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

Erik J. Roggeman, Aaron M. Scurto, Mark A. Stadtherr, John E. Chateauneuf* and Joan F. Brennecke

Dept. of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556

***Dept. of Chemistry**
Western Michigan University
Kalamazoo, MI 49008

Overall Goal: The development of an environmentally benign technique to remove metals from solid matrices.

Specific Goals:

The 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. The fundamental knowledge gained in this research is vital to computing phase behavior, and modeling and designing processes using CO_2 to separate organics and metal compounds from DOE mixed wastes. We have developed a comprehensive program to measure local solvation of metal chelates and to determine metal chelate stability in supercritical fluid mixtures using UV-vis and FTIR spectroscopy. These spectroscopic studies provide information on the solution microstructure, which is used in concert with 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 will be important in the design of processes using CO_2 to extract components from mixed wastes and in determining the optimum operating conditions.

DOE Needs Addressed

- Separation of metals and organics from mixed wastes
- Extraction of metals from contaminated soils
- Cleanup of radioactive decontamination waste
- Reprocessing of spent nuclear fuel

Liquid vs. CO_2 Extraction

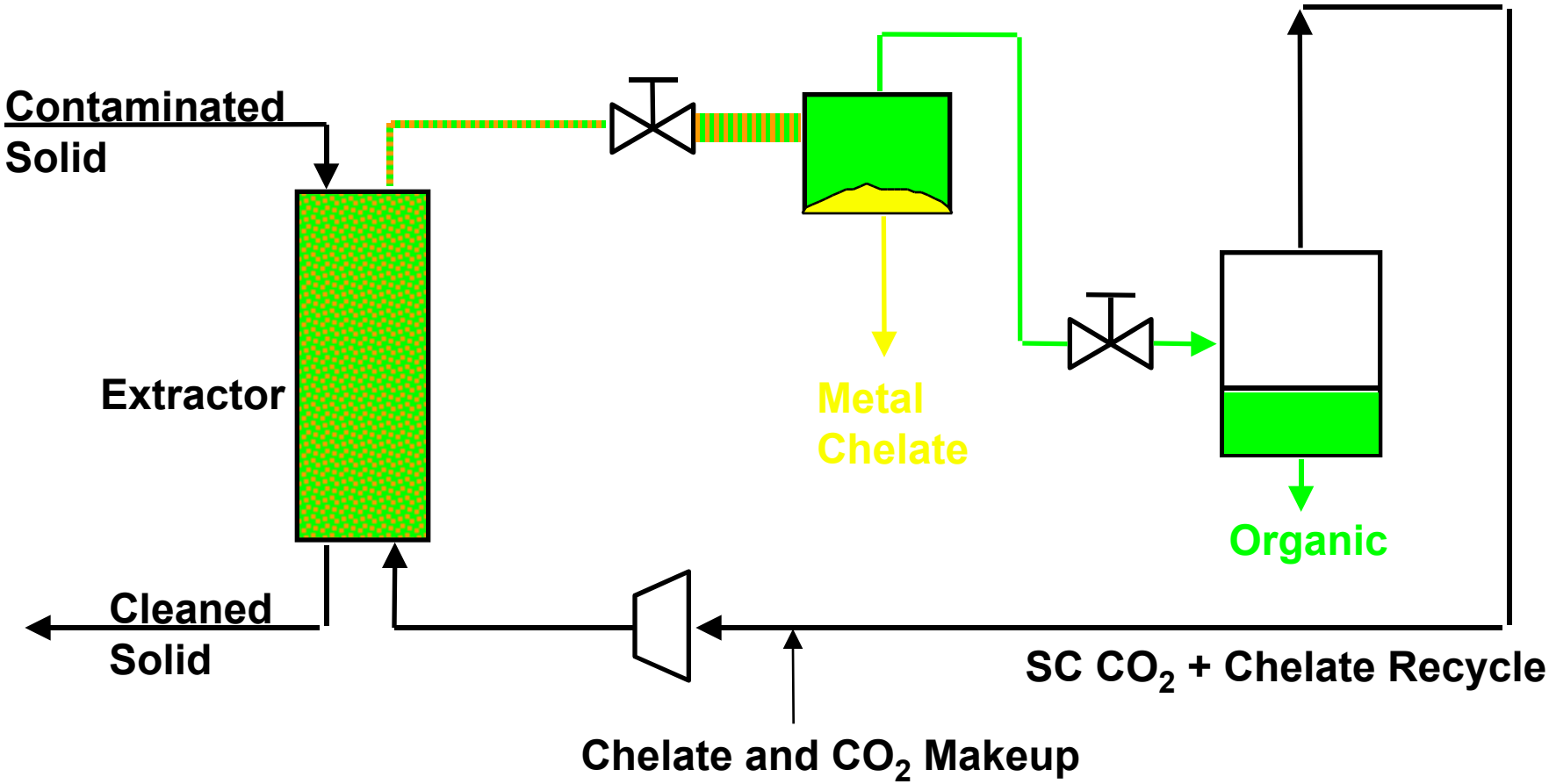
Liquid Extraction + Steam Stripping

- Residual organic solvent in solid matrix
- Organic contamination of aqueous phase
- Limited extraction efficiencies due to poor mass transfer
- Partial removal of organic co-contaminants
- Additional difficult organic solvent / organic co-contaminant / metal chelate separation steps

CO_2 Extraction

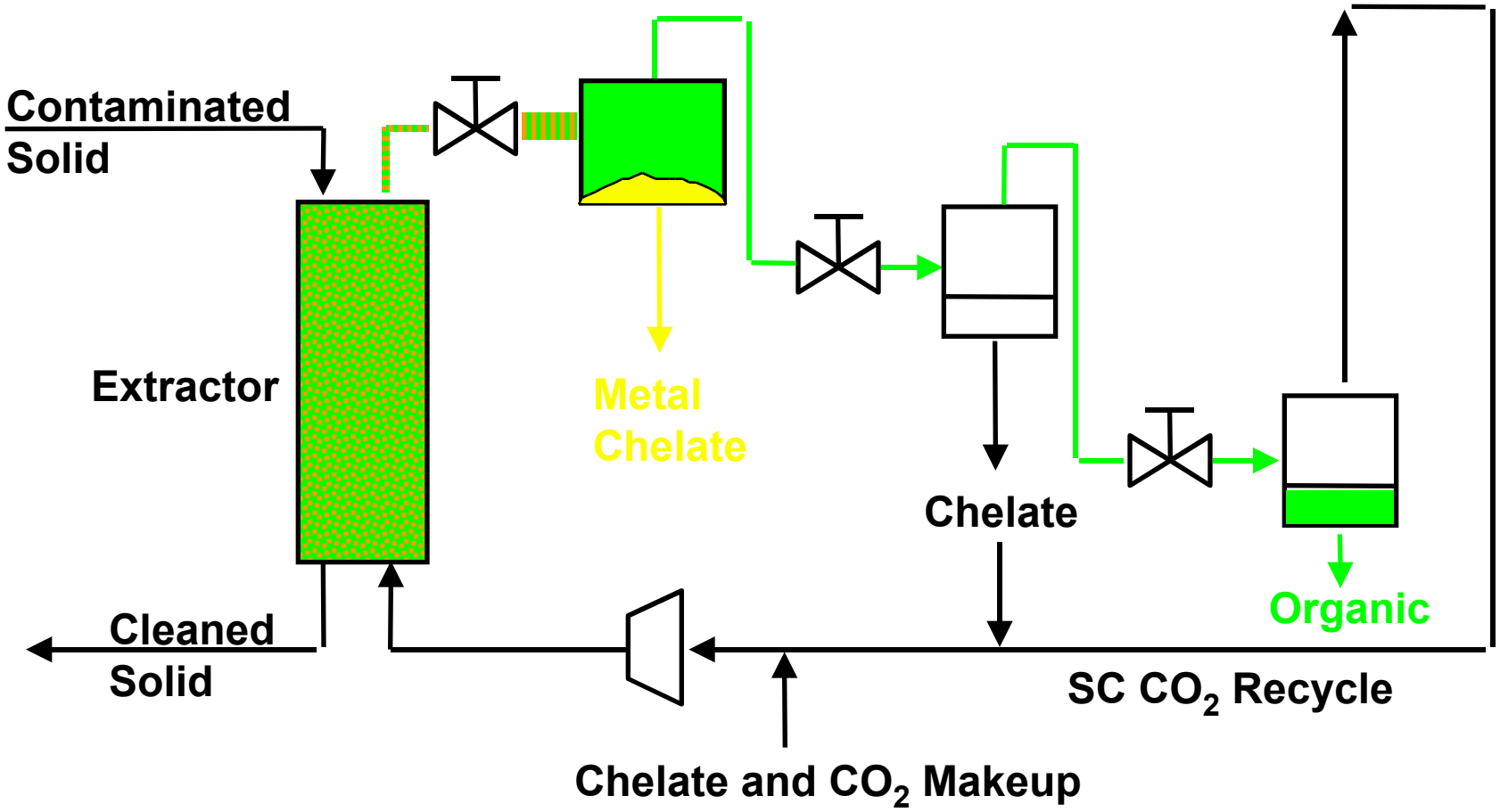
- High diffusivities
- No residual solvent in matrix
- Easy downstream separation (ΔT or ΔP)
- Mixed waste separation
  - Sequential organic and metal extraction
  - Co-extraction followed by sequential separation
- High Pressure Operation
- High capital and operating costs
- Low solubility of chelating agents and metal chelate complexes
  - designer ligands
  - cosolvents

