BINARY VAPOR-LIQUID EQUILIBRIUM MEASUREMENTS FOR SELECTED ASYMMETRIC MIXTURES AND EQUATION OF STATE DEVELOPMENT

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the degree of
DOCTOR OF PHILOSOPHY
May, 1994

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PREFACE

Solubilities of carbon monoxide in selected aromatic solvents (naphthalene, phenanthrene and pyrene) were measured at temperatures from 373.2 to 433.2 K and pressures to 23.3 MPa. Similarly, solubilities of hydrogen in selected heavy normal paraffins (n-decane, n-eicosane, n-octacosane and n-hexatriacontane) and aromatics (benzene, naphthalene, phenanthrene and pyrene) were measured at temperatures from 323.2 to 433.2 K and pressures to 21.7 MPa. These data were analyzed using the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state.

The newly acquired data agree well with the available literature data. Estimated uncertainties in the measured solubilities are less than 0.001 in mole fraction. These data constitute a complement to the previous measurements conducted at Oklahoma State University dealing with the solubility of light gases in n-paraffins, naphthenes, and aromatics. In general, the SRK and PR EOS represent the experimental data well when a single interaction parameter is used for each isotherm of each binary mixture.

A new equation of state (EOS) has been proposed based on the generalized van der Waals partition function for chain-like molecules. The new EOS utilizes an existing expression for the free volume of hard spheres in the repulsive term and an augmented generalized cubic equation of state attractive term. A square-well potential was used to describe the attractive energy between segments of molecules and temperature and density correction functions were introduced to amend the limiting low-density radial distribution function. A set of mixing rules was also proposed to extend the use of the new equation to mixtures. The predictive ability of the new equation of state was demonstrated through vapor-liquid equilibrium predictions involving pure fluids and n-paraffin binary mixtures containing ethane, carbon dioxide, and hydrogen. The new EOS predictions were compared to those of the PR, Simplified Perturbed-Hard Chain Theory (SPHCT) and Modified SPHCT EOS.

The new EOS provides improved predictions for pure-fluid vapor pressures and saturated densities and compares favorably with the PR, the SPHCT and the Modified SPHCT equations. EOS evaluations involving ethane + n-paraffins and carbon dioxide + n-paraffins binary mixtures, suggest that the new equation is best among the equations considered for *a priori* predictions.

I would like to express my sincere gratitude to my adviser, Dr. Khaled A. M. Gasem for his intelligent guidance, encouragement, and invaluable support. I also sincerely appreciate the advice and encouragement received from my graduate committee members: Drs. Robert L. Robinson, Jr., Arland H. Johannes and John N. Veenstra.

I will always cherish the good times I shared with my friends in Stillwater, particularly Ron Shaver, Mansour Bader, Gang-Choon Lee and Kyoung Ho Row. Times spent with them were both enjoyable and valuable. I also would like to express my appreciation to the undergraduate assistant, Matt Mohr, who helped me during the course of the experiment.

Most of all, I am in debt to my parents for their support and encouragement throughout the course of my study in the United States. I humbly dedicate this work to them for their love and sacrifice.

Finally, the financial support received from the Department of Energy of the United States under the contract number DE-FG22-90PC90302 is greatly appreciated.

TABLE OF CONTENTS

Chapter Page

SECTION II - EQUATION OF STATE DEVELOPMENT

LIST OF TABLES

Table Page

SECTION I - EXPERIMENTAL WORK

SECTION II - EQUATION OF STATE DEVELOPMENT

Table Page

LIST OF FIGURES

Figure Page

SECTION I - EXPERIMENTAL WORK

Figure Page

SECTION II - EQUATION OF STATE DEVELOPMENT

NOMENCLATURE

a	Energy parameter in the SRK or PR EOS
b	Molecular size parameter in the SRK or PR EOS
B	Second virial coefficient
c	Degrees of freedom parameter
C_{ij}, D_{ij}	Binary interaction parameters
g	Radial distribution function, molar Gibbs free energy
k	Boltzmann constant
K	Ratio of square-well width from hard sphere center to hard sphere radius
n	Number of data points, number of moles
N	Number of components in mixture, total number of molecules
p	Pressure
q	External molecular surface area
Q	Canonical partition function, equation of state constant
r	Radial distance from central molecule
R	Gas constant
SS	Objective function
T	Temperature
$\tilde{T}$	Reduced temperature (T/T^*)
u	Potential energy between molecules, equation of state constant

v	Molar volume
V	Total system volume
w	Equation of state constant
x	Liquid phase mole fraction
Y	Temperature dependent function in the new equation of state at low density limit
z	Mole fraction
Z	Compressibility factor

Greek letters

α	Temperature-dependent parameter in cubic equations of state, temperature correction function
β_1, β_2	Constants in repulsive term of the new equation of state
$\Delta(\rho)$	Density correction function to the limiting radial distribution function
ε	Characteristic energy parameter
ϕ	Intermolecular potential energy
η	Reduced density ($\tau v^*/v$)
κ	Acentric factor dependent parameter in cubic equations of state, equation of state constant
Λ	de Broglie wave length
$\Theta(T)$	Temperature correction function to the limiting radial distribution function
σ	Radius of hard sphere
τ	Geometrical constant (0.74048)
ω	Acentric factor

Subscripts

c	Critical state
calc	Calculated
expt	Experimental
f	Free
i, j	Component or data point identification number
l	Liquid
min	Minimum
r	Reduced property
v	Vapor

Superscript

att	Attractive
rep	Repulsive
*	Characteristic parameter

SECTION I - EXPERIMENTAL WORK

CHAPTER I

INTRODUCTION

Fluid phase equilibrium properties are widely used in the development of various chemical processes. For example, accurate knowledge of equilibrium properties is required in designing separation processes such as distillation and extraction, and in calculating mass transfer limits in processes involving multiple phases. Similarly, volumetric properties of pure fluids and mixtures are needed in designing chemical processes.

Equations of state, which cover a wide range of density, have been recognized as the most convenient models in vapor-liquid equilibrium and volumetric property predictions. In the 1870's, van der Waals established the concept of corresponding states and proposed his famous equation of state (EOS). Since then, numerous equations of state have been proposed and used in phase equilibrium and volumetric property calculations. Among these, the Soave-Redlich-Kwong (SRK) [1] and Peng-Robinson (PR) equations of state [2] are most widely used in industry.

Cubic equations of state such as SRK and PR may have one or two model parameters for each binary pair in a mixture [1, 2]. These binary interaction parameters cannot be predicted from existing theory. The parameters reflect the nature of unlike-molecular pair interactions and can be obtained from experimental measurements. In this section, binary solubility measurements of hydrogen in selected normal paraffins and aromatics are reported at temperatures from 323.2 to 433.2 K and pressures to 21.7 MPa.

The solubilities of carbon monoxide in selected aromatics are also reported at temperatures from 373.2 to 433.2 K and pressures to 23.3 MPa. The data were analyzed using the SRK and PR equations of state, and binary interaction parameters for these systems were obtained.

This experimental study was focused on the effects of temperature, pressure and solvent molecular size on the solubilities of light solute gases. There are several reasons for selecting the above binary systems for study. First, the solute gases such as hydrogen and carbon monoxide considered in the present work are major chemical components in coal conversion and hydrocarbon reforming processes. Since liquefied coals and heavy crude oils are potential alternative energy resources in the future, fluid phase equilibria of the chemicals involved in the processing or upgrading of these materials is of great interest. Second, the hydrocarbon solvents were selected to study the effect of solvent molecular size variations of normal paraffins and aromatics on the solubilities of the solute gases considered. Third, these systems were studied to expand the database at Oklahoma State University involving the solubilities of small molecules such as methane, ethane, carbon dioxide, carbon monoxide and hydrogen in the systematically selected hydrocarbon solvents. These equilibrium measurements for asymmetric mixtures are useful in direct industrial applications and in developing improved equation of state models.

A brief literature review on experimental methods for the measurement of gas solubilities in heavy hydrocarbon solvents is presented in Chapter II, along with the description of the apparatus and the experimental method used in this study. The solubility measurements and SRK and PR EOS representations of these data are given in Chapters III to V.

CHAPTER II

APPARATUS AND EXPERIMENTAL PROCEDURE USED IN THIS STUDY

Abstract

In this chapter, a brief literature review of the experimental methods used for high pressure vapor-liquid equilibrium measurements, the apparatus, and the experimental procedure used in this study are presented. The outlined description of the apparatus addresses specifications for the major components and modifications undertaken to complete the present study. The experimental procedure employed to measure solubilities of solute gases in selected solvents is also described in detail.

Literature Review

The phase rule states that a binary mixture in vapor-liquid equilibrium has two degrees of freedom. This implies that only two intensive thermodynamic variables are required to completely describe the equilibrium state of such a mixture. To evaluate or verify any thermodynamic model, such as an equation of state, at least three intensive thermodynamic variables should be measured for each of the systems considered. One of the more common combinations of intensive variables for binary mixtures in vapor-liquid equilibrium at high pressure involves temperature, pressure and liquid phase composition (T, p and x).

Recently, a review on experimental methods for investigating fluid phase equilibria at high pressure was conducted by Fornari and coworkers [3]. They classified the experimental methods used to measure fluid phase equilibrium properties as analytic and synthetic, based on the approach used to determine the phase compositions. The analytical approach was further subdivided into static, continuous flow and circulation methods based on the means used to achieve equilibrium conditions.

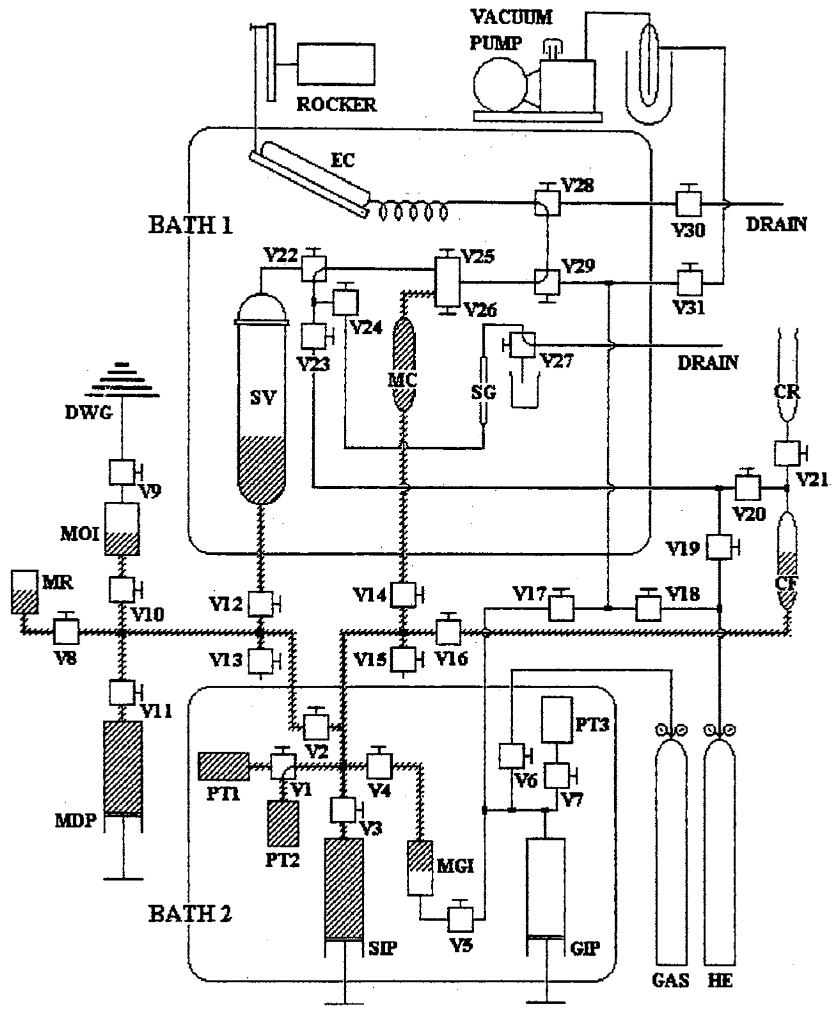
Among the various experimental techniques, the synthetic methods are commonly used for systems for which phase compositions are difficult to analyze [3]. Since composition analysis is not required, the experimental procedures are normally simpler than those of analytical methods. While the weak-point of these methods is the difficulty in obtaining tie lines in phase envelopes, they are widely used to obtain T-p-x measurements. Several studies utilizing the synthetic approach are found in the literature [4 - 9]. For example, Fall and Luks determined solubilities of carbon dioxide in n-dotriacontane and n-docosane by measuring the amount of solvent in the equilibrium cell (gravimetrically) and the volume of gas injected, at a given temperature and pressure. Their approach requires the equilibrium cell to be visible and easily detachable [6]. Similarly, Meskel-Lesavre and coworkers determined the composition of mixtures by weighing the equilibrium cell before and after each injection of solvent and solute [7]. For a mixture of known composition, they identified the bubble point by locating the discontinuity in the compressibility between the vapor-liquid two-phase region and the liquid single phase.

The other methods described in the literature are similar to the one used in this study. Typically, mercury is used as an incompressible fluid, and the volume of the equilibrium cell is varied by introduction or withdrawal of mercury. After injecting known amounts of solvent and solute into the cell, the bubble point can be determined visually by injecting mercury until all the vapor condenses [8]. Similarly, the bubble point pressure can be determined graphically by measuring pressures resulting from the changes of the mixture volume [4, 5, 9]. Since the system compressibility changes drastically when it crosses the phase boundary, the bubble point can be identified. Among the various synthetic methods for studying vapor-liquid equilibrium of fluid mixtures at high pressure described in the literature, this method is one of the most common [6, 7, 8].

Apparatus Used in This Study

A synthetic method was employed in the measurement of solute gas solubilities in heavy hydrocarbon solvents using a variable volume, static-type blind equilibrium cell. The volume of the cell was varied by the introduction or withdrawal of mercury. Figure 1 shows a detailed diagram of the apparatus. The major components of the experimental apparatus are housed in two constant-temperature air baths. One contains the equilibrium cell, a solvent-storage cell and a mercury-storage cell. The other contains a mercury injection pump, a solute injection pump and pressure transducers.

The apparatus, used in this study, is a modified version of that used by Darwish [4] and Yi [10]. Some modifications were undertaken on the apparatus used by Yi [10] to measure the solubilities of hydrogen in hydrocarbon solvents. First, the solvent injection pump, SIP in Figure 1, was replaced by a larger one, 25 cc in volume. This was done to accommodate the increase in the volume of the equilibrium cell and a higher operating pressure (over 13.79 MPa). Second, the equilibrium cell was replaced by a larger cell in volume. A reduction in the experimental uncertainties of the equilibrium composition is the main advantage for increasing the cell volume to 25 cc. The new equilibrium cell was applied only for hydrogen binaries. For carbon monoxide binaries, the old equilibrium cell was used. Third, an additional pressure transducer, PT2 in Figure 1, was installed to measure solute gas solubilities at pressures over 13.8 MPa. This new transducer was installed in parallel with the old pressure transducer, PT1 in Figure 1. The maximum capacity of the display connected to PT1 is 13.8 MPa and that of the corresponding display connected to PT2 is 138 MPa. When pressures greater than 13.8 MPa were expected, the pressure transducer PT1 was isolated by closing valve V2 in Figure 1 before



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 Experimental Apparatus

performing the experiment. Other minor modifications were also undertaken to improve the operations of the apparatus.

Following is a detailed description of the major components of the experimental apparatus and chemicals used in this study. The symbols used such as SV, MC and V1 are in reference to Figure 1.

Equilibrium Cell

The equilibrium cell used in the study of carbon monoxide binary systems is that used by Yi [10]. The cell was supplied by High Pressure Equipment Inc. and has a volume of 12.5 cc. The cell used to investigate solubilities of hydrogen in hydrocarbon solvent is a 19 cc, 316 stainless steel micro-reactor (Cat No. MS-16, 1 in OD, 1/2 in ID, 6 in L) supplied by High Pressure Equipment Inc. One end of the cell was plugged and the other end was connected to 1/16 in OD, 0.03 in ID stainless steel tubing through which the solvent, solute and mercury were injected. The plugged-end of the equilibrium cell was connected to a DC motor (1/4 hp, Bodine Electric Company, Model No. 42D5BEPM-E1) using a steel wire, and the other end of the cell was pivoted. The rotation of the motor causes the equilibrium cell to rock approximately 45 degrees above and below the horizontal level. Two stainless steel balls (diameter of 1/3 in) were placed inside the cell to enhance mixing while the cell is rocking.

Injection Pumps

All three hand pumps used in this study are positive displacement pumps. The solvent injection pump and the solute injection pump were supplied by Temco Inc. (Model No. HP-25-10). Each pump has a volume of 25 cc. The solvent injection pump was used to inject known amounts of solvent into the equilibrium cell, and to introduce and withdraw mercury to and from the equilibrium cell during the experiment. Similarly, the solute gas injection pump was used to inject specific amounts of the solute gas into the equilibrium cell. The maximum operating pressure of these pumps is 69 MPa (10,000 psi) and their resolution is 0.005 cc. The mercury-injection pump was supplied by Ruska Instruments Inc. (Model No. 2210-801) and has a volume of 500 cc. This pump was normally used for cleaning operations.

Storage Cells

The solvent storage cell (SV) is used to store degassed liquid solvent at the operating temperature of the experiment. It is a high pressure reactor (High Pressure Inc., Cat. No. OC-1, 2.5 in OD, 1 in ID, 10 in L). The mercury storage cell (MC) is a micro-reactor having a volume of 5 cc (High Pressure Inc., Cat. No. MS-11, 9/16 in OD, 5/16 in ID, 4 in L). Two additional stainless steel storage cells were used. They were the mercury reservoir (MR) and the cleaning fluid vessel (CF), which contained mercury and the cleaning solvent, respectively.

Constant Temperature Air Baths

The air bath containing the equilibrium cell, the solvent storage cell and the mercury storage cell was thermostated by a PID controller supplied by Omega Engineering Inc. (Cat. No. CN9000A). The temperature of the other bath was controlled by a PI controller supplied by Halikainen Instruments (Model NO. 1053A). Both air baths are temperature controlled within 0.1 °C of the set-point. In this study, the temperature of the bath containing the hand pumps and the pressure transducers was set to 50 °C.

The temperatures of both air baths were measured using platinum resistance thermometers equipped with digital displays supplied by Fluke Inc. (Model 2180A). The resolution of both displays is 0.01 °C.

Pressure Measurements

Injection and equilibrium pressures were measured using pressure transducers, which were connected to digital displays. All the pressure transducers and digital displays were supplied by Sensotec Inc. The pressure transducers, PT1 and PT2, are used to measure the pressure in the equilibrium cell, and the transducer PT3 is for measuring the pressure of solute gas. PT1 and PT3 (Model No. ST5E1890) have a range of 0 to 20.7 MPa, and PT2 (Model No. TJE/743-11) has a range of 0 to 69 MPa. The digital displays for PT1 and PT3 (Model No. 450D) are to 13.8 MPa with 0.007 MPa resolutions. The PT2 is connected to a digital display (Model No. GM), which has a maximum range of 138 MPa with a resolution of 0.07 MPa. This transducer is used when the pressure of the equilibrium cell exceeds 13.8 MPa.

Chemicals

All chemicals used in this work were supplied by commercial suppliers. Table I presents all of the chemicals used in this work, the names of suppliers, and the stated purity of each chemical. No further purification of the chemicals was attempted.

Experimental Procedures

A variable-volume, static-type blind equilibrium cell was used in this study. A brief description of the experimental procedure is presented here, and a detailed operation procedure of the apparatus is given in the supplementary materials [11]. After injecting known amounts of solvent and solute gas into the equilibrium cell, the bubble point of the mixture is identified graphically. This is accomplished by observing the discontinuity in the compressibility of the mixture as it passes from the two-phase state to the single liquid phase, at a given temperature. The volume of the equilibrium cell is varied by the introduction or withdrawal of mercury. For each injection of solvent into the equilibrium

TABLE I

SUPPLIERS AND STATED PURITIES OF CHEMICALS USED IN THIS WORK

Chemical Name	Supplier	Purity (mol %)
Carbon Monoxide	Matheson Gas Products	99.99
Hydrogen	Union Carbide Corporation	99.9995
n-Decane	Aldrich Chemical Company	99+
n- Eicosane	Aldrich Chemical Company	99
n- Octacosane	Alfa Products	99
n-Hexatriacontane	Alfa Products	99
Benzene	Aldrich Chemical Company	99+
Naphthalene	Aldrich Chemical Company	99+
Phenanthrene	Aldrich Chemical Company	98+
Pyrene	Aldrich Chemical Company	99+

cell, normally three bubble point data are obtained with three consecutive injections of solute gas. After each experiment, the equipment is cleaned for the subsequent experiment with a cleaning solvent (n-pentane).

Since the measured amounts of solvent and solute gas injected into the equilibrium cell are given in volumes, densities and molecular weights of the chemicals are required to calculate the mole fraction of the mixtures studied. The densities and molecular weights of the chemicals used in this work are shown in Appendix A.

Throughout the experimental work, error analysis was performed for each data point acquired. The error analysis method used in this study is described in Appendix C, along with a sample plot for pressure-to-solute gas mole fraction ratio (p/x_1) against mole fraction of solute gas (x_1). The precision of the data can be estimated from the amount of scatter in such a plot. The sample plot contains error bars for each data point as determined from the error analysis.

CHAPTER III

SOLUBILITIES OF CARBON MONOXIDE IN NAPHTHALENE, PHENANTHRENE AND PYRENE AT TEMPERATURES FROM 373.2 TO 433.2 K AND PRESSURES TO 23.3 MPA

Abstract

The solubilities of carbon monoxide in naphthalene, phenanthrene and pyrene were measured over the temperature range from 373.2 to 433.2 K and pressures to 23.3 MPa. The uncertainty in these solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. In general, the two equations represent the experimental data well over the complete temperature range when one interaction parameter is used for each binary system. Marginal improvements in equation of state predictions are realized when an additional interaction parameter is used.

Introduction

Accurate predictions for the phase behavior of fluid mixtures are at the heart of chemical process design and development. Industrial processes such as petroleum refining, coal conversion, enhanced oil recovery, and supercritical separation have created great demand for phase equilibrium data of asymmetric mixtures. Thermodynamic property predictions for these mixtures which include small solute gas molecules (such as carbon dioxide, methane, ethane, hydrogen and carbon monoxide) and heavy hydrocarbon solvents (effective carbon number of ten or greater) are severe tests to the current predictive models and the associated mixing theories.

Since carbon monoxide is one of the major products in the coal conversion process, fluid phase equilibria of mixtures containing carbon monoxide have received great interest. In this chapter, binary measurements for the solubility of carbon monoxide in the aromatic compounds naphthalene, phenanthrene and pyrene are presented. These data cover temperatures from 373.2 to 433.2 K and pressures to 23.3 MPa. The data have been correlated using the SRK [1] and PR [2] equations of state. Binary interaction parameters, C_{ij}, regressed from the experimental data, along with data from the literature, can be used to predict multicomponent phase behavior.

Results and Data Correlations

The carbon monoxide solubility measurements are presented in Tables II to IV. In general, the lowest temperature studied was dictated by the melting point of the solvents or the availability of literature data. The effect of temperature and pressure on the solubility of carbon monoxide in naphthalene is shown in Figure 2. Figure 2 indicates that the solubility of carbon monoxide increases as the temperature or pressure increases. The same trend has been observed for phenanthrene binaries, and for pyrene the temperature effect was not investigated.

A comparison of the present data for carbon monoxide + phenanthrene with those of DeVaney and coworkers [12] is shown in Figure 3. The comparison is given in terms of deviations of the predicted solubility using the SRK EOS (discussed below) from the experimental measurements. Figure 3 reveals that the solubility deviations are distributed unevenly around the zero line. This slight positive bias in the fit is attributed to the use of bubble point pressure differences as an objective function. The binary interaction parameters, C_{ij}, employed in the EOS predictions were obtained by linear extrapolation of

TABLE II

SOLUBILITY OF CARBON MONOXIDE (1) IN NAPHTHALENE (2)

x_1	p/MPa	x_1	p/MPa
373.2 K (100.0 °C, 212.0 °F)			
0.0239	4.79	0.0605	12.99
0.0267	5.37	0.0671	14.69
0.0395	8.14	0.0767	16.98
0.0489	10.24	0.0984	22.79
423.2 K (150.0 °C, 302.0 °F)			
0.0278	4.82	0.0635	11.58
0.0307	5.36	0.0685	12.56
0.0393	6.88	0.0770	14.24
0.0498	8.92	0.0972	18.46
0.0523	9.39		

TABLE III

SOLUBILITY OF CARBON MONOXIDE (1)
IN PHENANTHRENE (2)

x_1	p/MPa	x_1	p/MPa
383.2 K (110 .0 °C, 230.0 °F)			
0.0262	7.12	0.0648	19.56
0.0306	8.41	0.0655	20.00
0.0458	13.04	0.0750	23.28
0.0473	13.72		
423.2 K (150.0 °C, 302.0 °F)			
0.0231	5.47	0.0652	16.84
0.0249	5.94	0.0732	19.22
0.0436	10.78		

TABLE IV

SOLUBILITY OF CARBON MONOXIDE (1)
IN PYRENE (2)

x_1	p/MPa	x_1	p/MPa
433.2 K (160.0 °C, 320.0 °F)			
0.0247	6.65	0.0502	14.26
0.0284	7.71	0.0634	18.57
0.0472	13.38	0.0696	20.68

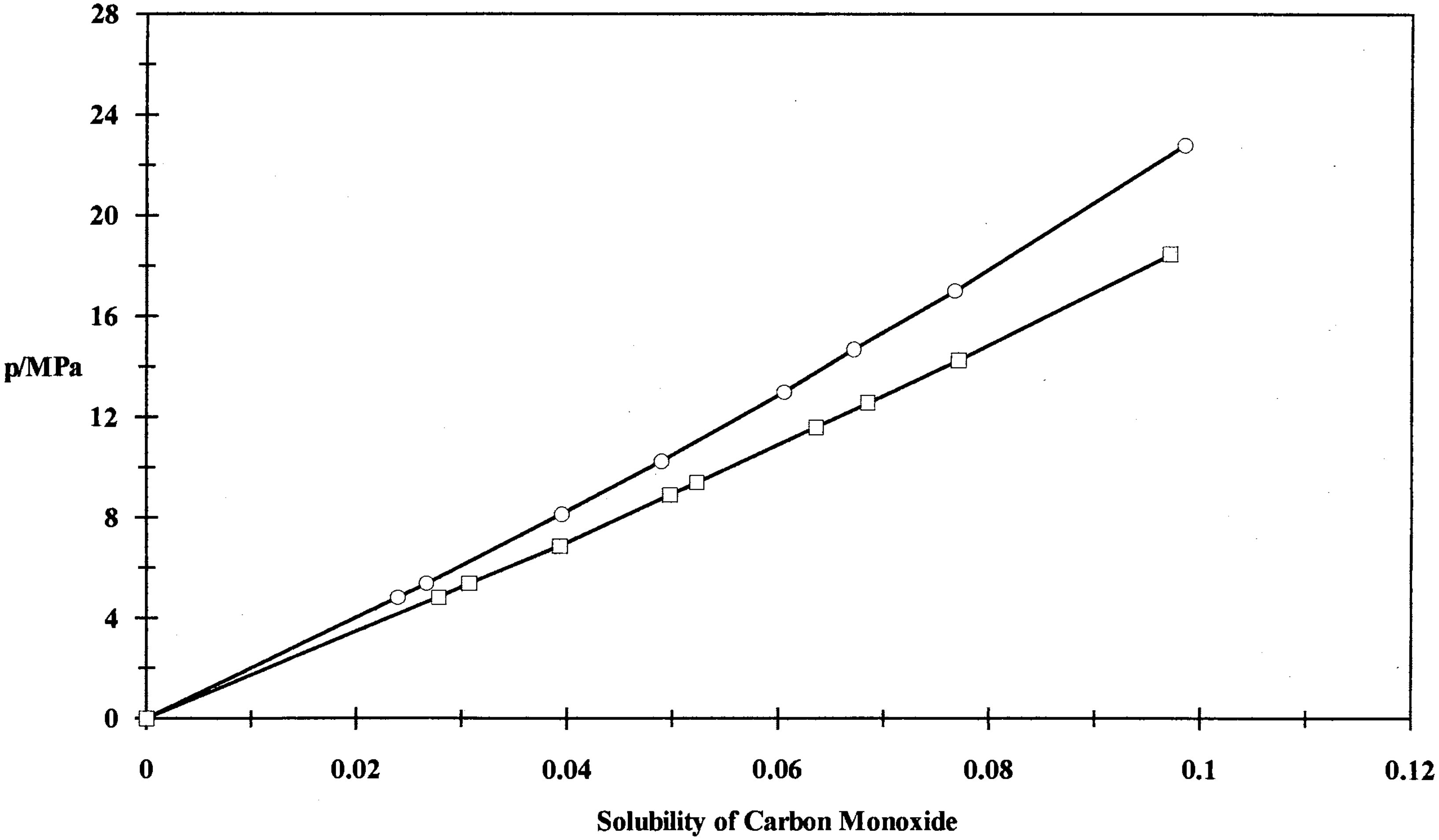


Figure 2. Solubility of Carbon Monoxide in Naphthalene. ○ 373.2 K; □ 423.2 K

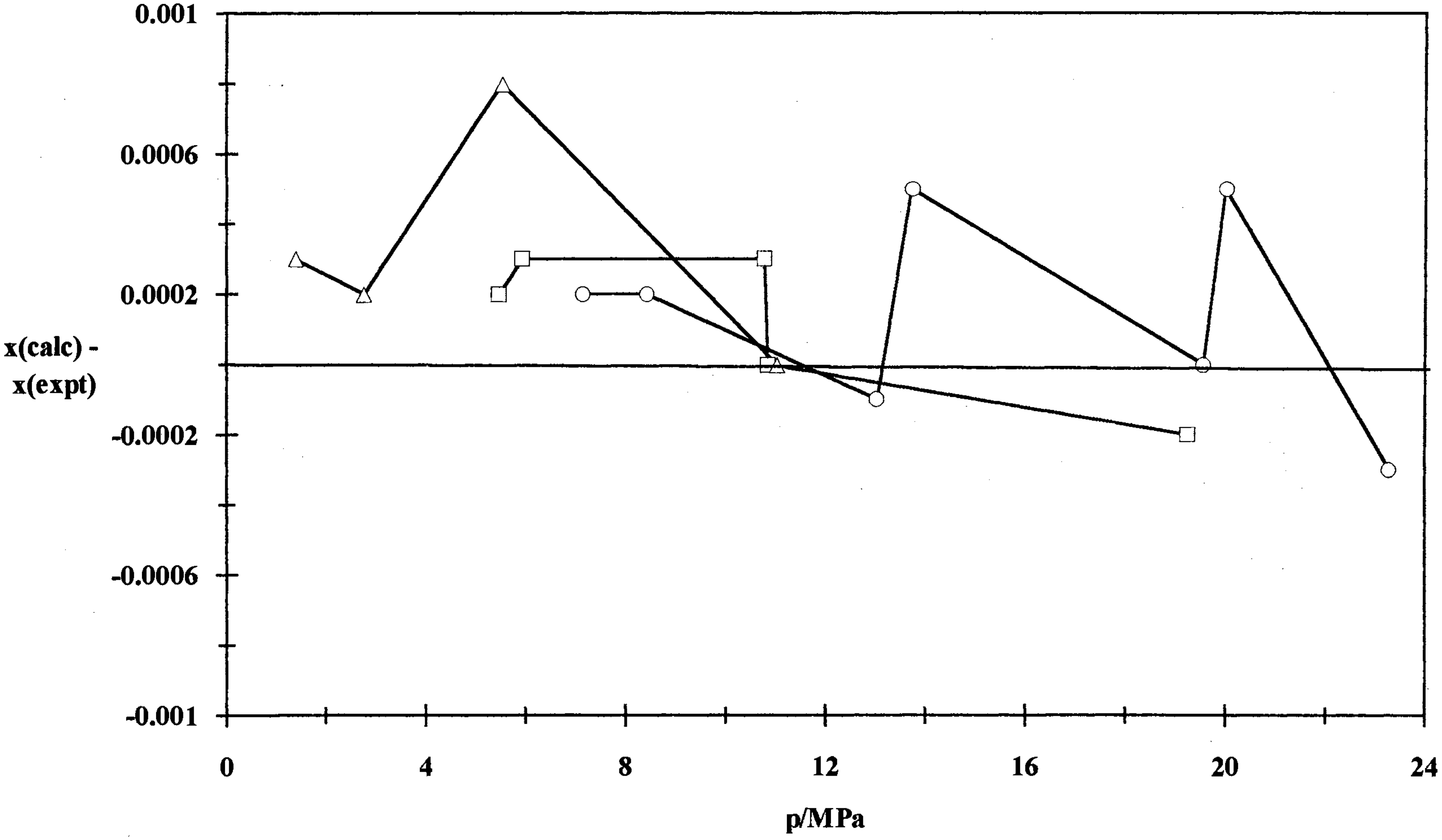


Figure 3. Comparison of Carbon Monoxide Solubilities in Phenanthrene. ○ 383.2 K This work; □ 423.2 K This work; Δ 377.6 K DeVaney (with $C_{ij} = 0.1567$)

the values fitted by present data for each isotherm. The figure shows good agreement between the present data and those of DeVaney and coworkers; deviations within the experimental uncertainty of 0.001 are observed. No literature data for the solubility of carbon monoxide in naphthalene and pyrene are available for comparison.

The SRK [1] and PR [2] cubic equations of state were used to correlate the experimental data . The SRK equation is given as follows:

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{3-1}$$

where

$$a(T) = a_c \alpha(T) \tag{3-2}$$

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

and

$$a_c = 0.42748\ R^2 T_c^2 / P_c \tag{3-4}$$

$$\alpha(T)^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \tag{3-5}$$

$$\kappa = 0.480 + 1.574\ \omega - 0.176\ \omega^2 \tag{3-6}$$

Similarly, the PR equation is given as follows:

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{3-7}$$

where

$$a(T) = a_c \alpha(T) \tag{3-8}$$

$$b = 0.07780\, RT_c / P_c \tag{3-9}$$

and

$$a_c = 0.45724\, R^2T_c^2 / P_c \tag{3-10}$$

$$\alpha(T)^{1/2} = 1 + \kappa(1 - T_r^{1/2}) \tag{3-11}$$

$$\kappa = 0.37464 + 1.54226\, \omega - 0.26992\, \omega^2 \tag{3-12}$$

To apply the SRK or PR equations of state to mixtures, the values of a and b can be determined using the following mixing rules [13]:

$$a = \sum_i^N \sum_j^N z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{3-13}$$

$$b = \sum_i^N \sum_j^N z_i z_j (1 + D_{ij}) \frac{b_i + b_j}{2} \tag{3-14}$$

In Equations (3-13) and (3-14), 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". Values of these parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of square errors in predicted bubble point pressures.

$$SS = \sum_i^n (p_{expt} - p_{calc})_i^2 \tag{3-15}$$

Further details on the data reduction techniques used in this study are given by Gasem [5]. 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 V.

TABLE V

CRITICAL PROPERTIES USED IN THE SRK AND PR EOS FOR CARBON MONOXIDE AND SELECTED AROMATICS

Component	P_c/MPa	T_c/K	ω	Reference
Carbon Monoxide	3.49	132.9	0.049	14
Naphthalene	4.05	748.4	0.302	15
Phenanthrene	3.30	873.2	0.540	16
Pyrene	2.60	938.2	0.830*	17

* Turek, E. A., (AMOCO Production Company, Tulsa, OK), Personal Communication (1988)

The equation-of-state representations of the solubilities for the systems considered are shown in Tables VI to VIII. In general, the SRK and PR equations are capable of describing the data with RMS errors within 0.001 in mole fraction for a given system when a single interaction parameter, C_{ij}, is used over the complete temperature range. As shown in Figure 4, the values of C_{ij} for both the SRK and the PR equations increase as the solvent molecular weight increases. The ability of equations of state to predict solubility is marginally improved (RMS = 0.0008) when an additional interaction parameter, D_{ij}, is employed.

As expected, improvements are realized by using temperature dependent interaction parameters; when two parameters (C_{ij} and D_{ij}) are fitted to each isotherm (for which the results are not presented here), the RMS errors are reduced to about 0.0004. The results in Tables VI-VIII show that the use of a single interaction parameter, C_{ij}, per binary system produces good equation-of-state representation (RMS within 0.001 in mole fraction) for the systems considered. In contrast to previous analysis involving CO_2, methane and ethane solubilities in heavy hydrocarbons [18-23], the low solubility of

TABLE VI

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF CARBON MONOXIDE (1) IN NAPHTHALENE (2)

T/K	Soave Parameters (PR Parameters)	Error in Carbon Monoxide Mole Fraction*	
	C_{12}	RMS	|MAX|
373.2	0.1252 (0.1506)	0.0004	0.0006
423.2	0.1140 (0.1375)	0.0004	0.0008
373.2 and 423.2	0.1219	0.0007	0.0019
	(0.1466)	0.0009	0.0023

* The RMS and Maximum errors in carbon monoxide mole fraction are essentially the same for the SRK and PR equations of state, unless separate results are shown.

TABLE VII

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF CARBON MONOXIDE (1) IN PHENANTHRENE (2)

T/K	Soave Parameters (PR Parameters)	Error in Carbon Monoxide Mole Fraction	
	C_{12}	RMS	|MAX|
383.2	0.1561 (0.1900)	0.0003	0.0005
423.2	0.1520 (0.1844)	0.0002	0.0003
383.2 and 423.2	0.1550 (0.1884)	0.0003	0.0006

TABLE VIII

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF CARBON MONOXIDE (1) IN PYRENE (2)

T/K	Soave Parameters (PR Parameters)	Error in Carbon Monoxide Mole Fraction	
	C_{12}	RMS	|MAX|
433.2	0.2158 (0.2551)	0.0003	0.0004

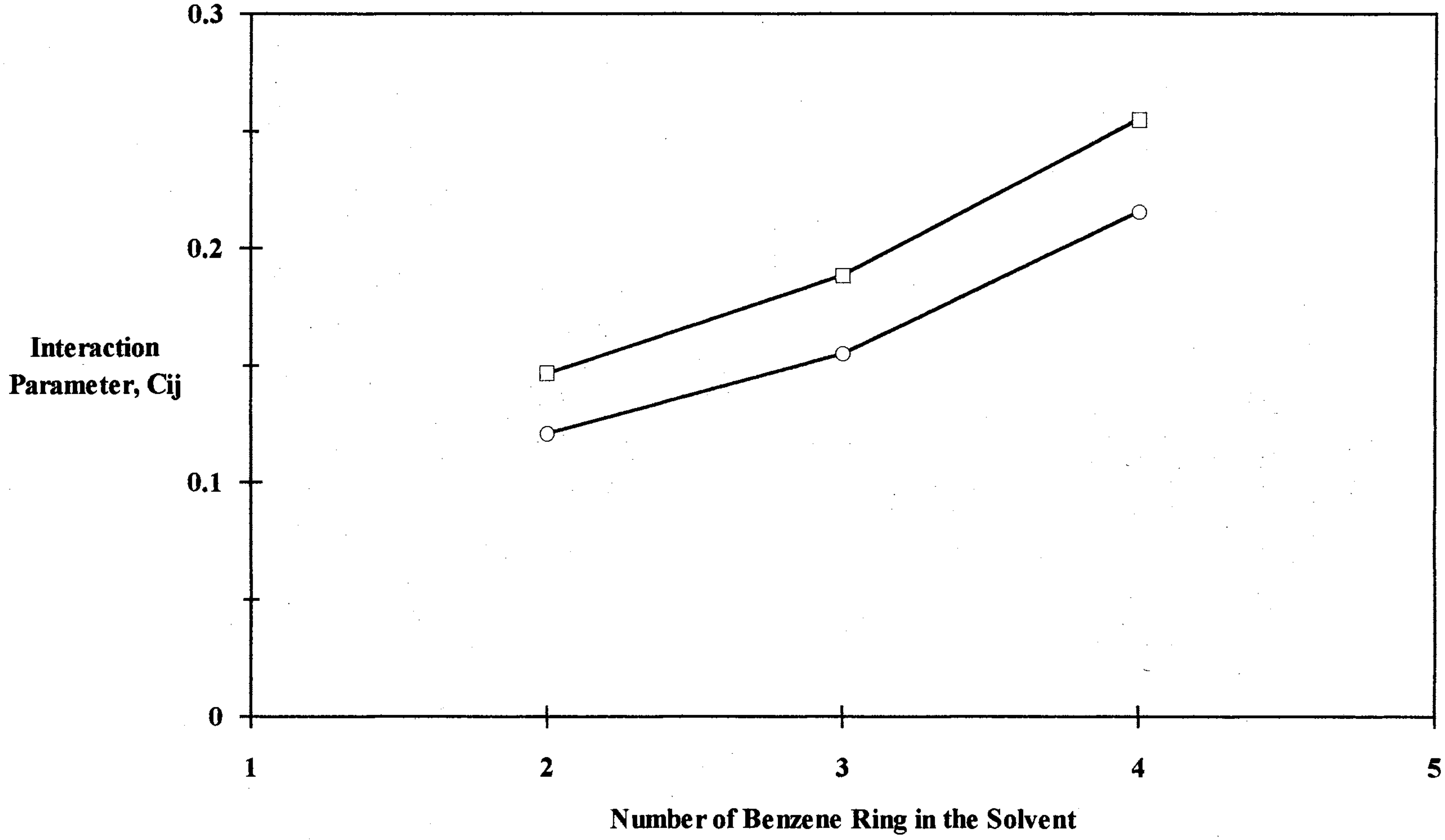


Figure 4. Binary Interaction Parameter Dependence on Solvent Molecular Weight for Carbon Monoxide in Aromatics.
○ The SRK Equation; □ The PR Equation

carbon monoxide in the aromatic solvents (at pressures to 23 MPa) has tempered the need for the second interaction parameter, D_{ij}. Moreover, a high degree of correlation is observed between C_{ij} and D_{ij} when both were regressed simultaneously. Thus, detailed study of data regressions including the second interaction parameter was not pursued.

