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The Latent Application of Ionic Liquids in Absorption Refrigeration

Shiqiang Liang, Wei Chen, Keyong Cheng,
Yongxian Guo and Xiaohong Gui
Institute of Engineering Thermophysics,
Chinese Academy of Sciences,
Beijing 100190,
China

1. Introduction

The absorption refrigeration technology, which went through more than 100 years, has attracted much attention all over the world, for the reason that it is environmental friendly and could make use of the low-grade energy, which refers to the ignored energy embedded in the exhaust steam of low pressure and low temperature. The absorption refrigeration is widely used in many fields, such as military, air conditioning, electric power, steelmaking, chemical industry, drugs manufacture and so on. In this section, the absorption refrigeration cycle and its working pairs are the key contents that will be introduced to the readers.

1.1 Principles

Absorption refrigeration uses a source of heat to provide the energy needed to drive the cooling process. The liquid refrigerant evaporates in a low partial pressure environment, thus extracting heat from its surroundings, and the absorbent absorbs the gaseous refrigerant to reduce its partial pressure in the evaporator and allowing more liquid to evaporate. The refrigerant-laden liquid is heated to boil refrigerant vapor out of the absorbent solution and compress the refrigerant vapor to a higher pressure, then it is condensed through a heat exchanger to replenish the supply of liquid refrigerant in the evaporator.

1.2 Absorption refrigeration cycle

The single effect absorption refrigeration cycle is shown in Figure 1, which is the most elementary one. As mentioned above, in absorption refrigeration system, an absorber, generator, pump and recuperative heat exchanger replace the compressor in the actual vapor-compression refrigeration systems. The cycle begins when high pressure liquid refrigerant from the condenser passes into the evaporator through an expansion valve, which reduces the pressure of the refrigerant to the low pressure existing in the evaporator. The liquid refrigerant vaporizes in the evaporator by absorbing heat from the material needing to be cooled and the resulting low-pressure vapor migrates to the absorber, where the vapor is absorbed by the solution coming from the generator, called strong solution.

Here we consider refrigerant as solvent. The resulting low concentration solution, called weak solution, is pumped to the generator, where the refrigerant is boiled off. The remaining strong solution flows back to the absorber and, thus, completes the cycle [1].
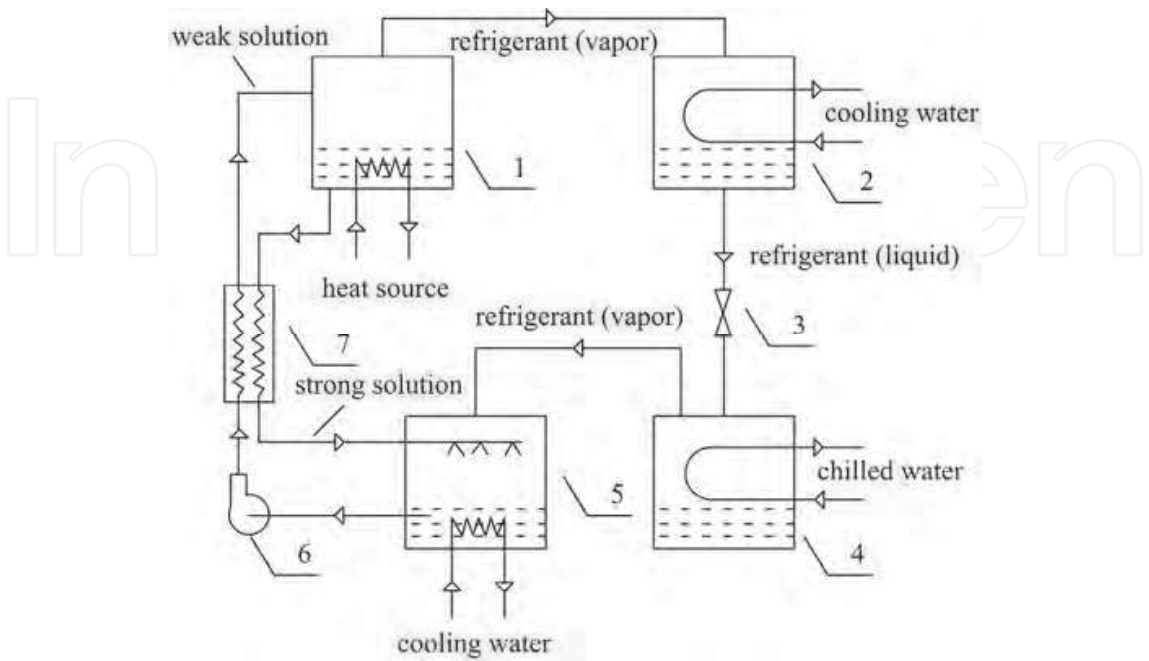

Fig. 1. Schematic diagram of single effect absorption refrigeration: 1- Generator, 2- Condenser, 3- Expansion valve, 4- Evaporator, 5- Absorber, 6- Solution pump, 7- Heat exchanger.
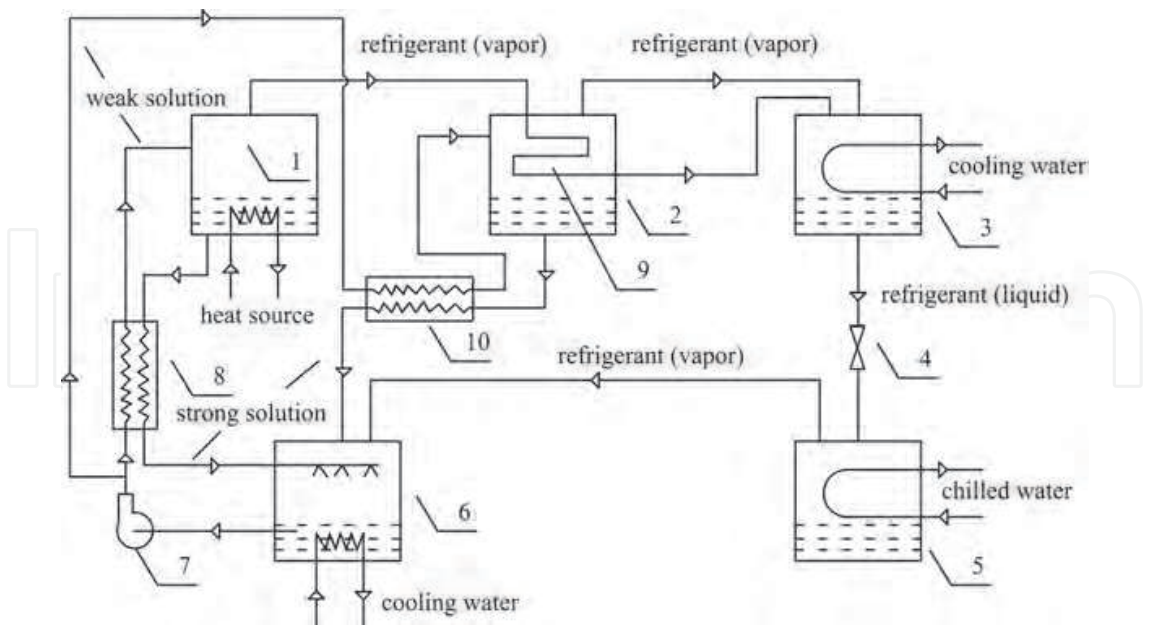

Fig. 2. Schematic diagram of double effect absorption refrigeration: 1- High pressure generator, 2- Low pressure generator, 3- Condenser, 4- Expansion valve, 5- Evaporator, 6- Absorber, 7- Solution pump, 8- High-temperature heat exchanger, 9- Condensing heat exchanger, 10- Low-temperature heat exchanger.

The another common cycle in the actual application, called double-effect absorption refrigeration cycle, is shown in Figure 2, which is mainly composed of a high pressure generator, low pressure generator, absorber, condenser and evaporator. Compared with the single one, the double effect absorption refrigeration system has two generators. The solution in high pressure generator, indirectly heated by the heat source, emits high pressure refrigerant vapor and forms strong solution. The solution in low pressure generator is heated by high pressure refrigerant vapor from the high pressure generator. The solution is concentrated in some degree and passes into high pressure generator. The energy is used twice, directly in the high pressure generator and indirectly in the low one. The double one is more complex and costly than the single one, but its efficiency is higher than the latter.

Besides above, there are some other absorption refrigeration cycles in order to make use of the energy more efficiently and completely, for example, the triple-effect absorption refrigeration cycle, the GAX cycle and the absorption/compression refrigeration cycle.

1.3 Working pairs

Many working fluids are suggested to be used as working pairs for absorption refrigeration in literature, but there is no ideal absorbent-refrigerant pair by now. Currently, the binary systems of NH_3-H_2O and LiBr-H_2O are well known as working fluid pairs to be applied in absorption refrigerators, but they both present advantages and disadvantages. The advantage for refrigerant NH_3 is that it can evaporate at lower temperatures (i.e. from -10 to 0°C) compared to H_2O (i.e. from 4 to 10°C). Therefore, for refrigeration, the NH_3-H_2O cycle is used. However, the NH_3/H_2O system is high-pressure and explosive, and the refrigerant NH_3 is poisonous, and its solution is alkaline and corrosive. The disparity in boiling point between NH_3 and H_2O is not large, which makes it necessary to utilize the distillation equipment. The coefficient of the performance for the H_2O-LiBr system is much higher than that for the NH_3-H_2O system. The only disadvantage is that H_2O-LiBr solution is corrosive to metal and easily crystallized, in addition, the working temperature and pressure of the H_2O-LiBr system are too low.

The refrigerant for the application being investigated should have the following properties: high latent heat of vaporization and low saturation pressures at normal operating temperature. Ammonia, water, methanol, and fluorocarbon refrigerants are at the top of the choice list. The important considerations influencing the choice of a suitable absorbent are: higher boiling point than refrigerant, strong ability to absorb the refrigerant, high thermal and chemical stability, low mass flow rate and heat capacity, non-poisonous, non-corrosive, non-flammable and so on. Ionic liquids are organic salts with a melting point below some arbitrary temperature, such as 100°C. Comparing with frequently-used solvents, ionic liquids exhibit distinctive properties, such as negligible vapor pressure, low combustibility, excellent thermal stability, wide liquid regions, and favorable solvating properties for a range of polar and non-polar compounds. If used as absorbents in absorption refrigeration system, their good solvating properties will make them useful in absorption of large amount of refrigerant under low temperature conditions to yield good COP, and their involatile will ensure them not contaminating with refrigerant stream when desorbed. Therefore, in recent years, RTILs are regarded as the potential candidates of absorbent in absorption refrigeration system [2, 3].

In the following sections, we'd like to introduce to readers a number of studies on the application of ionic liquids in absorption refrigeration system. Whether ionic liquids can be

used as refrigeration absorbent, there are two issues needed to be focused on. Firstly, we should make sure whether the physicochemical properties of ionic liquid and refrigerant's binary solution can meet the requests of absorption refrigerator's working pairs. Secondly, we should make sure whether the selected ionic liquid working pairs have competitive advantages in terms of performance compared with those traditional ones.

2. Physicochemical properties of ionic liquid and refrigerant's binary solution

2.1 Vapor liquid equilibrium (VLE)

VLE Properties of binary system containing ionic liquids are the most important factor to determine whether the binary solution is suitable for absorption refrigeration system. Ionic liquids can reduce the saturated vapor pressure of refrigerants with different magnitudes, which is associated with the kinds of ionic liquids and refrigerants.

Saturated vapor pressures of [BMIm]BF$_4$ + 2,2,2-trifluoroethanol (TFE) and [BMIm]Br + TFE mixtures were measured by K.S. Kim et al. [4] using the boiling point method in the concentration range of 40.0 ~ 90.0 mass% of ionic liquids and in the temperature range of 298.2 K ~ 323.2 K. The data were correlated with an Antoine-type equation. The average absolute deviations between experimental and calculated values were 0.6% and 0.4% for the [BMIm]BF$_4$ + TFE and the [BMIm]Br + TFE system, respectively. As shown in Figure 3, the [BMIm]Br + TFE system was found to be more favorable as working pairs in absorption heat pumps or chillers than the [BMIm]BF$_4$ + TFE from the results of VLE.
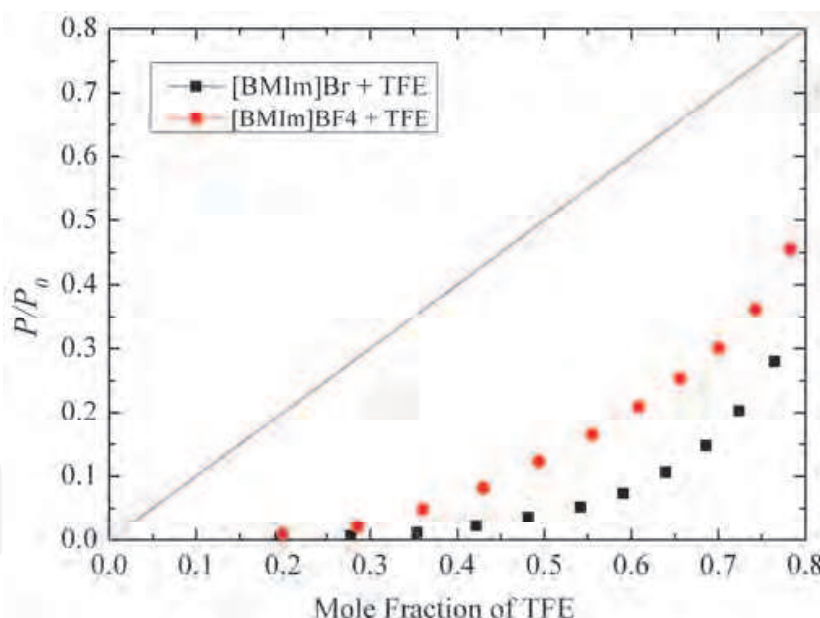

Fig. 3. The comparison of the saturated vapor pressures between the [BMIm]Br + TFE and [BMIm]BF$_4$ + TFE systems at 313.2 K.

