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Supercritical Fluid Extraction of Acidic, Polar Solutes from Aqueous Matrices: Partitioning Data for Pentachlorophenol between Carbon Dioxide and Water

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Supercritical fluid technologies as alternative methodologies to conventional procedures are being explored for the direct extraction of acidic and polar contaminants from aqueous matrices. In support of the knowledge required to implement these novel methods, the partitioning of pentachlorophenol between water and liquid and supercritical CO_2 has been characterized by determining distribution coefficients at (18.8, 41.7, and 59.8) °C from a saturated water solution (11.6×10^{-6} g/g solvent). The partitioning of pentachlorophenol from dilute solution (1.27×10^{-6} g/g solvent) was measured at (42.2 and 59.9) °C. Distribution coefficients were lower at this reduced concentration. Measurements were made at pressures up to about 280 bar. Comparison of the partitioning data to the solubility ratio of the solute in both phases contributes to the interpretation of relevant interactions in this complex system.

Introduction

Current procedures for extractions from water tend to require multiple steps and consume large volumes of toxic solvents that are hazardous and have high costs of production and disposal. Supercritical fluid methodologies provide means of enhancing method sensitivities owing to the potential of extracting and concentrating analytes in a single step. Selective extractions are possible owing to the variable densities of supercritical fluids. Fast extractions result from their low viscosities.

The determination of analytical levels of phenolic compounds in environmental matrices is complicated by the polar and acidic nature of this family of contaminants. Pentachlorophenol (PCP), the most acidic chlorophenol ($pK_a = 4.74$) (Curren and Burk, 1997), is found in natural water sources owing to its use as a wood preservative. The polar nature of water and its potential for hydrogen bonding with a solute combine to promote retention of phenols in water. Partial dissociation of this weak acid in water samples make extractions particularly difficult. Investigations into the partitioning behavior of several phenols between water and supercritical carbon dioxide (SC CO_2) have contributed to the interpretation of the interactions between the solute(s), water, and CO_2 (Hedrick et al., 1992; Akgerman and Carter, 1994; Ghonasgi at al, 1991a; Green and Akgerman, 1996). Water and SC CO_2 are somewhat soluble in each other (King et al., 1992; Wiebe, 1941), resulting in some important interactions. For instance, the pH of water-rich phase drops to about 3 owing to the formation of carbonic acid (Toews et al., 1995).

The successful implementation of supercritical fluid methodologies for water analyses will require a complete characterization of the extraction system. This may be accomplished in part by relating the solubility ratio of a solute in each phase to its partitioning between the phases. This ratio was previously considered by Ghonasgi et al. for benzene and a series of phenols. The solubilities of pentachlorophenol in water and CO_2 as a function of pressure have already been determined (Curren and Burk, 1997). Additional solubility data has been provided by Miller et al. (1997) and Madras et al. (1993). The distribution coefficient, K, of a solute is defined as the ratio of its mole fraction in the supercritical fluid-rich phase to its mole fraction in the water-rich phase. Such partitioning data for PCP has not been previously reported.

The effect of the initial concentration of a solute in the water phase on its partitioning between the phases has not been considered for chlorinated phenols. Starting concentrations have typically been in excess of 100×10^{-6} g/g solvent (Hedrick et al., 1992; Roop and Akgerman, 1990), greatly in excess of the concentrations of interest to the analytical chemist. No significant influence of concentration was found for the partitioning of phenol to supercritical CO_2 from solutions with initial concentrations of (0.2 to 10) wt % (Brudi et al., 1996). If partitioning is a function of concentration for chlorophenols, this has important implications in the analytical laboratory. Experiments at analytical concentrations will provide insight to the interactions relevant in environmental matrices. Optimization of extraction parameters such as pressure, temperature, pH, and ionic strength will eventually assist in the design of efficient extraction systems.