Process Concept



Chelating agent more volatile than organic contaminant

Process Concept



Chelating agent less volatile than organic contaminant

Extraction of Metals with CO_2

Previous Work

- Use chelating agents in CO_2 to remove metals from contaminated soils, sludges and wastewaters
- Can extract metals from filter paper, spiked sand, wastewater (Wang and Marshall, 1994; Wang et al., 1995)
- Measurements of solubilities in pure CO_2 (groups of Wai, Sievers, Taylor, etc.)
- Increased solubilities with added cosolvent (Wai et al., 1993)

$Hg(FDDC)_2$	CO_2	0.005 mol/L
150 atm, 50˚C	CO_2/5% CH_3OH	0.012 mol/L

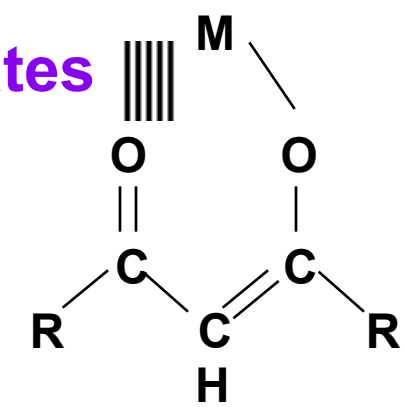
- Increased extraction efficiencies with added methanol and/or water (Lin et al., 1993)

Approach

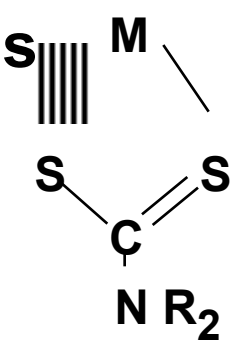
To study the influence of cosolvents on metal chelate solubility in CO_2 by:

- **measurements**
- **spectroscopy**
- **modeling**

β-diketonates



dithiocarbamates

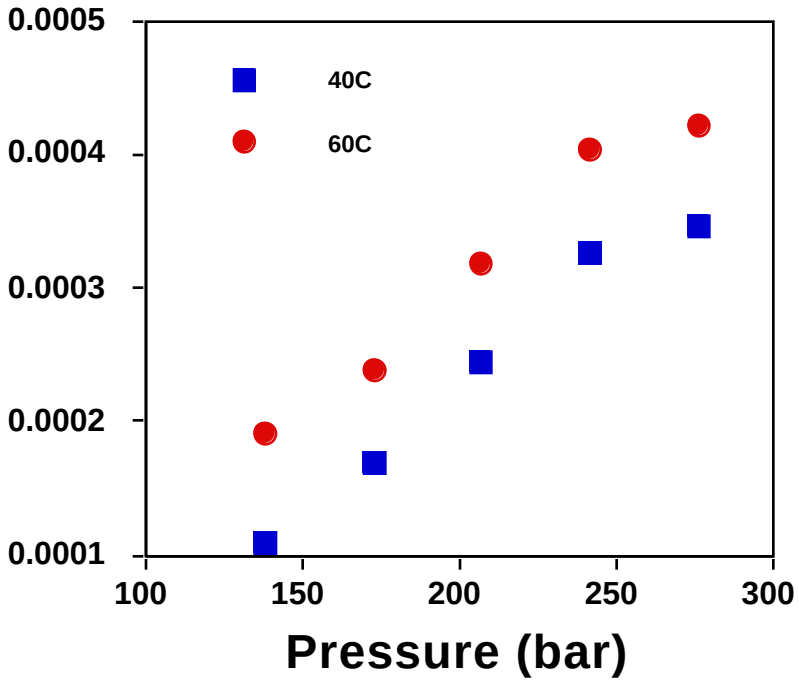


Outline of Results

- Measurements of the solubility of $Zn(thd)_2$ in CO_2 with and without cosolvents
- Spectroscopic study of preferential solvation of metal chelates by cosolvents
- Modeling of metal chelate solubility
- Other aspects of this project not covered in this poster:
  - metal chelate stability in CO_2 (in-situ FTIR and product analysis)
  - influence of water on solubility and extraction efficiency
  - tautomerization of β-diketonates in CO_2
  - development of a totally reliable computational method for metal chelate/SCF phase equilibrium calculations

