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Solubility of Methane in Benzene, Naphthalene, Phenanthrene, and Pyrene at Temperatures from 323 to 433 K and Pressures to 11.3 MPa

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Solubility data are presented for methane in each of four aromatic hydrocarbons, including benzene, naphthalene, phenanthrene, and pyrene. The measurements cover temperatures from 323 to 433 K at pressures to 11.3 MPa. Our data for methane in benzene are in reasonable agreement with the earlier measurements of Sage, while our data for phenanthrene are in excellent agreement with those of Malone. The solubilities are described with a root-mean-squared error of 0.001 in mole fraction by the Soave−Redlich−Kwong and Peng−Robinson equations of state when one interaction parameter is used over the complete temperature range for each binary system. Henry's constants and partial molar volumes at infinite dilution were also calculated on the basis of the Krichevsky−Kasarnovsky equation.

Introduction

Global energy concerns have prompted increasing efforts to develop processes to produce alternative forms of liquid fuels, such as those derived from coal. In such processes, multiple fluid phases are present in essentially all stages of feed preparation, conversion reactions, and product separation. For example, during the initial stages of coal dissolution in a coal-derived recycle solvent, various light gases are produced (e.g., CH_4, CO, CO_2, H_2S, H_2O, NH_3, and C_2 to C_5 saturated hydrocarbons) *(1)*. The effective design and operation of such conversion processes require accurate knowledge of the phase behavior of the fluid mixtures encountered. Studies of the solubilities of light gases in heavy hydrocarbons are also of interest in the processing of petroleum products, enhanced oil recovery, and supercritical fluid processes. Moreover, such studies are essential in the development and evaluation of solution theories for fluid mixtures.

Previously, we have reported and analyzed the solubility of carbon dioxide and ethane in a series of heavy hydrocarbons *(2−6)*. We have now completed an experimental study on the solubility of methane in a series of hydrocarbon solvents (paraffins, naphthenes, and aromatics). Methane solubilities in heavy normal paraffins and in naphthenes have been reported previously *(7)*. In the present work, the solubility of methane in benzene, naphthalene, phenanthrene, and benzo[*def*]phenanthrene (pyrene) are presented and correlated using the Soave−Redlich−Kwong (SRK) *(8)* and Peng−Robinson (PR) *(9)* equations of state (EOS). Solubilities were measured at temperatures from 311 to 423 K and pressures to 11.3 MPa. These data complement the available literature data and should prove useful in the development and testing of correlations to describe the phase behavior of multicomponent systems involving methane.

Experimental Method

The experimental apparatus used in this study is a modification of the one used by Raff *(6)*. A detailed description of the apparatus and experimental procedures is given elsewhere *(7, 10)*. Briefly, the apparatus is a variable-volume, static-type blind equilibrium cell. For a given binary mixture of known composition, the bubble point pressure is identified graphically from the discontinuity in compressibility of the mixture as it passes from the two-phase state to the single liquid phase. This method consists of introducing known amounts of well-degassed, pure components into a variable-volume thermostated equilibrium cell. The volume of the equilibrium mixture is varied by the introduction or withdrawal of mercury. Two steel balls are placed in the equilibrium cell and the cell is rocked 45° about the horizontal level to hasten the establishment of equilibrium. Details of the apparatus and experimental procedure are described by Darwish *(10)*.

Estimated uncertainties in experimental variables are 0.1 K in temperature and less than 0.001 in mole fraction. Uncertainties in the measured bubble point pressures depend on the steepness of the $p-x$ (pressure versus liquid phase mole fraction) relation and range from approximately 0.035 MPa for methane in benzene to 0.07 MPa for methane in naphthalene, phenanthrene, or pyrene *(7)*.

Materials

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

Results

The experimental results appear in Tables 1−4. Differences in the lowest temperature at which the various systems were studied were dictated by the melting points of the solvents, which (except for benzene) are solids at room temperature.

