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Solubilities of Some Chlorophenols in Supercritical CO_2 in the Presence and Absence of Cosolvents

Chandrasekhar Garlapati and Giridhar Madras*

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

The solubilities of three chlorophenols, namely, 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, in supercritical carbon dioxide were determined at temperatures from (308 to 318) K in the pressure range of (8.8 to 15.6) MPa. The solubilities were determined both in the absence of cosolvents and in the presence of two cosolvents, methanol and acetone. The solubilities (in the absence of cosolvents) in mole fraction of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol at 308 K were in the range of (0.0113 to 0.0215), (0.0312 to 0.0645), and (0.008 to 0.0173), respectively. The solubilities of the chlorophenols followed the order 2,4-dichlorophenol > 4-chlorophenol > phenol > 2,4,6-trichlorophenol > pentachlorophenol. The solubility data were correlated with the Charstil model and with the Mendez-Santiago and Teja model. The overall deviation between the experimental data and the correlated results was less than 6 % in averaged absolute relative deviation (AARD) for both of the models.

Introduction

Supercritical carbon dioxide ($SCCO_2$) is used in several applications in the environmental, food, and pharmaceutical industries, because of its attractive properties like moderate critical pressure, high critical density, and critical temperature close to ambient temperature.[1,2] However, carbon dioxide has limited utility in the extraction of polar compounds. The solvent power of $SCCO_2$ can be enhanced by adding (1 to 5) % in mole fraction of a polar cosolvent[3–5] like methanol, ethanol, and acetone.

Substituted phenols like nitro, chloro, and methyl groups are used in the preparation of drugs, fungicides, and insecticide, and hence the determination of their solubilities in supercritical fluids is important.[6–8] 4-Chlorophenol is used as an intermediate for the synthesis of other chlorophenols, intermediate dyes, fungicides, drugs, and topical antiseptics. 2,4-Dichlorophenol is used in the synthesis of intermediates for the production of drugs like sesone, nitrofen, and nemacide and is an ingredient in several antiseptics. 2,4,6-Trichlorophenol is used as an insecticide, as a germicide for preservation of wood, and as an ingredient of germicidal soaps. Considering the wide range of applications for these chlorophenols, determination of the solubilities of these compounds in supercritical fluids is important.

In this work, the solubilities of three solid chlorophenols in $SCCO_2$ in the absence of cosolvents and in the presence of methanol and acetone as cosolvents are reported. The solubilities of the chlorophenols are correlated with two models.

Experimental Section

Materials. CO_2 (CAS No. 124-38-9, 99 %) purchased from Vinayaka Gases (Bangalore, India) was purified to 99.9 %, by passing the gas through a bed of silica gel. 4-Chlorophenol (CAS No. 106-48-9, 99 %) from Alfa Aesar (U.S.A.) and 2,4-dichlorophenol (CAS No. 120-83-2, 98 %) and 2,4,6-trichlorophenol (CAS No. 88-06-2, 98 %) from Merck, Inc. (Germany) were used.

Equipment and Procedure. The solubility measurements were carried out using a flow apparatus based on the principles of the transpiration method described in literature.[9] A schematic diagram of the apparatus has been described in detail previously[10,11] and is shown in Figure S1 (see Supporting Information). In this method, two columns (300 mm × 14 mm) in series packed with the solutes were placed in the oven, where the temperature was maintained within ± 0.1 K. For each measurement, about 35 g (with an uncertainty of 0.01 mg) of pure solute was packed with glass wool layer-wise. Subsequently, carbon dioxide and cosolvents from the gas cylinder and cosolvent reservoirs were compressed into heated coils and then to an accumulator to make a supercritical mixture. In the system, the pressure was maintained within ± 0.02 MPa with a back pressure regulator. Then the supercritical mixtures were introduced to the bottom of the column. To ensure that the exiting CO_2 stream is saturated with the solute, experiments were conducted with $0.2\ \mathrm{mL \cdot min^{-1}}$ $SCCO_2$. The solute was then collected and measured gravimetrically. On the basis of the total flow of the supercritical fluid, the solubilities were determined. Solubility in terms of mole fraction is given by

$$y_2\ (\text{or})\ y_2' = \frac{n_{\text{solute}}}{n_{\text{scf}} + n_{\text{solute}}} \qquad (1)$$

