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1. Introduction

The rapid progress in the development of ionic liquids has generated enthusiasm for their application in many traditional fields and renewed interest in absorption refrigeration. New absorption refrigeration working pairs containing ionic liquids have gained widespread attention in the past decade. In a chapter entitled “The Latent Application of Ionic Liquids in Absorption Refrigeration” [1] that we have published 3 years ago with InTech in the book entitled “Applications of Ionic Liquids in Science and Technology” achieved impressive readership results and has so far been accessed more than 4000 times. Over the past 3 years, progress in this field has been outstanding, and a few commercially competitive new working pairs were discovered. In this chapter, we describe the latest progress in the development of a few mentionable new working pairs containing ionic liquids for absorption refrigeration and a type of completely new conceptual absorption refrigeration working pair that was proposed by us and is expected to lead to a major breakthrough in the development of absorption refrigeration.

2. Recent progress in absorption refrigeration working pairs containing ionic liquids

In the past 3 years, enthusiasm for studies on absorption refrigeration working pairs containing ionic liquids seems to have waned. The once preferred ionic liquid working pairs, such as Freon-IL, CO$_2$-IL, and NH$_3$-IL, do not receive attention from researchers any longer. However, some impressive progress is still being made for working pairs composed of a refrigerant and [RR’Im]DMP (1-R,3-R’-imidazolium dimethylphosphate).
2.1. [mmIm]DMP-CH$_3$OH

Zhao Jie et al. [2] measured the saturation vapor pressure of [mmIm]DMP-CH$_3$OH at $T = 303.15–363.15$ K and over a low methanol mole fraction range for $x$ including 0.529, 0.558, 0.582 and 0.605. Zhao Jin et al. [3] measured the saturation vapor pressure of [mmIm]DMP-CH$_3$OH at $T = 280–370$ K and over the high methanol mole fraction range for $x$ including 0.8222, 0.9123, 0.9418 and 0.9652. These experimental results were confirmed by Chen et al. [4] using the UNIFAC model and the Wilson model to predict the vapor pressure and the excess enthalpy, respectively. Figs. 1 and 2 show the predicted vapor pressure and excess enthalpy, respectively, at $T = 280–380$ K and $x = 0–1$.

![Figure 1. The predicted vapor pressure of [mmIm]DMP-CH$_3$OH.](image1)

![Figure 2. The predicted excess enthalpy of [mmIm]DMP-CH$_3$OH.](image2)
The thermodynamic performances of single effect [mmIm]DMP-CH$_3$OH absorption refrigeration have been simulated and analyzed. Fig. 3 shows the effects of the operating temperatures [condensing temperature ($T_C$), evaporating temperature ($T_E$), generating temperature ($T_G$), and absorption temperature ($T_A$)] on the circulation ratio, $f$, of the single system. From Fig. 3, the $f$ of [mmIm]DMP-CH$_3$OH is higher than that of LiBr/H$_2$O but still acceptable for operation, and the coefficient of performance (COP) of the [mmIm]DMP-CH$_3$OH absorption refrigeration will remain good, if the heat transfer areas of the regenerator are designed appropriately.

Fig. 4 shows the effects of the operating temperatures on the COP of the single system. From Fig. 4, the COP of the [mmIm]DMP-CH$_3$OH absorption refrigeration is lower than that of LiBr/H$_2$O absorption refrigeration under the same temperature conditions, but higher than that of H$_2$O/NH$_3$ absorption refrigeration under most temperature conditions. When the heat source temperature is greater than 400 K, [mmIm]DMP-CH$_3$OH absorption is still possible with a high COP close to that of LiBr/H$_2$O absorption refrigeration. In general, [mmim]DMP/methanol has excellent potential for application as the working pair in absorption refrigeration.
2.2. [dmIm]DMP-H$_2$O

Dong et al. [5] studied the thermophysical properties of the [dmIm]DMP-H$_2$O system. The vapor pressures of the [dmIm]DMP-H$_2$O system at mass fractions of ionic liquids, $\omega$, in the range of 0.10 to 0.90 were measured and correlated using a non-random two-liquid (NRTL) model. The experimental data and the model predictions are presented in Fig. 5.

![Figure 5. Vapor pressures of [dmIm]DMP-H$_2$O.](image)

The heat capacities of [dmIm]DMP-H$_2$O at a $\omega$ in the range of 0.10 to 0.90 and a temperature range of 303.15–353.15 K were determined by a BT2.15 Calvet microcalorimeter. Fig. 6 presents the experimental data and the corresponding correlation results.

![Figure 6. Heat capacities of [dmIm]DMP-H$_2$O.](image)
The performance characteristics of [dmIm]DMP-H$_2$O and LiBr-H$_2$O single effect absorption refrigeration at $t_E = 10 \, ^\circ C$, $t_C = 40 \, ^\circ C$, $t_A = 30 \, ^\circ C$, and $t_G = 80 \, ^\circ C$ were calculated and are listed in Table 1. It can be seen that the COP of the [dmIm]DMP-H$_2$O system is slightly lower than but close to that of the traditional working pair LiBr-H$_2$O.

<table>
<thead>
<tr>
<th>Working pair</th>
<th>$\omega_2$</th>
<th>$\omega_1$</th>
<th>$f$</th>
<th>COP</th>
</tr>
</thead>
<tbody>
<tr>
<td>[dmIm]DMP-H$_2$O</td>
<td>0.867</td>
<td>0.768</td>
<td>8.77</td>
<td>0.829</td>
</tr>
<tr>
<td>LiBr-H$_2$O</td>
<td>0.537</td>
<td>0.486</td>
<td>6.59</td>
<td>0.835</td>
</tr>
</tbody>
</table>

Table 1. Comparison of performance characteristics between the [dmIm]DMP-H$_2$O and LiBr-H$_2$O systems.

Fig. 7 shows the effects of changes in the $t_G$ on the COP for the [dmIm]DMP-H$_2$O and LiBr-H$_2$O systems with $t_E = 10 \, ^\circ C$, $t_C = 40 \, ^\circ C$, and $t_A = 30 \, ^\circ C$. It can be seen that as the $t_G$ is increased, the COPs of the [dmIm]DMP-H$_2$O and LiBr-H$_2$O systems stabilize after a sharp rise, and there is an optimum $t_G$ at which the COP reaches the highest value. When reaching the stable stage, the COP of the [dmIm]DMP-H$_2$O system is very close to that of the LiBr-H$_2$O system. Moreover, the operating temperature range has been extended and operational safety has been achieved for the [dmIm]DMP-H$_2$O working pair, because it has no limitation of crystallization. These findings indicate that [dmIm]DMP-H$_2$O has the potential to be novel working pair for absorption refrigeration.

2.3. [emIm]DMP-H$_2$O

Ren et al. [6] measured the vapor pressure of the [emIm]DMP-H$_2$O binary system at different IL mole fractions, $x$, ranging from 0.1 to 0.5, and the experimental data were fitted using the NRTL model (Fig. 8).
Figure 8. Vapor pressure of [emIm]DMP-H$_2$O with different mole fractions of IL and at different temperatures.

Figure 9. Specific heat capacities of [emIm]DMP-H$_2$O with different mole fractions of IL and at different temperatures.

The specific heat capacities of the [emIm]DMP-H$_2$O binary system were also measured at $T = 298.15$–$323.15$ K and with different IL mole fractions, $x$, ranging from 0.18 to 1. Fig. 9 presents the experimental data and the model predictions.

Based on the above thermophysical properties, Zhang et al. [7] investigated the thermodynamic performance of an absorption chiller employing the [emIm]DMP-H$_2$O working pair. Fig. 10 shows the effect of $t_c$ on the COP of the system at $t_c = 80$ °C, $t_g = 40$ °C, and $t_A = 35$ °C. The results indicated that, at the same $t_c$ and $t_A$, the COP of the [emIm]DMP-H$_2$O system is less than that of an aqueous solution of LiBr-H$_2$O but still greater than 0.7, whereas the $t_c$ is less than that of the LiBr-H$_2$O system. Thus, [emIm]DMP-H$_2$O has the potential to be a new working pair for use in an absorption chiller driven by low-grade waste heat or hot water generated by a common solar collector.
2.4. Summary

All three of the working pairs described above possess good theoretical cycle characteristics that are better than those of H$_2$O-NH$_3$, but still slightly lower than those of LiBr-H$_2$O. Due to the advantages of the negligible vapor pressure of the absorbent, no corrosion, and no crystallization, these three working pairs can be applied in a wider range of operating conditions than H$_2$O-NH$_3$ or LiBr-H$_2$O. Therefore, it is expected that these three working pairs have enormous potential in industrial applications and strong possibilities for commercial development.

