UNIVERSITY OF ILLINOIS

May 13 19 83

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Nancy Jane Marcus

ENTITLED Solubilities of Selected Compounds in Supercritical Fluids

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

Charles A. Eckert
Instructor in Charge

APPROVED: C. A. Eckert

HEAD OF DEPARTMENT OF Chemical Engineering

O-1364

SOLUBILITIES OF SELECTED COMPOUNDS IN SUPERCRITICAL FLUIDS

By

NANCY JANE MARCUS

Thesis
for the
DEGREE OF BACHELOR OF SCIENCE
IN
CHEMICAL ENGINEERING

College of Liberal Arts and Sciences
University of Illinois
Urbana, Illinois

1983

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

A supercritical fluid is any substance that exists above its critical temperature and critical pressure, where there is no phase boundary between the gas and liquid. Supercritical fluids exhibit solvent behavior more representative of a liquid than of a gas due to their liquid-like densities. Yet, the mass transfer chracteristics of supercritical fluids exceed that of liquids due to their gas-like viscosity and diffusivity between that of liquids and gases (1).

The phenomenon of enhanced solubility of compounds in supercritical fluids has been studied since 1879 (2), but recent industrial applications have led to increased interest in utilizing supercritical fluids as solvents in such diverse areas as chemical fuel fractionation and the food industry.

Supercritical pentane has been used to fractionate petroleum residuum (3) by dissolving the component asphaltene, resin and light oils to different degrees. The degree to which each solute dissolves is controlled by varying the system temperature and solvent density. Supercritical solvents have also been used to extract high-hydrocarbons and aromatics from coal (4). Both of these processes require less energy than standard liquid extraction processes at extreme temperatures.

Supercritical carbondioxide is now being used to selectively extract caffeine from green coffee beans (5). The liquid extraction of caffeine uses a toxic solvent which can leave a residue on the beans. Supercritical fluids can extract fats and oils from potato chips without removing the proteins or carbohydrates or damaging the chips (6).

COMPOUND SELECTION

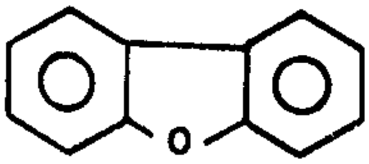
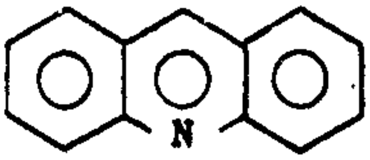
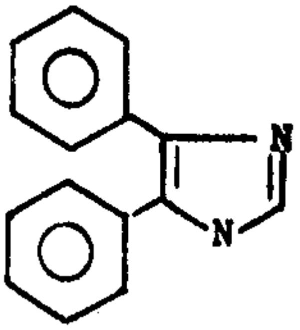
There are two basic criteria used for choosing a compound for study. The sample compound should be similar in structure to previously studied compounds so that existing theory can be used to describe its behavior. Previous supercritical studies have dealt with fused ring and substituted aromatic compounds such as naphthalene, phenanthrene, fluorene and pyrene (10). Also, the solid must have a melting point significantly above the critical point of the solvent. This criterion ensures that solid-solute and supercritical fluid interactions are occurring.

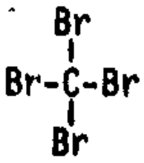
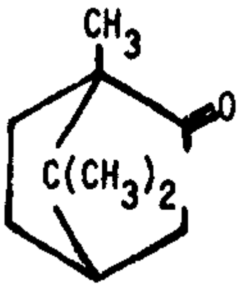
Two types of compounds were studied in non-polar gases. Acridine, dibenzofuran and 4,5-diphenylimidazole are polar solutes used to supplement other supercritical solubility work done by Hansen on these compounds (12). Hansen chose these compounds because they are representative of some of the functional groups found in coal. Since the optimum future use of coal is as an organic resource that can be converted to gaseous and liquid fuels and other chemicals, research is needed in the area of extracting and separating the various constituent compounds of coal. In order to best represent polar compounds, these solids have dipole moments close to or larger than 1 Debeye (see Table I).

Carbontetrabromide and camphor were chosen to utilize partial molar volume data on these solids, measured by Ziger (7). Ziger chose these solids because of their high volatility. Both vapor pressures are above 0.1 torr at room temperature (see Table I).

Carbondioxide was chosen as a solvent because it is plentiful, relatively cheap and is already well documented in supercritical studies. Ethylene has also been used extensively by other researchers.

TABLE I. SELECTED COMPOUNDS FOR SUPERCRITICAL SOLUBILITY STUDIES

Compound	Structure	Tmp (°C)	μ(D)
Dibenzofuran $C_{12}H_8O$		81-83	0.9
Acridine $C_{13}H_9N$		107	2.13
4,5-Diphenylimidazole $C_{15}H_{12}N_2$		232-233	4.34

Compound	Structure	Tmp (°C)	P_2^5 (25°C) torr
Carbontetrabromide	 $\mathrm{Br{-}\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}{-}Br}$	90-94	.713
Camphor		178	.259

THEORY

Although there are numerous industrial applications of supercritical extraction, the fundamental thermodynamic behavior of the supercritical phase is not well understood. The major goal of present supercritical fluid research is to develop an analytical semi-theoretical model to predict this behavior. Solubility measurements can then be used with various thermodynamic equilibria equations to obtain fundamental supercritical quantities.

An equation for the mole fraction of the solute in the fluid is obtained by equating the chemical potential for the two phases. The fugacity of the solid is:

$$f_2^S = f_2^{\circ S}\ (P^\circ)\ \exp \frac{V_2\ (P-P^\circ)}{RT} \qquad \text{Eq. 1}$$

The fluid phase can be described as either an "expanded" liquid or a nonideal gas. The fugacities are then:

$$f_2^L = X_2 f^\circ{}_2^L)P^\circ)\ {}_2(P^\circ{}_1 X_2)\ \exp {}_{P^\circ}^{P} \frac{\bar{v}_2(X_2,P)dP}{RT} \qquad \text{Eq. 2}$$

$$f_2^V = \phi_2 y_2 P \qquad \text{Eq. 3}$$

Most frequently, the gas approach is used. By equating Eq. 1 and Eq. 3, the mole fraction solute is:

$$y_2 = f^\circ{}_2^S\ \exp \frac{v_2\ (P-P^\circ)}{RT} / \phi_2 P \qquad \text{Eq. 4}$$

All parameters in this equation can be measured or easily evaluated with the exception of the fugacity coeffient, ϕ_2. ϕ_2 is a measure of the nonideality of the fluid phase and can be described with an equation of state;

$$\ln \phi_2 = \frac{1}{RT} {}_{P^{o}}^{P} [(\frac{\partial v}{\partial n_2})_{T_1P_1n_1} - \frac{RT}{P}]dP \qquad \text{Eq. 5}$$

where the derivative is the partial molar volume, $\bar{v}_2$. $\bar{v}_2$ is the most fundamental thermodynamic property characterizing the supercritical fluid, yet it is difficult to measure and cannot be obtained directly from y_2 vs. P data. This is because $\bar{v}_2$ is a complicated function of the isothermal compressibility. Ziger (7) has measured large negative values for $\bar{v}_2$ in the near critical region, some as large as -2×10^4 cc/mole.

The behavior of the vapor phase has been explained using a number of equations of state. Many of these use van der Waal (VDW) type models such as the Carnahan-Starling and Redlich-Kwong equations. The difficulty with using VDW theory lies in choosing the most physically meaningful method to obtain the adjustable VDW parameters.

The parameters used by Johnson and Eckert to model the fluid phase fit existing solid-fluid equilibrium data well (8,9,10). The advantage of both their Carnahan-Starling VDW and Augumented VDW models is that use of a corresponding states theory based on critical properties is avoided. Fluid-solute systems are highly asymmetric, with the large solute molecules and small solvent molecules having vastly different critical properties. Corresponding state approaches cannot describe the molecular interactions of such different molecules because, for instance, a small molecule will instantaneously interact with only part of a large molecule. So, a mixing rule which combines pure component critical properties of vastly different natures into a mixture critical property cannot be very accurate.

The solute properties used in the CS-VDW and AVDW models were the enthalpy of vaporization and the vapor pressure. CS-VDW predicts behavior in the relatively incompressible dense supercritical region, while the AVDW model is successful down to the critical density and converges with the CS-VDW model at higher densities (10). The difference between the two models is the attractive parameter. The CS-VDW model under-predicts the attractive forces in the mixture.

First estimates of relative degrees of solid solubilities in supercritical studies are given by the solute vapor pressures. At low pressures, the solubility decreases as temperature is raised because the solvent density decreases. At high pressures, the density is not as temperature dependent as at low pressures. In this region of liquid-like density, the solubility will increase with increasing temperature due mainly to the increase in solid vapor pressure (8). So, solubility is a strong function of density rather than pressure or temperature. Actually, the log of the solubility is linearly related to solvent density.

The most useful way to correlate the unique supercritical solubilities is to compare them to ideal solubilities. The enhancement factor is a dimensionless correction factor which can be applied to the ideal-gas expression of solute solubility as a measure of the extent that pressure enhances the solubility of the solid in the gas.

$$y_2 = \frac{P_2^5}{P} \cdot E \qquad \text{Eq. 6}$$

In supercritical fluids, E corresponds to non-idealities of 10^3-10^6 (8). The ideal gas solubility is simply the partial pressure of the solid at low pressure, ideal conditions.

Prausnitz (11) defines E as:

$$E = \frac{\phi_2^5(P_2^5)\ \exp\ {}_{ps}^{p}\ \frac{v_2^5 dP}{RT}}{\phi_2} \qquad \text{Eq. 7}$$

Note that the fugacity coefficient is needed to predict enhancement factors. Measurements of y_2 can be used to calculate enhancement with the equation:

$$E = \frac{y_2 P}{P_2^5} \qquad \text{Eq. 8}$$

APPARATUS

The original solubility apparatus was built and used by Johnson (10). The apparatus was then used and modified by Zieger (7) and Hansen (12). In this work, improvements to the system were made. A switching value assembly was added to the sample collection section for safety reasons since previously studied compounds were nonpolar and less toxic. The bath temperature range was increased using a glycol cooling system. There are four main sections of the apparatus (Figure 1): a pressurizing system, a pressure controlling system, a temperature controlled water bath containing the equilibrium cell (saturator) and the flow control and measurement system.

Pressurizing System

Using an air driven gas compressor (Haskell Model # AG-I52), the solvent gas is taken from a high pressure reservoir. This reservoir is heat treated stainless steel with all female fittings for 1/4" tubing. The approximate reservoir pressure is measured with a bourdon tube gauge.

Pressure Control

Pressure control within the system is maintained with a hand-controlled Tescom (series 26-1000) pressure regulator. This regulator is rated for a maximum pressure of 10,000 psi. Since changes in flowrate or inlet pressure can cause the regulator outlet pressure to vary, the regulator must be adjusted accordingly during an experimental run. Two Heise bourdon-tube gauges, ranges 0-2000 psi and 0-15,000 psi, indicate regulator outlet pressure. Pressure readings are accurate to ± 2 psi in the lower range and ± 5 psi in the upper range.

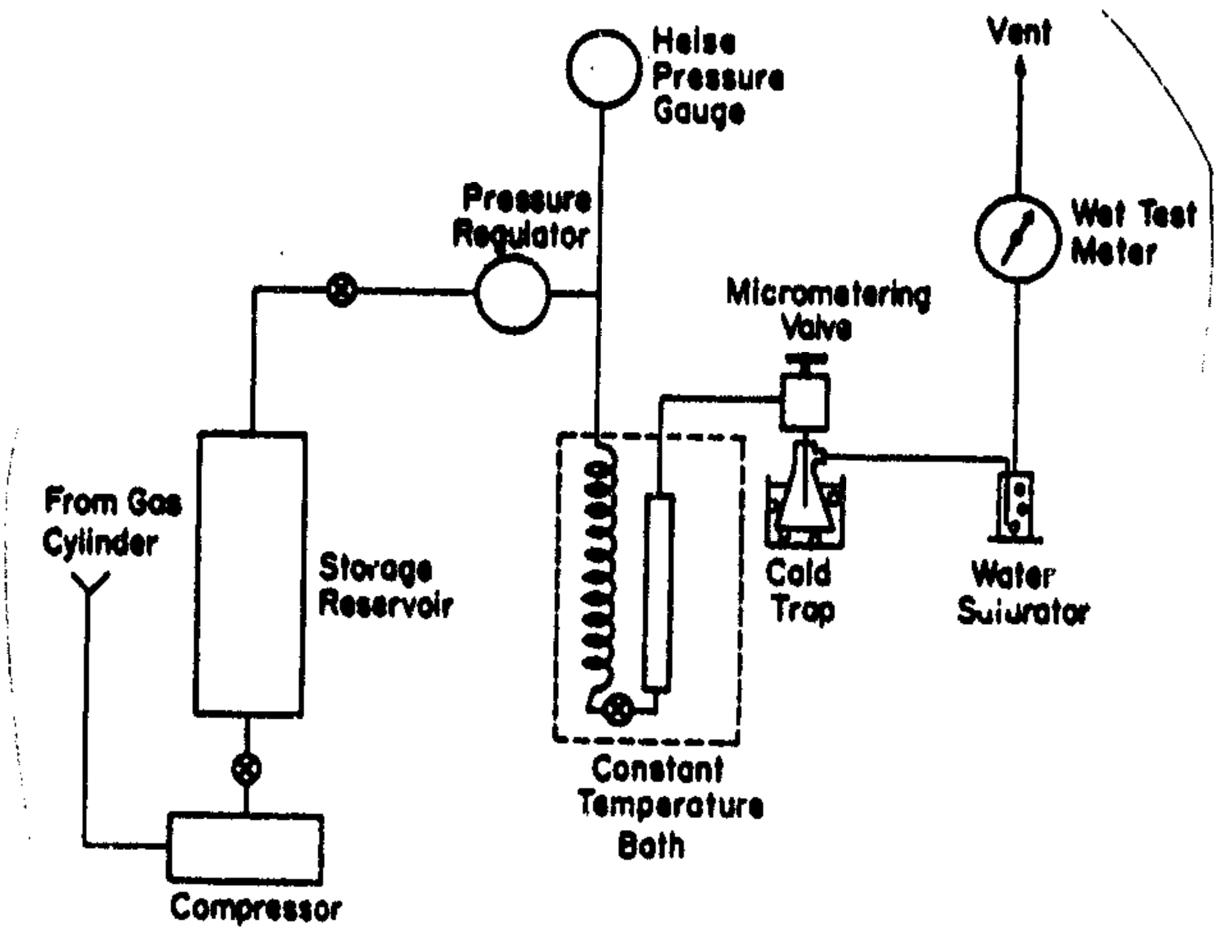


Figure 1. Schematic of flow equilibrium apparatus.

