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SYNTHESIS GAS SOLUBILITY IN FISCHER-TROPSCH SLURRY

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Summary

The objective of this research is to investigate the phase equilibrium behavior of synthesis gas and products in Fischer-Tropsch slurry reactor. A semi-flow apparatus has been designed and constructed for this purpose. The apparatus provides contact for a flowing gas stream with a stationary liquid and is suited for the determination of gas solubility in a molten wax of high melting point. To verify attainment of equilibrium, the new apparatus has been tested with a mixture of carbon dioxide and toluene. The test data agree well with the experimental results of Ng and Robinson from a static apparatus.

Measurements have been completed for eight binary mixtures: hydrogen, methane, ethane, and carbon dioxide in n-eicosane and in n-octacosane at three temperatures (100, 200, and 300° C) and five pressures (10, 20, 30, 40, and 50 atm).

Introduction

Recent intensified development of Fischer-Tropsch synthesis in a slurry reactor has created a need for information on gas solubility in the slurry media. Satterfield and co-workers (1-3), and others (4,5), have recently studied the effect of liquid composition on the rate of reaction and selectivity of the Fischer-Tropsch synthesis in a slurry reactor, and concluded that the solubility of synthesis gases in the slurry of interest was needed for interpretation of the synthesis reaction. The information is also important to the design and operation of the processes.

Previous studies on the solubility of synthesis gases and process products in heavy wax at conditions of temperature and pressure of the Fischer-Tropsch processes are limited. Albal and co-workers (5) reported the solubility data of synthesis gases (H_2,CO) in Gulf wax at temperatures of 348-523K. Matsumoto and Satterfield (6) investigated the hydrogen and carbon monoxide solubilities in three selected liquids: n-octacosane, phenanthrene, and fomblin. High temperature gas solubility data in paraffin wax are available by Peter and Weinert (7). In this work we designed and constructed a new apparatus for measurement of vapor-liquid equilibrium (VLE) for gas + slurry mixtures at conditions of Fischer-Tropsch synthesis in slurry reactors. The apparatus, of semi-flow type, provides contact for a flowing gas stream with a stationary liquid and is suitable particularly for the determination of gas solubility in a molten wax of high melting point. Measurements have been completed for eight binary mixtures: hydrogen, methane, ethane, and carbon dioxide in n-eicosane and in n-octacosa. at temperatures of 373-573K and pressures of 10-50 atm.

Experimental Section

Figure 1 shows the scheme of the semi-flow apparatus, which consists of two main sections: the quilibration section and the sampling section. All parts exposed to high temperature and pressure are constructed of 316 stainless steel.

The heart of the equilibration section is the thermostated nitrogen bath in which two stainless steel cells are placed in series. The first cell serves as a presaturator. and the second. as the equilibrium cell. The bath is a well insulated and regulated oven of 2.1 ft^3 internal volume. Nitrogen gas fills the bath in the course of experiments. Circulation of nitrogen in the bath is maintained by an electric fan mounted at the back of the bath. Two heating wires insulated in ceramic beads and controlled by rheostats are placed around the fan outlet to heat the bath. The bath temperature is controlled by a Halikainen Instrument Model 1053 through a secondary heater. The temperature uniformity in the bath was found to be within 0.5°C in the vicinity of the cells at bath temperature 100°C, and 1°C at 300°C.

The temperature of the equilibrium cell is measured by a type K chromel-alumel thermocouple inserted into the cell and calibrated to an accuracy of ± 0.1°C. To ensure the isothermal condition in the bath, a second thermocouple is placed outside the cell. Heating of the bath is controlled so that both thermocouples give the same reading within their accuracy in the course of an experiment. A model CMM 0-750 psi Heise gauge is used to read the pressure with an accuracy of ± 0.1% of the maximum range.

Both the cells are loaded at the beginning of a series of runs with a known amount of solvent. The bath is heated to the desired temperature before introducing the gas. Gas is supplied continuously to the system from the gas cylinder at the pressure of interest. To promote mixing and equilibration, the cells are packed with raschig rings, and the gas is sparged through the solvent in the cells. Equilibration requires about 20-40 minutes at the end of which the liquid composition attains a constant steady value. The gas flow rate is varied to test for constancy of gas composition when the gas composition is of interest.

Sampling Procedure

Liquid-phase effluent from the equilibrium cell is reduced in pressure and temperature before entering a trap for sampling. The heavy paraffin is retained as solid in the trap at ambient conditions and later weighed with an analytical balance. The corresponding quantity of liberated gas is determined volumetrically in a buret. For test mixtures of CO_2 + toluene, toluene condensate is retained as liquid in the trap at ambient condition. Minor corrections for the quantities of CO_2 dissolved in toluene and toluene vaporized into CO_2 were made to the directly observed sample weight and gas volume. No such corrections are needed for the paraffin experiments.

To prevent the entrainment of gas bubbles into the liquid samples and to retain the system at constant pressure in the course of liquid- phase sampling, the gas stream

