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Bubble-Point Pressures and Liquid Densities of Mixtures Blended with Difluoromethane, Pentafluoroethane, and 1,1,1-Trifluoroethane

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Measurements of the bubble-point pressures and the liquid densities of the binary difluoromethane + 1,1,1-trifluoroethane (R-32 + R-143a) and the ternary difluoromethane + pentafluoroethane + 1,1,1-trifluoroethane (R-32 + R-125 + R-143a) refrigerant mixtures at temperatures from 280 to 320 K in 10 K intervals are reported. The experimental apparatus used in the measurement is a magnetic densimeter coupled with a variable volume cell. The estimated uncertainties are ±12 mK in temperature, ±10 kPa in pressure, and ±0.2% in density, whereas the uncertainty in the determined composition of mixture is estimated to be ±0.3 mass %. On the basis of the measured bubble-point pressures, the optimization of the binary interaction parameter of the Peng−Robinson equation, which reproduces the available data within ±1%, is discussed. Empirical correlations for the saturated-liquid and compressed-liquid densities of mixtures composed of R-32, R-125, and R-143a with an accuracy within ±0.3% are also developed.

Introduction

Binary and/or ternary mixtures composed of difluoromethane (R-32), pentafluoroethane (R-125), and 1,1,1-trifluoroethane (R-143a) are expected to be potential alternatives to chlorodifluoromethane (R-22) and R-502, an azeotropic blend of 48.8 mass % R-22 and 51.2 mass % R-115 (pentafluorochloroethane). This is due to their near-azeotropic characteristics that promote behavior similar to that of a pure compound. In an extensive research program on the promising HFC (hydrofluorocarbon) refrigerant mixtures, we have already published measurements of bubble-point pressures and liquid densities of the binary mixtures R-32 + R-125 (Widiatmo et al., 1993) and R-125 + R-143a (Widiatmo et al., 1995; Fujimine et al., 1999). The aim of the present study is to conduct similar measurements of the binary mixture R-32 + R-143a and the ternary mixture R-32 + R-125 + R-143a in wide ranges of composition and temperature.

Experimental Section

A magnetic densimeter coupled with a variable-volume cell has been used in the present work to measure the liquid phase *PVTx* properties of the binary R-32 + R-143a and the ternary R-32 + R-125 + R-143a mixtures. The experimental apparatus is shown in Figure 1. The apparatus consists of a temperature control and measurement section, a pressure control and measurement section, and a density measurement section. The temperature is determined by means of a platinum resistance thermometer placed in the vicinity of the sample cell immersed in a thermostated fluid bath. The pressure is measured with a quartz pressure transducer, while the density is obtained by using a magnetic densimeter. By combining the magnetic densimeter with a variable-volume cell, it is possible to create a vapor−liquid coexisting state or a compressed-liquid phase in the liquid sample. The bubble-point condition is determined from careful visual observation of the appearance and disappearance of a bubble in a liquid sample. In the case of mixtures, the composition of the mixture is determined through weighing the supply vessels before and after sample condensation into the variable-volume cell. Detailed explanations of the present apparatus as well as experimental procedures have been reported elsewhere (Widiatmo et al., 1993).

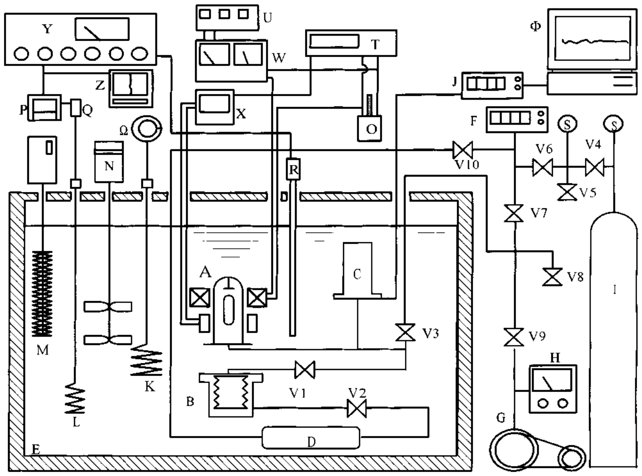

Figure 1. Experimental apparatus: (A) magnetic densimeter; (B) variable-volume cell; (C) digital quartz-pressure transducer; (D) damper; (E) thermostat; (F) digital-quartz pressure gauge; (G) vacuum pump; (H) vacuum gauge; (I) nitrogen gas; (J) digital quartz pressure computer; (K) main heater; (L) subheater; (M) cooler; (N) stirrer; (O) standard resistor; (P) PID controller; (R) standard platinum resistance thermometer; (S) pressure gauge; (T) digital multimeter; (U) current controller; (V1−10) valves; (W) DC power supply; (X) galvanometer; (Y) thermometer bridge; (Z) pen recorder; (Ω) transformer; (Φ) personal computer.

