# Supercritical Extraction of Organic Mixtures from Aqueous Solutions

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Supercritical extraction has been receiving wide attention in hazardous waste removal area (Eckert et al., 1986), and water contaminated with trace amounts of toxic organic mixtures is a common environmental problem. This paper focuses on the removal of toxic organic mixtures from dilute aqueous solutions using supercritical carbon dioxide. Studies of supercritical extraction related to aqueous solutions of organic compounds have concentrated on a single-compound extraction. Most environmental pollutants, however, are complex chemical mixtures and each component of the mixtures affects the solubilities and extraction parameters of all the other components in the mixture.

The objective of this study is to determine the equilibrium distribution coefficient of each component of a toxic organic mixture between water and supercritical carbon dioxide phase and to model the system that predicts the multicomponent system behavior. As a model system, we selected four compounds from different classes of water contaminants: benzene and toluene (single ring aromatic hydrocarbon solvents), naphthalene (a double ring aromatic hydrocarbon which may represent polycyclic aromatics), and parathion (an organophosphate pesticide). The Peng-Robinson equation of state (Peng and Robinson, 1976) with a composition-dependent mixing rule (Panagiotopoulos and Reid, 1986) was used to model the ternary system and then extended to predict the phase behavior of the six-component system. The model predicted the six-component system behavior with reasonable accuracy using only the information based on ternary system data. The distribution coefficients for all the compounds in the six-component system were greater than that component's distribution coefficient in the ternary system under the same conditions.

## Experimental Methods

Aqueous solutions were prepared by dissolving the individual compounds in water, resulting in four different binary solutions (water + one compound), and by dissolving the mixture of all four compounds in water, resulting in a five-component solution (water + four compounds). Deionized distilled water was saturated with benzene (99.9%, Fisher Scientific); toluene (99.9%, J.T. Baker); naphthalene (Fisher Scientific, lot 743721); and parathion (98.7%, Stauffer Chemical Company), respectively, and with a mixture of the four compounds. Table 1 shows the concentration of each compound in the binary and the five-component model aqueous solutions and the reported solubilities in water at room temperature.

The experimental apparatus used for this study and the operating procedures were described by Roop and Akgerman (1989). Extraction was conducted at 318 and 330 K with variation of pressure from 78 to 110 bar. System pressure was controlled within ±0.3 bar and temperature within ±1.2 K. In an extraction system, there should be only two phases. In supercritical fluid-water-organic component systems, it is possible to have more than two phases. We confirmed the presence of only two phases in our system by closing the material balance on benzene. A binary aqueous solution containing $^{14}C$ radiolabeled benzene was extracted. At equilibrium, samples taken from both the supercritical phase and the aqueous phase were analyzed by Beckman liquid scintillation counter (model 3801) to determine benzene concentration. The material balance closure was better than 95%. If a benzene-rich phase had formed, it is highly unlikely that only 5% of the benzene present in the system would distribute to that phase, the loss is due to evaporation during the trapping procedure of the supercritical-phase sample. Therefore, the analysis of aqueous-phase concentration before extraction and the overall material balance based on the analysis of both phases after extraction provided information on the number of phases and the composition of each phase. A gas chromatograph (HP 5890A) equipped with a flame ionization detector was used for the analysis of aqueous samples before and after extraction.

## Model for Phase Equilibria

The equilibrium compositions of both the aqueous and the supercritical fluid (SCF) phase at known temperature, pressure, and overall composition are carried out by the P–T flash calculation. The mole fraction of component $i$ in the aqueous

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**Table 1. Concentration of Organic Compounds in Model Aqueous Solutions**

| Compounds | Aqueous Solution Concentration (wt. %) | | |
|---|---|---|---|
| | Binary Solution | Five-Component Solution | Pure Solubility |
| Benzene | 0.1281 | 0.1251 | 0.1780* |
| Toluene | 0.0472 | 0.0467 | 0.0515* |
| Naphthalene | 0.0024 | 0.0029 | 0.0030** |
| Parathion | 0.0019 | 0.0026 | 0.0020† |

*From McAuliffe (1966)
**From Perry and Chilton (1973)
†From Martha (1983)

and SCF phase are $x_i$ and $y_i$, respectively, and the equilibrium distribution coefficient is given by $K_i = y_i/x_i$. At equilibrium, the distribution coefficient ($K$ value) is related to the fugacity coefficients of the two phases as follows.

$$K_i = \frac{\hat{\phi}_{iL}}{\hat{\phi}_{iF}} = \frac{y_i}{x_i} \tag{1}$$

On the basis of overall material balances,

$$x_i = z_i/[L + (1 - L)K_i] \tag{2}$$

$$y_i = K_i z_i/[L + (1 - L)K_i] \tag{3}$$

where $z_i$ is the overall composition of the $i$th component, and $L$ is the mole fraction of liquid. First, the densities of the two phases are estimated from an equation of state using initial guesses for $x_i$ and $y_i$. The fugacity coefficients are calculated by Eq. 4, and the first trial $K_i$ is determined by Eq. 1. After finding $L$ by iteration, a new set of $x_i$ and $y_i$ values is calculated by Eqs. 2 and 3.

