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Executive Summary

Experimental measurements that are required in order for us to develop an accurate thermodynamic model for our proposed separation process are continuing. In the previous quarter, vapor and liquid equilibrium compositions and mixture critical points were measured for the n-hexane/hexadecane system at 199.2, 251.7, 299.4, and 349.8 °C at pressures ranging from 6.2 to 39.4 bar. For the liquid phase, the three samples that were collected for a given temperature and pressure were always reproducible to better than $\pm 1\%$. For the vapor phase, the triplicate samples always agreed to within $\pm 2.5\%$. Temperature and pressure uncertainties for a given isotherm were always less than ± 0.4 °C and ± 0.14 bar, respectively. Considering all sources of error, the reported liquid and vapor compositions are believed to be accurate to better than ± 1.5 and $\pm 3\%$, respectively. Both SAFT and the Peng-Robinson equation were used to fit the measured data. Even though all necessary pure-component parameters for the SAFT equation were available for this system, it continues to significantly underpredict the concentration of the heavy component in the vapor phase and to overpredict the mixture critical pressure.

The group at North Carolina State University has been involved modeling the process using the ASPEN plus simulation program. First, the effectiveness of the Peng-Robinson (P-R) and the Redlich-Kwong-Soave (RKS) equations of state were examined. These cubic equations of state are both included in the ASPEN Plus program. Both models were used on fifteen sets of binary hydrocarbon data. RKS has been found to be slightly more accurate for most systems. However, P-R does better in predicting vapor-phase compositions which have low concentrations of the heavy component. Modeling of the overall process has started, using RKS to model the separation.

Technical Objectives

The objective of this research project is to evaluate the potential of SCF extraction for separating the catalyst slurry of a Fischer-Tropsch (F-T) slurry bubble column (SBC) reactor into two fractions: (1) a catalyst-free wax containing less than 10 ppm particulate matter and (2) a concentrated catalyst slurry that is ready for recycle or regeneration. The wax 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 major factors. First, the supercritical solvent must be able to dissolve the F-T wax; furthermore, this must be accomplished without entraining the solid catalyst. Second, the extraction must be controlled so as not to favor the removal of the low molecular weight wax compounds, i.e., a constant carbon-number distribution of the alkanes in the wax slurry must be maintained at steady-state column operation.

To implement our objectives, the following task structure is being implemented:

Task 1: Equilibrium Solubility Measurements

- a. apparatus modification and construction.
- b. experimental measurement of selected model systems.
- c. catalyst/wax separation studies.

Task 2: Thermodynamic Modeling

- a. programming and testing of SAFT equation for nonassociating systems.
- b. programming and testing of SAFT equation for associating systems.
- c. modeling measured results with the SAFT equation.
- d. pure component and mixture SAFT parameter determination for selected model systems.

Task 3: Process Design Studies

- a. integration of our SAFT program into a process simulation package.
- b. process configuration studies using above simulation package.

Detailed Description of Technical Progress

Task 1a. Apparatus Modification and Construction

Experimental results that were obtained for the first two binary systems to be measured indicate that we are obtaining accurate data of high quality. Because we have found our undergraduate assistants to be most helpful in assisting with the experiments, we have decided to postpone the automation of our apparatus indefinitely. The limited funds that we have can be used more effectively elsewhere. Modification of the apparatus to allow the measurement of alkanes that are solids at ambient conditions has begun and will continue into the next quarter.

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

Vapor-liquid equilibrium experiments for the n-hexane/hexadecane system have been completed. Measured compositions and corresponding pressures for the n-hexane/hexadecane binary at 199.2, 251.7, 299.4, and 349.8 °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 199.2 °C isotherm is plotted in Figure 2. 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. Figures 3 and 4 depict the modified Henry's Law constant and the modified Enhancement Factor, respectively, and indicate the high consistency of the measurements. It should be pointed out that H in Figure 3 is now defined as $H = (P - x_2 P_2^{sat})/x_1$ because the vapor pressure of hexadecane is nontrivial at the measured temperatures. For the hexane-squalane binary, the second term in the equation was essentially zero because of squalane's low vapor pressure.

For the liquid phase, the three samples collected at a given temperature and pressure were typically reproducible to better than $\pm 0.5\%$. In a few cases deviations of up to $\pm 1\%$ were obtained. For the vapor phase, the samples were also typically reproducible to $\pm 0.5\%$, but deviations between samples of up to $\pm 2.5\%$ were occasionally obtained.

Temperature and pressure uncertainties for a given isotherm were always less than ± 0.4 °C and ± 0.14 bar, respectively. Considering all sources of error, the reported liquid and vapor compositions are believed to be accurate to better than ± 1.5 and $\pm 3\%$, respectively.

Task 1c. Catalyst/Wax Separation Studies

No effort planned for this quarter.

Task 2a and 2b. Programming and Testing SAFT for Nonassociating and Associating Systems

No effort planned for this quarter.

Table I. Vapor-liquid equilibrium properties and properties calculated by Peng-Robinson and SAFT for the n-hexane/hexadecane system.