Solubility

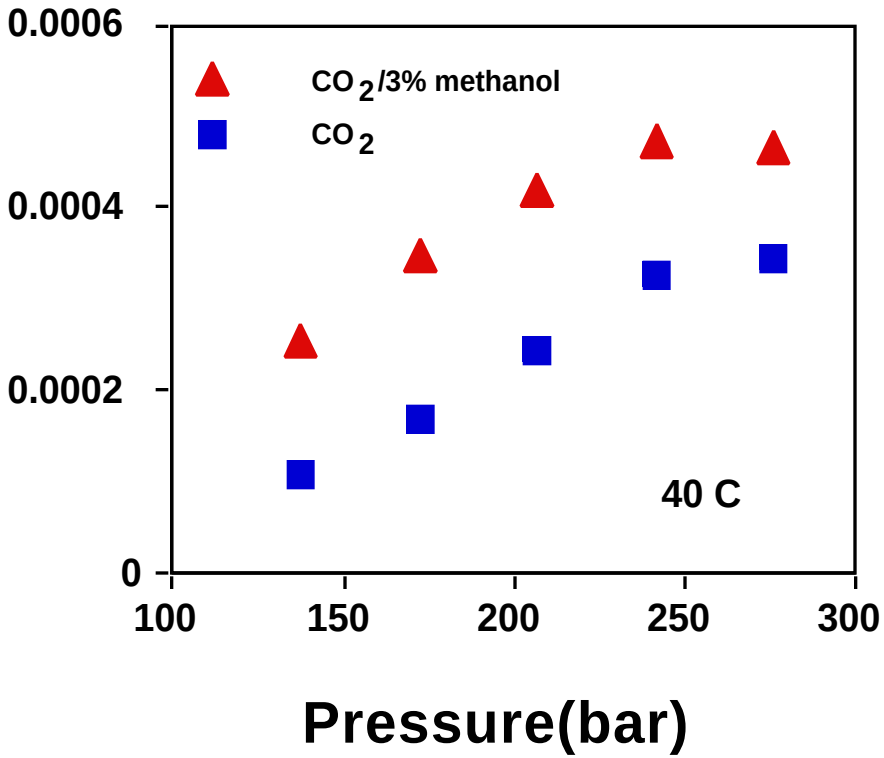
Zn^{II}(2,2,6,6-tetramethylheptane3,5-dionate)$_2$



