Investigation of Visualized Solid-Liquid Phase Equilibria for Pure and Mixed Refrigerants

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ABSTRACT

A pure-refrigerant Joule-Thomson (J-T) refrigerator has constraints on cooling capacity and operating temperature defined by the thermodynamic characteristics of the chosen refrigerant. The use of a mixed refrigerant (MR), which can efficiently overcome the limitations of a pure coolant, has attracted people's attention due to the high performance of its J-T effect and the variety of cooling temperatures available. Although MR have earned general acceptability for various J-T refrigerator applications, they have a significant operating challenge: that of clogging in the J-T expansion part, which is caused by a freezing problem. In this paper, the freezing points, i.e. solid-liquid phase equilibria of various MR have been examined using a visualization apparatus and analyzed by regular solution theory in the temperature range from 89 K to 182 K.

The visualization experimental apparatus was developed and tested to observe the freezing point with a camcorder while the temperature was monitored using instrumentation inside the glass test tube. The experimental apparatus consisted of three parts: 1) a cold part cooled using liquid nitrogen (LN_2), 2) a MR test part fabricated with a glass tube, and 3) a helium base part with glass bell jar to prevent frosting on the glass apparatus. The apparatus detected the freezing points of the selected pure refrigerants (R14, R218, R125 and N_2O) and a binary mixture of N_2O / R125 with a maximum error of 0.33% and 1.4%, respectively. Also, a multiple component MR made up of Ar, R14, R23, and R218 with various compositions was tested to search for the mole fraction which has the lowest freezing temperature.

INTRODUCTION

Recently, cryogenic refrigeration has been recognized as an important enabling technology in many areas such as natural gas liquefaction, sensor cooling, and superconducting applications. The Joule-Thomson (J-T) refrigeration cycle is one of the most fundamental refrigeration cycles for industrial applications because of its ease of fabrication, adjustability of cooling capacity, and high reliability due to no moving parts.[1,2] However, the low efficiency of a pure-refrigerant J-T refrigeration cycle—due to an irreversible process on the expansion valve—is a clear disadvantage.[3] In addition, the high pressure ratio, which is related to a specific refrigerant's characteristics, is also a challenge to achieve for a pure-refrigerant cryogenic J-T refrigerator. To make up for these shortcomings, mixed refrigerant (MR) J-T refrigerators have been developed.

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The MR J-T refrigeration cycle typically has high and low working pressure conditions of 2,000-3,000 kPa and 100-400 kPa, respectively.[1] Also, a wide range of cooling temperatures has been achieved using different compositions of working fluids.[4] The specific composition of the mixed refrigerant is commonly determined to maximize the efficiency and boost the potential refrigeration power with various freezing and boiling temperatures.[5] Although a well-designed MR can achieve high efficiency in the J-T refrigeration cycle, the component with the highest freezing temperature may clog or block the J-T expansion part, especially in the case of non-flammable mixed refrigerants (NF MR). Therefore, the freezing point of the MR at low pressure needs to be predicted and considered before finalization of a MR J-T refrigeration cycle.

The freezing points of pure refrigerants and binary MRs have generally been established by solid-liquid phase equilibria in past research. Nicola et al. investigated the freezing point of numerous binary mixtures using a closed vessel.[6,7,8] They applied the Rossini-method corrections to determine the freezing point from the experimental results. This method analyzed the solid-liquid equilibria using the time-temperature curve for the target MR. On the other hand, the Universal Functional-group Activity Coefficients (UNIFAC) method or the Universal Quasi-chemical Activity Coefficients (UNIQUAC) method are applied to calculate the solid liquid equilibria (SLE) of organic compounds and hydrocarbon mixtures.[9,10]

The above methods are well established to characterize the freezing point of binary mixtures or pure refrigerants. However, an SLE visualization apparatus has not yet been developed for visual investigation of the freezing phenomena under cryogenic conditions. Furthermore, there is little research that investigates the freezing temperature of mixtures containing more than three components.

