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TABLE II

SOLUBILITY OF METHANE IN BENZENE

Mole Fraction

DOE/PC/90523--T7

DE-FG22-86PC90523

PHASE EQUILIBRIUM DATA FOR DEVELOPMENT
OF CORRELATIONS FOR COAL FLUIDS

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Robert L. Robinson, Jr.
(Principal Investigator)
K. A. M. Gasem
N. Darwish

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

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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 requires 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 author's 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 , CH_4) in a series of heavy hydrocarbon solvents to permit evaluation of interaction parameters in models for phase behavior. Solubilities of the gases in the liquid 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; presentation of final results in formats useful in the design/optimization of coal liquefaction processes.

During the present report period, our solubility apparatus was modified to accomodate methane mixtures and to expedite data acquisition. The modifications resulted in a number of improvements including: improved mixing, low dead volume, and improved design and procedures for cleaning and degassing. Data have been obtained on the solubility of methane in cyclohexane and in benzene at 323.1, 373.1 and 423.1 K. These data are well described by the Soave and Peng-Robinson equations of state. The present data for methane + cyclohexane are in reasonable agreement with those reported by Schoch and co-workers (13) and Sage and Lacey (14). For methane + benzene, the data are in good agreement with those reported by Lin and co-workers (15), and Sage and Lacey (14).

In the coming report period, measurements will be continued on methane solubilities in n-tetratetracontane ($n-C_{44}$).

INTRODUCTION

Essentially all state-of-the-art models for phase behavior (including equations-of-state (EOS) and activity coefficient models) contain one (e.g., 1, 2), two (3, 4) or three (5) parameters which reflect the nature of 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 systems of interest. These "binary interaction parameters" have a dramatic effect on the predicted properties of mixtures and are thus required for accurate predictions. In most instances, predictions for multicomponent mixtures can be done directly from knowledge of "binary interaction parameters"; that is,

no higher-order parameters (i.e., "ternary interaction parameters", etc.) are generally required for complex mixtures.

Experimental measurements made on systematically chosen mixtures can be used to evaluate interaction parameters and, more importantly, furnish the basis for generalization of the parameters to permit interpolation (and perhaps extrapolation) to other solvents in the same homologous series. Such generalizations are particularly important, since complete studies of all possible solute/solvent pairs are obviously infeasible (3, 6-8). Toward this end, we have previously reported experimental measurements for ethane, CO_2 , and methane solubilities in a number of heavy hydrocarbon solvents (6, 9, 10, 11, 19). The present report on the solubility of methane in cyclohexane and in benzene constitutes a continuation of those studies.

DISCUSSION OF TECHNICAL PROGRESS

During the present report period, our experimental apparatus was modified to improve its performance in general and to facilitate solubility measurements involving CH_4 as the solute gas. Three specific equipment modifications were introduced.

First, our stirred equilibrium cell (for details see, e.g., 10) was replaced by a rocking cell similar to that used in our CO_2 solubility studies (9). This change was essential, since mixing in the stirred cell was inadequate for mixtures involving CH_4 . Using the new cell, the contents of the cell are mixed thoroughly by rocking the cell about 45° above and below the horizontal level. The pressurizing medium, which is mercury as before, has the additional role of enhancing mixing. To further enhance mixing, five steel balls are housed inside the rocking cell. This mechanism for mixing has proved to be superior to that in the previous stirred cell, as indicated by the time required to reach equilibrium. The new cell is an MS-15 microreactor

of 12.5 ml capacity (High Pressure Equipment). Second, to a large degree, the dead volume was eliminated from the cell and the pertinent connections. This was achieved by injecting mercury through the same line used to inject the solvent and the solute, thus chasing the remaining fluids in the line toward the cell.

The third modification in the apparatus involved the cleaning and the degassing portions of the apparatus. Using the old cleaning arrangement, the solvent (which may be solid at room temperature) can be easily trapped in some of the external lines, thus plugging these lines and causing unnecessary delays. This problem was eliminated in the new design by eliminating many unnecessary connections. Similarly, the degassing tubing and connections were modified to render them more reliable and less prone to leaks.

