Vapor–Liquid Equilibria of the Ternary Mixture $CH_4 + C_2H_6 + CO_2$ from Molecular Simulation

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The NpT + test-particle method for the calculation of vapor–liquid equilibria by molecular simulations is extended to ternary mixtures. It is applied to the system methane + ethane + carbon dioxide, for which all binary molecular interaction models are available from previous work. Methane is described as one-center Lennard-Jones fluid, ethane as two-center Lennard-Jones fluid, and carbon dioxide as two-center Lennard-Jones plus point quadrupole fluid. The unlike interactions are treated in the same way as the binary mixtures, using two parameters for each binary interaction. No ternary parameters are introduced. Vapor–liquid phase equilibria are calculated for the ternary mixture at the following temperature–pressure pairs: 233.15 K – 2 MPa; 250.5 K – 2 MPa; and 250.5 K – 3.04 MPa. Comparison of the simulation data with experimental and equation-of-state results shows excellent agreement. Bubble and dew densities are also reported.

Introduction

There is considerable interest in the prediction of phase equilibria of multicomponent mixtures. Routes for that purpose are models for the excess Gibbs energy, equations of state, and recently also molecular simulations. The advantage of the latter method is that it uses well-defined models for the interactions between two molecules and hence should not require any ternary or higher parameters.

Different molecular simulation methods have been suggested for the determination of phase equilibria. Ternary mixtures have been treated with the Gibbs ensemble (Panagiotopoulos, 1987), but so far only mixtures of spherical Lennard-Jones molecules have been considered (Tsang et al., 1995), which do not represent real mixtures. Here we will use the *NpT* + test particle method (Möller and Fischer, 1992; Lotfi et al., 1992; Vrabec and Fischer, 1995) and investigate the mixture methane + ethane + carbon dioxide. For the pure components, optimized intermolecular potentials have been suggested in previous articles (Lotfi, 1993; Vrabec et al., 1996; Möller and Fischer, 1994). The binary interactions between the unlike pairs of these molecules have been suggested recently in an investigation of the three binary mixtures methane + ethane, methane + carbon dioxide, and carbon dioxide + ethane (Vrabec and Fischer, 1996), which showed good to excellent predictions of the vapor–liquid equilibria (VLE). Therewith, all material is available for the prediction of the VLE of the ternary mixture, which is the purpose of this article.

Regarding the methodology, recall that previous investigations for pure fluids (Vrabec et al., 1993) and binary mixtures (Vrabec et al., 1995) showed qualitative agreement between the results of the *NpT* + test particle method and the Gibbs ensemble, but in nearly all cases smaller error bars and considerably less scatter of the data were produced from the *NpT* + test particle method.

In this article we will first describe the method for ternary mixtures, then repeat for the convenience of the reader the molecular models to be used, and finally we present the results in comparison with experimental and equation of state data.

The Method

We consider a ternary mixture consisting of the three components A, B, and C with a given complete set of like and

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unlike pairwise intermolecular potentials. For a VLE, thermodynamic quantities of interest are the temperature T, the vapor pressure p_σ, the liquid mole fractions x_A, x_B, and the vapor mole fractions y_A, y_B. The VLE requires the prescription of three independent variables, which we take to be the temperature and the liquid mole fractions. The idea of the N_pT + test particle method is to determine the chemical potentials μ_i of all components i in the liquid at fixed temperature and fixed mole fractions as functions of the pressure $\mu_i^l(p)$, and in the vapor at fixed temperature as functions of the pressure and the vapor mole fractions $\mu_i^v(p, y_A, y_B)$. From these μ-functions the three unknown quantities at coexistence, the vapor pressure, and the vapor mole fractions, are found by equating

$$\mu_i^l(p_\sigma) = \mu_i^v(p_\sigma, y_A, y_B), \qquad (i = A, B, C) \qquad (1)$$

for all three components.

The basic idea in the following is to write the chemical potentials as Taylor series. We note that the derivative of the chemical potential with respect to the pressure is the partial molar volume $\bar{v}_i$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} = \bar{v}_i. \qquad (2)$$

In the liquid phase the chemical potentials show a weak dependence on the pressure, therefore it is a sufficient approximation to use a simple first-order Taylor series for $\mu_i^l(p)$ around the pressure p_0^l

$$\mu_i^l(p) \approx \mu_i^l(p_0^l) + \bar{v}_i^l(p - p_0^l), \qquad (3)$$

which is our working equation for the liquid.

