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Solubilities of Carbon Monoxide in Heavy Normal Paraffins at Temperatures from 311 to 423 K and Pressures to 10.2 MPa

Srinivasa Srivatsan, Xiaohua Yi, Robert L. Robinson, Jr., and Khaled A. M. Gasem*

School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma 74078-0537

The solubilities of carbon monoxide in decane, eicosane, octacosane, and hexatriacontane were measured using a static equilibrium cell over the temperature range from 310.9 to 423.2 K and pressures to 10.2 MPa. The uncertainty in these new solubility measurements is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equations of state. In general, two binary interaction parameters per isotherm are needed to describe the data adequately.

Introduction

As a part of our ongoing research dealing with the phase behavior of asymmetric mixtures, the solubilities of methane, ethane, CO_2, and CO in systematically chosen solvents (heavy paraffinic, naphthenic, and aromatic hydrocarbons) have been measured and correlated *(1−7)*. In this study, we report new measurements on the solubility of carbon monoxide in the saturated hydrocarbon solvents decane, eicosane, octacosane, and hexatriacontane. These solubilities cover temperatures from 310.9 to 423.2 K and pressures to 10.2 MPa. The data have been correlated using the Soave−Redlich−Kwong (SRK) *(8)* and Peng−Robinson (PR) *(9)* equations of state (EOS). The binary interaction parameters, C_{ij} and D_{ij}, regressed from the new experimental data should be useful in the prediction of multicomponent phase behavior.

Experimental Method

A variable-volume, static-type blind equilibrium cell was used in this study. 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-phase liquid state. 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 enhance the establishment of equilibrium. Details of the apparatus and experimental procedure are described by Darwish *(7, 11)*. The measurement uncertainties are estimated to be ±0.1 K in temperature and less than ±0.001 in mole fraction. The estimated uncertainty in the bubble point pressure, which is dependent on the steepness of the pressure−composition relation, is of the order of ±0.05 MPa for the systems studied here. A detailed error analysis is given elsewhere *(11)*.

Materials

The carbon monoxide used in this study had a stated purity of 99.99+ mol % and was supplied by Matheson Gas Products. Decane, eicosane, and hexatriacontane were supplied by the Aldrich Chemical Co. and have stated purities of 99+, 99+, and 98 mol %, respectively. Octacosane was supplied by Alfa Products and had a reported purity of 99 mol %. No confirmation of the stated purity or further purification of these chemicals was attempted.

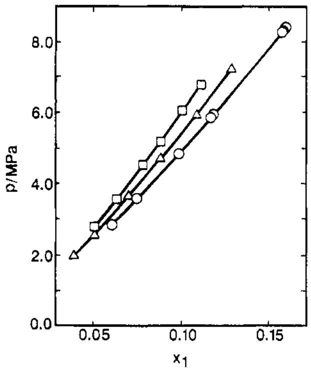

Figure 1. Bubble point data for carbon monoxide + eicosane: (□) 323.2 K; (△) 373.2 K; (○) 423.2 K.

Results and Data Correlation

The carbon monoxide solubility measurements are presented in Table 1. In general, the lowest temperature at which a particular system was studied was dictated by the melting point of the solvent or the availability of literature data (for comparison purposes). All hydrocarbons in this study are solids at room temperature except for decane. The effects of temperature and pressure on the solubility of carbon monoxide (liquid mole fraction of carbon monoxide, x_1) are illustrated in Figure 1 by the eicosane measurements; similar trends are observed for the other paraffin solvents. For a given total pressure, the solubility of carbon monoxide increases with increasing temperature. This is in contrast to the behavior observed for CO_2 and CH_4 solubilities in heavy normal paraffins *(13, 11)*. The difference may be explained in terms of the change in entropy of solution. For sparingly soluble gases in essentially nonvolatile solvents, it can be shown that *(17)*

$$\left(\frac{\partial \ln x_1}{\partial \ln T}\right)_{\mathrm{p}} = \frac{\Delta \bar{s}_1}{R} \qquad (1)$$

where x_1 is the mole fraction of the solute at equilibrium, T is the temperature, R is the gas constant, and $\Delta \bar{s}_1$ is the partial molar entropy change, defined as $\Delta \bar{s}_1 = \bar{s}_{1L} - s_{1V}$, where $\bar{s}_{1L}$ and s_{1V} are the partial molar entropy of the liquid and the molar entropy of the vapor, respectively.