J. Zhao et al. [5] measured the vapor pressure data for nine binary systems containing water, methanol or ethanol with the ionic liquids 1-methyl-3-methylimidazolium dimethylphosphate ([MMIm]DMP), 1-ethyl-3- methylimidazolium diethylphosphate ([EMIm]DEP) and 1-butyl-3-methylimidazo- lium dibutylphosphate ([BMIm]DBP) and one ternary system ethanol-water- [MMIm]DMP at varying temperature and ionic liquid mass percent ranging from 10% to 70% by a quasi-static method. The vapor pressure data of the

binary systems were correlated by the NRTL model. Similar work by J.F. Wang et al. [6] was conducted in 2007. As shown in Figure 4, based on the vapor pressure depression of binary systems interpolated at ionic liquid mole fraction 5% in the temperature range from 280 K to 370 K, the effect of ionic liquids on the vapor pressure lowering follows the order [MMIm]DMP > [EMIm]DEP > [BMIm]DBP for water, and [BMIm]DBP > [EMIm]DEP > [MMIm]DMP for methanol and ethanol.
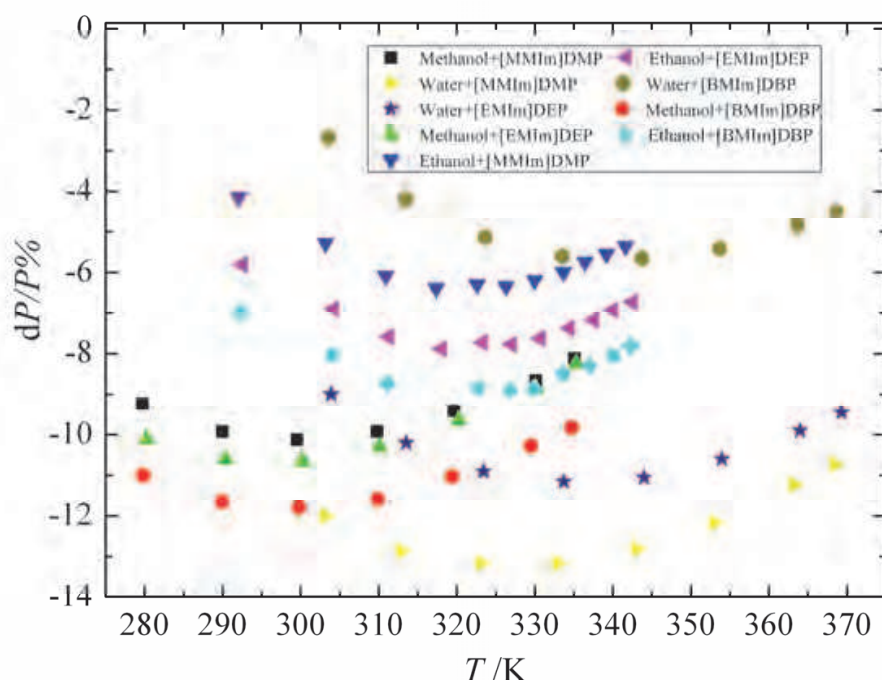

Fig. 4. Vapor pressure lowering ($dP/P\%$) of water, methanol and ethanol caused by different ILs at mole fraction of 0.05.

Solubilities of ammonia in ionic liquids, 1-ethyl-3-methylimidazolium acetate ([EMIm]Ac), 1-ethyl-3-methylimidazolium thiocyanate ([EMIm]SCN), 1-ethyl-3-methylimidazolium ethylsulfate ([EMIm]EtOSO$_3$), and N,N-dimethy- lethanolammonium acetate ([DMEA]Ac) were measured for the first time by A.Yokozeki and M.B. Shiflett [7] in 2007. Six mixture compositions of each binary system were involved from about 30 to 85 mole% of ammonia. Pressure-temperature-composition (P-T-x) data were claimed at isothermal conditions of 283, 298, 323, 348, and 373 K. The observed solubility of ammonia in ionic liquids is very high, and all cases show negative deviations from ideal solution behavior. Experimental P-T-x data were successfully correlated with the equation-of-state (EOS) model [8]. The experimental data and fitting results are shown in Figure 5 ~ 8. The opportunity for the absorption cycle application using the ammonia-RTIL system, replacing the traditional ammonia-water system, has been discussed [7].

S.P. Verevkin et al. [9] studied the vapor-liquid equilibria (VLE) of binary mixtures containing methanol, ethanol, 1-propanol and benzene in the ionic liquid [BMIm]NTf2 by using a static method. VLE measurements were carried out over the whole concentration range at four different temperatures in the range from 298.15 K to 313.15 K. Activity coefficients γi of these solvents in the ionic liquid have been determined from the VLE data and are described formally by using the NRTL equation.
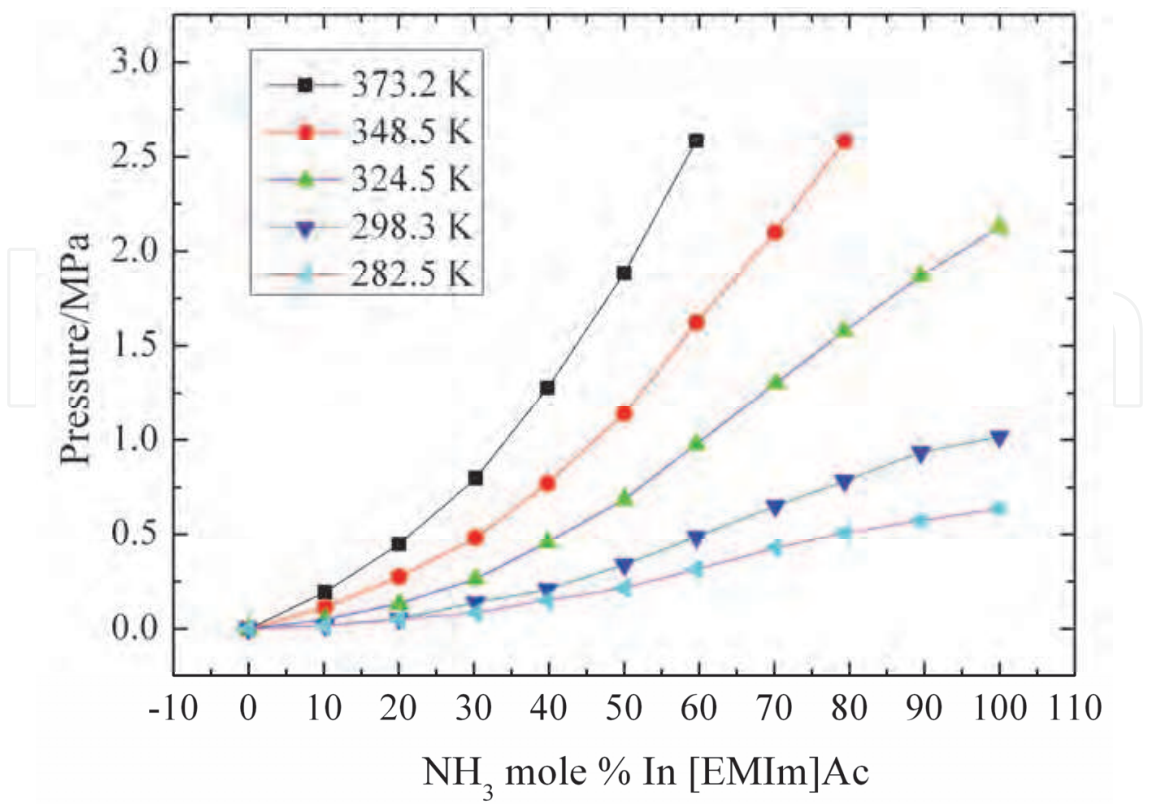
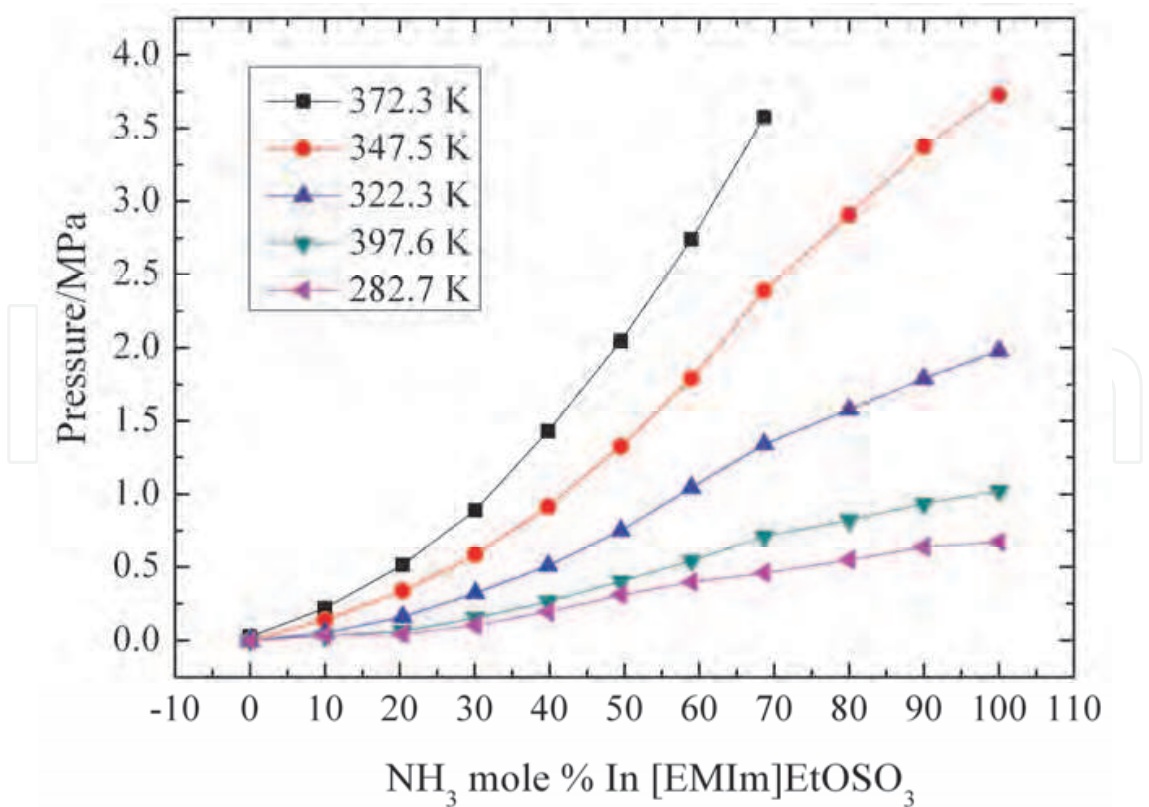Fig. 5. *P-T-x* phase diagram of NH$_3$ + [EMIm]Ac mixtures [7].

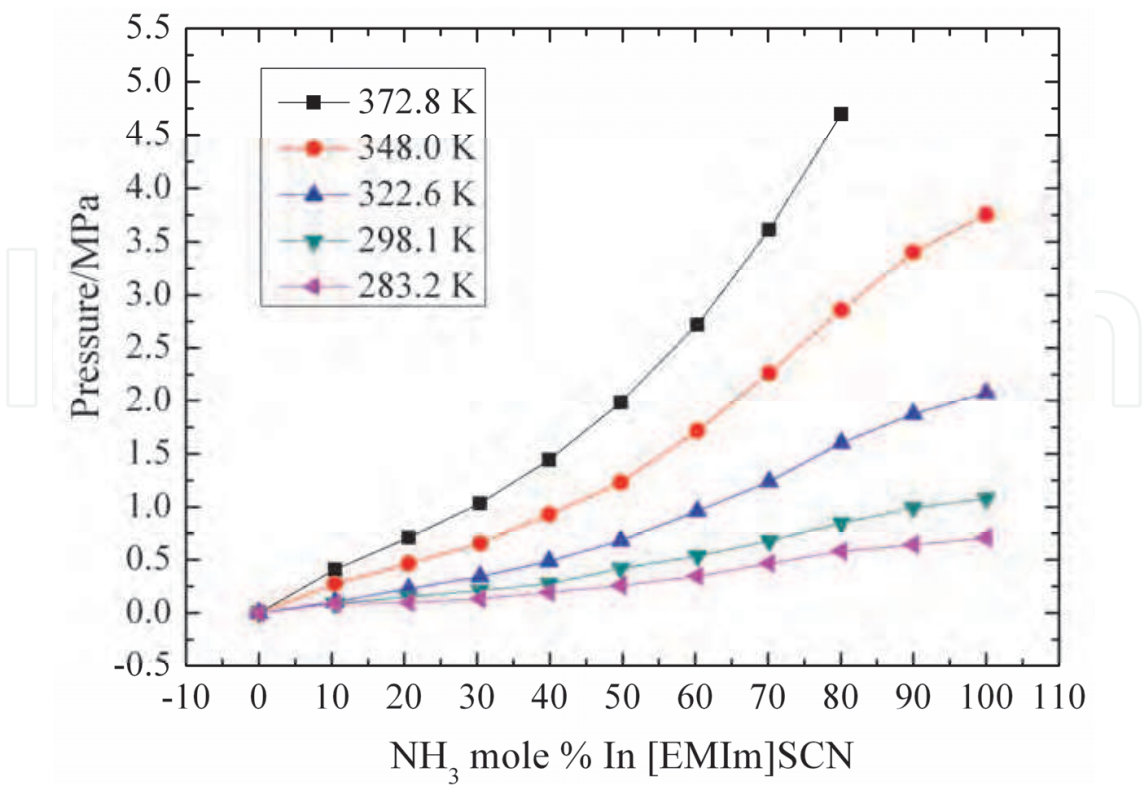Fig. 6. *P-T-x* phase diagram of NH$_3$ + [EMIm]EtOSO$_3$ mixtures [7].