Press. bar	Exp. Data mole fraction n-hexane		Calculated by Peng-Robinson mole fraction n-hexane				Calculated by SAFT mole fraction n-hexane			
	liquid	vapor	liquid	vapor	% error		liquid	vapor	% error	
					liquid	vapor			liquid	vapor
T = 199.2 °C										
6.18	0.4521	0.9858	0.4422	0.9852	2.2	4.0	0.3988	0.9859	11.8	1.0
7.91	0.5377	0.9893	0.5466	0.9890	1.7	2.5	0.5028	0.9896	6.5	3.2
9.63	0.6369	0.9918	0.6428	0.9916	0.9	1.9	0.6043	0.9922	5.1	4.6
11.36	0.7225	0.9938	0.7313	0.9936	1.2	2.5	0.7036	0.9941	2.6	5.5
13.08	0.8053	0.9954	0.8127	0.9953	0.9	1.2	0.8000	0.9958	0.7	9.2
14.80	0.8771	0.9970	0.8873	0.9969	1.2	2.6	0.8909	0.9974	1.6	14.6
16.53	0.9457	0.9986	0.9546	0.9985	0.9	3.6	0.9708	0.99917	2.7	40.9
17.35	0.9770	0.99939	0.9836	0.99940	0.7	4.3				
T = 251.3 °C										
7.908	0.3243	0.9372	0.3065	0.9365	5.5	1.1	0.3139	0.9439	3.2	10.7
11.36	0.4364	0.9537	0.4290	0.9537	1.7	0.6	0.4359	0.9612	0.1	16.2
14.80	0.5504	0.9640	0.5402	0.9630	1.9	2.8	0.5464	0.9707	0.7	18.6
18.26	0.6385	0.9696	0.6415	0.9688	0.5	2.6	0.6479	0.9769	1.4	24.0
21.70	0.7243	0.9734	0.7326	0.9729	1.1	2.0	0.7407	0.9815	2.3	30.3
25.15	0.8053	0.9766	0.8144	0.9760	1.1	2.7	0.8258	0.9853	2.5	37.3
28.60	0.8682	0.9782	0.8867	0.9784	2.1	0.9	0.9021	0.9891	3.9	50.1
32.05	0.9283	0.9788	0.9492	0.9796	2.3	3.7	0.9655	0.9938	4.0	70.6
33.77 ^a	0.9694	0.9694								
T = 299.4 °C										
7.91	0.1956	0.8067	0.1940	0.8043	0.8	1.2	0.1863	0.8207	4.8	7.2
14.80	0.3708	0.8834	0.3723	0.8805	0.4	2.5	0.3580	0.8964	3.4	11.1
21.70	0.5143	0.9113	0.5282	0.9056	2.7	6.5	0.5115	0.9232	0.5	13.4
25.14	0.5834	0.9172	0.5989	0.9114	2.7	7.0	0.5824	0.9307	0.3	16.3
28.59	0.6436	0.9199	0.6657	0.9143	3.4	7.0	0.6499	0.9360	1.0	20.2
32.04	0.7043	0.9196	0.7295	0.9142	3.6	3.3	0.7141	0.9398	1.4	25.1
35.49	0.7600	0.9152	0.7928	0.9092	4.3	7.1	0.7753	0.9420	2.0	31.6
38.93	0.8301	0.8925					0.8339	0.9423	4.6	46.3
39.45 ^a	0.8630	0.8630					0.8426	0.9420	2.4	57.7
T = 349.8 °C										
11.36	0.1816	0.6365	0.1735	0.6329	4.4	1.0	0.1780	0.6765	2.0	11.0
16.53	0.2805	0.7257	0.2784	0.7172	0.7	3.1	0.2803	0.7600	0.1	12.5
21.70	0.3723	0.7671	0.3785	0.7568	1.7	4.4	0.3761	0.8019	1.0	15.0
25.14	0.4341	0.7898	0.4432	0.7706	2.1	9.2	0.4370	0.8190	0.7	13.9
28.59	0.4955	0.7937	0.5077	0.7770	2.5	8.1	0.4959	0.8306	0.1	17.9
32.04	0.5573	0.7988	0.5738	0.7759	3.0	11.4	0.5532	0.8381	0.7	19.5
35.49	0.6167	0.7872	0.6482	0.7614	5.1	12.1	0.6096	0.8417	1.2	25.6
37.21	0.6506	0.7704	0.7091	0.7287	9.0	18.2	0.6379	0.8420	2.0	31.2
38.24 ^a	0.7211	0.7211					0.6550	0.8416	9.0	43.4

^a Vapor-liquid critical point.

Task 2c and 2d. Modeling VLE Data and Determining Pure Component/Mixture SAFT Parameters

The experimental data for the n-hexane/hexadecane binary were modeled using two equations of state, Peng-Robinson and the Statistical Associating Fluid Theory (SAFT). Using optimized interaction parameters, the P-R equation predicts the hexane concentration in the liquid phase to within an average error of 2.4%. In the vapor phase, the average error was 4.8% in the minor component (i.e., hexadecane) concentration. SAFT modeled the liquid phase well, with an average error of 2.3%. Unfortunately, just as for the hexane-squalane binary, SAFT does a poor job of modeling both the vapor phase, with an average error of 22%, and the mixture critical points. Table II shows the optimized binary interaction parameters for both equations of state, and a comparison of the goodness of fit of the two equations is shown for the isotherm at 299.4 °C in Figure 5.

Table II. Binary interaction parameters for the P-R and SAFT equations.

T (°C)	199.2 °C	251.3 °C	299.4 °C	349.8 °C
PR	-0.01	0.00	0.00	0.02
SAFT	0.02	0.01	0.025	0.03

Results for the SAFT equation are not what we had hoped. For the hexane/squalane system, we had no pure-component parameters for squalane, and had to assume that they were the same as for triacontane, $nC_{30}H_{62}$, in order to perform the necessary flash calculations. Thus, we had assumed that the inability of SAFT to model the vapor-phase composition accurately was due to the lack of good pure-component data. However, for the hexane/hexadecane system, pure-component parameters for hexadecane were readily available in the literature, and results are still less than satisfactory. Unfortunately, it is beginning to appear that, in its present form, SAFT may not be an appropriate equation for modeling the systems of interest.

