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Separation of Fischer-Tropsch Wax from Catalyst

Using Supercritical Fluid Extraction

Quarterly Technical Progress Report
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PATENT STATUS

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Executive Summary

Vapor and liquid equilibrium compositions have been measured for the n-hexane/squalane system at 196.6 °C, 251.1 °C, 301.3 °C, and 350.0 °C at pressures ranging from 5.5 to 54.8 bar. Mixture critical pressures at 35.6, 48.2, and 54.8 bar were obtained by the visual observation of critical opalescence within the view cell. Because of the large difference in molecular weight between squalane (MW = 422.83) and hexane (MW = 86.18), the reproducibility of the reported mole fractions are highly dependent on the squalane content in the phase of interest. For liquid phases containing less than 5 mol % squalane, samples are reproducible to within an error ±7% in squalane composition; for those containing more than 5 mol % squalane, the error was always less than ±2%. For the vapor phase, deviation between samples never exceeded ±7% of the squalane composition, and for most samples reproducibility was better than ±3%. The reported temperatures are accurate to within ±0.3 °C, and pressure variations during a run were always less than ±0.14 bar.

The experimental data were modeled using two equations of state, Peng-Robinson (PR) and the Statistical Associating Fluid Theory (SAFT). Using the P-R equation with the optimized binary interaction parameters, the n-hexane concentration in the liquid phase is predicted to an average error of 6%. In the vapor phase, the squalane concentration is predicted to an average error of 23%. Although the interaction parameters are relatively small, they do not follow a well-behaved trend that lends itself to extrapolation to other, unmeasured temperatures. The interaction parameter for SAFT is better behaved, as it is essentially constant over the temperature range explored. The fit to the liquid-phase concentration is excellent at all temperatures (i.e., no more than 2% devation in hexane concentration), but the predicted concentration of squalane in the vapor phase is off by an unacceptably large 73%. If, as we had originally intended, SAFT is to be used to model our proposed SCF extraction process, it must be capable of accurately predicting the partioning of the Fischer-Tropsch waxes between the liquid and vapor phases (i.e., K-values). Whether the inability of SAFT to model hexane-squalane simply means that we need to quantify the effect of branching, or that the basic model itself is flawed, will be the subject of future work.

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

Automation of the small-scale SCF apparatus is still under consideration. Some details of the control system still need to be examined.

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

Vapor-liquid equilibrium experiments for the n-hexane/squalane system were completed. Measured compositions and corresponding pressures for the n-hexane/squalane binary at 196.6 °C, 251.1 °C, 301.3 °C, and 350.0 °C are given in Table I and are depicted on a pressure-composition diagram in Figure 1. For clarity, the vapor-phase compositions are plotted in Figures 2 and 3. Both the liquid and vapor phases have been checked for consistency by the methods discussed in the previous quarterly report and are observed to be internally consistent (Figures 4 and 5).

Because of the large difference in molecular weight between squalane (MW = 422.83) and hexane (MW = 86.18), the reproducibility of the reported mole fractions are highly dependent on the squalane content in the phase of interest. This occurs because our analytical technique for determining phase compositions is based on wt %. For liquid phases containing less than 5 mol % squalane, samples are reproducible to within an error ±7% in squalane composition; for those containing more than 5 mol % squalane, the error was always less than ±2%. The reproducibility of the vapor-phase compositions was in general excellent when one considers the small amounts of squalane that were present in the vapor phase, especially at the lower temperatures. Deviation between samples for a given temperature and presssure never exceeded ±7 % of the squalane composition, and for most samples reproducibility was better than ±3 %.

The reported temperatures and pressures are believed to be accurate to ±0.3 °C and ±0.14 bar, respectively. Temperatures were measured with a scheme consisting of top- and bottom-phase thermocouples and a secondary standard RTD that was recently calibrated against a primary standard Rosemount 162CE RTD. The Heise pressure gauge used for our measurements was calibrated with a Budenburg 380H dead weight tester.

