Computational Chemistry Study of Amine Complexation

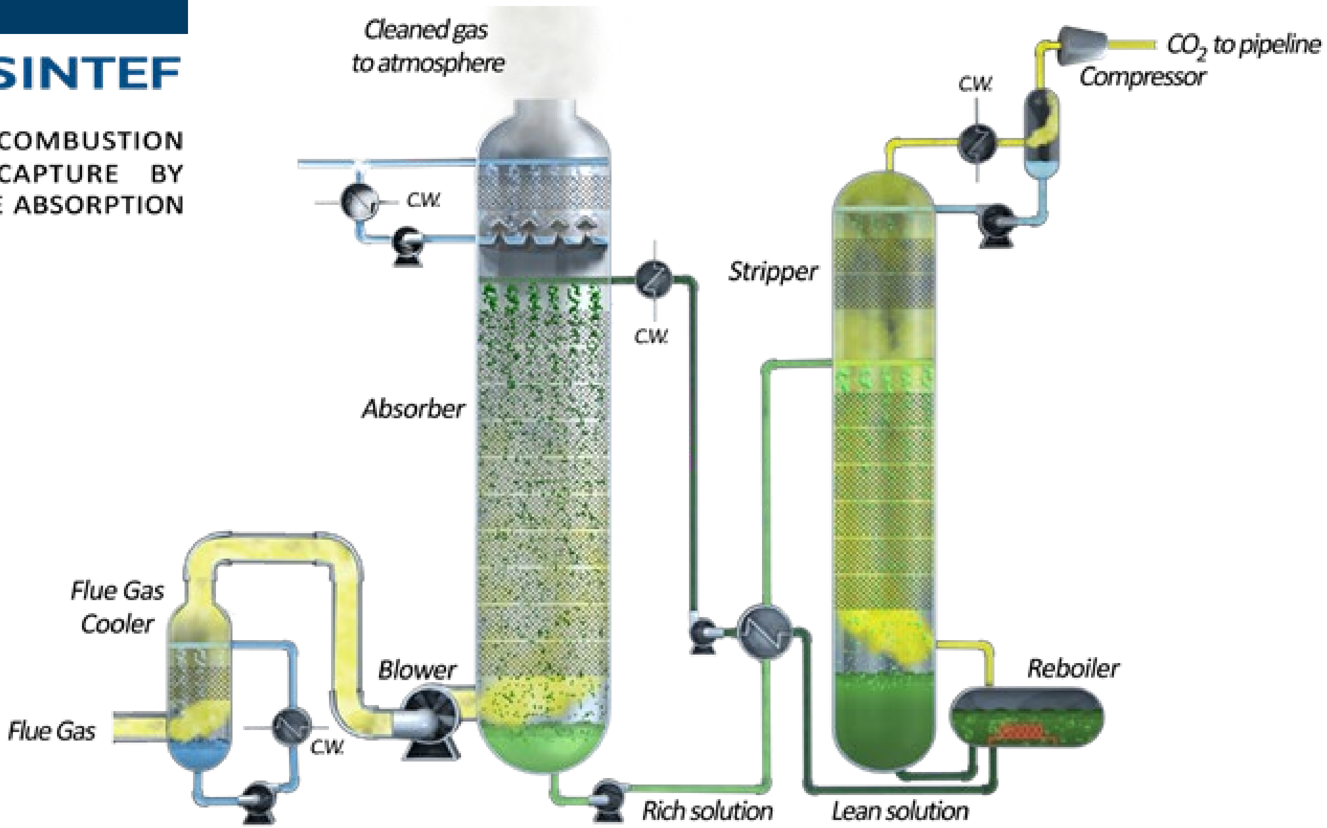
Stefan Andersson and Eirik Falck da Silva, SINTEF
PCCC8, Marseille, September 17, 2025
Eirik.silva@sintef.no

SINTEF

SINTEF

POST-COMBUSTION CO_2 CAPTURE BY AMINE ABSORPTION

Tiller full height absorber and desorber



SINTEF has had a central role in the development of slb Capturi solvent technology and in the development of the CESAR1 solvent

The importance of metal solubility in amine-based CO_2 capture

Metal ions can enter the solvent from materials in the plant or the flue gas

Metal from the plant entering the solvent is clearly undesirable

Metal ions are known to influence solvent degradation, often leading to higher degradation

Experimental data

- From the PhD thesis of Ingvild Eide-Haugmo, NTNU, 2011
- 30wt% amine kept at 135°C for 5 weeks. Tubes in 316 stainless steel. Metal analysis on the end samples with ICP-MS and amine degradation quantified by LC-MS.
- Experiments carried out both with unloaded amine and with CO_2 at 0.5 mol CO_2/mol amine loading.
- Experiments were also carried out with glass lining (avoiding any metal exposure)

Ingvild Eide-Haugmo

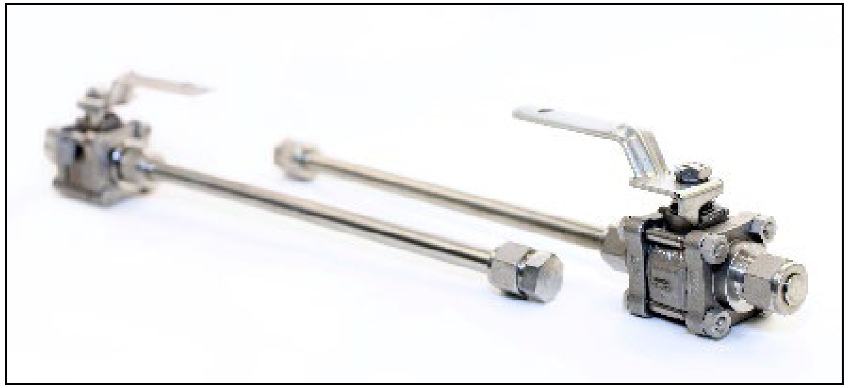
Environmental impacts and aspects of absorbents used for CO_2 capture

Thesis for the degree of Philosophiae Doctor

Trondheim, September 2011

Norwegian University of Science and Technology
Faculty of Natural Sciences and Technology
Department of Chemical Engineering

NTNU – Trondheim
Norwegian University of Science and Technology



Experimental results with loaded solvent

From the thesis of Ingvild Eide-Haugmo, NTNU, 2011
30wt% amine with CO2 at 0.5 mol CO2/mol amine loading. Tubes in 316 stainless steel. Results after 5 week experiments at 135°C. Metal analysis with ICP-MS.

DETA and EDA have proven to be very corrosive in pilot campaigns.

