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D. Dimitrelis and J.M. Prausnitz

July 1988

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**SOLUBILITIES OF N-OCTADECANE, PHENANTHRENE AND
N-OCTADECANE/PHENANTHRENE MIXTURES IN
SUPERCRITICAL PROPANE AT 390 AND 420 K
AND PRESSURES TO 60 BAR**

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ABSTRACT

Solubility data were obtained for n-octadecane, phenanthrene and a nearly equimolar n-octadecane/phenanthrene mixture in supercritical propane. Solubilities were measured in a flow apparatus at 390 and 420 K over the pressure range 35-60 bar. The experimental data have been correlated using the perturbed-hard-chain equation of state.

INTRODUCTION

Supercritical fluid extraction has received wide attention during the last few years for potential application in the specialty-chemicals, pharmaceutical and petroleum industry (1). At the center of this new technology lies enhanced solubility of the solute near the solvent's critical point. Experimental information on selected model systems is required to utilize molecular-thermodynamic models for representing the complex systems encountered in industrial applications.

Model systems using carbon dioxide or ethylene as the supercritical solvent have been studied extensively (2, 3, 4, 5). However, only a few studies have reported data for systems where the gaseous solvent has a critical temperature significantly above that of carbon dioxide (304.2 K) (6, 7). In this work we present solubilities of two model compounds (n-octadecane and phenanthrene) in supercritical propane.

Propane's critical point (369.8 K and 41.9 bar) makes it a suitable solvent for deasphalting processes in the petroleum industry. N-octadecane and phenanthrene represent two classes of hydrocarbon compounds, aliphatic and aromatic, found in heavy fossil fuels. Both are liquids in the temperature range investigated in this work; both exhibit essentially identical vapor pressures within this temperature range.

EXPERIMENTAL APPARATUS

Figure 1 shows a modified version of an apparatus described previously (8). Propane is pumped through the apparatus by a positive-displacement liquid pump from a cylinder. The desired pressure is adjusted by a back-

pressure regulator. High-pressure propane reaches the desired temperature upon flowing through a heat exchanger inserted in a constant-temperature fluidized-sand bath. Propane then passes through a packed-bed cell where it equilibrates with the heavy hydrocarbon at measured temperature and pressure. The temperature of the saturated fluid leaving the packed bed is raised to a level high enough to avoid precipitation of the heavy hydrocarbons; the fluid is then expanded and directed through a heated gas-sampling valve to take samples intermittently as discussed below. Gas samples are analyzed in a gas chromatograph; the area of the peaks is measured by an electronic integrator and displayed on a chart recorder. Finally, the propane stream passes through a condenser where the heavy hydrocarbon precipitates. Subsequently, the pure propane stream passes through a flowmeter where its cumulative volume is measured. The experimental procedure is automated once steady-state fluid flow is reached. Complete vaporization of the heavy hydrocarbon is signaled by a sharp decrease in the chromatogram peak area. To increase the rate of data acquisition, we use two flow systems in parallel.

When using a flow-solubility apparatus to study supercritical fluid-phase equilibria, it is necessary to exercise care when expanding from the experimental pressure to ambient pressure as required to facilitate downstream chemical or gravimetric analysis. In the retrograde region, there is a solubility minimum at intermediate pressures for a given temperature. Since isothermal expansion may decrease the equilibrium solubility, the solute may precipitate. Therefore, it is necessary to heat the expansion valve to a temperature for which the equilibrium solubility minimum is greater than the measured solubility in the equilibrium cell.

It is necessary to assure that, during the isobaric temperature increase between the equilibrium cell and the expansion valve, the solubility of the solute in the solvent increases monotonically. Otherwise, solute re-deposition at some intermediate location can falsify the experimental results because the measured solubility will be assigned erroneously to the temperature of the equilibrium cell and not to the unknown temperature of that intermediate location. High linear gas velocity downstream of the equilibrium cell can avoid this error by not allowing for establishment of thermodynamic equilibrium.

These two difficulties encountered in the retrograde region dictate upper limits for the experimentally-accessible ranges of temperature and pressure. Usually, the second difficulty is the more restrictive one, while the first depends on the temperature rating of the equipment downstream of the equilibrium cell. A molecular-thermodynamic model can provide guidance to assure meaningful results. The lower limits for the temperature- and pressure-range window are set by the sensitivity of the analytical technique used to analyze the gas samples. In our work, since we used gas chromatography without an internal standard, we were able to analyze only samples with a solute mole fraction greater than 10^{-4} .

The liquid pump is an Instrument Minipump Model 396-31 from Laboratory Data Control. To avoid vaporization of propane, the pump head is cooled to 283 K. To prevent hydrate formation (9), which clogs the discharge valve of the pump, water traces are removed from the propane stream by a Matheson Gas Purifier Model 450 placed upstream of the pump. The discharge pressure is adjusted by a Model 31 Back-Pressure Regulator from Circle Seal Controls. The pressure is measured with a Heise bourdon-tube pressure gauge

calibrated against a dead-weight gauge. The temperature of the fluidized-sand bath (Model SBS-4 by Techne) is controlled by a Thermotrol controller of Halikainen Instruments using a resistance-thermometer probe (RTD) Model PR-11 by Omega. The temperature is measured with an Iron/Constantan thermocouple whose reading is displayed on an Omega Trendicator Model 410, calibrated on the 1968 IPTS scale.

The packed-bed cells are made of stainless-steel tubes, 0.1 m in length and $5 \cdot 10^{-3}$ m inner diameter. The solute is introduced into the cell in solid form at three evenly spaced points separated with a 60/80-mesh Chromosorb-P column support. The mass of the heavy hydrocarbon is determined by weighing the funnel (made of ultra-thin weighing paper) with a Mettler mass balance Model HK 160 before and after loading.

