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Critical Parameters and Normal Boiling Temperatures of Five Fluorinated Ethers and Two Fluorinated Ketones†

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The critical parameters and normal boiling temperatures of five fluorinated ethers (1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether, *tert*-perfluorobutyl methyl ether, 1,1,1,2-tetrafluoro-2-difluoromethoxyethyl difluoromethyl ether, 2,3,3,5,5,6,6-heptafluoro-1,4-dioxane, and 2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane) and two fluorinated ketones (1,1,1,2,2-pentafluoro-3-butanone and 1,1,1,2-tetrafluoro-2-trifluoromethyl-3-butanone) were measured using static-type apparatuses, in which a small amount of a sample fluid of 5 cm^3 was required to determine the thermodynamic properties accurately. The uncertainties in the critical parameters were ±30 mK in temperature, ±2 kPa in pressure, ±0.2% in density, and ±10 mK in normal boiling temperature, respectively. Lydersen's group contribution method estimated the critical parameters fairly well, but no group contribution method could predict the normal boiling temperature reasonably.

Introduction

We are investigating many kinds of thermodynamic properties including critical properties, normal boiling points, vapor pressures, *pVT* relations, and viscosities for a series of fluorinated compounds such as ethers, alcohols, ketones, and others. They are expected to be new generation alternatives for CFCs and HCFCs used currently and have lower ozone-depletion indices and smaller global warming effects, together with high performance as refrigerants, blowing agents, or cleaning fluids.

In this work, we measured the critical parameters and the normal boiling temperatures of five fluorinated ethers and two fluorinated ketones and examined the applicability of group contribution techniques to the prediction of the critical parameters and the normal boiling temperatures.

Experimental Section

Materials. All fluorinated ethers and ketones were provided by Research Institute of Innovative Technology for the Earth, Japan. The sample fluids were distilled and dried over Merck molecular sieves (0.4 nm) to remove water. The purity expressed by the ratio of the peak areas of gas chromatography is listed in the third column in Table 1 as GC purity. 1,1-Difluoro-1-chloroethane, which was used to check the reliability of the critical parameter measurement, was also provided by Research Institute of Innovative Technology for the Earth, Japan, and its purity was >99.9 GC%. It was used as supplied. Methanol, which was used to check the reliability of the vapor pressure measurement, was supplied by Wako Pure Chemicals, and its purity was >99.9 wt %. It was used after drying over Merck molecular sieves (0.4 nm) to remove water.

Apparatuses and Procedures. A schematic diagram of an apparatus used for the measurement of critical parameters is shown in Figure 1. It consists of a view cell (A), an expansion vessel to discharge a sample fluid (B), and measuring devices of temperature and pressure. The first two vessels are placed in a thermostated oil bath (G) controlled by electric heaters (F1, F2). The view cell with 5.3 cm^3 inner volume is designed for a maximum working pressure of 7 MPa and a maximum working temperature of 473 K, and 10 mm thick sapphire windows are placed on both sides of the cell to observe the behavior of the meniscus between the vapor and liquid phases.

The critical temperature was measured using a Minco model S7929 calibrated 100 Ω platinum resistance thermometer and a type F26 resistance bridge made by Automatic Systems Laboratories Ltd. (T), inserted into the aluminum block mounted around the view cell. The critical pressure was measured using a Ruska model 2439-800 differential pressure null gauge (C) + a differential pressure null indicator (D) and a Paroscientific model 31K101 precise pressure transducer + a Paroscientific model 702 pressure computer (P1). To avoid the error caused by the condensation of the vapor of the sample fluid, we determined the vapor pressure of the sample by measuring the pressure of nitrogen gas supplied to the one side of a thin metallic diaphragm placed in the chamber of the differential pressure null gauge, where the pressure of the

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Table 1. Purity of Sample Fluids and Experimental and Predicted Results of Critical Parameters

