Final Report

DE-FG07-96ER14691
Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2

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This final report for DE-FG07-96ER14691, entitled "Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2," contains 1) a statement of the original objectives of the overall project, 2) an executive summary of the accomplishments realized, 3) background, 4) a detailed discussion of the results for the three year grant period, 5) a list of publications and presentations that resulted from this grant, and 6) a list of the personnel involved in the project. This is followed by the literature cited and the pertinent figures.

1. Objectives

The overall objectives of this project were to gain a fundamental understanding of the solubility and phase behavior of metal chelates in supercritical CO_2. Extraction with CO_2 is a excellent way to remove organic compounds from soils, sludges and aqueous solutions and recent research has demonstrated that together with chelating agents it is a viable way to remove metals, as well. In this project we sought to gain fundamental knowledge that is vital to computing phase behavior, and modeling and designing processes using CO_2 to separate organics and metal compounds from DOE mixed wastes. Our overall program was a comprehensive one to measure, model and compute the solubility of metal chelate complexes in supercritical CO_2 and CO_2/cosolvent mixtures. One aspect of this work was the measurement of local solvation of metal chelates using UV-visible spectroscopy, which provided information on the solution microstructure. We also focused on the measurement of the solubility of metal chelates in supercritical CO_2 and CO_2/cosolvent mixtures, as well as the phase behavior of the chelating agents themselves in CO_2. The purpose of these measurements was to provide information with which we could evaluate and develop thermodynamic models of the solubility behavior. Finally, we focused on the implementation of a more reliable computational technique, based on interval mathematics, to compute the phase equilibria using the thermodynamic models. These studies were undertaken because fundamental information about metal chelate solubility in supercritical CO_2 is important in the design of processes using CO_2 to extract components from mixed wastes and in determining the optimum operating conditions.

2. Executive Summary

The major accomplishments from this project are as follows.

- We have shown that Regular Solution Theory, which is the model used by essentially all previous researchers to estimate the solubility of metal chelate complexes in supercritical CO_2, is totally inadequate. It gives both quantitatively and qualitatively incorrect predictions. Its use for process design purposes would have catastrophic consequences. Rather, we have shown that equation of state models provide a much superior representation of the phase behavior with just one parameter fit to limited metal chelate/CO_2 solubility measurements, as long as some minimal thermodynamic data is available.
- From new solubility measurements, we show for the first time that over a wide range of pressures and temperatures the presence of organic co-contaminants would actually increase the solubility of metal chelates in supercritical CO_2.
- We have demonstrated that on a microscopic level organic co-contaminants that are dissolved in the CO_2 will enrich the immediate area around a solubilized metal chelate complex. However, in determining the extent to which the metal chelate solubility increases with the addition of co-contaminant, this microscopic behavior is secondary to the solutions' bulk density increase.
- We have developed a completely reliable computational technique, based on interval analysis, to compute the phase behavior of CO_2 mixtures that contain metal chelates and chelating agents using cubic equations of state. Unlike any conventional method (that may be prone to error through failure to converge or convergence to an incorrect solution), the new method that we have developed is guaranteed to provide the correct phase behavior for any particular cubic equation of state model.

Through a combination of phase behavior measurements, spectroscopy and the development of a new computational technique, we have achieved a completely reliable way to model metal chelate solubility in supercritical CO_2 and CO_2/co-contaminant mixtures. Thus, we can now design and optimize processes to extract metals from solid matrices using supercritical CO_2, as an alternative to hazardous organic solvents that create their own environmental problems, even while helping in metals decontamination.

3. Background

Extraction with supercritical CO_2 is an attractive possibility for the separation of DOE mixed wastes. Carbon dioxide is nontoxic and nonflammable and extraction with CO_2 has been successful for the decaffeination of coffee and tea, recovery of hops, edible oils and other natural products, the regeneration of activated carbon, the separation of organic solutions, and the fractionation of polymers. Supercritical CO_2 has also been used for the selective extraction of compounds from soils and other solid matrices (McHugh and Krukonis, 1990). Based on preliminary investigations at Rocky Flats and the University of Colorado, extraction with CO_2 has been proposed as a way to separate organics from DOE low-level mixed wastes at Hanford and Rocky Flats. However, an important issue is the fate of the metal compounds. The seminal work of several research groups over the last decade has shown not only that some metal chelates are sufficiently soluble in CO_2 or CO_2/cosolvent mixtures, but that metals can be successfully extracted from aqueous solutions and solid matrices with CO_2. Although not reviewed here, there have, in particular, been significant contributions in the form of numerous publications

from the groups of Professor Chen Wai at the University of Idaho, and Professor Robert Sievers at the University of Colorado.

An alternative to extraction of metals from solid matrices with chelating agents dissolved in CO_2 is the use of conventional organic solvents. Although it would require higher capital investment for the high pressure vessels, there are some significant advantages to the use of CO_2. Using chelating agents in conventional organic solvents is effective in removing metal contaminants but it leaves residual organic solvent in the solid matrix. Moreover, the effluent from the extractor presents a complicated separation problem, where metal chelates and organic co-contaminants must be separated from the organic solvent/chelating agent mixture that one would like to recycle. The residual organics in the solid matrix generally must be steam stripped, which produces an aqueous waste stream that is contaminated with organics. Thus, the clean-up effort would produce a waste of its own. Conversely, supercritical CO_2 leaves no residual solvent in the solid matrix, has higher diffusivity so it is more effective in permeating the matrix, and the solutes can be separated from the CO_2 by simple depressurization.

Since metal chelates have significantly lower solubilities in CO_2 than most liquid organics, one could devise a two-step extraction of solid matrices in which the organics were removed first and then the metals were removed by adding the chelating agent to the CO_2 solvent stream. Conversely, one can envision a process in which both organics and metals are extracted at a relatively high pressure (e.g., 200-400 bar). As our data will show below, there may be some significant process advantages to this configuration. The metal chelates and organics could be selectively separated by partial depressurizations. If the chelating agent was less volatile than the organic co-contaminants then excess chelating agent could be separated and re-added to the CO_2 recycle stream, as shown in Figure 1. Conversely, if the chelating agent was more volatile than the organic co-contaminants then the metal chelates and organics could be separated out by partial depressurizations, and the excess chelating that remained in solution could be directly recycled with the CO_2, as shown in Figure 2.

Although the feasibility of such a process has been demonstrated by previous researchers, what has been lacking is a quantitative and reliable method to model and compute the solubility of metal chelates in supercritical CO_2 and CO_2/co-contaminant mixtures, as well as the full multicomponent high pressure phase behavior of the process systems necessary for CO_2 extraction of metals from solid matrices. This is exactly what has been accomplished under the sponsorship of this grant, and the results are presented below.

4. Results and Discussion

The accomplishments realized under the sponsorship of this grant fall into four categories: A) Modeling, B) Solubility Measurements, C) Local Composition Measurements, and D) Computational Methods.

A) Modeling

Essentially all previous modeling of metal chelate solubilities in supercritical CO_2 had been done with Regular Solution Theory (Lagalante *et al.*, 1995; Wai *et al.*, 1996). The main

advantages of this model are that for solutions of components that are all liquids at the temperature of interest, the only information needed to predict the phase behavior is each components' liquid molar volume, v_L, and solubility parameter, δ. The solubility parameter is defined as $(\Delta U/ v_L)^{1/2}$, where ΔU is the internal energy of vaporization. If the component of interest is a solid then one requires the enthalpy change on melting, and the triple point temperature (which can generally be approximated by the normal melting point). If more accuracy is needed then the heat capacities of the solute as a liquid and a solid are needed. Although these properties are not always known for metal chelates, Regular Solution Theory (RST) has been used quite successfully to predict the solubility of metal chelates in liquids (Koshimura, 1978). However, this model is an excess Gibbs free energy (G^E) model developed by Scatchard and Hildebrand for liquid solutions only and it explicitly assumes no volume change on mixing. Clearly, this assumption is violated by supercritical fluid (SCF) mixtures, where large volume changes are expected to occur. In fact, G^E models are general not used for SCF mixtures because they do not explicitly include any sort of pressure dependence; clearly, pressure is an important variable for SCF mixtures. Thus, one would not expect RST to accurately model the solubility of metal chelates in SCFs, which is, in fact, the case.

