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Study on a Quaternary Working Pair of CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\)/H\(_2\)O for an Absorption Refrigeration Cycle

Yiqun Li \(^1\), Na Li \(^2\), Chunhuan Luo \(^{1,3}\) and Qingquan Su \(^{1,3,*}\)

\(^1\) School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China; liyiqun1616@gmail.com (Y.L.); luochunhuan@ustb.edu.cn (C.L.)

\(^2\) State Grid Energy Conservation Service CO., Ltd., Beijing 100083, China; b20150273@xs.ustb.edu.cn

\(^3\) Beijing Higher Institution Engineering Research Center of Energy Conservation and Environmental Protection, University of Science and Technology Beijing, Beijing 100083, China

\(*\) Correspondence: suqingquan@ustb.edu.cn

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Abstract: When compared with LiBr/H\(_2\)O, an absorption refrigeration cycle using CaCl\(_2\)/H\(_2\)O as the working pair needs a lower driving heat source temperature, that is, CaCl\(_2\)/H\(_2\)O has a better refrigeration characteristic. However, the crystallization temperature of CaCl\(_2\)/H\(_2\)O solution is too high and its absorption ability is not high enough to achieve an evaporation temperature of 5 \(^\circ\)C or lower. CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\) (15.5:5:1)/H\(_2\)O was proposed and its crystallization temperature, saturated vapor pressure, density, viscosity, specific heat capacity, specific entropy, and specific enthalpy were measured to retain the refrigeration characteristic of CaCl\(_2\)/H\(_2\)O and solve its problems. Under the same conditions, the generation temperature for an absorption refrigeration cycle with CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\) (15.5:5:1)/H\(_2\)O was 7.0 \(^\circ\)C lower than that with LiBr/H\(_2\)O. Moreover, the cycle’s COP and exergy efficiency with CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\) (15.5:5:1)/H\(_2\)O were approximately 0.04 and 0.06 higher than those with LiBr/H\(_2\)O, respectively. The corrosion rates of carbon steel and copper for the proposed working pair were 14.31 \(\mu\)m·y\(^{-1}\) and 2.04 \(\mu\)m·y\(^{-1}\) at 80 \(^\circ\)C and pH 9.7, respectively, which were low enough for engineering applications.

Keywords: absorption refrigeration; working pair; crystallization temperature; vapor pressure; COP; corrosivity

1. Introduction

Absorption refrigeration systems can effectively utilize not only industrial waste heat [1–4], but also low-grade renewable energy, including solar energy and geothermal energy for refrigeration [5–7]. As a traditional working pair, LiBr/H\(_2\)O has been widely used for refrigeration [8–12]. However, studies on new working pairs are still ongoing, because the required temperature of driving heat source for a refrigeration cycle using LiBr/H\(_2\)O even reaches 88.0 \(^\circ\)C [13–15], which is too high to use for some low-grade heat sources. Lin et al. [16] studied a double-stage air-cooled NH\(_3\)/H\(_2\)O absorption refrigeration system and found that it could effectively lower the temperature of driving heat source for utilizing solar energy. Malinina et al. [17] analyzed the influences of temperature and humidity on a solar energy refrigeration system with LiBr/H\(_2\)O and calculated the minimum heat-collecting temperatures that are based on solar energy in some cities. Mortazavi et al. [18] designed an absorption refrigeration system with a falling-film generator, which could use lower temperature waste heat or solar energy. Bourouis et al. [19] analyzed the performance of LiBr + LiNO\(_3\) + LiCl + LiI + H\(_2\)O in a vertical tube and found that the crystallization temperature was 35 \(^\circ\)C lower than LiBr solution. Sun et al. [20] studied LiBr-LiNO\(_3\) (mole ratio: 4:1)/H\(_2\)O and found the alternative working pair had higher COP and
less corrosivity than LiBr/H₂O. Chen et al. [21] studied the performance of an absorption refrigeration system using [emim]Cu₂Cl₅/NH₃ as working pair with the UNIFAC model, and results showed that the [emim]Cu₂Cl₅/NH₃ system possessed several advantages, including non-crystallization and non-corrosion. Bellos et al. [22] compared the exergy efficiency between LiCl/H₂O and LiBr/H₂O, results showed that LiCl/H₂O performed better at different ambient temperature levels. Wang et al. [23] measured the properties of different ammonia/ionic liquid working pairs. Luo et al. [24–28] studied various lithium nitrate-ionic liquid/water working pairs. They both found that the working pairs with ionic liquid had excellent characteristics for heating, whereas they were not suitable for refrigeration because of insufficient absorption ability. Li et al. [29–32] measured the thermophysical properties of several CaCl₂-based working pairs, and found that the CaCl₂-based working pairs had an excellent refrigeration characteristic. However, their strong corrosivity limited the practical applications.

In this work, to find a new working pair with excellent refrigeration characteristic for absorption refrigeration, various inorganic salts, including NaCl, KCl, LiCl, KNO₃, and LiNO₃, were added in CaCl₂/H₂O, and their crystallization temperature and saturated vapor pressure were measured. Furthermore, some other thermophysical properties and corrosivity of the proposed working pair were measured and the performance of an absorption refrigeration cycle with the proposed working pair was analyzed.

2. Experiments

2.1. Materials

Table 1 shows the purities of the reagents used in this work. Table 2 lists the detailed compositions of carbon steel and copper samples used in the corrosion experiments.

| Component | C   | Mn   | Si   | P   | S   | Zn   | Pb   | Sn   | Fe   | Cu   |
|------------|-----|------|------|-----|-----|------|------|------|------|------|
| Carbon steel Q235 | 0.16 | 0.53 | 0.3  | 0.035 | 0.04 | –    | –    | –    | balance | –    |
| Copper T6   | –   | –    | 0.006 | –    | 0.01 | 0.005 | 0.05 | 0.05 | 0.05 | balance |

2.2. Apparatus and Methods

To analyze the performance of a working pair, its properties, such as crystallization temperature, saturated vapor pressure, density, viscosity, specific heat capacity, dissolution enthalpy, and corrosion rate, need to be measured.

The crystallization temperature was measured by a dynamic method in a precision thermostat (HX-3010, Bilang, Shanghai). The prepared solution was put in the thermostat at a slightly higher initial temperature. The crystallization temperature was measured by reducing the temperature by 1 °C every 12 hours until crystallization appeared in the solution.

