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Distribution of a Complex Phenolic Mixture between Water and Supercritical Carbon Dioxide

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A complex phenolic mixture was successfully extracted from an aqueous solution by using near-critical and supercritical carbon dioxide, with and without entrainers. Experimental extractions were performed at 298 and 323 K at pressures up to 27.6 MPa to measure distribution coefficients. The Peng–Robinson equation of state with a recently published mixture combining rule quantitatively modeled the system and provided a qualitative prediction of the effect of adding a small amount of benzene as an entrainer.

Table I. Composition and Estimated Properties of Phenolic Mixture

component	wt %	T_c,^{a} K	P_c,^{b} MPa	accentric
phenol	0.76	692.1	6.13	0.461
phenol, 2-methyl	10.1	692.4	5.03	0.480
phenol, 2-methoxy	77.5	700.2	4.91	0.566
phenol, 2,3-dimethyl	5.5	716.6	4.32	0.530
phenol, methoxy, methyl	5.08	708.7	4.06	0.598
unidentified	~1			
av mixture properties		700.3	4.85	0.556

^{a} Joback's method (ref 2). ^{b} Lee–Kesler (ref 2).

Introduction

Recent attention has been given to supercritical extraction as a potential means of separating organic compounds from aqueous solutions. Phase equilibrium data and (to a limited extent) thermodynamic models have been reported in the literature for a variety of pure organic compounds distributed between water and a supercritical fluid. Many practical applications, however, involve processes for the extraction of multicomponent complex organic mixtures from water, such as applications in waste water treatment. Phase equilibrium behavior for such systems is quite complex, making experimental data and accurate thermodynamic models scarce. In addition, use of entrainers (or cosolvents) to increase the solvent power of supercritical fluids further complicates the phase behavior.

The objective of this study was to investigate the extraction of complex organic mixtures from water with supercritical fluids. This work is an extension of our study of the extraction of aqueous solutions of phenol, a model single-component compound. Therefore, as a model complex system, a multicomponent phenolic mixture (beechwood extract) was extracted from water by using near-critical and supercritical carbon dioxide (with and without entrainers). The fundamental thermodynamic parameter of interest for the extraction of organics from water is the distribution coefficient, defined as the ratio of the mole fraction of organic in the supercritical phase to the mole fraction of organic in the aqueous phase. We have measured the distribution coefficient of the phenolic mixture as a function of pressure and temperature. The Peng–Robinson equation of state (*1*) with a new mixing rule recently proposed by Panagiotopoulos and Reid (*2*) was used to model the pseudoternary system. In addition, the model was used to predict the effect of adding a small amount of an entrainer (benzene) to the system, and the predictions were verified experimentally.

The majority of the previous work in the area of high-pressure phase equilibria of supercritical fluids with aqueous solutions of organic compounds has focused on single-component oxygenated organic compounds in water. Kuk and Montagna (*3*) reported 2-propanol and ethanol extractions from water as a function of pressure and temperature using supercritical carbon dioxide. McHugh et al. (*4*) investigated the ethanol–water system but used ethane as the supercritical fluid for extraction. Paulaitis et al. (*5*) discussed some of the important phase equilibrium behavior of alcohol–water–supercritical fluid systems. Radosz (*6*) reports phase equilibrium data for the 2-propanol–water–carbon dioxide system. DeFillippi et al. (*7*) describes a process for removing ethanol from water, and Schultz and Randall (*8*) present a general correlation for the distribution coefficient of normal aliphatic alcohols as a function of carbon number. Systems other than alcohols, such as acetone (*9*) and aroma constituents of fruits and other foods (*8*), have also been investigated. In our previous work, we extracted phenol from water using near-critical and supercritical carbon dioxide and demonstrated the inadequacies of several cubic equations of state with conventional mixing rules (*10*). We also investigated the use of entrainers for aqueous systems and developed a method of qualitatively predicting a priori the effect of adding a small amount of cosolvent to our system (*11*). Benzene was found to be an appropriate entrainer for the extraction of phenol from water.

