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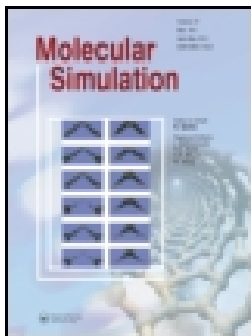Ramdin, M.; Jamali, S. H.; Becker, T. M.; Vlugt, T. J.H.

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ABSTRACT

Vapour–liquid equilibrium (VLE) and volumetric data of multicomponent mixtures are extremely important for natural gas production and processing, but it is time consuming and challenging to experimentally obtain these properties. An alternative tool is provided by means of molecular simulation. Here, Monte Carlo (MC) simulations in the Gibbs ensemble are used to compute the VLE of multicomponent natural gas mixtures. Two multicomponent systems, one containing a mixture of six components (N_2, CH_4, CO_2, H_2S, C_2H_6 and C_3H_8), and the other containing a mixture of nine components (N_2, CH_4, CO_2, H_2S, C_2H_6, C_3H_8, C_5H_{12}, C_7H_{16} and $C_{10}H_{22}$) are simulated. The computed VLE from the MC simulations is in good agreement with available experimental data and the GERG-2008 equation of state modelling. The results show that molecular simulation can be used to predict properties of multicomponent systems relevant for the natural gas industry. Guidelines are provided to setup Gibbs ensemble simulations for multicomponent systems, which is a challenging task due to the increased number of degrees of freedom.

1. Introduction

Reservoir engineers and technologists require accurate vapour–liquid equilibrium (VLE) and volumetric (PVT) data to estimate gas/condensate production rates, prevent solid/liquid formation in natural gas production/processing pipelines, and to design separation units to meet customer specifications [1,2]. However, natural gas is a complex mixture of many components with a variable composition, which makes it nearly impossible for experimentalists to measure the properties of all possible mixtures and conditions [3]. Typically, VLE and PVT data of multicomponent systems are computed with an equation of state (EoS), which requires experimental data of representative systems to calibrate the EoS parameters. In practice, three types of VLE experiments are performed [4,5]: (1) sampling experiments to measure the composition of one or more phases ($pTxy$), (2) bubble-point (PTx) and (3) dew-point (PTy) measurements. The last two types of measurements do not provide tie-line information, but are easier to perform compared to the more elaborate sampling experiments. In a bubble-point experiment, the gas-phase composition is unknown, while in a dew-point experiment the liquid-phase composition is unknown, but both can be computed from an EoS by, respectively, fitting to PTx and PTy data. However, computing high-pressure phase equilibria of (multiphase) multicomponent mixtures is a non-trivial task since EoSs often suffer from convergence and stability problems [6]. These limitations of EoSs are well-known and have been investigated in great detail by Michelsen [7–9]. For a recent overview of EoS modelling of natural gas systems, the reader is referred to [10–13].

Here, we investigate the accuracy of molecular simulations to compute $pTxy$ data of multicomponent natural gas mixtures. Note that EoS modelling is more practical and widely used in the natural gas industry, but molecular simulation can be a valuable tool especially in the absence of experimental data. Monte Carlo simulations in the Gibbs ensemble (GEMC) [14,15] are used to compute the VLE of two multicomponent systems. The first mixture contains N_2, CH_4, CO_2, H_2S, C_2H_6 and C_3H_8 and corresponds to the experimental system studied by Kalra and Robinson [16]. The second mixture contains N_2, CH_4, CO_2, H_2S, C_2H_6, and C_3H_8, C_5H_{12}, C_7H_{16} and $C_{10}H_{22}$ and corresponds to the experimental system (mixture 14) studied by Yarborough [17]. Although Gibbs ensemble simulations are often performed for unary, binary and ternary (confined) systems, its application to multicomponent (i.e., 4 or more components) systems is relatively rare [18–25]. The reason for this is two-fold; (1) experimental ($pTxy$) data for multicomponent systems are extremely scarce, which complicates validation of simulation results and (2) as it will become apparent in the next section, performing a multicomponent Gibbs ensemble simulation requires an increased effort compared to unary and binary systems. The VLE computed from the MC simulations are compared with experimental data and the GERG-2008 model, which is the reference EoS for natural gas systems [26].