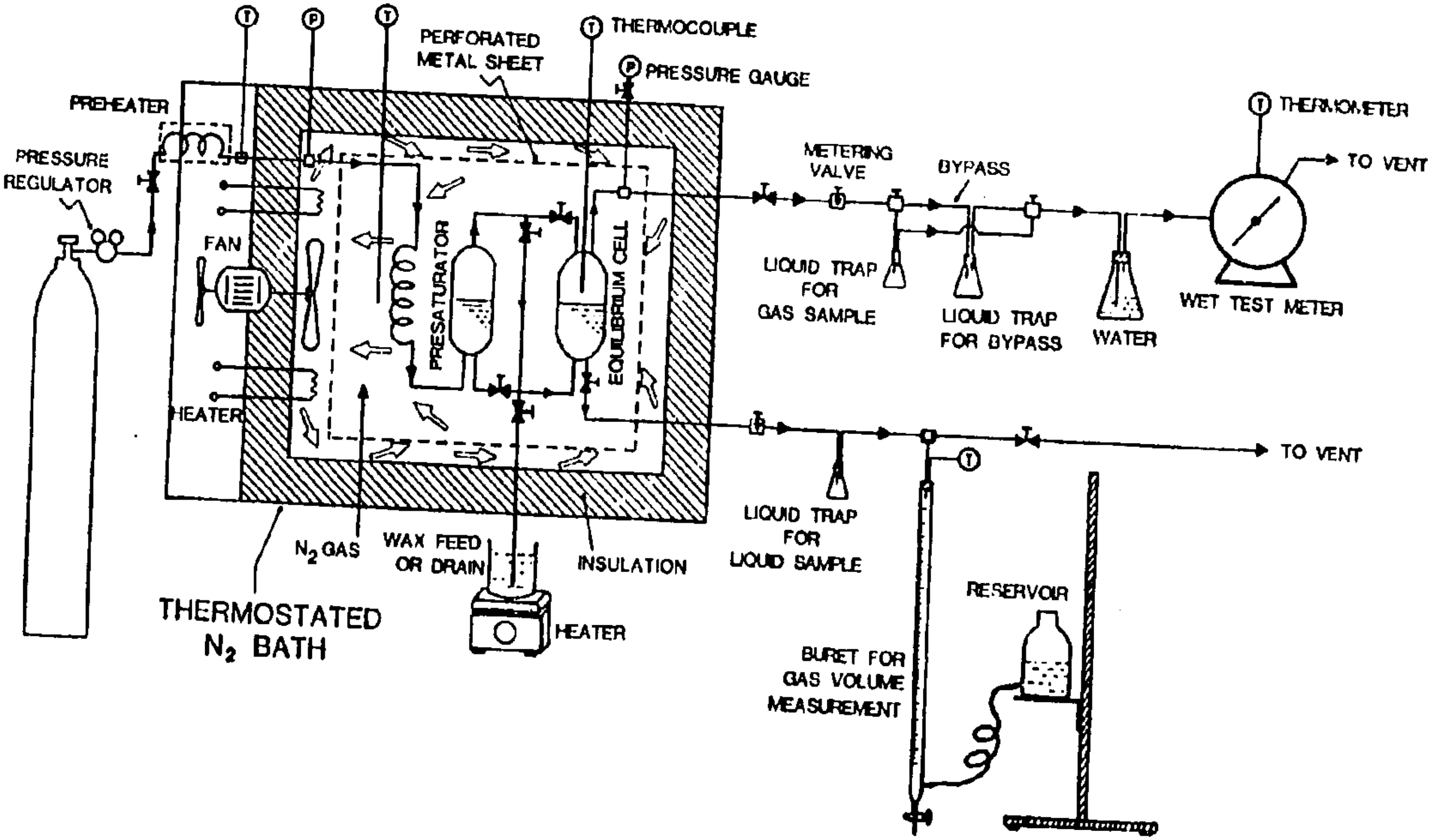


Figure 1. Vapor-liquid equilibrium apparatus

from the presaturator is redirected to enter the equilibrium cell from the top.

The sampling apparatus and procedure for the gas phase are similar to those described above for the liquid, except that a wet test meter was used in place of a buret to measure the gas due to the large volume of it that was liberated.

Materials

The sources and purities of chemicals used in this work are as follows:

Chemical	Supplier	Purity, %
H_2	Airco	99.8^+
CH_4	Matheson	99^+
C_2H_6	Matheson	99^+
CO_2	Matheson	99.8^+
Toluene	Malinckrodt	99
n-C_{20}	Alderich	99
n-C_{28}	Alfa	99

Results and Discussion

The apparatus has been tested with mixtures of carbon dioxide and toluene at 353K to verify attainment of equilibrium. As shown in Figures 2 and 3, the new data agree well with the experimental results of Ng and Robinson (8) from a static apparatus. Further tests for the attainment of equilibrium have been made by varying the gas flowrate. All of the results reported in this work were found to be independent of the flowrate.

Gas solubility measurements have been completed for eight binary mixtures: hydrogen, methane, ethane, and carbon dioxide in n-eicosane (n$-C_{20}$) and in n-octacosane (n$-C_{28}$) at three temperatures (100, 300, and 300°C). Along each isotherm, five pressures (10, 20, 30, 40, and 50 atm) were investigated for each system, except ethane binaries for which only four pressures (10-40 atm) were determined. The measurements at one temperature were made in the sequence of 10 atm, 30 atm, 50 atm, 40 atm, and 20 atm.

Figures 4-11 show the experimental results of gas solubilities for eight binary mixtures as a function of pressure at different temperatures. At least four replicate samples were taken at each condition of temperature and pressure. The multiple samples are generally reproducible to within 2% in the mole fraction of the gas component. Individual sample compositions are shown in the figures as separate points when they can be distinguished.

Gas solubility increases with pressure at the conditions of this study. Hydrogen was found to be significantly more soluble in both paraffin solvents at higher temperatures. The observed solubilities of carbon dioxide and ethane, on the other hand, decrease with increased temperature. The results for the methane binaries show a transition in solubilities with increasing temperature passing through a minimum value in the range of 100-300°C.

The composition of the saturated vapor phase has been determined. With the exception of experiments with n$-C_{20}$ at 300°C, the equilibrium gas was found to be almost pure, 99.5% or higher in the gas phase at all states studied, due to the extremely low volatility of the heavy paraffin solvents. Figure 12 shows the mole fraction of the light gas in the vapor for all four binary mixtures of gas + n$-C_{20}$ at 300°C. The mole fraction increase with pressure but decrease with pressure but decrease with temperature at the experimental conditions of this study.

Data Analysis by Krichevsky-Kasarnovsky Equation

The Krichevsky-Kasarnovsky equation (9) is expressed as

$$\ln\left(\frac{f_2}{x_2}\right) = \ln H_{2,1}^{P_1^\circ} + \frac{\bar{v}^{\infty}(P-P_1^\circ)}{RT} \qquad (1)$$

where subscript 1 refers to the solvent and subscript 2 to the solute. f_2 is the fugacity

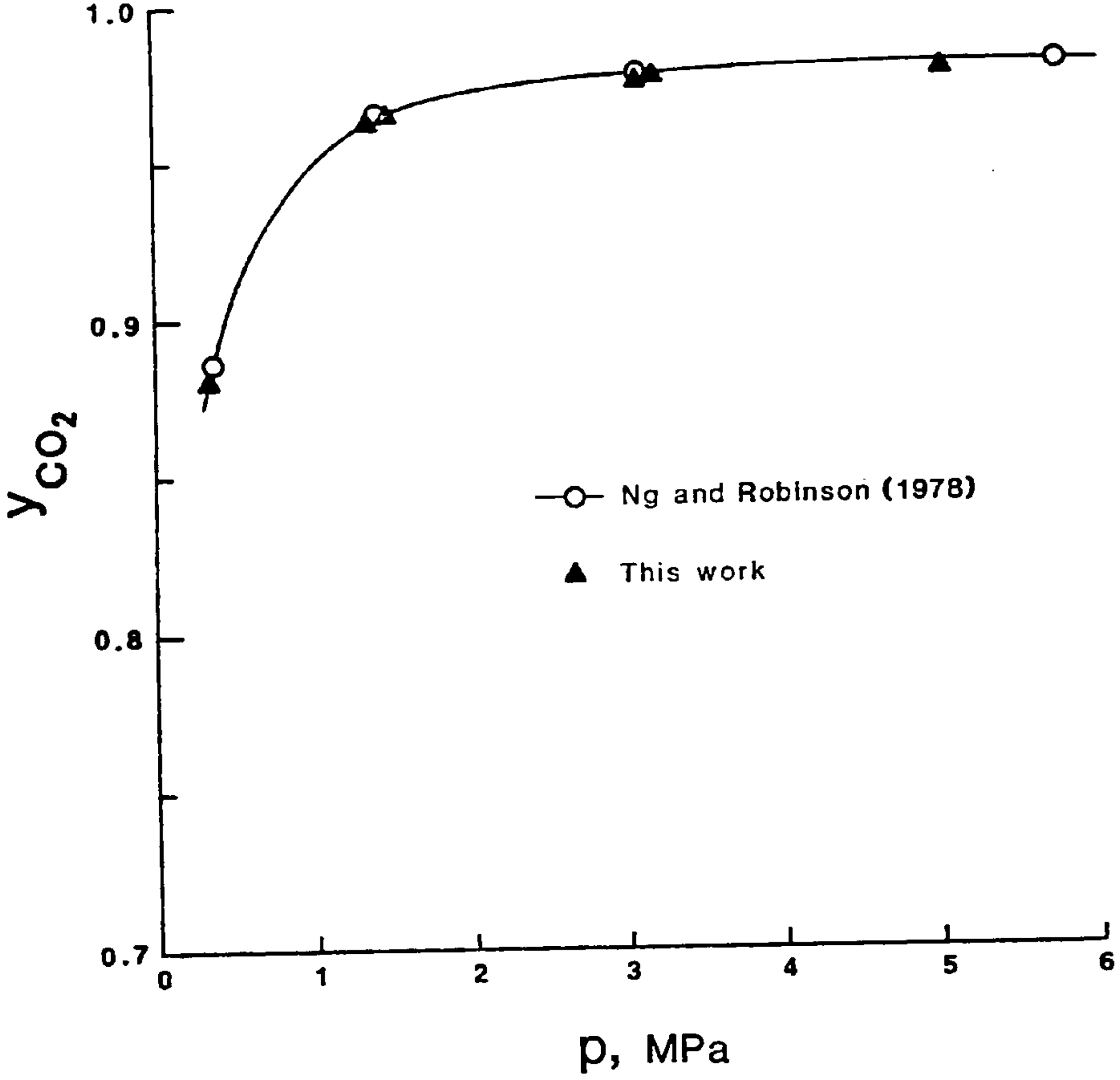


Figure 2. Mole fraction of CO_2 in saturated vapor in CO_2 + toluene mixtures at 353K