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

	Exp. Data mole fraction		Calculated by P-R mole fraction				Calculated by SAFT mole fraction			
Press.	n-hexane	squalane	n-hexane	squalane	% error		n-hexane	squalane	% error	
bar	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor
				T = 196.6 °C						
5.52	0.436	0.00017	0.454	0.00022	4.1	24.0	0.429	0.000036	-1.7	-79.1
6.89	0.526	0.00015	0.547	0.00019	4.1	24.1	0.511	0.000029	-2.8	-80.9
8.27	0.608	0.00013	0.631	0.00017	3.7	30.2	0.586	0.000024	-3.7	-81.7
9.45	0.679	0.00012	0.697	0.00016	2.7	29.1	0.647	0.000021	-4.7	-82.8
10.34	0.714	0.00011	0.743	0.00015	4.1	31.1	0.692	0.000019	-3.1	-83.2
10.69	0.729	0.00011	0.760	0.00014	4.3	29.9	0.709	0.000018	-2.7	-83.8
12.07	0.787	0.000097	0.823	0.00013	4.6	31.9	0.776	0.000016	-1.3	-83.5
13.24	0.841	0.000097	0.871	0.00011	3.6	13.8	0.833	0.000013	-0.9	-86.6
13.44	0.850	0.000096	0.879	0.00011	3.5	11.1	0.843	0.000012	-0.7	-87.5
15.38	0.921	0.000062	0.949	0.000062	3.1	0.2	0.942	0.000007	2.3	-89.0
16.55	0.956	0.000040	0.987	0.000019	3.2	-52.3	0.998	0.0000004	4.4	-99.0
17.31	0.978	0.000007								
17.41[a]	1.0	0.0								
				T = 251.1 °C						
8.62	0.428	0.00189	0.445	0.00179	-3.9	5.8	0.411	0.00050	-4.1	-73.7
11.38	0.514	0.00161	0.551	0.00166	7.2	-3.8	0.502	0.00042	-2.3	-73.8
16.13	0.631	0.00155	0.699	0.00167	10.8	-11.3	0.634	0.00035	0.5	-76.7
21.03	0.734	0.00169	0.811	0.00183	10.4	-7.6	0.745	0.00033	1.5	-80.6
25.17	0.813	0.00186	0.881	0.00206	8.4	-8.4	0.827	0.00034	1.7	-82.1
28.89	0.878	0.00232	0.931	0.00255	6.0	-10.9	0.896	0.00036	2.0	-84.3
34.13	0.954	0.00457					0.994	0.00024	4.2	-94.9
35.16	0.971	0.00629								
35.65[b]	0.985	0.0147								
				T = 301.3 °C						
10.00	0.323	0.0092	0.317	0.0084	-1.8	-8.7	0.324	0.0036	0.4	-60.9
15.10	0.466	0.0078	0.450	0.0079	-3.3	1.3	0.444	0.0029	-4.6	-62.8
19.99	0.550	0.0073	0.563	0.0085	2.4	16.4	0.540	0.0027	-1.8	-63.0
25.17	0.613	0.0075	0.666	0.0100	8.7	33.3	0.627	0.0027	-2.3	-63.5
30.34	0.701	0.0086	0.757	0.0125	8.0	45.3	0.703	0.0030	2.9	-65.1
34.82	0.756	0.0100	0.827	0.0164	9.4	64.0	0.761	0.0034	0.7	-66.0
38.96	0.802	0.0130	0.886	0.0233	10.4	79.2	0.811	0.0041	1.1	-68.5
42.40	0.845	0.0162					0.850	0.0049	0.6	-69.8
46.26	0.890	0.0262					0.892	0.0068	0.2	-74.0
46.95	0.901	0.0302					0.899	0.0073	-0.2	-75.8
48.23[b]	0.946	0.0543								
				T = 350.0 °C						
8.27	0.239	0.0362	0.193	0.0296	-19.3	-18.2	0.225	0.0175	6.0	-51.7
15.17	0.357	0.0256	0.337	0.0237	-5.5	-7.4	0.369	0.0121	3.5	-52.7
21.72	0.473	0.0238	0.459	0.0241	-3.0	-1.3	0.480	0.0107	1.4	-55.0
28.61	0.571	0.0242	0.575	0.0277	0.7	-14.5	0.578	0.0106	1.2	-56.2
35.51	0.660	0.0260	0.682	0.0352	3.4	35.4	0.660	0.0114	0.0	-56.2
42.40	0.728	0.0319	0.787	0.0512	8.1	60.5	0.732	0.0132	0.5	-58.6
49.30	0.801	0.0455					0.796	0.0165	0.6	-63.7
51.37	0.826	0.0547					0.814	0.0180	1.4	-67.0
53.43	0.856	0.0733					0.832	0.1980	2.8	-73.0
54.81[b]	0.896	0.104								

[a] Vapor pressure of pure n-hexane.
[b] Vapor-liquid critical point.

Previous work at Clemson has shown that equilibrium conditions are obtained with our continuous-flow apparatus design. Confirmation that equilibrium conditions do indeed exist for our current system of interest was obtained by collecting samples at varying flow rates at 301.3 °C and 34.8 bar. As shown in Table II, no effect of flow rate on composition was observed.

Table II. Measured equilibrium concentrations and flow rates for the n-hexane/squalane system at 301.3 °C and 34.82 bar.

	mole fraction n-hexane	
total flow rate (ml/hr)	liquid	vapor
100	0.757	0.0477
200	0.756	0.0474
300	0.757	0.0478

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.

