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Vapor-liquid equilibrium measurements for binary mixtures of R1234yf with R32, R125, and R134a

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ABSTRACT

Vapor-liquid equilibria (VLE) measurement results for three binary refrigerant mixtures of R1234yf with R32, R125, and R134a are presented. The VLE properties were measured at mass fractions of R1234yf from 25% to 80%. Equilibrium pressures were measured at temperatures from 273 K to 333 K at 10 K intervals for each binary refrigerant mixture. Measured data were correlated by using both the Peng-Robinson-type and Helmholtz-type equations of state combined with mixing rules. Binary interaction parameters included in each mixing rule were optimized to fit the measured VLE data of each binary mixture. It was found that the temperature glide of the refrigerant mixture R32/R1234yf was much larger than that of the other binary mixtures. Further, it was found that R134a/R1234yf had an azeotropic property around 50/50 wt%. The measured fundamental data of the vapor-liquid equilibrium are crucial for the optimization of binary refrigerant mixture systems.

Keywords:

Thermodynamic property, Equation of state, R1234yf, R32, R125, R134a, Binary mixture

Nomenclature

a	energy parameter in PR equation
b	size parameter in PR equation
E	objective function
k_{ij}	binary interaction parameter
P	pressure (Pa)
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	temperature (K)

v	molar volume ($\text{m}^3 \text{mol}^{-1}$)
x	composition in liquid phase
y	composition in gas phase

Greek letters

ζ_{ij}, ξ_{ij}	binary interaction parameter
ω	acentric factor

subscript

bubble	bubble point
cal	calculated results
c	critical
dew	dew point
exp	experimental results
i	component i
j	component j
red	reducing parameter

1. INTRODUCTION

Increasing concern regarding environmental protection and global warming has led to a reconsideration of the refrigerant technology used in stationary conditioners. The refrigerants currently used are either hydrofluorocarbons (HFCs), which have a high global warming potential (GWP), or hydrochlorofluorocarbons (HCFCs). Transitioning from these refrigerants to a low-GWP refrigerant is an issue of global importance. However, at present, there is no ideal candidate that can meet the requirements of both system performance and environmental performance.

In recent years, R1234yf has been widely accepted as a drop-in solution for mobile air conditioners because of its low GWP of 4 and its thermophysical properties, which are similar to those of R134a. In comparison with R410A, which is widely used in stationary air conditioners, R1234yf has smaller latent heat, which leads to larger mass flow rates, larger pressure drops in heat exchangers and connection pipes, and ultimately, lower coefficients of performance. One approach to resolve this problem is to use a refrigerant mixture of R1234yf with other refrigerants, i.e., R32, R125, or R134a, so as to obtain a larger latent heat. Mixing more than 22 wt% R125 or 36 wt% R134a with R1234yf has additional advantage to cancel the mild flammability of R1234yf (Yamada et al., 2010). The thermophysical properties of these refrigerant mixtures are essential for an investigation of their performance in refrigeration or the heat pump cycle. However, there is lack of information about their thermophysical properties. The only literature available is the modeling of vapor-liquid equilibrium for R32/Isobutane and R32/R1234ze(E) by Akasaka (2011).

In this study, the vapor-liquid equilibrium of three binary refrigerant mixtures of R1234yf with

R32, R125, and R134a were experimentally studied, and both a Peng-Robinson type and a Helmholtz type Equations of state are derived based on the measured data.

2. MEASUREMENTS

2.1. Materials

The R1234yf was provided by SynQuest Laboratories, Inc, and R32, R134a and R125 were provided by Takachiho Chemical Industrial Co., Ltd. For the R32/R1234yf mixture, the purities of R32 and R1234yf were higher than 99.9% and 99%, respectively. The purity of R1234yf sample guaranteed by the manufacture was 99%. Although the composition report provided by the manufacture showed a higher purity, there was no information showing what the containment was. Therefore, in this study, the R1234yf sample was firstly degassed five times using liquid nitrogen to get rid of non-condensation component. In order to eliminate the effect of possible condensation components, measurements of saturation temperature of R1234yf were conducted and the results were compared with that of 99.9% sample, the deviations of the measured saturation temperatures were found less than ± 0.05 K, therefore the effect of condensation component is consider negligible. For R125/R1234yf and R134a/R1234yf mixtures, the purity of all components was more than 99.9%.

