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Vapor-phase chemical equilibrium and combined chemical and vapor–liquid equilibrium for the ternary system ethylene + water + ethanol from reaction-ensemble and reactive Gibbs-ensemble molecular simulations

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ABSTRACT

Combined chemical and vapor–liquid equilibrium (ChVLE) data for the ternary system ethylene + water + ethanol are required for the conceptual design of a reactive separation process to obtain ethanol by the hydration of ethylene. Due to the absence of experimental data for the combined ChVLE of the reacting system, molecular simulation looks appealing to predict such data. In this work, the reaction-ensemble Monte Carlo (RxMC) method was used to calculate the chemical equilibrium of the ternary system in the vapor phase, and the reactive Gibbs-ensemble Monte Carlo (RxGEMC) method was used to calculate its combined ChVLE. A set of previously validated Lennard-Jones plus point-charge potential models were employed for ethylene, water, and ethanol. The RxMC predictions for the vapor-phase chemical equilibrium composition of the ternary system and the equilibrium conversion of ethylene to ethanol, at 200 °C and pressures of 30, 40, 50, and 60 atm, were found to be in good agreement with predictions made by use of a previously proposed thermodynamic model that combines the Peng–Robinson–Stryjek–Vera equation of state, the Wong–Sandler mixing rules, and the UNIQUAC activity coefficient model. The RxGEMC simulations were used to predict the reactive phase diagram (two-dimensional graph of pressure versus transformed liquid and vapor-phase ethylene mole fractions) at 200 °C. In contrast to the thermodynamic model, molecular simulation predicts a wider reactive phase diagram (due to a reactive dew-point line much richer in ethylene). However, these two independent approaches were found to be in very good agreement with regard to the predicted bubble-point line of the reactive phase diagram and the approximate location of the reactive critical point.

1. Introduction

The concept of process intensification could be applied in the petrochemical industry to the production of ethanol by the direct hydration of ethylene. In the intensified process, the simultaneous reaction and separation of the product (ethanol) and the reactants (ethylene and water) would occur in the same piece of equipment, a reactive separation column, into which gaseous ethylene and liquid water would be fed [1].

In a previous study [2], we corroborated the validity of a set of previously published Lennard-Jones plus point-charge potential models for ethylene [3], water [4], and ethanol [5] from the good agreement of Gibbs-ensemble Monte Carlo (GEMC) molecular simulation results for the vapor pressure and the VLE phase diagrams of those components with respect to calculations made by means of the most accurate (reference) multiparameter equations of state currently available for ethylene [6], water [7], and ethanol [8]. We found that these potential models are capable of predicting the available VLE phase diagrams of the binary systems ethylene + water [9] (at 200 and 250 °C), ethylene + ethanol [10] (at 150, 170, 190, 200, and 220 °C), and ethanol + water [11] (at 200, 250, 275, and 300 °C). We also found that molecular simulation predictions for the VLE phase diagrams of the ternary system ethylene + water + ethanol, at 200 °C and pressures of 30, 40, 50, 60, 80, and 100 atm, are in very good agreement with both the experimental data [12] and predictions that we had previously made [1] by use of a thermodynamic model that combines the Peng–Robinson–Stryjek–Vera (PRSV2) equation of state [13,14],

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Nomenclature

C	Number of species in the reacting system
k_B	Boltzmann constant
K_{eq}	Chemical equilibrium constant
L	Simulation box length
N	Total number of molecules
N_i	Initial number of molecules of component i for a reaction step
P	Pressure
P_{rx}	Probability of acceptance of a reaction step
P^0	Standard-state pressure
T	Absolute temperature
U	Configurational energy
V	Volume of the simulation box
x_i	Liquid-phase mole fraction of component i
X_i	Transformed liquid-phase mole fraction of component i
y_i	Vapor-phase mole fraction of component i
Y_i	Transformed vapor-phase mole fraction of component i

Greek symbols

α	Ewald sum convergence parameter
χ	Correction factor for the Lorentz–Berthelot combining rule
ν_i	Stoichiometric coefficient of component i
$\overline{\nu}$	Stoichiometric coefficient of the reaction
ζ	Reaction direction index

Subscripts

Coul	Coulombic
LJ	Lennard-Jones
t	Total

Superscripts

(b)	In the backward direction
(c)	By creation
(d)	By deletion
(f)	In the forward direction
0	Initial (in the feed)
real	Real-space contribution
recip	Reciprocal-space contribution
self	Self-interaction contribution

the Wong–Sandler (WS) mixing rules [15], and the UNIQUAC activity coefficient model [16]. This agreement between the predictions of two independent methods (molecular simulation and the thermodynamic model) gave us confidence for the subsequent use of simulation to predict the combined chemical and vapor–liquid equilibrium (ChVLE) of the ternary system and check the validity of predictions that we previously made [1] by means of the thermodynamic model.

