

Partition Coefficients of Environmentally Important Phenols in a Supercritical Carbon Dioxide–Water System from Cocurrent Extraction without Analysis of the Compressible Phase

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Partition coefficients of phenol, salicylic acid, and several environmentally important chloro- and nitrophenols in a supercritical CO₂–water system were measured using direct cocurrent extraction of aqueous solutions of the individual solutes with CO₂. Partitioning data on the nitrophenols and salicylic acid were obtained for the first time. To bypass the troublesome and error-prone analysis of the CO₂-rich phase, the present method employed only the solute concentrations in the aqueous phase before and after extraction to determine the partition coefficient. Unlike most previous engineering studies of phenol partitioning in a CO₂–water system, the concentrations of phenolic solutes approached infinite dilution in both phases. This makes the results relevant to analytical-scale SFE of environmental water samples with CO₂. Because of effective infinite dilution of the solutes, the partition coefficients provide a direct measure of relative CO₂-philicity/hydrophilicity of the individual phenols. Compared to the octanol–water partition coefficients of substituted phenols, the CO₂–water partition coefficients are more sensitive to substitution in the position neighboring the hydroxyl group.

Supercritical fluid extraction (SFE) is now well established in both its laboratory-scale and process-scale facets, benefiting from nontoxicity, environmental compatibility, handling safety, and affordable price of carbon dioxide, by far the most common extraction fluid. In analytical separations, SFE serves as a sample treatment technique to release low-volatility organic analytes from the sample matrix prior to subsequent quantitation performed by chromatographic methods. Within the last two decades, the initial emphasis on SFE of solid matrixes (soils, sludges, etc.) has increasingly been complemented by SFE of aqueous samples. The direct SFE of water-based matrixes has been assisted by low mutual solubility of water and CO₂ in the relevant region of temperature and pressure.^{1,2} The initial investigations into direct SFE of aqueous media were driven by the potential use of the

technique for environmental remediation by wastewater treatment.^{3,4} After the introductory tests of feasibility of the technique,^{5–7} analytical-scale SFE of aqueous media was applied to diverse classes of analytes, e.g., polycyclic aromatic hydrocarbons,⁸ pesticides,^{9,10} acidic pollutants,¹¹ nonionic surfactants,¹² steroids,¹³ pharmaceuticals,¹⁴ and metal–ligand complexes.^{15–17} Attention was paid to pH of the aqueous phase in a CO₂–water system at elevated temperatures and pressures¹⁸ and to the effect of pH on the recoveries of protic analytes from aqueous samples. It appears that the formation of carbonic acid in the aqueous phase may assist the extraction of acidic analytes¹⁹ and complicate the extraction of bases.²⁰ A short review of analytical-scale SFE of aqueous media is also available.²¹ In parallel with the work on analytical separations, extensive efforts were devoted to the background developments for process-scale SFE of aqueous media. In particular, phase equilibrium studies were carried out on solute partition coefficients

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(K values) between the aqueous and the gaseous phases. A large part of these studies were focused on phenol^{22–30} and chlorinated phenols^{25–27,31,32} although other types of solutes such as aromatic hydrocarbons,³³ chlorinated ethanes,³⁴ cyclic alcohols,²⁹ and organic amphiphiles³⁵ were also studied. Mutual cosolvency effects of multiple solutes were explored as functions of chemical diversity and relative concentrations of the solutes in the aqueous phase.^{26,29,33,35} Most of the phase equilibrium studies were performed to model process streams, and consequently, they employed rather high initial concentrations of solutes in the aqueous phase, sometimes approaching the saturation limit.^{22–25}

The purpose of the present work was to obtain new partitioning data that would be more relevant to analytical-scale SFE of environmental water samples. Therefore, the selection of solutes includes several chloro- and nitrophenols known as long-lived pollutants occurring in industrial effluents. To provide a realistic model of environmental water samples, the initial concentrations of individual solutes in the aqueous phase have to be very low. Expediency of such partitioning data for analytical-scale SFE consists of the possibility of extracting a large volume of an aqueous sample with supercritical CO₂ trapping and quantifying the extracted solutes after decompression of CO₂, and then using the partition coefficients for back-calculation of the amounts of solutes in the sample. Further, at very low concentrations of the solutes in typical samples of environmental water, the mutual effects on partition coefficients among the individual solutes are likely to be dampened although they may occur at higher concentrations of the solutes.^{26,29} Therefore, the partition coefficients obtained from single-solute measurements may still be useful for the purpose mentioned above.

