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Solubilities of Hydrogen in Hexane and of Carbon Monoxide in Cyclohexane at Temperatures from 344.3 to 410.9 K and Pressures to 15 MPa

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The solubilities of hydrogen in hexane and of carbon monoxide in cyclohexane were measured using a static equilibrium cell over the temperature range from 344.3 to 410.8 K and pressures to 15 MPa. The uncertainty in these new solubility measurements is estimated to be <0.001 in mole fraction. The data were analyzed using the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equations of state (EOS). In general, the two equations represent the experimental data within 0.002 mole fraction when a single interaction parameter (C_{ij}) is used for each isotherm.

Introduction

Previously, we have measured substantial amounts of data on the equilibrium phase compositions for binary mixtures of heavy hydrocarbon solvents with a variety of supercritical solutes, including hydrogen, methane, ethane, carbon monoxide, and carbon dioxide.[1−11] The present data on selected systems complement our earlier studies.

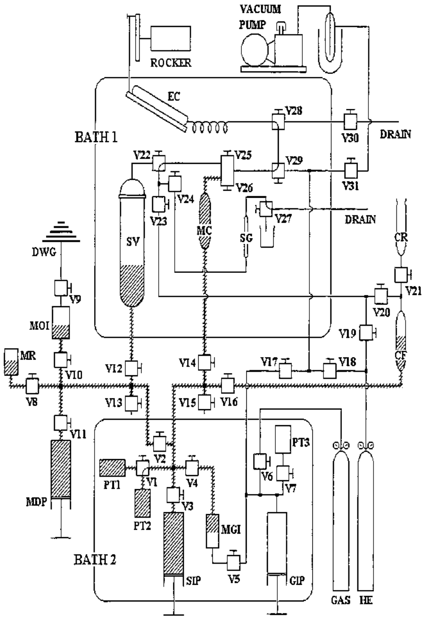
The data we have acquired are designed to facilitate the development and testing of models for prediction of the phase behavior in systems of interest in the production of fluid fuels from coal. These asymmetric mixtures, which contain small gas molecules in heavy hydrocarbon solvents, provide a severe test of current predictive models and their associated mixing theories.

In this work, measurements were made of the solubilities of hydrogen in hexane and carbon monoxide in cyclohexane. The Soave−Redlich−Kwong (SRK)[12] and Peng−Robinson (PR)[13] equations of state (EOS) were used to correlate the experimental data. Some experimental measurements have been reported previously for hydrogen + hexane at 344 K, 377 K, and 411 K; however, no data were found for the carbon monoxide + cyclohexane system.

Experimental Method

The experimental apparatus and procedures have been described by Darwish[2,3] and are summarized briefly here.

A schematic diagram of the apparatus is shown in Figure 1. Phase equilibrium is established in a variable-volume, thermostated, static-type blind cell. This equilibrium cell (EC, refer to Figure 1) is a 25 cm^3, 316 stainless steel microreactor. It is housed in a constant-temperature bath (BATH 1). Two steel balls are placed in the equilibrium cell, and the cell is rocked 45° above and below the horizontal position to hasten the establishment of equilibrium. The effective volume of the cell can be varied by the introduction or withdrawal of mercury.



CF	Cleaning Fluid Cylinder	MGI	Mercury-Gas Interface
CR	Cleaning Fluid Reservoir	MC	Mercury Storage Cell
DWG	Dead Weight Gauge	MOI	Mercury-Oil Interface
EC	Equilibrium Cell	MR	Mercury Reservoir
GAS	Solute Gas	PT's	Pressure Transducers
EC	Equilibrium Cell	SG	Sight Glass
GIP	Solute Gas Injection Pump	SIP	Solvent Injection Pump
HE	Helium Gas	SV	Solvent Storage Cell
MDP	Mercury Displacement Pump	V1-V31	Valves

Figure 1. Schematic diagram of experimental apparatus.

Degassed liquid solvent is stored, at the operating temperature of the experiment, in a solvent storage cell (SV) contained inside the high-temperature air oven (BATH 1). The equilibrium cell and solvent storage cell are from High-Pressure Equipment, Inc.