In Figure 3, we show the RST predictions for the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 at 40°C and 60°C. The data are new measurements taken in our laboratory and these will be discussed below. As shown in the figure, RST underpredicts the solubility by several orders of magnitude – note the logarithmic scale on the y-axis. The problem is worst in the low pressure region, where the predictions are off by as much as fourteen orders of magnitude! Also shown on the graph are the predictions for ideal solubility, i.e., assuming an activity coefficient of one. Another interesting feature of RST is that it gives the incorrect temperature dependence. RST predicts that the solubility of Fe(acetylacetonate)$_3$ in SC CO_2 should be greater at 40°C than at 60°C over the entire pressure range. In reality, solubilities of most solids in SC CO_2 exhibit a "crossover" pressure. At low pressures the solubility at a given pressure is greater at lower temperatures but at higher pressures the solubility is greater at higher temperatures. This is due to the competing effects of temperature that raises the sublimation pressure and density. At a given pressure the solution density will be lower at the higher temperature, and lower density generally means lower solubility of solutes. The density effect dominates at low pressures and the temperature effect on the sublimation pressure dominates at higher pressures. Not surprisingly, these entire trends are missed by RST. Thus, we conclude that RST is inadequate in modeling metal chelate solubilities in SCFs and that its use would provide gross errors in design calculations. For these calculations, the δ for CO_2 was taken from Giddings *et al*. (1968), who gave δ as a function of the reduced density. The molar volumes for CO_2, v_L, for CO_2 were calculated from the equation of state developed by Span and Wagner (1996). The δ and v_L for Fe(acetylacetonate)$_3$ of 23.80942 MPa$^{1/2}$ and 271 cm^3/mol, respectively, were taken from Koshimura (1978). The enthalpy of fusion and normal melting point temperature (used as an approximation of the triple point temperature) of Fe(acetylacetonate)$_3$ were 34.10 kJ/mol and 181.5K, respectively (Ribeiro da Silva *et al*., 1996; Beech and Lintonbon, 1971).

Conversely, equations of state have been used to model solid solubilities in SCFs with substantial success (Johnston *et al*., 1989). The solid/fluid equilibrium requirement is:

$$f_2^{\mathrm{S}} = P_2^{\mathrm{sub}}(T)\exp\left[\frac{v_2^S}{RT}(P - P_2^{\mathrm{sub}}(T))\right] = y_2 P\hat{\phi}_2^{\mathrm{F}}(T,P,\mathbf{y}) = \hat{f}_2^{\mathrm{F}},$$

where f_2^{S} is the fugacity of the solute in the pure solid phase, $\hat{f}_2^{\mathrm{F}}$ is the fugacity of the solute in the fluid phase solution, $P_2^{\mathrm{sub}}(T)$ is the sublimation pressure of pure solute, v_2^{S} is the molar volume of pure solute, and $\hat{\phi}_2^{\mathrm{F}}(T,P,\mathbf{y})$ is the fugacity coefficient of the solute in a fluid phase of composition $\mathbf{y} = (y_1, y_2, \ldots, y_C)^{\mathrm{T}}$. A cubic equation of state, such as the Peng-Robinson equation (Peng and Robinson 1976), can be used to calculate the fugacity coefficient.

$$P = \frac{RT}{(v-b)} - \frac{a}{[v(v+b)+b(v-b)]}$$

where,

$$a = \frac{0.45724R^2T_c^2}{P_c}[1+(0.3764+1.54226w-0.2699w^2)(1-T_r^{0.5})]^2$$

$$b = 0.07780\frac{RT_c}{P_c}$$

and w is the acentric factor. T_c and P_c are the critical temperature and pressure of the compound, respectively, and $T_r = \frac{T}{T_c}$. To extend this equation to mixtures, the conventional van der Waals mixing rules can be used:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}, \quad b = \sum_{i=1}^{n} x_i b_i, \text{ and } a_{ij} = (a_{ii}a_{jj})^{0.5}(1-k_{ij})$$

where the sums extend over all components, and a_{ii} and b_i indicate the pure component values for component i.

As shown in Figure 4-6, which now shows the data for Fe(acetylacetonate)$_3$ on a linear axis. The Peng-Robinson equation gives both qualitatively and quantitatively correct representation of the phase behavior. However, this model does require some unknown parameters and the differences in the three graphs are the way those parameters were fit or estimated. In Figure 4, the T_c, P_c, w of Fe(acetylacetonate)$_3$ and the binary interaction parameter, k_{ij}, between Fe(acetylacetonate)$_3$ and CO_2 were all fit to the experimental solubility data. While T_c, P_c, and w are available for many organic compounds, they are not available for essentially any of the metal chelates of interest. In Figure 5, we estimate T_c and P_c from a group contribution method developed by Joback (Prausnitz *et al.*, 1999) and fit w and k_{ij} to the experimental solubility data. In Figure 6, the only fit parameter is k_{ij}. The acentric factor was determined from its definition, $\omega \equiv -\log\left(\frac{P^{Vap}}{Pc}\right)_{T/Tc=.7} - 1.000$. For this equation, the vapor pressures were determined from the literature value of the enthalpy of vaporization (Beech and Lintonbon,

1971) and the vapor pressure at the triplet point. This was determined by extrapolating sublimation pressure data (Ribeiro da Silva *et al*., 1996) to the triple point, where the sublimation pressure and the vapor pressure are equal. The critical pressure and temperature were estimated from Joback's method (Prausnitz *et al*., 1999), which requires the normal boiling point. This, of course, could be determined from the vapor pressure equation evaluated at 1 atm. It gave a boiling point for Fe(acetylacetonate)$_3$ of 343ºC, which is close to published values of other tris acetylacetonates. All of these methods to calculate the solubility of the Fe(acetylacetonate)$_3$ in CO_2 using the Peng-Robinson equation of state require the solid density (Roof, 1956) and the sublimation pressure (Fedotova *et al*., 1992). As you can see, all three methods give equivalently good results. Thus, using minimal pure component thermodynamic data and standard estimation techniques, we are able to obtain quantitative estimates of the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 with only one interaction parameter fit to a few solubility measurements.

B) Solubility Measurements

To aid in the development of a new modeling technique based on cubic equations of state for metal chelates in supercritical CO_2, we measured the solubility of a representative metal chelate complex, Fe(acetylacetonate)$_3$ in supercritical CO_2 and CO_2/co-contaminant mixtures. Previous data for most compounds has only given a couple pressures or temperatures and we needed some complete isotherms with which to compare the modeling. These data were taken using an ISCO 220SX extractor that has been modified to use a variable micrometering restrictor valve (309-505 series) from Supercritical Fluid Technologies, Inc., along with an innovative flush system that we developed in our laboratory. We found that when studying this high melting metal chelate, the standard heated restrictor from ISCO plugged dependably, but the new system gives good results.