Methods

An aqueous solution was prepared by vigorously mixing distilled water and a phenolic mixture (beechwood extract) purchased from Matheson, Coleman & Bell (lot no. 330, 344113). Table I contains the composition and estimated properties of the phenolic mixture. After the aqueous and organic phases separated, the saturated aqueous phase (8700 ppm total organic carbon) was isolated. Carbon dioxide was purchased from Conroe Welding Supplies with a purity of at least 99.8%. Standard benzene, purchased from Fisher Scientific Co. (lot no. 724430), and radioactively labeled ^{14}C benzene, from Sigma Chemical Co. (0.02 mCi/mmol), were added together to create

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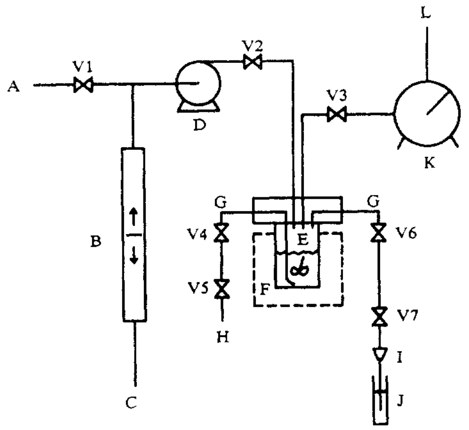

A	Carbon Dioxide Supply	H	Aqueous Sample Exit
B	High Pressure Compression Cylinder	I	Pressure Restricter
C	Nitrogen Inlet	J	Organic Solvent Trap
D	High Pressure Metering Pump	K	Wet Test Meter
E	Extraction Vessel	L	Exit Vent
F	Furnace	V1-V7	Valves
G	Narrow Bore Tubing		

Figure 1. Experimental apparatus for supercritical extraction.

a labeled benzene solution. All materials were used as received.

A schematic of the experimental apparatus used in this study is shown in Figure 1. The high-pressure equilibrium cell (300-mL autoclave) is initially charged with 150 mL of aqueous solution. A small amount of radioactively labeled entrainer (1-4 mol %) is added, if desired. The high-pressure compression cylinder (1 L, Welker) is filled with CO_2 from supply and then isolated through shut-off valve V1. The CO_2 is compressed by using nitrogen to produce liquid CO_2 at 10 MPa to avoid cavitation in the pump. The high-pressure metering pump (Milton Roy minipump) is then used to pump the liquid CO_2 into the extractor to the desired pressure (up to 31 MPa). The temperature of the system is controlled by a furnace. Once charged with supercritical CO_2 to the required pressure and temperature, the vessel contents are stirred for 1 h followed by a 2-h period for phase separation. Since the density of the CO_2 is similar to that of water at the conditions of this study, it was determined that 2 h was the minimum time required for the two phases to separate completely, as shown in Figure 2. Samples of both the aqueous phase and supercritical phase are taken. The double-valve sampling system V4-V5 allows a 0.3-mL sample of the aqueous phase to be collected from the bottom of the cell. A 1-mL sample of the supercritical phase from the top of the cell is isolated between valves V6 and V7. The sample is then bled across a restricter and through an organic solvent trap containing liquid scintillation counting solution (National Diagnostics, lot no. FE42) to obtain the entrainer concentration in the sample. After sampling, the enclosure is subsequently charged with additional CO_2 to a higher pressure, and the procedure is repeated. The system is depressurized through a wet test meter to monitor total CO_2 volume. A microcomputer data acquisition system is used to control and monitor the temperature and pressure of the system. A highly accurate pressure transducer (T-Hydronics Model TH-1V) and K-type thermocouple are used to provide electrical representations of the conditions of the system for the microcomputer. System pressure is measured to within 0.035 MPa and temperature to within 1 K.

Samples from the equilibrium cell were tested in a Dohrman carbon analyzer to determine the total organic carbon (TOC) content. When an entrainer was used, the samples were also tested in a Beckman liquid scintillation counter (Model 3801) to determine the entrainer concentration in the water. The concentration of the entrainer was subtracted off the TOC of the aqueous sample to determine the actual TOC content of the phenolic mixture in the water. This was then used to calculate the distribution coefficient.