In the research effort described in this paper, a visualization apparatus was fabricated to explore the solid-liquid phase equilibria of various MR candidates and was tested with pure refrigerants, binary MRs, and selected multicomponent MRs. To improve the accuracy of the experiments, video recording was conducted and interpreted frame by frame. The tested freezing point was compared with the analytical results calculated to verify the accuracy of the experimental procedure. Subsequently, numerous sets of MR (Ar, R14, R23, R218) were examined to obtain the lowest temperature without solidification (i.e. SLE). This information on SLE should be valuable for those designing an MR J-T refrigeration system with the described MR sets.

SOLID-LIQUID EQUILIBRIA ESTIMATION REGULAR SOLUTION THEORY

The SLE for a mixture can be estimated by numerous calculation methods. Commonly, the solubility characteristic of solids in liquids is applied to estimate the SLE. The solubility of a solid in a liquid is determined not only by the intermolecular forces between the solute and the solvent, but also by the melting point and the enthalpy of fusion of the solute.[11] In a binary solution or a binary mixture, the solubility of a solid x_2 at temperature T is given by,

$$\ln \gamma_2 x_2 = -\frac{\Delta h_f}{RT}\left(1-\frac{T}{T_{tp}}\right)+\frac{\Delta C_P}{R}\left(\frac{T_{tp}-T}{T}\right)-\frac{\Delta C_P}{R}\ln\frac{T_{tp}}{T} \quad (1)$$

where, γ_2 is the activity coefficient for solute, Δh_f is the enthalpy of fusion of the solute at the triple point temperature T_{tp}, and ΔC_P is the molar heat capacity difference between the subcooled liquid solute and the solid solute. To simplify this equation, the normal melting temperature T_m can be substituted for the triple-point temperature T_{tp}. Also, the terms related to molar heat capacity are not as important as the other terms, therefore a simplified form of the equation is[11],

$$\ln \gamma_2 x_2 = -\frac{\Delta h_f}{RT}\left(1-\frac{T}{T_m}\right) \quad (2)$$

In the ideal solution, the activity coefficient γ_2 is unity; however, for a non-ideal solution it may be significantly different from unity. Especially for the MR, most mixtures are nonpolar systems.

Thus, the activity coefficient can be calculated by regular solution theory given by Equations (3) and (4).[11]

$$RT\ln\gamma_1 = V_1^L\Phi_2^2\left[\left(\delta_1-\delta_2\right)^2+2l_{12}\delta_1\delta_2\right] \tag{3}$$

$$RT\ln\gamma_1 = V_1^L\Phi_2^2\left[\left(\delta_1-\delta_2\right)^2+2l_{12}\delta_1\delta_2\right] \tag{4}$$

where V_i^L is the liquid molar volume of pure liquid i at temperature T, and l_{12} is the binary parameter, which is difficult to obtain in a theoretical way. The value of l_{12}, though not predictable, is however, nearly zero. Therefore, the regular solution theory without binary parameter is simplified as follows (i.e. Scatchard-Hildebrand equation).

$$RT\ln\gamma_j = V_j^L\Phi_i^2\left(\delta_j-\delta_i\right)^2 \tag{5}$$

where Φ_i is the volume fraction of each component, and δ_i is the solubility parameter which is given by Equations (6) and (7), respectively.[11]

$$\Phi_i = \frac{x_iV_i^L}{\sum x_kV_k^L} \tag{6}$$

$$\delta_i = \sqrt{\frac{\Delta h_{fg,i}-RT}{V_i^L}} \tag{7}$$

The liquid molar volume V_i^L and solubility parameter δ_i should be estimated depending on the temperature to calculate the regular solution theory. These terms are calculated by REFPROP[12] and fitted with a parabolic function. The maximum error of the fitting formulas for molar volume is less than 0.5% in the temperature region between 80 K and 300 K.[12] The calculation errors for the solubility parameter are smaller than 1.5% within the same temperature range. The estimated molar volume-temperature diagram and solubility parameter-temperature diagram for various refrigerants are shown in Figures 1(a) and 1(b), respectively.

