Supercritical CO_2 Extraction of Organic Contaminants from Aqueous Streams

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Supercritical fluid extraction (SCFE) for the removal of organic toxins from water has been studied using a continuous-flow view cell system. Distribution coefficients (ratio of mole fraction of contaminant in supercritical CO_2 to mole fraction in the aqueous phase at equilibrium) have been determined for a homologous series of contaminants as individual components in pure water: benzene, phenol, p-chlorophenol, and m-cresol. Data were obtained at two temperatures (313 and 323 K) and over a pressure range of 9.65 to 17.23 MPa for each contaminant. The distribution coefficients of the contaminants follow a pattern that can be explained in terms of molecular interactions both with water in the aqueous phase (as quantified by the pure contaminant solubility in water) and with CO_2 in the SCF phase (as quantified by the pure contaminant solubility in near-critical CO_2 and crossover phenomena in SCF CO_2). These results have been accurately modeled using a hard-sphere, perturbation-theory-based Carnahan-Starling-DeSantis-Redlich-Kwong equation of state and simple van der Waals mixing rules.

Introduction

Supercritical fluid extraction (SCFE) is a unit operation, in which a supercritical fluid (SCF), a substance above its critical temperature and pressure, is used to preferentially solubilize specific components from a mixture containing low-vapor-pressure compounds. SCFE, in recent years, has attracted attention because of the increased extraction efficiency it sometimes provides over liquid-liquid extraction. The fluid density of SCFs (and hence solvent properties) can be varied from gas-like to liquid-like with relatively small changes in pressure.

Research on the use of SCF solvents as extraction media has intensified in recent years. The use of SCF solvents has been investigated for coal liquid extraction (Vasilakos et al., 1985), enhanced oil recovery, supercritical fluid chromatography, and extraction of essential oils, flavors and other natural products (McHugh and Krukonis, 1986; Paulaitis et al., 1983). However, few of these applications have reached the commercial stage. Applications that have been commercialized so far include propane deasphalting, extraction of edible oils, tertiary oil recovery with CO_2, decaffeination of coffee beans with CO_2, and hydrothermal manufacture of quartz (Modell, 1987).

A major factor limiting the commercial success of SCF extraction is the lack of reliable data for the design of the extraction units. Research involving SCFE has concentrated primarily on obtaining equilibrium solubilities of ambient-temperature solids in supercritical solvents (Paulaitis et al., 1983). For other solid and liquid systems, fewer studies are reported (Panagiotopoulos and Reid, 1986; Traub and Stephan, 1990), and virtually nothing is known about the extraction of organics from aqueous solutions.

SCFE can help remove toxins from soils and groundwaters (Groves et al., 1985; Brady et al., 1987; Dooley et al., 1987; Roop et al., 1988, 1989a,b; Ghonasgi et al., 1991); it is particularly useful in reducing the volume of toxins to be handled, which can then be destroyed through combustion or biodegradation.

The aim of this article is to provide data showing the effectiveness of supercritical CO_2 in removing contaminants from water. Benzene and substituted benzenes have been chosen for the study, because they themselves are common pollutants in aqueous streams, are chemically similar to many other common pollutants, and pure component solubilities in CO_2 are available for these compounds. Here, we report experimental vapor-liquid equilibria for CO_2 with benzene/water, phenol/water, *m*-cresol/water, and *p*-chlorophenol/water systems. We also model these data using a perturbation-theory-based equation of state (EOS). This EOS employs the closed form, hard-sphere

