Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2

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This progress report contains 1) a statement of the objectives of the overall project, 2) a discussion of the results obtained during the first year of the three year grant period, 3) a summary, 4) a description of the future work that will be pursued during the next year, and 5) accounting information. This is followed by the literature cited and the pertinent tables and figures.

1. Objectives

The overall objectives of this project are to gain a fundamental understanding of the solubility and stability 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. We seek 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 is a comprehensive one to measure local solvation of metal chelates and to determine metal chelate stability in supercritical fluid mixtures using UV-vis and FTIR spectroscopy. The spectroscopic studies provide information on the solution microstructure, which we are using in concert with our own and published solubility data to evaluate and develop thermodynamic models of the solubility behavior. Finally, we are implementing a more reliable computational technique, based on interval mathematics, to compute the phase equilibria using the thermodynamic models. This fundamental information about metal chelate stability and 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. Results and Discussion

In the first year of this grant we have obtained preliminary results in four areas: a) spectroscopic studies of metal chelates in pure CO_2 and CO_2/cosolvent mixtures, b) the effect of water on metal chelates in CO_2, c) measurements of metal chelate solubilities and d) the development of a completely reliable technique to perform high pressure CO_2 phase equilibrium computations.

a. Spectroscopic Studies of Metal Chelates in pure CO_2 and CO_2/Cosolvent Mixtures

One of the goals of this project is to use spectroscopy (UV-vis and FTIR) to measure the local environments around metal chelates in supercritical CO_2 and CO_2/cosolvent mixtures. Our progress in this area includes i) characterization of the absorption spectrum of $Fe^{III}(acetylacetone)_3$ in pure CO_2 as a function of temperature and pressure, ii) measurement of the the absorption spectrum of $Fe^{III}(acetylacetone)_3$ in various liquid solvents (that could be used as cosolvents) and comparison to literature values, iii) investigation of possible causes of the discrepancy between *our*

data and that published by Tingey et al., 1989, and iv) investigation of Na(diethyldithiocarbamate) and $Cu^{III}(acetylacetone)_2$ in liquid solvents to determine their potential use as solvatochromic probes in supercritical CO_2/cosolvent mixtures.

We began our investigation of solvatochromic shifts with $Fe^{III}(acetylacetone)_3$ because this is the compound reported in the one paper in the literature that sought to study local environments around metal chelate compounds in supercritical CO_2 (Tingey et al., 1989). The authors of that paper reported that the absorption maximum of $Fe^{III}(acetylacetone)_3$ showed significant shifts with temperature (i.e., changing density) in pure supercritical CO_2 (5 nm shifts) and in CO_2/methanol mixtures (up to 55 nm shifts). We characterized the UV-vis absorption of $Fe^{III}(acetylacetone)_3$ at its solubility limit in pure supercritical CO_2 at 40°C and 80°C at pressure from 1100 to 4740 psi, as shown in Figure 1 for 40°C. Contrary to the report in the literature (Tingey et al., 1989), the absorption maximum of $Fe^{III}(acetylacetone)_3$ does not shift with either temperature or pressure in pure CO_2. The two major absorption peaks remain stable at 350±l nm and 42±l nm (Zhang et al., 1997). The addition of a small amount of methanol to the CO_2 did not result in any shifts in the absorption spectrum. This is not surprising since the absorption peaks of $Fe^{III}(acetylacetone)_3$ in pure liquid methanol occur at 350 nm and 426 nm. In fact, our measurements, as well as some taken from the literature, of the absorption maxima of $Fe^{III}(acetylacetone)_3$ in various liquid solvents and some of our supercritical CO_2 values are shown in Table 1.

