802 *J. Chem. Eng. Data* **1996,** *41,* 802−805

Critical Properties of Fluorinated Ethers

Takeshi Sako,* Masahito Sato, Noriaki Nakazawa, and Masaru Oowa

Department of Chemical Systems, National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan

Masahiko Yasumoto, Haruaki Ito, and Shiro Yamashita

Research Institute of Innovative Technology for the Earth, Hongo 2-40-17, Bunkyo-ku, Tokyo 113, Japan

Using a static-type apparatus, we measured the critical temperatures, pressures, and densities of seven fluorinated ethers: $CF_3CHFOCHF_2$, $CF_3CF_2OCH_3$, $CF_3CH_2OCH_3$, $CF_3CF_2OCH_2CF_3$, $CF_3CF_2OCH_2CH_3$, CF_3,$CF_2CF_2OCH_3$, and $(CF_3)_2CFOCH_3$. The advantage of the measuring apparatus was that a small amount of a sample was sufficient to determine the critical properties accurately. The uncertainties of the critical properties measured in this work were ±30 mK in temperature, ±2 kPa in pressure, and ±0.2% in density, respectively. The critical properties of the compounds were compared with those estimated by the Lydersen group contribution method.

Introduction

We are investigating thermodynamic properties of a series of fluorinated ethers, which are under consideration as new generation alternatives for chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) used currently (Sako et al., 1994; Mochizuki et al., 1995). They have lower ozone-depletion indices and smaller global warming effects and show high performance as refrigerants, blowing agents, or cleaning fluids. Critical properties are fundamental properties and important to predict other physicochemical properties by equations of state or corresponding states theories. However only limited data from Wang et al. (1991) are available for fluorinated ethers such as $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, C-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3.

In this work, we measured the critical properties of seven fluorinated ethers by visual observation of the appearance and/or disappearance of the meniscus at the vapor + liquid interface of the sample. Furthermore we compared the results with Lydersen's prediction.

Experimental Section

The seven fluorinated ethers of 1,2,2,2-tetrafluoroethyl difluoromethyl ether ($CF_3CHFOCHF_2$), perfluoroethyl methyl ether ($CF_3CF_2OCH_3$), 2,2,2-trifluoroethyl methyl ether $_3CH_2OCH_3$), perfluoroethyl 2,2,2-trifluoroethyl ether $_3CF_2OCH_2CF_3$), perfluoroethyl ethyl ether ($CF_3CF_2OCH_2CH_3$), perfluoropropyl methyl ether ($CF_3CF_2CF_2OCH_3$), and perfluoroisopropyl methyl ether ($(CF_3)_2CFOCH_3$) were distilled and purified by preparative-scale gas chromatography. The collected fraction was dried over molecular sieves to remove water. The purity of the samples is presented in Table 1. The purity of HCFC-142b, which was used to check the reliability of the experimental apparatus, was more than 99.9%.

A schematic diagram of an apparatus used for the measurement of critical properties is shown in Figure 1. It consists of a view cell (A), an expansion vessel to discharge a sample (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). Figure 2 shows the detail of the view cell. The drawing on the top is the top view of the view cell, aluminum block, and a part of tubings and stop valve. That on the bottom is the cross-section of the view cell at the section S1−S2. It is designed for a maximum working pressure of 7 MPa and maximum working temperature of 473 K. On both sides of the cell, 10 mm thick sapphire windows are placed to observe the behavior of the meniscus between the vapor and liquid phases. The dimensions are 3 cm in length between both windows, 1.5 cm inner diameter, and 5.3 cm^3 inner volume.

Table 1. Purity of Samples

compound	purity/ mol %	compound	purity/ mol %
$CF_3CHFOCHF_2$	99.6	$CF_3CF_2OCH_2CH_3$	99.9
$CF_3CF_2OCH_3$	99.9	$CF_3CF_2CF_2OCH_3$	99.5
$CF_3CH_2OCH_3$	99.9	$(CF_3)_2CFOCH_3$	99.9
$CF_3CF_2OCH_2CF_3$	99.9		

The critical temperature of the sample was measured using a platinum resistance thermometer (T) (NAMAS Co., Type T25/02) calibrated on ITS-90 with an AC resistance bridge (Automatic Systems Laboratory, Model F250). The thermometer was inserted into the aluminum block mounted around the view cell. As the temperature of the aluminum block was assumed to be equal to that of the sample, careful attention was paid to confirm that the sample was in thermodynamic equilibrium by monitoring the temperature variation. The drift of the oil temperature in the thermostated bath was less than ±2 mK, and the temperature of the view cell was kept constant within a fluctuation of ±1 mK during the measurement of a given isotherm because the heat capacity of the cell was much larger than that of the fluid in the oil bath.

