Solubility of Methane in Hexane, Decane, and Dodecane at Temperatures from 311 to 423 K and Pressures to 10.4 MPa

Srinivasa Srivastan, Naif A. Darwish, Khaled A. M. Gasem, and Robert L. Robinson, Jr.*

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

The solubilities of methane in the normal paraffins hexane, decane, and dodecane were measured using a static equilibrium cell over the temperature range from 311 to 423 K and pressures to 10.4 MPa. The new solubility measurements are believed to have uncertainties of 0.002 in mole fraction, and they compare favorably with available literature data. The data were analyzed using the Soave–Redlich–Kwong and Peng–Robinson equations of state. In general, the two equations represent the experimental data well over the complete temperature range when two interaction parameters are used for each binary system.

Introduction

The ability to predict the phase behavior of fluid mixtures is important in the design and development of separation processes such as those encountered in petroleum refining, coal conversion, and supercritical extraction. As a result, a constant demand by industry exists for vapor–liquid equilibrium data at elevated pressures. Such data are required for the proper design, operation, and optimization of the various processes.

This study deals with experimental determination of the solubility of methane in selected hydrocarbons; i.e., given the pressure and temperature of a binary mixture (involving a solute gas and hydrocarbon solvent), the objective is to measure the concentration (mole fraction) of the solute gas dissolved in the liquid phase.

Binary vapor–liquid phase equilibrium for methane with heavy hydrocarbons (*n*-paraffins, naphthenes, and aromatics) has been studied by Darwish (*1*, *2*). The present work complements that earlier study by measuring the solubility of methane in hexane, decane, and dodecane. Solubilities were measured at temperatures from 311 to 423 K and pressures to 10.4 MPa.

Only binary mixture solubilities have been studied because binary data are particularly valuable in correlation development and testing. In general, all state-of-the-art models for vapor–liquid equilibrium describe the unlike molecule interactions using one to three parameters. The usual mixing rules in such models describe the unlike molecule interactions solely in terms of parameters that reflect pairwise interactions, which are conveniently obtained from data on binary mixtures.

The experimental data of this work together with the data available in the literature for the same systems were analyzed using the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) cubic equations of state (*3*, *4*). The ability of the cubic equations of state in representing these systems was evaluated, and binary interaction parameters from the present data are tabulated.

Experimental Method

The experimental apparatus used in this study employs a variable-volume, static-type blind equilibrium cell. The bubble point pressure of a synthetically prepared binary mixture is identified graphically from the discontinuity in compressibility of the mixture as it crosses from the liquid state to a two-phase condition. This method consists of introducing known amounts of two well-degassed pure components into a variable-volume thermostated equilibrium cell. The volume of the cell is varied by the introduction or withdrawal of mercury. Mechanical agitation of the equilibrium cell, required to ensure attainment of equilibrium, is accomplished by rocking the cell 45° about the horizontal level. Attainment of equilibrium in a reasonable time is ensured by the introduction of steel balls (slightly smaller in diameter than that of the equilibrium cell) into the cell.

Table I. Purities and Sources of Chemicals Used in This Study

chemical	source	purity/(mol %)
methane	Big 3 Industries, Inc.	99.97+
hexane	Aldrich Chemical Co.	99+
decane	Aldrich Chemical Co.	99+
dodecane	Alfa Products	99+

A detailed description of the apparatus and a step-by-step procedure for its operation are given by Darwish (*2*). Estimated uncertainties in experimental measurements are 0.1 K in temperature and less than 0.002 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 0.04 MPa (*2*) for the systems studied here.

Materials. All chemicals used in this study were purchased from commercial suppliers. No further purification was attempted. The chemicals, along with their reported purities and suppliers, are presented in Table I.

Results

The methane solubility data are presented in Tables II–IV. The effects of temperature and pressure on the solubility (liquid phase mole fraction of methane) are illustrated by the *n*-decane measurements shown in Figure 1. At a given total pressure, the solubility of the solute gas decreases with increasing temperature. This is the same behavior observed for CO_2 and CH_4 solubilities in heavy normal paraffins (*1*, *5*).

Comparisons of our results with those of other researchers appear in Figures 2–8. The comparisons are shown in terms of deviations generated by comparing solubilities predicted using the SRK equation of state (discussed below) to the experimental values. Interaction parameters, C_{ij} and D_{ij}, employed in the equation of state predictions were obtained by fitting our data for the isotherm under study.

