

Solubility of Methane in Cyclohexane and in *trans*-Decalin at Temperatures from 323 to 423 K at Pressures to 9.6 MPa

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Solubility data are presented for methane in the naphthenic solvents cyclohexane and *trans*-decalin (decahydronaphthalene) at temperatures from 323 to 423 K and pressures to 9.6 MPa. The data for methane + cyclohexane are in reasonable agreement with the measurements of Reamer et al. but differ significantly from some of the data of Schoch et al. Our new data can be described with root-mean-square errors of about 0.0005 mole fraction by the Soave–Redlich–Kwong and Peng–Robinson equations of state when a single interaction parameter per isotherm is employed in the equations. Addition of a second interaction parameter provides little improvement in the quality of representation of the data.

Introduction

Over a period of several years, we have measured high-pressure solubilities of a series of light gases (e.g., H₂, CO, N₂, CO₂, C₂H₆) in paraffinic, naphthenic, and aromatic solvents. Such data are valuable in developing and testing models for representation of the phase behavior in systems of interest in a variety of practical industrial applications, such as supercritical extraction, enhanced oil recovery, and production of fluid fuels from coal. We have presented correlations (Gasem et al., 1990, 1993) that have relied heavily on the use of our earlier data.

Recently, we have completed an experimental study of the solubility of methane in a series of aromatic, paraffinic, and naphthenic solvents. Solubility data have been presented for the binary systems of methane in the paraffins decane, eicosane, octacosane, hexatriacontane, and tetraetracontane (Darwish et al., 1993) and in the aromatics benzene, naphthalene, phenanthrene, and pyrene (Darwish et al., 1994). In the present work, solubility data for methane in the naphthenic solvents cyclohexane and *trans*-decalin are presented and correlated using the Soave–Redlich–Kwong (SRK) (Soave, 1972) and Peng–Robinson (PR) (Peng and Robinson, 1976) equations of state (EOS). Measurements were made at temperatures from 323 to 423 K and pressures to 9.6 MPa. These data provide a valuable complement to the available literature data and should prove useful in the development and testing of correlations to describe the phase behavior of multicomponent systems containing methane.

Experimental Section

The experimental apparatus used in this study was a modified version of the apparatus described in detail elsewhere (Darwish et al., 1993; Raff, 1986). Basically, it is a variable-volume, static-type blind equilibrium cell. For

a 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. Measurements are made by introducing known amounts of well-degassed, pure components into a variable-volume thermostated equilibrium cell. The volume of the equilibrium mixture is varied by introducing or withdrawing mercury from the cell. Two steel balls are placed in the cell, and the cell is rocked 45° above the horizontal level to hasten the establishment of equilibrium. Plots of equilibrium pressure versus the amount of mercury injected show clearly defined break points where the fluid passes from the two-phase to the single-phase state. A detailed description of the experimental procedure is given elsewhere (Park et al., 1995; Darwish, 1991).

Estimated uncertainties (ϵ) in the experimental measurements are 0.1 K in temperature, 0.003 MPa in pressure, and less than 0.001 in mole fraction. However, the estimated uncertainties in the reported bubble point pressures (ϵ_{bp}) at a specified mole fraction are of the order of 0.035 MPa (Darwish, 1991) for the systems in this study, since $(\epsilon_{bp})^2 = (\epsilon_p)^2 + (d[bp]/dx)^2(\epsilon_x)^2$. Thus the total uncertainty in the reported bubble point pressure (at specified mole fraction) depends on both the pressure and composition uncertainties and, in addition, the steepness of the bubble point pressure vs composition curve.

The methane used in the measurements had a stated purity of 99.97+ mol % and was supplied by Matheson. Cyclohexane and *trans*-decalin were from Aldrich Chemical Co. with quoted purities of 99+ mol %. No further analysis or purification of the chemicals was attempted.

Results and Discussion

The experimental data of this work are tabulated in Tables 1 and 2. The data have been correlated using the SRK and PR cubic equations of state in order (a) to assess the accuracy of these two EOS for the systems studied and

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

x_1	p/MPa	x_1	p/MPa
323.2 K			
0.042	1.41	0.155	5.40
0.069	2.35	0.174	6.10
0.098	3.34	0.207	7.38
0.124	4.25		
373.2 K			
0.029	1.25	0.152	5.91
0.052	2.09	0.178	7.02
0.083	3.24	0.194	7.63
0.100	3.91	0.201	7.94
0.138	5.40	0.212	8.41
423.2 K			
0.027	1.60	0.129	5.64
0.051	2.51	0.151	6.52
0.065	3.04	0.176	7.54
0.075	3.50	0.201	8.59
0.088	4.01	0.222	9.43
0.101	4.50		