Most previous studies on partitioning of low-volatility solutes between water and CO₂ employed continuous-flow methods with analysis of both phases to close the solute material balance. It should be noted that analysis of the compressed (and compressible), CO₂-rich phase may suffer from difficulties such as an incomplete trapping of the solute after decompression of the fluid solution or adverse effects of CO₂ on the detector response in a direct analysis of the high-pressure fluid solution by HPLC.³¹ These problems become even more serious at very low concentrations of the solute. The method used here is based on direct cocurrent extraction of a dilute aqueous solution with CO₂. To

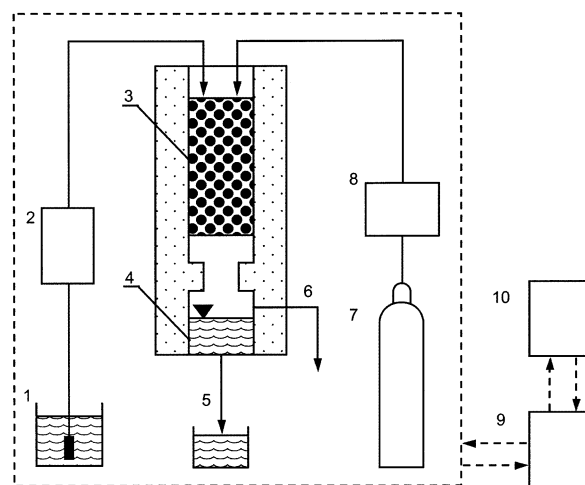


Figure 1. Schematic diagram of the extraction cell and the phase separator: 1, aqueous-phase reservoir; 2, aqueous-phase pump; 3, extraction column; 4, phase separator; 5, aqueous-phase restrictor; 6, CO₂-rich phase restrictor; 7, CO₂ cylinder; 8, liquid CO₂ pump; 9, control unit; 10, PC for input and display of operating parameters.

bypass the error-prone analysis of the CO₂-rich phase, the present method employs only the solute concentrations in the aqueous phase before and after extraction to determine the partition coefficient.

Naturally, application of our method has been qualified by the preconditions that the instrument operates within the regime of steady-state extraction and that the steady-state concentration of the solute in the aqueous effluent corresponds to equilibrium concentration.

EXPERIMENTAL SECTION

Apparatus Design. Figure 1 shows a schematic diagram of the essential part of the experimental setup for cocurrent extraction. The extraction column (i.d. 16 mm, internal length 191 mm) was mounted in a vertical position atop the phase separator (i.d. 16 mm, internal length 65 mm). Both parts were machined from stainless steel. The aqueous feed and the stream of pure CO₂ entered the column at the top and flowed down through the column packing. Preliminary tests of diverse packings of the extraction column revealed that the best efficiency was provided by spirals (o.d. 2.6 mm, length 2.3 mm) tightly wound from 0.3-mm-diameter, stainless steel wire. This packing was used in all experiments reported below. The void volume of the extraction column was 66% of the total volume. The lower end of the column was fitted with a 0.5-mm-thick perforated sheet of stainless steel to retain the packing within the column. The phase separator, an empty (i.e., not packed) cylindrical vessel, served to split the two-phase outflow from the extraction column into separate streams of the aqueous phase and the compressed gas. Because of its higher density at the operating conditions employed here, the aqueous phase collected at the bottom of the phase separator. The phase separator body contained three liquid-level sensors mounted at different vertical positions. The sensors were formed by contact wires housed in nonwetted PEEK tubing for insulation, and they utilized the different electrical conductivities of the aqueous and the gas phases for their operation; the phase separator body worked as a counter electrode. The lower and the

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upper sensors functioned as safety limits whereas the middle sensor served for a precise adjustment of the liquid level in the separator. The corresponding volume of bulk liquid at the bottom of phase separator was 5 mL. The temperature of the extraction column and the phase separator was controlled to ± 0.5 K.

