SOLUBILITY DATA FOR NITROGEN IN N-PARAFFINS AND EQUATION-OF-STATE METHODS TO DESCRIBE LIGHT GAS SOLUBILITIES IN HYDROCARBONS: SUPPLEMENTAL MATERIALS

By

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PREFACE

The binary vapor-liquid phase equilibria of nitrogen in normal heavy paraffins is investigated in this work. Solubilities of nitrogen in four solvents, n-decane, n-eicosane, n-octacosane, and n-hexatriacontane, were measured at temperatures from 323.2 to 423.2 K and pressures to 18.0 MPa. For all the binary mixtures, interaction parameters and Henry's constants were obtained for both the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS) using the newly acquired experimental data.

In addition, a database for the solubility of six supercritical fluids (carbon dioxide, carbon monoxide, nitrogen, hydrogen, methane and ethane) in aromatic and naphthenic solvents was generated. SRK and PR EOS binary interaction parameters were regressed from these data, and estimates for Henry's constants and infinite-dilution partial molar volumes were determined.

I wish to extend my sincere thanks and expressions of gratitude to my adviser Dr. K. A. M. Gasem. His intelligent guidance, authoritative knowledge and depth of experience have contributed significantly to the completion of this work.

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In addition, I would also like to thank Dr. Jongkee Park for the sacrifices he made in explaining and demonstrating the operation of the apparatus. He has proved indispensable as a guide in the use of various software packages used throughout this work as well. Mr. Matt Mohr and Mr. T. J. Mears, my undergraduate assistants, deserve special mention for their help in equipment repairs and setting up the database.

Most of all, to my parents, I dedicate this humble work in recognition of their encouragement and ever-present love.

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NOMENCLATURE

$a(T)$	equation of state cohesive energy parameter
AAD	arithmetic average of the absolute values of the deviations of n observations
b	equation of state covolume parameter
BIAS	arithmetic average of deviations of n observations
C_{ij}, D_{ij}	binary interaction parameters in the SRK or PR EOS
$H_{1,2}$	Henry's constant of solute 1 in solvent 2
f_1	fugacity of component 1
np	total number of data points
p	pressure
R	gas constant
RMS, RMSE	the root mean squared error of n observations
SS	objective function (defined in Eq. 2-15)
T	temperature
v	molar volume
V	solvent injection volume
x	liquid mole fraction of solute gas (solubility)
z	mole fraction (defined in Eq. 2-13)
%AAD	arithmetic average of percent absolute deviations of n observations

Greek letters

α	temperature dependent parameter in Eq. 2-5
$\hat{\varphi}_1$	fugacity coefficient of component 1 in a mixture
ω	acentric factor

σ	standard deviation
ρ	density
ε	prime error

Subscripts

c	critical state
cal	calculated
exp	experimental
i,j	component "i", "j" in a mixture
r	reduced property

Superscripts

l	liquid
v	vapor

CHAPTER I

INTRODUCTION

The phase behavior of asymmetric mixtures at high pressures is of practical and theoretical importance in many industrial applications, including enchanced oil and gas recovery, hydrotreating and coal gasification. Ideally, the phase behavior of complex systems can be predicted using equations of state (EOS) such as the Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR) EOS. However, the use of EOS for such predictions is limited by the availability of experimental phase behavior information that is needed to optimize these equations for more accurate predictions.

A wealth of vapor-liquid equilibrium data has been determined on several supercritical fluids such as CO_2 and methane in paraffins, aromatics and naphthenes. Several studies (17, 21, 54) have been devoted to evaluating the ability of various cubic equations of state to predict the phase behavior of such supercritical-fluid-containing mixtures. The PR and SRK EOS are the most widely used because of their simplicity and reasonable accuracy.

In contrast, the phase behavior of nitrogen mixtures containing n-paraffins is scarcely studied, compared with other supercritical gases. To date, n-hexadecane is the heaviest member of the normal paraffin homologous series for which nitrogen vapor-liquid equilibrium data exist (1).

The first objective of the present work was to determine the solubilities of nitrogen in heavy normal paraffins (n-decane, n-eicosane, n-octacosane and n-hexatriacontane). The newly aquired experimental data, together with the available literature data, were regressed using the SRK and PR EOS. The binary interaction parameters C_{ij} and D_{ij} for the SRK and PR EOS were obtained, as well as values for Henry's constants and partial molar volumes.

The second objective of this study was to set up a database which contains the equilibrium properties of six supercritical gases (nitrogen, hydrogen, carbon dioxide, carbon monoxide, methane and ethane) in aromatic or naphthenic solvents and to obtain the binary interaction parameters C_{ij} and D_{ij} for the SRK and PR EOS, as well as values for Henry's constants and partial molar volumes.

Chapter II describes previous experimental and theoretical work relevant to the present study. The experimental apparatus and procedures used in this study are presented in Chapter III. The experimental results and discussion are the topic of Chapter IV. In Chapter V, correlation of the solubility of nitrogen in n-paraffins is presented. Chapter VI is devoted to evaluating the cubic equations of state. Finally, conclusions and recommendations are given in Chapter VII.

CHAPTER II

LITERATURE REVIEW

This chapter contains a brief review of experimental and theoretical work directly pertinent to the present study. The topics surveyed are: experimental methods used to measure vapor-liquid equilibrium phase behavior, vapor-liquid equilibrium data for nitrogen and n-paraffins, and previous efforts to correlate the solubility of light gases in hydrocarbon solvents using cubic equations of state.

Experimental Apparatus

A rapid and accurate method for determining vapor-liquid equilibrium properties is needed in industry for the design and operation of various processes. Experimental equilibrium measurements are used directly for such purposes, or to develop correlations and predictive models. Various methods have been proposed to make such measurements. In general, the methods employed to determine compositions can be classified into analytical (direct sampling) methods and synthetic (indirect) methods. The analytical methods can be subgrouped on the basis of the technique used to achieve equilibrium conditions as static (2, 9), continuous flow (3) and circulation methods (4). Continuous flow and circulation methods are considered to be dynamic methods.

Analytical methods are commonly used to determine vapor-liquid equilibrium properties. These methods depend heavily on sampling. At high pressures, especially near the critical point, large disturbances to equilibrium can occur when withdrawing samples from the cell. Thus, this method works best for pressures far away from the critical point. Nevertheless, some improvements have been made to overcome this problem by reducing the amount of samples withdrawn (5), i.e., by using fast-acting pneumatic or electro-magnetic valves (6) or detachable sampling microcells (7).

Synthetic methods applied to multicomponent mixtures yield the p, T and x information. Several techniques based on these synthetic methods (9, 20, 31) are discussed in the literature. In a synthetic method, no sampling is necessary, and hence the difficulties related to the sampling process are avoided. Thus, the synthetic approach is commonly used for systems for which phase compositions are difficult to analyze. It is particularly well suited for measurements of phase equilibria at elevated pressures, and for complex multiphase equilibria. The main disadvantage of this method, however, is the difficulty associated in obtaining tie lines in the phase envelope.

Some analytical and synthetic methods incorporate the capacity for visual observations of the phase behavior (28). A visual equilibrium cell has the added advantage of observing the phase separation directly. A review of experimental apparatus covering the 1970s is given by Eubank, et al. (8). Fornari (10) gave the review covering the 1980s, and a more recent review is given by Park (31).

Experimental Data

Experimental vapor-liquid equilibrium (VLE) measurements for nitrogen + n-paraffins are needed to determine EOS binary interaction parameters for a more accurate prediction of the phase behavior of such systems. Most of the data reported in the literature are concerned with nitrogen + light alkane systems. Binary system studies involving nitrogen and methane, ethane, or propane have mostly addressed operations under cryogenic conditions (13). High temperature and high pressure VLE data of nitrogen and alkanes are scarce. A number of binary nitrogen + n-alkane systems were reviewed by Wisotzki and Schneider (11), and several new nitrogen + n-alkane systems (n = 8, 9, 10, 12) were measured by Llave and Chung (13). Nitrogen + n-decane binaries at temperatures from 310.9 K to 410.9 K were studied by Azarnoosh, et al. (12).

However, the heaviest n-paraffin among the nitrogen + n-paraffin mixtures studied is n-hexadecane (1). A summary of existing VLE data for nitrogen in normal paraffins is presented in Table I, along with the ranges of temperature, pressure, and mole fractions of nitrogen in the liquid phase. In the present EOS analysis, only solubility data (T, p, x) are used in order to achieve consistency among the different sources. During analysis of the data, pressures are restricted to below 90% of the mixture critical pressure to avoid the near-critical region where essentially all contemporary equations of state become inherently inaccurate.

Equation-of-State Correlation of Experimental Data

Among the many EOS currently in use, the SRK and PR equations have been found particularly useful for this purpose due to their simplicity and reasonable accuracy when dealing with hydrocarbon mixtures. The SRK (24) equation is given below:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{2-1}$$

where

$$a(T) = a_c \alpha(T) \tag{2-2}$$

$$b = 0.08664 RT_c / P_c \tag{2-3}$$

and

$$a_c = 0.42748 R^2 T_c^2 / P_c \tag{2-4}$$

$$\alpha(T)^{1/2} = 1 + K(1 - T_r^{1/2}) \tag{2-5}$$

$$K = 0.480 + 1.574\omega - 0.176\omega^2 \tag{2-6}$$

The PR (25) equation is given as follows:

TABLE I

BINARY DATA FOR NITROGEN IN NORMAL PARAFFINS

Solvent	Temperature Range, K	Pressure Range, bar	N_2 Mole Fraction Range	Reference
C_3	143.2 - 353.2	13.8 - 137.9	0.018 - 0.323	60
	230.0 - 290.0	11.9 - 219.2	0.018 - 0.528	61
nC_4	250.0 - 344.4	4.5 - 157.9	0.007 - 0.268	48
	310.9 - 422.0	35.7 - 290.9	0.011 - 0.375	49
	310.9 - 410.9	3.6 - 285.2	0.012 - 0.610	50
	310.9 - 410.9	16.3 - 144.2	0.025 - 0.490	51
nC_5	277.5 - 377.6	2.5 - 207.9	0.003 - 0.400	52
nC_6	310.9 - 444.3	17.2 - 344.6	0.021 - 0.700	53
nC_7	305.4 - 366.5	55.0 - 349.0	0.056 - 0.397	13
	305.5	91.0 - 998.5	0.100 - 0.661	7
	305.4 - 455.4	70.3 - 691.2	0.080 - 0.505	55
	453.2 - 497.2	12.0 - 294.5	0.008 - 0.670	6
	453.2 - 497.2	44.0 - 278.0	0.075 - 0.588	62
	453.2	15.2 - 276.6	0.018 - 0.580	63
nC_8	322.0 - 344.3	32.3 - 350.4	0.043 - 0.347	13
nC_9	322.0 - 344.3	37.2 - 347.4	0.048 - 0.332	13
nC_{10}	344.3	40.2 - 346.4	0.069 - 0.380	13
	310.9 - 410.9	2.8 - 344.7	0.033 - 0.398	12
nC_{12}	327.6 - 366.5	31.0 - 346.9	0.048 - 0.349	13
nC_{16}	462.7 - 703.4	20.1 - 254.6	0.038 - 0.555	1

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{2-7}$$

where

$$a(T) = a_c\alpha(T) \tag{2-8}$$

$$b = 0.07780RT_c / P_c \tag{2-9}$$

and

$$a_c = 0.45724R^2T_c^2 / P_c \tag{2-10}$$

$$\alpha(T)^{1/2} = 1+K(1-T_r^{1/2}) \tag{2-11}$$

$$K = 0.37464+1.54226\omega-0.26992\omega^2 \tag{2-12}$$

To apply the SRK or PR equations of state to mixtures, the values of a and b are determined using the following mixing rules (26):

$$a = \sum_i^N\sum_j^N z_iz_j(1-C_{ij})(a_ia_j)^{1/2} \tag{2-13}$$

$$b = 0.5\sum_i^N\sum_j^N z_iz_j(1+D_{ij})(b_i+b_j) \tag{2-14}$$

In Equations (2-13) and (2-14), the summations are over all chemical species and C_{ij} and D_{ij} are empirical interaction parameters characterizing the binary interactions between components "i" and "j". Most investigators use only one interaction parameter, C_{ij}. However, for mixtures involving heavy hydrocarbons, use of two interaction parameters, C_{ij} and D_{ij}, has proven more precise (27-30, 47).

Values of the interaction parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared errors in the predicted bubble point pressures:

$$SS = \sum_{n=1}^{np} (P_{exp} - P_{cal})^2 \tag{2-15}$$

Further details on the data reduction techniques are given by Gasem (27).

For binary systems, at constant temperature and pressure, Henry's law constant can be defined as:

$$H_{1,2} = \left(f_1 / x_1\right)_{\lim x_1 \to 0} = \left(\hat{\varphi}_1 \, p\right)_{\lim x_1 \to 0} \tag{2-16}$$

Estimates for Henry's constant can be obtained analytically or graphically using solubility data. Applying the graphical method, values of the solute vapor phase fugacity divided by the solute liquid phase concentration are plotted as a function of the solute liquid phase concentration and extrapolated to zero solute concentration. Henry's constant can also be determined analytically using an equation of state (58), such as the SRK or PR EOS.

Previous Efforts to Correlate the Solubility of Nitrogen in Normal Paraffins

Equations of state are widely used for calculating VLE properties of mixtures involving non-polar and slightly polar substances. Studies of phase equilibrium calculations using EOS have been reported in recent works (14, 17, 21, 27-30, 40, 44, 47, 54, 76-80). A few of the EOS developed over the years have been reviewed by Walas (81) and Takeuchi and Arai (82). Chao and Lin (15) examined the EOS predictions of VLE data for highly asymmetric mixtures. More recently, Park (31) proposed a new equation of state to predict VLE properties of these mixtures and compared it with the PR, the simplified-perturbed-hard-chain theory (SPHCT) and modified SPHCT EOS. Similarly, Shaver (32) modified the SPHCT equation of state and improved its performance for both equilibrium and volumetric property predictions.

Binary interaction parameters are generally incorporated in the mixing rules of an equation of state in order to obtain improved predictions. The optimal values of the binary interaction parameters are determined from binary VLE data by minimizing the difference between the calculated and experimental values of a selected equilibrium property. A number of optimality criteria that have been used in determining binary interaction parameters were summarized by Paunovic, et al. (16). They are (a) minimization of deviations in the predicted bubble point pressures (17, 64), (b) minimization of deviations in the predicted vapor and liquid component fugacities (16, 18), (c) minimization of deviations in the predicted K values (21, 65), (d) minimization of deviations in the predicted bubble point vapor composition (64), (e) minimization of the sum of variances of both the vapor and liquid compositions (66), and (f) minimization of the flash volume variances (67).

Among these criteria, the bubble point pressure criterion appears to be the most widely used method (27, 35, 67, 68). Graboski, et al. (67) and Kato, et al. (68) found the bubble point pressure criterion to be extremely sensitive to variations in the C_{ij} binary interaction parameter of the Redlich-Kwong EOS. Similarly, the fugacity criterion is also used frequently, where the whole pTxy data set is used to evaluate the optimum C_{ij} interaction parameter. By contrast, when the bubble point pressure criterion is applied, only part of the pTxy data set is used in calculating the interaction parameter (the temperature and the liquid phase compositions). Cited advantages of the fugacity criterion are: (1) iterative calculations, which are involved in bubble point pressure criterion, are not required (16); (2) the EOS accuracy for predicting other VLE properties is guaranteed, in contrast to the bubble point pressure criterion, which does not do so (18).

Myosan, et al. (17) correlated the phase behavior of systems containing nitrogen with the SRK EOS. In their study, the evaluation of the interaction parameters was made by comparison with experimental data for binary mixtures, and their optimum values were calculated by minimizing the following objective function:

$$SS = \sum_{n=1}^{np} \left(\frac{P_{cal} - P_{exp}}{P_{exp}}\right)^2 \tag{2-17}$$

A general correlation was developed for the SRK EOS interaction parameters of several gases in hydrocarbon solvents. They separated the effect of temperature on the interaction parameter (for a given solute) as follows:

$$C_{ij} = C_{ij}(T) + C_{ij}(\text{solvent}) \tag{2-18}$$

where a temperature-independent solvent interaction parameter is amended by a generalized correlation to account for temperature effects.

For nitrogen mixtures, Moysan, et al. (17) found that C_{ij} is mainly a function of temperature, and proposed the following correlation:

$$C_{ij} = 1 - A'(1 - B'T)/(1 - C'\sqrt{T}) \tag{2-19}$$

where, A' = 0.7046, B' = 0.00136 and C' = 0.0313. As such, the above correlation predicts the same value of the interaction parameter at a given temperature, regardless of the solvent in the mixture.

Correlation of binary interaction parameters for nitrogen mixtures was also undertaken by Valderrama, et al. (18) using five equations of state including the SRK and PR EOS. A binary interaction parameter was estimated by regressing the VLE data of several nitrogen mixtures at several temperatures for each EOS. The fugacity criterion which was developed by Paunovic, et al. (16) was used as the objective function:

$$SS = \sum_{n=1}^{np} |(f_1^V - f_1^L)/f_1^V| + |(f_2^V - f_2^L)/f_2^V| \tag{2-20}$$

where np is the number of data points in the pxy data set at a given temperature.

In their study, they found that both temperature and the size of the solvent strongly affect the C_{ij} value. This is in contrast to the assessment given by Moysan, et al. (17). They correlated the optimum interaction parameters for five EOS using the following correlation:

$$C_{ij} = A - B / T_{rj} \tag{2-21}$$

where T_{rj} is the reduced temperature of the solvent, and A and B are empirical coefficients. These coefficients were related to the structure of the solvents using the acentric factor of the solvent ω_j as follows:

$$A = A_0 + A_1\omega_j + A_2\omega_j^2 \tag{2-22}$$

$$B = B_0 + B_1\omega_j + B_2\omega_j^2 \tag{2-23}$$

All the coefficients for the SRK and PR EOS are given in Table II.

TABLE II

COEFFICIENTS A_i AND B_i IN THE GENERALIZED CORRELATION FOR THE SRK AND PR EOS INTERACTION PARAMETERS (18)

EOS	A_0	A_1	A_2	B_0	B_1	B_2
SRK	-0.4909	5.1567	-5.5304	-0.2540	2.3300	-2.3126
PR	-0.3432	4.1428	-3.8309	-0.1777	1.8079	-1.4731

Han, et al. (21) and Oellrich, et al. (22) proposed a different approach for handling interaction parameters. They treated C_{ij} as temperature independent in the SRK and PR EOS. Significant improvement was observed by introducing C_{ij} for each mixture. The optimum C_{ij} values were presented in their study for each mixture. However, no generalized correlation was given.

In general, nitrogen-containing, light hydrocarbon mixtures have been extensively investigated using cubic equations of state, and reasonable fits are obtained when binary interaction parameters are employed.

VLE Correlation of Supercritical Gases in Aromatics and Naphthenes

Many investigators have correlated the solubility of supercritical solutes in paraffins using equations of state (see, e.g., 27, 35, 47). Relatively less effort has been devoted to supercritical solutes in aromatic and naphthenic systems. Among them, Gray, et al. (34) studied a number of binary hydrogen + aromatics or naphthenes systems. Valderrama, et al. (36, 39) and Nishiumi, et al. (37) suggested correlations for the PR EOS interaction parameters of hydrogen systems. Several investigations (56, 57, 58) dealing with carbon dioxide in aromatics and naphthenes have appeared in the literature.

In addition, Nishiumi (54) successfully correlated the binary interaction parameters of the PR EOS in terms of the ratio of the critical molar volumes and the absolute difference between the acentric factors of each component. The correlation covers systems of hydrocarbons, carbon dioxide, nitrogen and hydrogen sulfide. Maysan, et al. (17) provided correlations of C_{ij} values for the SRK equation for mixtures of nitrogen, hydrogen, carbon dioxide, carbon monoxide and methane with n-paraffins, olefins, naphthenes and aromatics, respectively.

For hydrogen systems, Valderrama, et al. (36, 39) and Nishiumi, et al. (37) suggested correlations for the interaction parameter of the PR EOS. In 1983, Valderrama, et al. (39) presented a correlation in the form

$$C_{ij} = \alpha - \beta / T_{rj} \tag{2-24}$$

where α and β are empirical parameters and T_{rj} is the reduced temperature of the solvent. Using Equation (2-24), significant deviations in the predicted interaction parameters were observed for some systems, such as hydrogen + aromatics (39). Later, in 1986, a new correlation was proposed by Valderrama (36) as follows:

$$C_{ij} = A + BT + CT^2 \tag{2-25}$$

where A, B and C are constants specific to each mixture. The accuracy of the EOS predictions was substantially improved by using the new correlation.

Nishiumi, et al. (37) correlated the PR EOS interaction parameters for hydrogen containing binary mixtures as a function of temperature

$$C_{ij} = 1 - M_{ij} \tag{2-26}$$

where

$$\begin{aligned} M_{ij} &= 1.224 - 0.0044T + 3.251\times10^{-5}T^2 \quad \text{for } T > 461.75\text{ K} \\ &= 56.98 - 0.1655T + 1.199\times10^{-4}T^2 \quad \text{for } T \leq 461.75\text{ K} \end{aligned}$$

This correlation covers hydrogen-alkane, -cycloalkane, -aromatic systems as well as hydrogen systems involving some polar compounds. Precise representations were achieved using the above correlation. Absolute average deviation of 0.007 and 0.018 in the mole fraction of vapor and liquid phases were obtained using the optimized values at each temperature of the system and the generalized value from the correlation, respectively.

Kordas, et al. (57) gave a generalized correlation for the PR EOS interaction parameters for the systems of carbon dioxide with alkane, 1-alkenes, naphthenes and aromatics. The correlation for carbon dioxide + non-alkane systems was proposed as:

$$C_{ij} = a(\omega_j) + b(\omega_j)T_{ri} + c(\omega_j)T_{ri}^3 \tag{2-27}$$

$$\omega_j = A - e^{\frac{-MW\times SG}{B}} \tag{2-28}$$

where the interaction parameter is a function of the reduced temperature of CO_2 and the effective acentric factor of the non-alkane, which was calculated from Equation (2-28). The parameters a, b and c are functions of ω_j. The effective acentric factor values were correlated in terms of the molecular weight (MW) and the specific gravity at 15°C (SG). The values of A and B are 0.658 and 46.027, respectively. By applying this correlation, typical average relative errors in the bubble point pressure predictions were in the range of 2-6%.

Yau et al. (58) calculated the solubility of carbon dioxide in aromatics using the SRK equation of state. Henry's constants and infinite dilution partial molar volumes were also evaluated in their work.

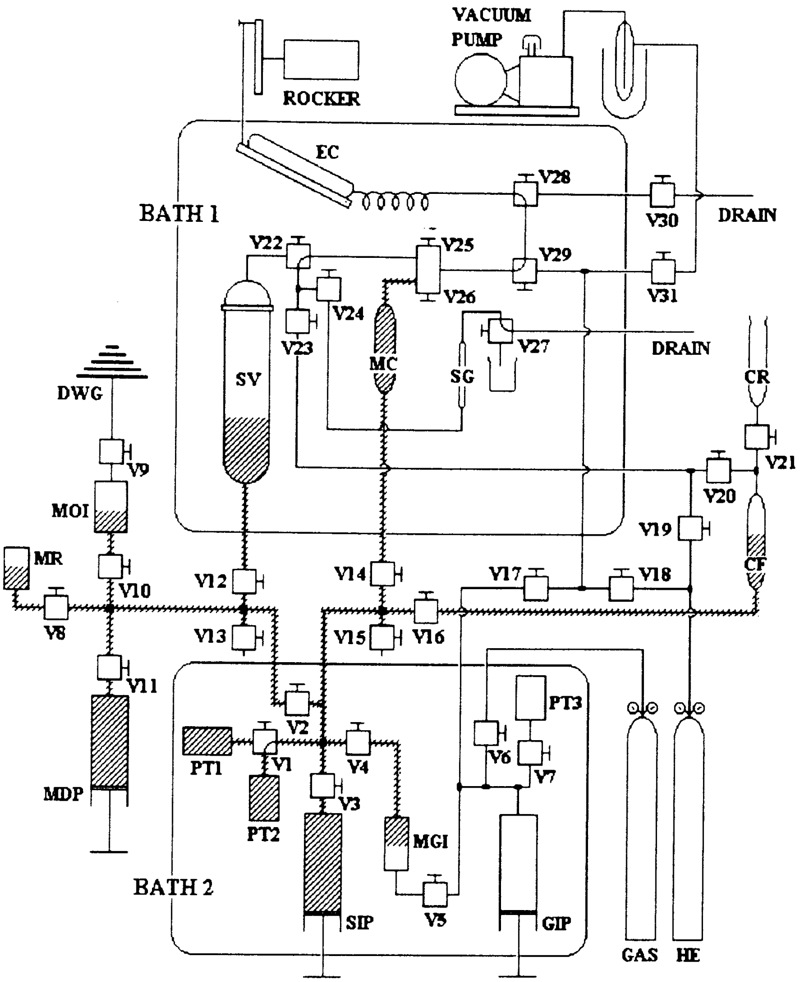
CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURES

Experimental Apparatus

The apparatus used in this study is briefly described here. A synthetic method was employed in measuring the solubilities of solute gases in heavy hydrocarbon solvents. A variable volume, static-type blind equilibrium cell was used. The experimental apparatus was originally built by Gasem (27) in 1982, and has been modified by Buffkin (29), Barrick (23), Darwish (28) and Park (31). No modifications were made to the apparatus during the course of this study. A detailed description of the apparatus and a step-by-step procedure for the operation are given by Park (31). The general schematic diagram of the apparatus as given by Park (31) is shown in Figure 1.

The equilibrium cell is a variable-volume, rocking type cell. It consists of a 316 stainless steel micro-reactor (Cat. No. MS-16, OD 1 in, ID 1/2 in, 19 cc in volume) supplied by High Pressure Equipment Inc. One end of the cell is plugged while the other end is connected to 1/16 in OD stainless steel tubing through which the solvent, solute and mercury are injected. Two stainless steel balls (diameter of 1/3 in) are placed inside the cell to enhance mixing. The volume of fluid mixture in the cell can be varied by the introduction and withdrawal of mercury using a screw pump. A solvent storage cell is used to store degassed liquid solvent at the operating temperature of the experiment. This is shown as SV in Figure 1 and is a high pressure reactor supplied by High Pressure Inc. (Cat. No. OC-1, OD 2.5 in, ID 1 in). The mercury storage cell (MC) is a 5 cc micro-reactor supplied by High Pressure Inc. (Cat. No. MS-11, OD 9/16 in, ID 5/16 in). The



CF - CLEANING FLUID CYLINDER
CR - CLEANING FLUID RESERVOIR
DWG - DEAD WEIGHT GAUGE
EC - EQUILIBRIUM CELL
GAS - SOLUTE GAS
GIP - SOLUTE GAS INJECTION PUMP
HE - HELIUM GAS
MDP - MERCURY DISPLACEMENT PUMP
MGI - MERCURY-GAS INTERFACE
MC - MERCURY STORAGE CELL
MOI - MERCURY-OIL INTERFACE
MR - MERCURY RESERVOIR
PT'S - PRESSURE TRANSDUCERS
SG - SIGHT GLASS
SIP - SOLVENT INJECTION PUMP
SV - SOLVENT STORAGE CELL
V'S - VALVES

Figure 1. Schematic Diagram of the Experimental Apparatus

cleaning fluid cell (CF) contains the cleaning solvent (n-pentane), which is injected into the equilibrium cell and the solvent storage cell by introducing mercury into the cleaning fluid cell.

Three positive displacement hand-pumps are used in this work. The solvent injection pump and the solute injection pump, each 25 cc in volume, were supplied by Temco Inc. (Model No. HP-25-10). The solvent injection pump is used for injecting solvent and measuring the amount injected. This pump is also used for transferring mercury to and from the equilibrium cell during the experiment. The solute injection pump is used to inject solute gas and measure the amount injected. The maximum operating pressure of these pumps is 68.9 MPa. The resolution of these pumps is 0.005 cc. The other pump was supplied by Ruska Instruments Inc. (Model No. 2210-801) and has a volume of 500 cc. This pump is normally used for cleaning operations and supplying mercury to the solvent injection pump.

Two air baths are used in the apparatus. One is used to house the solvent and solute injection pumps. The temperature in this bath is set at 50.00 °C and is controlled by a PI controller supplied by Halikainen Instruments (Model No. 1053A). The other bath contains the equilibrium cell, the solvent-storage cell and the mercury storage cell. The bath temperature is regulated by a PID controller supplied by Omega Engineering Inc. (Cat. No. CN9000A). Both air baths are controlled within 0.1 °C of the setpoint. The temperatures in the two air baths are measured using platinum resistance thermal detectors with digital displays supplied by Fluke Inc. (Model 2180A). The resolution of the displays is 0.01 °C.

Three pressure transducers are used in the apparatus. Two of them (PT1, PT2) are connected to the injection pump to measure the pressure in the equilibrium cell, the third (PT3) is connected to the solute injection pump to measure the pressure of the solute gas. All transducers are connected to digital displays. All pressure transducers and digital displays were supplied by Sensotec Inc. PT1 and PT3 (Model No. ST5E1890) have a range of 0 to 13.8 MPa whereas PT2 (Model No. TJE/743-11) has a range of 0 to 68.9 MPa. The digital displays for PT1 and PT3 (Model No. 450D) have maximum readings of 13.8 MPa and have 0.0007 MPa resolution. PT2 is connected to a digital display (Model No. GM) which has a maximum reading of 68.9 MPa and a resolution of 0.007 MPa.

All fittings, tubings and valves used in this study were supplied by High Pressure Equipment Company. The sizes of tubings used are 1/16, 1/8 and 1/4 in. All chemicals used in this work were supplied by commercial suppliers. No further purification of the chemicals was attempted. The suppliers and the stated purities are listed in Table III.

Experimental Procedures

According to the phase rule, a binary mixture in the state of two coexisting phases at equilibrium has two degrees of freedom. This means that only two independent intensive thermodynamic variables are required to describe the state of the system fully. For evaluation of any thermodynamic model such as an equation of state, at least one additional variable should be measured. In this work, the three measured variables are: temperature, pressure and the mole fraction of the solute (solubility) in the liquid phase.

The experimental procedure used in this study is simple. Known amounts of solvent and solute are injected into the equilibrium cell. The pressure in the equilibrium cell is changed by the introduction or withdrawal of mercury, which serves as an incompressible fluid "piston". In order to accelerate the approach to equilibrium, two stainless steel balls are placed in the equilibrium cell and the cell is rocked 45 degrees about the horizontal level. The bubble point pressure is identified by observing the break point in a pressure-volume curve as the mixture passes from two phases to a liquid phase. A typical pressure-volume plot is shown in Figure 2. Two to four points are measured in each run by subsequent solute injections. At least two runs are done for each isotherm to confirm the results. A detailed operating procedure is given by Park (31).

For the nitrogen system, the equilibrium time varied with the solvents and the

TABLE III

CHEMICALS AND THEIR PURITIES

Chemicals	Source	Purity (mol %)
Nitrogen	Liquid Air, Inc.	99.9999+
Carbon Monoxide	Matheson Gas Products	99.99+
Carbon Dioxide	Union Carbide	99.99+
trans-Decalin	Aldrich Chemical Company	99
n-Decane	Aldrich Chemical Company	99
n-Eicosane	Aldrich Chemical Company	99
n-Octacosane	Aldrich Chemical Company	99
n-Hexatriacontane	Alfa Chemical Company	99

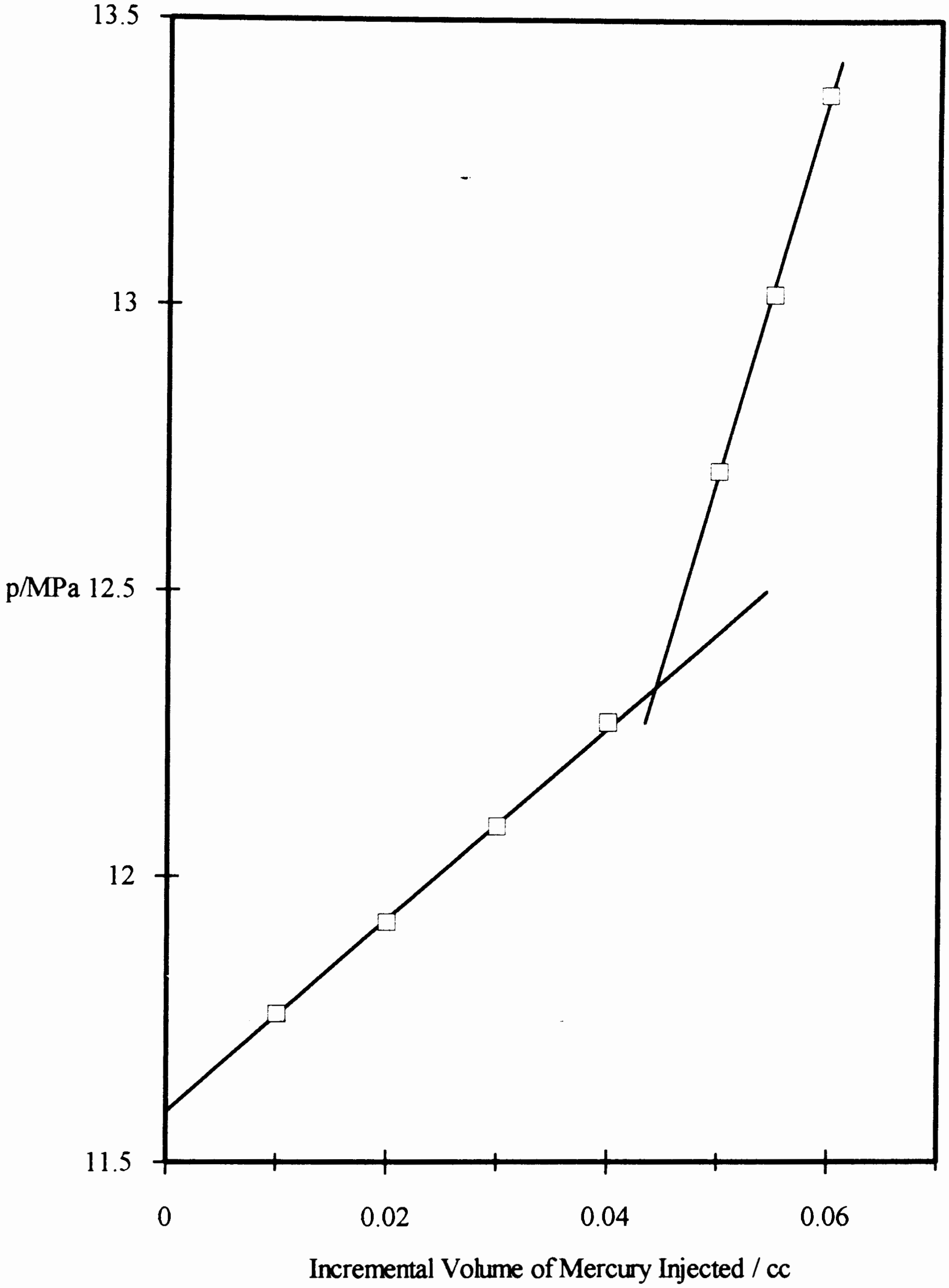


Figure 2. Graphical Determination of the Bubble Point for a Mixture of Nitrogen + n-Hexatriacontane at 373.2 K (x_{N_2} = 0.2089)

system temperature. Generally, it took at least 20 minutes to reach equilibrium for the systems studied in this work. At low temperature, it took about 10 more minutes to reach equilibrium.

