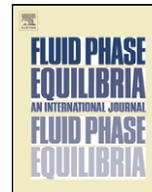




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Solubilities of cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid in supercritical carbon dioxide

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ABSTRACT

The solid solubilities of cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid in supercritical carbon dioxide were measured using a semi-flow apparatus. The experiments were taken at 308.2, 318.2 and 328.2 K. The pressure range was from 11 to 24 MPa. These data were confirmed as equilibrium solid solubilities based on a plug flow mass transfer model. The solid solubilities were further correlated using the equations of state or semi-empirical models. The correlation results are satisfactory with optimally fitted binary interaction parameters in the Peng–Robinson equation of state.

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1. Introduction

Supercritical technology is widely applied in extraction, chemical reaction and materials processing [1,2] where solid compounds are usually involved in those processes. Solid solubility data in supercritical fluids, especially in carbon dioxide, are essential to the development of the related industrial processes. Solid solubilities in supercritical carbon dioxide are reviewed or collected in recent literature [3,4]. It is noticed that more experimental data for organic and pharmaceutical compounds are still needed. The motivation of this study was to measure novel solubility data of solid acid compounds in supercritical carbon dioxide.

We have measured the solubilities of organic and pharmaceutical components in supercritical carbon dioxide using a semi-flow apparatus [5,6]. In this study, we applied the same apparatus to measure the solid solubilities of three acidic organic compounds, cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid, in supercritical carbon dioxide. The experimental temperatures were 308.2, 318.2 and 328.2 K. The pressure range was from 11 to 24 MPa. Cinnamic acid and phenoxyacetic acid are used in agriculture and pharmaceutical industries. 4-Methoxyphenylacetic acid is used in organic synthesis and also in pharmaceutical industries. These polar compounds all have the COOH function group. As far as we know, no solid solubility data for these compounds in supercritical carbon dioxide have been shown in literature.

In this research, we report new experimental data that are useful in process development or theoretical model correlation. The measured results in this study were firstly examined by a plug-flow mass transfer model to ensure that equilibrium solubilities were obtained. The experimental data were then correlated using either the equation of state or semi-empirical models. The correlation accuracy and the optimally fitted model parameters are presented in this study.

2. Experimental

2.1. Chemicals

Carbon dioxide (component 1) was purchased from San-Fu Chemical Co. (Taiwan) with a minimum purity of 99.8 mass%. Cinnamic acid and phenoxyacetic acid were purchased from Merck Company, and 4-methoxyphenylacetic acid was purchased from Acros Company. All pure chemicals had a minimum purity of 99 mass%, and were used without further purification. The properties of these pure components are listed in Table 1. The critical temperatures and pressures of the three solid compounds were estimated from the Joback correlation equation [7]. The acentric factors were estimated from the Ambrose method [8]. The structures of the three solid components are illustrated in Fig. 1.

2.2. Experimental apparatus and procedures

This study applied a semi-flow type apparatus to measure the solid solubilities of three organic compounds. The experimental

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Table 1
Purities and physical properties of the chemicals used in this study.

Compound	Molecular weight (10^{-3} kg/mol)	T_m (K)	V° (10^{-3} m ³ /mol)	T_c (K)	P_c (MPa)	ω	Purity (mass%)
Carbon dioxide (CO ₂)	44.010	–	–	304.12 [16]	7.374 [16]	0.225 [16]	>99.8
Cinnamic acid (C ₉ H ₈ O ₂)	148.159	406.15 [14]	0.1188 [14]	803.94 [7]	3.858 [7]	0.688 [8]	>99.0
Phenoxyacetic acid (C ₈ H ₈ O ₃)	152.148	371.65 [14]	0.1130 [15]	802.61 [7]	3.991 [7]	0.760 [8]	>99.0
4-Methoxyphenylacetic acid (C ₉ H ₁₀ O ₃)	166.173	360.15 [14]	0.1279 [15]	827.30 [7]	3.485 [7]	0.808 [8]	>99.0

apparatus is similar as that in our previous research [5]. It is consisted of three sections for the supply of supercritical CO₂, the equilibrium between the solid and the supercritical CO₂, and the analyses of the experimental results.

