

# SOLUBILITIES OF CARBON DIOXIDE IN CARBOXYLIC ACIDS UNDER HIGH PRESSURES

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The solubilities of carbon dioxide in lauric acid, palmitic acid and arachidic acid have been measured in a semiflow apparatus over the temperature range from 373.2 K to 473.2 K at pressures up to 5.07 MPa. A correlation is developed to describe the experimental data and to calculate the solubilities of carbon dioxide in these three heavy carboxylic acids. Henry's constants and the partial molar volumes at infinite dilution of carbon dioxide are determined from the measured solubility data.

## Introduction

Vapor-liquid equilibria (VLE) of CO<sub>2</sub> with carboxylic acids are of interest in some industrial processes, including the processing of pharmaceuticals, surfactants, soap, foods, and speciality chemicals. Limited data are available on systems involving CO<sub>2</sub> and the heavy carboxylic acids which are solid at room temperature. The work presented here is part of our continuing studies of the phase behavior of CO<sub>2</sub> in *n*-tetracosane and *n*-dotriacontane<sup>9)</sup>, in phenanthrene and pyrene<sup>11)</sup>, in phenol and catechol<sup>12)</sup>, and in naphthalene, diphenol, 2-methylnaphthalene, 1-naphthol and 2-naphthol<sup>4)</sup>. In the present study, the solubilities of CO<sub>2</sub> in lauric acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>-COOH), palmitic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>COOH) and arachidic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>COOH) have been measured in temperature ranges from 373.2 to 473.2 K and at pressures from 1.01 to 5.07 MPa. By way of the experimental data, the Krichevsky-Kasarnovsky equation<sup>5)</sup> was used to calculate Henry's constants and the partial molar volumes of CO<sub>2</sub> at infinite dilution. The isothermal VLE data obtained were correlated by using the modified Soave equation of state<sup>1)</sup> with one binary interaction parameter.

## 1. Experimental Section

A semiflow vapor-liquid equilibrium apparatus was used for the measurement of gas solubilities. A detailed description of the experimental equipment and sampling procedure have been reported<sup>3)</sup>. Briefly, in the course of an experiment the molten carboxylic acid was kept in a presaturator and an equilibrium cell,

which were housed in series in a thermostated nitrogen bath. Carbon dioxide passed continuously from a high-pressure cylinder through these two cells. To promote mixing and equilibration, the cells were packed with raschig rings.

Saturated liquid in the equilibrium cell was sampled by being withdrawn, reduced in pressure, and collected in a trap which was immersed in an ice bath. The trap with the solidified sample was weighed to determine the sample mass with an analytical balance, and the volume of liberated gas was measured 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 with a type J thermocouple inserted in the equilibrium cell. The pressure was measured with a Heise gauge to  $\pm 0.01$  MPa.

The purity of CO<sub>2</sub> used in this study was 99.5+ mol%. The lauric acid and palmitic acid, purchased from Merck, had minimum purities of 99 and 98 mol%, respectively. The arachidic acid, from Tokyo Kasei Kogyo Co., Ltd., had a minimum purity of 99 mol%. No further purification of the chemicals was attempted.

## 2. Results and Discussion

### 2.1 Experimental Data

Tables 1–3 present respectively the VLE data of liquid-phase mole fraction  $x_2$  and vapor-phase mole fraction  $y_2$  of CO<sub>2</sub> at various temperatures and pressures for CO<sub>2</sub> with lauric acid, palmitic acid, and arachidic acid. For each system, measurements were made at three temperatures: 373.2, 423.2 and 473.2 K. Along each isotherm, data were reported at five pressures: 1.01, 2.03, 3.04, 4.05 and 5.07 MPa. Each reported datum is the average value for at least three

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**Table 1.** VLE data for carbon dioxide (2)—lauric acid (1) system

$T$ [K]	$P$ [MPa]	$x_2$	$y_2$	$K_2$
373.2	1.01	0.0657	1.0000	15.2
	2.03	0.134	1.0000	7.48
	3.04	0.201	1.0000	4.98
	4.05	0.269	1.0000	3.72
	5.07	0.338	1.0000	2.98
423.2	1.01	0.0529	0.9996	18.9
	2.03	0.105	0.9996	9.57
	3.04	0.146	0.9998	6.84
	4.05	0.204	0.9999	4.89
	5.07	0.260	0.9999	3.84
473.2	1.01	0.0418	0.9951	23.8
	2.03	0.0843	0.9972	11.8
	3.04	0.124	0.9978	8.06
	4.05	0.172	0.9982	5.80
	5.07	0.214	0.9982	4.67

