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Evaluation of proper HFO refrigerant/ionic liquid mixture for absorption refrigeration system

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Abstract

This study is to evaluate ionic liquid as absorbents for absorption refrigeration system using Hydrofluoro-olefin (HFO) refrigerant. By examining properties of absorbent/refrigerant mixture, we found the most efficient absorbent/refrigerant pair for the absorption refrigeration system. First, we analyzed characteristics of ionic liquid as absorbent in absorption refrigeration system. Imidazolium ionic liquids have relatively low viscosity of about 10 mPa.s at 70 ^{o}C and high stability to water and air, so that we decided to apply imidazolium ionic liquid as absorbent. Then, we examined proper HFO refrigerant for the system. Among the refrigerants, R1336mzz(Z) and R1234ze(Z) are applicable for the absorption refrigeration system because both have low inflammability, and high critical points over 150 ^{o}C. Next, we analyzed characteristics of absorbent/refrigerant pair. When [OMIM][BF4] is used as absorbent, R1336mzz(Z) and R1234ze(Z) have the highest solubility of 0.05848 and 0.66149 at absorber, respectively. Lastly, we analyzed performance of the refrigeration system. Since difference of solubility of [OMIM][BF4]/R1234ze(Z) is large between absorber and generator, it shows the highest COP than other pairs.

Keywords: Absorption refrigeration system; Absrobent/refrigerant pair; Ionic liquid; Hydrofluoro-olefin; Non-Random two liquid model

1. Introduction

To maintain indoor thermal comfort in summer days, the use of refrigerator is rapidly increasing. Among various refrigeration system, absorption refrigeration system is promising due to its low operating cost and low heat source temperature. The absorption refrigeration system usually used H_2O/LiBr or NH_3/H_2O as refrigerant/absorbent pair. Those refrigerant/absorbent pairs, however, have fatal problems, such as crystallization of absorbent and corrosion [1-2]. Therefore, it is necessary to find proper refrigerant/absorbent pairs that can be used in absorption refrigeration system.

Ionic liquid has gained attraction as absorbent in absorption refrigeration system, because asymmetric structure between cation and anion of ionic liquid can help dissolve polar refrigerant, and it has good stability in air and water. Therefore, many studies are trying to apply ionic liquid in absorption refrigeration system. Firstly, research on finding substitute of LiBr in H_2O/LiBr absorption refrigeration system is conducted. Some researchers examined performance of absorption refrigeration system using H_2O/[EMIM][DMP] pair. The COP of refrigeration system using ionic liquid as absorbent is about 7% lower than that of H_2O/LiBr system, but it still showed relatively high COP over 0.7 [3]. Other researchers tried to increase COP of absorption refrigeration system using H_2O/[DMIM][DMP] pair [4]. They insisted that COP of the refrigeration system using H_2O/[DMIM][DMP] pair can provide higher COP of 0.78 compared to the system using H_2O/LiBr pair by proper system optimization. Others analyzed pair of water and various imidazolium-type ionic liquids for

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absorption refrigeration system, and showed that H2O/[EMIM][$(CH_3)_2PO_4$] showed the highest COP of 0.69 [5]. Others tried to apply EMISE to absorb water in absorption refrigeration system [6]. Although COP of absorption refrigeration system with H_2O/EMISE pair showed relatively high value of 0.66, the COP is lower than the refrigeration system with H_2O/LiBr pair. Although many previous studies analyzed application of ILs as absorbent to use water as refrigerant, water is frozen below zero temperature, so that operating range of the refrigeration system using water as refrigerant is limited. Therefore, research on various refrigerant for absorption refrigeration system is needed.