CHAPTER IV

BINARY VAPOR-LIQUID PHASE EQUILIBRIUM FOR NITROGEN + HEAVY NORMAL PARAFFINS

Abstract

The solubilities of nitrogen in n-decane, n-eicosane, n-octacosane, and n-hexatriacontane were measured at temperatures from 323.2 to 423.2 K and pressures to 18.0 MPa. The uncertainty in these solubility measurements was estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave-Redlich-Kwong and Peng-Robinson equations of state. In general, the two equations represent the experimental data well when one interaction parameter is used for each isotherm in each binary system.

Results and Discussions

The nitrogen solubility measurements are presented in Tables IV - VII. The effect of temperature and pressure on the solubility of nitrogen in each of the solvents studied is shown in Figures 3 - 6. In general, a trend of increasing solubility with increasing temperature and pressure is observed. This behavior is similar to that of carbon monoxide (30, 40) and hydrogen (31), and in contrast to the behavior observed for carbon dioxide (27), methane (28) and ethane (44). The effect of the molecular size of the solvent on the solubility is shown in Figure 7. The figure indicates that the solubility of nitrogen increases with increasing carbon number at a given temperature and pressure.

The EOS representations of the solubilities for the systems considered are shown

TABLE IV

SOLUBILITY OF NITROGEN (1) IN N-DECANE (2)

x_1	p/MPa	x_1	p/MPa
334.3 K (71.1 °C, 160.0 °F)			
0.0556	4.33	0.1178	9.84
0.0590	4.61	0.1202	10.06
0.0633	4.97	0.1539	13.40
0.1087	8.99	0.1578	13.81
377.6 K (104.4 °C, 220.0 °F)			
0.0568	4.05	0.1662	13.15
0.0689	4.97	0.1708	13.63
0.1158	8.73	0.1967	16.04
0.1271	9.66		
410.9 K (137.8 °C, 280.0 °F)			
0.0598	3.91	0.1343	9.25
0.0749	4.92	0.1690	11.99
0.1162	7.89	0.1894	13.61

TABLE V

SOLUBILITY OF NITROGEN (1) IN N-EICOSANE (2)

x_1	p/MPa	x_1	p/MPa
323.2 K (50.0 °C, 122.0 °F)			
0.0610	4.49	0.1292	10.61
0.0689	5.13	0.1413	11.90
0.0704	5.25	0.1789	16.22
0.0967	7.54	0.1866	17.23
373.2 K (100.0 °C, 212.0 °F)			
0.0629	4.03	0.1364	9.74
0.0715	4.61	0.1639	12.10
0.1199	8.33	0.1905	14.61
423.2 K (150.0 °C, 302.0 °F)			
0.0679	3.83	0.1445	8.89
0.0930	5.38	0.1728	11.09
0.1278	7.76	0.2121	14.24

TABLE VI

SOLUBILITY OF NITROGEN (1) IN N-OCTACOSANE (2)

x_1	p/MPa	x_1	p/MPa
348.2 K (75.0 °C, 167.0 °F)			
0.0726	4.30	0.1900	13.70
0.1108	6.93	0.1909	13.70
0.1245	8.04	0.2181	16.47
0.1334	8.70		
373.2 K (100.0 °C, 212.0 °F)			
0.0862	4.87	0.1698	10.89
0.0988	5.63	0.2071	14.18
0.1466	9.08	0.2289	16.10
423.2 K (150.0 °C, 302.0 °F)			
0.0896	4.46	0.1951	11.07
0.1010	5.11	0.2320	13.94
0.1689	9.31	0.2578	16.01

TABLE VII

SOLUBILITY OF NITROGEN (1) IN N-HEXATRICONTANE (2)

x_1	p/MPa	x_1	p/MPa
-------------------------------- 373.2 K (100.0 °C, 212.0 °F) --------------------------------			
0.1054	5.30	0.2089	12.23
0.1197	6.10	0.2628	16.81
0.1934	11.10	0.2749	17.99
-------------------------------- 423.2 K (150.0 °C, 302.0 °F) --------------------------------			
0.1185	5.28	0.2263	11.71
0.1240	5.56	0.2747	15.21
0.2040	10.22	0.2970	17.11

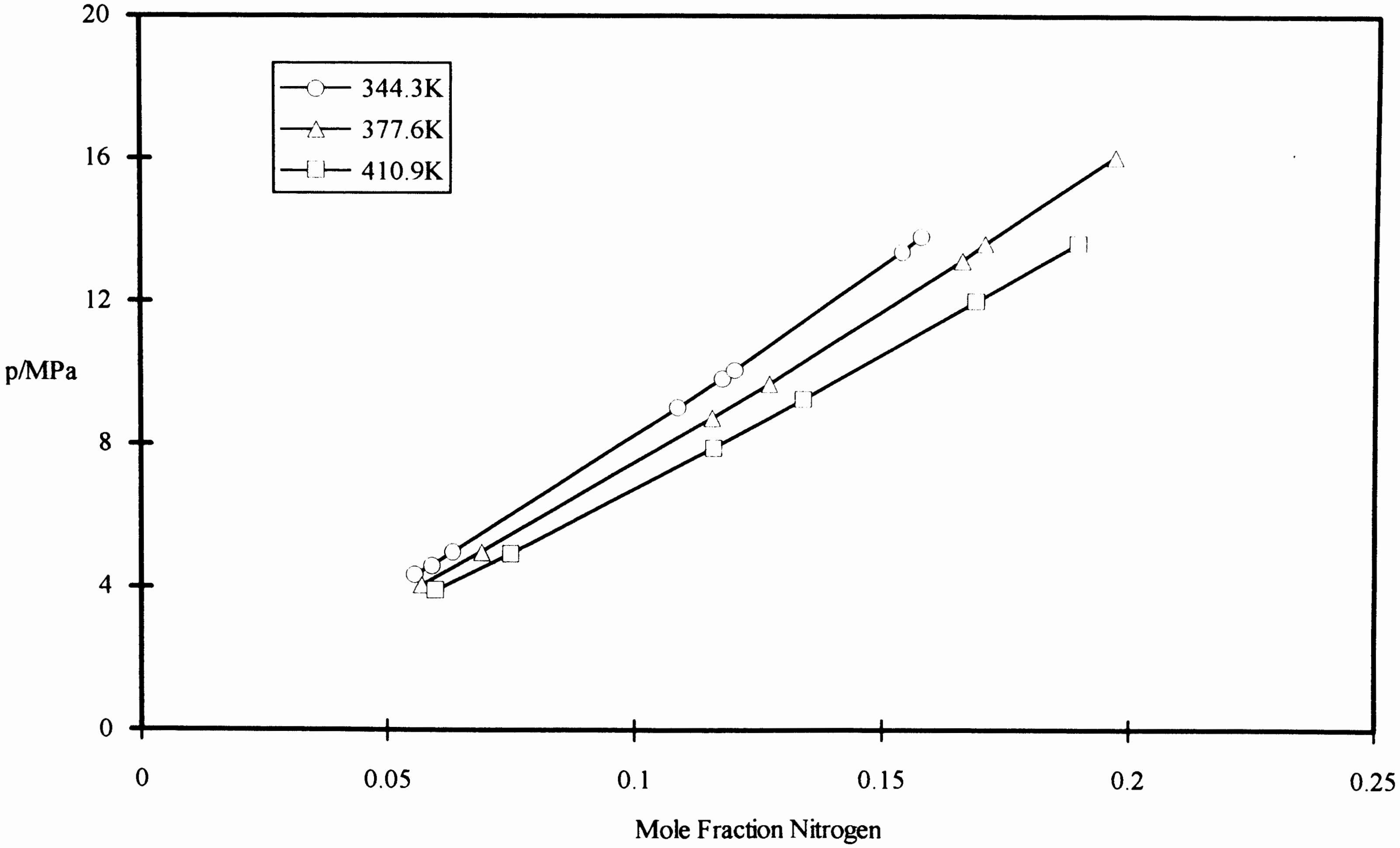


Figure 3. Solubility of Nitrogen (1) in n-Decane (2)

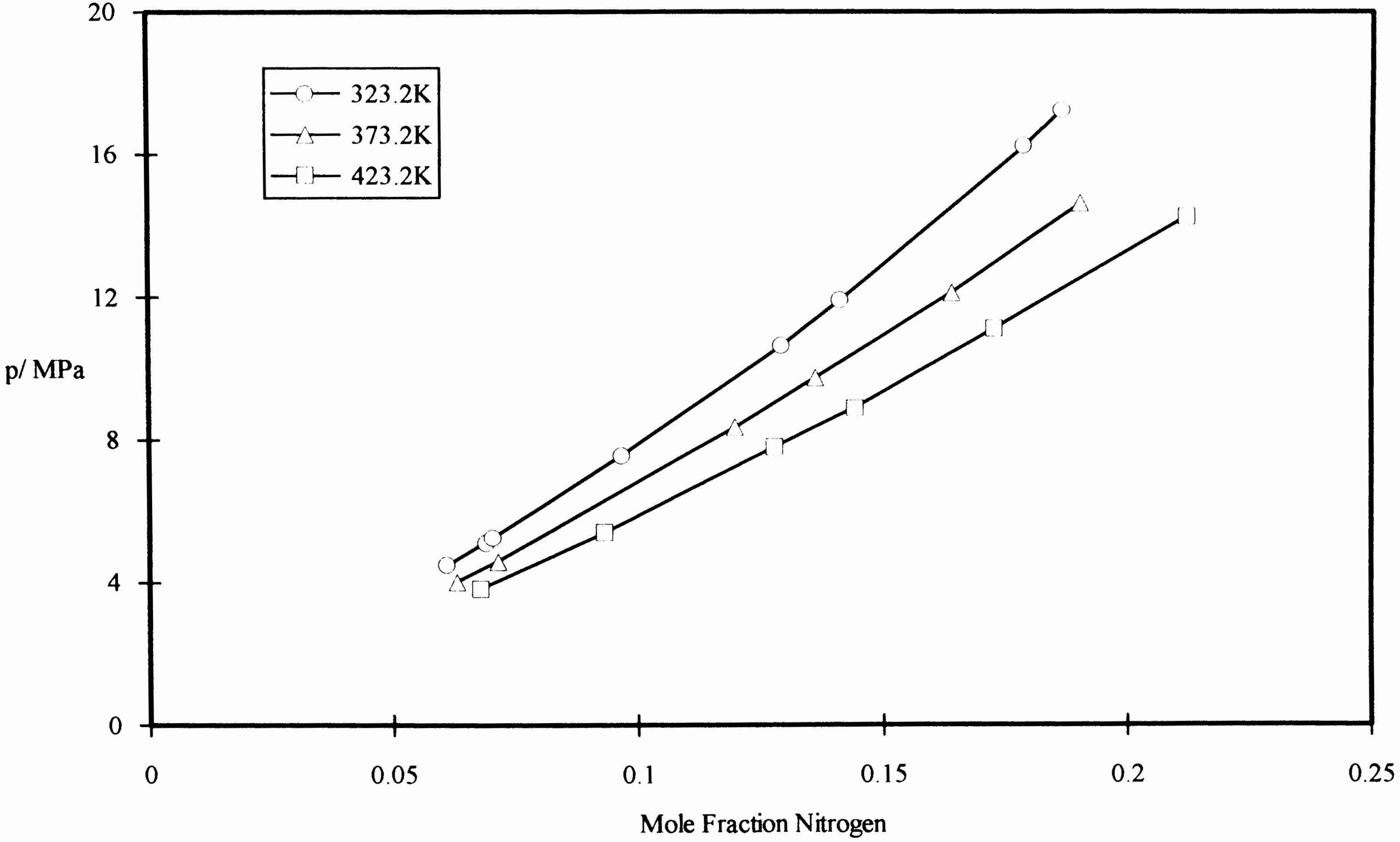


Figure 4. Solubility of Nitrogen (1) in n-Eicosane (2)

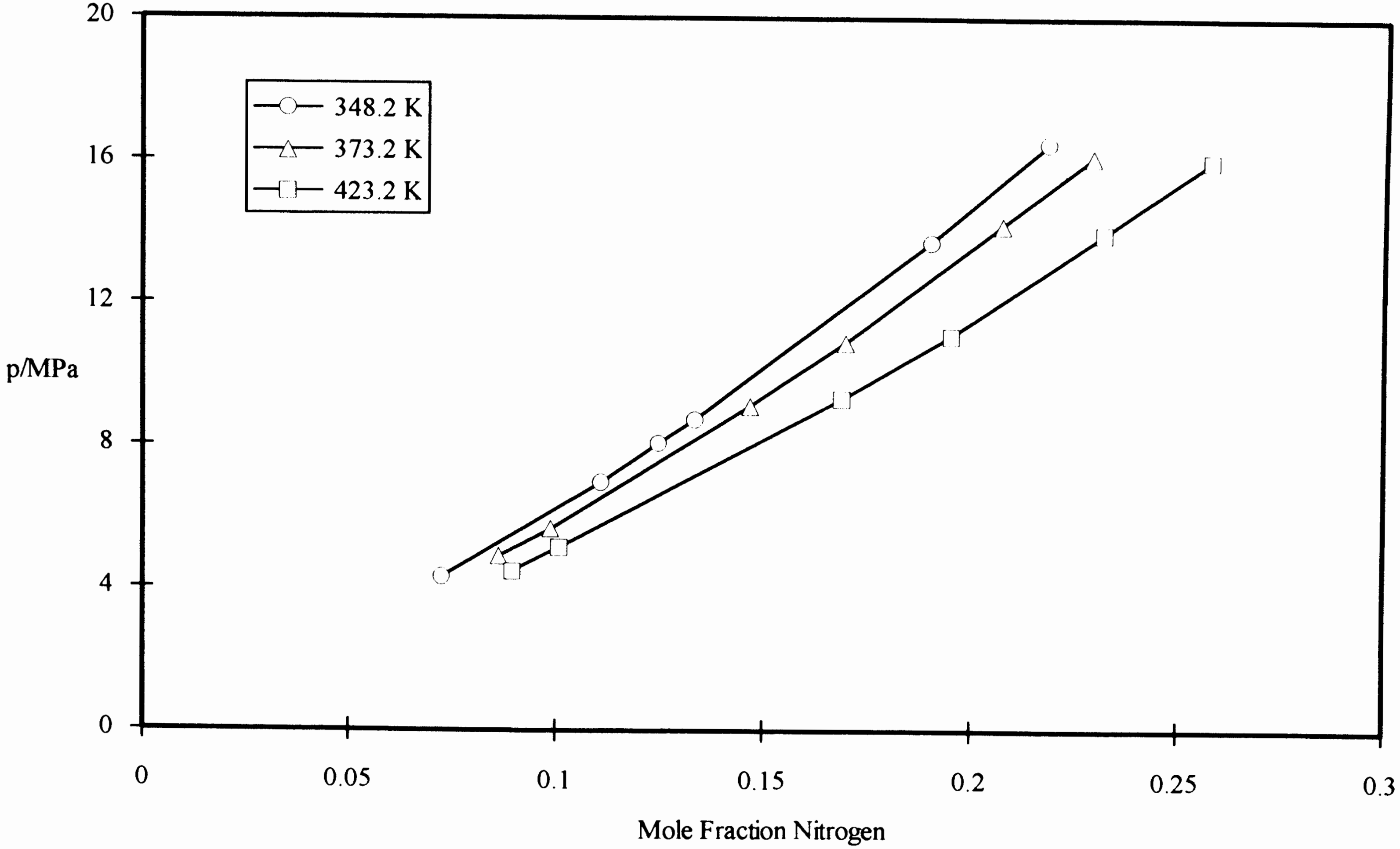


Figure 5. Solubility of Nitrogen (1) in n-Octacosane (2)

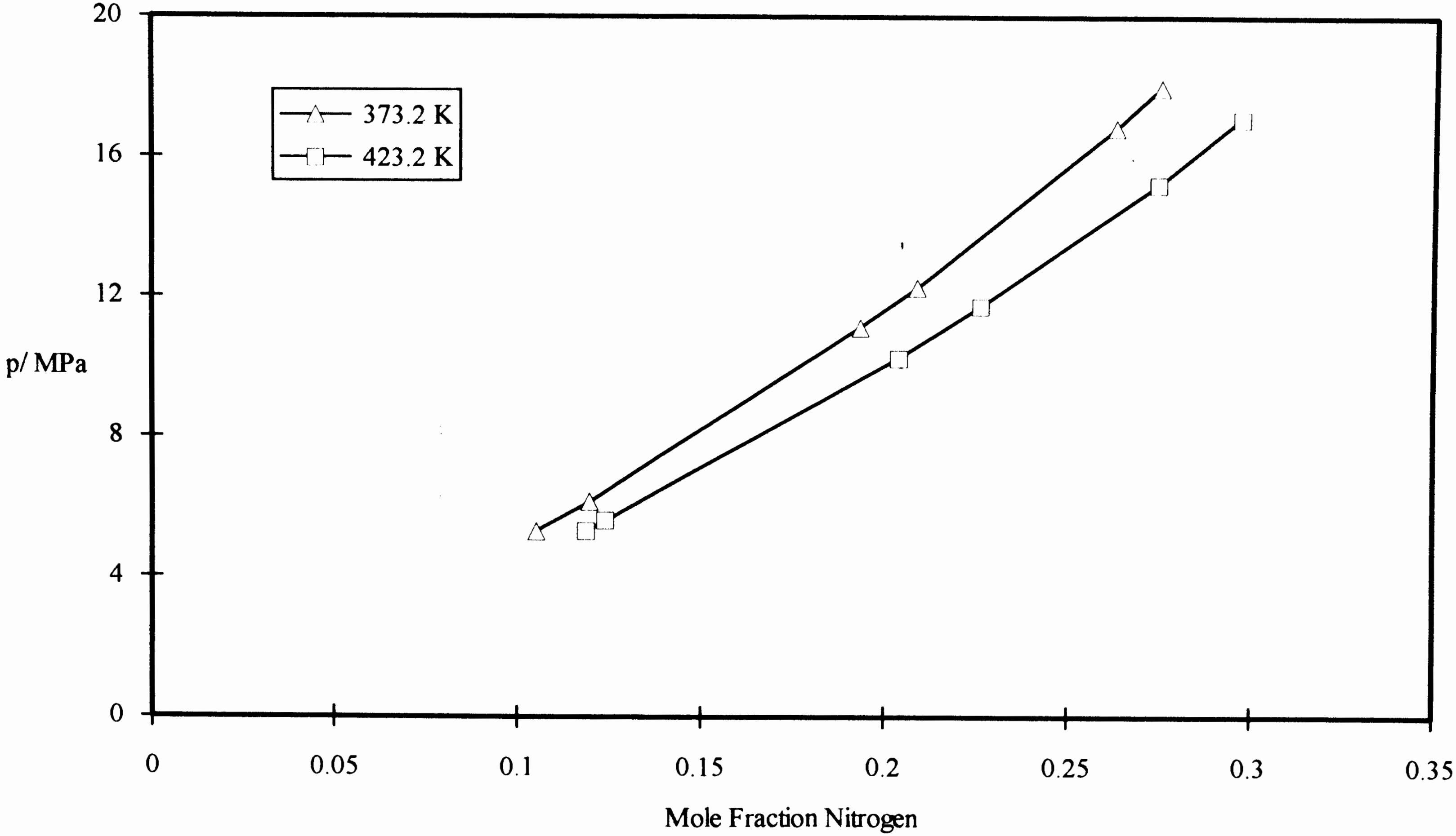


Figure 6. Solubility of Nitrogen (1) in n-Hexatriacontane (2)

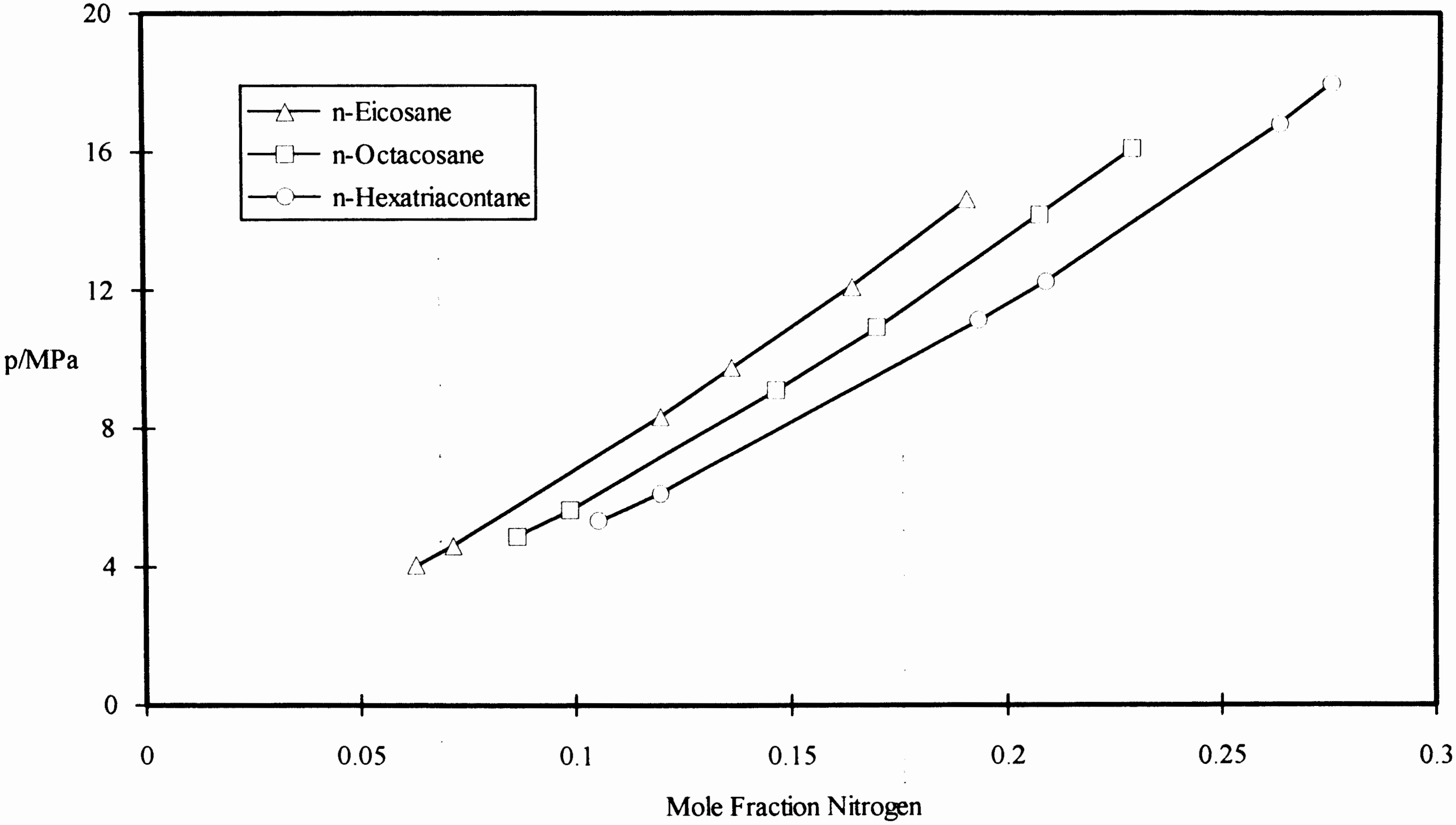


Figure 7. Bubble Point Pressure Data for Nitrogen (1) in n-Paraffins (2) at 373.2 K

in Tables VIII - XI. Optimum binary interaction parameters were obtained by minimizing the sum of the squares of pressure deviations from the experimental data, and Henry's constants were estimated. A detailed procedure for data reduction is given by Gasem (27). The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table XII. In general, the SRK and PR equations are capable of representing the data with RMS errors less than 0.006 in mole fraction for a given system when a single interaction parameter, C_{ij}, is used over the entire temperature and pressure range. Only a minor improvement is observed when the second interaction parameter, D_{ij}, is employed; RMS errors of 0.005 in mole fraction are obtained.

When a single interaction parameter, C_{ij}, is used for each isotherm, the SRK and PR equations of state are able to fit the data with RMS errors less than 0.002 in mole fraction with the exception of the system of nitrogen + n-hexatriacontane which has RMS errors of 0.004 in mole fraction at 423.2 K using the SRK EOS. For all the systems, RMS errors yielded by the PR equation of state at each isotherm are less than those of the SRK equation. When an additional interaction parameter, D_{ij}, is employed, for nitrogen in n-decane , n-eicosane and n-octacontane, no significant improvement was observed, as revealed in Tables VIII - X. However, for the nitrogen + n-hexatriacontane system, significant improvements in the EOS representation were achieved. The RMS error was dramatically reduced from 0.004 to 0.001, as shown in Figure 8. These results indicate that the SRK and PR equations of state can represent data of relatively low carbon number of nitrogen systems very well with one interaction parameter per isotherm. This behavior is also observed in methane (28), ethane (44) and other binary systems (31, 27, 30).

As shown in the EOS representation, the values of interaction parameters C_{ij} are larger than those typically obtained for the other solutes. Nevertheless, the temperature-dependent C_{ij} is not sufficient for correlating the larger molecules such as

TABLE VIII

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF THE SOLUBILITY OF NITROGEN (1) IN N-DECANE (2)

T/K	SRK Parameters (PR Parameters)		Error in Nitrogen Mole Fraction		SRK Henry's Contant (PR Henry's Contant) MPa
	C_{12}	D_{12}	RMS	|MAX|	
344.3	0.1440	0.0142	0.0001	0.0002	73.7
	(0.1634)	(0.0102)	(0.0001)	(0.0001)	(73.6)
	0.2163		0.0006	0.0008	71.8
	(0.2087)		(0.0005)	(0.0006)	(72.1)
377.6	0.1193	0.0190	0.0003	0.0006	67.8
	(0.1516)	(0.0114)	(0.0003)	(0.0005)	(67.7)
	0.2118		0.0010	0.0015	65.5
	(0.1991)		(0.0007)	(0.0010)	(66.3)
410.9	0.0753	0.0287	0.0002	0.0003	61.8
	(0.1258)	(0.0163)	(0.0002)	(0.0003)	(61.7)
	0.2164		0.0013	0.0016	59.3
	(0.1936)		(0.0008)	(0.0011)	(60.2)
344.3, 377.6 and 410.9	0.1225	0.0185	0.0004	0.0008	
	(0.1205)	(0.0191)	(0.0010)	(0.0024)	
	0.2146		0.0011	0.0022	
	(0.2026)		(0.0013)	(0.0032)	

TABLE IX

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF THE SOLUBILITY OF NITROGEN (1) IN N-EICOSANE (2)

T/K	SRK Parameters (PR Parameters) C_{12}	D_{12}	Error in Nitrogen Mole Fraction RMS	|MAX|	SRK Henry's Contant (PR Henry's Contant) MPa
323.2	0.3199	0.0011	0.0002	0.0004	67.1
	(0.3183)	(0.0003)	(0.0002)	(0.0003)	(67.3)
	0.3307		0.0002	0.0003	66.8
	(0.3211)		(0.0002)	(0.0003)	(66.9)
373.2	0.2700	0.0043	0.0004	0.0007	59.9
	(0.2873)	(0.0009)	(0.0004)	(0.0008)	(59.9)
	0.3153		0.0005	0.0010	59.1
	(0.2956)		(0.0004)	(0.0007)	(59.7)
423.2	0.2378	0.0063	0.0004	0.0006	52.7
	(0.2737)	(-0.0004)	(0.0004)	(0.0006)	(52.9)
	0.3038		0.0006	0.0010	51.8
	(0.2707)		(0.0004)	(0.0006)	(52.8)
323.2, 373.2 and 423.2	0.3380	-0.0013	0.0018	0.0047	
	(0.2784)	(0.0035)	(0.0038)	(0.0081)	
	0.3248		0.0018	0.0047	
	(0.3096)		(0.0038)	(0.0085)	

TABLE X

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF THE SOLUBILITY OF NITROGEN (1) IN N-OCTACOSANE (2)

T/K	SRK Parameters (PR Parameters)		Error in Nitrogen Mole Fraction		SRK Henry's Contant (PR Henry's Contant) MPa
	C_{12}	D_{12}	RMS	|MAX|	
348.2	0.3850	0.0048	0.0004	0.0007	54.2
	(0.3925)	(0.0032)	(0.0004)	(0.0007)	(54.1)
	0.4583		0.0009	0.0014	52.9
	(0.4343)		(0.0006)	(0.0011)	(53.3)
373.2	0.3873	0.0049	0.0007	0.0011	51.0
	(0.4019)	(0.0023)	(0.0007)	(0.0011)	(51.0)
	0.4624		0.0009	0.0015	49.8
	(0.4306)		(0.0007)	(0.0011)	(50.4)
423.2	0.3178	0.0099	0.0004	0.0006	45.4
	(0.3571)	(0.0050)	(0.0004)	(0.0006)	(45.5)
	0.4672		0.0016	0.0022	43.6
	(0.4177)		(0.0009)	(0.0011)	(44.5)
348.2, 373.2 and 423.2	0.3779	0.0055	0.0010	0.0020	
	(0.3574)	(0.0057)	(0.0012)	(0.0024)	
	0.4611		0.0014	0.0028	
	(0.4300)		(0.0014)	(0.0039)	

TABLE X

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF THE SOLUBILITY OF NITROGEN (1) IN N-OCTACOSANE (2)

T/K	SRK Parameters (PR Parameters)		Error in Nitrogen Mole Fraction		SRK Henry's Contant (PR Henry's Contant) MPa
	C_{12}	D_{12}	RMS	|MAX|	
348.2	0.3850	0.0048	0.0004	0.0007	54.2
	(0.3925)	(0.0032)	(0.0004)	(0.0007)	(54.1)
	0.4583		0.0009	0.0014	52.9
	(0.4343)		(0.0006)	(0.0011)	(53.3)
373.2	0.3873	0.0049	0.0007	0.0011	51.0
	(0.4019)	(0.0023)	(0.0007)	(0.0011)	(51.0)
	0.4624		0.0009	0.0015	49.8
	(0.4306)		(0.0007)	(0.0011)	(50.4)
423.2	0.3178	0.0099	0.0004	0.0006	45.4
	(0.3571)	(0.0050)	(0.0004)	(0.0006)	(45.5)
	0.4672		0.0016	0.0022	43.6
	(0.4177)		(0.0009)	(0.0011)	(44.5)
348.2, 373.2 and 423.2	0.3779	0.0055	0.0010	0.0020	
	(0.3574)	(0.0057)	(0.0012)	(0.0024)	
	0.4611		0.0014	0.0028	
	(0.4300)		(0.0014)	(0.0039)	

TABLE XI

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF THE SOLUBILITY OF NITROGEN (1) IN N-HEXATRIACONTANE

T/K	SRK Parameters (PR Parameters)		Error in Nitrogen Mole Fraction		SRK Henry's Contant (PR Henry's Contant) MPa
	C_{12}	D_{12}	RMS	|MAX|	
373.2	0.3687	0.0126	0.0006	0.0009	44.7
	(0.3958)	(0.0113)	(0.0006)	(0.0009)	(44.7)
	0.6258		0.0033	0.0045	41.1
	(0.5851)		(0.0029)	(0.0037)	(41.7)
423.2	0.3712	0.0148	0.0004	0.0006	39.3
	(0.4191)	(0.0115)	(0.0005)	(0.0006)	(39.4)
	0.6731		0.0037	0.0048	36.2
	(0.6059)		(0.0027)	(0.0034)	(37.1)
373.2 and 423.2	0.3975	0.0119	0.0046	0.0072	
	(0.4543)	(0.0083)	(0.0027)	(0.0044)	
	0.6398		0.0056	0.0086	
	(0.5918)		(0.0035)	(0.0054)	

TABLE XII

PHYSICAL PROPERTIES OF THE HEAVY N-PARAFFINS USED IN THE SRK AND PR EQUATIONS OF STATE

Component	P_c/MPa	T_c/K	ω	Reference
Nitrogen	3.390	126.2	0.0390	45
n-Decane	2.096	617.6	0.4885	46
n-Eicosane	1.069	766.6	0.8791	46
n-Octacosane	0.661	827.4	1.1617	46
n-Hexatricontane	0.428	864.0	1.4228	46

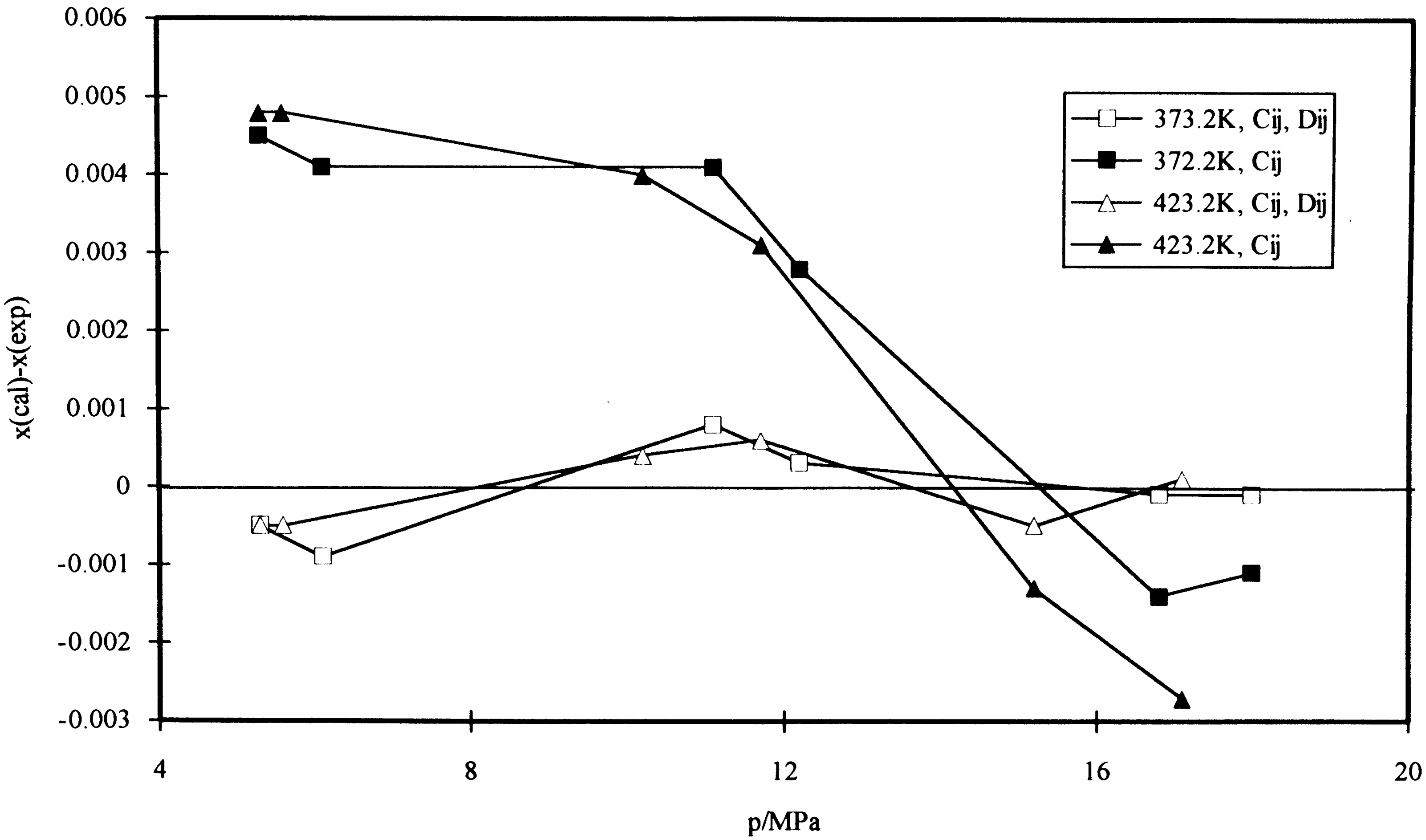


Figure 8. EOS Representation of the Solubility of Nitrogen in n-Hexatriacontane Using One Interaction Parameter, (C_{ij}) and Two Interaction Parameters, (C_{ij}, D_{ij})

n-hexatriacontane. This inadequacy may be attributed to poor mixing rules and/or poor estimates for the critical properties.

