

# Equilibrium Partitioning of 2,4-Dichlorophenol between Water and Near-Critical and Supercritical Carbon Dioxide

Aydin Akgerman\* and Brian D. Carter

Chemical Engineering Department, Texas A&M University, College Station, Texas 77843-3321

Distribution coefficients of 2,4-dichlorophenol between supercritical carbon dioxide and water are measured at 298.15 and 319.15 K over the pressure range 11–23 MPa using a single-stage equilibrium cell. The data are modeled by the Peng-Robinson equation of state with modified mixing rules. The data are also compared to literature data on distribution coefficients of phenol and *p*-chlorophenol.

## Introduction

Supercritical CO<sub>2</sub> extraction has been shown to be a viable technique for separation of organic compounds from water (1). The process is a promising technology especially for remediation of wastewaters contaminated with trace organics which are somewhat soluble in water such as chlorinated phenolic compounds. Supercritical extraction has the potential of being less energy intensive than distillation and other separation processes (2) and environmentally friendly. The extent of extraction is determined by the thermodynamic equilibrium distribution of the organic species between water and the supercritical fluid phases (equilibrium partitioning). Previous studies reported on equilibrium partitioning of phenol (3), benzene, toluene, naphthalene, and parathion both individually and in mixtures (4) and benzene, phenol, *p*-chlorophenol, and *m*-cresol (5). This study reports on equilibrium partitioning of 2,4-dichlorophenol.

## Experimental Technique

The experimental assembly consisted of a single-stage high-pressure vessel connected to a system equivalent to an on-line high-pressure liquid chromatograph (HPLC) system. This allowed for analysis of both the aqueous phase and the supercritical fluid (SCF) phase without expansion of the sample. The apparatus is shown schematically in Figure 1.

The containment vessel was a 300 cm<sup>3</sup> bolted closure packless autoclave with a MagneDrive II assembly manufactured by Autoclave Engineers, Inc. The two sampling ports of the autoclave were connected to Rheodyne sample injection valves that had 20- $\mu$ L sample loops. These valves were also connected, in series, to the HPLC sampling system. The mobile phase of the HPLC was pumped with an LDC/Milton Roy ConstaMetric III metering pump from a reservoir through the sampling valves and the detector before being either recycled to the original reservoir or bypassed into a container for contaminated solutions. The detector used was a Milton Roy critical extraction monitor which is a variable-wavelength high-pressure ultraviolet detector. The detector output was connected to a Hewlett-Packard Model 3393A integrator. Ideally, to determine the true distribution coefficients between the phases, the amount of organic compound placed in the autoclave should be less than or equal to the solubility in both phases. Hence, the total quantity of dichlorophenol was always less than the solubility in carbon dioxide (6) and in water (7) at the experimental conditions.

The system was charged with liquid CO<sub>2</sub> at 5.5 MPa. The temperature was monitored with a thermocouple and was

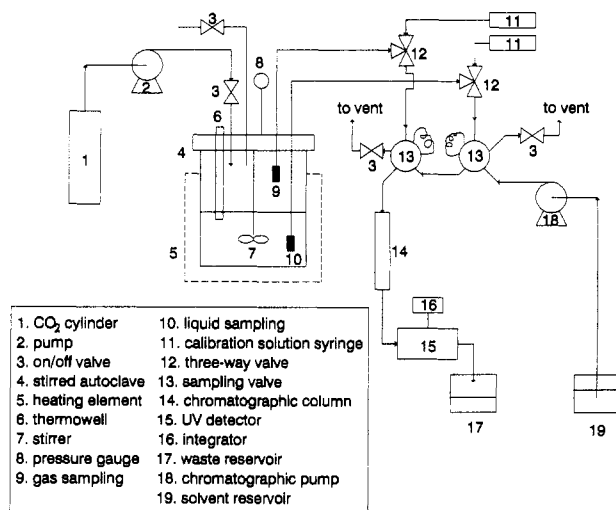


Figure 1. High-pressure equilibrium apparatus.

