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DE-FG22-90PC90302

March 3, 1994

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PROJECT TITLE: "Equilibrium and Volumetric Data and Model Development
for Coal Fluids"

PROJECT PERIOD: October 1, 1990 to September 30, 1993

SUMMARY

Under continued support from DOE, 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 predicting 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 the supercritical solutes hydrogen, methane, ethane, CO, and CO₂.

During the course of this project, solubility data were obtained on twenty-two binary mixtures of CO, hydrogen, or nitrogen in a series of paraffinic, naphthenic and aromatic solvents (decane, eicosane, octacosane, hexatriacontane, cyclohexane, decalin, benzene, naphthalene, phenanthrene, pyrene). The measurements were conducted at temperatures from 310 to 433 K, pressures to 22 MPa, and solute mole fraction from 0.01 to 0.30. Estimated errors of the measured gas solubilities in the selected solvents are less than 0.001.

Specific accomplishments of this project included (a) upgrading our experimental facility to permit highly accurate measurements of equilibrium phase compositions (solubilities) and phase densities, (b) measuring these properties for systematically-selected binary mixtures to provide critically needed input data for correlation development, (c) developing and testing models suitable for describing the phase behavior of coal-fluid mixtures, and (d) presenting the modeling results in generalized, practical formats suitable for use in process engineering calculations.

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**EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL
DEVELOPMENT FOR COAL FLUIDS**

**Final Report for the Period
October 1, 1990 to September 30, 1993**

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EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL DEVELOPMENT FOR COAL FLUIDS

ABSTRACT

The proper design, operation, and optimization of coal conversion and utilization processes depend heavily on knowledge of the phase behavior of the mixtures encountered in these processes. Frequently quoted statistics suggest that in conventional chemical plants 70% of the capital and 90% of the operation expenses are associated with phase separations. Since multiple stages occur in almost all stages of coal conversion processes - from feed preparation through conversion reactions to product separation - the proper description of phase behavior is important in each step of these processes.

The long term goal of our efforts is to develop accurate predictive methods for the description of equilibrium phase properties for a variety of types of mixtures and operating conditions. The specific objectives of the work described here included:

- (1) developing an experimental facility having the capability to provide data on equilibrium phase compositions (solubilities) and liquid densities, and doing so with greater accuracy and speed than our previous facility,
- (2) measuring equilibrium phase properties for systematically selected mixtures - specifically those containing important solute gases (such as nitrogen, hydrogen, carbon dioxide, methane, ethane, carbonyl sulfide, ammonia) in a series of heavy paraffinic, naphthenic and aromatic solvents (e.g., n-decane, n-eicosane, n-octacosane, n-hexatriacontane, cyclohexane, decalin, perhydrophenanthrene, perhydropyrene, benzene, naphthalene, phenanthrene, pyrene),
- (3) testing and developing correlation frameworks for representing the phase behavior of fluids of the type encountered in coal conversion processes, and
- (4) generalizing parameters in the correlation frameworks to enable accurate predictions for systems of the type studied, permitting predictions to be made for systems and conditions other than those for which experimental data are available.

During the course of this project, solubility data were obtained on twenty-two binary mixtures of CO, hydrogen, or nitrogen in a series of paraffinic, naphthenic and aromatic solvents (decane, eicosane, octacosane, hexatriacontane, cyclohexane, decalin, benzene, naphthalene, phenanthrene, pyrene). The measurements were conducted at temperatures from 310 to 433 K, pressures to 22 MPa, and solute mole fraction from 0.01 to 0.30. Estimated errors of the measured gas solubilities in the selected solvents are less than 0.001. In addition, vapor-liquid equilibrium measurements were obtained for the phase compositions and phase densities of CO₂

+ decane, CO₂ + trans-decalin, and ethane + 1-methylnaphthalene binary mixtures at 344.3 K and pressures up to the mixture critical points. These phase density data complement the previous measurements at Oklahoma State University for CO₂ solubilities in n-paraffins, naphthenes and aromatics. In general, the newly acquired data agree well with the available literature data.

The solubilities of CO, hydrogen, or nitrogen in paraffinic, naphthenic and aromatic hydrocarbons are described well by the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS). The precision of these descriptions varies; average errors are about 0.002 mole fraction when a single interaction parameter, C_{ij} , is used for each isotherm and 0.001 when two interaction parameters are employed for each isotherm.

The experimental data acquired in this project can (a) serve as an excellent basis for determining parameters in any selected phase behavior model, (b) provide valuable information for the development of improved equation-of-state models, and (c) improve our understanding of the phase behavior of hydrocarbon mixtures involving CO, hydrogen, or nitrogen. Moreover, our systematic studies of selected solutes in a series of solvents from the same molecular class facilitate generalized predictions that may encompass mixtures for which experimental data are lacking.

Aside from the routine analysis of our experimental data using SRK and PR EOS, three major tasks in EOS model evaluation and development were undertaken. **First**, a database for five supercritical fluids (CO₂, CO, methane, ethane, and hydrogen) in n-paraffins was generated to evaluate the SRK and PR EOS as a correlation framework to describe the phase behavior of these systems and as means to predict Henry's constants. Expressions for Henry's constant have been derived from the generalized cubic EOS. Five cases were included in the EOS evaluations, using bubble point pressure calculations. For each case, interaction parameters along with Henry's constants were obtained for both equations.

The SRK and PR EOS are capable of representing the phase behavior of CO₂, CO, methane, ethane, and hydrogen in n-paraffins. The two equations of state are nearly equivalent in predicting Henry's constants, and the predicted Henry's constants are in good agreement with the experimental values. The interaction parameters and Henry's constants provided by this work are useful for both practical applications and basic understanding of solution thermodynamics of the system studied.

Second, we have investigated several modifications to the simplified-perturbed-hard-chain theory (SPHCT) EOS. Sensitivity analyses of the original EOS parameters were done to aid in the EOS modifications. Also, a phenomenological volume translation similar to that introduced by Chou and co-workers was developed to improve the prediction of both vapor and liquid phase densities. These modifications resulted in a significant improvement in the prediction of

pure-fluid and mixture saturation properties, including vapor pressures, phase compositions and phase densities. The modified EOS is comparable to the original SPHCT equation in predicting the bubble point pressures of ethane + n-paraffin mixtures, with the modified equation providing improved results in the *a priori* predictive (no interaction parameters) mode. Simple correlations have been developed to represent the critical point constraints without the need for solving the complicated critical point constraint equations. The modified equation provides poorer results than the original SPHCT equation for the prediction of CO₂ + n-paraffin systems. This is attributed to deficiencies in the partition function of the original framework and the resulting uncertainties in the mixing rules used.

Third, a new equation of state was proposed based on the generalized van der Waals partition function for chain-like molecules. The repulsive term of the EOS utilizes an existing free volume expression for hard spheres, and the attractive term is 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 low-density limiting radial distribution function. In addition, a set of mixing rules was proposed to extend the use of the new equation to mixtures.

The predictive capabilities of the equation was compared to those of the PR, the SPHCT and Modified SPHCT EOS. Vapor pressures and saturated (liquid and vapor) densities of a variety of pure fluids, as well as bubble point pressures of selected binary mixtures, were used in model comparisons. The new EOS gives better predictions for pure-fluid vapor pressures and saturated densities than the PR and SPHCT EOS, and has comparable capability to the Modified SPHCT equation. EOS evaluations involving ethane + n-paraffin and carbon dioxide + n-paraffin mixture predictions suggest that the new equation is best among the equations for *a priori* predictions.

INTRODUCTION

Any effective over-all program to develop useful predictive methods for representing phase equilibrium properties of mixtures encountered in coal processes must incorporate a blend of theory and experiment. To validate any theoretical development requires pertinent, accurate data for mixtures exhibiting behaviors similar to those of interest, and such data must cover an adequate range of experimental conditions. Nevertheless, the quantity of data required can be reduced dramatically if experiments are designed carefully to serve specific, critical roles in the developing and testing the theoretical and correlational models. Accordingly, our research program included (a) evaluating existing literature data, (b) identifying viable correlation frameworks that contain a minimum of input parameters that are amenable to generalization, and (c) establishing an experimental facility able to provide the required data for the correlational effort.

The experimental portion of this project involved (a) upgrading our experimental facility to render it capable of functioning over a wider range of pressure, (b) acquiring critically-needed solubility data for the evaluation/development of models to describe the phase behavior of coal fluids, and (c) expanding our experimental capability to include saturated liquid and vapor phase density measurements. Combined data for solubilities and phase densities provide an improved basis for developing more theoretically-based, realistic equations of state.

Typical coal fluids contain a large number of individual components, spanning a wide range of molecular sizes, shapes, and specific chemical behaviors. However, the majority of these chemical species are formed from a relatively small number of functional groups in the molecules. Fortunately, this knowledge can be used to minimize experimentation if the mixtures for study are carefully selected to exhibit the most important classes of intermolecular (or inter-group) interactions. Our experimental measurements were planned to fulfill this role for the asymmetric mixtures encountered in coal conversion and utilization processes.

Asymmetric mixtures of light gases and heavy solvents occur frequently in feed and reactor product streams during the production and processing of coal fluids. Aided by support from the

Department of Energy and Oklahoma State University, an experimental phase equilibrium facility has been constructed and operated under the direction of the authors. Data have been obtained on a number of asymmetric mixtures, as illustrated by our vapor-liquid equilibrium (VLE) measurements, which are summarized in Table I* for about 80 different systems. These binary mixtures which involve small solute molecules (such as CO₂, CO, hydrogen, methane, ethane, and nitrogen) and heavy hydrocarbon solvents (effective carbon number of ten or greater) pose a challenge to the current predictive models and the associated mixing theories.

As a part of our on-going research dealing with the phase behavior of asymmetric mixtures, the solubilities of CO₂, CO, hydrogen, methane, ethane, and nitrogen in systematically-chosen solvents (heavy paraffinic, naphthenic and aromatic hydrocarbons) have been measured and correlated [1-7]. During the course of this project, new solubility data (the shaded entries in Table I) were obtained on twenty-two binary mixtures of CO, hydrogen, or nitrogen in a series of paraffinic, naphthenic and aromatic solvents (decane, eicosane, octacosane, hexatriacontane, cyclohexane, decalin, benzene, naphthalene, phenanthrene, pyrene). The measurements were conducted at temperatures from 310 to 433 K, pressures to 22 MPa, and solute mole fraction from 0.01 to 0.3. The data have been correlated using the SRK [8] and PR [9] equations of state. The binary interaction parameters, C_{ij} and D_{ij} , regressed from the new experimental data can be used to predict multicomponent phase behavior.

Measurements on binary mixtures have been central to our experimental program because they are the most valuable for correlation development and testing. The reason is that essentially all state-of-the-art models (including equations of state and activity coefficient models) contain one [e.g., 8, 9], two [2-4, 6, 10-14] or three [15] parameters which reflect the nature of unlike-molecule interactions. The "mixing rules" in such models almost always describe the unlike-molecule interactions solely in terms of parameters which reflect pairwise interactions -- and which can be established from data on binary mixtures. These parameters cannot, in general, be predicted *a priori* from existing theory; they must be established from

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* All tables and figures are given in Appendix B.

experimental data.

