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Thermodynamic Performance of a Double-Effect Absorption Refrigeration Cycle Based on a Ternary Working Pair: Lithium Bromide + Ionic Liquids + Water

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Abstract: For an absorption cycle, a ternary working pair LiBr–[BMIM]Cl(2.5:1)/H₂O was proposed as a new working pair to replace LiBr/H₂O. The thermodynamic properties including specific heat capacity, specific enthalpy, density, and viscosity were systematically measured and fitted by the least-squares method. The thermodynamic performance of a double-effect absorption refrigeration cycle based on LiBr–[BMIM]Cl(2.5:1)/H₂O was investigated under different refrigeration temperatures from 5 °C to 12 °C. Results showed that the ternary working pair LiBr–[BMIM]Cl(2.5:1)/H₂O had advantages in the operating temperature range and corrosivity. Compared with LiBr/H₂O, the operating temperature range was 20 °C larger, and the corrosion rates of carbon steel and copper were reduced by more than 50% at 453.15 K. However, the double-effect absorption refrigeration cycle with LiBr–[BMIM]Cl(2.5:1)/H₂O achieved a coefficient of performance (*COP_c*) from 1.09 to 1.46 and an exergetic coefficient of performance (*ECOP_c*) from 0.244 to 0.238, which were smaller than those based on LiBr/H₂O due to the higher generation temperature and larger flow ratio.

Keywords: Double-effect absorption refrigeration; ionic liquids; working pair; thermodynamic properties; thermodynamic performance

1. Introduction

An absorption heat pump (AHP), which can be driven by renewable energy or industrial waste heat for cooling or heating, is proven to have a great energy-saving potential in buildings. From the utilization of a driving heat source, the AHP cycle is divided into single-effect, double-effect, and multiple-effect AHP. The double-effect AHP has two generators, where the temperature of the driven heat source for the first generator is obviously higher than single-effect, and the vapor which is generated from the first generator is also the heat source of the second generator. The number of generators for multiple-effect AHP is correspondingly larger, and the grade of the driven heat source is further improved. The coefficient of performance (*COP*) of double-effect or multi-effect AHP is higher than single-effect AHP because the system can generate more vapor refrigerant per unit heat supplied. However, the improvement of *COP* is weakened upon increasing the number of effects due to the *COP* of each effect for double-effect or multiple-effect systems being lower than that for a single-effect system. Moreover, the higher number of effects leads to more system complexity. Therefore, the double-effect AHP cycle is more available commercially [1].

In the past few decades, many researchers studied the performance of a double-effect absorption heat pump system based on energy and exergy methods [2–8]. The effects of operation conditional

variables, such as the temperature in different working parts of the cycle, effectiveness of solution heat exchangers, circulation ratio, driving heat source, etc. on the thermodynamic performance were investigated. These studies had great significance in evaluating and optimizing the performance. However, among these systems, LiBr/H₂O was usually used as the working pair, which has risks of crystallization and corrosion at a high concentration and temperature. Thus, many researchers made continued efforts to resolve these issues using different methods such as corrosion inhibitors, anticorrosion materials, new working fluids, etc.

The addition of inhibitors is an economical way to reduce the corrosivity of LiBr/H₂O. OH⁻, chromate, tungstate, molybdate, nitrate, tetraborate, or some other complexes are usually added to the LiBr/H₂O solution as the inhibitors in absorption system [9–12]. These inhibitors are helpful to reduce the corrosion of metallic materials by forming a passive film on the metal sample surface. Nonetheless, at a high-level temperature, especially above 165 °C, the corrosion rate is too high for practical application. The corrosivity of LiBr/H₂O to various corrosion-resistant metals, including austenitic stainless steel, Cu–Ni alloys, and duplex stainless steel, was studied using the mass loss method and electrochemical method [13–17]. The corrosion rate decreases significantly when using high-nickel, high-molybdenum, and high-chromium alloys at a relatively low temperature and concentration; however, the metallic materials undergo pitting corrosion when the temperature and concentration are higher.

Some researchers worked on new working fluids instead of LiBr/H₂O which mainly included organic mixtures, salt solutions, and ionic liquids (ILs) [18]. However, among these working fluids, only a few were adopted in double-effect or multi-effect AHP systems. A quaternary working fluid LiNO₃–KNO₃–NaNO₃/H₂O was compatible with austenitic stainless-steel materials at high temperature up to approximately 260 °C, but the solubility of this working fluid was too low [19]. Organic fluid mixtures, such as trifluoroethanol (TFE)–tetraethylglycol dimethylether (TEGDME), methanol–TEGDME, TFE–*N*-methyl-2-pyrrolidone (NMP), and TFE–2-pyrrolidone (PYR), were investigated as new working fluids by several researchers [20,21]. These organic working fluids with wide working temperature ranges are stable at a higher temperature and not very corrosive to general metals, whereas TFE and methanol are inflammable and toxic. As mentioned above, the issue for double-effect or multi-effect AHP systems is still not well settled.

Recently, LiBr–[BMIM]Cl(2.5:1)/H₂O was proposed as a working pair in AHP [22]. The crystallization temperature, saturated vapor pressure, and corrosivity of this working pair were studied, and the results showed that its crystallization temperature and corrosivity were both lower than the common working pair LiBr/H₂O. To further evaluate this alternative working pair, some other important thermodynamic properties including density, viscosity, specific heat capacity, and specific enthalpy were systematically measured, and the performance of a double-effect absorption refrigeration cycle based on LiBr–[BMIM]Cl(2.5:1)/H₂O was investigated and compared with that using LiBr/H₂O.

2. Measuring Method and Thermodynamic Properties

The concentration purities of the reagents used in this work are shown in Table 1. The reagents were used without further purification.

Table 1. Provenance and mass fraction purity of the reagents.

Reagent	Mass Fraction Purity	Provenance
[BMIM]Cl ^a	>0.99	Shanghai Chengjie Chemical
LiBr	>0.995	Tianjin Jinke Chemical
KCl	>0.99	Sinopharm Chemical Reagent Beijing
Li ₂ CrO ₄	>0.99	Tianjin Jinke Chemical
Na ₂ SiO ₃	>0.995	Tianjin Guangfu Chemical
Polyaspartate	>0.99	Xiya Chemical
Pure water		Home made

^a [BMIM]Cl (1-butyl-3-methylimidazolium chloride): C₈H₁₅ClN₂.

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

The saturated vapor pressure was measured using a static method. The solution was poured into an autoclave and assembled with a precision digital absolute pressure gauge (AX-110, Aoxin, Xi'an, China) and a Pt-100 thermocouple. The assembly was then placed in a precision oil bath (DKU-30, Jinghong, Shanghai) after pumping into a vacuum. The data of the pressure gauge and thermocouple were collected after stabilization.

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

Both the specific heat capacity and dissolution enthalpy were measured using a micro reaction calorimeter (μ RC, THT Co., Milton Keynes, 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 using an isothermal method with a solid addition accessory. The specific enthalpy was obtained using the measured specific heat capacity and dissolution enthalpy.

The corrosion rates of carbon steel and copper in the solution were measured using a weight loss method. The sample was soaked in the solution for at least 200 h in a vacuum environment, and the mass change of the sample was weighed to calculate the corrosion rate.

All the thermodynamic properties were measured three times, and the averages were adopted. The detailed experimental apparatus and procedures were given in References [23–25]. The detailed data of the density, viscosity, specific heat capacity, and specific enthalpy for LiBr–[BMIM]Cl(2.5:1)/H₂O are listed in Appendix A.

3. Thermodynamic Analysis of a Double-Effect Absorption Refrigeration Cycle

3.1. Thermodynamic Calculation

The typical points of this serial double-effect absorption refrigeration cycle are marked in Figure 1. To analyze the performance of the cycle, some assumptions are given below.

