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Density and Viscosity of Linear Perfluoropolyethers Under High Pressures

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New experimental data on the density and viscosity of linear, unbranched perfluoropolyethers are presented at temperatures from 273 to 333 K and pressures up to 180 MPa. The measurements were carried out by a high-pressure burrette apparatus and a falling-cylinder viscometer. The uncertainties of the measurements are estimated to be less than 0.09% for the specific volume and 2.5% for the viscosity. The *P–V* data at each temperature are correlated satisfactorily by the Tait equation. The viscosity data are also analyzed and correlated with pressure or molar volume by several empirical and theoretical equations.

KEY WORDS: compressibility; density; fluorocarbon oil; free-volume equation; high pressure; perfluoropolyether; specific volume; Tait equation; viscosity.

1. INTRODUCTION

Perfluoropolyethers (PFPE) are one of the synthetic oils developed recently. The fluids, comprising only carbon, fluorine, and oxygen atoms, contain large amounts of tetrafluoroethyleneoxide $\text{-}\!\!(\!CF_2CF_2O\!)\!\!\text{-}$ units and partially enchained difluoroformyl $\text{-}\!\!(\!CF_2O\!)\!\!\text{-}$ units. These substances have peculiar properties such as chemical inertness, excellent thermal stability, and high flexibility of the polymer chain originating from the ether bonds. Two types of PFPE fluids are available commercially, one linear and unbranched and the other with short-chain branches. As the high flexibility of the polymer chain prevents crystallization, the fluids have low glass transition temperatures and wide ranges of liquid state with a

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good viscosity index. Due to the good elasthydrodynamic film-forming capability and nonflammability, PFPE should be a promising candidate of high-temperature lubricants and hydraulic fluids under extreme conditions. However, the literature provides only a limited number of physical-property data on the fluids [1–8], especially under high pressures. The present investigation was undertaken in order to obtain precise density and viscosity data of linear perfluoropolyethers $F\text{-}(CF_2CF_2CF_2O)_n\text{-}CF_2CF_3$ under high pressures.

2. EXPERIMENTAL

2.1. *PVT* Measurements

The specific volume was measured by a high-pressure burrette apparatus which has been described elsewhere [9]. The piezometer was thermostatically controlled to within ±10 mK in a liquid bath. The temperature was measured with standard mercury thermometers calibrated by the National Research Laboratory of Metrology, Japan, within an accuracy of ±50 mK. The pressure was measured by Heise Bourdon-tube gauges within ±0.10 MPa. The final uncertainty of the density obtained is estimated to be less than 0.09%.

2.2. Viscosity Measurements

The viscosity was measured using a falling-cylinder viscometer described in detail previously [10]. The falling time of the plummet was determined within ±0.1 ms by a time-interval counter. The viscometer was thermostatically controlled to ±50 mK by means of a water jacket. The pressure was measured by a strain gauge-type pressure transducer within ±0.1 MPa. The reproducibility of the falling-time measurements is within ±0.5%. The instrument was calibrated by the viscosity standard liquid JS-1000 provided by the National Research Laboratory of Metrology, Japan. The final uncertainty of the viscosity obtained is estimated to be less than 2.5%.

2.3. Materials

The sample fluids of perfluoropolyethers were supplied by Daikin Industries, Ltd., with the trade names Demnum S-20 and S-65. Typical physical properties of the fluids [8] are listed below.

	S-20	S-65
Average molecular weight	2500	4500
Pour point (K)	198	208
Refractive index (n_D^{20})	1.290	1.295
Surface tension ($mN \cdot m^{-1}$)	17.7	18.0
Glass transition temperature (K)	158	162

3. EXPERIMENTAL RESULTS

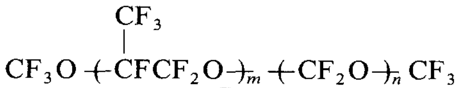
3.1. Density

The experimental results are given in Table I as functions of temperature and pressure. The isothermal pressure dependence of the specific volume of S-20 is also plotted in Fig. 1. A similar behavior is observed for S-65, although the specific volume of the latter is slightly lower than the former. The density of the fluids, ranging from 1800 to 2100 $kg \cdot m^{-3}$ in the present experimental conditions, is about twice those of common lubricating oils. The specific volume decreases monotonously with increasing pressure at each temperature. As shown in Fig. 2, it increases almost linearly with rising temperature, although the isobar has a quite small positive curvature at low pressures.

