

Report Title:

**VLE Measurements for Asymmetric Mixtures of
Fischer-Tropsch Hydrocarbons**

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Principal Author(s): **Mark C. Thies**

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Submitting Organization(s) **Clemson University
Department of Chemical Engineering
123 Earle Hall
Clemson, SC 29634-0909** (1)

Name & Address

(2)

(3)

(4)

(5)

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Abstract

The ability to model the thermodynamic phase behavior of long-chain and short-chain alkane mixtures is of considerable industrial and theoretical interest. However, attempts to accurately describe the phase behavior of what we call *asymmetric mixtures of hydrocarbons* (AMoHs) have met with only limited success. Vapor-liquid equilibrium (VLE) data are surprisingly scarce, and the limited data that are available suggest that cubic equations of state may not be capable of fitting (much less predicting) the phase behavior of AMoHs.

The following tasks, which address the problems described above, were accomplished during the one-year period of this Phase I UCR grant:

- A continuous-flow apparatus was modified for the measurement of AMoHs and used to measure VLE for propane + hexadecane mixtures at temperatures from 473 to 626 K and pressures up to the mixture critical pressures of about 100 bar.
- The extent to which cubic vs. modern, statistical mechanics-based equations of state (EoS) are applicable to AMoHs was evaluated. Peng-Robinson (PR) was found to be a surprisingly accurate equation for fitting AMoHs, but only if its pure component parameters were regressed to liquid densities and vapor pressures. However, even this form of PR was still not a predictive equation, as there was a significant variation of k_{ij} with temperature. In spite of its deficiencies in terms of vapor-phase predictions and modeling of the critical region, PC-SAFT was found to be the most appropriate EoS for truly predicting the phase behavior of highly asymmetric mixtures of alkanes.
- Finally, a dense-gas extraction (DGE) apparatus was designed and constructed for the fractionation of F-T waxes into cuts of pure oligomers. Such oligomers are needed in g-sized quantities to perform VLE measurements with long-chain alkanes with carbon numbers greater than 40. The dense gas and the solute mixture to be extracted are contacted in a packed column that has a separation power significantly greater than what can be achieved in one equilibrium stage. Thus, wax oligomer purities are expected to be much better than what can be obtained by conventional supercritical extraction processes.

VLE Measurements for Asymmetric Mixtures of Fischer-Tropsch Hydrocarbons

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Introduction

Asymmetric mixtures of hydrocarbons (i.e., mixtures containing hydrocarbons with large size differences) are frequently present during the processing of fossil fuel feedstocks, and an understanding of their sometimes complex phase behavior is essential for the optimal use of these feedstocks. For example, the problem of wax precipitation in natural gas reservoir pipelines is caused by retrograde condensation, a type of phase behavior that is characteristic of asymmetric mixtures [1]. In the petroleum industry, a light solvent is deliberately introduced into a residuum stream in the so-called ROSE process to create a highly asymmetric mixture, inducing a phase separation and maximizing the recovery of the more desirable lighter fractions [2].

The thermodynamics of asymmetric mixtures of hydrocarbons (AMoHs) also play an important role in the operation of the Fischer-Tropsch (F-T) slurry reactor, a key component in the conversion of coal to clean-burning, liquid fuels. The products of F-T synthesis are an asymmetric mixture of primarily paraffinic hydrocarbons and range in carbon number from C_1 to C_{200} . The distribution of these so-called “waxes” between the vapor and liquid phases has a significant impact on both the synthesis chemistry and hydrodynamics [3] in the reactor and, as a result, on reactor performance.

Attempts to accurately describe the phase behavior of systems such as those described above have met with only limited success. The problem is twofold: (1) Vapor-liquid equilibrium (VLE) data for asymmetric mixtures are relatively scarce, particularly for binary systems containing alkanes $>C_{20}$ in length. The data that have been measured were made primarily by our research group. (2) The limited data that are available suggest that the Peng-Robinson (PR) equation may not be capable of fitting (much less predicting) VLE for asymmetric mixtures containing n-alkanes longer than $\sim C_{20}$. These limited results also indicate that modern EoS based on statistical mechanics, such as SAFT, may have better predictive ability [4]. Thus, the objectives of this project were as follows:

1. VLE Measurements. Use a continuous-flow apparatus to measure VLE for binary mixtures of propane with model F-T waxes at the elevated temperatures and pressures relevant to F-T processing.
2. Modeling. Test both cubic and modern EoSs (e.g., SAFT) for their ability to correlate and predict VLE for those AMoHs for which we have high-quality experimental data.
3. Fractionation Apparatus. Design and construct a fractionation apparatus that can be used to produce gram-sized quantities of narrow molecular weight (MW) cuts of F-T waxes. Because of their prohibitively high cost in pure form, waxes $>C_{40}$ must first be produced before any VLE measurements can be made.

Finally, we note that only Phase I of the proposed research was funded (i.e., \$49,999 for one year plus a one-year no-cost extension).

Executive Summary

The ability to model the thermodynamic phase behavior of long-chain and short-chain alkane mixtures is of considerable industrial and theoretical interest. From an industrial standpoint, such asymmetric mixtures are relevant in the recovery of wax products from the Fischer-Tropsch (F-T) slurry reactor, which contains a vapor-liquid mixture of hydrocarbons ranging from C_1 to over C_{200} . Other examples include wax precipitation in natural gas pipelines and the ROSE process, which uses light, near critical solvents to recover oils from residua. From a theoretical perspective, modeling the phase behavior of asymmetric mixtures of hydrocarbons can serve as a useful test for the development of new equations of state (EoS). Long-chain alkanes are oligomers that bridge the gap between simple molecules and polymers. Unlike polymer systems, mixtures of long-chain alkanes and solvents are well-defined, have monodisperse constituents, and have quantifiable liquid and vapor compositions. However, unlike mixtures of simple molecules, these systems exhibit considerable solvent-solute size asymmetry. How well a theory predicts the phase behavior of these asymmetric mixtures provides insights into its ability to relate molecular features to macroscopic thermodynamic properties.