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Table 1. Bubble-Point Pressures and Saturated-Liquid Densities of R-32 + R-143a

x_{R-32}/mol·mol^{-1}	T/K	P/MPa	ρ/kg·m^{-3}	x_{R-32}/mol·mol^{-1}	T/K	P/MPa	ρ/kg·m^{-3}
0	249.98_1	0.281	1097.3	0.502_4	279.98_8	0.945	1005.9
0	259.98_4	0.401	1065.4	0.502_4	289.98_8	1.257	968.2
0	269.98_7	0.562	1032.7	0.502_4	299.98_7	1.642	925.3
0	279.98_8	0.764	998.4	0.502_4	309.98_7	2.108	878.0
0	279.98_8	0.762	996.9	0.502_4	319.98_7	2.667	822.7
0	289.98_8	1.015	959.4	0.749_7	279.98_8	0.992	1015.2
0	289.98_8	1.017	961.3	0.749_7	289.98_8	1.324	977.1
0	299.98_6	1.326	919.9	0.749_7	299.98_7	1.734	935.0
0	299.98_8	1.324	918.9	0.749_7	309.98_7	2.231	888.7
0	309.98_5	1.702	873.5	0.749_7	319.98_7	2.830	833.9
0	309.98_6	1.700	872.8	0.749_7	319.98_7	2.832	834.1
0	319.98_6	2.149	817.7	1.0	279.98_7	1.007	1030.0
0	319.98_6	2.150	818.6	1.0	279.98_7	1.007	1030.7
0	329.98_6	2.689	750.0	1.0	289.98_7	1.347	993.8
0.248_3	279.98_8	0.868	1001.4	1.0	289.98_7	1.349	993.2
0.248_3	289.98_8	1.152	963.6	1.0	299.98_6	1.773	952.6
0.248_3	299.98_7	1.502	920.9	1.0	299.98_6	1.772	951.9
0.248_3	309.98_7	1.925	873.8	1.0	309.98_6	2.293	907.5
0.248_3	319.98_7	2.433	818.5	1.0	319.98_4	2.918	856.5

Through the procedure adopted in the present study, the temperature, pressure, and density measurements can be performed within the uncertainties of ±12 mK, ±10 kPa, and ±0.2%, respectively. The uncertainty in the composition of the mixture is estimated to be not greater than ±0.3 mass %. Analyses of our sample purities by the manufacturers resulted in 99.99 mol % for R-32, 99.96 mol % for R-125, and 99.998 mol % for R-143a, respectively. No further purification has been done in the present work.

Results and Discussion

The bubble-point pressures and the liquid-phase *PVTx* properties of the binary R-32 + R-143a system have been measured for temperatures from 280 to 320 K at 10 K intervals and for compositions from 0 to 100 mass % in 25 mass % intervals. The measured bubble-point pressures and the saturated-liquid densities are listed in Table 1, while the liquid-phase *PVTx* properties are tabulated in Table 2.

Measurements of the bubble-point pressures and liquid-phase *PVTx* properties of the ternary R-32 + R-125 + R-143a mixture at a composition of 33.56/33.28/33.16 mol % were completed for temperatures from 280 to 320 K at 10 K intervals. The measured property data are given in Tables 3 and 4.

As we have reported previously (Widiatmo et al., 1993), the binary R-32 + R-125 system is an azeotropic mixture for which a minimum temperature exists in the vicinity of a composition with 80 mass% R-32. The binary R-125 + R-143a system is also considered an azeotropic blend with a maximum temperature, especially at lower temperatures. For the ternary R-32 + R-125 + R-143a system, the present measurements cover only a single composition so that the existence of any azeotrope in this ternary system cannot be identified experimentally. However, from our calculation of the bubble-point and dew-point pressures of the ternary R-32 + R-125 + R-143a system, it seems likely that the present ternary system is a nonazeotropic blend.

The bubble-point pressure representation in terms of the Peng−Robinson (PR) equation (Peng and Robinson, 1976) has been evaluated in the present work. Table 5 tabulates the parameters used in the original PR equation. The binary interaction parameters used in the calculation of the bubble-point pressures of the binary R-32 + R-143a and R-125 + R-143a systems were determined to be constant with temperature, while those of R-32 + R-125 were determined to be a function of temperature, as already reported (Widiatmo et al., 1997). The optimized binary interaction parameters k_{ij} are given in Table 6, where T denotes the temperature in K.

