HIGH PRESSURE SOLUBILITIES OF CARBON DIOXIDE AND ETHANE IN SELECTED PARAFFINIC, NAPHTHENIC AND AROMATIC SOLVENTS

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PREFACE

The isothermal solubilities of carbon dioxide in four solvents, benzene, n-decane, n-dodecane and n-tetradecane, were measured at temperatures ranging from 40 to 100°C. The isothermal solubilities of ethane were measured in n-decane at temperatures ranging from 100 to 280°F, in one- and two-ring naphthenic solvents (cyclohexane, trans-Decalin) at temperatures of 50, 100 and 150°C, and in 1-, 2-, 3- and 4-ring aromatic solvents (benzene, naphthalene, phenanthrene and pyrene) at temperatures ranging from 50 to 160°C. Binary interaction parameters for use in the Soave-Redlich-Kwong and Peng-Robinson equations of state have been optimized by regression of the obtained data for each system. Comparisons have been made regarding the accuracy of these equations in fitting the data with the use of one and two binary interaction parameters. Also compared are the results of the use of binary interaction parameters obtained through single and multiple-isotherm regressions of the data.

I wish to express my sincere thanks to my thesis advisor, Dr. R. L. Robinson, Jr., for the patience, wisdom and encouragement he provided during the course of this study.

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CHAPTER I

INTRODUCTION

Despite intense investigation of alternate energy sources, a heavy dependence on fossil fuels exists and will not be alleviated within the foreseeable future. With the dependence on fossil fuels, there exists a need for all amassable knowledge regarding the behavior of the components of these fuels to maximize efficiency in all stages of their production, refinement and use. Of primary importance is knowledge of the phase behavior of components of these fuels, since the design of so many of the processes involved in production and refinement rely on the knowledge of phase equilibrium.

Currently, there are a number of thermodynamic models commonly employed to predict phase equilibrium in multicomponent systems. Experimental data are needed for optimization of these models, particularly for binary systems formed by the dissolution of light gases into heavy hydrocarbons commonly found in crude oils and coal-liquids. Such data are extremely scarce, particularly for binaries of light gases with heavy aromatic and naphthenic solvents. Hence, the major objectives of this work are (a) the acquisition of data of binary systems of CO_2 with selected paraffinic and aromatic hydrocarbons to augment the work of previous researchers, and (b) data acquisition for systems of ethane with multi-ring naphthenic and aromatic solvents. Experience has shown that modification is needed in thermodynamic models for binary hydrocarbon systems in which there exists a large disparity between the sizes of the hydrocarbons.

Specific CO_2 binaries studied in this work include those containing benzene, n-decane, n-dodecane and n-tetradecane. Ethane binaries of interest include n-decane, one- and two-ring naphthenics (cyclohexane and trans-Decalin, respectively), and one-, two-, three-, and four-ring aromatic solvents (benzene, naphthalene, phenanthrene, and pyrene).

CHAPTER II

LITERATURE REVIEW

In conjunction with the experimental activity, a review of pertinent vapor-liquid equilibrium literature has been performed. Of specific interest are accounts of the development and use of binary interaction parameters to improve the abilities of the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state to predict phase behavior of hydrocarbon-hydrocarbon and CO_2-hydrocarbon binaries. Also of interest are previous studies of the phase behavior of the specific binary systems investigated in this study.

Previous Experimental Work

For most of the binaries investigated in the present study there exists at least one previous study. A summary of these is presented in Table I on the following page. Some of these are extremely useful because they provide experimental data for purposes of comparison. With the exception of the study by Nagarajan, all of the CO_2 + benzene studies include an isotherm obtained at 313.2 K (40°C) which makes this an ideal temperature at which to obtain data for this system for comparison purposes.

Some of the other systems have not been studied as extensively. The studies by Liu et al. (13) focus on three-phase solid-liquid-vapor equilibria at temperatures below 265 K. These data cannot be used for

TABLE I

SUMMARY OF PREVIOUS RESEARCH ON PHASE BEHAVIOR OF BINARY SYSTEMS INVESTIGATED IN THIS STUDY

System	Previous Researchers	Reference Number	Temperatures Investigated (K)	Pressures Investigated (MPa)
CO_2 + Benzene	Anderson and Barrick	1	313.2	1.644 - 5.572
	Nagarajan	2	344.3	6.895 - 10.960
	Gasem	3	313.2	0.754 - 5.171
	Gupta	4	313.2,353.2,393.2	0.740 - 13.395
	Ohgaki	5	298.15,313.15	0.894 - 7.750
	Donohue	6	313.35,352.95,393.15	2.119 - 6.270
CO_2 + n-Decane	Reamer and Sage	7	277.6 - 510.9	0.093 - 18.832
	Nagarajan	8	344.3	6.385 - 12.740
CO_2 + n-Dodecane	Anderson and Barrick	9	323.2,344.3	1.180 - 5.850
CO_2 + n-Tetradecane	Gasem	10	344.3	11.072 - 16.353
Ethane + n-Decane	Reamer and Sage	11	277.6 - 510.9	0.345 - 11.823
Ethane + Benzene	Kay and Nevens	12	266.7 - 560.9	2.068 - 9.652
	Liu, Luks and Kohn	13	175 - 265	0.075 - 0.816
	Ohgaki	14	298.2	0.775 - 3.800
Ethane + Cyclohexane	Liu, Luks and Kohn	13	145 - 255	0.096 - 0.199
Ethane + Trans-Decalin	Liu, Luks and Kohn	13	150 - 240	0.097 - 0.166

any direct comparison since the minimum temperature studied in all three of these systems is 323.2 K in the present study. Ohgaki et al. (14) conducted a study of vapor-liquid equilibrium in the ethane + benzene system at 25°C, but again this is below the minimum temperature of interest for ethane + benzene in this study.

Kay and Nevens (12) studied phase equilibria in the ethane + benzene system by determining bubble-point temperatures of constant-composition mixtures as a function of pressure. These bubble-point temperatures were measured for mixtures from zero to 1.0 liquid mole fraction ethane in increments of 0.1 liquid mole fraction at pressures from 100 to 1400 psia in 100 psia increments.

No studies have been performed previously on binary systems of ethane with naphthalene, phenanthrene or pyrene.

Historical Development of Binary Interaction Parameters

Cubic equations of state are commonly used to predict phase behavior of mixtures. The two most widely used equations are Soave's modification of the Redlich-Kwong equation (SRK) (23) and the Peng-Robinson equation (PR)(24). The parameters employed in these equations are easily calculated from critical properties and acentric factors of each component in the mixture. The equations are known for high accuracy in hydrocarbon systems; however, this accuracy is reduced when the mixtures contain non-hydrocarbons.

The use of an empirical adjustment factor has been suggested to compensate for this reduction in accuracy. The so-called binary interaction parameter, k_{12}, is incorporated into the calculation of the function a(T) in both the SRK and PR equations. This empirical constant corrects the energy of interaction between two different molecules so as to optimize the prediction of phase equilibria. Equations 3.8 and 3.9, in Chapter III of this work, show mathematically how these constants are employed in the SRK equation of state.

Huron (15) attempted use of k_{12} to improve accuracy in prediction of phase behavior in systems containing CO_2 and H_2S via the SRK equation. The binary interaction parameter was optimized by determining the value which, when used with the SRK equation, would minimize a certain objective function. Huron used as his objective function the following function, Q:

$$Q = \sum_{i=1}^{N} (y_i^{\,exp} - y_i^{\,calc})^2 + [(P_i^{\,exp} - P_i^{\,calc})/P_i^{\,exp}]^2 \quad (2.1)$$

where $(y_i^{exp} - y_i^{calc})$ and $(P_i^{exp} - P_i^{calc})$ are the differences between the experimental and calculated values of the mole fraction of one component and of the total system pressure, respectively, at fixed temperature and liquid mole fraction, for an experiment "i" in a set of N experiments. Huron concluded that phase equilibrium is effectively represented for hydrocarbon binary systems by setting k_{12} equal to zero, and that the use of any k_{12} of absolute value less than 0.04 would not significantly improve predictions. For mixtures of CO_2 with n-paraffins from methane to n-decane, values of k_{12} ranged from 0.096 to 0.128. Huron could not deduce any specific correlation between k_{12} and any characteristic parameter of the hydrocarbons (number of carbon atoms, acentric factor, molecular weight, critical constants). However, the possibility of an obscure correlation was suggested.

Graboski and Daubert (16) also declared the use of k_{12} unnecessary in hydrocarbon binaries. They found that the value of k_{12} lies in the range of 0.00 to 0.25 in hydrocarbon-nonhydrocarbon binaries, that the value of k_{12} generally increases with the molecular size of the hydrocarbon, and a correlation exists between k_{12} and the difference in solubility parameter of hydrocarbon and nonhydrocarbon. The criterion for optimization of the binary interaction parameter was the minimization of bubble point pressure variance, denoted by σ^2:

$$\sigma^2 = \sum_{i=1}^{N} [(P_i^{exp} - P_i^{calc})/P_i^{exp}]^2 \qquad (2.2)$$

where the variables have the same significances as in the study by Huron. Graboski and Daubert found this criterion superior to minimization of flash volume variance, since bubble point pressure is much more sensitive to the value of k_{12}. They applied their choice of criterion to binaries of hydrocarbons with H_2S, CO_2, CO and N_2. For CO_2 + hydrocarbon binaries they concluded that the value of k_{12} could be determined within limits of ±0.05 of the optimum by use of the following correlation:

$$k_{12}\ (CO_2) = 0.1294 + 0.0292\ (\Delta\delta) - 0.0222\ (\Delta\delta)^2 \qquad (2.3)$$

where $\Delta\delta$ is the solubility parameter difference.

Mundis, et al. (17) evaluated interaction parameters for the SRK equation by fitting the equation to infinite-dilution K-value data of CO_2 + methylcyclohexane and CO_2 + toluene systems at temperatures from 20 to -40°F and pressures to 1500 psia. The obtained values of k_{12} were 0.1719 and 0.1339, respectively. Comparison of the solubilities of CO_2

indicates greater solubility in the aromatic than in the naphthenic solvent. The authors offer no speculation as to whether these results could be extrapolated to other aromatic and naphthenic solvents with identical carbon and substituent arrangements.

Lin (18) evaluated binary interaction parameters for the Peng-Robinson equation for binaries of CO_2 and paraffins from methane through C_{18}, and selected one- and two-ring aromatic and naphthenic solvents. The criterion for optimization was minimization of the sum of deviations between calculated and experimental data for compositions (K-values). Values of k_{12} ranged from 0.093 to 0.136 for the normal paraffins and 0.078 to 0.180 for the naphthenics and aromatics. These variations appear to be random and the author recommends the use of 0.125 as a general parameter which adequately minimizes deviations from experimental data in most cases.

A previously unused criterion for k_{12} optimization is introduced by Paunovic et al. (19). The sum of absolute relative deviations between calculated vapor and liquid component fugacities, according to the author, would not involve iterations in calculating objective function values, and would thus provide a considerable reduction in computing time requirement. Binary interaction coefficients were calculated via this procedure for twelve binary systems consisting of hydrocarbons with CO_2, N_2, H_2 and H_2S. The mutual proximity of the k_{12} values obtained by the proposed method and the more conventional bubble point method was proven in this study, since in no case did the difference in k_{12} exceed 0.01. Of particular interest was the generation of k_{12} for the ethane + benzene data obtained by Ohgaki et al. (14) at 25°C. The authors obtained a value of 0.036 using their new method.

The use of two binary interaction parameters is recommended in a study by Turek et al. (21), for use with the generalized Redlich-Kwong equation. Within Turek's study a reference is made to the work of Yarborough (20), who recommends the use of k_{12} for hydrocarbon-nonhydrocarbon binaries as well as hydrocarbon binaries in which there exists a large disparity between the sizes of the two hydrocarbons. The latter recommendation will be evaluated in the present study.

Turek et al. (21) recommended a second binary interaction parameter l_{12}, to be introduced into the mixing rule for the calculation of the parameter "b" in the generalized Redlich-Kwong equation for modeling of CO_2 + hydrocarbon binaries. Their approach to parameter optimization employed a Marquardt optimization routine in which k_{12} and l_{12} were determined simultaneously along with Ω_{a,CO_2} and Ω_{b,CO_2}, pure component parameters for CO_2 which are generalized functions of reduced temperature and accentric factor and are used in calculation of the parameters a and b in the generalized Redlich-Kwong equation. The binary interaction parameters were made continuous functions of the hydrocarbon acentric factor and were optimized through simultaneous regression of several CO_2 + hydrocarbon systems. The optimization technique minimized fugacity deviations thus:

$$F = \sum_{k} \sum_{l=1}^{n_k} \sum_{i=1}^{2} [f_i^{V} (T,P,y_i^{exp}) - f_i^{L} (T,P,x_i^{exp})]_{k,l}^{2} \qquad (2.4)$$

where index l refers to an individual vapor-liquid equilibrium data point for binary system k, index i refers to an individual component in the binary, and n_k is the total number of points in the system k. This objective function requires exclusively vapor-liquid equilibrium data.

Optimum values of interaction parameters were obtained from the solubility data of this work using a regression package modified and explained by Gasem (25). The optimality criterion used by this package involves minimization of the weighted error in bubble-point pressures:

$$S = \sum_{i=1}^{N} \frac{(P_i^{exp} - P_i^{calc})^2}{\varepsilon_{bp}^2} \qquad (2.5)$$

where P_i^{exp} and P_i^{calc} are the experimental and calculated pressures for experiment "i" in a series of N experiments on a given binary system. ε_{bp} refers to the uncertainty associated with the experimental measurement of bubble-point pressure. A detailed description of the evaluation of this uncertainty is given at the close of Chapter III of this work.

CHAPTER III

REVIEW OF PHASE EQUILIBRIUM THERMODYNAMICS

Classical thermodynamics provides the mathematical framework for optimization of existing equations of state using the data obtained in this study. A review of phase equilibrium thermodynamics will develop the concepts used in current equations governing volumetric properties of binary systems.

In order for equilibrium to exist between any number of phases in an isolated system (constant energy and mass) of any number of components, the following criteria must be satisfied (22):

1) The entropy of the system is at its maximum value, and any differential change (with the system energy and moles of any component "i" held constant) will result in a differential entropy change, dS, of zero.
2) The first and second laws of thermodynamics, as applied to this system, mandate that for the differential change,

$$dU = TdS - PdV + \sum_{i=1}^{N} \tilde{\mu}_i \, dn_i \qquad (3.1)$$

with

U = system internal energy

T = system temperature

S = system entropy

P = system pressure

V = system volume

$\tilde{\mu}_i$ = chemical potential of species "i" in a mixture

n_i = number of moles of component "i".

If this equation is applied to two phases in equilibrium, vapor (denoted by') and liquid ("), the result is:

$$dU' = T'dS' - P'dV' + \sum \tilde{\mu}_i{}' dn_i{}' \qquad (3.2)$$

$$dU'' = T''dS'' - P''dV'' + \sum \tilde{\mu}_i{}'' dn_i{}'' . \qquad (3.3)$$

Since the net changes in internal energy, mass, and volume of an isolated system are necessarily zero at equilibrium, the above two equations may be rearranged and the above constraints applied to yield

$$dS = \left(\frac{1}{T'} - \frac{1}{T''}\right) dU' + \left(\frac{P'}{T'} - \frac{P''}{T''}\right) dV' - \sum \left(\frac{\tilde{\mu}_i{}'}{T'} - \frac{\tilde{\mu}_i{}''}{T''}\right) dn_i{}' . \qquad (3.4)$$

Recalling that the net entropy change of the system at equilibrium must also be zero, the coefficients of the terms of the right-hand side of the equation (3.4) are forced to zero. This further necessitates that, at equilibrium,

$$T' = T'' \tag{3.5}$$

$$P' = P'' \tag{3.6}$$

$$\tilde{\mu}_i' = \tilde{\mu}_i'' \qquad (i = 1,2,.....,N) \tag{3.7}$$

These are the criteria for equilibrium: equal pressures, temperatures and chemical potentials in each phase present. To apply the above relations in calculation of equilibrium properties, a mathematical model must be employed which relates the chemical potentials of the species in the equilibrium mixture to measureable system parameters (pressure, temperature, molar volume, phase compositions). The chemical potential is not easily manipulated in practical applications and is replaced by fugacity, which is easily described in terms of the above parameters.

To develop the concept of fugacity, the Gibbs energy of a phase, G, is considered (22)

$$dG = -SdT + VdP + \sum\tilde{\mu}_i \, dn_i \tag{3.8}$$

and from this expression the following Maxwell relation is obtained:

$$\left(\frac{\partial\tilde{\mu}_i}{\partial P}\right)_{T,n} = \tilde{V}_i \tag{3.9}$$

This expression reveals that chemical potential is an inconvenient parameter to work with in that is increases without bound as the pressure approaches zero.

For an ideal gas,

$$\left(\frac{\partial \tilde{\mu}_i}{\partial P}\right)_{T,n} = \frac{RT}{P} \qquad (3.10)$$

Upon integration, this expression becomes

$$\mu_i - \mu_i^{+} = RT \ln (P/P^{+}) \qquad (3.11)$$

where μ_i^{+} denotes the chemical potential of pure species i at a reference pressure P^{+}.

For an ideal gas mixture, equation (3.11) becomes:

$$\tilde{\mu}_i - \overset{+}{\mu_i} = RT \ln (Py_i\ /P^{+}). \qquad (3.12)$$

In a nonideal solution, the pressure exerted by species "i" would deviate from the partial pressure calculated by Dalton's law. To account for this deviation, the fugacity of species "i" (f_i) replaces the product Py_i in equation (3.12):

$$\tilde{\mu}_i - \overset{+}{\mu_i} \equiv RT \ln (f_i/P^{+}). \qquad (3.13)$$

Furthermore,

$$\lim_{p \to 0} (f_i/Py_i) \equiv 1.0 \qquad (3.14)$$

Equation (3.13), when applied to liquid and vapor phases, becomes

$$\tilde{\mu}_i' = \mu_i^{+} + RT \ln (f_i'/P^{+}) \qquad (3.15)$$

$$\tilde{\mu}_i'' = \mu_i^+ + RT \ln (f_i''/P^+). \qquad (3.16)$$

Recalling that chemical potential of each component is the same in all phases at equilibrium, the two equations may be combined to yield:

$$f_i' = f_i''. \qquad (3.17)$$

Fugacities of components in liquid and vapor phases are rarely described by direct definition. More often they are represented as deviations from ideal behavior, in the form of fugacity coefficients or activity coefficients. A fugacity coefficient of a species "i", ϕ_i, is defined thus:

$$\phi_i = \frac{\text{actual fugacity of component "i"}}{\text{fugacity of component "i" in ideal gas mixture}}$$

$$\text{or } \phi_i = \frac{f_i}{Py_i} \qquad (3.18)$$

In the liquid phase, ideality is usually equated with enthalpy and volume changes of zero upon mixing and random distribution of molecules. Fugacity of species i in such a liquid is given by:

$$f_i = x_i f_i^{oL} \qquad (3.19)$$

where

f_i^{oL} is the fugacity of component "i" in the pure liquid state at the system temperature and pressure.

The liquid fugacity is most often described in terms of the "activity coefficient, γ_i," thus (22):

$$\gamma_i = \frac{\text{actual fugacity of component "i"}}{\text{fugacity of component "i" in ideal mixture}} \tag{3.20}$$

or $$\gamma_i = \frac{f_i}{x_i f_i^{oL}}$$

Deviations of the volumetric behavior of gases from ideal behavior are similarly described by the gas compressibility factor (Z) which is defined as the ratio of the actual gas volume to the ideal gas volume at the system temperature and pressure (22).

$$Z = \frac{\text{actual gas volume}}{\text{ideal gas volume}} = \frac{\overline{V}}{RT/P} = \frac{P\overline{V}}{RT} \tag{3.21}$$

In terms of measurable parameters, the fugacity coefficient may be expressed as follows (22):

$$\ln \phi_i = \frac{1}{RT} \int_0^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln Z \tag{3.22}$$

or $$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP \tag{3.23}$$

The activity coefficient is related to measurable system parameters by the expression:

$$\ln \gamma_i = \frac{1}{RT} \int_0^P (\tilde{V}_i - \overline{V}_i)\, dP \tag{3.24}$$

where

$\tilde{V}_i$ = partial molar volume of component "i"

$\overline{V}_i$ = molar volume of pure component "i"

This study utilized two equations of state as models for the behavior of two-component mixtures at vapor-liquid equilibrium. Subsequently, the fugacity coefficients were evaluated using equation (3.22) and liquid and vapor fugacities were calculated.

The equations of state used in the study were Soave's modification of the Redlich-Kwong equation of state (SRK) and the Peng-Robinson equation of state (PR).

The Soave-Redlich-Kwong equation of state is of the form (23):

$$P = \frac{RT}{\overline{V} - b} - \frac{a(T)}{\overline{V}\ (\overline{V} + b)} \tag{3.25}$$

with

$$a(T) = \sum_i \sum_j y_i\ y_j\ a_{ij} \tag{3.26}$$

$$b = \sum_i \sum_j y_i\ y_j\ b_{ij} \tag{3.27}$$

$$a_{ij} = (a_i a_j)^{1/2}\ (1 - k_{ij}) \tag{3.28}$$

$$b_{ij} = 1/2\ (b_i + b_j)\ (1 + l_{ij}) \tag{3.29}$$

$$a_i = 0.4275\ R^2\ \frac{T_{ci}^{\ 2}\alpha_i(T_{ri})}{P_{ci}} \tag{3.30}$$

$$\alpha_i\ (T_{ri}) = [1 + m_i(1 - T_{ri}^{\ 0.5})]^2 \tag{3.31}$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^{\ 2} \tag{3.32}$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \tag{3.33}$$

with $\overline{V}$ = molar volume of fluid

T = system temperature, absolute

R = universal gas constant

T_{ci} = critical temperature of component i

P_{ci} = critical pressure of component i

T_{ri} = reduced temperature of component i, T/T_{ci}

ω_i = Pitzer acentric factor of component i

Here k_{ij} and l_{ij} are empirical adjustment factors, referred to usually as "binary interaction parameters", which may be used to optimize the fit of the SRK equation of experimental data.

The Peng-Robinson equation is of the form (24):

$$P = \frac{RT}{\overline{V} - b} - \frac{a(T)}{\overline{V}(\overline{V} + b) + b(\overline{V} - b)} \tag{3.34}$$

with a(T), b, a_{ij} and b_{ij} evaluated as in the SRK equation and

$$a_i = 0.45724 \frac{R^2 T_{ci}{}^2 \alpha_i(T_{ri})}{P_{ci}} \tag{3.35}$$

$$b_i = 0.07780 \frac{RT_{ci}}{P_{ci}} \tag{3.36}$$

$$\alpha_i = [1 + K(1 - T_{ri}{}^{0.5})]^2 \tag{3.37}$$

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{3.38}$$

The optimum values of k_{ij} and l_{ij}, i.e., the values of these factors which result in optimized fit of the equation of state to experimental data, were one goal of this study. These interaction parameters (k_{ij}, l_{ij}) were calculated by nonlinear regression of the experimental solubility data for the binaries studied, to minimize a deviation function, S, the weighted sum of errors in predicted bubble-point pressures:

$$S = \sum_{i=1}^{N} \frac{(P_i^{exp} - P_i^{calc})^2}{\varepsilon_{bp}^2} \tag{2.4}$$

with

$$\varepsilon_{bp}^2 = \varepsilon_p^2 + \left(\frac{\partial p}{\partial x}\right)^2 \varepsilon_{x1}^2 \tag{3.39}$$

ε_p uncertainty in pressure gauge reading

x_i = mol fraction of solute in the liquid phase

ε_{x_1} = uncertainty of the mol fraction of solute.

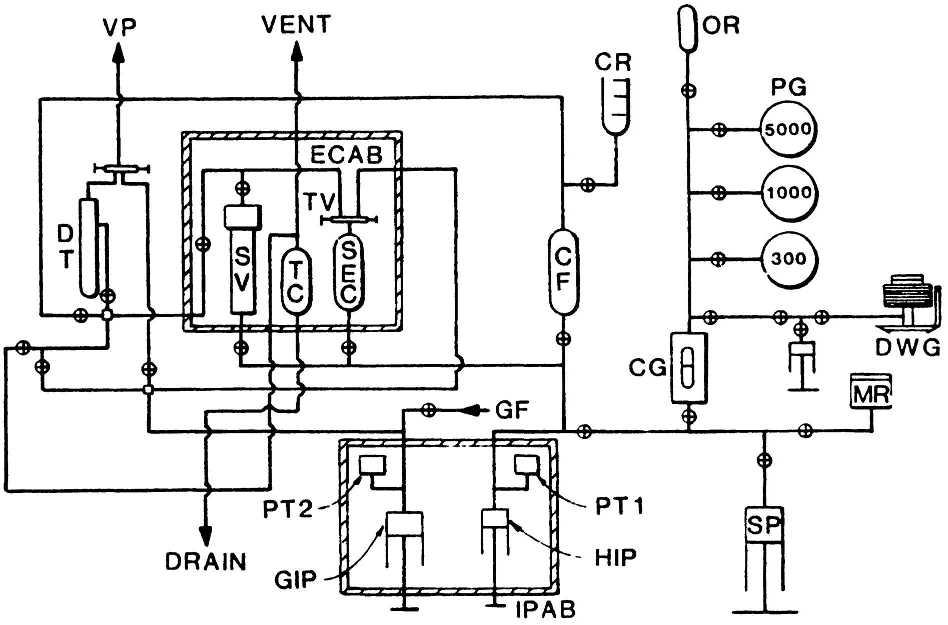
A detailed explanation of the data reduction techniques used in this study may be found in the work of Gasem (25). Evaluation of each term on the right-hand side of equation (3.39) is presented in Chapter V of this work.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus used in this study was designed, built and previously operated by Mr. Mark Barrick (1) and Mr. McRay Anderson (26). No modifications have been performed on the apparatus during the course of this experimentation. An extensive description of the apparatus is given in the Master of Science theses by Anderson and Barrick (1,26).

