

Final Report

Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids (DOE DE-FG07-98ER14924)

Joan F. Brennecke
Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556
(574) 631-5847
FAX (574) 631-8366
Email: jfb@nd.edu

July 3, 2003

This project was part of a collaborative effort with Argonne National Laboratories (EMSP Project Number 64965) and Loyola University. The investigators from the other institutions are listed below:

Dr. Mark L. Dietz (Lead Principal Investigator), Chemistry Division, Argonne National Laboratory, Argonne, IL 60439. Telephone: (630) 252-3647; e-mail: mdietz@anl.gov.

Dr. Richard E. Barrans, Jr. (Co-Investigator), Chemistry Division, Argonne National Laboratory, Argonne, IL 60439. (no longer at ANL)

Dr. Albert W. Herlinger (Co-Investigator), Department of Chemistry, Loyola University Chicago, Chicago, IL 60626. Telephone: (773) 508-3127; e-mail: Aherlin@wpo.it.luc.edu.

Graduate student/postdoctorate involvement:

Two graduate students at the University of Notre Dame were involved with this project. One, Dr. Aaron M. Scurto, graduated with his Ph.D. in August, 2002. He is currently pursuing a post-doctoral position at the Insitutut fur Technische Chemie und Makromolekulare Chemie at RWTH-Aachen in Germany. The other Christopher M. Lubbers, who graduated with his M. S. degree in August, 2000. He is currently employed by Goodyear in Akron, Ohio.

Research Objective:

Numerous types of actinide-bearing waste materials are found throughout the DOE complex. Most of these wastes consist of large volumes of non-hazardous materials contaminated with relatively small quantities of actinide elements. Separation of these wastes into their inert and radioactive components would dramatically reduce the costs of stabilization and disposal. For example, the DOE is responsible for decontaminating

concrete within 7000 surplus contaminated buildings. The best technology now available for removing surface contamination from concrete involves removing the surface layer by grit blasting, which produces a large volume of blasting residue containing a small amount of radioactive material. Disposal of this residue is expensive because of its large volume and fine particulate nature. Considerable cost savings would result from separation of the radioactive constituents and stabilization of the concrete dust. Similarly, gas diffusion plants for uranium enrichment contain valuable high-purity nickel in the form of diffusion barriers. Decontamination is complicated by the extremely fine pores in these barriers, which are not readily accessible by most cleaning techniques. A cost-effective method for the removal of radioactive contaminants would release this valuable material for salvage.

The objective of the overall (Argonne National Laboratory/Notre Dame/Loyola) project was to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction (SCDE) of actinide ions from solid wastes. Specifically, selected diphosphonic acids, which are known to form extremely stable complexes with actinides in aqueous and organic solution, were to be rendered carbon dioxide-soluble by the introduction of appropriate alkyl- or silicon-containing substituents. The metal complexation chemistry of these new ligands in SC-CO₂ were then to be investigated and techniques for their use in actinide extraction from porous solids developed. ANL and Loyola were fully responsible for synthesis, Notre Dame was responsible for measurement and modeling of the phase behavior of the ligands and metal ligand complexes with SC-CO₂, and ANL was responsible for actinide extraction from porous solids with the new ligands.

Results:

The University of Notre Dame goal was to measure the phase behavior of the various siloxane derivatized diphosphonic acid compounds synthesized by the groups at ANL and Loyola, in order to provide feedback on which compounds would be best as metal extractants in supercritical CO₂. Unfortunately, the ANL and Loyola groups found that those compounds were much more difficult to synthesize than originally anticipated. Over the four years of the grant (3 years plus a one year no-cost extension), we received only a very limited number of ligand samples. As indicated below, we investigated the phase behavior of the nine viable liquid samples that we received with CO₂. Therefore, we significantly expanded the scope of our part of the project by investigating the phase behavior with CO₂ of commercially available extractants and metal chelate complexes.

Our accomplishments to date fall into six categories: 1) VLE measurements of oligo(dimethylsiloxane) substituted *gem*-diphosphonates, 2) SFE measurements of two Eu complexes, 3) VLE of commercially-available β -diketones, 4) thermodynamic modeling of the VLE of the β -diketones, and 5) modeling of the solubility of metal β -diketonate complexes in multicomponent supercritical mixtures.

