Measurements of Vapor Pressures and *PVT* Properties of Heptafluoropropyl Methyl Ether

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Vapor pressures and *PVT* properties of heptafluoropropyl methyl ether ($CF_3CF_2CF_2OCH_3$, HFE-347mcc) have been measured at temperatures from 340 K to the critical temperature (437.7 K) and from (370 to 450) K along eight isochores, respectively. An isochoric cell apparatus was used in the present measurements with uncertainties estimated to be ±10 mK, ±2 kPa, and ±0.2 $kg·m^{-3}$ in temperature, pressure, and density, respectively. A vapor pressure correlation developed on the basis of the measured vapor pressures in addition to the other available data shows a satisfactory representation of the present data within ±2 kPa. Comparison of the measured *PVT* properties with the reported equation of state also shows a satisfactory agreement for engineering application within ±1% in pressure and ±2.2% in density.

Introduction

As a continuation to our earlier works on the new alternative refrigerants having zero ozone depletion potential and significantly low global warming potential as reported elsewhere (Ohta et al., 2001; Yoshii et al., 2001; Widiatmo et al., 2001), the present study aims to provide highly reliable vapor pressure and *PVT* property measurements of heptafluoropropyl methyl ether ($CF_3CF_2CF_2OCH_3$, HFE-347mcc), which is a promising candidate to replace trichlorofluoromethane (CCl_3F, R-11) especially for vapor-compression heat pump system application. The basic thermodynamic properties of HFE-347mcc are given briefly in Table 1. The present paper also discusses a comparison of the measured vapor pressures and *PVT* properties with vapor pressure correlation and equation of state (EOS) for HFE-347mcc already reported elsewhere (Widiatmo and Watanabe, 2001).

Table 1. Basic Thermodynamic Properties of HFE-347mcc

	$CF_3CF_2CF_2OCH_3$
T_c/K	437.7[a]
P_c/kPa	2476[b]
ρ_c/kg·m^{-3}	530[a]
M/kg·kmol^{-1}	200.067

[a] Sako et al. (1996). [b] Widiatmo and Watanabe (2001).

Experimental Studies

An isochoric apparatus with a spherical sample cell (~139 cm^3 in its inner volume) as shown in Figure 1 has been used throughout the present measurements. This apparatus has also been used in our earlier studies (Widiatmo et al., 2001) with a reliability being well confirmed through the measurements of 1,1,1-trifluoroethane (CF_3CH_3, HFC-143a). One may refer to our earlier work (Widiatmo et al., 2001) for the detailed explanation of the apparatus as well as the procedure of measurement.

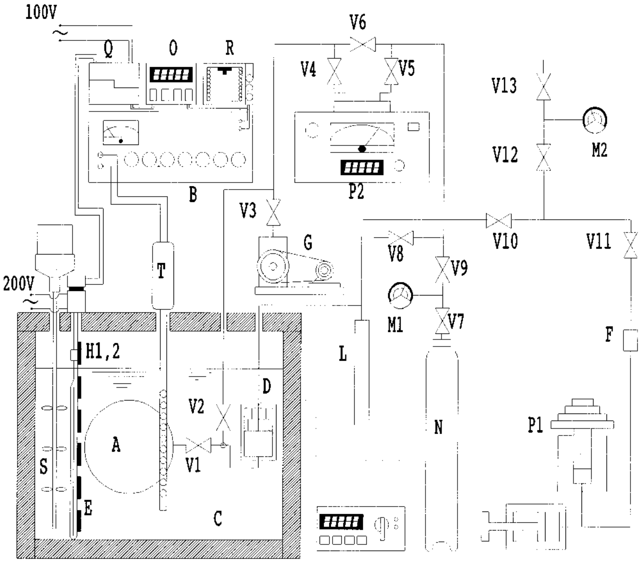

Figure 1. Experimental apparatus: A, sample cell; B, thermometer bridge; C, thermostated bath; D, differential pressure indicator; E, partition plate; F, dust filter; G, vacuum pump; H1,2, main/sub heater; I, digital resistance meter; J, pressure damper; M1,2, pressure gauges; N, nitrogen bottle; O, 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.

