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Modeling the Phase Equilibria of Asymmetric Hydrocarbon Mixtures Using Molecular Simulation and Equations of State

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Monte Carlo simulation (MC) is combined with equations of state (EoS) to develop a methodology for the calculation of the vapor–liquid equilibrium (VLE) of multicomponent hydrocarbon mixtures with high asymmetry. MC simulations are used for the calculation of the VLE of binary methane mixtures with long n-alkanes, for a wide range of temperatures and pressures, to obtain sufficient VLE data for the consistent fitting of binary interaction parameters (BIPs) for the EoS. The Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Perturbed Chain - Statistical Associating Fluid Theory (PC-SAFT) EoS are considered. The ability of each EoS to correlate the VLE data is assessed and the selected ones are used to predict the VLE of multicomponent gas condensate mixtures. MC simulations proved to be very accurate in predicting the VLE in all conditions and mixtures considered. The BIPs regressed from the simulation dataset lead to equally accurate modeling results for multicomponent mixtures, compared to those regressed from experimental data. © 2018 American Institute of Chemical Engineers *AIChE J*, 65: 792–803, 2019

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Introduction

The significant progress and development in the drilling technology has made possible the exploitation of deep, high pressure-high temperature (HPHT) oil reservoirs for hydrocarbon production.[1] Due to the depletion of conventional resources, the oil and gas industry is driven to explore and extract petroleum fluids from geological formations and wells located in the deep crust, which differ significantly from the conventional ones with respect to temperature (*T*), pressure (*P*), and composition.[1] The temperature in such reservoirs can vary from 150 to 260°C and the pressure from 70 to 200 MPa.[2] The fluid composition can be very asymmetric, with methane (CH_4) being the dominant component, mixed with long-chain normal alkanes (*n*-alkanes).[1,3]

The asymmetric nature of these reservoir fluids results in a more complex phase behavior, compared to those extracted from conventional wells.[3] A class of hydrocarbon mixtures that are present in HPHT reservoirs are the so-called gas condensate mixtures. The phase behavior of these systems differs from the phase behavior of conventional natural gas, because liquid can be condensed from the gas with pressure reduction at the temperature of the reservoir. As a result, the pressure decrease upon depletion of the reservoir can lead to significant loss of valuable product via liquid condensation, if precautions are not taken.[4] An important part of the gas production chain is the transportation of a methane rich stream from the point of extraction to the processing units and finally to the

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Additional Supporting Information may be found in the online version of this article.

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distribution network. The detailed design and optimization of uninterrupted transport processes require accurate knowledge of the physical properties and the phase equilibria conditions of the hydrocarbon mixtures as functions of temperature, pressure, and composition.

Experimental measurements of the physical properties and phase equilibrium of real reservoir fluids are relatively scarce. The modeling of these mixtures is a challenging task, due to the theoretical limitations in the available models and to the high uncertainties of the composition in such complex systems.[3] Current practice focuses on the experimental determination of these properties for synthetic mixtures comprised mainly of *n*-alkanes. A comprehensive review of the available experimental studies of asymmetric ternary and multicomponent hydrocarbon mixtures is given by Regueira et al.[5]

Experimental measurements for multicomponent mixtures are usually expensive and difficult to perform and do not cover the full range of working conditions. To that extent, thermodynamic models that can accurately predict the phase behavior and the physical properties of reservoir fluids are very important for the oil and gas industry, so that optimized and safe processes can be designed. Usually, the available experimental data of synthetic hydrocarbon mixtures are utilized for the assessment of existing models and the development of new ones. The agreement between model predictions and experimental data, for different mixtures, indicates how well these predictions can be extrapolated to conditions for which experimental data are not available.

To the best of our knowledge, there are two systematic research studies regarding the modeling of gas condensate mixtures. Yan et al.[6] made a comparative study between cubic such as Soave-Redlich-Kwong (SRK)[7] and Peng-Robinson (PR)[8] and higher order (simplified Perturbed Chain - Statistical Associating Fluid Theory,[9] sPC-SAFT, and Soave modified Benedict-Webb-Rubin[10]) equations of state (EoS), to assess the performance of each model in predicting physical properties and phase equilibria of reservoir fluids. The authors considered density predictions of each EoS for pure components that typically exist in reservoir fluids, isothermal vapor–liquid equilibrium (VLE) of relevant binary mixtures, VLE predictions of synthetic multicomponent mixtures, and *PVT* properties of real reservoir fluids. It was concluded that the predictions of the four models regarding the VLE of synthetic gases are very similar, with or without the use of k_{ij} parameters, if the mixtures are not very asymmetric. Discrepancies between the models are becoming more prominent for more asymmetric mixtures, while the values of the binary interaction parameters (BIPs) play an important role in the accurate prediction of the phase behavior. The authors mention that the k_{ij} parameters between hydrocarbons, other than CH_4, were set equal to zero, while the most important pairs contained CH_4, N_2, CO_2, and H_2S.

In a recent study, Novak et al.[11] evaluated the performance of the SRK, PR, PC-SAFT,[12] and Universal Mixing Rule - Peng Robinson UNIFAC (UMR-PRU)[13] models to predict dew points and liquid dropouts of synthetic and real gas condensates. The authors concluded that, in most cases, PC-SAFT predicts higher dew-point pressures than the experimentally measured ones for the synthetic gases, cubic EoS fail to describe the mixtures containing aromatic components, while the UMR-PRU model exhibits the lowest overall deviation from the experimental data. As a first step in their methodology, the authors evaluated the effect of the k_{ij} parameters on the calculations. It was shown that the use of k_{ij} parameters only between CH_4 and long-chain hydrocarbons (with 10 carbon atoms or more) yields practically the same results with those obtained when k_{ij} parameters for all binary pairs containing CH_4 are used. The exploitation of the complete matrix of binary pairs yields also very similar results. This finding indicates that the performance of each model in predicting the VLE of these multicomponent mixtures depends mainly on specific interaction pairs of molecules, that is, between CH_4 and long-chain hydrocarbons. It is important to note that the synthetic mixtures considered by Novak et al.[11] did not include N_2, CO_2, and H_2S, which would require additional k_{ij} parameters. Finally, it was emphasized that the regression of BIPs based on the respective binary mixture data is not always possible and there may be large uncertainties regarding the values of the parameters. This is a result of insufficient experimental VLE data for binary mixtures of CH_4 with long-chain hydrocarbons, especially at high pressures.

Fitting BIPs to binary mixture VLE data that do not span a wide temperature and pressure range may lead to false assessment of the correlative ability of different models. For example, even with one temperature independent k_{ij} parameter, some EoS can correlate better a wide temperature and pressure range of binary mixture VLE than others. The use of a limited number of experimental VLE data in the fitting process may result in similar performance, in terms of correlation of the phase behavior, with different thermodynamic models. The use of BIPs fitted to limited VLE data to predict the phase equilibria of multicomponent mixtures can lead to erroneous evaluation of the predictive capabilities of the models considered.