In order to accurately model the separation of multicomponent hydrocarbon systems using the Aspen Plus simulation package, the phase equilibria of the long-chain hydrocarbon systems must be accurately described. To do this, the group at North Carolina State University focused on two equations of state (EOSs) in the Aspen Plus

database: Peng-Robinson and Redlich-Kwong-Soave. Vapor-liquid equilibrium (VLE) has been calculated for each of 15 binary hydrocarbon systems using both equations of state, and the results were compared to experimental data available in the literature. The hydrocarbon systems modeled were all binary pairs of long-chain alkanes, similar to those found in Fischer-Tropsch wax distributions, and short-chain alkanes, similar to the supercritical fluids of interest.

In performing VLE calculations, the optimized binary interaction parameter (k_{ij}) for each system was determined. This was done using an optimization technique based on pressure and the vapor phase fraction of the heavy component, two important variables in the process design calculations. By choosing various values for k_{ij} , it was possible to calculate the average absolute deviation from experiment for each k_{ij} . These values were graphed to find the minimum error and corresponding binary interaction parameter. The VLE compositions at these optimum parameter values are used.

The average error of the results of the VLE calculations are shown in Table III. For the most part, the Redlich-Kwong-Soave EOS does a better job of predicting the experimental vapor-liquid equilibrium. However, the Peng-Robinson EOS does better in a few cases, namely the low temperature isotherms for the C6-C16 and C6-squalane systems. For these systems, where the concentration of the heavy component in the vapor phase is very low (10^{-5} mole fraction), the P-R equation does about twice as well as RKS in predicting the vapor-liquid equilibrium.

Figures 6 and 7 show graphical representations of these results. Figure 6 is a P-x-y diagram for the C5-C16 system at 245.5 °C. This graph shows experimental data compared with predictions based on the P-R, RKS and SAFT EOSs. The two cubic equations (P-R and RKS) appear to capture the vapor-liquid equilibrium of this system, with some small deviations in the liquid phase composition as the system approaches the mixture critical point. SAFT models the liquid phase well, but the equation misses badly on the vapor side. Figure 7 shows a blowup of the vapor phase data seen in Figure 6. Both cubic equations predict the vapor phase well, while the SAFT equation does not, especially near the mixture critical point. These calculations suggest that the phase equilibrium of binary hydrocarbon mixtures can be adequately predicted by either the Peng-Robinson or Redlich-Kwong-Soave EOS.

Table III: Equation of State Comparison - Binaries
 Absolute Average Deviations (P and y error / # of data points)

	Peng- Robinson	Redlich- Kwong-Soave
C5-C16 @ 245.5 °C	0.073	0.082
C5-C16 @ 306.5 °C	0.028	0.028
C5-C18 @ 306.5 °C	0.035	0.031
C5-C22 @ 245 °C	0.0908	0.061
C5-C22 @ 306.5 °C	0.069	0.048
C5-C22 @ 357.0 °C	0.082	0.046
C5-C24 @ 306.5 °C	0.133	0.086
C6-Squalane @ 196.6 °C	0.159	0.297
C6-Squalane @ 251.2 °C	0.145	0.22
C6-Squalane @ 301.4 °C	0.107	0.162
C6-Squalane @ 350.2 °C	0.133	0.21
C7-C19 @ 305.5 °C	0.061	0.035
C7-C23 @ 245.5 °C	0.078	0.132
C7-C23 @ 306.5 °C	0.091	0.069
C7-C23 @ 357.0 °C	0.091	0.071

Task 3. Process Design Studies

Modeling of the overall process on Aspen Plus has begun using the Redlich-Kwong-Soave equation of state. Initial studies were performed with an Anderson-Schulz-Flory distribution based on an alpha value of 0.8. This value was chosen because we wanted to start the simulations with a smaller number of products, for which necessary thermodynamic data, e.g., critical temperatures and pressures, was reasonably available in the literature. The simulation included two recycle loops; one loop recycled the unextracted product back to the reactor, and the other loop recycled uncondensed supercritical solvent back to the extraction unit along with a makeup feed. The calculations on both loops converged successfully. Several runs were performed with

hexane as the supercritical solvent. The temperature and pressure of the extraction unit and the ratio of solvent to waxy product were varied.

Plans for Next Quarter

Binary phase equilibrium experiments for the system n-hexane/hexadecanol are being initiated. Results for this system will be compared to those containing hexadecane, in an attempt to quantify the effect of alcohol groups on phase behavior. Future process modeling studies using ASPEN will focus on a product distribution based on alpha equal to 0.95. This distribution includes n-alkanes up to $C_{100}H_{202}$.