In the vapor phase the chemical potential shows a quite different behavior. Because of the dominating influence of its ideal part the chemical potential has typically a logarithmic course with respect to pressure and composition. This behavior cannot be well described by a simple first-order Taylor series. At this point, it is helpful to split the chemical potential into four parts

$$\mu_i = kT \ln \frac{p}{kT} + kT \ln y_i + \mu^{\text{id}}(T) + \mu_i^{\text{res}}, \qquad (4)$$

the ideal pressure dependent, the ideal composition dependent, the ideal temperature dependent, and the residual part. Now, only the latter has to be described by a Taylor series where a first-order expansion is sufficient. Treating the ideal parts analytically, we write

$$\begin{aligned}\mu_i^v(p, y_A, y_B) \approx{}& \mu_i^v(p_0^v, y_{A0}, y_{B0}) + \left(\frac{\partial \mu_i^{v,\text{res}}}{\partial p}\right)_{T,x}(p - p_0^v)\\ &+ kT \ln\left(\frac{p}{p_0^v}\right) + kT \ln\left(\frac{y_i}{y_{i0}}\right) + \left(\frac{\partial \mu_i^{v,\text{res}}}{\partial y_A}\right)_{T,p}(y_A - y_{A0})\\ &+ \left(\frac{\partial \mu_i^{v,\text{res}}}{\partial y_B}\right)_{T,p}(y_B - y_{B0}). \qquad (5)\end{aligned}$$

The derivative of the residual chemical potential with respect to the pressure is given by

$$\left(\frac{\partial \mu_i^{v,\text{res}}}{\partial p}\right)_{T,x} = \bar{v}_i^v - v^{\text{id}} = \bar{v}_i^v - \frac{kT}{p}, \qquad (6)$$

which is the residual partial molar volume. For the derivative of the residual chemical potential with respect to the vapor composition we make an approximation by difference ratios, for example,

$$\left(\frac{\partial \mu_i^{v,\text{res}}}{\partial y_A}\right)_{T,p} \approx \left(\frac{\mu_{i1}^{v,\text{res}} - \mu_{i0}^{v,\text{res}}}{y_{A1} - y_{A0}}\right)_{T,p} = \left(\frac{\Delta \mu_i^{v,\text{res}}}{\Delta y_A}\right)_{T,p}. \qquad (7)$$

By inserting Eqs. 6 and 7 in Eq. 5, we obtain our working equation for the vapor

$$\begin{aligned}\mu_i^v(p, y_A, y_B) \approx{}& \mu_i^v(p_0^v, y_{A0}, y_{B0}) + \left(\bar{v}_i^v - \frac{kT}{p}\right)(p - p_0^v)\\ &+ kT \ln\left(\frac{p}{p_0^v}\right) + kT \ln\left(\frac{y_i}{y_{i0}}\right) + \left(\frac{\Delta \mu_i^{v,\text{res}}}{\Delta y_A}\right)_{T,p}(y_A - y_{A0})\\ &+ \left(\frac{\Delta \mu_i^{v,\text{res}}}{\Delta y_B}\right)_{T,p}(y_B - y_{B0}). \qquad (8)\end{aligned}$$

In order to calculate the VLE by equating Eqs. 3 and 8 we have to determine all coefficients, which shall be described in the following. First, we have to set the temperature and the liquid composition for the required VLE. Then we choose an arbitrary pressure p_0^l, where $p_0^l = 0$ is a good guess for low temperatures, and perform one molecular simulation at this state point. This simulation can be done by molecular dynamics or the Monte Carlo technique, but it is necessary to use the isobaric-isothermal *NpT* ensemble (e.g., Andersen, 1980). We then obtain the chemical potential by Widom's test particle insertion (Widom, 1963) as

$$\mu_i = \mu^{id}(T) + kT \ln x_i - kT \ln \langle V \exp\{-\beta\psi_i\}\rangle / N, \qquad (9)$$

where ψ_i denotes the potential energy of the test particle of the species i, V is the instantaneous volume, and the brackets average in the *NpT* ensemble. Test particle insertion also yields the partial molar volume (Sindzingre et al., 1987; Heyes, 1992) as

$$\bar{v}_i = \frac{\langle V^2 \exp\{-\beta\psi_i\}\rangle}{\langle V \exp\{-\beta\psi_i\}\rangle} - \langle V \rangle. \qquad (10)$$

Evaluating Eqs. 9 and 10 in the liquid simulation yields us the coefficients for the liquid working equation, Eq. 3.

