

SEPARATION OF FISCHER-TROPSCH WAX FROM CATALYST
BY SUPERCRITICAL EXTRACTION

Quarterly Technical Report

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Executive Summary

Although alkanes are the major constituent of a Fischer-Tropsch wax, significant quantities (e.g., up to 30 wt %) of long-chain alcohol and alkene compounds can also be found in a F-T wax. With the lack of experimental data, the effect that the hydroxy and double-bond functional groups have on the phase behavior of systems containing long-chain hydrocarbons is unknown. Therefore, the phase behavior of the system n-hexane/1-hexadecanol was measured for comparison with the previously measured system n-hexane/hexadecane. Vapor and liquid equilibrium compositions and mixture critical points were measured at 198.9, 251.3, 299.2, and 349.9 °C at pressures ranging from 6.2 to 46.4 bar. Temperature and pressure measurements for all isotherms are believed to be accurate to better than ± 0.25 °C and ± 0.14 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to better than ± 3 and $\pm 4\%$, respectively.

Results indicate that the addition of the alcohol group to a C₁₆ hydrocarbon chain significantly affects the phase behavior with hexane, with the two-phase region extending to significantly higher (i.e., up to about 10 bar higher) pressures. The presence of the alcohol group was also found to be an impediment to obtaining a good fit of the experimental data with the Peng-Robinson equation.

Technical Objectives

The objective of this research project is to evaluate the potential of supercritical fluid (SCF) extraction for the recovery and fractionation of the wax product from the slurry bubble column (SBC) reactor of the Fischer-Tropsch (F-T) process. The wax, comprised mostly of branched and linear alkanes with a broad molecular weight distribution up to C_{100} , will be extracted with a hydrocarbon solvent that has a critical temperature near the operating temperature of the SBC reactor, i.e., 200-300 °C. Initial work is being performed using n-hexane as the solvent.

The success of the project depends on two factors. First, the supercritical solvent must be able to dissolve the F-T wax; furthermore, this must be accomplished at conditions that do not entrain the solid catalyst. Second, the extraction must be controlled so as not to favor the removal of the low molecular weight wax compounds. That is, a constant carbon-number distribution in the wax slurry must be maintained at steady-state column operation. Three major tasks are being undertaken to evaluate our proposed SCF extraction process. *Task 1:* Equilibrium solubility measurements for model F-T wax components in supercritical fluids at conditions representative of those in a SBC reactor. *Task 2:* Thermodynamic modeling of the measured VLE data for extending our results to real wax systems. *Task 3:* Process design studies of our proposed process. Additional details of the task structure are given below.

Task 1: Equilibrium Solubility Measurements

- a. apparatus modification and construction.
- b. experimental measurements of selected model systems.
- c. design and construction of new apparatus for measuring VLE of C_{36+} alkanes with hexane.

Task 2: Thermodynamic Modeling

- a. modeling VLE data using cubic equations of state.
- b. examination of theoretically based models, including the SAFT equation.

Task 3: Process Design Studies

- a. process configuration studies using the ASPEN PLUS simulation package.

Detailed Description of Technical Progress

Task 1a. Apparatus Modification and Construction

This task has been completed.

Task 1c. Design and Construction of New Apparatus

No effort planned for this quarter.

Task 1b. Experimental Measurements for n-Hexane/1-Hexadecanol System

Vapor-liquid equilibrium experiments for the n-hexane/1-hexadecanol system have been completed. Measured compositions and corresponding pressures for the n-hexane/1-hexadecanol binary at 198.9, 251.3, 299.2, and 349.9 °C are given in Table I and are depicted on a pressure-composition diagram in Figure 1. Mixture critical pressures and compositions are also reported at the three higher temperatures. For clarity, the vapor-phase composition of the 198.9 °C isotherm is plotted separately in Figure 2. Note that the inflection in the vapor-phase curve of Figure 2, which must exist according to theory, is detected, indicating the good quality of the measured results.

Because hexadecanol is a solid at room temperature (m.p. = 55 °C), the continuous-flow apparatus had to be modified before experiments could commence. The hexadecanol feed reservoir, feed lines, and pump head are heated with electrical heating tape and maintained at 75-100 °C. In addition to the lines containing pure hexadecanol, the sampling lines exiting the cell, which contain a mixture of solvent and solute, are heated to about 75 °C. The last 4 inches of sampling line tubing are not wrapped with tape so that the line can be inserted into a sealed sampling vial. To prevent this portion of the line from plugging due to hexadecanol solidification, it is made of copper, which remains hot by conduction. 2-6 g samples of each phase were typically collected.

For the liquid phase, the three samples collected at a given temperature and pressure were typically reproducible to better than $\pm 1.5\%$ deviation in 1-hexadecanol composition. In a few cases, deviations of up to $\pm 2.0\%$ were obtained. For the vapor phase, the samples were typically reproducible to $\pm 2.5\%$ in the minor component 1-hexadecanol, but deviations between samples of up to $\pm 3.5\%$ were occasionally obtained.

