

Accurate Computer Simulation of Phase Equilibrium for Complex Fluid Mixtures. Application to Binaries Involving Isobutene, Methanol, Methyl *tert*-Butyl Ether, and *n*-Butane

Martin Lísal,^{*,†,‡} William R. Smith,[†] and Ivo Nezbeda^{‡,§}

Department of Mathematics and Statistics, and School of Engineering, College of Physical and Engineering Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada, E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals, Academy of Sciences, 165 02 Prague 6, Czech Republic, and Department of Physics, J. E. Purkyně University, 400 96 Ústí n. Lab., Czech Republic

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We have developed a new method, called the reaction Gibbs ensemble Monte Carlo (RGEMC) method, for the computer simulation of the phase equilibria for multicomponent mixtures, given an intermolecular potential model for the constituent molecular species. The approach treats the phase equilibrium conditions as a special type of chemical reaction and incorporates knowledge of the pure-substance vapor pressure data into the simulations. Unlike macroscopic thermodynamic-based approaches like the Wilson and the universal quasichemical functional group activity coefficients (UNIFAC) approximations, no experimental information concerning the mixtures is required. In addition to the *PT*_{xy} phase equilibrium data, the volumetric properties of the mixture are calculated. We developed intermolecular potential models based on the optimized potentials for liquid simulations (OPLS) of Jorgensen and used the RGEMC method to predict phase equilibrium data for the binary systems isobutene + methyl *tert*-butyl ether (MTBE) and the binaries formed by methanol with isobutene, MTBE, and *n*-butane. The predictions are excellent, and of comparable accuracy to those obtained using the Wilson and the UNIFAC thermodynamic-based approaches, even though such approaches use experimental mixture information.

1. Introduction

Vapor–liquid phase equilibrium (VLE) calculations in chemistry and chemical engineering are traditionally carried out by means of empirically-based thermodynamic equation of state (EOS) and/or liquid-state activity-coefficient models.^{1,2} The main goal of such calculations is the prediction of the *PT*_{xy} behavior of the mixture (where *P* is the system pressure, *T* the temperature, and *x* and *y* denote the compositions of the coexisting phases). To implement these approaches, one requires as input information accurate data concerning the vapor–pressure behavior of each constituent pure fluid. These data are then combined with the mixture model; in addition, a mixture parameter appearing in the theory is often evaluated by means of an experimental measurement on the mixture. Given this input information, the system behavior is then calculated using standard thermodynamic relations.² The accuracy of these approaches in predicting the experimental data varies; as with all empirically-based methods, the path to further progress is not always clear.

An alternative, and much less well-developed approach, uses as input a molecular-based intermolecular potential model for the species and their interactions. The properties of the mixture are then calculated by computer simulation, using the Gibbs ensemble Monte Carlo (GEMC) method,³ the constant pressure–constant temperature (NPT) + test particle method,⁴ and/or the Gibbs–Duhem integration method.⁵ Molecular-based

simulation approaches have considerable advantage over the empirically-based approaches that predictions may be made in the absence of experimental data of any kind, provided one can construct an intermolecular potential model for the system. The construction of reasonably accurate such models is now a relatively straightforward task.⁶ Similarly, the computer simulation approaches can also calculate the volumetric properties of the mixture, which are often difficult to determine experimentally. However, the accuracy of these approaches for the calculation of phase equilibria has generally been inferior to results obtained from the empirically-based methods, especially for mixtures of any degree of complexity.⁷ This is illustrated by the results of De Pablo and Prausnitz,⁸ and De Pablo et al.,⁹ who applied the GEMC approach to binary alkane mixtures, of Gotlib et al.,¹⁰ Agrawal and Wallis,¹¹ and Strauch and Cummings,¹² who applied the GEMC approach to binary mixtures of methanol + ethane, methanethiol + propane, and methanol + water, respectively, and of Fischer et al., who applied the NPT + test particle method to binary mixtures of methane, ethane, and carbon dioxide,⁴ and to the ternary methane + ethane + carbon dioxide system.¹³

A goal of the aforementioned^{4,6,9,10,13} simulations studies has been to produce effective two-body potentials that can accurately reproduce experimental vapor pressure data for fluids and their mixtures. This goal may be unrealistic because it is likely that three- and higher-body potentials will ultimately be required to accurately calculate the fluid properties from the first principles. In this paper, for mixture *PT*_{xy} calculations we circumvent the problem of obtaining accurate two-body potentials by means of the incorporation of experimental pure-fluid phase equilibrium data into the mixture phase simulations.

* To whom correspondence should be addressed at the Academy of Sciences. E-mail: lisal@icpf.cas.cz.

[†] University of Guelph.

[‡] Academy of Sciences.

[§] J. E. Purkyně University.

A recently proposed molecular-based computer simulation technique that is similar in spirit to the GEMC method is the reaction ensemble Monte Carlo (REMC) method for calculating reaction equilibrium compositions, given an intermolecular potential model for the mixture species.¹⁴ This approach incorporates the ideal-gas driving terms for the reactions, $\{\Delta G_j^0(T)\}$, where $\Delta G_j^0(T)$ is the standard-state Gibbs energy change for reaction j . In addition to simple model molecular systems,¹⁴ the method has recently been applied to chemical reactions at the surfaces¹⁵ and to the bulk $\text{Br}_2 + \text{Cl}_2 + \text{BrCl}$ system.¹⁶

The main goal of this paper is to present a new computer simulation method for calculating phase equilibria in multi-component mixtures. The approach, which is a combination of the GEMC and REMC methods, incorporates knowledge of pure-component vapor–pressure data into the phase equilibrium calculations for the mixtures. Such data are also used by the empirically-based thermodynamic methods; however, unlike these approaches, our approach uses no mixture experimental data of any kind. The motivation for the method arises from considering phase equilibrium as a special case of a chemical reaction.¹⁷ We call the new approach the reaction Gibbs ensemble Monte Carlo (RGEMC) method.

Methyl *tert*-butyl ether (MTBE) is an important chemical used as an antiknock agent in unleaded gasoline. It is synthesized from a catalyzed reaction between isobutene and methanol, typically in the presence of inert C_4 's (e.g. *n*-butane or 1-butene), and the inerts and reaction product are separated by distillation. An important aspect of the modeling of the MTBE system is the prediction of its VLE behavior. We illustrate the RGEMC method on the binary mixtures formed by methanol with isobutene, MTBE, and *n*-butane; we also consider the thermodynamically simpler binary system isobutene + MTBE. These mixtures all display complex behavior, including azeotropy; they hence provide important test systems for predictive methods.

The phase equilibrium properties of the binaries of the MTBE system have been studied experimentally by Gmehling et al.¹⁸ and by Coto et al.¹⁹ Doherty and co-workers^{20,21} and others^{22,23} have calculated the VLE behavior employing thermodynamic approaches using empirically-based EOS and activity coefficient models. We compare the RGEMC results with the experimental data and with these approaches. We use the optimized potentials for liquid simulations (OPLS) considered previously^{24,25} for pure isobutene, methanol, and *n*-butane; the intermolecular potential model for pure MTBE is constructed using the OPLS²⁶ and Chemistry at Harvard Macromolecular Mechanics (CHARMM)²⁷ force fields. We extended these models to mixtures without the incorporation of mixture-dependent parameters.