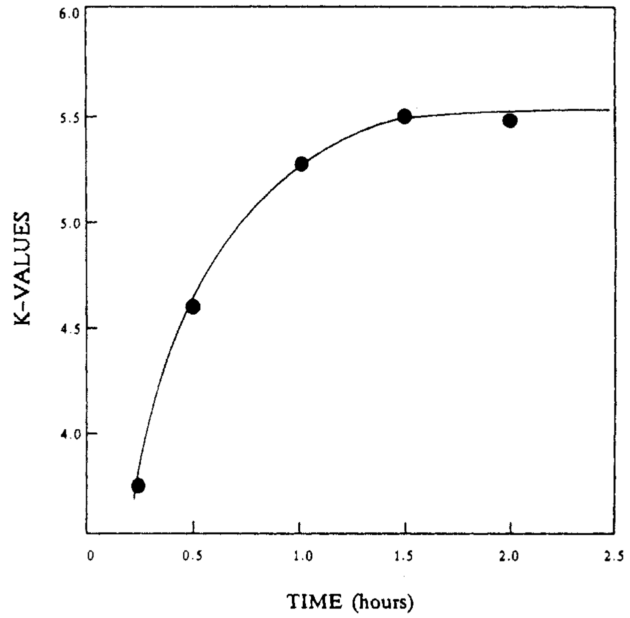

Figure 2. Time required to reach equilibrium for aqueous solution of phenolic mixture and supercritical carbon dioxide at 298 K and 27.6 MPa.

Table II. Experimentally Measured Reduction in Water TOC Content and Phenolic Mixture Distribution Coefficients at 298 K

pressure, MPa	TOC content, ppm	distribution coefficients
6.9	5030 ± 217	2.43 ± 0.27
13.8	3658 ± 61	3.85 ± 0.18
20.7	2955 ± 107	5.11 ± 0.26
27.6	2655 ± 48	5.74 ± 0.20

In order to confirm the existence of only two phases, we have used a Jerguson gauge (Model 11-R-20) for visual observation of the number of phases. The gauge was charged with the same volumetric ratio of the aqueous solution and CO_2, and only two phases were observed.

Results

Water samples were tested for TOC content. The ratio of the TOC of an aqueous sample to the TOC of the original solution is equivalent to the ratio of moles of phenolic solution in the sample to the total moles of phenolic solution. With this ratio (r), the distribution coefficient can be calculated with

$$K = \left(\frac{1 - r}{r}\right)\left(\frac{\text{total moles water}}{\text{total moles } CO_2}\right) \tag{1}$$

where it is assumed that the concentration of phenolics in both phases is small. The experimentally measured TOC content of the water and the distribution coefficients of the phenolic mixture at 298 K as a function of pressure are given in Table II. The TOC content of the water was reduced from the initial 8700 to 2655 ppm at 27.6 MPa, representing a 70% reduction in the phenolic concentration. Values of the distribution coefficient ranged from 2.43 at 6.9 MPa to 5.74 at 27.6 MPa. Three reproductions of the data yielded an average standard deviation of 6%.

As in our previous work with phenol (*11*), the data for the base pseudoternary system (phenolic mixture-water-carbon dioxide) were correlated with use of standard thermodynamic models. Equating the fugacity of all constituents in each phase

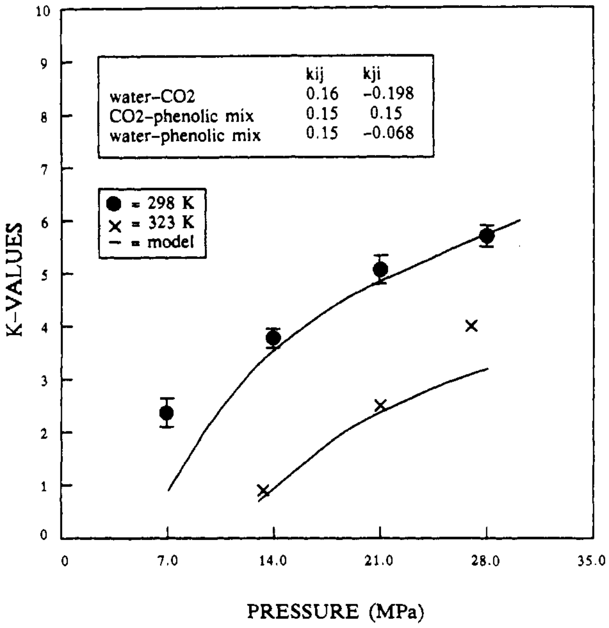

Figure 3. Distribution coefficients for phenolic mixture at 298 K and model data correlation. Prediction for 323 K and experimental verification.