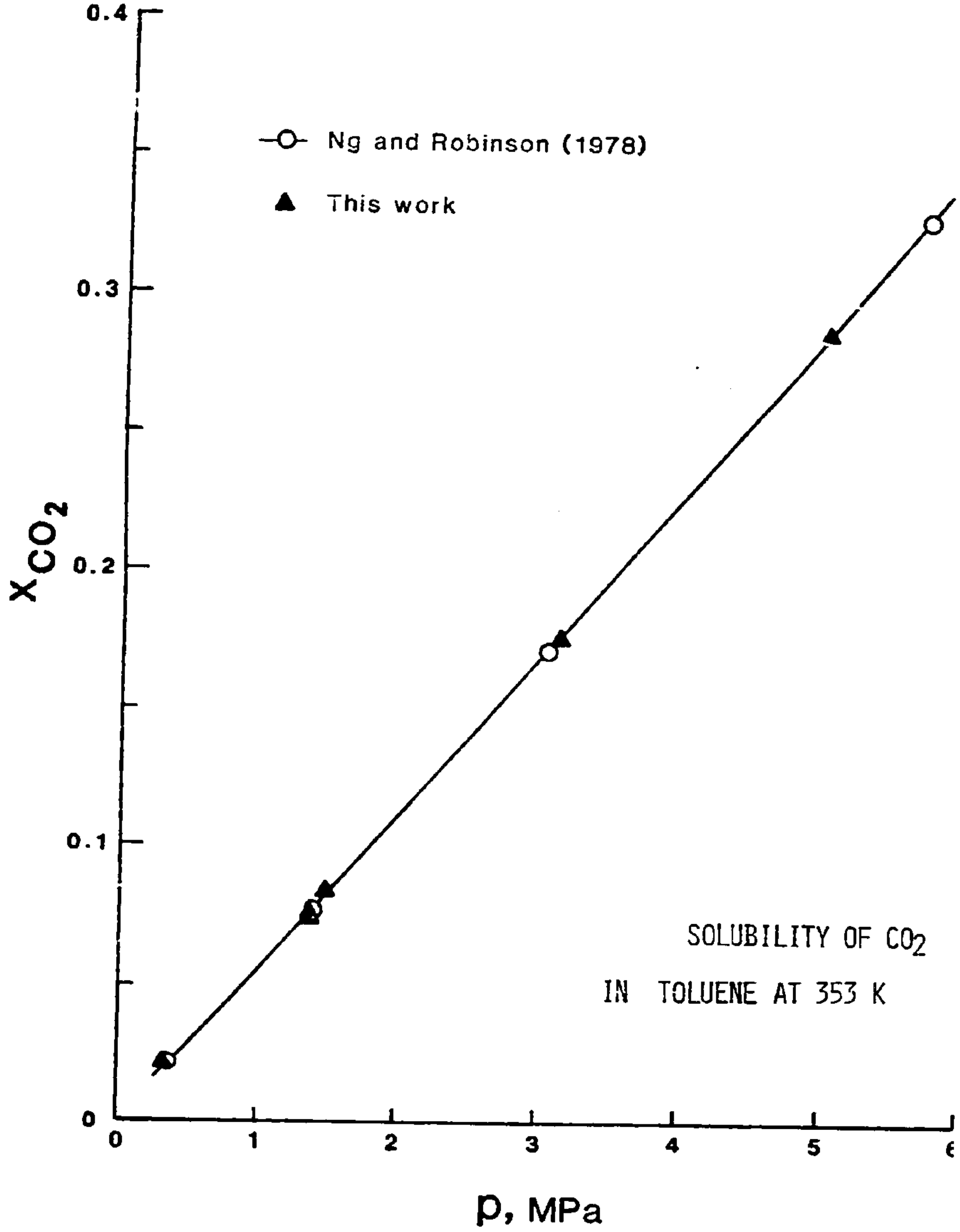
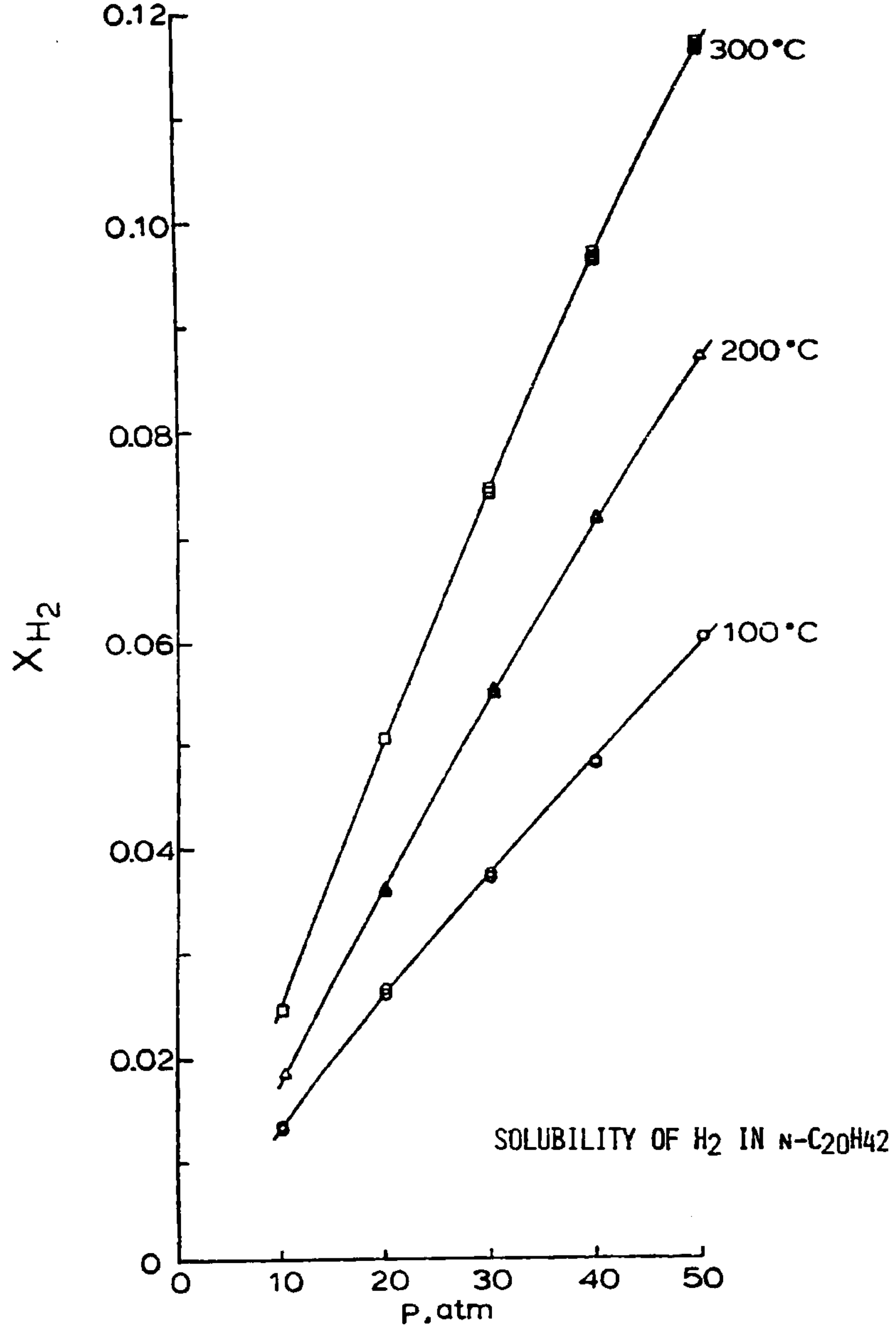