In the next section of this paper, we describe the RGEMC method. In the following section, we describe the intermolecular potential models used for the species involved. In the subsequent section, we discuss the details of the computer simulations. Subsequent sections discuss the results and present conclusions.

2. The Reaction Gibbs Ensemble Monte Carlo (RGEMC) Method

Vapor pressures, $P^{\text{sat}}(T)$, obtained from pure-fluid GEMC simulations differ from the experimental vapor pressures typically by about 10%.²⁸ This accuracy is not satisfactory for accurate prediction of the $PTxy$ phase equilibrium properties of mixtures. However, it is well-known that the pressure is very sensitive to the form and the parameters of intermolecular potential, whereas other properties are less sensitive.²⁹ Other workers^{10,30} have attempted to address these inaccuracies by modifying the intermolecular potential parameters of the

mixture, in some cases allowing them to be temperature-dependent.⁹ This is typically a very computationally intensive task.

Here, we present an alternative approach to improving the accuracy of mixture phase equilibrium calculations, which is very simple to implement. It relies upon utilizing available information concerning the pure-component vapor–pressure data, as are similarly used in the case of the empirically-based thermodynamic approaches. The key to the RGEMC approach is to consider phase equilibrium as a *chemical reaction*, a viewpoint often taken by workers concerned with the calculation of combined reaction and phase equilibrium.¹⁷

In the following, we assume that experimental vapor–pressure data are available for the pure-fluid components of the mixture, and that preliminary GEMC simulations have been performed for each pure component using the assumed intermolecular potential model. Then, for the gas phase in equilibrium with the liquid for each pure species, we have for the experimental (exp) and the simulation (GEMC) data, respectively:

$$\mu_{i,\text{exp}}^{\text{e,g}} = RT \ln f_{i,\text{exp}}^{\text{sat}} \quad (1)$$

$$\mu_{i,\text{GEMC}}^{\text{e,g}} = RT \ln f_{i,\text{GEMC}}^{\text{sat}} \quad (2)$$

where μ_i^{e} is the excess chemical potential of species i , R is the universal gas constant, f_i is the fugacity of species i , and superscript g denotes the gas phase. Combining the above equations gives

$$\mu_{i,\text{exp}}^{\text{e,g}} = \mu_{i,\text{GEMC}}^{\text{e,g}} + RT \ln \left(\frac{f_{i,\text{exp}}^{\text{sat}}}{f_{i,\text{GEMC}}^{\text{sat}}} \right) \quad (3)$$

$$\approx \mu_{i,\text{GEMC}}^{\text{e,g}} + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) \quad (4)$$

where the last approximation ignores the dependence of the fugacity coefficient ratio on the pressure. Equation 4 is equivalent to writing an accurate total chemical potential of the gaseous species as

$$\mu_i^{\text{g}} = \mu_i^0(T, P^0) + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) + \mu_{i,\text{GEMC}}^{\text{e,g}} \quad (5)$$

where $\mu_i^0(T, P^0)$ is the standard chemical potential in the ideal-gas state at the reference pressure P^0 .³¹ We may combine the first two terms to give

$$\mu_i^{\text{g}} = \mu_i^{0,*}(T, P^0) + \mu_{i,\text{GEMC}}^{\text{e,g}} \quad (6)$$

where $\mu_i^{0,*}(T, P^0)$ is a modified standard chemical potential given by

$$\mu_i^{0,*}(T, P^0) = \mu_i^0(T, P^0) + RT \ln \left(\frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \right) \quad (7)$$

We now use the REMC method for the mixture, incorporating the chemical-reaction-like term, $\mu_i^{0,*}(T, P^0)$ for each gaseous species. We consider phase equilibrium to result from the “chemical reactions”

$$A_i(\text{g}) = A_i(\text{l}) \quad (8)$$

TABLE 1: Lennard-Jones Well Depths ϵ_i and Sizes σ_i , Partial Charges q_i , Intermolecular Rotational Functions $V_i(\Phi)$, and Geometries of Isobutene, Methanol, MTBE, and *n*-Butane

isobutene (1) ²⁴				
atom	ϵ/k_B (K)	σ (Å)	q	geometry
CH ₂ (sp ²)	70.450 323	3.850	0.0	CH ₂ -C: 1.34 Å
C(sp ²)	52.837 742	3.750	0.0	C-CH ₃ : 1.50 Å
CH ₃ (sp ³ ,C ₃)	80.514 654	3.910	0.0	CH ₃ -C-CH ₃ : 124°
methanol (2) ^{24,25}				
atom	ϵ/k_B (K)	σ (Å)	q	geometry
O	85.546 821	3.070	-0.700	O-H: 0.945 Å
H	0.0	0.0	0.435	CH ₃ -O: 1.430 Å
CH ₃ (sp ³ ,C ₁)	104.165 83	3.775	0.265	CH ₃ -O-H: 108.5°
MTBE (3) ^{24,26}				
atom	ϵ/k_B (K)	σ (Å)	q	geometry
¹ CH ₃ (sp ³)	85.546 821	3.800	0.25	¹ CH ₃ -O: 1.41 Å
O	85.546 821	3.800	-0.50	O-C: 1.41 Å
C(sp ³)	25.160 83	3.800	0.25	C- ² CH ₃ : 1.53 Å
² CH(sp ³)	72.966 406	3.960	0.0	¹ CH ₃ -O-C: 112°
$V_3(\Phi) = V_0(1 + \cos 3\Phi)$ $V_0/k_B = 543.47391$ K ²⁷				O-C- ² CH ₃ : 112°
<i>n</i> -butane (4) ²⁴				
atom	ϵ/k_B (K)	σ (Å)	q	geometry
CH ₃ (sp ³ ,C ₂)	88.062 903	3.905	0.0	C-C: 1.53 Å
CH ₂ (sp ³)	59.379 558	3.905	0.0	C-C-C: 112°
$V_4(\Phi) = (V_1/2)(1 + \cos \Phi) + (V_2/2)(1 - \cos 2\Phi) + (V_3/2)(1 + \cos 3\Phi)$ $V_1/k_B = 765.895$ 65 K; $V_2/k_B = -158.513$ 23 K; $V_3/k_B = 1613.8156$ K				

where A_i denotes a particular species and l denotes the liquid phase. The phase equilibrium condition is the equality of the chemical potentials of each species in each phase, or equivalently that the total Gibbs energy change vanishes across the reaction. The standard Gibbs energy change for the reaction of eq 8 is

$$\Delta G_i^0(T) = RT \ln \left(\frac{P_{i,\text{GEMC}}^{\text{sat}}}{P_{i,\text{exp}}^{\text{sat}}} \right) \quad (9)$$