The phase equilibria of CH_4 binary mixtures with *n*-alkanes up to $n\text{-}C_{10}H_{22}$ are well studied in terms of experimental measurements. The mixture of CH_4 with $n\text{-}C_{16}H_{34}$ constitutes a very well-studied benchmark that is used also for the validation of experimental apparatuses. However, experimentally measured VLE data for mixtures with lower asymmetry, such as $CH_4\text{-}n\text{-}C_{12}H_{26}$ and $CH_4\text{-}n\text{-}C_{14}H_{30}$ are much scarcer and the available experimental data do not cover the full temperature and pressure range of conditions which are encountered in multicomponent applications. In cases of mixtures with higher asymmetry, the reported experimental data are also not sufficient. Table 1 summarizes the available VLE experimental data from literature for binary CH_4-*n*-alkane mixtures. As the asymmetry of a mixture increases, so does the temperature and pressure range where VLE is exhibited. Thus, experimental measurements have to be carried out at very high temperatures and pressures, which significantly increase the difficulty and the cost.

Molecular simulation is a powerful tool for the accurate prediction of phase equilibria and transport properties of pure components and binary mixtures.[14-17] During the past three decades, the rapid development of computers enabled the development of accurate potentials representing the intermolecular interactions and the simulation of the phase equilibria of various complex systems.[14,18] Monte Carlo simulation in the Gibbs Ensemble (GEMC) is the primary tool for calculating the phase coexistence of pure components and mixtures.[19,20] In the GEMC, two phases are simulated explicitly in two different simulation boxes without an interface. Molecules in the same simulation box interact with each other, but there are no interactions between molecules of different simulation boxes. Equilibrium is obtained by variation of the volume of each box and molecule exchange between the boxes. Although GEMC provides a straightforward route to determine accurate coexistence densities, the computation of critical parameters is not always easy.[21] To that end, alternative simulation methods such as the histogram reweighting in the grand-canonical ensemble,[22,23] the

Table 1. Experimental Binary VLE Data of CH_4-*n*-alkane Mixtures Examined in this Work

Temperature (K)	Pressure (MPa)	References
CH_4-*n*-$C_{10}H_{22}$		
244.26–277.59	1.56–6.90	59
263.15–303.15	1.60–36.53	60
310.90–410.90	1.04–8.65	61
423.15–583.05	3.04–18.68	62
237.15–423.15	0.053–10.13	63
310.93–510.93	0.14–36.20	64
293.15–472.47	11.30–35.98	65
CH_4-*n*-$C_{12}H_{26}$		
263.15–303.15	1.41–49.48	66
323.2–373.2	1.33–10.38	61
374.05	9.97–40.79	67
CH_4-*n*-$C_{16}H_{34}$		
290.00–360.00	2.15–70.35	68
293.15–313.15	2.09–69.55	69
303.20–323.20	0.06–0.51	70
324.00–413.20	7.60–31.90	71
462.45–703.55	2.05–25.26	72
623.10	2.50–18.00	73
CH_4-*n*-$C_{20}H_{42}$		
313.15	0.10–6.08	74
323.20–423.20	0.95–10.69	75
323.15–353.15	0.41–83.40	76
373.35–573.15	1.01–5.05	77
CH_4-*n*-$C_{24}H_{50}$		
325.00–425.00	1.93–104.05	78
373.15–573.15	1.01–5.07	79
374.05	20.10–84.30	80

Gibbs-Duhem integration technique,[24,25] and the iterative Monte Carlo scheme[26] (SPECS) can be very efficient, provided that the number of components is limited and the acceptance probability for insertions/deletions of molecules is sufficiently high. Nevertheless, GEMC combined with advanced techniques such as the configurational-bias Monte Carlo (CBMC)[27-29] or continuous fractional component Monte Carlo (CFCMC),[30-33] which increase the acceptance probability of the molecule exchange trial move, is still a very reliable and efficient tool for the phase equilibria calculation of hydrocarbon mixtures.

The aim of this work is to develop a methodology for the prediction of the VLE of multicomponent gas condensate mixtures by combining molecular simulation with thermodynamic models in the form of an EoS. Monte Carlo simulations in the Gibbs Ensemble with the TraPPE-UA force field[15] are used for the calculation of VLE data for various binary CH_4-*n*-alkane mixtures. In total, five binary mixtures are investigated: the mixtures of CH_4 with *n*-$C_{10}H_{22}$, *n*-$C_{12}H_{26}$, *n*-$C_{16}H_{34}$, *n*-$C_{20}H_{42}$, and *n*-$C_{24}H_{50}$. Initially, the GEMC simulation results are validated against the available experimental data and subsequently new calculations are performed at conditions in which no experimental measurements exist. Two sets of k_{ij} parameters for two cubic (SRK, PR) and one higher order (PC-SAFT) EoS are then regressed; one from the available experimental VLE data for the five binary mixtures and a second one using the GEMC simulation results. The aim is to compare the variation of the k_{ij} values when fitted to experimental data at the available range of conditions vs. the respective k_{ij} values fitted to GEMC simulation data which span an extensive temperature and pressure range. The ability of each EoS to correlate the VLE data depending on the available range of conditions is also assessed. Finally, the EoS considered in this work are used to predict the VLE of multicomponent gas condensate mixtures with both sets of k_{ij} parameters and a comparison between the models is performed. The gas condensate mixtures considered in this study consist mainly of *n*-alkanes. Although multicomponent mixtures including components like CO_2 and N_2, or even sour gases with high concentration of H_2S (and/or CO_2), better resemble reservoir fluids, the scope of this work is to concentrate on mixtures of alkanes, only. For the five binary CH_4-*n*-alkanes mixtures studied in this work, an extensive number of Monte Carlo (MC) simulations is required to cover the wide range of temperatures and pressures for the accurate prediction. The consideration of CO_2, N_2, and H_2S would require a significant number of additional MC simulations to validate and extend the binary mixture data. In addition, molecular simulation studies of hydrocarbons with polar molecules often require modifications of the binary interaction parameters used, mainly due to deficiencies in the force fields of the polar components.[34-39] This study will be the focus of a future work.