2.2. Apparatus

The VLE properties were measured using a static-type apparatus. A schematic of the apparatus is shown in Fig.1. The apparatus consists of a thermostat liquid bath, an equilibrium cell, a sampling system, and measurement instruments. The equilibrium cell used is a single-ended cylinder made of SS304 with inner volume of 150 mL. The outer diameter of the equilibrium cell is 50.8 mm, with a height of 124 mm and a thickness of is 2.4 mm. Temperature of the thermostat liquid bath was measured using a high-precision platinum resistance thermometer, and the results were transferred to a PC through a digital temperature indicator (Chino, CAB-F201). The total temperature measurement uncertainty was estimated to be within ± 0.015 K. The pressure inside the equilibrium cell was measured using a quartz oscillating pressure transmitter (Paroscientific, 1000–1 K), which had an uncertainty of ± 0.7 kPa (0.01% of full scale: 6,890 kPa).

The composition of the vapor phase was measured using a gas chromatograph (Shimadzu, GC-14B). The gas chromatograph was equipped with a flame ionization detector (FID) and a micro-packed column (Shinwa Chem., MICROPACKED ST). The inner volume of the sampling loop is 15 μ L. The uncertainty in the vapor phase composition is estimated to be within ± 0.01 mass fraction, which mainly includes the uncertainty of the calibration curves. The liquid phase composition was calculated from the amount of refrigerant mixtures initially charged to the equilibrium cell, the vapor phase composition data actually measured by the gas chromatograph, the

amount of refrigerant mixtures discharged to the gas chromatograph, and current pressure and temperature. normally when the volume of liquid exceeds half of the inner volume of the equilibrium cell, the difference between the overall composition and liquid composition is less than 0.1%. In our experiments, the initial changing liquid volume was set to be about 0.6 of the inner volume. The uncertainty of liquid phase composition is estimated from the uncertainty of charging composition, density of the vapor phase used, and the inner volume of equilibrium cell, sampling loop and the connecting tube. The estimated uncertainty of liquid phase composition is within ± 0.001 mass fraction.

2.3. Measurement procedure

2.3.1. Mixing process

Two sampling cells with the same inner volume of 150 mL were used for weighing the R1234yf and the other component. Degasification of the non-condensable gas was conducted for each component using liquid nitrogen, and the process was repeated five times. The weight of each component in the sampling cell was measured using an electronic balance (Sartorius, with an accuracy of ± 0.001 g) by subtracting the weight of the sampling cell. The component weight in the sampling cell was adjusted in accordance with the intended composition of the final mixture. Finally, both components were transferred from the sampling cells to the equilibrium cell using liquid nitrogen.

2.3.2. VLE Measurement

The equilibrium cell was placed in the thermostat liquid bath. The temperature of thermostat liquid bath and the pressure of the equilibrium cell were monitored continuously. When the variation of temperature smaller than 0.05 K and the change of pressure smaller than 1 kPa within 1 hour, the temperature and pressure are assumed stabilized. The saturated mixture vapor was then sampled using a 6-way switching valve to the sampling loop, and was injected into the gas chromatograph to measure the vapor phase composition. The liquid phase composition was calculated from the overall composition, the vapor phase composition measured, the amount of refrigerant mixtures discharged to the gas chromatograph, and current pressure and temperature. For each condition, measurements were conducted twice to confirm repeatability. The temperature of thermostat liquid bath was changed from 273-333 K at an interval of 10 K.

The sampling loop has a inner volume of 15 μL . The tubes connecting the equilibrium cell, switching valve and the vacuum pump have outer diameters of 1.6 mm and inner diameters of 0.8 mm. The inner volume of the connecting tube starting from the valve attached to the equilibrium cell to the valve attached to the vacuum pump is 96 μL . For each measurement, the same amount of vapor as that stored in sampling loop and the connecting tube need to be drew off from the

equilibrium cell, which will cause a slight change in the composition of the liquid phase. The effect of the loss of sample in each measurement was compensated using the inner volume of sampling loop and connecting tube and the measured gas phase composition.

3. RESULTS

The VLE properties were measured in the temperature range of 273–333 K in steps of 10 K. The overall concentration of the more volatile component was 20, 30, 40, 50, and 70 wt% for the R32/R1234yf mixture; 20, 30, 40, and 50 wt% for the R125/R1234yf mixture; and 25, 50, and 75 wt% for the R134a/R1234yf mixture. The results are shown in Figs. 2–4 on the isothermal VLE diagrams.