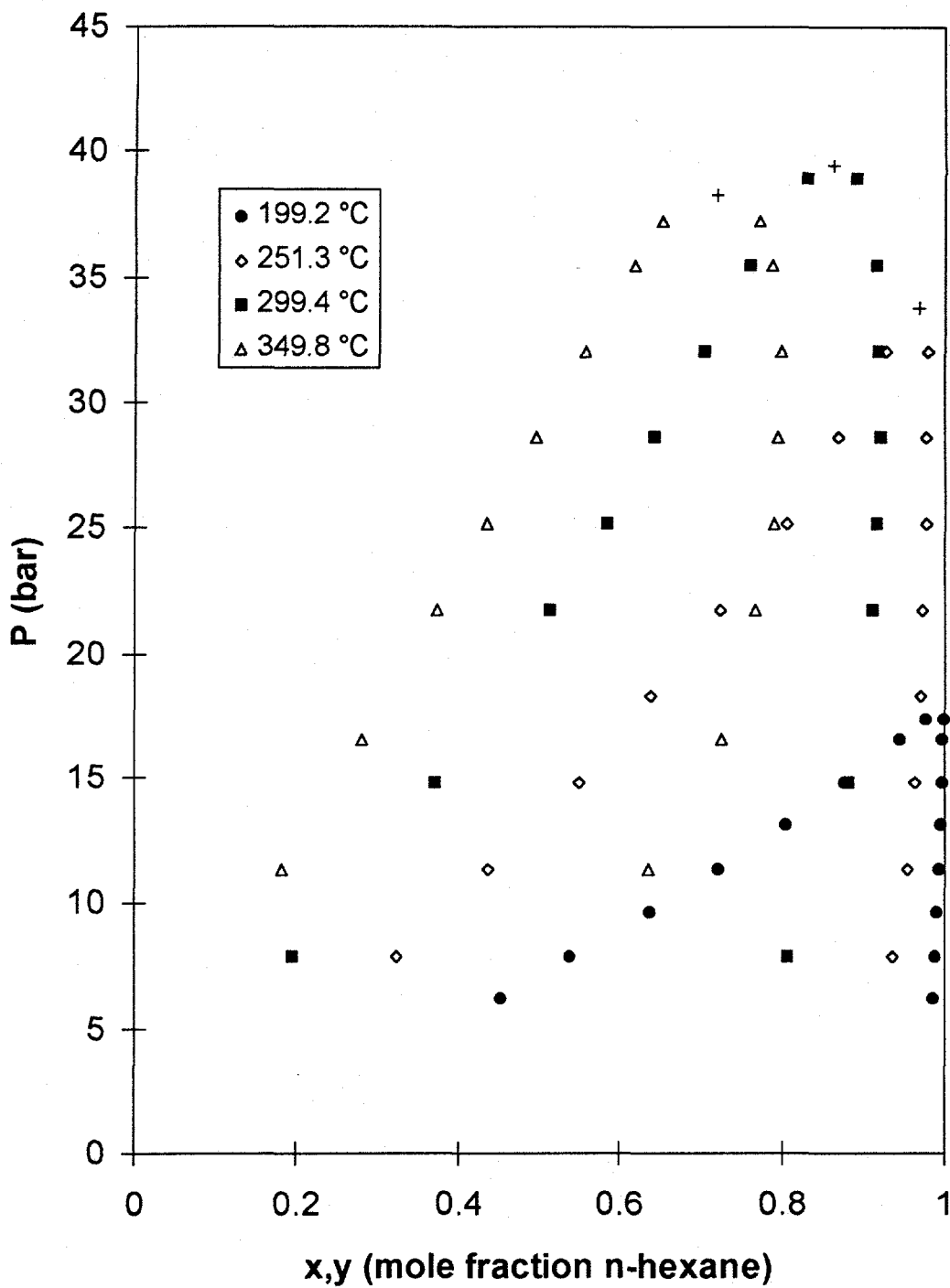


Figure 1. Pressure-vs-composition diagram for the n-hexane/hexadecane system at 199.2 , 251.3 , 299.4 , and 349.8 °C. The + are the mixture critical points.