In general, both the SRK and PR equations of state exhibit comparable abilities in representing the data using two interaction parameters. The RMS errors in mole fraction are comparable with the estimated uncertainties in the measurements. This excellent fit of the data illustrates both the ability of the equations of state and the precision of the experimental measurements.

Comparisons of the present solubility data for nitrogen in n-decane with those of Azarnoosh and McKetta (12) and Llave and Chung (13) are given in Figures 9 - 11. These comparisons are shown in terms of solubility deviations generated by comparing optimum SRK predictions to the experimental measurements. For this purpose, the interaction parameters, C_{ij}, of the SRK equation of state were regressed from the data obtained in this work at 344.3, 377.6 and 410.9 K. Figures 9 - 11 indicate significant disagreement between the present data and those of Azarnoosh and McKetta (12) and Llave and Chung (13). In addition, interaction parameters regressed from the present data, as expected, show substantial disagreement with those from Azarnoosh and McKetta (12) and Llave and Chung (13), as is evident in Table D.II, Appendix D. In comparison, Han, et al. (21) gave average temperature-independent values of C_{ij} of 0.188 and 0.228 for the SRK and PR equations, which show fair agreement with the present results. For the time being, no obvious explanation can be given for the large differences between the present work and those of McKetta, et al. and Llave, et al. No literature data for the solubility of nitrogen in n-eicosane, n-octacosane, and n-hexatriacontane are available for comparison.

The effect of temperature on the interaction parameter is presented in Figure 12, which indicates that the interaction parameter C_{ij} is only weakly temperature dependent. For each system, the interaction parameter C_{ij}, shows a slight linear dependence with temperature. The effect of the carbon number on the interaction parameter C_{ij}, is depicted

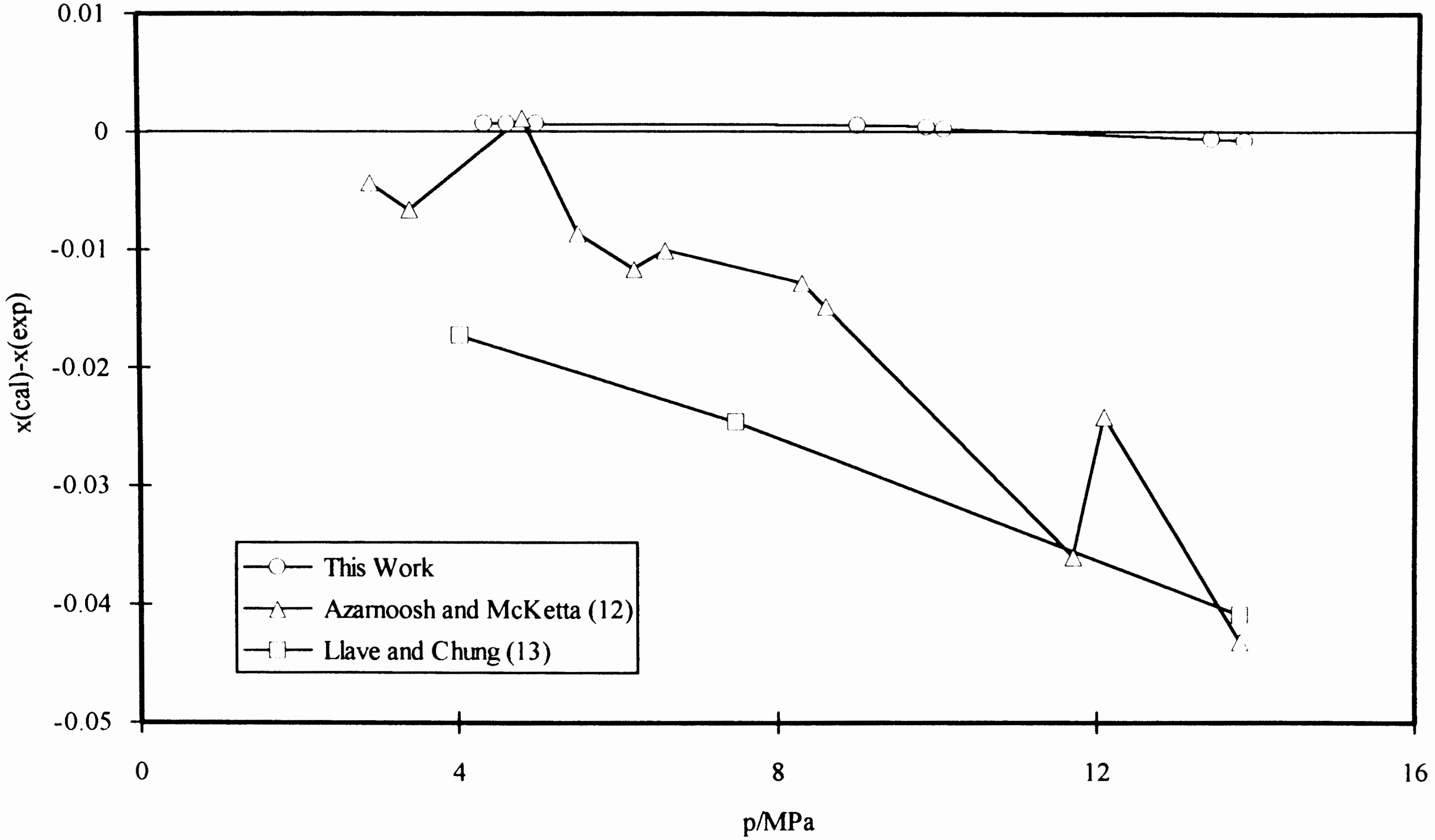


Figure 9. Comparison for the Solubilities of Nitrogen in n-Decane at 344.3 K

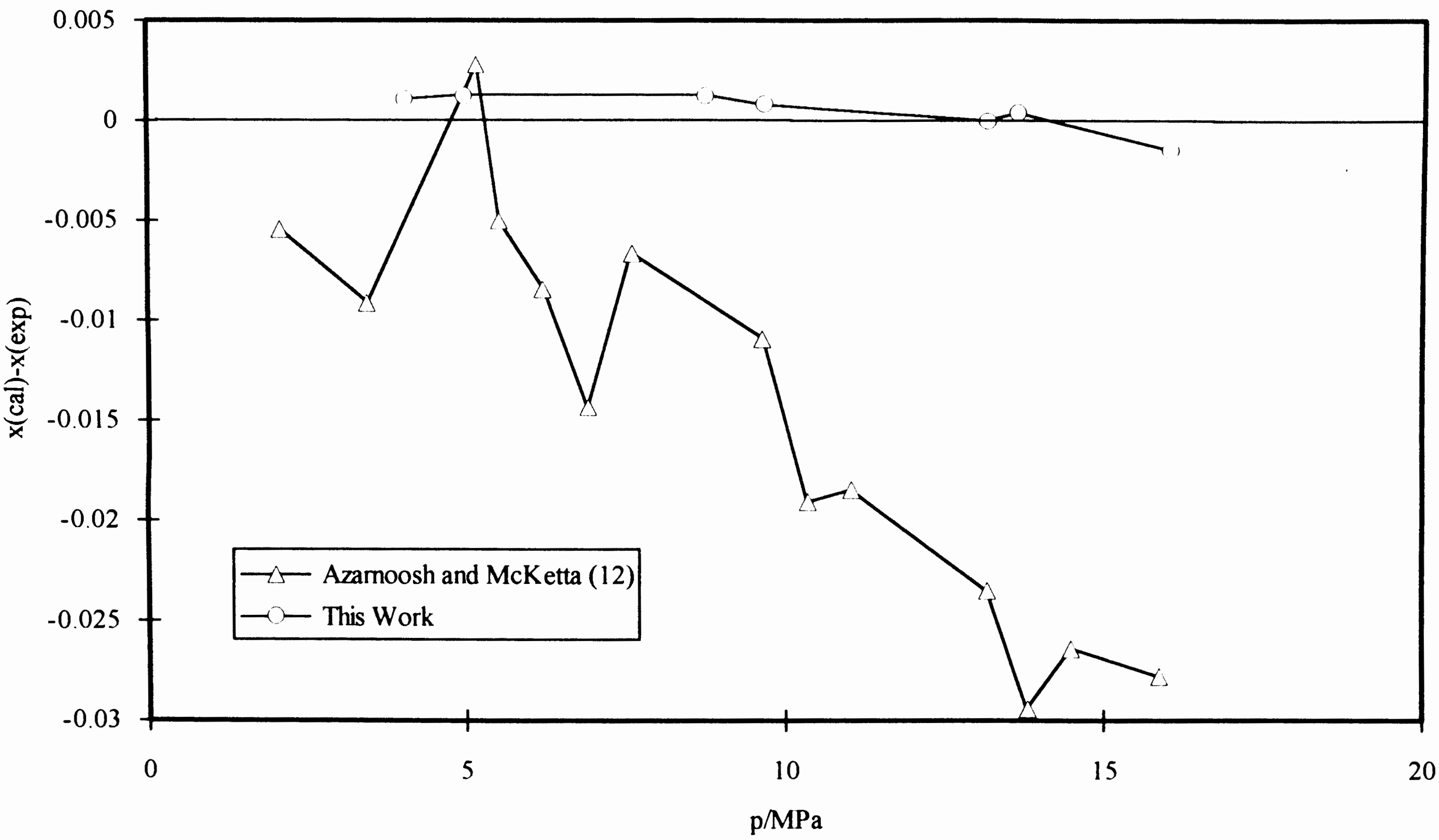


Figure 10. Comparison for the Solubilities of Nitrogen in n-Decane at 377.6 K

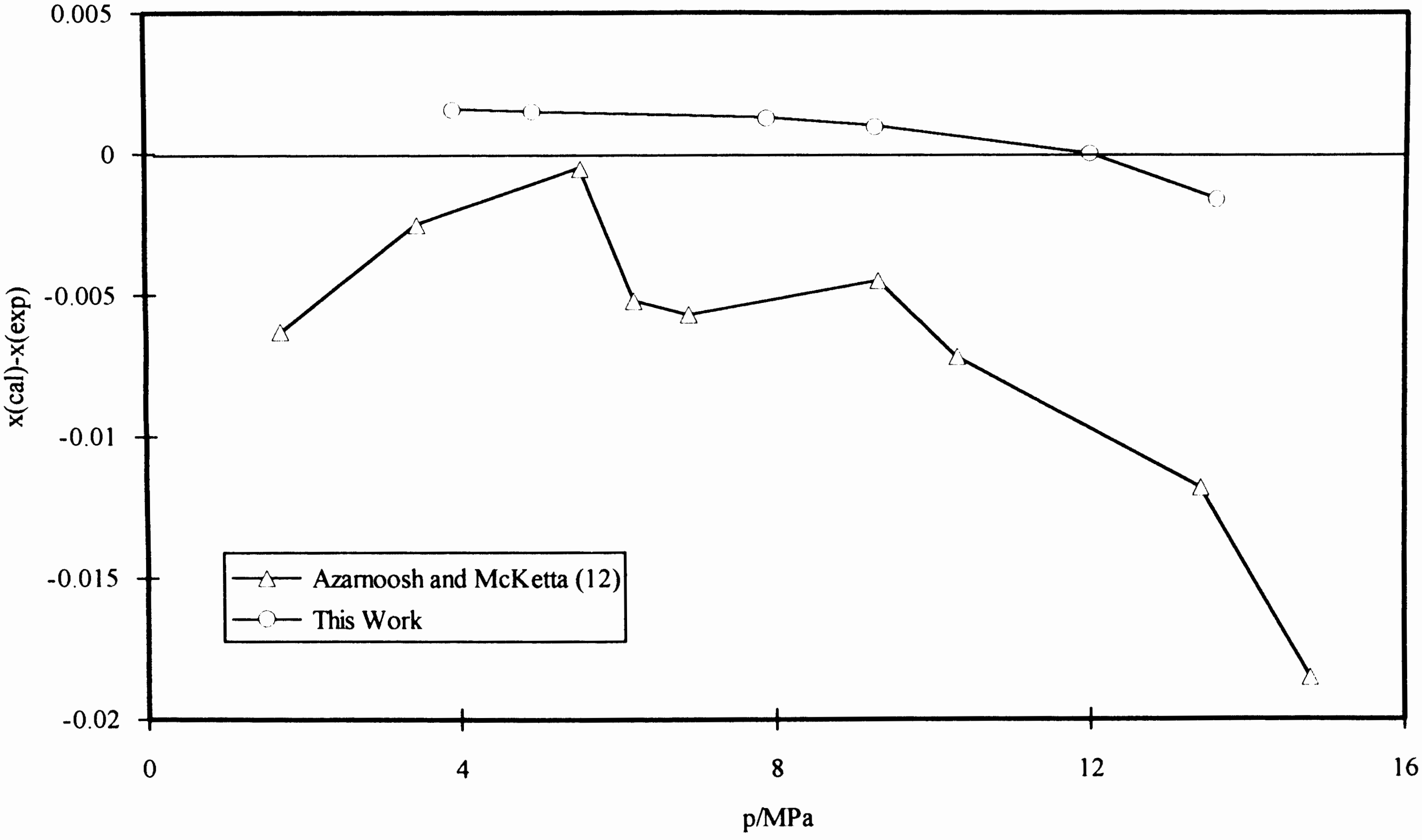


Figure 11. Comparison for the Solubilities of Nitrogen in n-Decane at 410.9 K

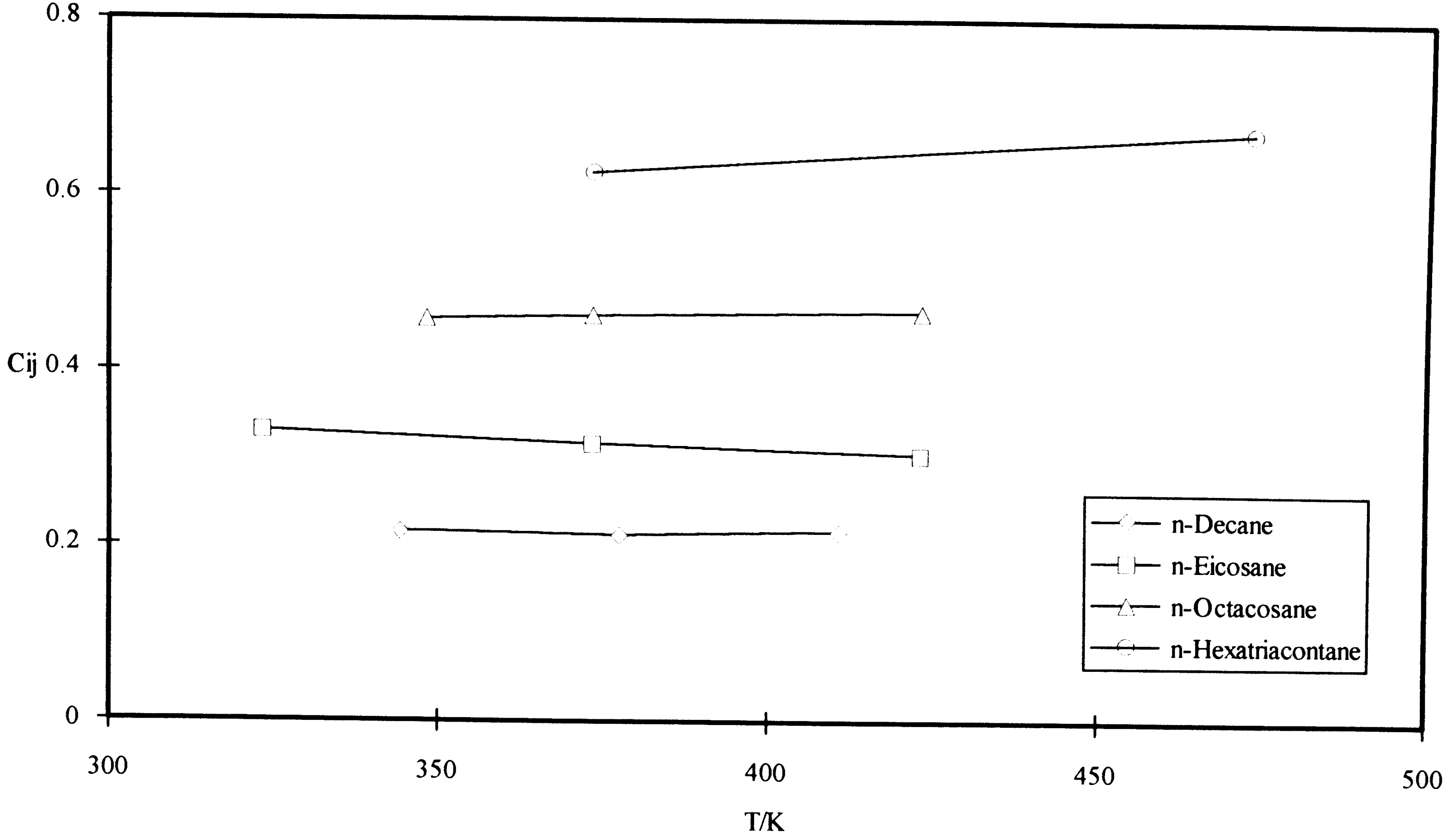


Figure 12. Soave Interaction Parameter C_{ij} for Nitrogen +n-Paraffins

in Figure 13. The interaction parameters for nitrogen in n-decane are extrapolated from the higher temperature data. The figure reveals the increasing trend of C_{ij} values for both the SRK and PR equations as the carbon number of the solvent increases. A similar trend has been observed for the other isotherms. A linear relation for the increase of C_{ij} with increasing carbon number is produced by the present nitrogen systems.

Henry's constants and partial molar volumes for nitrogen in n-decane, n-eicosane, n-octacosane, and n-hexatriacontane were determined. No literature data could be found for comparison purposes.

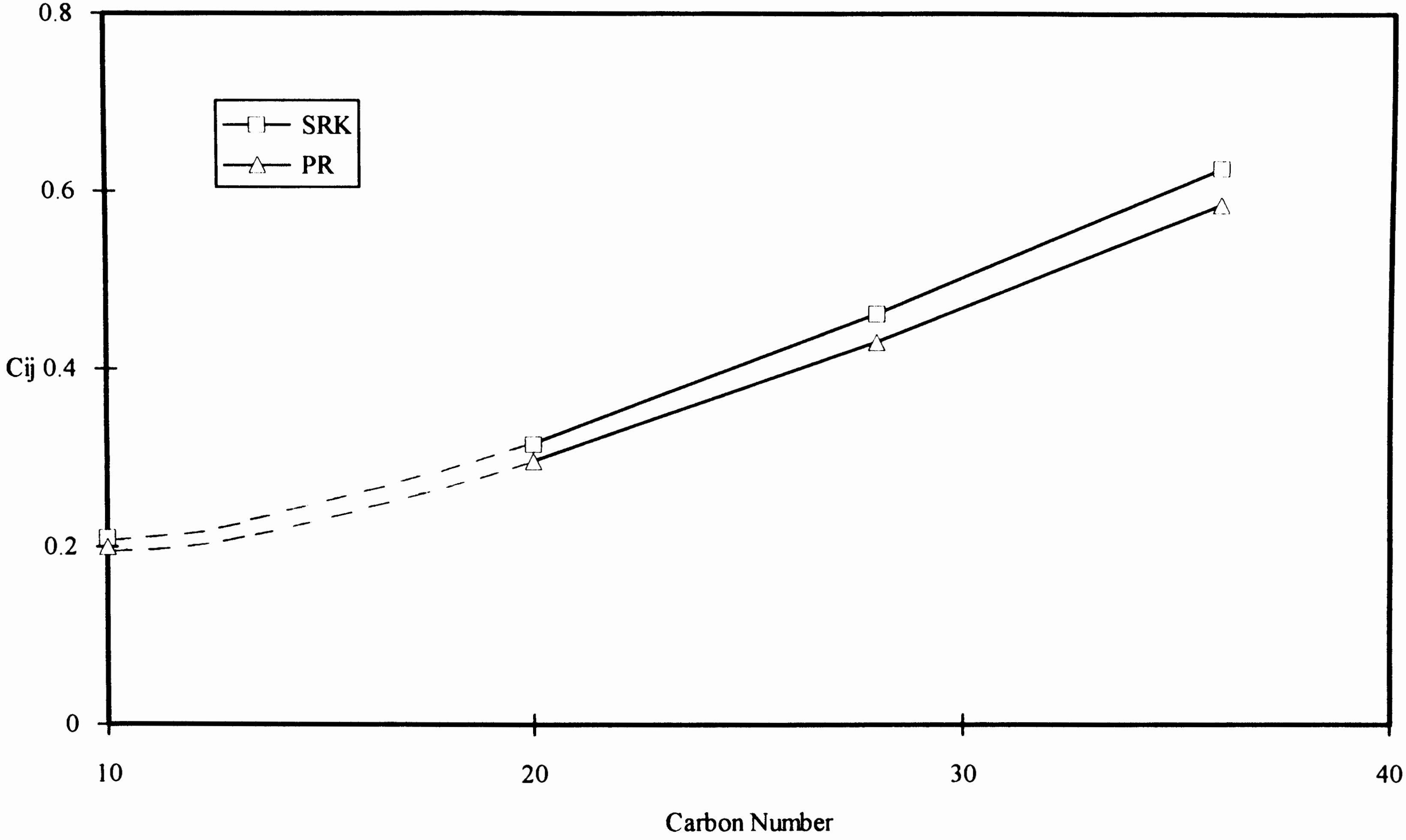


Figure 13. SRK and PR EOS Interaction Parameter C_{ij} for Nitrogen +n-Paraffins at 373.2 K

CHAPTER V

CORRELATION OF NITROGEN SOLUBILITIES IN NORMAL PARAFFINS

The prediction of vapor-liquid equilibrium (VLE) properties of hydrocarbon mixtures containing nitrogen is important in the chemical industry and receives particular attention in petroleum refining and enhanced oil recovery. Much effort has been made to calculate the VLE properties of these mixtures and, as mentioned in Chapter II, cubic equations of state have been used successfully in predicting the phase behavior of nitrogen-hydrocarbon mixtures.

Binary mixture data for the nitrogen + heavy n-paraffins (C_{10}, C_{20}, C_{28}, C_{36}) acquired in this work (as given in Tables IV - VII), combined with the literature data for these systems, were utilized in model evaluations. The literature data used in the evaluation are presented in Table I, along with the temperature and pressure ranges and the literature sources for the data. The data cover a temperature range from 143.2 to 703.4 K and pressures from 0.3 to 99.9 MPa. The solvents vary in carbon number from C_3 to C_{36}. All the data collected are isothermal bubble point pressures as a function of liquid mole fraction. The bubble point pressure data are restricted to pressures below 90% of the critical-point pressure to avoid the near-critical influence on the prediction accuracy. The data were analyzed using the SRK and PR equations of state, implemented in a software developed by Gasem (27). Some of the critical properties used in this work are shown in Table XII, and the rest are taken from the property data bank of Reid, et al. (70).

In the present work, five different cases were examined to test the abilities of the

TABLE XIII

SPECIFIC CASES STUDIED IN EOS MODEL EVALUATION

Case	Description
1. C_{ij}, $D_{ij} = 0$	A single value of C_{ij} is used for all the binary systems.
2. C_{ij}(CN), $D_{ij} = 0$	A separate value of C_{ij} is determined for each binary system, independent of temperature.
3. C_{ij} (CN), D_{ij} (CN)	Two interaction parameters are used for each binary system, independent of temperature.
4. C_{ij} (CN, T), $D_{ij} = 0$	A separate value of C_{ij} is determined for each isotherm of each system.
5. C_{ij} (CN, T), D_{ij} (CN, T)	Two interaction parameters are used for each isotherm of each system.

SRK and PR EOS. The various cases included are presented in Table XIII. For Cases 2 and 3, for each binary, data from different sources were analyzed separately. Optimum binary interaction parameters were obtained for each case, varying from one interaction parameter for all the binary systems to the use of two interaction parameters, C_{ij} and D_{ij}, for each isotherm of each system. Table XIV shows a summary of the results for the cases described in Table XIII using the SRK and PR EOS. Detailed results for each case containing the interaction parameters along with their uncertainties, Henry's constants, infinite dilution partial molar volumes, and the associated statistics are given in Appendix D. The overall model statistics are given for the bubble point pressure predictions. No generalization of the interaction parameters was attempted in this study.

The basic abilities of the SRK and PR EOS to predict bubble point pressures are evaluated using $C_{ij} = 0$ and $D_{ij} = 0$ (Case 1). However, the predictive abilities of both the SRK and PR equations of state are very poor for nitrogen binaries (RMSE = 59.1 bar, %AAD = 22.7 for SRK; RMSE = 66.3 bar, %AAD = 25.1 for PR). Thus, an average value of the interaction parameters of Case 2 is used ($C_{ij} = 0.15$ and $D_{ij} = 0$) to re-evaluate Case 1. The result of Case 1 appears in Table D.I, Appendix D. As shown by Table D.I, the predictive abilities of both the SRK and PR equations of state are still very poor for the nitrogen binary systems considered (RMSE = 36.5 bar, %AAD = 13.8 for SRK; RMSE = 31.5 bar, %AAD = 13.0 for PR), when a common interaction parameter is used. This indicates that the SRK and PR EOS prediction for the nitrogen binary mixtures could lead to large errors when a single interaction parameter is used to represent the entire range of temperature and solvent size. The observed results may be attributed to two factors. First, all of the EOS predictions are performed at temperatures far greater than the critical temperature of nitrogen. Second, the variation in the hydrocarbon molecular size is not well accounted for by a common value for the interaction parameter.

The effect of the carbon number of the solvent is considered in Case 2. Using an interaction parameter, C_{ij}, for each paraffin results in dramatic improvements in the EOS

TABLE XIV

RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF NITROGEN + N-PARAFFIN SYSTEMS

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	36.46	8.56	19.10	13.8
2	10.89	-2.71	7.11	5.8
3	5.96	-0.14	3.88	3.9
4	9.80	-2.86	6.28	5.3
5	3.95	0.10	2.49	2.6
	PENG-ROBINSON EQUATION OF STATE			
1	31.54	6.45	17.23	13.0
2	9.85	-2.07	6.51	5.4
3	5.73	0.05	3.70	3.7
4	8.62	-2.30	5.56	4.8
5	3.86	0.12	2.40	2.5

predictions over Case 1 (RMSE = 10.9 bar, %AAD = 5.8 for SRK; RMSE = 9.9 bar, %AAD = 5.4 for PR). This indicates that an interaction parameter to account for variation in molecular size is essential for reasonable predictions. Figures 14 and 15 show the interaction parameter for this case. The figure reveals that the interaction parameter is dependent on the carbon number, especially for larger carbon numbers, where C_{ij} increases with increasing carbon number. In comparison, the values of the interaction parameters obtained in this study for Case 2 are about 20% lower than those of Han, et al. (21) who used a different objective function, which minimizes deviations in the predicted K values. On the other hand, Oellrich, et al. (22) gave a value for the interaction parameter of nitrogen + hexane which is identical to the present work.

When two interaction parameters are employed for each system, a significant improvement is achieved (RMSE = 6.0 bar, %AAD = 3.9 for SRK; RMSE = 5.7 bar, %AAD = 3.7 for PR). The improvement in the prediction further demonstrates the need for the use of binary interaction parameters to account for unlike molecular interactions, and to some extent, empirically amend the model deficiency due to asymmetry in mixing. Case 4 describes the effects of temperature and carbon number on the interaction parameters. Some improvement over Case 1 is achieved with the use of a single interaction parameter, C_{ij}, specific to each isotherm of a given system (RMSE = 9.8 bar, %AAD = 5.3 for SRK; RMSE = 8.6 bar, %AAD = 4.8 for PR). Comparison of Cases 3 and 4 indicates that use of D_{ij} leads to better predictions than accounting for temperature effects.

Figure 16 shows the dependence of C_{ij} on temperature and carbon number of the solvent. Although it is difficult to see a uniform pattern in the data, a few trends are observed. The first trend shows that each binary system exhibits some temperature dependence, although the dependence differs for each system. The second trend demonstrates the increased value of C_{ij} as the carbon number of the solvent increases. Similar behavior is observed using the Peng-Robinson EOS. Compared with Case 2, Case

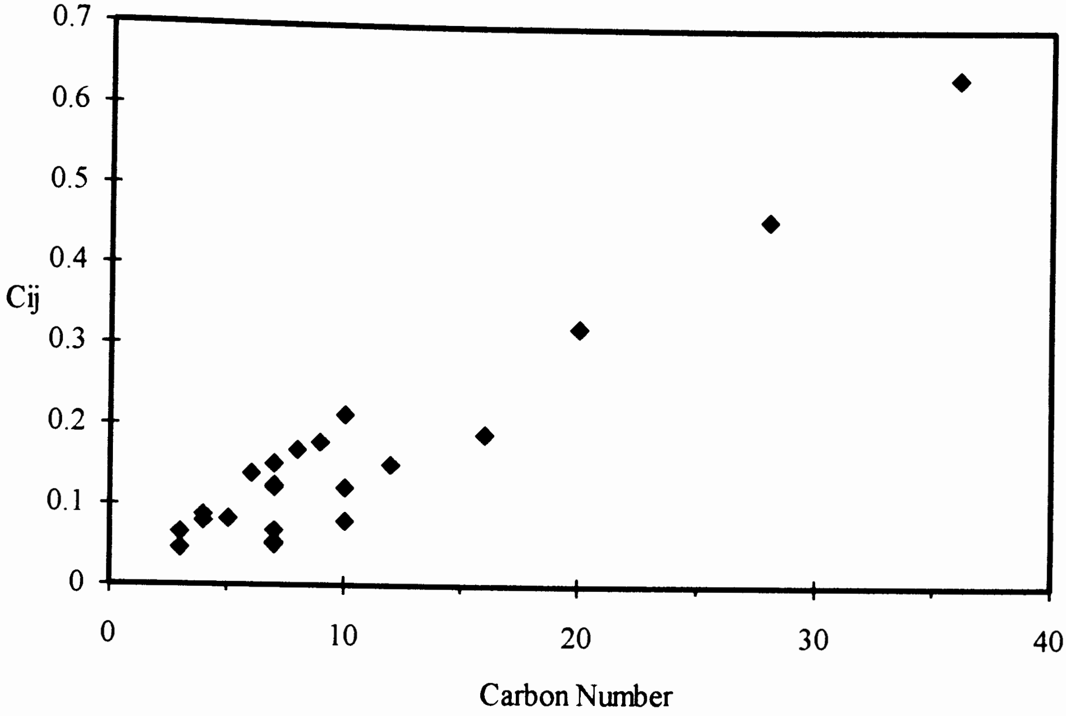


Figure 14. SRK EOS Interaction Parameters for Nitrogen + n-Paraffins (Case2)

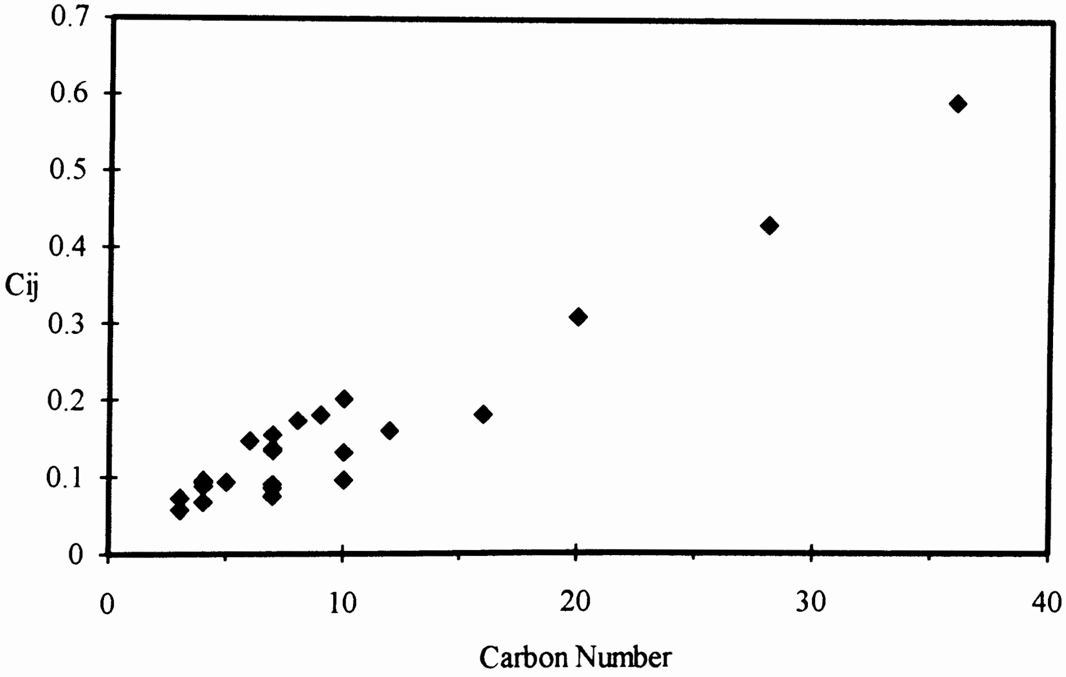


Figure 15. PR EOS Interaction Parameters for Nitrogen + n-Paraffins (Case2)

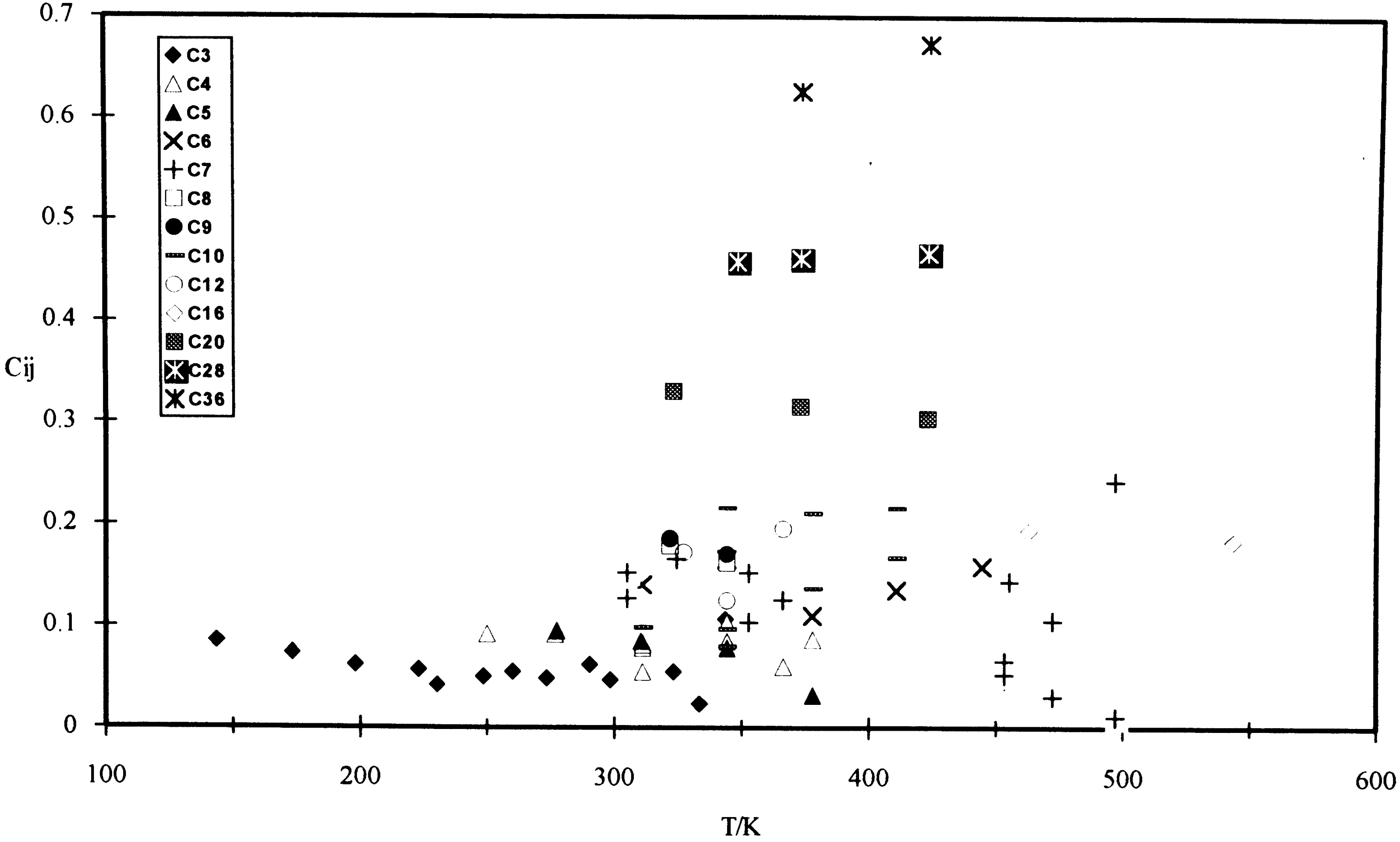


Figure 16. SRK EOS Interaction Parameters for Nitrogen + n-Paraffins (Case 4)

4 yields only slightly (about 10%) lower over-all RMSE values. However, Case 2 uses fewer interaction parameters (one per system) than Case 4, which needs one parameter per isotherm. Thus the use of a single interaction parameter C_{ij} for each mixture seems to be superior to Case 4 for describing the bubble pressure of the nitrogen + n-paraffin systems with comparable accuracy. This case has been studied by Valderrama (18). As discussed in Chapter II, he presented a correlation of the interaction parameter as functions of the reduced temperature and the accentric factor of the solvent. Applying his correlation leads to interaction parameters which are higher than those of the present work.