The success of the flash calculation depends on the accuracy of the fugacity coefficients. Cubic equations of state are frequently employed to calculate the fugacity coefficients. In this approach, the results are very sensitive to the mixing rules and their parameters. We used the Peng-Robinson equation of state (Peng and Robinson, 1976) combined with a composition-dependent mixing rule (Panagiotopoulos and Reid, 1986) for fugacity coefficient expression as follows.

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z - 1) - \ln (Z - B) - \frac{A}{2\sqrt{2}B}\left[\frac{\sum_k x_k(a_{ki} + a_{ik}) - \sum_k \sum_j x_k^2 x_j (k_{kj} - k_{jk})\sqrt{a_k a_j}}{a} + \frac{x_i \sum_k x_k (k_{ik} - k_{ki})\sqrt{a_i a_k}}{a} - \frac{b_i}{b}\right] \ln\left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right] \tag{4}$$

where

$$A = \frac{aP}{R^2T^2} \tag{5}$$

$$B = \frac{bP}{RT} \tag{6}$$

$$Z = \frac{PV}{RT} \tag{7}$$

For mixture parameters $a$ and $b$, the van der Waals one fluid mixing rules apply

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{8}$$

$$b = \sum_i x_i b_i \tag{9}$$

and

$$a_{ij} = [1 - k_{ij} + (k_{ij} - k_{ji})x_i]\sqrt{a_i a_j} \tag{10}$$

Equation 10 is the composition-dependent mixing rule with two adjustable interaction parameters, $k_{ij}$ and $k_{ji}$.

To model our six-component system, a total of 36 interaction parameters are required. The number of parameters to be determined, however, can be reduced by applying the following assumptions.

1. Interaction parameters are zero for hydrocarbon pairs (Reid et al., 1987) and for very dilute component pairs.

2. For nonpolar component pairs, which include $CO_2$, benzene, toluene, and naphthalene, $k_{ij} = k_{ji}$.

The values of the first parameter, $k_{ij}$, were available in the literature except for parathion binaries. The second parameter, $k_{ji}$, which is usually not available in the literature, was determined by regressing the experimental data for each ternary system. Interaction parameters determined from ternary data at 318 K were used to predict the six-component system behavior at 318 and 330 K. Table 2 shows the determined interaction parameters, $k_{ij}$ and $k_{ji}$, as well as the values obtained from the literature. The negative interaction parameters are common for component pairs if one of the components is polar. Since the critical constants and acentric factor of parathion were not available in the literature, the Ambrose method and Lee-Kesler equations (Reid et al., 1987) were used to calculate $T_c$ (856.9 K), $P_c$ (26.3 bar) and $\omega$ (0.874) of parathion.

## Results and Discussion

The distribution coefficients ($K$ values) of benzene, toluene, naphthalene, and parathion between supercritical $CO_2$ and water were obtained as a function of pressure at 318 and 330 K (Table 3). The worst-case errors were estimated from the reproducibility of GC analysis for each compound, which would

**Table 2. Interaction Parameters ($k_{ij}$ and $k_{ji}$) of Six Compounds for Composition-Dependent Mixing Combining Rule Equation 10***

| Component | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1 | 0.0 | 0.16 | 0.26 | 0.26 | 0.40 | 0.40 |
| 2 | −0.198 | 0.0 | 0.075 | 0.081 | 0.115 | −0.428 |
| 3 | −0.024 | 0.075 | 0.0 | 0.0 | 0.0 | 0.0 |
| 4 | −0.106 | 0.081 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5 | −0.110 | 0.115 | 0.0 | 0.0 | 0.0 | 0.0 |
| 6 | −0.097 | 0.428 | 0.0 | 0.0 | 0.0 | 0.0 |

*Component: 1 = water; 2 = carbon dioxide; 3 = benzene; 4 = toluene; 5 = naphthalene; 6 = parathion—$k12$ and $k21$ from Panagiotopoulos and Reid (1986), $k23$ = $k32$ and $k24$ = $k42$ from Nishiumi and Arai (1988), $k25$ = $k52$ from Haselow and Han (1986), $k13$ and $k14$ from Tsonopoulos and Wilson (1983), $k15$ from Tsonopoulos (1974), the other values from fitting ternary data at 318 K.