3.2. Viscosity

The viscosity data are presented in Table II as functions of temperature and pressure. The isothermal pressure dependences of the viscosity of S-20 and S-65 are illustrated in Fig. 3 together with the experimental data of Cantow et al. [7] for Fomblin YR and Z25 fluids, which are structurally different PFPE fluids as follows [7, 8].

Fomblin YR



$$CF_3O{-}(\overset{\overset{CF_3}{|}}{C}FCF_2O{-})_m{-}(CF_2O{-})_n\,CF_3$$

$(m:n = 40:1,\ \bar{M}_r = 9060)$

Fomblin Z25 $CF_3O{-}(CF_2CF_2O{-})_m{-}(CF_2O{-})_n\,CF_3$

$(m:n = 4:6,\ \bar{M}_r = 16{,}800)$

The viscosity of S-20 and S-65 increases monotonously with increasing pressure having small positive curvatures. The viscosity of S-65 (average molecular weight, 4500) is greater than that of S-20 (average molecular weight, 2500). The viscosity behavior of the linear polymer Z25 is quite

Table I. Density ρ (in $kg \cdot m^{-3}$) of Perfluoropolyethers (Pressure P in MPa)

273.15 K		293.15 K		303.15 K		313.15 K		333.15 K	
P	ρ	P	ρ	P	ρ	P	ρ	P	ρ
				S-20					
0.1	1894.1	0.1	1855.3	0.1	1835.9	0.1	1816.8	0.1	1777.9
3.6	1901.4	3.6	1863.5	3.6	1844.3	3.6	1825.8	3.6	1788.6
7.8	1909.3	7.4	1871.5	7.2	1852.9	7.1	1834.3	7.2	1798.2
14.3	1921.4	14.0	1884.7	13.4	1866.0	13.5	1848.6	13.8	1815.0
20.4	1931.7	20.9	1897.9	20.7	1880.7	20.7	1864.0	21.0	1831.2
28.1	1944.1	27.9	1910.5	27.8	1893.7	27.7	1877.5	27.6	1845.0
34.5	1953.5	34.6	1921.4	34.4	1904.9	34.5	1889.3	34.5	1858.5
41.4	1963.2	41.8	1932.9	41.3	1916.0	41.1	1900.3	41.4	1870.9
48.1	1972.7	48.4	1941.8	48.3	1927.2	48.3	1911.9	48.3	1882.5
55.0	1981.6	55.0	1951.6	55.1	1936.6	55.7	1922.9	55.1	1893.4
62.9	1991.4	62.2	1961.2	62.3	1946.4	62.0	1931.7	62.1	1903.7
69.0	1998.2	69.3	1970.4	69.0	1954.8	69.0	1941.1	68.8	1913.3
75.7	2006.1	75.7	1977.7	76.0	1963.7	75.8	1950.0	75.9	1922.9
82.7	2013.5	83.4	1986.8	82.6	1971.4	82.9	1958.5	82.8	1931.4
96.5	2028.0	96.1	2000.6	96.3	1986.7	96.5	1973.9	96.2	1948.0
109.6	2040.4	111.0	2016.5	109.9	2001.0	110.1	1988.4	109.8	1963.1
123.9	2053.3	124.5	2028.7	122.9	2013.5	123.6	2001.6	124.8	1978.7
137.2	2064.8	138.0	2041.2	137.3	2026.7	137.5	2014.9	137.3	1990.6
151.0	2076.2	151.3	2052.6	151.0	2038.9	151.0	2027.1	151.1	2003.4
164.8	2087.0	165.1	2063.8	164.3	2050.0	164.5	2038.6	164.8	2015.6
178.0	2097.4	179.0	2074.6	178.2	2060.8	177.9	2049.3	178.9	2027.1
				S-65					
		0.1	1869.6	0.1	1850.6	0.1	1831.5	0.1	1797.8
		6.3	1883.1	5.2	1863.5	5.6	1845.5	7.1	1818.2
		15.2	1902.4	10.1	1873.8	16.3	1869.2	11.0	1828.4
		22.3	1914.4	14.9	1883.4	21.7	1880.2	15.1	1837.4
		29.5	1925.3	20.1	1893.5	28.6	1891.5	30.4	1868.5
		38.1	1937.6	24.6	1900.7	34.3	1901.0	35.3	1876.2
		49.0	1954.4	29.7	1909.3	40.0	1909.8	41.7	1888.3
		60.0	1969.4	34.3	1917.8	48.6	1922.7	48.0	1897.7
		73.0	1984.4	40.7	1927.6	60.1	1939.4	63.1	1921.2
		76.9	1989.5	50.0	1941.1	67.0	1948.4	67.9	1926.9
		85.5	1998.8	60.0	1953.9	83.4	1969.3	77.5	1939.8
		91.4	2005.8	66.0	1962.0	89.7	1975.7	89.7	1954.9
		102.9	2018.8	76.8	1974.1	100.4	1987.5	100.8	1967.6
		121.6	2034.4	89.3	1988.9	120.1	2007.3	119.0	1987.2
		133.8	2045.9	100.4	2000.2	140.3	2025.7	139.4	2006.9
				114.8	2015.0	168.8	2049.6		
				137.5	2035.3				

