

Monte Carlo simulations of vapor-liquid-liquid equilibrium of ternary petrochemical mixtures

Suren Moodley^a, Kim Bolton^b, and Deresh Ramjugernath^a

^aThermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal, King George V Avenue, 4041, South Africa

^bSchool of Engineering, University of Borås, SE-501 90 Borås, Sweden

Gibbs ensemble Monte Carlo simulations in the isobaric-isothermal (NPT) and isochoric-isothermal (NVT) ensembles have been performed to calculate several vapor-liquid-liquid equilibrium state points for three ternary petrochemical mixtures: methane/n-heptane/water (1), n-butane/1-butene/water (2) and n-hexane/ethanol/water (3). Since mixture (1) exhibits a high degree of mutual insolubility amongst its components, and hence has a large three-phase composition region, simulations in the NPT ensemble were successful in yielding three distinct and stable phases at equilibrium. The results were in very good agreement with experimental data at 120kPa, but minor deviations were observed at 2000kPa. Obtaining three phases for mixture (2) with the NPT ensemble is very difficult (we did not succeed in the present study) since it has an extremely narrow three-phase region at equilibrium, and hence the NVT ensemble was used to simulate this mixture. The simulated results were, once again, in excellent agreement with experiment. The success of the NVT simulation, compared to NPT, is due to the fact that the total volume can spontaneously partition itself favorably amongst the three boxes and only one intensive variable (T) is fixed, whereas the pressure and the temperature are fixed in an NPT simulation. NPT simulations yielded three distinct phases for mixture (3), but quantitative agreement with experiment was obtained at very low ethanol concentrations only.

1. Introduction

Mixtures of hydrocarbons and water are ubiquitous in the petrochemical industry and are usually obtained from crude oil feed stocks. Their separation via distillation, and other separation processes that rely on thermodynamic data, is important as pure hydrocarbons (or mixtures containing these chemicals) are processed in downstream units for various purposes, such as blending into gasoline or as feeds to isomerization units. Thus, the measurement and characterization of their phase equilibria is of importance for designing efficient separation processes and equipment. Traditionally, such thermodynamic data is obtained via controlled laboratory experiments in which the mixture is allowed to equilibrate at temperatures and pressures of interest, and the compositions of the individual phases are then analyzed, usually via gas chromatography, to obtain the mole or mass fractions of each component in each phase [1-3]. For example, due to their importance in the petrochemical industry, experiments have been done on methane/n-heptane/water, n-butane/1-butene/water, and n-hexane/ethanol/water systems [4-6], and have revealed that these systems show a wide variation in their mutual solubilities, hence making them interesting targets to test the validity and accuracy of computational models.

Predictive methods exist which reduce the need for experiments, such as the numerous equation of state (EOS) models [7-9]. An alternative computational method to obtain phase equilibrium data is Monte Carlo molecular simulation [10]. The Gibbs ensemble method [11] has become the standard method for the molecular simulation of phase equilibrium of fluid mixtures. Gibbs ensemble simulations are performed in two or more microscopic regions within the bulk phases, far away from the interfaces and surfaces that therefore do not need to be included in the modeling. Additionally, molecular simulations also provide insight into the atomic structure of fluid phases, and this helps in understanding phenomena which would otherwise be difficult to explain through conventional measurement techniques. While there is an abundance of studies that have focused on the simulation of the vapor-liquid equilibrium (VLE) [12-

14] and liquid-liquid equilibrium (LLE) [15-17] of mixtures, there has been much less focus on their vapor-liquid-liquid (VLL) coexistence [24, 29].

In this work, we present results for selected vapor-liquid-liquid (VLLE) points of three ternary mixtures (methane/n-heptane/water, n-butane/1-butene/water, and n-hexane/ethanol/water) that were calculated by employing widely-used force fields and the Gibbs ensemble Monte Carlo (GEMC) method, and consequently the suitability of this method for predicting VLLE is discussed. Although the simulation results will be compared with the corresponding experimental data for each mixture, this work was of a qualitative nature, and hence sought to determine whether Gibbs ensemble Monte Carlo simulations in conjunction with two popular force fields (see Section 2), can be used to predict the VLLE of ternary mixtures that exhibit a wide variety of phase behavior. Accordingly, no attempt is made to reproduce complete phase diagrams of the selected ternary mixtures. This paper is structured as follows: first, the force fields used in the modeling are presented along with the simulation details. The results are then presented, together with a discussion that explains the findings of this work. Finally, concluding remarks are given regarding the way forward for further three-phase Monte Carlo fluid phase equilibrium studies.

