

Visual investigation of solid-liquid phase equilibria for non-flammable mixed refrigerant

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Abstract. Non-flammable mixed refrigerant (NF-MR) Joule Thomson (J-T) refrigerators have desirable characteristics and wide cooling temperature range compared to those of pure J-T refrigerators. However, the operating challenge due to freezing is a critical issue to construct this refrigerator. In this paper, the solid-liquid phase equilibria (i.e. freezing point) of the NF-MR which is composed of Argon, R14 (CF₄), and R218 (C₃F₈), has been experimentally investigated by a visualized apparatus. Argon, R14 and R218 mixtures are selected to be effectively capable of reaching 100 K in the MR J-T refrigerator system. Freezing points of the mixtures have been measured with the molar compositions from 0.1 to 0.8 for each component. Each test result is simultaneously acquired by a camcorder for visual inspection and temperature measurement during a warming process. Experimental results show that the certain mole fraction of Argon, R14, and R218 mixture can achieve remarkably low freezing temperature even below 77 K. This unusual freezing point depression characteristic of the MR can be a useful information for designing a cryogenic MR J-T refrigerator to reach further down to 77 K.

1. Introduction

Cryogenic Joule-Thomson (J-T) refrigeration cycle is the most fundamental refrigerator for large industrial applications such as gas liquefaction process[1]. This refrigerator has a lot of advantages, such as ease of fabrication, cooling power adjustability and high reliability due to no moving parts in cryogenic condition. However, J-T refrigerators with pure cryogenic refrigerants have inherent drawback that the low thermodynamic efficiency is somewhat indispensable due to an irreversible process at the expansion device. Moreover, extremely high pressure ratio between the high pressure and the low pressure parts is also a challenging issue to develop a pure refrigerant cryogenic J-T refrigerator. Therefore, mixed refrigerant (MR) J-T refrigerators been proposed and utilized as alternative devices in recent years to alleviate these shortcomings.

MR J-T refrigerator has achieved wide range of cooling temperatures by different compositions of working fluids [2]. The specific composition of the MR is carefully determined to maximize the thermodynamic efficiency and boost their potential refrigeration power with various boiling temperatures of its constituents [3].

MR has been commonly blended with flammable refrigerant such as methane (C1), ethane or ethylene (C2), propane (C3) and butane (C4) etc [4]. The flammable MR compositions enable the MR J-T refrigerator to attain high thermodynamic efficiency. However, explosiveness and combustible problem are the critical issues of the operation safety. These dangerous potential factors can be eliminated by using non-flammable refrigerants such as nitrogen (N₂), argon (Ar), R14 (CF₄), R23



(CHF₃) and R218 (C₃F₈).

Although the well-designed non-flammable MR may achieve high thermodynamic efficiency in its J-T refrigeration cycle, the component of high freezing temperature can actually clog or block the J-T expansion part. It is well-known that, non-flammable refrigerants have relatively high freezing temperatures compared to those of flammable refrigerants which have similar molecular structures (i.e. carbon number). Thereby, the freezing point of the non-flammable MR should be identified and thoughtfully considered at the design stage of cryogenic non-flammable MR J-T refrigeration cycle.

The freezing points of pure refrigerants and a few binary MRs were interpreted by solid-liquid equilibria (SLE) in the past research. Nicola et al. investigated the freezing point of numerous binary mixtures with the closed vessel [5], [6]. Campesitri et al. modelled the solid-liquid equilibrium prediction for binary mixtures of Ar, O₂, N₂, Kr, Xe and C1 [7]. Aforementioned studies were well established to characterize the freezing point of binary mixture or pure refrigerant, however, SLE for ternary MR under cryogenic condition has been rarely investigated. The only research for freezing of cryogenic MR is for the MR of Ar, R14, R23 and R218 in a certain molar composition[8]. This research mentioned that R23 is the main parameter of freezing point for Ar, R14, R23 and R218 mixture.

In this paper, freezing point depressions for ternary MR sets, which are composed of Ar, R14 and R218, are extensively investigated by a visualized apparatus. The tested MR is frozen by liquid nitrogen (LN₂, 77 K), and it is melted down with the evaporation of LN₂ by natural heat ingress. On-time video recording is conducted and interpreted frame by frame to measure the accurate freezing temperature for selected MR. The 27 test sets measured the actual freezing point of MR which have molar compositions from 0.1 to 0.8 for each pure components. Accordingly, the selected measurement details of the whole ternary MRs are presented in this paper.

