# Measurements and Modeling of Vapor-Liquid Equilibrium Properties for Low GWP refrigerants R1123/R1234yf/R32 Ternary Mixtures

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**Abstract**

There is an immediate need to replace existing refrigerants that have significant greenhouse effects with next-generation, low-GWP type refrigerants. While preserving refrigerant performance, to reduce flammability and/or toxicity and to improve compatibility with lubricating oils, various multi-component refrigerant mixtures are potential candidates. In this study, regarding the HFO1123/HFO1234yf/HFC32 ternary mixtures, we performed precise measurements of vapor-liquid equilibrium properties and tried to verify the reliability of two kind of thermodynamic property models. Measurements were conducted at temperatures from 303.15 to 328.15 K and at saturation pressures up to 3.7 MPa. The expanded uncertainties ($k$ = 2) in temperature, pressure, and component measurements were estimated to be less than 0.03 K, 1.4 kPa, and 0.43 mol%, respectively. One of the models used is the Helmholtz free energy type equation of state with the latest parameters. We used this equation of state to predict the VLE data for the ternary mixtures. Another model is the Peng-Robinson equation of state modified by Mathias and Copeman. We used the optimized parameters of pures and binary mixtures published by the present authors, for the present calculations of each ternary mixtures without any additional parameters specified to the ternary mixtures. Systematic comparisons between the predicted values and the present measurement results for the ternary mixtures were discussed.

## 1. Introduction

The multi-component mixtures containing R32/R1234yf binary pair are expected as a candidate for a next-generation refrigerant with a low environmental load for small and medium-sized refrigeration and air-conditioning systems. The authors' group has already reported the measurement results of the vapor-liquid equilibrium properties (bubble point and dew point pressures, hereinafter abbreviated as VLE properties), that are indispensable for determining the regression parameters of the thermodynamic equations of state, for a total of three binary mixtures, consisting of two of the three components R32 and R1234yf plus R1123 [1]. These measured values revealed that the existing equation of state has a pressure deviations of up to several percent (corresponding to an error of up to about 2 atm). The recently published Helmholtz free energy type equations of state by Akasaka and Lemmon [5] and Akasaka [6] (hereinafter abbreviated as Akasaka and Lemmon model) can represent these measured values well and will be implemented in the next version of the thermophysical property calculation software REFPROP ver. 10 [7]. It has become clear that highly accurate measured values are still required to ensure the reliability of the equations of state. However, the thermodynamic properties of mixtures of three or more components are generally estimated using only the coefficients and exponents for the substances up to the binary mixtures, and the model which includes parameters specific to the ternary mixtures has rarely reported. This seems to be no problem in the case of mixtures in which there is no strong influence of intermolecular force due to special polarities, associations, hydrogen bonds, etc. in the fluid, but in view of the current situation of the above binary mixture model, the verification by comparison with the measured value is strongly required.

Therefore, we performed the precise measurement of VLE properties for the ternary R32/R1123/R1234yf mixtures by means of the two different types of the measurement apparatus, in order to evaluate the reliability of the estimation results of ternary mixtures by the above REFPROP ver. 10.0 original model and the new Akasaka and Lemmon model. In addition, after estimating the ternary mixtures from the modified Peng-Robinson equation of state that regressed on the measured values of the binary mixture of the authors' group, the systematic comparison and verification of the models with the measured values are also performed. In this report, we attempted to verify the reliability of the estimated values of thermodynamic properties for multi-component mixtures.

## 2. Measurements of the VLE properties for the ternary mixtures

### 2.1. Recirculation type VLE property measurement apparatus

The VLE property is one of the thermodynamic properties indispensable for optimizing the mixing parameters of the equation of state. In this study, we used two types of

measurement methods, one in which the sample was in the two-phase region and the other in which the sample was approached from the liquid-phase region to the two-phase region and evaporated under reduced pressure. The former will be introduced in this section, and the latter will be introduced in the next section. In the common VLE property measurement, a part of the sample is extracted from a mixture sample in which the temperature and pressure are kept in equilibrium, and the composition is measured. In this study, a recirculation type VLE property measurement apparatus developed by the AKICO Co., Ltd., Japan, was used. In the recirculation type, two circulation loops that simulate the phase change of the gas phase and the liquid phase in the optical cell are reproduced by the liquid feed pump, and the sample is sandwiched in the temperature equilibrium state to prevent equilibrium failure. The sandwiched sample had a gas phase of about 2 cm$^3$ and a liquid phase of about 0.5 cm$^3$, and was mixed sufficiently uniformly with helium (purity 99.999 vol%) in a separate system placed in the oven, and then the composition of each was measured by means of the gas chromatograph (GC-3200, GL Sciences Inc., Japan).