A specially designed high-temperature, high-pressure expansion valve is used to expand the compressed-fluid mixture from the packed-bed cell so that the fluid can be sampled and metered. Details are presented elsewhere (10). The gas-sampling valve is a VALCO 10-port, high-temperature sampling valve with a $5.7 \cdot 10^{-7}$ m³ sample loops. A 10-port valve with two sample loops is used such that the fluid streams from two different packed-bed equilibrium cells can be sampled alternatively. Sampling is automated using a VALCO Digital Valve Interface, a VALCO 2-Position Helical-Drive Air Actuator and a mechanical timer. A typical run lasts one to two days; samples are taken automatically every half hour.

Gas samples are analyzed using a Perkin-Elmer Model 990 Gas Chromatograph with a hydrogen-flame ionization detector under constant-temperature, differential (compensated-mode) operation. The

chromatographic column is a 2-m long, 2.2×10^{-3} -m inner diameter stainless-steel tube packed with a 3% OV-101 Chromosorb W-HP column support. The output from the gas chromatograph is measured and recorded using a Spectra-Physics single-channel integrator and displayed on a Honeywell strip-chart recorder.

The cumulative volume of propane is measured through integration of the propane flow over time by a Matheson Mass Flowmeter, Series 8100; the output signal is fed to a Totalizer Model 8122.

The results of the intermittent fluid-phase analysis are plotted against the corresponding cumulative propane volume (at standard temperature and pressure) having passed through the equilibrium cell. The solubility is obtained using the equal-area data-reduction technique described elsewhere (8).

MATERIALS

The propane cylinder was supplied by Matheson with full-length eductor tubes for liquid withdrawal. Propane was of CP grade with a 99.0% minimum purity in the liquid phase. The solutes were supplied by Aldrich. Purity was 98+% for anthracene, 97% for n-octadecane and 98+% for phenanthrene.

The accuracy in reported temperature is better than ± 0.15 K; the accuracy in reported pressure is better than $\pm 1\%$ over the entire range. Finally, the accuracy in the reported solubility is better than $\pm 5\%$.

EXPERIMENTAL RESULTS

To check the apparatus, solubility data were obtained for anthracene. Table 1 presents the solubility of anthracene in propane at 420 K. Figure 2 compares our measurements with those reported by Rössling and Franck (6) who used a static apparatus. The solid line shows a correlation of our measurements using the perturbed-hard-chain equation as described below. The discrepancy between the two data sets is larger than the estimated experimental error.

Figure 3 shows the enhancement factor for anthracene as a function of pressure. The enhancement factor is defined as the ratio of the solute's partial pressure over its vapor pressure at given temperature and pressure. The data of Rössling and Franck are normalized using their own vapor-pressure measurements, while our data are normalized using the sublimation-pressure equation reported in API Publication 709 (11). The resulting enhancement factors for the two sets of measurements are within the reported experimental error. The difference between the two sets of solubility data is not larger than the variation in the sublimation pressure reported in the literature for anthracene.

Tables 2 and 3 present solubilities of n-octadecane and phenanthrene respectively in supercritical propane at 390 and 420 K and pressures to 60 bar. Table 4 presents the solubility of a n-octadecane/phenanthrene mixture in supercritical propane. The composition of the liquid phase on a propane-free basis is 46 mole-% phenanthrene and 54 mole-% n-octadecane. The vapor-phase mole fraction of the heavies is the sum of the n-octadecane and phenanthrene mole fraction in the vapor phase.

DATA CORRELATION AND DISCUSSION

We used the perturbed-hard-chain (PHC) equation of state (12, 13) to correlate our experimental results. Since our measurements are near propane's critical point, we adjusted the equation-of-state parameters for propane to represent better the properties of propane in its near-critical region. We used

$$\begin{aligned}T^* &= 245.69 \text{ K} \\v^* &= 4.316 \cdot 10^{-5} \text{ m}^3/\text{mole} \\c &= 1.51\end{aligned}$$

As discussed elsewhere (10), the choice of equation-of-state parameters has an effect on mixture calculations near the solvent's critical point. Overprediction of the solvent's critical temperature and pressure (even by few degrees or few bars) can adversely affect solubility calculations in the solvent's near-critical region. For n-octadecane and phenanthrene, we used the parameters reported by Cotterman et al. (12).

Figure 4 shows calculated and experimental results for the solubility of n-octadecane in propane. Using only one adjustable binary parameter $k_{12}^B = -0.06$, we were able to correlate our measurements for both isotherms over the entire pressure range. Dense-fluid parameter k_{12} was set to zero. The model correctly predicts that the propane/n-octadecane mixtures conform to type D phase behavior according to the classification of Kohn et al. (14).

Figure 5 shows calculated and experimental (15) Henry's constants for propane in n-octadecane. The calculations are performed using the binary parameter obtained from the solubility measurements. The measurements are correlated within experimental error over a wide range of temperature. Thus, the gas-phase solubility data appear to be consistent with the liquid-phase solubility data.

Figure 6 shows calculated and experimental results for the solubility of phenanthrene in propane. No binary parameter was necessary for the correlation of the experimental data. The equation of state predicts that at the lower temperature there is liquid-liquid immiscibility between a phenanthrene-rich and a propane-rich liquid phase. As discussed by Kohn et al. (14), such phase behavior is common for binary mixtures for which the triple point of the heavier component (the freezing point of phenanthrene is 373.7 K) is slightly higher than the critical temperature of the lighter component.

Figure 7 shows calculated and experimental solubilities of n-octadecane/phenanthrene mixtures in propane at two different temperatures and pressures. The liquid-phase composition on the abscissa is on a propane-free basis. The calculated solubilities are the sum of the vapor-phase mole fractions for n-octadecane and phenanthrene. For the two-solute system, there is an enhancement of the overall solubility compared with the solubilities of the individual heavy hydrocarbons.

The results indicate that calculations using the binary constants (propane/n-octadecane and propane/phenanthrene) do not correlate the vapor-phase composition for this ternary mixture. It is also necessary to

include a binary constant for the liquid phase containing the two heavy hydrocarbons. Because no experimental information is available for n-octadecane/phenanthrene vapor-liquid equilibria, we assume that the dense-fluid parameter k_{12} for n-octadecane/phenanthrene is similar to that for n-hexadecane/phenanthrene. Correlation of vapor-liquid equilibria data for n-hexadecane/phenanthrene (16) using the PHC equation gives k_{12} equal to 0.03. The solid line in Figure 7 shows calculated results using one interaction parameter per binary. These calculated results correlate the measured data well.