On the vapor side, in general, more effort is required, as the dependence of the chemical potential on the composition is needed. Hence, we perform three vapor simulations at the prescribed temperature, an arbitrarily chosen pressure p_0^v, and three arbitrary compositions (y_{A0}, y_{B0}), (y_{A1}, y_{B0}),

(y_{A1}, y_{B1}). In all these simulations the chemical potentials and partial molar volumes are evaluated. On the basis of the three sets of chemical potential, we can calculate the two difference ratios approximating the dependence of the chemical potential on composition. Thereafter the vapor working Eq. 8 is known as well.

Beside the phase equilibrium properties introduced earlier, other quantities are also of interest, such as the bubble and the dew density. In all four simulation runs we have determined the density ρ

$$\rho = N/\langle V \rangle, \tag{11}$$

and the isothermal compressibility β_T

$$\beta_T = \frac{1}{kT}\frac{1}{\langle V \rangle}[\langle V^2 \rangle - \langle V \rangle^2], \tag{12}$$

so that we can obtain the bubble and the dew density from first-order Taylor series by inserting the vapor pressure and vapor composition

$$\rho' \approx \rho_0^l + \beta_T^l \rho_0^l (p_\sigma - p_0^l), \tag{13}$$

$$\rho'' \approx \rho_0^v + \beta_T^v \rho_0^v (p_\sigma - p_0^v) + \left(\frac{\Delta \rho^v}{\Delta y_A}\right)_{T,p} (y_A - y_{A0}) + \left(\frac{\Delta \rho^v}{\Delta y_B}\right)_{T,p} (y_B - y_{B0}). \tag{14}$$

With respect to the vapor composition, the derivatives of the density are again approximated as difference ratios of the three vapor simulation results. The bubble and dew enthalpy can be calculated in the same way.

So far, the *NpT* + test particle method for ternary mixtures requires four simulation runs, one in the liquid and three for the vapor. If a simple equation of state (e.g., virial expansion, perturbed virial expansion) can be used instead of Eq. 8, the number of simulation runs is reduced to one per coexistence point.

Molecular Models

The investigation is performed for the mixture of methane + ethane + carbon dioxide. In this ternary system six different pairwise interactions occur: first, the three like interactions, CH_4-CH_4, C_2H_6-C_2H_6, and CO_2-CO_2, and second, the three unlike interactions, CH_4-C_2H_6, CH_4-CO_2, and CO_2-C_2H_6.

For the like interactions we use the optimized molecular models introduced previously. Methane is modeled as a one-center Lennard-Jones fluid (Lotfi, 1993), ethane as a two-center Lennard-Jones fluid (Vrabec et al., 1996), and carbon dioxide as a two-center Lennard-Jones plus point quadrupole fluid (Möller and Fischer, 1994). The parameters are given in Table 1. The vapor pressures and bubble densities of these model fluids were determined with the help of the *NpT* + test particle method and the model parameters were fitted to experimental saturation data.

Table 1. Parameters for Molecular Interactions for Methane Modeled as Lennard-Jones Fluids, for Ethane as Two-Center Lennard-Jones Fluid, and for Carbon Dioxide as Two-Center Lennard-Jones Plus Point Quadrupole Fluid

Substance	σ Å	ϵ/k K	L^*	Q^{*2}
Methane	3.7275	148.99	—	—
Ethane	3.5000	135.57	0.67	—
Carbon dioxide	3.0354	125.317	0.699	3.0255