In general, the RMS errors in mole fraction are comparable to the estimated uncertainties for the measurements. These results illustrate both the ability of the equations of state and the precision of the experimental measurements.

Conclusions

Data have been obtained for the solubility of carbon monoxide in naphthalene, phenanthrene and pyrene at temperatures from 373.2 to 433.2 K and pressures up to 23.2 MPa. These data are well described by the SRK and PR equations of state using a single interaction parameter. The present data combined with previous OSU measurements involving n-paraffins should serve as an excellent complement to the literature data, and should prove highly useful in model development.

CHAPTER IV

SOLUBILITIES OF HYDROGEN IN N-DECANE, N-EICOSANE, N-OCTACOSANE AND N-HEXATRIACONTANE AT TEMPERATURES FROM 323.2 TO 423.2 K AND PRESSURES TO 17.4 MPA

Abstract

The solubilities of hydrogen in n-decane, n-eicosane, n-octacosane and n-hexatriacontane were measured over the temperature range from 323.2 to 423.2 K and pressures to 17.4 MPa. The uncertainty in these new solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS). In general, the two equations represent the experimental data well when a single interaction parameter, C_{ij}, is used for each isotherm of each binary system. However, the interaction parameter is highly dependent on temperature.

Introduction

Vapor-liquid equilibrium properties of mixtures involving hydrogen and heavy hydrocarbon solvents are of interest in many industries. In particular, design and development of chemical processes such as coal conversion and hydrocarbon reforming processes require accurate phase behavior predictions for these systems. Since the

It has been argued that cubic equations of state such as the SRK and PR equations, which are widely used in industry, do not have good predictive capabilities for the phase behavior of the mixtures containing hydrogen [24-27]. This is attributed to the low critical temperature value used to determine the EOS pure component parameters for hydrogen. EOS parameters then obtained are different from the general trend describing other small molecules such as methane, ethane, carbon dioxide, and carbon monoxide.

A number of investigators have attempted to correlate the phase behavior of hydrogen + hydrocarbon binary systems. Prausnitz and his coworkers modified the SRK equation of state to improve the predictive capability for the systems containing hydrogen [24]. The same approach was pursued by Graboski and Daubert [25]. Lin compared the predictive abilities of the modified SRK equations of state with the original SRK equation and concluded that the original SRK EOS is better than the modified versions for the systems containing heavy hydrocarbons [27]. Preliminary analysis of the present data support Lin's findings. Therefore, the original SRK and PR equations were elected for this work, along with the experimental values for hydrogen's critical properties and acentric factor.

In this chapter, binary measurements for the solubilities of hydrogen in n-decane, n-eicosane, n-octacosane and n-hexatriacontane are presented. These data cover temperatures from 323.2 to 423.2 K and pressures to 17.4 MPa. The data have been correlated using the Soave-Redlich-Kwong (SRK) [1] and Peng-Robinson (PR) [2] equations of state. The binary interaction parameter, C_{ij}, regressed from the experimental measurements can be used to predict multicomponent phase behavior within the limit of experimental conditions considered in this work.

Results and Data Correlations

The hydrogen solubility measurements are presented in Tables IX to XII. In general, the lowest temperature studied for a given system was dictated by the melting point of the solvent or the availability of literature data. The effect of temperature and pressure on the solubility of hydrogen in n-decane is shown in Figure 5. A trend of increasing solubility with increased temperature and pressure is observed. A similar trend is observed for the rest of the solvents studied.

Nederbragt presented solubility data of hydrogen in n-decane at 80 °C [28]. Similarly, Sebastian and coworkers reported the same kind of data at elevated temperatures (464.5 K and above) [29]. Since the data taken in this work are different in temperature from these literature data, a comparison was not attempted. Comparisons for the data acquired on hydrogen + n-eicosane, hydrogen + n-octacosane and hydrogen + n-hexatriacontane binaries with those of Huang [30] at 373.2 K are shown in Figures 6, 7 and 8, respectively. The actual temperatures for Huang's data were 373.4 K for the hydrogen + n-eicosane and 373.3 K for the hydrogen + n-octacosane; thus, deviations of 0.2 K were assumed insignificant for the purposes of data comparison. The comparisons are shown in terms of deviations of the predicted solubilities using the SRK EOS from the experimental measurements, as discussed in Chapter III. The binary interaction parameter, C_{ij}, employed in the EOS predictions was obtained by fitting the present data for the isotherm under study. Figures 6, 7 and 8 show reasonable agreement between the data of the present work and those of Huang.

The SRK [1] and PR [2] cubic equations of state were used to correlate the experimental data. These equations and the corresponding mixing rules are given in Chapter III. Values of the binary interaction parameters were determined by fitting the experimental data to minimize the objective function, which is expressed as the sum of the squared errors in the predicted bubble point pressures. Further details for the data

TABLE IX

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

x_1	p/MPa	x_1	p/MPa
---------- 344.3 K (71.1 °C, 160.0 °F) ----------			
0.0369	4.46	0.0958	12.46
0.0576	7.13	0.1094	14.46
0.0682	8.60	0.1288	17.39
---------- 373.2 K (100.0 °C, 212.0 °F) ----------			
0.0418	4.41	0.0963	10.85
0.0557	5.96	0.1124	12.93
0.0760	8.36	0.1286	15.04
---------- 423.2 K (150.0 °C, 302.0 °F) ----------			
0.0435	3.71	0.0914	8.13
0.0561	4.82	0.1232	11.32
0.0851	7.48	0.1264	11.66

TABLE X

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

x_1	p/MPa	x_1	p/MPa
---------------------------- 323.2 K (50.0 °C, 122.0 °F) ----------------------------			
0.0320	3.26	0.0964	10.51
0.0333	3.40	0.0978	10.71
0.0644	6.77	0.1152	12.91
0.0663	7.02		
---------------------------- 373.2 K (100.0 °C, 212.0 °F) ----------------------------			
0.0273	2.23	0.0811	7.01
0.0296	2.41	0.0989	8.69
0.0371	3.09	0.1147	10.40
0.0686	5.81	0.1289	11.82
0.0776	6.73		
---------------------------- 423.2 K (150.0 °C, 302.0 °F) ----------------------------			
0.0410	2.81	0.0874	6.24
0.0573	3.97	0.1064	7.75
0.0756	5.33	0.1246	9.30

TABLE XI

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

x_1	p/MPa	x_1	p/MPa
---------------------------- 348.2 K (75 .0 °C, 167.0 °F) --------------------------------------			
0.0451	3.53	0.1138	9.59
0.0763	6.14	0.1294	11.11
0.0894	7.31	0.1485	13.10
---------------------------- 373.2 K (100.0 °C, 212.0 °F) --------------------------------------			
0.0572	4.02	0.1123	8.41
0.0614	4.34	0.1572	12.43
0.1076	8.00		
---------------------------- 423.2 K (150.0 °C, 302.0 °F) --------------------------------------			
0.0503	2.86	0.1235	7.47
0.0524	2.95	0.1407	8.74
0.0747	4.34	0.1511	9.53
0.0921	5.43	0.1728	11.24
0.1047	6.23		

TABLE XII

SOLUBILITY OF HYDROGEN (1) IN N-HEXATRIACONTANE (2)

x_1	p/MPa	x_1	p/MPa
---------------------------- 373.2 K (100.0 °C, 212.0 °F) --			
0.0677	4.11	0.1453	9.62
0.0813	4.99	0.2001	14.32
0.1287	8.32	0.2271	16.75
---------------------------- 423.2 K (150.0 °C, 302.0 °F) --			
0.0720	3.56	0.1545	8.39
0.0881	4.42	0.1941	11.08
0.1355	7.24	0.2080	12.00

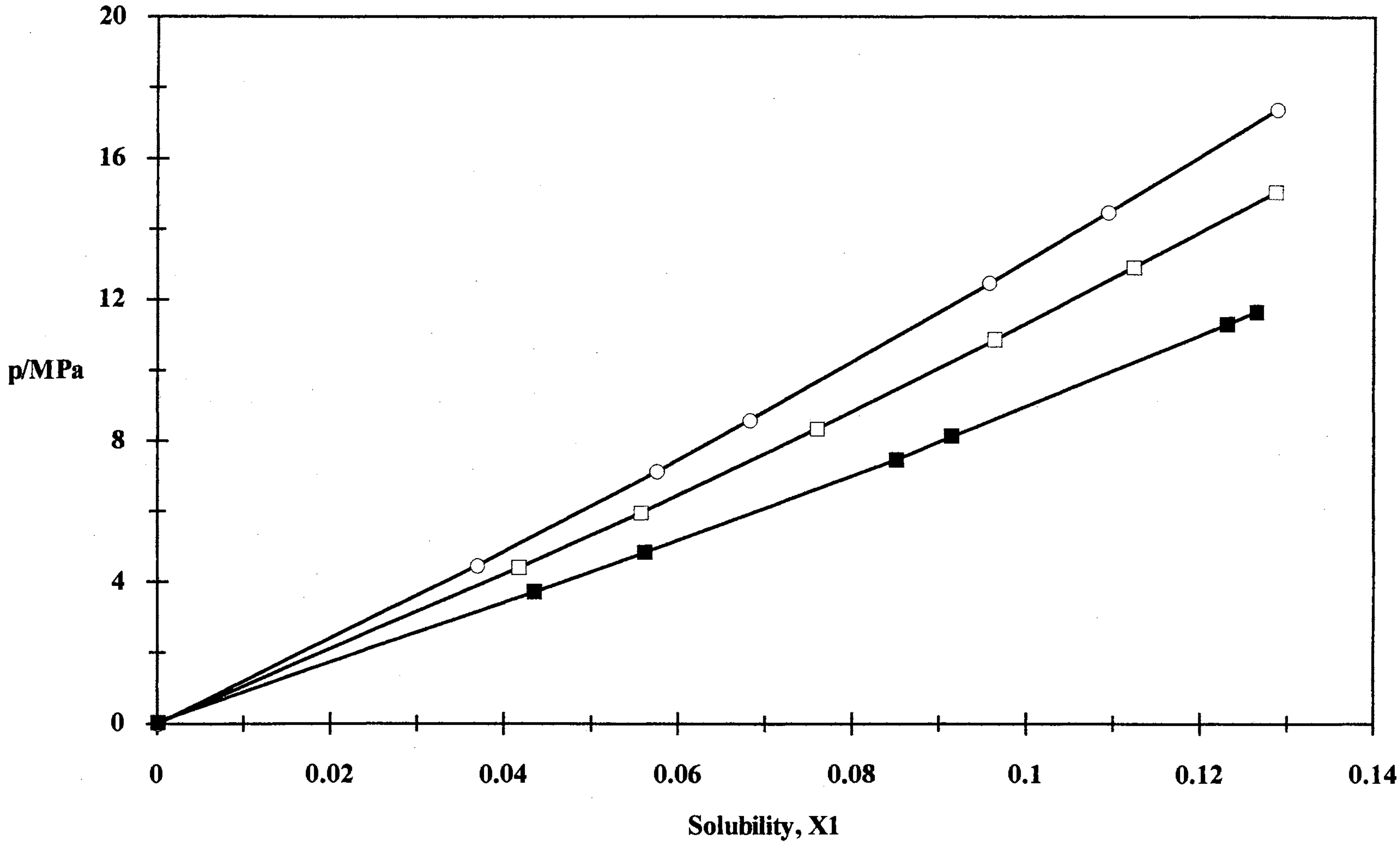


Figure 5. Solubility of Hydrogen in n-Decane. ○ 344.3 K; □ 373.2 K; ■423.2 K

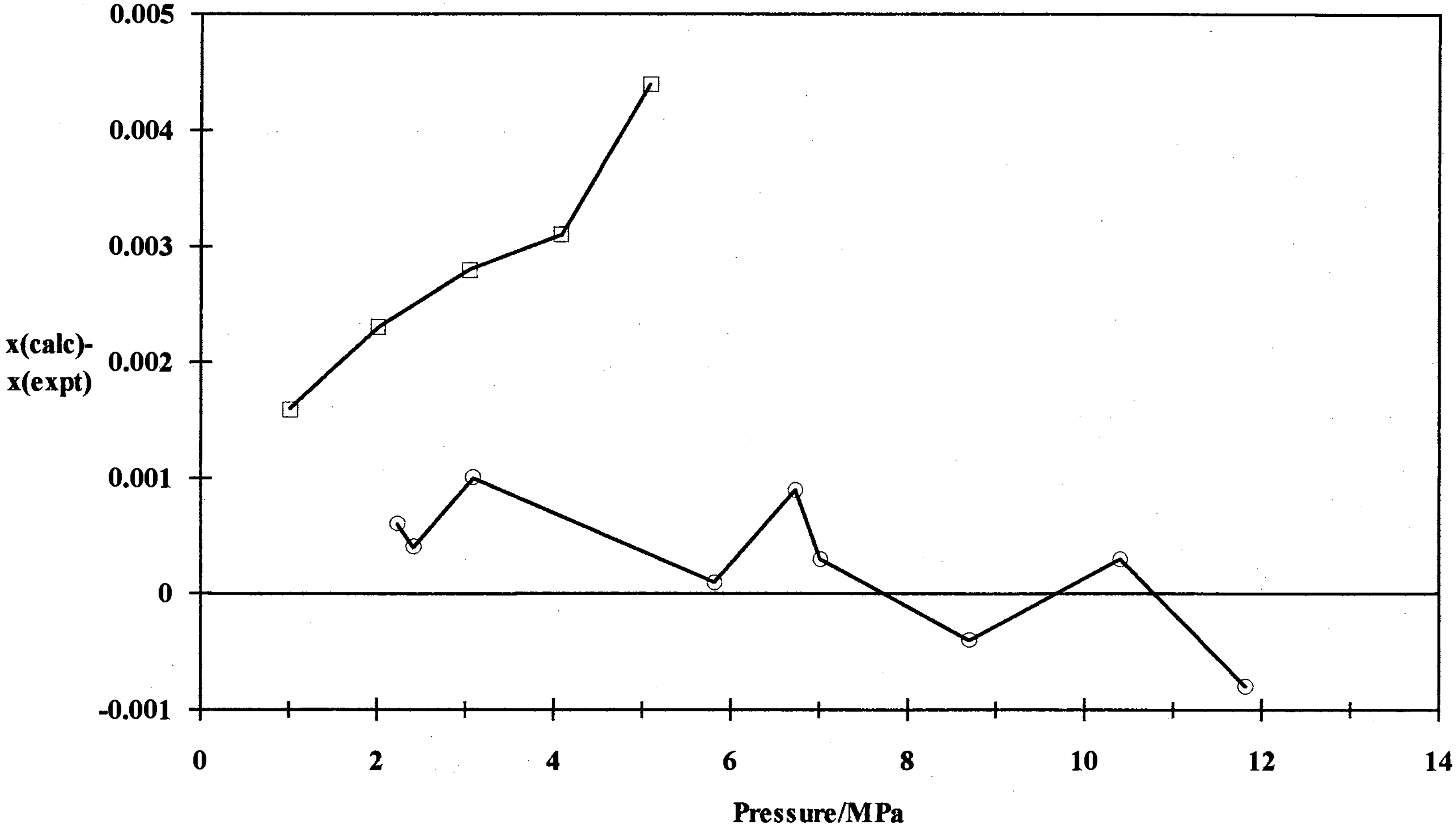


Figure 6. Comparison of Hydrogen Solubilities in n-Eicosane at 373.2 K. ○ This work; □ Huang

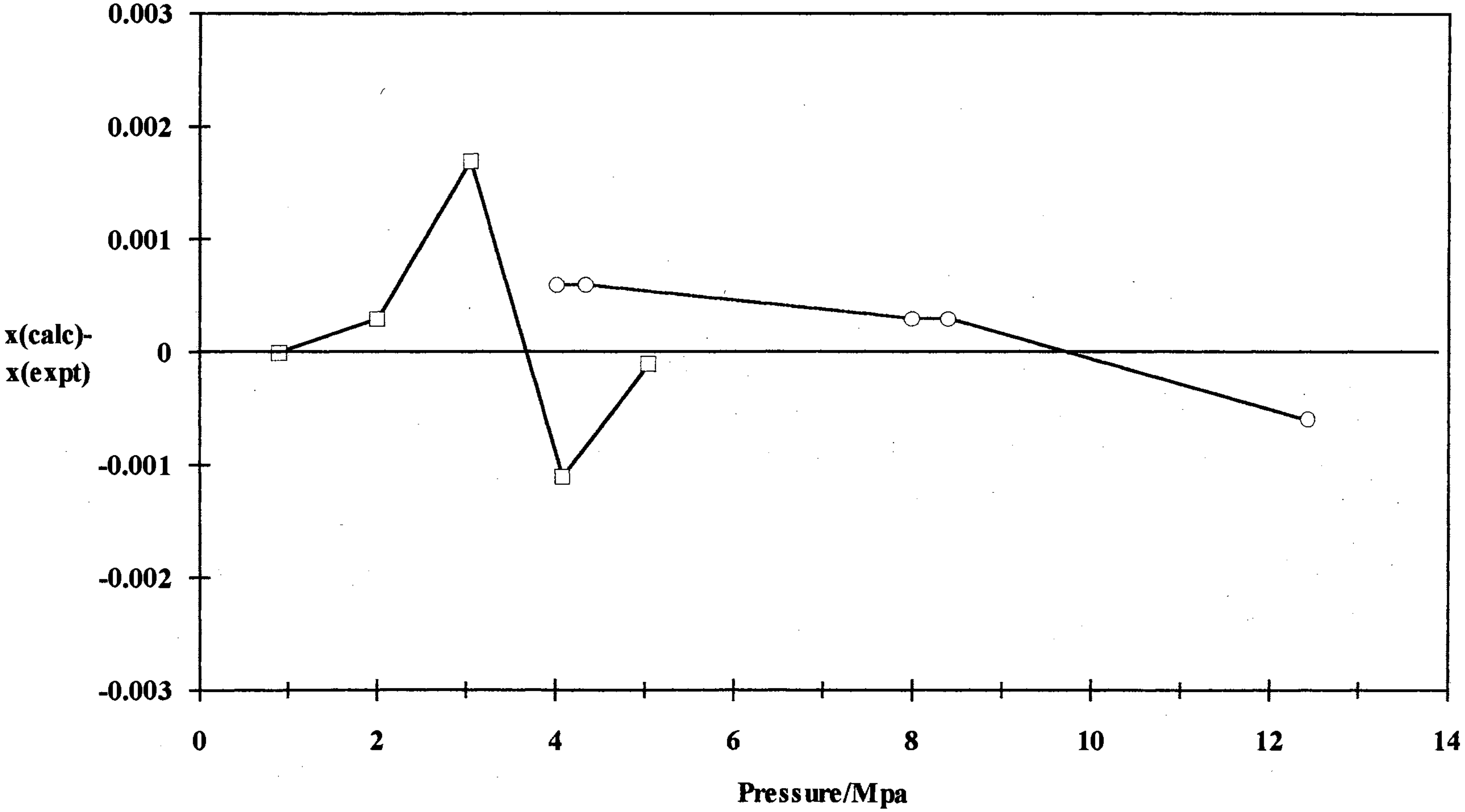


Figure 7. Comparison of Hydrogen Solubilities in n-Octacosane at 373.2 K. ○ This work; ☐ Huang

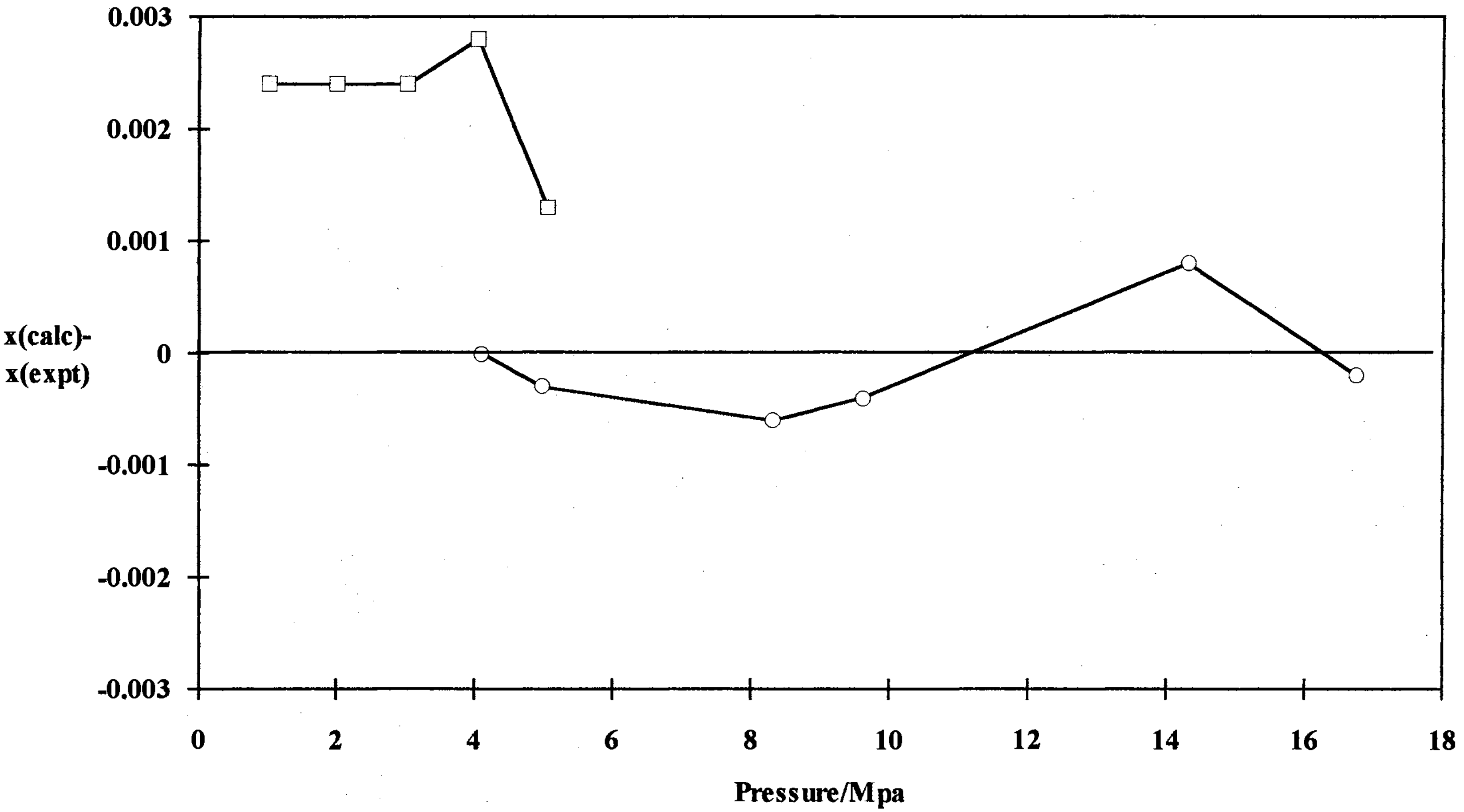


Figure 8. Comparison of Hydrogen Solubilities in n-Hexatriacontane at 373.2 K. ○ This work; □ Huang

reduction techniques used in this study are given by Gasem [5]. 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 XIII.

TABLE XIII

CRITICAL PROPERTIES USED IN THE SRK AND PR EOS FOR HYDROGEN AND SELECTED N-PARAFFINS

Component	P_C/MPa	T_C/K	ω	Reference
Hydrogen	1.300	33.2	-0.218	14
n-Decane	2.097	617.5	0.4885	5
n-Eicosane	1.117	770.5	0.8738	5
n-Octacosane	0.826	845.4	1.1073	5
n-Hexatriacontane	0.682	901.1	1.2847	5

The EOS representations of the solubilities for the systems considered are shown in Tables XIV to XVII. In general, the SRK and PR equations are capable of describing the data with RMS errors within 0.001 in mole fraction for a given system when a single interaction parameter, C_{ij}, is used for each isotherm of each binary mixture. As shown in the EOS representations, the values of the interaction parameters are relatively large (greater than 0.4 for all binary mixtures studied in this work) compared to those of systems containing methane, ethane, carbon dioxide. [18-23]. The temperature effect on C_{ij} for hydrogen + n-decane mixtures are shown in Figure 9. As the temperature increases, the value of C_{ij} increases for these mixtures. The same trend is observed for hydrogen + n-eicosane mixtures. However, the C_{ij} values for hydrogen + n-octacosane and hydrogen + n-hexatriacontane decrease as the temperature increases.

TABLE XIV

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN N-DECANE (2)

T/K	Soave Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
344.3	0.4200	0.0011	0.0015
	(0.3935)	(0.0008)	(0.0011)
373.2	0.4685	0.0008	0.0011
	(0.4135)	(0.0005)	(0.0010)
423.2	0.5835	0.0008	0.0012
	(0.4620)	(0.0004)	(0.0006)

TABLE XV

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN N-EICOSANE (2)

T/K	Soave Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
323.2	0.3682	0.0007	0.0010
	(0.3781)	(0.0006)	(0.0008)
373.2	0.3849	0.0006	0.0010
	(0.3656)	(0.0004)	(0.0007)
423.2	0.4070	0.0005	0.0008
	(0.3490)	(0.0002)	(0.0004)

TABLE XVI

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN N-OCTACOSANE (2)

T/K	Soave Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
348.2	0.2911	0.0005	0.0009
	(0.3283)	(0.0003)	(0.0007)
373.2	0.2560	0.0005	0.0006
	(0.2915)	(0.0002)	(0.0003)
423.2	0.1697	0.0005	0.0009
	(0.2056)	(0.0006)	(0.0011)

TABLE XVII

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN N-HEXATRIACONTANE (2)

T/K	Soave Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
373.2	0.0828	0.0005	0.0008
	(0.1876)	(0.0008)	(0.0011)
423.2	-0.0560	0.0005	0.0007
	(0.0695)	(0.0008)	(0.0013)

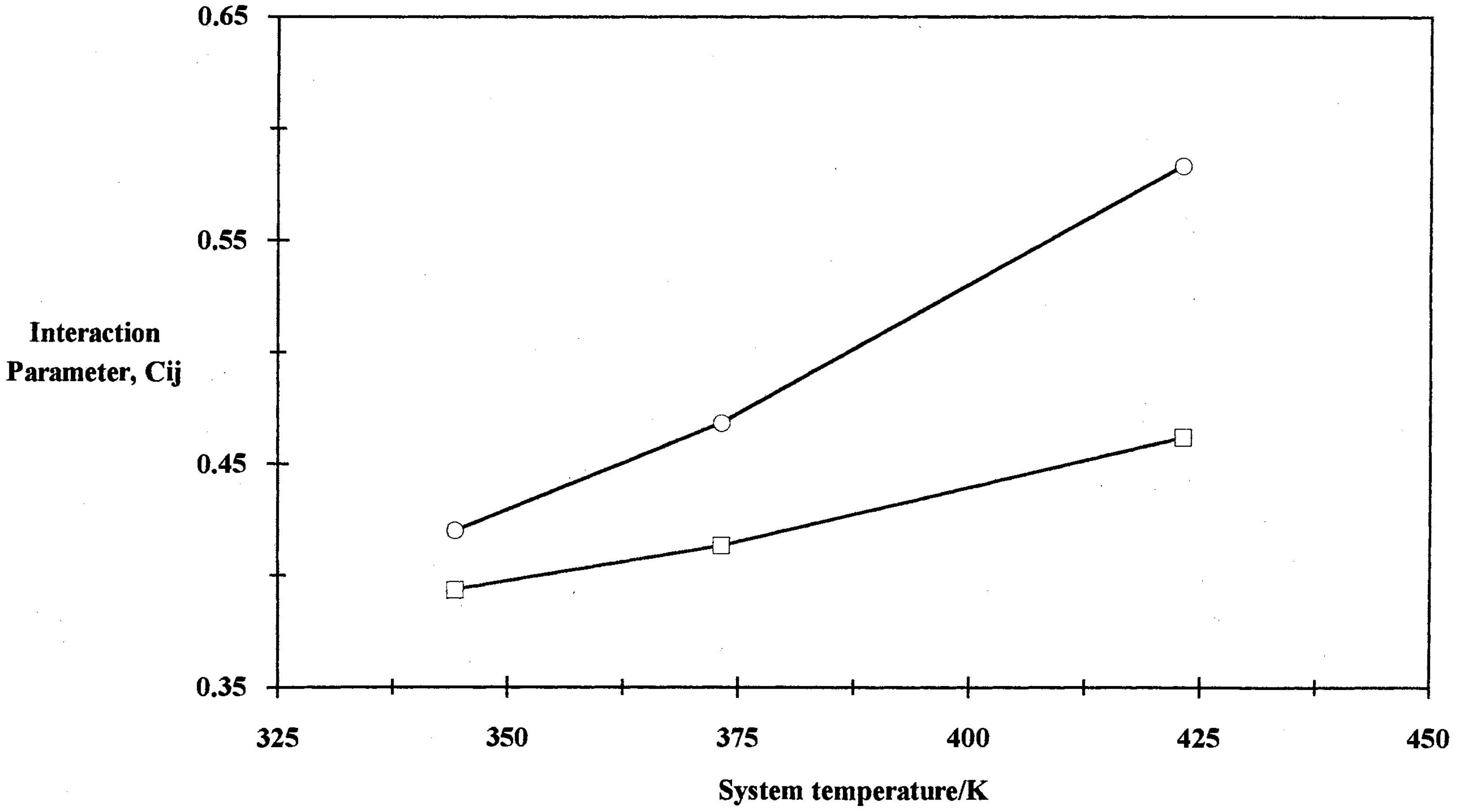


Figure 9. Temperature Dependence of C_{ij} for Hydrogen + n-Decane Mixtures.
○ The SRK Equation; □ The PR Equation

The effect of solvent molecular weight at 373.2 K is shown in Figure 10. The figure shows the decreasing trend of C_{ij} values for both the SRK and the PR equations as the solvent molecular weight increases. The trend is the same for the different isotherms studied. As indicated by Tables XIV to XVII, C_{ij} is highly dependent on temperature. Moreover, preliminary evaluations have indicated that the second interaction parameter D_{ij} was negligible for all the binary systems studied. Thus, regressions including the second interaction parameter, D_{ij}, were not pursued further.

The SRK and PR equations of state have similar predictive capability for most of the binary systems considered. However, while the SRK equation of state shows better results for hydrogen + n-hexatriacontane binary systems, the PR equation shows better results for hydrogen + n-decane systems. In general, the RMS errors in mole fraction for both equations are comparable to the estimated uncertainties for the measurements. Hence, the results illustrate both the ability of the equations of state and the precision of the experimental data.

Conclusions

Data have been obtained for the solubility of hydrogen in n-decane, n-eicosane, n-octacosane and n-hexatriacontane at temperatures from 323.2 to 423.2 K and pressures up to 17.4 MPa. These data are well described by the SRK and PR equations of state using a single interaction parameter for each isotherm. The newly acquired data for hydrogen solubilities should prove to be a valuable addition to the present OSU database on asymmetric mixtures. Collectively such data are essential in modeling the phase behavior of these systems.

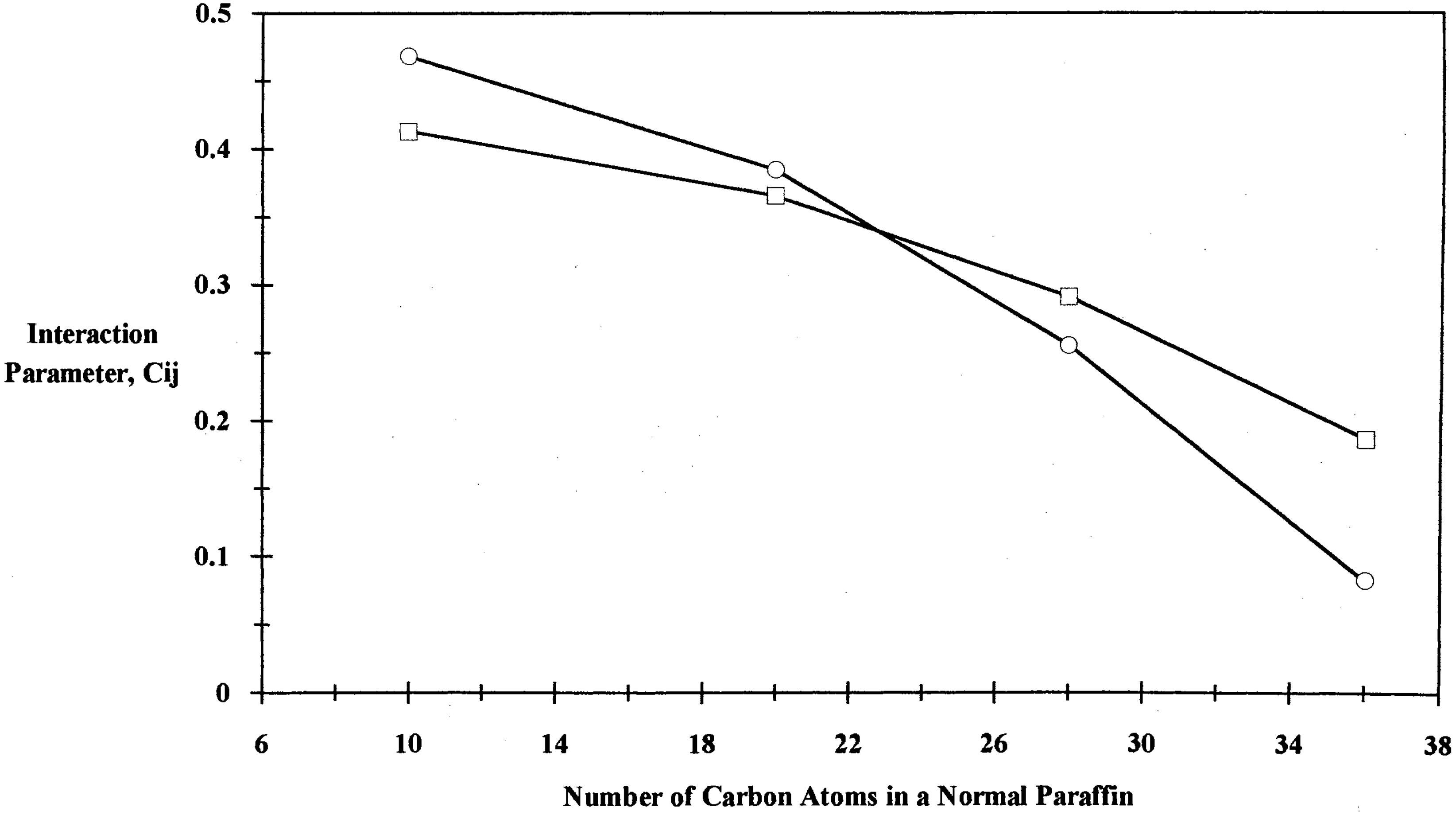


Figure 10. Binary Interaction Parameter Dependence on Solvent Molecular Weight for Hydrogen in n-Paraffin Binary Mixture at 373.2 K. ○ The SRK Equation; □ The PR Equation

CHAPTER V

SOLUBILITIES OF HYDROGEN IN BENZENE, NAPHTHALENE, PHENANTHRENE AND PYRENE AT TEMPERATURES FROM 323.2 TO 433.2 K AND PRESSURES TO 21.7 MPA

Abstract

The solubilities of hydrogen in benzene, naphthalene, phenanthrene and pyrene were measured using a static equilibrium cell over the temperature range from 323.2 to 433.2 K and pressures to 21.7 MPa. The uncertainty in these new solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. In general, the two equations represent the experimental data well when a single interaction parameter, C_{ij}, is used for each isotherm. The present data suggest that the interaction parameter is highly dependent on temperature. Regressions including a second interaction parameter were not considered.

Introduction

Interest in coal liquefaction and gasification has created a great demand for phase equilibrium data of mixtures containing hydrogen. Also, numerous industrial processes such as petroleum refining, hydrocarbon reforming, enhanced oil recovery, and supercritical separation require fluid phase equilibrium data and accurate models for asymmetric mixtures. These mixtures, which involve small gas molecules (such as carbon dioxide, hydrogen, methane, ethane, and carbon monoxide) and heavy hydrocarbon solvents, often elude the current predictive models and the associated mixing theories.

In this chapter, binary measurements for the solubility of hydrogen in selected aromatic solvents (benzene, naphthalene, phenanthrene and pyrene) are presented. These data cover temperatures from 323.2 to 433.2 K and pressures to 21.7 MPa. The new measurements are a complement to the previous measurements for hydrogen solubilities in normal paraffins presented in Chapter IV. The acquired data have been correlated using the SRK [1] and PR [2] equations of state and compared with the available literature data.

Results and Data Correlations

The newly acquired data for hydrogen solubility in benzene, naphthalene, phenanthrene and pyrene are presented in Tables XVIII to XXI. The effect of temperature and pressure on the solubility of hydrogen in benzene is shown in Figure 11. A trend of increasing solubility with increasing temperature and pressure is observed. A similar trend is also observed for the hydrogen binaries of naphthalene and phenanthrene. This behavior is identical to that obtained for carbon monoxide in aromatics as presented in Chapter III, as well as that of hydrogen in selected heavy normal paraffins given in Chapter IV. In contrast, the solubility of methane, ethane and carbon dioxide in hydrocarbon solvents exhibited a trend of decreasing solubilities with increasing temperature [18-23]. For hydrogen + pyrene systems, the temperature effect on hydrogen solubility was not studied.

