Phase Equilibria of Mixtures Containing Chain Molecules Predicted through a Novel Simulation Scheme

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A new iterative Monte Carlo simulation scheme is presented for the efficient prediction of fluid-phase equilibria of mixtures containing long chain molecules. Using realistic molecular potentials, the high-pressure vapor-liquid and liquid-liquid equilibria of binary mixtures of ethane or ethylene with C_{16} to C_{40} normal alkanes are calculated. Excellent agreement between experimental data and molecular simulation is obtained in all cases. [S0031-9007(98)06144-4]

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The phase equilibria of light solvent—heavy-hydrocarbon mixtures are of extreme importance for the petrochemical, polymer, and oil industry. Traditional approaches for the calculation of such equilibria are based on cubic (Peng-Robinson and Soave [1]) and higher order equations of state (EoS; such as statistical associating fluid theory (SAFT) [2] and perturbed hard sphere chain (PHSC) [3]). Several adjustable parameters are required in order to obtain quantitative agreement with experimental data.

Molecular simulation is an attractive alternative to this type of calculation, because it does not invoke any approximations, and predictions are based on well-defined molecular characteristics. Popular phase equilibrium schemes include the Gibbs ensemble Monte Carlo [4] and grand canonical Monte Carlo [5] methods, which require insertions, deletions, or exchanges of molecules between the phases in order to reach equilibrium. For a heavy hydrocarbon, such moves have very low probability of success, even if special bias techniques are used [6]. Several alternative techniques have been developed in order to overcome sampling difficulties associated with the transfer of long molecules in the phases under consideration. Mehta and Kofke [7,8] developed an iterative scheme for the simulation of pure fluid and mixture phase equilibria using the Gibbs-Duhem integration technique. According to their scheme, the calculation proceeds along the binodal, starting from a known coexistence point. Numerical (e.g., predictor-corrector) techniques are invoked in order to integrate the Clapeyron equation. Escobedo and de Pablo [9] applied a similar approach to idealized mixtures in the framework of an expanded grand canonical ensemble [10]. More recently, Mehta and Kofke [11] proposed a pseudo grand canonical ensemble where particle transfers are replaced by volume fluctuations. Camp and Allen [12] extended this ensemble to a pseudo Gibbs ensemble, in order to simulate directly the two phases. Both techniques require evaluation of the chemical potential and the pressure at each density sampled by the system during the run.

In this Letter, a new iterative Monte Carlo scheme is introduced for the simulation of phase equilibria of long chain systems (SPECS), which involves the simultaneous simulation of two phases. The scheme is presented here for binary mixtures consisting of a light solvent (component 1) and a heavy hydrocarbon (component 2), but can be easily generalized for multicomponent mixtures. The two phases are simulated under the same fugacity of the light solvent (f_1), temperature (T), and pressure (P). The number of heavy hydrocarbon molecules (N_2) in each phase remains constant. Insertions and deletions of the solvent molecules are performed in both phases in order to attain the imposed value of the solvent fugacity. Equilibrium is achieved by equalizing the fugacities of the heavy hydrocarbon in each of the two phases, using an iterative scheme based on the Gibbs-Duhem equation.

A low-density, solvent-rich phase I and a high-density, heavy hydrocarbon-rich phase II, are simulated in the $f_1 N_2 PT$ ensemble. A good initial estimate for f_1 is necessary for the first iteration of the SPECS scheme. This is obtained relatively easily by simulating the low-density phase in the $N_1^{\mathrm{I}} N_2^{\mathrm{I}} PT$ ensemble, under constant number of light solvent and heavy hydrocarbon molecules, at the temperature and pressure of interest. N_1^{I} and N_2^{I} are chosen to correspond to the range of low-density phase compositions of interest. The excess chemical potential of the solvent is calculated by standard Widom insertions [13], and its fugacity is obtained from the expression,

$$\ln f_1 = \beta \mu_1^{\mathrm{ex}} - \ln\left(\frac{\beta}{x_1 \rho}\right), \tag{1}$$

where the excess chemical potential μ_i^{ex} is defined as the difference between the chemical potential of component i in the bulk phase and the chemical potential of component i in a pure ideal gas phase at the same temperature and molar density of the component: $\mu_i^{\mathrm{ex}} = \mu_i - \mu_{i,\mathrm{pure}}^{ig}(T, \rho x_i)$; x_i is the mole fraction of component i, ρ is the total molar density of the bulk phase, and $\beta = 1/(k_B T)$, where k_B is the Boltzmann's constant.