The SRK *(8)* and PR *(9)* cubic equations of state describe the data well. Optimum binary interaction parameters for these equations were obtained by minimizing the sum of squares of deviations between the predicted and experimental saturation pressures. A detailed description of the EOS mixing rules that we employed and the procedures for the data reductions are given elsewhere *(7, 10)*. The input properties for the pure components (acentric factor, ω, critical temperature, T_c, and critical pressure, p_c) required by the SRK and PR equations of state, together with their literature sources, are presented in Table 5.

Figures 1 and 2 illustrate the effects of temperature and pressure on the methane solubility (liquid-phase mole

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Table 1. Solubility of Methane (1) in Benzene (2)

x_1	p/MPa	x_1	p/MPa
	323.2 K		
0.0275	1.46	0.1191	6.40
0.0533	2.80	0.1341	7.23
0.0751	3.97	0.1493	8.11
0.1141	6.14	0.1665	9.09
	373.2 K		
0.0289	1.73	0.0996	5.51
0.0389	2.26	0.1255	6.98
0.0605	3.42	0.1522	8.48
0.0750	4.21	0.1642	9.14
	423.2 K		
0.0287	2.05	0.1032	5.92
0.0316	2.21	0.1147	6.52
0.0552	3.42	0.1450	8.09
0.0736	4.38	0.1511	8.46

Table 2. Solubility of Methane (1) in Naphthalene (2)

x_1	p/MPa	x_1	p/MPa
	373.2 K		
0.0245	1.96	0.0640	5.30
0.0302	2.40	0.0860	7.35
0.0503	4.06	0.1002	8.69
	423.2 K		
0.0243	1.94	0.0598	4.93
0.0309	2.48	0.0750	6.25
0.0446	3.64	0.0998	8.48

Table 3. Solubility of Methane (1) in Phenanthrene (2)

x_1	p/MPa	x_1	p/MPa
	383.2 K		
0.0197	2.04	0.0600	6.73
0.0296	3.16	0.0714	8.17
0.0444	4.82	0.0898	10.71
	423.2 K		
0.0206	2.15	0.0595	6.62
0.0296	3.13	0.0742	8.42
0.0451	4.86	0.0902	10.46

Table 4. Solubility of Methane (1) in Pyrene (2)

x_1	p/MPa	x_1	p/MPa
	423.2 K		
0.0198	2.35	0.0699	8.97
0.0347	4.23	0.0751	9.71
0.0489	6.04	0.0855	11.30
0.0599	7.58		

Table 5. Critical Properties and Acentric Factors Used in the SRK and PR Equations of State

component	p_c/MPa	T_c/K	ω	ref
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	0.83^a	23

^{a} Reference 24.

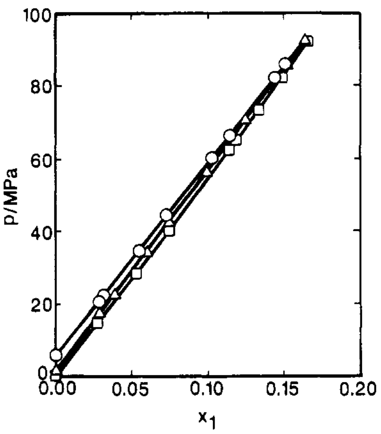

Figure 1. Bubble point pressure data for methane + benzene: □, 323.2 K; △, 373.2 K; ○, 423.2 K.

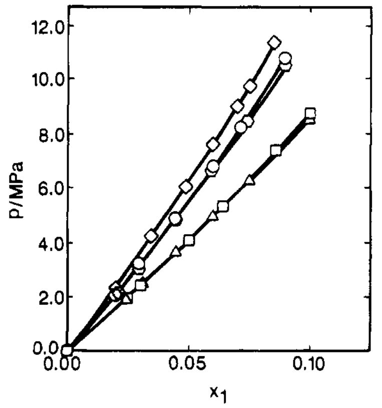

Figure 2. Bubble point pressure data for methane + aromatic hydrocarbons: □, naphthalene, 373.2 K; △, naphthalene, 423.2 K; ○, phenanthrene, 347.2 K; ○, phenanthrene, 423.2 K; ◇, pyrene, 433.2 K.