A number of experimental studies on the solubility of hydrogen in benzene have appeared in the literature. Connolly reported smoothed vapor-liquid equilibrium (T-P-x-y) data for this binary at elevated temperatures (433.2 to 533.2 K) [8]. Thompson and Edmister provided vapor-liquid equilibrium data for the hydrogen binary mixtures of benzene and cyclohexane [31]. Similarly, Brainard and Williams reported experimental

TABLE XVIII

SOLUBILITY OF HYDROGEN (1)
IN BENZENE (2)

x_1	p/MPa	x_1	p/MPa
---------------------------- 323.2 K (50.0 °C, 122.0 °F) --			
0.0123	4.07	0.0290	9.80
0.0138	4.56	0.0351	11.97
0.0245	8.22	0.0455	15.73
---------------------------- 373.2 K (100.0 °C, 212.0 °F) --			
0.0103	2.55	0.0316	7.57
0.0173	4.15	0.0477	11.51
0.0233	5.60	0.0523	12.71
---------------------------- 423.2 K (150.0 °C, 302.0 °F) --			
0.0207	4.05	0.0400	7.40
0.0254	4.85	0.0569	10.44
0.0381	7.07	0.0585	10.73

TABLE XIX

SOLUBILITY OF HYDROGEN (1) IN NAPHTHALENE (2)

x_1	p/MPa	x_1	p/MPa
373.2 K (100.0 °C, 212.0 °F)			
0.0157	5.29	0.0362	12.35
0.0165	5.50	0.0530	18.53
0.0346	11.80	0.0553	19.39
423.2 K (150.0 °C, 302.0 °F)			
0.0166	4.29	0.0385	9.95
0.0189	4.84	0.0470	12.46
0.0273	7.06	0.0534	14.08
0.0337	8.77	0.0567	15.21

TABLE XX

SOLUBILITY OF HYDROGEN (1) IN PHENANTHRENE (2)

x_1	p/MPa	x_1	p/MPa
383.2 K (110.0 °C, 230.0 °F)			
0.0165	6.33	0.0398	15.78
0.0228	8.85	0.0492	19.79
0.0328	12.83	0.0535	21.69
423.2 K (150.0 °C, 302.0 °F)			
0.0187	5.89	0.0391	12.53
0.0226	7.14	0.0514	16.74
0.0354	11.31	0.0557	18.35

TABLE XXI

SOLUBILITY OF HYDROGEN (1) IN PYRENE (2)

x_1	p/MPa	x_1	p/MPa
433.2 K (160.0 °C, 320.0 °F)			
0.0158	5.17	0.0358	11.91
0.0185	6.05	0.0498	16.97
0.0325	10.80	0.0575	19.73

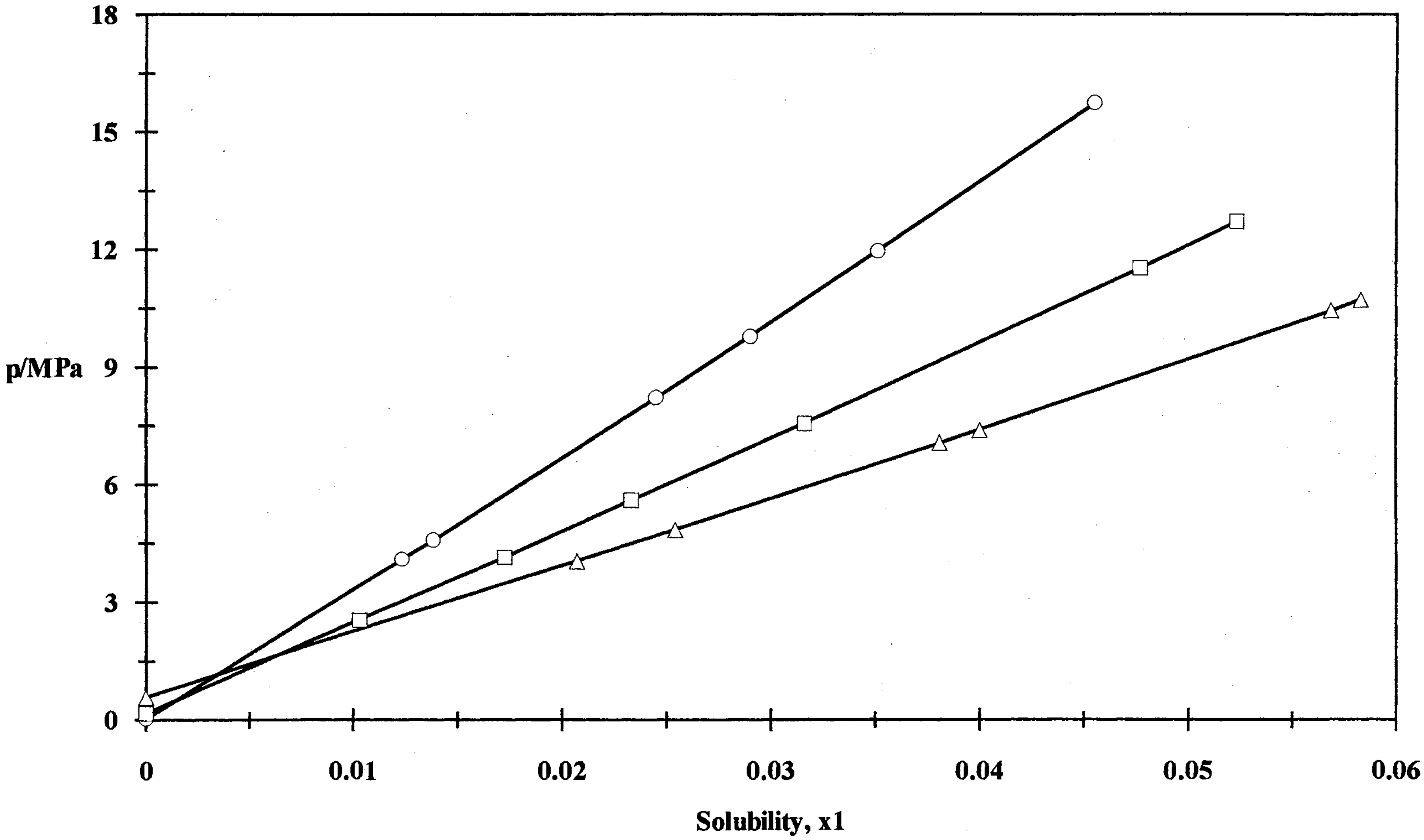


Figure 11. Solubility of Hydrogen in Benzene. ○ 323.2 K; □ 373.2 K; △ 423.5 K

data for the hydrogen binary systems involving benzene and cyclohexane along with quaternary vapor-liquid equilibrium data for mixtures containing hydrogen, benzene, cyclohexane and n-hexane [32]. These binary vapor-liquid equilibrium data were compared with the present work data. For comparison purposes, the interaction parameter, C_{ij}, of the SRK equation of state regressed from the present data was used in the prediction of solubilities. In comparisons with Connolly's and Thompson's data, the interaction parameter C_{ij} was extrapolated to the reported temperature of 433.2 K. For literature data within the temperature range of the present work, values of the interaction parameters were estimated using linear interpolation.

The solubility deviation plot for hydrogen + benzene is shown in Figure 12. All the data, except those of Brainard, are in good agreement with the present data. Among the data reported by Thompson and Edmister, the data point at 338.7 K and 48.25 MPa (6000 psia) showed a deviation of -0.0086 in solubility and even larger deviations at higher pressures. Similarly, three higher pressure points at 394.3 K showed large deviations. This implies that the regressed interaction parameters cannot be extrapolated away from the original conditions where the data regression was performed. Accordingly, literature data higher in pressure than 41.3 MPa (3000 psia) were not included in the deviation plot of Figure 12. Binary measurements for hydrogen + phenanthrene were reported by Malone and Kobayashi at 423.2 K [33]. A comparison of data on hydrogen + phenanthrene mixtures is shown in Figure 13. The figure indicates good agreement between the literature data and the measurements obtained in this study. No literature data for hydrogen + naphthalene and hydrogen + pyrene are available for comparison.

The equations of state, the corresponding mixing rules, and the data reduction techniques used in this study are the same as those used in Chapter III. However, regressions including the second interaction parameter, D_{ij}, were not considered in this work. The input parameters for the pure components (acentric factors, critical

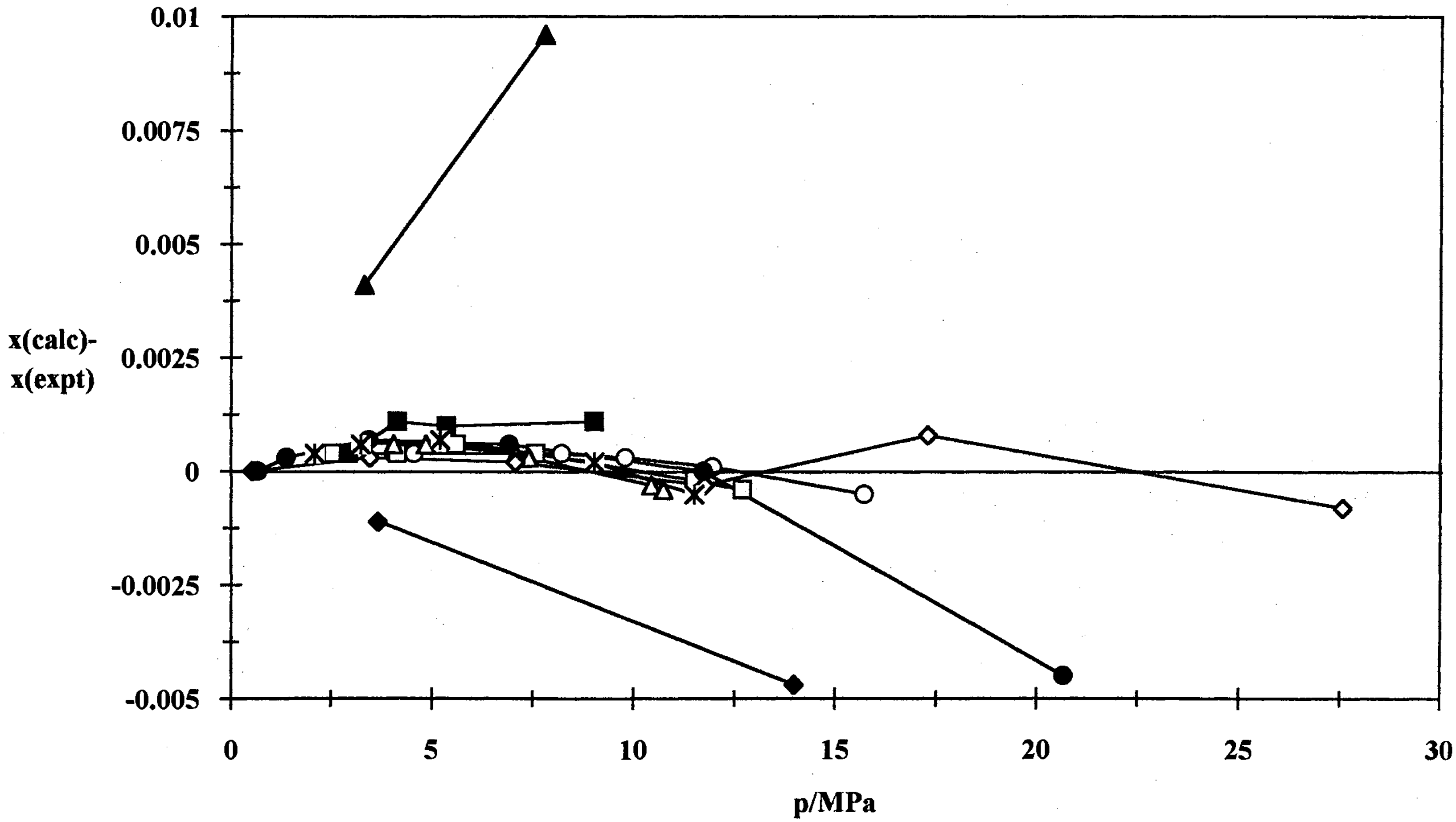


Figure 12. Comparison of Hydrogen Solubilities in Benzene. ○ 323.3 K □ 373.2 K △ 423.2 K This work; ◇ 338.7 K ● 394 K ■ 433.2 K Thompson; ▲ 366.5 ◆ 422.0 K Brainard; * 433.2 K Connolly

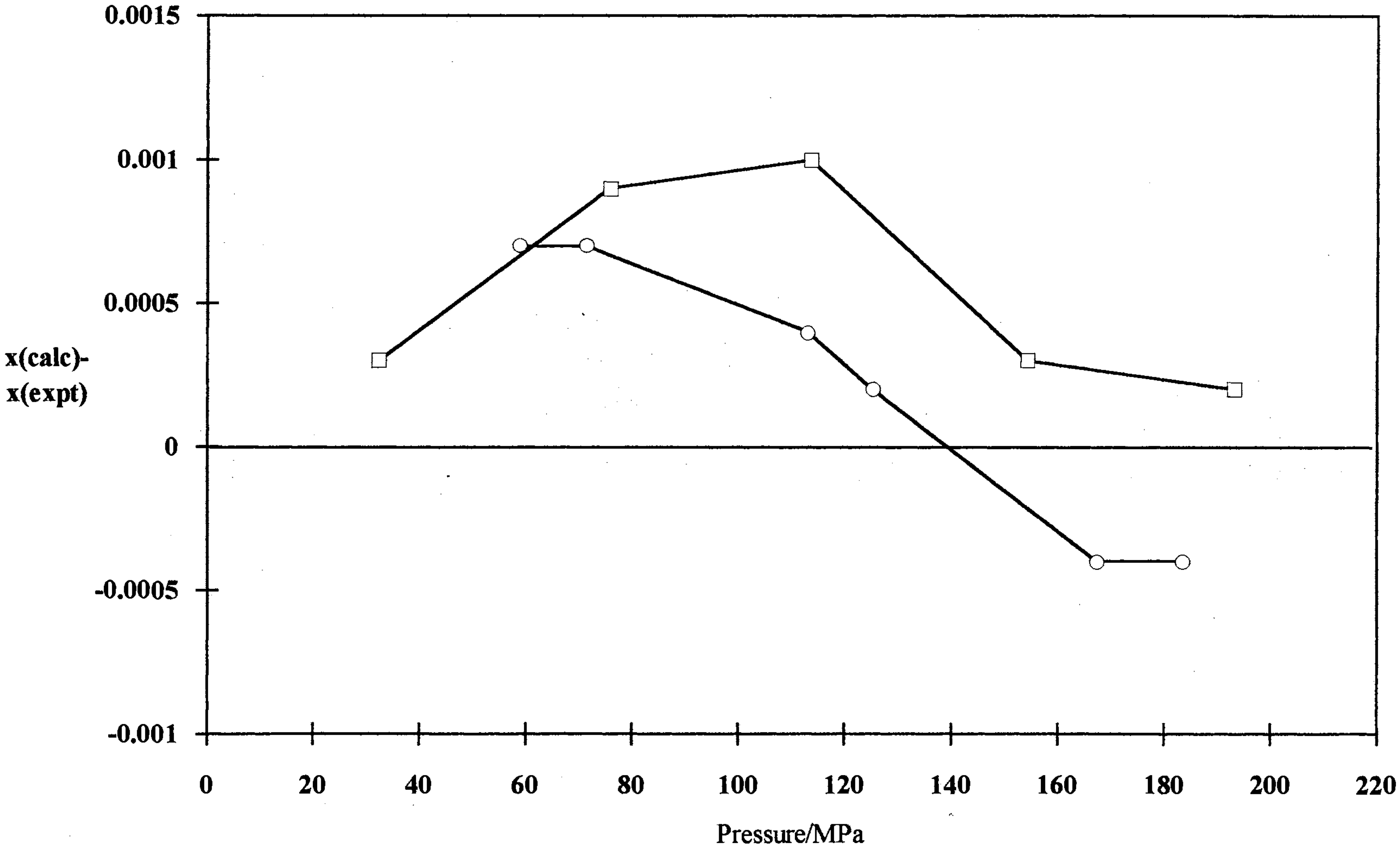


Figure 13. Comparison of Hydrogen Solubilities in Phenanthrene at 423.2 K. ○ This work; ☐ Malone

temperatures and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table XXII.

TABLE XXII

CRITICAL PROPERTIES USED IN THE SRK AND PR EOS FOR HYDROGEN AND SELECTED AROMATICS

Component	p_c/MPa	T_c/K	ω	Reference
Hydrogen	1.30	33.2	-0.218	14
Benzene	4.89	562.2	0.209	34
Naphthalene	4.05	748.4	0.302	15
Phenanthrene	3.30	873.2	0.540	16
Pyrene	2.60	938.2	0.830*	17

* Turek, E. A., (AMOCO Production Company, Tulsa, OK), Personal Communication (1988)

A preliminary study indicated that both SRK and PR equations of state do not represent the hydrogen solubility data adequately without interaction parameters. As expected, interaction parameters are required for systems which are highly asymmetric like the binary mixtures studied in the present work. The EOS representations of the solubilities for the systems considered are shown in Tables XXIII to XXVI. In general, the SRK and PR equations are capable of describing the data with RMS errors usually within 0.001 in mole fraction, when a single interaction parameter, C_{ij}, is used for each isotherm. The data reduction indicates that C_{ij} is highly dependent on temperature. Generally, the values of C_{ij} of both the SRK and PR equations increase as temperature increases for all the binary mixtures studied. The temperature effect on the interaction parameter is shown in Figure 14 for hydrogen + benzene binaries. The figure indicates

TABLE XXIII

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN BENZENE (2)

T/K	SRK Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
323.2	0.3479	0.0004	0.0005
	(0.3681)	(0.0003)	(0.0005)
373.2	0.4168	0.0004	0.0006
	(0.3991)	(0.0004)	(0.0005)
423.2	0.5450	0.0005	0.0006
	(0.4627)	(0.0003)	(0.0004)
344.3, 373.2 and	0.3818	0.0028	0.0058
423.2	(0.3861)	(0.0019)	(0.0039)

TABLE XXIV

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN NAPHTHALENE (2)

T/K	SRK Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
373.2	0.3685	0.0006	0.0009
	(0.3895)	(0.0006)	(0.0008)
423.2	0.4278	0.0005	0.0007
	(0.4127)	(0.0004)	(0.0006)
373.2 and 423.2	0.3865	0.0011	0.0016
	(0.3971)	(0.0007)	(0.0010)

TABLE XXV

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN PHENANTHRENE (2)

T/K	SRK Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
383.2	0.3245 (0.3766)	0.0005 (0.0005)	0.0007 (0.0007)
423.2	0.3665 (0.3940)	0.0005 (0.0004)	0.0007 (0.0006)
383.2 and 423.2	0.3376 (0.3824)	0.0008 (0.0006)	0.0012 (0.0009)

TABLE XXVI

SRK AND PR EOS REPRESENTATIONS OF THE SOLUBILITY OF HYDROGEN (1) IN PYRENE (2)

T/K	SRK Parameters (PR Parameters)	Error in Hydrogen Mole Fraction	
	C_{12}	RMS	|MAX|
433.2	0.4309 (0.4620)	0.0005 (0.0005)	0.0007 (0.0006)

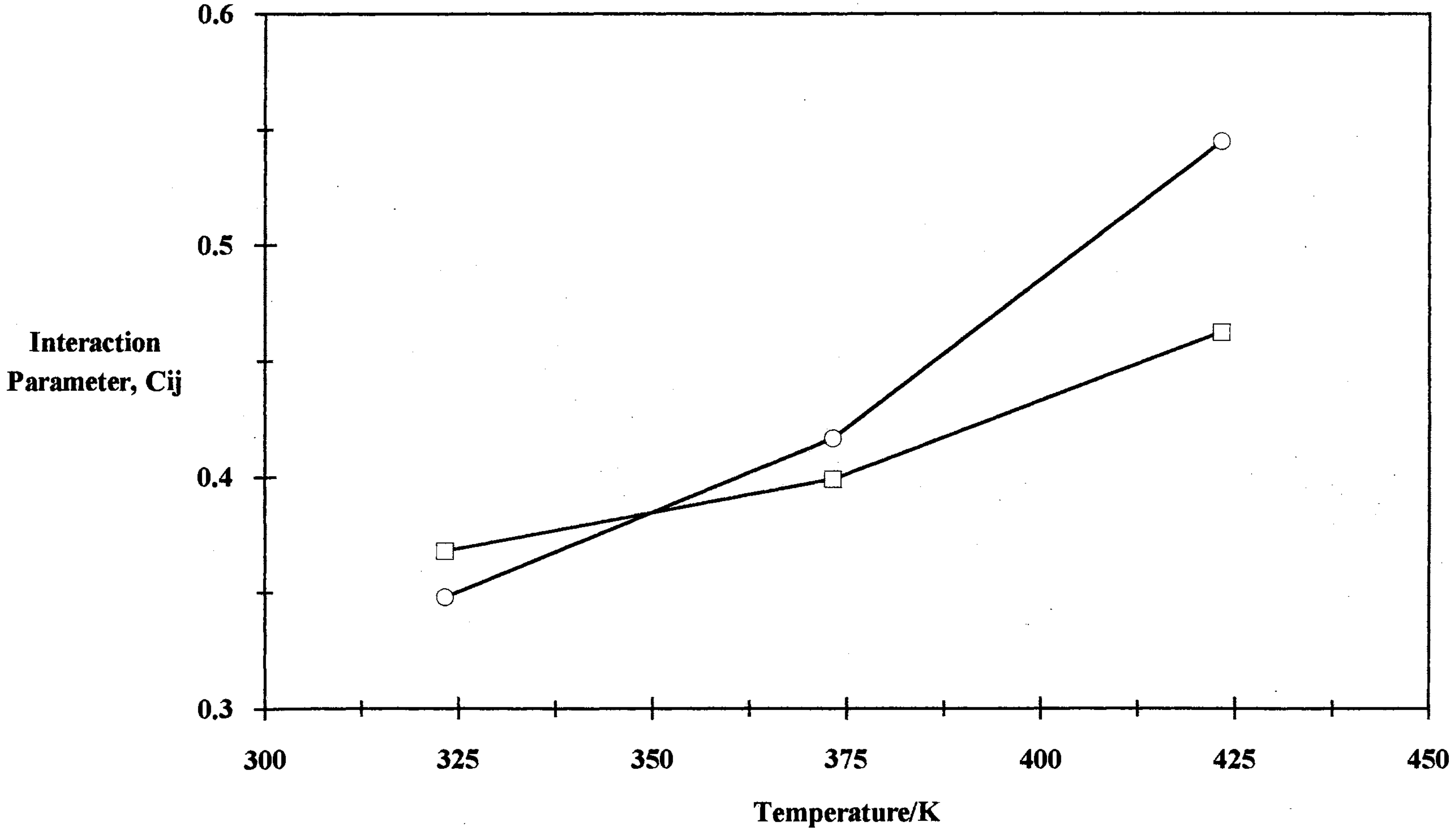


Figure 14. Temperature Effect on the Value of C_{ij} for Hydrogen + Benzene Mixtures.
○ The SRK Equation; □ The PR Equation

that C_{ij} increases as the temperature increases; a similar trend was observed for the hydrogen + naphthalene and hydrogen + phenanthrene binaries. The SRK and PR equations of state, in general, exhibit comparable capabilities in representing the present data using a single interaction parameter for each isotherm.

Conclusions

Data have been obtained for the solubilities of hydrogen in benzene, naphthalene, phenanthrene and pyrene at temperatures from 323.2 to 433.2 K and pressures up to 21.7 MPa. These data showed good agreement with the literature data within the range of the experimental conditions considered. The present data are well described by the SRK and PR equations of state. Interaction parameters for these equations have been obtained for the binary systems considered. The acquired data are a complement to the previous measurements for the solubility of hydrogen in n-paraffins. Combined, these data should serve an important role in designing chemical processes and in model development involving asymmetric mixtures.

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APPENDIXES

APPENDIX A

DENSITY AND MOLECULAR WEIGHT DATA USED IN CALCULATING MIXTURE COMPOSITIONS

The composition of a mixture is calculated from the volumes of solvent and solute injected to the equilibrium cell; thus, density and molecular weight data are required in the calculation of mixture compositions. Moreover, since the temperatures of the two air baths are different, and mercury is used as an incompressible fluid between the injection pump and the solvent storage cell, a correction for the volume of solvent injected is necessary (by the amount of thermal expansion or contraction of mercury). All such data used in calculating mixture compositions are presented in the Tables A.I and A.II with their respective sources.

For hydrogen, the densities are calculated with the equation of state provided by McCarty [35]. The range of injection pressure for hydrogen was between 300 and 450 psia. The accuracy of the equation used in calculating hydrogen density is within the experimental error range of the original data shown by McCarty. The injection pressure and the density of hydrogen, shown in Table A.II, represent typical values used in the experiment.

TABLE A.I

DENSITY DATA OF MERCURY AND SOLVENTS USED IN CALCULATING MIXTURE COMPOSITIONS

Name	Molecular Weight, g/mol	Temperature, K	Density, g/cc	Reference
Mercury		323.2	13.4729	36
		344.3	13.4217	36
		348.2	13.4124	36
		373.2	13.3522	36
		383.2	13.3283	36
		423.2	13.2330	36
		433.2	13.2093	36
n-Decane	142.28	344.3	0.6908	37
		373.2	0.6679	37
		423.2	0.6269	37
n-Eicosane	282.56	323.2	0.7693	37
		373.2	0.7347	37
		423.2	0.7040	37
n-Octacosane	394.77	348.2	0.7716	37
		375.2	0.7555	37
		423.5	0.7235	37
n-Hexatriacontane	506.99	375.2	0.7666	37
		423.2	0.7357	37

TABLE A.I (Continued)

Benzene	78.11	323.2	0.8468	38
		373.2	0.7908	38
		423.2	0.7293	38
Naphthalene	128.17	373.2	0.9628	38
		423.5	0.9219	38
Phenanthrene	178.23	383.2	1.0613	38
		423.2	1.0326	38
Pyrene	202.26	433.2	1.1065	39

TABLE A.II

DENSITIES OF SOLUTE GASES USED IN THE CALCULATION OF MIXTURE COMPOSITION

Name	Temperature, K	Pressure, psia	Density, mol/cc	Reference
Carbon Monoxide	323.2	367.4	0.0009441	40
Hydrogen	323.2	360.0	0.0009112*	35

* A sample value calculated from the equation of state provided by McCarty [35]

APPENDIX B

ERROR ANALYSIS FOR THE ACQUIRED SOLUBILITY DATA

Several procedural steps are undertaken to avoid any systematic error in the experiment. These include calibration of instruments used in the experiment and performing reproducibility tests on the experimental data. The platinum resistance temperature sensors used to measure temperatures of both air baths are regularly checked by measuring the ice point of distilled water. The sensors are also checked with a quartz thermometer (HP-2804A) having an accuracy of 0.04 °C. Temperature differences between the sensors and the quartz thermometer were less than 0.1 °C, within the experimental range. The three pressure transducers used in the experiment were regularly calibrated with the dead weight gauge attached to the apparatus. A detailed calibration procedure is provided by Darwish [4].

To establish the reliability of the apparatus, the vapor pressure of n-pentane at 100 °C was measured and compared to literature data [38]. The deviations in the vapor pressure measurements were less than 1.0 psia. Also solubilities of carbon monoxide in benzene were measured at 100 °C and compared with the data reported by Yi [10]. The data acquired in the present work showed good agreement with those of Yi; deviations were within the experimental error bars, as shown in Figure B.1.

Accumulative random errors in the solubility and bubble point pressure measurements were estimated. Error sources in this work include uncertainties in (a) the amount of solvent and solute injected, (b) the densities of solvent and solute, and (c) the instrumental and procedural errors in the bubble point pressure measurements. In this analysis, uncertainties in the measured temperatures were assumed negligible. The expected variance σ_Y^2 of an any observable Y, which is a function of the measured variables X_1, X_2,...,X_n, can be expressed in terms of the variance of each independent variable and the instrumental error of Y as follows:

$$\sigma_Y^2 = \sum_{i=1}^{n}\left(\frac{\partial Y}{\partial X_i}\right)^2 \sigma_{X_i}^2 + \varepsilon_Y^2 \tag{B-1}$$

where $\sigma_{X_i}^2$ is the variance of the independent variable X_i and ε_Y is the instrumental error in Y. The uncertainty in solubility is expressed according to Equation (B-1) as follows:

$$\sigma_{x_1}^2 = x_1^2(1-x_1)^2\left(\left(\frac{\sigma_{\rho_1}}{\rho_1}\right)^2 + \left(\frac{\sigma_{\rho_2}}{\rho_2}\right)^2 + \left(\frac{\sigma_{V_2}}{V_2}\right)^2 + \sum_{i=1}^{m}\left(\frac{\sigma_{V_{1,i}}}{V_{1,i}}\right)^2\right) \tag{B-2}$$

where m is the total number of solute injections used to synthesize the mixture in the equilibrium cell with the desired mole fraction. A detailed derivation for Equation (B-2) is given by Gasem [5]. Estimated values for the uncertainties in densities and injected volumes are provided by Darwish [4] as follows:

Relative uncertainty in solute density : $\frac{\sigma_{\rho_1}}{\rho_1} = 0.0015$

Relative uncertainty in solvent density : $\frac{\sigma_{\rho_2}}{\rho_2} = 0.0015$

Uncertainty in the volume of solute injected: $\sigma_{V_{1,i}} = 0.0075$

Uncertainty in the volume of solvent injected: $\sigma_{V_2} = 0.0075$

These estimates are assumed to be applicable to the systems studied in this work. With these uncertainties in the independent variables, uncertainty in the measured solubility is estimated.

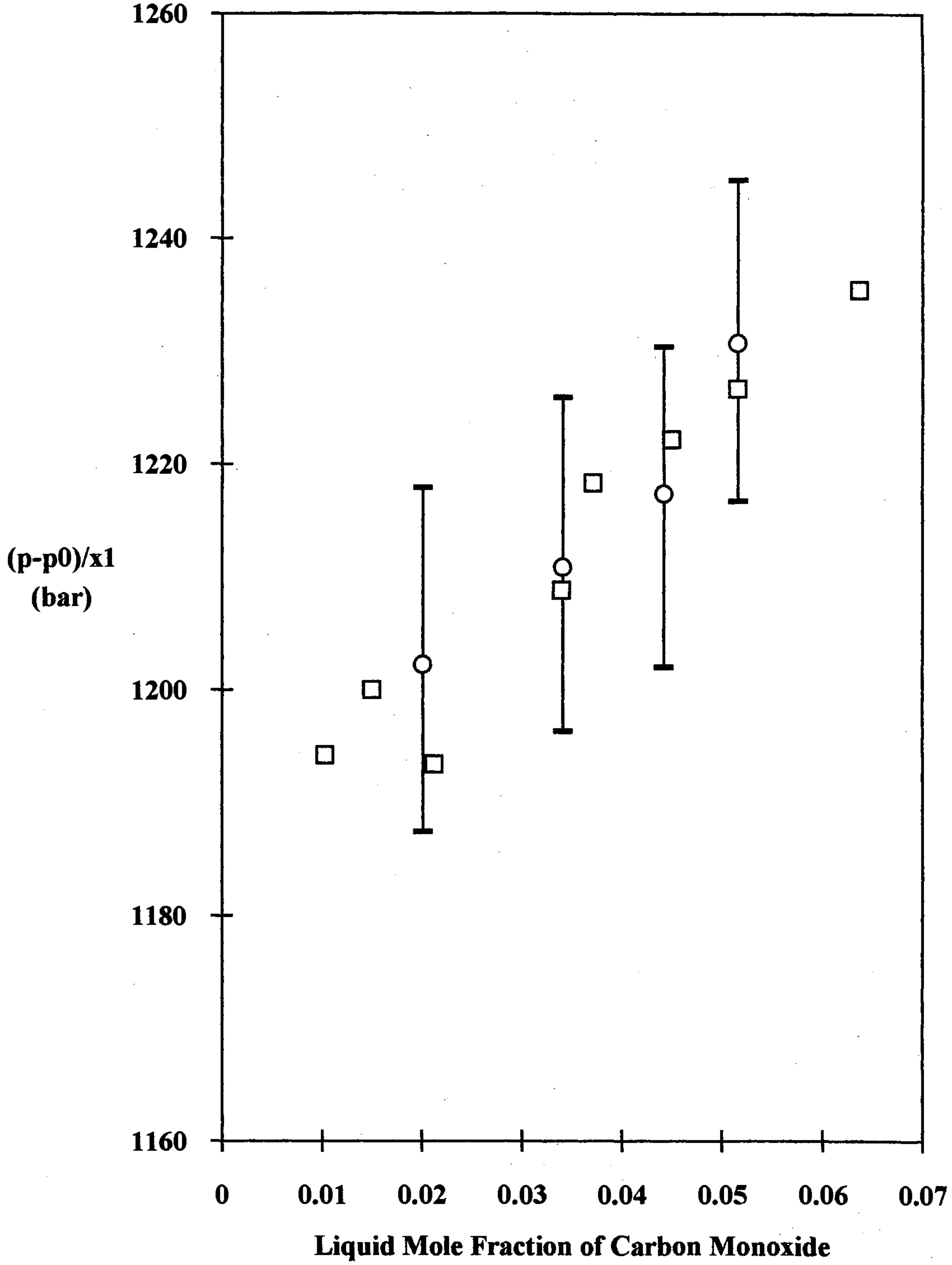

Figure B.1. Reproduciibility Plot for Carbon Monoxide Solubilities in Benzene.
○ Present Work; □ Yi [10]

Similarly, the expected uncertainty in the bubble point pressure is given as [5]:

$$\sigma_p^2 = \left(\frac{\partial p}{\partial x_1}\right)^2 \sigma_{x_1}^2 + \left(\frac{\partial p}{\partial T}\right)^2 \sigma_T^2 + \varepsilon_p^2 \tag{B-3}$$

where ε_p is an instrumental error in pressure measurement. Since the second term in the right hand side of Equation (B-3) is small compared to the other terms, it was neglected in this study. In quantifying the uncertainty in the bubble point pressure, the rate of change of the bubble point pressure with respect to solubility ($\partial p/\partial x_i$) is determined from a second order polynomial fit of the measured solubilities (x_i) in terms of pressure (p). The prime instrumental error in pressure ε_p was assumed to be 0.004p (psi) [4]. The estimated uncertainties in the solubility and in the bubble point pressure measurements used to establish the reliability of the apparatus are shown in Table B.I. Similarly, a sample reproducibility plot shown in terms of $(p-p_0)/x_1$ verses x_1 for the solubilities of hydrogen in n-octacosane, along with the calculated error bars, is presented in Figure B.II. Details on the error analysis used in the present work are provided by Darwish [4].

TABLE B.I

LIQUID MOLE FRACTION AND BUBBLE POINT PRESSURE ERROR ESTIMATES FOR THE CARBON MONOXIDE + BENZENE MIXTURES

Carbon Monoxide Solubility (x_1)	Bubble Point Pressure (bar)	σ_{x_1}	σ_p (bar)
0.0201	25.94	0.0001	0.186
0.0341	43.09	0.0002	0.262
0.0442	55.61	0.0002	0.324
0.0516	65.31	0.0003	0.365

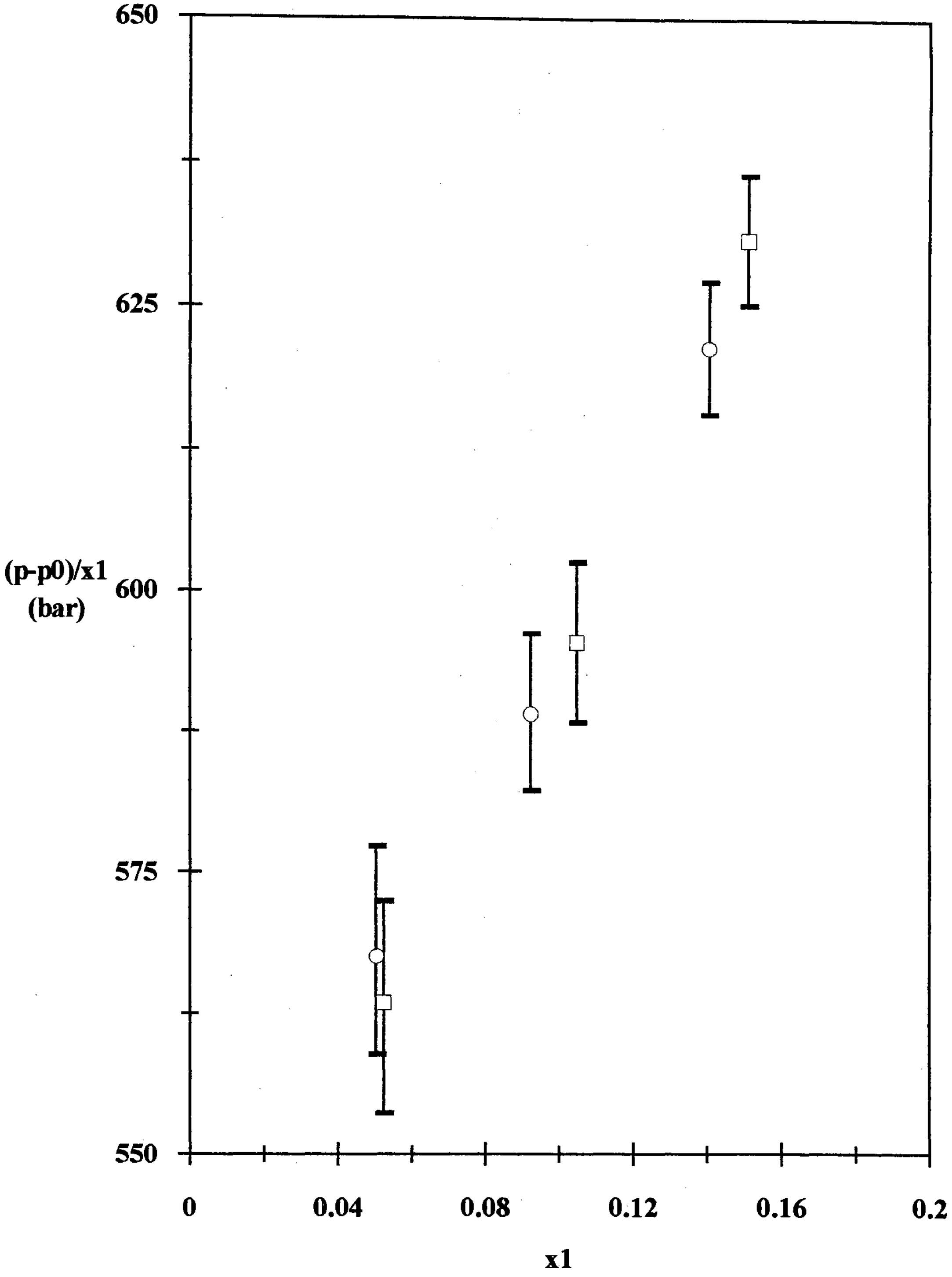

Figure B.II. The Reproducibility Plot for Hydrogen + n-Octacosane at 150 °C. ○ First Run; □ Second Run

SECTION II - EQUATION OF STATE DEVELOPMENT

CHAPTER I

INTRODUCTION

Most chemical processes involve vapor and liquid fluid phases, and a great portion of such processes operate near equilibrium conditions. Thus, accurate knowledge of fluid phase equilibrium and volumetric properties is required in designing and optimizing these processes. An equation of state (EOS) has been considered the most convenient thermodynamic model for these purposes.

The observed deviations in the volumetric (p-v-T) behavior of a real simple fluid from that of an ideal gas are caused by the repulsive and attractive intermolecular forces. One of the earliest models, which takes into account these forces quantitatively, is the van der Waals EOS. In van der Waals EOS, the excluded volume of molecules is taken into account as repulsive pressure, and the attractive pressure is assumed inversely proportional to the square of the molar volume of a system at a given temperature. Although the van der Waals EOS is proposed on intuitive grounds, it is capable of predicting the coexistence of vapor and liquid phases and the presence of the critical state. This equation formed the basis for other cubic equations of state, including the Soave-Redlich-Kwong (SRK) [1] and Peng-Robinson (PR) [2] equations, which are widely used in industry.

The SRK and PR equations have the same repulsive term as the van der Waals EOS. However, this repulsive term is theoretically defective, especially for dense fluids; typically, it over-predicts the repulsive compressibility factor at a given temperature and molar volume [3]. In addition, according to molecular simulation results of Nicolas et al. [4] and Vimalchand et al. [5], the attractive term of the SRK equation under-predicts the attractive compressibility factor. However, the simultaneous cancellation of errors from the repulsive and attractive terms leads to a reasonable predictive capability for the cubic equations [6]. These and other well recognized defects in the repulsive and attractive terms of the cubic equations limit their applicability for some systems. For example, cubic equations of state often do not represent properly the phase behavior of asymmetric mixtures and mixtures containing polar components.