Pure CO₂ was firstly liquefied to 272.2 K and was then pressurized to a desired pressure by a HPLC pump (Thermo Separation Product). The exit pressure was controlled using a back-pressure regulator (Tescom). The high pressure CO₂ passed through a pre-heating coil immersed in a water bath. It reached a specific supercritical state and was then charged into the pre-equilibrium and equilibrium cells. The pre-equilibrium cell had a volume of 150 cm³ where 25 g solid sample was distributed in five layers of glass beads. The volume of the equilibrium cell was 300 cm³ in which 50 g of solid sample was distributed in 10 layers. At the ends of both cells, filters were equipped to prevent any entrainment. The experimental temperature and pressure were detected in the equilibrium cell by calibrated thermocouple (Ins Co.) and pressure gauge (Heise Co.), respectively. The accuracies for their readings were ± 0.1 K and ± 0.03 MPa, respectively.

The supercritical CO₂ flew through the equilibrium cell and then expanded to atmospheric pressure after a needle valve. The needle valve was wrapped with a heating tape to keep the temperature above the melting point of the solid by 20–30 K in order to avoid any precipitation in the line. Solid was separated from the gas phase upon de-pressurization, and was dissolved into a flask with organic solvent of ethyl acetate. The flow rate of the gas was recorded by a wet test meter (Ritter TG1). The solution in the collecting flask was sonicated for more than 10 min. Its composition was measured by a UV–vis spectrometer (Jasco, UV-975). A sharp absorption peak in the UV–vis spectrometer was observed at the wavelength of 254 nm for cinnamic acid and phenoxyacetic acid, and was at 274 nm for 4-methoxyphenylacetic acid. Calibrations of the UV measurements were satisfactory with a R^2 regression coefficient better than 0.999.

At least three solid solubility data were taken at each experimental temperature and pressure. The uncertainty of experimental measurements was better than $\pm 5\%$.

3. Results and discussion

The experimental solubility data in supercritical CO₂ have been examined by applying a fluid–solid mass transfer model [9]. The detail procedures have been presented in our previous work [5]. The basic criterion of this mass transfer model is to calculate the ratio of the measured solid solubility relative to its saturated value, $X = C/C_{\text{sat}}$, under various experimental conditions (temperature, pressure, and flow rate). If the values of X are close to unity, the experimentally measured solid solubilities are accepted as equilibrium data. In our experiments, the X values under various experimental conditions were all greater than 0.999, and the mass transfer effect is confirmed to be negligible in this study.

The measured solid solubility data in supercritical CO₂ for cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid are presented in Tables 2–4, respectively. The densities of supercritical CO₂ at various experimental conditions were calculated from the Peng–Robinson equation of state [10]. These values were most near to the experimental values from IUPAC, and are also included in these tables. Generally, the solubilities for all three solid compounds increased with pressure at a fixed temperature. At a constant temperature, phenoxyacetic acid showed the largest solubility in supercritical CO₂. This may be due to the relatively higher solid vapor pressure as indicated in the following correlation results using equation of state (EOS). Cinnamic acid and 4-methoxyphenylacetic acid had similar and competitive solid solubilities at each experimental temperature. These solid solubility data were further correlated using the equation of state, or semi-empirical equation approaches.