The saturated vapor pressure was measured by a static method. The solution was poured into an autoclave that was assembled with a precision digital absolute pressure gauge (AX-110, Aoxin, Xi’an) and a Pt-100 thermocouple. The autoclave was placed in a precision oil bath (DKU-30, Jinghong,
Shanghai) after vacuuming. The data of pressure gauge and thermocouple were obtained, respectively, after stabilization.

The density and viscosity were measured in a precision viscometer oil bath (SYP1003-H, Zhongxi, Beijing). Density measurement was carried out by a capillary pycnometer with a capillary diameter of approximately 1 mm. Ubbelohde capillary viscometers with different fine capillaries was used to carry out the viscosity measurement.

The specific heat capacity and dissolution enthalpy were measured by a micro reaction calorimeter (μRC, THT Co., UK). The measurement of specific heat capacity was conducted by making a 1 °C “step-change” in the measurement temperature. The dissolution enthalpy was measured by an isothermal method, with a solid addition accessory.

The corrosion rate of carbon steel and copper in the solution were measured by a weight loss method. The sample was immersed in the solution for 200 hours. The corrosion rate was calculated according to the mass change of the sample.

References [24–28] give the detailed procedures. All the above experiments were carried out at 101.3 kPa and 25 °C. The properties of water and LiBr/H₂O were measured and compared with literature values to validate the above methods. In addition, three parallel experiments were carried out for each measurement to verify the reproducibility. Table 3 lists the accuracy of the instruments.

| Instrument                        | Parameter          | Accuracy       |
|----------------------------------|--------------------|----------------|
| Analytical balance               | 0–2100 g           | ±0.1 g         |
| Precision thermostat             | −30–150 °C         | ±0.5 °C        |
| Oil bath                         | 20–300 °C          | ±1.0 °C        |
| Digital absolute pressure gauge  | 0–110 kPa          | ±0.01 kPa      |
| Precision viscometer oil bath    | 0–230 °C           | ±0.05 °C       |
| Capillary pycnometer             | 50 mL              | ±0.03%         |
| Ubbelohde capillary viscometer   | 0.36 mm, 0.46 mm,  | ±0.02%         |
| Micro reaction calorimeter       | 0.58 mm, 073 mm    |                |
|                                  | 0–180 °C           | ±0.001 °C      |

3. Results and Discussion

3.1. CaCl₂/H₂O

To find a working pair with excellent refrigeration characteristic, the saturated vapor pressures of CaCl₂/H₂O were measured and are shown in Figure 1a. Figure 1b presents the comparison of the refrigeration characteristic between LiBr/H₂O and CaCl₂/H₂O, it shows that, for an identical pressure of 6.290 kPa, which is a typical pressure in the condenser and generator, CaCl₂/H₂O had a lower generation temperature than LiBr/H₂O, meaning that the refrigeration characteristic of CaCl₂/H₂O was better than LiBr/H₂O.

Figure 2 shows the absorption temperature of CaCl₂/H₂O under an absorption pressure of 0.872 kPa, which corresponds to the typical evaporation temperature of 5 °C. The crystallization temperature of CaCl₂/H₂O is also plotted in Figure 2 to illustrate the limitation from the crystallization of absorbent. The absorption temperature increased with increasing the concentration, and meet the crystallization temperature at 33.0 °C, which was the maximum absorption temperature under the given conditions. Generally, the absorption temperature in absorber for a refrigeration cycle is 37.0 °C, so the binary working pair of CaCl₂/H₂O could not be applied for the refrigeration cycle, because of its high crystallization temperature and insufficient absorption ability.

To improve the absorption ability and reduce the crystallization temperature of CaCl₂/H₂O, some salts, including NaCl, KCl, LiCl, KNO₃, and LiNO₃, were combined with CaCl₂/H₂O, and their saturated vapor pressures and crystallization temperatures were measured.
2019 from 78.6 g to 117.4 g and H\(_2\)O was 95.0 g. The crystallization temperatures of CaCl\(_2\)/H\(_2\)O were higher than those of CaCl\(_2\)/H\(_2\)O under the same concentrations.

Figure 3c shows CaCl\(_2\)-LiCl/H\(_2\)O with adding 10.0 g LiCl to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 78.6 g to 117.4 g and H\(_2\)O was 90.0 g. The crystallization temperatures of CaCl\(_2\)-LiCl/H\(_2\)O was reduced greatly when compared with that of CaCl\(_2\)/H\(_2\)O at 50.0 wt.\%, whereas with the concentration increasing, the effect of LiCl addition on the crystallization temperature obviously decreased.

Figure 3d shows CaCl\(_2\)-KNO\(_3\)/H\(_2\)O with adding 10.0 g KNO\(_3\) to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 78.6 g to 117.4 g and H\(_2\)O was 90.0 g. The crystallization temperatures of CaCl\(_2\)-KNO\(_3\)/H\(_2\)O were lower than those of CaCl\(_2\)/H\(_2\)O under the same concentrations.

**Figure 1.** (a) Saturated vapor pressure of CaCl\(_2\)/H\(_2\)O; (b) Comparison of the refrigeration characteristic between LiBr/H\(_2\)O and CaCl\(_2\)/H\(_2\)O.

**Figure 2.** Crystallization temperature and absorption temperature for CaCl\(_2\)/H\(_2\)O.

### 3.2. Measurement of Crystallization Temperature \(T_C\)

The \(T_C\) of CaCl\(_2\)-NaCl/H\(_2\)O, CaCl\(_2\)-KCl/H\(_2\)O, CaCl\(_2\)-LiCl/H\(_2\)O, CaCl\(_2\)-KNO\(_3\)/H\(_2\)O, CaCl\(_2\)-LiNO\(_3\)/H\(_2\)O, and CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\)/H\(_2\)O were measured. Figure 3 gives the comparison of \(T_C\) between these CaCl\(_2\)-based working pairs and CaCl\(_2\)/H\(_2\)O. Here, the concentration is the solution’s total solute mass concentration.

Figure 3a shows CaCl\(_2\)-NaCl/H\(_2\)O with adding 5.0 g NaCl to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 42.9 g to 61.3 g and H\(_2\)O was 95.0 g. The crystallization temperatures of CaCl\(_2\)-NaCl/H\(_2\)O were higher than those of CaCl\(_2\)/H\(_2\)O under the same concentrations.

Figure 3b shows CaCl\(_2\)-KCl/H\(_2\)O with adding 5.0 g KCl to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 78.6 g to 117.4 g and H\(_2\)O was 95.0 g. The crystallization temperatures of CaCl\(_2\)-KCl/H\(_2\)O were approximately 20.0 °C lower than those of CaCl\(_2\)/H\(_2\)O under the same concentrations.