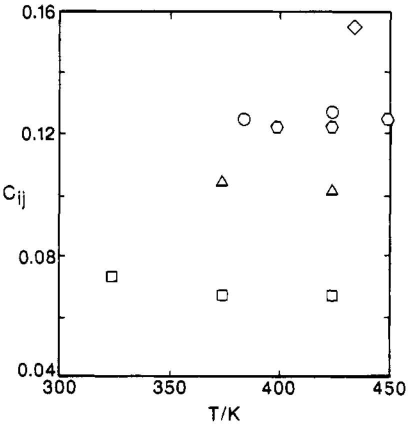

Figure 3. SRK interaction parameter, $C_{ij}(T)$, for methane + aromatic hydrocarbons: (this work) □, benzene; △, naphthalene; ○, phenanthrene; ◇, pyrene; (Malone (*16*)) ○, phenanthrene.

fraction of methane, x_1). The solubilities of methane in these aromatic hydrocarbons exhibit weak dependence on temperature as Figure 2 reveals for the solubility of methane in naphthalene and phenanthrene. Similarly, Figure 3 shows that the SRK interaction parameter, C_{ij}, for these systems is relatively insensitive to temperature. Figure 4 shows a very regular trend with chemical structure for the SRK interaction parameter, C_{ij}, when a single value is used over the complete temperature range for each binary system. However, the values of the interaction parameter, C_{ij}, are strongly influenced by the critical properties employed in the EOS predictions. This is important, since values of these parameters must be estimated for phenanthrene and pyrene, for which experimental properties are not available. For example, when the acentric factor of pyrene was taken as 0.344, as reported by API (*23*), the optimum C_{ij} was found to be 0.41. This is significantly different from the value of 0.15 obtained using an acentric factor of 0.83, as recommended by Turek (*24*).

The equation-of-state descriptions of the solubilities for all systems are given in Tables 6–9. In general, the SRK and PR equations are capable of describing the data with rms errors 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, where the rms error is 0.0013. For methane solubility in

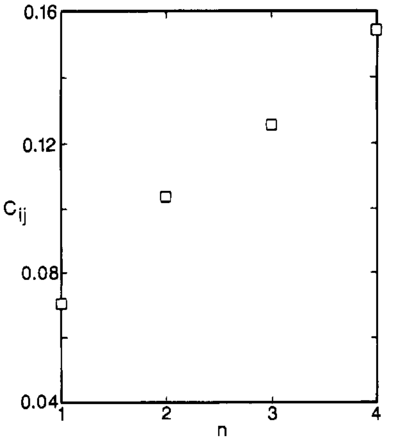

Figure 4. SRK interaction parameter, C_{ij}, for methane + aromatic hydrocarbons. n is the number of aromatic rings in the solvent.

Table 6. SRK and PR Equation-of-State Representations of the Solubility of Methane in Benzene

	SRK params (PR params)		error in mole fraction[a]	
T/K	C_{12}	D_{12}	rms	|max|
323.2	0.0328 (0.0361)	0.0222 (0.0272)	0.0002	0.0004
	0.0729 (0.0825)		0.0010	0.0017
373.2	0.0259 (0.0306)	0.0232 (0.0263)	0.0001	0.0001
	0.0668 (0.0742)		0.0009	0.0012
423.2	0.0367 (0.0385)	0.0172 (0.0191)	0.0002	0.0004
	0.0666 (0.0696)		0.0005	0.0008
323.2, 373.2, 423.2	0.0240 (0.0191)	0.0260 (0.0353)	0.0008	0.0014
	0.0705 (0.0786)		0.0013	0.0029

[a] Errors are essentially identical for the SRK and PR EOS.

Table 7. SRK and PR Equation-of-State Representations of the Solubility of Methane in Naphthalene

	SRK params (PR params)		error in mole fraction[a]	
T/K	C_{12}	D_{12}	rms	|max|
373.2	0.1034 (0.1008)	0.0003 (0.0054)	0.0002	0.0004
	0.1043 (0.1165)		0.0002	0.0003
423.2	0.0727 (0.0770)	0.0090 (0.0117)	0.0001	0.0002
	0.1014 (0.1110)		0.0002	0.0003
373.2, 423.2	0.0931 (0.0868)	0.0032 (0.0095)	0.0003	0.0007
	0.1033 (0.1146)		0.0003	0.0008

[a] Errors are essentially identical for the SRK and PR EOS.

benzene, somewhat improved predictions are realized (rms = 0.0008) when an additional parameter, D_{ij}, is used, as indicated by results given in Table 6.