The bubble points of the binary mixtures are measured utilizing the stirred equilibrium cell (referred to as SEC in Figure 1). This cell is a commercial stainless steel tubular reactor vessel with inlets at the top and bottom. At the beginning of a data run the equilibrium cell is partially filled with mercury with an evacuated space of about 20 cm^3 at the top of the cell. An arbitrary amount of solvent is injected into this space (typically 5-6 cm^3). The volume of solute gas needed to produce a specific solute mole fraction is calculated and this amount of solute gas is injected. After completing these injections, the effective volume of the cell is decreased by injection of incremental amounts of mercury into the cell with the hydrocarbon injection pump (HIP) and the cell pressure is recorded after each injection. The cell pressure is monitored as a function of the amount of mercury injected. At the bubble point, the change in pressure with respect to volume of injected mercury increases abruptly. The bubble point pressure is



CF - CLEANING FLUID CYLINDER
CG - MERCURY-OIL CONTACT GAUGE
CR - CLEANING FLUID RESERVOIR
DT - DEGASSING TRAP
DWG - DEAD-WT. GAUGE
ECAB - EQUILIBRIUM CELL AIR BATH
GF - GAS FEED LINE
GIP - GAS INJECTION PUMP
HIP - HYDROGEN INJECTION PUMP
IPAB - INJECTION PUMP AIR BATH
MR - MERCURY RESERVOIR

OR - OIL RESERVOIR
PG - PRESSURE GAUGES
PT1 - PRESSURE TRANSDUCER
PT2 - PRESSURE TRANSDUCER
SEC - STIRRED EQUILIBRIUM CELL
SP - SCREW PUMP (FOR CLEANUP ONLY)
SV - SOLVENT STORAGE CYLINDER
TC - TRASH CYLINDER
TV - THREE-WAY VALVE
VP - TO VACUUM PUMP

Figure 1. Schematic Diagram of Bubble-Point Apparatus

identified as the pressure at which this sharp discontinuity occurs.

The experimental procedures used in this study have remained the same with two exceptions. The first of these is that the gas pressure transducer (referred to as PT2 in Figure 1) is now periodically calibrated along with the hydrocarbon pressure transducer (PT1).

The hydrocarbon transducer calibration procedure is described in the aforementioned theses. This procedure is executed as prescribed. Then, the following procedure for calibration of the gas pressure transducer is executed:

1. The Ruska dead-weight gauge is isolated from the hydrocarbon pressure transducer by closing valves DW1, DW2, DW3, IV1, and V10. (Refer to Figure 2.)
2. The gas and hydrocarbon systems, normally isolated from one another, are coupled through a gas-mercury interface located inside the temperature-controlled pump bath. The interface consists of 100 ml Hoke cylinder containing 50 ml of mercury. During calibration, valve V12 is opened, coupling the gas system with the interface, and valve V13 is opened, completing the coupling of the gas and hydrocarbon systems through the interface and equalizing the pressures in both systems.
3. The combined system is charged with helium to approximately 1500 psia, and the system is allowed to equilibrate. Then, the gas and hydrocarbon pressure transducer readings are recorded. A correction factor of 1.8 psi is subtracted from the hydrocarbon transducer reading to counter the head pressure contributed by the mercury in the gas-mercury interface gauge. A new variable

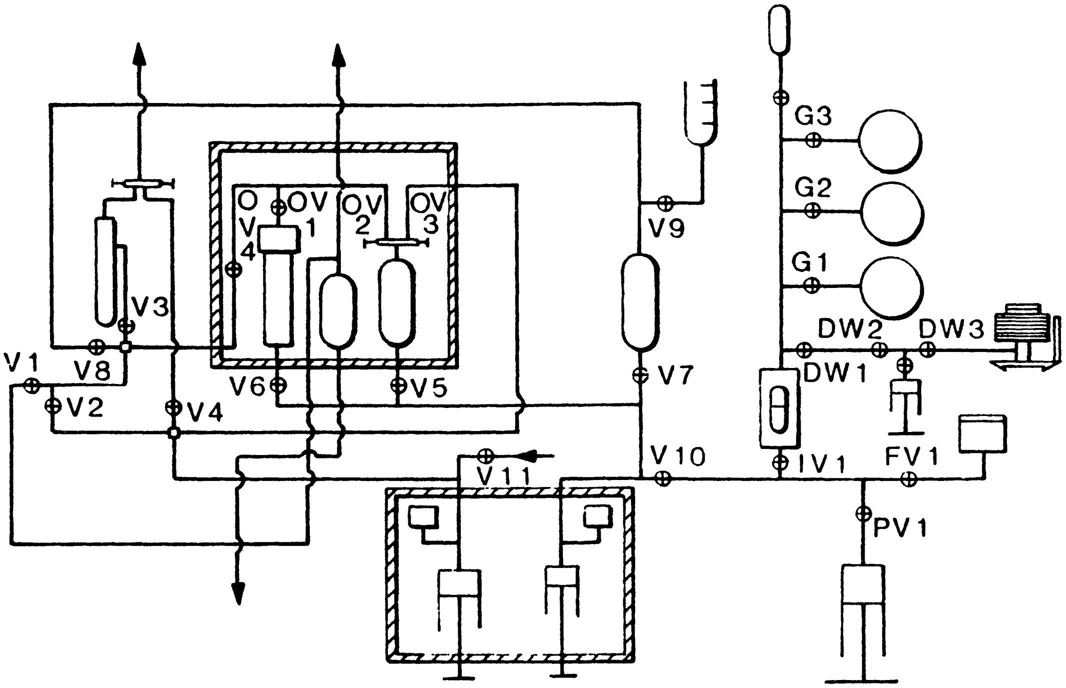


Figure 2. Schematic Diagram for Valve Identification

Δ, is defined as:

$$\Delta = P_H - 1.8 - P_G \qquad (4.1)$$

where:

P_H = hydrocarbon pressure transducer reading.

P_G = gas pressure transducer reading.

4. The pressure in the new combined gas-hydrocarbon system is lowered in increments of approximately 80 psi by bleeding helium from the system through V2. After each pressure decrease the system is allowed to equilibrate for approximately ten minutes and values of P_H, P_G, and Δ are then recorded. This process is continued until the pressure is decreased to atmospheric.
5. The hydrocarbon pressure transducer calibration procedure outlined by Anderson and Barrick yields values of a correction factor, δ, which is defined thus:

$$\delta = P_D - P_H \qquad (4.2)$$

where

P_D = accurate dead-weight gauge pressure.

P_H = hydrocarbon pressure transducer reading.

By combining expressions for Δ and δ an expression is determined which corrects the gas transducer reading to the accurate dead-weight gauge pressure:

$$P_D - P_G = \Delta(P_G) + \delta(P_G + \Delta) \qquad (4.3)$$

where

$\Delta(P_G)$ = the value of Δ evaluated at P_G.

$\delta(P_G + \Delta)$ = the value of δ evaluated at $P_G + \Delta$.

The data set consisting of P_H and corresponding δ is used to fit a cubic polynomial in which P_H and δ are the independent and dependent variables, respectively.

An expression for Δ consisting of a cubic polynomial in P_G is obtained in a similar fashion. The two analytical expressions are then combined to yield a third expression which gives $P_D - P_G$ as a function of P_G. These cubic polynomials typically fitted the tabulated transducer corrections with RMS error of less than 0.1 psi, with maximum absolute deviations of less than 0.2 psi.

The second modification in the experimental procedure deals with the computer program used in calculation of correction factors for the hydrocarbon pressure transducer. Anderson and Barrick included a head correction factor of -8.7 psi owing to the fact that there existed a mercury head of this magnitude between the level of the centerline of the equilibrium cell and the level of the hydrocarbon transducer. The correction factor calculated by the program would thus account for this head correction as well. The head correction was removed from the program and is now subtracted manually from each bubble-point pressure obtained.

Ethane requires somewhat different injection conditions than CO_2. Appendix A explains the analysis of uncertainties associated with ethane density and how it is calculated as a function of pressure. The resulting plot is shown on the following page (Figure 3) for percent uncertainty in ethane density as a function of pressure at 50°C. The plot indicates that this uncertainty is minimized at pressures between approximately 500 and 600 psia. Injection of ethane in this pressure range is preferable because it minimizes the uncertainty in the ethane density and in turn minimizes uncertainty in the material balance calculation of composition.

A small section of the tubing in the gas system is exposed to the atmosphere. This is the section which links the gas injection pump, inside the pump bath, to the gas injection valve inside the oven. Between these two enclosed, temperature-controlled environments is a gap of about six inches through which the tubing passes. Therefore the ethane should be injected at a pressure lower than its saturation pressure at room temperature (approximately 570 psia at 77°F) to avoid liquid formation in this section of the line. The ethane injection pressure is kept below 530 psia in all cases to maintain a safe margin from this pressure.

A computer program is used for the determination of ethane density. The program utilizes an equation of state developed for ethane by the U.S. National Bureau of Standards(36) and calculates ethane

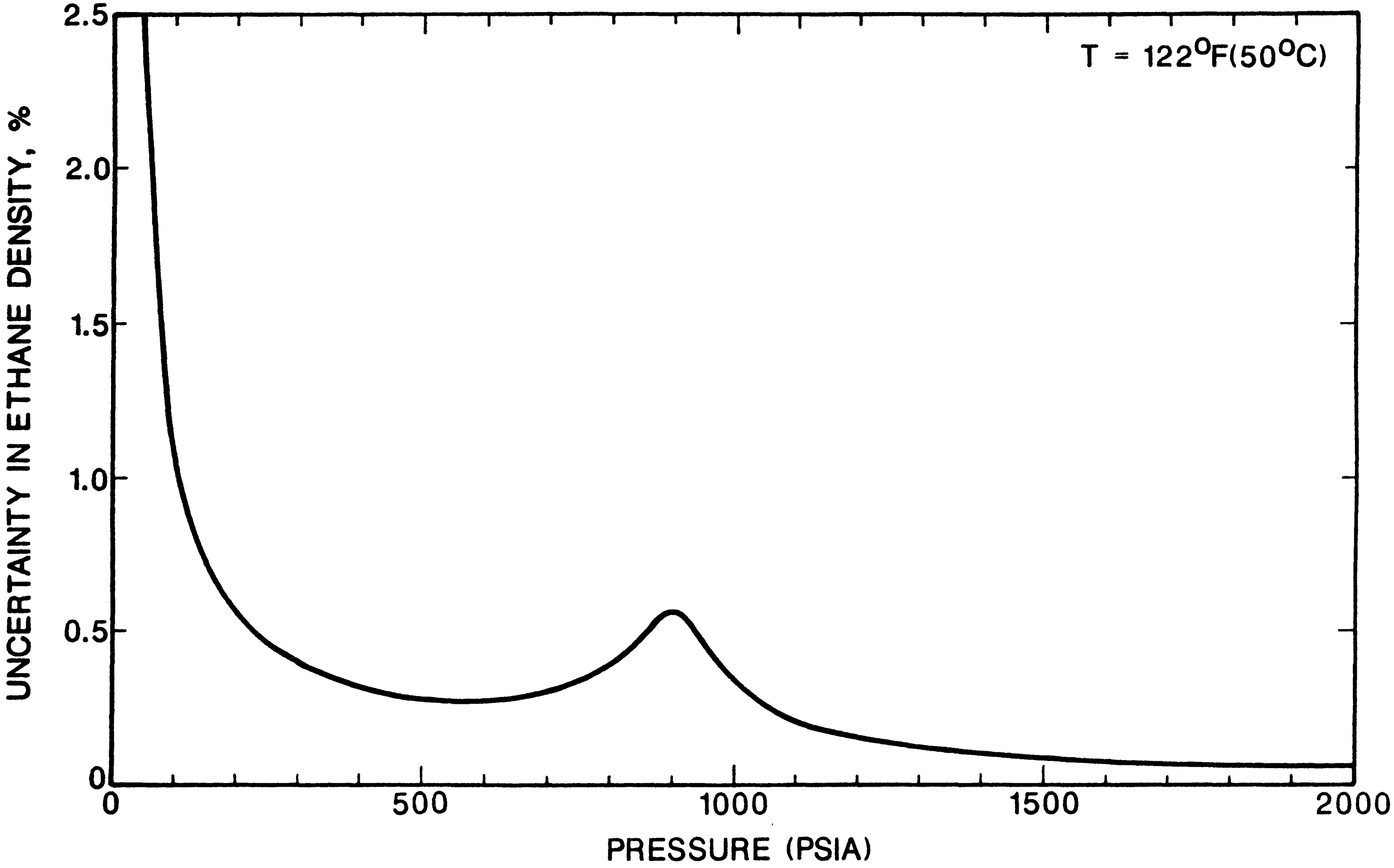


Figure 3. Uncertainty Associated with Measurement of Ethane Density

density as a function of the injection pressure and temperature. Details and a listing of the program are given in Appendix C.

Chemicals

All materials used in this study were obtained from commercial suppliers and no further purification was attempted. The suppliers and claimed purities of the chemicals are are given in Table II.

TABLE II

CHEMICALS AND THEIR PURITIES

Chemical	Source	Stated Purity (Mole %)
Carbon Dioxide	Union Carbide Company	99.99
Ethane	Matheson	99.99
n-Pentane	Burdick and Jackson Labs	Reagent Grade
n-Decane	Aldrich Chemical Company	99+
n-Dodecane	Alfa Products	99+
n-Tetradecane	Alfa Products	99
Cyclohexane	Aldrich Chemical Company	99.9
trans-Decalin	Aldrich Chemical Company	99+
Benzene	Aldrich Chemical Company	99.9
Naphthalene	Aldrich Chemical Company	99+
Phenanthrene	Aldrich Chemical Company	98+
Pyrene	Aldrich Chemical Company	99+

CHAPTER V

ANALYSIS OF ERRORS IN EXPERIMENTAL DATA

Two types of errors are commonly encountered when measuring experimental quantities: random errors which result from non-recurring aberrations and systematic errors which involve repeated, uniform flaws in the experimental procedure or measurement of experimental quantities. Random errors can be treated in a statistical fashion, but systematic errors must be remedied by eliminating erroneous methods of measurement.

In this study, vapor pressures of pure components were measured periodically to safeguard against undetected systematic error. In addition, the CO_2 + benzene system was studied at 40°C owing to the abundance of previous experimental data at this temperature. A significant deviation from the relatively narrow region (Figure 4) in which these data overlap would indicate the presence of a systematic error in one or more experimental measurements. The data obtained in this study fall on the upper limit of this region but agree within the limits of experimental uncertainty.

Analysis of random error begins with the evaluation of prime errors in quantities measured during an experiment, such as pressure or temperature. Random error is evaluated by determining how these errors propagate throughout calculations using these measured quantities, such as the calculation of a mole fraction.

Following a series of calibrations of the thermometers, precision displacement pumps and transducers used in this study the prime errors were estimated to be:

$$\varepsilon_T = 0.05 \text{ K} \tag{5.1}$$

$$\varepsilon_v = 0.0025 \text{ cm}^3 \tag{5.2}$$

$$\varepsilon_p = 0.05 \text{ psi} \tag{5.3}$$

where ε_T, ε_v and ε_p are the uncertainties associated with measurements of temperature, volume and pressure, respectively. The temperature estimate is based on the ability of the temperature controller to maintain a constant set point. The pressure transducers used in data aquisition were coupled with digital readouts which display pressures to 0.1 psia. The uncertainty in pressure was consequently estimated to be 0.05 psia, since a pressure could vary by this amount with no change in the pressure reading. Similarly, the precision injection pumps used in this study were graduated to 0.005 cm^3. The pump piston position could vary by 0.0025 cm^3 before the change would be discernable.

The estimated error in liquid mole fraction for this study may be calculated using the following equation (1):

$$\varepsilon_{x_1} = x_1 x_2 \left[(\varepsilon_{\rho_1}/\rho_1)^2 + (\varepsilon_{v_1}/\textstyle\sum V_{i_1})^2 + (\varepsilon_{\rho_2}/\rho_2)^2 + (\varepsilon_{v_2}/v_2)^2 \right]^{1/2} \tag{5.4}$$

where subscripts 1 and 2 refer to the solute and solvent, respectively.

The uncertainty in CO_2 density (denoted above by ε_{ρ_1}) was estimated to be 0.15% based on the variations of temperature and pressure in the uncertainty program of Appendix A. The uncertainty in ethane density was calculated with the same program using appropriate parameters (critical properties, acentric factor) for ethane. The uncertainty for ethane was estimated to be 0.28%.

Anderson and Barrick (1,26) performed two density measurements on liquid pyrene at 160°C. A difference of 0.003 g/cm^3 was found between the two measurements, and was assumed to be the maximum error in hydrocarbon density measurement.

A data run for a CO_2 system typically consisted of a hydrocarbon injection volume of 7 cm^3 and three CO_2 injections of 3 cm^3 each. Substituting these values, and the estimated CO_2 and pyrene densities into equation (5.4) yields:

$$\varepsilon_{x_{CO_2}} = 0.0031\ x_1 x_2 \tag{5.5}$$

Data runs for ethane systems necessitated injection of somewhat larger amounts of ethane, due to the lower molecular weight and injection pressure of the ethane. Typically, the total amount of ethane injected in a given run was 35 cm^3. Substituting this volume and the estimated uncertainty in ethane density into equation (5.4) yields:

$$\varepsilon_{x_{C_2H_6}} = 0.0039\ x_1 x_2\ . \tag{5.6}$$

Random error in bubble-point pressures due to prime and propagated errors may be estimated by use of the following equation (26):

$$\varepsilon_{pb}^{2} = \varepsilon_{p}^{2} + (\partial P/\partial x_1)^2\, \varepsilon_{x_1}^{2} + (\partial P/\partial T)^2 \varepsilon_T^{2}. \tag{5.7}$$

The maximum error in liquid mole fraction is given by setting $x_2 = x_1 = 0.5$ in equations (5.5) and (5.6). If the resulting expression is substituted into equation (5.7) and the temperature term is assumed negligible,

$$\varepsilon_{pb}^{2} = 0.05^2 + (0.0008)^2\, (\partial P/\partial x_1)^2 \tag{5.8}$$

for CO_2 systems and

$$\varepsilon_{pb}^{2} = 0.05^2 + (0.0010)^2\, (\partial P/\partial x_1)^2 \tag{5.9}$$

for ethane systems. The maximum error in bubble point pressure was calculated for each system by substituting the maximum value of $\partial P/\partial x_1$ encountered in that system into equations (5.8) or (5.9). The results are shown in Table III.

The value of $\partial P/\partial x_1$ may be evaluated either analytically or numerically: an analytical solution would require the differentiation with respect to solute mole fraction of the SRK (or PR) equation of state and substitution of bubble-point pressure measured for a system and the solute mole fraction (x_1) corresponding to that pressure. In this work $\partial P/\partial x_1$ was estimated simply by calculating the difference between the highest and second highest bubble point pressures measured for a system, calculating the difference between the solute mole fractions corresponding to these pressures, and dividing the pressure

TABLE III

MAXIMUM EXPECTED ERRORS IN BUBBLE POINT PRESSURES

System	Maximum Expected Error (psi)
CO_2 + Benzene	1.3
CO_2 + n-Decane	1.9
CO_2 + n-Dodecane	2.7
CO_2 + n-Tetradecane	3.2
Ethane + Decane	0.9
Ethane + Cyclohexane	2.2
Ethane + Benzene	2.7
Ethane + trans-Decalin	3.2
Ethane + Naphthalene	4.6
Ethane + Phenanthrene	11.8
Ethane + Pyrene	9.6

difference by the solute mole fraction difference.

Table III shows that the maximum expected error is greater for ethane + phenanthrene than for ethane + pyrene, even though ethane is less soluble in pyrene than in phenanthrene. This occurs because bubble point pressures as high as 1700 psia were measured for ethane + phenanthrene but pressures to only 1450 psia were measured for ethane + pyrene. The value of $\partial P/\partial x_1$ increases with pressure, and the maximum value of $\partial P/\partial x_1$ found for ethane + phenanthrene was sufficiently higher than that found for ethane + pyrene to result in a greater value of ε_{pb} for ethane + phenanthrene.

CHAPTER VI

EXPERIMENTAL RESULTS AND DISCUSSION

This study began with the measurement of the vapor pressure of propane at 40°C to determine whether the apparatus could reproduce known vapor pressure data. The propane vapor pressure was found to be 199.3 psia. Use of Antoine equation constants determined by Sage and Lacey (28) results in a calculated value of 198.5 psia. This discrepancy is acceptable since in this study accuracy is claimed to within 2 psi.

CO_2 + Benzene

The CO_2 + benzene binary system was investigated next at 40°C. This particular system and temperature were selected since six other investigators had performed studies and thus a large amount of data was available for comparison.

The data obtained in this study for the CO_2 + benzene system are listed in Table IV, and the data of Table IV are compared with the data of the previous researchers in Figure 4. In this figure, the ordinate is the bubble-point pressure less the vapor pressure of benzene at 40°C, divided by the corresponding CO_2 liquid mole fraction. Plots of this type magnify errors in uniformity of the data by the reciprocal of the CO_2 liquid mole fraction. The plots also show how the data deviate from Raoult's law. The negative slope in the plotted data indicates a negative deviation from Raoult's law.

TABLE IV

SOLUBILITY OF CO_2 IN BENZENE

Mole fraction CO_2	Pressure MPa	(psia)
-------------------------313.2 K (40°C, 104°F)-------------------------		
0.100	1.252	(181.7)
0.154	1.864	(270.4)
0.189	2.246	(325.8)
0.253	2.909	(422.0)
0.269	3.089	(448.1)
0.338	3.706	(537.6)
0.358	3.917	(568.3)
0.403	4.268	(619.1)
0.408	4.319	(626.5)
0.500	4.998	(725.1)
0.541	5.264	(763.7)
0.582	5.516	(800.2)

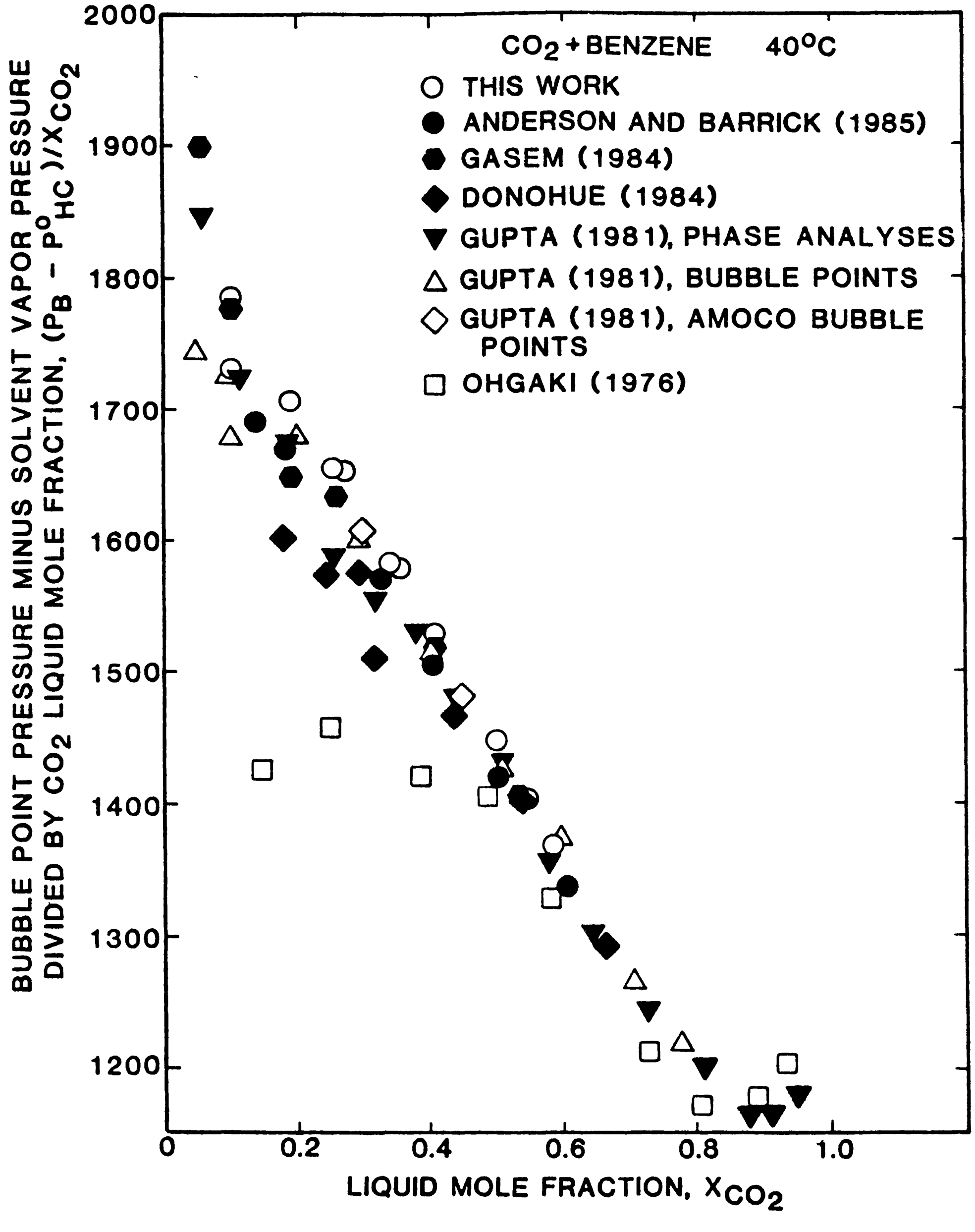


Figure 4. Comparison of Bubble-Point Data for CO_2 + Benzene at 40°C

The data obtained in this study appear to be marginally higher in pressure than the otherwise highest set of data, that obtained by Gasem (3). There exists a uniform, almost constant deviation of between 2 and 3 psi between the data of this work and that of Gasem. This discrepancy is not significant however and data from all sources seem to agree within reasonable limits, with the exception of the Ohgaki data which show strong negative deviations in pressure from the data of the other researchers, particularly at mole fractions less than 0.5.

