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**Separation of Fischer-Tropsch Wax from Catalyst**

**Using Supercritical Fluid Extraction**

Quarterly Technical Progress Report  
1 January 1996 - 31 March 1996

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## Executive Summary

Pressure-composition diagrams have been generated for the n-hexane/squalane system at 196.6 °C and 251.1 °C. Vapor and liquid equilibrium compositions were measured at pressures ranging from 80 psia to the mixture critical pressure at 251.1 °C, which occurred at 517 psia. Reproducibility of a given liquid-phase sample was found to be between 0.04 and 0.1 mol % squalane. At 197 °C, the reproducibility of the vapor-phase samples was to within  $\pm 0.0006$  mol % squalane. At 251 °C, the vapor-phase samples were reproducible to within  $\pm 0.01$  mol % squalane. Temperature uncertainty within an isotherm was less than  $\pm 0.3$  °C, and pressure variations during a run were always less than  $\pm 2$  psia. Methods for examining the internal consistency of the measured data were applied. For the liquid phase, the method involves using a modified Henry's law constant. For the vapor-phase compositions at 251 °C, a modified enhancement factor has been used. The modified Henry's law constant method has shown that most of the liquid-phase data are of good quality. However, the runs at 80, 100, and 120 psia at a temperature of 196.6 °C deviate badly from the established trends (sample contamination may have been a problem) and so will have to be discarded. The enhancement factor results indicate that all vapor-phase data at 251.1 °C are consistent and of good quality. Pressure-vs.-composition diagrams to be measured at 300 and 350 °C will complete our measurements for this binary mixture.

## 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

After completing measurements at 197 and 251 °C, the bath temperature was raised to 300 °C in preparation for measurement of the next isotherm. Unfortunately, at that time the differential thermocouple (DT) circuits started to give erroneous temperature measurements, with a temperature difference between the vapor- and liquid-phase thermocouples of over 1°C appearing in the view cell. The problem in the DT circuits appears to have been caused by a temperature difference at the junction between the positive chromel wires and the copper extension wires (which run out of the oven and connect to the terminal block). This temperature difference was caused by the fact that the copper tube (where the junctions are placed to keep them isothermal) was in close proximity to the heating elements. Insulation has been placed between the copper tube and the heating elements to solve this problem.

In order to decrease the residence time of the squalane in the oven, a piece of tubing was replaced. The original squalane line was approximately twenty-five feet long; the new tubing is only three feet long. To minimize the chance of significant squalane degradation occurring at elevated temperatures, all experiments over 300 °C will be performed using the shorter tubing.

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

Vapor-liquid equilibrium experiments for the n-hexane/squalane system, which were initiated in the previous quarter, were continued. Measured compositions and corresponding pressures for the n-hexane/squalane binary at 196.6 °C and 251.1 °C are given in Table I and are depicted on a pressure-composition diagram in Figure 1. For clarity, Figures 2 and 3 show enlargements of the hexane-rich vapor-phase compositions at 196.6 °C and 251.1 °C, respectively. The method of sample analysis has been fully described in the previous quarterly report. Reproducibility of a given sample was found to be between 0.04 and 0.1 mol % squalane for the liquid phases. At 196.6 °C and 251.1 °C, the reproducibility of the vapor-phase samples was to within  $\pm 0.0006$  mol % and

$\pm 0.01$  mol % squalane, respectively. Temperature and pressure uncertainties for a given isotherm were  $\pm 0.3$  °C and  $\pm 2$  psi, respectively.