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

Two equations of state were tested for their ability to correlate our experimental data, Peng-Robinson (PR) and Statistical Associating Fluid Theory, or SAFT. Peng-Robinson is a popular cubic equation of state that has been in both academic and industrial use for almost 20 years. It works well for ideal or nearly ideal solutions that are well-defined. SAFT, developed in the late 80s, is a noncubic equation of state based on perturbation theory. However, unlike earlier perturbation models, the reference fluid incorporates both chain length and molecular association. The advantages of SAFT are reported to be its ability to model undefined mixtures and highly nonideal systems, and

the fact that both its pure component and interaction parameters are well-behaved. However, compared to cubic equations of state it is, to say the least, complex.

In order to use PR in its most commonly applied form, a knowledge of both pure component critical properties and acentric factors is required. Although these data are readily available for n-hexane, they are not for squalane. Furthermore, several popular methods for estimating T_c and P_c could not be used because no boiling-point data are available for squalane. Thus, the method of Fedors[1] , which requires only structural information, was employed and gave a T_c of 848 K. Another structural contribution method by Ambrose[1] was used to calculate a P_c of 6.0 bar. To determine the acentric factor, Hutchenson's[2] program for the PR equation, which requires pure component vapor pressures as the input, was used. Using the calculated critical properties and two vapor pressure values from the literature, we obtained an acentric factor of 0.9695. With this information, flash calculations were then performed for the n-hexane/squalane system using PR.

Binary interaction parameters (δ_{ij}) were determined for each temperature by optimizing the fit of the equation to the experimentally measured liquid and vapor compositions. As seen in Table III, the δ_{ij}s are relatively small; however, they do not follow a well-behaved (e.g., linear) trend. Based on these results, the parameter values that one would use for extrapolating to unmeasured temperatures are uncertain. Using the P-R equation with the optimized interaction parameters, the n-hexane concentration in the liquid phase is predicted to an average error of 6%. In the vapor phase, the squalane concentration is predicted to an average error of 23 %. Results at 350.0 °C are shown in Figure 6 and are representative of the fits obtained at the other temperatures.

Table III. Binary interaction parameters for the PR and SAFT equations.

T (°C)	196.6 °C	251.1 °C	301.3 °C	350.0 °C
PR	-0.03	-0.05	0.0	0.05
SAFT	0.02	0.01	0.02	0.02

[1] Reid, Prausnitz, and Poling, Properties of Liquids and Gases, 4th ed., Chapter 2.
[2] Hutchenson, Ph.D. Dissertation, Clemson University, Dec. 1990.

SAFT was also used to model the binary system n-hexane/squalane. The pure component parameters for hexane were calculated from the correlations for n-alkanes given in the publication by Huang and Radosz[3]. For this initial work, the same correlation was also used for squalane, because no correlation for branched alkanes exists at this time. Thus, squalane was assumed to act no differently than triacontane (n-C_{30}). As with P-R, the fit of SAFT to the experimentally measured data was also optimized using an interaction parameter (k_{ij}). For SAFT, k_{ij} was essentially optimized against the liquid composition only because varying k_{ij} had little effect on the vapor-phase concentration. The k_{ij}s obtained are shown above in Table III. Compared to PR, we see that the interaction parameter for SAFT is better behaved; for extrapolating to temperatures above or below those measured, k_{ij} can be estimated with confidence to be about 0.02. Unfortunately, for the correlations used, SAFT does not do a good job of correlating the measured data. Although the fit to the liquid-phase concentration is excellent at all temperatures (i.e., no more than 2% devation in hexane concentration), the predicted concentration of squalane in the vapor phase is off by an unacceptably large 73 %. Results for SAFT at 350.0 °C are seen in Figure 6.

A complete listing of the phase compositions calculated using both equations of state, as well as the percent deviation between experimental and calculated values, is shown in Table I.

If, as we had originally intended, SAFT is to be used to model our proposed SCF extraction process, it must be capable of accurately predicting the partioning of the Fischer-Tropsch waxes between the liquid and vapor phases (i.e., K-values). Whether the inability of SAFT to model hexane-squalane simply means that we need to quantify the effect of branching, or that the basic model itself is flawed, will be the subject of future work.

Task 3. Process Design Studies

No effort planned for this quarter.

[3] Huang and Radosz, 'Equation of state for small, large, polydisperse, and associating molecules', I & EC Res. **1990,** *29,* 2284-2294.

Plans for Next Quarter

Equilibrium phase compositions and mixture critical points will be measured and correlated for binary mixtures of n-hexane with an n-alkane such as hexadecane or eicosane. In addition, currently available VLE data will be used to evaluate the ability of SAFT to accurately predict both liquid and vapor compositions for mixtures of light and heavy alkanes.