- The cycle is under a steady state.
- The kinetic and potential energies are negligible.
- Enthalpy of the fluid does not change when flowing through the expansion valve.
- The refrigerant leaving the condenser is saturated liquid.
- The refrigerant leaving the evaporator is saturated vapor.

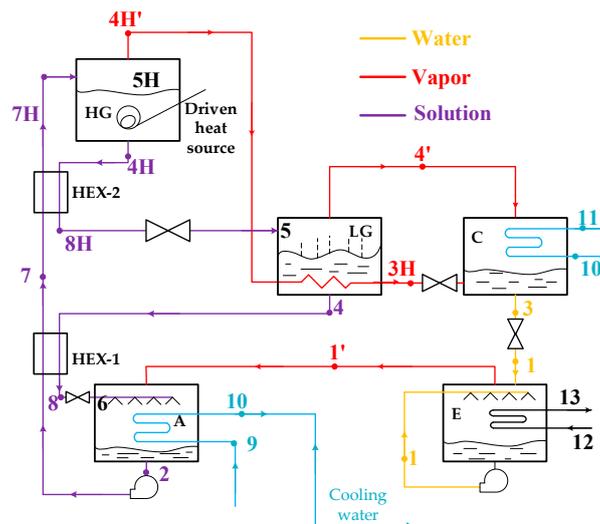


Figure 1. Schematic diagram of a double-effect absorption heat pump (AHP) cycle.

Based on energy, mass, and species conservations, the thermodynamic calculations of this cycle can be calculated using the following equations:

(1) High-pressure generator (HG)

$$m_{7H} = m_{4H} + m_{4H'}, \quad (1)$$

$$m_{7H}w_{7H} = m_{4H}w_{4H}, \quad (2)$$

$$q_{HG} = m_{4H'}h_{4H'} + m_{4H}h_{4H} - m_{7H}h_{7H}. \quad (3)$$

(2) Low-pressure generator (LG)

$$m_{8H} = m_{4'} + m_{4}, \quad (4)$$

$$m_{8H}w_{8H} = m_{4'}w_{4'}, \quad (5)$$

$$q_{LG} = m_{4'}h_{4'} + m_{4}h_{4} - m_{8H}h_{8H}. \quad (6)$$

As the calefaction heat in LG comes from the steam produced by the HG, the specific heat load q_{LG} can also be calculated using Equation (7).

$$q_{LG} = m_{4H'}(h_{4H'} - h_{3H}). \quad (7)$$

(3) Condenser

$$m_3 = m_{4'} + m_{3H}, \quad (8)$$

$$q_C = m_{4'}h_{4'} + m_{3H}h_{3H} - m_3h_3. \quad (9)$$

(4) Evaporator

$$m_{1'} = m_3, \quad (10)$$

$$q_E = m_{1'}h_{1'} - m_3h_3. \quad (11)$$

(5) Absorber

$$m_2 = m_8 + m_{1'}, \quad (12)$$

$$m_2w_2 = m_8w_8, \quad (13)$$

$$q_A = m_{1'}h_{1'} + m_8h_8 - m_2h_2. \quad (14)$$

(6) Solution heat exchangers

$$q_{HEX-1} = m_2(h_7 - h_2) = m_8(h_4 - h_8), \quad (15)$$

$$q_{HEX-2} = m_{7H}(h_{7H} - h_7) = m_{4H}(h_{4H} - h_{8H}), \quad (16)$$

$$\eta_{SHE-1} = \frac{t_4 - t_8}{t_4 - t_2}, \quad (17)$$

$$\eta_{SHE-2} = \frac{t_{4H} - t_{8H}}{t_{4H} - t_7}. \quad (18)$$

(7) Solution pump

$$w_{sp} = \frac{m_7 \Delta p}{\rho_7 \eta_{sp}} = \frac{a(m_{4H'} + m_{4'}) \Delta p}{\rho_7 \eta_{sp}}, \quad (19)$$

$$a = \frac{m_7}{m_{4H'} + m_{4'}} = \frac{w_4}{w_4 - w_7}, \quad (20)$$

where Δp (Pa) is the sum of the total pressure drops and the difference in pressure between the high-pressure generator and the absorber. Frictional and minor pressure losses along the pipelines were calculated using Equations (21)–(24).

$$p_f = \lambda \frac{l}{d} \frac{\rho V^2}{2}, \quad (21)$$

$$p_m = \zeta \frac{\rho V^2}{2}, \quad (22)$$

$$\lambda = 0.11 \left(\frac{K}{d} + \frac{68}{\text{Re}} \right)^{0.25}, \quad (23)$$

$$\text{Re} = \frac{Vd}{\nu}. \quad (24)$$

(8) COP and ECOP

From the above equations, the coefficient of performance (COP) and exergetic coefficient of performance (ECOP) of the double-effect absorption refrigeration cycle were calculated using Equations (25) and (26).

$$\text{COP} = \frac{q_E}{q_{HG} + w_{sp}}, \quad (25)$$

$$\text{ECOP} = \frac{q_E(T_0/T_E - 1)}{q_{HG}(1 - T_0/T_{HG}) + w_{sp}}. \quad (26)$$

3.2. Thermodynamic Calculation Results

In this work, the crystallization temperature and saturated vapor pressure of LiBr–[BMIM]Cl(2.5:1)/H₂O were obtained from Reference [22] and the thermodynamic properties of LiBr/H₂O were obtained from References [25–29]. The properties of water and vapor were obtained from References [30–32]. Under the conditions in Table 2, the parameters of each point in Figure 1 could be obtained using the fitted equations of the properties and conservation equations with the Matlab program. Results for LiBr–[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O are listed in Tables 3 and 4, respectively. The specific heat loads in different parts of the absorption refrigeration cycle are listed in Table 5.

Table 2. Refrigeration conditions of the double-effect absorption cycle.

Refrigeration Conditions			
Cooling water temperature at inlet	32 °C	Chilled water temperature at the inlet (t_{12})	12 °C
Cooling water temperature at outlet	42 °C	Chilled water temperature at the outlet (t_{13})	7 °C
Temperature difference at the evaporator	2 °C	Efficiency of the solution heat exchangers	0.90
Temperature difference at the absorber, condenser, and generators	3 °C	Difference of the mass concentration of the both working pairs	4%

Table 3. State parameters of streams in the cycle with LiBr–[BMIM]Cl(2.5:1)/H₂O.

Points	Stream	Position	w	t (°C)	p (kPa)	h (kJ·kg ⁻¹)	m (kg·s ⁻¹)
1'	Vapor	Outlet of the evaporator	0	5.0	0.872	2928.53	1.00
1	Water	Inlet of the evaporator	0	5.0	0.872	439.63	1.00
2	Weak solution	Outlet of the absorber	67.7	42.4	0.872	317.82	17.90
3	Water	Outlet of the condenser	0	45.0	9.58	606.99	1.00
3H	Water	Outlet of the low-pressure generator	0	101.8	108.52	845.47	0.60
4'	Vapor	Outlet of the low-pressure generator	0	98.8	9.58	3101.76	0.40
4	Strong solution	Outlet of the low-pressure generator	71.7	98.8	9.58	463.13	16.90
4H'	Vapor	Outlet of the high-pressure generator	0	164.9	108.52	3227.07	0.60
4H	Medium solution	Outlet of the high-pressure generator	70.0	164.9	108.52	582.94	17.30
5	Medium solution	Low-pressure generator	70.0	95.2	9.58	437.43	17.30
6	Strong solution	Absorber	71.7	48.0	0.872	363.76	16.90
7	Weak solution	Outlet of the solution heat exchanger	67.7	87.4	-	411.65	17.90
7H	Weak solution	Outlet of the solution heat exchanger	67.7	154.3	-	552.29	17.90
8	Strong solution	Outlet of the solution heat exchanger	71.7	48.0	-	363.76	16.90
8H	Medium solution	Outlet of the solution heat exchanger	70.0	95.2	-	437.43	17.30
9	Cooling water	Inlet of the absorber	0	32.0	-	-	-
10	Cooling water	Outlet of the absorber	0	39.4	-	-	-
11	Cooling water	Outlet of the condenser	0	42.0	-	-	-
12	Chilled water	Inlet of the evaporator	0	12.0	-	-	-
13	Chilled water	Outlet of the evaporator	0	7.0	-	-	-

Table 4. State parameters of streams in the cycle with LiBr/H₂O.