For a system that exhibits simple phase equilibria, Mullins<sup>1</sup> has proposed a modified Henry's law constant method for checking the consistency of measured liquid compositions. The modified Henry's law constant takes the form

$$H_1 = \frac{P}{x_1} \quad (1)$$

where  $P$  is the system pressure,  $x_1$  is the mole fraction of n-hexane in the liquid, and  $H_1$  is the modified Henry's law constant for n-hexane in squalane. Typically, a plot of  $H$  versus liquid mole fraction will show a well-behaved trend. Figures 4 and 5 show the plots of the modified Henry's law constants versus liquid mole fraction n-hexane at 196.6 °C and 251.1 °C, respectively. The points on the plots are the experimental data, while the straight lines have been obtained from a linear regression of the data. For the data at 196.6 °C, the regression does not include the three points at the lowest n-hexane liquid mole fraction; it is clear that these points are in error. Aside from these three points, the experimental data are of good quality, with the difference between the regressed and measured Henry's law constants always being less than 2.5%.

The method implemented to examine deviations in the vapor-phase compositions uses a modified enhancement factor  $E$ , which is defined as

$$E = \frac{y_2 P}{P_2^{sat}} \quad (2)$$

where  $y_2$  is the mole fraction squalane in the vapor phase,  $P$  is the system pressure, and  $P_2^{sat}$  is the estimated vapor pressure of squalane. Because no data are available for the vapor pressure of squalane below 360 °C, the vapor pressure of triacontane ( $C_{30}$ ) was calculated using the computer simulation package HYSIM and was used in the place of squalane. It should be noted that the vapor pressure does not have to be particularly accurate for the purpose of examining data because it is a constant at a given temperature. Figure 6 shows the plot of the natural logarithm of the enhancement factor versus the system pressure for the experimental data at 251.1 °C. As Figure 6 clearly depicts, the

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<sup>1</sup> Mullins, J. C., Clemson University, personal communication, 1996.

data form a smooth curve, indicating that the collected data is internally consistent. The vapor phase at 196.6 °C cannot be examined with this method because n-hexane is still below its critical point and the data terminate at the vapor pressure of pure n-hexane, see Figure 1.

Table I - Vapor-Liquid Equilibrium Data for n-Hexane/Squalane

Pressure (psia)	Mole Fraction Squalane		Pressure (psia)	Mole Fraction Squalane	
	Liquid	Vapor		Liquid	Vapor
<u>T=196.6 °C</u>			<u>T=251.1 °C</u>		
80	0.586	0.000196	125	0.572	0.00189
100	0.523	0.000169	165	0.486	0.00161
120	0.431	0.000149	234	0.369	0.00154
121	0.379	0.000131	305	0.266	0.00169
137	0.321	0.000122	365	0.187	0.00186
150	0.286	0.000113	419	0.122	0.00232
155	0.271	0.000111	440	0.108	0.00277
175	0.213	0.0000974	495	0.0457	0.00457
192	0.159	0.0000960	510	0.0294	0.00623
195	0.150	0.0000901	517 <sup>b</sup>	0.0147	0.0147
223	0.079	0.0000620			
240	0.044	0.0000397			
251	0.022	0.0000065			
253 <sup>a</sup>	0.0	0.0			

<sup>a</sup> Vapor pressure of pure n-hexane.

<sup>b</sup> Vapor-liquid critical point.

#### 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.

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

Efforts have not begun as planned. Modeling will begin as soon as the n-hexane/squalane isotherms at 300 and 350 °C are completed.



### Task 3. Process Design Studies

No effort planned for this quarter.

#### **Plans for Next Quarter**

Pressure-vs.-composition diagrams will be measured for the n-hexane/squalane system at 300 and 350 °C; this will complete our measurements for this binary mixture. The system will then be modeled with both SAFT and Peng-Robinson. Additional modifications to the apparatus are being considered. In particular, it would be desirable to have automation of the vapor-phase micrometering valve. Our experience with our other continuous-flow apparatus indicates that such a change would both increase productivity and improve pressure control.

