AmirKabir University of Technology
(Tehran Polytechnic)

AmirKabir Jounrnal of Science & Research
Mechanical Engineering
(ASJR-ME)
Vol. 48, No. 3, Autumn 2016, pp. 85-88

Vapor-Liquid-Liquid Equilibrium Calculation for Water and Normal-Hexane Binary Mixture Using Monte Carlo Molecular Simulation

M. Honari[1]*, B. Behzadi[2], M.R. Dehghani[3]

1- M.Sc., Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran
2- Associate Professor, Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran
3- Associate Professor, Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

(Received 12 March, 2012, Accepted 25 July, 2015)

ABSTRACT

In this work, phase equilibrium of pure and binary systems have been studied using the Monte Carlo molecular simulation method. The Gibbs ensemble method has been applied for this purpose. At first, vapor-liquid phase equilibrium of pure water and normal hexane was studied. Pure water vapor-liquid equilibrium was simulated using SPC-E, COMPASS and AMBER force fields. Also n-hexane vapor-liquid equilibrium was simulated using AMBER, CHARM-27 and TraPPE-UA force fields. Finally, the simulation in the Gibbs ensemble was used for liquid-liquid-vapor phase equilibrium calculations for mixture of water and n-hexane. Simulation results are in very good agreement with experimental data in pure cases while for the binaries, the results are fairly comparable to experimental data.

KEYWORDS:

Phase Equilibrium, Molecular Simulation, Monte Carlo Simulation, Gibbs Ensemble, Force Fields

* Corresponding Author, Email: mohamad_honari@chemeng.iust.ac.ir

1- Introduction

In recent years wide studies have been performed on the vapor-liquid and liquid-liquid phase equilibrium simulation for multi component mixtures. There are many studies on the Monte Carlo molecular simulation of biphasic fluid equilibrium [1-3]. Three-phase vapor-liquid-liquid equilibrium has also been studied for mixtures containing three or more components. However, the study of three-phase equilibrium for binary systems rarely has been performed [4, 5].

2- Theory and Simulation Methodology

In this study, the Gibbs ensemble was used for the Monte Carlo simulation. The Gibbs method is applicable in NVT and NPT ensemble. In both of the Gibbs method formulations, the total number of particles is constant [6, 7]. Degree of freedom for the three-phase equilibrium in a two-component system is equal to 1. It must be mentioned that degrees of freedom refers to the number of intensive properties such as temperature and pressure, which are independent of the other intensive variables. So for this system, it cannot be considered as constant over one intensive variable. NPT method cannot be used, as needs to fix pressure and temperature simultaneously, for the simulation of binary mixture at three-phase equilibrium. In this regard NVT method can be used only [8, 9].

For all simulations the MCCCS towhee code was used, that utilizes the GEMC method in NVT ensemble. The Coupled-decoupled Configurational Bias (CB) algorithm was used also for all simulations. The cut-off radius was considered as 10 Å, and the minimum length of the simulation box was considered as well as 20 Å (twice the cut-off radius). An analytical tail correction was used to correct the error which occurred by cutting the potential [10, 11].

Simulations performed for 105, 160, 210, 310, 520, 830, 1050 and 1560 number of molecules separately. For all cases except of 105 and 160 number of molecules, 1×10^4 Monte Carlo cycles used to achieve equilibrium and then 1×10^4 Monte Carlo cycles used to density calculations. Figure 1 shows the variation of reduced density versus the number of cycles for different number of molecules.

Also water and n-hexane as pure component were simulated at different number of molecules. Figure 2 (a) shows the water and n-hexane liquid density versus number of molecules of simulations.

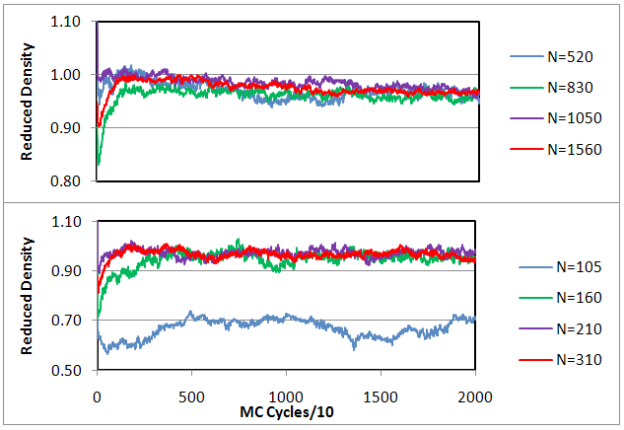

Figure 1. Reduced density versus MC cycles for different number of molecules

It can be seen that for molecules number greater than 310, similar results are obtained. Figure 2 (b) shows the CPU time versus molecule number. Considering both accuracy and time of simulations, for all simulations approximately 520 molecules were considered.

