

Solubility of Carbon Dioxide in Phenol and in Catechol

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 phenol and catechol has been measured in a semiflow vapor-liquid equilibrium apparatus over the temperature range from 75 to 150 °C for CO₂/phenol and from 125 to 200 °C for CO₂/catechol at pressures up to 50 atm. Henry's constant and the partial molar volume at infinite dilution are determined from the solubility data.

Introduction

Vapor-liquid equilibrium (VLE) data are an essential element in the design and development of some industrial processes. The solubilities of carbon dioxide in aromatic solvents are of interest in a number of industrial processes, including processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. The work presented here is part of our continuing studies on the phase behavior of carbon dioxide in *n*-tetracosane and in *n*-dotriacontane (1) and carbon dioxide in phenanthrene and in pyrene (2). In the present study, the solubilities of carbon dioxide in phenol and in catechol at temperatures ranging from 75 to 150 °C and from 125 to 200 °C, respectively, and pressures from 10 to 50 atm have been measured. Henry's constant and the partial molar volume at infinite dilution of the dissolved gas are obtained by fitting the Krichevsky-Ilinskaya equation (3) to the data.

Experimental Section

A semiflow vapor-liquid equilibrium apparatus is used for the measurement of gas solubility in this work. The experimental facilities and sampling procedure have been described elsewhere (4). Briefly, in the course of an experiment, the molten aromatic solvent was kept in a presaturator and an equilibrium cell, which were housed in series in a thermostated nitrogen bath. Carbon dioxide from a high-pressure cylinder continuously passed through these two cells. Upon saturation, the sample in the equilibrium cell was withdrawn, reduced in pressure, and collected in a trap. The collected aromatic solvent 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 °C by a type J thermocouple inserted in the equilibrium cell. Pressure was measured by a Heise gauge to ±1.5 psi.

Materials. The purity of carbon dioxide used in this work is 99.5+ mol %. Phenol was purchased from Wako Pure Chemical Industries, Ltd., and catechol from Aldrich Chemical Co., Inc., with a minimum purity of 99 mol %. The chemicals were used without further purification.

Results

Table I presents vapor-liquid equilibrium data for carbon dioxide with phenol at four temperatures: 75, 100, 125, and 150 °C. Table II presents vapor-liquid equilibrium data for carbon dioxide with catechol at four temperatures: 125, 150, 175, and 200 °C. At each temperature, five pressures (10, 20, 30, 40, and 50 atm) were investigated for all systems. The

Table I. VLE Data for the Carbon Dioxide-Phenol System

<i>T</i> , °C	<i>P</i> , atm	<i>x</i> ₂	<i>y</i> ₂	<i>K</i>
75	10	0.0311	0.9985	32.09
	20	0.0644	0.9991	15.51
	30	0.0925	0.9992	10.80
	40	0.1220	0.9992	8.191
	50	0.1535	0.9991	6.510
100	10	0.0227	0.9939	43.75
	20	0.0520	0.9965	19.15
	30	0.0762	0.9976	13.08
	40	0.1016	0.9975	9.823
	50	0.1292	0.9966	7.711
125	10	0.0226	0.9851	43.53
	20	0.0456	0.9919	21.74
	30	0.0666	0.9929	14.92
	40	0.0887	0.9935	11.21
	50	0.1069	0.9924	9.282
150	10	0.0209	0.9603	46.01
	20	0.0411	0.9786	23.83
	30	0.0604	0.9844	16.30
	40	0.0799	0.9870	12.35
	50	0.1010	0.9885	9.788

Table II. VLE Data for the Carbon Dioxide-Catechol System

<i>T</i> , °C	<i>P</i> , atm	<i>x</i> ₂	<i>y</i> ₂	<i>K</i>
125	10	0.0152	0.9969	65.76
	20	0.0304	0.9981	32.82
	30	0.0444	0.9985	22.50
	40	0.0594	0.9984	16.81
	50	0.0716	0.9986	13.94
150	10	0.0130	0.9939	76.69
	20	0.0260	0.9967	38.33
	30	0.0397	0.9975	25.13
	40	0.0528	0.9975	18.90
	50	0.0655	0.9979	15.24
175	10	0.0123	0.9875	80.35
	20	0.0258	0.9925	38.54
	30	0.0378	0.9947	26.31
	40	0.0508	0.9957	19.61
	50	0.0625	0.9962	15.94
200	10	0.0116	0.9772	84.02
	20	0.0244	0.9886	40.48
	30	0.0367	0.9896	26.94
	40	0.0486	0.9921	20.41
	50	0.0605	0.9937	16.42