2. Methods

The MCCCSTowhee code [18], which utilizes the GEMC method in the isobaric-isothermal (NPT) and isochoric-isothermal (NVT) ensembles, was used for all simulations. The default coupled-decoupled configurational-bias Monte Carlo (CBMC) [19] settings as implemented in the simulation program were used in all simulations [18]. This presented no problems as the coupled-decoupled algorithm was initially designed to address problems in growing branched alkanes [19], while this study focused on simpler straight chain molecules which are also correctly treated by the algorithm.

The TraPPE-UA and SPC-E force fields were used to model the hydrocarbon and water interactions, respectively. A minimum allowable box length of 17.0 Å was used and Lennard-Jones non-bonded interactions were truncated spherically at 8.5 Å (half of the minimum box length) and analytical tail corrections [20] were applied. A hard-inner cutoff radius of 0.8 Å was used, so that any attempts to insert or move a molecule within this spherical region were automatically rejected, thereby improving the simulation efficiency. The Ewald summation technique ($K_{\max} = 5$; $\kappa \times L = 5$), with tin-foil boundaries [21-23], was used to calculate the contribution of the long-range electrostatic interactions to the total potential energy. Initially, the pure components were equilibrated in separate simulation boxes, where only volume, translation, rotation and configurational-bias re-growth moves were allowed. The probabilities of performing each move type were {volume;translation;rotation;configurational-bias re-growth} = {0.01;0.33;0.33;0.33}. These probabilities have been used in previous studies of similar systems [19, 24]. Equilibrating pure phases in their respective simulation boxes increased the efficiency of the subsequent equilibration of the mixture since, especially for mixtures exhibiting a high degree of mutual insolubility, when swap moves were enabled very few molecules were transferred between the phases (boxes). The initial simulation box volumes for liquid phases were estimated by using a temperature-dependent density correlation [25], while vapor phase box volumes were estimated using the ideal gas equation of state. For NPT simulations, the initial estimates for the box volumes are important only from a computational time perspective, since the Gibbs ensemble technique spontaneously finds the equilibrium box volumes by varying their sizes independently. Molecules were initially arranged on a cubic lattice and block averages were calculated every $N_{\text{MC}}/5$ cycles, where N_{MC} is the total number of Monte Carlo cycles used in a simulation. Each cycle consists of N moves, and N is the total number of molecules in the simulation. The block averages were used to determine the average mole fractions and densities, as well as their standard deviations.

The pre-equilibration runs consisted of at least 2.5×10^4 Monte Carlo cycles. During these pre-equilibration runs, the maximum allowable centre-of-mass translations, rotations and volume displacements were updated every ten cycles for the first five thousand cycles, to yield acceptance rates of approximately 50% for each move type. Thereafter, swap moves were allowed with equal probabilities between each pair of simulation boxes with the total probability set to 10% and the remaining probabilities were equally distributed among translation, rotation and CBMC re-growths, while the volume-change probability remained at 1%. Equilibration runs consisted of at least 1.5×10^5 MC cycles during which the densities, potential energies, pressures and compositions were monitored for convergence. That is, equilibration had been achieved once the trends in these properties did not change with increasing simulation time. Further details, specific to each mixture, are provided in 2.1, 2.2 and 2.3.

2.1 Methane/water/n-heptane

Simulations at $T = 275\text{K}$ for two pressures, 120 kPa and 2000 kPa, were done in the NPT ensemble for a mixture consisting of 400 methane, 350 water and 250 n-heptane molecules. A pre-equilibration run of 5×10^3 cycles was used to obtain a 50% acceptance rate for molecular translations, box volume changes and molecular rotations (except for methane, which is monatomic in the TraPPE-UA potential model). Thereafter 2.5×10^4 cycles were propagated to further equilibrate the pure components before swap moves were allowed for equilibration runs of at least 1×10^5 cycles. Aside from using a hard inner cut-off radius of 0.7 \AA , truncating non-bonded Lennard-Jones beyond 10 \AA and accepting a minimum box length of 20 \AA , all simulation parameters are the same as those mentioned above.

2.2 n-Butane/1-butene/water

Two GEMC simulations in the NPT ensemble were done at $T = 310.93$ K and at $P = 404.72$ and $P = 101.33$ kPa for a mixture of 300-butane, 450 1-butene and 250 water molecules. Additionally, a simulation in the NVT ensemble was performed; the only difference between these simulation conditions and those mentioned above was that the total system volume was fixed (15% less than the total ‘equilibrium’ volume obtained from the NPT simulation at 404.72 kPa).

