

Gaseous Thermal Conductivities of Fluorinated Methyl Ethyl Ethers

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Gaseous thermal conductivities of six fluorinated methyl ethyl ethers, which are potential replacements for traditional blowing agents, have been measured by a transient hot-wire method. Temperature and pressure ranges of the measurements are from 303 K to 343 K and up to 0.4 MPa, respectively. The uncertainty of the thermal conductivities obtained is estimated to be within $\pm 1\%$. Simple correlation equations were developed to represent the temperature and pressure dependences on the experimental thermal conductivities. Comparisons of the thermal conductivities between the present fluorinated ethers and those of traditional blowing agents CFC 11 (trichlorofluoromethane) and HCFC 141b (1,1-dichloro-1-fluoroethane) are given.

Introduction

Although a number of hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) have been developed as possible substitutes for restricted chlorofluorocarbons (CFCs), it is not easy to satisfy both the industrial and environmental requirements. In the case of blowing agents, HFC 245fa and cyclopentane are presently expected to be promising alternatives to the traditional agent CFC 11 (trichlorofluoromethane). But the considerably high value of global warming potential (GWP) for HFC 245fa and the high flammability for cyclopentane suggest a necessity for developing new substitutes for these compounds. Therefore, the development of a new type of compound in which chlorine is replaced by atoms with low toxicity and low flammability such as oxygen, nitrogen, sulfur, or silica has been undertaken. The following six hydrofluorocarbon ethers (HFEs), which are potential alternatives for the traditional blowing agents, have been recently synthesized and their gaseous thermal conductivities have been measured.

HFE 227me: $\text{CF}_3\text{CHFOCF}_3$ (trifluoromethyl 1,2,2,2-tetrafluoroethyl ether)

HFE 236me: $\text{CF}_3\text{CHFOCHF}_2$ (difluoromethyl 1,2,2,2-tetrafluoroethyl ether)

HFE 245mc: $\text{CF}_3\text{CF}_2\text{OCH}_3$ (methyl perfluoroethyl ether)

HFE 245mf: $\text{CF}_3\text{CH}_2\text{OCHF}_2$ (difluoromethyl 2,2,2-trifluoroethyl ether)

HFE 245qc: $\text{CH}_2\text{FCF}_2\text{OCHF}_2$ (difluoromethyl 1,1,2-trifluoroethyl ether)

HFE 254pc: $\text{CHF}_2\text{CF}_2\text{OCH}_3$ (methyl 1,1,2,2-tetrafluoroethyl ether)

The measurements were performed with a transient hot-wire apparatus with extremely thin platinum wires to account for the low values of thermal conductivities in the gas phase. The thermal conductivities were compared to those of the restricted blowing agent CFC 11 and some

alternative substances HFCs and HCFCs that had been previously measured in the same apparatus as this work (Yamamoto et al., 1993; Tanaka et al., 1995). There exist very few reliable experimental works on thermophysical properties for the available HFEs, and rapid accumulation of accurate experimental data is required.

Experimental Section

According to the principle of transient hot-wire method, the working equation is given as follows (de Groot et al., 1974; Healy et al., 1976):

$$\Delta T = \frac{q}{4\pi\lambda} \ln \frac{4\kappa t}{a^2 C} \quad (1)$$

Here λ is the thermal conductivity and ΔT is the temperature rise of the platinum wire, q is the heat generated per unit length of the platinum wire, κ is the thermal diffusivity of the sample fluid ($=\lambda/\rho C_p$), a is the radius of the hot-wire, and C is the exponential of Euler's constant. To compensate for the heat flux in the axial direction through the sample fluid at the ends of the wire, two platinum wires of different length (main wire, 50 mm; compensating wire, 25 mm) are arranged in opposing arms of a bridge circuit and the deviation from the balance point owing to the initiation of the heating cycle is measured. The out-of-balance voltage is amplified and monitored by a computer together with the temperature and pressure. The hot-wire cell is jacketed and maintained isothermally at ± 10 mK by circulating water. Temperature and pressure are measured with a thermistor to within ± 10 mK and with a strain gauge-type pressure transducer within ± 0.1 MPa, respectively. The detail of the apparatus is described elsewhere (Yamamoto et al., 1993). Most of the recent measurements of liquid thermal conductivity are performed by a transient hot-wire method, because of its advantages of a high precision and simplicity of handling. That is not the case for gaseous thermal conductivity, however, and special attention should be paid to the obtained experimental results. The power supplied to the bridge circuit is initially consumed to heat up the platinum wires themselves. The heat capacity of the gaseous sample