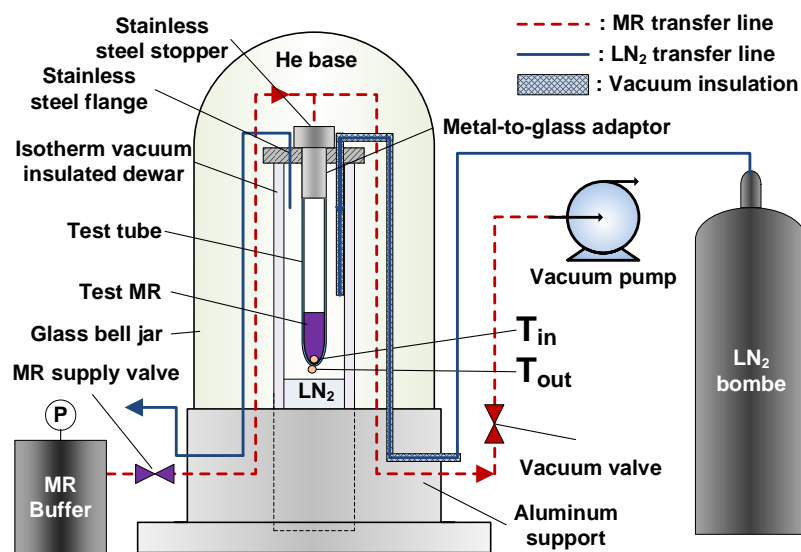


Figure 1. Schematics of the experimental apparatus [8]

2. Experimental apparatus and methodology

2.1 Experimental apparatus

A visualized experimental setup was developed and introduced in the past research[8]. Figure 1 shows the schematic of the experimental apparatus. Experimental apparatus mainly consists of with 3 parts; helium base, double layered vacuum insulation liquid nitrogen (LN₂) container, and MR test tube section. The developed complete experimental apparatus is illustrated as Figure 2 (a). The detailed view of the measurement part is shown as Figure 2 (b). Helium base part is primarily a machined aluminium support and glass bell jar made by Kurt J. Lesker. The height of bell jar is 457 mm (18 in) and the outer diameter

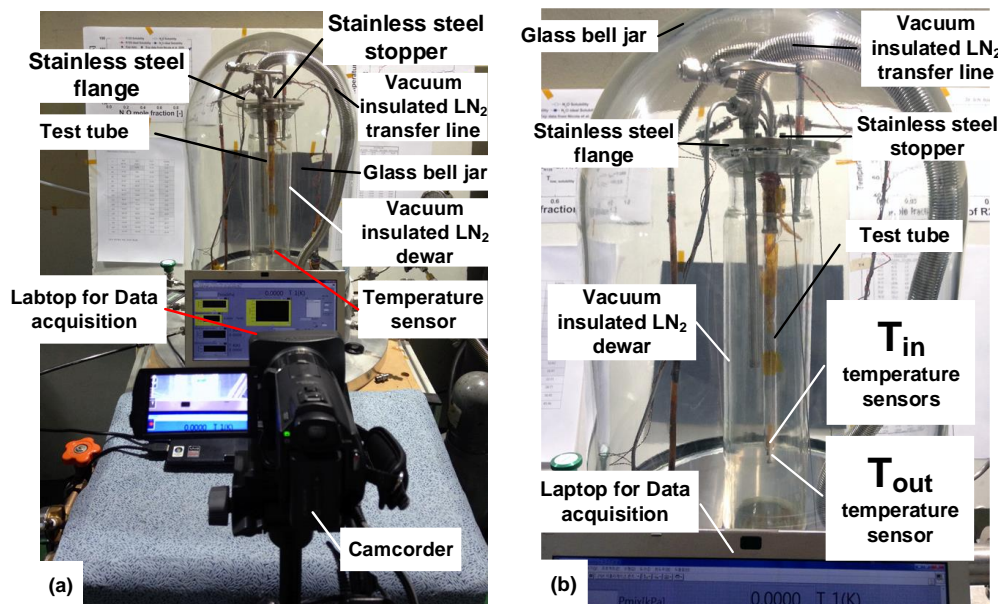


Figure 2. Photograph of visualized experimental apparatus (a) total apparatus and (b) test part [8]

is 320 mm (12.5 in). Helium gas is circulated before LN₂ charging and after LN₂ charging during the experiment to prevent the frost formation at the surface of the LN₂ container. The LN₂ container is a double layered vacuum insulation glass dewar made by KGW-Isotherm. The surface of the dewar has no silver coating because the transparency of the test section is required. The top of the dewar is covered by stainless steel flange which holds the LN₂ supply line, MR test tube section, and LN₂ vent line.

