Modeling the thermodynamic properties and phase behaviour of organic sulfur molecules with a group contribution based statistical associating fluid theory approach (GC-SAFT-VR)

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ABSTRACT

Leveraging the demonstrated accuracy of the group contribution statistical associating fluid theory for potentials of variable range (GC-SAFT-VR) equation of state to predict the phase equilibrium and thermodynamic properties of fluids, we use this approach to study organic sulfur molecules and their mixtures. Knowledge of the phase equilibria and thermodynamic properties of sulfur containing compounds, while of interest in a number of fields, is important to the development of petroleum products with lower sulfur content. In this work the CH=(thiophene) and —S- functional groups are characterized by fitting to experimental data for pure thiophene and cross interactions determined in order to extend the GC-SAFT-VR equation of state to the study of organic sulfur molecules. Theoretical predictions are compared with experimental results for the phase behavior of 3-methylthiophene, 2-methylthiophene, and benzothiophene, as well as their binary mixtures with alkanes, alkenes, aromatics, carbon dioxide, and alcohols. As far as we are aware, this work is the first SAFT-based study of mixtures containing thiophene molecules with aromatics, alcohols, and hydrocarbon molecules. The GC-SAFT-VR approach is found to accurately predict the phase behavior of the sulfur organic compounds studied, providing a method to determine the phase behavior of these compounds without heavy reliance on experimental data.

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1. Introduction

Organic sulfur containing molecules (e.g., thiols, sulfides, and thiophene) present in petroleum fuels impair the effectiveness of emission control systems and contribute to significant air pollution. These molecules also present significant processing problems within the oil and gas industry. For example, thiophene, which is a major impurity present in crude oil, is problematic as conventional removal technologies such as hydrodesulphurization are not very effective on thiophene containing systems [1]. Due to recent environmental concerns, many countries have employed stricter regulations on the sulfur content in fuels [2]. For example, in 2015 the U.S. Environmental Protection Agency introduced new vehicle emissions standards that lower the sulfur content of gasoline in an effort to reduce air pollution from passenger cars and trucks. With stricter fuel regulations, minimizing the cost of producing petroleum-based fuels will require new technological advances and innovations. One proposed method to extract thiophene and its derivatives from petroleum is to utilize supercritical CO_2 as a solvent [3]. Knowledge of the phase behavior and volumetric properties of mixtures containing CO_2, thiophene, and other solvents at high pressures are therefore needed for the continued development of new desulfurization processes. Specifically, the determination of the vapor liquid equilibrium (VLE) and the thermodynamic properties of hydrocarbon based sulfur compounds are essential to investigate the feasibility of the separation of sulfur impurities from petroleum; however, experimental investigations of organic sulfur systems are limited.

With limited experimental data available, the use of traditional cubic equations of state to study these systems is difficult, since such equations contain adjustable parameters whose values are

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determined from the correlation of system specific experimental data. Molecular-based equations of state, such as the statistical associating fluid theory (SAFT) [4,5], utilize more physically based parameters and therefore typically provide a more predictive approach and are attractive alternatives. SAFT, based on Wertheim's first order thermodynamic perturbation theory [6,7], takes into account the effect of molecular shape, size, and interactions on the thermodynamic properties and as such results in molecular parameters with less dependence on the thermodynamic conditions at which they were fit, thus offering a more predictive approach than typical cubic equations of state.

The advantages of the SAFT family of equations have been exploited by several authors to study organic sulfur systems. For example, in the work of Zuniga-Moreno et al. [8], the phase behavior of carbon dioxide + thiophene was studied using the perturbed chain statistical associating fluid theory (PC-SAFT) equation of state (EoS) [9]. The molecular parameters for carbon dioxide were taken from the literature [10] while the parameters for thiophene were obtained by fitting to vapor pressure and saturated liquid density data from the triple point to the critical point. The liquid densities of thiophene at six different temperatures were then calculated using the molecular parameters determined, finding deviations of less than 1%. In order to model the volumetric properties of the mixture, a binary interaction parameter was determined from a fit to vapor liquid equilibria data at 4 different temperatures. Densities and excess molar volumes were then calculated utilizing the fitted binary interaction parameter and found to provide predictions within 1% of experimental results for thiophene rich mixtures; however, deviations increased with increasing concentrations of carbon dioxide and for excess molar volumes (ranging from 35 to 130%).

More recently, also utilizing the PC-SAFT equation, Khelassi-Sefaour et al. [11] studied thiophene, pyridine, and the ionic liquid, 1-ethyl-3-methylimidazolium thiocyanate (EMIM][SCN]) at pressures close to atmospheric and temperatures between 273 K and 363 K. These mixtures are of interest due to the use of ionic liquids in extractive desulfurization of gasoline and diesel [12]. The parameters for thiophene were taken from the work of Zuniga-Moreno et al. [8] and a temperature dependent binary interaction parameter fitted to the VLE behavior of the thiophene + [EMIM][SCN] binary mixture. We note however, that even with fitted cross interaction parameters, the model was found to have difficulty representing the vapor-liquid-liquid equilibrium behavior, predicting VLE when liquid-liquid equilibrium (LLE) is observed experimentally.