2.3 Water/ethanol/n-hexane

Four state points at atmospheric pressure and temperatures of 329.45, 329.51, 329.77 and 330.54 K were investigated for mixtures of compositions $[z_{\text{water}}; z_{\text{ethanol}}; z_{\text{n-hexane}}] = [0.2; 0.31; 0.49]$, $[0.2; 0.245; 0.555]$, $[0.2; 0.145; 0.655]$ and $[0.2; 0.06; 0.74]$, respectively, for a total of 750 molecules in each NPT-Gibbs ensemble simulation. Equilibration periods consisted of at least 1×10^5 Monte Carlo cycles, followed by production runs of at least 5×10^4 cycles.

3. Results and Discussion

3.1 Methane/water/n-heptane

Simulations in the NPT ensemble for this mixture successfully yielded three distinct phases at equilibrium. This was seen by the difference in the three phase densities shown in Table 1. In addition, as

seen in the table, there was very good quantitative agreement with experiment at both pressures, although at 2000 kPa the mole fraction of n-heptane in the hydrocarbon liquid phase was significantly lower than experiment. n-Heptane is virtually insoluble in water at 275.5 K (experimental mole fractions at 120 kPa and 2000 kPa are 1×10^{-6} and 1.1×10^{-5} , respectively) and simulation times could have been drastically reduced if swap moves for n-heptane from the hydrocarbon liquid box to the aqueous phase box were disallowed, since the trial coupled-decoupled regrowth of n-heptane uses multiple trial sites during the regrowth and is therefore time-consuming.

The good agreement between the simulated and experimental data is partially due to the high degree of mutual insolubility amongst the three components at the conditions simulated. This is because the SPC/E and TraPPE force fields were fitted to the individual single component systems, and in dilute regions for these highly non-ideal mixtures the unlike-pair intermolecular interactions do not play a dominant role. The simulations therefore yield liquid densities and compositions in agreement with experiment. One of the reasons that the SPC-E force field was used instead of the SPC force field is that it provides better water liquid densities [26]. Furthermore, in all of the mixtures that were simulated, water was the least volatile component and would be predominantly in the liquid phases. The NPT method was also successful in yielding three distinct, stable phases at equilibrium. As illustrated in Figures 1a and 1b, the methane/water/n-heptane mixture is a good example of a ternary mixture that exhibits highly non-ideal behavior with a very large three-phase composition region. In such mixtures, one is free to choose from many different compositions during the simulation, while at the same time staying in the three phase region and far from the phase boundaries. There is thus very little risk of a simulation reverting to one or two phases, or for phase swapping between simulation boxes.

3.2 n-Butane/1-butene/water

This mixture exhibits an extremely narrow three-phase region (see Figure 1c) and is therefore difficult to simulate in the NPT ensemble. The two simulations at 404.72 kPa and 101.33 kPa (both at 310.93 K) yielded a water-rich liquid phase in one box and a hydrocarbon-rich vapor phase in the remaining two simulation boxes (seen by almost identical densities and compositions in the hydrocarbon-rich boxes). Analysis of the block averages from different periods along the trajectories confirmed that two stable hydrocarbon-rich vapor phases existed, and that there was no swapping of liquid and vapor phases between these boxes during the simulation. The NPT simulations yielded a two phase system despite the fact that the initial compositions were selected by locating the central point of the triangular three-phase region, so as to stay as far as possible from the phase boundaries.

The NVT ensemble may be preferred over the NPT ensemble for VLLE simulations for mixtures that have extremely narrow three phase regions. The constant pressure Gibbs ensemble method is not recommended for the study of single-component phase coexistence [11, 20], since the probability of locating a biphasic region, which lies on a line in a P-T diagram, is extremely small – by analogy, the probability of locating such a VLL coexistence point within an extremely narrow triangular region for a ternary mixture (which essentially resembles a single line) is extremely small as well. This can be explained by the fact that only one intensive thermodynamic variable, namely, temperature, is fixed in NVT simulations; according to the Gibbs phase rule for a non-reacting ternary three-phase system, there will be an additional degree of freedom thus making more VLL states accessible. This increases the stability of the simulation since configurations (fluctuations) can be accepted within the MC simulation without the system moving out of the three phase region. The NVT ensemble was therefore used to study the n-butane/1-butene/water system, with the volume based on the equilibrium values of the three box volumes obtained from the NPT simulation at 404.72 kPa. Since the NPT simulation yielded a liquid

water phase and two hydrocarbon-rich phases, the total volume from the NPT simulation was decreased by 15% before using it in the NVT ensemble. All other simulation conditions, except pressure, were the same as in the NPT simulations. As shown by the densities in Table 2, three distinct and stable phases were obtained. The table also shows that the simulated compositions are in excellent agreement with experimental data, almost completely reproducing the experimental three-phase composition boundary.