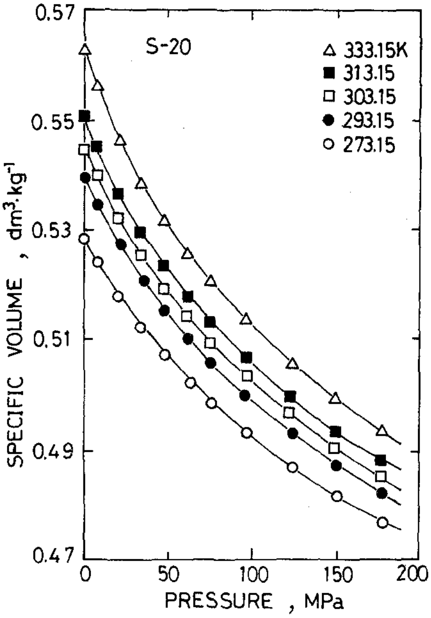


Fig. 1. Isothermal pressure dependences of the specific volume of S-20.

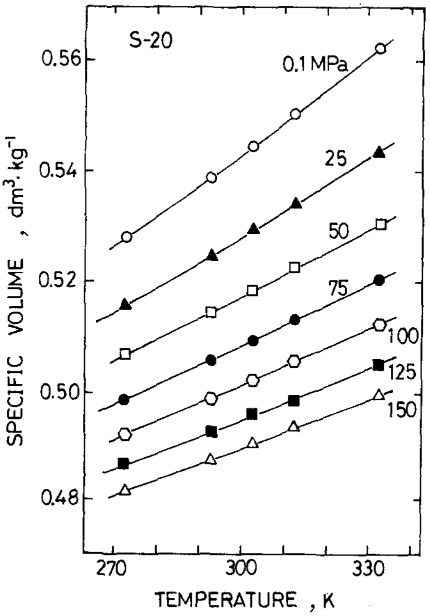


Fig. 2. Isobaric temperature dependences of the specific volume of S-20.

Table II. Viscosity η (in Pa · s) of Perfluoropolyethers

P (MPa)	S-20 at T(K)			S-65 at T(K)		
	293.15	303.15	313.15	293.15	303.15	313.15
0.1	0.107	0.0704	0.0486	0.272	0.174	0.117
9.9	0.150	0.0982	0.0672	0.381	0.241	0.161
19.7	0.206	0.132	0.0902	0.517	0.325	0.216
29.5	0.275	0.175	0.118	0.684	0.430	0.283
39.3	0.362	0.228	0.152	0.901	0.558	0.366
49.1	0.469	0.292	0.194	1.162	0.716	0.465
58.9	0.601	0.370	0.244	1.490	0.905	0.581
68.8	0.771	0.464	0.303	1.881	1.131	0.725
78.6	0.968	0.586	0.374	2.350	1.409	0.895
88.4	1.210	0.724	0.458	2.921	1.739	1.086
98.2	1.500	0.889	0.566	3.603	2.120	1.319

