



Low Temperature Vapor-Liquid equilibria of Binary mixtures by Molecular Simulation and Peng-Robinson equation of state

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Abstract: The Gibbs ensemble Monte Carlo method (GEMC) technique is used for determining composition and densities of vapor and liquid phases in equilibrium for binary mixtures of Lennard-Jones fluids. In the present study, VLE data for pure nitrogen and the binary systems nitrogen + methane at 183.15, 172.04 and 149.82 K and nitrogen + ethane at 194.26, 172.04 and 149.82 K mixtures have been investigated using Monte Carlo simulations in the Gibbs ensemble and Peng-Robinson equation of state modeling. GEMC has been considered and after the simulation, they display a decent match with experimental and results of Peng-Robinson equation of state of the vapor-liquid equilibrium for the two studied mixtures.

Keywords: vapor-liquid equilibrium, molecular simulation, Peng-Robinson equation of state.

Introduction

Thermodynamics of vapor-liquid equilibria plays an important role in many chemical processes associated with phase separation. Knowledge of phase equilibria is usually obtained from experimental observation of particular interest is the phase equilibria of mixtures containing methane and ethane, which are typically found in the petrochemical industry. Since the measurement of vapor-liquid equilibria is time-consuming and expensive, there is a demand to reduce the experimental work by employing suitable equations of state. Conventional approaches for predicting phase equilibria properties use empirical equations of state such as the Peng-Robinson equation of state (PR-EOS)¹. Although equations of state can be an excellent tool, they depend on a range of experimental data to evaluate parameters, and often lack predictive power for complex systems. A promising approach to study phase equilibria is computer simulation based on molecular modeling, which can predict vapor-liquid equilibria of fluid systems under a wide range of conditions, and also remarkable advantage over the empirical or semiempirical

models. Computer simulations can even be used to predict behavior at conditions under which experimental data are difficult or impossible to obtain. Recently great progress of simulation has been made. Many novel algorithms have been proposed, such as the NPT + test particle method^{2,3}, the Gibbs-Duhem integration method^{4,5}, the Histogram Reweighting Grand Canonical Monte Carlo^{6,7}, and Gibbs Ensemble Monte Carlo method (GEMC)^{8,9}.

Some molecular simulation works have already been reported on the VLE behavior of the pure components and the binary mixtures of nitrogen, methane and ethane^{10,11}. However, no studies have previously been reported on the VLE behavior of the binary systems nitrogen + methane at 183.15, 172.04 and 149.82 K, and nitrogen + ethane at 194.26, 172.04 and 149.82 K and obtaining results are compared with predicted PR-EOS and the experimental data.

Methodology and Model

Molecular Model

The first step in running a molecular simulation is making a model of the molecule or molecules are used. In these simulations, the Lennard-Jones potential is used to calculate the energy of the interactions by Eq. (1).

$$U_{ij}(r) = 4 \times \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (1)$$

Where U the configurational energy of interaction between the centers of two is beads i and j a distance r apart. ε_{ij} and σ_{ij} are energy and size parameters for the ij interaction. σ has units of length which represents the diameter of the bead. ε has units of energy, and represents the depth of the potential well. For interactions between different types of beads, the Lorentz-Berthelot combining rules are used by Eqs. (2) and (3).

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad (2)$$

$$\varepsilon_{ij} = (\varepsilon_{ii} \times \varepsilon_{jj})^{1/2} \quad (3)$$

Running a Simulation

Vapor-liquid equilibria of the binary mixtures were calculated via Monte Carlo Gibbs ensemble (GEMC) simulations in the isothermal-isobaric (NPT) ensemble using the simulation Gibbs Ensemble code. Each system consisted of 500 molecules in the sum, with varying number of the molecules of both components, depending on the mixture studied. The Ewald sum technique¹² was employed to deal with the electrostatic interactions with a cutoff radius adjusted to half the box length. The cutoff radius for the Lennard-Jones interactions was set to 12 Å, and standard long-range corrections to the energy and pressure were applied.

Gibbs ensemble simulation contains three steps, step 1: displacements of molecules within each phase (to satisfy internal equilibrium); step 2: fluctuations in the volume of the two phases (to satisfy equality of pressures); and step 3: transfers of molecules between phases (to satisfy equality of chemical potentials of all components).

In this paper, one cycle of the Gibbs ensemble was constructed with step 1 (each molecule was tried to move one time), step 2 (one time of volume change), again step 1 (each molecule was tried to move one time), and step 3 (molecular transfers were continued until 1% of molecules were exchanged, but the maximum number of the trial transfers was limited to 200000). The equilibrium properties were obtained as the averages over 500000 cycles after 300000 equilibration cycles. The numbers of the molecules were determined to satisfy that the cut-off radius was longer than four times the molecular size σ .

