

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 CO₂ with carboxylic acids are of interest in some industrial processes, including the processing of pharmaceuticals, surfactants, soap, foods, and specialty chemicals. Limited data are available on systems involving CO₂ 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 CO₂ in *n*-tetracosane and *n*-dotriacontane⁹⁾, in phenanthrene and pyrene¹¹⁾, in phenol and catechol¹²⁾, and in naphthalene, diphenol, 2-methylnaphthalene, 1-naphthol and 2-naphthol⁴⁾. In the present study, the solubilities of CO₂ in lauric acid (CH₃(CH₂)₁₀-COOH), palmitic acid (CH₃(CH₂)₁₄COOH) and arachidic acid (CH₃(CH₂)₁₈COOH) 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 equation⁵⁾ was used to calculate Henry's constants and the partial molar volumes of CO₂ at infinite dilution. The isothermal VLE data obtained were correlated by using the modified Soave equation of state¹⁾ 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 reported³⁾. 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Saturated liquid in the equilibrium cell was sampled by being withdrawn, reduced in pressure, and collected in a trap which was immersed in an ice bath.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 ± 0.01 MPa.

The purity of CO₂ 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 CO₂ at various temperatures and pressures for CO₂ 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 CO₂ listed in Tables 1–3 were calculated

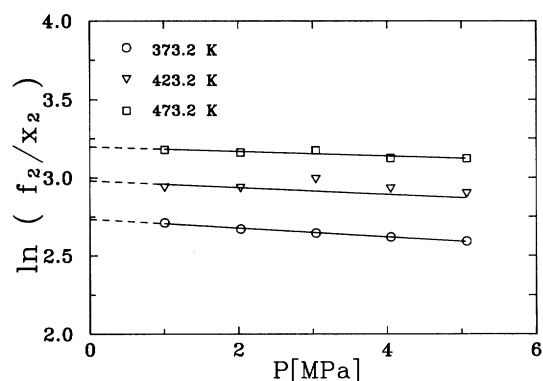


Fig. 1. Plot of $\ln(f_2/x_2)$ versus pressure P for system CO₂ + lauric acid

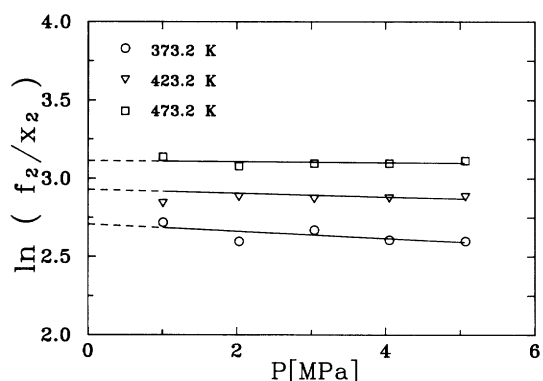


Fig. 2. Plot of $\ln(f_2/x_2)$ versus pressure P for system CO₂ + palmitic acid

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 CO₂ 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 CO₂ dissolved in the carboxylic acids can be determined from the measured solubility data according to the Krichevsky-Kasarnovsky equation⁵⁾

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

where subscript 1 refers to the solvent, carboxylic acid, and 2 to the solute, CO₂, H_2 is Henry's constant, \bar{v}_2^∞ is the partial molar volume of CO₂ 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 CO₂ by using the equation of state proposed by Huang *et al.*²⁾. 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

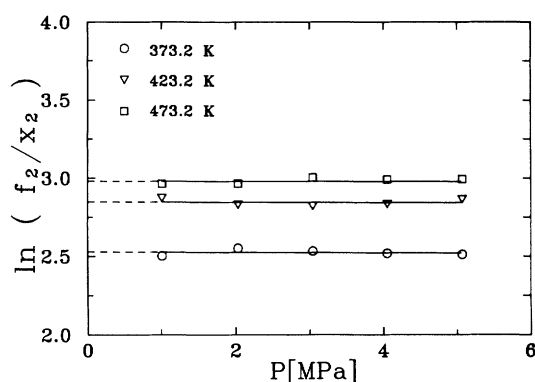


Fig. 3. Plot of $\ln(f_2/x_2)$ versus pressure P for system CO_2 + arachidic acid

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

and the slopes give the partial molar volumes of CO_2 at infinite dilution. The values of Henry's constants and the partial molar volumes of 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 CO_2 in paraffinic⁹⁾ and aromatic^{11,12)} solvents, the solubilities of CO_2 in lauric acid, palmitic acid and arachidic acid may be correlated well by the modified Soave equation¹⁾ 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,

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

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

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

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

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

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

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

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

The critical data and acentric factor of CO_2 required in the equations were taken from the property data bank of Reid *et al.*⁸⁾. The critical properties and acentric factors of heavy carboxylic acids were estimated by Lydersen's method⁷⁾ 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^∞

Solvent	T [K]	H_2 [MPa]	\bar{v}_2^∞ [cm ³ mol ⁻¹]
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

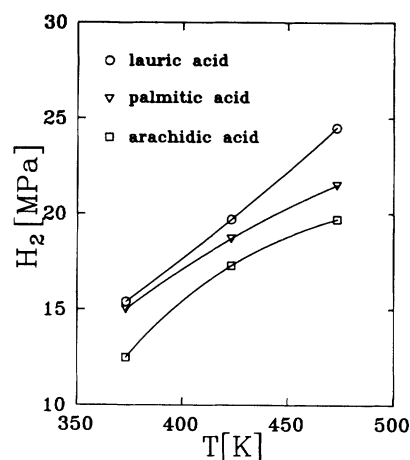


Fig. 4. Plot of Henry's constants versus temperature for CO_2 + carboxylic acid systems

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

Substance	T_c	P_c [MPa]	ω
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

correlations⁶⁾ 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 Physics¹⁰⁾, 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 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 Δy_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.