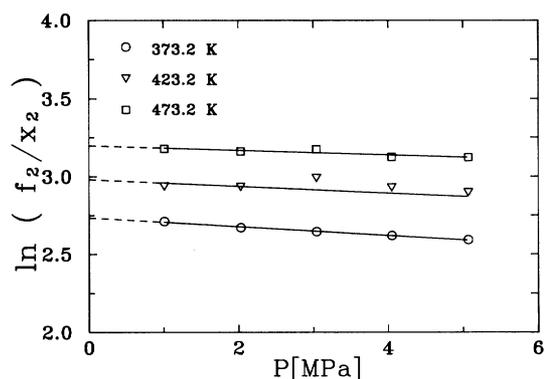
**Table 2.** VLE data for carbon dioxide (2)—palmitic acid (1) system

$T$ [K]	$P$ [MPa]	$x_2$	$y_2$	$K_2$
373.2	1.01	0.0652	1.0000	15.3
	2.03	0.144	1.0000	6.95
	3.04	0.196	1.0000	5.10
	4.05	0.272	1.0000	3.67
	5.07	0.336	1.0000	2.98
423.2	1.01	0.0582	0.9999	17.2
	2.03	0.110	0.9999	9.07
	3.04	0.165	0.9999	6.07
	4.05	0.216	0.9998	4.63
	5.07	0.264	0.9998	3.79
473.2	1.01	0.0436	0.9989	22.9
	2.03	0.0917	0.9993	10.9
	3.04	0.134	0.9995	7.46
	4.05	0.177	0.9997	6.65
	5.07	0.216	0.9998	4.63

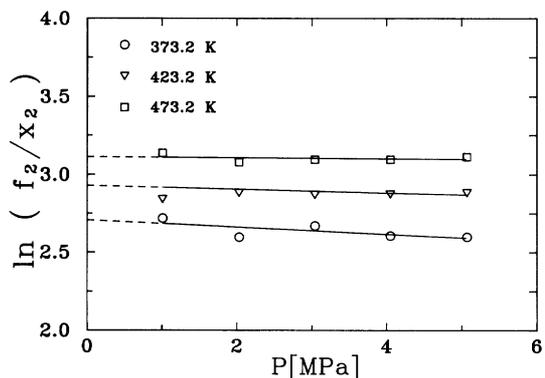
**Table 3.** VLE data for carbon dioxide (2)—arachidic acid (1) system

$T$ [K]	$P$ [MPa]	$x_2$	$y_2$	$K_2$
373.2	1.01	0.0809	1.0000	12.4
	2.03	0.151	1.0000	6.64
	3.04	0.225	1.0000	4.45
	4.05	0.297	1.0000	3.36
	5.07	0.366	1.0000	2.73
423.2	1.01	0.0564	1.0000	17.1
	2.03	0.116	1.0000	8.62
	3.04	0.173	1.0000	5.78
	4.05	0.225	1.0000	4.45
	5.07	0.269	1.0000	3.72
473.2	1.01	0.0518	0.9995	19.3
	2.03	0.103	0.9996	9.74
	3.04	0.147	0.9996	6.81
	4.05	0.196	0.9998	5.09
	5.07	0.243	0.9999	4.11

replicate samples. The compositions were generally reproducible within 2% for  $x_2$  and 0.05% for  $y_2$ . The  $K_2$  values of  $\text{CO}_2$  listed in Tables 1–3 were calculated



**Fig. 1.** Plot of  $\ln(f_2/x_2)$  versus pressure  $P$  for system  $\text{CO}_2$  + lauric acid



**Fig. 2.** Plot of  $\ln(f_2/x_2)$  versus pressure  $P$  for system  $\text{CO}_2$  + palmitic acid

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 mole fractions of  $\text{CO}_2$  in liquid and vapor phase increase with increasing pressure and decreasing temperature under the conditions of this work.

