MEASUREMENTS OF VAPOR-LIQUID EQUILIBRIUM PROPERTIES FOR THE BINARY REFRIGERANT, CARBON DIOXIDE + DIMETHYL ETHER

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ABSTRACT

Carbon dioxide is widely used as environmentally friendly refrigerant. In Japan, its major applications are for hot water supply systems. Therefore, some new blends of carbon dioxide with lower condensing pressure are being considered. A binary mixture of carbon dioxide and dimethyl ether is one of the candidates for such purpose. Some retrofit experiments or performance examinations with numerical models have already been reported, however, there are few experimental studies for its fundamental thermophysical properties. In the present study, therefore, vapor-liquid equilibrium (VLE) of the binary refrigerant carbon dioxide + dimethyl ether are presented. Bubble-point/dew-point pressures and composition are measured by means of a newly developed VLE apparatus. The apparatus consists of a thermostated equilibrium cell, high-pressure syringes and gas-chromatograph. The measurement uncertainty of the present apparatus is 0.007 K for temperature, 0.01% F.S. for pressure, and 0.30 mol% for composition, respectively. The present apparatus covers a wide range of temperature from 240 K to 380 K and pressures up to 7 MPa, while it was designed as small as possible, a rapid measurement was realized. As a preliminary result, \( P T_{xy} \) data along the saturation boundary at 288.1 K are presented in this paper.

1. INTRODUCTION

Carbon dioxide (CO\(_2\)) is one of the promising alternative refrigerant candidate since its ODP is zero and the GWP=1. Since the operating pressure range of the heat-pump cycle using carbon dioxide is relatively high, there is the disadvantage that the size of the system becomes larger than those with most of other working fluids. It is particularly a drawback for mobile air-conditioner applications, however, some stationary systems are still suitable for this working fluid. In 2001, a heat pump water heater using carbon dioxide as the working fluid was developed and released in Japan. As the total primary energy efficiency of the system is higher than boilers, 2 millions sales were recorded by the end of 2009.

In order to improve the performance of the CO\(_2\) based heat-pump water heater, there is the possibility to use some blended working fluids. Among several components, dimethyl ether (DME) is one of the promising candidate. By mixing DME with CO\(_2\), the operating pressure is lowered but the flammability remains low.

A review has been conducted on experimental and numerical research for the binary mixture, CO\(_2\)+DME. Koyama et al. (2006) reported the performance of heat pump system with CO\(_2\)+DME (90 mass% of CO\(_2\)). Afroz et al. (2008) reported a heat-transfer coefficient and the pressure drop of the CO\(_2\)+DME (39 mass% and 21 mass% of CO\(_2\)).

The cycle simulation results were also reported by Onaka et al. (2009). They reported that the COP improves when mixing 10 mass% of DME.

Considering the thermodynamic property for the present binary mixture, there exist limited number of studies except for vapor-liquid equilibrium (VLE) properties by Tsang et al. (1981), Jonasson et al. (1995) and Laursen et al. (2002). As for the thermodynamic property calculation model, REFPROP can predict the binary thermodynamic properties but it is not based on these experimental data. Akasaka (2009) reported a simple multi-fluid mixture model for a set of binary systems including
CO₂. He obtained three mixture parameters to calculate the thermodynamic property of the binary CO₂ + DME.

For further detailed investigation, a comprehensive approach to research the mixture thermodynamic property is desired for the present binary blend. Single-phase properties such as PVTx properties are needed to develop more accurate mixture thermodynamic model. On the other hand, extensive measurement of VLE properties is also important, since the existing literature data is relatively old or limited in measured temperatures.

The author has planned to measure a set of mixture thermodynamic properties such as VLE properties, PVTx properties and other caloric and transport properties for CO₂ + DME. As a first step, in the present study, the VLE property measurements were conducted. To cover a wider temperature range rapidly, VLE property measurement system was newly designed and developed. It covers the temperatures from (240 to 380) K, (0.3 to 7) MPa. Preliminary results for CO₂ + DME is presented in this paper. The experimental results were also compared with existing thermodynamic property models to discuss their reproducibility in VLE properties.