The bubble-point pressure deviation from the PR equation is depicted in Figure 2. Also shown in Figure 2 are the available bubble-point pressures reported by Kleemiss (1997), Nagel and Bier (1995), Zhelezny et al. (1995), and Higashi (1993). Except for some data by Higashi which show strong temperature dependence, and a single datum by Nagel and Bier, the optimized PR equation represents the available measured data within ±1%, as shown in Figure 2. Thus, the optimized PR equation can be utilized to calculate the temperature glide of the refrigerant mixtures. From such calculations it has been confirmed that the temperature glide of mixtures consisting of R-32, R-125, and R-143a is smaller than 1 K, as typically shown in Figure 3. This small temperature glide may indicate the mixtures are nearly azeotropic.

Figure 2 also illustrates the deviation of the measured bubble-point pressures of the ternary R-32 + R-125 + R-143a system from the PR equation, which merely requires the binary interaction parameters of the binary R-32 + R-125, R-32 + R-143a, and R-125 + R-143a systems given in Table 6. Figure 2 indicates that the PR equation optimized with the proposed procedure represents satisfactorily the bubble-point pressure of the ternary system. The deviation of the measured bubble-point pressures from the optimized PR equation does not exceed ±5 kPa.

The measured saturated liquid densities of refrigerant mixtures composed of R-32, R-125, and R-143a are represented using the saturated-liquid density correlation given in eq 1. This type of equation has also successfully been applied to binary refrigerant mixtures composed of R-32, R-125, and R-134a (Widiatmo et al., 1995).

$$\frac{\rho_s}{\rho_{Cm}} - 1 = A_m\left(1 - \frac{T}{T_{Cm}}\right)^{a_m} + B_m\left(1 - \frac{T}{T_{Cm}}\right)^{b_m} + C_m\left(1 - \frac{T}{T_{Cm}}\right)^{c_m} \quad (1)$$

In eq 1, ρ_s denotes the saturated-liquid density (in kg·m^{-3}), ρ_{Cm} and T_{Cm} denote the critical density (in kg·m^{-3}) and temperature (in K), respectively, and the subscript m denotes the mixture. The critical temperatures and critical densities for refrigerant mixtures are correlated by eqs 2 and 3, while the compositional dependence of the parameters a_m, b_m, c_m, A_m, B_m, and C_m was simply correlated by eq 4, where L_i denotes any arbitrary coefficient. The critical