Temperature Control

Temperature control is achieved using a Hallikairen Thermotrol (Model # 1053) in an insulated stirred water bath. This heat is balanced in two ways. For moderate to high bath temperatures, water at about 15°C is circulated through the bath in copper coils. For bath temperatures below ambient temperature, ethylene glycol is cooled to below 0°C in a refrigeration unit and pumped through a second set of copper coils. For the highest bath temperatures, two auxiliary heaters are used. Their output is controlled by two variable voltage transformers. The bath temperature is easily maintained from 12°C to 70°C and is accurate to ± 0.1°C. Bath temperature is read with a calibrated mercury thermometer to ± .05 C.

Flow Control and Measurement

The micrometering valve (Autoclave Engineering Model HT-A10960) situated between the saturator and the sample collection section reduces the high system pressure to atmospheric pressure. Within the valve, the pressure drop occurs between a shallow tempered stem and a seat with a .062" orifice. Flow control is achieved by varying the open area between the stem and seat. A uniquely machined stainless steel adapter, length 2 3/4", connects the micrometering valve to the high temperature switching valve. The switching valve has two outlets, accepting a sample trap and a waste trap, simultaneously.

To obtain smooth flow rates, solute precipitation must be prevented between the saturator and cold traps. Clogging due to precipitation is minimized by heating the micrometering value, connector, and switching valve. To melt clogged solute, 85 watt cartridge heaters are installed in 3/8" holes drilled in the valve housings. An aluminum block around the connector also holds a heater. All heaters are controlled with variable voltage transformers.

The collection traps are constructed from 6" side-arm test-tubes. A thin walled copper tube enters the trap through a drilled Teflon stopper. Above the stopper a 90° bend leads to a coned brass end which is secured to the switching valve with a high pressure fitting. The trap is plugged with steel wool to prevent entrained solute from escaping. Stainless steel wool or glass wool was used for the carbontetrabromide runs. The traps are immersed in an ice-water bath to enhance precipitation. This bath is constructed of clear plexiglass for visual checks of the amount of solute collected. An acetone-dry ice bath within the ice-water bath was used for the more volatile compounds: carbontetrabromide and camphor.

Gas flow is monitored with two gas-washers and measured with a wet test meter (Precision Scientific) in series with a soap bubble meter. The gas washers provide a quick check of gross gas flow rate and of which trap is collecting solute. The bubble meter can measure instantaneous flow rates while the wet-test meter measures the total solvent volume.

PROCEDURE

Solubility measurements were performed using a modified procedure of the one developed by Johnston (10).

The apparatus is prepared for an experimental run by firmly packing the saturator with 5 to 10 grams of finely ground solute. Each end of the saturator is plugged with a small bead of steel wool to prevent bulk movement of the solute from flow pressure. The saturator is connected to the tubing and left in the bath for at least three hours prior to a run to ensure the solute is at the bath temperature. The saturator is repacked when about 60% of the solute has been collected. The valves and connector are heated to 75°C above the melting point of the solute. The feed gas is compressed to about 1000 psi above the experimental pressure.

From .1 to .2 ft^3 of gas is passed through the saturator and into the waste trap to ensure equilibrium conditions. When equilibrium is attained, the flow is switched to the sample trap and a run is begun. Previously, traps were connected directly to the single outlet micrometering valve. When the sample trap was substituted for the waste trap, either flow was reduced and equilibrium lost or dangerous nitrogen, oxygen, and sulfer substituted aromatic compounds entered the room in vapor form. The switching valve eliminates these problems.

At the start of a run, the flow meter reading is recorded. Flowrates, bath temperature and system pressure are checked every few minutes during a run. Gas flowrate is typically held between 10 and 30 seconds per .01 ft^3 gas. This flowrate can vary 20% without affecting results (10). The more soluble compounds are run at the slower flowrates for easier collection. When an estimated sample weight of at least .1 gram has been collected, the flow is switched back to the waste trap and the final flow meter reading is recorded. The time required for a sample run depends on the solute solubility. Under the most insoluble conditions, such as acridine in ethylene at low pressures and temperatures, runs can take two hours. For very soluble conditions such as dibenzofuran at high temperatures, runs can take less than two minutes.

Collected solute weights were determined by weighing the traps before and after each run. An analytical balance was used to measure weight to ten thousands of a gram, accurate to ± .0004 g. The traps were re-used for runs of the same solute. Sample traps were gassed with nitrogen before each time they were weighed. This procedure eliminated weighing errors due to differences between the solvent densities and air density. An exception to this procedure was used with carbontetrabromide due to its high volatility. Traps used for this solid were pregassed with carbondioxide for initial weighings of runs with fluid carbon dioxide and were not gassed before final weighings. When carbontetrabromide was run in supercritical ethylene, the traps were not gassed with nitrogen before either weighing. Also, traps used for this solid were never reused.

CHEMICALS

The gases used were supplied by Linde Specialty Gases and Air Products. The ethylene was 99.8% pure and the carbondioxide was 99.99% pure. Dibenzofuran 98% min purity and acridine 97% purity were supplied by Aldrich. The acridine was further purified to 98% min purity by a hot ethanol, water recrystallization. Carbontetrabromide at 98% min purity was supplied by Alpha Products.

EXPERIMENTAL

Solubility _versus_ pressure data were measured for dibenzofuran, acridine, and carbontetrabromide in ethylene and for carbontetrabromide in carbondioxide. For each experimental run, the system temperature and pressure, total volume of gas that flowed through the collection trap, and the weight of the solid collected were measured. Gas density was calculated from measurements of the wet-test meter temperature and pressure and atmospheric pressure using the ideal gas law with a residual temperature function (see Appendix III). The data is presented as mole fraction solute _versus_ pressure and _versus_ supercritical fluid density for each isotherm (see Tables II, II, IV and V).

Because the system is dilute, the fluid density is approximated by the pure solvent density at system conditions. Pure solvent densities are obtained from IUPAC monographs for carbondioxide (13) and ethylene (14). Above the critical point these densities are accurate to ± 0.2%, but close to the critical point accuracy is probably not as good, since the fluids are highly compressible.

The mole fraction _versus_ pressure for these four systems are plotted in Figures 2, 3, 4 and 5.

At low pressures, the carbontetrabromide is more than twice as soluble as dibenzofuran in ethylene. But, at higher pressures, the carbontetrabromide is only about 1.3 times more soluble as the dibenzofuran. Carbontetrabromide is about 30 times as soluble as acridine in ethylene. Carbontetrabromide is three times more soluble in ethylene than in carbondioxide. The 35°C isotherm of carbontetrabromide in carbondioxide shows some leveling off of solubility

TABLE II. SOLUBILITY DATA FOR DIBENZOFURAN AND ETHYLENE SYSTEM

	Pressure (10^5Pa)	10^2y	Estimated Density (g/cc)	Run #
T = 50°C	483.6	4.79300	.486016	697
	483.6	4.28464	.486016	698
	414.6	4.40294	.475461	694
	414.6	3.61056	.475465	695
	345.7	2.83255	.463260	687
	345.7	3.00449	.463260	689
	311.2	2.51380	.456280	490
	276.8	2.08689	.448339	665
	276.8	2.19914	.448335	693
	242.3	1.56995	.439660	683
	207.8	1.38424	.429569	662
	207.8	1.11209	.429569	664
	173.3	0.86502	.417065	684
	138.9	0.40686	.401658	656
	138.9	0.63849	.401658	657
	138.9	0.40444	.401658	658
	104.4	0.17589	.381605	685
	69.9	0.01345	.345828	660
	69.9	0.01173	.345828	661
T = 35°C	483.6	1.35709	.486017	721
	483.6	1.44202	.486017	723
	414.7	1.09234	.475462	718
	414.7	1.49843	.475462	719
	414.7	1.10534	.475462	720
	380.2	1.34305	.469556	733
	380.2	1.24221	.469556	737
	380.2	1.1447	.469556	739
	345.7	1.27455	.463262	713
	311.2	1.08707	.456208	725
	276.8	1.37442	.448337	709

TABLE II. Continued.......

276.8	1.26774	.448337	710
276.8	0.93018	.448337	711
242.3	0.97589	.439660	726
207.8	0.77490	.429566	707
207.8	0.83360	.429566	708
173.3	0.56050	.417066	727
138.9	0.41827	.401652	703
138.9	0.29901	.401652	704
138.9	0.22415	.401652	705
104.4	0.21565	.381606	728
69.9	0.01383	.345813	702

TABLE III. SOLUBILITY DATA FOR ACRIDINE AND ETHYLENE SYSTEM

	Pressure (10^5Pa)	10^2y	Estimated Density (g/cc)	Run #
T = 35°C	483.6	.10631	.4599	645
	483.6	.10690	.4599	646
	483.6	.07733	.4599	647
	483.6	.10445	.4599	648
	414.7	.07157	.4472	641
	414.7	.09055	.4472	642
	414.7	.15880	.4472	644
	380.2	0.7921	.4400	649
	345.7	.07149	.4322	621
	345.7	.08133	.4322	639
	345.7	.08362	.4322	640
	311.2	.06143	.4232	650
	276.8	.07607	.4129	630
	276.8	.04635	.4129	631
	276.8	.07035	.4129	632
	276.8	.09919	.4129	633
	276.8	.07044	.4129	638
	242.3	.05286	.4012	651
	207.8	.06774	.3870	623
	207.8	.04973	.3870	624
	207.8	.08210	.3870	627
	207.8	.06855	.3870	628
	207.8	.07427	.3870	635
	173.3	.02814	.3674	652
	138.9	.02454	.3387	620
	138.9	.03928	.3387	634
	138.9	.04975	.3387	637
	104.4	.02367	.2938	653
	69.9	.00178	.1534	618
	69.9	.00064	.1534	626

TABLE IV. SOLUBILITY DATA FOR CARBONTETRABROMIDE IN ETHYLENE SYSTEM

	Pressure (10^5Pa)	10^2y	Estimated Density (g/cc)	Run #
T = 12°C	414.7	7.00837	.4732	854
	414.7	6.82747	.4732	855
	345.7	6.52929	.4608	851
	345.7	6.50780	.4608	852
	345.7	6.48550	.4608	853
	311.2	5.83597	.4536	857
	276.8	5.35662	.4455	848
	276.8	4.74906	.4455	849
	276.8	4.70200	.4455	850
	276.8	5.54576	.4455	858
	207.8	4.17318	.4263	845
	207.8	4.14173	.4263	846
	207.8	4.10382	.4263	847
	173.3	3.41949	.4133	860
	138.9	3.29788	.3972	842
	138.9	3.32235	.3972	843
	104.4	.70991	.3759	861
	69.9	1.13699	.3351	841
T = 25°C	69.9	.91586	.2258	809
	69.9	.92292	.2258	818
	59.6	.09814	.338	815
	59.6	.09044	.1338	816
	59.6	.10101	.1338	817
	53.4	.07238	.1030	810
	53.4	.06594	.1030	811
	53.4	.06658	.1030	812

TABLE V. SOLUBILITY DATA FOR CARBONTETRABROMIDE IN CARBONDIOXIDE

	Pressure (10^5Pa)	10^2y	Estimated Density (g/cc)	Run #
T = 35°C	207.8	2.08161	.8717	797
	207.8	1.88322	.8717	798
	207.8	2.16374	.8717	799
	138.9	1.52613	.7912	800
	138.9	1.73613	.7912	801
	118.2	1.69219	.7469	807
	107.9	1.34068	.7247	802
	107.9	1.52026	.7247	806
	97.5	1.35122	.6957	803
	97.5	1.57066	.6957	804
	87.2	1.03320	.5989	805