The CO_2 + benzene data were used in a nonlinear regression program which determined the values of the binary interaction parameters, k_{12} and l_{12}, which optimized the fit of the Soave-Redlich-Kwong and Peng-Robinson equations of state to the experimental data. The program was also used to determine the optimum value of k_{12} in the case where l_{12} is set equal to zero. Table V reports these optimized parameters and resulting RMS and maximum errors in bubble point pressures for CO_2 + benzene as well as other CO_2-containing systems, the discussions of which follow in this section.

Examination of Table V reveals that the parameters for the SRK and PR equations are not significantly different in their optimized values. For this and all subsequent systems in this study, errors are reported only for the SRK equation parameters since errors generated by the PR equation parameters were essentially identical. Also evident is the superior fit of both equations to the experimental data when two binary interaction parameters were used in a prediction program to calculate solubilities (liquid mole fractions) for the data of the previous researchers. Figure 5 shows the deviation of the experimental solubility from the calculated solubility for every point in each data

TABLE V

SOAVE AND PENG-ROBINSON EQUATION OF STATE REPRESENTATIONS OF CO_2 SOLUBILITY DATA

Tempterature K (°F)	Soave Parameters (P-R Parameters)		Error in CO_2 Mole Fraction	
	k_{12}	l_{12}	RMS	Max.
--------CO_2 + Benzene--------				
313.2 (104)	0.073	0.033	0.003	0.006
	(0.072)	(0.034)		
	0.103	----	0.023	0.040
	(0.102)	----		
--------CO_2 + n-Dodecane--------				
323.2 (122)	0.128	-0.002	0.003	0.004
	(0.115)	(-0.001)		
	0.125	----	0.002	0.003
	(0.113)	----		
344.3 (160)	0.127	-0.002	<0.001	0.002
	(0.113)	(-0.001)		
	0.124	----	0.001	0.002
	(0.110)	----		
373.2 (212)	0.123	-0.004	<0.001	<0.001
	(0.107)	(-0.004)		
	0.117	----	0.002	0.003
	(0.102)	----		
323.2, 344.3 and 373.2	0.124	-0.001	0.004	0.006
	(0.110)	(0.000)		
	0.123	----	0.004	0.006
	(0.110)	----		

TABLE V (Continued)

Tempterature K (°F)	Soave Parameters (P-R Parameters)		Error in CO_2 Mole Fraction	
	k_{12}	l_{12}	RMS	Max.
CO_2 + n-Decane				
344.3 (160)	0.118	0.006	0.002	0.004
	(0.104)	(0.006)		
	0.125	----	0.004	0.006
	(0.112)	----		
CO_2 + n-Tetradecane				
344.3 (160)	0.107	0.000	0.004	0.007
	(0.093)	(0.001)		
	0.107	----	0.004	0.007
	(0.094)	----		

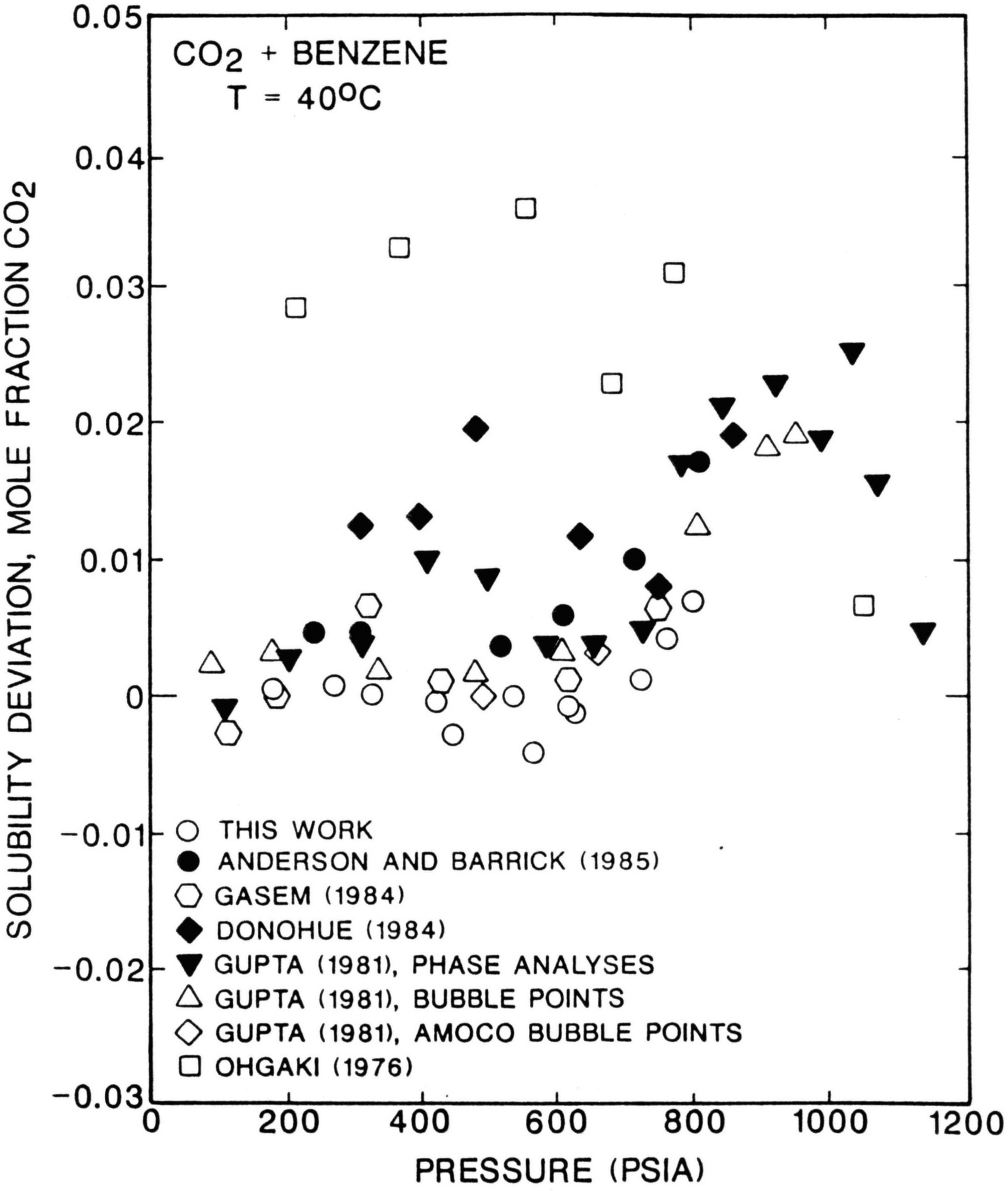


Figure 5. Comparison of Solubility Data for CO_2 + Benzene at 40°C

set. All previous data deviate positively from the data obtained in this study. However, the data of Gupta and Gasem typically differ by less than 0.005 mole fraction CO_2 from the data of this study. In light of this and the accuracy of the propane vapor pressure data, the experimental procedure was deemed satisfactory.

CO_2 + n-Dodecane

The CO_2 + n-dodecane system was studied next. Originally, the reason for this study was to measure data at 100°C to complement the data of Anderson and Barrick (9) at 50°C and 160°F (71.1°C. An isotherm was first measured at 50°C to check consistency with the data of Anderson and Barrick. However, considerable discrepancies were found to exist between the two data sets, as is shown in Figure 6. Differences approached 20 psi at low mole fractions ($x_{CO_2} = 0.1$) and narrowed with increasing mole fraction. The two bubble-point curves merged at approximately 0.4 liquid CO_2 mole fraction.

Results are quite similar for data obtained at 160°F. Differences are greatest (approximately 10 psi) at $x_{CO_2} = 0.1$ and convergence in the two data sets occurs at 0.4 liquid CO_2 mole fraction.

The last isotherm was measured at 100°C, to fulfill the original objective of the study of this system. The complete data set for the system is displayed in Table VI (optimized binary interaction parameters appear in Table V). Interaction parameters were calculated for each individual isotherm and for the lumped data of all three isotherms. Examination of the resulting errors in solubility reveal that error is minimized by the generation of interaction parameters for individual isotherms. This indicates that binary interaction parameters are indeed

TABLE VI

SOLUBILITY OF CO_2 IN N-DODECANE

Mole Fraction CO_2	Pressure MPa	(psia)
-----323.2 K (50°C, 122°F)-----		
0.103	0.986	(143.1)
0.202	2.084	(302.4)
0.325	3.539	(513.4)
0.359	3.969	(575.8)
0.482	5.570	(808.1)
0.501	5.825	(845.1)
-----344.3 K (71.1°C, 160°F)-----		
0.080	0.929	(134.7)
0.175	2.133	(309.5)
0.206	2.544	(369.0)
0.279	3.594	(521.4)
0.355	4.771	(692.1)
0.424	5.887	(854.0)
0.479	6.850	(993.8)
-----373.2 K (100°C, 212°F)-----		
0.092	1.279	(185.6)
0.177	2.596	(376.6)
0.239	3.597	(521.8)
0.360	5.845	(847.9)
0.377	6.184	(897.1)
0.453	7.782	(1128.9)
0.522	9.380	(1360.8)

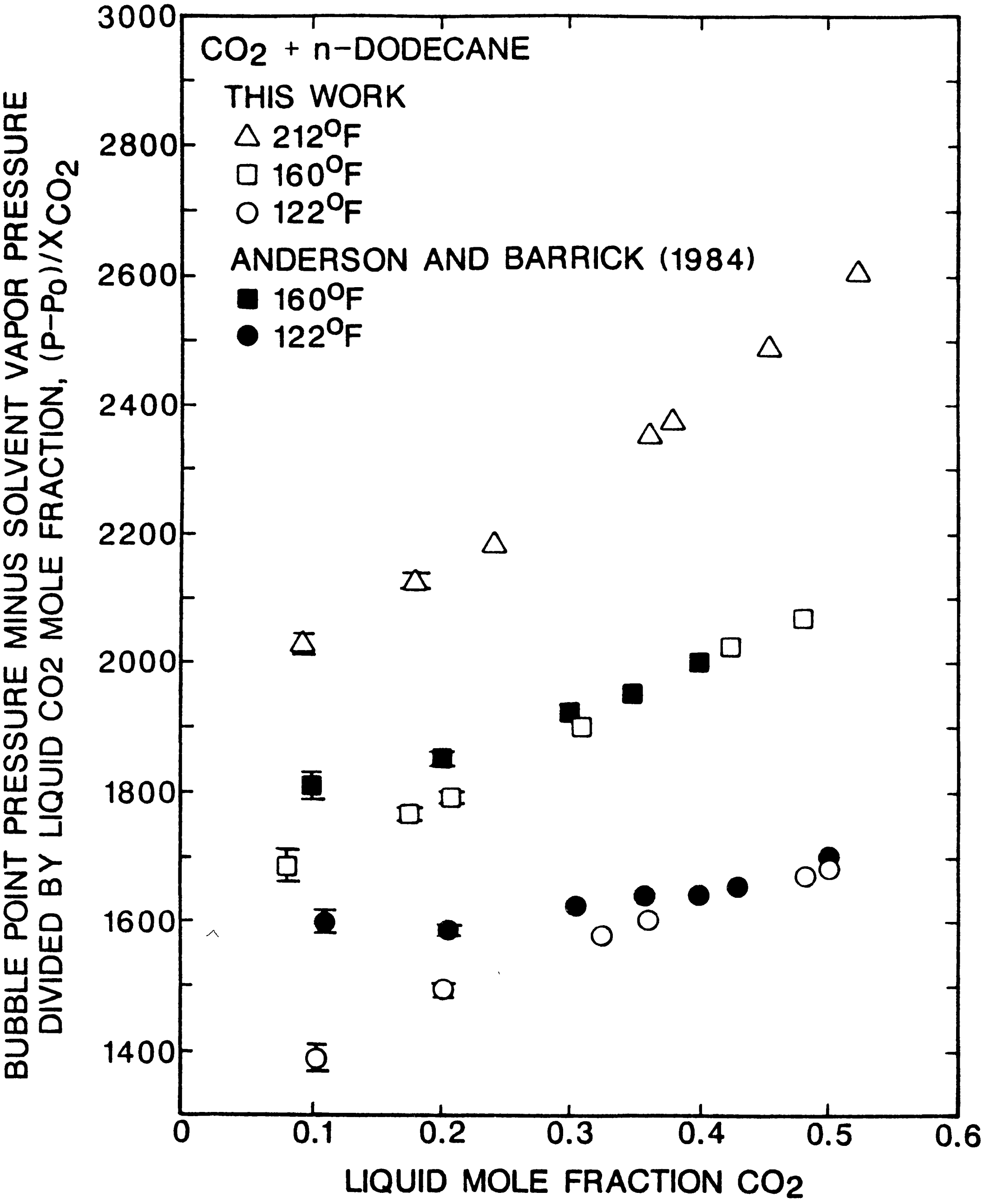


Figure 6. Comparison of Bubble-Point Data for CO_2 + n-Dodecane

functions of temperature.

The deviation of calculated from experimental solubility is shown for each point obtained in the present study and by Anderson and Barrick in Figure 7. Of particular interest is the exceptional fit of the SRK equation at 100°C. In no case does the deviation in solubility exceed 0.005 liquid mole fraction CO_2.

CO_2 + n-Decane

The third system investigated was CO_2 + n-decane at 160°F. This was done primarily to establish the ability of the experimental apparatus to reproduce data obtained by previous researchers, as with the study of the CO_2 + benzene system at 40°C. Three separate data runs were performed on this system; the resulting data are displayed in Table VII. The system had been investigated previously by both Reamer and Sage (7) and Nagarajan et al. (8), whose data are compared to those obtained in this study in Figure 8. The data of this work appears to be consistent with that of Sage at 0.1 liquid CO_2 mole fraction, and again at 0.6, but at mole fractions in between the data of Sage deviate positively from the data of this work, with a maximum deviation of about 15 psi occurring at a mole fraction of 0.33. The data of Nagarajan appear to deviate positively from the data of this work at a constant value of 15 psi.

The error bars shown in Figure 8, and all similar figures of this chapter, correspond to ±2 psi in bubble-point pressure for representation purposes. In each case, this pressure uncertainty is divided by the mole fraction, resulting in a decrease of the length of the bars with increasing mole fraction.

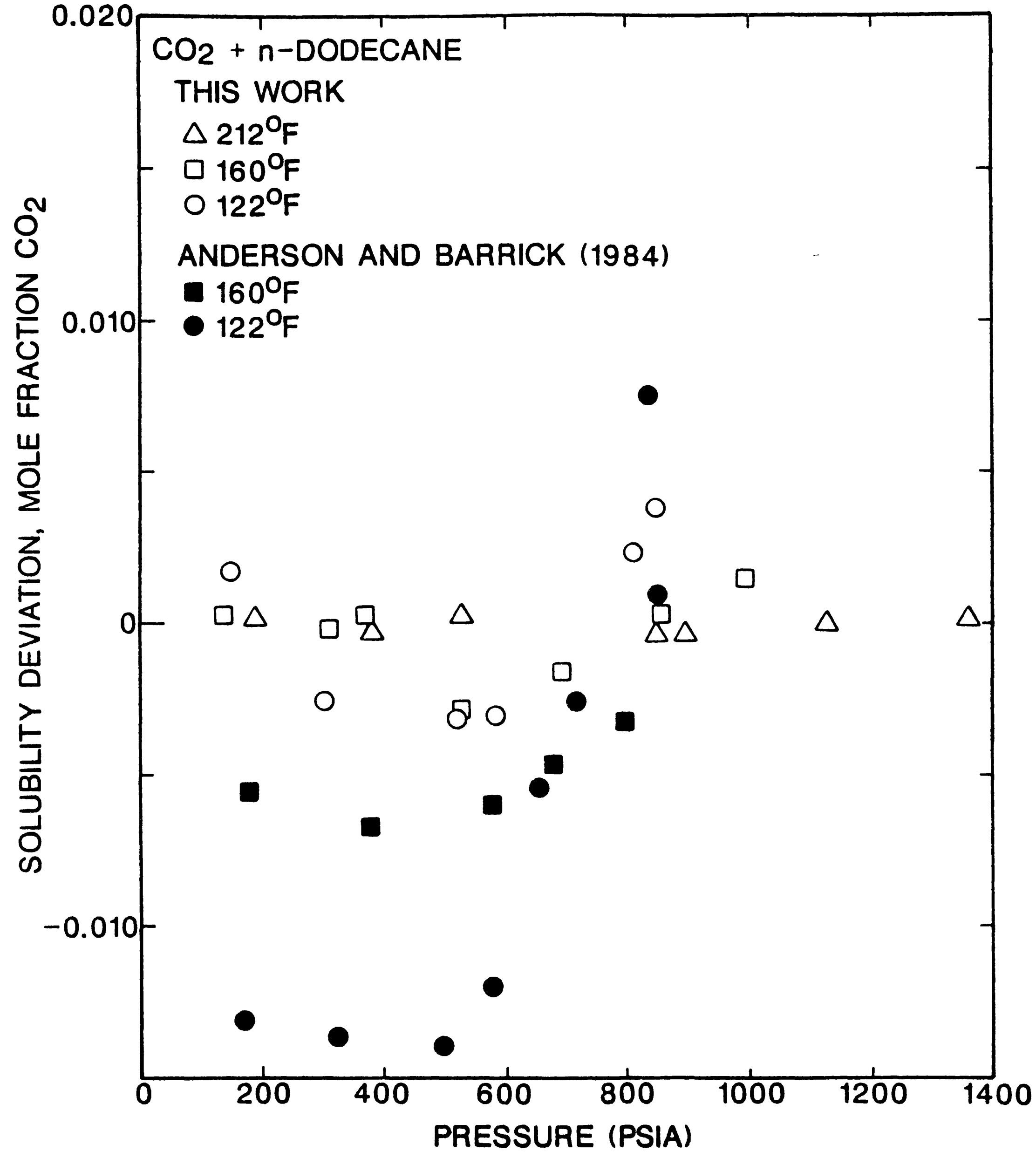


Figure 7. Comparison of Solubility Data for CO_2 + n-Dodecane

TABLE VII

SOLUBILITY OF CO_2 IN N-DECANE

Mole Fraction CO_2	Pressure MPa	(psia)
------------------------344.3 K (71.1°C, 160°F)--------------------------		
0.104	1.259	(182.7)
0.200	2.534	(367.6)
0.310	4.083	(592.4)
0.358	4.740	(687.7)
0.402	5.465	(792.8)
0.432	5.893	(854.9)
0.458	6.335	(919.0)
0.487	6.807	(987.5)
0.541	7.666	(1112.1)
0.599	8.633	(1252.4)

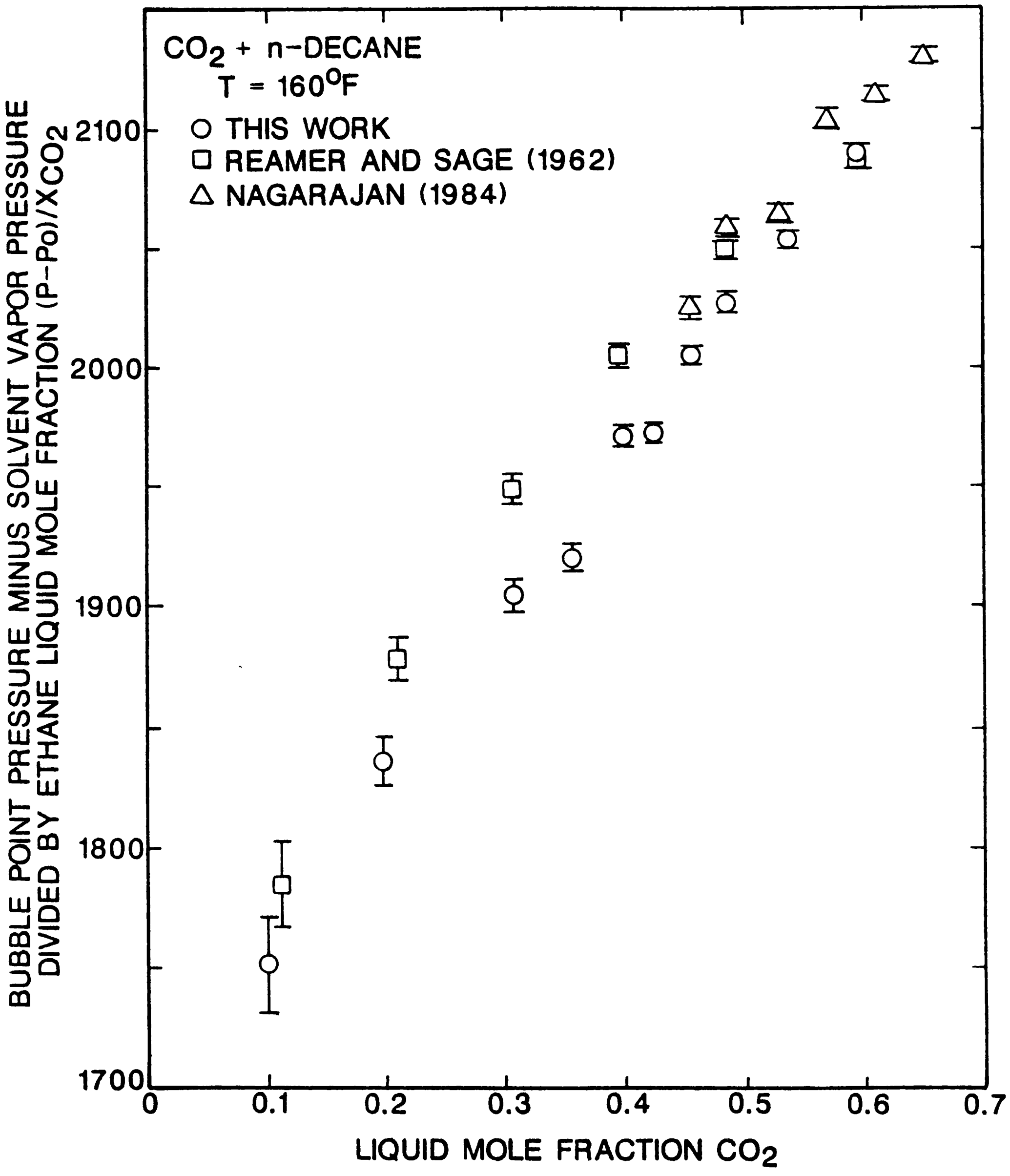


Figure 8. Comparison of Bubble-Point Data for CO_2 + n-Decane at 160°F

The Soave and Peng-Robinson representations of the CO_2 + n-decane system are displayed in Table V. The RMS error in CO_2 liquid mole fraction resulting from the use of k_{ij} only is twice that generated by the use of two parameters. Figure 9 shows graphically the SRK representation of the data for optimization of two interaction parameters.

CO_2 + n-Tetradecane

The final CO_2-containing system studied was CO_2 + n-tetradecane at 160°F. The primary purpose of this study was to resolve a discrepancy between the data of Gasem (10) and the data of Nagarajan (8). The data obtained by these researchers corresponded to system pressures of 1600 psia and above. Therefore, in order to obtain data useful in comparison to previous data, mole fractions were prepared which corresponded to bubble-point pressures approaching the limit of the pressure transducers used in this study (2000 psia). The collected data for the CO_2 + tetradecane system are listed in Table VIII and the data of this work and overlapping data of Gasem are compared graphically in Figure 10. As the figure indicates, the data of Gasem deviate negatively from the data of this study in terms of bubble-point pressures.

The highest point shown for the present data study in Figure 10, corresponding to a liquid CO_2 mole fraction of 0.77, was not included in the data regression due to the fact that it alone doubled the RMS error in solubility when included. It is shown in the figure solely for purposes of comparison to the data of Gasem.