Table 2. Liquid Phase *PVTx* Properties of R-32 + R-143a

x_{R-32}/mol·mol^{-1}	T/K	P/MPa	ρ/kg·m^{-3}
0^a	249.98_1	0.281	1097.3
0	249.98_1	0.504	1097.9
0	249.98_1	1.001	1099.9
0	249.98_1	1.500	1101.3
0	249.98_1	1.993	1103.0
0	249.98_1	2.529	1104.6
0	249.98_1	3.006	1106.1
0^a	259.98_4	0.401	1065.4
0	259.98_4	1.015	1068.4
0	259.98_4	1.538	1070.4
0	259.98_4	2.014	1072.2
0	259.98_4	2.513	1074.1
0	259.98_4	3.021	1076.2
0^a	269.98_7	0.562	1032.7
0	269.98_7	1.031	1035.7
0	269.98_7	1.532	1038.0
0	269.98_7	2.055	1040.7
0	269.98_7	2.524	1043.0
0	269.98_7	3.013	1045.2
0^a	279.98_8	0.764	998.4
0^a	279.98_8	0.762	996.9
0	279.98_8	1.003	1000.1
0	279.98_8	1.303	1002.6
0	279.98_8	1.602	1004.3
0	279.98_8	1.901	1006.1
0	279.98_8	2.202	1007.8
0	279.98_8	2.503	1009.7
0	279.98_8	3.007	1013.7
0^a	289.98_8	1.015	959.4
0^a	289.98_8	1.017	961.3
0	289.98_8	1.218	962.9
0	289.98_8	1.501	965.2
0	289.98_8	1.804	967.7
0	289.98_8	2.203	970.8
0	289.98_8	2.603	973.7
0	289.98_8	3.003	976.8
$0.502_4{}^a$	279.98_8	0.945	1005.9
0.502_4	279.98_8	1.507	1008.9
0.502_4	279.98_8	2.017	1011.9
0.502_4	279.98_8	2.509	1014.1
0.502_4	279.98_8	3.015	1016.4
$0.502_4{}^a$	289.98_8	1.257	968.2
0.502_4	289.98_8	1.535	970.1
0.502_4	289.98_8	2.013	974.0
0.502_4	289.98_8	2.514	977.3
0.502_4	289.98_8	3.015	980.2
$0.502_4{}^a$	299.98_7	1.642	925.3
0.502_4	299.98_7	2.029	929.0
0.502_4	299.98_7	2.502	933.8
0.502_4	299.98_7	3.005	937.8
$0.502_4{}^a$	309.98_7	2.108	878.0
0.502_4	309.98_7	2.530	883.6
0.502_4	309.98_7	3.004	889.7
$0.502_4{}^a$	319.98_7	2.667	822.7
0.502_4	319.98_7	3.000	829.7
$0.749_7{}^a$	279.98_8	0.992	1015.2
0.749_7	279.98_8	1.511	1017.1
0.749_7	279.98_8	2.009	1020.6
0.749_7	279.98_8	2.504	1023.1
0.749_7	279.98_8	3.005	1025.3
$0.749_7{}^a$	289.98_8	1.324	977.1
0.749_7	289.98_8	2.003	982.0
0.749_7	289.98_8	2.504	984.8
0.749_7	289.98_8	3.004	988.0
$0.749_7{}^a$	299.98_7	1.734	935.0
0.749_7	299.98_7	2.514	941.5
0^a	299.98_6	1.326	919.9
0^a	299.98_6	1.324	918.9
0	299.98_6	1.506	922.1
0	299.98_6	2.002	927.4
0	299.98_6	2.500	932.6
0	299.98_6	3.003	937.2
0^a	309.98_6	1.702	873.5
0^a	309.98_6	1.700	872.8
0	309.98_6	2.003	878.1
0	309.98_6	2.505	885.5
0	309.98_6	3.002	891.8
0^a	319.98_6	2.149	817.7
0^a	319.98_6	2.150	818.6
0	319.98_6	2.510	827.6
0	319.98_6	2.998	837.9
0^a	329.98_6	2.689	750.0
0	329.98_6	3.013	764.0
$0.248_3{}^a$	279.98_8	0.868	1001.4
0.248_3	279.98_8	1.501	1005.1
0.248_3	279.98_8	2.021	1008.6
0.248_3	279.98_8	2.513	1011.4
0.248_3	279.98_8	3.008	1013.7
$0.248_3{}^a$	289.98_8	1.152	963.6
0.248_3	289.98_8	1.550	966.7
0.248_3	289.98_8	2.015	970.2
0.248_3	289.98_8	2.511	974.1
0.248_3	289.98_8	3.002	977.7
$0.248_3{}^a$	299.98_7	1.502	920.9
0.248_3	299.98_7	1.997	926.1
0.248_3	299.98_7	2.505	931.1
0.248_3	299.98_7	3.004	935.6
$0.248_3{}^a$	309.98_7	1.925	873.8
0.248_3	309.98_7	2.513	882.2
0.248_3	309.98_7	3.006	889.0
$0.248_3{}^a$	319.98_7	2.433	818.5
0.248_3	319.98_7	2.995	831.0
0.749_7	299.98_7	3.000	945.3
$0.749_7{}^a$	309.98_7	2.231	888.7
0.749_7	309.98_7	2.488	891.4
0.749_7	309.98_7	3.004	897.3
$0.749_7{}^a$	319.98_7	2.830	833.9
$0.749_7{}^a$	319.98_7	2.832	834.1
0.749_7	319.98_7	3.000	837.3
1.0^a	279.98_7	1.007	1030.0
1.0^a	279.98_7	1.007	1030.7
1.0	279.98_7	1.532	1033.1
1.0	279.98_7	2.029	1035.1
1.0	279.98_7	2.523	1037.1
1.0	279.98_7	3.017	1039.3
1.0^a	289.98_7	1.347	993.8
1.0^a	289.98_7	1.349	993.2
1.0	289.98_7	1.515	994.3
1.0	289.98_7	2.005	996.7
1.0	289.98_7	2.503	999.5
1.0	289.98_7	3.005	1002.2
1.0^a	299.98_6	1.773	952.6
1.0^a	299.98_6	1.772	951.9
1.0	299.98_6	2.015	953.3
1.0	299.98_6	2.508	957.1
1.0	299.98_6	3.018	960.6
1.0^a	309.98_6	2.293	907.5
1.0	309.98_6	2.519	909.5
1.0	309.98_6	3.016	914.1
1.0^a	319.98_4	2.918	856.5
1.0	319.98_4	3.007	857.5

[a] Experimentally determined bubble-point.

temperatures and critical densities of single-component refrigerants are listed in Table 5; the numerical values for the parameters a, b, c, A, B, and C for pure substances are given in Table 7.