be propagated to the calculation of the $K$ values. The distribution coefficients of the four compounds differed by two orders of magnitude. The $K$ values of benzene and toluene, which are highly soluble in supercritical $CO_2$, were of the order $10^3$, which indicated up to 99% reduction in the concentration of aqueous phase in a single-equilibrium-stage extraction. The initial concentration of benzene in the binary aqueous solution was 0.029 mol % (0.1281 wt. % in Table 1). After extraction at 318 K and 90.2 bar, the equilibrium concentration of benzene in aqueous phase ($x_i$) was $3.8 \times 10^{-4}$ mol %, and that of benzene in supercritical phase ($y_i$) was 0.618 mol %. The corresponding $K$ value of benzene in the ternary system became 1626.3 ± 47.4. Similarly, when $K$ value of toluene was 2143.7 ± 50.4, the corresponding $x_i$ was $8.21 \times 10^{-5}$ mol %, and $y_i$ was 0.176 mol %. The maximum reductions in the aqueous-phase concentration of naphthalene and parathion at 318 K were 95% at 100 bar and 54% at 108 bar, respectively. The distribution coefficients of the four compounds in both the ternary and the six-component systems increased with pressure for each isotherm. For the six-component system, the distribution coefficients decreased overall at a higher temperature, due to the density reduction of supercritical $CO_2$. The variation of $CO_2$ density with temperature had a dominating effect on the distribution coefficients, compared to the change in volatility of the dilute organic components with temperature.

The distribution coefficient of each constituent of the six-component system increased compared to those of the ternary systems. Figure 1 shows increase in the benzene's $K$ value as a function of number of components in the system at 318 K and 90.2 bar. According to the model, the most increase in the benzene's $K$ value was at the presence of toluene, while naphthalene and parathion had little effect on the benzene's $K$ value. Therefore, the presence of similar compounds like benzene and toluene would facilitate the extraction of each compound. Figure 2 shows the percentage increase in average $K$ values of the four components in the six-component system at three different pressures, based on experimental data at 318 K. Percentage increase in the $K$ value of benzene was 37.3%, toluene 11.5%, naphthalene 201.5%, and parathion 113.6%, respectively. These results show that the effect of benzene and toluene on the $K$ values of other components was large, and that of naphthalene and parathion was relatively small. Therefore, benzene and toluene can be regarded as entrainers to enhance the extraction of naphthalene and parathion from water. We

**Table 3. Distribution Coefficients of the Four Compounds***

| $P$ (bar) | $K_t$ (318 K) | $P$ (bar) | $K_s$ (318 K) | $P$ (bar) | $K_s$ (330 K) |
|---|---|---|---|---|---|
| *Benzene* | | | | | |
| 79.8 | 856.7 | 80.5 | 910.7 | 81.9 | 444.2 |
| 90.2 | 1,626.3 | 91.6 | 2,554.0 | 97.2 | 810.0 |
| 100.6 | 2,756.0 | 104.1 | 3,730.0 | 110.3 | 1,005.0 |
| *Toluene* | | | | | |
| 79.1 | 1,096.0 | 80.5 | 808.4 | 81.9 | 647.0 |
| 93.7 | 2,143.7 | 91.6 | 2,568.0 | 97.2 | 1,433.0 |
| 107.6 | 5,083.0 | 104.1 | 5,236.0 | 110.3 | 2,092.0 |
| *Naphthalene* | | | | | |
| 81.3 | 125.0 | 79.9 | 205.0 | 81.3 | 65.1 |
| 89.6 | 211.1 | 91.0 | 766.2 | 96.5 | 98.0 |
| 99.9 | 347.2 | 103.4 | 1,088.0 | 109.6 | 291.3 |
| *Parathion* | | | | | |
| 79.8 | 13.0 | 80.5 | 22.2 | 81.9 | 6.7 |
| 90.2 | 14.4 | 91.6 | 29.1 | 97.2 | 11.8 |
| 107.6 | 18.3 | 104.1 | 46.3 | 110.4 | 15.4 |

| *Worst Case Error in K Values* | |
|---|---|
| Benzene | ±47.4 |
| Toluene | ±50.4 |
| Naphthalene | ±7.1 |
| Parathion | ±1.5 |

*$P$ = pressure; $K_t$ = $K$ value in ternary system; $K_s$ = $K$ value in six-component system