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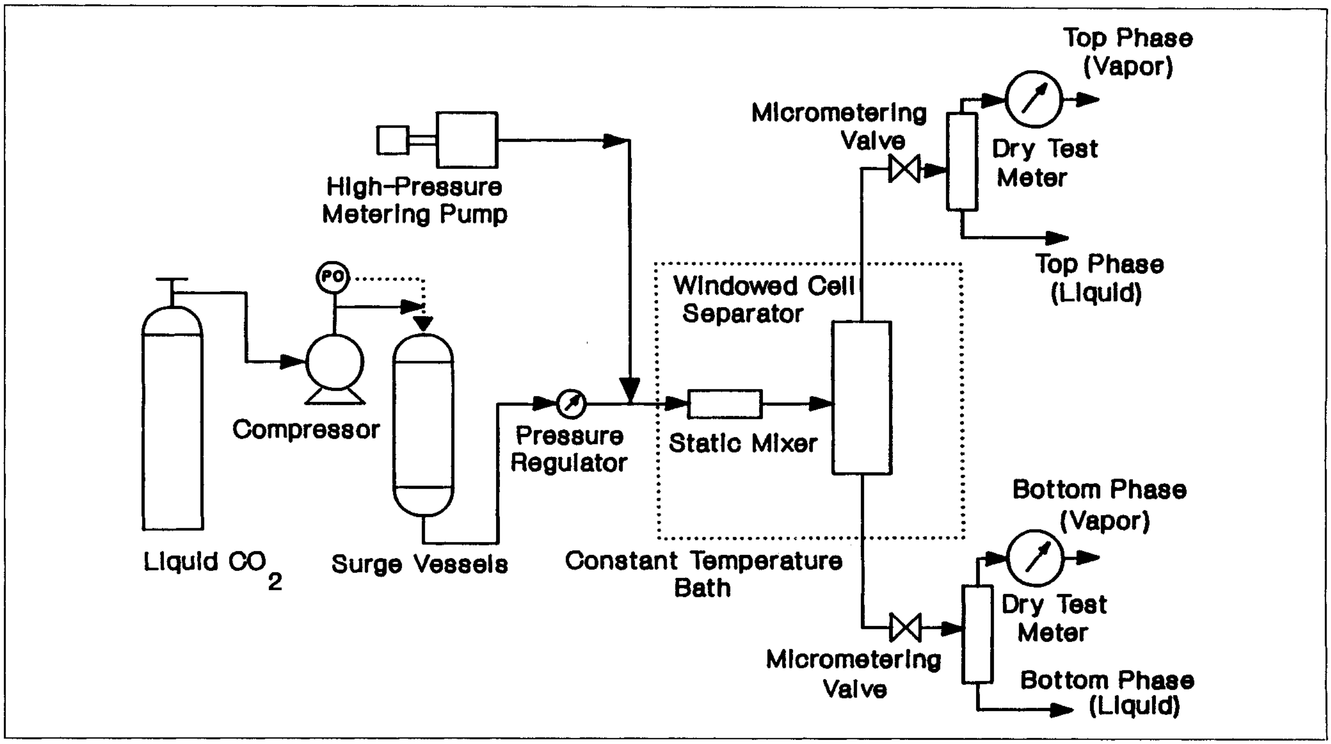

Figure 1. Supercritical fluid-liquid equilibrium apparatus.

equation of Carnahan and Starling (1969, 1972). The attractive term in this EOS is similar to the attractive term in the Redlich-Kwong EOS, as previously utilized by DeSantis et al. (1976).

Experimental Methods: Apparatus and Analysis

A continuous-flow apparatus was constructed for measuring phase equilibria in systems containing containing liquids and supercritical fluids. The flow cell concept was pioneered by Simnick et al. (1977).

Our experimental apparatus is similar to that of Radosz (1987), as shown in Figure 1. Liquid CO_2 (Liquid Carbonic, 99.9%) is fed by a diaphragm compressor (Superpressure 46-13421) and compressed to a pressure between 200 and 350 bar. The compressed CO_2 is then stored in surge tanks to dampen any pressure fluctuations. From the surge tanks, the CO_2 flows at ~0.7 g/s to a 21 element static mixer (Komax, model 250-021), where the pressure is controlled by a Tescom regulator (model 44-1124) to ±0.4 bar. The pressure in the static mixer is monitored by a Heise digital pressure gauge (model 710A). The liquid phase is delivered by a Ruska high-pressure metering pump (model 2252-BI). The concentrations of the contaminants fed, along with their solubilities in water, are given in Table 1. The CO_2, contaminant and water attain equilibrium in the static mixer; a second mixer can be added to verify equilibrium. A 30-cm^3 windowed cell (Jerguson 15-7-20) with de-entrainer section serves as the high-pressure separator and makes it possible to visually observe phase separation. The apparatus was tested for pressure drop using an Omega pressure transducer (model PK 301-4) downstream from the cell. Negligible pressure drop was observed. Downstream of the cell, two micrometering valves (Autoclave 30VRMM-4812), one for the SCF and one for the liquid phase, reduce the pressure to atmospheric, separating each phase into vapor and liquid; in this manner four samples are generated.

