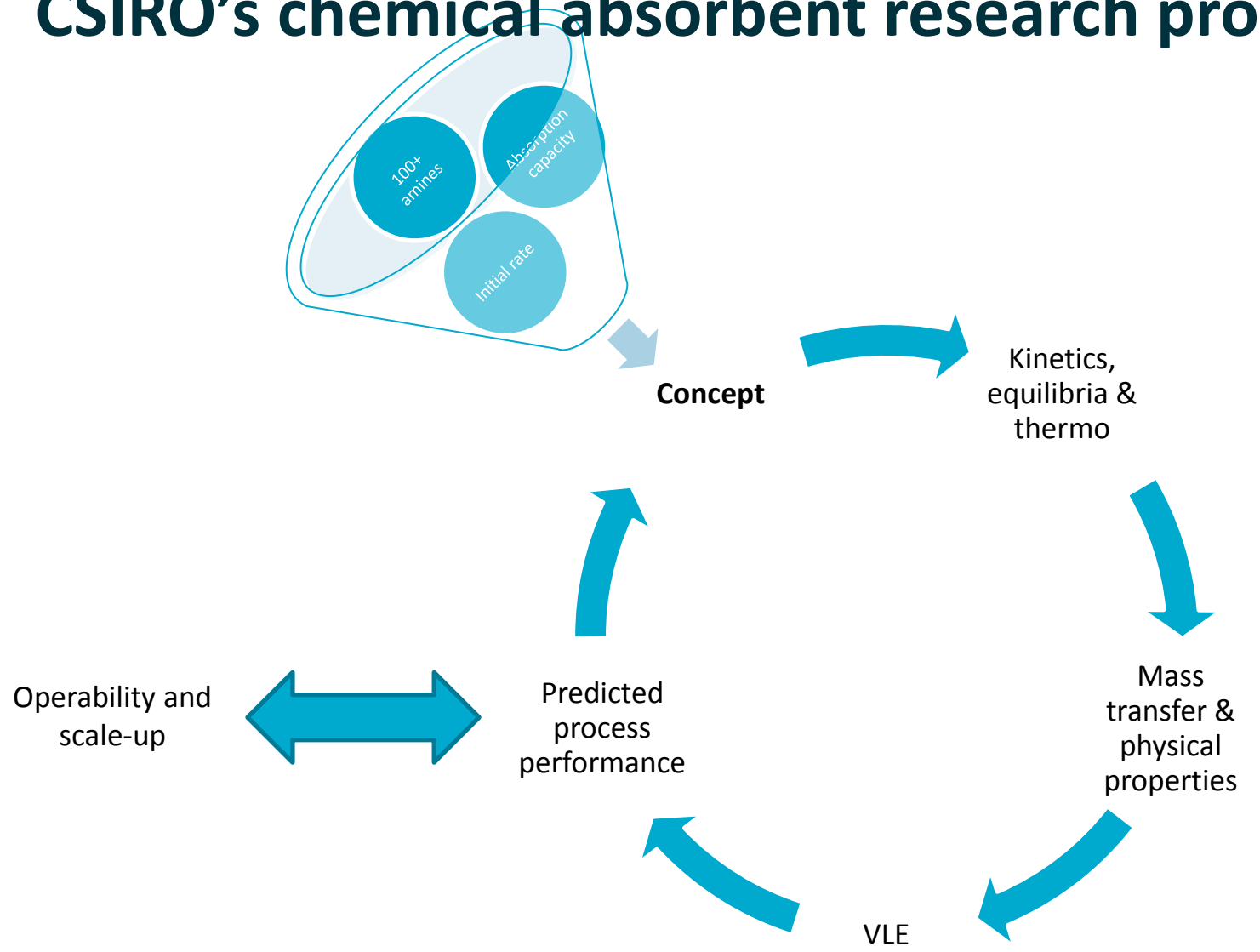
Development of reactive chemical absorbents at the CSIRO

HiPerCap Workshop, March 25 2015

Graeme Puxty
Research Team Leader

CSIRO's chemical absorbent research program



CSIRO's chemical absorbent research program

Near-term

- **Absorbent formulations based on readily available compounds** – typically aqueous amines and low cost additives
- Advanced aqueous ammonia

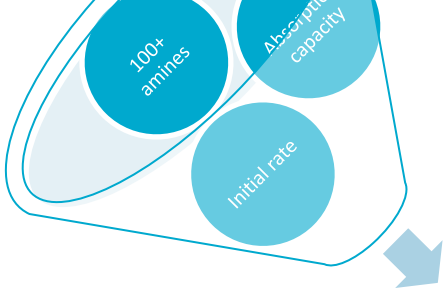
Mid-term

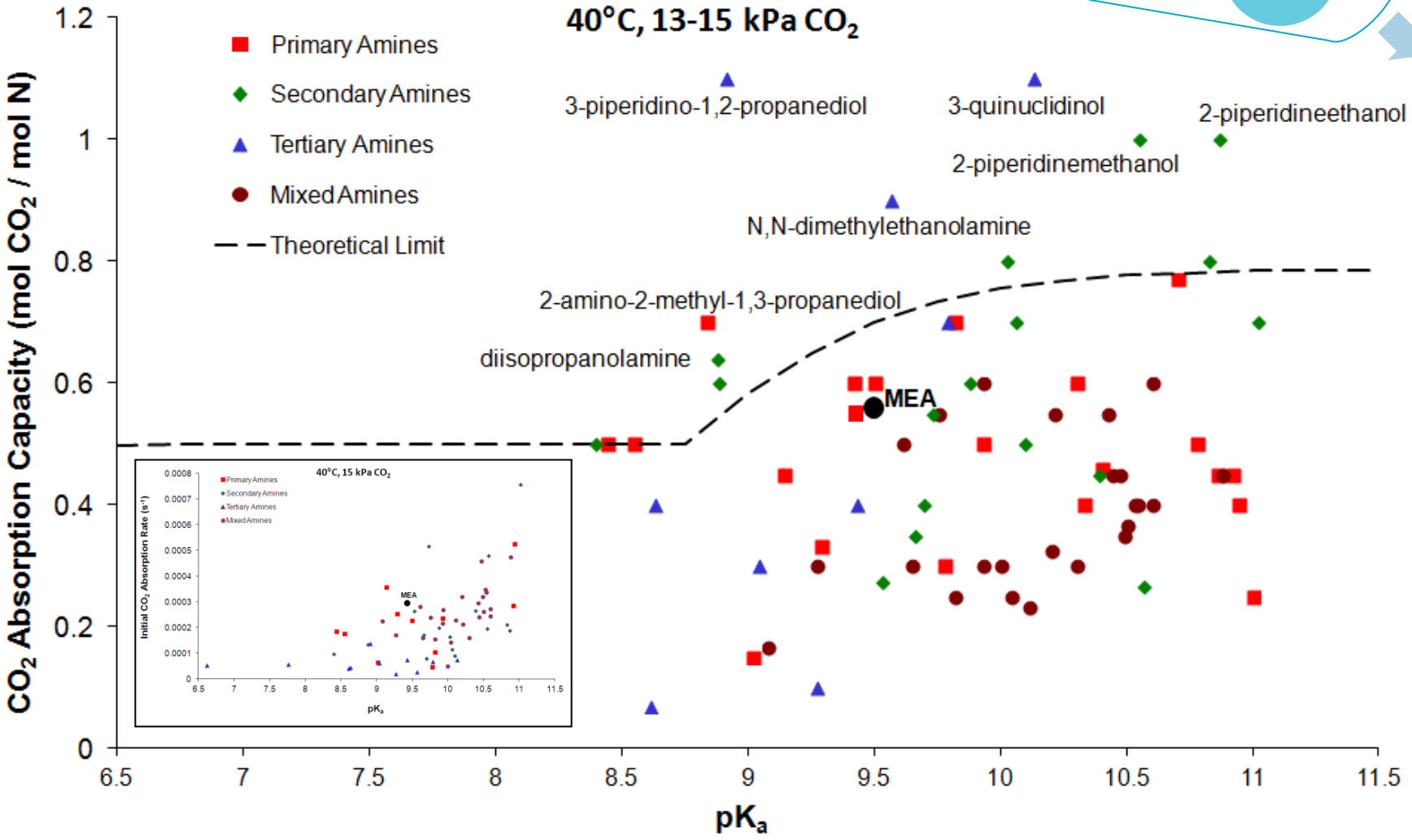
- **New compounds** designed specifically for CO_2 capture – new amine compounds

Long-term

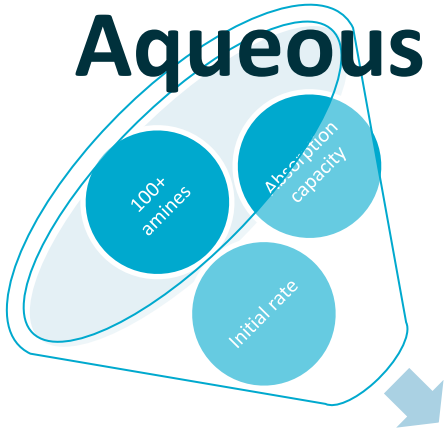
- **New absorbent systems and associated process concepts:**
  - Light-swing absorbents
  - Phase change absorbents
  - Enzymes

Aqueous amine screening study





Aqueous amine screening study

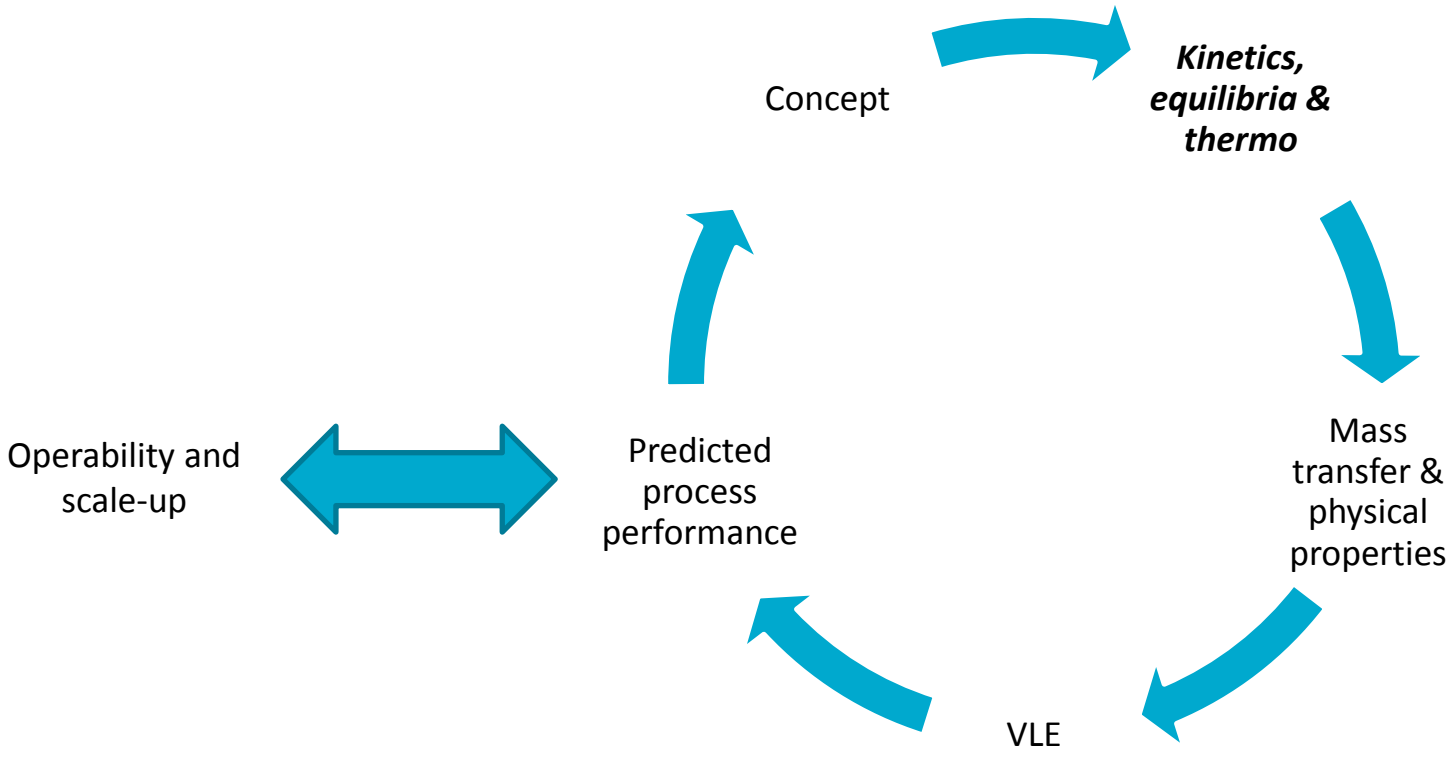


- **Over 100 amines screened** for CO_2 absorption capacity and initial absorption rate at a single set of conditions (40°C, 13-15 kPa CO_2)
- A combination of model predictions and experimental results allowed identification of **7 amines that performed better than expected**
- **Cyclic compounds** looked the most interesting
- Results have been **patented and published**:

