Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture

Jiafei Zhang, David W. Agar

Trondheim
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Motivation

Concepts

Solvent performance

Challenges and amelioration

Summary
Outline

- Motivation
- Concepts
- Solvent performance
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Global warming
Shortcomings of conventional solvents
Advantages of novel biphasic solvents

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Motivation

Technical shortcomings of conventional solvents:
- e.g. monoethanolamine (MEA)
- High energy consumption
- High quality of heat: 130-150 °C
- Significant amine loss by degradation

Major superiorities of novel biphasic solvents:
- Regeneration temperature 80°C
- Use of waste heat for desorption
- Good chemical stability
- High net CO₂ loading capacity

Challenges?

New generation absorbents

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Prof. Dr. David W. Agar
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Liquid-liquid phase separation (LLPS)

(a) Homogeneous absorption
(b) Heterogeneous desorption

Lipophilic amine
Phase change
TBS absorbent
Other CO₂ capture process with LLPS
Novel amines

**Alkanolamine vs lipophilic amine**

- **Alkanolamine**
  - (H)R\_N\_R(H)
  - R(OH)

- **Lipophilic amine**
  - (H)R\_N\_R(H)

**Examples of lipophilic amine**

- Hexylamine (I) HA
- Dipropylamine (II) DPA
- N,N-Dimethylcyclohexylamine (III) DMCA
Phase change

- Thermomorphic phase transition
- Low temperature $\rightarrow$ single phase
- High temperature $\rightarrow$ dual phases

Lower critical solution temperature (LCST)

Concepts II

Phase change

- Thermomorphic phase transition
- Low temperature $\rightarrow$ single phase
- High temperature $\rightarrow$ dual phases

Lower critical solution temperature (LCST)
Novel absorbent: thermomorphic biphasic solvent (TBS)

- Absorption: single phase
- Regeneration: two phases

- Lean solvent → cooling to 30-40°C: homogeneous
- Rich solvent → heating to 70-80°C: biphasic
Other CO₂ capture process with LLPS

- ‘Self-Concentration’ CO₂ Capture Process
  - Univ. of Kentucky

- DMX™ process with demixing solvents
  - IFP Energies Nouvelles

Outline

- Motivation
- Concepts
- **Solvent performance**
- Challenges and amelioration
- Summary

- Amine selection
- Absorption
- Desorption
- Chemical stability
Screening tests – searching new amines

- > 50 lipophilic amines (alkylamines)
- < 10 comparable to MEA or MDEA

Criteria

- **High loading capacity**: > 0.7 mol/mol (20% CO₂)
- **Fast absorption rate**: comparable to MEA
- **Good regenerability**: better than MDEA
- **Low degradability**: comparable to AMP & MDEA
- **Moderate heat of reaction**: lower than MEA

A: partially soluble in water, **rapid absorption rate**
B: less miscible with water, **high regenerability**

Recommended absorbent: Solvent blend A+B

A: as **absorption activator** → e.g. DPA, A1
B: as **regeneration promoter** → e.g. DMCA, EPD

**Blending A+B exploits the strengths of both components**
Absorption

Reactivity
- Rapid reaction rate
- Comparable to MEA (when $\alpha < 0.5$)

Loading capacity (net)
- Alkanolamine 40-120 °C with steam stripping
- TBS absorbent 30-80 °C without steam stripping
- CO$_2$ absorbed in TBS: 3.4 mol/kg
- Higher than MEA and AMP
Solvent performance III

Desorption

- Liquid-liquid phase separation
- Low regeneration temperature
  - ca. 80°C
  - Low value heat
- High regenerability
  - > 80% at 80°C for most TBS
  - > 98% at 80°C for optimised TBS
- Estimated energy consumption
  - MEA: 4.0 GJ/t_{CO₂}
  - TBS: 2.5 GJ/t_{CO₂}

Ref.: Geuzebroek, et al., TCCS-5, 2009
Cyclic loading capacity

- Higher CO₂ loading
- Lower residual loading
- Better than benchmarks

Chemical stability

- Low temperature (80°C) for desorption → less thermal degradation
- Low oxidability → less oxidative degradation
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**Motivation**

**Concepts**

**Solvent performance**

**Challenges and amelioration**

- Vaporisation loss
- Phase transition
- Regeneration techniques
- Process development

**Summary**
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Challenges and amelioration I

- Amine vaporisation loss
  - High volatility
  - Significant volatile loss

Countermeasures

- T for feed (top) at 30 °C
  - Reduced vaporisation

- Hydrophobic solvent scrubbing
  - e.g. Diphyl
  - Recovery >80%

- Water wash when using A1 as primary solvent
  - Reduced amine loss
  - Comparable to MEA or AMP

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<th>Amine</th>
<th>Temp.</th>
<th>Loss</th>
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<tr>
<td></td>
<td>°C</td>
<td>%/day</td>
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<tr>
<td>A1</td>
<td>30</td>
<td>&lt;0.5</td>
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<tr>
<td></td>
<td>40</td>
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<tr>
<td>DMCA</td>
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<tr>
<td></td>
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<tr>
<td></td>
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<td></td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>MEA</td>
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<tr>
<td>AMP</td>
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</table>
**Phase transition**

- Lower critical solution temperature (LCST): 
  most lipophilic amines $< 20^\circ$C
- Problem: 
  biphasic solvent in absorber

**Countermeasures**

- **Concentrating**
  - Negative on vaporisation loss
  - Limited at 4M
- **Using more A1**
  - Negative on regeneration
  - LCST $\approx 20^\circ$C
- **Partial deep regeneration**
  - Residual loading 0.1
  - Increasing LCST to 30°C
- **Adding solubiliser**
  - $< 10$wt%
  - Increasing LCST to 40°C
Regeneration techniques

Challenges

- Low temperature 80°C
- Without steam
- How to intensify the regeneration?

Regeneration intensification

- + Regeneration promoter
- Agitation
- Nucleation
- Nucleation + Agitation
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Challenges and amelioration III

Regeneration techniques

- Agitation
- Nucleation

Stirring

Porous particles for CO₂ bubble formation

Solution: A₁+B₁, 2+1M at 75 °C

Desorber CO₂ (mol/L)

Time (min)

1/40 wt.
1/60 wt.
1/80 wt.
N₂ stripping

CO₂ release rate [g/L/hr]

Method

DMCA+A₁
DMCA+DPA
None 100 rpm 250 rpm 500 rpm 750 rpm 1000 rpm Stripping

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Process development

**Challenges and amelioration IV**

**Flow sheeting diagram**

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**Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture**  
*Jiafei Zhang*
Bench-scale experimentation in packed absorption columns

At TU Dortmund

At Shell G.S.

Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture
**Summary**

**Novel absorbent:** lipophilic amine → TBS

- Rapid absorption rate (due to activator A)
- High regenerability (due to regeneration promoter B)
- Excellent net CO₂ loading capacity
- Low energy requirement
- High chemical stability

**Novel concept:** phase transition

- LLPS ⇒ enhanced regeneration
- Regeneration at 80°C ⇒ use of waste heat ⇒ reduces CO₂ capture process costs
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Thank you for your attention

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