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, obtain VLE data for the binary systems methane + xenon at 189.78 and 208.29 K and xenon + ethane at 161.40 and 182.24 K mixtures have been investigated using Monte Carlo simulations in the Gibbs ensemble and PR-EOS modeling. GEMC have been considered and after the simulation, they display a decent match with experimental and results of PR-EOS data of the vapor-liquid equilibrium for the two studied mixtures.

Keywords: Gibbs ensemble, Monte Carlo, Peng-Robinson EOS (PR-EOS), Vapor-liquid Equilibrium.

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 are the phase equilibria of mixtures containing alkanes and xenon, 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 xenon, methane and ethane. However, no studies have previously been reported on the VLE behavior of the binary systems methane + xenon at 189.78 and 208.29 K and xenon + ethane at 161.40 and 182.24 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).

\[ U = \epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right) \]

Where \( U \) is the configurational energy of interaction between the centers of two beads \( i \) and \( j \) a distance \( r \) apart. \( \epsilon_{ij} \) and \( \sigma_{ij} \) are energy and size parameters for the \( ij \) interaction. \( \sigma \) has units of length which represents the diameter of the bead. \( \epsilon \) 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).

\[ \epsilon_{ij} = (\epsilon_{ii} + \epsilon_{jj})^{1/2} \]  \hspace{1cm} (2)

\[ \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})^{1/2} \]  \hspace{1cm} (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 400 molecules in the sum, with varying number of the molecules of both components, depending on the mixture studied. The Ewald sum technique\(^{10}\) 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 10 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 400000 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 \( \sigma \).

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 EOS\(^{11}\) is defined by

\[ p = \frac{RT}{v - b} - \frac{a}{v(v + b) + \beta(v - b)} \]  \hspace{1cm} (4)

Where the temperature dependent parameter \( \alpha \) is defined by

\[ \alpha = \left( \frac{0.45724 R^{2/3}}{\rho_c} \right) [1 + 0.37464 + 1.54226 \omega - 0.87964 \omega^2] \left(1 - \frac{R}{\rho_c} \right)^2 \]  \hspace{1cm} (5)
The volume constant parameter $b$ is

$$b = 0.077T_0 \frac{H_T}{\rho_0}$$

The values of critical temperature $T_c$, critical pressure $p_c$, acentric factor $\omega$, and the ideal gas constant $R$ of the pure substances are given in Table 1.\(^{12}\)

**Results and Discussion**

The molecular interaction parameters are given in Table-2.\(^{13}\) The results section is divided into two parts: methane + xenon and xenon + ethane mixtures.

| Table 1. Pure substance parameters of the Peng-Robinson EOS. |
|-----------------|--------|--------|
|                | Xe     | CH$_4$  | C$_2$H$_6$ |
| $T_c$/K         | 289.74 | 190.56  | 305.32     |
| $p_c$/MPa       | 5.8404 | 4.599   | 4.872      |
| $\omega$        | 0.00   | 0.011   | 0.099      |

| Table 2. Pair-potential parameters. |
|-----------------|--------|--------|
|                | Xe     | CH$_4$  | C$_2$H$_6$ |
| $\sigma$/Å      | 4.260  | 4.015   | 4.782      |
| $\epsilon$/K     | 213.96 | 140.42  | 216.12     |

**Methane + Xenon**

Simulation results for the pressure-composition (P-xy) diagrams of the system methane + xenon at 189.78 and 208.29 K are presented in Fig.1 together with experimental data\(^{14}\) and predicted of Peng-Robinson EOS. The Gibbs Ensemble Monte Carlo simulation results for methane - xenon are found to be in good agreement with experiment at the two temperatures considered in this study. We can observe a perfect agreement between simulation, experimental and Peng-Robinson EOS.

**Xenon + Ethane**

Simulation results for the pressure-composition (P-xy) diagrams of the system xenon + ethane at 161.40 and 182.24 K are presented in Fig.2 together with experimental data\(^{15}\) and predicted of Peng-Robinson EOS. The Gibbs Ensemble Monte Carlo simulation results for xenon-ethane are found to be in relatively good agreement with experiment at the two temperatures considered in this study. The best agreement for vapor composition is obtained at all temperatures studied for all pressures.

**Concluding Remarks**

The Gibbs Ensemble Monte Carlo is used to study the vapor-liquid equilibria properties of xenon, methane and ethane. Simulation results for the pressure-composition diagrams of the system methane + xenon and xenon+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.
Fig. 1. Pressure-Composition diagram (P-xy) for methane + xenon at 189.78 and 208.29 K

Fig. 2. Pressure-Composition diagram (P-xy) for xenon + ethane at 161.40 and 182.24 K

References


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