The MR test tube section is utilized with a joining apparatus between the sealed glass tube and the half of a Double Ended Kovar-to-7052 Glass with the outer diameter of 12.7 mm (1/2 in), made by Larson Electronic glass. This joined test tube is soldered between the metal-glass adaptor and the stainless steel flange. Top side of the test tube is sealed with stainless steel stopper and indium wire. MR supply line and MR vent line are made with the outer diameter of 3.2 mm (1/8 in) stainless steel tube. Temperature sensor feedthrough line is fabricated with the same stainless steel tube and sealed by Stycast 2850 FT epoxy. All connection lines that attached at the stainless steel stopper are brazed to secure the sealing inside the MR test tube section.

Lakeshore silicon diode DT-670-SD temperature sensors are used to measure the temperature of the inside and the outside of the test tube. The accuracy of temperature sensor is ± 0.02 K. Two temperature sensors are positioned inside of the test tube to enhance the accuracy of measurement. Outer temperature sensor is installed by a temperature holder which is soldered at the surface of the test tube.

Honeywell model FP2000 pressure transducer with the operating range of 75 psi is used at the inlet of the test tube to determine the precise thermodynamic state of the refrigerant. The resolution of the pressure transducer is ± 0.5 kPa. The whole measurement data are collected by National Instrument NI-USB-6343. The SONY camcorder HXR-MC50N records the freezing and melting phenomenal image with 30 frame per second (30 fps).

A machined aluminium chamber is prepared to be used for the MR buffer. The volume of MR buffer is set as 608 cc to collect the sufficient mass of frozen MR inside the test tube. This volume is changeable according to the glass test tube size and its maximum allowable pressure.

Making an accurate test mixture is one of the main challenges to verify the freezing point for certain MR. The standard number 6142 (KS I ISO 6142:2008) requires that the standard gas mixture needs to be precisely provided with gravimetric method (mass gauging). However, the system size is too small to achieve good composition accuracy by the gravimetric method. To overcome this problem, the pressure ratio method is performed to prepare the selected MR. This is because each pure component

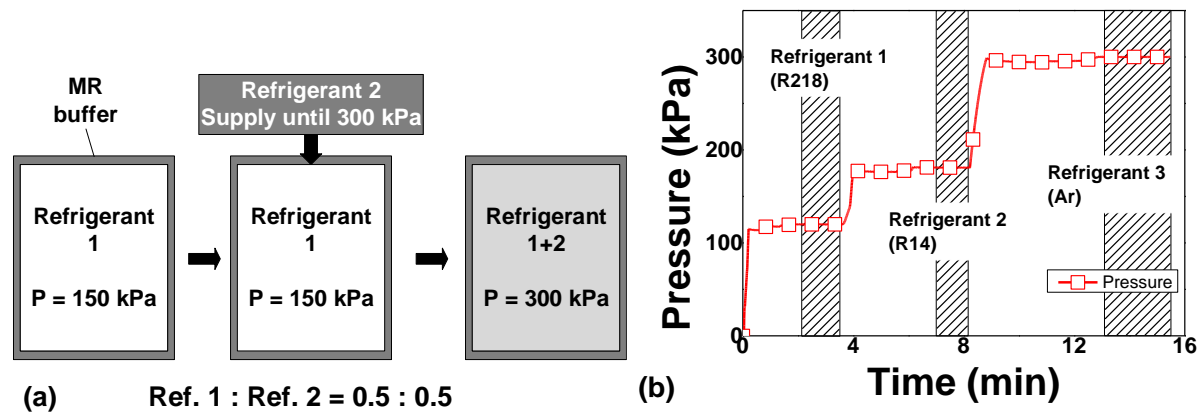


Figure 3. Explanation of MR charging method (a) schematics of refrigerant charging and (b) Pressure - time diagram of actual charging condition [8]

for MR satisfies the ideal gas law at the atmospheric condition.

