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**PHASE EQUILIBRIUM DATA FOR DEVELOPMENT OF CORRELATIONS
FOR COAL FLUIDS**

Final Report for the Period September 15, 1986–September 15, 1990

**By
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**By
Oklahoma State University
Stillwater, Oklahoma**

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PROJECT TITLE: "Phase Equilibrium Data for Development of
Correlations for Coal Fluids"

PROJECT PERIOD: 15 September 1986 to 15 September 1990

SUMMARY

During the course of this project, solubility data were obtained for ethane in n-hexane (n-C₆), n-eicosane (n-C₂₀), n-octacosane (n-C₂₈), n-hexatriacontane (n-C₃₆), and n-tetratetracontane (n-C₄₄) over the temperature range 311 to 423 K and pressures to 10 MPa. Similar data were obtained on eleven binary mixtures of methane in a series of paraffinic, naphthenic, and aromatic solvents which include n-decane (n-C₁₀), n-C₂₀, n-C₂₈, n-C₃₆, n-C₄₄, cyclohexane, trans-decalin, benzene, naphthalene, phenanthrene, and pyrene. Temperatures, pressures, and solute mole fractions were in the range of 311 to 433 K, 0.7 to 11.3 MPa, and 0.02 to 0.35 mole fraction methane, respectively. To accommodate the methane mixtures and to expedite data acquisition, our stirred equilibrium cell solubility apparatus was modified. These modifications resulted in a number of improvements including: improved mixing, lower dead volume, and improved procedures for cleaning and degassing. The newly-acquired solubility data are well described by the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS).

As part of our model development efforts, three tasks were undertaken. First, an evaluation was completed of the abilities of the simplified-perturbed-hard-chain-theory (SPHCT) and the SRK equations of state to represent the phase behavior of both pure n-paraffins and mixtures involving ethane + n-paraffins. In general, comparable predictions of pure fluid properties (vapor pressures and saturated liquid densities) and phase compositions were obtained from the SPHCT and SRK EOS. For the heavier paraffins (n-C₂₀ and above); however, the SPHCT produces better results. Second, simple generalized correlations for the optimum SRK and PR EOS interaction parameters were developed for methane + n-paraffins (extending from C₃ to n-C₄₄) and methane + aromatics. The generalized EOS parameters result in bubble point pressure predictions with root-mean-square errors, RMSE, of 1.2 and 0.6 bar for methane + n-paraffins and methane + aromatics, respectively. Third, a new framework for the reduction and correlation of saturation properties, using a scaled-variable-reduced-coordinate approach, was developed. Correlations based on the proposed method result in precise representation of vapor pressures (percentage average absolute deviations, %AAD, within 0.1), saturated liquid densities (%AAD within 0.1) and saturated vapor densities (%AAD within 0.2) for diverse chemical species.

PHASE EQUILIBRIUM DATA FOR DEVELOPMENT OF CORRELATIONS FOR COAL FLUIDS

ABSTRACT

The effective design and operation of processes for conversion of coal to fluid fuels require accurate knowledge of the phase behavior of the fluid mixtures encountered in the conversion processes. Multiple phases are present in essentially all stages of feed preparation, conversion reactions, and product separation; knowledge of the behavior of these multiple phases is important in each step. The overall objective of the authors' work is to develop accurate predictive methods for representations of vapor-liquid equilibria in systems encountered in coal-conversion processes. The objectives pursued in the present project include:

- (1) Measurements of binary vapor-liquid phase behavior data for selected solute gases (e.g., C_2H_6 , CH_4) in a series of paraffinic, naphthenic, and aromatic hydrocarbon solvents to permit evaluations of interaction parameters in models for phase behavior. Solubilities of the gases in the liquid phase have been determined.
- (2) Evaluation of existing equations of state and other models for representations of phase behavior in systems of the type studied experimentally; development of new correlation frameworks as needed.
- (3) Generalization of the interaction parameters for the solutes studied to a wide spectrum of heavy solvents; presentation of final results in formats useful in the design/optimization of coal liquefaction processes.

During the course of this project, solubility data were obtained for ethane in n-hexane ($n-C_6$), n-eicosane ($n-C_{20}$), n-octacosane ($n-C_{28}$), n-hexatriacontane ($n-C_{36}$), and n-tetratetracontane ($n-C_{44}$) over the temperature range 311 to 423 K and pressures to 10 MPa [1,2]. Similar data were obtained

on eleven binary mixtures of methane in a series of paraffinic, naphthenic, and aromatic solvents which include n-decane (n-C₁₀), n-C₂₀, n-C₂₈, n-C₃₆, n-C₄₄, cyclohexane, trans-decalin, benzene, naphthalene, phenanthrene, and pyrene. Temperatures, pressures, and solute mole fractions were in the range of 311 to 433 K, 0.7 to 11.3 MPa, and 0.02 to 0.35 mole fraction methane, respectively. To accommodate the methane mixtures and to expedite data acquisition, our stirred equilibrium cell solubility apparatus was modified. These modifications resulted in a number of improvements including: improved mixing, lower dead volume, and improved procedures for cleaning and degassing. The newly-acquired solubility data are well described by the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS).

As part of our model development efforts, three tasks were undertaken. First, an evaluation was completed of the abilities of the simplified-perturbed-hard-chain-theory (SPHCT) and the SRK equations of state to represent the phase behavior of both pure n-paraffins and mixtures involving ethane + n-paraffins. In general, comparable predictions of pure fluid properties (vapor pressures and saturated liquid densities) and phase compositions were obtained from the SPHCT and SRK EOS. For the heavier paraffins (n-C₂₀ and above); however, the SPHCT produces better results [4]. Second, simple generalized correlations for the optimum SRK and PR EOS interaction parameters were developed for methane + n-paraffins (extending from C₃ to n-C₄₄) and methane + aromatics. The generalized EOS parameters result in bubble point pressure predictions with root-mean-square errors, RMSE, of 1.2 and 0.6 bar for methane + n-paraffins and methane + aromatics, respectively. Third, a new framework for the reduction and correlation of saturation properties, using a scaled-variable-reduced-coordinate approach, was developed [3]. Correlations based on the proposed method result in

precise representation of vapor pressures (percentage average absolute deviations, %AAD, within 0.1), saturated liquid densities (%AAD within 0.1) and saturated vapor densities (%AAD within 0.2) for diverse chemical species.

INTRODUCTION

The energy needs in the United States have provided strong impetus for the conversion of coal to liquid and gaseous products. Multiple phases exist during the feed preparation, conversion reactions, and product separation stages of coal conversion processes. For example, during initial stages of coal dissolution in a coal derived recycle solvent, many light gases (e.g., CH_4 , C_2H_6 , CO , CO_2 , H_2S , H_2O , NH_3) are produced. Therefore, effective design, operation, and optimization of coal conversion processes depend heavily on accurate knowledge of the phase behavior in the mixtures encountered in each step of the conversion and refining processes. Frequently quoted statistics [6] suggest that in conventional chemical plants 70% of the capital and 90% of the operating expenses are associated with phase separations. Almost uniformly, conferences on (and reviews of) data needs rate phase equilibrium data as a top-priority item [6-9].

Analytical models for the description of phase behavior are a necessity in process design and optimization calculations. Essentially all state-of-the-art models for phase behavior contain one [10,11], two [12,13] or three [14] interaction parameters to account for unlike molecular pair interactions. These parameters, in general, cannot be predicted a priori from existing theory, but they can be established from experimental measurements on the binary pairs which form the system of interest. These "empirical" interaction parameters have a dramatic effect on the predicted properties of mixtures and are thus required for accurate predictions. In most instances, successful modeling of the behavior of complex multicomponent mixtures requires accurate information on the pure compounds and on the binary interactions that exist between the different molecular species.

Experimental measurements made on systematically chosen mixtures can be used to evaluate EOS interaction parameters and, more importantly, furnish the basis for generalization of the parameters to allow interpolation (and perhaps extrapolation) to other solvents in the same homologous series. As a result, the primary goal of the present project has been to perform measurements of the solubilities of light gases (e.g., C_2H_6 and CH_4) in a series of systematically selected solvents from among the n-paraffins, naphthenes, and aromatic hydrocarbons. The specific experimental plan undertaken involved measuring C_2H_6 and CH_4 solubilities in a series of progressively heavier solvents of a given molecular class (e.g., for n-paraffins: n- C_{10} , n- C_{20} , n- C_{28} , n- C_{36} , n- C_{44}). To facilitate the CH_4 measurements necessitated some modifications on the solubility apparatus designed originally by Gasem [15]. These modifications resulted in a number of improvements including: improved mixing, lower dead volume, and improved procedures for cleaning and degassing.

Data taken purposely for parameter development in selected correlation frameworks need not be exhaustively definitive for each binary system. A few data points on each of a few isotherms can fix the parameters adequately. The critical need is for the systematic study of a series of carefully selected binary systems. This permits the resultant model parameters to be correlated (generalized) to provide parameters for systems which have not been measured [4,17,31]. Such generalizations are particularly important, since complete studies of all possible solute/solvents pairs is obviously infeasible. Over the course of this project, our newly-acquired data on C_2H_6 and CH_4 solubilities in heavy hydrocarbons, combined with reliable data from the literature, have been used to develop generalized-parameter correlations for the SPHCT and the SRK EOS.

Several results of this project have been reported or published elsewhere [1-4]. This final report is devoted mainly to results not yet published elsewhere, mainly the experimental study of methane solubilities in a series of heavy n-paraffins, naphthenes, and aromatics.