1) VLE measurements of oligo(dimethylsiloxane) substituted *gem*-diphosphonates

We have measured the bubble points (i.e., the liquid phase compositions) of nine siloxane substituted *gem*-diphosphonates with CO₂ at 40°C and pressures to about 95 bar. These compounds were oligo(dimethylsiloxane) substituted *gem*-diphosphonate esters, i.e., not actual diphosphonic acids that could be used as metal ligands. These were measured with the static high pressure apparatus described in the original proposal. At low pressures, the incorporation of CO₂ into the diphosphonate-rich phases depends strongly upon the number and nature of the substituent groups present. The parent diphosphonic ester with no siloxane functionality, absorbs less CO₂ than one with a linear trisiloxane substituent. A compound bearing two such trisiloxane groups absorbs even more CO₂. The specific structure of the siloxane substituent is also important. Siloxy-substitution at the phosphonate alkyl esters also enhances the uptake of CO₂. Siloxane substitution also enhances the CO₂ affinity of diphosphonates bearing larger alkyl ester groups. The ligand-rich phases of all these compounds consist primarily of CO₂ even at 90 bar. Extrapolating the mass fraction trends to higher pressure suggests that the mixture critical points of all these compounds with CO₂ are at pressures of about 100-130 bar at 40 °C. Above the critical pressure, the CO₂/diphosphonate mixtures would be single phases at all compositions. Although siloxane substituents increase the molecular mass and reduce the volatility of the diphosphonates, they clearly enhance the affinity for CO₂.

2) SFE measurements of two Eu complexes

We attempted to measure the solubility of two Europium complexes of diphosphonic acid in CO₂. These compounds were made with conventional diphosphonic acid ligands; i.e., ones that have not been derivatized to increase CO₂ solubility. They were examined as a baseline – to determine how low the solubilities of metal complexes with conventional diphosphonic acids were. The compounds were Eu₂(TMSP[MDP])₃ and Eu₂(EH₂[MDP])₃. We determined that we were able to detect both of these compounds by fluorescence spectroscopy and developed an analytical method to do that. The solubility measurements we made at 40 °C and 300 bar, using the dynamic extraction apparatus described in the original proposal. We found that there were absolutely no detectable amounts of either compound in the extract. Based on the estimated detection limits, we determined that the solubility of both of these compounds must be less than 5 x 10⁻⁸ mole fraction.

3) VLE of commercially-available β-diketones

We measured the bubble points of ten commercially available β-diketones. They are 2,4-pentanedione (acac), 2,2,6,6-tetramethyl-3,5-heptanedione (thd), 2,2,7-trimethyl-3,5-octanedione (tod), 1-phenyl-butane-1,3-dione (Bzac), 1,1,1-trifluoro-2,4-pentanedione (tfa), 1,1,1,5,5,5-hexafluoropentane-2,4-dione (HFA), 4,4,4-trifluoro-1-(2-furyl)-butane-1,3-dione (FTFA), 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dione (TTFA), 4,4,4-trifluoro-1-phenyl-butane-1,3-dione (BTFA), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-octane-3,5-dione (fod). Using the static high pressure apparatus, we measured the liquid phase

compositions, molar volumes and mixture critical points of these ten compounds at temperatures between 30 and 60°C and pressures to about 95 bar. All of these compounds have high CO₂ solubilities and many have mixture critical points below 100 bar. An example of some of the data is shown in Figure 1, below. As expected, the CO₂ solubility decreases with increasing temperature. Mixture molar volumes decrease dramatically with increasing pressure but then level off, as is typical for high pressure liquid/CO₂ systems. Although higher molecular weight, the fluorinated compounds do take up more CO₂ than their non-fluorinated counterparts. For instance, the CO₂ solubility in fod is greater than in tfa. Moreover, the CO₂ solubility in both of these fluorinated compounds is greater than in the non-fluorinated chelating agents.

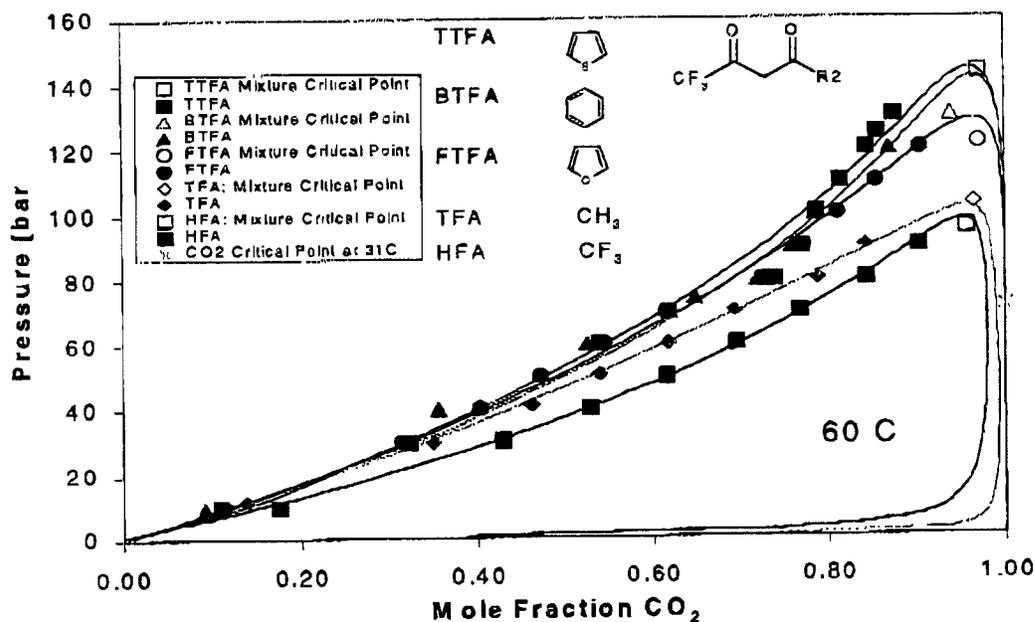


Figure 1 Phase behavior of various β -diketone ligands with CO₂.