Injection of solvent into the initially evacuated equilibrium cell is done volumetrically by injecting mercury at the bottom of the solvent cylinder, thus displacing an equal quantity of solvent into the rocking cell. Solute gas is then injected into the rocking cell. The solvent injection pump (SIP) and the gas injection pump (GIP) are from Temco, Inc. After each solute injection, the bubble point pressure of the mixture is determined. This is done by sequentially injecting known amounts of mercury into the cell to alter

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Table 1. Solubility of Hydrogen (1) in Hexane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		344.3 K			
0.0105	1.24	0.0226	2.67	0.0408	4.69
0.0107	1.29	0.0286	3.36	0.0420	4.93
0.0136	1.65	0.0289	3.36	0.0612	7.07
0.0197	2.30	0.0352	4.11	0.0727	8.70
		377.6 K			
0.0122	1.38	0.0680	6.84	0.1131	11.71
0.0394	3.93	0.0763	7.71	0.1288	13.48
0.0554	5.46	0.0912	9.31	0.1430	15.11
0.0628	6.24	0.1037	10.65		
		410.9 K			
0.0179	1.97	0.0678	6.00	0.0979	8.61
0.0302	2.95	0.0814	7.18	0.1169	10.32
0.0408	3.78	0.0854	7.52	0.1204	11.08
0.0520	4.70	0.0920	8.09		

the system volume. After each mercury injection, the equilibrium cell is rocked to bring the system to equilibrium and the pressure is recorded. The bubble point pressure (for the mixture of known composition) is identified graphically from the discontinuity in the pressure versus total-volume-of-mercury-injected relation as the mixture passes from the more compressible two-phase state to the less compressible single-liquid-phase state.

The air bath housing the equilibrium cell (BATH 1) is thermostated by a proportional-integral (PI) controller supplied by Omega Engineering, Inc. The temperature of the air bath housing the injection pump (BATH 2) is controlled by a PI controller from Halikainen Instruments. The temperatures in the air baths are measured using platinum resistance thermometers equipped with digital displays from Fluke, Inc. Pressures are measured with transducers from Sensotec, Inc. The transducers are calibrated periodically against a Ruska Instrument Corporation dead weight tester (DWG) with a certification traceable to the National Institute of Standards and Technology.

Measurement uncertainties are estimated to be 0.1 K in temperature, 0.007 MPa in pressure, and <0.001 in mole fraction. However, the estimated uncertainties (ϵ_{bp}) in the reported bubble point pressures (p_{bp}) at a specified mole fraction range from <0.02 MPa to about 0.2 MPa, since $(\epsilon_{bp})^2 = (\epsilon_p)^2 + (d[p_{bp}]/dx)^2(\epsilon_x)^2$. Thus, the total uncertainty in the reported bubble point pressure (at a specified mole fraction) depends on both pressure and composition uncertainties and, in addition, the steepness of the bubble point pressure versus composition curve.

Materials

The hydrogen (99.995 mol %) used in this study was supplied by Union Carbide Corporation, and the carbon monoxide (99.99%) by Matheson Gas Products. The hexane (99.9%) and cyclohexane (99+) were supplied by the Aldrich Chemical Co. No further purification of these chemicals was attempted.

Results and Discussion

The experimental data are presented in Tables 1 and 2. The measurements in this study cover the temperature range from 344.3 to 410.8 K and pressures to 15 MPa. The solute liquid composition range for the data acquired extends from 0.01 to 0.15 in mole fraction. A graphical representation of the experimental data is given in Figure 2 for the carbon monoxide + cyclohexane system, which indicates increasing solubility with increased temperature.

Table 2. Solubility of Carbon Monoxide (1) in Cyclohexane (2)

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
		344.3 K			
0.0166	1.59	0.0489	4.68	0.1088	10.66
0.0173	1.68	0.0708	6.81	0.1316	13.03
0.0367	3.50	0.0712	6.73	0.1321	12.83
0.0368	3.45	0.0910	8.67	0.1543	15.22
		377.6 K			
0.0200	1.90	0.0544	4.83	0.1110	9.90
0.0209	1.95	0.0732	6.55	0.1320	11.74
0.0376	3.37	0.0898	7.94	0.1321	11.86
0.0376	3.39	0.0901	8.04	0.1544	13.96
0.0539	4.80				
		410.9 K			
0.019	1.98	0.071	5.92	0.100	8.28
0.027	2.51	0.071	5.98	0.118	9.68
0.044	3.86	0.087	7.18	0.135	11.07
0.044	3.81	0.100	8.26	0.135	11.08
0.061	5.13				