EXPERIMENTAL METHOD

The experimental apparatus used in this study (shown in Figure 1) is a modified version of the apparatus originally designed by Gasem [15], and most recently used by Raff [1,5]. A brief description of the modified apparatus and the experimental procedure, which is detailed elsewhere [18], is presented in this section.

The central part of the facility is a high-pressure, variable-volume, rocking equilibrium cell (EC), constructed from a 316 stainless steel tubular reactor (High Pressure Equipment Inc., Cat. No. MS-14) with an internal volume of 12.5 cc, a length of 10 in., inside diameter, ID, of 5/16 in. and outside diameter, OD, of 9/16 in. The equilibrium cell is connected at one "active" end to a simple pivoting assembly, while the other "dead" end is connected to an aluminum drive wheel, which is, in turn, driven by a 1/50 hp variable speed motor (Bodine Electric Company, type NSH-12R). The equilibrium cell is brought from a 45° above to 45° below the horizontal level at a controlled speed of about 15 rpm using a motor speed controller (Bodine Electric Company, model 901, type BSH-200). Injections of solvent, solute, and mercury to the cell were made through a 1/16 in. OD, 0.03 in. ID stainless steel tubing welded into the pivoted end of the cell. The effective volume of the cell can be varied by the introduction and withdrawal of mercury using a screw pump. Five steel balls 3/16 in. in diameter are housed inside the cell to further promote mixing. Thus, the mercury acts in combination with the steel balls inside the cell to give excellent mixing.

Unique features of the equilibrium cell just described are its size and simplicity; being small in volume, the cell can be cleaned efficiently, since all its contents are disposed of upon cleaning and no mercury from the previous run is retained in the cell for the next run, as was the case in our previous cells.

The quality of mixing obtained from the cell described above is superior to that of the previous cells, as revealed by the equilibration times. For methane + n-C₃₆, the equilibration time is less than five minutes, compared to more than 30 minutes in the stirred cell previously used in the apparatus.

The apparatus is designed specifically to accommodate heavy solvents (which may be solid at room temp.). This is accomplished by placing the solvent storage vessel (SV1) inside the high-temperature air bath. The reservoir is a high pressure reactor (High Pressure Equipment Inc., Model OC-3) which can be filled with solvent (liquid or solid) by removing the top of the bomb.

Injection of solvent (liquid at operating temperatures) is done volumetrically by injecting mercury at the bottom of the solvent storage vessel (SV1) using a 10 cc positive displacement pump (HP), (Temco Inc., Model 10-1-12H) thus displacing an equal quantity of solvent into the equilibrium cell (EC). Sequential injections of solute (CH₄) are also made volumetrically using a 25 cc positive displacement pump (GP), (Temco Inc., Model 25-1-10Hat). These pumps were rated to 10,000 psia with a resolution of 0.005 cc. The gas pump, GP, is filled directly with solute gas, while the hydrocarbon pump, HP, contains mercury and is used for two purposes. It can inject mercury into the solvent storage cell, SV1, thus displacing an equivalent volume of solvent to the equilibrium cell, or it can inject mercury directly into the equilibrium

cell, to provide a pressure-volume traverse of the mixture under study (described below).

After each injection of solute into the solvent in the equilibrium cell, the bubble point of the mixture is determined by varying the system volume (injecting mercury into the cell) and observing the break point in the pressure-volume relationship as the system passes from a two-phase to an all-liquid condition, as illustrated in Figure 2.

Temperature is controlled and measured within 0.05°C with a platinum resistance thermometer. Pressures are measured by precision transducers, PT1 and PT2, (Sensotec Inc., Model ST5E1890), calibrated periodically against a dead-weight tester (Ruska Instrument, Inc., Model 2400.1). The injection pumps and transducers are housed in an air bath in which the temperature is held at $50 \pm 0.05^\circ\text{C}$ using a proportional integral controllers (Halikainen, Model 1053 A).

Imprecision in the measured bubble point pressures depends on the specific mixture under study and is of the order of 0.3 bar (0.002 in mole fraction) for CH_4 + n-paraffins, light aromatics and naphthenic solvents and 0.9 bar (0.001 in mole fraction) for CH_4 + heavy (solid at room temperature) aromatic solvents. Detailed analysis of experimental errors is given elsewhere [18].

MATERIALS

All chemicals used in this study were provided by commercial suppliers, and no further purification was attempted. The chemicals studied in this work, together with their reported purities and suppliers, are presented in Table I.

EXPERIMENTAL RESULTS AND DISCUSSION

Ethane Systems

Our binary solubility data for ethane in n-paraffins (n-C₆, n-C₂₀, n-C₂₈, n-C₃₆, and n-C₄₄) have been published elsewhere [1,2].

Methane Systems

Methane solubilities in eleven solvents have been studied; the specific systems and temperatures are summarized in Table II. Differences in the lowest temperature at which the systems were studied were dictated by the melting points of the solvents, which are solid at room temperature. Typical data obtained in this study are shown in Figure 3. These results may be visualized as the solubility of CH₄ at a given pressure or, alternatively, the bubble point pressure of a mixture of a given composition. For each isotherm studied, the data represent a combination of at least two separate experimental runs. Such multiple runs provide a useful check on the data; any inconsistencies between runs can reveal experimental errors that might not be detected within a single run. The experimental data for methane systems appear in Tables III-XIII.

EOS DATA CORRELATION AND COMPARISONS

The experimental data have been correlated using the SRK [11] and PR [10] cubic EOS (see Appendix A for details). Optimum binary interaction parameters were obtained by minimizing the sum of squares of pressure deviations from the experimental values. Detailed procedure for data reduction is given by Gasem [15]. The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the SRK and PR EOS, together with the literature sources are presented in Table XIV. Literature

sources available on methane binaries investigated in this study, which are suitable for comparison purposes, are presented in Table XV.

Ethane + n-Paraffins

Equations-of-state representations for ethane in n-C₆, n-C₂₀, n-C₂₈, n-C₃₆, and n-C₄₄ have been analyzed previously, using the SRK and PR EOS [1,2].

Methane + n-Paraffins

The equation-of-state representations of the binary solubilities for methane + n-paraffins are documented in Tables XVI-XX. The equations are capable of describing the data with root-mean-square errors, RMSE, within 0.002 in mole fraction when a single pair of interaction parameters, C_{ij} and D_{ij} , is used over the complete temperature range for any system studied (except for methane + n-eicosane system which has an RMSE of 0.0036 in mole fraction). When two parameters are fitted to each isotherm, RMSE is less than 0.0015 for each system.

Comparisons of our results with those reported by various investigators appear in Figures 4-13. The comparisons are shown in terms of deviations of the solubilities from values predicted using the SRK EOS. Interaction parameters employed in the equation-of-state predictions were obtained by fitting our data for each isotherm in each system. In cases where the literature data are reported at temperatures different from ours, solubility prediction were obtained using temperature independent parameters, C_{ij} and D_{ij} , regressed from our data over the complete range of temperature for the system. This method of comparison was employed because the interaction parameters, C_{ij} and D_{ij} , when regressed simultaneously, did not always show a clear dependence on temperature, so interpolation between isotherms becomes difficult.

Figures 4-9 show comparisons for methane + n-decane. The data obtained from the new apparatus are in excellent agreement with those obtained from our old apparatus for methane + n-C₁₀ at 100, 160, and 220°F. As shown in Figures 4-6, the new solubilities are predicted within 0.001. Reasonable agreement is observed between the present study and that of Reamer [19] at temperatures of 160, 220 and 280°F; solubilities, as shown in Figures 5-7, agree within 0.003 over the whole pressure range of this study. However, the agreement is not as good at 100°F, as Figure 4 shows. At temperatures higher than 280°F the agreement is reasonable over the pressure range of this study.

According to Mohindra [20], Reamer's data at 100, 160, 220 were found to be thermodynamically inconsistent. The best agreement between this work and that of Reamer [20] is at 280°F where the solubilities, as shown in Figure 7, agree within 0.0015. Similarly, good agreement (solubility deviation within 0.002) between this study and that of Lin [21] is revealed by Figure 8. Except at very low pressures (< 100 psia), this study is in significant disagreement with those of Lavender [22] and Beaudoin [23], which were reported to be internally inconsistent [20]. Figure 9 shows solubility deviations for methane + n-decane when temperature-independent parameters, C_{1j} and D_{1j} , are used to fit the whole set of data of the present work; solubilities of methane in n-C₁₀ are predicted with RMSE within 0.002.

Comparison of methane + n-C₂₀ data appears in Figure 10. Equation-of-state parameters regressed from our data predict lower solubilities (higher bubble point pressures) for the 392°F isotherm and higher solubilities (lower bubble point pressures) for the 212°F isotherm than reported by Huang, et al. [24]. Solubilities, as Figure 10 reveals, agree within 0.0025 for the 212°F isotherm and 0.004 for the 392°F isotherm.

Comparisons for methane + n-C₂₈ and methane + n-C₃₆ are shown in Figures 11 and 12. The agreement between this study and that of Huang, et al. [25] for methane + n-C₂₈ (in terms of solubility deviation) is within 0.004 for the 212°F isotherm and 0.002 for the 392°F isotherm. For methane + n-C₃₆, the agreement between this work and that of Tsai, et al. [26] is within 0.004 mole fraction for the 212°F isotherm, and 0.003 mole fraction for the 392°F isotherm (Figure 12). For methane + n-C₄₄ no literature data are available for comparisons; the ability of the equations of states to represent our data is shown in Figure 13.