Dynamic method using Isco SFX220 extractor

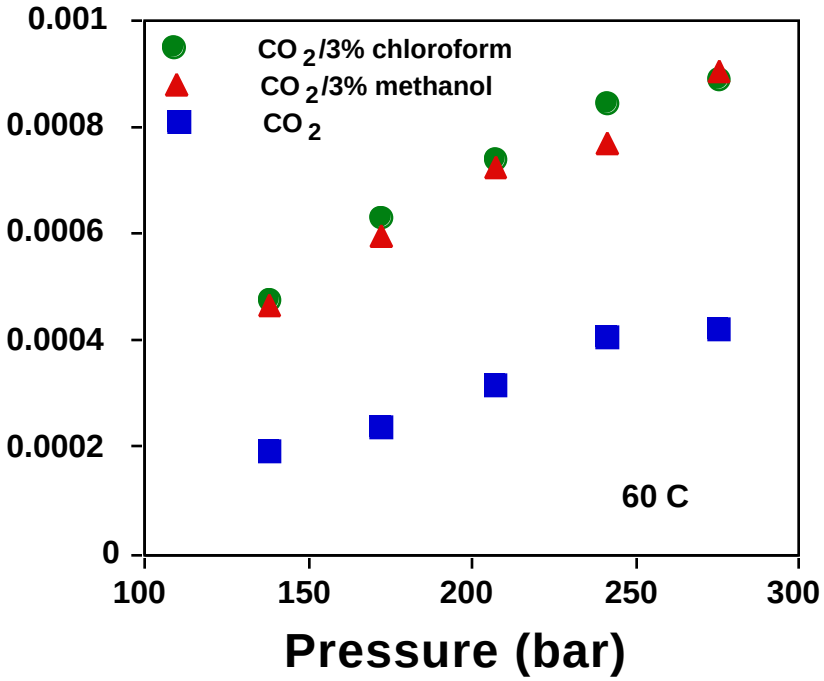
Solubility

Zn^{II}(2,2,6,6-tetramethylheptane3,5-dionate)$_2$

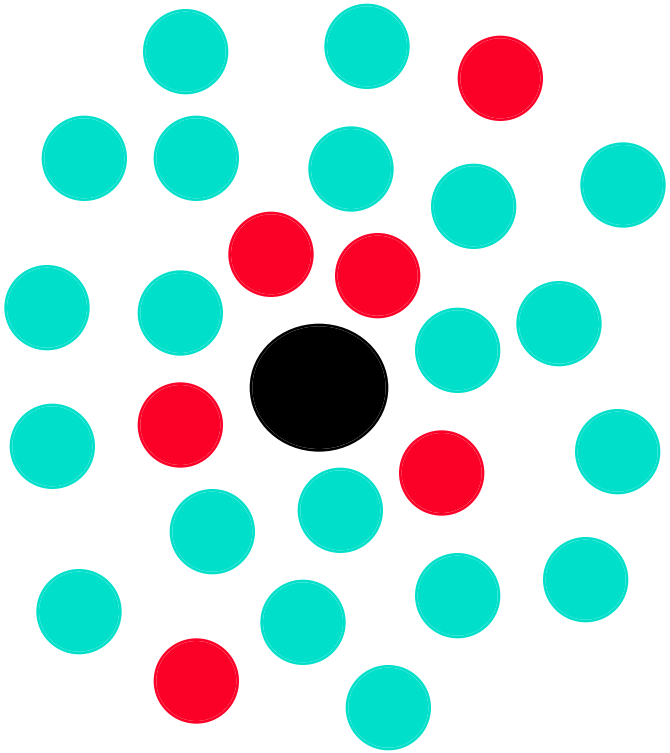


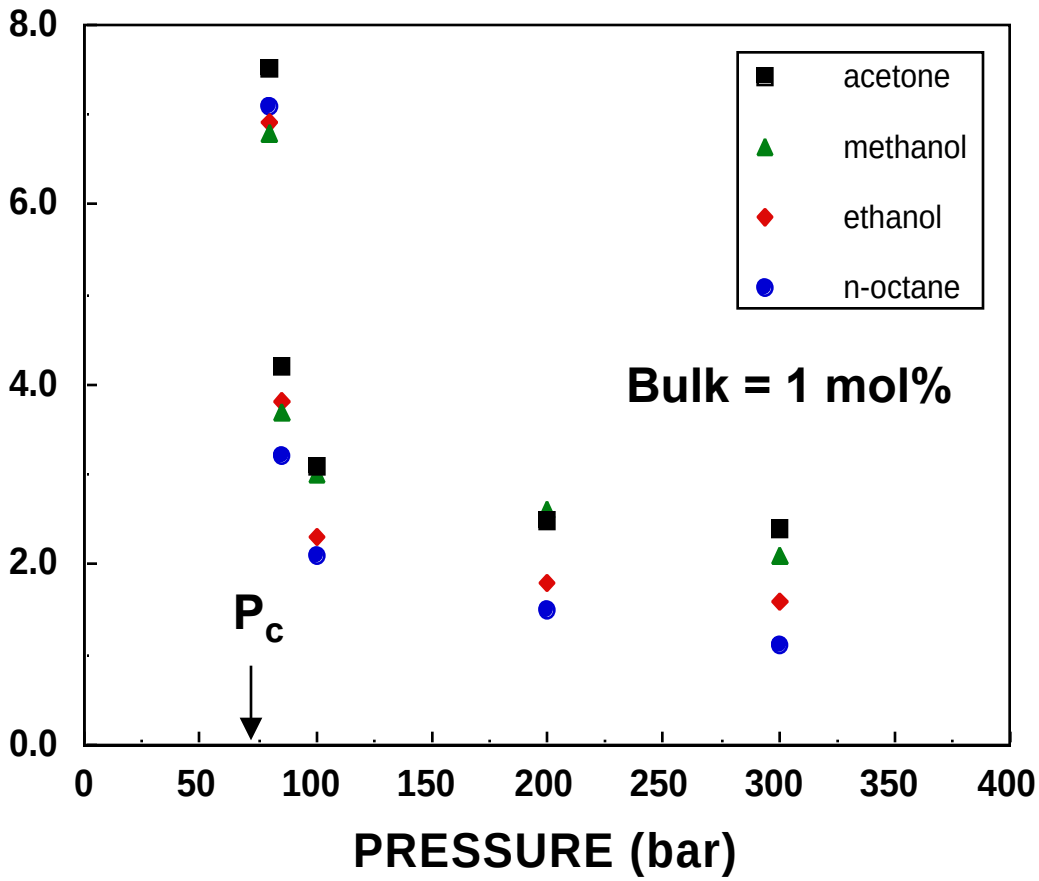
Effect of Cosolvents on Solubility

Zn^{II}(2,2,6,6-tetramethylheptane3,5-dionate)$_2$



Local Composition Enhancement





(Kim and Johnston, 1987)