reported data were the average values of at least four replicate samples at each experimental condition. The samples were generally reproducible within 2% in the mole fraction of carbon dioxide for the liquid phase and 0.05% for the vapor phase. *K* values of carbon dioxide listed in Tables I and II were calculated from the average values of *x* and *y* according to the definition $K = y/x$. It can be seen that the solubility of carbon dioxide increases with pressure and decreases with rising temperature under the conditions of the experiment.

Correlation. As was the case for our previously measured solubility of carbon dioxide in the paraffinic (1) and aromatic (2) solvents, the present data may be represented adequately by the modified Soave equation (5) with one interaction parameter. For the modified Soave equation, the specific relations are

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

where

* To whom all correspondence should be addressed.

Table III. Critical Properties and Acentric Factors Used in the Equation of State

substance	T_c , K	P_c , atm	ω	ref
carbon dioxide	304.1	72.8	0.239	6
phenol	694.2	60.5	0.438	6
catechol	772.2	77.7	0.641	7-9

Table IV. Correlation of VLE Data with the Modified Soave Equation

solvent	T , °C	P range, atm	data pts	k_{ij}	$\Delta P/P$, %	$\Delta y \times 10^4$
phenol	75	10-50	5	0.0753	1.69	2.24
	100	10-50	5	0.0772	4.42	5.15
	125	10-50	5	0.0719	0.90	13.08
	150	10-50	5	0.0631	1.28	20.76
catechol	125	10-50	5	-0.0377	0.85	12.35
	150	10-50	5	-0.0399	2.05	12.10
	175	10-50	5	-0.0541	1.58	8.46
	200	10-50	5	-0.0653	1.57	25.27

Table V. Thermodynamic Parameters for Carbon Dioxide Solubility

solvent	T , °C	H_2 , atm	A , J/mol	\bar{v}_2^∞ , cm ³ /mol
phenol	75	326	1347	45.3
	100	379	1465	48.6
	125	430	1531	52.1
	150	467	1597	56.3
catechol	125	637	1762	43.3
	150	721	1877	45.6
	175	765	1887	48.1
	200	797	1960	51.2

$$a = \sum_i \sum_j z_i z_j a_{ij} \quad (2)$$

$$b = \sum_i z_i b_i \quad (3)$$

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \quad (4)$$

$$a_i = 0.42748 \alpha_i R^2 T_{c,i}^2 / P_{c,i} \quad (5)$$

$$b_i = 0.08664 RT_{c,i} / P_{c,i} \quad (6)$$

$$\alpha_i = [1 + m_i (1 - T_r^{0.5})]^2 \quad (7)$$

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \quad (8)$$

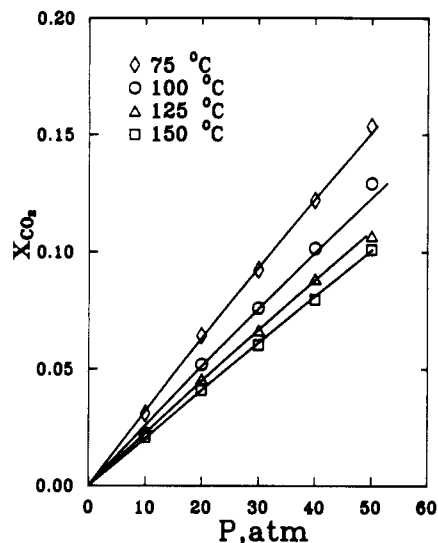
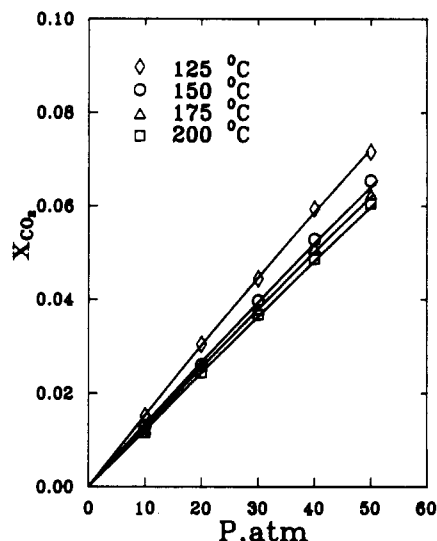
The critical data and acentric factors of carbon dioxide and phenol required in the equations were taken from the property data bank of Reid et al. (8). The critical temperature and pressure of catechol were calculated by means of the Ambrose method (7, 8). The acentric factor of catechol was estimated by the Lee-Kesler correlations (9). Those critical data and acentric factors are listed in Table III. The optimum values of k_{ij} were determined by minimizing the bubble pressure variance.

