Measurements of Vapor Pressures and *PVT* Properties of Pentafluoroethyl Methyl Ether and 1,1,1-Trifluoroethane

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Measurements of the vapor pressures and the *PVT* properties of pentafluoroethyl methyl ether ($CF_3CF_2OCH_3$, HFE-245mc) at temperatures from 310 K to the critical temperature (406.8 K) and from (360 to 440) K along 12 isochores, respectively, are reported. Similar measurements on 1,1,1-trifluoroethane (CF_3CH_3, HFC-143a) from (300 to 345.62) K for vapor pressures and from the vicinity of critical temperature to 430 K along 3 isochores for *PVT* properties have also been conducted. The measurements were performed by using a constant volume method with uncertainties of ±10 mK in temperature, ±1.4 kPa in pressure, and ±0.2 $kg\cdot m^{-3}$ in density. Comparison of the measured vapor pressures of HFE-245mc with the reported correlation shows an excellent agreement within ±2 kPa. An equation of state recently developed by the present authors was also found to be effective to represent the present *PVT* properties of HFE-245mc within ±1% in pressure in the vapor phase and within ±0.05% in density in the liquid phase.

Introduction

Because of the significant global warming impact of hydrofluorocarbons (HFCs), which are currently applied as long-term alternative refrigerants, the Research Institute of Innovative Technology for the Earth (RITE), Kyoto, Japan, has proposed the hydrofluoroethers (HFEs), which have zero ozone depletion potential (ODP) and significantly low global warming potential (GWP), as new-generation alternative refrigerants. Earlier related studies include those by Wang et al. (1991) and Salvi-Narkhede et al. (1992), who reported measurements of vapor pressures, liquid molar volumes, and critical properties of some fluorinated ethers. Sako et al. (1994, 1996) published vapor pressure and critical property measurements of fluorinated ethers proposed by the RITE. In 1998 Beyerlein et al. reported the vapor pressures and bubble-point pressures of several compounds including fluorinated ethers. Kul et al. (2000, 2001) conducted vapor pressure measurements for some pure fluorinated ethers and bubble-point pressure measurements for several HFE mixtures with HFCs of ethane derivatives using the same apparatus used by Beyerlein et al. (1998).

Among the candidates proposed by the RITE, pentafluoroethyl methyl ether ($CF_3CF_2OCH_3$, HFE-245mc) is a promising candidate to replace 1,2-dichloro-1,1,2,2-tetrafluoroethane ($CClF_2CClF_2$, R-114), especially for vapor-compression heat pump system application. The basic thermodynamic properties of HFE-245mc are given in Table 1. Our earlier works for HFE-245mc include that by Ohta et al. (2001), who reported vapor pressure, saturated-liquid and compressed-liquid density measurements, and that by Yoshii et al. (2001), who completed a series of saturation density measurements in the critical region and determined the critical temperature and critical density. The present paper aims to provide highly accurate sets of data for vapor pressures and *PVT* properties of HFE-245mc, especially in its gaseous phase. For the reconfirmation of the reliability of the experimental apparatus used throughout the present study, measurements of vapor pressures and *PVT* properties of 1,1,1-trifluoroethane (HFC-143a) have been conducted. Comparison of the measured vapor pressures for HFE-245mc with the other available data is presented in terms of the vapor pressure and saturated-liquid density correlations reported (Widiatmo and Watanabe, 2001), whereas the measured *PVT* properties are compared with the equation of state developed (Widiatmo and Watanabe, 2001).

Table 1. Basic Thermodynamic Properties of HFE-245mc

	$CF_3CF_2OCH_3$
T_c/K	406.83[a]
P_c/kPa	2887[b]
ρ_c/$kg\cdot m^{-3}$	509[a]
M/$kg\cdot kmol^{-1}$	150.054

[a] Yoshii et al. (2001). [b] Widiatmo and Watanabe (2001).