Points	Stream	Position	w	t (°C)	p (kPa)	h (kJ·kg ⁻¹)	m (kg·s ⁻¹)
1'	Vapor	Outlet of the evaporator	0	5.0	0.872	2928.53	1.00
1	Water	Inlet of the evaporator	0	5.0	0.872	439.63	1.00
2	Weak solution	Outlet of the absorber	58.8	42.0	0.872	279.65	15.71
3	Water	Outlet of the condenser	0	45.0	9.58	606.99	1.00
3H	Water	Outlet of the low-pressure generator	0	100.9	104.80	841.27	0.55
4'	Vapor	Outlet of the low-pressure generator	0	97.9	9.58	3100.02	0.45
4	Strong solution	Outlet of the low-pressure generator	62.8	97.9	9.58	384.89	14.71
4H'	Vapor	Outlet of the high-pressure generator	0	158.8	104.80	3215.43	0.55
4H	Medium solution	Outlet of the high-pressure generator	60.9	158.8	104.80	500.33	15.16
5	Medium solution	Low-pressure generator	60.9	93.1	9.58	375.97	15.16
6	Strong solution	Absorber	62.8	47.6	0.872	293.15	14.71
7	Weak solution	Outlet of the solution heat exchanger	58.8	85.8	-	365.55	15.71
7H	Weak solution	Outlet of the solution heat exchanger	58.8	148.3	-	485.58	15.71
8	Strong solution	Outlet of the solution heat exchanger	62.8	47.6	-	293.15	14.71
8H	Medium solution	Outlet of the solution heat exchanger	60.9	93.1	-	375.97	15.16
9	Cooling water	Inlet of the absorber	0	32.0	-	-	-
10	Cooling water	Outlet of the absorber	0	39.0	-	-	-
11	Cooling water	Outlet of the condenser	0	42.0	-	-	-
12	Chilled water	Inlet of the evaporator	0	12.0	-	-	-
13	Chilled water	Outlet of the evaporator	0	7.0	-	-	-

Table 5. The specific heat load at different parts of double-effect absorption heat pump (AHP). COP—coefficient of performance; ECOP—exergetic coefficient of performance.

Working Pairs	q_{HG} (kW)	q_{LG} (kW)	q_C (kW)	q_E (kW)	q_A (kW)	q_{SHE-1} (kW)	q_{SHE-2} (kW)	COP_c	$ECOP_c$
LiBr-[BMIM]Cl/H ₂ O	2134.14	1502.46	1142.50	2321.54	3388.27	1681.85	2520.97	1.09	0.244
LiBr/H ₂ O	1715.86	1366.15	1258.22	2321.54	2847.43	1349.08	1885.17	1.35	0.312

From Tables 3 and 4, the calculation results show good mass and species conservation. The energy conservation can be further verified from Table 5 by Equation (27). The total heat input is defined as $q_E + q_G$, and the total heat output is defined as $q_A + q_C$. The total heat input and output for LiBr-[BMIM]Cl/H₂O were 4455.68 kW and 4530.77 kW, respectively. The relative deviations between the total heat input and total heat output of the cycle were 1.68% for LiBr-[BMIM]Cl/H₂O and 1.69% for LiBr/H₂O. The mass flow rate of the cooling water in the absorber was nearly identical to that in the condenser. Considering an acceptable relative deviation, the above mathematic equations and Matlab program in this work could be used to analyze the performance of a double-effect absorption

refrigeration cycle. To further comprehensively compare it with LiBr/H₂O, the thermodynamic performance of LiBr–[BMIM]Cl/H₂O was calculated under various evaporation temperature from 5 °C to 12 °C. The chilled water temperatures (t_{11} and t_{12}) were changed with the evaporation temperature. The other operation conditions in Table 2 were kept invariant in the calculation.

$$\begin{cases} \left| \frac{(q_E + q_{HG}) - (q_C + q_A)}{(q_E + q_{HG})} \right| < 0.02 \\ D_{c1} = \frac{q_A \times \rho_A}{4.186 \times (t_{10} - t_9)} = 108 \text{ kg} \cdot \text{s}^{-1} \\ D_{c2} = \frac{q_C \times \rho_c}{4.186 \times (t_{11} - t_{10})} = 106 \text{ kg} \cdot \text{s}^{-1} \end{cases} \quad (27)$$

3.3. Thermodynamic Analysis and Discussion

3.3.1. Generation Temperature and Corrosion

For a high-temperature absorption system, the generation temperature in the high-pressure generator has great influence on the required grade of the driving heat source and the corrosion to materials. As shown in Figure 2, as the evaporation temperature t_E varied from 5 °C to 12 °C, the generation temperature t_{HG} in the HG decreased from 164.9 °C to 140.4 °C and from 158.9 °C to 137.3 °C for LiBr–[BMIM]Cl/H₂O and LiBr /H₂O, respectively. The double-effect absorption refrigeration system based on LiBr–[BMIM]Cl/H₂O needs a higher generation temperature, leading to it requiring a higher grade of the driving heat source and facing a stronger corrosivity. The generation temperature t_{LG} in the LG also decreased with the increasing t_E . The difference in t_{LG} between LiBr–[BMIM]Cl(2.5:1)/H₂O and LiBr /H₂O was slight.

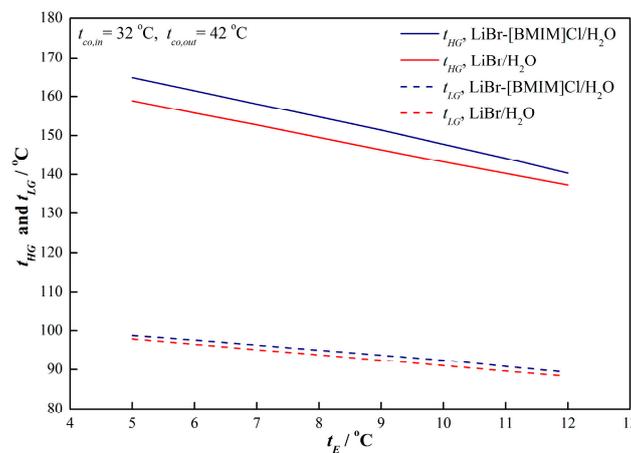


Figure 2. Variations of t_{HG} and t_{LG} with the evaporation temperature t_E .

The corrosion problem, which is generally faced in high-pressure generators, usually limits the applications of a high-temperature absorption system. To study the corrosivity of LiBr–[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O, the corrosion rates of carbon steel and copper in 70.0% LiBr–[BMIM]Cl(2.5:1)/H₂O at 165 °C and 60.9% LiBr/H₂O at 159 °C, adding environmentally friendly complex inhibitors of Na₂SiO₃ at $w = 0.004$ and polyaspartate (PASP) at $w = 0.001$, were investigated using a weight loss method [33]. Figure 3 shows that the corrosion rates of carbon steel and copper in LiBr–[BMIM]Cl(2.5:1)/H₂O were smaller than those in LiBr/H₂O. Compared to carbon steel, copper exhibited much greater corrosion rates in both working pairs.