2. Simulation details

Figure 1 shows the resemblance between sampling experiments and the Gibbs ensemble simulations [14,15]. Monte Carlo

simulations in the *NVT*-Gibbs or the *NPT*-Gibbs ensemble can be used to compute *pTxy* data of mixtures [27]. In both ensembles, the total number of molecules (N) and temperature (T) are fixed, while the volume (V^i) of the individual simulation boxes is allowed to change. In the *NVT*-Gibbs ensemble, the volume of the two boxes is coupled in such a way that the total volume ($V^T = V^1 + V^2$) is constant, but in the *NPT*-Gibbs ensemble the volume of the boxes can change independently to satisfy the imposed pressure (P). As a consequence of the Gibbs phase-rule, only the NVT-Gibbs ensemble can be used to compute VLE properties of unary systems. The Gibbs phase-rule for a non-reacting system is given by,

$$f = 2 + N - \pi \qquad (1)$$

where f is the number of degrees of freedom, N the number of components and π the number of phases. Clearly, for an unary system ($N = 1$) with two phases in equilibrium ($\pi = 2$) there is only one degree of freedom, which shows that the *NVT*-Gibbs is the only eligible ensemble for pure components. In principle, both ensembles can be used to compute the VLE of binary and multicomponent systems. In experiments, the composition of equilibrium phases are sampled and analysed at constant pressure and temperature conditions. Therefore, *NPT*-Gibbs ensemble simulations are more practical and allow a direct comparison with experiments. The central problem in Gibbs ensemble simulations, regardless of the chosen ensemble (*NVT* or *NPT*), is the initial distribution of the molecules in the boxes (1) to keep the size of both boxes larger than twice the cut-off radius and (2) to allow a quick phase split. Condition (1) is required to avoid unphysical interactions of particles due to the nearest neighbour convention [27]. Condition (2) essentially means that a good initial guess of the phase compositions should be provided for convergence of the system towards equilibrium. Note that this condition also holds for equation of state modelling. In fact, the size of the boxes is governed by the density of the systems, while the phase composition is governed by the distribution constant, K_i, defined as [28]:

$$K_i = \frac{y_i}{x_i} \qquad (2)$$

where y_i and x_i are the composition of component i in the gas- and liquid-phase, respectively. It is clear that in the absence of experimental data one would need an EoS to perform a flash calculation to obtain the density of the phases and the distribution constant of the components. The requirement of an EoS to setup a Gibbs ensemble simulation is a major drawback of the method limiting its application to complex multicomponent systems. Here, we seek alternative ways to estimate the K_i's avoiding the use of EoSs. Note that in the Gibbs ensemble only a reasonable guess for the K_i's needs to be provided, which can be obtained from ideality considerations or ad-hoc correlations. For example, Raoult's law can be used to estimate the distribution constants as [31]:

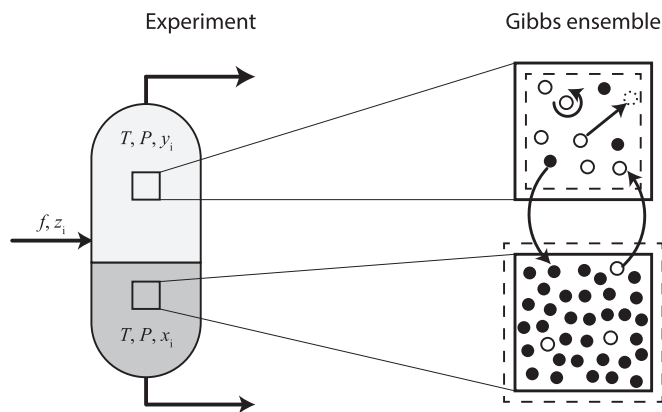$$K_i = \frac{y_i}{x_i} = \left(\frac{P_i^{\text{sat}}}{P} \right)_T \qquad (3)$$