Peng-Robinson Equation of State

Cubic EOS offer a compromise between generality and simplicity that is suitable for numerous purposes. They are excellent tools to correlate experimental data and are therefore often used for many technical applications. In the present work, the Peng- Robinson EOS with the Van der Waals one-fluid mixing rule was adjusted to binary experimental data and validated regarding the ternary mixture. The Peng-Robinson EOS¹³ is defined by

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (4)$$

Where the temperature dependant parameter a is defined by

$$a = \left(0.45724 \frac{R^2 T_c^2}{p_c} \right) \left[1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (5)$$

The volume constant parameter b is

$$b = 0.07780 \frac{RT_c}{p_c} \quad (6)$$

The values of critical temperature T_c , critical pressure p_c , acentric factor ω , and the ideal gas constant R of the pure substances are given in Table-1¹⁴.

Results and Discussion

The molecular interaction parameters are given in Table-2¹⁵. The results section is divided into three parts: pure nitrogen, nitrogen-methane and nitrogen-ethane mixtures.

Pure Nitrogen

Eight runs are done for the pure nitrogen system from 85 K to 120 K at 5 degree intervals using the Gibbs Ensemble Program. The liquid and vapor phases are initially set up with densities of 500 kg/m³ and 50 kg/m³, respectively. Simulation results for the temperature–density coexistence curve of pure nitrogen are presented in Fig.1. The results turn out to be in relatively good agreement with the experimental data reported¹⁶.

The critical temperature was determined by fitting simulated saturated liquid and vapor densities to density scaling law for the critical temperature¹⁷:

$$\rho_{liq} - \rho_{vap} = A_1 (T_c - T)^\beta \quad (7)$$

Where A_1 fitting constant and β is the critical exponent.

The critical density was obtained from the law of rectilinear diameters¹⁸;

$$\frac{\rho_{\text{liq}} - \rho_{\text{vap}}}{2} = \rho_c + A_2(T_c - T) \quad (8)$$

Where A_2 is a fitting constant.

The constants β and A were fitted to experimental temperature-density data.

Nitrogen + Methane

Simulation results for the pressure-composition (P-xy) diagrams of the system Nitrogen-Methane at 183.15, 172.04 and 149.82 K are presented in Fig.2 together with experimental data¹⁹ and predicted of Peng-Robinson EOS. The Gibbs Ensemble Monte Carlo simulation results for Nitrogen- Methane are found to be in good agreement with experiment at the three temperatures considered in this study. We can observe a perfect agreement between simulation, experimental and Peng-Robinson EOS. For the temperature of 149.82 K coincidence between experiment and simulation is also quite good.

Nitrogen + Ethane

Simulation results for the pressure-composition (P-xy) diagrams of the system Nitrogen-Methane at 194.26, 172.04 and 149.82 K are presented in Fig.3 together with experimental data²⁰ and predicted of Peng-Robinson EOS. The Gibbs Ensemble Monte Carlo simulation results for Nitrogen-Methane are found to be in relatively good agreement with experiment at the three temperatures considered in this study. The best agreement for vapor composition is obtained at all temperatures studied for all pressures.

Conclusion

The Gibbs Ensemble Monte Carlo is used to study the vapor-liquid equilibria properties of nitrogen, methane and ethane. Simulation results for the temperature-density coexistence curve of pure nitrogen as well as the pressure-composition diagrams of the system Nitrogen + Methane and Nitrogen + Ethane at several different temperatures are compared to experimental data and Prediction of Peng- Robinson EOS. Comparison of the simulated results with experimental data demonstrated that Gibbs Ensemble Monte Carlo simulations can be used to predict vapor-liquid equilibria with accuracy close to experiments.

Table 1: Pure substance parameters of the Peng-Robinson EOS

	N ₂	CH ₄	C ₂ H ₆
T _c /K	126.2	190.56	305.32
p _c /MPa	3.398	4.599	4.872
ω	0.037	0.011	0.099

Table 2: Pair-potential parameters.

	N ₂	CH ₄	C ₂ H ₆
$\sigma/\text{\AA}$	3.919	4.015	4.782
ϵ/K	91.85	140.42	216.12

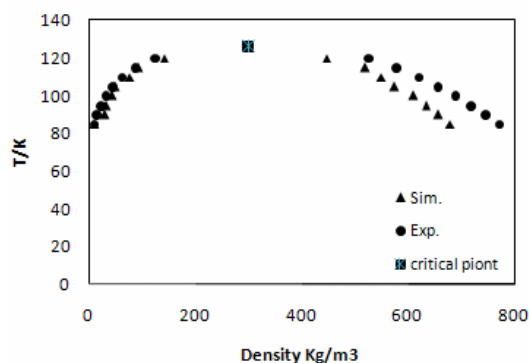


Fig.1. Phase diagram for pure nitrogen system compared with experimental results.

