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Journal of Fluorine Chemistry 73 (1995) 33–39

JOURNAL OF FLUORINE CHEMISTRY

Development of quantitative structure–activity relationships for perfluoropolyalkyl ethers

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Received 7 May 1994; accepted 16 November 1994

Abstract

Quantitative structure–activity relationships (QSAR) have been developed for the viscosity of perfluoropolyalkyl ethers as a function of the carbon to oxygen ratio and the bending energy. These treatments permit the prediction of viscosity/temperature and viscosity/molecular weight profiles. Molecular structures have been determined for a series of perfluoropolyalkyl ethers using molecular mechanics.

Keywords: Structure–activity relationships; Perfluoropolyalkyl ethers; Viscosity; Molecular mechanics; Molecular structures

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1. Introduction

Perfluoropolyalkyl ethers comprise a family of materials with high thermal and thermal oxidative stabilities and wide liquid ranges [1–5]. On the basis of these characteristics, compositions of the ethers are utilized in applications where extremes of temperature are encountered and in boundary lubrications [6,7] where long-term performance is mandatory. The properties are strongly dependent on structural arrangements. In broad terms, the lower the C/O ratio, the better the viscosity/temperature profile, the poorer the thermal oxidative stability in the presence of metals, metal alloys and salts [8].

Perfluoropolyalkyl ethers of the general structures $-[CF(CF_3)CF_2O]_n-$, $-[CF_2O]_x[CF_2CF_2O]_y-$ (wherein $x>y$) and $-[CF_2CF_2CF_2O]_n-$ are available commercially. A number of other arrangements have been synthesized in research quantities by the direct fluorination of hydrocarbon precursors [9]. None of the relatively high molecular weight materials exhibiting desirable viscosities and volatilities are monomolecular. All consist of telomer mixtures due to the nature of their syntheses. An ability to correlate the structural arrangements and molecular weights, or rather molecular weight ranges, with the viscosity characteristics would permit the identification of optimum perfluoropolyalkyl ethers for specific applications. Predictions of fluoroelastomer/chlorofluorocarbon swell [10] and polysilahydrocarbon structure–viscosity [11] have been successfully accomplished using quantitative structure–activity relationships (QSAR). These studies have provided the basis for the present undertaking. Furthermore, extending these treatments to stability correlations would allow the selection of the best compromise candidates for applications where extremes of temperature in oxidizing atmospheres and in the presence of metals/metal alloys are to be encountered. The investigations reported here were directed toward the development of structure–viscosity relationships.

2. Experimental details

2.1. General

For mass spectrometric (MS) analyses a Du Pont 21-491B double-focusing mass spectrometer attached to Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, was employed in conjunction with Du Pont 21-094 data acquisition and processing system. For GC analyses, a 10 ft × 1/8 in stainless-steel column packed with 4% OV-101 on 80–100 mesh Chromosorb G was employed; the conditions used were 35–300 °C at 8 °C min^{-1}. Molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Viscosities were measured with Cannon–Manning semi-micro viscometers. Molecular mechanics energy calculations are based on MM2 devel-

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SSDI 0022-1139(94)03208-4

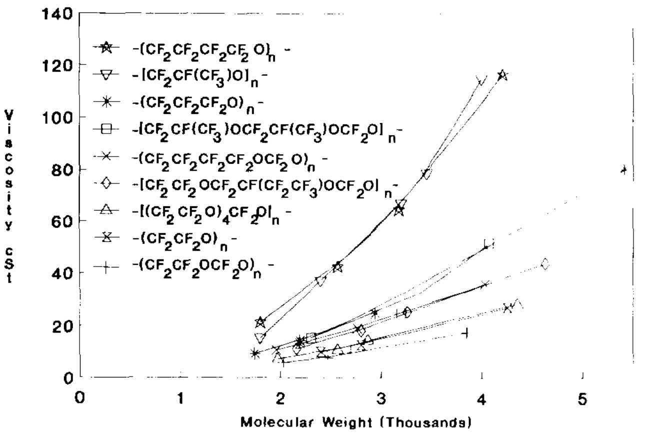


Fig. 1. Viscosity/molecular weight profiles for perfluoropolyalkyl ethers at 40 °C.