3. A new conceptual chemical absorption refrigeration working pair consisting of ammonia and a metal chloride-containing ionic liquid

3.1. The proposal

Adsorption refrigeration is a type of environmentally friendly refrigeration that has been studied for many years. The most commonly used working pairs in adsorption refrigeration systems are ammonia–activated carbon, methanol–activated carbon, water–zeolite, ammonia–calcium chloride, and methanol–calcium chloride. The first three are physical adsorption working pairs, and the last two are chemical adsorption working pairs. The following review begins with the NH$_3$-CaCl$_2$ system.

Calcium chloride reacts with ammonia to form coordination compounds:

\[
\begin{align*}
\text{CaCl}_2 \cdot 8\text{NH}_3 + \Delta H_1 & \iff \text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 & \text{at } T_1 \\
\text{CaCl}_2 \cdot 4\text{NH}_3 + \Delta H_2 & \iff \text{CaCl}_2 \cdot 2\text{NH}_3 + 2\text{NH}_3 & \text{at } T_2 \\
\text{CaCl}_2 \cdot 2\text{NH}_3 + \Delta H_3 & \iff \text{CaCl}_2 + 2\text{NH}_3 & \text{at } T_3
\end{align*}
\]

Figure 10. Effects of $t_\text{E}$ on the COP of the [emIm]DMP-H$_2$O system.
where $\Delta H_1 - \Delta H_3$ are the enthalpies of the reaction, and $T_{e1} - T_{e3}$ are the equilibrium temperatures. Benefiting from the reaction, the most impressive advantage of the NH$_3$-CaCl$_2$ system lies in its higher adsorption capacity compared to the others, while the main disadvantages are the low performances of heat and mass transfer and the phenomena of swelling and agglomeration in the process of adsorption [8]. Much effort has been spent attempting to overcome these defects. For example, Kai Wang et al. [9] proposed a new type of compound adsorbent composed of CaCl$_2$ and an expanded graphite adsorbent, which could mitigate the deterioration of the adsorption capacity that occurs in the long-term adsorption/desorption process. Using the compound adsorbent, Liwei Wang et al. [10] designed a multi-effect heat pipe-type adsorption refrigeration system, and a COP for their system of 0.39 was reported at a low $T_e$ of -20 °C. Obviously, these improvements have little effect, and many other similar efforts [11] proved futile. The essence of all these failures can be attributed to the fact that the adsorbent is a solid. Except for CaCl$_2$, typical metal chlorides used as an ammonia adsorbent include SrCl$_2$, LiCl$_2$, and ZnCl$_2$, among others. If only the solid metal chlorides could be dissolved in ionic liquids, there would be no problem that could not be solved in the absorption or adsorption systems. Fortunately, a few ionic liquids containing metal chlorides have been synthesized, including [bmim]Zn$_2$Cl$_5$ [12], that offer high hydrothermal stability and negligible vapor pressure to perfectly meet the absorbent criteria for absorption refrigeration. Compared with a solid adsorbent or other ionic liquids, the advantage of the ionic liquid [bmim]Zn$_2$Cl$_5$ is self-evident. The chemical reaction between NH$_3$ and Zn$^{2+}$ will largely enhance the solubility of NH$_3$ in the absorbent and reduce the pressure of vapor phase as well as in the NH$_3$-CaCl$_2$ system, and no defects in heat and mass transfer, swelling, or agglomeration are a problem. Some other metal cations such as Ni$^{2+}$ [13], Cu$^{2+}$ [14], and Fe$^{3+}$ [15] were also found to dissolve in ionic liquids, and thus, a family of new conceptual chemical absorption refrigeration working pairs consisting of ammonia and metal chloride-containing ionic liquids seems ready to be developed.

### 3.2. VLE behavior of the binary system of NH$_3$-[bmim]Zn$_2$Cl$_5$

In order to reveal the promising latent application of NH$_3$-[bmim]Zn$_2$Cl$_5$ as a working pair in absorption refrigeration, the vapor pressure data of the binary system of [bmim]Zn$_2$Cl$_5$/NH$_3$ are urgently needed. In our previous work [16], VLE data for the binary system of NH$_3$-[bmim]Zn$_2$Cl$_5$ were measured and fitted using the modified UNIFAC (Dortmund) model.

#### 3.2.1. Experimental data [16]

<table>
<thead>
<tr>
<th>100x$_3$</th>
<th>$p_{exp}$/kPa</th>
<th>$p_{cal}$/kPa</th>
<th>100x$_3$</th>
<th>$p_{exp}$/kPa</th>
<th>$p_{cal}$/kPa</th>
<th>100x$_3$</th>
<th>$p_{exp}$/kPa</th>
<th>$p_{cal}$/kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>85.78±0.04</td>
<td>67.4</td>
<td>65.6</td>
<td>91.34±0.05</td>
<td>699.6</td>
<td>704.5</td>
<td>87.34±0.05</td>
<td>1287.2</td>
<td>1188.0</td>
</tr>
<tr>
<td>86.84±0.04</td>
<td>77.4</td>
<td>77.0</td>
<td>92.39±0.05</td>
<td>829.7</td>
<td>828.8</td>
<td>89.05±0.05</td>
<td>1516.9</td>
<td>1517.5</td>
</tr>
<tr>
<td>87.76±0.05</td>
<td>87.7</td>
<td>88.6</td>
<td>93.67±0.06</td>
<td>1040.8</td>
<td>1029.9</td>
<td>90.58±0.06</td>
<td>1787.3</td>
<td>1787.5</td>
</tr>
<tr>
<td>88.92±0.05</td>
<td>103.5</td>
<td>106.7</td>
<td>$T$ = 403.15 K</td>
<td>$T$ = 483.15 K</td>
<td>$T$ = 483.15 K</td>
<td>$T$ = 483.15 K</td>
<td>$T$ = 483.15 K</td>
<td>$T$ = 483.15 K</td>
</tr>
<tr>
<td>90.42±0.06</td>
<td>134.9</td>
<td>137.2</td>
<td>84.79±0.03</td>
<td>488.6</td>
<td>489.8</td>
<td>83.62±0.02</td>
<td>1081.2</td>
<td>1080.8</td>
</tr>
</tbody>
</table>
Table 2. The $p$-$T$-$x$ data of binary solutions [bmim]Zn$_2$Cl$_5$ (1) + NH$_3$ (2)

<table>
<thead>
<tr>
<th>$100x_1$</th>
<th>$p^{\text{H}}$/kPa</th>
<th>$p^{\text{T}}$/kPa</th>
<th>$100x_2$</th>
<th>$p^{\text{H}}$/kPa</th>
<th>$p^{\text{T}}$/kPa</th>
<th>$100x_3$</th>
<th>$p^{\text{H}}$/kPa</th>
<th>$p^{\text{T}}$/kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.76±0.06</td>
<td>170.8</td>
<td>174.2</td>
<td>85.90±0.04</td>
<td>544.9</td>
<td>546.5</td>
<td>84.83±0.03</td>
<td>1183.8</td>
<td>1182.7</td>
</tr>
<tr>
<td>92.77±0.07</td>
<td>210.6</td>
<td>210.8</td>
<td>86.86±0.05</td>
<td>602.3</td>
<td>603.5</td>
<td>85.88±0.04</td>
<td>1283.9</td>
<td>1284.4</td>
</tr>
<tr>
<td>93.99±0.08</td>
<td>285.6</td>
<td>269.6</td>
<td>88.08±0.05</td>
<td>687.5</td>
<td>689.4</td>
<td>87.21±0.05</td>
<td>1434.2</td>
<td>1435.1</td>
</tr>
</tbody>
</table>