Fig. 7. *P-T-x* phase diagram of NH₃ + [EMIm]SCN mixtures [7].
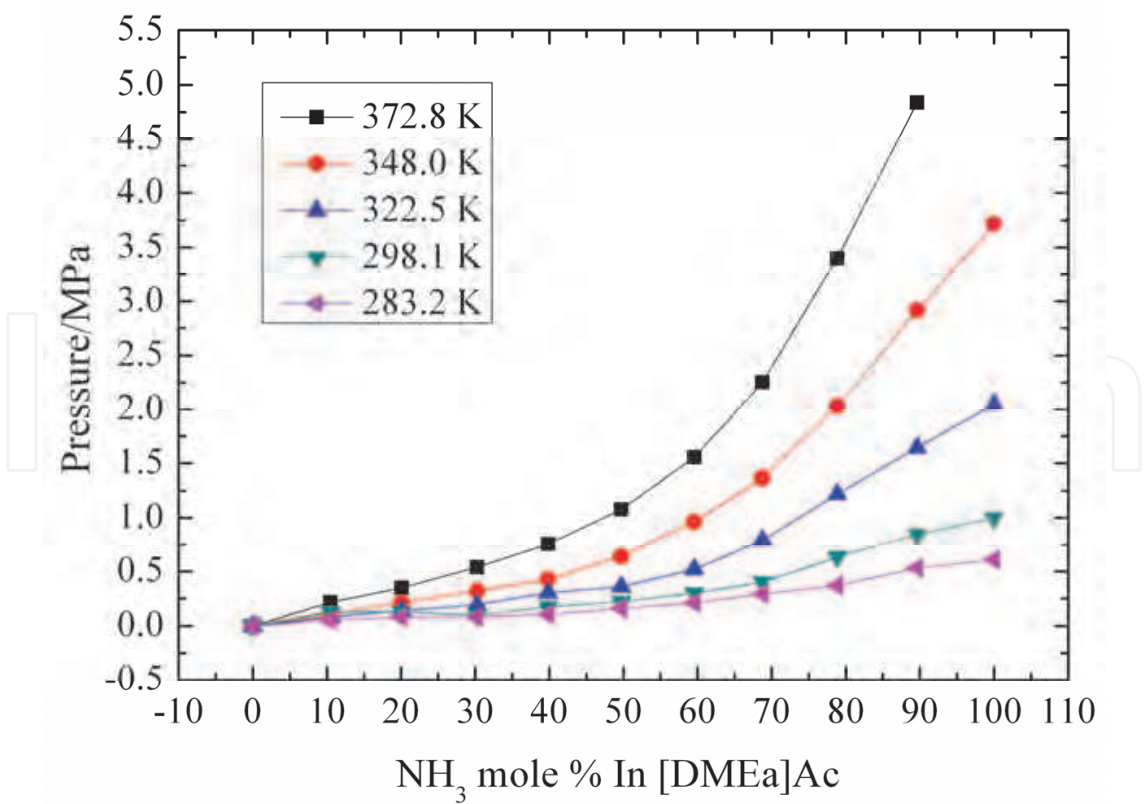

Fig. 8. *P-T-x* phase diagram of NH₃ + [DMEA]Ac mixtures[7].

Liang et al. [10] measured the saturated vapor pressure of the [MMIm]DMP-methanol solutions at 30°C ~ 90°C on condition that the mole fraction of [MMIm]DMP is 12.6%, 29.9%, 39.5%, 41.8%, 44.2% and 47.1%, respectively. The experimental data were correlated with the NRTL model, and the model parameters and the correlation deviation were calculated. The selected NRTL model with five parameters is applicable to the medium to high concentration zones, and the correlation deviation is 0.0159. With this NRTL model, the saturated vapor pressure of the [MMIm]DMP-methanol solutions when the mole fraction of [MMIm]DMP is 17.8% and 30.0% is predicted. As the low concentration solutions, the relationships between the saturated vapor pressure of the medium to high concentrations and the temperature are similar to the pure solvent, which obey the Antoine equation. The saturated vapor pressure of the [MMIm]DMP-methanol solutions when the mole fraction of [MMIm]DMP is 12.6% and 30.0% is also calculated by the NRTL model with three parameters by J. Zhao [5]. All the above T-P-x data are shown in Figure 9.
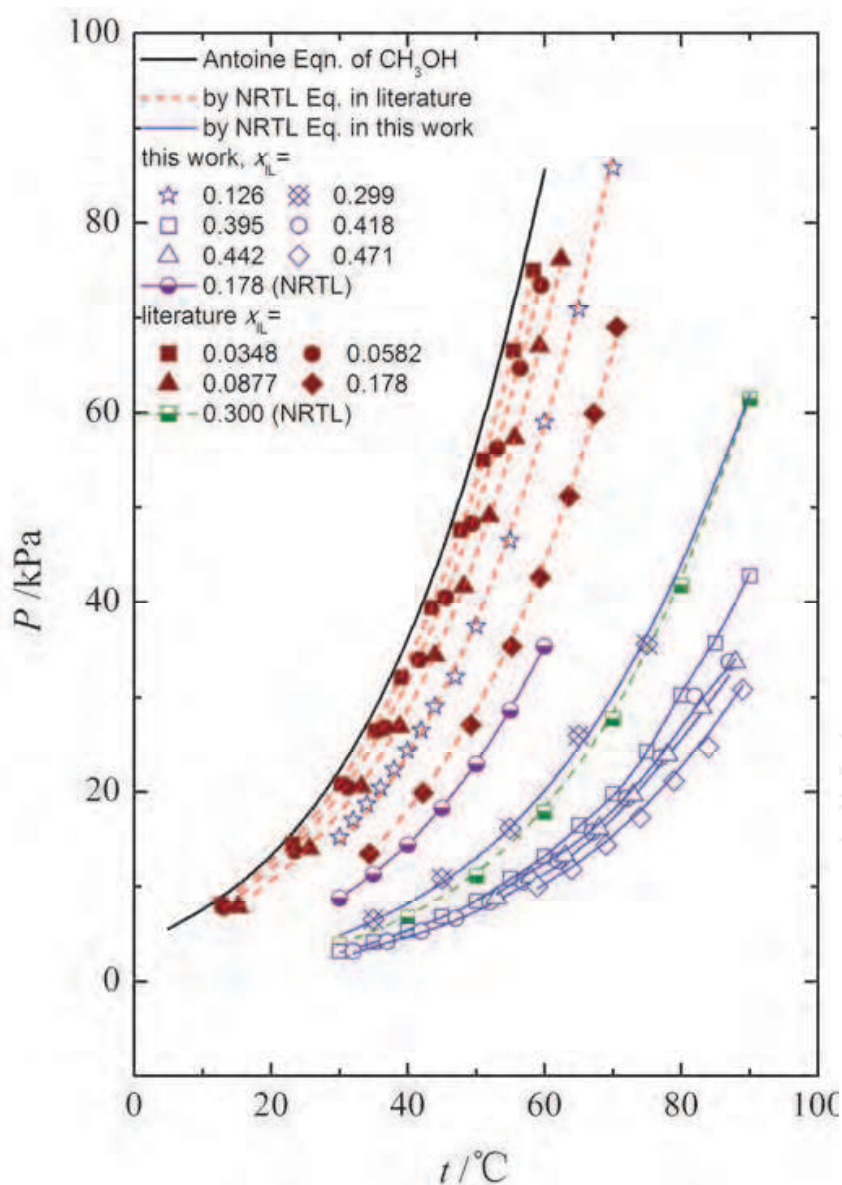

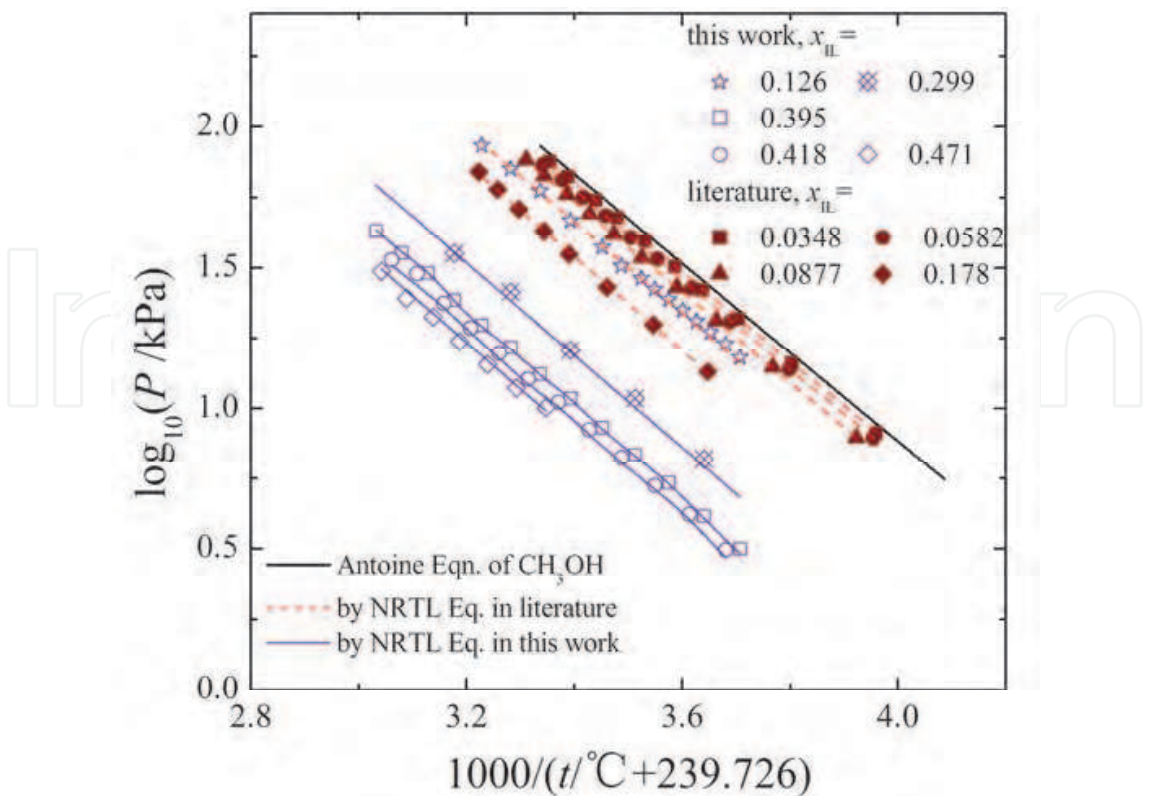Fig. 9. Saturated vapor pressure of [MMIm]DMP/CH₃OH solutions.

Fig. 10. Relationship of log P.vs.$1000/(t+C)$.

As shown in Figure 10, with the increase of the mole fraction of [MMIm]DMP, the saturated vapor pressure was significantly reduced. The saturated vapor pressure of the [MMIm]DMP-methanol solution at normal temperatures is lower than that of pure methanol at 5°C. This means that the normal temperatures solution can absorbs the low-temperature methanol vapor, which makes the [MMIm]DMP-methanol solution suitable for absorption refrigeration as the working pair.

The solution of working pair can absorb the refrigerant vapor when the saturated vapor pressure of solution is lower than that of the pure refrigerant at the evaporating temperature. As shown in table 1, when the evaporation temperature and the cooling water temperature are 10°C and 30°C, respectively, the lowest mole fraction of [MMIm]DMP in solution is 20.8%. When the evaporation temperature and the cooling water temperature are 5°C and 40°C, respectively, the lowest mole fraction of [MMIm]DMP in solution is 39.3%.

Evaporation Temperature /°C	Vapor Pressure /kPa (Refrigerant)	Minimum Concentration	Vapor Pressure /kPa (Solution)	Minimum Concentration	Vapor Pressure /kPa (Solution)
		Cooling Water Temperature /°C			
		30		40	
5	5.570	0.270	≤5.569	0.393	≤5.561
7	6.284	0.245	≤6.252	0.362	≤6.262
10	7.504	0.208	≤7.500	0.317	≤7.504

Table 1. Minimum concentration (mole fraction) of absorption solution.

The refrigerant can be separated from the solution of working pair when the saturated vapor pressure of solution is higher than that of the pure refrigerant at the condensing temperature. As shown in Table 2, when the regeneration temperature is 90°C, the mole fraction of [MMIm]DMP in the concentrated solution is relatively high. When the regeneration temperature and condensing temperature is 90°C and 40°C, the largest mole fraction of [MMIm]DMP in the concentrated solution is 44.5%. From the above two tables, there is a large optimization space between the lower and higher limit of mole fraction of [MMIm]DMP. Just from the perspective of vapor liquid equilibrium, the [MMIm]DMP-methanol system can be used as working pair of absorption refrigeration with a large adjustable redundancy.