As shown in Figs. 2 and 3, in the R32/R1234yf and R125/R1234yf systems, azeotropic behavior was not observed under the measurement conditions. On the other hand, for the R134a/R1234yf mixture, as shown in Fig. 4, azeotropic behavior was observed. The vapor pressures of R134a and R1234yf are very similar, and the azeotropic point exists around 50 wt% of R134a. All the measured data are provided in Appendix.

4. DISCUSSION

4.1. Equation of state

Measured data were correlated with two types of equation of state, the Peng-Robinson (PR) type and the Helmholtz type.

The PR equation (Peng and Robinson, 1976) is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (1)$$

with

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \left\{ 1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right\}^2 \quad (2)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (3)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (4)$$

where a and b are energy and size parameters, respectively. R is the universal gas constant. T , P , and v are temperature, pressure, and molar volume, respectively. ω is the acentric factor. Subscript c indicates the critical value.

For multi-component mixtures, the following mixing rule is used:

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad b_m = \sum_i x_i b_i \quad (5)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i \cdot a_j}, \quad (k_{ij} = k_{ji}) \quad (6)$$

where x_i is the concentration of i th component. Subscripts m , i , and j indicate the value of the mixture, component i , and component j , respectively. k_{ij} is binary interaction parameter and is generally determined by fitting the measured VLE data.

For a binary mixture, equations (5) and (6) reduce as follows:

$$a_m = x_1^2 a_1 + x_2^2 a_2 + 2(1 - k_{12}) \sqrt{a_1 \cdot a_2} \quad (7)$$

$$b_m = x_1 b_1 + x_2 b_2 \quad (8)$$

The substance constants used for calculation are shown in Table 1. The values for HFCs are quoted from REFPROP ver. 9.0 database (Lemmon *et al.* 2010); those for R1234yf are taken from Tanaka and Higashi (2009).

The Helmholtz-type equations of state used in this study for R32, R125, R134a, and R1234yf are the same as those in REFPROP ver. 9.0, as reported in Tillner-Roth and Yokozeki (1994), Lemmon and Jacobsen (2005), Tillner-Roth and Baehr (1998), and Richter *et al.* (2010), respectively.

The mixing model by Lemmon and Jacobsen (2004) was employed. This mixing model is used in REFPROP ver. 9.0 with default binary interaction parameters for mixtures of R1234yf with R32, R125, and R134a. The mixing model without a departure function is expressed as follows:

$$T_{\text{red}}(\mathbf{x}) = \sum_{i=1}^n x_i T_{c,i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \zeta_{ij} \quad (9)$$

$$v_{\text{red}}(\mathbf{x}) = \sum_{i=1}^n x_i v_{c,i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \xi_{ij} \quad (10)$$

where T , v , and x are temperature, molar volume, and composition, respectively. Subscript red indicates the reducing parameter. ζ_{ij} and ξ_{ij} are binary interaction parameters, and they were determined by fitting to measured data. In REFPROP ver. 9.0, it is assumed that $\xi_{ij} = 0$, because the effect of ξ_{ij} is small.

In this work, binary interaction parameters k_{ij} in the PR equation and ζ_{ij} in the Helmholtz equation were optimized by fitting to measured VLE data. The objective function in optimization is as follows:

$$E = \sum \left(\frac{P_{\text{exp}}}{P_{\text{cal}}} - 1 \right)_{\text{bubble}}^2 + \sum \left(\frac{P_{\text{exp}}}{P_{\text{cal}}} - 1 \right)_{\text{dew}}^2 \quad (11)$$

where E is objective function, P_{exp} and P_{cal} are measured and calculated saturated pressures, subscripts bubble and dew denote the bubble point and dew point, respectively.

Parameter ζ was set to 0. k_{ij} was varied between 0 ~ 1, while ζ_{ij} was varied between -100 ~ 0 to obtain optimized value by which the objective function takes minimum value.

Using optimized and not-optimized interaction parameters in each equation of state, saturated pressure was calculated and compared with measured values. Results are shown in Table 2. It was found that both equations of state with optimized interaction parameters can successfully represent measured saturated pressure. The average absolute deviation was less than 1.13%. On the other hand, REFPROP ver. 9.0 with a default interaction parameter predicts saturation pressure with an average absolute deviation of 3.6–5.3%.