			T_c/K			p_c/MPa			ρ_c/kg·dm^{-3}		
compound	formula	GC purity	exp	Lydersen	δT_c[a]	exp	Lydersen	δp_c[b]	exp	Lydersen	$\delta \rho_c$[c]
1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether	$C_5F_{10}H_{12}O$	99.5	447.40	436.37	−11.03	2.140	1.998	−0.142	0.582	0.588	0.006
tert-perfluorobutyl methyl ether	$C_5F_9H_{12}O$	99.5	462.72	448.40	−14.32	2.366	2.415	0.049	0.558	0.554	−0.004
1,1,1,2-tetrafluoro-2-difluoromethoxyethyl difluoromethyl ether	$C_4F_8H_2O$	99.76	449.81	450.29	0.48	2.421	2.309	−0.112	0.571	0.581	0.010
2,3,3,5,5,6,6-heptafluoro-1,4-dioxane	$C_4F_8H_{12}O$	99.5	452.88	463.51	10.63	2.866	3.692	0.826	0.597	0.637	0.040
2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane	$C_5F_{10}H_{12}O$	99.63	435.06	466.90	31.84	2.645	3.277	0.632	0.569	0.641	0.072
1,1,1,2,2-pentafluoro-3-butanone	$C_5F_{10}H_{12}O$	99.4	453.03	453.78	0.75	2.912	3.357	0.445	0.486	0.486	0.000
1,1,1,2-tetrafluoro-2-trifluoromethyl-3-butanone	$C_5F_{10}H_{12}O$	99.8	467.64	456.78	−10.86	2.522	2.791	0.269	0.518	0.512	−0.006
avg dev			11.42			0.354			0.020		

[a] $\delta T_c = T_c(\text{calc}) - T_c(\text{exp})$. [b] $\delta p_c = p_c(\text{calc}) - p_c(\text{exp})$. [c] $\delta \rho_c = \rho_c(\text{calc}) - \rho_c(\text{exp})$.

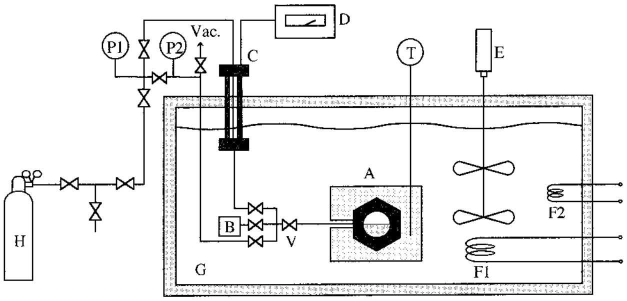

Figure 1. Experimental apparatus for measuring critical parameters: A, view cell; B, expansion vessel; C, differential pressure null gauge; D, differential pressure null indicator; E, agitator; F1, main heater; F2, subheater; G, oil bath; H, nitrogen gas cylinder; P1, P2, pressure gauges; T, Pt resistance thermometer; V, stop valves; Vac, vacuum line.

nitrogen gas was well-balanced with the vapor pressure of the sample fluid on the opposite side of the diaphragm. The critical density at the critical temperature was determined from the mass of the sample fluid confined in the view cell, where the inner volume of the cell was calibrated with water of a known density (JSME, 1980).

The experimental procedure is described below. The sample fluid was degassed in a reservoir by successive evaporate−condensate cycles under vacuum to remove noncondensable gases, and then it was transferred to the evacuated view cell in the oil bath. The temperature of the oil bath was increased while observing the existence of the meniscus. Within 100 mK below the critical temperature, the temperature was raised very slowly in 10 mK increments, and it took 1 h to reach the equilibrium condition. The same procedure was repeated until the meniscus disappeared and the strong critical opalescence was observed at the critical point. Both the temperature and pressure at the maximum critical opalescence were recorded. Then the temperature was raised to around 200 mK above the critical temperature to reach an uniform phase of a supercritical fluid and decreased slowly by the same procedure as that for raising the temperature near the critical point. The temperature was decreased in 10 mK increments, and it took 1 h until the meniscus reappeared and the strong critical opalescence was observed again in the critical point. The temperature and pressure at this point were recorded as the critical parameters again. The critical temperature and pressure were assumed to be the mean values obtained from these two measurements: increasing and decreasing temperature processes. To determine accurate critical parameters, it was important to keep the meniscus level at the middle of the view cell during the measurements.