Figure 3. Solubility of CO_2 in toluene at 353K

Figure 4. Solubility of hydrogen in n-eicosane



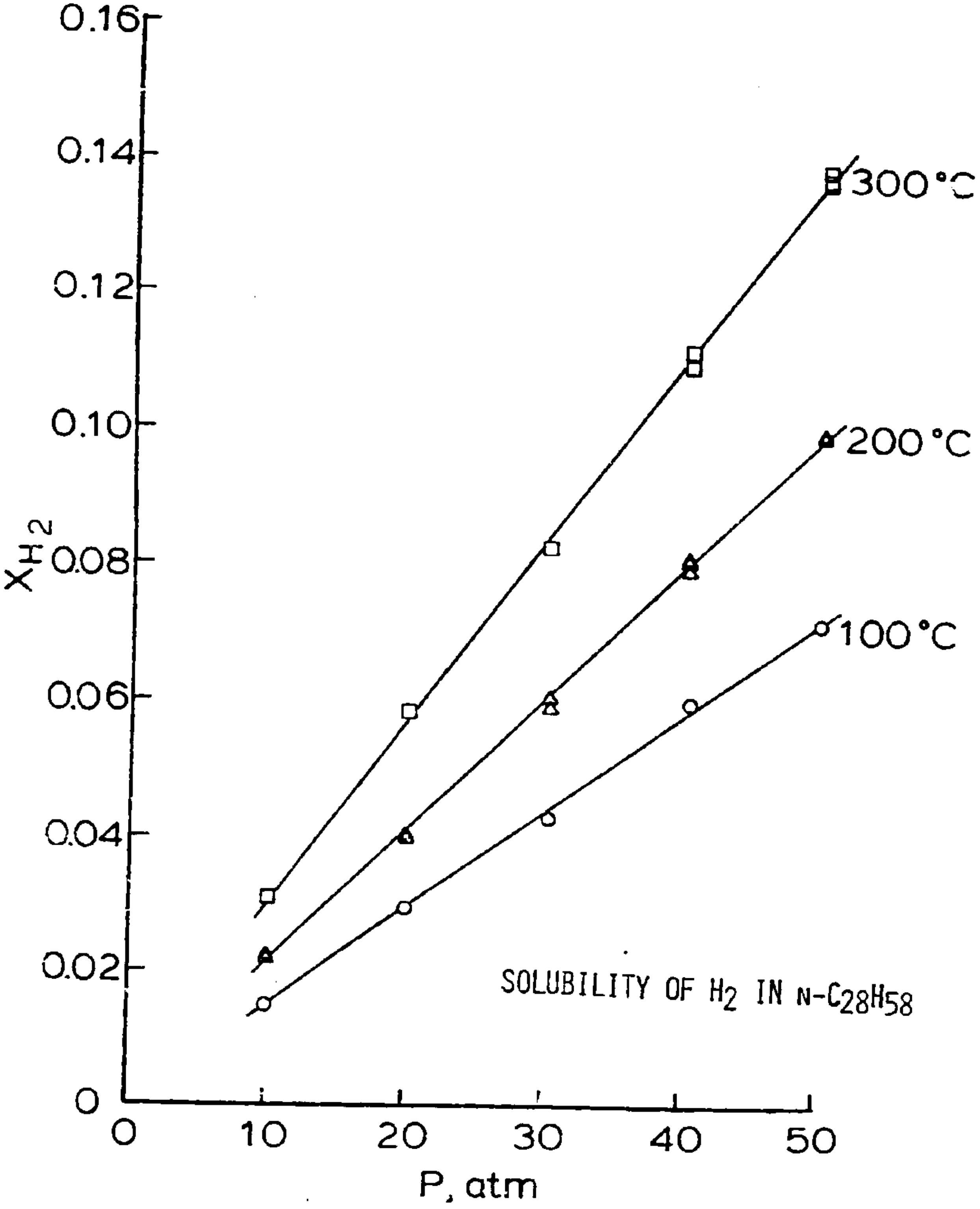