4.2. Temperature Glide

Temperature glide was calculated using the optimized PR equation for the three binary systems studied. Results are shown in Fig. 5. It can be seen that a relatively large temperature glide of 8 K is present at a composition of 20 wt% R32 in the R32/R1234yf mixture. For R125/R1234yf, a maximum temperature glide of 3.7 K was obtained at a composition of 50 wt% R125. This may cause a deterioration in heat transfer performance and a deviation in the mixing rate because of refrigerant leakage. For the R134a/R1234yf mixture, the temperature glide was negligibly small (approximately 0.2 K), and thus, the mixture behaves like a pure refrigerant in the heat pump and refrigeration cycle.

5. CONCLUSION

Vapor-liquid equilibrium of three binary refrigerant mixtures of R1234yf with R32, R125, and R134a were experimentally studied, and both Peng-Robinson type and Helmholtz type Equations of state are derived. The following results were obtained.

- A) For the R32/R1234yf and R125/R1234yf mixtures, non-azeotropic behavior was observed in the measurement range of 273–333 K.
- B) The R134a/R1234yf mixture has an azeotropic point at a composition of 50/50 wt%.
- C) Based on the measured VLE data, the PR and Helmholtz equations of state with mixing rules were successfully optimized. The average absolute deviation of calculated saturation pressure was less than 1.13%.
- D) Temperature glides were estimated for each binary mixture. It was found that the maximum temperature glide for R32/R1234yf is 8 K and that for R125/R1234yf is 3–4 K.

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APPENDIX

Table A.1 Data of VLE Measurements for (1) R32/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(0/100)				(50/50)			
273.33	318.7	0.000	0.000	273.32	723.2	0.497	0.679
283.15	438.2	0.000	0.000	283.13	973.5	0.497	0.651
293.16	592.2	0.000	0.000	293.14	1290.0	0.496	0.649
303.17	783.3	0.000	0.000	303.18	1675.4	0.495	0.643
313.18	1017.8	0.000	0.000	313.18	2142.1	0.495	0.627
323.10	1298.0	0.000	0.000	323.12	2692.4	0.495	0.610
333.11	1636.4	0.000	0.000	333.15	3347.1	0.497	0.601
(20/80)				(70/30)			
273.33	569.5	0.196	0.408	273.37	775.1	0.698	0.780
283.16	763.0	0.195	0.392	283.08	1044.1	0.697	0.784
293.15	1006.0	0.194	0.370	293.14	1388.6	0.696	0.779
303.15	1300.6	0.194	0.352	303.17	1807.4	0.695	0.772
313.18	1648.0	0.193	0.341	313.18	2319.9	0.695	0.768
323.10	2061.8	0.192	0.324	323.21	2929.4	0.694	0.761
333.12	2548.8	0.193	0.294	333.10	3646.4	0.693	0.754
(30/70)				(100/0)			
273.32	636.4	0.297	0.521	273.33	817.8	1.000	1.000
283.14	854.0	0.297	0.502	283.14	1106.9	1.000	1.000
293.15	1128.3	0.296	0.490	293.16	1475.2	1.000	1.000
303.15	1462.3	0.296	0.475	303.18	1927.6	1.000	1.000
313.17	1860.0	0.296	0.454	313.20	2480.1	1.000	1.000
323.11	2328.8	0.296	0.428	323.22	3144.2	1.000	1.000
333.10	2885.7	0.298	0.425	333.14	3927.5	1.000	1.000
(40/60)				(x_1/x_2) Mixing ratio in mass			
273.34	686.8	0.397	0.591				
283.14	922.5	0.396	0.582				
293.13	1219.7	0.395	0.573				
303.15	1582.0	0.395	0.559				
313.19	2015.7	0.394	0.549				
323.10	2526.1	0.395	0.511				
333.12	3130.5	0.397	0.494				