The excellent agreement between the simulated and experimental phase compositions is, once again, partially due to n-butane and 1-butene having low solubilities in water (the experimental mole fractions are 2.25×10^{-5} and 12.69×10^{-5} , respectively). Since the force field is developed for the individual components, one expects reasonable results in the dilute region. Similarly, the mole fraction of water in the vapor and hydrocarbon-rich phases is also in excellent agreement with experimental data. In contrast, there are large mole fractions of both hydrocarbons in the vapor and liquid hydrocarbon-rich phases, and their good agreement with experiment indicates that the force field – including cross terms for the interactions between these molecules – is valid. This is consistent with previous simulations based on the force field used here [27], which showed that the unlike-pair interactions between saturated alkane pseudoatoms and vinylic alkene pseudoatoms yield compositions in good agreement with experiment.

3.3 Water/ethanol/n-hexane

Due to the availability of experimental data for multiple VLLE state points for this mixture, four different conditions were studied in the NPT-Gibbs ensemble. The sizes of the experimental three-phase regions were reasonable at each state point of interest. The number of water molecules in each simulation was kept constant at 150 molecules to ensure reasonable statistics for the aqueous phase in each simulation, as well as for water in the hydrocarbon phases.

The equilibration runs for these mixtures, especially at high ethanol concentrations, required at least 1.5×10^5 Monte Carlo cycles to ensure that there is no change in the average mole fractions with increasing simulation time, and to obtain reasonable statistical uncertainties in the mole fractions of each component in each phase. Figure 2 shows the ternary composition diagrams for the four NPT simulations that were performed, each time increasing the number of ethanol molecules (while decreasing the number of n-hexane molecules to preserve the total number of molecules used in each simulation).

As can be seen in Figure 2, at very low ethanol concentrations, the shape of the three-phase region is qualitatively correct. An increase in the ethanol mole fraction decreases the area of the experimental three-phase region. This was not obtained from the simulations, where the three-phase regions became progressively larger. In fact, n-hexane molecules dissolved in the water phase only at the highest simulation temperature (330.54 K), with a mole fraction $x_3 = 0.0000004$. This is in poor agreement with the corresponding experimental solubility of $x_3^{\text{exp}} = 0.001$.

Thus, an increase in the alcohol mole fraction diminished the ability of the force fields to even qualitatively predict the equilibrium solubilities and hence the three-phase regions. This may be attributed to the simplicity of the Lorentz-Berthelot mixing rules, and that the unlike-pair attractions are not sufficiently strong. As mentioned earlier, previous two-phase studies [28] show systematic deviations for alcohol/alkane mixtures from experimental data by over-estimating the alkane solubility in both phases. This is evident in the mixture studied here in the vapor and ethanol rich phases (see Figure 2). Clearly, good agreement was obtained only at low concentrations of ethanol. Better results would have been obtained if the binary simulations were carried out to obtain force field parameters that yield a better prediction of the vapor-liquid and liquid-liquid phase envelopes of mixtures of alkanes/alcohols,

alkanes/water and alcohols/water over large composition ranges. This would have required successive modifications of the unlike-pair interactions for the size and energy parameters in many simulations for each binary mixture until satisfactory agreement with experimental data was obtained (for example, see [24]). These studies are left for future work.

4. Conclusions

The aim of this study was to investigate the ability of the Gibbs ensemble, using Monte Carlo molecular simulations, in predicting the VLLE at several state points for three industrially-relevant mixtures using two common potential models, TraPPE-UA and SPC-E. The simulation results for each mixture were then compared to the corresponding experimental data.

The NVT-Gibbs ensemble is preferred over the constant pressure variant for VLLE simulations for mixtures that have narrow three-phase regions, since NVT simulations fix only one intensive variable and thereby increases the stability of the simulation since configurations can be accepted within the MC simulation without the system moving out of the three-phase region.

The simulated mole fractions obtained for the methane/n-heptane/water and n-butane/1-butene/water systems are in good agreement with experimental data. In contrast, simulations of the water/ethanol/n-hexane mixture showed large deviations from experiment, especially at large ethanol mole fractions. This is mainly attributed to the fact that the Lorentz-Berthelot mixing rules for the unlike-pair attractions, which are important for systems that show a substantial degree of mutual solubility, have not been developed or parameterized for generic (n-alkane + alcohol + water) systems. Indeed, experimental laboratory measurements are currently the preferred method for the acquisition of VLLE data and

consequently the generation of phase diagrams, given the limited accuracy of simulations of highly non-ideal chemical systems (which are dependent on force field models and mixing rules), as well as the extremely long simulation times [30]. However, the continual development of force field models, as well as the production of increasingly powerful computational resources, can make molecular simulations a practical alternative for generating reliable phase equilibrium data.