The REMC method requires as input an intermolecular potential model and the standard Gibbs energy changes for each reaction i , the latter incorporated in the ideal-gas driving term Γ_i for the reaction, given by

$$\Gamma_i \equiv \exp \left[-\frac{\Delta G_i^0(T)}{RT} \right] = \frac{P_{i,\text{exp}}^{\text{sat}}}{P_{i,\text{GEMC}}^{\text{sat}}} \quad (10)$$

By considering the mixture phase equilibrium as resulting from the set of reactions denoted by eq 8, we may implement the REMC method by utilizing the following transition probability expressions for the transfer of particles between liquid and vapor boxes in the mixture simulation. When the phase equilibrium is treated as the chemical reaction (8), the transition probability $k \rightarrow l$ for the transfer of a particle from a liquid box (l) into a vapor box (g) is¹⁴

$$P_{kl}^{l \rightarrow g} = \min \left\{ 1, \Gamma_i \exp \left[-\beta \Delta U_{kl}^l - \beta \Delta U_{kl}^g + \ln \frac{N^l V^g}{(N^g + 1) V^l} \right] \right\} \quad (11)$$

and similarly, the transition probability $k \rightarrow l$ for the transfer

of a particle from a vapor box (g) into a liquid box (l) is¹⁴

$$P_{kl}^{g \rightarrow l} = \min \left\{ 1, \frac{1}{\Gamma_i} \exp \left[-\beta \Delta U_{kl}^g - \beta \Delta U_{kl}^l + \ln \frac{N^g V^l}{(N^l + 1) V^g} \right] \right\} \quad (12)$$

In eqs 11 and 12, $\beta = 1/(k_B T)$ and k_B is Boltzmann's constant, $\Delta U_{kl}^\alpha = U_l^\alpha - U_k^\alpha$ is the change in configurational energy in box α , V^α is the volume of box α , and N^α is the total number of molecules in box α . In eqs 11 and 12, the ideal-gas driving term Γ_i for the phase equilibrium reaction i is given by eq 10.

3. Intermolecular Potential Models

The intermolecular potentials used in our simulations are extensions of the OPLS potential models of Jorgensen et al. for liquid hydrocarbons, alcohols, and alkyl ethers^{24–26} to a multicomponent mixture involving isobutene, methanol, MTBE, and *n*-butane. The molecules are described by interaction sites located on the nuclei, in which the CH_{*n*} groups are treated as united atoms centered on the carbons. The interactions among the molecules are represented by site–site potentials; the interaction between atom a and b in different molecules is described by the Lennard-Jones (LJ) and Coulombic potentials

$$u_{ab}(r_{ab}) = \frac{A_{ab}}{r_{ab}^{12}} - \frac{C_{ab}}{r_{ab}^6} + \frac{q_a q_b e^2}{4\pi\epsilon_0 r_{ab}} \quad (13)$$

In eq 13, the parameters A_{ab} and C_{ab} can be expressed in terms of LJ parameters via

$$A_{aa} = 4\epsilon_a \sigma_a^{12} \quad C_{aa} = 4\epsilon_a \sigma_a^6 \quad (14)$$

TABLE 2: Molar Volume V and Configurational Energy U (Sum of the Lennard-Jones and Coulombic Energies) from the Monte Carlo Simulations of This Work, Previous Works, and Experiments for Liquid Isobutene, Methanol, MTBE, and n -Butane at Pressure of 1 atm and Room Temperature (The Simulation Uncertainties Are Given in the Last Digits as Subscripts)

component	T (K)	V (cm ³ /mol)			U (kJ/mol)		
		this work	refs 24 and 25	exptl ³⁵	this work	refs 24 and 25	exptl ³⁵
isobutene (1)	298.15	99.26 ₉₁	99.00 ₇₃	95.39	-17.85 ₁₈	-17.87 ₉	-18.11
methanol (2)	298.15	41.99 ₅₅	42.22 ₁₈	40.73	-35.82 ₃₄	-35.94 ₈	-35.47
MTBE (3)	293.15	117.1 ₇	n.a.	118.83	-28.49 ₂₀	n.a.	-27.59
n -butane (4)	298.15	101.7 ₁₀	101.59 ₇	101.46	-19.23 ₂₁	-19.16 ₁₃	-18.61

TABLE 3: Vapor–Liquid Equilibrium Data for Isobutene, Methanol, MTBE, and n -Butane from the Gibbs Ensemble Monte Carlo Simulations of This Work^a

isobutene (1)					
T (K)	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)	P^{sat} (bar)
400	-2.51 ₃₃	-12.51 ₃₅	852.7 ₁₁₂₀	135.0 ₃₉	25.41 ₁₈₁
380	-1.73 ₁₆	-13.86 ₁₉	1249 ₁₁₀	122.6 ₁₇	18.34 ₁₂₂
350	-1.11 ₁₁	-15.47 ₁₈	2266 ₂₂₅	111.5 ₁₃	10.51 ₈₈
320	-0.59 ₇	-16.89 ₁₆	4635 ₅₁₄	103.7 ₉	5.13 ₅₀
methanol (2)					
T (K)	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)	P^{sat} (bar)
450	-5.94 ₅₇	-21.39 ₆₉	660.8 ₃₈₈	66.18 ₃₆₅	24.07 ₂₆₇
420	-5.02 ₆₁	-24.95 ₃₃	1184 ₉₅	54.78 ₁₀₆	13.23 ₂₀₈
400	-2.78 ₇₅	-25.91 ₅₂	2672 ₃₀₄	52.06 ₂₃₄	8.35 ₃₇
360	-1.65 ₇₃	-29.41 ₃₅	7672 ₃₄₈₄	48.44 ₁₁₄	2.94 ₅₁
320	-0.49 ₃₈	-31.90 ₁₈	41950 ₆₀₃₀	46.36 ₅₁	0.59 ₃₀
MTBE (3)					
T (K)	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)	P^{sat} (bar)
480	-2.79 ₂₁	-17.55 ₃₆	1465 ₁₀₅	170.4 ₃₄	19.26 ₁₀₀
440	-1.43 ₂₁	-20.27 ₂₇	2932 ₃₆₄	150.5 ₁₉	10.08 ₃₇
400	-0.86 ₁₀	-22.86 ₂₁	5807 ₆₃₃	136.8 ₁₁	5.05 ₅₁
360	-0.37 ₁₅	-24.98 ₁₆	15390 ₂₂₆₀	128.2 ₇	1.84 ₂₆
320	-0.14 ₉	-27.22 ₁₇	44410 ₁₈₇₆	120.6 ₆	0.59 ₂₄
n -butane (4)					
T (K)	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)	P^{sat} (bar)
410	-2.50 ₁₃	-13.63 ₁₇	985.1 ₄₉₅	136.0 ₁₇	23.39 ₆₇
380	-1.51 ₁₅	-15.34 ₁₈	1774 ₁₆₉	122.2 ₁₄	13.84 ₉₉
350	-0.86 ₉	-16.84 ₁₂	3344 ₃₃₂	113.1 ₈	7.44 ₆₂
320	-0.46 ₇	-18.22 ₁₃	6760 ₉₅₇	106.1 ₆₆	3.57 ₄₈

^a T is the temperature, U is the configurational energy (sum of the Lennard-Jones and Coulombic energies), V is the molar volume, and P^{sat} is the vapor pressure. Superscripts g and l denote the vapor and liquid phases, respectively. The simulation uncertainties are given in the last digits as subscripts.