Figure 3c shows CaCl\(_2\)-LiCl/H\(_2\)O with adding 10.0 g LiCl to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 66.7 g to 100.0 g and H\(_2\)O was 90.0 g. The crystallization temperature of CaCl\(_2\)-LiCl/H\(_2\)O was reduced greatly when compared with that of CaCl\(_2\)/H\(_2\)O at 50.0 wt.\%, whereas with the concentration increasing, the effect of LiCl addition on the crystallization temperature obviously decreased.

Figure 3d shows CaCl\(_2\)-KNO\(_3\)/H\(_2\)O with adding 10.0 g KNO\(_3\) to CaCl\(_2\)/H\(_2\)O, in which CaCl\(_2\) were from 78.6 g to 117.4 g and H\(_2\)O was 90.0 g. The crystallization temperatures of CaCl\(_2\)-KNO\(_3\)/H\(_2\)O were lower than those of CaCl\(_2\)/H\(_2\)O under the same concentrations. Moreover, it decreased with
increasing concentration in the range of 49.0 wt.% to 53.5 wt.%, whereas it increased with further increasing concentration.

Figure 3. Comparison of $T_C$ between CaCl$_2$/H$_2$O and other CaCl$_2$-based working pairs: (a) CaCl$_2$-NaCl/H$_2$O; (b) CaCl$_2$-KCl/H$_2$O; (c) CaCl$_2$-LiCl/H$_2$O; (d) CaCl$_2$-KNO$_3$/H$_2$O; (e) CaCl$_2$-LiNO$_3$/H$_2$O; and, (f) CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O.

Figure 3e shows CaCl$_2$-LiNO$_3$/H$_2$O with adding 35.0 g LiNO$_3$ to CaCl$_2$/H$_2$O, in which CaCl$_2$ were from 42.9 g to 100.0 g and H$_2$O was 65.0 g. The crystallization temperatures of CaCl$_2$-LiNO$_3$/H$_2$O were significantly reduced when compared with those of CaCl$_2$/H$_2$O under the same concentrations. Corresponding to the concentrations ranging from 55.0 wt.% to 62.0 wt.%, which is a practical concentration range for an absorption refrigeration cycle, the crystallization temperatures of CaCl$_2$-LiNO$_3$/H$_2$O were from -10.0 °C to 7.0 °C, which are sufficiently low to solve the absorbent
crystallization problem in summer. However, the addition amount of 35.0 g LiNO$_3$ was relatively large, and it is a disadvantage from the aspect of cost due to LiNO$_3$ being much more expensive than CaCl$_2$. To depress the cost increase, a part of LiNO$_3$ was replaced with KNO$_3$ for CaCl$_2$-LiNO$_3$/H$_2$O. Figure 3f shows CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O with adding 25.0 g LiNO$_3$ and 5.0 g KNO$_3$ to CaCl$_2$/H$_2$O, in which CaCl$_2$ were from 66.7 g to 117.4 g and H$_2$O was 70.0 g. A reduction of crystallization temperature up to 30.0 $^\circ$C was achieved from 58.0 wt.% to 65.0 wt.%, which indicated that the crystallization problem would not occur in this concentration range.

3.3. Measurement of Saturated Vapor Pressure $p$

$p$ of CaCl$_2$-LiNO$_3$/H$_2$O and CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O with different mass ratios were measured and are shown in Tables 4 and 5.

| $x$/g | Saturated Vapor Pressure $p$ (kPa) at Each Temperature $T$ ($^\circ$C) |
|-------|---------------------------------------------------------------|
|       | CaCl$_2$(x)-LiNO$_3$(35.0 g)/H$_2$O(65.0 g)                   |
| 42.9  | $T$ 20.0 25.0 30.5 35.0 40.0 45.3 50.4 55.7 60.2 65.1 70.3 75.1 80.2 85.2 90.0 95.0 100.0 |
|       | $p$ 0.457 0.641 0.934 1.256 1.693 2.369 2.378 4.431 5.707 5.136 |
| 47.1  | $T$ 65.2 70.3 75.1 80.2 85.2 90.0 95.0 100.0  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 51.5  | $T$ 20.0 25.0 30.2 35.0 40.1 45.3 50.0 55.2 59.9  |
|       | $p$ 0.372 0.520 0.733 1.010 1.377 1.910 2.617 3.564 4.565 |
| 56.3  | $T$ 65.3 70.3 75.0 79.9 85.0 90.4 95.0 100.0  |
|       | $p$ 0.330 0.460 0.674 0.921 1.233 1.688 2.336 3.217 4.188 |
| 61.3  | $T$ 65.3 70.3 75.0 79.9 85.0 90.4 95.0 100.0  |
|       | $p$ 6.269 7.846 10.244 13.031 17.682 20.953 25.300 30.728 |
| 66.7  | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 72.4  | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 78.6  | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 85.2  | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 92.3  | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |
| 100.0 | $T$ 20.0 25.0 30.3 35.3 40.1 45.1 50.0 55.7 60.1  |
|       | $p$ 6.823 8.739 11.035 14.118 17.692 21.770 26.701 32.102 |

Table 4. $p$ of CaCl$_2$-LiNO$_3$/H$_2$O with different mass ratio.
Table 5. $p$ of CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O with different mass ratio.