Temperature and pressure uncertainties for a given isotherm were always less than ± 0.25 °C and ± 0.14 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to ± 3 and $\pm 4\%$, respectively. Both the liquid and vapor phases have been checked for consistency by the modified Henry's Law and modified Enhancement Factor methods. These methods were discussed in the first quarter report for 1996; as shown in Figures 3 and 4, they demonstrate that the measurements are consistent. It should be pointed out that H in Figure 3 is defined as $H = (P - x_2 P_2^{\text{sat}})/x_1$ because the vapor pressure of 1-hexadecanol is nontrivial at the highest temperatures measured.

Table I. Vapor-liquid equilibrium properties for the n-hexane/1-hexadecanol system.

press., bar	mole fraction n-hexane		press., bar	mole fraction n-hexane	
	liquid	vapor		liquid	vapor
T = 198.9 °C			T = 299.2 °C		
6.18	0.372	0.99548	7.91	0.174	0.9135
7.91	0.474	0.99627	11.36	0.244	0.9337
9.63	0.572	0.9969	14.80	0.322	0.9449
11.36	0.665	0.99742	18.26	0.402	0.9508
13.08	0.775	0.99793	23.15	0.496	0.9555
14.80	0.866	0.99845	28.59	0.607	0.9568
16.53	0.941	0.999212	35.49	0.712	0.9530
17.35	0.977	0.999721	38.93	0.785	0.9442
			42.38	0.856	0.9251
			43.21 ^a	0.891	0.891
T = 251.3 °C			T = 349.9 °C		
7.91	0.335	0.975	11.36	0.165	0.8157
11.36	0.412	0.9812	18.25	0.287	0.8663
14.80	0.519	0.984	21.70	0.341	0.8727
18.26	0.607	0.9861	28.59	0.459	0.886
21.70	0.693	0.9871	32.04	0.509	0.887
25.15	0.780	0.9872	35.49	0.558	0.8863
28.60	0.860	0.9877	38.93	0.626	0.8843
32.05	0.931	0.9866	42.38	0.675	0.8736
34.36 ^a	0.9699	0.9699	46.41 ^a	0.801	0.801

^a Vapor-liquid critical point

To verify that equilibrium conditions exist, samples were collected at varying flow rates. As can be seen in Table II, no effect of flow rate on the equilibrium

compositions at 199.2 °C and 11.36 bar was observed within the experimental uncertainties reported above.

Table II. Measured equilibrium compositions and flow rates for the n-hexane/1-hexadecanol system at 199.2 °C and 11.36 bar.

total flow rate (mL/hr)	mole fraction 1-hexadecanol	
	liquid	vapor
100	0.324	0.00257
200	0.328	0.00254
300	0.328	0.00262

The results for the n-hexane/1-hexadecanol system were compared to the n-hexane/hexadecane system to examine the effect of the alcohol group on phase behavior. Figure 5 shows a pressure-temperature diagram of the critical-point curves for both systems. The critical point of pure 1-hexadecanol was estimated by the method of Ambrose [1], and the critical point of hexadecane is available in the literature [1,2]. Because the critical points of hexadecane and 1-hexadecanol are quite similar, it is surprising how much larger the two-phase region is for the alcohol-containing system. The implications of this result are important for modeling our proposed process. Even when the carbon chain is 16 carbons long, the presence of an alcohol group still has a significant impact on the phase behavior of waxes with SCF solvents, and must be explicitly considered. At what carbon chain length the effect of the alcohol group will become negligible remains an open question.

Task 2a. Modeling VLE Data with Cubic Equations of State

The experimental data for the n-hexane/1-hexadecanol binary were modeled using the Peng-Robinson equation of state (P-R). Table III shows the optimized binary interaction parameters and the average absolute percent error between the calculated and measured compositions for P-R. Figures 6 and 7 show the fit of P-R to the experimental data. Calculated and experimental data are shown in Figure 6 for the liquid phase, and in Figure 7 for the vapor phase, for the three isotherms above the critical point of hexane. Although good fits of the liquid phase were obtained at higher temperatures, the solubility of hexadecanol in the vapor phase at these conditions is significantly overpredicted.

Table III. Results of the optimization of Peng-Robinson to the experimental data.

Temperature (°C)	Optimized k_{ij}	x error (%)	y error (%)
198.9	0.04	17.2	14.2
251.3	0.01	6.1	2.4
299.2	0.02	3.5	15.2
349.9	0.03	2.3	42.7

Because the critical point of hexadecanol had to be estimated, it is possible that the difficulties in adequately modeling the n-hexane/1-hexadecanol system are due to inaccuracies in the estimated critical properties. The system n-hexane/hexadecane was reexamined to help resolve this issue. Instead of using the experimental literature values for hexadecane, the critical properties were calculated using method of Ambrose [1]. The acentric factor was regressed from vapor pressure data using the method of Hutchenson [3]. Table IV shows the experimental and calculated values for T_c , P_c , and ω . Using the calculated properties for hexadecane, the system was modeled using P-R. Figure 8 shows the comparison of modeling n-hexane/hexadecane using the calculated and the experimental values for critical properties. As can be seen in Figure 8, P-R does a good job of modeling the hexane/hexadecane system, whether the constants are experimental or calculated. This suggests that P-R is not capable of accounting for the hydrogen bonding caused by the alcohol.

