Absorption heat pump cycles with NH3 – ionic liquid working pairs

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HIGHLIGHTS

● Nine NH3/IL pairs are investigated in AHPs for building heating.
● COP of four NH3/IL pairs beats that of the NH3/H2O.
● Idealized NH3/IL mixture can reach a COP of 1.84.
● [Emim][SCN] is currently a feasible candidate to be used in AHPs with PHX.

ABSTRACT

Ionic liquids (ILs), as novel absorbents, draw considerable attention for their potential roles in replacing water or LiBr aqueous solutions in conventional NH3/H2O or H2O/LiBr absorption refrigeration or heat pump cycles. In this paper, performances of 9 currently investigated NH3/ILs pairs are calculated and compared in terms of their applications in the single-effect absorption heat pumps (AHPs) for the floor heating of buildings. Among them, 4 pairs were reported for the first time in absorption cycles (including one which cannot operate for this specific heat pump application). The highest coefficient of performance (COP) was found for the working pair using [mmim][DMP] (1.79), and pairs with [emim][Tf2N] (1.74), [emim][SCN] (1.73) and [bmim][BF4] (1.70) also had better performances than that of the NH3/H2O pair (1.61). Furthermore, an optimization was conducted to investigate the performance of an ideal NH3/IL pair. The COP of the optimized mixture could reach 1.84. Discussions on the contributions of the generator heat and optimization results revealed some factors that could affect the performance. It could be concluded that the ideal IL candidates should show high absorption capacities, large solubility difference between inlet and outlet of the generator, low molecular weights and low heat capacities. In addition, an economic analysis of the AHP using NH3/[emim][SCN] working pair with plate heat exchangers was carried out based on heat transfer calculations. The results indicated that the NH3/IL AHP is economically feasible. The efforts of heat transfer optimization in the solution heat exchanger and a low expense of ILs can help the IL-based AHP systems to become more promising.

1. Introduction

The Paris Agreement adopted by 195 countries in the 2015 Paris climate conference (COP 21) reset the global ambition: limiting the temperature rise from pre-industrial levels well below 2 K. Efforts responding to climate change are also accelerating the way the energy sector is developing [1]. Heating and cooling, especially for buildings, take up the majority of the energy consumption and the greenhouse gases emission. According to the European Commission, heating and cooling consumed 50% (22.85 EJ) of the final energy consumption in the EU in 2012. 45% of energy for heating and cooling in the EU was used in the residential sector, 37% in industry and 18% in services [2]. In the US, 41% (42.2 EJ) of the primary energy in 2010 was consumed by the buildings sector, compared to 30% by the industrial sector and 29% by the transportation sector. Heating and cooling took 59% of the buildings energy consumption [3]. As an increasingly significant energy consumer in the buildings sector, China is the largest energy-consuming economy in the world, and buildings energy used in China was the second-largest in the world after the US, representing nearly 16% of total global energy consumption in buildings in 2012 (more than 18 EJ) [4].

Absorption refrigeration and heat pump cycles are drawing considerable attention because they can take effective advantage of low-grade heat from concentrating solar collectors or waste heat, providing opportunities for clean and sustainable energy utilization [5–8]. Working pairs H2O/LiBr and NH3/H2O have been widely used in
certain applications in absorption systems, while many challenges do exist, such as crystallization possibilities of the H$_2$O/LiBr pair and the difficulty in the separation of the NH$_3$/H$_2$O pair [9]. Thus, the investigation of alternative solvents is still a relevant topic [10-14,9].

Ionic liquids (ILs), whose properties can be adjusted by the design of anion and cation combination for a task-specific purpose, have drawn considerable attention for their potential roles in replacing conventional absorbents used in absorption refrigeration and heat pump cycles in the past years. Researchers recognized the strengths of ILs in applications, such as high boiling point, good affinity with refrigerants, and high chemical and thermal stabilities [9]. Nevertheless, there are also some challenges related to the technical feasibility and costs when introducing them, thus many efforts are still needed before the ILs are accepted in practice.

In order to preselect promising ILs to be used in absorption systems, many researchers did performance investigations. The majority of investigations were focused on performance predictions, in which the frequently studied refrigerants include H$_2$O [15,16], hydrocarbons (HCs) [17], hydrofluorocarbons (HFC) [18,19], and CO$_2$ [20]. Since NH$_3$ based absorption systems hold strengths such as sub-zero degree applications and free of air infiltration, research related to these mixtures is most relevant. Nevertheless, there is only limited work which has been reported. Yokozeki and Shiflett [21,22] measured solubility data for NH$_3$ with a set of ILs, and calculated the thermodynamic performance of these mixtures in a single-effect cycle. Kotenko [23] also developed thermodynamic simulations for absorption heat pumps (AHPs) with 4 NH$_3$/ILs mixtures in Aspen Plus, and compared their performances with that of the NH$_3$/H$_2$O system. Their results showed that the efficiency of some of the investigated NH$_3$/IL AHP processes, at specified operating conditions, was higher than that of conventional NH$_3$/H$_2$O systems. Chen et al. [24,25] investigated vapor-liquid equilibria (VLE) for metal ion-containing ionic liquid [bmim][Zn$_2$Cl$_6$] with NH$_3$, and compared the thermodynamic performance of this mixture with that of the NH$_3$/NaSCN pair. The performance of the former system is better than that of the latter one when the generator temperature is high and the absorber and the condenser temperatures are low. Ruiz et al. [26] modeled NH$_3$/IL absorption using COSMO-based Aspen simulations and analyzed cycle performance for conventional and task-specific ILs.

In these performance prediction studies of absorption systems, the enthalpy of the NH$_3$/IL solution is always an essential thermodynamic property. Most researchers obtained this property by adding an excess enthalpy to the sum of enthalpies of the two pure components. The excess enthalpy could be obtained from the VLE data via a variety of models. Some researchers [27,15,28] used the non-random two-liquid (NRTL) activity coefficient model to predict it. However, Shiflett and Yokozeki [27] found that an accurate prediction of the mixing enthalpy with NRTL is very difficult, because the excess enthalpy is derived from

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**Nomenclature**

- $A$ area ($m^2$)
- $C$ cost (k€)
- $C_p$ heat capacity ($kJkg^{-1}K^{-1}/kJkmol^{-1}K^{-1}$)
- $c$ coefficient in heat capacity (-)
- $f$ circulation ratio (-)
- $G$ parameters in NRTL model (-)
- $h$ specific enthalpy ($kJkg^{-1}$)
- $m$ mass flow rate ($kg s^{-1}$)
- $M_w$ molecular weight ($kg kmol^{-1}$)
- $P$ pressure (Pa)
- $Q$ heat flow (W)
- $q$ quality ($kg kg^{-1}$)
- $T$ temperature ($K/°C$)
- $w$ mass concentration ($kg kg^{-1}$)
- $x$ molar concentration ($kmol kmol^{-1}$)