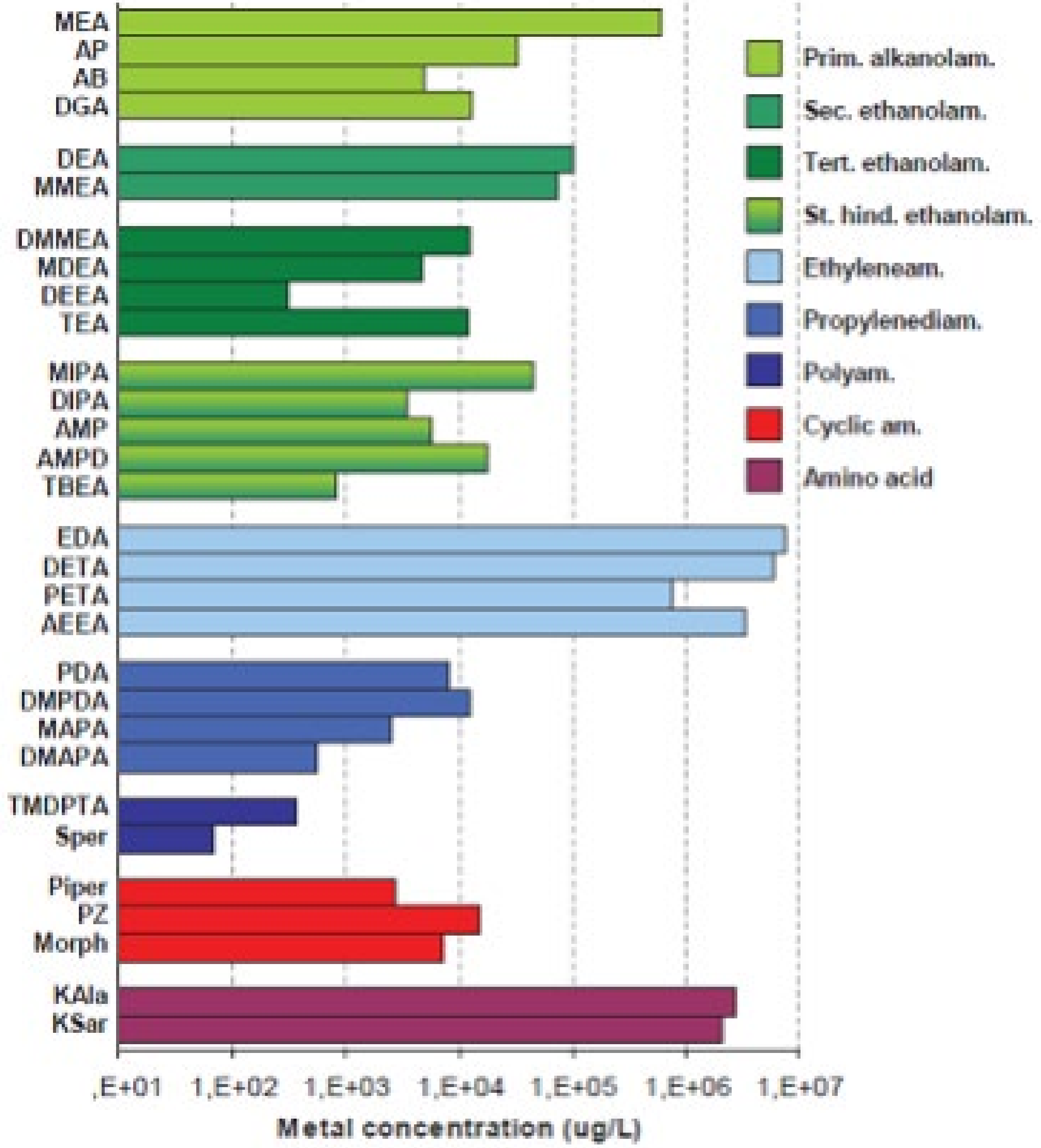


Figure 4-76: End point results for iron concentration in degraded amine solutions.

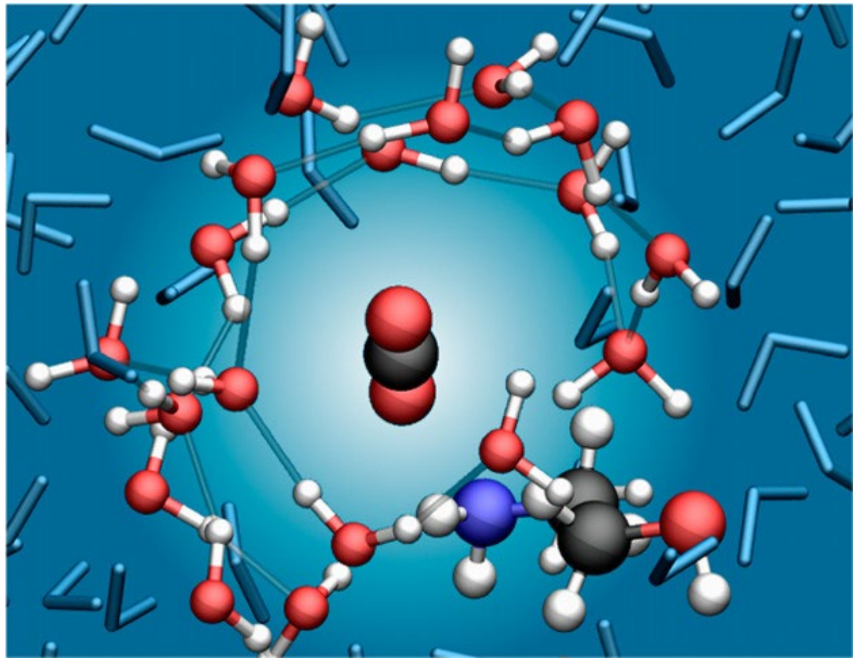
How to think about computational chemistry

- Molecular Mechanics
- Molecular dynamics
- Semi-Empirical methods
- Continuum solvent models
- Hartree-Fock methods
- Density Functional theory
- Coupled Cluster

$$\hat{H}\Psi = E\Psi$$

Hamiltonian Operator (Energy operator)

Energy eigenvalue



Guido, Ciro A., et al. "The fate of a zwitterion in water from ab initio molecular dynamics: Monoethanolamine (MEA)-CO2." *Journal of chemical theory and computation* 9.1 (2013): 28-32.

Computational Chemistry of amine complexation to metal ions

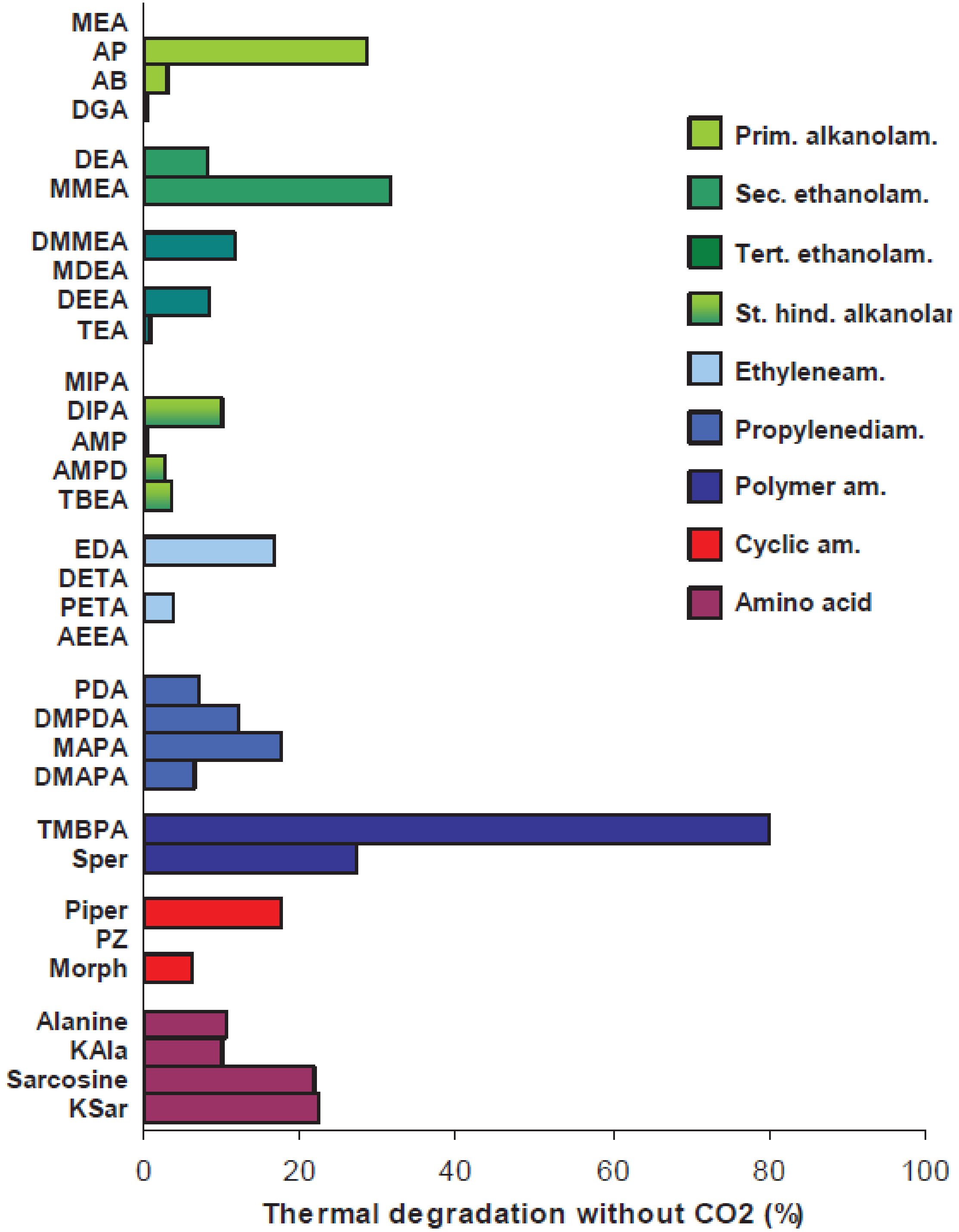
- Hypothesis: Binding strength between iron ion (Fe^{2+} and Fe^{3+}) and amine molecules correlates with metal solubility/corrosivity
  - $Fe^{2+/3+} + x \text{ amin} \rightleftharpoons (\text{Fe-amin}_x)^{2+/3+}$