The data for the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 at 40°C and 60°C has already been presented in Figures 4-6. The solubilities increase with increasing pressure, as expected. Moreover, the system exhibits a "crossover" pressure at around 200 bar, as described above. We also measured the solubility increase of Fe(acetylacetonate)$_3$ in supercritical CO_2 when 3 mol % of chloroform was added to the system. This data is shown in Figure 7 and, to our knowledge, is the first complete isotherm of the solubility increase of a metal chelate when a cosolvent is present. We chose $CHCl_3$ as a typical organic co-contaminant that might be present with radioactive or heavy metals at a DOE site. As can be seen in the figure, the presence of the $CHCl_3$ increases the solubility of Fe(acetylacetonate)$_3$ by about a factor of three. Thus, for a given volume of material that had to be cleaned, this would represent a significant reduction in the size of the vessel needed. Since pressure vessels are expensive, representing the majority of the capital investment cost of most supercritical extraction processes, this would substantially decrease the cost associated with a CO_2-based decontamination process. The modeling of this system is discussed below.

C) Local Composition Measurements

To better understand the Fe(acetylacetonate)$_3$/co-contaminant/SC CO_2 system, we undertook a program to use spectroscopy to measure the local composition of $CHCl_3$ around

Fe(acetylacetonate)$_3$ in SC CO_2. Based on literature results for polar organic solutes in SCF mixtures, it appeared that an important contributor to the increased solubilities and increased extraction efficiencies of metal chelates in CO_2/cosolvent mixtures might be the preferential solvation of the metal chelate by the cosolvent. We used UV-vis spectroscopy to measure the preferential solvation of Fe(acetylacetonate)$_3$ by chloroform in SC CO_2 at 60°C. Initially, we had planned to measure preferential solvation by solvatochromic shifts since there was a report of this method being used with Fe(acetylacetonate)$_3$ in the literature (Tingey *et al*. 1989). Unfortunately, the UV-visible absorption peaks of Fe(acetylacetonate)$_3$ do not shift with changing solvent environment. Fortunately, Fe(acetylacetonate)$_3$ does show significant changes in the intensity of the metal to ligand charge transfer band ~431 nm, with higher intensities observed in nonpolar solvents. Thus, the ratio of the intensity of a more stable intraligand band ~272 nm to the intensity of the 431 nm band is a sensitive measure of the local environment around the metal chelate complex. We have used this technique to measure the preferential solvation of Fe(acetylacetonate)$_3$ in SC CO_2/3 mole % chloroform mixtures. The results indicate that the local environment around the Fe(acetylacetonate)$_3$ is highly enriched with chloroform (up to seven times the bulk composition) and that it is largest at lower pressures, as shown in Figure 7. This is very similar to trends observed for the preferential solvation of polar organic solutes in SCFs but is the first measurement of preferential solvation of a metal chelate in a supercritical fluid mixture. Thus, the local environment around the metal chelate is substantially enriched with the chloroform and this is particularly pronounced at the lower pressures.

These results suggest that the solubility increase of Fe(acetylacetonate)$_3$ in SC CO_2 when 3 mol % $CHCl_3$ is added to the CO_2 may be due to the increased local composition of the $CHCl_3$ around the metal chelate. To determine the extent to which is phenomenon is important, we predicted the solubility increase that one would expect based solely upon the density increase that one gets at a particular pressure and temperature when one adds 3 mol % chloroform to CO_2. This can be done simply with the equation of state modeling. Using the best fit k_{ij} for Fe(acetylacetonate)$_3$/CO_2 from the binary solubility data, a k_{ij} for $CHCl_3$/CO_2 estimated from binary data in the literature, and a k_{ij} of zero for the $CHCl_3$/Fe(acetylacetonate)$_3$ pair, we estimated the solubility of Fe(acetylacetonate)$_3$ in a CO_2/3 mol% $CHCl_3$ mixture. As can be seen in Figure 7, the Peng-Robinson equation very accurately predicts the solubility increase observed for this system with the addition of a co-contaminant. Since the Peng-Robinson equation of state does not incorporate any knowledge of local composition increases, at least for this system, this result suggests that the main factor in determining the solubility increase is the increase density of the CO_2/chloroform mixture. Nonetheless, the preferential solvation of the metal chelate by the co-contaminant does exist, and it may play some role in determining the solubility of the metal chelate in CO_2/co-contaminant mixtures.

D) Computational Methods

As mentioned above, conventional flash algorithms can fail to converge or converge to incorrect solutions for the types of high pressure phase equilibrium calculations that are needed to design and optimize processes to extract metals with supercritical CO_2. Whether determining the best-fit k_{ij} from experimental data, or calculating the solubility of a solid at new conditions using a particular EOS model, there are two computational pitfalls that can be encountered in the calculation of solid-fluid equilibrium:

1. Solid solubilities in SCFs are usually computed by locating a mole fraction which satisfies the equifugacity equation relating the solute fugacity in the supercritical fluid, as predicted by the EOS, and the fugacity of the pure solid (see equation in modeling section above). However, at certain values of temperature, pressure, and k_{ij}, there can exist multiple solutions to the equifugacity condition. A common method for solving the equifugacity equation is successive substitution or some similar approach (McHugh and Krukonis, 1990), using some small value of the solid solubility in the fluid phase as the initial guess. In general, this strategy will only find the smallest solubility root and may miss any larger values, if present, that satisfy the equifugacity equation. Thus, what is needed is a completely reliable method to determine *all* the roots to the equifugacity equation.
2. Equifugacity is a necessary but not sufficient condition for stable solid-fluid equilibrium. Solutions to the equifugacity equation must be tested for global thermodynamic phase stability. One widely used technique to determine phase stability is based on tangent plane analysis (Baker *et al*., 1982); this method can distinguish the stable case from the metastable or unstable cases, but cannot distinguish metastable from unstable. Since we are interested in determining the thermodynamically stable solutions to the equifugacity equations, we have used the tangent plane analysis. Tangent plane analysis itself, however, presents a difficult computational problem, which again can be addressed by using a completely reliable equation solving technique.

To address these problems, we have developed a completely reliable method for determining all the solutions to the equifugacity equation, and then using a method that can test those solutions for stability with complete certainty. Thus, we present a methodology that is guaranteed to identify the correct, thermodynamically stable composition of a fluid phase in equilibrium with a pure solute, as will be encountered in the extraction of metals from solid matrices with CO_2.

The method that we have used to formulate this problem is given in detail by Xu *et al.* (2000). It is based on the equifugacity condition for the solute, which is given above in the modeling section. We have used the Peng-Robinson equation of state with standard van der Waals mixing rules. The computation of phase stability is based on the tangent plane distance D, which is simply the distance from the tangent plane to the Gibbs energy surface. The application of this method to solid/fluid equilibrium is discussed in more detail in Xu *et al*. (2000).

To solve this problem, we have applied interval mathematics, in particular an interval Newton/generalized bisection (IN/GB) technique, to find, or, more precisely, to find very narrow enclosures of, all solutions of a nonlinear equation system, or to demonstrate that there are none. The algorithm that we used has been described by Hua *et al*. (1998a,b), and it is given in more detail by Schnepper and Stadtherr (1996). Properly implemented, this technique provides the power to find, *with mathematical and computational certainty*, enclosures of *all solutions* of a system of nonlinear equations (Kearfoot, 1996), or to determine with certainty that there are none, provided that initial upper and lower bounds are available for all variables. This is made possible through the use of the powerful existence and uniqueness test provided by the interval Newton method. The technique can also be used to enclose with certainty the *global minimum* of a nonlinear objective function.