Table 1. Solubility of Contaminants in Water

Component	Feed Concentration (g/100 g of water)	Solubility (g/100 g of water)
Phenol	7.8	8.2*
p-Chlorophenol	1.5	2.71*
m-Cresol	0.3	0.5*
Benzene	0.05	0.178*

**Perry's Chemical Engineers' Handbook*, Robert Perry and Don Green, 6th ed.

**Tsonopoulous and Wilson (1983)

The cell, mixer, and de-entrainer are kept in a constant temperature water bath controlled by a Haake model E1 controller circulator to ±0.2°C. Once the temperature of the bath has reached the desired value, the CO_2 flow is started and the liquid pump turned on. The liquid level in the cell is kept steady by adjusting the lower micrometering valve. It takes about 45 minutes for the system to reach steady state with constant effluent stream composition.

The liquid samples are weighed, and these values are compared to the weight of liquid sample delivered by the metering pump to close the water, phenol, *m*-cresol, and *p*-chlorophenol material balances to within ±5%. Closure of the water-benzene material balance is difficult due to benzene's volatility. For benzene, gas samples from the upper phase were collected in glass sample bottles, and portions of these were injected directly into a gas chromatography (GC). Liquid samples were also analyzed by direct GC injections. Based on these GC measurements, the water-benzene balance closed within ● 10%. The flow rates of CO_2 were measured by a dry test meter (Singer model DTM-200) for both the upper and lower phases. These flow rates were periodically checked using a soap-bubble meter.

At each pressure and temperature, two sets of samples have been collected and the average compositions are reported. To test the apparatus and procedure, the vapor-liquid equilibria of the CO_2/water system at 313 K were measured and compared with literature data (Wiebe and Gaddy, 1940, 1941), with agreement within 1%. At lower pressures, our data for phenol distribution coefficients compare well with earlier data (Roop et al., 1988, 1989a,b), and this also serves as a test of our system (Ghonasgi et al., 1991).

The concentrations of phenol (Mallinckrodt, 88 wt. % in water), *m*-cresol (Eastman, 99.9%) and *p*-chlorophenol (Sigma, 99.9%) in the liquid samples were determined by visible spectroscopy (Perkin Elmer Lambda 6 spectrophotometer at 500 nm) of a dye complex of the compounds (APHA, 1985). The concentrations could be determined accurately within 2%. Benzene (Mallinckrodt, 99.9%) concentrations were obtained by direct injections of the samples into a GC (Varian 3400). The column used was an Alltech Superox II (polyethyleneglycol), fused silica capillary column, 30-m-long, 0.32-mm-ID.

Thermodynamic Considerations

During the last decade, equations of state have been used increasingly to correlate and model the complex phase behavior of fluid mixtures under a variety of conditions. Cubic EOS are among the more popular models that have been employed. Motivation for EOS-based modeling of the experimental data obtained in this study is twofold: (1) to enable prediction of equilibria beyond the temperatures or pressures investigated; and (2) to test the consistency and quality of the data.

Supercritical fluid-liquid equilibria, in particular supercritical fluid-water equilibria, can be difficult to model (Johnston et al., 1989). Further, the components in the systems studied here differ significantly in size, shape, and polarity. In this regard, the selection of an EOS can be crucial. Our modeling strategy is summarized as follows:

- The EOS should be simple to handle and should be based on a theoretical fluid that can be used as a reference to which real fluid behavior is compared.
- The EOS should contain parameters that, in typical cases, can be obtained from pure component and binary data.
- The EOS should be able to represent the behavior of mixtures of components from pure-component and binary data.