Attempts to accurately describe the phase behavior of these *asymmetric mixtures of hydrocarbons* (AMoHs), as we like to call them, have met with only limited success. The problem is twofold: (1) Vapor-liquid equilibrium (VLE) data for asymmetric mixtures are relatively scarce, particularly for binary systems containing alkanes C_{20} and longer. (2) The limited data that are available suggest that the commonly used cubic equations of state may not be capable of either fitting or predicting VLE for asymmetric mixtures containing n-alkanes longer than $\sim C_{20}$.

In order to address these two issues, several tasks were completed as part of this Phase I one-year research grant and are described below.

VLE measurements were made for the propane + hexadecane binary system. A continuous-flow apparatus was used to perform vapor-liquid equilibrium (VLE) measurements for binary mixtures of propane with hexadecane ($n-C_{16}H_{34}$) at 472.9, 522.9, 573.6, and 625.8 K. Both bubble- and dew-point compositions were measured from pressures of ~ 15 bar to the mixture critical point for each isotherm. Samples were generally reproducible to better than $\pm 1\%$ deviation in the minor component for both phases, and the reported compositions are believed to be accurate to $\pm 2\%$ deviation. With this work, we demonstrated that we have an apparatus capable of measuring highly accurate VLE data, including data in the mixture critical region, for AMoHs.

The Peng-Robinson (PR) and SAFT equations of state were rigorously evaluated for their ability to model AMoHs. The goal of this work was to determine the extent to which cubic vs. modern, statistical mechanics-based (SM-based) equations of state (EoS) are applicable to highly asymmetric mixtures of alkanes. In particular, the PR equation and two implementations of Statistical Associating Fluid Theory (SAFT) were evaluated. We denote one implementation of SAFT, which uses the Chen and Kreglewski dispersion term, as CK-SAFT; the second implementation, which uses the Gross and Sadowski dispersion term, is denoted as perturbed-chain SAFT, or PC-SAFT.

Our modeling work indicates that PR is a surprisingly accurate equation for fitting asymmetric mixtures of alkanes, but only if its pure component parameters are regressed to liquid densities and vapor pressures (we call this version PR-reg). Furthermore, the pure component parameters that are obtained when fitting to vapor pressure and liquid density data are well-behaved, suggesting that one may be able to estimate these parameters for asymmetric mixtures for which no data are available. However, even if these trends hold, PR-reg would still not be a predictive equation, as there is a significant variation of k_{ij} with temperature.

In spite of its deficiencies in terms of vapor-phase predictions and modeling of the critical region, PC-SAFT is the most appropriate EoS for predicting the phase behavior of highly asymmetric mixtures of alkanes. Furthermore, PC-SAFT is the only tested EoS that accurately reproduces the liquid volume behavior of the pure n -alkanes with temperature. Thus, we recommend that one use PC-SAFT with a k_{ij} of zero to predict VLE for asymmetric mixtures of n -alkanes when no data are available. Good estimates of liquid-phase compositions will be obtained up to within 5-10 bar of the predicted mixture critical point.

A dense-gas extraction (DGE) apparatus was designed and constructed for the fractionation of F-T waxes into cuts of pure oligomers. A semibatch, multistage extraction unit was constructed to study the DGE of F-T waxes. Such a multistage contacting device has a separation power significantly greater than what can be achieved in one equilibrium stage. Thus, product purities are much better than what is normally obtained by conventional supercritical extraction processes. The apparatus is rated for 400 °C and 200 bar and can hold a charge of up to 15 g of wax. Briefly, the equipment consists of a pump and preheater for supplying solvent, a 1.8 cm i.d. x 115 cm tall column that contains a stillpot, a 70 cm high section of packing, and a reflux finger at the top. A regulating valve is used to control both the column pressure and the flow of overhead product exiting the column.

For a typical experimental run, the extraction solvent reservoir is filled with the desired solvent (e.g., hexane). The compressed solvent then flows through the preheater, where it is heated to the desired dense-gas conditions. The dense-gas solvent then flows into the bottom of the charge cartridge, which contains a charge of polydisperse (e.g., F-T) wax. The solvent mixes with the wax charge in the stillpot, selectively extracting a particular narrow MW range of the wax, depending on the stillpot temperature and pressure. The dense-gas mixture of solvent and extracted wax then rises from the stillpot and enters the packed section of the column. Upon exiting the packed section, the dense-gas mixture contacts the reflux finger, which is housed in the top 14 cm of the column. This finger, which is maintained at a temperature different from the column, serves to condense liquid down the column as reflux, further purifying the overhead vapor fraction. The overhead vapor product exits out the side of the column and is expanded to ambient pressures by means of a regulating valve. The product is then collected and condensed in an ice bath.

Using this apparatus, we now have the ability to isolate long-chain alkanes of C₄₀ and above to purities of approximately 90%. Thus, for the first time ever, the opportunity exists for DOE to perform comprehensive VLE studies on oligomeric alkanes, a fundamentally important class of compounds that bridge the gap between simple molecules and polymers.