Table IV. Experimental and calculated parameters for hexadecane.

	T_c (K)	P_c (bar)	ω
experimental	722	14.1	0.722
calculated	722.3	14.5	0.765

Task 2b. Examination of Theoretically Based Equations of State

No effort planned this quarter.

Task 3a. Process Configuration Studies Using the ASPEN PLUS Simulation Package

Work is ongoing, but no report was planned for this quarter.

Plans for Next Quarter

Binary phase equilibrium experiments for the system n-hexane/tetracosane are being initiated. Modeling of the C₆/C₂₄ binary will commence upon completion of experiments. Process design studies that use several different solvents as the SCF solvent will be completed and then presented in the next quarterly report.

References

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2. Ambrose, D., and Tsonopoulos, C., "Vapor-Liquid Critical Properties of Elements and Compounds. 2. Normal Alkanes," *J. Chem. Eng. Data***40**, 531-546 (1995).
3. Hutchenson, K. W., "Fractionation of Petroleum Pitch by Supercritical Fluid Extraction: Experimental Phase Behavior and Thermodynamic Modeling," Ph. D. Dissertation, Clemson University, Clemson, SC (1990).

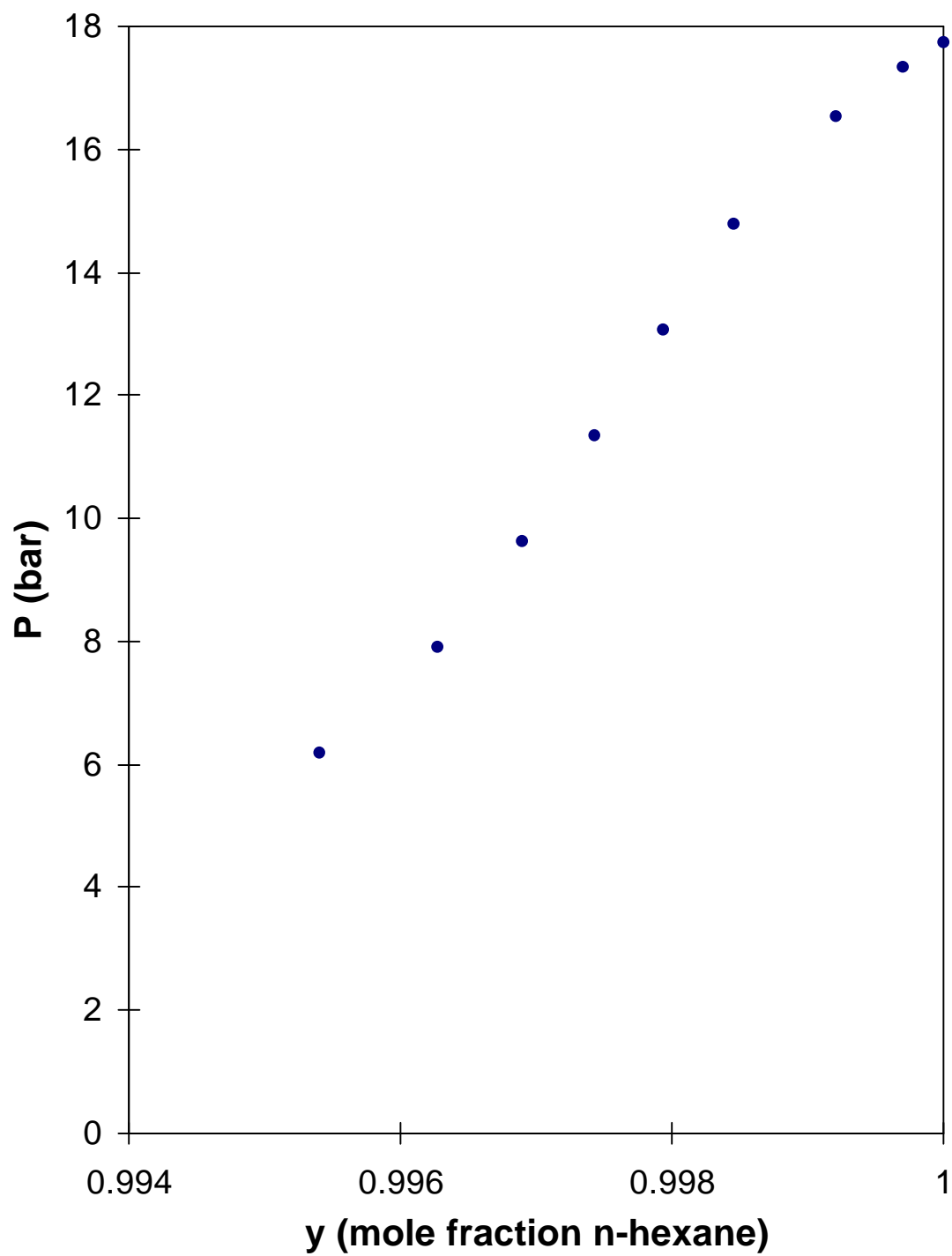


Figure 2. Vapor-phase compositions at 198.9 °C.