where y_2 is the mole fraction of solute in pure $SCCO_2$, y_2' is the mole fraction of solute in $SCCO_2$ with cosolvent, n_{solute} is moles of solute calculated based on mass collected, and n_{scf} is moles of $SCCO_2$ mixture based on total flow. Each measurement was carried out for a minimum of three times, and the relative uncertainty was less than ± 2.5 %. More details of the experimental apparatus and procedure are provided elsewhere.[10,11] Experiments with cosolvents were conducted with 3.0 % in mole fraction of acetone and with 3.0 % in mole fraction of methanol in $SCCO_2$. The presence of a cosolvent increases both the critical temperature and the pressure of the mixture. The critical loci

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* Corresponding author. Tel.: +91 80 22932321. Fax: +91 80 23600683. E-mail: giridhar@chemeng.iisc.ernet.in (G.M.).

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Table 1. Solubilities of Chlorophenols in $SCCO_2$ ($y_2 \cdot 10^3$)

	T/K						
p/MPa	308	313	308	313	308	313	318
	4-chlorophenol		2,4-dichlorophenol		2,4,6-trichlorophenol		
8.8	11.3	3.8	31.2	9.7	8.0	2.4	1.3
9.8	15.2	11.2	43.1	30.5	11.2	7.8	3.8
10.7	16.4	14.2	48.6	38.4	12.8	10.2	6.4
11.7	18.8	18.4	54.8	52.4	14.4	13.8	12.0
12.7	19.2	19.8	56.4	56.6	15.5	14.6	14.2
13.7	20.0	21.8	60.8	63.4	16.1	16.8	16.9
14.7	20.9	22.6	62.8	66.4	16.8	17.4	18.9
15.6	21.5	23.8	64.5	70.2	17.3	18.8	20.0

of $SCCO_2$-acetone and $SCCO_2$-methanol were obtained from literature,[12–14] and all experiments were conducted at pressures above the critical pressure of the mixture at the operating temperature.

Preparation of Cosolvent Mixtures. The mixtures of CO_2 with methanol or acetone were prepared by adjusting the flow rates of CO_2 (Q_{CO_2}) and cosolvents (Q_{cos}). The volumetric flow of cosolvent required to achieve a composition of X % in moles of the cosolvent (i.e., solute free basis) in the binary mixture at a given density of CO_2 (at a given temperature and pressure) can be readily determined from material balance[4,10]

$$Q_{\mathrm{cos}} = \frac{Q_{CO_2}\rho_{CO_2}\mathrm{MW}_{\mathrm{cos}}X}{\rho_{\mathrm{cos}}\mathrm{MW}_{CO_2}(1 - X)} \qquad (2)$$

In eq 2, MW_{CO_2} and $\mathrm{MW}_{\mathrm{cos}}$ are the molecular weights of CO_2 and cosolvent, respectively. The carbon dioxide and entrainer densities are denoted by ρ_{CO_2} and ρ_{cos}, respectively. The density of pure carbon dioxide was calculated by the equation of state proposed by Span and Wagner.[15]

Results and Discussion

The reliability of the apparatus was tested by determining the solubilities of fatty acids in $SCCO_2$ in both the presence and the absence of cosolvents. Good agreement was obtained with the literature data within ± 6 %, as reported previously.[10,11]

Solubility Data. The solubility data for 4-chlorophenol and 2,4-dichlorophenol in $SCCO_2$ at 308 and 313 K at pressures between (8.8 and 15.6) MPa are shown in Table 1. The solubilities of 4-chlorophenol and 2,4-dichlorophenol at 318 K were not investigated because these compounds melt at 311 K and 313 K, respectively. The solubility data for 2,4,6-trichlorophenol in $SCCO_2$ at 308 K, 313 K, and 318 K at pressures between (8.8 and 15.6) MPa are shown in Table 1. The experimental data and the data reported[6] for 4-chlorophenol and 2,4-dichlorophenol at 309 K are compared in Figure 1.

