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Solubility of Carbon Dioxide in Phenanthrene and in Pyrene

Jun-Shun Yau and Fuan-Nan Tsai*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 70101, ROC

The solubility of carbon dioxide in phenanthrene and pyrene has been measured in a semiflow vapor-liquid equilibrium apparatus over the temperature range from 423.15 to 523.15 K for phenanthrene and from 473.15 to 573.15 K for pyrene at pressures up to 50 atm. Henry constants, the partial molar volumes of carbon dioxide at infinite dilution, and the Margules parameters are determined from the solubility data.

Introduction

This work is a continuation of our studies on the phase behavior of carbon dioxide (CO₂) with hydrocarbon solvents that are of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Previously reported data include the solubility of CO₂ in *n*-tetracosane or *n*-dotriacontane (1) and in naphthalene or biphenyl (2). Barrick et al. (3) reported the solubility of CO₂ in phenanthrene or pyrene at temperatures to 439.15 K. In the present study, the vapor-liquid equilibria of CO₂ in three-ring and four-ring aromatic solvents phenanthrene and pyrene have been measured at temperature ranges from 423.15 to 523.15 K and 473.15 to 573.15 K, respectively, and pressures from 10 to 50 atm. Henry constants, the partial molar volumes of CO₂ at infinite dilution, and the Margules parameters are obtained by fitting the Krichevsky-Ilinskaya equation (4) to the solubility data.

Experimental Section

The experimental apparatus used for the measurement of gas solubility was a semiflow vapor-liquid equilibrium apparatus. A detailed description of the experimental equipment and sampling procedure has been reported (5). Briefly, CO₂ passed continuously from a high-pressure cylinder through two cells in series while both were filled with a molten aromatic hydrocarbon. The first cell is the presaturator and the second the equilibrium cell. Upon saturation, the sample from the latter was withdrawn, released under pressure, and collected in a trap. The condensed aromatic hydrocarbon was weighed with an analytical balance, and the liberated gas from the trap was measured volumetrically in a buret for the liquid phase and in a wet test meter for the gas phase. The temperature of the equilibrium cell was measured to an accuracy of 0.2 K by a type J thermocouple inserted in the equilibrium cell. The pressure was measured by a Helse gauge to ± 0.1 atm.

* To whom correspondence should be addressed.

Table I. VLE Data for the Carbon Dioxide (1)-Phenanthrene (1) System for Temperature *T*, Pressure *P*, Liquid (*x*₂) and Vapor (*y*₂) Mole Fractions of Carbon Dioxide, and *K*₂ = *y*₂/*x*₂ Values

<i>T</i> /K	<i>P</i> /atm	<i>x</i> ₂	<i>y</i> ₂	<i>K</i> ₂
423.15	10	0.0201	0.9994	49.62
	20	0.0402	0.9996	24.85
	30	0.0605	0.9996	16.51
	40	0.0796	0.9997	12.56
	50	0.0987	0.9997	10.13
473.15	10	0.0178	0.9966	55.96
	20	0.0348	0.9980	28.70
	30	0.0522	0.9982	19.13
	40	0.0699	0.9986	14.29
	50	0.0882	0.9987	11.32
523.15	10	0.0161	0.9856	61.26
	20	0.0332	0.9920	29.89
	30	0.0486	0.9940	20.44
	40	0.0658	0.9950	15.11
	50	0.0803	0.9955	12.40

Table II. VLE Data for the Carbon Dioxide (2)-Pyrene (1) System for Temperature *T*, Pressure *P*, Liquid (*x*₂) and Vapor (*y*₂) Mole Fractions of Carbon Dioxide, and *K*₂ = *y*₂/*x*₂ Values

<i>T</i> /K	<i>P</i> /atm	<i>x</i> ₂	<i>y</i> ₂	<i>K</i> ₂
473.15	10	0.0145	0.9994	68.92
	20	0.0285	0.9997	35.10
	30	0.0433	0.9997	23.09
	40	0.0587	0.9998	17.05
	50	0.0737	0.9998	13.56
523.15	10	0.0127	0.9964	78.77
	20	0.0282	0.9982	35.37
	30	0.0421	0.9987	23.75
	40	0.0551	0.9988	18.14
	50	0.0684	0.9989	14.61
573.15	10	0.0128	0.9867	76.84
	20	0.0265	0.9927	37.43
	30	0.0409	0.9945	24.35
	40	0.0540	0.9968	18.45
	50	0.0686	0.9980	14.54

Materials. Carbon dioxide used in this work had a minimum purity of 99.5 mol %. The phenanthrene and pyrene were purchased from Tokyo Kasei Kogyo Co., Ltd., with a minimum purity of 98 mol %. No further purification of the chemicals was attempted.