The effect of the molecular size of the paraffin solvent on the optimum interaction parameters is shown in Figure 14. The parameters, C_{ij} and D_{ij} , tend to increase linearly with carbon number (or, equivalently, with molecular weight). The effect of carbon number becomes more clear when optimizing only C_{ij} holding D_{ij} fixed (zero in this case) as Figure 15 shows. A constant value of 0.032 for C_{ij} , for the binary mixtures of methane in paraffinic solvents with carbon number less than or equal to 30, is suggested by Figure 15. For paraffinic solvents with higher carbon number, C_{ij} tends to increase linearly with carbon number for the set of critical properties and acentric factors used in this study. The corresponding RMSE in solubility are shown in the same graph.

The effects of temperature and carbon number on C_{ij} and D_{ij} , when regressed simultaneously, are shown in Figure 16. For a given binary mixture (except methane + n-C₂₈), C_{ij} increases with both temperature and carbon number. No general conclusion can be drawn regarding the effects of temperature and carbon number on D_{ij} for this case, as Figure 16 shows. When only C_{ij} is optimized (setting D_{ij} at zero), no pronounced effects of temperature and carbon number are noticed for the binary mixtures of methane

with n-C₁₀, n-C₂₀ and n-C₂₈ (Figure 17). However, for methane + n-C₃₆ and methane + n-C₄₄, C_{1j} increases with both, temperature and carbon number, which might be attributed to the uncertainty in the estimated critical properties of these solvents.

Methane + Naphthenes

The equation-of-state representations of the binary solubilities for methane + naphthenes are documented in Tables XXI and XXII. The PR EOS is capable of describing the data with RMSE within 0.002 in mole fraction when a single interaction parameters, C_{1j} , is used over the complete temperature range of the systems studied. Using an additional interaction parameter, D_{1j} , in the PR EOS produces no further improvements as shown in Tables XXI and XXII for the case of temperature-independent interaction parameters. In contrast, the SRK EOS does not represent the data as well and, as shown in the same tables, the PR equation with one parameter represents the data better than the SRK equation with two parameters. When two parameters are fitted to each isotherm, the RMSE is less than 0.0005 and the two equations give comparable representation of the data.

Comparisons of our results with those reported by various investigators appear in Figures 18-20. The comparisons are shown in terms of deviations of the solubilities from values predicted using the PR EOS. The available literature data for methane + cyclohexane are reported at temperatures different from ours. Therefore, the prediction of solubilities is performed using temperature independent parameters, C_{1j} and D_{1j} , obtained from our data.

Comparisons for methane + cyclohexane are shown in Figures 18 and 19. Good agreement (solubility deviation within 0.002) is observed between the present data and those of Reamer [27] at temperatures 160, 220, and 280°F. However, the agreement is not as good at 100 and 340°F, as shown in Figure

18. Excellent agreement is observed between this work and that of Schoch, et al. [28], at 220°F, where the solubility deviations are within 0.001 (Figure 19). Significant disagreement, however, is observed at 100 and 160°F as shown in Figure 19. Nothing definite can be said regarding the disagreement with those data of Sage [29], since they are outside the range of pressure of this study. For methane + t-decalin, no literature data are available for comparisons; the ability of the equations of state to represent our data is displayed in Figure 20.

The effects of temperature on C_{1j} and D_{1j} for methane + cyclohexane, when regressed simultaneously, are shown in Figure 21. The parameters exhibit a minimum at a temperature around 170°F, which is the same behavior observed when only one parameter, C_{1j} is regressed holding the other, D_{1j} , constant (zero in this case) as Figure 22 shows. These variations are, however, only slightly outside the uncertainties in the regressed parameter. The same trend is observed for the parameter C_{1j} regressed from Reamer's data (Figure 22). Also shown are the corresponding RMSE of our data and those of Reamer over the same pressure range. The high precision of the present data is evident from Figure 22.

When C_{1j} and D_{1j} for methane + t-decalin are regressed simultaneously, the two parameters exhibit opposite behaviors with temperature. While D_{1j} shows a minimum, C_{1j} exhibits a maximum as indicated in Figure 23. Simpler dependence of C_{1j} on temperature, for methane + t-decalin, is observed when only C_{1j} is optimized. In this case, C_{1j} shows a monotonic behavior with temperature as is shown in Figure 24.

The influence of the chemical structure of the solvent on the parameter C_{1j} is shown in Figure 25, where C_{1j} assumes higher values for the higher molecular weight solvent.

Methane + Aromatics

Equation-of-state representations of the solubilities for the systems under study are documented in Tables XXIII-XXVI. In general, the SRK and PR equations are capable of describing the data with RMSE of 0.0005 in mole fraction when a single interaction parameter, C_{ij} , is used over the complete temperature range. Methane + benzene is an exception; the RMSE is 0.0013 in mole fraction. For methane solubility in benzene, improved equation-of-state predictions are realized (RMSE = 0.0008) when an additional parameter, D_{ij} , is used, as indicated by results given in Table XXIII.

Comparisons of our results with those of various investigators appear in Figures 26-30. The comparisons are shown in terms of deviations of the solubilities from values predicted using the SRK EOS. Interaction parameters, C_{ij} or C_{ij} and D_{ij} , employed in the equation-of-state predictions were obtained by fitting our data over the complete temperature range of the system under study. The comparisons for the methane + benzene system are shown in Figures 26 and 27. Reasonable agreement (solubility deviations are within 0.004) is observed between our data and those of Lin, et al. [30] at 298°F (Figure 26). The best agreement observed is between the results of this work and those of Sage, et al. [29] at 160°F (Figure 31), where the solubility deviations are within 0.001. However, significant disagreement with Elbishlawi and Spencer [32], Legret, et al. [33], and Schoch, et al. [34] are seen in both figures.

Figures 28 and 29 show comparisons for methane + phenanthrene. These comparisons are shown in terms of both solubility deviation (Figure 28) and pressure deviations (Figure 29). Interaction parameters employed in the equation-of-state solubility prediction were obtained by fitting the data of Malone and Kobayashi [35], since their data cover a wider range of pressures

than do ours. The agreement between the two data sets is excellent. The maximum pressure deviation is shown to be within 10 psia, which is within the experimental error of the measured bubble point pressure [18]. Comparable solubility differences (Figure 28) are no greater than 0.0005.

For methane + naphthalene and methane + pyrene, no previous data are available for comparisons. The ability of the SRK and PR equations of state to precisely represent these data is illustrated by Figures 30-32. The low scatter in pressure and solubility deviations illustrate the high precision of the present data.

Figure 33 shows that the Soave interaction parameter, C_{1j} , for these systems is relatively insensitive to temperature. Figure 34 shows the effect of chemical structure on the lumped Soave interaction parameter, C_{1j} , (i.e., when a single value for C_{1j} is used over the complete temperature range of each system). A linear dependence of C_{1j} on the chemical structure is observed.

KRICHEVSKY-KASARNOVSKY ANALYSIS

In the range of methane mole fractions reported in this study, the binary solubilities of methane in heavy n-paraffins (n-C₁₀, n-C₂₀, n-C₂₈, n-C₃₆, and n-C₄₄,) and methane in heavy aromatics (naphthalene, phenanthrene and pyrene) are represented within 0.0015 and 0.0002 mole fraction, respectively, by the Krichevsky-Kasarnovsky (KK) equation [36] (definition of variables are given in the Nomenclature):

$$\ln(f_{\text{CH}_4}/x_{\text{CH}_4}) = \ln(H_{\text{CH}_4}) + (\bar{v}_{\text{CH}_4}^{\infty}/RT) (P - P_{\text{HC}}) \quad (1)$$

Values of the methane fugacity, f_{CH_4} , required for the KK equation were obtained from Bender's equation of state for methane [37], since the vapor phase is essentially pure methane.

Solubility data of this work for methane + n-paraffins and methane + aromatics, as well as those found in the literature, were analyzed using Equation 1, above. The regressed Henry's constants and the infinite-dilution partial molar volumes of methane are presented in Table XXVII. The solubility data of methane in cyclohexane, t-decalin, and benzene were excluded from this analysis because of the appreciable vapor pressures of these solvents at the reported temperatures.

MODEL DEVELOPMENT EFFORTS

Equations of state provide the most efficient method for correlating thermodynamic properties. Recently, intensive theoretical studies have been devoted to the development of equations of state useful in engineering applications. Consequently, a consensus is emerging that our current theoretical abilities permit us to seek models which are capable of describing accurately the phase behavior of a variety of chemical species exhibiting varying degrees of shape-size effects, polarity and association.

With this in mind, our choices of equations of state to represent the phase behavior of systems of interest in coal processing were guided by two basic considerations:

1. the practical need to incorporate our experimental findings in simple and industrially widely-used cubic equations of state such as the SRK and PR equations (see, 4, 17, 31), and
2. the need to develop equations of state which are theoretically more rigorous, thus potentially more capable of correlating both equilibrium and volumetric properties of asymmetric mixtures (see, 43-46, 4).

Two sets of model parameters are required for accurate EOS predictions; pure-substance parameters and "binary interaction" parameters. The first set

are the pure substance parameters, which are typically defined in terms of pure fluid properties such as T_c , P_c , and w (or characteristic temperature, pressure, and volume which are derived from saturation properties).