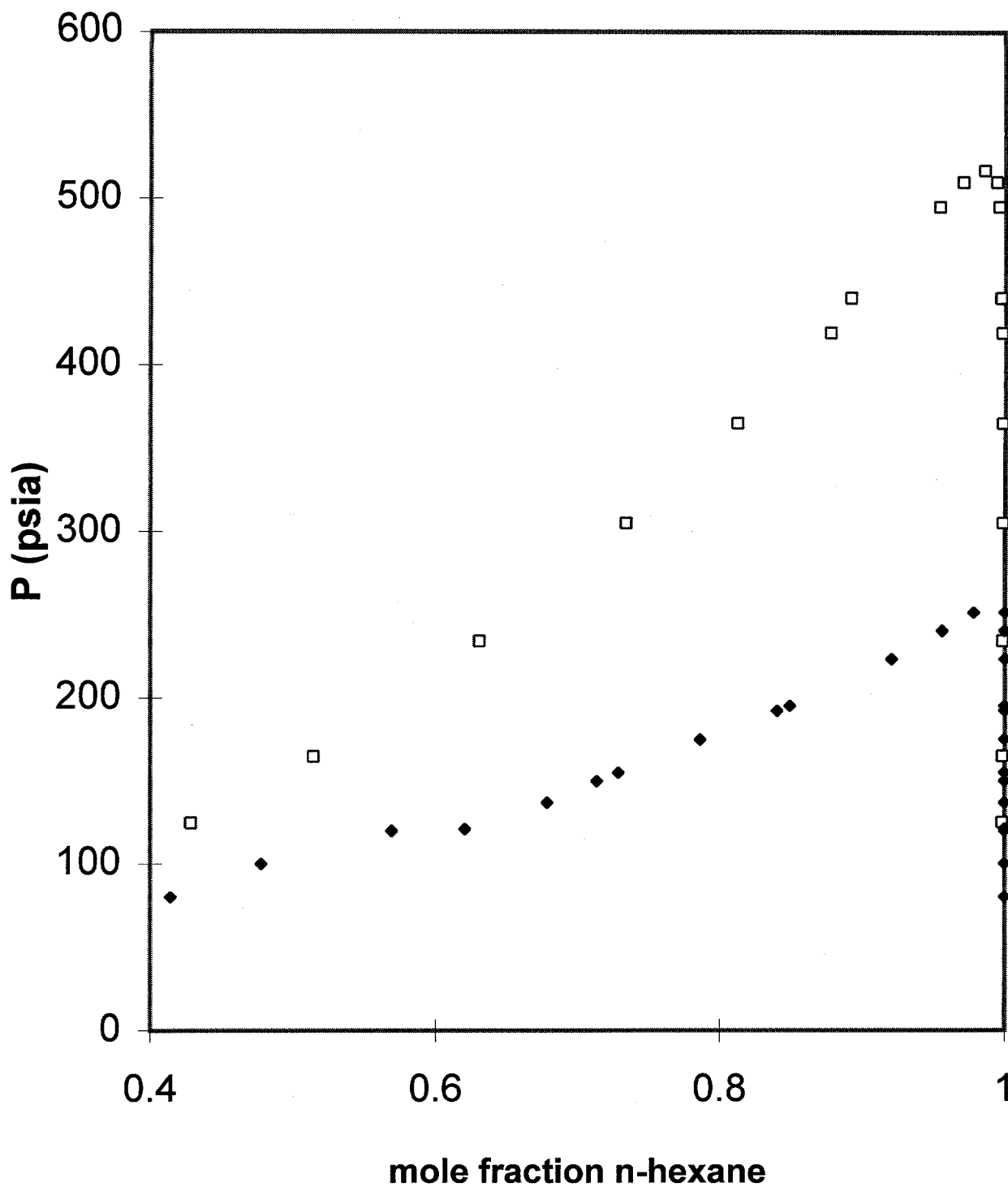