Figure 2 shows a comparison of our data for the methane + hexane system with those of four other researchers (*6*–*9*) at a temperature of 310.9 K. The observed deviations in solubility between our data and those of the other researchers are less than 0.006 except for one point (of Schoch et al. (*6*)), with our data generally showing lower methane solubility

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Table II. Solubility Data for Methane (1) + Hexane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		310.9 K			
0.0496	1.08	0.1898	4.30	0.2803	6.63
0.0996	2.18	0.2296	5.30	0.3234	7.84
0.1202	2.65	0.2494	5.85		
0.1493	3.36	0.2573	6.03		
		338.7 K			
0.0623	1.58	0.1498	3.80	0.2216	5.76
0.0628	1.58	0.1500	3.80	0.2510	6.64
0.1006	2.57	0.1997	5.23	0.2875	7.78
		377.6 K			
0.0506	1.55	0.1502	4.24	0.2499	7.11
0.0509	1.57	0.1550	4.40	0.2507	7.13
0.0622	1.90	0.1708	4.83	0.2939	8.46
0.0805	2.35	0.2006	5.72	0.2972	8.52
0.1004	2.93	0.2378	6.76		

Table III. Solubility Data for Methane (1) + Decane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		310.9 K			
0.0495	1.04	0.1512	3.42	0.2913	7.47
0.0750	1.60	0.1997	4.70	0.3080	8.04
0.0997	2.17	0.2522	6.24		
		344.3 K			
0.0505	1.22	0.1274	3.21	0.2271	6.17
0.0741	1.79	0.1537	3.95	0.2484	6.87
0.0962	2.39	0.2007	5.35		
		377.6 K			
0.0552	1.44	0.1247	3.41	0.2401	7.12
0.0837	2.21	0.1691	4.74	0.2755	8.35
0.0969	2.60	0.2107	6.10		
		410.9 K			
0.0737	2.06	0.1761	5.15	0.2506	7.75
0.1260	3.58	0.2019	6.02	0.2754	8.65
0.1516	4.37	0.2259	6.86		

Table IV. Solubility Data for Methane (1) + Dodecane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		323.2 K			
0.0615	1.33	0.2105	5.21	0.3566	10.38
0.1023	2.27	0.2530	6.54		
0.1515	3.55	0.3022	8.24		
		373.2 K			
0.0998	2.54	0.1817	4.98	0.2505	7.32
0.1013	2.59	0.2020	5.62	0.3023	9.27

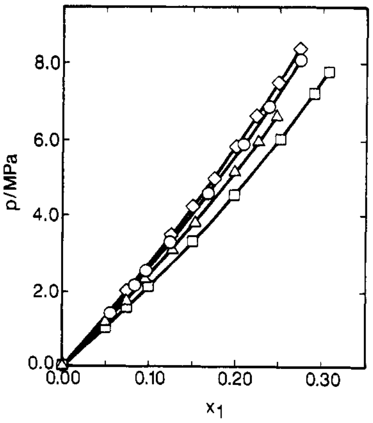

Figure 1. Solubility of methane in decane: □, 310.9 K; △, 344.3 K; ○, 377.6 K; ◇, 410.9 K.

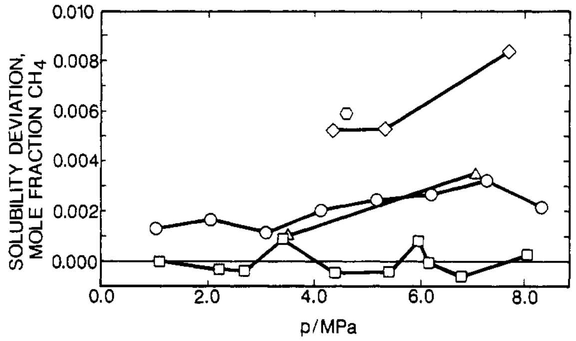

Figure 2. Comparison of methane solubilities in hexane at 310.9 K: □, this work; ◇, Schoch (*6*); △, Poston (*7*); ○, Shim (*8*) (323.2 K); ○, Sage (*9*).

