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Solubilities of Acidic Pesticides in Water and Liquid and Supercritical Carbon Dioxide

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The potential of supercritical fluid technology for water analysis has been recognized for nearly a decade. In an effort to broaden the knowledge required to implement methods for the direct extraction of water samples, we have investigated the partitioning of chlorinated, acidic pesticides and phenols between water and carbon dioxide. A high-pressure stainless steel extraction vessel with on-line HPLC detection was constructed for solubility and partitioning experiments. The solubility of pentachlorophenol in both water and liquid CO_2 was determined at ambient temperatures as a function of pressure. A solubility isotherm was also constructed at 28.1 °C for CO_2. Solubility isotherms of 2,4-dichlorophenoxyacetic acid in liquid and supercritical (SC) CO_2 have been measured at (21.0, 26.3, and 34.8) °C. Naphthalene solubility in SC CO_2 was measured at 34.7 °C and compared with literature values to ensure correct function of the apparatus. Measurements were performed at pressures up to 250 bar.

Introduction

The presence of organic contaminants in natural waters has been a topical issue among scientists and the general public for many years. Specifically, the abundant use of acidic, chlorinated pesticides in agriculture has resulted in the potential exposure of humans and wildlife to carcinogenic and toxic residues. Conventional extraction methods for the detection of water pollutants are time-consuming, require multiple steps in procedure, and employ large volumes of expensive, toxic organic solvents. Acidic pesticides have proven to be typically difficult to remove from aqueous matrices due to their high affinity for water. The development of rapid, clean, and accurate methods of analysis is required to address these limitations.

Several methods have been developed for the direct supercritical fluid extraction of aqueous matrices (Hedrick and Taylor, 1989; Ghonasgi et al., 1991; Brewer and Kruus, 1993; Roop et al., 1989). Currently, the chemistry underlying the extraction of acidic, organic species from water using supercritical carbon dioxide (SC CO_2) is not completely understood. Several investigations into the solubilities of pesticides and phenols in supercritical fluids have been reported (Van Leer and Paulaitis, 1980; Madras et al., 1993; Macnaughton and Foster, 1994; Schäfer and Baumann, 1988; Macnaughton et al., 1995). Other authors have measured distribution coefficients in support of the interpretation of analyte partitioning between water and SC CO_2 (Ghonasgi et al., 1991; Roop et al., 1989; Gupta et al., 1991; Hedrick et al., 1992; Akgerman and Carter, 1994). The pH of water is expected to drop to about 3 during an extraction due to the dissolution of CO_2 to form carbonic acid (Toews et al., 1995).

Successful implementation of novel methodologies will require a more complete understanding of the interactions among the water phase, the supercritical CO_2, and the analyte(s) to be extracted. This may be accomplished by further determining analyte solubilities in both phases as a function of pressure and temperature, recognizing partitioning trends, and defining distribution coefficients. The measurement of the ratio of an analyte in water and SC CO_2 should aid in the interpretation of analyte distribution during an extraction. The effect of this ratio has been explored by Ghonasgi et al. with respect to the distribution of benzene, *p*-chlorophenol, *m*-cresol, and phenol between water and CO_2. Only solubilities in water at atmospheric pressure were considered. Solubilities have previously been reported by Schäfer and Baumann, and Macnaughton and Foster, for 2,4-dichlorophenoxyacetic acid (2,4-D) solubility in SC CO_2. Pentachlorophenol (PCP) results have also been reported by Madras et al.