Results

Tables I and II present the direct experimental vapor-liquid equilibrium data for liquid-phase mole fraction *x*₂ and vapor-phase mole fraction *y*₂ of CO₂ at temperature *T* and pressure *P* for CO₂ with phenanthrene and pyrene, respectively. Each

Table III. Critical Temperatures T_c , Critical Pressures P_c , and Acentric Factors ω Used in Equations 6-9

substance	T_c /K	P_c /atm	ω	ref
carbon dioxide	304.1	72.85	0.239	7
phenanthrene	873.2	32.57	0.540	3, 8
pyrene	938.2	25.66	0.344	3, 9

reported datum is the average value of at least four replicate samples. The sample compositions were generally reproducible within 2% in the mole fraction of CO_2 for the liquid phase and 0.02% for the gas phase. The K_2 values of CO_2 listed in Tables I and II were calculated from the average values of x_2 and y_2 according to the definition $K_2 = y_2/x_2$. It can be seen that the solubility of CO_2 increases with pressure and decreases with rising temperature under the conditions of this work.

Correlation. The solubility of CO_2 in aromatic solvents phenanthrene and pyrene is correlated by the modified Soave equation (6) with one interaction parameter, k_{12} :

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (1)$$

where v is the molar volume.

$$a = z_1^2 a_{11} + 2z_1 z_2 a_{12} + z_2^2 a_{22} \quad (2)$$

$$b = z_1^2 b_{11} + 2z_1 z_2 b_{12} + z_2^2 b_{22} \quad (3)$$

$$a_{12} = (a_{11} a_{22})^{0.5} (1 - C_{12}) \quad (4)$$

$$b_{12} = 0.5(b_{11} + b_{22})(1 - D_{12}) \quad (5)$$

$$a_i = 0.42748 \alpha_i R^2 T_{c,i}^2 / P_{c,i} \quad i = 1, 2 \quad (6)$$

$$b_i = 0.08664 R T_{c,i} / P_{c,i} \quad (7)$$

$$\alpha_i = [1 + m_i (1 - T_{r,i}^{0.5})]^2 \quad (8)$$

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \quad (9)$$

$T_{c,i}$, $P_{c,i}$, $T_{r,i}$, and ω_i are, respectively, the critical temperature, critical pressure, reduced temperature, and acentric factor of component i .

In fitting equations of state to experimental data, the values for the optimized interaction parameters are dependent on the properties ($T_{c,i}$, $P_{c,i}$, and ω_i) used in the evaluation of the pure-component parameters (a and b) in the equations. Table III presents the properties utilized in the present work. The optimum values of C_{12} and D_{12} were determined by minimizing the bubble pressure variance.

Table IV. Correlation of VLE Data with the Modified Soave Equation: Temperature T , Pressure P Range, C_{12} and D_{12} Values, Equations 4 and 5, Average Relative Percent Deviation in Pressure $100 \Delta P/P$, and Average Absolute Deviation in Vapor Phase Mole Fraction of Carbon Dioxide Δy_2

solvent	T /K	P range/atm	data pts	C_{12}	D_{12}	$100 \Delta P/P^a$	$\Delta y_2^b / 10^{-4}$
phenanthrene	383.15 ^c	18-105	7	0.1562		2.88	
	423.15	10-50	5	0.1698		2.03	2.52
				0.1821	-0.2117	0.36	2.53
	473.15	10-50	5	0.1682		2.00	7.34
				0.1817	-0.2148	0.85	7.15
	523.15	10-50	5	0.1698		1.49	13.04
pyrene	423.15-523.15	10-50	15	0.1849	-0.2079	1.12	13.73
				0.1693		1.80	7.56
				0.1818	-0.2012	0.87	7.76
	433.15 ^c	7-105	7	0.3038		2.20	
	473.15	10-50	5	0.3897		3.61	5.70
				0.4214	-0.5094	0.83	5.31
	523.15	10-50	5	0.4247		3.74	21.12
				0.4669	-0.5700	2.69	20.10
	573.15	10-50	5	0.4658		3.42	66.46
			0.5222	-0.6076	0.74	62.17	
473.15-573.15	10-50	15	0.4128		5.76	35.24	
			0.4285	-0.2219	6.07	34.67	

^a $\Delta P/P = (1/n) \sum_{i=1}^n |(P_{i,\text{calcd}} - P_{i,\text{exptl}}) / P_{i,\text{exptl}}|$. ^b $\Delta y_2 = (1/n) \sum_{i=1}^n |y_{2,\text{calcd},i} - y_{2,\text{exptl},i}|$. ^c Solubility data were measured by Barrick et al. (3).