Experimental

VLE measurements. A continuous-flow apparatus (see Fig. 1) was used to perform VLE measurements for binary mixtures of propane with hexadecane ($n\text{-C}_{16}\text{H}_{34}$). This apparatus was designed and constructed at Clemson University and has a number of unique features that have been incorporated over the course of almost 20 years of high-pressure VLE work by Prof. Thies's research group. The essential features of the apparatus have been described in detail in the literature [5], so only a brief description is given here.

For a given experimental run, propane and the heavy wax component are pumped to the system at a combined flow rate of 100-200 mL/h. The two components are preheated within the isothermal nitrogen bath in separate lines and are then combined in a specially designed mixing tee that assists in the rapid approach to equilibrium.

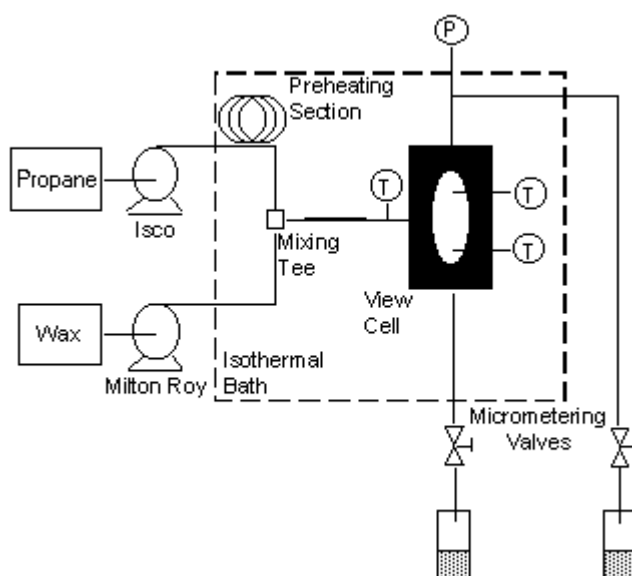


Figure 1. Continuous-flow apparatus for measuring VLE data of F-T waxes in light hydrocarbon solvents at elevated temperatures and pressures.

After passing through an expansion and a contraction to ensure adequate mixing, the two-phase stream enters the view cell (volume ~ 12 mL), where the two phases are allowed to separate. The vapor and liquid phases flow out the top and bottom of the cell, respectively, and are reduced to ambient pressure after passing through micrometering (MM) valves. The top-phase MM valve is used to control the pressure, while the bottom-phase MM valve is used to control the liquid level within the cell. The sample lines exiting the MM valves terminate in GC syringe needles, which are used to pierce the septa of the airtight collection vials. After collecting about 5 g in each vial, the entire sample is weighed. The wax composition of each phase is then determined by removing the septa and letting the liquid wax sample degas. Previous experience with similar systems indicates that the accuracy of this technique is quite good, that is, to within $\pm 2\%$ deviation [5].

Design and Construction of Fractionation Apparatus for F-T Waxes. The classic technique for the separation of high MW fossil fuels into narrow MW fractions is gel permeation chromatography (GPC). However, GPC is too tedious and expensive for isolation of the g-sized quantities of wax oligomers that we need to perform VLE measurements. Thus, we propose a separation technique that we call dense-gas extraction (DGE) be investigated. (The terms destraction and gas extraction [6] have also been used.) With DGE, the extractive solvent is a dense gas in the vicinity of its critical temperature, with the pressure being high enough so that the solvent has significantly more extractive power than an ideal gas. Pressures can be either well below those typically used in supercritical extraction or at supercritical conditions, depending on the solubility of the solute to be extracted into the gaseous, solvent-rich phase. Typically, the dense gas and the solute mixture to be extracted are contacted in a multistage or differential contacting device that has a separation power significantly greater than what can be achieved in one equilibrium stage. Thus, product purities are much better than what is normally obtained by conventional supercritical extraction processes. Both the system phase behavior and mass transfer properties can also dramatically affect the achievable separation.

A semibatch, multistage extraction unit was constructed to study the DGE of F-T waxes. The apparatus, which is shown in Fig. 2, is rated for 400 °C and 200 bar and can hold a charge of up to 15 g of wax. Briefly, the equipment consists of a pump and preheater for supplying solvent, a 1.8 cm i.d. x 115 cm tall column that contains a stillpot, a 70 cm high section of packing, and a reflux finger at the top. A regulating valve is used to control both the column pressure and the flow of overhead product exiting the column.

In preparation for an experiment, the stillpot (i.e., the first 23 cm of the column, which is packing-free) is charged with F-T wax. This is accomplished by loading the charge cartridge with wax and introducing the cartridge into the bottom of the stillpot. For a typical experimental run, the extraction solvent reservoir is filled with the desired solvent (e.g., hexane). The compressed solvent then flows through the preheater, where it is heated to the desired dense-gas conditions. The dense-gas solvent then flows into the bottom of the charge cartridge. The solvent mixes with the wax charge in the stillpot, selectively extracting a portion of the wax. The dense-gas mixture of solvent and extracted wax then rises from the stillpot and enters the packed section of the column, which is filled with 4 mm random packing (Cannon Instrument Co., part no. 3947-A20). Upon exiting the packed section, the dense-gas mixture contacts the reflux finger, which is housed in the top 14 cm of the column. This finger serves as a condenser. If the temperature of the finger or the packed column is different from the stillpot temperature, a wax-rich liquid phase can condense. This liquid phase flows down the column as reflux, further purifying the overhead vapor fraction. The overhead vapor product exits out the side of the column, adjacent to the top of the reflux finger, and is expanded to ambient pressures by means of the regulating valve (Autoclave Engineers, part no. 30VM4084-GY). The product is then collected and condensed in an ice bath.

