Vapor–Liquid Equilibria of Binary Mixtures Containing Methane, Ethane, and Carbon Dioxide from Molecular Simulation

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The $NpT+$ test particle method is used in order to predict vapor–liquid equilibria of the mixtures methane +ethane, methane +carbon dioxide, and carbon dioxide+ethane by molecular simulations. The pure-component molecular models were fitted to the experimental vapor pressures and saturated liquid densities in previous papers, which used the same simulation method for the determination of the phase equilibria. For each binary mixture the two unlike interaction parameters were determined from one experimental excess volume and one excess enthalpy. Based on these molecular models the vapor–liquid phase equilibria were calculated for each mixture at three temperatures. Comparison of the pressure-composition data with experimental results shows the high predictive power of this molecular based procedure. This statement is confirmed by additional comparisons of the pressure-composition diagrams and the pressure-density diagrams with results from equations of state.

KEY WORDS: biogas; molecular interactions; molecular simulations; natural gas; vapor–liquid equilibria.

1. INTRODUCTION

The calculation of thermodynamic properties from molecular models is a long-lasting aim and has been considerably facilitated by the use of computer simulations. A topic of special interest also with respect to practical applications is the easy and accurate simulation of phase equilibria. In that field, recently, remarkable progress was made. One frequently used method

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is the Gibbs ensemble, which was introduced by Panagiotopoulos [1] and applied to pure fluids and mixtures [2–5]. Alternatively, the $NpT+$ test particle method was proposed [6] and first applied to pure fluids [7–9], including carbon dioxide [10]. Recently, the method was extended to mixtures and applied to argon + methane [11] and a series of Lennard–Jones mixtures [12]. The purpose of the present paper is to demonstrate that the $NpT+$ test particle method also works well for nonspherical and polar molecules. In particular, we want to consider three key mixtures, namely, methane + ethane, methane + carbon dioxide, and carbon dioxide + ethane. The first and third of these mixtures are of great technical interest in energy and petroleum engineering; the second mixture is known as biogas.

The calculation of thermodynamic properties by statistical mechanics requires models for the intermolecular potentials between the like and the unlike molecules. For the determination of the pure-component interactions, an established procedure assumes a physically reasonable model for the interaction with few adjustable parameters to be fitted to the saturated properties of the liquid. Such effective intermolecular potentials are available for the substances under present consideration [10, 13, 14]. In addition, it was suggested earlier [15] to determine the unlike interaction parameters by fitting to one experimental excess volume and one excess enthalpy. This work has to be done here for the three unlike interactions of the binary mixtures.

The paper is organized such that we give an outline of the method in the next section. Then the molecular models are given for the pure components and determined for the unlike interactions. Finally, vapor–liquid equilibria are presented for each system at three temperatures and compared to experimental data and to equation of state (EOS) results.

2. OUTLINE OF THE METHOD

We consider a binary mixture consisting of components $A$ and $B$ ($i=A, B$) with a given complete set of like and unlike intermolecular potentials between the particles. The basic idea of the $NpT+$ test particle method for the determination of vapor–liquid phase equilibria of binary mixtures is to construct at a prescribed temperature $T$ and a prescribed liquid composition $x$, the chemical potentials as functions of the pressure $\mu_i^L(p)$, and in the vapor as functions of the pressure and the vapor composition $\mu_i^V(p, y_A)$ by simulations. Because of the prescription of the pressure it is essential to use the isobaric isothermal $NpT$ ensemble, but it should be mentioned that it does not matter whether molecular dynamics or Monte Carlo simulation technique is used. When the construction is done, the vapor pressure $p_\alpha$ and the vapor composition in equilibrium $y$ can be