Based on these considerations, we decided to utilize a hard-sphere, perturbation-theory-based EOS. The compressibility factor includes "repulsive-only" reference and "attractive-only" perturbation terms (Henderson, 1979; Gubbins, 1972):

$$Z = Z_o + Z_{pert}. \tag{1}$$

where Z_o is for a hard-sphere reference fluid as represented by the Carnahan-Starling equation (1969, 1972). For the attractive term, several models are now available (Brennecke and Eckert, 1989; Kreglewski, 1984). For this work, we used a simple Redlich-Kwong attractive term, which was first utilized by DeSantis et al. (1976) in this context. The full EOS then becomes:

$$Z = \frac{1 + \xi + \xi^2 - \xi^3}{(1-\xi)^3} - \frac{a}{RT(V+b)} \tag{2}$$

where ξ is the packing fraction, $\xi = b/4V$. The molecular volume b is assumed to be a function of temperature; the attractive parameter a is also a function of temperature. Equation 2 is hereafter referred to as the Carnahan-Starling-DeSantis-Redlich-Kwong (CSDRK) EOS.

Morrison and McLinden (1986) applied this equation to model phase equilibria and PVT data for 11 different chlorofluorocarbon refrigerants and their mixtures in the subcritical region. A similar EOS has already been found suitable for modeling solid-SCF equilibria of nonpolar systems (Dieters and Swaid, 1984). Besides the simplicity of the attractive term, these considerations have contributed to the choice of this EOS.

The first step in the modeling was to determine the parameters a and b for pure components; they were determined from the specific volumes of saturated liquid and vapor, and pure-component vapor pressures (Armstrong et al., 1976; Daubert and Danner, 1984) using the error minimization algorithm of Morrison and McLinden (1986). These parameters were fitted to polynomial functions of temperature:

$$a(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \tag{3}$$

and

Table 2. Coefficients of Temperature-Dependent Polynomials, Eqs. 3 and 4

	a_o,b_o	a_1,b_1 $\times 10^3$	a_2,b_2 $\times 10^6$	a_3,b_3 $\times 10^9$	Temp. Range
CO_2	*a* 1,132.54	−2,498.12	0.0	0.0	310–330 K
	b 0.0877861	−0.158615	0.0	0.0	
Water	*a* 2,190.18	−5,961.48	8,372.69	−4,957.22	275–600 K
	b 0.0552198	−0.124815	0.182367	−0.112957	
Phenol	*a* 8,591.55	−3,101.82	−24,391.9	24,074.97	325–625 K
	b 0.202111	−0.117618	−0.0561736	0.0	
m-Cresol	*a* 1,1031.2	−946.556	−4,618.94	4,860.72	303–453 K
	b 0.236166	−0.0948683	−0.12444	0.0	
p-Chlorophenol	*a* 14,188.1	−22,623.2	−886.943	0.0	323–493 K
	b 0.292965	−0.291233	0.0	0.0	
Benzene	*a* 6,077.94	−10,033.8	444.24	0.0	290–370 K
	b 0.186068	−0.166537	0.0	0.0	

$$b(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3. \tag{4}$$

Polynomial coefficients resulting from the regression are listed in Table 2. For CO_2, it was necessary to extrapolate values of $b(T)$ from Eq. 4, whereas the values of $a(T)$ were regressed using literature PVT data as discussed earlier (Ghonasgi et al., 1991).

Quadratic mixing rules were utilized to model mixture properties:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} \omega_i \, \omega_j \, a_{ij} \tag{5}$$

and

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} \omega_i \, \omega_j \, b_{ij} \tag{6}$$

where ω is the mole fraction in either the liquid or vapor phase, and N is the number of components in the mixture. The unlike interaction parameters a_{ij} and b_{ij}, $i \neq j$, are given by:

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \tag{7}$$

and

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2} \right) \tag{8}$$

where k_{ij} is the binary interaction parameter. Here, only one parameter, k_{ij}, is needed for each binary pair.