Case 5 is the most complex one; two interaction parameters are applied to each isotherm of each system. An enhanced fit for the data is seen in Table D.IV (RMSE = 4.0 bar, %AAD = 2.6 for SRK; RMSE = 3.9 bar, %AAD = 2.5 for PR). The results show further improvement when a second interaction parameter is also used specific to each isotherm of each system. These results indicate that the interaction parameters for n-paraffins are temperature and carbon number dependent. Moreover, the detailed results given in Table D.V, Appendix D, show no discernible difference between the light and heavy solvents, all being fitted equally well. Although the level of complexity in this case may be excessive for routine applications, the precision offered is excellent. As such, Case 5 is considered as the optimum case to assess the correlative capability of cubic equations of state.

It should be noted that some of the regressed interaction parameters contain large uncertainties, which may be attributed to the imprecision of the data. For example, for nitrogen + n-heptane mixture, the uncertainty in the interaction parameter C_{ij} obtained from the data of Brunner, et al. (62) is over thirty percent, as shown in Table D.IV. Care should be taken when using these data, since similar data for other members of the homoglous series are well described by the same model.

Henry's constants and partial molar volumes for nitrogen in n-paraffins are determined in this work using the SRK and PR EOS. Examination of Table D.V,

Appendix D shows that, in general, Henry's constant increases with increasing temperature when the temperature is not much in excess of the nitrogen critical temperature, and decreases when the temperature is much higher than the nitrogen critical temperature. Thus, for a wide temperature range, Henry's constant goes through a maximum (47). However, no simple generalization was made regarding the temperature effect on Henry's constant. Henry's constant and partial molar volume data for these systems could not be found in the literature for comparison with the present results.

CHAPTER VI

VAPOR-LIQUID EQUILIBRIUM PREDICTIONS USING CUBIC EQUATIONS OF STATE

Estimates of the solubility of important supercritical gases such as carbon dioxide, carbon monoxide or hydrogen in hydrocarbon solvents are required in many chemical process applications, including hydrotreating and coal gasification. When the available experimental data cannot meet the demands of VLE calculations, accurate predictive models provide reliable estimates.

An extensive literature search was conducted to identify the available VLE data involving supercritical fluids of interest to the energy sector. A broad database containing carbon dioxide, carbon monoxide, hydrogen, nitrogen, methane and ethane with aromatic and naphthenic solvents has been assembled in this work. All the data considered are constant-temperature bubble point pressures for different liquid mole fractions. A summary of the database employed in the evaluation including ranges of temperature, pressure and solute liquid-phase mole fraction, along with their sources, is presented in Table E.I - E.VI, Appendix E. The data cover a wide range of temperature and pressures and are restricted to 90% of the critical pressure.

The data are represented using the Peng-Robinson and Soave-Redlich-Kwong equations of state. Optimum values of interaction parameters are determined by fitting the experimental data to minimize an objective function expressed as the sum of the squared errors in the predicted bubble point pressures, as mentioned in Chapter II. In fitting the equation of state to experimental data, the values for the optimized interaction parameters are dependent on the properties T_c, P_c, and ω, which are used in the evaluation of the pure-component parameters (a and b) in Equations (2-13, 2-14). The pure fluid properties employed in this study are presented in Table XV.

In this work, a method established in earlier work (27) for evaluating cubic equations of state and modified (47) to include Henry's constants and infinite dilute partial molar volumes is pursued. As described in Chapter V, five different cases are examined to test the abilities of the EOS in representing the solubility data. Owing to the poor predictions obtained without interaction parameters, an average value for the interaction parameters obtained in Case 2 is used for Case 1. Results for the SRK and PR equations of state for the five cases studied, together with Henry's constants and the infinite dilution partial molar volumes are discussed below. Detailed results of the evaluation of the five cases for the six supercritical solutes (carbon dioxide, carbon monoxide, hydrogen, nitrogen, methane and ethane) in aromatics or naphthenes using the PR equation of state are presented in Tables I - V, Appendixes F - K. These tables provide the interaction parameters along with their uncertainties, Henry's constants, infinite dilution partial molar volumes and statistics assessing the quality of the fit.

Nitrogen + Aromatics and Naphthenes

The summarized results for nitrogen in aromatics or naphthenes are listed in Table XVI. As expected, the RMS errors in the bubble point pressure are extremely large. The predictive abilities of both the SRK and PR equations of state as given by Case 1 are poor for the nitrogen binaries (RMSE = 47.4 bar and %AAD = 16.2 for SRK; RMSE = 50.4 bar and %AAD = 16.2 for PR). Thus, the effect of temperature and/or the molecular size must be considered for better predictions.

Significant improvement in the EOS predictions is observed with an interaction parameter for each binary mixture as specified by Case 2 (RMSE = 18.9 bar and %AAD = 7.6 for SRK; RMSE = 18.0 bar and %AAD = 6.9 for PR). However, the error in bubble point pressure is still large. As indicated in Table F.II, Appendix F, the largest RMSE is

TABLE XV

PHYSICAL PROPERTIES OF AROMATICS AND NAPHTHENES USED IN THE SRK AND PR EQUATIONS OF STATE

Chemical	T_c (bar)	P_c (K)	ω	Source
Nitrogen	126.3	33.9	0.039	45
Hydrogen	33.2	13.0	-0.218	70
Ethane	305.4	48.8	0.099	70
Methane	190.4	46.0	0.011	70
Carbon Monoxide	132.9	35.0	0.066	70
Carbon Dioxide	304.1	73.8	0.239	70
Cyclopentane	511.7	45.1	0.196	70
Cyclohexane	553.5	40.7	0.212	70
Methylcyclohexane	572.2	34.7	0.236	70
Ethylcyclohexane	609.0	30.0	0.243	70
Propylcyclohexane	639.0	28.0	0.258	70
Benzene	562.2	48.9	0.212	70
Toluene	591.8	41.0	0.263	70
Ethylbenzene	617.2	36.0	0.302	70
Propylbenzene	638.2	32.0	0.344	70
Isopropylbenzene	631.1	32.1	0.326	70
Butylbenzene	660.5	28.9	0.393	70
Hexylbenzene	697.2	23.0	0.470	19
Heptylbenzene	714.2	21.1	0.514	19
Octylbenzene	729.2	19.5	0.557	19
o-Xylene	630.3	37.3	0.310	70
m-Xylene	617.1	35.4	0.325	70
p-Xylene	616.2	35.1	0.320	70
Mesitylene	637.3	31.3	0.399	70
Naphthalene	748.4	40.5	0.302	70
1-Methylnaphthalene	772.0	36.0	0.310	70
2-Methylnaphthalene	761.0	35.0	0.382	70
Tetralin	720.2	33.0	0.297	69
trans-Decalin	687.1	31.4	0.270	71
Pyrene	938.2	26.0	0.830	31
Phenanthrene	873.2	33.0	0.540	73
Diphenymethane	770.0	28.6	0.442	70
Quinoline	794.5	57.8	0.320	74
Diphenyl	789.0	38.5	0.372	70
m-Cresol	705.8	45.6	0.454	70
Styrene	647.0	39.9	0.257	70
Anisole	645.6	42.5	0.347	58

TABLE XV (Continued)

Chemical	T_c (bar)	P_c (K)	ω	Source
Benzaldehyde	694.8	45.4	0.316	70
1-Naphthol	826.1	46.9	0.520	58
2-Naphthol	822.4	46.9	0.520	58
Phenol	694.2	61.3	0.438	70
Catechol	772.2	78.7	0.641	58

TABLE XVI

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF NITROGEN + AROMATICS AND NAPHTHENES

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	47.36	-8.51	29.14	16.2
2	18.85	-2.38	12.19	7.6
3	13.68	-1.59	8.97	6.5
4	12.66	-3.95	8.44	6.0
5	6.79	-4.41	3.48	3.0
	PENG-ROBINSON EQUATION OF STATE			
1	50.39	-12.73	30.52	16.2
2	18.00	-1.36	11.37	6.9
3	11.27	-0.97	7.73	6.1
4	11.33	-3.23	7.42	5.3
5	5.62	-0.05	3.11	2.9

29 bar. Also, the optimum values of C_{ij} obtained from different data sources for the same mixture show considerable difference. Richon, et al. (38), for example, have shown unreasonable discrepancies between the results reported by Llave, et al. (13) and their measurements for mixtures of the nitrogen + toluene. Thus, the quality of the experimental data used, together with the temperatures and pressures considered, are the predominant factors in the determination of the interaction parameter. Figures 17 and 18 present the interaction parameters for this case against the molecular weight. As shown in the figures, the interaction parameters for aromatics are about 0.1 higher than those of naphthenes, and all the parameters are strongly dependent on the molecular weight. Some of the binaries have been studied by Han, et al. (21). Generally, the present work yields higher parameter values than those of Han, et al. The disagreements may be attributed to differences in the critical properties and the objective function used.

Substantial improvement is achieved in the quality of the predictions (RMSE = 13.7 bar and %AAD = 6.5 for SRK; RMSE = 11.3 bar and %AAD = 6.10 for PR) by introducing the second interaction parameter D_{ij} over the entire temperature range (Case 3). This indicates the need to account for variations in the solvent molecular size. The effect of temperature on the interaction parameter C_{ij} is taken into consideration in Case 4. This resulted in 30% improvement over Case 2, which demonstrates the temperature dependence of C_{ij}. The predictive ability of Case 4 is similar to that of Case 3. Thus, both temperature and molecular size effects are equally important.

When an additional interaction parameter D_{ij} for each isotherm is introduced (Case 5), an adequate representation of nitrogen binary mixtures is achieved. This improved fit is revealed in Table XXI with RMSE = 6.8 bar and %AAD = 3.0 for SRK; RMSE = 5.6 bar and %AAD = 2.9 for PR. In this case, the overall error was lowered by 12 bar when compared with Case 2, which indicates that the interaction parameters for the nitrogen binary systems are strongly dependent on temperature and molecular size. However, even with two interaction parameters being employed for each isotherm, the RMSE is still large

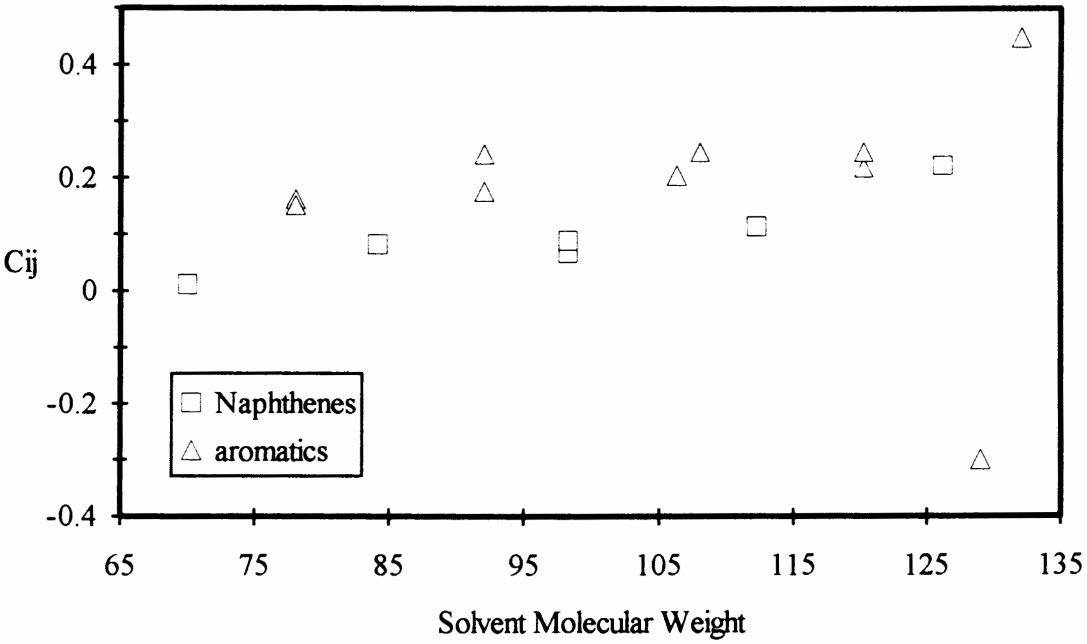


Figure 17. SRK EOS Interaction Parameters for Nitrogen + Aromatics and Naphthenes (Case 2)

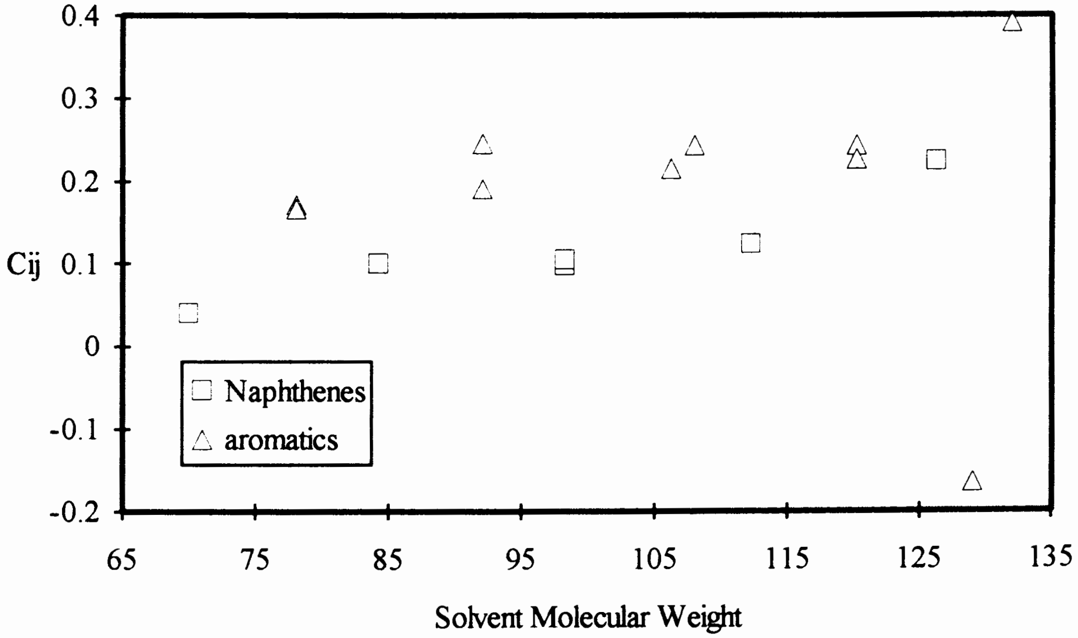


Figure 18. PR EOS Interaction Parameters for Nitrogen + Aromatics and Naphthenes (Case 2)

(up to 6 bar), and only reasonable results are obtained.

Both equations do not represent the bubble point pressure very well, especially, for nitrogen in toluene, m-xylene and mesitylene systems; the RMSE (Case 5) in bubble point pressure is 26 bar for the mesitylene binary. The experimental data for these systems were taken from the same source in the literature (38). By disregarding the two isotherms which give the largest RMSE, the overall RMSE is reduced from 6 to 4 bar using the PR EOS. Thus, some of the lack-of-fit may be attributed to inconsistency in the experimental data and to the solvent functional group.

In comparison with the nitrogen + n-paraffin systems, the present systems are more demanding due to the solvent molecular structure and polarity. The values of interaction parameters (extending from 0 to 0.3) are not so regular as those of the nitrogen + n-paraffins, which have a range extending from 0 to 0.7. For both types of systems, the interaction parameters increase with increasing solvent molecular weight.

Carbon Dioxide + Aromatics and Naphthenes

A summary of the results for carbon dioxide in aromatics or naphthenes is given in Table XVII. The predictive abilities for Case 1 using both the SRK and PR equations of state are inadequate to represent the carbon dioxide binary system (RMSE = 15.6 bar and %AAD = 13.2 for SRK; RMSE = 15.4 bar and %AAD = 12.4 for PR).

Substantial improvement is observed in the quality of the EOS predictions when a single interaction parameter is used for each binary mixture (Case 2) (RMSE = 3.8 bar and %AAD = 6.0 for SRK; RMSE = 4.0 bar and %AAD = 6.2 for PR). As indicated in Tables G.II, Appendix G (85), the optimum values of C_{ij} obtained from different data sets (originating from different literature sources) for the same binary mixture system show considerable scatter. This can be attributed, at least in part, to inconsistency among the data from different sources. Yau, et al. (59), for example, have shown significant discrepancies between the results reported by Devaney, et al. (83) and their measurements

TABLE XVII

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF CARBON DIOXIDE + AROMATICS AND NAPHTHENES

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	15.62	-1.35	6.95	13.2
2	3.81	-0.90	2.59	6.0
3	2.22	-0.03	1.20	2.9
4	3.10	-0.74	2.16	5.2
5	1.21	0.03	0.68	1.8
	PENG-ROBINSON EQUATION OF STATE			
1	15.39	-0.48	6.75	12.4
2	3.95	-0.90	2.62	6.2
3	2.33	-0.02	1.22	2.9
4	3.08	-0.78	2.17	5.2
5	1.65	-0.02	0.68	1.8

for the carbon dioxide + phenanthrene mixture. In addition, the differences in the interaction parameters were further amplified during data regression as a result of variations in the temperature and pressure range. Thus, the quality of the experimental data used together with the ranges of temperature and pressure considered are the predominant factors in determining the values of the interaction parameter.

Figures 19 and 20 present the interaction parameters for this case plotted against the solvent molecular weight. As shown, the majority of the binary systems fall within the range of ± 0.1 from the commonly encountered value of 0.12. Only the interaction parameters for the carbon dioxide + pyrene, anisole, benzaldelyde, catechol and quinoline differ in behavior. This may be attributed to the high polarity of those solvents, apart from pyrene. While the interaction parameter values show scatter, the optimum value of the interaction parameter for most systems is about 0.12. Nevertheless, it is difficult to generalize these interaction parameters with satisfactory results. Lin (56) has reported a constant value of $C_{ij} = 0.125$ using the PR EOS for binary mixtures of carbon dioxide with a variety of hydrocarbons. This value is close to the estimate from the present work. For each mixture, most of the interaction parameters are close to the values reported in this study. The variations are mostly due to differences in the objective function used. In Lin's study, deviations in the predicted K values for both components were minimized. In contrast, Han,et al. (21) evaluated the binary interaction parameters for several binary mixtures which show significant disagreement with the present work.

Moderate improvement is observed in the EOS predictions (RMSE = 2.2 bar and %AAD = 2.9 for SRK; RMSE = 2.3 bar and %AAD = 2.9 for PR) when the second interaction parameter D_{ij} is introduced over the entire temperature range (Case 3). Case 4 addresses the temperature effect on the interaction parameter C_{ij}. In this case, a minor improvement is observed over Case 2. The predictive ability of Case 4 is worse than that of Case 3. This demonstrates that the effect of molecular size is more important than that of temperature, except for highly polar solvents such as catachol and quinoline.

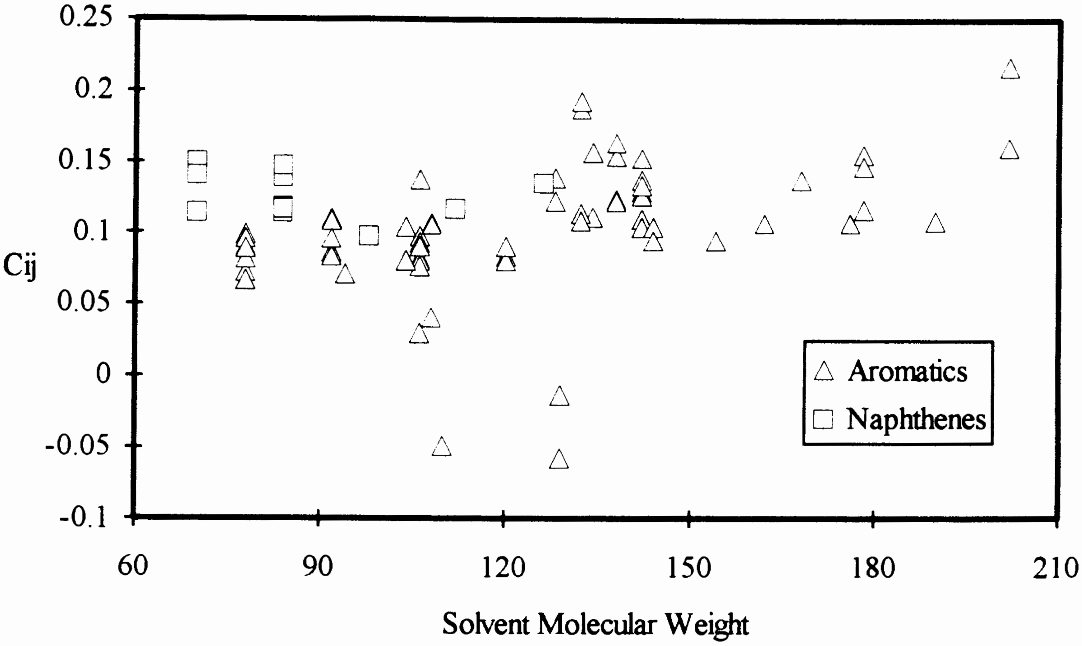


Figure 19. SRK EOS Interaction Parameters for Carbon Dioxide + Aromatics and Naphthenes (Case 2)

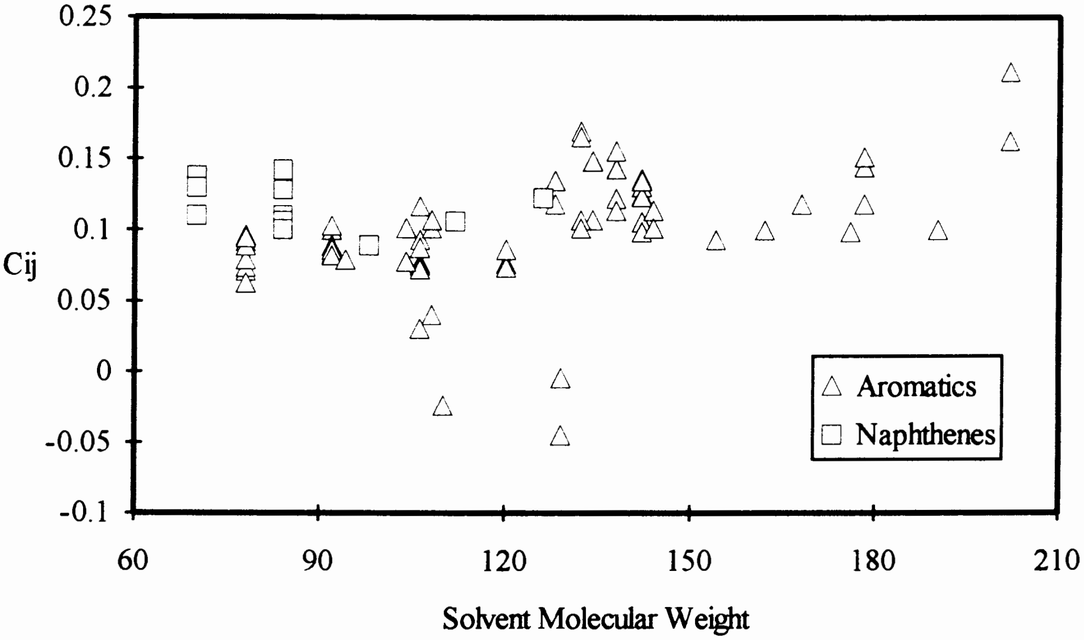


Figure 20. PR EOS Interaction Parameters for Carbon Dioxide + Aromatics and Naphthenes (Case 2)

Therefore, one interaction parameter for each binary mixture may be adequate with little loss in the accuracy of the EOS predictions. This case was evaluated by Yau, et al. (58) for carbon dioxide in twenty-eight aromatic solvents. Their results are generally in good agreement with the ones reported here. A generalized correlation of the interaction parameter for this case was given by Kordas, et al. (57). No comparison can be made between this work and Kordas's due to differences in the data sets used.

As expected, when an additional interaction parameter D_{ij} for each isotherm is introduced (Case 5), excellent representation is achieved for carbon dioxide binary mixtures. This improved fit is revealed in Table XVI with RMSE = 1.2 bar and %AAD = 1.8 for SRK; RMSE = 1.7 bar and %AAD = 1.8 for PR. Case 5 provides the best representation for the carbon dioxide binary system.

Compared with the carbon dioxide + n-paraffin systems, the values of the interaction parameters for Case 2 are about 0.2 larger than those of Bader (47) and seem to increase slightly with increasing molecular weight, which is in contrast to the behavior observed for the carbon dioxide + n-paraffins. For both types of systems, the effect of temperature on interaction parameters is not very significant.

Finally, the prediction results using the PR and SRK equations are compared. For all the carbon dioxide binary mixtures studied in this work, both equations represent the bubble point pressure reasonably well. With one interaction parameter for each binary, both equations of state give fairly good representation. Generally, the interaction parameters C_{ij} for the PR equation is slightly lower than those for the SRK equation.

Carbon Monoxide + Aromatics

A limited amount of literature data is available for carbon monoxide + aromatic systems. A summary of the results for carbon monoxide in aromatics is given in Table XVIII. The results indicate that the predictive abilities of both the SRK and PR equations of state for Case 1 are poor for these systems (RMSE = 7.7 bar and %AAD = 6.5 for

TABLE XVIII

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF CARBON MONOXIDE + AROMATICS

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	7.69	-2.75	5.21	6.5
2	2.58	-0.24	1.69	2.8
3	2.28	-0.10	1.60	2.4
4	0.79	-0.25	0.62	1.3
5	0.65	-0.13	0.43	0.9
	PENG-ROBINSON EQUATION OF STATE			
1	14.32	-8.20	9.24	9.6
2	2.44	-0.03	1.86	2.9
3	2.43	0.03	1.82	2.9
4	0.75	-0.23	0.59	1.2
5	0.47	-0.04	0.29	0.6

SRK; RMSE = 14.3 bar and %AAD = 9.6 for PR).

The effect of solvent molecular weight on the interaction parameter is represented by Case 2. Significant improvement in the EOS predictions is observed when an interaction parameter for each binary mixture is used (RMSE = 2.6 bar and %AAD = 2.8 for SRK; RMSE = 2.4 bar and %AAD = 2.9 for PR). As indicated in Figures 21 and 22, the interaction parameter is highly dependent on the molecular weight; it increases with increasing molecular weight. In contrast to the carbon dioxide systems, the interaction parameter C_{ij} for the PR EOS is much higher than that for the SRK EOS.

Only marginal improvement is observed in the quality of the EOS (RMSE = 2.3 bar and %AAD = 2.4 for SRK; RMSE = 2.4 bar and %AAD = 2.9 for PR) by introducing the second interaction parameter D_{ij} over the entire temperature range (Case 3). This clearly demonstrates that there is no need for employing a second interaction parameter to account for the molecular size effects.

Substantial improvement in the EOS representations over Case 2 is revealed in Table H.IV, Appendix H (85) by introducing the temperature-dependent interaction parameters (RMSE = 0.8 bar and %AAD = 1.3 for SRK; RMSE = 0.8 bar and %AAD = 1.2 for PR). When an additional interaction parameter D_{ij} is introduced for each isotherm, to account for the molecular size effects (Case 5), only moderate improvement is revealed in Table XVIII (RMSE = 0.7 bar and %AAD = 0.9 for SRK; RMSE = 0.5 bar and %AAD = 0.6 for PR). The overall error was marginally reduced compared with Case 4.

The values of the interaction parameters for Case 2 continually increase with increasing molecular weight. However, for the carbon monoxide + n-paraffin systems, C_{ij} increases to a maximum, then decreases with increasing molecular weight. For both types of systems, the effects of the solvent molecular weight and temperature on the interaction parameters are important. Overall, C_{ij} depends highly on the temperature and the molecular weight. However, there seems to be no need for the use of D_{ij} to account for the molecular size effects. For all the mixtures studied in this work, both the SRK and PR

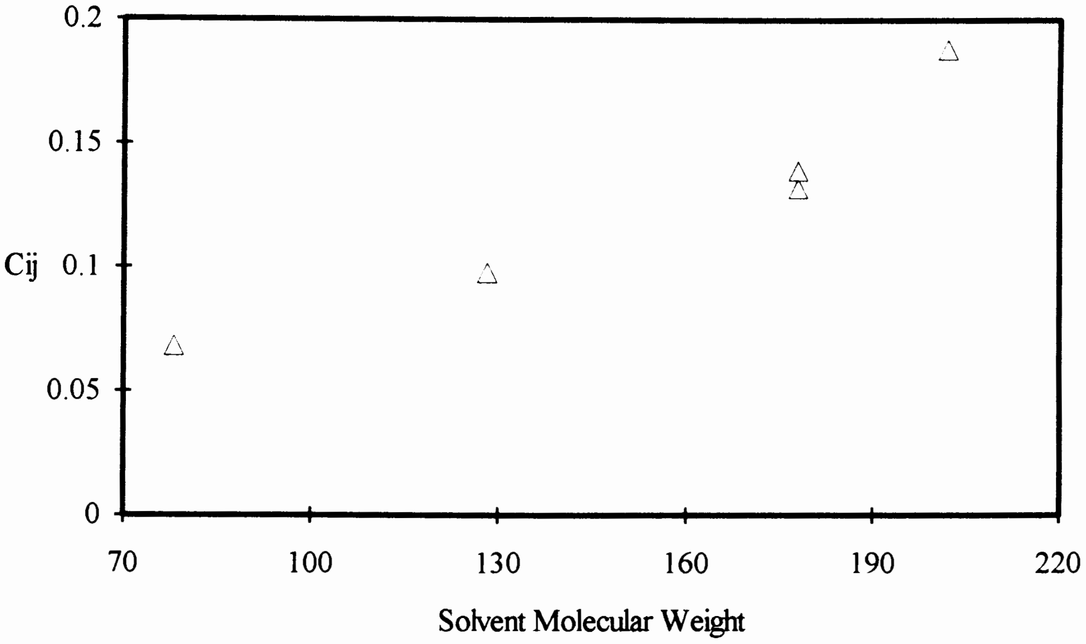


Figure 21. SRK EOS Interaction Parameters for Carbon Monoxide + Aromatics (Case 2)

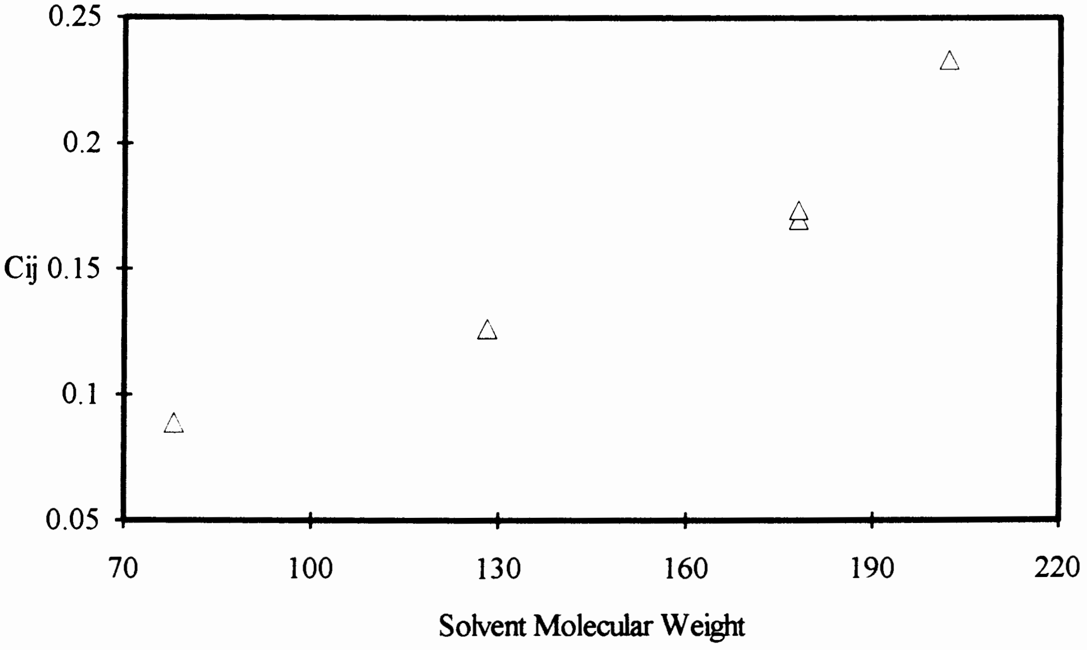


Figure 22. PR EOS Interaction Parameters for Carbon Monoxide + Aromatics (Case 2)

equations represent the bubble point pressure reasonably well.

