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Solubilities of Carbon Monoxide in Aromatic Hydrocarbons at Temperatures from 323 to 433 K and Pressures to 23.3 MPa

Jongkee Park, Xiaohua Yi, Khaled A. M. Gasem, and Robert L. Robinson, Jr.*

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

The solubilities of carbon monoxide in benzene, naphthalene, phenanthrene, and pyrene were measured using a static equilibrium cell over the temperature range from 323.2 to 433.2 K and pressures to 23.3 MPa. The uncertainty in these 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 (EOS). In general, the two equations represent the experimental data well over the complete temperature range when one interaction parameter is used for each binary system. Marginal improvements in equation of state predictions are realized when an additional interaction parameter is used.

Introduction

Mixtures which involve small gas solute molecules (such as hydrogen, methane, ethane, CO, and CO_2) and heavy hydrocarbon solvents (effective carbon numbers of 10 or greater) pose a significant challenge to the abilities of current predictive models and their associated mixing theories. As a part of our ongoing research dealing with the phase behavior of asymmetric mixtures, the solubilities of methane, ethane, CO, and CO_2 in systematically-chosen solvents (heavy paraffinic, naphthenic, and aromatic hydrocarbons) have been measured and correlated *(1−8)*. In this study, we report new binary measurements for the solubility of CO in the aromatic compounds benzene, naphthalene, phenanthrene, and pyrene; these data complement our recent data on CO in heavy paraffinic compounds *(8)*. The present measurements cover temperatures from 323.2 to 433.2 K and pressures to 23.3 MPa.

The data have been correlated using the Soave−Redlich−Kwong (SRK) *(9)* and PR Peng−Robinson *(10)* equations of state (EOS). Binary interaction parameters, C_{ij} and D_{ij}, regressed from the new experimental data, along with data from the literature, can be used in predictions of multicomponent phase behavior.

Experimental Section

Method. A variable-volume, static-type blind equilibrium cell was used in this study. The apparatus and procedures have been described in detail previously *(6, 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 on the order of 0.06 MPa for the systems studied here. A detailed error analysis is given by Darwish *(11)*.

Materials. The carbon monoxide used in this study had a stated purity of 99.99% and was supplied by Matheson Gas Products. Benzene, naphthalene, phenanthrene, and pyrene were supplied by the Aldrich Chemical Co. and had stated purities of 99+%, 99+%, 98+%, and 99+%, respectively. No further purification of these chemicals was attempted.

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

x_1	p/MPa	x_1	p/MPa
Benzene			
323.2 K			
0.0099	1.47	0.0478	7.33
0.0197	2.94	0.0546	8.42
0.0296	4.45	0.0597	9.26
0.0398	6.04		
373.2 K			
0.0103	1.41	0.0371	4.70
0.0150	1.98	0.0450	5.68
0.0212	2.71	0.0516	6.51
0.0340	4.29	0.0637	8.05
433.2 K			
0.0148	2.12	0.0428	4.86
0.0252	3.13	0.0548	6.05
0.0398	4.56	0.0590	6.46
Naphthalene			
373.2 K			
0.0239	4.79	0.0605	12.99
0.0267	5.37	0.0671	14.69
0.0395	8.14	0.0767	16.98
0.0489	10.24	0.0984	22.79
423.2 K			
0.0278	4.82	0.0635	11.58
0.0307	5.36	0.0685	12.56
0.0393	6.88	0.0770	14.24
0.0498	8.92	0.0972	18.46
0.0523	9.39		
Phenanthrene			
383.2 K			
0.0262	7.12	0.0648	19.56
0.0306	8.41	0.0655	20.00
0.0458	13.04	0.0750	23.28
0.0473	13.72		
423.2 K			
0.0231	5.47	0.0652	16.84
0.0249	5.94	0.0732	19.22
0.0436	10.78		
Pyrene			
433.2 K			
0.0247	6.65	0.0502	14.26
0.0284	7.71	0.0634	18.57
0.0472	13.38	0.0696	20.68