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References

- [1] S.L. Clifford, D. Ramjugernath, J.D. Raal, *Fluid Phase Equilib.* 237(1-2) (2005) 89.
- [2] M.A. Joseph, J.D. Raal, D. Ramjugernath, *Fluid Phase Equilib.* 182(1-2) (2001) 157.
- [3] P. Naidoo, D. Ramjugernath, J.D. Raal, *Fluid Phase Equilib.* 269 (2008) 104.
- [4] R. Susilo, J.D. Lee, P. Englezos, *Fluid Phase Equilib.* 231 (2005) 20.
- [5] A.H. Wehe, J.J. McKetta, *J. Chem. Eng. Data*, 6(2) (1961) 167.
- [6] V. Gomis, A. Font, R. Pedraza, M.D. Saquete, *Fluid Phase Equilib.* 259 (2007) 66.
- [7] I.G. Economou, C. Tsonopoulos, *Chem. Eng. Sci.* 52(4) (1997) 511.
- [8] S. Aparicio-Martinez, K.R. Hall, *Fluid Phase Equilib.* 254 (2007) 112.

- [9] N.M. Al-Saifia, E.Z. Hamadb, P. Englezosa, *Fluid Phase Equilib.* 271 (2008) 82.
- [10] N. Metropolis, A.W. Rosenbluth, M. Rosenbluth, A.H. Teller, E. Teller, *J. Chem. Phys.* 21 (1953) 1087.
- [11] A.Z. Panagiotopoulos, *Mol. Phys.* 61 (1987) 813.
- [12] B. Smit, S. Karaborni, J.I. Siepmann, *J. Chem. Phys.* 102 (1995) 2126.
- [13] J.J. Potoff, J.I. Siepmann, *AIChE J.* 47 (2001) 1676.
- [14] R. Khare, A.K. Sum, S.K. Nath, J.J. de Pablo, *J. Phys. Chem. B* 108 (2004) 10071.
- [15] J. Jiang, Q. Yan, H. Liu, Y. Hu, *Macromolecules* 30(26) 1997 8459.
- [16] S.M. Lambert, D.S. Soane, J.M. Prausnitz, Fluid Phase Equilib. 0378-3812 Fluid properties and phase equilibria for chemical process design. International conference No. 6, Cortina d'Ampezzo , Italy (19/07/1992) 1993, vol. 83 (20 ref.), pp. 59-68
- [17] E. Johansson, K. Bolton, D.N. Theodorou, P. Ahlström, *J. Chem. Phys.* 126 (2007) 224902.
- [18] <http://towhee.sourceforge.net>
- [19] M.G.Martin, J.I. Siepmann, *J. Phys. Chem. B* 103 (1999) 4508.
- [20] D. Frenkel, B. Smit, Understanding Molecular Simulations: From Algorithms to Applications, Vol. 1 of Computational Science Series (2nd edition), Academic Press, San Diego, 2002.
- [21] S.W. de Leeuw, J.W. Perram, E.R. Smith, *Proc. R. Soc. Lond. A* 373 (1980) 27.
- [22] S.W. de Leeuw, J.W. Perram, E.R. Smith, *Proc. R. Soc. Lond. A* 373(1752) 57.
- [23] S.W. de Leeuw, J.W. Perram, E.R. Smith, *Proc. R. Soc. Lond. A* 388(1794) 173.
- [24] L. Zhang, J.I. Siepmann, *J. Phys. Chem. B*, 109 (2005) 2911.
- [25] R.H. Perry, D. W. Green, Perry's Chemical Engineers' Handbook, McGraw-Hill, New York, 2007.
- [26] C. Boulougouris,, I.G. Economou, D.N. Theodorou, *J.Phys. Chem. B*, 102 (1998) 1029.
- [27] C.D. Wick, M.G. Martin, J.I. Siepmann, *J. Phys. Chem. B* 104 (2000) 8008.
- [28] B. Chen, J.J. Potoff, J.I. Siepmann, *J. Phys. Chem. B* 105 (2001) 3093.

[29] J.N. Canongia Lopes, D.J. Tildesley, *Mol. Phys.* 92(2) (1997) 187.

[30] S. Moodley, Molecular Simulation of Vapour-Liquid-Liquid Equilibrium, MscEng Dissertation, University of KwaZulu Natal, Durban, South Africa, 2008.