Solvation from Extinction Coefficients

$Fe^{III}(acac)_3$

Solvent	Transition (nm) Intraligand	CT	$I_{intraligand}/I_{CT}$
Hexane, ambient	271	429	7.7
CO_2,40˚C,88 bar	273	428	7.6
CO_2,40˚C,97 bar	273	428	7.8
CO_2,40˚C,327 bar	273	428	8.5
$CHCl_3$, 60˚C, 1 bar	274	437	8.5
$CHCl_3$, 60˚C, 214 bar	274	437	11.2
Methanol, 40˚C, 1 bar	273.5	426	16.1
Methanol, 60˚C, 1 bar	273.5	426	20.8

Barnum, D. W., J. Inorg. Nucl. Chem., 1961, 21, 221-237
Singh, P. R. and R. Sahai, Aust. J. Chem., 1969, 22, 1169-1175

Solvation from Extinction Coefficients

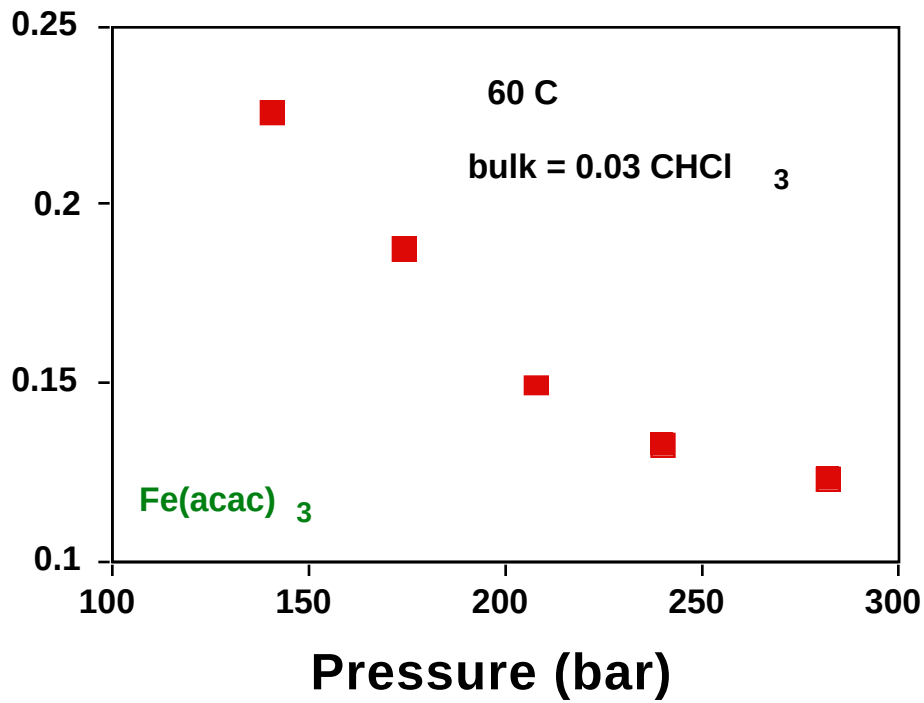
$Fe^{III}(acac)_3$

$$E_m = x_{12} z_m \left(E_1 / z_{12} \right) + x_{32} z_m \left(E_3 / z_{32} \right)$$

x_{12} = local composition of CO_2 around the solute
x_{32} = local compositionof chloroform around the solute
E_m = peak intensity ratio in mixture
E_1 = peak intensity ratio in pure CO_2
E_3 = peak intensity ratio in pure chloroform
z_m = coordination number in mixture = number of molecules around solute
z_{12} = coordination number around solute in pure CO_2
z_{32} = coordination number around solute in pure chloroform

Local Compositions

$Fe^{III}(acac)_3$ in a 3 mole% $CHCl_3$ / CO_2 mixture



Increase of β-diketonate solubility in CO_2/cosolvent mixtures:

- **Partially due to greater bulk density at given T and P**
- **Also, due to preferential solvation of the metal chelate by the cosolvent**

