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

2/28/00 (covers entire grant period 9/15/96-9/14/99)

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Training

A total of one post-doctoral research associate and six graduate students, from the University of Notre Dame and Western Michigan University, were involved with this project over its three year span from 9/15/96-9/14/99.

DOE Problems Addressed

The DOE problem addressed by this grant is the separation of organics and radioactive metals from DOE mixed wastes. The objective was to investigate the fundamentals of using supercritical CO₂ to solubilize both volatile organic compounds and metal chelates, with applications to extractions from soils, sludges and aqueous solutions.

Research 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.

Research Progress and Implications

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.

Work on this project is complete. Currently, we are investigating the possible use of specially designed diphosphonic acid ligands for metal solubilization in supercritical CO₂ in collaboration with Argonne National Laboratories and Loyola University – Chicago under DOE EMSP grant DE-FG07-98ER14924.

The final report for this grant, including lists of publications and presentations, was submitted for posting on the main DOE EMSP website (<http://204.134.132.56/main.htm>).