The critical pressure was measured by a differential pressure null gauge (C) (Ruska Co., Model 2439-702), a differential pressure null indicator (D) (Ruska Co., Model 2416-711), and a precise pressure gauge (P1) (Paroscientific, Inc., Digiquartz pressure transducer 2200AT and 2900AT). In order to avoid the error caused by the condensation of the vapor of the sample, 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 dif-

---

* Tel: 81-298-54-4735. Fax: 81-298-56-8587. E-mail: sako@nimc.go.jp.

S0021-9568(95)00327-X CCC: $12.00

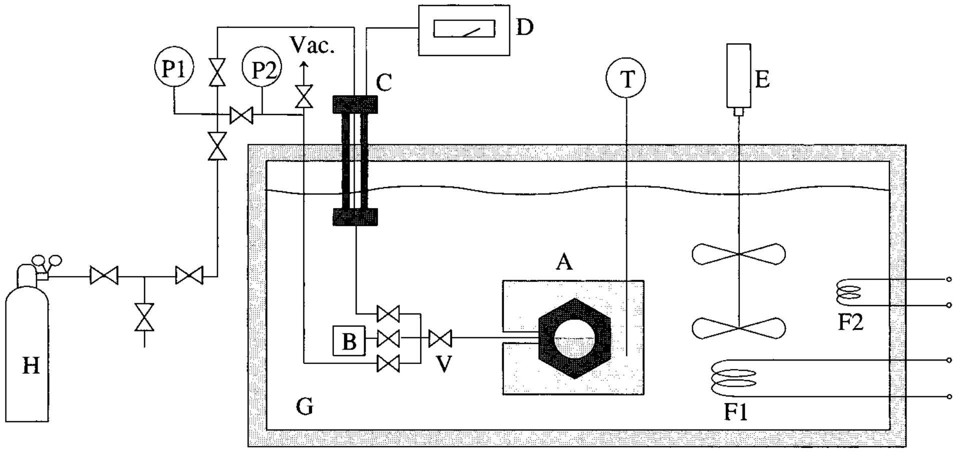

Figure 1. Experimental apparatus for measurement of critical properties: A, view cell; B, expansion vessel; C, differential pressure null gauge; D, differential pressure null indicator; E, agitator; F1, main heater; F2, subheater; G, oil bath; H, nitrogen gas cylinder; P1, P2, pressure gauges; T, Pt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

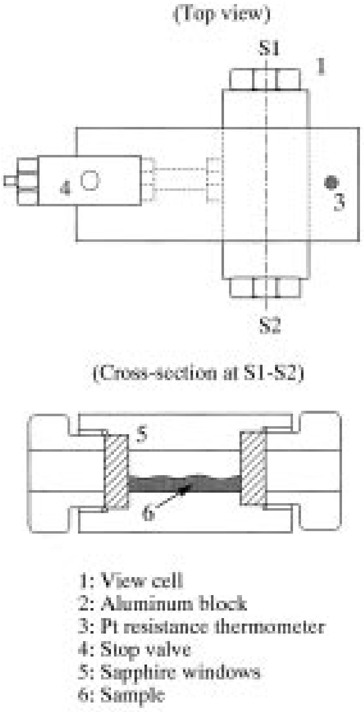

Figure 2. View cell.

ferential pressure null gauge, where the pressure of the nitrogen gas was well-balanced with the vapor pressure of the sample in the opposite side of the diaphragm.

The critical density was determined from the mass of the sample confined in the view cell at the critical point. Prior to the measurement, the inner volume of the cell was calibrated by filling water with a known density (JSME, 1983) and corrected with respect to the effect of the thermal expansion on the basis of the data of the linear thermal expansion coefficient for the 316 stainless steel (Touloukian, 1976). There was no significant effect of the pressure on the change in the inner volume of the cell. The sample in the cell was sucked from the cell, collected into a trap bottle cooled with liquid nitrogen, and weighed with a precise balance with an uncertainty of 0.1 mg.

The experimental uncertainties were estimated to be within ±30 mK in the critical temperature, ±2.0 kPa in the critical pressure, and ±0.2% in the critical density, respectively.

