PHASE BEHAVIOR OF LIGHT GASES IN HYDROCARBON
AND AQUEOUS SOLVENTS

Report for the Period
from September 1, 1998 to March 31, 1999

K. A. M. Gasem
R. L. Robinson, Jr.
(Principal Investigators)
W. Gao
K. H. Row

Oklahoma State University
School of Chemical Engineering
Stillwater, Oklahoma 74078-0537

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DISCLAIMER

PHASE BEHAVIOR OF LIGHT GASES IN
HYDROCARBON AND AQUEOUS SOLVENTS

ABSTRACT

Under previous support from the U. S. Department of Energy, an experimental facility has been established and operated to measure valuable vapor-liquid equilibrium data for systems of interest in the production and processing of coal fluids. To facilitate the development and testing of models for prediction of the phase behavior for such systems, we have acquired substantial amounts of data on the equilibrium phase compositions for binary mixtures of heavy hydrocarbon solvents with a variety of supercritical solutes, including hydrogen, methane, ethane, carbon monoxide, and carbon dioxide.

The present project focuses on measuring the phase behavior of light gases and water in Fischer-Tropsch (F-T) type solvents at conditions encountered in indirect liquefaction processes and evaluating and developing theoretically-based correlating frameworks to predict the phase behavior of such systems. Specific goals of the proposed work include (a) developing a state-of-the-art experimental facility to permit highly accurate measurements of equilibrium phase compositions (solubilities) of challenging F-T systems, (b) measuring these properties for systematically-selected binary, ternary and molten F-T wax mixtures to provide critically needed input data for correlation development, (c) developing and testing models suitable for describing the phase behavior of such mixtures, and (d) presenting the modeling results in generalized, practical formats suitable for use in process engineering calculations.

During the present reporting period, the solubilities of hydrogen in n-hexane, carbon monoxide in cyclohexane, and nitrogen in phenanthrene and pyrene were measured using a static equilibrium cell over the temperature range from 344.3 to 433.2 K and pressures to 22.8 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 Peng-Robinson (PR) equation of state (EOS). In general, the PR EOS represents the experimental data well when a single interaction parameter (C_{ij}) is used for each isotherm.

In addition, the predictive capability of the modified Park-Gasem-Robinson (PGR) equation of state (EOS) was evaluated for selected carbon dioxide + normal paraffins, ethane + normal paraffins, and hydrogen + normal paraffins. A set of mixing rules was proposed for the modified EOS to extend its predictive capabilities to mixtures. The predicted bubble point pressures for the ethane + n-paraffin and carbon dioxide + n-paraffin binaries were compared to those of the Peng-Robinson (PR), simplified-perturbed-hard-chain theory (SPHCT) and original PGR equations. The predictive capability of the proposed equation is better or comparable to the PR, SPHCT and original PGR equations of state for the ethane binaries (%AAD of 1.9) and carbon dioxide binaries (%AAD of 2.0). For the hydrogen binaries, the modified PGR EOS showed much better performance (%AAD of 1.7) than the original PGR equation and comparable to the PR equation.

A technical report on our recent measurements and a manuscript we have prepared for publication are attached.

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PROJECT TITLE: "Phase Behavior of Light Gases in Hydrocarbon and Aqueous Solvents"

PRINCIPAL INVESTIGATORS: K. A. M. Gasem

R. L. Robinson, Jr.

AFFILIATION: School of Chemical Engineering
Oklahoma State University
Stillwater, OK 74078
(405) 744-5280

PROJECT PERIOD: September 1, 1998 to March 31, 1999

EXECUTIVE SUMMARY

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Solubilities of Hydrogen in n-Hexane, Carbon Monoxide in Cyclohexane, and Nitrogen in Phenanthrene and Pyrene at Temperatures from 344.3 to 433.2 K and Pressures to 22.8 MPa

Wuzi Gao
Robert L. Robinson, Jr.
Khaled A. M. Gasem

School of Chemical Engineering
Oklahoma State University
Stillwater, Oklahoma 74078-0537

Abstract

The solubilities of hydrogen in n-hexane, carbon monoxide in cyclohexane, and nitrogen in phenanthrene and pyrene were measured using a static equilibrium cell over the temperature range from 344.3 to 433.2 K and pressures to 22.8 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 Peng-Robinson (PR) equation of state (EOS). In general, the PR EOS represents the experimental data well when a single interaction parameter (C_{ij}) is used for each isotherm.

Introduction

In the recent past, we have measured substantial amounts of data on the equilibrium phase compositions for binary mixtures of heavy hydrocarbon solvents with a variety of supercritical solutes, including hydrogen, methane, ethane, carbon monoxide, and carbon dioxide (Anderson et al., 1986; Darwish, 1991; Darwish et al., 1993; Gasem et al., 1989; Gasem and Robinson, 1985; Park et al., 1995; Srivatsan et al., 1995). The present data on selected systems complement our earlier studies.

The data we have acquired are designed to facilitate the development and testing of models for prediction of the phase behavior in systems of interest in the production of fluid fuels from coal. These asymmetric mixtures, which contain small gas molecules in heavy hydrocarbon solvents, provide a severe test of current predictive models and their associated mixing theories (Park et al., 1995).

In the work described here, measurements were made of the solubilities of hydrogen in n-hexane, carbon monoxide in cyclohexane, and nitrogen in phenanthrene and pyrene.

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Some prior literature information exists for hydrogen +n-hexane at 344 K, 377 K and 411 K; however, no data have been reported previously for the other systems.

Experimental Method

The experimental apparatus and procedures have been described by Darwish (Darwish, 1991; Darwish et al., 1993) and are summarized briefly here.

Phase equilibrium is established in a variable-volume, thermostated, static-type blind cell. Two steel balls are placed in the equilibrium cell, and the cell can be rocked 45 degrees above and below the horizontal position to hasten the establishment of equilibrium. The effective volume of the cell can be varied by the introduction or withdrawal of mercury.

A known amount of degassed liquid solvent is injected volumetrically into the initially evacuated equilibrium cell. A known amount of solute gas is then injected into the rocking cell from a gas-injection pump. After each solute injection, the bubble point pressure of the mixture is determined by sequentially injecting known amounts of mercury into the equilibrium cell to alter the system volume. After each mercury injection, the equilibrium cell is rocked to bring the system to equilibrium, and the pressure is recorded. The bubble point pressure (for the mixture of known composition) is identified graphically from the discontinuity in a pressure vs. total-volume-of-mercury-injected plot as the mixture passes from the more compressible two-phase state to the less compressible single-liquid-phase state. Additional solute is then added to the cell and the above procedure repeated at the new (higher) solute mole fraction.

Measurement uncertainties are estimated to be ±0.1 K in temperature and less than ±0.001 in composition (mole fraction). However, the estimated uncertainties (ε_{bp}) in the reported bubble point pressures (P_{bp}) at a specified mole fraction are of the order of 0.07 MPa (Darwish, 1991) for the systems in this study, since $(\varepsilon_{bp})^2 = (\varepsilon_p)^2 + (d[P_{bp}]/dx)^2(\varepsilon_x)^2$. Thus the total uncertainty in the reported bubble point pressure (at specified mole fraction) depends on both pressure and composition uncertainties and, in addition, the steepness of the bubble point pressure vs. composition curve.

Materials

The hydrogen (99.995 mol %) used in this study was supplied by Union Carbide Corporation, the carbon monoxide (99.99 %) by Matheson Gas Products, and the nitrogen (99.995+ %) was supplied by Sooner Airgas, Inc. The hexane (99.9 %), cyclohexane (99+ %), phenanthrene (98%) and pyrene (98 %) were supplied by the Aldrich Chemical Company. No further purification of these chemicals was attempted.

Results and Discussion

The experimental data are presented in Tables 1 - 3. As expected, a trend of increasing solubility with increasing temperature and pressure is observed.

The PR EOS (Peng and Robinson, 1976) was used to correlate the experimental data. The PR EOS is given below.

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

where

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

$$b = 0.0778 RT_c / P_c \tag{3}$$

and

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

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

$$k = 0.37464 + 1.54226w + 0.26992w^2 \tag{6}$$

where p is the pressure, R is the gas constant, T is the temperature, a and b are EOS constants, v is the molar volume, T_c is the critical temperature, p_c is the critical pressure, T_r is the reduced temperature, $\alpha(T)$ expresses the temperature dependence in the parameter a, and ω is the acentric factor.

To apply the PR equations of state to mixtures, the values of a and b can be determined using the mixing rules (Gasem et al., 1989):

$$a = \sum_i^N \sum_j^N z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{7}$$

$$b = 0.5 \sum_i^N \sum_j^N z_i z_j (1 + D_{ij})(b_i + b_j) \tag{8}$$

where z_k represents the mole fraction of component "k" in a mixture, and N is the number of components in mixture.

In Equations 7 and 8, 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". Interaction parameter values were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared percent deviations in predicted bubble point pressures, i.e.:

$$SS = \sum_{i}^{n} \frac{(p_{exp} - p_{calc})_i^2}{p_{exp}^2} \qquad (9)$$

where n is the number of data points, p_{exp} is the experimental pressure, and p_{cal} is the calculated pressure. Further details of the data reduction technique are given by Gasem (Gasem et al., 1985; Gasem, 1986). The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the PR EOS are presented in Table 4.

Details of the EOS representations of the solubilities are shown in Tables 5. In general, the PR EOS is capable of describing the data with RMS errors within 0.002 in mole fraction when one interaction parameter, C_{ij}, is used for each isotherm. When a single interaction parameter is regressed for a given system for the complete temperature range, the RMS errors are within 0.004. If two interaction parameters, C_{ij} and D_{ij}, are used for each isotherm, the quality of the predictions improves, resulting in RMS errors less than 0.001 in mole fraction; however, the interaction parameters are erratic in their temperature dependence, indicating a high correlation between the parameters C_{ij} and D_{ij}. For that reason, and because a single interaction parameter represents the data adequately, no results for two interaction parameters are presented here.

Our data for hydrogen+n-hexane are compared with the previous measurements of Nicholes et al (1957) at 344 K, 377 K and 411 K in Figure 10. Some disagreement exists between our data and those of Nicholes at 344 K, while at 377 K and 410 K, good agreements are achieved, within 0.002. The comparisons are shown in terms of deviations (δx) of the solubilities (liquid mole fraction nitrogen) from values predicted using the PR EOS, using temperature independent C_{ij} and D_{ij} values determined from the present data.

The figure facilitates a sensitive analysis of differences in data sets. The difference in the deviations between data sets (not the magnitude of the deviation of either set from the reference EOS model) is of interest in these data comparisons. The differences in deviations (δx) between data sets are independent of the reference model employed. That is, for two data sets A and B, at a fixed temperature and pressure: $\delta x_A - \delta x_B = [(x_{expt})_A - (x_{EOS})] - [(x_{expt})_B - (x_{EOS})] = (x_{expt})_A - (x_{exptl})_B$.