When these cubic equations are applied to asymmetric mixtures, the common mixing rules based on molecule-molecule interactions are used. This also contributes to their deficiency, since a small molecule in an asymmetric mixture is more likely to interact with only a part (segment) of a large molecule. Thus, in general, models based on interactions between segments of molecules are more realistic for such mixtures.

Efforts to develop theoretically-based equations of state incorporating sound repulsive and attractive terms have been made. For hard spheres, there is no attractive energy between particles. Hence, an equation of state for hard spheres is merely the repulsive contribution of a real fluid equation of state accounting for the excluded volume. Computer simulation results [7], virial-type analytical derivation [8], and a simple correlation for the analytical derivation [9] for the repulsive behavior of hard spheres are discussed in the literature. The Carnahan and Starling equation [9] closely represents the computer simulation results [7] and the analytical derivation [8]. As such, a number of equations of state utilizes the Carnahan and Starling repulsive term [10-15].

The perturbed-hard-chain theory equation of state (PHCT) is one of the most accurate equations for representing the phase behavior of chain molecules. The attractive term of this equation is based on the molecular simulation results of Alder et al. [16], in which molecules are assigned square-well potential interactions. One of the shortcomings of the equation is that the attractive contribution has 24 terms. Because of the complexity of the attractive term and the corresponding mixing rules, the PHCT EOS has been used sparingly as a general purpose equation of state for calculating the phase behavior of mixtures.

A simplified form of the PHCT equation (SPHCT equation) was proposed by Kim and coworkers [12]. They replaced the attraction term of the PHCT equation with the local composition model of Lee et al. [17]. This equation has a comparable predictive capability to the SRK and PR equations in representing the phase behavior of simple molecules, and has a better capability for handling some asymmetric mixtures [18, 19]. Although this equation has the advantages of a segment-interaction model, it suffers from several shortcomings. The SPHCT equation often fails to generate accurately the vapor-liquid phase envelope for pure fluids. In addition, it fails to predict adequately pure fluid vapor pressures below 0.007 bar [18], and it yields worse vapor density predictions than those of the PR EOS [19]. A modification to improve the SPHCT EOS predictions was recently undertaken by Shaver [19]. The Modified SPHCT EOS is better than the original SPHCT EOS in representing equilibrium and volumetric properties for a variety of pure fluids.

Another well-known equation of state based on statistical mechanics is the Chain-of-Rotators (COR) EOS proposed by Chien and coworkers [20]. The COR EOS repulsive term utilizes the hard dumbbell equation [21] and the same type of attractive term as the PHCT EOS. The COR EOS has shown good performance in representing fluid phase behavior, but it is more complex than the PHCT EOS.

This work is focused on developing a simple equation of state capable of representing the phase behavior of simple, normal, and asymmetric mixtures involving molecules of diverse molecular sizes. The present work is an effort to overcome some of the above-mentioned shortcomings in the existing equations. The new equation is theoretically based and its parameters are evaluated from both equilibrium and volumetric properties of pure fluids. This EOS is intended to be accurate in predicting fluid phase equilibrium and volumetric properties of pure fluids from the triple point to near the critical point, as well as mixture properties over a wide range of conditions.

The new equation of state was derived from the generalized van der Waals partition function for chain-like molecules proposed by Donohue and Prausnitz [11]. The equation has a simple repulsive term proposed by Elliott and coworkers [6]. The performance of this repulsive term is similar to that of the Carnahan and Starling equation. Since the attractive term of the generalized cubic equation of state under-predicts compressibility factors of fluids, a correction term is added to the attractive term of the generalized cubic equation. The temperature dependence of the new equation is based on an empirically augmented square-well potential for segment interactions. The new equation has three substance-specific parameters for each pure fluid.

Detailed derivation of the equation is presented in Chapter II along with a brief literature review on equations of state. Chapter III presents the EOS parameter evaluations and an assessment of the pure fluid property predictions. The predictive capability of the new equation is compared to that of the PR, SPHCT, and Modified SPHCT equations. Predictions for the vapor pressure and saturated vapor and liquid densities of a variety of pure fluids are compared to those of the other equations. Bubble point pressure calculations for the binary mixtures of ethane + n-paraffins, carbon dioxide + n-paraffins, and hydrogen + n-paraffins with the new equation are shown in Chapter IV. Comparisons are also undertaken with the PR, SPHCT and Modified SPHCT equations regarding the representation of bubble point pressures for these binary mixtures.

CHAPTER II

A NEW EQUATION OF STATE

Abstract

A new equation of state utilizing segment-segment molecular interactions is proposed. The van der Waals partition function for chain-like molecules of Donohue and Prausnitz [11] is used in developing the equation. Each molecular segment is considered as a hard sphere with its free volume adopted from the expression given by Elliott and coworkers [6]. A square-well potential is used to represent the segment-segment attraction energy. The density dependence of the radial distribution function of the new equation leads to the attractive term of an augmented generalized cubic equation of state.

Introduction

Since the thermodynamic properties of fluid mixtures are one of the basic requirements in designing and operating chemical processes, there has been continuous demand from industry for accurate thermodynamic models. There are two different common approaches in the vapor-liquid equilibrium calculations. One is the equation of state approach and the other is the activity coefficient model approach. Activity coefficient models such as the Wilson [25], NRTL [26] and UNIFAC [27] are very convenient in calculating K-values in vapor-liquid equilibrium or distribution coefficients in liquid-liquid equilibrium of highly nonideal systems. However, these activity coefficient models cannot provide the volumetric properties of fluid mixtures. Moreover, these models normally show poor performance for high pressure systems.

The van der Waals type equations of state provide both volumetric and equilibrium properties. Among the equations of state, the SRK equation [1] and PR equation [2] are widely used in industry. Although these equations are mostly empirical, their predictive capabilities for equilibrium properties of mixtures containing simple and normal fluids are good. In applying these equations to asymmetric mixtures, however, the molecular size disparity strains the capability of these cubic equations, which employ molecule-molecule interactions.

Recent interest in asymmetric mixtures has generated new requirements for thermodynamic models and equilibrium data for systems containing small molecules and heavy solvents. Also the development of fast computers makes it possible to perform Monte Carlo simulations and molecular dynamics simulations to delineate molecular interactions. These simulation results have stimulated the development of theoretically-based equations of state. In this work, a new simple equation of state for chain-like molecules is proposed by utilizing an existing free volume expression and a new expression for the attractive term.

Literature Review

The van der Waals type equations of state can describe adequately the phase behavior of simple and normal fluid mixtures. However, these empirical equations are intrinsically limited in their applicability to mixtures containing molecules of diverse molecular sizes and polar species. Recently developed equations of state such as the Perturbed-Hard-Chain Theory (PHCT) equation [10, 11], the Chain-of-Rotators (COR) equation [20], the Simplified Perturbed-Hard-Chain Theory (SPHCT) equation [12] and the Cubic Chain-of-Rotators (CCOR) equation [22, 23], which originated from statistical mechanics, have been proven useful in predicting the fluid phase equilibria of industrially important mixtures.

The PHCT equation is one of the accurate equations for representing vapor-liquid equilibrium properties of chain-like hydrocarbons. This equation consists of repulsive and attractive contributions given in terms of compressibility factors as:

$$Z = 1 + c\left(Z^{rep} + Z^{att}\right) \tag{2-1}$$

where c is the degrees of freedom parameter. The repulsive term of this equation is adopted from the Carnahan and Starling (C-S) expression [9], and the attractive term is based on the molecular simulation results of Alder and coworkers [16] for molecules having a square-well potential. The weak point of this equation is that its attractive term has as many as 24 terms. Because of the complex attraction term and the corresponding mixing rules, the PHCT equation has limited use in practical applications. A simplified version of this equation was provided by Kim and coworkers [12] using the Lee-Lombardo-Sandler (LLS) local composition model [17] as the attractive term of their equation. The predictive capability of this equation is comparable with that of the Soave-Redlich-Kwong (SRK) equation, which is commonly used in industry [18]. Typically, this equation shows better performance than the SRK equation in predicting phase properties of heavy hydrocarbons. However, the SPHCT equation requires more computer time than a cubic equation such as the SRK for calculating thermodynamic properties in two-phase region. This is because the SPHCT equation requires more computer time to identify the volume (compressibility factor) liquid root of the equation in each iteration of the equilibrium calculations.

The COR equation has a rotational term in the expression for the compressibility factor, along with the repulsive and attractive terms. The equation is given as:

$$Z = 1 + Z^{rep} + cZ^{rot} + \left(1 + cf(T)\right)Z^{att} \tag{2-2}$$

The repulsive term of the COR equation is that of the C-S equation, and the rotational term is from the hard-dumbbell equation provided by Boublik and Nezbeda [21]. The basic assumption in the rotational term is that a chain molecule consists of a series of hard dumbbell molecules. Each dumbbell has three translational degrees of motion and two rotational degrees of motion. The attractive term of the COR equation is given by Alder and coworkers [16]. The equation shows comparable or better performance than the PHCT equation in predicting vapor pressures and saturated liquid and vapor densities of some paraffins and aromatics [20]. However, the COR equation is considered more complex than the PHCT equation. Thus, Lin et al. [22] simplified the COR equation using simple correlations for the repulsive term and the rotational term along with two empirical expressions in the attractive term. One of these expressions is similar to that of the SRK equation. Evaluations of the simplified COR equation using two binary interaction parameters for some hydrogen binary mixtures were conducted [22, 23], and the results were compared to those of the SRK equation using one interaction parameter. The simplified COR equation showed better precision than the SRK equation for the systems considered. However, no evaluation of the equation with one interaction parameter is available in the literature.

Following is a brief review on equation-of-state repulsive and attractive terms. This is a very active area of research, thus only studies pertinent to the present work are discussed.

The repulsive term of an equation of state for real fluids is often used to describe hard-sphere, hard-disc or hard-chain interactions in which no attractive energy between molecules is involved. Monte Carlo or molecular dynamics simulation results are available in the literature for the repulsive contribution to fluid compressibility for different densities [7, 24]. Among the equations of state for hard-spheres, Carnahan and Starling [9] provided one of the better known and more accurate expressions. Their expression, given below, is a simple correlation of the virial-type analytical derivation for the hard-sphere compressibility factor [8].

$$\begin{aligned} Z^{rep} &= \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \\ &= 1+\frac{4\eta-2\eta^2}{(1-\eta)^3} \end{aligned} \qquad (2\text{-}3)$$

where $\eta = \frac{1}{6}\left(\pi\sqrt{2}\right)\left(\frac{v^*}{v}\right)$ and v^* is the molar close packed volume for hard spheres.

Several equations of state, using an attractive term similar to that of existing cubic equations of state and the C-S repulsive term, have been proposed in the literature [13 - 15]. In general, these equations showed better or comparable performance to the PR and SRK equations in calculating fluid phase equilibrium properties of simple mixtures.

Recently, an empirical expression for hard spheres is proposed by Elliott and coworkers [6] as follows:

$$Z^{rep} = 1+\frac{4\eta}{1-1.9\eta} \qquad (2\text{-}4)$$

This equation is based on computer simulations for hard spheres [7] and the work done by Carnahan and Starling; expectedly, the functional behavior of above Equation (2-4) is very similar to that of C-S. Also, a similar empirical expression for the compressibility factor of hard spheres, which is used in the CCOR equation proposed by Lin and coworkers, is given as [22]:

$$\begin{aligned} Z^{rep} &= \frac{1+3.08\eta}{1-1.68\eta} \\ &= 1+\frac{4.76\eta}{1-1.68\eta} \end{aligned} \qquad (2\text{-}5)$$

The expressions for the repulsive compressibility factors (Equations (2-3) to (2-5)) are compared with the molecular dynamics calculations of Erpenbeck and Wood [7] and that of the van der Waals equation in Figure 1. All the above equations for hard spheres except that of the van der Waals equation show good agreement with the results of molecular simulations for hard spheres. All expressions for the repulsive term and the computer simulation results indicate that system pressure diverges as η increases. In contrast, variation in the limiting behavior is evident. The limiting value of η is 1/4 for van der Waals equation [6] and 1 for the C-S equation. That of Lin and coworkers is 1/1.68, and for Elliott and coworkers it is 1/1.9. As η approaches its limiting value, pressure approaches infinity; thus, these limiting values stand for the extreme-condensed state.

Aside from the classical equation of state [1, 2], attractive terms have been obtained from the correlation of computer simulation results of molecules having a square-well potential [10, 11, 20], from a local composition model [12] or from empirical studies [6, 13 - 15]. For the PHCT and COR equations of state, the attractive term was obtained by extending the computer simulations for spherical molecules having square-well potentials to chain-like molecules. The original simulations were performed for a wide range of densities [16], and the results were correlated to produce an EOS attractive expression having 24 terms [10, 11, 20]. The attractive term of the SPHCT equation of state was obtained by extending the LLS lattice model of Lee et al. [17] to chain-like molecules. The density-dependent attractive term was obtained based on the local composition model and assuming that each segment of a molecule occupies one site in a quasi-crystalline lattice and that of neighboring segments occupy adjacent sites [12]. Other equation of state attractive terms in the literature [1, 2, 6, 13 - 15] are mostly empirical.

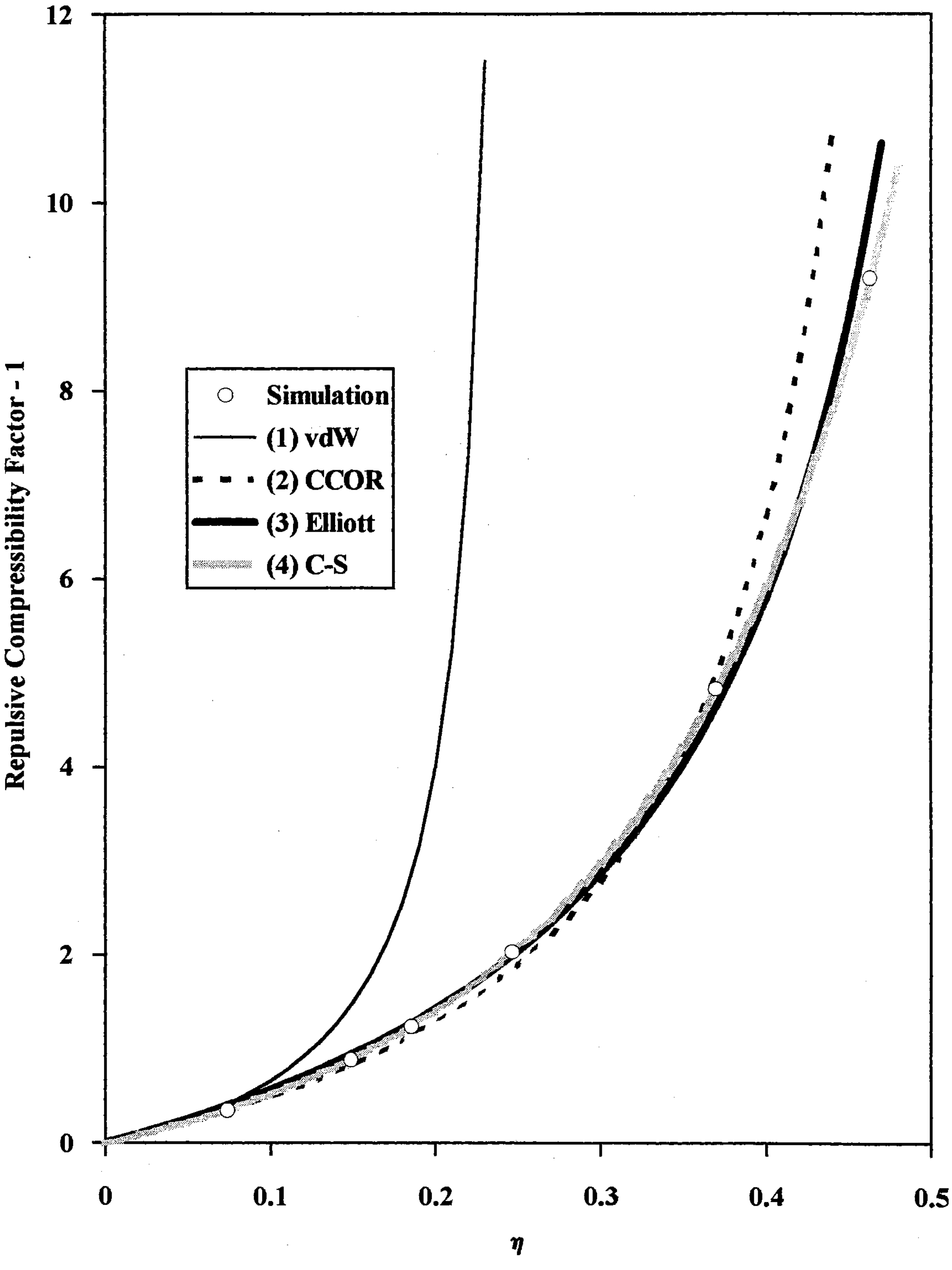

Figure 1. Comparison of Repulsive Compressibility Factor Expressions.
○ Simulation Results of Erpenbeck et al.; (1) van der Waals; (2) CCOR; (3) Elliott et al.; (4) Carnahan and Starling

Many other expressions for intermolecular interactions, such as the Lennard-Jones potential and Buckingham potential [28], are not reviewed here since these are not within the scope of this work.

Equation of State Development

Difficulties in modeling at the molecular level are the major hindrance in developing a thermodynamic model for dense fluids. If the interaction energy between molecules and the free volume of a system are well defined, thermodynamic properties can be calculated accurately with the aid of statistical mechanics. A typical example of the statistical mechanical connection between the behavior of particles and bulk thermodynamic properties is the canonical partition function. Once a partition function is established, thermodynamic properties can be derived. Among the expressions for partition functions, the generalized van der Waals partition function has been the starting point for developing equations of state having repulsive and attractive terms. This generalized van der Waals partition function requires a free volume expression and intermolecular potential energy to account for dispersion effects or attractive interactions between molecules. Detailed discussion on this partition function is given by Vera and Prausnitz [3].

Donohue and Prausnitz extended the generalized van der Waals partition function to chain-like molecules [11]. They assumed that the kinetic energy of a chain-like molecule is affected by the translational, rotational and vibrational degrees of freedom and that the total degrees of freedom for a chain-like molecule is 3c instead of 3 in the generalized van der Waals partition function. Then, the partition function for chain-like molecules [11] becomes

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \left(\frac{V_f}{V}\exp\left(\frac{-\phi}{2ckT}\right)\right)^{Nc} \qquad (2\text{-}6)$$

where V_f is the free volume of hard-spheres and Λ is the de Broglie wave length. For simple molecules, such as methane and argon, the degrees of freedom parameter c is 1 and the partition function of Equation (2-6) becomes the generalized van der Waals partition function.

The relationship between system pressure and the partition function is given as:

$$\frac{p}{kT} = \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \tag{2-7}$$

For a given canonical partition function, an equation of state can be derived using the fundamental relationship given in Equation (2-7). The present chapter is mainly concerned with deriving a pressure-explicit equation of state, utilizing the above equation.

By taking the logarithm of Equation (2-6) and applying Stirling Approximation on lnN!, the following equation is obtained:

$$\ln Q = -N \ln N + N + N \ln V - N \ln \Lambda^3 + Nc\left(\ln V_f - \ln V - \frac{\phi}{2ckT}\right) \tag{2-8}$$

Then, applying the expression for Q (Equation (2-8)) to Equation (2-7), one obtains

$$\frac{pV}{NkT} = 1 + c\left(\frac{V}{V_f}\frac{\partial V_f}{\partial V} - 1 - \frac{V}{2ckT}\frac{\partial \phi}{\partial V}\right)_{N,T} \tag{2-9}$$

To rewrite Equation (2-9) on a molar basis, the definition of the molar volume ($v = V(N_A/N)$) is introduced into Equation (2-9).

$$\frac{pv}{RT} = 1 + c\left(\frac{v}{v_f}\frac{\partial v_f}{\partial v} - 1 - \frac{v}{2ckT}\frac{\partial \phi}{\partial v}\right)_{T} \tag{2-10}$$

where N_A is Avogadro's number, and N is the total number of molecules in a system. Thus, an equation of state for chain-like molecules can be obtained from above Equation

(2-10), once the free volume expression and the potential energy for a given system are known.

The free-volume expression given by Elliott and coworkers [6] shown in the Equation (2-4) is used in this work. Since, as shown in Figure 1, this free volume expression closely approximates the molecular dynamics simulation results and leads to a simpler expression for the repulsive term compared with C-S equation. This leads to

$$\frac{v}{v_f}\frac{\partial v_f}{\partial v} - 1 = \frac{4\eta}{1-1.9\eta} \tag{2-11}$$

where $\eta = \frac{\tau v^*}{v}$ and $\tau = 0.7405$

The attractive term in the partition function is expressed in terms of the segment number within the interaction range by Kim and coworkers as follows [12]:

$$\frac{-\phi}{2ckT} = \frac{1}{2}\int_{1/\tilde{T}=0}^{1/\tilde{T}} N_c(\rho,T)d(1/\tilde{T}) \tag{2-12}$$

where $\tilde{T} = \frac{T}{T^*} = \frac{ckT}{\varepsilon q}$

The coordination number, N_c, is defined as the number of segments within the interaction range of a central molecule, and ε is the potential energy between segments. Applying the square-well potential between two segments, N_c is given as:

$$N_c = \frac{N}{V}\int_{\sigma}^{K\sigma} g(r;\rho,T)\, s4\pi r^2 dr \tag{2-13}$$

where σ is the radius of a hard-sphere, $K\sigma$ is the potential well width from σ, s is the number of segments in the central molecule, and $g(r;\rho,T)$ is the radial distribution function. Equation (2-13) transforms the quest for N_c to that of finding a workable, yet accurate distribution function.

At the low density limit, the radial distribution function is given as [29]:

$$\lim_{\rho \to 0} g(r;\rho,T) = \exp\left(\frac{-u(r)}{kT}\right) \qquad (2\text{-}14)$$

where u(r) is the potential energy between molecules. Since the degrees of freedom parameter (c), which represents the ratio of the total system energy (translational, rotational and vibrational energy) to the translational energy [12], is introduced into the attraction energy term in the partition function of chain-like molecules, it is also introduced in the potential energy term of the radial distribution function as follows:

$$\lim_{\rho \to 0} g(r;\rho,T) = \exp\left(\frac{-u(r)}{ckT}\right) \qquad (2\text{-}15)$$

Integration of Equation (2-13) for a square-well potential fluid leads to

$$\lim_{\rho \to 0} N_c = \frac{N}{V}\frac{4\pi}{3}\sigma^3\left(K^3 - 1\right) s\exp\left(\frac{\varepsilon^*}{ckT}\right) \qquad (2\text{-}16)$$

where ε^* is the total square well potential energy for a central molecule. By replacing ε^* by εq, Equation (2-16) becomes

$$\lim_{\rho \to 0} N_c = \frac{N}{V}\frac{4\pi}{3}\sigma^3\left(K^3 - 1\right) s\exp\left(\frac{\varepsilon q}{ckT}\right) \qquad (2\text{-}17)$$

Substituting Equation (2-17) into Equation (2-12), the potential energy expression at the low density limit becomes

$$\lim_{\rho \to 0} \frac{-\phi}{2ckT} = \left(\frac{K^3 - 1}{2}\right)\left(\frac{v^*}{v}\right)\int_{1/\tilde{T}=0}^{1/\tilde{T}} \exp\left(\frac{1}{\tilde{T}}\right) d\left(1/\tilde{T}\right) \qquad (2\text{-}18)$$

where $T^* = \dfrac{\varepsilon q}{ck}$ and $\tilde{T} = \dfrac{T}{T^*}$

By integrating Equation (2-18), the following expression for potential energy at the low density limit is obtained.

$$\lim_{\rho \to 0} \frac{-\phi}{2ckT} = \alpha_0 \left(\frac{v^*}{v}\right)\left(\exp\left(\frac{1}{\tilde{T}}\right) - 1\right) \tag{2-19}$$

where $\alpha_0 = (K^3 - 1)/2$

To extend the limiting potential energy expression to real fluids, two empirical functions ($\Delta(\rho)$ and $\Theta(T)$) which are dependent on density and temperature, respectively, are used to amend the limiting definition of the radial distribution function given in Equation (2-19):

$$\frac{-\phi}{2ckT} = \alpha_0 \Theta(T) \Delta(\rho) \left(\frac{v^*}{v}\right)\left(\exp\left(\frac{1}{\tilde{T}}\right) - 1\right) \tag{2-20}$$

Based on Equation (2-10), the attractive term of the equation of state becomes

$$\begin{aligned} \frac{-v}{2ckT}\left(\frac{\partial \phi}{\partial v}\right)_{N,T} &= \alpha_0 \Theta(T)\left(\exp\left(\frac{1}{\tilde{T}}\right) - 1\right) v^* \left(\frac{\partial \Delta(\rho)}{\partial v} - \frac{\Delta(\rho)}{v}\right) \\ &= \alpha_0 \Theta(T)\left(\exp\left(\frac{1}{\tilde{T}}\right) - 1\right)\left(\frac{\partial \Delta(\rho)}{\partial v_r} - \frac{\Delta(\rho)}{v_r}\right) \end{aligned} \tag{2-21}$$

where $v_r = v/v^*$. Combining Equations (2-10), (2-11), and (2-21) translates the task for EOS development to that of defining the $\Delta(\rho)$ and $\Theta(T)$ functions of the attractive term.

The attractive term of the generalized cubic equation of state is known to be reasonable for simple and normal molecules. However, several studies have indicated that the attractive term of cubic equations of state such as the SRK equation under-predicts compressibility factors compared to molecular simulation results [6]. In this work, an augmented generalized cubic equation of state attractive term is used. The augmented term is expected to give more flexibility to the equation when applied to chain-like molecules near the critical point. The following expression for the density-dependent function $\Delta(\rho)$ leads to the attractive term of the proposed equation of state.

$$\frac{\partial \Delta(\rho)}{\partial v_r} - \frac{\Delta(\rho)}{v_r} = -\frac{v_r}{v_r^2 + uv_r + w} - \frac{Q}{v_r + 1} \tag{2-22}$$

The actual form of the density correction function, $\Delta(\rho)$, is given by integrating Equation (2-22) as:

$$\Delta(\rho) = \frac{-v_r}{\sqrt{u^2 - 4w}} \ln \frac{2v_r + u - \sqrt{u^2 - 4w}}{2v_r + u + \sqrt{u^2 - 4w}} + Qv_r \ln \frac{v_r + 1}{v_r} \qquad \text{if } u^2 > 4w \tag{2-23}$$

or

$$\Delta(\rho) = \frac{-2v_r}{\sqrt{4w - u^2}} \tan^{-1} \frac{2v_r + u}{\sqrt{4w - u^2}} + Qv_r \ln \frac{v_r + 1}{v_r} \qquad \text{if } u^2 < 4w \tag{2-24}$$

From Equations (2-10), (2-11), (2-21) and (2-22) the following equation of state is obtained.

$$Z = 1 + c\left(\frac{\beta_1 \tau}{v_r - \beta_2 \tau} - \frac{\alpha Y v_r}{v_r^2 + uv_r + w} - \frac{Q\alpha Y}{v_r + 1}\right) \tag{2-25}$$

where $\beta_1 = 4$ and $\beta_2 = 1.9$ as given by Elliott and coworkers [6],

$$\alpha = \alpha_0 \Theta(T) \tag{2-26}$$

and

$$Y = \exp\left(\frac{1}{\bar{T}}\right) - 1 \tag{2-27}$$

Based on preliminary studies using the new EOS form given by Equation (2-25) and work done by Shaver [19], the temperature correction function $\Theta(T)$ used in this work is given as:

$$\Theta(T) = 1 + \kappa_1 \tilde{T}^{1/2} + \kappa_2 \tilde{T} + \kappa_3 \tilde{T}^2 + \kappa_4 \tilde{T}^{-1} \tag{2-28}$$

where κ_1, κ_2, κ_3 and κ_4 are generalized EOS constants.

Limiting Behavior of the Equation of State

As the system molar volume approaches infinity at any temperature, the repulsive term of the equation becomes unity, and the attraction term vanishes. This is because the terms inside the parentheses in Equation (2-25) vanish as the system molar volume approaches infinity. Hence, the equation of state reduces to the ideal gas law at the limit of infinite system molar volume. At the extreme-compressed state where pressure approaches infinity, the molar volume or the compressibility factor is known from the denominator of the repulsive term of the equation of state. It is given as follows:

$$v_{min} = \beta_2 \tau v^* \tag{2-29}$$

The minimum molar volume (v_{min}) of Equation (2-29) is the smallest possible molar volume. This implies that the compressibility factor at a given temperature and pressure is always larger than the Z_{min}, which is defined as:

$$Z_{min} = \frac{\beta_2 \tau p v^*}{RT} \tag{2-30}$$

As the temperature approaches infinity, the attractive term vanishes because the temperature-dependent term of the equation (αY) converges to zero, as shown in Figure 2. Moreover, when the molecular size (characteristic volume, v^*) is zero and the temperature becomes infinity, the equation also satisfies the ideal gas law limit.

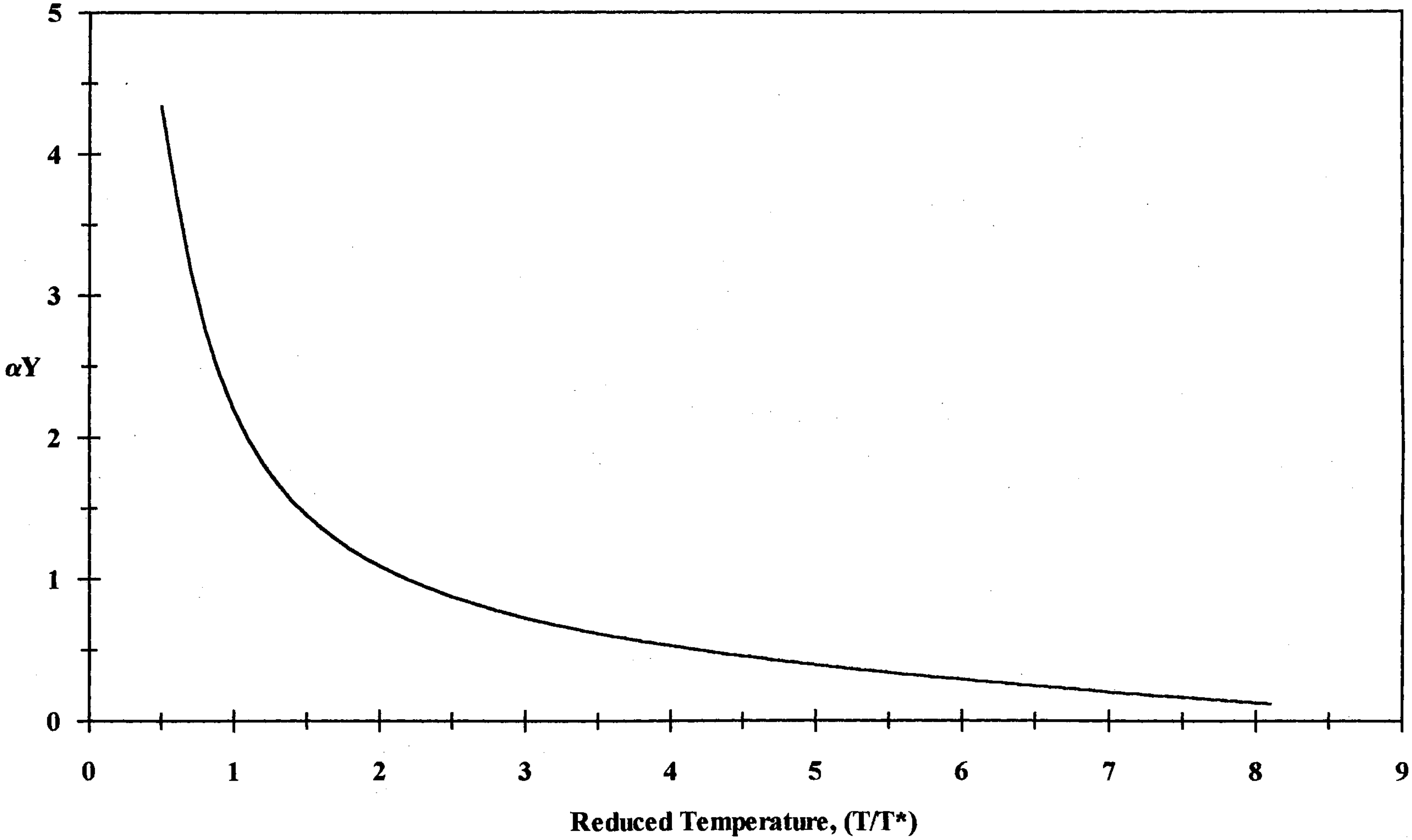

Figure 2. The Temperature-Dependent Term of the Equation of State (αY) as a Function of Reduced Temperature.

CHAPTER III

EVALUATION OF THE NEW EQUATION OF STATE FOR SELECTED PURE FLUIDS

Abstract

The predictive capability of the proposed equation of state for vapor pressure and phase densities was evaluated for selected normal paraffins, normal alkenes, cycloparaffins, light aromatics, argon, carbon dioxide and water. The generalized EOS constants and substance-specific characteristic parameters in the proposed equation of state were obtained from the pure component vapor pressures and saturated liquid and vapor molar volumes. The calculated phase properties are compared to those of the Peng-Robinson (PR) [2], Simplified Perturbed-Hard-Chain Theory (SPHCT) [12] and Modified SPHCT equations of state [19]. Generally, the performance of the proposed equation of state is better than the PR, SPHCT and Modified SPHCT equations in predicting the pure fluid properties considered. In addition, the second virial coefficients for propane, argon and methane were calculated using the new EOS, and compared with experimental values.

Introduction

The interaction energy between particles and the free volume of the fluid are difficult to describe accurately. Even if the potential energy between particles and free volume are known accurately, it is very difficult to implement the information in a simple equation of state. Naturally, several assumptions are necessary in the derivation of an equation of state. Such assumptions evoke a lack of fit with experimental data.

Therefore, the substance-specific model parameters of the equation are assumed adjustable and are regressed using pure fluid experimental data to render the equation useful for practical applications.

Typically, the EOS constants and the component-specific parameters are determined from vapor-liquid equilibrium phase properties. Since a pure component in vapor-liquid equilibrium has only one degree of freedom, any experimental data set containing more than one thermodynamic intensive property can be used to evaluate the constants and the parameters in an equation of state. Temperature, pressure, and saturated liquid and vapor molar volumes (or densities) are the commonly used thermodynamic properties in the development and evaluation of pure-fluid equations of state.

Equation of State

The pressure explicit form of the equation derived in the previous chapter may be written as:

$$\frac{\mathrm{pv}}{\mathrm{RT}} = 1 + \mathrm{c}\left(\frac{\beta_1 \tau}{\mathrm{v_r} - \beta_2 \tau} - \frac{\alpha \mathrm{Y} \mathrm{v_r}}{\mathrm{v_r^2} + \mathrm{u}\mathrm{v_r} + \mathrm{w}} - \frac{\mathrm{Q}\alpha\mathrm{Y}}{\mathrm{v_r} + 1} \right) \qquad (3\text{-}1)$$

where

$$\alpha = \alpha_0\left(1 + \kappa_1 \tilde{\mathrm{T}}^{1/2} + \kappa_2 \tilde{\mathrm{T}} + \kappa_3 \tilde{\mathrm{T}}^2 + \kappa_4 \tilde{\mathrm{T}}^{-1}\right) \qquad (3\text{-}2)$$

and

$$\mathrm{Y} = \exp\left(\frac{1}{\tilde{\mathrm{T}}}\right) - 1,\ \tilde{\mathrm{T}} = \frac{\mathrm{T}}{\mathrm{T}^*} \text{ and } \mathrm{v_r} = \frac{\mathrm{v}}{\mathrm{v}^*} \qquad (3\text{-}3)$$

The equation of state shown in Equation (3-1) is fifth order in volume (or in compressibility factor). The expanded form of the equation in terms of the compressibility factor (Z) is

$$Z^5 + AZ^4 + BZ^3 + CZ^2 + DZ + E = 0 \tag{3-4}$$

The coefficients of Equation (3-4) (A, B, C, D and E) are constant for a given temperature and pressure. This expanded form of the equation of state and definitions for these coefficients are presented in Appendix A. During equilibrium calculations, the expanded form, Equation (3-4), is solved to identify liquid and vapor roots of Z.

The fugacity coefficient required in the equilibrium calculations by the equation of state is given below:

$$\ln\phi = -c\frac{\beta_1}{\beta_2}\ln\frac{v_r - \beta_2\tau}{v_r} + c\alpha Y\frac{2}{\sqrt{4w - u^2}}\left(\tan^{-1}\frac{2v_r + u}{\sqrt{4w - u^2}} - \frac{\pi}{2}\right) - c\alpha YQ\ln\frac{v_r + 1}{v_r}$$
$$+\frac{c\beta_1\tau}{v_r - \beta_2\tau} - \frac{c\alpha Y v_r}{v_r^2 + uv_r + w} - \frac{c\alpha YQ}{v_r + 1} \tag{3-5}$$

A detailed derivation is presented in Appendix B.

Methods

The equation of state proposed in this work was constructed to have a set of universal constants for all compounds (u, w, Q, α_0, and κ_1 - κ_4) and substance-specific pure component parameters (T^*, v^* and c). Experimental vapor pressure data along with liquid and vapor phase molar volumes at different temperatures were used to evaluate all the EOS constants. Data sets used in this work are of the types T-p-v_l-v_v, T-p-v_l, T-p, or T-v_l as shown in the next section. The objective function (SS) minimized to determine the EOS constants is given as:

$$SS = \sum_{i=1}^{N}\left(\left(\frac{p_{expt} - p_{calc}}{p_{expt}}\right)^2 + \left(\frac{v_{l,expt} - v_{l,calc}}{v_{l,expt}}\right)^2 + \left(\frac{v_{v,expt} - v_{v,calc}}{v_{v,expt}}\right)^2\right)_i \qquad (3\text{-}6)$$

When vapor density data were not available, the last term of Equation (3-6) was omitted from the objective function. For the data set containing only T-p data, only the first term of Equation (3-6) was included in the objective function. Similarly, for data points containing only temperature and liquid molar volume (T-v_l), only the second term was included in the objective function. The calculated vapor pressure, saturated liquid and vapor molar volumes at different temperatures, appearing in the objective function, were obtained using the equation of state.

The constants in the equation (u, w, Q, α_0 and κ_1 - κ_4) were obtained mainly from the methane, propane, butane and propene saturation data, since these four compounds have a wide saturation range in reduced temperature. The regressed EOS constants are shown in Table I, along with the constants appearing in the repulsive term. A multiple nonlinear regression method was used to regress the constants and the pure component parameters in the equation (T^*, v^* and c). Details on the equilibrium calculation method and the regression technique used in this work are given by Gasem [30].

In principle, the pure component parameters can be obtained by solving the equations for the critical point constraints, and using vapor-liquid equilibrium data [19]. Using such a strategy would reduce the number of the substance-specific parameters in the equation of state, provided that the critical properties are available. However, parameter regressions including the critical point constraints are not considered in the present work.

In each iteration step to calculate the vapor pressure and saturated liquid and vapor molar volumes, the liquid and vapor roots (compressibility factors) of the equation of state are identified. Since the EOS (Equation (3-4)) is fifth order in compressibility factor, the conventional Newton's Method often does not lead to the correct solutions of the equation. Thus, a robust technique was used to solve Equation (3-4) as follows. For

TABLE I

EQUATION OF STATE CONSTANTS

Constant	Value
τ	0.74048
β_1	4.0000
β_2	1.9000
u	-2.6192
w	2.0000
Q	7.3708
α_0	1.4000
κ_1	0.092687
κ_2	0.18011
κ_3	-0.030748
κ_4	-0.33149

a liquid root, the initial value of Z_l was taken as the Z_{min} in Equation (2-28) of the previous chapter. The right hand side of Equation (3-4) was calculated repeatedly with increasing Z_l (1% each time) until its sign changed from negative to positive. Then, the Z value was set as the new initial guess, and Newton's Method was applied. The convergence criterion used requires that the relative difference of the compressibility factor from the previous iteration is smaller than $1.0\text{x}10^{-8}$. A similar technique was used to obtain the vapor root. The initial guess for Z_v was set to a value of three, which is large enough for all the experimental data used in this work. The right hand side of Equation (3-4) was calculated repeatedly with decreasing value of Z_v (5 % reduction every iteration). When a sign change was observed, Newton's method was applied with the updated Z_v as an initial guess.