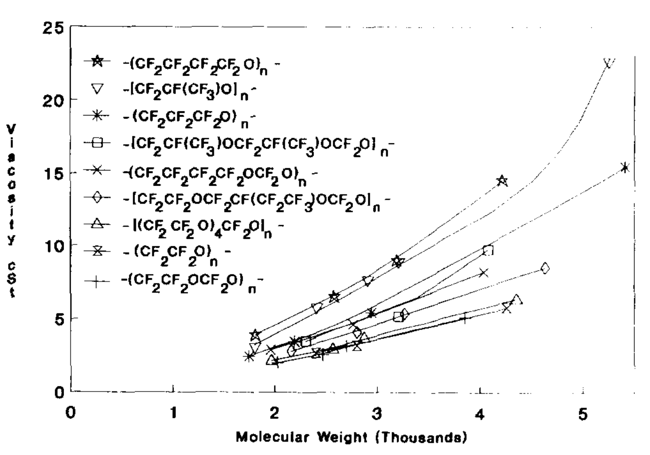


Fig. 2. Viscosity/molecular weight profiles for perfluoropolyalkyl ethers at 100 °C.

oped by Allinger [12] modified by Hypercube Inc. (MM$^+$; Hyperchem 3.0 software). The MM$^+$ parameters were optimized by us using a PM3 data set developed by J.J.P. Stewart specifically for perfluoroalkyl ethers; the latter was provided by the US Air Force. The bond lengths and angles used are listed below. Bond lengths: C–C = 1.554 Å, C–O = 1.354 Å, C–F = 1.312 Å. Angles: C–C–C = 112.2°, C–C–O = 108.2°, C–O–C = 124.7°, O–C–O = 109.4°. Regression analyses were performed using an SPSS 4.01 computer program.

2.2. Materials

Poly(hexafluoropropene oxide), $F(CF(CF_3)CF_2O)_nC_2F_5$, which were oils of different molecular weight, were obtained from Du Pont (Krytox 143 series); the linear isomer, $-[CF_2CF_2CF_2O]_n-$, was received from Daikin Co. (Demnum S-20). The remainder of the perfluoropolyalkyl ethers were prepared by Exfluor Research Corp. and were provided by the US Air Force.

All the materials, with the exception of the Krytox 143 series, were fractionally distilled and the molecular weight and 40 °C and 100 °C viscosities determined for each individual fraction. The viscosity/molecular weight profiles are presented in Figs. 1 and 2; the materials are listed in Table 1.

3. Results and discussion

As mentioned earlier, the perfluoropolyalkyl ethers studied were telomer mixtures. This is illustrated by the chromatograms given in Figs. 3 and 4 for $-(CF_2CF_2CF_2O)_n-$ and $-(CF_2CF_2O)_n-$, respectively. The repeating pattern of peaks represents specifically terminated chains as determined by GC–MS. The three-peak pattern in $-(CF_2CF_2CF_2O)_n-$ corresponds to: large peak, $C_3F_7O(CF_2CF_2CF_2O)_nC_2F_5$ (GC–MS, *m/e*: 999 $[C_3F_7(OCF_2CF_2CF_2)_5]$; 833 $[C_3F_7(OCF_2CF_2CF_2)_4]$; 667 $[C_3F_7(OCF_2CF_2CF_2)_3]$; also 949 $[C_2F_5(OCF_2CF_2CF_2)_5]$; 783 $[C_2F_5(OCF_2CF_2CF_2)_4]$; 617 $[C_2F_5(OCF_2CF_2CF_2)_3]$); second peak, $C_3F_7O(CF_2CF_2CF_2O)_nC_3F_7$ (GC–MS, *m/e*: 999; 833; 667); third peak, $C_2F_5O(CF_2CF_2CF_2O)_{n+1}C_2F_5$ (GC–MS, *m/e*: 949; 783; 617). In the case of $-(CF_2CF_2O)_n-$, based on GC–MS in the two-peak sequence the large peak is $CF_3O(CF_2CF_2O)_nCF_3$ (GC–MS, *m/e*: 881 $[CF_3(OCF_2$-

Table 1
Perfluoropolyalkyl ether listing and viscosity data

Structure	MW 2500 viscosity (cSt)		MW 4000 viscosity (cSt)	
	40 °C	100 °C	40 °C	100 °C
$-(CF_2CF_2OCF_2O)_n-$	8.61	2.78	18.5	5.5
$-(CF_2CF_2O)_n-$	10.7	2.88	23.5	5.0
$-[(CF_2CF_2O)_4CF_2O]_n-$	10.8	3.03	25.0	5.5
$-[CF_2CF_2OCF_2CF(CF_2CF_3)OCF_2O]_n-$	15.0	3.55	35.0	7.0
$-(CF_2CF_2CF_2CF_2OCF_2O)_n-$	16.5	4.05	35.7	8.15
$-[CF_2CF(CF_3)OCF_2CF(CF_3)OCF_2O]_n-$	17.1	3.80	37.0	7.0
$-(CF_2CF_2CF_2O)_n-$	18.9	4.30	49.0	9.0
$-[CF_2CF(CF_3)O]_n-$	40.8	6.05	115.0	12.0
$-(CF_2CF_2CF_2CF_2O)_n-$	41.8	6.36	106.0	13.0