The fugacity of the light solvent, as calculated from phase I, is imposed on phase II, so that both phases are simulated under the same f_1, P, and T. The imposed value of f_1 is achieved by insertions and deletions of light solvent molecules. These Monte Carlo moves are accepted according to criteria derived from the probability density of the f_1N_2PT ensemble in each phase, given by the expression,

$$p_{\mathrm{eq}}(N_1, V, \mathbf{r_1}, \mathbf{r_2}; f_1, N_2, P, T) = \mathrm{const}\frac{V^{N_2}}{N_1!}(\beta f_1 V)^{N_1}\exp(-\beta PV)\frac{\exp[-\beta U_{\mathrm{tot}}(\mathbf{r_1}, \mathbf{r_2}; V, N_1, N_2)]}{(Z_{1,\mathrm{intra}})^{N_1}}, \tag{2}$$

where $\mathbf{r_1}, \mathbf{r_2}$ are sets of atomic position vectors defining the configuration of the molecules of species 1 and 2, respectively; V is the volume of the phase; U_{tot} is the total energy, which includes contributions from nonbonded interactions, bond angle, and dihedral angle changes; and $Z_{1,\mathrm{intra}}$ is a dimensionless configurational integral over all of the orientations and conformations of a single solvent molecule.

The SPECS scheme proceeds with the calculation of the chemical potential (or, equivalently, the fugacity) of the heavy hydrocarbon in both phases. As Widom insertions of long chains are very inefficient for the reliable estimation of the chemical potential, the "chain increment ansatz" [14] is invoked. According to this approximation, the excess chemical potential of a chain molecule of length n is a linear function of its length beyond a minimum length n_{small}: $\mu^{\mathrm{ex}}(n) = \mu^{\mathrm{ex}}(n_{\mathrm{small}}) + (n - n_{\mathrm{small}})\mu^{\mathrm{ex}}_{\mathrm{seg}}$. The quantity $\mu^{\mathrm{ex}}_{\mathrm{seg}}$ is defined as the difference between the excess chemical potential of a chain of length $n + 1$ and the excess chemical potential of a chain of length n: $\mu^{\mathrm{ex}}_{\mathrm{seg}} = \mu^{\mathrm{ex}}(n + 1) - \mu^{\mathrm{ex}}(n)$. By invoking the ansatz, the excess chemical potential of a chain of length n can be calculated by virtual insertions of shorter chains of length n_{small} and virtual augmentations of system chains by one segment for the calculation of the excess segmental chemical potential $\mu^{\mathrm{ex}}_{\mathrm{seg}}$. In previous work [15], this ansatz was validated for chains of 6 to 16 segments treated with two realistic united-atom models in both liquid and vapor phases. This approach greatly facilitates the chemical potential calculations of the heavy hydrocarbon in both phases. To improve sampling efficiency, the short chains of length n_{small} are inserted at uniformly distributed positions in each of the two phases, using configurational bias techniques [15].

The condition of phase equilibrium is satisfied if the fugacities of component 2 are found equal in the two phases, since equal fugacities of component 1 are imposed and the simulation in both phases is performed under the same temperature and pressure. If, as expected, the fugacities of component 2 are not equal, both phases are simulated again in the f_1N_2PT ensemble using a revised common value of f_1, which is estimated through a Newton-Raphson scheme designed to equalize f_2 in the two phases. This scheme, based on the Gibbs-Duhem equation, has the simple form,

$$\Delta \ln f_1 = (1 - x_1^{\mathrm{I}})x_2^{\mathrm{II}}\frac{\ln f_2^{\mathrm{II}} - \ln f_2^{\mathrm{I}}}{1 - x_1^{\mathrm{I}} - x_2^{\mathrm{II}}}. \tag{3}$$

The iterations proceed until $\Delta \ln f_1$ reaches a sufficiently small value.