The literature contains numerous correlations [38-42] for predicting saturation properties; many of these correlations however suffer from a limited range of applicability and poor suitability for generalization. Furthermore, the need for specialized correlations for each saturation property amplifies the need for an efficient and reliable unified framework for the prediction of saturation properties. Toward this end, we have used the corresponding states theory to develop a unified framework for the correlation of saturation properties. Detailed description of this framework as it applies to vapor pressure, saturated liquid and vapor density predictions is given by Shaver et al. [3, 68].

The second set of parameters, the interaction parameters, are used to account for unlike-molecule pair interactions. These interaction parameters, which are known to have dramatic effects on the VLE predictive capability of the EOS, are a mixture property which must be determined from experimental measurements or from correlations based on such measurements. Therefore, experimental measurements were utilized to evaluate interaction parameters and, more importantly, they furnish the basis for generalization of the parameters to permit interpolations (and modest extrapolations) to other solvents in the same homologous series.

Over the course of the present project, three major tasks concerning model evaluation and development were completed, as described below.

Correlation of Pure Fluid Saturation Properties

A new framework for the reduction and correlation of pure-fluid saturation properties, using a scaled-variable-reduced-coordinate approach,

was developed. Correlations based on the proposed method result in precise representation of vapor pressures (%AAD within 0.1), saturated liquid densities (%AAD within 0.1) and saturated vapor densities (%AAD within 0.2) of diverse chemical species. These results have been published previously [68].

Evaluation of SPHCT and SRK EOS

An evaluation was completed of the abilities of the simplified-perturbed-hard-chain-theory (SPHCT) and the SRK EOS to represent the phase behavior of both pure n-paraffins and mixtures involving ethane + n-paraffins. The SPHCT EOS exhibits reasonable ability to represent vapor pressures and saturated liquid densities of n-paraffins extending from methane to n-C₆₄ (%AAD of 4 and 7%, respectively). For the ethane + n-paraffins binaries, in general, comparable predictions of phase compositions are obtained from the SPHCT and the SRK EOS. For the heavier paraffins (n-C₂₀ and heavier), however, the SPHCT EOS produces better results.

Simple generalized correlations have been developed for the SPHCT and SRK input variables (T^* , v^* , and c for SPHCT; T_c , p_c , and w for SRK). Using such correlations, a single parameter (C_{1j}) produces useful predictions for ethane in the complete n-paraffins series (RMSE of 1.5 bar bubble point pressures) including the heaviest members of the series.

Correlation of Methane Solubilities Using SRK and PR EOS

The ability of the Soave-Redlich-Kowong (SRK) and Peng-Robinson (PR) equations of state (EOS) to represent the phase behavior of binary mixtures of methane + n-paraffins and methane + aromatics has been evaluated. In this evaluation, our experimental data on the solubility of methane in five heavy n-paraffins (n-C₁₀, n-C₂₀, n-C₂₈, n-C₃₆ and n-C₄₄) and four aromatics

(benzene, naphthalene, phenanthrene, and pyrene), together with data from the literature, were used. The database used for this purpose, together with the literature sources, is shown in Table XXVIII. Optimum interaction parameters are presented for each system considered for a variety of cases--ranging from using a single interaction parameter, C_{ij} , to represent the full database to the most detailed case of employing two interaction parameters, C_{ij} and D_{ij} , for each isotherm in each specific system.

1. Model Evaluation

Seven different models were examined in this study. These are presented in Table XXIX where a systematic progression in complexity of the models is evident. These evaluations were performed using the SRK EOS; however, the conclusions drawn here apply equally well to the PR EOS since an equivalence in the phase behavior predictions from the two equations has been observed [17,18,47]. Generalization of the EOS parameters (discussed later) was performed for both the SRK and PR EOS.

Table XXX presents a summary of results for the cases described in Table XXIX, where definitions of the statistical quantities used to evaluate the results are given in the Nomenclature. The overall model statistics are given for the bubble point pressure predictions for the seven cases, for both methane + n-paraffins and methane + aromatics. Also, given in Table XXX is the RMSE in the predicted mole fraction when the interaction parameters are set at their optimum values for each evaluation case.

The results obtained for model evaluation reveal an increase in accuracy which parallels the complexity of the models employed. For SRK EOS, a gradual decrease in the RMSE in bubble point pressures for methane + n-paraffins, from 6.0 to 0.3 bar, is obtained in going from Case 1 ($C_{ij} = D_{ij} = 0$) to Case 7 ($C_{ij}(T); D_{ij}(T)$). Similarly, for methane + aromatics, the pressure RMSE is

reduced from 14.3 to 0.2 bar. Such results when expressed as "normalized RMSE", with respect to the best case (Case 7), NRMSE, show a twenty two-fold and a eighty four-fold reduction in the observed error deviation for methane + n-paraffins and methane + aromatics, respectively (see Table XXX).

2. Generalization of Interaction Parameters

Three different generalization procedures (explained in Table XXXI) were examined in this study. The generalizations were carried out employing both the SRK and PR EOS. The methane + n-paraffins database used in parameter-generalization is identical to the database employed in the evaluation cases considered previously. For methane + aromatics, however, only our data were considered, since the available literature data are not adequately described by our model. Coefficients for the generalized-parameter correlations are presented in Table XXXII for the three cases given in Table XXXI.

Table XXXIII presents a summary of results for the cases described in Table XXXI, where overall model statistics are given for the bubble point pressure predictions for both methane + n-paraffins and methane + aromatics.

Regarding generalization of the SRK and the PR EOS interaction parameter, C_{ij} , the simplest and most direct procedure is to use a single interaction parameter to represent the whole set of binaries of the same homologous series. This case of generalization (Case 1 in Table XXXI), however, is not capable of representing the phase behavior of n-paraffins and aromatics involving methane, as evident from Table XXXIII. The generalization given by Case 2 represents a compromise between simplicity and accuracy where bubble point pressures are predicted within 2 bars using a simple polynomial (second order in acentric factor) for C_{ij} .

Case 3 represents a working strategy of generalization regarding accuracy and simplicity where four parameters are needed to predict bubble point

pressures within 1.2 bar. The developed correlations for the co-volume parameter, b , (one for n-paraffins and another for aromatics) are purely empirical and are not recommended for uses other than those presented in this work.

Figure 35 presents the error profile for the generalized predictions and illustrates the molecular size effects on the quality of the predictions. As indicated in the figure, Case 1 is shown to work well for solvents below $n\text{-C}_{20}$, after which the RMSE in the predicted bubble point pressures increases rather linearly with the carbon number until it reaches about 17 bar for $n\text{-C}_{44}$. Results of Case 2 represent substantial improvements over those of Case 1 where the pressures are predicted with an RMSE less than 4 bar for the whole range of carbon numbers. The best results, however, are obtained from Case 3 where the RMSE in the predicted pressures is below 2 bar.

CONCLUSIONS

Solubility data were obtained for ethane in n-hexane ($n\text{-C}_6$), n-eicosane ($n\text{-C}_{20}$), n-octacosane ($n\text{-C}_{28}$), n-hexatriacontane ($n\text{-C}_{36}$), and n-tetratetracontane ($n\text{-C}_{44}$) over the temperature range from 311 to 423 K and pressures to 10 MPa. Similar data were obtained on eleven binary mixtures of methane in a series of paraffinic, naphthenic, and aromatic solvents which include $n\text{-C}_{10}$, $n\text{-C}_{20}$, $n\text{-C}_{28}$, $n\text{-C}_{36}$, $n\text{-C}_{44}$, cyclohexane, trans-decalin, benzene, naphthalene, phenanthrene, and pyrene. Temperatures, pressures, and solute mole fractions were in the general range of 311 to 433 K, 0.7 to 11.3 MPa, and 0.02 to 0.35 mole fraction CH_4 , respectively. The newly-acquired solubility data are well described by the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state (EOS).

Model development efforts involved three major tasks. First, an evaluation was completed of the abilities of the simplified-perturbed-hard-

chain-theory-theory (SPHCT) and the SRK equations of state to represent the phase behavior of both pure n-paraffins and mixtures involving ethane + n-paraffins. In general, comparable predictions of pure fluid properties (vapor pressures and saturated liquid densities) and phase compositions were obtained from the SPHCT and SRK EOS. For the heavier paraffins (n-C₂₀ and above), however, the SPHCT produces better results. Second, simple generalized correlations for the optimum SRK and PR EOS interaction parameters were developed for methane + n-paraffins (extending from C₃ to n-C₄₄) and methane + aromatics. The generalized EOS parameters result in bubble point pressure predictions with RMSE of 1.2 and 0.6 bar for methane + n-paraffins and methane + aromatics, respectively. Third, a new framework for the proper reduction and correlation of saturation properties, using a scaled-variable-reduced-coordinate approach, was developed. Correlations based on the proposed method result in precise representation of vapor pressures (%AAD within 0.1), saturated liquid densities (%AAD within 0.1) and saturated vapor densities (%AAD within 0.2) of diverse chemical species.

The data from this work should form a valuable basis for systematically evaluating other models that may be developed for description of phase behavior in systems of the type studied. Additional studies are needed to provide systematic data for other solutes of importance in the production and refining of coal-derived liquids.