adjusted with the Furnatrol II controller. Experiments were made at three pressures at 298.15  $\pm$  1 and 319.15  $\pm$  1 K. After the autoclave was brought to the desired temperature and pressure, the contents were vigorously mixed for a period of not less than 2 h by agitation. Following this mixing period, the contents of the autoclave were allowed to settle for 2 h and the aqueous and the supercritical phases were sampled. A 2-h period was deemed necessary for the phases to fully separate (3). Ethanol was used as the mobile phase in the HPLC. The detector was calibrated using solutions of known concentrations similar to those expected. During measurements, the SCF phase was always sampled first, because the SCF phase is more sensitive to pressure changes that accompany the sampling of either phase. To flush the sample loop, a valve was opened, allowing the SCF to expand into a known volume bounded by a second valve. The first valve was shut and the second opened to release a volume of about 1.5 mL of SCF. The sampling valve was then switched so that the pulse traveled through the HPLC system, and the corresponding area was recorded by the integrator. Similarly, when the water phase was sampled, water was flushed through the sample loop and into a graduated cylinder to measure the amount that had been removed from the autoclave (about 1 mL). Then the sampling valve was turned to inject the sample, and the resulting peak was again recorded. The process of pressurizing, mixing, settling, and sampling was repeated for each pressure experiment.

After completion of measurements at three pressures, the HPLC was recalibrated, and the water and SCF sampling valves were recalibrated. Water and carbon dioxide both

\* To whom correspondence should be addressed.

Table 1. Interaction Parameters

<i>i</i>	<i>j</i>	$k_{ij}$	$k_{ji}$
$T = 297 \text{ K}$			
H <sub>2</sub> O	CO <sub>2</sub> <sup>a</sup>	0.160	-0.198
H <sub>2</sub> O	DiCIP	0.410	-0.015
C <sub>2</sub> O	DiCIP	0.168	0.168
$T = 319 \text{ K}$			
H <sub>2</sub> O	CO <sub>2</sub> <sup>a</sup>	0.160	-0.198
H <sub>2</sub> O	DiCIP	0.458	-0.011
C <sub>2</sub> O	DiCIP	0.136	0.136

<sup>a</sup> H<sub>2</sub>O-CO<sub>2</sub>  $k_{ij}$  and  $k_{ji}$  values are from Panagiotopoulos and Reid (8); all other values were fit from experimental data. The objective function minimized was  $\sum [(y_i/x_i)_{\text{calc}} - (y_i/x_i)_{\text{expt}}]^2$ .

Table 2. Distribution Coefficients  $K_i$  for 2,4-Dichlorophenol with Accompanying Mole Fractions in CO<sub>2</sub>

pressure	$K_i^a$	$y_i$
$T = 297 \text{ K}$		
11.1	38.8	0.000 196
16.0	43.1	0.000 205
19.4	43.6	0.000 223
$T = 319 \text{ K}$		
11.1	13.9	0.000 181
16.6	32.5	0.000 223
22.9	36.6	0.000 228

<sup>a</sup> Precision of  $\pm 10\%$  based on repeat experiments.

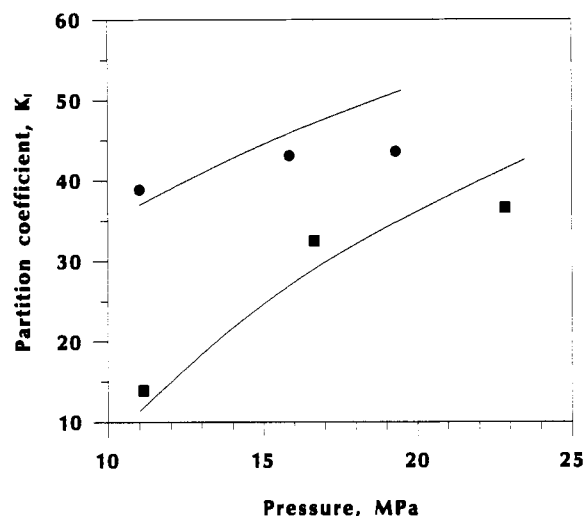


Figure 2. Comparison between experimental data and the thermodynamic model for partition coefficients,  $K_i$ , of dichlorophenol between water and carbon dioxide: ■, 319.15 K; ●, 298.15 K; —, model.