| y/g  | Saturated Vapor Pressure $p$ (kPa) at Each Temperature $T$ (°C) | CaCl$_2$(y g)-LiNO$_3$(25.0 g)-KNO$_3$(5.0 g)/H$_2$O(70.0 g) |
|------|-------------------------------------------------------------|----------------------------------------------------------------|
| 66.7 | $T$ 20.0 25.0 30.1 35.5 40.0 45.3 50.0 54.9 60.0          | $p$ 0.352 0.511 0.741 1.064 1.434 1.987 2.638 3.508 4.660       |
|      |                                                              | $T$ 65.1 70.1 75.2 80.0 87.2 89.9 95.0 100.0                  |
|      |                                                              | $p$ 6.119 8.024 10.490 13.001 17.346 23.450 28.590            |
| 72.4 | $T$ 20.0 25.0 30.2 34.9 40.6 45.6 50.0 55.2 60.4          | $p$ 0.315 0.455 0.650 0.911 1.353 1.850 2.403 3.250 4.283       |
|      |                                                              | $T$ 65.1 69.9 75.2 80.3 85.0 89.7 94.9 100.0                  |
|      |                                                              | $p$ 5.560 7.106 9.469 11.911 14.327 17.200 21.021 26.025       |
| 78.6 | $T$ 20.0 25.0 29.9 35.1 40.5 45.0 50.0 55.0 60.0          | $p$ 0.295 0.371 0.530 0.762 1.049 1.427 1.940 2.638 3.508       |
|      |                                                              | $T$ 65.1 69.9 75.2 80.3 85.0 89.7 94.9 100.0                  |
|      |                                                              | $p$ 5.560 7.106 9.469 11.911 14.327 17.200 21.021 26.025       |
| 85.2 | $T$ 20.0 25.0 30.0 35.0 40.5 45.0 50.0 55.0 60.0          | $p$ 0.219 0.312 0.445 0.627 0.928 1.239 1.740 2.311 3.200       |
|      |                                                              | $T$ 65.1 69.9 75.2 80.3 85.0 89.7 94.9 100.0                  |
|      |                                                              | $p$ 5.560 7.106 9.469 11.911 14.327 17.200 21.021 26.025       |
| 92.3 | $T$ 20.0 25.0 30.0 35.4 39.9 45.0 50.0 55.1 60.1          | $p$ 0.198 0.285 0.399 0.581 0.793 1.136 1.563 2.150 2.925       |
|      |                                                              | $T$ 65.2 70.0 75.3 79.9 85.2 90.0 95.5 100.2                  |
|      |                                                              | $p$ 3.875 5.048 6.683 8.448 10.859 13.429 16.906 19.867       |
| 100.0| $T$ 41.0 44.9 50.0 55.0 60.2 65.0 70.1 75.1 80.3          | $p$ 0.673 0.889 1.244 1.730 2.454 3.349 4.519 5.911 7.656       |
|      |                                                              | $T$ 85.2 89.9 94.9 99.9 100.0                                  |
|      |                                                              | $p$ 9.761 12.060 14.960 18.163                                 |
| 108.3| $T$ 60.0 65.2 70.0 75.2 80.1 84.8 90.4 95.1 100.1         | $p$ 2.205 3.045 4.051 5.252 6.686 8.464 10.993 13.110 15.587 |
|      |                                                              | $T$ 82.0 85.1 90.0 95.0 100.3                                  |
|      |                                                              | $p$ 5.921 6.971 9.009 11.303 14.387                           |

The measured $p$ was fitted by Equation (1) [33–35].

$$\log p = \sum_{i=0}^{4} [A_i + B_i / (T + 273.15 - C_i)] w^i$$

where $A_i$, $B_i$, and $C_i$ are the regression parameters. Equation (2) obtains the average absolute relative deviation (AARD) between the measured values and the fitted values.

$$\text{AARD} = 1/N \sum_{i=1}^{N} \left| \frac{P_{\text{exp}} - P_{\text{fit}}}{P_{\text{fit}}} \right|$$

where $N$ is total number of data, $P_{\text{exp}}$ is the measured or obtained value, and $P_{\text{fit}}$ is the fitted value.

The regression parameters and AARD were obtained and are shown in Tables 6 and 7, respectively. Figures 4 and 5 plot the measured $p$ and fitted value of CaCl$_2$-LiNO$_3$/H$_2$O and CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O, respectively. The fitted value agreed well with the measured $p$. 60.2 wt.% for CaCl$_2$(63.2 g)-LiNO$_3$(35.0 g)/H$_2$O(65.0 g) and 60.5 wt.% for CaCl$_2$(77.3 g)-LiNO$_3$(25.0 g)-KNO$_3$(5.0 g)/H$_2$O(70.0 g) were obtained, respectively, by Equation (1) at 37.0 °C and 0.872 kPa, which are the typical absorption temperature and absorption pressure for a refrigeration cycle. Meanwhile, the absorption temperatures of these two working pairs were 70.5 °C and 69.2 °C, respectively, at 6.290 kPa, which is the typical generation pressure. Therefore, CaCl$_2$(77.3 g)-LiNO$_3$(25.0 g)-KNO$_3$(5.0 g)/H$_2$O(70.0 g),
with a solute mass ratio of 15.5:5:1, had been proposed as an alternative working pair for LiBr/H₂O. The proposed working pair is expressed as CaCl₂-LiNO₃-KNO₃(15.5:5:1)/H₂O in this paper.

Table 6. Regression parameters for CaCl₂-LiNO₃/H₂O and average absolute relative deviation (AARD) value.

| i  | Aᵢ   | Bᵢ    | Cᵢ    | AARD  |
|----|------|-------|-------|-------|
| 0  | 4.896×10⁻¹ | -1.985×10⁰ | -3.624×10⁰ |       |
| 1  | -1.172×10⁻¹ | 5.756×10⁻¹ | -1.189×10¹ |       |
| 2  | 1.024×10⁻²  | -2.990×10⁻¹ | -3.963×10¹ | 1.55% |
| 3  | -1.768×10⁻⁴ | 3.046×10⁻³ | -1.894×10¹ |       |
| 4  | 9.452×10⁻⁷  | -8.957×10⁻⁶ | -4.335×10⁰ |       |

Table 7. Regression parameters for CaCl₂-LiNO₃-KNO₃/H₂O and AARD value.

| i  | Aᵢ   | Bᵢ    | Cᵢ    | AARD  |
|----|------|-------|-------|-------|
| 0  | -2.262×10⁻² | -3.844×10⁻¹ | 5.668×10⁻¹ |       |
| 1  | 5.616×10⁻¹  | 1.184×10⁰  | 1.367×10⁰  |       |
| 2  | -2.523×10⁻² | -1.498×10⁻² | 5.033×10⁰  | 2.34% |
| 3  | 4.274×10⁻⁴  | -3.524×10⁻³ | -3.042×10¹ |       |
| 4  | -2.421×10⁻⁶ | 2.944×10⁻⁵  | -1.620×10¹ |       |

Figure 4. p of CaCl₂-LiNO₃/H₂O with different mass ratio.