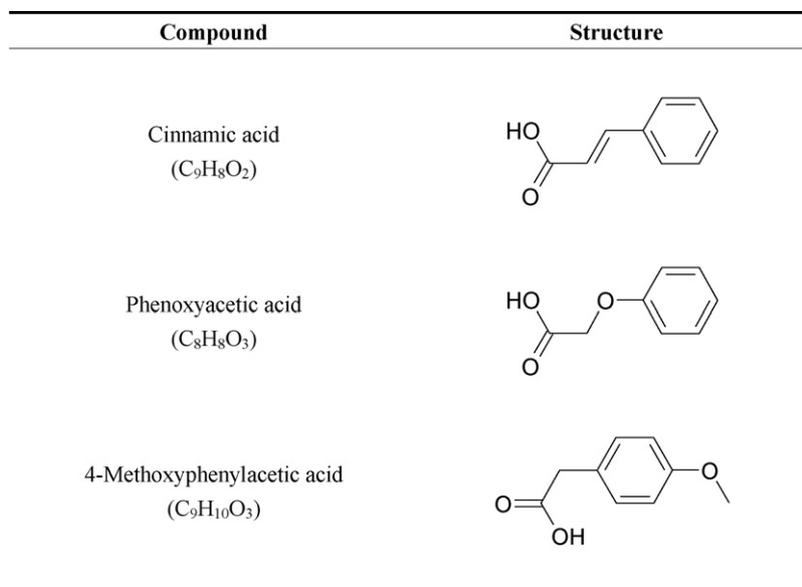


Fig. 1. Structures of solid compounds in this study.

Table 2
Solubility of cinnamic acid (2) in supercritical CO₂ (1).

T (K)	P (MPa)	10 ⁴ y ₂	ρ ₁ (kg/m ³)
308.2	14.91	1.23	814.04
	16.85	1.78	836.73
	18.99	2.00	857.44
	20.99	2.40	874.00
	23.12	2.47	889.50
318.2	12.30	0.41	670.57
	13.75	0.79	715.12
	15.17	1.19	745.83
	16.78	1.79	772.71
	18.71	2.20	798.43
	20.85	2.77	821.74
328.2	23.05	3.58	841.93
	12.58	0.35	546.67
	14.71	0.95	645.63
	16.85	1.81	701.75
	18.51	2.38	732.66
	20.09	2.94	756.41
	21.88	3.56	778.94
23.61	4.25	797.60	

3.1. Equation of state method

At solid–supercritical fluid phase equilibrium, the equal fugacity criterion is applied and the solid solubility is expressed as:

$$y_i = \frac{p_i^{\text{vp}} \exp[V_i^{\text{S}}(p - p_i^{\text{vp}})/RT]}{\hat{\phi}_i^{\text{SCF}} p} \quad (1)$$

where V_i^{S} is the solid molar volume, p_i^{vp} is the solid vapor pressure, and $\hat{\phi}_i^{\text{SCF}}$ is the fugacity coefficient of solid in the supercritical fluid phase. The solid vapor pressure was expressed by the conventional equation:

$$\ln p_i^{\text{vp}} = A - \frac{B}{T} \quad (2)$$

where A and B were two empirical parameters. Two EOS were employed in this study in data regression: the

Table 3
Solubility of phenoxyacetic acid (3) in supercritical CO₂ (1).

T (K)	P (MPa)	10 ⁴ y ₃	ρ ₁ (kg/m ³)
308.2	12.37	1.15	774.48
	14.09	1.55	802.83
	15.68	2.22	823.61
	17.44	2.54	842.82
	19.26	2.84	859.81
	20.83	3.25	872.76
	22.43	3.46	884.68
	318.2	12.58	1.06
14.16		1.81	724.91
15.02		2.15	742.96
16.61		2.67	770.16
18.44		3.51	795.15
20.02		4.52	813.21
22.02		5.03	832.87
328.2		11.75	0.57
	13.40	1.68	593.08
	15.02	2.58	655.49
	16.58	3.56	695.92
	18.02	4.86	724.30
	19.54	5.83	748.63
	20.92	6.74	767.34
	22.23	7.92	782.93

Table 4
Solubility of 4-methoxyphenylacetic acid (4) in supercritical CO₂ (1).