TABLE 4: Critical Temperature T_c , Pressure P_c , and Molar Volume V_c , and Constants A , B , and C for the Antoine Vapor–Pressure Equation (eq 19) for Pure Isobutene, Methanol, MTBE, and n -Butane Obtained from our Gibbs Ensemble Monte Carlo Simulation Results of Table 3 (The Corresponding Experimental Values^{35,37,20} Are Given in Parentheses)

component	T_c (K)	P_c (bar)	V_c (cm ³ /mol)	A	B	C
isobutene (1)	432.7 (417.9)	40.0 (40.0)	247 (239)	8.4977389 (9.132635)	-1817.1451 (-2125.74886)	-54.720771 (-33.160)
methanol (2)	495.6 (512.6)	51.5 (80.9)	118 (118)	10.765146 (11.986965)	-3106.2980 (-3643.31362)	-40.414885 (-33.434)
MTBE (3)	532.4 (496.4)	38.4 (33.7)	334 (327)	10.355395 (9.203235)	-3759.4247 (-2571.58460)	28.103582 (-48.406)
n -butane (4)	452.0 (425.2)	43.7 (38.0)	257 (255)	9.9881261 (9.382695)	-2859.4255 (-2320.51670)	8.3404439 (-24.932)

where ϵ_a and σ_a are the LJ well depth and size, respectively, for atom a , r_{ab} is the distance between atoms a and b in different molecules; q_a and q_b are the partial charges on these atoms, ϵ_0 is the permittivity of free space, and e is the unit charge. The OPLS combining rules for A_{ab} and C_{ab} are

$$A_{ab} = \sqrt{A_{aa}A_{bb}} \quad C_{ab} = \sqrt{C_{aa}C_{bb}} \quad (15)$$

The molecular bond lengths and angles were fixed, on the basis

of microwave results,^{24,25} and internal rotations of the monomers were included. The values of the potential parameters, intermolecular rotational potential functions, and molecular bond lengths and angles are given in Table 1.

4. Computational Details

For the pure fluids, we used constant pressure–constant temperature (NPT) Monte Carlo (MC) simulations²⁹ and constant volume–constant temperature (NVT) GEMC³² and

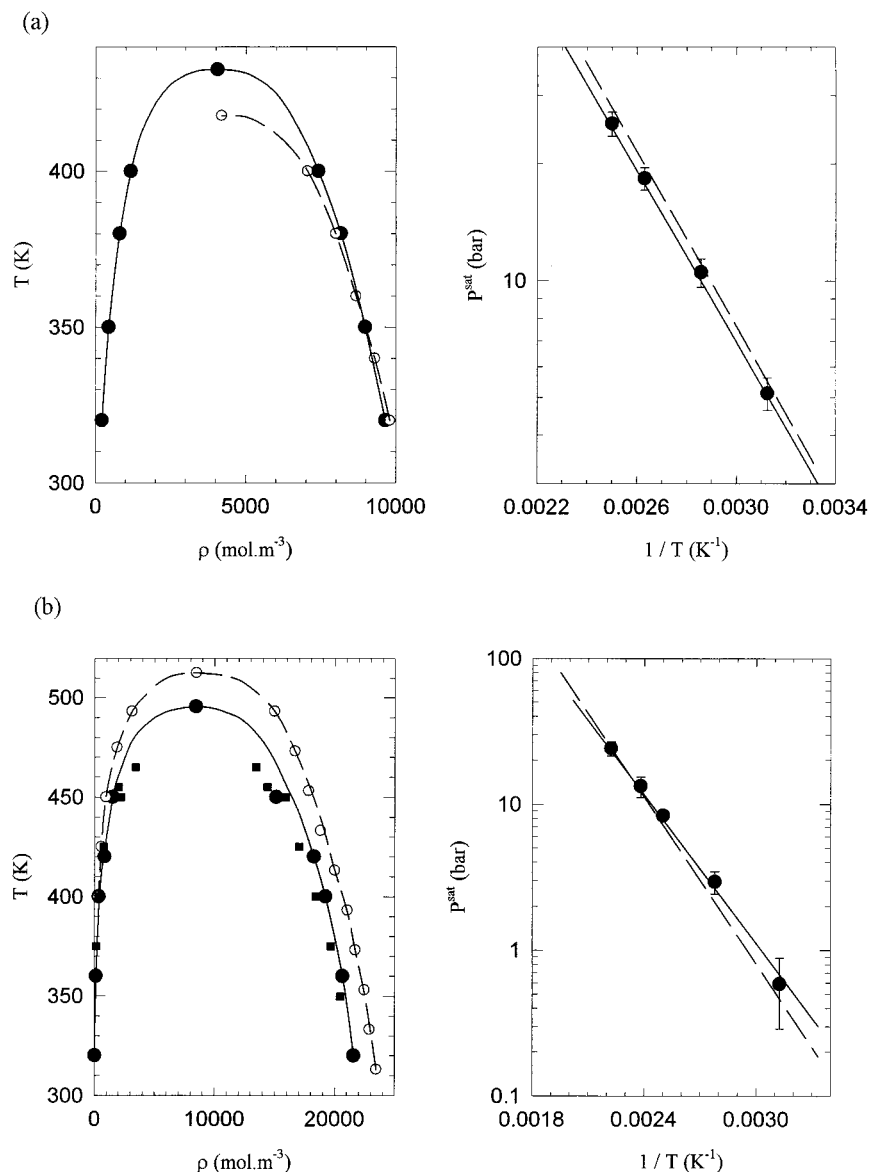


Figure 1. Vapor–liquid coexistence curves for (a) isobutene and (b) methanol. Filled circles are the Gibbs ensemble Monte Carlo (GEMC) simulation results of this work and open circles are the experimental data.^{39,40,42} Filled squares are the GEMC simulation results of Van Leeuwen and Smit³⁸ for methanol. The curves drawn through the coexistence densities are guides for the eye only. The solid line through the GEMC simulation vapor pressures represents fits of the data to the Antoine equation, and the dashed line represents the experimentally correlated vapor pressures using the Antoine equation.²⁰

NVT RGEMC simulations to determine pure liquid properties and vapor–liquid coexistence curves, respectively. For the NPT MC and NVT GEMC and NVT RGEMC simulations, we used $N = 256$ and 512 particles, respectively, in cubic boxes with the minimum image convention and periodic boundary conditions, and with cut-off radius r_c equal to one-half the box length. The LJ long-range corrections for the configurational energy and the virial were included,²⁹ assuming that the radial distribution functions are unity beyond the cut-off radius. We treated the Coulombic long-range interactions by the reaction-field method.³³ Equation 13 can then be rewritten as

$$u_{ab}(r_{ab}) = \frac{A_{ab}}{r_{ab}^{12}} - \frac{C_{ab}}{r_{ab}^6} + \frac{q_a q_b e^2}{4\pi\epsilon_0 r_{ab}} \left[1 + \frac{\epsilon_{RF} - 1}{2\epsilon_{RF} + 1} \left(\frac{r_{ab}}{r_c} \right)^3 \right] \quad (16)$$

where ϵ_{RF} is the dielectric constant. For moderately and highly polar liquids, the factor $(\epsilon_{RF} - 1)/(2\epsilon_{RF} + 1)$ is very close to

0.5 (corresponding to $\epsilon_{RF} = \infty$, i.e., the conducting boundary condition), and thus we assumed $\epsilon_{RF} = \infty$ in all cases.