We then sought to determine the origin of the discrepancy between our data and that published by Tingey et al., 1989. The main difference in our techniques was that we started with pure isolated metal chelate solid, $Fe^{III}(acetylacetone)_3$, which we then placed in the high pressure optical cell with supercritical CO_2. Tingey and coworkers synthesized the $Fe^{III}(acetylacetone)_3$ in situ; i.e., they placed $FeCl_3$ in the stainless steel optical cell and contacted it with supercritical CO_2 containing a large excess (approximately 1000x) of chelating agent (i.e., acetylacetone). To reproduce this process, we synthesized $Fe^{III}(acetylacetone)_3$ in situ in ethanol using 0.086 mM $FeCl_3 \cdot 6H_2O$ with acetylacetone concentrations ranging from 1.7 to 18.1 mM. As shown in Figure 2, the absorption of the metal chelate with a large excess of the chelating agent present is strongly dependent on the concentration of the chelating agent. Thus, it is likely that the thermochromic shifts reported by Tingey et al. for $Fe^{III}(acetylacetone)_3$ are just due to the varying concentration of the chelating agent that is present in large excess, rather than any intrinsic characteristic of the metal chelate solvation in supercritical CO_2. It should also be noted that large excesses of chelating agents like acetylacetone are certainly capable of complexing with metals from the wall of a stainless steel optical cell. Since Cr and Ni are also present in stainless steel, it is likely that Tingey et al. were observing a mixture of Fe, Cr and Ni acetylacetone complexes, which all have different characteristic absorbances. For instance, we have measured the maximum absorbance of $Cr^{III}(acetylacetone)_3$ in supercritical CO_2 at 330.5 nm.

In an effort to find an alternate solvatochromic probe we have characterized the UV-vis absorption spectra of $Cr^{III}(acetylacetone)_3$, $Cu^{III}(acetylacetone)_2$ and Na(diethyldithiocarbamate) in supercritical CO_2 and liquid solvents. The major absorption maxima for these compounds are shown in Table 2. None of these compounds exhibit sufficient solvatochromic shifts in order to accurate determine local compositions when small amounts of a liquid cosolvent is added to the CO_2. Currently, we are investigating some of the metal dithizone complexes and examining solvent induced changes in the FTIR spectra of the various metal chelates as a potential means of measuring local compositions in metal chelate/CO_2 cosolvent mixtures.

b. Effect of Water on Metal Chelates in CO_2

In any practical extraction of metal contaminants from soils or sludges using supercritical CO_2, water will inevitably be present. Although the solubility of water in CO_2 is less than 1 mole % (Dohrn et al., 1993) our investigations show that it may have substantial influence on the stability of some metal chelate complexes.   In addition, several researchers have found that the addition of a small amount of water can significantly increase the extraction efficiency of metals from solid matrices with supercritical CO_2 (Laintz et al., 1992; Lin et al., 1994; Lin et al., 1995b; Phelps et al., 1996). Thus, understanding the effects of water on metal chelate stability and solubility is vitally important.

Fe^{III}(acetylacetone)$_3$ is dramatically affected by the presence of water. In pure liquid water, the absorption peak at about 430 nm completely disappears. This peak and the one at about 350 nm are uniquely characteristic of the Fe^{III}(acetylacetone)$_3$ metal chelate complex. The peak at about 273 nm is indicative of the metal chelate but is also present in the spectrum of the chelating agent (acetylacetone) alone. The ratio of the peak intensity at about 273 nm to the peak intensity at about 430 nm is characteristic of the solvent around the Fe^{III}(acetylacetone)$_3$ (Singh and Sahai, 1969; Barnum, 1961). As shown in Table 1, this ratio is higher for polar solvents and essentially infinity for pure liquid water.   The spectroscopic changes may be indicative of partial metal chelate dissociation.

$$M^{n+} + n(Hacac) \Longleftrightarrow M(acac)_n + nH^{+}$$
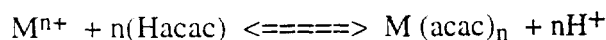
In nonpolar solvent (like hexane and CO_2) one would expect the equilibrium constant to be quite large, with essentially all of the metal present in the complexed form. However, polar solvents may affect this equilibrium. Alternately, water molecules closely associated with (solvation or present as additional neutral ligands) the metal chelate complex may also significantly alter its spectroscopic characteristics.

We have conducted some preliminary investigations of the effect of water on Fe^{III}(acetylacetone)$_3$ in supercritical CO_2. The addition of just 0.2 μL of water to the optical cell of approximately 3 mL volume results in a drastic increase in the $I(\pi_3-->\pi_4)/I(n-->d*)$ ratio, as shown in Figure 3 for both 40°C and 80°C (Zhang et al., 1997).   The behavior is time dependent because there is no explicit agitation in the optical cell and the system had not yet reached equilibrium when the experiments were terminated.   Nonetheless, qualitative observations of the dramatic effect of water on Fe^{III}(acetylacetone)$_3$ in supercritical CO_2 can be made.   Similar increases in $I(\pi_3-->\pi_4)/I(n-->d*)$ of Fe^{III}(acetylacetone)$_3$ can be obtained by adding 10 μL of water to approximately 3 mL of methylene chloride. The dramatic changes in the peak at 350 nm in supercritical CO_2 with such a small amount of added water may be an indication of preferential solvation of the metal chelate by the water, which may have important implications on solubilities and extraction efficiencies.