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* gasem@master.ceat.okstate.edu

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

x_1	p/MPa	x_1	p/MPa
Decane, 310.9 K			
0.0448	2.84	0.1097	7.57
0.0873	5.81	0.1247	8.78
0.0953	6.45	0.1399	10.00
Decane, 344.3 K			
0.0385	2.36	0.0883	5.64
0.0538	3.30	0.1171	7.69
0.0770	4.85	0.1363	9.15
Decane, 377.6 K			
0.0388	2.22	0.1197	7.37
0.0619	3.62	0.1400	8.81
0.0895	5.39	0.1599	10.20
Eicosane, 323.2 K			
0.0516	2.80	0.0902	5.16
0.0645	3.56	0.1024	6.05
0.0797	4.51	0.1136	6.78
Eicosane, 373.2 K			
0.0403	1.19	0.0899	4.72
0.0516	2.58	0.1107	5.93
0.0715	3.65	0.1308	7.24
Eicosane, 423.2 K			
0.0616	2.83	0.1205	5.94
0.0716	3.57	0.1590	8.24
0.1004	4.83	0.1593	8.27
0.1187	5.86	0.1614	8.38
Octacosane, 348.2 K			
0.0553	2.33	0.1014	4.62
0.0604	2.55	0.1320	6.37
0.0854	3.82	0.1493	7.57
Octacosane, 373.2 K			
0.0463	2.01	0.1131	5.02
0.0577	2.42	0.1463	6.80
0.1005	4.42		
Octacosane, 423.2 K			
0.0551	2.19	0.1623	7.08
0.1027	4.18	0.1853	8.41
0.1315	5.59		
Hexatriacontane, 373.2 K			
0.0494	1.80	0.1192	4.75
0.0634	2.34	0.1603	6.76
0.0899	3.44	0.2002	8.95
Hexatriacontane, 423.2 K			
0.0568	1.85	0.1289	4.66
0.0705	2.37	0.1742	6.61
0.1040	3.60	0.2099	8.40

Equation 1 shows that the solubility increases with temperature whenever the partial molar entropy change of the solute is positive. The partial molar entropy change can be written as

$$\Delta\bar{s}_1 = (s_{1L} - s_{1V}) + (\bar{s}_{1L} - s_{1L}) \qquad (2)$$

where s_{1L} is the entropy of the (hypothetical) pure liquid at the temperature of the solution. The first term on the right-hand side of eq 2 is negative since the entropy of the liquid is lower than that of saturated vapor at the same temperature. Assuming ideal entropy of mixing for the two liquids, the second term in eq 2 can be written as

$$\bar{s}_{1L} - s_{1L} = R \ln(1/x_1) \qquad (3)$$

From eq 3, it is seen that the lower the value of x_1, the larger is the term $(\bar{s}_{1L} - s_{1L})$ and, thus, for very sparingly soluble gases, $\Delta\bar{s}_1$ is positive and the solubility increases with temperature.

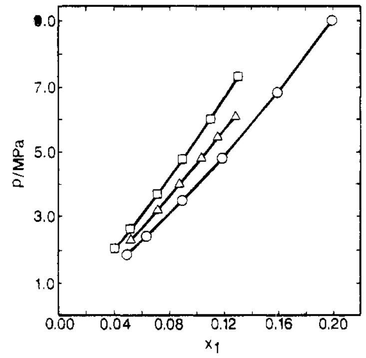

Figure 2. Bubble point pressure data for carbon monoxide + paraffins at 373.2 K: (□) C_{20}; (△) C_{28}; (○) C_{36}.

