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High-Pressure Solubilities of Hydrogen, Nitrogen, and Carbon Monoxide in Dodecane from 344 to 410 K at Pressures to 13.2 MPa

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The solubilities of hydrogen, nitrogen, and carbon monoxide in dodecane were measured using a static equilibrium cell over the temperature range from 344.3 to 410.9 K at pressures to 13.24 MPa. The uncertainty in these measurements is estimated to be less than 0.001 in mole fraction. The data are represented with root-mean-square errors of less than 0.003 mole fraction by the Soave−Redlich−Kwong and Peng−Robinson equations of state when a single empirical interaction parameter, C_{ij}, is used for each binary system.

Introduction

Over the past several years, we have performed extensive experimental measurements on the vapor−liquid phase equilibrium behavior of light gases in heavy hydrocarbon solvents. These highly asymmetric mixtures were selected to mimic the behavior of systems found in several important industrial processes, including reservoir fluid recovery, supercritical extractions, and production of coal-derived fluids.

Our previous measurements have included the solubilities of hydrogen (Park et al., 1995), nitrogen (Tong, 1994), and carbon monoxide (Srivatsan et al., 1995) in a series of normal paraffin solvents ranging from decane through hexatriacontane. However, the solvent dodecane was not reported as part of those studies. No experimental data for these solutes in dodecane have been reported before; thus, the present measurements provide a valuable complement to our previous work. The combined measurements on the solubilities of these light gases in normal paraffin solvents offer a useful basis for developing and testing predictive models for the phase behavior of highly asymmetric mixtures.

Experimental Method

The experimental apparatus and procedures have been described by Park (Park et al., 1996) and are summarized briefly here.

Phase equilibrium is established in a variable-volume, thermostated, static-type blind cell. Two steel balls are placed in the equilibrium cell, and the cell can be 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.

A known amount of degassed liquid solvent is injected volumetrically into the initially evacuated equilibrium cell. A known amount of solute gas is then injected into the rocking cell from a gas-injection pump. After each solute injection, the bubble point pressure of the mixture is determined by sequentially injecting known amounts of mercury into the equilibrium cell to alter 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 a pressure vs total-volume-of-mercury-injected plot as the mixture passes from the more compressible two-phase state to the less compressible single-liquid-phase state. Additional solute is then added to the cell, and the above procedure repeated at the new (higher) solute mole fraction.

Measurement uncertainties are estimated to be ±0.1 K in temperature, ±0.007 MPa in pressure, and less than ±0.001 in mole fraction. These estimates are based on our experience in performing such measurements, including calibrations of the temperature and pressure measurement apparatus against reference-standard calibration equipment in our laboratory. However, the uncertainties (ϵ_{bp}) in the reported bubble point (bp) pressures *at a specified mole fraction* are of the order of ±0.06 MPa for the systems in this study, since $(\epsilon_{bp})^2 = (\epsilon_p)^2 + (d[bp]/dx)^2(\epsilon_x)^2 + (d[bp]/dT)^2(\epsilon_T)^2$. (The temperature term is so small that it can be omitted.) 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.

Materials

The hydrogen (99.995 mol %) used in this study was supplied by Union Carbide Corporation, the carbon monoxide (99.99%) by Matheson Gas Products, the nitrogen (99.995+%) by Sooner Airgas, Inc., and the dodecane (99+%) by Aldrich Chemical Company. No further purification of these chemicals was attempted.

Results and Correlation

The experimental measurements are reported in Table 1. Analysis of the data reveals that the solubility of each of these solutes increases with increasing temperature and pressure, with carbon monoxide being the most soluble and hydrogen the least soluble in dodecane.