To further study the influence of water on metal chelates in supercritical CO_2, we have designed and constructed a high pressure FTIR optical cell, as shown in Figure 4. The optical cel can be configured for a variety of pathlengths using stepped windows that protrude various distances towards the center of the cell. Initial experiments with supercritical CO_2 are in progress. Complementary studies of the effect of added water on the FTIR spectra of Fe^{III}(acetylacetone)$_3$ in methylene chloride indicate a dramatic decrease in the C-O stretching band at about 1430 cm^{-1}. Thus, our continuing work is focusing on the combined use of UV-vis and FTIR spectroscopy to

determine the influence of water in supercritical CO_2 on the stability, complexation equilibria and local environment of metal chelate complexes. Understanding this basic chemistry is exceedingly vital in predicting and modeling the solubilities and extractability of metals into supercritical CO_2 containing chelating agents.

c. Measurements of Metal Chelate Solubilities

A limited number of solubility measurements are available in the literature for metal chelate complexes in supercritical CO_2 (Laintz et al., 1991; Wai et al., 1993a,b: Lin et al., 1995a; Wai and Smart, 1996; Lagalante et al., 1995; Sievers et al., 1996; Ashraf-Khorassani et al., 1996; M'Hamdi et al., 1991; Saito et al., 1990). To complement these measurements we have assembled a supercritical CO_2 extraction unit consisting, of an ISCO Model 260D syringe pump and SFX supercritical fluid extractor. As an example, our measurements of the solubility of $Zn^{II}(2,2,6,6-$ tetramethylheptane-3,5-dionate)$_2$ are shown in Figure 5 for 40°C and 50°C. As expected, the solubilities increase with increasing pressure. We are particularly interested in the effect of cosolvents, including water which would be present in any extraction of contaminated soil samples, on the solubility. These experiments are in progress. These solubility data will be extremely important in developing appropriate models for and reliably computing metal chelate solubilities in supercritical CO_2 and supercritical CO_2/cosolvent mixtures.

d. Development of a Completely Reliable Technique to Perform High Pressure CO_2 Phase Equilibrium Computations.

The reliable prediction of phase equilibrium from thermodynamic models will be a key problem in the design and operation of processes using supercritical CO_2 to extract metals from contaminated soils and sludges. The solution of phase stability and, subsequently, phase equilibrium problems is well known to pose computational difficulties, as standard methods may converge to false or trivial solutions. In this project we are developing and applying a new method, based on interval mathematics, that is capable of solving the phase stability and equilibrium problems with mathematical and computational certainty that the correct result has been obtained. In particular, in the first year of this project we have extended the applicability of the interval method to a wide variety of equation of state models (Hua et al., 1997a). This includes the Peng-Robinson equation, that can be used to predict solubilities of chelating agents and metal chelate compounds in supercritical CO_2 and CO_2/cosolvent mixtures. Also, we have greatly enhanced the efficiency of the method by reducing or eliminating the overestimation of function ranges that are inherent in standard interval arithmetic. For example, in the equation of state models needed to describe the solubility of chelating agents and metal chelates in supercritical CO_2, the energy and size parameters are mole fraction weighted averages. Special bounding procedures for such averages were developed and can be used to substantially improve the efficiency of the interval approach (Tessier et al., 1997; Hua et al., 1997b). Thus far, our work has focused on the general computational procedure. Future work will focus on specific applications to metal chelates in supercritical CO_2 and CO_2/cosolvent mixtures.

