Performance analysis of double-effect absorption heat pump cycles using NH$_3$/ILs pairs

Meng WANG*, Carlos A. INFANTE FERREIRA

Process and Energy Department,
Delft University of Technology
Content

- Introduction
- Methods
- Results and discussion
- Conclusions
Content

● Introduction
● Methods
● Results and discussion
● Conclusions
Background

World Total Final Energy Consumption (IEA)

- Industry Heating: 24%
- Buildings Heating: 21%
- Other Heat: 18%
- Transport: 10%
- Electricity: 3%
- Non-Energy Use: 24%

Absorption heat pump (AHP)

- High temp. driving heat
- Low temp. heat from surroundings
- Mid temp. heat application

- Highly efficient space heating & cooling
- Utilization of low-grade energy: waste heat, concentrated solar heat
Motivation

Working pairs

- Crystallization (H₂O/Libr)
- Additional process and equipment (NH₃/H₂O)

Ionic liquid (IL)

Strengths:
- High boiling point
- High chemical and thermal stability
- Good affinity with refrigerants
- Adjustable design of anion and cation
Most researches were based on single-effect absorption systems.

In this work, we intend to explore the NH$_3$/IL in double-effect AHP.
Content

- Introduction
- Methods
- Results and discussion
- Conclusions
Double-effect AHP cycle

- Double-effect absorption cycle in a parallel configuration

Assumptions:
- In a steady state.
- Equilibrium at outlets of GENs.
- 3 K subcooling at solution outlet of ABS
- Saturated state at outlets of CON or EVA is.
- 10 K of pinch in SHXs, 5 K in iHX, 75% effectiveness in HX
- Heat losses, pressure losses and pumping work are neglected.

\[
COP_{\text{cooling}} = \frac{\dot{Q}_e}{\dot{Q}_h} \quad COP_{\text{hp}} = \frac{\dot{Q}_d + \dot{Q}_c}{\dot{Q}_h} \\
DR = \frac{n_{\dot{m}_1}}{n_{\dot{m}_4}} \quad CR = \frac{n_{\dot{m}_5}}{n_{\dot{m}_4}} = \frac{1 - w_{13}}{w_5 - w_{13}}
\]
Content

● Introduction
● Methods
● Results and discussion
● Conclusions
Operation limits analysis

\[ w_9 < w_8(w_5) \]
\[ w_{11b} < w_{7c}(w_5) \]

VLE
Range of \( T_{15} \)
For a cooling operation \( (T_{hg}/T_a/T_c/T_e = 175/30/40/10 \, ^\circ C) \)

**\( T_{15} \) ranges**

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>( T_{15_min} ) (°C)</th>
<th>( T_{15_max} ) (°C)</th>
<th>Range of ( T_{15} ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Bmim}][\text{BF4}])</td>
<td>70.</td>
<td>121.</td>
<td>50.</td>
</tr>
<tr>
<td>([\text{Bmim}][\text{PF6}])</td>
<td>72.</td>
<td>111.</td>
<td>39.</td>
</tr>
<tr>
<td>([\text{Emim}][\text{BF4}])</td>
<td>70.</td>
<td>118.</td>
<td>48.</td>
</tr>
<tr>
<td>([\text{Emim}][\text{EtSO4}])</td>
<td>72.</td>
<td>84.</td>
<td>13.</td>
</tr>
<tr>
<td>([\text{Emim}][\text{SCN}])</td>
<td>73.</td>
<td>120.</td>
<td>47.</td>
</tr>
<tr>
<td>([\text{Emim}][\text{Tf2N}])</td>
<td>73.</td>
<td>112.</td>
<td>40.</td>
</tr>
<tr>
<td>([\text{Hmim}][\text{BF4}])</td>
<td>88.</td>
<td>92.</td>
<td>4.</td>
</tr>
<tr>
<td>([\text{Mmim}][\text{DMP}])</td>
<td>67.</td>
<td>128.</td>
<td>61.</td>
</tr>
<tr>
<td>([\text{Omim}][\text{BF4}])</td>
<td>76.</td>
<td>102.</td>
<td>26.</td>
</tr>
<tr>
<td>(\text{H2O})</td>
<td>69.</td>
<td>121.</td>
<td>52.</td>
</tr>
</tbody>
</table>

- Most ILs can be operated for a cooling application.
- \([\text{Emim}][\text{EtSO4}]\) and \([\text{Hmim}][\text{BF4}]\) have smaller operating range.
For a heating operation \( (T_{hg}/T_{a}/T_{c}/T_e = 175/45/45/10 \, ^\circ C) \)

\( T_{15} \) ranges

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>T15_min (°C)</th>
<th>T15_max (°C)</th>
<th>Range of T15 [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X [Hmim][BF4]</td>
<td>130.</td>
<td>70.</td>
<td>-59.</td>
</tr>
<tr>
<td>X [Mmim][DMP]</td>
<td>91.</td>
<td>104.</td>
<td>12.</td>
</tr>
<tr>
<td>X [Omim][BF4]</td>
<td>111.</td>
<td>76.</td>
<td>-34.</td>
</tr>
</tbody>
</table>