Equation-of-state representations of the experimental data are illustrated for carbon monoxide in dodecane in

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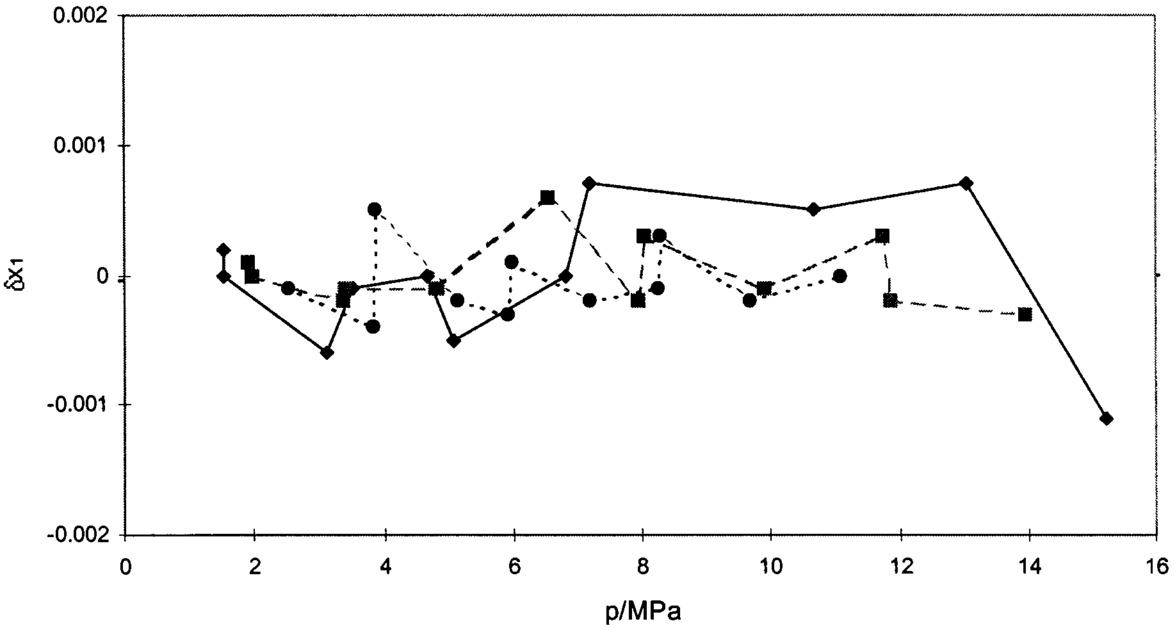

Figure 1. Solubility of carbon monoxide (1) in dodecane (2) at (◆) 344.3 K, (■) 377.6 K, and (●) 410.9 K. δx_1 is the difference between the measured solubility and the value predicted by the Peng–Robinson equation of state.

Table 1. Solubility of Hydrogen, Nitrogen, and Carbon Monoxide in Dodecane

x_1	p/MPa	x_1	p/MPa	x_1	p/MPa	x_1	p/MPa	x_1	p/MPa	x_1	p/MPa
	Hydrogen				Nitrogen				Carbon Monoxide		
	344.3 K				344.3 K				344.3 K		
0.0297	3.36	0.0703	8.26	0.0314	2.30	0.0804	6.30	0.0240	1.52	0.0804	5.08
0.0302	3.37	0.0802	9.38	0.0422	3.15	0.0915	7.27	0.0256	1.53	0.0857	5.39
0.0505	5.80	0.0900	10.79	0.0559	4.23	0.1046	8.45	0.0500	3.12	0.1113	7.18
0.0506	5.81	0.1010	12.00	0.0675	5.22	0.1165	9.55	0.0546	3.35	0.1150	7.87
	377.6 K				377.6 K				377.6 K		
0.0144	1.42	0.0804	8.43	0.0195	1.41	0.0801	5.90	0.0113	0.69	0.0945	5.73
0.0355	3.56	0.0904	9.55	0.0350	2.43	0.0950	6.97	0.0118	0.71	0.0992	6.03
0.0550	5.59	0.1000	10.64	0.0493	3.53	0.1101	8.27	0.0197	1.17	0.1300	8.14
0.0707	7.39	0.1204	13.24	0.0651	4.65	0.1242	9.42	0.0208	1.23	0.1368	8.54
								0.0568	3.34		
	410.9 K				410.9 K						
0.0209	1.77	0.0803	7.13	0.0202	1.29	0.0801	5.31		410.9 K		
0.0348	2.92	0.0956	8.55	0.0354	2.31	0.0955	6.48	0.0245	1.34	0.1049	5.95
0.0500	4.31	0.1108	10.14	0.0498	3.21	0.1100	7.43	0.0447	2.47	0.1202	6.91
0.0652	5.62	0.1252	11.54	0.0649	4.32	0.1251	8.66	0.0603	3.32	0.1335	7.75
								0.0718	3.91	0.1493	8.75
								0.0904	5.07		