Thus, the composition of MR is varied simply proportional to the pressure ratio. Figure 3 (a) illustrates the refrigerant charging method, and Figure 3 (b) represents the actual pressure-time diagram during the experiment. Thereby, the selected MR is precisely blended with a certain pressure ratio and it is completely mixed with a magnetic stirrer (mixer). This mixer is illustrated in Figure 4 (a) and this mixer with MR buffer is shown in Figure 4 (b). The accuracy of blending method is confirmed by standard gas and gas chromatography (Agilent 7890B gas chromatograph). The errors between the standard gas analysis results and those of the developed MRs are estimated smaller than 2%. Therefore, this mixing method has good accuracy to provide a desired MR composition.

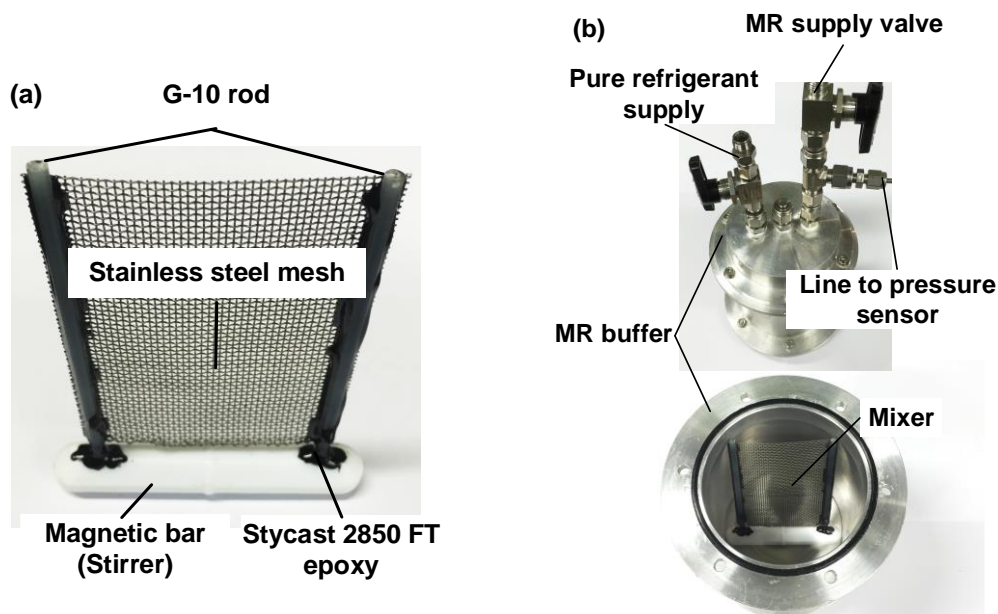


Figure 4. Photograph of (a) mixer and (b) MR buffer with mixer

2.2 Experimental procedure and condition

The experimental procedure of the freezing point measurement is as follows.

- 1) Evacuate MR buffer and MR test tube by vacuum pump approximately $6 \times 10^{-4} \text{ Pa}$ (5 mTorr).
- 2) Close the MR supply valve. MR test tube holds the vacuum condition until target MR is prepared.
- 3) Blend the target MR in the MR buffer with mixer.

- 4) Close the vacuum valve and charge the target MR into the test tube.
- 5) Feed LN₂ in the LN₂ container. Target MR liquefy and freeze by LN₂.
- 6) Stop LN₂ supply if LN₂ level is reached sufficient height (i.e. above the solidified MR position).
- 7) Record the temperature of the whole solidified MR until it melts completely.
- 8) Perform the same experiment to achieve the reliability of experimental results (2-3 times).

Table 1. Properties of selected refrigerants

Refrigerant	Triple point temperature [K]	Critical point temperature [K]
Ar	83.8	150.7
R14	89.5	227.5
R23	118.0	229.3
R218	125.5	345.0

Table 1 shows the temperature of triple and critical points of the selected refrigerants[9]. As mentioned in the previous research, the freezing point of mixture of Ar, R14, R23 and R218 is identified approximately as 116 K for certain composition [8]. This research speculated that the R23 is the main component to freeze the selected quaternary MR (Ar, R14, R23 and R218). Furthermore, the freezing point of quaternary MR without R23 (i.e. ternary MR) has been measured as 97 K, in the previous research. This freezing temperature is unusually low compared to those of R23 including cases. Therefore, the target MR in this paper, has been selected Ar, R14 and R218 to verify the freezing point depression of the mixture. Table 2 represents the whole experimental points of the selected MR composition. Each test MR contains the pure refrigerant mole fraction between 10% and 80%. Variation of the mole fraction for each pure component is set as 10%. Accordingly, 36 MR sets are selected for the measurement of the freezing point.