The aqueous feed and CO₂ were delivered to the top of the extraction column by a pair of reciprocating pumps (model PU-980, Jasco Corp., Tokyo, Japan). Both pumps were controlled by a single control unit connected to a PC through an RS-232C interface. The control unit also served to adjust the pressure and the temperatures of extraction column and phase separator and to maintain the liquid level in the phase separator. The PC was used just for input and display of the operating parameters. The aqueous-feed pump was operated in constant-flow mode to provide flow rates ranging from 0.25 to 10.0 mL/min. The CO₂ pump was operated in constant-pressure mode with the pressure controlled to ± 0.05 MPa. To secure a steady flow of liquid CO₂, the pump head was fitted with a cooling jacket and cooled to 5 °C by circulating water from an external cryostatic bath (model LT D6/20, Grant Instruments Ltd., Barrington, Cambridge, U.K.).

The CO₂-rich effluent exited from the phase separator through a fused-silica capillary restrictor. Typical dimensions of the restrictor were 65-cm length and 75- μ m i.d. The aqueous effluent eluted from the phase separator through a 40-cm piece of 200- μ m-i.d. fused-silica tubing with an on-column UV detection cell created by stripping off the polyimide coating. The outlet of the detection tubing was connected to the fused-silica capillary restrictor with a typical length of 25 cm and 50- μ m i.d. Determination of the partition coefficient of a solute comprised measurements at different relative flow rates of the aqueous and the CO₂-rich effluents (see the Results and Discussion section below). The different relative flow rates were realized by a suitable selection of both restrictors or by successive cutting of the aqueous-phase restrictor while the CO₂ restrictor was kept fixed.

Solute concentrations in the aqueous effluent were determined on-line by a UV spectrophotometric detector equipped with a capillary flow cell (model SpectraFocus, Thermo Separation Products, Inc., Fremont, CA). The detection was carried out at the wavelength of the absorption maximum of the respective solute. In addition to on-line detection, off-line arrangement of solute detection was also tested by employing salicylic acid, and all results for this solute refer to the off-line arrangement. After degassing the aqueous effluent in an ultrasonic bath and adding a proper reagent (54 mg of FeCl₃·6H₂O, 10 mL of acetic acid, and water to 100 mL), the concentration of the complex of salicylic acid with Fe³⁺ was measured at 530 nm by employing a VIS spectrophotometer (model Spekol 11, Carl Zeiss, Jena, Germany).

The time-averaged flow rate of the aqueous phase was derived from the volume of outgassed aqueous effluent collected at ambient pressure in a graduated cylinder. The time-averaged flow rate of the CO₂-rich phase was measured after expansion and thermal equilibration of the gas by a wet gas meter (model G01, Spektrum s. r. o., Skuteč, Czech Republic), employing water as a working fluid. Typical flow rates of the aqueous phase were within 0.25–2.0 mL/min, and typical flow rates of the CO₂-rich phase at the temperature and pressure of the extraction column ranged within 0.3–4.0 mL/min. Considering the low volumetric flow rates and the large free cross section of the extraction column (~ 1.3

cm²), the pressure drop across the column could be considered negligible.

Reagents. Carbon dioxide (purity >99.99 mol %) was supplied by SIAD s. r. o. (Braňany u Mostu, Czech Republic). Water was redistilled prior to use. Salicylic (2-hydroxybenzoic) acid (purity >99 mol %) was supplied by Sigma-Aldrich s. r. o. (Prague, Czech Republic) and used as received. Phenol, 2-nitrophenol, 4-nitrophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 3-methyl-4-chlorophenol, 2,4-dimethylphenol, and 2-methyl-4,6-dinitrophenol were taken from the EPA 604-N Phenols Kit (Supelco, Sigma-Aldrich s. r. o.).

Procedure. Stock solutions (100 mg/L) of the individual solutes were prepared in redistilled water. In salicylic acid, the concentration of the stock solution was 10 mg/L. Before the measurements with a solute, the stock solution was degassed in an ultrasonic bath, and the wavelength of the absorption maximum and absorbance of the solution were checked. The apparatus was started up with distilled water in the aqueous-phase reservoir. After stabilization of the operating parameters, distilled water was replaced with the proper stock solution, and response data acquisition was started at the rate of 10 entries/s.