## 2.2 Correlation with Krichevsky-Kasarnovsky Equation

Henry's constants and the partial molar volumes at infinite dilution of  $\text{CO}_2$  dissolved in the carboxylic acids can be determined from the measured solubility data according to the Krichevsky-Kasarnovsky equation<sup>5)</sup>

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

where subscript 1 refers to the solvent, carboxylic acid, and 2 to the solute,  $\text{CO}_2$ ,  $H_2$  is Henry's constant,  $\bar{v}_2^\infty$  is the partial molar volume of  $\text{CO}_2$  at infinite dilution, and  $P_1^s$  is the vapor pressure of the solvent. The fugacity  $f_2$  in Eq. (1) can be calculated from pure  $\text{CO}_2$  by using the equation of state proposed by Huang *et al.*<sup>2)</sup>. According to Eq. (1) a linear relation should be obtained between  $\ln(f_2/x_2)$  and  $P$  for a given gas and solvent at constant temperature. Figures 1–3 show the linear results that are obtained. By Eq. (1), the intercepts at  $P = P_1^s$  of these plots give Henry's constants according to the definition

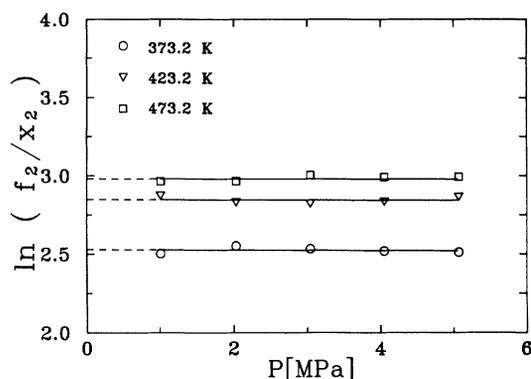


Fig. 3. Plot of  $\ln(f_2/x_2)$  versus pressure  $P$  for system  $\text{CO}_2$  + arachidic acid

$$H_2 = \lim_{x_2 \rightarrow 0} (f_2/x_2) \quad (2)$$

and the slopes give the partial molar volumes of  $\text{CO}_2$  at infinite dilution. The values of Henry's constants and the partial molar volumes of  $\text{CO}_2$  at infinite dilution so determined are listed in Table 4.

Figure 4 shows the calculated values of Henry's constants as a function of temperature for each system. It can be seen that Henry's constants increase with increasing temperature and decreasing carbon number of carboxylic acid.

### 2.3 Correlation of Solubility Data

As was the case for our previously measured solubilities of  $\text{CO}_2$  in paraffinic<sup>9)</sup> and aromatic<sup>11,12)</sup> solvents, the solubilities of  $\text{CO}_2$  in lauric acid, palmitic acid and arachidic acid may be correlated well by the modified Soave equation<sup>1)</sup> with one binary interaction parameter  $k_{12}$ :

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (3)$$

where  $v$  is the molar volume,

$$a = z_1^2 a_{11} + 2z_1 z_2 a_{12} + z_2^2 a_{22} \quad (4)$$

$$b = z_1 b_1 + z_2 b_2 \quad (5)$$

$$a_{12} = (a_{11} a_{22})^{0.5} (1 - k_{12}) \quad (6)$$

$$a_i = 0.42748 \alpha_i R^2 T_{c,i}^2 / P_{c,i} \quad (i=1, 2) \quad (7)$$

$$b_i = 0.0866 RT_{c,i} / P_{c,i} \quad (8)$$

$$\alpha_i = [1 + m_i (1 - T_{r,i}^{0.5})]^2 \quad (9)$$

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \quad (10)$$

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

The critical data and acentric factor of  $\text{CO}_2$  required in the equations were taken from the property data bank of Reid *et al.*<sup>8)</sup>. The critical properties and acentric factors of heavy carboxylic acids were estimated by Lydersen's method<sup>7)</sup> and the Lee-Kesler

Table 4. Thermodynamic parameters for carbon dioxide solubilities: Henry's constants  $H_2$  and the partial molar volumes of carbon dioxide at infinite dilution  $\bar{v}_2^\infty$