Regeneration Temperature /°C	Maximum Concentration	Vapor Pressure /kPa	Maximum Concentration	Vapor Pressure /kPa
	Cooling Water Temperature /°C (Condensing pressure of CH_3OH /kPa)			
	30 (22.135)		40 (35.876)	
80	0.480	≥22.153	0.349	≥35.936
85	0.531	≥22.201	0.397	≥35.925
90	0.580	≥22.240	0.445	≥35.996

Table 2. Maximum concentration (mole fraction) of absorption solution.

Liang et al. [11] measured the saturated vapor pressure of the [BMIm]Cl-methanol solutions at 30°C~80°C on condition that the mole fraction of [BMIm]Cl is 19.2%, 21.6%, 31.6%, 43.8% and 51.7%, respectively. The experimental data were correlated with the NRTL model, and the model parameters and the correlation deviation were calculated. The data of experiment and prediction by the NRTL model is shown in Figure 11.
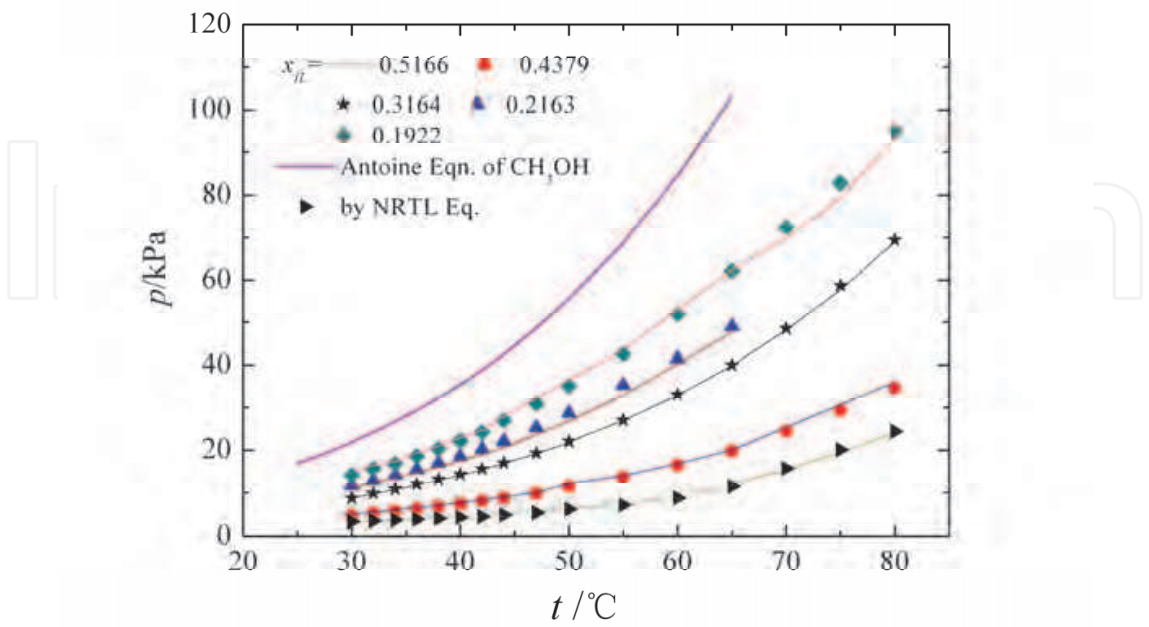

Fig. 11. Saturated vapor pressure of [BMIm]Cl/CH_3OH solutions.

As shown in Table 3, when the evaporation temperature and the cooling water temperature are 10°C and 30°C, respectively, the lowest mole fraction of [BMIm]Cl in solution is 34.3%. When the evaporation temperature and the cooling water temperature are 5°C and 40°C, respectively, the lowest mole fraction of [BMIm]Cl in solution is 49.0%.

Evaporation Temperature /°C	Vapor Pressure /kPa (Refrigerant)	Minimum Concentration	Vapor Pressure /kPa (Solution)	Minimum Concentration	Vapor Pressure /kPa (Solution)
		Cooling Water Temperature /°C			
		30		40	
5	5.570	0.408	≤5.309	0.490	≤5.485
7	6.284	0.381	≤6.086	0.472	≤6.049
10	7.504	0.343	≤7.271	0.439	≤7.221

Table 3. Minimum concentration (mole fraction) of absorption solution.

As shown in Table 4, when the temperature of heat resource is 80°C, the mole fraction of [BMIm]Cl in the concentrated solution is relatively high. When the temperature of heat resource and condensing temperature is 80°C and 40°C, the largest mole fraction of [MMIm]DMP in the concentrated solution is 42.0%. From the above two tables, there is a large optimization space between the lower and higher limit of mole fraction of [BMIm]Cl. Just from the perspective of vapor liquid equilibrium, the [BMIm]Cl-methanol system can be used as working pair of absorption refrigeration with a large adjustable redundancy.

Regeneration Temperature /°C	Maximum Concentration	Vapor Pressure /kPa	Maximum Concentration	Vapor Pressure /kPa
	Cooling Water Temperature /°C (Condensing pressure of CH_3OH /kPa)			
	30 (22.135)		40 (35.876)	
70	0.439	≥24.113	0.354	≥37.101
75	0.472	≥24.014	0.394	≥36.456
80	0.512	≥24.050	0.420	≥37.291

Table 4. Maximum concentration of absorption solution.

2.2 Viscosity

Viscosity is an important physical parameter of the binary system containing ionic liquids, and it can largely influence the application of ionic liquids in absorption refrigeration. The viscosities of binary system containing ionic liquids and water, methanol, TFE has been reported in the literature [12~16]. Viscosities of the binary system are reducing exponentially when the mole fraction of refrigerant and temperature increase. The excess logarithmic viscosities of the binary system in the whole composition range are all positive. Liang et al. [17] measured viscosities of binary systems [MMIm]DMP-methanol, [BMIm]Cl-methanol by the capillary tube method at temperatures (293.15 K to 353.15 K) when the mole fraction of ionic liquids is 20%, 40%, 60%, 80%, 100%, respectively. The experimental

data are correlated with the Arrhenius-like equation, Redlich-Kister equation and Seddon equation. The experimental data and correlate results are shown in Figure 12 and Figure 13.
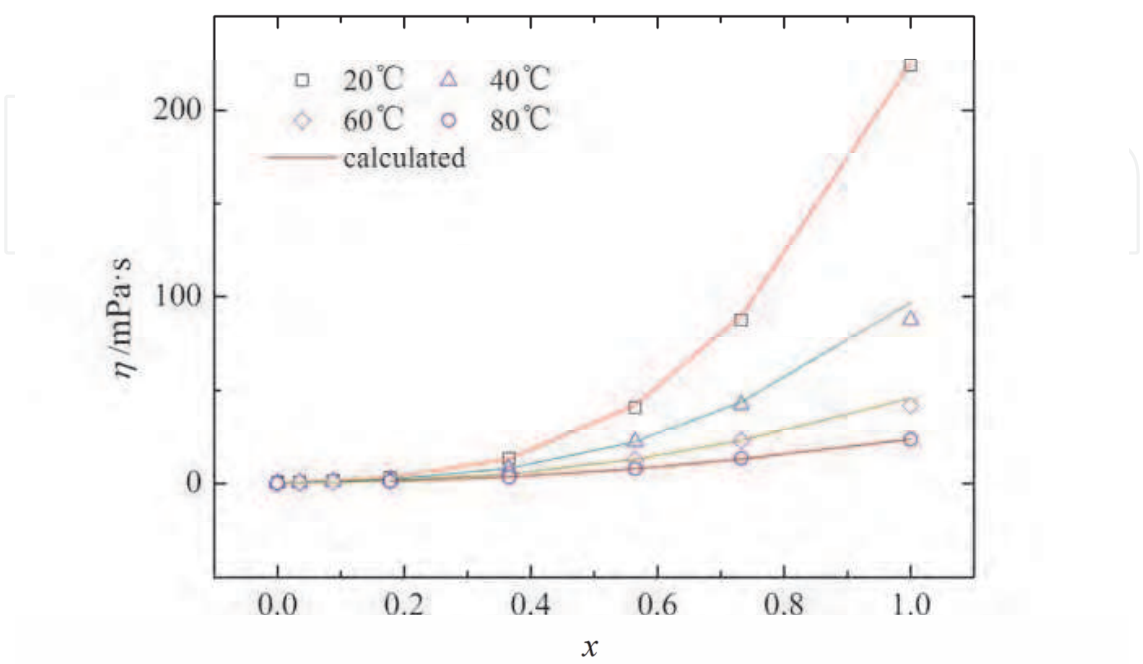

Fig. 12. Viscosities of binary systems [MMIm]DMP-methanol.
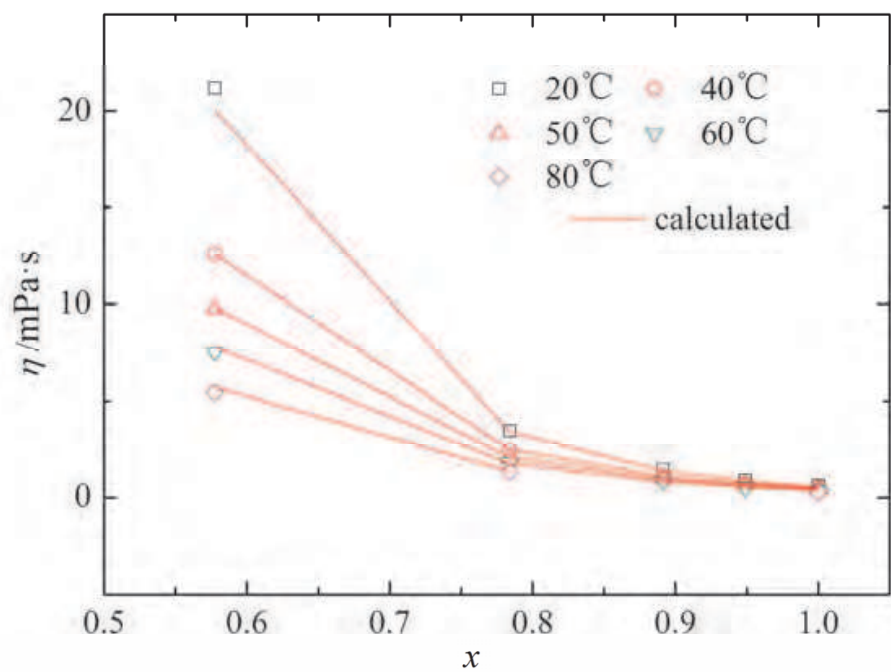

Fig. 13. Viscosities of binary systems [BMIm]Cl-methanol.

As shown in Figure 12 and Figure 13, viscosities of binary systems [MMIm]DMP- methanol, [BMIm]Cl-methanol reduce rapidly with the increase of temperature, especially in the high concentration region. Viscosities of [MMIm]DMP and [BMIm]Cl are very large, but the methanol can reduce their viscosities to a great extent. Viscosity of [MMIm]DMP at 293.15 K is 223.6736 mPa·s, while viscosities of [MMIm]DMP-methanol is 87.5429 mPa·s on condition that the mole fraction of [BMIm]DMP is 73.3%. [BMIm]Cl is solid at 293.15 K, while viscosities of [mmim]Cl-methanol is 20.1732 mPa·s on condition that the mole fraction of [BMIm]Cl is 42.2%.

2.3 Heat capacity

Heat capacity is a physical quantity which is the important bridge connecting the macroscopic observable thermodynamics quantity and the microscopic molecular structure. On the basis of heat capacity, the h-ω diagram is mapped, from which we can analyze COP of the whole absorption refrigeration cycle.

Fredlake [18] measured the heat capacities of thirteen imidazolium based ionic liquids at temperature (298.15 K ~ 323.15 K). Heat capacities for nine ionic liquids have been determined with the "three-step" method using two different differential scanning calorimeters (DSC) by Anja et al. [19], the measurements cover a temperature range from 315 K to 425 K. Waliszewski et al. [20] measured the heat capacities of ionic liquids: [EMIm]BF$_4$, [EMIm]NTf$_2$, [BMIm]BF$_4$ and [MPPy]NTf$_2$ at temperature (283.15 K ~ 358.15 K). Z. H. Zhang et al. [21] measured the molar heat capacities of the room temperature ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate (EMIES) by an adiabatic calorimeter at temperature (78 K ~ 390 K). The results show that the heat capacities of ionic liquids ranges from 1.2 to 1.9 J·g-1·K-1, which is smaller than that of water, methanol and ammonia.

Tao et al. [22] measured the heat capacity of the binary system [EMIm]BF$_4$-water at temperature (298.15 K ~ 343.15 K) when the mass fraction change from 25% to 100%. The heat capacity falls when the mass fraction of [EMIm]BF$_4$ increases. Rebelo et al. [23] measured the heat capacity of [BMIm]BF$_4$ at temperature (278.15 K ~ 333.15 K), the capacity ranges from 355 to 385 J·mol-1·K-1. They also measured excess heat capacity of binary system of [BMIm]BF$_4$-water. The results show that excess heat capacity is positive with the mole fraction ranging from 0 to 56.4%, while in the high concentration region excess heat capacity is negative. This indicates that the addition of water augments the heat capacity of ionic liquids.

Liang et al. [17] measured the heat capacities of binary system [MMIm]DMP-methanol and [BMIm]Cl-methanol at temperature (30 K ~ 80 K) with various of mole fractions. The experimental data are correlated with the following equation:

$$C_P = A + B \cdot t$$

where C_P is heat capacity, t is temperature, $A = A_1 \cdot \omega_2 + A_2 \cdot \omega + A_3$, $B = B_1 \cdot \omega_2 + B_2 \cdot \omega + B_3$. The fitting parameters and average absolute deviation is shown in Table 5. The experimental data and correlate results are shown in Figure 14 and Figure 15.