In the work of Chen et al. [12], thiophene + ionic liquid mixtures were also studied using the PC-SAFT approach. Thiophene parameters were again taken from the work of Zuniga-Moreno et al. [8], while the parameters for the ionic liquids were characterized by fitting to density data for the ionic liquids of interest. In this work, the phase behavior of the binary mixtures of thiophene +1,3-dimethylimidazolium methylphosponate ([DMIM][SCN]) and [EMIM][SCN], were compared to experimental results and found to be in good agreement for VLE data. However, as observed in the work of Khelassi-Sefaour, VLE was again observed instead of the experimentally determined LLE for thiophene + [EMIM][SCN].

As discussed above, previous applications of SAFT have met with limited success in terms of developing a predictive approach to describe the phase behavior of thiophene mixtures. However, we note that these were homonuclear approaches, in that all segments in the model chain have the same size and energy of interaction, and that the ring structure of the thiophene molecule is not explicitly described. In this work, we employ a group contribution SAFT-based approach that allows for a model in which the thiophene ring is explicitly described through the connection of several smaller segments. Specifically, we use the group contribution statistical associating fluid theory for potentials of variable range (GC-SAFT-VR), which combines the hetero-SAFT-VR equation [13], which forms chain molecules from hetero-nuclear segments interacting through attractive potentials of variable attractive range, with a group contribution approach (GC) [14,15]. The GC-SAFT-VR approach thus describes molecules as chains of tangentially bonded segments of different size and/or energy parameters that represent various functional groups within the molecule. The location of association sites can also be specified within a molecule, enabling heterogeneity in molecular architecture to be captured within a SAFT model. In recent studies [14–16], the GC-SAFT-VR approach has been successfully applied to study a wide range of associating and non-associating molecules including hydrocarbons [14], ketones [14], alcohols [15], polymers [15], fatty acid methyl esters [17], fluorinated molecules [18], and aromatics [16]. Of particular relevance, is the application to benzene and alkyl benzene molecules in which the benzene ring was explicitly considered through the connectivity of several smaller groups and found to result in more accurate predictions than other group-contribution approaches [16].

In this work the applicability of the GC-SAFT-VR approach is expanded by characterizing the CH=(thiophene) and −S- functional groups and determining their cross interactions with other groups of interest. The theoretical predictions are compared with experimental results for pure thiophene, 3-methylthiophene, and benzothiophene, as well as binary mixtures containing these fluids with alkanes, alkenes, aromatics, carbon dioxide, and alcohols. The remainder of the paper is organized as follows: the GC-SAFT-VR equation is presented in Section 2, the functional group parameter estimation and results for pure fluids and binary mixtures are discussed in Section 3, and conclusions drawn in Section 4.

2. Molecular model and theory

As an extension of the hetero-SAFT-VR equation [13], which allows the description of molecules formed from chains of tangentially bonded segments of different size and/or energy parameters, the GC-SAFT-VR approach was proposed by Peng et al. [13,14] to model molecules as chains of tangentially bonded segments that represent various functional groups within a molecule. The segments representing each functional group interact via a square well potential, which can be described by,

$$u_{ki,lj}(r) = \begin{cases} +\infty & \text{if} & r < \sigma_{ki,lj} \\ -\varepsilon & \text{if} & \sigma_{ki,lj} \leq r \leq \lambda_{ki,lj}\sigma_{ki,lj} \\ 0 & \text{if} & r \leq \lambda_{ki,lj}\sigma_{ki,lj} \end{cases} \tag{1}$$

where $u_{ki,lj}$ represents the interaction between a functional group of type i present in molecule k with a functional group of type j in molecule l, σ is the segment diameter, ε is the depth of the square well, λ is the potential range, and r is the distance between the two groups. Unlike size and energy interactions can be obtained from Lorentz-Berthelot based combining rules,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{3}$$

$$\lambda_{ij} = \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \tag{4}$$

when similar cross interactions are expected. For interactions

involving polar functional groups, which are expected to deviate from these simple combining rules, an advantage of the group-contribution approach is that the unlike interactions can be fitted in most cases to pure component experimental data for molecules containing the functional groups of interest. Additional fitting to experimental data, as required in homonuclear approaches is not needed. As such, a predictive equation for the study of mixture phase behavior can be developed.

The GC-SAFT-VR approach has been presented in several papers [14–16,18] and so here we provide only a brief overview of the theory. The Helmholtz free energy is described as the sum of four separate contributions, viz

$$\frac{A}{Nk_BT} = \frac{A^{ideal}}{Nk_BT} + \frac{A^{mono}}{Nk_BT} + \frac{A^{chain}}{Nk_BT} + \frac{A^{assoc}}{Nk_BT} \quad (5)$$

where N is the total number of molecules in the system, T is the temperature, k_B is the Boltzmann constant, and A^{ideal}, A^{mono}, A^{chain}, and A^{assoc} are the contributions to the free energy due to the ideal, monomer, chain, and association interactions, respectively. The monomer free energy, A^{mono}, is given by a second order high temperature expansion using Barker and Henderson perturbation theory for mixtures [19].

$$\frac{A^{mono}}{Nk_BT} = \sum_{k=1}^{n} \sum_{i=1}^{n'_k} m_{ki} x_k \left(a^{HS} + \frac{a_1}{k_BT} + \frac{a_2}{(k_BT)^2} \right) \quad (6)$$

where n'_k is the number of types of functional groups i present in molecule k and m_{ki} is the number of segments of type i in chains of component k.