Experimental Section

A schematic diagram of the extraction vessel and the online plumbing to an HPLC unit is shown in Figure 1 and has been described before (Curren and Burk, 1997). A screw cap was fitted onto a stainless steel body for a total system internal volume of 105 mL. The temperature was monitored with a thermocouple swaged into a threaded opening on one side of the cell. The vessel, and all tubing prior to and including the sample loops, was thermostated inside a Tenney Junior oven. 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. A $^1/_4$ in. ball

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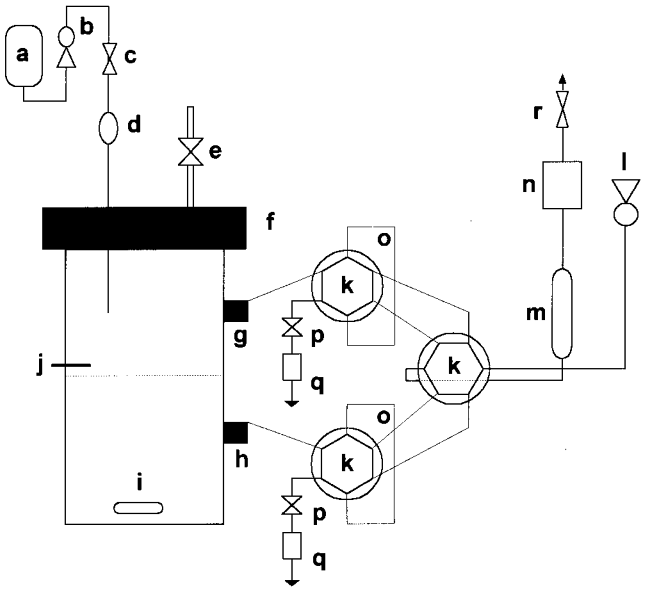

Figure 1. Experimental apparatus: (a) liquid CO_2, (b) pump, (c) entrance valve, (d) pressure gauge, (e) $^1/_4$ ball valve, (f) screw cap, (g) upper sample port, (h) lower sample port, (i) stir bar, (j) thermocouple, (k) six-port valve, (l) HPLC pump, (m) HPLC column, (n) UV detector, (o) sample loop,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

valve in the cap allowed access to the interior of the vessel without having to unscrew the cap. Two sample ports made from $^1/_{16}$ in. tubing were welded to one side of the vessel, allowing withdrawal of samples from each phase. A Suprex SFE-50 syringe pump delivered liquid and supercritical CO_2. All standard and sample aliquots were manually injected into a combined Waters 6000A−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% water brought to pH 3 with phosphoric acid with a flow rate of 1.2 mL/min. A wavelength of 224 nm was used. A back-pressure regulator prevented formation of bubbles in the detector.

For the partitioning experiments, water either saturated with pentachlorophenol [$(11.6 \pm 0.6) \times 10^{-6}$ g/g solvent] or diluted to one-tenth this concentration [$(1.27 \pm 0.17) \times 10^{-6}$ g/g solvent] was placed in the cell. Prior to pressurization, the vessel headspace was purged of ambient air by flushing CO_2 out through the ball valve. At each pressure increment, the cell was isolated for equilibration by closing the entrance and exit valves. For sampling, the upper and lower exit valves were simultaneously opened and samples of CO_2 and water were collected in separate sample loops (2, 10, or 112 μL). The water fraction was collected each time so that the amount of water removed from the bulk solution could be determined by weighing. To ensure system equilibration, stirring times, settling times, flow rate, and sampling times were varied. It was determined through replicate injections that a minimum of 40 min stirring and a 15 min settling period were required for phase equilibration and separation. The CO_2-rich fraction was immediately injected into the HPLC. Once the chromatography was complete, the mobile phase was redirected through the lower sample loop for the analysis of the water-rich fraction. Pentachlorophenol standards of appropriate concentrations were prepared in both water-saturated CO_2 and pure water by doping the standards with very small, concentrated aliquots of PCP prepared in optima-grade methanol. A minimum r^2 value of 0.99 was obtained for each calibration curve.