$T = 343.15$ K

| $85.65±0.03$ | 119.6 | 117.8 | 91.11±0.06 | 1000.0 | 1003.1 | 90.49±0.06 | 1970.7 | 1972.3 |
| 86.72±0.04 | 137.4 | 136.5 | 92.19±0.07 | 1170.8 | 1170.1 | 88.94±0.05 | 1862.0 | 1862.2 |
| 87.63±0.05 | 155.8 | 155.6 | 93.51±0.07 | 1432.6 | 1439.7 | 83.48±0.02 | 1185.0 | 1185.3 |

$T = 363.15$ K

| $88.80±0.05$ | 183.4 | 184.8 | $T = 423.15$ K | 84.71±0.03 | 1294.9 | 1293.3 |
| 90.31±0.06 | 230.9 | 234.5 | 84.39±0.03 | 668.4 | 669.3 | 85.77±0.04 | 1400.7 | 1400.5 |
| 91.66±0.06 | 286.5 | 294.5 | 85.53±0.04 | 740.5 | 741.4 | 87.11±0.05 | 1559.8 | 1559.2 |

$T = 383.15$ K

| $89.41±0.06$ | 1100.9 | 1101.8 | 83.32±0.02 | 1300.6 | 1300.4 |
| 85.45±0.03 | 202.5 | 202.2 | 90.88±0.06 | 1313.0 | 1314.9 | 84.57±0.03 | 1414.3 | 1414.3 |
| 86.52±0.04 | 230.7 | 230.7 | 91.99±0.07 | 1523.0 | 1523.6 | 85.65±0.04 | 1525.2 | 1525.2 |

$T = 323.15$, 343.15, 363.15, 383.15, 403.15, 423.15, 443.15, 463.15, 483.15, 503.15, 523.15, 543.15, and 563.15 K are summarized in Table 2.

The uncertainties in the NH$_3$ mole fraction in the binary solution, which can be due to the random and systematic errors in the experimental method and the calculation accuracy of the ammonia equation of state (EOS), are also presented in the table.

The pressure-temperature-composition ($p$-$T$-$x$) data of the binary solutions [bmim]Zn$_2$Cl$_5$ (1) + NH$_3$ (2) with NH$_3$ mole fractions of $x_2 = 0.83–0.94$ at $T = 323.15$, 343.15, 363.15, 383.15, 403.15, 423.15, 443.15, 463.15, 483.15, 503.15, 523.15, 543.15, and 563.15 K are summarized in Table 2.
3.2.2. The modified UNIFAC (Dortmund) model [16]

Because of the non-volatilization of the ionic liquid [bmim]Zn$_2$Cl$_5$, the vapor phase of the binary system [bmim]Zn$_2$Cl$_5$ (1) + NH$_3$ (2) consists only of NH$_3$, and the total pressure $p$ of the binary solution can be given by [17],

$$p = x_2 \gamma_2 P_2^S \exp \left( \frac{V_2^L - B_2(p - P_2^S)}{RT} \right)$$  \hspace{1cm} (1)

where $x_2$ is the mole fraction of NH$_3$ in the binary solution, $\gamma_2$ is the activity coefficient of NH$_3$, $V_2^L$ is the liquid mole volume of NH$_3$, $B_2$ is the second virial coefficient in the ammonia EOS, and $P_2^S$ is the vapor pressure of pure NH$_3$. When the temperature $T$ is below the $T_C$, $P_2^S$ is equal to the saturation vapor pressure, $P_S$, which can be calculated by [18],

$$\ln P_2^S = \frac{1}{T_r - 0.101947} \left( -4.2522 T_r^2 + 7.929445 T_r^3 + 0.38077837 T_r^7 - 4.039557 \right)$$  \hspace{1cm} (2)

where $T_r$ is the ratio of the solution temperature $T$ and $T_C$. When the temperature $T$ is higher than the $T_C$, $P_2^S$ is defined as the pure NH$_3$ pressure at $T$ and the critical mole fraction $V_C$, which can be calculated by the RK type EOS as follows [19]:

$$P_2^S = \frac{RT}{V_C - b} \left( \frac{a(T)}{V_C(V_C + b)} \right)$$  \hspace{1cm} (3)

$$a(T) = 0.42748 \alpha(T) R^2 T_r^2 \frac{1}{P_C}$$  \hspace{1cm} (4)

$$b = 0.08664 RT_c / P_C$$  \hspace{1cm} (5)

where the temperature dependent term $\alpha(T)$ can be written by:

$$\alpha(T) = \sum_{k=0}^{2} \beta_k (1/T_r - T_C)^k$$  \hspace{1cm} (6)

The EOS constants for NH$_3$ $\beta_k$ and the critical parameters $T_C$, $V_C$, and $P_C$ are given in Table 3.

<table>
<thead>
<tr>
<th>$\beta_0$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$T_C / K$</th>
<th>$P_C / kPa$</th>
<th>$V_C / m^3mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00027</td>
<td>0.45689</td>
<td>-0.05772</td>
<td>406.15</td>
<td>11424</td>
<td>0.00427</td>
</tr>
</tbody>
</table>

Table 3. EOS constants and critical parameters for NH$_3$. 
In the UNIFAC model, the excess Gibbs free energy is composed of two contributing parts, the combinatorial part and the residual part, and the activity coefficient $\gamma_i$ can be given as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$  \hspace{1cm} (7)

where $\gamma_i^C$ is the combinatorial activity coefficient and $\gamma_i^R$ is the residual activity coefficient.

The combinatorial activity coefficient $\gamma_i^C$ describes the repulsive interaction attributed to the molecular size and shape, which can be calculated by:

$$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + \frac{Z}{2} \ln \frac{\vartheta_i}{\varphi_i} + \ell_i - \frac{\varphi_i}{x_i} \sum_{j} x_j f_j$$  \hspace{1cm} (8)

$$\ell_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1)$$  \hspace{1cm} (9)

$$\vartheta_i = q_i x_i / \sum_j q_j x_j$$  \hspace{1cm} (10)

$$\varphi_i = r_i x_i / \sum_j r_j x_j$$  \hspace{1cm} (11)

$$q_i = \sum v_k^{(i)} Q_k$$ \hspace{1cm} (12)

$$r_i = \sum v_k^{(i)} R_k$$  \hspace{1cm} (13)

where $Z$ is normally set to 10, $v_k^{(i)}$ is the number of group $k$ in component $i$, and $R_k$ and $Q_k$ are the volume and surface parameters of the group $k$, respectively. The values of $R_k$ and $Q_k$ for the group used in our experiment are listed in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>[bmim]$^+$</th>
<th>Zn$^{2+}$</th>
<th>Cl$^-$</th>
<th>NH$_3$$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_i$</td>
<td>6.0534 [20]</td>
<td>3.0 [21]</td>
<td>0.6560 [20]</td>
<td>0.8239 [22]</td>
</tr>
<tr>
<td>$Q_i$</td>
<td>4.7910 [20]</td>
<td>3.0 [21]</td>
<td>0.6730 [20]</td>
<td>0.7780 [22]</td>
</tr>
</tbody>
</table>

Table 4. Volume parameters $R_i$ and surface parameters $Q_i$.