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 the present measurements are ±10 mK in temperature, ±2 kPa in pressure, and 0.2 $kg·m^{-3}$ in density, respectively. The purity of the

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Table 2. Experimental Vapor Pressures of HFE-347mcc

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
340.00	290.1	385.00	888.8	421.50	1843.5
350.00	381.4	390.00	988.4	425.00	1966.9
350.00	382.6	390.00	989.4	430.00	2154.0
350.00	381.2	390.00	987.6	430.00	2154.8
360.00	494.7	393.50	1062.9	430.00	2154.8
360.00	495.1	400.00	1216.6	435.00	2358.4
360.00	495.4	400.00	1217.4	435.00	2357.4
365.00	559.4	405.00	1345.4	435.00	2358.6
370.00	630.7	410.00	1483.4	437.00	2444.6
370.00	631.8	410.00	1484.2	437.00	2445.2
370.00	630.5	420.00	1793.2	437.50	2466.8
370.00	630.3	420.00	1793.7		
380.00	794.6	420.00	1792.3		
380.00	796.2	420.00	1794.1		
380.00	795.6	420.00	1791.7		

HFE-347mc sample was 99.4 mass% according to the Research Institute of Innovative Technology for the Earth (RITE), Kyoto, Japan, and no further purification was conducted in the present study.

Results and Discussion

Vapor pressures of HFE-347mcc have been measured at temperatures from 340 K to the critical temperature (437.7 K) to obtain 41 data points as listed in Table 2. *PVT* property measurements were completed from (370 to 450) K, as summarized in Table 3, along eight isochores. Saturated-vapor and saturated-liquid densities have also been determined from the intersection between the vapor pressure curve and isochores. As we reported in our earlier paper (Widiatmo et al., 2001), 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. We also found that the uncertainty of the saturated-vapor densities (0.1 kg·m^{-3}) and saturated-liquid densities (0.2 kg·m^{-3}) is not significantly affected by the uncertainties of determined saturation temperature and pressure. The determined saturated-vapor and saturated-liquid densities are presented in Table 4 together with their uncertainties, $\delta\rho$.

Table 3. Experimental *PVT* Properties of HFE-347mcc

T/K	P/kPa	ρ/kg·m^{-3}	T/K	P/kPa	ρ/kg·m^{-3}
	a Series			e Series	
371.50	652.2	54.043	436.50	2417.3	363.361
372.00	658.2	54.041	437.00	2433.8	363.361
372.50	662.0	54.040	437.50	2450.0	363.351
373.00	664.2	54.039	438.00	2466.1	363.342
374.00	667.2	54.036	438.50	2482.1	363.333
375.00	670.4	54.033	439.00	2498.1	363.323
380.00	685.6	54.020	440.00	2529.8	363.304
390.00	715.4	53.993	445.00	2685.6	363.210
400.00	744.5	53.966	450.00	2838.3	363.115
410.00	772.8	53.939			
420.00	800.8	53.911		f Series	
430.00	828.3	53.884	438.00	2490.2	536.912
440.00	855.6	53.856	440.00	2583.1	536.856
450.00	882.4	53.828	445.00	2820.0	536.717
			450.00	3060.1	536.577
	b Series				
394.00	1072.7	94.979		g Series	
394.50	1079.7	94.977	435.50	2391.8	718.590
395.00	1083.5	94.974	436.00	2426.8	718.572
396.00	1089.7	94.970	436.50	2462.1	718.553
400.00	1113.5	94.951	437.00	2497.8	718.535
405.00	1142.7	94.927	438.00	2569.0	718.497
410.00	1171.2	94.903	440.00	2714.7	718.423
415.00	1199.3	94.878			
420.00	1227.0	94.854		h Series	
425.00	1254.7	94.830	422.00	1878.1	895.179
430.00	1281.8	94.806	422.50	1940.5	895.156
435.00	1308.6	94.781	423.00	2003.1	895.133
440.00	1335.1	94.757	423.50	2066.0	895.110
445.00	1361.6	94.732	424.00	2128.8	895.087
450.00	1387.8	94.707	424.50	2192.1	895.064
			425.00	2255.5	895.041
	c Series		430.00	2897.0	894.811
417.00	1691.3	171.704	435.00	3551.0	894.580
418.00	1711.6	171.696	440.00	4214.7	894.349
			445.00	4883.3	894.117
	d Series		450.00	5563.1	893.884
422.50	1873.8	199.623			
423.00	1883.4	199.618			
423.50	1891.3	199.613			
424.00	1899.2	199.608			
425.00	1914.5	199.598			
430.00	1989.0	199.547			
435.00	2064.1	199.495			
440.00	2136.4	199.443			
445.00	2207.6	199.392			
450.00	2277.7	199.340			

