

Separation of Fischer-Tropsch Wax from Catalyst by Supercritical Extraction

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**Separation of Fischer-Tropsch Wax from Catalyst
by Supercritical Extraction**

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Executive Summary

Previous results with alkanes longer than C_{16} (e.g., squalane and tetracosane) indicate that conventional cubic equations may not be capable of modeling vapor-liquid equilibrium (VLE) for Fischer-Tropsch waxes with alkane solvents such as hexane. In contrast, with SAFT we have been able to predict liquid-phase compositions with good accuracy. Because more data are needed to confirm these trends, the system n-hexane/hexatriacontane ($nC_{36}H_{74}$) was investigated. Equilibrium phase compositions and mixture critical points were measured at 248.5, 299.9 and 348.7 °C at pressures ranging from 7.84 to 64.51 bar.

The SAFT equation of state was used to model the three completed isotherms for the hexane/ C_{36} system. As has been previously observed, liquid-phase compositions are accurately predicted with a small, constant k_{ij} of 0.03. Thus, these results provide even further evidence of SAFT's predictive power. However, the weaknesses of SAFT that have been previously noted also continue to occur. Namely, SAFT consistently overpredicts the mixture critical pressure and underpredicts the solubility of the F-T wax in the supercritical (i.e., vapor) phase. The latter of these deficiencies is of particular concern for modeling our proposed extraction process.

Nevertheless, we need to recognize that SAFT represents a significant improvement over conventional cubic equations of state. Namely, by setting k_{ij} to 0.03, liquid-phase compositions can be predicted for F-T wax/solvent systems up to at least C_{36} over a wide range of temperatures and pressures.

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/Hexatriacontane System

Vapor-liquid equilibrium experiments for the n-hexane/hexatriacontane ($nC_{36}H_{74}$) system have been completed. Measured compositions and corresponding pressures at 248.5, 299.9, and 348.7 °C are given in Table I and are depicted on a pressure-composition diagram in Figure 1. Mixture critical points were also measured at the two higher temperatures; however, because of the very low amount of C_{36} that exists at the mixture critical point at 248.5 °C, no measurement could be made. For clarity, vapor-phase compositions for the three isotherms are also shown in Figure 2.

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 the minor component composition. For the vapor phase, the samples at 299.9 and 348.7 °C were typically reproducible to $\pm 2.0\%$ in the minor component (i.e., hexatriacontane). At 248.5 °C, the reproducibility was not as good (i.e., $\pm 3.0\%$) because of the lower solute concentrations in the vapor phase. Temperature and pressure measurements for a given isotherm are believed to be accurate to ± 0.4 °C and ± 0.17 bar, respectively. Considering all sources of error, the reported liquid- and vapor-phase compositions are believed to be accurate to ± 2.5 and $\pm 3.5\%$, respectively.

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

Efforts to model the hexane/hexatriacontane system with the Peng-Robinson equation are currently underway. Results will be presented in the next quarterly report.

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

press., bar	mole fraction hexatriacontane		press., bar	mole fraction hexatriacontane	
	liquid	vapor		liquid	vapor
T = 248.5 °C			T = 348.7 °C		
7.91	0.591	0.0000795	7.91	0.765	0.00466
13.08	0.411	0.0000777	14.80	0.626	0.00347
18.25	0.292	0.0000883	25.14	0.449	0.00364
23.42	0.199	0.000146	35.49	0.330	0.00493
28.59	0.117	0.000310	45.83	0.240	0.00812
33.76	0.0376	0.00115	56.17	0.160	0.0157
35.14	0.0191	0.00231	62.38	0.116	0.0306
35.42 ^a	--- ^b	--- ^b	64.51 ^a	0.0702	0.0702
T = 299.9 °C					
7.84	0.711	0.000773			
14.80	0.535	0.000619			
21.70	0.412	0.000745			
28.59	0.301	0.00103			
35.49	0.221	0.00179			
42.38	0.165	0.00331			
49.28	0.102	0.00841			
53.48 ^a	0.0358	0.0358			

^a Vapor-liquid critical point

^b Unable to maintain critical opalescence because of the low C₃₆ solubility at the critical point

Task 2b. Examination of Theoretically Based Equations of State

The Statistical Associated Fluid Theory (SAFT) equation of state has been used to model the data for the C₆/C₃₆ binary. Interaction parameters were optimized as described previously. The optimized binary interaction parameters and the average absolute percent deviation between the calculated and measured compositions for the SAFT equation are shown in Table II. Calculated and experimental data are shown in Figures 3 and 4 for the liquid and vapor phase compositions, respectively. As was observed for the C₆/C₂₄ system, a small, constant k_{ij} of 0.03 was found to provide the best fit of the data for all measured temperatures. Furthermore, Radosz (1998) has recently shown that SAFT also accurately predicts liquid-phase compositions for ethane/long alkane mixtures when a k_{ij} of 0.03 is used. Taken together, these results provide compelling evidence that SAFT is indeed a predictive equation for mixtures of light gases and solvents with long alkanes up to at least C₃₆.