Database Used in the Present Work

A database of 21 pure compounds described previously by Shaver [19] was used in this work. The database covers almost the entire vapor-liquid coexistence region (from the triple point to a reduced temperature of about 0.98). The near-critical data were excluded to avoid the numerical difficulties associated with calculating vapor pressures at those points. Only vapor pressure data were available for six compounds, and for some compounds limited saturated liquid density data were available. Specific ranges of saturated data used for pure fluids and their sources are presented in Table II. Beyond the data used by Shaver [19], data for heavy normal hydrocarbons (n-C_{20}, n-C_{28}, n-C_{36} and n-C_{44}) and hydrogen were also used to evaluate the pure component parameters of the equation for those compounds. The temperature, pressure and saturated density ranges for these heavy normal hydrocarbons and hydrogen with their sources are also shown in Table II.

TABLE II

SOURCES AND RANGES OF PURE-FLUID SATURATION DATA USED

Compound	Temperature Range, K	Pressure Range, bar	Liquid Density Range, g/cm^3	Vapor Density Range, g/cm^3	Source
Methane	90.68 - 188.0	0.1172 - 42.412	0.2299 - 0.4512	2.514x10^{-4} - 0.0986	32
Ethane	90.348 - 295.0	1.131x10^{-5} - 39.16	0.3309 - 0.6519	4.557x10^{-8} - 0.0925	33
Propane	85.47 - 360.0	3.0x10^{-9} - 35.55	0.3453 - 0.6574	2.72x10^{-5} - 0.1054	34
n-Butane	134.86 - 420.0	6.736x10^{-6} - 34.83	0.3281 - 0.7353	3.492x10^{-8} - 0.1335	35
n-Octane	243.15 - 553.15	3.16x10^{-4} - 19.97	0.3818 - 0.7102	0.0003 - 0.09873	36
n-Decane	330.85 - 613.15	0.01333 - 20.366	0.324 - 0.6996	*	37
n-Tetradecane	394.26 - 573.15	0.0129 - 2.605	0.6685**	*	37
Ethene	103.986 - 276.0	0.0012 - 43.73	0.3242 - 0.6549	4.01x10^{-6} - 0.1115	38
Propene	87.89 - 360.0	9.54x10^{-9} - 42.202	0.3292 - 0.7688	5.49x10^{-11} - 0.1338	39
1-Butene	119.95 - 413.15	5.0x10^{-7} - 36.18	0.345 - 0.618	*	37
1-Hexene	156.15 - 493.15	5.0x10^{-7} - 26.86	*	*	37
Cyclopropane	171.85 - 393.15	0.01333 - 51.252	*	*	37
Cyclobutane	204.95 - 453.15	0.01333 - 45.191	*	*	37
Cyclohexane	279.82 - 543.15	0.05328 - 35.889	0.3130 - 0.7102	*	37

TABLE II (Continued)

Compound	Temperature Range, K	Pressure Range, bar	Liquid Density Range, g/cm^3	Vapor Density Range, g/cm^3	Source
Cyclooctane	308.45 - 633.15	0.01333 - 31.309	*	*	37
trans-Decalin	334.06 - 492.03	0.01333 - 1.9998	0.7726 - 0.8355	*	37, 40
Benzene	278.68 - 555.0	0.0478 - 44.8502	0.4355 - 0.8965	1.62x10^{-4} - 0.1750	40
Toluene	270.0 - 580.0	0.0076 - 35.56	0.2914 - 0.8873	2.87x10^{-5} - 0.1318	41
1-Methyl Naphthalene	380.83 - 551.47	0.01333 - 1.9998	0.9230 - 0.9619	*	37
Argon	84.0 - 146.0	0.7052 - 49.05	0.8296 - 1.413	0.004194 - 0.2680	38
Carbon Dioxide	216.55 - 298.15	5.179 - 64.356	0.7138 - 1.1778	0.0138 - 0.2424	42
Water	273.16 - 633.15	0.006117 - 186.55	0.5281 - 0.9998	4.855x10^{-6} - 0.1437	43
n-Eicosane	473.15 - 623.15	0.01533- 1.110	0.5903 - 0.6668		37
n-Octacosane	323.15 - 704.45	7.0x10^{-9} - 1.01325	0.6226 - 0.7876		37
n-Hexatriacontane	373.15 - 769.15	6.9x10^{-8} - 1.01325	0.6399 - 0.7667		37
n-Tetratetracontane	373.15 - 818.15	6.9x10^{-8} - 1.01325	0.7450 - 0.7760		37
Hydrogen	14.000 - 32.000	0.074 - 11.07	0.0460 - 0.0769	1.388x10^{-4} -0.0175	41

* Saturated density data for these compounds were not available.

** Only one saturated liquid density value was available for n-tetradecane.

Results and Discussions

Saturation Property Predictions

Errors in the predicted vapor pressures for 21 selected compounds are shown in Table III along with those of the PR, SPHCT and Modified SPHCT equations. The critical properties, required in the PR equation, and the pure component parameters for the SPHCT and Modified SPHCT equations are given by Shaver [19], as shown in Tables III to V. The errors are expressed using the Root Mean Squared Error (RMSE) and the Absolute Average Percent Deviation (%AAD). The RMSE and %AAD are defined as follows

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{N}\left(Y_{\mathrm{expt},i} - Y_{\mathrm{calc},i}\right)^2}{N}} \qquad (3\text{-}7)$$

$$\%\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Y_{\mathrm{expt},i} - Y_{\mathrm{calc},i}}{Y_{\mathrm{expt},i}}\right| \times 100 \qquad (3\text{-}8)$$

where Y stands for any property to be evaluated. In this case, Y is vapor pressure.

The comparisons shown in Table VI are based on vapor pressures greater than 0.007 bar. This is because the SPHCT and Modified SPHCT equations cannot predict vapor pressure accurately below 0.007 bar [18, 19]. For the new equation, vapor pressures were also calculated using data over the full saturation range (from the triple point to a reduced temperature of about 0.98). The quality of fit (RMSE = 1.12 bar and %AAD = 1.83) is almost the same as that of the reduced data set (vapor pressures greater than 0.007 bar) shown in Table VI. This indicates that the new equation has a predictive capability for vapor pressures within 2.0 % for the entire two-phase region. The overall %AAD of the new equation is about half of those of the PR and SPHCT equations.

TABLE III

CRITICAL PROPERTIES USED IN THE PR EOS FOR PURE-FLUID EVALUATIONS

Compound	T_c (K)	p_c (bar)	ω	Source
Methane	190.56	45.95	0.0110	32
Ethane	305.40	48.20	0.0990	44
Propane	369.80	42.42	0.1530	44
n-Butane	425.16	37.96	0.1990	44
n-Octane	569.35	24.96	0.3980	18
n-Decane	617.50	20.97	0.4890	18
n-Tetradecane	691.58	15.62	0.6442	30
n-Eicosane	766.60	10.69	0.8791	45
Ethene	282.34	50.40	0.0910	38
Propene	365.57	46.65	0.1440	38
1-Butene	419.95	40.43	0.1910	44
1-Hexene	504.03	31.43	0.2850	44
Cyclopropane	398.25	55.75	0.1300	44
Cyclobutane	460.00	49.85	0.1810	44
Cyclohexane	553.50	40.74	0.2100	44
Cyclooctane	647.20	35.67	0.2360	44
trans-Decalin	687.10	31.40	0.2700	44
Benzene	561.75	48.76	0.2120	44
Toluene	591.80	41.04	0.2630	44
1-Metylnaphthalene	772.00	36.00	0.3100	44
Argon	150.86	49.05	0.0010	38
Carbon Dioxide	304.20	73.76	0.2390	44
Water	647.13	220.55	0.3440	43

TABLE IV

PURE-FLUID PARAMETERS FOR THE SPHCT EOS

Compound	T^* (K)	v^* (cm^3/mol)	c
Methane	80.050	18.889	1.0298
Ethane	120.73	26.988	1.2485
Propane	136.94	35.876	1.5015
n-Butane	151.73	43.922	1.6867
n-Octane	177.91	74.084	2.6453
n-Decane	186.03	93.130	3.0697
n-Tetradecane	196.70	127.416	3.9218
n-Eicosane	205.98	181.657	5.1600
Ethene	111.58	24.684	1.2379
Propene	133.85	31.881	1.5267
1-Butene	157.89	40.457	1.5212
1-Hexene	255.90	26.597	1.0854
Cyclopropane	252.76	13.699	0.6646
Cyclobutane	312.12	13.976	0.6413
Cyclohexane	199.49	49.825	1.7077
Cyclooctane	212.41	69.815	2.1068
trans-Decalin	381.13	29.826	0.9682
Benzene	192.59	41.457	1.8866
Toluene	205.78	52.971	1.8921
1-Metylnaphthalene	398.18	28.382	1.1351
Argon	63.250	14.275	1.0270
Carbon Dioxide	104.32	14.486	1.9258
Water	225.08	9.0710	2.0233

TABLE V

PURE-FLUID PARAMETERS FOR THE MODIFIED SPHCT EOS

Compound	T^* (K)	v^* (cm^3/mol)	c
Methane	95.230	18.858	1.0003
Ethane	142.28	26.795	1.2423
Propane	165.27	35.123	1.4273
n-Butane	185.28	43.721	1.5594
n-Octane	227.31	78.542	2.1875
n-Decane	239.20	96.459	2.4906
n-Tetradecane	256.16	133.68	3.0646
n-Eicosane	276.49	195.23	3.7096
Ethene	131.95	23.773	1.2299
Propene	164.70	31.885	1.3884
1-Butene	183.89	40.798	1.5329
1-Hexene	210.80	59.210	1.8164
Cyclopropane	181.03	29.372	1.3473
Cyclobutane	203.12	36.629	1.4884
Cyclohexane	239.26	52.475	1.6060
Cyclooctane	273.29	67.898	1.7514
trans-Decalin	286.08	80.275	1.8482
Benzene	242.48	44.417	1.6142
Toluene	249.65	53.890	1.7578
1-Metylnaphthalene	314.20	76.076	2.0217
Argon	76.030	14.098	0.9760
Carbon Dioxide	131.05	15.858	1.6258
Water	266.06	10.568	1.9416

TABLE VI

COMPARISON OF PURE FLUID VAPOR PRESSURE PREDICTIONS

Component	Peng-Robinson*		SPHCT*		Modified SPHCT*		This Work	
	RMSE bar	%AAD	RMSE bar	%AAD	RMSE bar	%AAD	RMSE bar	%AAD
Methane	0.162	1.57	0.444	3.81	0.239	1.30	0.383	1.56
Ethane	0.075	3.52	0.721	4.41	0.056	0.51	0.685	2.52
Propane	0.074	5.76	0.721	3.73	0.101	0.94	0.053	0.04
n-Butane	0.094	1.72	0.764	4.49	0.167	0.88	0.311	1.71
n-Octane	0.050	2.00	0.408	4.16	0.128	1.68	0.259	2.50
n-Decane	0.063	3.90	0.489	3.60	0.115	1.05	0.551	2.22
n-Tetradecane	0.030	7.26	0.021	1.26	0.027	1.24	0.036	1.81
Ethene	0.056	2.77	0.923	4.08	0.134	0.48	0.719	2.05
Propene	0.053	1.22	0.655	3.97	0.143	0.72	0.710	2.27
1-Butene	0.052	10.34	0.685	3.28	0.158	0.83	0.271	0.81
1-Hexene	0.039	1.12	0.227	0.85	0.117	1.09	0.171	1.61
Cyclopropane	0.072	1.57	0.384	0.96	0.188	0.51	0.150	0.47
Cyclobutane	0.061	0.52	0.378	1.16	0.199	1.21	0.411	0.91
Cyclohexane	0.029	2.09	0.668	2.15	0.083	1.21	0.284	1.02
Cyclooctane	0.176	7.34	1.029	3.95	0.220	2.12	0.182	1.04
trans-Decalin	0.049	11.86	0.009	0.84	0.006	1.21	0.002	0.12
Benzene	0.082	2.10	0.447	3.79	0.156	1.25	0.963	2.65
Toluene	0.056	1.75	1.105	4.13	0.141	1.10	0.162	0.96
1-Metylnaphthalene	0.080	19.33	0.010	0.68	0.006	1.20	0.002	0.12
Argon	0.110	0.39	0.338	2.32	0.216	0.74	1.012	2.67
Carbon Dioxide	0.344	2.21	0.651	2.96	0.212	0.45	0.582	2.31
Water	0.829	4.69	3.763	6.97	1.968	2.79	4.824	6.48
Overall	0.236	3.56	1.041	3.02	0.467	1.14	1.268	1.75

* from Shaver [19]

Among the equations considered, the Modified SPHCT equation showed the best predictions.

In the prediction of vapor pressures for n-decane and n-tetradecane, the new equation, the SPHCT equation and the Modified SPHCT equation show better performance than the PR equation. This implies that the equations based on segment-segment interactions are superior to the equation based on molecule-molecule interactions, in predicting the vapor pressure for heavy compounds. The new equation shows relatively worse prediction for water than for other compounds (RMSE is 4.83 bar and %AAD is 6.48). This indicates that the equation fails to predict accurately vapor pressures of highly polar fluids like water. In general, however, the performance of the new equation is better than those of the PR and the SPHCT equations of state in predicting vapor pressures of pure fluids over the full saturation range.

Errors in the prediction of saturated liquid and vapor densities for selected compounds are shown in Tables VII and VIII. The results in these tables are for vapor pressures greater than 0.007 bar. For the new equation, saturated densities were also calculated using the complete data set. For saturated liquid densities, the overall RMSE is 0.027 g/cm^3 and the overall %AAD is 3.54. For saturated vapor densities, the overall RMSE is 0.005 g/cm^3 and the overall %AAD is 3.05. The overall RMSE and %AAD for the reduced data set and the complete data set are almost equal. This indicates that the errors in the predicted phase densities are evenly distributed from the triple point to near the critical point.

The new equation is better than the other equations considered in representing saturated liquid densities of pure fluids. While the PR and SPHCT equations show comparable performance in predicting the saturated liquid densities of pure fluids (%AAD of 6.65 and 6.87, respectively), the Modified SPHCT equation shows the worst results for saturated liquid density predictions (%AAD of 10.05). For saturated vapor density predictions, the overall %AAD of the SPHCT equation is almost double that observed for

TABLE VII

COMPARISON OF PURE FLUID LIQUID DENSITY PREDICTIONS

	Peng-Robinson*		SPHCT*		Modified SPHCT*		This Work	
Component	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD
Methane	0.036	8.75	0.028	6.97	0.034	9.88	0.017	4.57
Ethane	0.030	5.45	0.045	7.82	0.047	9.82	0.010	2.14
Propane	0.032	5.56	0.047	7.79	0.046	8.12	0.014	2.70
n-Butane	0.029	5.04	1.049	7.88	0.049	8.75	0.022	4.29
n-Octane	0.030	5.19	0.062	9.88	0.058	9.88	0.042	7.72
n-Decane	0.043	7.14	0.068	11.49	0.073	12.84	0.028	4.94
n-Tetradecane	0.079	8.83	0.002	0.25	0.013	1.93	0.020	2.89
Ethene	0.041	7.10	0.037	7.35	0.043	8.14	0.011	2.17
Propene	0.041	6.60	0.039	7.55	0.045	8.31	0.022	4.20
1-Butene	0.024	3.90	0.024	3.72	0.053	10.03	0.017	2.93
Cyclohexane	0.018	2.60	0.029	4.10	0.064	10.27	0.022	3.93
Benzene	0.038	5.56	0.072	9.28	0.077	11.78	0.043	6.21
Toluene	0.027	2.89	0.060	7.24	0.064	8.34	0.033	4.81
Argon	0.145	10.00	0.077	5.93	0.084	6.97	0.018	1.41
Carbon Dioxide	0.047	4.36	0.051	4.49	0.109	10.73	0.047	4.46
Water	0.156	19.54	0.077	8.28	0.172	21.58	0.032	3.56
Overall	0.062	6.65	0.052	6.87	0.077	10.05	0.028	3.87

* from Shaver [19]

TABLE VIII

COMPARISON OF PURE FLUID VAPOR DENSITY PREDICTIONS

Component	Peng-Robinson*		SPHCT*		Modified SPHCT*		This work	
	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD	RMSE g/cm^3	%AAD
Methane	0.002	3.14	0.007	6.61	0.001	1.39	0.006	5.03
Ethane	0.001	4.01	0.006	7.05	0.002	1.80	0.002	1.98
Propane	0.001	6.12	0.006	5.26	0.002	2.23	0.004	3.58
n-Butane	0.001	2.12	0.010	6.53	0.003	1.92	0.005	2.21
n-Octane	0.001	2.25	0.009	8.11	0.003	4.48	0.005	4.09
Ethene	0.001	2.88	0.008	6.52	0.002	2.01	0.002	1.65
Propene	0.000	1.56	0.009	6.11	0.003	2.58	0.003	1.50
Benzene	0.002	2.78	0.014	7.13	0.005	3.77	0.008	3.02
Toluene	0.004	4.04	0.009	5.12	0.001	2.35	0.003	2.17
Argon	0.003	1.36	0.014	3.98	0.005	1.33	0.003	1.43
Carbon Dioxide	0.001	2.65	0.015	4.64	0.005	2.72	0.007	2.25
Water	0.003	5.99	0.017	11.29	0.006	3.29	0.010	6.55
Overall	0.002	3.14	0.011	6.01	0.003	2.25	0.006	3.13

* from Shaver [19]

the PR equation and the new equation; both are comparable in their predictions of saturated vapor densities (%AAD of 3.1). The Modified SPHCT equation is the best among the equations considered in representing saturated vapor densities, while it is the worst for saturated liquid densities without volume translation.

Figure 3 shows the experimental and calculated phase envelope for propane, which is known for its wide pressure range in the two-phase region. The calculated properties were obtained from the vapor-liquid equilibrium calculations at the experimental temperatures. The figure shows that the proposed equation has the capability to predict the vapor-liquid phase envelope from the triple point to the critical point.

The EOS pure component parameters obtained are shown in Table IX. In general, the characteristic temperature (T^*) increases as the normal boiling point of the compound increases. The characteristic volume (v^*) increases as the molecular size of the compound increases except for polar compounds such as carbon dioxide and water. The degrees of freedom parameter (c) shows a trend similar to the characteristic volume. For normal paraffins, the pure component parameters are plotted as function of their carbon number in Figures 4 to 6. The characteristic temperature shows an asymptotic behavior as the carbon number in the compound increases. The characteristic volume and the degrees of freedom parameter are almost linear relative to the carbon number of the compound. These trends are similar to those of the SPHCT equation, and should be amenable to simple generalization. It should be noted that the pure component parameters for n-eicosane and n-octacosane deviate slightly from the trends. This may be attributed to the presence of some correlation among the parameters.

Second Virial Coefficients

For pure fluids, the second virial coefficient of the proposed equation of state is given as:

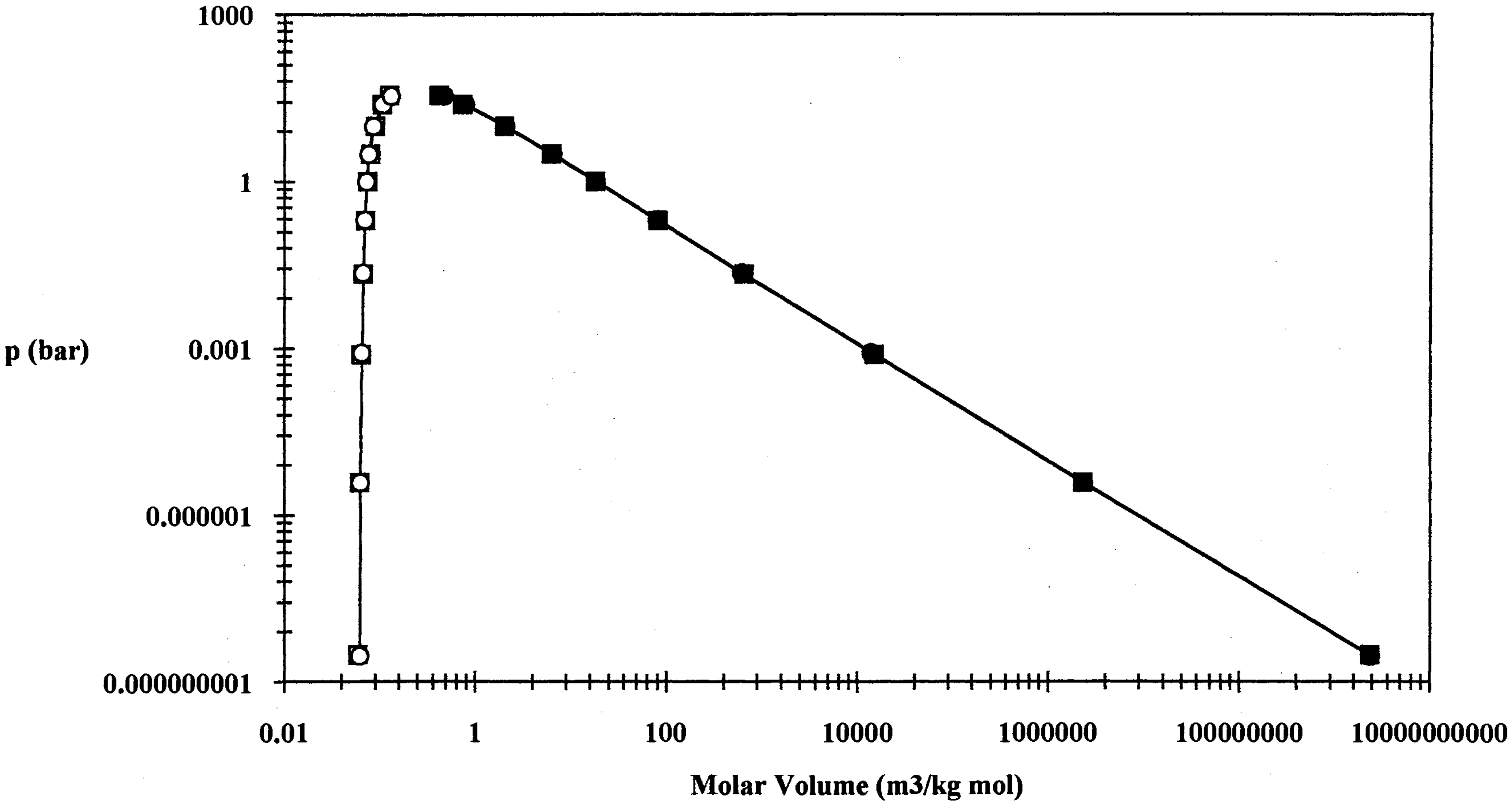

Figure 3. Experimental and Calculated Vapor pressure and Phase Molar Volumes for Propane.
☐ Calculated Liquid Phase ■ Vapor Phase;
○ Experimental Liquid Phase ● Vapor Phase [34]

TABLE IX

PURE-FLUID PARAMETERS FOR THE PROPOSED EQUATION

Compound	T* (K)	v* (cm^3/mol)	c
Methane	81.287	23.180	1.0000
Ethane	121.46	30.817	1.2545
Propane	143.01	40.915	1.3990
n-Butane	157.04	50.202	1.5973
n-Octane	189.10	84.736	2.3581
n-Decane	201.84	105.16	2.5979
n-Tetradecane	206.31	155.95	3.5223
n-Eicosane	208.53	204.99	5.2086
n-Octacosane	218.51	286.38	6.5399
n-Hexatriacontane	230.91	395.89	7.0828
n-Tetratetracontane	234.06	491.49	8.1107
Ethene	112.58	27.566	1.2402
Propene	138.78	36.804	1.4365
1-Butene	158.68	47.191	1.5180
1-Hexene	170.35	73.850	2.0271
Cyclopropane	156.97	33.757	1.3242
Cyclobutane	177.17	41.313	1.4512
Cyclohexane	205.40	59.327	1.6119
Cyclooctane	227.67	77.828	1.8601
trans-Decalin	203.89	161.70	2.4709
Benzene	205.02	48.701	1.6738
Toluene	212.37	60.107	1.7995
1-Metylnaphthalene	232.47	136.22	2.5651
Argon	64.055	16.928	1.0000
Carbon Dioxide	111.31	18.052	1.6565
Water	231.08	10.352	1.9365
Hydrogen	20.555	18.434	0.38545

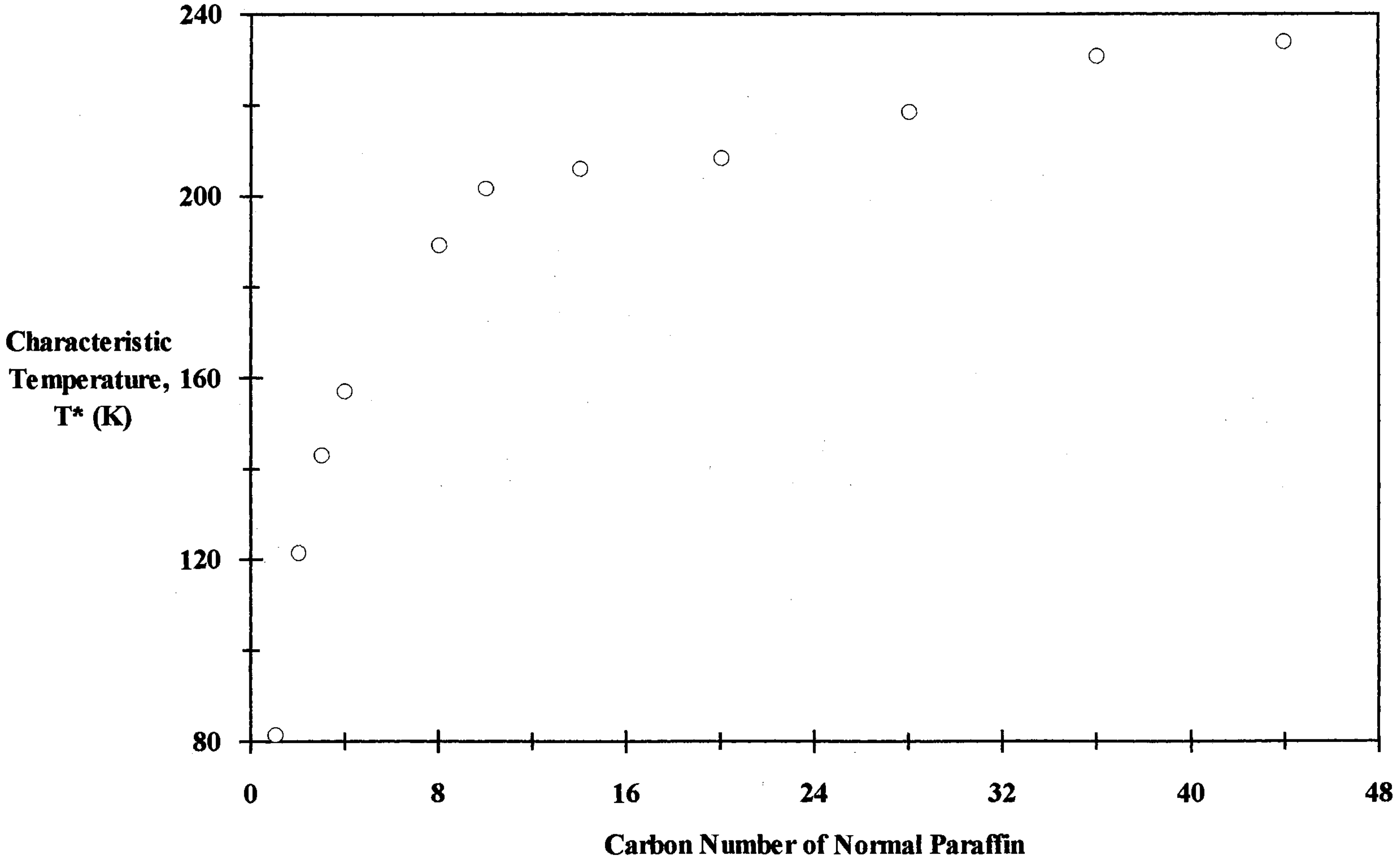

Figure 4. Characteristic Temperatures of Normal Paraffins

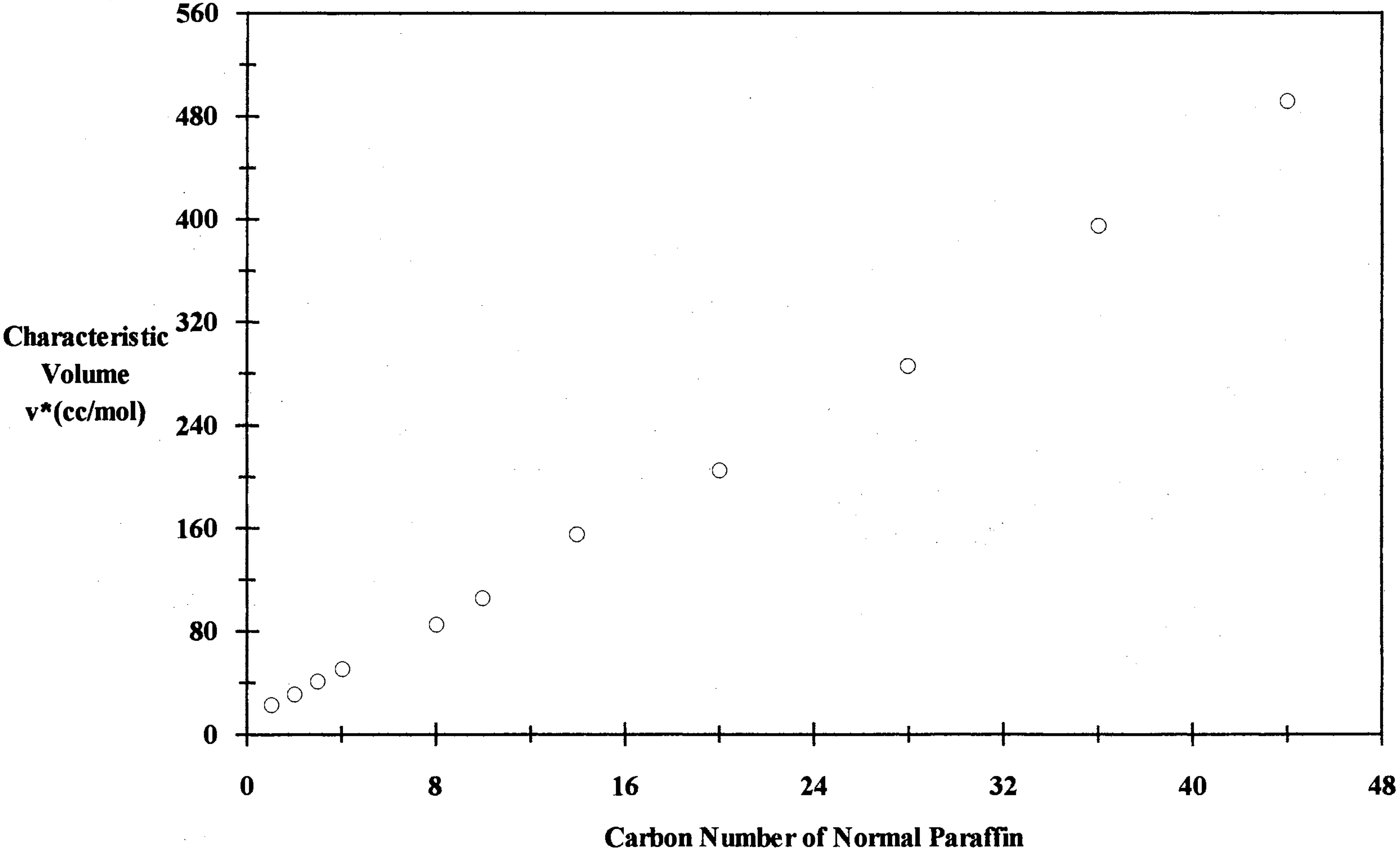

Figure 5. Characteristic Volumes of Normal Paraffins

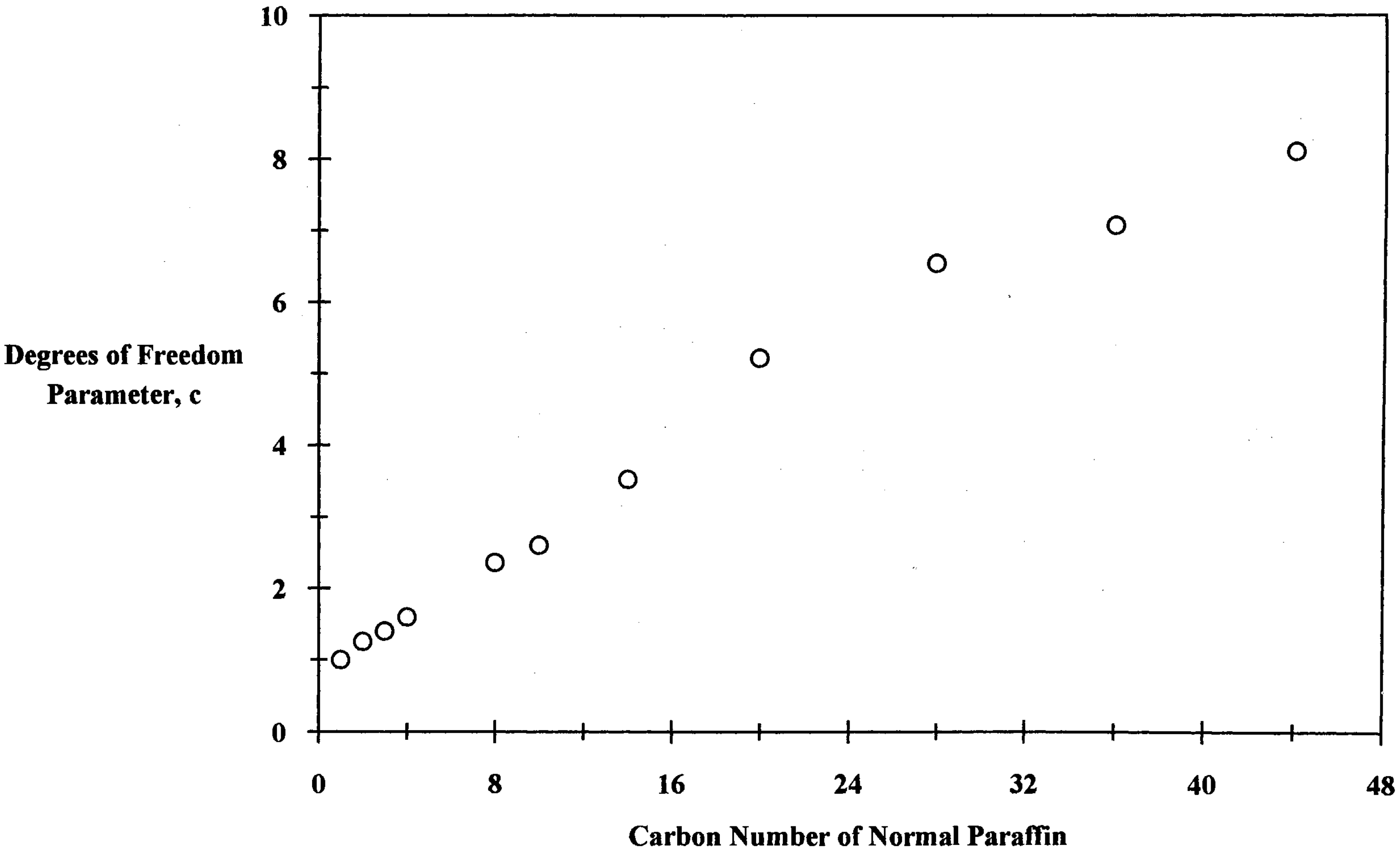

Figure 6. Degrees of Freedom Parameters of Normal Paraffins

$$B = \beta_1 \tau c v^* - (1 + Q) c \alpha Y v^* \tag{3-9}$$

The second virial coefficients for propane, argon and methane were evaluated using the above expression, and the results were compared to the smoothed experimental data presented by Dymond and Smith [31]. Figure 7 shows the calculated and experimental second virial coefficients for the selected pure fluids. The figure indicates good agreement between calculated and experimental values for reduced temperatures greater than two. For lower temperature, however, the new EOS over-predicts the second virial coefficient.

Conclusions and Recommendations

The EOS constants and the pure component parameters for selected compounds are obtained for the new equation of state. For the systems considered, the vapor pressure predictive capability of the new equation is better than PR and SPHCT equations of state over the full saturation range. Similarly, the new equation has better predictive capability for saturated liquid densities than PR and SPHCT equations, while all the equations considered are comparable in representing saturated vapor densities. The Modified SPHCT equation is the best among the equations considered in representing vapor pressures greater than 0.007 bar and saturated vapor densities. However, without volume translation, the Modified SPHCT equation showed poor representations for saturated liquid densities (AAD of 10 %).

In general, the new equation has a better predictive capability than PR and SPHCT in representing vapor pressures and saturated liquid and vapor densities for the selected systems and comparable abilities to the Modified SPHCT. The pure component parameters show a systematic trend with increasing carbon number. This indicates that the pure component parameters can be generalized. The second virial coefficients were calculated for selected compounds, and were compared to experimental values. Both the

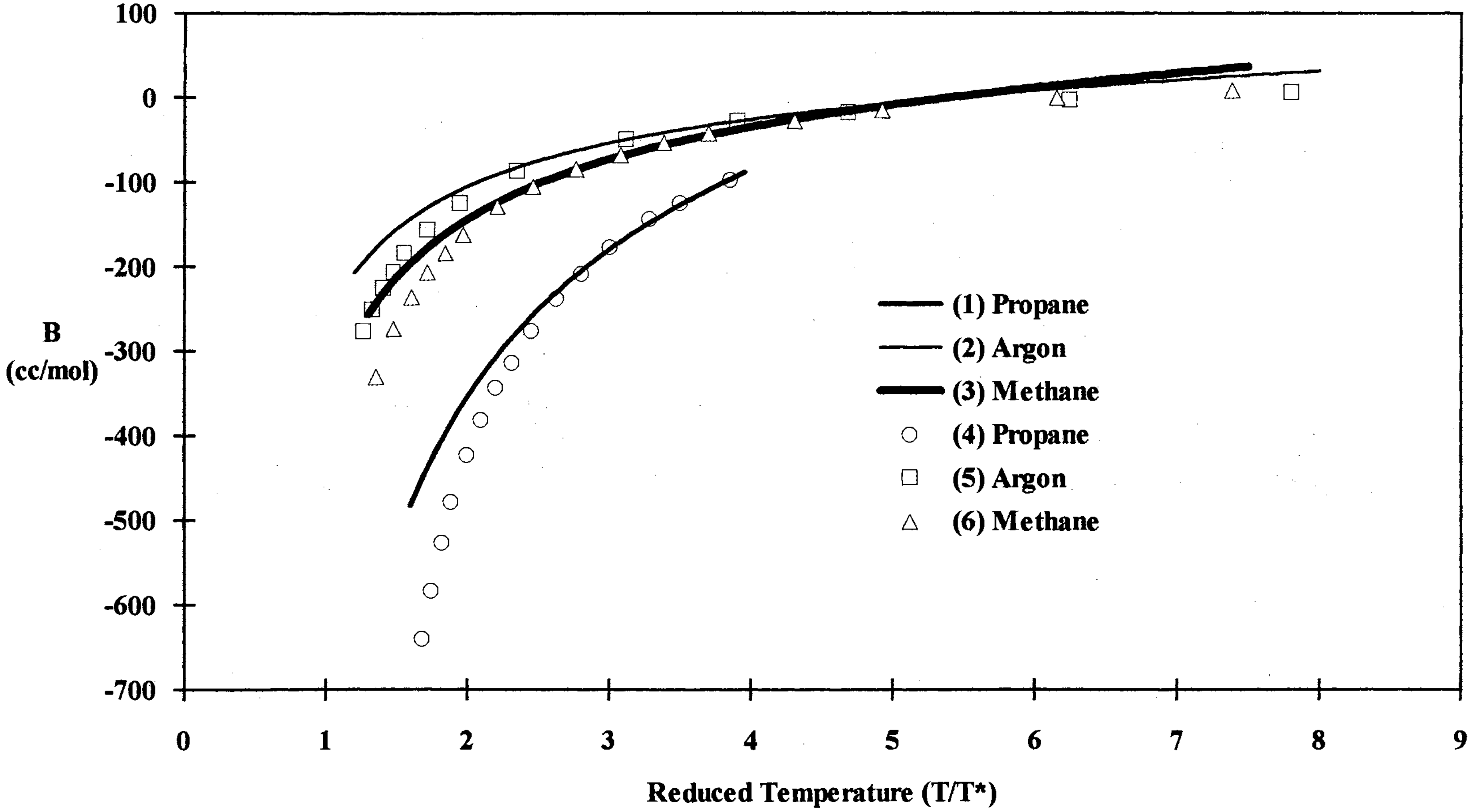

Figure 7. Second Virial Coefficients for Propane, Argon and Methane.
(1), (2) and (3): Calculated Values;
(4), (5) and (6): Experimantal Values [31]

calculated and experimental values show very good agreement above a reduced temperature (T/T^*) of two.