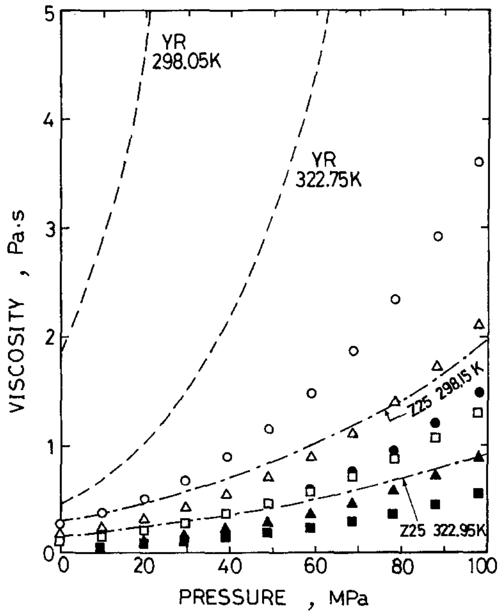


Fig. 3. Isothermal pressure dependences of the viscosity of perfluoropolyethers. S-20: (●) 293.15 K; (▲) 303.15 K; (■) 313.15 K. S-65: (○) 293.15 K; (△) 303.15 K; (□) 313.15 K.

similar to our results. On the other hand, the viscosity of YR with bulky CF_3 side groups increases drastically with increasing pressure. In order to compare the pressure dependence of the viscosity, it is convenient to use the relative viscosity defined as η/η_0, where η and η_0 are the viscosities at high pressures and atmospheric pressure, respectively. As shown in Fig. 4, the relative viscosities of S-20 and S-65 are substantially the same in the present experimental conditions. The relative viscosity increases with lowering temperature. The relative viscosity of YR is remarkably greater than the others, whereas both pressure and temperature dependences of the relative viscosity of Z25 are much lower. These differences should come from their chemical structures [7]. The bulky side groups in YR may be responsible for the high viscosity and high pressure sensitivity of this fluid. The aboundant ether bonds in Z25 may cause high flexibility of the polymer chain and low pressure sensitivity of the viscosity.

The viscosity of S-20 and S-65 decreases with rising temperature at constant pressure. The absolute value of the temperature coefficient of the viscosity $[(\partial\eta/\partial T)_p]$ increases with increasing pressure. As shown typically

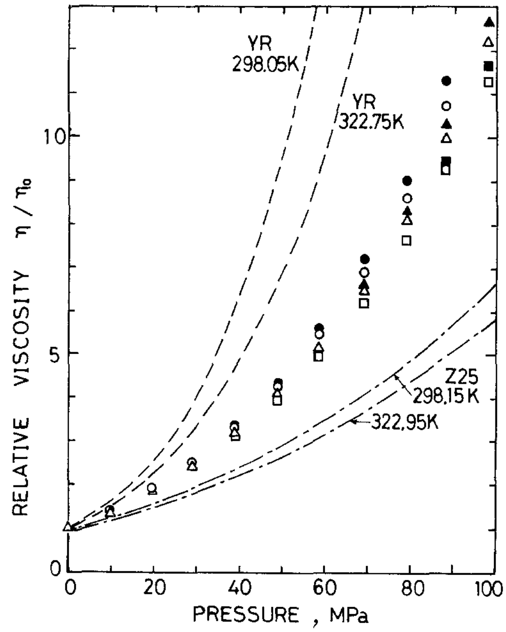


Fig. 4. Isothermal pressure dependences of the relative viscosity of perfluoropolyethers. S-20: (●) 293.15 K; (▲) 303.15 K; (■) 313.15 K. S-65: (○) 293.15 K; (△) 303.15 K; (□) 313.15 K.

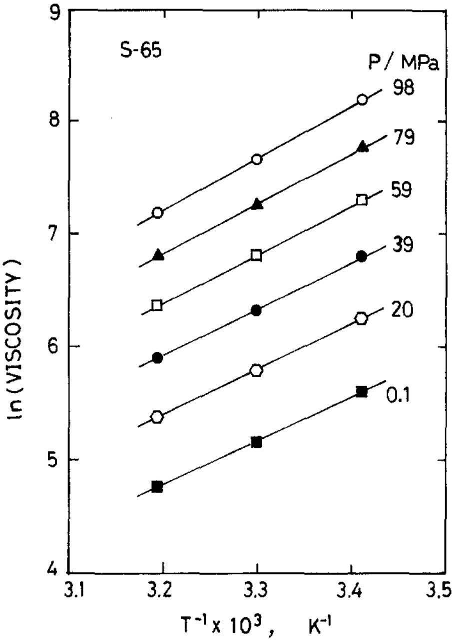


Fig. 5. ln η vs T^{-1} diagram of S-65; viscosity is in mPa · s.

in Fig. 5, the temperature dependence of the viscosity can be represented satisfactorily by the Andrade equation:

$$\ln \eta = A + B/T \tag{1}$$

throughout the present experimental conditions. It should be noted that S-65 shows a higher temperature sensitivity than S-20.