Nevertheless, SAFT still has problems that must be addressed before it can be used to model our proposed extraction process. Just as for previously measured systems,

Table II. Optimized binary interaction parameters for the SAFT equation and deviations between experimental and calculated results.

Temperature (°C)	Optimized k_{ij}	x error (%)	y error (%)
248.5	0.03	10.4	29.4
299.9	0.03	6.1	23.1
348.7	0.03	2.3	18.1

$${}^a \text{AAPD} = \sum_i \left| \frac{(x_i[\text{exp}] - x_i[\text{calc}])}{x_i[\text{exp}]} \right| \times 100\%$$

SAFT significantly underpredicts vapor-phase compositions and overpredicts the observed mixture critical pressure. This overprediction of the mixture critical pressure is at least partly due to the fact that SAFT does not predict the pure component critical points correctly, with the predicted vapor pressure curve extending more than 20 °C above the true critical temperature (see Figure 5). The anomalous behavior that is observed for the vapor phase at 248.5 °C (see Figure 4) probably occurs because SAFT predicts a vapor pressure at this temperature instead of the observed mixture critical point. Further investigation is required to confirm this premise.

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

No effort planned for this quarter.

Plans for Next Quarter

VLE measurements for the hexane/hexatriacontane system at 200 °C will be attempted. All results for this system will then be fit to both the Peng-Robinson and SAFT equations. The ability of SAFT to predict liquid-phase compositions for all VLE data relevant to our proposed process will be investigated. Finally, design and construction of a new apparatus for high molecular weight components will be completed.

References

Radosz, M. and H. Adidharma, "Square-Well SAFT Equations of State for Homopolymeric and Heteropolymeric Fluids", presented at 8th International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, The Netherlands, April 1998.