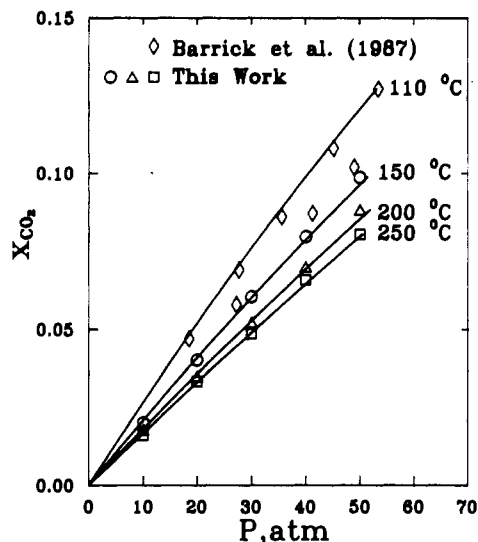
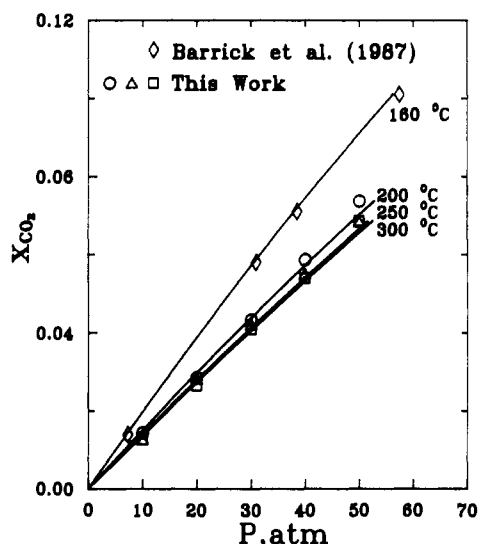
**Figure 1. Comparison of calculated mole fraction x_2 of carbon dioxide in phenanthrene (lines) with experimental data (symbols) as a function of pressure P and temperature T .****Figure 2. Comparison of calculated mole fraction x_2 of carbon dioxide in pyrene (lines) with experimental data (symbols) as a function of pressure P and temperature T .**

Table V. Thermodynamic Parameters for Carbon Dioxide Solubility: Henry Constant H_2 , Margules Constant A , and Partial Molar Volumes at Infinite Dilution \bar{v}_2^∞

solvent	T/K	H_2 /atm	A /(J mol ⁻¹)	\bar{v}_2^∞ /(cm ³ mol ⁻¹)
phenanthrene	423.15	466	860	58.9
	473.15	542	1006	68.0
	523.15	587	1232	80.5
pyrene	473.15	646	1185	82.4
	523.15	690	1460	98.3
	573.15	701	1837	119.6

The calculated results are shown in Table IV. Representations using one (C_{12}) and two (C_{12} , D_{12}) interaction parameters are shown for cases where (a) the parameters were optimized for each isotherm separately and (b) multiple isotherms were treated simultaneously. Figures 1 and 2 compare calculated and experimental solubilities of CO₂ in phenanthrene and pyrene, respectively, with one interaction parameter. It indicates that the agreement is satisfactory over the entire temperature and pressure ranges. In Figure 1 we include the CO₂ solubility data of Barrick et al. (3) at 383.15 and 423.15 K which are systematically higher than those of the present work. Figure 2 also includes the solubility data of CO₂ in pyrene of Barrick et al. (3) at 433.15 K for comparison, though their data were not taken at temperatures identical with those of this work.

Henry constants H_2 , the partial molar volumes of CO₂ at infinite dilution \bar{v}_2^∞ , and the Margules parameters A were determined by fitting the Krichevsky–Ilinskaya equation (4):

$$\ln(f_2/x_2) = \ln H_2 + A(x_1^2 - 1)/RT + \bar{v}_2^\infty(P - P_1^s)/RT \quad (10)$$

where f_2 is the fugacity of CO₂ and P_1^s is the saturated vapor pressure of solvents, in combination with the modified Soave equation using the optimum one interaction parameter C_{12} of Table IV by the Bender et al. approach (10). The resulting parameters are listed in Table V. The values of all the parameters increase with temperature.

Glossary

A	Margules constant, J mol ⁻¹
a	parameter in the modified Soave equation, eq 1, atm cm ⁶ mol ⁻²
b	parameter in the modified Soave equation, eq 1, cm ³ mol ⁻¹
C, D	binary interaction parameter

f	fugacity, atm
H	Henry constant, atm
K	vaporization equilibrium ratio, y/x
P	pressure, atm
R	molar gas constant, 82.0569 atm cm ³ K ⁻¹ mol ⁻¹
T	temperature, K
v	molar volume, cm ³ mol ⁻¹
\bar{v}	partial molar volume, cm ³ mol ⁻¹
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
z	mole fraction (liquid or vapor phase)

Greek Letters

ω	acentric factor
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Superscripts

s	saturated property
∞	infinite dilution

Subscripts

1	component 1 (solvent)
2	component 2 (solute, CO ₂)
c	critical property
i	component i
r	reduced property

Registry No. CO₂, 124-38-9; phenanthrene, 85-01-8; pyrene, 129-00-0.

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