caused perturbations which, unfortunately, emerged at the same time as the solute peaks. These perturbations were due to either pressure effects originating from switching of sample valves or slight changes in the absorbance of ethanol affected by water or carbon dioxide. These perturbations were small in comparison with the solute peaks, and the areas obtained for the pure CO<sub>2</sub> and pure water peaks were simply measured and subtracted from the areas of the solute peaks before conversion to concentrations using the calibration curves.

### Thermodynamic Model

The Peng-Robinson equation of state with mixing rules proposed by Panagiotopoulos and Reid (8) for highly polar asymmetric systems was shown to work well for supercritical CO<sub>2</sub> + water systems (4). In this model the partition coefficient is given by

Table 3. Solubilities of Various Phenols in Water and Supercritical CO<sub>2</sub> and the Distribution Coefficients at 319 K and 16.5 MPa

compound	mole fraction solubility in CO <sub>2</sub>	solubility in H <sub>2</sub> O (g/100 g)	$K_i^a$
phenol	0.016 25 (6)	8.20 (7)	1.57 (5)
<i>p</i> -chlorophenol	0.020 43 (6)	2.71 (7)	3.80 (5)
2,4-dichlorophenol	0.075 83 (6)	0.45 (7)	32.5 (this work)

<sup>a</sup> Interpolated from data in ref 5.

$$K_i = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V} = \frac{y_i}{x_i} \quad (1)$$

where the fugacity coefficients are

$$\ln \hat{\phi}_i = \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left[ \frac{\sum_k x_k (a_{ki} + a_{ik})}{a_m} - \frac{\sum_k \sum_j x_k^2 x_j (k_{kj} - k_{jk}) (a_k a_j)^{1/2} - x_i \sum_k x_k (k_{ik} - k_{ki}) (a_i a_k)^{1/2}}{a_m} - \frac{b_i}{b_m} \right] \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (2)$$

with

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (3)$$

$$b_m = \sum_i x_i b_i \quad (4)$$

$$a_{ij} = (1 - k_{ij} + (k_{ij} - k_{ji})x_i)(a_i a_j)^{1/2} \quad (5)$$

$$B = b_m P / RT \quad (6)$$

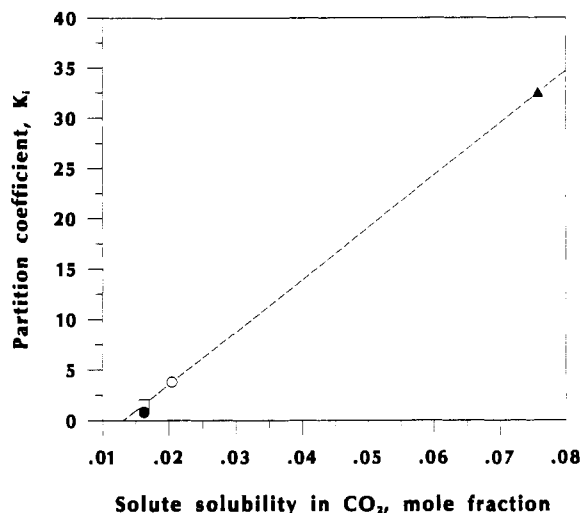
$$A = a_m P / R^2 T^2 \quad (7)$$

$$Z = PV / RT \quad (8)$$

The composition-dependent mixing rule contains two adjustable interaction parameters,  $k_{ij}$  and  $k_{ji}$ , which must be evaluated from experimental data or taken from the literature. Table 1 summarizes the interaction parameters used in the model. The  $k_{ij}$  and  $k_{ji}$  values for H<sub>2</sub>O + CO<sub>2</sub> are from Panagiotopoulos and Reid (8).