Models and Methods

Equations of state

An EoS is a mathematical relation that correlates the temperature, pressure, and molar volume (v) of a pure component at a thermodynamic equilibrium state. According to the Gibbs phase rule for a single-phase pure component, the EoS can be solved for one of these quantities while the other two are set.[40] The usual case is that the EoS is solved for the volume, at constant temperature and pressure, and then all other thermodynamic properties can be determined, using specific thermodynamic relations. The most well-known EoS are the SRK and PR which belong to the family of cubic EoS (cubic dependency on volume) and are empirical modifications of the pioneering van der Waals EoS.[41] Mixture properties can be calculated by a cubic EoS using appropriate combining and mixing rules. In this work, the SRK and PR EoS were applied to mixtures via the van der Waals one fluid theory (vdW1f) mixing rules, using only one temperature-independent BIP (k_{ij}) in the attractive term.

SAFT based models are theoretically derived EoS based on rigorous perturbation theory.[42-44] A SAFT model that has gained tremendous industrial popularity is the PC-SAFT EoS.[12] PC-SAFT was derived using the hard chain fluid as the reference system and the second order Barker–Henderson perturbation theory[45] was applied for the Helmholtz free energy term that accounts for the dispersion interactions. The pair potential used is the modified square well potential, proposed by Chen and Kreglewski.[46] The chain and association terms in PC-SAFT EoS are the same as the ones used in the SAFT EoS proposed by Huang and Radosz.[47,48] The reader can refer to the original publications[12,49] for the exact mathematical relations. In this work, the PC-SAFT EoS was used to calculate mixture properties with the vdW1f mixing rules as proposed by Gross and Sadowski,[12] while specific combining rules (Lorentz–Berthelot-based with a BIP incorporated into the Berthelot rule) were applied to calculate the segment dispersive energy and diameter parameters for the unlike interactions. More details on the Cubic and PC-SAFT EoS are provided in the Supporting Information.

Monte Carlo simulation

Monte Carlo simulations were performed in the Gibbs-NPT ensemble to compute the VLE of mixtures.[14,19,20] In the Gibbs-NPT ensemble, the volume of the two boxes can be changed independently and different kinds of MC moves are performed to satisfy the equilibrium conditions, that is, the equality of temperature, pressure, and chemical potential of each component in

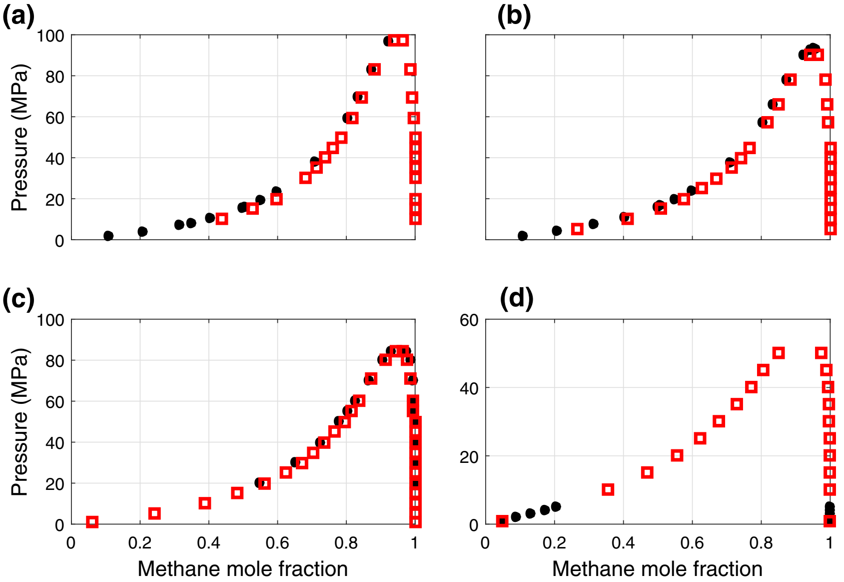

Figure 1. Pressure – composition VLE for the CH_4-*n*-$C_{24}H_{50}$ mixture at various temperatures; (a) *T* = 330 K, (b) *T* = 350 K, (c) *T* = 374.05 K, (d) *T* = 523.15 K. Experimental data[78-80] are represented by black data points and GEMC simulation data by red squares.

[Color figure can be viewed at wileyonlinelibrary.com]

the coexisting phases. In each MC step, a trial move is selected at random to displace, regrow, rotate, or exchange a chosen hydrocarbon chain or change the volume of a randomly selected box. GEMC relies on a sufficient number of molecule exchanges between the simulation boxes. Unfortunately, the acceptance probabilities for these exchanges can be close to zero for the case of long molecules or when densities are high (e.g., a liquid phase at low temperature).

Although GEMC has been used to study a wide range of mixtures, simulation data for asymmetric mixtures of hydrocarbons are scarce. This should be attributed, among others, to the low acceptance probability for the exchange of the long-chain hydrocarbons. At these conditions, advanced simulation techniques such as CBMC[27-29] or CFCMC[30,31] are used to increase the acceptance probability of the molecule exchange trial move. Details for these simulation techniques are given in the Supporting Information. In this work, all simulations were performed using the CBMC method, while the CFCMC method was used to verify the results for systems where the exchange of molecules between the boxes is expected to be more difficult (e.g., CH_4-*n*-$C_{20}H_{42}$ and CH_4-*n*-$C_{24}H_{50}$ at low temperatures and high pressures).

In this work, the TraPPE united atom (TraPPE-UA) force field was used for all the *n*-alkanes.[15] In the TraPPE-UA, CH_4, CH_3, and CH_2 groups are modeled as pseudo-atoms with no charges. The non-bonded intramolecular and intermolecular interactions between the pseudo-atoms are represented by the 12–6 Lennard-Jones (LJ) potential. The LJ parameters used in this study can be found in the work by Martin and Siepmann.[15] Force field and computational details for the MC simulations are given in the Supporting Information. All GEMC simulations were carried out with RASPA.[50,51]

Results and Discussion

Monte Carlo simulations

The computed VLE from the GEMC simulations depends heavily on the accuracy of the force fields used. As mentioned in the previous section, TraPPE-UA was used in all our simulations. The choice of this force field was based on various reasons: Siepmann and coworkers reported the VLE of pure alkanes up to *n*-$C_{12}H_{26}$,[15] showing that the TraPPE-UA force field is sufficiently accurate in reproducing the VLE of these hydrocarbons. In addition, the use of united atom force fields is advantageous due to the significant reduction of interaction sites compared to their full atom counterparts (e.g., TraPPE-EH[52]). One of the drawbacks of the TraPPE-UA force field is the tendency to slightly overestimate the vapor pressures and densities.[15] However, the saturated liquid densities and critical temperatures are predicted accurately.[15] Therefore, since the liquid phase properties at high temperatures are represented well by the TraPPE-UA force field, it is expected that the k_{ij} parameters, which are typically fitted to bubble-point data, will not be affected by the deficiency of the model to accurately describe the gas-phase.