The temperature of the column at a given location can be controlled to ± 1.0 °C, giving a total uncertainty in the reported temperatures of ± 2 °C. Column pressure can be controlled to within ± 0.07 bar of the desired setpoint by means of the regulating valve (see Fig. 2), which was actuated via a National Instruments NuDrive motion control device (Model 4CX-001) along with a DC servomotor and gear reducer (ECM Motor Co., Model 5471). The system pressure was measured with a pressure transducer (Heise, Model HPO) that was monitored by National Instruments Labview software.

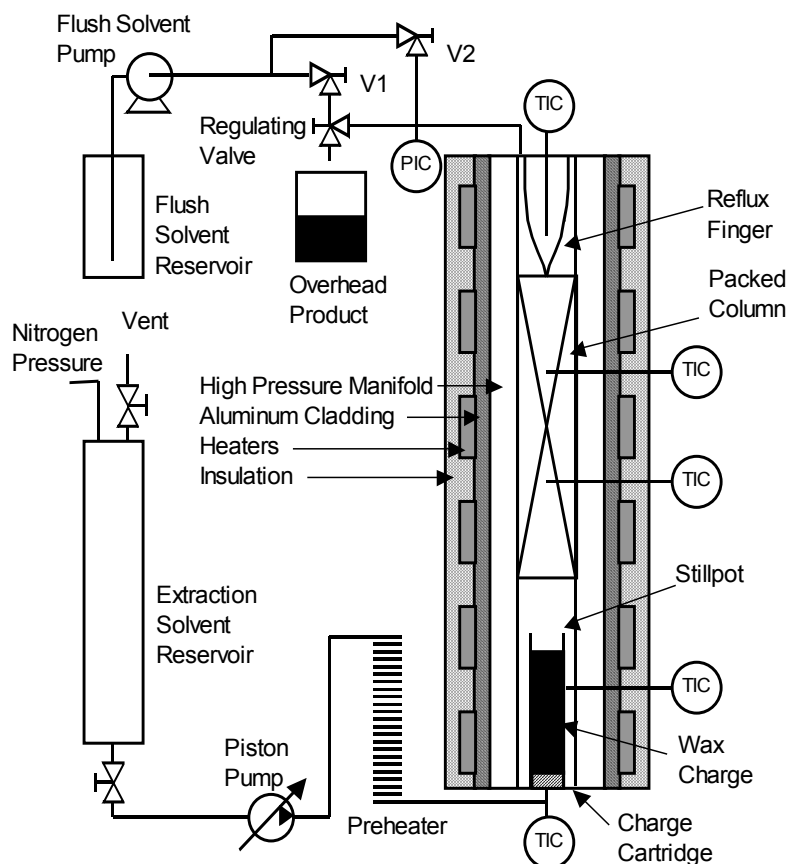


Figure 2. Schematic of the DGE apparatus designed and constructed for the isolation of high MW n-alkane oligomers from F-T waxes.

As Phase II funding for this project was not obtained, no fractionation runs with F-T waxes were performed with this column. The column is currently being used to fractionate the carbonaceous pitches that serve as precursors for high-performance carbon fibers with performance significantly superior to column chromatography in terms of both purity and yield being obtained [7]. Thus, if funding could be obtained, we are confident that our DGE setup could be used to produce the desired high MW alkanes at purities of at least 90%.

Results and Discussion

VLE measurements for Binary Mixtures of Propane with Hexadecane. The continuous-flow apparatus described above was used to measure vapor and liquid equilibrium compositions and corresponding pressures for the propane + hexadecane system at 472.9, 522.9, 573.6, and 625.8 K. For each of these isotherms, mixture critical pressures and compositions were also measured. Results are given in the form of a pressure vs. composition diagram in Fig. 3. Triplicate samples were collected for each measured vapor- and liquid-phase composition; these samples were generally reproducible to better than $\pm 1\%$ deviation in the minor component for both phases. Considering all known sources of error, the reported accuracy of our VLE measurements is believed to be $\pm 2\%$, based on the minor component. The accuracy of the mixture critical pressures and critical point compositions (i.e., the maximum-pressure data points for a given

