

Environmental Management Science Program

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Spectroscopy, Modeling and Computation of Metal Chelate Solubility in Supercritical CO₂

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Research Objective

The overall objectives of this project are to gain a fundamental understanding of the solubility and stability of metal chelates in supercritical (SC) 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. We seek 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 contaminated soils and 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 (SCF) 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 SC CO₂ is important in the design of processes using CO₂ to extract components from mixed wastes and in determining the optimum operating conditions.

Research Progress and Implications

This report summarizes work after 1 year and 8 months (9/15/96-5/14/98) of a 3 year project. Thus far, progress has been made in: 1) the measurement of the solubility of metal chelates in SC CO₂ with and without added cosolvents, 2) the spectroscopic determination of preferential solvation of metal chelates by cosolvents in SC CO₂ solutions, and 3) the development of a totally reliable computational technique for phase equilibrium computations.

- 1) An important factor in the removal of metals from solid matrices with CO₂/chelate mixtures is the equilibrium solubility of the metal chelate complex in the CO₂. While there are several researchers measuring the solubility of metal chelates in pure CO₂, we know of only one data point showing the influence of added cosolvents on solubility. Conversely, there are several reports that added methanol or the presence of water can significantly enhance extraction efficiencies. Therefore, we have measured the solubility of a simple b-diketonate complex, Zn(2,2,6,6-tetramethylheptane-3,5-dionate)₂, at 40°C and 60°C in SC CO₂ and in SC CO₂ modified with 3 mole % methanol. At all conditions, the solubilities increase with increasing pressure and range between 0.002 and 0.005 mol/L in pure CO₂ at pressure between 2000 and 4000 psi. The addition of 3 mol % methanol results in an increase in the solubility of the metal chelate complex. At pressures from 2000 to 4000 psi the solubilities are 0.004 to 0.009 mol/L and 0.006 to 0.015 mol/L in 3 mol% methanol/CO₂ mixtures at 40°C and 60°C, respectively.
- 2) Based on literature results for polar organic solutes in SCF mixtures, an important contributor to the increased solubilities and increased extraction efficiencies of metal chelates in CO₂/cosolvent mixtures may be the preferential solvation of the metal chelate by the cosolvent. We have used UV-vis spectroscopy to measure the preferential solvation of Fe(acetylacetonate)₃ (Fe(acac)₃) by methanol in SC CO₂ at 40°C and 60°C. Initially, we had planned to measure

preferential solvation by solvatochromic shifts since there was a report of this method being used with $\text{Fe}(\text{acac})_3$ in the literature (Tingey et al. *J. Phys. Chem.* 1989, 93, 2140). Unfortunately, the UV-vis absorption peaks of $\text{Fe}(\text{acac})_3$ do not shift with changing solvent environment. Fortunately, $\text{Fe}(\text{acac})_3$ 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 $\text{Fe}(\text{acac})_3$ in SC CO_2 /3 mole % methanol mixtures. The results indicate that the local environment around the $\text{Fe}(\text{acac})_3$ is highly enriched with methanol (up to 16 times the bulk composition) and that it is largest at higher pressures. This is very different from trends observed for the preferential solvation of polar organic solutes in SCF. Careful examination of the spectra obtained revealed subtle changes in the spectra of $\text{Fe}(\text{acac})_3$ in CO_2 /methanol mixtures that are not present in either pure CO_2 or pure methanol, which may indicate specific chemical interactions. Nonetheless, the increases in local composition of the methanol around $\text{Fe}(\text{acac})_3$ mirror the solubility enhancement and extraction efficiency increases observed when methanol is used as a cosolvent. Currently, we are using $\text{Fe}(\text{acac})_3$ with other cosolvents. Small amounts of water in CO_2 causes dramatic changes in the intensity ratios in $\text{Fe}(\text{acac})_3$, indicating a high degree of preferential solvation, as well as potential acid-assisted ligand exchange.

- 3) The purpose of solubility measurements and spectroscopic measurements of preferential solvation is the development of appropriate models of CO_2 /ligand and CO_2 /metal chelate complex phase behavior. Moreover, the reliable prediction of phase equilibrium from thermodynamic models is a key problem in the design and operation of processes using SC 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. We have extended the applicability of the interval method to a wide variety of equation of state models, including the Peng-Robinson equation, that can be used to predict solubilities of chelating agents and metal chelate compounds in SC 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. Thus far, our work has focused on the development of the general computational procedure.

Planned Activities

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Other Access To Information

A list of publications and presentations that are a result of this project will be available after 7/1/98 at: <http://www.nd.edu/~jfb/doesmsp/pubs.html>.