and expressing them in terms of fugacity coefficients yields the usual expression for the distribution coefficient

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^{L}}{\hat{\phi}_i^{SC}} \tag{2}$$

The fugacity coefficients were determined by applying the Peng-Robinson equation of state

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V - b_m) + b_m(V - b_m)} \tag{3}$$

and the van der Waals-one-fluid mixing rules

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad b_m = \sum_i x_i b_i \tag{4}$$

to the fundamental thermodynamic relationship

$$\ln \hat{\phi}_i = \int_v^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,v,n_j} - \frac{RT}{v} \right] dv - \ln z \tag{5}$$

In addition, a new combining rule recently proposed by Panagiotopoulos and Reid (*2*) was used, which relaxes the assumption that the binary interaction parameters $k_{ij} = k_{ji}$, yielding a second interaction parameter per binary

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij} + (k_{ij} - k_{ji})x_i) \tag{6}$$

Equation 4 reduces to the conventional combining rule when $k_{ij} = k_{ji}$. Although this combining rule does not reproduce the correct functional dependence of the mixture second virial coefficient on composition, it offers computational advantages over more complex local composition, density-dependent mixing rules (*12-14*). Binary interaction parameters for the phenolic mixture were assumed to be the same as those obtained for phenol (*11*). The k_{ij} and k_{ji} for the two major components (water and carbon dioxide) are the most critical to describe the phase equilibria and were obtained from Panagiotopoulos and Reid (*2*). Tsonopoulos (*15*) provides general values for carbon dioxide and the phenolic mixture, as well as the interaction parameter for water and phenol. The parameter for phenol and water (a single parameter out of six), which was not available in the literature, was adjusted to fit the data at 298 K and held constant throughout the rest of the study. The results of the model are shown in Figure 3, as well as the interaction parameters used and the experimental values for comparison. The model was then used to predict the effect of increasing the temperature. The distribution coefficients were predicted to decrease when the temperature is increased to 323 K, and these predictions were verified experimentally. At 323 K, the distribution coefficient decreased and only reached 4.1 at 26.2 MPa.

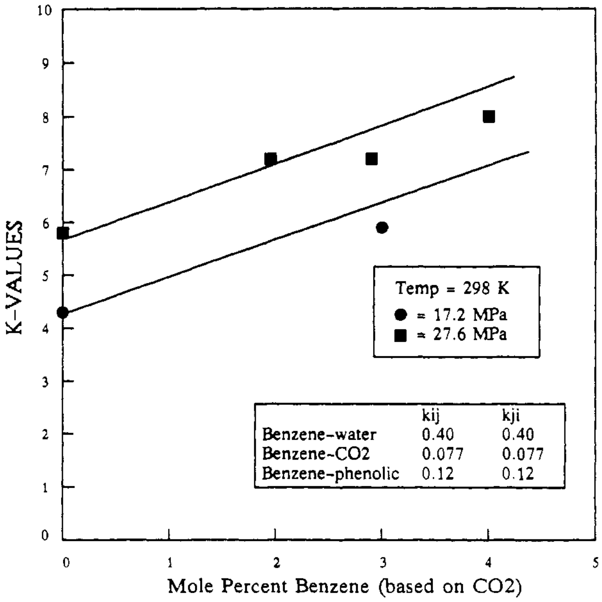

Figure 4. Model prediction and experimental verification of the effect of benzene as an entrainer at 298 K for 17.2 and 27.6 MPa.

The model was then extended to a quaternary system to predict the effect of adding a small amount of an entrainer. Two of the entrainers investigated in our single-component study of phenol (methanol and benzene) were chosen as perspective cosolvents for the extraction of the phenolic mixture. With the interaction parameters from the phenol study, methanol was predicted to have no effect on the distribution of the phenolic mixture and therefore was not tested experimentally. Figure 4 shows the predicted effect of benzene on the extraction of the phenolic mixture (again using the same interaction parameters used in the phenol study). Since a favorable effect was predicted, experiments were performed with use of up to 4 mol % benzene (based on carbon dioxide). The experimental results are also shown in the figure. As predicted, benzene did increase the distribution of the phenolic mixture up to 50%. These results agree with the results of our single-component study, in which the distribution coefficient of phenol was increased with the addition of benzene (*11*).