The calculated results with the optimum values of k_{ij} for each isotherm are listed in Table IV. For the majority of isotherms, the calculated bubble pressures agree with experimental data within 4% on the average. Figures 1 and 2 show the comparisons of calculated and experimental solubilities of carbon dioxide in the two aromatic solvents studied, respectively. It can be seen that the calculated results are in agreement with experimental data over the entire temperature and pressure ranges of data.

Henry's constant and the partial molar volume at infinite dilution are determined by fitting the Krichevsky-Ilinskaya equation (3) to the data. The equation is

$$\ln(f_2/x_2) = \ln H_2 + A(x_1^2 - 1)/RT + \bar{v}_2^\infty(P - P_1^s)/RT \quad (9)$$

When the Krichevsky-Ilinskaya equation and the modified

**Figure 1. Comparison of calculated solubility of carbon dioxide in phenol with experimental data.****Figure 2. Comparison of calculated solubility of carbon dioxide in catechol with experimental data.**

Soave equation are combined, Henry's constant, the partial molar volume at infinite dilution, and the Margules parameter can be calculated (10). The expressions of the three parameters can be derived from the modified Soave equation according to the following relations:

$$H_2 = P_1^s \Phi_2^{L,\infty} \quad (10)$$

$$\bar{v}_2^\infty = - \left[\frac{(\partial P / \partial n_2)_{V,T,n_1}}{(\partial P / \partial V)_{T,n_1,n_2}} \right]_{n_2=0} \quad (11)$$

$$A = - \frac{RT}{2} \frac{\partial}{\partial x_2} (\ln \Phi_2^L + \ln P)_{x_2=0} \quad (12)$$

When the optimum values of k_{ij} in Table IV are substituted into these expressions, the three Krichevsky-Ilinskaya parameters are obtained. The resulting parameters are listed in Table V. The values of all parameters increase with temperature.

Glossary

A	Margules constant
a, b	parameters in the modified Soave equation
f	fugacity
H	Henry's constant

<i>K</i>	vaporization equilibrium ratio, y/x
<i>k</i>	binary interaction parameter
<i>n</i>	number of moles
<i>P</i>	pressure
<i>R</i>	universal gas constant
<i>T</i>	temperature
<i>V</i>	total volume
<i>v</i>	molar volume
\bar{v}	partial molar volume
<i>x</i>	mole fraction in the liquid phase
<i>y</i>	mole fraction in the vapor phase
<i>z</i>	mole fraction (liquid or vapor phase)

Greek Letters

Φ	fugacity coefficient
ω	acentric factor

Superscripts

L	liquid phase
s	saturated property
∞	infinite dilution

Subscripts

1	component 1 (solvent)
2	component 2 (solute)

<i>c</i>	critical property
<i>i, j</i>	components <i>i</i> and <i>j</i>
<i>r</i>	reduced property

Registry No. CO₂, 124-38-9; phenol, 108-95-2; catechol, 120-80-9.