T (K)	P (MPa)	10 ⁴ y ₄	ρ ₁ (kg/m ³)
308.2	11.61	0.51	758.80
	14.30	0.99	805.82
	15.68	1.37	823.61
	17.75	1.59	845.89
	19.26	2.08	859.81
	21.13	2.25	875.08
	23.61	2.78	892.81
	318.2	12.65	0.47
14.03		0.88	721.90
15.61		1.33	753.83
17.33		1.87	780.63
18.85		2.51	800.10
20.30		3.09	816.15
21.54		3.83	828.42
23.06		4.17	842.01
328.2	14.23	0.61	628.69
	15.47	0.98	668.55
	17.13	1.61	707.53
	18.99	2.94	740.35
	20.50	4.17	761.93
	22.09	5.17	781.35
	23.47	6.34	796.19

Soave–Redlich–Kwong EOS [11]:

$$p = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b)} \quad (3)$$

and the Peng–Robinson EOS [10]:

$$p = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \quad (4)$$

In these EOS, \underline{V} was the molar volume and the EOS parameters (a and b) were determined from the critical constants of the pure compounds. The van der Waals mixing rules (VDW2) with two binary interaction parameters (k_{ij} and l_{ij}) were used in this study:

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (5)$$

$$b_m = \sum_i \sum_j x_i x_j \frac{(b_i + b_j)}{2} (1 - l_{ij}) \quad (6)$$

If parameter l_{ij} was taken as zero and only a single parameter k_{ij} was used, it was denoted as the VDW1 mixing rules. The binary interaction parameters together with the parameters in the solid vapor pressure equation were optimally fitted to the experimental solid solubility data by minimizing the following objective function:

$$\text{obj} = \sum_k \frac{|y_{i,k}^{\text{exp}} - y_{i,k}^{\text{cal}}|}{y_{i,k}^{\text{exp}}} \quad (7)$$

The summation was over all experimental k th points. The superscripts exp and cal represented the experimental and calculated values, respectively. Table 5 presents the optimally fitted parameters from the EOS method. The binary interaction parameters were taken as temperature-independent and their values are all in reasonable range. Both EOS with the VDW2 mixing rules yielded satisfactory results where the absolute average deviation in solid solubility (AADY) is around 5%.

3.2. Semi-empirical correlation equation method

Two commonly used semi-empirical equations were applied in this study for solid solubility data correlation. The Chrastil equation

Table 5
Correlated results of solubility data in SCCO₂ using various EOS mixing rules.

Mixing rules	Peng–Robinson EOS			Soave–Redlich–Kwong EOS		
	k_{ij}	l_{ij}	AADY (%)	k_{ij}	l_{ij}	AADY (%)
CO ₂ (1) + Cinnamic acid (2)				$\ln P_2^{vp}(10^{-6} \text{ MPa}) = 40.92 - (14527.28/T(K))$		
VDW1	0.0237	–	6.16	0.0281	–	6.57
VDW2	0.0405	0.0457	5.37	0.0457	0.0471	5.48
CO ₂ (1) + Phenoxyacetic acid (3)				$\ln P_3^{vp}(10^{-6} \text{ MPa}) = 43.78 - (14557.64/T(K))$		
VDW1	0.1440	–	12.14	0.1525	–	12.92
VDW2	0.2311	0.2464	4.41	0.2386	0.2530	4.73
CO ₂ (1) + 4-Methoxyphenylacetic acid (4)				$\ln P_4^{vp}(10^{-6} \text{ MPa}) = 55.95 - (21101.81/T(K))$		
VDW1	–0.1438	–	14.04	–0.1381	–	13.48
VDW2	–0.2448	–0.2663	4.80	–0.2332	–0.2654	5.15

$$\text{AADY} (\%) = \frac{100}{n} \sum_{k=1}^n \frac{|y_{j,k}^{\text{exp}} - y_{j,k}^{\text{cal}}|}{y_{j,k}^{\text{exp}}}$$

[12] expressed the solid solubility in a three-parameter form (n , C , and D):

$$\ln S_i(\text{kg/m}^3) = n \ln \rho_1(\text{kg/m}^3) + \frac{C}{T} + D \quad (8)$$

$$S_i = \frac{\rho_1 M_i y_i}{M_1 (1 - y_i)} \quad (9)$$

Mendes–Santiago and Teja [13] also proposed the following equation that fitted the solid solubility using three parameters (E , F , and G):

$$T \ln(y_i P(\text{MPa})) = E + F \rho_1(\text{kg/m}^3) + GT \quad (10)$$

The parameters in the above two semi-empirical equations were optimally fitted to the experimental solid solubility data using the same objective function in Eq. (7). Table 6 illustrates the correlation results from the two semi-empirical equations. The grand AADY value over all experimental solubility data was around 8% that was larger than that from the EOS correlation.