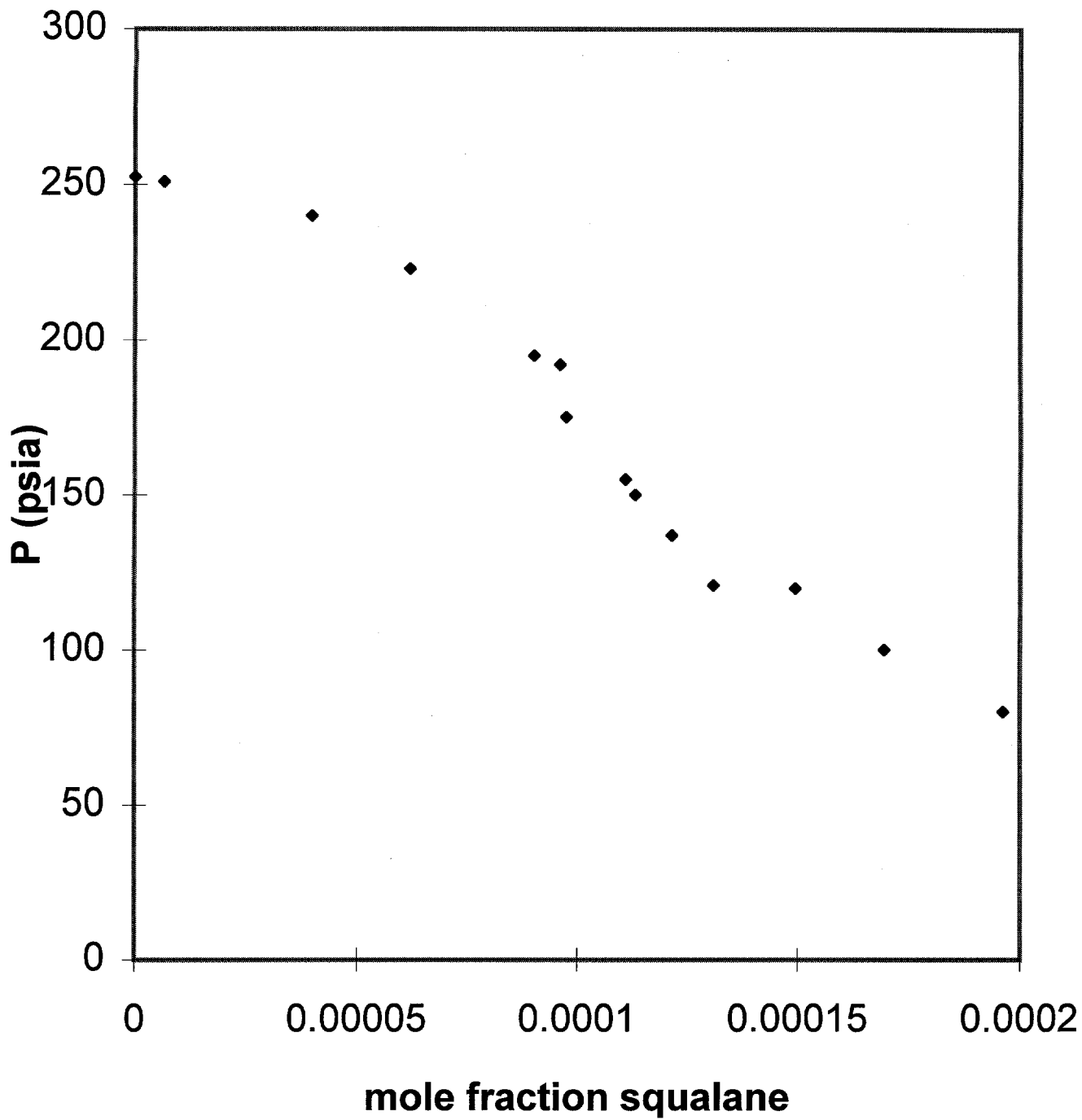