M. I. Attalla, G. D. Puxty, A. W. Allport, M. Bown, Q. Yang and R. C. Rowland, Carbon dioxide capturing process, involves contacting carbon dioxide containing gas stream with aqueous alkanolamine solution, where alkanolamine solution is selected from group consisting of Tricine and salts. WO2009121135-A1 (2009).

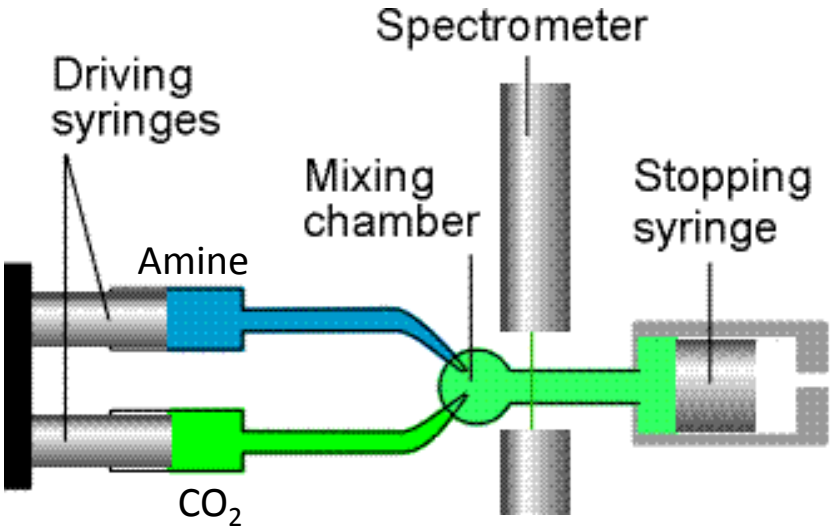
G. Puxty, R. Rowland, A. Allport, M. Attalla, Q. Yang, M. Bown, R. Burns and M. Maeder, Carbon dioxide post combustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. *Environmental Science & Technology*, 43 (2009) 6427-6433.

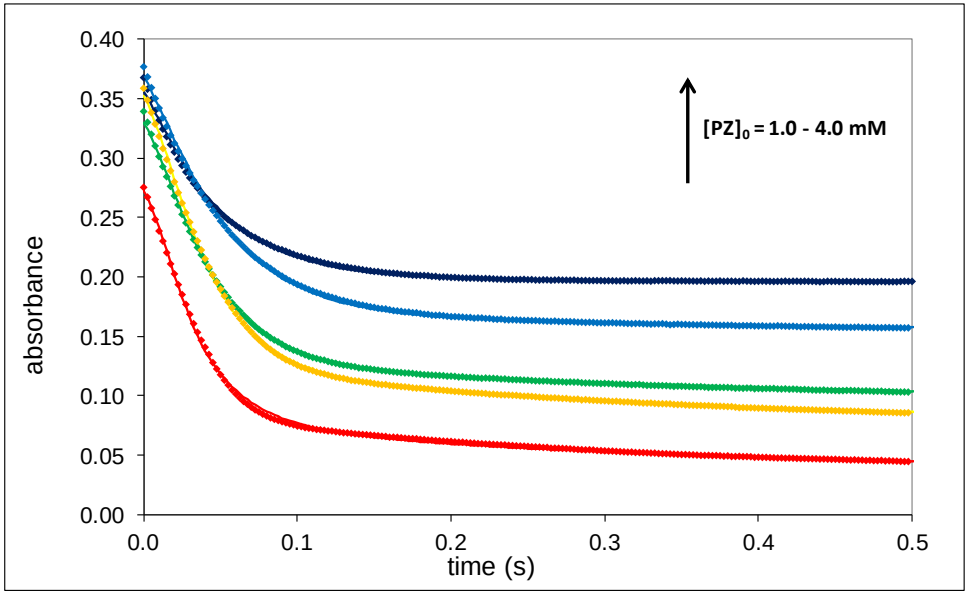
Understanding the chemistry



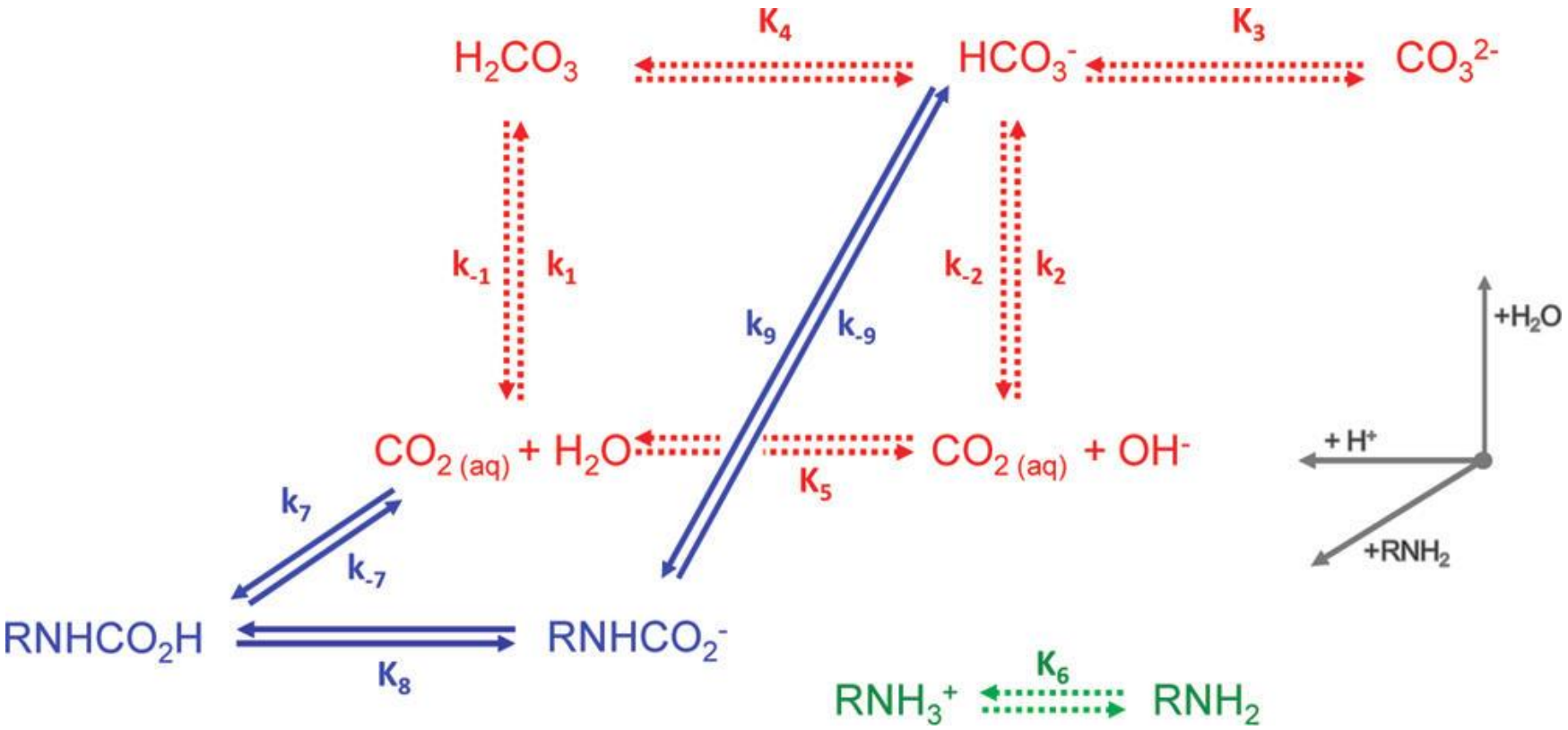
Kinetics, equilibria and thermodynamics

- Stopped-flow and UV-visible spectroscopy used to determine CO_2-amine reaction kinetics
- ^{1}H-NMR used to determine CO_2-amine reaction equilibria





What we learned – mechanistic understanding



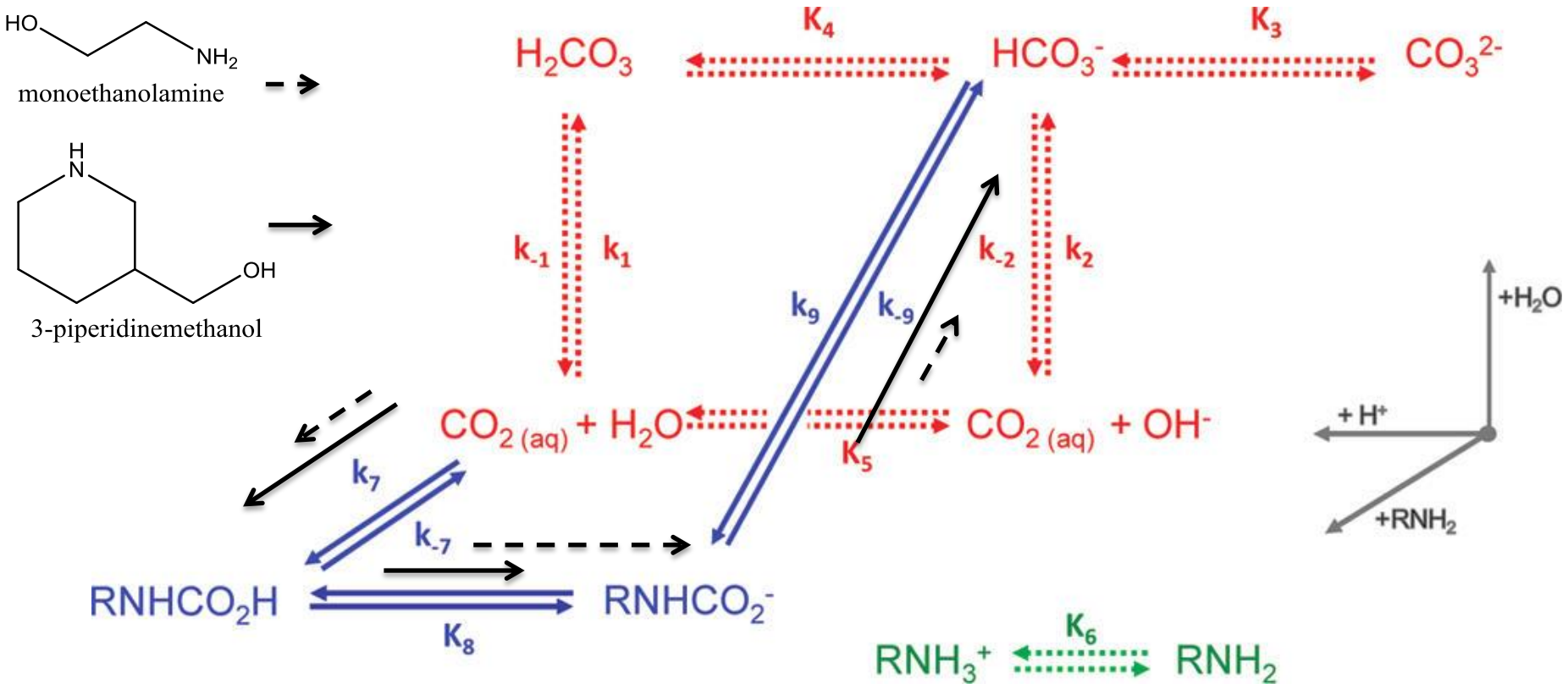
Fernandes, D., et al., *Protonation constants and thermodynamic properties of amines for post combustion capture of CO2. Journal of Chemical Thermodynamics, 2012.* ***51: p. 97-102.***