Figure 1. Resemblance of experiments and the Gibbs ensemble simulations. In an experiment, a stream with a known overall composition (z_i) is flashed at a constant temperature and pressure yielding a gas and a liquid-phase with composition y_i and x_i, respectively. In a Gibbs ensemble simulation, two simulation boxes are used to simulate properties of coexisting phases away from the gas/liquid interface. In an experiment, the conditions for phase equilibrium (i.e., the equality of temperature, pressure and chemical potentials) are met using a stable thermostatic bath, a pressure controller and a stirrer to enhance mass-transfer. Equivalently, in the Gibbs ensemble simulations, four kinds of MC moves (translation, rotation, volume change and molecule transfer with CBMC [29]) are performed to satisfy the equilibrium conditions [30]. In experiments and in simulations, sampling of the phases is only performed after ensuring that equilibrium is reached.

where P_i^{sat} and P denote the saturation pressure of component i and the flash/total pressure, respectively. Equation (3) assumes an ideal gas phase (i.e., $\phi = 1$) and an ideal liquid phase (i.e., $\gamma = 1$). Unfortunately, Equation (3) cannot be used when some of the components are supercritical, which would require extrapolation of the saturation pressures often leading to erroneous results. In some cases, the K_i's of the supercritical compounds can be obtained from Henry's law [31]:

$$K_i = \frac{y_i}{x_i} = \frac{H_i}{P} \qquad (4)$$

where H_i is the Henry constant of component i. Equation (4) is difficult to apply for multicomponent systems, since Henry constant data might not be available for all the components present in the liquid mixture. Alternatively, one can use correlations to estimate the distribution constants. An example of such a correlation is provided by Wilson [32]:

$$K_i = \frac{P_{ci}}{P} \exp\left[5.37(1 + \omega_i)\left(1 - \frac{T_{ci}}{T}\right) \right] \qquad (5)$$

where P_{ci}, T_{ci} and ω_i are, respectively, the critical pressure (psia), critical temperature (in °R) and the accentric factor of component i. P and T are the pressure (psia) and temperature (in °R) of the system in equilibrium. Equation (5) is mainly developed for hydrocarbons and applicable for low to moderate pressures assuming that the K-values are composition independent. Many more correlations for K-values exist and the reader is referred to [1,2,33,34] for an overview. Equations (3) and (5) have a limited application range, but can be very useful to setup a Gibbs ensemble simulation for natural gas systems.

To perform a Gibbs ensemble simulation, one requires force fields, which are potentials to describe the intra and intermolecular interactions of all components in the mixture. The TraPPE united-atom (UA) force field have been used to describe N_2,

CH_4, CO_2, H_2S, C_2H_6, C_3H_8, C_5H_{12}, C_7H_{16} and $C_{10}H_{22}$ [35–37]. The molecules N_2, CH_4, CO_2, H_2S and C_2H_6 were considered rigid in the simulations, while the higher alkanes were considered flexible. The internal degrees of freedom of the flexible molecules were sampled using the configurational-bias Monte Carlo (CBMC) scheme [29]. Interactions between dissimilar atoms were described by the Lorentz–Berthelot mixing rules [38]. The electrostatic interactions were described by the Ewald method using a relative precision of 10^{-5} [27]. Note that only N_2, CO_2 and H_2S contain partial charges, whereas the alkanes are uncharged. The Lennard-Jones (LJ) interactions were truncated at 14 Å and tail corrections were applied [27]. Given an initial/overall composition, z_i, the following steps are required to setup a Gibbs ensemble simulation: (1) Choose the total number of particles (N_T). Note that the VLE is independent of N_T, but it should be chosen such that the statistics and the computational time are acceptable. (2) Compute the K-values of all components from an EoS or the correlations outlined in the previous section and distribute molecules in both boxes accordingly. The initial molecule distribution can be computed from a known z_i and K_i, by simultaneously solving Equation (2) and the component-balance equation,