Figure 5. Solubility of hydrogen in n-octacosane

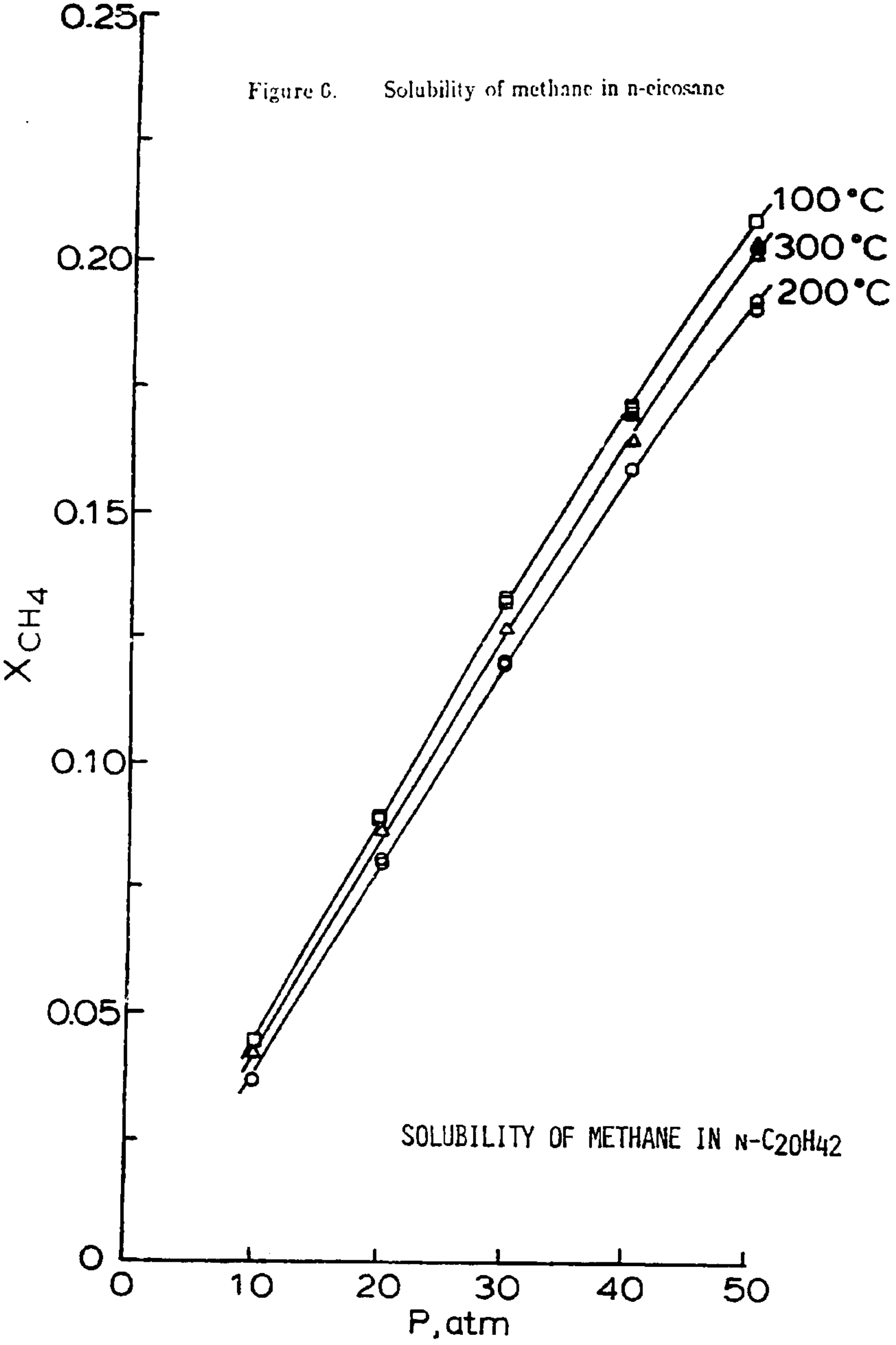


Figure 6. Solubility of methane in n-eicosane

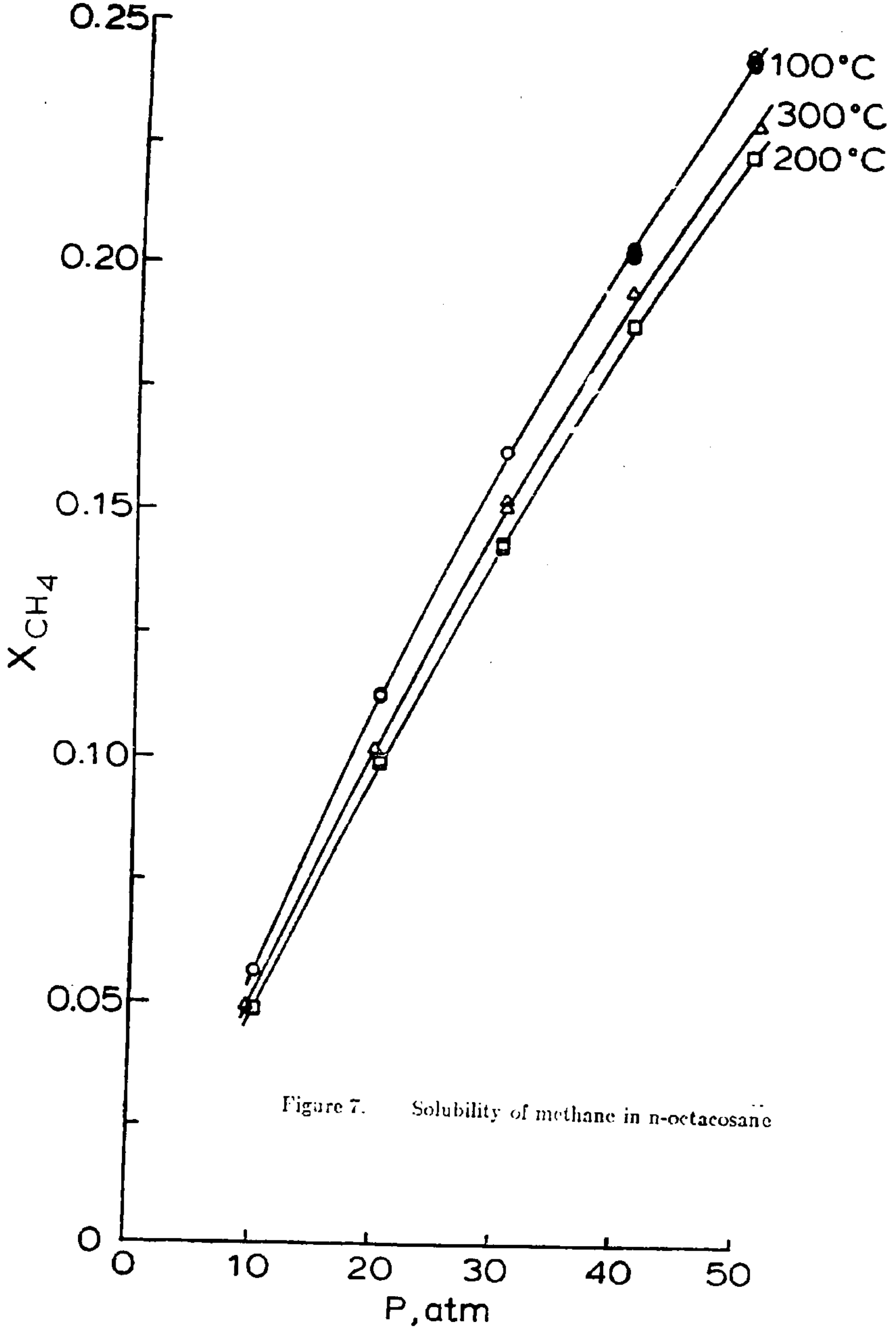