Experimental Studies

Measurements throughout the present work have been conducted using a constant volume apparatus shown in Figure 1. This apparatus is similar to that used in our earlier studies (Piao et al., 1990) with a reliability well confirmed. A prescribed mass of the sample with research grade purity (99.9967 mol% for HFE-245mc and 99.94 mass% for HFC-143a according to the analysis by the chemical manufacturers) is confined in a spherical thick-walled sample cell (A) made of stainless steel with ~139 cm^3 in its inner volume, and it is installed in a thermostated fluid bath (C).

The sample temperature is not detected directly but is considered to be the same as that of the heat transfer medium, silicone oil, within the thermostated fluid bath; a series of measurements have been performed under a

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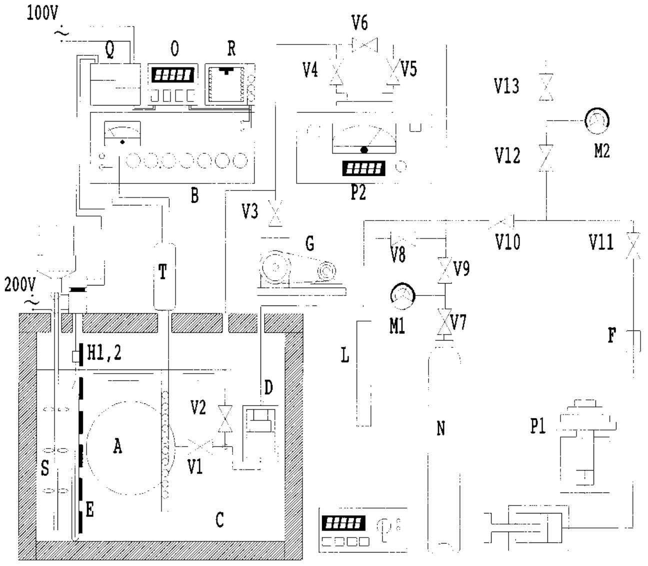

Figure 1. Experimental apparatus: A, sample cell; B, thermometer bridge; C, thermostated bath; D, differential pressure indicator; E, partition plate; F, dust filter; G, vacuum pump; H1,2, main/sub heater; I, digital resistance meter; J, pressure damper; M1,2, pressure gauges; N, nitrogen bottle; O, PID controller; P1, air piston type pressure gauge; P2, Bourdon-tube pressure gauge; Q, thyristor regulator; R, pen recorder; S, stirrer; T, platinum resistance thermometer; V1−13, valves.

well-established thermal equilibrium condition between the sample and bath fluid. The temperature of the bath fluid detected by a standard 25 Ω platinum resistance thermometer (T) is automatically controlled within ±2 mK of its fluctuation using a PID controller (O) and is measured with a thermometer bridge (B).

The sample pressure is then measured, with the aid of an air-piston pressure gauge (P1), as that of nitrogen gas supplied from its bottle (N), which serves as a pressure transferring medium existing at the upper space of the stainless steel membrane equipped in a differential pressure indicator (D).

The sample density, on the other hand, is determined on the basis of the sample mass weighed by a precision chemical balance within the estimated uncertainty of ±3 mg and the inner volume of the sample cell associated with required minor corrections owing to thermal expansion and hydrostatic pressure deformation.

The experimental uncertainties of the present measurements have been estimated on the basis of the ISO recommendation (1993) associated with a coverage factor of 2. The expanded uncertainties of measurements are ±10 mK in temperature, ±1.4 kPa in pressure, and ±0.07% in density, respectively.

Results and Discussion

Preceding the measurements on HFE-245mc, the vapor pressures and *PVT* properties of HFC-143a have been measured from 300 K up to the critical temperature (345.857 K) and from the vicinity of critical temperature up to 430 K along three isochores, respectively. The measured results for the vapor pressures of HFC-143a are listed in Table 2, whereas those for the *PVT* properties are given in Table 3.