The contribution to the free energy due to chain formation, A^{chain}, from a mixture of hetero-segmented square-well monomer segments is given by,

$$\frac{A^{chain}}{Nk_BT} = -\sum_{k=1}^{n} x_k \sum ln y_{ki,kj}^{SW} \left(\sigma_{ki,kj} \right) \quad (7)$$

where the first sum is over all components in the mixture and the second sum considers the chain formation and connectivity of the segments within a given chain. The background correlation function is given by,

$$y_{ki,kj}^{SW} \left(\sigma_{ki,kj} \right) = \exp \left(\frac{-\varepsilon_{ki,kj}}{k_BT} \right) g_{ki,kj}^{SW} \left(\sigma_{ki,kj} \right) \quad (8)$$

where $g_{ki,kj}^{SW}(\sigma_{ki,kj})$ is the radial distribution function for the square well monomers at the contact distance $\sigma_{ki,kj}$ and is approximated by a first-order high-temperature perturbation expansion.

Finally, the contribution due to association interactions, (A^{Assoc}) [20], between sites on different functional groups that form the molecules of interest is expressed as:

$$\frac{A^{Assoc}}{Nk_BT} = \sum_{k=1}^{n} x_k \sum_{i=1}^{n'_k} v_{ki} \sum_{a=1}^{ns'_i} n_{ia} \left(\ln X_{kia} + \frac{1 - X_{kia}}{2} \right) \quad (9)$$

where the first sum is over the number of components n, the second over all types of functional groups in the molecule k (n'_k), and the third sum over the total number of site types in a functional group i (ns'_i). The fraction of molecules of type i not bonded at site a, $X_{a,i}$, is obtained from the solution of the mass balance equations and is given in terms of the total number density for the system, shown as [4,5]:

$$X_{kia} \frac{1}{1 + \rho \sum_{l=1}^{n} x_l \sum_{j=1}^{n'_l} v_{lj} \sum_{b=1}^{ns'} n_{jb} x_{ljb} \Delta_{kia,lib}} \quad (10)$$

Here $\Delta_{a,b,i,j}$ is the parameter that characterizes the association between site a in molecule i and site b in molecule j in the mixture and is given by:

$$\Delta_{kia,ljb} = K_{kia,ljb}^{HB} f_{kia,ljb} g_{ki,lj}^{SW} \left(\sigma_{ki,lj} \right) \quad (11)$$

where $K_{kia,ljb}^{HB}$ is the volume available for bonding, $f_{kia,ljb}$ the Mayer f-function, and $g_{ki,lj}^{SW}$ the radial distribution function for the square well monomers. At this point, it is important to note that in the usual homonuclear model of SAFT the sites on a molecule are distributed over the whole molecule and not located on a particular segment, as is often shown in schematic representations of SAFT models. However, in the GC- SAFT-VR equation, because of the hetero-segmented chain model used, the location of the association sites can be specified on a given functional group and hence their position within the model chain defined [15].

3. Results and discussion

3.1. Pure compounds

Thiophene (C_4H_4S) belongs to a class of heterocyclic compounds containing a five membered ring with one sulfur atom, as shown in Fig. 1. In the proposed molecular model of thiophene, the ring is described by four CH=groups and one -S- group connected using 5 bonds following the work of Das et al. [16] in which a model was developed that captures the effects of $\pi-\pi$ electronic interactions in ring molecules. The molecular parameters (σ, ε, λ, m) for the CH=(thiophene) and -S- groups were determined by adjusting the model parameters to experimental vapor pressure and saturated liquid density data for the thiophene molecule following the same procedure as described in previous work [14–16]. Due to the similarities between the thiophene and the alkylbenzene molecule, the segment number, m, was fixed at 0.35, which is the m value determined for the CH=group used in the alkylbenzene molecules (CH=(aBz)) group [16]. During the fitting process, experimental data points near the critical region and vapor pressures near the triple point were excluded from the fitting process as this data is known to skew the results of the fitting [21].

The parameters obtained from the fitting process are reported in Tables 1–3 and give absolute deviations in vapor pressure (AADP) and saturated liquid density (AADL) of 2.4% and 0.037%, respectively. As compared to the homonuclear approach used in the work of Zuniga-Moreno et al. [8], we find a lower value for the AADL but a slightly higher deviation in pressure. In Fig. 2, the GC-SAFT-VR correlations are shown for vapor pressure and saturated liquid density in comparison with the experimental data [23].

After determining the optimal parameters for the newly defined functional groups that comprise the thiophene molecule, the phase
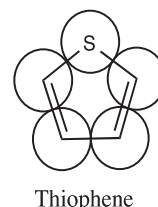

Thiophene

Fig. 1. Schematic representation of thiophene molecular model.

Table 1
GC-SAFT-VR parameters for the segment size σ and segment number m of each functional group studied.