$$\nu_{Cm} = \sum x_i \nu_{Ci} + \sum\sum x_i x_j \Delta\nu_{ij}({\nu_{Ci}}^{1/3} + {\nu_{Cj}}^{1/3}){\nu_{Ci}}^{1/3}{\nu_{Cj}}^{1/3} \quad (2)$$

$$\nu_{Cm} T_{Cm} = \sum\sum x_i x_j \Delta T_{ij}\sqrt{\nu_{Ci} T_{Ci} \nu_{Cj} T_{Cj}} \quad (3)$$

$$L_m = \sum L_i x_i + \sum\sum x_i x_j \Delta L_{ij} \quad (4)$$

ν with any subscript throughout the present paper denotes the molar volume (in cm^3·mol^{-1}). The subscript i

Table 3. Bubble-Point Pressures and Saturated-Liquid Densities of R-32 + R-125 + R-143a

x_{R-32}/ mol·mol^{-1}	x_{R-125}/ mol·mol^{-1}	T/K	P/MPa	ρ/kg·m^{-3}
0.335_6	0.332_8	279.98_8	0.900	1121.7
0.335_6	0.332_8	289.98_8	1.201	1078.8
0.335_6	0.332_8	299.98_7	1.574	1030.1
0.335_6	0.332_8	309.98_7	2.023	975.9
0.335_6	0.332_8	319.98_7	2.563	911.2

Table 4. Liquid-Phase *PVTx* Properties of R-32 + R-125 + R-143a

x_{R-32}/ mol·mol^{-1}	x_{R-125}/ mol·mol^{-1}	T/K	P/MPa	ρ/kg·m^{-3}
0.335_6[a]	0.332_8	279.98_8	0.900	1121.7
0.335_6	0.332_8	279.98_8	1.506	1125.9
0.335_6	0.332_8	279.98_8	2.014	1129.2
0.335_6	0.332_8	279.98_8	2.507	1132.4
0.335_6	0.332_8	279.98_8	3.015	1135.3
0.335_6[a]	0.332_8	289.98_8	1.201	1078.8
0.335_6	0.332_8	289.98_8	1.511	1081.5
0.335_6	0.332_8	289.98_8	2.012	1086.0
0.335_6	0.332_8	289.98_8	2.502	1090.1
0.335_6	0.332_8	289.98_8	3.011	1094.3
0.335_6[a]	0.332_8	299.98_7	1.574	1030.1
0.335_6	0.332_8	299.98_7	2.002	1035.3
0.335_6	0.332_8	299.98_7	2.498	1040.7
0.335_6	0.332_8	299.98_7	3.005	1046.0
0.335_6[a]	0.332_8	309.98_7	2.023	975.9
0.335_6	0.332_8	309.98_7	2.498	983.6
0.335_6	0.332_8	309.98_7	3.000	991.3
0.335_6[a]	0.332_8	319.98_7	2.563	911.2
0.335_6	0.332_8	319.98_7	2.997	922.8

[a] Experimentally determined bubble-point.

Table 5. Parameters Used in the PR Equation

properties	R-32	R-125	R-143a
T_C/K	351.26[a]	339.17[b]	345.88[c]
P_C/MPa	5.780[d]	3.620[b]	3.764[c]
ρ_C/kg·m^{-3}	427[a]	577[b]	431[c]
M/g·mol^{-1}	52.024	120.02	84.04
ω	0.277	0.306	0.263

[a] Higashi (1996). [b] Higashi (1994). [c] Higashi and Ikeda (1995). [d] Qian et al. (1993).

Table 6. Binary Interaction Parameters for the Binary Systems

binary system	k_{ij} (T in K)
R-32 + R-125	$-0.0466 + 0.000169T$
R-32 + R-143a	0.0116
R-125 + R-143a	-0.0126

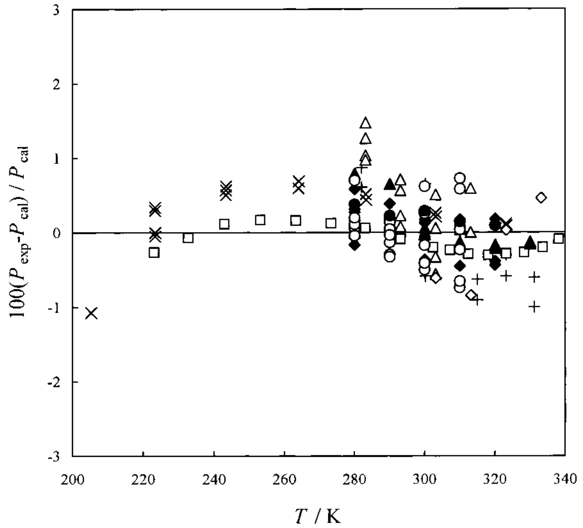

Figure 2. Bubble-point pressure deviation from the PR equation: (◆) this work (R-32 + R-143a); (●) this work (R-32 + R-125 + R-143a); (▲) Fujimine et al. (1999) (R-125 + R-143a); (□) Kleemiss (1997) (R-125 + R-143a); (×) Nagel and Bier (1996) (R-125 + R-143a); (+) Zhelezny et al. (1995) (R-125 + R-143a); (○) Widiatmo et al. (1993) (R-32 + R-125); (△) Higashi (1993) (R-32 + R-125); (◇) Kleemiss (1997) (R-32 + R-125).