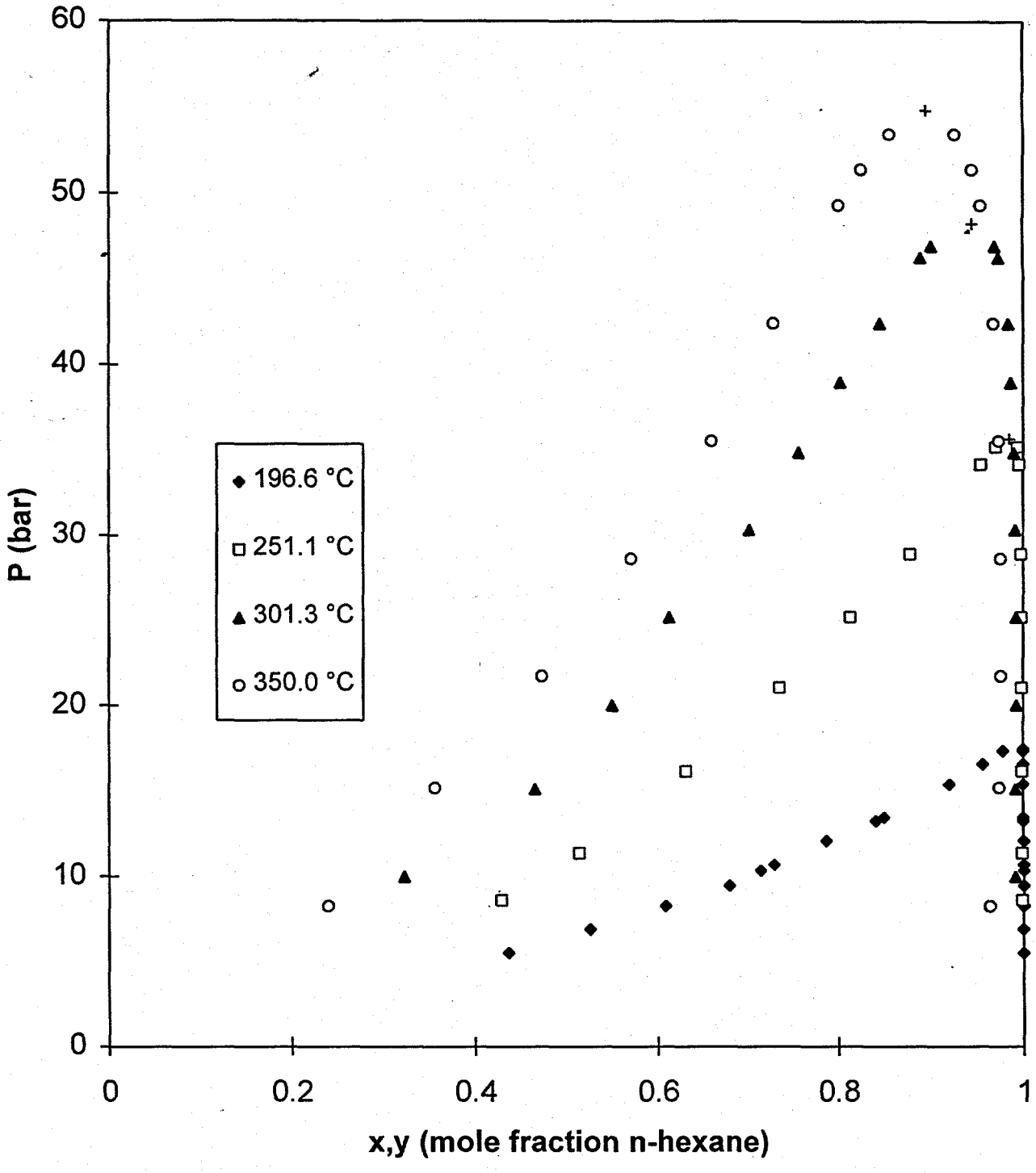

Figure 1. Pressure-vs-composition diagram for the n-hexane/squalane system at 196.6 °C, 251.1 °C, 301.3 °C, and 350.0 °C. The + are the mixture critical temperatures.