The experimental procedure is described below. Firstly, we confirmed the thermal stability of all samples by heating them for at least 6 h at 473 K and analyzing with gas chromatography whether the pyrolysis products from the samples existed or not. The stable sample was degassed in a reservoir by successive evaporation−condensation 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 gradually by 200 to 300 mK/min while the existence of the meniscus was observed. The temperature increase was reduced to 10 mK/h when the critical point was approached within 30 mK. The meniscus disappeared, and the strong critical opalescence was observed in close vicinity of the critical point. The temperature and pressure at the maximum critical opalescence were recorded. Then the temperature was raised a little above the critical temperature to reach a uniform phase of a supercritical fluid and decreased by 10 mK/h. The temperature and pressure at the reappearance of the meniscus and maximum critical opalescence were recorded again. The critical temperature and pressure were assumed to be the mean values obtained from these two measurements. In order to determine accurate critical properties, it was important to keep the meniscus level at the middle of the view cell during the measurements.

We repeated the measurement of the critical properties twice for the same sample. The critical pressure was measured in the first experiment with the pressure-measuring device, and the critical temperature and density were determined in the second experiment without the pressure-measuring device. More accurate values of the critical temperature and density were obtained when the differential pressure null gauge was not connected to the measuring line. This was because the disturbance caused by the deformation of the diaphragm of the gauge was avoided.

The measurement apparatus and procedure of normal boiling points, which are necessary to predict the critical temperature, were described elsewhere (Sako et al., 1994).

Results and Discussion

There is some experimental error in determining the critical properties by visual observation. Figure 3 shows the extent of 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 properties determined from the disappearance of the

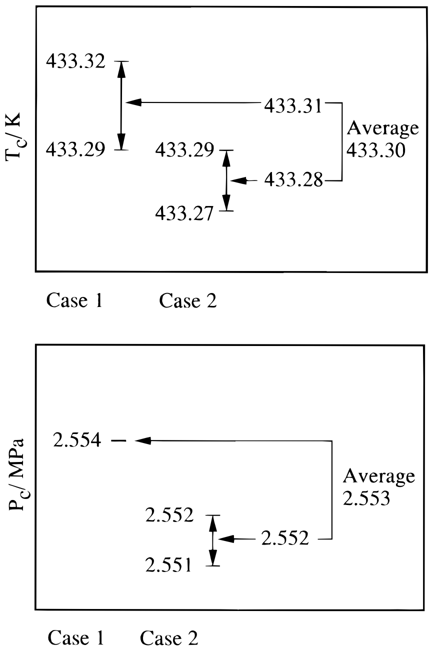

Figure 3. Uncertainty to determine critical properties of $(CF_3)_2$-$CFOCH_3$: (case 1) in case of increasing temperature; (case 2) in case of decreasing temperature.

Table 2. Comparison of Experimental with Literature Critical Properties of CH_3CClF_2

critical property	experimental	Yada et al. (1991)	Mears et al. (1955)
/K	410.34	410.29	410.25
/MPa	4.048	4.041	4.123
/g·cm^{-3}	0.444	0.446	0.435

meniscus on increasing temperature (case 1) and those determined from the reappearance on decreasing temperature (case 2). This gave an uncertainty of 20 to 30 mK in the critical temperature and of 1 to 3 kPa in the critical pressure. The second one was the indistinctness of the maximum critical opalescence at the critical point. There was a temperature region of 20 to 40 mK and a pressure region of 1 to 2 kPa where the intensity of the opalescence was almost unchanged, the uncertainty in the critical temperature being larger than that in the critical pressure. The final values were the averages of each step, as shown in Figure 3.

To check the reliability of the experimental apparatus and procedure, we measured the critical properties of HCFC-142b (CH_3CClF_2). The comparison between the experimental results and the literature values reported by Yada et al. (1991) and Mears et al. (1955) is presented in Table 2. The difference from the data of Yada et al. was almost within the experimental uncertainties for the three kinds of critical properties. On the other hand, the critical properties measured by Mears et al. deviated from our data except for the critical temperature.

The critical properties were measured for seven fluorinated ethers. The experimental results are given in Table 3. The fluorinated ethers were classified into three groups: fluorinated methyl ethyl ethers, fluorinated diethyl ethers, and fluorinated methyl propyl ethers. No experimental data on the critical properties were available in the literature. The normal boiling points are given in Table 3. For many compounds, the critical temperature reduced as the normal boiling point decreased. The critical properties of some compounds, for example $CF_3CH_2OCHF_2$ and $CHF_2CF_2OCH_3$, could not be determined because of their thermal decomposition.