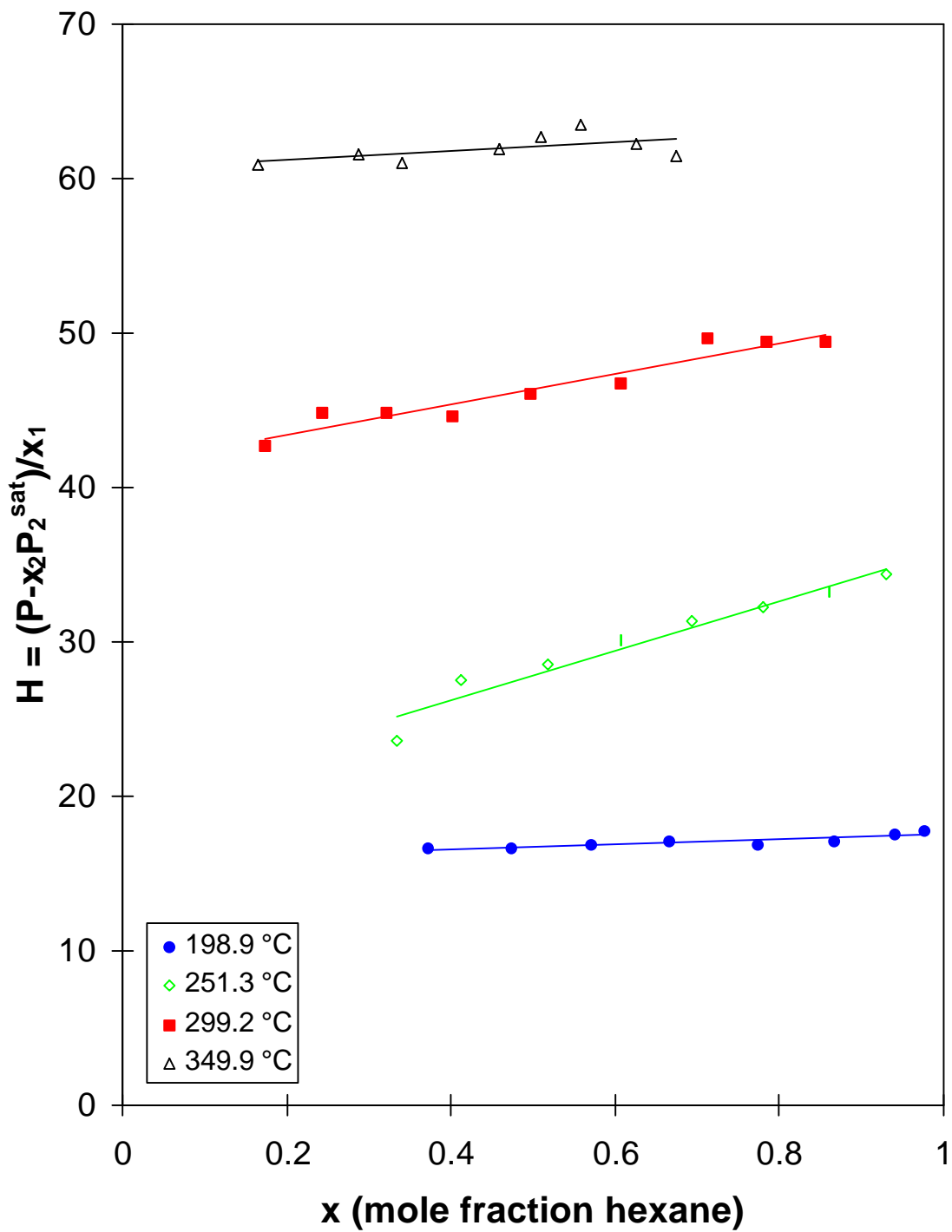


Figure 3. Modified Henry's Law constant vs liquid composition at 198.9 °C, 251.3 °C, 299.2 °C, and 349.9 °C.