**Greek letter**

- $\alpha$ parameter in NRTL model (-)
- $\gamma$ activity coefficient (-)
- $\tau$ parameter in NRTL model (-)

**Subscript and superscript**

- 0 reference state
- 1,2 ... state point
- abs absorber
- c critical (property)
- con condenser
- E excess (enthalpy)
- eva evaporator
- gen generator
- NH$_3$ species of NH$_3$
- IL species of IL
- phx plate heat exchanger
- r refrigerant stream
- s strong solution stream

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**Abbreviation**

- ABS absorber
- AHP absorption heat pump
- CON condenser
- COP coefficient of performance
- EOS equation of state
- EVA evaporator
- GA genetic algorithm
- GAX generator/absorber heat exchanger
- GEN generator
- HC hydrocarbon
- HFC hydrochlorofluorocarbon
- HK heat exchangers
- IL ionic liquid
- NRTL non-random two-liquid activity coefficient model
- OHTC overall heat transfer coefficient
- PHX plate heat exchanger
- REC rectifier
- RMSD root-mean-square deviation
- RK Redlich-Kwong (equation of state)
- SHX solution heat exchanger
- VLE vapor-liquid equilibrium/vapor-liquid equilibria
- [bmim][BF$_4$] 1-ethyl-3-methylimidazolium tetrafluoroborate
- [bmim][BF$_4$] 1-ethyl-3-methylimidazolium tetrafluoroborate
- [bmim][BF$_4$] 1-ethyl-3-methylimidazolium thiocyanate
- [bmim][EtSO$_4$] 1-ethyl-3-methylimidazolium ethylsulfate
- [bmim][SCN] 1-ethyl-3-methylimidazolium thiocyanate
the temperature derivative of the activity coefficient, and the temperature-dependency in any activity model is always in a purely empirical form. Therefore then they turned to a cubic equation of state (EOS) method for excess enthalpy predictions [21,22]. Meanwhile, for the pure components part, one of the challenges is the heat capacity of the IL. In the work of Yokozeki and Shiflett [21,22], this part was obtained from a group function contribution method [29]. However, Cai et al. [20] pointed out that this group function contribution method is not always accurate. In the prediction work of Chen et al. [25], experimental heat capacity data of ILs were employed in the enthalpy predictions. Therefore, according to the previous studies, the combination of EOS based method for the excess enthalpy with the experimental heat capacity data of ILs may provide a more accurate way for the performance prediction of AHPs.

Previous experimental studies were carried out either by substituting the working pairs in a traditional commercial system [30–32] with H2O/ILs pairs, or restricted to small scales systems [33]. Apart from these studies, the understanding of ILs in more practical aspects, for example the heat and mass transfer aspects, is still limited. However, researches of IL-based working pairs is emerging recently taking more practical aspects into account. Meyer et al. [34] studied the combined heat and mass transfer phenomena of H2O/[emim][Tf2N] in an absorption refrigeration system by using analytical functions. Aiyi and Coronas [35] developed a measurement setup to study the absorption capacity of the NH3 vapor in ILs in a pool type absorber. Wadekar [36] simulated the heat transfer behavior of IL ([bmm][Tf2N]) in different heat exchangers (HXs). The results showed that the heat transfer performance was not particularly attractive, but heat transfer enhancement technology can improve it effectively. Boman et al. [37] screened working pairs including the IL-based ones for a single-effect AHP based on both thermodynamic and heat transfer principles. The shell-and-tube HXs of IL-based AHP systems need more heat exchanger area due to the poor heat transfer performance of the ILs. Chugh et al. [38] implemented a membrane-based semi-open absorption system using IL for heating, dehumidification and cooling application. The experimental test achieved a heating coefficient of performance (COP) of 1.4.

In this paper, a thermodynamic model of single-effect AHPs is first proposed accompanied with an accurate method to estimate enthalpies of solutions. With this model, the performance behaviors of 9 commercialized ILs with NH3 which have sufficient published data (VLE data with NH3 and pure heat capacities of ILs) for this calculation. The performance of four of these pairs in absorption systems is reported for the first time. The influence of the GEN temperatures on the circulation ratio (j) and on the COP is also studied. As one of the most original parts of this study, the developed NRTL and heat capacity models have been made generic, by integrating them with a genetic algorithm (GA) in the thermodynamic AHP model, to determine the maximum COP of the AHP cycle and explore how the thermodynamic properties of the ideal ILs should show. In addition, the heat transfer calculations for each heat exchanger of an AHP are carried out considering all heat exchangers are plate heat exchangers (PHXs). Based on that, the feasibility of applying IL in an AHP system is analyzed by investigating its economic performance.

2. Methods

2.1. Thermodynamic model of the cycle

Thermodynamic models of the single-effect AHP systems have been frequently reported in the literature, see for instance Kiss and Infante Ferreira [39]. In this section, only the details required for the following steps of this paper will be discussed.

Fig. 1 depicts a schematic diagram of a single-effect absorption refrigeration/heat pump cycle. The system is mainly composed of an absorber (ABS), a generator (GEN), a condenser (CON), an evaporator (EVA), along with a solution heat exchanger (SHX), a pump and two throttle valves.

To qualitatively illustrate the temperature and pressure relationship of each state, the process is also plotted in a ln P – (−1/T) diagram in Fig. 2. In the ABS, the weak NH3/IL solution 5 (weak in the refrigerant, NH3) absorbs the saturated pure NH3 refrigerant vapor 1 from the EVA, and then it turns into strong solution 2. The heat Qabs is delivered to the heating system by the ABS. The outlet solution 2 from the ABS is then pumped to a high pressure level and enters the SHX as a cold flow. The outlet flow of the cold side, stream 4, then goes into the GEN, where the driving heat Qgen is input. With the heat input, strong solution 4 releases some refrigerant vapor 8, then becomes the poor solution 7 and enters the SHX. In the SHX, the weak solution 7 is cooled by the cold side to a state of 6 and then throttled to a low pressure level through a valve, before going back to the ABS. The superheated refrigerant vapor 8 from the GEN is condensed to a saturated pure liquid refrigerant in the CON, where the heat Qcon is delivered to the heating system. After that, the saturated liquid refrigerant 9 expands to a low pressure level through a valve, and extracts heat Qeva from the surrounding in the EVA. The
The activity coefficients $P_{c}$ can be obtained through the NRTL activity coefficient model after correlating VLE data,

$$
\ln P_{\text{m}} = x_{A}^{2} \left[ G_{21} \frac{1}{x_{1}G_{21} + (x_{2} + x_{1}G_{12})^{2}} + G_{12} \frac{1}{x_{2}G_{12} + (x_{1} + x_{2}G_{21})^{2}} \right]
$$