The NPT MC, NVT GEMC, and NVT RGEMC simulations were organized in cycles as follows. Each cycle consisted of two and three steps, respectively: n_D translational and rotational moves, n_V volume moves, and n_T particle transfers (in the case of the NVT GEMC and NVT RGEMC simulations). The types of moves were selected at random with fixed probabilities, chosen so that the appropriate ratio of moves was obtained. In the case of the NPT MC simulations, the ratio $n_D:n_V$ was set at $N:1$. In the case of the NVT GEMC and NVT RGEMC simulations, $n_D:n_V:n_T$ was set at $N:1:5000$. The acceptance ratios for translational and rotational moves, and for volume changes, were adjusted to approximately 30%. After an initial equilibration period of $1-2 \times 10^4$ cycles, we generated (depending on the thermodynamic conditions) between 0.5 and 1×10^5 cycles to accumulate averages of the desired quantities. The precision of the simulated data was obtained using block averages, with 500 cycles per block. In addition to ensemble averages of the

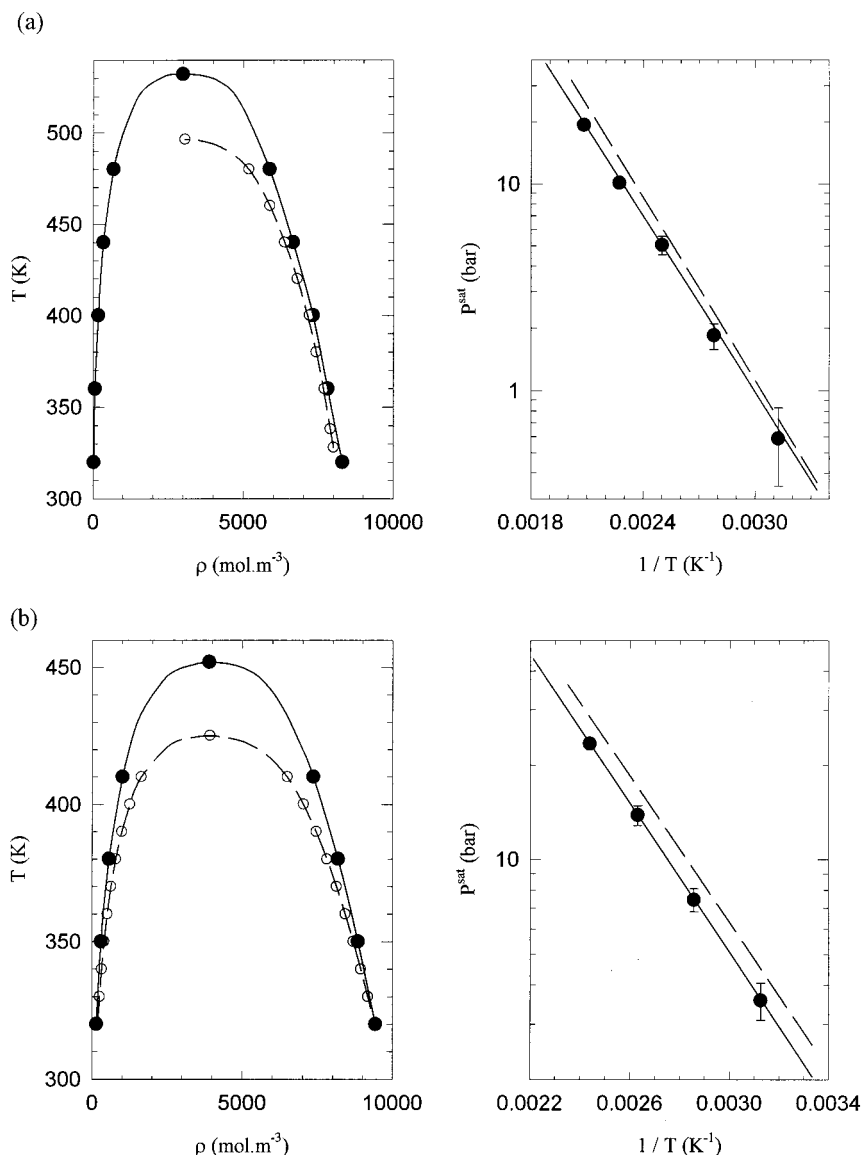


Figure 2. Vapor–liquid coexistence curves for (a) MTBE and (b) *n*-butane. Filled circles are the Gibbs ensemble Monte Carlo (GEMC) simulation results of this work and open circles are the experimental data.^{40,41} The curves drawn through the coexistence densities are guides for the eye only. The solid line through the GEMC simulation vapor pressures represents fits of the data to the Antoine equation, and the dashed line represents the experimentally correlated vapor pressures using the Antoine equation.²⁰

quantities of direct interest, we also monitored the convergence profiles of the thermodynamic quantities, to keep the development of the system under careful control.³⁴

For the binaries, we used NPT RGEMC and NPT GEMC simulations to determine the vapor–liquid coexistence curves. As for the pure fluid simulations, the NPT RGEMC and NPT GEMC simulations were organized in cycles as follows. Each cycle consisted of three steps: n_D translational and rotational moves, n_V volume moves, and n_T particle transfers. The three types of moves were selected at random with fixed probabilities, chosen so that the appropriate ratios of each type of move were obtained. The ratio $n_D:n_V:n_T$ in the cycle was set to $N:2:5000$. The other simulation details were the same as those in the case of the pure simulations. The initial equilibration period required $0.5\text{--}1 \times 10^5$ cycles and final production runs were carried out using between 1 and 2×10^5 cycles.

5. Results and Discussion

5.1 Pure Fluids. Our new MC simulation results for the pure liquids at $P = 1$ atm and room temperature are given in

Table 2, where they are compared with previously published simulation results^{24,25} and with the experimental data.³⁵ The results show that our NPT MC simulation results agree within their statistical uncertainties with the previously published simulation results^{24,25} and the simulation results for liquid molar volumes and configurational energies of all pure fluids are within 2–4% of the experimental values.³⁵ Also, the model for MTBE constructed using the OPLS²⁶ and CHARMM²⁷ force fields reproduces the experimental liquid molar volume and configurational energy³⁵ within 2 and 4%, respectively.