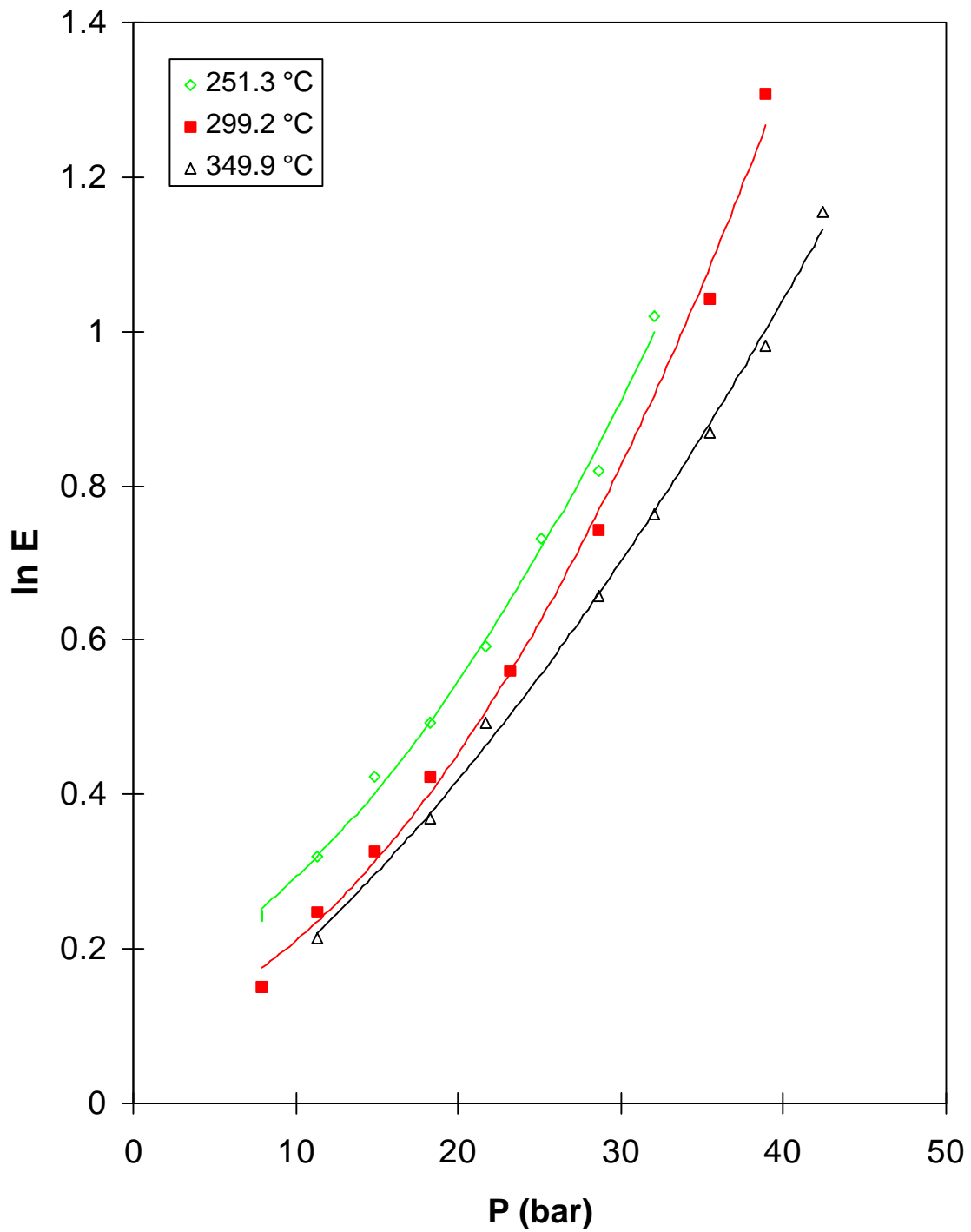


Figure 4. Natural logarithm of the enhancement factor vs pressure at 251.3 °C, 299.2 °C, and 349.9 °C.