The solubilities for mixtures with more than three components can be calculated by averaging the solubility parameters. The activity coefficient for a multicomponent mixture is calculated as follows[11],

$$RT\ln\gamma_k = V_k^L\left(\delta_k-\bar{\delta}\right)^2 \tag{8}$$

where, $\bar{\delta}$ is the averaged of solubility parameter which is obtained by Equation (9).

$$\bar{\delta} = \sum_i \Phi_i\delta_i \tag{9}$$

To confirm the adequacy of the measurement technique of our experimental apparatus, the

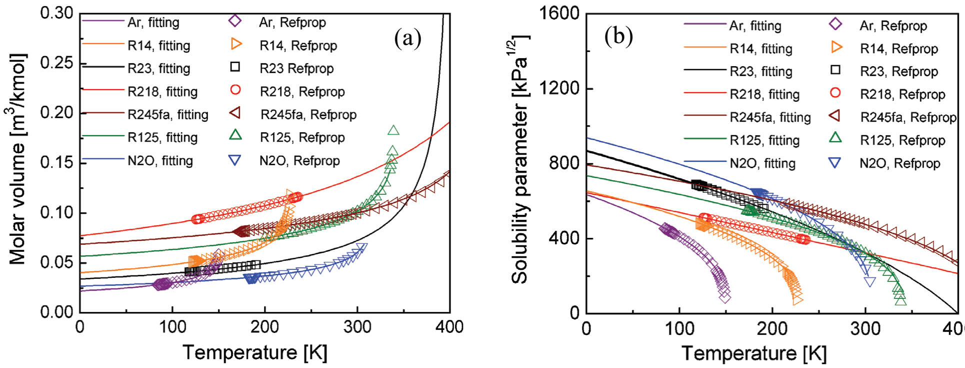

Figure 1. Curve fit of (a) molar volume-temperature, and (b) solubility parameter-temperature for various refrigerants applied in this research

Table 1. Triple point temperature for pure refrigerants

Refrigerants	T_{tp} [K]
R14	89.5
R23	118.0
R218	125.4
R245fa	171.1
R125	172.5
Nitrous oxide (N_2O)	182.3

aforementioned estimation methods will be applied for checking the experimental results.

Test Refrigerant Selection

Table 1 displays the target pure refrigerants used in this investigation. Non-flammable pure refrigerants were selected to confirm the accuracy of the measurement method of the experimental apparatus over the temperature range from 89 K to 182 K. These refrigerants were also utilized in the binary mixed refrigerants and multicomponent mixtures.

From previous research, it is known that the freezing temperatures of a few sets of binary mixed refrigerants are well predicted with the ideal solution (whose the activity coefficient is equal to one).[6] For example, research results for the R125 + N_2O binary mixture reveal that this mixture obeys the ideal solution. In this paper, the R125 + N_2O binary mixed refrigerant is therefore used to verify the accuracy of the experimental procedures for MRs. In contrast, the R245fa + R125 binary MR is utilized in this experimental apparatus to find the acceptance of the regular solution theory.

For multicomponent MR, various mixtures of Ar, R14, R23, R218 were explored in this research. This set of MR (Ar, R14, R23 and R218) is one of the most suitable combinations for a cryogenic MR J-T refrigerator with the aim of cooling below 120 K—such as natural gas liquefaction. For reference, the freezing point of Ar:R14:R23:R218 = 0.17:0.30:0.20:0.33 is obtained as 116 K from previous research.[13] Various compositions of this MR were analyzed in this research to further determine the multicomponent mixture with the lowest achievable freezing point.

EXPERIMENT

Experimental Apparatus

A visualization experimental setup was developed and is introduced in this paper. Figure 2 shows a schematic of the experimental apparatus. A photograph of the whole experimental apparatus is shown in Figure 3(a), and the test part of the experimental apparatus is shown in Figure 3(b).

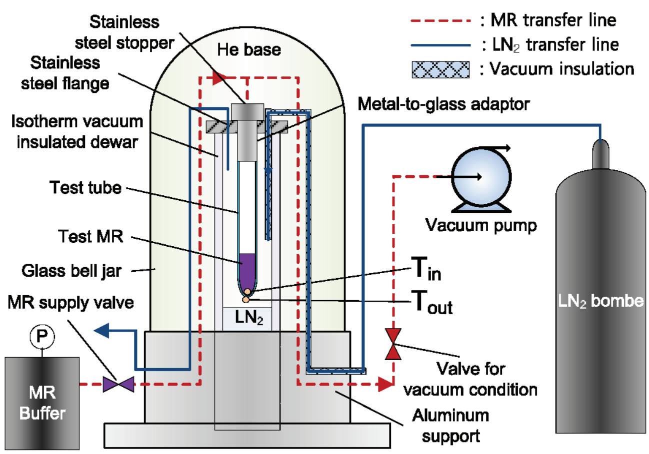

Figure 2. Schematic diagram of visualized experimental apparatus for freezing point detection