Results and Data Correlation

The CO 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). The effect of temperature and

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* rrobins@master.ceat.okstate.edu

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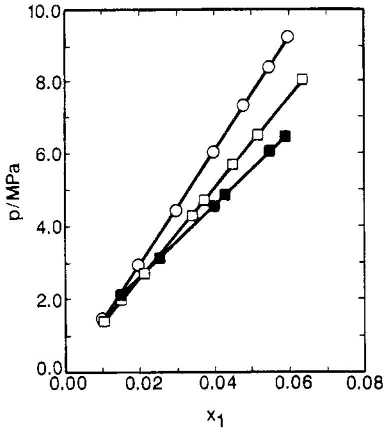

Figure 1. Solubility of carbon monoxide in benzene at (○) 323.2, (□) 373.2, and (■) 433.2 K.

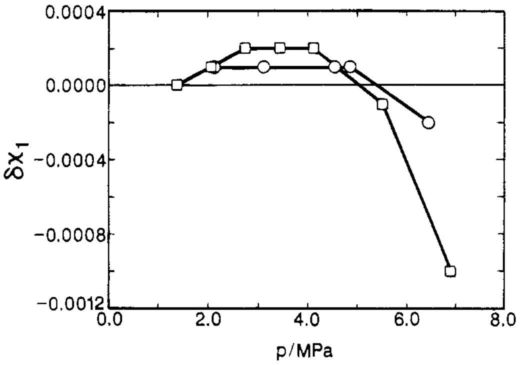

Figure 2. Comparison of carbon monoxide solubilities in benzene at 433.2 K: (○) this work, (□) Connolly *(12)*. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

pressure on the solubility of CO in benzene is shown in Figure 1. A similar trend of increasing solubility with increased temperature and pressure is observed for the other solvents studied (with the exception of pyrene, for which the effect of temperature was not investigated).

A comparison of our data on CO + benzene and those of Connolly *(12)* at 433.2 K is shown in Figure 2. The comparison is shown in terms of deviations, δx_1, of the solubility predicted using the SRK EOS (discussed below) from the experimental measurements, i.e., $\delta x_1 = x_1(\mathrm{SRK}) - x_1(\mathrm{exptl})$. The binary interaction parameter, C_{ij}, employed in the EOS predictions was obtained by fitting our data for that isotherm. Figure 2 shows very good agreement between our data and those of Connolly; the deviations are generally within the experimental uncertainty of 0.001.

A comparison of the present data for carbon monoxide + phenanthrene with those of DeVaney and co-workers *(13)* is shown in Figure 3. The binary interaction parameters, C_{ij}, employed in the EOS predictions were obtained by linear extrapolation of values fitted to the present data for each isotherm. Figure 3 reveals that the solubility deviations are not distributed evenly around the zero line; this is not uncommon when the parameters are determined from fits to bubble point pressures and comparisons shown in terms of mole fractions. The figure shows good agreement between the present data and those of DeVaney and co-workers; deviations are generally within 0.0005. No literature data for the solubility of carbon monoxide in naphthalene or pyrene are available for comparison.

The SRK *(9)* and the PR *(10)* cubic equations of state were used to correlate the experimental data. The SRK equation is given below; similar relations are given else-

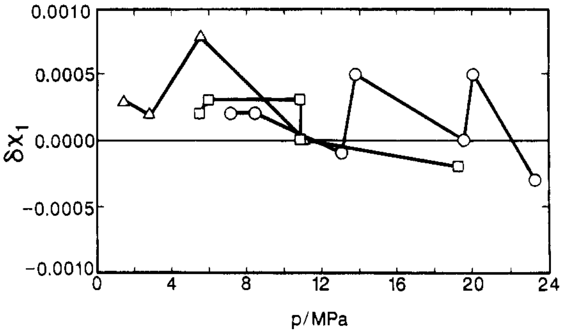

Figure 3. Comparison of carbon monoxide solubilities in phenanthrene at 383.2, 423.2, and 377.6 K: (○) 383.2 K, (□) 423.2 K, this work; (△) 377.6 K, DeVaney et al. *(13)*. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

where for the PR equation *(10)*.