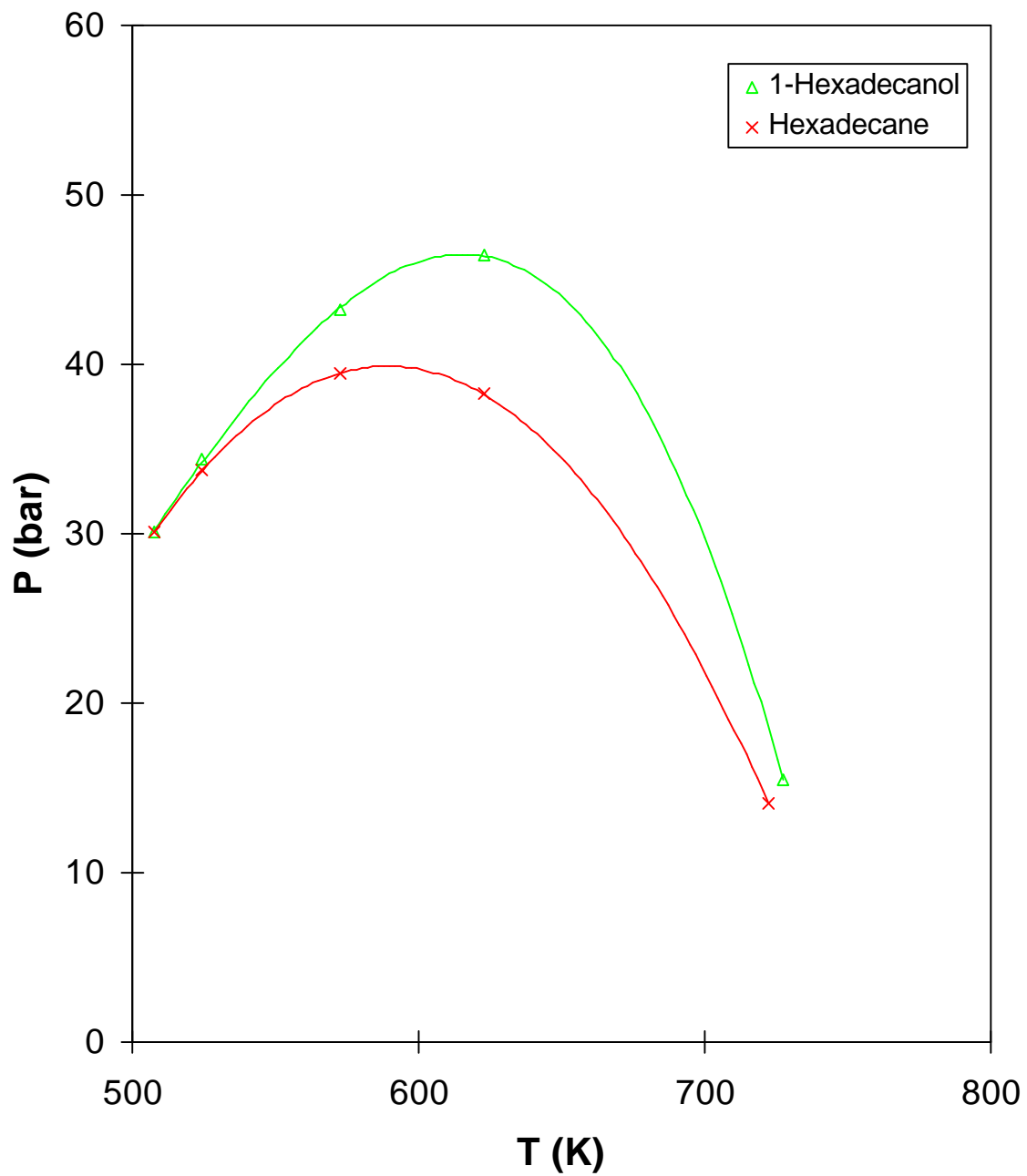


Figure 5. Critical-point curves for hexadecane and 1-hexadecanol with hexane.