The measured CO<sub>2</sub>/water distribution coefficients ( $y_i/x_i$ ) for 2,4-dichlorophenol as a function of pressure at two temperatures are shown in Table 2. The precision was generally better than 4% for the composition in both the aqueous and SCF phases while the average overall mass balance was better than 96% with the exception of the measurement at 319 K and 11.1 MPa where the mass balance closure was 90%.

$K_i$  increases with pressure as expected and is always higher at the lower temperature, indicating that the crossover point was not encountered in the pressure range studied. The parameters obtained from these experiments were used in the Peng-Robinson equation of state to model dichlorophenol behavior in the water + carbon dioxide system. Figure 2 compares results from the model with the experimental data. The model agrees well, both qualitatively and quantitatively, with the experimental results.



**Figure 3.** Partition coefficient,  $K_i$ , for various phenols as a function of their solubility in  $\text{CO}_2$  in mole fraction at 319.15 K and 16.5 MPa:  $\square$ , phenol (5);  $\bullet$ , phenol (3);  $\circ$ , *p*-chlorophenol (5);  $\blacktriangle$ , 2,4-dichlorophenol (this study).

In Table 3, the  $K_i$  values show an increase from phenol to chlorophenol to dichlorophenol. The solubilities in water are in the order phenol > chlorophenol > dichlorophenol, while the solubilities in  $\text{CO}_2$  are in the order dichlorophenol > chlorophenol > phenol. Since dichlorophenol has the lowest solubility in water and the highest solubility in  $\text{CO}_2$ , it is only reasonable to expect 2,4-dichlorophenol to have the highest

$K_i$  value. The  $K_i$  values for these compounds show a linear relationship with their solubility in  $\text{CO}_2$  as shown in Figure 3. The  $K_i$  values for chlorophenol and phenol were obtained from Ghonasgi et al. (5), and the  $K_i$  value for phenol is from Roop and Akgerman (3).

#### Literature Cited

- (1) Akgerman, A.; Roop, R. K.; Hess, R. K.; Yeo, S.-D. Supercritical Extraction in Environmental Control. In *Supercritical Fluid Technology - Reviews in Modern Theory and Applications*; Bruno, T. J., Ely, J. F., Eds.; CRC Press: Boca Raton, FL, 1991; pp 479-509.
- (2) King, B.; Boyes, A.; Bott, T.; Mubarak, A. Economic Aspects of the Design of Near-Critical Extraction Processes. *I. Chem. E. Symp. Ser.* 1987, 103, 351.
- (3) Roop, R. K.; Akgerman, A. Entrainer Effect for Supercritical Extraction of Phenol from Water. *Ind. Eng. Chem. Res.* 1989, 28, 1542.
- (4) Yeo, S.-D.; Akgerman, A. Supercritical Extraction of Organic Mixtures from Aqueous Solutions. *AIChE J.* 1990, 36, 1743.
- (5) Ghonasgi, D.; Gupta, S.; Dooley, K. M.; Knopf, F. C. Supercritical  $\text{CO}_2$  Extraction of Organic Contaminants from Aqueous Streams. *AIChE J.* 1991, 37, 944.
- (6) Van Leer, R. A.; Paulaitis, M. E. Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* 1980, 25, 258.
- (7) Perry, R. H.; Chilton, C. H. *Chemical Engineer's Handbook*, 5th ed.; McGraw-Hill: New York, 1973; pp 3-32.
- (8) Panagiotopoulos, A. Z.; Reid, R. C. New Mixing Rule for Cubic Equations of State of Highly Polar, Asymmetric Systems. *ACS Symp. Ser.* 1986, 300, 571.

Received for review October 5, 1993. Revised February 18, 1994. Accepted March 3, 1994.\* This work was supported by the National Science Foundation through Grant BES9114848.

\* Abstract published in *Advance ACS Abstracts*, April 15, 1994.