The expanded uncertainties with the coverage factor; $k$=2 (confidence width 95%), are estimated as 0.03 K for temperature measurement, 1.38 kPa for pressure measurement, and 0.007 mol · mol$^{-1}$ for composition measurement. As an example, Fig. 1 shows the measurement results [4] of the R1123/R1234yf binary mixtures. The baseline is REFPROP ver. 10.0 (original model). It can be seen that the REFPROP ver. 10.0 has a systemic deviation of up to about 6%. This deviation corresponds to about 2 atm. In the Akasaka and Lemmon model, correlation was performed using this data as the input data, and the deviation is reduced. The solid line and broken line show the calculation results from the modified Peng-Robinson equation of state, which will be described later.
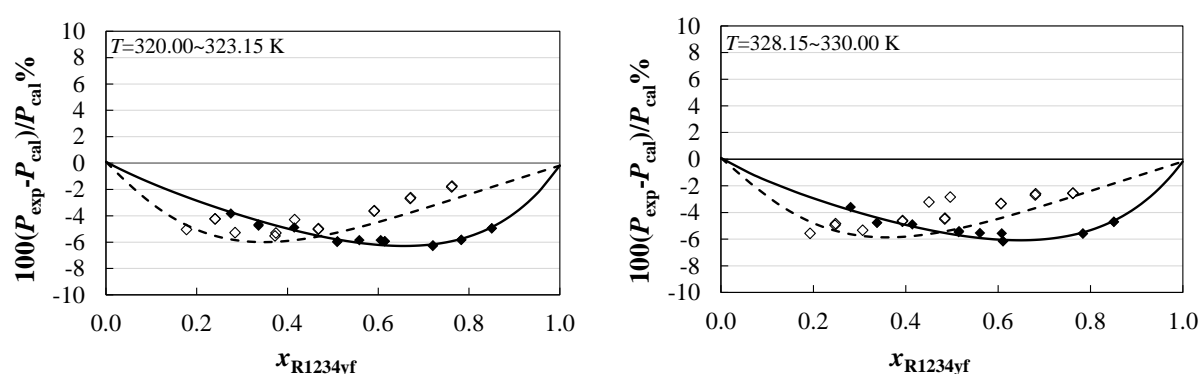


Fig.1 Deviations between the experimental VLE properties [4] and the predictions of the REFPROP ver. 10.0 [7] for R1123/R1234yf mixtures. ◆; bubble point pressures, ◇; dew point pressures, — · ----; values from the modified Peng–Robinson equation of state [4].

Measurements for the ternary mixtures were also performed on the same principle. In order to derive the mass fraction from the area fraction measured by the gas chromatograph, as shown in Fig. 2, the calibration curve equations for the three types of binary mixture were combined.
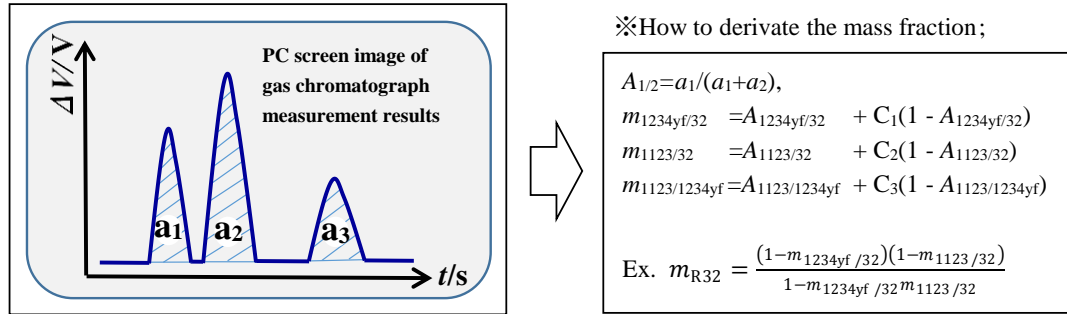