Experimental Section

A schematic diagram of the extraction vessel and the on-line plumbing to the HPLC unit is shown in Figure 1. The setup is similar to that reported by Akgerman and Carter. The vessel was designed and constructed at the *Science Technology Centre* at Carleton University (Ottawa). The screw cap is made of hardened stainless steel to prevent seizing with the stainless steel body. Unless specified, all tubing is $^1/_{16}$ in. stainless steel with a 0.03 in. i.d. The total internal volume of the system from the entrance Valco two-port valve, in line prior to the pressure gauge, to the exit shut-off valve of the same type was 105 mL. A $^1/_{16}$ in. Swagelok−$^1/_8$ in. universal pipe thread union was screwed into a threaded opening on one side of the vessel. The centre of the union was drilled out such that a $^1/_{16}$ in. steel thermocouple could be fed through and swaged in place. Temperature was monitored with an Omega microprocessor thermometer capable of 0.1 °C precision. The vessel, and all tubing prior to and including the sample loop, was thermostated in a water bath which was heated electrically. A magnetic stir bar was placed inside the cell and the entire apparatus placed over a magnetic stirrer for solution mixing. The pressure was continually monitored using a Bourdon gauge with a (0−6000) psi range and 25 psi precision. The $^1/_4$ in. ball valve in the cap allowed access to the interior of the vessel without having to dismantle the apparatus. Two sample ports were made by welding sections of $^1/_{16}$ in. tubing to one side of the vessel. These ports allowed withdrawal of samples from each phase during partitioning experiments. The frit downstream from the upper sample port prevented solid from entering the extraction loop during the solubility tests. A packed

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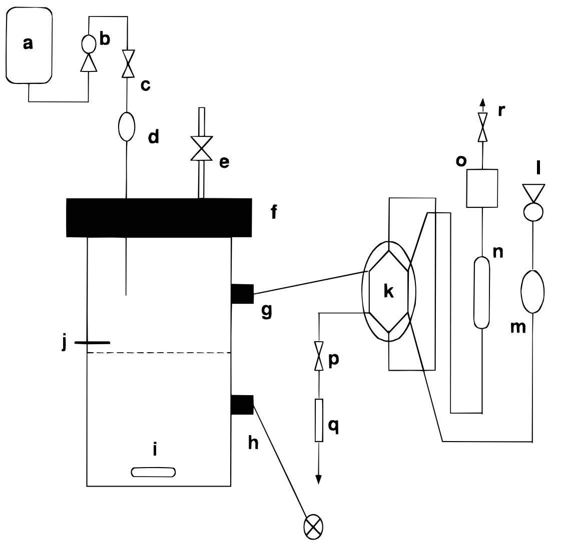

Figure 1. Experimental apparatus: (a) liquid CO_2, (b) pump, (c) entrance valve, (d) pressure gauge, (e) $^1/_4$ in. ball valve, (f) screw cap, (g) upper sample port, (h) lower sample port, (i) stir bar, (j) thermocouple, (k) six-port valve, (l) HPLC pump, (m) HPLC injector, (n) HPLC column, (o) UV detector, (p) exit valve, (q) restrictor, (r) back-pressure regulator.

plunger pump delivered liquid CO_2 through a section of $^1/_8$ in. stainless steel tubing welded to the vessel cap. The pump head was cooled to prevent vaporization of the CO_2. A Suprex SFE-50 syringe pump was used for delivery of pressurized distilled, deionized, unbuffered water at ambient temperatures. The syringe pump was also used for delivery of SC CO_2 during naphthalene solubility experiments. All standard and sample aliquots except naphthalene were manually injected into a Varian LC Star System with a 250 × 4.6 mm 5 μM C_{18} column and ultraviolet detection. The mobile phase composition was 95% methanol + 5% v/v acetic acid (0.5% v/v) in water with a flow rate of 1.2 mL/min. Wavelengths of 280, 286, and 224 nm were used for the analyses of pentachlorophenol (Aldrich, 99%) in CO_2, 2,4-D (Aldrich, 98%) in CO_2, and pentachlorophenol in water respectively. A back-pressure regulator prevented vaporization of methanol in the detector. A Waters 6000A chromatography pump was used for solvent delivery for naphthalene standard and sample analyses. Detection was at a wavelength of 320 nm.

To determine analyte solubility, 2−3 g of solid solute were placed in the vessel. Prior to pressurization, the apparatus was purged of ambient air by flushing CO_2 or water through the access valve. At each pressure increment the cell was isolated for equilibration by closing the Valco two-port valves. For sampling, the exit valve was opened and saturated CO_2 or water purged through a 2 or 10 μL sample loop before expanding through a stainless steel restrictor or open-ended piece of tubing into a hot water collection bath. To ensure saturation of the fluid, the stirring rate, equilibration times, flow rate, and sampling times were varied. Typical equilibration and sampling times for 2,4-D and PCP were 5−30 min and 20−180 s, respectively, for solubility in CO_2. Naphthalene solubility experiments required equilibration times between 15 and 20 h. Equilibration was allowed to occur from 5 h to several days for PCP solubility experiments in water. All solutions were accepted as saturated when further increases in equilibration times did not yield higher apparent solubilities. Calibration curves were constructed by injecting analyte standards prepared in HPLC-grade methanol of appropriate concentrations. A minimum r^2 value of 0.99 was obtained for each curve.