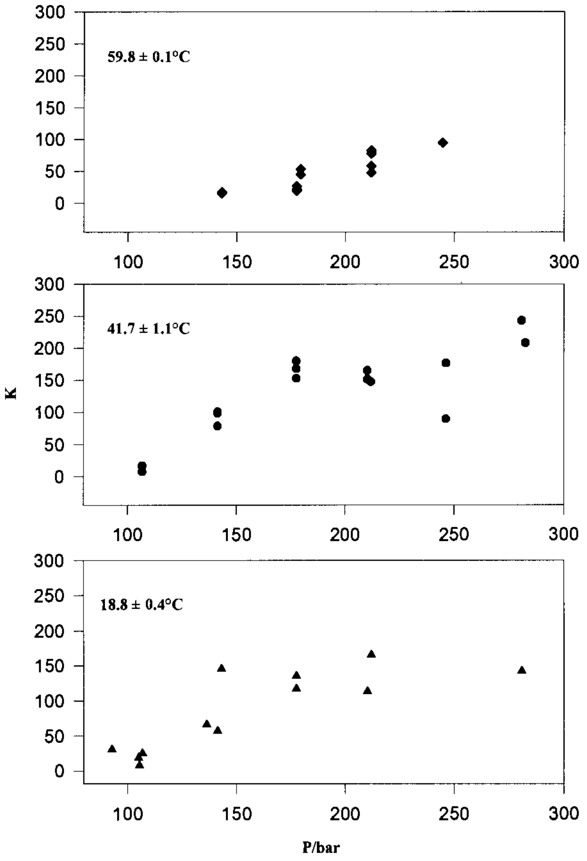

Figure 2. Distribution coefficient, *K*, for pentachlorophenol between water initially saturated in PCP and CO_2.

Results and Discussion

The partitioning of pentachlorophenol from solute-saturated water to CO_2 at sub- and supercritical conditions is quantified in Figure 2 as a function of pressure. The partitioning data is included in Table 1. Some high values (over 100) were observed for K, owing to the large amount of PCP which partitioned to the CO_2-rich phase. The limit of detection for the analysis of the water-rich fractions was a maximum of 0.08 and 0.1×10^{-6} g/g solvent using the 112 and 10 μL sample loops, respectively. This allowed for a maximum *K* value of about 240 to be determined. The data are less precise at higher pressures as the limit of detection is approached in the water-rich fractions. At 18.8 and 41.7 °C the distribution coefficient is similar in magnitude over the pressure ranges studied. However, increasing the temperature to 59.8 °C has caused analyte partitioning to the supercritical phase to drop significantly. Several variables may contribute to this effect. The reduced density, and consequent solvating power, of CO_2 at the higher temperature apparently dominates the effect of temperature on solute vapor pressure. This trend has already been observed for various phenolic compounds (Hedrick et al., 1992; Akgerman and Carter, 1994; Ghonasgi et al., 1991b). The difference in CO_2 density between the lower two isotherms is not as significant and falls within 10% at the upper pressure range. The density effect is further shown in Figure 3. The partitioning of PCP at the highest isotherm will only rival that at the lower temperatures with an increase in density, thus requiring a substantial increase in pressure.

Another variable to consider is the increase in the dissociation constant of pentachlorophenol with increasing temperature. According to Gibb's free energy relationship

Table 1. Distribution Coefficient, *K*, of Pentachlorophenol between Water Initially Saturated with PCP (11.6 (±0.6) × 10^{-6} g/g Solvent) and Liquid and Supercritical CO_2

P/bar	ρ/g cm^{-3}	K^a
	$T = (18.8 \pm 0.4)$ °C	
93	0.873	31
106	0.890	20 ± 9
136	0.910	67
142	0.914	120 ± 50
177	0.941	130 ± 10
211	0.956	140 ± 30
281	0.986	142
	$T = (41.7 \pm 1.1)$ °C	
107	0.651	12 ± 5
141	0.766	90 ± 10
177	0.811	170 ± 10
211	0.851	150 ± 10
246	0.874	130 ± 40
282	0.905	230 ± 20
	$T = (59.8 \pm 0.1)$ °C	
143	0.577	17 ± 1
177	0.688	23 ± 4
179	0.693	49 ± 5
212	0.746	70 ± 20
245	0.746	95

[a] Standard deviation included for results averaged from three or more trials; range included for results averaged from two trials; no uncertainty included for single trials.