NOMENCLATURE

A, B	correlation constants
a, b	equation of state parameters
AAD	absolute average deviation
c	"degrees of freedom" parameter
C_{ij} , D_{ij}	interaction parameters between components i and j in mixing rules for equations of state
f_{CH_4}	methane fugacity
H_{CH_4}	Henry's constant of methane in a hydrocarbon solvent
m	generalization parameter
P	pressure
P_{HC}	vapor pressure of hydrocarbon solvent
R	universal gas constant
RMSE	root mean square error
T	temperature
T^*	characteristic temperature
V	molar volume
$\bar{v}_{CH_4}^\infty$	infinite dilution methane partial molar volume
v^*	characteristic volume
x	mole fraction in the liquid phase

Greek Symbols

α	temperature function for parameter a
β	temperature function for parameter b
ω	acentric factor
σ	expected uncertainty

Subscripts

c	critical state
i, j	component index
r	reduced property

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Table I
Suppliers and Purities of Chemicals
Used in this Study

Chemicals	Supplier	Purity (molt)
Methane	Big 3 Industries, Inc.	99.97+
Ethane	Matheson	99.97+
Ammonia	Matheson	99.99+
n-Propane	Big 3 Industries, Inc.	99.99+
n-Pentane	Fisher Scientific	Spec. Grade
n-Decane	Aldrich Chemical Company	99.00+
n-Eicosane	Aldrich Chemical Company	99.00+
n-Octacosane	Aldrich Chemical Company	99.00+
n-Hexatriacontane	Aldrich Chemical Company	98.00+
n-Tetratetracontane	Alpha Morton Thiokol Inc.	96.00+
Benzene	J.T Baker Chemical Comp.	99.80+
Cyclohexane	Aldrich Chemical Company	99.90+
t-Decalin	Aldrich Chemical Company	99.00+
Naphthalene	Aldrich Chemical Company	99.00+
Phenanthrene	Aldrich Chemical Company	98.00+
Pyrene	Aldrich Chemical Company	99.00+

Table II
Binary Mixtures of Methane Studied in This Project

Solvent	Temperature Range, °F	Methane Mole Fraction Range, x_{CH_4}
n-C ₁₀	100 - 280	0.01 - 0.32
n-C ₂₀	122 - 302	0.04 - 0.25
n-C ₂₈	167 - 302	0.05 - 0.30
n-C ₃₆	212 - 302	0.05 - 0.30
n-C ₄₄	212 - 302	0.05 - 0.25
Benzene	122 - 302	0.03 - 0.17
Naphthalene	212 - 302	0.02 - 0.10
Phenanthrene	230 - 302	0.02 - 0.09
Pyrene	320	0.02 - 0.09
Cyclohexane	122 - 302	0.02 - 0.22
t-Decalin	122 - 302	0.02 - 0.20

Table III
Solubility Data for Methane in n-Decane (n-C₁₀)

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
310.9 K (37.8°C, 100°F)		
0.050	10.4	(151)
0.075	16.0	(232)
0.100	21.7	(315)
0.151	34.2	(495)
0.200	47.0	(682)
0.252	62.4	(905)
0.291	74.7	(1084)
0.308	80.4	(1166)
344.3 K (71.1°C, 160°F)		
0.051	12.2	(177)
0.074	17.9	(260)
0.096	23.9	(346)
0.127	32.1	(466)
0.154	39.5	(572)
0.201	53.5	(776)
0.227	61.7	(895)
0.248	68.7	(996)
377.6 K (104.4°C, 220°F)		
0.055	14.4	(209)
0.084	22.1	(320)
0.097	26.0	(377)
0.125	34.1	(495)
0.169	47.4	(688)
0.211	61.0	(884)
0.240	71.2	(1032)
0.276	83.5	(1212)
410.9 K (137.8°C, 280°F)		
0.074	20.6	(298)
0.126	35.8	(520)
0.152	43.7	(633)
0.176	51.5	(747)
0.202	60.2	(873)
0.226	68.6	(995)
0.251	77.5	(1124)
0.275	86.5	(1254)

Table IV
Solubility Data for Methane in n-Eicosane (n-C₂₀)

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
323.2 K (50.0°C, 122.0°F)		
0.051	9.5	(138)
0.099	18.9	(274)
0.119	23.2	(337)
0.150	30.2	(438)
0.177	36.8	(533)
0.212	45.5	(659)
373.2 K (100.0°C, 212.0°F)		
0.075	15.8	(230)
0.113	24.8	(359)
0.150	34.3	(498)
0.200	48.2	(699)
0.251	64.2	(930)
0.251	64.0	(929)
423.2 K (150.0°C, 302.0°F)		
0.074	16.8	(243)
0.156	38.5	(558)
0.200	51.6	(749)
0.250	67.7	(982)
0.251	67.9	(985)
0.275	76.7	(1113)
0.301	86.3	(1251)
0.350	106.9	(1550)

Table V
Solubility Data for Methane in n-Octacosane (n-C₂₈)

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
348.2 K (75.0°C, 167.0°F)		
0.057	9.3	(134)
0.084	13.6	(197)
0.137	23.8	(345)
0.149	26.1	(379)
0.199	37.2	(540)
0.237	46.3	(672)
0.252	50.2	(728)
373.2 K (100.0°C, 212.0°F)		
0.074	12.6	(183)
0.127	23.6	(343)
0.152	28.4	(413)
0.175	34.3	(498)
0.277	61.7	(895)
0.325	77.4	(1123)
423.2 K (150.0°C, 302.0°F)		
0.074	14.1	(204)
0.109	21.3	(308)
0.154	31.6	(458)
0.202	43.3	(628)
0.251	56.7	(822)
0.299	70.9	(1029)

Table VI
Solubility Data for Methane in n-Hexatriacontane (n-C₃₆)

Mole Fraction Methane	Bubble Point Pressure bar (psia)	
373.2 K (100.0°C, 212.0°F)		
0.057	8.7	(126)
0.138	22.7	(329)
0.168	28.0	(407)
0.232	42.1	(610)
0.260	48.6	(705)
0.266	49.5	(719)
0.315	63.7	(924)
423.2 K (150.0°C, 302.0°F)		
0.051	8.4	(122)
0.102	17.4	(253)
0.152	26.7	(387)
0.198	36.9	(535)
0.248	48.9	(709)
0.300	63.1	(915)
0.351	79.3	(1150)

Table VII

Solubility Data for Methane in n-Tetratetracontane (n-C₄₄)

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
373.2 K (100.0°C, 212.0°F)		
0.050	6.8	(98)
0.100	13.8	(200)
0.126	17.8	(256)
0.152	22.1	(321)
0.171	25.1	(363)
0.177	26.2	(379)
0.250	40.6	(589)
0.311	54.6	(792)
423.2 K (150.0°C, 302.0°F)		
0.086	12.5	(181)
0.121	18.1	(262)
0.157	24.2	(351)
0.211	34.2	(496)
0.254	43.7	(633)
0.279	48.9	(709)
0.304	55.7	(808)

Table VIII
Solubility Data of Methane in Cyclohexane

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
323.2 K (50.0°C, 122.0°F)		
0.042	14.1	(201)
0.069	23.5	(341)
0.098	33.4	(484)
0.124	42.5	(616)
0.155	54.0	(783)
0.174	61.0	(885)
0.207	73.8	(1071)
373.2 K (100.0°C, 212.0°F)		
0.029	12.5	(181)
0.052	20.9	(303)
0.083	32.4	(469)
0.100	39.1	(567)
0.138	54.0	(783)
0.152	59.1	(858)
0.178	70.2	(1018)
0.194	76.3	(1106)
0.201	79.4	(1151)
0.212	84.1	(1220)
423.2 K (150.0°C, 302.0°F)		
0.027	16.0	(232)
0.051	25.1	(365)
0.065	30.4	(441)
0.075	35.0	(508)
0.088	40.1	(582)
0.101	45.0	(653)
0.129	56.4	(818)
0.151	65.2	(945)
0.176	75.4	(1094)
0.201	85.9	(1246)
0.222	94.3	(1368)

Table IX
Solubility Data of Methane in t-Decalin

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
323.2 K (50.0°C, 122.0°F)		
0.026	8.9	(129)
0.050	17.5	(253)
0.075	26.6	(385)
0.100	36.7	(532)
0.134	50.1	(726)
0.150	57.3	(832)
373.2 K (100.0°C, 212.0°F)		
0.050	20.4	(296)
0.100	42.0	(609)
0.120	51.1	(741)
0.150	65.7	(953)
0.170	75.3	(1092)
0.180	81.1	(1176)
0.200	91.1	(1322)
423.2 K (150.0°C, 302.0°F)		
0.030	13.5	(196)
0.075	33.9	(492)
0.100	46.0	(667)
0.127	58.6	(850)
0.135	63.0	(914)
0.176	83.6	(1213)
0.200	96.2	(1396)

Table X
Solubility Data for Methane in Benzene

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
323.2 K (50.0°C, 122.0°F)		
0.028	14.6	(212)
0.053	28.0	(407)
0.075	39.7	(576)
0.114	61.4	(891)
0.119	64.0	(929)
0.134	72.3	(1049)
0.149	81.1	(1177)
0.167	90.9	(1318)
373.2 K (100.0°C, 212.0°F)		
0.029	17.3	(250)
0.039	22.6	(327)
0.061	34.2	(496)
0.075	42.1	(611)
0.100	55.6	(806)
0.126	69.8	(1012)
0.152	84.8	(1230)
0.164	91.4	(1326)
423.2 K (150.0°C, 302.0°F)		
0.029	20.5	(297)
0.032	22.2	(321)
0.055	34.2	(496)
0.074	43.8	(636)
0.103	59.2	(859)
0.115	65.3	(946)
0.145	80.9	(1174)
0.151	84.6	(1227)