Table 2. Solubility of Methane (1) in *trans*-Decalin (2)

x_1	p/MPa	x_1	p/MPa
323.2 K			
0.026	0.89	0.100	3.67
0.050	1.75	0.134	5.01
0.075	2.66	0.150	5.73
373.2 K			
0.050	2.04	0.170	7.53
0.100	4.20	0.180	8.11
0.120	5.11	0.200	9.11
0.150	6.57		
423.2 K			
0.030	1.35	0.135	6.30
0.075	3.39	0.176	8.36
0.100	4.60	0.200	9.62
0.127	5.86		

Table 3. Critical Properties and Acentric Factors Used in the SRK and PR Equations of State^a

component	critical properties		acentric factor
	pressure/MPa	temp/K	
methane	4.60	190.4	0.011
cyclohexane	4.07	553.5	0.212
<i>trans</i> -decalin	3.14	687.1	0.27

^a Reid et al. (1987).

(b) to facilitate comparisons of our data with the results of earlier studies. Optimum binary interaction parameters in the EOS were obtained by minimizing the sum of squares of pressure deviations from the experimental values. The detailed procedure for data reduction is given by Gasem (1989). The EOS input parameters for the pure components (acentric factors, critical temperatures, critical pressures) appear in Table 3.

The equations of state, when fitted to individual isotherms, reproduced the measured bubble point pressures with average absolute errors of about 0.5%. Using the EOS parameters determined by minimizing errors in bubble point pressures also provided good representations of the methane solubilities (mole fractions at specified pressures), as documented in Tables 4 and 5.

Both the SRK and PR EOS are capable of describing the data for both systems with root-mean-square (rms) errors of less than 0.003 in mole fraction when a single interaction parameter, C_{ij} , is used over the complete temperature range of this study. When a C_{ij} value is optimized for each isotherm of data, the rms errors for either EOS drop to about 0.0005, which is within the expected experimental

Table 4. SRK and PR Equation-of-State Representations of Solubility of Methane in Cyclohexane

T/K	Soave parameters (P-R parameters)		error in predicted methane mole fraction ^a	
	C_{12}	D_{12}	rms	max
323.2	0.024	0.004	0.0003	0.0005
	(0.029)	(0.007)		
373.2	0.032		0.0005	0.0008
	(0.042)			
	0.016	0.007	0.0005	0.0011
	(0.019)	(0.011)		
423.2	0.029		0.0006	0.0012
	(0.036)			
	0.041	0.005	0.0005	0.0009
323.2, 373.2, 423.2	(0.042)	(0.005)		
	0.051		0.0005	0.0009
	(0.051)			
	0.032	0.001	0.0025	0.0055
	(0.025)	(0.009)	(0.0019)	(0.0047)
	0.034		0.0025	0.0055
	(0.041)		(0.0020)	(0.0034)

^a Errors are essentially identical for the SRK and PR EOS for isotherm-by-isotherm fits to the data.

Table 5. SRK and PR Equation-of-State Representations of Solubility of Methane in *trans*-Decalin

T/K	Soave parameters (P-R parameters)		error in predicted methane mole fraction ^a	
	C_{12}	D_{12}	rms	max
323.2	0.060	-0.003	0.0004	0.0007
	(0.059)	(0.001)		
	0.050		0.0005	0.0007
373.2	(0.061)			
	0.056	-0.002	0.0005	0.0010
	(0.063)	(-0.003)		
	0.050		0.0007	0.0013
423.2	(0.057)			
	0.056	0.000	0.0006	0.0010
	(0.060)	(-0.001)		
323.2, 373.2, 423.2	0.056		0.0006	0.0010
	(0.059)			
	0.052	0.000	0.0008	0.0016
	(0.059)	(0.000)	(0.0007)	(0.0013)
	0.051		0.0008	0.0016
	(0.059)		(0.0007)	(0.0013)

^a Errors are essentially identical for the SRK and PR EOS for isotherm-by-isotherm fits to the data.

uncertainty of the data. Using an additional interaction parameter, D_{ij} , produces very minor improvements, as shown in the tables. The excellent fit of the equations to the data on an isotherm-by-isotherm basis illustrates both the abilities of the EOS and the precision of the data. The absence of clear temperature trends in the regressed interaction parameters is attributed to their sensitivity to small errors in the experimental data. (In fact, the regressed parameters are essentially invariant to two decimal places for methane + *trans*-decalin in Table 5.)