Figure 5. p of CaCl₂-LiNO₃-KNO₃/H₂O with different mass ratio.
The $p$ of this working pair was measured in order to analyze the cycle performance with CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O, as shown in Table 8.

| wt/wt.% | Saturated Vapor Pressure $p$ (kPa) at Each Temperature $T$ (°C) |
|---------|---------------------------------------------------------------|
| 50.0    | $T$ 20.1 25.7 30.2 35.3 40.6 45.0 50.7 55.4 60.0 $p$ 0.634 0.901 1.225 1.705 2.371 3.064 4.325 5.626 7.206 |
|         | $T$ 65.2 70.7 75.0 80.9 85.7 90.0 95.2 100.0 $p$ 9.336 12.075 14.800 19.100 23.536 27.931 33.519 40.578 |
| 55.0    | $T$ 21.2 28.0 32.1 35.0 39.9 45.1 52.0 55.6 60.0 $p$ 0.443 0.712 0.939 1.148 1.569 2.210 3.407 4.249 5.387 |
|         | $T$ 65.2 70.2 75.0 80.9 85.0 90.4 95.0 100.0 $p$ 7.060 9.016 11.301 14.825 17.699 21.912 26.011 31.898 |
| 60.0    | $T$ 21.0 26.1 30.0 35.0 41.0 45.0 50.0 55.1 60.4 $p$ 0.280 0.412 0.541 0.769 1.166 1.492 2.071 2.855 4.026 |
|         | $T$ 65.5 70.2 75.0 80.0 85.4 90.4 95.2 100.1 $p$ 5.355 6.901 8.873 11.106 14.063 17.268 21.176 25.912 |
| 65.0    | $T$ 25.1 30.0 35.0 40.5 45.0 50.0 55.6 60.5 65.6 $p$ 0.226 0.341 0.490 0.744 0.985 1.339 1.958 2.675 3.665 |
|         | $T$ 71.1 75.4 80.1 85.2 90.0 94.6 100.5 $p$ 4.971 6.282 7.749 9.894 12.395 15.241 19.243 |

The measured $p$ was fitted by Equation (3) and the AARD was obtained to be 1.82% by Equation (2).

$$\log p = 1.243 - 8.293/(T + 273.15 + 3.466 \times 10^3) + (1.698 \times 10^{-1} - 3.894 \times 10/(T + 273.15 + 1.944 \times 10^2)) \times w + (-1.503 \times 10^{-3} + 3.797 \times 10^{-1}/(T + 273.15 + 2.836 \times 10^2)) \times w^2$$  \hspace{1cm} (3)

Figure 6 shows the measured $p$ and fitted value. The measured $p$ agreed well with the fitted value, which indicated that the $p$ of CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O could be obtained with the given corresponding concentration and temperature.

![Figure 6. $p$ of CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O.](image)

Figure 7 compares the refrigeration characteristic of CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O and LiBr/H\textsubscript{2}O. The generation temperature of CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O was 74.0 °C, which was 7.0 °C lower than that of LiBr/H\textsubscript{2}O. In other words, the temperature that is required for the driving heat source could be reduced by 7.0 °C through using CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O instead of LiBr/H\textsubscript{2}O.
3.4. Measurement of Density $\rho$

$\rho$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was measured by a capillary pycnometer method. Table 9 lists the results.

| $w$/wt.% | $T$   | Density $\rho$ (g cm$^{-3}$) at Each Temperature $T$ (°C) |
|---------|-------|------------------------------------------------------|
| 50.0    |       | 1.4614 1.4563 1.4488 1.4412 1.4352 1.4278 1.4215 1.4141 1.4067 |
| 55.0    | 20.0  | 1.5181 1.5111 1.5042 1.4977 1.4906 1.4834 1.4761 1.4696 1.4618 |
| 60.0    | 20.0  | 1.5784 1.5713 1.5642 1.5547 1.5495 1.5420 1.5351 1.5287 1.5229 |
| 65.0    | 40.0  | 1.6245 1.6185 1.6131 1.6058 1.5991 1.5915 1.5820 |

The measured $\rho$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was fitted by Equation (4) and AARD was obtained to be 0.22% by Equation (2).

$$
\rho = 1.923 \times 10^{-2} - 1.139 \times (T + 273.15) + 1.690 \times 10^{-3} \times (T + 273.15)^2 \\
+ (-1.034 \times 10^3 + 6.162 \times (T + 273.15) - 9.146 \times 10^{-3} \times (T + 273.15)^2) \times w \\
+ (1.859 \times 10^3 - 1.107 \times 10 \times (T + 273.15) + 1.642 \times 10^{-2} \times (T + 273.15)^2) \times w^2 \\
+ (-1.108 \times 10^3 + 6.595 \times (T + 273.15) - 9.781 \times 10^{-3} \times (T + 273.15)^2) \times w^3 
$$

Figure 8 shows the measured $\rho$ and the fitted value. The measured $\rho$ was highly consistent with the fitted value. The density linearly decreased with the temperature increasing, and it increased with the concentration increasing.
3.5. Measurement of Viscosity $\eta$

The measured $\eta$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was measured by the Ubbelohde capillary viscometer method. Table 10 shows the results.

| w/wt.% | Viscosity $\eta$ (mPa·s) at Each Temperature $T$ (°C) |
|--------|--------------------------------------------------|
| 50.0   | $T$, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 |
| 55.0   | $H$, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 |
| 60.0   | $T$, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 |
| 65.0   | $H$, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 |

The measured $\eta$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was fitted by Equation (5) and the AARD was obtained to be 0.82% by Equation (2).

$$\eta = 8.099 \times 10^{-4} - 4.721 \times 10^{4} / (T + 273.15) + 8.480 \times 10^{6} / (T + 273.15)^2$$

$$+(-2.286 \times 10^2 + 1.169 \times 10^5 / (T + 273.15) - 2.278 \times 10^7 / (T + 273.15)^2) \times w$$

$$+(2.534 \times 10 - 1.816 \times 10^4 / (T + 273.15) - 4.422 \times 10^5 / (T + 273.15)^2) \times w^2$$

$$+(2.224 \times 10^2 + 4.127 \times 10^5 / (T + 273.15) + 2.716 \times 10^2 / (T + 273.15)^2) \times w^3$$

(5)

Figure 9 shows the measured $\eta$ and the fitted value. The measured $\eta$ agreed well with the fitted value. $\eta$ exponentially decreased with the temperature increasing, whereas it increased with the concentration increasing.
3.6. Measurement of Specific Heat Capacity \( C_p \)

\( C_p \) of CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\)(15.5:5:1)/H\(_2\)O was measured with a micro reaction calorimeter. Table 11 lists the results.