Table XI
Solubility Data for Methane in Naphthalene

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
373.2 K (100.0°C, 212°F)		
0.025	19.6	(284)
0.030	24.0	(349)
0.050	40.6	(590)
0.064	53.0	(769)
0.086	73.5	(1065)
0.100	86.9	(1260)
423.2 K (150.0°C, 302.0°F)		
0.024	19.4	(281)
0.031	24.8	(360)
0.045	36.4	(528)
0.060	49.3	(715)
0.075	62.5	(907)
0.100	84.8	(1229)

Table XII
Solubility Data for Methane in Phenanthrene

Mole Fraction Methane	Bubble Point Pressure bar	(psia)
383.2 K (110.0°C, 230.0°F)		
0.020	20.4	(296)
0.030	31.6	(458)
0.044	48.3	(700)
0.060	67.3	(977)
0.071	81.7	(1185)
0.090	107.1	(1553)
423.2 K (150.0°C, 302.0°F)		
0.021	21.5	(312)
0.030	31.3	(454)
0.045	48.6	(705)
0.060	66.2	(960)
0.074	84.2	(1221)
0.090	104.6	(1517)

Table XIII
Solubility Data for Methane in Pyrene

Mole Fraction Methane	Bubble Point Pressure bar	(psia)
433.2 K (160.0°C, 320°F)		
0.020	23.5	(341)
0.035	42.3	(614)
0.049	60.4	(875)
0.060	75.8	(1099)
0.070	89.7	(1301)
0.075	97.1	(1408)
0.086	113.0	(1639)

Table XIV
Critical Properties and Acentric Factors Used
in the SRK and PR Equations of State

Component	Pressure (bar)	Temperature (K)	Acentric Factor	Reference
Methane	46.60	190.5	0.0110	48
n-C ₁₀	20.97	617.5	0.4885	49
n-C ₂₀	10.69	766.6	0.8941	50
n-C ₂₈	6.61	827.4	1.1617	50
n-C ₃₆	4.28	864.0	1.4228	50
n-C ₄₄	2.90	866.6	1.6664	50
Cyclohexane	40.66	553.4	0.213	51
t-Decalin	29.08	681.5	0.286	51
Benzene	48.98	561.7	0.225	52
Naphthalene	41.14	748.4	0.315	53
Phenanthrene	33.0	873.2	0.540	54
Pyrene	26.0	938.2	0.830 ^a	55

^a Ref. [56]

Table XV
Experimental Data for Methane + Hydrocarbons
Used for Comparison Purposes in This Study

Solvent	Temperature Range, °F	Methane Mole Fraction Range, x_{CH_4}	Reference Number
n-C ₁₀	320 - 460	0.10 - 0.40	21
	77 - 302	0.03 - 0.30	23
	100 - 280	0.00 - 0.32	19
	100 - 220	0.05 - 0.44	22
n-C ₂₀	212 - 392	0.05 - 0.20	24
n-C ₂₈	212 - 392	0.05 - 0.25	25
n-C ₃₆	212 - 392	0.06 - 0.27	26
Cyclohexane	100 - 220	0.10 - 0.30	28
	100 - 220	0.37 - 0.45	29
	70 - 240	0.04 - 0.30	27
Benzene	298 - 442	0.03 - 0.25	21
	100	0.20 - 0.53	34
	100 - 220	0.18 - 0.28	29
	150	0.01 - 0.21	32
	104	0.10 - 0.37	33
Phenanthrene	257 - 302	0.02 - 0.18	35

Table XVI

SRK and PR Equation-of-State Representations of
Solubility of Methane in n-Decane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	Mole Fraction RMS	MAX
310.9 (100.0)	0.054	-0.009	0.0003	0.0005
	(0.054)	(-0.008)		
	0.033		0.0019	0.0028
	(0.037)			
344.3 (160.0)	0.046	-0.007	0.0003	0.0005
	(0.045)	(-0.006)		
	0.028		0.0009	0.0013
	(0.030)			
377.6 (220.0)	0.054	-0.010	0.0003	0.0005
	(0.053)	(-0.010)		
	0.031		0.0012	0.0019
	(0.030)			
410.9 (280.0)	0.069	-0.015	0.0004	0.0007
	(0.067)	(-0.017)		
	0.035		0.0013	0.0019
	(0.030)			
310.9, 344.3 377.6, 410.3	0.057	-0.011	0.0007	0.0017
	(0.057)	(-0.011)		
	0.032		0.0017	0.0032
	(0.033)			

* Errors are essentially identical for the SRK and PR EOS

Table XVII
SRK and PR Equation-of-State Representations
of Solubility of Methane in n-Eicosane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
323.1 (122.0)	0.072	-0.008	0.0005	0.0007
	(0.069)	(-0.007)		
	0.029		0.0015	0.0024
	(0.031)			
373.1 (212.0)	0.096	-0.016	0.0002	0.0003
	(0.091)	(-0.016)		
	0.017		0.0032	0.0046
	(0.016)			
423.1 (302.0)	0.106	-0.020	0.0005	0.0008
	(0.101)	(-0.022)		
	0.021		0.0047	0.0067
	(0.015)			
323.1, 373.1 423.1	0.058	-0.008	0.0036	0.0070
	(0.039)	(-0.005)		
	0.022		0.0039	0.0066
	(0.019)			

* Errors are essentially identical for the SRK and PR EOS

Table XVIII

SRK and PR Equation-of-State Representations of
Solubility of Methane in n-Octacosane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
348.1 (167.0)	0.136	-0.013	0.0007	0.0016
	(0.127)	(-0.014)		
	0.033		0.0039	0.0056
	(0.029)			
373.1 (212.0)	0.170	-0.017	0.0009	0.0014
	(0.158)	(-0.018)		
	0.041		0.0057	0.0069
	(0.034)			
423.1 (302.0)	0.122	-0.012	0.0004	0.0007
	(0.112)	(-0.014)		
	0.025		0.0025	0.0038
	(0.012)			
348.1, 373.1 423.1	0.153	-0.015	0.0014	0.0028
	(0.140)	(-0.016)		
	0.034		0.0044	0.0098
	(0.027)			

* Errors are essentially identical for the SRK and PR EOS

Table XIX

SRK and PR Equation-of-State Representations of
Solubility of Methane in n-Hexatriacontane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
373.1 (212.0)	0.192	-0.010	0.0013	0.0023
	(0.179)	(-0.012)		
	0.091		0.0042	0.0065
	(0.078)			
423.1 (302.0)	0.223	-0.012	0.0010	0.0016
	(0.208)	(-0.015)		
	0.110		0.0050	0.0074
	(0.092)			
373.1, 423.1	0.220	-0.013	0.0020	0.0040
	(0.201)	(-0.014)		
	0.099		0.0053	0.0110
	(0.084)			

* Errors are essentially identical for the SRK and PR EOS

Table XX

SRK and PR Equation-of-State Representations of
Solubility of Methane in n-Tetratetracontane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
373.1 (212.0)	0.243	-0.008	0.0009	0.0018
	(0.229)	(-0.009)		
	0.138		0.0040	0.0059
	(0.123)			
423.1 (302.0)	0.263	-0.008	0.0011	0.0017
	(0.249)	(-0.010)		
	0.161		0.0029	0.0041
	(0.139)			
373.1, 423.1	0.258	-0.008	0.0023	0.0040
	(0.242)	(-0.010)		
	0.148		0.0045	0.0079
	(0.130)			

* Errors are essentially identical for the SRK and PR EOS

Table XXI

SRK and PR Equation-of-State Representations of
Solubility of Methane in Cyclohexane

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
323.2 (122.0)	0.023	0.005	0.0002	0.0003
	(0.028)	(0.008)		
	0.032		0.0004	0.0006
	(0.042)			
373.2 (212.0)	0.023	0.004	0.0003	0.0005
	(0.027)	(0.005)		
	0.029		0.0004	0.0006
	(0.036)			
423.2 (302.0)	0.034	0.010	0.0004	0.0007
	(0.038)	(0.008)		
	0.050		0.0006	0.0010
	(0.050)			
323.2, 373.2 423.2	0.040	-0.003	0.0026	0.0049
	(0.035)	(0.004)	(0.0020)	(0.0038)
	0.034		0.0026	0.0053
	(0.041)		0.0020	(0.0034)

* Errors are essentially identical for the SRK and PR EOS

Table XXII

SRK and PR Equation-of-State Representations of
Solubility of Methane in trans-Decalin

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	RMS	MAX
323.2 (122.0)	0.073	0.002	0.0003	0.0005
	(0.073)	(0.004)		
	0.078		0.0004	0.0006
	(0.084)			
373.2 (212.0)	0.096	-0.004	0.0004	0.0005
	(0.094)	(-0.003)		
	0.085		0.0004	0.0007
	(0.087)			
423.2 (302.0)	0.079	0.007	0.0002	0.0004
	(0.080)	(0.006)		
	0.098		0.0005	0.0007
	(0.095)			
323.2, 373.2 423.2	0.115	-0.011	0.0022	0.0037
	(0.102)	(-0.005)	(0.0014)	(0.0023)
	0.087		0.0023	0.0039
	(0.088)		0.0014	(0.0024)

* Errors are essentially identical for the SRK and PR EOS

Table XXIII

SRK and PR Equation-of-State Representations of
Solubility of Methane in Benzene

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Methane*	
	C ₁₂	D ₁₂	Mole Fraction RMS	MAX
323.2 (122.0)	0.033	0.022	0.0002	0.0004
	(0.036)	(0.027)		
	0.073 (0.083)		0.0010	0.0017
373.2 (212.0)	0.026	0.023	0.0001	0.0001
	(0.031)	(0.026)		
	0.067 (0.074)		0.0009	0.0012
423.2 (302.0)	0.037	0.017	0.0002	0.0004
	(0.039)	(0.019)		
	0.067 (0.070)		0.0005	0.0008
323.2, 373.2 423.2	0.024	0.026	0.0008	0.0014
	(0.019)	(0.035)		
	0.071 (0.079)		0.0013	0.0029