The fugacity coefficients, φ_i, were calculated from

$$RT \ln \varphi_i = \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial n_i} \right) V, T, n_{j \neq i} - \frac{RT}{V} \right] dV - RT \ln Z. \tag{9}$$

The resulting expression for φ_i using the CSDRK-EOS is as derived by DeSantis et al. (1976):

$$\ln \varphi_i = \frac{4\xi - 3\xi^2}{(1-\xi)^2} + \frac{b_{ii}(4\xi - 2\xi^2)}{b(1-\xi)^3} + \frac{2}{RT\,b} \ln \left(\frac{V}{V+b} \right) \sum_{j=1}^{N} x_i a_{ji} + \frac{b_{ii} a}{RT\,b^2} \ln \left(\frac{V+b}{V} \right) - \frac{b_{ii} a}{RT(bV + b^2)} - \ln Z. \tag{10}$$

The binary interaction parameters for the CO_2-contaminant systems were obtained from available low-temperature binary solubility data: phenol and *p*-chlorophenol (Van Leer and Paulaitis, 1980), *m*-cresol (Lee and Chao, 1988), and benzene (Gupta et al., 1982). Details of this fitting procedure are provided elsewhere (Ghonasgi et al., 1991).

The k_{ij} for the water-CO_2 system was obtained from regression of the binary equilibrium data of Wiebe and Gaddy (1940, 1941). Our approach was found to work well for the modeling of the water-CO_2 system. Water–supercritical-fluid systems are considered to be difficult to model using the EOS approach (Johnston et al., 1989; Wenzel and Rupp, 1978). Besides providing us with the k_{ij}, this binary system has also served as a test of our modeling approach (Ghonasgi et al., 1991). The contaminant-water binary interaction parameters were computed from the actual ternary data (one datum at low pressure from each isotherm). These equilibrium calculations were performed by equating the total pressure and fugacities in the two phases. The distribution coefficient is:

$$K_i = \frac{y_i}{x_i} = \frac{\varphi_i^L}{\varphi_i^{SCF}}. \tag{11}$$

The temperature and the liquid (water-rich)-phase compositions were fixed in these calculations. A bubble point algorithm similar to that of Anderson and Prausnitz (1980a,b) was utilized to compute the equilibrium mole fraction. The objective function in the iterative calculation scheme was:

$$\ln \left(\sum_{i=1}^{N} y_i \right) = \ln \left(\sum_{i=1}^{N} K_i x_i \right) = 0 \tag{12}$$

The remaining unknown is the system pressure that was obtained upon convergence. The k_{ij}'s for all the binary systems are reported in Table 3. It is interesting to point out that k_{ij} values are nearly independent of the system temperature except for the water-CO_2 system. In the case of this system, complex carbonic acid formation may occur at the temperatures studied and can lead to changes in k_{ij} values. Further details regarding the algorithm and the EOS are reported in an earlier article (Ghonasgi et al., 1991).

In modeling the ternary systems, it was found that the contaminant concentrations were low enough in both the phases to assume zero concentration of toxins (infinite dilution). We thus ignored the effect of the contaminants on the fugacities of the binary water-CO_2 system. The contaminant distribution coefficients were then calculated assuming infinite dilution using Eq. 11, allowing us to obtain K as a function of temperature and pressure only. This strategy was used to avoid the complications resulting from erroneous measurements of CO_2 concentration in the water-rich phase and to reduce the number of variables needed to specify K. We tested and found virtually no effect of this assumption on the modeling of the measured ternary data (Ghonasgi et al., 1991).