Table 4. Experimental Saturation Densities of HFE-347mcc

saturated vapor				saturated liquid			
T/K	P/kPa	ρ/kg·m^{-3}	$\delta\rho$/%	T/K	P/kPa	ρ/kg·m^{-3}	$\delta\rho$/%
371.45	654.1	54.04	0.19	435.11	2363.2	718.59	0.03
393.93	1074.5	94.97	0.11	421.84	1857.5	895.18	0.02
422.25	1871.6	199.62	0.05				
436.11	2406.2	363.36	0.03				

Figure 2 shows the deviation of the available vapor pressures from our reported vapor pressure correlation (Widiatmo and Watanabe, 2001). Sako et al. in their earlier work (1994) reported the vapor pressures of HFE-347mcc in terms of a vapor pressure correlation, which is illustrated in Figure 2 as a solid line. Ohta et al. (2001) measured the vapor pressures by using a magnetic densimeter coupled with a variable volume cell at temperatures from (250 to 370) K. As shown in Figure 2, our reported vapor pressure correlation reproduces well the present vapor pressures and those by Ohta et al. (2001) within ±2 kPa. Several data by Ohta et al. show values lower than the present vapor pressures at temperatures at which they both exist. The difference, however, among them was 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 18 kPa near the critical point, which exceeds their claimed uncertainty of vapor pressure measurements. Our earlier study on HFE-245mc (Widiatmo et al., 2001) also found similarly a considerable difference of the vapor pressures by Sako et al. (1994) from other reported data. 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 3 depicts the density deviation of available saturated-liquid density data from our reported saturated-liquid density correlation (Widiatmo and Watanabe, 2001). Ohta et al. (2001) reported vapor pressure and liquid density measurements from (250 to 370) K in 10 K intervals, whereas the present measurements determined saturated-liquid densities only at 422 and 435 K, and there are no data available at temperatures between 370 and 422

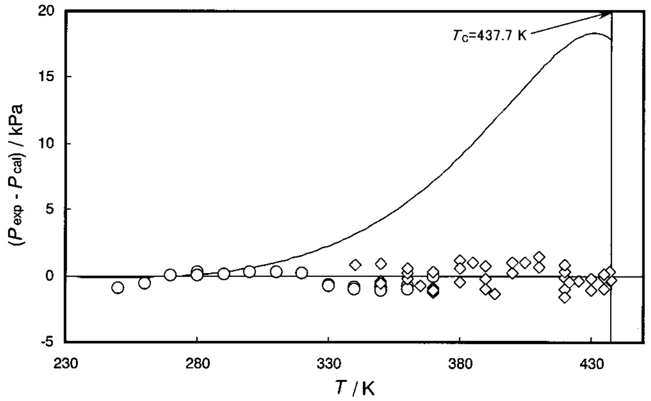

Figure 2. Vapor pressure deviation of HFE-347mcc from Widiatmo and Watanabe eq: ◊, this work; ○, Ohta et al. (2001); −, Sako et al. (1994).