Table A.2 Data of VLE Measurements for (1) R32/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(20/80)				(40/60)			
273.32	567.6	0.196	0.417	273.32	683.9	0.391	0.608
283.13	760.8	0.195	0.391	283.14	918.1	0.389	0.588
293.15	1003.9	0.195	0.374	293.16	1212.7	0.386	0.575
303.16	1299.1	0.194	0.358	303.17	1570.8	0.382	0.556
313.18	1648.4	0.193	0.335	313.19	1994.2	0.381	0.527
323.10	2061.7	0.193	0.308	323.10	2493.1	0.378	0.506
333.11	2548.8	0.194	0.292	333.11	3068.8	0.370	0.501
(30/70)				(50/50)			
273.31	632.8	0.290	0.522	273.33	724.2	0.498	0.653
283.13	848.4	0.288	0.510	283.14	974.6	0.497	0.648
293.14	1118.4	0.285	0.493	293.15	1291.3	0.497	0.643
303.17	1446.0	0.281	0.474	303.15	1678.2	0.497	0.630
313.18	1831.9	0.277	0.460	313.19	2142.8	0.497	0.618
323.11	2283.9	0.277	0.413	323.10	2692.9	0.497	0.598
333.13	2813.1	0.269	0.412	333.11	3348.6	0.499	0.594

(x_1/x_2) Mixing ratio in mass

Table A.3 Data of VLE Measurements for (1) R125/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(0/100)				(40/60)			
273.31	318.3	0.000	0.000	273.33	460.3	0.398	0.574
283.13	438.1	0.000	0.000	283.11	621.6	0.398	0.559
293.17	592.8	0.000	0.000	293.17	828.3	0.397	0.546
303.19	784.8	0.000	0.000	303.19	1081.1	0.397	0.530
313.20	1020.1	0.000	0.000	313.09	1382.6	0.397	0.514
323.13	1302.6	0.000	0.000	323.15	1750.2	0.398	0.497
333.12	1641.7	0.000	0.000	333.12	2181.2	0.399	0.473
(20/80)				(50/50)			
273.34	385.0	0.199	0.351	273.35	489.4	0.498	0.667
283.17	525.4	0.199	0.334	283.17	662.2	0.497	0.656
293.17	704.7	0.199	0.325	293.09	879.3	0.496	0.647
303.09	923.2	0.198	0.310	303.11	1147.3	0.496	0.631
313.10	1192.2	0.199	0.299	313.12	1471.6	0.496	0.616
323.11	1515.5	0.199	0.289	323.14	1860.3	0.497	0.593
333.13	1899.4	0.200	0.270	333.14	2319.4	0.498	0.578
(30/70)				(100/0)			
273.36	415.4	0.299	0.438	273.41	676.8	1.000	1.000
283.07	563.1	0.299	0.428	283.15	909.4	1.000	1.000
293.10	753.6	0.299	0.417	293.20	1204.9	1.000	1.000
303.11	987.7	0.299	0.402	303.13	1566.5	1.000	1.000
313.10	1271.4	0.299	0.392	313.16	2008.1	1.000	1.000
323.12	1612.6	0.299	0.376	323.18	2538.5	1.000	1.000
333.14	2017.3	0.300	0.360	333.14	3169.4	1.000	1.000

 (x_1/x_2) Mixing ratio in mass

Table A.4 Data of VLE Measurements for (1) R125/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(0/100)				(40/60)			
273.35	318.7	0.000	0.000	273.32	452.8	0.398	0.572
283.08	437.6	0.000	0.000	283.17	615.0	0.398	0.560
293.11	592.5	0.000	0.000	293.14	819.6	0.398	0.546
303.14	783.9	0.000	0.000	303.11	1070.7	0.397	0.529
313.16	1020.2	0.000	0.000	313.18	1378.2	0.397	0.516
323.19	1305.5	0.000	0.000	323.18	1743.3	0.398	0.498
333.21	1646.1	0.000	0.000	333.19	2176.8	0.399	0.484
(20/80)				(50/50)			
273.31	384.9	0.199	0.349	273.40	489.7	0.498	0.666
283.14	525.2	0.199	0.339	283.13	660.7	0.498	0.657
293.16	704.5	0.199	0.331	293.14	880.1	0.498	0.643
303.14	925.1	0.198	0.318	303.19	1150.7	0.498	0.625
313.17	1194.9	0.199	0.307	313.17	1475.3	0.498	0.612
323.16	1517.7	0.199	0.297	323.17	1863.0	0.499	0.592
333.16	1901.1	0.200	0.284	333.17	2326.2	0.500	0.580
(30/70)				(100/0)			
273.31	418.3	0.299	0.463	273.36	678.3	1.000	1.000
283.15	569.2	0.298	0.448	283.08	910.1	1.000	1.000
293.19	762.1	0.298	0.434	293.11	1206.8	1.000	1.000
303.19	998.8	0.298	0.421	303.12	1569.3	1.000	1.000
313.15	1283.8	0.298	0.404	313.15	2010.0	1.000	1.000
323.17	1628.0	0.299	0.386	323.16	2539.9	1.000	1.000
333.18	2036.7	0.300	0.373	333.19	3175.6	1.000	1.000