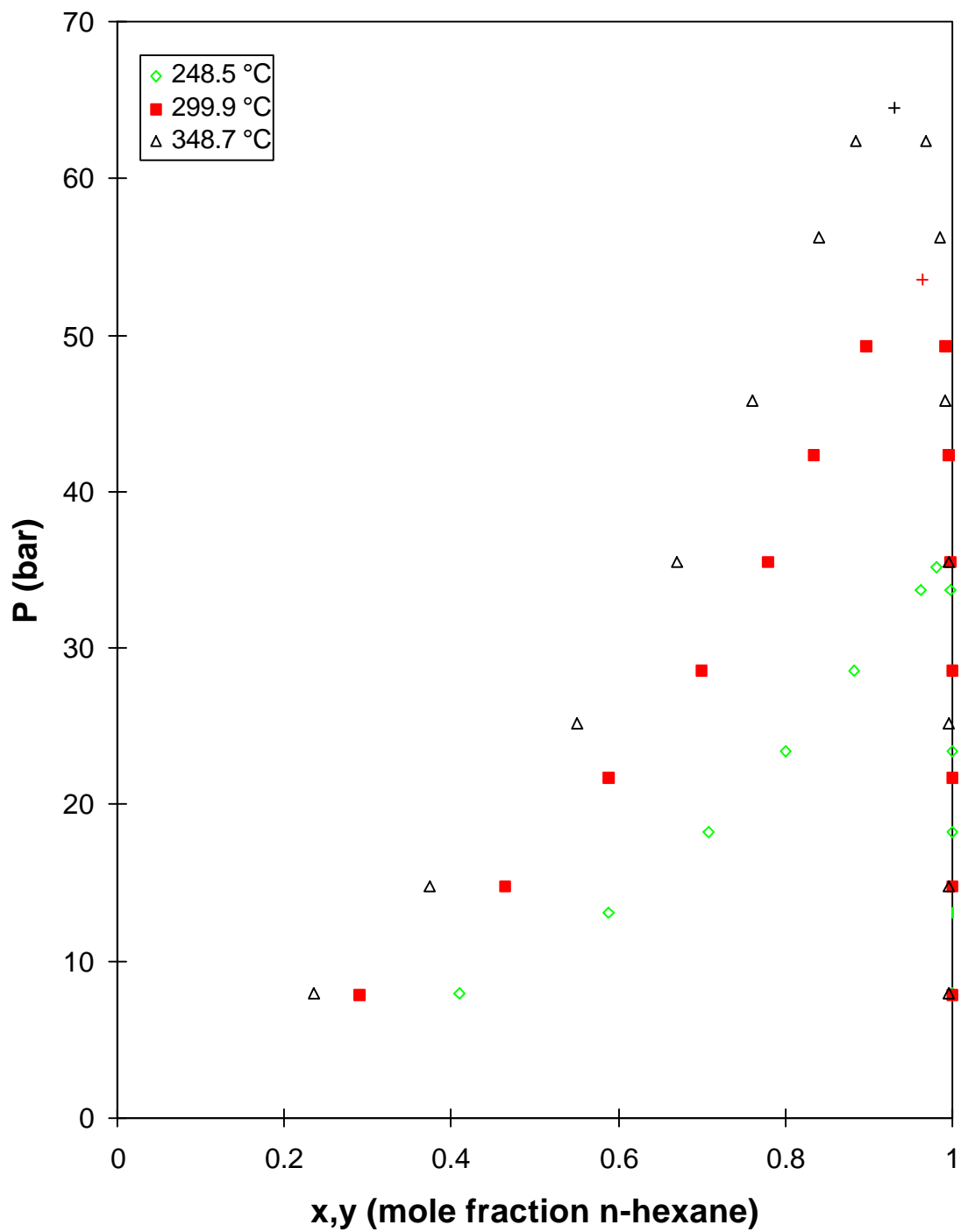


Figure 1. Pressure vs composition diagram for the n-hexane/hexatriacontane binary at 248.5 °C, 299.9 °C, and 348.7 °C. The + are the mixture critical points.