4. DISCUSSION

4.1. Correlation of Density with Pressure

For each specific volume isotherm, the experimental data are correlated with pressure by the Tait equation:

$$\frac{v_0 - v}{v_0} = \frac{\rho - \rho_0}{\rho} = C \ln\left(\frac{D + P}{D + P_0}\right) \tag{2}$$

where v_0 and ρ_0 are the specific volume and density at atmospheric pressure P_0 ($=0.1$ MPa), respectively, and C and D are specific constants for substance and temperature. The optimum values of the constants are listed in Table III together with the deviations of the experimental data from Eq. (2).

The isothermal compressibility

$$\beta_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{3}$$

of S-20 calculated using the Tait equation is plotted against pressure in Fig. 6. It decreases monotonously with increasing pressure and decreasing temperature. The isothermal compressibility of S-20 is slightly greater than that of S-65.

4.2. Correlation of Viscosity with Pressure

Various empirical equations have been presented to represent the viscosity as functions of pressure and temperature. Among them, a polynomial equation and the Tait-type equation [11, 12] are employed to fit our viscosity data. After the data analysis it is found that the viscosity isotherms can be represented satisfactorily by a cubic equation of pressure as follows:

$$\frac{\eta-\eta_0}{\eta_0} = a(P-P_0) + b(P-P_0)^2 + c(P-P_0)^3 \tag{4}$$

where η_0 is the viscosity at atmospheric pressure P_0, and a, b, and c are the empirical coefficients, which are listed in Table IV. Equation (4) can repre-

Table III. Coefficients in the Tait Equation (2)

Fluid	T (K)	10^2C	D (MPa)	V_0 ($\mathrm{dm^3 \cdot kg^{-1}}$)	Mean dev. (%)	Max. dev. (%)
S-20	273.15	7.704	70.93	0.52796	0.012	0.036
	293.15	7.826	62.53	0.53898	0.009	0.021
	303.15	7.703	57.11	0.54466	0.010	0.027
	313.15	7.719	53.10	0.55046	0.010	0.026
	333.15	7.713	45.61	0.56245	0.009	0.019
S-65	293.15	7.494	61.97	0.53487	0.032	0.090
	303.15	7.269	55.50	0.54036	0.023	0.050
	313.15	7.548	54.65	0.54601	0.025	0.083
	333.15	7.494	46.42	0.55622	0.034	0.091

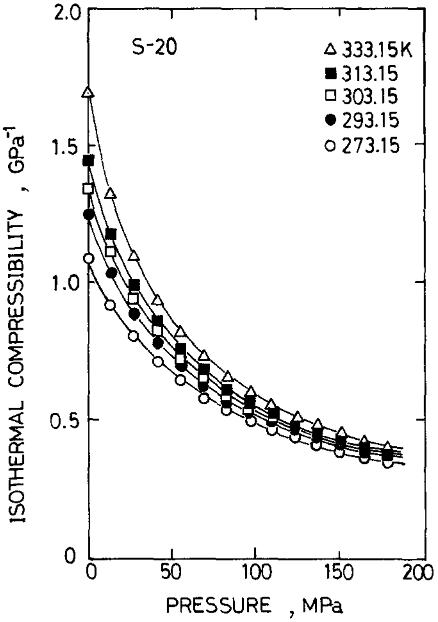


Fig. 6. Pressure dependences of the isothermal compressibility of S-20.

sent the viscosities of S-20 and S-65 with mean deviations of 0.38 and 0.24% and maximum deviations of 1.2 and 0.68%, respectively. The Tait-type equation [11, 12] and other empirical equations of pressure with two adjustable parameters, on the other hand, were found to give an unsatisfactory fitting to our results, which may be ascribed to the considerably strong pressure dependence of the viscosity for these fluids.