Figure 7. Solubility of methane in n-octacosane

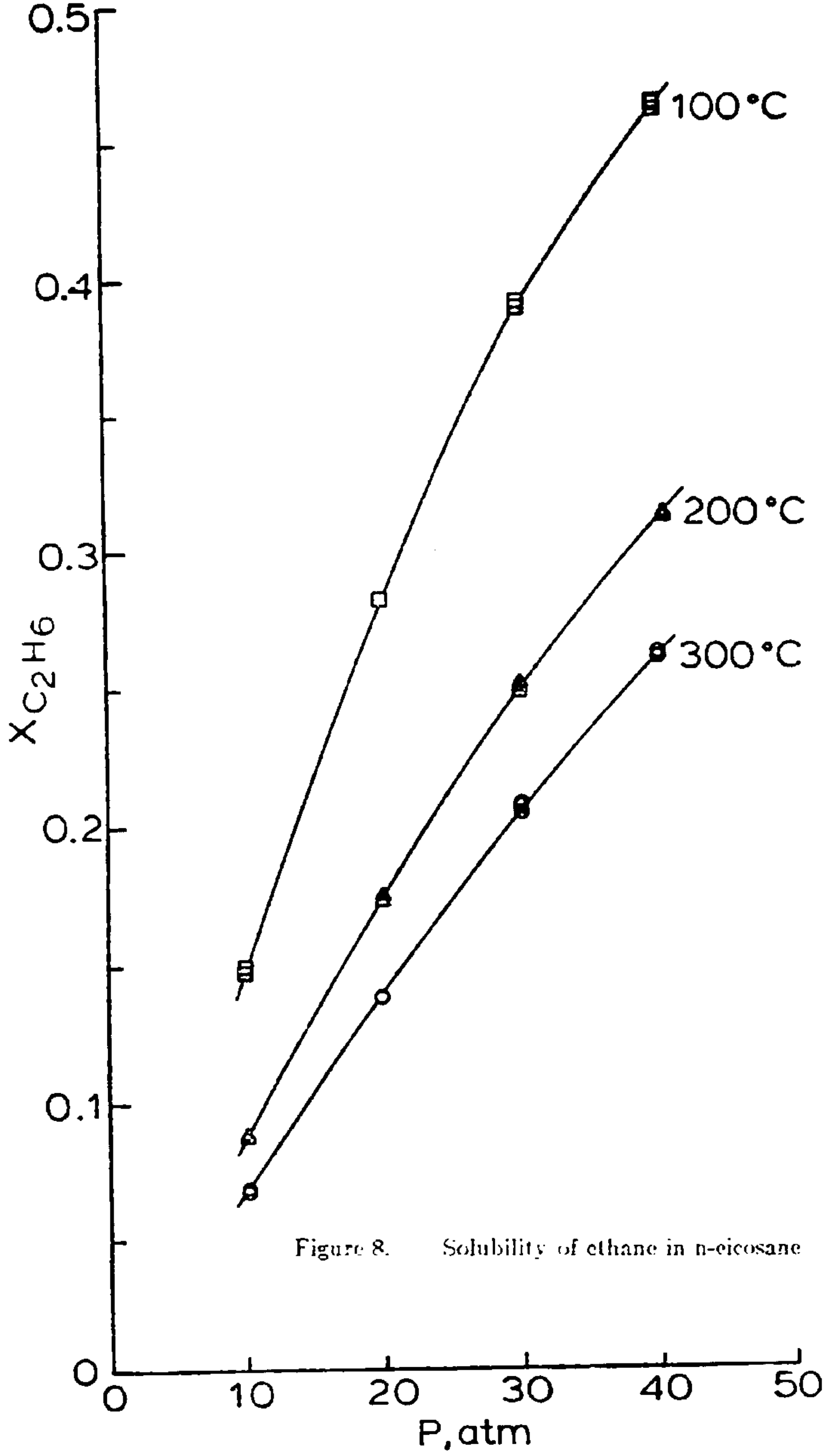


Figure 8. Solubility of ethane in n-eicosane