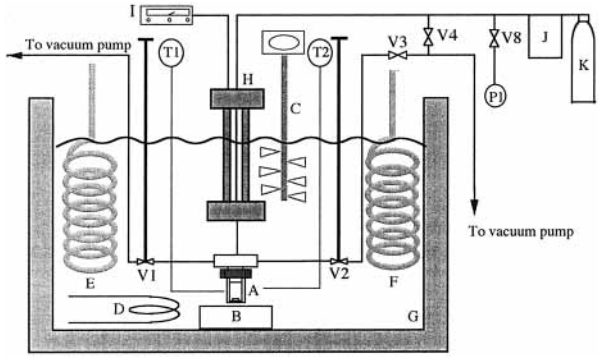

Figure 2. Experimental apparatus for measuring normal boiling temperatures: A, equilibrium cell; B, magnetic stirrer; C, agitator; D, heater; E, cooler 1 (273 K); F, cooler 2 (243 K); G, oil bath; H, differential pressure null gauge; I, differential pressure null indicator; J, pressure control pack; K, nitrogen gas cylinder; P1, pressure gauge; T1, Pt resistance thermometer; T2, monitoring thermometer; V, stop valves.

A schematic diagram of an apparatus for the measurement of normal boiling temperatures is shown in Figure 2. It consists of an equilibrium cell placed in an oil bath and temperature and pressure measurement devices. The equilibrium cell (A) with 2 cm^3 in internal volume was designed for a maximum working pressure of 600 kPa and a maximum working temperature of 373 K. The cell was placed in the oil bath (G) controlled by an electric heater (D) and coolers (E, F) within an accuracy of 0.01K. The equilibrium temperature of the sample fluid was measured with a NAMAS type T25-02 calibrated 100 Ω platinum resistance thermometer (T1), and the vapor pressure was measured using the same differential pressure null gauge (H) + null indicator (I) and the same pressure computer (P1) except for a precise pressure transducer. In this experiment, a Parascientific model 2100A precise pressure transducer was employed for a low-pressure measurement (the maximum working pressure was 690 kPa).

Results and Discussion

There were experimental uncertainties in the determination of the critical parameters by the visual observation method. Figure 3 shows the uncertainties for the determination of the critical temperature and pressure of a fluorinated ether using the experimental apparatus shown in Figure 1. The first uncertainty was the disagreement between the critical parameters from the disappearance of the meniscus on increasing the temperature (case 1) and those determined from the reappearance on decreasing the temperature (case 2). This gave an uncertainty of 20 to 30 mK in the critical temperature and of 1 to 3 kPa in the

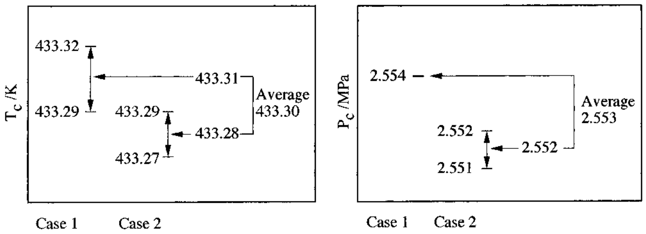

Figure 3. Uncertainty in the determination of critical parameters of 1,1,1,2-tetrafluoro-2-trifluoromethylethyl methyl ether: case 1, in the case of increasing temperature; case 2, in the case of decreasing temperature.

Table 2. Comparison of Experimental and Literature Critical Parameters of 1,1-Difluoro-1-chloroethane

critical parameters	exp results	Yada et al. (1991)
T_c/K	410.34	410.29
p_c/MPa	4.048	4.041
ρ_c/g·cm^{-3}	0.444	0.446

critical pressure. The second one was the indistinctness of the maximum critical opalescence at the critical point. There was a temperature range of 20 to 40 mK and a pressure range of 1 to 2 kPa where the intensity of the opalescence did not vary significantly. The final critical temperature and pressure were the average of case 1 and case 2, as shown in Figure 3. The experimental uncertainties were estimated to be within ±30 mK in the critical temperature, ±2 kPa in the critical pressure, and ±0.2% in the critical density, respectively.

To check the reliability of the experimental apparatus and procedure, measurements were made on the critical parameters of 1,1-difluoro-1-chloroethane (HCFC-142b). Table 2 shows the comparison of our measured data with literature data by Yada et al. (1991). Our results agreed well with the literature values within the experimental uncertainties for three kinds of critical parameters.