(7)

where,

$$
G_{12} = \exp(-\tau_{12})
$$

(8a)

$$
G_{11} = \exp(-\tau_{11})
$$

(8b)

$$
\tau_{12} = \tau_{12}^{(0)} + \left( \frac{G_{12}}{T} \right)\frac{1}{G_{12}}
$$

(8c)

$$
\tau_{11} = \tau_{11}^{(0)} + \left( \frac{G_{11}}{T} \right)\frac{1}{G_{11}}
$$

(8d)


### 2.2. Properties

#### 2.2.1. Vapor-liquid equilibria for the NH$_3$/ILs binary solutions

Vapor-liquid equilibria describe the relationships between parameters $P-T-x_{i}$ which can be used to identify the state points in the cycle. NRTL models for the prediction of VLE of mixtures have been frequently reported in the literature, see for instance [39]. In this section, only the details required for the following steps of this paper will be discussed.

For the NH$_3$/IL system, due to the non-volatility of ILs, the equilibrium criteria are simplified as,

$$
P = Y_{\text{NH3}}X_{\text{NH3}} \frac{P_{\text{NH3}}^{\text{ref}}} {P_{\text{NH3}}}
$$

(6)

where, $P_{\text{NH3}}^{\text{ref}}$ can be obtained from NIST Refprop [40]. The activity coefficient $\tilde{N}_{\text{NH3}}$ can be obtained through the NRTL activity coefficient model after correlating VLE data,

$$
\ln \tilde{N}_{\text{NH3}} = x_{A}^{2} \left[ G_{21} \frac{1}{x_{1}G_{21} + (x_{2} + x_{1}G_{12})^{2}} + G_{12} \frac{1}{x_{2}G_{12} + (x_{1} + x_{2}G_{21})^{2}} \right]
$$

(7)

The enthalpy data of pure NH$_3$ are directly obtained from NIST’s Refprop [40]. For a real solution, the total enthalpy can be estimated using the following method, depending on its state.

For a saturated solution at an equilibrium condition $T, P$ and $w_{\text{NH3}}$, the total enthalpy is,

$$
h_{\text{sol}}(T,P,w_{\text{NH3}}) = h_{\text{sol}}^{\text{ref}} = w_{\text{NH3}} h_{\text{NH3}}(T) + w_{\text{IL}} h_{\text{IL}}(T) + h_{\text{f}}(T,P,w_{\text{NH3}})
$$

(9)

where the enthalpies of NH$_3$ are chosen at their saturated liquid states. For the ILs, the enthalpies are calculated with the help of their pure heat capacities $c_{p}^{\text{IL}}$,

$$
h_{\text{IL}}(T) = h_{0}(T) + \int_{T_{0}}^{T} c_{p}^{\text{IL}} dT
$$

(10)

The calculation of the excess enthalpy, $h_{f}$, can be obtained using an

### Table 1

Molecular weight and critical data of the investigated ILs.

<table>
<thead>
<tr>
<th>ILs</th>
<th>$M_{w}$ [kg kmol$^{-1}$]</th>
<th>$T_{c}$ [K]</th>
<th>$P_{c}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mmim][DMP]</td>
<td>222.18</td>
<td>816.8</td>
<td>2.72</td>
</tr>
<tr>
<td>[emim][BF$_4$]</td>
<td>197.97</td>
<td>596.2</td>
<td>2.36</td>
</tr>
<tr>
<td>[hmim][BF$_4$]</td>
<td>254.08</td>
<td>690.0</td>
<td>1.79</td>
</tr>
<tr>
<td>[bmim][BF$_4$]</td>
<td>282.13</td>
<td>737.0</td>
<td>1.60</td>
</tr>
<tr>
<td>[mmim][DMP]</td>
<td>226.02</td>
<td>643.2</td>
<td>2.04</td>
</tr>
<tr>
<td>[bmim][BF$_4$]</td>
<td>284.18</td>
<td>719.4</td>
<td>1.73</td>
</tr>
<tr>
<td>[emim][Tf$_2$N]</td>
<td>391.31</td>
<td>1249.3</td>
<td>3.27</td>
</tr>
<tr>
<td>[emim][EtSO$_4$]</td>
<td>236.29</td>
<td>1067.5</td>
<td>4.05</td>
</tr>
<tr>
<td>[emim][BF$_4$]</td>
<td>169.25</td>
<td>1013.6</td>
<td>2.23</td>
</tr>
</tbody>
</table>

* The critical data are obtained using the group-contribution-function method [42].
equation of state (EOS) and mixing rules. Yokozeki and Shillett [21,22,41] employed a modified Redlich-Kwong (RK) type of cubic EOS to fit the vapor pressure data and to predict the excess enthalpy. This method is also used for the prediction of the mixing heat in the present work. The detailed approach has been reported in the mentioned references. The values of the critical temperature and pressure of ILs needed for the following calculations, along with their molecular weights, are listed in Table 1.

For subcooled solutions at condition $T$, $P$ and $w_{w_{H_2O}}$, its enthalpy can be obtained by subtracting the subcooled part from a corresponding saturated solution,

$$h^\text{w}(T,P,w_{w_{H_2O}}) = h(T,sat,P,w_{w_{H_2O}}) - \int_{T}^{T_{sat}} C_{p}^{w} \, dT$$  \hspace{1cm} (11)

In this study, the weighted average heat capacity of both components has been implemented to express $C_{p}^{w}$.

$$C_{p}^{w}(w_{w_{H_2O}}) = w_{w_{H_2O}}C_{p}^{w_{H_2O}} + (1-w_{w_{H_2O}})C_{p}^{w_{IL}}$$  \hspace{1cm} (12)

This treatment has been verified for $H_2O/[mmim][DMP]$ with $C_{p}^{w}$ data in [15] showing that the relative deviation is always smaller than 4%.