- Methods:
  - **DFT** (B3LYP, M11 and r2SCAN) → ΔG for gas phase reaction
  - Basis sets: def2-TZVPP for energies and structure, 6-31G** for vibrational frequencies
  - **continuum solvation model** (SMD) for given solvent (water so far) → ΔG for solvation
  - Combination of the two: **ΔG for reaction in solution**

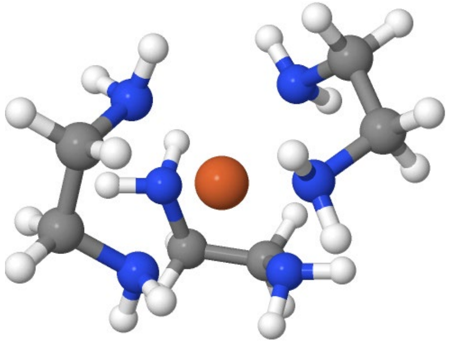
- Amines investigated so far:
  - MEA, 3-aminopropanol (AP), Diethylaminoethanol (DEEA), 2-amino-2-methylpropanol (AMP), Ethylenediamine (EDA), Diethylenetriamine (DETA), N-(2-hydroxyethyl)-ethylenediamine (AEEA), 1,3-propane-diamine (PDA), 3-amino-1-methylaminopropane (MAPA), Dimethylaminopropylamin (DMAPA), piperazine

A comment:

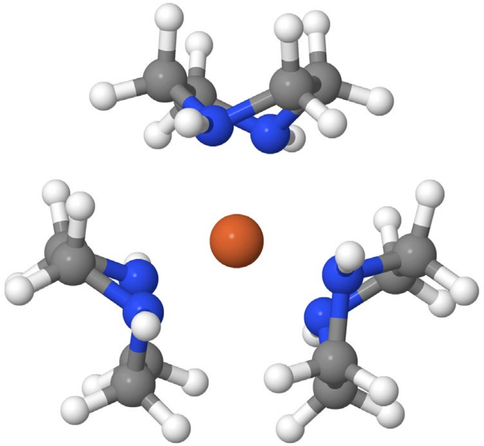
- In the experiments the solvent will to some extent have degraded
- In the comparison with computational chemistry results we are ignoring effect of degradation products on metal solubility