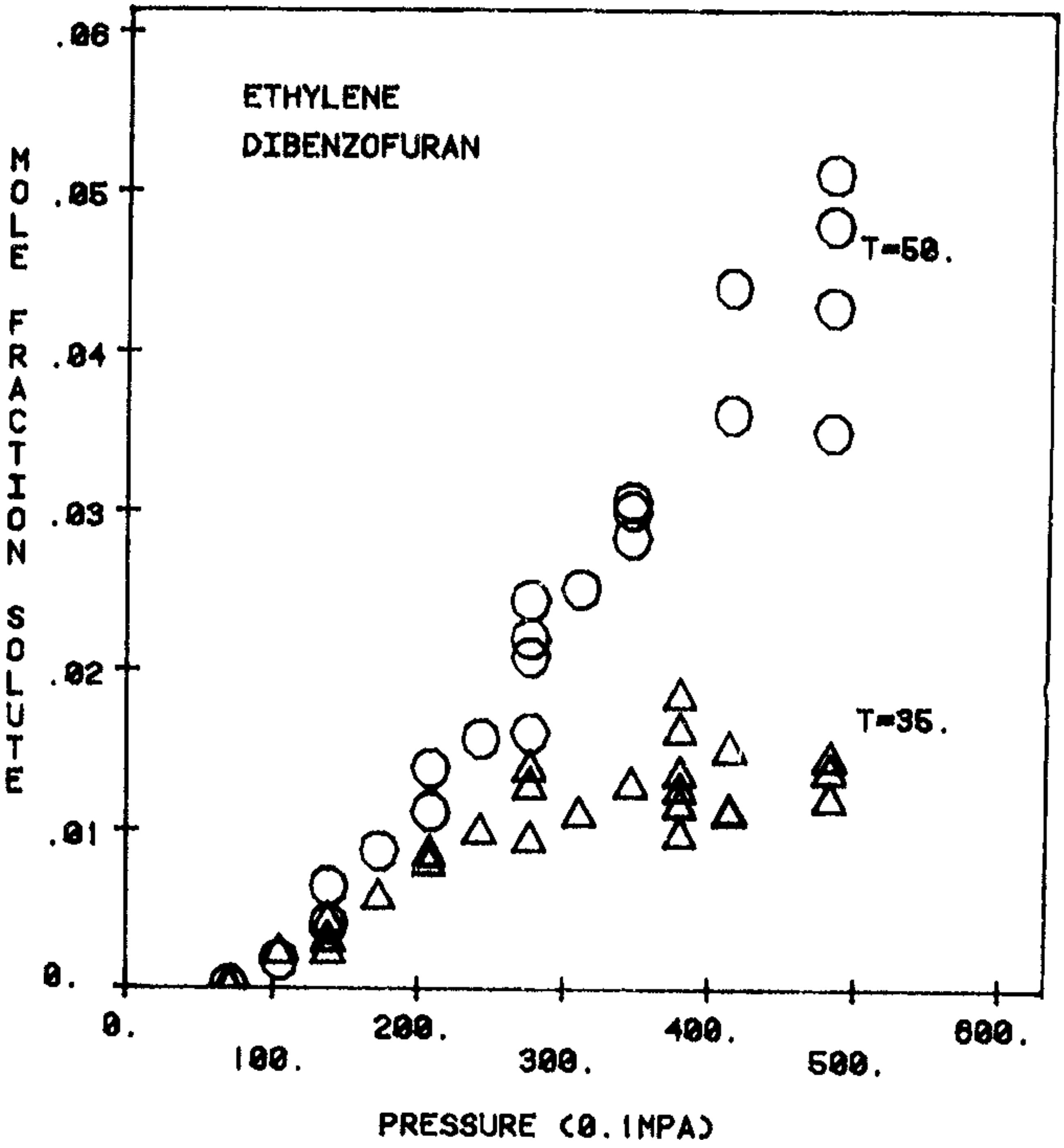


Figure 2. Solubility *versus* pressure isotherms for dibenzofuran in ethylene.

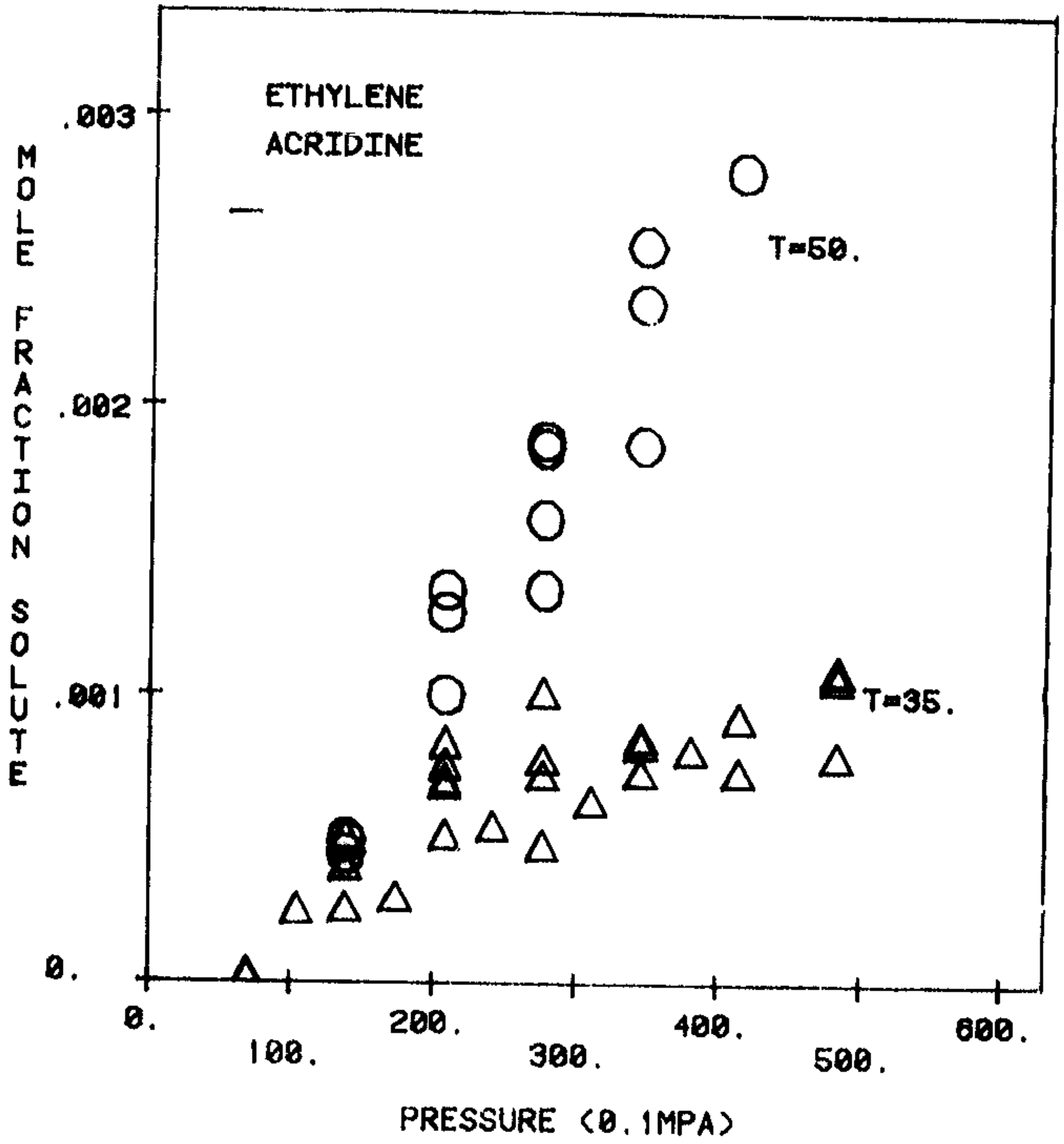


Figure 3. Solubility *versus* pressure isotherms for acridine in ethylene.

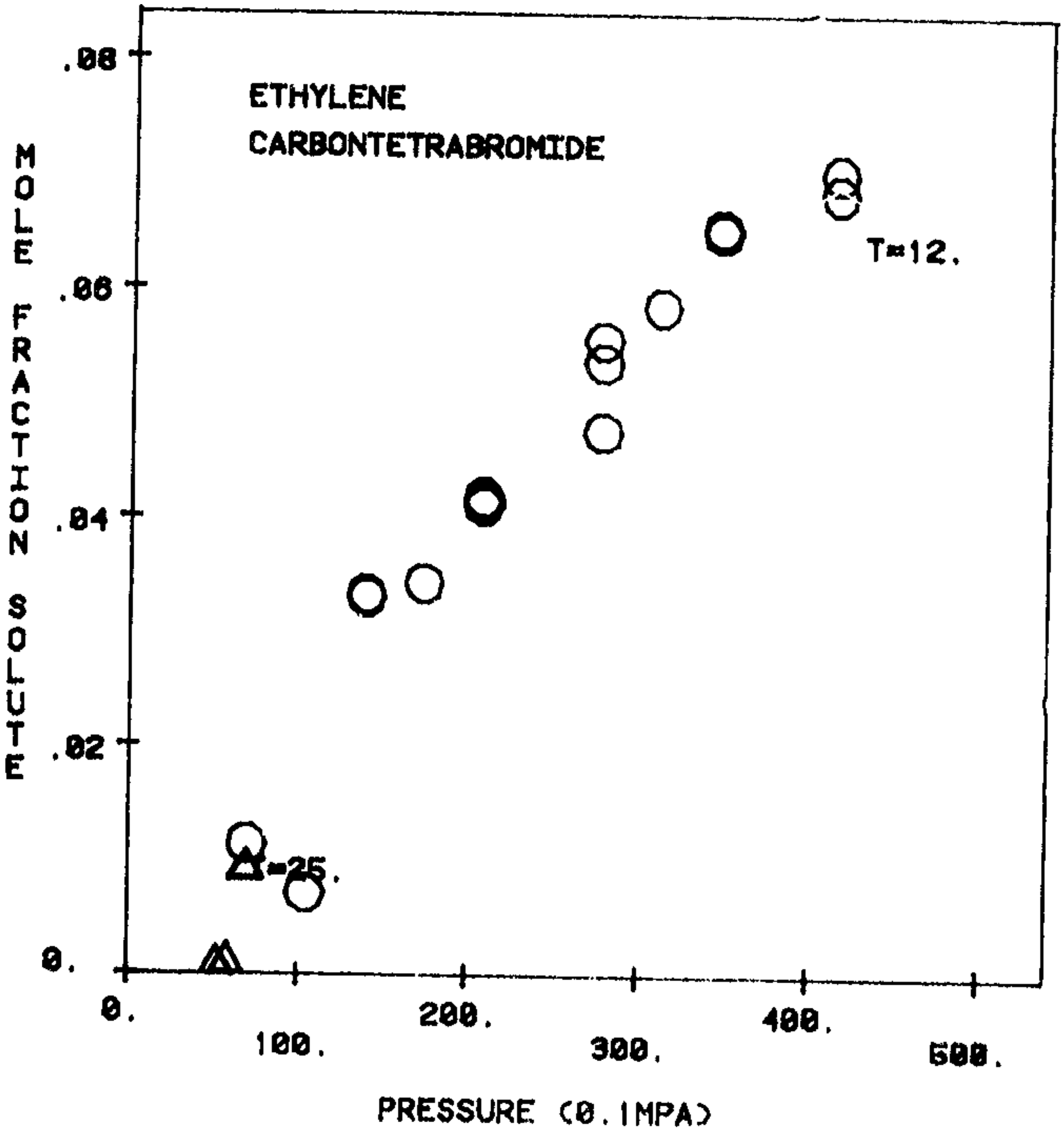


Figure 4. Solubility *versus* pressure isotherms for carbontetrabromide in ethylene.

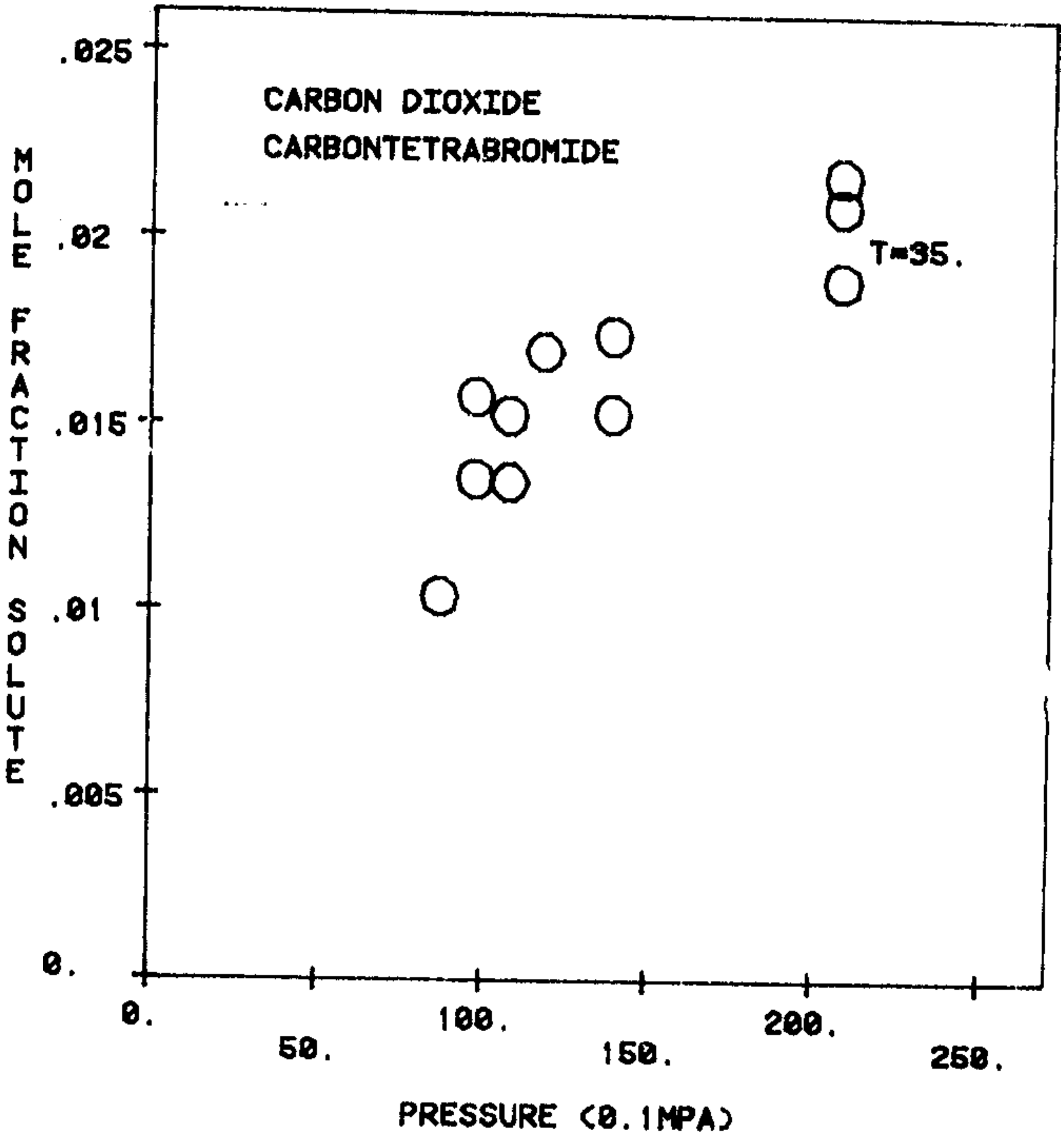


Figure 5. Solubility *versus* pressure isotherms for carbontetrabromide in carbondioxide.

above 100 (.1 MPa) while the 12^{o}C isotherm in ethylene does not. For both dibenzofuran and acridine, the 35^{o}C isotherm exhibits leveling off while the 50^{o}C isotherm does not.