Phase	Methane		n-Heptane		Water		Specific density [kg.m ⁻³]
	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	
P = 120kPa							
Vapor	0.9839 (32)	0.963987 (1230)	0.0154 (5)	0.0292 (1149)	0.0006 (6)	0.0068 (81)	0.911 (16)
Hydrocarbon-rich liquid	0.008336 (701)	0.015111 (1045)	0.991663 (701)	0.984045 (1025)	0.000001 (1)	0.000844 (20)	702.5 (1)
Water-rich liquid	0.000019 (1)	0.000047 (9)	0	0.000001 (1)	0.99998 (1)	0.999953 (1)	1008 (63)
P = 2000kPa							
Vapor	0.99822 (57)	0.994973 (150)	0.00172 (58)	0.004291 (148)	0.000059 (75)	0.000737 (3)	14.78 (59)
Hydrocarbon-rich liquid	0.125 (2)	0.076446 (6872)	0.8746 (25)	0.922922 (6847)	0.000002 (2)	0.000632 (26)	685.2 (9)
Water-rich liquid	0.00007 (4)	0.000523 (43)	0	0.000011 (1)	0.99993 (4)	999466 (11)	1016 (23)

Table 1 – Simulation results for 3-box NpT simulations at 275.5 K for methane/n-heptane/water at 120 kPa and 2000kPa. The statistical uncertainty in the final digit(s) of each value is/are shown as in parentheses. Sim. refers to simulation results, and Exp. refers to experimental data [4]. The specific densities are those obtained from the simulations; no experimental densities were reported.

Phase	n-Butane		1-Butene		Water		Specific density [kg.m-3]
	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	
NVT ensemble							
$P = 548$ (2) kPa							
Vapor	0.372 (5)	0.373	0.624 (5)	0.614	0.0040 (8)	0.0128	13.56 (59)
Hydrocarbon-rich liquid	0.419 (4)	0.42	0.581 (4)	0.579	0.00004 (1)	0.0012	563.2 (9)
Water-rich liquid	0.0000051 (102)	2.25×10^{-5}	0.0000019 (38)	12.7×10^{-5}	0.99999 (1)	0.9998506	993 (7)
NpT ensemble							
$P = 548$ kPa							
Vapor	0.371 (14)	0.373	0.625 (16)	0.614	0.0042 (28)	0.0128	13.24 (4)
Hydrocarbon-rich liquid	0.419 (9)	0.42	0.581 (9)	0.579	0.000047 (31)	0.0012	577 (1)
Water-rich liquid	0	2.25×10^{-5}	0.00000074 (1)	12.7×10^{-5}	0.9999993 (1)	0.9998506	994 (8)

Table 2 – Simulation results for n-butane/1-butene/water at 310.93 K in the NVT and NpT ensembles. The NVT simulation used 30% of the total equilibrium volume from an NpT simulation at 404.72 kPa. The statistical uncertainty in the final digit(s) of each value is/are shown in parentheses – note that statistical uncertainties for the experimental data were not reported in the reference publication [5]. Sim. refers to simulation results, and Exp. refers to experimental data. The specific densities are those obtained from the simulations; no experimental densities were reported.

	Mole fractions						
Phase	Water		Ethanol		n-Hexane		Specific density [kg.m-3]
T = 330.540 K	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	
Vapor	0.0637 (39)	0.137	0.0664 (12)	0.162	0.8699 (28)	0.702	3.0152 (56)
Hydrocarbon-rich liquid	0.00021 (6)	0.0002056	0.00305 (25)	0.021	0.99674 (3)	0.976	621 (6)
Water-rich liquid	0.9642 (59)	0.869	0.0358 (58)	0.131	$4_9 \times 10^{-7} *$	0.001	965 (6)
T = 329.770 K							
Vapor	0.0535 (33)	0.122	0.1696 (35)	0.202	0.7769 (38)	0.676	3.0152 (563)
Hydrocarbon-rich liquid	0.0005 (4)	0.005	0.0131 (40)	0.060	0.9864 (44)	0.935	621 (6)
Water-rich liquid	0.950 (16)	0.704	0.0496 (16)	0.293	0	0.003	965 (6)
T = 329.510 K							
Vapor	0.0470 (18)	0.114	0.2283 (47)	0.221	0.7247 (36)	0.665	2.825 (16)
Hydrocarbon-rich liquid	0.2089 (108)	0.008	0.6953 (156)	0.087	0.0958 (220)	0.905	730 (9)
Water-rich liquid	0.9517 (164)	0.555	0.0483 (164)	0.433	0	0.012	961 (8)
T = 329.450 K							
Vapor	0.0570 (44)	0.110	0.2310 (59)	0.229	0.7120 (27)	0.661	2.80 (1)
Hydrocarbon-rich liquid	0.1332 (207)	0.012	0.7084 (242)	0.113	0.1584 (437)	0.875	714 (8)

Water-rich liquid	0.9129 (132)	0.489	0.0871 (132)	0.492	0	0.019	938 (8)
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Table 3 – Simulation results for 3-box NpT simulations for n-hexane/ethanol/water at four different compositions at 101.33kPa. The statistical uncertainty in the final digit(s) of each value is/are shown in parentheses – note that statistical uncertainties for the experimental data were not reported in the reference publication. Sim. refers to simulation results, and Exp. refers to experimental data [6]. The specific densities are those obtained from the simulations; no experimental densities were reported. *Uncertainty shown as a subscript.