If $T$ of a stream is higher than $T_{sat}$, part of the $NH_3$ in the solution will be boiled off. For this case, the total enthalpy can be expressed as,

$$h^\text{w}(T,P,w_{w_{H_2O}}) = (1-q)h^\text{sat} + qh^\text{vap}$$  \hspace{1cm} (13)

where, $h^\text{sat}$ and $h^\text{vap}$ are the specific enthalpies for the saturated solution part and the vapor part, respectively. $q$ is the quantity, which can be identified as,

$$q = \frac{w_{w_{H_2O}}}{1-w_{w_{H_2O}}}$$  \hspace{1cm} (14)

2.3. Optimization problem

The properties of ILs can be adjusted by the design of anion and cation combinations for a task-specific purpose. However, because of the large number of anions and cations, the number of possible combinations is considerable. In this paper, the determination of screen criteria of task-specific ILs for AHPs will also be discussed. These criteria are identified via the optimization of the cycle performance.

In the optimization, the objective is the maximization of the COP which depends on solubility (concentration of weak and strong solutions) and enthalpy values as will be discussed in Section 3.5. Making use of an NRTL model, a total of eight parameters are identified which affects the attained COP value. They are $\alpha$, $\gamma_{fi}^{(0)}$, $\gamma_{fi}^{(1)}$, $\gamma_{fi}^{G}$ and $\gamma_{fi}^{L}$ of the NRTL model for VLE, $c_{fi}$, $c_{j}$ in linear molar $C_{j}$ expression and the molecular weight $M_{w}$. Once the COP reaches the optimal value, corresponding optimal variables can be determined for the optimum IL and mixture. Meanwhile, in order to obtain a practical and reasonable result, constraints of these optimal variables are needed. They are determined in terms of experimental data which are collected and discussed in Section 3.1.

The GA is better at finding global solutions than gradient-based solvers. GA selectively generates new candidate points to evaluate based upon a method that is similar to breeding between two “parents” to generate a “child”. They are useful for problems that are highly nonlinear, such as the present problem. One of the concerns is the computational efficiency. To check a large amount of individuals from generation to generation is time-consuming. Luckily, the present optimization problem is not so CPU-intensive. In addition, the selection of individuals in the current generation is random, which can also lead to local minima. To overcome this drawback, instead of using GA for only one optimization, we try thousands of optimizations based on GA independently to remove local minima. The non-physical optimization results will be rejected. Finally, the optimum value for the objective function can be identified. The GA toolbox of Matlab has been used to identify the optimum combination of parameters. The effect of the settings for what concerns population size, elicit count, crossover fraction and generations has been investigated by studying the effect of variations and finally the settings proposed in the Matlab toolbox, respectively, 200, 10, 0.8 and 500, have been adopted.

3. Results and discussion

3.1. Correlations and summaries of properties

3.1.1. Vapor liquid equilibria

With the experimental VLE data of binary $NH_3/IL$s, the binary parameters, $\alpha$, $\gamma_{fi}^{(0)}$, $\gamma_{fi}^{(1)}$ and $\gamma_{fi}^{G}$ of the NRTL model (Eq. (7) and (8)), can be correlated and will allow for the determination of the operating concentrations. The correlated results and accuracies are listed in Table 2. In this work, most of the data have been correlated with a root-mean-square deviation (RMSD) smaller than 5.62% as shown in Table 2. Only the model for the pair $NH_3/[omim][BF_4]$ showed slightly larger deviation: 8.7%.

3.1.2. Heat capacities

Experimental heat capacity ($C_{p}$) data of 61 ILs at 298.15 K, reviewed by Paulechka [46], are plotted in Fig. 4 in mole-based and mass-based units, respectively. It is quite interesting to see that the mole-based $C_{p}$ data are distributed in a linear trend with respect to the molecular weight. The mass-based $C_{p}$ data are centralized near 1.44 kJ kg$^{-1}$ K$^{-1}$ in a nearly constant range between 1 and 2 kJ kg$^{-1}$ K$^{-1}$. This trend provides a general relationship between $C_{p}$ and $M_{w}$ for ILs, which will be used in the property optimization as a constraint. Even though the relationship is not very accurate, it still can be helpful to identify how this property impacts on the performance of the mixture in the AHP.

For the same ILs involved in the NRTL correlation in Table 2, the mole-based $C_{p}$ values are also plotted as a function of temperature in Table 2.

<table>
<thead>
<tr>
<th>Working pairs</th>
<th>$\alpha$</th>
<th>$\gamma_{fi}^{(0)}$</th>
<th>$\gamma_{fi}^{(1)}$</th>
<th>$\gamma_{fi}^{G}$</th>
<th>$\gamma_{fi}^{L}$</th>
<th>Data points</th>
<th>RMSD $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NH_3/[mmim][DMP]$</td>
<td>0.24032</td>
<td>7.82</td>
<td>−2300.68</td>
<td>−4.43</td>
<td>1000.39</td>
<td>30</td>
<td>3.31%</td>
</tr>
<tr>
<td>$NH_3/[emim][BF_4]$</td>
<td>0.99952</td>
<td>−0.01</td>
<td>236.41</td>
<td>−1.26</td>
<td>164.59</td>
<td>25</td>
<td>5.14%</td>
</tr>
<tr>
<td>$NH_3/[mmim][BF_4]$</td>
<td>0.99998</td>
<td>−14.8</td>
<td>5081.74</td>
<td>−2.67</td>
<td>478.85</td>
<td>25</td>
<td>4.29%</td>
</tr>
<tr>
<td>$NH_3/[emim][BF_4]$</td>
<td>0.90702</td>
<td>−7.01</td>
<td>2690.74</td>
<td>−2.4</td>
<td>283.17</td>
<td>25</td>
<td>8.71%</td>
</tr>
<tr>
<td>$NH_3/[mmim][PF_5]$</td>
<td>−0.01285</td>
<td>−48.23</td>
<td>8961.06</td>
<td>32.62</td>
<td>−5490.64</td>
<td>30</td>
<td>2.62%</td>
</tr>
<tr>
<td>$NH_3/[mmim][TiN]$</td>
<td>−0.00422</td>
<td>−100</td>
<td>14710.17</td>
<td>71.51</td>
<td>−9046.21</td>
<td>30</td>
<td>5.62%</td>
</tr>
<tr>
<td>$NH_3/[ESO4]$</td>
<td>0.71604</td>
<td>11.17</td>
<td>−4089.25</td>
<td>−7.53</td>
<td>2451.46</td>
<td>29</td>
<td>4.32%</td>
</tr>
<tr>
<td>$NH_3/[SCN]$</td>
<td>−0.27082</td>
<td>−10.66</td>
<td>3120.01</td>
<td>5.6</td>
<td>−1967.71</td>
<td>36</td>
<td>4.59%</td>
</tr>
<tr>
<td>$NH_3/H_2O$</td>
<td>−0.24355</td>
<td>24.17</td>
<td>−18636.43</td>
<td>7.26</td>
<td>−3370.40</td>
<td>111</td>
<td>3.24%</td>
</tr>
</tbody>
</table>

$^*$ The experimental VLE data used are from, 1 [43, 2, 3 and 4 [44], 5, 6 and 7 [21, 8 and 9 [22] and 10 [45]. Data of the $NH_3/H_2O$ pair are used as a reference.