Since the mole fraction is a stronger function of density than of pressure, plots of mole fraction versus density represent the data better (see Figures 6, 7, 8 and 9). The log mole fraction versus density plots show that this relationship is relatively linear (see Figures 10, 11, 12 and 13).

As discussed earlier, the non-idealities of the solid-fluid system are included in the enhancement factor. To calculate enhancement factors, the vapor pressures of the solutes are required. Vapor pressure valves for acridine are tabulated from 8^{o}C to 50^{o}C (15). Dibenzofuran vapor pressures were extrapolated from vapor pressures of the liquid (12,16). Carbontetrabromide vapor pressures were calculated using the Antoine equation and constants from literature (17).

The log enhancement factor versus density is linear for every system (see Figures 14, 15, 16 and 17).

The uncertainty in the solubility data corresponds directly to the uncertainty in the collected solute weights. This uncertainty was estimated by Johnston (10) to be about 2-5%. Uncertainties in temperature, pressure, and gas flow are negligible except very near the solvent critical point. Near the critical point small deviations in pressure can cause 2% uncertainty in solubility. The relative error for the solubility data is calculated using the sums of squares methods (12).

Measurement of anthracene solubility in ethylene at 70^{o}C agreed well with data reported by Johnston (10) (see Appendix I).

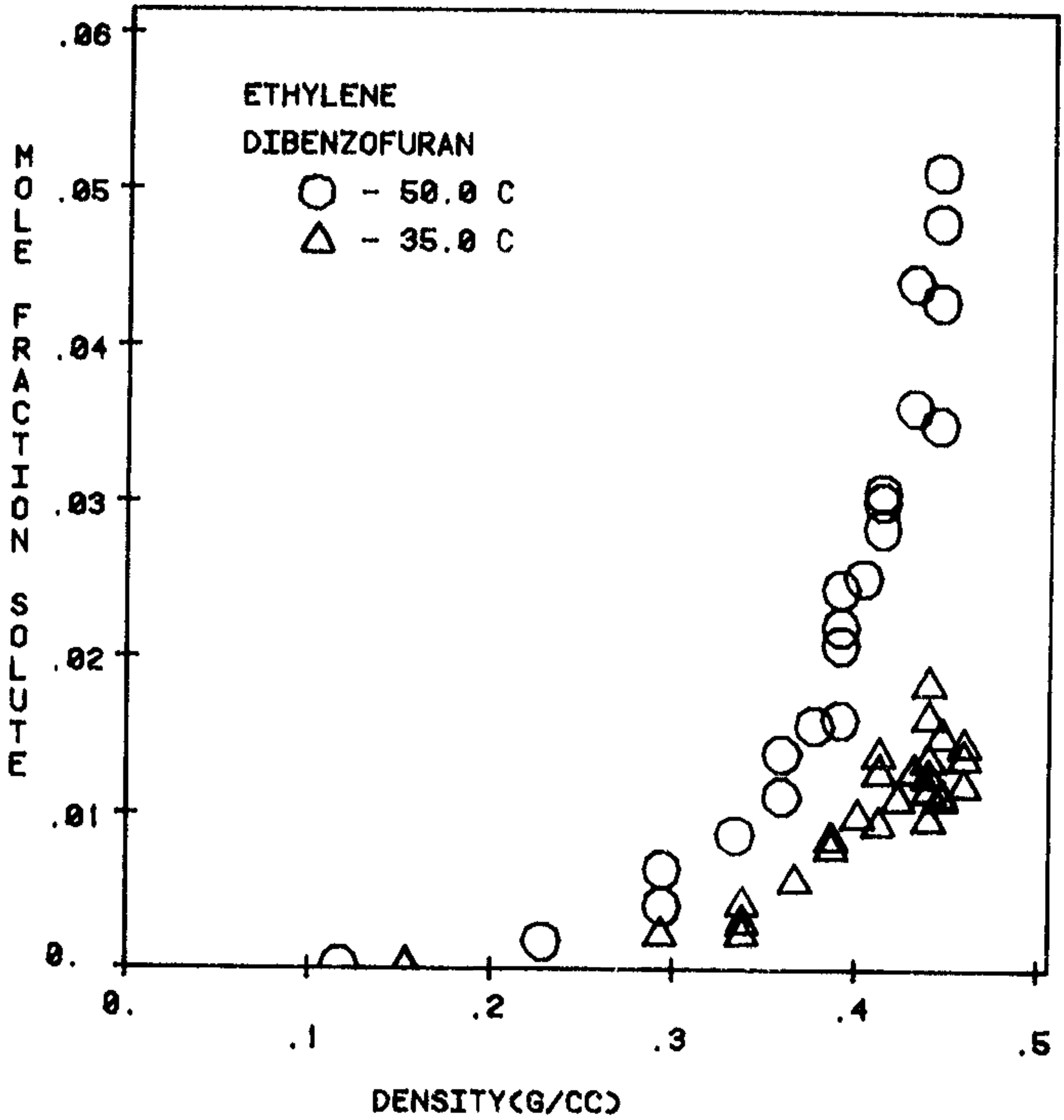


Figure 6. Solubility *versus* density isotherms for dibenzofuran in ethylene.

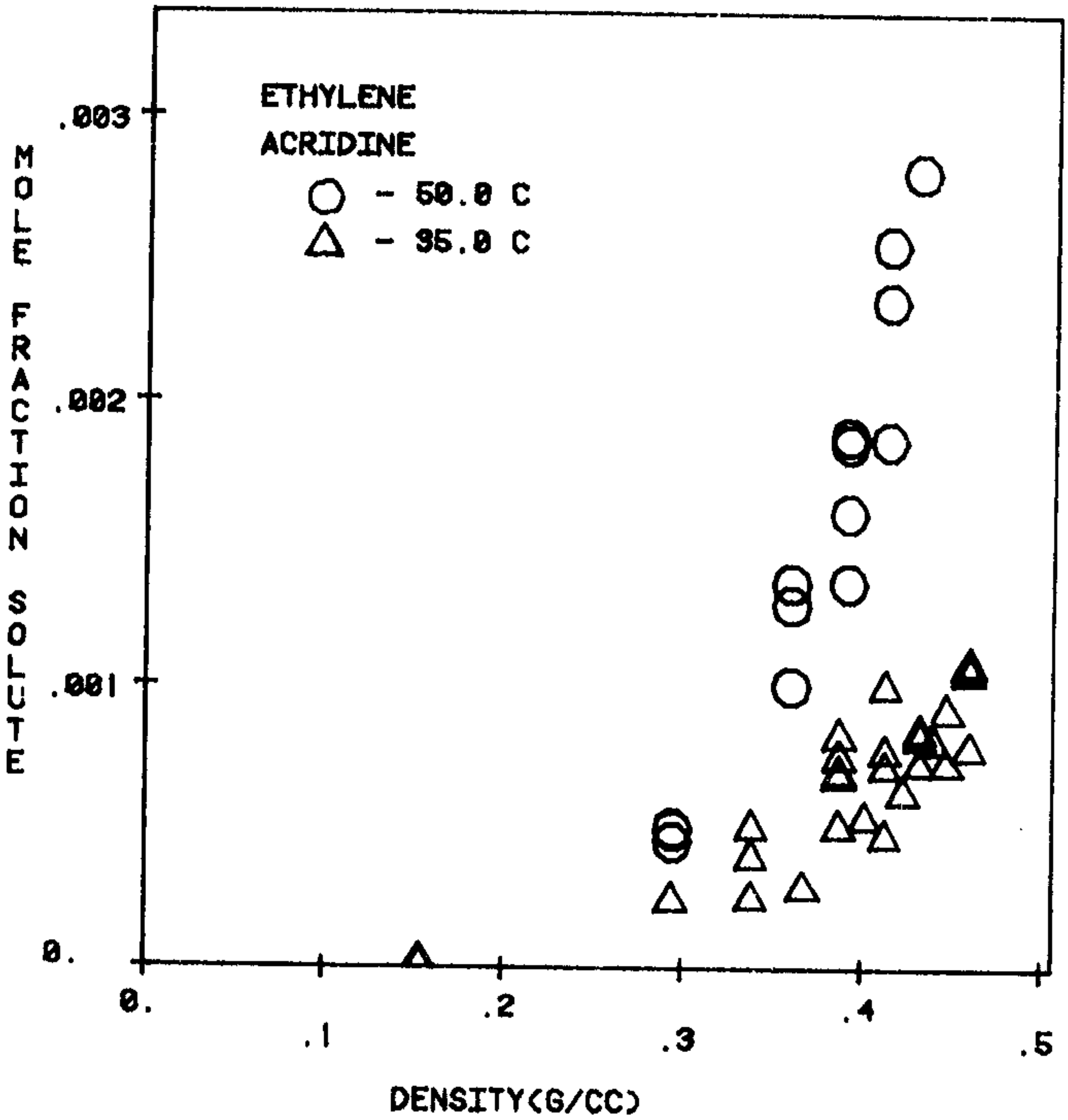


Figure 7. Solubility *versus* density isotherm for acridine in ethylene.

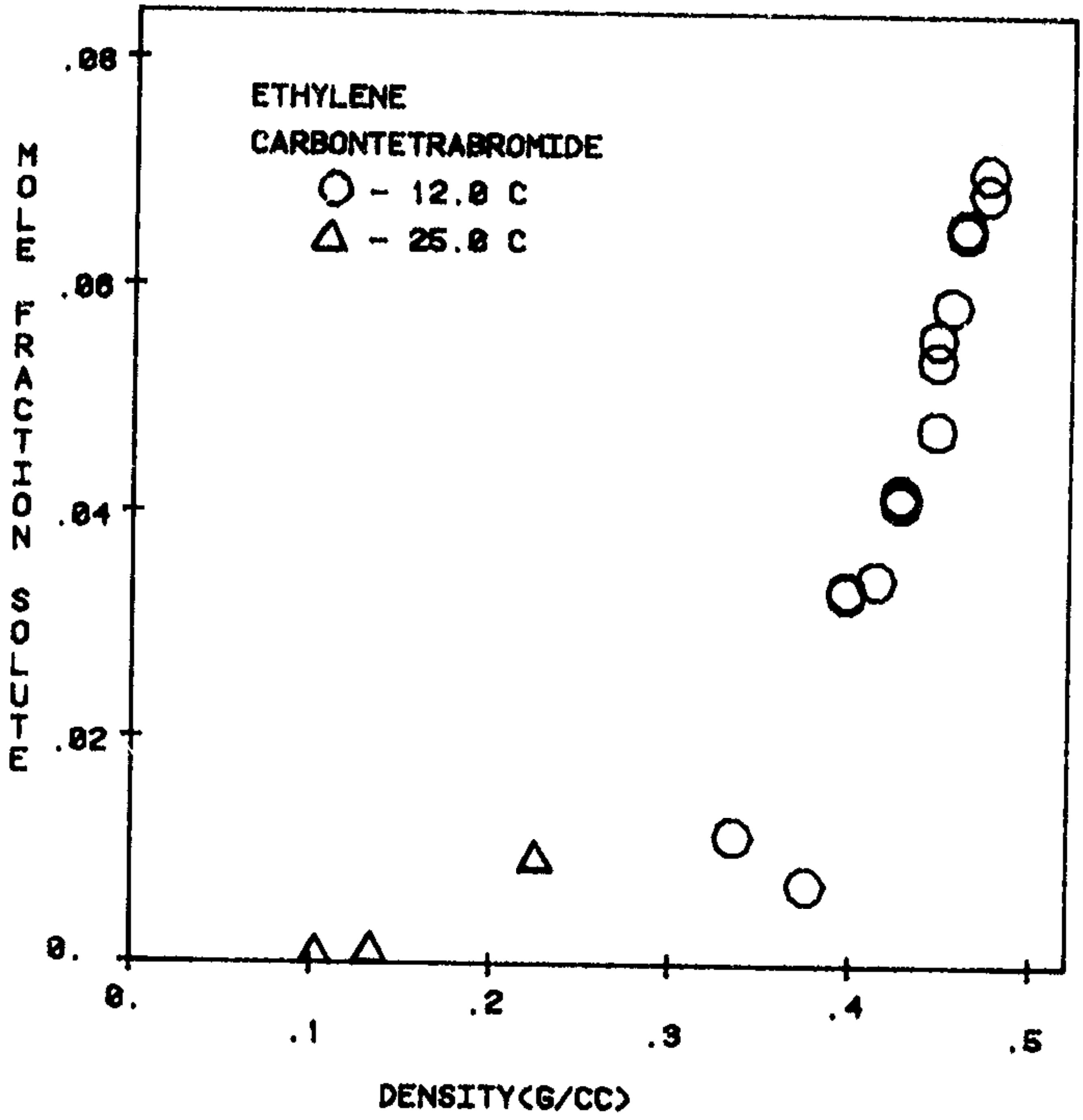


Figure 8. Solubility *versus* density isotherms for carbontetrabromide in ethylene.