To validate the TraPPE-UA force field, the VLE of binary mixtures of CH_4 with different long-chain *n*-alkanes were computed in the Gibbs-NPT ensemble and compared with available experimental data. In Figure 1, the simulated VLE data for the most asymmetric mixture (i.e., CH_4-*n*-$C_{24}H_{50}$) at temperatures ranging from 330 to 523.15 K are plotted against the available experimental data. Excellent agreement between the two sets of data is observed, even at conditions close to the critical points. Similarly, good agreement is observed for all the mixtures considered, justifying the choice of the TraPPE-UA force field. Relevant comparisons between experiments and simulations can be found in the Supporting Information (Figures S1–S5).

Equation of state modeling

The accurate phase equilibrium modeling of asymmetric hydrocarbon mixtures with EoS relies heavily on the BIPs between CH_4 and long-chain hydrocarbons.[11] In this work, temperature independent k_{ij} parameters are used in the combining rules of the adopted EoS. A different model selection would require the use of different BIPs, for example, energetic

Table 2. %AARD Between Experimental VLE Data and EoS Calculations for the Mixture Bubble Pressure and Corresponding k_{ij} Values

EoS			CH_4-n-$C_{10}H_{22}$	CH_4-n-$C_{12}H_{26}$	CH_4-n-$C_{16}H_{34}$	CH_4-n-$C_{20}H_{42}$	CH_4-n-$C_{24}H_{50}$
SRK	Pr.	%AARD	9.37	17.49	13.06	13.26	17.49
	Cor.	%AARD	4.30	5.92	4.81	13.62	14.58
		k_{ij}	0.0349	0.0421	0.0565	0.0392	0.0428
PR	Pr.	%AARD	10.13	19.63	14.14	14.45	19.23
	Cor.	%AARD	4.01	5.81	4.96	15.06	16.23
		k_{ij}	0.0389	0.0461	0.0595	0.0421	0.0494
PC-SAFT	Pr.	%AARD	12.85	18.15	21.51	21.64	25.29
	Cor.	%AARD	5.55	5.31	8.47	4.94	5.69
		k_{ij}	0.0208	0.0213	0.0364	0.0375	0.0408
NP			87	40	59	49	67

$$\%\text{AARD} = \frac{100}{\text{NP}}\sum_{i=1}^{\text{NP}}\left|\frac{P_i^{\text{calculated}} - P_i^{\text{experimental}}}{P_i^{\text{experimental.}}}\right|$$

NP is the number of experimental data points and P_i is the bubble pressure.
"Pr." refers to predictions ($k_{ij} = 0$), whereas "Cor." refers to correlations (calculations with $k_{ij} \neq 0$).

interactions in Excess Gibbs Energy models, interactions between groups in group contribution schemes, and so forth.[53-55] Except for the thermodynamic model itself, the number of BIPs, their temperature dependency, and so forth affects the general correlative ability of the model.

Supporting Information Tables S1 and S2 summarize the pure component parameters used for the cubic and PC-SAFT EoS, respectively. The critical properties and the acentric factor for the cubic EoS were taken from the DIPPR[56] database, while the PC-SAFT EoS parameters were taken from Gross and Sadowski,[12] except for the n-$C_{24}H_{50}$ parameters, which were taken from the MAPS platform v4.0.[57]

Comparison of calculations from the various methods

A major aim in this work is to evaluate k_{ij} parameters by fitting the EoS to GEMC simulation data generated here, and to experimental data available in the literature. As shown in the previous section, GEMC simulations can provide accurate VLE predictions for the binary mixtures considered. In this work, GEMC simulations were also performed at conditions where no experimental data are available. The aim was to cover the entire temperature range from the normal melting temperature to the critical temperature of the long-chain n-alkane in every mixture. We aim to show that molecular simulation based on accurate force fields is a powerful tool that can be used to complement experiments and provide useful insight at conditions in which measurements are difficult to be carried out (e.g., high temperature and pressures). The pressure range examined in the simulations spans from low values up to approximately the binary mixture critical point. To avoid conditions where solidification may occur, the lowest isotherm is ~10 K higher than the normal melting point and the highest one is ~50 K lower than the critical temperature of the long-chain n-alkane, respectively.

In this work, two sets of k_{ij} parameters were obtained: One by minimizing the root-mean-square deviation between the bubble pressure values calculated by the EoS and experimental data and the second one by minimizing the same deviation between EoS calculations and GEMC data. Table 2 summarizes the Percentage Average Absolute Relative Deviation (% AARD) between experimental VLE data and EoS calculations for each mixture and the corresponding k_{ij} values. Table 3 summarizes the % AARD and the respective k_{ij} values for the case where GEMC simulation VLE data were used. In the rest of the paper, the % AARD and k_{ij} parameters calculated from the experimental VLE data will be referred to as % AARD-EXP and k_{ij}^{EXP}, while those calculated from GEMC simulations as % AARD-MC and k_{ij}^{MC}, respectively. As a general trend, it should be pointed out that the k_{ij} values are relatively small in all cases, and EoS predictions are in reasonable agreement with both experimental and GEMC data, even when $k_{ij} = 0$. An assessment of these calculations is shown in Tables 2 and 3.

In Figure 2, the variation of % AARD-EXP and % AARD-MC with the carbon number of the long-chain n-alkane in each binary mixture is presented. All the binary mixtures considered in this work include only n-alkanes and one might

Table 3. %AARD Between GEMC Simulation VLE Data and EoS Calculations for the Mixture Bubble Pressure and Corresponding k_{ij} Values Regressed from Monte Carlo Simulation Data

EoS			CH_4-n-$C_{10}H_{22}$	CH_4-n-$C_{12}H_{26}$	CH_4-n-$C_{16}H_{34}$	CH_4-n-$C_{20}H_{42}$	CH_4-n-$C_{24}H_{50}$
SRK	Pr.	%AARD	16.44	10.62	11.97	13.06	15.52
	Cor.	%AARD	3.93	4.34	7.31	8.38	12.41
		k_{ij}	0.0379	0.0368	0.0526	0.0436	0.0355
PR	Pr.	%AARD	18.30	11.84	12.12	14.95	17.52
	Cor.	%AARD	3.79	3.90	7.30	8.93	12.66
		k_{ij}	0.0416	0.0406	0.0538	0.0497	0.0434
PC-SAFT	Pr.	%AARD	13.52	15.16	18.27	20.49	21.85
	Cor.	%AARD	3.79	6.26	7.28	8.68	8.97
		k_{ij}	0.0150	0.0237	0.0332	0.0344	0.0343
NP			53	64	54	69	86

$$\%\text{AARD} = \frac{100}{\text{NP}}\sum_{i=1}^{\text{NP}}\left|\frac{P_i^{\text{calculated}} - P_i^{\text{experimental}}}{P_i^{\text{experimental}}}\right|$$

NP is the number of experimental data points and P_i is the bubble pressure.
"Pr." refers to predictions ($k_{ij} = 0$), whereas "Cor." refers to correlations (calculations with $k_{ij} \neq 0$).