Due to environmental issue, research of low global warming point (GWP) refrigerant has been actively conducted, so that researchers tried to apply ionic liquid as absorbent with low GWP refrigerant. Some researchers analyzed application of [HMIM][PF_6] and [HMIM][Tf_2N] as absorbent for R134a refrigerant [7]. When [HMIM][Tf_2N] is used as absorbent, about 0.1 higher COP is obtained compared to the absorption refrigeration system using [HMIM][PF_6] as absorbent. Other researchers analyzed performance of absorption refrigeration system with HFO/ionic liquid pairs [8]. Since high solubility of R32 to [C_2MIM][Tf_2N], the COP of the system with R32/[C_2MIM][Tf_2N] pair showed the highest value of 0.734 among various working pairs. Others examined six imidazolium-type ionic liquids as absorbent for using R1234yf as refrigerant [9]. Among the ionic liquids, [HMIM][Tf_2N] showed the highest COP of 0.35 among IL absorbents. The R1234yf /[HMIM][Tf_2N] pair, however, showed lower COP than conventional working fluids due to low specific volume of R1234yf. Although various studies have been conducted to find proper ionic liquid for absorption refrigeration system, studies on finding proper ionic liquid for absorbing hydrofluoroolefin refrigerant is insufficient.

2. Methods

The purpose of this study is to find proper working fluid/absorbent mixture for double effect absorption refrigeration system. Therefore, we have to develop the refrigeration system model and express behavior of the mixture. The double effect absorption refrigeration system model is developed using MATLAB. Properties of HFO refrigerants are obtained by REFPROP 10.0, and that of the mixture is calculated using COSMO-RS.

The absorption cooling system is largely composed of a generator, a condenser, an evaporator, and an absorber. The double-effect absorption system is a device that aims to improve performance by adding a regenerator and a condenser, respectively, to the existing system. The working pressure of the double-effect absorption cooling system is divided into three levels, and the concentration is also divided into three levels. The schematic diagram is shown in fig 1. For the study of this system, it is necessary to assume the understanding of the phenomena of each component. The whole system is calculated assuming a steady state. At the outlet point of the low-pressure condenser, the refrigerant from the low-temperature condenser is assumed to condense to saturation, where the pressure determines the operating pressure at the mid-level. The refrigerant vaporized in the evaporator is also assumed to be saturated, where the pressure determines the low level operating pressures in the evaporator and absorber. In the absorber, the gaseous refrigerant is absorbed by the working fluid with a low concentration to become a saturated working fluid with a high concentration that satisfies the phase equilibrium state under the operating conditions. In the high-pressure regenerator and the low-pressure regenerator, the refrigerant is separated due to the difference in boiling point between the two liquids constituting the working fluid. Since only the refrigerant is separated in the regenerator, the concentration of the outlet is calculated using the same amount of absorbent. Concentration calculation and thermal equilibrium are calculated through the following equations.

$$\sum \dot{m}_i = \sum \dot{m}_o \tag{1}$$

$$\sum \dot{m}_i \, h_i = \sum \dot{m}_o \, h_o \tag{2}$$

$$\dot{m}_\imath x_i = \dot{m}_o x_o \tag{3}$$

When calculating the coefficient of performance of the cycle, the energy consumed by the pump is very small and is therefore neglected.

$$COP = \frac{Q_{Evaporator}}{Q_{High\ Pressure\ Generator} + W_{Pump}} \cong \frac{Q_{Evaporator}}{Q_{High\ Pressure\ Generator}} \tag{4}$$

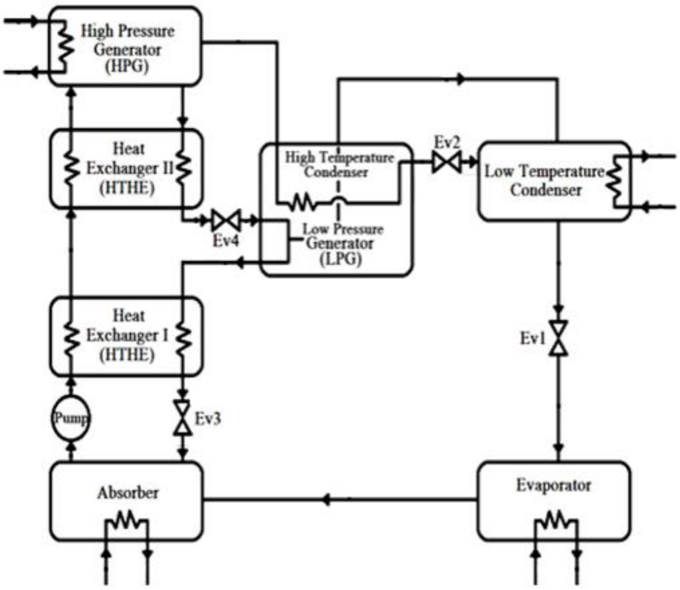


Fig. 1. Schematic of double effect absorption refrigerator.