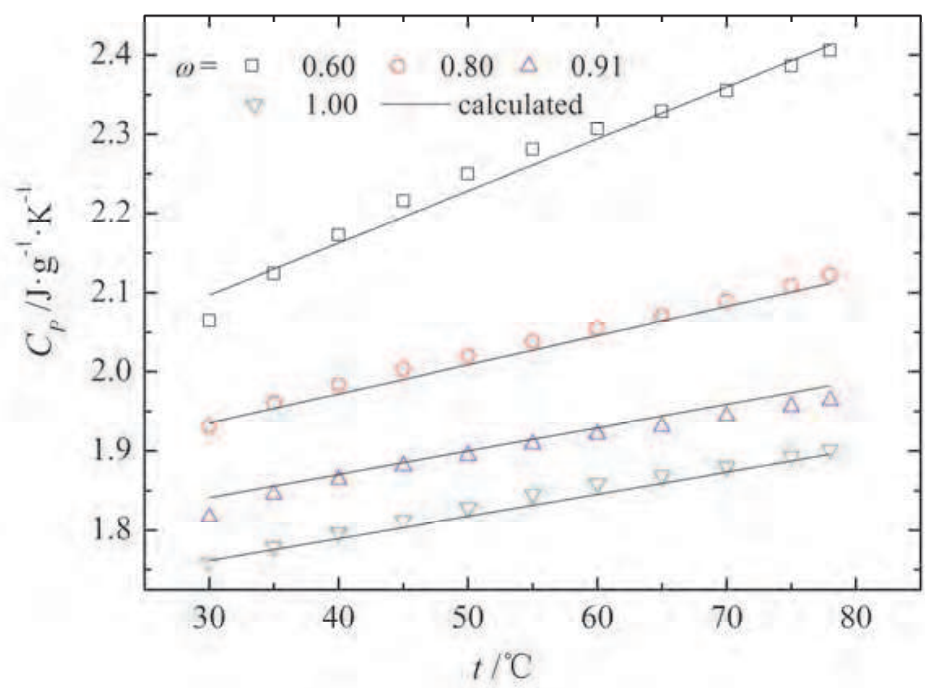| Binary System	A_1	A_2	A_3	B_1	B_2	B_3	ARD
[MMIm]DMP-methanol	-0.9057	0.8936	1.6894	0.0251	-0.0496	0.0273	0.0060
[BMIm]Cl-methanol	-0.7312	0.6737	1.6857	0.0200	-0.0315	0.0166	0.0019

Table 5. Fitting parameters.

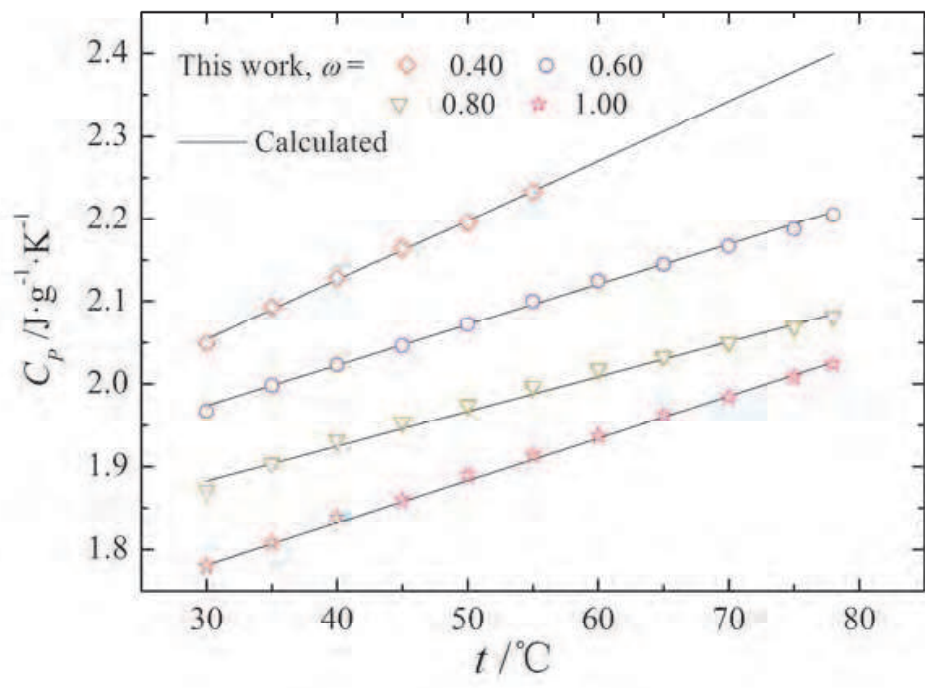Fig. 14. Heat capacities of binary systems [MMIm]DMP-methanol.

Fig. 15. Heat capacities of binary systems [BMIm]Cl-methanol.

The heat capacity of traditional working pair LiBr-H_2O is very low, which is only 2 J·g^{-1}·K^{-1} at 373.15 K with the mass fraction of 55%. The heat capacities of binary system [MMIm]DMP-methanol and [BMIm]Cl-methanol on the same condition is close to that of LiBr-H_2O solution. This means that the evaporating of methanol out of solution requires only a small amount of heat, which is favorable for enhancing COP of absorption refrigeration cycle.

2.4 Summary

This section investigates the application potential in binary system containing ionic liquids and refrigerant as working pairs for absorption refrigeration from three aspects: vapor liquid equilibrium, viscosity and heat capacity. The saturated vapor pressure and heat capacity in plenty of these binary systems are relatively low. The density and viscosity in these systems are moderate. Compared with the traditional working pairs, the new ones have their own advantages. They are non-corrosive and non-crystalline. Since ionic liquids are non-evaporative, this new kind of absorption refrigeration system is no need to set up distillation equipment. The physical and chemical properties in binary system containing ionic liquids and frequently-used refrigerants are still not perfect, and the studies on the application of ionic liquids in absorption refrigeration are still inadequate. With the increasing of the quantity of ionic liquids and the deepening of studies on their physical and chemical properties, ionic liquid absorption refrigeration must become an important part of refrigeration in near future.

3. Theoretical cycle and efficiency analysis of novel absorption refrigeration system using ionic liquids

3.1 Single-effect absorption refrigeration system

A. Yokozeki [7, 8] measured the solubility, vapor-liquid equilibrium of binary solutions containing ionic liquids, and computed the specific heat capacity at constant pressure, enthalpy, Gibbs energy, and entropy based on the EOS equation. According to the results conducted, various parameters of ideal single-effect absorption refrigeration system were computed. The quality circulation rate f, solution concentration in generator X_g, solution concentration in absorber X_a, and COP are shown in Table 6 when the temperatures of the generator, absorber, condenser, and evaporator are 373 K, 313 K, 303 K, and 283 K respectively. The results present that when ionic liquids are used as working pairs with NH_3, Freon, water, and CO_2 respectively, COP of absorption refrigeration systems are higher than that systems using NH_3/H_2O or $H_2O/LiBr$.

Wang et al. [24] used TFE-[BMIm]Br in double-effect parallel absorption refrigeration system, and the effect of the effectiveness of solution heat exchanger η on COP was analyzed. In the Figure 16, ω_1, ω_2, ω_3, ω_4 stand for COP in four kinds of process respectively. The results show that COP increases markedly with the improvement of η. Therefore, it is important to use high effect solution heat exchanger for double-effect parallel absorption refrigeration. Considering COP of the system and actual heat transfer performance of the heat exchanger, η is chosen to be 0.9. The effects of evaporating temperature, absorbing temperature, high pressure generating temperature on COP, solution circulation ratio, and operating pressure of the system are presented.

Binary System	f	$x_g/\%$	$x_a/\%$	COP	Literatures
NH_3+[BMIm]PF_6	17.27	94.5	89.0	0.575	[7]
NH_3+[BMIm]BF_4	12.98	95.7	88.3	0.557	[7]
NH_3+[HMIm]Cl	14.26	93.9	87.3	0.525	[7]
NH_3+[EMIm]Tf_2N ,	24.57	96.3	92.4	0.589	[7]
NH_3+[EMIm]AC	12.55	92.3	85.0	0.573	[7]
NH_3+[EMIm]$EtOSO_3$	17.55	85.2	89.8	0.485	[7]
NH_3+[EMIm]SCN	12.42	92.7	85.3	0.557	[7]
NH_3+ H_2O	2.54	59.5	36.1	0.646	[26]
R22+[BMIm]PF_6	5.12	89.70	72.20	0.319	[27]
R32+[BMIm]PF_6	7.35	90.40	78.10	0.385	[27]
R32+[BMIm]BF_4	6.41	90.20	76.10	0.330	[27]
R134+[BMIm]PF_6	4.38	88.80	68.50	0.348	[27]
R134a+[BMIm]PF_6	10.66	92.40	83.70	0.254	[27]
CO_2+[BMIm]PF_6	25.76	88.54	85.12	0.008	[29]
H_2O+[BMIm]BF_4	18.20	98.56	93.14	0.525	[28]
H_2O+LiBr	4.08	66.30	50.00	0.833	[26]

Table 6. Parameters of single-effect absorption refrigeration system.

From Figure 17, it can be concluded that double-effect parallel absorption refrigeration using TFE-[BMIm]Br is more suitable for air conditioning. However, COP is relatively low when evaporation temperature is below zero. As shown in Figure 18, COP increases with the high pressure generating temperature. Considering the heat stability of TFE-[BMIm]Br, it is not suitable for the operation when the high pressure generating temperature is more than 500 K.
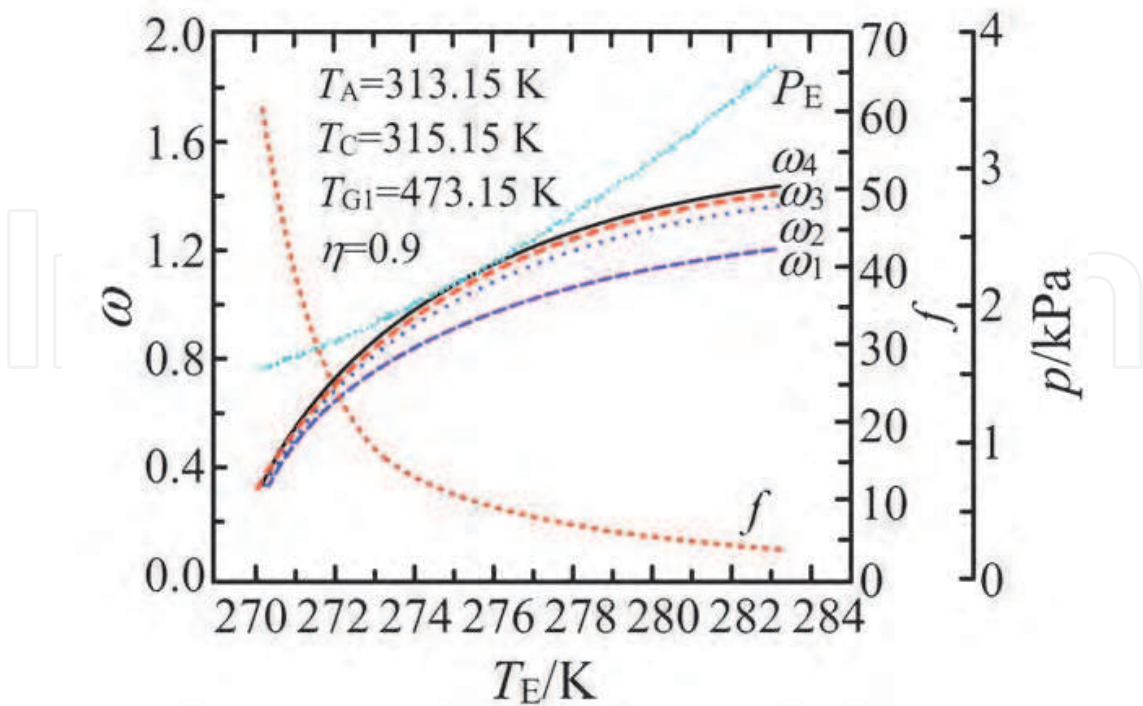

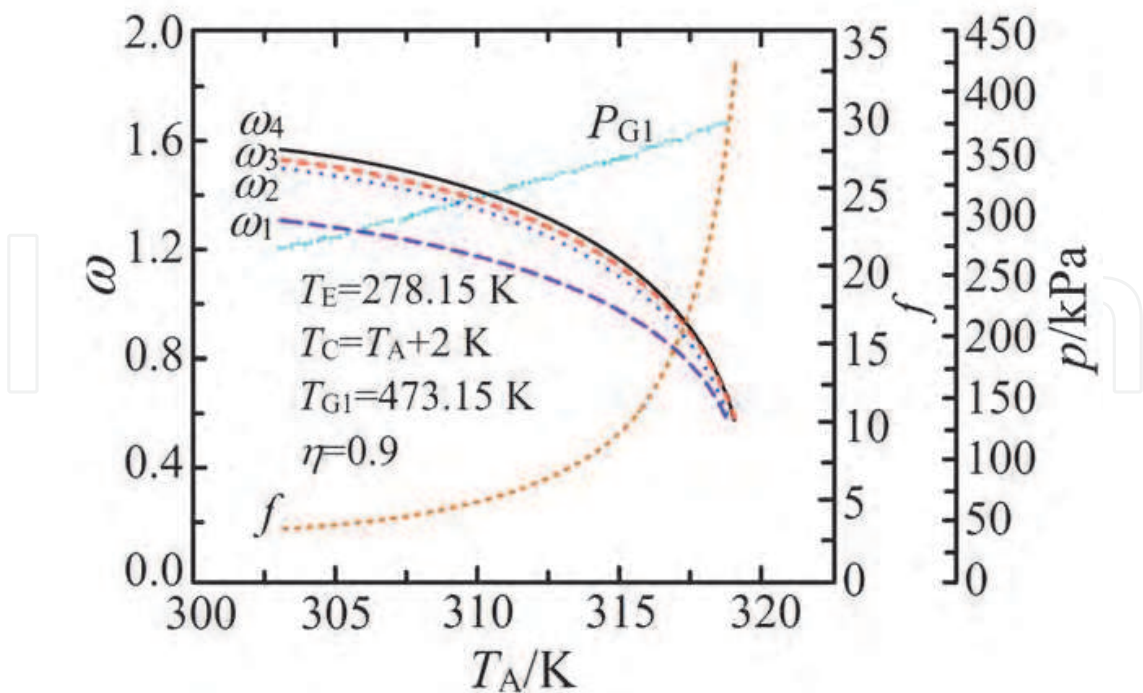Fig. 16. The effect of evaporation temperature on performances.