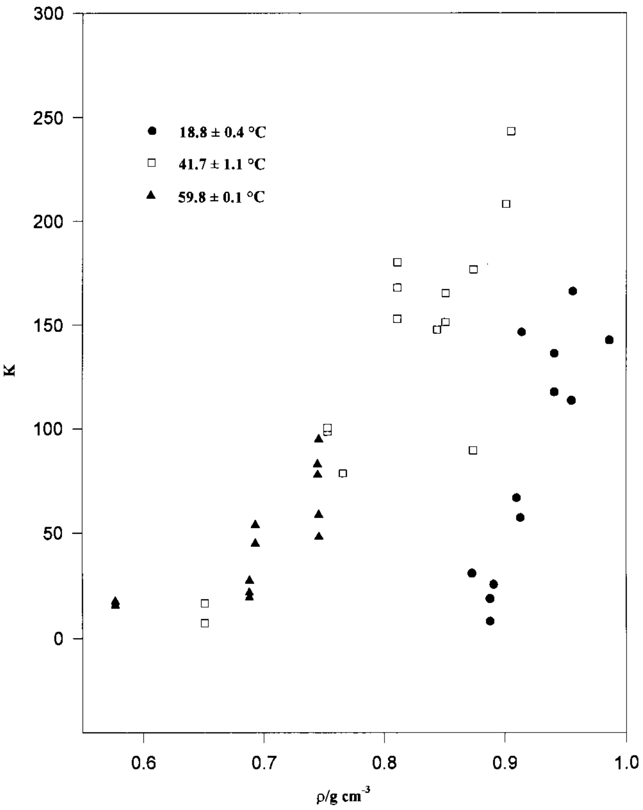

Figure 3. Distribution coefficient, *K*, as a function of density from water initially saturated with PCP.

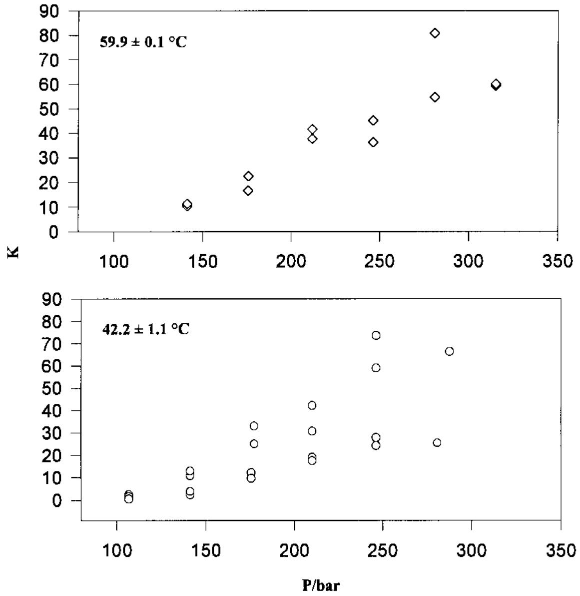

Figure 4. Distribution coefficient, *K*, for pentachlorophenol between water and CO_2 from dilute solution.

Table 2. Distribution Coefficient, *K*, of Pentachlorophenol between Dilute Solution (1.27 (±0.17) × 10^{-6} g/g Solvent) and Supercritical CO_2

P/bar	ρ/g cm^{-3}	K^a
	$T = (42.2 \pm 1.1)$ °C	
107	0.628	2.5
107	0.646	1.1 ± 0.5
141	0.762	8 ± 5
176	0.814	20 ± 10
210	0.848	30 ± 10
246	0.876	50 ± 20
281	0.903	26
288	0.907	66
	$T = (59.9 \pm 0.1)$ °C	
141	0.566	11 ± 1
176	0.683	20 ± 3
212	0.745	40 ± 2
246	0.788	41 ± 5
281	0.821	70 ± 10
315	0.848	60 ± 1

[a] Standard deviation included for results averaged from three or more trials; range included for results averaged from two trials; no uncertainty included for single trials.

$\{RT\mathrm{p}K_a\}$, the pK_a value drops from 4.8 to 4.2 over the temperature range studied. This results in approximately 6% pentachlorophenoxide anions in the water-rich phase at the extraction conditions of pH 3 and 59.8 °C. Pentachlorophenol will only partition to the CO_2-rich phase in its un-ionized form. A moderate increase in water pH also occurs from 18.8 to 59.8 °C (Toews et al., 1995) owing to the reduction of CO_2 solubility in water (Wiebe, 1941). The higher the pH, the greater the dissociation of acidic PCP. Although the amount of water in CO_2 coincidentally increases with temperature, making the CO_2-rich phase more polar and possibly a better solvent for PCP, solubility values remain minimal, between 0.1 and 0.3% v/v.