The unlike interactions $A-B$ are usually expressed through the unlike interaction parameters η and ξ and the like potential parameters as

$$\sigma_{AB} = \eta \frac{1}{2}(\sigma_A + \sigma_B), \tag{15}$$

and

$$\epsilon_{AB} = \xi \sqrt{\epsilon_A \epsilon_B}. \tag{16}$$

The parameters η and ξ were determined for the three required unlike interactions in an earlier article (Vrabec and Fischer, 1996) by a method of Möller et al. (1992). This method allows the unlike interaction parameters to be fit to one experimental excess volume and one experimental excess enthalpy. The values are listed in Table 2. It should be emphasized that all parameters used here are the same as for the investigation of the binary mixtures $CH_4 + C_2H_6$, $CH_4 + CO_2$, and $CO_2 + C_2H_6$ by Vrabec and Fischer (1996). No ternary parameters were introduced.

Results and Discussion

For the ternary mixture methane + ethane + carbon dioxide VLE data were calculated at three temperature–pressure pairs: 233.15 K–2 MPa, 250.5 K–2 MPa, and 250.5 K–3.04 MPa. According to our method, prescribed quantities were the temperature and the liquid composition. Vapor pressure and vapor composition were predicted. The choice of the prescribed quantities, in particular the liquid composition, was made in order to make a direct comparison to experimental data possible. It should be mentioned here that our simulation runs were performed with $N = 500$ particles, which meant that the liquid molar fractions had to be multiples of $1/N = 0.002$. The raw data for both liquid and vapor, Eqs. 3 and 8, were obtained by molecular dynamics simulations.

Altogether, 23 VLE points are given in Table 3, including 8 binary systems. Additionally, the bubble and dew densities are presented. The statistical uncertainties of all values in the phase equilibrium were obtained by the error propagation

Table 2. Unlike Interaction Parameters for the Three Binary Mixtures

Mixture	η	ξ
Methane + ethane	1.00140	0.99923
Methane + carbon dioxide	0.99220	0.95580
Ethane + carbon dioxide	1.00000	0.94691

Table 3. Vapor–Liquid Equilibria of the Ternary Mixture Methane + Ethane + Carbon Dioxide as Obtained from the *NpT* + Test Particle Method*

x_{CH_4}	x_{CO_2}	p_σ MPa	y_{CH_4}	y_{CO_2}	ρ' mol·l^{-1}	ρ'' mol·l^{-1}
T = 233.15 K (p = 2 MPa)						
0.150	0.000	2.004 (37)	0.5825 (73)	0.0000	16.032 (24)	1.247 (26)
0.120	0.134	2.037 (39)	0.4508 (60)	0.1683 (28)	16.488 (29)	1.283 (25)
0.104	0.216	2.077 (64)	0.3983 (53)	0.2447 (37)	16.883 (31)	1.298 (28)
0.080	0.442	1.991 (34)	0.3462 (54)	0.3780 (58)	18.302 (31)	1.250 (25)
0.068	0.562	1.922 (41)	0.3319 (53)	0.4268 (63)	19.312 (28)	1.206 (23)
0.060	0.682	1.974 (49)	0.3381 (65)	0.4619 (73)	20.583 (34)	1.226 (30)
0.050	0.806	2.13 (14)	0.3544 (84)	0.4981 (96)	22.300 (33)	1.269 (55)
0.042	0.958	2.11 (11)	0.465 (18)	0.535 (18)	24.891 (30)	1.257 (66)
T = 250.5 K (p = 2 MPa)						
0.070	0.000	1.951 (19)	0.3095 (51)	0.000	14.816 (25)	1.137 (26)
0.040	0.096	1.997 (33)	0.1754 (30)	0.1762 (27)	15.159 (33)	1.202 (25)
0.014	0.236	2.116 (48)	0.0608 (13)	0.3598 (53)	15.772 (35)	1.288 (31)
0.000	0.336	2.056 (32)	0.0000	0.4691 (63)	16.232 (36)	1.284 (30)
0.000	0.920	2.145 (72)	0.0000	0.8607 (51)	22.235 (45)	1.277 (52)
0.002	0.952	1.905 (62)	0.0205 (10)	0.8889 (42)	22.770 (41)	1.107 (48)
0.008	0.992	2.25 (18)	0.0898 (36)	0.9102 (36)	23.676 (40)	1.236 (67)
T = 250.5 K (p = 3.04 MPa)						
0.174	0.000	3.011 (38)	0.5146 (51)	0.0000	14.804 (35)	1.870 (38)
0.140	0.114	3.041 (31)	0.4100 (50)	0.1476 (20)	15.174 (48)	1.950 (39)
0.110	0.244	3.085 (41)	0.3303 (42)	0.2751 (32)	15.802 (40)	1.993 (39)
0.078	0.488	3.150 (69)	0.2603 (37)	0.4409 (42)	17.241 (51)	1.993 (45)
0.062	0.670	3.018 (45)	0.2490 (39)	0.5325 (48)	18.862 (46)	1.892 (43)
0.058	0.742	3.041 (71)	0.2581 (48)	0.5605.(58)	19.708 (58)	1.895 (49)
0.054	0.826	3.07 (13)	0.2764 (63)	0.5955 (74)	20.886 (42)	1.901 (69)
0.054	0.946	3.135 (75)	0.3646 (94)	0.6354 (94)	23.059 (40)	1.897 (64)