Methane + Aromatics and Naphthenes

The summarized results for methane in aromatics or naphthenes are listed in Table XIX. These results of Case 1 indicate that the predictive abilities of both the SRK and PR equations of state are unsatisfactory for the methane binary systems (RMSE = 22.1 bar and %AAD = 10.6 for SRK; RMSE = 18.9 bar and %AAD = 10.3 for PR).

When a single interaction parameter for each binary mixture is used (Case 2), some improvement in the EOS predictions is observed (RMSE = 6.6 bar and %AAD = 4.0 for SRK; RMSE = 6.1 bar and %AAD = 3.7 for PR). As shown in Table I.II, Appendix I (85), the optimum values of C_{ij} obtained from different data sources for the same mixture system show considerable difference. This is similar to earlier observations concerning other solute mixtures studied in this work. Figures 23 and 24 present the interaction parameters for this case. As shown in the figures, the interaction parameter of aromatics increases with increasing molecular weight except for methane + quinoline. The C_{ij} interaction parameters of the PR EOS are slightly higher than those of the SRK EOS.

Moderate improvement in the EOS predictions is observed (RMSE = 5.1 bar and %AAD = 3.3 for SRK; RMSE = 4.6 bar and %AAD = 3.0 for PR) by introducing the second interaction parameter D_{ij} over the entire temperature range (Case 3). The temperature effect on the interaction parameter C_{ij} is considered in Case 4, which resulted in about 25% improvement over Case 2. The EOS ability of representation is similar to that of Case 3. This demonstrates that the effect of temperature is as important as that of molecular size.

When an additional interaction parameter D_{ij} for each isotherm is introduced (Case 5), a further improved fit is revealed in Table XIX (RMSE = 2.3 bar and %AAD = 1.6 for SRK; RMSE = 2.1 bar and %AAD = 1.5 for PR). Case 5 shows a 50% improvement over Case 4, which indicates that molecular size effects are very important.

TABLE XIX

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF METHANE + AROMATICS AND NAPHTHENES

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	22.12	2.72	12.86	10.6
2	6.57	-0.96	3.92	4.0
3	5.07	-0.08	3.00	3.3
4	4.78	-0.99	2.96	3.2
5	2.30	0.19	1.25	1.6
	PENG-ROBINSON EQUATION OF STATE			
1	18.93	-0.74	11.66	10.3
2	6.06	-0.84	3.59	3.7
3	4.55	0.01	2.69	3.0
4	4.34	-0.88	2.67	2.9
5	2.13	0.15	1.15	1.5

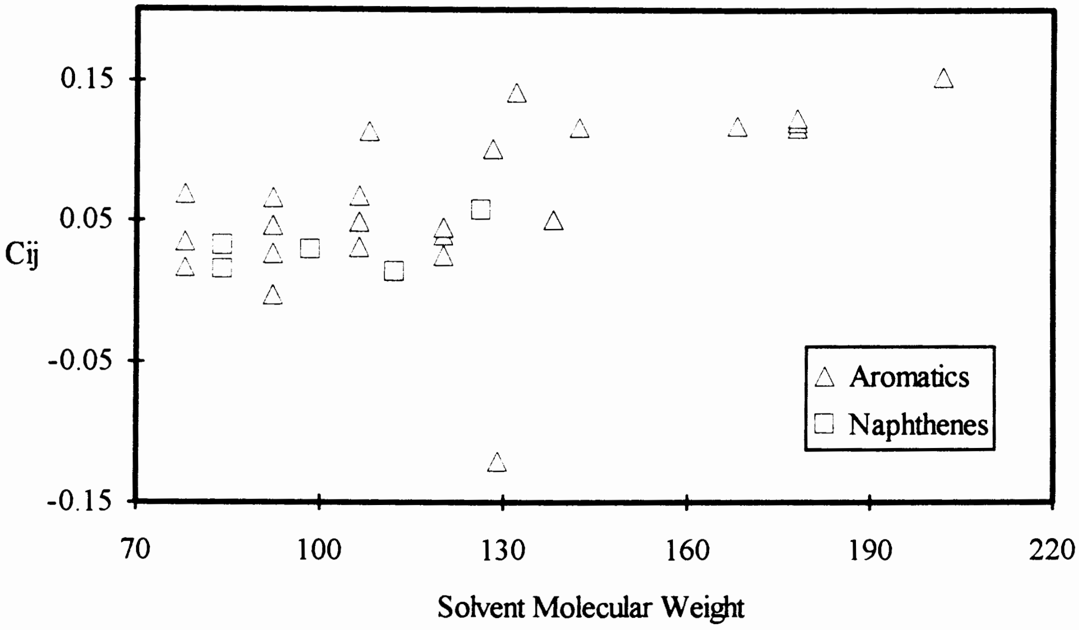


Figure 23. SRK EOS Interaction Parameters for Methane + Aromatics and Naphthenes (Case 2)

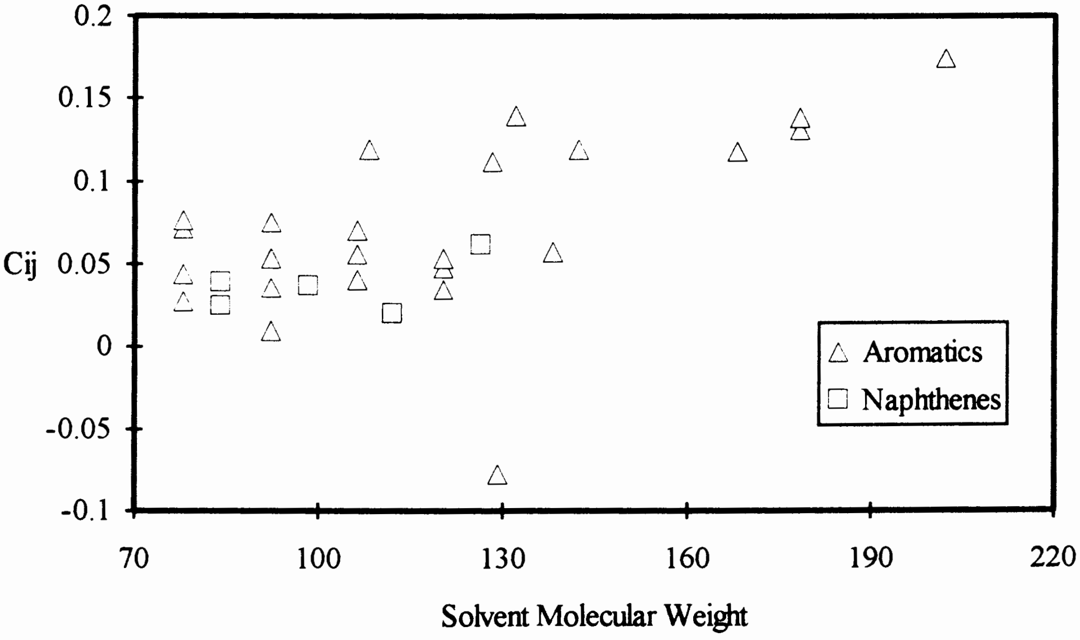


Figure 24. PR EOS Interaction Parameters for Methane + Aromatics and Naphthenes (Case 2)

For the heavier solvents, the C_{ij} of the present systems increases with increasing molecular weight while it has a relative constant value at molecular weights of less than 130. In comparison, a decrease in C_{ij} with the carbon number is observed for the heavier n-paraffin systems (47). At low molecular weights, the values of the interaction parameters for both types of systems are similar and yield an average value of about 0.05. However, the EOS representation for the present systems is worse than that for methane + n-paraffins systems. This is mainly attributed to the solvent chemical structure and the polarity of aromatics and naphthenes.

Finally, the EOS predictions using the PR and SRK equations are compared. For all the methane binary mixtures studied in this work, both the SRK and PR EOS represent the bubble point pressure fairly well.

Ethane + Aromatics and Naphthenes

The summarized results for ethane in aromatics or naphthenes are listed in Table XX. These results of Case 1 suggest that the predictive abilities of both the SRK and PR equations of state are poor for the ethane binary systems (RMSE = 21.3 bar and %AAD = 12.3 for SRK; RMSE = 23.9 bar and %AAD = 13.6 for PR). Thus, using a single interaction parameter for all ethane binary systems, the representation of the data by both equations is not satisfactory.

When an interaction parameter for each binary mixture is used (Case 2), a dramatic improvement is observed in the EOS predictions (RMSE = 3.3 bar and %AAD = 4.7 for SRK; RMSE = 3.5 bar and %AAD = 4.9 for PR). As shown in Table J.II, Appendix J (85), the optimum values of C_{ij} obtained from different sources for the same solvent show considerable difference, see, e.g., the ethane +1-methylnaphthalene mixture. Figures 25 and 26 present the interaction parameters for this case against the solvent molecular weight. As shown in the figures, the interaction parameters of aromatics increase with increasing molecular weight. Only the interaction parameters of benzaldehyde + ethane

TABLE XX

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF ETHANE + AROMATICS AND NAPHTHENES

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	21.25	-6.64	8.55	12.3
2	3.29	-0.63	2.09	4.7
3	2.22	-0.06	1.43	3.5
4	2.58	-0.55	1.55	2.7
5	0.87	0.06	0.55	1.5
	PENG-ROBINSON EQUATION OF STATE			
1	23.85	-8.01	9.66	13.6
2	3.45	-0.81	2.17	4.9
3	2.30	-0.09	1.42	3.4
4	2.89	-0.68	1.74	4.0
5	0.83	0.07	0.51	1.5

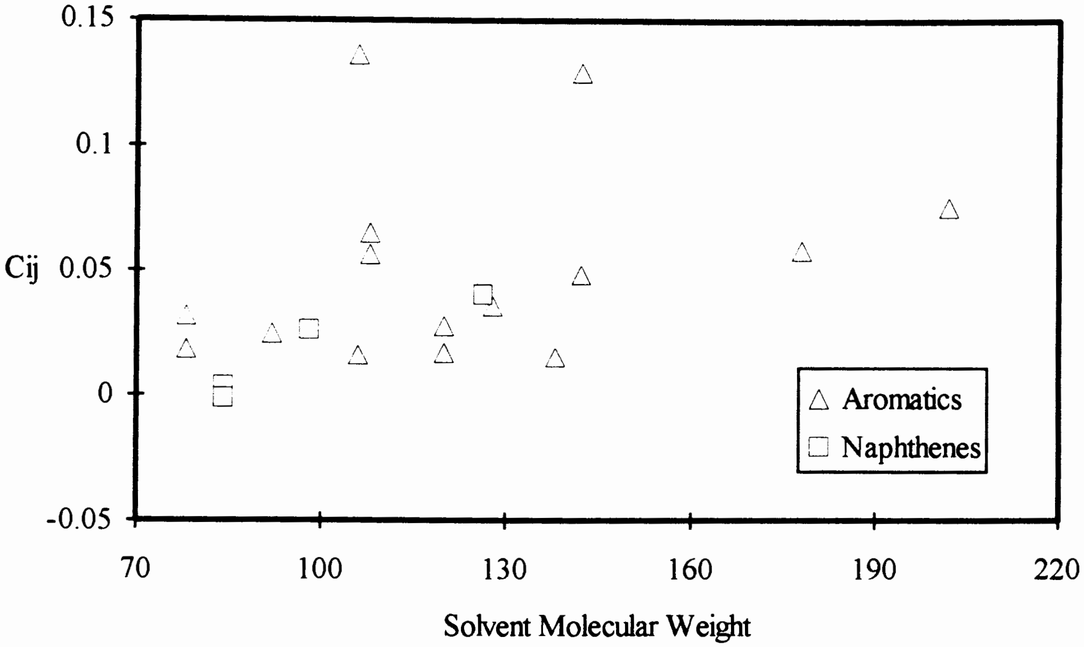


Figure 25. SRK EOS Interaction Parameters for Ethane + Aromatics and Naphthenes (Case 2)

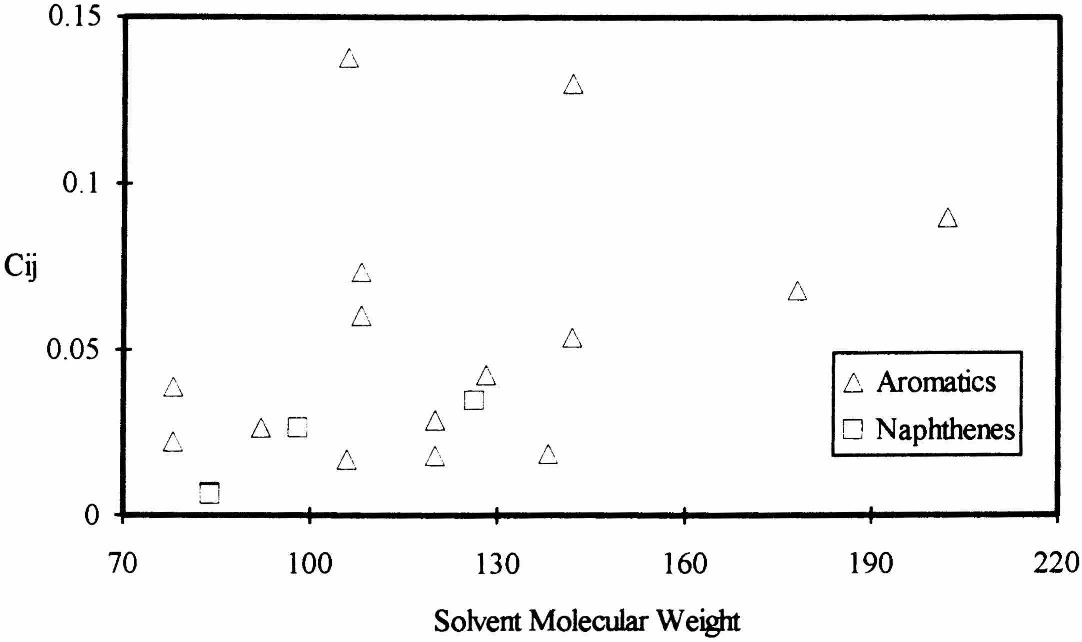


Figure 26. PR EOS Interaction Parameters for Ethane + Aromatics and Naphthenes (Case 2)

and 1-methylnaphthalene + ethane are vastly different from the rest of the ethane binaries.

Moderate improvement is realized in the quality of the EOS predictions by introducing the second interaction parameter D_{ij} over the entire temperature range, as specified by Case 3 (RMSE = 2.2 bar and %AAD = 3.5 for SRK; RMSE = 2.3 bar and %AAD = 3.4 for PR). The temperature effect on the interaction parameter C_{ij} is accounted for in Case 4. No improvement over Case 3 and only marginal improvement over Case 2 is observed. This demonstrates that C_{ij} depends heavily on the molecular size. Further, an additional interaction parameter D_{ij} for each isotherm is introduced (Case 5). In this case, considerable improvement is achieved with RMSE = 0.9 bar and %AAD = 1.5 for SRK; RMSE = 0.8 bar and %AAD = 1.5 for PR. The overall error was lowered by 70% using both the PR and SRK EOS compared with Case 4.

In comparison, C_{ij} values of the present system increase with increasing molecular weight. However, for the ethane + n-paraffin systems, minor variations in C_{ij} values are observed for carbon numbers below 20. For light molecular weights (MW < 130), both systems have very close C_{ij} values, that are similar to those of the methane systems. The EOS representation is good for both types of systems.

Generally, both the SRK and PR equations represent the bubble point pressure of all the ethane binary mixtures studied in this work equally well. For these systems, the solvent molecular size has a major effect on the interaction parameters of both equations.

Hydrogen + Aromatics and Naphthenes

The summarized results for hydrogen in aromatics or naphthenes are listed in Table XXII. As expected, for Case 1, the predictive abilities of both the SRK and PR equations of state are deficient for the hydrogen binary systems (RMSE = 46.4 bar and %AAD = 17.3 for SRK; RMSE = 58.4 bar and %AAD = 18.7 for PR). To improve the representation of both equations for hydrogen binary systems, evaluations accounting for variations in the solvent molecular size and temperature are considered.

TABLEXXI

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES OF HYDROGEN + AROMATICS AND NAPHTHENES

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
	SOAVE-REDLICH-KWONG EQUATION OF STATE			
1	46.40	7.55	24.70	17.3
2	15.47	-5.71	10.35	8.0
3	11.91	-4.59	7.68	7.0
4	10.27	-3.64	6.27	5.2
5	4.51	-0.96	2.13	1.9
	PENG-ROBINSON EQUATION OF STATE			
1	58.35	18.68	28.02	18.7
2	13.52	-4.45	8.73	6.6
3	10.45	-3.61	6.42	5.7
4	8.77	-2.86	5.18	4.2
5	2.86	-0.31	1.30	1.4

When an interaction parameter for each binary mixture is used (Case 2), considerable improvement in the EOS representations is obtained with (RMSE = 15.5 bar and %AAD = 8.0 for SRK; RMSE = 13.5 bar and %AAD = 6.6 for PR). However, the error in bubble point pressures is still notably large. As indicated in Table K.II, Appendix K (85), the greatest RMSE is 29 bar. Also, the optimum values of C_{ij} obtained from different data sources for the same mixture system show considerable difference, as exemplified by the hydrogen + 1-methylnaphthalene binary mixture. Figures 27 and 28 present the interaction parameters for this case against the solvent molecular weight. As shown in the figures, the interaction parameters are widely scattered. The difference between the largest and smallest interaction parameter is about 1.0. The interaction parameters for hydrogen systems are larger in magnitude than for other solutes. And while most of the interaction parameters fall within 0.2 - 0.7, some are much larger, as seen for the hydrogen + tetralin binary.

By introducing the second interaction parameter D_{ij} over the entire temperature range (Case 3), substantial improvement in the quality of the EOS fit is achieved (RMSE = 11.9 bar and %AAD = 7.0 for SRK; RMSE = 10.5 bar and %AAD = 5.7 for PR). This indicates the need to account for molecular size effects. Case 4 considers the temperature effect on the interaction parameter C_{ij}. Accounting for C_{ij}'s temperature variations resulted in a 30% improvement over Case 2. As mentioned earlier in Chapter II, Case 4 has been attempted by Valderrama and coworker (36, 39). In one study (39), they correlated interaction parameters for the PR EOS in terms of the accentric factor and the reduced temperature of the solvent. Later on, they proposed another correlation for the PR EOS interaction parameters which was applied to a wider temperature range and results in a more accurate representation of the hydrogen + aromatics systems (36).

When an additional interaction parameter D_{ij} for each isotherm is introduced (Case 5), the best representation of hydrogen binary mixtures is achieved. This enhanced fit is revealed in Table XXI with RMSE = 4.5 bar and %AAD = 1.9 for SRK; RMSE = 2.9 bar

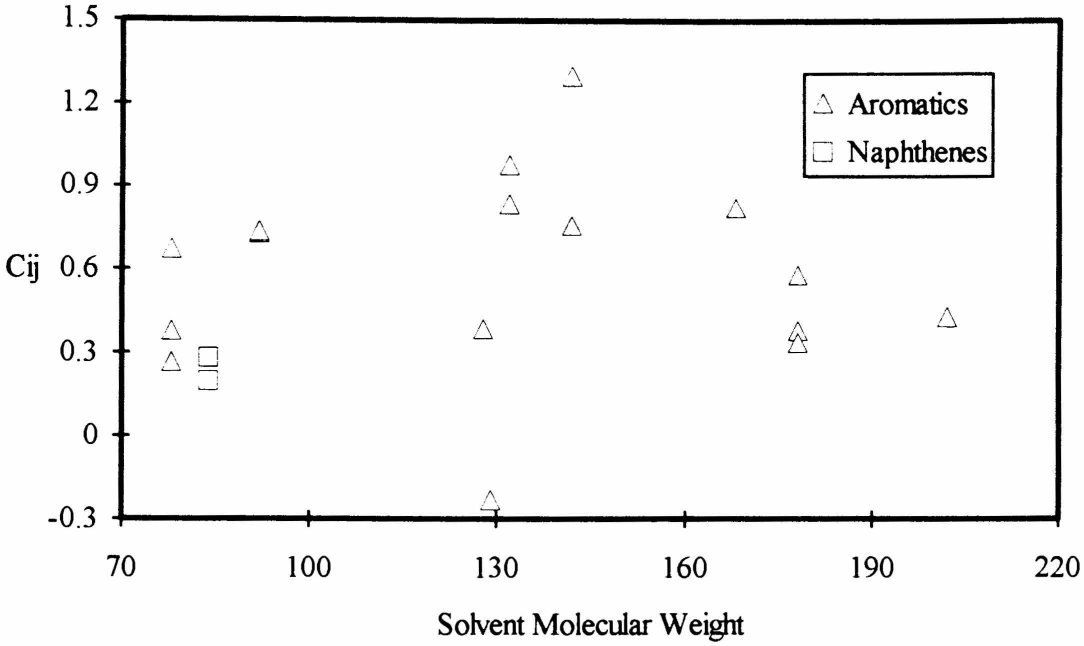


Figure 27. SRK EOS Interaction Parameters for Hydrogen + Aromatics and Naphthenes (Case 2)

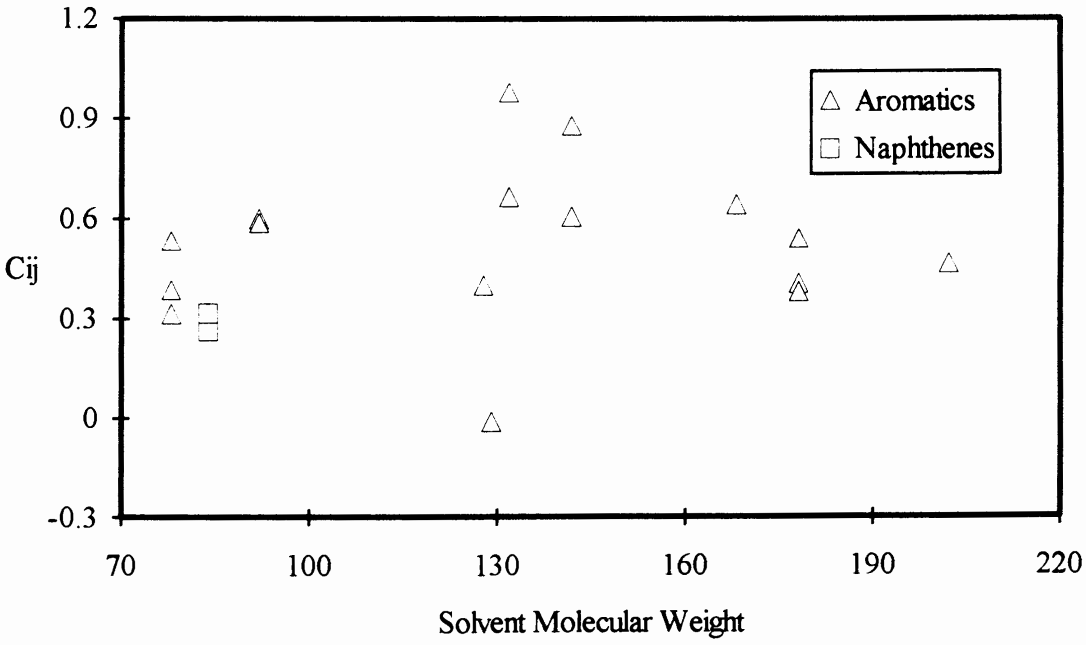


Figure 28. PR EOS Interaction Parameters for Hydrogen + Aromatics and Naphthenes (Case 2)

and %AAD = 1.4 for PR. Therefore, the effect of molecular size must be considered for hydrogen binary systems as noticed in Case 3.

Although substantial improvement is realized in Case 5, the EOS representation, as expressed by the RMSE, is not very good. These results may be attributed to the low critical temperature and pressure of hydrogen and the negative value of the accentric factor, and/or inconsistency in the experimental data. For example, the RMSE in bubble point pressure for the hydrogen + benzene mixture (84) is as high as 15 bar for Case 5.

In general, the interaction parameter for hydrogen binary systems is strongly temperature and molecular size dependent. For all the hydrogen mixtures studied in this work, neither equation represents the bubble point pressure very well. However, on a relative basis, the predictive capabilities of the SRK and PR EOS are very good. This behavior may be attributed to the steep slope of a p-x plot for these systems, which indicates that hydrogen does not easily dissolve in the hydrocarbon solvents. Thus, slight changes in solubility can cause large errors in the bubble point pressure. Moreover, the PR EOS gives a little better representation than the SRK EOS.

Discussion

The vapor-liquid equilibrium data of six supercritical gases in aromatic and naphthenic solvents are correlated using the SRK and PR EOS for five specific cases (Table XIII). A summary of the overall results is presented in Table XXII. As shown in the table, the SRK and PR EOS are capable of representing the phase behavior of carbon dioxide, carbon monoxide, methane, ethane, hydrogen and nitrogen in aromatic and naphthenic solvents. However, neither equation represents the bubble point pressure very well for the nitrogen and hydrogen systems. The basic abilities (Case 1) of both SRK and PR EOS are grossly inadequate to represent all the systems studied here. Particularly, for nitrogen and hydrogen systems, large differences are observed (for hydrogen systems, RMSE = 46.7 bar and %AAD = 18.1 for SRK; RMSE = 58.6 bar and %AAD = 19.6 for

TABLE XXII

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES: SUPERCRITICAL GASES + AROMATICS AND NAPHTHENES

	RMS Error in Bubble Point Pressure, bar (%AAD)					
CASE NUMBER	CO_2	CO	CH_4	C_2H_6	H_2	N_2
	SOAVE-REDLICH-KWONG EQUATION OF STATE					
1. C_{ij}, $D_{ij} = 0$	15.62 (13.2)	7.69 (6.5)	22.12 (10.6)	21.25 (12.3)	46.40 (17.3)	47.36 (16.2)
2. C_{ij}(MW), $D_{ij} = 0$	3.81 (6.0)	2.58 (2.8)	6.57 (4.0)	3.29 (4.7)	15.47 (8.0)	18.85 (7.6)
3. C_{ij}(MW), D_{ij} (MW)	2.22 (2.9)	2.28 (2.4)	5.07 (3.3)	2.22 (3.5)	11.91 (7.0)	13.68 (6.5)
4. C_{ij}(MW, T), $D_{ij} = 0$	3.10 (5.2)	0.79 (1.3)	4.78 (3.2)	2.58 (2.7)	10.27 (5.2)	12.66 (6.0)
5. C_{ij}(MW, T), D_{ij} (MW, T)	1.21 (1.8)	0.65 (0.9)	2.30 (1.6)	0.87 (1.5)	4.51 (1.9)	6.79 (3.0)
	PENG-ROBINSON EQUATION OF STATE					
1. C_{ij}, $D_{ij} = 0$	15.39 (12.4)	14.32 (9.6)	18.93 (10.3)	23.85 (13.6)	58.35 (18.7)	50.39 (16.2)
2. C_{ij}(MW), $D_{ij} = 0$	3.95 (6.2)	2.44 (2.9)	6.06 (3.7)	3.45 (4.9)	13.52 (6.6)	18.00 (6.9)
3. C_{ij}(MW), D_{ij} (MW)	2.33 (2.9)	2.43 (2.9)	4.55 (3.0)	2.30 (3.4)	10.45 (5.7)	11.27 (6.1)
4. C_{ij}(MW, T), $D_{ij} = 0$	3.08 (5.2)	0.75 (1.2)	4.34 (2.9)	2.89 (4.0)	8.77 (4.2)	11.33 (5.3)
5. C_{ij}(MW, T), D_{ij} (MW, T)	1.65 (1.8)	0.47 (0.6)	2.13 (1.5)	0.83 (1.5)	2.86 (1.4)	5.62 (2.9)

PR and for nitrogen systems, RMSE = 47.4 bar and %AAD = 16.2 for SRK; RMSE = 50.4 bar and %AAD = 16.2 for PR). The best representation of the experimental data can be achieved by using two interaction parameters for each isotherm of each mixture (Case 5 for PR: RMSE = 1.7 bar and %AAD = 1.8 for carbon dioxide systems; RMSE = 0.5 bar and %AAD = 0.6 for carbon monoxide systems; RMSE = 2.2 bar and %AAD = 1.7 for methane systems; RMSE = 0.8 bar and %AAD = 1.5 for ethane systems; RMSE = 5.7 bar and %AAD = 2.1 for hydrogen systems; RMSE = 5.8 bar and %AAD = 2.9 for nitrogen systems).

Table XXII reveals that the effects of temperature and molecular size are different for different binary systems. For the carbon dioxide and ethane systems, the effect of molecular size is more important than the effect of molecular size in the carbon monoxide systems. For the rest of the systems, the effects of temperature and molecular size are almost equally important.

Based on the earlier discussion concerning each solute, it can be stated that the EOS interaction parameters are dependent on the dissimilarity in the molecular species, i.e., the more dissimilarity in molecular type, the greater the values required for such parameters. This is well illustrated by the hydrogen systems. The largest C_{ij} value is greater than 1 for systems such as hydrogen + methylnaphthane. Similar behavior is observed for hydrogen + n-paraffins (47); as illustrated by the hydrogen + n-octane mixture, which has an interaction parameter greater than 1.

The overall results given in Tables XXII and XXIII suggest the SRK and PR equations represent the bubble point pressure of supercritical gases in n-paraffins better than that of supercritical gases in aromatics and naphthenes. These results may be attributed to variations in the molecular structure and polarity of some aromatics and naphthenes. Table XXIII reveals that the predictive capability of the SRK and PR EOS without interaction parameters (Case 1) varies for different solutes. However, on a relative basis, the deviations produced using two parameters per isotherm (Case 5) are

TABLE XXIII

SUMMARY OF THE RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES: SUPERCRITICAL GASES + N-PARAFFINS

CASE NUMBER	RMS Error in Bubble Point Pressure, bar (%AAD)					
	CO_2 (47)	CO (47)	CH_4 (47)	C_2H_6 (47)	H_2 (47)	N_2
SOAVE-REDLICH-KWONG EQUATION OF STATE						
1. C_{ij}, $D_{ij} = 0$	10.36 (21.6)	6.23 (10.4)	3.28 (9.2)	5.15 (8.0)	23.88 (17.9)	34.46 (13.8)
2. C_{ij}(CN), $D_{ij} = 0$	2.10 (4.7)	2.17 (3.4)	1.51 (5.0)	2.50 (4.3)	12.04 (7.1)	10.89 (5.8)
3. C_{ij}(CN), D_{ij} (CN)	1.45 (3.5)	1.93 (3.1)	0.83 (2.6)	2.13 (3.9)	8.88 (7.0)	5.96 (3.9)
4. C_{ij}(CN,T), $D_{ij} = 0$	1.07 (2.9)	1.02 (1.9)	1.11 (4.0)	1.05 (1.6)	4.09 (3.3)	9.80 (5.3)
5. C_{ij}(CN, T), D_{ij} (CN, T)	0.41 (1.1)	0.43 (0.7)	0.32 (1.1)	0.57 (1.1)	1.25 (1.2)	3.95 (2.6)
PENG-ROBINSON EQUATION OF STATE						
1. C_{ij}, $D_{ij} = 0$	9.48 (20.1)	6.57 (10.9)	3.51 (9.9)	5.73 (8.7)	26.67 (20.2)	31.54 (13.0)
2. C_{ij}(CN), $D_{ij} = 0$	2.24 (4.9)	2.22 (3.4)	1.51 (4.7)	2.85 (4.8)	11.03 (6.4)	9.85 (5.4)
3. C_{ij}(CN), D_{ij} (CN)	1.55 (3.7)	1.95 (3.1)	0.83 (2.7)	2.48 (4.3)	7.73 (6.1)	5.73 (3.7)
4. C_{ij}(CN,T), $D_{ij} = 0$	1.07 (2.9)	1.10 (1.9)	1.10 (4.0)	1.04 (1.5)	3.10 (2.4)	8.62 (4.8)
5. C_{ij}(CN, T), D_{ij} (CN, T)	0.44 (1.1)	0.43 (0.7)	0.32 (1.1)	0.57 (1.0)	1.27 (1.1)	3.86 (2.5)

about 1% for all the solutes considered except the nitrogen systems (47). In comparison, Table XXII shows that the predictive capability of the SRK and PR EOS (Case 5) varies for the different solutes and greater relative errors are observed (1-3%). Moreover, neither equation is precise in representing the nitrogen systems.

Tables XXII and XXIII reveal that the RMS errors of the nitrogen systems are at least five times greater than those of the carbon dioxide systems, aside from Case 1. However, absolute average percent deviation (%AAD) of the nitrogen systems is only twice as high as that of the carbon dioxide systems. These results may be attributed to the low solubility of nitrogen compared with carbon dioxide at the same temperature and pressure. Thus, the bubble point pressure is very sensitive to the solubility of nitrogen. The unsatisfactory results may have also resulted from the low critical temperature and pressure of nitrogen and/or inconsistency in the experimental data.

The quality of representation of the bubble point pressures using the SRK and PR EOS is presented in Tables XXIV and XXV for six supercritical gases in n-paraffins, aromatics and naphthenes based on the absolute average percent deviations. Both equations provide excellent representations for carbon monoxide systems. With a single interaction parameter for each mixture, both equations represent the bubble point pressure of carbon monoxide systems with reasonable accuracy. The excellent fit of the EOS for the carbon monoxide systems may be partially attributed to the limited amount of data, which have originated mostly from OSU. For carbon dioxide + aromatics and naphthenes systems, while the use of two interaction parameters for each mixture yields good representation for the bubble point pressure, the use of one interaction parameter for each isotherm of each mixture gives poor representation. Similar behavior is observed for methane + n-paraffins. With a single interaction parameter for each mixture, both equations are adequate to describe the carbon monoxide, methane and ethane systems. In comparison, two interaction parameters for each isotherm of each mixture are required for hydrogen + aromatics and naphthenes systems to produce very good representations.