Figure 8 presents the selectivity of propane for an equimolar n-octadecane/phenanthrene mixture. Selectivity is defined as the ratio of equilibrium K-factors for phenanthrene and n-octadecane. Propane is slightly more selective for phenanthrene than for n-octadecane. This selectivity difference cannot be attributed to vapor-pressure effects since the vapor pressures of the two model compounds are essentially the same over the temperature range investigated. The observed selectivity may be related to weak interactions between the quadrupole moment of phenanthrene and weak dipole moment of propane.

At the lower temperature, the selectivity decreases initially with pressure but then increases as the pressure approaches the mixture critical point for the binary systems. At the higher temperature we observe an azeotrope.

Propane appears to be more selective for aromatic than for aliphatic hydrocarbons, confirming the results of previous work on the selectivity of propane for a continuous oil mixture containing saturated and aromatic

hydrocarbons (17). Propane is a more selective solvent at temperatures near its critical; at higher temperatures, selectivity decreases while solvent power increases.

GLOSSARY

c Prigogine's Parameter
k Binary Interaction Parameter
PHC Perturbed-Hard-Chain Equation of State
T Temperature
v Molar Volume

Superscripts:

B Second Virial Coefficient
* Perturbed-Hard-Chain Equation-of-State Parameters

Subscripts:

ij Interaction between Component i and Component j

REGISTRY NO. Propane, 74-98-6; Anthracene, 120-12-7; N-Octadecane, 593-45-3; Phenanthrene, 85-01-8.

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LIST OF TABLE CAPTIONS:

Table 1. Solubility of Anthracene in Propane

Table 2. Solubility of n-Octadecane in Propane

Table 3. Solubility of Phenanthrene in Propane

Table 4. Solubility of a Nearly Equimolar Mixture of
n-Octadecane/Phenanthrene in Propane

LIST OF FIGURE CAPTIONS:

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Figure 2. Calculated and Experimental Solubilities of Anthracene in Propane at 420 K.

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Figure 4. Calculated and Experimental Solubilities of n-Octadecane in Propane.

Figure 5. Predicted and Experimental Henry's Constant for Propane in n-Octadecane (Binary Parameter k_{12}^B from Solubility Data for n-Octadecane in Propane).

Figure 6. Calculated and Experimental Phase Equilibria for Propane/Phenanthrene.

Figure 7. Calculated and Experimental Solubilities for n-Octadecane/Phenanthrene Mixture in Propane.

Figure 8. Calculated Solubility Ratio (Selectivity) for an Equimolar n-Octadecane/Phenanthrene Liquid Mixture in Propane.

Table 1. Solubility of Anthracene in Propane

T (K)	P (bar)	mole %
419.5	46.1	0.0351
419.5	48.3	0.0400
420.0	52.6	0.0478
419.6	56.3	0.0541

Table 2. Solubility of n-Octadecane in Propane

T (K)	P (bar)	mole %
389.9	36.1	0.0257
389.9	40.3	0.0408
390.0	46.1	0.0729
419.5	45.9	0.110
419.6	52.5	0.160
419.6	53.0	0.174
419.6	60.7	0.302

Table 3. Solubility of Phenanthrene in Propane

T (K)	P (bar)	mole %
389.7	36.3	0.0319
390.0	40.7	0.0433
390.0	44.7	0.0630
419.0	45.7	0.0901
419.1	53.5	0.136
419.1	58.9	0.189

Table 4. Solubility of a Nearly Equimolar Mixture of n-Octadecane/Phenanthrene in Propane