$$x_i N_T^L + y_i N_T^G = z_i N^T, \tag{6}$$

using the constraints $\sum x_i = \sum y_i = \sum z_i = 1$. In Equation (6), x_i and y_i are the liquid- and gas-phase mole fractions of component i, respectively. N_T^L and N_T^G are the total number of molecules in the liquid- and gas-phase. (3) Estimate the size of both boxes corresponding with the molecule distribution of the previous step. The density of each subsystem can be estimated from an NPT simulation or from an EoS. Since the cut-off radius in our simulation is 14 Å, the size of both boxes should be at least 28 Å. Typically, the size of the gas box is twice the size of the liquid box. However, note that the box size (volume) is an output of the Gibbs ensemble simulation and controlled by the total number of particles (N_T) at given T and P. Hence, if the equilibrium box size is less than twice the cut-off radius, one should simply increase the total number of particles keeping z_i fixed. (4) Start the Gibbs ensemble simulation with the estimated molecule distribution and box sizes. The GEMC simulations were started with an equilibration run of 50,000 MC cycles followed by a production run of 0.2 million cycles. The number of steps in a MC cycle equals the total number of particles in the simulation box. The reported error bars represent the 95% confidence interval obtained from four independent simulations with different random seed numbers and initial configurations.

Furthermore, it is important to choose the state-points (T, P) carefully, since Gibbs ensemble simulations become unstable near critical points [39]. Therefore, one should avoid simulations near critical points of pure components and/or mixtures. Protocols to setup efficient Gibbs ensemble simulations are provided by Cortés Morales et al. [40]. Here, the simulation conditions were chosen based on the availability of experimental data. The total number of molecules in our simulation was varied from around 500 to 1500 and Equation (5) was used to estimate the K-values. In Table 1, the properties of the studied

components and the initial composition (z_i) of the mixtures are listed.

3. Results and discussion

To compute the VLE of multicomponent natural gas mixtures, MC simulations in the NPT-Gibbs ensemble were performed using RASPA [41,42], a molecular simulation tool. The simulations were performed at different temperatures and pressures. In Figure 2, the K-values computed from the MC simulations at two temperatures were compared with the experimental data of Kalra and Robinson [16], and the GERG-2008 EoS modelling [26]. The results show that the MC simulation is in good agreement for N_2 and CH_4. The K-values of CO_2 and H_2S are slightly underestimated, while the K-values of C_2H_6 and C_3H_8 are slightly, but systematically, overestimated. However, the temperature and pressure dependency of the K-values are correctly captured by the MC simulations. In Figure 3, the coexistence densities of the vapour and liquid-phase computed from the MC simulations are compared with the experiments of Kalra and Robinson [16], and the GERG-2008 EoS modelling. The gas-phase densities are in good agreement with the experimental data, but the MC simulations slightly overpredict the liquid-phase densities. This overprediction is due to the UA description of the alkanes, which results in a more dense packing of the molecules in the liquid [43]. Furthermore, the GERG-2008 EoS is able to correctly describe this six-component (Mix 1) natural gas mixture. The MC simulations were extended to a more challenging nine-component natural gas system (Mix 2), which was experimentally studied by Yarborough [17]. In Figure 4, the K-values computed from the MC simulations are compared with experimental data and the GERG-2008 EoS. The K-values of N_2 and CH_4 from the MC simulations are in good agreement with experiments, but again the K-values of CO_2 and H_2S are slightly underestimated, while the K-values of the higher alkanes, especially n-pentane, n-heptane and n-decane, are systematically overestimated. Moreover, the GERG-2008 modelling results are, except for nitrogen, in good agreement with experiments. For N_2, the GERG-2008 EoS overestimate the K-values, while the MC data are in good agreement with the experiments. In Figure 5, the coexistence densities of the vapour and liquid-phase computed from the MC simulations are compared with the GERG-2008 EoS modelling. Again, the gas-phase densities are in good agreement with the EoS results, but the liquid-phase densities are slightly overpredicted. Furthermore, the GERG-EoS failed to converge for the Yarborough mixture beyond a pressure of 10 MPa, which exemplifies the difficulties associated with the modelling of multicomponent mixtures at high pressures.