The reaction-ensemble Monte Carlo (RxMC) method [17–19] has been used successfully by several authors for the computation of the chemical equilibrium of some reactions of industrial interest, such as the dimerization of nitric oxide [20–22], the esterification reaction of ethanol and acetic acid to yield ethyl acetate and water [23], the hydrogenation of benzene to cyclohexane [24], the synthesis of ammonia [20,25,26], the combined hydrogenation of ethylene and propylene [27], and the detonation of nitromethane [28] and other energetic liquids [29]. A very comprehensive review of the RxMC method and its various applications has been made by Turner et al. [19]. In this work, the RxMC method was implemented in order to compute the vapor-phase chemical equilibrium of the ternary system ethylene + water + ethanol (i.e., for the vapor-phase hydration of ethylene to ethanol) and compare the simulation predictions with those obtained by means of the PRSV2-WS-UNIQUAC thermodynamic model described in the first of our previous works [1].

The reactive Gibbs-ensemble Monte Carlo (RxGEMC) method [18,30,31] is a combination of the reaction-ensemble (RxMC) [17–19] and the Gibbs-ensemble (GEMC) [32–39] methods, and it has already been used for the computation of the combined ChVLE of dimerization and combination reactions [18,30], the etherification reaction of isobutene and methanol to yield methyl-*tert*-butyl ether [31], and the dimerization reactions of nitrogen dioxide [40] and nitric oxide [41]. In this work, the RxGEMC method was implemented in order to compute the combined ChVLE for the hydration of ethylene to ethanol and compare the simulation predictions with those previously obtained [1] from the thermodynamic model.

The outline of the paper is as follows. The RxMC and the RxGEMC simulation methods are described in Sections 2.1 and 2.2, respectively. In Section 3.1, simulation results for the vapor-phase chemical equilibrium of the hydration reaction are reported, discussed, and compared with calculations previously carried out [1] by means of the PRSV2-WS-UNIQUAC thermodynamic model. In Section 3.2, simulation results for the combined ChVLE of the hydration reaction are reported, discussed, and compared with the predictions previously made [1] by use of the thermodynamic model.

2. Simulation methods

The Lennard-Jones (LJ) plus point-charge intermolecular potential models recently devised by Weitz and Potoff [3] for ethylene, Huang et al. [4] for water, and Schnabel et al. [5] for ethanol were used to carry out the simulations of the present work. These potential models were fully described in our previous simulation study [2]. However, for the convenience of the reader, some details like the local coordinates and charges of the sites, and the values of the size and energy parameters of the LJ contribution can be found in Table S1 (in Supplementary data). The potential model for ethylene, which comprises two LJ sites (with positive point charges) and one negative point charge, was found by Weitz and Potoff [3] to yield more accurate predictions for the saturated liquid densities, vapor pressures, critical density, and normal boiling point of ethylene as compared to other two united-atom models (NERD and TraPPE-UA). The potential model for water, which comprises one LJ site and two positive and one negative point charges, was found by Huang et al. [4] to yield more accurate predictions for the saturated liquid densities, vapor pressures, and heat of vaporization of water as compared to other four united-atom models (TIP4P, TIP4P-Ew, TIP4P/2005, and SPC/E). The potential model for ethanol, which comprises three LJ sites and two positive and one negative point charges, was found by Schnabel et al. [5] to yield more accurate predictions for the saturated liquid densities, vapor pressures, and heat of vaporization of ethanol as compared to other two united-atom models (OPLS-UA and TraPPE-UA). In our previous work [2], the validity of these models was corroborated from the good agreement found between our simulation results for the vapor pressure and the VLE phase diagrams of ethylene, water, and ethanol, and calculations carried out by means of the most accurate (reference) multiparameter equations of state currently available for those components [6–8].

2.1. Simulation method for the vapor-phase chemical equilibrium

In the reaction-ensemble Monte Carlo (RxMC) method, a single simulation box is used to simulate the vapor-phase chemical