We have applied the IN/GB algorithm to the solution of the equifugacity condition, thus determining with certainty *all* the roots within the given initial interval, or determining with certainty that there are none. In the latter case, this is mathematical proof that there is no solid phase present at equilibrium. The second step in the method we developed is the testing of the equifugacity roots, just found, for stability. Again this is done using the IN/GB algorithm, thus guaranteeing that all the stationary points of the tangent plane distance *D*, or equivalently, the global minimum of *D*, are enclosed.

This method is the first application of a global optimization method to the solid/fluid equilibrium problem. The solid/fluid phase equilibria computed as part of this grant exploited this new method to make sure that the correct solutions were identified. The application of this new method to a variety of problems, several of which exhibit very complex behavior, can be found in Xu *et al*. (2000).

In summary, we have produced four major accomplishments under the auspices of this grant. First, we have shown that Regular Solution Theory gives both quantitatively and qualitatively incorrect predictions of the solubility of metal chelates in supercritical CO_2. Conversely, we have shown that cubic equation of state models provide a very good representation of the phase behavior with just one parameter fit to limited metal chelate/CO_2 solubility measurements. In addition, from new solubility measurements, we have shown for the first time that over a wide range of pressures and temperatures the presence of organic co-contaminants would actually increase the solubility of metal chelates in supercritical CO_2. Although we found that on a microscopic level organic co-contaminants that are dissolved in the CO_2 will enrich the immediate area around a solubilized metal chelate complex, this has no significant affect in determining the solubility enhancement that is observed when the co-contaminants are present. Finally, we have developed a completely reliable computational technique, based on interval analysis, to compute the phase behavior of CO_2 mixtures that contain metal chelates and chelating agents using cubic equations of state. Unlike any conventional method (that may be prone to error through failure to converge or convergence to an incorrect solution), the new method that we have developed is guaranteed to provide the correct phase behavior for any particular cubic equation of state model. Through a combination of phase behavior measurements, spectroscopy and the development of a new computational technique, we have achieved a completely reliable way to model metal chelate solubility in supercritical CO_2 and CO_2/co-contaminant mixtures. Thus, we can now design and optimize processes to extract metals from solid matrices using supercritical CO_2, as an alternative to hazardous organic solvents that create their own environmental problems, even while helping in metals decontamination.

5. List of Publications and Presentations

Below are lists of publications and presentations that acknowledged at least partial support from this Department of Energy grant.

Publications

1. James Z. Hua, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Phase Stability Using Interval Analysis: Cubic Equation of State Models," Computers and Chemical Engineering, 22, 1998, p. 1207-1214.

2. James Z. Hua, Joan F. Brennecke and Mark A. Stadtherr, "Enhanced Interval Analysis for Phase Stability: Cubic Equation of State Models," Ind. Eng. Chem. Res., 37, 1998, p. 1519-1527.

3. Robert W. Maier, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Homogeneous Azeotropes," AIChE J., 44, 1998, 1745-1755.

4. Erik J. Roggeman, Aaron M. Scurto, Mark A. Stadtherr, and Joan F. Brennecke, "Spectroscopy, Measurement and Modeling of Metal Chelate Solubility in Supercritical CO_2," Proceedings of the 8th International Symposium on Supercritical Fluid Chromatography and Extraction, St. Louis, MO, July 12-16, 1998.

5. James Z. Hua, Robert W. Maier, Steven R. Tessier, Joan F. Brennecke and Mark A. Stadtherr, "Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach," Fluid Phase Equilibria, 158-160, 1999, 607-615.

6. Joan F. Brennecke and John E. Chateauneuf, "Homogeneous Organic Reactions as Mechanistic Probes in Supercritical Fluids," Chemical Reviews, 99 (2), 1999, 433-452.

7. Mark A. Stadtherr, "High Performance Computing: Are We Just Getting Wrong Answers Faster?" *AIChE CAST Communications*, **22**(1), 6-14 (1999).

8. Mary J. Kremer, Karen A. Connery, Matthew M. DiPippo, Junbo Feng, John E. Chateauneuf and Joan F. Brennecke, "Spectroscopy to Measure Solvation, Kinetics, and Equilibrium in Supercritical Fluids," Proceedings of the 6th Meeting on Supercritical Fluids: Chemistry and Materials, Nottingham, UK, April 10-13, 1999.

9. Stephan R. Tessier, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Phase Stability Analysis for Excess Gibbs Energy Models," Chemical Engineering Science, in press,1999.

10. R. W. Maier, J. F. Brennecke and M. A. Stadtherr, "Computing Homogeneous Azeotropes Using Interval Analysis," Chem. Eng. & Tech., in press, 1999.

11. Chao-Yang Gau, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Nonlinear Parameter Estimation in VLE Modeling," submitted to Fluid Phase Equilibria, 1999.

12. Robert W. Maier, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Reactive Azeotropes," submitted to Computers and Chemical Engineering, 1999.

13. Gang Xu, Aaron M. Scurto, Marcelo Castier, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of High Pressure Solid-Fluid Equilibrium," Ind. Eng. Chem. Res., in press, 1999.

Invited Presentations

1. Mark A. Stadtherr, James Z. Hua, and Joan F. Brennecke, "Phase Stability Analysis for Equation of State Models," Institute for Operations Research and the Management Sciences, National Meeting, Dallas, October 26-29, 1997.

2. Joan F. Brennecke, "Supercritical Fluids for Environmental Applications: A Chemical Engineering Perspective," Department of Chemistry, Western Michigan University, November 6, 1997.

3. Mark A. Stadtherr, "Reliable Process Modeling Using Interval Analysis," Department of Chemical Engineering Seminar, Carnegie-Mellon University, Pittsburgh, PA, February 24, 1998.

4. Joan F. Brennecke, "Dense Phase Fluids: Phase Behavior," Department of Energy/Environmental Protection Agency Dense Phase Fluids and Alternative Reaction Media Workshop, Sante Fe, NM, April 13-16, 1998.

5. Joan F. Brennecke, "Thermodynamic and Kinetic Studies in Supercritical Fluids," Department of Chemistry, Loyola University of Chicago, April 16, 1998.

6. Erik J. Roggeman, Aaron M. Scurto, Mark A. Stadtherr, and Joan F. Brennecke "Spectroscopy, Measurement and Modeling of Metal Chelate Solubility in Supercritical CO_2," 8th International Symposium on Supercritical Fluid Chromatography and Extraction, St. Louis, MO, July 12-16, 1998.

7. Joan F. Brennecke, Mark A. Stadtherr and John E. Chateauneuf, "Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2", Department of Energy EMSP Scientific Workshop, Rosemont, IL, July 27-30, 1998.

8. Joan F. Brennecke, "Understanding Metal Chelates in Supercritical CO_2," Department of Chemical Engineering, University of Texas at Austin, Austin, TX, September 9, 1998.

9. Joan F. Brennecke, "Using Spectroscopy to Understand Metal Chelates in Supercritical CO_2," Department of Chemical Engineering, University of Massachusetts, Amherst, MA, October 1, 1998.

10. Mark A. Stadtherr, "High Performance Computing: Are We Just Getting Wrong Answers Faster?", Computing and Systems Technology Division Awards Dinner, AIChE Annual Meeting, Miami Beach, FL, November 15-20, 1998.

11. John E. Chateauneuf, "The Use of Reaction Intermediates to Investigate Supercritical Fluid Solvent Effects: The Development of Supercritical Fluids as Environmentally Benign Reaction Media," Department of Chemistry, Central Michigan University, Mt. Pleasant, MI, March 1 (1999).