Based on the present work, the following tasks are recommended.

1. The ability of the equation of state to predict the volumetric properties in the single phase region (superheated vapor and sub-cooled liquid regions) should be evaluated. Further, the EOS constants and the pure component parameters of the equation should be obtained from data covering the entire p-v-T surface, including volumetric properties in the single phase region.
2. The calorimetric properties for various compounds should be calculated to further evaluate the equation of state.
3. Evaluations of the equation with the parameters obtained from regressions including the critical-point constraints should be pursued.
4. Generalization of the pure component parameters for n-paraffins should be undertaken to expand the applicability of the equation of state.

CHAPTER IV

EVALUATION OF THE NEW EQUATION FOR SELECTED BINARY MIXTURES

Abstract

A set of mixing rules has been proposed for the new equation of state to extend its predictive capabilities to mixtures. The equation was evaluated using data for binary mixtures of ethane + n-paraffins, carbon dioxide + n-paraffins and hydrogen + n-paraffins. Two binary interaction parameters were introduced in the mixing rules, one for characteristic temperature (T^*) and the other for characteristic volume (v^*). Several case studies for the use of interaction parameters were pursued for the binary mixtures considered. The cases studied include bubble point pressure predictions (1) without interaction parameters, (2) with a single interaction parameter for all binaries for a given solute gas, (3) with one interaction parameter for each solvent, and (4) with one interaction parameter for each isotherm of each solvent.

The predicted bubble point pressures for the ethane and carbon dioxide binaries were compared to those of the Peng-Robinson (PR), Simplified Perturbed-Hard-Chain Theory (SPHCT) and Modified SPHCT equations of state for each case studied. For the hydrogen binaries, comparisons were limited to the PR equation using a system-dependent or temperature-dependent interaction parameter. The predictive capability of the proposed equation is better or comparable to the PR, SPHCT and Modified SPHCT equations for both the ethane and carbon dioxide binary systems. For the hydrogen systems, the PR equation shows better performance than the new equation.

Introduction

A large portion of the separation and purification processes (such as distillation, extraction, crystallization) rely on accurate knowledge of equilibrium properties. Currently, accurate description of vapor-liquid equilibrium of asymmetric mixtures is of interest in coal conversion, enhanced oil recovery and supercritical separations. These asymmetric mixtures pose a challenge to the current thermodynamic models. In the present chapter, the proposed equation of state is tested for the prediction of vapor-liquid equilibrium of selected asymmetric mixtures.

In vapor-liquid equilibrium calculations, equations of state are considered the most convenient models. To extend the use of such equations to mixtures, mixing rules are required. The one-fluid theory, which treats a mixture as a hypothetical pure fluid at a given temperature and molar volume, is most commonly used for mixture equations of state. The one-fluid theory is described well by Leland et al. [46]. Two- and three-fluid models are also available in the literature. The cell models for liquid solutions proposed by Scott are typical two- and three-fluid models [47].

A number of studies on mixing rules for virial type equations of state have appeared in the literature. Lin and Robinson tested six different mixing rules for the pure component potential parameter ε_{ii} used for predicting interaction second virial coefficients for rare-gas pairs [48]. They suggested that the harmonic average of pure potential parameters, in the pair potential model of Dymond and Alder [49], is the best among the models tested. Similarly, several mixing rules for the mean-density-approximation equation of state are proposed and tested for various binary and ternary systems [50 - 52].

For an equation of state which covers the density range extending from ideal gas to saturated liquid, the van der Waals one-fluid theory is the most widely used mixing rule [53]. For cubic equations of state such as the PR and SRK equations, the use of geometric average for the attractive energy parameter (a_{ij}) and the arithmetic average for the covolume (b_{ij}) is most common [1, 2, 30, 54].

Huron and Vidal showed that any mixing model which gives a finite excess Gibbs free energy at infinite pressure can be used to construct a mixing rule [55]. They proposed several mixing rules for cubic equations with the condition of a finite excess Gibbs free energy at infinite pressure. Their mixing rules for the SRK equation are as follows:

$$b = \sum_{i} z_j b_{ii} \tag{4-1}$$

and

$$a = b\left(\sum_{i} z_i \frac{a_{ii}}{b_{ii}} - \frac{g_{\infty}^{E}}{\ln 2} \right) \tag{4-2}$$

where g_{∞}^{E} is the excess Gibbs free energy of a system at infinite pressure. According to Equation (4-2), any excess Gibbs free energy expression at infinite pressure can be used to estimate "a" of the SRK equation.

Typical examples of the excess Gibbs free energy models are the local composition models of Wilson [25] and NRTL [26]. Radosz et al. [56] proposed a set of general mixing rules for the SRK equation, which is similar to that suggested by Smith [53], for asymmetric mixtures. Their mixing rules are as follows:

$$b = \sum_{i} \sum_{j} z_i z_j b_{ij} \quad \text{and} \quad a\,b^{-0.25} = \sum_{i} \sum_{j} z_i z_j a_{ij} b_{ij}^{-0.25} \tag{4-3}$$

where

$$b_{ij}^{1/3} = \frac{1}{2}\left(b_i^{1/3} + b_j^{1/3}\right) \quad \text{and} \quad a_{ij} b_{ij}^{-0.25} = \sqrt{a_i a_i \left(b_i b_j\right)^{-0.25}}\left(1 - C_{ij}\right) \tag{4-4}$$

The exponent -0.25 in Equations (4-3) and (4-4) is a regressed value from experimental data. This asymmetric mixing rule is of interest for mixtures containing large variations in component sizes.

Modifications of the conventional mixing rules by applying composition dependent cross-terms have also been described in the literature [57 - 59]. Adachi and Sugie [59] used the linear mixing rule for the covolume parameter "b" and the following quadratic mixing rule for "a" of the Redlich-Kister equation.

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{4-5}$$

where

$$a_{ij} = \left(1 - C_{ij}\right)\left(a_i a_j\right)^{1/2} \text{ with } C_{ij} = l_{ij} + m_{ij}\left(z_i - z_j\right) \tag{4-6}$$

where l_{ii} and m_{ii} are binary interaction parameters. Recently, Wong and Sandler have proposed mixing rules for the van der Waals type equations, which satisfy the quadratic composition dependence of the second virial coefficient [60]. Their mixing rules are as follows:

$$b = \frac{\sum_i \sum_j z_i z_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \frac{F(z)}{RT}} \tag{4-7}$$

and

$$a = b\,F(z) \tag{4-8}$$

where F(z) is an arbitrary function of composition vector z. They determined F(z) from the excess Helmholtz free energy at infinite pressure, and showed that their mixing rules are better than the conventional mixing rules for some mixtures.

The lack of fit of an equation of state in representing equilibrium properties of mixtures is typically due to inherent deficiencies in the equation and/or the applied mixing rules. Normally, binary interaction parameters are required to improve the predictive capability of an equation of state. The role of the interaction parameters becomes especially important for asymmetric mixtures or mixtures containing polar components [30]. In principle, binary interaction parameters (characterizing interaction between different species in the mixtures under study) are commonly obtained from a small amount of experimental data. These binary interaction parameters thus obtained can be generalized to expand the capability of the equation of state.

The mixing rules used in the present work are based on the one-fluid theory. Two binary interaction parameters are introduced to amend the characteristic temperature and the characteristic volume, respectively. These interaction parameters are evaluated for ethane, carbon dioxide and hydrogen binary mixtures with n-paraffins. Normally, ternary or higher order interaction parameters have no merit in the practical sense.

Equation of State for Mixtures

Mixing rules are required to extend the applicability of an equation of state to mixtures. A basic requirement for establishing the viability of a set of mixing rules is to verify that the mixture's second virial coefficient has a quadratic dependence on composition [60]. For pure fluids, the second virial coefficient of the proposed equation of state is given in Equation (3-9) in Chapter III. To satisfy the quadratic composition dependence of the second virial coefficient for a mixture, the following relationships should be satisfied.

$$\left\langle \beta_1 \tau c v^* - (1+Q) c\alpha Y v^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j \left(\beta_1 \tau c v^* - (1+Q) c\alpha Y v^*\right)_{ij} \tag{4-9}$$

A set of mixing rules satisfying the condition shown in Equation (4-9) is proposed. In the cross-terms, the geometric average for the energy parameter (ε_{ij}) and the arithmetic average for the size parameter (σ_{ij}) are adopted. The proposed mixing rules are similar to those of the SPHCT equation.

$$\left\langle cv^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j c_i v_{ji}^* \qquad (4\text{-}10)$$

$$\left\langle v^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j v_{ij}^* \qquad (4\text{-}11)$$

and

$$\left\langle c\alpha Y v^* \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i z_j c_i \alpha_{ij}\left(\exp\left(\frac{T_{ij}^*}{T}\right) - 1\right) v_{ji}^* \qquad (4\text{-}12)$$

where

$$v_{ij}^* = \frac{s_i \sigma_{ij}^3}{\sqrt{2}} \qquad (4\text{-}13)$$

$$\alpha_{ij} = \alpha_0\left(1 + \kappa_1\left(\frac{T}{T_{ij}^*}\right)^{1/2} + \kappa_2\left(\frac{T}{T_{ij}^*}\right) + \kappa_3\left(\frac{T}{T_{ij}^*}\right)^2 + \kappa_4\left(\frac{T}{T_{ij}^*}\right)^{-1}\right) \qquad (4\text{-}14)$$

$$T_{ij}^* = \frac{\varepsilon_{ij} q_i}{c_i k} \qquad (4\text{-}15)$$

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right)\left(1 + D_{ij}\right) \qquad (4\text{-}16)$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\left(1 - C_{ij}\right) \qquad (4\text{-}17)$$

The properties in angular brackets, $\langle\ \rangle$, are for mixtures. In the mixing rules shown in Equations (4-10) and (4-12), the cross-term of the characteristic volume v^*_{ji} is adopted instead of v^*_{ij}. The effect of switching indices is that the mixture properties in Equations (4-10) and (4-12) are more biased toward the component with the smaller characteristic volume. As an example, a mixture property $\langle c\alpha Y v^*\rangle$ is shown in Figure 8 as a function of ethane composition in the binary mixture of ethane + n-decane at 310.9 K.

For mixtures, the equation of state proposed in Chapter II becomes

$$Z = 1 + \frac{\beta_1 \tau \langle cv^* \rangle}{v - \beta_2 \tau \langle v^* \rangle} - \frac{\langle c\alpha Y v^* \rangle v}{v^2 + u\langle v^* \rangle v + w\langle v^* \rangle^2} - \frac{Q\langle c\alpha Y v^* \rangle}{v + \langle v^* \rangle} \tag{4-18}$$

When the hard core radius (σ) shown in Equation (4-13) is the same for all components in a mixture, v^*_{ij} may be expressed as:

$$v^*_{ij} = v^*_{ii}\left(1 + D_{ij}\right)^3 \tag{4-19}$$

For ethane binary mixtures, Equation (4-19) is applied in calculating v^*_{ij}. According to the preliminary calculations, σ of carbon dioxide is almost the same as that of normal paraffins; thus, Equation (4-19) is also used in evaluating the equation for carbon dioxide binaries. Since the value of σ for hydrogen is not known explicitly, it is also assumed to be equal to that of a normal paraffin segment. This assumption along with a zero value for D_{ij} leads to the linear mixing rule for the characteristic volume of a mixture, as shown in Equation (4-24). Actually, the values of the characteristic volume (v^*) for methane, carbon dioxide and hydrogen are not significantly different from each other, and all three of them are considered to be monomers. Hence, for simplicity, using the same value of σ for all components is acceptable. If different values of σ are used for the various compounds, the new equation becomes a four-parameter equation of state. This is another reason for not using a different value of σ for each compounds in this work.

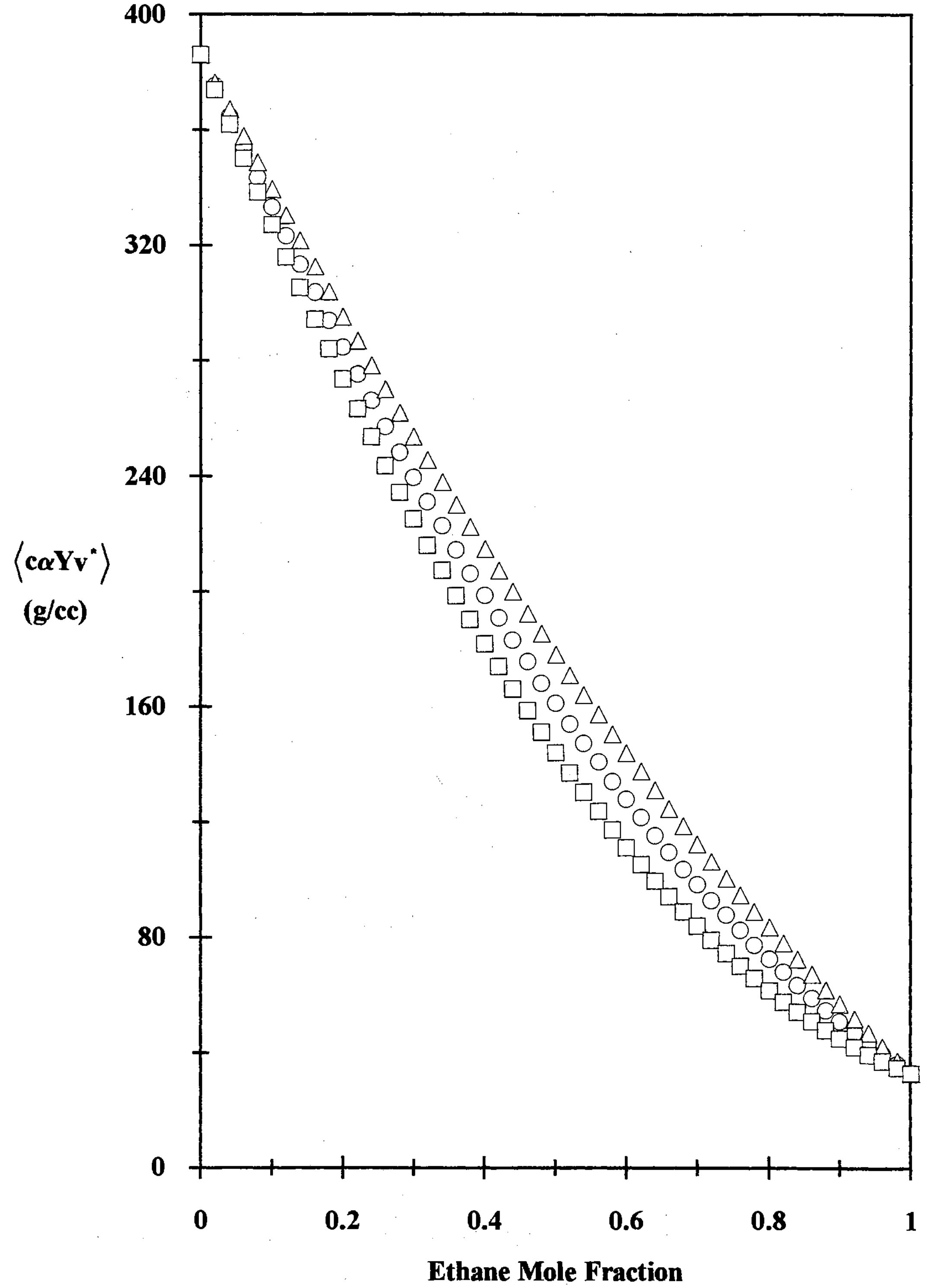

Figure 8. Variations of $\langle c\alpha Y v^* \rangle$ with Composition for Ethane + n-Decane System at 310.9 K. ○ $C_{ij} = 0.0$; □ $C_{ij} = 0.3$; Δ $C_{ij} = -0.3$

Similarly, in evaluating the equation of state for the selected mixtures, ε_{ij}/k is assumed constant. Accordingly, the expression for T_{ij}^* may be written as:

$$T_{ij}^* = T_{ii}^*\left(1 - C_{ij}\right) \tag{4-20}$$

This expression is used throughout the evaluation of the equation for the mixtures considered. If no interaction parameter (C_{ij}, D_{ij}) is used in Equations (4-19) and (4-20), the mixing rules in Equations (4-10) and (4-12) are equivalent to the following expressions:

$$\left\langle cv^*\right\rangle = \left\langle c\right\rangle\left\langle v^*\right\rangle \tag{4-21}$$

and

$$\left\langle c\alpha Y v^*\right\rangle = \left\langle c\alpha Y\right\rangle\left\langle v^*\right\rangle \tag{4-22}$$

where

$$\left\langle c\right\rangle = \sum_{i=1}^{N} z_i c_i \tag{4-23}$$

$$\left\langle v^*\right\rangle = \sum_{i=1}^{N} z_i v_{ii}^* \tag{4-24}$$

and

$$\left\langle c\alpha Y\right\rangle = \sum_{i=1}^{N} z_i c_i \alpha_{ii}\left(\exp\left(\frac{T_{ii}^*}{T}\right) - 1\right) \tag{4-25}$$

Database Used for Mixture Evaluations

The databases used in evaluating the proposed equation of state for mixtures were extracted from those used by Shaver [19] for ethane and carbon dioxide binaries with n-paraffins. The ethane + n-paraffin binary database consists of bubble point pressures and ethane solubilities (liquid phase composition) at different temperatures. The database covers a solvent molecular size extending from n-butane (C_4) to n-tetratetracontane (C_{44}), temperatures from 310.9 to 423 K and pressures to 82.4 bar. In the present work, the normal paraffin solvents selected are n-butane, n-octane, n-decane, n-eicosane, n-octacosane, n-hexatriacontane and n-tetratetracontane. The normal paraffin solvents selected for evaluating the carbon dioxide binaries are n-butane, n-decane, n-eicosane, n-octacosane, n-hexatriacontane and n-tetratetracontane. The carbon dioxide binary database covers temperatures from 310.9 to 510.9 K and pressures to 172.4 bar. Details on the databases for ethane and carbon dioxide binaries used in the present work are described by Shaver [19]. Another database for hydrogen + n-paraffins was used to evaluate the new equation. This database covers solvent molecular size variations from n-butane to n-hexatriacontane, temperatures from 323.2 to 573.3 K and pressures to 173.9 bar. Ranges of temperature, pressure and mole fraction considered in the hydrogen database are shown in Table X, accompanied with their respective literature sources.

Results and Discussions

Bubble point pressure predictions were performed at various temperatures and liquid phase compositions using the new equation of state. Experimental pressures were used as a measure for the quality of fit of the equation. The equation was evaluated using the binary mixtures of ethane and carbon dioxide with normal paraffins. Results were generated for four different cases involving the use of interaction parameters, as described in Table XI. Similar evaluations were conducted using the PR, SPHCT and Modified SPHCT equations for purposes of comparison. The critical properties for the PR equation and the generalized pure component parameters for the SPHCT and Modified SPHCT equations used in this work are given elsewhere [19].

TABLE X

HYDROGEN BINARY SYSTEM SOLUBILITY DATA USED IN EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Source
n-C_4	327.7 - 394.3	27.78 - 168.8	0.0190 - 0.2660	61
n-C_{10}	344.3 - 423.2	37.07 - 173.9	0.0369 - 0.1288	*
n-C_{20}	323.2 - 573.3	9.940 - 118.2	0.0113 - 0.1289	*, 62
n-C_{28}	348.2 - 573.2	9.859 - 131.0	0.0206 - 0.1728	*, 62
n-C_{36}	373.2 - 573.2	10.22 - 167.5	0.0154 - 0.2272	*, 62

* Present work, in Chapter VI of Section I

TABLE XI

SPECIFIC CASES FOR INTERACTION PARAMETERS USED IN EQUATION OF STATE EVALUATIONS

Case	Interaction Parameter	Description
1	$C_{ij} = 0$*	The simple mixing rule without any interaction parameter.
2	C_{ij}	A single value of C_{ij} is determined for all binary systems for each solute gas.
3	$C_{ij}(CN)$	A separate value of C_{ij} is determined for each binary mixture. The value of C_{ij} is dependent only on the normal paraffin carbon number for a given solute.
4	$C_{ij}(CN, T)$	A separate value of C_{ij} is determined for each binary mixture at each temperature. The value of C_{ij} is dependent both on the normal paraffin carbon number and system temperature for a given solute.

* For all cases, $D_{ij} = 0$.

The model evaluation cases studied are listed in Table XI. Case 1 represents the EOS evaluation for the mixtures considered with no interaction parameter ($C_{ij} = 0$). Case 2 represents the EOS evaluation with a single interaction parameter for each solute gas for all the normal paraffin solvents selected. Case 3 addresses the ability of the equation when a common value of C_{ij} for each binary system is used. In case 4, a different value of C_{ij} is used for each isotherm in each binary mixture. EOS evaluations including the second interaction parameter, D_{ij}, are not considered in this work.

For the hydrogen binaries, evaluations were undertaken only with the new equation and the PR equation for Cases 3 and 4. The SPHCT and Modified SPHCT equations are not evaluated for hydrogen binaries, since pure component parameters of the equations are not available. Attempts were made to regress the pure component parameters of hydrogen for the SPHCT equation. However, convergence problems persisted during the equilibrium calculations, especially near the critical point.

To obtain the optimum values of the interaction parameters, the following objective function was used in all model evaluations:

$$SS = \sum_{i=1}^{N} \left(\frac{p_{expt} - p_{calc}}{p_{expt}} \right)_i^2 \qquad (4\text{-}26)$$

where p_{expt} and p_{calc} represent experimental and calculated bubble point pressures, respectively. The prediction of bubble point pressure with interaction parameter(s) regressed through the above objective function leads to the possible minimum value of absolute average percent deviation. Details of the regression technique and bubble point calculation method used in this work are described by Gasem [30].

The fugacity coefficient expression for component "i" in a mixture required in the equilibrium calculations was derived for the new equation of state, as given below:

$$
\begin{aligned}
\ln \phi_i = & -\frac{\beta_1}{\beta_2}\left(\frac{1}{\langle v^* \rangle}\frac{1}{n}\frac{\partial n^2\langle cv^* \rangle}{\partial n_i} - \frac{\langle cv^* \rangle}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)\ln\frac{v_r - \beta_2\tau}{v_r} \\
& + \left(\beta_1\tau\frac{\langle cv^* \rangle}{\langle v^* \rangle}\frac{1}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)\frac{1}{v_r - \beta_2\tau} - \left(\frac{\langle c\alpha Yv^* \rangle}{\langle v^* \rangle}\frac{1}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)\frac{v_r}{v_r^2 + uv_r + w} \\
& + \left(\frac{1}{\langle v^* \rangle}\frac{\partial n\langle c\alpha Yv^* \rangle}{\partial n_i} - \frac{\langle c\alpha Yv^* \rangle}{\langle v^* \rangle}\frac{1}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w - u^2}}\left(\tan^{-1}\frac{2v_r + u}{\sqrt{4w - u^2}} - \frac{\pi}{2}\right) \\
& - \left(\frac{1}{\langle v^* \rangle}\frac{\partial n\langle c\alpha Yv^* \rangle}{\partial n_i} - \frac{\langle c\alpha Yv^* \rangle}{\langle v^* \rangle}\frac{1}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)Q\ln\frac{v_r + 1}{v_r} \\
& - \left(\frac{\langle c\alpha Yv^* \rangle}{\langle v^* \rangle}\frac{1}{\langle v^* \rangle}\frac{\partial n\langle v^* \rangle}{\partial n_i}\right)\frac{Q}{v_r + 1} - \ln Z \qquad (4\text{-}27)
\end{aligned}
$$

where

$$
\frac{\partial n\langle c\alpha Yv^* \rangle}{\partial n_i} = \sum_{j=1}^{N} z_j\left(c_i\alpha_{ij}Y_{ij}v_{ji}^* + c_j\alpha_{ji}Y_{ji}v_{ij}^*\right) - \langle c\alpha Yv^* \rangle \qquad (4\text{-}28)
$$

$$
\frac{\partial n\langle v^* \rangle}{\partial n_i} = \sum_{j=1}^{N} z_j\left(v_{ij}^* + v_{ji}^*\right) - \langle v^* \rangle \qquad (4\text{-}29)
$$

and

$$
Y_{ij} = \exp\left(\frac{T_{ij}^*}{T}\right) - 1 \qquad (4\text{-}30)
$$

A detailed derivation for the fugacity coefficient is presented in Appendix C. In each iteration of the equilibrium calculations, the equation of state was solved to obtain liquid and vapor compressibility roots. The expanded form of the equation of state (shown in Appendix A) was used, and the same solution technique used in evaluating pure fluid properties was employed in solving the equation for mixtures.

Ethane + Normal Paraffin Binaries

Bubble point pressure calculations were performed for the four evaluation cases using the equations of state selected. A summary of the results is shown in Table XII. Detailed statistics for each isotherm of each binary mixtures are shown in Tables D.I to D.XVI in Appendix D. The new equation shows the best results in Case 1 (AAD of 7.47 %) while the SPHCT equation is the worst (AAD of 16.6 %). This implies that the new equation is the most accurate among the equations considered in predicting bubble point pressures without any interaction parameter. With the introduction of interaction parameters (Cases 2 to 4), the SPHCT equation is the best among the equations considered. The results indicate that while the predictive capability of the SPHCT equation is improved with the introduction of interaction parameters, the rest of the equations are not affected as much. The quality of fit for Case 4 is 4.1%, 3.0%, and 2.8% for the PR, the Modified SPHCT and the new equation, respectively. In general, the new equation shows better performance than those of the PR and Modified SPHCT equations. The new equation yielded better performance than the PR equation except for Case 3, and it gave better results than the Modified SPHCT equation except for Case 2.

Figure 9 shows the effect of solvent molecular size on the interaction parameter of Case 3. While both the new equation and the Modified SPHCT equation require small values for the interaction parameters (-0.02 to 0.02), the interaction parameters are relatively large for the PR and SPHCT equations. The figure also indicates that the variations in the interaction parameters are relatively small for the SPHCT equation, the Modified SPHCT equation and the new equation compared to that of the PR equation. This suggests that equations based on segment-segment interactions are more suitable for asymmetric mixtures, and accordingly extrapolations using such equations should prove useful.

TABLE XII

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

	Peng-Robinson		SPHCT		Modified SPHCT		This work	
Case Number	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	2.06	9.52	4.83	16.6	2.21	8.81	3.95	7.47
2	2.04	9.40	1.76	5.41	2.54	6.72	3.39	7.14
3	1.79	4.38	1.29	3.22	2.57	6.32	2.47	5.15
4	1.77	4.13	0.78	1.62	1.18	3.00	1.34	2.79

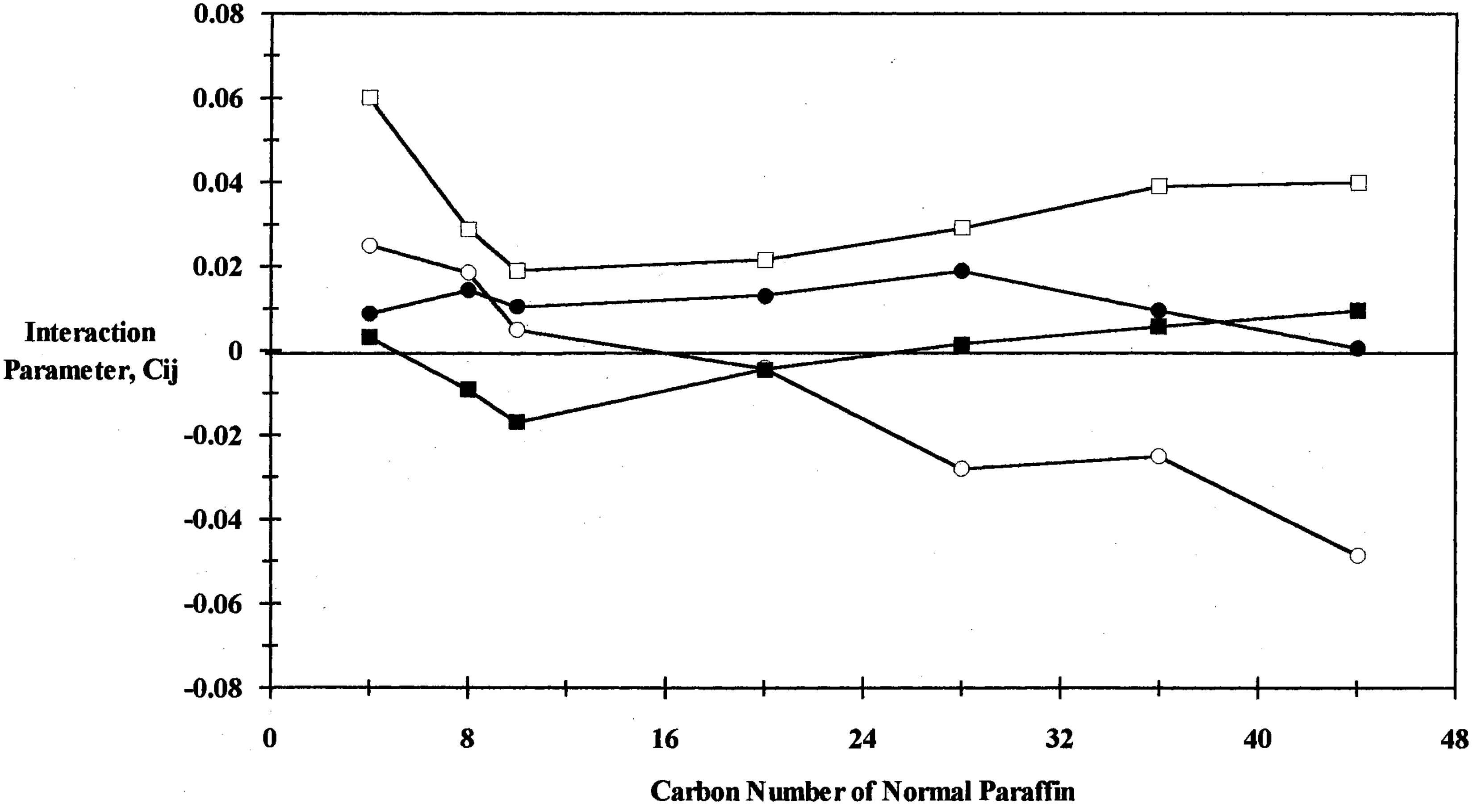

Figure 9. Case 3 Binary Interaction Parameters for the Ethane in n-Paraffins.
○ The PR Equation; □ The SPHCT Equation;
● The Modified SPHCT; ■ The Present Equation

Carbon Dioxide + Normal Paraffin Binaries

A summary of the bubble point pressure calculations for all cases studied is presented in Table XIII. Detailed calculation results are shown in Tables D.XVII to D.XXXII in Appendix D. For the raw prediction case (Case 1), the new equation of state shows the best results among the equations considered. Moreover, while the SPHCT and Modified SPHCT equations had convergence problems for the high pressure data points in the first case, the new equation and the PR equation did not have such problems. In all cases studied, the Modified SPHCT equation shows the worst predictions. The new equation and the Modified SPHCT equation are relatively insensitive to the introduction of the interaction parameters for Cases 1 to 3 compared to the PR and SPHCT equations. For the most complex case studied (Case 4), the predictive capability of the new equation (AAD of 2.07 %) is intermediate to those of the PR (AAD of 2.55 %) and SPHCT (AAD of 1.87 %) equations. For all equations of state studied, temperature-dependent interaction parameters (Case 4) are needed to obtain reasonable predictions.

Figure 10 shows the interaction parameters of Case 3 for all the equations considered. The interaction parameter values for the new equation are relatively constant (0.03) to variation in the solvent molecular size. Similarly, all the interaction parameter values are within a narrow range for the SPHCT equation. Figure 11 shows the temperature dependence of the interaction parameters for the new equation. It shows a very strong temperature dependence for the binaries containing heavy components. These results suggest that the interaction parameter values are weakly dependent on the solvent molecular size for heavy component binaries (C_{20} and above), while their temperature dependence is distinctive (almost linear with a slope of -0.0006/K).

The relatively poor predictions of the new equations for Cases 2 and 3 may be attributed to several factors. First, the partition function of the present EOS does not explicitly account for polar effects. If the polar effects were included in the partition

TABLE XIII

SUMMARY OF RESULTS FOR REPRESENTATION OF BUBBLE POINT PRESSURES FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS

	Peng-Robinson		SPHCT		Modified SPHCT		This work	
Case Number	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	13.5	19.9	14.8*	26.8*	12.2*	24.7*	8.83	17.9
2	2.50	5.44	6.03	9.25	12.3	17.0	9.04	14.3
3	2.76	3.25	2.73	4.59	9.60	12.8	5.95	10.0
4	2.17	2.55	2.10	1.87	4.32	5.17	2.36	2.07

* Approximately 1/4 of the higher pressure data points were predicted as being single phase.

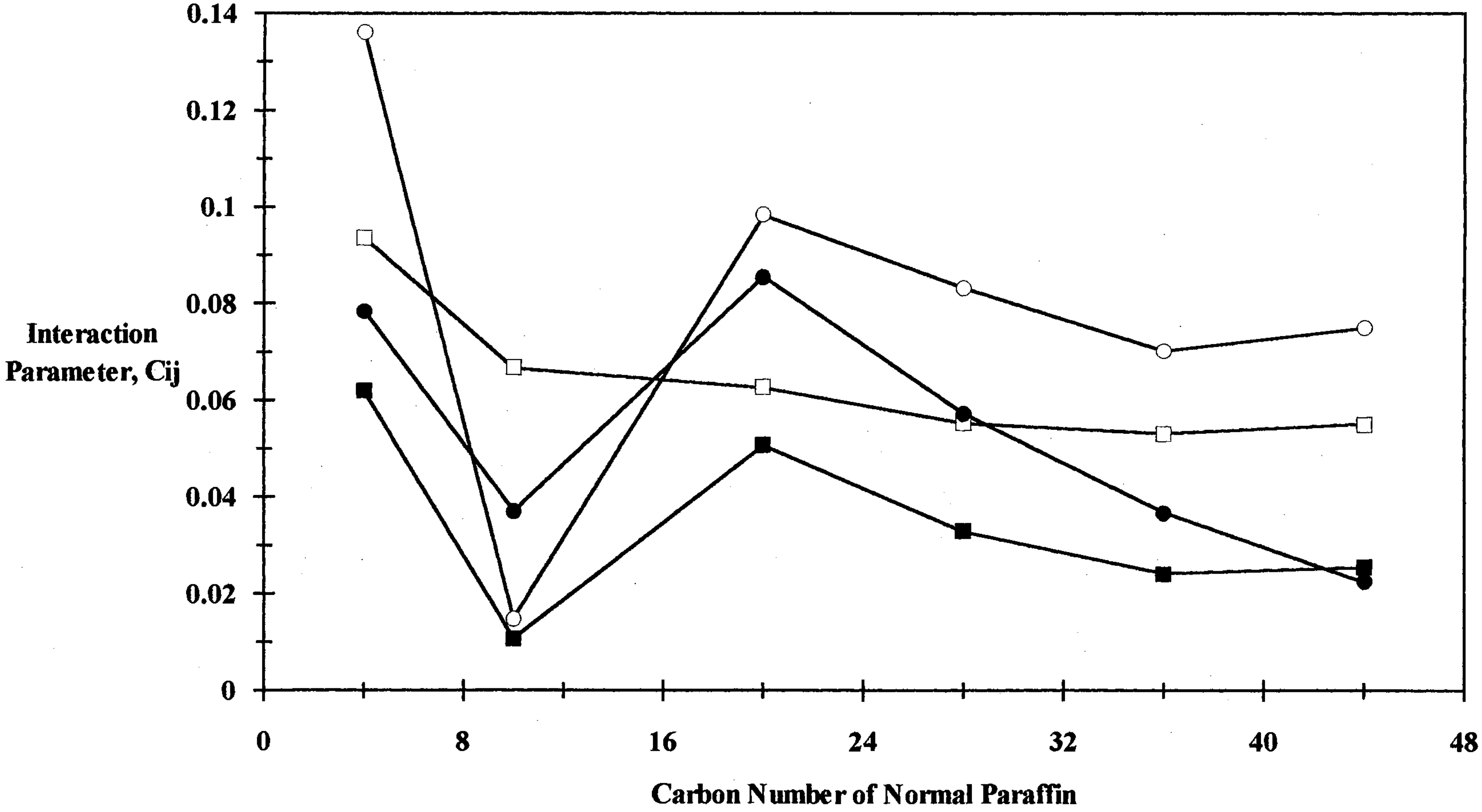

Figure 10. Case 3 Binary Interaction Parameters for the Carbon Dioxide in n-Paraffins.
○ The PR Equation; ☐ The SPHCT Equation;
● The Modified SPHCT; ■ The Present Equation

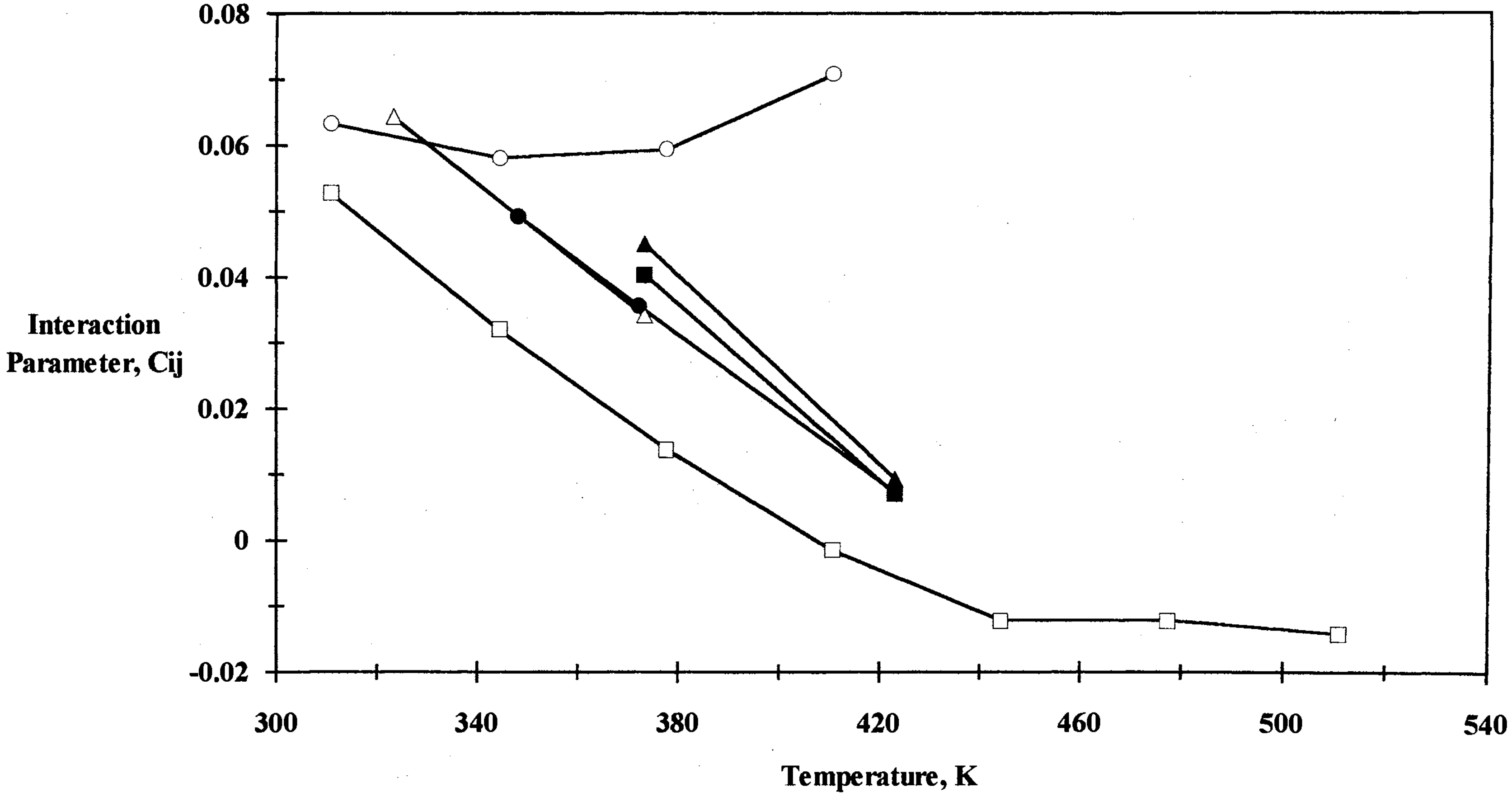

Figure 11. Temperature-Dependent Interaction Parameters of the New Equation of State: Case 4 for the CO_2 + n-Paraffins Binary Mixtures.
○ n-C_4 Binaries; □ n-C_{10} Binaries; Δ n-C_{20} Binaries;
● n-C_{28} Binaries; ■ n-C_{36} Binaries; ▲ n-C_{44} Binaries

function for the segment-segment interaction models (the SPHCT, the Modified SPHCT and the new equation), better performances of the models would be expected for systems containing polar compounds such as carbon dioxide [see, e.g., 63]. Second, in evaluating the new equation for carbon dioxide binaries, a common value of the square-well potential depth (ε) is used for all compounds. Actually, the attraction energy between a carbon dioxide molecule and a normal paraffin segment is expected to be different. This assumption is considered likely to limit the capability of the equation [see, e.g., 64]. Third, the mixing rules applied in evaluating the carbon dioxide binaries may not be adequate because the interaction parameter, C_{ij}, shows an almost linear dependence on temperature. This indicates that the temperature-dependent mixture property in Equation (4-12), $\langle c\alpha Yv^{*}\rangle$, is not optimum for the carbon dioxide binaries.