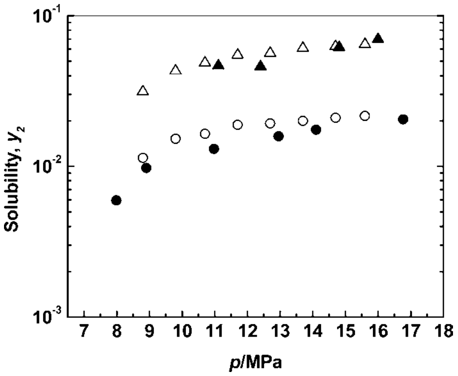

Figure 1. Solubilities of 4-chlorophenol at 308 K, ○, this work; 4-chlorophenol at 309 K, ●, ref 6; 2,4-dichlorophenol at 308 K, Δ, this work; 2,4-dichlorophenol at 309 K, ▲, ref 6, in $SCCO_2$.

The crossover pressures have been observed, and they are from (12.0 to 12.5) MPa, (12.5 to 13.0) MPa, and (13.5 to 14.0) MPa for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, respectively.

The results obtained in this study indicate that the solubilities of chlorophenols vary in the following order: 2,4-dichlorophenol > 4-chlorophenol > 2,4,6-trichlorophenol in pure $SCCO_2$. A comparison can also be made with existing data[6,16,17] for the solubilities of pentachlorophenol and phenol. The solubility data shows that pentachlorophenol has a lower solubility than 2,4,6-trichlorophenol and the solubility of phenol is less than 4-chlorophenol but more than that of 2,4,6-trichlorophenol. Thus, the overall order for solubilities is 2,4-dichlorophenol > 4-chlorophenol > phenol > 2,4,6-trichlorophenol > pentachlorophenol. The order of solubilities is simply the order of the pure-solute vapor (sublimation) pressures.

Cosolvent Effect. The solubility data for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol in $SCCO_2$ in the presence of cosolvents are shown in Table 2. Methanol and acetone are commonly used cosolvents. Though both are polar solvents, methanol is both a hydrogen bond acceptor and a donor, while acetone is a hydrogen bond acceptor. Thus methanol is self-associated, while acetone is nonassociated.[18] The results obtained with cosolvents in this study indicate that the solubilities of chlorophenols in the presence of methanol as the cosolvent are higher compared to that observed with acetone as the cosolvent.

An enhancement in solubility is observed as a result of the cosolvent. The solubility enhancement effect can be quantified by e, which is defined as the ratio of the solubility obtained with cosolvent to that obtained without the cosolvent. The average cosolvent enhancement factors (averaged over all pressures) are listed in Table 2. From the value of e, it is apparent that methanol is a better cosolvent than acetone. This may be due to the higher hydrogen bonding ability of methanol

Table 2. Solubilities of Chlorophenols ($y_2' \cdot 10^3$) in $SCCO_2$ + 3.0 % in Mole Fraction Cosolvent at $T = 313$ K

	T/K = 313					
	methanol			acetone		
p/MPa	4-chlorophenol	2,4-dichlorophenol	2,4,6-trichlorophenol	4-chlorophenol	2,4-dichlorophenol	2,4,6-trichlorophenol
8.8	17.1	35.7	8.2	11.0	30.8	6.5
9.8	34.6	69.1	19.4	21.8	61.2	11.8
10.7	40.6	81.4	22.6	24.6	72.6	18.6
11.7	42.1	89.9	28.1	28.7	80.8	20.4
12.7	46.2	93.8	29.4	29.5	86.4	21.9
13.7	48.6	95.2	31.5	30.6	87.6	24.3
14.7	50.3	95.9	32.6	30.9	88.8	25.2
15.6	52.1	96.3	33.6	31.1	89.6	26.6
e	2.69	1.71	2.31	1.70	1.54	1.66

Table 3. Correlation Parameters for the Solubilities of Chlorophenols without and with Cosolvents (Methanol and Acetone) Obtained Using Eq 6 and Eq 8

system	correlation parameters					AARD/%
4-chlorophenol-SCCO$_2$		$A = 1245$		$B = 94760$		1.97
2,4-dichlorophenol-SCCO$_2$		$A = 1204$		$B = 100500$		3.24
2,4,6-trichlorophenol-SCCO$_2$		$A = 1452$		$B = 103800$		3.86
4-chlorophenol-SCCO$_2$-methanol	$C = 886$		$D = 67350$		$F = 36190$	3.25
2,4-dichlorophenol-SCCO$_2$-methanol	$C = 1349$		$D = 61830$		$F = 21650$	1.91
2,4,6-trichlorophenol-SCCO$_2$-methanol	$C = 921$		$D = 80530$		$F = 37400$	2.64
4-chlorophenol-SCCO$_2$-acetone	$C = 1295$		$D = 63580$		$F = 19840$	4.42
2,4-dichlorophenol-SCCO$_2$-acetone	$C = 1462$		$D = 63830$		$F = 16050$	4.98
2,4,6-trichlorophenol-SCCO$_2$-acetone	$C = 1244$		$D = 90960$		$F = 18140$	5.87