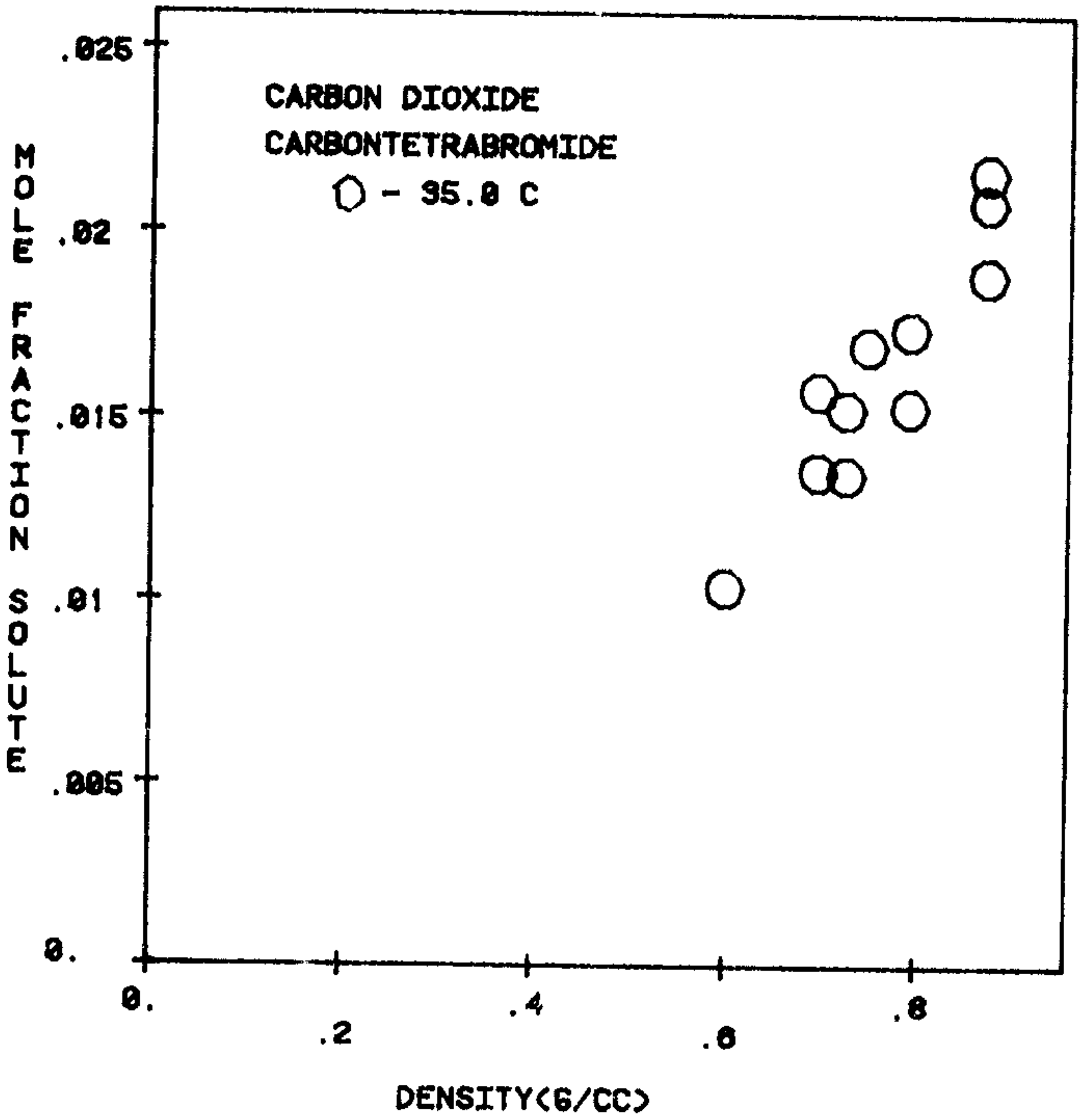


Figure 9. Solubility *versus* density isotherms for carbontetrabromide in carbondioxide.

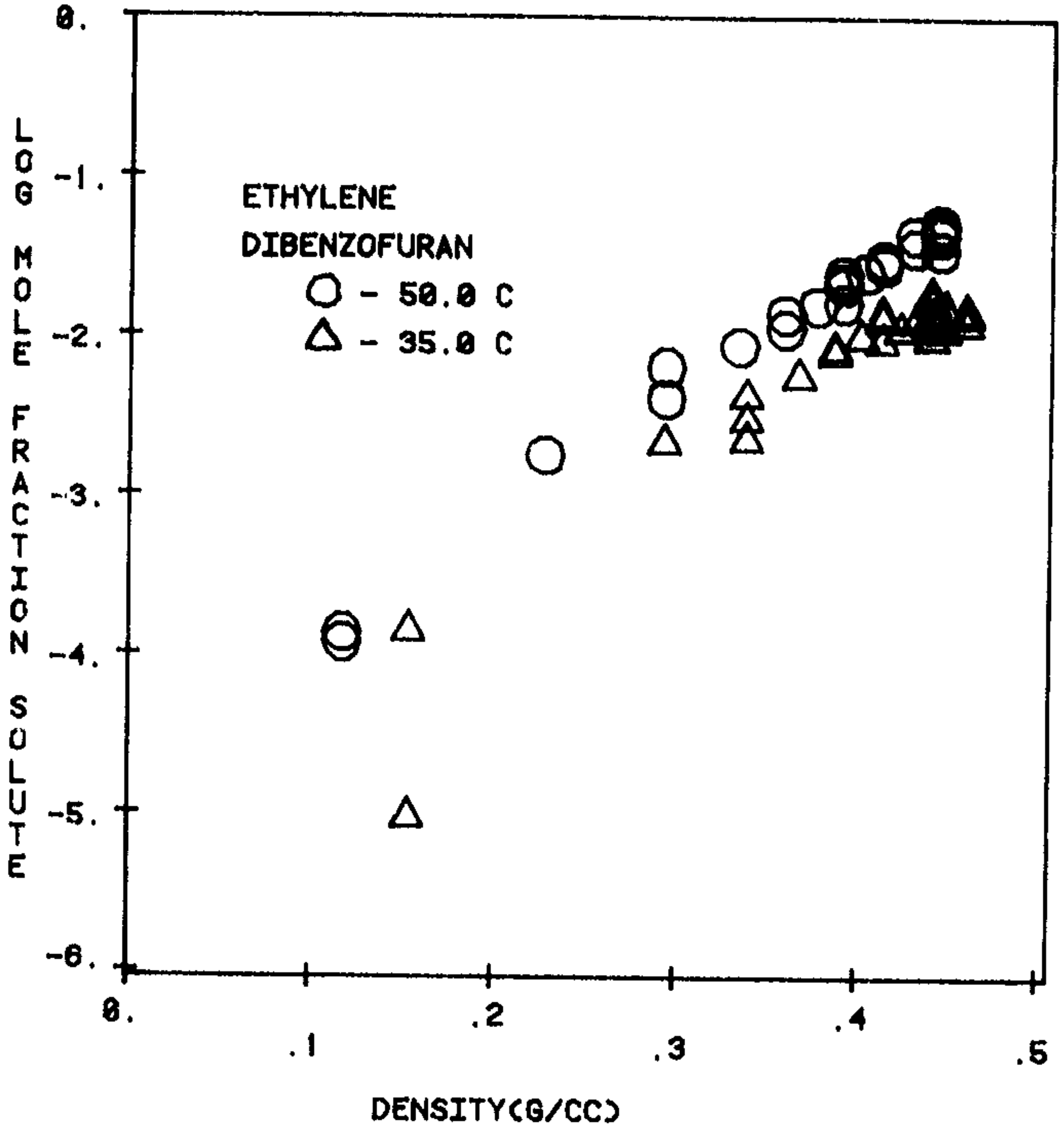


Figure 10. Log solubility *versus* density isotherms for dibenzofuran in ethylene.

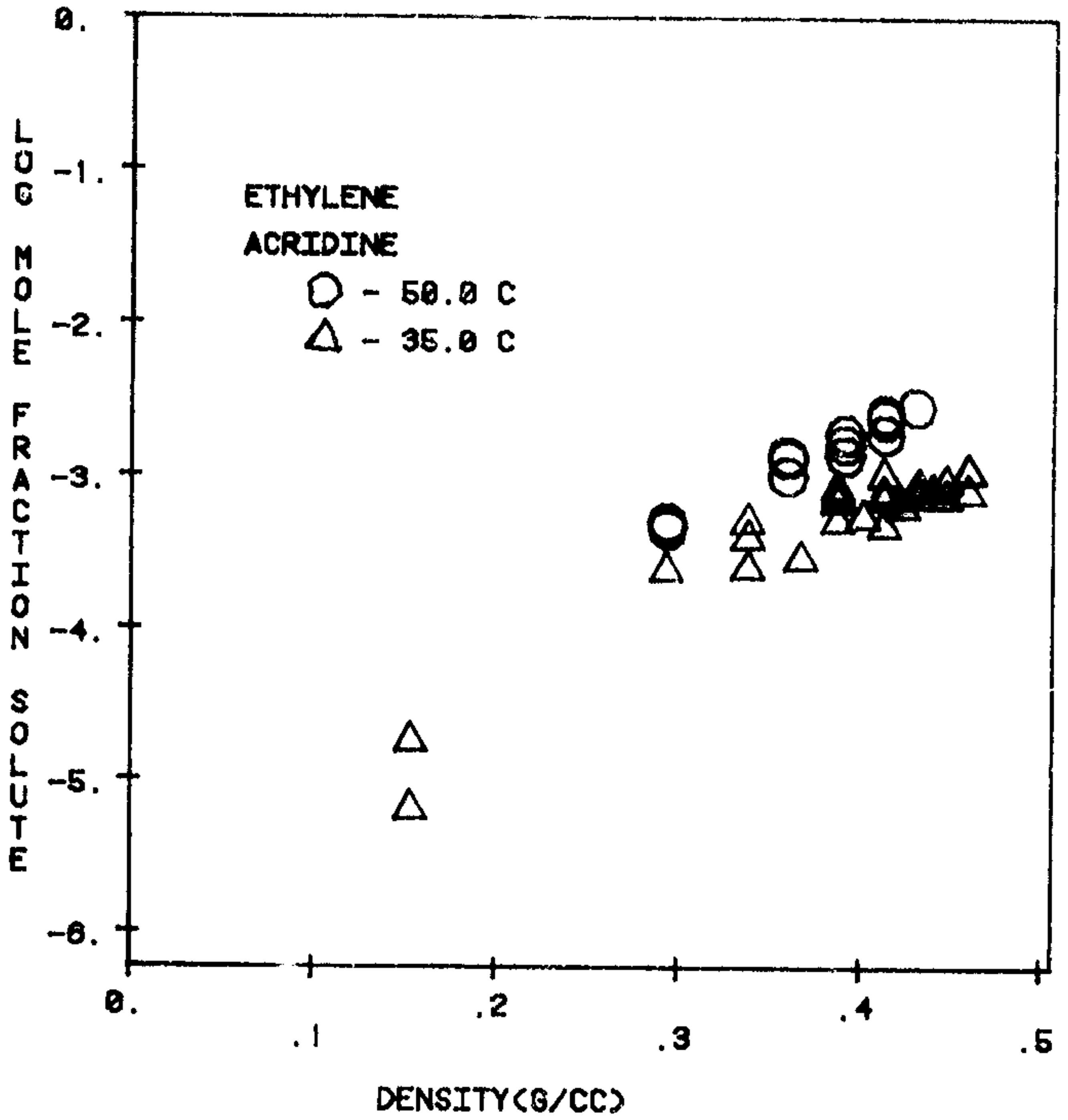


Figure 11. Log solubility *versus* density isotherms for acridine in ethylene.

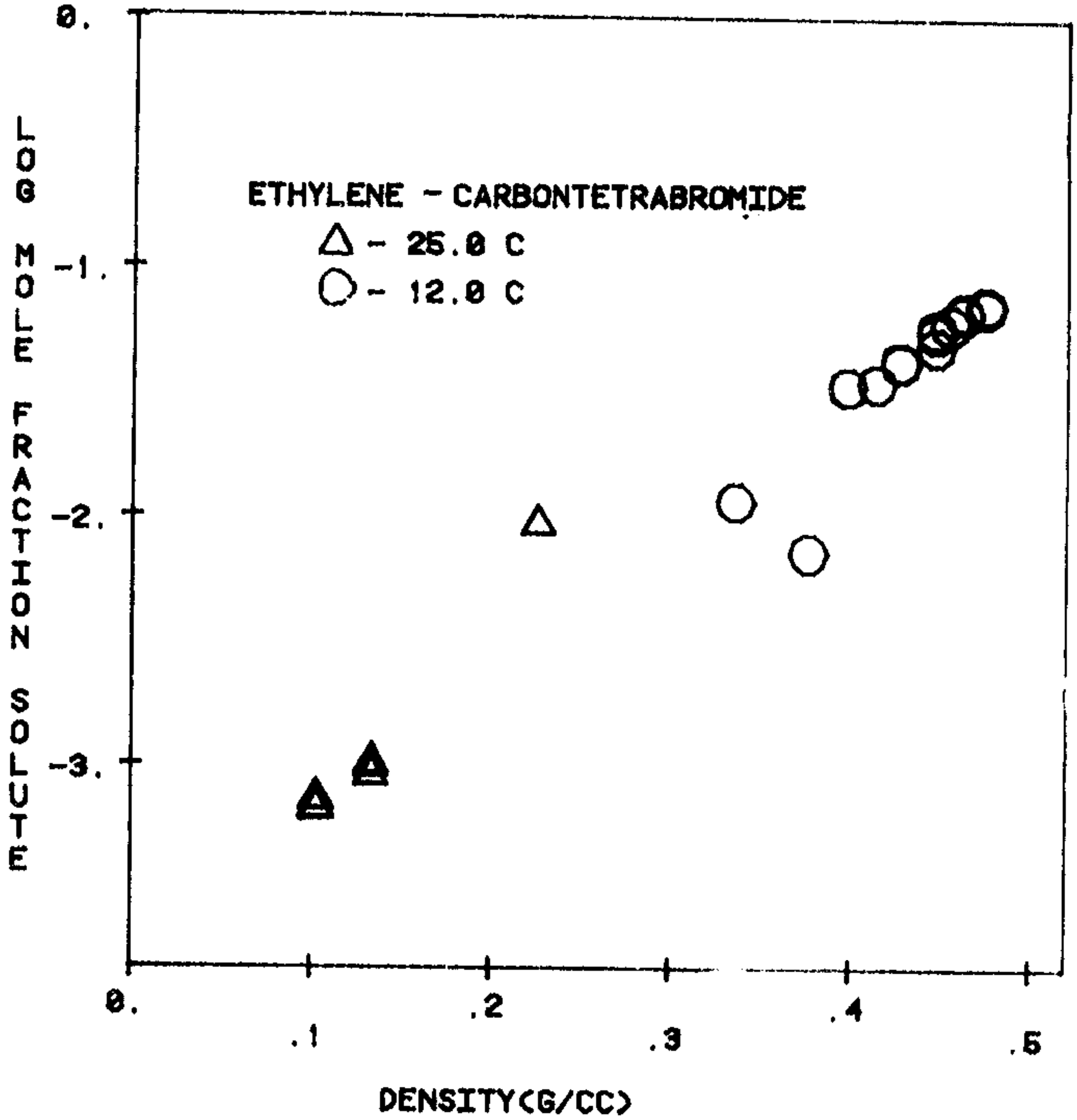


Figure 12. Log solubility *versus* density isotherms for carbontetrabromide in ethylene.

