P_{\text{exp}}}{P_{\text{exp}}} \right| \times 100
\]

\[
AAD \rho_{\text{liq}}(\%) = \frac{1}{Npt} \sum_{i=1}^{Npt} \left| \frac{\rho_{\text{theo}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right| \times 100
\]

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Table A.1 Average absolute deviation in vapor pressures and saturated liquid densities obtained between experimental data and theoretical results for pure benzene and alkylbenzenes.
where $N_{p}$ is the number of experimental points being evaluated, $P_{exp}$ and $P_{theo}$ are the experimental and calculated pressure; $\rho_{exp}$ and $\rho_{theo}$ are the experimental and calculated saturated liquid density, respectively.

References


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