The RMS error in solubility for the data of this system was 0.004 liquid CO_2 mole fraction as Table V indicates. This unusually high

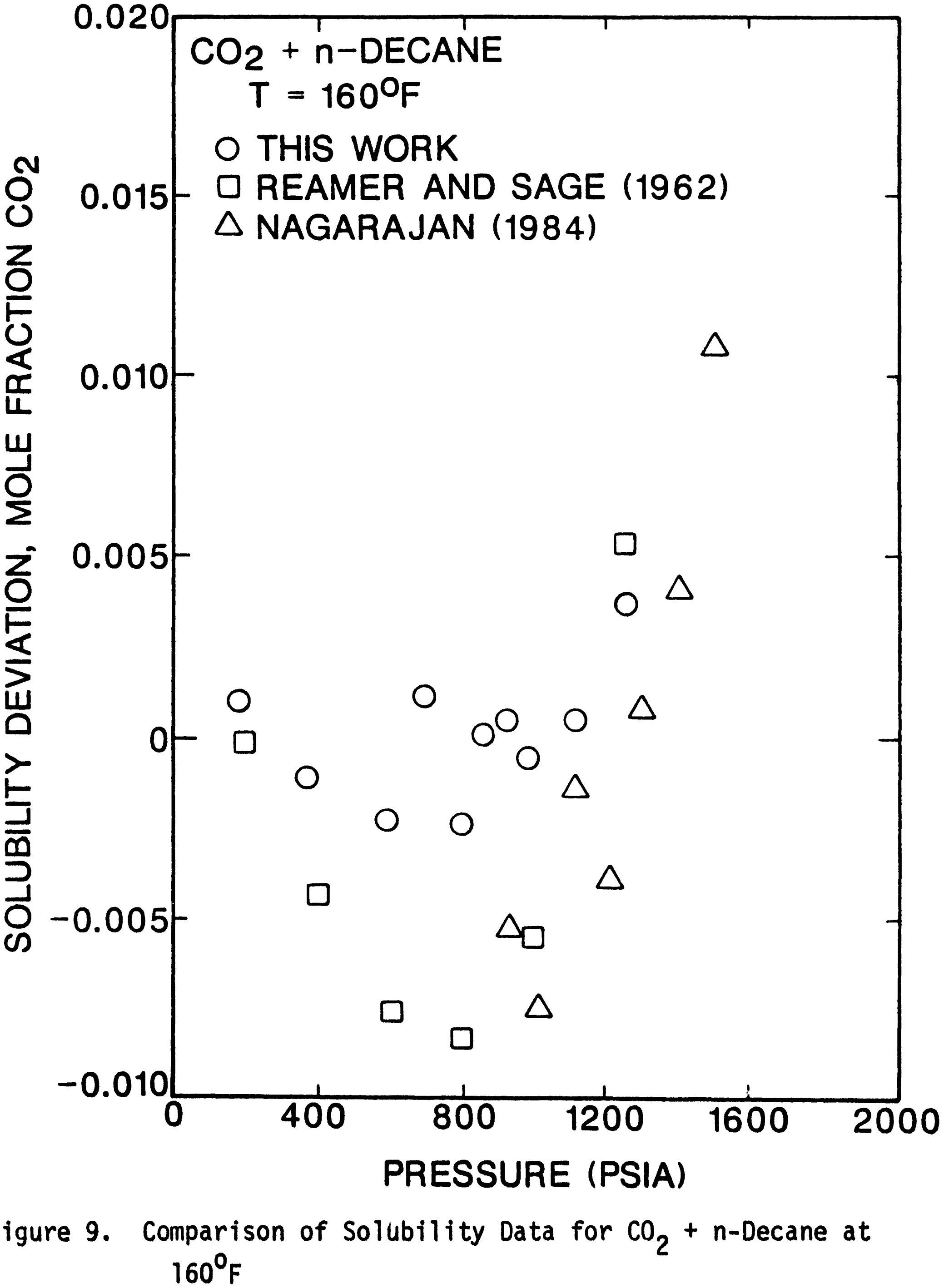


Figure 9. Comparison of Solubility Data for CO_2 + n-Decane at 160°F

TABLE VIII

SOLUBILITY OF CO_2 IN n-TETRADECANE

Mole Fraction CO_2	Pressure MPa	(psia)
344.3 K (71.1°C, 160°F)		
0.136	1.548	(224.5)
0.260	3.169	(459.8)
0.410	5.512	(799.7)
0.509	7.341	(1065.0)
0.659	10.533	(1528.0)
0.703	11.553	(1676.0)
0.721	12.052	(1748.4)

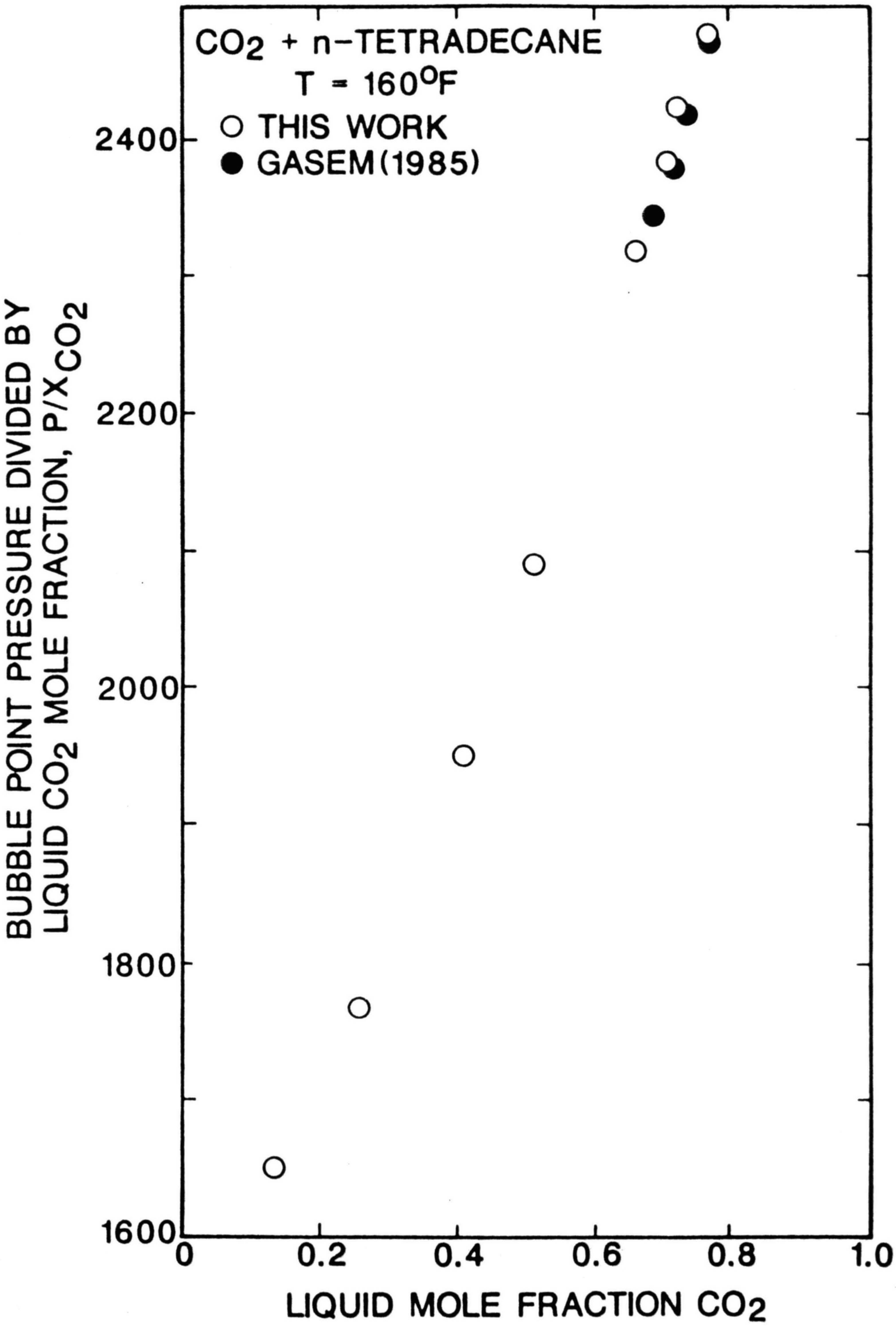


Figure 10. Comparison of Bubble-Point Data for CO_2 + n-Tetradecane at 160°F

solubility error may be attributable to the fact that bubble-point pressures were measured for this system which greatly exceed the highest pressures obtained for most other isotherms. The data of Gasem show positive deviations on the order of 0.006 in solubility from the optimized fit of the SRK equation to the data of this study, as is demonstrated by Figure 11. Deviations appear to be systematically increasing with CO_2 liquid mole fraction.

The densities and volumes used to calculate solubilities in all of the CO_2 systems studied are listed in Table IX. These densities and volumes are listed so that revised calculations of mole fractions may be performed if discrepancies are found between the densities of the components used in this study and densities reported by some other researcher. A detailed procedure for recalculation of mole fractions is presented later in this chapter.

Ethane + n-Decane

The ethane + n-decane system was originally studied at 100°F to resolve a discrepancy between data obtained in 1962 by Reamer and Sage (11) and new data obtained by Luks and co-workers (29). The data obtained in this study show bubble-point pressures as much as 20 psi below those of Sage (equivalent to 0.025 mole fraction ethane higher solubility). Luks and co-workers found similar deviations from the data of Reamer and Sage; in fact, their bubble points are marginally lower than those reported here.

On the basis of these findings, a complete investigation of the ethane + n-decane system was conducted, matching the temperatures investigated by Reamer and Sage. Data were obtained for 100, 160, 220

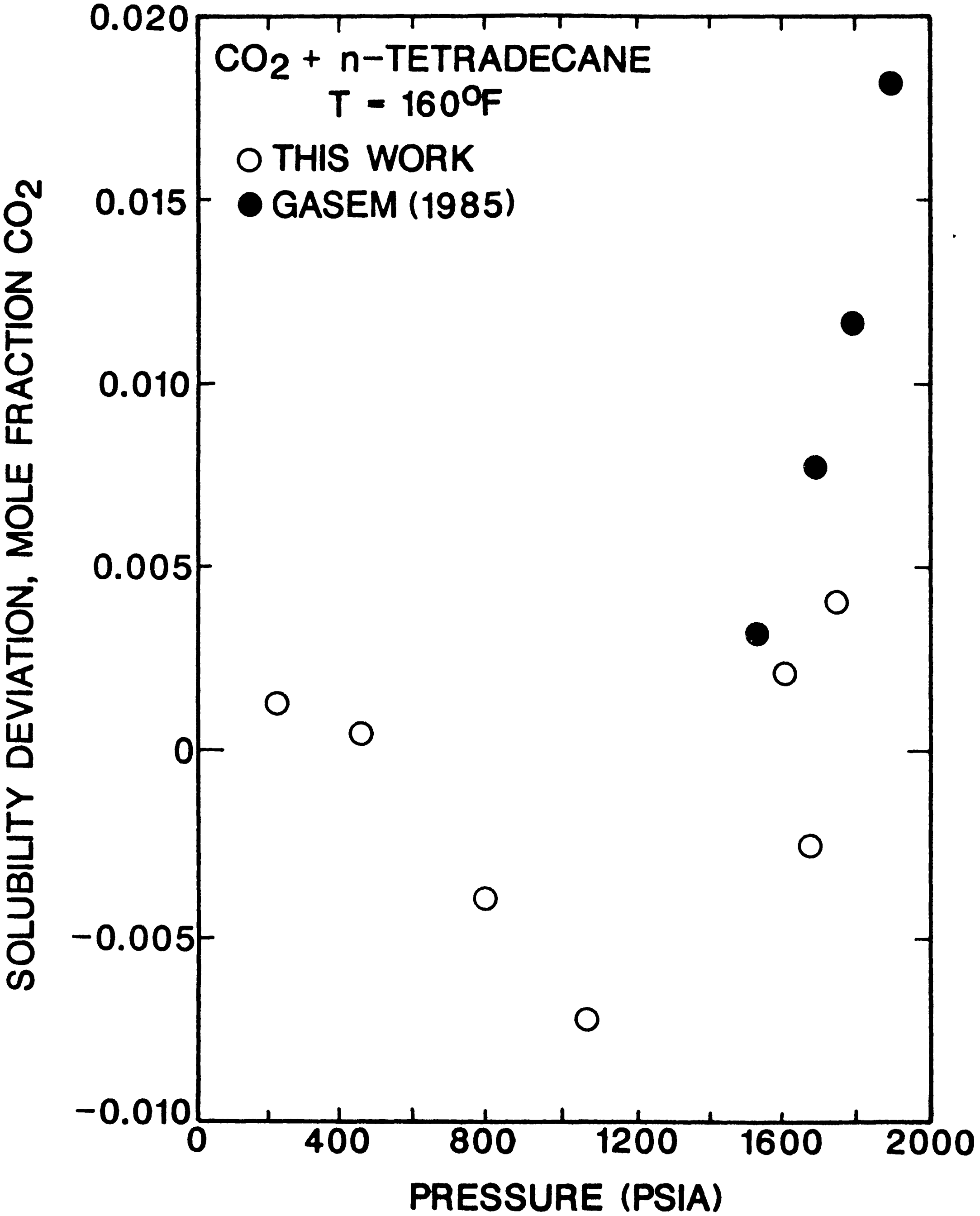


Figure 11. Comparison of Solubility Data for CO_2 + n-Tetradecane

TABLE IX

DENSITIES AND VOLUMES USED TO CALCULATE SOLUBILITIES IN CO_2 SYSTEMS

Solvent * Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for CO_2 at 50°C (psia)	Calculated CO_2 density (g/cm^3) ρ_{CO_2}	Volume of CO_2 Injected (cm^3) $V_{i_{CO_2}}$	Solvent Injection Number
Benzene 40°C					
0.8577	7.20	875.7	0.1366	2.83	1
		875.2	0.1365	6.55	1
		875.6	0.1365	7.82	1
		887.4	0.1393	17.93	1
	6.30	876.4	0.1367	5.18	2
		876.5	0.1368	6.15	2
		876.5	0.1368	11.12	2
	6.67	852.5	0.1315	5.71	3
		852.5	0.1315	8.61	3
		838.5	0.1282	12.26	3
	5.78	874.0	0.1362	3.74	4
		873.7	0.1353	7.73	4
n-Dodecane 50°C					
0.7271	4.96	878.9	0.1373	1.72	1
		878.9	0.1373	2.08	1
		877.7	0.1370	3.02	1
	4.93	897.9	0.1417	0.74	2
		896.8	0.1415	2.40	2
		896.8	0.1415	2.95	2
n-Dodecane 160°F					
0.7189	4.75	862.7	0.1336	1.96	1
		862.7	0.1336	2.21	1
		861.5	0.1336	1.40	1
		861.3	0.1333	1.40	1
	5.04	877.4	0.1370	0.60	2
		877.3	0.1369	0.85	2
		877.3	0.1369	1.20	2

TABLE IX (Continued)

Solvent * Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for CO$_2$ at 50°C (psia)	Calculated CO$_2$ density (g/cm^3) ρ_{CO_2}	Volume of CO$_2$ Injected (cm^3) $V_{i_{CO_2}}$	Solvent Injection Number
---n-Dodecane 100°C---					
0.6900	5.03	890.8	0.1401	0.65	1
		890.8	0.1401	1.36	1
		890.9	0.1401	1.86	1
	5.26	908.8	0.1443	1.40	2
		908.8	0.1443	2.25	2
		907.7	0.1441	1.72	2
		907.7	0.1441	1.72	2
---n-Decane 160°F---					
0.6908	3.96	859.8	0.1330	5.39	1
		859.8	0.1330	0.66	1
		859.4	0.1329	1.46	1
		878.3	0.1372	1.95	1
	3.90	860.2	0.1330	2.81	2
		860.2	0.1330	1.39	2
	6.05	836.9	0.1283	1.17	3
		824.1	0.1244	1.40	3
		823.1	0.1243	3.05	3
		822.1	0.1242	2.11	3
---n-Tetradecane 160°F---					
0.7266	6.36	870.2	0.1353	1.19	1
		835.8	0.1285	4.30	1
		839.6	0.1285	13.36	1
	5.98	828.9	0.1261	2.68	2
		828.9	0.1261	5.25	2
		874.2	0.1362	6.32	2
		874.2	0.1362	4.64	2

*Solvent Density References: Benzene (33), n-Decane (33), n-Dodecane (33), n-Tetradecane (33).

and 280°F, and these data are listed in Table X and displayed, along with those of Reamer and Sage, in Figure 12. The trend is similar for data obtained at each temperature: the data of this study deviate strongly at low ethane mole fractions and converge with the Reamer and Sage data at mole fractions between 0.6 and 0.7.

Table XI shows the optimized binary interaction parameters obtained through single and lumped-isotherm regressions of bubble-point data for the ethane + n-decane system as well as all other ethane-containing systems studied in this work. In Figure 13, the maximum solubility deviation of the Reamer and Sage data appears to occur at bubble-point pressures between 200 and 300 psia. The deviation is greatest for the 100°F data and decreases with increasing temperature. Figure 14 is an alternative method of comparison of the two sets of data: the logarithm of bubble-point pressure is shown as a function of the inverse of temperature for constant compositions. Highlighted in this figure are the excellent agreement between the data of this work and those of Luks, and the similarity in magnitudes of the disagreements of both of these data sets from that of Reamer and Sage. Once again, the data of Reamer and Sage deviate most strongly from the data of this work at 100°F, with the deviation decreasing as temperature increases.

The remainder of this work is a systematic study of the solubility of ethane in one- and two-ring naphthenic solvents (cyclohexane, trans-Decalin) and one-, two-, three-, and four-ring aromatic solvents (benzene, naphthalene, phenanthrene and pyrene). For the solvents which exist as liquids at room temperature, isotherms were measured at 50, 100 and 150°C. For the solvents with melting points above room temperature, isotherms selected for study were affected by melting point, but

TABLE X

SOLUBILITY OF ETHANE IN N-DECANE

Mole Fraction Ethane	Pressure MPa	(psia)
310.9 K (37.8°C, 100°F)		
0.108	0.423	(61.4)
0.127	0.491	(71.3)
0.211	0.833	(120.9)
0.271	1.093	(158.6)
0.300	1.226	(177.8)
0.308	1.281	(185.8)
0.413	1.768	(256.5)
0.471	2.077	(301.3)
0.501	2.246	(325.8)
0.601	2.812	(408.0)
344.3 K (71.1°C, 160°F)		
0.105	0.598	(86.7)
0.203	1.182	(171.5)
0.305	1.899	(275.4)
0.422	2.764	(401.0)
0.510	3.546	(514.4)
0.579	4.167	(604.4)
0.631	4.690	(680.3)
377.6 K (104°C, 220°F)		
0.106	0.807	(117.0)
0.202	1.600	(232.1)
0.328	2.787	(404.3)
0.408	3.618	(524.8)
0.505	4.790	(694.8)
0.600	6.033	(875.1)
410.9 K (137.7°C, 280°F)		
0.105	1.005	(145.8)
0.215	2.131	(309.1)
0.323	3.415	(495.3)
0.404	4.487	(650.9)
0.500	5.925	(859.4)
0.582	7.253	(1052.1)
0.638	8.236	(1194.6)

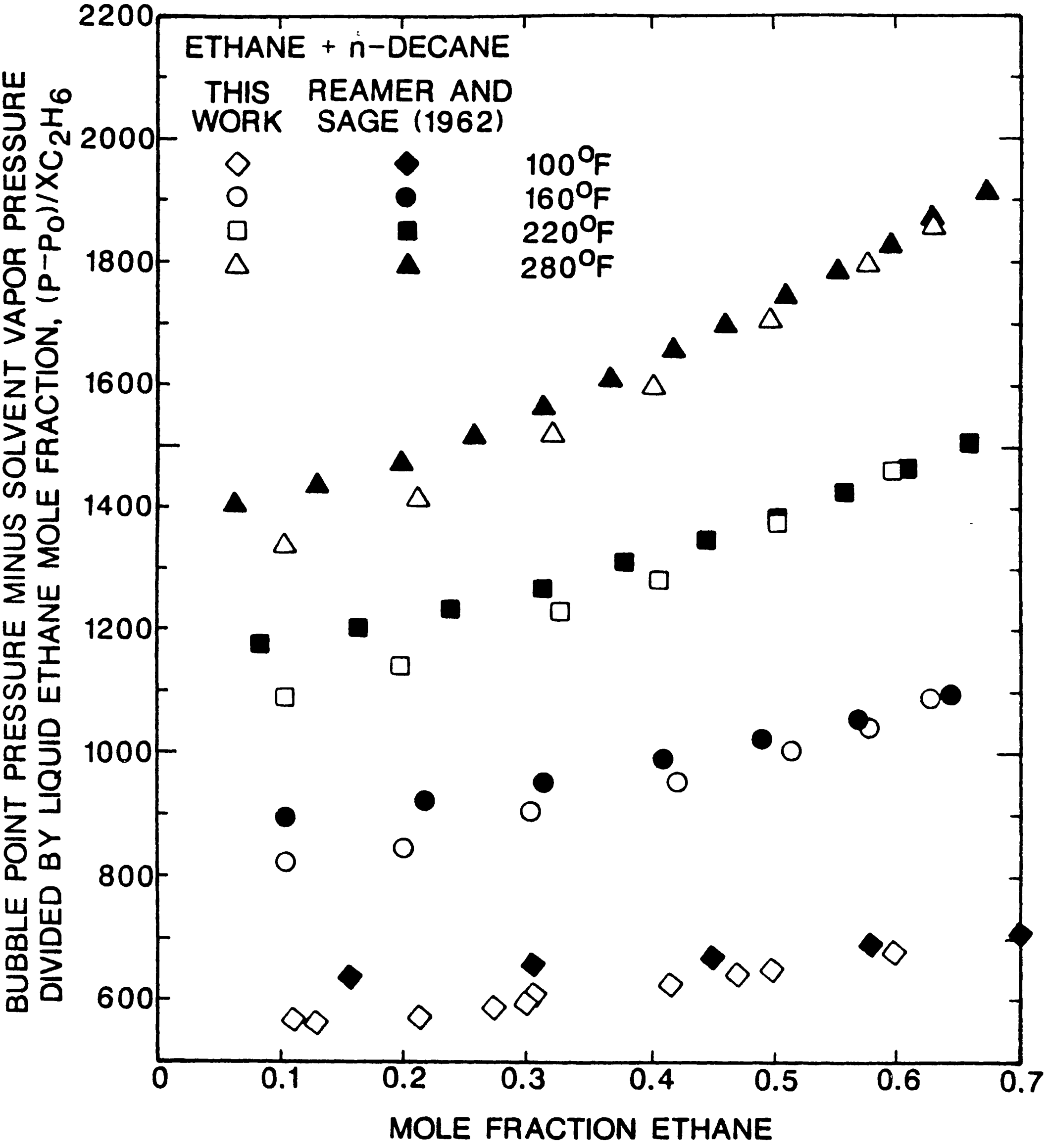


Figure 12. Comparison of Bubble-Point Data for Ethane + n-Decane

TABLE XI

SOAVE AND PENG-ROBINSON EQUATION OF STATE REPRESENTATIONS OF ETHANE SOLUBILITY DATA

Temperature K (°F)	Soave Parameters (P-R Parameters) k_{12}	l_{12}	Error in C_2H_6 Mole Fraction RMS	Max.
----------Ethane + n-Decane----------				
310.9 (100)	0.008	-0.002	0.002	0.004
	(0.010)	(-0.002)		
	0.005	--	0.004	0.008
	(0.006)	--		
344.3 (160)	0.010	-0.007	0.002	0.002
	(0.010)	(-0.007)		
	0.001	--	0.006	0.010
	(0.003)	--		
377.6 (220)	0.011	-0.012	0.001	0.002
	(0.011)	(-0.011)		
	-0.002	--	0.007	0.013
	(-0.002)	--		
410.9 (280)	0.019	-0.020	< 0.001	0.001
	(0.016)	(-0.019)		
	-0.002	--	0.010	0.020
	(-0.003)	--		
310.9, 344.3	0.010	-0.006	0.004	0.008
377.6, 410.9	(0.010)	(-0.006)		
	0.002	--	0.007	0.016
	(0.003)	--		
----------Ethane + Cyclohexane----------				
323.2 (122)	-0.006	0.012	0.001	0.002
	(0.001)	(0.011)		
	0.007	--	0.008	0.016
	(0.013)	--		

TABLE XI (Continued)

Temperature K (°F)	Soave Parameters (P-R Parameters) k_{12}	 l_{12}	Error in C_2H_6 Mole Fraction RMS	 Max.
------------------------Ethane + Cyclohexane (Cont.)--------------------				
373.2 (212)	-0.002	0.003	0.001	0.002
	(0.001)	(0.005)		
	0.001	--	0.002	0.003
	(0.006)	--		
423.2 (302)	0.011	-0.002	< 0.001	0.001
	(0.009)	(0.002)		
	0.009	--	< 0.001	0.001
	(0.011)	--		
323.2, 373.2 and 423.2	-0.003	0.008	0.004	0.005
	(0.001)	(0.010)		
	0.006	--	0.005	0.013
	(0.011)	--		
------------------------Ethane + Benzene-------------------------------				
323.2 (122)	0.010	0.025	0.003	0.007
	(0.017)	(0.025)		
	0.034	--	0.023	0.045
	(0.040)	--		
373.2 (212)	0.004	0.024	0.002	0.004
	(0.007)	(0.026)		
	0.025	--	0.010	0.023
	(0.030)	--		
423.2 (302)	0.009	0.013	< 0.001	0.002
	(0.008)	(0.019)		
	0.019	--	0.005	0.010
	(0.022)	--		
323.2, 373,2 and 423.2	0.006	0.026	0.005	0.101
	(0.009)	(0.028)		
	0.029	--	0.014	0.033
	(0.035)	--		

TABLE XI (Continued)

Temperature K (°F)	Soave Parameters (P-R Parameters) k_{12}	l_{12}	Error in C_2H_6 Mole Fraction RMS	Max.
------------------------Ethane + trans-Decalin------------------------				
323.2 (122)	0.022	0.007	0.003	0.005
	(0.025)	(0.008)		
	0.032	--	0.005	0.008
	(0.036)	--		
373.2 (212)	0.030	-0.002	< 0.001	0.002
	(0.031)	(-0.001)		
	0.027	--	0.002	0.003
	(0.030)	--		
423.2 (302)	0.039	-0.003	< 0.001	0.002
	(0.037)	(-0.001)		
	0.035	--	0.002	0.003
	(0.036)	--		
323.2, 373.2 and 423.2	0.026	0.004	0.004	0.005
	(0.028)	(0.005)		
	0.031	--	0.004	0.008
	(0.034)	--		
----------------------Ethane + Naphthalene----------------------------				
373.2 (212)	0.004	0.019	0.001	0.002
	(0.005)	(0.021)		
	0.028	--	0.010	0.018
	(0.031)	--		
423.2 (302)	-0.026	0.020	< 0.001	0.001
	(-0.025)	(0.022)		
	0.005	--	0.005	0.012
	(0.008)	--		
373.2 and 423.2	0.007	0.010	0.012	0.025
	(0.008)	(0.012)		
	0.021	--	0.013	0.028
	(0.024)	--		

TABLE XI (Continued)

Temperature K (°F)	Soave Parameters (P-R Parameters) k_{12}	l_{12}	Error in C_2H_6 Mole Fraction RMS	Max.
----------Ethane + Phenanthrene----------				
383.2 (230)	0.038 (0.042)	0.013 (0.016)	0.002	0.003
	0.061 (0.071)	-- --	0.006	0.007
423.2 (302)	0.037 (0.041)	0.011 (0.015)	< 0.001	<0.001
	0.061 (0.071)	-- --	0.002	0.004
383.2 and 423.2	0.039 (0.044)	0.011 (0.015)	0.002	0.005
	0.061 (0.071)	-- --	0.004	0.007
----------Ethane + Pyrene----------				
433.2 (320)	0.174 (0.162)	0.013 (0.016)	0.001	0.002
	0.205 (0.200)	-- --	0.002	0.003