Parallel to our experimental program, we have pursued model development and testing with the goal of providing more accurate capabilities to predict equilibrium and volumetric properties of mixtures encountered in coal processing. Our intention in the model development activities has been to strike a balance between (a) fulfilling immediate needs in coal processing by using semi-empirical models (such as van der Waals-type equations of state), and (b) the ultimate goal of providing rigorous, accurate and *a priori* predictive capability based on more rigorous theories at the molecular level. In this project, our efforts in EOS model development have emphasized and sought equations with features that

- originate from the generalized van der Waals or perturbation theory, amended by the Flory lattice model for chain-like interactions, and they should be supported in their makeup by molecular simulations;
- employ segment-segment interactions [e.g., 16-18] so they can accommodate substances of differing molecular sizes over wide density ranges;
- characterize the EOS parameters based on our current insights on pair correlation functions, and incorporate the known limiting behavior of these parameters [19, 20];
- include the ability to represent all the thermodynamic properties of interest (T , ρ , ρ , x , y , H , S) over the full operating range; and
- are relatively simple to use, numerically efficient, and modest in terms of the demands placed on experimental measurements required for tuning purposes.

Our study of the perturbed-hard-chain-theory (PHCT) equation [14] has shown that it offers a promising balance between simplicity and theoretical rigor. Accordingly, we have further explored the merits of this framework during the course of this project. Specifically we have (a) evaluated the predictive capability of the SPHCT EOS as compared to the widely used cubic equations of state, (b) modified the SPHCT equation [21] to improve its predictions, and (c) developed a new EOS model targeting the types of mixtures encountered in the coal industry [22].

No simple, analytic and completely predictive EOS has yet been derived from theory.

Therefore, model parameters must be based on experimental data for the most accurate predictions. If experimental measurements are performed on systematically chosen mixtures, they can be used to evaluate interaction parameters. More importantly, they can furnish the basis for generalization of the parameters to permit interpolation (and even extrapolation) to other solvents in the same homologous series. This has been documented by our data [1-7, 10-14] on the binary solubilities of hydrogen, methane, ethane, H_2 , CO, CO_2 , and N_2 in n-paraffins. These data, along with information from the literature, have been used to (a) test and improve the ability of the SRK, PR and SPHCT equations of state to describe the behavior of mixtures of interest, (b) provide optimum interaction parameters for these equations and (c) present simple generalized correlations for the interaction parameters. Our work, as well as similar model development studies conducted by others who utilized our data [e.g., 23, 24], confirm the value of systematically-planned measurements of the type studied in the present project.

Given below are brief descriptions of (a) the experimental methods employed in this study, (b) our recent experimental results and data correlation, and (c) examples of our model development efforts. Detailed presentation and discussion of the various topics have been reported elsewhere [21, 22, 25, 26].

EXPERIMENTAL METHOD

Solubility Measurements

A synthetic method was employed in the measurements 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.

Different generations of our solubility apparatus [2, 3, 10, 22] have produced large amounts of precise equilibrium data for the asymmetric mixtures catalogued in Table I. The apparatus, used in this study, is a modified version of that used by Darwish [10] and Yi [27]. Some modifications were undertaken on the apparatus used by Yi [27] 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 cell of larger volume. A reduction in the experimental uncertainties of the equilibrium composition is the main advantage of increasing the cell volume to 25 cc. The new equilibrium cell was used only for hydrogen binaries. Third, an additional pressure transducer PT2 was installed to measure pressures over 13.79 MPa. This new transducer was installed in parallel with the old one (PT1). Other minor modifications were also undertaken to improve the operation of the apparatus. Following is a description of the major components of the experimental apparatus and the procedure used in this study.

The equilibrium cell used in the study of carbon monoxide binary systems is that used by Yi [27]. The cell, which is 12 cc in volume, was supplied by High Pressure Equipment Inc. The cell used to investigate solubilities of hydrogen in hydrocarbon solvents is a 25 cc, 316 stainless steel micro-reactor (Cat No. MS-16, 1 in OD, 1/2 in ID) 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 steel wire, and the other end was pivoted. The motor was used to rock the equilibrium cell 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.

Three positive displacement hand pumps were used in this study. The solvent injection pump and the solute injection pump, each 25 cc in volume, were supplied by Temco Inc. (Model

No. HP-25-10). The solvent injection pump 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 68.95 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.

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). 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). 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.

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 resolutions of both displays are 0.01 °C.

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 20.68 MPa, and PT2 (Model No. TJE/743-11) has a range of 0 to 68.95 MPa. The digital displays for PT1 and PT3 (Model No. 450D)

are to 13.79 MPa with 0.007 MPa resolutions. The transducer PT2 is connected to a digital display (Model No. GM), which has a maximum range of 137.9 MPa with a resolution of 0.07 MPa. This transducer is used when the pressure of the equilibrium cell exceeds 13.79 MPa.

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 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).

Imprecision in the measured bubble point pressures depends on the specific mixture under study and is of the order of 0.05 MPa (0.001 in mole fraction) for the systems considered in this study. Detailed error analysis is given elsewhere [22, 26].

Phase Density Measurements

We have also expanded our experimental capabilities and initiated a new program for measuring phase densities. To accomplish this, our existing fluid recirculation vapor-liquid equilibrium apparatus, developed over the past eight years through funding from a consortium of oil companies, was used during the course of this project. In previous studies [e.g., 28], this apparatus has been used to measure simultaneously the phase compositions, phase densities and interfacial tensions for systems of interest to petroleum production (at conditions up to 450 K and 20 MPa). The basic components of the apparatus have been described elsewhere [28, 29]. Recently, however, it has been automated by installation of computerized data acquisition and control systems. All equipment was interfaced to a Northgate 386 personal computer through an ACRO 900 interface unit and monitored through Labtech Control software. The apparatus is shown schematically in Figure 2. The two Mettler/Paar 512 vibrating U-tube densitometers

were used for vapor and liquid density measurements. Figure 3 shows typical experimental phase density data obtained using this apparatus. The data cover the full saturation range of the binary system ethane + 1-methylnaphthalene, including the near critical region. The newly acquired phase densities data along with complete error analysis are reported elsewhere [21].

MATERIALS

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

RESULTS AND DATA CORRELATION

Carbon Monoxide + Hydrocarbons

The CO solubility measurements are presented in Table III. In general, the lowest temperature at which a particular system was studied was dictated by the melting point of the solvent or the availability of literature data; all hydrocarbons in this study are solids at room temperature, except for decane and benzene. The effect of temperature and pressure on the solubility of carbon monoxide in eicosane is shown in Figure 4. The trend of increasing solubility with increased temperature and pressure is observed for all the n-paraffinic and aromatic solvents studied, with the exception of pyrene (for which the effect of temperature has not been investigated).

Comparisons of our binary data for the solubility of CO in eicosane, octacosane, and hexatriacontane with those of Huang and coworkers [30] are shown in Figures 5, 6 and 7, respectively. The comparisons are shown in terms of deviations of the experimental measurements from the solubility predicted using the SRK EOS (discussed in Appendix A). The binary interaction parameters, C_{ij} and D_{ij} , employed in the EOS predictions were obtained by fitting our data for the isotherm under study. Figures 6-8 indicate reasonable agreement between our data and those of Huang. No literature data for the solubility of CO in decane are

available for direct comparison.

A comparison of our data on CO + benzene binary with those of Connolly [33] at 433.2 K is shown in Figure 8. The comparison is shown in terms of deviations of the experimental measurements from the solubility predicted using the SRK EOS. The single binary interaction parameter, C_{ij} , employed in the EOS predictions was obtained by fitting our data for that isotherm. Figure 8 shows very good agreement between our data and those of Connolly; deviations within the experimental uncertainty of 0.001 are observed. No literature data for the solubility of CO in naphthalene, phenanthrene and pyrene are available for comparison.

The EOS representations of the solubilities of CO in n-paraffins are shown in Table IV. Using the physical properties given in Table IX, relatively large C_{ij} values are obtained for eicosane, but no correlation with carbon number is observed. For the eicosane and octacosane, the SRK and PR equations are capable of describing the data with RMS errors within 0.004 in mole fraction when a single interaction parameter, C_{ij} , is used over the complete temperature range. For these two binaries, only marginal improvements in the EOS predictions are realized when a second interaction parameter, D_{ij} , is employed. For the hexatriacontane system, however, the use of either one or two interaction parameters, over the complete temperature range does not fit the data well (RMS errors of 0.007).

When one interaction parameter, C_{ij} , is fitted to each isotherm for the systems of eicosane and octacosane, the RMS errors are less than 0.0015 in mole fraction (except for the octacosane system at 348.15 K), and the two equations of state give comparable representation of the data. No significant improvements are obtained for either system when a second interaction parameter, D_{ij} , is used (except for the octacosane system at 348.15 K) as revealed by the results in Table IV. For the hexatriacontane system, the use of the second interaction parameter for each isotherm significantly improves the predictions. The need for the second interaction parameter may reflect the inadequacy in the original EOS mixing rules for the highly asymmetric mixtures produced by the larger hexatriacontane molecules.

The EOS representations of the CO solubilities in aromatic solvents are also shown in

Table IV. 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. The ability of equations of state is marginally improved (RMS = 0.0008) when an additional interaction parameter, D_{ij} , is employed. In contrast to our previous experience with the CO₂, methane and ethane systems [1-7], the low solubility of CO in the four aromatic solvents (at pressures to 23 MPa) has tempered the need for the second interaction parameter, D_{ij} . Moreover, a high degree of correlation was observed between C_{ij} and D_{ij} when both were used simultaneously. 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 RMS errors in mole fraction are, in general, within the estimated uncertainty of 0.001 when the full potential of the EOS model is realized using two interaction parameters, C_{ij} and D_{ij} , per isotherm. The results obtained illustrate both the ability of the equation of state and the precision of our reported data.

Hydrogen + Hydrocarbons

The hydrogen solubility measurements are presented in Table V. In general, the lowest temperature at which a particular system was studied 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 decane is shown in Figure 9. A trend of increasing solubility with increased temperature and pressure is observed for all the n-paraffin solvents studied as well as for benzene, naphthalene, and phenanthrene. However, the temperature effect was not studied for hydrogen + pyrene system.

Comparisons of our binary data for the solubility of hydrogen in eicosane, octacosane, and hexatriacontane with those of Huang and coworkers [32] at 373.2 K are shown in Figures 10, 11 and 12, respectively. Minor temperature variations of up to 0.2 K in Huang's data were neglected for the purposes of data comparison. The comparisons are shown in terms of

deviations of the experimental measurements from the solubility predicted using the SRK EOS. The binary interaction parameter, C_{ij} , employed in the EOS predictions was obtained by fitting our data for the isotherm under study. Figures 10-12 indicate reasonable agreement between our data and those of Huang. No literature data for the solubility of hydrogen in decane are available for direct comparison.

A comparison of our data on hydrogen + benzene with those of the literature is shown in Figure 13. For comparison purposes, the interaction parameter, C_{ij} , of the SRK EOS regressed from our data was used in the prediction of solubilities. In our comparison with the data reported by Connolly [33] and Thompson and Edminster [34], the interaction parameter C_{ij} was extrapolated to their reported temperature of 433.2 K. In the other comparisons, the values of interaction parameters were linearly interpolated. As Figure 13 illustrates, all the data except those of Brainard show good agreement. A comparison of data on hydrogen + phenanthrene is shown in Figure 14. The observed deviations indicate remarkably good agreement between the data of Malone [35] and those measured in this study.

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 systems containing hydrogen [52]. The same kind of approach was pursued by Garboski and Daubert [36]. 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 [37]. Preliminary analysis of the present data supported Lin's findings. We therefore elected to use the original SRK and PR equations of states, along with the experimental values for critical properties and acentric factor of hydrogen.