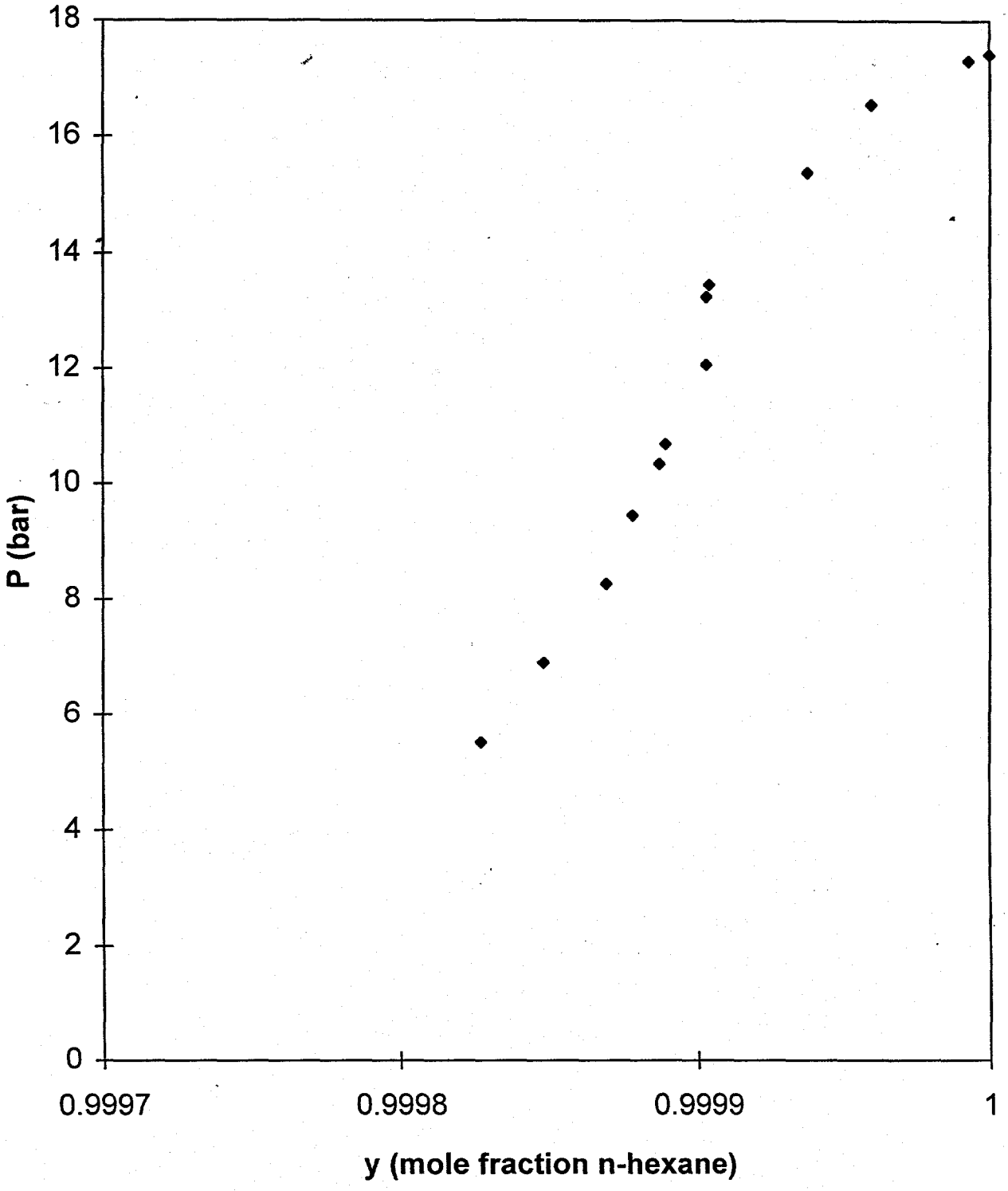

Figure 2. Vapor-phase compositions at 196.6 °C.