The mismatch between experiments and MC data for some of the components can be attributed to the inadequacy of the molecular models (i.e., force fields) to accurately describe: (1) the pure component properties (e.g., vapour pressures), and (2) the cross-interactions using the simple Lorentz–Berthelot mixing rules. For example, the force field of alkanes slightly overpredicts the vapour pressures [35,36], which explains the overestimation of the gas-phase compositions and the K-values. The solubility of CO_2 in alkanes in the liquid-phase is generally overestimated by the TraPPE-UA [44] force field and other UA

Table 1. Molecular weights (MW), critical parameters (T_c, P_c) [31], acentric factors (ω) [31] and the initial composition of the studied mixtures. Mix 1 corresponds to the six-component system of Kalra and Robinson [16], and Mix 2 corresponds to the nine-component mixture of Yarborough [17].

Component	MW/g/mol	T_C/K	P_C/MPa	ω	Mix 1[a]	Mix 2
N_2	28.01	126.2	3.398	0.037	0.077	0.030
CH_4	16.04	190.6	4.599	0.011	0.712	0.718
CO_2	44.01	304.1	7.374	0.225	0.019	0.030
C_2H_6	30.07	305.3	4.872	0.099	0.066	0.046
H_2S	34.08	373.4	8.963	0.090	0.099	0.030
C_3H_8	44.10	369.8	4.248	0.152	0.028	0.025
$n-C_5H_{12}$	72.15	469.7	3.370	0.252		0.053
$n-C_7H_{16}$	100.21	540.2	2.740	0.350		0.038
$n-C_{10}H_{22}$	142.29	617.8	2.110	0.490		0.030

[a] Estimated from reported molar volumes and phase compositions.

Table 2. Comparison of the K-values computed from the MC simulations and the Wilson equation for the Yarborough mixture (Mix 2) at 310.9 K and 3.65 MPa.

Component	$K_i^{exp.}$	$K_i^{sim.}$	K_i^{Wilson}
N_2	13.8	14.3	25.4
CH_4	5.1	5.9	10.3
CO_2	2.8	2.1	2.3
C_2H_6	1.3	1.6	1.5
H_2S	1.1	0.8	0.8
C_3H_8	0.45	0.68	0.36
$n-C_5H_{12}$	0.059	0.12	0.030
$n-C_7H_{16}$	0.008	0.022	0.004
$n-C_{10}H_{22}$	0.0005	0.002	0.0002
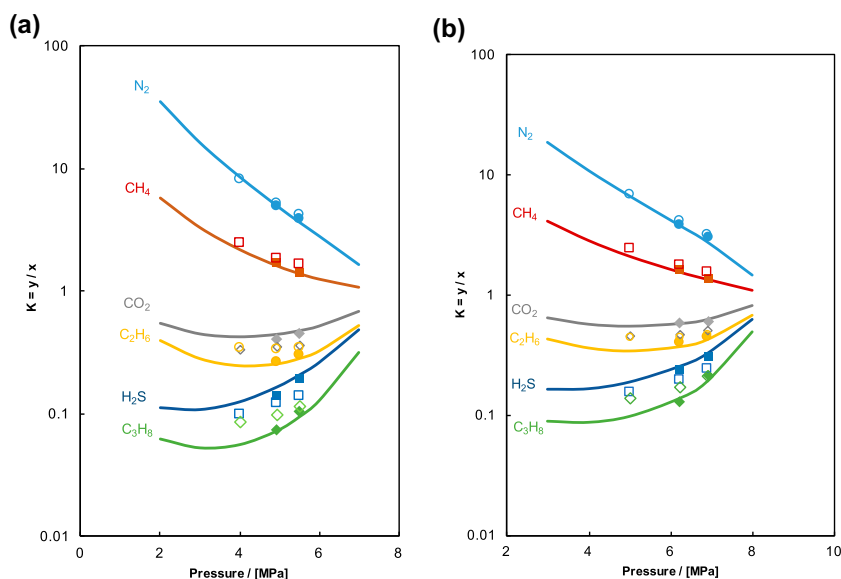
Figure 2. (Colour online) Comparison of K-values from experiments (closed symbols), MC simulations (open symbols) and GERG-2008 EoS modelling (lines) at (a) 213.7 K and (b) 227.6 K for the mixture of Kalra and Robinson (Mix 1) [16]. Error bars of the simulation results are smaller than the symbol size.