T (K)	P (bar)	mole %
388.7	42.7	0.0676
419.7	54.5	0.227

APPARATUS FOR MEASURING THE SOLUBILITY OF HEAVY HYDROCARBONS
IN SUPERCRITICAL PROPANE

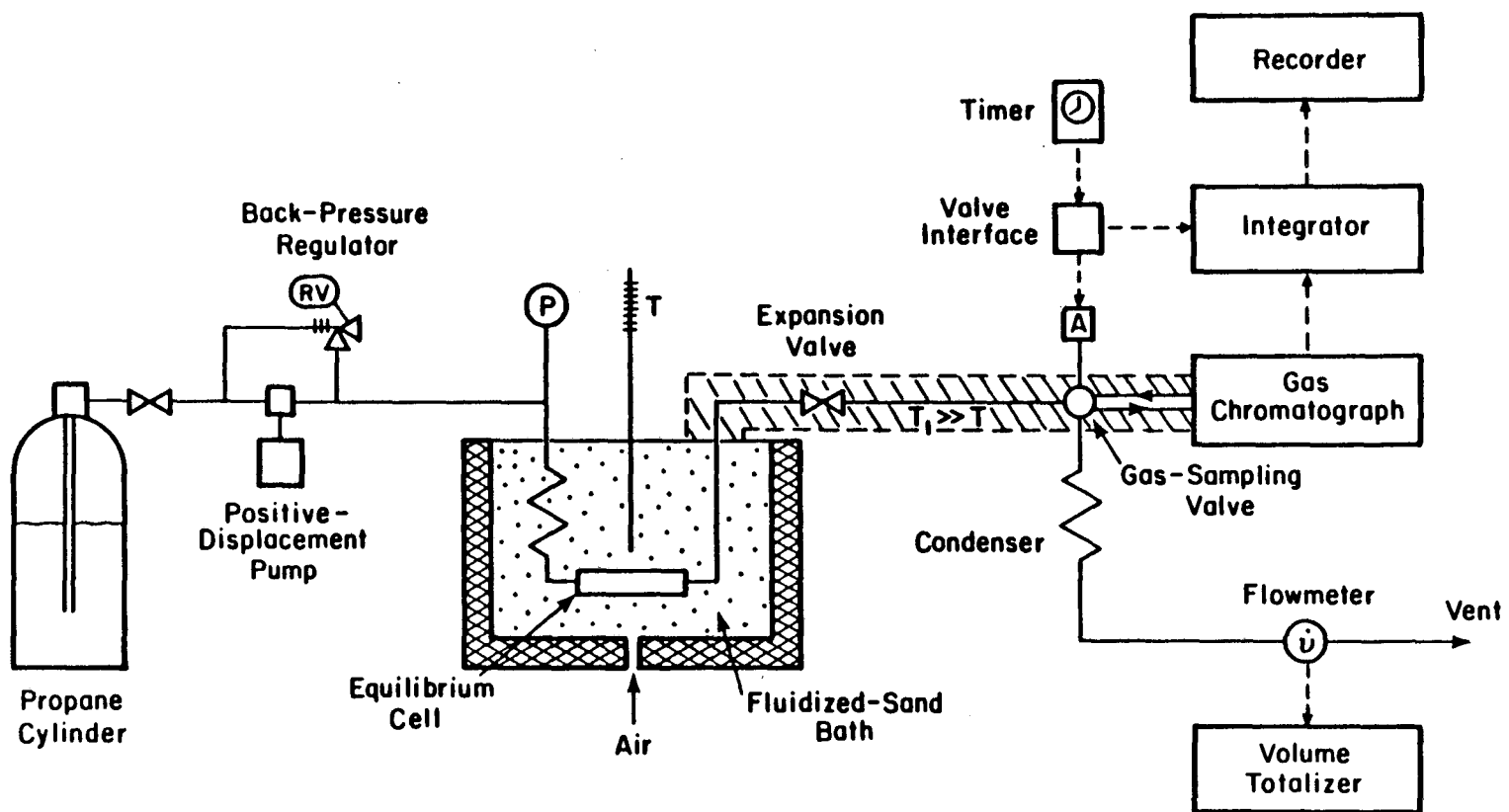
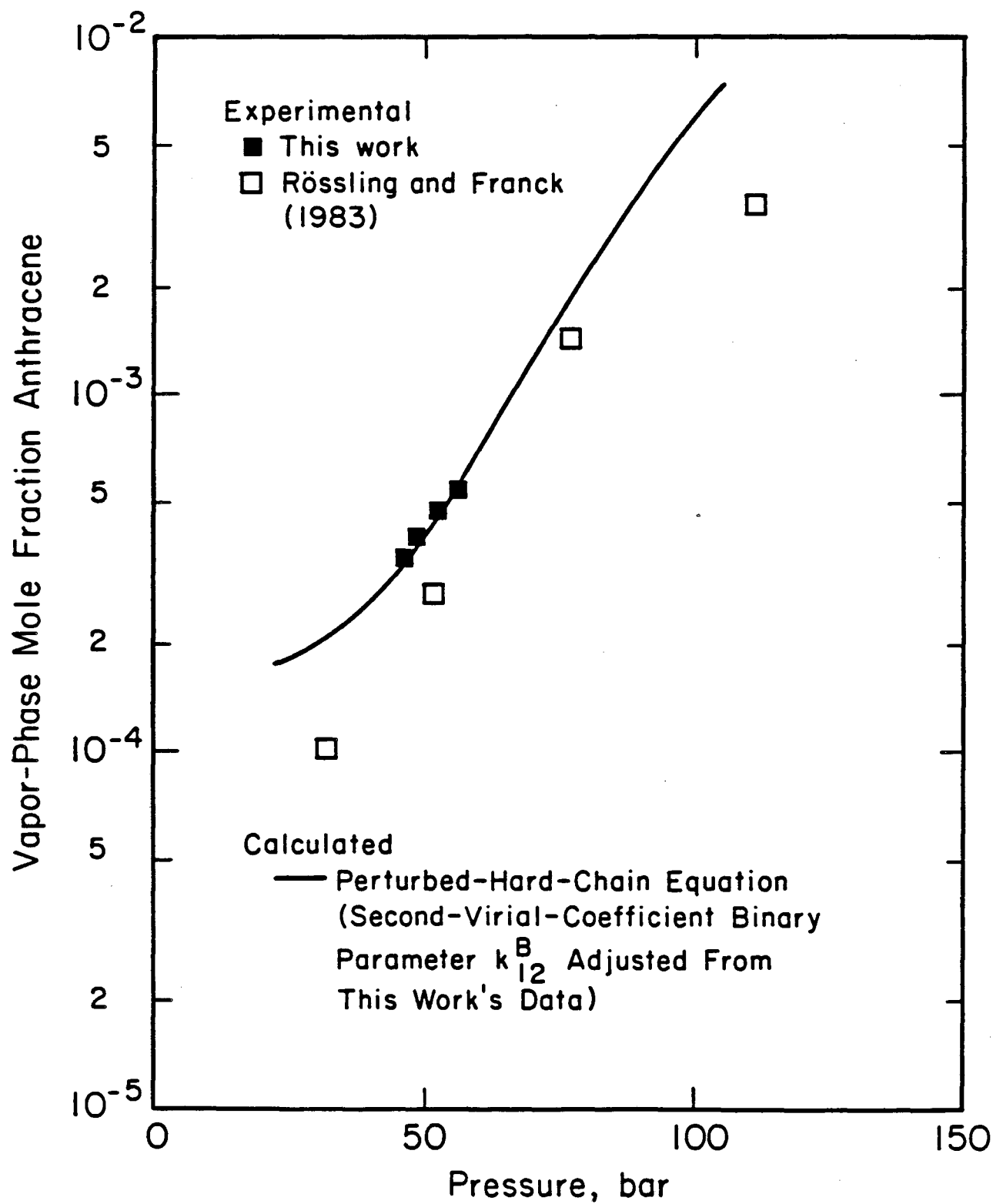