Only [Bmim][BF4], [Emim][SCN] and [Mmim][DMP] can be operated for heating
Effects of distribution ratio on COP and $f$

$(T_{hg}/T_a/T_c/T_e = 175/30/40/10\, ^\circ C, \text{NH}_3/\text{IL})$

- Optimum DR = 0.5.
- Best NH$_3$/IL pair can beat NH$_3$/H$_2$O pair in a DE absorption refrigeration cycle.
- Circulation ratios of NH$_3$/IL pairs are much higher than NH$_3$/H$_2$O.
Cooling performance

- Effects of driving T on COP and capacity

$\text{NH}_3/\text{[Emim]}[\text{SCN}]$ pair (solution flow of 0.54 kg/s)

- As $T_{hg}$ rises, the COP increases, but the increment becomes smaller.
- Cooling capacity increases at an approximately linear trend.
- A lower cooling temperature leads to a lower COP and a lower cooling capacity.
Heating performance

- Effects of distribution ratio on COP and $f$

\[
\frac{T_{hg}}{T_a} / \frac{T_c}{T_e} = 200/45/45/10 \, ^\circ\text{C, NH}_3/\text{IL}
\]

- Optimum DR = 0.6.
- Their optimum COPs are below 2.0, worse than the NH$_3$/H$_2$O pair.
- Heating application is not as good as the cooling.
Heating performance

- Effects of driving T on COP and capacity

\( \text{NH}_3/[[\text{Emim}][\text{SCN}]] \) pair (solution flow of 0.54 kg/s)

- As \( T_{hg} \) rises, the COP increase (due to the decomposition temp., the peak didn’t reach).
- Cooling capacity increases with \( T_{hg} \) rises.
- A lower environment temperature leads to a lower COP and a lower heating capacity.
Content

● Introduction
● Methods
● Results and discussion
● Conclusions
Conclusions

- DE-AHP with NH$_3$-ILs as working fluids has been investigated for the first time.
- Best performing ammonia pairs are those with [Bmim][BF$_4$], [Emim][SCN] and [Mmim][DMP].
- Optimum DR of system is around 0.5~0.6.
- Cooling applications with NH$_3$/IL is more promising.
- NH$_3$/ILs have the potential to show a better performance than NH$_3$/H$_2$O pair for cooling.
Question?

Meng WANG*, Carlos A. INFANTE FERREIRA
M.Wang-2@tudelft.nl
Process and Energy Department,
Delft University of Technology
Vapor Liquid Equilibria (VLE) for NH$_3$/ILs

- Equilibrium criterion
  \[ \gamma_{NH_3} = \frac{P}{x_{NH_3} P_{sat}} \]

- $P_{sat}$ is from Antoine equation.

- Activity coefficient $\gamma$ is from NRTL model,
  \[ \ln \gamma_i = x_i^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{G_{12} \tau_{12}}{(x_2 + x_1 G_{12})^2} \right] \]

  where
  \[
  \begin{align*}
  G_{12} &= \exp(-\alpha \tau_{12}) \\
  G_{21} &= \exp(-\alpha \tau_{21}) \\
  \tau_{12} &= \tau_{12}^{(0)} + \frac{\tau_{12}^{(1)}}{T} \\
  \tau_{21} &= \tau_{21}^{(0)} + \frac{\tau_{21}^{(1)}}{T}
  \end{align*}
  \]
● Enthalpies of solutions

» Saturated solution \((T, P, w_{NH_3})\)

\[
h(T, P, w_{NH_3}) = w_{NH_3} h_{NH_3}(T) + w_{IL} h_{IL}(T) + \Delta h_{mix}(T, P, w_{NH_3})
\]

– for IL \(h_{IL}(T) = h_0(T_0) + \int_{T_0}^{T} C_p^IL dT\)

– mixing enthalpy neglected

» Subcooled solution \((T, P, w_{NH_3})\)

\[
h(T, P, w_{NH_3}) = h(T_{sat}, P, w_{NH_3}) - \int_T^{T_{sat}} C_p^{sol}(w_{NH_3}) dT
\]

– \(C_p\) of solution (no excess contribution)

\[
C_p^{sol}(w_{NH_3}) = w_{NH_3} C_p^{NH_3} + (1 - w_{NH_3}) C_p^{IL}
\]
● Excess effects in the heat capacity of solutions are not dominant.

Method 1

Method 2

Excess effect of $C_p$ is limited
● Different $\Delta h_{\text{mix}}$ source for NH$_3$/[bmim][BF$_4$] solution

• Very few impact of $\Delta h_{\text{mix}}$ on total enthalpy of NH$_3$/IL solution.