4) Thermodynamic modeling of the VLE of the β -diketones

In addition, we conducted thermodynamic modeling of the bubble points and liquid molar volumes of the ten commercially available β -diketone complexes. We used the Peng Robinson equation of state with Van der Waals 1 mixing rules. The critical temperatures, pressures and acentric factors of these compounds were not available so they were estimated or extrapolated from available data using standard techniques. The only parameters fit to the bubble point and liquid molar volume data are a temperature-independent k_{ij} for each compound. The magnitude of these k_{ij} values is quite small, indicating that very little correction is needed to the geometric mean mixing rule. The Peng-Robinson equation of state does a superb job of modeling the bubble point data. The liquid molar volumes are not as accurate but do show the correct trends.

As far as we know, these are the first vapor liquid equilibrium measurements of any β -diketone chelating agents with CO_2 . This information is important for determining what conditions are necessary to obtain a single phase CO_2 /chelating agent mixtures to be fed to the extractor. It is also important in modeling the solubility of metal chelate complexes when excess chelating agent is present (see below).

5) Modeling of the solubility of metal β -diketonate complexes in multicomponent supercritical mixtures

The solubility of a variety of metal chelate complexes in supercritical CO_2 are available in the literature. However, in a real metal extraction process, one would inevitably have excess ligand present in order to allow high removal of the metal contaminant. Thus, what is really of interest is the solubility of the metal chelate complex in a CO_2 /excess ligand mixture. Using published metal chelate/ CO_2 solubility data and the chelating agent/ CO_2 VLE data measured above, we have been able to estimate the solubility of metal chelates in CO_2 /excess ligand mixtures using the Peng-Robinson equation of state. For instance, we are able to predict the solubility of $\text{Cr}(\text{acac})_3$ in a CO_2 /acac mixture. The model predicts that there should be some significant solubility increase just by having the excess ligand present.

Summary:

In this project, we measured the phase behavior of CO_2 with the series of oligo(dimethylsiloxane) substituted *gem*-diphosphonate esters. They showed high affinity for CO_2 , thus validating the hypothesis that the addition of silyl groups should significantly increase the solubility of diphosphonates in CO_2 . We have also investigated the phase behavior of a series of ten commercially available β -diketones, showed that their phase behavior with CO_2 could be accurately modeled with the Peng-Robinson equation of state, and used that model to predict increases in the solubility of metal chelate complexes in SC CO_2 when excess ligand is present.

University of Notre Dame Publications resulting from this project:

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

Erik J. Roggeman, Aaron M. Scurto and Joan F. Brennecke, "Spectroscopy, Solubility and Modeling of Cosolvent Effects on Metal Chelate Complexes in Supercritical Carbon Dioxide Solutions," Ind. Eng. Chem. Res., 40, 2001, p. 980-989.

Aaron M. Scurto, Christopher M. Lubbers, and Joan F. Brennecke, "Thermodynamic Aspects of the in-situ Extraction of Metals with Supercritical Fluids," Proceedings of the 2nd International Meeting on High Pressure Chemical Engineering, Hamburg, Germany, March 7-9, 2001.

Joan F. Brennecke, Aaron M. Scurto, Christopher M. Lubbers, Lynnette A. Blanchard, Jennifer L. Anthony and Edward J. Maginn, "Environmental Applications of Supercritical Fluids," Proceedings of the 4th Brazilian Conference on Supercritical Fluids, Salvador, Bahia, Brazil, October 9-11, 2001.

Aaron M. Scurto, Christopher M. Lubbers and Joan F. Brennecke, "Supercritical CO₂ for the Extraction of Metals," Proceedings of the 5th International Symposium of the ESQIE-IPN, Mexico City, Mexico, May 29 - 31, 2002.

Aaron M. Scurto, Gang Xu, Joan F. Brennecke and Mark A. Stadtherr, "Phase Behavior and Reliable Computation of High Pressure Solid-Fluid Equilibrium with Cosolvents," submitted to Ind. Eng. Chem. Res., 2003.

Chris M. Lubbers, Aaron M. Scurto, and Joan F. Brennecke, "Experimental Measurement and Modeling of the Vapor-Liquid Equilibrium of β -Diketones with CO₂," ACS Symposium Series, A. S. Gopalan, ed., in press, 2003.