PC screen image of gas chromatograph measurement results

$\Delta V / V$

$a_1$ $a_2$ $a_3$

$t/s$

※How to derivate the mass fraction;

$A_{1/2} = a_1/(a_1+a_2),$

$m_{1234yf/32} = A_{1234yf/32} + C_1(1 - A_{1234yf/32})$

$m_{1123/32} = A_{1123/32} + C_2(1 - A_{1123/32})$

$m_{1123/1234yf} = A_{1123/1234yf} + C_3(1 - A_{1123/1234yf})$

Ex. $m_{R32} = \dfrac{(1-m_{1234yf/32})(1-m_{1123/32})}{1-m_{1234yf/32}\,m_{1123/32}}$

Fig. 2 Derivation the mass fraction from the measurement results by gas chromatography (for ternary mixtures).

### 2.2. Isothermal/variable volume bellows type $P\rho Tx$ property measurement apparatus

On the other hand, as a completely different method, it is also possible to elucidate the VLE property with high precision by gradually reducing the pressure from the liquid phase region at an isothermal temperature and detecting the phase change before and after entering the two-phase region on the measured data. In this study, this method was reproduced using the bellows type variable volume method. On the top of Fig. 3, the distribution of the present measured value on the isothermal line of the $P\rho Tx$ property for the ternary R32/R1123/R1234yf mixtures are shown on the $P\rho$ diagram. The composition is measured and adjusted by the gravimetrically method and gas chromatograph, and is 33.5/33.4/33.1 mol%. The broken line connects the measured values of each isotherm, and it can be confirmed that the phase change is clearly shown. From these refraction points, the bubble point pressure value and the saturated liquid density value at each temperature are determined, and the results compared with the values estimated by REFPROP ver. 10.0 [7] are shown on second and subsequent rows of Fig. 3. The upper part shows the relative deviations of the bubble point pressure, and the lower part shows the relative deviation of the saturated liquid density. It can be seen that the saturated liquid density is generally well estimated except near the critical temperature. However, the bubble point pressure shows a systemic deviation of about 2% at the maximum, and it can be said that REFPROP ver. 10.0 needs to be corrected. The comparison results with the Akasaka and Lemmon model will be described in Chapter 4.
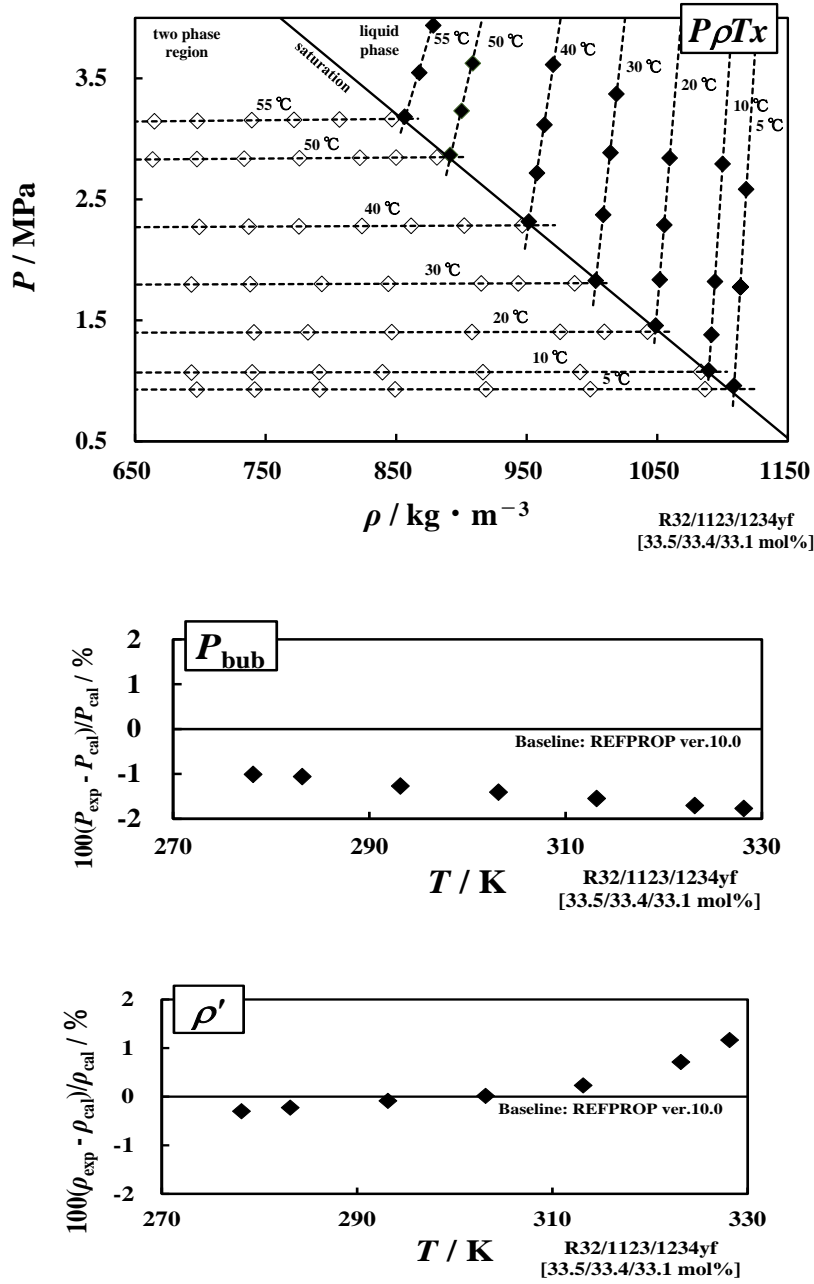
Fig. 3 Measurement results of the *PρTx* properties and saturation properties for R32/R1123/R1234yf ternary mixtures.