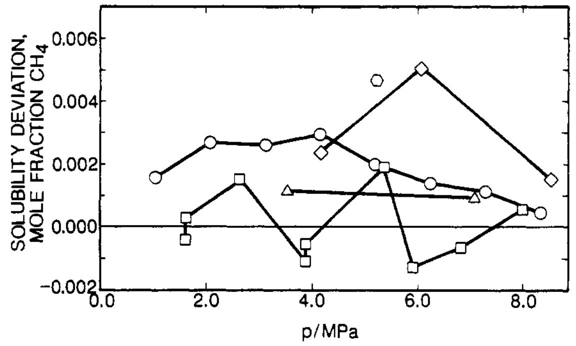

Figure 3. Comparison of methane solubilities in hexane at 344.3 K: □, this work; ◇, Schoch (*6*); △, Poston (*7*); ○, Shim (*8*) (348.2 K); ○, Sage (*9*).

(higher bubble point pressures). Similarly, Figures 3 and 4 show the results of comparisons with the same researchers at 344.3 and 377.6 K, respectively. In general, the differences in solubilities between our data and those in the literature are less than 0.005 at 344.3 K and 0.003 at 377.6 K. Our data are in good agreement (deviations <0.003) with those of Poston (*7*) and Shim (*8*) on all three isotherms of study. In all the above comparisons, interaction parameters, C_{ij} and D_{ij}, regressed from our data were used to predict solubility deviations for the data reported by Shim at temperatures slightly different from ours.

Figures 5–8 show comparisons for methane + decane. Reasonable agreement is observed between the present study and that of Reamer (*10*) at temperatures of 344.3, 377.6, and 410.9 K; solubilities, as shown in Figures 6 and 7, agree within 0.003 over the whole pressure range of this study. However, the agreement is not as good at 310.9 K, as Figure 5 shows. According to Mohindra (*11*), Reamer's data at 310.9, 344.3, and 377.6 K were found to be thermodynamically inconsistent. The best agreement between this work and that of Reamer (*10*) is at 410.9 K where the solubilities, as shown in Figure 8, agree within 0.0015. Similarly, good agreement (solubility deviation within 0.002) between this study and that of Lin (*12*) is also revealed by Figure 8. Except at very low pressures (<0.7 MPa), this study is in significant disagreement with that of Lavender (*13*), whose data were reported to be internally inconsistent (*11*).

No comparisons are available for the methane + dodecane system due to the absence of published data.

Equation of State Data Correlation. The experimental data have been correlated using the SRK (*3*) and PR (*4*) cubic equations of state. For the SRK equation the specific relations used are

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

where

$$a(T) = a_c\alpha(T) \tag{2}$$

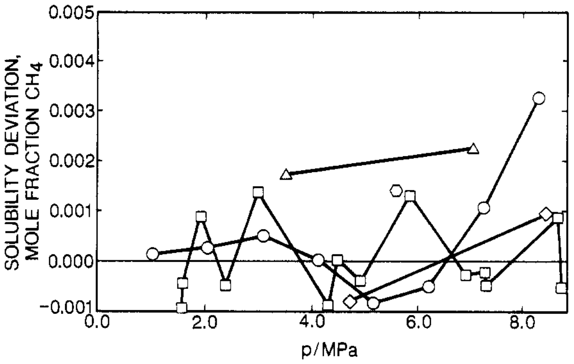

Figure 4. Comparison of methane solubilities in hexane at 377.6 K: □, this work; ◇, Schoch (*6*); △, Poston (*7*); ○, Shim (*8*) (373.2 K); ○, Sage (*9*).

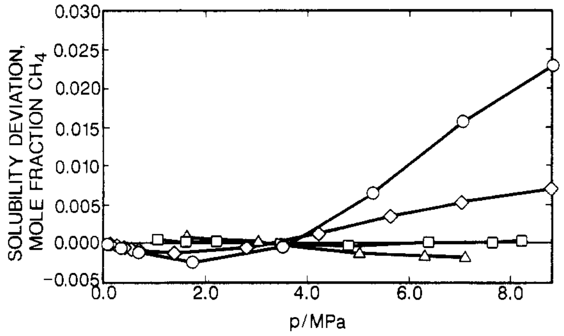

Figure 5. Comparison of methane solubilities in decane at 310.9 K: □, this work, run 1; △, this work, run 2; ○, Lavender (*13*); ◇, Reamer (*10*).