compared to that of acetone.[18,19] The solubilities of the chlorophenols in SCCO$_2$ are more influenced by pressure than by cosolvents. For example, the solubility enhancement of 4-chlorophenol at 313 K by 3.0 % in mole fraction of methanol is only 2.69. In comparison, an increase in the pressure from (8.8 to 15.6) MPa increases the solubility by a factor of 6.13 at 313 K. A similar behavior has been observed for the solubilities of the other two chlorophenols in the presence of cosolvents.

Modeling of Solubilities. The equation of state approach needs physicochemical properties of solutes such as critical pressure, critical temperature, and acentric factor. These are usually obtained by group contribution methods.[20,21] Therefore, methods that do not require critical properties of the solute are often used. Solvate complex models are used[22–27] for this purpose. In this work, the Chrastil models[22] and the models proposed by Mendez-Santiago−Teja[28,29] were used to correlate solubilities of solids in supercritical fluids in both the presence and the absence of cosolvents. The required experimental sublimation pressures of the chlorophenol derivatives are obtained from literature.[30] In all of these models, the correlation constants are temperature independent.

Chrastil Model. The model proposed by Chrastil[22] is based on the formation of solvate complex between the solute and the solvent molecules. The Chrastil model relates the solubility of the solute and density of the pure solvent and is[31,32]

$$C/\mathrm{kg}\cdot\mathrm{m}^{-3} = (\rho/\mathrm{kg}\cdot\mathrm{m}^{-3})^{\kappa}\exp\left(\frac{a}{T/\mathrm{K}} + b\right) \qquad (3)$$

where C is the concentration of solute in saturated supercritical gas, κ is an association number, ρ is the supercritical fluid density, T is temperature, a is a function of the enthalpy of solvation and enthalpy of vaporization, and b is a function of association and molecular weights of solute and supercritical fluid. In eq 3, the constants κ, a, and b are independent of temperature and needed to be fitted by experimental data. The values of κ, a, and b for the chlorophenols are reported in Table S1 (see Supporting Information). Figures S2a, S3a, and S4a (see Supporting Information) represent the comparison of correlated results with the experimental values for chlorophenols in SCCO$_2$. It is clear that the plot of $\ln(C/\mathrm{kg}\cdot\mathrm{m}^{-3})$ with $\ln(\rho/\mathrm{kg}\cdot\mathrm{m}^{-3})$ is linear, confirming the validity of the experimental data and Chrastil model.

The Chrastil equation was modified to correlate solubilities of solids in SCCO$_2$ in the presence of cosolvents[24,31,32]

$$C'/\mathrm{kg}\cdot\mathrm{m}^{-3} = (\rho/\mathrm{kg}\cdot\mathrm{m}^{-3})^{\kappa}(m/\mathrm{kg}\cdot\mathrm{m}^{-3})^{\gamma}\exp\left(\frac{a}{T/\mathrm{K}} + b\right) \qquad (4)$$

where C' is the concentration of solute in saturated supercritical mixture, m is the concentration of cosolvent, and γ is the association number for cosolvent. When temperature T and the concentration of entrainer are kept constant, eq 4 can be written as[31]

$$\ln(C'/\mathrm{kg}\cdot\mathrm{m}^{-3}) = \kappa\ln(\rho/\mathrm{kg}\cdot\mathrm{m}^{-3}) + b'' \qquad (5)$$

where $b'' = \gamma\ln(m) + (a/T) + b$.

These constants are obtained by correlating the experimental data with eq 5. The values of κ and b'' are reported in Table S1 (see Supporting Information). Figures S2b, S3b, and S4b (see Supporting Information) represent the comparison of the correlated results with the experimental values for chlorophenols in SCCO$_2$ in the presence of the cosolvents, methanol and acetone. It is clearly observed that the plots of ln $(C'/\mathrm{kg}\cdot\mathrm{m}^{-3})$ with ln $(\rho/\mathrm{kg}\cdot\mathrm{m}^{-3})$ is linear, confirming the validity of the experimental data and modified Chrastil model.