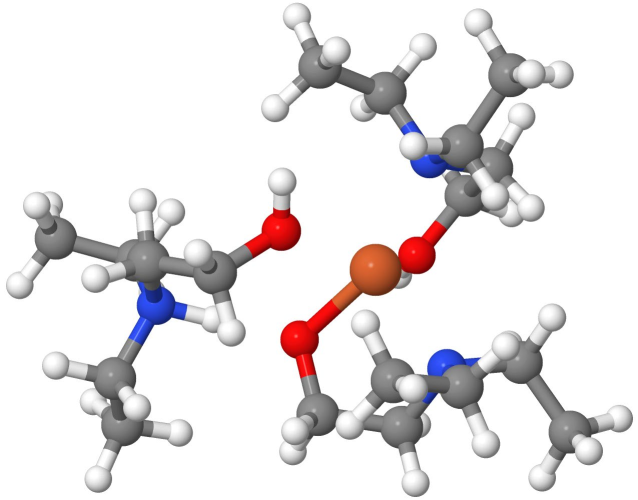
Molecular structures



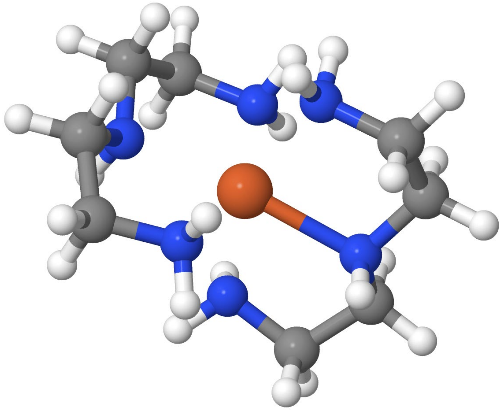
$(Fe\text{-}EDA_3)^{2+}$



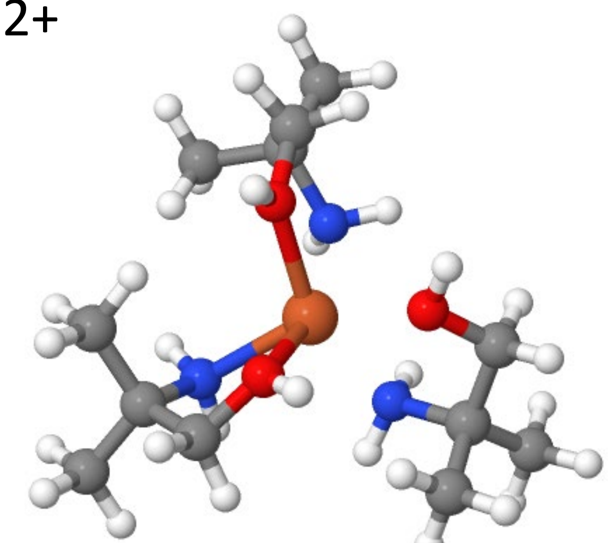
$(Fe\text{-}Pz_3)^{2+}$



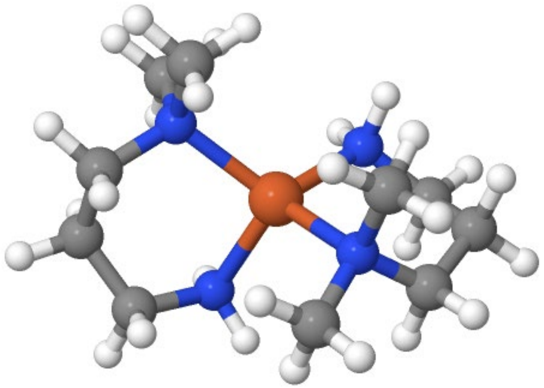
$(Fe\text{-}DEEA_3)^{2+}$



$(Fe\text{-}DETA_2)^{2+}$



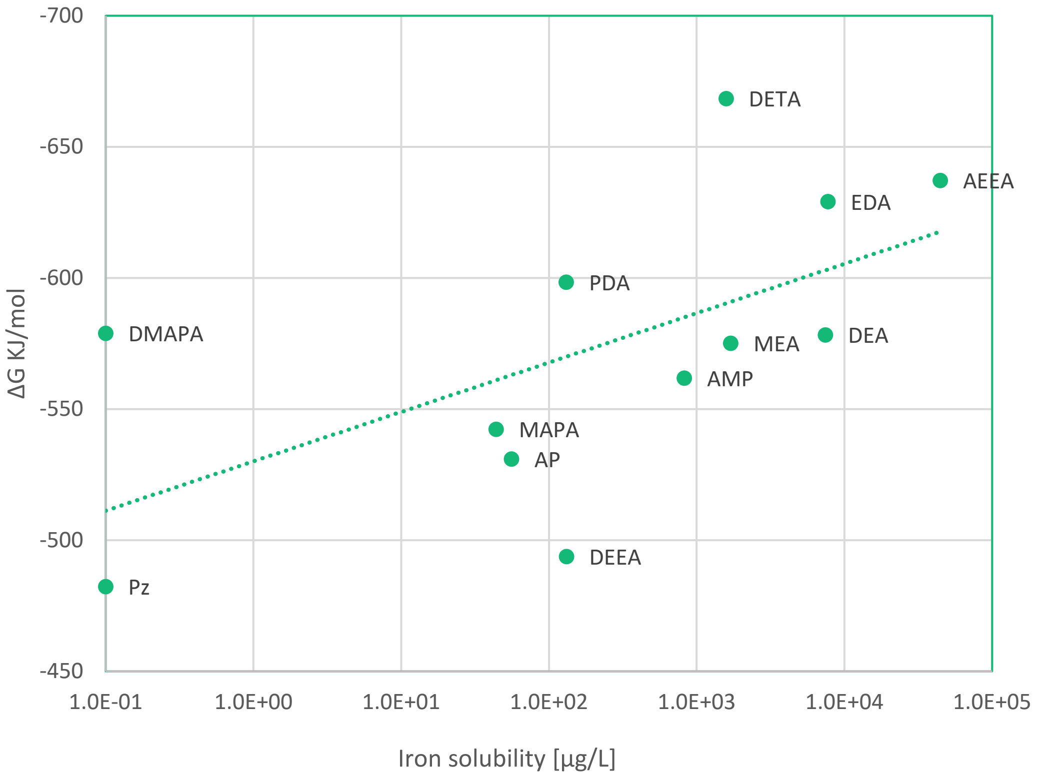
$(Fe\text{-}AMP_3)^{2+}$



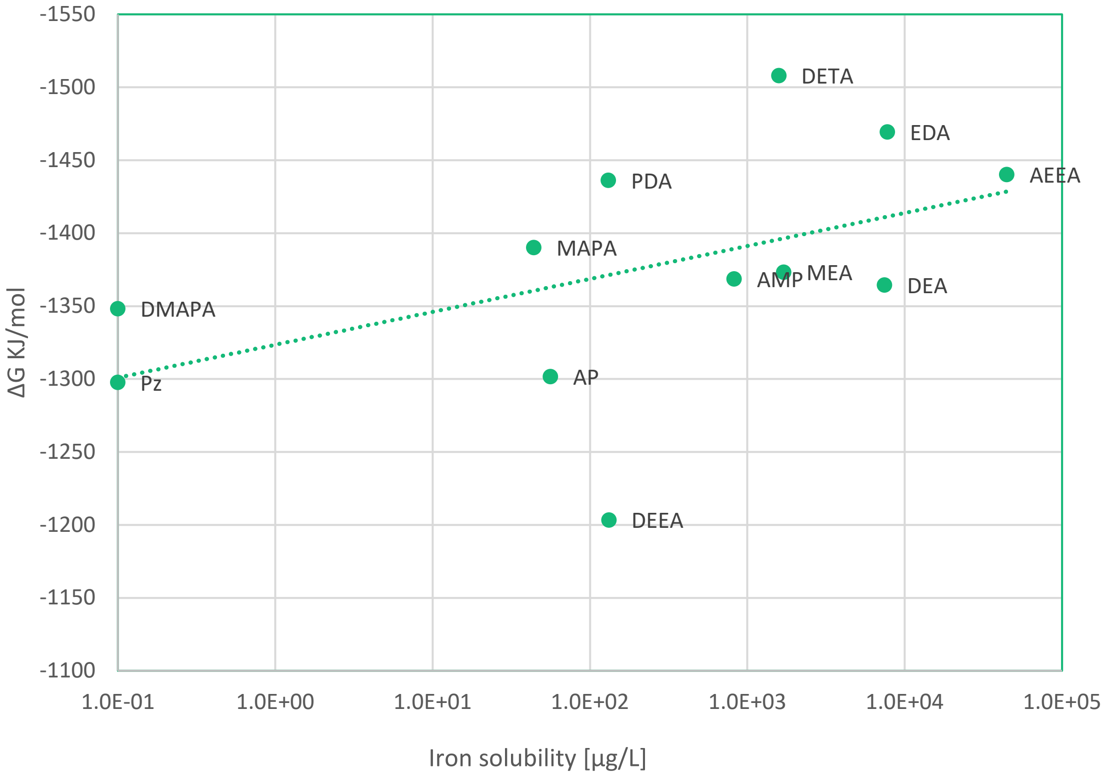