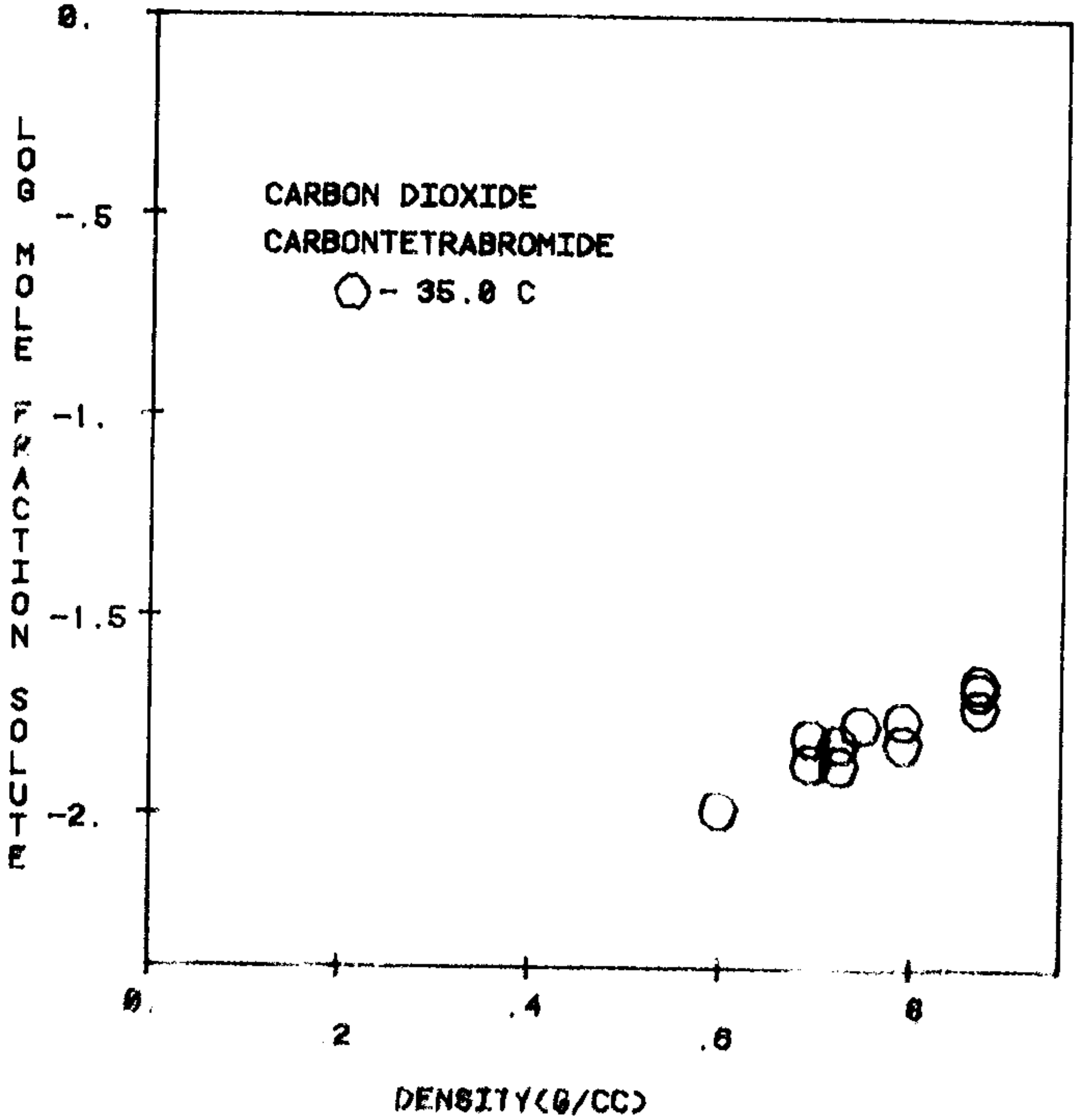


Figure 13. Log solubility versus density isotherms for carbontetrabromide in carbondioxide.

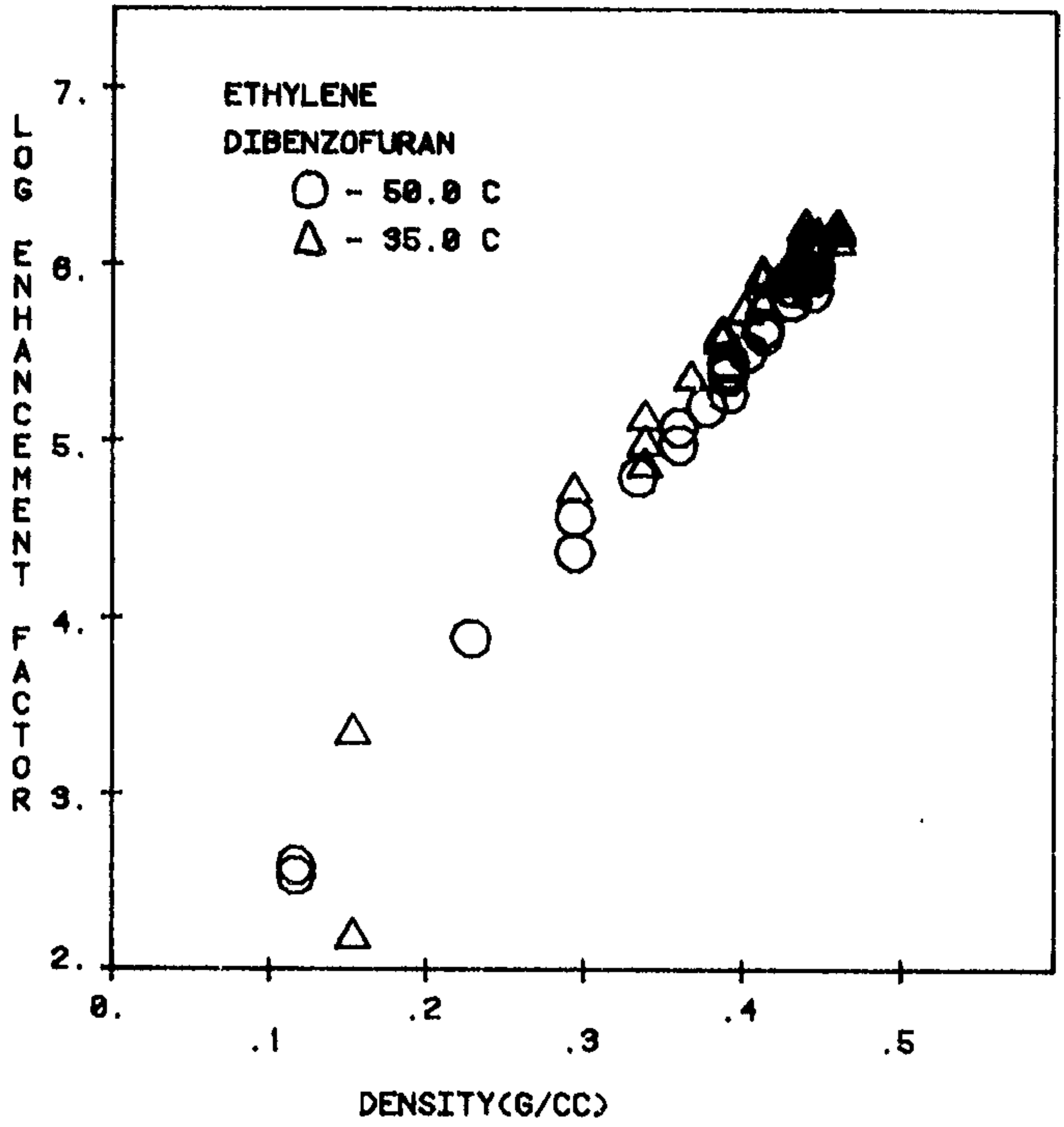


Figure 14. Log enhancement factor <u>versus</u> density for dibenzofuran in ethylene.

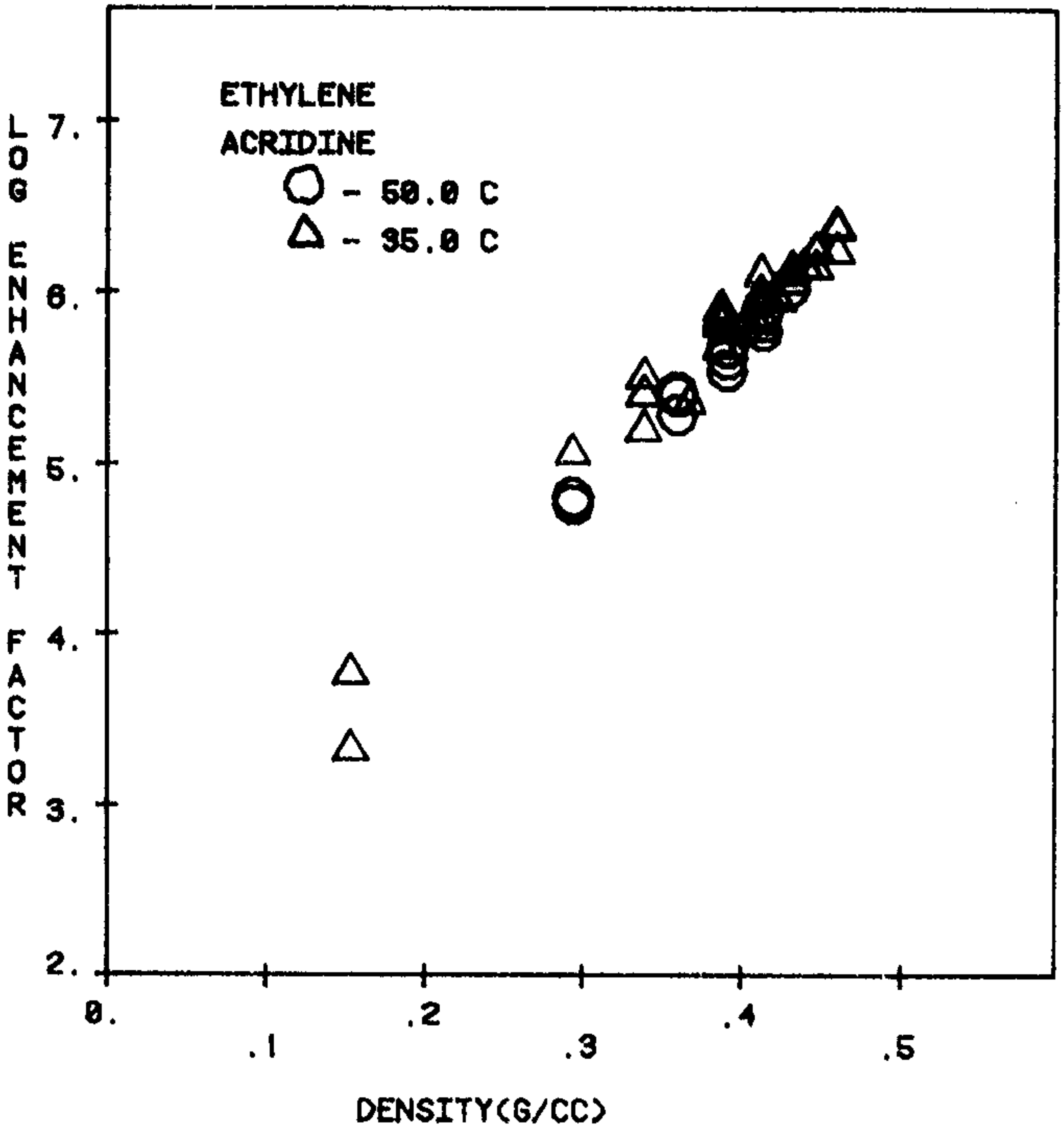


Figure 15. Log enhancement factor versus density for acridine in ethylene.