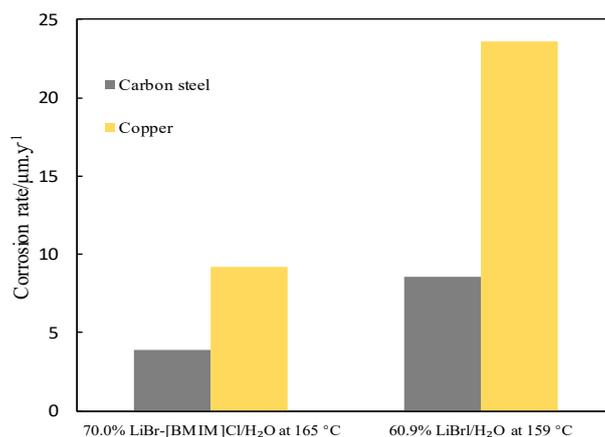


Figure 3. Corrosion rates of carbon steel and copper in LiBr-[BMIM]Cl/H₂O and LiBr/H₂O.

In order to further analyze the corrosion phenomenon of copper, the surface morphologies of the metal samples soaked in the solutions of LiBr-[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O were photographed using a scanning electron microscope (SEM), as shown in Figure 4. The copper surface for LiBr-[BMIM]Cl(2.5:1)/H₂O was homogeneously covered with the solid corrosion products. In addition to the complex inhibitors, the organic cations in the imidazolium-based ionic liquids [BMIM]Cl would be adsorbed onto the metal surface to form an organic film, which would be helpful for inhibiting the ion transport and reducing the corrosion rate. In contrast, there was no protective layer overlaid on the copper surface for LiBr/H₂O. Thus, the corrosivity of the ternary working pair was less than LiBr/H₂O. Under the generation temperature around 160 °C in the high-pressure generator, LiBr-[BMIM]Cl/H₂O had a strong anti-corrosion effect on the metal materials, which is beneficial for the lifetime of a high-temperature absorption system.

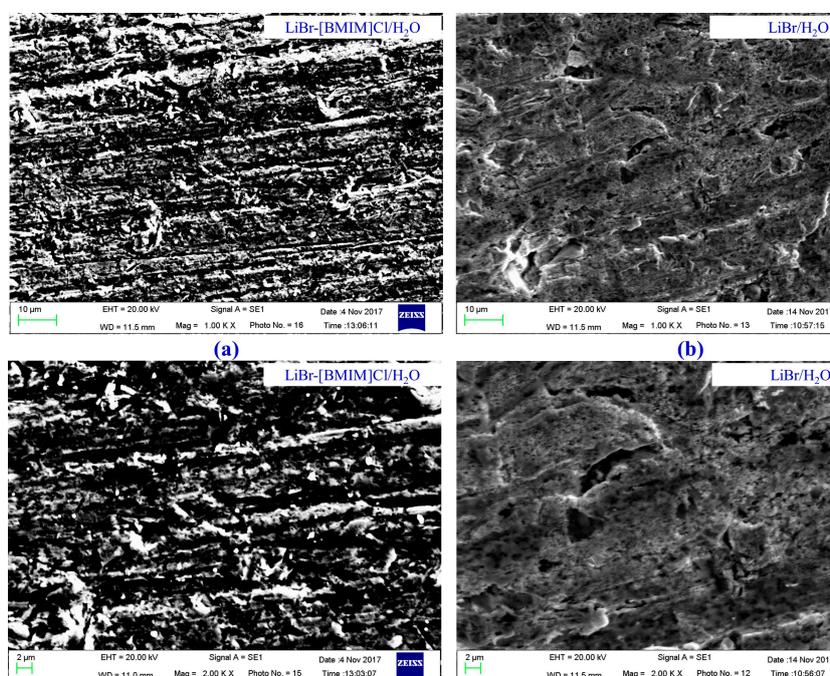


Figure 4. SEM micrograph of copper surface in the working pair with $w = 0.004 \text{ Na}_2\text{SiO}_3$ and $w = 0.001$ polyaspartate: (a) LiBr-[BMIM]Cl/H₂O; (b) LiBr/H₂O.

3.3.2. Crystallization Problem

In addition to the corrosion issue, crystallization is another critical problem limiting the practical application of a high-temperature absorption refrigeration system. Crystallization risk generally occurs as the strong solutions flow through the solution heat exchangers (HEX), especially at the outlet of the HEX-1 (point 8). Thus, the operating temperature range, which is defined to be the difference between the t_8 and crystallization temperature t_{cr} , is not only closely related to the temperature t_8 but also depends on the concentration of the strong solution. Figure 5 shows the variation of the mass fractions of strong solution w_{LG} with the evaporation t_E . w_{LG} decreased from $w = 0.717$ to $w = 0.680$ and from $w = 0.628$ to $w = 0.586$ for LiBr–[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O, respectively, as t_E increased from 5 °C to 12 °C, whereby the former had a larger strong solution concentration. However, as shown in Figures 6 and 7, the operating temperature range of LiBr–[BMIM]Cl(2.5:1)/H₂O was still larger than that of LiBr/H₂O because of its lower crystallization temperature. As t_E increased from 5 °C to 12 °C, the operating temperature range for LiBr–[BMIM]Cl/H₂O varied from 34.8 °C to 56.9 °C, which was approximately 20 °C larger than that for LiBr/H₂O. In particular, at the lower refrigeration temperature, the operating temperature range for LiBr/H₂O was around 10 °C, and the crystallization risk could not be ignored due to the fluctuation of the concentration.

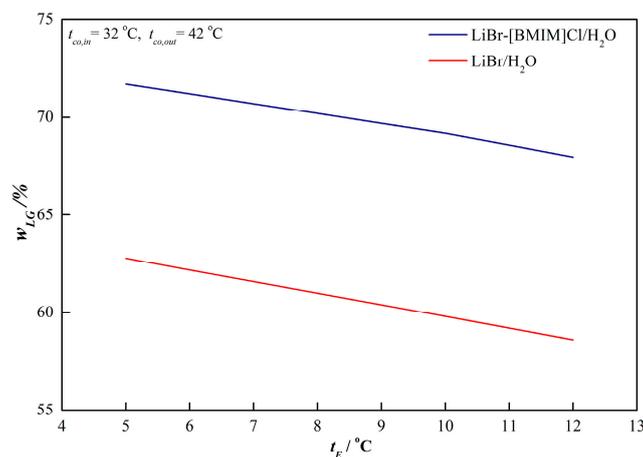


Figure 5. Variations of w_{LG} with the evaporation temperature t_E .

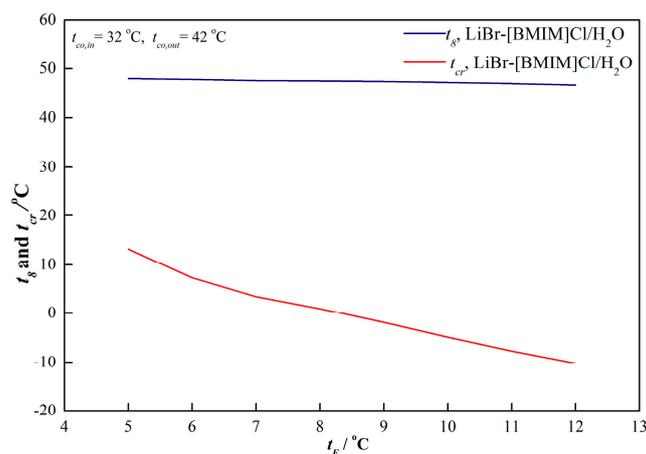


Figure 6. Variations of t_8 and t_{cr} for LiBr–[BMIM]Cl/H₂O with the evaporation temperature t_E .

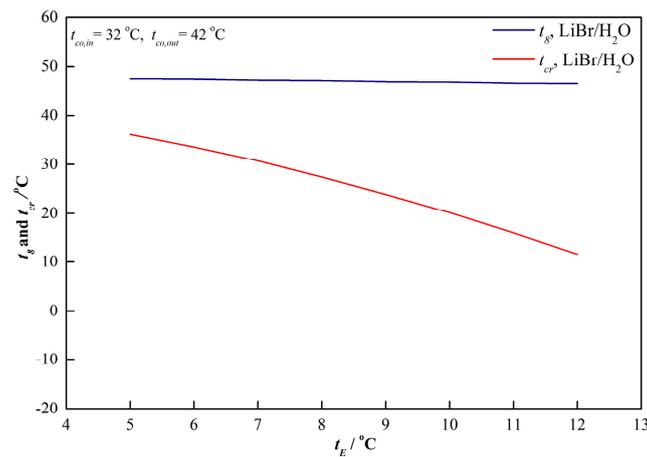


Figure 7. Variations of t_g and t_{cr} for LiBr/H₂O with the evaporation temperature t_E .