The iterative phase equilibrium scheme described above is efficient for any binary mixture of differently sized molecules that are present in appreciable amounts in both phases. SPECS is designed to take full advantage of the ease with which light solvent molecules are inserted or deleted from a simulated phase and of the chain increment ansatz, which greatly facilitates the chemical potential calculations required for the heavy hydrocarbon.

In the case of very long hydrocarbon molecules that exhibit very low solubility in the low-density phase I, consisting mainly of the light solvent, the general scheme outlined above can be slightly modified to accelerate convergence. If the heavy hydrocarbon is in high dilution in phase I, then its fugacity varies linearly with its mole fraction in that phase (Henry's law), while the fugacity of the solvent follows the Lewis rule [1] and is thus insensitive to small changes in composition. The adjustment of composition in phase I needed to equalize the fugacities of component 2 in the two phases can be estimated readily as $x^{\mathrm{I}}_{2,\mathrm{revised}}/x^{\mathrm{I}}_{2,\mathrm{initial}} = f^{\mathrm{II}}_{2,\mathrm{target}}/f^{\mathrm{I}}_{2,\mathrm{initial}}$, where $x_{2,\mathrm{initial}}$ and $f_{2,\mathrm{initial}}$ have been estimated from the initial $N_1^{\mathrm{I}}N_2^{\mathrm{I}}PT$ simulation of phase I, and $f^{\mathrm{II}}_{2,\mathrm{target}}$ is the fugacity of the heavy hydrocarbon in phase II, obtained from Widom insertions in that phase. In this way, the composition of the low-density phase I that is in equilibrium with the high-density phase II can be found within two to three $N_1^{\mathrm{I}}N_2^{\mathrm{I}}PT$ simulations without invoking Eq. (3). The equilibrium composition is the one that equates the fugacities of the heavy hydrocarbon in both phases, since the fugacities of the light solvent are equal by design.

The SPECS scheme is applicable to real mixtures of industrial interest. Binary mixtures of ethane (C_2H_6) with n-hexadecane (n-$C_{16}H_{34}$) and with n-eicosane (n-$C_{20}H_{42}$), and mixtures of ethylene (C_2H_4) with n-$C_{20}H_{42}$ and n-tetracontane (n-$C_{40}H_{82}$) at high pressure were examined in this work. A united atom representation was used for all molecules. Nonbonded inter- and intramolecular interactions were modeled with a Lennard-Jones (LJ) potential. The long chain molecules were described with a potential model [16] that invokes the same LJ parameters for both the end and internal segments ($\epsilon/k_B = 49.3$ K, $\sigma = 3.94$ Å) and a torsional potential with global minimum in the trans and local minima in the gauche+ and gauche− conformations. Bond lengths and bond angles were fixed at 1.54 Å and 112°, respectively. This potential was used recently for the phase equilibrium of pure *n*-hexadecane, and simulation results were in good agreement with experimental data for the saturated liquid density over a wide temperature range [17].

The parameters used for ethane, taken from Ref. [18], were $\epsilon/k_B = 112.2$ K, $\sigma = 3.64$ Å and site-site distance $l = 1.84$ Å. Those for ethylene, estimated in this work, were $\epsilon/k_B = 91.4$ K, $\sigma = 3.63$ Å, and $l = 1.48$ Å. These sets of parameters reproduce the vapor-liquid saturated densities of the two pure light solvents at temperatures below the critical point. The regular Lorentz-Berthelot combining rules were used for the cross LJ parameters.

Results are shown in Fig. 1 for the ethane mixtures and in Fig. 2 for the ethylene mixtures. Both figures display pressure-composition diagrams at constant temperature. Experimental data [19–21] and predictions from two widely used EoS, namely, SAFT and Peng-Robinson, are shown for comparison. No adjustable binary interaction parameters were used in the EoS. Simulation results are in very good agreement with the experimental data even for the most asymmetric mixture studied ($C_2H_4-n\text{-}C_{40}H_{82}$). EoS predictions deviate significantly from the experimental data, especially for the mixture containing $n\text{-}C_{40}H_{82}$. In principle, EoS require several adjustable parameters in order to correlate accurately the experimental data for such mixtures. On the other hand, simulations use as input only pure component parameters which are identical for all chain lengths of the heavy hydrocarbons, and give predictions that are in excellent agreement with experimental data, even for the most asymmetric mixtures. This methodology, therefore, can be used to predict reliably the phase equilibria of complex fluid mixtures in the absence of experimental data.