$^*$ RMSD is obtained based on the deviations between the correlated and experimental pressure data by $\text{RMSD}(P) = \sqrt{\frac{\sum_{i=1}^{N}(P_{\text{cor}}(i)-P_{\text{exp}}(i))^2}{N}}$.
parameters of the linear expression and is based on the experimental \( C_p \) data from literature [47–53]. The accuracies of all correlations are also listed. Notice that for most fluids the available data are limited to 100 °C, so that the relation is extrapolated when calculating values up to 130 °C. This may lead to larger errors than reported in Table 3.

### 3.2. Performance comparison

To compare the performances in detail, some calculated results are listed in Table 4 at a specific condition \( T_{\text{gen}}/T_{\text{eva}}/T_{\text{con}} = 120/45/45/10 \) °C. This operating conditions range is specified based on applications in floor heating. Apart from the solubility levels of the in- and outlet of the ABS and performance parameters \( f \) and \( \text{COP} \), the conditions at the GEN inlet (state point 4) are also checked. Qualities \( q_p \) are listed to show if there is vapor boiled-off before entering the GEN. The table also includes the results for the \( \text{NH}_3/\text{H}_2\text{O} \) system and optimum results obtained in Section 3.5. The single-effect AHP cycle with \( \text{NH}_3/\text{H}_2\text{O} \) as working fluids, reported by Kotenko [23], operates at similar conditions as applied in the current work. His predicted heating COP for a system with a rectifier and slightly lower evaporating temperature \( T_{\text{eva}} = 5 \) °C is around 1.59, which is quite close to the values obtained in the current work of 1.61.

Two facts resulting from the circulation ratio, \( f \), can influence the cycle performance. One is its impact on the pumping power. A higher value of \( f \) means a larger mass flow rate through the pump (at the same flow of refrigerant stream), which can increase the power consumption of the solution pump. The second one is due to the relationship between \( f \) and the energy and mass balances for the GEN and for the ABS, which will be discussed in detail in Section 3.3. In all, a small \( f \) is preferable. Because of the significant difference in molecular weights between \( \text{NH}_3 \) and ILs, the mass concentrations of \( \text{NH}_3/\text{ILs} \) pairs are much lower than that of the \( \text{NH}_3/\text{H}_2\text{O} \) system. As a result, the circulation ratios of \( \text{NH}_3/\text{ILs} \) mixtures (29.2–112.3) are significantly higher than that of conventional \( \text{NH}_3/\text{H}_2\text{O} \) (4.6). Promisingly, 4 of the ILs based systems hold higher COP values than that for the \( \text{NH}_3/\text{H}_2\text{O} \) system. These ILs are [mim][DMP] (1.79), [emim][Tf2N] (1.74), [emim][SCN] (1.73) and [bmim][BF4] (1.70). Although the performance of the \( \text{NH}_3/\text{H}_2\text{O} \) system could be improved by implementing advanced cycles, such as the generator/absorber heat exchanger (GAX) cycle, that would also increase the complexity and investment of the system. These promising results show the potential of \( \text{NH}_3/\text{ILs} \) working pairs which can be executed with a simple cycle, making these pairs superior alternatives.

Previously Yokozeki and Shiflett [21,22] have compared the performance of some of the investigated mixtures in single-effect absorption refrigeration cycles. Their results are also included in Table 4 for reference. At their considered operations conditions, the \( \text{NH}_3/\text{H}_2\text{O} \) pair has been identified to perform better than the considered \( \text{NH}_3/\text{ILs} \) pairs. This is different from the current work, in which the \( \text{NH}_3/\text{H}_2\text{O} \) pair is not identified as the superior one for a heat pump operation. Yokozeki and Shiflett [21,22] did not include the effect of the rectifier when calculating the performance of the \( \text{NH}_3/\text{H}_2\text{O} \) pair. The rectifier is essential to guarantee the purity of the produced refrigerant. This is the main reason why their COP of the \( \text{NH}_3/\text{H}_2\text{O} \) pair was overestimated. Besides, although the experimental VLE data of Yokozeki and Shiflett [21,22] have been used for these fluids in the present work, the NRTL parameters have been independently correlated. The fitted VLE behaviors are not identical but quite similar to the ones reported by Yokozeki and Shiflett [21,22]. The difference in COP results for the \( \text{NH}_3/\text{IL} \) pairs is mainly due to the method used to predict the specific heat of the working pairs. For example, Yokozeki and Shiflett [21,22] made use of the group contribution function method to predict these values, while in this study the reported experimental values have been used as discussed in Section 3.1. Problems encountered when using the group contribution function method for the prediction of the specific heat of ionic liquids have previously been reported by Cal et al. [20], as already

![Fig. 4. \( C_p \) values of 61 ILs at 298.15 K (upper: mole-based, lower: mass-based). These 61 data points have been collected from experimental \( C_p \) data reviewed by Paulechka [46]. They are selected because they are the only ones having uncertainties lower than 15%.](image-url)

![Fig. 5. Experimental \( C_p \) (mole-based) values of the investigated ILs as a function of temperature.](image-url)

### Table 3

<table>
<thead>
<tr>
<th>ILs</th>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>Data points</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mim][DMP]</td>
<td>−153.898</td>
<td>1.476</td>
<td>4</td>
<td>0.94%</td>
</tr>
<tr>
<td>[emim][BF4]</td>
<td>214.067</td>
<td>0.308</td>
<td>12</td>
<td>0.18%</td>
</tr>
<tr>
<td>[bmim][BF4]</td>
<td>275.962</td>
<td>0.520</td>
<td>9</td>
<td>0.00%</td>
</tr>
<tr>
<td>[emim][BF4]</td>
<td>323.894</td>
<td>0.588</td>
<td>100</td>
<td>0.21%</td>
</tr>
<tr>
<td>[bmim][BF4]</td>
<td>250.201</td>
<td>0.397</td>
<td>20</td>
<td>0.66%</td>
</tr>
<tr>
<td>[bmim][PF6]</td>
<td>282.070</td>
<td>0.452</td>
<td>1528</td>
<td>0.91%</td>
</tr>
<tr>
<td>[emim][Tf2N]</td>
<td>363.188</td>
<td>0.478</td>
<td>16</td>
<td>0.01%</td>
</tr>
<tr>
<td>[emim][EtSO4]</td>
<td>245.526</td>
<td>0.462</td>
<td>146</td>
<td>0.60%</td>
</tr>
<tr>
<td>[emim][SCN]</td>
<td>116.474</td>
<td>0.547</td>
<td>10</td>
<td>0.61%</td>
</tr>
</tbody>
</table>

* The experimental \( C_p \) data used are from [47] [48], [49], 4, 5 and 6 [50], 6 [51], 7 [52] and 9 [53].