3. Summary

In the first year of this grant to study "Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO_2" we have obtained important results about possible solvatochromic probes of the local environmental around metal chelates in CO_2, the important influence of small amounts of water in CO_2 on the stability and solvation of metal chelates, the solubility of $Z^{II}(2,2,6,6-$tetramethylheptane-3.5-dionate)$_2$ in supercritical CO_2 and a new completely reliable technique to perform high pressure CO_2 phase equilibrium computations. We

found that $Fe^{III}(acetylacetone)_3$ is not a good solvatochromic probe but is dramatically affected by water in supercritical CO_2. The effect of the supercritical CO_2 solvent, as well as cosolvents, on the stability, complex reaction equilibrium, and solvation of metal chelates is vitally important in predicting solubilities in supercritical CO_2 and CO_2 mixtures. Water is of particular interest because it would be naturally occurring in the extraction of metals from contaminated soils or sludges. Moreover, the advances we have made in the reliability of the computation of high pressure phase behavior will be vital in the design and operation of extraction units to remove metal contaminants from soils, sludges and wastewater.

4. Future Work

The planned work for the remaining two years of this project includes:

a) measuring local compositions around metal chelates in CO_2/cosolvent mixtures as a function of temperature and pressure with an appropriate solvatochromic probe (either UV-vis or FTIR),

b) using a combination of UV-vis and FTIR spectroscopies to quantify changes in the complexation equilibrium, stability, and solvation of $Fe^{III}(acetylacetone)_3$ when small amounts of water are added to supercritical CO_2 and to common liquid solvents like methylene chloride,

c) using FTIR spectroscopy to study temperature and pressure effects on the keto-enol equilibria of ß-diketones, which is a vital step in metal chelate complex formation,

d) measuring the solubilities of additional compounds, in pure supercritical CO_2 and with added cosolvents (including water),

e) using data on the solubility of metal chelates in supercritical CO_2 to fit pure component parameters of the metal chelates, seeing if these parameters can be correlated or predicted from known physical properties, and using these parameters to predict metal chelate solubilities in CO_2/cosolvent mixtures, and

f) applying the newly developed interval method to specific examples of chelating agent/CO_2 equilibria and metal chelate solubilities in supercritical CO_2, using various equation of state models.

These studies will provide a fundamental understanding of metal chelation equilibrium, stability, solvation and solubility in supercritical CO_2 and CO_2/cosolvent mixtures. This information, when used with the newly developed reliable computational technique for phase equilibrium calculations, will provide the information and techniques necessary, to design and determine oppropriate operating parameters for units to extract metals from contaminated soils and sludges

5. Accounting Information

The budgeted amounts and actual amounts spent for the first year of the grant (9/15/96-9/14/97) in the various categories are shown below:

Category	Budget	Actual
salaries	11,930	20,282
benefits	913	2,853
capital equipment	9,900	9,900
supplies	4,732	1,978
subcontract to Western Michigan University	30,031	30,031
indirect costs	20,818	24,627
total	78,323	89,671

Thus, the grant is overspent by \$11,348 for the first year. The reason for this is that I was able to have a post-doctoral research associate (Dr. Jianwei Zhang) working on the project for four months. His salary of \$9,667 plus benefits and associated indirect costs accounts for the overexpenditure. Fortunately, this can be covered by salary and indirect costs budgeted for the second year of the grant. The item of capital equipment purchased was the ISCO model 260D syringe pump, which is described in the research progress section above.

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Table 1 Absorption maxima of $Fe^{III}(acetylacetone)_3$ in supercritical CO_2 and various liquid solvents.

Solvent	Transition (nm)			
	$\pi_3 \rightarrow \pi_4$	$d\varepsilon \rightarrow \pi_4$	$n \rightarrow d^*$	$I(\pi_3 \rightarrow \pi_4)/I(n \rightarrow d^*)$
CO_2, 40°C, 1278 psi	273	351	428	7.6
CO_2, 40°C, 1405 psi	273	350	428	7.8
CO_2, 40°C, 4740 psi	273	350	428	8.5
hexane	271	352	429	7.7
methanol	273.5	350	426	10.2
ethanol	273	352.5	431	9.3
ethanol[a]	273	351	431	9.33
ethanol[b]	272	351	431	9.33
water	276	350	---	---
CH_2Cl_2	274	354.5	437.5	7.4
$CHCl_3$[a]	274	353	437	16.2
chloroform[b]	273	353	437	8.91

[a]   P. R. Singh and R. Sahai, 1969
[b]   D. W. Barnum, 1961

Table 2 Absorption maxima of $Cr^{III}(acetylacetone)_3$, $Cr^{III}(acetylacetone)_2$ and Na(diethyldithiocarbamate) in supercritical CO_2 and various liquid solvents.