Our new GEMC VLE simulation data for the pure fluids are given in Table 3. We estimated the critical temperatures T_c and densities ρ_c from a least-squares fit of the rectilinear diameter law³⁶

$$\frac{\rho_g + \rho_l}{2} = \rho_c + C_1(T - T_c) \quad (17)$$

and the critical scaling relation³⁶

TABLE 5: Vapor–Liquid Equilibrium Data for the Isobutene + MTBE System at the Temperature 350 K from the Gibbs Ensemble Monte Carlo (GEMC) and Reaction Gibbs Ensemble Monte Carlo (RGEMC) Simulations of This Work^a

GEMC: isobutene (1) + MTBE (3); $T = 350$ K								
P (bar)	x_1	x_3	y_1	y_3	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)
1.51 ₂₅	0	1	0	1	−0.26 ₁₁	−25.62 ₁₆	20770 ₃₇₅₀	126.13 ₇
3.0	0.1723 ₁₁₅	0.8277 ₁₁₅	0.6107 ₂₀₆	0.3893 ₂₀₆	−0.40 ₁₂	−23.49 ₂₆	9085 ₉₆	123.8 ₉
5.5	0.4300 ₂₅₉	0.5700 ₂₅₉	0.8206 ₁₄₉	0.1794 ₁₄₉	−0.62 ₁₈	−20.75 ₃₂	4756 ₇₀	119.6 ₁₂
8.0	0.7557 ₁₆₈	0.2443 ₁₆₈	0.9393 ₁₁₅	0.0607 ₁₁₅	−0.84 ₁₃	−17.54 ₂₂	3143 ₆₀	115.0 ₈
10.51 ₈₈	1	0	1	0	−1.11 ₁₁	−15.47 ₁₈	2266 ₂₂₅	111.5 ₁₃
RGEMC: isobutene (1) + MTBE (3); $T = 350$ K								
P (bar)	x_1	x_3	y_1	y_3	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)
1.93 ₄₀	1	0	1	0	−0.46 ₁₆	−25.51 ₁₇	14070 ₃₁₆₀	126.3 ₇
3.0	0.1193 ₁₀₈	0.8807 ₁₀₈	0.4557 ₁₄₂	0.5443 ₁₄₂	−0.47 ₁₂	−24.11 ₂₅	8995 ₁₃₃	124.5 ₉
5.5	0.3642 ₁₉₄	0.6358 ₁₉₄	0.7492 ₁₅₁	0.2508 ₁₅₁	−0.68 ₁₇	−21.46 ₃₀	4718 ₈₀	120.5 ₉
8.0	0.6554 ₂₁₇	0.3446 ₂₁₇	0.8907 ₁₁₆	0.1093 ₁₁₆	−0.91 ₁₄	−18.53 ₂₇	3081 ₇₄	116.2 ₇
11.04 ₇₆	1	0	1	0	−1.18 ₁₂	−15.44 ₁₇	2115 ₁₈₆	111.7 ₁₁

^a T is the temperature, x_i and y_i are the mole fractions of liquid and vapor, respectively, P is the pressure, U is the configurational energy (sum of the Lennard-Jones and Coulombic energies), and V is the molar volume. Superscripts g and l denote the vapor and liquid phases, respectively. The simulation uncertainties are given in the last digits as subscripts.

TABLE 6: Vapor–Liquid Equilibrium Data for the Isobutene + Methanol, Methanol + MTBE and Methanol + *n*-Butane Systems from the Reaction Gibbs Ensemble Monte Carlo Simulations of This Work^a

isobutene (1) + methanol (2); $T = 323.15$ K								
P (bar)	x_1	x_2	y_1	y_2	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)
0.52 ₈	0	1	0	1	−0.55 ₅₅	−31.68 ₃₂	47300 ₇₆₀	46.49 ₇₈
2	0.0321 ₁₂₁	0.9679 ₁₂₁	0.7339 ₂₂₈	0.2661 ₂₂₈	−0.29 ₁₃	−31.48 ₄₅	12960 ₂₆₀	47.23 ₁₁₄
4	0.1297 ₁₆₆	0.8703 ₁₆₆	0.8547 ₂₀₇	0.1453 ₂₀₇	−0.48 ₇	−29.45 ₄₉	6209 ₁₃₀	53.56 ₁₂₃
6	0.3192 ₄₆₃	0.6808 ₄₆₃	0.9017 ₁₄₅	0.0983 ₁₄₅	−0.66 ₁	−26.36 ₉₃	3962 ₇₁	64.31 ₂₉₈
6.17 ₅₄	1	0	1	0	−0.71 ₉	−16.76 ₁₂	3771 ₃₉₅	104.3 ₇
methanol (2) + MTBE (3); $T = 338.15$ K								
P (bar)	x_1	x_2	y_1	y_2	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)
1.36 ₂₇	0	1	0	1	−0.29 ₁₂	−26.15 ₂₁	21960 ₅₀₀	124.2 ₈
1.55	0.0993 ₁₆₄	0.9007 ₁₆₄	0.2277 ₁₅₃	0.7723 ₁₅₃	−0.52 ₂₇	−26.28 ₂₈	17220 ₃₉₀	116.2 ₁₅
1.55	0.7296 ₁₅₆	0.2704 ₁₅₆	0.5168 ₂₇₉	0.4832 ₂₇₉	−0.88 ₁₇	−30.54 ₂₃	16940 ₄₇₀	66.21 ₁₁₈
1.4	0.8228 ₉₇	0.1772 ₉₇	0.5967 ₃₄₄	0.4033 ₃₄₄	−0.54 ₁₈	−31.28 ₁₈	18930 ₇₂₀	58.94 ₉₂
1.2	0.9297 ₈₄	0.0703 ₈₄	0.7195 ₂₂₅	0.2805 ₂₂₅	−0.76 ₃₁	−32.37 ₃₃	22030 ₁₃₁₀	50.24 ₇₄
1.08 ₁₆	1	0	1	0	−0.99 ₂₇	−30.81 ₁₇	21080 ₂₂₅₀	47.22 ₄₁
methanol (2) + <i>n</i> -butane (4); $T = 350$ K								
P (bar)	x_1	x_2	y_1	y_2	U_g (kJ/mol)	U_l (kJ/mol)	V_g (cm ³ /mol)	V_l (cm ³ /mol)
10.17 ₉₈	0	1	0	1	−1.28 ₁₃	−16.90 ₁₃	2259 ₂₉₃	112.7 ₉
9.5	0.6247 ₁₇₀	0.3753 ₁₇₀	0.1903 ₂₄₁	0.8097 ₂₄₁	−1.10 ₁₈	−23.63 ₂₄	2575 ₈₂	74.15 ₁₄
8	0.8521 ₁₂₉	0.1479 ₁₂₉	0.2334 ₂₆₇	0.7666 ₂₆₇	−0.91 ₁₅	−27.45 ₂₉	3160 ₁₁₀	57.54 ₁₀
6	0.9276 ₁₃₅	0.0724 ₁₃₅	0.3173 ₂₀₁	0.6827 ₂₀₁	−0.84 ₂₁	−28.96 ₂₇	4361 ₁₈₂	52.05 ₁₄
4	0.9700 ₁₀₀	0.0300 ₁₀₀	0.3904 ₂₀₅	0.6096 ₂₀₅	−0.62 ₁₄	−31.60 ₄₃	6775 ₂₀₈	47.74 ₁₀
1.59 ₂₉	1	0	1	0	−1.27 ₅₁	−30.06 ₂₈	11620 ₁₁₂₀	47.88 ₅₆