*The numbers in parentheses indicate the statistical uncertainties in the last digits.

law. Figures 1 to 3 compare the present work with the experimental data (Knapp et al., 1990) and with the equation of state results (Ely et al., 1989). The experiment can be used to directly compare 21 of the 23 listed VLE points.

We now discuss the vapor pressures in Table 3. In 12 of 21 cases the predicted vapor pressures agree within their statistical uncertainies, and in 9 cases within 2 times their uncertainties with the experiment. The system at 250.5 K–2 MPa shows the highest disagreement, which is caused by the fact that the very low liquid mole fractions of methane had to be prescribed in multiples of 0.002.

A direct comparison of the predicted vapor compositions with experimental data is possible for 37 mole fractions, of which 28 agree within their statistical uncertainty, and 8

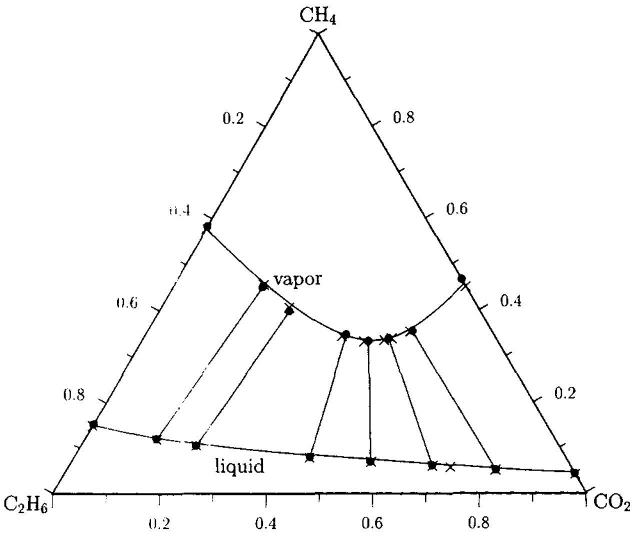

Figure 1. Ternary system at 233.15 K and 2 MPa.

Present results (●) are given in comparison to experimental VLE of Knapp et al. (1990) (×) and to EOS results of Ely et al. (1989) (——).

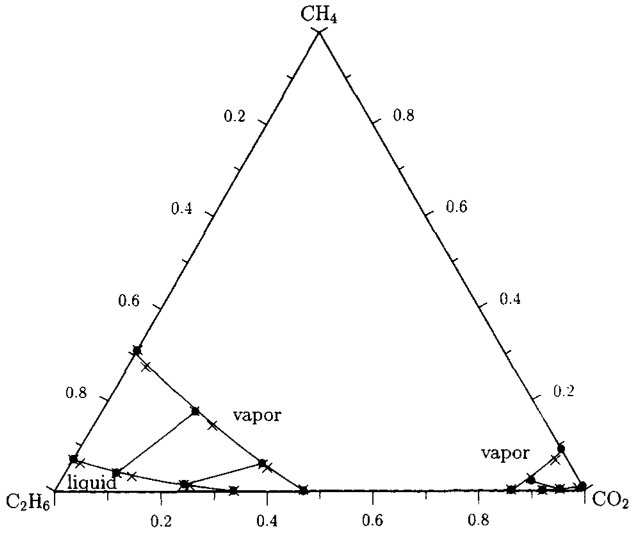

Figure 2. Ternary system at 250.5 K and 2 MPa.