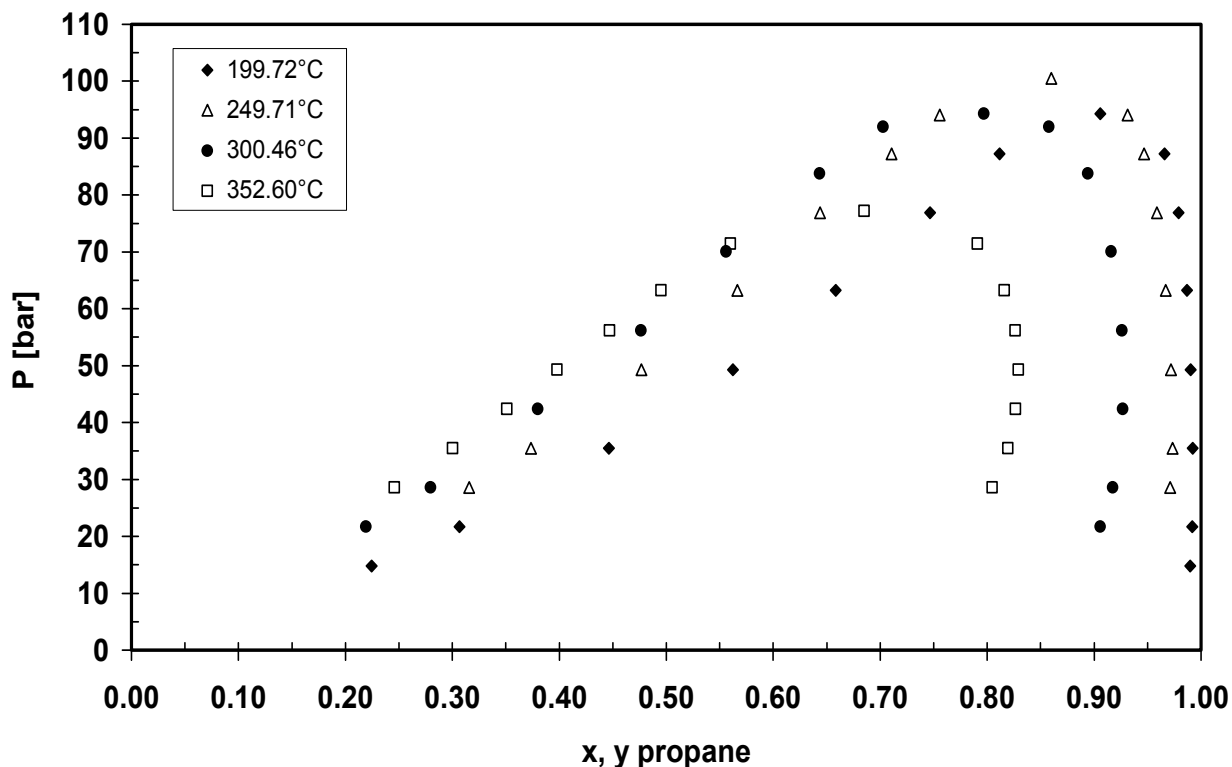


Figure 3. Pressure vs. composition diagram for the propane + hexadecane system.

isotherm) is believed to be comparable to that of the other measured compositions.

VLE Modeling of AmoHs Using Peng-Robinson and SAFT Equations of State. The goal of this work was to determine the extent to which cubic vs. modern, statistical mechanics-based (SM-based) equations of state (EoS) are applicable to highly asymmetric mixtures of alkanes. In particular, the Peng-Robinson (PR) equation [8] and two implementations of Statistical Associating Fluid Theory (SAFT) were evaluated. We denote one implementation of SAFT, which uses the Chen and Kreglewski dispersion term and was proposed by Huang and Radosz [9,10], as CK-SAFT; the second implementation, which uses the Gross and Sadowski dispersion term, is denoted as perturbed-chain SAFT, or PC-SAFT [11].

All of these equations were tested for their predictive and their correlative ability, with our experimental VLE data for hexane-hexadecane (C_6 - C_{16}), hexane-tetracosane (C_6 - C_{24}), and hexane-hexatriacontane (C_6 - C_{36}) being used for the analysis [5,12]. The PR equation was chosen because of its widespread use in industry and its simplicity. CK-SAFT and PC-SAFT were chosen because of their molecular basis, their widespread use among researchers, and their growing use by practicing engineers. Our goal was to use the above VLE data to (1) determine the limits of applicability of the cubic equations, which work well for alkane mixtures of similarly sized molecules, and (2) test the ability of the two SAFT equations to predict the effect of molecular shape on fluid properties. These results are presented in detail elsewhere [13], so a shortened description of this work is presented below.

Each of the three tested EoS was fit to the binary VLE data described above. For each measured pressure vs. composition isotherm, the optimum binary interaction parameter was obtained by minimizing the total absolute percent deviation between measured and calculated liquid and vapor compositions summed over all data points. The calculation was always carried out with the minor component in a given phase, so vapor-phase solubilities were weighted approximately the same as those in the liquid phase. Representative pressure-composition isotherms generated by each of the EoS are compared with experimental measurements (at either 622K or 623K) in Figs. 4 through 7.

With the conventional Peng-Robinson equation, a good fit to experimental data can be obtained for the C₆-C₁₆ system at all investigated temperatures (Fig. 4). Furthermore, for this system the k_{ij} can be set to 0.00 with little loss in accuracy. However, as the chain length of the wax component increases, the goodness of fit deteriorates significantly. Moreover, for the C₆-C₂₄ and C₆-C₃₆ binaries the optimum k_{ij} 's exhibit large changes in magnitude as a function of temperature. Part of the reason for the poor fits to liquid-phase compositions is that PR does not correctly predict the liquid-density behavior of pure long-chain *n*-alkanes. In fact, we discovered that PR grossly underpredicts liquid densities for the longer alkanes—and these predictions become worse with increasing molecular weight [4,13].

By regressing the PR parameters to liquid density and vapor pressure data (we call this version of Peng-Robinson PR-reg), good agreement is obtained between calculated and experimental liquid and vapor compositions for all tested systems (Fig. 5). We believe that the significant improvements in VLE fits for the binary mixtures containing C₂₄ and C₃₆ are due in no small part to the good liquid density fits that are obtained with PR-reg, in dramatic contrast with PR. Although PR-reg gives much improved fits to phase compositions away from the mixture critical points, the mixture critical pressures are overpredicted for all tested systems. Such behavior is typical for equations of state that do not account for critical exponent behavior and whose pure component parameters are fit to co-existence curve data. For the more asymmetric mixtures, the k_{ij} 's are better behaved with PR-reg than with PR, as they are smaller in magnitude and monotonically decrease with increasing temperature.

An interesting observation regarding the PR-reg approach is that the pure component parameters $a(T_c)$ and b in PR-reg are linear functions of *n*-alkane carbon number [4,13]. This behavior is analogous to that observed with CK-SAFT and PC-SAFT. Furthermore, the change in the third parameter, κ , with carbon number is also essentially linear.