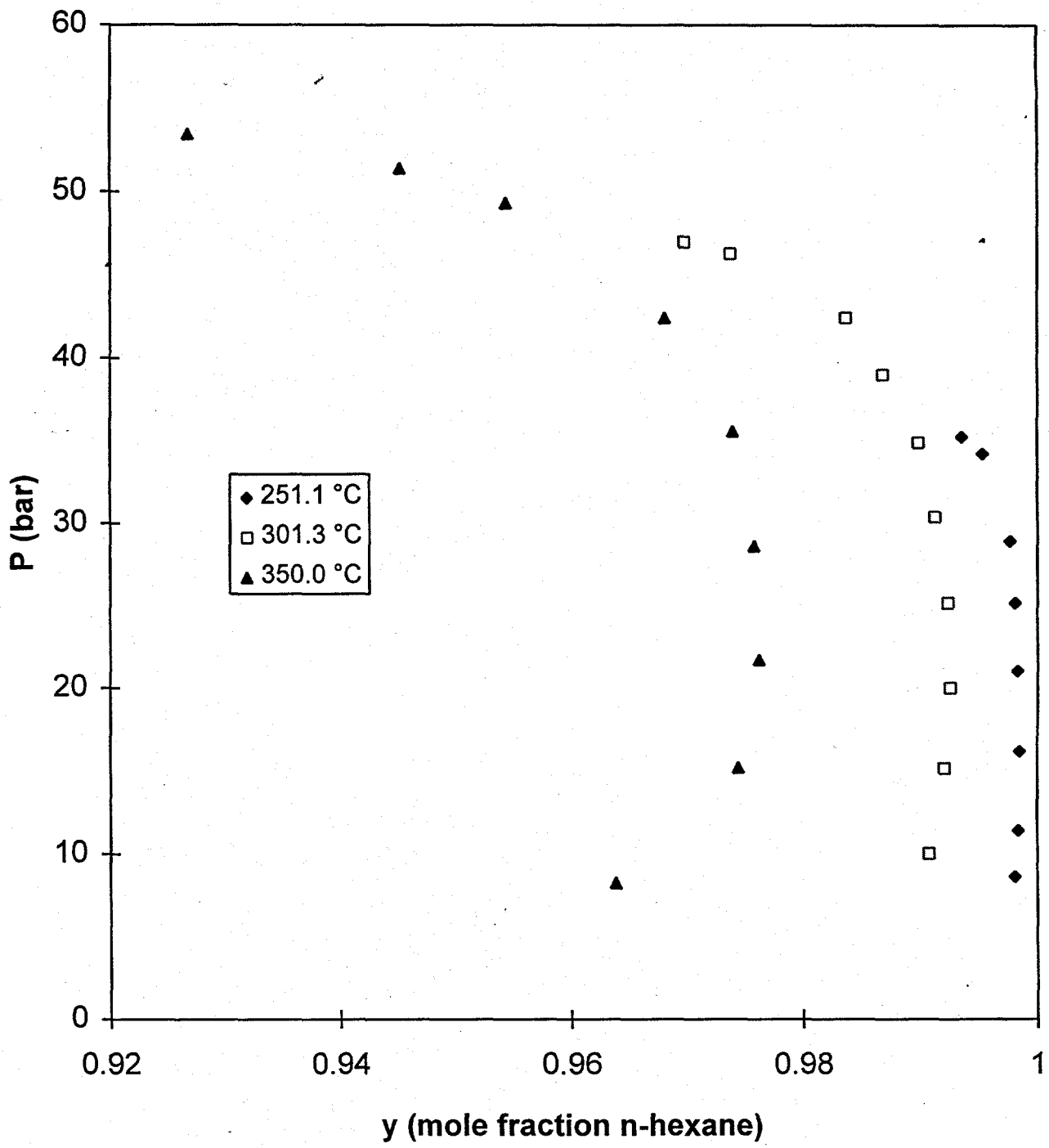

Figure 3. Vapor-phase compositions at 251.1 °C, 301.3 °C, and 350.0 °C.

