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Critical Properties of 1,2,2,2-Tetrafluoroethyl Trifluoromethyl Ether (HFE-227me) + Trifluoromethoxymethane (HFE-143m) and + Methyl Pentafluoroethyl Ether (HFE-245mc)

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Critical properties of binary mixtures of 1,2,2,2-tetrafluoroethyl trifluoromethyl ether (HFE-227me) with two hydrofluoroethers, trifluoromethoxymethane (HFE-143m) and methyl pentafluoroethyl ether (HFE-245mc), were measured. The uncertainties were ± 10 mK in temperature, ± 0.5 kPa in pressure, and ± 1.0 kg·m^{-3} in density. The experimental data were correlated with equations proposed by Higashi.

Introduction

Hydrofluoroethers (HFEs) are environmentally benign compounds having zero ODP and low GWP and are expected to be the new refrigerants.[1,2] The Research Institute of Innovative Technology for the Earth (RITE) synthesized and evaluated about 150 HFEs.[3,4] Of these, trifluoromethoxymethane (CF_3OCH_3, HFE-143m) and pentafluoromethoxyethane ($CF_3CF_2OCH_3$, HFE-245mc) were found to be possible alternatives for dichlorodifluoromethane (CCl_2F_2, CFC-12) and 1,2-dichloro-1,1,2,2-tetrafluoroethane ($CClF_2CClF_2$, CFC-114), respectively. Unfortunately, they are slightly combustible (ASHRAE class 2).[5,6] Thus, for safety reasons, the HFEs are expected to be used in binary mixtures with inflammable compounds.

The critical properties (critical temperature, pressure, and density) are the most important physical properties for the development of an equation of state to calculate and estimate the thermodynamic properties of fluids in industry. However, reliable information on the thermophysical properties of these mixtures has not been reported. In previous papers, we described the construction of an apparatus for the precise measurement of critical properties[7] and its application to the newly synthesized compounds and their mixtures.[5,8,9] In the present article, using this apparatus, we have measured the critical properties of binary mixtures of 1,2,2,2-tetrafluoroethyl trifluoromethyl ether (HFE-227me) with two HFEs, HFE-143m and HFE-245mc.

Experimental

Materials. Table 1 summarizes the properties of samples used in this study. They were all supplied by RITE. The mole fraction based purities were analyzed by gas chromatography (Hewlett-Packard, model HP-6890; thermal conductivity detector).

Apparatus and Procedures. The critical points of HFE-227me and its mixtures were measured by observing the behavior of the meniscus at the vapor−liquid interface in an optical cell. The apparatus used in this study is the same as that in the previous papers.[5,7−10] Briefly, the apparatus is composed of a rectangular-shaped optical cell (ca. 5 cm^3 in volume) and two variable-volume vessels to control the inner volume of the apparatus and a differential null-pressure detector. The optical cell was connected to the two variable-volume vessels and the differential null-pressure detector by a valve. The central axis of these vessels and the detector were adjusted to be at the same level. They were immersed in a constant temperature oil bath. The temperature of the oil bath was controlled to within ± 3 mK in the range of (300 to 450) K. Under these conditions, the uncertainty in the critical temperature was estimated to be ± 10 mK. The uncertainty in pressure was estimated to be less than ± 0.5 kPa.

In experiments, critical properties were measured by the appearance and disappearance of the meniscus at the critical density with changing temperature, whereas the density was maintained at the critical value by the two variable-volume vessels.

After the critical property measurements, the samples inside the optical cell and the null-pressure detector were trapped in a cold trap separately and weighed. The critical density was then determined from the mass of the sample and the known internal volume of the optical cell. The composition of the samples in the null-pressure detector and the optical cell was analyzed by gas chromatography. The uncertainties in the density and the mole fractions both in the optical cell and in the null-pressure gauge were ± 1.0 kg·m^{-3} and ± 0.5 %, respectively.

A detailed description of the experimental apparatus and procedures including the sample preparation were given in the previous papers.[5,7−10]