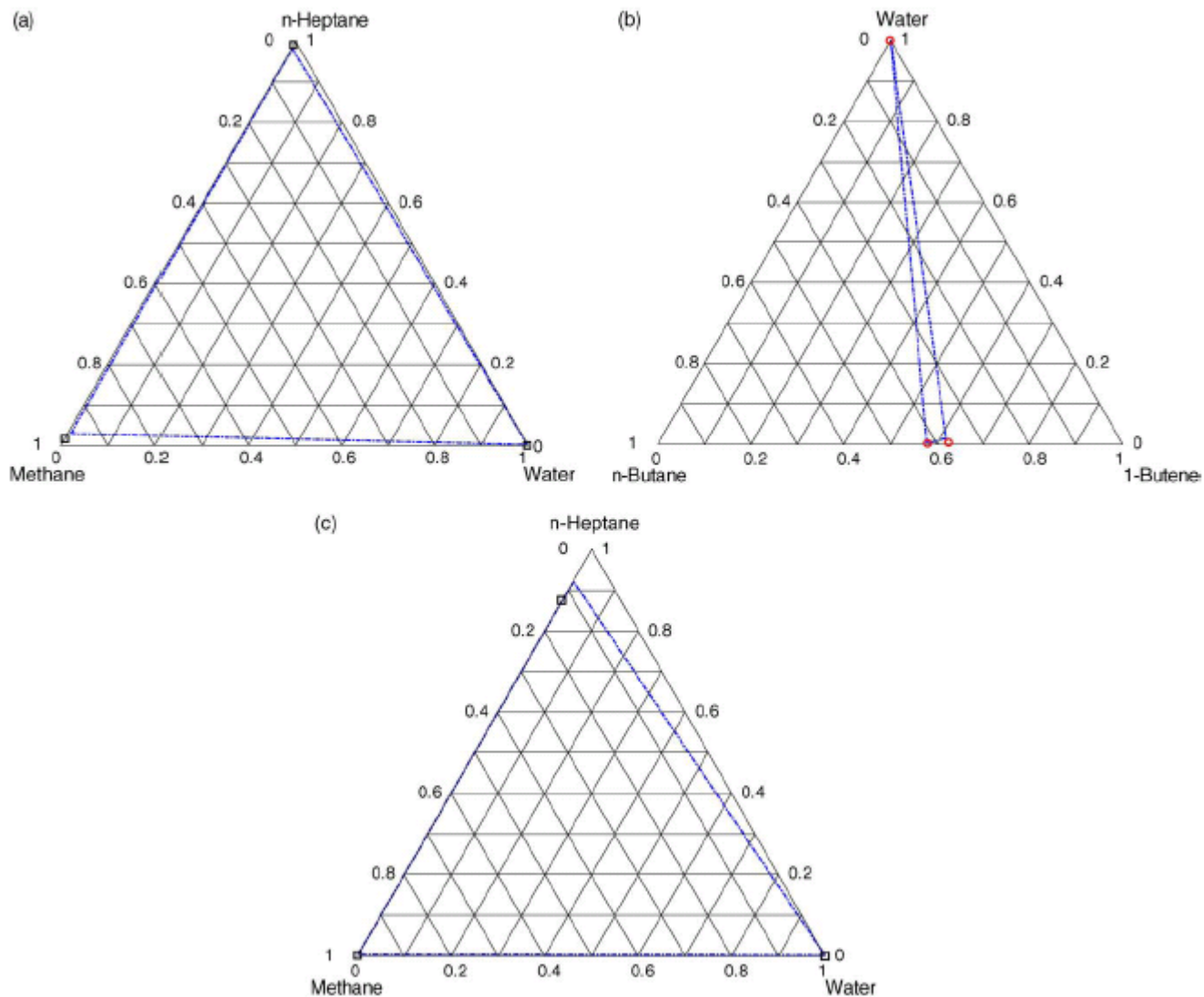


Fig. 1. VLLE ternary composition diagrams for (a) methane/water/n-heptane at 275.5K and 120 kPa, (b) methane/water/n-heptane at 275.5K and 2000 kPa, and (c) nbutane/1-butene/water at 310.93K (NVT ensemble). The experimental three-phase regions are shown as triangles, with the vertices corresponding to the experimental phase compositions listed in Tables 1 and 2, while the simulation results are shown as symbols.