Fig. 5. With respect to the temperature, the \( C_p \) values of different ILs also show approximately linear trends. Thus, the molar \( C_p \) value of each IL is represented by a linear expression. Table 3 lists the correlated
discussed in the introduction.

3.3. Contributions to the generation heat

Considering the energy balance of the 4 main devices, the COP of a heat pump system can also be expressed as,

\[
\text{COP} = \frac{Q_{\text{abs}} + Q_{\text{eva}}}{Q_{\text{gen}}} = \frac{Q_{\text{abs}} + Q_{\text{eva}}}{Q_{\text{gen}}} = 1 + \frac{Q_{\text{eva}}}{Q_{\text{gen}}}
\]

The EVA heat, \(Q_{\text{eva}}\), is equal for all fluids. Thus, the difference in COP results from the GEN heat, \(Q_{\text{gen}}\). A higher \(Q_{\text{gen}}\) gives a lower heat pump COP.

To make this clear, relevant expressions of the total enthalpies in Section 2.2 along with Eq. (4) and (14) are substituted into Eq. (2).

Taking into account the heat and mass balances of the GEN, the heat input in the GEN, \(Q_{\text{gen}}\), can be rewritten as,

\[
Q_{\text{gen}} = m_{\text{f}}[h_{\text{f}} - h_{\text{NH}_3}]_{\text{sat}} + (1-f)\{q_{\text{fl}} + (q_{\text{fl}}-h_{\text{fl}})_{\text{abs}}\} + (f-1)\{w_{\text{IL}}(1-h_{\text{NH}_3})_{\text{sat}}\} + \{(f-1)\{w_{\text{IL}}(1-h_{\text{NH}_3})_{\text{sat}}\} - (f-1)\{w_{\text{IL}}(1-h_{\text{NH}_3})_{\text{sat}}\} \}
\]

\(Q_{\text{gen}}\) is split into 4 terms in this expression. The first term is the latent heat effect from the condensation of \(\text{NH}_3\) vapor (while also includes the sensible heat associated with the superheated state, while very small). The second one denotes the excess heat. The other two terms represent the contributions of sensible heat, in which, the term in the third line is the sensible heat change of the \(\text{NH}_3\) component while the term in the last line is that of the IL component.

In order to analyze the performance, each of the above contributions to the GEN heat, for the operating condition \(T_{\text{gen}}, T_{\text{eva}} = 120/45/45/10\) °C, is depicted in Fig. 6 for all the \(\text{NH}_3/\text{ILs}\) working pairs.

The values of \(T_{\text{f}}\) are almost identical for the same cases, indicating that the latent heats per unit mass flow, \(h_c\), are more or less the same for all cases. The difference in latent heat in Fig. 6 is due to the different mass flows, 1–9. Large values of \(f\) or \(q\) can lead to a low value of the latent heat contribution. The q has an obvious negative correlation with the latent heat contribution, which can be observed in Fig. 6, e.g. pairs with [omim][BF_4] and [bmim][PF_6]. A higher q implies more vapor is boiled off before the flow enters the GEN. In this way, the heat duty of the GEN is reduced. The q value results mainly from the VLE properties of the \(\text{NH}_3/\text{ILs}\) systems.

Again, due to the almost equal values of \(T_{\text{f}}\), the sensible heats per unit mass flow from \(\text{NH}_3\) component are identical for all the mixtures. The difference in \(\text{NH}_3\) sensible heats is mainly caused by the factor, \((f-1)(w_{\text{NH}_3})\). Also the circulation ratio, \(f\), has a stronger impact compared with \((w_{\text{NH}_3})\). This is also true for the contribution of the sensible heat of the ILs: since the mass-based \(C_p\) values of ILs and temperature differences between inlet and outlet \(\Delta T\) are approximately the same, the sensible heat of the ILs per unit mass flow, \(C_p\Delta T\), are similar for all the ILs. The difference in sensible heat contributions is mainly due to the required circulation ratio, \(f\). Smaller \(f\) of pairs with [bmim][BF_4], [emim][Tf_2N] and [emim][SCN] lead to smaller sensible heat contributions and correspondingly higher COPs. This indicates that the circulation ratio \(f\) is dominant in this case. The solubility difference at the in- and outlet of the ABS will determine the \(f\) values.

Since the VLE properties are usually studied with mole-based units, when considering mass-based properties, say \(f\) here, \(M_w\) also plays a role. For the \(\text{NH}_3\) absorption system, a larger molecular weight of the absorbent leads to a smaller mass concentration change when the molar change is maintained. This also implies that smaller molecular weight of the absorbent is preferable in terms of performance.

The contribution of excess heat will be discussed in Section 3.4.

3.4. Influence of heat source temperature on the performance

To investigate the influence of heat source temperature on the performance, condensing temperature \(T_{\text{gen}}\), absorbing temperature \(T_{\text{abs}}\) and evaporating temperature \(T_{\text{eva}}\) are set to be 45 °C, 45 °C and 10 °C, respectively, while the temperature of the heat source, \(T_{\text{eva}}\), varies in a range from 100 °C to 130 °C. Because all the experimental VLE conditions are lower than 130 °C, \(T_{\text{gen}}\) is maintained below 130 °C in all calculations.

---

Table 4
Performance comparison when different working pairs are used in the AHP cycle \(T_{\text{gen}}, T_{\text{eva}}, T_{\text{abs}}, T_{\text{eva}} = 120/45/45/10\) °C and the refrigeration COP \(T_{\text{gen}}, T_{\text{eva}}, T_{\text{abs}}, T_{\text{eva}} = 100/40/30/10\) °C of corresponding pairs from Yokozeki and Shiflett [21,22].