The pressure at vapor-liquid phase equilibrium in the absorber and the two regenerators of the double-effect absorption chiller is calculated using Raoult's law, which introduces the activity coefficient.

$$y_i P = x_i \gamma_i P_i^{sat} \tag{5}$$

x_i denotes the mole fraction in the liquid phase, and y_i denotes the mole fraction in the vapor state. The activity coefficient is introduced in consideration of the fact that the gas has not great non-ideality with respect to the actual gas, but the liquid phase has large non-ideality. The enthalpy of various working fluids used in a double-effect absorption chiller is calculated as follows.

$$h = h_{Ref} x_{Ref} + h_{IL} x_{IL} + h_{mix} \tag{6}$$

$$h_{IL} = h_o + \int_{T_o}^{T} C_{p,IL} dT \tag{7}$$

$$h_{mix} = -RT^2 \left[\frac{\partial \left(\frac{G^E}{RT} \right)}{\partial T} \right]_P \tag{8}$$

3. Results and discussion

3.1. HFO refrigerants and ionic liquid absorbents

In this study, we examined HFO refrigerants that are usually used in refrigeration system. Most of GWPs of HFO refrigerants and flammability are also low, so most HFO refrigerants are applicable to the refrigeration system. Moreover, these refrigerants have lower freezing point than water, so we can generate more cold heat source with refrigeration system using HFO refrigerants than that using water. Next, we examined possibility of application of HFO refrigerants to double effect absorption refrigeration system. The desirable operating ranges of HFO refrigerants are listed in Fig. 2. Here, we assumed that the desirable operating range is between triple point and critical point. Heat source temperature of double effect absorption refrigeration system is usually over 120 °C. Therefore, when refrigerants which has low critical point than heat source temperature, the thermodynamic cycle will be operated in super critical state. Unfortunately, the studies on super critical state of HFO refrigerant are insufficient. Therefore, the refrigerant which has higher critical point than heat source temperature is recommended, such as, R1336mzz(Z) and R1234ze(Z).

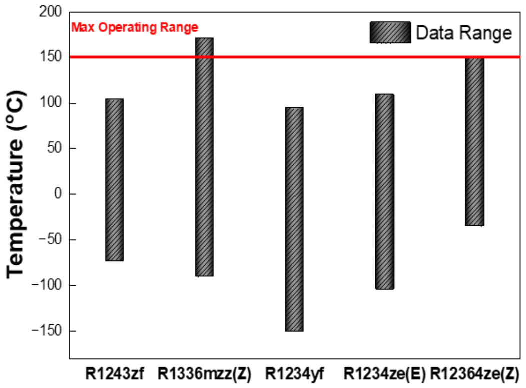


Fig. 2. Comparison of operating ranges of HFO refrigerants.

Next, proper ionic liquids are examined. Ionic liquids consist of large cation and small anion. This asymmetry leads to weak attractive force, so that ionic liquids have low melting point. Characteristics of ionic liquids are determined by combination of cation and anion. Especially, flow characteristics of ionic liquids are mainly determined by structure of cation. The characteristics of various cation are listed in table 1.

Table 1. Characteristics of $N(SO_2CH_3)_2$ anion-based ionic liquids

Name	Chemical Formula	Molecular weight (g/mol)	Volume (cm^3/mol)
1-Ethyl-3-methylimidazolium	$C_6H_{11}N_2^+$	111.17	259.5
1-Methyl-1-propyrrolidinium	$C_8H_{18}N^+$	128.24	287.0
Trimethylpropylammonium	$C_6H_{16}N^+$	102.20	268.7
1-Ethyl-2,3,5-trimethylpyrazolium	$C_8H_{15}N_2^+$	139.22	288.4
1-Methyl-1-propylpiperidinium	$C_9H_{20}N^+$	142.26	300.8

Among the flow characteristics, viscosity is one of important factors that affects performance of the refrigeration system. Therefore, we examined viscosities of ionic liquids based on cations shown in Fig. 3. In this study, we examined viscosity of ionic liquids with 1-ethyl-3-methylimidazolium (EMIM), N-methyl-N-propylpyrrolidinium (P13), trimethyl propylammonium (TMPA), and 1-ethly-2,3,5-trimethylpyrazolium (ETMP) comparing with H2O/LiBr solution of 59.9 wt%. Most ionic liquids have higher viscosity than that of H_2O/LiBr solution. Among the ionic liquids, however, imidazolium type ionic liquid has relatively low viscosity. Over 50 ^oC, viscosity of EMIM is lower than 20 mPa.s. Therefore, we concluded that EMIM ionic liquids are promising for absorption refrigeration system.