Conway, W., et al., *Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO2(aq) and HCO3- with Monoethanolamine (MEA) in Aqueous Solution. Journal of Physical Chemistry A, 2011.* ***115(50): p. 14340-14349.***

McCann, N., et al., *Kinetics and Mechanism of Carbamate Formation from CO2(aq), Carbonate Species, and Monoethanolamine in Aqueous Solution. Journal of Physical Chemistry A, 2009.* ***113(17): p. 5022-5029.***

McCann, N., et al., *Molecular Interactions between Amine and Carbonate Species in Aqueous Solution - Kinetics and Thermodynamics. Greenhouse Gas Control Technologies 9, 2009.* ***1(1): p. 995-1002.***

What we learned – what is it about cyclic compounds?



Conway, W., et al., *Toward the Understanding of Chemical Absorption Processes for Post-Combustion Capture of Carbon Dioxide: Electronic and Steric Considerations from the Kinetics of Reactions of CO2(aq) with Sterically hindered Amines. Environmental Science & Technology, 2013.* ***47(2): p. 1163-1169.***

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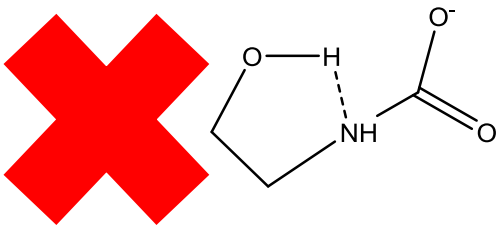
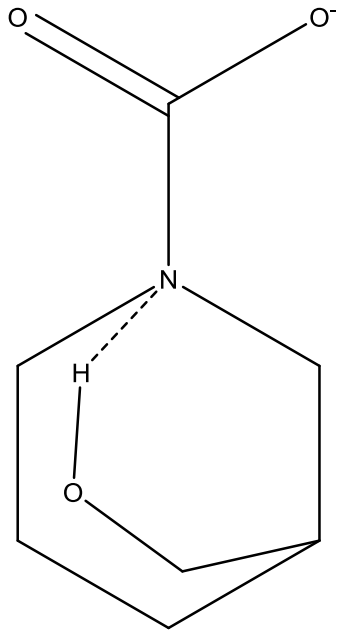
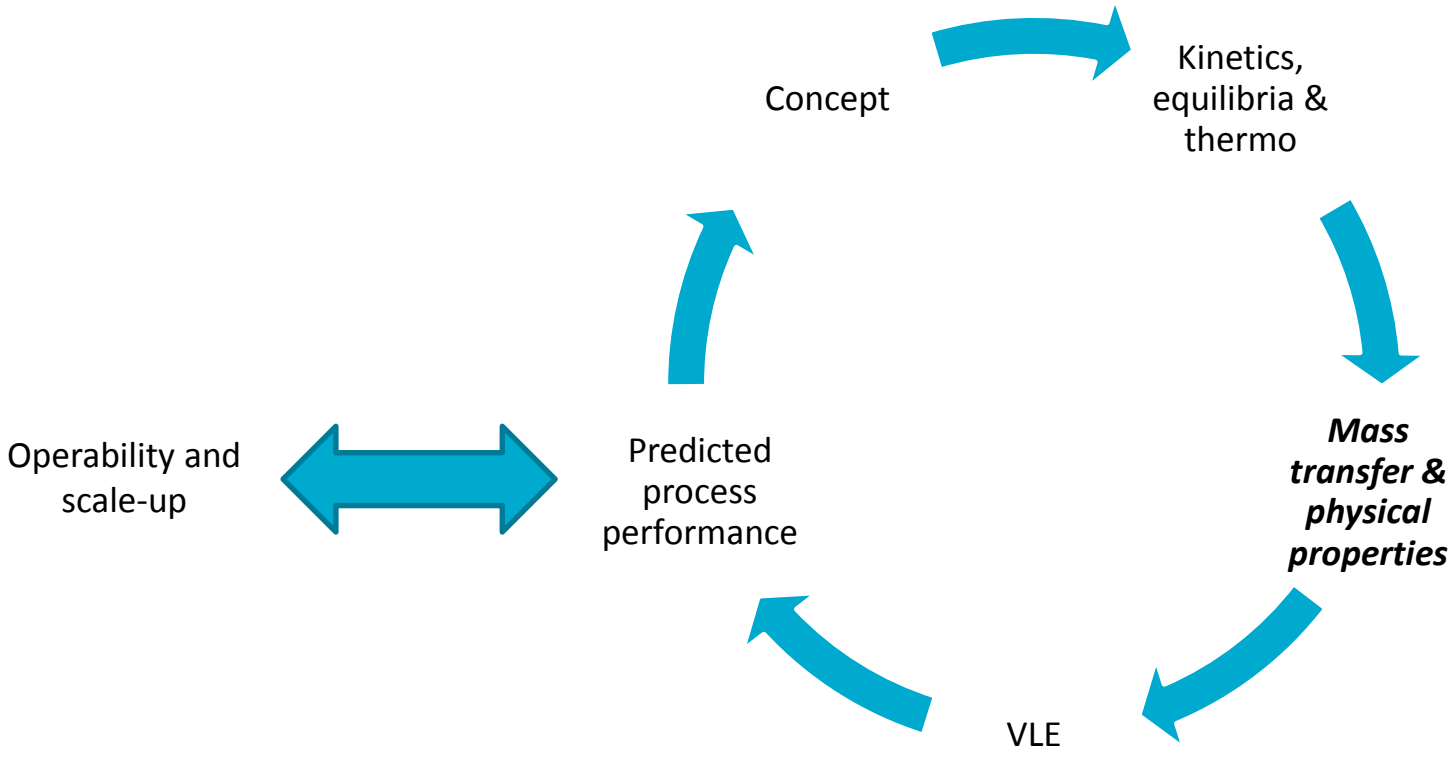


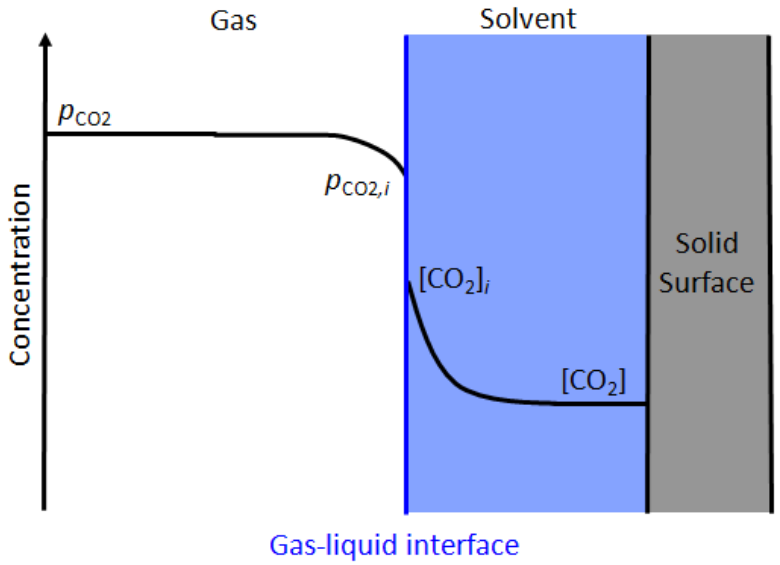


Understanding absorption rates

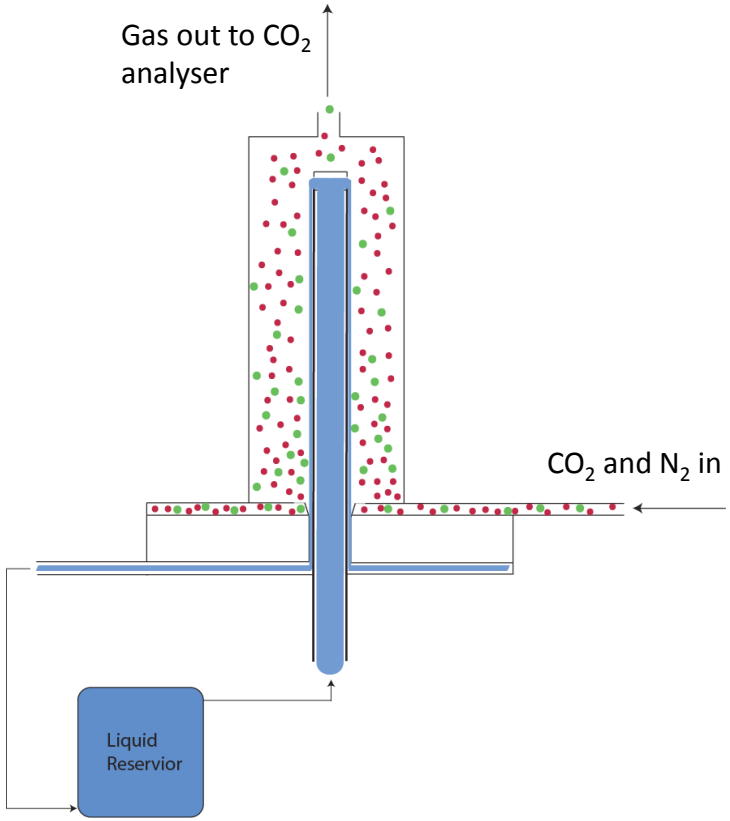


What influences mass transfer?