Table 2. Vapor Pressures of HFC-143a

T/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa
300.00	1325.3	325.00	2408.3	340.13	3340.1
305.00	1504.7	328.13	2581.7	342.13	3482.4
308.13	1625.5	330.00	2688.6	342.50	3508.1
310.00	1700.0	330.00	2688.4	343.13	3556.8
310.00	1700.1	333.13	2878.1	344.13	3631.6
313.13	1833.7	335.00	2994.0	345.00	3696.3
315.00	1916.0	335.13	3004.3	345.00	3695.6
318.13	2061.1	338.12	3201.7	345.12	3708.2
320.00	2151.1	340.00	3328.8	345.62	3748.3
320.00	2151.1	340.00	3328.1		
323.13	2310.1	340.12	3339.4		

Table 3. *PVT* Properties of HFC-143a

T/K	*P*/kPa	ρ/kg·m^{-3}	*T*/K	*P*/kPa	ρ/kg·m^{-3}
a Series			c Series		
348.12	3949.0	430.4	346.13	3787.3	438.8
353.12	4355.0	430.3	353.12	4365.3	438.7
363.12	5178.0	430.1	363.12	5208.8	438.5
373.12	6007.1	429.9	373.12	6062.5	438.3
383.13	6840.2	429.7	383.12	6922.7	438.1
393.12	7674.9	429.5	393.13	7785.7	437.8
403.13	8510.1	429.3			
413.13	9343.7	429.1			
423.13	10176.3	428.8			
433.13	11008.2	428.6			
b Series					
350.00	4101.0	435.9			
360.00	4931.3	435.7			
370.00	5774.8	435.5			
380.00	6628.2	435.3			
390.08	7489.2	435.0			
400.00	8338.2	434.8			
410.00	9194.4	434.6			
420.00	10049.6	434.4			
430.00	10904.6	434.2			

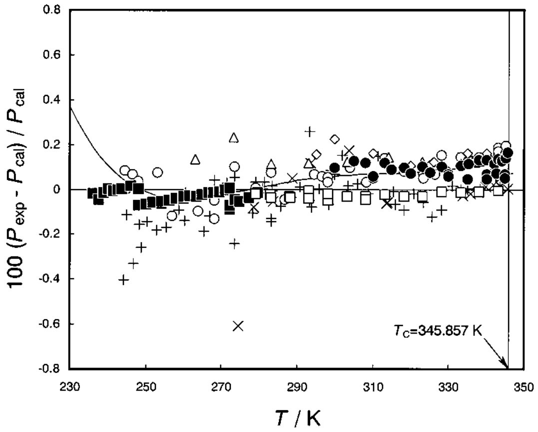

Figure 2. Vapor pressure deviation of HFC-143a from Lemmon and Jacobsen eq: ●, this work; ×, Fukushima et al. (1993); +, Giuliani et al. (1994); △, Fujiwara et al. (1995); ◇, Zhang et al. (1995); ○, Giuliani et al. (1995); ■, Weber et al. (by ebulliometer, 1996); □, Weber et al. (by *PVT* apparatus, 1996); —, Giuliani et al. (1995).

Figure 2 illustrates the deviation of the measured vapor pressures of HFC-143a from the vapor pressure correlation by Lemmon and Jacobsen (2000), which was used as an ancillary correlation in developing the equation of state for HFC-143a accepted by the International Energy Agency (IEA) Annex-18 as the Recommended International Equation of State. Also shown are the reported vapor pressures by Fukushima et al. (1993), Giuliani et al. (1994, 1995), Zhang et al. (1995), Fujiwara et al. (1995), and Weber et al. (1996), who used the isochoric cell method and ebulliometer in their measurements. The solid curve in Figure 2 is vapor pressures calculated from the correlation by Giuliani et al. (1995). As shown in Figure 2 the present measurements agree well with the data by Giuliani et al. (1995), Zhang et al., Fujiwara and Piao (1995), and some data by Fukushima et al. (1993). Smooth correlation