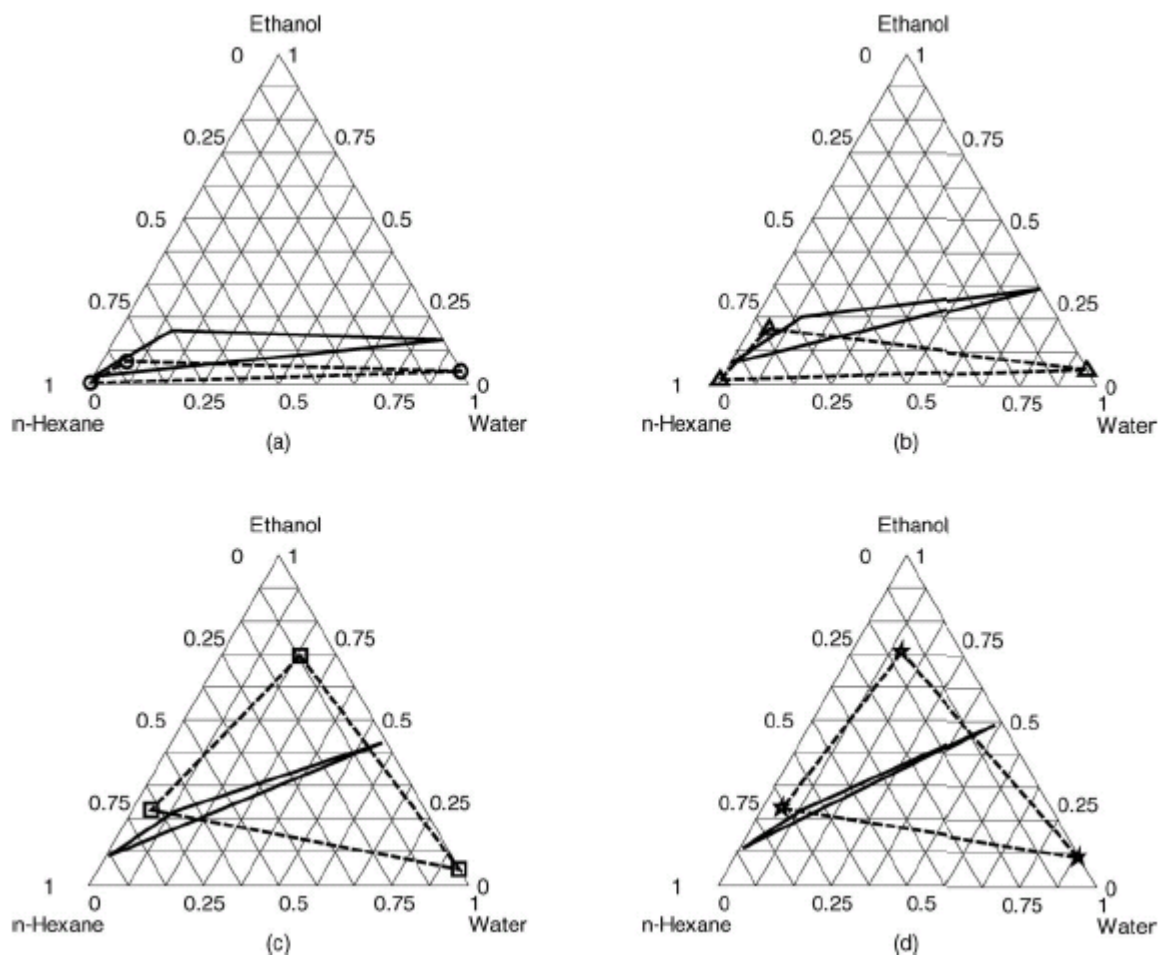


Fig. 2. VLLE diagrams for water/ethanol/n-hexane at 101.33 kPa using a total 750 molecules. (a) 329.45K using 232 ethanol molecules. (b) 329.51K using 184 ethanol molecules. (c) 329.77K using 108 ethanol molecules. (d) 330.54K using 45 ethanol molecules. Experimental three-phase envelopes are enclosed by solid lines, with the vertices corresponding to the experimental data listed in [Table 3](#), while simulation envelopes are enclosed by dashed lines joining the symbols which indicate phase compositions.