- Chemical reaction kinetics
  (and equilibria as a function of CO_2 loading)
- Viscosity and surface tension
  (impacts diffusivity and flow)

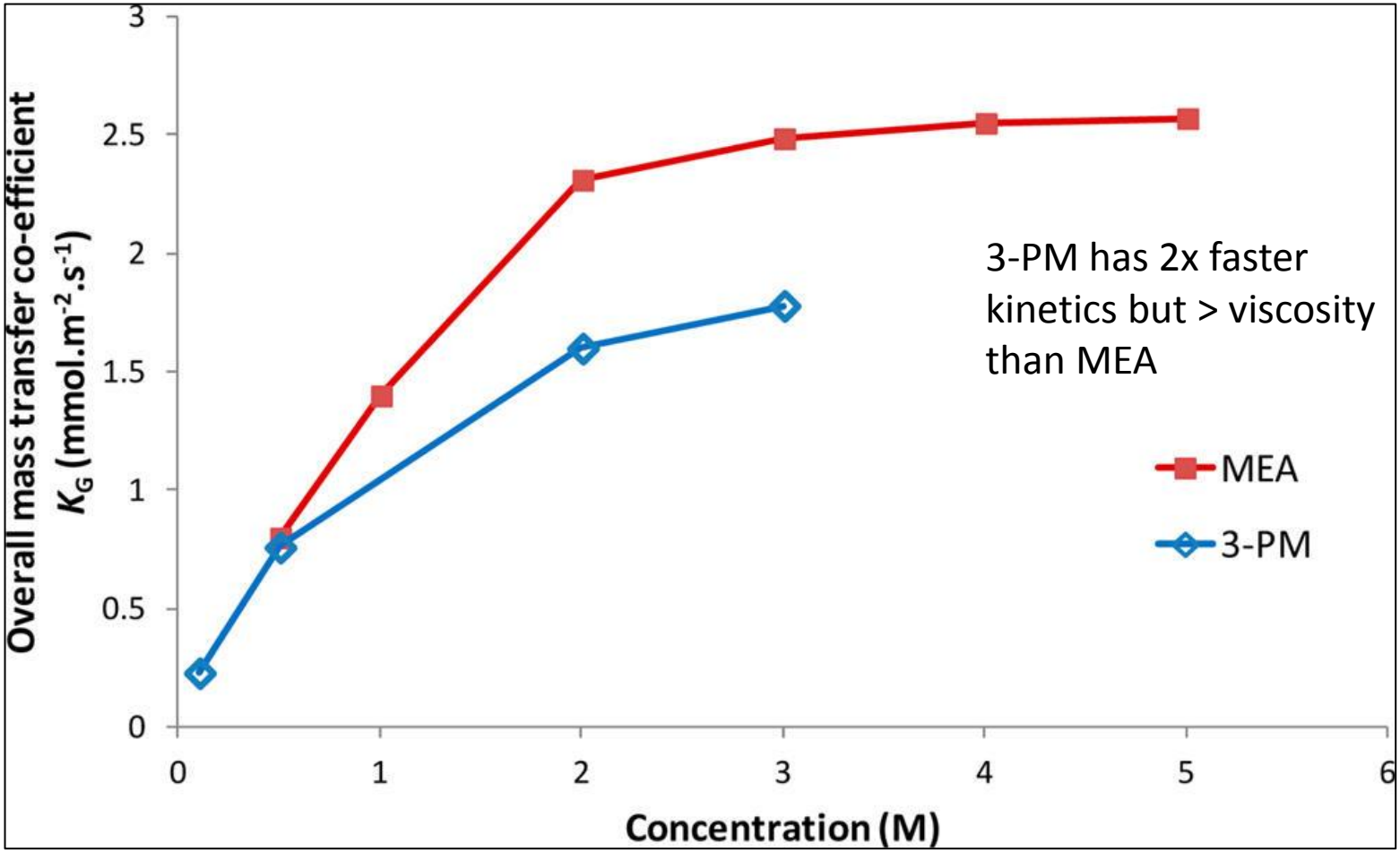


Wetted-wall reactor



The impact of viscosity

Faster kinetics ↑ ↓ Larger viscosity



Conway, W., et al., *CO2 Absorption into Aqueous Solutions Containing 3-Piperidinemethanol: CO2 Mass Transfer, Stopped-Flow Kinetics, H-1/C-13 NMR, and Vapor-Liquid Equilibrium Investigations. Industrial & Engineering Chemistry Research, 2014.* ***53(43): p. 16715-16724.***

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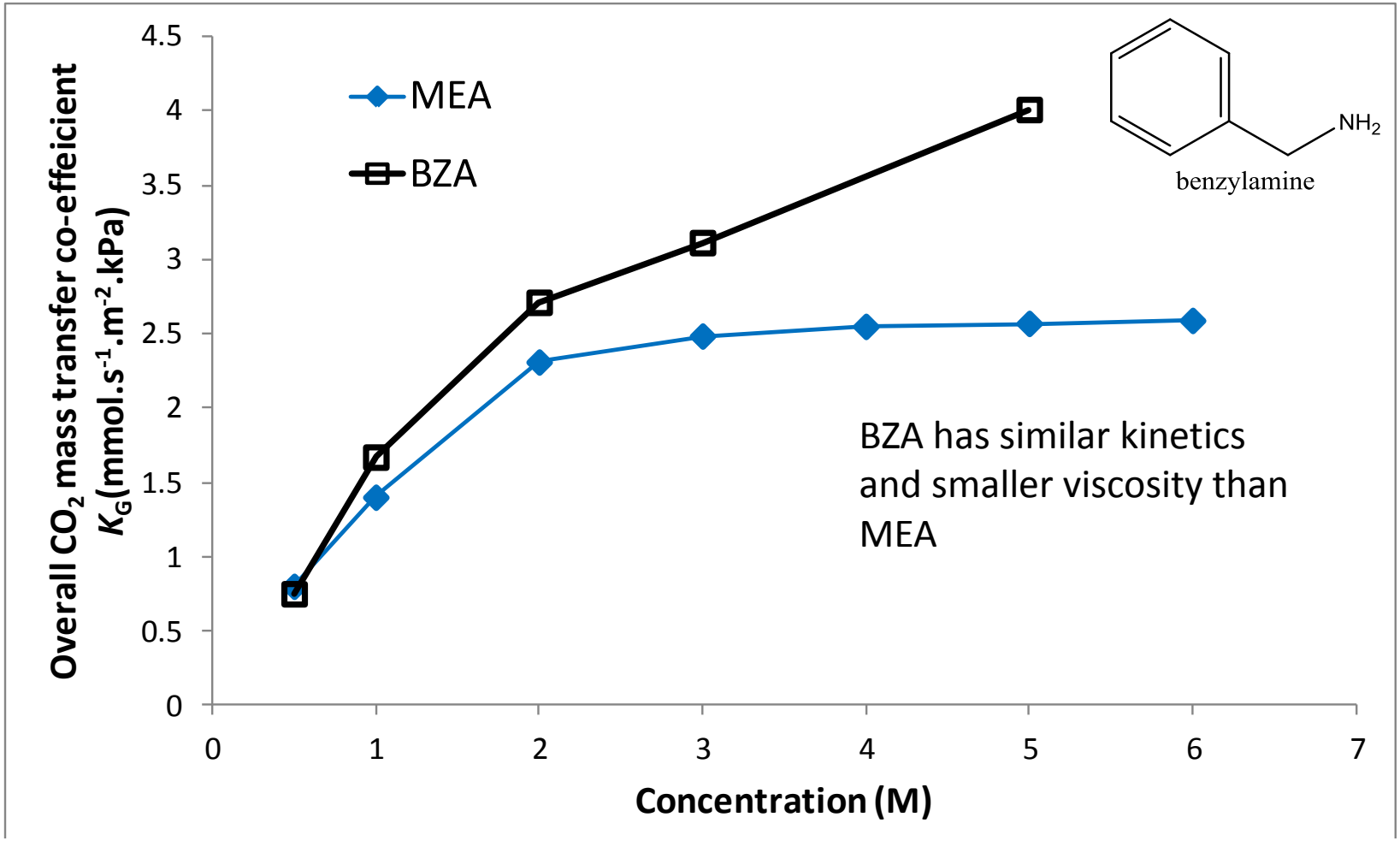
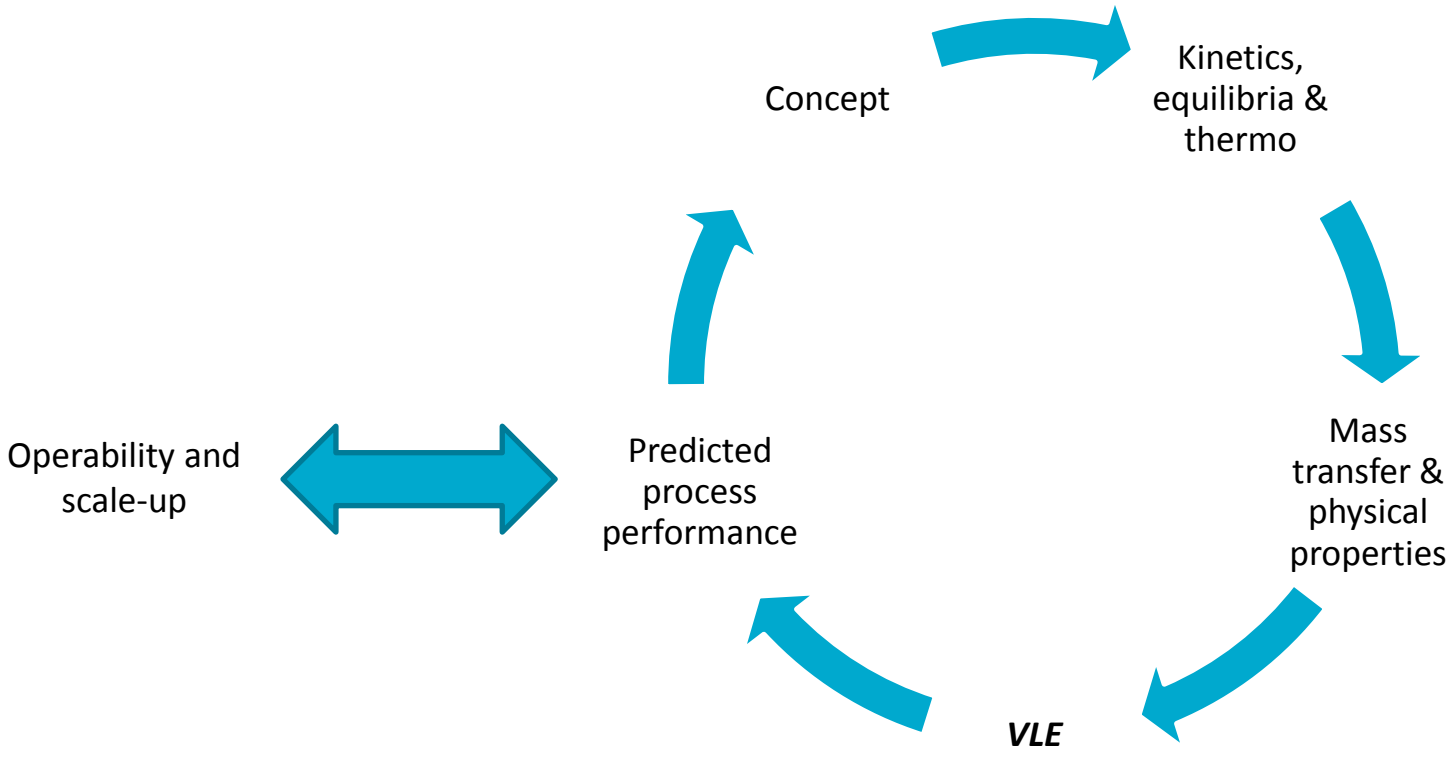


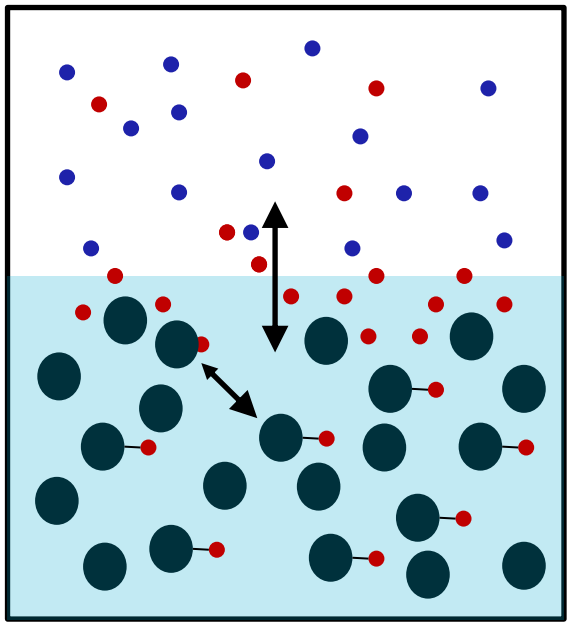
Conway, W., et al., *Rapid CO2 absorption into aqueous benzylamine (BZA) solutions and its formulations with monoethanolamine (MEA), and 2-amino-2-methyl-1-propanol (AMP) as components for post combustion capture processes. Chemical Engineering Jounral, 2015.* ***264: p. 954-961.***