The time needed to reach the steady state ranged from 30 min to 3 h, depending largely on the flow rate of the aqueous phase. The partition coefficients of salicylic acid and phenol were measured at temperatures within 313–363 K (40–90 °C) and pressures within 15–30 MPa. The partition coefficients of the other phenolic solutes were measured at 333–353 K (60–80 °C) and 20 MPa.

RESULTS AND DISCUSSION

Steady-State Extraction and Solute Partition Coefficients.

After entering the extraction column, the solute, water, and CO₂ start to partition between the aqueous phase and the CO₂-rich phase toward equilibrium distribution. When the extraction column reaches a steady state, the sum of solute masses in the aqueous and the CO₂-rich phases in every cross section of the column remains constant. The solute distribution in each phase along the column axis is governed by the balance between convection and solute mass transfer. The solute concentrations at the end of a sufficiently long and efficient column may be expected to be close to equilibrium values. The overall solute mass balance of the extraction column may be written as

$$F_1^L x_1 = F_2^L x_2 + F_2^G y_2 \quad (1)$$

where F^L and F^G are molar flow rates of the aqueous and the CO₂-rich phase, x and y are mole fractions of the solute in the aqueous and the CO₂-rich phase, and subscripts 1 and 2 refer to the inlet and the outlet of the extraction column, respectively. It should be noted that because of partitioning of water and CO₂ between the liquid phase and the compressed gas, the molar flow rates F_1^L and F_2^L are not the same. Assuming an equilibrium distribution of the solute between the two phases at the column outlet,

$$y_2 = Kx_2 \quad (2)$$

where K is the partition coefficient of the solute. The mole fraction-based form of the partition coefficient is preferred here to the

molar concentration-based form although the latter has been conventional in analytical chemistry. The reason is that, in compressible or near-critical mixtures, changes in temperature or pressure can induce large changes in density or molar volume. Therefore, the molar concentration is not a suitable composition variable in such mixtures because it varies with temperature or pressure even when no change in composition occurs. If the mole fractions of the solute in both phases are very low, an effective state of infinite dilution of the solute in both phases can be assumed, and the solute partition coefficient can be considered to be invariant with respect to both x_2 and y_2 . Then, substituting for y_2 in eq 1 from eq 2, one obtains

$$\frac{x_2}{x_1 - (F_2^L/F_1^L)x_2} = \frac{1}{K} \frac{F_1^L}{F_2^G} \quad (3)$$

Provided that the preconditions mentioned above are fulfilled, eq 3 suggests that cocurrent extraction can be used to measure the solute partition coefficient without the need to determine y_2 , i.e., without the need for troublesome analysis of the compressed, CO₂-rich phase. To determine the partition coefficient of a solute at a particular temperature and pressure, the extraction column was allowed to reach the steady state in several separate runs with different relative flow rates F_1^L/F_2^G as set by a proper choice of the outlet restrictors. The values of the left-hand side of eq 3 were then plotted against the respective relative flow rates F_1^L/F_2^G , and the solute partition coefficient was determined from the slope of the plot. The molar flow rates F_1^L , F_2^L , and F_2^G were obtained from the rates measured at ambient conditions by employing high-pressure mutual solubilities of water and CO₂.¹ In the temperature and pressure range of our measurements, the mole fraction solubility of CO₂ in water is ~ 0.023 , and the mole fraction solubility of water in CO₂ is ~ 0.007 . The value of F_2^G was also corrected for saturation of the gas stream with water vapor in the wet gas meter at ambient conditions. The equation of state (EOS) published by Ely et al.³⁶ was employed to describe the PVT behavior of pure CO₂.