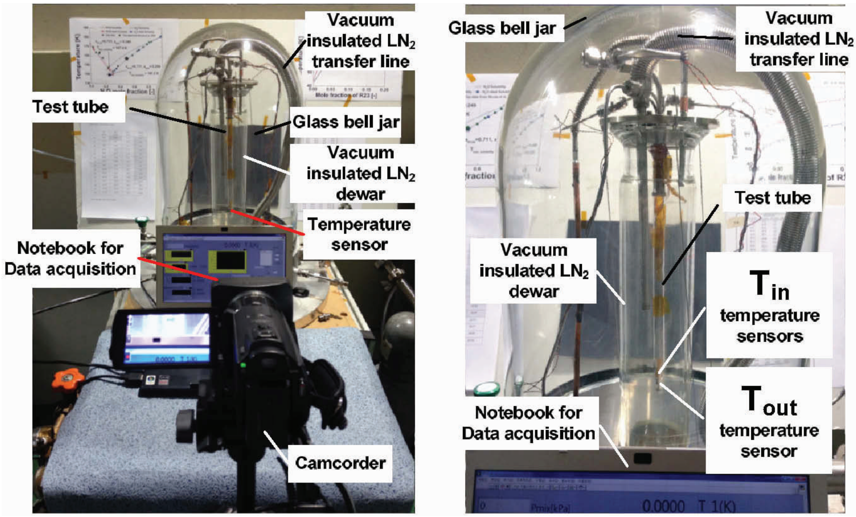

Figure 3. Photograph of experimental apparatus (a) complete view and (b) test part

The experimental apparatus contains three parts: 1) the helium base part, 2) the liquid nitrogen (LN_2) container, and 3) the MR test tube.

The helium base part is fabricated with a glass bell jar that is positioned above the machined aluminum support. Helium gas is charged to approximately 130 kPa during the experiment to prevent frost formation at the surface of the LN_2 container. The LN_2 container is composed of a double-layered vacuum insulation glass dewar made by KGW-Isotherm. The surface of the glass dewar is completely transparent without silver coating because transparency of the test section is required. The top of the glass dewar is covered by a stainless steel plate that holds the LN_2 supply line, test tube, and the LN_2 vent line. The test tube of the MR is attached by soldering with a glass-to-metal adapter. The top side of the test tube is sealed with a stainless steel stopper and indium wire seal.

The MR supply line, MR vent line, and temperature sensor feedthrough line are made with 1/8-inch stainless steel tube. These lines are brazed to the stainless steel stopper to construct the sealing inside of the test tube. Two Lakeshore silicon-diode DT-670-SD temperature sensors are applied to measure the temperature of the inside and the outside of the test tube. In particular, the two temperature sensors are positioned inside of the test tube to enhance the accuracy of the measurement. A Honeywell model FP2000 pressure transducer with an operating range of 75 psi is used at the inlet of the test tube to determine the precise thermodynamic state of the refrigerant. The accuracy of the temperature sensor is ±0.02 K, and that of the pressure transducer is ± 0.5 kPa.

The entire suite of measurement instrumentation is connected to a data acquisition system (National Instrument NI-USB-6343) to collect the experimental results. A SONY camcorder HXR-MC50N is used to visually capture an image of the freezing and melting phenomena. This allows the SLE of the various refrigerants and MRs to be analyzed by both the recorded image and the temperature-pressure data.

To conveniently demonstrate the SLE of the refrigerants, LN_2 was selected as the coolant to freeze them. The experimental procedure of the visualization apparatus is as follows:

A. Evacuate the test tube and MR buffer until 6×10^{-4} kPa (5 mTorr) by vacuum pump.
B. Close MR supply valve and prepare the target MR with the required molar composition.
C. Charge the target MR into the test tube.
D. Feed LN_2 into the LN_2 container.
E. Freeze the target MR.
F. Stop feeding LN_2 when the level of LN_2 is reached to the top of the frozen MR in the test tube.
G. Record the temperature of the whole solidified MR until it melts completely.
H. Repeat the same experiment to establish the reliability of the experimental results.