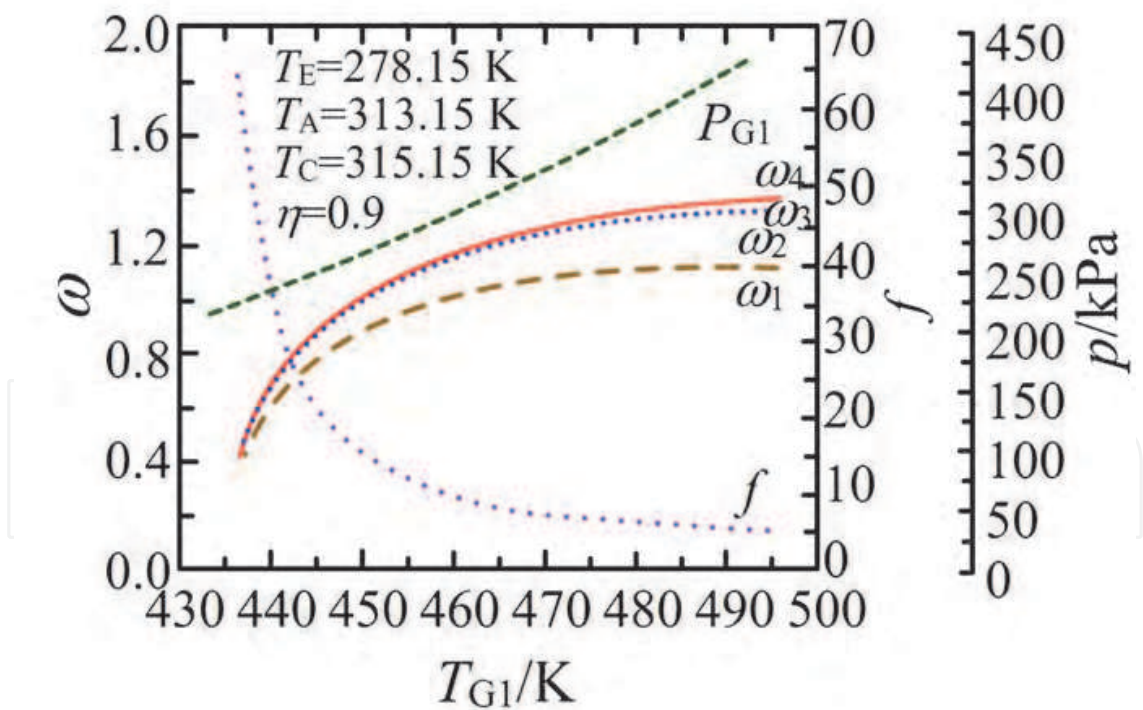Fig. 17. The effect of absorption temperature on performances.

Fig. 18. The effect of generation temperature on performances.

Liang et al. [25] used [MMIm]DMP-CH$_3$OH to analyze the effectiveness of absorption refrigeration system. In order to analyze the effect of various temperatures on the effectiveness of the system, different values were set, and loads of heat equipment, solution concentration, circulation ratio, gas-emission scope, and COP were computed.

As shown in Figure 19, for single-effect absorption refrigeration system, COP increases with the improvement of heat source temperature and evaporating temperature. When heat source and evaporating temperature are 120°C and 10°C respectively, COP gets 0.895. However, it is not suitable for evaporating temperature to be too low. For example, if evaporating temperature is 5°C, and heat source temperature is below 80 °C, solution concentration will not meet the requirements of solution circulation.
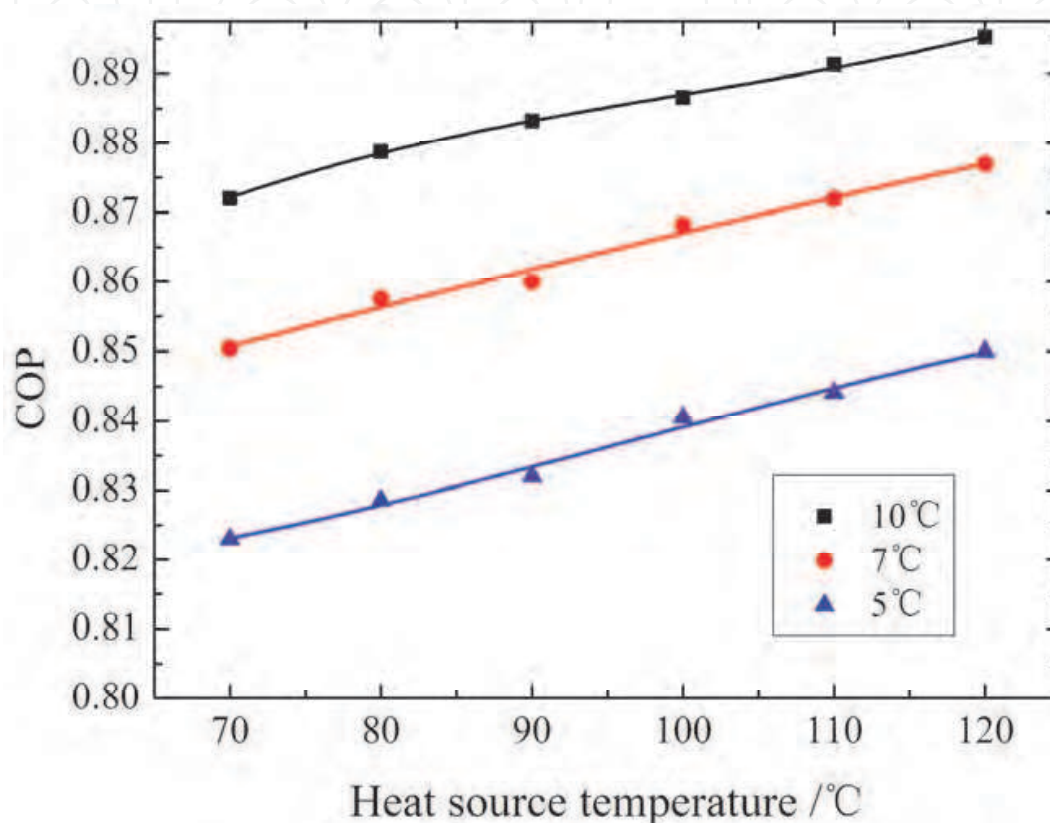

Fig. 19. The effect of heat resource temperature on COP.

Figure 20 and 21 show the variation tendency of gas-emission scope, circulation ratio with heat resource temperature and evaporating temperature. With the improvement of heat source temperature and evaporating temperature, gas-emission scope increases, while circulation ratio decreases. The smaller the gas-emission scope, the bigger the circulation ratio, and the more the heat absorbed by solution liquid, the lower COP. When the evaporating temperatures are 5°C, 7°C, and 10°C respectively, the heat source temperatures should be above 60°C, 70°C and 80°C respectively. Otherwise, the gas-emission scopes will be too small and the circulation ratios will be too big, which will lead to lower effectiveness of the system, huge equipment, and high operating cost. Figure 22, 23 and 24 show the changes of COP, gas-emission scope, and circulation ratio with heat source temperatures at various evaporation temperatures. COP of the system increases with the reduction of the following parameters: condensing temperature, absorbing temperature and circulation ratio, while increases with the improvement of gas-emission scope.
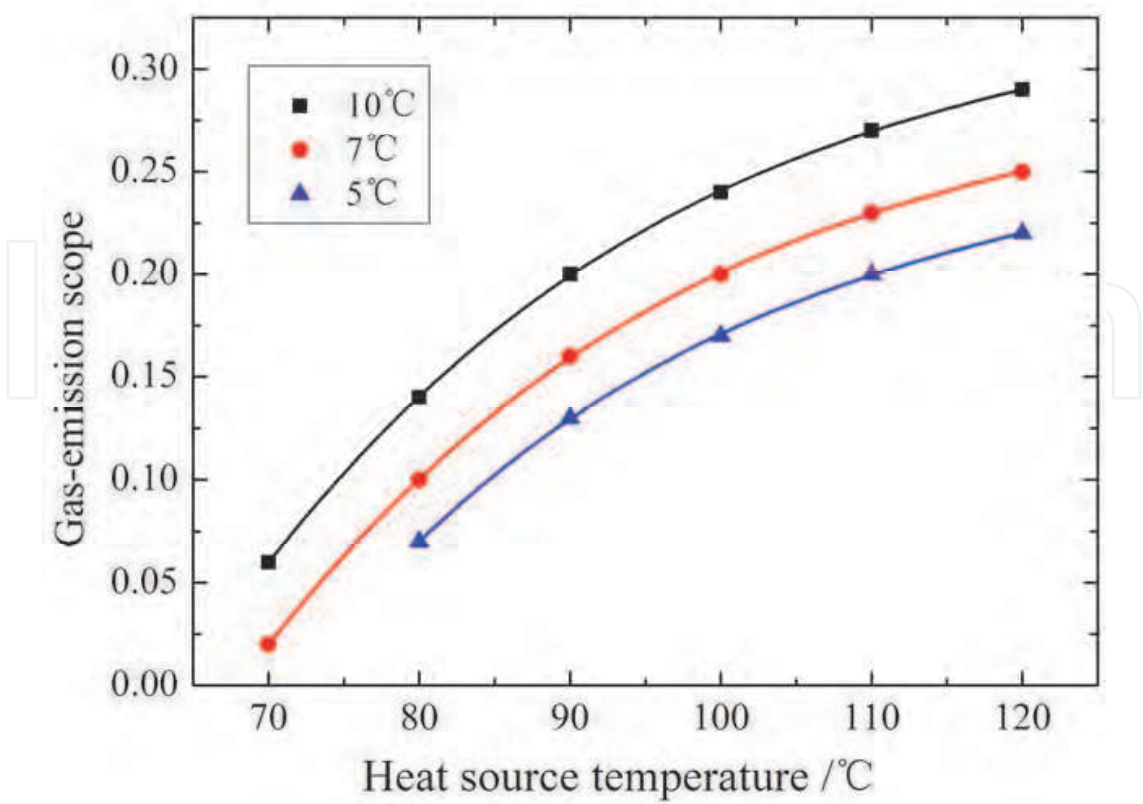
Fig. 20. The effect of heat resource temperature on gas-emission scope.
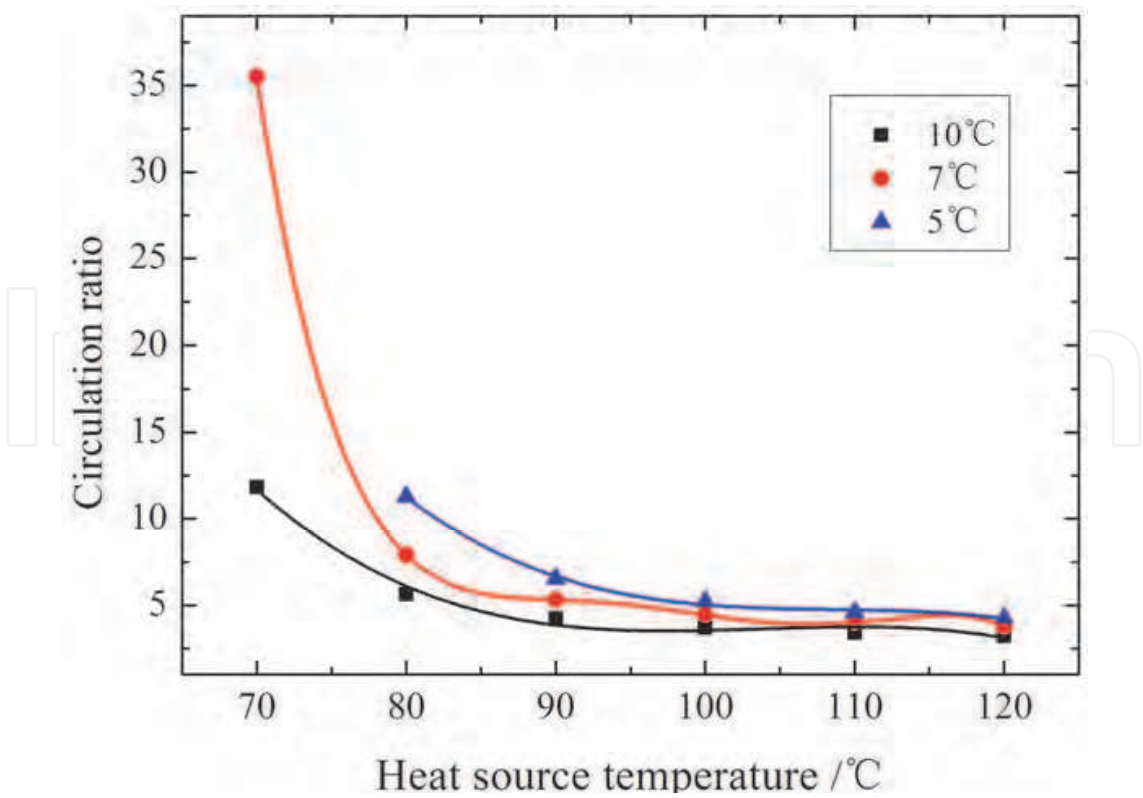

