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Critical Parameters and Vapor Pressure Measurements of Potential Replacements for Chlorofluorocarbons—Four Hydrofluoroketones and a Hydrofluoroamine

Katsuto Otake,[*,†,‡] Masahiko Yasumoto,[‡,§] Yasufu Yamada,[§] Jyunji Murata,[§] and Shingo Urata[§]

Institute for Green Technology, and Research Center for Developing Fluorinated Greenhouse Gas Alternatives, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan, and Research Institute of Innovative Technology for the Earth, Hongo 2-40-17, Bunkyo-ku, Tokyo 113-0000, Japan

Critical parameters and vapor pressures of five possible replacement compounds for chlorofluorocarbons—four hydrofluoroketones and a hydrofluoroamine—were measured with an accuracy of ±10 mK, ±0.5 kPa, and ±1 kg·m^{-3}. Critical temperatures, pressures, and densities were in the ranges from 450 to 500 K, from 2.3 to 3 MPa, and from 450 to 550 kg·m^{-3}, respectively. Among the fSMive compounds examined**,** one of the hydrofluoroketones, HFK-354pc (CHF$_2$CF$_2$C(=O)CH$_3$), was relatively unstable.

Introduction

Chlorofluorocarbons (CFCs) have been utilized extensively as refrigerants, cleaning solvents, and other process fluids due to their chemical stability and suitable physical properties. However, their undesirable ozone layer depletion potential (ODP) make their use likely to be restricted soon. To meet the requirements of the Kyoto Protocol (1997), it will be necessary to develop alternative substances that can satisfy the technical specifications of industry while reducing ODP. Hydrogen-containing fluorinated ethers, ketones, and amines have been developed as alternatives to CFCs and hydrochlorofluorocarbons (HCFCs).[1] They have almost zero ODP because of the absence of chlorine atoms in the molecules.[2] For evaluation of the use of these compounds in industrial systems, the most important basic properties needed in the process design are values of physical properties such as vapor pressures and the critical parameters—critical temperature, critical pressure, and critical density. In this article, the critical parameters and vapor pressures of four hydrofluoroketones and a hydrofluoroamine are measured by the visual method. The apparatus used for the visual determination of these properties, together with the results of validation tests and the measured results of 21 hydrofluoroethers, have been reported previously.[3]

Experimental Section

Materials. All compounds were supplied by the Research Institute of Innovative Technology for the Earth (RITE). Their purities were monitored with a gas chromatograph (Hewlett-Packard, model HP-6890) equipped with a thermal conductivity detector. Table 1 summarizes the sample codes, molecular formula, molar based purity, and normal boiling point for all the compounds used in this study.[4,5] Decomposition of these substances is easily promoted by impurities such as water, and thus, a preliminary stability check was conducted. The check was carried out using a simple apparatus which consisted of a cylinder connected to a pressure gauge. The sample to be tested was placed in the cylinder and maintained at a temperature 50 K higher than its estimated critical temperature for a period of 12 h. The estimated critical temperature was determined by Joback's method.[6] In the previous work,[3] thermal decomposition was detected mainly by a steep increase in pressure during the test. In this work, as the pressure increase is small, chemical stability was checked in terms of the change of the sample color before and after the test and also by gas chromatographic analysis. The procedures and apparatus for the stability check and dehydration were described in the previous report.[3] Substances judged to be thermally unstable were treated with molecular sieves 3A. The molecular sieves were pretreated at 620 K under vacuum for 2 h.

Apparatus. The critical points of the compounds were measured by observing the behavior of the meniscus at the vapor−liquid interface in an optical cell. Figure 1 is a schematic representation of the experimental apparatus. It was composed of four main parts: (A) a rectangular shaped optical cell (ca. 5 cm^3 in volume), (B) two variable volume vessels, (C) a differential null-pressure detector, and (D) aluminum blocks that acted as thermal masses to minimize temperature fluctuations. The optical cell was connected to the two variable volume vessels and the differential null-pressure detector by a valve (V$_1$). The central axis of these vessels and the gauge were arranged at the same level. The temperature of the oil bath was controlled to within ±3 mK in the range 400 to 450 K and to ±5 mK from 450 to 550 K. The uncertainty in the critical temperature is estimated to be ±10 mK. The uncertainties in pressure and density were estimated to be less than

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* Corresponding author. Phone: +81-298-61-4567 or +81-298-61-4819. Fax: +81-298-61-4567. E-mail: katsuto-otake@aist.go.jp.

[†] Institute for Green Technology, National Institute of Advanced Industrial Science and Technology.