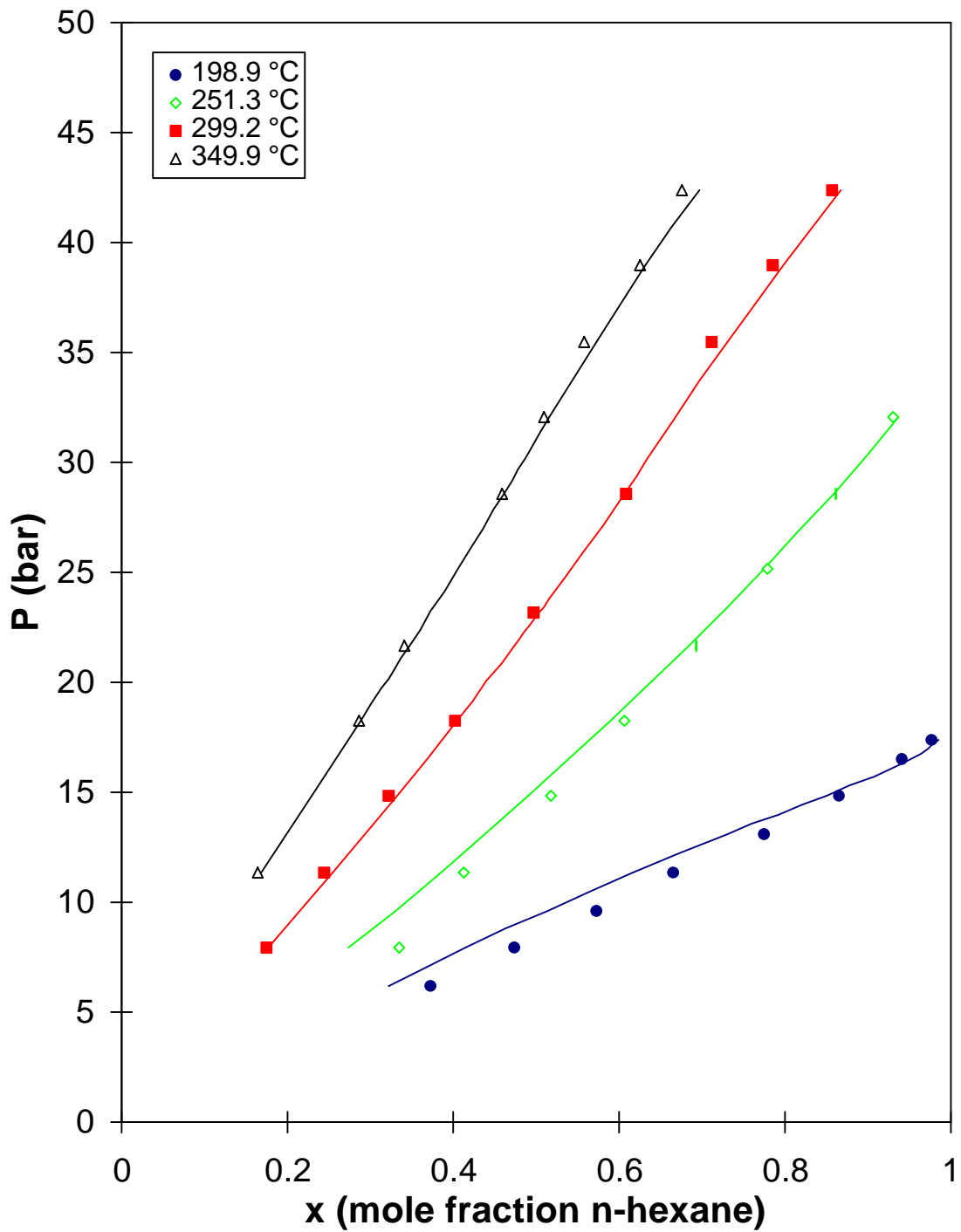


Figure 6. Comparison of Peng-Robinson calculations with experimental data for the liquid-phase compositions.