No literature data on the solubilities for the other systems are available for comparison.

Conclusions

Measurements have been obtained for the solubilities of hydrogen in n-hexane, carbon monoxide in cyclohexane, and nitrogen in phenanthrene and pyrene at temperatures from 344.3 K to 433.2 K at pressures up to 22.8 MPa. The data are described well by the PR EOS. Interaction parameters for the PR EOS have been obtained for the binary systems studied.

Financial Support

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Legend to Figures

Figure 1.   Solubility data for hydrogen (1) in n-hexane (2) at (♪) 344.3 K, (O) 377.6 K, (
ρ) 410.9 K. Solid symbols are for this study, and empty ones for Nicoles (1957),
δx_1 is the difference between the measured solubility and the value predicted by the
PR equation.
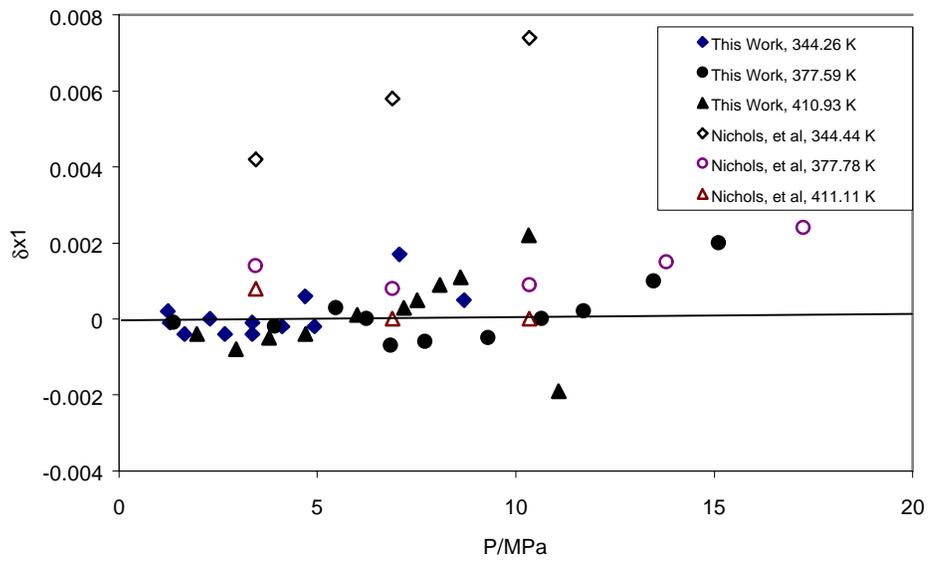
Figure 1.

Table 1. Solubility of Hydrogen in n-Hexane

x_1	p/MPa		x_1	p/MPa
		344.3 K		
0.0105	1.24		0.0289	3.36
0.0107	1.29		0.0352	4.11
0.0136	1.65		0.0408	4.69
0.0197	2.30		0.0420	4.93
0.0226	2.67		0.0612	7.07
0.0286	3.36		0.0727	8.70
		377.6 K		
0.0122	1.38		0.0912	9.31
0.0394	3.93		0.1037	10.65
0.0554	5.46		0.1131	11.71
0.0628	6.24		0.1288	13.48
0.0680	6.84		0.1430	15.11
0.0763	7.71			
		410.9 K		
0.0179	1.97		0.0854	7.52
0.0302	2.95		0.0920	8.09
0.0408	3.78		0.0979	8.61
0.0520	4.70		0.1169	10.32
0.0678	6.00		0.1204	11.08
0.0814	7.18			

Table 2. Solubility of Carbon Monoxide in Cyclohexane

x_1	p/MPa		x_1	p/MPa
		344.3 K		
0.0166	1.59		0.0712	6.73
0.0173	1.68		0.0910	8.67
0.0367	3.50		0.1088	10.66
0.0368	3.45		0.1316	13.03
0.0489	4.68		0.1321	12.83
0.0708	6.81		0.1543	15.22
		377.6 K		
0.0200	1.90		0.0898	7.94
0.0209	1.95		0.0901	8.04
0.0376	3.37		0.1110	9.90
0.0376	3.39		0.1320	11.74
0.0539	4.80		0.1321	11.86
0.0544	4.83		0.1544	13.96
0.0732	6.55			
		410.9 K		
0.019	1.98		0.087	7.18
0.027	2.51		0.100	8.26
0.044	3.86		0.100	8.28
0.044	3.81		0.118	9.68
0.061	5.13		0.135	11.07
0.071	5.92		0.135	11.08
0.071	5.98			

Table 3. Solubility of Nitrogen in Phenanthrene and Pyrene

x_1	p / MPa		x_1	p / MPa
		Phenanthrene		
		383.2 K		
0.0222	10.47		0.0337	16.12
0.0241	11.45		0.0411	19.85
0.0300	14.33		0.0431	20.82
		410.9 K		
0.0254	10.44		0.0452	18.60
0.0298	12.47		0.0491	20.35
0.0404	16.74		0.0517	21.40
		Pyrene		
		433.2 K		
0.0178	7.59		0.0354	15.48
0.0256	11.09		0.0492	21.90
0.0310	13.50		0.0512	22.88

Table 4. Critical Pressures, p_c, Critical Temperatures, T_c, and
Acentric Factors, ω, Used in the PR Equation of State

Component	p_c / MPa	T_c / K	ω	Ref
Carbon Monoxide	3.50	132.9	0.066	Reid et al. (1987)
Hydrogen	1.30	33.2	-0.218	Reid et al. (1987)
Nitrogen	3.39	126.2	0.039	Reid et al. (1987)
Cyclohexane	4.07	553.5	0.212	Reid et al. (1987)
n-Hexane	3.01	507.5	0.299	Reid et al. (1987)
Phenanthrene	3.30	873.2	0.540	API (1979a)
Pyrene	2.60	938.2	0.830[a]	API (1979b)

[a]Turek, 1988

Table 5. PR Equation of State Representations of System Solubility

T/K	C_{12}	Error in Predicted Solute Mole Fraction	
		RMS	|MAX|
Hydrogen in n-Hexane			
344.3	0.3948	0.0006	0.0017
377.6	0.4294	0.0007	0.0020
410.9	0.5419	0.0011	0.0022
344.3, 377.6 and 410.9	0.4321	0.0038	0.0121
Carbon Monoxide in Cyclohexane			
344.3	0.0640	0.0018	0.0045
377.6	0.0505	0.0012	0.0027
410.9	0.0469	0.0014	0.0029
344.3, 377.6 and 410.9	0.0560	0.0019	0.0047
Nitrogen in Phenanthrene			
383.2	0.4050	0.0009	0.0015
410.9	0.4010	0.0013	0.0018
383.2 and 410.9	0.4030	0.0011	0.0020
Nitrogen in Pyrene			
433.2	0.4960	0.0011	0.0018

THE MODIFIED PGR EQUATION OF STATE: ASYMMETRIC MIXTURE PREDICTIONS

K. H. Row
K. A. M. Gasem

School of Chemical Engineering
Oklahoma State University
423 Engineering North
Stillwater, OK 74078

ABSTRACT

The predictive capability of the modified Park-Gasem-Robinson (PGR) equation of state (EOS) for bubble point pressures was evaluated for selected carbon dioxide + normal paraffins, ethane + normal paraffins, and hydrogen + normal paraffins. A set of mixing rules was proposed for the modified EOS to extend its predictive capabilities to mixtures. The predicted bubble point pressures for the ethane + n-paraffin and carbon dioxide + n-paraffin binaries were compared to those of the Peng-Robinson (PR), simplified-perturbed-hard-chain theory (SPHCT) and original PGR equations. The predictive capability of the proposed equation is better than or comparable to the PR, SPHCT and original PGR equations of state for the ethane binaries (absolute-averaged-percent deviation (%AAD) of 1.9) and the carbon dioxide binaries (%AAD of 2.0). For the hydrogen binaries, the modified PGR EOS showed much better performance (%AAD of 1.7) than the original PGR equation and comparable to the PR equation.

INTRODUCTION

Accurate knowledge of equilibrium properties is one of the key factors in most calculations for chemical processes such as separation and purification. Equations of state are widely used for mixtures of nonpolar and slightly polar substances. The present work describes tests of the modified PGR EOS for vapor-liquid equilibrium predictions of selected asymmetric mixtures.

The one-fluid approach, introduced by van der Waals, is the most commonly used method for extending equations of state to nonpolar mixtures (8). This approach assumes that the properties of a mixture are equivalent to those of a hypothetical pure component at the same temperature and pressure, with the characteristic constants properly averaged over the composition (8). The averaging function of the one-fluid mixing approach is quadratic in mole fraction and expressed as

$$A = \sum \sum x_i x_j A_{ij} \tag{1}$$

On the right hand side of Equation (1), A_{ii} is an equation of state constant for pure component i and A_{ij} ($i \neq j$) is obtained by an appropriate combining rule with or without binary interaction parameters. The standard method for introducing a binary interaction parameter, C_{ij}, into the mixing rule is to assume a corrected geometric mean rule for the energetic interaction parameter such as 'a' in the cubic equation of state

$$a_{ij} \equiv \left(a_i a_j\right)^{1/2} \left(1 - C_{ij}\right) \tag{2}$$

This classical one-fluid method is very simple and reliable, primarily for nonpolar mixtures.

The van der Waals mixing rules fail to give satisfactory results for complex mixtures at extreme conditions of pressure or density; this has led to the development of new mixing rules. Several researchers propose mixing rules used in conjunction with a "shape factor" approach. Lee et al. (10) extended the van der Waals one-fluid mixing rule by using an additional corresponding-states parameter. Johnson and Rowley (11) employed mixing rules based on a three-parameter principle of corresponding states (PCS) proposed by Wong et al. (12) for their extension of the Lee-Kesler method (ELK) to polar mixtures. The mixing rules in explicit corresponding-states format require the use of one binary parameter, and the computation time differs according to the reference equation of state. Applicability of these mixing rules is limited primarily to nonpolar and weakly polar mixtures (8-10).