Mendez-Santiago and Teja Models. Solubilities of Organic Solids in SCF. The models of Mendez-Santiago and Teja[28,29] are based on the theory of dilute solutions and relate

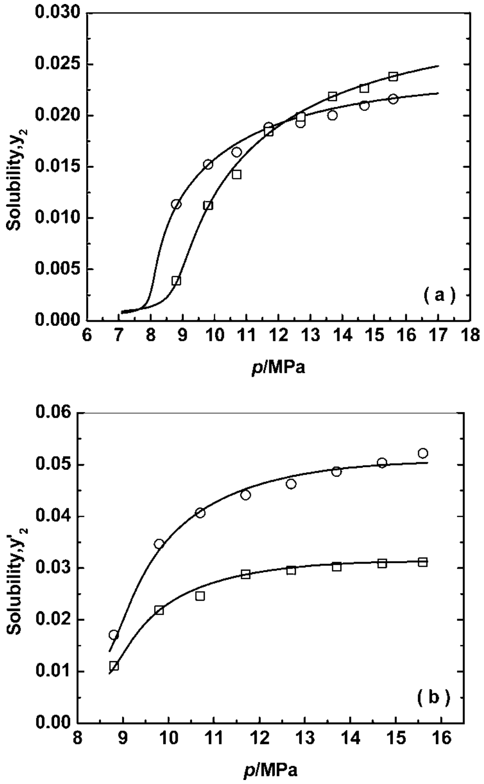

Figure 2. Comparison of the experimental solubility data of 4-chlorophenol in SCCO$_2$ without (y_2) and with (y'_2) cosolvents: (a) ○, experimental values at 308 K, without cosolvent; Δ, experimental values at 313 K, without cosolvent and (b) ○, experimental values at 313 K, with 3.0 % in mole fraction acetone; Δ, experimental values at 313 K, with 3.0 % in mole fraction methanol. The solid lines are model correlations based on the Mendez-Santiago−Teja model (eqs 6 and 8). All of the correlation parameters are given in Table 3.

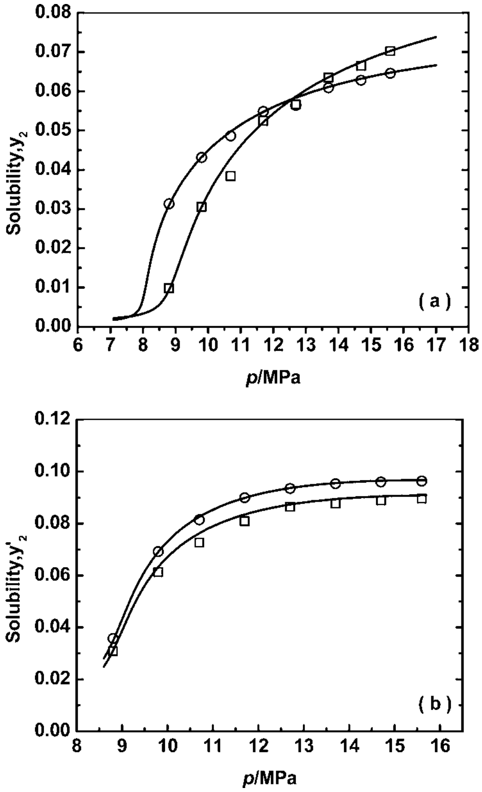

Figure 3. Comparison of the experimental solubility data of 2,4-dichlorophenol in SCCO$_2$ without (y_2) and with (y_2') cosolvents: (a) ○, experimental values at 308 K, without cosolvent; Δ, experimental values at 313 K, without cosolvent and (b) ○, experimental values at 313 K, with 3.0 % in mole fraction acetone; Δ, experimental values at 313 K, with 3.0 % in mole fraction methanol. The solid lines are model correlations based on the Mendez-Santiago−Teja model (eqs 6 and 8). All of the correlation parameters are given in Table 3.

the solubility of solid, y_2 (in mole fraction), with the density of SCCO$_2$, ρ (mol·mL^{-1}).