Groups	σ (Å)	m_i
-S-	3.919	0.85
CH=(Thiophene)	3.511	0.35
CH= (Benzene)	3.028	0.619
CH=(ABz)	3.928	0.35
C=	2.112	0.382

Table 2
GC-SAFT-VR segment-segment dispersion energy range parameters $\lambda_{ki,lj}$ Values denoted with a * do not utilize Lorentz Bethelot combining rules.

Type	-S-	CH (Thiophene)	CH= (Benzene)	CH= (ABz)	C=
CH$_3$	1.51701	1.37585	1.60988	1.49148	1.38398
CH$_2$	1.60490*	1.47417	1.70485	1.58024	1.50425
CH	1.74358	1.61842	1.86298	1.71841	1.68251
CH$_2$=CH	1.5538	1.4115	1.6539	1.5277	1.4286
OH terminal	1.51444	1.39819	1.58961	1.49323	1.40881
CO$_2$	1.53501*	1.37340	1.64607	1.50580	1.38242
-S-	1.54086	1.40447	1.63435	1.51589	1.41898
CH(Thiophene)	1.40447	1.25224	1.48521	1.37830	1.22993
CH=(Benzene)	1.63435	1.48521	1.75536	1.60607	1.52422
CH=(ABz)	1.51589	1.37830	1.60607	1.49099	1.38674
C=	1.41898	1.22993	1.52422	1.38674	1.19284

behavior of the derivatives of thiophene, namely 3-methylthiophene, 2-methylthiophene, and benzothiophene, were then predicted as a means of testing and validating the new parameters. The molecular models for the derivatives of thiophene

are shown in Fig. 3, where the red spheres represent the CH=(thiophene) group, the yellow spheres represent the C= segments, and the light blue spheres represent the CH=(benzene) groups. The parameters for the C= and CH=(benzene) groups were taken from previous work [16]. The vapor pressure and saturated liquid density of each molecule were then predicted, with no additional fitting to experimental data. Comparing theoretical predictions with experimental results, for the 3-methylthiophene molecule the AADP and AADL was found to be 2.3% and 5.7% respectively. While for the 2-methylthiophene molecule [24], which contains the same functional groups as the 3-methylthiophene molecule [24] but in a different arrangement, the AADP and AADL were calculated and determined to be 7.1% and 6.7%, respectively. Finally the prediction of the vapor pressure and saturated liquid density of the benzothiophene [24] molecule gives an AADP and AADL of 4.9% and 6.5%, respectively. Although these deviations are higher than what one might obtain by fitting directly to the experimental data for each pure compound, we consider them to be good given that they were not determined by fitting to experimental data for the molecules studied and so are complete predictions. Additionally, the polar nature of the molecules studied is not explicitly included in the model, but taken into account implicitly using the square well potential parameters.

3.2. Binary mixtures

We now consider constant temperature and pressure slices of the phase diagrams of binary mixtures of the organic sulfur molecules studied with several fluids including: alkanes, alkenes, alcohols, carbon dioxide, and aromatics. First, we consider binary mixtures of thiophene with linear alkanes, namely, hexane, hexene,

Table 3
GC-SAFT-VR segment-segment dispersion energy well depth parameters $\varepsilon_{ki,lj}/k_B$ (K). Values denoted with a * do not utilize Lorentz Bethelot combining rules.

| Type	-S-	CH (Thiophene)	CH= (Benzene)	CH= (ABz)	C=
CH$_3$	404.97297	209.60988	185.23752	293.44157	153.86132
CH$_2$	407.5407*	210.93894	186.41204	295.30218	154.83689
CH	264.61765	136.96340	121.03800	191.74075	100.53614
CH$_2$=CH	385.6702	202.8312	179.2470	283.9518	148.8855
OH terminal	611.90479	316.71568	279.88961	443.38342	232.48089
CO$_2$	354.32107*	183.39297	232.48089	256.73943	134.61715
-S-	678.12000	362.37497	320.23988	507.30377	265.99648
CH(Thiophene)	362.37497	187.56159	165.75289	262.57526	137.67707
CH=(Benzene)	320.23988	165.75289	146.48000	232.04436	121.66868
CH=(ABz)	507.30377	262.57526	232.04436	367.59000	192.73984
C=	265.99648	137.67707	121.66868	192.73984	101.06000
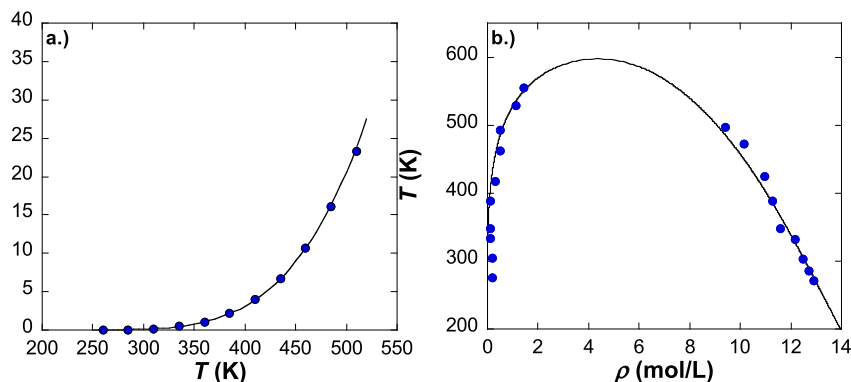
Fig. 2. GC-SAFT-VR correlation for a) the vapor pressure curve and b) the saturated liquid density for thiophene (C$_4$H$_4$S) using the parameters determined in this work as compared to experimental data (symbols) [22].
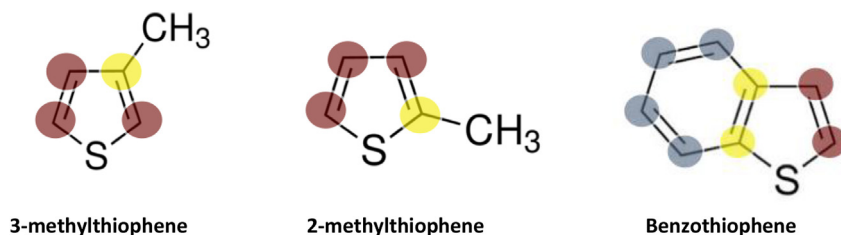
Fig. 3. Schematic representation of the molecular models used to describe the thiophene derivatives studied.