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Table 1. Thermophysical Properties of Methyl Ethyl Ethers

	M^a	F-ratio ^b	T_b/K	P_{sat}^c/kPa	$\rho_{liq}^d/(kg \cdot m^{-3})$	purity/%
HFE 227me	186.03	.875	263.6			99.9
HFE 236me	168.04	.750	296.5	108.1	1454.0	99.9
HFE 245mc	150.05	.625	278.7			99.9
HFE 245mf	150.05	.625	302.2	86.9	1390.8	99.9
HFE 245qc	150.05	.625	316.3	49.3	1426.2	99.9
HFE 254pc	132.07	.500	310.3	63.1	1288.0	99.9

^a Molar mass. ^b F-atom/(H-atom + F-atom). ^c Vapor pressure at 298.15 K. ^d Liquid density at 296.15 K.

is considerably smaller than that of platinum wire, and this heat capacity difference leads to an unexpectedly too small temperature rise on the wire surface at the very beginning of the supply of power. One of the best ways to minimize this heat capacity effect is to use an extremely thin wire. In the present work, therefore, a high-purity platinum wire whose radius is only $2.5 \mu m$ is used as a hot-wire. Besides this heat capacity effect, the working equation is derived assuming an infinite extent around a hot-wire to achieve the complete temperature decline to a bulk temperature. In other words, the working equation requires that the temperature gradient exists only in the sample fluid close to the hot-wire. But in the gas phase, the temperature field around the hot-wire usually extends beyond the radius of isothermal outer wall, and if the growth of the outer boundary breaks the assumption of the infinite extent of sample fluid, the negative departure from the linear relationship between ΔT and $\ln \tau$ in eq 1 is observed near the end of the measurement. In the case of gaseous sample, therefore, the measurements should be completed during a very short time interval in which neither the heat capacity effect nor the outer boundary effect appears. The usual sampling rate of present measurements is set at 3 kSamples/s, and the data collected for about 200 ms midway, in which the linear relationship between ΔT and $\ln \tau$ is maintained, are used to determine the thermal conductivity. The typical temperature rise ΔT during this time interval is in the range of 0.2 to 0.3 K.

Taxis and Stephan (1994) have recently researched the application of the transient hot-wire method to gases at low pressures. According to their work, the heat capacity and outer boundary effects on our apparatus have been strictly analyzed using the experimental data for argon which had been measured in advance. As the result of this, it has been confirmed that reliable gaseous thermal conductivities can be determined with our apparatus using the data points that have been collected during a very short time interval mentioned above. The detail of this confirmation is described elsewhere (Matsuo and Tanaka, 1994).

HFEs used in this experiment were synthesized at the National Institute of Materials and Chemical Research, and their purity is given in Table 1 together with some fundamental thermophysical properties reported by RITE (1996). The uncertainty of the experimental results was estimated considering the possible error sources, i.e., the precision of temperature and pressure measurement, uncertainty of wires dimensions, resolution of the A/D converter, stability of supplied power, and temperature drift of bridge resistances. The overall uncertainty obtained as a summation of above sources is less than 1%, and the reproducibility of measurement is well within this value. But, in general, the measurements of gaseous thermal conductivities are much more difficult than those of liquid thermal conductivities and the large discrepancies beyond 5% from author to author are frequently reported. Our previous results for some halogenated ethanes (Yamamoto et al., 1993) obtained with the same apparatus as the