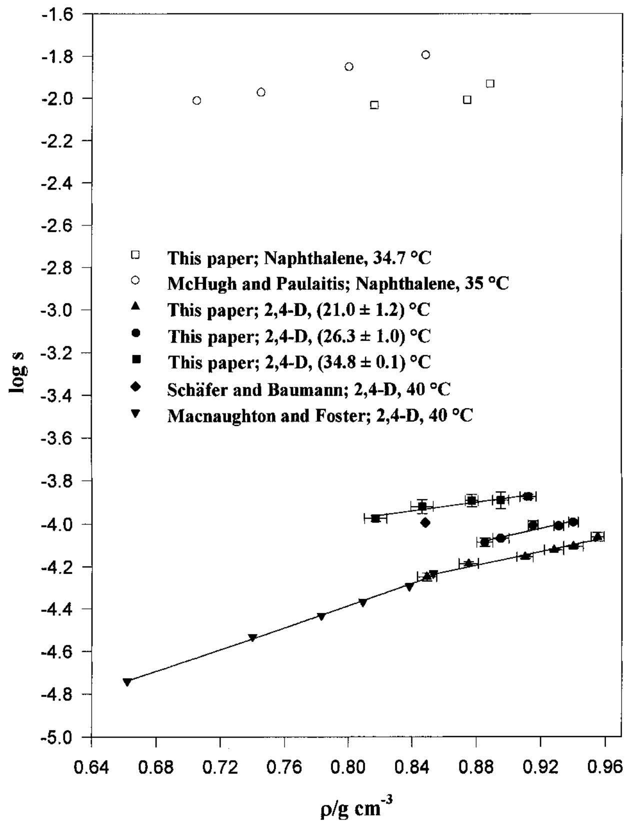

Figure 2. Log *s* of 2,4-D and naphthalene in CO_2 as a function of density.

Table 1. Mole Fraction, *s*, of 2,4-D in Liquid and Supercritical Carbon Dioxide

P/bar	$10^5 s$	*P*/bar	$10^5 s$
	T = 21.0 ± 1.2 °C		
83.2	5.63	170	7.52
109	6.50	200	7.79
142	6.98	241	8.63
	T = 26.3 ± 1.0 °C		
145	8.16	230	9.70
165	8.51	248	10.1
204	9.80		
	T = 34.8 ± 0.1 °C		
141	10.6	226	12.8
167	12.0	254	13.3
203	12.7		

Results and Discussion

The solubility, *s*, measurements for naphthalene in supercritical CO_2 at 34.7 °C are shown in Figure 2. The close proximity of these results to those obtained by McHugh and Paulaitis (1980) validates continued use of the apparatus for solubility and partitioning experiments. Solubility isotherms are shown in Figure 2 for 2,4-D in liquid and SC CO_2 at 21.0, 26.3, and 34.8 °C with pressures up to about 250 bar. Each isotherm demonstrates an increase in analyte solubility with increased pressure as a result of the effects of solvent density and solute vapor pressure. Pressure and solubility data are listed in Table 1. Included in Figure 2 are the measurements obtained by Schäfer and Baumann, and Macnaughton and Foster, for this solute in SC CO_2 at 40 °C. Increased solubility values were expected as this is a temperature 5° greater than the highest isotherm reported in our work. Previously, differences in results were attributed by Macnaughton and Foster to a lack of solute purification which would cause the measurements by Schäfer and Baumann to be inordinately high due to the dissolution of impurities. Our