Figure 1. Pressure-composition diagram for n-hexane/squalane at 196.6 °C and 251.1 °C.



**Figure 2. Pressure-composition diagram of the vapor phase at 196.6 °C.**

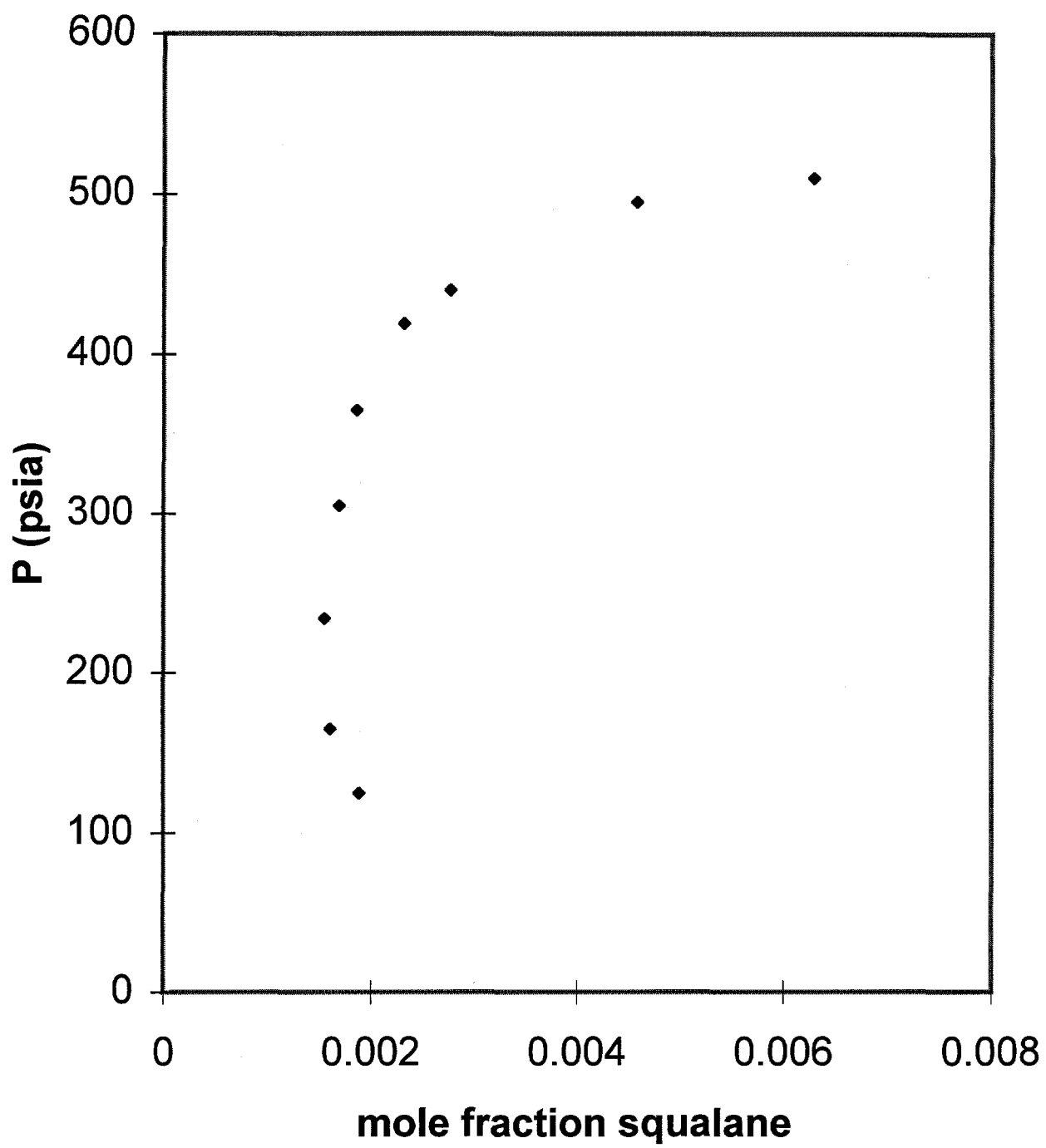