The experimental results are given in Table 1. No experimental data on the critical parameters were available in the literatures. The experimental data were compared with the Lydersen's estimation (1955), which is one of the successful group contribution methods. The calculated results and the deviation between the experimental and calculated values are also given in Table 1. This method could estimate the critical properties of the fluorinated compounds fairly well, although it was developed mainly to apply to hydrocarbons.

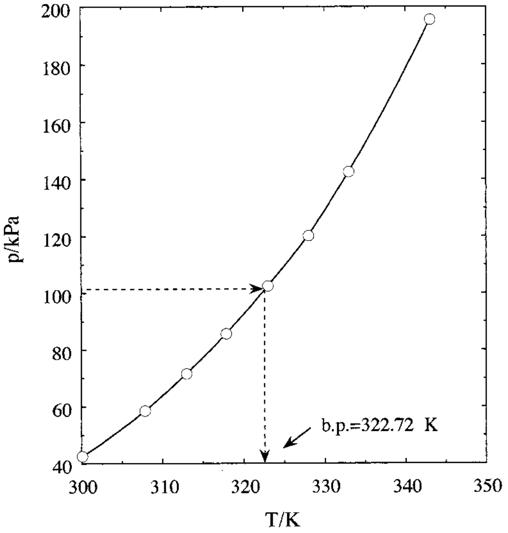

Figure 4. Vapor pressure of 1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether.

Figure 4 shows how to determine the normal boiling temperature from the vapor pressure data in the vicinity of an atmospheric pressure. The vapor pressure data were correlated by the Antoine equation:

$$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K} + C) \qquad (1)$$

The normal boiling temperature at 101.325 kPa was then determined from the Antoine equation.

Table 3. Vapor Pressures in the Vicinity of the Normal Boiling Temperature and Antoine Constants in Eq 1

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether[a]		*tert*-perfluorobuthyl methyl ether[b]		1,1,1,2-tetrafluoro-2-difluoro-methoxyethyl difluoromethyl ether[c]		2,3,3,5,5,6,6-heptafluoro-1,4-dioxane[d]	
300.09	42.53	295.36	31.11	303.44	55.26	299.00	61.39
307.84	58.55	302.92	42.14	308.38	66.40	302.88	71.08
312.96	71.55	312.89	61.99	313.18	79.77	312.72	100.21
317.90	85.65	322.97	89.67	317.94	93.68	313.84	104.36
322.99	102.43	327.01	103.29	323.04	113.06	322.97	144.42
327.80	120.11	333.00	126.11	327.99	133.93	332.98	199.37
333.02	142.53			333.15	159.16	343.01	269.24
343.05	195.53			338.17	186.89	353.10	356.38
				343.23	219.00	363.17	465.19
avg dev = 0.29%	max. dev = 0.50%	avg dev = 0.17%	max. dev = 0.24%	avg dev = 0.25%	max. dev = 0.73%	avg dev = 0.57%	max. dev = 0.97%
2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane[e]		1,1,1,2,2-pentafluoro-3-butanone[f]		1,1,1,2-tetrafluoro-2-trifluoromethyl-3-butanone[g]			
295.95	73.95	300.99	60.48	297.47	30.68		
303.45	95.51	304.97	71.05	302.85	38.28		
308.32	115.21	312.87	95.80	312.91	57.01		
313.11	136.95	317.98	115.52	322.99	82.76		
322.97	189.59	322.95	137.36	327.97	98.55		
333.03	259.77	333.03	191.60	328.99	102.24		
343.17	350.06	344.57	273.83	333.01	116.91		
353.13	458.54	353.16	348.90	343.07	161.54		
363.19	595.05						
avg dev = 0.67%	max. dev = 0.96%	avg dev = 0.10%	max. dev = 0.26%	avg dev = 0.10%	max. dev = 0.19%		

[a] $A = 5.7616$, $B = 934.79$, $C = -73.833$. [b] $A = 7.4136$, $B = 1942.6$, $C = 32.712$. [c] $A = 7.7968$, $B = 2192.6$, $C = 58.666$. [d] $A = 6.7157$, $B = 1448.9$, $C = -5.1005$. [e] $A = 6.0278$, $B = 992.85$, $C = -58.133$. [f] $A = 6.1903$, $B = 1101.7$, $C = -51.093$. [g] $A = 6.5372$, $B = 1379.5$, $C = -24.354$.