$(Fe\text{-}DMAPA_2)^{2+}$

Calculations vs. experimental iron solubilities -Unloaded solution

With Fe^{2+}

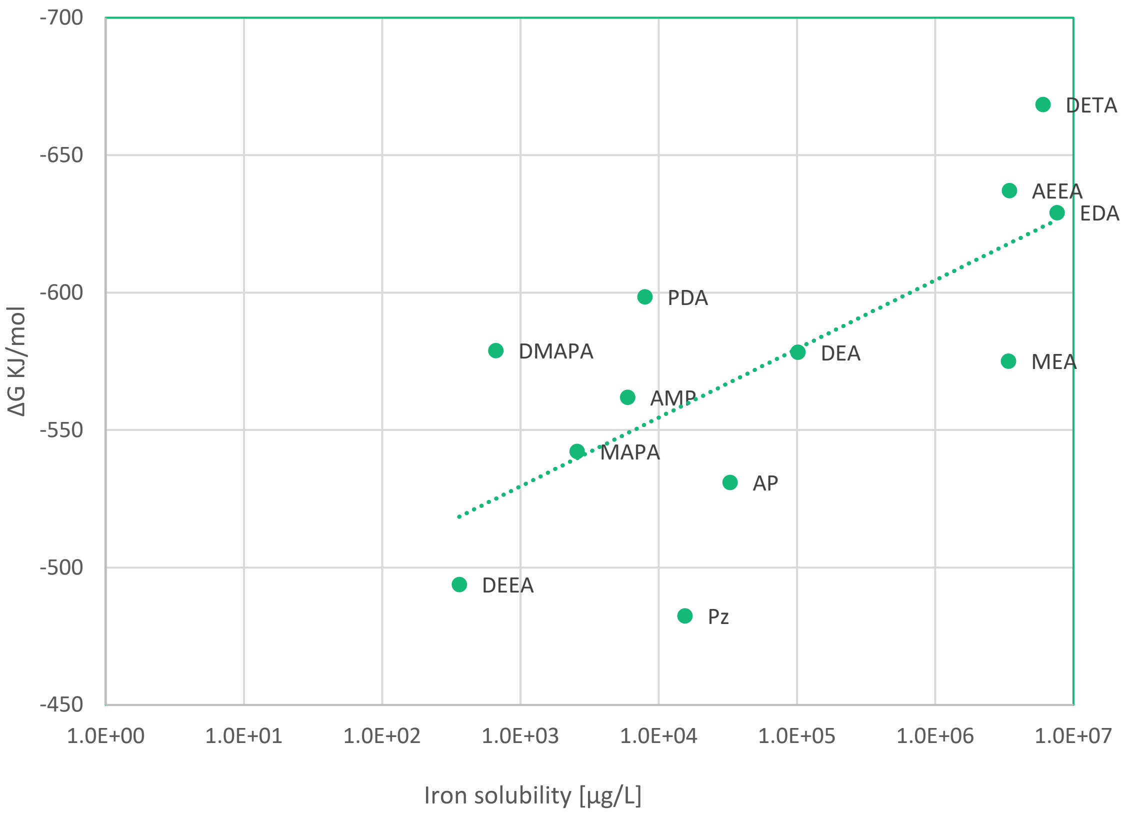


With Fe^{3+}

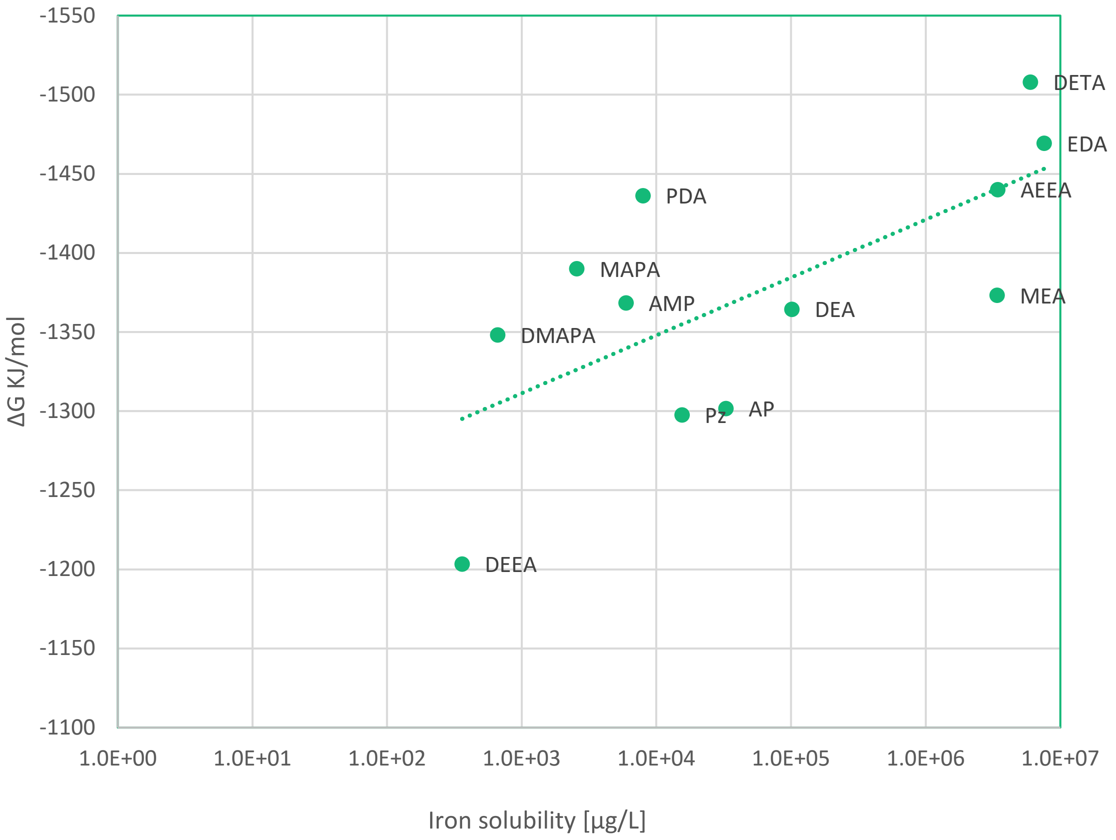


Calculations vs. experimental iron solubilities -Loaded solution

With Fe^{2+}



With Fe^{3+}

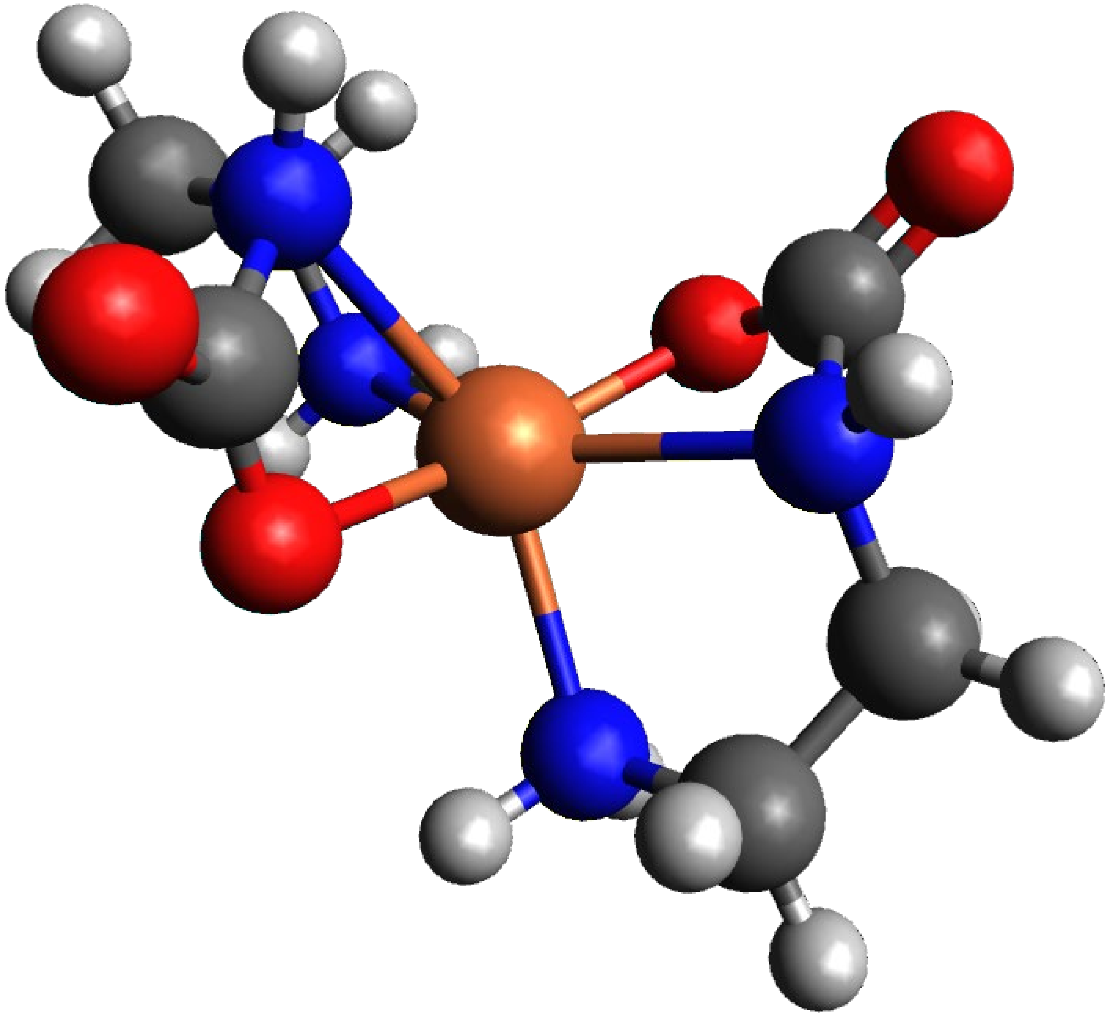


Ongoing & Future Work

- Study of the complexation power of different species such as carbamates