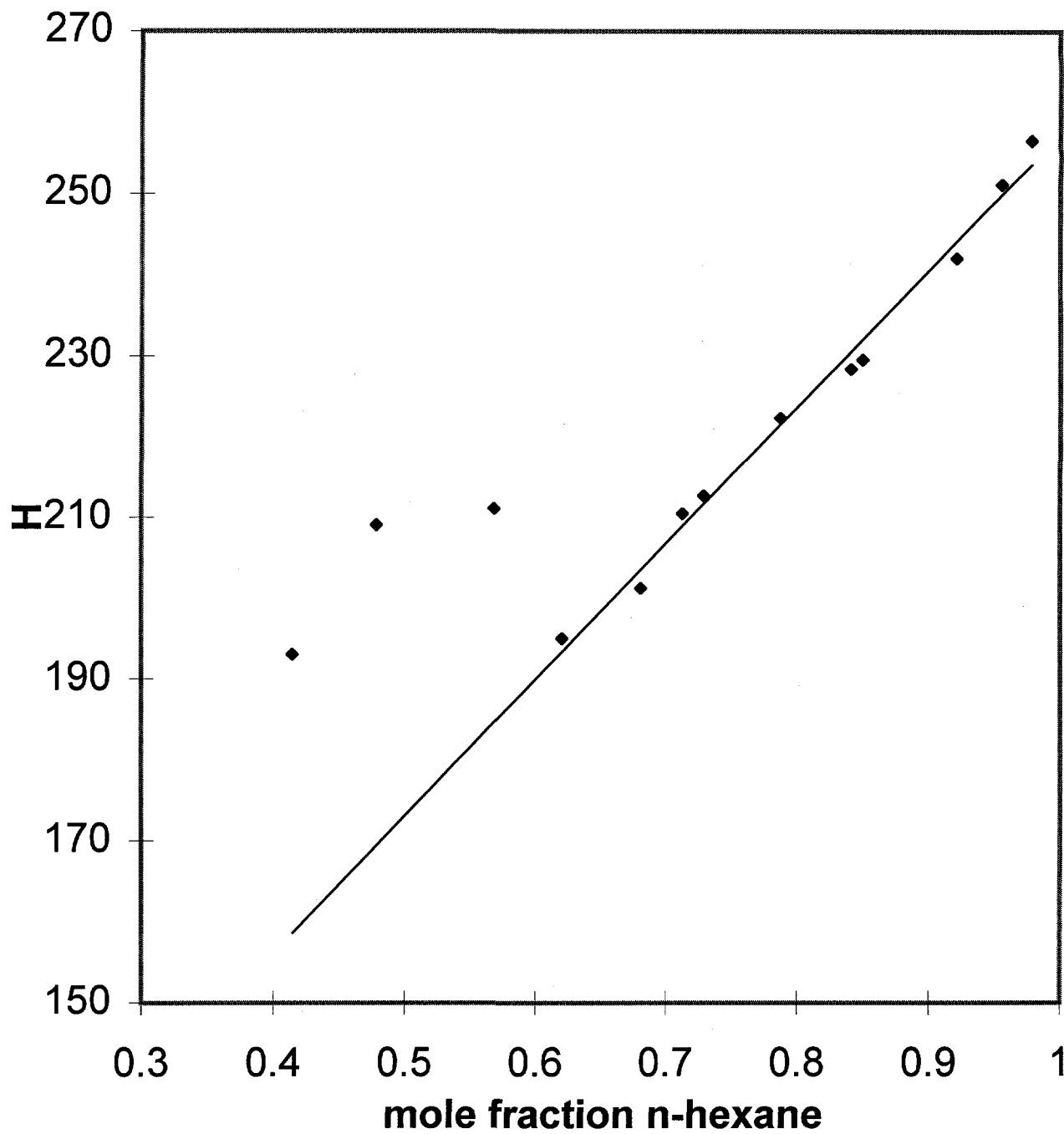
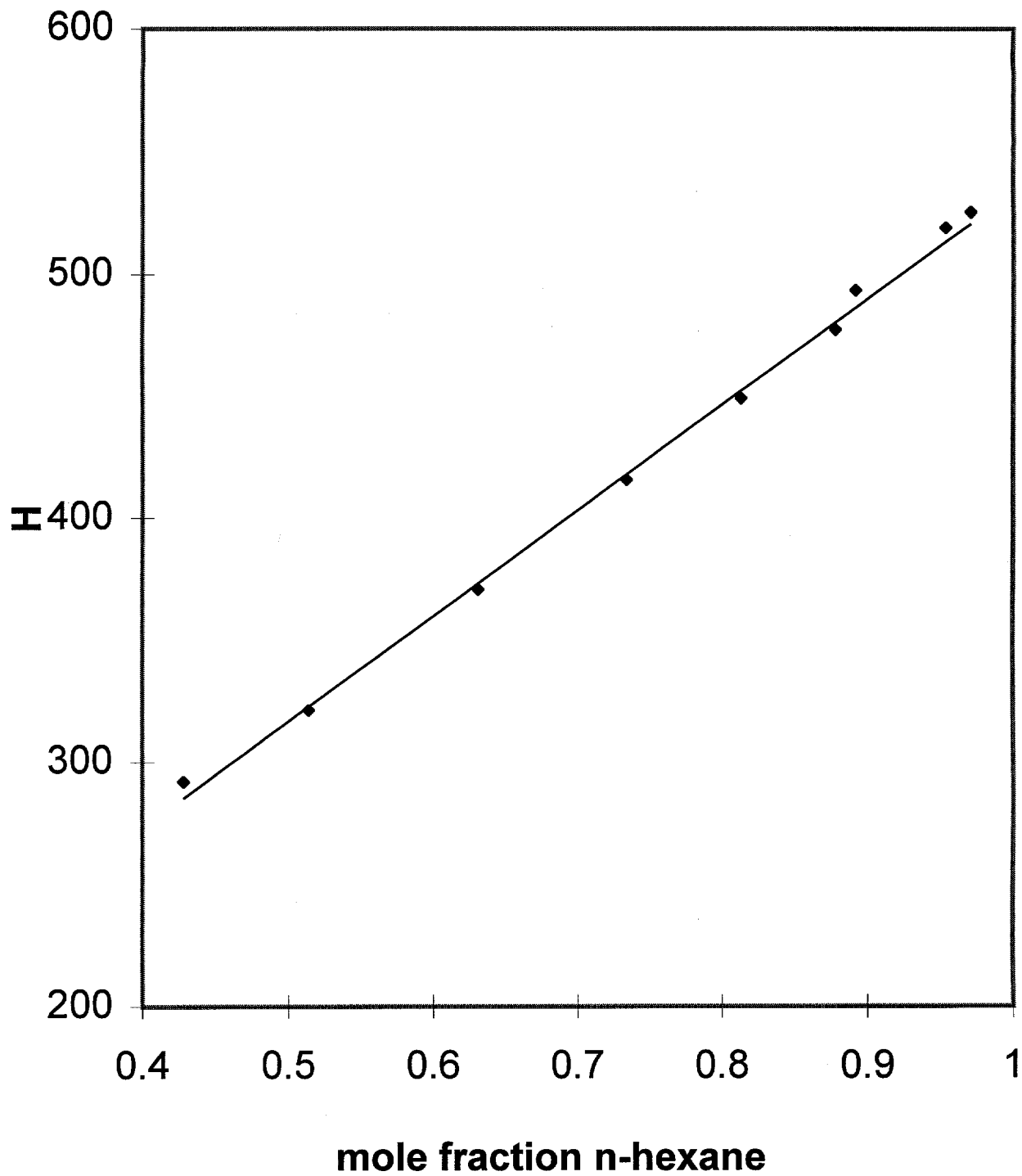