Huron and Vidal claimed that any mixing model that gives a finite excess Gibbs free energy at infinite pressure can be used to construct a mixing rule (13) for the SRK equation. Their mixing rules are

$$\langle b \rangle = \sum_i z_i b_{ii}$$

(3)

and

$$\langle a \rangle = \langle b \rangle \left(\sum_i z_i \frac{a_{ii}}{b_{ii}} - \frac{G^{ex}(T, x_i)}{C^*} \right)$$

(4)

where values of C* for SRK and PR are 0.6931 and -0.6232, respectively. Since Huron and Vidal developed the basic idea of excess Gibbs free energy mixing rules, similar models have been proposed. Vidal derived the infinite-pressure limit of the excess Gibbs energy calculated from the Redlich-Kwong equation with quadratic mixing rules (14). The local composition models of Wilson (5) and NRTL (6) are typical examples of the excess Gibbs energy models. Wong and Sandler introduced a similar mixing rule (Wong-Sandler mixing rule) that is also based on the idea of equating free energies at infinite pressure (5). However, the Wang-Sandler mixing rule makes use of the excess Helmholtz free energy of mixing rather than the Gibbs free energy. This mixing rule is simpler than the mixing rules that use the excess Gibbs free energy.

Mansoori and Leland (16) introduced density-dependent mixing rules. They postulated that for mixtures of molecules differing in size, better results could be obtained by allowing the mixture parameters to be a function of composition and density.

The inaccuracy of an equation of state in representing equilibrium properties of mixtures may be due to inherent deficiencies in the equation and/or the mixing rules applied. Normally, binary interaction parameters are required to improve the predictive capability of an equation of state. These binary interaction parameters (characterizing interaction between different species in the mixture) are commonly obtained from a small amount of experimental data. The parameters thus obtained can be generalized to expand the capability of the equation of state.

In the present work, the one-fluid mixing rules of van der Waals with one binary interaction parameter are introduced to improve the VLE prediction capability. These interaction parameters are evaluated for ethane, carbon dioxide and hydrogen binary mixtures with n-paraffins.

THE MODIFIED PGR EOS

The pressure explicit form of the modified PGR EOS given earlier [27] may be written as

$$\frac{pv}{RT} = 1 + c\left(\frac{\beta_1 \tau}{v_r - \beta_2 \tau} - \frac{Z_M Y v_r}{v_r^2 + uv_r + w} - \frac{Q_1 Z_M Y}{v_r + Q_2}\right) \qquad (5)$$

where

$$Y = \exp(F_t) - 1 \qquad (6)$$

$$F_t = \omega_1\left(\frac{1}{2\widetilde{T}}\right)^{1/2} + \omega_2\left(\frac{1}{2\widetilde{T}}\right) + \omega_3\left(\frac{1}{2\widetilde{T}}\right)^{3/2} + \omega_4\left(\frac{1}{2\widetilde{T}}\right)^2 \qquad (7)$$

The universal constants in this equation are shown in Table I. These EOS constants, including u, w, Z_M, Q_1, Q_2 and ω_1 - ω_4 are regressed from pure fluid experimental data as described in our companion study [27]. The repulsive-term constants are as reported by Elliot and coworkers ($\beta_1 = 4$, $\beta_2 = 1.9$) [28].

To extend the PGR EOS to mixtures, the mixing rules employed by Park (4) are used in this study after appropriate modification is made for the temperature-dependent part in the attractive term. Similar to the SPHCT EOS, the geometric average for the energy parameter (ε_{ij}) and the arithmetic average for the volume parameter (σ_{ij}) were selected for use.

$$\langle cv^* \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j c_i v_{ji}^* \qquad (8)$$

$$\langle v^* \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j v_{ij}^* \qquad (9)$$

where

$$v_{ij}^* = \frac{s_i \sigma_{ij}^3}{\sqrt{2}} \qquad (10)$$

and z_i and z_j are the mole fractions of component i and j, respectively. When the employed mixing rules are applied to the modified temperature-dependent term of Equation (6), the resulting expression is

$$\langle cYv^* \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i z_j c_i \left(\exp(F_t)_{ij} - 1 \right) v_{ji}^* \qquad (11)$$

where

$$(F_t)_{ij} = \omega_1 \left(\frac{T_{ij}^*}{2T} \right)^{1/2} + \omega_2 \left(\frac{T_{ij}^*}{2T} \right) + \omega_3 \left(\frac{T_{ij}^*}{2T} \right)^{3/2} + \omega_4 \left(\frac{T_{ij}^*}{2T} \right)^2 \qquad (12)$$

$$T_{ij}^* = \frac{\varepsilon_{ij} q_i}{c_i k} \qquad (13)$$

$$\sigma_{ij} = \frac{1}{2} \left(\sigma_{ii} + \sigma_{jj} \right) \left(1 + D_{ij} \right) \qquad (14)$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \left(1 - C_{ij} \right) \qquad (15)$$

The properties in angular brackets, $\langle \ \rangle$, are for the mixture. The D_{ij} and C_{ij} in Equations (14) and (15) are the co-volume and energetic interaction parameters, respectively. In this study, the co-volume interaction parameter was set to zero and the energetic interaction parameter was the only concern.

According to the expressions shown above, the modified version of the PGR EOS for mixture systems becomes

$$Z = 1 + \frac{\beta_1 \tau \langle cv^* \rangle}{v - \beta_2 \tau \langle v^* \rangle} - \frac{Z_M \langle cYv^* \rangle v}{v^2 + u \langle v^* \rangle v + w \langle v^* \rangle^2} - \frac{Q_1 Z_M \langle cYv^* \rangle}{v + Q_2 \langle v^* \rangle} \qquad (16)$$

When the hard core radii, σ_{ij}, in Equation (14) are the same and the co-volume interaction parameter, D_{ij}, is set to zero for all components in a mixture, v_{ij}^* may be expressed as

$$v_{ij}^* = v_{ii}^*$$

$$(17)$$

$$v_{ji}^* = v_{jj}^*$$

For ethane binary mixtures, Equation (17) is applied in calculating v_{ij}^*. For carbon dioxide binary systems, Park (4) performed preliminary calculations of the hard sphere radius, σ, of carbon dioxide and normal paraffins and found that they are almost equivalent. Thus, Equation (17) is also used for carbon dioxide + normal paraffins binary systems. Due to a scarcity of information about the hard sphere radius for hydrogen, the same assumption, which was used by Park, is used in this work. 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 (17). These assumptions simplify the mixture version of the EOS. Another reason for this simplification is to avoid the use of multiple interaction parameters.

As suggested in several previous works (1-4), a constant characteristic energy term in Equation (12) is used throughout the evaluation of the modified EOS for the binary mixtures considered in this study. As a consequence, the expression for T_{ij}^* can be written as

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

$$(18)$$

$$T_{ji}^* = T_{jj}^*\left(1 - C_{ij}\right)$$

THE BINARY MIXTURE DATABASE

The databases used in evaluating the modified EOS for mixtures are the same as those used by Park (4) for ethane, carbon dioxide and hydrogen binaries with n-paraffins. The ethane + n-paraffin binary database consists of bubble point pressures (p at fixed x) or, equivalently, ethane solubilities (x at fixed p) at different temperatures. The database covers solvent molecular sizes 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 the evaluation of 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. The database for hydrogen + n-paraffins covers solvent molecular size variations from n-butane to n-hexatriacontane, temperatures from 323.2 to 573.3 K and pressures up to 173.9 bar. Ranges of temperature, pressure and mole fraction considered in the ethane, carbon dioxide and hydrogen binary mixture database are shown in Tables II through IV.

RESULTS AND DISCUSSION

Bubble point pressure predictions were performed at various temperatures and liquid phase compositions using the modified PGR EOS. Results were generated for three cases involving the use of interaction parameters, as described in Table V. Case 1 with no interaction parameter ($C_{ij} = 0$) represents the raw predictive ability of the equation to predict bubble point pressures. Case 2 is the most commonly used representation of the interaction parameter in literature, in which a separate C_{ij} is used for each binary mixture system. In Case 3, a separate C_{ij} is used for each isotherm of each binary system. Similar evaluations were conducted using the PR, SPHCT and original PGR equations for ethane and carbon dioxide binary mixtures. For hydrogen binaries, evaluations were undertaken only with the original PGR equation and the PR equation for Cases 2 and 3. The SPHCT equation was not evaluated for hydrogen binaries because pure component parameters for the equation are not available.

The following objective function was used in all model evaluations to obtain the optimum interaction parameters:

$$SS = \sum_{i=1}^{N} \left(\frac{p_{calc} - p_{exp}}{p_{exp}} \right)_i^2 \tag{22}$$

where p_{exp} is the experimental bubble point pressure and p_{calc} is the calculated bubble point pressure. The regressed parameters through the above objective function leads to the minimum value of average absolute percentage deviation (%AAD) in bubble point pressure. The same regression and calculation methods used for the original PGR EOS evaluation were applied in this study. Details on the regression technique and bubble point calculation method used in this work are described by Gasem (24).

The required fugacity coefficient expression for component i in a mixture was derived for the modified PGR EOS

$$\ln\phi_i = -\frac{\beta_1}{\beta_2}\left(\frac{1}{\langle v^*\rangle}\frac{1}{n}\frac{\partial n^2\langle cv^*\rangle}{\partial n_i} - \frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\ln\frac{v_r - \beta_2\tau}{v_r}$$

$$+\left(\beta_1\tau\frac{\langle cv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{1}{v_r - \beta_2\tau} - \left(\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{1}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Z_M v_r}{v_r^2 + uv_r + w}$$

$$+\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_1} - \frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{2}{\sqrt{4w - u^2}}\left(\tan^{-1}\frac{2v_r + u}{\sqrt{4w - u^2}} - \frac{\pi}{2}\right)$$

$$-\left(\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle cYv^*\rangle}{\partial n_1} - \frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{Q_2}\ln\frac{v_r + Q_2}{v_r}$$

$$-\left(\frac{\langle cYv^*\rangle}{\langle v^*\rangle}\frac{Z_M}{\langle v^*\rangle}\frac{\partial n\langle v^*\rangle}{\partial n_i}\right)\frac{Q_1}{v_r + Q_2} - \ln Z \tag{20}$$

where

$$\frac{\partial n\langle cYv^*\rangle}{\partial n_i} = \sum_{j=1}^{N}z_j\left(c_i Y_{ij}v_{ji}^* + c_j Y_{ji}v_{ij}^*\right) - \langle cYv^*\rangle \tag{21}$$

$$\frac{\partial n\langle v^*\rangle}{\partial n_i} = \sum_{j=1}^{N}z_j\left(v_{ij}^* + v_{ji}^*\right) - \langle v^*\rangle \tag{22}$$

and

$$Y_{ij} = \exp\left[\omega_1\left(\frac{T_{ij}^*}{2T}\right)^{1/2} + \omega_2\left(\frac{T_{ij}^*}{2T}\right) + \omega_3\left(\frac{T_{ij}^*}{2T}\right)^{3/2} + \omega_4\left(\frac{T_{ij}^*}{2T}\right)^2\right] - 1 \tag{23}$$

Detailed derivation of the fugacity coefficient expression for components in a mixture is given elsewhere [4].

Results for the modified PGR, the original PGR, the original SPHCT and the PR equations of state for the three cases studied are discussed below.