Mixtures with a high degree of asymmetry exhibit a lower critical solution temperature (LCST) [1] and become immiscible in the vicinity of the solvent critical point. This behavior has been attributed to free volume effects, since the temperature increase results in higher density dissimilarities between the components. In Fig. 3, experimental data and molecular simulation predictions are shown for $C_2H_4-n\text{-}C_{40}H_{82}$ at 296.4 bar. Simulation results are in very good agreement with the experimental data. SAFT captures this behavior only qualitatively, while Peng-Robinson predicts complete miscibility under these conditions. Peng-Robinson was designed for small- and intermediate-size hydrocarbons, and such inaccuracy for asymmetric mixtures is expected.

In conclusion, a new iterative simulation scheme (SPECS) was presented for the efficient calculation of

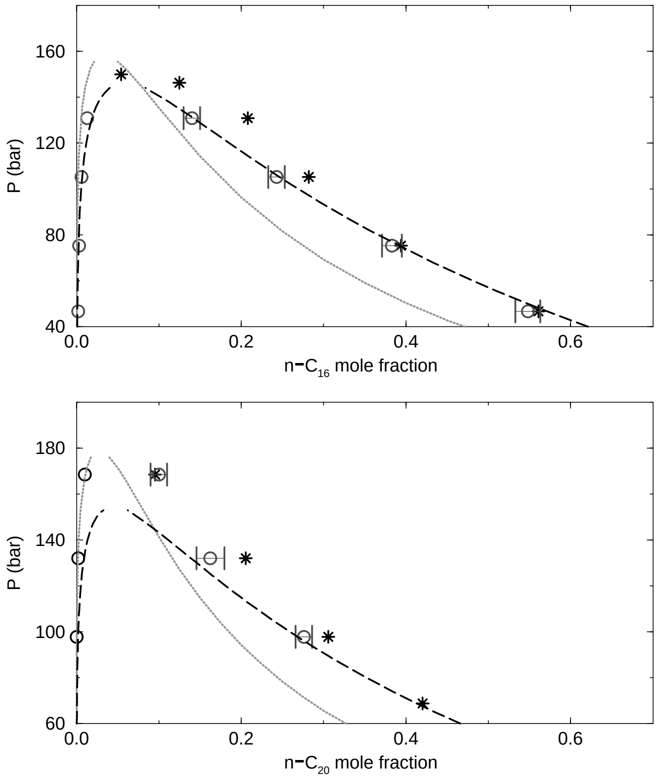

FIG. 1. Pressure–heavy hydrocarbon mole fraction phase diagrams for binary systems of $C_2H_6-n\text{-}C_{16}H_{34}$ (top) and $C_2H_6-n\text{-}C_{20}H_{42}$ (bottom) at $T = 402.8$ K. Experimental data (stars) [19,20], SPECS (circles), SAFT (dotted lines), and Peng-Robinson EoS (dashed lines) predictions.