3.3.3. Solution Pump Power

In most previous studies, the solution pump power was ignored because of its negligible value. In this work, the solution pump power was calculated based on the measured densities and viscosities. As exhibited in Figure 8, the solution pump power decreased with increasing t_E . According to Equation (19), the flow ratio a had a great impact on the solution pump power. As shown in Figure 9, the flow ratio a had a similar tendency with w_{sp} . Moreover, the double-effect absorption refrigeration cycle using LiBr–[BMIM]Cl(2.5:1)/H₂O had a larger flow ratio because of a higher mass fraction of the strong solution, which led to a larger w_{sp} . Compared to the heat load in other parts in the absorption cycle, the solution pump power from 2 kW to 3.5 kW was really negligible, but the calculation was necessary for selecting the solution pump.

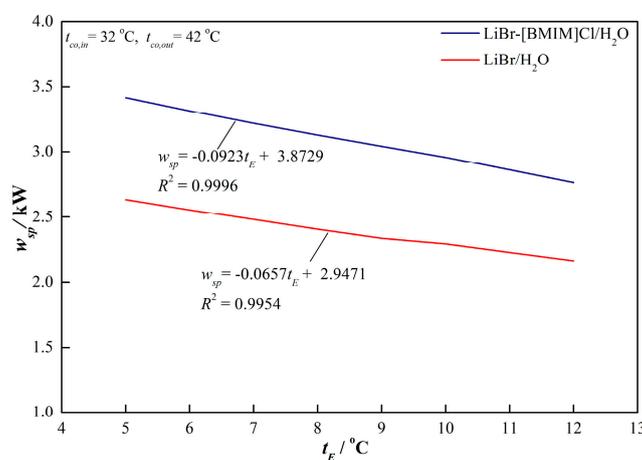


Figure 8. Variations of w_{sp} with the evaporation temperature t_E .

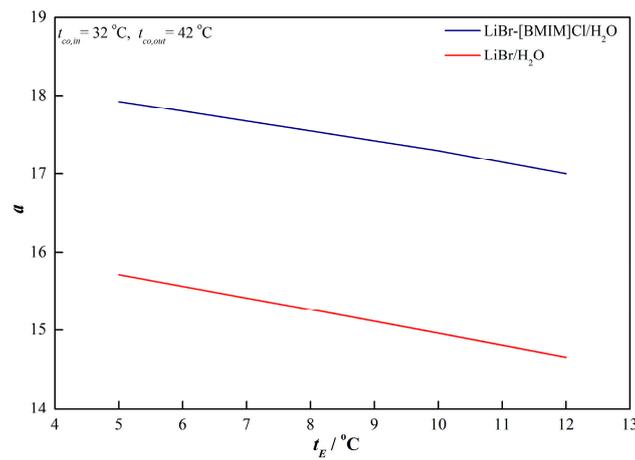


Figure 9. Variations of a with the evaporation temperature t_E .

3.3.4. COP_c

COP_c , the coefficient of performance for cooling, shows the energy utilization efficiency. The variation of COP_c with t_E is shown in Figure 10. As t_E varied from 5 °C to 12 °C, COP_c increased from 1.09 to 1.46 and from 1.35 to 1.49 for LiBr-[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O, respectively. Obviously, the latter had a larger COP_c . On the basis of Equation (25), COP_c can be further described by Equation (28).

$$COP = \frac{h_{1'} - h_3}{a \times \left(\frac{w_{HG} - w_A}{w_{HG}} \times h_{4h'} + \frac{w_A}{w_{HG}} \times h_{4h} - h_{7h} \right) + w_{sp}}. \quad (28)$$

Under a certain condensation temperature, h_3 is a constant. $h_{1'}$ increases with increasing t_E . As shown in Figures 8 and 9, both w_{sp} and a decreased with increasing t_E . The sum in the brackets was a positive value and also decreased with increasing t_E . Consequently, the COP_c showed a positive relationship with t_E . Because the double-effect absorption refrigeration cycle with LiBr-[BMIM]Cl(2.5:1)/H₂O had a larger a and w_{sp} , as well as a higher generation temperature corresponding to a higher $h_{4h'}$, it achieved a smaller COP_c compared to LiBr/H₂O. However, the COP_c of LiBr-[BMIM]Cl(2.5:1)/H₂O increased with a much larger slope and got close to that based on LiBr/H₂O at $t_E = 12$ °C. This was mainly because the specific heat load in the high-pressure generator was reduced sharply due to the larger a . Additionally, the generation temperature and the corresponding $h_{4h'}$ were reduced more rapidly compared with that for LiBr/H₂O.

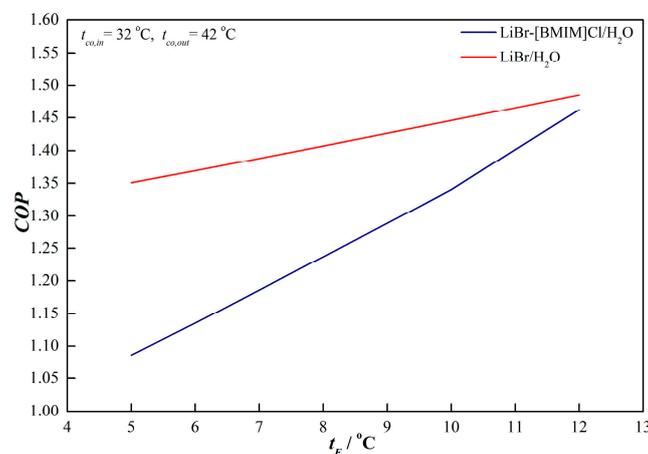


Figure 10. Variations of coefficient of performance (COP) with the evaporation temperature t_E .

3.3.5. $ECOP_c$

COP_c , which is based on the first law of thermodynamics, is important to analyze the thermal performance of an absorption system, $ECOP_c$ is usually used for further evaluating the performance of the absorption system based on the second law of thermodynamics. As we know, exergy is a measure of the usefulness and quality of energy, meaning the potential of the heat-to-work through a reversible thermodynamic process. Naturally, the analysis of $ECOP_c$ is significant for a double-effect absorption refrigeration cycle. As shown in Figure 11, $ECOP_c$ varied from 0.244 to 0.238 and from 0.312 to 0.247 upon increasing t_E from 5 °C to 12 °C for LiBr–[BMIM]Cl(2.5:1)/H₂O and LiBr/H₂O, respectively. Compared to COP_c , $ECOP_c$ had a different variation tendency. $ECOP_c$ for LiBr–[BMIM]Cl(2.5:1)/H₂O firstly increased slightly and then decreased with increasing t_E , and $ECOP_c$ for LiBr/H₂O also changed nonlinearly. This was mainly because $ECOP_c$ had a relationship with both the quantity and quality of energy. In Equation (26), the specific heat loads q_E and q_{HG} transformed from the driving heat source were the measures of quantity. $(T_0/T_E - 1)$ and $(1 - T_0/T_{HG})$ were the efficiency of the heat-to-work by the Carnot engine operating between a constant temperature T and ambient temperature T_0 , i.e., the Carnot factor, showing the quality of the heat.