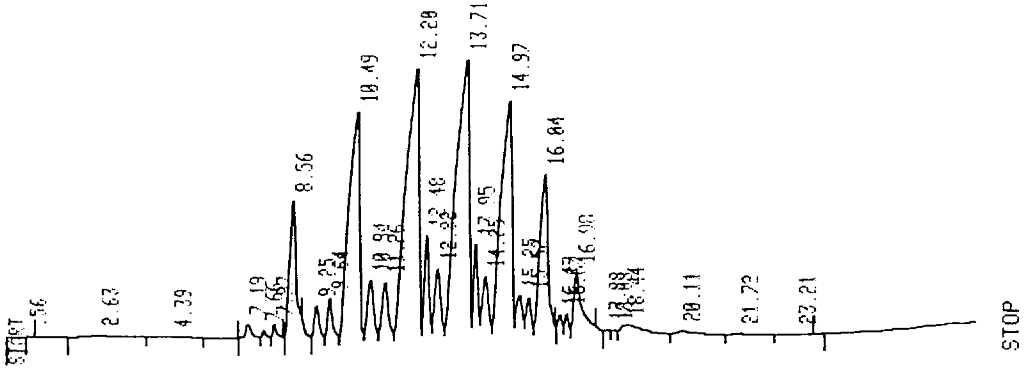


Fig. 3. Gas chromatogram of $-(CF_2CF_2CF_2O)_n-$.

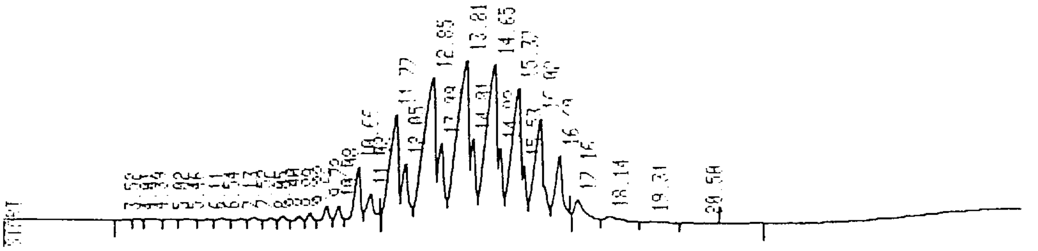


Fig. 4. Gas chromatogram of $-(CF_2CF_2O)_n-$.

Table 2
Structural descriptors considered [a]

Carbon to oxygen ratio
Total number of carbons
Total number of oxygens
Total number of tertiary carbons
Number of segments in repeating group
Number of carbons in segment 1
Number of oxygens in segment 1
Carbon to oxygen ratio in segment 1
Number of carbons adjacent in segment 1
Number of tertiary carbons in segment 1
Number of carbons in branch of segment 1
Number of oxygens in branch of segment 1
Carbon to oxygen ratio in branch of segment 1
Number of carbons in segment 2
Number of oxygens in segment 2
Carbon to oxygen ratio in segment 2
Number of carbons adjacent in segment 2
Number of tertiary carbons in segment 2
Number of carbons in branch of segment 2
Number of oxygens in branch of segment 2
Carbon to oxygen ratio in branch of segment 2

[a] Group and segment defined for $[(CF_2CF_2O)_4CF_2O]$, for example, are as follows: group = $[(CF_2CF_2O)_4CF_2O]$; segment = $(CF_2CF_2O)_4$, CF_2O. The same values are assigned for type 2 as type 1 segments when only one type of segment is present.

$CF_2)_7]$; 765 $[CF_3(OCF_2CF_2)_6]$; 649 $[CF_3(OCF_2CF_2)_5]$; 533 $[CF_3(OCF_2CF_2)_4]$; the small peak is $C_2F_5(CF_2CF_2O)_nCF_3$ (GC–MS, *m/e*: 1047 $[C_2F_5(OCF_2CF_2)_8]$; 931 $[C_2F_5(OCF_2CF_2)_7]$; 815 $[C_2F_5(OCF_2CF_2)_6]$; 699 $[C_2F_5(OCF_2CF_2)_5]$; 583 $[C_2F_5(OCF_2CF_2)_4]$; also 765; 649; 533).

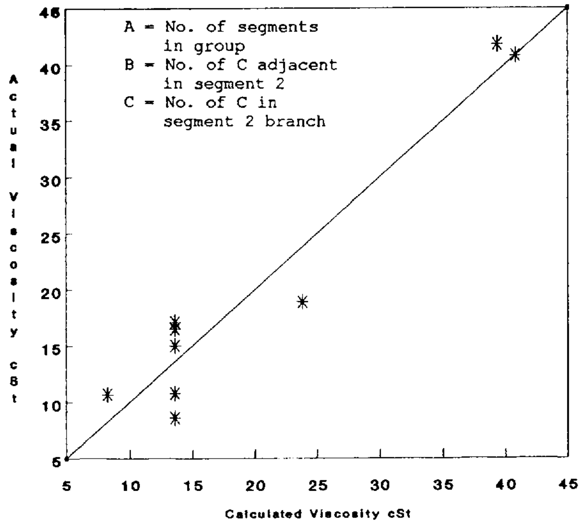


Fig. 5. Calculated versus actual viscosity at 40 °C as a function of three descriptors.