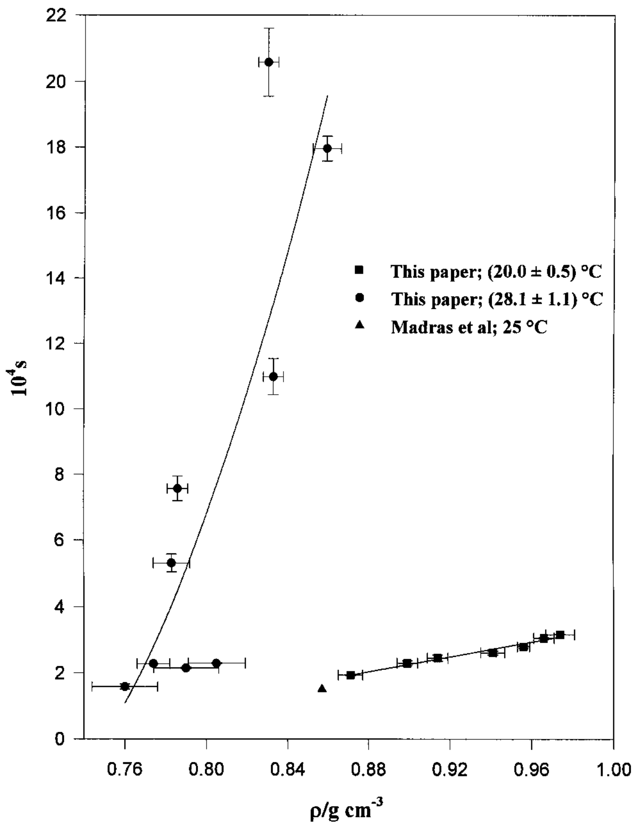

Figure 3. Mole fraction, *s*, of PCP in CO_2 as a function of density.

Table 2. Mole Fraction, *s*, of Pentachlorophenol in Liquid Carbon Dioxide

P/bar	10^4s	*P*/bar	10^4s
	$T = 20.0 \pm 0.5$ °C		
97.4	1.93	220	2.78
127	2.29	252	3.04
153	2.45	269	3.15
189	2.60		
	$T = 28.1 \pm 1.1$ °C		
84.4	5.31	94.8	2.29
87.9	1.58	110	11.0
88.0	7.56	111	20.6
89.9	2.14	141	18.0
91.3	2.28		

static system with on-line monitoring allowed for the accurate determination of solute–solvent equilibrium without mass transfer problems. Although the analytes were not purified in our work on-line detection by HPLC allowed for direct measurement of solute concentration without interference from impurities. No impurities were observed in the 2,4-D sample or standard aliquots. The solubility of pentachlorophenol was determined in liquid CO_2 at 20.0 °C and 28.1°C with varied pressure. As shown in Table 2, solubility increased with solvent density, and is expected to further increase with temperature. The data point at 25 °C reported by Madras et al. is included in Figure 3. Standard and sample chromatograms for PCP in CO_2 indicated a 1% impurity which was not identified.

The solubility of pentachlorophenol in unbuffered water was measured at 23.6 °C for pressures from 1 to 171 bar; a data point was obtained at 20.5 °C and 208 bar which has also been included in Figure 4. Table 3 summarizes pressure and solubility data at the indicated temperatures and lists actual concentration values, *c*, for PCP in water. At the time of analysis, we were not capable of constant temperature regulation at ambient conditions. Nonetheless, variation in this temperature range was expected to have only a limited effect on solubility. The solubility of PCP in water at atmospheric pressure has been reported in the range of 14–19 μg/mL (Freiter, 1979) and as 18 μg/mL at 27 °C (Carswell and Nason, 1938). Our work has yielded a value of 13.4 μg/mL under similar conditions.