## 3. Estimation of the thermodynamic properties for the ternary mixtures

### 3.1. Helmholtz free energy type equations of state

The Helmholtz free energy type equation of state for the ternary R32/R1123/R1234yf mixtures implemented in REFPROP ver. 10.0 is shown in Eq. (1).

$$\phi_{\text{mix}} = \sum_{i=1}^{n}\left[x_i\left(\phi_i^{\text{id}} + \phi_i^{\text{r}}\right) + x_i \ln x_i\right] + \sum_{j=1}^{n-1}\sum_{k=j+1}^{n} x_j x_k F_{jk}\phi_{jk}^{\text{excess}} \tag{1}$$

Here, $\phi$ is the dimensionless Helmholtz free energy. The first term on the right side is the contribution from each equation of state for components (and the change in entropy due to mixing), and the second term on the right side is the excess term (mixing law) that corrects the deviation (excess amount) from the measured value. As can be seen from Eq. (1), the calculation of the multi-component system of ternary mixtures or more is performed using only the parameters up to the binary mixtures. The Akasaka and Lemmon model has almost the same functional form, and the parameters of the binary mixtures are regressed to the measured values of the authors' group and optimized. For more detailed information of the reproducibility of these binary mixtures, references to the literatures [5,6] are recommended.

### 3.2. Cubic type equations of state

The cubic type equation of state by the authors is shown in Eqs. (2-5). The correlation of this equation of state [2-4] was initially intended for experimental design and data evaluation. However, since the authors' data can be reproduced well by the Akasaka and Lemmon model, we also used this cubic type model to estimate values for ternary mixtures this time. This is a modification of the Peng-Robinson equation of state [8] by Mathias and Copeman [9], and it has been modified to be able to correlate the saturated vapor pressure of a pure substance by making the $\alpha$ function a polynomial of temperature. Eqs. (4,5) show the mixing law applied to $a\alpha$ and $b$ in Eq. (2). Even in these equations, the calculation of a multi-component system of ternary or more mixtures is performed using only the parameters related to the components up to the binary mixtures.

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)} \tag{2}$$

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_c}}\right) + c_2\left(1 - \sqrt{\frac{T}{T_c}}\right)^2 + c_3\left(1 - \sqrt{\frac{T}{T_c}}\right)^3\right]^2 \tag{3}$$

$$a\alpha = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}\alpha_{ij} \quad , \quad a_{ij,i\neq j}\alpha_{ij} = \left(1 - k_{ij}\right)\sqrt{a_i\alpha_i a_j\alpha_j} \tag{4}$$

$$b = \sum_{i=1}^{n} x_i b_i \tag{5}$$

## 4. Results and discussions

Figure 4 shows the deviation plots of the present measurement values of VLE properties of the ternary mixtures. The upper figure shows the absolute pressure deviation [kPa],