Understanding vapour-liquid-equilibria



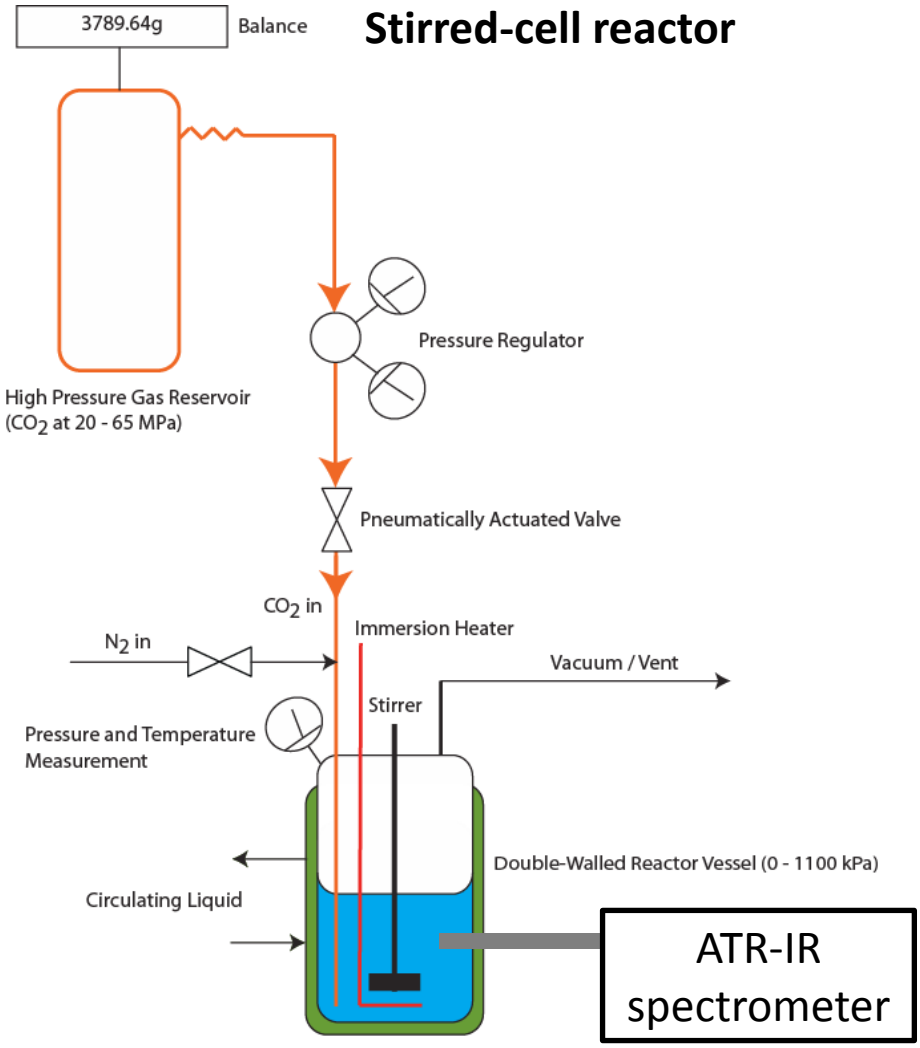
What influences VLE?

- Chemical equilibria
- Chemical thermodynamics



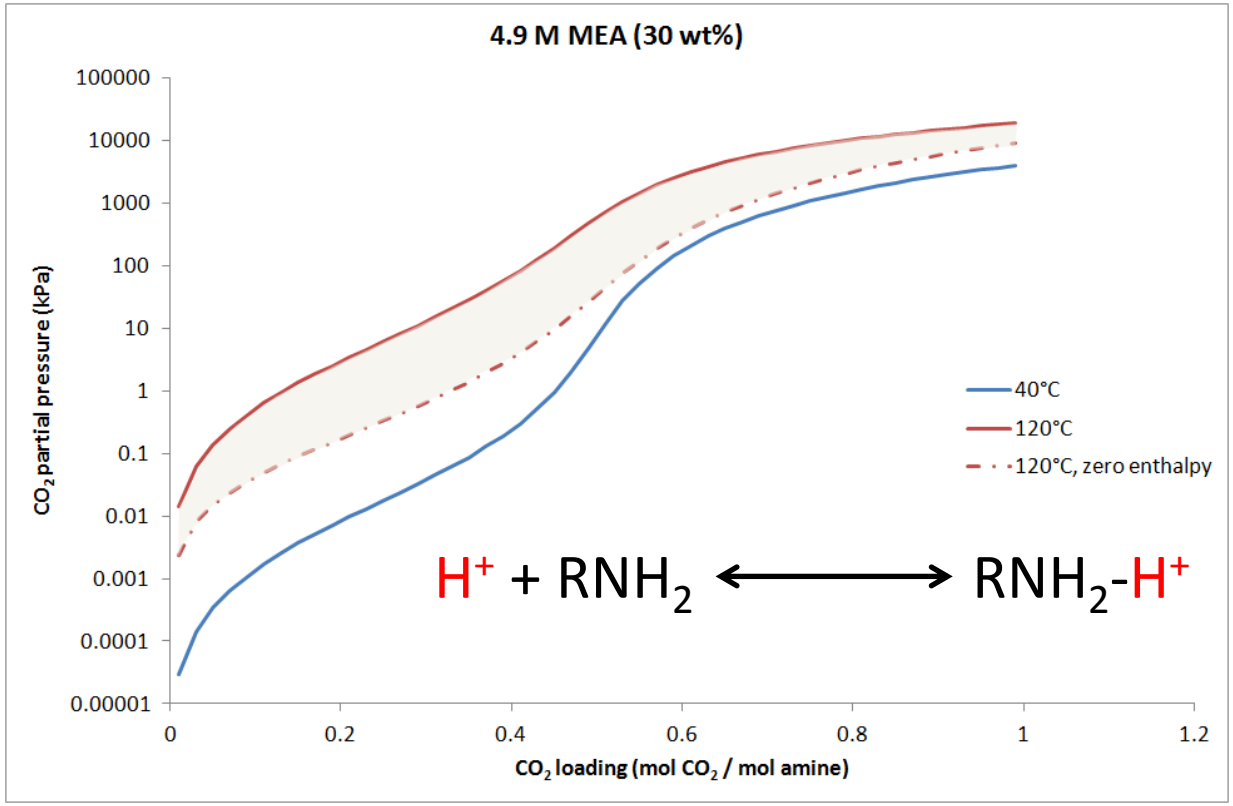
Gas

Liquid

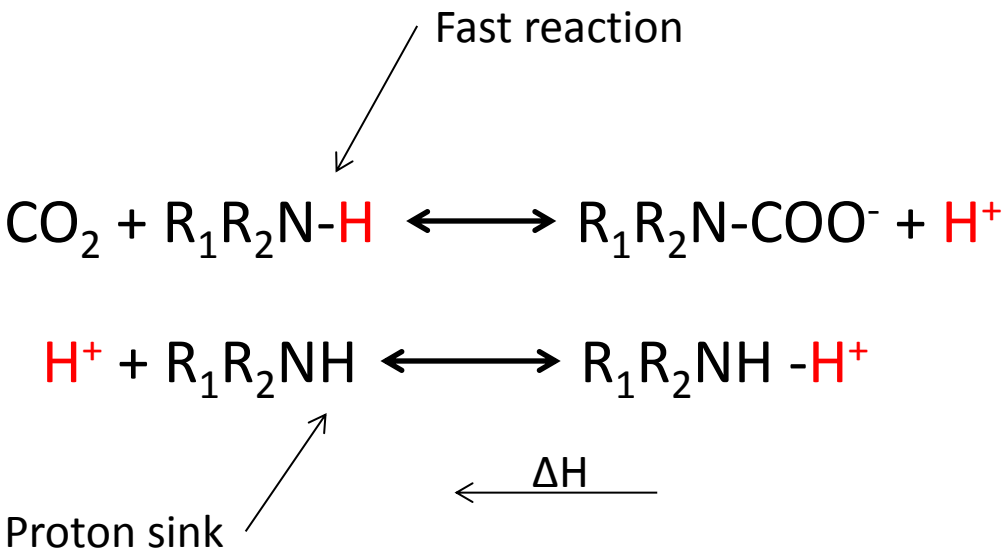


What sort of VLE behaviour do we want?

- Large absorption capacity at low temperature and low CO_2 partial pressure
- Large reduction in capacity with increasing temperature



Putting it together

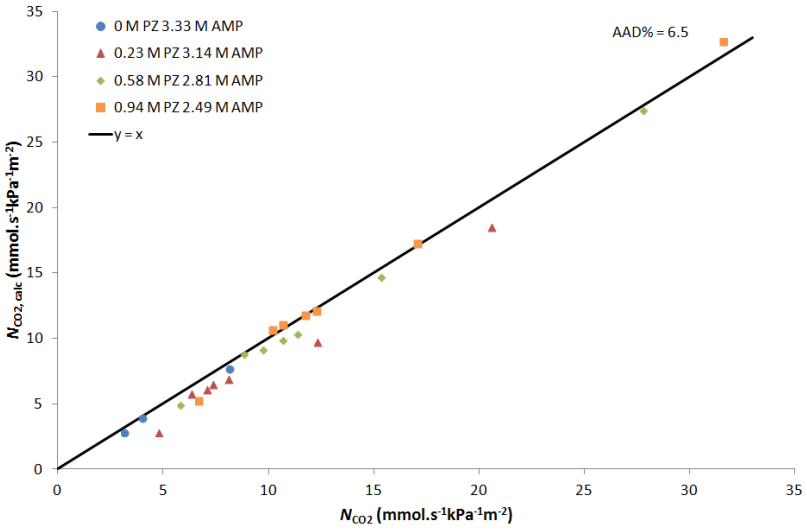


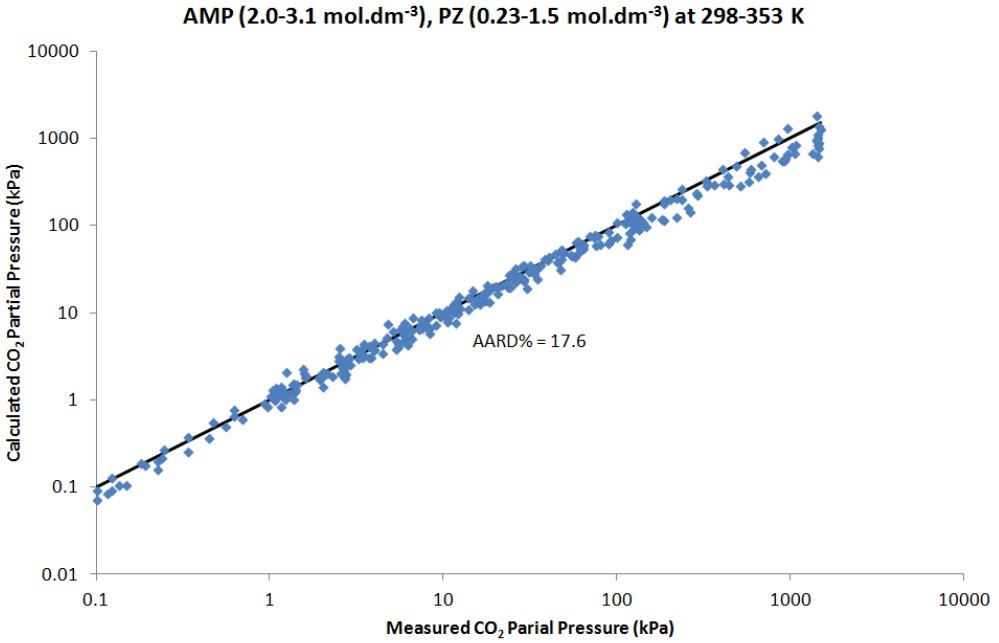
- Stable against degradation
- Non-corrosive
- Environmentally benign
- Low volatility and viscosity
- Negligible nitrosamine formation