Table 11. \( C_p \) of CaCl\(_2\)-LiNO\(_3\)-KNO\(_3\)(15.5:5:1)/H\(_2\)O.

| \( w \)/wt.% | \( T \) (°C) | 10.0 | 20.0 | 30.0 | 40.0 | 50.0 | 60.0 | 70.0 | 80.0 | 90.0 | 100.0 |
|-------------|-------------|------|------|------|------|------|------|------|------|------|------|
| 50.0 \( C_p \) | 2.438       | 2.444 | 2.458 | 2.473 | 2.487 | 2.501 | 2.518 | 2.527 | 2.542 | 2.563 |       |
| 55.0 \( C_p \) | 2.313       | 2.321 | 2.335 | 2.350 | 2.366 | 2.380 | 2.400 | 2.417 | 2.432 | 2.452 |       |
| 60.0 \( C_p \) | 2.189       | 2.193 | 2.206 | 2.216 | 2.227 | 2.241 | 2.254 | 2.266 | 2.286 | 2.303 |       |
| 65.0 \( C_p \) | 2.039       | 2.045 | 2.057 | 2.071 | 2.085 | 2.098 | 2.110 | 2.127 | 2.130 | 2.146 |       |

The measured \( C_p \) was fitted by Equation (6) and AARD was obtained to be 0.21\% by Equation (2).

\[
C_p = 2.575 + 1.951 \times 10^{-2} \times (T + 273.15) - 2.200 \times 10^{-4} \times (T + 273.15)^2 \\
+ (1.121 \times 10^{-2} - 6.433 \times 10^{-4} \times (T + 273.15) + 7.593 \times 10^{-6} \times (T + 273.15)^2)w \\
+ (-3.259 \times 10^{-4} + 5.570 \times 10^{-6} \times (T + 273.15) - 7.020 \times 10^{-8} \times (T + 273.15)^2)w^2
\]  

Figure 10 shows the measured \( C_p \) and the fitted value. \( C_p \) linearly increased with increasing the temperature.
3.7. Calculation of Specific Enthalpy $h$

3.7.1. $C_p$ of CaCl$_2$, LiNO$_3$, KNO$_3$ and H$_2$O

The $C_p$ of solid KNO$_3$ was measured and is shown in Table 12, $C_p$ of CaCl$_2$, LiNO$_3$, and H$_2$O are given in Reference Literature [29].

| Reagent | Specific Heat Capacity $C_p$ (kJ·kg$^{-1}$·K$^{-1}$) at Each Temperature $T$ (°C) |
|---------|----------------------------------------------------------------------------------|
| KNO$_3$ | $T$  10.0  20.0  30.0  40.0  50.0  60.0  70.0  80.0  90.0  100.0 |
|         | $C_p$  0.930  0.952  0.968  0.974  0.988  1.040  1.053  1.072  1.090  1.119 |

3.7.2. Measurement of Dissolution Enthalpy $\Delta H_{mix}$

$\Delta H_{mix}$ of KNO$_3$, LiNO$_3$, and CaCl$_2$ with a mass ratio of 15.5:5:1 were measured at 25.0 °C and are shown in Table 13.

| w/wt.% | 50.0  | 55.0  | 60.0  | 65.0  |
|--------|-------|-------|-------|-------|
| $\Delta H_{mix}$/kJ·kg$^{-1}$ | 149.310 | 150.501 | 150.275 | 151.292 |

3.7.3. Calculation of Specific Enthalpy $h$

$h$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O can be obtained from the measured $C_p$ and $\Delta H_{mix}$ [25,36,37]. Table 14 lists the obtained results.

The obtained $h$ was fitted by Equation (7) and AARD was obtained to be 0.07% by Equation (2).

$$h = 3.151 \times 10^2 - 1.193 \times w + 6.998 \times 10^{-3} \times w^2$$
$$+ (2.971 - 2.553 \times 10^{-3} \times w - 1.817 \times 10^{-4} \times w^2) (T + 273.15)$$
$$+ (-1.775 \times 10^{-3} + 1.198 \times 10^{-4} \times w - 1.304 \times 10^{-6} \times w^2) (T + 273.15)^2$$

(7)

Figure 11 shows the obtained $h$ and the fitted value. $h$ linearly increased with increasing the temperature, and the slope of line slightly increased with reducing the concentration.
was obtained to be 0.84% by Equation (2).

Calculation of Specific Entropy $s$

$s$ of a solution can be also obtained from the measured $C_p$ and $\Delta H_{\text{mix}}$ [38]. $s$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was obtained and is shown in Table 15.

Table 15. $s$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O.

| w/wt.% | $s$ (kJ kg$^{-1}$ K$^{-1}$) at Each Temperature $T$ (°C) |
|--------|-----------------------------------------------------|
|        | 50.0 | 55.0 | 60.0 | 65.0 |
| 50.0   | 10.0 | 1.412 | 1.578 | 1.658 | 1.736 | 1.813 | 1.889 | 1.963 | 2.306 | 2.108 |
| 55.0   | 10.0 | 1.417 | 1.576 | 1.652 | 1.727 | 1.800 | 1.872 | 1.943 | 2.014 | 2.083 |
| 60.0   | 10.0 | 1.422 | 1.500 | 1.645 | 1.716 | 1.785 | 1.852 | 1.919 | 1.985 | 2.050 |
| 65.0   | 10.0 | 1.431 | 1.502 | 1.638 | 1.704 | 1.769 | 1.832 | 1.895 | 1.955 | 2.016 |

The obtained $s$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was fitted by Equation (8) and the AARD was obtained to be 0.84% by Equation (2).

$$s = -2.662 \times 10 + 1.370 \times 10^2 \times w - 2.828 \times 10^2 \times w^2 + 1.967 \times 10^2 \times w^3$$
$$+ (2.333 \times 10^{-1} + 1.315 \times w + 2.735 \times w^2 - 1.892 \times w^3) (T + 273.15) + (-6.999 \times 10^{-4} + 4.199 \times 10^{-3} \times w - 8.788 \times 10^{-3} \times w^2 + 6.062 \times 10^{-3} \times w^3) (T + 273.15)^2$$
$$+ (7.282 \times 10^{-7} - 4.461 \times 10^{-6} \times w + 9.373 \times 10^{-6} \times w^2 - 6.469 \times 10^{-6} \times w^3) (T + 273.15)^3$$

(8)
Figure 12 shows the obtained $s$ and the fitted value. $s$ increased with the temperature increasing and decreased with the concentration increasing when the temperature was above 28 °C, whereas it changed little with the concentration when the temperature was below 28 °C.

![Figure 12.](image)

**Figure 12.** $s$ of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O.

3.9. Application for an Absorption Refrigeration Cycle

3.9.1. Absorption Refrigeration Cycle Using CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O

Figure 13a shows the schematic of an absorption refrigeration cycle. Figure 13b is the $P$-$T$ diagram of the cycle, and the points that are marked in the two diagrams are one-to-one correspondence.

![Figure 13.](image)

**Figure 13.** (a) Schematic of the absorption refrigeration cycle; (b) $P$-$T$ diagram of the absorption refrigeration cycle.