- Explore the complexation power of different degradation products

- Try to understand what role these complexes play in solvent degradation

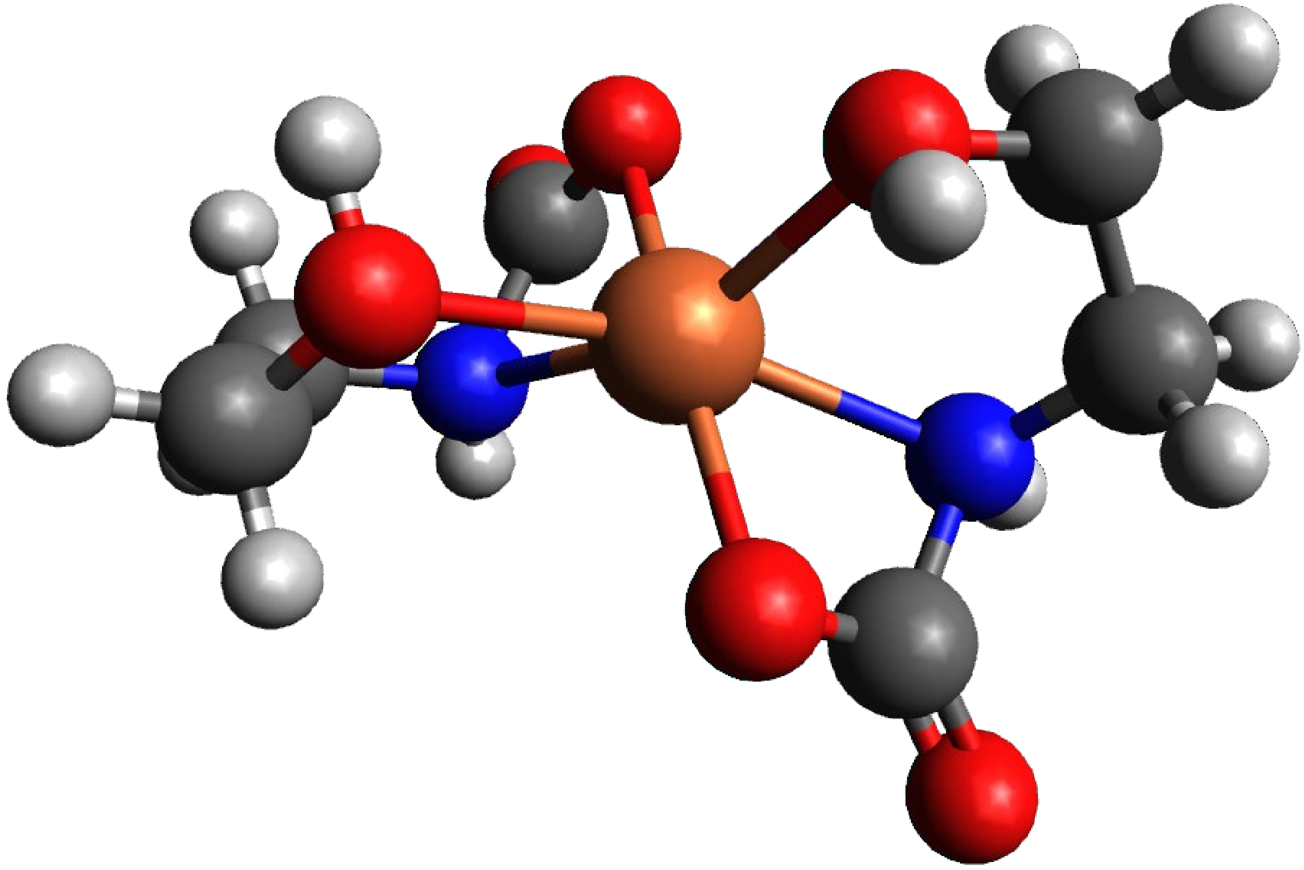
Fe^{2+} - EDA carbamate



- ΔG / kJ/mol
  - 1 EDA carbamate: **-393**
  - 2 EDA carbamate: **-518**

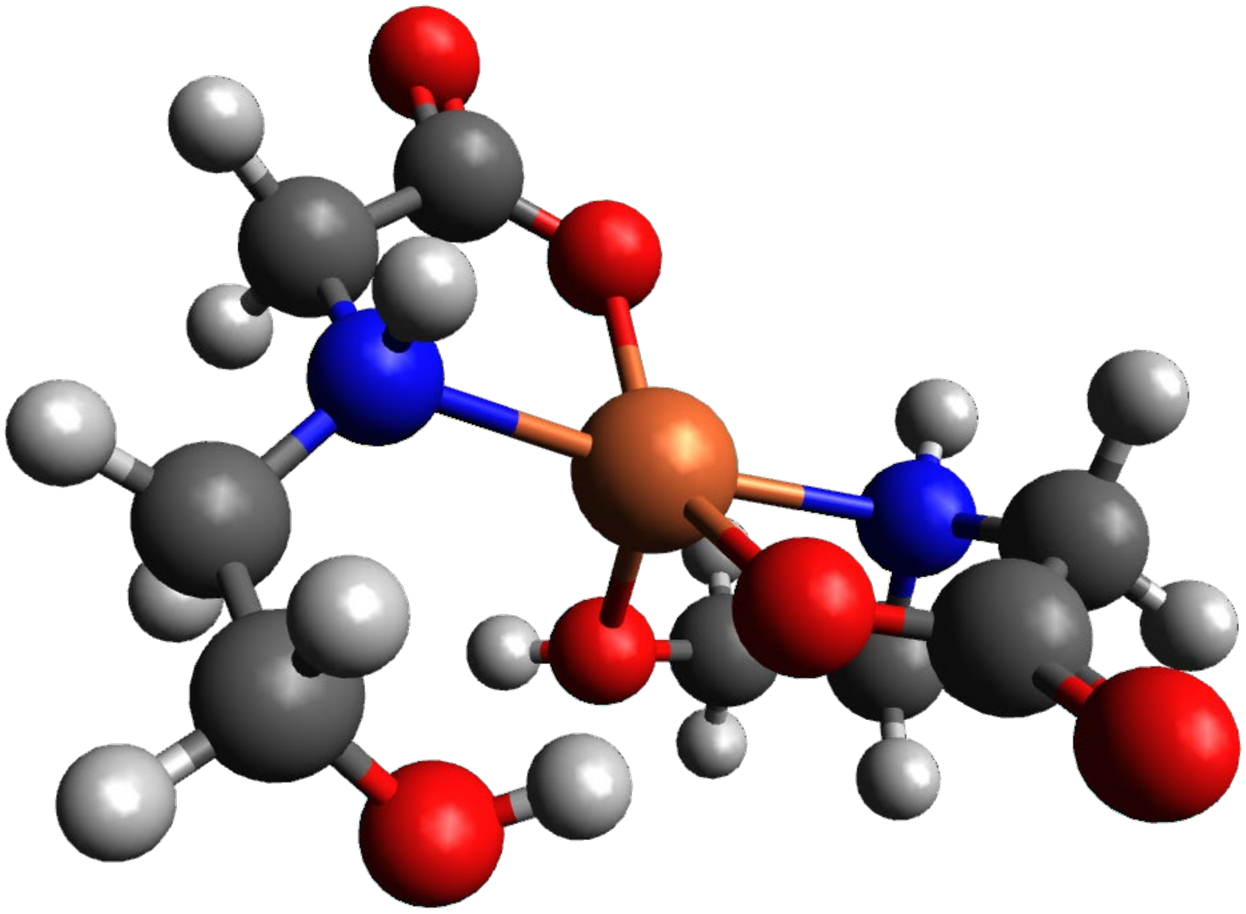
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)