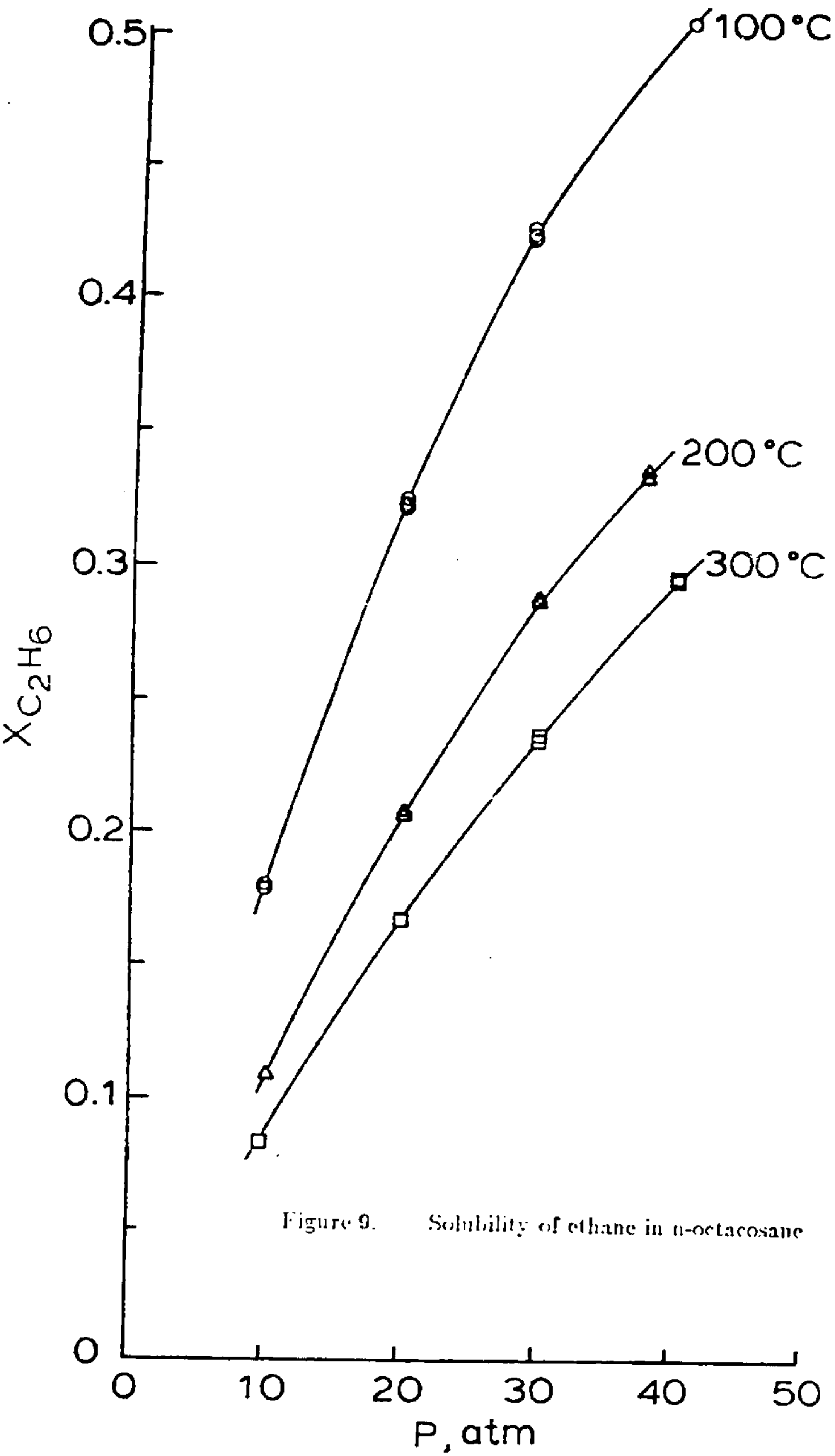


Figure 9. Solubility of ethane in n-octacosane

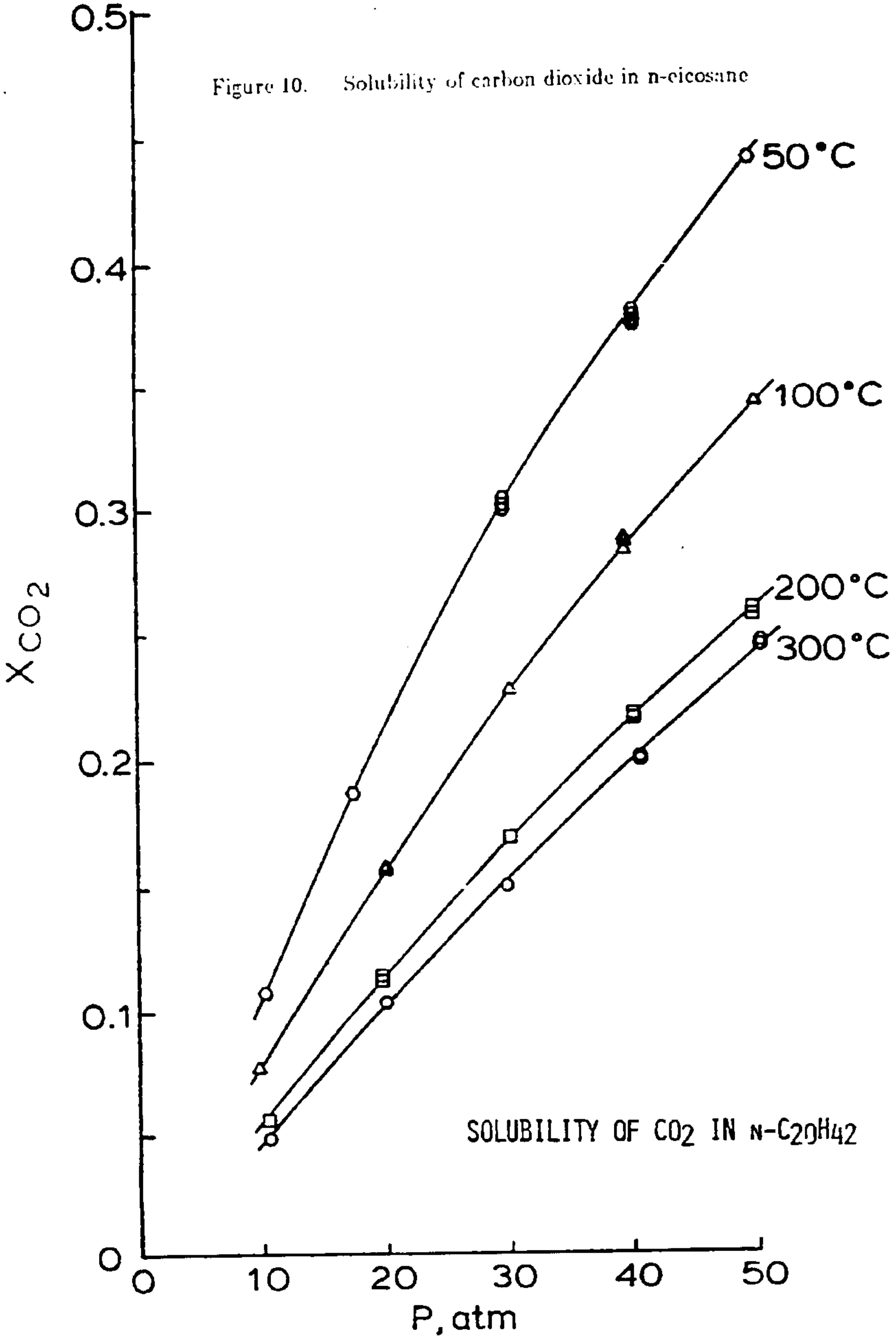
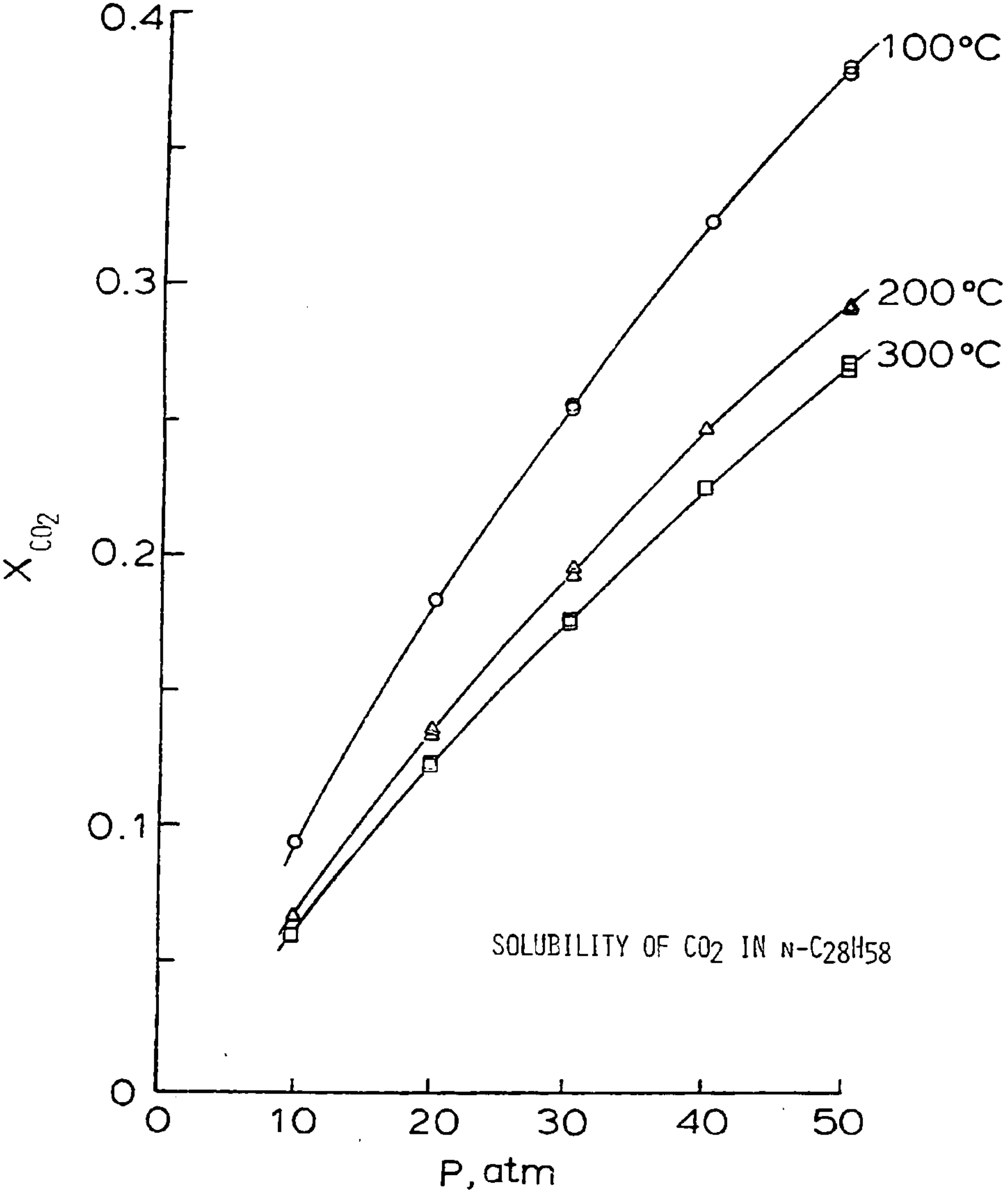