12. John E. Chateauneuf, "The Development of Supercritical Fluids as Environmentally Benign Reaction Media: The Influence of SCF Solvation on Chemical Reactivity," Department of Chemistry and the Center for Photochemical Sciences, Bowling Green State University, OH, March 3 (1999).

13. John E. Chateauneuf, J. Zhang, J. Brink, M. Slominis and M. Perkovic, "Investigation of Free Radical and Radical Ion Reactivity with Supercritical Carbon Dioxide," (poster presentation) American Chemical Society 217th National Meeting, Anaheim, CA, March 22 (1999). Sci-Mix,

14. Joan F. Brennecke, "Spectroscopy to Measure Solvation, Kinetics, and Equilibrium in Supercritical Fluids, " 6th Meeting on Supercritical Fluids: Chemistry and Materials, Nottingham, UK, April 10-13, 1999.

15. Joan F. Brennecke, "Pollution Prevention with Supercritical CO_2," Department of Civil Engineering, Northwestern University, Evanston, IL, April 30, 1999.

16. Mark A. Stadtherr, Gang Xu, Benito Stradi, Robert W. Maier and Joan F. Brennecke, "Reliable Computation of Phase Behavior Using Interval Methods," SIAM Annual Meeting, Atlanta, GA, May 12-15, 1999.

17. John E. Chateauneuf, "Reactions in Supercritical Fluids: The Development of Supercritical Fluids as Environmentally Benign Reaction Media," Department of Chemistry, Andrews University, Berrien Springs, MI, May 19, (1999).

18. Joan F. Brennecke, "Environmental Applications of Supercritical Fluids," Escola de Quimica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, May 25, 1999.

19. Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Phase Behavior Using Interval Analysis," Escola de Quimica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, May 27, 1999.

20. Joan F. Brennecke, "Spectroscopic Measurements of Local Compositions," PLAPIQUI, Universidad Nacional del Sur, Bahia Blanca, Argentina, June 1, 1999.

21. Joan F. Brennecke, "Application of Supercritical Chemical Engineering Processes in Environmental Protection and Remediation," PLAPIQUI, Universidad Nacional del Sur, Bahia Blanca, Argentina, June 4, 1999.

22. John E. Chateauneuf, “Reactions in Supercritical Fluids: The development of Supercritical Fluids as Environmentally Benign Reaction Media,” Department of Chemistry, Argonne National Laboratory, Argonne, IL, June 30, (1999).

23. John E. Chateauneuf, “Free Radical Reactions in Supercritical Fluids,” Gordon Research Conference on Free Radical Reactions, Holderness School, Plymouth, NH, July 11-16, (1999).

24. John E. Chateauneuf, “The Use of Reaction Intermediates to Probe Supercritical Fluid Solvent Effects,” American Chemical Society 218th National Meeting, New Orleans, LA, August 22-26 (1999). Symposium on Chemistry of Reactive Intermediates and Modeling in Hydrocarbon Conversion.

25. Mark A. Stadtherr, “Recent Advances in Reliable Nonlinear Equation Solving,” AspenWorld 2000, Orlando, FL, to be presented Feb. 6-11, 2000.

26. Mark A. Stadtherr, “Reliable Process Modeling Using Interval Analysis,” Department of Chemical Engineering Seminar, University of Kansas, Lawrence, KS, to be presented March 29, 2000.

Contributed Presentations

1. Jianwei Zhang, Erik J. Roggeman, John E. Chateauneuf and Joan F. Brennecke, “Cosolvent Effects on Metal Chelates in Supercritical CO_2," Annual AIChE Meeting, Los Angeles, CA, Nov. 16-21, 1997.

2. Robert W. Maier, Joan F. Brennecke and Mark A. Stadtherr, "A New Approach for Reliable Computation of Homogeneous Azeotropes in Multicomponent Mixtures," Annual AIChE Meeting, Los Angeles, CA, Nov. 16-21, 1997.

3. James Z. Hua, Joan F Brennecke and Mark A. Stadtherr, "Combined Local and Global Approach to Reliable Computation of Phase Equilibria," Annual AIChE Meeting, Los Angeles, CA, Nov. 16-21, 1997.

4. James Z. Hua, Robert W. Maier, Steven R. Tessier, Joan F. Brennecke and Mark A. Stadtherr, “Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach,” (poster presentation) Eighth International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, The Netherlands, April 26-May 1, 1998.

5. Erik J. Roggeman, Aaron M. Scurto, Joan F. Brennecke and John E. Chateauneuf, “Spectroscopic Measurements of Preferential Solvation and Novel Solubility Measurements of Metal Chelate Complexes in Pure and Modified Supercritical CO_2,” 1998 Midwest Thermodynamics and Statistical Mechanics Conference, Notre Dame, IN, May 18-19, 1998.

6. Robert W. Maier, Mark A. Stadtherr and Joan F. Brennecke, "Reliable Computation of Homogeneous Azeotropes," 1998 Midwest Thermodynamics and Statistical Mechanics Conference, Notre Dame, IN, May 18-19, 1998.

7. Erik J. Roggeman, Aaron M. Scurto, John E. Chateauneuf and Joan F. Brennecke, "Cosolvent Effects to Enhance Metal Extraction with Supercritical CO_2," Annual AIChE Meeting, Miami, FL, Nov. 15-20, 1998.

8. Mark A. Stadtherr, Robert W. Maier, Benito A. Stradi, Gang Xu and Joan F. Brennecke, "Reliable Computation of High Pressure Phase Behavior," Annual AIChE Meeting, Miami, FL, Nov. 15-20, 1998.

9. Robert W. Maier, Joan F. Brennecke and Mark A. Stadtherr, "Computation of Reactive Azeotropes Using Interval Analysis," Annual AIChE Meeting, Miami, FL, Nov. 15-20, 1998.

10. John E. Chateauneuf, J. Zhang, J. Brink, M. Slominis and M. Perkovic, "Investigation of Free Radical and Radical Ion Reactivity with Supercritical Carbon Dioxide," (poster presentation) American Chemical Society 217th National Meeting, Anaheim, CA, March 24 (1999). Physical Chemistry Division, Free Radicals in the Condensed Phase Symposium.

11. Gang Xu, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Solid-Fluid Equilibria Using Interval Analysis," Midwest Thermodynamics and Statistical Mechanics Conference, Detroit, MI, May 17-18, 1999.

12. John E. Chateauneuf, "The Use of Reaction Intermediates to Probe Supercritical Fluid Solvent Effects," (poster presentation) American Chemical Society 218th National Meeting, New Orleans, LA, August 23 (1999).

13. Robert W. Maier, Joan F. Brennecke, and Mark A. Stadtherr, "A New Approach for Reliably Computing All Azeotropes of Multicomponent Mixtures," Annual AIChE Meeting, Dallas, TX, Oct. 31 – Nov. 5, 1999.

14. Mark A. Stadtherr, Robert W. Maier, and C.-Y. Gau, "New Interval Methodologies for Reliable Process Modeling", AIChE Annual Meeting, Dallas, TX, Oct. 31–Nov. 5, 1999.

15. Gang Xu, Joan F. Brennecke and Mark A. Stadtherr, "Reliable Computation of Solid-Supercritical Fluid Equilibria Using Interval Analysis," Annual AIChE Meeting, Dallas, TX, Oct. 31 – Nov. 5, 1999.

16. Gang Xu, Aaron M. Scurto, Marcelo. Castier, Mark A. Stadtherr, and Joan F. Brennecke "Reliable Computation of High Pressure Solid-Fluid Equlibrium", 5th International Symposium on Supercritical Fluids, Atlanta, GA, to be presented April 8-12, 2000.