The residual activity coefficient $\gamma_i^R$ accounts for the intermolecular forces resulting from the corresponding group interaction, which is described as the summation of the group activity coefficient $\Gamma$ for group $k$ of component $i$. 
\[ \ln \gamma_k^i = \sum_{k}^{N} \ln \gamma_k^i ((\ln \Gamma_k^i - \ln \Gamma_k^{i(0)}) \]  

(14)

where \( \Gamma_i \) and \( \Gamma_k^{i(0)} \) are the activity coefficients for group \( k \) in binary solution and in the component \( i \), respectively, and can be described as:

\[ \ln \Gamma_k^i = Q_k^i \left[ 1 - \ln \left( \sum_{m} \sum_{n} \theta_m \phi_{m,n} \right) - \sum_{m} \left( \sum_{n} \theta_m \phi_{m,n} \right) \right] \]

(15)

\[ \theta_m = Q_m X_m / \sum_{n=1}^{N} Q_n X_n \]

(16)

\[ X_m = \sum_{j=1}^{M} \nu_{m,j} x_j / \sum_{j=1}^{M} \sum_{n=1}^{N} \nu_{n,j} x_j \]

(17)

Eqs. 15–17 can also be used to calculate \( \ln \Gamma_k^{i(0)} \), except that the group composition variable \( X_m \) is now the group fraction of group \( k \) in component \( i \). For the modified UNIFAC (Dortmund) model, the group interaction parameters between groups \( n \) and \( m \), \( \phi_{n,m} \), is described as:

\[ \phi_{n,m} = \exp \left( \frac{a_{nm}}{K} - b_{nm} T + c_{nm} T \right) \]

(18)

where \( a_{nm} \) (K\(^{-1}\)), \( b_{nm} \), and \( c_{nm} \) (K) are the adjustable interaction parameters for correlating the experimental vapor pressure data. The corresponding correlation results are listed in Table 5.

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>( a_{nm} / K^1 )</th>
<th>( b_{nm} )</th>
<th>( c_{nm} / K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>[bmim](^{+})</td>
<td>0.00617</td>
<td>-1.9768</td>
<td>-378.1920</td>
</tr>
<tr>
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<td>[bmim](^{+})</td>
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<td>[bmim](^{+})</td>
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<td>-82.6723</td>
<td>-5307.7958</td>
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<td>Zn(^{2+})</td>
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<td>59.8376</td>
<td>-5434.4813</td>
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</tbody>
</table>

Table 5. Adjustable interaction parameters for UNIFAC model
The $P-T-x$ phase diagrams with symbols for experimental data and lines for the UNIFAC model calculations are shown in Fig. 11. It can be seen from the figure that with an increase in the NH$_3$ mole fraction, the vapor pressure also increases, and the rising trend becomes increasingly more obvious. With an increase in the binary solution temperature, the vapor pressure increases rapidly. When the temperature is below the T$_c$ of NH$_3$, the rate of increase becomes more rapid, but when the temperature is higher than the T$_c$ of NH$_3$, the rate of increase tends to slow and the vapor pressure even declines slightly.

Figure 11. $P-T-x$ phase diagrams (Lines: calculated with the UNIFAC model. Symbols: experimental data) [16].

Figure 12. Comparison of experimental data and the UNIFAC model calculations [16].
A comparison of the experimental data and the UNIFAC model calculations is shown in Fig. 12. All deviations are below 5.0% and are mainly produced by the uncertainties in the volumes of the high pressure vessel (0.7%) and liquid phase of binary system (1.1%), the weights of \([\text{bmim}]\text{Zn}_2\text{Cl}_5\) (0.01%) and \(\text{NH}_3\) (0.05%), the temperature distribution in the high pressure vessel (0.7%), EOS calculation accuracy (1.2%), and the fitting uncertainty (1.6%). Based on the above uncertainties, the total uncertainty of the measurements is estimated to be within 4.3%.

3.2.3. Comparison with normal ionic liquids and \(\text{ZnCl}_2\)

Fig. 13 compares the vapor pressures of \([\text{bmim}]\text{Zn}_2\text{Cl}_5/\text{NH}_3\) solutions with \(x_2 = 0.9507\) and 0.9231 to those of \(\text{ZnCl}_2\) \(6\text{NH}_3\) [23] at \(T = 330–420\) K. When \(x_2 = 0.9507\), the \(\text{NH}_3\) mass fraction of the binary solution is equal to the \(\text{NH}_3\) mass fraction in \(\text{ZnCl}_2\) \(6\text{NH}_3\), and when \(x_2 = 0.9231\), the mole ratio of \(\text{NH}_3\) and \(\text{Zn}^{2+}\) is 6, which is equal to that in \(\text{ZnCl}_2\) \(6\text{NH}_3\). From Fig. 13, the vapor pressures of \(\text{NH}_3\) in \([\text{bmim}]\text{Zn}_2\text{Cl}_5\) with \(x_2 = 0.9507\) and 0.9231 are 2–3 times higher than that of \(\text{ZnCl}_2\) \(6\text{NH}_3\), which can be attributed to the effects of the ionic liquid \([\text{bmim}]\text{Cl}\) on the complexation reaction production of \(\text{NH}_3\) and \(\text{Zn}^{2+}\) ions.

![Figure 13. Comparison of vapor pressures of \(\text{NH}_3\)-[bmim]Zn\(_2\)Cl\(_5\) solution and ZnCl\(_2\) 6NH\(_3\) [16].](image)

Fig. 14 compares the vapor pressure of the \(\text{NH}_3\)-[bmim]Zn\(_2\)Cl\(_5\) solution and ammonia solutions containing ionic liquids [19] [emim][Ac], [emim][SCN], [emim][EtOSO\(_3\)], and [DMEA][Ac] at \(T = 348\) K and \(x_2 = 0–1\). From Fig. 14, the vapor pressure of \(\text{NH}_3\) in [bmim]Zn\(_2\)Cl\(_5\) is one order of magnitude smaller than that in normal ionic liquids at \(x_2 = 0–0.95\), which means that the complexion reaction of \(\text{NH}_3\) and \(\text{Zn}^{2+}\) ions can largely reduce the vapor pressure of \(\text{NH}_3\) in the ionic liquid and largely enhance the solubility of \(\text{NH}_3\) in the ionic liquid.

Based on the results in Figs. 13 and 14, the absorption characteristics of [bmim]Zn\(_2\)Cl\(_5\) are much better than those of normal ionic liquids but slightly lower than those of ZnCl\(_2\). Additionally,
the liquid form of [bmim]ZnCl₂ offers a major advantage over ZnCl₂, which will completely resolve the abovementioned limitations to improve the cycle performance for ZnCl₂/NH₃ adsorption refrigeration. Therefore, working pairs of NH₃-[bmim]ZnCl₂ have good latent application potential in absorption refrigerator and heat pump operation.

3.3. Heat capacities and excess enthalpies of the NH₃-[bmim]ZnCl₂ system

In order to investigate the cycle characteristics of [bmim]ZnCl₂/NH₃ absorption refrigeration, data for the heat capacities of [bmim]ZnCl₂ and excess enthalpies of [bmim]ZnCl₂/NH₃ are urgently needed. In our previous work, the heat capacities of [bmim]ZnCl₂ for \( T = 210.15–383.15 \) K were obtained by differential scanning calorimetry (DSC), and the excess enthalpies of [bmim]ZnCl₂/NH₃ at various ammonia mole fractions for \( T = 288.15–333.15 \) K were measured experimentally. The data for excess enthalpies were fit by a five-parameter NRTL model. Based on the heat capacity of [bmim]ZnCl₂ and the excess enthalpy of [bmim]ZnCl₂/NH₃, the enthalpies of [bmim]ZnCl₂/NH₃ solution at \( x_1 = 0–1 \) for \( T = 273.15–343.15 \) K were calculated.

3.3.1. Heat capacities of [bmim]ZnCl₂

Fig. 15 shows the result of TG scanning for [bmim]ZnCl₂, which was determined using a TGA/SDT instrument. Onset of a 2.5% weight loss in a nitrogen atmosphere occurs at 676.15 K, and approximately 40% of the mass is gone by 774.15 K, which is a typical volatilization temperature for imidazolium salts. Continued heating of [bmim]ZnCl₂ eventually results in a constant weight near 1043.15 K, with a residual weight of 36.4%. These results indicate that [bmim]ZnCl₂ possesses high thermal stability at \( T < 673.15 \) K.
Figure 15. Thermogravimetric (TG) scan results for \([\text{bmim}]\text{Zn}_2\text{Cl}_5\).

Figure 16. DSC scanning results for \([\text{bmim}]\text{Zn}_2\text{Cl}_5\): (a) variations in heat flow, \(q_m\), and specific heat capacity, \(c_p\), along with temperature variations for \([\text{bmim}]\text{Zn}_2\text{Cl}_5\); (b) \(c_p-T\) diagram of \([\text{bmim}]\text{Zn}_2\text{Cl}_5\) for \(T = 243.15-383.15\) K.