- No single amine we investigated delivers on all these features
- Two options:
  - Amine formulations
  - New molecules

Intelligent formulation design

- Once we know the kinetics, equilibria and thermodynamics of an individual amine we can predict the behaviour of a mixture



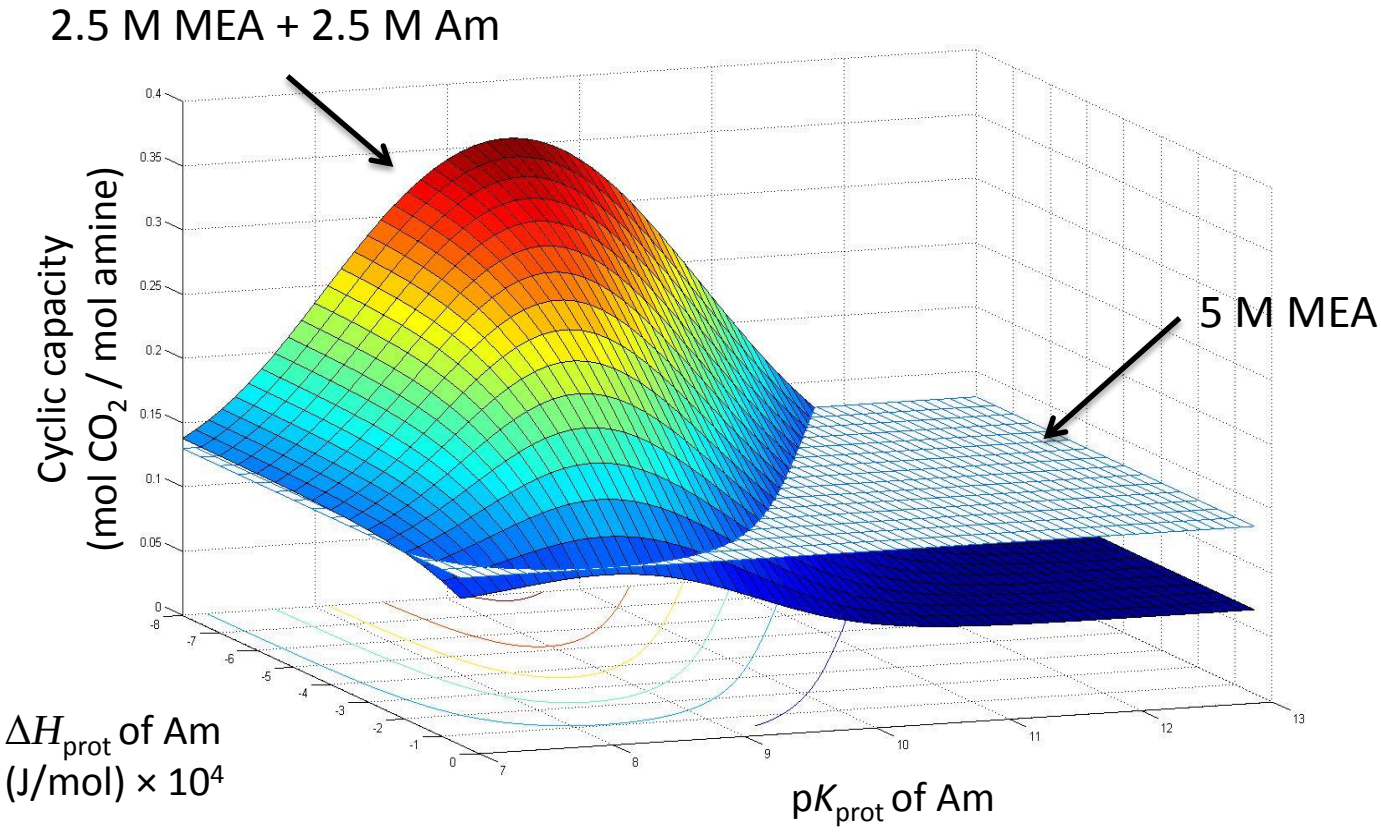


Puxty, G. and M. Maeder, *A simple chemical model to represent CO2-amine-H2O vapour-liquid-equilibria. International Journal of Greenhouse Gas Control, 2013.* ***17: p. 215-224.***

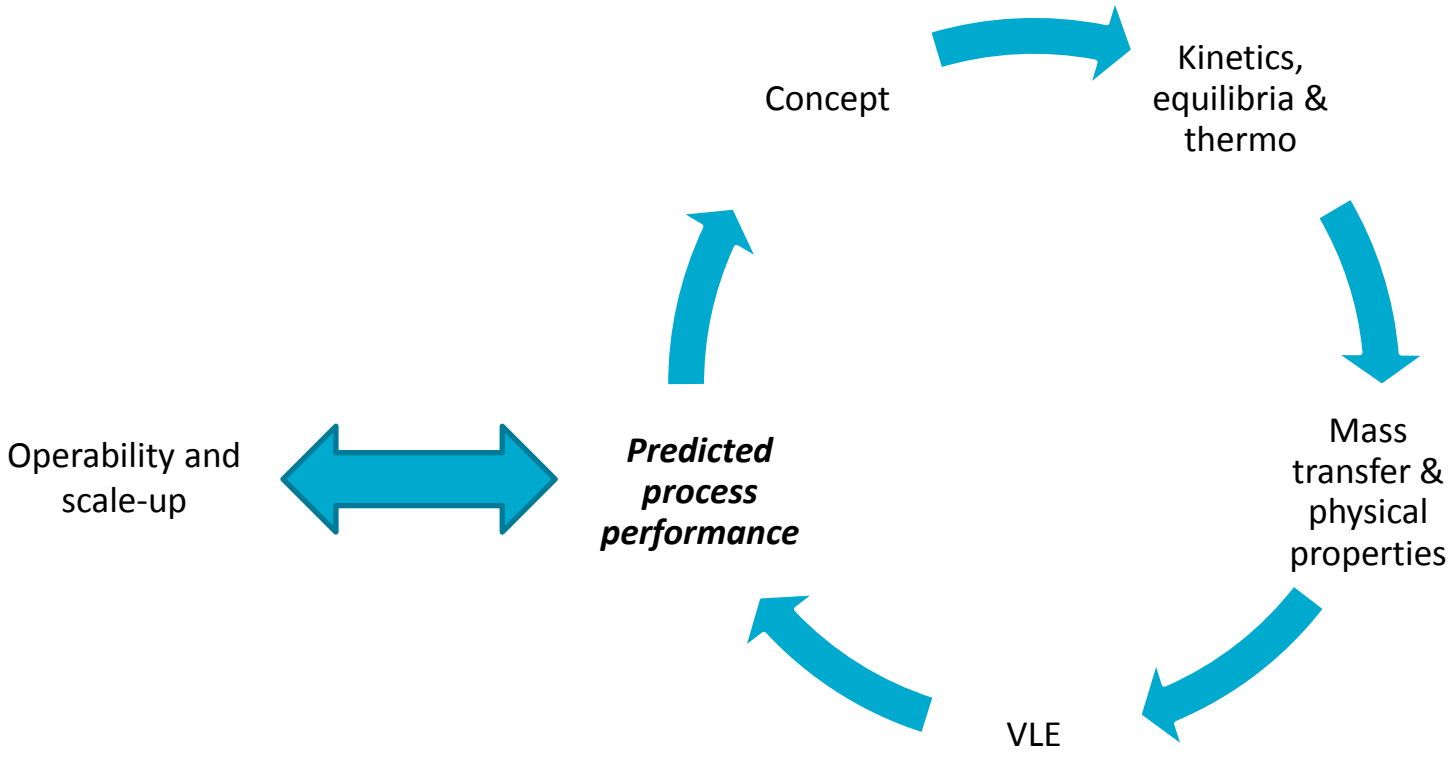
Puxty, G. and R. Rowland, *Modeling CO2 Mass Transfer in Amine Mixtures: PZ-AMP and PZ-MDEA. Environmental Science & Technology, 2011.* ***45(6): p. 2398-2405.***

Intelligent formulation design

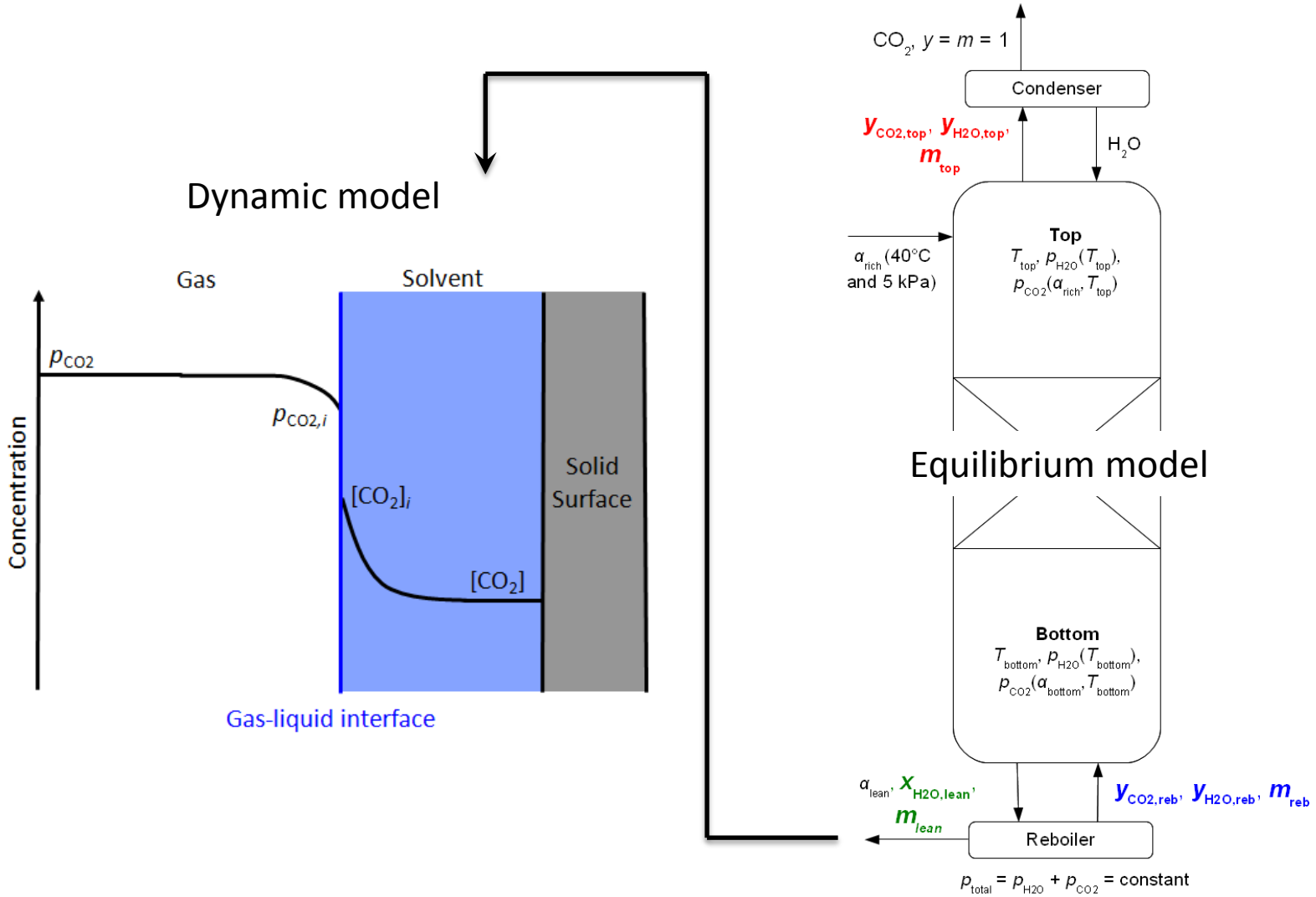
- We can vary the properties of constituent amines and investigate the impact on capture performance