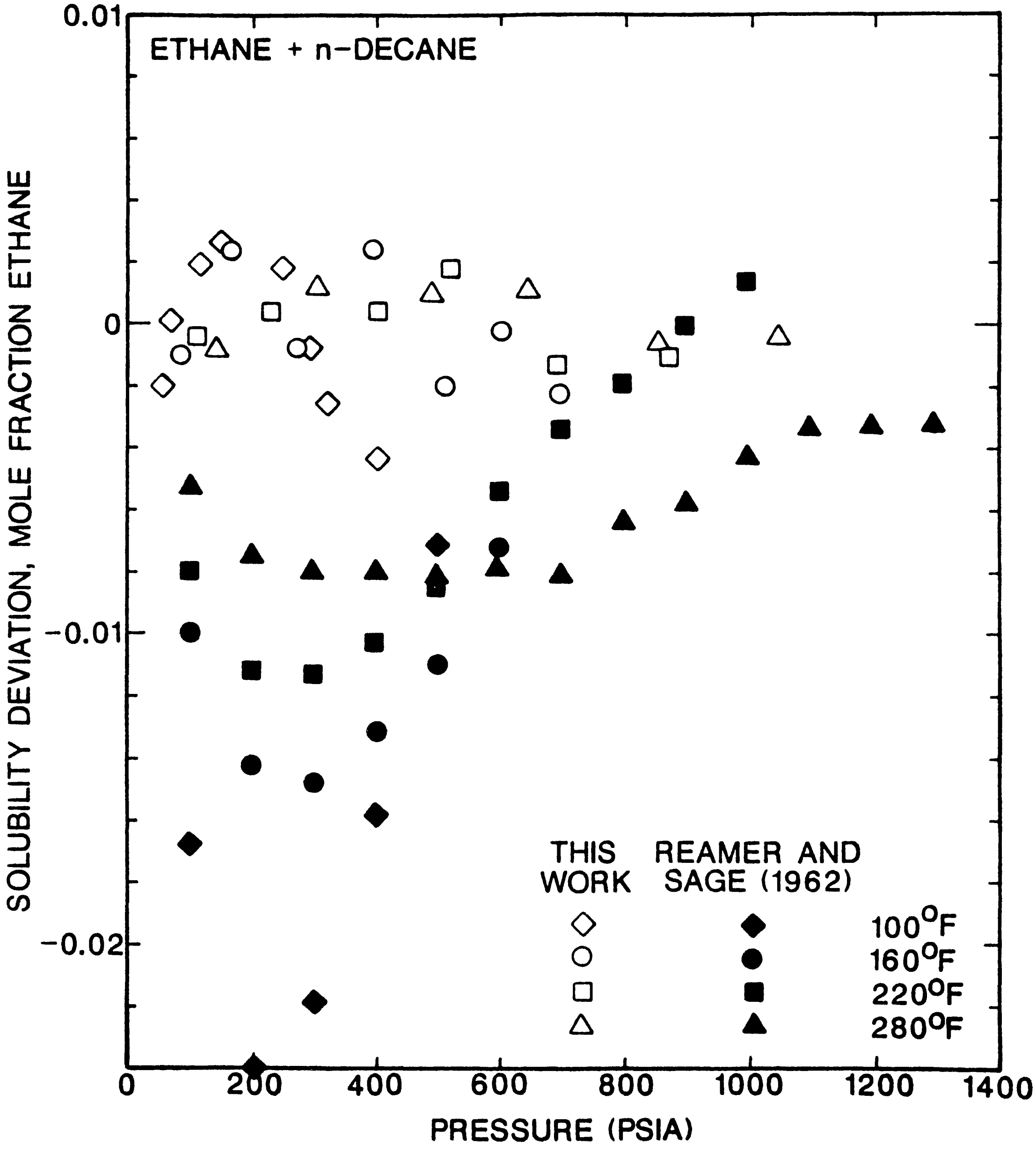


Figure 13. Comparison of Solubility Data for Ethane + n-Decane

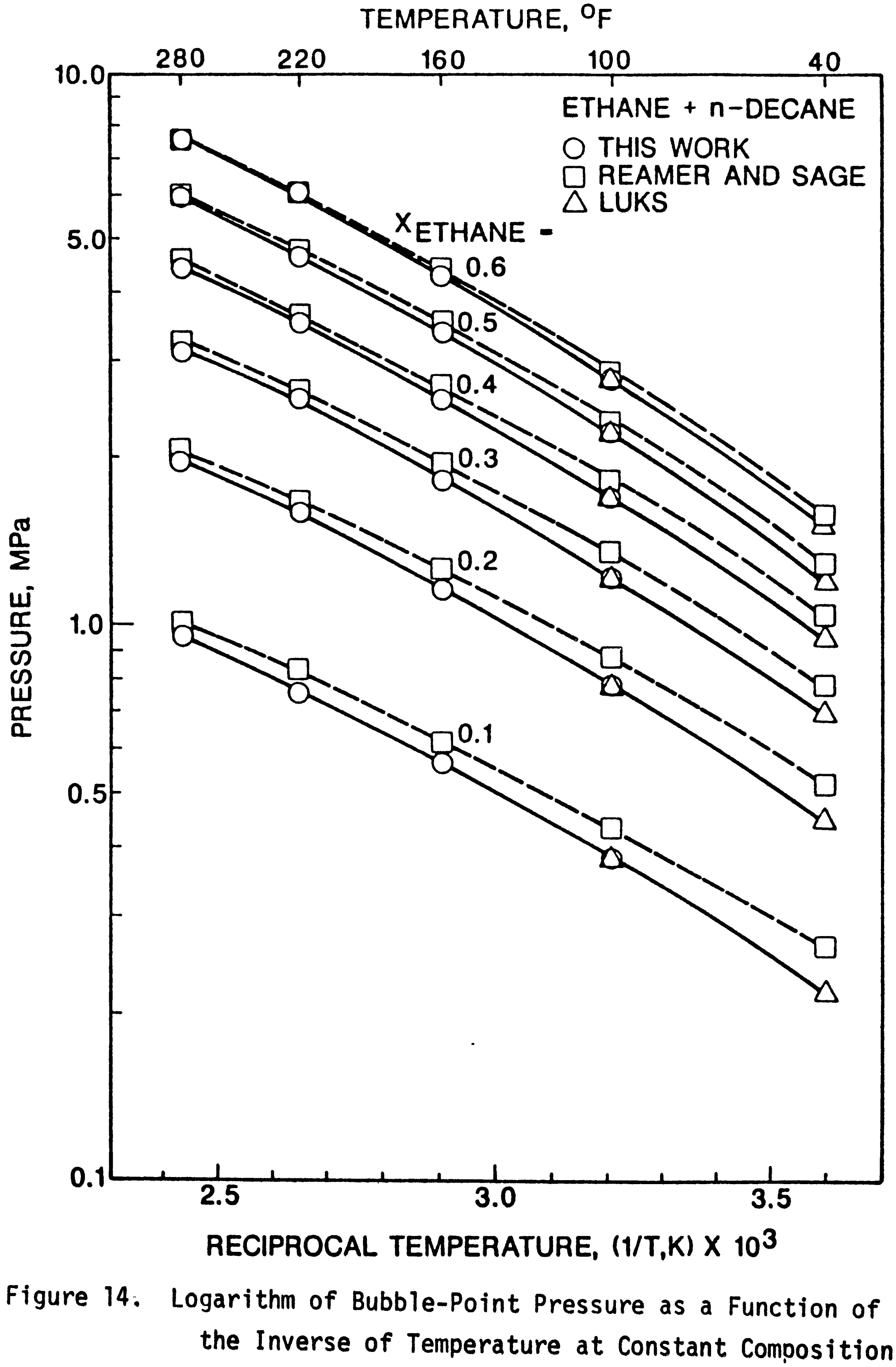


Figure 14. Logarithm of Bubble-Point Pressure as a Function of the Inverse of Temperature at Constant Composition for Ethane + n-Decane

attempts were made to stay as close as possible to the format used for the other solvents.

Ethane + Cyclohexane

The ethane + cyclohexane system was studied first. As mentioned in the literature review section of this paper, no high-pressure vapor-liquid equilibrium studies had been previously performed on this system. Prior to measurement of the 100 and 150°C isotherms, vapor pressures of pure cyclohexane were measured as a routine safeguard against systematic errors. Vapor pressures of 26.6 and 82.0 psia were measured for cyclohexane at 100 and 150°C, respectively. Use of the Antoine constants reported by Reid (27) yields vapor pressures of 25.3 and 80.1 psia for the two respective temperatures. These vapor pressure measurements fall within the error limit of ±2 psi established for the experimental apparatus.

The data obtained for the ethane + cyclohexane system are presented in Table XII. The customary plots of $(P-P^\circ)/x_{C_2H_6}$ vs. liquid ethane mole fraction and solubility deviations for the system data are displayed in Figures 15 and 16. The optimized binary interaction parameters provide an excellent fit to the experimental data, as Figure 16 indicates. In only one case was the solubility deviation greater than 0.002 liquid mole fraction. The optimized binary interaction parameters are displayed in Table XI. The trend in interaction parameter values seems to be a decrease in l_{ij} and simultaneous increase in k_{ij} with increasing temperature.

TABLE XII

SOLUBILITY OF ETHANE IN CYCLOHEXANE

Mole Fraction Ethane	Pressure	
	MPa	(psia)
323.2 K (50°C, 122°F)		
0.050	0.326	(47.3)
0.075	0.472	(68.5)
0.150	0.909	(131.8)
0.200	1.193	(173.0)
0.356	2.121	(307.7)
0.419	2.489	(361.1)
0.550	3.259	(472.8)
0.601	3.567	(517.5)
373.2 K (100°C, 212°F)		
0.049	0.625	(90.7)
0.131	1.419	(205.8)
0.209	2.178	(315.9)
0.301	3.122	(452.9)
0.401	4.154	(602.6)
0.500	5.221	(757.4)
0.543	5.725	(830.6)
423.2 K (150°C, 302°F)		
0.100	1.882	(273.0)
0.204	3.311	(480.3)
0.276	4.348	(630.8)
0.351	5.411	(785.0)
0.447	6.786	(984.4)
0.518	7.771	(1127.4)

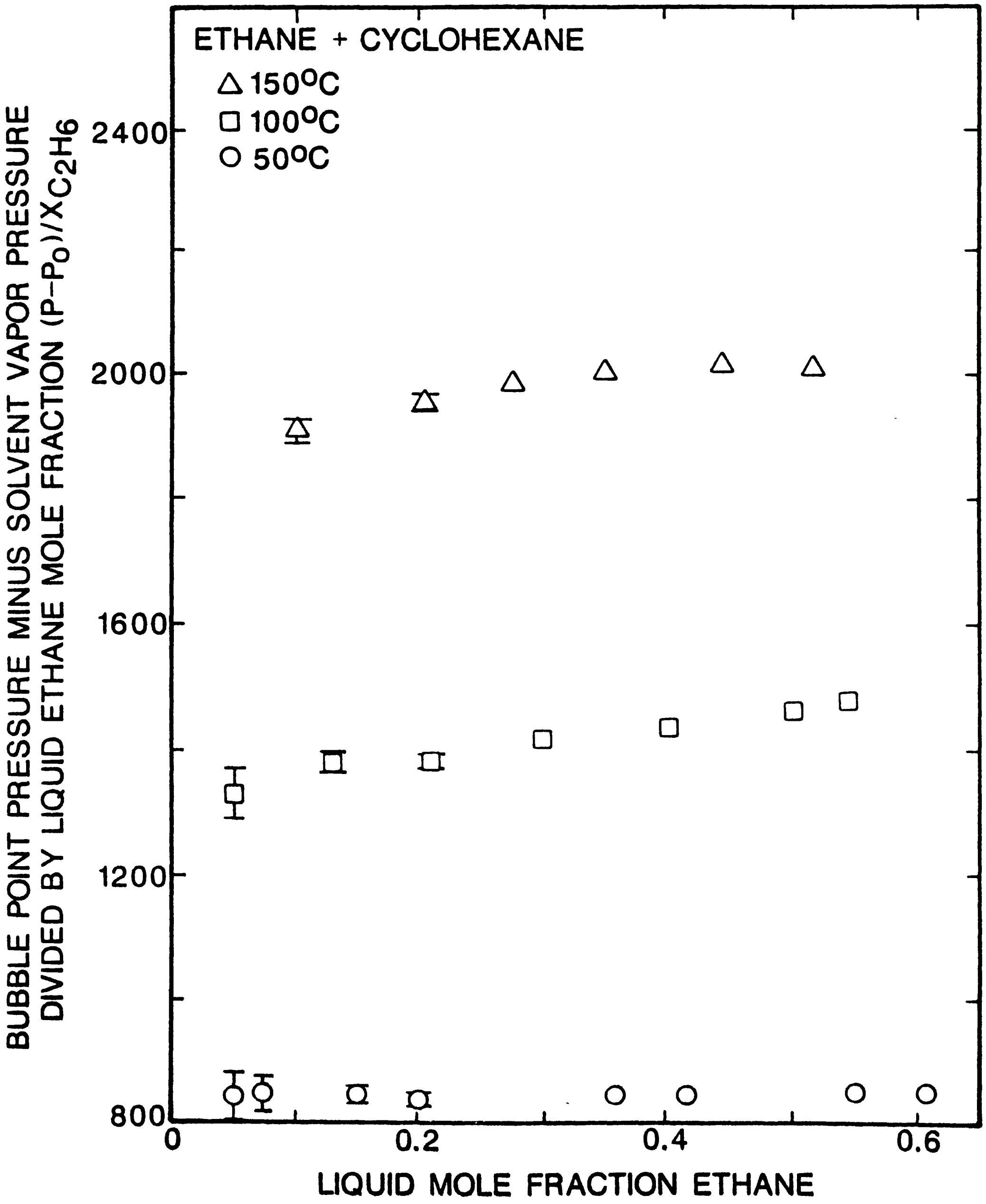


Figure 15. Bubble-Point Data for Ethane + Cyclohexane

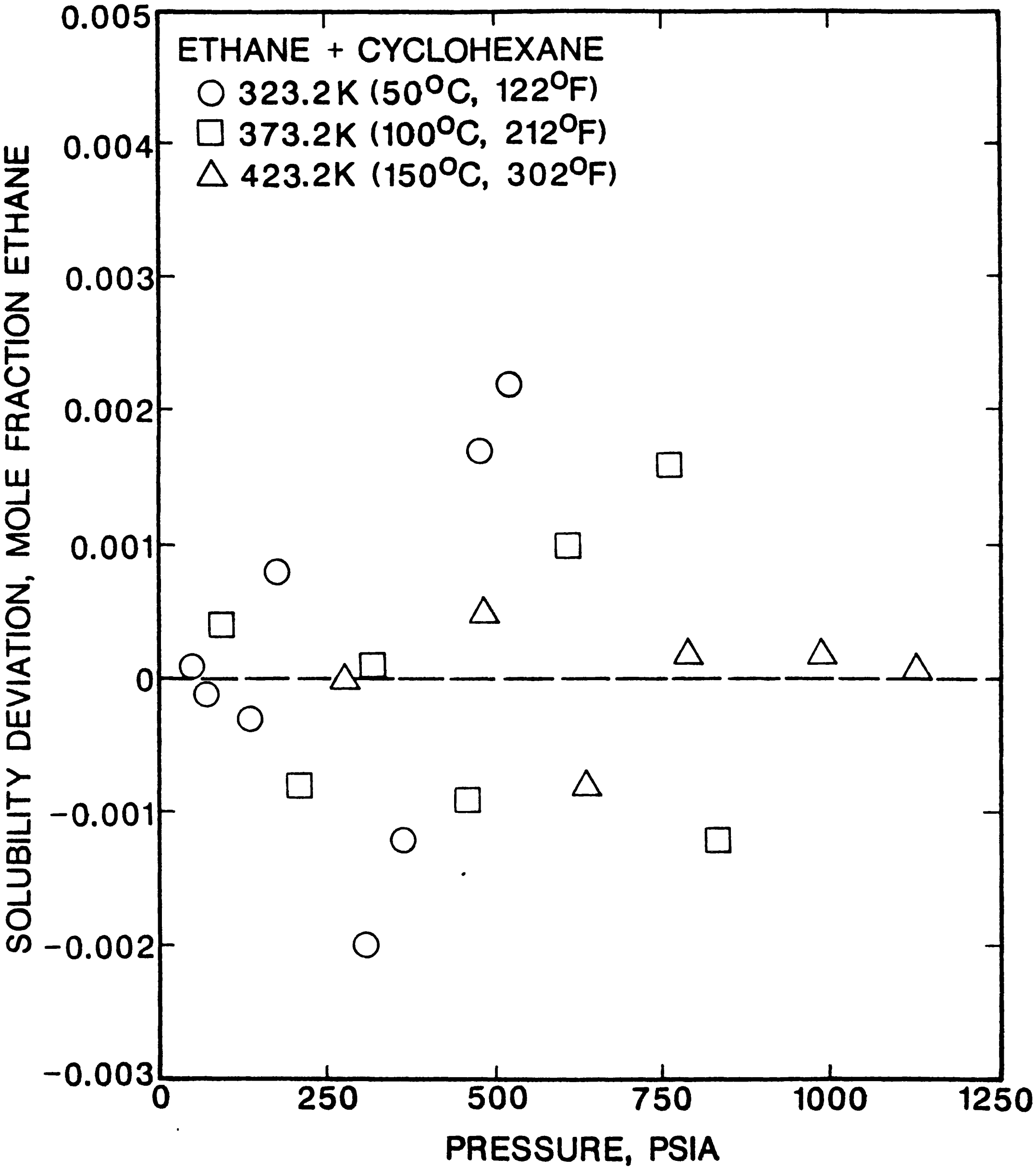


Figure 16. Soave and Peng-Robinson Representations of Ethane Solubility in Cyclohexane

Ethane + trans-Decalin

The ethane + trans-Decalin system was studied at 50, 100 and 150°C also. As with ethane + cyclohexane, no previous high-pressure solubility data exist. The collected data appear in Table XIII. Solubility errors in excess of 0.005 mole fraction ethane occur for the 50°C isotherm, but data points in the 100 and 150°C isotherms show absolute deviations of less than 0.002 in every case. The trend in binary interaction parameters, as shown in Table XI, is similar to that found in the ethane + cyclohexane system with a decrease in l_{ij} and simultaneous increase in k_{ij} as the system temperature increases. In Figure 17, these optimized parameters are plotted as functions of solvent liquid density for both naphthenic solvents studied. This plot was constructed to determine if any correlation exists between solvent liquid density and the interaction parameter values, and if these results could be extrapolated to naphthenics with higher numbers of rings. Examination of the figure reveals that obvious trends exist between solvent density and BIP values for individual solvents but no continuous correlation is obvious for naphthenics in general.

Ethane + Benzene

The remainder of the study focused on the solubility of ethane in aromatic solvents. The first of these, benzene, is the only solvent on which previous research had been conducted. High-pressure solubility data were collected by Ohgaki et. al (14) and by Kay and Nevens (12). Ohgaki obtained data at only 25°C, so these data could not be used for direct comparison. Kay and Nevens obtained bubble-point temperatures for mixtures ranging from zero to 1.0 liquid mole fraction ethane in

TABLE XIII

SOLUBILITY OF ETHANE IN TRANS-DECALIN

Mole Fraction Ethane	Pressure MPa	(psia)
323.2 K (50°C, 122°F)		
0.054	0.351	(50.9)
0.054	0.345	(50.1)
0.104	0.651	(94.5)
0.212	1.338	(194.2)
0.320	2.079	(301.8)
0.365	2.411	(350.1)
0.483	3.265	(474.0)
0.524	3.576	(519.2)
373.2 K (100°C, 212°F)		
0.104	1.077	(156.3)
0.152	1.569	(227.8)
0.204	2.163	(314.1)
0.305	3.369	(489.2)
0.400	4.629	(672.1)
0.484	5.789	(840.5)
0.561	6.921	(1004.9)
423.2 K (150°C, 302°F)		
0.065	0.985	(143.0)
0.099	1.457	(211.6)
0.193	2.972	(431.5)
0.252	3.949	(573.3)
0.303	4.832	(701.6)
0.408	6.813	(989.1)
0.501	8.678	(1259.9)

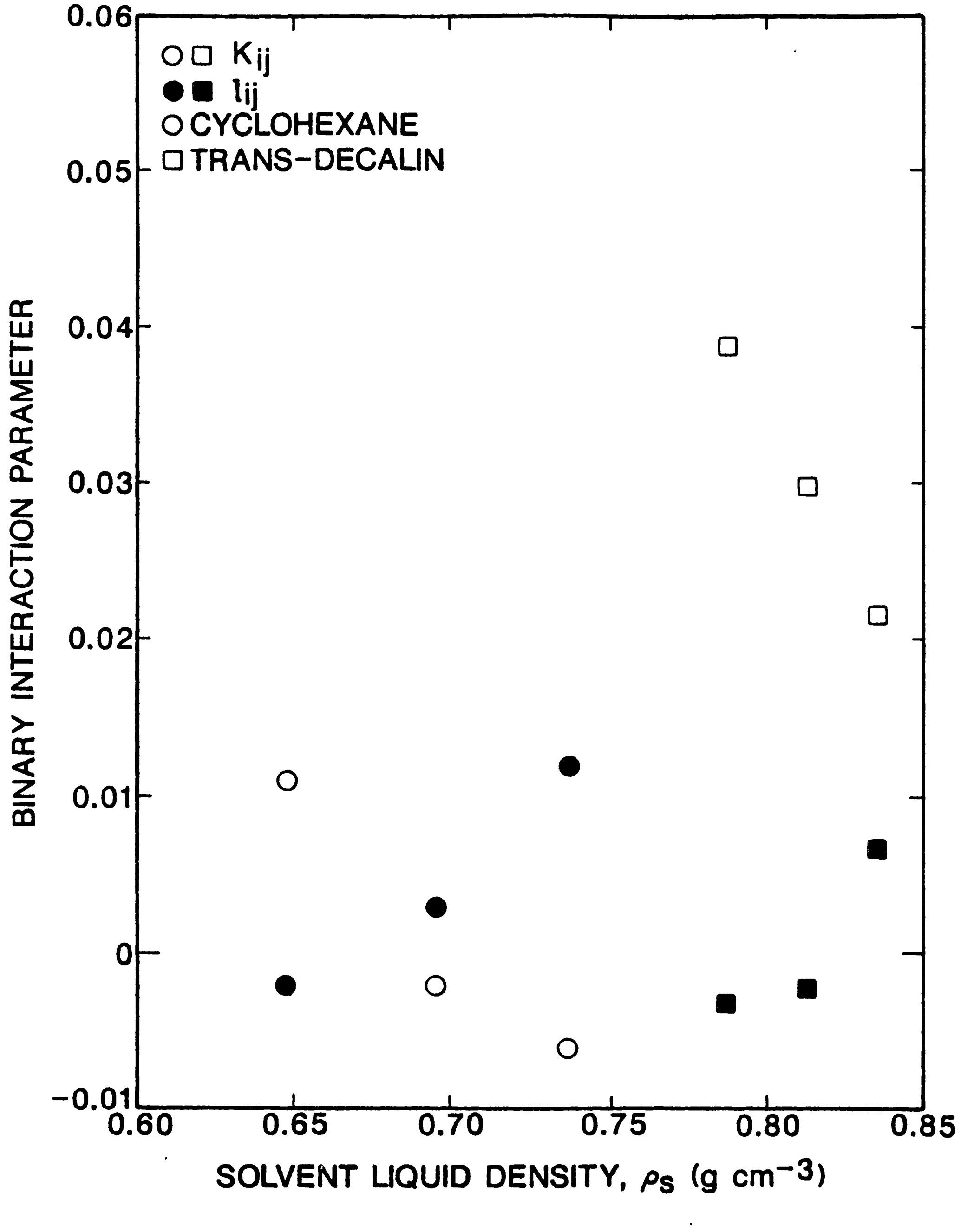


Figure 17. Binary Interaction Parameters as Functions of Solvent Liquid Density for Naphthenic Solvents

increments of 0.1 mole fraction, at constant system pressure of from 100 to 1400 psia in 100-psi increments. Because of the method of experimentation, no data points existed at the exact temperatures of interest in the present study. Therefore a graphical interpolation procedure was implemented, to facilitate comparisons. Kay and Nevens data were plotted in isobars on a temperature vs. liquid ethane mole fraction diagram and equilibrium compositions were estimated for each of the three temperatures by interpolating graphically between data points on each isobar.

As a precaution against systematic error, the vapor pressure of benzene was measured at 100°C and 150°C prior to solubility data collection at those temperatures. Vapor pressures of 28.6 and 83.7 psia were measured for 100°C and 150°C, respectively. Use of the Antoine equation constants reported by Reid (27) gives vapor pressures of 26.1 and 84.3 psia for the respective temperatures. The first reading is significantly different from that reported by Reid but the second differs by only 0.6 psi.