Comparisons of our results with those of various researchers appear in Figures 5 and 6. The comparisons are shown in terms of deviations , δx_1, of the solubilities from values predicted using the SRK *(8)* equation of state. 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 for each system. These figures permit sensitive analysis of the differences in the solubilities measured by various researchers.

Table 8. SRK and PR Equation-of-State Representations of the Solubility of Methane in Phenanthrene

	SRK params (PR params)		error in mole fraction[a]	
T/K	C_{12}	D_{12}	rms	|max|
383.2	0.1313 (0.1247)	−0.0014 (0.0040)	0.0001	0.0002
	0.1246 (0.1418)		0.0001	0.0002
423.2	0.1204 (0.1189)	0.0014 (0.0054)	0.0002	0.0003
	0.1268 (0.1420)		0.0002	0.0003
383.2, 423.2	0.1257 (0.1228)	−0.0001 (0.0044)	0.0002	0.0005
	0.1255 (0.1419)		0.0002	0.0005

[a] Errors are essentially identical for the SRK and PR EOS.

Table 9. SRK and PR Equation-of-State Representations of the Solubility of Methane in Pyrene

	SRK params (PR params)		error in mole fraction[a]	
T/K	C_{12}	D_{12}	rms	|max|
433.2	0.124 (0.126)	0.006 (0.009)	0.0001	0.0002
	0.159 (0.180)		0.0002	0.0004

[a] Errors are essentially identical for the SRK and PR EOS.

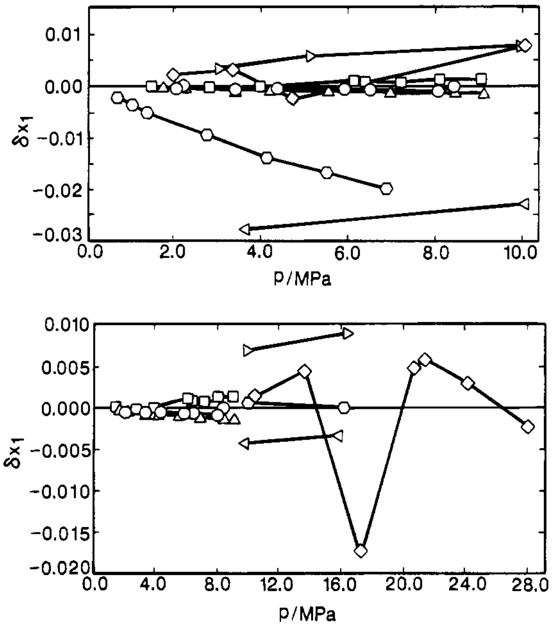

Figure 5. Comparison of methane solubilities in benzene: (a, top) (this work) □, 323.2 K; △, 373.2 K; ○, 423.2 K; (Elbislawi *(13)*) ○, 338.8 K; (Legret (14)) <, 313.2; (Lin *(11)*) ◇, 421.0 K; >, 462.1 K. (b, bottom) (this work) □, 323.2 K; △, 373.2 K; ○, 423.2 K; (Sage *(12)*) ▷, 311.1 K; ○, 344.3 K; ◁, 377.6 K; (Schoch *(15)*) ◇, 421.0 K. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

The comparisons for methane + benzene, Figure 5, reveal reasonable agreement (solubility differences within 0.004) between our results and those of Lin et al. *(11)* at 421 K (Figure 5a). Better agreement is observed with the results of Sage et al. *(12)* at 344 K (Figure 5b), where the solubility differences are within 0.001. However, significant disagreements with Elbishlawi and Spencer *(13)*, Legret et al. *(14)*, and Schoch et al. *(15)* are seen in both figures.