17. Gang Xu, Aaron M. Scurto, Marcelo. Castier, Mark A. Stadtherr, and Joan F. Brennecke "Reliable Computation of High Pressure Solid-Fluid Equlibrium", COBEQ 2000, Águas de São Pedro, Brazil, to be presented Sept. 24-27, 2000.

6. List of Personnel Involved with This Project

University of Notre Dame

Graduate Students:
- Erik J. Roggeman, M.S. Thesis: Spectroscopy and Solubility Measurements of Metal Chelate Complexes in Supercritical Carbon Dioxide Solutions, 7/98
- Gang Xu, Ph.D. expected 2001
- Aaron M. Scurto, Ph.D. expected 2002
- William D. Haynes, Ph.D. expected 2002

Postdoctoral Associates:
- Jianwei Zhang, currently employed at Monsanto in St. Louis, MO

Faculty:
- Joan F. Brennecke, Professor of Chemical Engineering
- Mark A. Stadtherr, Professor of Chemical Engineering

Western Michigan University (subcontract)

Graduate Students:
- Jingsheng Zhang, M.S. expected 2000
- Honshu Jin M. S. Thesis: Spectroscopic Investigations of Carbocation Reactivity in Supercritical Carbon Dioxide, 7/99

Faculty:
- John E. Chateauneuf, Assistant Professor of Chemistry

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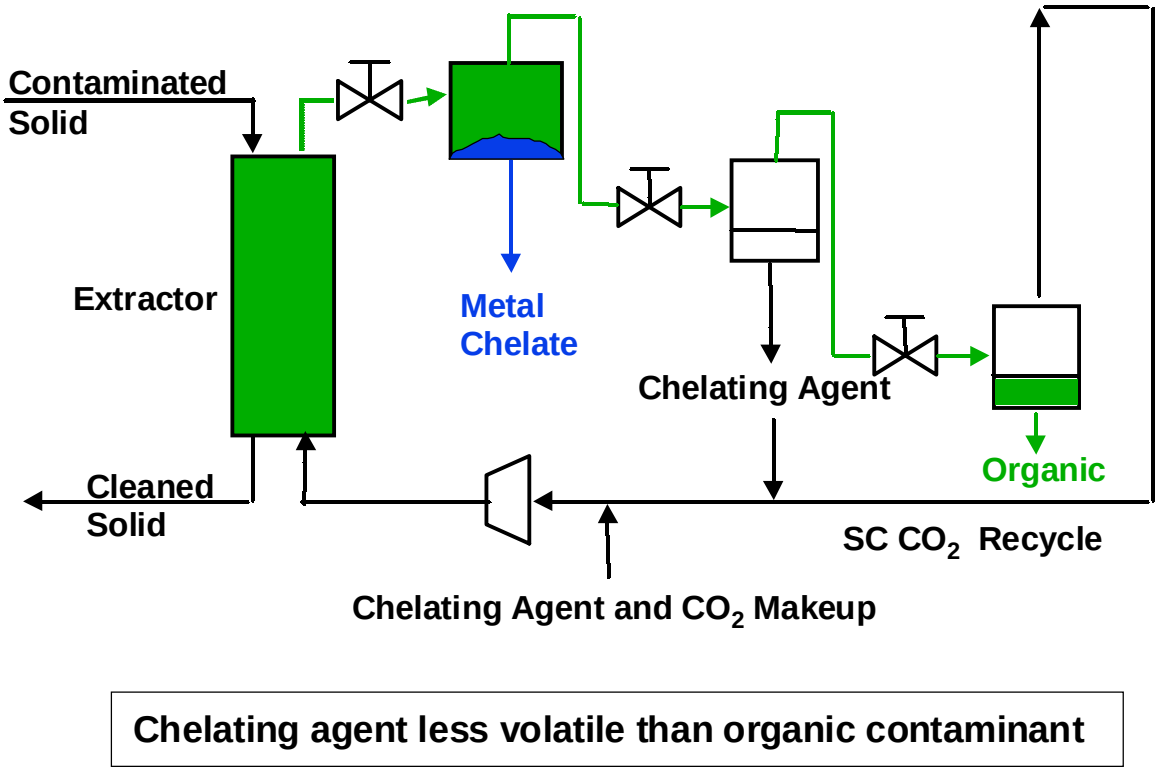

Figure 1 Schematic of metal extraction process using chelating agents dissolved in supercritical CO_2, in which the chelating agent is less volatile than any organic co-contaminants that might be present.

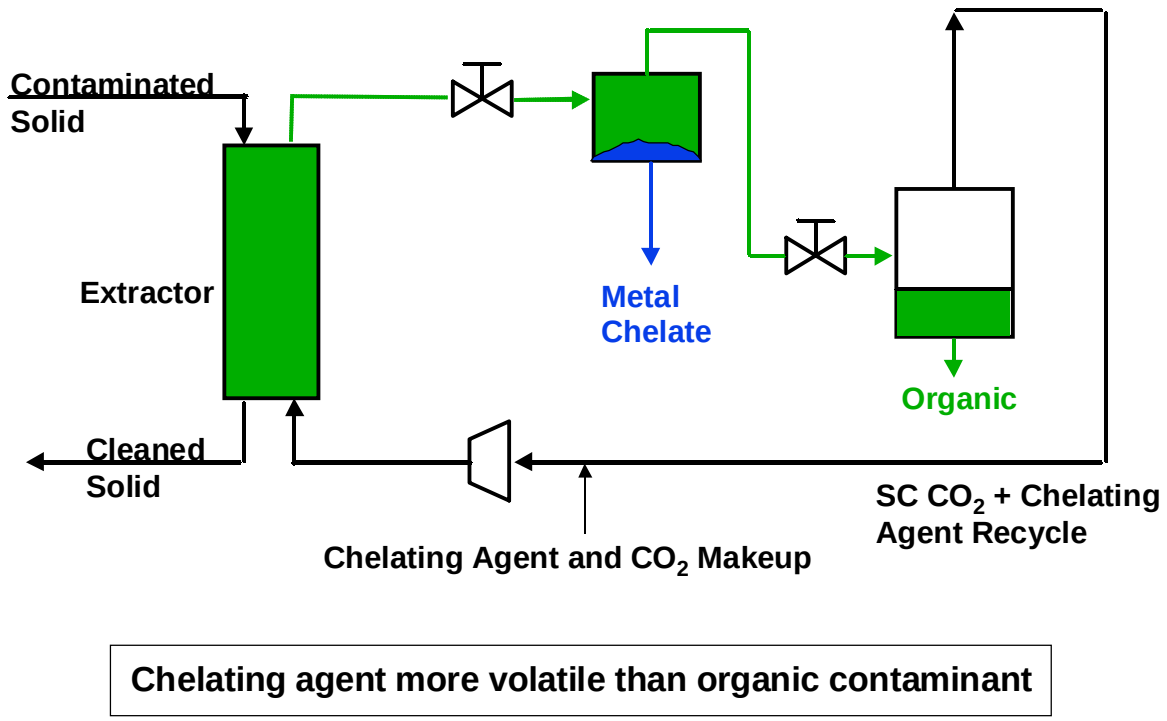

Figure 2 Schematic of metal extraction process using chelating agents dissolved in supercritical CO_2, in which the chelating agent is significantly more volatile than any organic co-contaminants that might be present.