The ethane + benzene data obtained in this study is summarized in Table XIV. The data of this work and the interpolation of Kay and Nevens' data are compared directly in Figure 18, and the solubility deviations are compared in Figure 19. At 50°C, agreement is excellent, and well within the combined experimental uncertainties in the two data sets. At 100°C, agreement is good for ethane mole fractions above 0.25, but at lower compositions the data of Kay and Nevens are as much as 20 psi above the results of the present work at 150°C, the slope of the bubble-point curve itself is steeper for the Kay and Nevens data than for the present work, with the intersection of the two curves apparently

TABLE XIV

SOLUBILITY OF ETHANE IN BENZENE

Mole Fraction Ethane	Pressure MPa	(psia)
323.2 K (50°C, 122°F)		
0.051	0.478	(69.4)
0.101	0.911	(132.1)
0.200	1.665	(241.6)
0.317	2.488	(361.0)
0.464	3.353	(486.4)
0.503	3.568	(517.6)
0.600	4.044	(586.7)
373.2 K (100°C, 212°F)		
0.090	1.341	(194.6)
0.114	1.651	(239.5)
0.216	2.900	(420.7)
0.255	3.380	(490.3)
0.353	4.494	(651.9)
0.403	5.049	(732.4)
0.502	6.056	(878.5)
423.2 K (150°C, 302°F)		
0.049	1.397	(202.7)
0.101	2.284	(331.4)
0.202	3.953	(573.5)
0.302	5.542	(804.0)
0.399	7.063	(1024.6)
0.465	8.012	(1162.3)
0.499	8.459	(1227.1)

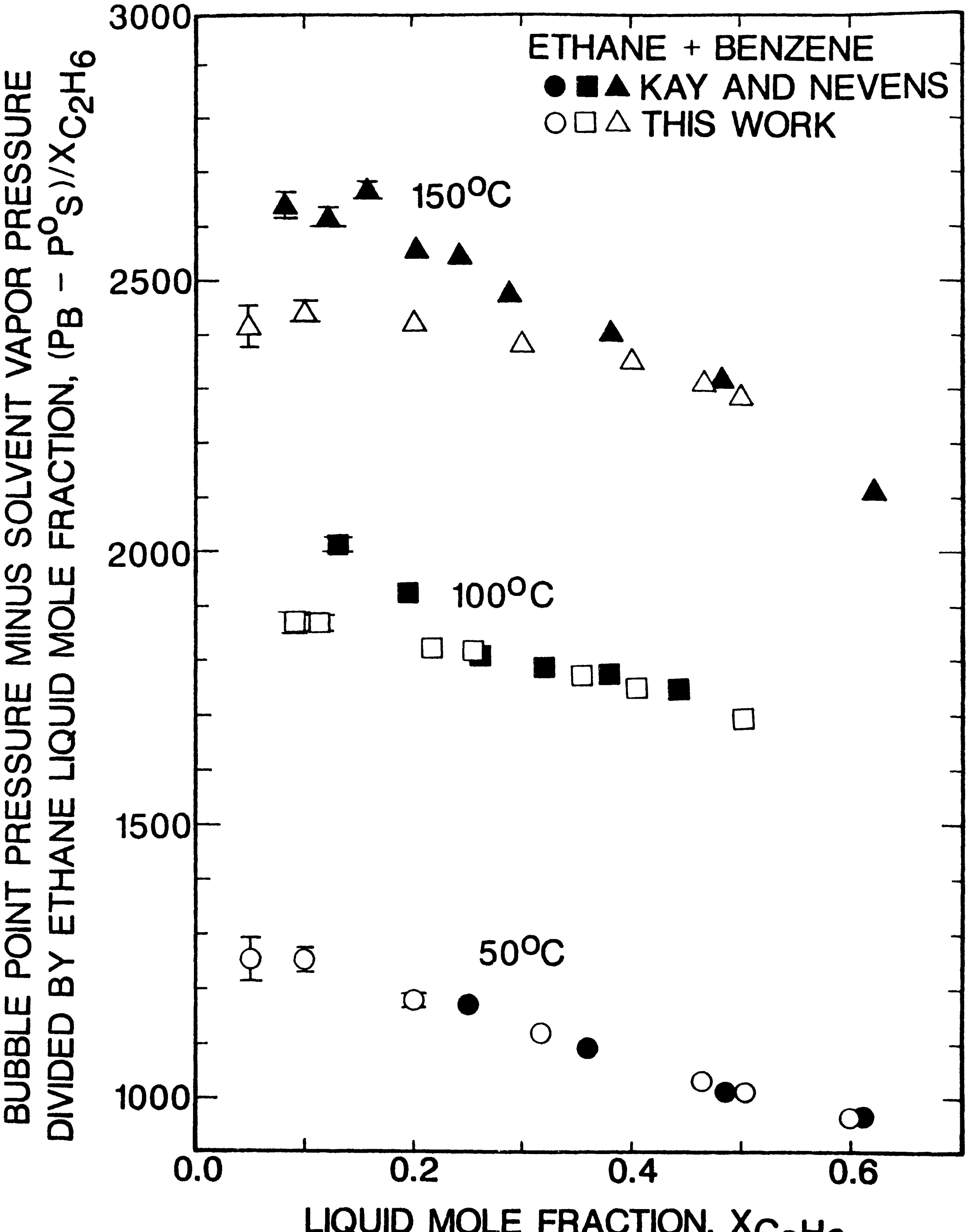


Figure 18. Comparison of Bubble-Point Data for Ethane + Benzene

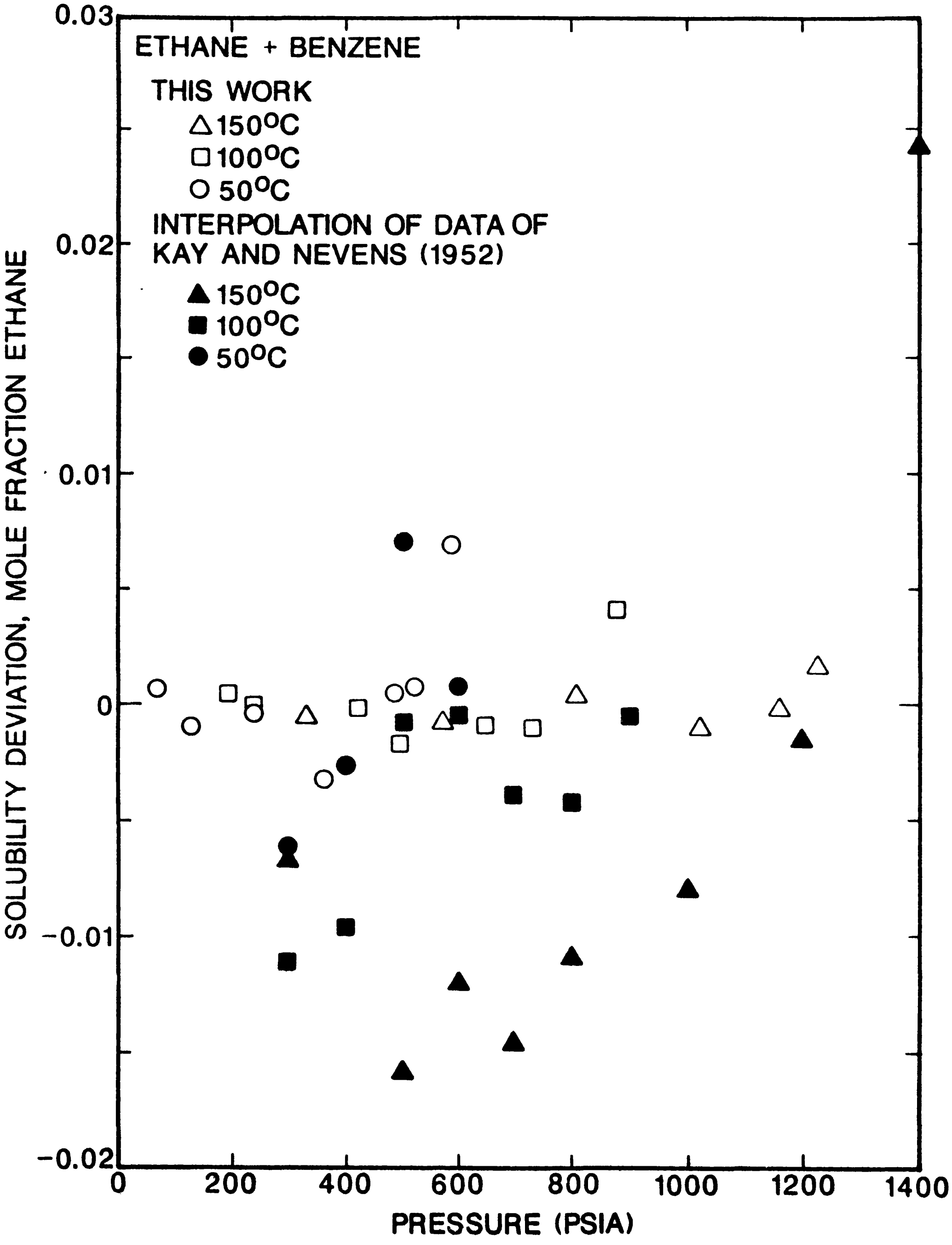


Figure 19. Comparison of Solubility Data for Ethane + Benzene

at 0.5 mole fraction. The pressure differences translate into solubility differences of less than 0.005 at 50°C, rising to 0.015 at 150°C.

Following Figure 19 is a plot of the logarithm of bubble-point pressure as a function of the inverse of temperature for the ethane + benzene data obtained in this study, along with those of Kay and Nevens and Ohgaki (Figure 20). The plot shows the positive deviations of the Kay and Nevens data from the data of this work at 150°C, with some degree of disagreement at 100°C. Agreement is excellent with the Ohgaki data and the data of Kay and Nevens below 100°C for all mole fractions. The optimized binary interaction parameters for ethane + benzene are shown in Table XI. There is no clear correlation between the parameters and system temperature; l_{ij} decreases with increasing temperature, but not uniformly, and k_{ij} shows no definite pattern.

Ethane + Naphthalene

For the remaining three systems, ethane in naphthalene, phenanthrene and pyrene, no previous data exist. The melting point of naphthalene (85°C) made the measurement of a 50°C isotherm impractical, therefore two isotherms of data were measured (100 and 150°C). These data are presented in Table XV. The 150°C isotherm was obtained by a different method than used for all other isotherms measured: the initial injections of naphthalene and ethane were performed at 100°C, and the oven temperature was raised to 150°C after the injection was completed. This was done to avoid difficulties in the degassing of the naphthalene. Antoine equation constants reported by Reid (27) result in vapor pressures for naphthalene of 0.4 psia at 100°C and 2.6 psia at

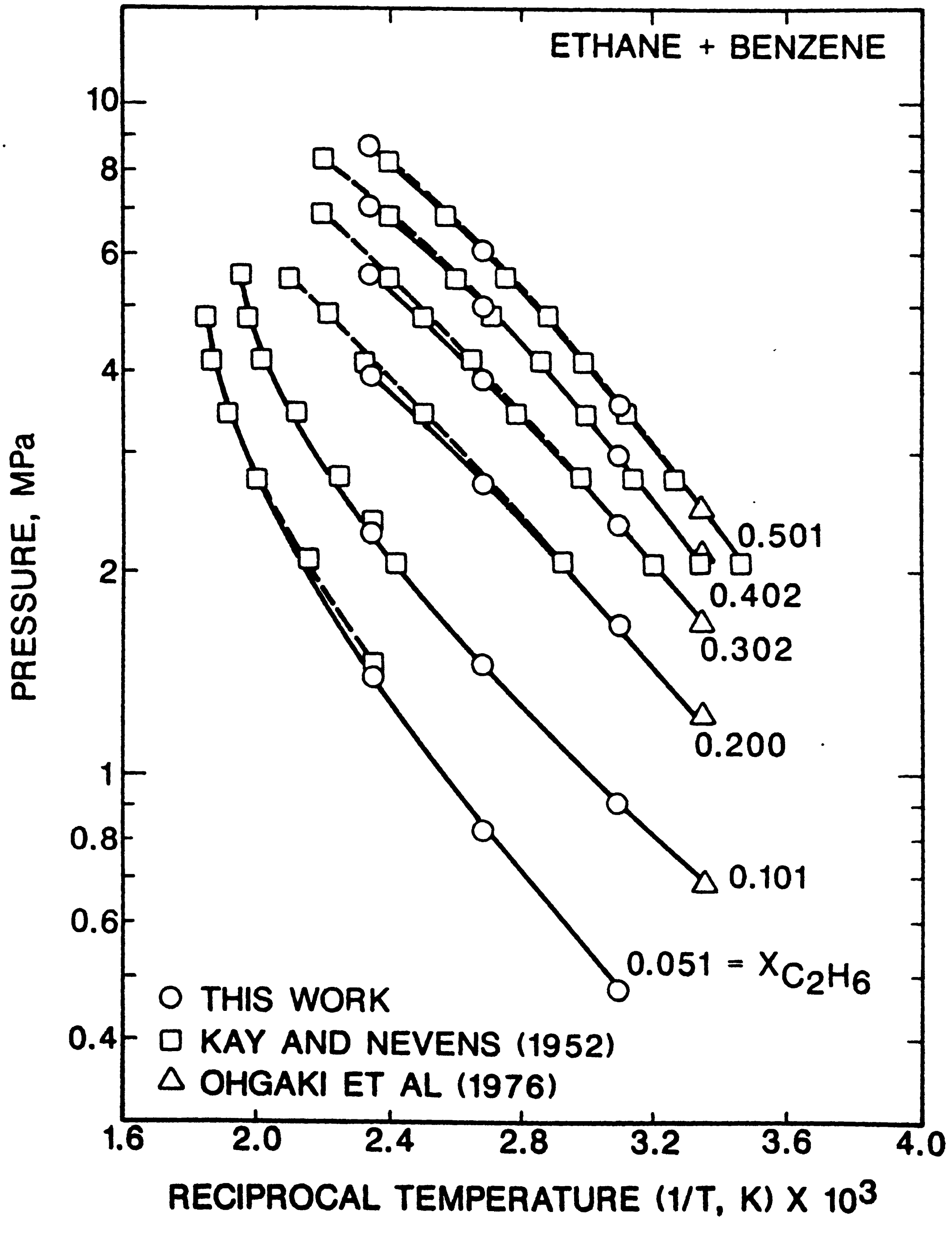


Figure 20. Logarithm of Bubble-Point Pressure as a Function of the Inverse of Temperature at Constant Composition for Ethane + Benzene

TABLE XV

SOLUBILITY OF ETHANE IN NAPHTHALENE

Mole Fraction Ethane	Pressure MPa	(psia)
373.2 K (100°C, 212°F)		
0.133	2.574	(373.2)
0.159	3.118	(452.2)
0.208	4.098	(594.2)
0.264	5.257	(762.3)
0.331	6.719	(974.3)
0.388	7.933	(1150.4)
0.392	8.077	(1171.3)
0.430	8.900	(1290.6)
0.467	9.777	(1417.8)
0.493	10.428	(1512.2)
423.2 K (150°C, 302°F)		
0.085	2.145	(311.1)
0.123	3.156	(457.6)
0.208	5.374	(779.3)
0.269	7.098	(1029.0)
0.307	8.156	(1182.8)
0.324	8.692	(1260.4)
0.380	10.307	(1494.6)

150°C. During the degassing procedure a vacuum pump is directly coupled with the solvent storage cylinder. When the pressure in the storage cylinder decreases to the vapor pressure of the solvent, the solvent begins to vaporize and is carried out with the remaining gas. A section of tubing linking the degassing trap with the storage cylinder is exposed to room temperature. Although this section of tubing has been thoroughly wrapped with heating tape, there is no guarantee that the naphthalene, during degassing, would not form a solid plug in it and isolate the vacuum from the storage cylinder. Also, there was no means to detect the formation of such a plug without disturbing the degassing procedure. Degassing at 100°C, where the naphthalene vapor pressure is low, minimizes the risk of this occurring.

The SRK and PR equations fit the ethane + naphthalene data very well; in no case does solubility error exceed 0.002. Of particular interest in this system is the fact that parameters generated by regression of the lumped isotherms result in rms error twelve times that of the error generated by individual isotherm regression.

Ethane + Phenanthrene

The ethane + phenanthrene system was studied at 110 and 150°C, since the phenanthrene melting point of 100°C would make measurements at that temperature impractical. The data obtained at these two temperatures are listed in Table XVI. The SRK and PR equations seem to fit the data well since the solubility deviation exceeds 0.002 in only one instance. Table XI lists the optimized binary interaction parameters, and for this particular system, k_{ij}'s are essentially equal for both temperatures, and l_{ij}'s behave similarly. Ethane +

TABLE XVI

SOLUBILITY OF ETHANE IN PHENANTHRENE

Mole Fraction Ethane	Pressure MPa	(psia)
383.2 K (110°C, 230°F)		
0.081	2.264	(328.2)
0.126	3.720	(539.3)
0.187	5.710	(827.9)
0.204	6.533	(947.2)
0.307	11.207	(1624.9)
0.313	11.653	(1689.5)
423.2 K (150°C, 302°F)		
0.081	2.760	(400.2)
0.121	4.266	(618.5)
0.184	6.844	(992.3)
0.204	7.702	(1116.7)
0.240	9.419	(1365.7)
0.249	9.881	(1432.6)

phenanthrene was the only system containing an aromatic solvent for which this pattern occurred.

Ethane + Pyrene

The last system of interest in this work was ethane + pyrene. The pyrene melting point of 151°C necessitated a temperature of 160°C for study. This is the only isotherm obtained for the pyrene system, since the portion of the experimental apparatus housed insided the cell bath contains various Teflon and Viton seals for which 160°C is the upper limit of endurance. The data obtained for the ethane + pyrene system appear in Table XVII. Table XI lists the optimized binary interaction parameters for the system.

Comparison of the binary interaction parameter values for this system with those for all other ethane systems studies reveals a large inconsistency in the value of k_{ij} for ethane + pyrene. For no other system does the value of k_{ij} exceed 0.04, but for ethane + pyrene it assumes a value of 0.174. This unexpectedly large value of k_{ij} may be attributable to the fact that the equations of state used in this study require critical properties of the mixture components and those of pyrene must be estimated since the exact critical properties are not measurable. The critical properties for used for pyrene can only be estimated since pyrene undergoes thermal decomposition before its critical point can be attained for measurement. The critical properties each solvent are tabulated in Table XVIII.

Figures 21 through 23 present the binary interaction parameters obtained for the ethane + aromatic systems as functions of three different solvent parameters. Figure 21 shows the parameters as

TABLE XVII

SOLUBILITY OF ETHANE IN PYRENE

Mole Fraction Ethane	Pressure MPa	(psia)
------------------------433.2 K (160°C, 320°F)--------------------------		
0.072	2.857	(414.3)
0.090	3.677	(533.3)
0.125	5.216	(756.5)
0.155	6.889	(999.1)
0.174	7.806	(1132.0)
0.209	9.918	(1438.3)

TABLE XVIII

CRITICAL PROPERTIES USED IN EQUATIONS OF STATE

Solvent	Pressure (MPa)	Temperature (K)	Acentric Factor	Reference
n-Decane	2.096	617.6	0.4885	(30)
n-Dodecane	1.823	658.3	0.562	(27)
n-Tetradecane	1.621	694.0	0.679	(27)
Cyclohexane	4.073	553.4	0.433	(27)
trans-Decalin	2.908	681.5	0.286	(27)
Benzene	4.897	562.1	0.2125	(30)
Naphthalene	4.053	748.4	0.302	(27)
Phenanthrene	3.30	873.2	0.540	(31)
Pyrene	2.60	938.2	0.344	(32)

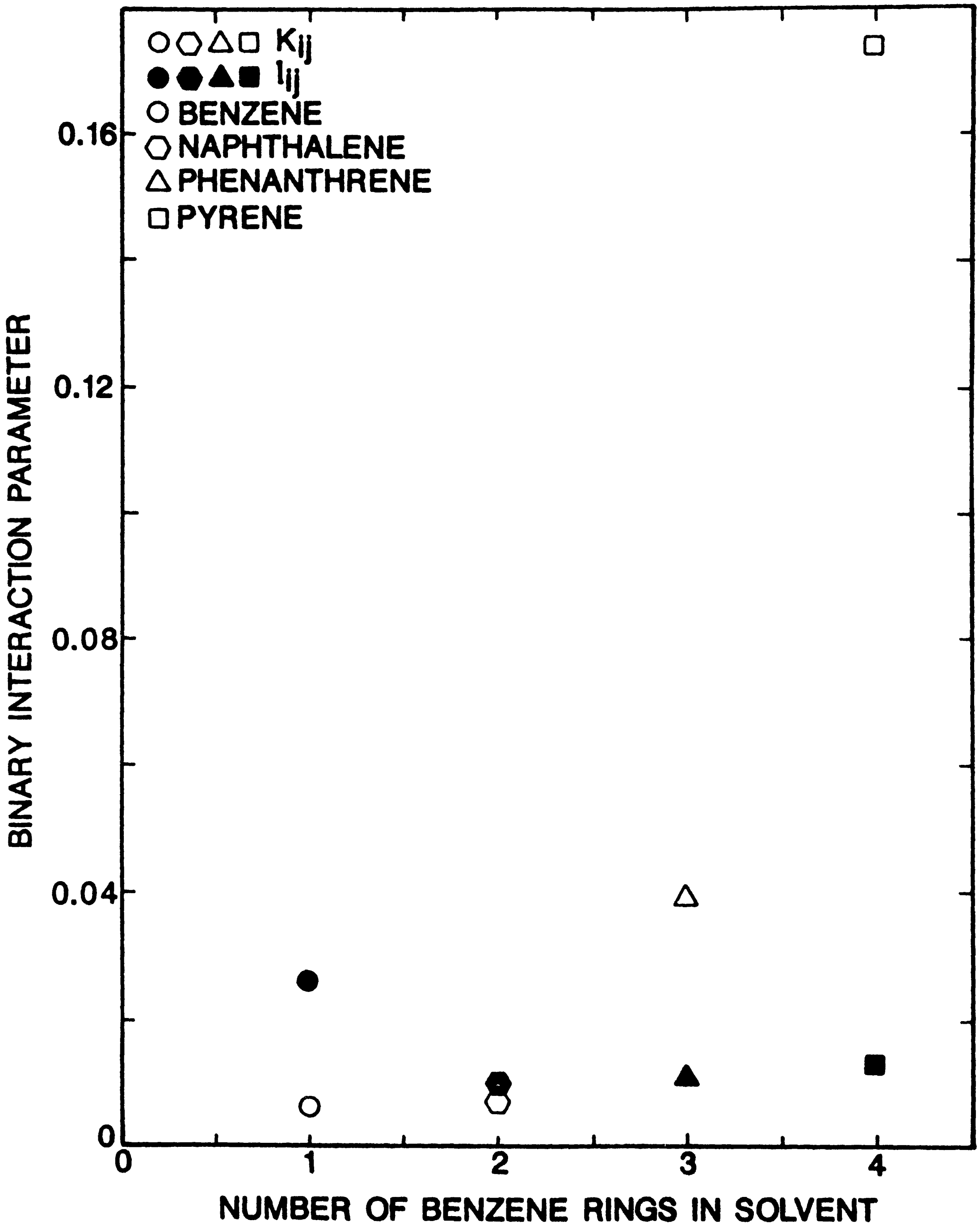


Figure 21. Binary Interaction Parameters as Functions of Numbers of Benzene Rings in Aromatic Solvents

functions of the number of benzene rings in the solvent, and Figure 22 shows the parameters as functions of solvent molecular weight. The parameters displayed in these two figures were obtained through simultaneous regression of all isotherms for a given solvent. The value of k_{ij} seems to increase with the solvent molecule size, though not in a uniform fashion. The value of l_{ij} appears relatively constant with the exception of the benzene parameter which deviates positively from the pattern established by the other three.

Figure 23 displays binary interaction parameters as functions of solvent liquid density. In this figure, the value of l_{ij} seems to be reasonably constant with the maximum at a solvent density of 0.84. The behavior of k_{ij} is highly erratic and thus no obvious correlation exists between k_{ij} and solvent density. The value of k_{ij} increases with molecule size when naphthalene is omitted.