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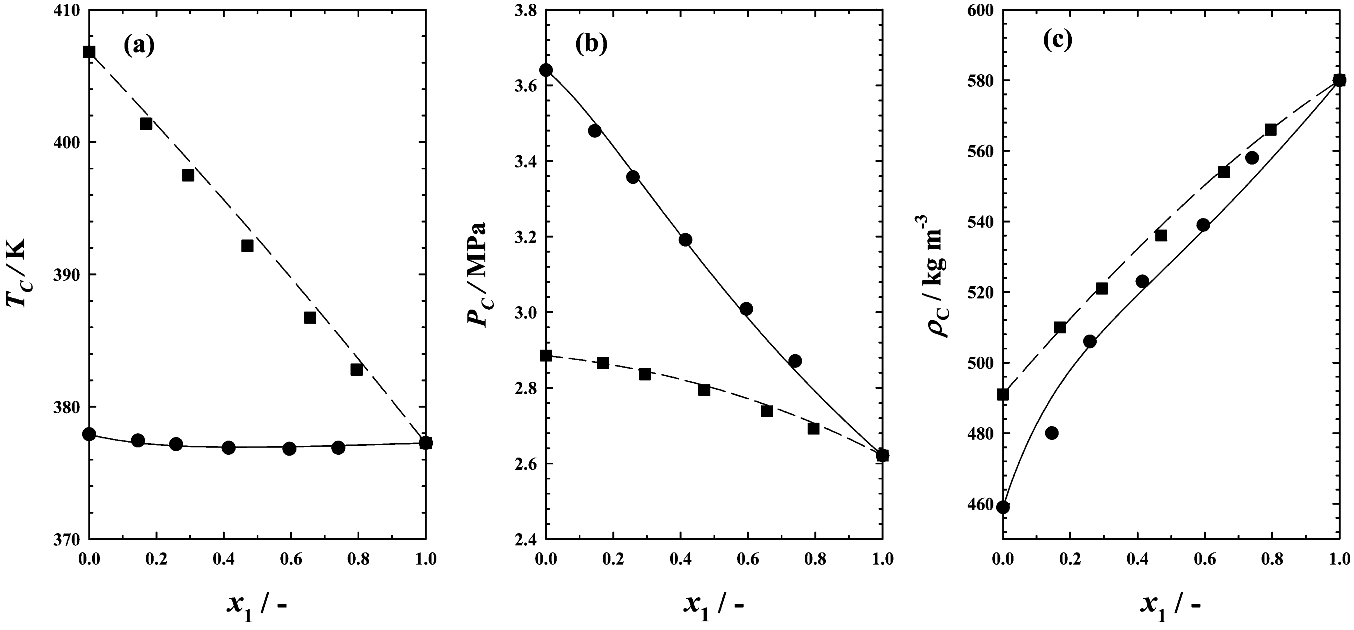

Figure 1. Critical properties of the binary mixtures of HFE-227me (1) and HFEs (2). (a) Critical temperature, (b) critical pressure, and (c) critical density for: ●, HFE-143m; ■, HFE-245mc. Lines are the correlated results of eqs 1 to 6: —, HFE-143m; ---, HFE-245mc.

Table 1. Compounds Used in This Study

sample code (molecular formula)	name	CAS No.	purity	boiling point K	T_C K	P_C MPa	ρ_C kg·m^{-3}	ref
HFE-143m (CF_3OCH_3)	trifluoromethoxymethane	421-14-7	99.9	249.15	377.92 ± 0.01	3.640 ± 0.0005	459 ± 1.0	5
HFE-227me ($CF_3CHFOCF_3$)	1,2,2,2-tetrafluoroethyl trifluoromethyl ether	2356-62-9	99.9	263.41	377.26 ± 0.01	2.621 ± 0.0005	580 ± 1.0	this work
HFE-245mc ($CF_3CF_2OCH_3$)	methylpentafluoroethylether	22410-44-2	99.9	278.66	406.82 ± 0.01	2.885 ± 0.0005	491 ± 1.0	8

Correlation. Critical data measured in this study were correlated by equations proposed by Higashi:[11,12]

$$T_{Cm} = \theta_1 T_{C1} + \theta_2 T_{C2} + 2\theta_1\theta_2\Delta_T \qquad (1)$$

$$V_{Cm} = \theta_1 V_{C1} + \theta_2 V_{C2} + 2\theta_1\theta_2\Delta_V \qquad (2)$$

$$P_{Cm} = \theta_1 P_{C1} + \theta_2 P_{C2} + 2\theta_1\theta_2\Delta_P \qquad (3)$$

$$V_{Cm} = M_m/\rho_{Cm} \qquad (4)$$

$$M_m = x_1 M_1 + (1 - x_1) M_2 \qquad (5)$$

$$\theta_i = \frac{x_i V_{Ci}^{2/3}}{\sum_{j=1}^{2} x_j V_{Cj}^{2/3}} \quad i = 1,2 \qquad (6)$$

where T_{Ci}, V_{Ci}, and P_{Ci} are the critical temperature, critical volume, and critical pressure of component i, respectively; x is the mole fraction; M_i is the molecular weight of component i; ϑ_i is the surface ratio of component i given by eq 6; and Δ_T, Δ_V, and Δ_P are the fitting properties for critical temperature, volume, and pressure, respectively. Subscript m means mixture.