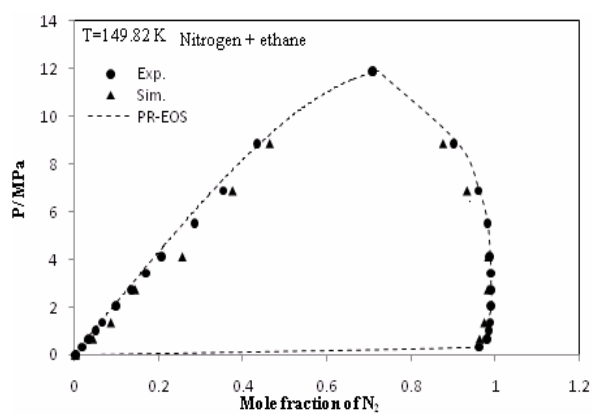
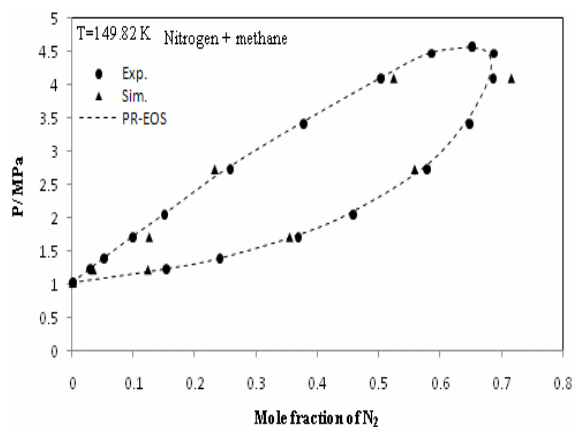
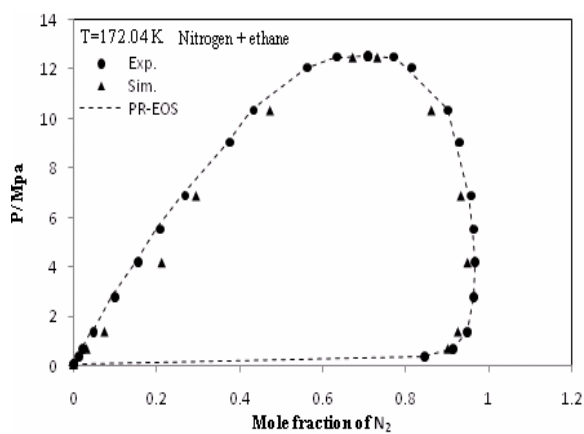
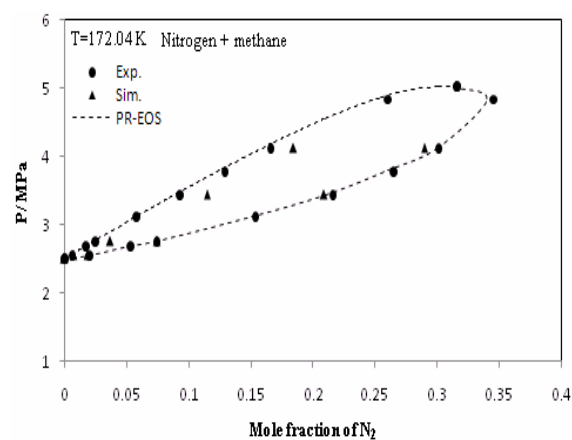
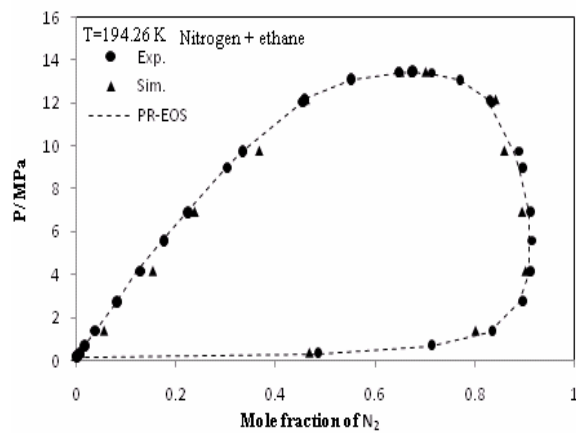
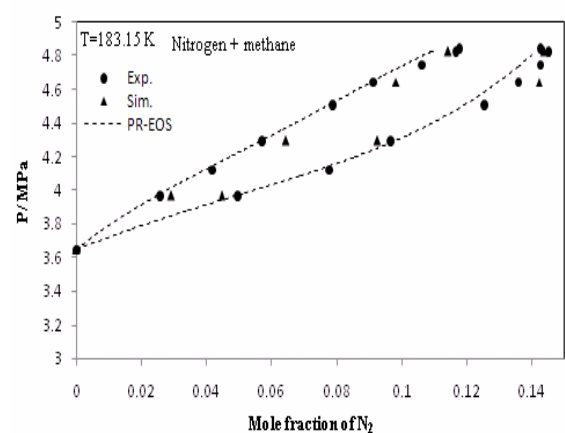


Fig. 2: Pressure-Composition diagram (P-xy) for nitrogen- methane system at 183.15 ,172.04, 149.82 K

Fig. 3: Pressure-Composition diagram (P-xy) for nitrogen-ethane system at 194,172.04, 149.82 K

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