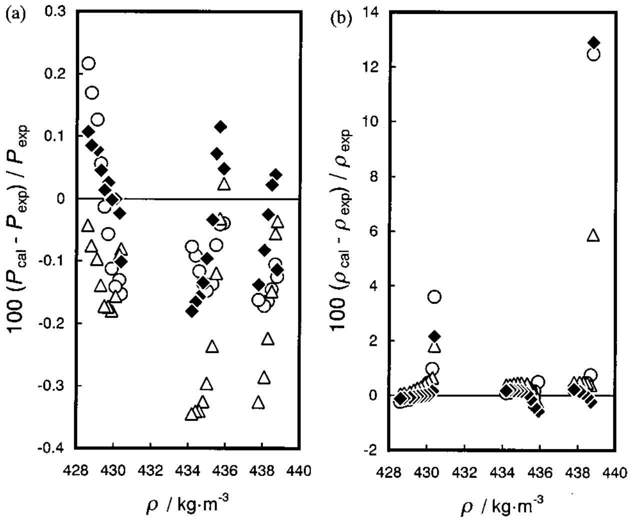

Figure 3. *PVT* property deviation of HFC-143a: a, pressure deviation; b, density deviation; ◆, from equation by Outcalt and McLinden (1997); △, from equation by Li et al. (1999); ○, from equation by Lemmon and Jacobsen (2001).

between the present vapor pressures and those by Weber et al. (1996) obtained by ebulliometer at lower temperatures can also be observed from Figure 2. This fact may reflect the reliability of the present isochoric apparatus for vapor pressure measurement. Compared to those data, some of the data by Fukushima et al. (1993), data by Giuliani et al. (1994), and those by Weber et al. (1996) obtained by the isochoric apparatus show systematic small differences of 0.1%.

Comparisons are made between the present *PVT* properties of HFC-143a and the available equation of state recently reported by Outcalt and McLinden (1997) that was adopted in REFPROP ver. 6.01 (McLinden et al., 1998), by Li et al. (1999), and by Lemmon and Jacobsen (2000) as shown in Figure 3. The abscissa in Figure 3 denotes the density. The equation by Outcalt and McLinden (1997) and the internationally recommended one by Lemmon and Jacobsen (2000) show almost the same data reproducibility within ±0.2% in pressure. The Li equation represents relatively well the present measurements within ±0.2% in pressure for densities lower than the critical density. It then shows significant deviation to reach ±0.35% in pressure from those higher than the critical density. In relation with the density deviation in liquid phase, those three equations represent the present measurements within ±0.7%, except two data points, which exist very near the saturation condition. These results, therefore, also confirm the reliability of the present apparatus for the *PVT* property measurements.

One hundred and thirteen vapor pressures of HFE-245mc at temperatures from 310 K to the critical temperature have been obtained through the present measurements together with 135 *PVT* properties along 13 different isochores. The measured vapor pressures are presented in Table 4, whereas the *PVT* properties are given in Table 5. Saturated-vapor and saturated-liquid densities have also been determined as the intersection between the vapor pressure curve and respective isochores. The intersection between the vapor pressure curve and the specified isochore in a pressure−temperature ($P-T$) diagram leads to a saturation temperature−pressure point with their estimated uncertainties. This pair of $P-T$ values is then used as input values to estimate the required correction to the inner volume of the spherical sample cell due to the thermal expansion and pressure deformation. The saturated density can accordingly be determined from the corrected volume and the sample mass initially charged into the sample cell. The determined saturated-vapor and saturated-liquid densities are presented in Tables 6 and 7 together with their uncertainties, $\delta\rho$. Here, we found that the uncertainty of the saturated-vapor densities (0.1 kg·m^{-3}) and saturated-liquid densities (0.2 kg·m^{-2}) is not significantly affected by the uncertainties of determined saturation temperature and pressure.