The EOS representations of the hydrogen solubilities in n-paraffins are shown in Table VI. In general, the SRK and PR equations are capable of describing the data with RMS errors within 0.001 in mole fraction when a single interaction parameter, C_{ij} , is used per isotherm. Using the physical properties given in Table VII, relatively large C_{ij} values are obtained for

decane, along with a decreasing trend for C_{ij} with solvent carbon number. The atypical values observed for C_{ij} are attributed to the low value of the critical temperature of hydrogen and the resulting acentric factor ($\omega = -0.218$).

When a single interaction parameter is used for a given hydrocarbon solvent the RMS errors are within 0.005. This level of variation is significantly beyond the precision of the experimental data and is an indication of a strong temperature dependence in the interaction parameter. Data regressions involving the second interaction parameter, D_{ij} , result in negligible values for this parameter (not given here) and no significant improvement in the quality of the fit. This is in clear contrast to our previous studies of hydrocarbon mixtures involving methane, ethane, and CO_2 [1-7].

The EOS representations of the hydrogen solubilities in aromatic solvents are also shown in Tables VI. In general, the SRK and PR equations are capable of describing the data with RMS errors usually less than 0.001 in mole fraction when a single interaction parameter, C_{ij} , is used for each isotherm. Data reduction indicates that the interaction parameter, C_{ij} , is highly dependent on temperature. Moreover, the SRK and PR EOS, in general, exhibit comparable abilities in representing the data using a single interaction parameter. Data regressions which included a second interaction parameter, D_{ij} , were omitted in this study due to atypical values of interaction parameters obtained. The high correlation between the parameters C_{ij} and D_{ij} are not unexpected in systems exhibiting such low solubilities.

The SRK and PR equations of state, in general, exhibit comparable abilities in representing the reported data within their experimental precision; however, some differences in the quality of the fit are observed for the various hydrocarbons. Specifically, the PR EOS produced better fits for decane, while the SRK EOS gave better results for hexatriacontane.

Nitrogen + Hydrocarbons

Currently, few data are available for mixtures involving nitrogen and heavy hydrocarbons. For example, hexadecane is the heaviest member of the normal paraffin homologous series for which nitrogen vapor-liquid equilibrium data exist [38]. Therefore, the present data constitute a

valuable addition to the literature. The nitrogen solubility data are presented in Table VII. The effect of temperature and pressure on the solubility of nitrogen in n-decane is shown in Figure 15. A trend of increasing solubility with increased temperature and pressure is observed within the experimental range considered. The solubilities of nitrogen in n-eicosane, octacosane and hexatricontane exhibit the same trend as that of nitrogen in n-decane.

Comparisons of our data for nitrogen in n-decane with those of Azarnoosh and McKetta [39] and Llave and Chung [40] are given in Figures 16-18. These comparisons are shown in terms of solubility deviations generated by comparing optimum SRK predictions with the experimental measurements. For this purpose, the interaction parameters, C_{ij} , of the SRK equation of state were regressed from our data at 344.3, 377.6, and 423.2 K. Figures 16-18 indicate disagreement between our data and those of Azarnoosh and McKetta [39] and Llave and Chung [40]. No literature data for the solubility of hydrogen in n-eicosane, octacosane, or hexatricontanodecane are available for direct comparison.

The EOS representations of the solubilities for the systems considered are shown in Table IX. In general, the SRK and PR equations are capable of describing the data with RMS errors usually less than 0.001 in mole fraction when a single interaction parameter, C_{ij} , is used per isotherm. Our data reduction indicates that the interaction parameter, C_{ij} , is highly dependent on temperature. Moreover, the SRK and PR equations of state, in general, exhibit comparable abilities in representing the present data using a single interaction parameter for each isotherm.

Henry's Constants

By definition, Henry's constant of a gas solute (1) in a hydrocarbon solvent (2) is given as:

$$H_{1,2} = \lim_{x_1 \rightarrow 0} (f_1 / x_1) = \lim_{x_1 \rightarrow 0} (\phi_1 p) \quad (1)$$

Estimates for Henry's constant were obtained for the present data using SRK and PR equations of state in accordance with the above definition [25]. Values for Henry's constant, along with

the interaction parameters associated with them, are given in Tables IV, VI and VIII. In general, values of Henry's constant obtained from the PR EOS are slightly larger than those obtained using SRK EOS. Further discussion relating to Henry's constants for the various solutes in n-paraffins is given in the following section addressing model evaluation and development.

MODEL DEVELOPMENT

Accurate predictions for the phase behavior of fluid mixtures are at the heart of chemical process design and development. Industrial processes such as coal conversion as well as petroleum refining, enhanced oil recovery, and supercritical separation have created great demand for phase equilibrium data of asymmetric mixtures. Currently, these mixtures which involve small solute molecules (such as hydrogen, methane, ethane, CO₂ and CO) and heavy hydrocarbon solvents (effective carbon number of ten or greater) pose a challenge to the current predictive models and the associated mixing theories.

For the types of asymmetric mixtures encountered in coal fluids, solubility data are often adequate for evaluation of model parameters if interest is restricted to predicting only equilibrium phase compositions (i.e., not volumetric properties). For such predictions, the simple classical equations of state have been very useful, as demonstrated in our mixture studies involving methane, ethane, H₂, N₂, CO and CO₂ solutes [1-7, 10-14, 25, 26] -- but even here, they exhibit a strained ability for some systems. However, advances in molecular thermodynamics (aided by simulation studies) now facilitate the development of EOS models capable of representing accurately both equilibrium phase compositions and volumetric properties (densities). In recent studies, we have directed our attention in model development to such equations of state, focusing initially on evaluation of the hard-chain-perturbation theory [e.g., 14, 16].

In a typical application, we used data acquired at OSU on the solubility of hydrogen, methane, ethane, CO and CO₂ in n-paraffins, along with data from the literature, to develop

parameter generalizations of both cubic (SRK) and simplified-perturbed-hard-chain-theory (SPHCT) [16] equations of state [12, 14, 41, 42]. These results, illustrated by the methane and CO evaluations in Table X, demonstrate the relative abilities of the two equations of state. While not shown in the overall statistics of Table X, the SPHCT gives markedly better predictions for mixtures containing longer-chain solvents typical of those encountered in coal fluids. This improvement may be attributed to the SPHCT's description of the mixture in terms of segment-segment interactions, in contrast to the molecule-molecule interactions on which the cubic SRK EOS is based.

Aside from the ability to correlate existing experimental data, the true measure of any correlation framework is the ability to provide predictions for (a) systems for which there are no data, and (b) properties not included in the data reduction. Figure 19 examines the variation of the SPHCT interaction parameter (C_{ij}) for n-paraffin solvents with the various solute gases. The figure reveals a very reasonable interpolation (and even extrapolation) capability for the SPHCT, as indicated by the essentially linear dependence of C_{ij} on the solvent carbon number. This contrasts to a much stronger, non-linear variation (not shown here) in the parameters for cubic EOS models for representing the same data.

The above example reveals the manner in which systematic experimental measurements can permit valuable conclusions to be drawn; in this case, we concluded that (a) a single interaction parameter could adequately represent the data and (b) that the SPHCT parameter exhibits some dependence on the molecular size of the paraffin solvent molecule (albeit significantly less than for the SRK and PR equations of state [14, 41]). These results also clearly suggest that improvements (relative to the SPHCT EOS) are required to realize the full potential of segment-segment interaction models, where the interaction parameters should be essentially independent of molecular size.

Seeking such a model, we have recently investigated several modifications to the SPHCT EOS [21]. Sensitivity analyses of the original EOS parameters were performed to aid in the EOS modifications. The effect of applying critical-point constraints to the SPHCT EOS was

also studied. These studies have resulted in modifying the attractive portion of the EOS to improve vapor pressure predictions by the constrained equation. Moreover, a phenomenological volume translation similar to that introduced by Chou and co-workers [43] was developed to improve the prediction of both vapor and liquid phase densities.

Our proposed changes in the SPHCT EOS have resulted in significant improvement for prediction of pure-fluid vapor pressures, phase compositions and densities (overall, less than half the error obtained from the SPHCT and PR equations). The modified equation is comparable to the original SPHCT equation for the prediction of ethane + n-paraffin mixtures, with the modified equation providing improved results in the predictive mode (no interaction parameter); thus, indicating that the modified equation would provide better *a priori* predictions for systems lacking experimental data.

Following are sample studies describing some of our model evaluation and development efforts. Complete and detailed analysis is given elsewhere [22, 25]. The works included here illustrate the strategy we have pursued in model development, which involves (1) evaluation of the widely-used cubic equations of state, (2) evaluation and modification of theoretically-based EOS models, and (3) development of new EOS models targeting the types of mixtures encountered in the coal industry.

Cubic EOS Models

The purpose of this modeling effort was to (i) further evaluate the viability of cubic equations of state as a correlating framework for supercritical fluid mixtures, and (ii) predict Henry's constants for such mixtures. Thus, a database consisting of binary data acquired at Oklahoma State University on CO₂, methane, ethane, CO and hydrogen with n-paraffins, along with data from the literature were employed to: (1) test the ability of cubic equations of state (SRK and Peng-Robinson) to describe the phase behavior of these systems, (2) provide optimum interaction parameters for such equations, (3) assess the reliability of cubic equations of state in predicting Henry's constants based on the available experimental data.

Database Used and Data Reduction

Binary mixture data for CO₂, CO, methane, ethane, and hydrogen with n-paraffins previously acquired at Oklahoma State University, along with data from the literature, were used in our study. A summary of the database employed in the evaluation including ranges of temperature, pressure and mole fraction of the coexisting phases, together with their sources is given elsewhere [25]. Most of the utilized data, covering n-paraffins from C₃ to nC₄₄, were isothermal bubble point pressure measurements as a function of solute liquid mole fraction. The data employed were limited to pressures below 90% of the solute critical pressure in order to decrease the influence on the regressed interaction parameters of data near the critical region, where equations of state are inherently incapable of accurate predictions.

Values of critical temperature (T_c), critical pressure (p_c) and acentric factor (ω) for each pure fluid, along with the binary interaction parameters, constitute the model input variables for the SRK and Peng-Robinson equations of state. The values of the input variables for the n-paraffins C₁ - C₂₀ are taken from the property data bank of Reid and workers [63]. For n-paraffins heavier than C₂₀, the values of the input variables are estimated by the Asymptotic Behavior Correlation [44]. The pure-fluid properties employed in this study are presented in Table XI. It should be noted that values of EOS interaction parameters are significantly affected by the values used for T_c , p_c and ω , especially for heavier n-paraffins. Thus, care should be exercised in discussing observed trends in these parameters.

Since most of the available data is in the T-p-x form (no vapor phase measurements), only the measured properties T, p, and x were used in the data reductions. Uncertainties in the temperature measurements are assumed to be insignificant and, since uncertainties in the pressure measurements are mostly unavailable, the following least squares objective function, SS, was employed for the EOS interaction parameter evaluations:

$$SS = \sum_{i=1}^N \left[(p_{cal} - p_{exp}) \right]_i^2 \quad (1)$$

p_{cal} and p_{exp} are the calculated and experimental bubble point pressures, respectively. A

Marquart [45] nonlinear regression procedure was employed in the calculations. According to Equation (1), the root-mean-square error (RMSE) provides an appropriate measure for the overall performance of the model for a given data set, more so than %AAD.

Equation of State Evaluation

In this study, a method we have established in earlier work [e.g., 44] for evaluation of cubic equations of state was pursued and modified to include Henry's constant predictions. Table XII presents five specific cases used in the evaluations. No generalization of the parameters is included in such cases; however, specific parameter values are evaluated as required by the model for a given case.