Table 2. Critical Properties of HFE-227me (1) + HFE-143m (2) Binary Systems

x_1[a]	T_C K	P_C MPa	ρ_C kg·m^{-3}	x_1[b] (optical cell base deviation/%)[d]	x_1[c] (optical cell base deviation/%)[e]
0	377.92	3.640	459	0.0000	0.0000
0.1455	377.45	3.480	480	0.1437 (1.24)	0.1441 (0.96)
0.2585	377.16	3.357	506	0.2578 (0.27)	0.2585 (0.00)
0.4147	376.89	3.191	523	0.4091 (1.35)	0.4151 (−0.10)
0.5954	376.82	3.009	539	0.5932 (0.37)	0.5948 (0.10)
0.7403	376.89	2.871	558	0.7378 (0.34)	0.7393 (0.14)
1	377.26	2.621	580	1.0000	1.0000
			AAD/%	0.71	0.26

[a] Mole fraction in the optical cell. [b] Mole fraction calculated from the mass ratio. [c] Mole fraction in the null-pressure detector and variable-volume vessels. [d] Deviation = ($x_{\text{optical cell}} - x_{\text{feed}}$)/$x_{\text{optical cell}}$. [e] deviation = ($x_{\text{optical cell}} - x_{\text{null-pressure detector}}$)/$x_{\text{optical cell}}$.

Results and Discussion

Critical Properties of Mixtures. Figure 1 shows the critical loci of the two binary systems investigated in this study. Numerical values are tabulated in Tables 2 and 3. Similar to the mixtures previously reported,[5,8] the critical density data showed a wider spread compared with the critical temperature and pressure. The larger the difference in boiling point and critical temperature, the wider the data spread. This is presumably due to the characteristics of the critical point where the density changes sharply with only minute changes in temperature and/or pressure.

From the tables, it is also clear that there are composition differences between samples recovered from the optical cell and the null pressure detector. The larger the boiling point and critical temperature difference, the larger the average absolute deviation (AAD) of the composition. As reported previously,[5,8] this fact suggests that there was a temperature difference between the optical cell and the null pressure detector. However,

Table 3. Critical Properties of HFE-227me (1) + HFE-245mc (2) Binary Systems

	T_C	P_C	ρ_C	x_1[b]	x_1[c]
x_1[a]	K	MPa	kg·m^{-3}	(optical cell base deviation/%)[d]	(optical cell base deviation/%)[e]
0.0000	406.82	2.885	491	0.0000	0.0000
0.1694	401.38	2.866	510	0.1715 (−1.24)	0.1710
0.2941	397.49	2.836	521	0.2578 (−1.84)	0.2948
0.4706	392.17	2.794	536	0.4753 (−1.00)	0.4715
0.6565	386.73	2.738	554	0.6592 (−0.41)	0.6587
0.7952	382.80	2.692	566	0.7965 (−0.16)	0.7948
1.0000	377.26	2.621	580	1.0000	1.0000
			AAD/%	0.93	0.35

[a] Mole fraction in the optical cell. [b] Mole fraction calculated from the mass ratio. [c] Mole fraction in the null-pressure detector and variable-volume vessels. [d] Deviation = $(x_{\text{optical cell}} - x_{\text{feed}})/x_{\text{optical cell}}$. [e] Deviation = $(x_{\text{optical cell}} - x_{\text{null-pressure detector}})/x_{\text{optical cell}}$.

Table 4. Correlated Results

system	parameters	AAD/%
HFE-227ea + HFE-143m	$\Delta_T = -1.2005$	0.04
	$\Delta_p = 0.3441$	0.53
	$\Delta_v = -40.8037$	0.84
HFE-227ea + HFE-245mc	$\Delta_T = -0.0887$	0.00
	$\Delta_p = 0.0786$	0.06
	$\Delta_v = -4.9893$	0.12

as the AADs are smaller than 1 % for the two systems investigated, there will be only minor effects on the critical property measurements.

Correlation of the Critical Properties. The correlated results are shown as lines in Figure 1 and are summarized in Table 4. As shown in the table, the AADs of the critical properties are less than ± 1 %. The AAD of the critical density is larger than that of critical temperature as described above.

Conclusion

We have measured the critical properties of binary mixtures of HFE-227me with two hydrofluoroethers, HFE-143m and HFE-245mc, with uncertainties of ± 10 mK in temperature, ± 0.5 kPa in pressure, and ± 1.0 kg·m^{-3} in density. The data spread in the critical density was larger than that of critical temperature and pressure data. This is presumably due to the difficulty in measuring the density close to the critical point where it changes sharply with only minimal changes in temperature and pressure.

The experimental results were correlated with equations proposed by Higashi.[11,12] The maximum average absolute deviation was less than 1 % for all critical properties. A minute composition difference less than 1 % was observed between the optical cell and the null-pressure detector for both the binary systems.

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