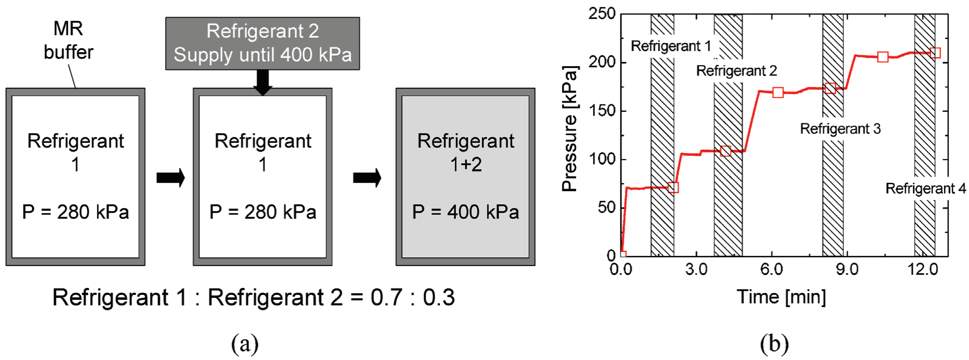

Figure 4. Diagram for MR charging method: (a) schematics, and (b) Pressure-time diagram of actual charging condition

A MR buffer was utilized to produce the exact composition of MR in the experiments. As stated above, the tested MR obeys the ideal gas equation at room temperature; therefore, the composition of MR is simply proportional to the pressure ratio. In this manner, the composition of MR is determined proportionally to the pressure ratio of pure refrigerant to total pressure of MR buffer. Figure 4(a) displays a schematic of the mixing method for the target MR, and Figure 4(b) shows the pressure-time diagram obtained under experimental conditions for an actual four-component MR.

Experimental Results for Pure Refrigerant and Binary MR

As mentioned above, pure refrigerants and binary MR were tested in the experiment to verify the accuracy of experimental method. Table 2 represents the experimental results of pure refrigerants and binary MRs. The measurement error with a pure refrigerant was less than 0.6% in this experimental apparatus. Furthermore, the maximum experimental error was 1.4% for a binary MR.

The experimental error for the R125+N_2O binary MR was obtained by comparing it to the calculation results for an ideal solution. By contrast, that of the R245fa + R125 binary MR was compared with the calculation results for a regular solution. Figures 5(a) and (b) display comparisons of the experimental results and the calculation results for R125+N_2O and R245fa + R125, respectively. The experimental results for the R125 + N_2O binary MR are well matched with the other literature in the error of 1.4%.[6] Similarly, the experimental results for the R245fa + R125 binary MR have errors less than 1.32% when compared to the calculation results for a regular solution. Thus, the visualization experimental procedure in this paper is considered appropriate for measuring the freezing point of both a pure refrigerant and a MR.

Table 2. Experimental results of pure refrigerants and binary mixed refrigerants

Refrigerants	From literature [K]	Experimental result [K]	Error [%]
R14	89.5	89.6	0.1
R23	118.0	118.0	0.05
R125	172.5	172.0	0.33
R245fa	171.05	170.0	0.64
N_2O	182.3	182.3	0.13
R125+N_2O	141.5 – 182.3 (Varied due to mole fraction)	143.6 – 182.3 (Varied due to mole fraction)	1.40 (Ideal)
R245fa+R125	144.3 – 172.5 (Varied due to mole fraction)	145.7 – 172.0 (Varied due to mole fraction)	1.32 (Regular)

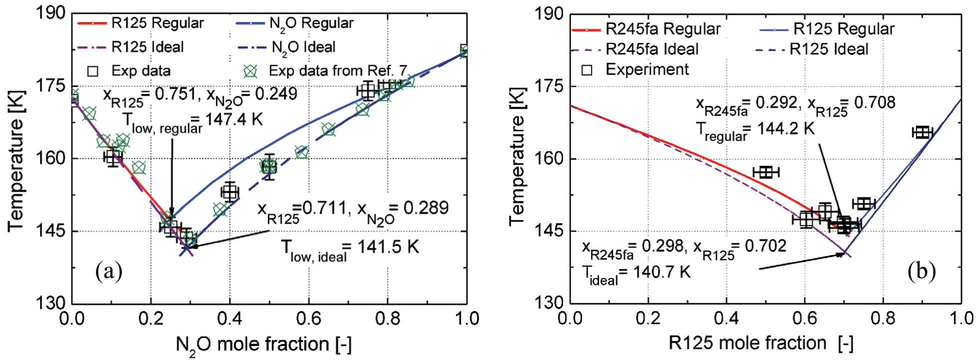

Figure 5. Comparisons of experimental results and calculation results for (a) R125+N_2O binary MR, and (b) R245fa+R125 binary MR