Fig. 16(a) shows the variation in the specific heat flow, \(q_m\), and the specific heat capacity, \(c_p\), along with temperature variations for \([\text{bmim}]\text{Zn}_2\text{Cl}_5\). The specific heat flow increases with an increase in temperature. The rate of increase of the specific heat flow rises at \(T < 243.15\) K, and the variation in the rate of increase of the specific heat flow is minor for \(T > 243.15\) K. The specific heat capacity increases with an increase in the \([\text{bmim}]\text{Zn}_2\text{Cl}_5\) temperature at \(T < 243.15\) K, and the rate of increase also increases. The specific heat capacity presents an increasing trend after a decline for \(T > 243.15\) K. These results indicate that the melting temperature of \([\text{bmim}]\text{Zn}_2\text{Cl}_5\) is near 243.15 K. By careful observation, it is found that variations in the specific heat capacity with \(T > 251.15\) K can be well fitted by the following quadratic equation:

\[
c_p = 2.39327 - 0.00691T + 0.000011767T^2
\]  

(19)
Fig. 16(b) shows the $c_p$-$T$ diagram for $T = 243.15$–$383.15$ K. The symbols represent the experimental data, and the lines represent the calculated conic curve. It can be seen that variation in the specific heat capacity with temperature is accurately described by the quadratic curve.

### 3.3.2. Experimental data for excess enthalpy of NH$_3$-[bmim]Zn$_2$Cl$_5$

Temperature-component-molar excess enthalpy ($T$-$x$-$H^E$) data for the binary systems [bmim]Zn$_2$Cl$_5$ (2) + NH$_3$ (1) at ammonia mole fractions of $x_1 = 0.60$–0.95 and $T = 288.15$, 303.15, 318.15, and 333.15 K are summarized in Table 6. Uncertainties in the temperature, ammonia mole fraction, and molar excess enthalpy are also presented in the table. The uncertainties are due to random errors as well as systematic errors for the experimental apparatus and the calculation accuracy of the UNIFAC model for the VLE of NH$_3$/[bmim]Zn$_2$Cl$_5$. With an increase in the ammonia mole fraction, $x_1$, the molar excess enthalpy presents an increasing trend after an initial decline.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$x_1$</th>
<th>$H^E$/J/mol</th>
<th>$T$/K</th>
<th>$x_1$</th>
<th>$H^E$/J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>0.617</td>
<td>-6052</td>
<td>318.15</td>
<td>0.631</td>
<td>-6237</td>
</tr>
<tr>
<td>288.15</td>
<td>0.709</td>
<td>-6446</td>
<td>318.15</td>
<td>0.725</td>
<td>-6795</td>
</tr>
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<td>288.15</td>
<td>0.819</td>
<td>-6385</td>
<td>318.15</td>
<td>0.796</td>
<td>-6825</td>
</tr>
<tr>
<td>288.15</td>
<td>0.935</td>
<td>-4778</td>
<td>318.15</td>
<td>0.877</td>
<td>-6301</td>
</tr>
<tr>
<td>303.15</td>
<td>0.614</td>
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<td>333.15</td>
<td>0.622</td>
<td>-6233</td>
</tr>
<tr>
<td>303.15</td>
<td>0.718</td>
<td>-6657</td>
<td>333.15</td>
<td>0.698</td>
<td>-6851</td>
</tr>
<tr>
<td>303.15</td>
<td>0.782</td>
<td>-6665</td>
<td>333.15</td>
<td>0.773</td>
<td>-6870</td>
</tr>
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<td>303.15</td>
<td>0.866</td>
<td>-6242</td>
<td>333.15</td>
<td>0.854</td>
<td>-6638</td>
</tr>
<tr>
<td>303.15</td>
<td>0.947</td>
<td>-4393</td>
<td>333.15</td>
<td>0.931</td>
<td>-5412</td>
</tr>
</tbody>
</table>

**Table 6.** Mole excess enthalpy of binary systems [bmim]Zn$_2$Cl$_5$ (1) + NH$_3$ (2).

### 3.3.3. NRTL model

Based on the local composition representation of the excess Gibbs energy, $G^E$, Renon and Prausnitz [24] proposed the NRTL model. The $G^E$ for the NRTL model can be described by:

$$ G^E = \frac{RT}{x_1 x_2} \left( \frac{r_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{r_{12} G_{12}}{x_1 + x_2 G_{12}} \right) \quad (20) $$

$$ r_{12} = \frac{g_{12} - g_{22}}{RT}, \quad r_{21} = \frac{g_{21} - g_{11}}{RT} \quad (21) $$
\[ G_{12} = \exp(-\alpha \tau_{12}), \ G_{21} = \exp(-\alpha \tau_{21}) \]  

(22)

where \( g_{ij} \) and \( g_{jj} \) are the interaction energy between \( ij \) and \( jj \) component pairs, respectively, and \( \alpha \) is the non-random parameter. The relationship between \( G^E \) and the activity coefficient is given by:

\[
G^E = RT \sum_i \ln \gamma_i + \sum_{ij} \frac{\partial G^E}{\partial x_i} \tau_{ij} \rho \eta_{ij}
\]  

(23)

Therefore, the activity coefficients of components 1 and 2 in a binary mixture can be written as:

\[
\ln \gamma_1 = x_2 \left[ \tau_{12} \left( \frac{G_{11}}{x_1 + x_2 G_{21}} \right)^2 + \left( \frac{x_2 G_{12}}{(x_1 + x_2 G_{21})^2} \right) \right]
\]  

(24)

\[
\ln \gamma_2 = x_1 \left[ \tau_{21} \left( \frac{G_{22}}{x_2 + x_1 G_{12}} \right)^2 + \left( \frac{x_1 G_{21}}{(x_2 + x_1 G_{12})^2} \right) \right]
\]  

(25)

The definition of the activity coefficient for ammonia, \( \gamma_1 \), is presented in our previous work [16]. For the NRTL model, the interaction energy between the \( ij \) and \( jj \) component pairs are defined as:

\[ g_{12} - g_{22} = A_1 + B_1 T \]  

(26)

\[ g_{21} - g_{11} = A_2 + B_2 T \]  

(27)

The Gibbs-Helmholtz equation for excess enthalpy is:

\[
\frac{H^E}{T^2} = \left. \frac{\partial \left( \frac{G^E}{T} \right)}{\partial T} \right|_{P,x}
\]  

(28)

For the five-parameter NRTL model, the excess enthalpy can be calculated by:

\[
H^E = -x_1 x_2 \left[ \frac{A_1 G_{12} \left[ x_1 \tau_{12} (\alpha \tau_{12} - 1) - x_2 G_{21} \right]}{(x_1 + x_2 G_{21})^2} + \frac{A_2 G_{12} \left[ x_2 \tau_{12} (\alpha \tau_{12} - 1) - x_1 G_{21} \right]}{(x_2 + x_1 G_{12})^2} \right]
\]  

(29)

The correlation results are shown in Table 7.
Table 7. Binary parameters and non-random parameters for NRTL model

<table>
<thead>
<tr>
<th>α</th>
<th>A J/mol⁻¹</th>
<th>B J/mol⁻¹ K⁻¹</th>
<th>A J/mol⁻¹</th>
<th>B J/mol⁻¹ K⁻¹</th>
</tr>
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<tbody>
<tr>
<td>0.1043</td>
<td>14062.6306</td>
<td>419.6197</td>
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</table>

Figure 17. T-x-H° diagram of [bmim]Zn₂Cl₅/NH₃ for T = 288.15–333.15 K.

Fig. 17 shows the T-x-H° diagram for the binary system of [bmim]Zn₂Cl₅/NH₃ at T = 288.15–333.15 K. The symbols represent the experimental data, and the lines represent the calculations from the NRTL model. From Fig. 17, with an increase in the NH₃ mole fraction, the excess enthalpy shows an increasing trend after a decline. There are minimum excess enthalpies for each temperature: -6555.7, -6707.1, -6846.3, and -6974.7 J/mol appear at x₁ = 0.772, 0.774, 0.776, and 0.777 for T = 288.15, 303.15, 318.15, and 333.15 K, respectively.