[‡] Research Center for Developing Fluorinated Greenhouse Gas Alternatives, National Institute of Advanced Industrial Science and Technology.

[§] Research Institute of Innovative Technology for the Earth.

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Table 1. Properties of Samples

sample code	molecular structure	CASRN	purity/mol %	T_b/K	compound name
HFK-447mcc	$CF_3CF_2CF_2C(=O)CH_3$	355-17-9	99.9	337.40	1,1,1,2,2,3,3-heptafluoropentan-4-one
HFK-465mc	$CF_3CF_2C(=O)CH_2CH_3$	378-72-3	99.5	335.24	1,1,1,2,2-pentafluoropentan-3-one
HFK-354pc	$CHF_2CF_2C(=O)CH_3$	679-97-0	99.1	340.83	1,1,2,2-tetrafluorobutan-3-one
HFK-549mccc	$CF_3CF_2CF_2CF_2C(=O)CH_3$	678-18-2	99.8	360.47	1,1,1,2,2,3,3,4,4-nonafluorohexan-5-one
HFAM-348mm-f	$(CF_3)_2NCH_2CHF_2$	176674-31-0	99.99	324.50	2,2-difluoroethylbis(trifluoromethyl)amine

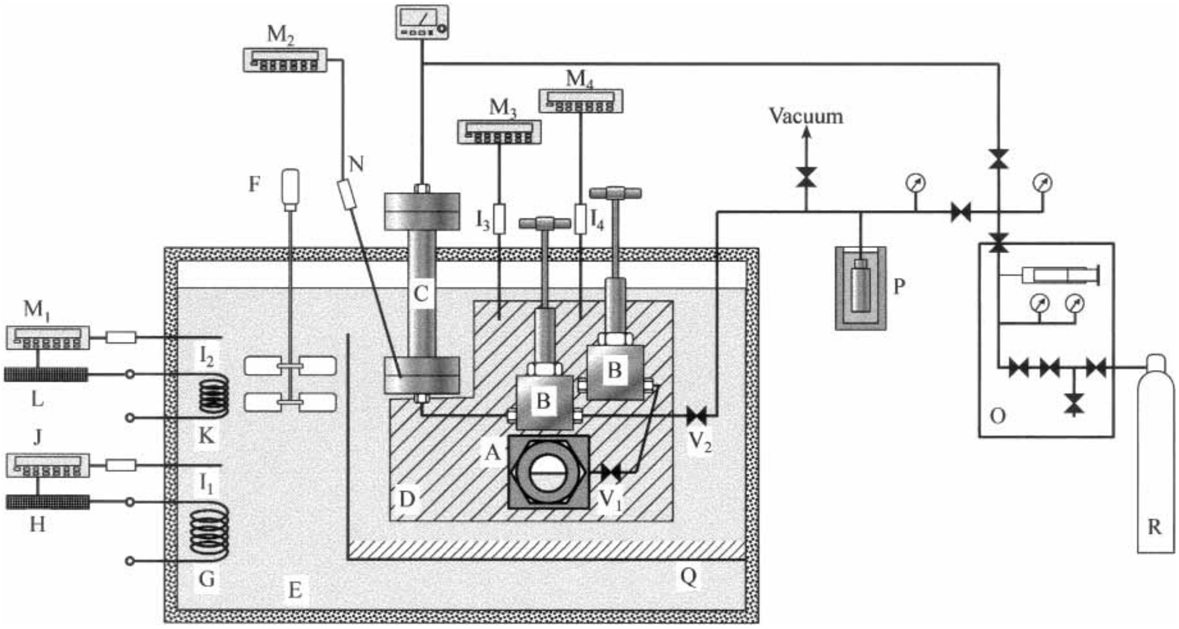

Figure 1. Schematic experimental apparatus: A, optical cell; B, variable volume vessel; C, differential null-pressure detector; D, aluminum blocks; E, constant temperature oil bath; F, stirrer; G, main heater; H, main heater controller; I, platinum resistance thermometer; J, thyristor regulator; K, subheater; L, subheater controller; M, platinum resistance thermometer; N, platinum resistance thermometer; O, quartz crystal pressure gauge; P, cold trap; Q, rectifier fin; R, N_2 cylinder.