Hydrogen + Normal Paraffin Binaries

The critical properties used in the evaluation of the PR equation are the same as the values used in Chapter IV of Section I. In Cases 1 and 2, the new equation predicted a single phase for some higher pressure data points. So, evaluations and comparisons were performed only for Cases 3 and 4. A summary of the bubble point pressure calculations for the two cases studied are presented in Table XIV.

Detailed calculation results are shown in Tables D.XXXIII to D.XXXVI in Appendix D. The PR EOS shows significantly better performance than the new equation in Case 3 (%AAD of 4.5 and 33, respectively) while both equations are comparable in Case 4 (%AAD of 2.0 and 2.7, respectively). This indicates that the interaction parameters of the new equation is strongly dependent on temperature. The values of the interaction parameters for both the new equation and the PR equation are abnormally large, which may imply some deficiency in the model, the EOS parameters, or the mixing rules.

TABLE XIV

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

	Peng-Robinson		This work	
Case Number	RMSE (bar)	%AAD	RMSE (bar)	%AAD
3	5.23	4.52	30.3	33.2
4	3.23	2.04	3.35	2.69

Since hydrogen is a quantum gas, its molecular potential energy is expected to be significantly different from those of other compounds [64]. Thus, the phase behavior of systems involving hydrogen is different from other binary mixtures such as methane, ethane, carbon dioxide with n-paraffins. Actually, the new equation was developed for chain-molecules and the square-well potential energy model (with constant energy well depth) was adopted. Hence, poor predictive capability of the equation for systems containing hydrogen is understandable. Using common values for the hard core radius and the potential well depth for all compounds constitutes a poor assumption to use in the hydrogen binary evaluations. The hard core radius and the potential well depth for a hydrogen molecule are expected to be different from those of normal paraffin segments. In addition, as mentioned earlier in discussions dealing with carbon dioxide binary evaluations, the current mixing rules may not be adequate for the hydrogen binaries studied.

Conclusions and Recommendations

A set of mixing rules has been proposed for the newly proposed equation of state to extend its use to mixtures. The equation of state was evaluated using the binary mixtures of ethane, carbon dioxide, and hydrogen with n-paraffins. The systems selected contain simple mixtures such as ethane + n-butane binary mixtures and asymmetric mixtures such as ethane + n-tetratetracontane systems. For all binary systems studied, the new equation of state has the capability of predicting bubble point pressures within 3 %AAD with a single interaction parameter for each isotherm. For the binary systems of ethane and carbon dioxide with n-paraffins, the bubble point pressure predictive capability of the new equation is compared to those of the PR, SPHCT and Modified SPHCT equations.

For the *a priori* prediction case (Case 1), the new equation shows the best results among the equations tested. For ethane binaries, the segment-segment interaction models

(SPHCT equation, Modified SPHCT equation and the new equation) shows better performance than the model based on molecule interactions (PR) in Case 4. This indicates that models based on segment interactions are more suitable for asymmetric mixtures such as ethane and n-paraffin mixtures. For carbon dioxide binaries, the equations based on segment interactions do not do as well in comparison with ethane binaries. For hydrogen binaries, the PR equation yields better predictions than the new equation.

This work suggests that fundamental changes in the partition function are necessary for systems containing polar components like carbon dioxide or quantum gases like hydrogen. Also, the hard core radius and the potential well depth for various compounds should be further studied to improve mixture predictions. The mixing rules and/or combination rules should be studied further to provide for improved representation of mixtures. Efforts should be made to eliminate the interaction parameter temperature dependence. The databases selected in the evaluations of the equation are limited to binary mixtures involving ethane, carbon dioxide and hydrogen with n-paraffin solvents. Further evaluations of the EOS using diverse systems are recommended.

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APPENDIXES

APPENDIX A

EXPANDED FORM OF THE EQUATION OF STATE

The fifth order expanded form of the equation is obtained by rearranging the equation of state given in Chapters III and IV in the following manner:

$$Z^5 + AZ^4 + BZ^3 + CZ^2 + DZ + E = 0 \tag{A-1}$$

where

$$A = \delta(u - \beta_2\tau + 1) - 1$$

$$B = \delta^2(w - \beta_2\tau u + u - \beta_2\tau) - \delta(u - \beta_2\tau + 1 + \lambda - \gamma - Q\gamma)$$

$$\begin{aligned} C = & -\delta^3(\beta_2\tau w - w + \beta_2\tau u) \\ & -\delta^2(w - \beta_2\tau u + u - \beta_2\tau + \lambda + u\lambda - \gamma + \beta_2\tau\gamma - uQ\gamma + \beta_2\tau Q\gamma) \end{aligned}$$

$$D = -\delta^3(\delta\beta_2\tau w - \beta_2\tau w + w - \beta_2\tau u + u\lambda + w\lambda + \beta_2\tau\lambda - wQ\gamma + \beta_2\tau uQ\gamma)$$

$$E = \delta^4(\beta_2\tau w - w\lambda - \beta_2\tau wQ\gamma)$$

The terms δ, λ and γ appearing in the coefficients are defined as follows:

- When applying the equation of state for pure fluids

$$\delta = \frac{pv^*}{RT}, \qquad \lambda = c\beta_1\tau \quad \text{and} \quad \gamma = c\alpha Y$$

- When applying the equation of state for mixtures

$$\delta = \frac{p\langle v^*\rangle}{RT}, \qquad \lambda = \beta_1\tau\frac{\langle cv^*\rangle}{\langle v^*\rangle} \quad \text{and} \quad \gamma = \frac{\langle cv^*\alpha Y\rangle}{\langle v^*\rangle}$$

APPENDIX B

FUGACITY COEFFICIENT FOR PURE FLUIDS

The fugacity coefficient for pure fluids can be evaluated using the following equation [65]:

$$\ln \phi = -\frac{1}{RT}\int_{\infty}^{v}\left(p - \frac{RT}{v}\right)dv + Z - 1 - \ln Z \tag{B-1}$$

From the pure-fluid equation of state given in Chapter III, the following expression is obtained for the integrand:

$$p - \frac{RT}{v} = RT\left(\frac{c\beta_1\tau v^*}{v\left(v - \beta_2\tau v^*\right)} - \frac{c\alpha Y v^*}{v^2 + uv^*v + wv^{*2}} - \frac{c\alpha YQv^*}{v\left(v + v^*\right)}\right) \tag{B-2}$$

Integrating Equation (B-2) and substituting the result to Equation (B-1), the following fugacity coefficient expression is derived:

$$\ln \phi = -c\frac{\beta_1}{\beta_2}\ln\frac{v_r - \beta_2\tau}{v_r} + c\alpha Y\frac{2}{\sqrt{4w - u^2}}\left(\tan^{-1}\frac{2v_r + u}{\sqrt{4w - u^2}} - \frac{\pi}{2}\right) - c\alpha YQ\ln\frac{v_r + 1}{v_r}$$

$$+\frac{c\beta_1\tau}{v_r - \beta_2\tau} - \frac{c\alpha Y v_r}{v_r^2 + uv_r + w} - \frac{c\alpha YQ}{v_r + 1} \tag{B-3}$$

Values for the EOS constants, substance-specific parameters and expressions for α and Y are described in Chapter III.

APPENDIX C

FUGACITY COEFFICIENT EXPRESSION FOR COMPONENTS IN A MIXTURE

The fugacity coefficient of component "i" in a mixture may be derived for the equation of state considered by the following definition [65].

$$\ln \phi_i = -\int_{\infty}^{V}\left(\frac{1}{RT}\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{1}{V}\right)dV - \ln Z \qquad \text{(C-1)}$$

where V is the total system volume. From the mixture equation of state shown in Equation (4-18), the following expression can be obtained by multiplying both sides of the equation by the total number of moles and then taking the partial derivative of pressure with respect to the number of moles of component "i" in a mixture. The partial derivatives shown from this point on are at constant: temperature, total system volume, and number of moles for all components except component "i".

$$
\begin{aligned}
\frac{1}{RT}\left(\frac{\partial p}{\partial n_i}\right)-\frac{1}{V} = {} & \frac{\beta_1\tau\dfrac{\partial n\langle cv^*\rangle}{\partial n_i}}{V\left(V-\beta_2\tau n\langle v^*\rangle\right)}-\frac{\dfrac{\partial\langle c\alpha Yv^*\rangle}{\partial n_i}}{V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2} \\
& -\frac{Q\dfrac{\partial n\langle c\alpha Yv^*\rangle}{\partial n_i}}{V\left(V+n\langle v^*\rangle\right)}+\frac{\beta_1\tau n^2\langle cv^*\rangle\beta_2\tau\dfrac{\partial n\langle v^*\rangle}{\partial n_i}}{V\left(V-\beta_2\tau n\langle v^*\rangle\right)^2} \\
& +\frac{un^2\langle c\alpha Yv^*\rangle\dfrac{\partial n\langle v^*\rangle}{\partial n_i}V}{\left(V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2\right)^2}+\frac{2wn^3\langle c\alpha Yv^*\rangle\langle v^*\rangle\dfrac{\partial n\langle v^*\rangle}{\partial n_i}}{\left(V^2+un\langle v^*\rangle V+w\left(n\langle v^*\rangle\right)^2\right)^2} \\
& +\frac{Qn^2\langle c\alpha Yv^*\rangle\dfrac{\partial n\langle v^*\rangle}{\partial n_i}}{V\left(V+n\langle v^*\rangle\right)^2} \qquad \text{(C-2)}
\end{aligned}
$$

Here, "n" is the total number of moles in a mixture. Integrating Equation (C-1) with the integrand given in Equation (C-2) leads to the following expression for the fugacity coefficient of component "i" in a mixture.

$$
\begin{aligned}
\ln\phi_i = {} & -\frac{\beta_1}{\beta_2}\left(\frac{1}{\left\langle v^*\right\rangle}\frac{1}{n}\frac{\partial n^2\left\langle cv^*\right\rangle}{\partial n_i}-\frac{\left\langle cv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)\ln\frac{v_r-\beta_2\tau}{v_r} \\
& +\left(\beta_1\tau\frac{\left\langle cv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)\frac{1}{v_r-\beta_2\tau} \\
& -\left(\frac{\left\langle c\alpha Yv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)\frac{v_r}{v_r^2+uv_r+w} \\
& +\left(\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle c\alpha Yv^*\right\rangle}{\partial n_i}-\frac{\left\langle c\alpha Yv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w-u^2}}\left(\tan^{-1}\frac{2v_r+u}{\sqrt{4w-u^2}}-\frac{\pi}{2}\right) \\
& -\left(\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle c\alpha Yv^*\right\rangle}{\partial n_i}-\frac{\left\langle c\alpha Yv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)Q\ln\frac{v_r+1}{v_r} \\
& -\left(\frac{\left\langle c\alpha Yv^*\right\rangle}{\left\langle v^*\right\rangle}\frac{1}{\left\langle v^*\right\rangle}\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i}\right)\frac{Q}{v_r+1} \\
& -\ln Z \qquad \text{(C-3)}
\end{aligned}
$$

where

$$\frac{\partial n\left\langle c\alpha Yv^*\right\rangle}{\partial n_i} = \sum_{j=1}^{N} z_j\left(c_i\alpha_{ij}Y_{ij}v_{ji}^* + c_j\alpha_{ji}Y_{ji}v_{ij}^*\right)-\left\langle c\alpha Yv^*\right\rangle \qquad \text{(C-4)}$$

$$\frac{\partial n\left\langle v^*\right\rangle}{\partial n_i} = \sum_{j=1}^{N} z_j\left(v_{ij}^* + v_{ji}^*\right)-\left\langle v^*\right\rangle \qquad \text{(C-5)}$$

and

$$Y_{ij} = \exp\left(\frac{T_{ij}^*}{T}\right)-1 \qquad \text{(C-6)}$$

The expression for α_{ij} is defined in Chapter IV.

APPENDIX D

MIXTURE EQUATION OF STATE EVALUATIONS

This appendix contains detailed tables for all cases studied in the evaluations of the equations of state considered (PR, SPHCT, Modified SPHCT, the new EOS). Tables D.I to D.XVI contain detailed results for ethane binaries and tables D.XVII to D.XXXII contain those for carbon dioxide binaries. Tables D.XXXIII to D.XXXVI are the results for the hydrogen binaries. For hydrogen binaries, only the PR and the new EOS were evaluated for Cases 3 and 4.

The numerical values given in the following tables are duplicates of computer outputs, and as such the number of significant figures appearing in these tables do not reflect precision.

TABLE D.I

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	1.71	-1.50	1.50	3.4	6
2	4	366.5	.0000	.0000	2.08	-1.80	1.80	4.2	8
3	4	394.3	.0000	.0000	0.77	-0.60	0.60	1.6	5
4	8	323.1	.0000	.0000	1.44	-1.35	1.35	4.4	11
5	8	348.1	.0000	.0000	1.92	-1.78	1.78	7.2	13
6	8	373.1	.0000	.0000	1.37	-1.28	1.28	6.7	9
7	10	310.9	.0000	.0000	0.58	-0.47	0.47	3.1	10
8	10	344.3	.0000	.0000	0.66	-0.44	0.50	1.5	7
9	10	377.6	.0000	.0000	0.56	-0.10	0.47	1.7	6
10	10	410.9	.0000	.0000	1.22	-0.32	1.02	2.6	7
11	20	323.1	.0000	.0000	1.40	0.78	1.30	11.4	6
12	20	373.1	.0000	.0000	1.94	0.61	1.79	7.1	6
13	20	423.1	.0000	.0000	2.80	2.27	2.60	9.7	7
14	28	348.1	.0000	.0000	2.54	2.51	2.51	17.2	10
15	28	373.1	.0000	.0000	2.46	2.39	2.39	15.8	7
16	28	423.1	.0000	.0000	3.38	3.28	3.28	15.9	7
17	36	373.1	.0000	.0000	2.67	2.58	2.58	20.3	7
18	36	423.1	.0000	.0000	2.35	2.07	2.07	11.6	6
19	44	373.1	.0000	.0000	3.30	3.23	3.23	26.2	9
20	44	423.1	.0000	.0000	2.33	2.25	2.25	15.7	7

MODEL OVERALL STATISTICS

RMSE	=	2.0641	BAR	NO PT	=	154
AAD	=	1.7577	BAR	%AAD	=	9.522
MIN DEV	=	-3.4157	BAR	MIN %DEV	=	-13.093
MAX DEV	=	4.2122	BAR	MAX %DEV	=	48.666
BIAS	=	0.5036	BAR	C-VAR	=	0.073
RESTRICTIONS	:	NONE		R-SQR	=	.920698

TABLE D.II

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	-.0033	.0000	1.83	-1.57	1.57	3.6	6
2	4	366.5	-.0033	.0000	2.25	-1.94	1.94	4.6	8
3	4	394.3	-.0033	.0000	0.71	-0.52	0.52	1.4	5
4	8	323.1	-.0033	.0000	1.69	-1.60	1.60	5.3	11
5	8	348.1	-.0033	.0000	2.22	-2.06	2.06	8.3	13
6	8	373.1	-.0033	.0000	1.60	-1.49	1.49	7.8	9
7	10	310.9	-.0033	.0000	0.79	-0.68	0.68	4.7	10
8	10	344.3	-.0033	.0000	0.97	-0.76	0.76	2.3	7
9	10	377.6	-.0033	.0000	0.82	-0.45	0.57	1.5	6
10	10	410.9	-.0033	.0000	1.50	-0.71	1.13	2.4	7
11	20	323.1	-.0033	.0000	1.38	0.49	1.26	10.5	6
12	20	373.1	-.0033	.0000	2.06	0.09	1.79	6.6	6
13	20	423.1	-.0033	.0000	2.55	1.80	2.37	8.9	7
14	28	348.1	-.0033	.0000	2.29	2.24	2.24	15.7	10
15	28	373.1	-.0033	.0000	2.18	2.11	2.11	14.5	7
16	28	423.1	-.0033	.0000	3.09	2.99	2.99	14.9	7
17	36	373.1	-.0033	.0000	2.46	2.37	2.37	19.1	7
18	36	423.1	-.0033	.0000	2.18	1.82	1.89	10.8	6
19	44	373.1	-.0033	.0000	3.12	3.04	3.04	25.1	9
20	44	423.1	-.0033	.0000	2.17	2.10	2.10	14.9	7

MODEL OVERALL STATISTICS

RMSE	=	2.0395	BAR	NO PT	=	154
AAD	=	1.7650	BAR	%AAD	=	9.401
MIN DEV	=	-3.6288	BAR	MIN %DEV	=	-14.300
MAX DEV	=	3.9556	BAR	MAX %DEV	=	47.482
BIAS	=	0.2517	BAR	C-VAR	=	0.072
RESTRICTIONS	:	NONE		R-SQR	=	.909172

TABLE D.III

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0251	.0000	1.14	-0.85	0.95	2.0	19
2	8	323.1	.0185	.0000	0.34	-0.02	0.30	1.7	33
3	10	310.9	.0049	.0000	0.64	-0.10	0.49	2.0	30
4	20	323.1	-.0042	.0000	3.21	-1.44	2.34	7.0	19
5	28	348.1	-.0281	.0000	1.88	-0.76	1.42	6.5	24
6	36	373.1	-.0251	.0000	2.75	-1.29	1.86	7.6	13
7	44	373.1	-.0485	.0000	2.16	-1.07	1.55	8.5	16

MODEL OVERALL STATISTICS

RMSE = 1.7909 BAR
AAD = 1.1042 BAR
MIN DEV = -7.8518 BAR
MAX DEV = 1.8167 BAR
BIAS = -0.6441 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 4.389
MIN %DEV = -14.733
MAX %DEV = 20.774
C-VAR = 0.102
R-SQR = .883702

TABLE D.IV

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0250	.0000	1.05	-0.75	0.88	1.8	6
2	4	366.5	.0378	.0000	0.90	-0.29	0.71	1.5	8
3	4	394.3	-.0018	.0000	0.70	-0.52	0.52	1.4	5
4	8	323.1	.0137	.0000	0.44	-0.26	0.40	1.3	11
5	8	348.1	.0211	.0000	0.34	0.10	0.29	1.7	13
6	8	373.1	.0199	.0000	0.33	0.06	0.28	1.7	9
7	10	310.9	.0064	.0000	0.20	-0.06	0.15	1.0	10
8	10	344.3	.0020	.0000	0.48	-0.24	0.35	1.3	7
9	10	377.6	-.0025	.0000	0.75	-0.37	0.51	1.5	6
10	10	410.9	-.0043	.0000	1.60	-0.83	1.19	2.5	7
11	20	323.1	-.0224	.0000	2.29	-1.09	1.55	7.4	6
12	20	373.1	-.0144	.0000	3.21	-1.60	2.48	6.4	6
13	20	423.1	-.0305	.0000	3.72	-1.79	2.70	6.3	7
14	28	348.1	-.0424	.0000	1.49	-0.62	1.11	6.1	10
15	28	373.1	-.0439	.0000	2.02	-0.97	1.56	6.9	7
16	28	423.1	-.0552	.0000	2.53	-1.10	1.75	5.9	7
17	36	373.1	-.0634	.0000	2.18	-0.97	1.42	7.5	7
18	36	423.1	-.0458	.0000	2.79	-1.25	2.22	7.7	6
19	44	373.1	-.0923	.0000	2.60	-1.29	1.86	10.5	9
20	44	423.1	-.0706	.0000	1.37	-0.63	0.99	5.4	7

MODEL OVERALL STATISTICS

RMSE = 1.7707 BAR
AAD = 1.0647 BAR
MIN DEV = -8.0823 BAR
MAX DEV = 1.3691 BAR
BIAS = -0.6522 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 4.131
MIN %DEV = -16.312
MAX %DEV = 18.783
C-VAR = 0.097
R-SQR = .845846

TABLE D.V

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	3.54	-2.91	2.91	7.1	6
2	4	366.5	.0000	.0000	4.43	-3.70	3.70	9.0	8
3	4	394.3	.0000	.0000	2.61	-1.83	1.83	5.2	5
4	8	323.1	.0000	.0000	3.39	-3.25	3.25	10.5	11
5	8	348.1	.0000	.0000	4.43	-4.10	4.10	16.1	13
6	8	373.1	.0000	.0000	3.91	-3.59	3.59	18.5	9
7	10	310.9	.0000	.0000	1.54	-1.47	1.47	11.8	10
8	10	344.3	.0000	.0000	2.97	-2.75	2.75	11.3	7
9	10	377.6	.0000	.0000	4.35	-3.94	3.94	12.7	6
10	10	410.9	.0000	.0000	6.85	-6.14	6.14	13.6	7
11	20	323.1	.0000	.0000	2.85	-2.54	2.54	14.6	6
12	20	373.1	.0000	.0000	6.21	-5.75	5.75	15.4	6
13	20	423.1	.0000	.0000	7.93	-7.13	7.13	16.8	7
14	28	348.1	.0000	.0000	3.98	-3.70	3.70	20.9	10
15	28	373.1	.0000	.0000	4.87	-4.31	4.31	21.7	7
16	28	423.1	.0000	.0000	6.07	-5.42	5.42	20.4	7
17	36	373.1	.0000	.0000	4.98	-4.39	4.39	25.9	7
18	36	423.1	.0000	.0000	7.80	-7.02	7.02	25.1	6
19	44	373.1	.0000	.0000	5.10	-4.46	4.46	25.6	9
20	44	423.1	.0000	.0000	5.42	-4.86	4.86	27.6	7

MODEL OVERALL STATISTICS

RMSE	=	4.8309	BAR	NO PT	=	154
AAD	=	4.0893	BAR	%AAD	=	16.600
MIN DEV	=	-12.3584	BAR	MIN %DEV	=	-30.459
MAX DEV	=	0.0000	BAR	MAX %DEV	=	0.000
BIAS	=	-4.0893	BAR	C-VAR	=	0.171
RESTRICTIONS	:	NONE		R-SQR	=	.888396

TABLE D.VI

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0279	.0000	2.64	-2.13	2.13	4.9	6
2	4	366.5	.0279	.0000	3.18	-2.96	2.96	6.8	8
3	4	394.3	.0279	.0000	2.66	-2.28	2.28	5.9	5
4	8	323.1	.0279	.0000	1.62	-0.14	1.32	4.5	11
5	8	348.1	.0279	.0000	0.84	-0.52	0.61	2.5	13
6	8	373.1	.0279	.0000	0.82	-0.76	0.76	4.1	9
7	10	310.9	.0279	.0000	1.68	1.52	1.52	10.7	10
8	10	344.3	.0279	.0000	1.76	1.62	1.62	6.5	7
9	10	377.6	.0279	.0000	0.78	0.73	0.73	2.7	6
10	10	410.9	.0279	.0000	1.47	-0.99	1.03	1.6	7
11	20	323.1	.0279	.0000	2.21	1.87	1.87	10.3	6
12	20	373.1	.0279	.0000	2.77	2.19	2.19	4.5	6
13	20	423.1	.0279	.0000	0.49	-0.45	0.45	1.0	7
14	28	348.1	.0279	.0000	0.45	0.27	0.34	1.6	10
15	28	373.1	.0279	.0000	0.33	-0.13	0.29	2.6	7
16	28	423.1	.0279	.0000	1.08	-1.03	1.03	4.5	7
17	36	373.1	.0279	.0000	1.18	-1.09	1.09	7.2	7
18	36	423.1	.0279	.0000	2.95	-2.69	2.69	9.9	6
19	44	373.1	.0279	.0000	1.46	-1.25	1.25	6.8	9
20	44	423.1	.0279	.0000	2.32	-2.14	2.14	12.9	7

MODEL OVERALL STATISTICS

RMSE = 1.7610 BAR
AAD = 1.3343 BAR
MIN DEV = -4.8777 BAR
MAX DEV = 4.9758 BAR
BIAS = -0.4749 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 5.414
MIN %DEV = -16.319
MAX %DEV = 12.290
C-VAR = 0.062
R-SQR = .965439

TABLE D.VII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0600	.0000	1.79	-1.14	1.50	3.3	19
2	8	323.1	.0290	.0000	1.12	-0.31	0.85	3.5	33
3	10	310.9	.0190	.0000	1.67	-0.62	1.01	3.0	30
4	20	323.1	.0216	.0000	1.55	-0.49	1.19	3.6	19
5	28	348.1	.0292	.0000	0.67	0.00	0.55	2.7	24
6	36	373.1	.0391	.0000	0.83	-0.02	0.58	2.3	13
7	44	373.1	.0401	.0000	0.66	-0.08	0.58	4.1	16

MODEL OVERALL STATISTICS

RMSE	=	1.2928	BAR	NO PT	=	154
AAD	=	0.9051	BAR	%AAD	=	3.223
MIN DEV	=	-5.4258	BAR	MIN %DEV	=	-9.238
MAX DEV	=	2.4013	BAR	MAX %DEV	=	9.263
BIAS	=	-0.3969	BAR	C-VAR	=	0.073
RESTRICTIONS	:	NONE		R-SQR	=	.930075

TABLE D.VIII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0546	.0000	1.47	-0.82	1.20	2.6	6
2	4	366.5	.0653	.0000	1.45	-0.43	1.19	2.6	8
3	4	394.3	.0874	.0000	0.41	-0.06	0.34	0.8	5
4	8	323.1	.0209	.0000	1.70	-0.97	1.21	3.1	11
5	8	348.1	.0308	.0000	0.63	-0.10	0.50	2.1	13
6	8	373.1	.0350	.0000	0.29	0.05	0.25	1.6	9
7	10	310.9	.0157	.0000	0.21	0.12	0.17	1.4	10
8	10	344.3	.0184	.0000	0.15	0.03	0.12	0.7	7
9	10	377.6	.0233	.0000	0.32	-0.11	0.22	0.5	6
10	10	410.9	.0302	.0000	1.06	-0.52	0.75	1.4	7
11	20	323.1	.0174	.0000	0.18	0.04	0.12	0.7	6
12	20	373.1	.0223	.0000	0.86	0.37	0.66	1.7	6
13	20	423.1	.0295	.0000	0.15	0.00	0.14	0.4	7
14	28	348.1	.0266	.0000	0.29	0.07	0.22	1.2	10
15	28	373.1	.0304	.0000	0.64	0.31	0.49	2.4	7
16	28	423.1	.0347	.0000	0.51	0.20	0.34	1.2	7
17	36	373.1	.0369	.0000	0.64	0.19	0.34	1.6	7
18	36	423.1	.0432	.0000	0.30	0.14	0.25	1.0	6
19	44	373.1	.0364	.0000	0.26	-0.09	0.23	1.5	9
20	44	423.1	.0482	.0000	0.52	0.23	0.42	2.4	7

MODEL OVERALL STATISTICS

RMSE	=	0.7800	BAR	NO PT	=	154
AAD	=	0.4687	BAR	%AAD	=	1.624
MIN DEV	=	-3.9036	BAR	MIN %DEV	=	-7.409
MAX DEV	=	1.7994	BAR	MAX %DEV	=	5.068
BIAS	=	-0.0866	BAR	C-VAR	=	0.043
RESTRICTIONS	:	NONE		R-SQR	=	.988390

TABLE D.IX

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	2.55	-2.43	2.43	5.2	6
2	4	366.5	.0000	.0000	2.98	-2.82	2.82	6.1	8
3	4	394.3	.0000	.0000	1.42	-1.22	1.22	2.9	5
4	8	323.1	.0000	.0000	1.20	-0.88	1.10	4.7	11
5	8	348.1	.0000	.0000	1.69	-1.60	1.60	8.5	13
6	8	373.1	.0000	.0000	1.64	-1.56	1.56	9.1	9
7	10	310.9	.0000	.0000	1.66	-1.62	1.62	14.1	10
8	10	344.3	.0000	.0000	1.04	-0.81	0.94	5.8	7
9	10	377.6	.0000	.0000	0.95	0.04	0.75	3.0	6
10	10	410.9	.0000	.0000	2.02	1.40	1.44	2.4	7
11	20	323.1	.0000	.0000	3.84	-3.58	3.58	22.3	6
12	20	373.1	.0000	.0000	2.44	-2.27	2.27	8.3	6
13	20	423.1	.0000	.0000	1.40	0.54	0.99	2.2	7
14	28	348.1	.0000	.0000	4.04	-3.83	3.83	22.3	10
15	28	373.1	.0000	.0000	3.02	-2.82	2.82	16.0	7
16	28	423.1	.0000	.0000	0.95	0.17	0.70	2.9	7
17	36	373.1	.0000	.0000	2.58	-2.40	2.40	15.8	7
18	36	423.1	.0000	.0000	1.27	0.82	0.97	2.9	6
19	44	373.1	.0000	.0000	1.28	-1.16	1.16	7.3	9
20	44	423.1	.0000	.0000	2.38	1.82	1.82	7.8	7

MODEL OVERALL STATISTICS

RMSE	=	2.2050	BAR	NO PT	=	154
AAD	=	1.8074	BAR	%AAD	=	8.811
MIN DEV	=	-5.6507	BAR	MIN %DEV	=	-26.777
MAX DEV	=	4.1967	BAR	MAX %DEV	=	13.239
BIAS	=	-1.2815	BAR	C-VAR	=	0.078
RESTRICTIONS	:	NONE		R-SQR	=	.940362

TABLE D.X

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0113	.0000	1.83	-1.54	1.54	3.1	6
2	4	366.5	.0113	.0000	1.97	-1.72	1.72	3.6	8
3	4	394.3	.0113	.0000	1.87	-1.51	1.56	3.4	5
4	8	323.1	.0113	.0000	0.81	0.53	0.63	1.7	11
5	8	348.1	.0113	.0000	0.86	0.05	0.74	3.9	13
6	8	373.1	.0113	.0000	0.59	-0.26	0.53	3.4	9
7	10	310.9	.0113	.0000	0.64	-0.51	0.61	6.4	10
8	10	344.3	.0113	.0000	1.73	1.10	1.26	4.0	7
9	10	377.6	.0113	.0000	2.96	2.26	2.26	5.4	6
10	10	410.9	.0113	.0000	4.87	4.11	4.11	8.1	7
11	20	323.1	.0113	.0000	2.20	-2.11	2.11	14.3	6
12	20	373.1	.0113	.0000	2.63	1.16	2.03	5.2	6
13	20	423.1	.0113	.0000	4.98	3.93	3.93	7.8	7
14	28	348.1	.0113	.0000	2.46	-2.37	2.37	14.3	10
15	28	373.1	.0113	.0000	1.10	-1.06	1.06	7.9	7
16	28	423.1	.0113	.0000	3.35	2.48	2.48	7.1	7
17	36	373.1	.0113	.0000	1.05	-0.85	0.97	7.5	7
18	36	423.1	.0113	.0000	4.18	3.45	3.45	10.5	6
19	44	373.1	.0113	.0000	0.92	0.61	0.61	2.9	9
20	44	423.1	.0113	.0000	4.57	3.74	3.74	18.0	7

MODEL OVERALL STATISTICS

RMSE	=	2.5351	BAR	NO PT	=	154
AAD	=	1.7490	BAR	%AAD	=	6.716
MIN DEV	=	-3.1092	BAR	MIN %DEV	=	-18.938
MAX DEV	=	9.4879	BAR	MAX %DEV	=	24.207
BIAS	=	0.4737	BAR	C-VAR	=	0.090
RESTRICTIONS	:	NONE		R-SQR	=	.862507

TABLE D.XI

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0087	.0000	2.05	-1.79	1.80	3.8	19
2	8	323.1	.0143	.0000	1.02	0.54	0.84	3.1	33
3	10	310.9	.0104	.0000	2.70	1.34	1.82	6.0	30
4	20	323.1	.0132	.0000	4.05	1.68	3.00	9.1	19
5	28	348.1	.0189	.0000	3.03	0.76	2.00	8.8	24
6	36	373.1	.0095	.0000	2.68	0.81	1.99	8.8	13
7	44	373.1	.0007	.0000	1.87	0.25	1.44	7.4	16

MODEL OVERALL STATISTICS

RMSE	=	2.5675	BAR	NO PT	=	154
AAD	=	1.7559	BAR	%AAD	=	6.316
MIN DEV	=	-3.3368	BAR	MIN %DEV	=	-17.477
MAX DEV	=	10.6875	BAR	MAX %DEV	=	19.635
BIAS	=	0.5753	BAR	C-VAR	=	0.146
RESTRICTIONS	:	NONE		R-SQR	=	.801171

TABLE D.XII

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0225	.0000	1.36	-0.65	1.20	2.5	6
2	4	366.5	.0253	.0000	1.07	-0.32	0.87	1.9	8
3	4	394.3	.0320	.0000	0.92	-0.16	0.80	1.9	5
4	8	323.1	.0107	.0000	0.78	0.46	0.60	1.7	11
5	8	348.1	.0157	.0000	1.32	0.74	1.09	4.0	13
6	8	373.1	.0156	.0000	0.78	0.27	0.60	2.7	9
7	10	310.9	.0194	.0000	0.79	0.36	0.54	3.6	10
8	10	344.3	.0091	.0000	1.38	0.71	1.05	3.9	7
9	10	377.6	.0031	.0000	1.35	0.64	0.94	2.7	6
10	10	410.9	-.0032	.0000	1.35	0.67	0.93	1.9	7
11	20	323.1	.0284	.0000	1.45	0.51	0.95	4.5	6
12	20	373.1	.0107	.0000	2.47	0.97	1.94	5.2	6
13	20	423.1	-.0001	.0000	1.36	0.50	0.97	2.2	7
14	28	348.1	.0286	.0000	0.80	0.24	0.58	3.1	10
15	28	373.1	.0208	.0000	1.32	0.59	1.01	4.9	7
16	28	423.1	.0013	.0000	1.16	0.44	0.78	2.7	7
17	36	373.1	.0195	.0000	1.28	0.40	0.71	3.5	7
18	36	423.1	-.0021	.0000	0.81	0.35	0.62	2.3	6
19	44	373.1	.0081	.0000	0.46	0.10	0.29	1.4	9
20	44	423.1	-.0096	.0000	0.78	0.34	0.61	3.5	7

MODEL OVERALL STATISTICS

RMSE = 1.1791 BAR
AAD = 0.8260 BAR
MIN DEV = -2.1992 BAR
MAX DEV = 5.0885 BAR
BIAS = 0.3702 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 2.996
MIN %DEV = -10.058
MAX %DEV = 9.000
C-VAR = 0.065
R-SQR = .889005

TABLE D.XIII

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0000	.0000	.59	-.07	.53	1.2	6
2	4	366.5	.0000	.0000	.97	-.65	.80	1.7	8
3	4	394.3	.0000	.0000	1.18	-.81	1.01	2.2	5
4	8	323.2	.0000	.0000	2.97	2.64	2.64	7.6	11
5	8	348.2	.0000	.0000	3.19	2.40	2.47	7.2	13
6	8	373.2	.0000	.0000	2.14	1.60	1.60	6.4	9
7	10	310.9	.0000	.0000	1.16	.87	.88	4.9	10
8	10	344.3	.0000	.0000	4.92	4.09	4.09	13.6	7
9	10	377.6	.0000	.0000	7.94	6.70	6.70	19.1	6
10	10	410.9	.0000	.0000	12.14	10.66	10.66	22.6	7
11	20	323.2	.0000	.0000	.69	-.61	.61	4.7	6
12	20	373.2	.0000	.0000	4.40	3.11	3.18	6.0	6
13	20	423.2	.0000	.0000	6.06	4.97	4.97	10.4	7
14	28	348.2	.0000	.0000	1.06	-1.02	1.02	6.3	10
15	28	373.2	.0000	.0000	.51	-.13	.45	3.7	7
16	28	423.2	.0000	.0000	3.25	2.51	2.51	7.6	7
17	36	373.2	.0000	.0000	1.51	-1.40	1.40	9.2	7
18	36	423.2	.0000	.0000	.87	.62	.68	2.0	6
19	44	373.2	.0000	.0000	2.02	-1.75	1.75	9.8	9
20	44	423.2	.0000	.0000	.40	-.34	.35	3.3	7

MODEL OVERALL STATISTICS

RMSE	=	3.9497	BAR	NO PT	=	154
AAD	=	2.3574	BAR	%AAD	=	7.467
MIN DEV	=	-3.2600	BAR	MIN %DEV	=	-11.496
MAX DEV	=	19.0434	BAR	MAX %DEV	=	23.362
BIAS	=	1.6170	BAR	C-VAR	=	.140
RESTRICTIONS	:	NONE		R-SQR	=	.760359

TABLE D.XIV

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	-.0044	.0000	.65	-.42	.58	1.2	6
2	4	366.5	-.0044	.0000	1.30	-1.10	1.14	2.4	8
3	4	394.3	-.0044	.0000	1.44	-1.11	1.23	2.7	5
4	8	323.2	-.0044	.0000	2.52	2.05	2.05	5.4	11
5	8	348.2	-.0044	.0000	2.50	1.67	1.89	5.7	13
6	8	373.2	-.0044	.0000	1.53	.99	1.06	4.0	9
7	10	310.9	-.0044	.0000	.69	.36	.46	2.8	10
8	10	344.3	-.0044	.0000	4.00	3.22	3.22	10.0	7
9	10	377.6	-.0044	.0000	6.80	5.64	5.64	15.7	6
10	10	410.9	-.0044	.0000	10.76	9.38	9.38	19.7	7
11	20	323.2	-.0044	.0000	1.38	-1.31	1.31	8.6	6
12	20	373.2	-.0044	.0000	2.82	1.57	2.02	4.5	6
13	20	423.2	-.0044	.0000	4.43	3.50	3.50	7.0	7
14	28	348.2	-.0044	.0000	1.78	-1.70	1.70	10.1	10
15	28	373.2	-.0044	.0000	.93	-.91	.91	6.4	7
16	28	423.2	-.0044	.0000	2.17	1.55	1.55	4.2	7
17	36	373.2	-.0044	.0000	2.15	-1.97	1.97	12.4	7
18	36	423.2	-.0044	.0000	.33	-.28	.30	1.8	6
19	44	373.2	-.0044	.0000	2.63	-2.29	2.29	12.9	9
20	44	423.2	-.0044	.0000	.90	-.88	.88	6.2	7