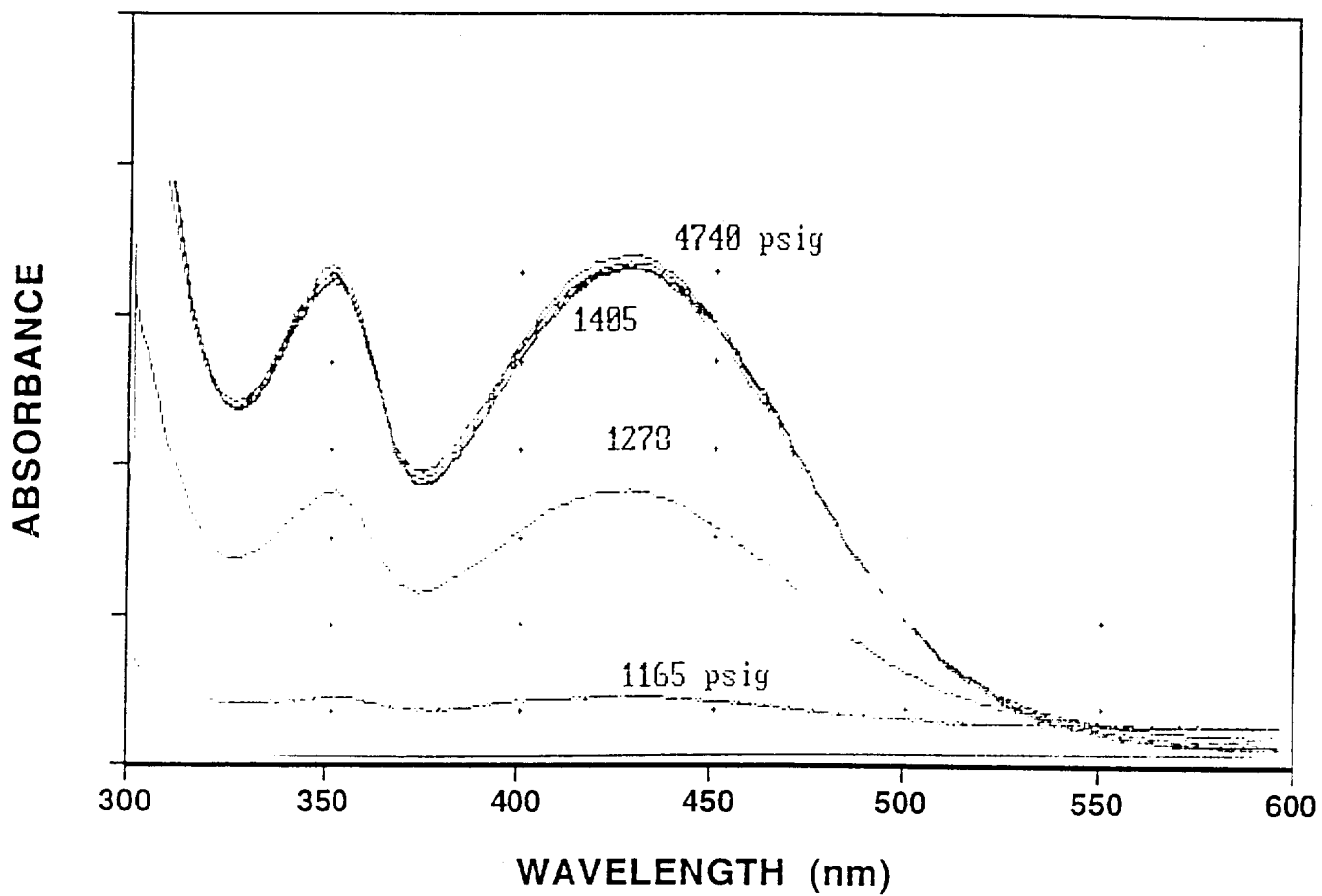| Compound	Solvent	major peaks (nm)
$Cr^{III}(acetylacetone)_3$	water	256.5, 330.5
	CO_2 at 40°C and 2500 psia	332, 558
$Cu^{III}(acetylacetone)_2$	hexane	292
	ethanol	292
	chloroform	294
Na(diethyldithiocarbamate	acetonitrile	263, 300.5
	ethanol	259, 290.5
	hexane	278
	CO_2 at 40°C and 2200 psia	268, 425