Case 1 represents the initial evaluation of the EOS models in which the raw ability of each model is assessed. In Case 2, the common industrial practice of using a single interaction parameter is considered for each binary mixture. Case 3 addresses the improvements realized when a separate pair of interaction parameters are considered for each binary mixture, independent of temperature. A single interaction parameter is used for each isotherm of each binary mixture in Case 4. Case 5 represents the ultimate correlative capability of the equations of state models in which two interaction parameters are considered for each isotherm of each mixture.

The interaction parameters for each of these cases are obtained using the objective function of Equation (1) through the bubble point pressure calculations. The resultant interaction parameters for the SRK and Peng-Robinson equations of state for the five cases studied, combined with pure component vapor pressures (based on the Antoine equation), are also used to estimate Henry's constants. The ability of cubic EOS models to predict Henry's constants is assessed using the optimum predictive case (Case 5) where two interaction parameters per isotherm are used.

A summary of the overall results is presented below for five supercritical fluids (carbon dioxide, methane, ethane, carbon monoxide and hydrogen) with n-paraffins. Detailed evaluation

for hydrogen + n-paraffins is included in the following section to exemplify the EOS evaluation effort we have undertaken.

For each case described in Table XIII, interaction parameters for both SRK and PR equations of state were obtained along with the predicted Henry's constants [25]. As indicated by Table XIII the SRK and PR equations of state are capable of representing the phase behavior of carbon dioxide, methane, ethane, carbon monoxide and hydrogen in n-paraffin systems. The results indicate that the progression in accuracy parallels the level of complexity of the model, i.e., the more interaction parameters, the better the fit. A good representation of the experimental data can be achieved by using two binary interaction parameters for each binary system of each isotherm (Case 5 for both SRK and PR: RMSE = 0.4 bar and %AAD = 1.1 for CO₂ systems; RMSE = 0.4 bar and %AAD = 0.7 for C₁ systems; RMSE = 0.3 bar and %AAD = 1.1 for C₂ systems; RMSE = 0.6 bar and %AAD = 1.1 for CO systems; RMSE = 1.3 bar and %AAD = 1.2 for H₂ systems).

Table XIII reveals an interesting result in that while the predictive capability of the SRK on PR EOS without interaction parameters (Case 1) vary for the different solutes, on a relative basis, the deviations produced using two parameters per isotherm (Case 5) are about 1% for all solutes. The need for interaction parameters is dependent on the dissimilarity in the molecular species; the more dissimilarity in molecular type, the greater the need for C_{ij} and D_{ij}, and the larger the values observed for such parameters. This is well illustrated by carbon monoxide and hydrogen + n-paraffin systems, which show atypical values for C_{ij} and D_{ij}.

The predicted Henry's constants by the SRK and PR EOS are in good agreement with the experimental values when two interaction parameters are used per isotherm. The equations of state are nearly equivalent in predicting Henry's constants [25].

Hydrogen + n-Paraffin Systems

A summary of the results for the five evaluation cases described in Table XII, applied to hydrogen in n-paraffins using both the SRK and PR equations of state is given in Table XIV.

Detailed tables for each case containing the resultant interaction parameters along with their uncertainties, Henry's constants, and complete statistics are given elsewhere [25].

The raw prediction abilities (Case 1) of both SRK and PR equations of state are grossly inadequate to represent hydrogen binary systems (RMSE = 23.9 bar and %AAD = 17.9 for SRK; RMSE = 26.7 bar and %AAD = 20.2 for PR). The unsatisfactory results are attributed to the low critical temperature and pressure of hydrogen and the resultant negative value of the acentric factor. This may also explain the atypical values obtained for the interaction parameters. In contrast to the other supercritical fluids in n-paraffins, the use of a single interaction parameter for each binary mixture C_{ij} (CN) (Case 2) does not drastically improve the quality of fit (RMSE = 12 bar and %AAD = 7.1 for SRK; RMSE = 11 bar and %AAD = 6.4 for PR). It is worth mentioning that the binary data of hydrogen + n-octane requires a value of C_{ij} (CN) greater than 1 for both equations of state. Such a deficiency may be attributed to the fact that these data are at temperatures relatively close to the critical temperature of n-octane [50, 51]. As shown by Figures 20 and 21, it is difficult to suggest a constant value of C_{ij} for all hydrogen + n-paraffins. However, a value of 0.4 for C_{ij} seems reasonable for most of the systems. Marginal improvements are achieved when two interaction parameters, C_{ij} (CN) and D_{ij} (CN), for each binary system are employed (RMSE = 8.9 bar and %AAD = 7.0 for SRK; RMSE = 7.7 bar and %AAD = 6.1 for PR). On the other hand, significant improvements in the predictive abilities of both equations of state are achieved when C_{ij} (T) is used (Case 4; RMSE = 4.1 bar and %AAD = 3.3 for SRK; RMSE = 3.1 bar and %AAD = 2.4 for PR). The prediction capabilities of both equations of state reveal further improvement when both C_{ij} (T) and D_{ij} (T) are employed (Case 5; RMSE = 1.3 bar and %AAD = 1.2 for SRK; RMSE = 1.3 bar and %AAD = 1.1 for PR).

The level of improvements observed for Cases 4 and 5 strongly demonstrates the temperature dependence of the interaction parameters. The SRK and PR equations of state generally give comparable results in representing the experimental data to within their uncertainties, in general.

Experimental Henry's constants are available for various n-paraffin solvents with hydrogen, which permit an excellent assessment for the reliability of cubic equations of state to predict Henry's constant. Table XV provides such data along with those regressed from the Krichevsky-Kasarnovsky (KK) equation and those predicted by SRK and PR equations of state (Case 5). In addition, Figures 22 and 23 show the experimental and predicted (Case 5) Henry's constants by both equations of state for hydrogen in propane, n-butane, n-hexane, n-heptane, n-octane, n-decane and n-hexadecane, respectively. Typically, Henry's constants are measured at the saturation pressure of the solvent. However, in certain applications they are adjusted to zero pressure. For instance, to facilitate the comparison for hydrogen + n-butane system, the reported Henry's constants at zero pressure were adjusted to their respective values at the saturation pressure of n-butane.

Figures 22 to 23 demonstrate clearly the ability of both cubic equations of state to accurately predict Henry's constants for hydrogen binary systems over a wide range of temperature. As can be seen, Henry's constants uniformly fall with rising temperature over the entire temperature range. Such a trend may be attributed to the low critical temperature of hydrogen.

New EOS Development

Cubic equations of state often fail to adequately represent the phase behavior of asymmetric mixtures and mixtures containing polar components. Further, 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.

Further, molecular dynamics calculations have demonstrated that inadequacies currently exist in characterizing EOS parameters and their temperature dependence [50, 51]. For

example, the functional form of the parameter in the attractive term in the SRK and PR equations does not conform to theoretical limits at high temperatures [51]. This conclusion at the molecular level could shed light on the well-documented difficulty these equations have in describing the behavior of mixtures containing quantum gases (e.g., helium, hydrogen) [11, 52], since these gases are at extremely high (reduced) temperatures at typical processing conditions.

As another example, prior to our recent work [21], development of the SPHCT EOS included little or no attention to its near-critical behavior. Although this analytic EOS does, as expected, exhibit classical near-critical behavior, some improvements are possible by considering the critical constraints in defining the EOS parameters. The fact is clear that previous studies involving both cubic and PHCT equations of state [14, 53] have devoted inadequate attention to issues of EOS parameterization.

Efforts to develop theoretically-based equations capable of handling asymmetric mixtures of state have been made. 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. Recently developed equations of state such as the Perturbed-Hard-Chain Theory (PHCT) equation [54, 55], the Chain-of-Rotators (COR) equation [56], the Simplified Perturbed-Hard-Chain Theory (SPHCT) equation [16] and the Cubic Chain-of-Rotators (CCOR) equation [57, 58], which originated from statistical mechanics, have been proven useful in predicting the fluid phase equilibria of industrially important mixtures.

A simplified form of the PHCT equation (SPHCT equation) was proposed by Kim and coworkers [16]. They replaced the attraction term of the PHCT equation with the local composition model of Lee et al. [59]. 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 [14, 21]. Although this equation has the advantages of a segment-interaction model, it suffers from several shortcomings, such as its frequent failure 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 [14], and it yields worse vapor density predictions than those of the PR EOS [21]. A modification to improve the SPHCT EOS predictions was recently undertaken by Shaver [21]. The Modified SPHCT EOS is better than the original SPHCT EOS in representing equilibrium and volumetric properties for a variety of pure fluids.

The model development work reported in this section is focused on developing a simple EOS 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 of state. 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.

Detailed derivation of the equation is presented elsewhere [22]. The predictive capability of the new equation was 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 were compared to those of the other equations. Bubble point pressure calculations for binary mixtures of ethane + n-paraffins, CO₂ + n-paraffins, and hydrogen + n-paraffins with the new equation were performed. Comparisons were also undertaken with the PR, SPHCT and Modified SPHCT equations regarding representation of bubble point pressures for these binary mixtures. Following is a brief outline for the modeling efforts described in detail in the Ph.D. dissertation of J.K. Park [22].

A New Equation of State

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 [55] 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 [60]. 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 EOS.

The pressure explicit form of the new EOS may be written as:

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

where

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

$$\alpha = \alpha_0 (1 + \kappa_1 \tilde{T}^{1/2} + \kappa_2 \tilde{T} + \kappa_3 \tilde{T}^2 + \kappa_4 \tilde{T}^{-1}) \quad (3)$$

and

$$Y = \exp\left(\frac{1}{\tilde{T}}\right) - 1, \quad \tilde{T} = \frac{T}{T^*} \quad \text{and} \quad v_r = \frac{v}{v^*} \quad (4)$$

The new EOS shown in Equation (2) is fifth order in volume (or in compressibility factor). It was constructed to have a set of universal constants for all compounds (u , w , Q , α_0 , and $\kappa_1 - \kappa_4$) 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:

$$SS = \sum_{i=1}^N \left(\left(\frac{p_{\text{exp } i} - p_{\text{calc}}}{p_{\text{exp } i}} \right)^2 + \left(\frac{v_{l,\text{exp } i} - v_{l,\text{calc}}}{v_{l,\text{exp } i}} \right)^2 + \left(\frac{v_{v,\text{exp } i} - v_{v,\text{calc}}}{v_{v,\text{exp } i}} \right)^2 \right) \quad (5)$$

When vapor density data were not available, the last term of Equation (5) was omitted from the objective function. For the data set containing only T-p data, only the first term of Equation (5)

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 appearing in the objective function were obtained using the EOS.

The constants in the equation (u , w , Q , α_0 and $\kappa_1 - \kappa_4$) were obtained primarily 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 XVI, along with 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 [44].