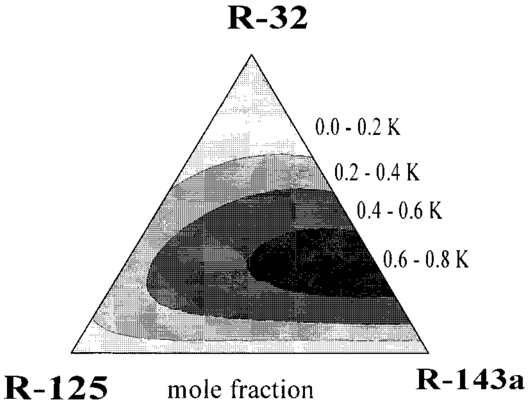

Figure 3. Temperature glide of mixtures blended with R-32, R-125, and R-143a at 500 kPa.

or j denotes a property of single components, while the subscript ij denotes a binary mixture. Δv_{ij} and ΔT_{ij} in eqs 2 and 3 are cross-parameters for the critical molar volume and critical temperature of the mixtures, respectively. ΔL_{ij} in eq 4 represents the cross-parameter for a_m, b_m, c_m, A_m, B_m, and C_m in eq 1. Any cross-parameter l_{ij} in the present paper fulfills the conditions $l_{ij} = l_{ji}$ and $l_{ij,i=j} = 0$.

Higashi (1996), Nagel and Bier (1995, 1996), and Kishizawa et al. (1999a,b) reported the critical temperatures and densities for the binary R-32 + R-125 and R-125 + R-143a systems. Mizukawa et al. (1999) of our laboratory have recently completed their measurements on the critical temperatures and densities of the binary R-32 + R-143a system. Those reported and/or referred data were adopted to develop eq 2 for the respective properties. Equations 2 and 3 are modifications of those used by Thomson et al. (1982), by introducing cross-parameters, Δv_{ij} and ΔT_{ij}, that play a role to indicate whether the properties deviate to positive or negative against the averaged values. In relation to the critical temperature and density of the ternary R-32 + R-125 + R-143a system, there are no reported data available at present. They are calculated in the present work from eqs 2 and 3 by introducing the cross-parameters of its constituent binary systems. The cross-parameters for the critical properties of refrigerant mixtures are summarized in Table 8.

Equation 4 is used by replacing L with a_m, b_m, c_m, A_m, B_m, and C_m in eq 1. The subscripts 1, 2, and 3 in eq 2 represent R-32, R-125, and R-143a, respectively. The basic data sets used to optimize a_m, b_m, c_m, A_m, B_m, and C_m include the present work and those by Widiatmo et al. (1993, 1995) for the binary R-32 + R-125 and R-125 + R-143a systems and by Fujimine et al. (1999) for the binary R-125 + R-143a system. The cross-parameters used in eq 4 are given in Table 9.

Figure 4 illustrates the deviation of measured saturated-liquid densities from eq 1. Also shown in Figure 4 are our saturated liquid density data of the binary R-32 + R-125 and R-125 + R-143a systems reported earlier (Widiatmo et al., 1993, 1995) and the data by Ikeda et al. (1995) in a reduced density range similar to that for the present study. Ikeda and co-workers reported saturated-liquid density

Table 7. Parameters Used in Eq 1

coefficient	R-32	R-125	R-143a
A_i	0.991 467	2.228 14	1.046 23
B_i	1.805 72	0.451 997	1.699 42
C_i	2.343 30	0	0
a_i	0.280	0.370	0.257
b_i	0.530	1.130	0.599
c_i	4.450	0	0

Table 8. Cross-Parameters in Eqs 2, 3, 9, and 10

binary system	$2\Delta v_{ij}$	$2\Delta T_{ij}$	$2\Delta P_{ij}$	$2\Delta\omega_{ij}$
R-32 + R-125	0	2.0446	−0.7290	0.042
R-32 + R-143a	−0.0228	1.9769	−0.3777	0.037
R-125 + R-143a	−0.0055	1.9984	0.0050	0.009