Table 2. Critical Properties of Hydrofluoroketones and a Hydrofluoroamine

	experimental												
	first run				second run								
	temp decrease		temp increase		temp decrease		temp increase		avg		avg		
sample code	T_c/K	P_c/MPa	T_c/K	P_c/MPa	T_c/K	P_c/MPa	T_c/K	P_c/MPa	T_c/K	σ	P_c/MPa	σ	ρ_c/kg·m^{-3}
HFK-447mcc	476.53	2.577	476.55	2.578	476.54	2.577	476.57	2.578	476.55	0.030	2.578	0.001	538
HFK-465mc	475.53	2.641	475.55	2.644	475.52	2.642	475.55	2.643	475.54	0.026	2.642	0.002	494
HFK-549mccc	498.95	2.198	498.98	2.200	498.96	2.197	498.98	2.199	498.97	0.026	2.198	0.002	520
HFAM-348mm-f	460.17	2.641	460.22	2.643	460.19	2.641	460.21	2.643	460.20	0.038	2.642	0.002	579

			deviation					
estimated by Joback's method[6]			critical temp		critical pressure		critical density	
T_c/K	P_c/MPa	ρ_c/kg·m^{-3}	ΔT_c/K	T_c(err)/%	ΔP_c/MPa	P_c(err)/%	$\Delta\rho_c$/kg·m^{-3}	ρ_c(err)/%
479.30	3.012	452	−2.75	−0.58	−0.434	−16.83	86	15.99
477.78	2.791	512	−2.24	−0.47	−0.149	−5.64	−18	−3.64
497.49	2.357	529	1.48	0.30	−0.159	−7.23	−9	−1.73
457.59	2.718	552	2.61	0.57	−0.076	−2.88	27	4.66

±0.5 kPa and ±1 kg·m^{-3}, respectively. A detailed description of the experimental apparatus was given in the previous paper.[3] Thermal expansion of the optical cell and expansion due to the inner pressure of the cell were neglected in this study.

Procedures. The sample was loaded into the optical cell from the dehydration apparatus. After the optical cell was connected to the apparatus, the remaining part of the apparatus was evacuated. After closing V_1 and opening V_2, the temperature was raised to the desired value in 10 K increments. For each change in conditions, approximately 1 h of equilibration time was allowed, and the temperature and saturated vapor pressure were recorded. The position of the meniscus was controlled by the variable volume vessels (B) to be 1 to 2 mm higher than the center of the optical windows.

Near the critical temperature, when the critical opalescence began to appear, the temperature step was decreased to 10 mK. The inner volume of the apparatus was controlled by the variable volume vessels so that the critical opalescence could be equally observed in both liquid and gas phases. The critical point was determined by changing the temperature from supercritical to subcritical and vice versa.

In the case of decreasing temperature, the critical opalescence becomes most intense at temperature T_{CL}, and

Table 3. Critical Properties of HFK-354pc with and without Dehydration

	experimental											
	first run				second run							
	temp decrease		temp increase		temp decrease		temp increase			estimated by Joback's method		
	T_c/K	P_c/MPa	T_c/K	P_c/MPa	T_c/K	P_c/MPa	T_c/K	P_c/MPa	ρ_c/kg·m^{-3}	T_c/K	P_c/MPa	ρ_c/kg·m^{-3}
without dehydration			473.46	1.721			473.80	1.796				
with dehydration	500.17	3.658	500.21	3.666	500.20	3.620			453	497.48	3.493	450

Table 4. Vapor Pressures of the Samples

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
HFK-447mcc ($CF_3CF_2CF_2C({=}O)CH_3$)							
302.45	0.0251	372.77	0.3024	422.87	0.9769	468.04	2.2259
314.15	0.0414	382.79	0.3950	432.93	1.1902	473.05	2.4223
323.18	0.0596	392.82	0.5031	442.96	1.4346	475.51	2.5150
352.69	0.1666	402.82	0.6415	452.99	1.7230	475.62	2.5205
362.68	0.2243	412.86	0.7970	463.02	2.0432		
HFK-465mc ($CF_3CF_2C({=}O)CH_2CH_3$)							
299.34	0.0252	337.54	0.1146	372.77	0.3298	422.89	1.0348
302.57	0.0292	342.69	0.1360	382.80	0.4257	432.92	1.2587
314.02	0.0480	347.51	0.1581	392.82	0.5421	442.94	1.5102
323.62	0.0700	352.71	0.1878	402.85	0.6838	452.98	1.8060
327.65	0.0813	362.75	0.2521	412.87	0.8429	463.01	2.1470
332.67	0.0971						
HFK-354pc[a] ($CHF_2CF_2C({=}O)CH_3$)							
297.98	0.0195	342.64	0.1203	402.85	0.6332	463.00	2.0255
303.14	0.0254	352.81	0.1680	412.87	0.7884	473.03	2.3941
312.49	0.0392	362.75	0.2266	422.89	0.9803	481.09	2.7236
324.19	0.0612	372.78	0.3006	432.92	1.1812	489.16	3.0917
333.60	0.0878	382.74	0.3904	442.86	1.4229	497.23	3.4653
337.67	0.1013	392.81	0.5010	452.97	1.7061		
HFK-549mccc ($CF_3CF_2CF_2CF_2C({=}O)CH_3$)							
332.69	0.0403	372.80	0.1547	412.92	0.4385	453.03	1.0148
342.71	0.0584	382.83	0.2052	422.94	0.5475	463.06	1.2008
352.75	0.0826	392.86	0.2691	432.97	0.6760	472.98	1.4520
362.72	0.1139	402.89	0.3460	443.00	0.8395	481.14	1.6682
HFAM-348mm-f ($(CF_3)_2NCH_2CHF_2$)							
293.10	0.0297	333.20	0.1377	373.35	0.4445	413.53	1.1108
303.11	0.0457	343.24	0.1903	383.38	0.5720	423.55	1.3566
313.12	0.0676	353.28	0.2577	393.44	0.7219	433.59	1.6422
323.16	0.0976	363.30	0.3414	403.49	0.9003		