Table 4. Experimental Vapor Pressures of HFE-245mc

T/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa
310.00	301.8	350.00	890.4	370.00	1393.0	395.00	2306.7
310.00	301.9	350.00	889.6	370.00	1394.8	395.50	2329.9
310.00	302.4	351.00	910.5	370.00	1393.3	396.00	2352.6
313.15	332.9	351.50	921.6	370.00	1394.0	396.00	2350.8
315.00	351.1	352.00	932.6	371.00	1423.5	398.00	2442.6
315.00	351.5	352.50	943.7	373.15	1490.8	398.15	2451.0
320.00	406.8	353.00	954.6	375.00	1548.6	399.15	2497.9
320.00	407.3	353.15	958.7	376.00	1581.1	400.00	2537.9
320.00	406.6	353.50	965.6	378.00	1646.8	400.00	2538.5
323.15	445.4	354.00	977.8	379.00	1682.7	400.00	2537.6
325.00	468.3	354.00	976.8	380.00	1716.2	400.15	2545.7
325.00	467.8	355.00	999.5	380.00	1715.5	400.50	2562.1
330.00	536.7	355.00	999.0	380.00	1716.8	401.15	2594.2
330.00	537.7	355.00	999.9	381.00	1750.9	402.15	2643.6
330.00	537.3	356.00	1022.7	382.00	1788.2	403.15	2694.0
330.00	536.8	358.00	1070.4	383.15	1829.5	403.50	2711.4
333.15	584.6	359.00	1096.4	384.00	1861.5	404.00	2737.3
335.00	612.5	360.00	1120.4	385.00	1897.6	404.15	2745.3
335.00	612.2	360.00	1119.7	385.00	1898.9	405.00	2788.8
338.00	661.3	360.00	1121.0	386.00	1935.4	405.00	2789.1
340.00	696.6	360.00	1119.3	386.50	1954.5	405.15	2797.9
340.00	697.4	360.00	1121.2	387.00	1973.8	406.00	2842.2
340.00	696.0	361.00	1145.3	387.00	1974.4	406.15	2851.2
341.00	714.0	363.15	1202.5	388.15	2020.6		
343.15	754.3	364.00	1225.5	389.00	2054.5		
345.00	787.8	365.00	1250.6	390.00	2094.1		
345.00	788.7	365.00	1251.9	390.00	2095.4		
346.00	807.7	365.00	1251.5	391.00	2134.8		
348.00	847.3	366.00	1278.4	393.15	2227.1		
350.00	888.9	368.00	1335.2	394.00	2263.9		

Figure 4 illustrates the deviation of the available vapor pressures from our reported correlation (Widiatmo and Watanabe, 2001). The solid line represents the vapor pressure correlation developed by Sako et al. (1994). As shown in Figure 4, our earlier correlation reproduces well the present vapor pressures and those by Ohta et al. (2001) within ±2 kPa. Several data by Ohta et al. show smaller values than the present measurements at the temperatures at which they overlap. However, the difference among them is still within the uncertainty of vapor pressure measurements claimed by Ohta et al. On the other hand, the correlation by Sako et al. shows systematic deviation to reach −11 kPa (−0.4%) in the vicinity of the critical point. Such deviations even exceed their claimed uncertainty of vapor pressure measurements. In this connection, Sako (1997) informed the present authors of the fact that their vapor pressure measurements were not as accurate as the experimental uncertainty claimed in their paper (1994).

Figure 5 shows the vapor−liquid coexistence curve of HFE-245mc. Ohta et al. (2001) reported the saturated-liquid densities (○) from 260 to 370 K, whereas Yoshii et al. (2001) made saturated-vapor and saturated-liquid density measurements (△) in the vicinity of the critical point, where two data points (at 406.5 K for saturated liquid and at 406.46 K for saturated vapor) almost overlap with the present measurements (◇).