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

where

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

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

and

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

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

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

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 α, 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)*

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

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

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 the mixture.

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 the experimental data to minimize the objective function, SS, which represents the sum of squared errors in predicted bubble point pressures:

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

where n is the number of data points, p_{exp} is the experimental pressure, and p_{cal} is the calculated pressure.

Table 2. Critical Pressures, p_c, Critical Temperatures, T_c, and Acentric Factors, 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	0.049	15
benzene	4.830	562.1	0.212	16
naphthalene	4.052	748.4	0.302	17
phenanthrene	3.300	873.2	0.540	18
pyrene	2.600	938.2	0.830[a]	19

[a] Turek, E. A., Amoco Production Company, Tulsa, OK. Personal communication, 1988.

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

T/K	SRK parameter (PR parameter) C_{12}	error in carbon monoxide mole fraction[a] RMS	|MAX|
	Benzene		
323.2	0.0953 (0.1157)	0.0002	0.0003
373.2	0.0700 (0.0886)	0.0002	0.0003
433.2	0.0803 (0.1048)	0.0001	0.0002
323.2, 373.2, 433.2	0.0884 (0.1070)	0.0008	0.0023
	Naphthalene		
373.2	0.1252 (0.1506)	0.0004	0.0006
423.2	0.1440 (0.1375)	0.0004	0.0008
373.2, 423.2	0.1219 (0.1466)	0.0007 0.0009	0.0019 0.0023
	Phenanthrene		
383.2	0.1561 (0.1900)	0.0003	0.0005
423.2	0.1520 (0.1844)	0.0002	0.0003
383.2, 423.2	0.1550 (0.1884)	0.0003	0.0006
	Pyrene		
433.2	0.2158 (0.2551)	0.0003	0.0004

[a] The RMS and maximum errors in carbon monoxide mole fraction are essentially the same for the SRK and PR equations of state.

Further details of the data reduction techniques used in this study are given by Gasem *(14)*. The input parameters for the pure components (acentric factor, ω, critical temperature, T_c, and critical pressure, p_c) required by the SRK and PR equations of state, together with the literature sources, are presented in Table 2.

The EOS representations of the solubilities for the systems considered are shown in Table 3. In general, the SRK and PR equations are capable of describing the data with root-mean-squared errors (RMS) within 0.001 in mole fraction for a given system when a single interaction parameter, C_{ij}, is used over the complete temperature range. The ability of equations of state is marginally improved (RMS = 0.0008) when an additional interaction parameter, D_{ij}, is employed.

The good results from the use of a single interaction parameter, C_{ij}, per binary system are in contrast to our previous experience with the CO_2, methane, and ethane systems *(1–8)*; the low solubility of CO in the four aromatic solvents (at pressures to 23 MPa) has apparently tempered the need for the second interaction parameter, D_{ij}. A high degree of correlation was observed between C_{ij} and D_{ij} when both were used simultaneously.

As expected, improvements are realized by using temperature dependent interaction parameters; when two parameters (C_{ij} and D_{ij}) are fitted to each isotherm (for which the results are not presented here), the RMS errors are reduced to about 0.0004. In general, the RMS errors in mole fraction are comparable to the estimated uncertainties for the measurements. This illustrates both the ability of the equations of state and the precision of the reported data.

Conclusions

Results have been obtained for the solubility of carbon monoxide in benzene, naphthalene, phenanthrene, and pyrene at temperatures from 323.2 to 433.2 K and pressures up to 23.2 MPa. These results are well described by the SRK and PR equations of state.

Acknowledgment

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