2. EXPERIMENTAL

![Diagram of VLE apparatus](image)

**Figure 1.** Cross section of the VLE apparatus. AR: transparent acrylic rod for meniscus observation, CS: copper sheath for SPRT, EC: equilibrium cell, SPRT: standard platinum resistance thermometer, HS: high-pressure stainless syringe, LA: linear actuators for HS, PT: pressure transducer, TV: three-way-valves, TI: thermal insulator, VA: actuators for TV, VC: vacuum pump.

For refrigerant VLE property measurements, a circulation type apparatus was developed and used for many years. (Shimawaki, 2002, 2003, Kayukawa, 2005, Akasaka, 2007, Tanaka, 2009) The performance of the apparatus was excellent, however, covered temperature range from 260 K to 330 K was not enough to satisfy the entire range of the refrigeration cycle.

In the present study, therefore, a compact-type VLE property measurement system was newly developed to cover wider temperature range. The measurement principle is basically the same but the
magnetic pumps were replaced with the high-pressure stainless-steel syringes to circulate the vapor/liquid phases. The cross section of the apparatus is shown in figure 1. Mixture refrigerant sample was charged in an equilibrium cell with sapphire glass window (Taiatsu Glass, Co.). The size of the inner volume of the cell is 45 cc, 23 mm diameter and 100 mm length. Meniscus of the mixture sample can be observed by means of a digital camera. An acrylic solid cylinder was placed between the sapphire glass window and the camera whose end surface was closely fitted to the glass surface in order to prevent a dew condensation at the glass surface when measuring at low temperatures. The mixture sample is stirred by means of a tiny Teflon stirrer bar placed in the center pit of the cell. The stirrer bar is magnetically-rotated. A couple of ports at the top and bottom of the cell lead to the high-pressure syringes of 2 cc. These syringes are alternately reciprocated by a couple of linear-actuators so as to keep the inner volume constant. By repeating these suction/injection processes, the composition of the vapor/liquid phases become uniform in the cell and the syringes.

2.1. Composition measurement
Composition of the vapor/liquid phases at equilibrium state was measured by a gas-chromatograph (Agilent, 6890N). After considerable circulation by the syringes, sample vapor and liquid was respectively sent to the gas-chromatograph by switching the three-way valves between the cell and the syringes. Vapor sample was pushed out from the syringe through the thin PEEK capillary (0.25 mm I.D.) then sent to the gas-sampling valve (switching volume: 0.25 cc) installed in the gas-chromatograph. To avoid the separation of the component while passing the expansion of the sample vapor, switching of the gas-sampling valve was operated a few seconds after the operation of the three-way valve, at that time the capillary flow became constant. Liquid sample was also sent to the gas-chromatograph in which the liquid-sampling valve (switching volume: 1 µL) through the PEEK capillary. For liquid sampling, it is important to keep the sample at liquid-phase, therefore, a back-pressure valve is added after the liquid-sampling valve to keep the pressure at 7 MPa or higher. Without this setup, liquid sample at low temperatures may not be measured correctly since the low-pressure liquid sample will vaporize at the ambient temperature. Similarly, the mixture vapor sampled at the higher temperatures was expanded by the syringe to avoid the condensation along the capillary tube.
The vapor/liquid composition is calculated from area-percent results of the gas-chromatograph, based on the calibration parameters for each pure component. A known composition gas sample was prepared in a stainless-steel bottle of 1.0 L volume by measuring each pure sample mass. The gas sample composition is known to be 2.5×10⁻⁵ of mole fraction or better. When considering the reproducibility, integration uncertainty of the chromatogram, the composition measurement capability of the gas-chromatograph is estimated to be 0.02 mol%. As for overall uncertainty of the composition measurement including the sampling process, it is estimated to be about 0.30 mol%.