To extend the use of the proposed EOS 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. For mixtures, the proposed EOS may expressed as:

$$Z = 1 + \frac{\beta_1 \tau \langle cv^* \rangle}{v - \beta_2 \tau \langle v^* \rangle} - \frac{\langle c\alpha Y v^* \rangle v}{v^2 + u \langle v^* \rangle v + w \langle v^* \rangle^2} - \frac{Q \langle c\alpha Y v^* \rangle}{v + \langle v^* \rangle} \quad (6)$$

where the angular brackets, $\langle \rangle$, signify a mixture quantity. The proposed mixing rules are similar to those of the SPHCT equation.

$$\langle cv^* \rangle = \sum_{i=1}^N \sum_{j=1}^N z_i z_j c_i v_{ji}^* \quad (7)$$

$$\langle v^* \rangle = \sum_{i=1}^N \sum_{j=1}^N z_i z_j v_{ij}^* \quad (8)$$

and

$$\langle \alpha Y v^* \rangle = \sum_{i=1}^N \sum_{j=1}^N z_i z_j c_i \alpha_{ij} \left(\exp \left(\frac{T_{ij}^*}{T} \right) - 1 \right) v_{ji}^* \quad (9)$$

where

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

$$\alpha_{ij} = \alpha_0 \left(1 + \kappa_1 \left(\frac{T}{T_{ij}^*} \right)^{1/2} + \kappa_2 \left(\frac{T}{T_{ij}^*} \right) + \kappa_3 \left(\frac{T}{T_{ij}^*} \right)^2 + \kappa_4 \left(\frac{T}{T_{ij}^*} \right)^{-1} \right) \quad (11)$$

$$T_{ij}^* = \frac{\epsilon_{ij} q_i}{c_i k} \quad (12)$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}) (1 + D_{ij}) \quad (13)$$

and

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} (1 - C_{ij}) \quad (14)$$

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.

Evaluation of the New EOS for Pure Fluids

Errors in the predicted vapor pressures for 21 selected compounds are shown in Table XVII 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 [21]. The comparisons shown in Table XVII 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 [14]. 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 XVII. 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. 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 comparable if not 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 XVIII and XIX. 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/cm³ and the overall %AAD is 3.54. For saturated vapor densities, the overall RMSE is 0.005 g/cm³ 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 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 24 shows the experimental and calculated phase envelope for propane, which is known for its wide temperature 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 near the critical point.

The EOS pure component parameters obtained are shown in Table XX. 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 CO_2 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 a function of carbon number in Figures 25 to 27. 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 in carbon number. 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 degree of correlation among the parameters.

Evaluation of the New EOS for Selected Binary Mixtures

A set of mixing rules has been proposed for the new EOS to extend its predictive capabilities to mixtures. The equation was evaluated using data for binary mixtures of ethane + *n*-paraffins, CO_2 + *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 CO₂ binaries were compared to those of the PR, SPHCT, and Modified SPHCT equations of state. 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 than or comparable to the PR, SPHCT and Modified SPHCT equations for both the ethane and CO₂ binary systems. For the hydrogen systems, the PR equation shows better performance than the new equation.

The cases studied are listed in Table XXI. 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 for hydrogen 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:

$$SS = \sum_{i=1}^N \left(\frac{p_{\text{expt}} - p_{\text{calc}}}{p_{\text{expt}}} \right)_i^2 \quad (15)$$

where p_{expt} and p_{calc} represent experimental and calculated bubble point pressures, respectively. Details of the regression technique and bubble point calculation method used in this work are described by Gasem [44].

a) 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 XXII. Detailed statistics for each isotherm of each binary mixtures are shown elsewhere [22]. 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 28 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.

b) CO₂ + Normal Paraffin Binaries

A summary of the bubble point pressure calculations for all cases studied is presented in Table XXIII. Detailed calculation results are shown elsewhere [22]. For the raw prediction case (Case 1), the new EOS 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 29 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 30 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 (C₂₀ 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 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 CO₂ [e.g., 61]. Second, in evaluating the new equation for CO₂ binaries, a common value of the square-well potential depth (ϵ) is used for all compounds. Actually, the attraction energy between CO₂ molecule and a normal paraffin segment is expected to be different. This assumption is considered likely to limit the capability of the equation [e.g., 62]. Third, the mixing rules applied in evaluating the CO₂ 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 CO₂ binaries.

c) Hydrogen + Normal Paraffin Binaries

The critical properties used in the evaluation of the PR equation are given in Table IX. In Cases 1 and 2, the new equation predicted a single phase for some higher pressure data points. Thus, 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 XXIV. Details are shown elsewhere [22].

The PR EOS shows significantly better performance than the new equation in Case 3 (%AAD of 4.5 and 33, respectively) while the equations are comparable in Case 4 (%AAD of 2.0 and 2.7, respectively). This indicates that the interaction parameter of the new equation is strongly dependent on temperature. The values of 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. Since hydrogen is a quantum gas, its molecular potential energy is expected to be significantly different from those of other compounds [62]. Thus, the phase behavior of systems involving hydrogen is different from other binary mixtures such as methane, ethane, CO₂ 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 in the hydrogen binary evaluations. The hard core radius and the potential well depth for hydrogen molecules are expected to be different from those of normal paraffin segments. In addition, as mentioned earlier in discussions dealing with CO₂ binary evaluations, the current mixing rules may not be adequate for the hydrogen binaries studied.

Summary

The EOS constants and the pure component parameters for selected compounds have been obtained for the new EOS. 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 showed better predictive capability than the PR and SPHCT in representing vapor pressures and saturated liquid and vapor densities 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.

A set of mixing rules has been proposed for the newly proposed EOS to extend its use to mixtures. The EOS was evaluated using the binary mixtures of ethane, CO₂, and hydrogen with n-paraffins. The systems selected contain simple mixtures such as ethane + n-butane and asymmetric mixtures such as ethane + n-tetradecane. For all binary systems studied, the new EOS has the capability to predict bubble point pressures within 3 %AAD with a single interaction parameter for each isotherm. For the binary systems of ethane and CO₂ with n-

paraffins, the bubble point pressure predictive capability of the new equation is comparable 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 PR model based on molecule interactions (Case 4). This indicates that models based on segment interactions are more suitable for asymmetric mixtures such as ethane and n-paraffin mixtures. For CO₂ binaries, the equations based on segment interactions do not do as well as for the 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 CO₂ 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 improved representation of mixtures. Efforts should be made to eliminate the temperature dependence of the interaction parameter. The databases selected in the evaluations of the equation are limited to binary mixtures involving ethane, CO₂ and hydrogen with n-paraffin solvents. Further evaluations of the EOS using diverse systems are recommended.

CONCLUSIONS

Solubility data were obtained on twenty-two binary mixtures of the solutes CO, hydrogen, and nitrogen in a series of paraffinic, naphthenic and aromatic solvents (decane, eicosane, octacosane, hexatriacontane, cyclohexane, decalin, benzene, naphthalene, phenanthrene, pyrene). The measurements were conducted at temperatures from 310 to 433 K, pressures to 22 MPa, and solute mole fraction from 0.01 to 0.3. Estimated errors of the measured gas solubilities in the selected solvents are less than 0.001. In addition, vapor-liquid equilibrium measurements were obtained for the phase compositions and phase densities of CO₂ + decane,

CO₂ + trans-decalin, and ethane + 1-methylnaphthalene binary mixtures at 344.3 K and pressures up to the mixture critical points. These phase density data complement the previous measurements at Oklahoma State University for CO₂ solubilities in n-paraffins, naphthenes and aromatics. In general, the newly acquired data agree well with the available literature data.

The solubilities of CO, hydrogen, and nitrogen in paraffinic, naphthenic and aromatic hydrocarbons are described well by the SRK and PR EOS. The precision of these descriptions varies; average errors are about 0.002 mole fraction when a single interaction parameter, C_{ij} , is used for each isotherm and 0.001 when two interaction parameters are employed for each isotherm.

The experimental data acquired in this project can (a) serve as an excellent basis for determining parameters in any selected phase behavior model, (b) provide valuable information for the development of improved EOS models, and (c) improve our understanding of the phase behavior of hydrocarbon mixtures involving CO, hydrogen, or nitrogen. Moreover, our systematic studies of selected solutes in a series of solvents from the same molecular class facilitate generalized predictions that may encompass mixtures for which experimental data are lacking.

Expressions for Henry's constant have been derived from a generalized cubic EOS. Five cases were used in the EOS evaluations through the use of bubble point pressure calculations. For each case, interaction parameters along with Henry's constants were obtained for both equations. The SRK and PR EOS are capable of representing the phase behavior of CO₂, CO, methane, ethane, and hydrogen in n-paraffins. The equations of state are nearly equivalent in predicting Henry's constants. The predicted Henry's constants from both equations are in good agreement with the experimental values. The interaction parameters, Henry's constants provided by this work are useful for both practical applications and basic understanding of solution thermodynamics of the system studied.

We have also investigated several modifications to the simplified-perturbed-hard-chain theory (SPHCT) EOS. Sensitivity analyses of the original EOS parameters were done to aid in

the EOS modifications. Also, a phenomenological volume translation, similar to that introduced by Chou and co-workers, was developed to improve the prediction of both vapor and liquid phase densities. These modifications resulted in a significant improvement in the prediction of pure-fluid and mixture saturation properties, including vapor pressures, phase compositions and phase densities. The modified EOS is comparable to the original SPHCT equation in predicting the bubble point pressures of ethane + n-paraffin mixtures with the modified equation providing improved results in the *a priori* predictive (no interaction parameters) mode. Simple correlations have been developed to represent the critical point constraints without the need of solving the complicated critical point constraint equations. The modified equation provides poorer results than the original SPHCT equation for the prediction of CO₂ + n-paraffin systems. This is attributed to deficiencies in the partition function in the original framework and the resulting uncertainties in the mixing rules used.

Further, a new EOS was proposed based on the generalized van der Waals partition function for chain-like molecules. The repulsive term of the EOS utilizes an existing free volume expression for hard spheres, and the attractive term is 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 are introduced to amend the low-density limiting radial distribution function. In addition, a set of mixing rules was proposed to extend the use of the new equation to mixtures.

The predictive capability of the equation was compared to those of the PR, the SPHCT and Modified SPHCT EOS. Vapor pressures, and saturated liquid and vapor densities of a variety of pure fluids as well as bubble point pressures of selected binary mixtures were used in model comparison. The new EOS gives better predictions for pure-fluid vapor pressures and saturated densities than the PR and SPHCT EOS, and has comparable capability to the Modified SPHCT EOS. EOS evaluations involving ethane + n-paraffin and carbon dioxide + n-paraffin mixture predictions suggest that the new equation is best among the equations considered for *a priori* predictions.

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NOMENCLATURE

$a(T)$	Energy parameter in the SRK or PR EOS
b	Molecular size parameter in the SRK or PR EOS
c	Degrees of freedom parameter
C_{ij}, D_{ij}	Binary interaction parameters
$H_{1,2}$	Henry's constant of solute 1 in solvent 2
f_i	fugacity of component 1
k	Boltzmann constant
n	Number of data points, number of moles
N	Number of components in mixture, total number of molecules
p	Pressure
Q, u, w	Equation of state constants in Eq. (2)
R	Gas constant
SS	Objective function (defined in Eq. (9))
T	Temperature
$\tilde{T}$	Reduced temperature (T/T^*)
v	Molar volume
x	Liquid phase mole fraction
Y	Temperature dependent function in the new equation of state at low density limit
Z	Compressibility factor
z	Mole fraction

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
ε	Characteristic energy parameter
φ_1	Fugacity coefficient of component 1
η	Reduced density ($\tau v^*/v$)
κ	Acentric factor dependent parameter in cubic equations of state; equation of state constant
σ	Radius of hard sphere
τ	Geometrical constant (0.74048)
ω	Acentric factor

Subscripts

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

Superscript

*	Characteristic parameter

APPENDIX A
SRK and PR EOS Data Correlation

EOS Data Correlation

The SRK [8] and PR [9] cubic equations of state were used to correlate the experimental data. The SRK equation is given below; similar relations are given elsewhere for the Peng-Robinson equation [9].