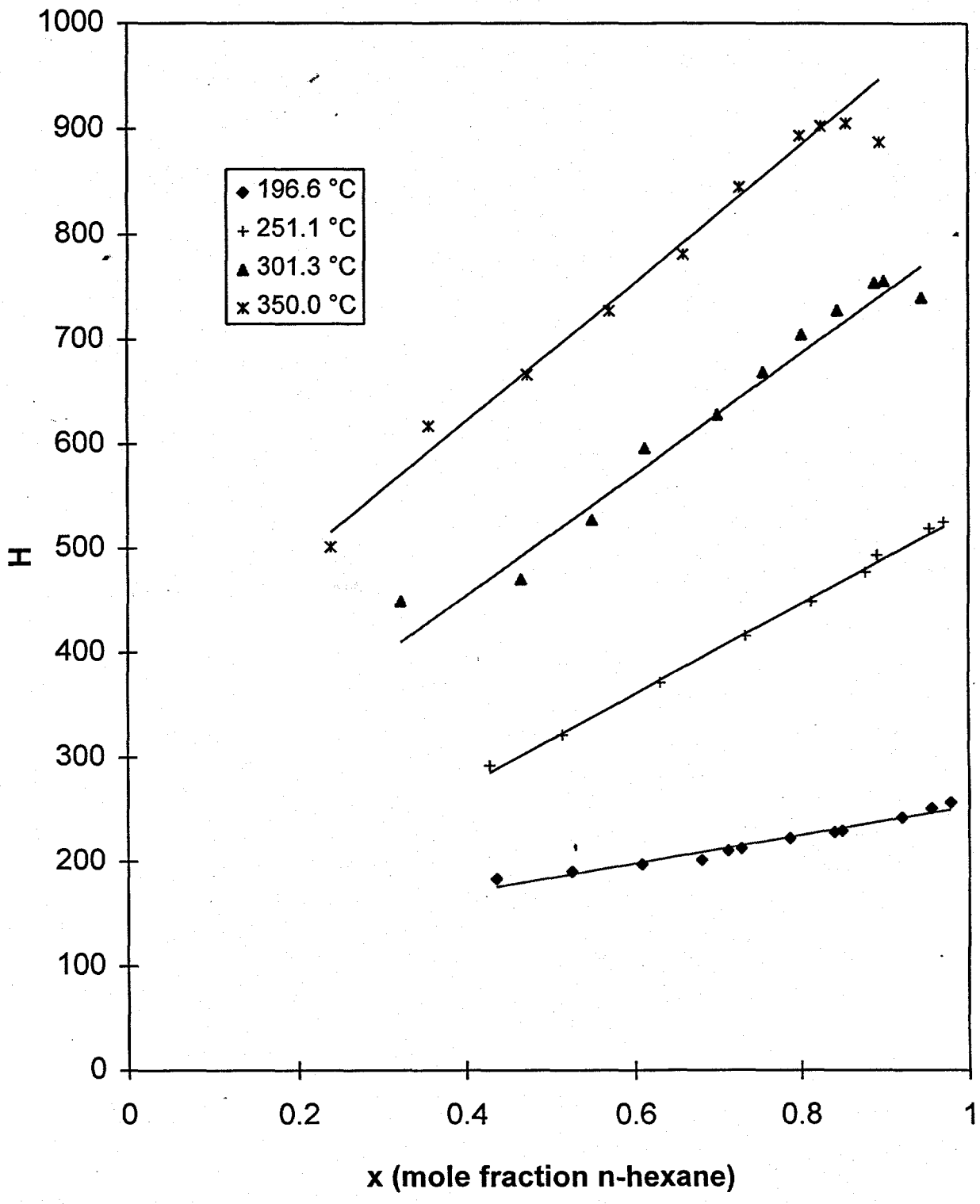

Figure 4. Modified Henry's Law constant vs liquid composition at 196.6 °C, 251.1 °C, 301.3 °C, and 350.0 °C.