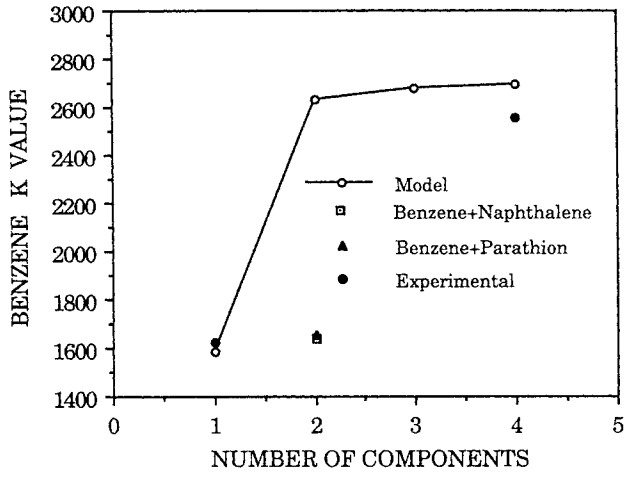


**Figure 1. Distribution coefficient (*K* value) of benzene as a function of number of components in supercritical carbon dioxide and water mixture at 318 K and 90.2 bar.**

Number of components: 1 = benzene; 2 = benzene + toluene; 3 = benzene + toluene + naphthalene; 4 = benzene + toluene + naphthalene + parathion

found that this multicomponent effect is significant even in very dilute systems, and it can be explained by interactions among supercritical $CO_2$, water, and each of the mixture components.

The interaction parameters (Table 2) based on the ternary system data were used to predict the distribution coefficients of both the ternary and six-component system behavior at 318 and 330 K. Our model predicted the multicomponent system behavior at two temperatures with reasonable accuracy, only from a single temperature ternary information. The interaction parameters of the components in the system were regarded as temperature-independent. The results also verified the assumptions that the interaction parameters for hydrocarbon pairs and very dilute component pairs are zero, and $k_{ij} = k_{ji}$ for nonpolar component pairs. Table 4 shows the average absolute deviation

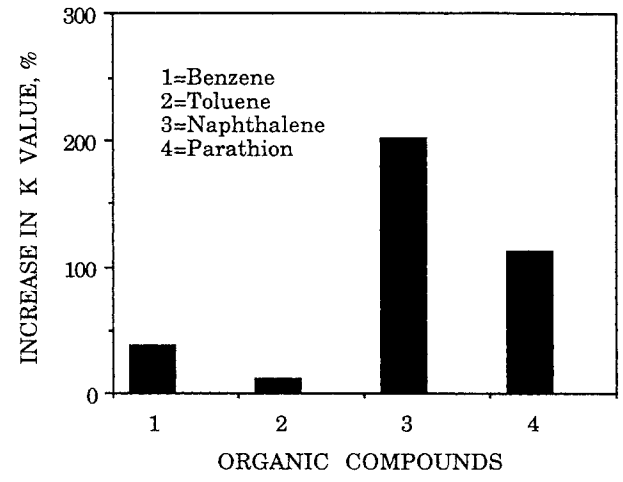


**Figure 2. Percentage increase in distribution coefficient of each compound in six-component system vs. ternary system at 318 K.**

**Table 4. Average Absolute Deviation between Predicted and the Worst-Case Experimental Distribution Coefficients in Six-Component System***

| Compounds | Avg. Abs. Dev. in *K* Values (%) at 318 K | Avg. Abs. Dev. in *K* Values (%) at 330 K |
|---|---|---|
| Benzene | 21.9 | 30.5 |
| Toluene | 26.7 | 30.7 |
| Naphthalene | 22.5 | 18.4 |
| Parathion | 71.2 | 50.1 |

*Average absolute deviation (%) $= (100/n)\sum_i |(K_{iexp} - K_{ical})/K_{iexp}|$

between predicted and experimental distribution coefficients. The worst-case *K* values which include the error terms in Table 3 were used to calculate the deviation. The agreement between the model and the experimental data may be considered to be acceptable when orders of magnitude differences in the *K* values are taken into consideration. The large prediction error is due partly to the experimental error in pressure and temperature control, but is due mostly to the inaccuracy involved in the GC analysis of aqueous samples which contain very small amounts of volatile compounds. Some of the compounds in water could be lost during sample handling, and the flame ionization detector does not have high sensitivity when aqueous samples are used directly. For parathion, the large deviation is possible due to the high acentricity of parathion ($\omega = 0.874$).

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## Notation

$a$ = force constant in Peng-Robinson equation of state
$b$ = volume constant in Peng-Robinson equation of state
$K$ = distribution coefficient
$k_{ij}, k_{ji}$ = interaction parameter between components $i$ and $j$
$L$ = liquid phase mole fraction
$R$ = ideal gas constant
$T$ = temperature
$V$ = volume
$x_i$ = mole fraction in the liquid phase
$y_i$ = mole fraction in the supercritical phase
$Z$ = compressibility factor

### *Greek letters*

$\omega$ = acentric factor
$\hat{\phi}$ = fugacity coefficient

### *Subscripts*

$i, j, k$ = components
$c$ = critical
$F$ = supercritical fluid phase
$L$ = liquid phase

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