The working conditions are given, as follows: the evaporation temperature was 5.0 °C; the absorption temperature and condensation temperature were 37.0 °C; and, the evaporation and condensation pressures were 0.872 kPa and 6.290 kPa, respectively. The concentration of dilute solution for CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was figured out to be 60.5 wt.% by Equation (3), and the strong solution was 63.5 wt.%, with a concentration difference of 3.0 wt.%, thus, the generation temperature of the cycle was determined to be 74.0 °C by Equation (3). The same method was applied to calculate the generation temperature while using LiBr/H$_2$O and other CaCl$_2$-based
working pairs, including CaCl\textsubscript{2}-LiBr-LiNO\textsubscript{3}-KNO\textsubscript{3}(16.2:2:2:1)/H\textsubscript{2}O, CaCl\textsubscript{2}-LiNO\textsubscript{3}-LiBr(8.72:1:1)/H\textsubscript{2}O, and CaCl\textsubscript{2}-LiBr(1.35:1)/H\textsubscript{2}O. Table 16 lists the results.

| Working Pair                                                                 | CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3} (15.5:5:1)/H\textsubscript{2}O | LiBr/ H\textsubscript{2}O | CaCl\textsubscript{2}-LiBr-LiNO\textsubscript{3}-KNO\textsubscript{3} (16.2:2:2:1)/H\textsubscript{2}O | CaCl\textsubscript{2}-LiNO\textsubscript{3}-LiBr (8.72:1:1)/H\textsubscript{2}O | CaCl\textsubscript{2}-LiBr (1.35:1)/H\textsubscript{2}O |
|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-----------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Dilute solution/wt.%                                                         | 60.5                                                                            | 56.4            | 58.5                                                                             | 57.3                                                                             | 55.8                                                                             |
| Strong solution/wt.%                                                         | 63.5                                                                            | 59.4            | 61.5                                                                             | 60.3                                                                             | 58.8                                                                             |
| Generation temperature/\degree C                                              | 74.0                                                                            | 81.0            | 74.8                                                                             | 73.3                                                                             | 74.8                                                                             |

As seen in Table 16, the generation temperature was reduced by 7.0 \degree C through the use of CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O instead of LiBr/H\textsubscript{2}O. The generation temperature differences between the four CaCl\textsubscript{2}-based working pairs were relatively small.

3.9.2. Analysis of COP and Exergy Efficiency

To analyze the performance of a refrigeration cycle with CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O, the state parameters of typical points in Figure 13 were obtained by Equations (3), (7) and (8). Table 17 lists the results.

| Point | Stream        | p/kPa | T/\degree C | w/wt.\% | h/kJ kg\textsuperscript{-1} | D/kg s\textsuperscript{-1} | s/kJ kg\textsuperscript{-1} K\textsuperscript{-1} |
|-------|---------------|-------|-------------|----------|----------------------------|-----------------------------|------------------------------------------|
| 1     | Water         | 0.872 | 5.0         | 0        | 439.6                      | 1.0                         | 0.07621                                  |
| 1’    | Vapor         | 0.872 | 5.0         | 0        | 2927.9                     | 1.0                         | 9.02690                                  |
| 2     | Dilute solution | 0.872 | 37.0         | 60.5     | 349.2                      | 21.2                        | 0.09149                                  |
| 3     | Water         | 6.290 | 37.0         | 0        | 573.5                      | 1.0                         | 0.53190                                  |
| 4     | Strong solution | 6.290 | 74.0         | 63.5     | 424.4                      | 20.2                        | 0.33201                                  |
| 4’    | Vapor         | 6.290 | 74.0         | 0        | 3054.2                     | 1.0                         | 8.5368                                   |
| 5     | Dilute solution | 6.290 | 69.2         | 60.5     | 420.9                      | 21.2                        | 0.31351                                  |
| 6     | Strong solution | 0.872 | 41.0         | 63.5     | 353.7                      | 20.2                        | 0.11525                                  |
| 7     | Dilute solution | –     | 63.9         | 60.5     | 409.9                      | 21.2                        | 0.27782                                  |
| 8     | Strong solution | –     | 44.3         | 63.5     | 360.7                      | 20.2                        | 0.13754                                  |

The coefficient of performance (COP) for the absorption refrigeration cycle can be defined as:

$$
\text{COP} = \frac{Q_E}{Q_G} = \frac{h_{1'} - h_3}{h_{1'} - h_4 + \alpha (h_4 - h_7)}
$$

where \(\alpha\) represents circulating ratio.

COP was obtained to be 0.801 when using CaCl\textsubscript{2}-LiNO\textsubscript{3}-KNO\textsubscript{3}(15.5:5:1)/H\textsubscript{2}O as the working pair. The COPs for other working pairs were obtained with the same method, and the results are listed in Table 18.
Table 18. Coefficient of performance (COP) of the cycle with different working pairs.

| Working Pair   | CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O | LiBr/H$_2$O | CaCl$_2$-LiBr-LiNO$_3$-KNO$_3$ (16.2:2:2:1)/H$_2$O | CaCl$_2$-LiNO$_3$-LiBr (8.72:1:1)/H$_2$O | CaCl$_2$-LiBr (1.35:1)/H$_2$O |
|----------------|---------------------------------------------|-------------|---------------------------------------------|-------------------------------------|--------------------------------|
| COP            | 0.801                                       | 0.762       | 0.793                                       | 0.805                               | 0.788                          |

Table 18 shows that, through using CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O instead of LiBr/H$_2$O, the COP was improved by 0.04. Moreover, the exergy destruction in each part of the cycle were analyzed to further compare the performance between CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O and LiBr/H$_2$O. Exergy is defined as the maximum possible reversible work that can be obtained from a stream:

$$E = (h - h_0) - (T_0 + 273.15)(s - s_0)$$

where $T_0$ represents the environment temperature that was taken as 25$ ^\circ $C in this paper.

The exergy destructions for each part of the absorption refrigeration cycle were obtained as follows [39].