[a] Thermally unstable. Shown for reference.

a further decrease in temperature gave a clearly identical meniscus. In most cases, the meniscus appeared upon condensation at 10 mK lower than T_{CL}. On the other hand, in the case of increasing the temperature, the disappearance of the meniscus and the reappearance of the critical opalescence did not seem to be as clear as in the case of decreasing the temperature. When the temperature was increased from the subcritical to supercritical conditions, the interface between the gas and liquid phases appeared as a thick line at temperature T_{CH} and became thinner before disappearing. For most experiments, T_{CH} was about 10 to 20 mK higher than T_{CL}. In this study, the numerical average of T_{CL} and T_{CH} was taken as the critical temperature. The critical pressure was determined from a linear interpolation of the $T-P$ curve near the critical point. The critical density was determined from the sample mass trapped in the cold trap following the measurements and the known inner volume.

The vapor pressures were correlated using the Antoine equation,[6]

$$\log P = A - \frac{B}{T + C} \tag{1}$$

and the Wagner equation,[6]

$$\ln P_r = \frac{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^{2.5} + D(1 - T_r)^5}{T_r} \tag{2}$$

where P is the pressure in MPa and T is the temperature in K. T_r and P_r are the reduced temperature and pressure, given by $T_r = T/T_c$ and $P_r = P/P_c$, respectively. T_c is the critical temperature, and P_c is the critical pressure.

Results and Discussion

The critical parameters of three out of four hydrofluoroketones and a hydrofluoroamine are shown in Table 2 together with values estimated by the method of Joback.[6] As shown by the standard deviations, the reproducibilities of the critical temperature and pressure were good and within ±20 mK and ±2 kPa, respectively. Joback's method predicted critical temperature and pressure within ±0.6% and −8%, respectively, except for HFK-447mcc.

Compound HFK-354pc was found to be thermally unstable. Table 3 shows the critical parameters of HFK-354pc with and without dehydration. Although the thermal stability improved with dehydration, HFK-354pc was too unstable to allow a measurement of the critical temperature and pressure.

Table 4 shows the vapor pressure of the compounds. Table 5 shows numerical values of eqs 1 and 2 determined on the basis of the experimental data. All data were equally weighted for the fit. The average absolute deviations (AADs) between calculated and experimental values are also shown in Table 5. Wagner's representation gave better agreement than Antoine's equation for all samples.

Table 5. Numerical Values of Coefficients for the Antoine and Wagner Equations and Average Absolute Deviation (AAD)

	temp range/K		parameters for the Antoine equation (eq 1)				parameters for the Wagner equation (eq 2)				
	T_{min}	T_{max}	A	B	C	AAD/%	A	B	C	D	AAD/%
HFK-447mcc	298	T_c	3.307 45	1233.688 44	−50.908 66	0.64	−8.262 56	2.624 68	−6.822 91	7.461 69	0.33
HFK-465mc	299	T_c	3.164 74	1146.076 89	−58.490 06	0.75	−8.973 25	4.895 88	−8.775 89	4.864 39	0.29
HFK-354pc[a]	297	497	3.170 20	1143.663 87	−63.147 07	0.72					
HFK-549mccc	294	T_c	3.285 02	1318.937 26	−50.839 27	0.47	−7.830 73	0.906 48	−3.863 19	4.069 68	0.37
HFAM-348mm-f	293	T_c	3.324 16	1214.573 77	−42.862 24	0.38	−8.151 88	1.973 51	−4.547 64	5.122 46	0.12

[a] Thermally unstable. Shown for reference.

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