Table 9. Cross-Parameters in Eq 4

binary system	$2\Delta a_{ij}$	$2\Delta b_{ij}$	$2\Delta c_{ij}$	$2\Delta A_{ij}$	$2\Delta B_{ij}$	$2\Delta C_{ij}$
R-32 + R-125	0.030	−0.283	18.472	0.961	−0.972	−2.450
R-32 + R-143a	0.204	−0.019	11.420	1.135	−1.423	−2.266
R-125 + R-143a	0.027	−0.303	0	0.587	−0.770	0

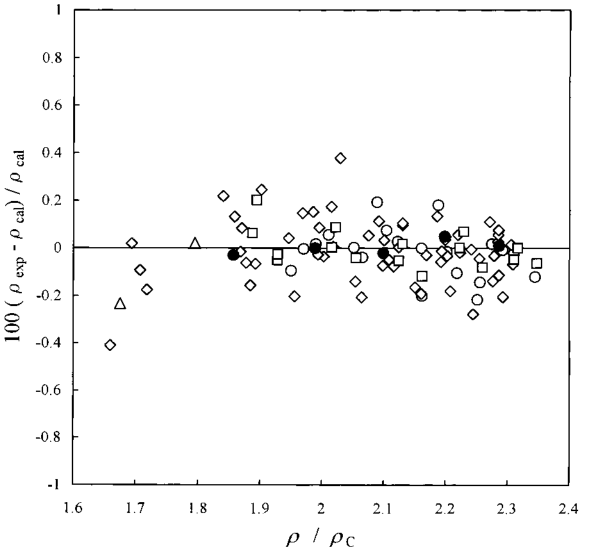

Figure 4. Saturated-liquid density deviation from eq 1: (□) this work (R-32 + R-143a); (●) this work (R-32 + R-125 + R-143a); (○) Widiatmo et al. (1993) (R-32 + R-125); (◇) Fujimine et al. (1999) (R-125 + R-143a); (△) Ikeda and Higashi (1995) (R-125 + R-143a).

data near the critical temperature of the binary R-125 + R-143a system. Their measurements were performed to obtain direct measurements of the critical temperature and density. The present saturated-liquid densities of the binary R-32 + R-143a system are underestimated by eq 1, as indicated in Figure 4. This is due to the procedure of determining the critical temperature, pressure, density, and all coefficients on the basis of the measured compressed-liquid densities instead of the saturated ones. However, the deviation falls within the claimed uncertainty of the density measurement, ±0.2%.

Figure 4 shows that eq 1 excellently represents most of the saturated-liquid density data within ±0.3% except those very near the critical point ($0.989 < T_r < 1$) by Ikeda et al. (1995). The deviations of the data by Ikeda et al. from eq 1 range from +0.66 to −1.5%. The measured saturated-liquid densities of the ternary R-32 + R-125 + R-143a system are also satisfactorily represented. It should be noted that the representation for the ternary mixture was developed from only the cross-parameters of the corresponding binary mixtures in eqs 1−4.

The measured compressed-liquid densities of the refrigerant mixtures in the present study are represented by eq 5, which is a modification of the Sato equation (1981). Equation 5 has also been applied successfully in our previous work concerning the binary and ternary mixtures of R-32, R-125, and R-134a (Widiatmo et al., 1997).

$$\ln \frac{\rho_s}{\rho} = E \ln\left(\frac{P + D}{P_s + D}\right) \qquad (5)$$

In eq 5, ρ_s and P_s are the saturated-liquid density (in kg·m^{-3}) and the bubble-point pressure (in MPa), respectively. ρ_s is obtained from eq 1, while P_s is from eq 6.

$$\ln \frac{P_s}{P_{Cm}} = 5.92715 - \frac{6.09649}{T_r} - 1.28863 \ln T_r + 0.169347 T_r^{6} + \omega_m\left(13.4902 - \frac{13.8756}{T_r} - 11.1704 \ln T_r + 0.385433 T_r^{6}\right) \qquad (6)$$

D and E are given in eqs 7 and 8

$$\frac{D}{P_{Cm}} + 1 = 13.406\tau + 66.7486\tau^2 - 97.1726\tau^3 + \tau^4 \exp(-22.4997 + 226.792\omega_m - 451.956\omega_m^{2}) \qquad (7)$$

$$E = -0.147397 + 0.192097\omega_m \qquad (8)$$

T_r in eq 6 is T/T_{Cm}, and τ is $1 - T_r$; T_{Cm} is calculated from eqs 2 and 3. Equation 6 is the presently adopted bubble-point pressure correlation that is different from that proposed in our previous paper (Widiatmo et al., 1997). This improvement became feasible thanks to the existence of the reported critical pressure data by Nagel and Bier (1995, 1996) for the binary R-32 + R-125 and R-125 + R-143a systems. The mixing rule for the critical pressure (in MPa) P_{Cm} is given by eq 9, whereas that for the acentric factor ω_m is given by eq 10.