heptane, and methylbutane. To our knowledge this is the first time the SAFT approach has been applied to the study of these mixtures. The molecular group parameters for the alkanes, branched alkanes, and alkenes, (i.e., CH_3, CH_2, CH, and CH_2=CH) were taken from previous work [14]. The cross interaction between the CH_2 and -S-groups was found to deviate from Lorentz-Berthelot behavior and fitted to VLE data for thiophene + heptane at 1.0133 bar, as experimental data for a molecule containing both groups was unavailable. Using these parameters, in Fig. 4, the predicted phase behavior for thiophene + hexane at constant temperatures of 338.15 K and 323.15 K is presented (Fig. 4a) and excellent agreement is obtained with experimental results. The system thiophene + n-hexane shows positive deviations from Raoult's law and maximum pressure azeotropy [25], due to the close nature of the thiophene (T_b = 357.31 K) and n-hexane (T_b = 341.88 K) boiling points; the closer the boiling points of the pure components and the less ideal the mixture, the greater the likelihood of an azeotrope. If hexane is changed to hexene, which involves only the change of a single group within the model, the theoretical predictions are again found to be in good agreement with the experimental results as shown in Fig. 4b, with the theory correctly predicting no azeotropic behavior. Similarly, if the chain length of the alkane is increased from hexane to heptane, as in Fig. 4c, the theory correctly captures the change in phase behavior without any

fitting to the experimental data. Finally, if a representative branched molecule is considered as in Fig. 4d which presents a *Txy* slice of the thiophene + methylbutane phase diagram at 1.0133 bar, again good agreement with experimental data is observed. We note deviations from experimental data are observed at the pure limit in some cases due to deviations associated with the pure hydrocarbon predictions.

We now study the phase behavior of binary mixtures of aromatic compounds + thiophene. The CH=(benzene), CH=(alkylbenzene), C= and CH_3 group parameters needed to describe toluene and benzene are taken from previous work [16] and combined with the parameters for thiophene presented herein. In Fig. 5a, a constant temperature *Pxy* slice of the benzene + thiophene phase diagram is predicted at 298 K and in Fig. 5b a constant pressure *Txy* slice of the toluene + thiophene binary mixture is presented. In both cases, good agreement is obtained between the theoretical predictions and experimental results, although we observe small deviations for both mixtures due to over prediction of the pure toluene and benzene vapor pressure. We also note that the thiophene + toluene binary mixture shows nearly ideal phase behavior, with the theory predicting a type 1 phase diagram.

Turning to binary mixtures of thiophene and carbon dioxide, in Fig. 6, we present *Px* slices of the CO_2 + thiophene phase diagram
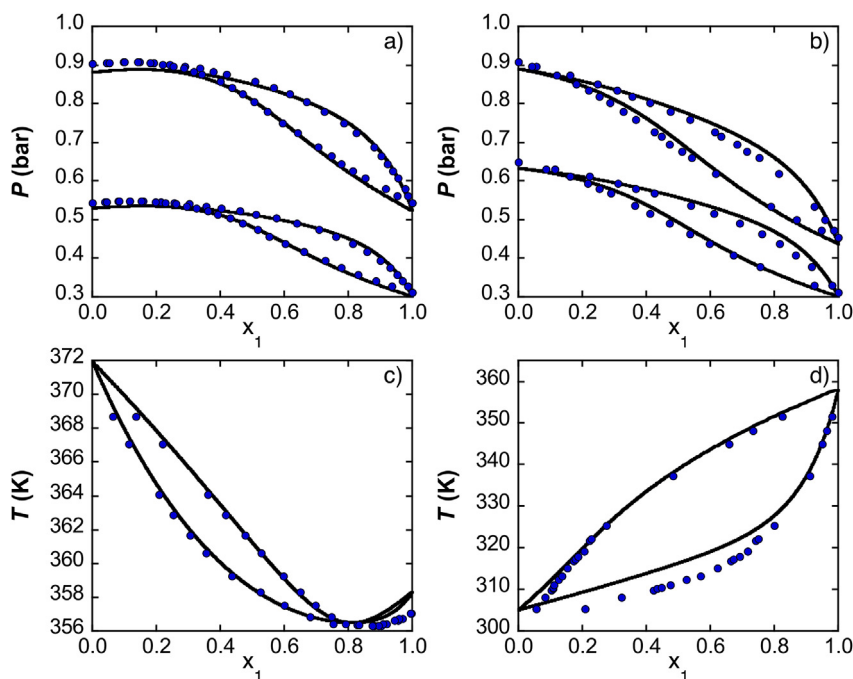