 (x_1/x_2) Mixing ratio in mass

Table A.5 Data of VLE Measurements for (1) R134a/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(0/100)				(75/25)			
273.31	318.3	0.000	0.000	273.32	315.3	0.750	0.711
283.13	438.1	0.000	0.000	283.20	439.9	0.750	0.725
293.17	592.8	0.000	0.000	293.17	600.7	0.750	0.728
303.19	784.8	0.000	0.000	303.17	801.8	0.750	0.735
313.20	1020.1	0.000	0.000	313.19	1048.8	0.750	0.736
323.13	1302.6	0.000	0.000	323.20	1359.1	0.750	0.737
333.12	1641.7	0.000	0.000	333.21	1726.4	0.750	0.738
(25/75)				(100/0)			
273.32	328.5	0.250	0.264	273.31	295.5	1.000	1.000
283.15	452.8	0.250	0.266	283.19	415.9	1.000	1.000
293.11	612.5	0.250	0.267	293.16	572.6	1.000	1.000
303.17	812.2	0.250	0.270	303.19	769.5	1.000	1.000
313.18	1058.2	0.250	0.269	313.19	1017.3	1.000	1.000
323.19	1355.6	0.250	0.266	323.12	1316.8	1.000	1.000
333.20	1711.1	0.250	0.265	333.14	1680.7	1.000	1.000
(50/50)				(x_1/x_2) Mixing ratio in mass			
273.33	324.3	0.500	0.482				
283.16	449.8	0.500	0.489				
293.13	611.6	0.500	0.490				
303.08	812.2	0.500	0.498				
313.18	1065	0.500	0.500				
323.19	1369	0.500	0.498				
333.20	1733	0.500	0.499				

Table A.6 Data of VLE Measurements for (1) R134a/(2) R1234yf

T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]	T [K]	P [kPa]	x_1 [g g ⁻¹]	y_1 [g g ⁻¹]
(0/100)				(50/50)			
273.35	318.7	0.000	0.000	273.33	324.8	0.500	0.481
283.08	437.6	0.000	0.000	283.17	450.5	0.500	0.487
293.11	592.5	0.000	0.000	293.12	612.1	0.500	0.491
303.14	783.9	0.000	0.000	303.18	815.6	0.500	0.496
313.16	1020.2	0.000	0.000	313.11	1064.1	0.500	0.495
323.19	1305.5	0.000	0.000	323.21	1370.6	0.500	0.497
333.21	1646.1	0.000	0.000	333.16	1732.4	0.500	0.495
(25/75)				(75/25)			
273.32	326.3	0.250	0.261	273.34	315.6	0.750	0.713
283.18	450.9	0.250	0.265	283.14	439.2	0.750	0.721
293.15	610.8	0.250	0.263	293.18	601.1	0.750	0.726
303.20	810.4	0.250	0.267	303.20	802.1	0.750	0.729
313.20	1056.6	0.250	0.268	313.20	1053.7	0.750	0.741
323.20	1353.3	0.250	0.267	323.19	1358.1	0.750	0.745
333.21	1708.9	0.250	0.262	333.19	1724.5	0.750	0.744

(x_1/x_2) Mixing ratio in mass

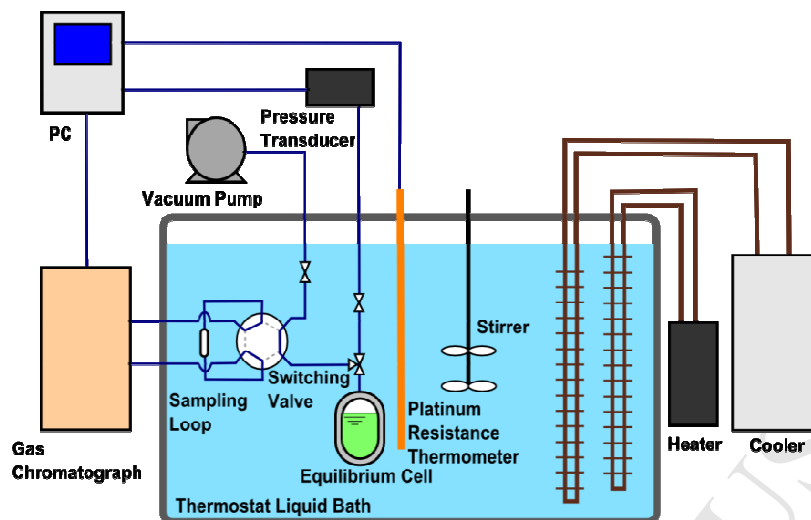


Figure 1. Schematic of vapor-liquid equilibrium measurement apparatus.