Table XIX summarizes the densities of ethane and solvents and the volume of each injected during every data run performed in this work. The references from which the solvent densities were obtained are also listed in Table XIX. The solubilities of ethane for all bubble points obtained in this work may be recalculated in the event that discrepancies are found between ethane or solvent densities used in this work and those reported by some other source. Using a different ethane or solvent density, revised ethane solubilities may be calculated using the following equation:

$$x_{C_2H_6} = \frac{(\rho_{C_2H_6} \sum_{i=1}^{N} V_{i,C_2H_6}) / MW_{C_2H_6}}{(\rho_{C_2H_6} \sum_{i=1}^{N} V_{i,\, C_2H_6})/MW_{C_2H_6} + \rho_s V_s / MW_s} \qquad (6.1)$$

where: x is the solubility

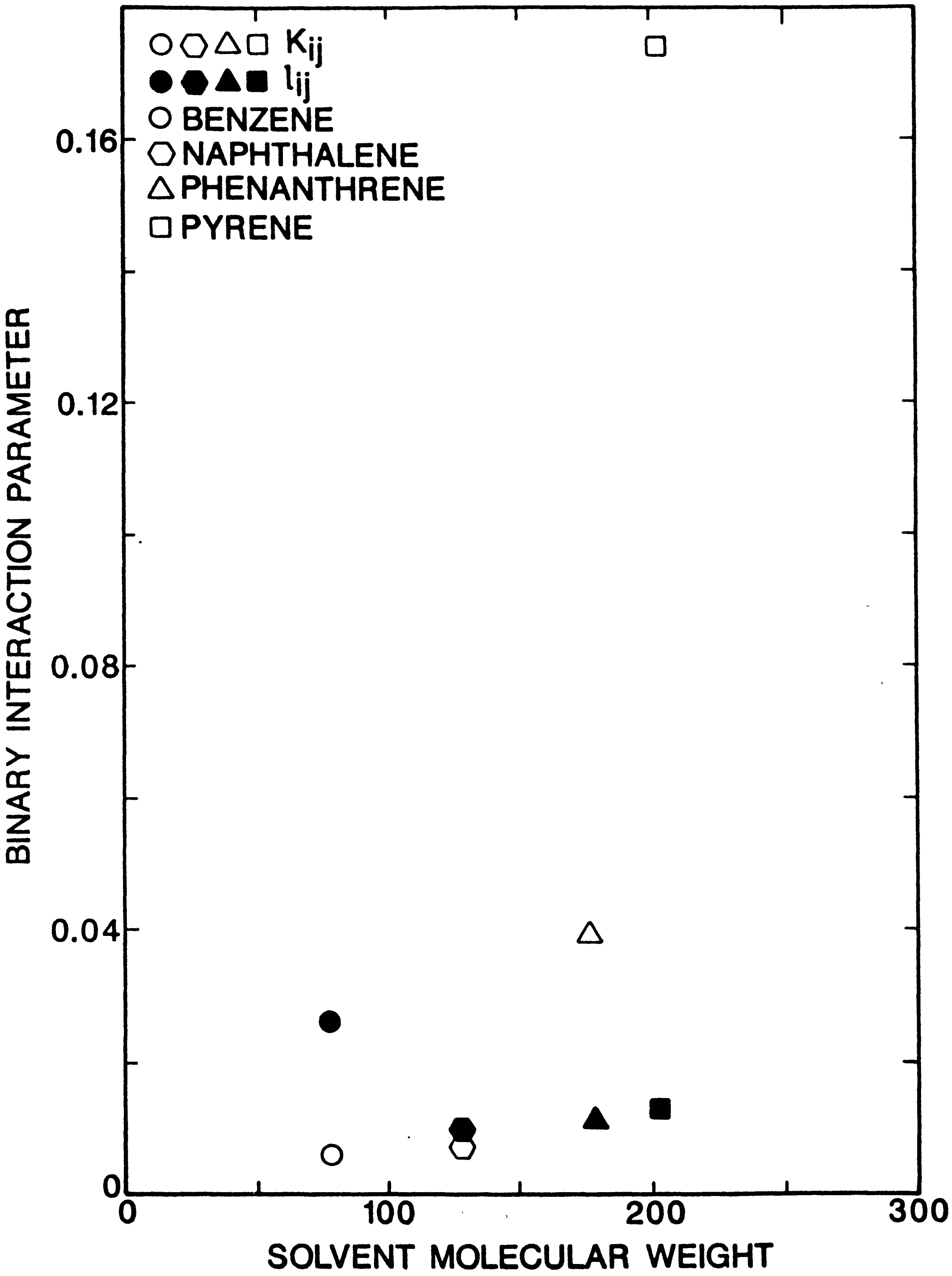


Figure 22. Binary Interaction Parameters as Functions of Molecular Weights of Aromatic Solvents

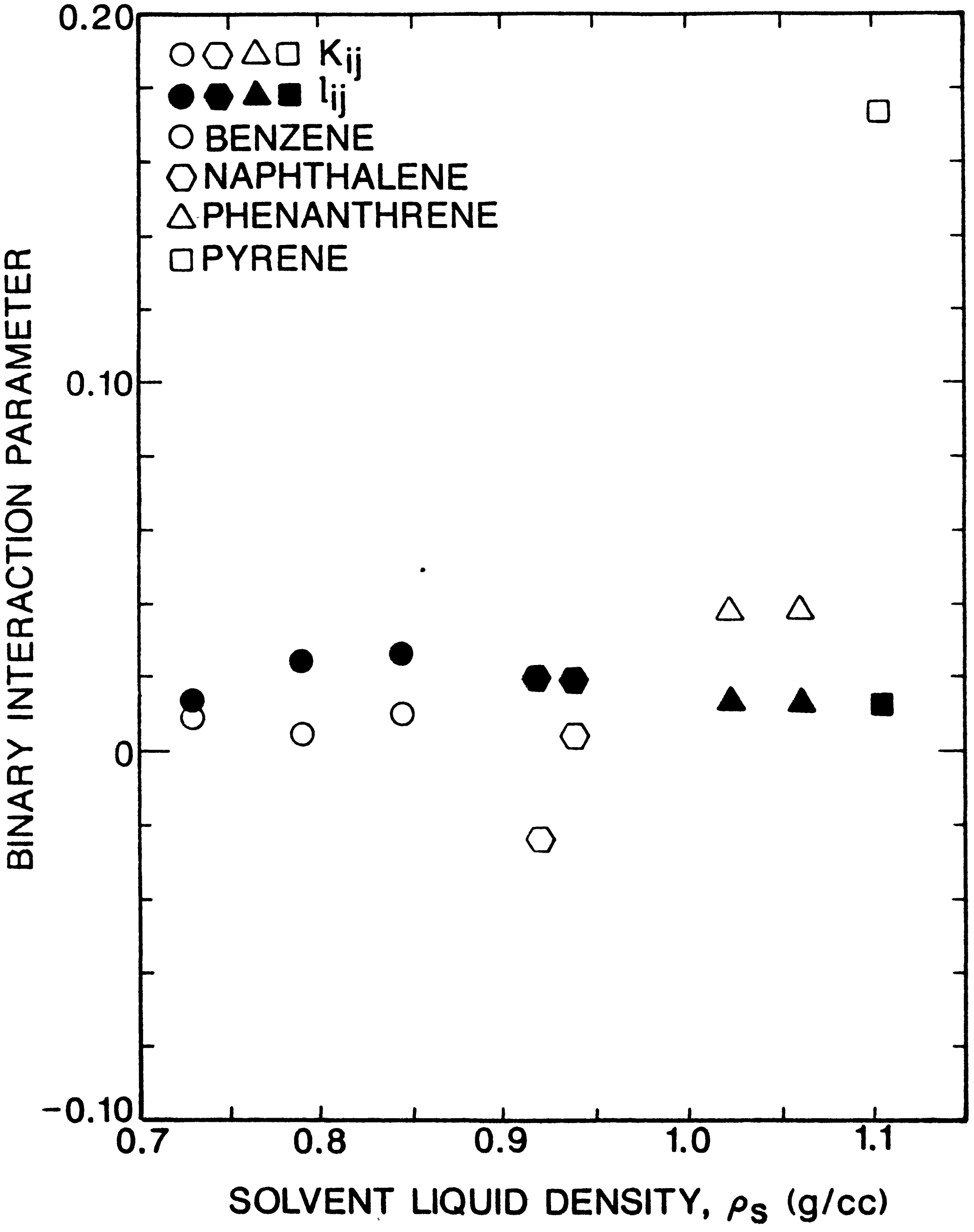


Figure 23. Binary Interaction Parameters as Functions of Aromatic Solvent Liquid Densities

TABLE XIX

DENSITIES AND VOLUMES USED TO CALCULATE SOLUBILITIES IN ETHANE SYSTEMS

Solvent* Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for C_2H_6 at 50°C (psia)	Calculated Ethane density (g/cm^3) $\rho_{C_2H_6}$	Volume of Ethane Injected (cm^3) $V_{iC_2H_6}$	Solvent Injection Number
n-Decane 100°F					
0.7167	6.46	610.7	0.0676	1.76	1
		626.4	0.0704	2.03	1
		626.4	0.0704	2.23	1
	6.59	624.7	0.0701	2.07	2
		500.8	0.0506	4.46	2
		500.9	0.0506	6.54	2
	6.55	500.8	0.0506	7.30	3
		485.2	0.0484	11.47	3
		485.2	0.0484	10.29	3
	5.57	495.6	0.0499	0.96	4
		493.1	0.0499	14.11	4
n-Decane 160°F					
0.6908	5.53	511.0	0.0520	1.82	1
		510.6	0.0520	4.99	1
		524.5	0.0540	9.02	1
		524.7	0.0540	9.98	1
	6.28	524.7	0.0540	4.31	2
		505.4	0.0512	8.51	2
		505.5	0.0512	11.55	2
n-Decane 220°F					
0.6641	5.03	509.4	0.0520	1.62	1
		509.4	0.0520	7.75	1
		509.6	0.0520	10.99	1
	5.81	505.6	0.0513	4.02	2
		505.7	0.0513	3.75	2
		505.9	0.0513	8.43	2

TABLE XIX (Continued)

Solvent* Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for C_2H_6at 50°C (psia)	Calculated Ethane density (g/cm^3) $\rho_{C_2H_6}$	Volume of Ethane Injected (cm^3) $V_{iC_2H_6}$	Solvent Injection Number
------n-Decane 280°F------					
0.6367	5.61	513.3	0.0523	3.94	1
		513.3	0.0523	5.85	1
		513.3	0.0523	10.26	1
	5.24	528.0	0.0545	1.52	2
		525.0	0.0545	4.65	2
		525.0	0.0545	6.78	2
		528.0	0.0545	9.82	2
------Cyclohexane 50°C------					
0.7362	6.21	492.0	0.0494	2.68	1
		492.0	0.0494	5.60	1
		492.0	0.0494	15.61	1
		492.0	0.0494	16.58	1
		502.7	0.0509	1.34	2
		502.7	0.0509	3.16	2
		502.7	0.0509	9.60	2
		505.5	0.0512	24.08	2
------Cyclohexane 100°C------					
0.6956	4.22	499.6	0.0504	1.08	1
		499.6	0.0504	4.44	1
		499.6	0.0504	8.44	1
		498.7	0.0503	10.77	1
		505.6	0.0513	3.71	2
		505.9	0.0513	6.88	2
		505.9	0.0513	14.06	2
------Cyclohexane 150°C------					
0.6474	5.01	494.9	0.0498	2.59	1
		494.9	0.0498	3.37	1
		494.9	0.0498	6.64	1
		494.9	0.0498	12.45	1
	4.59	507.1	0.0515	6.34	2
		506.7	0.0515	8.94	2

TABLE XIX (Continued)

Solvent* Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for C_2H_6 at 50°C (psia)	Calculated Ethane density (g/cm^3) $\rho_{C_2H_6}$	Volume of Ethane Injected (cm^3) $V_{iC_2H_6}$	Solvent Injection Number
Benzene 50°C					
0.8469	4.91	507.8	0.0516	1.66	1
		507.8	0.0516	6.10	1
		507.8	0.0516	19.07	1
		507.8	0.0516	19.81	1
	5.58	506.5	0.0513	3.98	2
		506.7	0.0514	12.48	2
		501.2	0.0506	1.97	2
Benzene 100°C					
0.7907	4.00	537.4	0.0558	2.17	1
		537.8	0.0559	3.83	1
		519.1	0.0532	6.20	1
		519.0	0.0532	10.54	1
	4.48	543.3	0.0567	3.09	2
		543.4	0.0567	5.14	2
		543.4	0.0567	7.98	2
Benzene 150°C					
0.7295	5.16	517.0	0.0528	3.08	1
		517.0	0.0529	8.78	1
		499.2	0.0504	16.19	1
	5.04	500.6	0.0506	1.46	2
		500.6	0.0506	5.62	2
		500.6	0.0506	11.51	2
		501.1	0.0506	5.77	2
trans-Decalin 50°C					
0.8450	6.22	511.7	0.0521	1.25	1
		511.7	0.0521	4.65	1
		503.7	0.0510	6.89	1
		503.8	0.0510	8.04	1
	6.20	507.4	0.0520	1.24	2
		510.9	0.0520	1.32	2
		510.9	0.0520	7.75	2
		510.7	0.0520	13.82	2

TABLE XIX (Continued)

Solvent* Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for C_2H_6 at 50°C (psia)	Calculated Ethane density (g/cm^3) $\rho_{C_2H_6}$	Volume of Ethane Injected (cm^3) $V_{iC_2H_6}$	Solvent Injection Number
------------------------------trans-Decalin 100°C---------------------					
0.8124	5.90	512.0	0.0522	2.31	1
		512.0	0.0522	2.80	1
		512.0	0.0522	8.22	1
		511.7	0.0521	12.20	1
	5.91	515.4	0.0526	3.55	2
		515.4	0.0526	5.14	2
		515.4	0.0526	9.91	2
------------------------------trans-Decalin 150°C---------------------					
0.7865	7.91	497.7	0.0502	2.95	1
		497.9	0.0502	8.74	1
		497.9	0.0502	6.91	1
	5.27	472.4	0.0467	1.33	2
		471.9	0.0467	3.30	2
		471.9	0.0467	1.87	2
		471.8	0.0467	12.93	2
------------------------------Naphthalene 100°C-----------------------					
0.9628	5.86	520.2	0.0534	3.79	1
		520.4	0.0534	5.11	1
		520.4	0.0534	7.13	1
		520.3	0.0534	8.14	1
	5.21	520.3	0.0534	4.18	2
		536.0	0.0557	9.38	2
		536.1	0.0557	5.14	2
	5.67	511.8	0.0521	6.46	3
		511.8	0.0521	5.71	3
		511.8	0.0521	6.35	3
------------------------------Naphthalene 150°C-----------------------					
0.9628$^+$	5.67	519.3	0.0532	3.38	1
		519.4	0.0532	5.49	1
		519.4	0.0532	2.66	1
		519.4	0.0532	3.22	1

$^+$Injection made at 100°C

TABLE XIX (Continued)

Solvent* Density (g/cm^3) ρ_{HC}	Volume of Solvent Injected (cm^3) V_{HC}	Injection Pressure for C_2H_6 at 50°C (psia)	Calculated Ethane density (g/cm^3) $\rho_{C_2H_6}$	Volume of Ethane Injected (cm^3) $V_{iC_2H_6}$	Solvent Injection Number
------Naphthalene 150°C------					
	5.63	533.8	0.0553	2.14	2
		532.5	0.0551	3.91	2
		532.6	0.0551	4.17	2
------Phenanthrene 110°C------					
1.0613	5.75	513.6	0.0524	2.84	1
		513.6	0.0524	2.20	1
		513.6	0.0524	3.93	1
	5.41	513.8	0.0524	1.64	2
		513.9	0.0524	2.60	2
		513.6	0.0524	3.96	2
------Phenanthrene 150°C------					
1.0613$^+$	5.57	513.6	0.0524	2.63	1
		513.6	0.0524	2.24	1
		513.6	0.0524	1.43	1
1.0326	5.82	514.0	0.0524	1.69	2
		514.0	0.0524	2.67	2
		514.3	0.0525	1.72	2
$^+$Injection made at 110°C					
------Pyrene 160°C------					
1.1065	5.91	518.4	0.0531	1.81	1
		518.7	0.0531	1.56	1
		519.0	0.0531	1.48	1
	6.20	518.5	0.0531	1.49	2
		518.5	0.0531	1.25	2
		518.5	0.0531	1.32	2

***Density references:** **n-Decane (33), Cyclohexane (33), trans-Decalin (34), Benzene (33), Naphthalene (35), Phenanthrene (35), Pyrene (1).**

ρ is the density

V_i is the volume injected during injection "i" in a series

of N injections

MW is the molecular weight

In the course of this study many routine problems were encountered, such as leaks, faulty equipment and failure of parts necessitating replacements. All of these were costly in the respect that they required extensive trouble-shooting and repair time.

One problem encountered deserves individual mention. Originally, ethane of CP Grade (99.0+%), supplied by Linde Division of Union Carbide, was used in measurement of bubble points in ethane systems. Four isotherms were measured using this grade of ethane. The data for ethane + benzene at 50°C were compared with the data of Kay and Nevens and an almost constant difference of 30 psi was found between the data of this work and that of Kay and Nevens. Consequently, new ethane of 99.99+% stated purity was obtained from Matheson and the isotherm was remeasured. Figure 24 shows the standard plot of $p/x_{C_2H_6}$ for the ethane + n-decane system using data obtained from the use of both grades of ethane. This clearly establishes that the ethane of 99.99% purity is a necessity in conducting studies of thermophysical properties of ethane-containing systems where precise knowledge of the ethane mole fraction is required. The impurity in the 99% ethane (likely ethylene) obviously gave rise to increased bubble point pressures.

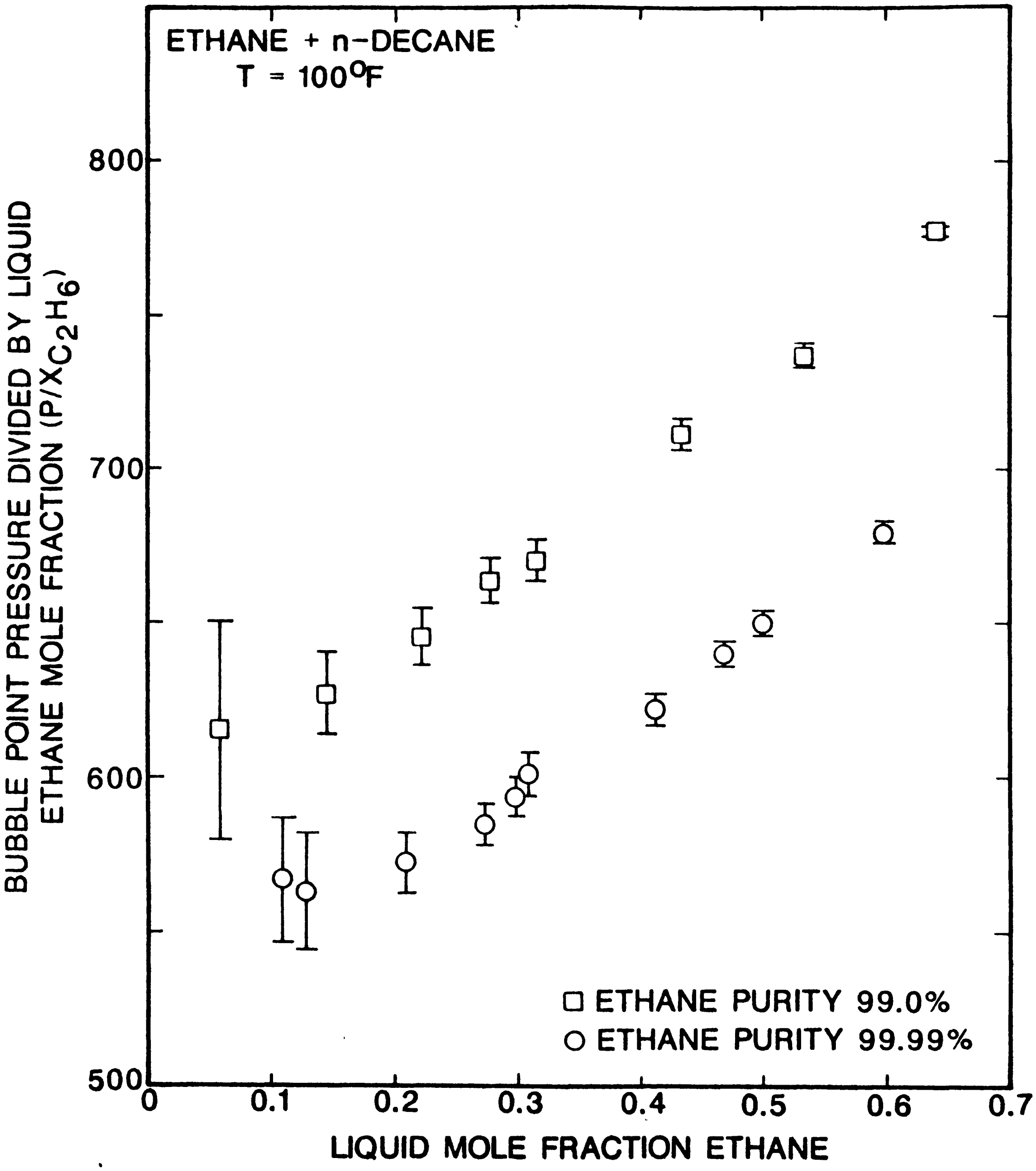


Figure 24. Comparison of Bubble-Point Data for Ethane + n-Decane Using Different Purities of Ethane

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Accomplished in this study were the measurement of high pressure solubilities of CO_2 in n-decane, n-dodecane, n-tetradecane and benzene, and the solubilities of ethane in n-decane, 1- and 2-ring naphthenic solvents and 1-, 2-, 3-, and 4-ring aromatic solvents. Based on the findings herein, the following conclusions and recommendations are drawn.

Conclusions

1. Measurement of the vapor pressure of propane obtained with the apparatus agrees within 0.8 psi of that reported in literature data.
2. The measurements of the solubility of CO_2 in benzene at 40°C are consistent within combined experimental uncertainty to those of Gasem and Gupta.
3. The precision of the solute and solvent injection pumps utilized in this study enables calculations of compositions of binary systems with a precision of 0.0005 solute mole fraction. Bubble-point pressure have been measured with digital pressure gauges accurate to 0.1 psia. Therefore the measurements of gas solubilities for the following systems have been performed with an accuracy equal to or surpassing that of previous studies:

System	Pressure psia	Temperatures, °F
CO_2 + Benzene	180 - 800	104
CO_2 + n-Decane	180-1250	160
CO_2 + n-Dodecane	130-1360	122-212
CO_2 + n-Tetradecane	220-1750	160
Ethane + n-Decane	60-1200	100-280
Ethane + Benzene	70-1230	122-302

4. This study is the first of its kind in which high-pressure gas solubilities have been determined for the following system:

System	Pressures (psia)	Temperatures (°F)
Ethane + Cyclohexane	40-1130	122-302
Ethane + trans-Decalin	50-1260	122-302
Ethane + Naphthalene	310-1520	212-302

System	Pressures (psia)	Temperatures (°F)
Ethane + Phenanthrene	330-1690	230-302
Ethane + Pyrene	410-1440	320

5. Binary interaction parameters have been optimized by regression of the data obtained for each system, for the cases of individual isotherms, lumped isotherms, the use of a single parameter (k_{ij}), and the use of two parameters (k_{ij}, l_{ij}). These optimizations have been performed for both the SRK and PR equations of state.
6. Solubilities of CO_2 and ethane in hydrocarbons are predicted by the SRK and PR equations with an average RMS error of 0.002 liquid CO_2 or ethane mole fraction when two binary interaction parameters per isotherm are used. The use of only one binary interaction parameter (k_{ij}) in these equations results in RMS errors in predicted CO_2 or ethane solubility ranging from one to twelve times the solubility error generated by the use of two interaction parameters. In most cases, the RMS error generated by the use of one interaction parameter is at least twice that generated by the use of two.
7. Both k_{ij} and l_{ij} are temperature dependent, although no straightforward correlations were developed between these quantities. Data at narrower temperature intervals is required to draw a sufficient analytical correlation between temperature and k_{ij} and l_{ij} values for a particular system.

Recommendations

1. A study of the solubility of nitrogen in the aromatic and naphthenic solvents used in this study would provide extremely useful data. With industrial interest increasing in the use of nitrogen displacement of hydrocarbons as an enhanced oil recovery technique, a new demand will exist for phase behavior data for N_2 + hydrocarbon systems. At present, such data are extremely scarce.
2. Measurements should be conducted on solubilities of CO_2, ethane and N_2 in mixtures of paraffinic, naphthenic and aromatic solvents. This will help to delineate the effects of the aromatic, naphthenic and/or paraffinic character of mixtures on the phase behavior on the success of binary interaction parameters (from binary system studies) employed in the SRK or PR equations to model such mixtures.

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APPENDIXES

APPENDIX A

EXPLANATION AND PRESENTATION OF COMPUTER PROGRAM USED TO EVALUATE PERCENT UNCERTAINTIES IN CO_2 AND ETHANE DENSITIES

The uncertainty in the density of the solute gas is given by the following relation, where the uncertainty in density is denoted by ε_ρ^2 :

$$\varepsilon_\rho^2 = \left(\frac{\partial\rho}{\partial T}\right)_p^2 \varepsilon_T^2 + \left(\frac{\partial\rho}{\partial p}\right)_T^2 \varepsilon_p^2$$

where ε_T and ε_p are the experimental uncertainties associated with temperature and pressure measurements. For the particular apparatus used in this study, ε_T is assigned a value of 0.2°C and ε_p is assigned a value of 1 psi.

The partial derivatives of density with respect to temperature and pressure are evaluated using the SRK equation. To avoid solution of a cubic equation, temperature and density are specified and pressure is then calculated from the equation of state and the uncertainty in density is calculated at that pressure.

The following computer program implements the preceding steps in calculating percent uncertainty in density of the solute gas (CO_2 or ethane) at the injection temperature of 50°C. The program is adaptable to any pure component by simply entering the critical constants and acentric factor of that component.

```
//RH02   JOB (15348,000-00-0000),'0000',TIME=(00,5),CLASS=F,
// MSGCLASS=X,NOTIFY=*
/*PASSWORD ?
/*JOBPARM FORMS=9031,LINECT=76,ROOM=K
// EXEC WATFIV
//WATFIV.SYSIN DD *
$JOB            ,TIME=(0,5)
C234567890123456
      REAL M,MOLWT
      EPSP=0.05
      EPST=0.05
      W=0.091
      PC=707.8
      TC=549.8
      TIN=582.
      TINC=20.
      TFIN=582
      VIN=500.
      VINC=10.
      VFIN=40.
      MOLWT=30.
      T=TIN
 47   V=VIN
      R=669.9
C
      WRITE(6,70)
 70   FORMAT(/5X,'PRESSURE',5X,'TEMPERATURE',5X,'VOLUME',5X,
     C 'UNCERTAINTY',5X,'PERCENT UNCERTAINTY')
      WRITE(6,71)
 71   FORMAT(6X,'(PSIA)',10X,'(F)',8X,'(CM/MOL)',4X,'IN DENSITY',11X,'IN
     C DENSITY')
      WRITE(6,72)
 72   FORMAT(47X,'(G/CM3)')
      WRITE(6,73)
 73   FORMAT(4X,'__________',3X,'______________',3X,'_________',3X,'_______
     C__________',3X,'_________________________',/)
C
C  CALCULATE A AND B @ARAMETERS FOR SRK EQUATION
C
      A=(0.4275*R**2*TC**2)/PC
      B=(0.08664*R*TC)/PC
      TR=T/TC
C
C
C  CALCULATE VALUE OF A(T) FOR SRK EQUATION
C
C
      M=0 480+1.574*W-0.176*W**2
      AT=A*(1+M*(1-SQRT(TR)))
C
C
C   CALCULATE PARTIALS OF A(T) WITH RESPECT TO TEMPERATURE
C
C
      DAT=(-A/2)*M*(1/SQRT(T*TC))
C
C
C   CALCULATE PRESSURE VIA SRK
C
 46   P=(R*T)/(V-B)-AT/(V*(V+B))
C2345678
C
C
C
C     CALULATE DP/DT AND DP/DV
C
C
      DPDT=R/(V-B)-DAT/(V*(V+B))
      PART1=-(R*T)/(V-B)**2
      PART2=AT*(1/(V*(V+B)))*(1/(V+B)+1/V)
      DPDV=PART1+PART2
C
```

```
C
C   CALCULATE PARTIALS OF DENSITY WITH RESPECT TO TEMP AND PRESS
C
C
      DRHODP=-1/(V**2)*1/DPDV
      DRHODT=DPDT/(V**2*DPDV)
C
C   CALCUALTE UNCERTAINTY,  DENSITY, AND % UNCERTAINTY
C
      EPSROM=SQRT((DRHODP*EPSP)**2+(DRHODT*EPST)**2)
      EPSRHO = EPSROM
      EPSRHO=EPSRHO*MOLWT
      RHO=MOLWT/V
      PERC=(EPSRHO/RHO)*100
      TF=T-460
      WRITE(6,50)P,TF,V,EPSRHO,PERC
   50 FORMAT(3X,F10.2,7X,F6.2,5X,F10.2,5X,F10.8,7X,F10.8)
      IF(V.EQ.VFIN)GO TO 53
      V=V-VINC
      GO TO 46
   53 IF(T.EQ.TFIN)GO TO 54
      T=T+TINC
      GO TO 47
   54 STOP
      END
$ENTRY
$IBSYS
//
```

APPENDIX B

EXPLANATION AND PRESENTATION OF PROGRAM USED TO CALCULATE CO_2 DENSITY

The following program implements an equation of state developed by IUPAC (37) for high-accuracy determination of CO_2 density. The equation of state actually consists of two equations; an analytical equation which retains accuracy in all regions except in close proximity to the critical point, and a scaling equation which works only in a small region around the critical point. A switching function coordinates these two pressures according to the distance from the critical point to the (ρ,T) point at which the calculation is being made.