* Errors are essentially identical for the SRK and PR EOS

Table XXIV

SRK and PR Equation-of-State Representations of
Solubility of Methane in Naphthalene

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Mole Fraction*	
	C ₁₂	D ₁₂	RMS	MAX
373.2 (212.0)	0.103	0.000	0.0002	0.0004
	(0.101)	(0.005)		
	0.104		0.0002	0.0003
	(0.117)			
423.2 (302.0)	0.073	0.009	0.0001	0.0002
	(0.077)	(0.012)		
	0.101		0.0002	0.0003
	(0.111)			
373.2, 423.2	0.093	0.003	0.0003	0.0007
	(0.087)	(0.010)		
	0.103		0.0003	0.0008
	(0.115)			

* Errors are essentially identical for the SRK and PR EOS

Table XXV

SRK and PR Equation-of-State Representations of
Solubility of Methane in Phenanthrene

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Mole Fraction*	
	C ₁₂	D ₁₂	RMS	MAX
383.2 (230.0)	0.131	-0.001	0.0001	0.0002
	(0.125)	(0.004)		
	0.125		0.0001	0.0002
	(0.142)			
423.2 (302.0)	0.120	0.001	0.0002	0.0003
	(0.119)	(0.005)		
	0.127		0.0002	0.0003
	(0.142)			
383.2, 423.2	0.126	-0.000	0.0002	0.0005
	(0.123)	(0.004)		
	0.126		0.0002	0.0005
	(0.142)			

* Errors are essentially identical for the SRK and PR EOS

Table XXVI

SRK and PR Equation-of-State Representations of
Solubility of Methane in Pyrene

Temperature K (°F)	Soave Parameters (P-R Parameters)		Error in Mole Fraction	
	C ₁₂	D ₁₂	RMS	MAX
433.2 (320.0)	0.124	0.006	0.0001	0.0002
	(0.126)	(0.009)		
	0.159		0.0002	0.0004
	(0.180)			

Table XXVII

Henry's Constants and Infinite-Dilution Partial Molar
Volumes for Methane in n-Paraffins
and Methane + Aromatics

Temp., K	Ref.	Henry's Constant, bar	Partial Mol. Vol., cm ³ /g-mole	RMS Error Mole Fraction
- - - - - Methane + n-Paraffins - - - - -				
n-Decane (n-C ₁₀)				
298.2	23	199 (+1)*	735 (+30)*	0.0015
310.9	This Work	203 (+4)	695 (+13)	0.0002
310.9	19	195 (+1)	960 (+35)	0.0023
310.9	22	196 (+3)	980 (+70)	0.0080
323.2	23	217 (+1)	875 (+18)	0.0014
344.3	This Work	233 (+1)	665 (+32)	0.0003
344.3	19	221 (+1)	950 (+25)	0.0013
344.3	22	220 (+3)	1100 (+65)	0.0060
348.2	23	240 (+1)	855 (+30)	0.0013
373.2	23	261 (+2)	850 (+55)	0.0019
377.6	This Work	252 (+1)	750 (+23)	0.0003
377.6	19	251 (+2)	760 (+75)	0.0007
377.6	22	250 (+4)	1050 (+110)	0.0037
410.9	This Work	266 (+1)	770 (+40)	0.0006
410.9	19	293 (+1)	128 (+290)	0.0046
423.2	21	270 (+5)	765 (+180)	0.0013
423.2	23	305 (+3)	93 (+135)	0.0015
n-Eicosane (n-C ₂₀)				
323.2	This Work	178 (+1)	1230 (+80)	0.0005
373.2	This Work	199 (+1)	1470 (+25)	0.0003
373.4	24	208 (+1)	1075 (+45)	0.0003
423.2	This Work	217 (+1)	1520 (+25)	0.0007
473.5	24	226 (+3)	1490 (+220)	0.0009
n-Octacosane (n-C ₂₈)				
348.2	This Work	153 (+1)	1855 (+110)	0.0007
373.2	This Work	162 (+2)	2080 (+150)	0.0013
373.4	25	165 (+2)	1720 (+200)	0.0014
423.2	This Work	179 (+1)	1950 (+75)	0.0005
473.5	25	192 (+3)	1740 (+230)	0.0012
n-Hexatriacontane (n-C ₃₆)				
373.2	This Work	147 (+1)	2000 (+50)	0.0010
373.4	26	143 (+2)	2075 (+155)	0.0013
423.2	This Work	157 (+1)	2195 (+40)	0.0006
473.5	26	159 (+3)	2420 (+290)	0.0019

Table XXVII (Continued)

Henry's Constants and Infinite-Dilution Partial Molar
Volumes for Methane in n-Paraffins
and Methane + Aromatics

Temp. K	Ref.	Henry's Constant, bar	Partial Mol. Vol., cm ³ /g-mole	RMS Error Mole Fraction
n-Tetratetracontane (n-C ₄₄)				
373.2	This Work	128 (+1)	2270 (+90)	0.0009
423.2	This Work	135 (+1)	2585 (+60)	0.0009
- - - - - Methane + Aromatics - - - - -				
Naphthalene				
373.2	This Work	770 (+4)	338 (+50)	0.0005
423.2	This Work	780 (+2)	350 (+25)	0.0001
Phenanthrene				
383.2	This Work	1006 (+4)	495 (+30)	0.0001
423.2	This Work	1013 (+3)	530 (+25)	0.0002
398.2	35	1019 (+2)	480 (+ 5)	0.0002
423.2	35	1019 (+4)	490 (+15)	0.0003
448.2	35	1014 (+2)	514 (+10)	0.0002
Pyrene				
433.2	This Work	1152 (+4)	510 (+25)	0.0003

* Values in parentheses are the standard deviations in the estimated parameters

Table XXVIII

Experimental Data for Methane + n-Paraffins and Methane +
Aromatics Used for Model Evaluation and EOS
Parameter Generalizations

Paraffin Carbon Number, CN	Temperature Range, °F	Methane Mole Fraction Range, x_{CH_4}	Ref.	Number of Points
- - - - - Methane + n-Paraffins - - - - -				
3	100 - 190	0.03 - 0.49	57	62
4	160 - 220	0.03 - 0.39	58, 59	9
6	122 - 302	0.01 - 0.39	60	37
7	100 - 340	0.10 - 0.40	61	12
8	77 - 302	0.02 - 0.29	62	28
9	122 - 302	0.03 - 0.31	63	39
10	100 - 400	0.01 - 0.32	This Work, 19	53
16	372	0.08 - 0.32	64	4
20	122 - 392	0.04 - 0.25	This Work, 24	19
28	212 - 392	0.05 - 0.30	This Work, 25	18
36	212 - 392	0.05 - 0.30	This Work, 26	19
44	212 - 302	0.05 - 0.25	This Work	15
- - - - - Methane + Aromatics - - - - -				
Benzene	122 - 302	0.03 - 0.17	This Work	22
Naphthalene	212 - 302	0.02 - 0.10	This Work	12
Phenanthrene	230 - 302	0.02 - 0.09	This Work	12
Toluene	300 - 442	0.02 - 0.20	21	7
m-Xylene	100 - 400	0.04 - 0.22	65	7
n-Butylbenzene	158 - 212	0.02 - 0.14	66	12
Diphenylmethane	373	0.03 - 0.15	67	4
Pyrene	320	0.02 - 0.09	This Work	7

Table XXIX

Specific Cases for Interaction Parameters
Used in the EOS Model Evaluation

Case	Description
1 $C_{ij} = 0$ $D_{ij} = 0$	The 'raw' ability of the EOS, using one-fluid mixing rules with no interaction parameters; permits prediction from pure-component data.
2 C_{ij}	A single value of C_{ij} is used for application to all binary systems.
3 C_{ij}, D_{ij}	Two interaction parameters are determined for application to all binary systems.
4 C_{ij}	A separate value of C_{ij} is determined for each binary system, independent of temperature; this is the most commonly used EOS representation in the literature.
5 C_{ij}, D_{ij}	Two interaction parameters are determined for application to each binary systems, independent of temperature.
6 $C_{ij}(T)$	A separate value of C_{ij} is determined for each binary system at each temperature; this case permits C_{ij} to be temperature dependent.
7 $C_{ij}(T),$ $D_{ij}(T)$	A separate pair of parameters is determined for each binary system at each temperature.

Table XXX

**Summary of Results for Model Evaluation for
Methane + Hydrocarbons Using the SRK EOS**

Case Number	Bubble Point Pressure RMSE (bar)	BIAS (bar)	AAD (bar)	%AAD	NRMSE ^a in Mole Fraction	RMSE ^b
- - - - - Methane + n-Paraffins - - - - -						
1	5.95	-1.86	4.37	10.53	22.0	0.022
2	5.56	0.51	3.29	8.76	20.6	0.019
3	2.62	-0.24	1.89	4.67	9.7	0.010
4	1.46	0.02	1.00	2.72	5.4	0.006
5	1.29	-0.11	0.91	2.49	4.8	0.005
6	0.68	0.09	0.49	1.54	2.5	0.003
7	0.27	-0.04	0.17	0.55	1.0	0.002
- - - - - Methane + Aromatics - - - - -						
1	14.27	-11.33	11.33	20.83	83.9	0.022
2	5.34	-0.18	3.90	6.93	31.4	0.007
3	1.84	0.14	1.21	2.75	10.8	0.004
4	0.57	-0.08	0.40	0.93	3.4	0.0011
5	0.49	-0.01	0.34	0.79	2.9	0.0009
6	0.42	-0.10	0.31	0.77	2.5	0.0008
7	0.17	-0.001	0.14	0.37	1.0	0.0003

^a NRMSE = RMSE/(RMSE, Case 7)

^b Solubility is calculated from SRK EOS using the optimum interaction parameter(s) for each case.