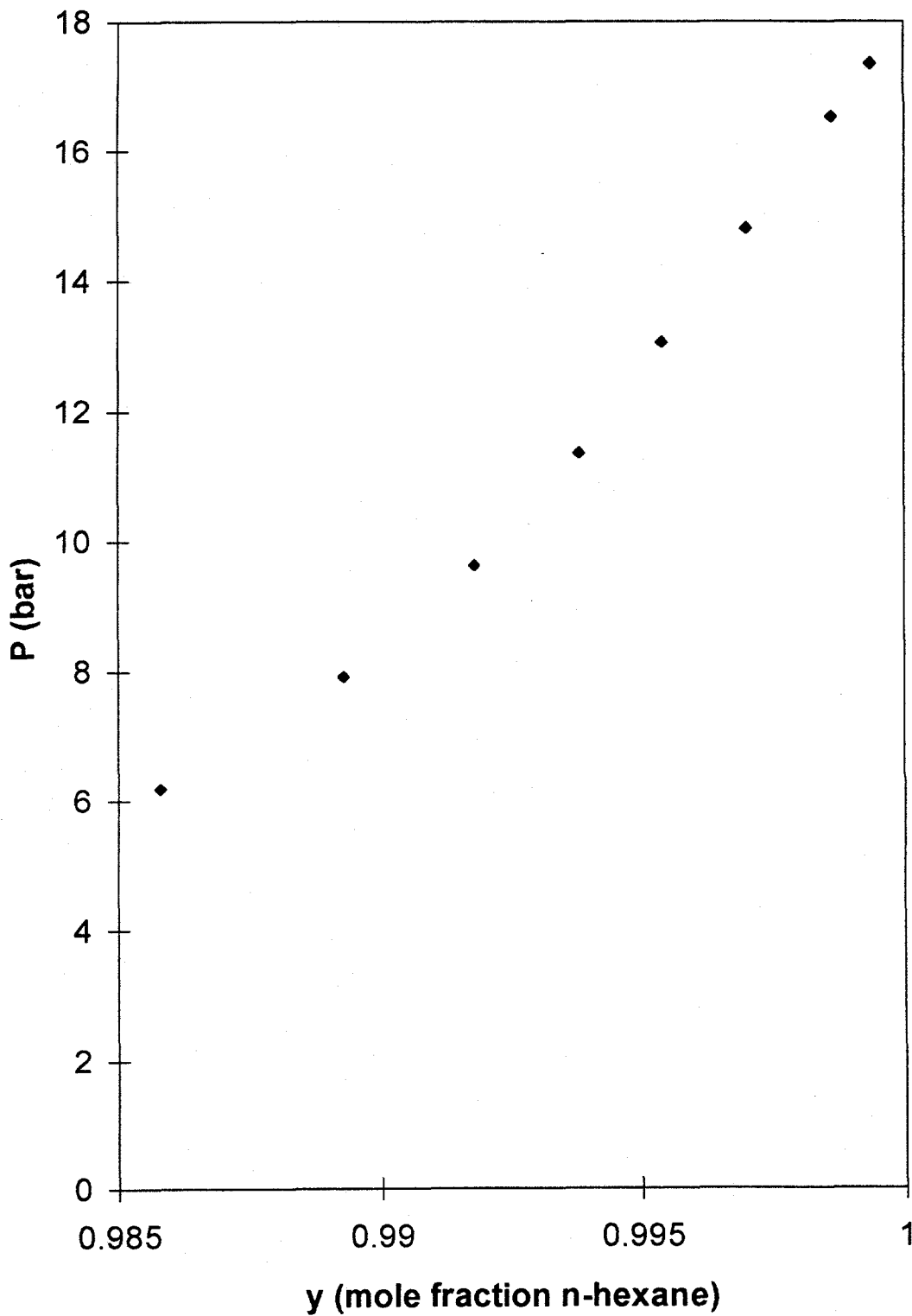


Figure 2. Vapor-phase composition at 199.2 °C.

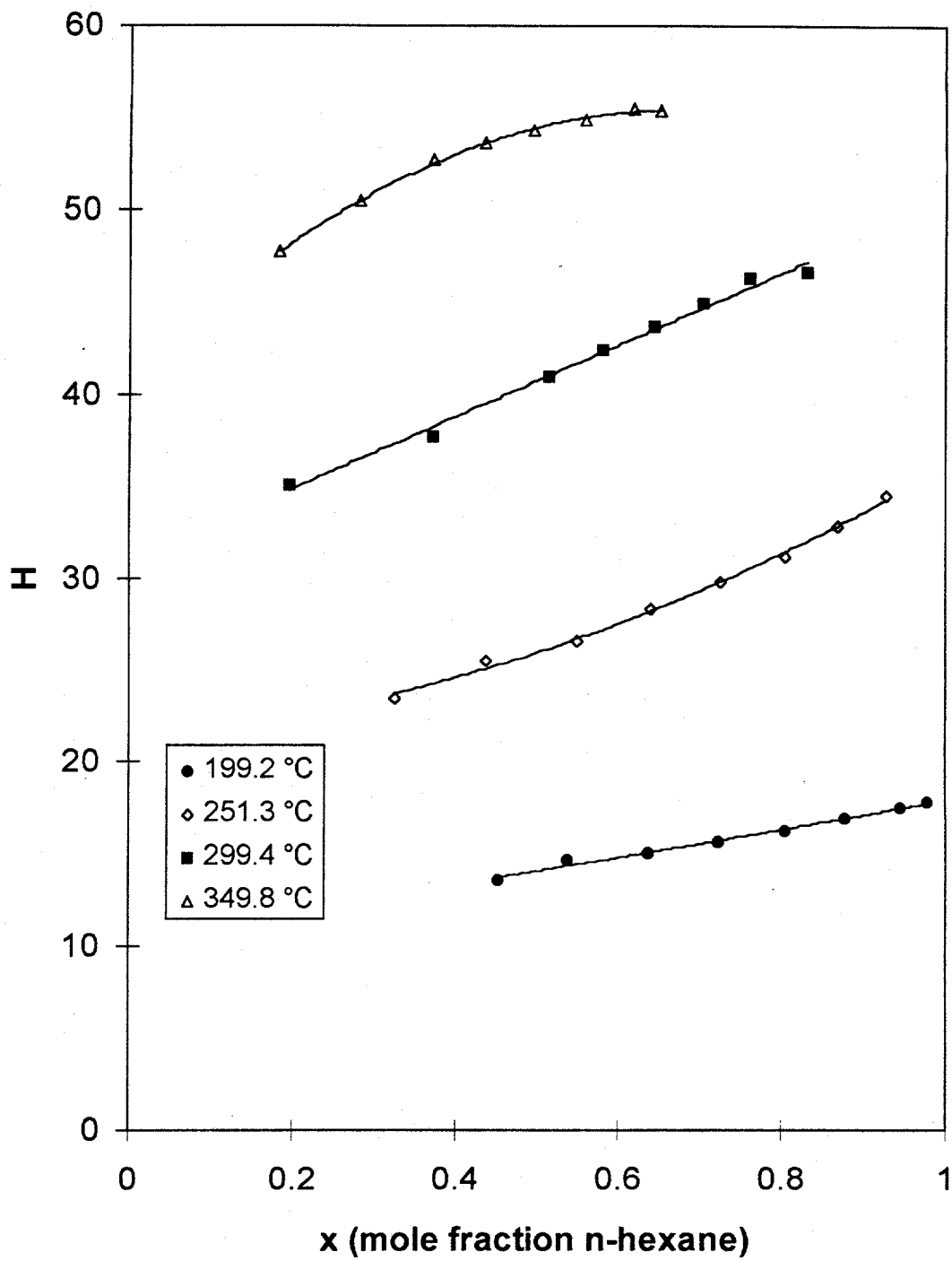


Figure 3. Modified Henry's Law constant vs liquid composition at 199.2 , 251.3 , 299.4 , and 349.8 °C.