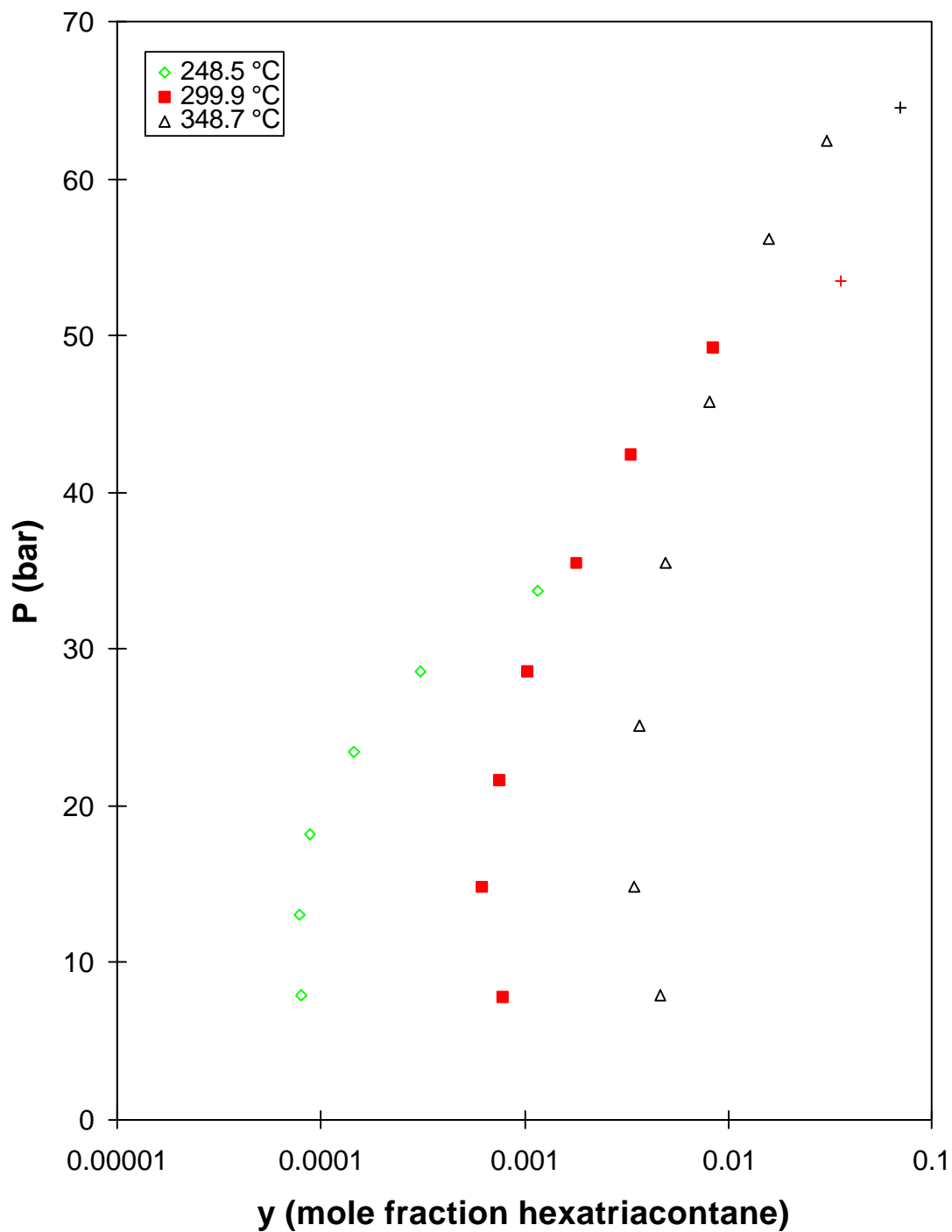


Figure 2. Vapor-phase compositions for the n-hexane/hexatriacontane binary at 248.5 °C, 299.9 °C, and 348.7 °C. The + are the mixture critical points.