Present results (●) are given in comparison to experimental VLE of Knapp et al. (1990) (×) and to EOS results of Ely et al. (1989) (——).

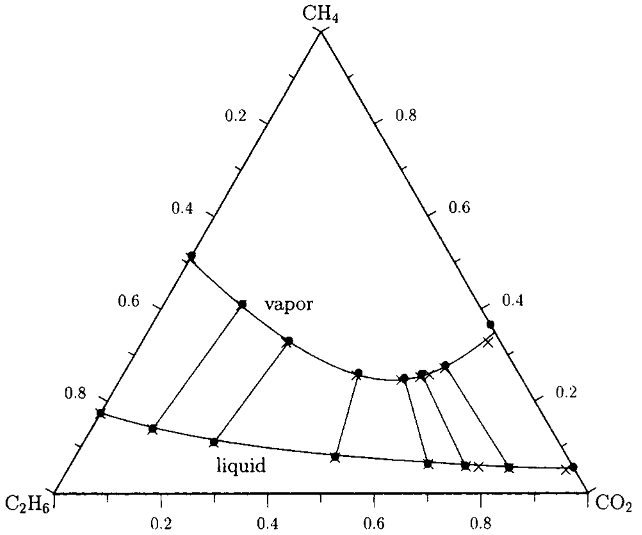

Figure 3. Ternary system at 250.5 K and 3.04 MPa.

Present results (●) are given in comparison to experimental VLE of Knapp et al. (1990) (×) and to EOS results of Ely et al. (1989) (——).

within 2 times their uncertainty. Observing Figures 1 to 3 it can be said that on average our data show a better agreement with the experiment than the equation of state.

Summarizing we can state that we were able to predict the VLE of the ternary mixture methane + ethane + carbon dioxide with very high accuracy from molecular simulation without introducing any ternary parameters. There are two things to say about the further application of the method: (1) in our experience, sufficiently accurate models for the intermolecular potentials between the pure components are very crucial in the prediction of thermodynamic data by molecular simulations; and (2) the method is open for improvement, in particular with respect to the number of simulations in the vapor phase. It is worth mentioning that recently an equation was presented (Boda and Szalai, 1996) that allows us to determine the variation of the chemical potential with respect to the composition $\partial\mu/\partial y$ as fluctuation from one simulation, so that the number of simulation runs in the vapor phase can be reduced to one.

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Notation

k = Boltzmann's constant
L^* = reduced elognation [$L^* = L/\sigma$]
N = number of particles in the simulation box
Q^{*2} = reduced quadrupole moment [$Q^{*2} = Q^2/\epsilon\sigma^5$]

Greek letters

β = Boltzmann's factor
ϵ = energy parameter of the Lennard-Jones potential
η = binary size interaction parameter
ξ = binary energy interaction parameter
σ = size parameter of the Lennard-Jones potential

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Appendix

This appendix summarizes some details of our molecular dynamics simulations. All runs were performed in the *NpT* ensemble with 500 particles. Periodic boundary conditions and the minimum image convention were used, with a cutoff radius of 4σ, where σ is the size parameter of carbon dioxide; long-range corrections were also considered. In the case of quadrupolar interactions, no long-range corrections had to be made. The translational equations of motion were solved with a fifth-order predictor–corrector method. The time step was taken to be 0.0015 in the usual units. Each run was started from a fcc-lattice with 6,000 equilibration time steps; its production length was 50,000 time steps. The pressure was kept constant by the method of Andersen (1980), where the membrane mass was set to 5×10^{-7} in the vapor and 10^{-4} in the liquid; the temperature was kept constant by momentum scaling after each time step. In order to calculate the chemical potentials and the partial molar volumes, Widom's test particle insertion (Widom, 1963) was applied, using 500 test particles for the liquid and 250 for the vapor, after each time step. When quadrupolar particles were inserted, their potential energy ψ was set to infinity when distances were smaller than 0.4σ (Möller and Fischer, 1994). The uncertainties of the results were calculated according to the method of Fincham et al. (1986).

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