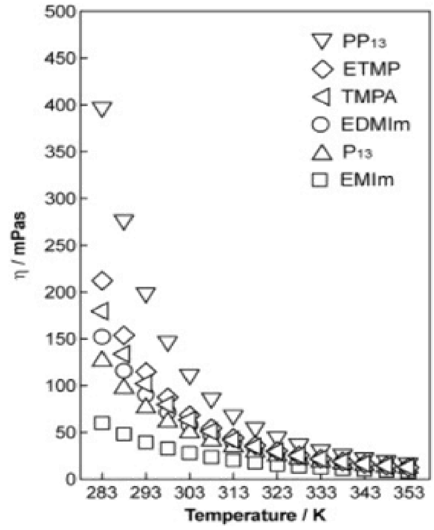
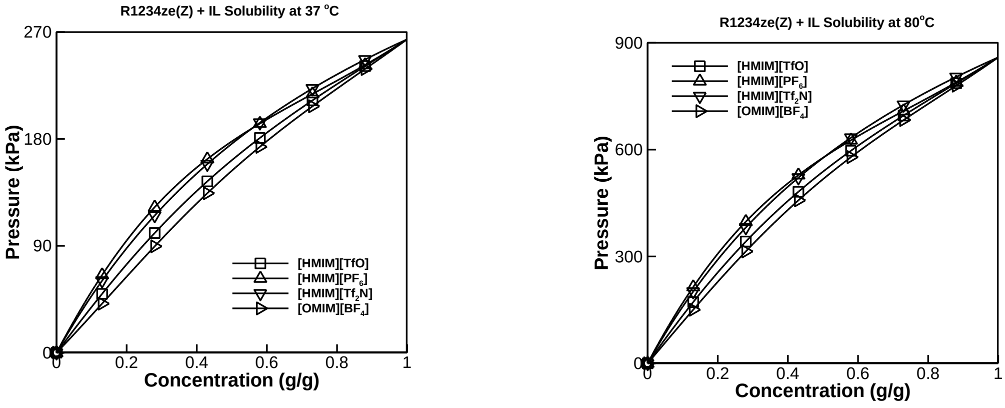


Fig. 3. Changes in viscosity of ionic liquids depending on various cation with Tf_2N anion [10].

3.2. Examination of HFO refrigerants/ionic liquid absorbents solution

In this section, we analyzed application of HFO refrigerant/ionic liquid mixture for double absorption refrigeration system. Here, heat source temperature of the refrigeration system is 140 °C, and temperatures of pressure generator and absorber are 37 °C and 80 °C, respectively. Candidate of HFO refrigerants are R1336mzz(Z) and R1234ze(Z) and that of ionic liquids are imidazolium type ionic liquids. Results of the mixture is compared to water/ionic liquid pair.

Solubility of R1234ze(Z) with various ionic liquids are shown in Fig. 4. Here, solubility of refrigerant is expressed using concentration that is defined by mass fraction of refrigerant weight and solution weight. Since the highest concentration is observed absorber and the lowest concentration is observed in low-pressure generator. Therefore, we compared concentration in low-pressure generator and absorber. The Concentration of R1234ze(Z) is increased according to saturation pressure. For example, concentration of R1234ze(Z) /[OMIM][BF_4] mixture increased from 0.15 to 0.32 when saturation pressure increased from 30 kPa to 90 kPa. The concentration of the mixtures, however, inversely proportional to temperature. For example, the solubility of R1234ze(Z)/[OMIM][BF_4] mixture at 100 kPa decreased from 0.37 to 0.14 when the temperature increased from 37 °C to 80 °C.