Experimental Results for Multi-Component MR

The measurement accuracy of the SLE by the visualization experimental apparatus was verified by the preliminary experimental results. The next step was to measure the SLE for the four-component MR set of Ar, R14, R23, and R218 using the same experimental apparatus. Firstly, the MR composition of Ar:R14:R23:R218 = 0.17:0.30:0.20:0.33 was selected to compare with measurements in previous research.[13] The calculation result using regular solution theory for this composition is shown in Table 3. The results are expressed as the maximum mole fraction of the target MR of each component that can exist in the liquid state. The shaded part in Table 3 denotes that the refrigerant should be solidified at the corresponding temperature. According to the calculation results, the liquid-only temperature for the target MR may be limited by the component of R23. Consequently, reducing the mole fraction of R23 should be an effective method to lower the temperature of SLE. Figure 6 shows the calculation result with the same ratio for the rest of the MR while the molar composition of R23 is varied. The calculation results using regular solution theory suggest that the temperature of SLE for the target MR could be decreased up to 46 K in the absence of R23.

Additional experiments were conducted using several sets of molar composition. The tested MR had a variation scale of 0.025 mole fraction of R23. For example, the MR set which had the second largest composition of R23 is composed of the mole fraction of Ar:R14:R23:R218 = 0.17:0.30:0.175:0.33. The aforementioned mole fraction is converted as Ar:R14:R23:R218 = 0.17:0.31:0.18:0.34. Similarly, nine sets of MR which had these variations of R23 fraction were measured for SLE using the visualization experimental apparatus.

Table 3. Calculation result of regular solution theory for Ar:R14:R23:R218 = 0.17:0.30:0.20:0.33

Temperature [K] \ Mole fraction [%]	Ar [17%]	R14 [30%]	R23 [20%]	R218 [33%]
90	63.12	95.76	5.79	82.10
95	65.30	100.66	8.38	85.38
100	66.40	105.29	11.67	88.41
105	66.33	109.65	15.71	91.17
106	66.17	110.50	16.62	91.69
107	65.95	111.33	17.55	92.21
108	65.68	112.16	18.52	92.71
109	65.35	112.97	19.51	93.20
110	64.97	113.78	20.54	93.68
115	62.20	117.71	26.16	95.92
120	57.88	121.46	32.53	97.87

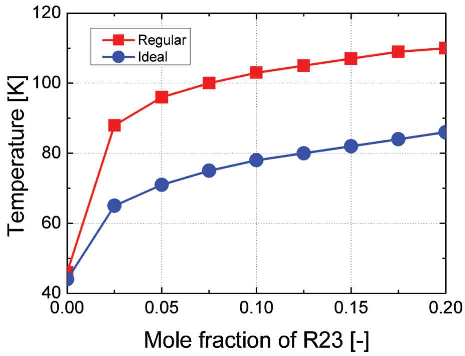

Figure 6. Calculation results of regular solution and ideal solution for various mole fraction of R23

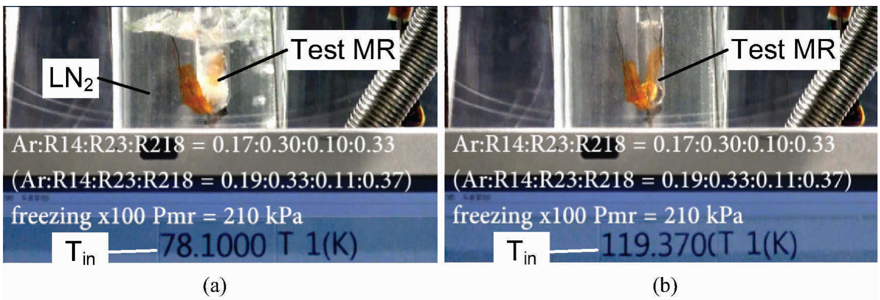

Figure 7. Recorded image of the experiment with Ar:R14:R23:R218 = 0.17:0.30:0.10:0.33 (Ar:R14:R23:R218 = 0.19:0.33:0.11:0.37) (a) solid (freezing) state and (b) liquid (melting) state