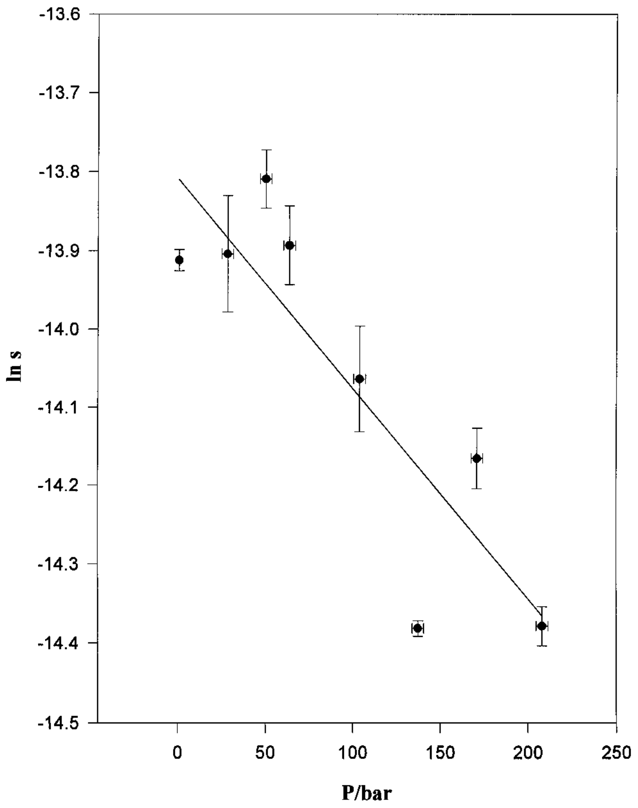

Figure 4. ln *s* of PCP in water as a function of pressure.

Table 3. Mole Fraction, *s*, of Pentachlorophenol in Water

P/bar	*c*/mg L^{-1}	10^7s	*P*/bar	*c*/mg L^{-1}	10^7s
		$T = 23.6 \pm 0.5$ °C			
1	13.4	9.08	104	11.6	7.82
28.5	13.6	9.17	137	8.4	5.68
50.3	14.9	10.1	171	10.4	7.05
63.8	13.7	9.26			
		$T = 20.5 \pm 0.4$ °C			
208	8.4	5.69			

Dissolution of a solute in water requires disruption or distortion of the attractive forces between water molecules. The solubility of PCP is minimal due to limited hydrogen bonding with surrounding water molecules. The presence of chlorine atoms in both ortho positions likely causes repulsion between the phenol group and any points of attachment, and intramolecular hydrogen bonding is promoted (Blackman et al., 1955). Due to the partial dissociation of PCP in water, the pH is lowered to about 5 as pentachlorophenoxide anion is very soluble (Arcand et al., 1993). We measured the pH of PCP saturated water at 1 atm to be 4.6. As undissociated PCP is fairly insoluble in water, it will quickly reach a maximum concentration once the minimum pH is achieved. Previous experiments have shown solubility maxima in water at 1–2 kbar for alkylbenzenes (Sawamura et al., 1989). Other experiments with solid naphthalene have demonstrated a linear decrease in solubility with pressures up to 3 kbar (Sawamura et al., 1993). Our results show a fairly linear decrease in solubility over the range of 1–208 bar for PCP, a phenomenon which may be better understood following determination of the volume change upon solution of PCP in water. The volume change of a solute upon solution, ΔV, is the difference between its partial molar volume at infinite dilution, $\bar{V}°_w$, and the molar volume of the pure crystal, V_c (Sawamura et al., 1993):

$$\Delta V = \bar{V}°_w - V_c \tag{1}$$

An infinitely dilute solution assumes the degree of mutual solubility is small. The hydrated PCP appears to have a compressibility similar to that of the molecular crystal resulting in a volume change which is positive. Using the relationship

$$\Delta V = -RT[\delta \ln x/\delta p]_T \tag{2}$$

the volume change of pentachlorophenol has been calculated from the slope of Figure 4 as 66 $cm^3\ mol^{-1}$. Compression of the analyte in aqueous solution likely caused PCP to precipitate out of solution with increased pressure.

Conclusions

The partitioning of an analyte between water and supercritical CO_2 will be affected by the solubility of the analyte in the two phases. There are three factors which may influence these solubilities as the pressure is increased. First, most analytes will become more soluble in the CO_2. We have shown that this is true for 2,4-D and PCP. Second, the solubility of the analyte in the aqueous phase may increase or decrease. Our results suggest that the solubility of PCP in water actually decreases with increasing pressure. Third, the aqueous phase will become more acidic due to dissolution of CO_2. This will cause protonation of acidic species, and the protonated forms are expected to be more soluble in CO_2. From all three points of view, the partitioning of this species is thus expected to increase with increasing pressure.