Equation of State Modeling

$$y_i = \frac{\cancelto{1}{\varphi_i^{sat}} P_i^{sat} \exp[v^s(P-P_i^{sat})/RT]}{\varphi_i P}$$

y_i = solubility of metal chelate in CO_2 phase

φ_i^{sat} = fugacity coefficient at the sublimation pressure ~1.0

P_i^{sat} = sublimation pressure

v^s = solid molar volume

P = pressure

R = gas constant

T = temperature

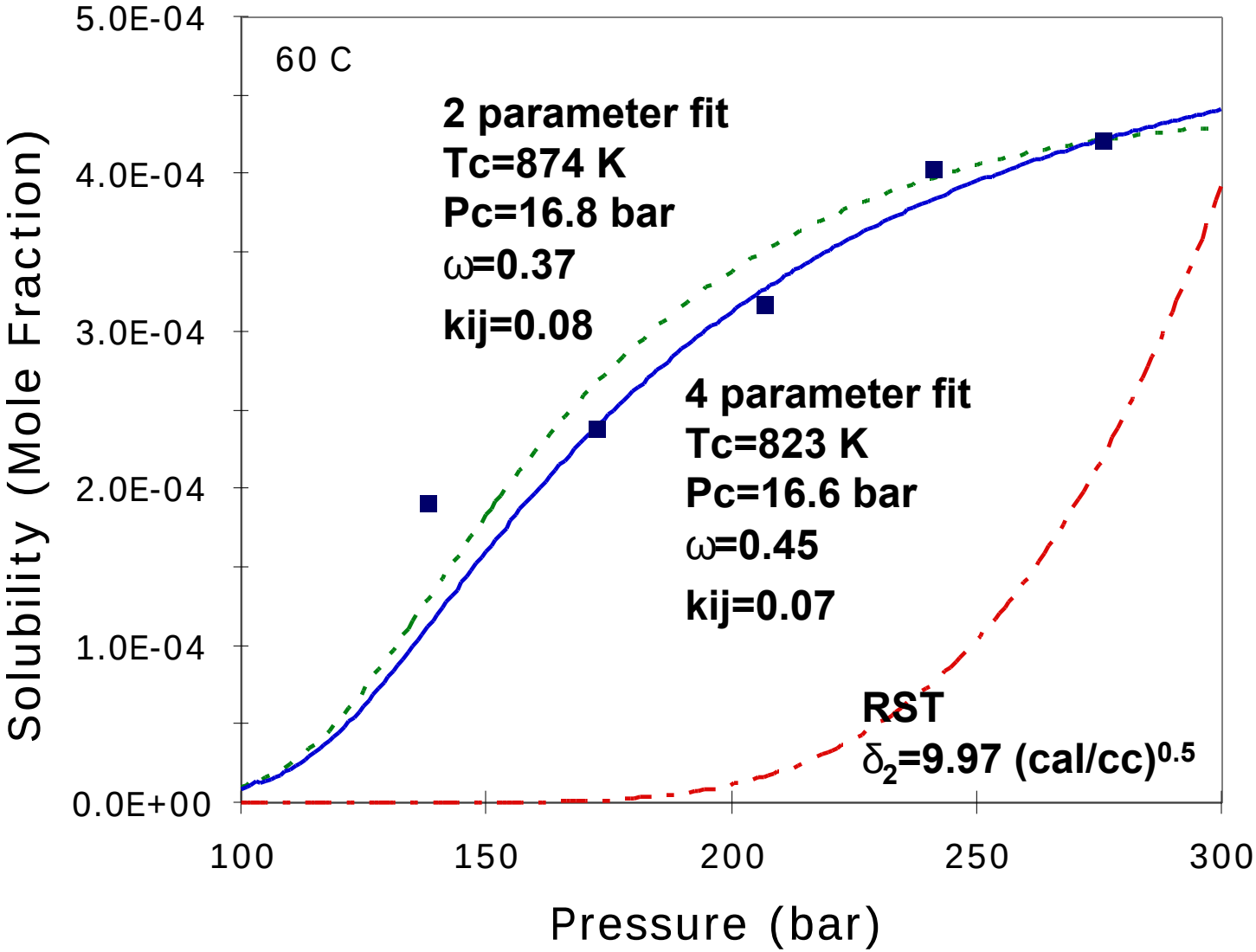
φ_i = fugacity coefficient from EOS = $f(T_c, P_c, \omega, y_i, k_{ij})$

Challenge: Thermodynamic properties (especially T_c, P_c and ω) are not known for metal chelate complexes