Approach to the Steady State. Figure 2 shows examples of the time courses of detector response in three runs with phenol. The shapes of the time profiles suggest that, to a first approximation, the system behaves as an exponential mixer with a transportation delay. The term "transportation delay" refers to the flow rate-dependent time to onset of nonzero response of the detector. The time is needed to transport the solute through the system from the aqueous-phase reservoir to the detection cell. Figure 2 indicates that the time period required to reach the steady state varies strongly with the flow rate of the aqueous phase. Therefore, the time profiles are largely a result of an exponential washout of the initially solute-free liquid at the bottom of the phase separator by solute-containing effluent from the extraction column. This finding is also supported by the shape of the lower curve pertaining to the smallest flow rate of the aqueous phase. The pulsations in the curve may reflect perturbations caused by individual drops of the liquid dripping from the lower end of the extraction column into the phase separator. The decreasing

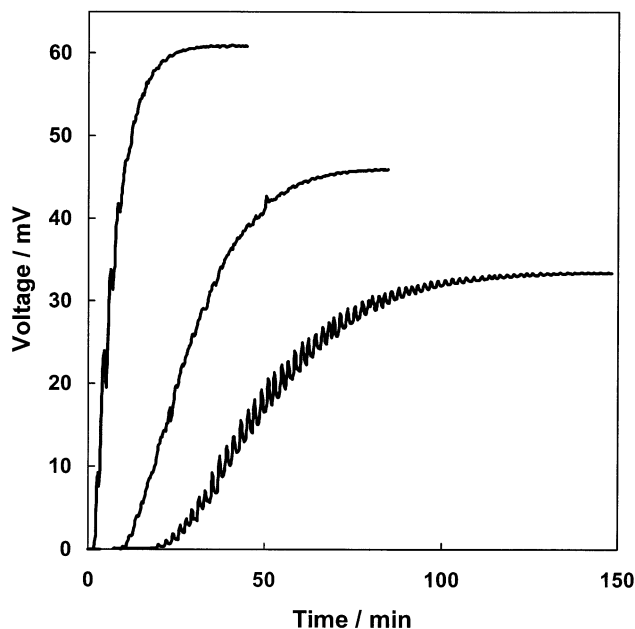


Figure 2. Time courses of the detector response (output voltage) in three runs with phenol at 333 K and 20 MPa. Upper curve: $F_1^L = 0.121$ mol/min, $F_1^G = 0.0284$ mol/min. Middle curve: $F_1^L = 0.0322$ mol/min, $F_1^G = 0.0232$ mol/min. Lower curve: $F_1^L = 0.0167$ mol/min, $F_1^G = 0.0284$ mol/min.

amplitude of the perturbations at longer extraction times reflects the gradual reduction in the composition difference between the liquid eluting from the column and the liquid exiting from the phase separator. At the steady state, the composition difference disappears.

Precision of Measurement. The present method relies on an accurate determination of the solute mole fraction x_2 in the aqueous effluent. Further, the functional form of eq 3 suggests that precision of the method will vary with the magnitude of the particular partition coefficient and with the flow rates employed. A detailed analysis of eq 3 shows clearly that the method is not suitable for either extremely hydrophilic solutes ($K \rightarrow 0$) or extremely hydrophobic solutes ($K \rightarrow \infty$) because, in these limiting cases, the resultant partition coefficient becomes highly sensitive to errors in the determination of x_2 . The sensitivity of $\log K$ to errors in the determination of x_2 is minimum if

$$K = F_2^L/F_2^G (\approx F_1^L/F_2^G) \quad (4)$$

Equation 4 provides an approximate guide for selecting an appropriate range of relative flow rates F_1^L/F_2^G when a partition coefficient of a particular expected value (see below) is being measured.

In addition to uncertainty in the determination of x_2 , the partition coefficients are also subject to errors caused by fluctuations in temperature, pressure, and flow rates of both phases. Reproducibility of the method was tested with salicylic acid and 2,4,6-trichlorophenol. In salicylic acid, representing relatively hydrophilic solutes, reproducibility was within $\pm 2\%$. In more hydrophobic 2,4,6-trichlorophenol, reproducibility dropped to $\pm 4\%$.