Table 4. Experimental and Predicted Results of Normal Boiling Temperatures

compound	T_b(exp)/K	T_b(Joback)/K	δT^a/K
1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether	322.72	316.0	−6.7
tert-perfluorobutyl methyl ether	326.50	316.7	−9.8
1,1,1,2-tetrafluoro-2-difluoromethoxyethyl difluoromethyl ether	319.95	322.6	2.6
2,3,3,5,5,6,6-heptafluoro-1,4-dioxane	312.72	346.0	33.3
2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane	304.98	346.0	41.0
1,1,1,2,2-pentafluoro-3-butanone	314.37	334.7	20.3
1,1,1,2-tetrafluoro-2-trifluoromethyl-3-butanone	328.78	352.9	24.1
avg dev		19.7	

[a] δT = normal boiling temperature (calc) − normal boiling temperature (exp).

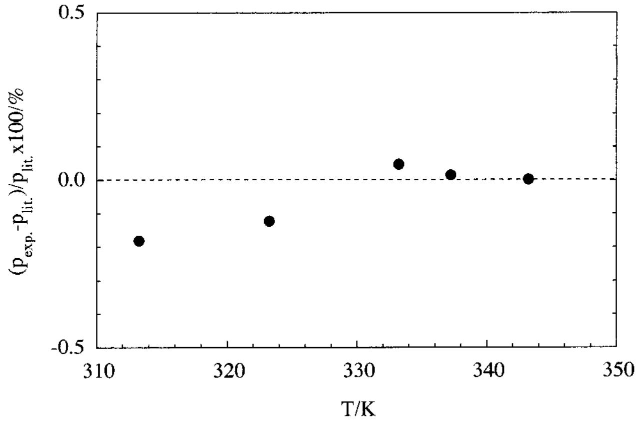

Figure 5. Deviation of vapor pressure of methanol from literature data.

To check the reliability of the experimental apparatus and procedure, we measured the vapor pressures of pure methanol. Figure 5 shows the difference between the experimental and literature data, including at the normal boiling temperature. The vapor pressures measured here agreed well with the literature data (Reid et al., 1987). Judging from the results, the uncertainties were ±10 mK in temperature and ±0.1 kPa in pressure.

Table 3 gives the vapor pressures in the vicinity of the normal boiling temperature, the Antoine constants in eq 1, and the percent average and maximum deviations for five fluorinated ethers and two fluorinated ketones. The percent average deviation was defined by $1/n\sum|p(\text{exp}) - p(\text{calc})|/p(\text{exp}) \times 100$, where n is the number of data points and p is the vapor pressure. The vapor pressure data for all fluorinated compounds were fitted by eq 1 smoothly. Table 4 lists the experimental normal boiling temperatures for five fluorinated ethers and two fluorinated ketones. The experimental results were compared with the Joback's estimation (1984) based on a group contribution method, and the deviation was too large to be used in engineering calculations.

Conclusions

The critical parameters and normal boiling temperatures of five fluorinated ethers (1,1,1,2,4,4,4-heptafluoroisobutyl trifluoromethyl ether, *tert*-perfluorobutyl methyl ether, 1,1,1,2-tetrafluoro-2-difluoromethoxyethyl difluoromethyl ether, 2,3,3,5,5,6,6-heptafluoro-1,4-dioxane, 2-trifluoromethyl-4,4,5,5-tetrafluoro-1,3-dioxolane) and two fluorinated ketones (1,1,1,2,2-pentafluoro-3-butanone, 1,1,1,2-tetrafluoro-2-trifluoromethyl-3-butanone) were measured using the static-type apparatuses, which could realize the rapid and accurate determination of these properties with a small amount of the sample of 2 to 5 cm^3. Lydersen's group contribution method estimated the critical parameters fairly well, but no group contribution method could predict the normal boiling temperature well.

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