Fig. 4. Phase behavior of thiophene (1) + (a) hexane (2) at 338.15 K and 323.15 K (top to bottom), (b) hexene (2) at 333.15 K and 323.15 K (top to bottom), (c) heptane (2) at 1.0133 bar and (d) methylbutane (2) at 1.0133 bar. The solid lines represent the GC-SAFT-VR predictions and the symbols the experimental data [26].
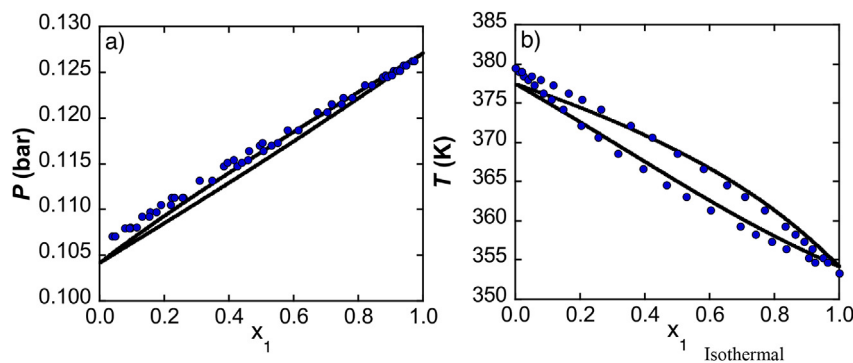
Fig. 5. Isothermal vapor-liquid equilibria for thiophene (1) (a) + toluene (2) at 298 K and (b) + benzene (2) at 0.9003 bar. The solid lines represent the GC-SAFT-VR predictions and the symbols the experimental data [27,28].
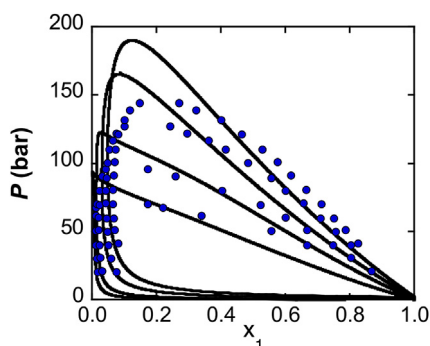

Fig. 6. Isothermal vapor-liquid equilibria for thiophene (1) + CO_2 (2) at 383 K, 363 K, 334 K, and 314 K (top to bottom). The solid lines represent the GC-SAFT-VR predictions and the symbols the experimental data [32].

over a range of temperatures from 314 K–383 K [29]. Here a single fitted cross interaction between the CO_2 molecule and the −S−

group was determined by fitting to VLE data for the mixture at 363.15 K; mixture data must be used since the CO_2 is a molecular group and so a pure component containing the two groups of interest cannot be used to determine the interaction between the groups. The model parameters were then used to predict the phase behavior at the remaining temperatures with no additional fitting to experimental data. Aside from the over-prediction of the critical region, which is expected from an analytical equation of state [30,31], the theoretical predictions describe the experimental results well. As can be seen from the figures, the proposed model is able to capture the changes in phase behavior as a function of temperature and at a similar level of agreement to the work of Zuniga-Moreno et al. [8]; however, we note that in this work only one isotherm was used to determine the one fitted cross interaction.

Next mixtures of strongly associating fluids such as alcohols with compounds containing thiophene are studied and the theory's ability to capture the complex interactions between the lone pair of electrons present on the alcohol oxygen atom and the thiophene
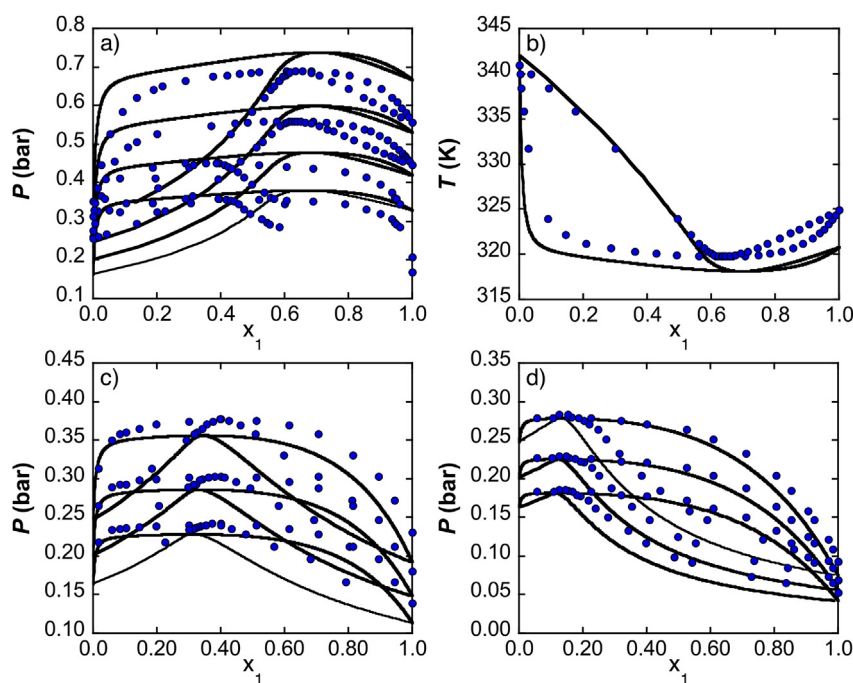