Because the parameters for CK-SAFT and for PR-reg were both obtained from the regression of vapor pressures and liquid densities, a comparison between these two equations is of particular interest. As seen in Figs. 5 and 6, the two EoS give comparable fits to the liquid phase, but PR-reg is significantly better in fitting the vapor phase at moderate and higher pressures. In addition, CK-SAFT is unable to reproduce the correct phase behavior in the critical region; for example, at 623 K the fit is only fair because the critical region dominates the phase behavior for the C₆-C₁₆ system. As was the case with PR-reg, CK-SAFT overpredicts the mixture critical point – and for essentially the same reasons.

However, the fits for CK-SAFT improve considerably for the more asymmetric systems where

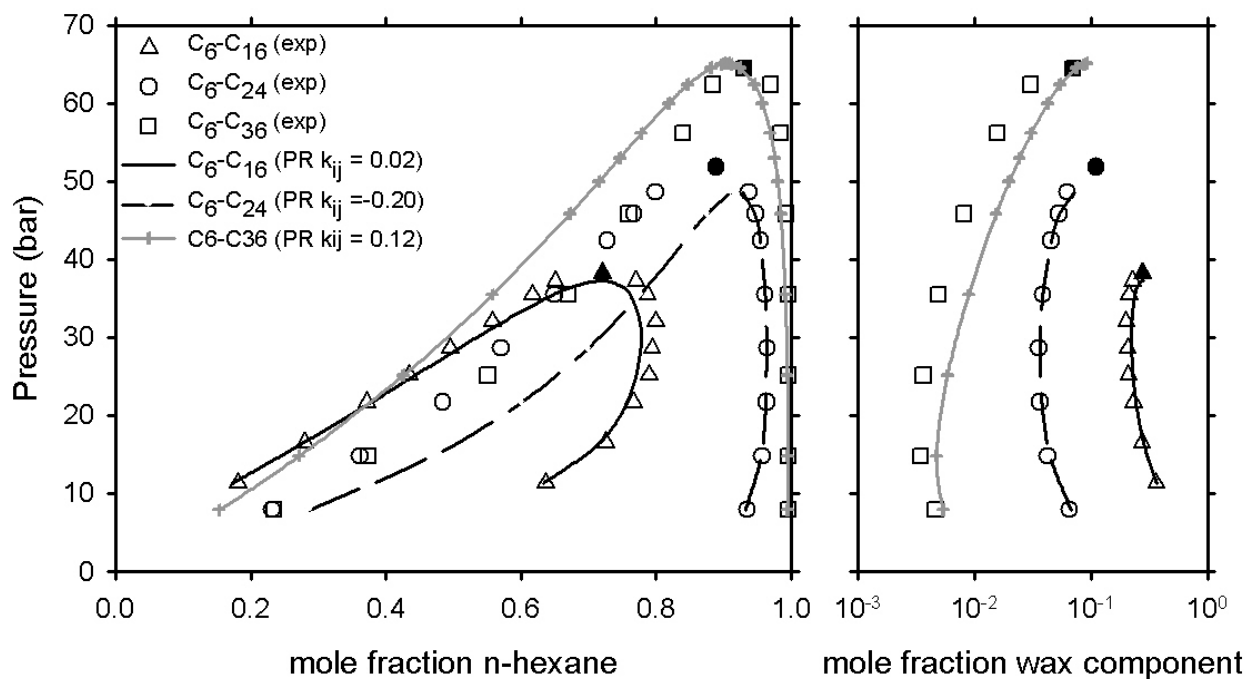


Figure 4. PR fits to mixture data at $T=622K$ or $623K$. The vapor compositions are expanded on the right and the mixture critical points are filled.