$$b = 0.08664RT_c/P_c \tag{3}$$

and

$$a_c = 0.42748R^2T_c^{\,2}/P_c \tag{4}$$

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

$$k = 0.480 + 1.574w - 0.176w^2 \tag{6}$$

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

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

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

In eqs 7 and 8, the summations are over all chemical species and C_{ij} and D_{ij} are empirical interaction parameters characterizing the binary interactions between components "i" and "j". Values of these parameters were determined by fitting experimental binary mixture data to minimize the objective function, SS, which represents the sum of squared errors in predicted bubble point pressures:

$$\mathrm{SS} = \sum_i^n (p_{\mathrm{exptl}} - p_{\mathrm{calcd}})_i^{\,2} \tag{9}$$

Further details of the data reduction techniques employed in this study are given by Gasem (*14*). The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table V.

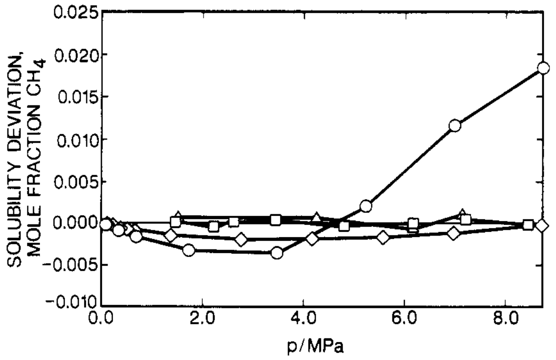

Figure 6. Comparison of methane solubilities in decane at 344.3 K: □, this work, run 1; △, this work, run 2; ○, Lavender (*13*); ◇, Reamer (*10*).

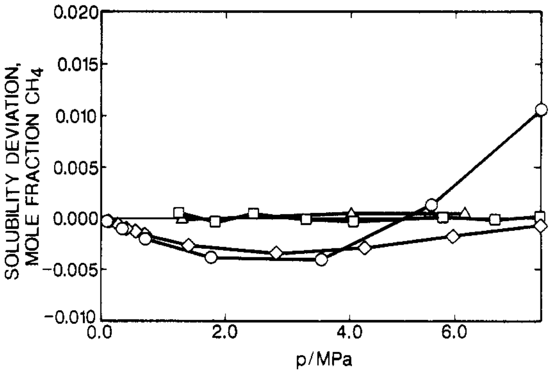

Figure 7. Comparison of methane solubilities in decane at 377.6 K: □, this work, run 1; △, this work, run 2; ○, Lavender (*13*); ◇, Reamer (*10*).

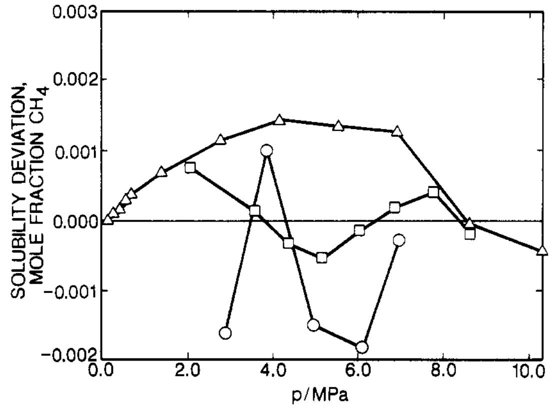

Figure 8. Comparison of methane solubilities in decane: □, this work, 410.9 K; △, Reamer (*10*), 410.9 K; ○, Lin (*10*), 423.2 K.

Table V. Critical Pressure, P_c, Critical Temperature, T_c, and Acentric Factor, w, Used in the SRK and PR Equations of State

component	P_c/MPa	T_c/K	w	ref
methane	4.660	190.5	0.011	15
hexane	3.030	507.9	0.298	16
decane	2.097	617.5	0.4885	16
dodecane	1.806	658.3	0.571	16

The equation of state representation of the solubility for the systems considered is shown in Tables VI–VIII. In general, the SRK and PR equations are capable of describing the data with RMS errors within 0.005 in mole fraction for a given system when a single interaction parameter, C_{ij}, is used over the complete temperature range. The quality of the EOS representation is improved when an additional interaction parameter, D_{ij}, is employed, resulting in RMS errors of about

Table VI. SRK and PR Equation of State Representations of the Solubility of Methane (1) + Hexane (2)