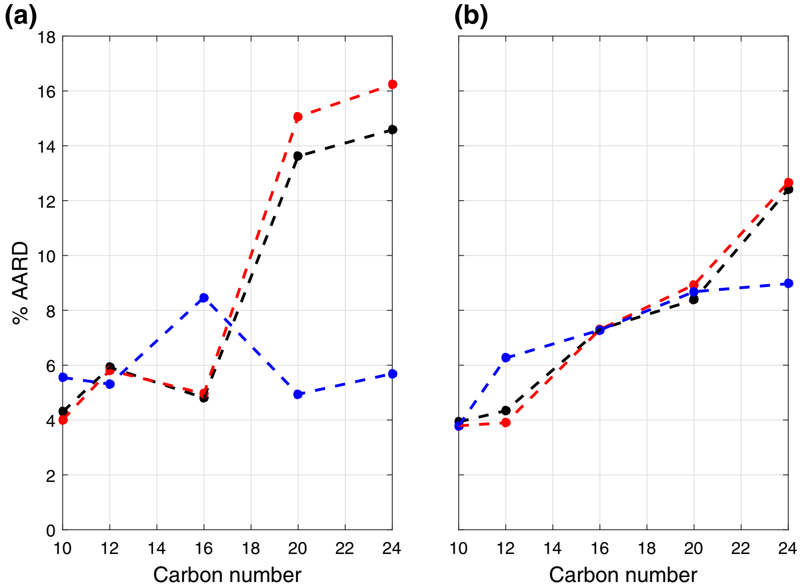

Figure 2. % AARD vs. carbon number of the long-chain hydrocarbon for binary CH_4 mixtures.

Left panel shows the % AARD when k_{ij} parameters are fitted to experimental data. Right panel shows the % AARD when k_{ij} parameters are fitted to GEMC simulation data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS. [Color figure can be viewed at wileyonlinelibrary.com]

expect that the % AARD will increase as the asymmetry of each mixture increases, that is, with the carbon number. However, this is not always the case here. The two cubic EoS essentially deviate from the expected behavior because of the % AARD-EXP value of CH_4-n-$C_{16}H_{34}$ mixture, which has a lower value compared to CH_4-n-$C_{12}H_{26}$ mixture. The most prevalent deviation from the expected behavior is presented by PC-SAFT EoS which correlates with almost the same accuracy in terms of % AARD-EXP values (~5.3%) the VLE of CH_4 mixtures with n-$C_{10}H_{22}$, n-$C_{12}H_{26}$, n-$C_{20}H_{42}$, and n-$C_{24}H_{50}$. A distinctively higher value (% AARD-EXP = 8.47) is presented for the CH_4-n-$C_{16}H_{34}$ mixture. The relative constant k_{ij} can be attributed partly to the strong theoretical basis of PC-SAFT that captures accurately the properties of long hydrocarbon molecules.

The same trend presented for the % AARD-EXP of the cubic EoS in this work is also followed by the respective values reported by Yan et al.,[6] while the absolute values are also similar. The k_{ij}^{EXP} values regressed in this work are in very good agreement with those reported by Novak et al.[11] that also used the DIPPR[56] database for the pure component parameters of the cubic EoS and the Gross and Sadowski[12]

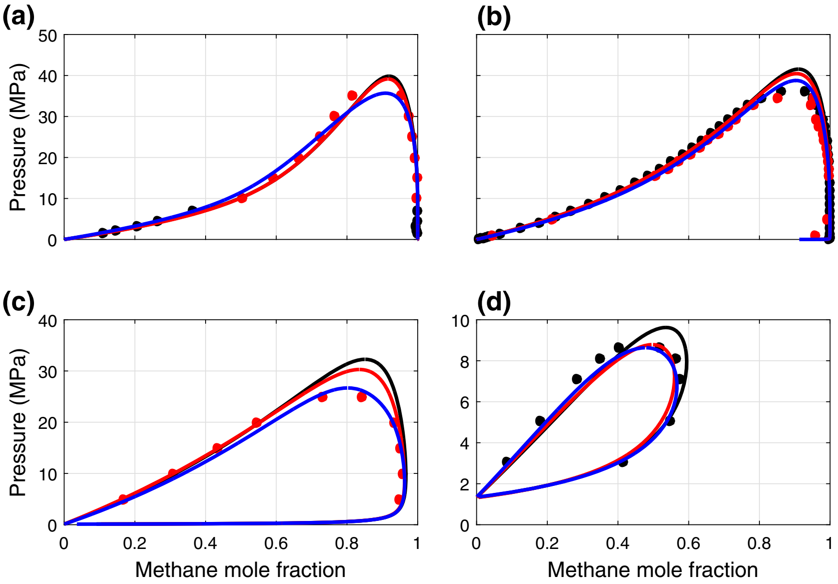

Figure 3. Pressure – composition VLE for the CH_4-n-$C_{10}H_{22}$ mixture at various temperatures; (a) T = 244.26 K, (b) T = 310.93 K, (c) T = 450 K, (d) T = 583.05 K. Experimental data[59,62,64] are represented by black data points. GEMC simulation data are represented by red data points. Calculations with EoS are represented by lines and are performed with k_{ij} parameters fitted to GEMC simulation data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS.

[Color figure can be viewed at wileyonlinelibrary.com]

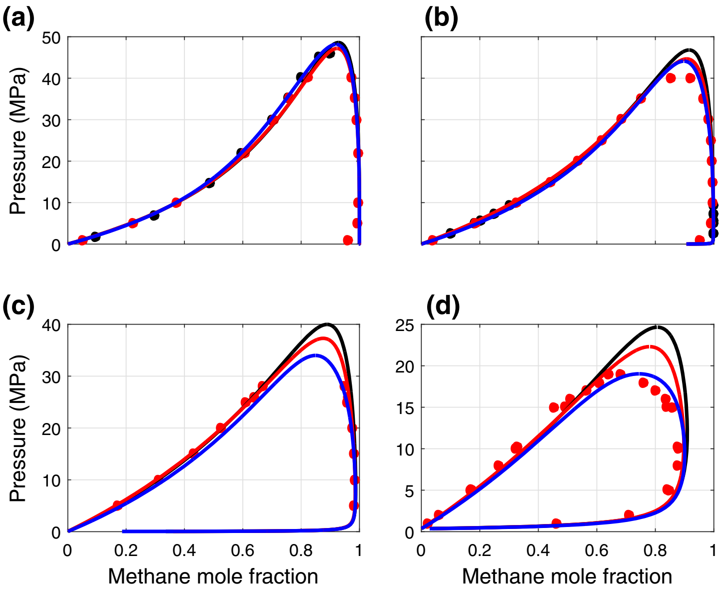

Figure 4. **Pressure – composition VLE for the CH_4-*n*-$C_{12}H_{26}$ mixture at various temperatures; (a) *T* = 303.15 K, (b) *T* = 373.2 K, (c) *T* = 450 K, (d) *T* = 550 K. Experimental data[61,66] are represented by black data points. GEMC simulation data are represented by red data points. Calculations with EoS are represented by lines and are performed with k_{ij} parameters fitted to GEMC simulation data. Black lines correspond to SRK, red to PR and blue to PC-SAFT EoS.**