Ethane + n-Paraffin Systems

Bubble point pressure calculations for the three evaluation cases described above were performed for the selected equations of state. A summary of the results is presented in Table VI. The modified version of the PGR equation showed the best results in Case 1 (root-mean-squared error (RSME) of 1.55 bar and %AAD of 5.0) while the SPHCT equation was the worst (RSME of 4.83 bar and %AAD of 16.6). This implies that the modified PGR 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 and 3), the modified PGR equation was still the best among the equations considered. When the interaction parameters are considered to be independent of system temperature (Case 2), the prediction capability of the modified equation exceed that of the other equations (RSME of 1.19 bar and %AAD of 2.8). In Case 3, the modified equation was shown to be comparable to the original SPHCT equation, which showed the best results. The quality of fit for Case 3 is 4.1%, 1.6%, 2.8% and 1.9% for the PR, the SPHCT, the original PGR and the modified PGR equations, respectively. The modified PGR equation performed much better than the PR and original PGR equations.

Figure 1 shows the effect of the solvent molecular size on the optimum interaction parameter for Case 2. For systems whose solvents are lighter than C_{20}, the optimum interaction parameters obtained from the modified PGR equation are close to the arithmetic mean of those from the SPHCT and the original PGR equations. Both the original and modified PGR equations require smaller values for the interaction parameters than the original SPHCT equations. The figure indicates that both the SPHCT and modified PGR equations result in fairly constant interaction parameters with increasing carbon number compared to those of the PR EOS. This typical of an EOS based on segment-segment interactions (3).

The effect of temperature on the optimum interaction parameters is shown in Figures 2 to 5, in which the C_{ij}'s of Case 3 are plotted for the modified PGR equation, the original PGR equation, the SPHCT equation and the PR equation, respectively. As can be seen from these figures, the modified PGR equation has interaction parameters that are less sensitive to temperature than the other equations selected. This weak temperature dependence of the interaction parameters may indicate the adequacy of the mixing rules used. The C_{ij}'s of the original and modified PGR equations behave like those of the cubic EOS. The values decrease as the temperature increases while the interaction parameters

of the SPHCT equation exhibit the opposite trend. Comparison of Figures 2 and 15 indicate that interaction parameters from both equations exhibit similar trends. Also, a compactness in the parameter dispersion is observed.

Carbon Dioxide + n-Paraffin Binaries

A summary of the bubble point pressure calculations of carbon dioxide + n-paraffin binary mixtures for three cases described in Table V is presented in Table VII. For the zero interaction parameter case (Case 1), the modified PGR equation showed the best results among the equations considered. Convergence problems were observed with the SPHCT equation for the high-pressure data points. This is because the SPHCT EOS was derived for nonpolar compounds. The original PGR equation performed the worst for all cases. The original PGR equation and the modified PGR equation were less sensitive to the introduction of the interaction parameters than the PR equation and the SPHCT equation, which showed great improvements in the RSME and %AAD. Once the interaction parameters were introduced, both the original and modified PGR equations gave larger errors than the PR and SPHCT equations.

The relatively poor predictions of the modified PGR equations for Case 2 may be caused by the character of the partition function of the PGR and modified PGR equations. The partition function of the PGR EOS did not explicitly account for polar effects (4). If the polar effects were considered in the partition function for the segment-segment interaction models, better performances of the model would be expected. Assumptions used in the simple one-fluid mixing rules may be another factor for these poor results. As in the case of the original PGR and SPHCT equations, a common value of the hard core radius (σ) and the square-well potential depth (ε) are used for all compounds. Actually, the hard core radius for the carbon dioxide molecule is different from that of a segment in normal paraffins. Similarly, the attractive energy between the carbon dioxide molecule and a segment in normal paraffins is expected to be different. This assumption may limit the capability of the equation.

For Case 3, the predictive capability of the modified PGR equation (%AAD of 2.0) is almost identical to that of the SPHCT (%AAD of 1.9) and original PGR (%AAD of 2.1) equations. However, the RMSE of the modified PGR equation (RMSE of 0.86 bar) was much smaller than that of the other equations considered (RMSE of 2.17 bar, 2.10 bar and 2.36 bar for the PR, SPHCT and PGR equations, respectively), which implies that the errors of the modified equation are more evenly distributed throughout the isotherms.

For all equations of state studied, temperature-dependent interaction parameters (Case 3) are needed to obtain accurate predictions.

Figure 6 shows the effect of carbon number on the optimum interaction parameter of Case 2 for all the equations considered. As with the ethane systems, the modified PGR equation requires smaller interaction parameters than the PR, SPHCT, and original PGR equations. The interaction parameter values of the modified PGR and SPHCT equations are less scattered than those of the other equations. The parameter values for the modified PGR and SPHCT equations are relatively constant (0.02 and 0.06, respectively) with increase in solvent molecular size. This makes extrapolations to heavier molecular weight compounds for the CO_2 systems more reliable.

The effect of temperature on the interaction parameters can be seen in Figures 7 to 10 from Case 3. Unlike the ethane + n-paraffin systems, Figure 7 shows a very strong temperature dependence for the binaries containing heavy components. The figures indicate that the interaction parameters are more sensitive to temperature than to the solvent molecular weight. The magnitude of the temperature dependence for the modified PGR equation is greater than that of the SPHCT equation and less than the PR and original PGR equations. This observation matches the results for Case 3 in Table VII.

Hydrogen + n-Paraffin Binaries

A summary of the bubble point pressure calculations of hydrogen + n-paraffin binary mixtures for selected cases are presented in Table VIII. Since all equations showed convergence problems for the zero interaction parameter case (Case 1), evaluations and comparisons were made only for Cases 2 and 3.

The modified PGR equation performed worse than the PR equation in Case 2 (%AAD of 5.8 and 4.5, respectively) while the RSME values of the modified PGR were lower than that of the PR equation (RSME of 4.06 bar and 5.23 bar, respectively). The original PGR equation showed considerable errors in Case 2. The modified PGR equation appeared preferable to the PR and original PGR equations when temperature-dependent interaction parameters were introduced (%AAD of 1.7, 2.0 and 2.7 and RSME of 1.09 bar, 3.22 bar and 3.35 bar, respectively). Overall, the modified PGR equation is the most accurate among the equations considered in predicting bubble point pressures.

Figure 11 shows the effect of carbon number on the optimum interaction parameter of Case 2 for the equations considered. Unlike the ethane and carbon dioxide

systems, the modified PGR equation does not contain smaller interaction parameters than the PR and original PGR equations. Apparently, except for the n-C$_4$ system, the interaction parameters of the original and modified PGR equation are almost equivalent in magnitude with opposite signs. Overall, the interaction parameter values for the selected equations are less sensitive to the carbon number and may be treated as constants. This makes extrapolations to heavier molecular weight compounds for the H$_2$ systems more reliable.

The effects of temperature on the optimum interaction parameter are shown in Figures 12 to 14 for Case 3. Both the modified and original PGR equations have interaction parameters that are less sensitive to molecular weight of the solute than the PR equation. The interaction parameters for the modified PGR equation showed less variation with temperature than that of the original PGR equation, which may imply that the simple one-fluid mixing rules were sufficient to describe the characteristics of binary mixture systems. Also, the behaviors of the C$_{ij}$ values were opposite to those of the original PGR equation. This observation was similar to that obtained from Figure 11. The C$_{ij}$'s from the PR equation show more of scatter than the other equations of state.

Since hydrogen is a quantum gas, its molecular potential energy is expected to be significantly different from that of other compounds. Thus, the phase behavior of systems involving hydrogen is different from other binary mixtures such as methane, ethane, carbon dioxide with n-paraffins, and the characteristics of the interaction parameters showed noticeable differences. Nevertheless, modified equation was more accurate than the other equations, for systems containing hydrogen.

CONCLUSIONS AND RECOMMENDATIONS

The modified Park-Gasem-Robinson (PGR) EOS was evaluated using binary mixture systems of ethane, carbon dioxide and hydrogen with n-paraffins. The systems contain simple mixtures such as ethane + n-butane and asymmetric mixtures such as ethane + n-tetratetracontane systems. Simple van der Waals one-fluid mixing rules with one interaction parameter, C$_{ij}$, were used in the evaluation. Throughout the evaluations, the modified PGR equation predicted bubble point pressures within 2 %AAD with one temperature dependent interaction parameter (Case 3).

For ethane + n-paraffins and carbon dioxide + n-paraffin systems, the bubble point pressure prediction results of the modified PGR equation were compared to those of the PR, SPHCT and original PGR equations. With no interaction parameter, the modified

PGR equation showed the best results among the equations tested. For ethane binaries, the segment-segment interaction models such as the SPHCT, original PGR and modified PGR equations showed better performance than the PR equation in Case 3. The modified PGR equation showed better results than the SPHCT equation in Case 2. For carbon dioxide binaries, the modified equation showed worse performance than the PR and SPHCT equations in Case 2. In Case 3, the modified PGR equation showed comparable results to the SPHCT equation.

For hydrogen + n-paraffin systems, the bubble point pressure predictions of the modified PGR equation were compared to those of the PR and original SPHCT equations. In Case 2, the modified PGR equation gave worse predictions than the PR equation. However, in Case 3, the modified equation performed better than the PR and original PGR equations.

The effects of the carbon number and system temperature on the interaction parameters were studied. The interaction parameters of the modified equation showed less sensitivity to the carbon number for each binary system. The modified equation also showed weak temperature dependence, resulting in more flexibility. The modified PGR equation has less scattered interaction parameters with the carbon number and, thus, is more suitable for extrapolation.