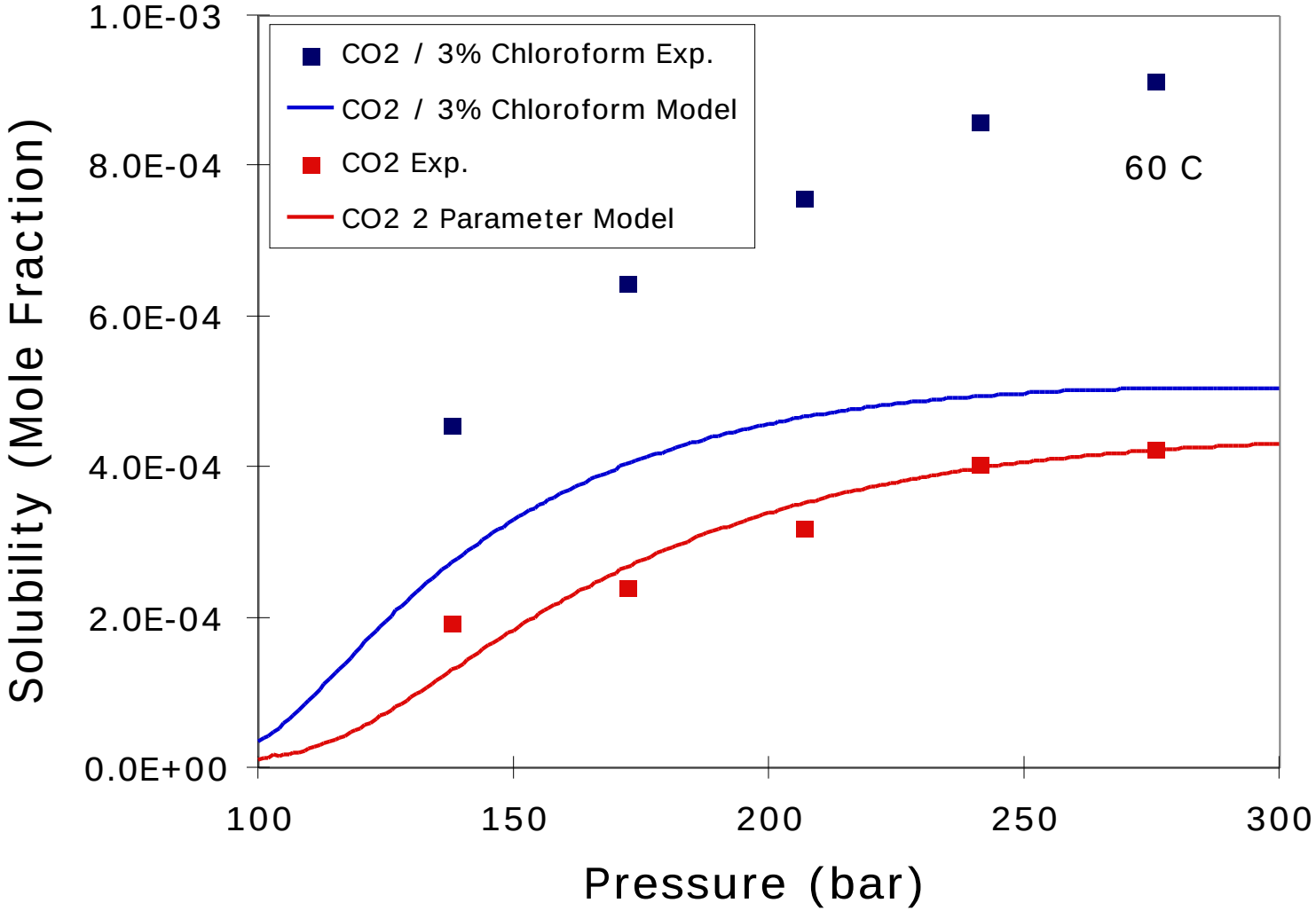
Regular Solution Theory Modeling

- Previous modeling of metal chelate solubility in supercritical CO_2 was done by assuming solid/liquid equilibria and using Regular Solution Theory to model the liquid phase nonidealities (Lagalante et al., 1995)
- However, this approach is inadequate because:
  - It does not correctly capture the density (pressure) dependence of the solubility
  - It predicts increasing solubility with decreasing temperature, contrary to experimental observations
  - Regular solution theory assumes $s^E = v^E = 0$, which is not a good approximation for supercritical fluid solutions

$Zn(thd)_2$ Solubility from EOS



Solubility Increases with Cosolvent



Conclusions

- CO_2 + chelating agents can be used to extract metals from solid matrices
- New data for the solubility of $Zn(thd)_2$ in supercritical CO_2 with and without cosolvents
- Solubility data indicate that organic co-contaminants like chloroform and methanol can increase metal chelate solubility
- Spectroscopy shows that the solubility increase is due, at least in part, to preferential solvation of the metal chelate by the organic co-contaminant
- Metal chelate solubilities in supercritical CO_2 can be modeled adequately with the Peng-Robinson equation of state, although there is a dirth of physical and thermodynamic property data for metal chelates
- Estimation of co-contaminant solubility enhancement will require that the preferential solvation be addressed more explicitly

Acknowledgments

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