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ones for PC-SAFT. Taking into account the possible differences in tolerance values for the fitting of BIPs, the calculation procedure for the VLE and the exact experimental data used by the various authors, it can be assessed that the agreement with prior work is sufficiently good.

As it can be observed from Figure 2b, the % AARD-MC for all three EoS always increases with the carbon number, following the expected behavior. The three EoS present similar % AARD-MC values for the mixtures of CH_4 with *n*-$C_{10}H_{22}$, *n*-$C_{16}H_{34}$, and *n*-$C_{20}H_{42}$, while PC-SAFT presents two distinct values for the CH_4-*n*-$C_{12}H_{26}$ and CH_4-*n*-$C_{24}H_{50}$ mixtures when compared to the cubic EoS. The two cubic EoS present very similar % AARD-MC values for all the binary mixtures considered. Comparing the % AARD-MC values to the respective % AARD-EXP, it is observed that the CH_4-*n*-$C_{10}H_{22}$ value remains almost constant for the cubic

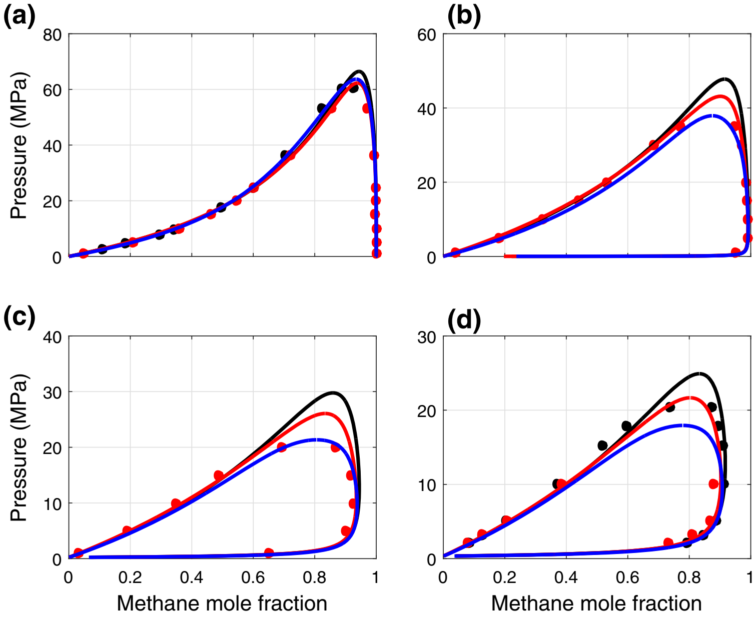

Figure 5. **Pressure – composition VLE for the CH_4-*n*-$C_{16}H_{34}$ mixture at various temperatures; (a) *T* = 340 K, (b) *T* = 500 K, (c) *T* = 600 K, (d) *T* = 623.15 K. Experimental data[68,72] are represented by black data points. GEMC simulation data are represented by red data points. Calculations with EoS are represented by lines and are performed with k_{ij} parameters fitted to GEMC simulation data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS.**

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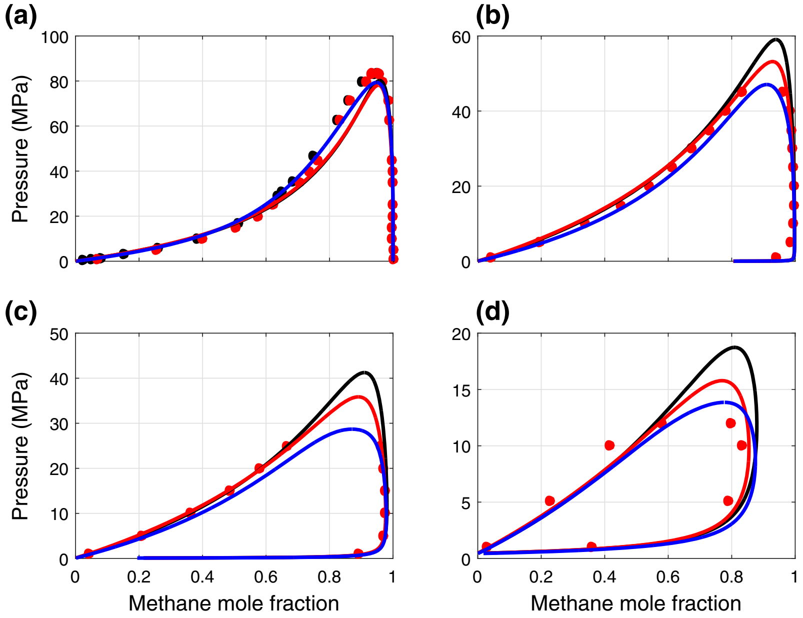

Figure 6. Pressure – composition VLE for the CH_4-*n*-$C_{20}H_{42}$ mixture at various temperatures; (a) T = 323.15 K, (b) T = 500 K, (c) T = 600 K, (d) T = 700 K. Experimental data[76] are represented by black data points. GEMC simulation data are represented by red data points. Calculations with EoS are represented by lines and are performed with k_{ij} parameters fitted to GEMC simulation data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS.

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EoS, while others change significantly resulting in a totally different assessment between the three models. A more detailed analysis for each mixture and the correlative ability of the EoS considered is presented below.