NOMENCLATURE

a	Energy parameter in the SRK or PR equation of state
A	EOS constant
b	Molecular size parameter in the SRK or PR equation of state
c	Degree of freedom parameter
C_{ij}, D_{ij}	Binary interaction parameters
F	Function defined by Equation (7)
G	Molar Gibbs free energy
n	Number of data points; number of moles
N	Number of components in mixture; total number of molecules
p	Pressure
Q	EOS constant
s	Number of segments
SS	Objective function
T	Temperature
T*	Characteristic temperature parameter
u	Potential energy between molecules; equation of state constant
v	Molar volume
v*	Characteristic volume parameter
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
Z_M	Constant

Greek letters

β_1, β_2 Constants in repulsive term of the new equation of state

ε Square-well potential energy between segments

σ Radius of hard sphere

τ Geometrical constant (0.74048)

ω Acentric factor

Subscripts

c   Critical state

calc   Calculated

exp   Experimental

f   Free

i, j   Component or data point identification number

l   Liquid

min   Minimum

r   Reduced property

v   Vapor

Superscripts

ex   Excess

o   Ideal gas

*   Characteristic parameter

~   Reduced temperature

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TABLE I

UNIVERSAL CONSTANTS FOR THE MODIFIED
PGR EQUATION OF STATE

Constant	Value
τ	0.74048
u	-2.8969
w	2.6944
Q_1	10.5121
Q_2	1.0226
Z_M	1.4264
ω_1	0.076354
ω_2	2.0124
ω_3	-0.22322
ω_4	-0.70301

TABLE II

ETHANE + N-PARAFFIN SYSTEMS USED IN MODIFIED

EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Reference (# of pts)
n-C_4	338.7 - 394.3	32.4 - 50.3	0.118 - 0.753	17 (19)
n-C_8	323.2 - 373.2	4.1 - 52.7	0.047 - 0.863	18 (33)
n-C_{10}	310.9 - 410.9	4.2 - 82.4	0.105 - 0.638	19 (30)
n-C_{20}	323.2 - 423.2	5.0 - 76.9	0.118 - 0.653	20 (19)
n-C_{28}	348.2 - 423.2	5.6 - 51.8	0.102 - 0.520	21 (24)
n-C_{36}	373.2 - 423.2	3.7 - 47.6	0.087 - 0.531	20 (13)
n-C_{44}	373.2 - 423.2	3.9 - 31.7	0.099 - 0.516	20 (16)

TABLE III

CARBON DIOXIDE + N-PARAFFIN SYSTEMS USED IN MODIFIED

EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Reference (# of pts)
$n\text{-}C_4$	310.9 - 410.9	5.5 - 75.4	0.002 - 0.908	22 (52)
$n\text{-}C_{10}$	310.9 - 510.9	3.5 - 172.4	0.045 - 0.864	23 (70)
$n\text{-}C_{20}$	323.2 - 373.2	6.2 - 67.6	0.073 - 0.501	24 (22)
$n\text{-}C_{28}$	323.2 - 423.2	8.1 - 96.0	0.070 - 0.617	24 (23)
$n\text{-}C_{36}$	373.2 - 423.2	5.2 - 86.5	0.062 - 0.502	24 (18)
$n\text{-}C_{44}$	373.2 - 423.2	5.8 - 70.8	0.082 - 0.502	24 (14)

TABLE IV

HYDROGEN + N-PARAFFIN SYSTEMS USED IN MODIFIED

EQUATION OF STATE EVALUATIONS

Solvent	Temperature Range, K	Pressure Range, bar	H_2 Mole Fraction Range	Reference (# of pts)
n-C_4	327.7 - 394.3	27.78 - 168.8	0.0190 - 0.2660	25 (60)
n-C_{10}	344.3 - 423.2	37.07 - 173.9	0.0369 - 0.1288	4 (21)
n-C_{20}	323.2 - 573.3	9.940 - 118.2	0.0113 - 0.1289	4, 26 (37)
n-C_{28}	348.2 - 573.2	9.859 - 131.0	0.0206 - 0.1728	4, 26 (35)
n-C_{36}	373.2 - 573.2	10.22 - 167.5	0.0154 - 0.2272	4, 26 (27)

TABLE V

CASE STUDIES USED IN EVALUATING THE
MODIFIED PGR EQUATION OF STATE

Case	Interaction Parameter	Description
1	$C_{ij} = 0$	A simple mixing rule with no interaction parameter.
2	$C_{ij}(CN^*)$	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.
3	$C_{ij}(CN^*, T)$	A separate value of C_{ij} is determined for each binary mixture at each temperature. The value of C_{ij} is dependent only on the normal paraffin carbon number and system temperature for a given solute.

* Carbon number of the specific n-paraffin

TABLE VI

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

Case Number	Peng-Robinson		SPHCT		Original PGR		This Work	
	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	2.1	9.5	4.8	16.6	3.4	7.7	1.6	5.0
2	1.8	4.4	1.3	3.2	2.5	5.1	1.2	2.8
3	1.8	4.1	0.8	1.6	1.3	2.8	0.7	1.9

TABLE VII

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

Case Number	Peng-Robinson		SPHCT		Original PGR		This Work	
	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
1	13.5	19.9	14.8*	26.8*	8.8	17.9	7.9	14.3
2	2.8	3.3	2.7	4.6	6.0	10.0	3.3	7.0
3	2.2	2.5	2.1	1.9	2.4	2.1	0.9	2.0

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

TABLE VIII

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

Case Number	Peng-Robinson		Original PGR		This Work	
	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
2	5.2	4.5	30.3	33.2	4.06	5.8
3	3.2	2.0	3.35	2.7	1.09	1.7