Figure 18. Absolute deviations and relative deviations with the NRTL model.
Fig. 18 shows the absolute deviations and relative deviations between the experimental data and the values predicted by the NRTL model for excess enthalpy data. The results indicate that all deviations for excess enthalpy data are less than 3.9%. The measurement deviations are mainly produced by the uncertainties in volumes of the high pressure vessels (0.5%), the little tank (0.5%) and the liquid phase of binary system (0.2%); the weights of [bmim]Zn₂Cl₅ (0.01%), NH₃ (0.05%) and water (0.01%); temperature distributions in the water bath (1.4%) and the bath container (1.2%); and the UNIFAC calculationaccuracies (0.9%). Based on the above uncertainties, the total uncertainty of measurement is estimated to be less than 4.8%.

3.3.4. Enthalpy of [bmim]Zn₂Cl₅/NH₃ solution

The enthalpy of a solution of [bmim]Zn₂Cl₅/NH₃ at T and a given NH₃ mass fraction ω₁ can be calculated by:

\[ h = (1 - ω₁)h₁ + ω₁h₂ + h^E \]  

(30)

The enthalpy of [bmim]Zn₂Cl₅, \( h_1 \), can be calculated by:

\[ h_1 = \int_{T_0}^{T} c_p \, dT \]  

(31)

where \( c_p \) is the specific heat capacity of [bmim]Zn₂Cl₅, which can be calculated using Eq. (1), and \( T_0 \) is defined as 273.15 K. The enthalpy of NH₃ can be calculated by [19]:

\[ h_2 = \sum_{i=0}^{N} a_i (T - 273.15)^i \]  

(32)

Figure 19. Calculations for enthalpies of [bmim]Zn₂Cl₅/NH₃ solution at \( x_1 = 0-1 \) for \( T = 273.15-343.15 \) K.
Fig. 19 shows the calculated enthalpies for [bmim]Zn$_2$Cl$_5$/NH$_3$ solution at $\omega_1 = 0–1$ and $T = 273.15–343.15$ K. Based on the VLE properties and the enthalpies of [bmim]Zn$_2$Cl$_5$/NH$_3$ solutions, the thermodynamic performances of the [bmim]Zn$_2$Cl$_5$/NH$_3$ absorption system can be investigated.

3.4. Thermodynamic analysis of an absorption system using NH$_3$-[bmim]Zn$_2$Cl$_5$ as the working pair [25]

In our previous work, the modified UNIFAC model was used to describe the VLE properties of [bmim]Zn$_2$Cl$_5$/NH$_3$ [16] and the NRTL model was used to predict the excess enthalpic properties of [bmim]Zn$_2$Cl$_5$/NH$_3$. Based on a single-effect absorption refrigeration model, the thermodynamic performance of the [bmim]Zn$_2$Cl$_5$/NH$_3$ absorption system was simulated and compared with that of the NaSCN/NH$_3$ adsorption system. The coefficients of performance for cooling (COP) and heating (COP*) and circulation ratios under the condition of a subzero evaporating temperature were calculated and analyzed.

3.4.1. System description and simulation

Fig. 20 shows a schematic diagram of the single effect absorption system. The main system is composed of the generator (G), the absorber (A), the condenser (C), the evaporator (E), the regenerator (R), the valves (V), and the solution pump (P). In Fig. 20, the status point numbers are given, and the fluids at each point are marked: $i$ denotes the [bmim]Zn$_2$Cl$_5$/NH$_3$ solution from the absorber with a high NH$_3$ mass fraction, $ii$ denotes the [bmim]Zn$_2$Cl$_5$/NH$_3$ solution from the generator with a low NH$_3$ mass fraction, and $iii$ denotes the refrigerant NH$_3$. The symbols $q_c$, $q_C$, $q_A$, and $q_G$ represent the heat flow of the evaporator, the condenser, the absorber, and the generator, respectively.

![Figure 20. Schematic diagram of the single effect absorption system [25].](image)
In order to simulate the thermodynamic performance of an absorption system using 
[bmim]Zn$_2$Cl$_5$/NH$_3$ as a working pair, several assumptions were made as follows [25]:

1. The simulation is conducted under steady state;
2. The vapor pressure losses are neglected, the pressure of the evaporator is equal to that of 
the absorber, and the pressure of the condenser is equal to that of the generator;
3. The refrigerant flowing out of the condenser is in a saturated liquid state, and the 
refrigerant flowing out of the evaporator is in a saturated gas state;
4. The heat recovery rate of the regenerator is set to 0.80 [26]; and
5. The thermal losses and pumping work are negligible.

The mass and energy conservation equations for the evaporator are given by:

\[ m_E = m_{in} \]  \hspace{1cm} (33)

\[ q_E = m_i h_i - m_{in} h_{in} \]  \hspace{1cm} (34)

The mass and energy conservation equations for the condenser are given by:

\[ m_C = m_{in} \]  \hspace{1cm} (35)

\[ q_C = m_i h_i - m_{in} h_{in} \]  \hspace{1cm} (36)

For the absorber, the mass conservation equation of the solution, the mass conservation 
equation of IL, and the energy conservation equation are given by:

\[ m_s = m_{in} + m_{abs} \]  \hspace{1cm} (37)

\[ m_i (1 - \omega_s) = m_{in} + m_{IL} (1 - \omega_{IL}) \]  \hspace{1cm} (38)

\[ q_A = m_i h_i + m_{IL} h_{IL} - m_{abs} h_{abs} \]  \hspace{1cm} (39)

For the generator, the mass conservation equation of the solution, the mass conservation 
equation of IL, and the energy conservation equation are given by:

\[ m_i = m_{in} + m_{out} \]  \hspace{1cm} (40)
\[ m_2(1 - \omega_2) = m_1 + m_3(1 - \omega_3) \]  
(41)

\[ q_G = m_2h_3 + m_1h_1 - m_2h_2 \]  
(42)

For the regenerator, the energy conservation equation is given by:

\[ m_2(h_2 - h_s) = m_1(h_{i0} - h_s) \]  
(43)

Based on the above assumptions and the conservation equations for mass and energy conservation, the heat flow values of \( q_G, q_C, q_E, \) and \( q_A; \) mass flow values of \( m_2 \) and \( m_3; \) and mass fractions of \( \omega_2 \) and \( \omega_3 \), can be calculated. The circulation ratio \( (f) \) is calculated by:

\[ f = \frac{m_1}{m_2} = \frac{1 - \omega_2}{\omega_2 - \omega_3} \]  
(44)

The COP for cooling is defined by:

\[ COP = \frac{q_h}{q_G} \]  
(45)

The exergy efficiency \( (\eta_{ex}) \) for cooling is given by:

\[ \eta_{ex} = \frac{\theta_G \left( T_G - 1 \right)}{\theta_C \left( 1 - \frac{T_C}{T_G} \right)} \]  
(46)

The COP* for heating is defined as:

\[ COP^* = \frac{q_A + q_C}{q_G} = 1 + \frac{q_E}{q_G} \]  
(47)

The exergy efficiency for cooling \( (\eta_{ex}^*) \) is given by:

\[ \eta_{ex}^* = \frac{\theta_C \left( 1 - \frac{T_h}{T_C} \right) + \theta_A \left( 1 - \frac{T_A}{T_C} \right)}{\theta_G \left( 1 - \frac{T_G}{T_A} \right)} \]  
(48)
3.4.2. Results and discussion

Fig. 22 shows variations in the COP and $\eta_{\text{ex}}$ of [bmim]$\text{ZnCl}_2$/NH$_3$ absorption refrigeration with variations in $t_A$ and $t_C$ at a $t_G = 90$ °C and $t_E = -10$ °C. These results show that both the COP and $\eta_{\text{ex}}$ decline with increases in $t_A$ and $t_C$. This is because increases in $t_A$ and $t_C$ lead to a decrease in the mass fraction of solution from the absorber ($\omega_2$) and an increase in the mass fraction of solution from the generator ($\omega_3$). These changes in both $\omega_2$ and $\omega_3$ result in a decrease of $q_E$.