The equation is written such that ρ and T are specified and P is calculated. In this study a program calculating ρ from specified P and T is highly preferable. Therefore a numerical Newton-Raphson convergence algorithm envelopes the equation and calculates the correct ρ through a series of modifications of an initial guess, given by the ideal gas law.

The program has the capability to handle a variety of input pressure and temperature units as well as to generate a variety of output units. In addition, arrays may be generated by specifying initial and final temperatures with a set temperature increment and similar specifications on pressure.

```
$JOB            ,TIME=(0,5),NOLIST
C2345678901234567890
C
C
C       CALCULATE PRESSURE USING ANALYTICAL EQUATION OF STATE
C
C
C
      IMPLICIT REAL *8 (A-G,O-Z)
      DIMENSION BIJ(10,7),A(4),C(2),D(2)
      DATA BIJ/-7.25854437D-01,4.47869183D-01,-1.72011999D-01,
     C4.46304911D-03,2.55491571D-01,5.94667298D-02,
     C-1.47960010D-01,1.36710441D-02,3.92284575D-02,
     C-1.19872097D-02,-1.68332974D00,1.26050691D00,
     C-1.83458178D00,-1.76300541D00,2.37414246D00,
     C1.16974683D00,-1.69233071D00,-1.00492330D-01,
     C4.41503812D-01,-8.46051949D-02,2.59587221D-01,
     C5.96957049D00,-4.61487677D00,-1.11436705D01,
     C7.50925141D00,7.43706410D00,-4.68219937D00,
     C-1.63653806D00,8.86741970D-01,4.64564370D-02,
     C3.76945574D-01,1.54645885D01,-3.82121926D00,
     C-2.78215446D01,6.61133318D00,1.50646731D01,
     C-3.13517448D00,-1.87082988D00,0.0D00,0.0D00,
     C-6.70755370D-01,1.94449475D01,3.60171349D00,
     C-2.71685720D01,-2.42663210D00,9.57496845D00,
     C0.0D00,0.0D00,0.0D00,0.0D00,-8.71456126D-01,
     C8.64880497D00,4.92265552D00,-6.42177872D00,
     C-2.57944032D00,0.0D00,0.0D00,0.0D00,0.0D00,0.0D00,
     C-1.49156928D-01,0.0D00,0.0D00,0.0D00,0.0D00,0.0D00,
     C0.0D00,0.0D00,0.0D00,0.0D00/
      DATA A/-6.8849249D00,-9.5924263D00,1.3679755D01,
     C-8.6056439D00/
      DATA C/3.822502D-01,4.2897885D-01/
      WRITE(6,73)
   73 FORMAT(//15X,'****** DETERMINATION OF CARBON DIOXIDE DENSITY *****
     C*')
      WRITE(6,74)
   74 FORMAT(//20X,'ENTER TEMPERATURE UNITS')
      WRITE(6,175)
  175  FORMAT(20X,'1-FARENHEIT, 2-RANKINE, 3-KELVIN, 4-CELSIUS?')
      READ(9,176) L1
  176  FORMAT(I1)
      WRITE(6,177)
  177  FORMAT(/20X,'ENTER PRESSURE UNITS')
      WRITE(6,178)
  178  FORMAT(20X,'1-PSIA, 2-ATM, 3-BAR ?')
      READ(9,79) L2
   79 FORMAT(I1)
      WRITE(6,81)
   81 FORMAT(/20X,'ENTER DESIRED DENSITY UNITS')
      WRITE(6,82)
   82 FORMAT(20X,'1-G/CM3, 2-LB/FT3 ?')
      READ(9,83) L3
   83 FORMAT(I1)
      WRITE(6,199)
  199 FORMAT(//5X,'FIX DECIMAL POINT WHEN ENTERING ALL REQUESTED DATA
     C'//)
      WRITE(6,84)
   84 FORMAT(/5X,'ENTER INITIAL TEMPERATURE')
      READ(9,86) T
   86 FORMAT(D10.4)
      WRITE(6,87)
   87 FORMAT(/5X,'ENTER FINAL TEMPERATURE')
      READ(9,88) TFIN
   88 FORMAT(D10.4)
      WRITE(6,89)
   89 FORMAT(/5X,'ENTER TEMPERATURE INCREMENT')
      READ(9,91)TINC
   91 FORMAT(D10.4)
      WRITE(6,92)
   92 FORMAT(/5X,'ENTER INITIAL PRESSURE')
      READ(9,93)P
```

```
   93 FORMAT(D10.4)
      WRITE(6,94)
   94 FORMAT(/5X,'ENTER FINAL PRESSURE')
      READ(9,95) PFIN
   95 FORMAT(D10.4)
      WRITE(6,96)
   96 FORMAT(/5X,'ENTER PRESSURE INCREMENT')
      READ(9,97)PINC
   97 FORMAT(D10.4)
      WRITE(6,135)
  135 FORMAT(/5X,'OUTPUT UNITS ARE:')
      IF(L1.EQ.1)GO TO 251
      IF(L1.EQ.2)GO TO 252
      IF(L1.EQ.4)GO TO 253
      IF(L1.EQ.3)GO TO 302
  251 T=(T+459.669)/1.8
      TFIN=(TFIN+459.669)/1.8
      TINC=TINC/1.8
      WRITE(6,136)
  136 FORMAT(5X,'TEMPERATURE - DEGREES FARENHEIT')
      GO TO 254
  252 T=T/1.8
      TFIN=TFIN/1.8
      TINC=TINC/1.8
      WRITE(6,137)
  137 FORMAT(5X,'TEMPERATURE - DEGREES RANKINE')
      GO TO 254
  253 T=T+273.15
      TFIN=TFIN+273.15
      WRITE(6,138)
  138 FORMAT(5X,'TEMPERATURE - DEGREES CELSIUS')
      GO TO 254
  302 WRITE(6,303)
  303 FORMAT(5X,'TEMPERATURE - DEGREES KELVIN')
  254 IF(L2.EQ.1)GO TO 155
      IF(L2.EQ.2)GO TO 156
      IF(L2.EQ.3)GO TO 305
  155 P=0.068947*P
      PINC=0.068947*PINC
      PFIN=0.068947*PFIN
      WRITE(6,141)
  141 FORMAT(5X,'PRESSURE - PSIA')
      GO TO 257
  156 P=1.01325*P
      PINC=1.01325*PINC
      PFIN=1.01325*PFIN
      WRITE(6,142)
  142 FORMAT(5X,'PRESSURE - ATMOSPHERES')
      GO TO 257
  305 WRITE(6,306)
  306 FORMAT(5X,'PRESSURE - BAR')
  257 IF (L3.EQ.1)GO TO 310
      WRITE(6,311)
  311 FORMAT(5X,'DENSITY - POUNDS PER CUBIC FT')
      GO TO 340
  310 WRITE(6,312)
  312 FORMAT(5X,'DENSITY - GRAMS PER CM3')
  340 WRITE(6,98)
   98 FORMAT(//10X,'PRESSURE',8X,'TEMPERATURE',8X,'CO2 DENSITY',13X,'Z')
      WRITE(6,99)
   99 FORMAT(9X,'----------',6X,'-------------',6X,
     C'--------------',7X,'----------'/)
  401 PIN=P
  402 P=PIN
   78 TC=304.21
      PC=73.825
      RHOC=0.010589
      R=83.143
      IF(T.GT.TC)GO TO 22
      PSUM=0.0
      DO 23 I=1,4
          PCONST=A(I)*(TC/T-1)**I
```

```
          PSUM=PSUM+PCONST
  23  CONTINUE
      PSAT=PC*DEXP(11.3774*(1-T/TC)**1.935+PSUM)
      IF(P.LT.PSAT)GO TO 22
      SUM=0.0
      DO 26 I=1,2
          CON=C(I)*(1-T/TC)**((I+1.0)/3.0)
          SUM=SUM+CON
  26  CONTINUE
      RHO=RHOC*(1+1.9073793*(1-T/TC)**0.347+SUM)
  28  GO TO 41
  22  RHO=P/(R*T)
  41  M=0
  31  SUM=0.0
      TAU=304.2/T
      OMEGA=RHO/0.01063
      DO 100 J=1,7
        DO 90 I=1,10
            CONST=BIJ(I,J)*(TAU-1)**(J-1)*(OMEGA-1)**(I-1)
            SUM=SUM+CONST
  90    CONTINUE
 100  CONTINUE
      Z=1.0+OMEGA*SUM
      R=83.143
      PA=RHO*Z*R*T
C
C
C
C
C   CALCULATE CRITICAL EQUATION PARAMETERS
C
C
      DELT=DABS((T-TC)/TC)
      DELRHO=DABS((RHO-RHOC)/RHOC)
      R=DELT +(0.6471102*DELRHO**2)**1.4409
  25  X=R-0.6471102*R**0.306*DELRHO**2-DELT
      ABSX=DABS(X)
      IF (ABSX.LT.1E-5)GO TO 20
      DX=1-0.198016*DELRHO**2/R**0.694
      R=R-X/DX
      GO TO 25
   20 THETA=0.670302*DELRHO/R**0.347
      QT1=37.26895-82.70074*THETA**2+57.08947*THETA**4.0
      IF (T.GE.TC)GO TO 30
      CCAL=-53.81157
      GO TO 40
  30  CCAL=-34.92493
  40  QT2=CCAL*DABS(1.0-1.440248*THETA**2.0)**1.934872
      QTHETA=QT1+QT2
      DELP=R**1.9348*QTHETA+6.98*DELT+28.362
     C   *R**1.5879*THETA*(1-THETA**2)
      PS=PC*(1+DELP)
C
C   THE FINAL EQUATION
C
      EXP1=1-DEXP(-(0.01/R)**1.5)
      EXP2=1-DEXP(-(0.05/R)**3.0)
      FR=1-EXP1*EXP2
      PCALC=FR*PA+(1-FR)*PS
      ERR=DABS(P-PCALC)/P
      IF(ERR.LT.1E-4)GO TO 160
      IF(M.EQ.0)GO TO 131
      DRHODP=(RHODEL-RHOOLD)/(PCALC-POLD)
      RHO=RHOOLD+DRHODP*(P-POLD)
      GO TO 41
 131  M=1
      POLD=PCALC
      RHOOLD=RHO
      DEL=0.0001
      RHODEL=RHO+DEL
      RHO=RHODEL
      GO TO 31
```

```
  160 RHO=RHO*44.009                                                    00002160
      IF(L1.EQ.1)GO TO 350                                              00002170
      IF(L1.EQ.2)GO TO 351                                              00002180
      IF(L1.EQ.4)GO TO 352                                              00002190
      GO TO 353                                                         00002200
  350 HT4=1.8*T-459.669                                                 00002210
      GO TO 453                                                         00002220
  351 HT4=1.8*T                                                         00002230
      GO TO 453                                                         00002240
  352 HT4=T-273.15                                                      00002250
      GO TC 453                                                         00002251
  353 HT4=T                                                             00002252
  453 IF(L2.EQ.1)GO TO 354                                              00002260
      IF(L2.EQ.2)GO TO 255                                              00002270
      GO TO 356                                                         00002280
  354 HP4=14.504*P                                                      00002290
      GO TO 256                                                         00002310
  255 HP4=P/1.01325                                                     00002320
      GO TO 256                                                         00002323
  356 HP4=P                                                             00002325
  256 IF(L3.EQ.1)GO TO 378                                              00002330
      HRHO4=RHO*62.371                                                  00002340
      GO TO 379                                                         00002341
  378 HRHO4=RHO                                                         00002350
  379 R=83.143                                                          00002351
      Z=(PCALC*44.009)/(RHO*R*T)                                        00002352
      HZ=Z                                                              00002353
      WRITE(6,170)HP4,HT4,HRHO4,HZ                                      00002355
  170 FORMAT(7X,F10.2,8X,F10.2,10X,F10.6,8X,F10.5/)                     00002356
      P=P+PINC                                                          00002370
      IF(PINC.EQ.0.0)GO TO 75                                           00002375
      IF (P.GT.PFIN)GO TO 75                                            00002380
      GO TO 78                                                          00002390
   75 T=T + TINC                                                        00002400
      IF(TINC.EQ.0.0)GO TO 77                                           00002405
      IF (T.GT.TFIN)GO TO 77                                            00002410
      GO TO 402                                                         00002420
   77 STOP                                                              00002430
      END                                                               00002440
$ENTRY                                                                  00002450
$IBSYS                                                                  00002460
//                                                                      00002470
```

APPENDIX C

EXPLANATION AND PRESENTATION OF PROGRAM USED TO CALCULATE ETHANE DENSITY

The following program was developed by The National Bureau of Standards (36) for precise determination of ethane density. As with the IUPAC CO_2 equation, the pressure is calculated at a specified temperature and density. Therefore, a Newton-Raphson convergence scheme is employed to determine the density which corresponds to the input pressure.

```
$JOB            ,TIME=(0,5),NOLIST
C234567890123456
      IMPLICIT REAL *8  (A-G,O-Z)
      DIMENSION A(7),B(4),C(7),D(8)
      DATA A/1.3D00,-11.3899624306D00,18.8452282876D00,
     C -7.6354151345D00,5.4284431006D00,-1.3623270362D00,
     C 0.7692492586D00/
      DATA B/0.333D00,0.719684501D00,0.281866182D00,-0.289937306D00/
      DATA C/0.35D00,1.202348669D00,0.110005895D00,0.137169205D00,
     C -0.980317935D00,1.338756298D00,-0.807762749D00/
      DATA D/1.00D00,0.667D00,2.00D00,0.48752227313D00,0.33198750982D00,
     C 0.06854249828D00,-.43113918548D00,0.03779460468D00/
      WRITE(6,1)
  1   FORMAT(//10X,'***  DETERMINATION OF ETHANE DENSITY AT 122 F ***')
      DK=1.5154D-06
      MW=.3007D02
      DC=0.6800D01
      DT=.21680D02
      TT=.90348D02
      R=0.0831434D00
      PT=.11308D-04
      TC=.30533D03
      PC=0.48714D02
   8  WRITE(6,2)
  2    FORMAT(/10X,'ENTER ETHANE PRESSURE,PSIA')
      READ(9,19)P
  19  FORMAT(D10.4)
      P=P/14.503
      IF(P.EQ.0.0)GO TO 3
      T=323.14
      RHO=P/(R*T)
      TVAP=300
 222  MM=0
  41  M=0
 51   IF(RHO.LE.DC)GO TO 31
      XLD=(TC-TVAP)/(TC-TT)
      CAPY=B(2)+B(3)*XLD**(1.-B(1))+B(4)*XLD
      Y=CAPY*(XLD**B(1)-XLD)+XLD
      RHOVS=Y*(DT-DC)+DC
      GO TO 55
 31   XVD=(TC-TVAP)/(TC-TT)
      UVD=(TC/TVAP-1)/(TC/TT-1)
      CAPY=C(2)*UVD+C(3)*XVD**C(1)+C(4)*XVD**1.000+C(5)*XVD**1.333+C(6)
     C *XVD**1.667+C(7)*XVD**2.00
      AL=DLOG(DC/DK)
      CAP=CAPY*AL
      EX=DEXP(CAPY*AL)
      RHOVS=DC/EX
  55  ERR=DABS(RHOVS-RHO)
      IF(ERR.LT.0.0001)GO TO 61
      IF(M.EQ.0)GO TO 71
      DTDRHO=(TDEL-TOLD)/(RHOVS-RHOOLD)
      TVAP=TOLD+DTDRHO*(RHO-RHOOLD)
      GO TO 41
 71   M=1
      RHOOLD=RHOVS
      TOLD=TVAP
      DEL=0.0001
      TDEL=TVAP+DEL
      TVAP=TDEL
      GO TO 51
  61  XVP=(1-TT/TVAP)/(1-TT/TC)
      UVP=(TVAP-TT)/(TC-TT)
      PVAP=DEXP(A(2)+A(3)*XVP+A(4)*UVP+A(5)*UVP**2+A(6)*UVP**3+A(7)
     C *UVP*(1-UVP)**A(1))
C
C
C      CALCULATE PRESSURE FROM PVAP,TVAP
C
      SIG=RHOVS/DC
      P1=PVAP+SIG*R*DC*(T-TVAP)
      BB=D(4)+D(5)*SIG+D(6)*SIG**2.
```

```
      CC=(SIG-1.)*(SIG-2.0)*(D(7)+D(8)*SIG**2)                          00000770
      F=DABS((SIG-1.0)**3)/((DT/DC-1.0)**3)                             00000780
      THETA=TVAP*DEXP(-1.0*F)                                           00000790
      OMSIG=1.0-THETA/TVAP                                              00000800
      OMEGA=1.0-THETA/T                                                 00000810
      X3=TVAP/TC                                                        00000820
      PSISIG=0.6667/X3+(1-0.6667)*(1.0-OMSIG+OMSIG*DLOG(RHOVS))         00000830
      X4=T/TC                                                           00000840
      PSI=0.6667/X4+(1.0-0.6667)*(1.0-OMEGA+OMEGA*DLOG(OMEGA))          00000850
      CAPPSI=PSI-PSISIG                                                 00000860
      PHI=DSQRT(T/TC)*DLOG(T/TVAP)                                      00000870
      F=BB*PHI+CC*CAPPSI                                                00000880
      PCALC=P1+SIG**2*R*DC*TC*F                                         00000890
      ERR=DABS(P-PCALC)/P                                               00000940
      IF(ERR.LT.1.0E-4)GO TO 501                                        00000950
      IF(MM.EQ.0)GO TO 221                                              00000960
      DRHODP=(RHODEL-RHOLD2)/(PCALC-POLD)                               00000970
      RHO=RHOOLD+DRHODP*(P-POLD)                                        00000980
      GO TO 222                                                         00000990
  221 MM=1                                                              00001000
      POLD=PCALC                                                        00001010
      RHOLD2=RHO                                                        00001020
      DEL=0.01                                                          00001030
      RHODEL=RHO+DEL                                                    00001040
      RHO=RHODEL                                                        00001050
      GO TO 41                                                          00001060
  501  HRHO=RHO                                                         00001090
      HP=P*14.503                                                       00001091
      WRITE(6,777)HP,HRHO                                               00001100
  777 FORMAT(/5X,'ETHANE DENSITY AT ',F8.2,' PSIA IS ',F11.5,' G/CM3')  00001110
      GO TO 8                                                           00001120
    3 STOP                                                              00001130
      END                                                               00001140
$ENTRY                                                                  00001150
$IBSYS                                                                  00001160
//                                                                      00001170
```

APPENDIX D

EXPLANATION AND PRESENTATION OF PROGRAM USED TO CALIBRATE PRESSURE TRANSDUCERS

The calibration procedure for the hydrocarbon pressure transducer consists of a direct coupling of the transducer to the Ruska dead weight gauge and acquisition of transducer readings for each combination of weights placed atop the rotating dead-weight column.

The following program calculates the factors to be added to the hydrocarbon transducer readings to correct them to the accurate dead-weight gauge pressure. The Ruska dead weight pressure is calculated from an equation outlined in the manual accompanying the dead weight gauge (38). After the reference pressure is calculated, the transducer reading is subtracted from it to yield the transducer correction. A table is printed which lists the transducer correction factor as a function of transducer reading. A useful list of weight combinations is shown in Table A. The table lists the dead weight reference pressure corresponding to each combination of weights.

TABLE A

WEIGHT COMBINATIONS USED IN HYDROCARBON TRANSDUCER CALIBRATION

Weight Combination	Resulting Reference Pressure, psig
Q	49.94
P	79.90
O	129.84
O, P	179.77
M	229.71
M, Q	249.68
M, P	279.65
N, O, P	379.52
M, N	429.08
M, N, O	529.33
L, O	629.21
L, M	729.08
L, M, O	829.03
L, M, N	928.83
L, M, N, O	1028.70
A, O	1128.58
A, N	1228.42
A, M, O	1328.30
A, M, N	1428.17
A, M, N, O	1528.05
A, L, O	1627.93

```
//PRSS   JOB (15348,000-00-0000),'0000',TIME=(00,20),CLASS=A,
// MSGCLASS=X,NOTIFY=*
/*PASSWORD ?
/*JOBPARM FORMS=2972,LINECT=76,ROOM=K
// EXEC WATFIV
//WATFIV.SYSIN DD *
$JOB
C
C
C       THIS PROGRAM CALCULATES TRANSDUCER CORRECTIONS FOR THE PRESSURE
C       HYDROCARBON TRANSDUCER LOCATED IN EN412 FROM DEAD WEIGHT
C       TEST DATA.
C
C
C          USER I.D.:U14702F
C          PROGRAM NAME: TCPRSS.CNTL
C
C
C
      DIMENSION SUMMAS(21),GAUGEP(2,21),DWP(2,21),GC(2,21),
     .          TRANSP(2,21).HEAD(2),GAUGE(2)
      DOUBLE PRECISION C1,C2
      DATA C1,C2,C3,C4/0.998951759,0.0260416,1.0,0.000017/
      DATA C5,C6/25.0,0.2356E-08/
      DATA TEMP/24.2/
      DATA HEAD/8.7,0.0/
      DATA NUMP,TARMAS/21,0.78107/
      DATA MONTH,NDATE,NYEAR/8,1,85/
      WRITE(6,1)
  1   FORMAT(/5X,'ENTER ATMOSPHERIC PRESSURE,PSIA')
      READ(9,2)PATM
  2   FORMAT(F10.4)
      DO 20 N=1,2
        DO 10 M=1,NUMP
          READ (5,5) TRANSP(N,M)
    5    FORMAT (F9.3)
   10   CONTINUE
   20 CONTINUE
      DO 40 N=1,2
        DO 30 M=1,NUMP
          GAUGEP(N,M) = TRANSP(N,M)
   30   CONTINUE
   40 CONTINUE
      READ (5,50) (SUMMAS(I),I=1,NUMP)
   50 FORMAT (F10.6)
      DO 70 N=1,2
        DO 60 M=1,NUMP
          DWPN = (SUMMAS(M) + TARMAS)*C1
          DWPD = C2*(C3 + C4*(TEMP - C5))*(C3 - C6*GAUGEP(N,M))
          DWP(N,M) = DWPN/DWPD
          TRUEP = DWP(N,M) + PATM
          GC(N,M) = TRUEP - GAUGEP(N,M)
   60   CONTINUE
   70 CONTINUE
      WRITE (6,120) MONTH,NDATE,NYEAR
  120 FORMAT (////40X,'DATE:',1X,I2,'/',I2,'/',I2//)
      WRITE (6,130)
  130 FORMAT (10X,'INPUT UNITS ARE DEG C AND PSIA'/////)
      WRITE (6,80)
   80 FORMAT (////20X,'HYDROCARBON TRANSDUCER CORRECTIONS'//)
      WRITE (6,90)
   90 FORMAT (15X,'TRANS PRESS',5X,'D.W. PRESS',5X,'TRANSD CORR'//)
      WRITE (6,100) (TRANSP(1,M),DWP(1,M),GC(1,M),M=1,NUMP)
  100 FORMAT (18X,F7.2,8X,F7.2,9X,F5.2)
      WRITE (6,110)
  110 FORMAT (/1X,'----------------------------------------------------
     .---------------------------------------',/////)
C 110 FORMAT (////25X,'GAS TRANSDUCER CORRECTIONS'//)
C     WRITE (6,90)
C     WRITE (6,100) (TRANSP(2,M),DWP(2,M),GC(2,M),M=1,NUMP)
      STOP
      END
```

```
$ENTRY                                                                 00000660
     64.2                                                              00000670
     94.0                                                              00000680
    143.5                                                              00000690
    193.1                                                              00000700
    242.7                                                              00000710
    262.6                                                              00000720
    292.4                                                              00000730
    391.5                                                              00000740
    441.4                                                              00000750
    540.6                                                              00000760
    639.7                                                              00000770
    739.8                                                              00000780
    838.0                                                              00000790
    937.1                                                              00000800
   1036.2                                                              00000810
   1135.4                                                              00000820
   1234.3                                                              00000830
   1333.5                                                              00000840
   1432.4                                                              00000850
   1531.5                                                              00000860
   1630.6                                                              00000870
      0.0                                                              00000880
      0.0                                                              00000890
      0.0                                                              00000900
      0.0                                                              00000910
      0.0                                                              00000920
      0.0                                                              00000930
      0.0                                                              00000940
      0.0                                                              00000950
      0.0                                                              00000960
      0.0                                                              00000970
      0.0                                                              00000980
      0.0                                                              00000990
      0.0                                                              00001000
      0.0                                                              00001010
      0.0                                                              00001020
      0.0                                                              00001030
      0.0                                                              00001040
      0.0                                                              00001050
      0.0                                                              00001060
      0.0                                                              00001061
      0.0                                                              00001062
   0.52072                                                             00001070
   1.30181                                                             00001080
   2.60359                                                             00001090
   3.9054                                                              00001100
   5.20714                                                             00001110
   5.72786                                                             00001120
   6.50896                                                             00001130
   9.11255                                                             00001140
  10.41429                                                             00001150
  13.01788                                                             00001160
  15.62153                                                             00001170
  18.22508                                                             00001180
  20.83067                                                             00001190
  23.43223                                                             00001200
  26.03582                                                             00001210
  28.63949                                                             00001220
  31.24224                                                             00001230
  33.84582                                                             00001240
  36.44938                                                             00001250
  39.05297                                                             00001260
  41.65662                                                             00001261
```

VITA

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Candidate for the Degree of

Master of Science

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