Flow Rate Range for Determination of the Solute Partition Coefficients. The proper range of the relative flow rates F_1^L/F_2^G

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Table 1. Partition Coefficients of Phenol and Salicylic Acid in a CO₂–Water System

temp/K	solute	pressure/MPa			
		15	20	25	30
313	phenol	1.10	1.31	1.35	1.36
	salicylic acid	0.24	0.32	0.40	0.41
323	phenol	0.92	1.13	1.36	1.42
	salicylic acid	0.17	0.27	0.38	0.39
333	phenol	0.85	1.26	1.60	1.73
	salicylic acid	0.12	0.21	0.33	0.38
343	phenol	0.76	1.27	1.53	1.67
	salicylic acid	0.08	0.17	0.30	0.37
353	phenol	0.63	1.06	1.43	1.58
	salicylic acid	0.04	0.14	0.26	0.35
363	phenol	0.53	0.99	1.37	1.61
	salicylic acid		0.10	0.21	0.31

should be selected to include the expected value of K according to eq 4. In relatively hydrophilic solutes with $K \approx 1$, the measurements were carried out at the relative flow rates F_1^L/F_2^G below 3. In more hydrophobic solutes, the flow rate range only extended up to $F_1^L/F_2^G \approx 10$ because, for apparatus reasons, it was difficult to stabilize low flow rates of CO₂ needed to reach higher values of F_1^L/F_2^G . Linearity of the plots based on eq 3 was usually very good.

Concentration Dependence of the Solute Partition Coefficient. In an individual solute, measurements of partition coefficients were carried out with a single stock solution. The only exception was phenol, where the results obtained with the 100 mg/L solution were checked by limited measurements with a 10 mg/L solution. No significant differences were found between the partition coefficients resulting from both stock solutions. In a 100 mg/L solution, the mole fraction (x_1) of phenol is 1.92×10^{-5} and the mole fraction of 2-methyl-4,6-dinitrophenol is 9.12×10^{-6} , with the values for the other solutes ranging in between. Therefore, if the operating temperature and pressure are well removed from the vapor–liquid critical point of any component of the system, the solute can be considered to be infinitely dilute in both phases.

Solute Partition Coefficients as Functions of Temperature and Pressure. Table 1 lists the partition coefficients of phenol and salicylic acid. There are no literature data on partition coefficients of salicylic acid in a CO₂–water system, but there have been numerous studies of the partition coefficients of phenol. A comparison of the previous and the present results on phenol at 323 K is shown in Figure 3. The literature data were obtained using either a flow apparatus^{24,27} or a high-pressure static equilibrium cell²⁸ with phenol concentration in the aqueous feed ranging from 1% (w/w)^{27,28} to 8% (w/w).²⁴ A high concentration of phenol in the aqueous feed appears to increase the partition coefficient.²⁴ However, large differences in the literature results^{27,28} obtained with 1% (w/w) solutions of phenol make it difficult to identify a clear-cut trend in the partition coefficient at lower concentrations. The present results pertaining to an even lower concentration of phenol in the aqueous feed (0.01% w/w) are relatively close to the data of Brudi et al.²⁸ This is consistent with the findings by Brudi et al.²⁸ and by us that the partition coefficient of phenol at 323 K is essentially independent of concentration.

Substituent Effects on the Partition Coefficients of Phenols. Table 2 shows the partition coefficients of several substituted

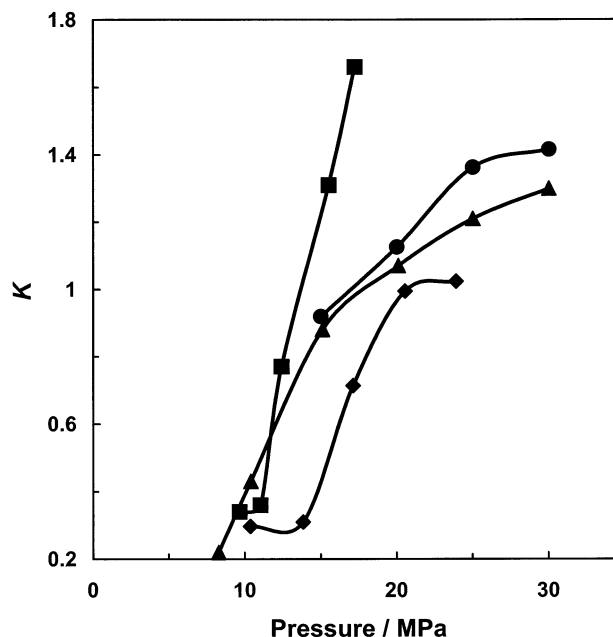


Figure 3. Partition coefficients of phenol at 323 K. (●) this work; (■) ref 24; (◆) ref 27; (▲) ref 28.