Figure 10. Solubility of carbon dioxide in n-eicosane

Figure 11. Solubility of carbon dioxide in n-octacosane



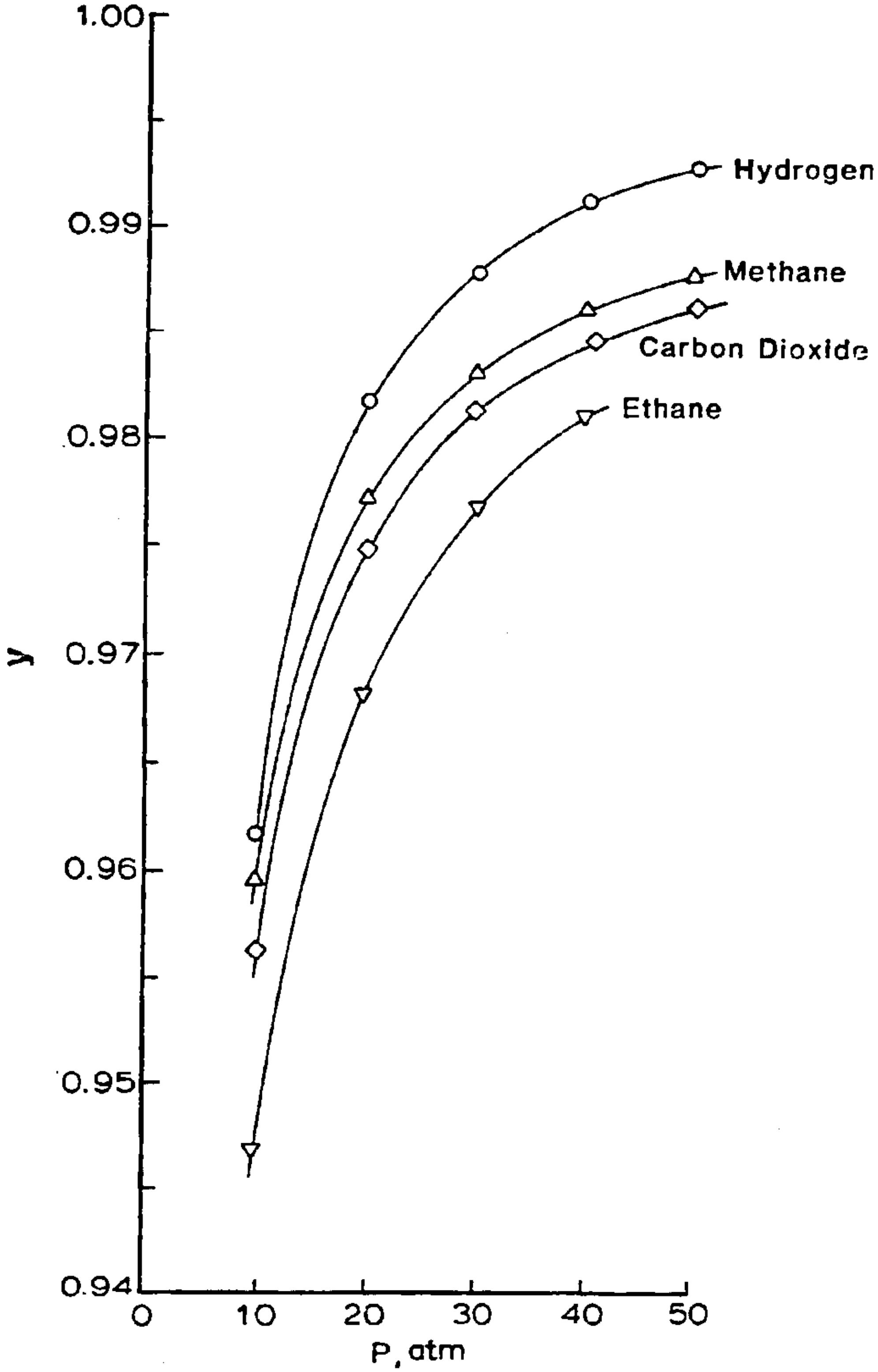


Figure 12. Vapor-phase compositions of gas in mixtures with n-eicosane at 300°C

of gas component in the mixture. x_2 is the mole fraction of gas in the liquid phase. P_1° denotes the vapor pressure of hydrocarbon solvent. $H_{2,1}^{P_1^\circ}$ is the Henry's constant for gas in the hydrocarbon solvent at P_1°, and $\bar{v}^\infty$ the partial molar volume at infinite dilution of the gaseous solute in the liquid phase. This equation has been found to represent well the solubilities of sparingly soluble gases up to very high pressures, if the temperature is well below the critical temperature of the solution.

Figure 13 illustrates the excellent representation of the experimental results from this work by the Krichevsky-Kasarnosky equation at 100°C. f_1 was calculated from the Lee-Kesler correlation (10) under the assumption that the vapor phase is pure solute. For hydrogen gas, the temperature range of this work is well beyond that of the Lee-Kesler correlation. We, thus, assumed $f_1 = P$. At 100°C, the vapor pressures of both $n-C_{20}$ and $n-C_{28}$ solvents are completely negligible in comparison to the total pressure.

Similar results are found for the other two temperatures, 200 and 300°C. We, therefore, conclude that the Krichevsky-Kasarnovsky equation is adequate to represent the solubility data at the experimental conditions of this work.

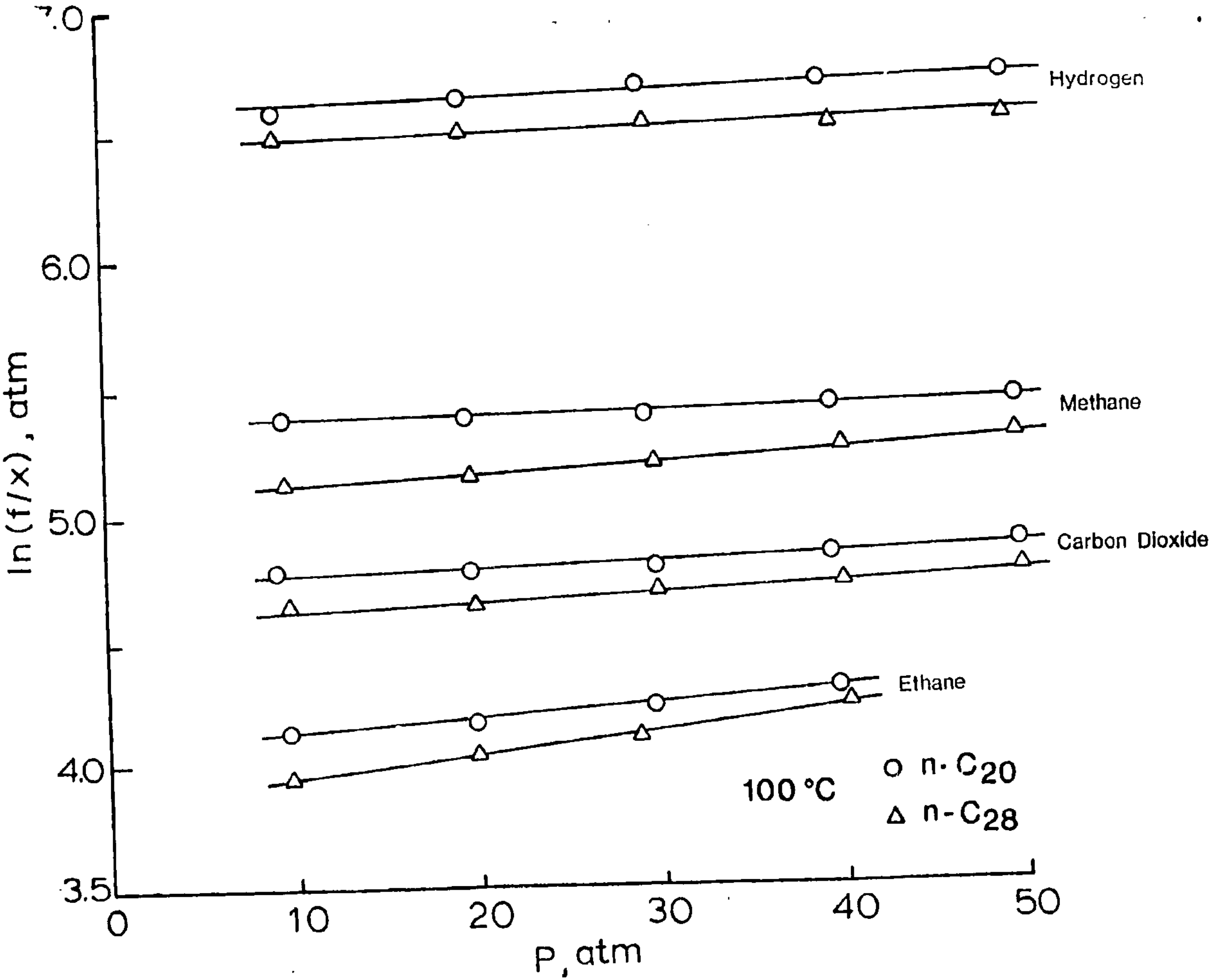


Figure 13. Correlation of data with the Krichevsky-Kasarnovsky equation

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