The experimental critical properties were compared with Lydersen's estimation (1955) given by

$$T_c/\mathrm{K} = T_b[0.567 + \sum\Delta_T - (\sum\Delta_T)^2]^{-1}$$

$$P_c/\mathrm{atm} = M(0.34 + \sum\Delta_p)^{-2}$$

$$V_c/\mathrm{cm^3{\cdot}mol^{-1}} = 40 + \sum\Delta_v \qquad (1)$$

where T_b is the normal boiling point presented in Table 3, M is the molecular weight, and Δ are group parameters. This is one of the successful group contribution methods and is often used in an engineering calculation. The calculated results are given in Table 3. The mean and maximum deviations were 3.46 K and 6.73 K in critical temperature, 0.137 MPa and 0.268 MPa in critical pressure, and 0.021 g·cm^{-3} and 0.038 g·cm^{-3} in critical density, respectively. The Lydersen method could estimate the critical properties of the fluorinated ethers fairly well, although it was developed mainly to apply to hydrocarbons. The deviation among C_3 ethers was a little larger than that among C_4 ethers.

Conclusions

The critical properties determined in this work and the vapor pressures measured in the previous work suggested that the fluorinated ethers are potential alternatives for chlorofluorocarbons and hydrochlorofluorocarbons as refrigerants of heat pumps, blowing agents, and cleaning fluids. The Lydersen estimation technique of the critical properties could be used for rough calculation for fluorinated ethers.

Literature Cited

The Japan Society of Mechanical Engineers (JSME). *JSME Data Book: Thermophysical properties of fluids*; JSME: Tokyo, 1983; p 208.

Lydersen, A. L. Estimation of critical properties of organic compounds. *Repr.—Wis., Eng. Exp. Stn.* **1955**, 3.

Mears, W. H.; Stahl, R. F.; Orfeo, S. R.; Shair, R. C.; Kells, L. F.; Thompson, W.; McCann, H. Thermodynamic properties of halogenated ethanes and ethylenes. *Ind. Eng. Chem.* **1955**, *47*, 1449–1454.

Mochizuki, Y.; Nagasaki, N.; Suga, A.; Gotoh, Y.; Ito, H.; Yamashita, S. Physical properties of fluorinated ethers. *Proceedings of ACS 12th Winter Fluorine Conference* **1995**, *1*, 55.

Table 3. Critical Properties Measured in This Study and Those Estimated by Lydersen's Method

no.	compound	T_b/K exp	T_C/K exp	T_C/K Lydersen	P_C/MPa exp	P_C/MPa Lydersen	ρ_C/g·cm^{-3} exp	ρ_C/g·cm^{-3} Lydersen
1	$CF_3CHFOCHF_2$	296.50	428.95	425.64	3.050	2.782	0.533	0.540
2	$CF_3CF_2OCH_3$	278.74	406.80	409.41	2.887	2.958	0.499	0.523
3	$CF_3CH_2OCH_3$	304.77	448.98	455.71	3.513	3.429	0.412	0.431
4	$CF_3CF_2OCH_2CF_3$	301.04	421.68	419.41	2.330	2.228	0.533	0.571
5	$CF_3CF_2CF_2OCH_3$	307.38	437.70	435.31	2.481	2.369	0.530	0.550
6	$(CF_3)_2CFOCH_3$	302.56	433.30	428.49	2.553	2.369	0.542	0.550
7	$CF_3CF_2OCH_2CH_3$	301.26	431.23	433.34	2.533	2.673	0.448	0.480
	mean deviation		3.46		0.137		0.021	

Sako, T.; Sato, M.; Nakazawa, N.; Oowa, M.; Sekiya, A.; Ito, H.; Yamashita, S. Thermodynamic properties of fluorinated ethers as alternative refrigerants. *Proceedings of the International Conference CFC's, the day after*, **1994**, 1, 485−491.

Touloukian, Y. S.; Kirby, R. K.; Taylor, R. E.; Desai, P. D. *Thermal expansion*, *Metallic elements and alloys*, *Thermophysical properties of matter*; IFI/Plenum: New York, 1976; Vol. 12.

Wang, B-H.; Adcock, J. L.; Mathur, S. B.; van Hook, W. A. Vapor pressures, liquid molar volumes, vapor non-idealities, and critical properties of some fluorinated ethers: $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2H$, c-$CF_2CF_2CF_2O$, CF_3OCF_2H, and CF_3OCH_3; and of CCl_3F and CF_2ClH. *J. Chem. Thermodyn.* **1991**, *23*, 699−710.

Yada, N.; Kumagai, K.; Tamatsu, T.; Sato, H.; Watanabe, K. Measurement of the thermodynamic properties of HCFC 142-b. *J. Chem. Eng. Data* **1991**, *36*, 12−14.

Received for review December 23, 1995. Accepted April 11, 1996.[⊗] This work was supported by New Energy and Industrial Technology Development Organization (NEDO).

JE950327T

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1996.