T/K	Soave parameters (PR parameters)		error in methane mole fraction[a]	
	C_{12}	D_{12}	RMS	|max|
310.9	0.028	−0.002	0.0005	0.0009
	(0.030)	(−0.000)		
	0.026		0.0006	0.0008
	(0.030)			
344.3	0.053	−0.014	0.0011	0.0019
	(0.052)	(−0.013)		
	0.032		0.0017	0.0026
	(0.033)			
377.6	0.040	0.002	0.0008	0.0014
	(0.040)	(0.001)		
	0.042		0.0008	0.0015
	(0.040)			
310.9, 344.3, and 377.6	0.043	−0.008	0.0031	0.0061
	(0.041)	(−0.006)	0.0021	0.0043
	0.032		0.0033	0.0064
	(0.033)		0.0023	0.0046

[a] The RMS and maximum errors in CH_4 mole fraction are essentially the same using the SRK and PR equations of state, unless separate results are shown.

Table VII. SRK and PR Equation of State Representations of the Solubility of Methane (1) + Decane (2)

T/K	Soave parameters (PR parameters)		error in methane mole fraction[a]	
	C_{12}	D_{12}	RMS	|max|
310.9	0.054	−0.009	0.0003	0.0005
	(0.054)	(−0.008)		
	0.033		0.0019	0.0028
	(0.037)			
344.3	0.046	−0.007	0.0003	0.0005
	(0.045)	(−0.006)		
	0.028		0.0009	0.0013
	(0.030)			
377.6	0.054	−0.010	0.0003	0.0005
	(0.053)	(−0.010)		
	0.031		0.0012	0.0019
	(0.030)			
410.9	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, and 410.9	0.057	−0.011	0.0007	0.0017
	(0.057)	(−0.011)		
	0.032		0.0017	0.0032
	(0.033)			

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

0.002 in mole fraction.

As expected, more significant improvements are realized by using temperature-dependent interaction parameters; when two parameters (C_{ij} and D_{ij}) are fitted to each isotherm, the RMS errors are within 0.001. The results in Tables VI–VIII suggest that the use of two parameters per binary system produces an adequate EOS representation for the systems considered.

In general, the RMS errors in mole fraction are comparable to the estimated uncertainties for the measurements. These results illustrate both the ability of the equations of state and the precision of the reported data.

Conclusions

Data have been obtained on the solubility of methane in a series of n-paraffin solvents (hexane, decane, and dodecane) at temperatures from 311 to 423 K and pressures to 10.4 MPa. These data are well described by the Soave–Redlich–Kwong and Peng–Robinson equations of state. The newly acquired data, combined with our earlier measurements involving heavy n-paraffins (*1*), will be of value in (a) establishing interaction parameters in other equations of state for light gases in hydrocarbon solvents and (b) the development and evaluation of solution theories of mixing.

Table VIII. SRK and PR Equation of State Representations of the Solubility of Methane (1) + Dodecane (2)

T/K	Soave parameters (PR parameters)		error in methane mole fraction[a]	
	C_{12}	D_{12}	RMS	|max|
323.2	0.066	−0.013	0.0004	0.0006
	(0.065)	(−0.012)		
	0.034		0.0039	0.0052
	(0.037)			
373.3	0.066	−0.016	0.0002	0.0004
	(0.064)	(−0.017)		
	0.021		0.0028	0.0034
	(0.022)			
323.2 and 473.2	0.073	−0.017	0.0022	0.0035
	(0.073)	(−0.017)	0.0031	0.0049
	0.030		0.0045	0.0084
	(0.032)		0.0050	0.0091

[a] The RMS and maximum errors in CH_4 mole fraction are essentially the same using the SRK and PR equations of state, unless separate results are shown.

List of Symbols

$a(T)$	energy parameter in the SRK or PR EOS
C_{ij},D_{ij}	binary interaction parameters in the SRK or PR EOS
N	number of components in mixture
n	number of data points
p	pressure
R	gas constant
RMS	root mean square error
SS	objective function (defined by eq 9)
T	temperature
v	molar volume
x	liquid mole fraction of methane (solubility)
w	acentric factor
Z	compressibility factor
z_i	mole fraction of component i in a mixture

Greek Letters

α	temperature-dependent parameter in eq 2

Subscripts

c	critical state
calcd	calculated
exptl	experimental
i	component i in a mixture
r	reduced property

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