To ensure proper operation of the modified apparatus, well-documented VLE data from the literature were reproduced. The test systems included carbon dioxide + benzene, carbon dioxide + n-decane, carbon dioxide + n-hexatriacontane and methane + n-eicosane. Data were then obtained on the solubility of methane in cyclohexane and in benzene at 323.1, 373.1, and 423.1 K. These data are well described by the Soave and Peng-Robinson equations of state.

Table I presents experimental solubility data for methane + cyclohexane at 323.1, 373.1, and 423.1 K, and Table II presents data for methane + benzene at 323.1, 373.1, and 423.1 K. Comparisons of the present data for methane + cyclohexane system with those reported by Schoch and co-workers (13) and Sage and Lacey (14) appear in Figure 1. Figure 2 shows similar comparisons of the present data and those reported by others (14-18) for the methane + benzene system. These comparisons are shown in terms of deviations of the measured solubilities from values predicted using the Soave EOS (1), where interaction

parameters for the EOS predictions were obtained by optimizing the fit to the present data.

Since the literature data were reported at temperatures and pressures which differ from the present work, no comparisons could be made at specific temperatures; instead, the present data were regressed over their complete temperature range, and the resulting parameters were used to predict solubilities.

Figure 1 reveals reasonable agreement among the present data for methane + cyclohexane (323.1-423.1 K, 200-1400 psi), Schoch and co-workers (13) (311.1-377.6 K, 600-1800 psi) and Sage and Lacey (14) (311.1-377.6 K, 2045-2240 psi). The different data sets differ by no more than 0.008 in mole fractions; however, our data show that the temperature dependence of the interaction parameters must be taken into account for accurate representation of the data. Figure 2 shows a similar comparison for methane + benzene, where the temperature dependence of the EOS parameters is neglected in this case, also. Obvious disagreement is indicated between Lin's data (15) and data reported by Elbishlawi (18) and Legret (16). Our data for this system, along with the data reported by Sage (14), are well within the range of the various investigators.

The EOS representations of the solubilities for the systems under study are documented in Tables III and IV. The equations are capable of describing the data for methane + cyclohexane with RMS errors within 0.003 in mole fraction when a single set of interaction parameters, C_{ij} , D_{ij} , is used over the complete temperature range. When two parameters are fitted to each isotherm, RMS errors are less than 0.0003, as shown in Table III. For methane + benzene data, when two parameters are used over the complete temperature range, an RMS within 0.001 is obtained; however when two parameters are fitted

to each isotherm, RMS errors are less than 0.0002, as shown in Table IV. These results illustrate both the ability of the EOS and the precision of our reported data. The results in Tables III, and IV also reveal that both methane + cyclohexane and methane + benzene data are adequately represented by a single interaction parameter, i.e. using only C_{ij} .

CONCLUSIONS

Data have been obtained on the solubility of methane in cyclohexane and in benzene at 323.1, 373.1, and 423.1 K. These data are well described by the Soave and Peng-Robinson equations of state. These results will be of value in establishing EOS interaction parameters for light hydrocarbon gases in such solvents.

GLOSSARY

C_{ij}, D_{ij}

interaction parameters between components i and j in mixing rules for equation of state

P

pressure

R

universal gas constant

T

temperature

x

mole fraction in the liquid phase

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TABLE I
SOLUBILITY OF METHANE IN CYCLOHEXANE

Mole Fraction Methane	pressure	
	MPa	psia
- - - - - 323.1 K (50°C, 122°F) - - - - -		
0.042	1.412	204.8
0.069	2.352	341.1
0.098	3.338	484.1
0.124	4.246	615.9
0.155	5.400	783.2
0.174	6.098	884.5
0.207	7.382	1070.7
- - - - - 373.1 K (100°C, 212°F) - - - - -		
0.029	1.247	180.9
0.052	2.086	302.5
0.083	3.235	469.2
0.100	3.911	567.2
0.138	5.397	782.7
0.152	5.912	857.5
0.178	7.018	1017.8
0.194	7.627	1106.2
0.201	7.938	1151.3
0.212	8.412	1220.0