FIGURE 1

CALCULATED AND EXPERIMENTAL SOLUBILITY
OF ANTHRACENE IN PROPANE AT 420 K



CALCULATED AND EXPERIMENTAL ENHANCEMENT FACTOR FOR ANTHRACENE IN PROPANE AT 420 K

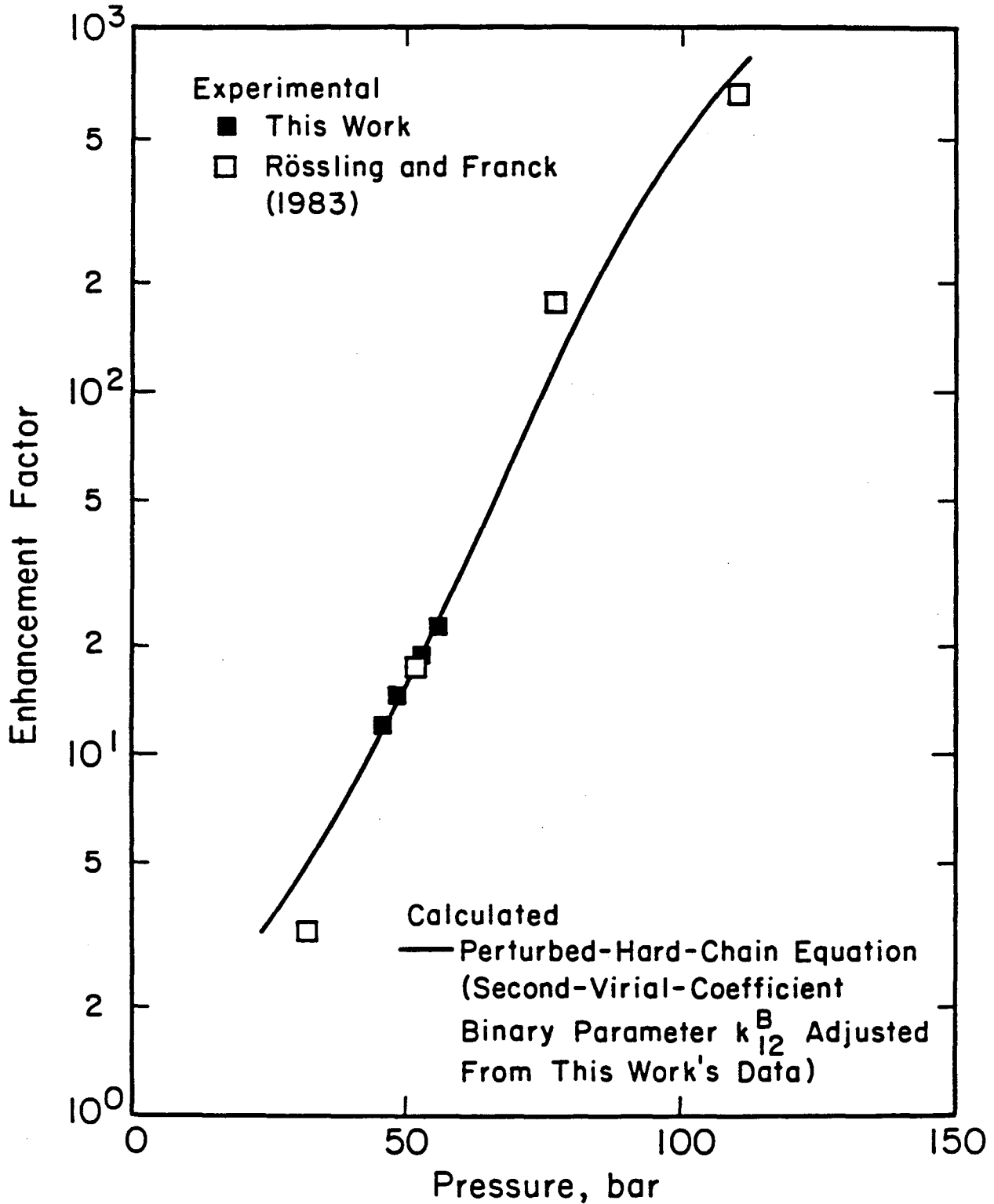


FIGURE 4