Figure 4 demonstrates the effect on partitioning of reducing the initial concentration of pentachlorophenol in the water to 1.27 ppm from 11.6 ppm. The lower concentration more closely resembles contamination levels in natural water sources. Partitioning to the CO_2-rich phase has become smaller at this concentration. Distribution coefficient values are included in Table 2. Interactions between water and PCP are easily disrupted as the presence of chlorine molecules on the solute in both ortho positions minimizes hydrogen bonding with surrounding water molecules. Solute–solute bonding between PCP molecules is likely to be more important in a more concentrated solution and may result in dimers that would have improved solubility in the CO_2-rich phase and would be less soluble in the polar water-rich phase. Pentachlorophenol will also more readily partition to the CO_2 as a

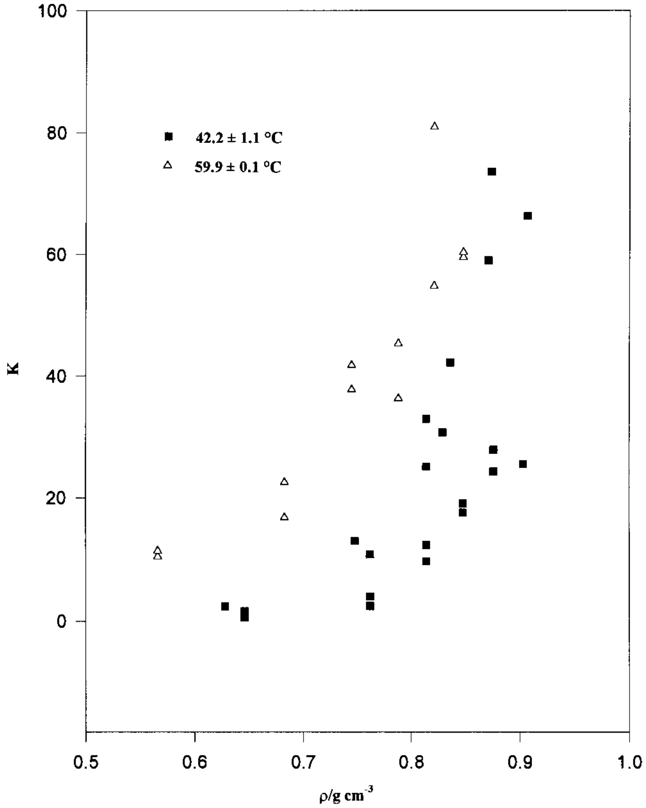

Figure 5. Distribution coefficient, *K*, as a function of density for PCP from dilute solution.

consequence of fewer and weaker solute−solvent (H_2O) interactions.

The partitioning of PCP from the dilute solution shows a greater dependence on temperature than that from PCP-saturated water. At constant pressure, partitioning is improved as temperature is increased from 42.2 to 59.9 °C. Figure 5 shows that over the CO_2 density range of about 0.60 to 0.85 g/mL the partitioning of PCP to the CO_2-rich phase is favored at the highest isotherm, 59.9 °C. As the solvent density increases along all isotherms, *K* shows a consistent increase on all plots at both concentrations owing to the improved solvating power of CO_2.

The mass balance of pentachlorophenol in both phases was determined by comparing the areas obtained for each fraction to the appropriate calibration curves. On-line HPLC analysis of the CO_2-rich fraction required calibration in water-saturated fluid as it was determined that at analytical concentrations a solvent effect on chromatography existed. Peak areas for the CO_2 standards were significantly greater than for standards prepared in either methanol or water. Chromatograms showed a positive absorbance for CO_2 immediately followed by a negative well, both of which preceded the solute peak. The mass balance calculation accounted for the volume of water removed from the cell at each pressure increment of an isotherm. Knowledge of the mole fraction of CO_2 in the water-rich phase (King et al., 1992; Wiebe and Gaddy, 1940; Wiebe, 1941) allowed for the determination of the volume of the aqueous solution according to the apparent molar volume of $CO_{2(aq)}$ (Hnedkovský et al., 1996). The average mass balances obtained were at or above 80% for all isotherms. Sampling problems were frequently encountered for the first few injections of the water-rich fraction at low pressures. The areas obtained were inordinately large and the points were excluded from the partitioning plots as *K* would be very small.