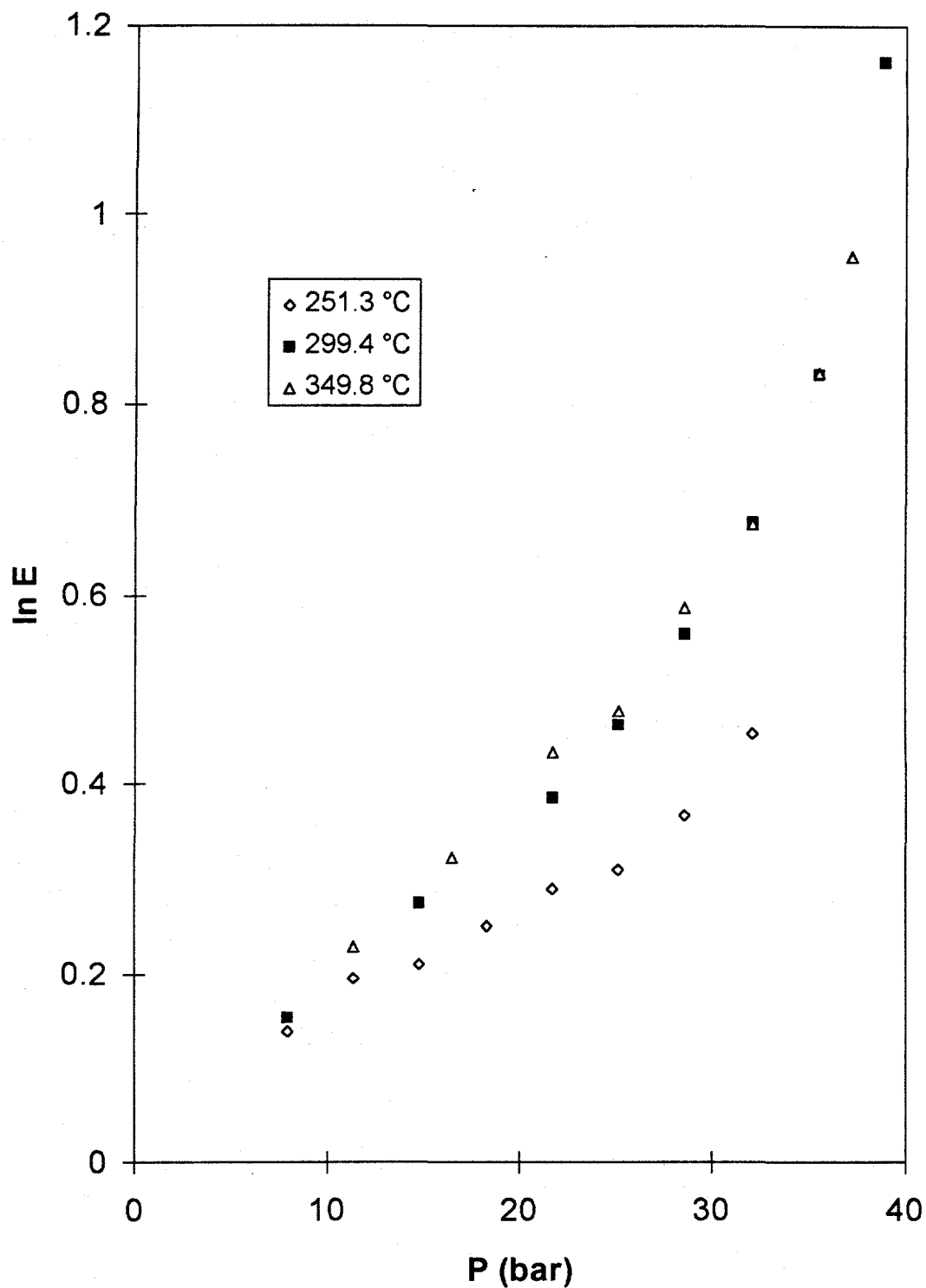


Figure 4. Natural logarithm of the enhancement factor vs pressure at 251.3, 299.4, and 349.8 °C.