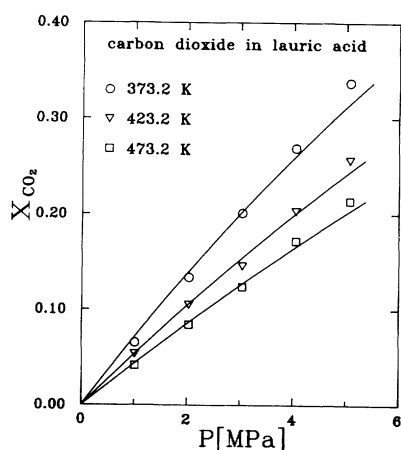


Fig. 5. Comparison of calculated mole fraction x_2 of carbon dioxide in lauric acid (lines) with experimental data (points) as a function of pressure P and temperature T

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

Conclusion

This study has presented new experimental data on the solubilities of CO_2 in heavy carboxylic acids such as lauric acid, palmitic acid, and arachidic acid. The liquid- and vapor-phase mole fractions of 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 CO_2 at infinite dilution for the 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

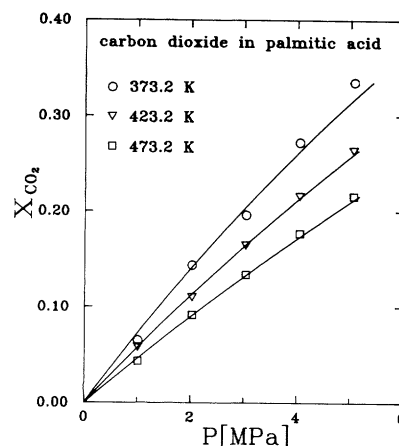


Fig. 6. Comparison of calculated mole fraction x_2 of carbon dioxide in palmitic acid (lines) with experimental data (points) as a function of pressure P and temperature T

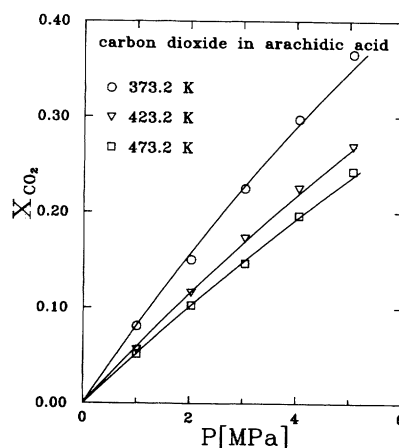


Fig. 7. Comparison of calculated mole fraction x_2 of carbon dioxide in arachidic acid (lines) with experimental data (points) as a function of pressure P and temperature T

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 ⁶ mol ⁻²]
b	= parameter in the modified Soave equation	[cm ³ mol ⁻¹]
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 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)	[—]
α	= parameter in the modified Soave equation	[—]
ω	= acentric factor	[—]

〈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

Literature Cited

- 1) Graboski, M. S. and T. E. Daubert: *Ind. Eng. Chem. Process Des. Dev.*, **17**, 443 (1978).
- 2) Huang, F. H., M. H. Li, L. L. Lee, K. E. Starling and F. T. H. Chung: *J. Chem. Eng. Japan*, **18**, 490 (1985).
- 3) Huang, S. H., H. M. Lin, F. N. Tsai and K. C. Chao: *Ind. Eng. Chem. Res.*, **27**, 162 (1988).
- 4) Jan, D. S. and F. N. Tsai: *Ind. Eng. Chem. Res.*, **30**, 1965 (1991).
- 5) Krichevsky, I. R. and J. S. Kasarnovsky: *J. Am. Chem. Soc.*, **57**, 2168 (1935).
- 6) Lee, B. I. and M. G. Kesler: *AIChE J.*, **21**, 510 (1975).
- 7) Lydersen, A. L.: Estimation of Critical Properties of Organic Compounds, Univ. Wisconsin Coll. Eng., Eng. Exp. Stn. Rep. **3**, Madison, Wis., April (1955).
- 8) Reid, R. C., J. M. Prausnitz and B. E. Poling: *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York (1988).
- 9) Tsai, F. N. and J. S. Yau: *J. Chem. Eng. Data*, **35**, 43 (1990).
- 10) Weast, R. C., D. R. Lide, M. J. Astle and W. H. Beyer: *CRC Handbook of Chemistry and Physics*, 70th ed., 1989–1990.
- 11) Yau, J. S. and F. N. Tsai: *J. Chem. Eng. Data*, **37**, 295 (1992).
- 12) Yau, J. S. and F. N. Tsai: *J. Chem. Eng. Data*, **37**, 141 (1992).