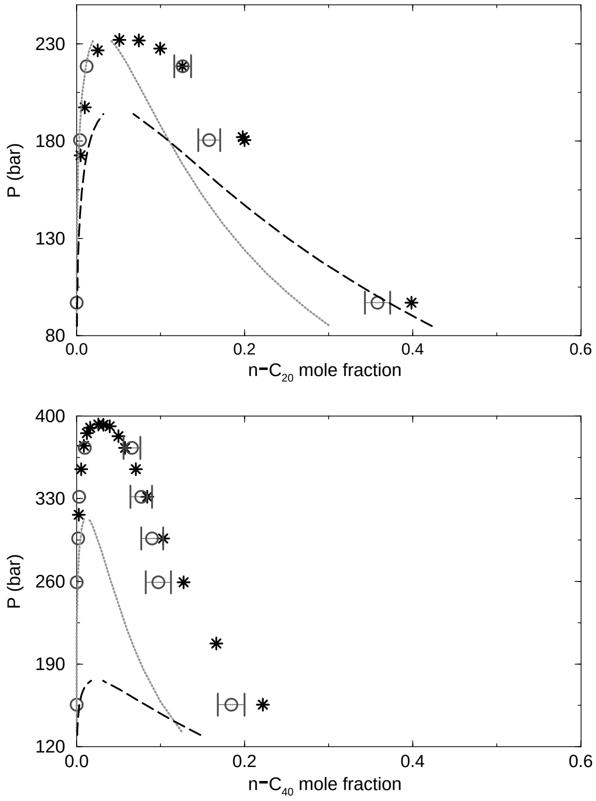

FIG. 2. Pressure–heavy hydrocarbon mole fraction phase diagrams for binary $C_2H_4-n\text{-}C_{20}H_{42}$ (top) and $C_2H_4-n\text{-}C_{40}H_{82}$ (bottom) at $T = 398.15$ K. Experimental data (stars) [21], SPECS (circles), SAFT (dotted lines), and Peng-Robinson EoS (dashed lines) predictions.

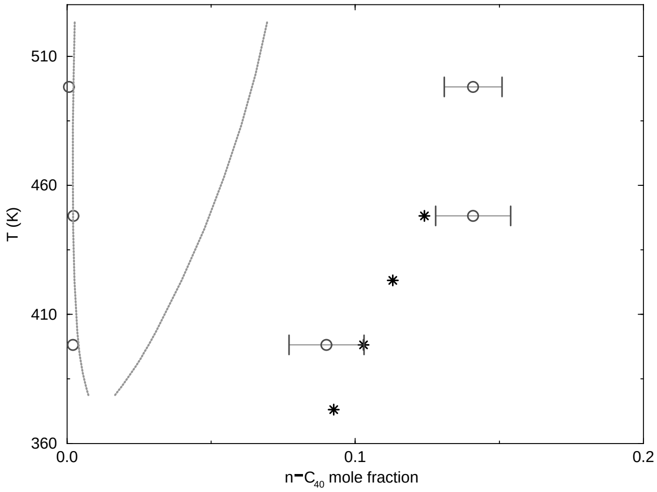

FIG. 3. High-pressure phase equilibria of LCST-type for $C_2H_4-n\text{-}C_{40}H_{82}$ mixture at $P = 296.4$ bar. Experimental data (stars) [21], SPECS (circles), and SAFT (dotted lines) predictions. Peng-Robinson EoS predicts complete miscibility at these conditions.

mixture phase equilibria of different size molecules, which overcomes the problems of large molecule insertion or exchange faced by state-of-the-art simulation methods. The scheme was applied to binary mixtures of ethane and ethylene with heavy hydrocarbons. Pressure-composition phase diagrams were calculated and found to be in very good agreement with experimental data for all of the mixtures examined. Predictions from the SPECS scheme are clearly superior to those from equations of state commonly used in industry, such as SAFT and Peng-Robinson, which deviate significantly from the experimental data, especially for highly asymmetric mixtures [22].

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[22] After this manuscript was submitted for publication, J. J. de Pablo and co-workers presented a preprint with calculations for the mixtures $C_2H_6-n\text{-}C_{20}H_{42}$ and $C_2H_4-n\text{-}C_{20}H_{42}$ using a different united atom model than the one used here that was fitted to pure heavy hydrocarbon coexistence densities. Their calculations are in very close agreement with results presented herein. For example, at 402.8 K and 97 bar, the mole fraction of C_2H_6 in the $n\text{-}C_{20}H_{42}$-rich phase is 0.724 ± 0.010 according to our model, 0.727 according to de Pablo's model, and 0.6943 from experimental data (Ref. [20]). For the binary mixture $C_2H_4-n\text{-}C_{20}H_{42}$ at 398 K and 97 bar, the mole fraction of C_2H_4 in the $n\text{-}C_{20}H_{42}$-rich phase is 0.642 ± 0.015 from our model, 0.60 from de Pablo's model, and 0.6014 from experimental data (Ref. [21]). It is evident, therefore, that a realistic potential model able to predict accurately the pure component density, such as the one used here and the one proposed by de Pablo, provides accurate estimates of mixture phase equilibria driven mainly by large density differences between the components (free volume effects), as is the case for the mixtures examined here.