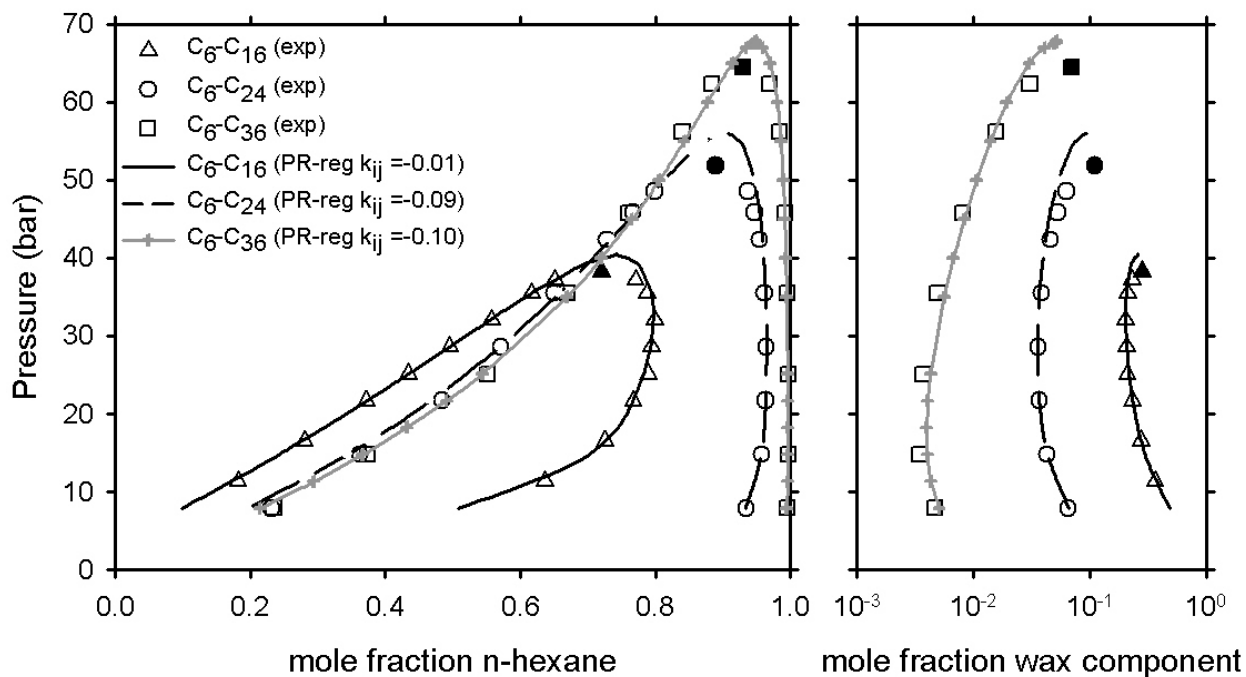


Figure 5. PR-reg fits to mixture data at $T=622K$ or $623K$. The vapor compositions are expanded on the right and the mixture critical points are filled.

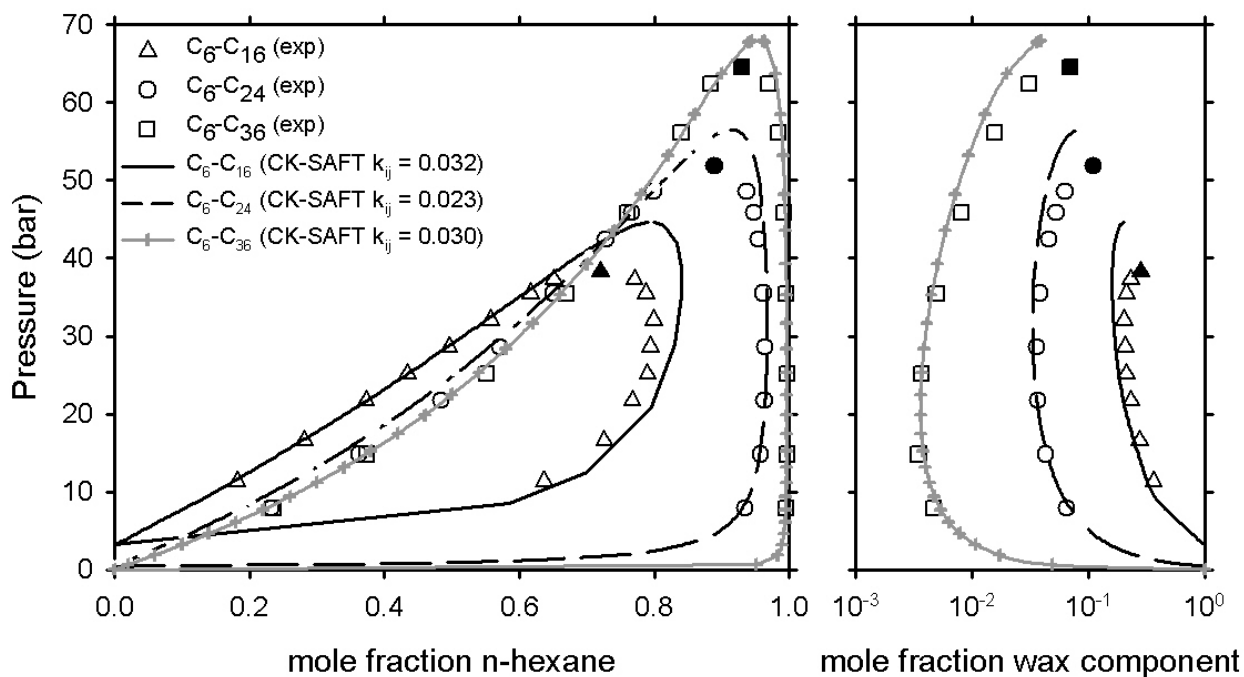


Figure 6. CK-SAFT fits to mixture data at $T=622K$ or $623K$. The vapor compositions are expanded on the right and the mixture critical points are filled.

