PHASE BEHAVIOR OF COAL FLUIDS:
DATA FOR CORRELATION DEVELOPMENT

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ABSTRACT

The effective design and operation of processes for conversion of coal to fluid fuels requires accurate knowledge of the phase behavior of the fluid mixtures encountered in the conversion process. Multiple phases are present in essentially all stages of feed preparation, conversion reactions and product separation; thus, 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 representation of vapor-liquid equilibria in systems encountered in coal conversion processes. The objectives of the present project include:

- (1) Measurements of binary vapor-liquid phase behavior data for selected solute gases (e.g. CO_2 and C_2H_6) in a series of heavy hydrocarbon solvents to permit evaluation of interaction parameters in models for phase behavior. Both solubilities of the gases in the liquid phase and of the heavy solvents in the gas phase will be determined.
- (2) Measurements on ternary systems in which high-melting-point solvents are dissolved in more volatile aromatics to provide mixed solvents; this will facilitate measurements at lower temperatures than would be possible in the pure high-melting-point aromatic solvents, which would be solid at operating conditions.
- (3) Evaluation of existing equations-of-state and other models for representation of phase behavior in systems of the type studied experimentally; development of new correlation frameworks as needed.
- (4) Generalization of the interaction parameters for the solutes studied to a wide spectrum of heavy solvents; presentations of final results

in formats useful in the design/optimization of coal liquefaction processes.

During the present report period, binary solubility data were measured for methane in four aromatic hydrocarbons at temperatures from 323 to 433 K (122 to 320°F) and pressures up to 11.3 MPa (1640 psia). The hydrocarbons studied are: benzene, naphthalene, phenanthrene and pyrene. The present data for methane + benzene are in fair agreement with the earlier measurements of Sage, et al. Excellent agreement is observed between our data and those of Malone and Kobayashi for methane + phenanthrene. The new data can be described with a root-mean-square (RMS) error of 0.001 in mole fraction by the Soave-Redlich-Kwong (SRK) equation of state when one interaction parameter is used over the complete temperature range for each system. Henry's constants and partial molar volumes at infinite dilution are evaluated from the data using the Krichevsky-Kasarnovsky correlation.

INTRODUCTION

The unpredictability of the energy situation has prompted increasing efforts to investigate alternative forms of liquid fuels such as coal-derived syncrudes. Multiple phases are present in essentially all stages of coal feed preparation, conversion reactions, and product separation. For example, during the initial stages of coal dissolution in a coal-derived recycle solvent, many light gases are produced (e.g., CH_4 , CO , CO_2 , H_2S , H_2O , NH_3 , and $\text{C}_2\text{-C}_5$) [1]. Therefore, the effective design and operation of such conversion processes requires accurate knowledge of the phase behavior of the fluid mixtures encountered. Studies of solubility of light gases in heavy hydrocarbons is also of interest in the processing of petroleum products, enhanced oil recovery and supercritical fluid processes. Moreover, such studies are indispensable in the development and evaluation of solution theories.

Previously, we have reported and analyzed data on the solubility of carbon dioxide and ethane in a series of heavy hydrocarbons [2-6]. Recently, we have completed an experimental study on the solubility of methane in a series of heavy hydrocarbons (paraffins, naphthenes, and aromatics). Data on methane solubilities in heavy normal paraffins and in naphthenes have been reported previously [7]. In the present work, solubility data for the binary systems of methane in benzene, naphthalene, phenanthrene and pyrene were measured and correlated using Soave [8] and Peng-Robinson (PR) [9] equations of state. Solubilities were measured at temperatures from 311 to 423 K (122 to 320°F) and pressures up to 11.3 MPa (1640 psia). These data complement the available literature data and should prove useful in the development and testing of correlations describing the phase behavior of multicomponent systems involving methane.

EXPERIMENTAL SECTION

Apparatus and Procedure:

The experimental apparatus used in this study is a modified version of the apparatus used by Raff [6]. The modifications, described elsewhere [7], resulted in a number of improvements including: improved mixing, low dead volume, and improved procedures and designs for cleaning and degassing. Estimated experimental uncertainties are 0.1 K in temperature and less than 0.001 in mole fraction. The uncertainty in the measured bubble-point pressure depends on the steepness of the p-x relation and is of the order of ± 10 psia [7].

Materials:

The methane had a stated purity of 99.97⁺ mol% and was supplied by Matheson. Benzene was supplied by J. T. Baker Chemical Company and had a purity of 99.8+ mol%. Naphthalene, phenanthrene and pyrene were from Aldrich Chemical Company with quoted purities of 99⁺, 98⁺ and 99⁺ mol%, respectively. No further purification of the chemicals was attempted.