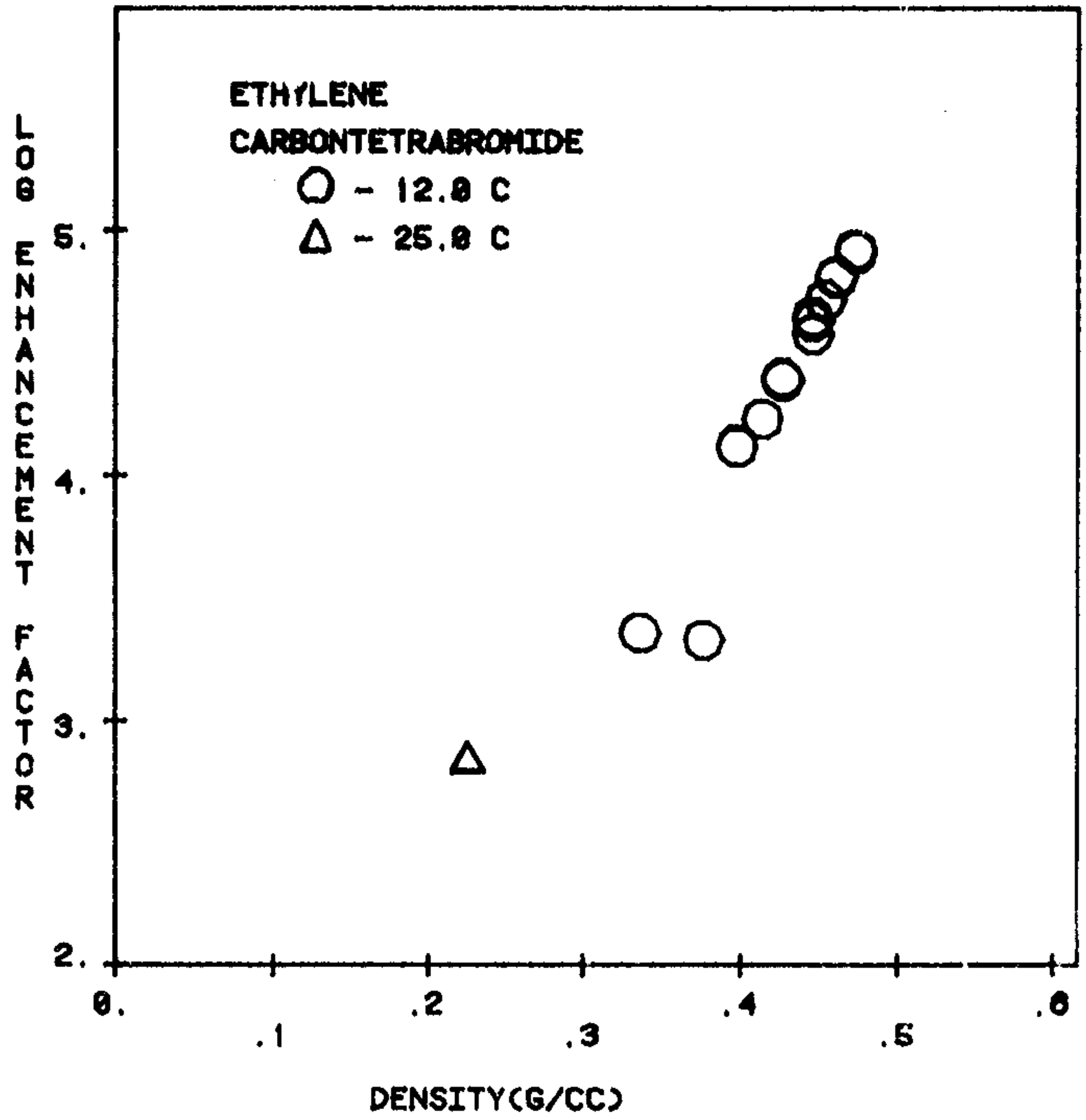


Figure 16. Log enhancement factor versus density for carbontetrabromide in ethylene.

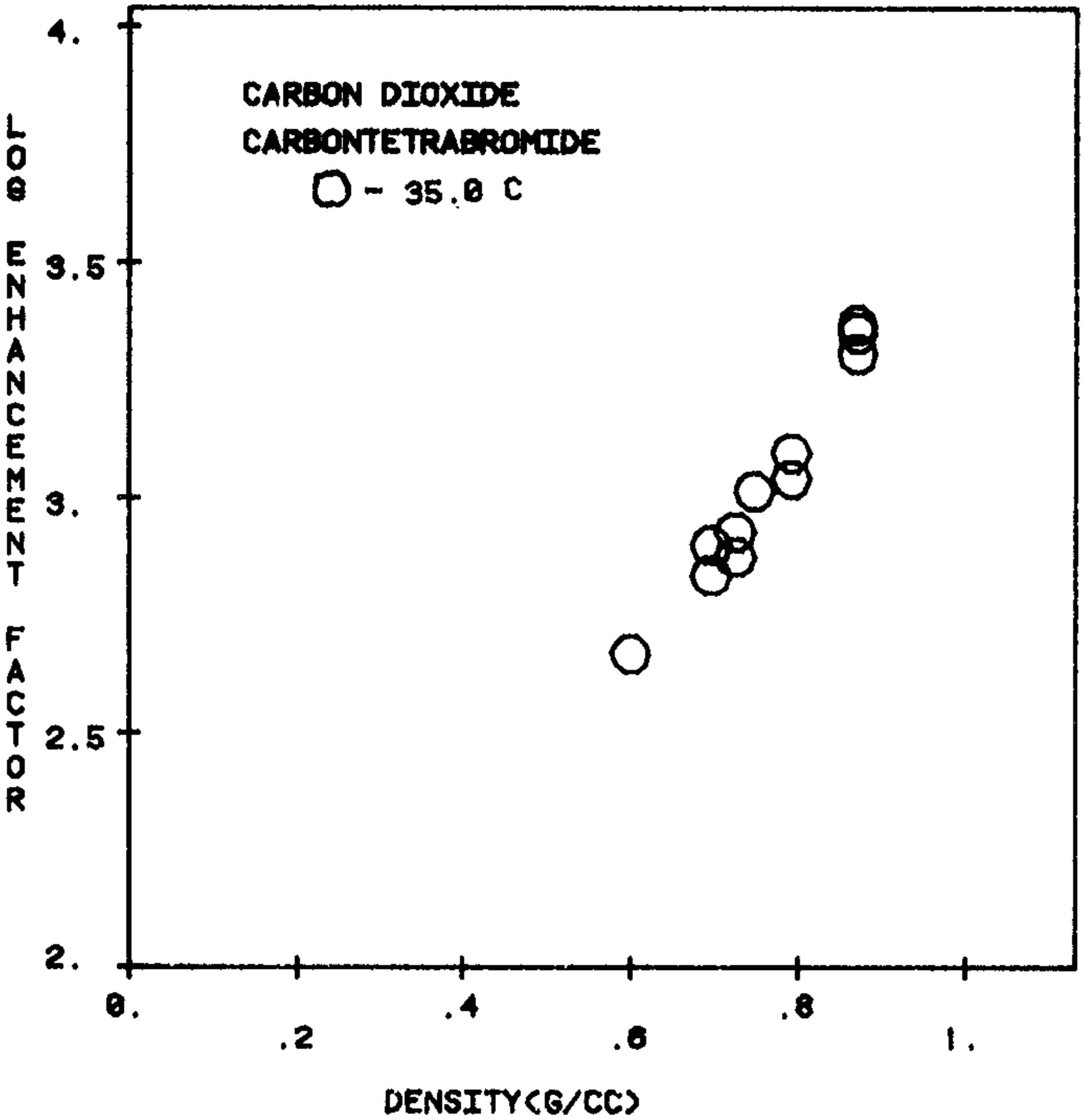


Figure 17. Log enhancement factor <u>versus</u> density for carbontetrabromide in carbondioxide.

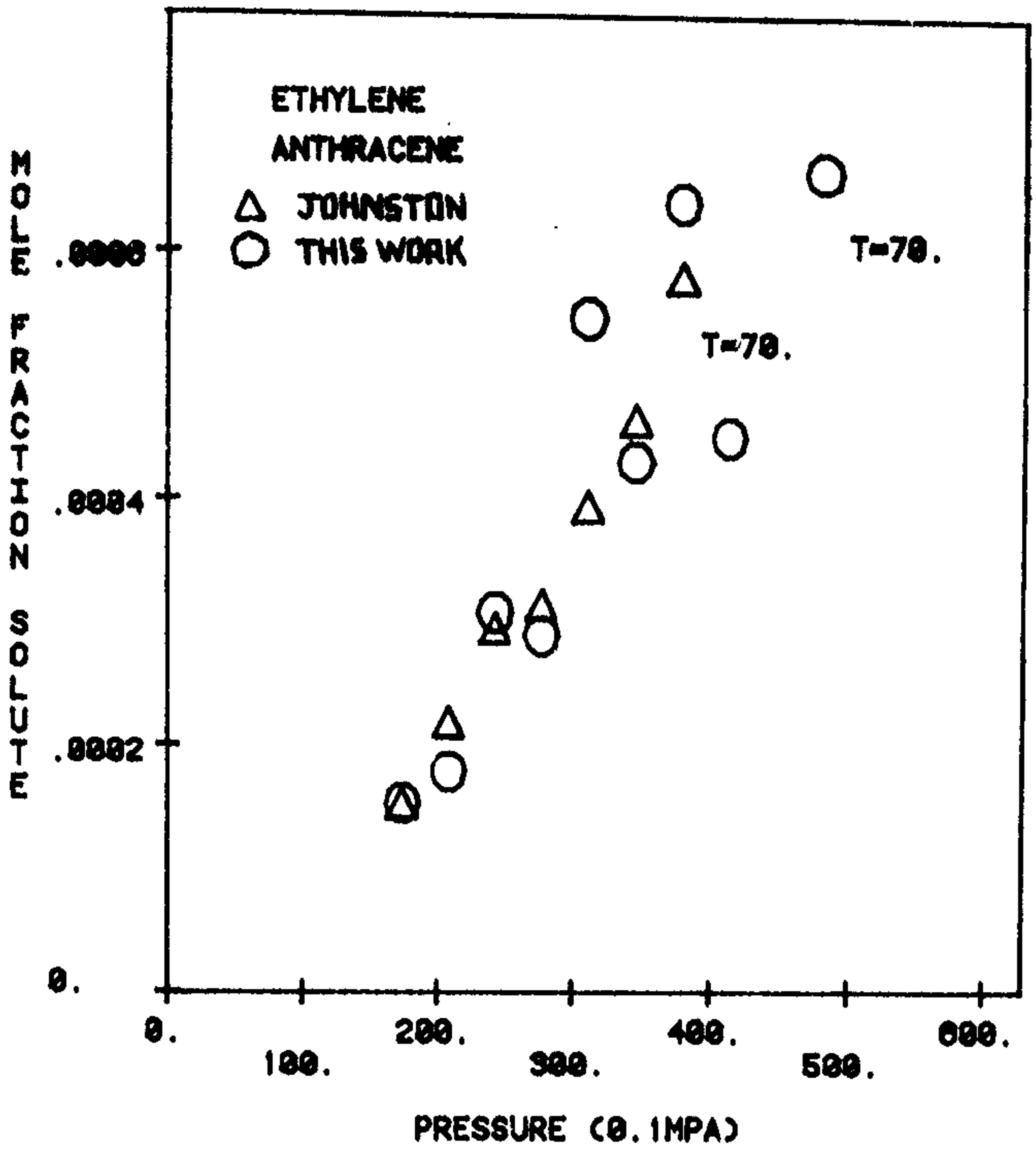
CONCLUSION

This study has enlarged the solid-fluid equilibrium data base with compounds representative of coal-constituents and also with highly volatile compounds.

1. The most meaningful representation of the non-idealities of the solid-fluid system is the enhancement factor.
2. The log enhancement factor is roughly linear with density over several orders of magnitude.

APPENDIX I

COMPARISON OF ANTRACENE IN ETHYLENE DATA


ETHYLENE
ANTHRACENE
△ JOHNSTON
○ THIS WORK
T=70.
T=70.
MOLE FRACTION SOLUTE
.0006
.0004
.0002
0.
0.
100.
200.
300.
400.
500.
600.
PRESSURE (0.1MPA)

APPENDIX II

OTHER SYSTEMS

The compound 4,5-diphenylimidazole was run in ethylene at a system temperature of 50°C and a pressure of 3000 psi. Six trials of this system were run. Although as much as 5.1 ft^3 of fluid was passed through the saturator, negligible solid was collected. It was decided that 4,5-diphenylimidazole was too insoluble to be studied further.

The opposite problem occurred with camphor in ethylene. Even at the low system temperature of 12°C and low pressure of 800 psi, the compound was extremely soluble. Some trials at this low pressure yielded mole fractions of 3.3% or greater. This high solubility was impossible to measure accurately or with small scatter because the saturator would empty of solute before positive flow equilibrium could be achieved. Another problem was that clogging occurred in the micrometering valve regardless of valve temperature.