TABLE VIII

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

Case Number	Peng-Robinson		Original PGR		This Work	
	RMSE (bar)	%AAD	RMSE (bar)	%AAD	RMSE (bar)	%AAD
2	5.2	4.5	30.3	33.2	4.06	5.8
3	3.2	2.0	3.35	2.7	1.09	1.7
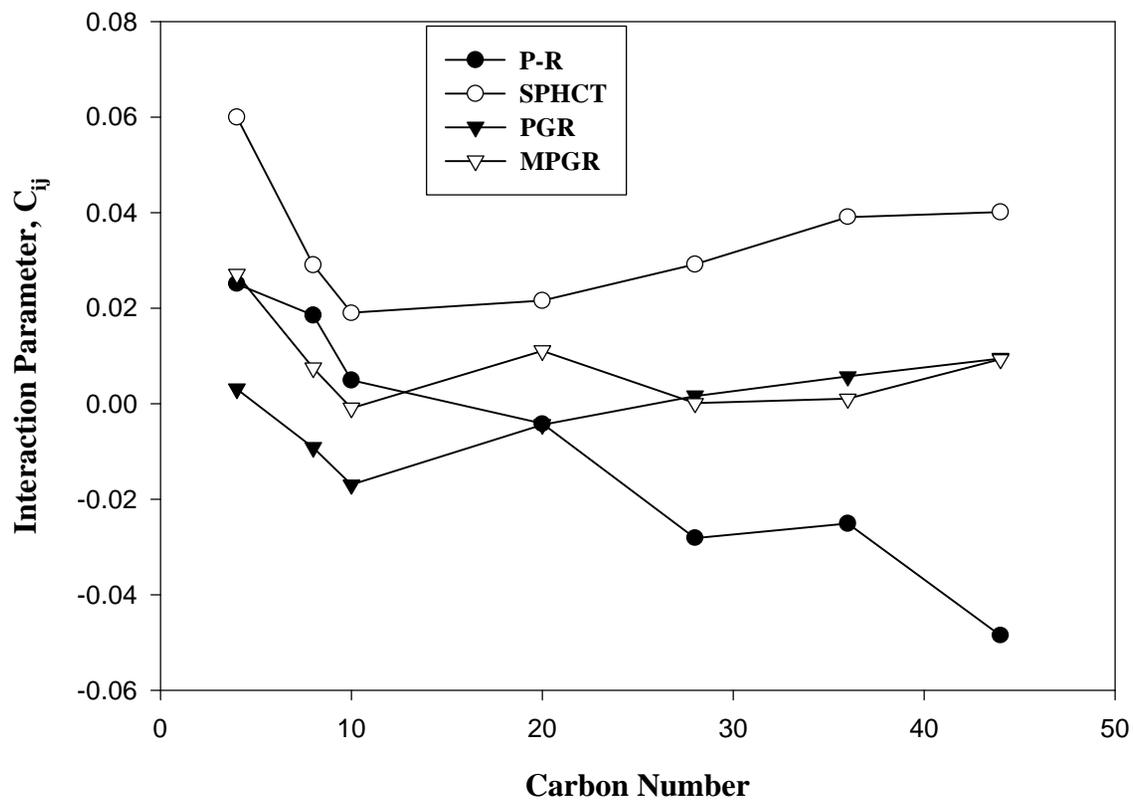
Figure 1.   Equation of State Interaction Parameters, C_{ij}, for Ethane + n-Paraffin Systems.
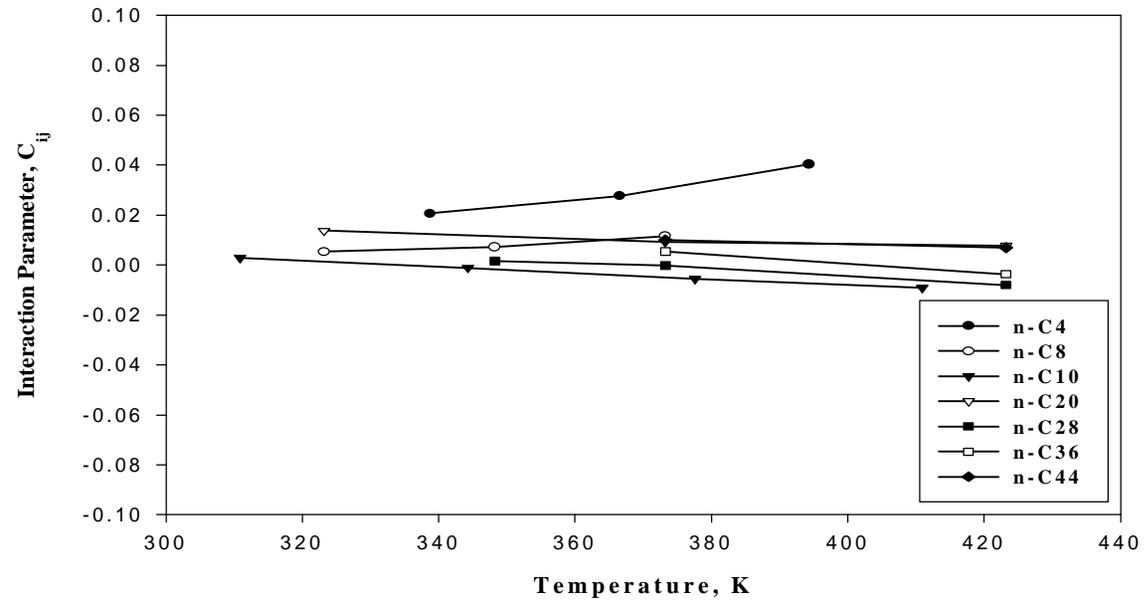
Figure 2.   Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.
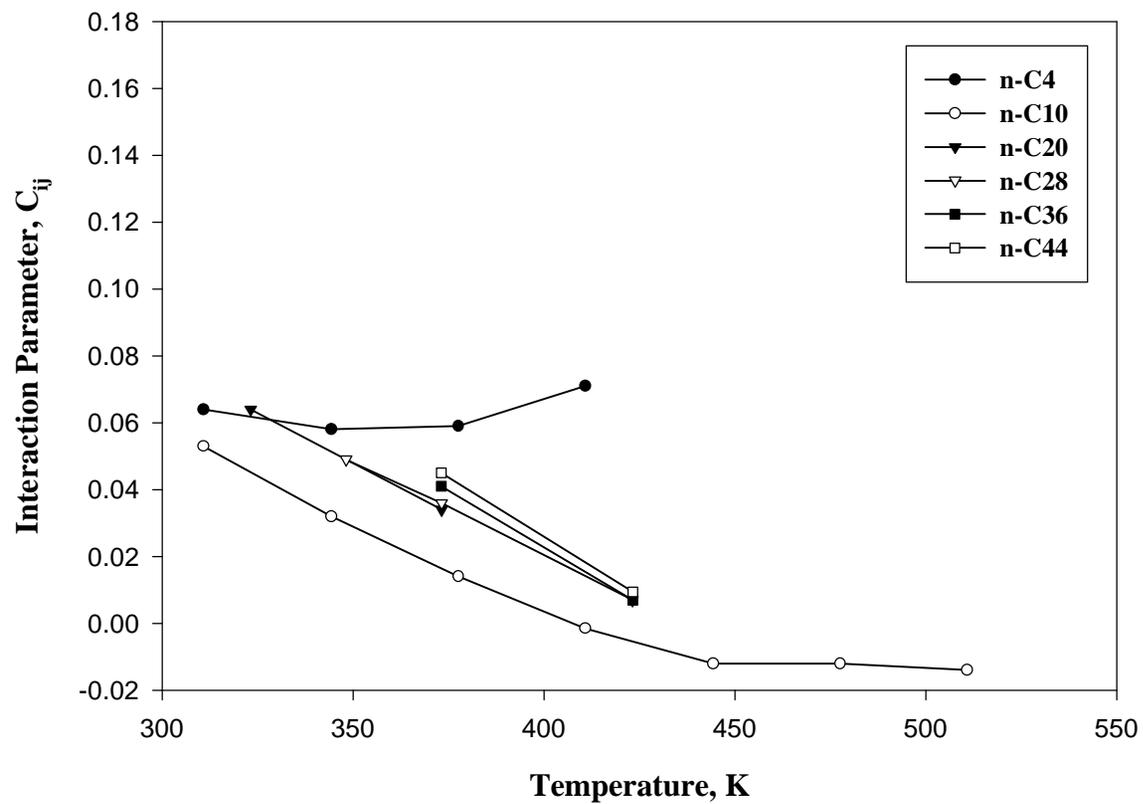
Figure 3.   PGR equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.
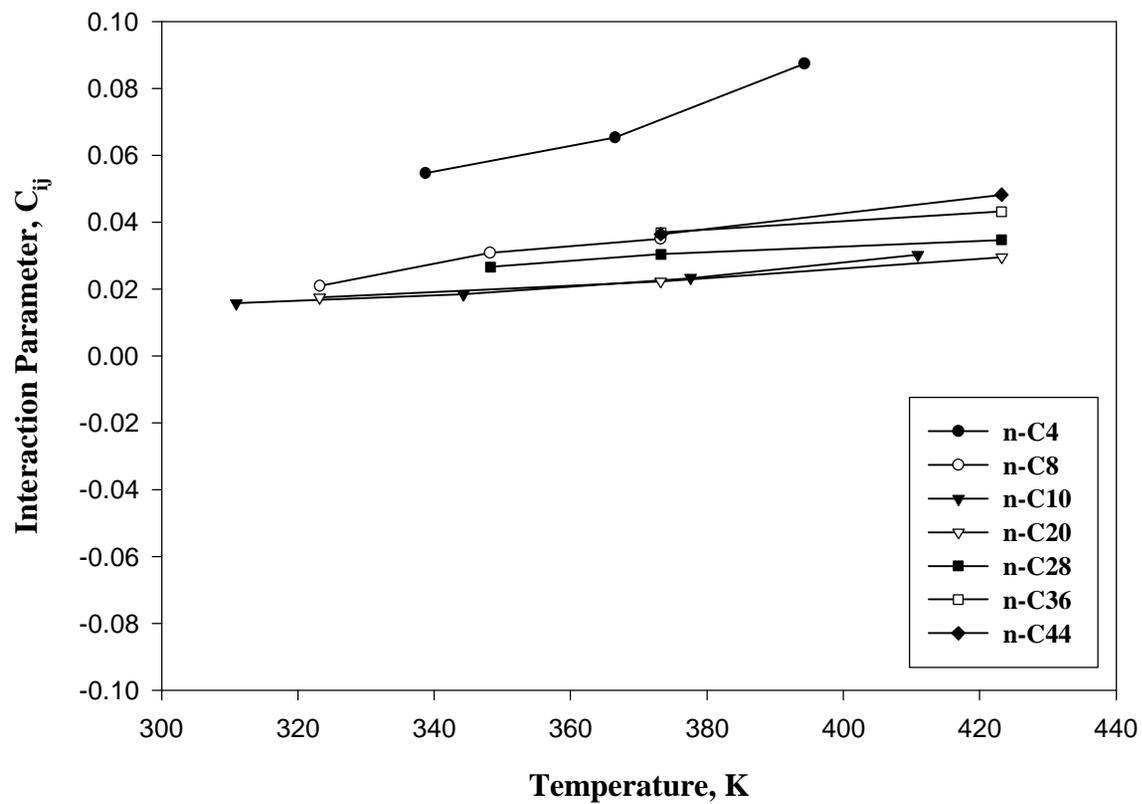
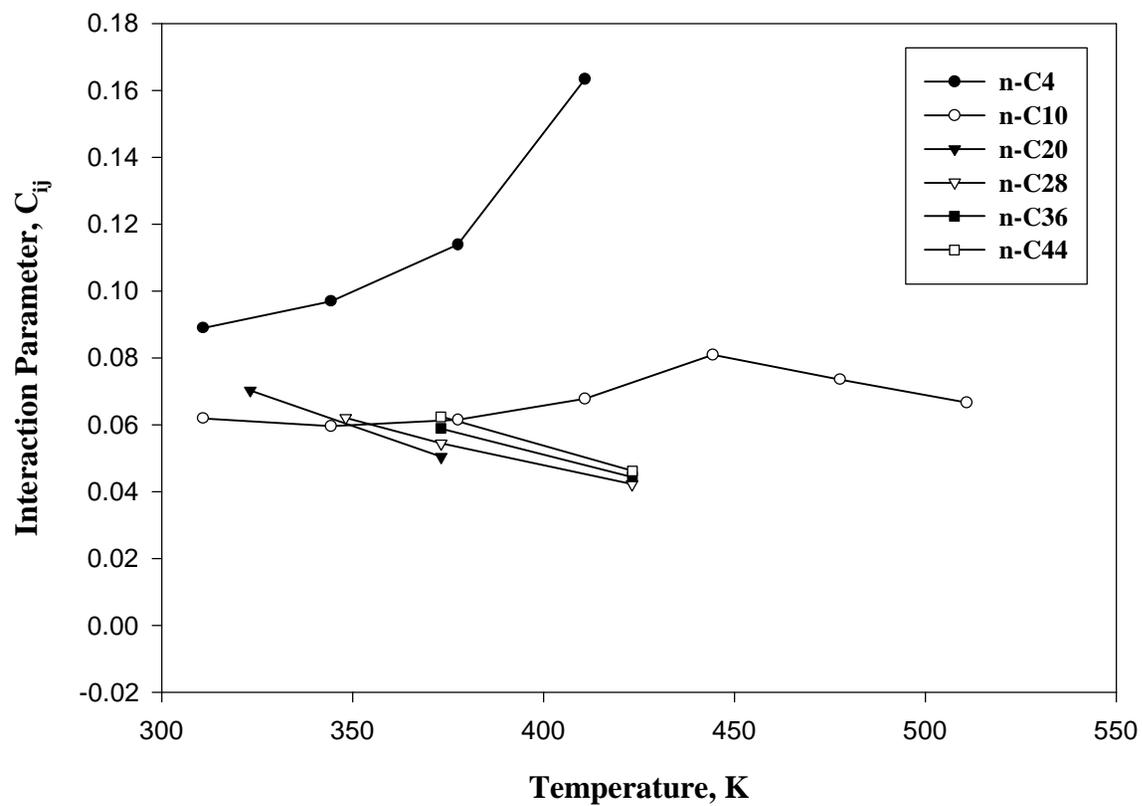Figure 4.   SPHCT Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Ethane + n-Paraffin Systems.
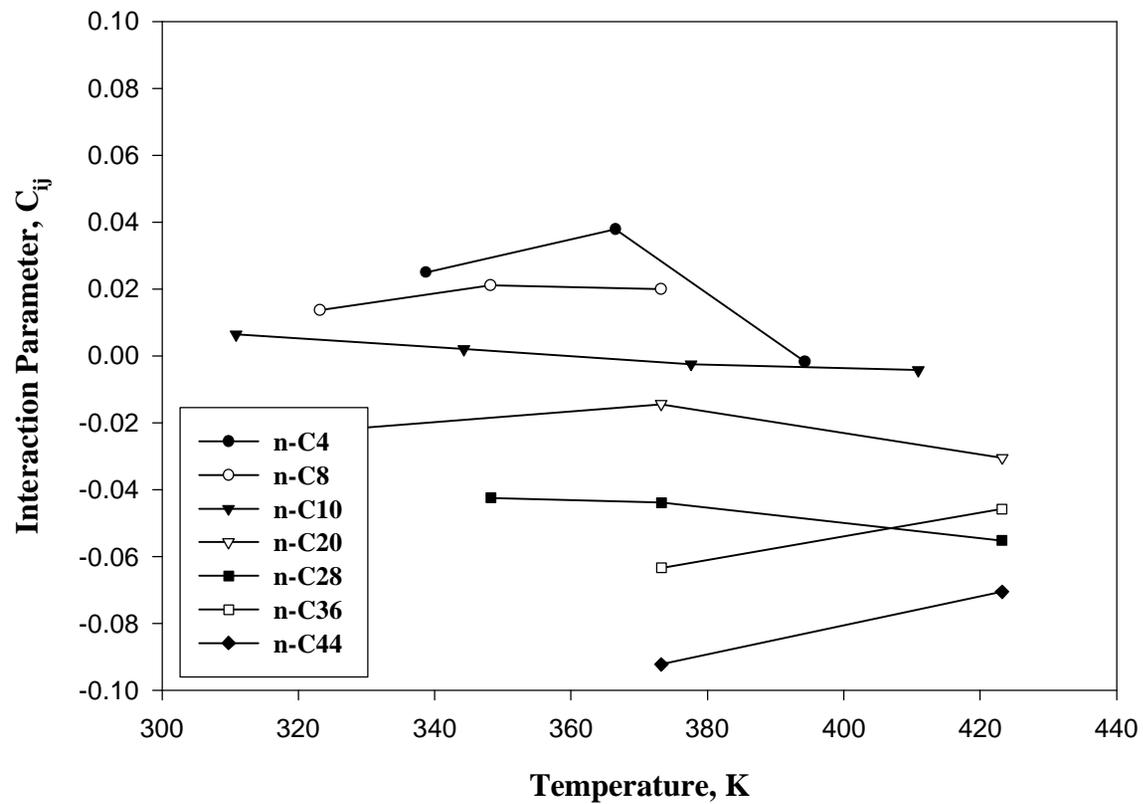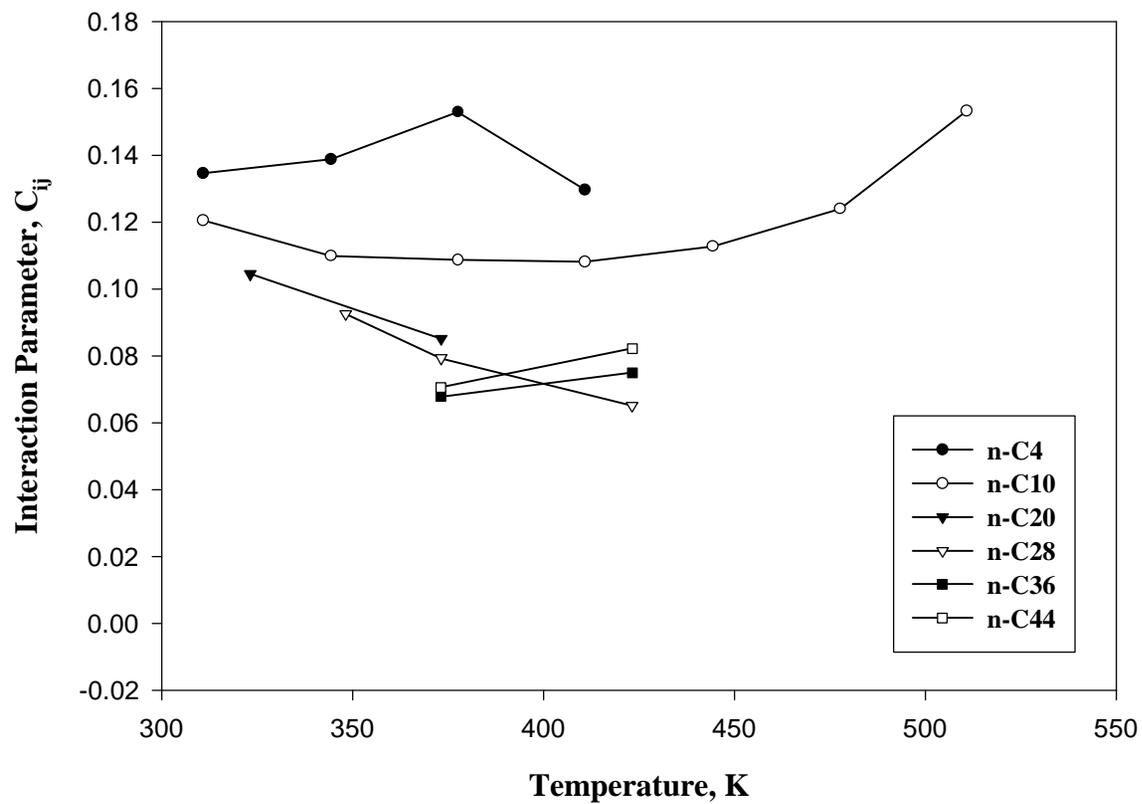
Figure 5.   PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence
for Ethane + n-Paraffin Systems.
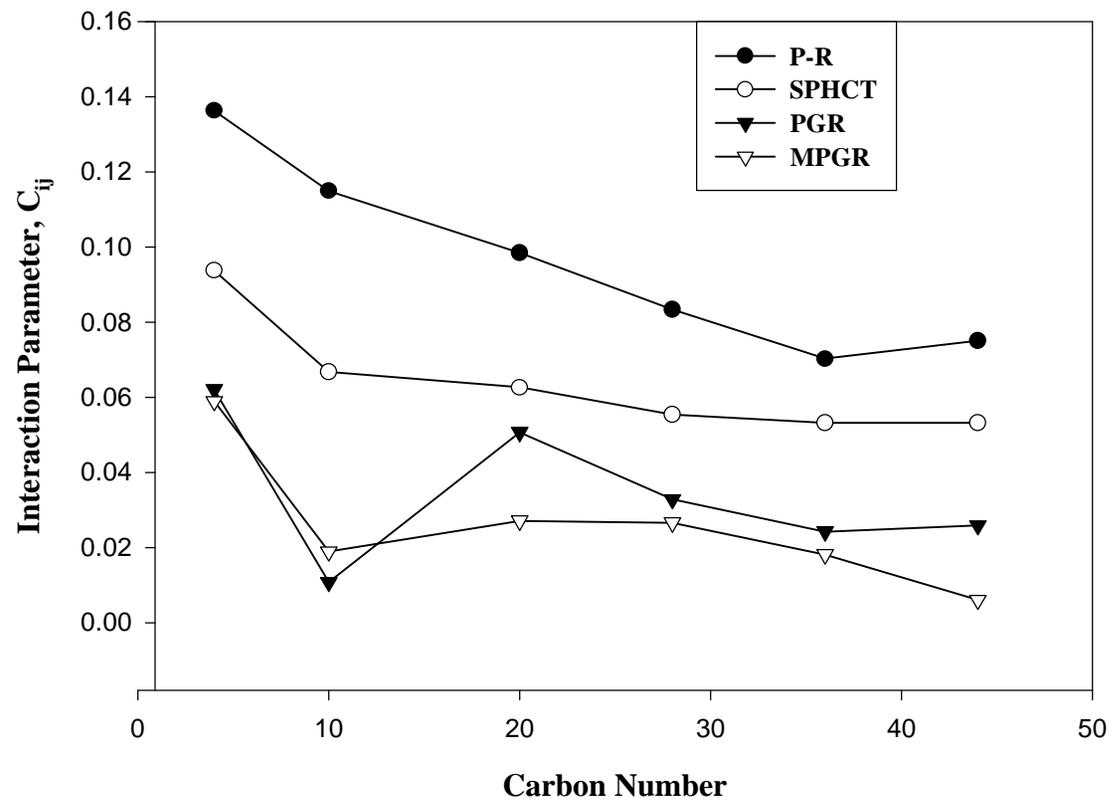
Figure 6.   Equation of State Interaction Parameters, C_{ij}, for the Carbon Dioxide + n-Paraffin Systems.
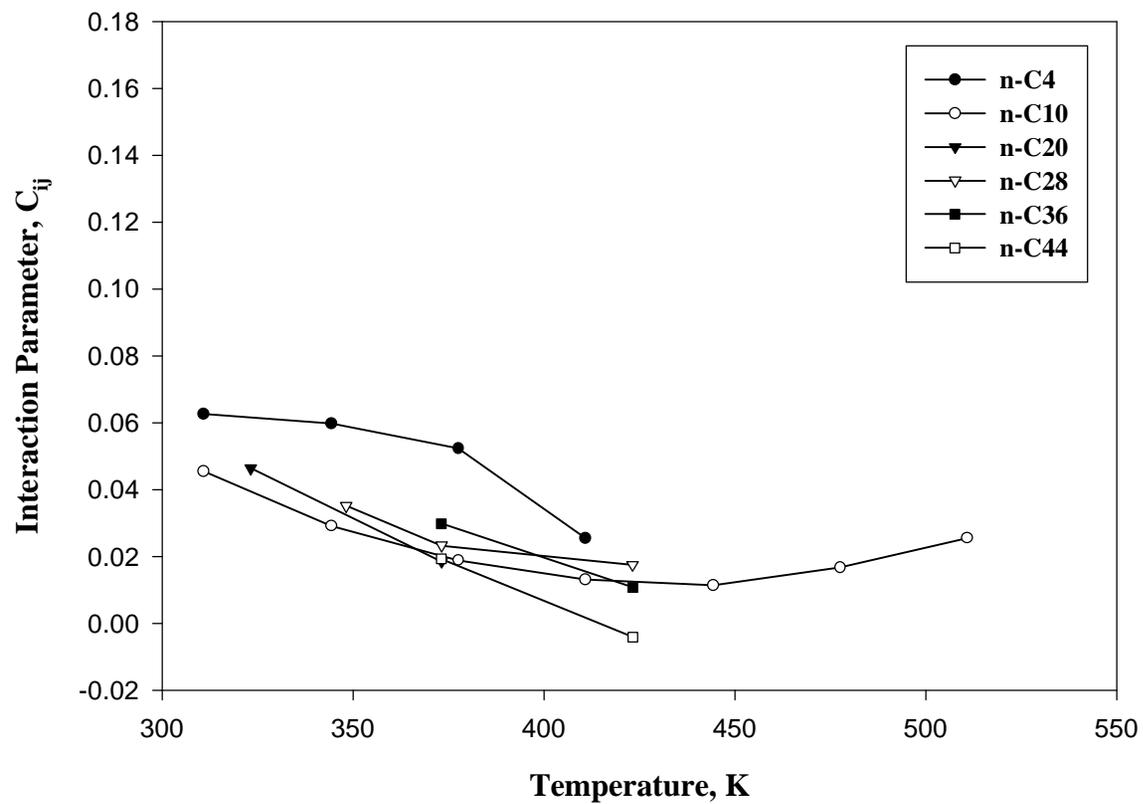
Figure 7.   Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