force fields [45,46], which also explains the underprediction of the K-values in the MC simulations. Similarly, the TraPPE-UA force field overestimates the liquid-phase solubility of alkanes in alkanes [35,47,48], which consequently result in the over-prediction of the K-values, e.g. for n-pentane, n-heptane and n-decane. We note that the explicit-hydrogen version of the TraPPE force field (TraPPE-EH) for alkanes yields a better description of vapour pressures and VLE of CO_2, H_2S, CH_4 and higher alkane mixtures [36,37,43,49,50]. However, the TraPPE-EH force field for the current study would be computationally too expensive, since every methane molecule would have four

additional interaction sites, while higher alkanes would have $2n + 2$ additional sites, where n is the number of carbon atoms. Considering that we have more than 1000 molecules (mainly methane, but also a considerable fraction of higher alkanes) and that the computational time scales with $\sim N^2$, where N is the number of interaction sites, it is clear that the computational time would increase significantly. The computational time for the VLE calculations of the Yarborough mixture was approximately four weeks on a Xeon-E52620 machine.

Furthermore, the Lorentz–Berthelot mixing rules [38], which are similar to the van der Waals mixing rules without binary
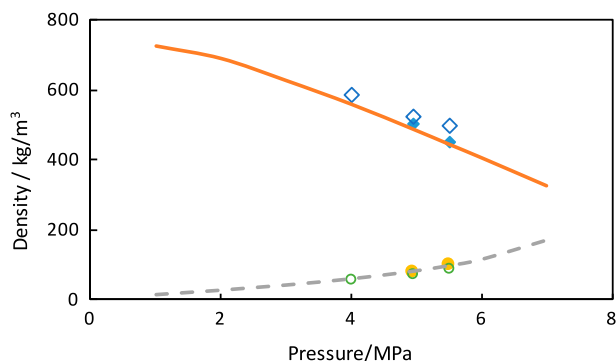
Figure 3. (Colour online) Comparison of coexistence densities from experiments (closed symbols), MC simulations (open symbols) and GERG-2008 EoS modelling (lines) at 213.7 K for the mixture of Kalra and Robinson (Mix 1) [16].
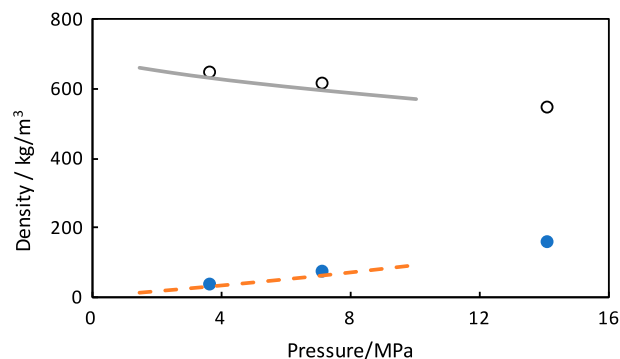

Figure 5. (Colour online) Comparison of coexistence densities from MC simulations (open symbols) and GERG-2008 EoS modelling (lines) at 310.9 K for the mixture of Yarborough (Mix 2) [17]. The GERG-2008 EoS did not converge for pressures beyond 10 MPa.