<table>
<thead>
<tr>
<th>Working pairs</th>
<th>Heat pump performance</th>
<th>Refrigeration performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(w_2) [kg kg(^{-1})]</td>
<td>(w_7) [kg kg(^{-1})]</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[mim]][\text{DMP}])</td>
<td>0.057</td>
<td>0.031</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]][\text{BF}_4])</td>
<td>0.054</td>
<td>0.034</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[bmim]][\text{BF}_4])</td>
<td>0.080</td>
<td>0.072</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[bmim]][\text{PF}_6])</td>
<td>0.057</td>
<td>0.023</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{Tf}_2\text{N}])</td>
<td>0.061</td>
<td>0.046</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{EtSO}_4])</td>
<td>0.044</td>
<td>0.025</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{SCN}])</td>
<td>0.056</td>
<td>0.039</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{BF}_4])</td>
<td>0.043</td>
<td>0.025</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{SCN}])</td>
<td>0.082</td>
<td>0.049</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{Tf}_2\text{N}])</td>
<td>0.043</td>
<td>0.025</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{EtSO}_4])</td>
<td>0.056</td>
<td>0.039</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{[emim]}[\text{SCN}])</td>
<td>0.082</td>
<td>0.049</td>
</tr>
</tbody>
</table>

\(^*\) Concentration data are all for the \(\text{NH}_3\) component. The subscript 2 and 7 represent outlet conditions of the ABS and the GEN, respectively, which are locations with strong and weak solution flows. The subscript 4 represents the inlet conditions of the GEN.

---

Fig. 6. Contributions to the GEN heat \(Q_{\text{gen}}\) by the 4 terms of Eq. (16). The 4 terms are latent heat, absorption heat and sensible heats of both components. 1–8 denotes \(\text{NH}_3\) based working fluids with \([\text{mim}][\text{DMP}], [\text{emim}][\text{BF}_4], [\text{bmim}][\text{BF}_4], [\text{bmim}][\text{BF}_4], [\text{bmim}][\text{PF}_6], [\text{emim}][\text{Tf}_2\text{N}], [\text{emim}][\text{EtSO}_4]\) and \([\text{emim}][\text{SCN}].\)
with both molecular weight and temperature as $\text{°C}$. Large concentration differences and vapor activity are observed for the optimum IL, which is depicted in Fig. 7. Optimum properties including vapor pressure, $P$, and a higher COP. Besides, since the molecular weight $M_w$ is exactly its lowest limit, 170. The optimum molecular weight $M_w$ is exactly its lowest limit, 170. For the same molar solubility difference, a lower value of $M_w$ will lead to a higher value of mass solubility difference which will then lead to a lower $f$ and a higher COP. Besides, since the molecular weight $M_w$ has a linear ascending relationship with mole-based $C_p$, a lower mole-based $C_p$ is observed for the optimum IL, which is depicted in the lowest position in Fig. 5. The optimum properties including vapor pressure, $P$, and $M_w$ allow us to screen the ideal ILS for AHP cycles. The challenge for future work is identifying ILS which show properties close to the optimized ideal mixture. It is clear that a low molecular weight, low $C_p$ and large concentration difference between in- and outlet of the ABS are essential requirements.

### 3.6. Outlook of economic and technical feasibilities

In an economic analysis, the COP values are related to the operational costs of the AHP while the capital costs are related to the...
investment in equipment and working fluids. To determine the sizes of the main components, which are the heat exchangers, the duty and overall heat transfer coefficient of each main heat exchanger are first estimated taking the local flow and fluid properties into account. A conventional NH₃/H₂O AHP with shell-and-tube HXs is here compared with an NH₃/IL AHP. IL [emim][SCN] is selected as absorbent for the NH₃/IL AHP since it is one of the best performing ILs and because its viscosity and current price are the lowest among the studied ILs as shown in Table 7.

Boman et al. [37] have recently shown that the IL-based AHP systems need more heat exchanger area due to the poor heat transfer performance of the ILs, caused by their higher viscosity, lower thermal conductivity and heat capacity. In this section, PHXs are considered mainly due to its compact size and good performance of heat and mass transfer. The compact design of PHXs keeps the system volume small so that a smaller amount of expensive working fluid is sufficient to fill the system.

### 3.6.1. Equipment sizing

The floor heating system for a building in a moderate climate area, for example, the Netherlands, is taken for the economic comparison of the AHPs. The heating load will generally not exceed 60 W/m² [59]. A 3750 m² building will have a heating capacity of 225 kW and its yearly heating requirement will be, approximately, 337.5 MWh.

PHX with plate sizes 0.191 m × 0.0618 m (width × length) and plate spacing of 1.5 mm have been considered for all heat exchangers except for the SHX. The dimensions of the SHX were 0.390 m × 0.990 m with an identical plate spacing.

The overall heat transfer coefficient for each heat exchanger has been estimated taking the local fluid properties into account. A conventional NH₃/H₂O AHP with shell-and-tube HXs is here compared with an NH₃/IL AHP. IL [emim][SCN] is selected as absorbent for the NH₃/IL AHP since it is one of the best performing ILs and because its viscosity and current price are the lowest among the studied ILs as shown in Table 7.

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### 3.6.2. Economic analysis

For the economic calculation, a cost equation based on DACE [64] PHX costs has been applied to the areas reported in Table 8:

$$C_{\text{phx}} = 1.934 	imes 10^{0.6231}$$

with $C_{\text{phx}}$ expressed in k€ and $A$ expressed in m², for the SS316 PHX in the area range of 40 to 300 m². The cost of SS316 shell-and-tube HXs is taken from the same source for the area range of 30 to 200 m²:

$$C_{\text{hx}} = 3.743 	imes 10^{0.5948}$$
Table 8
Equipment size for both AHP systems, based on the same conditions applied in Table 4.

