Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO$_2$

Final Report

J. F. Brennecke
M. A. Stadtherr
J. E. Chateauneuf

September 1999

Work Performed Under Contract No. DE-FG07-96ER14691

For
U.S. Department of Energy
Assistant Secretary for
Energy Research
Washington, DC

By
University of Notre Dame
Notre Dame, IN
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
SPECTROSCOPY, MODELING AND COMPUTATION OF METAL CHELATE SOLUBILITY IN SUPERCritical CO₂

FINAL REPORT

J. F. Brennecke
M. A. Stadtherr
J. E. Chateauneuf

September 1999

Work Performed Under Contract No. DE-FG07-96ER14691

Prepared for the
U.S. Department of Energy
Assistant Secretary for
Energy Research
Washington, DC

Prepared by
University of Notre Dame
Notre Dame, IN
Final Report

DE-FG07-96ER14691
Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO₂

9/15/96-9/14/99

Joan F. Brennecke and Mark A. Stadtherr
Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556

John E. Chateauneuf
Department of Chemistry
Western Michigan University
Kalamazoo, MI 49008

This final report for DE-FG07-96ER14691, entitled “Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO₂,” 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 CO₂. Extraction with CO₂ is an 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 CO₂ 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 CO₂ and CO₂/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 CO₂ and CO₂/cosolvent mixtures, as well as the phase behavior of the chelating agents themselves in CO₂. 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 CO₂ is important in the design of processes using CO₂ 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 CO₂, 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/CO₂ 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 CO₂.
- We have demonstrated that on a microscopic level organic co-contaminants that are dissolved in the CO₂ 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 CO₂ 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 CO₂ and CO₂/co-contaminant mixtures. Thus, we can now design and optimize processes to extract metals from solid matrices using supercritical CO₂, as an alternative to hazardous organic solvents that create their own environmental problems, even while helping in metals decontamination.

3. Background

Extraction with supercritical CO₂ is an attractive possibility for the separation of DOE mixed wastes. Carbon dioxide is nontoxic and nonflammable and extraction with CO₂ 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 CO₂ 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 CO₂ 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 CO₂ or CO₂/cosolvent mixtures, but that metals can be successfully extracted from aqueous solutions and solid matrices with CO₂. 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, $\delta$. The solubility parameter is
defined as $(\Delta U/v_L)^{1/2}$, where $\Delta U$ 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 $\delta$ for CO$_2$ was taken from
Giddings et al. (1968), who gave $\delta$ 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 $\delta$ 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:
\[ f_2^S = P_2^{\text{sub}}(T) \exp \left( \frac{v_2^S}{RT} (P - P_2^{\text{sub}}(T)) \right) = y_2 P \hat{\phi}_2^F(T, P, y) = \hat{f}_2^F, \]

where \( f_2^S \) is the fugacity of the solute in the pure solid phase, \( \hat{f}_2^F \) is the fugacity of the solute in the fluid phase solution, \( P_2^{\text{sub}}(T) \) is the sublimation pressure of pure solute, \( v_2^S \) is the molar volume of pure solute, and \( \hat{\phi}_2^F(T, P, y) \) is the fugacity coefficient of the solute in a fluid phase of composition \( y = (y_1, y_2, \ldots, y_c)^T \). 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,

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

\[ b = 0.07780 \frac{RT}{P_c} \]

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:

\[ a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij}, \quad b = \sum_{i=1}^{n} x_i b_i, \quad \text{and} \quad a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \]

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, \( \omega = -\log \left( \frac{P_{\text{ref}}}{P_c} \right) \), \(-1.000\). For this equation, the vapor pressures were determined from the literature value of the enthalpy of vaporization (Beech and Lintonbon,
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 343°C, which is close to published values of other tris acetylacetonates. All of these methods to calculate the solubility of the Fe(acetylacetonate)₃ in CO₂ 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 CO₂ 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 CO₂, we measured the solubility of a representative metal chelate complex, Fe(acetylacetonate)₃, in supercritical CO₂ and CO₂/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 micrometreing 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 CO₂ 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 CO₂ 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 CHCl₃ 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 CHCl₃ 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 CO₂-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 CO₂ system, we undertook a program to use spectroscopy to measure the local composition of CHCl₃ 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 $k_f$, 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


Invited Presentations


8. Joan F. Brennecke, "Understanding Metal Chelates in Supercritical CO\textsubscript{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\textsubscript{2}," Department of Chemical Engineering, University of Massachusetts, Amherst, MA, October 1, 1998.


Contributed Presentations


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

Literature Cited in Report


McHugh, M. A; Krukonis, V. J. (1990), Supercritical Fluid Extraction: Principles and Practice; Butterworth-Heinemann: Boston.


Contaminated Extractor

Chelating Agent

Cleaned Organic Solid SC CC)2 Recycle

Chelating Agent and CO₂ Makeup

Chelating agent less volatile than organic contaminant

Figure 1 Schematic of metal extraction process using chelating agents dissolved in supercritical CO₂, 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 I 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 I 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.