Table 2. Effects of Substituents and Temperature on the Partition Coefficients of Phenols at 20 MPa

solute	temperature/K			K_{333}/K_{353}
	333	343	353	
phenol	1.26	1.27	1.06	1.2
salicylic acid	0.21	0.17	0.14	1.5
2-nitrophenol	72	43	30	2.4
4-nitrophenol	0.18	0.17	0.16	1.2
2-chlorophenol	13	10	8.4	1.5
2,4-dichlorophenol	67	23	17	4.0
2,4,6-trichlorophenol	145	68	46	3.2
3-methyl-4-chlorophenol	5.9	4.8	3.8	1.6
2,4-dimethylphenol	10	8.8	7.5	1.4
2-methyl-4,6-dinitrophenol	55	36	21	2.7

phenols at 333–353 K and 20 MPa. In all solutes, with a possible exception of phenol, the partition coefficients decrease with increasing temperature, suggesting a decrease in solvent power of the CO₂-rich phase relative to the aqueous phase. The last column in Table 2 indicates that the effect of temperature is more important in less hydrophilic solutes. At the three temperatures shown in Table 2, the solute-to-solute patterns in the partition coefficients are the same. Because of the importance of CO₂–water cosolvency effects, hydrogen bonding, and acid–base interactions in the present systems, a detailed thermodynamic analysis of the partition coefficients is beyond the scope of this contribution. Instead, a qualitative discussion of the substituent effects will be given here, and the relationship between the CO₂–water partition coefficients and the octanol–water partition coefficients of the solutes will be discussed.

Considering an effective infinite dilution of a solute in both phases, the CO₂–water partition coefficient provides a direct measure of the relative CO₂-philicity/hydrophilicity of the solute at the particular temperature and pressure, and the solute-to-solute differences can be interpreted in terms of solute molecular structure and solute–solvent interactions. Because of the electron-

drawing effect of the nitro group on the hydroxyl group, 4-nitrophenol appears to be even more hydrophilic than salicylic (2-hydroxybenzoic) acid. Intermolecular hydrogen bonds between water molecules and oxygen atoms of the nitro group may also contribute to the hydrophilicity of 4-nitrophenol. In salicylic acid, the intramolecular hydrogen bond between the hydroxyl and carboxyl groups detracts from hydrophilicity. Compared to the 4-isomer, 2-nitrophenol is less hydrophilic, both because of the intramolecular hydrogen bond between the hydroxyl and nitro groups and because of steric hindrance of the dissociable proton by the nitro group. The clear trend in the partition coefficients when going from 2-chlorophenol through 2,4-dichlorophenol to 2,4,6-trichlorophenol reflects the fact that increasing chlorine substitution makes the molecule more bulky, more polarizable, and more apt for interaction with carbon dioxide molecules through dispersion forces. The hydrophilic effect of the hydroxyl group seems dampened by steric hindrance and by a weak intramolecular hydrogen bond to the chlorine atom in the ortho position. The partition coefficients of 3-methyl-4-chlorophenol and 2,4-dimethylphenol primarily reflect the enhanced polarizabilities of these molecules as compared to phenol. In 2,4-dimethylphenol, steric hindrance of the dissociable proton by the neighboring methyl group can also be important. The partition coefficient of 2-methyl-4,6-dinitrophenol seems to be an outcome of all the features mentioned above—intra- and intermolecular hydrogen bonding, steric hindrance, and increased polarizability as compared to phenol.