Table 2. Thermal Conductivity of Methyl Ethyl Ethers

P/MPa	$\lambda/mW \cdot m^{-1} \cdot K^{-1}$	P/MPa	$\lambda/mW \cdot m^{-1} \cdot K^{-1}$	P/MPa	$\lambda/mW \cdot m^{-1} \cdot K^{-1}$
HFE 227me					
$T = 303.15 K$		$T = 313.15 K$		$T = 323.15 K$	
0.05	12.13	0.05	12.93	0.05	13.62
0.10	12.31	0.10	13.06	0.10	13.70
0.15	12.48	0.15	13.20	0.15	13.79
0.20	12.67	0.20	13.34	0.20	13.89
0.25	12.84	0.25	13.46	0.25	13.99
0.30	13.03	0.30	13.61	0.30	14.09
0.35	13.22	0.35	13.76	0.35	14.21
		0.38	13.85	0.40	14.33
HFE 236me					
$T = 303.15 K$		$T = 323.15 K$		$T = 333.15 K$	
0.05	11.94	0.05	13.96	0.05	14.88
0.10	12.24	0.10	14.12	0.10	14.99
		0.14	14.27	0.14	15.10
$T = 313.15 K$					
0.05	13.04				
0.10	13.26				
0.115	13.34				
HFE 245mc					
$T = 303.15 K$		$T = 313.15 K$		$T = 323.15 K$	
0.05	12.24	0.05	12.98	0.05	13.78
0.10	12.58	0.10	13.23	0.10	13.94
0.15	12.93	0.15	13.47	0.15	14.11
0.19	13.22	0.20	13.74	0.20	14.28
		0.21	13.80	0.23	14.39
HFE 245mf					
$T = 305.15 K$		$T = 317.15 K$			
0.078	12.34	0.099	13.37		
HFE 245qc					
$T = 317.15 K$		$T = 323.15 K$		$T = 333.15 K$	
0.07	12.81	0.076	13.46	0.08	14.25
HFE 254pc					
$T = 323.15 K$		$T = 333.15 K$		$T = 343.15 K$	
0.05	13.49	0.05	14.09	0.05	14.71
0.10	13.79	0.10	14.34	0.10	14.82
0.12	13.92	0.15	14.60	0.15	14.93
				0.17	14.98

present work are not exceptions, and considerably large disagreements from the literature values that are beyond combined uncertainty were observed. It is not completely deniable, therefore, that there might exist an overlooked error source or inadequate correction.

Results and Discussion

The thermal conductivities obtained at various temperatures and pressures are given in Table 2, and those for HFE 227me are typically shown as in Figure 1. The thermal conductivity of HFE 227me increases monotonically with both increasing pressure and increasing temperature. Similar temperature and pressure dependences were observed for other HFEs. According to the residual transport-property concept, thermal conductivity for a pure fluid is separated into three different contributions, i.e., dilute-gas term, excess term which accounts for the density dependence, and critical enhancement term, and usually

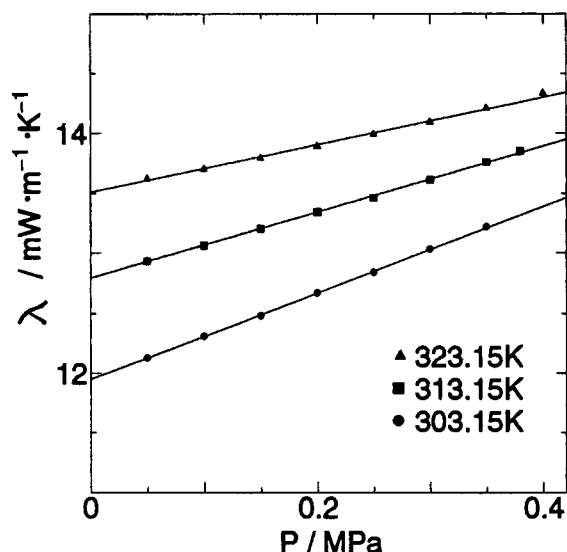


Figure 1. Thermal conductivities of HFE 227me as a function of pressure.