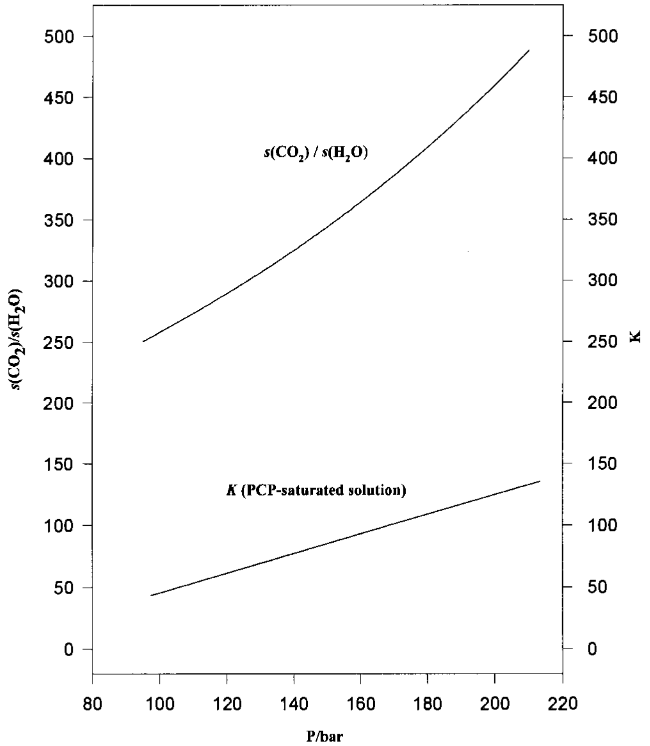

Figure 6. Comparison of the solubility ratio of PCP between CO_2 and water to the distribution coefficient, *K*, from water initially saturated with PCP.

Figure 6 compares the partitioning of pentachlorophenol from saturated solution at 18.8 °C to its solubility ratio between pure water and CO_2 at ambient temperature. To facilitate the comparison, the distribution line (*K*) was obtained by extrapolating the best fit line through the data points in Figure 2. Solubility data was previously determined in both phases as a function of pressure (Curren and Burk, 1997). Best fit lines were determined for each set of solubility data, and the quotient as a function of pressure was calculated. The upper solubility line is curved in Figure 6 as the solubility of PCP in water decreases with pressure owing to a positive volume change upon solution while the solubility in CO_2 is coincidentally increasing. The difference in the magnitude of the upper curve to the *K* line demonstrates the relevance of molecular interactions other than those involved in the solubilization of the pure solute in the pure phases. Specifically, the solute is being retained in the water-rich phase either through enhanced interactions in this phase, or there are interactions in the CO_2-rich phase that are less favorable. Potential interactions occurring in either phase with respect to pH and pK_a have already been discussed. The ionic strength of the water should be affected by the presence of carbonate ions, thus influencing the magnitude of ion−solute interactions. Hydrogen bonds between water and PCP in the CO_2-rich phase should also be relevant. Measurements of the ionic strength and dielectric constants of both phases will provide information on the dissociation of PCP and any dipolar interactions in either phase. Complete characterization of this system will enable the optimization of extraction parameters. Extractions with carbon dioxide can then be shown to be viable alternative methodologies to existing technologies.

Conclusions

The determination of the distribution coefficient of pentachlorophenol between water and CO_2 from saturated

(11.6 ppm) solution at (18.8, 41.7, and 59.8) °C as a function of pressure indicates that in this temperature range solute partitioning is improved at the lower temperatures. However, temperature has a positive effect on the partitioning of PCP to the CO_2-rich phase from dilute solution (1.27 ppm). Partitioning is improved as the temperature is increased from (42.2 to 59.9) °C. Solute partitioning increases along all isotherms as a function of increasing pressure owing the greater solvating power of CO_2. Relevant interactions exist in the water-rich phase that enhance partitioning of PCP from saturated solution, as shown by higher values in K when compared to the dilute system.

A comparison of the partitioning of PCP at the lowest isotherm from saturated solution to its solubility ratio between the pure phases suggests interactions exist that are only relevant when the two phases come into contact. This is evidenced by retention of the solute in the water-rich phase during partitioning experiments, giving K values lower than those predicted by the solubility ratio. It is necessary to determine the ratio of pentachlorophenol solubility in water-saturated CO_2 and CO_2-saturated water to resolve the difference and provide a more complete understanding of this complex system.

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