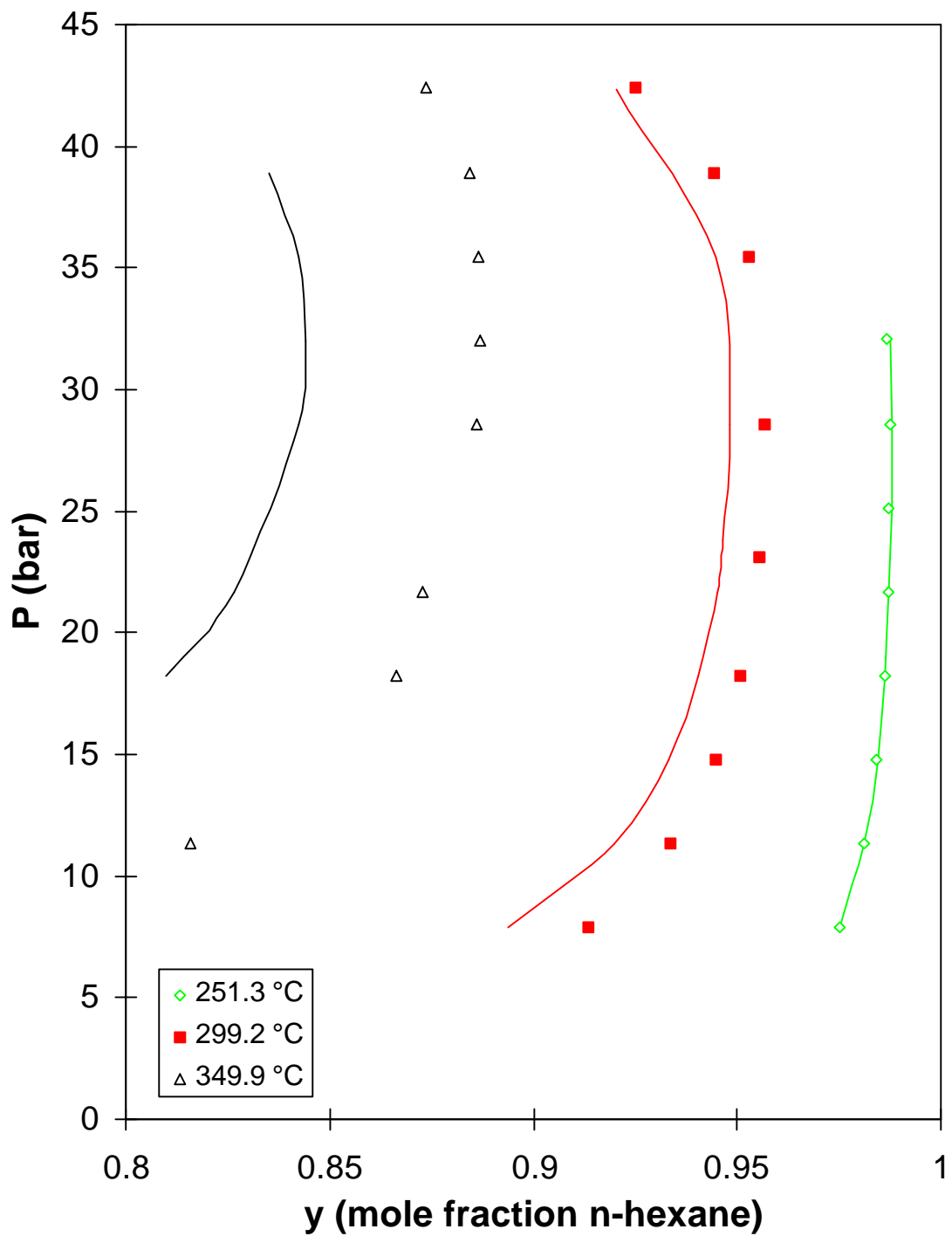


Figure 7. Comparison of Peng-Robinson calculations with experimental data for the vapor-phase compositions.

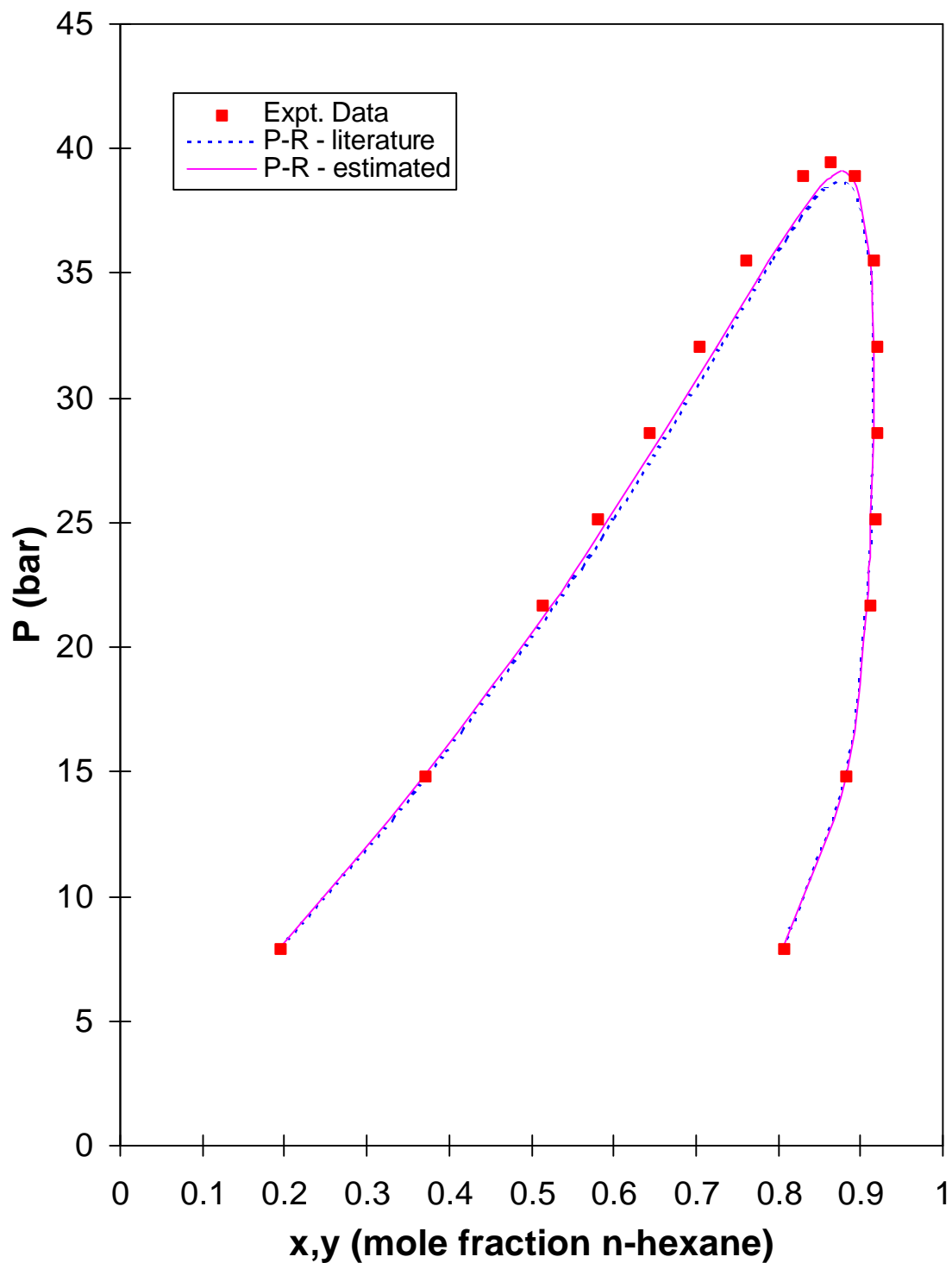


Figure 8. Modeling of n-hexane/hexadecane with Peng-Robinson using estimated and literature values for critical properties at 299.4 °C.