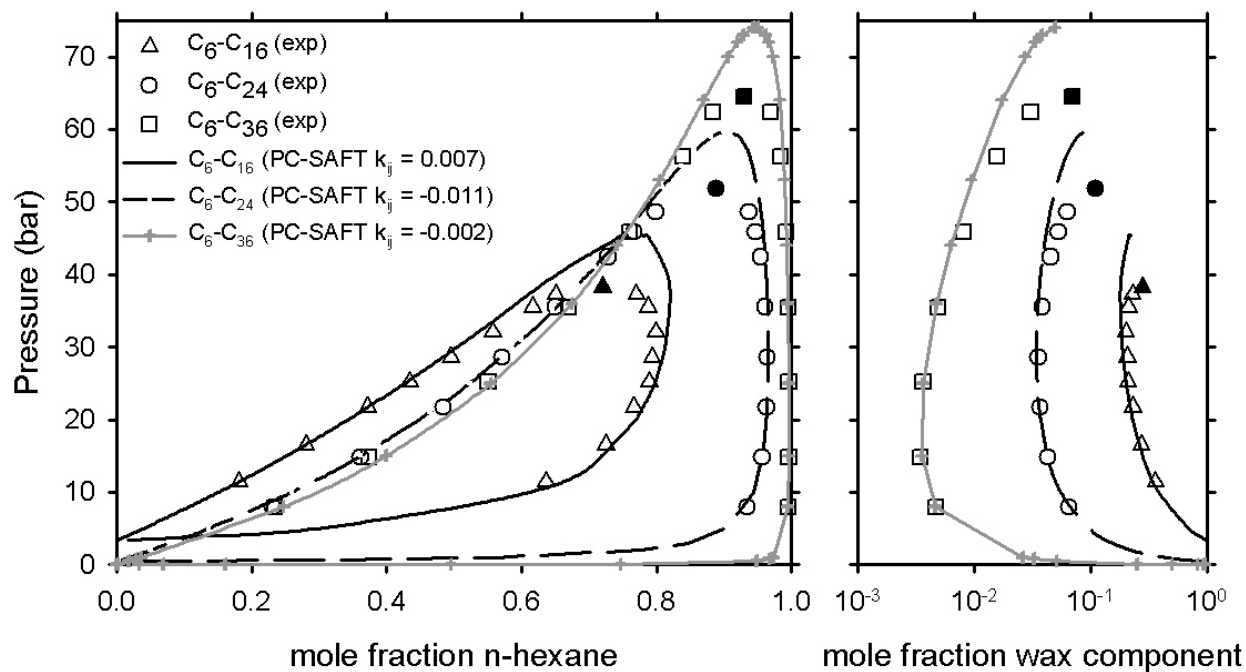


Figure 7. PC-SAFT fits to mixture data at $T=622K$ or $623K$. The vapor compositions are expanded on the right and the mixture critical points are filled.

the critical region has less of an impact on the overall phase behavior (Fig. 6). These results are particularly encouraging when one recalls that, as stated earlier, the pure component parameters for C_{24} are true predictions, and that the vapor pressure data used by Huang and Radosz [9] to fit their C_{36} pure component parameters are inconsistent with our experimental results.

In contrast to PR-reg, the optimum k_{ij} 's for CK-SAFT are nearly constant for the more asymmetric (i.e., C_6 - C_{16} and C_6 - C_{24}) systems. In fact, if one assumes a constant k_{ij} of 0.030, good estimates of liquid-phase compositions are obtained for these two systems.

Comparison of PC-SAFT with experimental results is given in Fig. 7. At low to moderate pressures (i.e., far away from the critical region), this equation provides a good fit to both liquid- and vapor-phase compositions; the higher temperature fits are especially good. These results are consistent with the fact that PC-SAFT gave the best fits to pure component data of any EoS considered in this work [13]. Furthermore, the optimized k_{ij} 's are closer to zero than for any of the other tested EoS. However, the mixture critical pressures are significantly overpredicted, and this deficiency is responsible for much of the reported deviations from the experimental data.

In our work with PR and PR-reg, we had no choice but to come up with a vapor pressure estimate for C_{36} . In marked contrast, with PC-SAFT we did not use any pure component data for C_{36} , but estimated the necessary parameters from Gross and Sadowski's correlation [11]. It is of particular note that the VLE predictions of PC-SAFT for the C_6 - C_{36} binary are essentially equivalent in goodness of fit to those obtained for C_6 - C_{24} (Fig. 7), even though the C_{24} parameters had been fit to pure component data. The above illustrates a significant advantage of the various versions of SAFT: for the n -alkanes, well-behaved correlations are available for estimating the pure component parameters of segment size, segment energy, and segment number.

Finally, because PC-SAFT k_{ij} 's were found to be the closest to zero when optimized, the ability of this EoS to truly predict VLE compositions was evaluated. The liquid-phase predictions of PC-SAFT were found to be in very good agreement with experimental data, generally to better than 5% deviation in the minor component. It is interesting to note that PC-SAFT also gave the best fits to pure component liquid molar volume data [13]. Good liquid-phase predictions are also obtained with CK-SAFT by setting the k_{ij} 's equal to 0.03. However, neither EoS can be used to predict vapor-phase compositions with any degree of confidence.

Conclusions

A continuous-flow apparatus was used to measure vapor and liquid equilibrium compositions for binary mixtures of propane with hexadecane at elevated temperatures and pressures. Measurements such as these are important for improving our understanding of the nonideal phase behavior of asymmetric mixtures of alkanes, where size differences, instead of intermolecular forces, dominate the observed nonidealities. Our experimental work indicates that highly reproducible data (i.e., to within $\pm 2\%$ deviation) can be obtained, but care must be taken to ensure that equilibrium compositions are obtained.

Our modeling work indicates that Peng-Robinson is a surprisingly accurate equation for fitting

asymmetric mixtures of alkanes, but only if its pure component parameters are regressed to liquid densities and vapor pressures. Furthermore, the pure component parameters that are obtained when fitting to vapor pressure and liquid density data are well-behaved, suggesting that one may be able to estimate these parameters for asymmetric mixtures for which no data are available. However, even if these trends hold, PR-reg would still not be a predictive equation, as there is a significant variation of k_{ij} with temperature.

In spite of its deficiencies in terms of vapor-phase predictions and modeling of the critical region, PC-SAFT is the most appropriate EoS for predicting the phase behavior of highly asymmetric mixtures of alkanes. Furthermore, PC-SAFT is the only tested EoS that accurately reproduces the liquid volume behavior of the pure n -alkanes with temperature. Thus, we recommend that one use PC-SAFT with a k_{ij} of zero to predict VLE for asymmetric mixtures of n -alkanes when no data are available. Good estimates of liquid-phase compositions will be obtained up to within 5-10 bar of the predicted mixture critical point.

Finally, a dense-gas extraction apparatus suitable for the fractionation of F-T waxes into its oligomeric alkanes has been designed, constructed, and tested. Using this apparatus, we now have the ability to isolate long-chain alkanes of C_{40} and above to purities of approximately 90%. Thus, for the first time ever, the opportunity exists for DOE to perform comprehensive VLE studies on oligomeric alkanes, a fundamentally important class of compounds that bridge the gap between simple molecules and polymers.

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