Table 2. Experiment composition of selected MR (Ar, R14 and R218)

Mole fraction Exp. Number	Ar (-)	R14 (-)	R218 (-)
1	0.1	0.1	0.8
2	0.1	0.2	0.7
3	0.1	0.3	0.6
⋮	⋮	⋮	⋮
34	0.7	0.1	0.2
35	0.7	0.2	0.1
36	0.8	0.1	0.1

3. Experimental results and discussion

3.1 Experimental results

Figure 5 (a) and (b) show the sample images of the freezing point measurement. Figure 5 (a) illustrates the frozen state of the tested MR (Ar:R14:R218 = 0.4:0.1:0.5), and Figure 5 (b) presents the melting point of the tested MR. Each recording result is precisely identified the freezing image by frame scale.

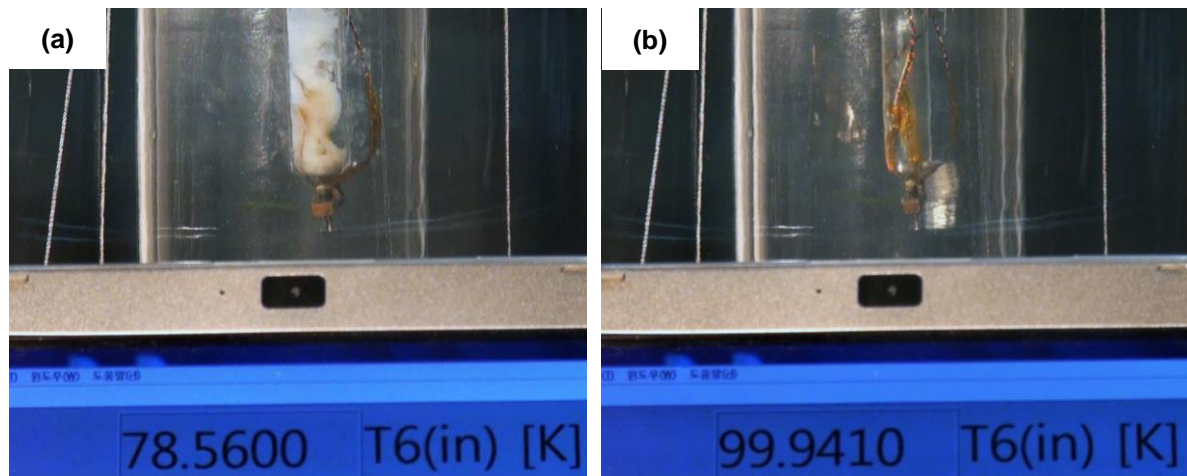


Figure 5. Recorded image of the experimental result for Ar:R14:R218 = 0.4:0.1:0.4 (a) frozen state with LN₂ and (b) melting point

Figure 6 displays the measurement results of the whole molar composition of MR. Each vertex of the Figure 6 is the freezing point of pure component, and dots are the measurement points for each selected MR. MR set which has R218 fraction higher than 0.5, was measured the freezing temperature higher than 100 K. These results are obvious due to the high freezing point of pure R218. However, high composition of R14 cases show very different tendencies. MR sets which have the R14 fraction higher than 0.4, were measured the freezing temperature lower than 77 K. The freezing point of R14 is well known as 89.5 K, however, substantial depression of freezing point for certain composition of MR sets are measured even below that of pure component. Figure 7 (a) presents the unfrozen image of the selected MR (Ar:R14:R218 = 0.2:0.6:0.2) immersed in LN₂ with the test tube. Figure 7 (b) illustrates the image after LN₂ evaporation for same case. Interestingly, MR cases containing high Ar mole fraction