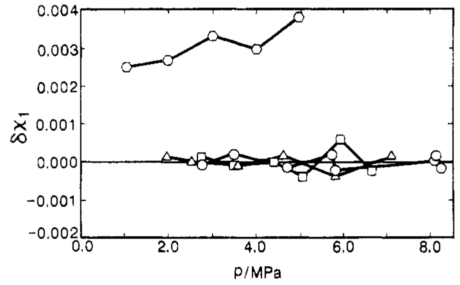

Figure 3. Comparison of solubilities for carbon monoxide in eicosane. δx_1 is the deviation of the predicted solubility using the SRK EOS from that measured. This work: (□) 323.2 K; (△) 373.2 K; (○) 423.2 K. Huang *(12)*: (○) 373.2 K.

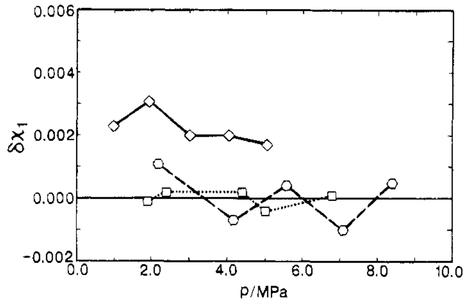

Figure 4. Comparison of solubilities for carbon monoxide in octacosane. δx_1 is the deviation of the predicted solubility using the SRK EOS from that measured. This work: (□) 373.2; (○) 423.2 K. Huang *(12)*: (◇) 373.2 K.

The effect of molecular weight (or, equivalently, the carbon number) of the solvent is shown in Figure 2. For a given temperature and pressure, the solubility of the gas (on a molar basis) increases with increasing molecular weight of the solvent. This could be because of the increased number of sites along the chain of the normal paraffin with which the carbon monoxide molecule can interact; i.e., longer chains (higher carbon number) offer more sites to accommodate the solute molecule than shorter ones.

Comparisons of our binary data for the solubility of carbon monoxide in eicosane, octacosane, and hexatriacontane with those of Huang and co-workers *(12)* are shown in Figures 3, 4, and 5, respectively. The comparisons are shown in terms of deviations, δx_1, of the solubility predicted using the SRK EOS (discussed below) from the experimental measurements, i.e., $\delta x_1 = x_1(\mathrm{SRK}) - x_1(\mathrm{exp})$. The binary interaction parameters, C_{ij} and D_{ij}, employed in the EOS predictions were obtained by fitting our data for the isotherm under study. Figures 3−5 indicate reasonable agreement between our results and those of Huang. In general, our data show solubilities 0.002−0.004 higher than those of Huang. No literature data for the solubility of carbon monoxide in decane are available for direct comparison.

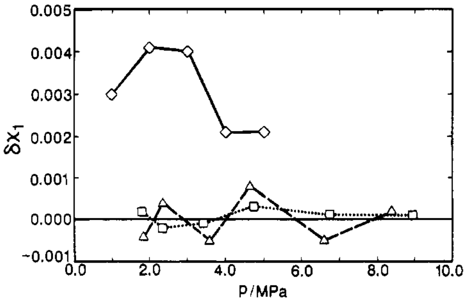

Figure 5. Comparison of solubilities for carbon monoxide in hexatriacontane. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation. This work: (□) 373.2 K; (△) 423.2 K. Huang *(12)*: (◇) 423.2 K.

Table 2. Critical Pressure, p_c, Critical Temperature, T_c, and Acentric Factor, ω, Used in the SRK and PR Equations of State

component	p_c/MPa	T_c/K	ω	ref
carbon monoxide	3.494	132.9	0.0491	14
decane	2.108	617.6	0.4900	14
eicosane	1.117	770.5	0.8738	13
octacosane	0.826	845.4	1.1073	13
hexatriacontane	0.682	901.1	1.2847	13

The SRK *(8)* and PR *(9)* cubic equations of state were used to correlate the experimental data. The SRK equation is given below [similar relations are given elsewhere for the Peng–Robinson equation *(9)*]

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{4}$$

where

$$a(T) = a_c\alpha(T) \tag{5}$$

$$b = 0.08664RT_c/p_c \tag{6}$$

and

$$a_c = 0.42748R^2T_c^{\,2}/p_c \tag{7}$$

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{\,1/2}) \tag{8}$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \tag{9}$$

where p is the pressure, R is the gas constant, T is the temperature, a and b are 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 in the parameter a, and ω is the acentric factor.