$$P_{Cm} = \sum x_i P_{Ci} + \sum\sum x_i x_j \Delta P_{ij} \qquad (9)$$

$$\omega_m = \sum x_i \omega_i + \sum\sum x_i x_j \Delta\omega_{ij} \qquad (10)$$

The cross-parameters ΔP_{ij} in eq 9 for the binary R-32 + R-125 and R-125 + R-143a systems were optimized on the basis of the critical pressure data by Nagel and Bier (1995, 1996). Since, for the binary R-32 + R-143a system, neither critical temperature nor critical pressure data are available, the critical pressure of this binary mixture is derived from the bubble-point pressure data with the aid of eq 6. The optimized values of ΔP_{ij} for all the mixtures of present interest are tabulated in Table 8. Similar to that of the binary R-32 + R-143a system, there is no report of a critical pressure measurement of the ternary R-32 + R-125 + R-143a system. Therefore, in the present work, the critical pressure of the ternary system is calculated from eq 9 by introducing the cross-parameter ΔP_{ij} of its constituent binary mixtures.

Equation 6 takes a functional form similar to that used by Lee and Kesler (1975), introducing the mixing rule for the acentric factor ω_m given in eq 10. The coefficients in eq 6 have been optimized so as to fulfill the criteria given below for a vapor pressure correlation:

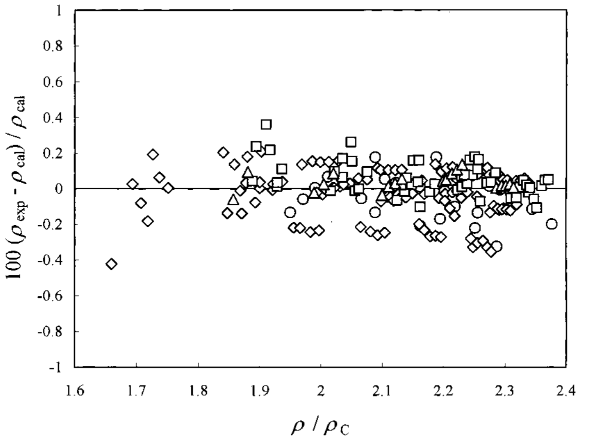

Figure 5. Liquid density deviation from eq 5: (□) this work (R-32 + R-143a); (△) this work (R-32 + R-125 + R-143a); (○) Widiatmo et al. (1993) (R-32 + R-125); (◇) Fujimine et al. (1999) (R-125 + R-143a).

(1) at $T = T_{Cm}$, $P_s = P_{Cm}$

(2) at $T = T_{Cm}$, $d\alpha/dT_r = 0$, where α is the Riedel factor defined as $\alpha = T_r \; d \ln P_r/dT_r$

(3) $\omega = -\log(P_s/P_{Cm})_{T_r=0.7} - 1$

The basic input data are the present bubble-point pressure data in addition to those by Widiatmo et al. (1993, 1995, 1997) to cover the binary and ternary mixtures of R-32, R-125, and R-134a and those by Fujimine et al. (1999). Using eq 6, the present bubble-point pressures are reproduced within ±2%.

Equations 7 and 8 are also revised versions from our previous representations (Widiatmo et al., 1997), by applying the functional forms similar to those used by Thomson et al. (1982). The coefficients of these equations are determined on the basis of the present compressed-liquid densities complimented with those of our previous work (Widiatmo et al., 1997).

By incorporating eqs 6−8 with eq 5, the result leads to a compressed-liquid density representation within ±0.3%, as shown in Figure 5 except a single datum by Fujimine et al. (1999) for the binary R-125 + R-143a system. Figure 5 shows not only the deviation of the compressed-liquid densities but also that of the saturated-liquid densities of the binary and ternary mixtures of R-32, R-125, and R-143a. It is important to note that eq 5 is developed mostly on the basis of compressed-liquid densities at pressures below 4 MPa. Since engineering applications of those refrigerants in air conditioning and refrigeration are limited to that pressure range, it seems worthwhile to claim the importance of eq 5 in engineering applications. Since eq 5 is also developed on the basis of the compressed-liquid densities of the mixtures blended with R-32, R-125, and/or R-134a, it also works effectively to reproduce the corresponding experimental data for the binary and ternary mixtures of R-32, R-125, and R-134a.

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