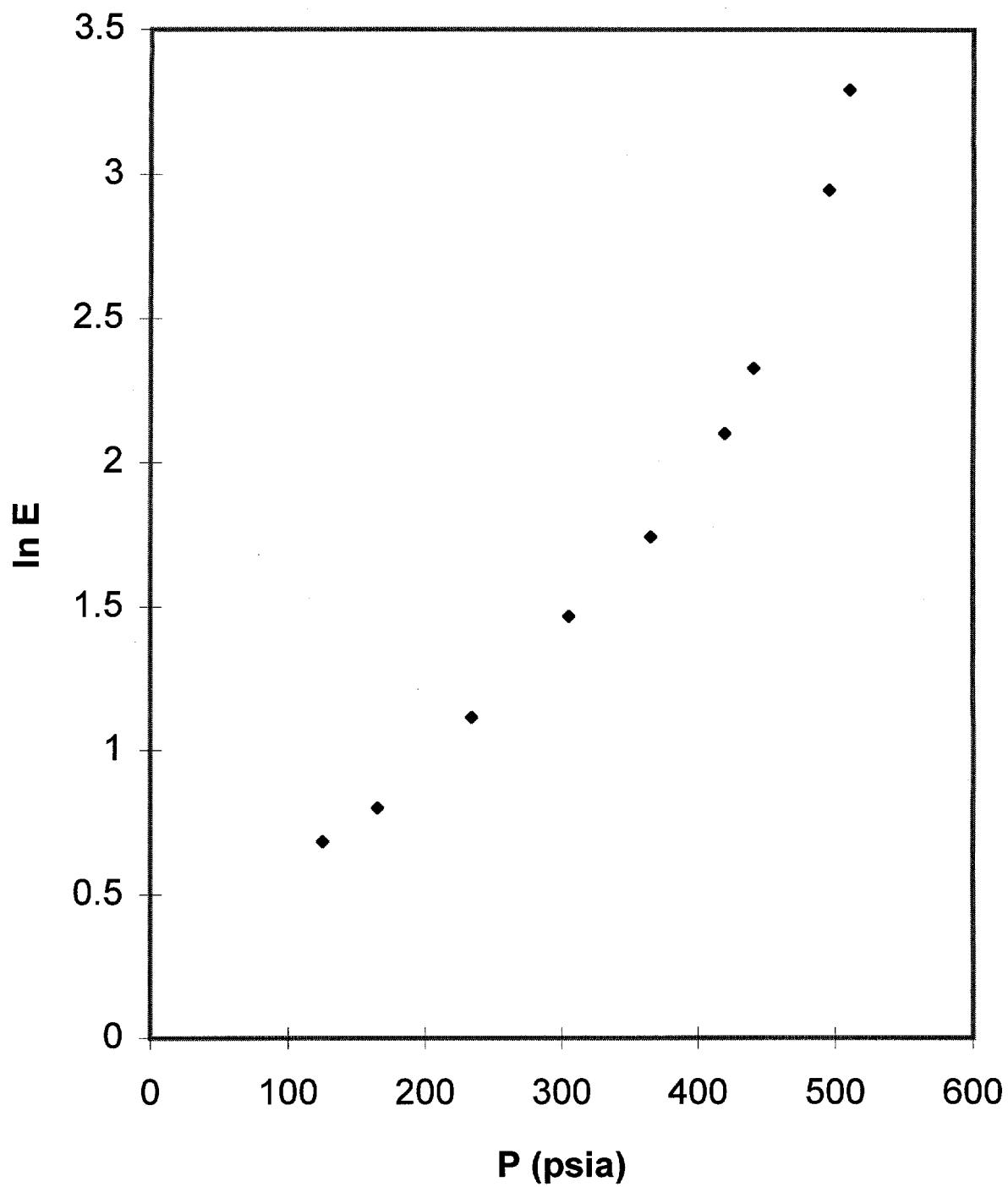
Figure 3. Pressure-composition diagram of the vapor phase at 251.1 °C.



**Figure 4. Modified Henry's law constant vs liquid mole fraction n-hexane at 196.6 °C.**



**Figure 5. Modified Henry's law constant vs liquid mole fraction n-hexane at 251.1 °C.**



**Figure 6. Natural logarithm of the modified enhancement factor vs pressure at 251.1 °C.**