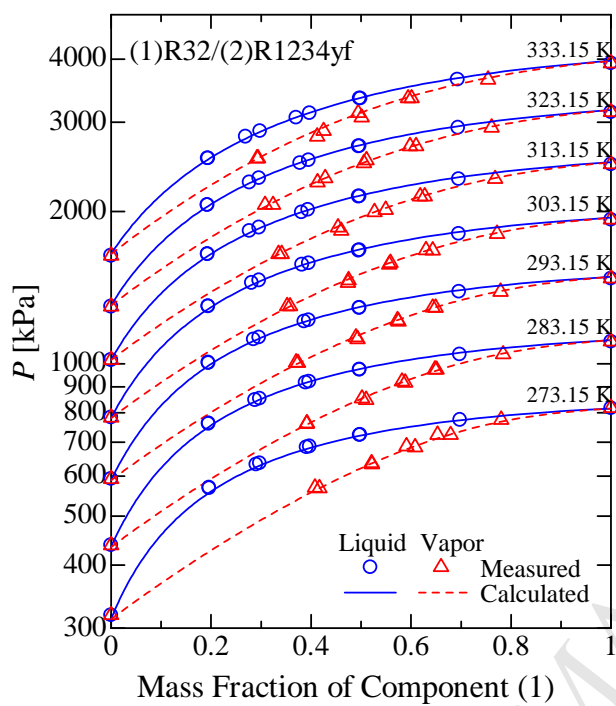


Figure 2. Results of VLE measurements for R32/R1234yf.