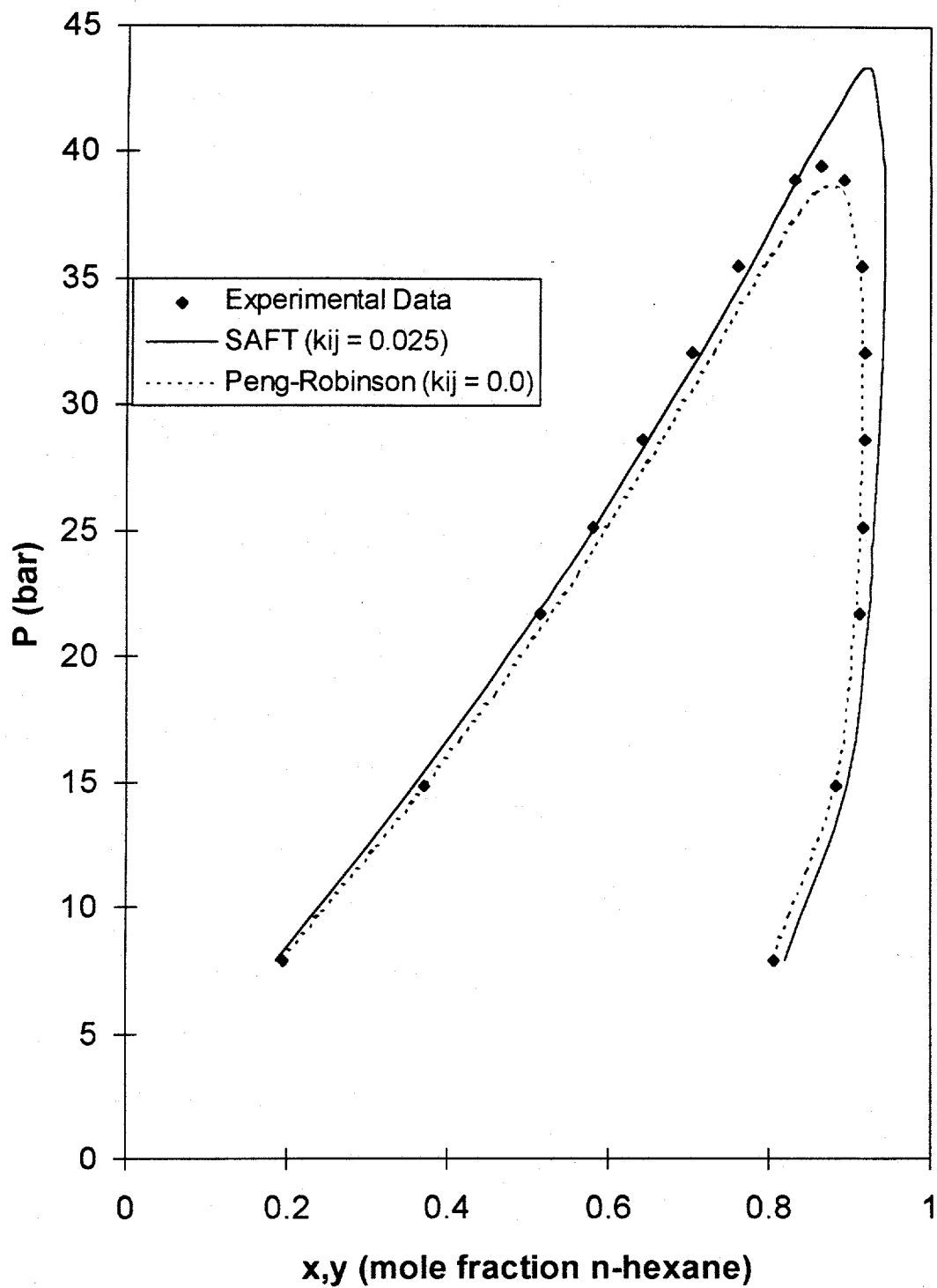


Figure 5. Comparison of Peng-Robinson and SAFT equations with experimental data at 299.4 °C.