Comparisons of our results with those reported by others appear in Figures 1 and 2. The comparisons are shown in terms of deviations (δx) of the solubilities from values predicted using the PR EOS, using temperature-independent C_{ij} and D_{ij} values determined from the present data. These figures facilitate a sensitive analysis of differences in data sets. The difference in the deviations between data sets (not the magnitude of the deviation of either set from the reference EOS model) is of interest in these data comparisons. The differences in deviations (δx) between data sets are independent of the reference model employed. That is, for two data sets A and B, at a fixed temperature and pressure: $\delta x_A - \delta x_B = [(x_{\text{expt}})_A - (x_{\text{EOS}})] - [(x_{\text{expt}})_B - (x_{\text{EOS}})] = (x_{\text{expt}})_A - (x_{\text{expt}})_B$.

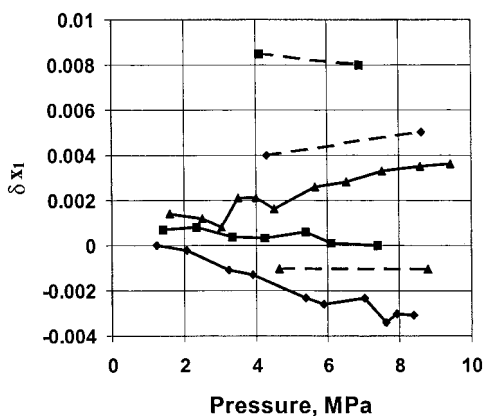


Figure 1. Comparison of methane solubilities in cyclohexane. Solid lines are this work (■, 323 K; ◆, 373 K; ▲, 423 K), and dashed lines are Schoch et al. (■, 311 K; ◆, 344 K; ▲, 378 K). δx_1 is the deviation (mole fraction methane) of the data from the PR EOS fit to our data.

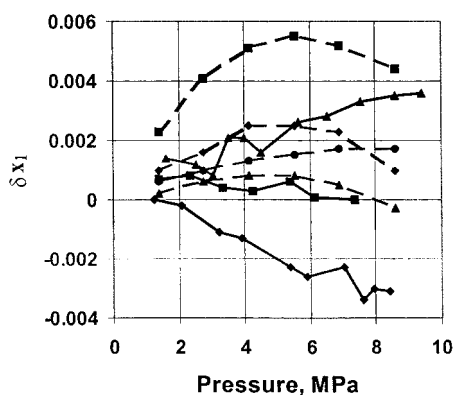


Figure 2. Comparison of methane solubilities in cyclohexane, continued. Solid lines are this work (■, 323 K; ◆, 373 K; ▲, 423 K), and dashed lines are Reamer et al. (■, 311 K; ◆, 344 K; ▲, 378 K; ●, 411 K). δx_1 is the deviation (mole fraction methane) of the data from the PR EOS fit to our data.

The available literature data for methane + cyclohexane are reported at temperatures different from our measurements. Comparisons with the data of Schoch et al. (1940) appear in Figure 1. Good agreement is observed between their data at 377.6 K and ours at 373.2 K, since the two deviation curves are separated by no more than about 0.002. Significant disagreement, however, is observed at 310.9 and 344.3 K, where differences in the two data sets are on the order of 0.006 to 0.008 mole fraction, with the solubilities of Schoch et al. being higher than those of the present work. Figure 2 shows comparisons with the data of Reamer et al. (1958). At the lowest temperatures, disagreements of up to 0.005 are evident, while at higher temperatures differences between the two data sets are on the order of 0.003. Sage et al. (1936) also studied this system, but those data are at pressures beyond the range of our measurements.

For methane + *trans*-decalin, no literature data are available for comparison. Our data show that, for a given temperature and pressure, the solubility of methane is higher in *trans*-decalin than in cyclohexane (i.e., the gas solubility increases with increasing molecular weight of the naphthenic solvent).

Conclusions

Data have been obtained on the solubility for methane in cyclohexane and in *trans*-decalin at temperatures from 323 to 423 K and pressures to 9.6 MPa. These data are well described by the Soave–Redlich–Kwong and Peng–Robinson equations of state.

Acknowledgment

We thank Mr. Wuzi Gao for assistance with the equation-of-state calculations.

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Received for review May 13, 1997. Accepted November 26, 1997. This work was supported by the U.S. Department of Energy under Contract No. DE-FG22-86PC90523.

JE970110U