RESULTS AND DISCUSSION

Equilibrium Data:

The experimental results appear in Tables I-IV. Differences in the lowest temperature at which the systems were studied are dictated by the melting point of the solvents, which are solids at room temperature.

Equation of State Data Correlation:

The experimental data have been correlated using the SRK [8] and PR [9] equations of state. Optimum binary interaction parameters were obtained by minimizing the squares of pressure deviations from the experimental values. Detailed procedures for the data reduction are given by Gasem [10]. The input

parameters of the pure components (acentric factors and critical temperatures and pressures) required by the SRK and PR equations of state, together with their literature sources, are presented in Table V.

Figures 1 and 2 show the effects of temperature and pressure on methane solubility. The solubility of methane in heavy aromatic hydrocarbons exhibits weak dependence on temperature, as Figure 2 reveals for the solubility of methane in naphthalene, phenanthrene and pyrene. Figure 3 shows that the Soave interaction parameter, C_{ij} , for these systems is relatively insensitive to temperature. Figure 4 shows the effect of chemical structure on the lumped Soave interaction parameter, C_{ij} (i.e., when a single value of C_{ij} is used over the complete temperature range of each system). A nonlinear dependence of C_{ij} with the chemical structure, as given by the number of aromatic rings, is observed. However, this variation of C_{ij} with chemical structure is similar to that reported for ethane [4] and CO_2 [6] in the same solvents. The possibility exists that this variation is an artifact of the critical properties and acentric factors used for the pure solvents, since those of phenanthrene and pyrene must be estimated.

Equation-of-state representation of the solubilities for the systems under study is illustrated in Tables VI-IX. In general, the SRK and PR equations are capable of describing the data within an RMS error of 0.0005 in mole fraction, when a single interaction parameter, C_{ij} , is used over the complete temperature range. The methane + benzene system, which has an RMS error of 0.0013 in mole fraction, is an exception. For methane solubility in benzene, improved equation-of-state predictions are realized (RMS error = 0.0008) when an additional parameter, D_{ij} , is used, as indicated by results given in Table VI.

Comparisons of our results with those of various investigators appear in Figures 5-8. The comparisons are shown in terms of deviations of the solubilities from values predicted using the SRK [8] equation of state. Interaction parameters 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 5 and 6. Reasonable agreement is observed between our result and those of Lin, et al. [11] at 298°F (Figure 5), and good agreement is observed with the results of Sage, et al. [12] at 160 and 220°F (Figure 6). However, significant disagreements with Elbishlawi and Spenser [13], Legret, et al. [14], and Schoch, et al. [15] are seen in both figures.

Figures 7 and 8 show comparisons for methane + phenanthrene; these comparisons are shown in terms of both solubility deviations (Figure 7) and pressure deviations (Figure 8). Interaction parameters employed in the equation-of-state solubility predictions were obtained by fitting the data of Malone and Kobayashi [16], since his data cover a wide range of pressures. The agreement between the two data sets is good. The maximum pressure deviation is shown to be less than + 10 psia, which is within the experimental error of our bubble point pressure measurements [7]. For methane + naphthalene and methane + pyrene systems, no previous data are available for comparisons.

Krichevsky-Kasarnovsky Analysis:

In the range of methane mole fractions reported in this study, the binary solubilities of methane in naphthalene, phenanthrene and pyrene are represented within 0.0002 mole fraction by the Krichevsky-Kasarnovsky (KK) equation [17]:

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

Values of the methane fugacity, $\hat{f}_{\text{CH}_4}$, required for the KK equation were obtained from Bender's equation of state for methane [18], since the vapor phase is essentially pure methane. The resultant Henry's constants and infinite-dilution partial molar volumes of methane regressed from our data are presented in Table X and Figure 9.

CONCLUSIONS

Data have been obtained for the solubility of methane in benzene, naphthalene, phenanthrene, and pyrene at temperatures from 323 to 433 K (122 to 320°F) and pressures to 11.2 MPa (1640 psia). The data are well described by the Soave-Redlich-Kwong and Peng-Robinson equations of states and the Krichevsky-Kasarnovsky correlation.