TABLE XXIV

QUALITY OF REPRESENTATION OF THE BUBBLE POINT PRESSURES: SUPERCRITICAL GASES + AROMATICS AND NAPHTHENES

CASE NUMBER	CO_2	CO	CH_4	C_2H_6	H_2	N_2
		SOAVE-REDLICH-KWONG EQUATION OF STATE				
1. C_{ij}, $D_{ij} = 0$	P*	P	P	P	P	P
2. C_{ij}(MW), $D_{ij} = 0$	P	G	A	A	P	P
3. C_{ij}(MW), D_{ij} (MW)	G	G	A	A	P	P
4. C_{ij}(MW, T), $D_{ij} = 0$	P	VG	A	G	P	P
5. C_{ij}(MW, T), D_{ij} (MW, T)	VG	E	VG	VG	VG	G
		PENG-ROBINSON EQUATION OF STATE				
1. C_{ij}, $D_{ij} = 0$	P	P	P	P	P	P
2. C_{ij}(MW), $D_{ij} = 0$	P	G	A	A	P	P
3. C_{ij}(MW), D_{ij} (MW)	G	G	G	A	P	P
4. C_{ij}(MW, T), $D_{ij} = 0$	P	VG	G	A	A	P
5. C_{ij}(MW, T), D_{ij} (MW, T)	VG	E	VG	VG	VG	G

*P = poor; %AAD > 5 A = adequate; 3 < %AAD <5 G = good; 2 < %AAD <3

VG = very good; 1 < %AAD < 2 E = excellent; %AAD < 1

TABLE XXV

QUALITY OF REPRESENTATION OF THE BUBBLE POINT PRESSURES: SUPERCRITICAL GASES + N-PARAFFINS

CASE NUMBER	CO_2 (47)	CO (47)	CH_4 (47)	C_2H_6 (47)	H_2 (47)	N_2
			SOAVE-REDLICH-KWONG EQUATION OF STATE			
1. C_{ij}, $D_{ij} = 0$	P*	P	P	P	P	P
2. $C_{ij}(CN)$, $D_{ij} = 0$	A	A	A	A	P	P
3. $C_{ij}(CN)$, D_{ij} (CN)	A	A	G	A	P	A
4. $C_{ij}(CN,T)$, $D_{ij} = 0$	G	VG	A	VG	A	P
5. $C_{ij}(CN, T)$, D_{ij} (CN, T)	VG	E	VG	VG	VG	G
			PENG-ROBINSON EQUATION OF STATE			
1. C_{ij}, $D_{ij} = 0$	P	P	P	P	P	P
2. $C_{ij}(CN)$, $D_{ij} = 0$	P	G	A	A	P	P
3. $C_{ij}(CN)$, D_{ij} (CN)	G	G	G	A	P	A
4. $C_{ij}(CN,T)$, $D_{ij} = 0$	G	VG	A	A	A	P
5. $C_{ij}(CN, T)$, D_{ij} (CN, T)	VG	E	VG	VG	VG	G

*P = poor; %AAD > 5
A = adequate; 3 < %AAD <5
G = good; 2 < %AAD <3
VG = very good; 1 < %AAD < 2
E = excellent; %AAD < 1

However, for nitrogen + aromatics and naphthenes systems, even with two interaction parameters for each isotherm of each mixture, both equations can only represent the bubble point pressure with reasonable accuracy.

All systems can be described very well by Case 5 using the SRK and PR EOS, except the nitrogen systems. The experimental uncertainty of the OSU data is typically within 1% of the bubble point pressure. Aside from the nitrogen binaries, the EOS representations of bubble point pressure yield deviations twice the size of the experimental uncertainty for all the other systems. The predictive abilities of the SRK and PR EOS for the systems containing n-paraffins are similar to those of the systems containing aromatics and naphthenes. Moreover, the SRK and PR equations of state, in general, exhibit comparable abilities in representing the present data.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The present study deals with the experimental determination of solubility data for nitrogen in selected n-paraffins and evaluation of the SRK and PR equations of state abilities to represent asymmetric mixtures involving light gases and hydrocarbon solvents. A broad database for carbon dioxide, methane, ethane, carbon monoxide, hydrogen, and nitrogen with aromatics and naphthenes has been generated in this work. The data have been correlated using the PR and SRK equations. Bubble point pressure calculations have been performed using the GEOS computer software (27) to determine (a) the SRK and PR EOS interaction parameters for each binary along with their uncertainties, (b) Henry's constants, (c) infinite dilution partial molar volumes, and (d) statistics assessing the quality of the fit. The following conclusions and recommendations may be stated based on this work.

Conclusions

1. The solubilities of carbon monoxide in n-decane and carbon dioxide in trans-decalin at 160°F were measured. The carbon monoxide + n-decane data are in excellent agreement with the literature data; deviations are within 0.0006 in mole fraction. The carbon dioxide + trans-decalin data are in reasonable agreement with previous measurements.
2. The solubilities of nitrogen in selected n-paraffin solvents (n-decane, n-eicosane, n-octaconsane, and n-hexatriacontane) were measured at temperatures from 323.2 to 423.2 K and pressures up to 18.0 MPa (2069 psia). The uncertainty in these

solubility measurements is estimated to be less than 0.001 in mole fraction.

3. Optimum binary interaction parameters as well as Henry's constants for the newly acquired data were obtained using the SRK and PR equations of state. The equations exhibit comparable abilities in representing the data using two interaction parameters; the RMS errors in mole fraction are less than 0.001.
4. The nitrogen + n-paraffin systems are well represented by both the SRK and PR equations of state. The interaction parameter is highly dependent on the carbon number of the solvent and slightly dependent on temperature. Two interaction parameters for each system are needed to represent the bubble point of nitrogen in n-paraffins with reasonable accuracy (%AAD of 3.9 for SRK; %AAD of 3.7 for PR).
5. The abilities of the PR and SRK EOS to represent the bubble point pressure (solubility) of light gases in hydrocarbon solvents vary for different solutes. For example, while carbon monoxide mixtures are fitted excellently by both equations, nitrogen mixtures are only adequately represented.
6. When two interaction parameters are used, both the SRK and PR EOS represent the bubble point pressure of methane, ethane, carbon dioxide, and carbon monoxide binary systems with RMS errors of less than two bar. For the nitrogen binary systems, the RMS errors are as high as six bar. Both equations, in general, exhibit comparable abilities in representing the data.

Recommendations

1. Further studies are recommended on nitrogen + aromatics or naphthenes (e.g., benzene, naphthalene, phenanthrene, pyrene). Such studies will complement the existing database and provide an improved basis for comprehensive evaluation of the nitrogen phase behavior.
2. Although the interaction parameters for six supercritical gases in aromatics and naphthenes have been extensively studied, the development of generalized

correlations for estimating the EOS interaction parameters for different systems is desirable and should have wide applications.

special mention for their help in equipment repairs and setting up the database.

Most of all, to my parents, I dedicate this humble work in recognition of their encouragement and ever present love.

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APPENDIXES

APPENDIX A

Computer Program Used to Calculate the Density of Nitrogen

This program implements an equation of state developed by IUPAC (75) for high-accuracy determination of nitrogen density as a function of temperature and pressure. The equation of state may be written as:

$$p = \rho RT \left[1 + \sum_{i=1}^{32} N_i (X)_i\right] \qquad \text{(A-1)}$$

where, N_i are the coefficients of the equation, $(X)_i$ are in terms of temperature and density (75). To calculate ρ for a specified T and p, a numerical successive substitution algorithm is employed with the initial guess given by the ideal gas law.

To validate the implementation of Equation (A-1), a comparison was made between calculated densities and values reported in the literature. As shown in Table A.I, the maximum percent deviation is 0.032, which resulted from the round-off error of the listed values.

TABLE A.I

COMPARISON OF NITROGEN DENSITIES

Pressure psia	Temperature K	$\rho_{cal.} \times 10^4$ g-mole/cc	$\rho_{ref} \times 10^4$ g-mole/cc	$\lvert \rho_{cal} - \rho_{ref} \rvert / \rho_{ref}$ %
290.08	26.85	8.0402	8.0386	0.020
	76.85	6.8520	6.8540	0.029
362.59	26.85	10.0543	10.0543	0.000
	76.85	8.5570	8.5543	0.032
435.11	26.85	12.0687	12.0685	0.002
	76.85	10.2580	10.2585	0.004

```
C    ***********************************************************
C    * THIS PROGRAM IS USED TO CALCULATE NITROGEN DENSITY *
C    ***********************************************************

     IMPLICIT REAL*8 (A-H, M-Z)
     DATA N1, N2, N3 / .185927462121, 1.30155934655, -2.64054394027/,
   * N4, N5, N6 / .292709245322, -.287482987766, .161225592835/,
   * N7, N8, N9 / -.135129830972, 1.37262707287E-5 , 13.6860808703/,
   * N10,N11,N12/ .0012897330086, 0.315240491447, -.548670430729/,
   * N13,N14,N15/ .0744966916902, -.151712926147, -.728119881405/,
   * N16,N17,N18/ .112790673192, -.0187922799332, .0460360632178/,
   * N19,N20,N21/ -.00251321896106, -12.5428246147, -.722843603762/,
   * N22,N23,N24/ -9.07779852949, .333590008958, -2.10175282124/,
   * N25,N26,N27/ -.24475274962, -.611651799016, -.0244254052253/,
   * N28,N29,N30/ -.0230295508018, .0157620487302, -.0126428070667/,
   * N31,N32,ALPHA/ -.00146576723582, 9.15063203408E-5, -.70371896/

     DATA PC,TC,DENC,RR/ 34., 126.2, 0.01121, 83.1434/

     WRITE(*,*) 'ENTER PRESSURE, IN PSIA'
     READ(*,*) PP

C    CHANGE UNIT TO 'BAR'
     PP=PP*1.01325/14.696

     WRITE(*,*) 'ENTER TEMPERATURE, IN DEGREE'
     READ(*,*) TEMP

C    CHANGE UNIT TO 'K'
     TEMP=TEMP+273.15

C    CALCULATE INITIAL VALUE OF DENSITY
     DEN=PP/(RR*TEMP)

C    SUCCESSIVE SUBSTITION METHOD
10   OMEGA=DEN/DENC
     TT=TC/TEMP
     ZZ=1.+OMEGA*(N1+N2*TT**0.5+N3*TT+N4*TT**2.+N5*TT**3.)
   *    +OMEGA**2.*(N6+N7*TT+N8*TT**2.+N9*TT**3.)
   *    +OMEGA**3.*(N10+N11*TT+N12*TT**2.)+OMEGA**4.*(N13*TT)
   *    +OMEGA**5.*(N14*TT**2.+N15*TT**3.)+OMEGA**6.*(N16*TT**2.)
   *    +OMEGA**7.*(N17*TT**2.+N18*TT**3.)+OMEGA**8.*(N19*TT**3.)
   *    +(OMEGA**2.)*DEXP(ALPHA*OMEGA**2.)*((N20*TT**3.+N21*TT**4.)
   *    +(OMEGA**2.)*(N22*TT**3.+N23*TT**5.)
   *    +(OMEGA**4.)*(N24*TT**3.+N25*TT**4.)
   *    +(OMEGA**6.)*(N26*TT**3.+N27*TT**5.)
   *    +(OMEGA**8.)*(N28*TT**3.+N29*TT**4.)
   *    +(OMEGA**10.)*(N30*TT**3.+N31*TT**4.+N32*TT*5.))
     DEN1=PP/(RR*TEMP*ZZ)
     DEV=(DEN1-DEN)/DEN
     IF ( ABS(DEV) .GT. 1.E-5) THEN
     DEN=DEN1
     GOTO 10
     END IF
     WRITE(*,*)'DENSITY OF NITROGEN= ',DEN1, '  G-MOLE/CC'
     STOP
     END
```

APPENDIX B

Estimated Uncertainty in the Density of Nitrogen

The uncertainty of the nitrogen density depends on the temperature and pressure of the solute. In this work, all the nitrogen injections were done at 50 °C and near 370 psia. The uncertainty in the density of nitrogen can be given as (28):

$$\sigma_{\rho_{N_2}} = [(\partial\rho_{N_2}/\partial p)_T^{\,2}(\sigma_p)^2 + (\partial\rho_{N_2}/\partial T)_p^{\,2}(\sigma_T)^2]^{\frac{1}{2}} \tag{B-1}$$

where

$\sigma_{\rho_{N_2}}$ = is the uncertainty in nitrogen density

σ_P = is the uncertainty in pressure

σ_T = is the uncertainty in temperature

The values for σ_P and σ_T are 0.05 psia and 0.1 K, respectively, according to Barrick (23), and are unique to the apparatus used in this work. The partial derivatives of the pressure were evaluated by directly differentiating Equation (A-1), which leads to:

$$(\partial p/\partial\rho)_T = RT\,[1+\sum_{i=1}^{32} N_i(X_\rho)_i] \tag{B-2}$$

$$(\partial p/\partial T)_\rho = R\rho\,[1+\sum_{i=1}^{32} N_i(X_T)_i] \tag{B-3}$$

in which $(X_\rho)_i$ and $(X_T)_i$ are in terms of temperature and density (75). Also

$$(\partial\rho/\partial p)_T = 1/(\partial p/\partial\rho)_T \tag{B-4}$$

$$(\partial\rho/\partial T)_p = -(\partial p/\partial T)_\rho(\partial\rho/\partial p)_T = -\frac{(\partial p/\partial T)_\rho}{(\partial p/\partial\rho)_T} \qquad \text{(B-5)}$$

Substituting into Equation (B-1), the uncertainty of nitrogen density could be evaluated for selected pressures and temperatures. Typically, the value of the uncertainty is about 0.03% in nitrogen density for the present experiments.

APPENDIX C

ERROR ANALYSIS

Measurement errors are two types, systematic errors and random errors. A systematic error is one that invariably has the same magnitude and the same sign under the same conditions. Systematic errors are attributable to known conditions and vary with these conditions. Such errors can be evaluated and applied, with signs reversed, as corrections to measured quantities or eliminated by modifying the experimental procedure (41).

Although systematic errors are generally cumulative, it is sometimes possible to employ precautionary procedures to prevent their accumulation, which may impair the accuracy of the final result. In this work, the systematic errors are detected by calibrating the pressure transducers and temperature sensors periodically. Calibration of the pressure transducers was made against a dead weight test. The detailed calibration procedure is given by Darwish (28). The temperature sensors were checked by measuring the ice point of pure water and calibrated regularly against an HP-2804A quartz thermometer (accuracy of 0.04 °C) at the experimental temperature.

To verify the reliability of the apparatus and the procedure of the experiment, two kinds of reproducibility tests were conducted: vapor pressure measurement and bubble point pressure measurements of binary mixtures. The vapor pressure of n-pentane at 101.85 °C was measured. Compared with values reported in the literature (43), the measured vapor pressure of this work and the reported literature value agree to within 1 psia. The slight difference is within the experimental uncertainty of the apparatus. Two binary mixtures (carbon monoxide + n-decane and carbon dioxide + trans-decalin) were chosen as test systems for bubble point pressure measurements at 160.0 °F. The experimental data of the two systems are presented in Tables C.I and C.II. The interaction parameters, C_{ij}, of the SRK EOS were regressed from the data obtained in this work. For the binary system of carbon monoxide + n-decane, the data were compared with the earlier work of Yi (40). As shown in Figure C.1, the different data sets are in excellent agreement with a maximum deviation of less than 0.001 in mole fraction for both data set. For the carbon dioxide + trans-decalin binary, comparison of this work with those of Gasem (33) and Shaver (32) are presented in Figure C.2. While excellent agreement is observed between the present work and the data reported by Shaver at higher pressures, significant disagreement exists among the various sources at lower pressure. These comparisons provide an acceptable measure of the internal consistency of the experimental setup and the procedure used.

Random errors are less predictable than systematic errors and are usually treated by statistical methods. In this work, there were three prime errors associated with temperature, pressure and volume, which propagate during the course of an experiment. Those prime errors were determined as follows according to Darwish (28):

$$\varepsilon_T = 0.1\ ^\circ\mathrm{C} \tag{C-1}$$

$$\varepsilon_P = 0.004p\ \mathrm{psia} \tag{C-2}$$

$$\varepsilon_V = 0.0075\ \mathrm{cc} \tag{C-3}$$

Error propagation is used to estimate the overall uncertainty in solubility due to uncertainties in temperature, pressure and volume. Uncertainty is an interval around the measured value of the variable within which the true value could exist. In general, the variable (y) can be expressed as a function of a set of independent variables (x_i), i.e.,

$$y = f(\,x_1, x_2, x_3, \ldots\ldots x_i\,) \tag{C-4}$$

The expected variance of y can be stated as (42):

TABLE C.I

SOLUBILITY OF CARBON MONOXIDE (1) IN N-DECANE (2)

x_1	p/MPa	x_1	p/MPa
------------------------------ 344.3 K (71.1 °C, 160.0 °F) ------------------------------			
0.0564	3.49	0.1194	7.86
0.0608	3.79	0.1542	10.47.
0.1127	7.35	0.1679	11.61

TABLE C.II

SOLUBILITY OF CARBON DIOXIDE (1) IN TRANS-DECALIN (2)

x_1	p/MPa	x_1	p/MPa
------------------------------ 344.3 K (71.1 °C, 160.0 °F) ------------------------------			
0.0454	0.93	0.2670	5.33
0.1012	2.01	0.3194	6.47
0.1552	3.09	0.3242	6.55
0.1894	3.75	0.3684	7.48
0.2140	4.26	0.4103	8.32
0.2557	5.10	0.4297	8.72
0.2587	5.20		

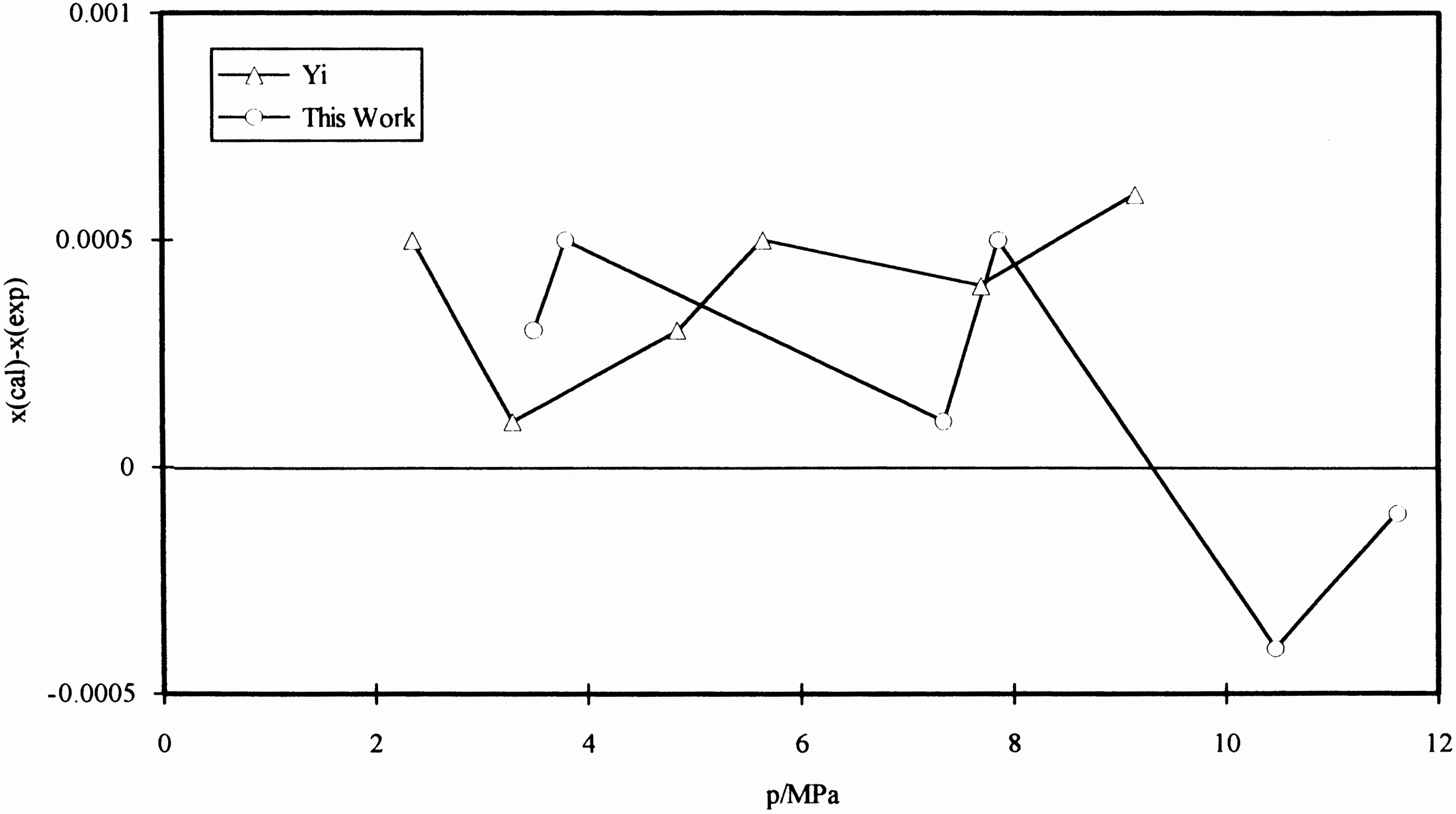

Figure C.1. Comparison for the solubility of Carbon Monoxide in n-Decane at 344.3 K

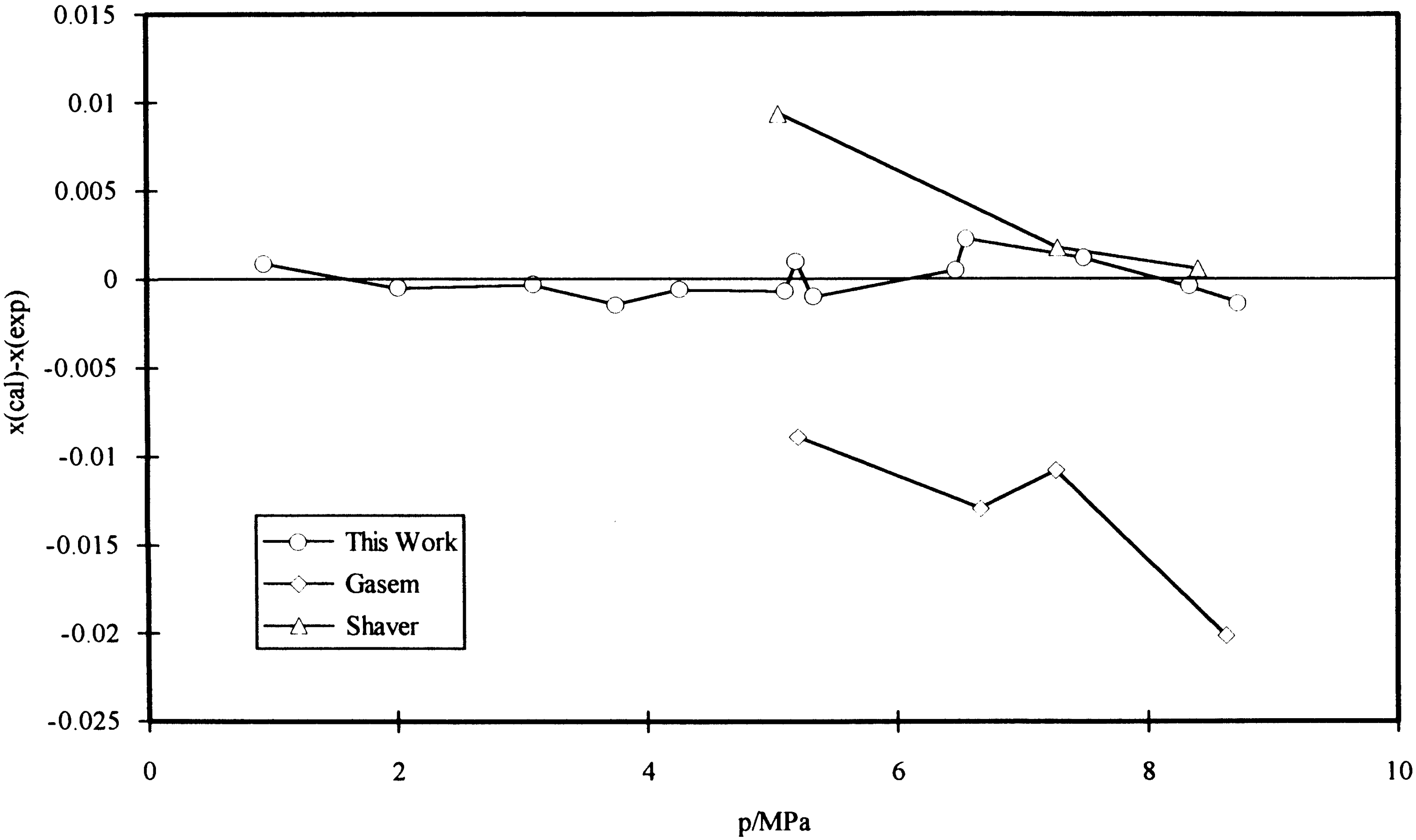

Figure C.2. Comparison for the solubility of Carbon Dioxide in trans-Decalin at 344.3 K

$$\sigma^2{}_y = \sum_{i=1}^{n}(\frac{\partial f}{\partial x})^2\sigma^2{}_{x_i} + \varepsilon^2{}_y \qquad \text{(C-5)}$$

in which, σ_{xi} is the standard derivation of x_i, ε_y is the instrumental error in y if y itself is also a measured variable. Otherwise, this term equals zero. In this investigation, uncertainty in solubility and bubble point pressure were evaluated. The uncertainty in solubility is in the form of (28):

$$\sigma_{x_1}{}^2 = x_1{}^2(1-x_1)^2[(\frac{\sigma_{\rho_1}}{\rho_1})^2 + (\frac{\sigma_{\rho_2}}{\rho_2})^2 + (\frac{\sigma_{V_2}}{V_2})^2 + \sum_{i=1}^{n}(\frac{\sigma_{V_{1i}}}{V_{1i}})^2] \qquad \text{(C-6)}$$

in which, n is the number of gas injections. All variances are specified conservatively as (28):

$(\sigma_{\rho_1}/\rho_1) = 0.0015$ (relative uncertainty in nitrogen density)
$(\sigma_{\rho_2}/\rho_2) = 0.0015$ (relative uncertainly in solvent density)
$(\sigma_{V_2}/V_2) = 0.0015$ (relative uncertainty in solvent injection volume)
$\sigma_{V_{1i}} = 0.0075$ (uncertainty in gas injection volume)

A typical run is composed of three nitrogen injections with a total about 5 cc. Substitution of these values in Equation (C-6) yields:

$$\sigma_{x_1} = 0.003x_1x_2 \qquad \text{(C-7)}$$

which results in a maximum estimated error in nitrogen liquid mole fraction measurement of 0.0006.

Bubble point pressure of a given binary mixture is a function of the temperature and composition of the mixture. The uncertainty of the bubble point pressure can be expressed as (28):

$$\sigma_P{}^2 = (\frac{\partial p}{\partial x_1})_T \sigma_{x_1}{}^2 + (\frac{\partial p}{\partial T})_{x_1}{}^2 \sigma_T{}^2 + \varepsilon_P{}^2 \qquad \text{(C-8)}$$

where, ε_P is specified in Equation (C-2).

Compared with the other terms, the temperature effect is generally negligible. By replacing ε_P with 0.004p psia in Equation (C-8), the estimated uncertainty in bubble point pressure is:

$$\sigma_P{}^2 = (0.004p)^2 + (\frac{\partial p}{\partial x_1})_T{}^2 \sigma_{x_1}{}^2 \qquad \text{(C-9)}$$

The partial derivative of pressure with respect to the solubility of nitrogen is estimated by employing a second order polynomial to fit p-x data at the specified isotherm of each system. The calculated uncertainty in bubble point pressure is about 12 psia.

APPENDIX D

NITROGEN + N-PARAFFINS

This appendix provides detailed calculation results of the representation of bubble point pressures of nitrogen + n-paraffin systems for the five cases using the Peng-Robinson equation of state. For each case, the interaction parameters along with their uncertainties, Henry's constants, infinite dilution partial molar volumes and complete statistics including the root mean squared error (RMSE), bias, absolute average deviation (AAD), and absolute average percent deviation (%AAD) are presented. For Cases 2 and 3, the values of Henry's constants and infinite dilution partial molar volumes are at the highest temperature of that data set.

TABLE D.1

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + N-PARAFFINS SYSTEM: CASE 1

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Propane 60	143.2	.1500 .0000	.0000 .0000	416*	33*	134.83	122.79	122.79	156.95	6**
60	173.2	.1500 .0000	.0000 .0000	528	38	162.13	122.70	122.70	120.66	6
60	198.2	.1500 .0000	.0000 .0000	578	43	83.20	64.78	64.78	67.33	6
60	223.2	.1500 .0000	.0000 .0000	591	50	50.92	39.51	39.51	40.90	6
60	248.2	.1500 .0000	.0000 .0000	575	60	37.52	29.98	29.98	32.87	6
60	273.2	.1500 .0000	.0000 .0000	534	77	27.29	21.28	21.28	22.29	6
60	298.2	.1500 .0000	.0000 .0000	473	108	20.03	14.69	14.69	14.33	6
60	323.2	.1500 .0000	.0000 .0000	394	179	12.42	8.27	8.27	7.43	4
60	333.2	.1500 .0000	.0000 .0000	358	239	12.44	8.74	8.91	8.90	4
60	343.2	.1500 .0000	.0000 .0000	317	350	2.98	1.76	2.18	3.09	4
61	230.0	.1500 .0000	.0000 .0000	590	52	105.35	78.83	78.83	54.73	9
61	260.0	.1500 .0000	.0000 .0000	558	67	37.53	25.72	25.72	23.66	9
61	290.0	.1500 .0000	.0000 .0000	495	95	22.33	16.40	16.40	13.84	13

TABLE D.1 (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Butane	250.0	.1500	.0000	672	52	17.67	13.34	13.34	17.06	10
48		.0000	.0000							
48	277.0	.1500	.0000	647	62	15.21	11.30	11.3	13.45	12
		.0000	.0000							
48	311.1	.1500	.0000	585	84	16.09	12.56	12.56	12.44	16
		.0000	.0000							
48	344.4	.1500	.0000	498	128	8.75	6.80	6.85	7.91	12
		.0000	.0000							
51	310.9	.1500	.0000	586	84	30.35	19.48	23.53	17.24	6
		.0000	.0000							
51	344.3	.1500	.0000	499	127	12.66	5.39	10.13	9.35	6
		.0000	.0000							
51	377.5	.1500	.0000	390	245	8.84	6.12	7.29	6.46	8
		.0000	.0000							
50	310.9	.1500	.0000	586	84	34.34	19.90	20.58	11.21	9
		.0000	.0000							
49	310.9	.1500	.0000	586	84	31.31	11.93	20.36	15.19	5
		.0000	.0000							
49	366.5	.1500	.0000	429	189	13.03	9.96	9.96	8.30	4
		.0000	.0000							
n-Pentane	277.4	.1500	.0000	692	56	22.97	18.62	18.77	15.04	7
52		.0000	.0000							
52	310.7	.1500	.0000	652	70	16.82	10.66	10.66	10.22	14
		.0000	.0000							
52	344.3	.1500	.0000	586	94	14.16	8.07	8.09	7.06	11
		.0000	.0000							
52	377.6	.1500	.0000	502	138	20.04	13.8	13.80	15.44	10
		.0000	.0000							
n-Hexane	310.9	.1500	.0000	677	64	13.47	-1.24	11.34	7.34	11

TABLE D.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
53		.0000	.0000							
53	344.2	.1500	.0000	628	81	13.77	-8.30	9.68	4.04	11
		.0000	.0000							
53	377.6	.1500	.0000	560	109	17.65	4.19	11.90	7.07	11
		.0000	.0000							
53	410.9	.1500	.0000	479	160	8.98	-2.18	7.29	7.28	8
		.0000	.0000							
53	444.3	.1500	.0000	385	277	8.89	-4.89	8.49	8.06	6
		.0000	.0000							
n-Heptane	305.4	.1500	.0000	699	59	25.01	1.76	14.62	5.30	15
55		.0000	.0000							
55	352.6	.1500	.0000	643	78	42.78	12.98	26.90	7.03	6
		.0000	.0000							
55	399.8	.1500	.0000	554	115	72.67	36.95	37.09	9.22	5
		.0000	.0000							
55	455.4	.1500	.0000	420	224	9.88	-3.32	7.61	4.93	5
		.0000	.0000							
13	305.4	.1500	.0000	699	59	10.49	-3.73	9.75	5.36	6
		.0000	.0000							
13	352.6	.1500	.0000	643	78	9.68	-6.69	8.58	5.82	5
		.0000	.0000							
7	305.5	.1500	.0000	699	59	39.59	16.80	26.45	5.80	43
		.0000	.0000							
14	324.3	.1500	.0000	682	65	18.27	-16.70	16.70	11.28	6
		.0000	.0000							
14	366.5	.1500	.0000	620	87	9.97	6.96	7.60	3.37	5
		.0000	.0000							
6	453.2	.1500	.0000	426	216	14.72	3.82	9.34	9.62	14
		.0000	.0000							

TABLE D.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
6	472.2	.1500 .0000	.0000 .0000	374	299	5.46	.53	4.27	6.62	11
6	497.2	.1500 .0000	.0000 .0000	300	545	5.12	-4.46	4.78	8.02	13
62	453.2	.1500 .0000	.0000 .0000	426	216	7.18	-5.87	6.14	4.75	6
62	472.2	.1500 .0000	.0000 .0000	374	299	16.81	9.20	13.54	9.74	5
62	497.2	.1500 .0000	.0000 .0000	300	545	9.97	5.12	8.06	7.75	5
63	453.2	.1500 .0000	.0000 .0000	426	216	13.50	5.83	7.89	5.64	10
n-Octane 13	322.0	.1500 .0000	.0000 .0000	684	62	15.76	-13.40	14.00	8.70	5
13	344.3	.1500 .0000	.0000 .0000	662	70	9.79	-8.97	8.97	8.13	7
n-Nonane 13	322.0	.1500 .0000	.0000 .0000	683	60	23.47	-20.16	20.16	11.26	6
13	344.3	.1500 .0000	.0000 .0000	665	68	13.54	-11.65	11.65	6.58	6
n-Decane 12	310.9	.1500 .0000	.0000 .0000	669	57	25.27	18.79	18.87	8.71	22
12	344.3	.1500 .0000	.0000 .0000	652	67	23.18	17.72	18.17	8.50	30
12	377.6	.1500 .0000	.0000 .0000	619	80	5.63	3.38	4.52	3.77	29
12	410.9	.1500 .0000	.0000 .0000	573	98	7.58	-5.44	5.89	4.01	20
13	344.3	.1500	.0000	652	67	33.45	28.73	28.73	16.32	6

TABLE D.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0000	.0000							
This work	344.3	.1500	.0000	652	67	10.79	-9.98	9.98	11.36	8
		.0000	.0000							
This work	377.6	.1500	.0000	619	80	8.89	-8.23	8.23	8.22	7
		.0000	.0000							
This work	410.9	.1500	.0000	573	98	5.52	-5.20	5.20	6.19	6
		.0000	.0000							
n-Dodecane	327.6	.1500	.0000	648	60	19.00	-17.76	17.76	10.24	6
13		.0000	.0000							
13	344.3	.1500	.0000	641	64	11.37	8.96	8.96	5.41	6
		.0000	.0000							
13	366.5	.1500	.0000	625	72	14.55	-6.44	12.05	11.52	4
		.0000	.0000							
n-Hexadecane	462.7	.1500	.0000	499	115	5.61	-4.39	4.39	3.12	8
1		.0000	.0000							
1	543.5	.1500	.0000	389	202	2.7	-2.35	2.35	2.27	7
		.0000	.0000							
1	623.7	.1500	.0000	264	480	6.48	-5.76	5.76	6.26	7
		.0000	.0000							
n-Eicosane	323.2	.1500	.0000	498	62	34.12	-30.03	30.03	29.77	8
This work		.0000	.0000							
This work	373.2	.1500	.0000	494	76	20.09	-18.14	18.14	19.83	6
		.0000	.0000							
This work	423.2	.1500	.0000	468	96	12.64	-11.46	11.46	13.06	6
		.0000	.0000							
n-Octacosane	348.2	.1500	.0000	368	79	41.91	-38.34	38.34	36.59	7
This work		.0000	.0000							
This work	373.2	.1500	.0000	366	88	36.84	-33.50	33.5	32.29	6
		.0000	.0000							

TABLE D.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
This work	423.2	.1500	.0000	352	111	28.64	-25.94	25.94	25.39	6
		.0000	.0000							
n-Hexatriacontane	373.2	.1500	.0000	272	108	56.31	-51.32	51.32	43.43	6
This work		.0000	.0000							
This work	423.2	.1500	.0000	263	136	44.90	-40.98	40.98	37.05	6
		.0000	.0000							
OVERALL STATISTICS						31.54	6.45	17.23	12.99	657

* Estimated value.