and the lower figure shows the relative pressure deviation [%]. The baselines are different for each plot for comparison, with ○ being the Akasaka and Lemmon equation [5,6], △ being the modified Peng-Robinson equation of state [2-4], and □ being the REFPROP ver. 10.0 original model [7]. The composition is ●▲■: Composition 1(R32/R1123/R1234yf = 0.335/0.334/0.331), ●▲■: Composition 2 (0.197/0.499/0.304), and ○△□: Composition 3(0.198/0.402/0.400).
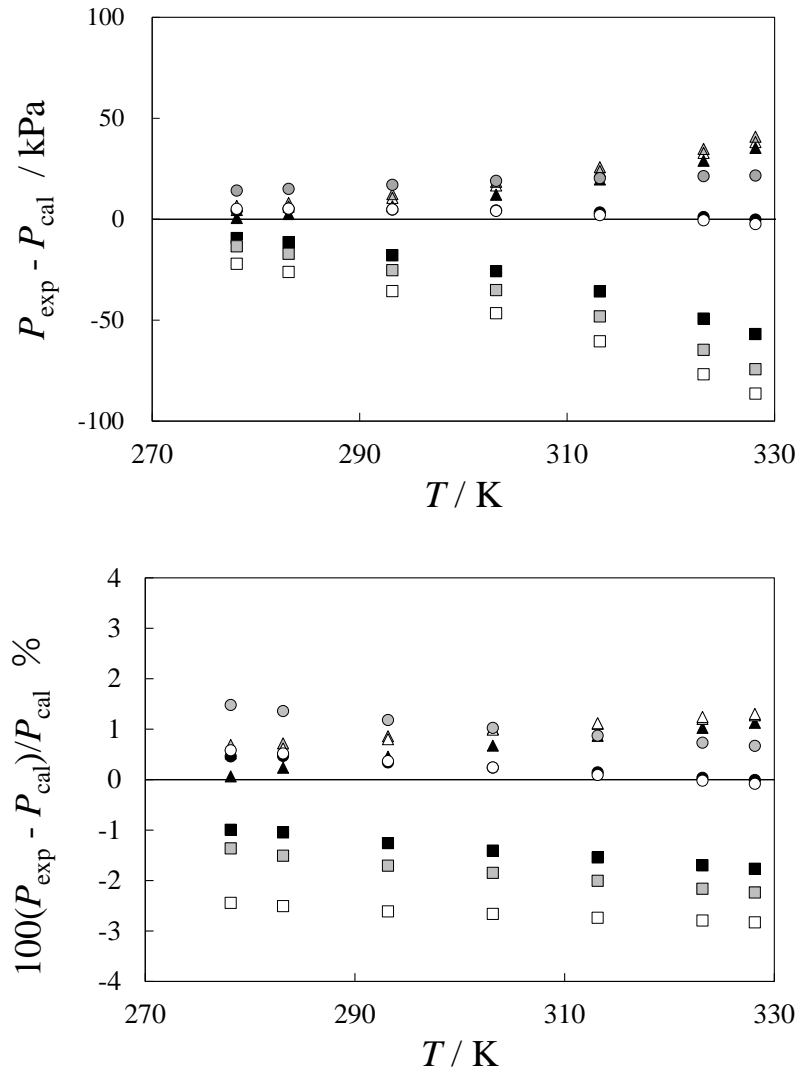


Fig. 4 Absolute (top) and relative (bottom) deviations of the bubble point pressures for R32/R1123/R1234yf ternary mixtures.

The Akasaka and Lemmon model, which has high reproducibility for the binary mixtures, reproduces the present bubble point pressure values within an absolute pressure deviation of 20 kPa and a relative pressure deviation of 1.5% or less. It can be seen that the reproducibility of the ternary mixtures is improved compared to REFPROP ver. 10.0. On the other hand, the estimated values from the modified Peng-Robinson equation of state are also in

good agreement with the Akasaka and Lemmon model. It was confirmed that high reproducibility for the binary mixture is necessary to ensure the reliability of the estimated value of the multi-component systems, and that the difference in the functional form of the equation of state does not have much effect. We plan to make similar comparisons further on the effects on other thermodynamic properties such as density and enthalpy. However, it was not possible recently, to clarify in detail the effects of azeotrope (pseudo-azeotrope) and the effects of intermolecular interactions. Quantitative evaluation of these points is awaited in the future.

## Acknowledgments

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