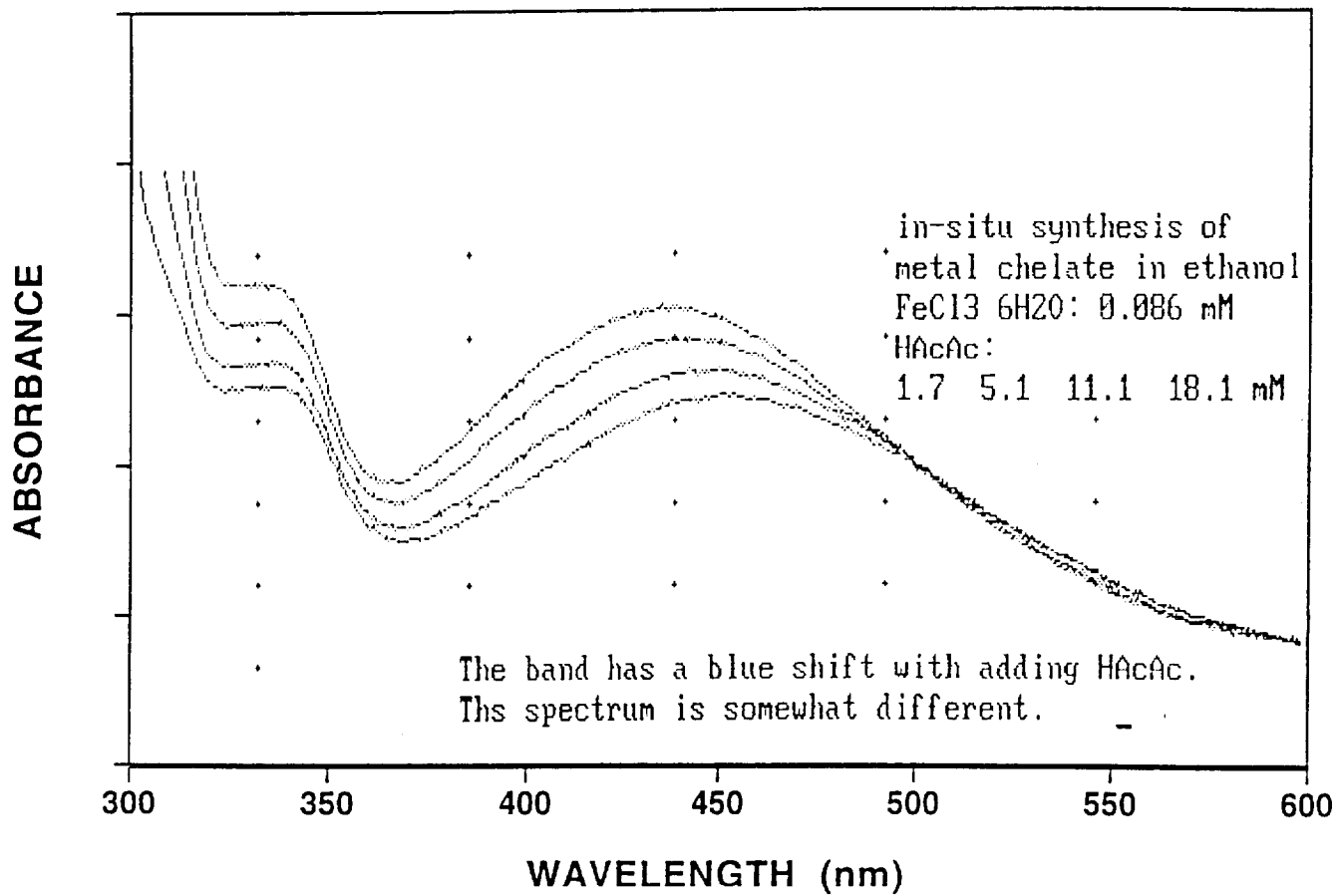FIGURE 1   Absorption Spectra of Fe(acetylacetone)$_3$ in Supercritical CO_2 at 4CC and various pressures.