$$T \ln E = A + B\rho \tag{6}$$

where E is the enhancement factor given by

$$E = \frac{y_2 p}{p^{\mathrm{sub}}} \tag{7}$$

where p and T are the system pressure and temperature in Pa and K, respectively, and p^{sub} is the sublimation pressure of the chlorophenol derivatives that was obtained from literature.[30] In eq 6, the constants A and B are also independent of temperature and needed to be fitted by experimental data. The values of A and B for the chlorophenols are reported in Table 3. The results obtained using these equations are shown in Figures 2a, 3a, and 4a. ρ is the density of SCCO$_2$ and is calculated from the equation of state proposed by Span and Wagner.[15]

Solubilities of Solutes in the Presence of Cosolvents. The solubilities obtained with cosolvent were correlated by the equation proposed by Mendez-Santiago and Teja[29]

$$T \ln E' = C + D\rho + Fy_{\mathrm{cos}} \tag{8}$$

where E' is the enhancement factor given by

$$E' = \frac{y_2' p}{p^{\mathrm{sub}}} \tag{9}$$

where C, D, and F are constants that need to be fitted by experimental data.

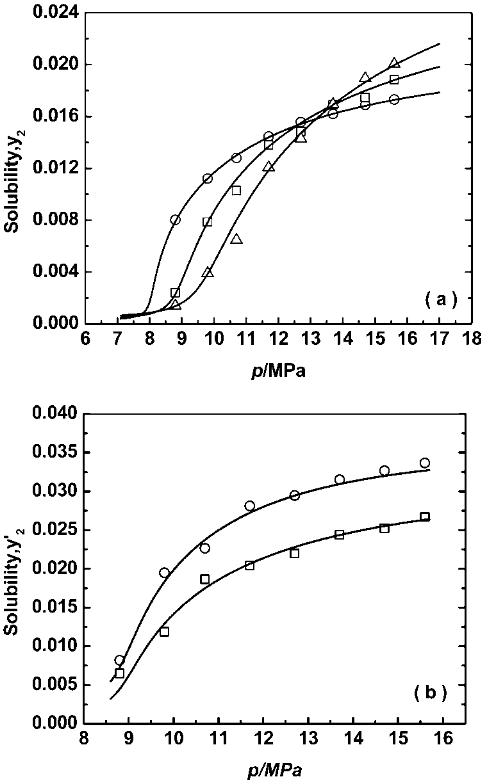

Figure 4. Comparison of the experimental solubility data of 2,4,6-trichlorophenol in SCCO$_2$ without (y_2) and with (y_2') cosolvents: (a) ○, experimental values at 308 K, without cosolvent; Δ, experimental values at 313 K, without cosolvent; □, experimental values at 318 K without cosolvent and (b) ○, experimental values at 313 K, with 3.0 % in mole fraction acetone; Δ, experimental values at 313 K, with 3.0 % in mole fraction methanol. The solid lines are model correlations based on the Mendez-Santiago−Teja model (eqs 6 and 8). All of the correlation parameters are given in Table 3.

All of the modeling results are reported in Table 3 along with the averaged absolute relative deviation (AARD/%). The model predictions of the solubilities of chlorophenols in SCCO$_2$, SCCO$_2$ + methanol, and SCCO$_2$ + acetone ternary systems at 313 K are shown in Figures 2b, 3b, and 4b.

Conclusions

The solubilities of three chlorophenols in SCCO$_2$ and in SCCO$_2$ + methanol and SCCO$_2$ + acetone at temperatures of 308 K, 313 K, and 318 K in the pressure range of (8.8 to 15.6) MPa were determined. The solubilities in SCCO$_2$ followed the order dichlorophenol > chlorophenol > trichlorophenol. The solubilities of chlorophenols are higher in the presence of methanol compared to those observed in the presence of acetone. The solubility data were correlated with Chrastil model and the model proposed by Mendez-Santiago and Teja. The overall deviation between the experimental data and the correlated results was less than 6 % for both of the models.

Supporting Information Available:

Figure S1 shows the schematic diagram of the apparatus used for measuring solubilities. Table S1 shows the correlation parameters based on Chrastil's model for solubilities of some chlorophenols in SCCO$_2$. Figures S2, S3, and S4 show the experimental solubility data of 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol in SCCO$_2$ without and with cosolvents and the correlation by Chrastil's model. This material is available free of charge via the Internet at http://pubs.acs.org.

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