The slopes of both the COP and $\eta_{\text{ex}}$ curves are less steep when $t_A$ and $t_C$ are lower, and as $t_A$ and $t_C$ continue to increase, the slopes become increasingly steep. This can be explained by the fact that, with the continuous increases in $t_A$ and $t_C$, the difference between $\omega_2$ and $\omega_3$ continues to become smaller. By comparison, the thermal performance of the [bmim]$\text{ZnCl}_2$/NH$_3$ system is better than that of the NaSCN/NH$_3$ system when $t_A$ and $t_C$ are low. However, when $t_A$ and $t_C$ are high, the thermal performance of the NaSCN/NH$_3$ system is better than that of the [bmim]$\text{ZnCl}_2$/NH$_3$ system, and the upper operating limit of $t_A$ and $t_C$ for NaSCN/NH$_3$ is higher than that for the [bmim]$\text{ZnCl}_2$/NH$_3$ system. This can also be explained by the properties of NH$_3$ solubility in [bmim]$\text{ZnCl}_2$ and NaSCN. The higher solubility of NH$_3$ in [bmim]$\text{ZnCl}_2$ ensures that the [bmim]$\text{ZnCl}_2$/NH$_3$ system possesses better thermal performance than the NaSCN/NH$_3$ system with operating conditions of low $t_A$ and $t_C$. The stronger combination of NH$_3$ and [bmim]$\text{ZnCl}_2$ demonstrates that the upper operating limit of $t_A$ and $t_C$ for the [bmim]$\text{ZnCl}_2$/NH$_3$ system are lower than those of the NaSCN/NH$_3$ system.

![Figure 21](image1.png)

**Figure 21.** Variations in the COP and $\eta_{\text{ex}}$ of [bmim]$\text{ZnCl}_2$/NH$_3$ absorption refrigeration with changes in $T_G$ for $t_A = t_C = 25$ °C and $t_E = -10$ °C [25].

Fig. 23 shows the effects of $t_C$ on the COP for $t_C = 110-230$ °C with $t_A = t_C = 35$ °C and $t_E = -10$ °C, -20 °C, -30 °C, or -40 °C. With an increase in $t_C$, the COP presents a trend of first increasing and then decreasing. The reason for this trend is that the increase in $t_C$ has both positive and negative effects on the COP. The positive and negative effects are the same as indicated by the analysis of the trend in COP shown in Fig. 2. When $t_C$ is lower, the positive effect is predominant, and
the COP increases with an increase in \( t_G \). With a further increase in \( t_G \), the negative effect is gradually enhanced, and the rate at which the COP increases is continually reduced until it finally becomes negative. When \( t_E \) is higher, the negative effect is predominant, and the COP decreases with an increase in \( t_E \). For \( t_E = -10 \, ^\circ C \), -20 \, ^\circ C \), -30 \, ^\circ C \), and -40 \, ^\circ C \), the maximum COPs for the [bmim]Zn\(_2\)Cl\(_5\)/NH\(_3\) system of 0.54, 0.48, 0.42, and 0.35 appear at \( t_G = 133 \, ^\circ C \), 161 \, ^\circ C \), 188 \, ^\circ C \), and 225 \, ^\circ C \), respectively. When \( t_E = -10 \, ^\circ C \) and -20 \, ^\circ C \), the maximum COPs for the NaSCN/NH\(_3\) system occur at \( t_G = 81 \, ^\circ C \) and 98 \, ^\circ C \), respectively [27]. These results indicate that the required temperature of the heat source for the [bmim]Zn\(_2\)Cl\(_5\)/NH\(_3\) system is higher than that of the NaSCN/NH\(_3\) system.
Fig. 24. Effects of $t_G$ on $f$ for $t_G = 110–230 \, ^\circ C$, $t_A = t_C = 35 \, ^\circ C$ and $t_E = -10 \, ^\circ C$, -20 $^\circ C$, -30 $^\circ C$, or -40 $^\circ C$ [25]. Fig. 24 shows effects of $t_G$ on the $f$ for $t_G = 110–230 \, ^\circ C$ with $t_A = t_C = 35 \, ^\circ C$ and $t_E = -10 \, ^\circ C$, -20 $^\circ C$, -30 $^\circ C$, or -40 $^\circ C$. With an increase in $t_G$, the $f$ declines, because the increase in $t_G$ is conducive to desorption of NH$_3$ in the generator. With an increase in $t_E$, the $f$ grows, because the increase in $t_E$ will decrease the absorption pressure of the absorber. Thus, the absorption ability of the absorber will be decreased. The $f$ is an important parameter for absorption refrigeration. An increase in the $f$ will lead to an increase in the amount of energy used to heat the solution from $t_A$ to $t_G$. If the $f$ is greater than 10, the COP decreases, even when the efficiency of the regenerator is greater than 0.9. For $t_E = -10 \, ^\circ C$, -20 $^\circ C$, and -30 $^\circ C$, the circulation ratios are less than 10 when $t_G$ is greater than 115$^\circ C$, 139 $^\circ C$, or 187 $^\circ C$, respectively. Based on the results shown in Figs. 23 and 24, the [bmim]Zn$_2$Cl$_5$/NH$_3$ system can be used when $t_E = -10$ to -30 $^\circ C$.

Fig. 25. Effects of $t_G$ on the COP* for $t_G = 170–300 \, ^\circ C$ with $t_A = t_C = 55 \, ^\circ C$, 57 $^\circ C$, 59 $^\circ C$, or 61 $^\circ C$ and $t_E = -10 \, ^\circ C$ [25]. Fig. 25 shows the effects of $t_G$ on the COP* for $t_G = 170–300 \, ^\circ C$ with $t_A = t_C = 55 \, ^\circ C$, 57 $^\circ C$, 59 $^\circ C$, or 61 $^\circ C$ and $t_E = -10 \, ^\circ C$. The COP* presents a trend of declining after increasing with an increase
in \( t_G \). For \( t_A = t_C = 55 \degree C, 57 \degree C, 59 \degree C, \) and \( 61 \degree C \), the maximum COP* values of 1.447, 1.422, 1.390, and 1.348 appear at \( t_G = 266 \degree C, 276 \degree C, 283 \degree C, \) and \( 289 \degree C \), respectively. The COP* decreases with increases in \( t_A \) and \( t_C \) because the increase in \( t_A \) is not conducive to absorption of NH\(_3\) in the absorber. In addition, the increase in \( t_C \) is not conducive to desorption of NH\(_3\) in the generator.

![Figure 26](image)

**Figure 26.** Effects of \( t_G \) on \( \eta^*_{ex} \) for \( t_G = 170–300 \degree C \) with \( t_A = t_C = 55 \degree C, 57 \degree C, 59 \degree C, \) or \( 61 \degree C \) and \( t_E = -10 \degree C \) [25].

Fig. 26 shows the effects of \( t_G \) on \( \eta^*_{ex} \) for \( t_G = 170–300 \degree C \) with \( t_A = t_C = 55 \degree C, 57 \degree C, 59 \degree C, \) or \( 61 \degree C \) and \( t_E = -10 \degree C \). With an increase in \( t_G \), the \( \eta^*_{ex} \) presents a trend of decreasing after initially increasing. For \( t_A = t_C = 55 \degree C, 57 \degree C, 59 \degree C, \) and \( 61 \degree C \), the maximum values of \( \eta^*_{ex} \) of 0.341, 0.368, 0.384, and 0.402 appear at \( t_G = 193 \degree C, 206 \degree C, 221 \degree C, \) and \( 246 \degree C \), respectively. It can be seen that the optimal \( \eta^*_{ex} \) occurs at a lower \( t_G \) than did the optimal COP*. This is because the increase in \( t_G \) leads to an increase in the exergy proportion in \( q_E \), which induces a decreasing trend in \( \eta^*_{ex} \) but has no effect on the COP*.