FIGURE 2 Absorption Spectra of Fe(acetylacetone)₃ Made In-situ from FeCl₃ Using Various Concentrations of Acetylacetone Chelate (Hacac) in Ethanol at Room Temperature.
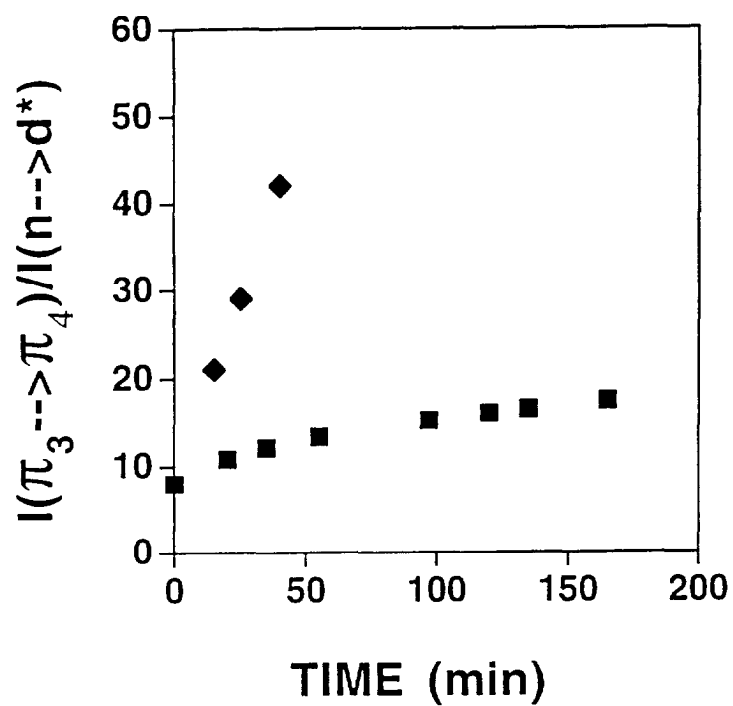
Figure 3 Ratio of Intensity of the Peaks at about 273 nm to that at about 430 nm in the Absorption Spectrum of $Fe^{III}(acetylacetone)_3$ as a Function of Time (without stirring in the optical cell). The experiments were conducted in Supercritical CO_2 at 40C (squares) and 80C (diamonds).
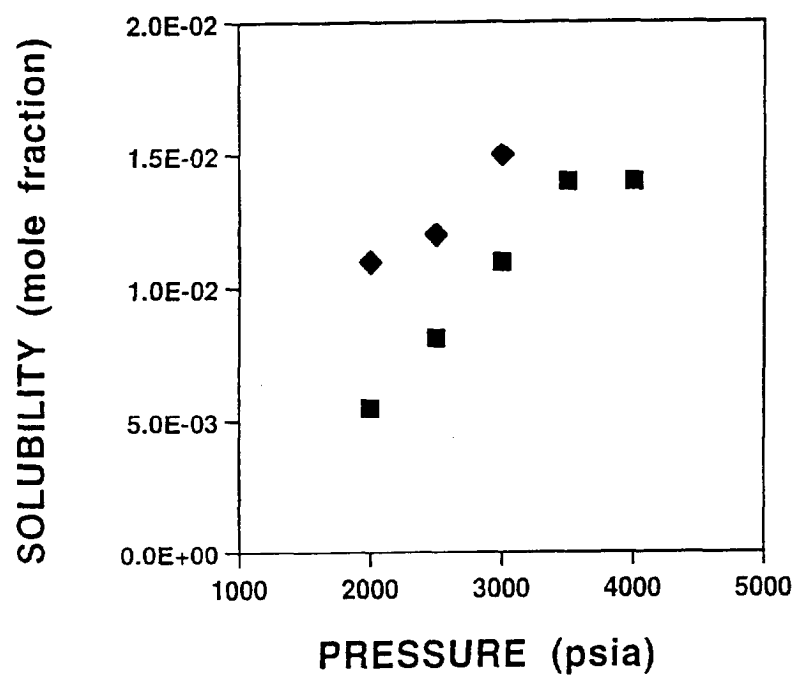
NOTES:
1) ALL DIMENSIONS ARE IN INCHES.
2) MATERIAL: 316 STAINLESS.
3) 1 PIECE REQUIRED.

OPTICAL CELL

UNIVERSITY of NOTRE DAME
COLLEGE OF ENGINEERING

DWG. NO. wr277-c1

Figure 4 Schematic of High Pressure FTIR Optical Cell

Figure 5 Solubility of $Zn^{II}(2,2,6,6\text{-tetramethylheptane3,5-dionate})_2$ in Supercritical CO_2 at 40C (squares) and 50C (diamonds).