Solvent	$T$ [K]	$H_2$ [MPa]	$\bar{v}_2^\infty$ [cm <sup>3</sup> mol <sup>-1</sup> ]
Lauric acid	373.2	15.4	-89
	423.2	19.7	-76
	473.2	24.5	-58
Palmitic acid	373.2	15.0	-72
	423.2	18.7	-42
	473.2	22.5	-12
Arachidic acid	373.2	12.5	-5.1
	423.2	17.3	-4.1
	473.2	19.7	-1.9

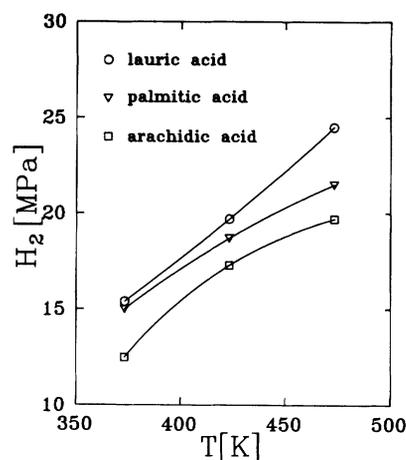


Fig. 4. Plot of Henry's constants versus temperature for  $\text{CO}_2$  + carboxylic acid systems

Table 5. Critical temperature  $T_c$ , critical pressure  $P_c$ , and acentric factors  $\omega$  used in Eqs. (7)–(10)

Substance	$T_c$	$P_c$ [MPa]	$\omega$
Carbon dioxide	304.10	7.382	0.239
Lauric acid	734.75	1.934	1.021
Palmitic acid	780.00	1.510	1.175
Arachidic acid	820.26	1.238	1.448

correlations<sup>6)</sup> respectively. The normal boiling points of lauric acid and palmitic acid needed in calculations for  $T_c$  were taken from the CRC Handbook of Chemistry and Physics<sup>10)</sup>, while the normal boiling point of arachidic acid was obtained by extrapolating those of lauric acid, palmitic acid, and stearic acid. These critical data and acentric factors are listed in Table 5. The optimum values of  $k_{12}$  were determined by minimizing the bubble pressure variance.

The calculated results with the optimum values of  $k_{12}$  for each isotherm are listed in Table 6. The average relative percent deviation in pressure is not more than 6%. Figures 5–7 compare calculated and experimental solubilities of  $\text{CO}_2$  in three heavy carboxylic acid solvents. They indicate that the modified Soave

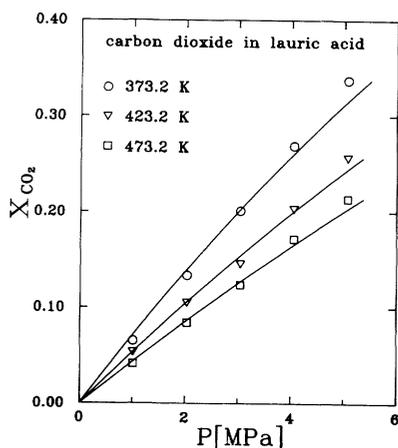
**Table 6.** Correlation of VLE data with the modified Soave equation for five data points at each temperature

Solvent	$T$ [K]	$P$ range [MPa]	$k_{12}$	$100$ $\Delta P/P^a$	$10^4$ $\Delta y_2^b$
Lauric acid	373.2	1.01–5.07	0.0235	5.37	0.16
	423.2	1.01–5.07	0.0073	2.99	1.14
	473.2	1.01–5.07	0.0088	4.13	2.31
Palmitic acid	373.2	1.01–5.07	0.0375	5.80	0.06
	423.2	1.01–5.07	0.0045	1.22	1.09
	473.2	1.01–5.07	0.0130	2.44	2.16
Arachidic acid	373.2	1.01–5.07	0.0072	3.02	0.03
	423.2	1.01–5.07	-0.0044	2.53	0.04
	473.2	1.01–5.07	-0.0448	1.49	2.85

$$^a \Delta P/P = \frac{1}{n} \sum_{i=1}^n \left| \frac{P_{i,\text{cal}} - P_{i,\text{exp}}}{P_{i,\text{exp}}} \right|$$

$$^b \Delta y_2 = \frac{1}{n} \sum_{i=1}^n |y_{2,\text{cal},i} - y_{2,\text{exp},i}|$$

where  $n$  is number of data.