** The data are not converged.

TABLE D.II

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + N-PARAFFINS SYSTEM: CASE 2

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Propane	(143.2-	.0909	.0000			12.04	3.58	8.31	8.85	30
60	248.2)	.0018	.0000	479	59					
60	(273.2-	.0557	.0000			4.66	-1.33	3.94	5.55	24
	343.2)	.0063	.0000	281	334					
61	(230.0-	.0564	.0000			5.59	-2.97	4.92	6.85	31
	290.0)	.0025	.0000	404	92					
n-Butane	(250.0-	.0955	.0000			2.42	-.27	1.70	3.05	49
48	344.4)	.0015	.0000	458	126					
51	(310.9-	.0944	.0000			9.04	-2.25	6.57	6.54	20
	377.6)	.0080	.0000	365	240					
49	(310.9-	.0894	.0000			13.55	-5.12	11.05	11.60	8
	366.5)	.0174	.0000	396	185					
50	(310.9)	.0672	0000			10.42	-4.53	8.11	9.60	9
		.0107	.0000	495	82					
n-Pentane	(277.5-	.0924	.0000			5.31	.11	3.20	5.04	42
52	377.6)	.0031	.0000	466	136					
n-Hexane	(310.9-	.1463	.0000			13.43	-3.55	10.05	6.70	47
53	444.3)	.0041	.0000	384	277					
n-Heptane	(305.4-	.1351	.0000			19.18	-7.88	14.16	6.36	30
55	455.4)	.0031	.0000	414	223					
7	(305.5)	.1362	.0000			20.54	-10.09	18.93	6.15	43
		.0014	.0000	678	59					
13	(305.4-	.1565	.0000			12.05	-1.76	10.20	6.33	22
	366.5)	.0038	.0000	626	87					
6	(453.2-	.0921	.0000			6.80	-4.29	5.77	9.51	38
	497.2)	.0098	.0000	290	538					

TABLE D.II (Continued)

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
62	(453.2-	.1187	.0000			10.80	-1.65	9.02	7.37	16
	497.2)	.0193	.0000	294	541					
63	(453.2)	.0750	.0000			5.43	-2.90	4.98	6.69	10
		.0122	.0000	399	213					
n-Octane	(322.0-	.1723	.0000			6.43	-2.49	5.30	4.87	12
13	344.3)	.0038	.0000	688	71					
n-Nonane	(322.0-	.1814	.0000			5.39	-1.02	4.44	2.76	12
13	344.3)	.0026	.0000	702	68					
n-Decane	(310.9-	.1112	.0000			4.16	-1.20	3.54	3.74	49
12	344.3)	.0012	.0000	610	66					
12	(377.6-	.1507	.0000			6.49	.01	5.11	3.89	49
	410.9)	.0024	.0000	573	98					
13	(344.3)	.0962	.0000			3.03	1.54	2.87	2.94	6
		.0025	.0000	595	66					
This work	(344.3-	.2026	.0000			1.19	-.10	.96	1.06	21
	410.9)	.0015	.0000	609	99					
n-Dodecane	(327.6-	.1600	.0000			14.37	-.41	12.71	8.82	16
13	366.5)	.0066	.0000	635	72					
n-Hexadecane	(462.7-	.1815	.0000			2.68	-.83	1.69	1.95	22
1	623.7)	.0040	.0000	267	482					
n-Eicosane	(323.2-	.3095	.0000			3.36	.86	2.89	3.17	20
This work	423.2)	.0041	.0000	548	97					
n-Octacosane	(348.2-	.4298	.0000			1.23	.00	.93	.85	19
This work	423.2)	.0017	.0000	450	113					
n-Hexatriacontane	(373.2-	.5917	.0000			2.52	-1.08	2.30	2.42	12
This work	423.2)	.0045	.0000	367	138					
OVERALL STATISTICS						9.85	-2.07	6.51	5.38	657

TABLE D.III

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + N-PARAFFINS SYSTEM: CASE 3

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Propane	(143.2-	-.0064	.0639			6.25	2.95	4.32	6.49	30
60	248.2)	.0094	.0061	531	67					
60	(273.2-	-.0283	.0750			3.74	-.76	2.74	3.30	24
	343.2)	.0197	.0168	296	363					
61	(230.0-	.0074	.0499			2.77	-.74	2.33	3.53	31
	290.0)	.0051	.0049	448	101					
n-Butane	(250.0-	.0566	.0227			1.58	.11	1.10	1.86	49
48	344.4)	.0031	.0013	468	130					
51	(310.9-	-.0112	.0882			6.60	-.11	5.06	6.97	20
	377.6)	.0274	.0213	404	270					
49	(310.9-	-.0966	.1519			3.74	1.43	2.88	4.22	8
	366.5)	.0233	.0168	482	227					
50	(310.9)	-.0390	.0956			2.66	.28	2.38	4.23	9
		.0109	.0088	641	99					
n-Pentane	(277.5-	.0177	.0410			3.75	1.00	2.36	4.09	42
52	377.6)	.0124	.0066	491	146					
n-Hexane	(310.9-	.0586	.0490			9.51	-1.20	7.08	6.27	47
53	444.3)	.0136	.0072	405	296					
n-Heptane	(305.4-	.0794	.0329			10.39	-.15	7.32	3.87	30
55	455.4)	.0068	.0038	437	236					
13	(305.4-	.0827	.0324			9.78	.47	8.15	5.84	22
	366.5)	.0229	.0099	678	94					
7	(305.5)	.0763	.0356			4.22	.78	3.59	1.52	43
		.0019	.0011	814	66					
6	(453.2-	-.0606	.1090			3.01	-.87	2.47	4.55	38
	497.2)	.0136	.0086	329	612					

TABLE D.III (Continued)

SYSTEM	T(K)	C_{12}	D_{12}	$H_{1,2}$	$\tilde{V}_1^\infty$	RMSE	BIAS	AAD	%AAD	NP
REFERENCE	Range	σ_C	σ_D	(bar)	(cc/mol)	(bar)	(bar)	(bar)		
62	(453.2-	-.0868	.1323			6.66	1.37	4.62	3.90	16
	497.2)	.0489	.0279	339	629					
63	(453.2)	-.0269	.0720			1.64	-.12	1.13	1.22	10
		.0101	.0064	457	241					
n-Octane	(322.0-	.0915	.0295			2.86	.40	1.94	2.97	12
13	344.3)	.0127	.0046	752	77					
n-Nonane	(322.0-	.1803	.0003			5.36	-1.13	4.45	2.76	12
13	344.3)	.0043	.0017	703	68					
n-Decane	(310.9-	.0842	.0000			3.83	-.44	3.02	2.86	49
12	344.3)	.0088	.0000	630	68					
12	(377.6-	.1868	-.0117			6.19	-.84	4.82	3.77	49
	410.9)	.0163	.0053	555	95					
13	(344.3)	.1334	-.0128			1.05	.12	.95	1.04	6
		.0077	.0026	562	63					
This work	(344.3-	.1207	.0190			.71	.20	.61	.74	21
	410.9)	.0141	.0032	625	105					
n-Dodecane	(327.6-	.1021	.0146			13.95	1.30	12.08	9.14	16
13	366.5)	.0595	.0148	671	76					
n-Hexadecane	(462.7-	.1792	.0006			2.68	-.79	1.69	1.96	22
1	623.7)	.0077	.0016	268	482					
n-Eicosane	(323.2-	.2768	.0037			3.35	1.00	2.86	3.14	20
This work	423.2)	.0453	.0053	554	100					
n-Octacosane	(348.2-	.3568	.0058			.97	.26	.79	.86	19
This work	423.2)	.0226	.0018	459	118					
n-Hexatriacontane	(373.2-	.4549	.0082			2.10	-.56	1.72	1.47	12
This work	423.2)	.0618	.0037	382	150					
OVERALL STATISTICS						5.73	.05	3.70	3.67	657

TABLE D.IV

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + N-PARAFFINS SYSTEM: CASE 4

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Propane	143.2	.0953	.0000	272*	33*	4.30	-.77	3.48	4.71	6
60		.0007	.0000							
60	173.2	.0842	.0000	358	37	5.77	-1.76	5.16	8.36	6
		.0025	.0000							
60	198.2	.0728	.0000	401	42	5.48	-1.48	4.79	7.62	6
		.0040	.0000							
60	223.2	.0678	.0000	432	49	6.13	-1.82	5.33	8.90	6
		.0065	.0000							
60	248.2	.0593	.0000	434	59	5.26	-1.10	4.42	6.28	6
		.0077	.0000							
60	273.2	.0562	.0000	422	75	5.27	-1.13	4.44	6.39	6
		.0103	.0000							
60	298.2	.0538	.0000	389	104	5.44	-1.20	4.49	5.97	6
		.0146	.0000							
60	323.2	.0629	.0000	343	172	4.36	-1.71	4.28	5.68	4
		.0219	.0000							
60	333.2	.0367	.0000	304	227	3.95	-1.48	3.87	5.41	4
		.0241	.0000							
60	343.2	.0988	.0000	297	341	1.44	-.57	1.41	2.45	4
		.0172	.0000							
61	230.0	.0530	.0000	416	51	5.25	-2.35	4.78	6.58	9
		.0030	.0000							
61	260.0	.0631	.0000	438	65	5.26	-2.19	4.32	6.19	9
		.0009	.0000							
61	290.0	.0676	.0000	414	93	4.90	-1.95	4.43	5.93	13
		.0065	.0000							

TABLE D.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Butane	250.0	.1016	.0000	576	51	1.49	-.59	1.27	2.66	10
48		.0016	.0000							
48	277.0	.1005	.0000	569	62	1.52	-.54	1.35	3.67	12
		.0017	.0000							
48	311.1	.0842	.0000	512	83	2.04	-.64	1.66	2.70	16
		.0025	.0000							
48	344.4	.0858	.0000	451	125	.91	-.41	.86	1.86	12
		.0022	.0000							
51	310.9	.0920	.0000	521	83	13.21	-2.66	10.14	8.66	6
		.0147	.0000							
51	344.3	.1050	.0000	465	126	8.35	-2.76	7.37	7.78	6
		.0192	.0000							
51	377.5	0943	.0000	365	240	4.16	-.82	3.34	3.98	8
		.0121	.0000							
50	310.9	.0672	.0000	495	82	10.42	-4.53	8.11	9.60	9
		.0107	.0000							
49	310.9	.0899	.0000	519	83	17.05	-8.45	16.58	17.14	5
		.0228	.0000							
49	366.5	.0733	.0000	388	184	1.46	-.44	1.24	1.95	4
		.0057	.0000							
n-Pentane	277.4	.1050	.0000	614	56	4.39	.04	3.53	4.34	7
52		.0041	.0000							
52	310.7	.0943	.0000	580	69	1.92	-.91	1.61	3.93	14
		.0020	.0000							
52	344.3	.0863	.0000	527	92	2.85	-1.14	2.25	3.99	11
		.0046	.0000							
52	377.6	.0481	.0000	439	135	2.50	.35	1.97	4.37	10
		.0051	.0000							
n-Hexane	310.9	.1466	.0000	672	64	13.26	-3.07	11.26	7.21	11

TABLE D.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
53		.0061	.0000							
53	344.2	.1666	.0000	646	81	10.61	-1.32	7.52	3.72	11
		.0062	.0000							
53	377.6	.1222	.0000	539	108	12.07	-5.66	11.06	8.46	11
		.0088	.0000							
53	410.9	.1391	.0000	473	159	8.64	-4.04	7.40	7.79	8
		.0149	.0000							
53	444.3	.1614	.0000	389	278	8.73	-3.50	8.09	7.56	6
		.0260	.0000							
n-Heptane	305.4	.1386	.0000	681	59	17.47	-10.11	14.66	6.73	15
55		.0032	.0000							
55	352.6	.1201	.0000	613	78	24.74	-12.27	20.97	8.49	6
		.0106	.0000							
55	399.8	.0572	.0000	495	113	21.29	-11.86	20.00	10.13	5
		.0186	.0000							
55	455.4	.1565	.0000	422	224	9.68	-1.55	8.21	5.18	5
		.0159	.0000							
13	305.4	.1569	.0000	710	59	8.70	1.41	8.07	5.27	6
		.0045	.0000							
13	352.6	.1560	.0000	650	79	9.03	-3.76	8.00	5.21	5
		.0077	.0000							
7	305.5	.1362	.0000	678	59	20.54	-10.09	18.93	6.15	43
		.0014	.0000							
14	324.3	.1691	.0000	708	66	12.50	-5.56	11.85	8.31	6
		.0077	.0000							
14	366.5	.1324	.0000	604	86	3.04	-1.03	2.43	1.49	5
		.0029	.0000							
6	453.2	.0760	.0000	399	213	7.49	-4.24	6.02	10.56	14
		.0135	.0000							

TABLE D.IV (Continued)

SYSTEM	T(K)	C_{12}	D_{12}	$H_{1,2}$	$\tilde{V}_1^{\infty}$	RMSE	BIAS	AAD	%AAD	NP
REFERENCE		σ_C	σ_D	(bar)	(cc/mol)	(bar)	(bar)	(bar)		
6	472.2	.1145	.0000	364	297	3.99	-2.11	3.40	6.78	11
		.0123	.0000							
6	497.2	.2107	.0000	312	551	4.08	-2.05	3.59	6.00	13
		.0225	.0000							
62	453.2	.1779	.0000	436	217	5.13	-1.57	4.79	3.75	6
		.0124	.0000							
62	472.2	.0607	.0000	350	294	8.82	-3.17	7.83	7.79	5
		.0306	.0000							
62	497.2	.0513	.0000	283	533	4.82	-2.36	4.22	5.69	5
		.0293	.0000							
63	453.2	.0750	.0000	399	213	5.43	-2.90	4.98	6.69	10
		.0122	.0000							
n-Octane	322.0	.1807	.0000	727	62	4.45	-.84	4.12	4.44	5
13		.0042	.0000							
13	344.3	.1663	.0000	681	71	5.81	-3.28	5.21	5.33	7
		.0047	.0000							
n-Nonane	322.0	.1876	.0000	736	61	2.53	-1.18	2.00	2.09	6
13		.0017	.0000							
13	344.3	.1737	.0000	693	68	3.71	-1.15	2.78	1.87	6
		.0029	.0000							
n-Decane	310.9	.1114	.0000	617	56	3.50	-1.39	3.13	3.67	22
12		.0013	.0000							
12	344.3	.1105	.0000	610	66	5.23	-1.04	4.33	3.68	30
		.0019	.0000							
12	377.6	.1425	.0000	612	80	4.74	.83	3.91	3.32	29
		.0022	.0000							
12	410.9	.1675	.0000	584	99	4.50	-.42	3.37	2.65	20
		.0029	.0000							
13	344.3	.0962	.0000	595	66	3.03	1.54	2.87	2.94	6

TABLE D.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0025	.0000							
This work	344.3	.2087	.0000	721	67	.46	-.17	.45	.62	8
		.0009	.0000							
This work	377.6	.1990	.0000	663	80	.59	-.20	.51	.64	7
		.0013	.0000							
This work	410.9	.1936	.0000	602	99	.59	-.22	.53	.78	6
		.0020	.0000							
n-Dodecane	327.6	.1783	.0000	683	60	5.87	-2.37	5.36	4.17	6
13		.0039	.0000							
13	344.3	.1355	.0000	625	64	7.59	1.82	4.97	3.15	6
		.0060	.0000							
13	366.5	.1915	.0000	665	72	8.26	3.97	7.24	11.97	4
		.0156	.0000							
n-Hexadecane	462.7	.1817	.0000	513	115	.56	.08	.45	.49	8
1		.0012	.0000							
1	543.5	.1693	.0000	393	202	.95	-.44	.80	1.00	7
		.0029	.0000							
1	623.7	.1998	.0000	269	482	3.84	-2.02	3.25	4.23	7
		.0145	.0000							
n-Eicosane	323.2	.3210	.0000	669	62	.19	-.04	.17	.22	8
This work		.0003	.0000							
This work	373.2	.2955	.0000	597	77	.35	.01	.28	.38	6
		.0010	.0000							
This work	423.2	.2705	.0000	528	97	.28	.03	.26	.35	6
		.0011	.0000							
n-Octacosane	348.2	.4342	.0000	533	80	.57	-.15	.49	.49	7
This work		.0012	.0000							
This work	373.2	.4303	.0000	504	89	.64	-.07	.55	.51	6
		.0017	.0000							

TABLE D.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
This work	423.2	.4174 .0020	.0000 .0000	445	113	.59	-.21	.52	.64	6
n-Hexatriacontane This work	373.2	.5850 .0048	.0000 .0000	417	109	2.09	-.89	2.04	2.20	6
This work	423.2	.6060 .0056	.0000 .0000	371	138	1.72	-.72	1.68	1.93	6
OVERALL STATISTICS						8.62	-2.30	5.56	4.78	663

TABLE D.V

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + N-PARAFFINS SYSTEM: CASE 5

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Propane	143.2	.0877	.0048	278*	34*	4.23	-.66	3.31	4.15	6
60		.0196	.0123							
60	173.2	.0314	.0371	420	41	4.78	-.16	3.32	3.16	6
		.0436	.0300							
60	198.2	.0177	.0405	466	46	4.58	-.08	3.16	2.99	6
		.0459	.0333							
60	223.2	-.0096	.0585	514	55	4.73	-.21	3.39	3.35	6
		.0485	.0343							
60	248.2	-.0083	.0532	494	65	4.57	-.01	3.18	3.32	6
		.0471	.0378							
60	273.2	-.0212	.0647	480	84	4.57	-.06	3.14	2.88	6
		.0697	.0570							
60	298.2	-.0378	.0849	449	120	4.57	-.07	3.17	3.03	6
		.0697	.0614							
60	323.2	-.0521	.1246	408	205	.52	.10	.48	.70	4
		.0112	.0112							
60	333.2	-.0818	.1434	366	275	.46	.06	.41	.50	4
		.0184	.0151							
60	343.2	-.0718	.1423	323	395	.38	-.03	.33	.63	4
		.0346	.0271							
61	230.0	.0196	.0350	480	55	1.75	.02	1.59	2.69	9
		.0049	.0049							
61	260.0	-.0044	.0644	522	74	.95	.28	.72	2.42	9
		.0047	.0042							
61	290.0	-.0242	.0882	491	108	.32	.05	.24	.41	13
		.0019	.0017							

TABLE D.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
n-Butane	250.0	.0388	.0333	619	56	.29	.04	.25	1.04	10
48		.0042	.0022							
48	277.0	.0425	.0330	607	66	.66	.05	.46	2.12	12
		.0079	.0045							
48	311.1	.0269	.0362	545	89	1.30	.02	.69	.90	16
		.0132	.0083							
48	344.4	.0287	.0363	471	133	.20	-.05	.15	.52	12
		.0045	.0028							
51	310.9	-.0081	.0843	645	98	9.87	1.25	7.25	11.43	6
		.0695	.0516							
51	344.3	-.0816	.1383	575	155	4.29	.27	3.66	5.83	6
		.0638	.0445							
51	377.5	.0235	.0693	401	264	3.47	.14	2.73	3.19	8
		.0436	.0391							
50	310.9	-.0390	.0956	641	99	2.66	.28	2.38	4.23	9
		.0109	.0088							
49	310.9	-.1073	.1590	763	110	1.05	-.06	.95	1.43	5
		.0075	.0053							
49	366.5	.0680	.0059	392	186	1.42	-.28	1.27	1.81	4
		.0226	.0191							
n-Pentane	277.4	.1580	-.0265	572	52	3.91	-.85	2.89	4.96	7
52		.0514	.0254							
52	310.7	.0462	.0258	616	74	.90	-.13	.72	1.88	14
		.0072	.0038							
52	344.3	.0184	.0411	575	101	1.13	.13	.81	1.43	11
		.0112	.0065							
52	377.6	.0301	.0144	452	138	2.38	.71	1.91	4.98	10
		.0218	.0169							
n-Hexane	310.9	.0447	.0515	793	74	8.96	1.95	7.83	9.73	11

TABLE D.V (Continued)

SYSTEM	T(K)	C_{12}	D_{12}	$H_{1,2}$	$\tilde{V}_1^\infty$	RMSE	BIAS	AAD	%AAD	NP
REFERENCE		σ_C	σ_D	(bar)	(cc/mol)	(bar)	(bar)	(bar)		
53		.0294	.0145							
53	344.2	.1013	.0355	711	89	8.97	1.45	7.14	6.06	11
		.0367	.0194							
53	377.6	.0212	.0731	657	126	2.69	.24	2.17	1.79	11
		.0080	.0053							
53	410.9	-.0227	.1059	576	191	.63	.19	.57	1.17	8
		.0044	.0028							
53	444.3	-.0488	.1489	479	339	3.16	.46	2.72	2.61	6
		.0469	.0299							
n-Heptane	305.4	.0884	.0283	783	64	7.18	.75	6.21	3.54	15
55		.0061	.0033							
55	352.6	.0479	.0522	763	90	9.99	1.59	7.89	4.91	6
		.0158	.0104							
55	399.8	.0054	.0619	620	131	4.23	.98	3.60	2.60	5
		.0074	.0070							
55	455.4	.1265	.0241	442	234	9.54	-.92	8.38	4.92	5
		.0999	.0770							
13	305.4	.1892	-.0135	676	56	8.39	.31	7.01	4.27	6
		.0564	.0234							
13	352.6	.0650	.0429	739	88	4.56	.00	3.87	2.72	5
		.0307	.0141							
7	305.5	.0763	.0356	814	66	4.22	.78	3.59	1.52	43
		.0019	.0011							
14	324.3	.0188	.0637	867	79	4.36	-.04	4.18	3.27	6
		.0230	.0098							
14	366.5	.1027	.0154	632	90	1.67	.20	1.32	1.40	5
		.0108	.0055							
6	453.2	-.0497	.0973	485	251	2.20	-.37	1.88	4.31	14
		.0120	.0079							

TABLE D.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
6	472.2	-.0217 .0264	.0864 .0150	412	337	1.80	-.31	1.41	3.40	11
6	497.2	-.0802 .0410	.1514 .0197	354	646	1.76	-.16	1.28	2.21	13
62	453.2	-.0785 .0340	.0574 .0188	478	239	2.82	.49	2.09	2.47	6
62	472.2	-.1536 .0815	.1567 .0523	449	368	4.66	.16	3.68	2.60	5
62	497.2	-.1206 .0285	.1332 .0205	333	626	1.38	-.30	1.24	1.62	5
63	453.2	-.0269 .0101	.0720 .0064	458	241	1.64	-.12	1.13	1.22	10
n-Octane 13	322.0	.1196 .0408	.0205 .0135	774	67	3.36	.64	2.40	4.03	5
13	344.3	.0882 .0122	.0303 .0047	753	78	1.98	-.11	1.36	2.05	7
n-Nonane 13	322.0	.1539 .0125	.0106 .0039	764	63	1.60	-.19	1.31	1.18	6
13	344.3	.1309 .0205	.0143 .0068	729	72	2.55	.21	1.81	1.41	6
n-Decane 12	310.9	.0851 .0106	.0080 .0032	641	59	3.02	-.56	2.53	2.56	22
12	344.3	.0908 .0138	.0064 .0044	626	68	5.05	-.40	3.93	3.15	30
12	377.6	.1855 .0148	-.0137 .0047	585	76	4.14	-.26	3.42	2.93	29
12	410.9	.1385 .0192	.0099 .0065	602	102	4.24	.32	3.23	2.81	20
13	344.3	.1334-	.0128	562	63	1.05	.12	.95	1.04	6

TABLE D.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0077	.0026							
This work	344.3	.1621	.0105	736	70	.07	.01	.06	.09	8
		.0027	.0006							
This work	377.6	.1503	.0117	678	83	.24	.02	.18	.19	7
		.0105	.0025							
This work	410.9	.1268	.0160	617	104	.15	.01	.12	.14	6
		.0082	.0020							
n-Dodecane	327.6	.0977	.0196	749	66	3.46	-.21	3.02	2.16	6
13		.0280	.0068							
13	344.3	.2242	-.0235	559	57	5.46	-.58	4.18	3.78	6
		.0476	.0125							
13	366.5	.5633	-.0816	519	46	2.65	.52	2.43	3.53	4
		.1018	.0223							
n-Hexadecane	462.7	.1948	-.0025	509	114	.58	-.05	.42	.42	8
1		.0077	.0015							
1	543.5	.1318	.0092	402	208	.37	.02	.29	.41	7
		.0070	.0017							
1	623.7	.0827	.0466	295	524	.60	.09	.55	.76	7
		.0086	.0031							
n-Eicosane	323.2	.3053	.0018	673	63	.25	.05	.17	.16	8
This work		.0009	.0001							
This work	373.2	.2875	.0009	599	78	.34	.04	.27	.41	6
		.0084	.0008							
This work	423.2	.2634	.0008	529	98	.29	.05	.26	.38	6
		.0060	.0006							
n-Octacosane	348.2	.3928	.0032	541	83	.38	.02	.33	.36	7
This work		.0112	.0009							
This work	373.2	.3913	.0031	511	92	.58	.07	.50	.56	6
		.0178	.0014							

TABLE D.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
This work	423.2	.3538 .0147	.0052 .0012	455	117	.27	.02	.24	.25	6
n-Hexatriacontane This work	373.2	.3955 .0164	.0113 .0010	447	125	.38	.05	.33	.40	6
This work	423.2	.4193 .0161	.0114 .0010	394	155	.30	.03	.28	.32	6
OVERALL STATISTICS						3.86	.12	2.40	2.47	663

APPENDIX E

DATABASE FOR SIX SUPERCRITICAL GASES IN AROMATIC OR NAPHTHENIC SOLVENTS

This appendix describes the solubility database for six supercritical gases (carbon dioxide, carbon monoxide, nitrogen, hydrogen, methane and ethane) in aromatic and naphthenic solvents. Tables E.I - E.VI present for each binary the range of temperature, pressure and solute liquid mole fraction and the literature sources. The references for the database are given at the end of this appendix.

TABLE E.I

NITROGEN BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	N_2 Mole Fraction Range	Reference
Cyclopentane	366.4 - 410.2	13.6 - 312.8	0.021 - 0.374	2
Cyclohexane	366.5 - 410.9	17.5 - 275.9	0.009 - 0.291	29
Methylclohexane	453.2 - 497.2	52.0 - 371.0	0.064 - 0.629	78
	310.9 - 477.6	4.4 - 168.7	0.005 - 0.268	76
Ethylcyclohexane	310.9 - 477.6	4.3 - 203.9	0.005 - 0.328	67
Propylcyclohexane	313.6 - 472.9	16.4 - 997.0	0.020 - 0.459	45
Benzene	303.2 - 398.2	62.1 - 307.1	0.035 - 0.204	72
	303.2 - 373.2	67.4 - 356.5	0.031 - 0.201	71
n-Propylbenzene	313.2 - 473.2	10.0 - 396.7	0.015 - 0.360	18
Toluene	323.2 - 348.2	36.4 - 353.5	0.018 - 0.159	71
	313.2 - 472.6	22.0 - 1000.0	0.018 - 0.390	45
m-Xylene	313.2 - 472.6	11.5 - 1001.0	0.019 - 0.351	45
Mesitylene	313.2 - 472.6	11.0 - 998.0	0.018 - 0.340	45
1-Methylnaphthalene	462.2 - 703.3	20.3 - 25.54	0.012 - 0.288	75
m-Cresol	462.2 - 663.6	30.9 - 254.2	0.009 - 0.350	77
Tetralin	463.6 - 662.8	20.7 - 255.6	0.015 - 0.573	77
Quinoline	462.1 - 703.7	20.4 - 253.7	0.009 - 0.252	74

TABLE E.I

NITROGEN BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	N_2 Mole Fraction Range	Reference
Cyclopentane	366.4 - 410.2	13.6 - 312.8	0.021 - 0.374	2
Cyclohexane	366.5 - 410.9	17.5 - 275.9	0.009 - 0.291	29
Methylclohexane	453.2 - 497.2	52.0 - 371.0	0.064 - 0.629	78
	310.9 - 477.6	4.4 - 168.7	0.005 - 0.268	76
Ethylcyclohexane	310.9 - 477.6	4.3 - 203.9	0.005 - 0.328	67
Propylcyclohexane	313.6 - 472.9	16.4 - 997.0	0.020 - 0.459	45
Benzene	303.2 - 398.2	62.1 - 307.1	0.035 - 0.204	72
	303.2 - 373.2	67.4 - 356.5	0.031 - 0.201	71
n-Propylbenzene	313.2 - 473.2	10.0 - 396.7	0.015 - 0.360	18
Toluene	323.2 - 348.2	36.4 - 353.5	0.018 - 0.159	71
	313.2 - 472.6	22.0 - 1000.0	0.018 - 0.390	45
m-Xylene	313.2 - 472.6	11.5 - 1001.0	0.019 - 0.351	45
Mesitylene	313.2 - 472.6	11.0 - 998.0	0.018 - 0.340	45
1-Methylnaphthalene	462.2 - 703.3	20.3 - 25.54	0.012 - 0.288	75
m-Cresol	462.2 - 663.6	30.9 - 254.2	0.009 - 0.350	77
Tetralin	463.6 - 662.8	20.7 - 255.6	0.015 - 0.573	77
Quinoline	462.1 - 703.7	20.4 - 253.7	0.009 - 0.252	74

TABLE E.II

CARBON DIOXIDE BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	CO_2 Mole Fraction Range	Reference
Cyclopentane	310.8 - 333.2	1.8 - 82.6	0.007 - 0.857	1
	366.8 - 412.1	10.3 - 120.0	0.033 - 0.735	2
	276.6 - 493.1	0.2 - 120.3	0.009 - 0.952	3
Cyclohexane	473.2 - 533.2	20.3 - 129.7	0.020 - 0.570	4
	348.2 - 423.2	19.8 - 104.3	0.103 - 0.577	5
	344.3	68.7 - 109.7	0.426 - 0.880	6
	273.2 - 303.2	7.7 - 58.1	0.081 - 0.806	7
	366.5 - 410.9	1.7 - 145.1	0.067 - 0.790	29
Methylcyclohexane	311.0 - 477.2	3.5 - 148.9	0.027 - 0.979	8
Ethylcyclohexane	310.9 - 477.6	1.8 - 164.3	0.012 - 0.973	44
Propylcyclohexane	313.1 - 472.8	20.5 - 183.5	0.209 - 0.792	45
Benzene	344.3	69.0 - 109.6	0.453 - 0.875	6
	298.2 - 313.2	8.9 - 77.5	0.106 - 0.933	9
	313.2 - 393.2	6.2 - 133.0	0.047 - 0.948	10
	313.4 - 393.2	5.0 - 62.7	0.017 - 0.661	11
	343.6 - 413.6	22.9 - 153.9	0.143 - 0.730	12
	273.2 - 303.2	8.3 - 63.1	0.124 - 0.928	7
	313.2	16.4 - 55.7	0.139 - 0.602	5
	313.2	12.5 - 55.2	0.100 - 0.582	42
	313.2	12.2 - 50.0	0.099 - 0.503	43
Naphthalene	373.2 - 423.2	13.9 - 104.5	0.047 - 0.336	23
	373.2 - 423.2	10.1 - 50.7	0.027 - 0.164	39
Phenanthrene	383.2 - 423.2	18.8 - 106.2	0.047 - 0.229	23
	423.2 - 523.2	10.1 - 50.7	0.016 - 0.099	35
	377.6 - 699.8	13.8 - 110.3	0.017 - 0.234	41
Pyrene	433.2	7.3 - 105.7	0.014 - 0.172	23
	473.2 - 573.2	10.1 - 50.7	0.013 - 0.074	35
Toluene	313.3 - 477.0	3.3 - 152.9	0.013 - 0.971	13
	393.3 - 542.9	9.8 - 52.0	0.017 - 0.226	14
	353.2 - 413.2	2.6 - 131.7	0.012 - 0.783	15
	353.4 - 393.2	5.2 - 64.5	0.019 - 0.361	11
	311.0	14.9 - 69.3	0.131 - 0.866	16
	476.3	17.1 - 147.2	0.030 - 0.528	30
Ethylbenzene	308.0 - 328.0	13.8 - 84.4	0.107 - 0.921	16
	312.6 - 366.2	24.0 - 142.5	0.210 - 0.845	17
n-Propylbenzene	313.2 - 472.9	11.0 - 193.5	0.032 - 0.848	18

TABLE E.II (Continued)

Solvent	Temperature Range, (K)	Pressure Range, (bar)	CO_2 Mole Fraction Range	Reference
Isopropylbenzene	299.3 - 383.2	7.2 - 171.2	0.050 - 0.986	19
Butylbenzene	310.2 - 373.2	5.1 - 55.7	0.028 - 0.527	20
	273.2 - 293.2	10.1 - 50.7	0.106 - 0.778	21
Hexylbenzene	288.2 - 318.2	6.5 - 92.4	0.069 - 0.978	22
Heptylbenzene	268.2 - 318.2	6.5 - 83.0	0.087 - 0.904	22
Octylbnezene	288.2 - 318.2	5.8 - 82.8	0.070 - 0.767	22
o-Xylene	312.6 - 366.2	14.7 - 149.3	0.120 - 0.936	17
m-Xylene	462.2 - 582.6	20.8 - 52.6	0.025 - 0.174	14
	312.6 - 366.2	13.3 - 153.6	0.116 - 0.841	17
	310.9 - 477.6	4.1 - 144.8	0.012 - 0.295	31
	303.2 - 343.2	6.7 - 271.5	0.076 - 0.238	36
p-Xylene	312.6 - 366.2	12.0 - 141.6	0.108 - 0.867	17
	353.2 - 393.2	4.6 - 61.5	0.026 - 0.397	11
Mesitylene	310.9 - 477.6	2.5 - 176.0	0.016 - 0.982	34
1-Methylnaphthalene	463.1 - 703.6	19.2 - 51.0	0.039 - 0.143	24
	353.2 - 413.2	18.2 - 144.5	0.046 - 0.488	15
	308.2 - 328.2	20.0 - 240.0	0.097 - 0.614	32
	372.6	37.2 - 206.7	0.130 - 0.601	38
2-Methylnaphthalene	307.2	8.8 - 69.8	0.054 - 0.434	25
	323.2 - 373.2	10.1 - 50.7	0.041 - 0.266	39
	307.2 - 373.2	15.2 - 65.9	0.054 - 0.416	20
1-Naphthol	393.2 - 453.2	10.1 - 50.7	0.017 - 0.094	39
2-Naphthol	413.2 - 473.2	10.1 - 50.7	0.016 - 0.092	39
Tetralin	462.0 - 664.7	20.0 - 51.3	0.023 - 0.137	26
	544.2	15.4 - 266.0	0.020 - 0.645	30
	344.3 - 377.6	40.7 - 243.8	0.185 - 0.801	37
	343.6 - 373.1	31.7 - 221.2	0.133 - 0.932	38
trans-Decalin	323.2 - 423.2	14.7 - 106.6	0.052 - 0.456	5
	345.4 - 523.6	45.1 - 221.4	0.135 - 0.741	27
	344.3	50.6 - 156.5	0.243 - 0.837	46
Diphenylmethane	462.8 - 703.8	19.2 - 51.0	0.039 - 0.143	24
Quinoline	343.2 - 541.0	43.6 - 225.4	0.082 - 0.513	27
	461.8 - 703.4	20.1 - 51.0	0.022 - 0.115	28
Diphenyl	373.2 - 473.2	10.1 - 50.7	0.025 - 0.177	39
m-Cresol	462.7 - 664.7	19.5 - 51.8	0.009 - 0.111	28
	308.2 - 328.2	20.0 - 240.0	0.081 - 0.537	32
Styrene	308.2 - 373.2	26.9 - 162.4	0.176 - 0.991	33
	308.0 - 328.0	14.4 - 83.1	0.001 - 0.006	16
Anisole	343.1 - 372.3	24.5 - 168.1	0.165 - 0.864	38