Figure 6 shows comparisons for methane + phenanthrene. Interaction parameters in the equation of state were obtained by fitting the data of Malone and Kobayashi

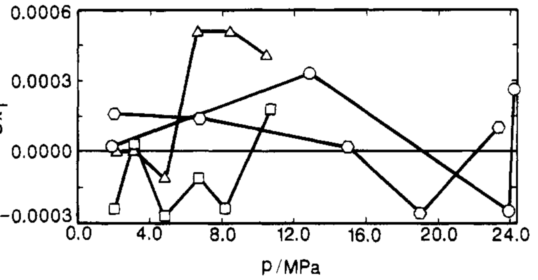

Figure 6. Comparison of methane solubilities in phenanthrene: (this work) □, 383.2 K; △, 423.2 K; (Malone *(16)*) ○, 398.2 K; ○, 423.2 K. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

(16), since their data covered a wide range of pressures. The agreement between the two data sets is excellent. The maximum solubility deviation is less than 0.0005 mole fraction, which is within the experimental error of the measured solubilities *(7)*.

For methane + naphthalene and methane + pyrene, no previous data are available for comparisons. The ability of the SRK and PR equations of state to represent precisely these data is documented in Tables 7 and 9. The low rms errors in solubility illustrate the precision of the present data.

Krichevsky–Kasarnovsky Analysis

In the range of methane mole fractions reported in this study, the solubilities of methane in naphthalene, phenanthrene, and pyrene are represented within 0.0005 mole fraction by the Krichevsky–Kasarnovsky (KK) equation *(17)*, expressed as

$$\ln(f_1/x_1) = \ln H_{1,p_2} + (v_1^{\infty}/RT)(p - p_2) \qquad (1)$$

where f_1, H_{1,p_2}, v_1^{∞}, R, and p_2 are the fugacity of methane, Henry's constant of methane at the hydrocarbon vapor pressure, the infinite dilution partial molar volume of methane, the universal gas constant, and the vapor pressure of the solvent, respectively. Values of the methane fugacity were obtained using Bender's equation of state for methane *(18)*, since the vapor phase is essentially pure methane. The solubility data of methane + benzene were excluded from the KK analysis because of the appreciable vapor pressures (and, hence, vapor-phase mole fractions) of benzene at the reported temperatures.

Henry's constants and infinite-dilution partial molar volumes of methane regressed from the solubility data of this work and other researchers, using eq 1, are presented in Table 10. Henry's constants of this work agree within 0.5 MPa with those of Malone *(16)*. Also, the partial molar volumes from this work and Malone *(16)* agree within their experimental uncertainties. However, care should be exercised in attributing physical significance to the partial molar volumes, which are known to be less accurate than the corresponding Henry's constants determined by KK analysis.

Conclusions

The solubility of methane in each of the aromatic solvents benzene, naphthalene, phenanthrene, and pyrene has been measured at temperatures ranging from 323 to 433 K and pressures to 11.3 MPa. These data are well described by the Soave–Redlich–Kwong and Peng–Robinson equations of state and by the Krichevsky–Kasarnovsky equation. These results should be useful for evaluating solution theories for representing light gas solubilities in aromatic solvents.

Table 10. Henry's Constants and Infinite-Dilution Partial Molar Volumes for Methane in Aromatic Hydrocarbons

T/K	ref	SRK Henry's constant/MPa (PR Henry's constant/MPa)	partial molar volume/ ($\mathrm{cm^3 \cdot mol^{-1}}$)	error in methane mole fraction rms
		Naphthalene		
373.2	this work	77.0 (4)[a]	338 (50)[a]	0.0005
423.2	this work	78.0 (2)	350 (25)	0.0001
		Phenanthrene		
383.2	this work	100.6 (4)	495 (30)	0.0001
423.2	this work	101.3 (3)	530 (25)	0.0002
398.2	16	101.9 (2)	480 (5)	0.0002
423.2	16	101.9 (4)	490 (15)	0.0003
448.2	16	101.4 (2)	514 (10)	0.0002
		Pyrene		
433.2	this work	115.2 (4)	510 (25)	0.0003

[a] Standard deviation of the estimated parameter.

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