Fig. 7. Binary mixtures of thiophene (1) + (a) methanol (2) at 323.15 K, 318.15 K, 313.15 K, and 308.15 K (top to bottom), (b) methanol (2) at 0.603 bar, (c) ethanol (2) at 318.15 K, 313.15 K, and 308.15 K (top to bottom), and (d) propanol (2) at 318.15 K, 313.15 K, and 308.15 K (top to bottom). The solid lines represent the GC-SAFT-VR predictions and the symbols the experimental data [27,33].

ring tested. The parameters for the OH, CH$_2$, and CH$_3$ groups needed to describe alcohols were taken from previous work [15] and combined with those for thiophene developed in this work; the theoretical results are thus true predictions. In Fig. 7a, we present four isotherms for the thiophene + methanol binary mixture at 323.15 K, 318.15 K, 313.15 K, and 308.15 K and in Fig. 7b a *Txy* slice of the phase diagram at 0.603 bar. Although the proposed model is able to capture the changes in phase behavior as a function of temperature, we observe some deviation for the thiophene + methanol mixture, due to the over prediction of the vapor pressure of pure methanol. As the chain length of the alcohol is increased, better agreement is observed, as the GC-SAFT-VR approach provides a better description of the pure limits for higher molecular weight of alcohols, as can be seen Fig. 7c and d where we present the phase behavior for ethanol + thiophene and propanol + thiophene respectively. The azeotrope is also predicted accurately, agreeing well in both pressure and composition with the experimental results, particularly for the longer alcohol molecules studied.

To test the accuracy of GC-SAFT-VR approach for molecules other than thiophene, the phase behavior of binary mixtures of 3-methylthiophene with alkanes, branched alkanes, and the aromatic molecule, toluene, has also been studied. These mixtures have not been studied previously with a SAFT based approach, perhaps because of the limited experimental data that is available for parameter estimation. The ability to use a group contribution SAFT approach to accurately describe these systems would therefore be attractive. In Fig. 8 the VLE for binary mixtures of 3-methylthiophene with hexane, hexene and heptane are presented. We observe that replacing the thiophene molecule with the 3-methylthiophene molecule eliminates the azeotropic behavior for both the hexane and hexene binary mixtures (c.f. Figs. 4a, 8a and 4b and 8b), thus allowing for easier separation. We note that good agreement is found between the experimental results and theoretical predictions in all cases, with the theory accurately capturing the changes in phase behavior with the increase in the number of CH$_2$ groups in the linear alkane. The phase behavior is also correctly predicted for saturated as well as unsaturated alkanes, again without fitting to the mixture experimental data.

Results for constant temperature *Px* slices of the 3-methylthiophene + 2-methylbutane phase diagram are compared with experimental data in Fig. 9a. From the figure we note that excellent agreement between the theoretical predictions and the experimental results is observed. However, for the 3-methylthiophene + 2-methypentane mixture, shown in Fig. 9b, we see a slight deviation at the pure limit of 2-methylpentane due to the over prediction of the pure vapor pressure of 2-methylpentane; however, the shape and curvature of the phase envelope are correctly predicted.

Finally, the phase behavior of mixtures containing the aromatic organic compound benzothiophene has been studied. The benzothiophene molecule is considerably more complex than thiophene and thus represents a more stringent test of the theory. Using the GC-SAFT-VR approach with no additional fitting, as shown in Fig. 10, we are able to accurately predict phase behavior of the binary mixtures of benzothiophene + dodecane and benzothiophene + octanol. To our knowledge no other SAFT study has been performed on these systems.