Figures 3–7 refer to *P-xy* phase diagrams for the binary mixtures considered at various temperatures, with the three EoS using k_{ij} parameters regressed from GEMC simulation data. Experimental and GEMC simulation data are plotted together (when available) at the selected temperatures, showing the very good agreement between the two datasets. Figure 3 shows the *P-xy* diagrams for the CH_4-*n*-$C_{10}H_{22}$ mixture at temperatures from 244.26 to 583.05 K. All EoS

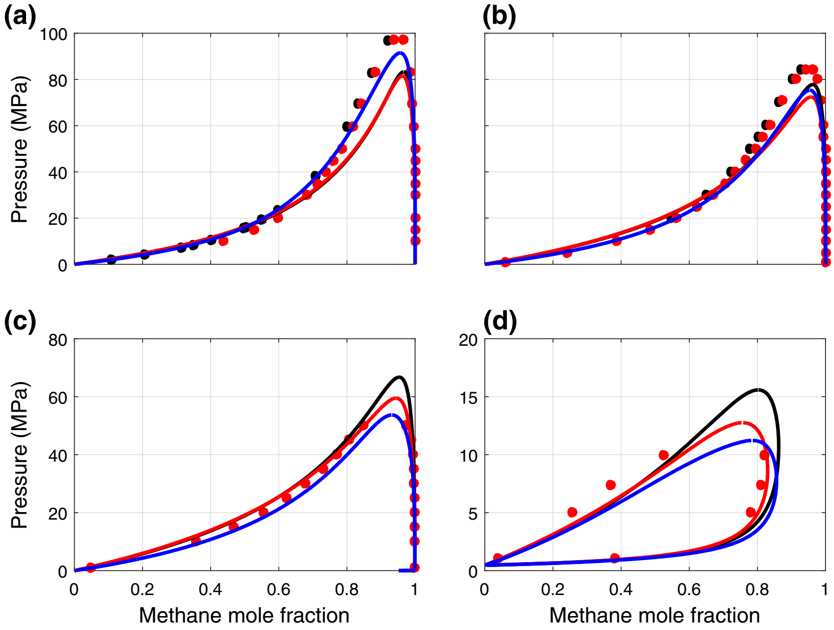

Figure 7. Pressure – composition VLE for the CH_4-*n*-$C_{24}H_{50}$ mixture at various temperatures; (a) T = 330 K, (b) T = 374.05 K, (c) T = 500 K, (d) T = 750 K. Experimental data[78,80] are represented by black data points. GEMC simulation data are represented by red data points. Calculations with EoS are represented by lines and are performed with k_{ij} parameters fitted to GEMC simulation data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS.

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Table 4. Composition in Mole Fractions of the Synthetic Gas Condensates Studied in this Work

Compound	SGC1	SGC2	SGC3	SGC4	SGC5	SGC6	SGC7
CH_4	0.8119	0.8512	0.7000	0.8997	0.7905	0.8232	0.8205
C_3H_8						0.0871	0.0895
n-C_4H_{10}	0.1385	0.0991	0.1200	0.0300			
i-C_5H_{12}					0.0023		
n-C_5H_{12}					0.1999	0.0505	0.0500
n-C_6H_{14}					0.0023		
n-C_8H_{18}			0.0700	0.0297			
n-$C_{10}H_{22}$	0.0496					0.0198	0.0199
n-$C_{12}H_{26}$		0.0497	0.0499	0.0207			
n-$C_{16}H_{34}$			0.0301	0.0149		0.0194	0.0201
n-$C_{20}H_{42}$			0.0300	0.0050			
n-$C_{24}H_{50}$					0.0050		

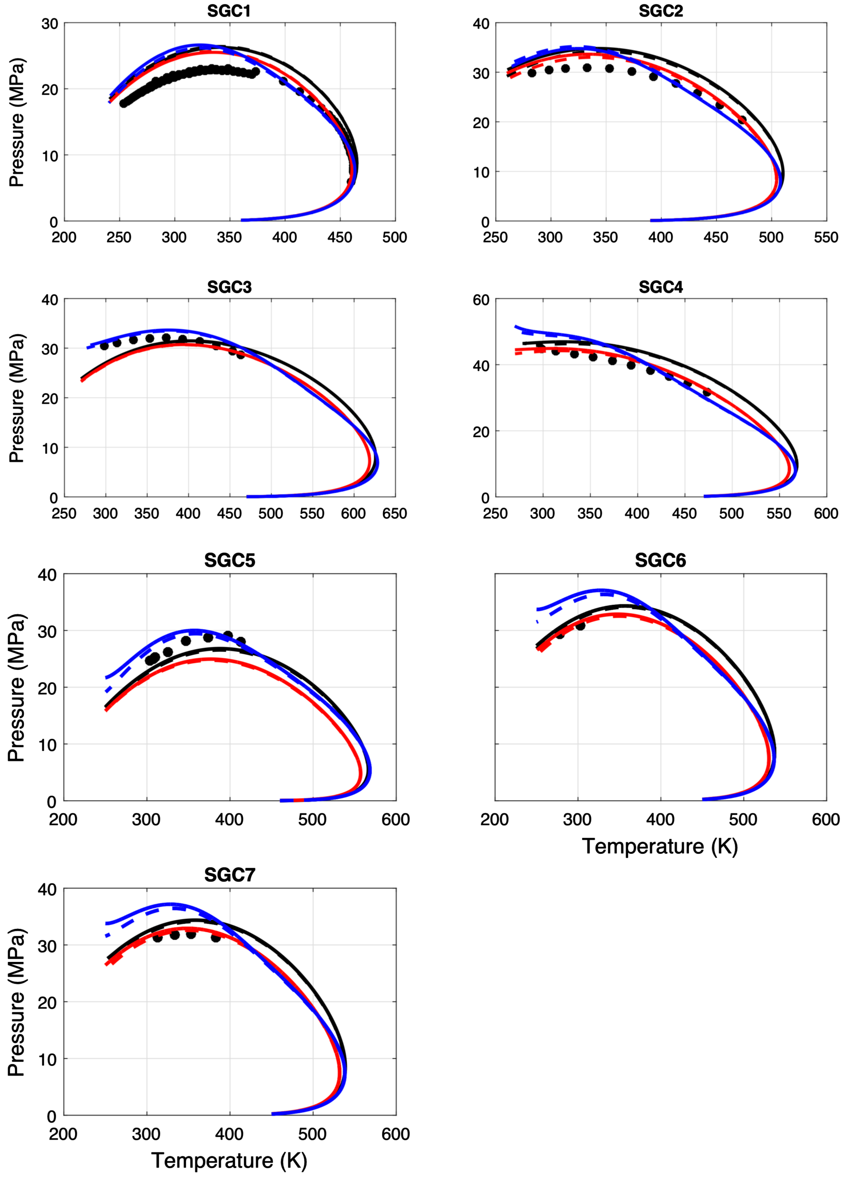

Figure 8. Constant composition phase envelopes for the synthetic gas condensate mixtures (SGC1, SGC2, SGC3, SGC4, SGC5, SGC6, and SGC7) studied in this work.