2.2. Temperature measurement and control
Equilibrium temperature is controlled by a circulation bath (Julabo, LH40) which covers a wide temperature range from 233 K to 473 K. The equilibrium cell, syringes and three-way-valves are tightly covered with aluminum blocks, in which silicone oil was circulated from the bath. When the heat loss is taken into account, the effective temperature range is from 240 K. Since the aluminum blocks are directly temperature-controlled, it is possible to measure VLE properties rapidly. Usually, the system reaches the completely thermally equilibrium within 30 minutes. The sample temperature is directly measured with a fine standard PRT (Netsushin, NSR-U160). The diameter of the PRT is as small as 1.0 mm, so that it is easy to detect the internal temperature of the high-pressure cell. The PRT is inserted into the cell with a thin copper sheath (2mm O.D., 1.1 mm I.D. and 50 mm long). The temperature fluctuation of the aluminum blocks was detected by another PRT to be not greater than 0.01 K. As a result, equilibrium temperature is stable with very small fluctuation being less than 0.003 K. The standard PRT sensor is calibrated based on ITS-90. The overall temperature measurement uncertainty is 7 mK.
3.3. Pressure measurement

The equilibrium pressure is directly measured by a quartz pressure transducer (Paroscientific, 31K), placed above the aluminum blocks. The transducer was calibrated with a dead-weight piston gauge at the pressure calibration section of the National Metrology Institute of Japan (NMIJ). The uncertainty of pressure measurement is 0.01% full scale (7 MPa).

3. RESULTS

As a preliminary result, a total of 24 sets of $PTxy$ (pressure, temperature, liquid-phase and vapor-phase composition) data were obtained at 288.10 K. For the bubble-point measurements, the mole fraction of CO$_2$ ranges from 0.0085 to 0.9300 where pressure ranges from 0.47 MPa to 4.53 MPa. The dew-point data, the measured mole fraction of CO$_2$ is from 0.060 to 0.989. The present results are illustrated in Figure 2, together with those obtained by Tsang et al. (1981). In Figure 2, the bubble-point and dew-point curves calculated from REFPROP and the mixture model reported by Akasaka (2009) are also included.

![Figure 2](image-url)  
Figure 2. Bubble-point and dew-point pressures for the binary systems, CO$_2$+ DME at 288.1 K. Curves are calculated by the simple multi-fluid model by Akasaka (2009) and REFPROP.
4. DISCUSSION

In the present study, measured VLE properties are compared with existing mixture thermodynamic models for CO2+ DME system. As shown in Figure 2, the present measurements are well reproduced by the mixture model by Akasaka (2009). The calculated AAD (average absolute deviation) is 2.3 % for the bubble-point pressures, where those for the experimental data by Tsang et al. (1981) is 1.5 % since the mixture parameters reported by Akasaka is optimized to their data. It is also noted that the measurement by Tsang et al. (1981) is obtained at 288.2 K which is 0.1 K higher than that of the present measurements.

The dew-point curve by REFPROP does not agree with the experimental data because it is not optimized to this particular binary blends and the default mixing parameters were used. The bubble-point curve by REFPROP agree well despite the use of generalized mixture model.

Considering the available experimental data for the binary system, CO2+ DME, there is lack of data at the temperature range below 273.15 K. Hence the additional VLE data at that temperature range are expected in order to evaluate and develop an effective mixture thermodynamic model for this important binary blend.

5. CONCLUSION

In the present study, the compact-type VLE measurement system was developed to measure a set of VLE properties for the binary system, CO2+ DME. The binary system of the interest is promising alternative candidate to improve the performance of the heat-pump cycles especially for water-heater applications. The VLE apparatus developed in this study has excellent capability to measure PTxy data with uncertainty of 0.007 K for temperature, 0.01 % for pressure and 0.30 mol% for vapor/liquid composition, respectively. As a preliminary result, A set of 24 PTxy data was obtained at 288.1 K. The present measurements agree well with the prediction of the multi-fluid model by Akasaka(2009).

For further investigation, intensive experimental research particularly at low temperatures are expected.

REFERENCES