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

where

$$a(T) = a_c \alpha(T) \quad (2)$$

$$b = 0.08664 RT_c / P_c \quad (3)$$

and

$$a_c = 0.42748 R^2 T_c^2 / P_c \quad (4)$$

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

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \quad (6)$$

To apply the SRK or PR equations of state to mixtures, the values of a and b can be determined using the mixing rules (4)

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

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

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". Values of these parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared errors in predicted

bubble point pressures

$$SS = \sum_i^n (P_{\text{exp}} - P_{\text{calc}})_i^2 \quad (9)$$

Further details of the data reduction techniques used in this study are given by Gasem [13]. 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.

APPENDIX B
TABLES AND FIGURES

TABLE I
BINARY VAPOR-LIQUID PHASE
EQUILIBRIUM DATA MEASURED AT OSU

SOLVENTS	SOLUTES*					
	<u>Carbon Monoxide</u>	<u>Hydrogen</u>	<u>Nitrogen</u>	<u>Methane</u>	<u>Ethane</u>	<u>Carbon Dioxide</u>
Paraffins						
n-C ₄						pTxy $\rho^L\rho^V$
n-C ₆	pTx	pTx	pTx	pTx	pTx	pTx
n-C ₁₀	pTx	pTx	pTx	pTx	pTxy $\rho^L\rho^V$	pTxy $\rho^L\rho^V$
n-C ₁₂	pTx	pTx		pTx	pTx	pTx
n-C ₁₄	pTx	pTx		pTx	pTx	pTxy $\rho^L\rho^V$
n-C ₂₀	pTx	pTx	pTx	pTx	pTx	pTx
n-C ₂₈	pTx	pTx	pTx	pTx	pTx	pTx
n-C ₃₆	pTx	pTx	pTx	pTx	pTx	pTx
n-C ₄₄				pTx	pTx	pTx
Naphthenes						
Cyclohexane	pTx	pTx		pTx	pTx	pTxy $\rho^L\rho^V$
trans-Decalin	pTx	pTx		pTx	pTxy $\rho^L\rho^V$	pTxy $\rho^L\rho^V$
Aromatics						
Benzene	pTx	pTx		pTx	pTxy $\rho^L\rho^V$	pTxy $\rho^L\rho^V$
Naphthalene	pTx	pTx		pTx	pTx	pTx
1-Methylnaphthalene					pTx	pTxy $\rho^L\rho^V$
Phenanthrene	pTx	pTx		pTx	pTx	pTx
Pyrene	pTx	pTx		pTx	pTx	pTx

Typical Measurement Conditions: Temperatures of 300–425 K and Pressures to 20.0 MPa

p = pressure; T = temperature; x, y = liquid and vapor mole fractions; ρ^L, ρ^V = liquid and vapor phase densities

TABLE II
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+

TABLE III

Solubility of Carbon Monoxide (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Decane			
310.9 K			
0.0448	2.84	0.1097	7.57
0.0873	5.81	0.1247	8.78
0.0953	6.45	0.1399	10.00
344.3 K			
0.0385	2.36	0.0883	5.64
0.0538	3.30	0.1171	7.69
0.0770	4.85	0.1363	9.15
377.6 K			
0.0388	2.22	0.1197	7.37
0.0619	3.62	0.1400	8.81
0.0895	5.39	0.1599	10.20
Eicosane			
323.2 K			
0.0516	2.80	0.0902	5.16
0.0645	3.56	0.1024	6.05
0.0797	4.51	0.1136	6.78
373.2 K			
0.0403	1.99	0.0899	4.72
0.0516	2.58	0.1107	5.93
0.0715	3.65	0.1308	7.24
423.2 K			
0.0616	2.83	0.1205	5.94
0.0761	3.57	0.1590	8.24
0.1004	4.83	0.1593	8.27
0.1187	5.86	0.1614	8.38

TABLE III (Continued)

Solubility of Carbon Monoxide (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Octacosane			
348.2 K			
0.0553	2.33	0.1014	4.62
0.0604	2.55	0.1320	6.37
0.0854	3.82	0.1493	7.57
373.2 K			
0.0463	2.01	0.1131	5.02
0.0577	2.42	0.1463	6.80
0.1005	4.42		
423.2 K			
0.0551	2.19	0.1623	7.08
0.1027	4.18	0.1853	8.41
0.1315	5.59		
Hexatriacontane			
373.2 K			
0.0494	1.80	0.1192	4.75
0.0634	2.34	0.1603	6.76
0.0899	3.44	0.2002	8.95
423.2 K			
0.0568	1.85	0.1289	4.66
0.0705	2.37	0.1742	6.61
0.1040	3.60	0.2099	8.40
Benzene			
323.2 K			
0.0099	1.47	0.0478	7.33
0.0197	2.94	0.0546	8.42
0.0296	4.45	0.0597	9.26
0.0398	6.04		
373.2 K			
0.0103	1.41	0.0371	4.70
0.0150	1.98	0.0450	5.68
0.0212	2.71	0.0516	6.51
0.0340	4.29	0.0637	8.05

TABLE III (Continued)

Solubility of Carbon Monoxide (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
433.2 K			
0.0148	2.12	0.0428	4.86
0.0252	3.13	0.0548	6.05
0.0398	4.56	0.0590	6.46
Naphthalene			
373.2 K			
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			
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		
Phenanthrene			
383.2 K			
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			
0.0231	5.47	0.0652	16.84
0.0249	5.94	0.0732	19.22
0.0436	10.78		
Pyrene			
433.2 K			
0.0247	6.65	0.0502	14.26
0.0284	7.71	0.0634	18.57
0.0472	13.38	0.0696	20.68

TABLE IV

**SRK and PR Equation-of-State Representations
of the Solubility of Carbon Monoxide (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction*	
	C ₁₂	D ₁₂	RMS	MAX
Decane				
310.9	0.1356	-0.0031	0.0003	0.0005
	(0.1378)	(-0.0023)		
	0.1204		0.0003	0.0007
	(0.1280)			
344.3	0.1115	-0.0004	0.0002	0.0003
	(0.1220)	(-0.0019)		
	0.1094		0.0002	0.0003
	(0.1137)			
377.6	0.0800	0.0043	0.0002	0.0004
	(0.1025)	(0.0004)		
	0.1006		0.0003	0.0005
	(0.1008)			
310.9, 344.3 and 377.6	0.1104	0.0007	0.0014	0.0032
	(0.0676)	(0.0118)		
	0.1136		0.0014	0.0032
	(0.1184)			
Eicosane				
323.2	0.2772	-0.0113	0.0003	0.0006
	(0.2698)	(-0.0112)		
	0.1602		0.0006	0.0009
	(0.1686)			
373.2	0.2257	-0.0105	0.0002	0.0004
	(0.2305)	(-0.0123)		
	0.1166		0.0006	0.0009
	(0.1214)			
423.2	0.2292	-0.0140	0.0002	0.0002
	(0.2419)	(-0.0185)		

TABLE IV (Continued)

**SRK and PR Equation-of-State Representations
of the Solubility of Carbon Monoxide (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction*	
	C ₁₂	D ₁₂	RMS	MAX
	0.0873 (0.0862)		0.0008	0.0012
323.2, 373.2 and 432.2	0.1439 (-0.1557)	-0.0018 (0.0323)	0.0040 (0.0053)	0.0072 (0.0113)
	0.1253 (0.1271)		0.0041 (0.0052)	0.0073 (0.0096)
Octacosane				
348.2	0.4522 (0.4341)	-0.0258 (-0.0270)	0.0005	0.0009
	0.0935 (0.1128)		0.0027	0.0038
373.2	0.1498 (0.1701)	-0.0071 (-0.0084)	0.0002	0.0004
	0.0438	(0.0699)	0.0008	0.0018
423.2	0.1413 (0.1711)	0.0100 (-0.0130)	0.0008	0.0011
	0.0031	(0.0239)	0.0012	0.0019
348.2, 373.2 and 423.2	0.0427 (-0.0142)	-0.0013 (0.0051)	0.0028	0.0050
	0.0246 (0.0448)		0.0030	0.0051
Hexatriacontane				
373.2	0.1966 (0.2185)	-0.0115 (-0.0127)	0.0001	0.0002
	0.0073 (0.0431)		0.0024	0.0028

TABLE IV (Continued)

**SRK and PR Equation-of-State Representations
of the Solubility of Carbon Monoxide (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction*	
	C_{12}	D_{12}	RMS	MAX
423.2	0.1328 (0.1688)	-0.0148 (-0.0172)	0.0005	0.0008
	-0.1154 (0.0672)		0.0026	0.0034
373.2 and 423.2	0.3102 (0.2199)	-0.0212 (-0.0162)	0.0068 (0.0075)	0.0117 (0.0116)
	-0.0409 (-0.0021)		0.0080 (0.0085)	0.0114 (0.0152)
Benzene				
323.2	0.0953 (0.1157)		0.0002	0.0003
373.2	0.0700 (0.0886)		0.0002	0.0003
433.2	0.0803 (0.0886)		0.0001	0.0002
323.2, 373.2 and 433.2	0.0884 (0.1070)		0.0008	0.0023
Naphthalene				
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 (0.1466)		0.0007 0.0009	0.0019 0.0023

TABLE IV (Continued)

**SRK and PR Equation-of-State Representations
of the Solubility of Carbon Monoxide (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction*	
	C_{12}	D_{12}	RMS	MAX
Phenanthrene				
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
Pyrene				
433.2	0.2158 (0.2551)		0.0003	0.0004

* Errors are essentially the same for the SRK and PR EOS whenever not mentioned.

TABLE V
Solubility of Hydrogen (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Decane			
344.3 K			
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			
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			
0.0435	3.71	0.0914	8.13
0.0561	4.82	0.1232	11.32
0.0851	7.48	0.1264	11.66
Eicosane			
323.2 K			
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			
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			
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 V (Continued)

Solubility of Hydrogen (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Octacosane			
348.2 K			
0.0452	3.53	0.1139	9.59
0.0764	6.14	0.1296	11.11
0.0895	7.31	0.1487	13.10
373.2 K			
0.0572	4.02	0.1123	8.41
0.0614	4.34	0.1572	12.43
0.1076	8.00		
423.2 K			
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		
Hexatriacontane			
373.2 K			
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			
0.0720	3.56	0.1545	8.39
0.0881	4.42	0.1941	11.08
0.1355	7.24	0.2080	12.00
Benzene			
323.2 K			
0.0123	4.07	0.0290	9.80
0.0138	4.56	0.0351	11.97
0.0245	8.22	0.0455	15.73

TABLE V (Continued)

Solubility of Hydrogen (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
373.2 K			
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			
0.0207	4.05	0.0400	7.40
0.0254	4.85	0.0569	10.44
0.0381	7.07	0.0585	10.73
Naphthalene			
373.2 K			
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			
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
Phenanthrene			
383.2 K			
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			
0.0187	5.89	0.0391	12.53
0.0226	7.14	0.0514	16.74
0.0354	11.31	0.0557	18.35
Pyrene			
433.2 K			
0.0158	5.17	0.0358	11.91
0.0185	6.05	0.0498	16.97
0.0325	10.80	0.0575	19.73