Figure 4. (Colour online) Comparison of K-values from experiments (closed symbols), MC simulations (open symbols) and GERG-2008 EoS modelling (lines) at 310.9 K for the mixture of Yarborough (Mix 2) [17]. The GER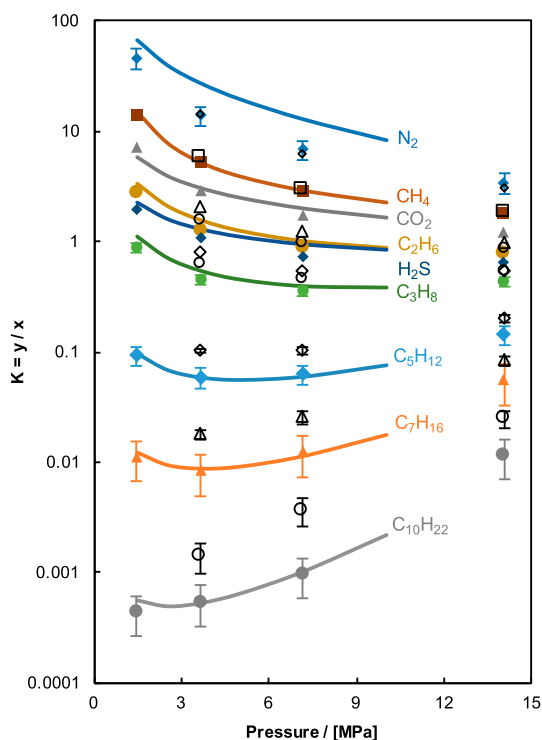G-2008 EoS did not converge for pressures beyond 10 MPa. Error bars are only shown for nitrogen and the higher alkanes, as for the other components the error bars are smaller than the symbol size.

interaction parameters [51], might not be adequate to describe such a complex asymmetric system. However, it is generally difficult to use a different mixing rule, since the force field parameters are typically fitted in combination with the Lorentz–Berthelot mixing rules, which would require re-fitting of all parameters. Another cause of uncertainty in the simulations is introduced using a relatively small system size to reduce the computational time. As a consequence, the number of molecules in the liquid-phase for a low-soluble component (e.g., N_2), and the number of molecules in the gas-phase for a low-volatile component (e.g., $C_{10}H_{22}$) is relatively small. This issue can only be solved using a relatively large number of molecules, which

is computationally prohibitive. In order to reduce computational time, the recently coarse-grained force fields developed by Herdes et al. [52] to model natural gas systems might be promising. In Table 2, we compare the K-values from experiments, the Wilson method and the MC simulations. The Wilson equation is known to yield poor results for super-critical components, non-hydrocarbons, high pressures and relatively large alkanes. However, the Wilson equation or any other K-value correlations can be useful to setup Gibbs ensemble simulations. Overall, these results show that molecular simulation can be useful to natural gas engineers.

4. Conclusion

Vapour–liquid equilibrium data (i.e., $PTxy$, PTx and PTy) are extremely important in natural gas processing. $PTxy$ data can be obtained from sampling experiments, but it is a challenging task for multicomponent mixtures. Bubble-point (PTx) or dew-point (PTy) measurements are easier to perform, but do not provide tie-line information. Typically, the unknown gas-phase or liquid-phase composition is computed from an equation of state by fitting bubble-point or dew-point data. Alternatively, molecular simulations can be used to compute the VLE of mixtures. Here, we used Monte Carlo Simulations in the Gibbs ensemble to compute the VLE of a six-component and a nine-component natural gas mixture using standard force fields from the literature. The $PTxy$ data from the MC simulations are compared with available experimental data and GERG-2008 equation of state modelling. Overall, a good agreement between experiments, EoS modelling and MC simulations is observed. Guidelines are provided to setup multicomponent Gibbs ensemble simulations without using equations of state or experimental data.

Disclosure statement

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