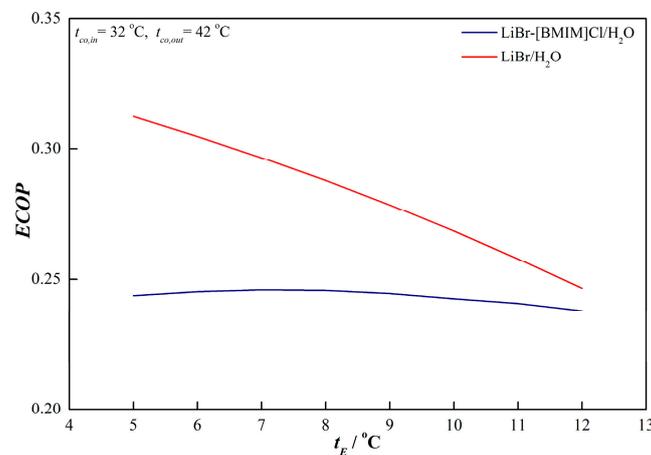


Figure 11. Variations of exergetic coefficient of performance ($ECOP$) with the evaporation temperature t_E .

To further investigate the effect of t_E on $ECOP_c$, the variations of q_E , q_{HG} , $(T_0/T_E - 1)$, and $(1 - T_0/T_{HG})$ are shown in Figure 12. q_{HG} , $(T_0/T_E - 1)$, and $(1 - T_0/T_{HG})$ decreased with increasing t_E and q_E increased with increasing t_E . The decreases in q_{HG} and $(1 - T_0/T_{HG})$ were beneficial for improving $ECOP_c$. The increase in q_E also had a positive contribution to $ECOP_c$, whereas the decrease in $(T_0/T_E - 1)$ had negative contribution to $ECOP_c$. $ECOP_c$ for LiBr–[BMIM]Cl/H₂O was somewhat less than that for LiBr/H₂O because of the larger q_{HG} and $(1 - T_0/T_{HG})$. q_{HG} for LiBr–[BMIM]Cl/H₂O decreased much more rapidly as t_E increased from 5 °C to 12 °C, resulting in the reduction of the $ECOP_c$ gap between both working pairs. q_E , q_{HG} , $(T_0/T_E - 1)$, $(1 - T_0/T_{HG})$, and w_{sp} almost changed linearly with the changing of t_E ; thus, Equation (26) for $ECOP_c$ can be further described as follows:

$$ECOP_c = \frac{f_E(t_E) \times \theta_E(t_E)}{f_{HG}(t_E) \times \theta_{HG}(t_E) + w_{sp}(t_E)}. \quad (29)$$

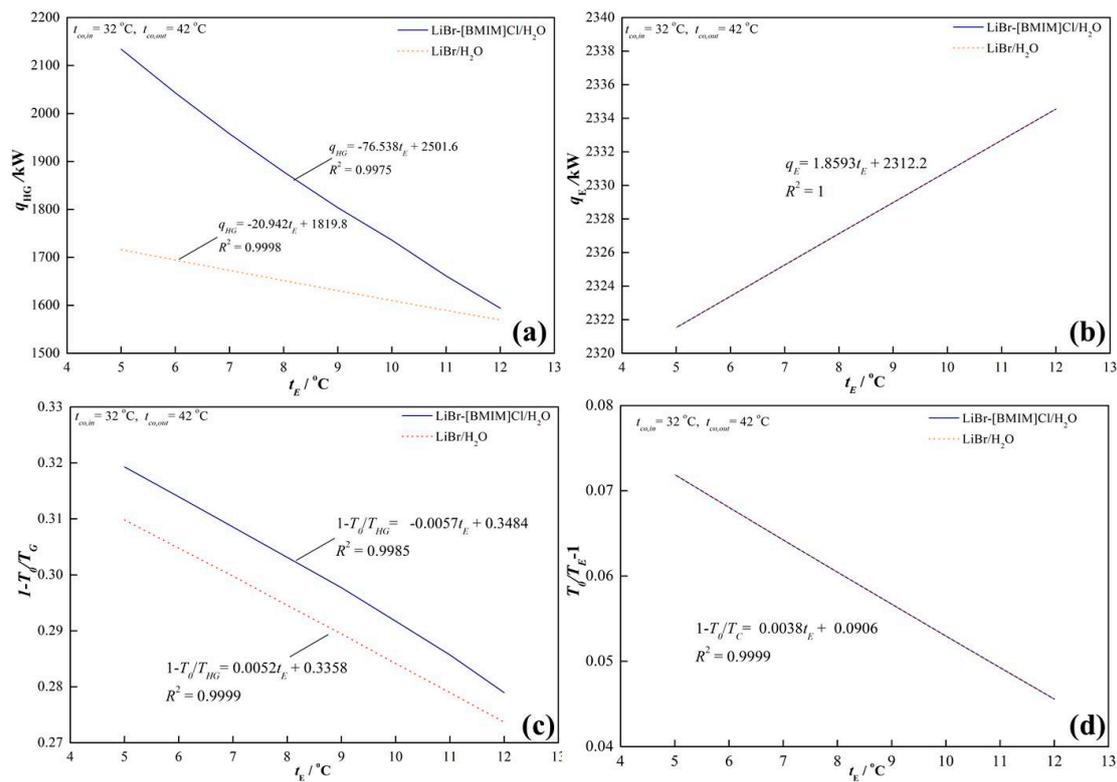


Figure 12. Variations of the specific heat loads and their quality with the evaporation temperature t_E . (a) q_E ; (b) q_{HG} ; (c) $(1 - T_0/T_{HG})$; (d) $(T_0/T_E - 1)$.

Obviously, the $ECOP_c$ changed nonlinearly upon increasing the t_E . As the first-order derivative of the $ECOP_c$ is equal to zero, the theoretical maximum value of the $ECOP_c$ could be obtained, and the values were 0.246 (about $t_E = 7$ °C) and 0.383 (about $t_E = -23$ °C) for LiBr-[BMIM]Cl/H₂O and LiBr/H₂O, respectively. As t_E was below the transform temperature, the decreases in q_{HG} and $(1 - T_0/T_{HG})$ had a dominant effect on the $ECOP_c$, resulting in an increase in $ECOP_c$. However, as the t_E further increased, the decline in $(T_0/T_E - 1)$ became the key factor leading to the reduction of the $ECOP_c$. Because q_{HG} and $(1 - T_0/T_{HG})$ for LiBr-[BMIM]Cl/H₂O were larger than those for LiBr/H₂O, the former had a larger transform temperature.

3.3.6. Concentration Difference between Weak and Strong Solution

The concentration difference between the weak solution and strong solution (dc) also affects the performance of the absorption refrigeration cycle. To analyze the influence of dc , the thermodynamic performance of LiBr-[BMIM]Cl/H₂O and LiBr/H₂O was calculated under various dc values from 3% to 7%.

As shown in Figure 13, the high-pressure generator temperature t_{HG} increased linearly with increasing dc for both LiBr-[BMIM]Cl/H₂O and LiBr/H₂O. At the same t_{HG} , the dc of LiBr/H₂O was about 1.8% small than that of LiBr-[BMIM]Cl/H₂O, which means LiBr/H₂O had a smaller circulation ratio, but higher crystallization temperature due to the high strong solution concentration. This was consistent with the previous analysis. The COP of the cycle for both working pairs also increased with increasing dc in Figure 14. The difference in t_{HG} or COP between LiBr-[BMIM]Cl/H₂O and LiBr/H₂O was tiny upon changing the dc .

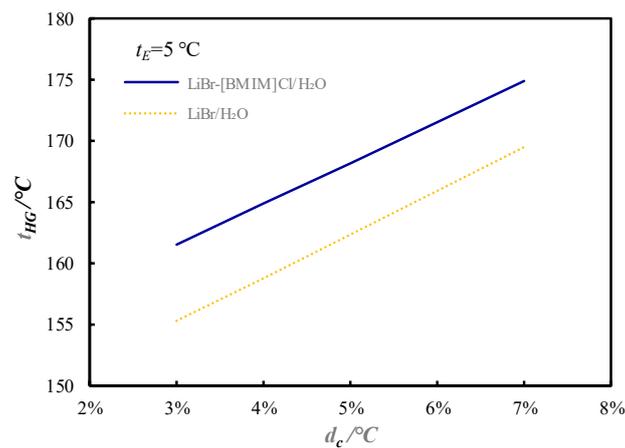


Figure 13. Variations of t_{HG} with different d_c .