Figure 8.   PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.
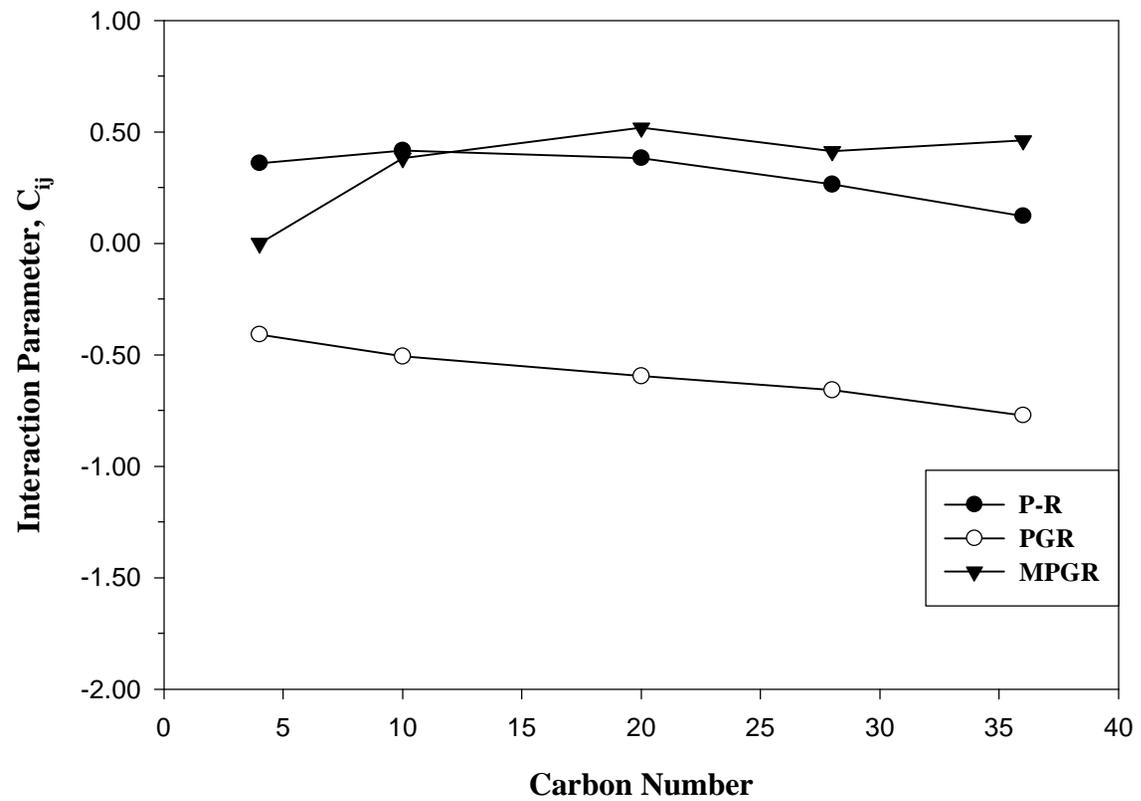
Figure 9.   SPHCT Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

Figure 10. PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Carbon Dioxide + n-Paraffin Systems.