Fe^{2+} - MEA carbamate



- ΔG / kJ/mol
  - 1 MEA carbamate: **-355**
  - 2 MEA carbamate: **-452**
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)

Fe^{2+} - deprotonated HEGly



- ΔG / kJ/mol
  - 1 HEGly: **-415**
  - 2 HEGly: **-563**
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)

Thank you for your attention!

eirik.silva@sintef.no

ACKNOWLEDGEMENT

These results have been produced with support from gigaCCS – Norwegian Research Centre of Excellence for Carbon Capture and Storage, performed under the Norwegian research programme Centre for Environment-friendly Energy Research (FME). The authors acknowledge the following partners for their contributions: Aibel, Aker BP, Ansaldo Energia, Aqualung Carbon Capture, Capsol Technologies, Cegal, Cignus Instruments, Climeworks, Elkem, Endress+Hauser SICK, Equinor, Eramet, Gassco, Hafslund Celsio, Havindustritilsynet, Heidelberg Materials, Hydro, IFE, Imperial College London, Krohne, Lunds Universitet, NaTRan, NGI, NORCE, NTNU, OMV Norge, Panametrics, Petrobras, Ruhr-Universität Bochum, Saipem, SLB, SLB Capturi, SINTEF, Universitetet i Bergen, Universitetet i Oslo, Università di Bologna, University of Western Australia, Vallourec, Vår Energi and the Research Council of Norway (350370).

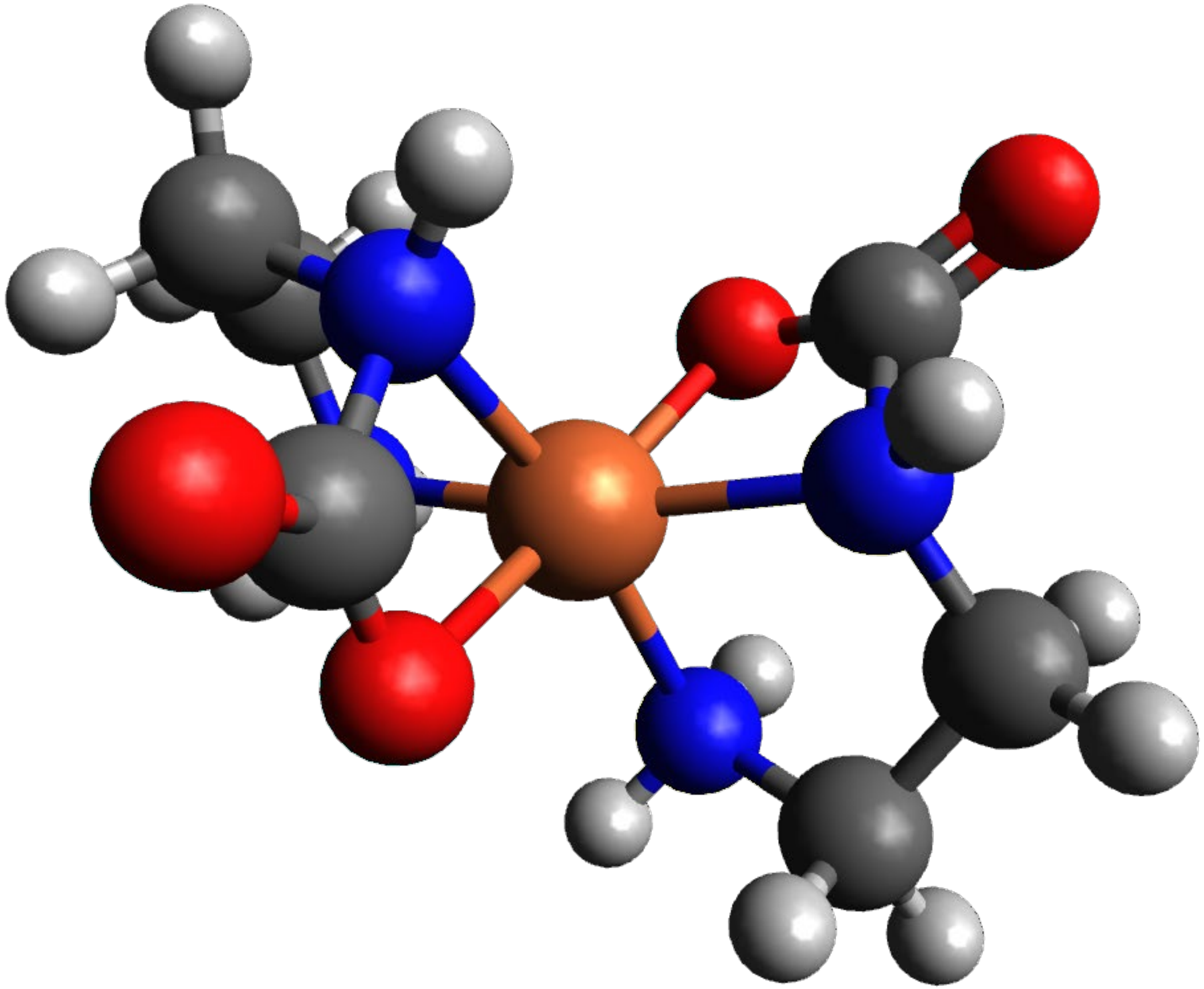
SolveMORE

Solvent Management Optimisation for Reducing Environmental footprint of the CO_2 capture process