Table XXXI

Specific Cases for Generalization of Interaction
Parameter, C_{ij} , in SRK and PR EOS.

Case	Description
1 $C_{ij} = C_{ij}^o$	A single value of C_{ij} is determined for application to all binary systems (same as Case 2 in Table XXIX)
2 $C_{ij} = f(\omega)$	C_{ij} is correlated in terms of acentric factor of the solvent using a second order polynomial. The leading term of this polynomial is the optimum interaction parameter for low molecular weight solvents (C_{ij}^s). The parameters optimized in this case are A_1 and A_2 below. $C_{ij} = A_0 + A_1\omega + A_2\omega^2$ where $A_0 = C_{ij}^s$
3 $C_{ij} = C_{ij}^s$ $b = f(T_r, \omega)$	C_{ij} is set to a prescribed value, C_{ij}^s, (the optimum for low molecular weight solvents) while β is considered as a function of reduced temperature and acentric factor. The parameters optimized in this case are B_0, B_1 and B_2. $C_{ij} = A_0 = C_{ij}^s$ $b(T_r, \omega) = b_c \beta(T_r, \omega)$ $\beta(T_r, \omega) = [1 + m(1 - T_r^{1/2})]^2$ $m = B_0 + B_1\omega + B_2\omega^2$

Table XXXII

Coefficients of C_{1j} and m Generalized Correlations

$$\beta(T_r, \omega) = [1 + m(1 - Tr^{1/2})]^2$$

$$m = B_0 + B_1\omega + B_2\omega^2$$

$$C_{1j} = A_0 + A_1\omega + A_2\omega^2$$

Coefficient	Case 2*		Case 3	
	SRK	(PR)	SRK	(PR)
- - - - - Methane + n-Paraffins - - - - -				
A_0	0.0371	(0.0371)	0.0371	(0.0371)
A_1	0.0646	(0.0632)	-	
A_2	-0.1487	(-0.1405)	-	
B_0	-		0.0946	(0.0644)
B_1	-		-0.4129	(-0.3333)
B_2	-		0.4258	(0.3922)
- - - - - Methane + Aromatics - - - - -				
A_0	0.0700	(0.0700)	0.0700	(0.0700)
A_1	0.3570	(0.4008)	-	
A_2	-0.2131	(-0.2347)	-	
B_0	-		-0.1650	(-0.2019)
B_1	-		0.1282	(0.1334)
B_2	-		-0.1518	(-0.1788)

* For case number, see Table XXXI.

Table XXXIII

Summary of Results for Model Generalization of Methane +
Hydrocarbons Using the SRK and PR EOS

Case No.	Bubble Point Pressure				RMSE ^a in Mole Fraction
	RMSE, bar SRK(PR)	BIAS, bar SRK(PR)	AAD, bar SRK(PR)	%AAD SRK(PR)	
- - - - - Methane + n-Paraffins - - - - -					
1	5.56(5.59)	0.52(0.64)	3.29(3.22)	8.76(8.60)	0.0190
2	1.89(1.84)	0.13(0.17)	1.29(1.26)	3.26(3.14)	0.0078
3	1.24(1.27)	-0.05(0.02)	0.95(0.93)	2.44(2.35)	0.0050
- - - - - Methane + Aromatic Hydrocarbons - - - - -					
1	6.05(7.67)	-0.49(-0.77)	4.50(5.76)	7.10(9.17)	0.0070
2	1.46(1.76)	-0.31(-0.34)	1.16(1.42)	2.17(2.60)	0.0016
3	0.63(0.70)	-0.19(-0.25)	0.47(0.52)	1.10(1.25)	0.0011

^a Solubility is calculated from SRK EOS using the generalized interaction parameter(s) for each case.

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Figure 2.
Graphical Determination of Bubble Point Pressure
Across Vapor-Liquid Phase Boundary

Figure 3

Bubble Point Pressure Data for Methane + n-Paraffins at 212 F

Figure 4
Comparison of Methane Solubilities in n-Decane at 100 F

Figure 5

Comparison of Methane Solubilities in n-Decane at 160 F

Figure 6

Comparison of Methane Solubilities in n-Decane at 220 F

Figure 7

Comparison of Methane Solubilities in n-Decane at 280 F

Figure 8

Comparison of Methane Solubilities in n-Decane for Studies Performed
at Temperatures Different from the Present Work

Figure 9

Comparison of Methane Solubilities in n-Decane Using Lumped Parameters, Cij and Dij,
of the Present Work

Figure 10

Comparison of Methane Solubilities in n-Eicosane

Figure 11

Comparison of Methane Solubilities in n-Octacosane

Figure 12
 Comparison of Methane Solubilities in n-Hexatriacontane

Figure 13

Comparison of Methane Solubilities in n-Tetradecane

Figure 14

Soave Interaction Parameters, C_{1j} and D_{1j} , for Methane + n-Paraffins at 212 F

Figure 15

Soave Interaction Parameter, C_{1j} , and Corresponding RMS Errors for Methane + n-Paraffins at 212 F

Figure 16
Soave Interaction Parameters, C_{ij} and D_{ij} , for Methane + n-Paraffins

Figure 17

Soave Interaction Parameter, C_{ij} , for Methane + n-Paraffins

Figure 18

Comparison of Methane Solubilities in Cyclohexane

Figure 19

Comparison of Methane Solubilities in Cyclohexane Using Lumped Parameters of This Work

LEGEND □-□-□ This Work: 122 F ▲-▲-▲ This Work: 212 F

Figure 20

Comparison of Methane Solubilities in t-Decalin

Figure 21

Soave Interaction Parameters, C_{1j} and D_{1j} , for Methane + Cyclohexane

Figure 22

Soave Interaction Parameter, C_{ij} , and Corresponding
RMS Errors for Methane + Cyclohexane

Figure 23
Soave Interaction Parameters, C_{ij} and D_{ij} , for Methane + t-Decalin

Figure 24
Soave Interaction Parameter, C_{ij} , and Corresponding
RMS Errors for Methane + t-Decalin

Figure 25
Soave Interaction Parameter, C_{ij} , for Methane + Cyclohexane
and Methane + t-Decalin

Figure 26
Comparison of Methane Solubilities in Benzene (a)

Figure 27
Comparison of Methane Solubilities in Benzene (b)

Figure 28

Comparison of Methane Solubilities in Phenanthrene

Figure 29

Prediction of Bubble Point Pressures of Methane in Phenanthrene Using the SRK Equation of State

Figure 30

Prediction of Bubble Point Pressures of Methane in Naphthalene Using the SRK Equation of State

LEGEND B-B-B This Work: 212 F A-A-A This work: 302 F

Figure 31

Prediction of Methane Solubilities in Naphthalene Using the SRK Equation of State

Figure 32
Prediction of Bubble Point Pressures and Solubilities of Methane in Pyrene Using the SRK Equation of State

Figure 33

Soave Interaction Parameter, $C_{ij}(T)$, for Methane + Aromatic Hydrocarbons

Figure 34

Soave Interaction Parameter, C_{ij} , for Methane + Aromatic Hydrocarbons

Figure 35

Molecular Size Effects on Generalized-Parameter SRK EOS Prediction for Methane + n-Paraffins

APPENDIX A
Description of SRK and PR EOS

Two equations of state used widely in industry are the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations which are explicit in pressure, P, and cubic in volume, V. The SRK equation of state is [11]

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

where

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

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

and

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

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

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

The PR equation of state is of similar form [10]

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (7)$$

where a(T) and b are given as

$$a(T) = a_c \alpha(T) \quad (8)$$

$$b = 0.0778 RT_c/P_c \quad (9)$$

$$a_c = 0.45724 R^2 T_c^2 / P_c \quad (10)$$

$$\alpha(T) = [1 + k (1 - T_r^{1/2})]^2 \quad (11)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (12)$$

To apply the SRK or PR equations of state to mixtures, the values of a and b can be determined using the mixing rules [17]

$$a_m = \sum \sum z_i z_j (1 - C_{ij}) (a_i a_j)^{1/2} \quad (13)$$

$$b_m = 0.5 \sum \sum z_i z_j (1 + D_{ij}) (b_i + b_j) \quad (14)$$

In Equations 13 and 14, the summations are over all chemical species and C_{ij} and D_{ij} are empirical binary interaction parameters characterizing the binary interactions between components "i" and "j". Values of these parameters are typically determined by fitting experimental binary mixture data to minimize some objective function, SS, which, in this work, is the weighted sum of squared errors in predicted bubble point pressures

$$SS = \sum \frac{(P_{iexp} - P_{icalc})^2}{(\sigma_{ip})^2} \quad (15)$$

where σ_{ip} is the uncertainty in the measured pressure [18] and the sum is over the data point analyzed. Further details of the data reduction techniques employed in this study are given by Gasem [15].

END

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