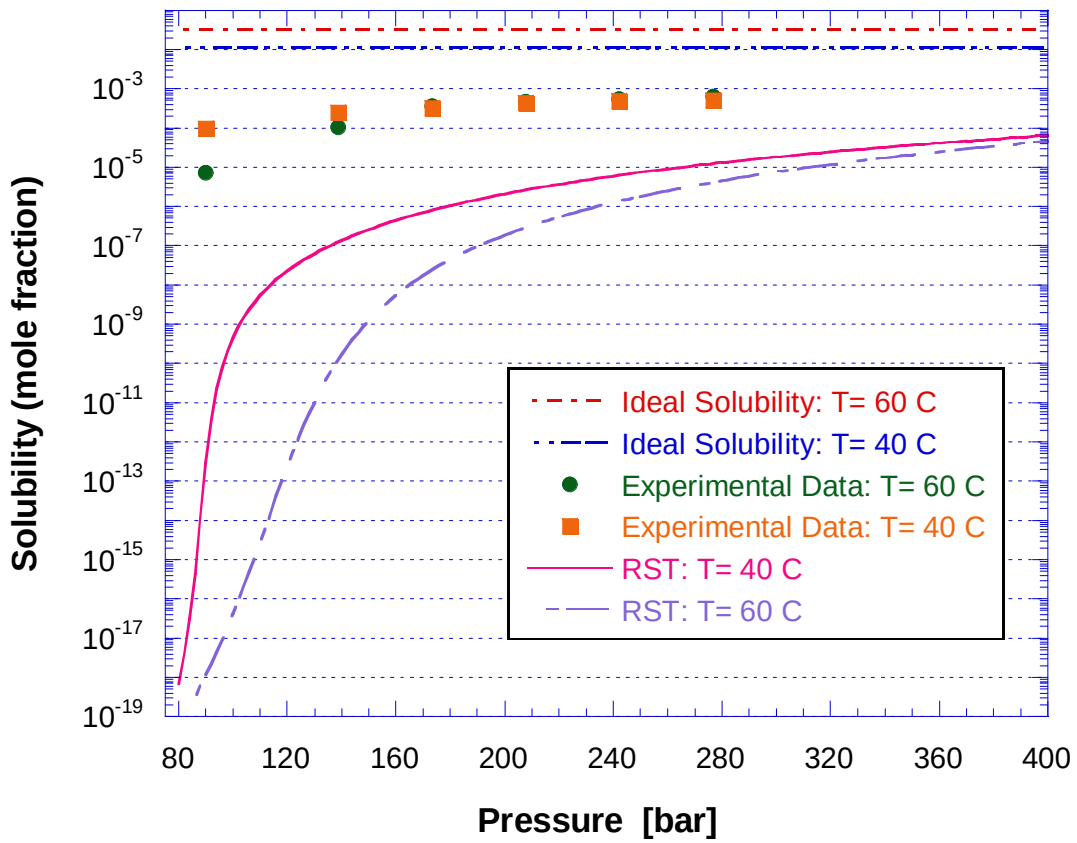

Figure 3 Solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 as predicted by Regular Solution Theory at 40°C and 60°C. Also included at the top of the graph are the predictions from ideal solution theory, in which the activity coefficient is assumed to be one.

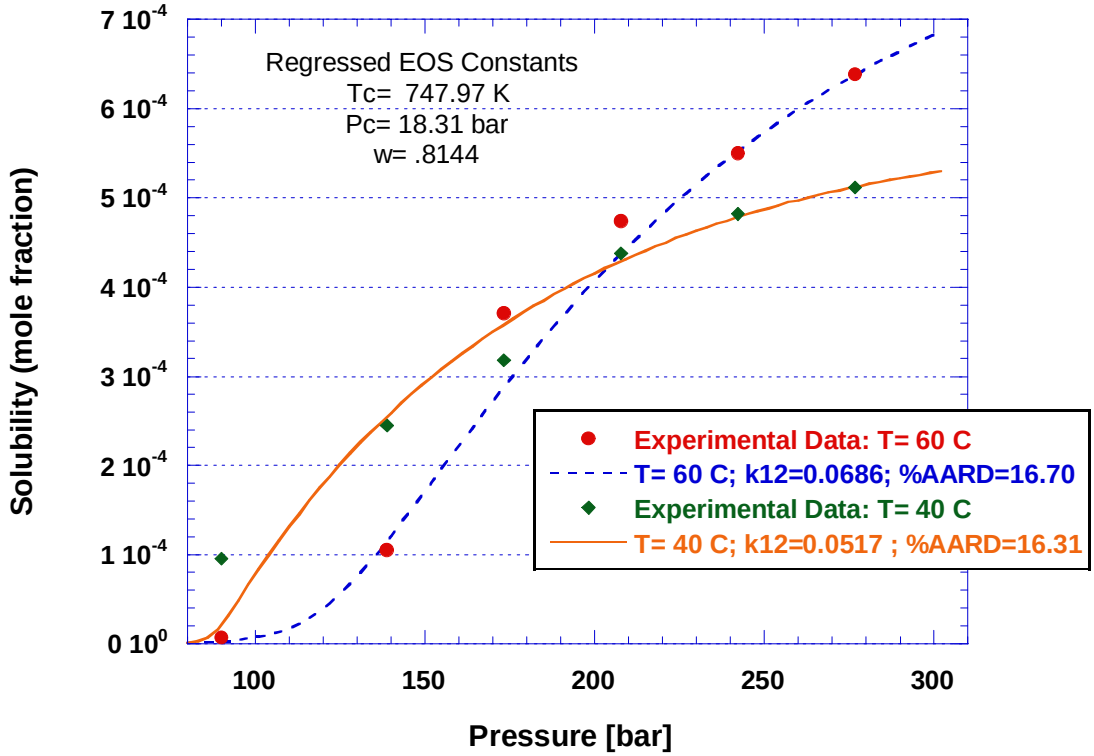

Figure 4 Modeling of the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 at 40°C and 60°C with the Peng-Robinson equation using van der Waal 1 mixing rules. Here three pure component parameters for the Fe(acetylacetonate)$_3$, as well as the binary interaction parameter, k_{ij}, are regressed from the experimental data. Shown on the graph are the regressed values, as well as the average relative deviation between the model and the experimental data.