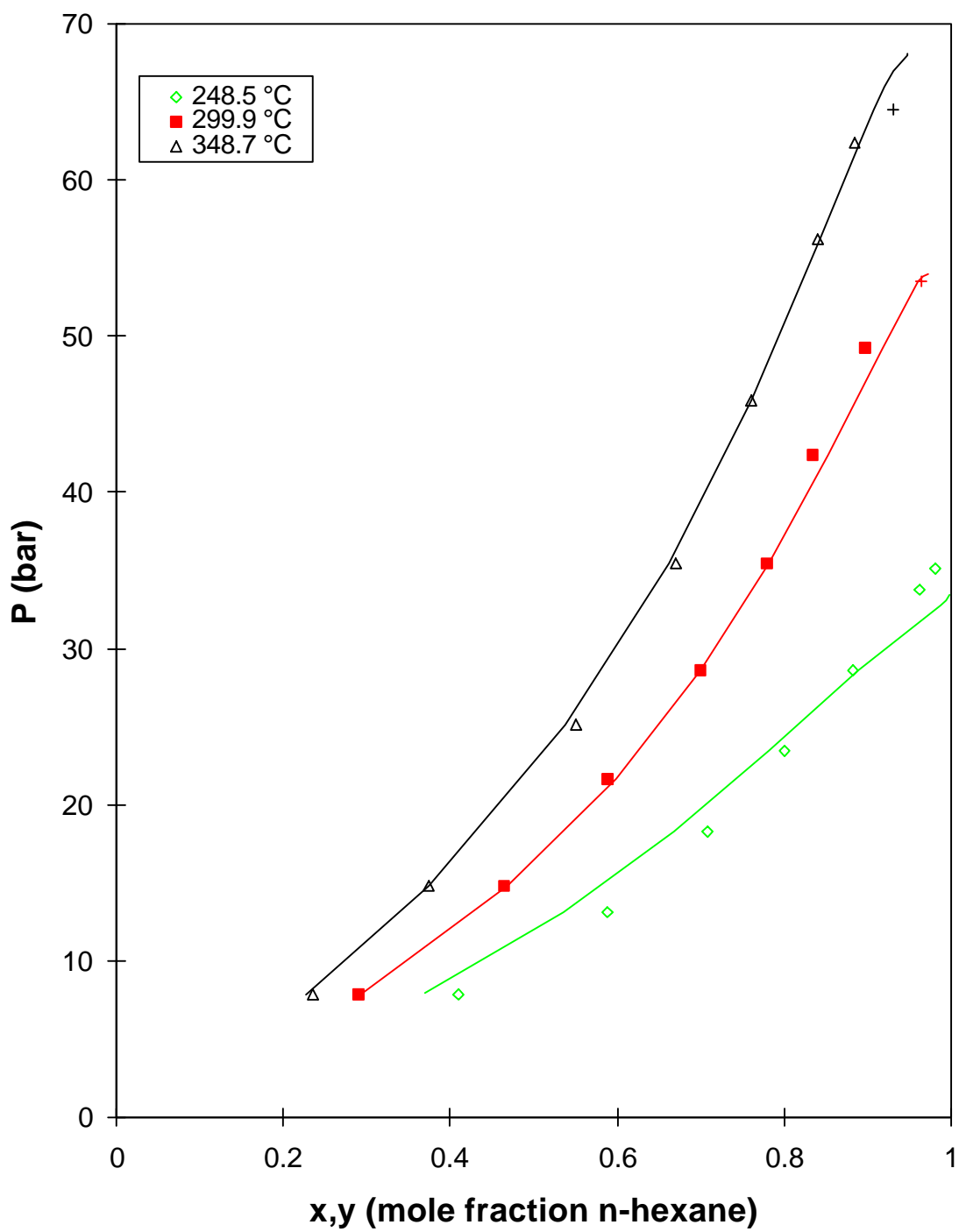


Figure 3. Comparison of SAFT calculations with experimental data for the liquid-phase compositions.

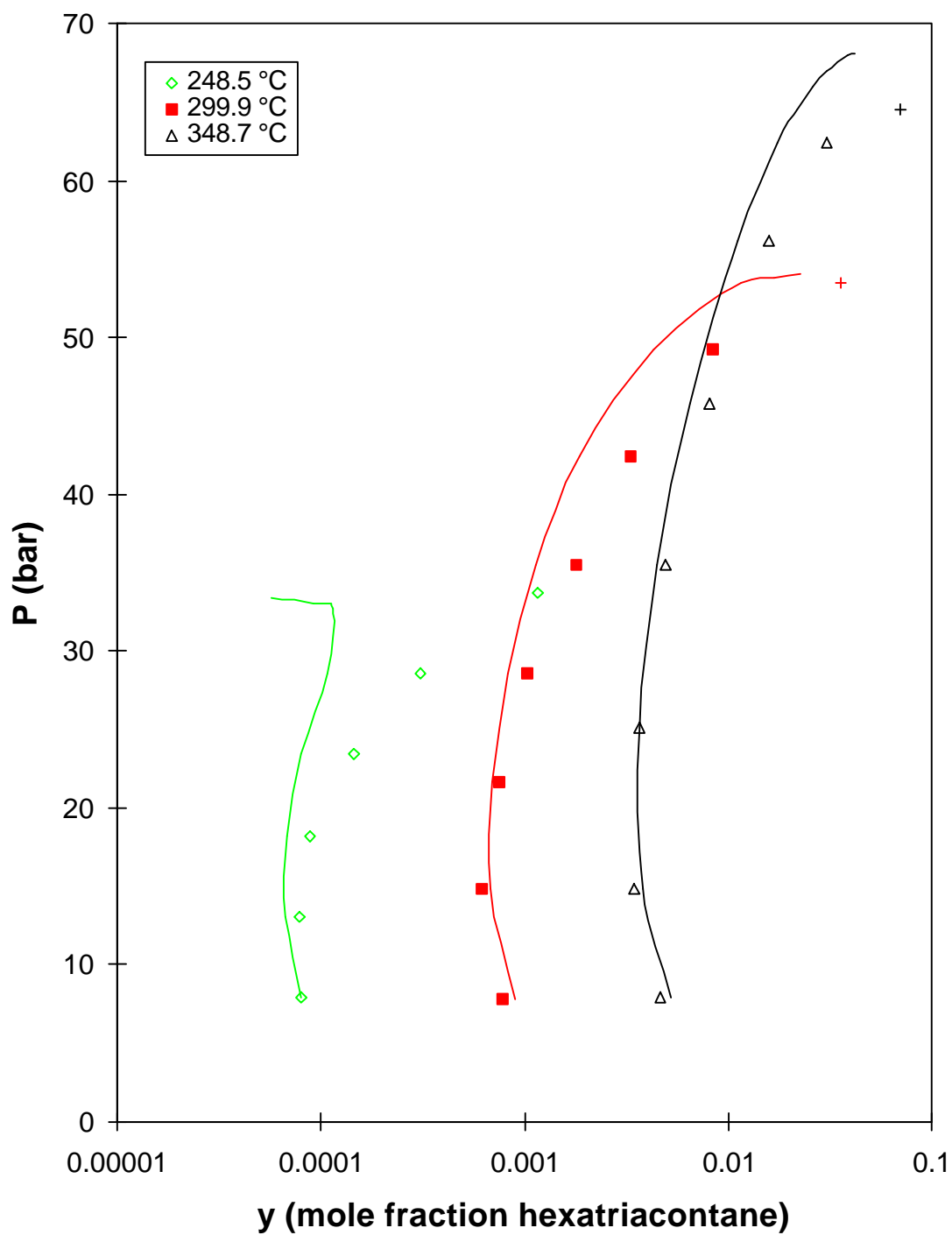


Figure 4. Comparison of SAFT calculations with experimental data for the vapor-phase compositions.