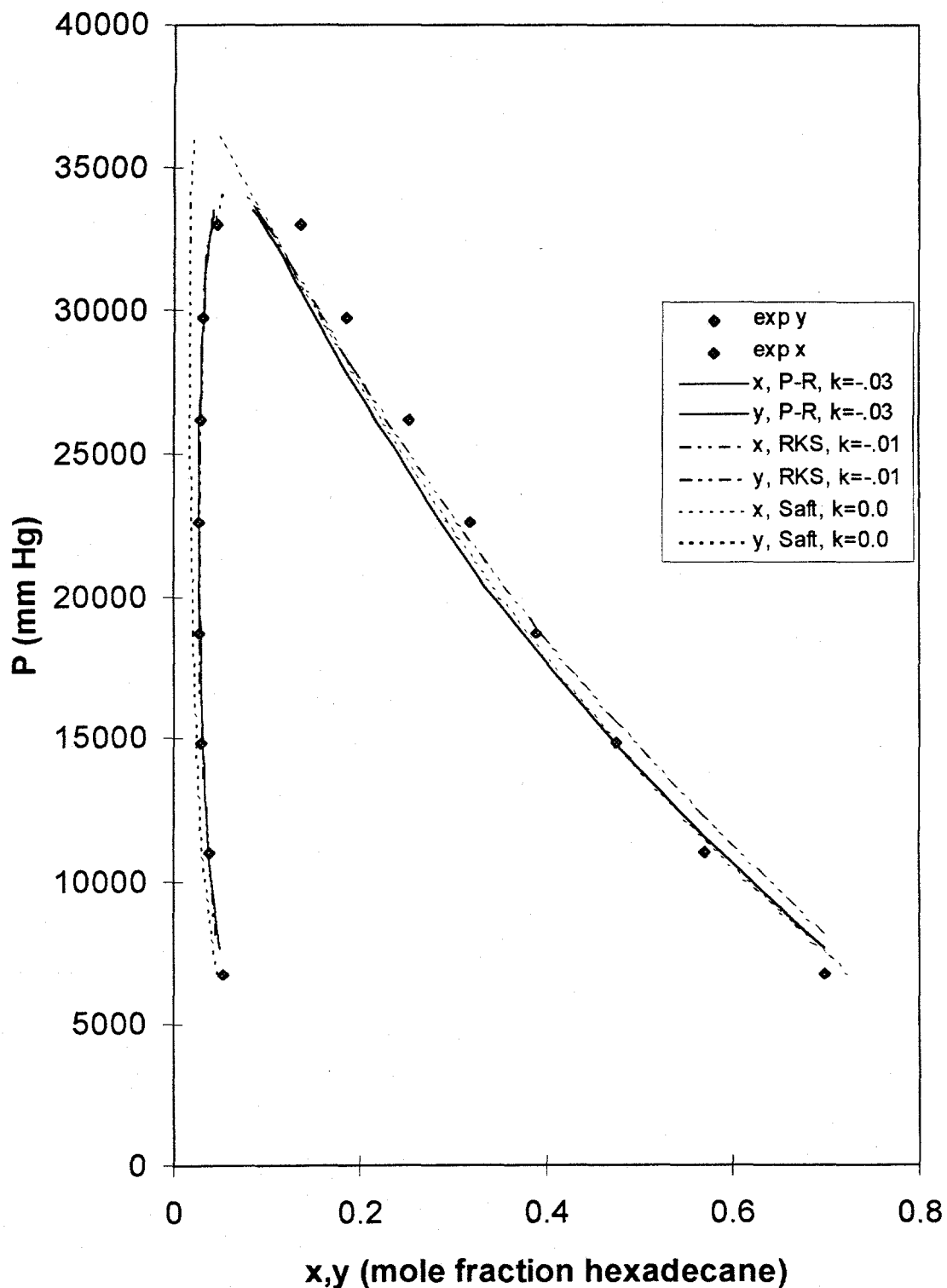


Figure 6. Comparison of P-R, SRK, and SAFT equations with experimental data for the pentane/hexadecane system at 245.5 °C.

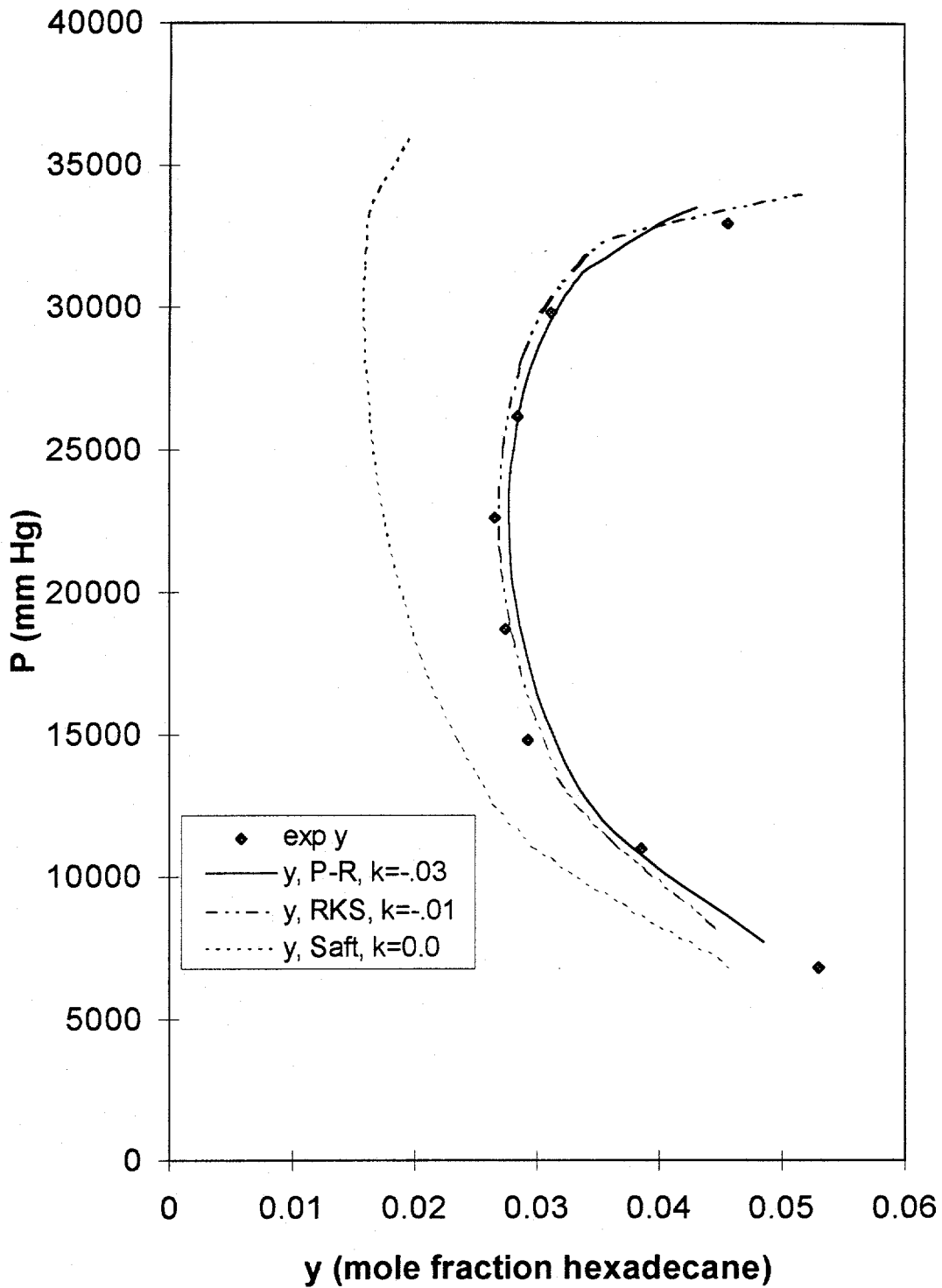


Figure 7. Comparison of P-R, SRK, and SAFT for vapor-phase modeling of the pentane/hexadecane system at 245.5 °C