Table IV. Coefficients in Eq. (4)

Fluid	T (K)	$10^2 a$ (MPa^{-1})	$10^4 b$ (MPa^{-2})	$10^6 c$ (MPa^{-3})	η_0 (Pa·s)	Mean dev. (%)	Max. dev. (%)
S-20	293.15	3.9625	2.4216	7.1752	0.107	0.29	1.10
	303.15	3.8705	2.1807	6.0759	0.0704	0.33	0.82
	313.15	3.8470	1.8937	5.2846	0.0486	0.52	1.24
S-65	293.15	3.8161	2.7935	6.1255	0.272	0.23	0.48
	303.15	3.7152	2.7939	5.1351	0.174	0.24	0.68
	313.15	3.5637	3.1396	3.9827	0.117	0.24	0.62

4.3. Correlation of Viscosity with Molar Volume

It is well known that the viscosity of various organic liquids can be correlated with the molar volume by the free-volume equations. The applicability of the free-volume equation presented by Dymond and Brawn [13] to the present results has been examined:

$$\ln \eta' = E + F\frac{V_0}{V - V_0} \tag{5}$$

The quantity η' is a kind of reduced viscosity defined as

$$\eta' = 100\,\eta V^{2/3}/(MT)^{1/2} \tag{6}$$

where η is viscosity in mPa·s, V molar volume in $\mathrm{cm^3 \cdot mol^{-1}}$, and M molecular weight in $10^{-3}\,\mathrm{kg \cdot mol^{-1}}$. The coefficients E, F, and V_0 are determined as adjustable parameters by the least-squares method. Equation (5) is found to represent the experimental data of S-20 and S-65 with mean deviations as $\ln \eta'$ of 0.042 and 0.023% and maximum deviations of 0.16 and 0.19%, respectively. The optimum values of the coefficients are listed in Table V.

4.4. Interpretation of Viscosity Behavior by Eyring's Theory

According to the Eyring model for viscous flow [14–17], a molecule under shear can move to the direction of shear by making a hole of suitable size. In this process an activation energy $\Delta E_{\mathrm{f}}^{\ddagger}$ is required. Besides making a hole, a molecule also needs an activation energy $\Delta E_{\mathrm{m}}^{\ddagger}$ to move against the intermolecular forces of the neighboring molecules. These processes can be treated in the same way as a chemical reaction. Thus, the resulting viscosity expression can be represented as follows:

$$\eta = \frac{Nh}{V}\exp\left(\frac{\Delta E^{\ddagger}}{RT}\right)\exp\left(-\frac{\Delta S^{\ddagger}}{R}\right)\exp\left(\frac{P\,\Delta V^{\ddagger}}{RT}\right) \tag{7}$$

Table V. Coefficients in Eq. (5)

Fluid	T (K)	E	F	V_0 ($\mathrm{cm^3 \cdot mol^{-1}}$)	Mean dev. (%)	Max. dev. (%)
S-20	293.15	−5.1090	7.8842	824.8	0.03	0.06
	303.15	−3.1057	5.9184	855.8	0.04	0.08
	313.15	−2.5827	5.3571	866.3	0.06	0.16
S-65	293.15	−1.2496	4.9357	1590.0	0.02	0.05
	303.15	−1.4789	5.2222	1561.9	0.01	0.02
	313.15	−1.6236	5.4538	1537.1	0.04	0.19

where N is the Avogadro number, h the Planck constant, and R the gas constant, and $\Delta E^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ are activation energy, entropy, and volume, respectively. The activation energy $\Delta E^{\ddagger}$ is regarded as the sum of $\Delta E_{\mathrm{f}}^{\ddagger}$ and $\Delta E_{\mathrm{m}}^{\ddagger}$ mentioned above and can be obtained from the Arrhenius plot:

$$\Delta E^{\ddagger} = R\left(\frac{\partial \ln \eta}{\partial(1/T)}\right)_P \tag{8}$$

The activation volume $\Delta V^{\ddagger}$ is regarded as the volume of the necessary hole for the molecule to move. It can be calculated in a similar manner as follows:

$$\Delta V^{\ddagger} = RT\left(\frac{\partial \ln \eta}{\partial P}\right)_T \tag{9}$$

In the present work, the activation energy was calculated by the Andrade equation (1) and the activation volume by the following equation:

$$\ln \eta = \alpha + \beta P + \gamma P^2 \tag{10}$$

The activation energy and volume thus obtained are listed in Tables VI and VII, respectively, together with the values for YR and Z25 cited from Cantow et al. [7].