gigaCCS

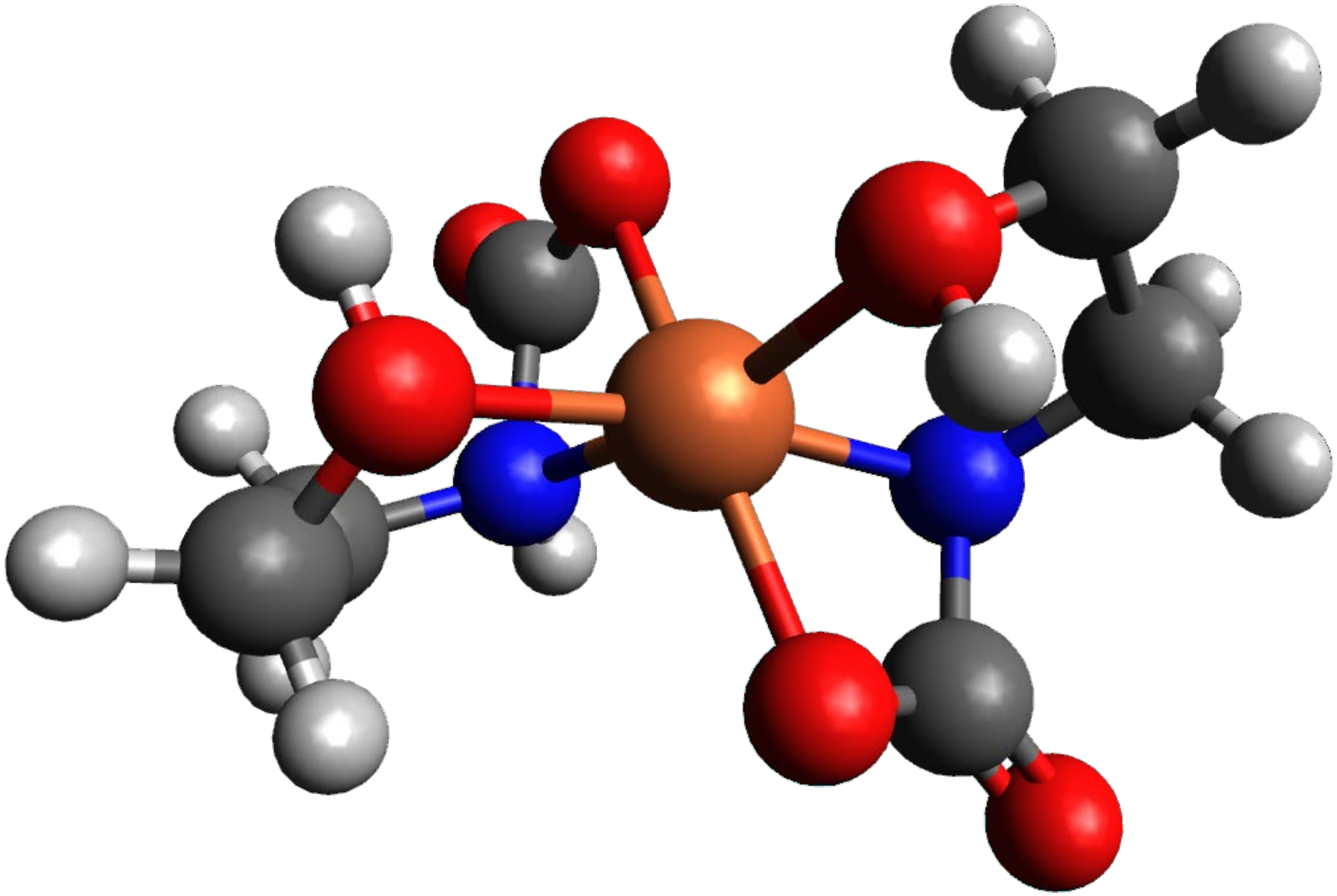
Teknologi for et
bedre samfunn

Fe^{2+} - EDA carbamate (singlet)



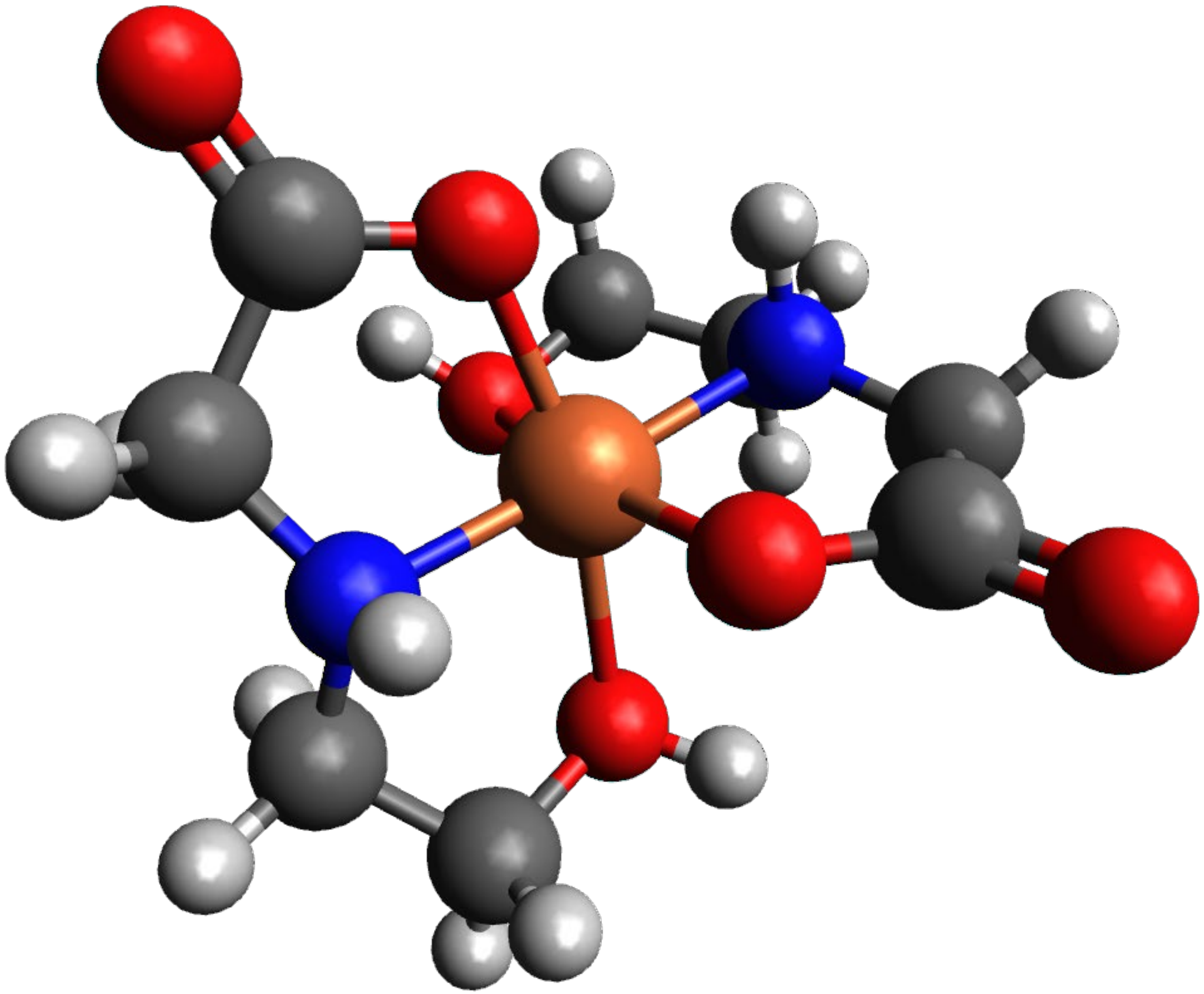
- ΔG / kJ/mol
  - 1 EDA carbamate: **-230**
  - 2 EDA carbamate: **-429**
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)

Fe^{2+} - MEA carbamate (singlet)



- ΔG / kJ/mol
  - 1 MEA carbamate: **-161**
  - 2 MEA carbamate: **-340**
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)

Fe^{2+} - deprotonated HEGly (singlet)



- ΔG / kJ/mol
  - 1 HEGly: **-242**
  - 2 HEGly: **-460**
- Method
  - B3LYP/def2-TZVPP
  - SMD solvation model (water)