(a) Change in solubility at absorber (b) Change in solubility at low pressure generator

Fig. 4. Comparison of solubility of R1234ze(Z) with various ionic liquids in double effect absorption refrigeration system.

Among the refrigerant/absorbent mixtures, R1234ze(Z)/[OMIM][BF_4] pair is the only promising pair for the double absorption refrigeration system. Because the concentration at absorber is lower than that in low-pressure generator when other refrigerant/absorbent mixtures except R1234ze(Z)/[OMIM][BF_4] pair. When we use [OMIM][BF_4] as absorbent, the concentration of refrigerant at absorber is 0.01 higher than that at low-pressure generator shown in Fig. 5. Therefore, R1234ze(Z)/[OMIM][BF_4] is good for double effect absorption refrigeration system.

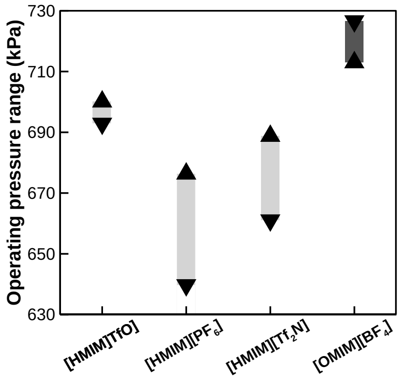
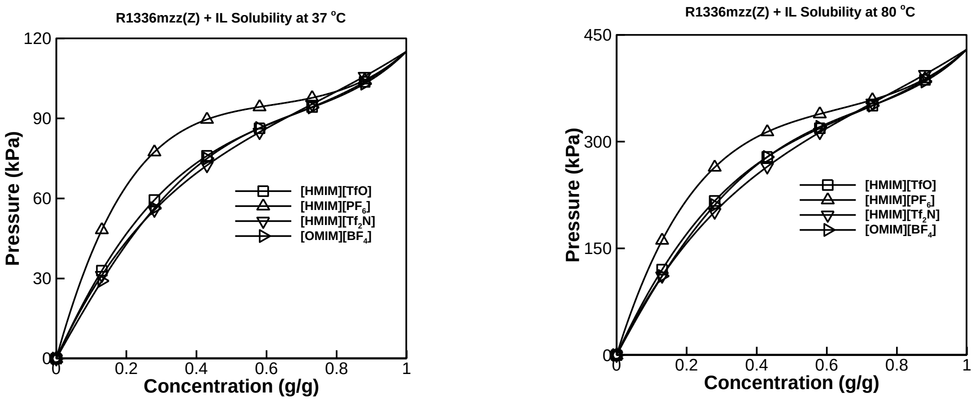


Fig. 5. Concertation of R1234ze(Z) at absorber and low-pressure generator with various ionic liquids.

Next, solubility of R1336mzz(Z) examined with various ionic liquids shown in Fig. 6. Similar to R1234ze(Z), solubility of R1336mzz(Z) is proportional to pressure, and inversely proportional to temperature. In case of R1336mzz(Z) with [HMIM][TfO], concentration is increase from 0.22 to 0.58 when saturation pressure increased from 150 kPa to 300 kPa. Concentration decreased from 0.8 to 0.15 when the temperature increased from 37 ºC to 80 ºC at saturation pressure of 100 kPa. Among the mixtures, R1336mzz(Z)/[HMIM][Tf2N] pair showed the highest solubility. At 600 kPa, concentration of R1336mzz(Z) with [HMIM][Tf_2N] is about 0.42.