Results and Discussion

The distribution coefficients were obtained at two temperatures, 313 K and 323 K. A pressure range of 9.6-17.23 MPa was investigated for phenol, whereas a pressure range of 9.65-16.54 MPa was investigated for other contaminants. These

Table 3. Binary Interaction Parameters

Temperature	k_{ij} 313 K	k_{ij} 323 K
Water-CO_2	0.009	0.021
Phenol-CO_2	0.0985	0.0985
m-Cresol-CO_2	0.0	0.0
p-Chlorophenol-CO_2	0.075	0.075
Benzene-CO_2	0.016	0.016
Water-Phenol	−0.18	−0.173
Water-*m*-Cresol	−0.25	−0.23
Water-*p*-Chlorophenol	−0.241	−0.236
Water-Benzene	−0.14	−0.138

Table 4. Distribution Coefficients and SCF-Phase Mole Fractions of Contaminants*

Pres. MPa	K_i	y_i
CO_2-Water-Phenol		
	Temperature = 313 K	
9.65	0.46	0.0061
11.025	1.12	0.013
12.404	1.27	0.014
15.51	1.54	0.015
17.23	1.73	0.019
	Temperature = 323 K	
9.65	0.34	0.0034
11.025	0.36	0.0046
12.404	0.77	0.0075
15.51	1.31	0.014
17.23	1.66	0.016
CO_2-Water-m-Cresol		
	Temperature = 313 K	
9.65	0.60	0.00022
11.025	1.40	0.00055
12.404	2.20	0.0006
13.80	2.70	0.0007
15.16	3.00	0.0008
16.54	3.90	0.00077
	Temperature = 323 K	
9.65	1.00	0.00036
11.025	1.12	0.0004
12.404	1.77	0.00069
13.80	3.12	0.00075
15.16	5.00	0.00087
16.54	6.02	0.001
CO_2-Water-p-Chlorophenol		
	Temperature = 313 K	
9.65	1.94	0.0030
11.025	3.00	0.0033
12.404	3.47	0.0035
13.80	4.96	0.0040
15.16	5.24	0.0047
16.54	5.38	0.0048
	Temperature = 323 K	
9.65	0.44	0.00081
11.025	0.68	0.0011
12.404	1.32	0.0014
13.80	2.00	0.0026
15.16	2.40	0.0029
16.54	2.75	0.0033
CO_2-Water-Benzene		
	Temperature = 313 K	
9.65	1,957.8	0.000202
11.025	3,809.6	0.000393
12.404	3,726.4	0.000390
13.80	3,645.9	0.000376
15.16	4,102.3	0.000423
16.54	4,941.2	0.000510
	Temperature = 323 K	
9.65	981.82	0.000101
11.025	1,648.1	0.000170
12.404	1,252.1	0.000129
13.80	2,324.6	0.000240
15.16	1,654.2	0.000171
16.54	2,553.1	0.000263

*Estimated error ±5% for systems containing phenol, *m*-cresol, and *p*-chlorophenol. Estimated error ±15% for the system containing benzene.

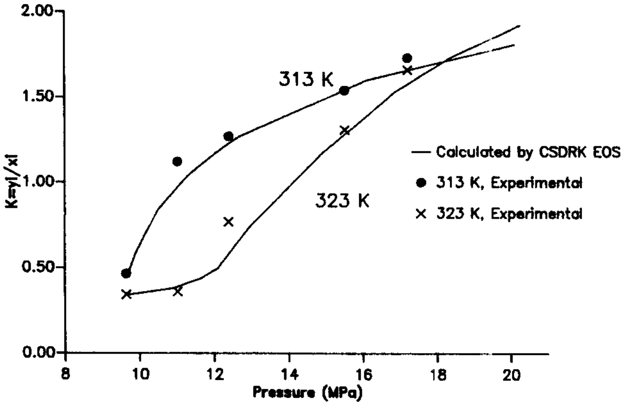

Figure 2. EOS and experimental *K* values for phenol at 313 K and 323 K.

results are reported in Table 4 and Figures 2-5. We observed a large scatter in the distribution coefficients for benzene. The *K* values for benzene are so large that even small errors in concentration measurements can generate significant scatter in the *K* values. Benzene concentrations in the water-rich phase are very small after the equilibration. Hence, the observed scatter in the *K* values. A comparison of the distribution coefficients for the four contaminants shows the following trend at 313 K:

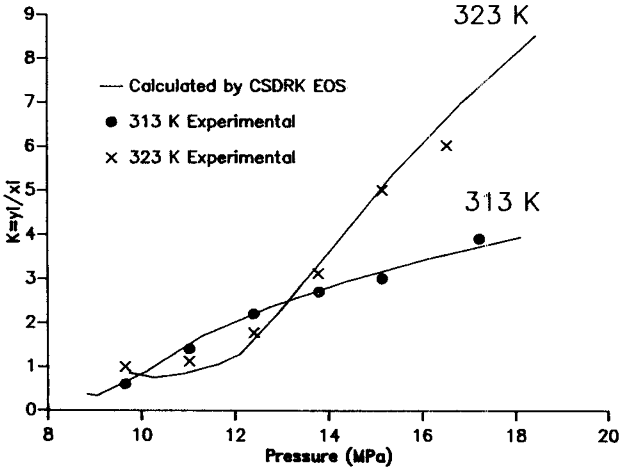

Figure 3. EOS and experimental *K* values for *m*-cresol at 313 K and 323 K.

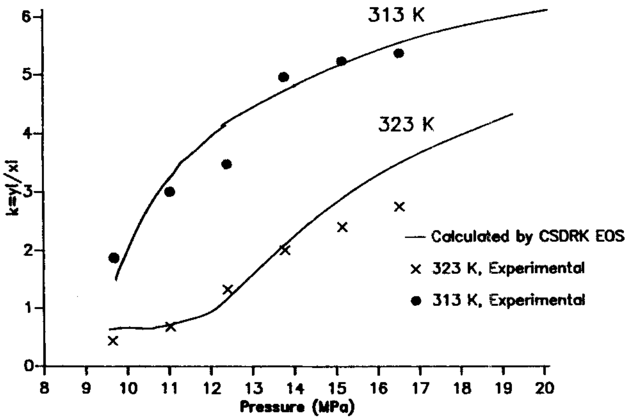

Figure 4. EOS and experimental *K* values for *p*-chlorophenol at 313 K and 323 K.

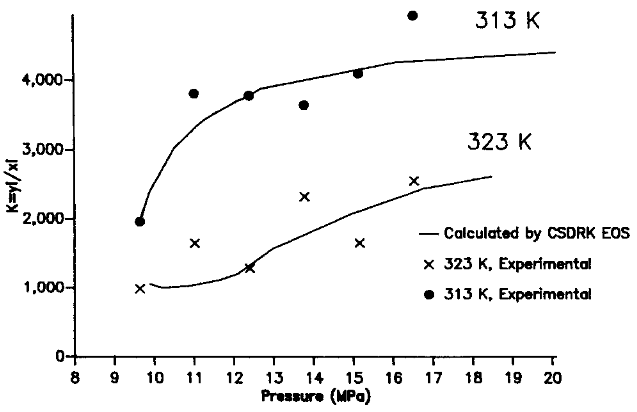

Figure 5. EOS and experimental K values for benzene at 313 K and 323 K.

benzene > p-chlorophenol > m-cresol > phenol

at 323 K, the order of m-cresol and p-chlorophenol in this list is reversed.

The results for benzene and phenol are easily explained. Benzene is the most hydrophobic of these contaminants, whereas phenol is the most hydrophilic. This is clearly reflected, as shown in Table 1, by the solubility of these contaminants in water at room temperature. The solubilities follow the trend:

phenol > p-chlorophenol > m-cresol > benzene.

In equilibria involving water and CO_2, benzene is found primarily in the CO_2-rich phase, whereas phenol is found primarily in the water-rich phase. Apparently, the K value for benzene is enhanced by a CO_2-benzene interaction, which results in a benzene/phenol K value ratio of $\sim 10^3$, even though the inverse molar solubility ratio in water is only ~ 40 for these two substances. This is due perhaps to the fact that benzene has a zero dipole moment, whereas phenol is polar.