TABLE I (Continued)
SOLUBILITY OF METHANE IN CYCLOHEXANE

Mole Fraction Methane	pressure	
	MPa	psia
----- 423.1 K (150°C, 302°F) -----		
0.027	1.599	231.9
0.051	2.513	364.5
0.065	3.039	440.7
0.075	3.501	507.8
0.088	4.000	581.6
0.101	4.504	653.3
0.129	5.640	818.0
0.151	6.521	945.8
0.176	7.542	1093.9
0.222	9.433	1368.1
0.201	8.590	1245.9

TABLE II
SOLUBILITY OF METHANE IN BENZENE

Mole Fraction Methane	pressure	
	MPa	psia
----- 323.1 K (50°C, 122°F) -----		
0.028	1.464	212.3
0.053	2.803	406.5
0.075	3.973	576.2
0.114	6.142	890.8
0.119	6.402	928.5
0.134	7.229	1048.5
0.149	8.112	1176.5
0.167	9.087	1317.9
----- 373.1 K (100°C, 212°F) -----		
0.029	1.726	250.3
0.039	2.255	327.1
0.061	3.418	495.8
0.075	4.209	610.5
0.100	5.559	806.3
0.126	6.980	1012.3
0.152	8.477	1229.5
0.164	9.142	1326.0
----- 423.1 K (150°C, 302°F) -----		
0.029	2.046	296.8
0.032	2.215	321.2
0.055	3.416	495.5

TABLE II (Continued)
SOLUBILITY OF METHANE IN BENZENE

Mole Fraction Methane	pressure	
	MPa	psia
0.074	4.383	635.7
0.103	5.921	858.7
0.115	6.525	946.3
0.145	8.092	1173.7
0.151	8.458	1226.7

TABLE III
SOAVE AND PENG-ROBINSON EQUATION OF STATE
REPRESENTATIONS OF METHANE SOLUBILITY IN CYCLOHEXANE

Temperature K(°F)	Soave Parameters (P-R Parameters)		Error in Methane* Mole Fraction	
	C_{ij}	D_{ij}	RMS	MAX
323.1 (122)	0.023	0.005	0.0002	0.0003
	(0.028)	(0.008)	--	--
	0.032	--	0.0004	0.0006
	(0.042)	--	--	--
373.1 (212)	0.023	0.004	0.0003	0.0005
	(0.027)	(0.005)	--	--
	0.029	--	0.0004	0.0006
	(0.036)	--	--	--
423.1 (302)	0.034	0.010	0.0003	0.0005
	(0.038)	(0.008)	--	--
	0.050	--	0.0006	0.001
	(0.050)	--	--	--
323.1, 373.1 423.1	0.040	-0.003	0.0026	0.005
	(0.035)	(0.004)	--	--
	0.034	--	0.0026	0.005
	(0.041)	--	--	--

* Errors are essentially identical for the Soave and the Peng-Robinson equations of state.

TABLE IV
SOAVE AND PENG-ROBINSON EQUATION OF STATE
REPRESENTATIONS OF METHANE SOLUBILITY IN BENZENE

Temperature K(°F)	Soave Parameters (P-R Parameters)		Error in Methane* Mole Fraction	
	C_{ij}	D_{ij}	RMS	MAX
323.1 (122)	0.033	0.022	0.0002	0.0004
	(0.036)	(0.027)	--	--
	0.073	--	0.0011	0.0017
	(0.083)	--	--	--
373.1 (212)	0.026	0.023	0.0001	0.0001
	(0.031)	(0.026)	--	--
	0.067	--	0.0009	0.0012
	(0.074)	--	--	--
423.1 (302)	0.037	0.017	0.0002	0.0004
	(0.039)	(0.019)	--	--
	0.067	--	0.0005	0.0008
	(0.070)	--	--	--
323.1, 373.1 423.1	0.024	0.026	0.0008	0.0014
	(0.019)	(0.035)	--	--
	0.071	--	0.0013	0.0029
	(0.080)	--	--	--

* Errors are essentially identical for the Soave and the Peng-Robinson equations of state

FIGURE 1
COMPARISON OF METHANE SOLUBILITIES
IN CYCLOHEXANE

FIGURE 2
COMPARISON OF METHANE SOLUBILITIES
IN BENZENE

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