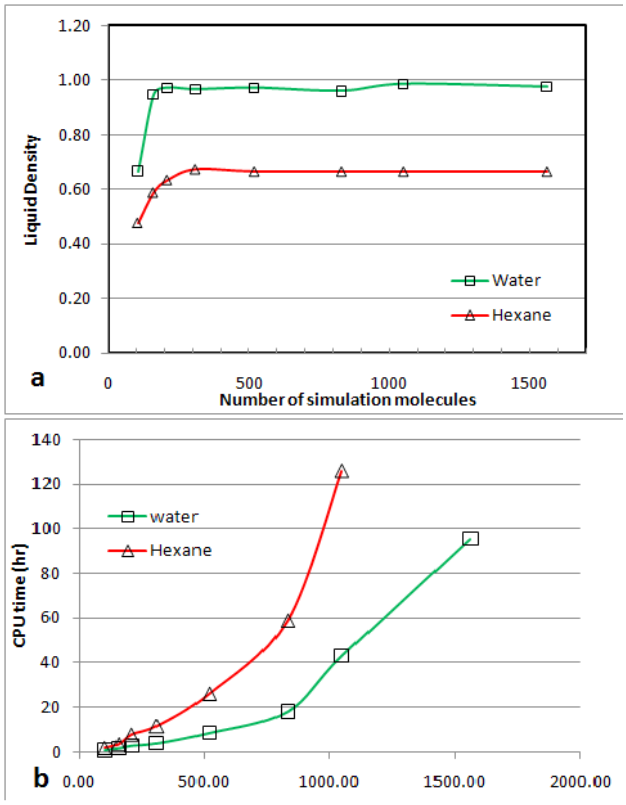

Figure 2. a) Liquid density for water and n-hexane in different number of molecules, b) CPU time for water and n-hexane simulation in different number of molecules

3- Simulation Results

Values of the %ARD for different force fields are shown in Table 1. Our results show that SPC-E model is more accurate than the other force fields.

Table 1. Comparison of different force fields' %ARD for simulations

		SPC-E	AMBER	COMPASS
%ARD	Liquid Density	1.35	2.03	3.62
%AAD	Vapor Density	0.89	0.68	1.29

Pure water and n-hexane were simulated in Gibbs NVT ensemble for 7 different temperatures and the simulation results were compared to available experimental data from NIST [12] in Figure 3 and Figure 4.

The results of simulation in Gibbs NVT ensemble successfully yielded three distinct equilibrium phases with different densities for n-Hexane-water system. The equilibrium mole fractions for water-n-hexane mixture in two liquid phases are in good agreement with experimental. The composition of components in vapor phase was not reported in literatures (there is not any comparison).

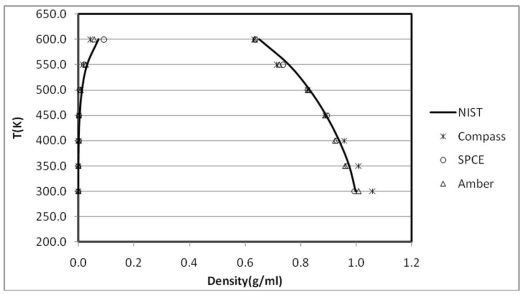

Figure 3. Pure water phase equlibria diagram

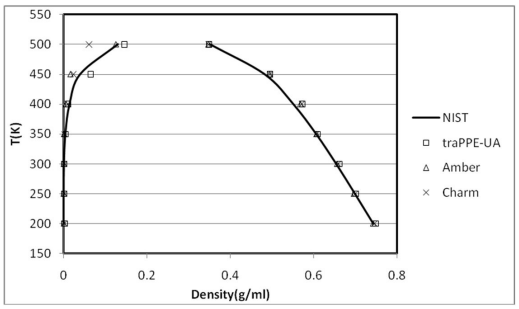

Figure 4. Pure n-hexane phase equlibria diagram

4- Conclusions

In summary, we report the first successful GEMC simulations of binary VLLE of realistic systems. Binary three-phase fluid equilibrium for complex chemical systems can be studied by using the NVT–GEMC method. Equilibrium mole fractions which obtained from the NVT simulations were in semi-quantitative agreement with experiments. The NPT simulations are incapable of producing stable binary three-phase equilibrium for the n-hexane–water system under the conditions studied here.

5- References

[1] Nath, S.K., et al., 1998. "Simulation of vapor-liquid equilibria for alkane mixtures." *Industrial and Engineering Chemistry Research*, 37(8): p. 3195-3202.

[2] Moodley, S., K. Bolton, and D. Ramjugernath, 2010. "Monte Carlo simulations of vapor-liquid-liquid equilibrium of some ternary petrochemical mixtures." *Fluid Phase Equilibria*, 299(1): p. 24-31.

[3] Moodley, S., et al., 2010. "Gibbs ensemble Monte Carlo simulations of binary vapour–liquid–liquid equilibrium: application to n-hexane–water and ethane–ethanol systems." *Molecular Simulation*, 36(10): p. 758-762.

[4] Cornell, W.D., et al., 1995. "A second generation force field for the simulation of proteins, nucleic acids, and organic molecules." *Journal of the American Chemical Society*, 117(19): p. 5179-5197.

[5] Neria, E., S. Fischer, and M. Karplus, 1996. "Simulation of activation free energies in molecular systems." *Journal of Chemical Physics*, 105(5): p. 1902-1921.

[6] Smit, B., P. De Smedt, and D. Frenkel, 1989. "Computer simulations in the Gibbs ensemble." *Molecular Physics*, 68(4): p. 931-950.

[7] Clifford, S., K. Bolton, and D. Ramjugernath, 2006. "Monte Carlo simulation of carboxylic acid phase equilibria." *Journal of Physical Chemistry B*, 110(43): p. 21938-21943.

[8] Frenkel, D. and B. Smit, 2002. "Understanding molecular simulation: from algorithms to applications", *Academic Press*.

[9] Errington, J.R., 2003. "Direct calculation of liquid-vapor phase equilibria from transition matrix Monte Carlo simulation." *Journal of Chemical Physics*, 118(22): p. 9915-9925.

[10] Allen, M.P. and D.J. Tildesley, 1989. "Computer simulation of liquids", *Clarendon Press*.

[11] N. Grønbech-Jensen, and M. Neumann, 1998. "Pressure calculation in polar and charged systems using Ewald summation: Results for the extended simple point charge model of water." *Journal of Chemical Physics*, 109(7): p. 2791-2797.

[12] Linstrom, P.J. and E. Mallard, NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology: Gaithersburg MD.