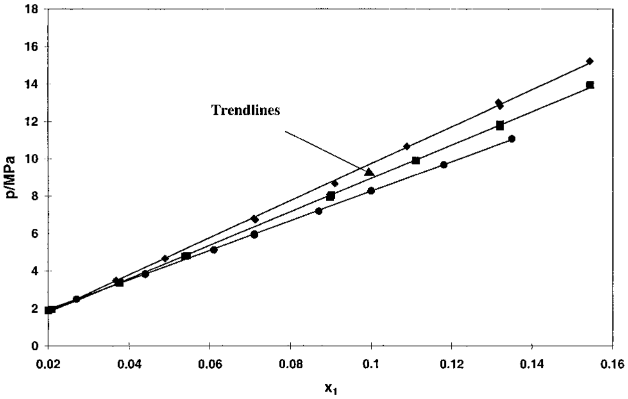

Figure 2. Solubility of carbon monoxide (1) in cyclohexane (2) at (◆) 344.3 K, (■) 377.6 K, and (●) 410.9 K.

The SRK and PR EOS were used to correlate the experimental data. The SRK equation of state is

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

where

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

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

and

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

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

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

Similarly, the PR equation of state is as follows:

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{7}$$

where

$$a = a_c\alpha(T) \tag{8}$$

$$b = 0.0778RT_c/P_c \tag{9}$$

Table 3. Critical Pressures, p_c, Critical Temperatures, T_c, and Acentric Factors, ω, Used in the PR Equation of State

component	p_c/MPa	T_c/K	ω	ref
hydrogen	1.30	33.2	−0.218	Reid et al.[16]
carbon monoxide	3.50	132.9	0.066	Reid et al.[16]
hexane	3.01	507.5	0.299	Reid et al.[16]
cyclohexane	4.07	553.5	0.212	Reid et al.[16]

and

$$a_c = 0.45724R^2T_c^2/p_c \tag{10}$$

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{1/2}) \tag{11}$$

$$k = 0.37464 + 1.54226\omega - 0.2699\omega^2 \tag{12}$$

where p is the pressure, R is the gas constant, T is the temperature, a and b are the EOS constants, v is the molar volume, T_c is the critical temperature, p_c is the critical pressure, T_r is the reduced temperature, $\alpha(T)$ expresses the temperature dependence of the parameter a, and ω is the acentric factor.

To apply the SRK and PR EOS to mixtures, the values of a and b were determined using the mixing rules (Gasem et al.[4]):

$$a = \sum_i^N\sum_j^N z_iz_j(1 - C_{ij})(a_ia_j)^{1/2} \tag{13}$$

$$b = 0.5\sum_i^N\sum_j^N z_iz_j(1 + D_{ij})(b_i + b_j) \tag{14}$$

where z_k represents the mole fraction of component k in a mixture and N is the number of components in the mixture. The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) required by the EOS are presented in Table 3.

In eqs 13 and 14, 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. Interaction parameter values were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared relative deviations in predicted bubble point pressures, that is

$$\mathrm{SS} = \sum_i^n\left(\frac{p_{\mathrm{calc}} - p_{\mathrm{exp}}}{p_{\mathrm{exp}}}\right)_i^2 \tag{15}$$

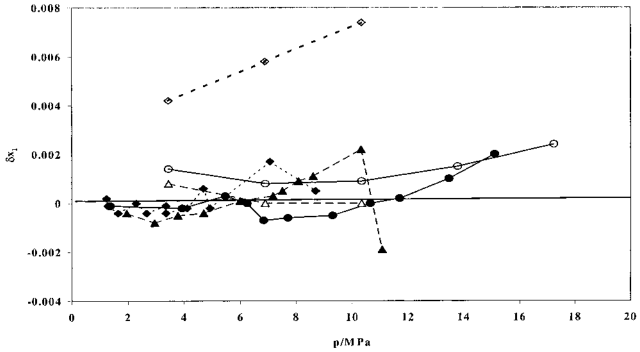

Figure 3. Comparison of solubility data for hydrogen (1) in hexane (2) at (◇) 344.3 K, (O) 377.6 K, and (△) 410.9 K. Solid symbols are this study, and open symbols are Nichols.[15]

where n is the number of data points, p_{calc} is the calculated pressure, and p_{exp} is the experimental pressure. Further details of the data reduction technique are given by Gasem.[5,14]

Details of the equation of state representations of the solubilities are shown in Table 4. In general, the PR equation of state is capable of describing the data with RMS errors within 0.002 in mole fraction when one interaction parameter, C_{ij}, is used for each isotherm. When a single interaction parameter is regressed for a given system for the complete temperature range, the RMS errors are within 0.004. If two interaction parameters, C_{ij} and D_{ij}, are used for each isotherm, the quality of the predictions improves, resulting in RMS errors < 0.001 in mole fraction; however, the interaction parameters are erratic in their temperature dependence, indicating a high correlation between the parameters C_{ij} and D_{ij}. For that reason, and because a single interaction parameter represents the data adequately, no results for two interaction parameters are presented here.