Table 3. Coefficients in Eq 2

	HFE 227me	HFE 236mc	HFE 245mc	HFE 254pc
a_1	13.499	13.805	13.609	13.134
$10^2 a_2$	6.699	9.924	9.355	7.908
$10^4 a_3$	-5.27	-3.93	3.83	-3.43
b_1	2.015	3.500	3.363	6.662
b_2	-0.07930	-0.11881	-0.17936	-0.21310
ave. dev./%	0.06	0.14	0.04	0.09
max. dev./%	0.17	0.25	0.11	0.21

expressed as a function of temperature and density. But there exist no gaseous density data for present HFEs, so the experimental thermal conductivities were correlated with temperature and pressure instead of density. Since the temperature and pressure ranges of present measurements are away from the critical regions, it is not necessary to take the contribution of critical enhancement into account. Because of the small ranges of temperature and pressure, it is found that the thermal conductivities are represented satisfactorily by the following simple polynomial equation.

$$\lambda = \{a_1 + a_2(T - 323.15) + a_3(T - 323.15)^2\} + \{b_1 + b_2(T - 323.15)\}P \quad (2)$$

The coefficients of eq 2 are given in Table 3 together with the average and maximum deviations. This correlation has not been undertaken for HFE 245mf and HFE 245qc, whose measurements were performed only at a single pressure close to saturation.

The thermal conductivities at atmospheric pressure, λ_0 , were determined in terms of the correlation eq 2, and the results are illustrated in Figure 2. Slightly higher and lower values for HFE 236me and HFE 245qc, respectively, are conspicuous, but the thermal conductivities are fairly close to one another and arranged in the following order at a particular temperature of 323.15 K:

$$\begin{aligned} \text{HFE 245qc} < \text{HFE 227me} < \text{HFE 254pc} < \\ (13.46) \quad 13.70 \quad 13.80 & \\ \text{HFE 245mc} < \text{HFE 236me} & (3) \\ 13.95 \quad 14.16 & \end{aligned}$$

Here the numerical values are calculated λ_0 in mW/m·K and the value in the parentheses for HFE 245qc indicates

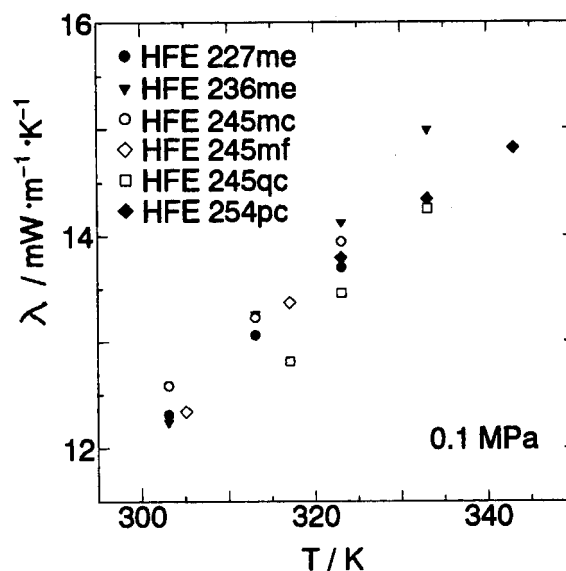


Figure 2. Thermal conductivities of HFEs at atmospheric pressure and various temperatures.

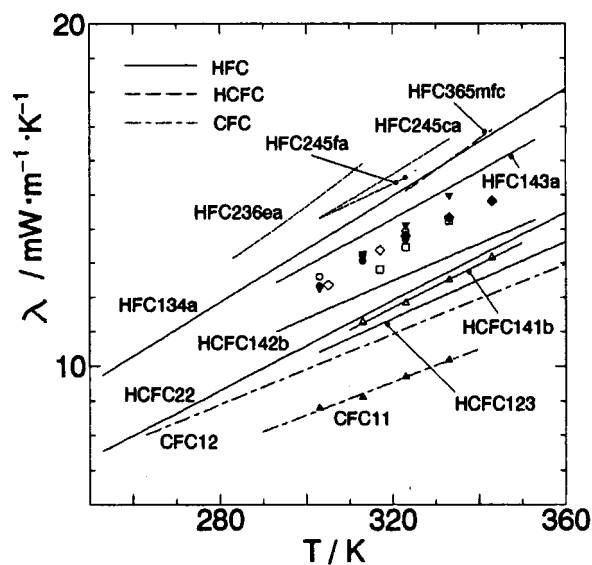


Figure 3. Comparison of the thermal conductivities at atmospheric pressure; ●, HFE 227me; ▼, HFE 236me; ○, HFE 245mc; ◇, HFE 245mf; □, HFE 245qc; ◆, HFE 254pc.