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

$$a = \sum_i^N\sum_j^N z_iz_j(1 - C_{ij})(a_ia_j)^{1/2} \tag{10}$$

$$b = 0.5\sum_i^N\sum_j^N z_iz_j(1 + D_{ij})(b_i + b_j) \tag{11}$$

where z_i and z_j are the mole fractions of components i and j in a mixture and N is the number of components in mixture.

In eqs 10 and 11, the summations are over all chemical species and C_{ij} and D_{ij} are empirical interaction parameters

Table 3. SRK and PR Equation of State Representations of the Solubility of Carbon Monoxide (1) in Hydrocarbons (2)

	SRK parameters (PR parameters)		error in mole fraction (using PR eq)[a]		SRK Henry constant/ MPa
T/K	C_{12}	D_{12}	RMS	|MAX|	
	Decane				
310.9	0.1356	−0.0031	0.0003	0.0005	60.4
	(0.1378)	(−0.0023)			
	0.1204		0.0003	0.0007	60.8
	(0.1280)				
344.3	0.1115	−0.0004	0.0002	0.0003	58.6
	(0.1220)	(−0.0019)			
	0.1094		0.0002	0.0003	58.6
	(0.1137)				
377.6	0.0800	0.0043	0.0002	0.0004	55.7
	(0.1025)	(0.0004)			
	0.1006		0.0003	0.0005	55.3
	(0.1008)				
310.9, 344.3,	0.1104	0.0007	0.0014	0.0032	
and 377.6	(0.0676)	(0.0118)			
	0.1136		0.0014	0.0032	
	(0.1184)				
	Eicosane				
323.2	0.2772	−0.0113	0.0003	0.0006	50.1
	(0.2698)	(−0.0112)			
	0.1602		0.0006	0.0009	51.7
	(0.1686)				
373.2	0.2257	−0.0105	0.0002	0.0004	46.8
	(0.2305)	(−0.0123)			
	0.1166		0.0006	0.0009	48.0
	(0.1214)				
423.2	0.2292	−0.0140	0.0002	0.0002	42.8
	(0.2419)	(−0.0185)			
	0.0873		0.0008	0.0012	44.3
	(0.0862)				
323.2, 373.2,	0.1439	−0.0018	0.0040	0.0072	
and 432.2	(−0.1557)	(0.0323)	(0.0053)	(0.0113)	
	0.1253		0.0041	0.0073	
	(0.1271)		(0.0052)	(0.0096)	
	Octacosane				
348.2	0.4522	−0.0258	0.0005	0.0009	37.9
	(0.4341)	(−0.0270)			
	0.0935		0.0027	0.0038	42.3
	(0.1128)				
373.2	0.1498	−0.0071	0.0002	0.0004	39.3
	(0.1701)	(−0.0084)			
	0.0438		0.0008	0.0018	40.0
	(0.0699)				
423.2	0.1413	−0.0100	0.0008	0.0011	36.7
	(0.1711)	(−0.0130)			
	0.0031		0.0012	0.0019	38.0
	(0.0239)				
348.2, 373.2,	0.0427	−0.0013	0.0028	0.0050	
and 423.2	(−0.0142)	(0.0051)			
	0.0246		0.0030	0.0051	
	(0.0448)				
	Hexatriacontane				
373.2	0.1966	−0.0115	0.0001	0.0002	34.2
	(0.2185)	(−0.0127)			
	0.0073		0.0024	0.0028	36.7
	(0.0431)				
423.2	0.1328	−0.0148	0.0005	0.0008	30.7
	(0.1688)	(−0.0172)			
	−0.1154		0.0026	0.0034	33.1
	(0.0672)				
373.2 and	0.3102	−0.0212	0.0068	0.0117	
423.2	(0.2199)	(−0.0162)	(0.0075)	(0.0116)	
	−0.0409		0.0080	0.0114	
	(−0.0021)		(0.0085)	(0.0152)	