![Figure 27](image)

**Figure 27.** Effects of \( t_G \) on the \( f \) for \( t_G = 170–300 \degree C \) with \( t_A = t_C = 55 \degree C, 57 \degree C, 59 \degree C, \) or \( 61 \degree C \) and \( t_E = -10 \degree C \) [25].
Fig. 27 shows the effects of $t_G$ on the $f$ for $t_G = 170–300 \, ^\circ\text{C}$ with $t_A = t_C = 55 \, ^\circ\text{C}$, $57 \, ^\circ\text{C}$, $59 \, ^\circ\text{C}$, or $61 \, ^\circ\text{C}$ and $t_E = -10 \, ^\circ\text{C}$. The variation in the $f$ is the same as that for the COP for cooling in Fig. 6. For $t_A = t_C = 55 \, ^\circ\text{C}$, $57 \, ^\circ\text{C}$, $59 \, ^\circ\text{C}$, and $61 \, ^\circ\text{C}$, the $f$ values are less than 10 when $t_G$ is greater than 220 °C, 244 °C, 263 °C, and 285 °C, respectively. Overall, the results in Figs. 21–27 indicate that the [bmim]Zn$_2$Cl$_5$/NH$_3$ absorption system is suitable for use in heating applications.

Figure 28. Effects of $t_G$ on the COP for $t_G = 75–130 \, ^\circ\text{C}$ with $t_A = 35 \, ^\circ\text{C}$, $t_C = 40 \, ^\circ\text{C}$, and $t_E = 5 \, ^\circ\text{C}$.

The theoretical cycle characteristic of the [bmim]Zn$_2$Cl$_5$/NH$_3$ absorption system is also compared with that of the LiBr/H$_2$O system. Fig. 28 shows the effects of $t_G$ on the COP for $t_G = 75–130 \, ^\circ\text{C}$ with $t_A = 35 \, ^\circ\text{C}$, $t_C = 40 \, ^\circ\text{C}$, and $t_E = 5 \, ^\circ\text{C}$ and a heat recovery rate of the regenerator of 0.75. For both systems, the COP initially exhibits a significant increase as the $t_G$ increases. As $t_G$ continues to increase though, the slope of the COP curve for the [bmim]Zn$_2$Cl$_5$/NH$_3$ system becomes less steep, whereas the COP curve for the LiBr/H$_2$O system presents a trend of a slight decrease after the increase. When $t_G < 95 \, ^\circ\text{C}$, the COP of the [bmim]Zn$_2$Cl$_5$/NH$_3$ system is slightly higher than that of the LiBr/H$_2$O system. When $95 < t_G < 115 \, ^\circ\text{C}$, the COP of the [bmim]Zn$_2$Cl$_5$/NH$_3$ system is slightly less than that of the LiBr/H$_2$O system. When $t_G > 115 \, ^\circ\text{C}$, the COP of the [bmim]Zn$_2$Cl$_5$/NH$_3$ system is higher than that of the LiBr/H$_2$O system. As $t_G$ continues to increase, the COP curve for the [bmim]Zn$_2$Cl$_5$/NH$_3$ system still maintains an upward trend with a small slope, but the COP curve of the LiBr/H$_2$O system shows a downward trend with a small slope. Although the COP of the [bmim]Zn$_2$Cl$_5$/NH$_3$ system is less than the COP of the LiBr/H$_2$O system at some specific temperatures, the overall theoretical cycle characteristic of the [bmim]Zn$_2$Cl$_5$/NH$_3$ system is slightly better than that of the LiBr/H$_2$O system, especially at higher $t_G$ values.

3.5. Summary

The vapor pressures of the binary solution of [bmim]Zn$_2$Cl$_5$/NH$_3$ with NH$_3$ mole fraction $x_2 = 0.83–0.94$ at $T = 323.15–563.15 \, \text{K}$ were measured via a static method with a total uncertainty of measurement below 4.3% [16]. The experimental data were fit using the modified UNIFAC
TG scanning of [bmim]Zn₂Cl₅ was carried out using a TGA/SDT instrument over the range of T = 323.15–1173.15 K. The results indicate that [bmim]Zn₂Cl₅ possesses high thermal stability for T < 637.15 K. Heat capacity data at T = 210.15–383.15 K were obtained by using a DSC 910S operated with a rate of temperature increase of 5 K/min and a nitrogen volume flow of 40 cm³/min. Molar excess enthalpy data for [bmim]Zn₂Cl₅/NH₃ at x₁ = 0.60–0.95 for T = 288.15, 303.15, 318.15, and 333.15 K were measured. The excess enthalpy data were fit using the NRTL model. Measurement uncertainties and the maximum deviation of correlations for the excess enthalpy data were lower than 4.8% and 3.9%, respectively. With an increase in the NH₃ molar fraction, excess enthalpy showed a trend of increasing after declining. Minimum excess enthalpies of -6555.7, -6707.1, -6846.3, and -6974.7 J/mol appeared at x₁ = 0.772, 0.774, 0.776, and 0.777 for T = 288.15, 303.15, 318.15, and 333.15 K, respectively. Based on the heat capacity of [bmim]Zn₂Cl₅ and the excess enthalpy of [bmim]Zn₂Cl₅/NH₃, the enthalpies of [bmim]Zn₂Cl₅/NH₃ solutions can be calculated, which makes it feasible to investigate the thermodynamic performances of the [bmim]Zn₂Cl₅/NH₃ absorption system.

Based on the modified UNIFAC model and the NRTL model, the thermodynamic performance of a single effect absorption system using [bmim]Zn₂Cl₅/NH₃ as the working pair was simulated and compared with those of the NaSCN/NH₃ adsorption system [25] and the H₂O-LiBr absorption system. The thermal performance of the [bmim]Zn₂Cl₅/NH₃ system is better than that of the NaSCN/NH₃ system when the t_c is high and t_s and t_c are low and also better than that of the H₂O-LiBr absorption system in some cases. With an increase in t_c, the COP and COP* present trends of declining after increasing, and the circulation ratios show a decreasing trend. When t_s = -30 °C and t_c = 35 °C, the maximum COP of the [bmim]Zn₂Cl₅/NH₃ system is still greater than 0.42. When t_s = -10 °C and t_c = 60 °C, the maximum COP is still greater than 1.40. Under these two operating conditions, the circulation ratios remain acceptable. Although the COP of the [bmim]Zn₂Cl₅/NH₃ system is less than that of the LiBr/H₂O system in some specific temperature ranges, the overall theoretical cycle characteristic of the [bmim]Zn₂Cl₅/NH₃ system is slightly better than that of the LiBr/H₂O system, especially when t_c is high. Overall, these results indicate that the [bmim]Zn₂Cl₅/NH₃ absorption system offers good thermal performance for use in both cooling and heating applications.

4. Conclusions and outlook

Ten years have passed since ionic liquids were introduced in the field of absorption refrigeration, and unfortunately, the research progress pertaining to absorption refrigeration working pairs containing ionic liquids has been disappointing to us. Most of the working pairs proposed
by researchers from all over the world are gradually fading from view due to a lack of practical applications. Particular attention was paid to ionic liquid working pairs containing [RR’Im]DMP (1-R,3-R’-imidazolium dimethylphosphate). When applied in absorption refrigeration, the cycle characteristics of the three representative working pairs of [dmIm]DMP-H$_2$O, [emIm]DMP-H$_2$O and [mmIm]DMP-CH$_3$OH are better than that of H$_2$O-NH$_3$, but still slightly lower than those of LiBr-H$_2$O. So far, the new conceptual chemical absorption refrigeration working pairs containing an ionic liquid, with [bmim]Zn$_2$Cl$_5$/NH$_3$ as the representative, are the most ideal ionic liquid-type working pairs for absorption refrigeration. The thermodynamic performances of absorption refrigeration using the proposed chemical working pairs are comparable to those achieved with the LiBr-H$_2$O system. Additionally, the ranges of operating conditions for the chemical working pairs are wider than those of the conventional working pairs. At present, promoting the industrial application of [bmim]Zn$_2$Cl$_5$/NH$_3$ is our next priority. The discovery of chemical absorption refrigeration working pairs containing an ionic liquid is a milestone in the development of absorption refrigeration technology. It is foreseeable that the application of ionic liquids in absorption refrigeration will achieve a major breakthrough in the development of this technology, with the continued discovery of similar ionic liquid working pairs based on the chemical reaction.

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References