The reversal in the ordering of the K values for m-cresol and p-chlorophenol can also be explained, upon examination of the pure-component solubilities in water and CO_2. At ambient temperature, p-chlorophenol is more soluble in water than m-cresol. Based solely on water solubility, the K values would be expected to follow the order observed at 323 K. Francis (1954) reported the solubilities of the pure compounds in near critical CO_2 at room temperature and 6.6 MPa. He found the solubility order:

benzene $\begin{pmatrix}\text{complete}\\\text{miscibility}\end{pmatrix}$

> p-chlorophenol (0.0297 mol/mol CO_2)

> m-cresol (0.0170 mol/mol CO_2)

> phenol (0.0145 mol/mol CO_2)

Based solely on these solubilities, the K values would be anticipated to follow the values obtained at 313 K. There are evidently two competing factors controlling the K values: the molecular interaction of the contaminant with water in the aqueous phase and the contaminant interaction with CO_2 in the SCF phase. For m-cresol and p-chlorophenol, as the temperature is increased from 313 to 323 K, the contaminant interactions with CO_2 in the SCF phase evidently become less significant while the aqueous-phase interactions remain important.

We can also study to some extent the effect of temperature and pressure on the K values of individual contaminants. We observe two distinct crossovers in temperature for phenol and m-cresol. It is interesting to note that these crossovers are similar, in shape and location, to the crossovers that are found in the curves for the pure-contaminant solubilities in SCF-CO_2 (Van Leer and Paulaitis, 1980; Lee and Chao, 1988). This result suggests that the presence of water in either phase has little effect on CO_2-contaminant interactions in the SCF phase besides the fact that the polarity of phenol and m-cresol is close to that of water. The qualitative features of the distribution coefficient isotherms in the presence of water are affected by the same considerations as are the solubility isotherms of the pure contaminants; these are contaminant vapor pressure and CO_2 compressibility (Brennecke and Eckert, 1989; Johnston et al., 1989). Of course, as previously emphasized, the exact magnitude of the K values for a particular contaminant also depends highly on the magnitudes of the solubility of the contaminants in water.

Figures 4 and 5 also suggest the existence of crossover phenomena in the equilibria of aqueous p-chlorophenol and benzene with SCF-CO_2 at slightly below the pressure range studied here. Similar behavior can also be expected for the equilibria of the pure contaminants with CO_2; however, we are unable to confirm this hypothesis due to the limited pure contaminant data available.

The modeling results using the CSDRK-EOS agree well with the experimental data qualitatively and quantitatively, except for benzene where the comparison is difficult due to the scatter in the data. This not only demonstrates the quality of the data (except benzene), but also the success of using the hard-sphere-based approach. In this regard, it is important to note that the values of the binary interaction parameters (k_{ij}) for the water-contaminant pairs depend very little on temperature. In fact, k_{ij} values obtained from one isotherm could have been used at the other temperature without any significant errors except for the water-CO_2 system. Clearly, this reaffirms our earlier observation (Ghonasgi et al., 1991) that an accurate pure fluid EOS is very important in the modeling of aqueous–SCF-phase equilibria. The magnitude of the values of the k_{ij} parameters for the water-contaminant pairs, however, is a cause of concern. Their absolute values are negative and somewhat large. This perhaps indicates a need for different mixing rules such as density-dependent mixing rules, which according to Lee and Sandler (1987) lead to much smaller values for k_{ij}, or the use of a better attraction term in Eq. 2.

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Notation

a = attraction constant, kJ·m^3/kmol
b = molecular volume parameter, m^3/kmol
k = binary interaction parameter
K = distribution coefficient
n = number of moles, kmol
N = number of components

P = pressure, MPa
R = gas constant, kJ/kmol·K
T = temperature, K
V = molar volume, m^3/kmol
x = mole fraction in the liquid phase
y = mole fraction in the gas phase
Z = compressibility factor

Greek letters

φ = fugacity coefficient
ξ = packing fraction
ω = mole fraction in liquid or gas phase

Subscripts

i, j = component indices
o = reference fluid
pert = attractive forces contribution

Superscripts

L = liquid phase
SCF = supercritical fluid phase

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