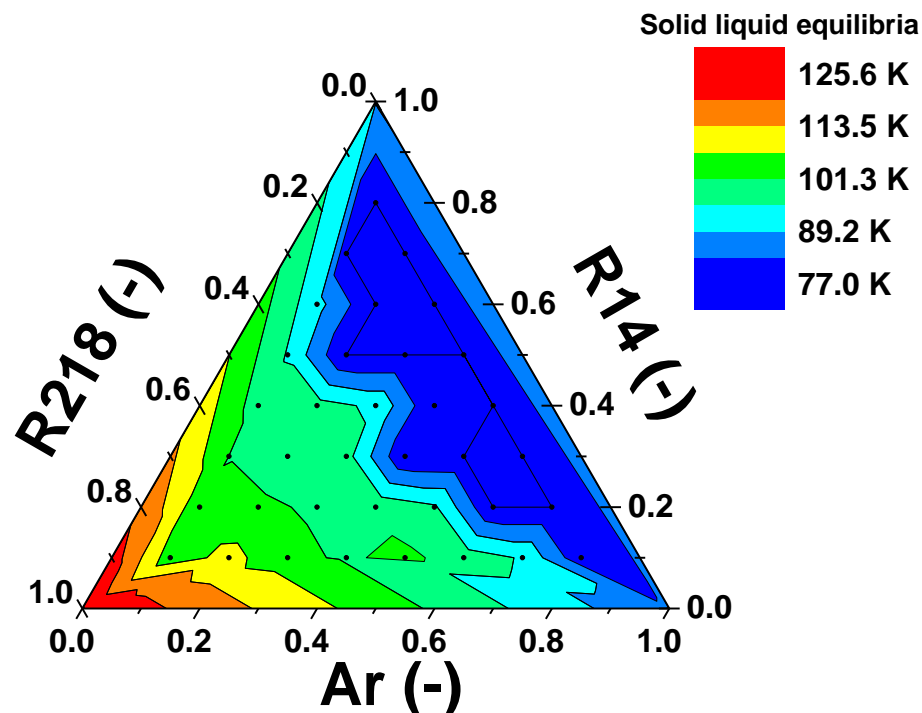


Figure 6. Freezing point measurement results of ternary MR (Ar, R14 and R218)

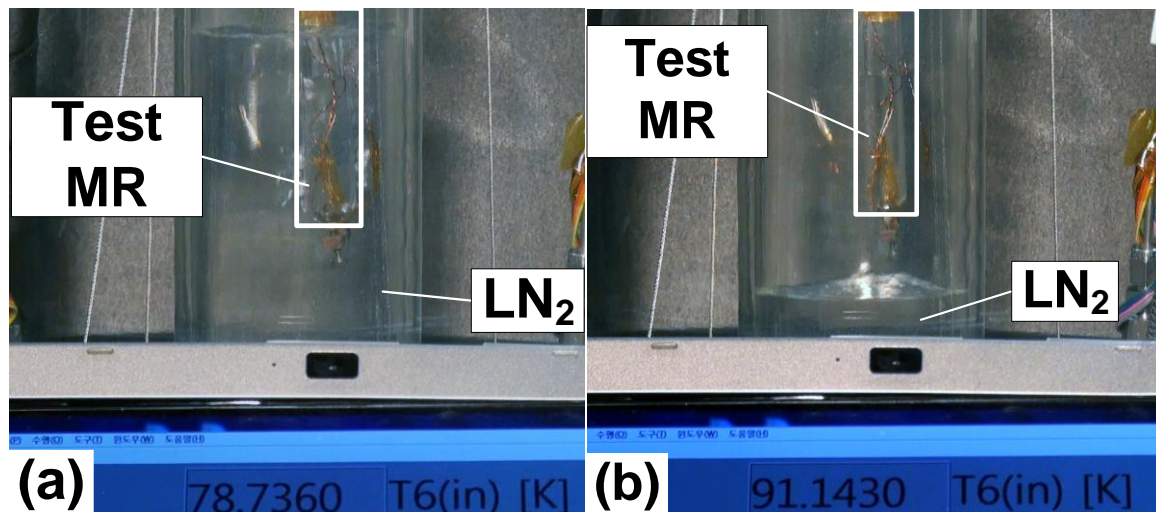


Figure 7. Recorded image of the experimental result for Ar:R14:R218 = 0.2:0.6:0.2 (a) unfrozen state in LN₂ condition and (b) after the LN₂ evaporation for same MR case

were obtained relatively high freezing point compared to those of high R14 mole fraction cases. Pure Ar has slightly lower freezing temperature than that of pure R14. However, the freezing point depression characteristic in the MR is reversed. This result is due to the solubility characteristics.