Table 5. Experimental *PVT* Properties of HFE-245mc

T/K	P/kPa	ρ/kg·m^{-3}
	a Series	
360.00	1093.1	75.05
365.00	1123.5	75.03
370.00	1153.1	75.01
375.00	1182.4	74.99
380.00	1211.1	74.97
385.00	1239.4	74.95
390.00	1267.5	74.94
395.00	1295.4	74.92
400.00	1322.8	74.90
405.00	1350.0	74.88
410.00	1376.9	74.86
415.00	1403.6	74.84
420.00	1430.1	74.82
425.00	1456.5	74.81
430.00	1482.7	74.79
435.00	1508.7	74.77
440.00	1534.5	74.75
	b Series	
375.00	1478.7	106.1
380.00	1524.4	106.0
385.00	1569.2	106.0
390.00	1613.1	106.0
395.00	1656.4	106.0
400.00	1699.2	105.9
405.00	1741.4	105.9
410.00	1783.1	105.9
415.00	1824.3	105.9
420.00	1865.2	105.8
425.00	1905.7	105.8
430.00	1945.9	105.8
435.00	1985.8	105.7
440.00	2025.3	105.7
	c Series	
387.50	1992.0	164.4
390.00	2034.0	164.4
395.00	2112.5	164.3
400.00	2189.1	164.3
405.00	2264.2	164.2
410.00	2337.9	164.2
415.00	2410.6	164.2
420.00	2482.3	164.1
425.00	2553.2	164.1
430.00	2623.3	164.0
435.00	2692.8	164.0
440.00	2761.7	164.0
	d Series	
401.00	2560.4	253.1
405.00	2668.4	253.0
410.00	2801.4	252.9
415.00	2927.7	252.9
420.00	3053.7	252.8
425.00	3178.0	252.8
430.00	3300.7	252.7
435.00	3421.8	252.6
	e Series	
404.50	2759.7	321.9
405.00	2778.0	321.9
405.50	2796.4	321.9
406.00	2814.9	321.9
407.00	2850.9	321.9
408.00	2887.0	321.8
410.00	2957.9	321.8
415.00	3132.4	321.7
420.00	3303.4	321.6
425.00	3471.8	321.6
430.00	3638.3	321.5
435.00	3803.3	321.4
440.00	3966.8	321.3
	f Series	
410.00	3027.5	397.8
415.00	3250.0	397.7
420.00	3469.8	397.6
425.00	3687.4	397.5
430.00	3903.6	397.4

T/K	P/kPa	ρ/kg·m^{-3}
	g Series	
407.15	2905.9	488.8
408.15	2960.7	488.8
413.15	3235.8	488.7
423.15	3792.8	488.4
433.15	4352.7	488.2
	h Series	
406.50	2872.6	602.6
407.00	2906.2	602.6
410.00	3114.7	602.5
415.00	3476.2	602.4
420.00	3847.1	602.2
425.00	4225.0	602.1
430.00	4608.0	601.9
435.00	4994.4	601.8
440.00	5384.4	601.6
	i Series	
405.00	2819.1	683.4
410.00	3259.6	683.2
415.00	3718.4	683.1
420.00	4188.0	682.9
425.00	4666.3	682.7
430.00	5151.1	682.6
435.00	5641.0	682.4
	j Series	
401.00	2592.3	745.6
401.50	2645.5	745.6
402.00	2698.0	745.6
403.00	2803.3	745.5
405.00	3017.6	745.4
410.00	3566.2	745.3
415.00	4128.4	745.1
420.00	4700.9	744.9
425.00	5281.0	744.7
430.00	5867.7	744.5
435.00	6459.6	744.3
	k Series	
397.00	2422.1	799.8
397.50	2484.8	799.8
398.00	2548.0	799.8
398.50	2611.2	799.8
399.00	2674.9	799.8
400.00	2802.7	799.7
402.00	3060.9	799.6
405.00	3453.4	799.5
410.00	4119.0	799.3
415.00	4795.7	799.1
420.00	5481.4	798.9
425.00	6174.7	798.7
430.00	6873.6	798.5
435.00	7577.2	798.3
440.00	8284.7	798.1
	l Series	
396.50	2378.4	802.7
397.00	2441.2	802.7
397.50	2504.5	802.7
398.00	2568.1	802.7
398.50	2632.0	802.6
399.00	2696.5	802.6
400.00	2825.5	802.6
402.00	3085.8	802.5
405.00	3481.9	802.4
410.00	4153.5	802.2
415.00	4835.5	802.0
	m Series	
395.00	2733.3	854.1
400.00	3513.6	853.9
405.00	4308.3	853.7
410.00	5112.8	853.5
415.00	5925.8	853.3
420.00	6746.2	853.1
425.00	7572.9	852.9
430.00	8404.4	852.7