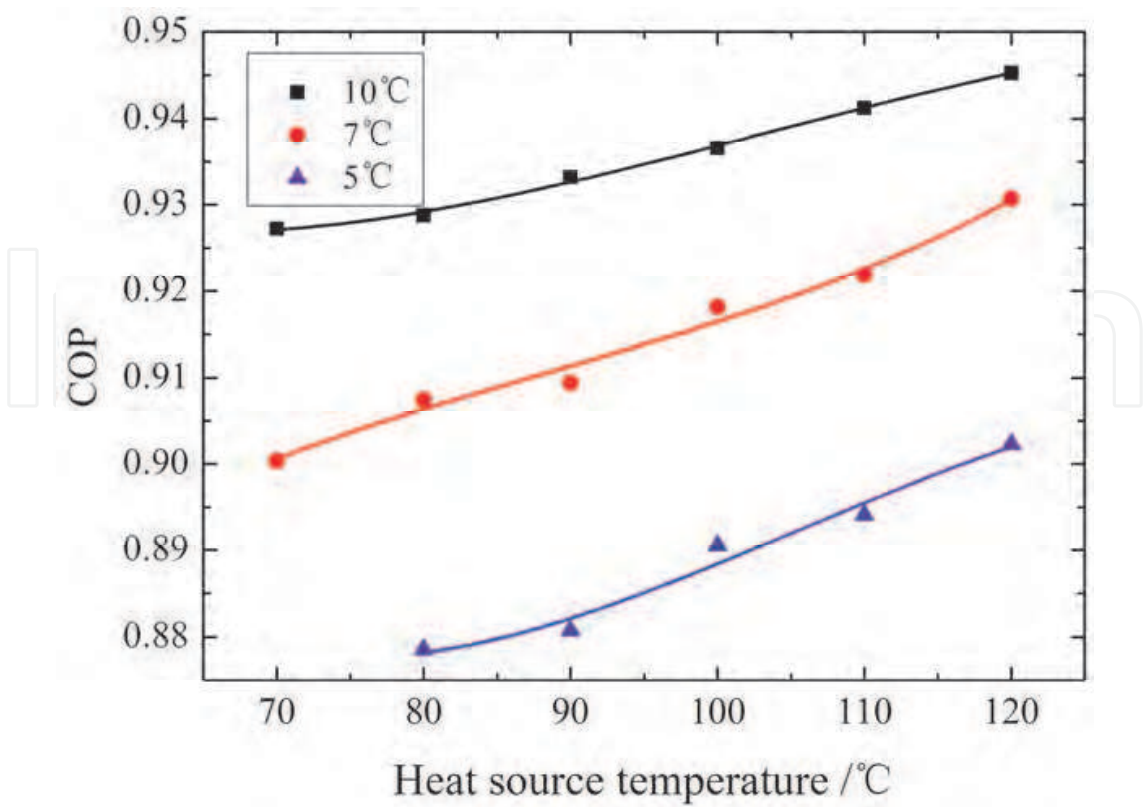Fig. 21. The effect of heat resource temperature on circulation ratio.

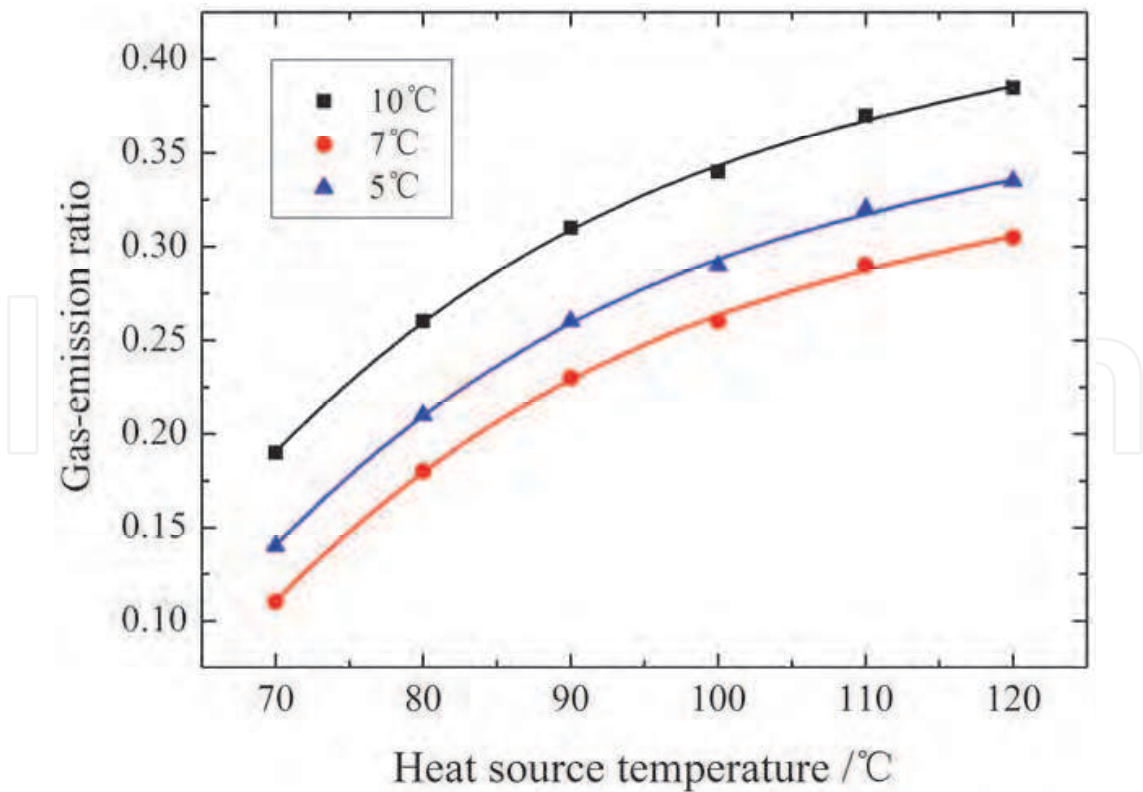Fig. 22. The effect of heat resource temperature on COP.

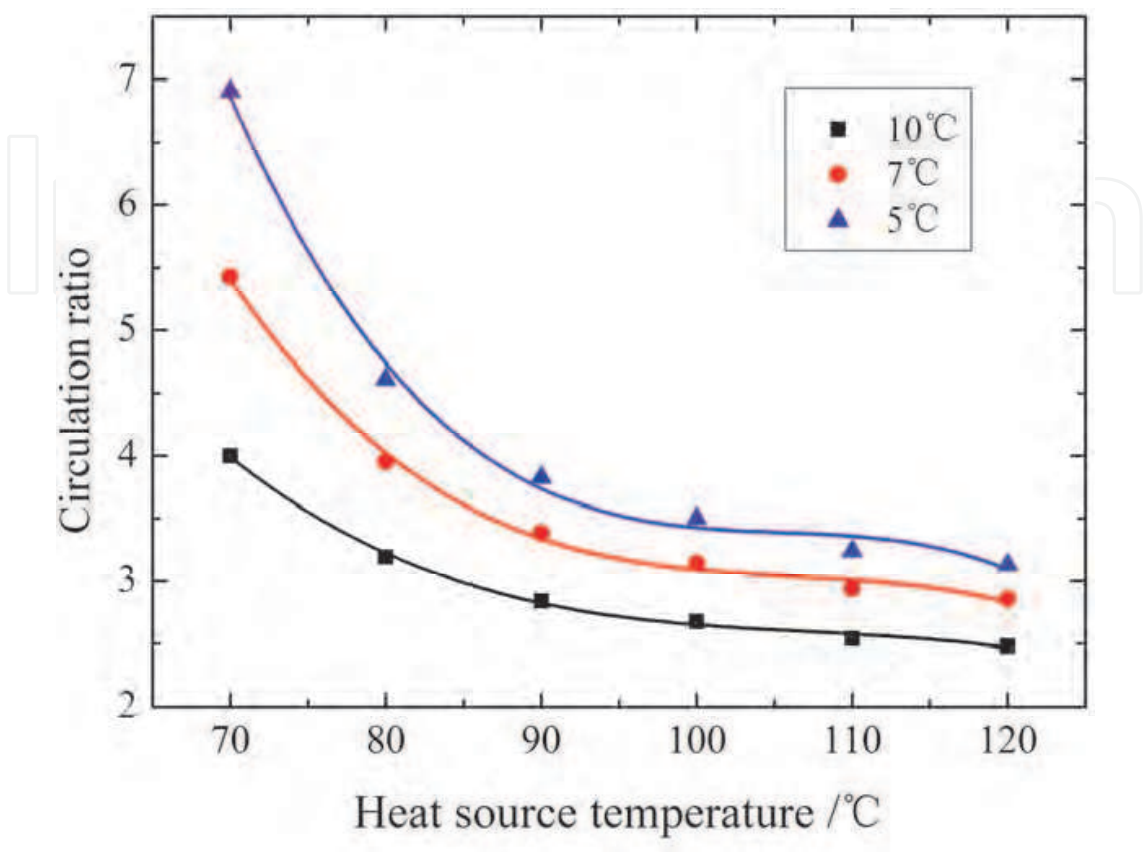Fig. 23. The effect of heat resource temperature on gas-emission scope.

Fig. 24. The effect of heat resource temperature on circulation ratio.

In order to compare the difference between the system using [MMIm]DMP-CH₃OH and that using the traditional working pairs, such as NH₃/H₂O, H₂O/LiBr, under the same working conditions, various parameters were analyzed, such as condensing pressure, evaporating pressure, circulation ratio, and COP. The results are shown in Table 7, the system using [MMIm]DMP-CH₃OH has the following advantages:

1. COP of the system using [MMIm]DMP-CH₃OH is higher than that using NH₃/H₂O and H₂O/LiBr.
2. Unit quality refrigerating capacity is higher than that using NH₃/H₂O, but lower than that using H₂O/LiBr.
3. Circulation ratio is higher than that using NH₃/H₂O, which is helpful to significantly reduce the volume of the equipment.
4. The system using [MMIm]DMP-CH₃OH reduces the requirements of the generating pressure and condensing pressure. The generating and condensing pressures for [MMIm]DMP-CH₃OH are far lower than that for NH₃/H₂O,while a little higher than that H₂O/LiBr. So maintaining and operating of the system are favorable.
5. The mass fraction of [MMIm]DMP-CH₃OH solution is in the range of 65% ~ 89%, and the gas-emission scope can get 0.24, which is far higher than that using H₂O/LiBr, and helpful to reduce the volume of the equipment.

Binary System	P_{con}, P_g /kPa	P_{eva}, P_a /kPa	f	x_g Mass%	x_a Mass%	Q_e /kW	COP
CH$_3$OH/[MMIm]DMP	35.43	7.4113	3.71	89	65	1242	0.886
NH$_3$/H$_2$O	1548	615	2.54	59.5	36.1	1112	0.646
H$_2$O/LiBr	7.38	1.23	4.08	66.3	50	2502	0.833

Table 7. Comparison of COP in the system with different working pairs.

3.2 Double-effect absorption refrigeration system

Single-effect absorption refrigeration system, with simple structure, convenient operation, and low heat source requirement, is suitable for the situation that the heat source temperature and operating pressure is not too high. However, while the heat source temperature is high, there are several drawbacks of the single system, such as low COP and low utilization rate of energy. In order to utilize energy more efficiently and fully, some other systems are developed, such as double-effect system, three-effect system and multiple-effect system.