TABLE E.II (Continued)

Solvent	Temperature Range, (K)	Pressure Range, (bar)	CO_2 Mole Fraction Range	Reference
Benzaldehyde	343.0 - 372.6	28.3 - 183.1	0.181 - 0.792	38
Phenol	348.2 - 423.2	10.1 - 50.7	0.021 - 0.154	40
Catechol	398.2 - 473.2	10.1 - 50.7	0.012 - 0.072	40

TABLE E.III

CARBON MONOXIDE BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	CO Mole Fraction Range	Reference
Benzene	323.2 - 433.2	14.1 - 92.6	0.010 - 0.064	47
Naphthalene	373.2 - 423.2	47.9 - 227.9	0.024 - 0.098	48
Phenanthrene	383.2 - 423.2	54.7 - 232.8	0.023 - 0.075	48
	377.6 - 699.8	13.8 - 110.3	0.005 - 0.093	41
Pyrene	433.2	66.5 - 206.8	0.025 - 0.070	48

TABLE E.IV

METHANE BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	CH_4 Mole Fraction Range	Reference
Cyclohexane	294.3 - 344.3	13.8 - 282.0	0.037 - 0.765	63
	323.2 - 423.2	12.5 - 94.3	0.027 - 0.222	64
Methylcyclohexane	313.4 - 473.2	25.2 - 277.1	0.065 - 0.737	53
Ethylcyclohexane	311.1 - 477.6	4.1 - 207.3	0.015 - 0.600	67
Propylcyclohexane	313.4 - 472.8	15.0 - 389.5	0.038 - 0.712	53
Benzene	423.2	6.9 - 330.9	0.014 - 0.695	54
	421.1 - 501.2	20.2 - 242.6	0.025 - 0.495	55
	313.2	36.6 - 374.2	0.099 - 0.688	52
	313.2 - 423.2	14.6 - 91.4	0.028 - 0.167	64
Phenanthrene	398.2 - 473.2	17.7 - 241.7	0.017 - 0.186	59
	383.2 - 423.2	20.4 - 107.1	0.020 - 0.090	64
	377.6 - 699.8	13.8 - 110.3	0.012 - 0.135	41
Naphthalene	373.2 - 423.2	19.4 - 86.9	0.024 - 0.100	64
Pyrene	433.2	23.5 - 113.0	0.020 - 0.086	64
Toluene	422.5 - 543.2	20.2 - 252.7	0.018 - 0.633	55
	313.2	101.0 - 424.5	0.237 - 0.744	52
	423.2	6.9 - 365.4	0.017 - 0.729	54
	323.2 - 423.2	11.7 - 89.2	0.026 - 0.181	66
n-Propylbenzene	313.2 - 472.8	21.4 - 527.0	0.044 - 0.805	53
m-Xylene	310.9 - 477.6	4.1 - 144.8	0.012 - 0.295	31
	313.2	100.3 - 465.2	0.246 - 0.783	52
	460.8 - 582.4	20.2 - 201.9	0.022 - 0.455	60
Mesitylene	313.2	101.7 - 519.1	0.278 - 0.808	52
	310.9 - 477.6	3.5 - 145.9	0.011- 0.325	34
1-Methylnapthalene	464.2 - 704.0	20.5 - 251.3	0.025 - 0.454	58
Tetralin	461.9 - 664.6	20.3 - 253.3	0.029 - 0.473	58
trans- Decalin	323.2 - 423.2	8.9 - 96.2	0.026 - 0.200	64
Diphenylmethane	462.5 - 702.9	20.1 - 253.0	0.032 - 0.439	58
m-Cresol	462.3 - 663.4	20.0 - 253.3	0.018 - 0.489	60
Quinoline	462.8 - 702.9	20.1 - 253.0	0.017 - 0.403	61

TABLE E.V

ETHANE BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, (K)	Pressure Range, (bar)	C_2H_6 Mole Fraction Range	Reference
Cyclohexane	323.2 - 423.2	3.3 - 77.7	0.049 - 0.601	70
	313.2	12.3 - 42.5	0.236 - 0.836	68
Methylcyclohexane	313.1 - 473.0	6.0 - 93.6	0.072 - 0.923	53
Propylcuclohexane	313.1 - 472.9	7.6 - 117.7	0.052 - 0.954	53
Benzene	323.2 - 423.2	4.8 - 84.6	0.049 - 0.600	70
	298.2	7.8 - 38.0	0.120 - 0.930	69
Naphthalene	373.2 - 423.2	21.5 - 104.3	0.085 - 0.493	70
Phenanthrene	383.2 - 423.2	22.6 - 116.5	0.081 - 0.313	70
Pyrene	433.2	28.6 - 99.2	0.072 - 0.209	70
Toluene	313.1 - 473.2	6.3 - 114.8	0.027 - 0.905	53
Propylbenzene	313.2 - 473.1	3.8 - 132.8	0.033 - 0.945	53
m-Xylene	313.1 - 473.1	5.1 - 120.0	0.036 - 0.925	53
Mesitylene	313.2 - 473.0	5.0 - 128.2	0.038 - 0.944	53
1-Methylnaphthalene	308.2 - 328.2	15.0 - 145.0	0.117 - 0.754	32
	372.5	32.4 - 122.0	0.094 - 0.348	38
m-Cresol	308.2 - 328.2	15.0 - 240.0	0.066 - 0.401	32
trans-Decalin	323.2 - 423.2	3.5 - 86.8	0.054 - 0.561	70
Benzaldehyde	372.5	24.1 - 93.8	0.051 - 0.242	38
Anisole	372.5	24.1 - 96.5	0.083 - 0.539	38

TABLE E.VI

HYDROGEN BINARY SYSTEM DATA EMPLOYED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Reference
Cyclohexane	338.7 - 394.3	6.9 - 690.4	0.003 - 0.350	87
	310.9 - 410.9	34.5 - 620.5	0.014 - 0.292	89
Benzene	433.2 - 533.2	19.0 - 178.0	0.007 - 0.132	85
	323.2 - 423.2	25.5 - 157.3	0.010 - 0.059	48
	338.7 - 433.2	5.3 - 689.3	0.002 - 0.243	87
Naphthalene	373.2 - 423.2	42.9 - 193.9	0.016 - 0.057	48
Phenanthrene	398.2 - 473.2	26.1 - 252.3	0.017 - 0.186	59
	383.2 - 423.2	58.9 - 216.9	0.017 - 0.056	48
	377.6 - 699.8	13.8 - 110.3	0.002 - 0.080	41
Pyrene	433.2	51.7 - 197.3	0.016 - 0.058	48
Toluene	542.2 - 568.2	34.6 - 327.0	0.019 - 0.514	80
	461.9 - 575.2	20.2 - 253.7	0.008 - 0.394	90
1-Methylnaphthalene	462.2 - 701.7	20.3 - 253.3	0.010 - 0.259	81
	730.1	50.9 - 277.8	0.043 - 0.336	88
Tetralin	462.8 - 662.3	20.3 - 253.3	0.012 - 0.282	83
	423.2 - 621.8	17.4 - 273.3	0.010 - 0.239	84
Quinoline	462.5 - 701.7	20.1 - 253.0	0.007 - 0.207	82
Diphenylmethane	462.8 - 701.7	20.3 - 253.3	0.012 - 0.306	79

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APPENDIX F

NITROGEN + AROMATICS AND NAPHTHENES SYSTEMS

This appendix provides detailed calculation results of the representation of bubble point pressures of nitrogen + aromatics and naphthenes for the five cases the using Peng-Robinson equation of state. For each case, the interaction parameters along with their uncertainties, Henry's constants, infinite dilution partial molar volumes and complete statistics including the root mean squared error (RMSE), bias, absolute average deviation (AAD), and absolute average percent deviation (%AAD) are presented. For some mixtures, the infinite dilution partial molar volumes show irregularity at the higher temperatures.

For Cases 2 and 3, the values of Henry's constants and infinite dilution partial molar volumes are at the highest temperature of that data set.

TABLE F.I

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + AROMATICS AND NAPHTHENES SYSTEM: CASE 1

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Methycyclohexane	310.9	.1500	.0000	957	55	13.19	10.72	10.72	14.38	7
76		.0000	.0000							
76	352.6	.1500	.0000	891	68	8.61	7.04	7.11	7.91	7
		.0000	.0000							
76	394.3	.1500	.0000	796	89	9.08	6.83	6.83	7.73	7
		.0000	.0000							
76	477.6	.1500	.0000	552	204	9.64	6.76	6.76	5.08	7
		.0000	.0000							
78	453.2	.1500	.0000	629	151	8.99	2.13	7.84	4.51	5
		.0000	.0000							
78	472.2	.1500	.0000	569	190	29.94	11.53	17.57	7.77	7
		.0000	.0000							
78	497.2	.1500	.0000	487	277	15.46	4.67	12.69	8.65	5
		.0000	.0000							
Ethylcyclohexane	310.9	.1500	.0000	839	55	13.91	9.65	9.65	11.61	11
67		.0000	.0000							
67	338.7	.1500	.0000	821	63	9.43	-7.00	7.22	9.83	11
		.0000	.0000							
67	394.3	.1500	.0000	745	86	8.01	5.42	6.04	9.12	9
		.0000	.0000							
67	477.6	.1500	.0000	566	167	18.9	14.00	14.00	15.19	10
		.0000	.0000							
m-Cresol	462.2	.1500	.0000	1975	68	21.56	-17.14	17.14	14.05	7
77		.0000	.0000							
77	542.7	.1500	.0000	1341	111	14.07	-10.31	10.31	7.69	7
		.0000	.0000							

TABLE F.I (Continued)

SYSTEM	T(K)	C_{12}	D_{12}	$H_{1,2}$	$\tilde{V}_1^{\infty}$	RMSE	BIAS	AAD	%AAD	NP
REFERENCE		σ_C	σ_D	(bar)	(cc/mol)	(bar)	(bar)	(bar)		
77	624.3	.1500	.0000	797	271	13.47	-11.74	11.74	8.67	6
		.0000	.0000							
77	663.6	.1500	.0000	551	628	11.70	-9.59	9.59	7.60	5
		.0000	.0000							
Tetralin	463.6	.1500	.0000	1040	86	37.57	-29.57	29.57	23.93	7
77		.0000	.0000							
77	544.0	.1500	.0000	800	145	36.06	-27.05	27.05	19.50	7
		.0000	.0000							
77	623.2	.1500	.0000	547	328	33.59	-27.65	27.65	19.18	6
		.0000	.0000							
Quinoline	462.1	.1500	.0000	3563	56	82.07	64.99	64.99	54.58	7
74		.0000	.0000							
74	541.9	.1500	.0000	2530	78	77.76	60.66	60.66	48.33	7
		.0000	.0000							
74	623.9	.1500	.0000	1711	127	72.01	54.78	54.78	41.72	7
		.0000	.0000							
74	703.7	.1500	.0000	1055	287	72.56	56.08	56.08	35.34	6
		.0000	.0000							
Cyclopentane	366.4	.1500	.0000	952	83	61.36	40.72	40.73	25.67	17
2		.0000	.0000							
2	410.2	.1500	.0000	762	128	37.52	22.77	25.63	10.08	14
		.0000	.0000							
Cyclohexane	366.4	.1500	.0000	997	73	18.92	12.58	14.13	11.73	9
29		.0000	.0000							
29	410.8	.1500	.0000	843	103	19.95	13.47	13.63	7.47	9
		.0000	.0000							
Propylcyclohexane	313.6	.1500	.0000	820	55	136.40	-116.18	116.18	26.68	7
45		.0000	.0000							
45	393.2	.1500	.0000	752	81	17.37	-15.03	15.03	9.40	10

TABLE F.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0000	.0000							
45	472.9	.1500	.0000	606	140	11.25	-1.05	8.06	5.87	11
		.0000	.0000							
1-Methylnaphthalene	462.6	.1500	.0000	1380	73	29.84	-23.54	23.54	19.08	7
75		.0000	.0000							
75	542.8	.1500	.0000	1089	110	21.70	-16.45	16.45	11.39	7
		.0000	.0000							
75	624.0	.1500	.0000	792	200	18.37	-15.85	15.85	11.99	6
		.0000	.0000							
75	703.3	.1500	.0000	499	562	17.24	-15.23	15.23	10.57	7
		.0000	.0000							
Toluene	313.2	.1500	.0000	1420	50	110.33	-96.71	96.71	20.15	8
45		.0000	.0000							
45	391.5	.1500	.0000	1142	74	31.58	-28.27	28.27	16.10	10
		.0000	.0000							
45	472.6	.1500	.0000	801	142	21.28	1.15	15.91	7.20	15
		.0000	.0000							
71	323.2	.1500	.0000	1390	52	65.03	-56.04	56.04	30.98	6
		.0000	.0000							
71	348.2	.1500	.0000	1306	58	51.95	-44.37	44.37	22.93	6
		.0000	.0000							
m-Xylene	313.2	.1500	.0000	1274	49	118.01	-100.40	100.40	22.74	7
45		.0000	.0000							
45	391.5	.1500	.0000	1066	71	59.09	-54.15	54.15	18.78	12
		.0000	.0000							
45	472.6	.1500	.0000	787	126	23.55	-20.37	20.37	13.52	10
		.0000	.0000							
Mesitylene	313.2	.1500	.0000	1201	49	164.80	-146.50	146.50	31.60	8
45		.0000	.0000							

TABLE F.I (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
45	393.2	.1500 .0000	.0000 .0000	1015	70	61.19	-58.21	58.21	21.37	9
45	472.6	.1500 .0000	.0000 .0000	775	117	27.13	-24.53	24.53	15.29	10
n-Propylbenzene 18	313.4	.1500 .0000	.0000 .0000	1152	49	73.59	-63.70	63.70	38.35	8
18	403.2	.1500 .0000	.0000 .0000	968	75	36.47	-32.22	32.22	19.99	8
18	473.2	.1500 .0000	.0000 .0000	765	120	14.42	-13.21	13.21	8.60	8
Benzene 71	303.2	.1500 .0000	.0000 .0000	1728	48	34.93	-30.64	30.64	14.40	5
71	348.2	.1500 .0000	.0000 .0000	1499	59	10.68	-10.43	10.43	6.83	5
71	373.2	.1500 .0000	.0000 .0000	1364	68	9.09	2.21	6.91	3.93	5
72	398.2	.1500 .0000	.0000 .0000	1226	81	7.12	-.05	5.86	3.79	7
72	303.2	.1500 .0000	.0000 .0000	1728	48	44.72	-41.76	41.76	19.12	3
72	348.2	.1500 .0000	.0000 .0000	1499	59	16.81	-15.86	15.86	9.13	6
72	373.2	.1500 .0000	.0000 .0000	1364	68	7.80	-6.60	6.74	4.51	6
OVERALL STATISTICS						50.39	-12.73	30.52	16.21	424

TABLE F.II

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + AROMATICS AND NAPHTHENES SYSTEM: CASE 2

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Methylcyclohexane	(310.9-	.1057	.0000			2.77	.26	1.63	2.32	28
76	477.6)	.0026	.0000	531	203					
78	(453.2-	.0992	.0000			14.86	-5.13	12.10	7.94	17
	497.2)	.0132	.0000	468	274					
Ethylcyclohexane	(310.9-	.1238	.0000			11.43	.28	7.38	9.87	41
67	477.6)	.0072	.0000	553	166					
Propylcyclohexane	(313.6-	.2239	.0000			28.09	8.09	17.57	5.46	28
45	472.9)	.0049	.0000	649	141					
Cyclopentane	(366.4-	.0419	.0000			13.61	-5.20	10.81	10.27	31
2	410.2)	.0068	.0000	661	125					
Cyclohexane	(366.5-	.1005	.0000			5.96	-1.68	4.83	5.64	18
29	410.9)	.0042	.0000	788	102					
m-Cresol	(462.2-	.2430	.0000			5.39	-1.21	3.38	2.82	25
77	663.6)	.0062	.0000	573	636					
Tetralin	(463.6-	.3922	.0000			9.28	-2.34	6.98	5.12	20
77	623.2)	.0121	.0000	616	338					
Quinoline	(462.1-	-.1639	.0000			19.44	3.91	13.05	10.01	27
74	703.7)	.0221	.0000	907	276					
1-Methylnaphthalene	(462.2-	.3045	.0000			3.96	-1.25	2.98	3.12	27
75	703.3)	.0048	.0000	527	572					
Toluene	(323.2-	.2464	.0000			11.07	-3.75	9.67	6.95	12
71	348.2)	.0045	.0000	1601	59					
45	(313.2-	.1924	.0000			28.67	1.49	18.83	7.47	33
	472.6)	.0035	.0000	836	43					
m-Xylene	(313.2-	.2154	.0000			18.41	-6.04	15.49	7.16	29
45	472.6)	.0027	.0000	841	128					

TABLE F.II (Continued)

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Mesitylene	(313.2-	.2279	.0000			27.08	-9.28	22.10	8.58	27
45	472.6)	.0034	.0000	838	118					
Propylbenzene	(313.2-	.2436	.0000			28.59	-4.23	21.20	11.42	24
18	473.2)	.0121	.0000	840	122					
Benzene	(303.2-	.1683	.0000			16.60	-.93	12.74	6.02	15
71	373.2)	.0055	.0000	1412	69					
72	(303.2-	.1737	.0000			14.29	-.14	9.60	4.58	22
	398.2)	.0052	.0000	1426	69					
OVERALL STATISTICS						18.00	-1.36	11.37	6.93	424

TABLE F.III

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + AROMATICS AND NAPHTHENES SYSTEM: CASE 3

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Methylcyclohexane	(310.9-	.0101	.0327			2.01	.46	1.49	3.01	28
76	477.6)	.0155	.0053	541	212					
78	(453.2-	-.0370	.0905			9.16	.95	6.54	3.83	17
	497.2)	.0317	.0186	536	311					
Ethylcyclohexane	(310.9-	-.1054	.0725			9.65	1.47	7.38	11.81	41
67	477.6)	.0583	.0181	592	188					
Propylcyclohexane	(313.6-	.0208	.0656			16.21	9.88	13.04	7.61	28
45	472.9)	.0272	.0084	717	161					
Cyclopentane	(366.4-	-.0098	.0325			13.03	-3.79	11.10	9.90	31
2	410.2)	.0311	.0185	698	132					
Cyclohexane	(366.5-	-.0246	.0544			3.16	.08	2.58	4.30	18
29	410.9)	.0181	.0077	853	112					
m-Cresol	(462.2-	.1894	.0126			5.20	-1.37	3.49	2.90	25
77	663.6)	.0482	.0112	574	642					
Tetralin	(463.6-	.8295	-.0982			5.92	-2.48	4.80	5.05	20
77	623.2)	.0867	.0196	590	299					
Quinoline	(462.1-	-1.1652	.2188			12.55	6.20	10.49	13.10	27
74	703.7)	.2006	.0427	987	342					
1-Methylnaphthalene	(462.2-	.3597	-.0112			3.84	-1.20	2.85	2.95	27
75	703.3)	.0407	.0081	525	566					
Toluene	(323.2-	-.1095	.1075			5.92	-.69	4.59	3.82	12
71	348.2)	.0754	.0226	1803	75					
45	(313.2-	.0106	.0599			13.68	-6.17	11.60	5.44	33
	472.6)	.0170	.0052	870	156					
m-Xylene	(313.2-	.1542	.0182			17.19	-7.19	13.73	6.79	29
45	472.6)	.0307	.0091	854	122					

TABLE F.III (Continued)

SYSTEM REFERENCE	T(K) Range	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Mesitylene	(313.2-	.0883	.0366			22.53	-12.88	19.15	7.64	27
45	472.6)	.0419	.0109	867	127					
Propylbenzene	(313.2-	-.0572	.0850			3.77	-.12	2.42	1.75	24
18	473.2)	.0085	.0022	923	143					
Benzene	(303.2-	-.1296	.1063			4.23	1.78	3.53	2.08	15
71	373.2)	.0196	.0069	1570	84					
72	(303.2-	-.1453	.1144			3.23	1.54	2.73	2.08	22
	398.2)	.0148	.0052	1603	85					
OVERALL STATISTICS						11.27	-.97	7.73	6.10	424

TABLE F.IV

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + AROMATICS AND NAPHTHENES SYSTEM: CASE 4

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Methycyclohexane	310.9	.1082	.0000	867	54	.99	.21	.91	2.69	7
76		.0014	.0000							
76	352.6	.1140	.0000	834	68	.71	.05	.63	2.20	7
		.0013	.0000							
76	394.3	.0997	.0000	741	88	1.60	-.21	1.07	1.58	7
		.0040	.0000							
76	477.6	.0720	.0000	516	201	2.61	-.84	2.15	2.48	7
		.0097	.0000							
78	453.2	.1326	.0000	618	150	5.99	-3.17	4.44	3.80	5
		.0080	.0000							
78	472.2	.0698	.0000	530	187	16.03	-7.80	14.51	9.37	7
		.0239	.0000							
78	497.2	.0871	.0000	464	274	10.30	-4.83	9.17	8.23	5
		.0303	.0000							
Ethylcyclohexane	310.9	.1134	.0000	772	55	4.87	-.10	3.48	5.67	11
67		.0047	.0000							
67	338.7	.1774	.0000	866	63	5.80	-1.47	4.68	6.27	11
		.0065	.0000							
67	394.3	.1142	.0000	709	85	3.02	-.31	2.23	5.45	9
		.0054	.0000							
67	477.6	.0463	.0000	517	164	9.75	.42	7.10	8.18	10
		.0229	.0000							
m-Cresol	462.2	.2448	.0000	2260	68	.94	-.19	.68	.51	7
77		.0015	.0000							
77	542.7	.2381	.0000	1455	113	2.66	.43	1.87	1.81	7
		.0065	.0000							

TABLE F.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
77	624.3	.2642	.0000	851	275	4.40	-1.98	3.50	3.22	6
		.0162	.0000							
77	663.6	.2158	.0000	567	633	9.65	-4.36	8.89	6.63	5
		.0463	.0000							
Tetralin	463.6	.3558	.0000	1319	88	1.92	-.10	1.42	1.06	7
77		.0035	.0000							
77	544.0	.4401	.0000	998	150	2.46	1.03	2.24	3.34	7
		.0065	.0000							
77	623.2	.4881	.0000	646	342	3.28	-1.56	2.94	3.18	6
		.0118	.0000							
Quinoline	462.1	-.0735	.0000	2467	55	1.21	.55	.92	2.28	7
74		.0018	.0000							
74	541.9	-.1627	.0000	1782	75	.65	.26	.62	1.00	7
		.0014	.0000							
74	623.9	-.2863	.0000	1234	121	.83	.41	.65	1.95	7
		.0028	.0000							
74	703.7	-.4602	.0000	786	266	1.62	.81	1.42	2.60	6
		.0089	.0000							
Cyclopentane	366.4	.0245	.0000	764	80	8.83	-3.54	7.10	10.61	17
2		.0060	.0000							
2	410.2	.0684	.0000	685	125	13.17	-5.57	11.85	8.13	14
		.0099	.0000							
Cyclohexane	366.4	.1071	.0000	924	73	5.58	-1.95	4.45	6.90	9
29		.0051	.0000							
29	410.8	.0897	.0000	777	102	4.78	-1.92	4.31	3.89	9
		.0058	.0000							
Propylcyclohexane	313.6	.2337	.0000	987	55	4.75	-.59	3.49	1.23	7
45		.0009	.0000							
45	393.2	.1846	.0000	790	81	4.82	-2.25	4.06	3.90	10

TABLE F.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0031	.0000							
45	472.9	.1354	.0000	599	139	10.06	-4.58	8.05	6.58	11
		.0095	.0000							
1-Methylnaphthalene	462.6	.2989	.0000	1667	74	.54	-.02	.48	.77	7
75		.0009	.0000							
75	542.8	.3007	.0000	1239	112	1.50	.52	1.38	2.82	7
		.0038	.0000							
75	624.0	.3114	.0000	868	204	3.53	-1.50	3.17	3.04	6
		.0128	.0000							
75	703.3	.3429	.0000	534	574	5.67	-2.14	4.88	4.10	7
		.0244	.0000							
Toluene	313.2	.1963	.0000	1602	50	18.10	-6.52	14.84	3.28	8
45		.0024	.0000							
45	391.5	.1980	.0000	1236	74	17.15	-6.85	14.12	8.96	10
		.0095	.0000							
45	472.6	.1263	.0000	782	141	18.40	-7.29	15.97	8.12	15
		.0114	.0000							
71	323.2	.2506	.0000	1779	52	12.26	-5.20	11.28	7.34	6
		.0068	.0000							
71	348.2	.2409	.0000	1583	59	8.26	-2.71	7.68	6.11	6
		.0054	.0000							
m-Xylene	313.2	.2150	.0000	1502	49	8.29	.15	7.89	2.53	7
45		.0015	.0000							
45	391.5	.2197	.0000	1192	72	23.07	-9.62	21.79	8.46	12
		.0077	.0000							
45	472.6	.1999	.0000	827	127	15.54	-7.40	13.29	9.36	10
		.0137	.0000							
Mesitylene	313.2	.2293	.0000	1454	49	31.49	-14.13	27.39	6.87	8
45		.0043	.0000							

TABLE F.IV (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
45	393.2	.2174	.0000	1128	70	32.62	-15.52	30.53	11.58	9
		.0132	.0000							
45	472.6	.2218	.0000	833	118	11.40	-5.90	9.76	7.98	10
		.0101	.0000							
n-Propylbenzene	313.4	.3010	.0000	1669	50	7.08	-2.67	5.97	4.49	8
18		.0040	.0000							
18	403.2	.2371	.0000	1100	76	10.42	-4.49	9.67	7.70	8
		.0086	.0000							
18	473.2	.1731	.0000	783	120	11.18	-5.74	10.03	6.75	8
		.0105	.0000							
Benzene	303.2	.1875	.0000	1927	48	1.36	-.51	1.16	1.02	5
71		.0007	.0000							
71	348.2	.1612	.0000	1537	59	6.83	-3.45	6.47	4.60	5
		.0046	.0000							
71	373.2	.1402	.0000	1339	68	6.58	-3.16	6.30	4.44	5
		.0053	.0000							
72	398.2	.1429	.0000	1212	81	6.37	-2.82	5.90	4.22	7
		.0059	.0000							
72	303.2	.2026	.0000	2012	48	1.19	-.45	.87	.61	3
		.0008	.0000							
72	348.2	.1781	.0000	1595	59	3.85	-1.53	3.53	2.40	6
		.0028	.0000							
72	373.2	.1587	.0000	1387	68	5.95	-2.65	5.36	3.35	6
		.0004	.0000							
OVERALL STATISTICS						11.33	-3.23	7.42	5.29	424

TABLE F.V

BUBBLE POINT CALCULATIONS USING PENG-ROBINSON EQUATION OF STATE FOR NITROGEN + AROMATICS AND NAPHTHENES SYSTEM: CASE 5

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
Methycyclohexane	310.9	.1005	.0025	871	55	1.01	.25	.93	2.86	7
76		.0089	.0030							
76	352.6	.1097	.0015	836	68	.72	.07	.65	2.23	7
		.0091	.0028							
76	394.3	.0655	.0121	753	91	1.53	-.04	1.16	1.73	7
		.0563	.0202							
76	477.6	-.0973	.0746	561	224	1.05	.19	.94	1.25	7
		.0311	.0137							
78	453.2	.0836	.0308	659	159	4.02	-.64	3.69	2.91	5
		.0255	.0154							
78	472.2	-.0818	.1089	657	223	5.60	.63	5.08	3.56	7
		.0281	.0171							
78	497.2	-.1869	.1669	585	341	1.04	.13	.83	.62	5
		.0186	.0099							
Ethylcyclohexane	310.9	.1006	.0040	780	56	4.85	.04	3.47	5.67	11
67		.0641	.0199							
67	338.7	-.0076	.0552	964	74	4.89	-.07	3.07	4.72	11
		.0327	.0101							
67	394.3	.0156	.0321	751	92	2.53	.48	2.05	6.72	9
		.0000	.0019							
67	477.6	.0120	.0139	528	160	9.73	.72	7.02	8.29	10
		.1908	.0750							
m-Cresol	462.2	.1668	.0169	2283	71	.74	.00	.49	.49	7
77		.0528	.0114							
77	542.7	.4124	-.0413	1414	104	2.39	-.13	1.96	2.26	7
		.1421	.0340							

TABLE F.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
77	624.3	-.1797	.1263	928	317	1.22	.09	1.03	1.18	6
		.0601	.0165							
77	663.6	-.5868	.2772	677	797	1.64	.41	1.56	1.39	5
		.1386	.0407							
Tetralin	463.6	.3565	-.0005	1316	88	1.94	-.36	1.45	1.15	7
77		.0082	.0020							
77	544.0	.6696	-.0526	953	136	1.75	.15	1.29	1.35	7
		.1041	.0239							
77	623.2	.2288	.0707	685	383	1.85	-.19	1.50	1.18	6
		.0892	.0240							
Quinoline	462.1	-.0219	-.0107	2445	53	1.06	.38	.81	2.07	7
74		.0276	.0056							
74	541.9	-.1128	-.0108	1764	73	.53	.08	.41	.59	7
		.0207	.0046							
74	623.9	-.2715	-.0035	1230	120	.82	.35	.68	1.89	7
		.0346	.0079							
74	703.7	-.4154	-.0130	777	261	1.55	.57	1.23	2.32	6
		.0793	.0224							
Cyclopentane	366.4	-.0764	.0594	871	90	5.99	-.15	4.84	9.12	17
2		.0232	.0132							
2	410.2	-.1212	.1287	865	153	3.55	.37	2.98	2.57	14
		.0167	.0104							
Cyclohexane	366.4	.0159	.0380	990	79	4.18	-.49	3.48	6.20	9
29		.0420	.0174							
29	410.8	-.0371	.0594	858	113	1.31	.20	1.10	1.77	9
		.0144	.0066							
Propylcyclohexane	313.6	.2158	.0056	1007	57	4.37	.29	3.99	1.56	7
45		.0214	.0067							
45	393.2	.1108	.0257	847	87	2.68	-.27	1.84	1.38	10

TABLE F.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^\infty$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
		.0163	.0056							
45	472.9	.0005	.0641	699	160	1.40	.49	1.26	1.99	11
		.0009	.0006							
1-Methylnaphthalene	462.6	.2813	.0034	1672	75	.53	.03	.46	.81	7
75		.0145	.0028							
75	542.8	.2950	.0012	1241	112	1.50	.59	1.39	2.88	7
		.0128	.0025							
75	624.0	-.0642	.0834	934	231	1.05	.18	.93	.95	6
		.0675	.0143							
75	703.3	-.2488	.1615	604	672	2.53	.33	2.15	1.70	7
		.1473	.0377							
Toluene	313.2	.0300	.0536	1774	57	14.56	-3.26	12.66	3.71	8
45		.0809	.0258							
45	391.5	-.2658	.1604	1575	101	4.14	.73	2.93	2.34	10
		.0483	.0160							
45	472.6	-.1314	.1304	980	174	5.68	.92	4.70	3.48	15
		.0245	.0114							
71	323.2	-.2650	.1525	2106	74	5.66	-.85	4.08	2.48	6
		.3119	.0900							
71	348.2	-.1013	.1058	1809	75	4.16	.95	2.77	4.37	6
		.0951	.0293							
m-Xylene	313.2	.2026	.0036	1514	50	8.27	.44	7.87	2.61	7
45		.0399	.0115							
45	391.5	-.1247	.1121	1494	93	8.69	1.56	6.68	4.70	12
		.0459	.0144							
45	472.6	-.1207	.1264	1026	159	2.10	.40	1.77	2.28	10
		.0151	.0056							
Mesitylene	313.2	-.0034	.0597	1671	60	25.79	-11.25	23.52	5.93	8
45		.0566	.0137							

TABLE F.V (Continued)

SYSTEM REFERENCE	T(K)	C_{12} σ_C	D_{12} σ_D	$H_{1,2}$ (bar)	$\tilde{V}_1^{\infty}$ (cc/mol)	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NP
45	393.2	-.2346 .0364	.1333 .0101	1527	98	6.47	1.23	5.69	3.04	9
45	472.6	-.0339 .0106	.0879 .0035	980	141	1.32	-.08	1.08	1.30	10
n-Propylbenzene 18	313.4	-.1992 .0062	.1190 .0014	1933	71	2.41	.60	1.97	3.29	8
18	403.2	-.0794 .0625	.0901 .0177	1291	95	4.59	.04	2.99	1.43	8
18	473.2	-.0349 .0111	.0780 .0040	914	141	1.63	-.32	1.45	.95	8
Benzene 71	303.2	.1932 .0086	-.0019 .0030	1922	48	1.42	-.55	1.17	1.06	5
71	348.2	-.0547 .0181	.0793 .0066	1713	70	1.27	-.25	.96	.93	5
71	373.2	-.0480 .0142	.0734 .0055	1489	79	1.02	-.20	.77	.79	5
72	398.2	-.0834 .0115	.0892 .0044	1354	95	.79	-.09	.72	.44	7
72	303.2	.1249 .0449	.0258 .0148	2065	51	.53	-.04	.50	.28	3
72	348.2	.0048 .0076	.0615 .0027	1712	68	.99	.07	.93	.68	6
72	373.2	-.0508 .0408	.0789 .0152	1533	80	2.29	.35	2.18	1.55	6
OVERALL STATISTICS						5.62	-.05	3.11	2.88	424

VITA

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Master of Science

Thesis: SOLUBILITY DATA FOR NITROGEN IN N-PARAFFINS AND EQUATION-OF-STATE METHODS TO DESCRIBE LIGHT GAS SOLUBILITIES IN HYDROCARBONS

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