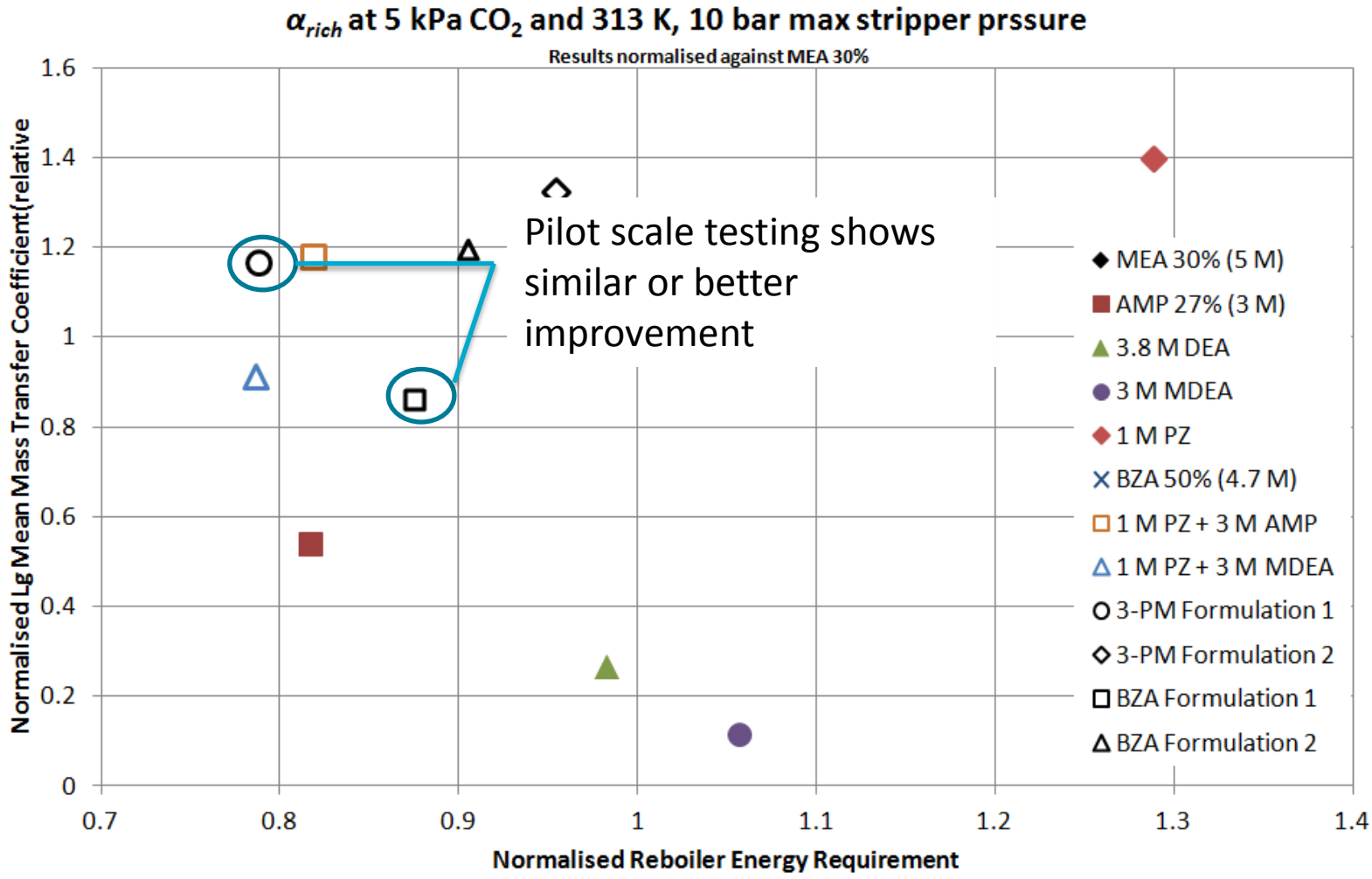
Predicting process performance



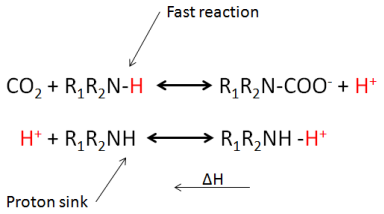
Equilibrium stripper + mass transfer prediction



Predicted process performance - formulations

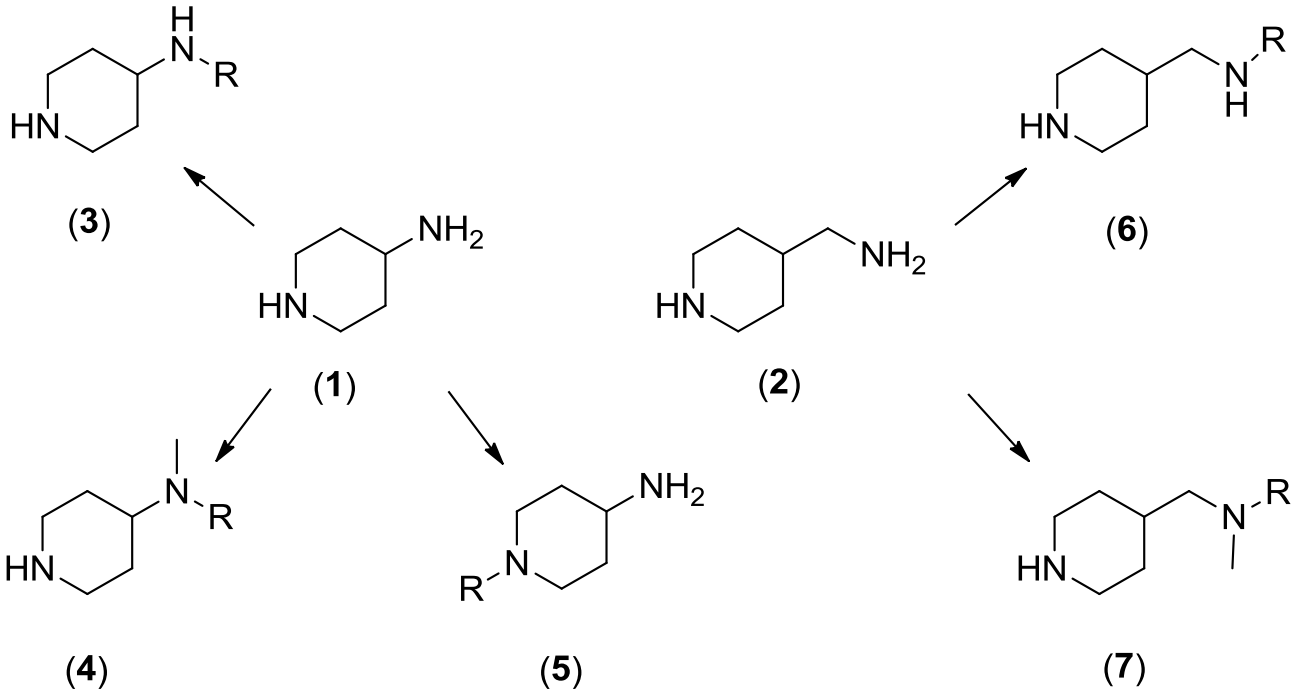


Intelligent molecular design



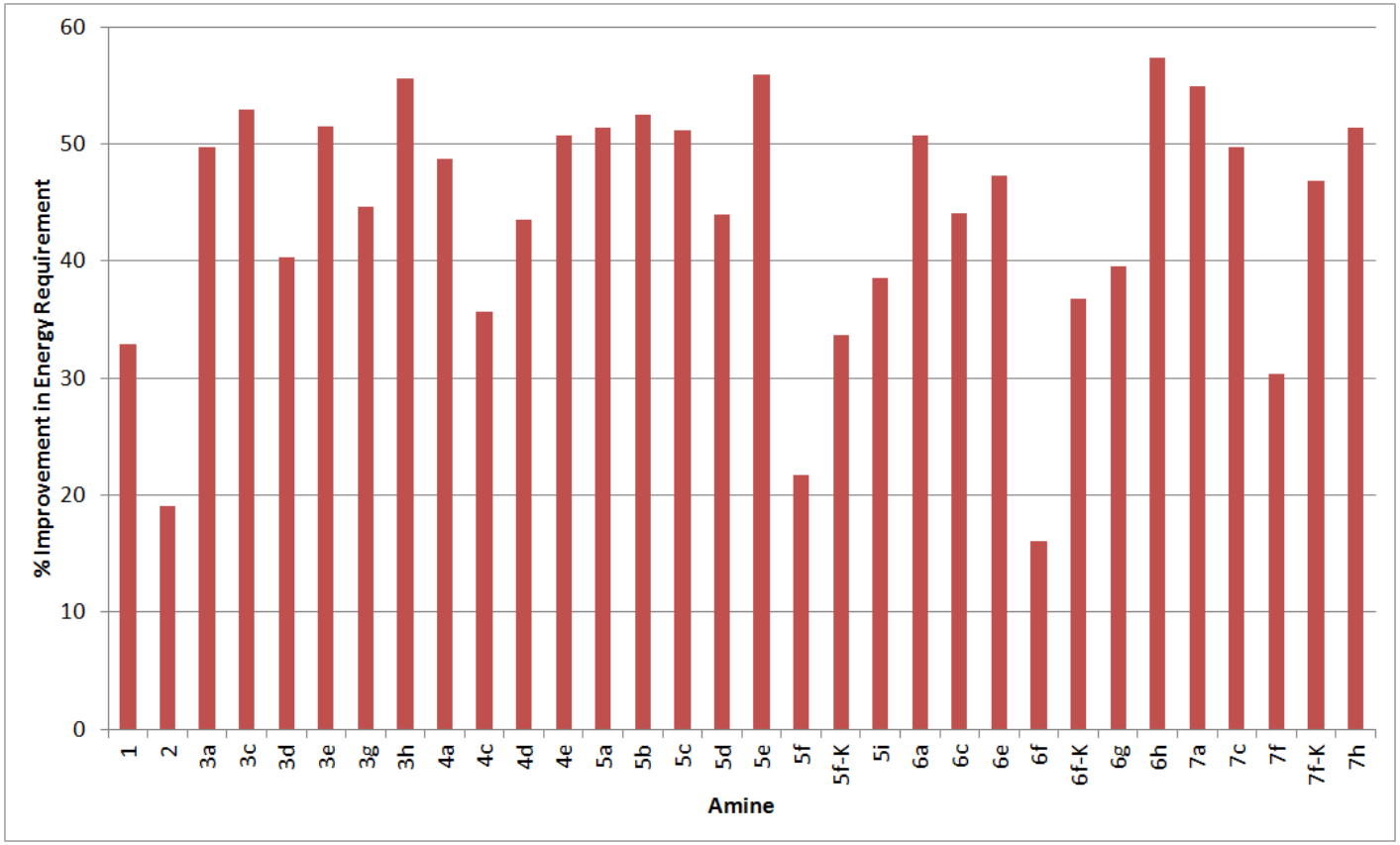
- Stable against degradation
- Non-corrosive
- Environmentally benign
- Low volatility and viscosity
- Negligible nitrosamine formation