Figs. 2–4 present the experimental data and the calculated results from the Peng–Robinson EOS for three solid compounds, respectively. Satisfactory agreement between measured and correlated results is observed. The cross-over pressures are estimated as 16.2–16.8 MPa for cinnamic acid, 13.4–14 MPa for phenoxyacetic acid, and 16–16.7 MPa for 4-methoxyphenylacetic acid, respectively.

Table 6
Correlated results of the solubility data in SCCO₂ using various empirical models.

Chrastil equation				Mendez–Santiago and Teja equation			
n	C	D	AADY (%)	E	F	G	AADY (%)
CO ₂ (1) + Cinnamic acid (2)							
8.21	-6.79×10^3	–34.00	9.28	-1.33×10^4	4.48	25.19	8.05
CO ₂ (1) + Phenoxyacetic acid (3)							
7.78	-9.11×10^3	–23.32	10.38	-1.54×10^4	4.53	32.25	9.23
CO ₂ (1) + 4-Methoxyphenylacetic acid (4)							
11.50	-1.02×10^4	–45.19	3.62	-1.73×10^4	5.58	34.84	3.87

$$\text{AADY} (\%) = \frac{100}{n} \sum_{k=1}^n \frac{|y_{j,k}^{\text{exp}} - y_{j,k}^{\text{cal}}|}{y_{j,k}^{\text{exp}}}$$

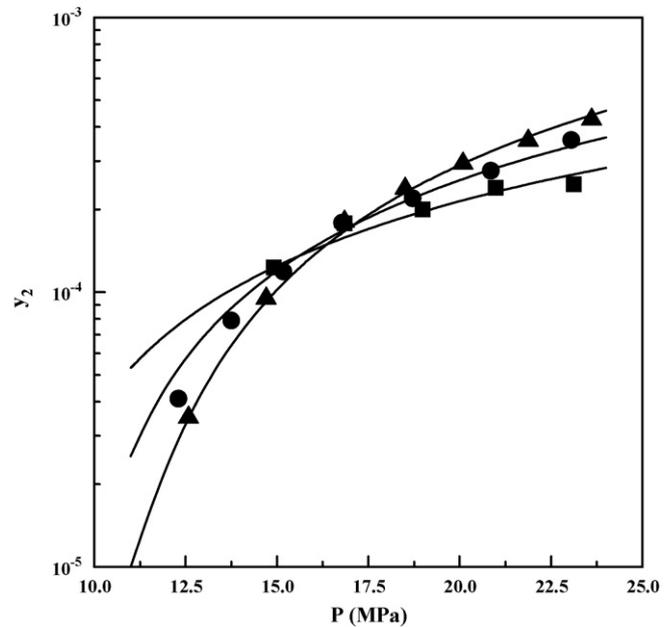


Fig. 2. Solubility data of cinnamic acid (2) in SCCO₂ (1): (■) 308.2 K, (●) 318.2 K, (▲) 328.2 K, and (–) Peng–Robinson equation of state with VDW2 mixing rule.