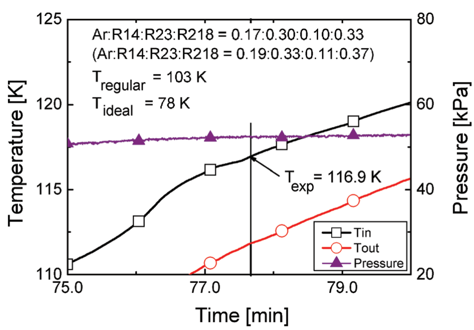

Figure 8. Measurement data of the experiment for Ar:R14:R23:R218 = 0.17:0.30:0.10:0.33

A representative experimental image of the MR (Ar:R14:R23:R218 = 0.17:0.30:0.10:0.33) is presented in Figure 7. Figures 7(a) and (b) show the recorded image during the experiments in solid state and liquid state, respectively. The experimental temperature-time data are shown in Figure 8. The temperature history shows a slight gradient change, although this small transition is difficult to notice. This non-separable temperature transition occurs by the temperature glide of the two-phase state of the MR. Thus, the melting temperature is identified by the recorded image when the whole frozen MR changed into liquid phase.

Figure 9 provides a comparison of the experimental results and the analytical calculation results. The measurement errors of the experiment are also depicted with the experimental results. The maximum error of mole fraction in the experimental results is 0.0025; this is determined by the pressure transducer error and the maximum error of temperature measurement (0.5 K) from the

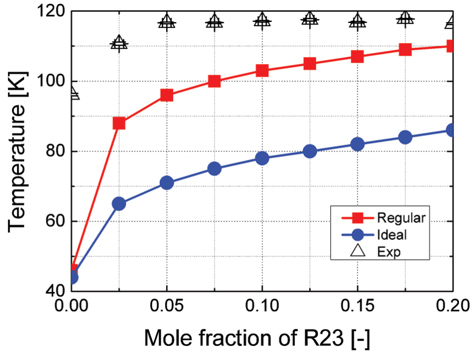

Figure 9. Comparison of experimental results and calculation results of regular solution and ideal solution

variation of temperature sensors inside of the test tube. Both analytical results (regular and ideal solution) display the gradual reduction of temperature of the SLE when the R23 mole fraction is decreased to 0.05. However, the experimental results demonstrate little change by R23 fraction when the molar composition of R23 is larger than 0.05. Moreover, the calculation result by the regular solution theory predicts 89 K, whereas the experimental result indicates 110 K when the mole fraction of R23 is 0.025. Furthermore, the temperature of SLE in the case of the MR that has no R23 composition shows a large gap between the experimental result (96 K) and the result of regular solution theory (46 K).

The largest discrepancy between the experimental results and the analytical calculations appears when the R23 composition is small. These errors may occur due to the absence of accurate binary parameters for each component. If the solubility parameter δ is similar between those components, then the contribution of the binary parameter l_{12} is important in the SLE.[11] Therefore, in the case of the Ar, R14, R23, R218 mixture, the six binary parameters in the regular solution theory should be investigated to predict a more accurate freezing temperature.

CONCLUSIONS

A visualization experimental apparatus was developed to estimate the SLE of the desired target MR. This apparatus successfully satisfied the prediction criteria with a maximum error of 0.4% for pure refrigerants when compared with literature, and a maximum error 1.4% for binary MRs in comparison to the analytical models. The MR set of Ar, R14, R23, and R218 was examined in this experimental apparatus to verify the lowest temperature without freezing problems for a cryogenic MR J-T refrigerator. The tested MR set indicates the lowest temperature of SLE as 96 K without R23, while the SLE temperature is approximately 116 K with more than 5% of R23. According to the measurement results in this paper, a MR J-T refrigerator which uses this set of MR should operate at temperatures above 120 K.

ACKNOWLEDGMENT

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