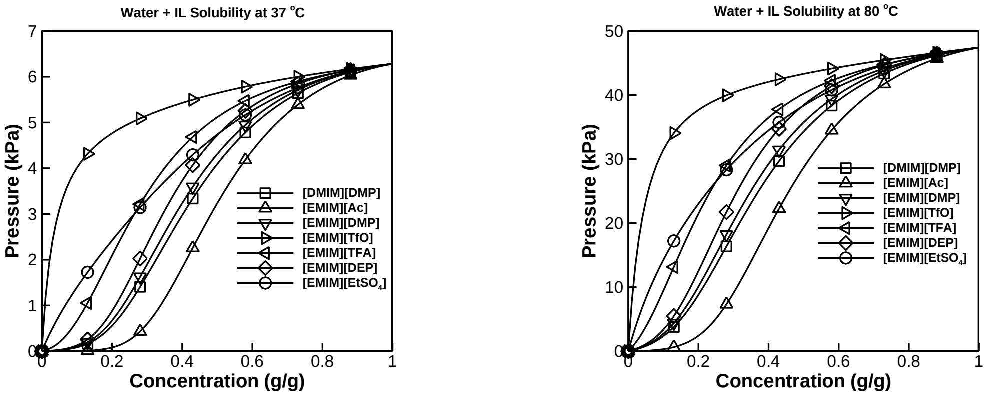
(a) Change in solubility at absorber

(b) Change in solubility at low pressure generator

Fig. 6. Comparison of solubility of R1336mzz(Z) with various ionic liquids in double effect absorption refrigeration system.

In case of R1336mzz(Z), however, the concentration of refrigerant at absorber is lower than that at generators. To operate absorption refrigeration system, the concentration of refrigerant at absorber should be higher than that at generator. Because refrigerants are absorbed to absorbent at absorber. Therefore, R1336mzz(Z) is inappropriate refrigerant for absorption refrigeration system in given condition.

Solubility of water with various ionic liquids also analyzed shown in Fig.7. Changes in solubility of water with ionic liquids are similar to other refrigerants. The higher the saturation pressure, the higher the solubility, and the higher the temperature, the lower the solubility. Among the mixture, H_2O/[EMIM][Ac] pair shows the largest solubility. In low-pressure generator, the concentration is about 0.65 at 5 kPa.



(a) Changes in solubility at absorber (b) Changes in solubility at low pressure generator

Fig. 7 Comparison of solubility of water with various ionic liquids in double effect absorption refrigeration system.

However, concentration difference between at absorber and low pressure generator is the largest for H_2O/[DMIM][DMP] mixture shown in Fig. 8. Therefore, H_2O/[DMIM][DMP] is suitable for the absorption refrigeration system.

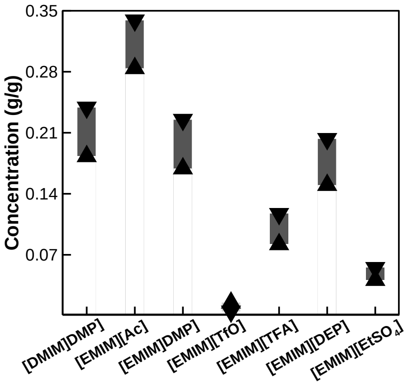


Fig. 8. Operating range of high pressure generator for the absorption refrigeration system using water with various ionic liquids.

4. Conclusion

In this study, proper HFO refrigerant/ionic liquid pairs for double effect refrigeration system are examined. We analyzed properties of various mixtures for the double effect absorption refrigeration system depending on working fluid/ionic liquid.

(1) Among HFO refrigerants, R1234ze(Z) and R1336mzz(Z) are promising refrigerants for double effect absorption refrigeration system. Because heat source temperature of double effect absorption refrigeration system is higher than the critical point of rest of HFO refrigerants. Therefore, only R1234ze(Z) and R1336mzz(Z) can be exited in stable condition under operating condition of double effect refrigeration system. In case of ionic liquid, imidazolium type ionic liquids are suitable for the refrigeration system. Because viscosity of imidazolium ionic liquid has relatively low value compared to other ionic liquids.

(2) The solubility of HFO refrigerant/ionic liquids are examined to find promising mixture for the absorption refrigeration system. For R1234ze(Z), [OMIM][BF4] is promising due to high solubility of 0.28 in low pressure generator at 300 kPa. It also has high concentration difference between absorber and generator, so that large amount of refrigerant can be supplied to evaporator. In case of R1336mzz(Z), however, concentration of refrigerant at absorber is lower than that at generators, it is not suitable refrigerant for the absorption refrigeration system. We also analyzed solubility of water to ionic liquid absorbent. Although the highest solubility can be found for H2O/[EMIM][Ac] mixture, concentration difference between absorber and generator is relatively small. Therefore, we recommended that H2O/[DMIM][DMP] is promising absorbent for water.

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