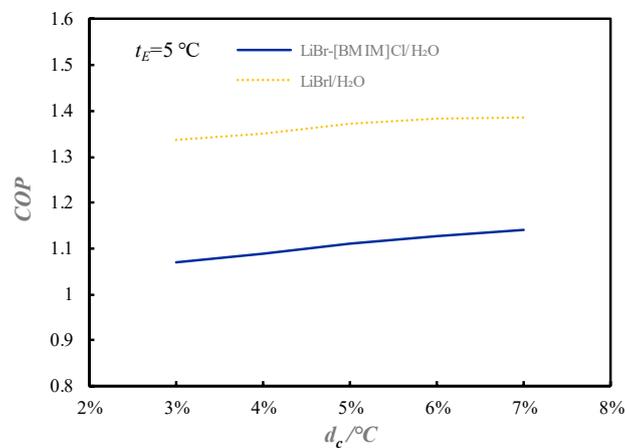


Figure 14. Variations of COP with different d_c .

4. Conclusions

Based on the properties of LiBr–[BMIM]Cl(2.5:1)/H₂O, the thermodynamic performance of a double-effect absorption refrigeration cycle with this working pair was analyzed and compared with LiBr/H₂O under different refrigeration temperatures from 5 °C to 12 °C. Results showed that the operating temperature range for LiBr–[BMIM]Cl(2.5:1)/H₂O was about 20 °C larger than that for LiBr/H₂O. The solution pump power was negligible as it was much less than the specific heat loads of other parts of the absorption cycle. The double-effect absorption refrigeration cycle using LiBr–[BMIM]Cl/H₂O achieved COP_c from 1.09 to 1.46, which was smaller than that using LiBr/H₂O due to the higher generation temperature and larger flow ratio. $ECOP_c$ for LiBr–[BMIM]Cl/H₂O varied from 0.244 to 0.238, which was also smaller than that for LiBr/H₂O. Although LiBr–[BMIM]Cl/H₂O had a higher generation temperature, it showed less corrosivity to carbon steel and copper compared to LiBr/H₂O. Thus, as a potential working pair, LiBr–[BMIM]Cl(2.5:1)/H₂O has some advantages for a double-effect absorption refrigeration cycle or other high-temperature AHP.

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Nomenclature

[BMIM]Cl	1-butyl-3-methylimidazolium chloride
a	circulation ratio
COP_c	coefficient of performance
C_p	specific heat capacity, $J \cdot g^{-1} \cdot K^{-1}$
$ECOP_c$	exergy coefficient of performance
h	specific enthalpy, $kJ \cdot kg^{-1}$
ILs	ionic liquids
m	mass flow rate of the solution, $kg \cdot s^{-1}$
p	vapor pressure, kPa
q	specific heat load, $kJ \cdot s^{-1}$
Re	Reynolds number
T	temperature, K
t	temperature, °C
w	mass fraction of absorbent
η	efficiency
ν	viscosity, $mm^2 \cdot s^{-1}$
ρ	density, $g \cdot cm^{-3}$
λ	frictional factor
ζ	factor of local resistance
θ	Carnot factor
A	absorber
C	condenser
cr	crystallization
E	evaporator
HEX-1, HEX-2	solution heat exchanger
HG	high-pressure generator
LG	low-pressure generator
sp	solution pump

Appendix A

Table A1. Saturated vapor pressure at absorbent mass fraction w of the system LiBr (1) + [BMIM]Cl (2) + H₂O (3) at $p = 0.1$ MPa.

T (K)	p (kPa)						
$w_{1+2} = 0.60$		$w_{1+2} = 0.65$		$w_{1+2} = 0.70$		$w_{1+2} = 0.75$	
296.4	0.71	309.7	0.82	303.7	0.55	356.7	2.90
316.4	2.06	323.3	1.70	313.4	0.96	367.5	4.89
326.7	3.69	334.3	3.00	323.8	1.51	379.0	8.35
336.5	5.98	345.9	5.57	332.4	2.91	389.5	12.77
346.7	9.69	355.9	8.85	345.1	4.86	399.8	19.03
357.8	15.28	365.3	13.34	355.3	7.80	410.4	27.76
367.5	22.05	375.2	19.82	364.7	12.57	420.3	38.98
377.8	32.60	384.5	28.22	375.1	18.59	429.9	56.05
388.6	48.40	395.8	41.96	384.8	28.815	441.6	76.89
400.2	71.00	405.7	59.23	396.5	40.84	449.6	98.50
408.7	92.65	415.4	79.80	405.6	58.25		
		423.2	100.70	416.5	79.00		

The fitting equation was as follows:

$$\lg p = \sum_{i=0}^4 [A_i + B_i / (T - C_i)] w^i \quad (A1)$$

Table A2. Values of A_i , B_i , and C_i for saturated vapor pressure.

i	A_i	B_i	C_i
0	-1.0265478	39.616964	210.51137
1	0.74875570	-549.1808	-302.38069
2	$-1.2196498 \times 10^{-2}$	18.494558	-594.34163
3	$-1.2684596 \times 10^{-4}$	4.44125×10^{-19}	-3.1545374
4	1.5837523×10^{-6}	-6.24780×10^{-4}	-306.48281

Table A3. Density at absorbent mass fraction w of the system LiBr (1) + [BMIM]Cl (2) + H₂O (3) at $p = 0.1$ MPa^a.

T (K)	ρ (g·cm ⁻³)								
$w_{1+2} = 0.55$		$w_{1+2} = 0.60$		$w_{1+2} = 0.65$		$w_{1+2} = 0.70$		$w_{1+2} = 0.75$	
303.15	1.384	303.15	1.434	303.15	1.49	303.15	1.549		
313.15	1.378	313.15	1.428	313.15	1.483	313.15	1.542		
323.15	1.372	323.15	1.422	323.15	1.477	323.15	1.535		
333.15	1.367	333.15	1.416	333.15	1.47	333.15	1.528	333.15	1.59
343.15	1.361	343.15	1.411	343.15	1.464	343.15	1.521	343.15	1.582
353.15	1.355	353.15	1.405	353.15	1.458	353.15	1.515	353.15	1.575
363.15	1.349	363.15	1.399	363.15	1.452	363.15	1.508	363.15	1.568
373.15	1.343	373.15	1.393	373.15	1.446	373.15	1.502	373.15	1.561

^a The mass ratio of LiBr to [BMIM]Cl was 2.5:1. Standard uncertainties u were $u(T) = \pm 0.05$ K, $u(w_{1+2}) = \pm 0.2$ wt.%, and $u(p) = \pm 3.0$ kPa, and the standard uncertainty u was $u(\rho) = \pm 0.003$ g·cm⁻³.

The fitting equation was as follows:

$$\rho = \sum_{i=0}^2 [(A_i + B_i T + C_i T^2)w^i]. \tag{A2}$$

Table A4. Values of A_i , B_i , and C_i for density.

i	A_i	B_i ($\times 10^{-3}$)	C_i ($\times 10^{-5}$)
0	0.384514	6.128884	-1.221983
1	2.024635	-16.63302	3.272392
2	8.490245×10^{-2}	8.778485	-2.017801

Table A5. Viscosity at absorbent mass fraction w of the system LiBr (1) + [BMIM]Cl (2) + H₂O (3) at $p = 0.1$ MPa^a.