GLOSSARY

C_{ij}, D_{ij}	interaction parameters between components i and j in mixing rules for equation of state
$\hat{f}_{CH_4}$	fugacity of methane in the liquid (or vapor) phase
P	pressure
P_{HC}	hydrocarbon vapor pressure
H_{CH_4}, P_{HC}	Henry's constant of methane at the hydrocarbon vapor pressure
R	universal gas constant
T	temperature
$\bar{v}_{CH_4}^\infty$	infinite dilution partial molar volume of methane
x	liquid phase mole fraction of methane

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Table I
Solubility Data of Methane in Benzene

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
----- 323.2 K (50.0°C, 122.0°F) -----		
0.0275	14.6	(212)
0.0533	28.0	(407)
0.0751	39.7	(576)
0.1141	61.4	(891)
0.1191	64.0	(929)
0.1341	72.3	(1049)
0.1493	81.1	(1177)
0.1665	90.9	(1318)
----- 373.2 K (100.0°C, 212.0°F) -----		
0.0289	17.3	(250)
0.0389	22.6	(327)
0.0605	34.2	(496)
0.0750	42.1	(611)
0.0996	55.1	(806)
0.1255	69.8	(1012)
0.1522	84.8	(1230)
0.1642	91.4	(1326)

Table I (Continued).

Solubility Data of Methane in Benzene

Mole Fraction Methane	Bubble Point Pressure bar (psia)
<hr style="border-top: 1px dashed;"/> ----- 423.2 K (150°C, 302°F) -----	
0.0287	20.5 (297)
0.0316	22.1 (321)
0.0552	34.2 (496)
0.0736	43.8 (636)
0.1032	59.2 (859)
0.1147	65.2 (946)
0.1450	80.9 (1174)
0.1511	84.6 (1227)

Table II
Solubility Data of Methane in Naphthalene

Mole Fraction Methane	Bubble Point Pressure bar (psia)	
----- 373.2 K (100°C, 212°F) -----		
0.0245	19.6	(284)
0.0302	24.0	(349)
0.0503	40.6	(590)
0.0640	53.0	(769)
0.0860	73.5	(1065)
0.1002	86.9	(1260)
----- 423.2 K (150°C, 302°F) -----		
0.0243	19.4	(281)
0.0309	24.8	(360)
0.0446	36.4	(528)
0.0598	49.3	(715)
0.0750	62.5	(907)
0.0998	84.8	(1229)

Table III

Solubility Data of Methane in Phenanthrene

Mole Fraction Methane	Bubble Point Pressure bar (psia)
----- 383.2 K (110°C, 230°F) -----	
0.0197	20.4 (296)
0.0296	31.6 (458)
0.0444	48.2 (700)
0.0600	67.3 (977)
0.0714	81.8 (1185)
0.0898	107.1 (1553)
----- 423.2 K (150°C, 302°F) -----	
0.0206	21.5 (312)
0.0296	31.3 (454)
0.0451	48.6 (705)
0.0595	66.2 (960)
0.0742	84.2 (1221)
0.0902	104.6 (1517)

Table IV
Solubility Data of Methane in Pyrene

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
----- 433.2 K (160°C, 320°F) -----		
0.0198	23.5	(341)
0.0347	42.3	(614)
0.0489	60.4	(875)
0.0599	75.8	(1099)
0.0699	89.7	(1301)
0.0751	97.1	(1408)
0.0855	113.0	(1639)

Table V
Pure Substance Properties Used in SRK
and PR Equations of State

Component	Pressure (MPa)	Temperature (K)	Acentric Factor	Reference
Methane	4.660	190.5	0.011	19
Benzene	4.898	561.7	0.225	20
Naphthalene	4.114	748.4	0.315	21
Phenanthrene	3.30	873.2	0.540	22
Pyrene	2.60	938.2	0.344	23

Table VI

Soave and Peng-Robinson Equation-of-State
Representations of Solubility of Methane in Benzene

Temperature K (°F)	SRK Parameters (PR Parameters)		Error in Mole Fraction	
	C ₁₂	D ₁₂	RMS	MAX
323.2 (122.0)	0.0328	0.0222	0.0002	0.0004
	(0.0361)	(0.0272)	(0.0002)	(0.0004)
	0.0729		0.0010	0.0017
	(0.0825)		(0.0014)	(0.002)

373.2 (212.0)	0.0259	0.0232	0.0001	0.0001
	(0.0306)	(0.0263)	(0.0001)	(0.0001)
	0.0668		0.0009	0.0012
	(0.0742)		(0.0011)	(0.0014)

423.2 (302.0)	0.0367	0.0172	0.0002	0.0004
	(0.0385)	(0.0191)	(0.0002)	(0.0004)
	0.0666		0.0005	0.0008
	(0.0696)		(0.0005)	(0.0009)