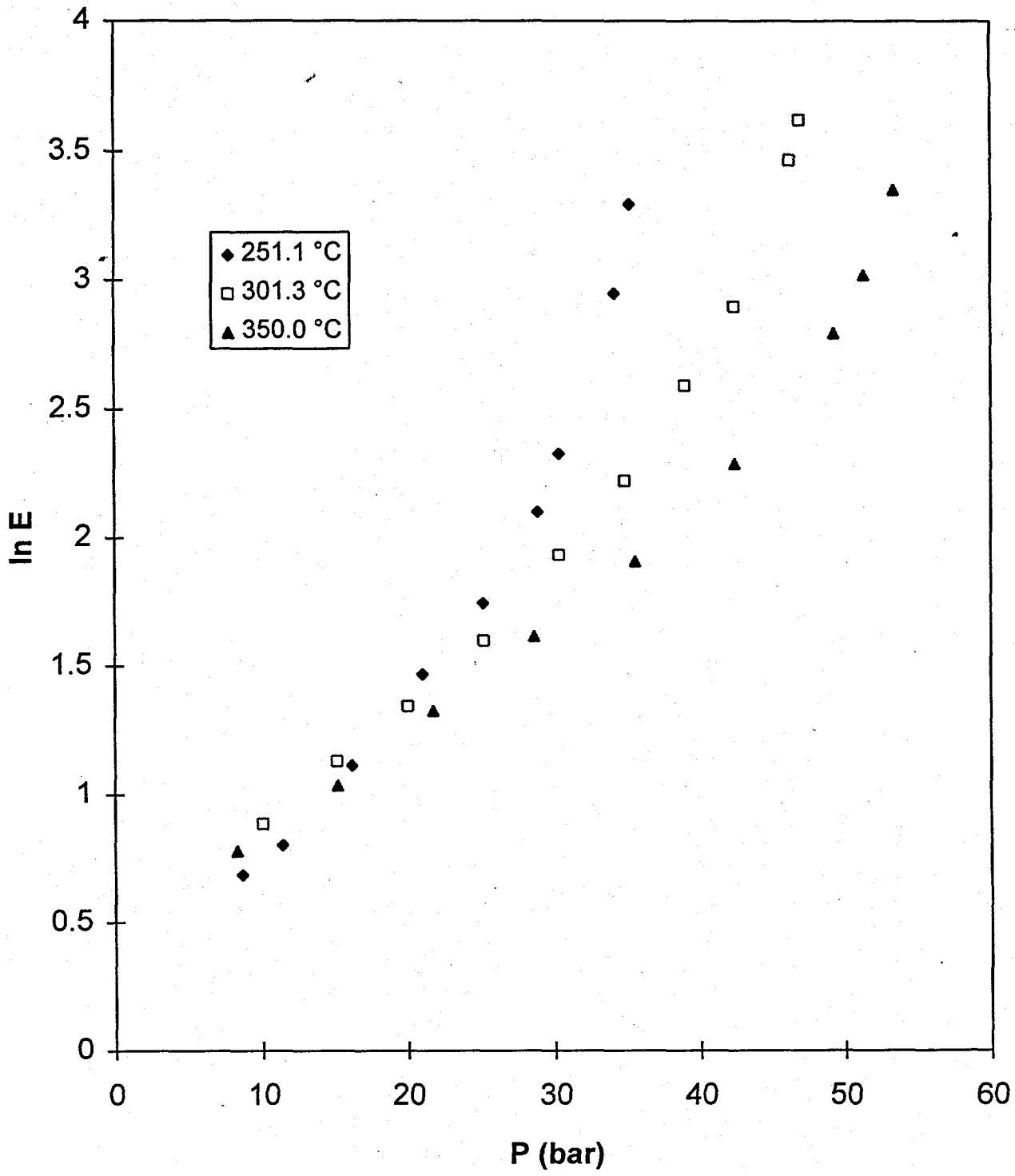

Figure 5. Natural logarithm of the enhancement factor vs pressure at 251.1 °C, 301.3 °C, and 350.0 °C.

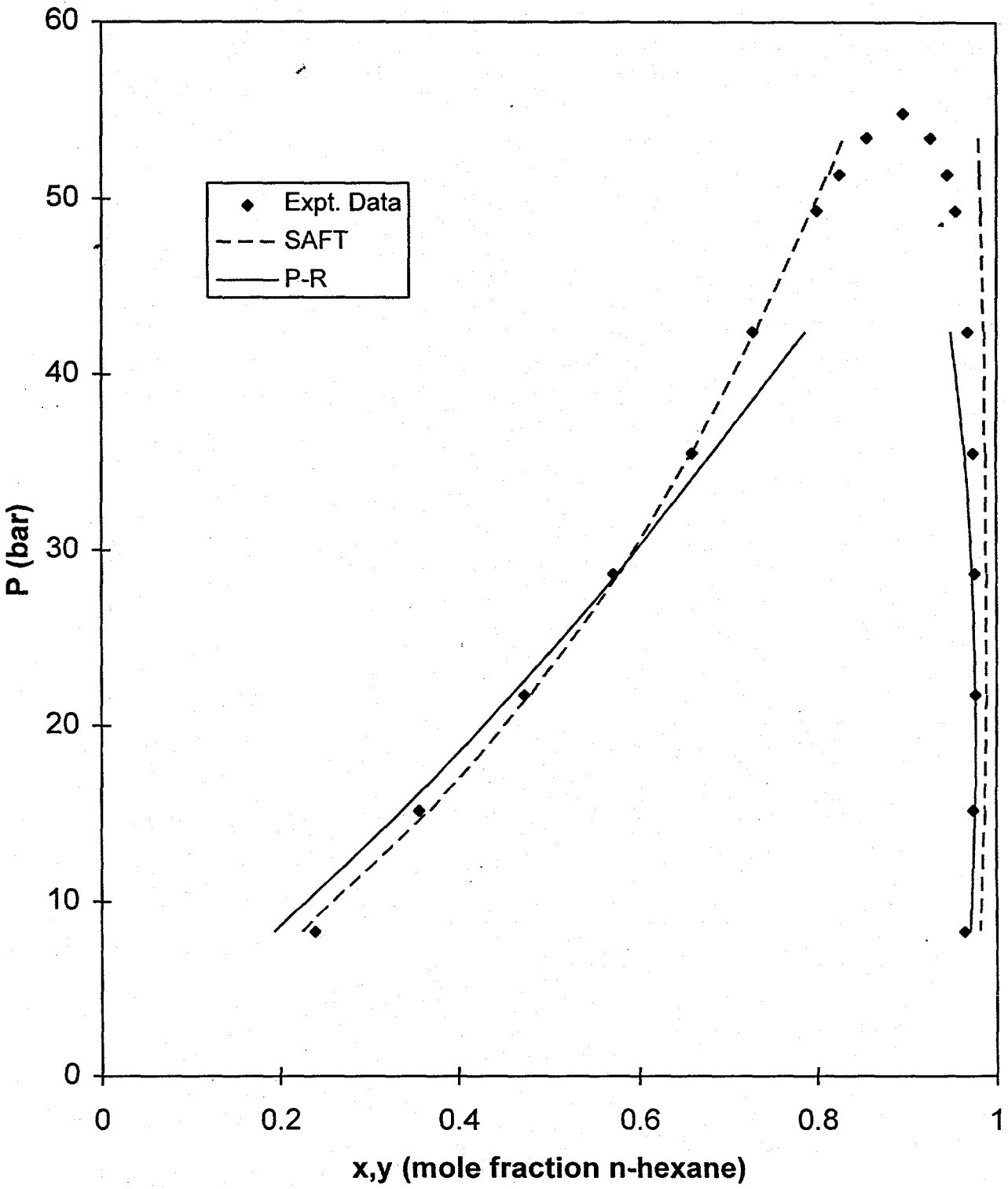

Figure 6. Comparison of Peng-Robinson and SAFT equations with experimental data at 350.0 °C.