Figure 1. In this figure, the data are shown in terms of the deviation, δx_1, in the solubility (liquid mole fraction) predicted by the Peng–Robinson (Peng and Robinson, 1976) equation of state (PR EOS) from the measured value; i.e., $\delta x_1 = x_1(\mathrm{PR}) - x_1(\mathrm{exptl})$. The solubility values for the PR EOS were calculated using a separate interaction parameter, C_{ij}, regressed from our data at each isotherm of our measurements. The C_{ij} values were optimized to minimize the root-mean-square (RMS) errors in the calculated bubble point pressures at fixed temperature and liquid mole fraction. The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) were taken from Reid et al. (1987).

Details of the EOS representations of the solubilities are shown in Table 2. In general, the Soave–Redlich–Kwong (SRK) EOS (Soave, 1972) and PR EOS are 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 0.003. If two interaction parameters, C_{ij} and D_{ij}, are used for each isotherm, the quality of the predictions improves, resulting in RMS errors less than 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.

Henry's Constants

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

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

where $\hat{f}_1$, x_1, and $\hat{\varphi}_1$ are the fugacity, liquid mole fraction, and fugacity coefficient, respectively, for the solute in the mixture. Estimates for Henry's constant were obtained for the present data using SRK and PR equations of state in accordance with the above definition. Values for the Henry's constants, along with the interaction parameters associated with them, are given in Table 2. In general, the

Table 2. SRK and PR Equation-of-State Representations of the Solubility of Hydrogen, Nitrogen, and Carbon Monoxide in Dodecane

T/K	SRK parameters (PR parameters), C_{12}	error in mole fraction		SRK Henry's Constant (PR Henry's Constant), MPa
		RMS	|MAX|	
		Hydrogen		
344.3	0.3723	0.0012	0.0030	105.3
	(0.3567)	(0.0011)	(0.0027)	(106.1)
377.6	0.4569	0.0010	0.0020	93.5
	(0.4002)	(0.0008)	(0.0013)	(94.6)
410.9	0.4688	0.0011	0.0026	79.3
	(0.3863)	(0.0006)	(0.0011)	(80.3)
344.3, 377.6, and 410.9	0.4194	0.0021	0.0063	
	(0.3775)	(0.0014)	(0.0047)	
		Nitrogen		
344.3	0.2162	0.0002	0.0004	70.8
	(0.2095)	(0.0002)	(0.0003)	(70.9)
377.6	0.2252	0.0008	0.0015	66.5
	(0.2086)	(0.0007)	(0.0012)	(66.8)
410.9	0.2352	0.0010	0.0021	61.2
	(0.2049)	(0.0008)	(0.0023)	(61.6)
344.3, 377.6, and 410.9	0.2226	0.0008	0.0016	
	(0.2082)	(0.0008)	(0.0023)	
		Carbon Monoxide		
344.3	0.1061	0.0016	0.0031	58.9
	(0.1120)	(0.0016)	(0.0032)	(58.9)
377.6	0.1009	0.0018	0.0041	56.6
	(0.1004)	(0.0017)	(0.0037)	(56.8)
410.9	0.0711	0.0008	0.0015	51.8
	(0.0671)	(0.0006)	(0.0012)	(52.2)
344.3, 377.6 and 410.9	0.0965	0.0022	0.0052	
	(0.0965)	(0.0027)	(0.0063)	

SRK EOS produced slightly lower $H_{1,2}$ values (~ 1% lower) than those obtained from the PR EOS.

Conclusions

Measurements are reported for the solubilities of hydrogen, nitrogen, and carbon monoxide in dodecane at temperatures from 344.3 K to 410.9 K at pressures up to 13.2 MPa. Interaction parameters and Henry's constants for both the SRK and the PR EOS have been obtained for the systems studied, and the each EOS represents the data adequately.

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