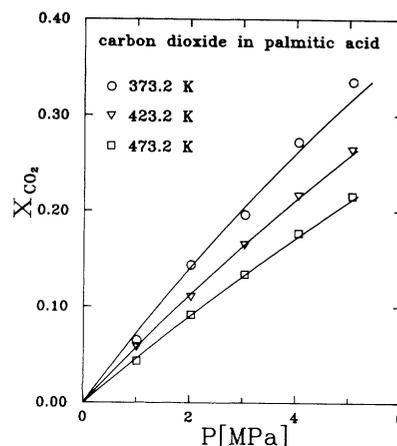
**Fig. 5.** Comparison of calculated mole fraction  $x_2$  of carbon dioxide in lauric acid (lines) with experimental data (points) as a function of pressure  $P$  and temperature  $T$

equation with one interaction parameter is adequate to correlate the solubility data.

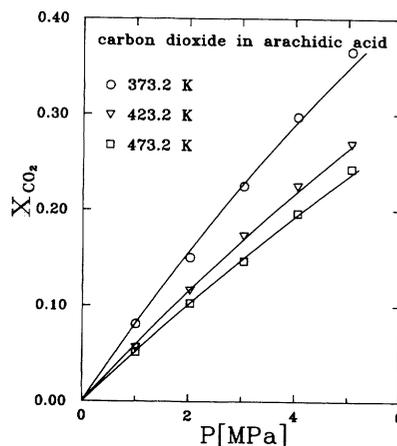
### Conclusion

This study has presented new experimental data on the solubilities of  $\text{CO}_2$  in heavy carboxylic acids such as lauric acid, palmitic acid, and arachidic acid. The liquid- and vapor-phase mole fractions of  $\text{CO}_2$  increase with pressure and decrease with rising temperature under the experimental conditions of this work. The solubility data obtained are satisfactorily correlated by applying a modified Soave equation of state with one interaction parameter.

Henry's constants and the partial molar volumes of  $\text{CO}_2$  at infinite dilution for the  $\text{CO}_2$ -heavy carboxylic acid systems can be obtained from the solubility data on the basis of the Krichevsky-Kasarnovsky equation. The Henry's constants obtained increase with increasing temperature and decreasing carbon number



**Fig. 6.** Comparison of calculated mole fraction  $x_2$  of carbon dioxide in palmitic acid (lines) with experimental data (points) as a function of pressure  $P$  and temperature  $T$



**Fig. 7.** Comparison of calculated mole fraction  $x_2$  of carbon dioxide in arachidic acid (lines) with experimental data (points) as a function of pressure  $P$  and temperature  $T$

of carboxylic acid in the temperature ranges from 373.2 to 473.2 K.

### Acknowledgment

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### Nomenclature

$a$	= parameter in the modified Soave equation	[MPa cm <sup>6</sup> mol <sup>-2</sup> ]
$b$	= parameter in the modified Soave equation	[cm <sup>3</sup> mol <sup>-1</sup> ]
$f$	= fugacity	[MPa]
$H$	= Henry's constant	[MPa]
$K$	= vaporization equilibrium ratio, $y/x$	[—]
$k$	= binary interaction parameter	[—]
$m$	= parameter in the modified Soave equation	[—]
$n$	= number of data	[—]
$P$	= pressure	[MPa]
$R$	= molar gas constant, 8.314	[MPa cm <sup>3</sup> K <sup>-1</sup> mol <sup>-1</sup> ]
$T$	= temperature	[K]
$v$	= molar volume	[cm <sup>3</sup> mol <sup>-1</sup> ]
$\bar{v}$	= partial molar volume	[cm <sup>3</sup> mol <sup>-1</sup> ]
$x$	= mole fraction in the liquid phase	[—]

$y$	= mole fraction in the vapor phase	[—]
$z$	= mole fraction (liquid or vapor phase)	[—]
$\alpha$	= parameter in the modified Soave equation	[—]
$\omega$	= acentric factor	[—]

<Superscripts>

$s$	= saturated property
$\infty$	= infinite dilution

<Subscripts>

1	= component 1 (solvent)
2	= component 2 (solute, CO <sub>2</sub> )
$c$	= critical property
$i$	= component $i$
$r$	= reduced property

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