^a T is the temperature, x_i and y_i are the mole fractions of liquid and vapor, respectively, P is the pressure, U is the configurational energy (sum of the Lennard-Jones and Coulombic energies), and V is the molar volume. Superscripts g and l denote the vapor and liquid phases, respectively. The simulation uncertainties are given in the last digits as subscripts.

$$\rho_l - \rho_g = C_2(T_c - T)^{1/3} \quad (18)$$

For each species, the estimated critical temperature and critical volume, $V_c = 1/\rho_c$, are given in Table 4 together with the corresponding experimental values.^{35,37}

We fitted the vapor pressure curves for all pure fluids to the Antoine equation:³⁵

$$\ln P^{\text{sat}} = A + \frac{B}{T + C} \quad (\text{bar, K}) \quad (19)$$

The Antoine constants are also given in Table 4 together with the critical pressures P_c obtained from the Antoine equation. In Table 4, we also list the corresponding experimental Antoine constants²⁰ and the experimental values of P_c .³⁷

The estimated critical temperatures in Table 4 are higher than the experimental values by about 10% for isobutene, MTBE, and *n*-butane. For methanol, the estimated critical temperature is lower than the experimental value by about 10%. The estimated critical molar volumes of all pure fluids are in very good agreement with experimental values. The estimated critical pressures are higher than the experimental values by about 15% for MTBE and for *n*-butane. For methanol, the estimated critical pressure is lower than the experimental value by nearly 40%.

The vapor–liquid coexistence curves for isobutene and for methanol are shown in Figure 1, and those for MTBE and *n*-butane are shown in Figure 2. The coexistence densities of methanol from the GEMC simulations of Van Leeuwen and Smit,³⁸ obtained using the same intermolecular potential model as that used in this work, are also plotted in Figure 1b. The

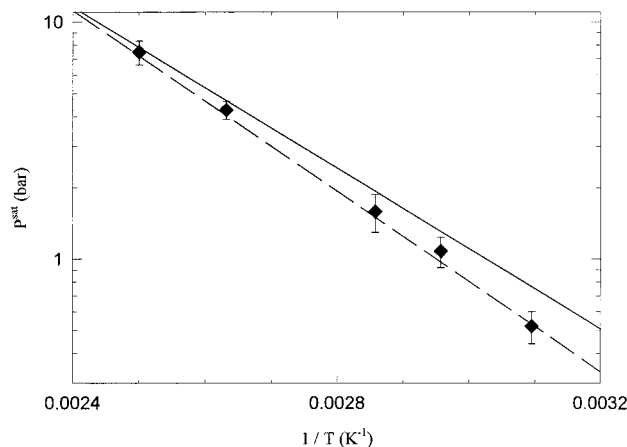


Figure 3. The vapor–pressure curve for pure methanol in the temperature interval considered for the binary fluid simulations of Figures 4 and 5. Filled diamonds are the reaction Gibbs ensemble Monte Carlo simulation results of this work; the solid line represents the correlated Gibbs ensemble Monte Carlo simulation vapor pressures of this work by the Antoine equation and the dashed line represents experimentally correlated vapor pressures using the Antoine equation.²⁰

agreement between our and Van Leeuwen and Smit's results is very good (By way of comparison, Van Leeuwen and Smit used only 216 molecules in their simulations, whereas our simulations used 512 molecules; they used the Ewald sum method for the Coulombic long-range interactions,²⁹ whereas our simulations used the reaction field method). Van Leeuwen and Smit did not report the simulation vapor pressures. Figures 1 and 2 show that the simulated coexistence densities are in good agreement with the experimental values.^{39–42} The agreement is better at lower temperatures, probably because the OPLS potential parameters used were adjusted to $P = 1$ atm and room temperature.

Figures 1 and 2 show that the pure-fluid simulation vapor pressures are lower than the experimentally correlated $P^{\text{sat}}(T)$,²⁰ typically by about 10% for isobutene, MTBE, and *n*-butane. For methanol, the simulation values $P^{\text{sat}}(T)$ are higher than the experimentally correlated $P^{\text{sat}}(T)$ values²⁰ for temperatures up to about 400 K; for higher temperatures, they are lower. Figures 1 and 2 show that the intermolecular potential models represent reasonably well the pure-fluid coexistence properties for temperatures up to about $0.8T_c$.

The basic approximation used for the calculation of the mixture phase equilibria is eq 4 for the pure fluids. To demonstrate its accuracy in the case of pure fluids, in Figure 3 we show the vapor pressure curve for pure methanol over the temperature interval considered for our binary simulations (see next section), as calculated by the RGEMC method. It is seen that the simulation points lie essentially on the experimental curve within their uncertainties. Similar results were obtained for the other pure fluids.

5.2. Binaries. We calculated the VLE behavior for the isobutene + MTBE system using both GEMC and RGEMC simulations, i.e., with $\Gamma_i = 1$ and $\Gamma_i = P^{\text{sat}}_{i,\text{exp}}/P^{\text{sat}}_{i,\text{GEMC}}$, respectively. Both sets of simulation data for this system are given in Table 5, and they are also shown, together with our calculated predictions using the Wilson²⁰ and the UNIFAC³⁵ methods, in Figure 4. Figure 4 shows that the GEMC simulation results are at much lower pressures in comparison to those of the Wilson and UNIFAC methods; the principal reason is due to the fact that the simulation pure-fluid vapor pressures are lower than the experimental values.²⁰ Figure 4 also shows that the RGEMC results are a significant improvement in comparison

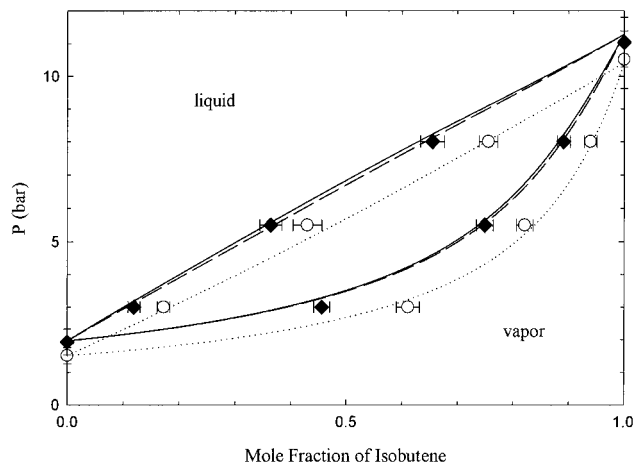


Figure 4. Figure 4. The pressure–composition diagram for the isobutene + MTBE system at the temperature 350 K. Open circles and filled diamonds are the Gibbs ensemble Monte Carlo (GEMC) and the reaction Gibbs ensemble Monte Carlo simulation results of this work, respectively. The solid and dashed lines represent our calculated predictions using the Wilson²⁰ and the UNIFAC methods,³⁵ respectively. The dotted curves drawn through the GEMC simulation data are guides for the eye only.

with the GEMC simulations. The vapor and liquid compositions are in excellent agreement with the predictions using the Wilson²⁰ and UNIFAC³⁵ methods.