The activation energy generally increases with increasing pressure. The activation energies of S-20 and S-65, where the molecular structure is common and only the molecular weights are different, are almost same. On the other hand, the activation energy of linear Z25 is about 40% lower than those of linear S-20 and S-65 in spite of its larger molecular weight 16800. It may be attributable to the considerably greater number of flexible ether bonds in Z25. The activation energy of YR, which has bulky CF_3 side groups, is about 30% greater than that of S-20 and S-65 and 110–130%

Table VI. Activation Energy for Viscous Flow $\Delta E^{\ddagger}$ (kJ · mol^{-1})

	P (MPa)				
Fluid	0.1	30	50	70	100
S-20	30	32	34	36	37
S-65	32	34	35	36	38
YR [7]	40	45	49	48	53
Z25 [7]	19	20	21	22	23

Table VII. Activation Volume for Viscous Flow $\Delta V^{\ddagger}$ ($cm^3 \cdot mol^{-1}$)

		P (MPa)		
Fluid	T (K)	0.1	50	100
S-20	293.15	81	65	48
	303.15	81	64	48
	313.15	81	64	47
S-65	293.15	80	63	47
	303.15	81	63	46
	313.15	82	63	45
YR [7]	298.15	117	95	—
	323.15	112	93	86
Z25 [7]	298.15	62	46	39
	323.15	62	47	37

larger than that of Z25. It is found, therefore, that the activation energy is related more closely to molecular structures than the average molecular weight of fluids.

According to the modern molecular theory of viscosity [15–17], a large molecule does not always flow as the whole molecular unit, but small portions of the long-chain molecule, so-called "segments," move from one hole to another in the liquid. Thus, the activation volume would correspond to the average volume necessary for the segments to move.

The activation volume of PFPE fluids generally decreases with increasing pressure. The activation volume of Z25 is about 25% smaller than those of S-20 and S-65, whereas that of YR is larger by 40–90%. It means that the more bulky a segment, the greater the required cavity. At elevated pressures, the number of holes of sufficient size gradually reduces, thus making the polymers less likely to flow, increasing its viscosity.

5. CONCLUSION

The density and viscosity of linear, unbranched perfluoropolyethers have been measured in the temperature range 273–333 K at pressures up to 180 MPa. The density data are satisfactorily correlated with pressure by the Tait equation (2). The viscosity also can be well represented by a cubic equation of pressure, Eq. (4), and a free-volume equation, Eq. (5). The viscosity data obtained were compared with those of other perfluoropolyethers with CF_3 side groups. Consequently, it is confirmed that the short-chain branches may be responsible for the high viscosity, high pressure sensitivity of η, large activation energy, and activation volume for viscous flow. It is hoped that the conclusions obtained could be made in general about any lubricating fluids.

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REFERENCES

1. D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, *Wear* **18**:85 (1971).
2. W. R. Jones, Jr., R. L. Johnson, W. O. Winer, and D. M. Sanborn, *ASLE Trans.* **18**:249 (1975).
3. C. E. Snyder, Jr., and R. E. Dolle, Jr., *ASLE Trans.* **19**:171 (1976).
4. W. R. Jones, Jr., and C. E. Snyder, Jr., *ASLE Trans.* **23**:253 (1980).
5. W. R. Jones, Jr., K. J. L. Paclorek, T. I. Ito, and R. H. Kratzer, *Ind. Eng. Chem. Prod. Res. Dev.* **22**:166 (1983).
6. S. Yasutomi, S. Bair, and W. O. Winer, *J. Tribol.* **106**:291 (1984).
7. M. J. R. Cantow, E. M. Barrall, Jr., B. A. Wolf, and H. Geerissen, *J. Polym. Sci. Polym. Phys.* **25**:603 (1987).
8. Y. Ohsaka, *Petrotech.* **8**:840 (1985).
9. H. Kubota, S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka, and T. Makita, *Rev. Phys. Chem. Jpn.* **49**:59 (1979).
10. Y. Tanaka, T. Yamamoto, Y. Satomi, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jpn.* **47**:12 (1977).
11. H. Kashiwagi and T. Makita, *Int. J. Thermophys.* **3**:289 (1982).
12. Y. Tanaka, Y. Matsuda, H. Fujiwara, H. Kubota, and T. Makita, *Int. J. Thermophys.* **8**:147 (1987).
13. J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Prop.* (ASME, New York, 1977), p. 660.
14. R. E. Powell, W. E. Roseveare, and H. Eyring, *Ind. Eng. Chem.* **33**:430 (1941).
15. Y. Tamai, *J. Jpn. Petrol. Inst.* **25**:127 (1982).
16. Y. Tamai and T. Kyotani, *J. Jpn. Petrol. Inst.* **25**:94, 281 (1982).
17. T. Kyotani, Y. Tamai, and Y. Horita, *ASLE Trans.* **26**:538 (1983).