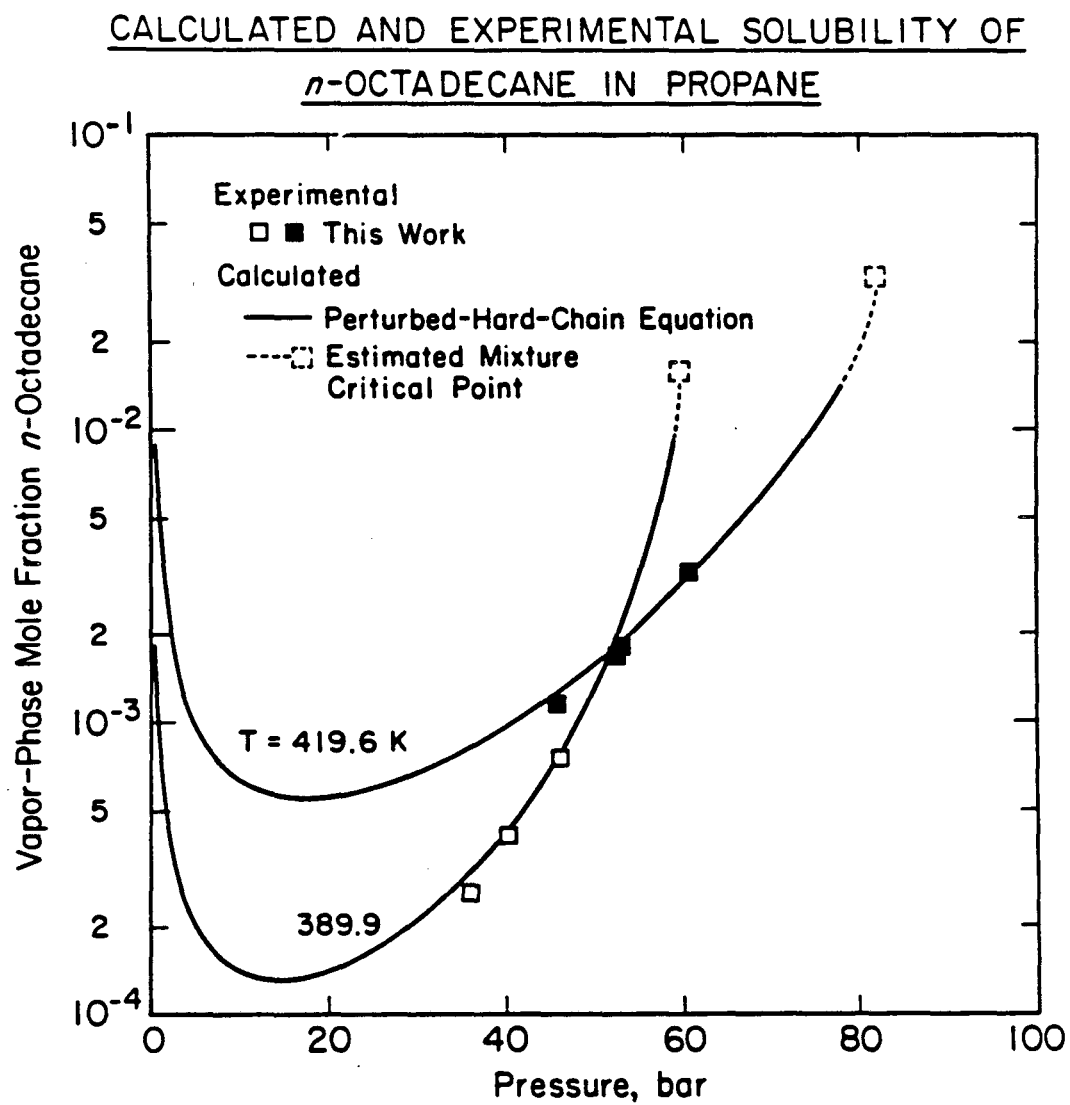
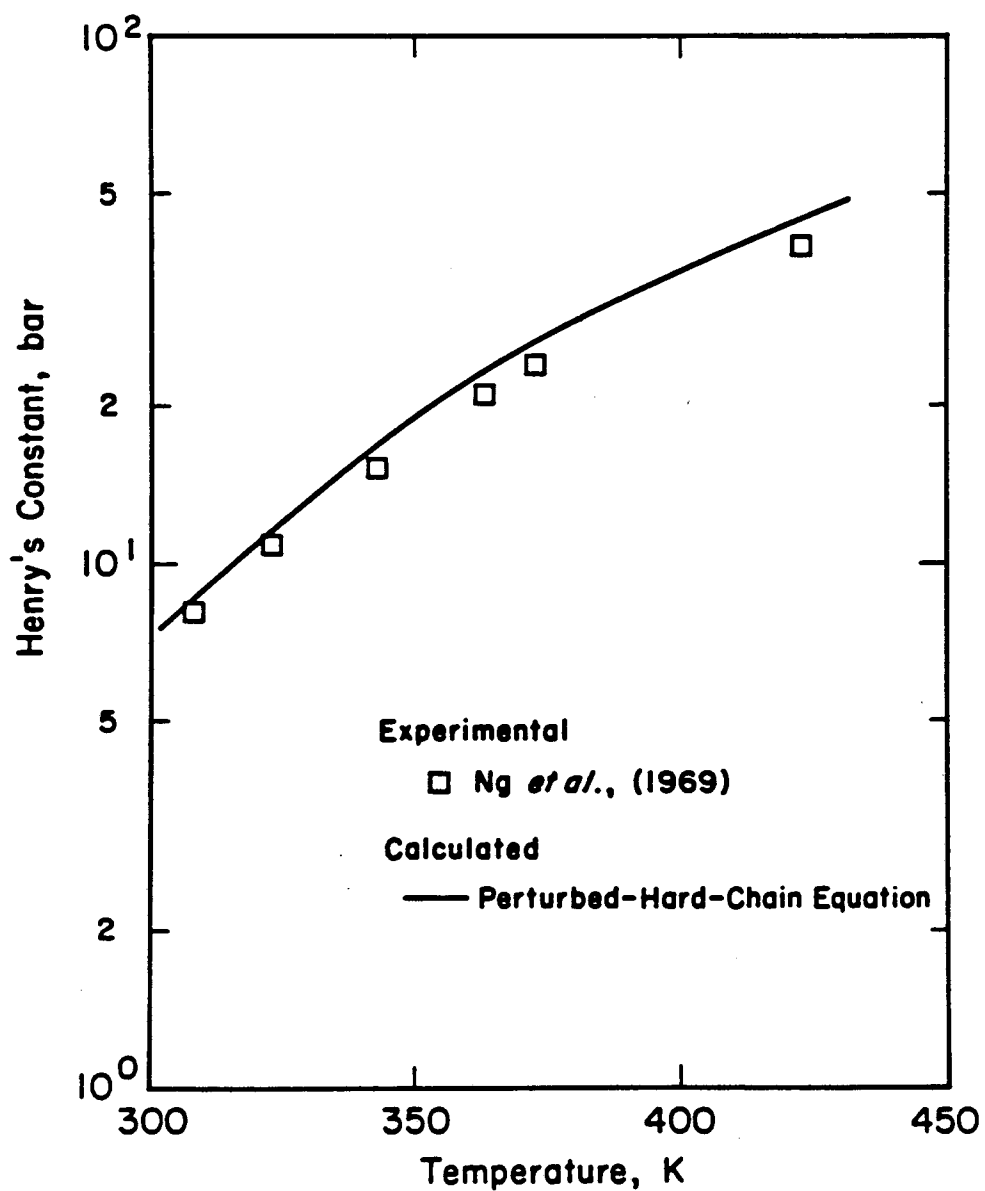


FIGURE 5

PREDICTED AND EXPERIMENTAL HENRY'S CONSTANT
FOR PROPANE IN *n*-OCTADECANE

(Binary Parameter k_{12}^B From Solubility Data For
n-Octadecane in Propane)