the raw datum at 0.076 MPa given in Table 2. As is shown in Figure 2, the temperature coefficients of λ_0 are a little different from one another and there exist some overlappings in the present temperature range of measurements. So notice should be taken of the partial breakdown of this order at different temperatures.

In Figure 3, these λ_0 for HFEs are compared with those for some CFCs, HCFCs, and HFCs that had been measured previously with the same apparatus (Yamamoto et al., 1993; Tanaka et al., 1995; Matsuo et al., in press). This figure shows that the thermal conductivities of present HFEs are considerably higher than those of the restricted blowing agents, CFC 11 and HCFC 141b, i.e., 35 to 46% higher than CFC 11 and 10 to 19% higher than HCFC 141b at 323.15 K, respectively. But it is also clear from this figure that HFEs indicate slightly lower thermal conductivities than the HFCs which are presently expected to be possible substitutes for the restricted blowing agents.

The comparison between HFEs and HFCs whose molecular structures are similar to each other was attempted in

Table 4. Comparison with the Corresponding HFCs

	M^a	$(M_{\text{HFE}}/M_{\text{HFC}})$	λ^b	$(\lambda_{\text{HFE}}/\lambda_{\text{HFC}})$	GWP ^c
HFE 236me (CF ₃ CHFOCHF ₂)	168.04		14.12		0.11
HFC 236ea (CF ₃ CHFCHF ₂)	152.03	(1.11)	16.89	(0.84)	
HFE 245qc (CH ₂ FCF ₂ OCHF ₂)	150.05		13.46 ^d		
HFC 245ca (CH ₂ FCF ₂ CHF ₂)	134.05	(1.12)	15.78	(0.85)	
HFE 245mf (CF ₃ CH ₂ OCHF ₂)	150.05		13.88		0.13
HFC 245fa (CF ₃ CH ₂ CHF ₂)	134.05	(1.12)	15.48	(0.90)	

^a Molar mass. ^b Thermal conductivity in mW/m·K (at 323.15 K and 0.10 MPa). ^c Referenced value to the absolute GWP for CFC 11. ^d Value at 0.076 MPa.

order to examine the effect of introducing the oxygen atom. Each HFC has the same molecular structure as the corresponding HFE except for the lack of an –O– bond. The result is given in Table 4 and HFEs are found to indicate 10 to 16% lower thermal conductivity than the corresponding HFCs at 323.15 K. Here in this table, the thermal conductivity for HFE 245qc is again the experimental datum at 0.076 MPa. According to the simple kinetic theory, a substance with higher molar mass indicates lower gaseous thermal conductivity. It might be proper, therefore, that HFEs indicate lower thermal conductivities, but it is confirmed that the addition of oxygen atom produces a better insulating performance. It can be concluded from Figure 3 and Table 4 that gaseous thermal conductivities are roughly arranged in the following order:



Although the gaseous thermal conductivity is one of the most essential properties of a blowing agent, the insulating performance is also strongly dependent on other thermophysical factors such as foam cell size, foam density, and rate of diffusion from foam. It should be noticed, therefore, that this order for thermal conductivity is not necessarily a rigid basis for the foam insulating performance. Furthermore, some chemical properties such as thermal stability, toxicity, and environmental factors should be also taken into consideration in selecting suitable alternative substances. Among some properties given in Table 4, it is noteworthy that the present HFEs possess considerably

lower GWPs (Sekiya and Misaki, 1996), which are roughly half those of HFCs. Judging from the present experimental results and these established properties, it could be concluded that the fluorinated methyl ethyl ethers investigated in this work possess superior potential as replacements for traditional blowing agents.

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