- Design new molecules to have the properties we want



Predicted process performance – new amines

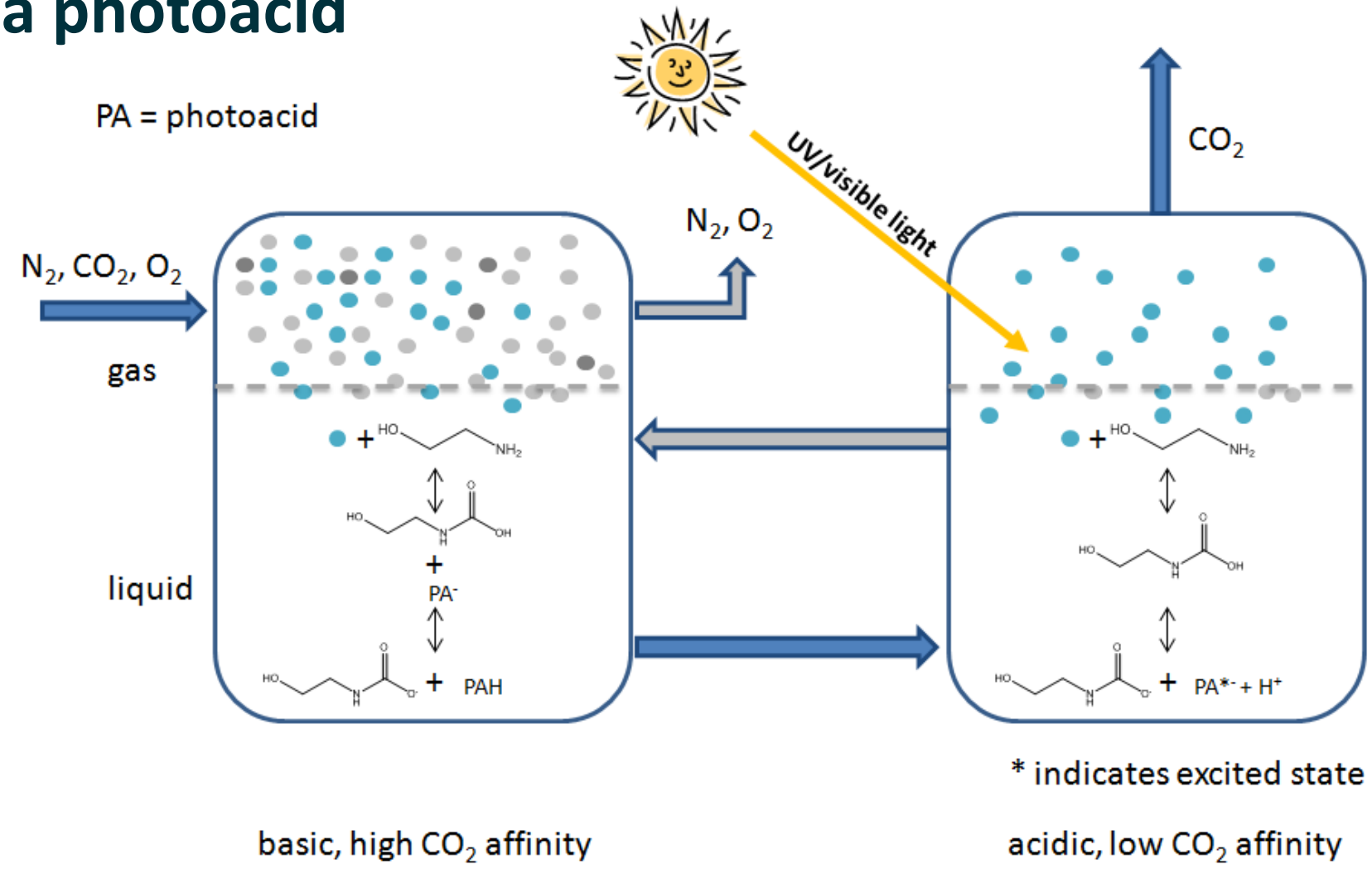
- Estimated improved energy performance (based on 2 M, measured cyclic capacity and molecular weight) relative to piperazine



Conclusions

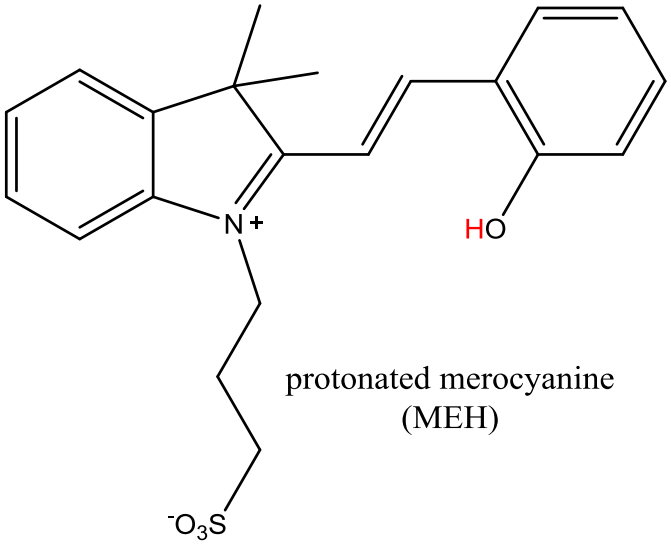
- Still substantial scope for improvement in both formulations and new amines molecules
- Pilot scale testing revealed good performance but operational challenges to be addressed:
  - viscosity, volatility, foaming, materials compatibility
- New molecules to be synthesises at large scale for more thorough testing

Something a bit different – photoswitching using a photoacid



Photoswitching

PAH

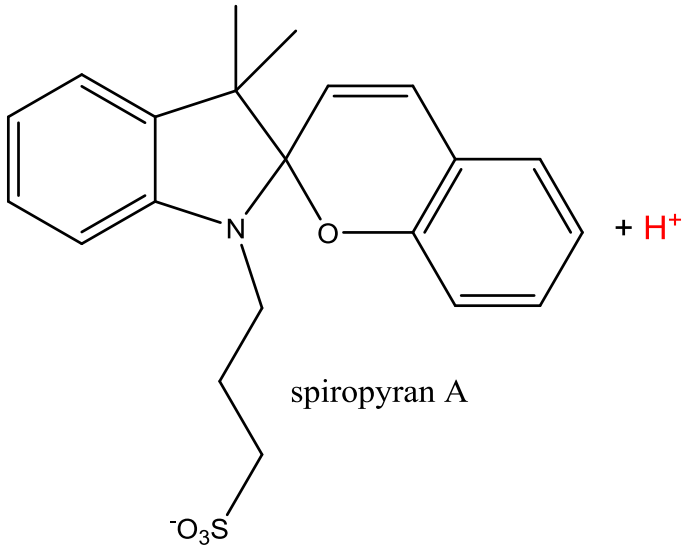


protonated merocyanine
(MEH)

light on

light off

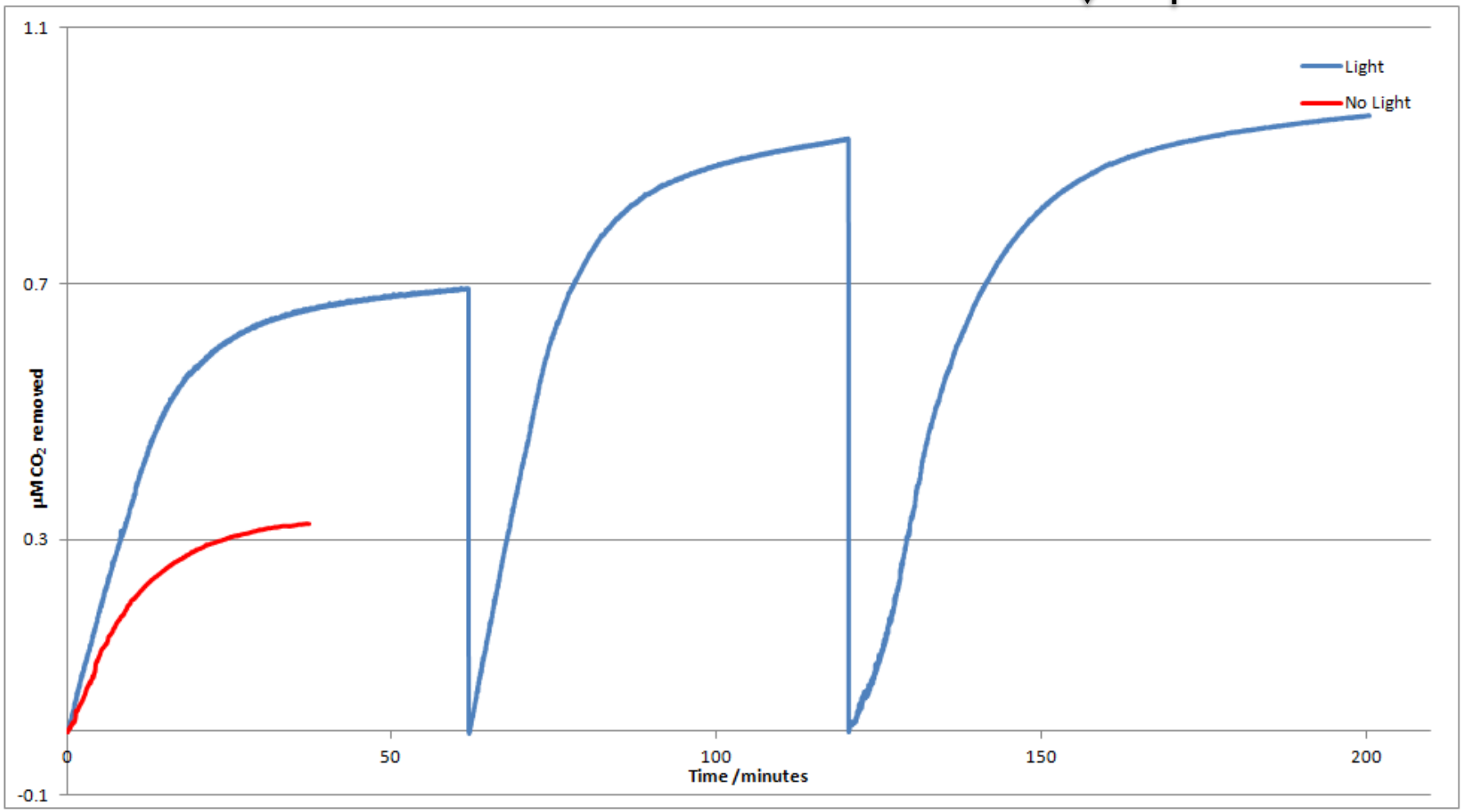
PA*-



spiropyran A

Photoswitching

Saturate with CO_2 ↓ ↑ Irradiate



The current team

Reactive chemical absorbents at CSIRO

Formulations/phase change	New compounds	Light-swing	Aqueous Ammonia
Will Conway Yaser Beyad Pauline Pearson	**Qi Yang** Will Conway	**Robert Bennett**	Hai Yu Kangkang Li Long Ji

The University of Newcastle

Marcel Maeder

Robert Burns

Duong Phan

Anh Nguyen

Sarah Clifford

Thank You

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