CALCULATED AND EXPERIMENTAL PHASE EQUILIBRIA FOR PROPANE/PHENANTHRENE

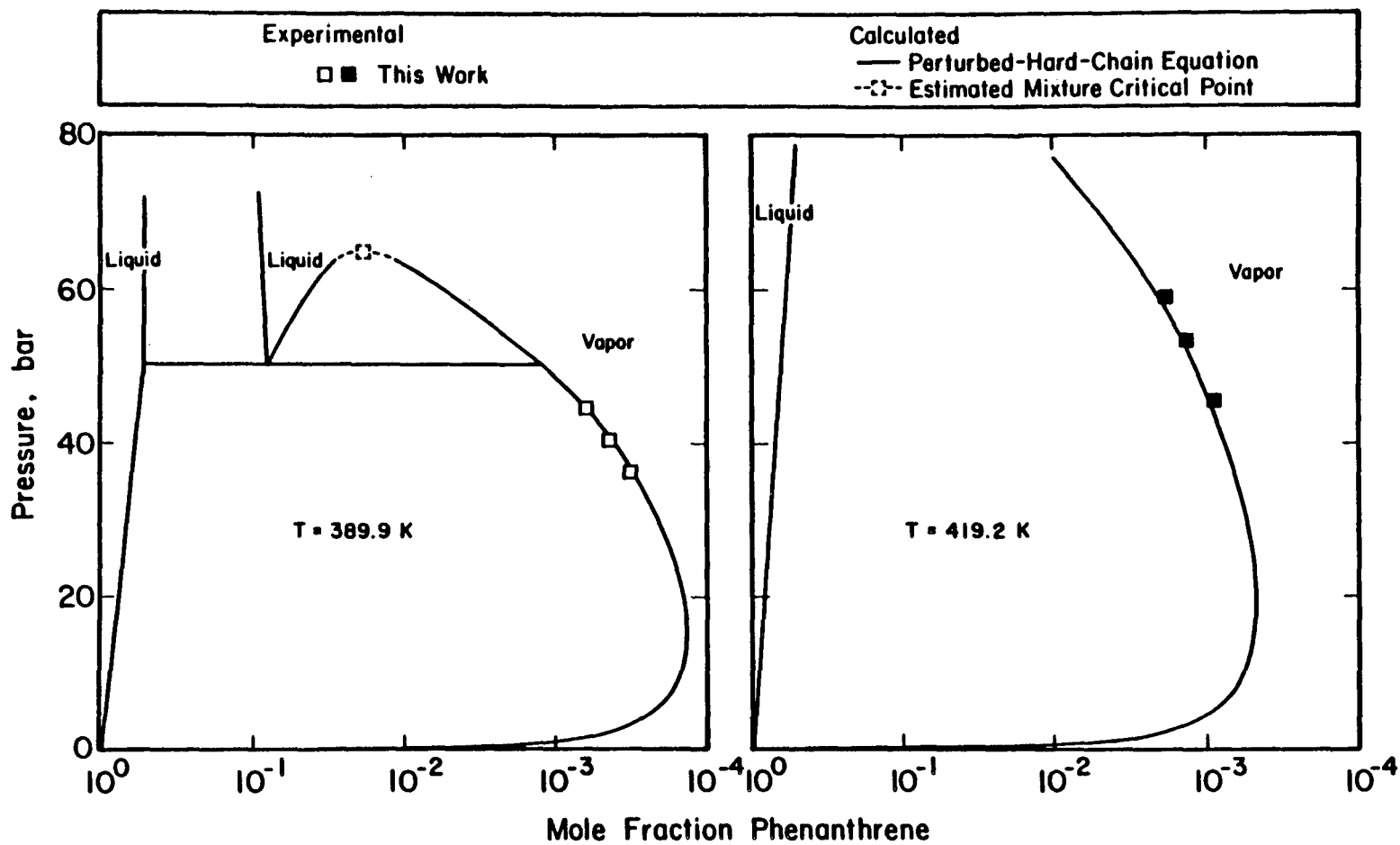
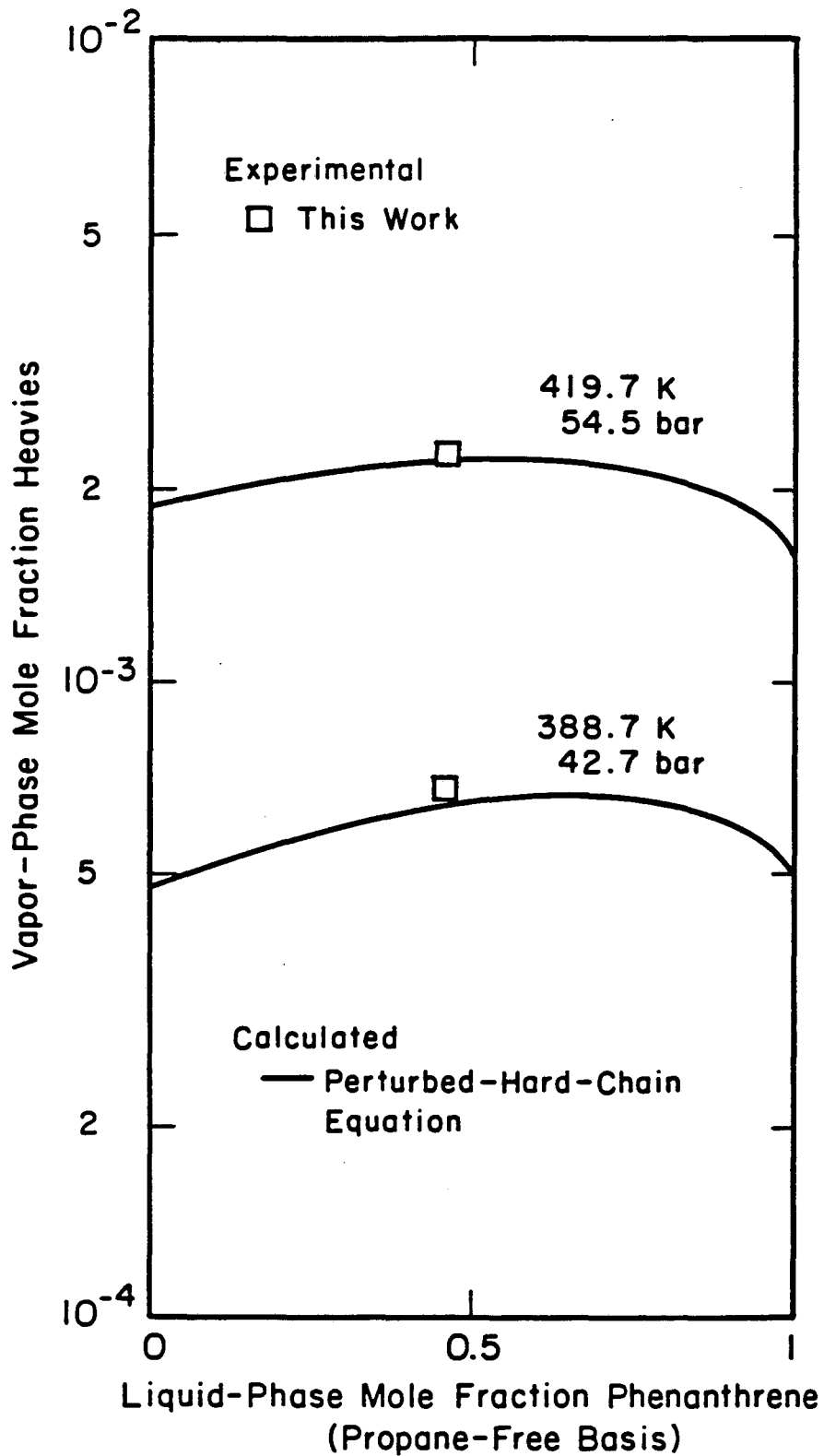
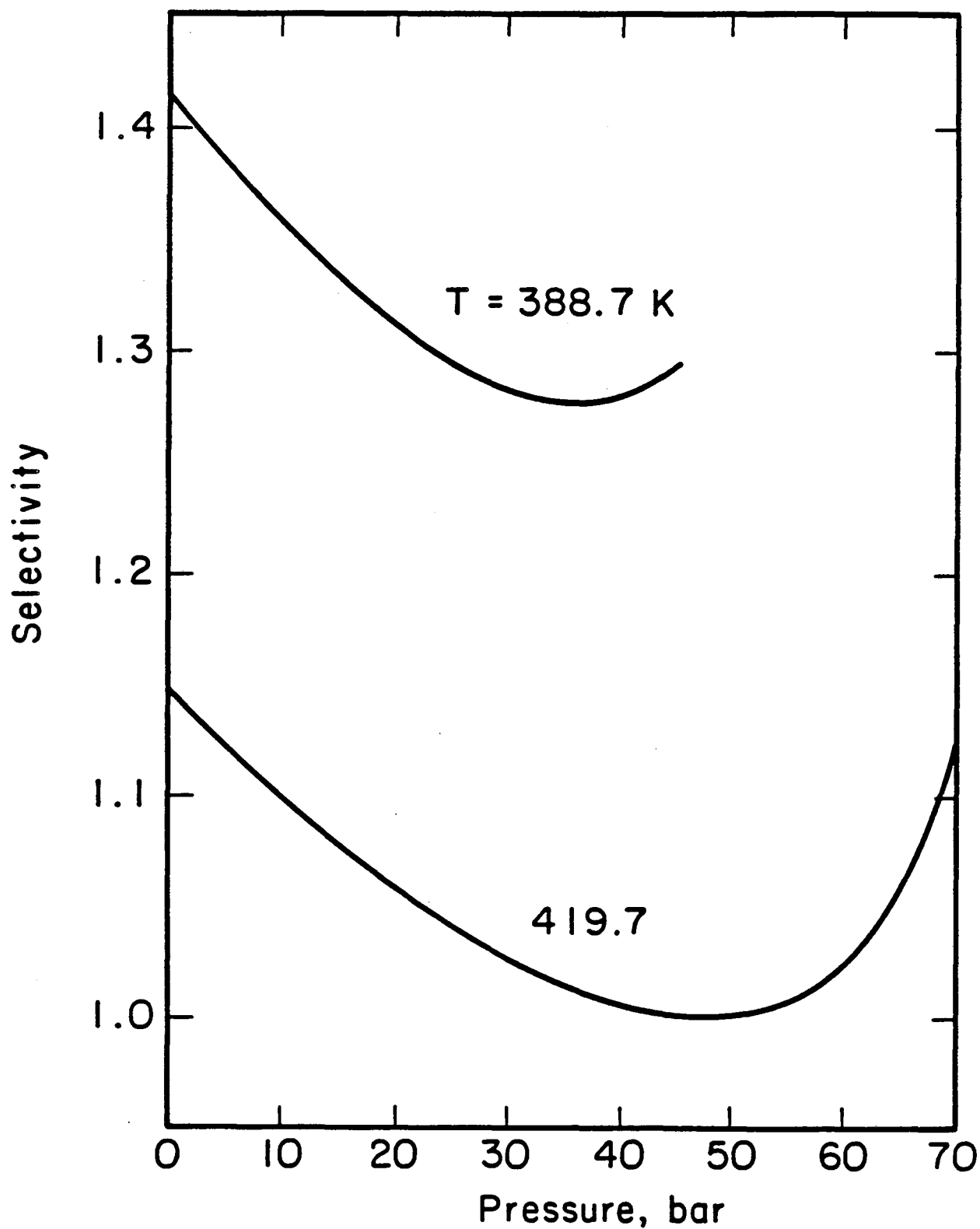


FIGURE 6

CALCULATED AND EXPERIMENTAL VAPOR-PHASE
MOLE FRACTION OF *n*-OCTADECANE AND
PHENANTHRENE IN PROPANE



CALCULATED SOLUBILITY RATIO (SELECTIVITY) FOR
AN EQUIMOLAR PHENANTHRENE/*n*-OCTADECANE
LIQUID MIXTURE IN PROPANE



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