4. Conclusion

In this paper, we have extended the application of the GC-SAFT-VR approach to study the phase behavior of organic sulfur molecules, namely, thiophene, 3-methylthiophene, and benzothiophene. These sulfur compounds found in crude oil cause many
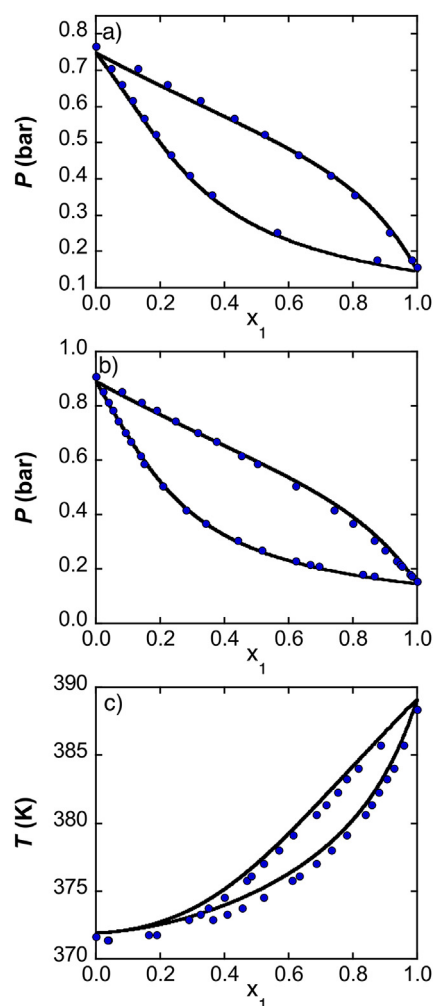

Fig. 8. Vapor−liquid equilibria for binary mixtures of 3-methylthiophene (1) + (a) hexane (2) at 333.15 K, (b) + hexene (2) at 333.15 K and (c) + heptane (2) at 1 bar. The solid lines represent the theoretical predictions and the symbols represent the experimental results [34].

handling, transportation, storage, and manufacturing difficulties due to their extreme toxicity and corrosiveness. A model and parameters have been proposed within the GC-SAFT-VR approach that allows the phase behavior of these molecules to be studied predictively. Molecular parameters were determined for thiophene by fitting to experimental vapor pressure and saturated liquid density data and the phase behavior of other derivatives of thiophene then predicted using the group-contribution approach without additional fitting to experimental results. The proposed model takes advantage of the earlier work of Das et al. [16] in that the ring molecules are fragmented into smaller groups and the ring structure retained to better capture the interactions associated with the ring. Binary mixtures of these molecules with other relevant fluids were then studied and found to be in overall excellent agreement with the experimental data. Two modified cross interactions were introduced to correct for deviations from ideal behavior, which is assumed by the use of Lorentz Berthelot combining rules for all other cross interactions. The cross interaction between the −S− group and the CH$_2$ group and CO$_2$ molecule were each fitted to isothermal vapor-liquid equilibrium data at a single temperature and the resulting parameters then used to predict the phase behavior at other temperatures and in other binary mixtures, with good agreement seen. Accordingly, we can
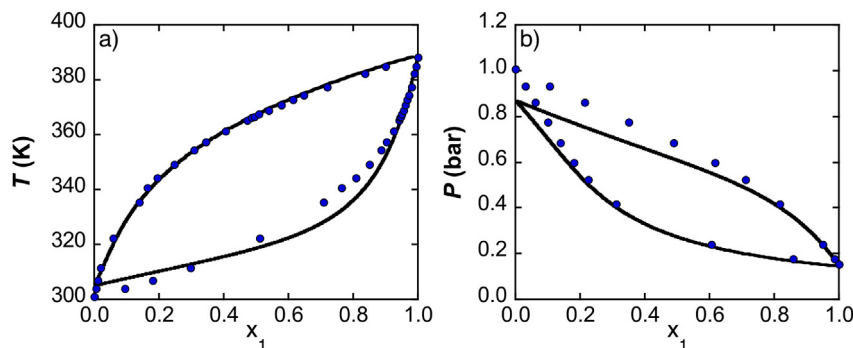
Fig. 9. Vapor—liquid equilibria for binary mixtures of (a) 3-methylthiophene + 2-methylbutane at 1 bar and (b) 3-methylthiophene + 2-methylpentane at 333.15 K. The solid lines represent the theoretical predictions and the symbols represent the experimental results [34].
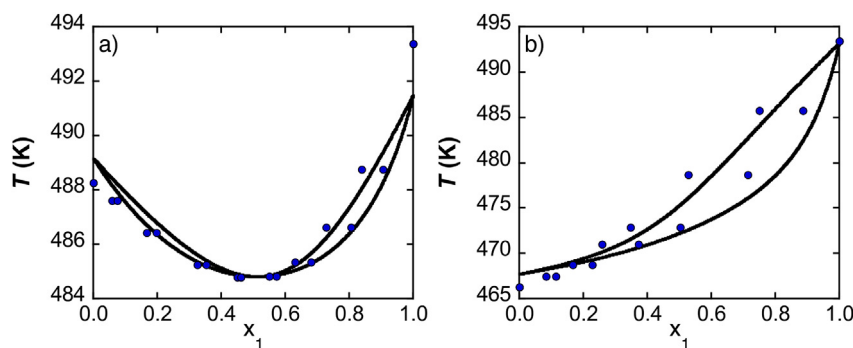

Fig. 10. Vapor—liquid equilibria for binary mixtures of benzothiophene (1) + (a) dodecane at 0.995 bar and (b) octanol at 0.995 bar. The solid lines represent the theoretical predictions and the symbols represent the experimental results [25].

conclude based on the limited experimental data available that the parameters developed can be applied successfully and in a predictive and transferable fashion to predict the phase equilibrium of pure fluids and mixtures of thiophene and its derivatives without reliance on additional experimental data.

Acknowledgments

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