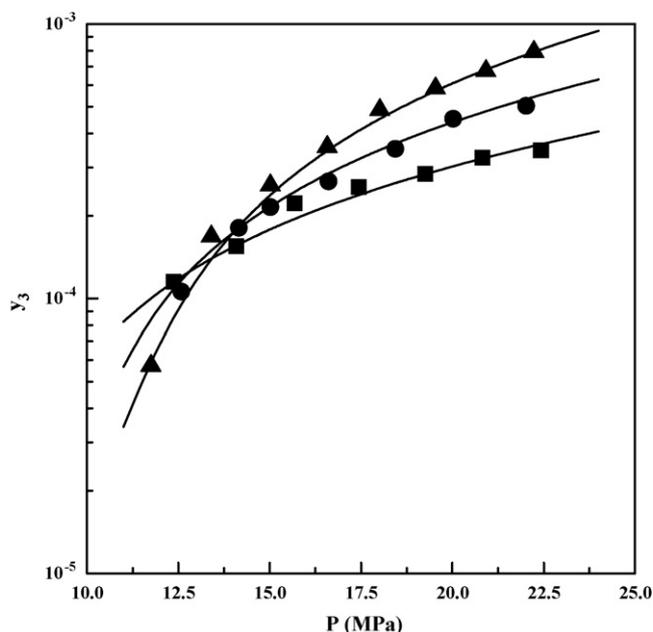


Fig. 3. Solubility data of phenoxyacetic acid (3) in SCCO_2 (1): (■) 308.2 K, (●) 318.2 K, (▲) 328.2 K, and (—) Peng–Robinson equation of state with VDW2 mixing rule.

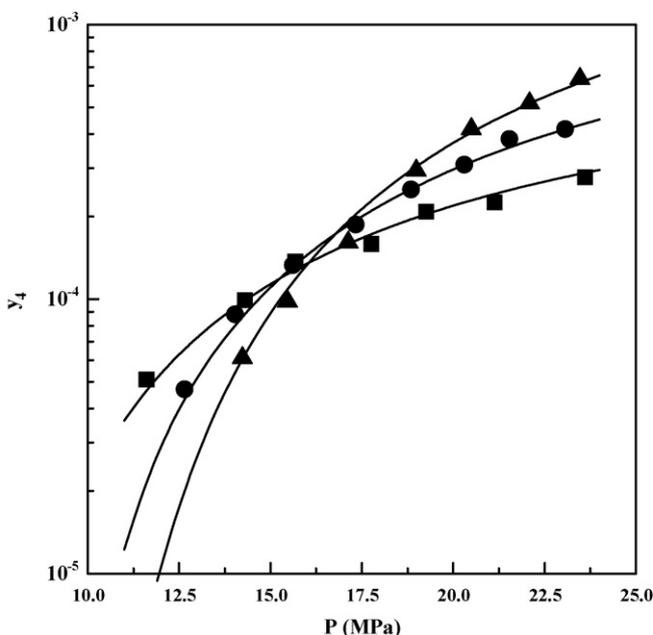


Fig. 4. Solubility data of 4-methoxyphenylacetic acid (4) in SCCO_2 (1): (■) 308.2 K, (●) 318.2 K, (▲) 328.2 K, and (—) Peng–Robinson equation of state with VDW2 mixing rule.

4. Conclusion

The solid solubilities in supercritical CO_2 were measured in this study for cinnamic acid, phenoxyacetic acid and 4-methoxyphenylacetic acid. The experimental temperatures were 308.2, 318.2 and 328.2 K where the pressure ranged from 11 to 24 MPa. The mass transfer effect was confirmed to be negligible in this study. The measured data were satisfactorily correlated using the Soave–Redlich–Kwong and Peng–Robinson EOS with VDW2 mixing rules where the absolute average deviation in solid solubility was 5%. The cross-over pressures for these solid compounds

were also determined from experimental results.

List of symbols

a, b	parameters in the equation of state
A, B	parameters in the solid vapor pressure equation
C	parameter in the Chrastil model, or the solid solubility
D	parameter in the Chrastil model
E, F, G	parameters in the Mendez–Santiago and Teja equation
k, l	binary interaction parameters
M	molecular weight
n	parameter in the Chrastil equation
obj	objective function defined in Eq. (7)
P	pressure
P_c	critical pressure
R	gas constant
S	solid solubility defined in Eq. (8)
T	temperature
T_c	critical temperature
T_m	melting temperature
\underline{V}	molar volume
\underline{V}^s	solid molar volume
X	relative saturated concentration of the solid solute
y	mole fraction

Greek letters

ϕ	fugacity coefficient
ρ	density
ω	acentric factor

Subscripts

1	component 1, CO_2
i, j	component i or j
k	the k th experimental point
m	mixture property
sat	saturated value

Superscripts

cal	calculated value
exp	experimental value
vp	vapor pressure

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