<table>
<thead>
<tr>
<th>Component</th>
<th>NH3/[emim][SCN]</th>
<th>Heat duty [kW]</th>
<th>OHTC [W m$^{-2}$ K$^{-1}$]</th>
<th>Area [m$^2$]</th>
<th>Plates number [-]</th>
<th>NH3/H$_2$O</th>
<th>Heat duty [kW]</th>
<th>OHTC [W m$^{-2}$ K$^{-1}$]</th>
<th>Area [m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEN</td>
<td>129.9</td>
<td>2390</td>
<td>2.7</td>
<td>39</td>
<td></td>
<td>138.4</td>
<td>1700</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>ABS</td>
<td>111.7</td>
<td>3010</td>
<td>2.3</td>
<td>33</td>
<td></td>
<td>138.3</td>
<td>880</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>REC</td>
<td>81.9</td>
<td>- 6980</td>
<td>2.1</td>
<td>31</td>
<td></td>
<td>21.2</td>
<td>800</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>EVA</td>
<td>95.1</td>
<td>5870</td>
<td>1.4</td>
<td>21</td>
<td></td>
<td>85.5</td>
<td>820</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>CON</td>
<td>113.3</td>
<td>400</td>
<td>53.9</td>
<td>233</td>
<td></td>
<td>86.7</td>
<td>700</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>SHX (option 1)</td>
<td>354.8</td>
<td>300</td>
<td>134.7</td>
<td>856</td>
<td></td>
<td>87.6</td>
<td>610</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>SHX (option 2)</td>
<td>292.6</td>
<td>400</td>
<td>53.9</td>
<td>233</td>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

The OHTC stands for the Overall heat transfer coefficient.

Table 9
Yearly energy requirements and yearly capital costs of the different AHP systems in comparison to a conventional boiler.

<table>
<thead>
<tr>
<th>Component</th>
<th>Heating efficiency [–]</th>
<th>Primary energy demand [MW h]</th>
<th>Primary energy cost [k€]</th>
<th>Yearly HX cost [k€]</th>
<th>Yearly work fluid cost [k€]</th>
<th>Total yearly cost [k€]</th>
<th>Yearly savings** [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler</td>
<td>0.85</td>
<td>397</td>
<td>21.8</td>
<td>–</td>
<td>–</td>
<td>21.8</td>
<td>–</td>
</tr>
<tr>
<td>AHP NH3/IL (option 1)</td>
<td>1.47</td>
<td>229</td>
<td>12.7</td>
<td>2.8</td>
<td>29.3</td>
<td>44.7</td>
<td>– 105.0</td>
</tr>
<tr>
<td>AHP NH3/IL (option 2)</td>
<td>1.31</td>
<td>258</td>
<td>14.3</td>
<td>1.6</td>
<td>8.1</td>
<td>23.8</td>
<td>– 9.2</td>
</tr>
<tr>
<td>AHP NH3/H$_2$O</td>
<td>1.37</td>
<td>246</td>
<td>13.7</td>
<td>2.5</td>
<td>0</td>
<td>15.7</td>
<td>28.0</td>
</tr>
</tbody>
</table>

The negative of the yearly saving indicates extra costs.

The yearly HX costs take into account a (linear) depreciation time of 15 years. The price of natural gas for households and commercial consumers has been taken as 55 €/MW h [65]. A boiler efficiency of 85% has been adopted, which has also been taken into account for the other AHP systems. The price of IL varies significantly depending both on production amounts and manufacturing technique. The prices of the [emim][SCN] listed in Table 7 are based on quotations in a lab scale production. It is also reported that, in large scale production, some ILs cost will reduce to 3.00 $/kg [66]. Honeywell UOP [67] reports the use of ILs to produce high-octane motor fuels and claims it is a “cost-effective solution”. This indicates that the application of ILs at an industrial scale does make their price economically more competitive. The values from the current vendors and the expected low value (3.00 $/kg) have been adopted in the present calculations. Table 9 shows the results of the economic comparison between the different AHP solutions and the use of a conventional boiler. All considered AHP options lead to both energy savings and costs savings, when the cost of IL is at a reasonable level (industrial scale production). The influence of the IL price is also shown. The NH3/IL AHP with a large minimum temperature approach in the SHX performs economically the best for current IL prices.

4. Conclusion

After a review of methods and a summary of available experimental properties, a thermodynamic model has been proposed to investigate single-effect AHPs with NH$_3$/ILs working pairs as working fluids for the purpose of the floor heating of buildings. With this model, the performance of the AHPs has been calculated for all 8 feasible NH$_3$/ILs pairs (one additional pair cannot operate under the considered conditions) and also for NH$_3$/H$_2$O. Additionally, a properties optimization work and economic analysis have been executed. Based on the work, the following conclusions could be drawn:

- The circulation ratio $f$ decreases and COP increases with an increase of the generator temperature (up to 130 °C).
- Under the considered conditions, the COP of the NH$_3$/[bmim][BF$_4$], NH$_3$/[emim][Tf$_2$N], NH$_3$/[emim][SCN] pair reaches the best performance (COP of 1.79), and along with NH$_3$/[bmim][BF$_4$], NH$_3$/[emim][Tf$_2$N], NH$_3$/[emim][SCN] all showing a higher COP than that of the NH$_3$/H$_2$O pair. Nevertheless, the circulation ratio $f$ is significantly higher than that for the NH$_3$/H$_2$O pair.
- The analysis of the generator heat requirement revealed that, high vapor quality values at the inlet of the GEN resulted in a high COP because of a lower latent heat contribution. The influence of circulation ratio, $f$, is mainly associated with the two sensible contributions (the sensible heat of both components), and a low $f$ would lead to a high COP. Neglecting the excess enthalpy, the performance changes, but the better working pairs still beat NH$_3$/H$_2$O pair in terms of COP.
- The optimum COP of this type of working pairs and for the condition

3.6.3. Other technical concerns

**STABILITY** Most ILs have been reported as being stable as liquids over a very wide temperature range. It has also been reported for some NH$_3$/IL mixtures that chemical reactions take place [24]. Chemical reactions make the cycles less reversible. The long term operation of these fluids might be a concern but NH$_3$/IL mixtures which do not undergo chemical reactions are expected to be capable of realizing a large number of operational cycles in a reliable way.

**VOLATILITY** There have also been concerns about the negligible vapor pressure of ionic liquids [68]. Although being small, very small concentrations of IL vapor may leave the generator and enter the condenser. After a large number of cycles, IL may accumulate in the evaporator requiring additional actions to bring it back to the absorber loop. Since no long term operation with these cycles has been reported, the practical performance of these mixtures still needs to be confirmed.
considered can be expected to reach 1.84 as demonstrated by the property-optimization study.
- To realize an ideal performance, the optimum IL candidates should show high absorption capabilities, large solubility differences between in- and outlet of the generator, low molecular weights and low heat capacities. The optimization study shows its potential to assist in the selection of IL as absorbers.
- Large circulation ratio combined with worse heat transfer performance in the solution heat exchanger lead to large demand of heat transfer area, which additionally requires a large amount of expensive ILS.
- An economic feasibility analysis indicates that, when the [emim] SCN would be produced at industrial scales, this NH2/IL AHPs lead to both significant energy (42%) and economic (29%) savings.

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