Measurements of PVT and Vapor-Liquid Equilibrium Properties of Low Global-Warming-Potential Refrigerants

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論 文 名　：Measurements of PVT and Vapor-Liquid Equilibrium Properties of Low Global-Warming-Potential Refrigerants （低 GWP 冷媒の PVT および気液平衡物性の測定）

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論 文 内 容 の 要 旨

The primary objective of this thesis is to investigate pressure-volume-temperature (PVT) properties of pure Hydro-Fluoro-Olefins (HFOs) and vapor-liquid equilibrium (VLE) properties of binary fluid-mixture systems of HFOs and difluoromethane (R32). For the next generation refrigerants, low global-warming-potential (GWP) HFOs and their blends are promising alternatives of Hydro-Fluoro-Carbons (HFCs). Since there are few valid data available for their thermodynamic properties, high-accurate data for the PVT properties of *cis*-1,3,3,3- tetrafluoropropene (R1234ze(Z)) at temperatures from 353 to 413 K, and the VLE properties of R32 + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf), R32 + trifluoroethylene (R1123), and R1123 + R1234yf are presented at temperatures from 273 to 313 K. In addition, comparisons with equations of state (EOSs) are performed, and the binary interaction parameters of a simple cubic EOS for the mixtures were determined based on the VLE data.

Chapter 1 gives the scientific background and literature review about the thermodynamic properties of HFOs and their blends with HFCs in this study. The vapor pressures, saturated liquid densities, saturated vapor densities, critical parameters and PVT properties are described. The historical development of refrigerants is also introduced.

Chapter 2 presents the details of the experimental apparatus for the PVT property measurement by a multiple expansion method (Burnett method) and introduces the measurement principle of the method. The temperature measurement by a standard platinum resistance thermometer (SPRT) and the modification of pressure measurement by an absolute pressure transducer are discussed. The basic mathematical analysis is introduced for the calculation of densities and determination of compressibility factors. The experimental procedure and special supply system for R1234ze(Z) are described. The uncertainties in the experiments are analyzed.

Chapter 3 presents the details of the apparatus for the VLE measurement. The temperature and pressure measurements are described, and the composition measurement is introduced. An extraction system is also introduced. For the measurement of composition, the conversion functions were determined by measuring the standard binary mixtures of R32, R1123 and R1234yf with a gas chromatograph. Experimental procedure is carefully described. The uncertainties in the experiment are analyzed.

Chapter 4 presents the experimental results from the Burnett method. Extensive experimental results are presented to confirm the reliability of the experimental apparatus. Helium was measured at temperatures of 353 K, 373 K, 393 K and 413 K. Based on the results, the cell constant was determined as 1.39760 ± 0.00005. The experimental data were compared with equation of state (EOS) by Ortiz-Vega et al., and the deviations are within 0.05 %. Nitrogen and 1,1,1,2-tetrafluoroethane (R134a) were measured at temperatures of 353 K and 413. The densities and pressures were compared with the EOS by Span et al. for nitrogen and that by Tillner-Roth et al. for R134a, respectively, and show the same magnitude of deviations within 0.1 %. The present experimental results of helium, nitrogen and R134a agree well with the EOSs. R1234ze(Z) was filled into the sample cell at the vapor-liquid equilibrium state. The vapor pressure and single gaseous PVT properties were measured at temperatures of 353 K, 373 K, 393 K and 413 K. The results were compared with the existing EOS by Akasaka et al. and other published data. The EOS agrees well with the present data within 0.1 % in vapor pressure, but it shows a deviation of 0.3 % in density. Therefore, it is expected to improve the accuracy of the EOS by using the present data as input data for the EOS formulation.

Chapter 5 presents the experimental results of VLE properties of binary mixtures. The mixtures of R32 + R1234yf, R32 + R1123 and R1123 + R1234yf were measured at the temperature region from 273 to 313 K at an interval of 10 K. For the binary mixture of R32 + R1234yf, the bubble and dew pressures were compared with the Kamiaka et al.'s data and the EOS by Akasaka. The present data agree with the EOS within 1.1 %, and Kamiaka et al's data show the same magnitude at similar mass fraction. For R32 + R1123 and R1123 + R1234yf, our experimental data are firstly obtained in the world, and no other valid data are available. The present data have clarified the VLE property surfaces of R32 + R1123 and R1123 + R1234yf. The binary interaction parameters of a simple cubic EOS, which is Peng-Robinson (PR) EOS, were determined to represent the present data.

Chapter 6 presents the overall conclusion of this thesis.