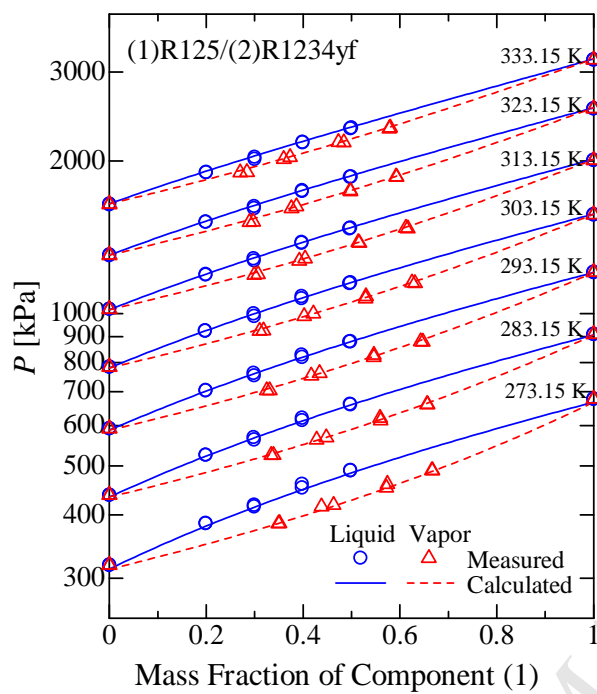


Figure 3. Results of VLE measurements for R134a/R1234yf

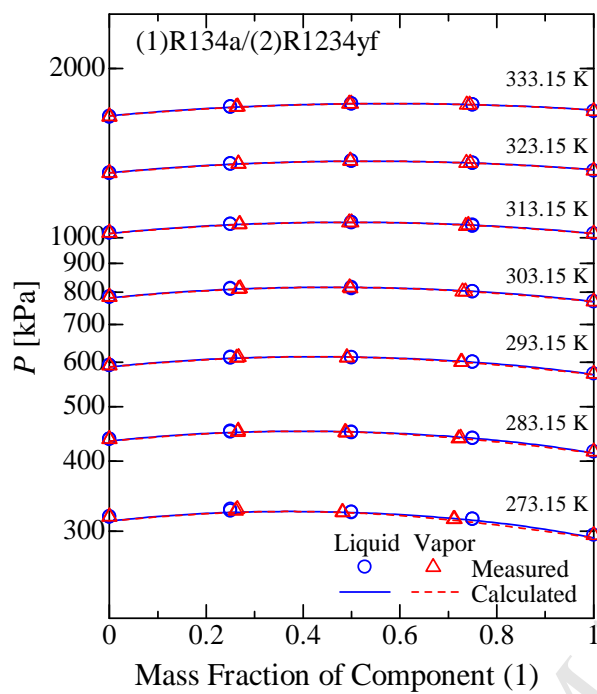


Figure 4. Results of VLE measurements for R134a/R1234yf

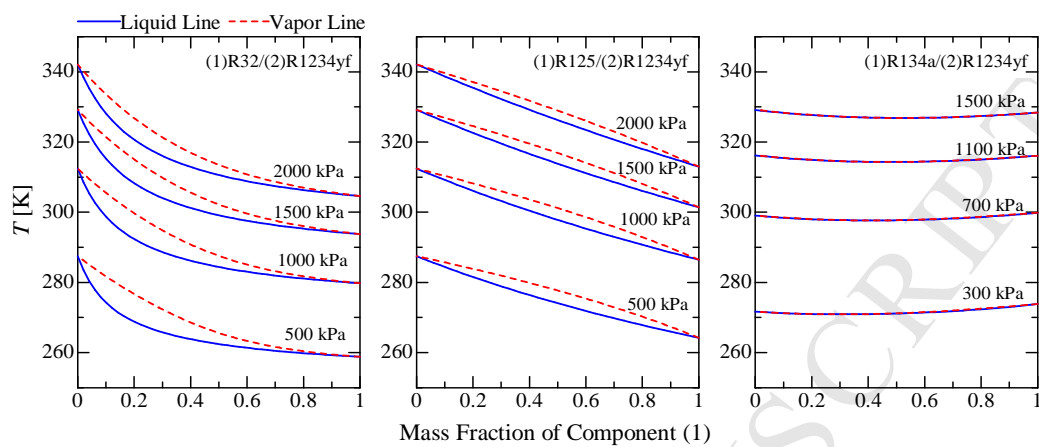


Figure 5. Isobaric VLE diagram

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Figure 1. Schematic of vapor-liquid equilibrium measurement apparatus.

Figure 2. Results of VLE measurements for R32/R1234yf.

Figure 3. Results of VLE measurements for R134a/R1234yf

Figure 4. Results of VLE measurements for R134a/R1234yf

Figure 5. Isobaric VLE diagram

Table 1 Substance constants of components.

Property	Unit	R32	R125	R134a	R1234yf
M	g mol^{-1}	52.02	120.02	102.03	114.04
T_c	K	351.26	339.17	374.21	367.85
P_c	kPa	5782	3618	4059	3382
ω	-	0.277	0.305	0.327	0.280

Table 2 Average absolute deviation of saturated pressure and binary interaction parameters.

Equation of State	Peng-Robinson		Helmholtz	
	Optimized (k_{12})	$k_{12} = 0$	Optimized (ζ_{12})	Default [REFPROP] (ζ_{12})
R32/R1234yf	0.63% (0.037)	6.31% (0)	1.13% (-33.80)	3.63% (-44.43)
R125/R1234yf	0.50% (0.004)	0.61% (0)	0.35% (-1.16)	5.27% (-18.90)
R134a/R1234yf	0.33% (0.020)	2.70% (0)	0.20% (-10.36)	4.35% (-25.96)

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Table A.1 Data of VLE Measurements for (1) R32/(2) R1234yf

Table A.2 Data of VLE Measurements for (1) R32/(2) R1234yf

Table A.3 Data of VLE Measurements for (1) R125/(2) R1234yf

Table A.4 Data of VLE Measurements for (1) R125/(2) R1234yf

Table A.5 Data of VLE Measurements for (1) R134a/(2) R1234yf

Table A.6 Data of VLE Measurements for (1) R134a/(2) R1234yf

Table 1 Substance constants of components.

Table 2 Average absolute deviation of saturated pressure and binary interaction parameters.

Vapor-liquid equilibria measurement results for three binary refrigerant mixtures of R1234yf with R32, R125, and R134a are presented. Equilibrium pressures were measured at temperatures from 273 K to 333 K at 10 K intervals for each binary refrigerant mixture. Measured data were correlated by using Helmholtz-type equation of state combined with a mixing rule.