MODEL OVERALL STATISTICS

RMSE	=	3.3909	BAR	NO PT	=	154
AAD	=	2.0970	BAR	%AAD	=	7.139
MIN DEV	=	-4.1886	BAR	MIN %DEV	=	-14.628
MAX DEV	=	17.1384	BAR	MAX %DEV	=	20.821
BIAS	=	.8657	BAR	C-VAR	=	.120
RESTRICTIONS	:	NONE		R-SQR	=	.793467

TABLE D.XV

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	.0031	.0000	.83	-.24	.67	1.5	19
2	8	323.2	-.0092	.0000	1.76	.92	1.27	4.2	33
3	10	310.9	-.0170	.0000	3.97	1.83	2.58	8.2	30
4	20	323.2	-.0044	.0000	3.22	1.37	2.34	6.7	19
5	28	348.2	.0016	.0000	2.08	.57	1.32	5.7	24
6	36	373.2	.0057	.0000	1.60	.52	1.19	5.2	13
7	44	373.2	.0095	.0000	.96	.11	.69	3.1	16

MODEL OVERALL STATISTICS

RMSE = 2.4671 BAR
AAD = 1.5251 BAR
MIN DEV = -1.9100 BAR
MAX DEV = 12.1146 BAR
BIAS = .8378 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 5.145
MIN %DEV = -16.910
MAX %DEV = 14.709
C-VAR = .140
R-SQR = .791705

TABLE D.XVI

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR ETHANE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	338.7	-.0028	.0000	.61	-.29	.56	1.2	6
2	4	366.5	.0041	.0000	.77	-.23	.62	1.4	8
3	4	394.3	.0097	.0000	.76	-.13	.67	1.6	5
4	8	323.2	-.0115	.0000	1.99	1.14	1.40	3.6	11
5	8	348.2	-.0079	.0000	2.01	1.10	1.54	5.3	13
6	8	373.2	-.0091	.0000	.97	.36	.73	3.2	9
7	10	310.9	-.0049	.0000	.64	.30	.43	2.8	10
8	10	344.3	-.0171	.0000	1.70	.87	1.25	4.4	7
9	10	377.6	-.0262	.0000	2.05	.96	1.38	3.9	6
10	10	410.9	-.0368	.0000	2.48	1.25	1.71	3.4	7
11	20	323.2	.0050	.0000	.66	.23	.42	1.8	6
12	20	373.2	-.0063	.0000	2.24	.93	1.72	4.5	6
13	20	423.2	-.0140	.0000	1.36	.51	.96	2.1	7
14	28	348.2	.0070	.0000	.43	.12	.31	1.6	10
15	28	373.2	.0031	.0000	.94	.44	.71	3.4	7
16	28	423.2	-.0100	.0000	.95	.37	.63	2.2	7
17	36	373.2	.0116	.0000	.74	.22	.39	1.8	7
18	36	423.2	-.0020	.0000	.45	.21	.36	1.4	6
19	44	373.2	.0127	.0000	.26	-.08	.23	1.4	9
20	44	423.2	.0046	.0000	.56	.25	.45	2.6	7

MODEL OVERALL STATISTICS

RMSE = 1.3364 BAR
AAD = .8393 BAR
MIN DEV = -1.2317 BAR
MAX DEV = 5.2837 BAR
BIAS = .4594 BAR
RESTRICTIONS : NONE

NO PT = 154
%AAD = 2.792
MIN %DEV = -11.404
MAX %DEV = 8.339
C-VAR = .073
R-SQR = .871744

TABLE D.XVII

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	6.93	-5.84	5.84	24.2	18
2	4	344.3	.0000	.0000	4.72	-3.22	3.22	12.4	17
3	4	377.6	.0000	.0000	2.44	-1.54	1.54	5.2	12
4	4	410.9	.0000	.0000	0.64	-0.35	0.35	1.0	5
5	10	310.9	.0000	.0000	14.61	-13.21	13.21	37.0	11
6	10	344.3	.0000	.0000	16.06	-13.05	13.05	26.9	8
7	10	377.6	.0000	.0000	16.06	-12.95	12.95	21.7	10
8	10	410.9	.0000	.0000	14.96	-12.26	12.26	18.6	10
9	10	444.3	.0000	.0000	17.91	-15.90	15.90	19.3	11
10	10	477.6	.0000	.0000	29.98	-23.13	23.13	23.1	11
11	10	510.9	.0000	.0000	15.86	-13.75	13.75	18.3	9
12	20	323.1	.0000	.0000	11.36	-9.91	9.91	34.7	13
13	20	373.1	.0000	.0000	11.52	-10.17	10.17	23.7	9
14	28	348.1	.0000	.0000	18.25	-13.90	13.90	26.4	8
15	28	373.1	.0000	.0000	13.09	-9.49	9.49	20.0	9
16	28	423.1	.0000	.0000	10.46	-7.31	7.31	13.2	6
17	36	373.1	.0000	.0000	6.73	-5.09	5.09	15.1	10
18	36	423.1	.0000	.0000	9.85	-7.11	7.11	13.6	8
19	44	373.1	.0000	.0000	7.43	-5.09	5.09	13.9	7
20	44	423.1	.0000	.0000	7.99	-5.60	5.60	12.9	7

MODEL OVERALL STATISTICS

RMSE	=	13.4546	BAR	NO PT	=	199
AAD	=	9.4400	BAR	%AAD	=	19.853
MIN DEV	=	-62.8435	BAR	MIN %DEV	=	-46.201
MAX DEV	=	0.0000	BAR	MAX %DEV	=	.000
BIAS	=	-9.4400	BAR	C-VAR	=	.271
RESTRICTIONS	:	NONE		R-SQR	=	.820315

TABLE D.XVIII

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.1039	.0000	1.70	-1.49	1.49	6.7	18
2	4	344.3	.1039	.0000	2.50	-2.16	2.16	5.6	17
3	4	377.6	.1039	.0000	2.75	-2.31	2.31	4.8	12
4	4	410.9	.1039	.0000	1.24	-0.74	0.74	1.6	5
5	10	310.9	.1039	.0000	2.29	-2.03	2.03	7.4	11
6	10	344.3	.1039	.0000	2.69	-0.84	2.45	4.7	8
7	10	377.6	.1039	.0000	1.92	-0.81	1.68	2.4	10
8	10	410.9	.1039	.0000	1.52	-1.02	1.10	1.4	10
9	10	444.3	.1039	.0000	2.27	-1.87	1.87	2.0	11
10	10	477.6	.1039	.0000	3.76	-3.23	3.23	3.6	11
11	10	510.9	.1039	.0000	5.81	-5.00	5.00	6.7	9
12	20	323.1	.1039	.0000	0.59	-0.24	0.33	1.0	13
13	20	373.1	.1039	.0000	2.40	2.33	2.33	6.5	9
14	28	348.1	.1039	.0000	1.93	0.43	1.70	6.4	8
15	28	373.1	.1039	.0000	2.05	1.61	1.96	8.4	9
16	28	423.1	.1039	.0000	2.37	2.20	2.20	9.4	6
17	36	373.1	.1039	.0000	2.02	1.88	1.88	9.6	10
18	36	423.1	.1039	.0000	2.40	1.05	2.15	7.5	8
19	44	373.1	.1039	.0000	1.65	0.80	1.55	9.1	7
20	44	423.1	.1039	.0000	2.22	0.03	1.76	6.7	7

MODEL OVERALL STATISTICS

RMSE	=	2.5022	BAR	NO PT	=	199
AAD	=	1.9837	BAR	%AAD	=	5.437
MIN DEV	=	-9.5693	BAR	MIN %DEV	=	-13.840
MAX DEV	=	4.4178	BAR	MAX %DEV	=	18.019
BIAS	=	-0.8117	BAR	C-VAR	=	0.050
RESTRICTIONS	:	NONE		R-SQR	=	.954917

TABLE D.XIX

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.1363	.0000	0.73	-0.30	0.49	1.2	52
2	10	310.9	.0149	.0000	3.26	0.19	2.11	2.9	70
3	20	323.1	.0984	.0000	1.40	0.08	1.16	3.4	22
4	28	348.1	.0833	.0000	4.01	-1.51	2.47	5.9	23
5	36	373.1	.0702	.0000	3.16	-1.19	1.85	4.9	18
6	44	373.1	.0750	.0000	3.29	-1.36	2.03	6.1	14

MODEL OVERALL STATISTICS

RMSE	=	2.7606	BAR	NO PT	=	199
AAD	=	1.5939	BAR	%AAD	=	3.253
MIN DEV	=	-12.7455	BAR	MIN %DEV	=	-13.270
MAX DEV	=	11.8705	BAR	MAX %DEV	=	11.582
BIAS	=	-0.3810	BAR	C-VAR	=	0.093
RESTRICTIONS	:	NONE		R-SQR	=	.996611

TABLE D.XX

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.1346	.0000	0.51	0.05	0.36	1.1	18
2	4	344.3	.1388	.0000	0.36	-0.05	0.23	0.6	17
3	4	377.6	.1530	.0000	0.21	-0.04	0.17	0.4	12
4	4	410.9	.1297	.0000	0.80	-0.61	0.61	1.4	5
5	10	310.9	.1205	.0000	2.29	0.88	1.74	4.5	11
6	10	344.3	.1099	.0000	3.72	0.92	2.73	4.1	8
7	10	377.6	.1087	.0000	2.43	0.57	1.73	1.8	10
8	10	410.9	.1081	.0000	1.44	0.11	1.14	1.3	10
9	10	444.3	.1128	.0000	1.06	-0.07	0.80	0.9	11
10	10	477.6	.1240	.0000	1.23	0.03	0.80	0.8	11
11	10	510.9	.1532	.0000	0.97	0.08	0.64	0.9	9
12	20	323.1	.1045	.0000	0.53	-0.16	0.31	1.0	13
13	20	373.1	.0852	.0000	0.97	-0.36	0.71	1.8	9
14	28	348.1	.0926	.0000	3.80	-1.62	2.63	6.0	8
15	28	373.1	.0793	.0000	3.72	-1.51	2.21	5.2	9
16	28	423.1	.0652	.0000	3.76	-1.73	2.46	5.5	6
17	36	373.1	.0678	.0000	2.06	-0.88	1.28	4.2	10
18	36	423.1	.0750	.0000	3.85	-1.47	2.38	5.4	8
19	44	373.1	.0706	.0000	3.12	-1.30	1.95	6.5	7
20	44	423.1	.0822	.0000	3.27	-1.27	2.01	5.5	7

MODEL OVERALL STATISTICS

RMSE	=	2.1705	BAR	NO PT	=	199
AAD	=	1.1769	BAR	%AAD	=	2.549
MIN DEV	=	-10.0086	BAR	MIN %DEV	=	-12.549
MAX DEV	=	8.5262	BAR	MAX %DEV	=	11.096
BIAS	=	-0.3020	BAR	C-VAR	=	0.066
RESTRICTIONS	:	NONE		R-SQR	=	.992398

TABLE D.XXI

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	8.07	-7.17	7.17	26.7	18
2	4	344.3	.0000	.0000	6.27	-4.60	4.60	15.7	17
3	4	377.6	.0000	.0000	4.24	-3.16	3.16	9.9	12
4	4	410.9	.0000	.0000	1.53	-0.89	0.89	2.7	5
5	10	310.9	.0000	.0000	16.08	-14.94	14.94	40.2	11
6	10	344.3	.0000	.0000	19.91	-17.09	17.09	31.1	8
7	10	377.6	.0000	.0000	19.91	-16.61	16.61	24.7	10
8	10	410.9	.0000	.0000	16.17	-13.86	13.86	19.9	10
9	10	444.3	.0000	.0000	7.63	-15.89	15.89	19.9	11
10	10	477.6	.0000	.0000	20.34	-17.89	17.89	20.5	11
11	10	510.9	.0000	.0000	22.72	-18.54	18.54	23.6	9
12	20	323.1	.0000	.0000	14.42	-12.95	12.95	46.9	13
13	20	373.1	.0000	.0000	14.04	-12.76	12.76	31.2	9
14	28	348.1	.0000	.0000	22.62	-18.74	18.74	41.6	8
15	28	373.1	.0000	.0000	16.47	-13.36	13.36	34.1	9
16	28	423.1	.0000	.0000	12.10	-9.66	9.66	23.2	6
17	36	373.1	.0000	.0000	11.60	-9.94	9.94	35.8	10
18	36	423.1	.0000	.0000	11.95	-10.11	10.11	24.4	8
19	44	373.1	.0000	.0000	12.32	-10.10	10.10	37.6	7
20	44	423.1	.0000	.0000	9.89	-8.30	8.30	25.0	7

MODEL OVERALL STATISTICS

RMSE = 14.7674 BAR
AAD = 11.6294 BAR
MIN DEV = -44.2786 BAR
MAX DEV = 0.0000 BAR
BIAS = -11.6294 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 26.801
MIN %DEV = -48.628
MAX %DEV = 0.000
C-VAR = 0.297
R-SQR = .854203

TABLE D.XXII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0489	.0000	4.33	-3.67	3.70	13.6	18
2	4	344.3	.0489	.0000	5.31	-4.21	4.21	11.2	17
3	4	377.6	.0489	.0000	7.55	-6.14	6.14	12.9	12
4	4	410.9	.0489	.0000	3.28	-2.20	2.20	5.2	5
5	10	310.9	.0489	.0000	6.93	-6.43	6.43	17.1	11
6	10	344.3	.0489	.0000	8.06	-7.13	7.13	11.0	8
7	10	377.6	.0489	.0000	10.03	-7.85	7.85	7.9	10
8	10	410.9	.0489	.0000	9.11	-6.78	6.78	5.7	10
9	10	444.3	.0489	.0000	7.78	-6.13	6.13	5.6	11
10	10	477.6	.0489	.0000	7.89	-6.64	6.64	6.9	11
11	10	510.9	.0489	.0000	7.96	-6.95	6.95	9.6	9
12	20	323.1	.0489	.0000	5.36	-4.89	4.89	18.2	13
13	20	373.1	.0489	.0000	0.33	-0.31	0.31	1.2	9
14	28	348.1	.0489	.0000	6.09	-5.16	5.16	11.9	8
15	28	373.1	.0489	.0000	1.68	-1.49	1.49	4.4	9
16	28	423.1	.0489	.0000	2.99	2.15	2.15	4.4	6
17	36	373.1	.0489	.0000	2.11	-1.89	1.89	7.5	10
18	36	423.1	.0489	.0000	1.57	1.30	1.30	2.9	8
19	44	373.1	.0489	.0000	3.02	-2.56	2.56	10.0	7
20	44	423.1	.0489	.0000	0.88	0.67	0.67	1.7	7

MODEL OVERALL STATISTICS

RMSE	=	6.0323	BAR	NO PT	=	199
AAD	=	4.4512	BAR	%AAD	=	9.246
MIN DEV	=	-20.0250	BAR	MIN %DEV	=	-21.991
MAX DEV	=	6.1210	BAR	MAX %DEV	=	6.615
BIAS	=	-4.1673	BAR	C-VAR	=	0.121
RESTRICTIONS	:	NONE		R-SQR	=	.857218

TABLE D.XXIII

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	344.3	.0937	.0000	2.02	-1.19	1.46	3.6	52
2	10	410.9	.0667	.0000	2.89	-0.78	2.16	3.7	70
3	20	323.1	.0626	.0000	3.52	0.76	2.83	8.3	22
4	28	348.1	.0553	.0000	3.41	0.40	2.25	5.1	23
5	36	373.1	.0531	.0000	2.17	0.55	1.68	5.1	18
6	44	373.1	.0551	.0000	2.11	0.37	1.70	5.7	14

MODEL OVERALL STATISTICS

RMSE	=	2.7316	BAR	NO PT	=	199
AAD	=	1.9881	BAR	%AAD	=	4.585
MIN DEV	=	-10.4195	BAR	MIN %DEV	=	-10.162
MAX DEV	=	11.0693	BAR	MAX %DEV	=	11.963
BIAS	=	-0.3814	BAR	C-VAR	=	0.092
RESTRICTIONS	:	NONE		R-SQR	=	.973538

TABLE D.XXIV

BUBBLE POINT CALCULATIONS USING THE SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0885	.0000	1.35	-0.72	0.86	2.1	18
2	4	344.3	.0970	.0000	1.90	-0.79	1.19	2.4	17
3	4	377.6	.1138	.0000	0.56	-0.18	0.49	1.4	12
4	4	410.9	.1634	.0000	2.18	-0.81	1.94	5.1	5
5	10	377.6	.0619	.0000	4.77	-2.21	3.00	3.4	10
6	10	410.9	.0596	.0000	4.63	-2.31	3.20	3.4	10
7	10	444.3	.0614	.0000	2.82	-1.36	2.11	2.3	11
8	10	477.6	.0678	.0000	1.28	-0.59	1.06	1.2	11
9	10	510.9	.0809	.0000	0.89	0.15	0.57	1.0	9
10	10	310.9	.0736	.0000	1.87	-0.40	1.05	2.0	11
11	10	344.3	.0666	.0000	3.94	-1.59	2.10	2.6	8
12	20	323.1	.0703	.0000	0.81	0.26	0.57	2.0	13
13	20	373.1	.0504	.0000	0.36	0.15	0.32	0.9	9
14	28	348.1	.0621	.0000	1.51	0.42	0.91	1.9	8
15	28	373.1	.0544	.0000	0.87	0.29	0.49	1.1	9
16	28	423.1	.0422	.0000	0.56	0.20	0.32	0.7	6
17	36	373.1	.0589	.0000	0.55	0.24	0.41	1.5	10
18	36	423.1	.0444	.0000	0.26	0.05	0.17	0.5	8
19	44	373.1	.0624	.0000	0.59	0.21	0.38	1.2	7
20	44	423.1	.0462	.0000	0.18	0.07	0.15	0.4	7

MODEL OVERALL STATISTICS

RMSE = 2.1033 BAR
AAD = 1.0788 BAR
MIN DEV = -12.3583 BAR
MAX DEV = 3.9206 BAR
BIAS = -0.4945 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 1.873
MIN %DEV = -9.225
MAX %DEV = 6.411
C-VAR = 0.064
R-SQR = .936515

TABLE D.XXV

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	7.19	-6.32	6.32	24.9	18
2	4	344.3	.0000	.0000	6.29	-4.88	4.89	14.8	17
3	4	377.6	.0000	.0000	3.87	-2.92	2.96	7.8	12
4	4	410.9	.0000	.0000	0.56	-0.39	0.43	1.1	5
5	10	377.6	.0000	.0000	16.35	-15.41	15.41	22.7	10
6	10	410.9	.0000	.0000	10.43	-9.75	9.75	13.9	10
7	10	444.3	.0000	.0000	5.86	-5.30	5.30	7.8	11
8	10	477.6	.0000	.0000	3.77	-2.10	3.32	4.9	11
9	10	510.9	.0000	.0000	3.34	-2.86	3.03	5.3	9
10	10	310.9	.0000	.0000	16.70	-15.64	15.64	44.9	11
11	10	344.3	.0000	.0000	18.73	-17.75	17.75	32.9	8
12	20	323.1	.0000	.0000	18.64	-16.96	16.96	62.5	13
13	20	373.1	.0000	.0000	16.37	-15.17	15.17	38.3	9
14	28	348.1	.0000	.0000	25.94	-22.28	22.28	52.5	8
15	28	373.1	.0000	.0000	17.60	-14.96	14.96	40.9	9
16	28	423.1	.0000	.0000	5.75	-5.11	5.11	15.3	6
17	36	373.1	.0000	.0000	12.33	-10.83	10.83	40.6	10
18	36	423.1	.0000	.0000	3.11	-2.99	2.99	9.2	8
19	44	373.1	.0000	.0000	10.95	-9.35	9.35	37.0	7
20	44	423.1	.0000	.0000	1.62	0.47	1.06	3.2	7

MODEL OVERALL STATISTICS

RMSE	=	12.2380 BAR	NO PT	=	199
AAD	=	9.1862 BAR	%AAD	=	24.662
MIN DEV	=	-44.5275 BAR	MIN %DEV	=	-66.755
MAX DEV	=	6.5165 BAR	MAX %DEV	=	5.647
BIAS	=	-9.0526 BAR	C-VAR	=	0.246
RESTRICTIONS	:	NONE	R-SQR	=	.979483

TABLE D.XXVI

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0457	.0000	3.48	-3.12	3.12	12.4	18
2	4	344.3	.0457	.0000	3.97	-3.28	3.29	7.9	17
3	4	377.6	.0457	.0000	3.40	-2.68	2.74	5.5	12
4	4	410.9	.0457	.0000	1.75	-1.41	1.50	3.4	5
5	10	377.6	.0457	.0000	10.56	5.88	6.89	6.6	10
6	10	410.9	.0457	.0000	19.51	14.14	14.14	12.3	10
7	10	444.3	.0457	.0000	23.05	17.94	17.94	17.0	11
8	10	477.6	.0457	.0000	24.31	18.84	18.84	17.8	11
9	10	510.9	.0457	.0000	14.15	10.80	10.80	12.1	9
10	10	310.9	.0457	.0000	8.27	-7.73	7.73	25.4	11
11	10	344.3	.0457	.0000	5.63	-2.86	5.27	11.8	8
12	20	323.1	.0457	.0000	12.84	-11.90	11.90	45.0	13
13	20	373.1	.0457	.0000	4.70	-4.60	4.60	13.3	9
14	28	348.1	.0457	.0000	12.67	-11.55	11.55	30.5	8
15	28	373.1	.0457	.0000	4.78	-4.37	4.37	15.9	9
16	28	423.1	.0457	.0000	13.48	9.03	9.03	15.7	6
17	36	373.1	.0457	.0000	3.55	-3.38	3.38	15.2	10
18	36	423.1	.0457	.0000	15.99	12.27	12.27	25.7	8
19	44	373.1	.0457	.0000	1.73	-1.15	1.67	9.2	7
20	44	423.1	.0457	.0000	18.63	14.40	14.40	38.9	7

MODEL OVERALL STATISTICS

RMSE	=	12.3312	BAR	NO PT	=	199
AAD	=	8.1315	BAR	%AAD	=	16.968
MIN DEV	=	-20.6909	BAR	MIN %DEV	=	-51.584
MAX DEV	=	51.0904	BAR	MAX %DEV	=	54.490
BIAS	=	1.6400	BAR	C-VAR	=	0.248
RESTRICTIONS	:	NONE		R-SQR	=	.649583

TABLE D.XXVII

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0786	.0000	0.70	-0.13	0.54	1.6	52
2	10	377.6	.0372	.0000	12.70	4.28	9.28	13.2	70
3	20	323.1	.0856	.0000	8.82	0.88	6.98	21.0	22
4	28	348.1	.0573	.0000	11.57	0.64	7.46	18.7	23
5	36	373.1	.0368	.0000	8.75	1.05	6.71	19.6	18
6	44	373.1	.0224	.0000	7.75	0.39	6.17	20.6	14

MODEL OVERALL STATISTICS

RMSE = 9.5954 BAR   NO PT = 199
AAD = 6.0800 BAR   %AAD = 12.746
MIN DEV = -13.2656 BAR   MIN %DEV = -46.914
MAX DEV = 41.8119 BAR   MAX %DEV = 45.189
BIAS = 1.7661 BAR   C-VAR = 0.322
RESTRICTIONS : NONE   R-SQR = .696139

TABLE D.XXVIII

BUBBLE POINT CALCULATIONS USING THE MODIFIED SPHCT EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0809	.0000	0.55	-0.13	0.34	0.9	18
2	4	344.3	.0747	.0000	0.95	-0.34	0.55	1.3	17
3	4	377.6	.0760	.0000	0.75	-0.15	0.63	1.6	12
4	4	410.9	.1008	.0000	0.24	0.07	0.22	0.6	5
5	10	344.3	.0555	.0000	8.24	2.23	6.19	10.1	8
6	10	310.9	.0736	.0000	4.10	-0.51	3.75	12.8	11
7	10	377.6	.0405	.0000	7.14	2.56	5.12	6.3	10
8	10	410.9	.0267	.0000	6.07	2.31	4.37	4.6	10
9	10	444.3	.0164	.0000	4.66	1.66	2.99	3.1	11
10	10	477.6	.0098	.0000	4.79	1.56	2.97	3.1	11
11	10	510.9	.0141	.0000	2.96	0.84	1.65	2.3	9
12	20	323.1	.1095	.0000	4.44	0.72	2.74	9.8	13
13	20	373.1	.0631	.0000	2.58	0.81	1.99	5.3	9
14	28	348.1	.0774	.0000	8.55	1.21	5.77	14.2	8
15	28	373.1	.0638	.0000	6.15	1.63	3.47	8.5	9
16	28	423.1	.0235	.0000	3.60	1.37	2.20	5.0	6
17	36	373.1	.0651	.0000	2.49	0.87	1.70	6.1	10
18	36	423.1	.0132	.0000	2.17	0.78	1.46	3.5	8
19	44	373.1	.0549	.0000	3.04	1.00	1.84	6.3	7
20	44	423.1	.0006	.0000	1.77	0.63	1.13	3.1	7

MODEL OVERALL STATISTICS

RMSE	=	4.3179	BAR	NO PT	=	199
AAD	=	2.4307	BAR	%AAD	=	5.171
MIN DEV	=	-4.7780	BAR	MIN %DEV	=	-27.935
MAX DEV	=	22.1302	BAR	MAX %DEV	=	24.596
BIAS	=	0.8530	BAR	C-VAR	=	0.132
RESTRICTIONS	:	NONE		R-SQR	=	.829526

TABLE D.XXIX

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 1)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0000	.0000	6.28	-5.59	5.59	21.8	18
2	4	344.3	.0000	.0000	6.23	-5.06	5.07	13.7	17
3	4	377.6	.0000	.0000	4.22	-3.36	3.42	8.0	12
4	4	410.9	.0000	.0000	1.69	-1.36	1.43	3.3	5
5	10	310.9	.0000	.0000	12.24	-11.43	11.43	32.2	11
6	10	344.3	.0000	.0000	11.74	-11.07	11.07	19.7	8
7	10	377.6	.0000	.0000	7.67	-6.83	6.83	8.6	10
8	10	410.9	.0000	.0000	3.65	-1.41	2.35	2.7	10
9	10	444.3	.0000	.0000	4.07	2.69	3.74	6.3	11
10	10	477.6	.0000	.0000	4.85	3.17	4.48	7.5	11
11	10	510.9	.0000	.0000	3.15	2.42	2.70	5.4	9
12	20	323.2	.0000	.0000	14.25	-12.86	12.86	46.9	13
13	20	373.2	.0000	.0000	10.86	-10.01	10.01	25.0	9
14	28	348.2	.0000	.0000	19.90	-16.67	16.67	37.6	8
15	28	373.2	.0000	.0000	12.24	-10.13	10.13	26.5	9
16	28	423.2	.0000	.0000	2.11	-1.86	1.86	5.4	6
17	36	373.2	.0000	.0000	9.17	-7.86	7.86	28.4	10
18	36	423.2	.0000	.0000	2.60	-2.12	2.12	5.0	8
19	44	373.2	.0000	.0000	10.21	-8.34	8.34	30.8	7
20	44	423.2	.0000	.0000	2.69	-2.21	2.21	6.5	7

MODEL OVERALL STATISTICS

RMSE	=	8.8322	BAR	NO PT	=	199
AAD	=	6.6248	BAR	%AAD	=	17.864
MIN DEV	=	-35.8569	BAR	MIN %DEV	=	-48.713
MAX DEV	=	6.5868	BAR	MAX %DEV	=	13.586
BIAS	=	-5.5621	BAR	C-VAR	=	.178
RESTRICTIONS	:	NONE		R-SQR	=	.974328

TABLE D.XXX

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 2)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0275	.0000	4.04	-3.61	3.61	13.8	18
2	4	344.3	.0275	.0000	4.90	-3.91	3.93	8.9	17
3	4	377.6	.0275	.0000	4.12	-3.11	3.18	6.1	12
4	4	410.9	.0275	.0000	1.52	-1.20	1.31	3.0	5
5	10	310.9	.0275	.0000	6.40	-6.06	6.06	17.6	11
6	10	344.3	.0275	.0000	1.74	-1.50	1.53	3.2	8
7	10	377.6	.0275	.0000	7.64	6.95	6.95	9.7	10
8	10	410.9	.0275	.0000	14.97	13.85	13.85	18.9	10
9	10	444.3	.0275	.0000	18.78	17.61	17.61	23.3	11
10	10	477.6	.0275	.0000	17.08	16.08	16.08	21.8	11
11	10	510.9	.0275	.0000	12.28	11.48	11.48	17.6	9
12	20	323.2	.0275	.0000	9.28	-8.43	8.43	31.0	13
13	20	373.2	.0275	.0000	2.04	-2.00	2.00	5.7	9
14	28	348.2	.0275	.0000	10.05	-8.56	8.56	19.8	8
15	28	373.2	.0275	.0000	2.60	-2.35	2.35	7.2	9
16	28	423.2	.0275	.0000	10.04	7.51	7.51	16.2	6
17	36	373.2	.0275	.0000	3.19	-2.78	2.78	10.4	10
18	36	423.2	.0275	.0000	8.07	6.84	6.84	16.3	8
19	44	373.2	.0275	.0000	4.50	-3.69	3.69	13.7	7
20	44	423.2	.0275	.0000	5.58	4.67	4.67	14.0	7

MODEL OVERALL STATISTICS

RMSE = 9.0436 BAR
AAD = 6.7366 BAR
MIN DEV = -17.4157 BAR
MAX DEV = 24.6053 BAR
BIAS = 1.4571 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 14.330
MIN %DEV = -33.192
MAX %DEV = 30.430
C-VAR = .182
R-SQR = .760530

TABLE D.XXXI

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0620	.0000	1.44	-.47	.99	2.4	52
2	10	310.9	.0107	.0000	7.41	1.02	6.47	12.2	70
3	20	323.2	.0507	.0000	5.93	.84	4.89	14.3	22
4	28	348.2	.0328	.0000	7.99	.00	5.16	12.2	23
5	36	373.2	.0242	.0000	5.32	.58	4.43	13.1	18
6	44	373.2	.0258	.0000	4.95	.08	4.11	13.7	14

MODEL OVERALL STATISTICS

RMSE	=	5.9508	BAR	NO PT	=	199
AAD	=	4.3592	BAR	%AAD	=	10.040
MIN DEV	=	-13.4236	BAR	MIN %DEV	=	-35.629
MAX DEV	=	25.1802	BAR	MAX %DEV	=	27.214
BIAS	=	.3859	BAR	C-VAR	=	.200
RESTRICTIONS	:	NONE		R-SQR	=	.913513

TABLE D.XXXII

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR CARBON DIOXIDE + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	310.9	.0643	.0000	.83	-.44	.51	1.2	18
2	4	344.3	.0582	.0000	2.10	-.92	1.33	2.8	17
3	4	377.6	.0594	.0000	1.68	-.49	1.30	2.9	12
4	4	410.9	.0708	.0000	.27	.09	.25	.7	5
5	10	310.9	.0528	.0000	1.25	.44	1.00	2.4	11
6	10	344.3	.0320	.0000	1.37	.47	.90	1.3	8
7	10	377.6	.0139	.0000	1.65	-.62	.79	.9	10
8	10	410.9	-.0015	.0000	4.11	-2.06	2.63	2.6	10
9	10	444.3	-.0121	.0000	5.02	-2.47	3.40	3.4	11
10	10	477.6	-.0121	.0000	4.95	-1.40	3.58	4.4	11
11	10	510.9	-.0142	.0000	3.59	-1.48	2.57	3.1	9
12	20	323.2	.0644	.0000	1.11	.33	.72	2.4	13
13	20	373.2	.0342	.0000	.92	.35	.74	1.9	9
14	28	348.2	.0493	.0000	2.26	.63	1.36	2.8	8
15	28	373.2	.0356	.0000	1.56	.51	.86	1.9	9
16	28	423.2	.0074	.0000	1.06	.41	.62	1.3	6
17	36	373.2	.0405	.0000	.41	.18	.31	1.1	10
18	36	423.2	.0071	.0000	.36	-.03	.23	.5	8
19	44	373.2	.0452	.0000	.24	.08	.18	.7	7
20	44	423.2	.0094	.0000	.17	-.04	.12	.3	7

MODEL OVERALL STATISTICS

RMSE = 2.3606 BAR
AAD = 1.2376 BAR
MIN DEV = -12.3006 BAR
MAX DEV = 5.9196 BAR
BIAS = -.4096 BAR
RESTRICTIONS : NONE

NO PT = 199
%AAD = 2.074
MIN %DEV = -7.136
MAX %DEV = 7.241
C-VAR = .072
R-SQR = .928749

TABLE D.XXXIII

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR HYDROGEN + N-PARAFFIN SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.3598	.0000	8.12	-1.15	6.14	5.9	60
2	10	344.3	.4177	.0000	2.53	0.14	1.79	1.8	21
3	20	323.1	.3836	.0000	1.35	0.35	1.09	2.5	37
4	28	348.1	.2649	.0000	3.05	-0.02	2.40	4.1	35
5	36	373.1	.1232	.0000	4.04	0.16	3.38	7.0	27

MODEL OVERALL STATISTICS

RMSE	=	5.2300	BAR	NO PT	=	180
AAD	=	3.4537	BAR	%AAD	=	4.521
MIN DEV	=	-14.9324	BAR	MIN %DEV	=	-16.713
MAX DEV	=	25.0888	BAR	MAX %DEV	=	4.892
BIAS	=	-0.2757	BAR	C-VAR	=	0.094
RESTRICTIONS	:	NONE		R-SQR	=	.947621

TABLE D.XXXIV

BUBBLE POINT CALCULATIONS USING THE PENG-ROBINSON EQUATION OF STATE FOR HYDROGEN + N-PARAFFIN SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	.3091	.0000	4.91	1.04	3.89	4.1	13
2	4	344.2	.3369	.0000	4.18	0.74	2.88	3.1	12
3	4	360.9	.3868	.0000	4.04	0.43	2.77	2.7	11
4	4	377.5	.4490	.0000	5.47	0.21	3.93	3.8	12
5	4	394.2	.4815	.0000	7.72	-0.56	5.56	4.9	12
6	10	344.3	.4043	.0000	1.64	0.40	1.11	1.0	9
7	10	373.1	.4174	.0000	0.77	0.20	0.55	0.6	6
8	10	423.1	.4636	.0000	0.36	0.09	0.33	0.5	6
9	20	323.1	.3856	.0000	1.00	0.37	0.83	1.1	7
10	20	373.1	.3703	.0000	0.52	0.16	0.40	0.7	9
11	20	373.3	.4690	.0000	0.53	0.24	0.47	1.9	5
12	20	423.1	.3523	.0000	0.23	0.08	0.20	0.4	6
13	20	473.5	.3154	.0000	0.31	0.09	0.22	0.8	5
14	20	573.2	.4234	.0000	0.25	0.03	0.23	1.0	5
15	28	348.1	.3330	.0000	0.41	0.15	0.33	0.4	6
16	28	373.1	.2934	.0000	0.22	0.07	0.17	0.2	5
17	28	423.1	.2026	.0000	0.44	-0.05	0.30	0.4	9
18	28	373.2	.2889	.0000	0.65	0.04	0.49	1.5	5
19	28	473.2	.2170	.0000	0.54	0.21	0.43	1.5	5
20	28	573.1	.1048	.0000	0.32	0.12	0.25	1.1	5
21	36	373.1	.2114	.0000	1.86	0.95	1.59	3.3	11
22	36	423.1	.0625	.0000	0.62	-0.22	0.54	0.8	6
23	36	473.0	.0210	.0000	1.04	0.43	0.75	2.9	5
24	36	573.1	-.1357	.0000	0.53	0.25	0.48	1.9	5

MODEL OVERALL STATISTICS

RMSE	=	3.2246	BAR	NO PT	=	180
AAD	=	1.6571	BAR	%AAD	=	2.041
MIN DEV	=	-6.9057	BAR	MIN %DEV	=	-11.208
MAX DEV	=	21.8876	BAR	MAX %DEV	=	12.970
BIAS	=	0.2754	BAR	C-VAR	=	0.106
RESTRICTIONS	:	NONE		R-SQR	=	.901963

TABLE D.XXXV

BUBBLE POINT CALCULATIONS USING THE NEW EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 3)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	-.4080	.0000	9.68	-.12	7.63	7.8	60
2	10	344.3	-.5060	.0000	32.16	-11.61	27.48	29.4	21
3	20	323.2	-.5951	.0000	36.07	-19.12	27.28	50.3	37
4	28	348.2	-.6579	.0000	36.48	-20.30	27.91	48.8	35
5	36	373.2	-.7714	.0000	39.94	-21.55	28.99	48.9	27

MODEL OVERALL STATISTICS

RMSE	=	30.2884	BAR	NO PT	=	180
AAD	=	21.1348	BAR	%AAD	=	33.163
MIN DEV	=	*******	BAR	MIN %DEV	=	-76.549
MAX DEV	=	39.4144	BAR	MAX %DEV	=	81.439
BIAS	=	-12.5053	BAR	C-VAR	=	.543
RESTRICTIONS		:	NONE	R-SQR	=	.854172

TABLE D.XXXVI

BUBBLE POINT CALCULATIONS USING THE PRESENT EQUATION OF STATE FOR HYDROGEN + N-PARAFFINS SYSTEMS (CASE 4)

ISO	CN	T(K)	C(I,J)	D(I,J)	RMSE	BIAS	AAD	%AAD	NO PT
1	4	327.6	-.3636	.0000	1.62	-.40	1.45	1.7	13
2	4	344.2	-.3991	.0000	1.98	-.58	1.36	1.5	12
3	4	360.9	-.4244	.0000	2.92	-1.00	2.22	2.5	11
4	4	377.6	-.4373	.0000	2.29	-.68	2.02	2.6	12
5	4	394.2	-.4438	.0000	2.55	-.39	2.18	2.5	12
6	10	344.3	-.4037	.0000	6.52	-2.77	4.97	4.7	9
7	10	373.2	-.4770	.0000	5.31	-2.20	4.25	4.4	6
8	10	423.2	-.6002	.0000	3.23	-1.26	2.51	3.1	6
9	20	323.2	-.3148	.0000	4.26	-1.88	3.18	4.0	7
10	20	373.2	-.4337	.0000	3.93	-1.79	2.79	4.2	9
11	20	373.3	-.4290	.0000	.69	-.17	.42	1.1	5
14	20	573.2	-.8041	.0000	.58	-.15	.43	1.2	5
15	28	348.2	-.3796	.0000	4.16	-1.65	3.30	3.9	6
16	28	373.2	-.4452	.0000	4.02	-1.51	2.96	3.8	5
17	28	423.2	-.5725	.0000	3.13	-1.21	2.20	3.2	9
18	28	373.2	-.4612	.0000	.89	-.38	.69	2.5	5
19	28	473.2	-.6855	.0000	.23	-.08	.13	.4	5
20	28	573.1	-.8729	.0000	.24	-.02	.21	.9	5
21	36	373.2	-.4864	.0000	6.27	-2.10	3.53	3.9	11
22	36	423.2	-.6249	.0000	3.58	-1.52	2.88	3.7	6
23	36	473.1	-.7559	.0000	.52	.24	.44	1.9	5
24	36	573.1	-.9712	.0000	.34	.17	.30	1.3	5

MODEL OVERALL STATISTICS

RMSE	=	3.3458	BAR	NO PT	=	180
AAD	=	2.0939	BAR	%AAD	=	2.686
MIN DEV	=	-16.6968	BAR	MIN %DEV	=	-9.968
MAX DEV	=	3.6105	BAR	MAX %DEV	=	8.266
BIAS	=	-.9943	BAR	C-VAR	=	.110
RESTRICTIONS		:	NONE	R-SQR	=	.871079

VITA 2

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