The compositions of the mixtures are listed in Table 4. Experimental data[5,81-83] are represented by points and calculations by lines. Solid lines correspond to calculations with k_{ij} parameters fitted to experimental binary VLE data. Dashed lines correspond to calculations with k_{ij} parameters fitted to GEMC simulation binary VLE data. Black lines correspond to SRK, red to PR, and blue to PC-SAFT EoS. [Color figure can be viewed at wileyonlinelibrary.com]

correlate accurately the two datasets with the % AARD-MC being almost equal for the cubic and PC-SAFT. Furthermore, the % AARD-EXP for the cubic EoS is similar to % AARD-MC, while a higher difference is presented for PC-SAFT. This higher variation of the % AARD value for PC-SAFT is attributed to the VLE data at 244.26 K. The k_{ij} parameters of PC-SAFT EoS generally show higher sensitivity to the dataset used for the regression, compared to the respective ones of cubic EoS.[6,58] However, similar sensitivity of the k_{ij} parameters for the three EoS is shown when high temperature VLE GEMC simulation data are added. This indicates that the higher sensitivity of the BIPs of PC-SAFT may be attributed mainly to the low temperature VLE correlation.

In Figure 4, the VLE correlation results for the CH_4-n-$C_{12}H_{26}$ mixture are presented with the three EoS. The isotherms at 303.15 and 373.2 K are correlated almost with the same accuracy by the three EoS. At higher temperatures (450 and 550 K), cubic EoS correlate slightly more accurately the equilibrium pressure away from the critical point compared to PC-SAFT, in expense of a more significant critical point over prediction. It is prevalent even at 373.2 K, that SRK presents the most significant over prediction of the critical point, with PR following and with PC-SAFT being the most accurate. Comparing the % AARD-EXP and % AARD-MC values for this mixture, it can be assessed that the addition of high-temperature VLE data for the regression shifts the % AARD to lower values for the cubic EoS, since they are more successful in correlating the high temperature VLE and to a higher value for PC-SAFT which correlates better the low temperature data. Note that the available experimental VLE data for this mixture are in the range of 263.15–373.2 K, while the critical temperature of n-$C_{12}H_{26}$ is 650 K. GEMC simulations were performed at isotherms from 283 to 600 K to obtain a wider range of pseudo-experimental data for CH_4-n-$C_{12}H_{26}$. Results are plotted in Figure 5 for the CH_4-n-$C_{16}H_{34}$ mixture with calculations from the three EoS and k_{ij}^{MC}. In this case, the difference between the three EoS in the critical point prediction becomes even more pronounced with the increase of temperature.

Figures 6 and 7 show the VLE results for the mixtures of CH_4 with n-$C_{20}H_{42}$ and n-$C_{24}H_{50}$. For these two mixtures, the improved correlation of the VLE behavior at low temperatures (323.15 and 330 K, respectively) with PC-SAFT EoS is more pronounced. At high temperatures, especially from 500 K and higher, cubic EoS correlate more accurately the equilibrium pressure than PC-SAFT. As with the previous mixtures, SRK EoS predicts the highest critical pressures, while PC-SAFT EoS predicts the lowest ones. At temperatures close to the normal melting temperature of the long-chain n-alkane of every mixture, the two cubic EoS predict almost the same critical pressure. The experimental data for the CH_4-n-$C_{20}H_{42}$ mixture span from 323.15 to 573.15 K, while GEMC simulation data cover a temperature range from 323 to 700 K. The respective range for the CH_4-n-$C_{24}H_{50}$ mixture is 330–573.15 K for the experiments and 330–750 K for the GEMC simulation data.

The two sets of k_{ij} parameters were used for the calculation of constant composition VLE of asymmetric multicomponent mixtures, comprised mainly of n-alkanes. The compositions of the mixtures studied are summarized in Table 4. The k_{ij} parameters between CH_4 and alkanes with lower molecular weight than n-$C_{10}H_{22}$ were taken from Novak et al.[11] Alternatively the interaction parameter values for these binary pairs could have been set equal to zero and almost the same modeling results would have been obtained, since their effect is negligible, as shown by Novak et al.

In Figure 8, the results for the multicomponent mixtures considered are presented, with the two cubic and PC-SAFT EoS. The difference between calculations with the two sets of k_{ij} parameters is practically negligible. The highest deviations between the two sets of calculations are presented with PC-SAFT EoS for the synthetic gas condensates (SGCs) 4, 5, 6, and 7. For SGC4, the deviations in the calculated equilibrium pressure start close to 280 K and are approximately 1 MPa. For SGCs 5, 6, and 7 the deviations appear close to 290 K and vary from 1 to 2.5 MPa. Both cubic EoS are much more insensitive to the choice of the set of k_{ij} parameters for the mixtures mentioned. Very low sensitivity to the choice of BIPs is manifested in SGC3 mixture with all three EoS. It should be noticed that the composition of SGC3 in terms of high molecular weight n-alkanes is higher compared to SGC4. This results in the equilibrium measurements being bubble points instead of dew points, as opposed to all the other mixtures studied. This is the only mixture in which PC-SAFT EoS is clearly more accurate than the cubic ones.

Conclusions

A predictive methodology was developed for the calculation of the VLE of multicomponent hydrocarbon mixtures with high asymmetry, combining molecular simulations and EoS. MC simulations in the Gibbs Ensemble were used for the calculation of the VLE of binary CH_4 mixtures with n-alkanes, to be used as a pseudo-experimental dataset, for a consistent fitting of the BIPs of the thermodynamic models. Two cubic (SRK, PR) and one higher order (PC-SAFT) EoS were used to correlate the binary-mixture VLE data and subsequently predict the multicomponent mixture VLE. GEMC simulations with the TraPPE-UA force field were validated with experimental VLE data for the binary mixtures considered. It was shown that accurate predictions can be retrieved even in very asymmetric mixtures. It is assessed that GEMC simulations can be carried out with high accuracy at temperatures and pressures in which no experimental VLE data exist, thus covering a wide range of conditions, suitable for fitting BIPs of thermodynamic models. k_{ij} parameters with the three EoS were regressed from both experimental and GEMC simulation data. It is shown that the use of a dataset that spans a wide range of temperatures and pressures consistently affects the k_{ij} values. It is also observed that for the CH_4-n-$C_{10}H_{22}$ mixture the three EoS correlate with equal accuracy the VLE behavior, while with increasing asymmetry, PC-SAFT EoS is more successful in correlating the low temperature data and cubic EoS the high temperature data. Finally, the BIPs regressed from GEMC simulation data lead to equally accurate modeling results for multicomponent mixtures, compared to those regressed from experimental binary mixture data. Consequently, molecular simulations using accurate force fields can be used to generate precise VLE data for binary mixtures of CH_4 with n-alkanes, in the absence of experimental data.

Associated Content

EoS and MC details; Critical temperature, pressure and acentric factor data; PC-SAFT EoS parameters; GEMC simulation data; comparison of GEMC and experimental data.

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