Table 6. Experimental Saturated-Liquid Densities

T/K	P/kPa	ρ/kg·m^{-3}	$\delta\rho$/%
406.51	2870.3	602.5	0.03
404.25	2750.0	683.4	0.03
400.92	2582.9	745.5	0.03
396.71	2384.0	799.8	0.03
396.47	2373.2	802.6	0.03
391.21	2144.3	854.2	0.02

Table 7. Experimental Saturated-Vapor Densities

T/K	P/kPa	ρ/kg·m^{-3}	$\delta\rho$/%
358.55	1084.6	75.04	0.13
371.84	1449.9	106.1	0.09
387.41	1991.2	164.4	0.06
399.74	2525.6	253.1	0.04
404.25	2750.3	321.9	0.03
406.46	2867.7	397.9	0.03

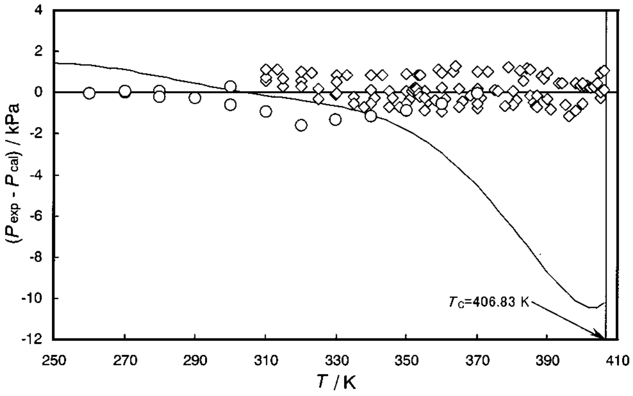

Figure 4. Vapor pressure deviation of HFE-245mc from Widiatmo and Watanabe eq: ◇, this work; ○, Ohta et al. (2001); —, Sako et al. (1994).

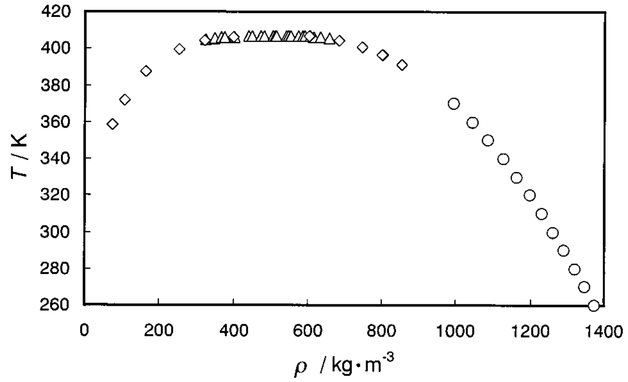

Figure 5. Vapor−liquid coexistence curve of HFE-245mc: ◇, this work; ○, Ohta et al. (2001); △, Yoshii et al. (2001).

Figure 6 depicts the saturated-liquid density deviation from our saturated-liquid density correlation reported elsewhere (Widiatmo and Watanabe, 2001). Except for a single datum (at 406.5 K) among the present measurements and the data in the vicinity of critical point by Yoshii et al., our correlation reproduces satisfactorily the data by Ohta et al. (2001) and the present measurements within ±0.15%.