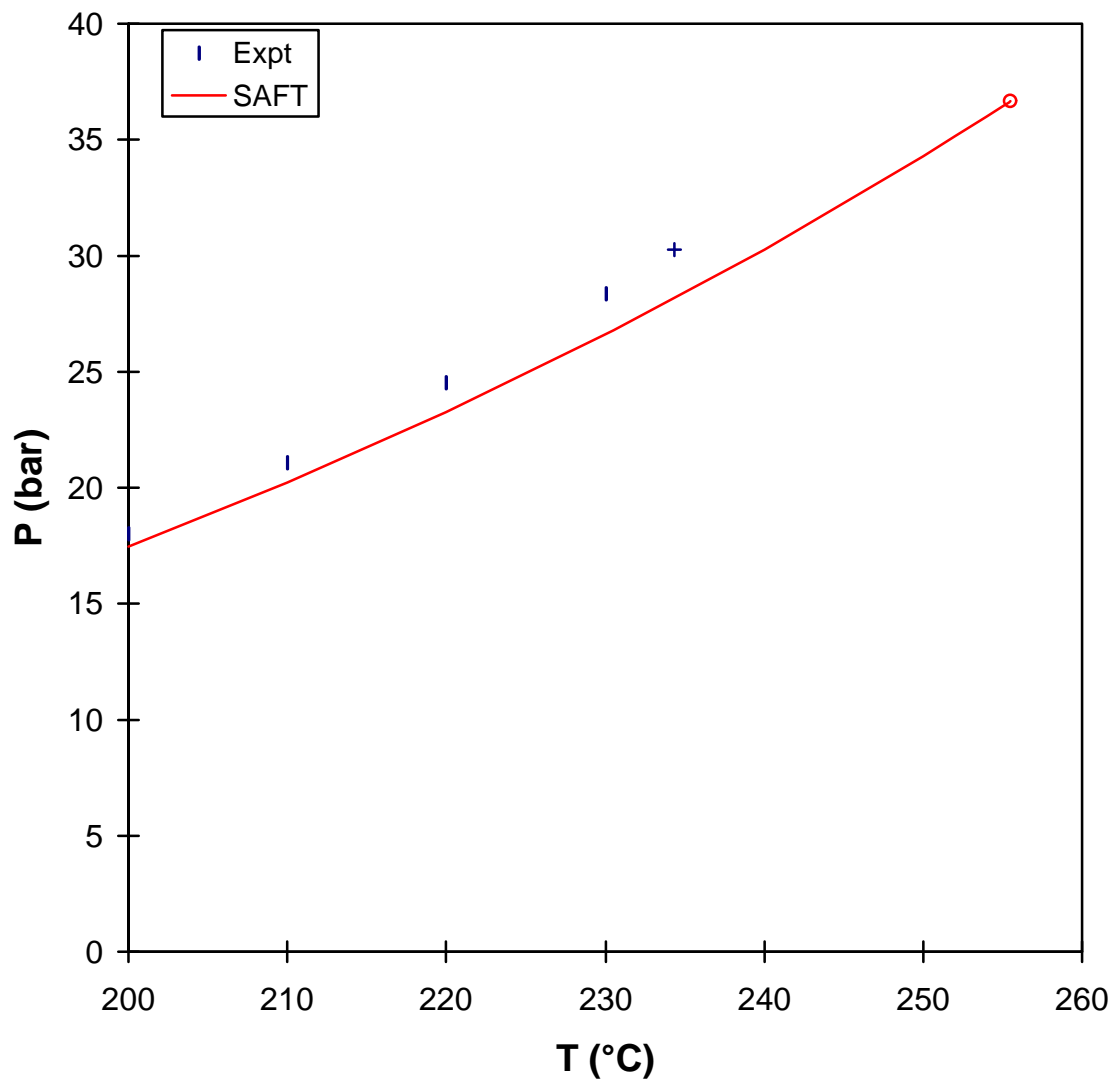


Figure 5. Experimental measurements and SAFT predictions for the vapor pressure of n-hexane. The + is the experimental critical point, and the o is SAFT's prediction.