Work in our laboratory is currently exploring the effects of changing the pH so that the relative contributions of protonation and solvation of acidic compounds (by the water and by the CO_2) can be determined.

Literature Cited

Akgerman, A.; Carter, B. D. Equilibrium Partitioning of 2,4-Dichlorophenol between Water and Near-Critical and Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1994**, *39*, 510−512.

Arcand, Y.; Hawari, J.; Guiot, S. R. Solubility of Pentachlorophenol in Aqueous Solutions: The pH Effect. *Water Res.* **1995**, *29*, 131−136.

Blackman, G. E.; Parke, M. H.; Garton, G. The Physiological Activity of Substituted Phenols. II. Relationships between Physical Properties and Physiological Activity. *Arch. Biochem. Biophys.* **1955**, *54*, 55−71.

Brewer, S. E.; Kruus, P. Direct Supercritical Fluid Extraction from Water. *J. Environ. Sci. Health* **1993,** *B28*, 671−685.

Carswell, T. S.; Nason, H. K. Properties and Uses of Pentachlorophenol. *Ind. Eng. Chem.* **1938**, *30*, 622−626.

Freiter, E. R. *Kirk−Othmer's Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley and Sons: New York, 1979; Vol. 5.

Ghonasgi, D.; Gupta, S.; Dooley, K. M.; Knopf, F. C. Supercritical CO_2 Extraction of Organic Contaminants from Aqueous Streams. *AIChE J.* **1991**, *37*, 944−950.

Gupta, S.; Ghonasgi D.; Dooley; K. M.; Knopf, F. C. Supercritical Carbon Dioxide Extraction of a Phenolic Mixture from an Aqueous Waste Stream. *J. Supercrit. Fluids* **1991**, *4*, 181−185.

Hedrick, J.; Taylor, L. T. Quantitative Supercritical Fluid Extraction/Supercritical Fluid Chromatography of a Phosphonate from Aqueous Media. *Anal. Chem.* **1989**, *61*, 1986−1988.

Hedrick, J. L.; Mulcahey, L. J.; Taylor, L. T. Supercritical Fluid Extraction of Phenols from Water. *Supercritical Fluid Technology*; Bright, F. V., McNally, M. E. P., Eds.; ACS Symposium Series 488; American Chemical Society: Washington, DC, 1992; p 206−220.

Macnaughton, S. J.; Foster, N. R. Solubility of DDT and 2,4-D in Supercritical Carbon Dioxide and Supercritical Carbon Dioxide Saturated with Water. *Ind. Eng. Chem. Res.* **1994**, *33*, 2757−2763.

Macnaughton, S. J.; Kikic, I.; Rovedo, G.; Foster, N. R.; Alessi, P. Solubility of Chlorinated Pesticides in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1995**, *40*, 593−597.

Madras, G. M.; Erkey, C.; Akgerman, A. A New Technique for Measuring Solubilities of Organics in Supercritical Fluids. *J. Chem. Eng. Data* **1993**, *38*, 422−423.

McHugh, M.; Paulaitis, M. E. Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1980**, *25*, 326−329.

Roop, R. K.; Akgerman, A.; Dexter, B. J.; Irvin, T. R. Extraction of Phenol from Water with Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1989,** *2*, 51.

Sawamura, S.; Kitamura, K.; Taniguchi, Y. Effect of Pressure on the Solubilities of Benzene and Alkylbenzenes in Water. *J. Phys. Chem.* **1989**, *93*, 4931−4935.

Sawamura, S.; Tsuchiya, M.; Ishigami, T.; Taniguchi, Y.; Suzuki, K. Effect of Pressure on the Solubility of Naphthalene in Water at 25 °C. *J. Solution Chem.* **1993**, *22*, 727−732.

Schäfer, K.; Baumann, W. Solubility of Some Pesticides in Supercritical CO_2. *Fresenius' Z. Anal. Chem.* **1988**, *332*, 122−124.

Toews, K. L.; Shroll, R. M.; Wai, C. M. pH-Defining Equilibrium between Water and Supercritical CO_2. Influence on SFE of Organics and Metal Chelates. *Anal. Chem.* **1995**, *67*, 4040−4043.

Van Leer, R. A.; Paulaitis, M. E. Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1980**, *25*, 257−259.

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