Evaporator:

$$\Delta E_E = D_3E_3 - D_1'E_1' + Q_E(T_0/T_E - 1)$$

Condenser:

$$\Delta E_C = D_4'E_4' - D_3E_3 - Q_C(1 - T_0/T_C)$$

Absorber:

$$\Delta E_A = D_8E_8 + D_1'E_1' - D_2E_2 - Q_A(1 - T_0/T_A)$$

Generator:

$$\Delta E_G = D_7E_7 - D_4E_4 - D_4'E_4' + Q_G(1 - T_0/T_G)$$

Heat exchanger:

$$\Delta E_{HEX} = D_2E_2 + D_4E_4 - D_7E_7 - D_8E_8$$

Table 19 compares the exergy destructions of the absorption cycle with CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O and LiBr/H$_2$O. Except the exergy destruction of the evaporator was equal because of the same evaporation condition, the exergy destructions of other parts for CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O were lower than those for LiBr/H$_2$O. For the absorption refrigeration cycle, the exergy efficiency ($\eta_E$) can be defined as:

$$\eta_E = \frac{Q_E(T_E/T_0 - 1)}{Q_G(1 - T_Q/T_0)}$$

Table 19. The exergy destruction in each part of absorption refrigeration cycle using CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O and LiBr/H$_2$O.

| Part                  | Exergy Destruction/kW |
|-----------------------|------------------------|
| CaCl$_2$-LiNO$_3$-KNO$_3$ (15.5:5:1)/H$_2$O | LiBr/H$_2$O |
| Evaporator            | 0.5                    | 0.5                     |
| Condenser             | 0.4                    | 0.8                     |
| Absorber              | 52.1                   | 55.3                    |
| Generator             | 282.6                  | 332.7                   |
| Heat exchanger        | 25.5                   | 31.4                    |
The $\eta_E$ of the absorption refrigeration cycle with CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O and LiBr/H$_2$O were obtained to be 0.327 and 0.272, respectively. When compared with COP, the difference in exergy efficiency between the two working pairs was more distinct, which further showed the advantage of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O as an alternative working pair.

Figures 14 and 15 show the changes of generation temperature and efficiencies (COP and $\eta_E$) for CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O, with the evaporation temperature varying from 5 $^\circ$C to 15 $^\circ$C. As shown in Figure 14a, the generation temperature decreased almost linearly with increasing the evaporation temperature. As shown in Figure 14b, the COP of the absorption refrigeration cycle increased with the evaporation temperature increasing, whereas the exergy efficiency decreased with the evaporation temperature increasing.

Figure 14. (a) Variation of the generation temperature with the evaporation temperature; and, (b) Variations of COP and $\eta_E$ with the evaporation temperature.

Figure 15. Variations of COP and $\eta_E$ with the heat exchanger efficiency.

Figure 15 shows the variations of COP and $\eta_E$ with the solution heat exchanger efficiency. COP and $\eta_E$ increased almost linearly with the heat exchanger efficiency increasing, and the increasing slope of COP was greater than that of $\eta_E$. 
3.10. Measurement of Corrosion Rate $R_C$

Generally, carbon steel is used as the structural material and copper is used as the heat exchange material for absorption heat pump. The $R_C$ of carbon steel and copper in 63.5 wt.% solution of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O were measured at 80.0 °C and pH 9.7. Figure 16 gives the comparison of $R_C$ in 63.5 wt.% solution of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O, 59.4 wt.% solution of LiBr/H$_2$O, and 60.3 wt.% solution of CaCl$_2$-LiNO$_3$-LiBr(8.72:1:1)/H$_2$O.

![Figure 16](image_url)

Figure 16. $R_C$ of carbon steel and copper for CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O, CaCl$_2$-LiNO$_3$-LiBr(8.72:1:1)/H$_2$O and LiBr/H$_2$O.

Figure 16 shows that the $R_C$ of carbon steel in 63.5 wt.% solution of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was 14.31 μm·y$^{-1}$. Although the corrosivity of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O to carbon steel was stronger than that of LiBr/H$_2$O, it was still acceptable for practical applications. On the other hand, the corrosivity of CaCl$_2$-LiNO$_3$-LiBr(8.72:1:1)/H$_2$O to carbon steel was too strong to be applied, even though it had the lowest generation temperature among the CaCl$_2$-based working pairs. The $R_C$ of copper in 63.5 wt.% solution of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O was 2.04 μm·y$^{-1}$, which was smaller than that in 59.4 wt.% solution of LiBr/H$_2$O and it could meet the requirements for engineering applications.

4. Conclusions

1. When compared with LiBr/H$_2$O, for an identical adsorption temperature at 0.872 kPa, which is a typical pressure of absorber, CaCl$_2$/H$_2$O had a lower absorption temperature at 6.290 kPa, which is a typical pressure of generator, meaning that CaCl$_2$/H$_2$O basically had a better refrigeration characteristic for an absorption refrigeration cycle. However, the absorption ability of CaCl$_2$/H$_2$O was not strong enough for achieving an evaporation temperature of 5 °C or lower, because of its high crystallization temperature.

2. The crystallization temperature was significantly lowered when combining CaCl$_2$/H$_2$O with LiNO$_3$ or LiNO$_3$+KNO$_3$. As a result, the absorption ability of CaCl$_2$-LiNO$_3$/H$_2$O or CaCl$_2$-LiNO$_3$-KNO$_3$/H$_2$O was essentially improved.

3. For an absorption refrigeration cycle using CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O as the working pair, the generation temperature that is required for achieving an evaporation temperature of 5 °C was 74.0 °C, which was 7.0 °C lower than that using LiBr/H$_2$O.

4. When compared with LiBr/H$_2$O under the same conditions, COP and $\eta_E$ of the absorption refrigeration cycle with CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O were improved by 0.04 and 0.06, respectively.
5. $R_C$ of carbon steel and copper in 63.5 wt.% solution of CaCl$_2$-LiNO$_3$-KNO$_3$(15.5:5:1)/H$_2$O at 80.0 °C and pH 9.7 were 14.31 and 2.04 µm·y$^{-1}$, respectively, which indicated that the corrosivity of the proposed working pair could meet the requirements for practical applications.

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**Nomenclature**

- $T$: temperature, °C
- $w$: mass concentration, %
- $T_C$: crystallization temperature, °C
- $p$: saturated vapor pressure, kPa
- $\rho$: density, g·cm$^{-3}$
- $\eta$: dynamic viscosity, mPa·s
- $C_p$: specific heat capacity, kJ·kg$^{-1}$·K$^{-1}$
- $\Delta H_{mix}$: dissolution enthalpy, kJ·kg$^{-1}$
- $h$: specific enthalpy, kJ·kg$^{-1}$
- $s$: specific entropy, kJ·kg$^{-1}$·K$^{-1}$
- AARD: average absolute relative deviation
- $a$: circulation ratio
- $COP$: coefficient of performance
- $E$: exergy
- $\Delta E$: exergy destruction
- $\eta_E$: exergy efficiency
- $R_C$: corrosion rate, µm·y$^{-1}$

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