Figure 7 represents the pressure deviation of the present measurements from our reported 16 term modified BWR type equation of state (Widiatmo and Watanabe, 2001). Also plotted in Figure 7 are the *PVT* property data by Ohta et al. (2001) in the liquid phase. An earlier reported equation of state for HFE-245mc by Tsuge et al. (1997) represents the present *PVT* properties within ±0.3% in pressure but does not work for the saturation condition and

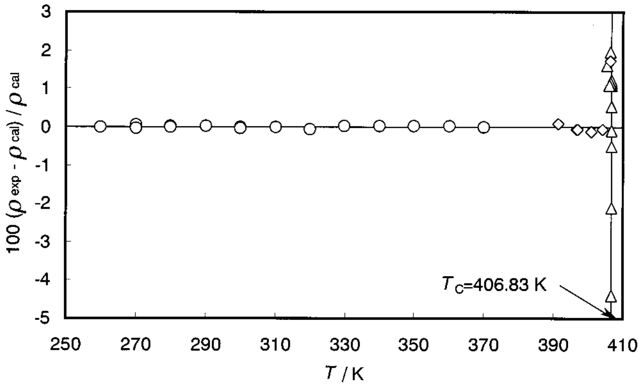

Figure 6. Saturated-liquid density deviation of HFE-245mc Widiatmo and Watanabe eq: ◇, this work; ○, Ohta et al. (2001); △, Yoshii et al. (2001).

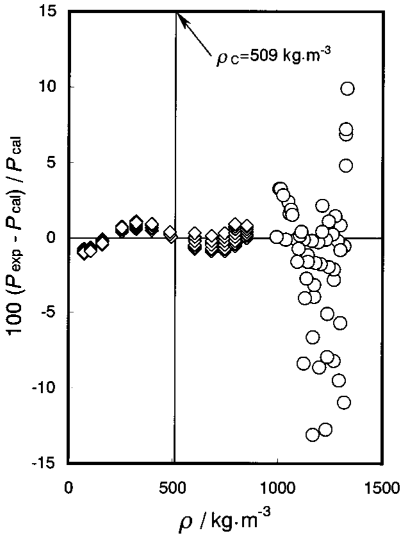

Figure 7. Pressure deviation of the *PVT* properties of HFE-245mc from Widiatmo and Watanabe eq: ◇, this work; ○, Ohta et al. (2001).

fails to represent the liquid phase *PVT* properties by Ohta et al., because that formulation was developed based on only the limited number of data available at that time. Our equation of state (EOS), as illustrated in Figure 7, did an excellent job of representing both the present measurements and the results by Ohta et al. in the liquid phase. Although the data by Ohta et al. have a much larger deviation from our EOS than the present measurements, such a result seems to be still acceptable in the liquid phase, in which the pressure gradient against density along an isotherm becomes significantly greater than that in the vapor phase. This statement is supported by the results given in Figure 8, which shows the density deviation of the available *PVT* properties from our EOS. In contrast to Figure 7, the liquid phase *PVT* properties by Ohta et al. are reproduced very well within ±0.1% in density. Significant density deviations are observed at densities between 321 and 398 kg·m^{-3}. Such a deviation may reflect an additional possibility remaining to develop the EOS for HFE-245mc with the aid of an increased number of terms.

Conclusions

The vapor pressures and *PVT* properties of HFC-143a and a new-generation refrigerant candidate HFE-245mc have been measured accurately in a wide range of temperatures and pressures. Vapor pressure and saturated-liquid density correlations and an equation of state have been confirmed to represent the measured properties.

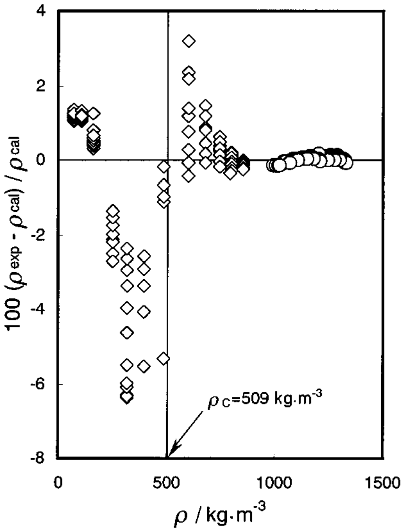

Figure 8. Density deviation of the *PVT* properties of HFE-245mc from Widiatmo and Watanabe eq: ◇, this work; ○, Ohta et al. (2001).

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