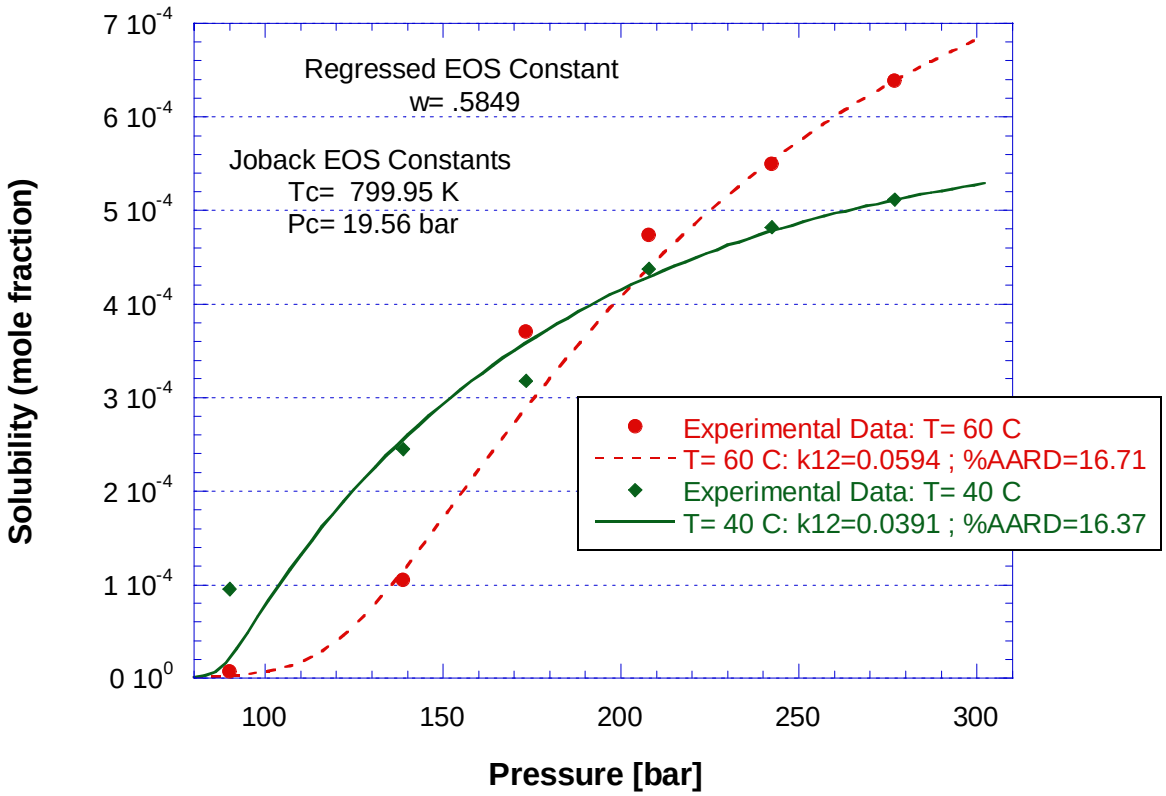

Figure 5 Modeling of the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 at 40°C and 60°C with the Peng-Robinson equation using van der Waal 1 mixing rules. Here only one pure component parameter (the acentric factor) for the Fe(acetylacetonate)$_3$, and the binary interaction parameter, k_{ij}, are regressed from the experimental data. Shown on the graph are the values of the critical temperature and pressure that were estimated with the Joback method, the regressed values of the acentric factor, and k_{ij}, as well as the average relative deviation between the model and the experimental data.

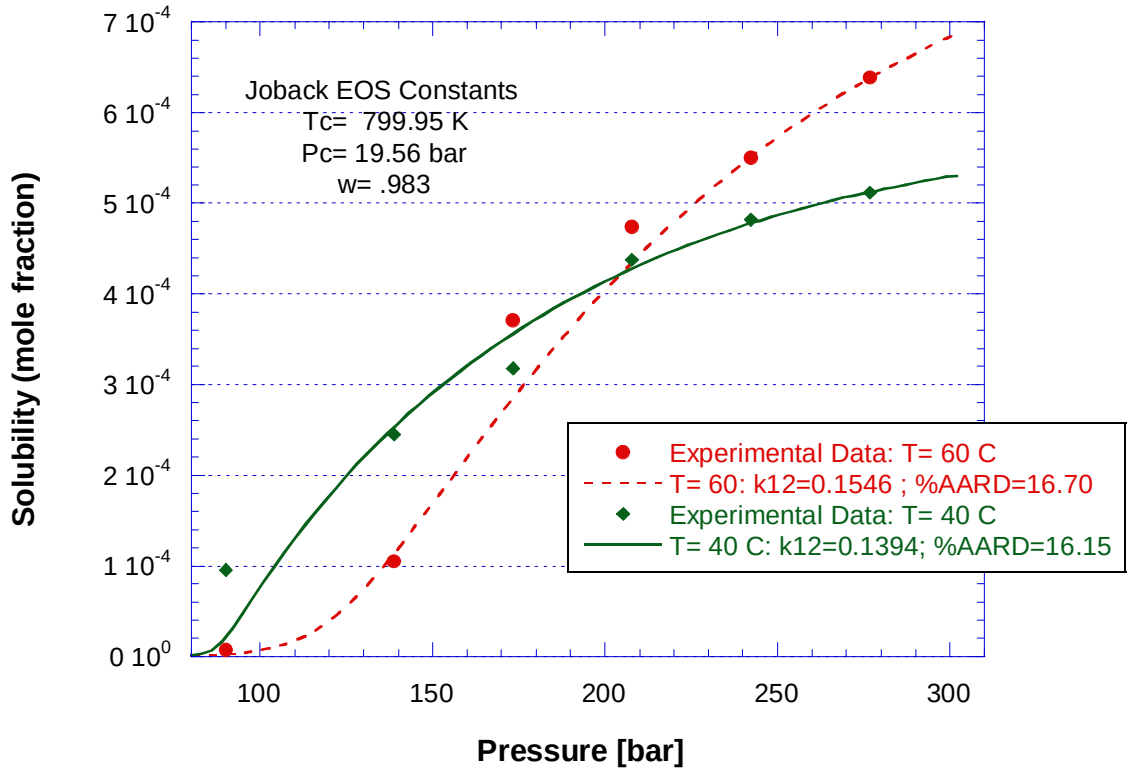

Figure 6 Modeling of the solubility of Fe(acetylacetonate)$_3$ in supercritical CO_2 at 40°C and 60°C with the Peng-Robinson equation using van der Waal 1 mixing rules. Here only the binary interaction parameter, k_{ij}, was regressed from the experimental data. Shown on the graph are the values of the critical temperature and pressure that were estimated with the Joback method, the acentric factor determined from pure component data, and the regressed value of k_{ij}, as well as the average relative deviation between the model and the experimental data.

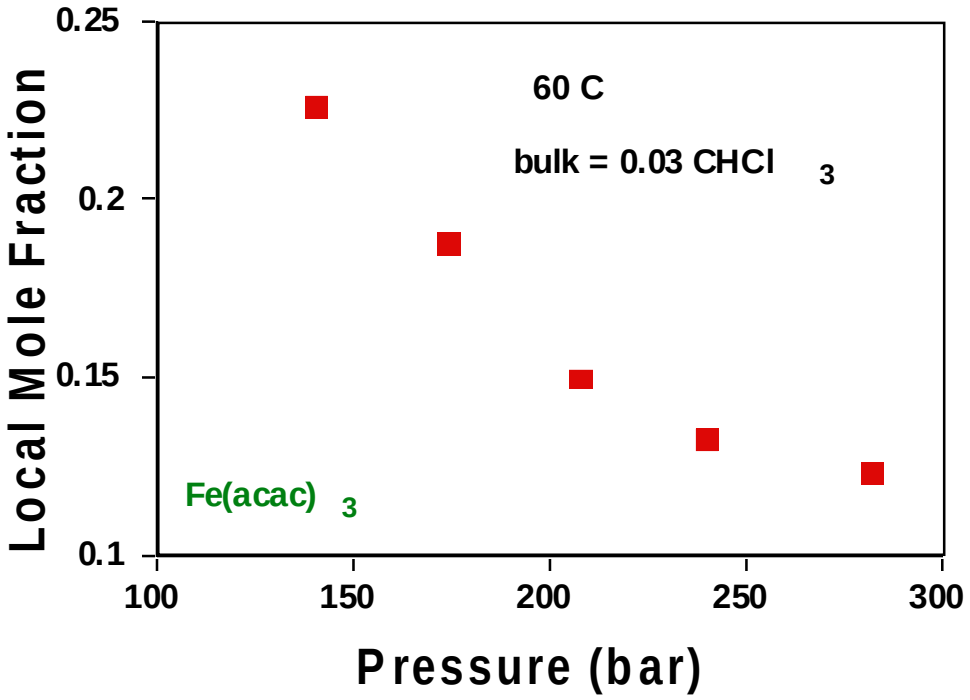

Figure 7 Local compositions of chloroform around Fe(acetylacetonate)$_3$ at 60°C, as measured by UV-visible spectroscopy.