[a] Errors are essentially identical for the SRK and PR EOS whenever not mentioned.

characterizing the binary interactions between components i and j. Values of these parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared errors in predicted bubble point pressures

$$\mathrm{SS} = \sum_{i}^{n} (p_{\mathrm{exp}} - p_{\mathrm{calc}})_i^2 \qquad (12)$$

where n is the number of data points, p_{exp} is the experimental pressure, and p_{cal} is the calculated pressure using the equation of state. Further details of the data reduction techniques used in this study are given by Gasem *(13)*. 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 2.

The EOS representations of the carbon monoxide solubilities are documented in Table 3. The SRK equation of state is capable of describing the decane, eicosane, and octacosane data with RMS errors of 0.004 in mole fraction when a single interaction parameter, C_{ij}, is used for each system over the complete temperature range. For these three binaries, only marginal improvements in the EOS predictions are realized when a second interaction parameter, D_{ij}, is also employed. For the hexatriacontane system, however, the use of either one or two interaction parameters over the complete temperature range does not fit the data well (RMS errors of 0.007 in mole fraction using C_{ij} and D_{ij}).

Table 3 reveals that the values obtained for the interaction parameters, C_{ij} and D_{ij}, when lumped over the complete temperature range, lie outside the range of values obtained for the parameters determined for the individual isotherms. This is possible since C_{ij} and D_{ij} are regressed simultaneously, and a high degree of parameter correlation exist between C_{ij} and D_{ij} *(7)*.

When one interaction parameter, C_{ij}, is fitted to each isotherm for the systems eicosane and octacosane, the RMS errors are less than 0.0015 in mole fraction (except for the octacosane system at 348.2 K), and the two equations of state give comparable representation of the results. No significant improvements are obtained for decane, eicosane, or octacosane by using two parameters for each isotherm except for the octacosane system at 348.2 K (Table 3). For the hexatriacontane system, however, the use of the second interaction parameter, D_{ij}, for each isotherm improves the predictions significantly (Table 3). The need for a second interaction parameter may reflect the inadequacy in the original EOS mixing rules for the highly asymmetric mixtures produced by the larger hexatriacontane molecules (see, e.g., *10, 15, 16*).

The RMS errors in mole fraction are, in general, within the estimated uncertainty of 0.001 when the full potential of the EOS model is realized using two interaction parameters (C_{ij} and D_{ij}) per isotherm.

Henry Constants

By definition, the Henry constant, $H_{1,2}$, for carbon monoxide (1) in a hydrocarbon solvent (2) is given as

$$H_{1,2} = \underset{\lim x_1 \to 0}{(f_1/x_1)} = \underset{\lim x_1 \to 0}{(\varphi_1 p)} \qquad (13)$$

where f_1, x_1, and φ_1 are the fugacity, liquid mole fraction, and fugacity coefficient of carbon monoxide, respectively. Estimates for the Henry constant were obtained for the present data using the SRK equation of state in accordance with the above definition. Values for the Henry constant, along with the associated interaction parameters, are given in Table 3. For the present systems, the SRK Henry constant estimates using C_{ij} and D_{ij} are lower than those obtained using C_{ij} only. Lin and co-workers *(18)* reported an experimental Henry constant at 373.2 K for the n-C_{36} binary. Their value of 36.4 MPa is in good agreement with our estimate using C_{ij} only (36.7 MPa) and 6% larger than our estimates using both C_{ij} and D_{ij} (34.2 MPa).

Conclusions

Measurements have been made on the solubility of carbon monoxide in decane, eicosane, octacosane, and hexatriacontane at temperatures from 310.9 to 423.2 K and pressures up to 10.2 MPa. These results are described well by the SRK and PR equations of state when two interaction parameters, C_{ij} and D_{ij}, are used per isotherm. The newly acquired data provide valuable information for the development of improved EOS models, and they also facilitate better understanding of the phase behavior of carbon monoxide–hydrocarbon mixtures.

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