T (K)	ν (mm ² ·s ⁻¹)	T (K)	ν (mm ² ·s ⁻¹)	T (K)	ν (mm ² ·s ⁻¹)	T (K)	ν (mm ² ·s ⁻¹)	T (K)	ν (mm ² ·s ⁻¹)
$w_{1+2} = 0.55$		$w_{1+2} = 0.60$		$w_{1+2} = 0.65$		$w_{1+2} = 0.70$		$w_{1+2} = 0.75$	
303.15	3.81	303.15	6.21	303.15	10.31	303.15	23.01		
313.15	3.01	313.15	4.88	313.15	7.82	313.15	16.13		
323.15	2.44	323.15	3.87	323.15	6.02	323.15	11.61		
333.15	1.99	333.15	3.06	333.15	4.66	333.15	8.39	333.15	21.29
343.15	1.68	343.15	2.49	343.15	3.71	343.15	6.35	343.15	14.14
353.15	1.46	353.15	2.11	353.15	3.05	353.15	4.94	353.15	10.00
363.15	1.30	363.15	1.83	363.15	2.60	363.15	4.03	363.15	7.46
373.15	1.18	373.15	1.63	373.15	2.22	373.15	3.34	373.15	5.81

^a The mass ratio of LiBr to [BMIM]Cl was 2.5:1. Standard uncertainties u were $u(T) = \pm 0.05$ K, $u(w_{1+2}) = \pm 0.2$ wt.%, and $u(p) = \pm 3.0$ kPa, and the relative standard uncertainty u_r was $u_r(\nu) = \pm 0.03$ ν .

The fitting equation was as follows:

$$\lg \nu = \sum_{i=0}^3 [(A_i + B_i/T + C_i/T^2)w^i]. \tag{A3}$$

Table A6. Values of A_i , B_i , and C_i for viscosity.

i	$A_i (\times 10^2)$	$B_i (\times 10^4)$	$C_i (\times 10^6)$
0	1.217521	-5.828088	3.460217
1	-3.896274	13.818580	8.897532
2	3.291964	-1.092322	-51.704210
3	-0.295650	-9.908650	46.722780

Table A7. Specific heat capacities at absorbent mass fraction w of the system LiBr (1) + [BMIM]Cl (2) + H₂O (3) at $p = 0.1$ MPa ^a.

T (K)	C_p (J·g ⁻¹ ·K ⁻¹)	T (K)	C_p (J·g ⁻¹ ·K ⁻¹)	T (K)	C_p (J·g ⁻¹ ·K ⁻¹)	T (K)	C_p (J·g ⁻¹ ·K ⁻¹)	T (K)	C_p (J·g ⁻¹ ·K ⁻¹)
$w_{1+2} = 0.55$		$w_{1+2} = 0.60$		$w_{1+2} = 0.65$		$w_{1+2} = 0.70$		$w_{1+2} = 0.75$	
303.15	2.30	303.15	2.20	303.15	2.05	303.15	1.94		
313.15	2.32	313.15	2.21	313.15	2.07	313.15	1.96		
323.15	2.33	323.15	2.22	323.15	2.08	323.15	1.96		
333.15	2.34	333.15	2.22	333.15	2.10	333.15	1.97	333.15	1.85
343.15	2.35	343.15	2.23	343.15	2.11	343.15	1.98	343.15	1.86
353.15	2.38	353.15	2.24	353.15	2.12	353.15	2.01	353.15	1.88
363.15	2.40	363.15	2.27	363.15	2.16	363.15	2.03	363.15	1.91
373.15	2.45	373.15	2.30	373.15	2.19	373.15	2.07	373.15	1.93

^a The mass ratio of LiBr to [BMIM]Cl was 2.5:1. Standard uncertainties u were $u(T) = \pm 0.01$ K, $u(w_{1+2}) = \pm 0.2$ wt.%, and $u(p) = \pm 3.0$ kPa, and the standard uncertainty u was $u(C_p) = \pm 0.05$ J·g⁻¹·K⁻¹.

The fitting equation was as follows:

$$C_p = \sum_{i=0}^2 [(A_i + B_i T + C_i T^2)w^i]. \tag{A4}$$

Table A8. Values of A_i , B_i , and C_i for specific heat capacity.

i	A_i	$B_i (\times 10^{-2})$	$C_i (\times 10^{-5})$
0	4.656718	-1.447759	3.392384
1	3.182206	-1.114172	-1.471251
2	-6.925005	2.383878	-1.126738

Table A9. Specific heat capacities (J·g⁻¹·K⁻¹) of ionic liquid [BMIM]Cl at $p = 0.1$ MPa and different temperatures.

283.15 K	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K
1.55	1.62	1.73	1.94	2.55	6.31	1.98	1.98	2.025	2.05

Table A10. Dissolution enthalpies (kJ·kg⁻¹) at various mass fractions w for LiBr-[BMIM]Cl/H₂O at 313.15 K and $p = 0.1$ MPa.

Mass fraction	0.55	0.60	0.65	0.70
Dissolution enthalpy/kJ·kg ⁻¹	-160.66	-173.93	-189.89	-168.04

Equations for calculating specific enthalpy were as follows:

$$\begin{cases} h(T, w) = \int_{T_0}^T C_p dT + h(T_0, w) \\ h(T_0, w) = \sum_{i=1}^3 w_i h_i + h^E(T_0, w) \\ h_i = \int_{T_0}^T C_{p,i} dT + 418.60 \end{cases} \quad (\text{A5})$$

where $h(T, w)$ (kJ/kg) is the specific enthalpy of LiBr–[BMIM]Cl/H₂O at temperature T (K), mass fraction w , $h(T_0, w)$ (kJ/kg) is the specific enthalpy of LiBr–[BMIM]Cl/H₂O at temperature T_0 (K), and mass fractions w , w_i , and h_i are the mass fractions and specific enthalpies of the pure components in the ternary system; $h^E(T_0, w)$ is the dissolution enthalpy of LiBr–[BMIM]Cl/H₂O at temperature T_0 (K), and mass fraction w , $C_{p,i}$ (kJ·kg^{−1}·K^{−1}) is the specific heat capacity of the pure components. The reference data of the specific enthalpies of pure water and pure absorbents were specified to be 418.60 kJ·kg^{−1} (100 kcal·kg^{−1}).

Table A11. Specific enthalpy h at absorbent mass fraction w of the system LiBr (1) + [BMIM]Cl (2) + H₂O (3) at $p = 0.1$ MPa ^a.

T (K)	h (kJ·kg ^{−1})						
$w_{1+2} = 0.55$		$w_{1+2} = 0.60$		$w_{1+2} = 0.65$		$w_{1+2} = 0.70$	
303.15	331.04	303.15	312.51	303.15	291.33	303.15	307.99
313.15	354.18	313.15	334.45	313.15	312.04	313.15	327.44
323.15	377.38	323.15	356.45	323.15	332.82	323.15	346.97
333.15	400.70	333.15	378.56	333.15	353.70	333.15	366.60
343.15	424.17	343.15	400.81	343.15	374.72	343.15	386.39
353.15	447.84	353.15	423.24	353.15	395.92	353.15	406.35
363.15	471.75	363.15	445.91	363.15	417.34	363.15	426.54
373.15	495.96	373.15	468.84	373.15	439.01	373.15	446.98

^a The mass ratio of LiBr to [BMIM]Cl was 2.5:1. Standard uncertainties u were $u(T) = \pm 0.01$ K, $u(w_{1+2}) = \pm 0.2$ wt.%, and $u(p) = \pm 3.0$ kPa, and the relative standard uncertainty u_r was $u_r(h) = \pm 0.02$ h .

The fitting equation was as follows:

$$h = \sum_{i=0}^2 [(A_i + B_i w + C_i w^2 + D_i w^3) T^i] \quad (\text{A6})$$

Table A12. Values of A_i , B_i , C_i , and D_i for specific enthalpy.

i	A_i	B_i	C_i	D_i
0	-1.184934×10^4	5.791208×10^4	-9.675233×10^4	5.399248×10^4
1	7.876601×10^{-1}	4.862318	−5.643877	2.016601×10^{-3}
2	4.233235×10^{-3}	-1.054922×10^{-2}	8.114677×10^{-3}	-2.862036×10^{-6}

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