APPENDIX III

COMPUTER PROGRAMS

```
      PROGRAM MOLCALC(CO2,TAPE4=CO2,
     +SDT,TAPE5=SDT,C2H4,TAPE3=C2H4,
     +SRT,TAPE7=SRT,INPUT,OUTPUT,TAPE9)
C
C     TAPE 3  DENSITY DATA FOR C2H4RNT
C     TAPE 4  DENSITY DATA FOR CO2RINT
C     TAPE 5  RAW DATA FROM SOLUBILITY RUNS
C     TAPE 7  OUTPUT GENERATED BY CALC FROM
C             TAPES 4&5
C     TAPE 9 RAW DATA FROM TAPE 5 AS A CHECK
      COMMON/DATA1/GWD(7),SWD(7),GMW,SMW,JJ,II,
     +NIS,ERW,PVP,N(10),M,NSM
      COMMON/DATA2/ST(10),NP,I,NRN(225),TWM(225),
     +PR(225),WTS(225),VOL(225),SPR(225)
      COMMON/DATA3/WP(225),PCH(225),ERM(225),
     +DNS(225),PCM(225),RHO(225),DER(225)
      INTEGER I,NIS
      READ(5,*) NSS
      WRITE(7,*) NSS
      DO 10 KK=1,NSS
      CALL START
      DO 10 K=1,NIS
      CALL READ
      CALL CALC
      CALL WRITE
 10   CONTINUE
      STOP
      END
C
      SUBROUTINE START
C      THIS SUBROUTINE READS IN:
C           GAS(FORMAT A4) AND GAS MW
C           SOLUTE(FORMAT A4) AND SOL MW
C           NUMBER OF ISOTHERMS,ERROR IN SOLUTE WT,
C             VAPOR PRESURE OF SOLUTE AT 25C
C             (IF NOT NEG)
      COMMON/DATA1/GWD(7),SWD(7),GMW,SMW,JJ,II,
     +NIS,ERW,PVP,N(10),M,NSM
      NSM=0
      N(1)=0
      M=0
      READ(5,025) GWD,GMW,JJ
      WRITE(9,25) GWD,GMW,JJ
      READ(5,025) SWD,SMW,II
      WRITE(9,25) SWD,SMW,II
      READ(5,030)NIS,ERW,PVP
      WRITE(9,030)NIS,ERW,PVP
      WRITE(7,25) GWD,GMW,JJ
      WRITE(7,25) SWD,SMW,II
      WRITE(7,*) NIS
 25   FORMAT(7A4,F6.2,5X,I2)
 30   FORMAT(I2,5X,F6.4,5X,F13.11)
      RETURN
      END
C
      SUBROUTINE READ
      COMMON/DATA1/GWD(7),SWD(7),GMW,SMW,JJ,II,
     +NIS,ERW,PVP,N(10),M,NSM
      COMMON/DATA2/ST(10),NP,I,NRN(225),TWM(225),
     +PR(225),WTS(225),VOL(225),SPR(225)
```

```
      INTEGER N,NIS,NRN,I
C      READ IN:
C                   NUMBER OF POINTS PER ISOTHERM &
C                            SYSTEM TEMP (C)
C                   THE RUN NUMBER
C                   WET METER TEMP (DEG F)
C                   BAROMETRIC PRESSURE (MM HG)
C                   WEIGHT SOLUTE (GRAMS)
C                   VOL (CUF)
C                   THE SYSTEM PRESSURE (PSIG)
      M=M+1
      IF(M  .GT.  1) NSM=NSM+N(M-1)
      READ(5,100) N(M), ST(M)
      WRITE(9,100)N(M), ST(M)
      NP=N(M)
      DO 10 J=1,NP
      IF(J  .EQ. 1) I=NSM
      I=I+1
      READ(5,200)NRN(I),TWM(I),PR(I),
     + WTS(I),VOL(I),SPR(I)
      WRITE(9,200)NRN(I),TWM(I),PR(I),
     + WTS(I),VOL(I),SPR(I)
   10 CONTINUE
  100 FORMAT(I2,6X,F6.2)
  200 FORMAT(I3,6X,F6.1,4X,F7.1,6X,F7.4,
     +5X,F7.4,5X,F6.1)
      RETURN
      END
      SUBROUTINE CALC
      COMMON/DATA1/GWD(7),SWD(7),GMW,SMW,JJ,I1,
     +NIS,ERW,PVP,N(10),M,NSM
      COMMON/DATA2/ST(10),NP,I,NRN(225),TWM(225),
     +PR(225),WTS(225),VOL(225),SPR(225)
      COMMON/DATA3/WP(225),PCW(225),ERM(225),
     +DNS(225),PCM(225),RHO(225),DER(225)
      REAL R
      DO 10 J=1,NP
      TURE=ST(M)
      IF(J  .EQ.  1) I=NSM
      I  =  I+1
      TWM(I)  =  (TWM(I)-32)/1.8 + 273.15
      WTS(I)=WTS(I)+PVP*VOL(I)*SMW*28316/
     +(82.05*TWM(I))
      WP(I)  =  EXP(18.3036-3816.44/(TWM(I)-46.15))
      PR(I)  =  (PR(I)-WP(I)-4.77)/760
C     WTM  ASSUMED TO OPERATE AT 1IN SUC
C     MEAN BAROMETER TEMP COR ASSUMED 02.9 MMHG
      IF(JJ    .EQ.  1     ) R=RETHY(TWM(I))
      IF(JJ    .EQ.  2     ) R=RESCO2(TWM(I),PR(I))
      DNS(I)  =PR(I)/(82.06*TWM(I)-R*PR(I))
     +*GMW*28316.754
      PCW(I)  =  WTS(I)/(DNS(I)*VOL(I)+WTS(I))*100
      PCM(I)  =  WTS(I)/SMW/((DNS(I)*VOL(I)/GMW)
     + +  (WTS(I)/SMW))*100
C     THE MOLPC ERROR(ERM) IS REPORTED AS % ER
C     SEE NOTEBOOK CII
C     FOR MTD OF DET'N, USE THE SUM OF SQS MTD
C     ASSUMED UNCERTAINTIES:
```

```
C                        SOLUTE WT ERROR EST (ERW)
C                        0.3DEG F FOR WTM TEMP
C                        0.004CUF FOR WTM VOL
C                        0.3MMHG FOR ATMOSPHERIC PRES
      DER(I)=DNS(I)*0.0028901*TWM(I)/PR(I)
     +*(0.2/TWM(I) + 0.00039/PR(I))
      ERM(I)=(100-PCM(I))*(((DER(I)/DNS(I))**2
     + +(0.004/VOL(I))**2+(ERW/WTS(I))**2)**.5)
      PR(I)=PR(I)*1.013
      SPR(I)=SPR(I)/14.503+PR(I)
      IF(J    .EQ.   1) CALL CPH4RNT(TURF,SPR(I),
     +RHO(I))
      IF(J    .EQ.   2) CALL CO2RINT(TURF,SPR(I),
     +RHO(I))
   10 CONTINUE
      RETURN
      END
C
      FUNCTION RESCO2(T,P)
      Z=0.99467+0.20542*(P-1)
      RESCO2=82.06*T*(1-Z)/P
      RETURN
      END
C
      FUNCTION RETHY(T)
      RETHY=30.5155*(10**5.)*T**(-1.73425)-32.622
      RETURN
      END

      SUBROUTINE CO2RINT(TEMP,PRES,RINT)
C     SEE FILE CO2RINT FOR DOC OF THIS SUBROUTINE
      DIMENSION P(19),T(7),R(19,7)
      REWIND 4
      READ(4,100) NR,NC
      READ(4,110) T(1),T(2),T(3),T(4),T(5),T(6),T(7)
      DO 20 J=1,NR
      READ(4,130) P(J),R(J,1),R(J,2),R(J,3),
     + R(J,4),R(J,5),R(J,6),R(J,7)
   20 CONTINUE
      TEMP=273.15+TEMP
      PRES=PRES
      IERRO=0
      M=0
      N=0
      DO 30 I=1,NC
      IF(T(I)  .LT.  TEMP) M=I
   30 CONTINUE
      DO 40 J=1,NR
      IF(P(J)  .LT.  PRES) N=J
   40 CONTINUE
      IF(M  .EQ.  NC) IERRO=1
      IF(N  .EQ.  NR) IERRO=1
      IF(M  .EQ.  0  .OR.  N  .EQ.  0) IERRO=1
      IF(M  .EQ.  0)  M=1
      IF(N  .EQ.  0)  N=1
      IF(M  .EQ.  NC)  M=M-1
      IF(N  .EQ.  NR)  N=N-1
      IF(IERRO  .EQ.  1)  PRINT 140,TEMP,PRES
      RINTL= R(N,M) + (TEMP-T(M))/(T(M+1)-T(M))
     + *(R(N,M+1)-R(N,M))
      RINTH=R(N+1,M)+(TEMP-T(M))/(T(M+1)-T(M))
     + *(R(N+1,M+1)-R(N+1,M))
      RINT= RINTL+(PRES-P(N))/(P(N+1)-P(N))
     + *(RINTH-RINTL)
```

```
 100  FORMAT(I2,2X,I2)
 110  FORMAT(5X,7F9.1)
 130  FORMAT(F6.1,7F9.6)
 140  FORMAT("VAL TO BE INT NOT BRACK BY DATA  ",
     +"T=",F6.1,",P=",F6.1)
      RETURN
      END
C
C
      SUBROUTINE C2H4RNT(TEMP,PRES,RINT)
C     SEE FILE C2H4RNT FOR DOC OF THIS SUBROUTINE
      DIMENSION P(19),T(6),R(19,6)
      REWIND 3
      READ(3,100) NR,NC
      READ(3,110) T(1),T(2),T(3),T(4),T(5),T(6)
      DO 20 J=1,NR
      READ(3,130) P(J),R(J,1),R(J,2),R(J,3),
     + R(J,4),R(J,5),R(J,6)
  20  CONTINUE
      TEMP=273.15+TEMP
      PRES=PRES
      IERRO=0
      M=0
      N=0
      DO 30 I=1,NC
      IF(T(I) .LT. TEMP) M=I
  30  CONTINUE
      DO 40 J=1,NR
      IF(P(J) .LT. PRES) N=J
  40  CONTINUE
      IF(M .EQ. NC) IERRO=1
      IF(N .EQ. NR) IERRO=1
      IF(M .EQ. 0 .OR. N .EQ. 0) IERRO=1
      IF(M .EQ. 0) M=1
      IF(N .EQ. 0) N=1
      IF(M .EQ. NC) M=M-1
      IF(N .EQ. NR) N=N-1
      IF(IERRO .EQ. 1) PRINT 140,TEMP,PRES
      RINTL= R(N,M) + (TEMP-T(M))/(T(M+1)-T(M))
     + *(R(N,M+1)-R(N,M))
      RINTH=R(N+1,M)+(TEMP-T(M))/(T(M+1)-T(M))
     + *(R(N+1,M+1)-R(N+1,M))
      RINT= RINTL+(PRES-P(N))/(P(N+1)-P(N))
     + *(RINTH-RINTL)
 100  FORMAT(I2,2X,I2)
 110  FORMAT(5X,6F9.1)
 130  FORMAT(F6.1,6F9.6)
 140  FORMAT("VAL TO BE INT NOT BRACK BY DATA  ",
     +"T=",F6.1,",P=",F6.1)
      RETURN
      END
      SUBROUTINE WRITE
      COMMON/DATA1/GWD(7),SWD(7),GMW,SMW,JJ,II,
     +NIS,ERW,PVP,N(10),M,NSM
C
      COMMON/DATA2/ST(10),NP,I,NRN(225),TWM(225),
     +PR(225),WTS(225),VOL(225),SPR(225)
      COMMON/DATA3/WP(225),PCW(225),ERM(225),
     +DNS(225),PCM(225),RHO(225),DEA(225)
      REAL PRES,SP,WP,ST,TWM,DNS,PCM,PCW,VOL,WTS
      WRITE(7,100)ST(I),NP
      WRITE(7,200)
```

```
      DO 10 J=1,NP
      IF(J .EQ. 1) I=NSM
      I = I+1
      PSIG=(SPR(I)-PR(I))*14.503
      PCM(I)=PCM(I)/100
C
C     OUTPUT TO TAPE7 IS SYSTEM P IN 0.1MPA(PSIG)
C                        SOLUTE MOLE FRACTION
C                        ERROR PER CENT OF Y2
C                        DENSITY (RHO) OF SCF
C                        DENSITY OF GAS IN WTM
C                        RUN NUMBER
C
     WRITE(7,300) SPR(I),PSIG,PCM(I),
    + ERR(I),RHO(I),DNS(I),NRN(I)
 10  CONTINUE
 100 FORMAT(2X,"THE ISOTHERM AT T=",F4.1,
    + " C, HAS ",I2," DATA POINTS")
 200 FORMAT(1X,"P (.1MPA) (GAUGE)",4X,
    +"Y2 MLFRC",6X,"ERROR %Y2",6X,"RHO G/CC",
    +5X,"WTM RHO G/FT3",5X,"RUN NO.")
 300 FORMAT(F10.3,1X,"(",F5.0,")",3X,
    +2(F10.7,5X),F8.6,5X,F9.5,12X,I3)
     RETURN
     END
```

APPENDIX IV

NOMENCLATURE

Symbols

ρ	density
P	pressure
T	temperature
y_2	mole fraction solute
E	enhancement factor
P^s	vapor pressure
ϕ	fugacity coefficient
v	volume
R	gas constant
f	fugacity
$\bar{v}$	partial molar volume
Pa	pascal

Subscripts

i	component i
1	solvent
2	solute
mp	melting point

Superscripts

s	saturation

Prefixes

m	milli (10^{-3})
M	mega (10^{6})

LITERATURE CITED

1. Gouw, T. H., and Jentost, R. E., J. Chromatogr. 68, 303 (1972).

2. Hannay, J. B., and Hogarth, J., Proc. Roy. Soc. (London), Ser. A, 29, 324-26 (1879)

3. Gearhart, J. A., and Garwin, L. "A New Economical Approach to Residuum Processing," presented at the 1976 National Petroleum Refiners Association, March 20, 1976, San Antonio, Texas.

4. Moddocks, P. R., and Gibson, J., Chem. Eng. Prog. 73, (6) 59 (1977).

5. Zosel, K., US-Patent, 3,806,619 (1974).

6. Chem. and Eng. News 59, (21) 27 (1981).

7. Ziger, D. H., PhD Dissertation, University of Illinois, Urbana, Illinois, 1982.

8. Johnston, K. P. and Eckert, C. A., AI. ChE. J. 27, 5, 773 (1981).

9. Johnston, K. P., Ziger, D. H. and Eckert, C. A. "Solubilities of Hydrocarbon Solids in Supercritical Fluids: The Augmented-van der Waal Treatment," University of Illinois, 1981.

10. Johnston, K. P., PhD Dissertation, University of Illinois, Urbana, Illinois, 1982.

11. Prausnitz, J. M., Molecular Thermodynamics of Fluid-Phase Equilibria Prentice-Hall, Inc.:Englewood Cliffs, New Jersey, 1969, p 163.

12. Hansen, P. C., Master's Dissertation, University of Illinois, Urbana, Illinois, 1983.

13. Angus, S., Armstrong, B. and de Reuck, K. M., Carbon Dioxide International Thermodynamic Tables of the Fluid State, Pergamon Press:Frankfurt, W. Germany, 1976.

14. Angus, S., Armstrong, B., and de Reuck, K. M., International Thermodynamic Tables of the Fluid State, Ethylene The Butterworth Group:London, England, 1974.

15. McEachern, D. M., Sandoval, O., and Iniquez, J. C., J. Chem. Thermo. 7, 299 (1975).

16. Cass, R. C., Fletcher, S. E., Mortimer, C. T., Springall, H. D., White, T. R., J. Chem. Soc. 1958, 1406 (1958).

17. CRC Handbook of Chemistry 60, C-677.