Conclusions

Near-critical and supercritical carbon dioxide was used to successfully extract a complex phenolic mixture from an aqueous solution. The system was quantitatively modeled at 298 K as a pseudoternary system (phenolic mixture-water-carbon dioxide) with estimated critical values for the mixture, the Peng-Robinson equation of state, a new mixing rule recently proposed by Panagiotopoulos and Reid (*2*), and the binary interaction parameters determined in our single-component study of phenol. The model correctly predicted, at least qualitatively, a drop in the distribution coefficient of the phenolic mixture with an increase in the temperature to 323 K. It also correctly predicted an increase in the distribution coefficient with the addition of benzene as an entrainer. Thus, the phase equilibrium behavior of the complex phenolic mixture distributed between water and a supercritical fluid was effectively modeled as a pseudoternary system with use of the binary interaction parameters of a structurally similar key component, phenol.

Glossary

a	attraction constant for equation of state
K	distribution coefficient
n	number of moles
P	pressure
r	moles of phenolic solution in sample/total moles of phenolic solution
R	gas constant
T	temperature
v	volume
x	mole fraction in liquid phase
y	mole fraction in supercritical phase
z	compressibility

Greek Letters

$\hat{\phi}$	fugacity coefficient

Subscripts

i	component i
j	component j
ij	cross term for components i and j

Superscripts

L	liquid phase
SC	supercritical phase

Registry No. PhOH, 108-95-2; CO_2, 124-38-9; benzene, 71-43-2.

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Excess Volumes and Viscosities of Binary Systems Containing 4-Methyl-2-pentanone

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Excess volumes and kinematic viscosities have been measured by means of a vibrating tube densimeter and an Ubbelohde viscometer for 12 binary systems containing 4-methyl-2-pentanone (MIBK). Excess volumes have been correlated by means of a polynomial expression, viscosities by means of the Mc Allister equation. The first component in all the binary systems studied is 4-methyl-2-pentanone (MIBK); the second component is 3-pentanone, 2-hexanone, cyclohexanone, *n*-heptane, toluene, *p*-xylene, ethylcyclohexane, 1,1,1-trichloroethane (chlorotene), *n*-butyl acetate, 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol, DAA), 1-methoxy-2-propanol (PGM), or 1-acetoxy-2-ethoxyethane (ethylcellosolve). All the systems have been measured at atmospheric pressure and 298.15 K.

Introduction

Mixing volumes and viscosity effects are important from both the theoretical and practical points of view: indeed, strong deviations from linearity are often encountered in liquid mixtures, even if they are of similar nature.

Different approaches have been suggested for the prediction of mixtures viscosity. Among these, the group contribution methods seem to be particularly promising. The development of a group contribution method requires the availability of an adequate data base. The data base should consist of a sufficient number of systems, all containing the chemical functional groups taken into account in the operating area of the method. The present work adds a contribution to the development of the general data base and, in this respect, makes up a continuation of the project started in ref 1.

In addition to the scientific interest, the characterization of mixtures containing 4-methyl-2-pentanone (MIBK) is useful for a number of practical applications in the fields of paints, varnishes, and printing inks: in particular, the systems MIBK/PGM (PGM = 1-methoxy-2-propanol), MIBK/DDA (DDA = diacetone alcohol), MIBK/toluene, and MIBK/*p*-xylene for air-drying epoxy polyamine and polyamide coatings and the systems MIBK/ethylcellosolve and MIBK/cyclohexanone for air-drying polyurethane coatings.

Experimental Section

All the chemicals used in the present study were supplied by Fluka and used as received. The stated purity of all the chemicals exceeded 99.0 mol %. Nitrogen and bidistilled water were used for the densimeter calibration and cyclohexane for the viscometer calibration. The purity of the cyclohexane and water was higher than 99.9 mole % and that of nitrogen higher than 99.9999 mole %. Densities and viscosities of the pure components at 298.15 K and atmospheric pressure were measured before preparing the mixtures and compared with literature values (see Table I).

All the solutions were prepared with use of a Mettler balance (precision of 1×10^{-5} g) and airtight stoppered bottles following a procedure described elsewhere (*1*). The possible error in the mole fraction is estimated to be lower than 3×10^{-5}.

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