Whereas Figure 4 shows that the isobutene + MTBE system follows Raoult's law, the binary mixtures of methanol with each of isobutene, MTBE, and *n*-butane are highly nonideal.⁴³ Experimental data exist for only the methanol + isobutene¹⁸ and the methanol + MTBE mixtures.¹⁹

Our new RGEMC simulation data for all the methanol binary systems are given in Table 6. The P_{xy} diagrams for these mixtures are shown in Figure 5 at individual temperatures. In Figure 5, we compare the results from our RGEMC simulations with available experimental data, and with our predictions using the Wilson and UNIFAC methods. For the methanol + isobutene system, the simulated compositions agree within their statistical uncertainties with the experimental data;¹⁸ the Wilson method also agrees quite well with the experimental values and is slightly better than the UNIFAC method. For the methanol + MTBE system, the simulated liquid compositions again agree within their statistical uncertainties with the experimental values;¹⁹ the simulated vapor compositions show small deviations from the experimental values. The UNIFAC method results are in excellent accord with the experimental results; the Wilson method overpredicts the experimental compositions. There are no experimental data for the methanol + *n*-butane system; hence, we compare our simulations only with predictions using the Wilson and UNIFAC methods. The simulated liquid compositions essentially agree within their statistical uncertainties with the predictions of the Wilson method; the UNIFAC method yields liquid compositions above those of both the simulated values and the Wilson method. The simulated vapor compositions are slightly lower than the values predicted by the Wilson and UNIFAC methods.

5.3 Extension to More Complex Systems. The RGEMC method may be applied to multicomponent systems exhibiting phase equilibrium, including the case of systems also exhibiting chemical reaction. A relatively simple example (recently studied by us¹⁶) of the latter situation is the $\text{Br}_2 + \text{Cl}_2 + \text{BrCl}$ system, which exhibits combined reaction and phase equilibrium behavior. The systems studied in the present paper show that the RGEMC method produces accurate results for mixture phase

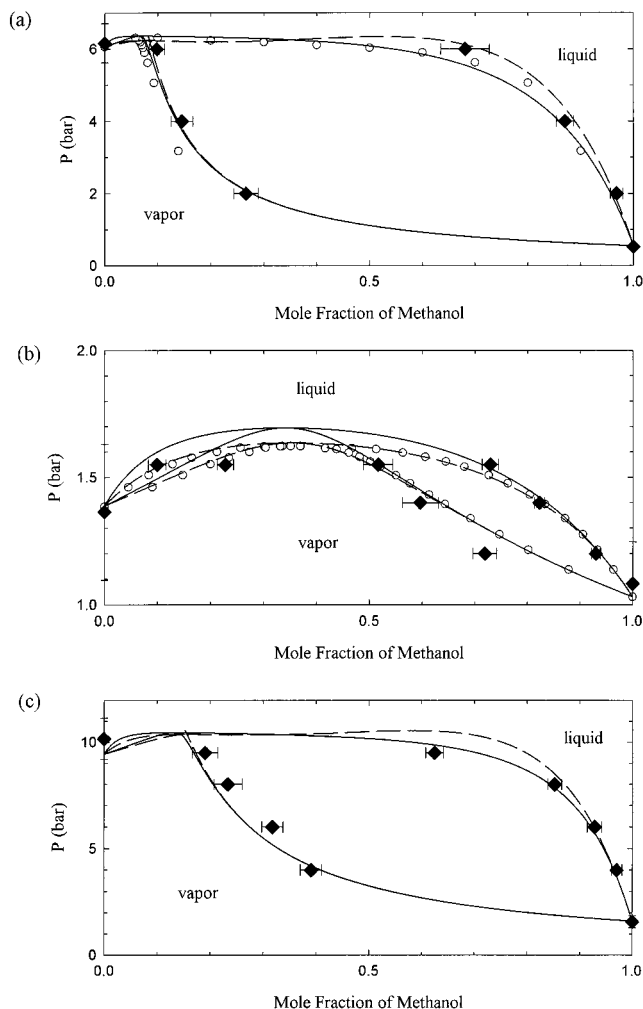


Figure 5. The pressure–composition diagram for the binary mixtures of methanol with isobutene, MTBE, and *n*-butane. Open circles are the experimental data (if available) and filled diamonds are the reaction Gibbs ensemble Monte Carlo simulation results of this work. The solid and dashed lines represent our calculated predictions using the Wilson²⁰ and the UNIFAC methods,³⁵ respectively. (a) The methanol + isobutene system at the temperature 323.15 K. Experimental data were taken from ref 18. (b) The methanol + MTBE system at the temperature 338.15 K. Experimental data were taken from ref 19. (c) The methanol + *n*-butane system at the temperature 350 K.

equilibria in the absence of chemical reactions, even for complex systems with (physically) associating components such as methanol. The method can also be applied in principle to systems that must be modeled as containing chemically associating fluids, such as acetic acid and hydrogen fluoride. Phase equilibria for these systems results from combined reaction and phase equilibrium among the monomeric and chemically associating species. Basic required data to apply the RGEMC method to such systems include ideal-gas partition function data for the associating species (e.g., in the simplest case, monomers and dimers), experimental data for the pure fluids, and intermolecular potential models for the associating species.

6. Conclusions

We have developed a new method for the computer simulation of the phase equilibrium properties of multicomponent mixtures, given an intermolecular potential model for the constituent molecular species. We used intermolecular potential models based on the OPLS potential models of Jorgensen et al.^{24–26} The model for MTBE is a new application of this approach.

The method, called the reaction Gibbs ensemble Monte Carlo (RGEMC) method, is a combination of the Gibbs ensemble Monte Carlo method³ and the reaction ensemble Monte Carlo method.¹⁴ The approach treats the phase equilibrium conditions as a special type of chemical reaction and incorporates knowledge of the pure-substance vapor–pressure data into the simulations. The RGEMC method utilizes only an intermolecular potential model and pure-component vapor pressure data. Unlike many thermodynamic-based approaches, no mixture information is required; also (unlike some thermodynamic-based approaches), the mixture volumetric properties are a byproduct of the calculations.

We have used the RGEMC method to predict phase equilibrium data for the binary system isobutene + MTBE and the binaries formed by methanol with isobutene, MTBE, and *n*-butane. The predictions are excellent, and of comparable accuracy to those obtained using the Wilson and the UNIFAC thermodynamic-based approaches.

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