TABLE VI

**SRK and PR Equation of State Representations
of the Solubility of Hydrogen (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction		SRK Henry's Constant (PR Henry's Constant) MPa
	C ₁₂	D ₁₂	RMS	MAX	
Decane					
344.3	0.4200 (0.3935)		0.0011 (0.0008)	0.0015 (0.0011)	110.54 (112.14)
373.2	0.4685 (0.4135)		0.0008 (0.0005)	0.0011 (0.0010)	96.76 (98.43)
423.2	0.5835 (0.4620)		0.0008 (0.0004)	0.0012 (0.0006)	76.97 (78.59)
344.3, 373.2 and 423.2	0.4523 (0.4082)		0.0039 (0.0023)	0.0077 (0.0046)	
Eicosane					
323.2	0.3682 (0.3781)		0.0007 (0.0006)	0.0010 (0.0008)	94.35 (95.04)
373.2	0.3849 (0.3656)		0.0006 (0.0004)	0.0010 (0.0007)	77.18 (78.12)
423.2	0.4070 0.3490)		0.0005 (0.0002)	0.0008 (0.0004)	63.88 (72.25)
323.2, 373.2 and 423.2	0.3772 (0.3706)		0.0010 (0.0009)	0.0015 (0.0018)	
Octacosane					
348.2	0.2911 (0.3283)		0.0005 (0.0003)	0.0009 (0.0007)	72.25 (72.91)
373.2	0.2560 (0.2915)		0.0005 (0.0002)	0.0006 (0.0003)	64.98 (65.74)

TABLE VI (Continued)

**SRK and PR Equation of State Representations
of the Solubility of Hydrogen (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction		SRK Henry's Constant (PR Henry's Constant) MPa
	C ₁₂	D ₁₂	RMS	MAX	
423.2	0.1697 (0.2056)		0.0005 (0.0006)	0.0009 (0.0011)	53.21 (53.99)
348.2, 373.2 and 423.2	0.2518 (0.2850)		0.0031 (0.0043)	0.0056 (0.0072)	
Hexatriacontane					
373.2	0.0828 (0.1876)		0.0005 (0.0008)	0.0008 (0.0011)	56.38 (57.08)
423.2	-0.0560 (0.0695)		0.0005 (0.0008)	0.0007 (0.0013)	46.50 (47.19)
373.2 and 423.2	0.0425 (0.1509)		0.0050 (0.0059)	0.0052 (0.0097)	
Benzene					
323.2	0.3479 (0.3681)		0.0004 (0.0003)	0.0005 (0.0005)	306.13 (306.97)
373.2	0.4168 (0.3991)		0.0004 (0.0004)	0.0006 (0.0005)	214.89 (216.46)
423.2	0.5450 (0.4627)		0.0005 (0.0003)	0.0006 (0.0004)	1561.0 (1576.4)
344.3, 373.2 and 423.2	0.3818 (0.3861)		0.0028 (0.0019)	0.0058 (0.0039)	

TABLE VI (Continued)

**SRK and PR Equation of State Representations
of the Solubility of Hydrogen (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction		SRK Henry's Constant (PR Henry's Constant) MPa
	C ₁₂	D ₁₂	RMS	MAX	
Naphthalene					
373.2	0.3685 (0.3895)		0.0006 (0.0006)	0.0009 (0.0008)	306.50 (307.90)
423.2	0.4278 (0.4127)		0.0005 (0.0004)	0.0007 (0.0006)	238.31 (240.17)
373.2 and 423.2	0.3865 (0.3971)		0.0011 (0.0007)	0.0016 (0.0010)	
Phenanthrene					
383.2	0.3245 (0.3766)		0.0005 (0.0005)	0.0007 (0.0007)	353.61 (354.29)
423.2	0.3665 (0.3940)		0.0005 (0.0004)	0.0007 (0.0006)	291.33 (292.85)
383.2 and 423.2	0.3376 (0.3824)		0.0008 (0.0006)	0.0012 (0.0009)	
Pyrene					
433.2	0.4309 (0.4620)		0.0005 (0.0005)	0.0007 (0.0006)	305.33 (306.15)

TABLE VII

Solubility of Nitrogen (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Decane			
344.3 K			
0.0556	4.33	0.1178	9.84
0.0590	4.61	0.1202	10.06
0.0633	4.97	0.1539	13.40
0.1087	8.99	0.1578	13.81
377.6 K			
0.0568	4.05	0.1662	13.15
0.0689	4.97	0.1708	13.63
0.1158	8.73	0.1967	16.04
0.1271	9.66		
410.9 K			
0.0598	3.91	0.1343	9.25
0.0749	4.92	0.1690	11.99
0.1162	7.89	0.1894	13.61
Eicosane			
323.2 K			
0.0610	4.49	0.1292	10.61
0.0689	5.13	0.1413	11.90
0.0704	5.25	0.1789	16.22
0.0967	7.54	0.1866	17.23
373.2 K			
0.0629	4.03	0.1364	9.74
0.0715	4.61	0.1639	12.10
0.1199	8.33	0.1905	14.61
423.2 K			
0.0679	3.83	0.1445	8.89
0.0930	5.38	0.1728	11.09
0.1278	7.76	0.2121	14.24

TABLE VII (Continued)

Solubility of Nitrogen (1) in Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
Octacosane			
348.2			
0.0726	4.30	0.1900	13.70
0.1108	6.93	0.1909	13.70
0.1245	8.04	0.2181	16.47
0.1334	8.70		
373.2 K			
0.0862	4.87	0.1698	10.89
0.0988	5.63	0.2071	14.18
0.1466	9.08	0.2289	16.10
423.2 K			
0.0896	4.46	0.1951	11.07
0.1010	5.11	0.2320	13.94
0.1689	9.31	0.2578	16.01
Hexatricosane			
373.2 K			
0.1054	5.30	0.2089	12.23
0.1197	6.10	0.2628	16.81
0.1934	11.10	0.2749	17.99
423.2 K			
0.1185	5.28	0.2263	11.71
0.1240	5.56	0.2747	15.21
0.2040	10.22	0.2970	17.11

TABLE VIII

**SRK and PR Equation-of-State Representations
of the Solubility of Nitrogen (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction		SRK Henry's Constant (PR Henry's Constant) MPa
	C ₁₂	D ₁₂	RMS	MAX	
Decane					
344.3	0.2163		0.0006	0.0008	7180
	(0.2087)		(0.0005)	(0.0006)	7210
377.6	0.2118		0.0010	0.0015	6550
	(0.1991)		(0.0007)	(0.0010)	6630
410.9	0.2164		0.0013	0.0016	5930
	(0.1936)		(0.0008)	(0.0011)	6020
344.3, 377.6 and 410.9	0.2146		0.0011	0.0022	
	(0.2026)		(0.0013)	(0.0032)	
Eicosane					
323.2	0.3307		0.0002	0.0003	6680
	(0.3211)		(0.0002)	(0.0003)	6690
373.2	0.3153		0.0005	0.0010	5910
	(0.2956)		(0.0004)	(0.0007)	5970
423.2	0.3038		0.0006	0.0010	5190
	(0.2707)		(0.0004)	(0.0006)	5280
323.2, 373.2 and 423.2	0.3248		0.0018	0.0047	
	(0.3096)		(0.0038)	(0.0085)	
Octacosane					
348.2	0.3850	0.0048	0.0004	0.0007	5420
	(0.3925)	(0.0032)	(0.0004)	(0.0007)	(5420)
	0.4583		0.0009	0.0014	5290
	(0.4343)		(0.0006)	(0.0011)	(5330)

TABLE VIII (Continued)

**SRK and PR Equation-of-State Representations
of the Solubility of Nitrogen (1) in Hydrocarbons (2)**

T/K	SRK Parameters (PR Parameters)		Error in Mole Fraction		SRK Henry's Constant (PR Henry's Constant) MPa
	C_{12}	D_{12}	RMS	MAX	
373.2	0.3873	0.0049	0.0007	0.0011	5100
	(0.4019)	(0.0023)	(0.0007)	(0.0011)	(5090)
	0.4624		0.0009	0.0015	4980
	(0.4306)		(0.0007)	(0.0011)	(5040)
423.2	0.3178	0.0099	0.0004	0.0006	4530
	(0.3571)	(0.0050)	(0.0004)	(0.0006)	(4540)
	0.4672		0.0016	0.0022	4360
	(0.4177)		(0.0009)	(0.0011)	(4450)
348.2, 373.2 and 423.2	0.3779	0.0055	0.0010	0.0020	
	(0.3574)	(0.0057)	(0.0012)	(0.0024)	
	0.4611		0.0014	0.0028	
	(0.4300)		(0.0014)	(0.0039)	
Hexatriacontane					
373.2	0.3687	0.0126	0.0006	0.0009	4470
	(0.3958)	(0.0113)	(0.0006)	(0.0009)	(4480)
	0.6258		0.0033	0.0045	4120
	(0.5851)		(0.0029)	(0.0037)	(4170)
423.2	0.3712	0.0148	0.0004	0.0006	3930
	(0.4191)	(0.0115)	(0.0005)	(0.0006)	(3940)
	0.6731		0.0037	0.0048	3620
	(0.6059)		(0.0027)	(0.0034)	(3710)
373.2 and 423.2	0.3975	0.0119	0.0046	0.0072	
	(0.4543)	(0.0083)	(0.0027)	(0.0044)	
	0.6398		0.0056	0.0086	
	(0.5918)		(0.0035)	(0.0054)	

TABLE IX

Critical Pressure, P_c , Critical Temperature, T_c , and Acentric Factor, ω , Used in the SRK and PR Equations of State

Component	P_c /MPa	T_c /K	ω	Reference
Carbon Monoxide	3.494	132.9	0.0491	69
Hydrogen	1.300	33.2	-0.218	69
Nitrogen	3.390	126.3	0.0390	38
Decane	2.097	617.5	0.4885	44
Eicosane	1.117	770.5	0.8738	44
Octacosane	0.826	845.4	1.1073	44
Hexatriacontane	0.682	901.1	1.2847	44
Benzene	4.830	562.1	0.212	65
Naphthalene	4.052	748.4	0.302	66
Phenanthrene	3.300	873.2	0.540	67
Pyrene	2.600	938.2	0.830*	68

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

TABLE X
MODEL EVALUATION RESULTS
FOR SPHCT AND SRK EQUATIONS-OF-STATE

<u>Case *</u>	<u>Regressed</u>	<u>Bubble Point Pressure</u>				<u>Solubility</u>	
	<u>Parameter</u>	<u>RMSE. Bar</u>		<u>% Ave. Abs. Dev.</u>		<u>RMSE. Mol.Frn.</u>	
		SPCHT	SRK	SPCHT	SRK	SPCHT	SRK
----- Carbon Monoxide + n-Paraffins -----							
1	none	14.3	9.0	24.7	13.1	0.0312	0.0170
2	C _{ij}	3.0	5.6	4.6	8.4	0.0054	0.0102
3	C _{ij} (CN)	1.6	2.0	2.4	2.8	0.0030	0.0040
4	C _{ij} (CN,T)	0.5	0.5	1.1	1.0	0.0009	0.0012
----- Methane + n-Paraffins -----							
1	none	13.3	14.4	25.8	17.2	0.0583	0.0577
2	C _{ij}	4.9	1.9	7.1	3.2	0.0160	0.0085
3	C _{ij} (CN)	2.8	0.95	4.8	2.0	0.0096	0.0038
4	C _{ij} (CN,T)	0.93	0.58	2.0	1.3	0.0044	0.0026

*Case:

1. none   C_{ij} = 0; this represents "raw ability" of the cubic EOS, using the basic mixing rules with no interaction parameters; permits predictions from pure component data only.
2. C_{ij}   A single value of C_{ij} is used for the complete homologous series.
3. C_{ij} (CN)   A separate value of C_{ij} is determined for each binary system, independent of temperature; this is the most commonly employed EOS representation in the literature. (CN = carbon number)
4. C_{ij} (CN,T)   A separate value of C_{ij} is determined for each binary system at each temperature; this case permits C_{ij} to be temperature dependent.