323.2, 373.2 423.2	0.0240	0.0260	0.0008	0.0014
	(0.0191)	(0.0353)	(0.0015)	(0.0027)
	0.0705		0.0013	0.0029
	(0.0786)		(0.0021)	(0.0038)

Table VII

Soave and Peng-Robinson Equation-of-State
Representation of Solubility of Methane in Naphthalene

Temperature K (°F)	SRK Parameters (PR Parameters)		Error in Mole Fraction	
	C ₁₂	D ₁₂	RMS	MAX
373.2 (212.0)	0.1034	0.0003	0.0002	0.0004
	(0.1008)	(0.0054)	(0.0002)	(0.0004)
	0.1043		0.0002	0.0003
	(0.1165)		(0.0002)	(0.0004)

423.2 (302.0)	0.0727	0.0090	0.0001	0.0002
	(0.0770)	(0.0117)	0.0001	0.0002
	0.1014		0.0002	0.0003
	(0.1110)		(0.0003)	(0.0004)

373.2, 423.2	0.0931	0.0032	0.0003	0.0007
	(0.0868)	(0.0095)	(0.0005)	(0.0011)
	0.1033		0.0003	0.0008
	(0.1146)		(0.0006)	(0.0013)

Table VIII

Soave and Peng-Robinson Equation-of-State
Representation of Solubility of Methane in Phenanthrene

Temperature K (°F)	SRK Parameters (P-R Parameters)		Error in Mole Fraction	
	C ₁₂	D ₁₂	RMS	MAX
383.2 (230.0)	0.1313	-0.0014	0.0001	0.0002
	(0.1247)	(0.0040)	(0.0001)	(0.0002)
	0.1246		0.0001	0.0002
	(0.1418)		(0.0002)	(0.0004)

423.2 (302.0)	0.1204	0.0014	0.0002	0.0003
	(0.1189)	(0.0054)	(0.0002)	(0.0003)
	0.1268		0.0002	0.0003
	(0.1420)		(0.0002)	(0.0003)

383.2, 423.2	0.1257	-0.0001	0.0002	0.0005
	(0.1228)	(0.0044)	(0.0002)	(0.0003)
	0.1255		0.0002	0.0005
	(0.1419)		(0.0002)	(0.0004)

Table IX

Soave and Peng-Robinson Equation-of-State
Representation 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)	0.2416	0.0317	0.0001	0.0002
	(0.2349)	(0.0313)	(0.0001)	(0.0002)
	0.4127		0.0005	0.0008
	(0.3865)		(0.0005)	(0.0009)

Table X

Henry's Constants and Infinite-Dilution Partial Molar
Volumes for Methane in Aromatic Hydrocarbons

Temperature K(°F)	Henry's Const. MPa	Partial Mol. Vol. m ³ /g-mole	RMS Error Mole Fraction
----- Naphthalene -----			
373.2 (212.0)	77.3	338	0.0005
423.2 (302.0)	78.4	350	0.0001
----- Phenanthrene -----			
383.2 (230.0)	100.5	495	0.0001
423.2 (302.0)	101.4	531	0.0002
----- Pyrene -----			
433.2 (320.0)	115.2	510	0.0003

Figure 1.

Bubble Point Pressure Data for Methane + Benzene System

LEGEND

□-□-□ CH4 + Naph.: 212	△-△-△ CH4 + Naph.: 302
○-○-○ CH4 + Phen.: 230	★-★-★ CH4 + Phen.: 302
◇-◇-◇ CH4 + Pyrene: 320	

Figure 2.

Bubble Point Pressure Data for Methane + Aromatic Hydrocarbons

Figure 3.

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

Figure 4.

Soave Interaction Parameters (Lumped C_{ij}) for Methane + Aromatic Hydrocarbons

Figure 5.

Comparison of Methane Solubilities in Benzene

SOURCE: □-□-□ This Work: 122 F △-△-△ This Work: 212 F ○-○-○ This Work: 302 F
 ◇-◇-◇ Schoch: 298 F *-*-* Sage: 100 F *-*-* Sage: 160 F
 --* Sage: 220 F

FIGURE 6
 Comparison of Methane Solubilities in Benzene

Figure 7.

Comparison of Methane Solubilities in Phenanthrene

Figure 8.

Comparison of Methane Solubilities in Phenanthrene

Figure 9.

Henry's Constants of Methane in Aromatic Hydrocarbons

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