Literature Cited

- (1) Tsai, F. N.; Yau, J. S. *J. Chem. Eng. Data* 1990, 35, 43.
- (2) Yau, J. S.; Tsai, F. N. *J. Chem. Eng. Data*, in press.
- (3) Krichevsky, I. R.; Ilinskaya, A. A. *Zh. Fiz. Khim.* 1945, 19, 621.
- (4) Huang, S. H.; Lin, H. M.; Tsai, F. N.; Chao, K. C. *Ind. Eng. Chem. Res.* 1988, 27, 162.
- (5) Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev.* 1978, 17, 443.
- (6) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1988.
- (7) Ambrose, D. *Correlation and Estimation of Vapor-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds*; NPL Rep. Chem. 92; National Physical Laboratory: Teddington, Sept 1978; corrected March 1980.
- (8) Ambrose, D. *Correlation and Estimation of Vapor-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds*; NPL Rep. Chem. 98; National Physical Laboratory: Teddington, 1979.
- (9) Lee, B. I.; Kesler, M. G. *AIChE J.* 1975, 21, 510.
- (10) Bender, E.; Klein, U.; Schmitt, W.; Prausnitz, J. M. *Fluid Phase Equilib.* 1984, 15, 241.

Received for review February 10, 1991. Revised June 13, 1991. Accepted February 5, 1992. Acknowledgment is made to the National Science Council of the Republic of China (Grant NSC 79-0402-E006-17) for financial support of this work.

Isobaric Vapor-Liquid Equilibria for the Binary Systems CH₃SiHCl₂ with (CH₃)₃SiCl, (CH₃)₂SiCl₂, CH₃SiCl₃, or SiCl₄

Trandafir Rugină and Liviu Săcărescu*

Institute of Macromolecular Chemistry "P. Poni", Aleea Grigore Ghica Vodă 41A, 6600 Iași, Romania

This paper reports isobaric vapor-liquid equilibrium (VLE) data for four binary systems containing dichloromethylsilane, CH₃SiHCl₂, and chlorotrimethyl-, dichlorodimethyl-, trichloromethyl-, or tetrachlorosilane, (CH₃)_{4-n}SiCl_n ($n = 1-4$). The VLE data were determined ebullometrically at atmospheric pressure, and the experimental temperatures were corrected for 760 mmHg. The pure component vapor pressures were calculated using literature Antoine constants. The VLE data were then correlated by means of the Wilson, nonrandom two-liquid (NRTL), and Gothard equations.

Introduction

Vapor-liquid equilibrium (VLE) data for binary methylchlorosilane systems are scarce. In view of the importance of these data for the design of rectification columns in manufacturing silicon derivatives, we developed a data base for this class of substances. All the VLE data published until now on methylchlorosilanes were tested using a rectification process computer simulator and were verified on an industrial pilot plant.

Experimental Section

Materials. The methylchlorosilanes were Fluka products with 98% stated purity. They were purified by distillation on a laboratory column until no impurities were chromatographically detectable.

The physicochemical constants of the purified substances are compared with literature data in Table I.

Apparatus and Procedure. The experimental apparatus was a Swietoslowski-type ebullometer (1).

The experimental boiling temperatures, t^* , were measured to within 5.10^{-2} °C with a Beckmann thermometer calibrated in our laboratory with benzene for high boiling points and CH₃HSiCl₂ for low boiling points. The atmospheric pressure, P^* , was read on a Hg barometer to within 0.1 mmHg. The liquid, x_i , and vapor, y_i , mole fraction compositions of the two phases at equilibrium were determined by means of a gas chromatograph (2) packed with a mixture of 70% FS 1265 + 30% SE-30 on AW/DHCS Chromosorb P, 60-80 mesh. The overall uncertainty in the equilibrium mole fractions is estimated to be $(0.1-1) \times 10^{-2}$. The t^* values at pressure P^* were corrected for normal pressure, $P^\circ = 760$ mmHg, using the following equation (3):

$$t = t^* + ((dt_1/dP)x_1 + (dt_2/dP)x_2)(P^\circ - P^*) \quad (1)$$

where t_i is the boiling temperature of pure component i calculated with the Antoine equation from

$$t_i/^\circ\text{C} = B_i/[A_i - \log(P^\circ/\text{mmHg})] - C_i \quad (2)$$

The experimental data are shown in Tables II-V.

Results

The liquid-phase activity coefficients, γ_i , were calculated from the experimental P - x - y data at each temperature. The