3.2 Discussion of the experimental result

The freezing point depression of the mixture may interpreted as the solubility of the solid in the solvent or a liquid [10]. In these ternary MR (Ar, R14 and R218) cases, the solid refrigerant is mainly formed with R218, which has the highest freezing temperature. The solid phase of R218 has two possibilities to dissolve into liquid state, which is R14 or Ar. As mentioned before, the freezing point depression of MRs were intensively obtained for the R14 rich sets compared to those of Ar rich sets. For example, the freezing point of R14 rich MR (Ar:R14:R218 = 0.2:0.5:0.3) turns out to be below 77 K, while, that of Ar rich MR (Ar:R14:R218 = 0.5:0.2:0.3) is 96.1 K. These typical results prove that the solubility characteristic between R14 and R218 is stronger than that of Ar and R218. In other words, the solid state of R218 is easily dissolved into the liquid state of R14 rather than that of Ar. This characteristic also could be found and illustrated in Figure 8 (a) and (b). Figure 8 (a) represents the experimental results of freezing point measurement for the same mole fraction of Ar and R218, and Figure 8 (b) displays those

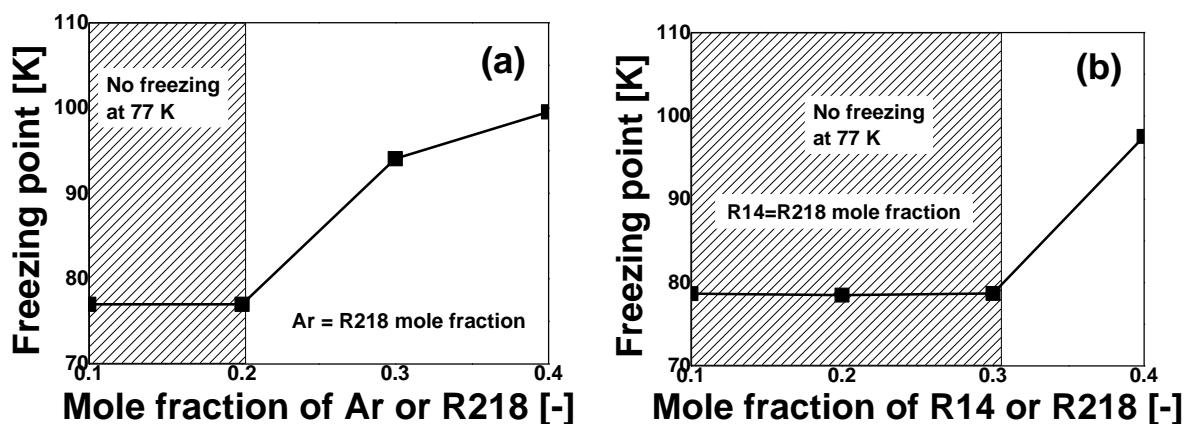


Figure 8. Freezing point measurement results for selected MR (a) same mole fraction between Ar and R218 and (b) same mole fraction between R14 and R218

of same mole fraction between R14 and R218.

Furthermore, there is a remarkable freezing point depression for certain MR set. The selected MR sets which contain molar ratio higher than 2 between R14 and R218, show the freezing temperatures below 77 K. Thus, the molar ratio between R14 and R218 plays the most critical role to decrease the freezing point. If this molar ratio is maintained more than 2 in ternary MR for any Ar fraction, its freezing point becomes lower than 77 K. This result can be inferred from the eutectic formation of R14 and R218. If an MR technology is applied to reach temperature below 77 K in a non-flammable MR J-T refrigerator, the MR in the case of Ar, R14 and R218, must contain the higher molar ratio than 2 between R14 and R218.

4. Conclusion

In this study, the freezing points of ternary MR sets, which contain Ar, R14 and R218, were investigated by visualized apparatus. The freezing point depression is clearly noticeable due to mixing phenomena in composition to that of pure R218. Especially, this depression strongly appeared with MR which has R14 rich composition. The molar ratio between R14 and R218 is a key parameter to drop the freezing temperature. If this molar ratio is higher than 2, freezing state of MR does not appear even in LN₂ environment (77 K). The MR compositions investigated in this paper can provide valuable information for selecting the proper working fluid of non-flammable cryogenic MR J-T refrigerator below 100 K.

Acknowledgement

This work was supported by the Power Generation & Electricity Delivery of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 2014101050231B).

5. Reference

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