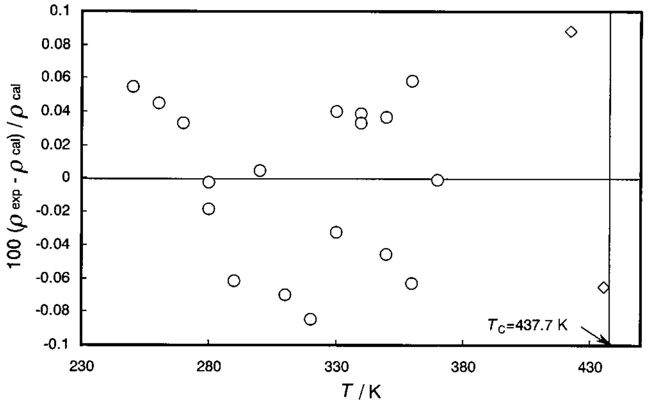

Figure 3. Saturated-liquid density deviation of HFE-347mcc from Widiatmo equation: ◊, this work; ○, Ohta et al. (2001).

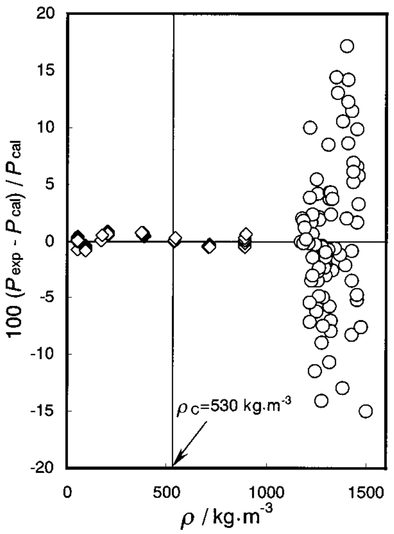

Figure 4. Pressure deviation of the *PVT* properties of HFE-347mcc from Widiatmo and Watanabe eq: ◊, this work; ○, Ohta et al. (2001).

K. The correlation represents those data very well within ±0.1% in density.

Figure 4 represents the pressure deviation of the available *PVT* properties from our reported EOS, including the present *PVT* properties and those by Ohta et al. (2001) in the liquid phase. The EOS was a modified BWR type one consisting of 17 terms and was also developed on the basis of the present measurements. In the vapor phase, as shown in Figure 4, the EOS does an excellent job of representing the present *PVT* properties within ±1% in pressure. The same result has also been obtained for the present *PVT* properties available along two isochores in the liquid phase. However, in relation with the data by Ohta et al., eq 3 exhibits greater data scatter within ±15% in pressure. Such a result seems to be still acceptable in the liquid phase because an isothermal gradient on the pressure−volume ($P-v$) plane increases more steeply, so that a minute difference in liquid density yields a significant pressure deviation.

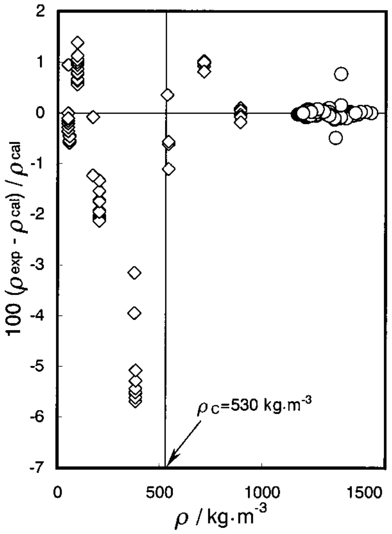

Figure 5. Density deviation of the *PVT* properties of HFE-347mcc from Widiatmo and Watanabe eq: ◊, this work; ○, Ohta et al. (2001).

Most of the liquid phase *PVT* properties by Ohta et al. (2001) are represented satisfactorily, as shown in Figure 5, by our EOS within ±0.01% in density. This fact supports the previous statement in connection with the pressure deviation of the *PVT* properties by Ohta et al. from the EOS. The EOS also does a good job of representing the present liquid phase *PVT* properties within ±1% in density. In the vapor phase, except those at densities of ~363 kg·m^{-3}, the present *PVT* properties are relatively well correlated within ±2.2% in density. Significant deviation at densities of ~363 kg·m^{-3} may reflect a possibility to develop an EOS with an increased number of terms.

Conclusions

The vapor pressures and *PVT* properties of a new-generation alternative candidate HFE-347mcc 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 satisfactorily to represent the measured properties. They have also been discussed with the existing data in the literature.

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