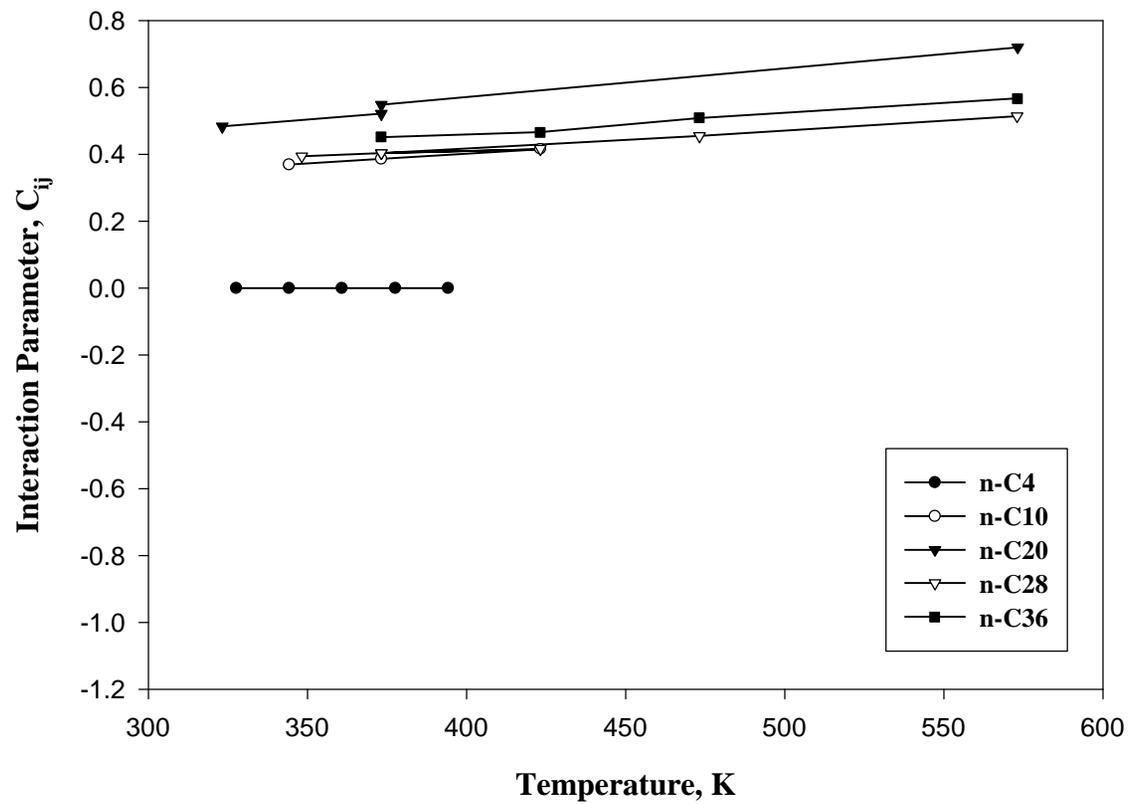Figure 11. Equation of State Interaction Parameters, C_{ij}, for the Hydrogen + n-Paraffin Systems.

Figure 12. Modified PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.
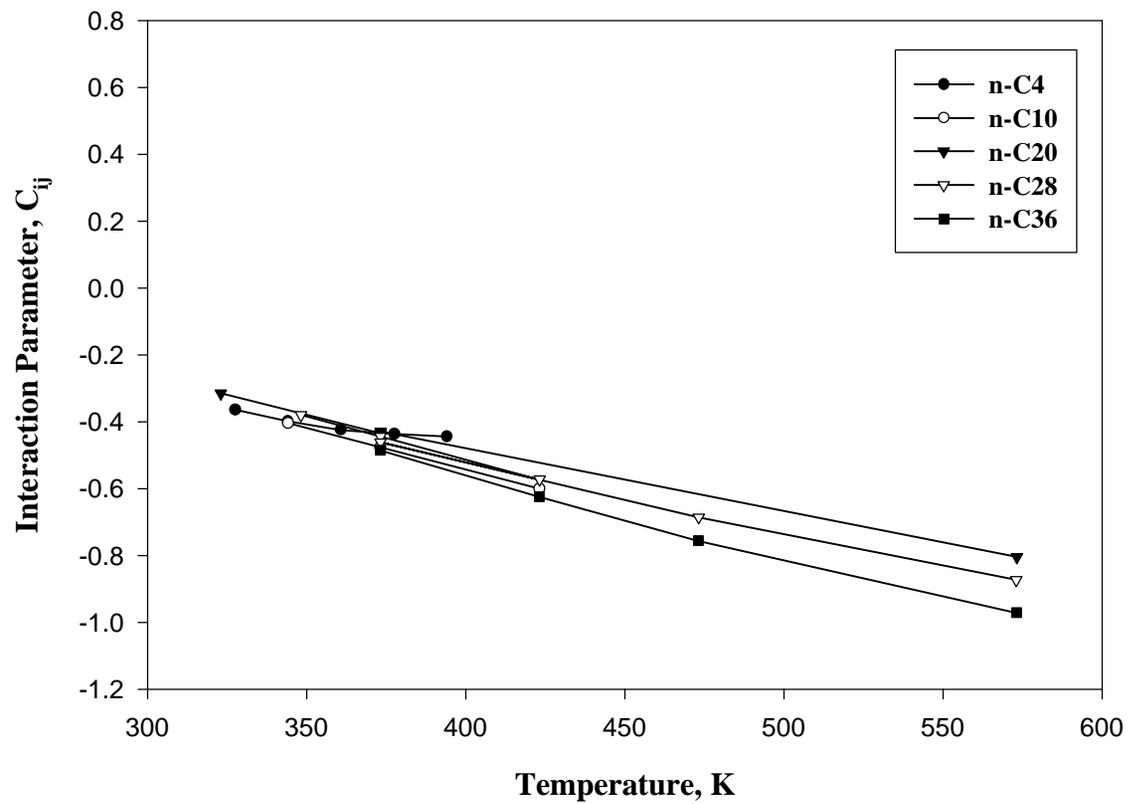
Figure 13.   PGR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.
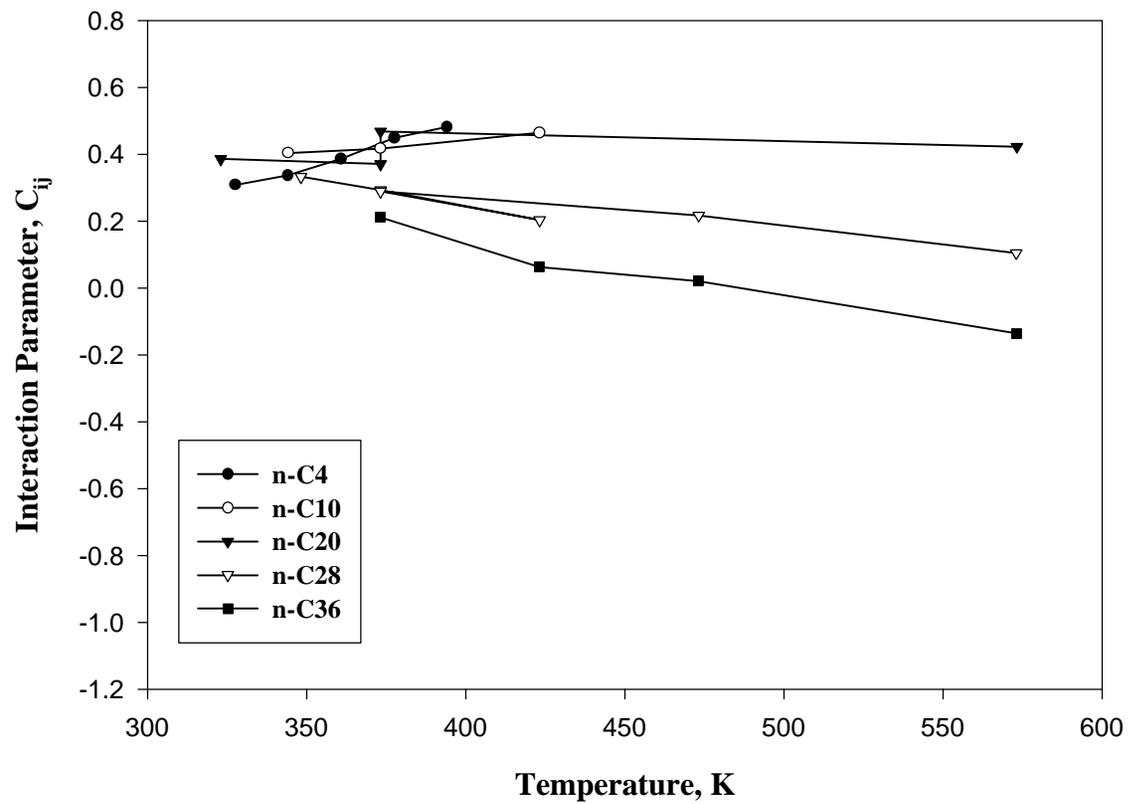
Figure 14.   PR Equation Interaction Parameter, C_{ij}, Temperature and Carbon Number Dependence for Hydrogen + n-Paraffin Systems.