Liang et al. analyzed the effectiveness and equipment load of double-effect absorption refrigeration system using [MMIm]DMP-CH$_3$OH under various heat source temperature and evaporating temperature. Different generating temperatures, condensing temperatures, absorbing temperatures, and evaporating temperatures were set. The loads of heat equipment, solution concentration, circulation ratio, gas-emission scope, and COP were computed. The results are shown in Figure 25, 26 and 27.
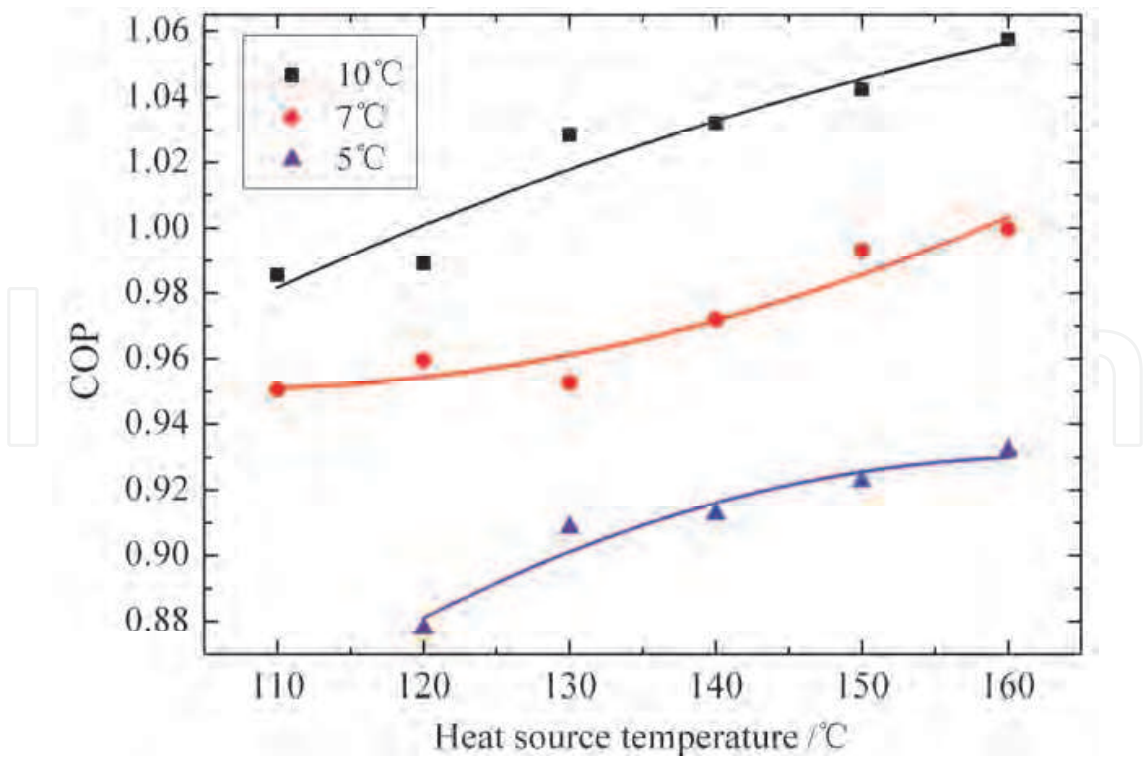

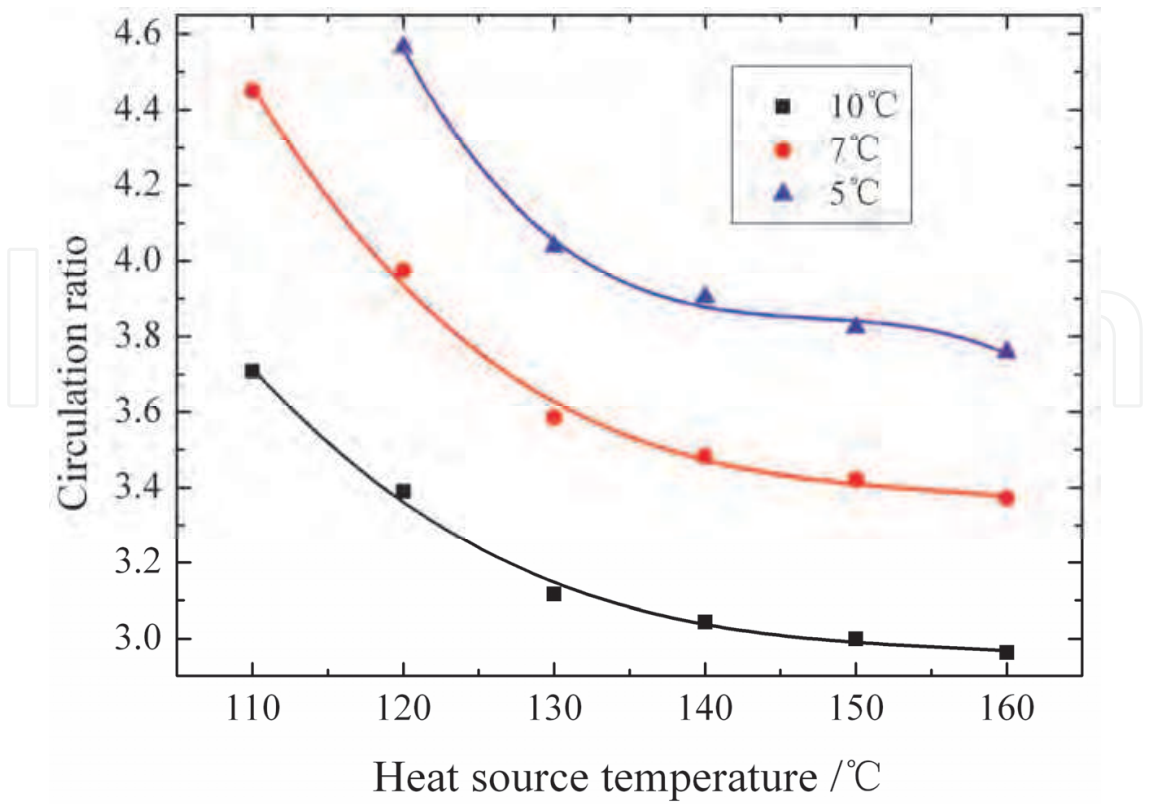Fig. 25. The effect of heat resource temperature on COP.

Fig. 26. The effect of heat resource temperature on gas-emission scope.
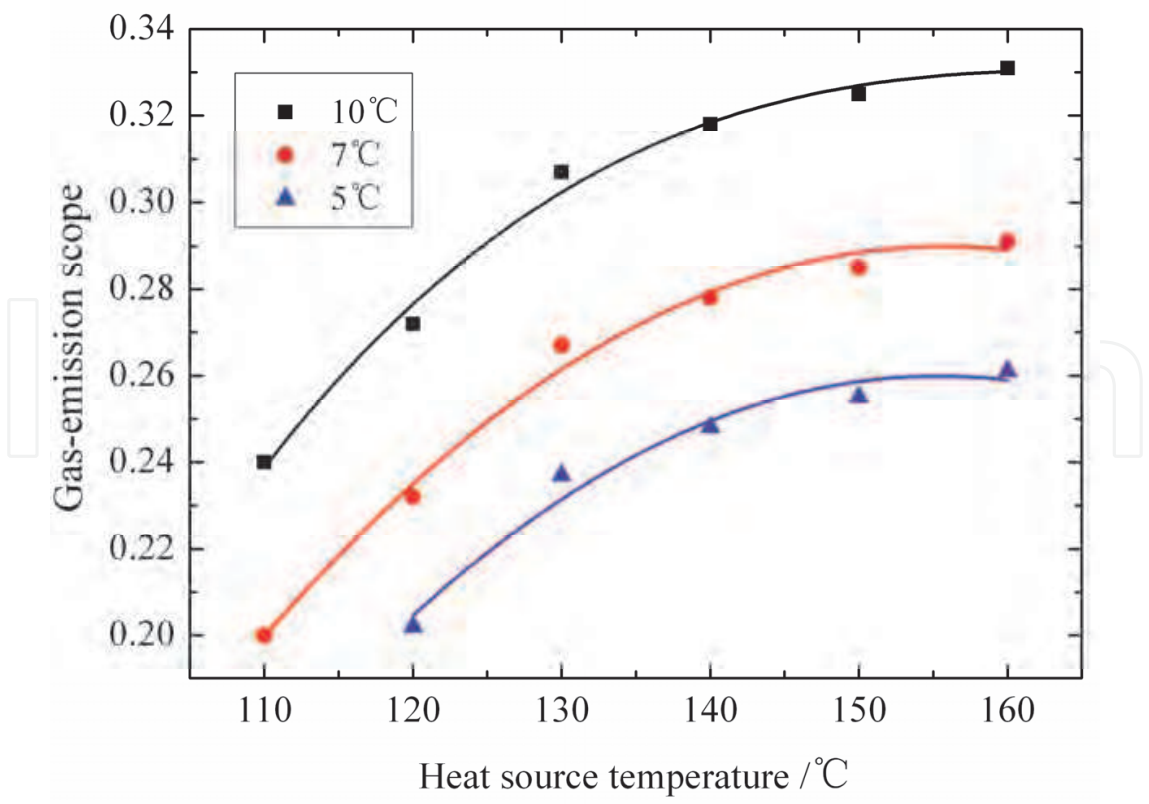

Fig. 27. The effect of heat resource temperature on circulation ratio.

Single-effect absorption refrigeration system, with simple structure, convenient operation, and low heat source requirement, is suitable for the situation that the heat source temperature and operating pressure is not too high. However, while the heat source temperature is high, there are several drawbacks of the single system, such as low COP and low utilization rate of energy. In order to utilize energy more efficiently and fully, some other systems are developed, such as double-effect system, three-effect system and multiple-effect system.

Liang et al. analyzed the effectiveness and equipment load of double-effect absorption refrigeration system using [MMIm]DMP-CH₃OH under various heat source temperature and evaporating temperature. Different generating temperatures, condensing temperatures, absorbing temperatures, and evaporating temperatures were set. The loads of heat equipment, solution concentration, circulation ratio, gas-emission scope, and COP were computed. The results are shown in Figure 25, 26 and 27.

Figure 25 shows that COP of the system increases with the improvement of the heat source temperature and evaporating temperature. For example, COP gets 1.06 when the heat source temperature and evaporating temperatures are 160°C and 10°C respectively. However, the evaporating temperature should not be too low. When the evaporating temperature is 5°C, and heat source temperature is under 120°C, the solution concentration of [MMIm]DMP-CH₃OH will be too low, the circulation ratio will be too high, and the double-effect system will lose its predominance in comparing with the single-effect one.

Figure 26 and Figure 27 show the variation tendency of gas-emission scope and circulation ratio with heat source temperature and evaporating temperature for double-effect absorption refrigeration system. With the improvement of heat source temperature and evaporating temperature, gas-emission scope increases, while circulation ratio decreases. The smaller the gas-emission scope, the bigger the circulation ratio, and the more the heat absorbed by solution liquid, the lower COP. When the evaporating temperatures are 5°C, 7°C, and 10°C respectively, the heat source temperatures should be above 120°C, 110°C and 100°C respectively. Otherwise, gas-emission scope is too small and circulation ratio is too big, so that compared with single-effect absorption refrigeration system, double-effect absorption refrigeration system will not have any advantage. Furthermore, the structure double-effect absorption refrigeration system is huger, and the cost is higher.

In order to compare the difference between the system using [MMIm]DMP-CH₃OH and that using the traditional working pairs, such as NH₃/H₂O, H₂O/LiBr, under the same working conditions, various parameters were analyzed, such as condensing pressure, evaporating pressure, circulation ratio, and COP. The results are shown in Table 8, the system using [MMIm]DMP-CH₃OH has the following advantages:

1. COP of double-effect absorption refrigeration system using [MMIm]DMP-CH₃OH is almost the same with that of the system using H₂O/LiBr.
2. Since methanol is chosen as refrigerant, evaporation latent heat of methanol is smaller than that of water, and unit quality refrigerating capacity of methanol is smaller than that of H₂O/LiBr.
3. Circulation ratio of the system using [MMIm]DMP-CH₃OH is smaller, and gas-emission scope is larger. Compared with that of the system using H₂O/LiBr, it is helpful to simplify the structure of the equipment.
4. The requirements of operating pressure, condensing pressure, and vacuum for the system using [MMIm]DMP-CH₃OH are lower, which benefits the operation and the maintaining of the system.

Binary System	Deflation Ratio	ω_a	ω_{r1}	ω_{r2}	Circulation Ratio	Q_e/kW	COP
CH$_3$OH/[MMIm]DMP	0.255	0.72	0.957	0.975	3.82	1242	0.923
H$_2$O/LiBr	0.05	56.93	60	61.93	12.38	2502	0.930

Table 8. Comparison of COP in the system with different working pairs.

3.3 Summary

Based on the physical and chemical properties of binary system containing ionic liquids and refrigerant, A. Yokozeki et al. from American, J.Z. Wang et al. and S.Q. Liang et al. from China calculated some fundamental parameters of refrigeration cycle by the EOS model, including several key parameters, such as COP, circulation ratio and gas-emission scope. They also analyzed the flux characteristics of some fundamental parameters with different heat source temperature, condensing temperature, evaporating temperature and absorption temperature. The pressure of the whole cycle is moderate, and there is no distillation equipment, no corrosion and no crystallization in the new type of absorption refrigeration. Compared with the double effect cycle, the single effect cycle is more economical and practical when this new working pairs containing ionic liquids is used. Since the working pairs used by different researchers are not the same, COP of different cycles is different from each other. Further research will focus on the practical applications of the new type absorption refrigeration.

4. Conclusions and outlook

Based on the low-grade heat source, absorption refrigeration, which owns many advantages such as simple and quiet, along with energy-saving and environmental protection, has huge spaces for development. It is revealed that the binary system, containing ionic liquids and refrigerants as working pairs of absorption refrigeration, has large application potential through the researches on the physical and chemical properties. The new type ionic liquid absorption refrigeration can overcome same defects belonging to the traditional type, such as corrosion, crystallization and requirement of distillation equipment. However, the large-scaled industrial application of the new technology is still restricted by several factors as follows. Firstly, COP of some working pairs containing ionic liquids is still not high, requiring that better working pairs with high COP should be screened out. Secondly, the researches are still at the academic stage in defect of the studies on practical design and structure optimization. The experimental units are all theoretical simulation ones, and until now the suitable absorption refrigeration units in practice have not been produced. In addition, the manufacturing costs for the new type of absorption refrigeration are high, for the reason that the price of ionic liquids is high, which prevents the market from popularizing this technology. Overall, the ionic liquid absorption refrigeration has a huge space for development and good market prospect, and it will certainly bring innovative promotion and ground-breaking progress for the absorption refrigeration technology.

5. Acknowledgments

6. References

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Applications of Ionic Liquids in Science and Technology
Edited by Prof. Scott Handy

This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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