In environmental and pharmaceutical sciences, hydrophilicity of substances has often been measured by 1-octanol–water partition coefficients, K_{ow} . For the solutes of this study, Figure 4 shows the relationship between the CO_2 –water partition coefficients (333 K, 20 MPa) and the octanol–water partition coefficients at ambient conditions.^{37,38} Except for salicylic acid containing two dissociable protons, all other ortho-substituted phenols are located in the upper part of the plot ($\log K \geq 1$). Along the x-axis of the plot, no distinction between the ortho-substituted and the other phenols is apparent. Therefore, compared to octanol–water partition coefficients, the CO_2 –water partition coefficients are much more sensitive to the effects of the neighboring substituent on the hydroxyl group. This finding is well illustrated by the two isomers of nitrophenol. The difference in $\log K$ values between 2- and 4-nitrophenol is 2.6 whereas the difference in $\log K_{ow}$ values is only -0.12 . The cause of the diverse solute-to-solute patterns in both sets of partition coefficients consists of different chances for solute–solvent hydrogen bonding in nonaqueous phases of the two partitioning systems. Unlike CO_2 , 1-octanol can form hydrogen bonds with phenols. Further, it is well known that, at ambient conditions, there is about one water molecule for every four 1-octanol molecules in water-saturated 1-octanol. On the contrary, the mole fraction solubility of water in CO_2 at 333 K and 20 MPa is only ~ 0.007 .¹ Therefore, as regards the possibility of forming solute–solvent hydrogen bonds, the coexisting phases in 1-octanol–water system are more similar to each other than the coexisting phases in the CO_2 –water system. Consequently, the CO_2 –water partition coefficients are more sensitive to substituent effects on hydrogen bonds because, in the 1-octanol–

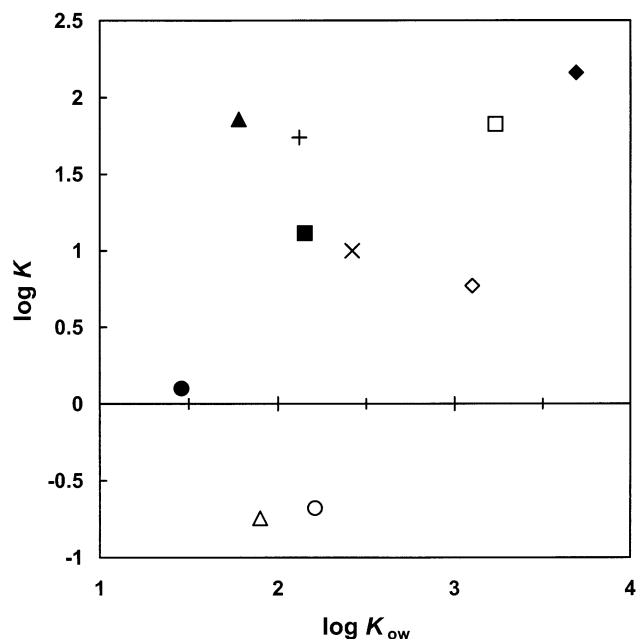


Figure 4. CO_2 –water partition coefficients at 333 K and 20 MPa versus octanol–water partition coefficients at ambient conditions:^{37,38} (●) phenol; (○) salicylic acid; (▲) 2-nitrophenol; (△) 4-nitrophenol; (■) 2-chlorophenol; (□) 2,4-dichlorophenol; (◆) 2,4,6-trichlorophenol; (◇) 3-methyl-4-chlorophenol; (×) 2,4-dimethylphenol; (+) 2-methyl-4,6-dinitrophenol.

water system, the effects on hydrogen bonds partly compensate between the coexisting phases.

CONCLUSIONS

A novel apparatus for dynamic extraction of aqueous media with supercritical carbon dioxide has been described and used to measure the CO_2 –water partition coefficients of several substituted phenols. With a judicious selection of flow rates of both phases, the apparatus can provide reasonable values of the partition coefficients of low-volatility solutes in a CO_2 –water system without the need for analysis of the compressed, CO_2 -rich effluent. Relative values of partition coefficients of substituted phenols conform to expectations based on substituent effects, steric effects, and effects of inter- and intramolecular hydrogen bonds. Compared to partitioning of phenols in the 1-octanol–water system, the partitioning in the CO_2 –water system appears to be more selective with respect to ortho-substituted phenols. The explanation for this finding comes from the different relative chances for phenols to form solute–solvent hydrogen bonds in nonaqueous phases of the 1-octanol–water and the CO_2 –water systems.

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