Our data for hydrogen + hexane are compared with the previous measurements of Nichols et al.[15] at 344 K, 377 K, and 411 K in Figure 3. Some disagreement exists

Table 4. SRK and PR Equation-of-State Representations of Solubility Measurements

	SRK parameters (PR parameters)	deviation in predicted solute mole fraction		SRK Henry's const (PR Henry's const)
T/K	C_{12}	RMSE	|max|	MPa
	Hydrogen + Hexane			
344.3	0.4501	0.0007	0.0019	107.1
	(0.3948)	(0.0006)	(0.0017)	(107.6)
377.6	0.5124	0.0013	0.0034	86.1
	(0.4294)	(0.0007)	(0.0020)	(87.6)
410.9	0.7117	0.0012	0.0031	71.7
	(0.5419)	(0.0011)	(0.0022)	(72.9)
344.3, 377.6, and 410.9	0.5128	0.0046	0.0131	
	(0.4321)	(0.0038)	(0.0121)	
	Carbon Monoxide + Cyclohexane			
344.3	0.0442	0.0018	0.0046	87.7
	(0.0640)	(0.0018)	(0.0045)	(87.6)
377.6	0.0330	0.0014	0.0031	84.4
	(0.0505)	(0.0012)	(0.0027)	(84.5)
410.9	0.0341	0.0015	0.0032	72.6
	(0.0469)	(0.0014)	(0.0029)	(72.9)
344.3, 377.6, and 410.9	0.0387	0.0025	0.0064	
	(0.0560)	(0.0019)	(0.0047)	

between our data and those of Nichols at 344 K, while at 377 K and 410 K agreement within 0.002 is achieved. The comparisons are shown in terms of deviations (δx) of the solubilities (liquid mole fraction nitrogen) from values predicted by the PR equation of state, using temperature independent C_{ij} and D_{ij} values determined from the present data. The figure facilitates 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 equation of state model) are 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, $\delta x_A - \delta x_B = [(x_{expt})_A - (x_{EOS})] - [(x_{expt})_B - (x_{EOS})] = (x_{expt})_A - (x_{exptl})_B$.

No literature data on the solubilities for the carbon monoxide + cyclohexane system are available for comparison; as such, the newly acquired measurements should serve as a valuable complement to the existing database.

Henry's Constants

By definition, Henry's constant for a solute (1) in a hydrocarbon solvent (2) is given as

$$H_{1,2} = \lim_{x_1 \to 0} (\hat{f}_1^{\,L}/x_1) = \lim_{x_1 \to 0} (\hat{\varphi}_1 p) \qquad (16)$$

where $\hat{f}_1^{\,L}$, x_1, and $\hat{\varphi}_1$ are the liquid-phase fugacity, liquid mole fraction, and fugacity coefficient, respectively, for the solute. Estimates for Henry's constant were obtained for the present data using the SRK and PR EOS in accordance with the above definition, using one regressed interaction parameter per isotherm, $C_{ij}(T)$. As shown in Table 4, the SRK equation of state produces slightly lower $H_{1,2}$ values than those obtained from the PR equation of state.

Conclusions

Measurements have been obtained for the solubilities of hydrogen in hexane and of carbon monoxide in cyclohexane at temperatures from 344.3 K to 410.9 K at pressures up to 15 MPa. The estimated uncertainties of the measured gas solubilities in the selected solvents are within 0.001 mole fraction. The Soave−Redlich−Kwong (SRK) and the Peng−Robinson (PR) equations of state (EOS) have been used to analyze the data. Interaction parameters for both the SRK and the PR EOS Henry's constants have been obtained for the systems studied. The precision of these descriptions varies; average errors are about 0.002 mole fraction when a single interaction parameter, C_{ij}, is used for each isotherm.

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