TABLE XI
PURE-FLUID PROPERTIES USED IN EQUATION OF STATE
EVALUATIONS

Component	T_c (K)	p_c (bar)	ω
H ₂	33.2	13.0	-0.218
CO	132.9	35.0	0.066
CO ₂	304.1	73.8	0.239
C ₁	190.4	46.0	0.011
C ₂	305.4	48.8	0.099
C ₃	369.8	42.5	0.153
nC ₄	425.2	38.0	0.199
nC ₅	469.7	33.7	0.251
nC ₆	507.5	30.1	0.299
nC ₇	540.3	27.4	0.349
nC ₈	568.8	24.9	0.398
nC ₉	594.6	22.9	0.445
nC ₁₀	617.7	21.2	0.489
nC ₁₁	638.8	19.7	0.535
nC ₁₂	658.2	18.2	0.575
nC ₁₆	722.0	14.1	0.742
nC ₁₈	748.0	12.0	0.790
nC ₁₉	756.0	11.1	0.827
nC ₂₀	767.0	11.1	0.907
nC ₂₁	780.2	10.5	0.896
nC ₂₂	791.7	10.2	0.938
nC ₂₄	809.5	9.3	0.987
nC ₂₈	845.4	8.3	1.107
nC ₃₂	875.1	7.4	1.202
nC ₃₆	901.1	6.8	1.285
nC ₄₄	944.3	6.0	1.418

TABLE XII
SPECIFIC CASES USED IN EQUATION-OF-STATE MODEL EVALUATIONS

Case	Description
1. $C_{ij} = 0, D_{ij} = 0$	The "raw predictive ability" of the cubic equations of state, using basic mixing rules with no interaction parameters. This case permits predictions based on pure component data only.
2. $C_{ij}(\text{CN}), D_{ij} = 0$	A separate value of C_{ij} is determined for each binary system, independent of temperatures. This is the most commonly employed equations of state representation in the literature.
3. $C_{ij}(\text{CN}), D_{ij}(\text{CN})$	A separate value of C_{ij} and D_{ij} is determined for each binary system, independent of temperature. This case assesses the benefits of including a second interaction parameters.
4. $C_{ij}(T), D_{ij} = 0$	A separate value of C_{ij} is determined for each binary system at each temperature. This case permits C_{ij} to be temperature dependent.
5. $C_{ij}(T), D_{ij}(T)$	Separate values of C_{ij} and D_{ij} are determined for each binary system at each temperature. This case represents the ultimate correlative capability of the equations of state.

TABLE XIII**SUMMARY OF RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES:
SUPERCRITICAL FLUIDS + N-PARAFFINS**

CASE NUMBER	RMS Error in Bubble Point Pressure, bar (%AAD)				
	CO ₂	C ₁	C ₂	CO	H ₂
SOAVE-REDLICH-KWONG EQUATION OF STATE					
1	10.36 (21.6)	6.23 (10.4)	3.28 (9.2)	5.15 (8.0)	23.88 (17.9)
2	2.10 (4.7)	2.17 (3.4)	1.51 (5.0)	2.50 (4.3)	12.04 (7.1)
3	1.45 (3.5)	1.93 (3.1)	0.83 (2.6)	2.13 (3.9)	8.88 (7.0)
4	1.07 (2.9)	1.02 (1.9)	1.11 (4.0)	1.05 (1.6)	4.09 (3.3)
5	0.41 (1.1)	0.43 (0.7)	0.32 (1.1)	0.57 (1.1)	1.25 (1.2)
PENG-ROBINSON EQUATION OF STATE					
1	9.48 (20.1)	6.57 (10.9)	3.51 (9.9)	5.73 (8.7)	26.67 (20.2)
2	2.24 (4.9)	2.22 (3.4)	1.51 (4.7)	2.85 (4.8)	11.03 (6.4)
3	1.55 (3.7)	1.95 (3.1)	0.83 (2.7)	2.48 (4.3)	7.73 (6.1)
4	1.07 (2.9)	1.10 (1.9)	1.10 (4.0)	1.04 (1.5)	3.10 (2.4)
5	0.44 (1.1)	0.43 (0.7)	0.32 (1.1)	0.57 (1.0)	1.27 (1.1)

TABLE XIV**SUMMARY OF RESULTS FOR THE REPRESENTATION OF BUBBLE POINT PRESSURES: HYDROGEN + N-PARAFFIN SYSTEMS**

Case Number	BUBBLE POINT PRESSURE			
	RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD
SOAVE-REDLICH-KWONG EQUATION OF STATE				
1	23.88	-15.67	16.60	17.9
2	12.04	-3.22	7.08	7.1
3	8.88	-3.21	5.67	7.0
4	4.09	-1.35	2.60	3.3
5	1.25	0.05	0.76	1.2
PENG-ROBINSON EQUATION OF STATE				
1	26.67	-16.09	18.30	20.2
2	11.03	-2.33	6.37	6.4
3	7.73	-2.45	4.91	6.1
4	3.10	-0.89	1.89	2.4
5	1.27	0.06	0.76	1.1

TABLE XV
REPRESENTATION OF HENRY'S CONSTANTS
FOR HYDROGEN + N-PARAFFINS

CN	T(K)	H _{1,2} (bar)			
		EXP.	KK EQ.	SRK**	PR**
n-C4	327.7	1013 (46)	--	1011	1013
	344.3	864 (46)	--	831	844
	361.0	743 (46)	--	739	740
	377.6	634 (46)	--	632	640
	394.3	499 (46)	--	506	512
n-C6	277.6	1135 (47)	--	1205	1206
	311.0	1013 (47)	--	1159	1161
	344.2	922 (47)	--	1041	1044
	377.2	800 (47)	--	920	927
	411.2	709 (47)	--	731	733
	444.2	598 (47)	--	593	598
n-C7	424.2	679 (48)	--	690	693
	471.7	474 (48)	--	512	521
	498.9	418 (48)	--	391	396
n-C10	344.3	n.a.*	1147 (22)	1159	1169
	373.2	n.a.	994 (22)	1007	1008
	423.2	n.a.	813 (22)	798	800
	462.5	679 (49)	--	649	653
	503.4	537 (49)	--	547	552
	543.0	405 (49)	--	420	426
n-C20	323.2	n.a.	995 (22)	973	980
	373.2	n.a.	798 (22)	789	790
	423.2	n.a.	668 (22)	652	653
	473.6	n.a.	543 (30)	530	537
	573.3	n.a.	382 (30)	372	371
n-C28	348.2	n.a.	758 (22)	734	739
	373.2	n.a.	665 (22)	661	663
	423.2	n.a.	551 (22)	534	533
	473.3	n.a.	488 (30)	472	476
	573.2	n.a.	341 (30)	345	350

TABLE XV (Continued)

**REPRESENTATION OF HENRY'S CONSTANTS
FOR HYDROGEN + N-PARAFFINS**

CN	T(K)	H _{1,2} (bar)			
		EXP.	KK EQ.	SRK**	PR**
n-C36	373.2	n.a.	570 (22)	573	574
	423.2	n.a.	450 (22)	463	461
	473.1	n.a.	438 (30)	398	403
	573.2	n.a.	317 (30)	323	312

** Case 5

* n.a. = not available.

TABLE XVI
NEW 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

TABLE XVII
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-Methylnaphthalene	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 [21]

TABLE XVIII

COMPARISON OF PURE FLUID LIQUID 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	0.036	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 [21]

TABLE XIX

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 [21]

TABLE XX
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

TABLE XXI
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	$C_{ij}(\text{CN})$	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	$C_{ij}(\text{CN}, T)$	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, $D_{ij} = 0$.

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

Case Number	Peng-Robinson		SPHCT		Modified SPHCT		This work	
	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

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

Case Number	Peng-Robinson		SPHCT		Modified SPHCT		This work	
	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.

TABLE XXIV

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

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

- C/ - CLEANING FLUID CYLINDER
- C/R - 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

Figure 2. Schematic Diagram for Fluid Recirculation Phase Density Apparatus

Figure 3. Liquid and Vapor Phase Density Data from the Fluid Recirculation Apparatus

Figure 4. Solubility of Carbon Monoxide in Eicosane. $\circ$ 323.2 K; $\square$ 373.2 K; $\blacksquare$ 423.2 K.

Figure 5. Comparison of Solubilities for Carbon Monoxide in Eicosane.

This work: □ 323.2K, ○ 423.2K, △ 373.2K; Huang (30): ○ 373.2K

Figure 6. Comparison of Solubilities for Carbon Monoxide in Octacosane.

This work: □ 323.2K, ○ 373.2K; Huang (30): ◇ 373.2K

Figure 7. Comparison of Solubilities for Carbon Monoxide in Hexatriacontane at 373.2 K.

This work: □ 373.2K, △ 423.2K; Huang (30): ◇ 423.2K

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Figure 8. Comparison of Solubilities for Carbon Monoxide in Benzene at 433.2 K.

○ This work; □ Connolly (33)

Figure 9. Solubility of Hydrogen in Decane. ○ 344.2 K; □ 373.2 K; ■ 423.2 K.

Figure 10. Comparison of Solubilities for Hydrogen in Eicosane at 373.2 K.

○ This work; □ Huang (32)

Figure 11. Comparison of Solubilities for Hydrogen in Octacosane at 373.2 K.

○ This work; □ Huang (32)

Figure 12. Comparison of Solubilities for Hydrogen in Hexatriacontane at 373.2 K.

○ This work; □ Huang (32)

Figure 13a. Comparison of Hydrogen Solubilities in Benzene. $\circ$ 323.3 K $\square$ 373.2 K $\triangle$ 423.2 K This work; $\diamond$ 338.7 K $\bullet$ 394 K $\blacksquare$ 433.2 K Thompson; $\blacktriangle$ 436.5 $\blacklozenge$ 422.0 K Brainard; $\boxtimes$ 433.2 K Connolly; --- See Figure 13b

Figure 13b. 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; ⊠ 433.2 K Connolly

Figure 14. Comparison of Hydrogen Solubilities in Phenanthrene at 423.2 K. ○ This work; □ Malone

Figure 15. Solubility of Nitrogen in n -Decane

Figure 16. Deviation Plot of Nitrogen Solubilities in n-Decane at 344.3 K.

○ This work; Δ Azarnoosh and McKetta, □ Llave and Chung

Figure 17. Deviation Plot of Nitrogen Solubilities in n-Decane at 377.6 K.

○ This work; Δ Azarnoosh and McKetta

Figure 18. Deviation Plot of Nitrogen Solubilities in n-Decane at 410.9 K.

○ This work; Δ Azarnoosh and McKetta

Figure 19. SPHCT Interaction Parameters for Solute Gases in n-Paraffin Solvents

Figure 20. Binary Interaction Parameters for Supercritical Fluids in n-Paraffins Using Soave-Redlich-Kwong Equation of State (Case 2)

Figure 21. Binary Interaction Parameters for Supercritical Fluids in n-Paraffins Using Peng-Robinson Equation of State (Case 2)

Figure 22. Henry's Constants for Hydrogen + Butane System

Figure 23. Henry's Constants for Hydrogen + Decane System

Figure 25. Characteristic Temperatures of Normal Paraffins

Figure 26. Characteristic Volumes of Normal Paraffins

Figure 27. Degrees of Freedom Parameters of Normal Paraffins

Figure 28. Binary Interaction Parameters for the Ethane in n-Paraffins (Case 3)

Figure 29. Case 3 Binary Interaction Parameters for the Carbon Dioxide in n-Paraffins

Figure 30. Temperature-Dependent Interaction Parameters of the New Equation of State

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