Although the copolymers had more complex chromatograms, in the majority of instances the end-groups, in the given sequence of peaks, were identified. The assignments agreed with the ^{19}F NMR data performed on the bulk samples both in this laboratory and by Bierschenk et al. [9].

For a comparison of inherent viscosities and the determination of viscosity–structure relationships, materials of identical molecular weights or molecular weight ranges are required. The essentially linear viscosity/

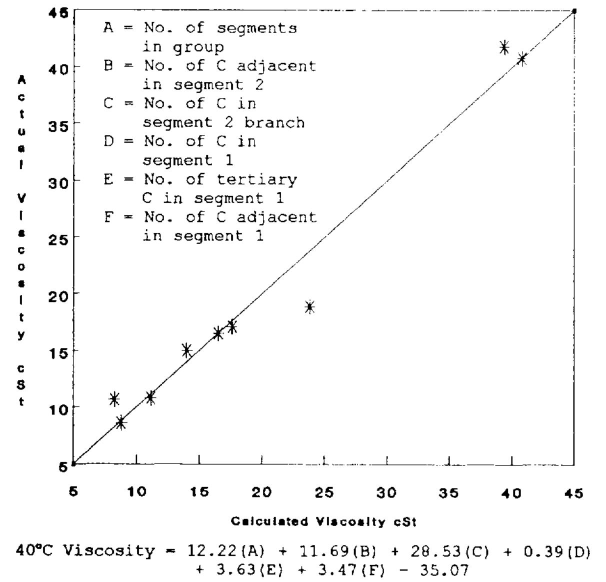


Fig. 6. Calculated versus actual viscosity at 40 °C as a function of six descriptors.

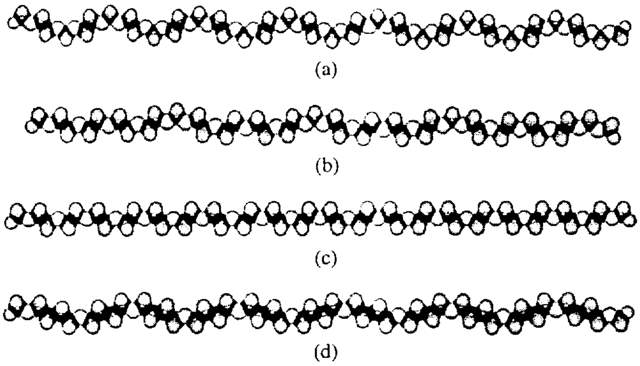


Fig. 7. The conformations obtained with molecular mechanics for perfluoropolyalkyl ethers: (a) $CF_3O(CF_2CF_2OCF_2O)_{13}CF_3$, (b) $CF_3O[(CF_2CF_2O)_4CF_2O]_4CF_3$, (c) $CF_3O(CF_2CF_2O)_{20}CF_3$, (d) $CF_3O(CF_2CF_2CF_2CF_2O)_{11}CF_3$.

molecular weight dependence for perfluoropolyalkyl ethers is evident from the data presented in Figs. 1 and 2. To develop QSAR expressions, the descriptors listed in Table 2 were employed in multivariate linear regression analysis. Using three descriptors with $n=9$ (data points) gave an r value (Pearson correlation coefficient) of 0.963 and an s value (standard error estimate) of 4.27. The data point scatter is illustrated in Fig. 5. With six descriptors, r was raised to 0.985, s was 4.33; the actual plot is presented in Fig. 6. In view of these results and difficulty in encoding more complex structures, an approach involving energy parameters was next investigated.

The flexibility of a molecule, i.e. the ease of bending, is one of the major factors affecting the flow, i.e. the viscosity. In perfluoropolyalkyl ethers, the carbon to oxygen ratio portrays this property to a degree. However, the latter relationship breaks down completely in the case of branched materials, as is evident from a comparison of the relative viscosities of the isomers $-(CF_2CF_2CF_2O)_n-$ and $-(CF(CF_3)CF_2O)_n-$. Also, in the case of longer CF_2 chains, the C/O ratio provides an inadequate correlation as exemplified by the large difference in the relative viscosities of $-(CF_2CF_2CF_2O)_n-$ and $-(CF_2CF_2CF_2CF_2O)_n-$. The molecular conformations of the perfluoropolyalkyl ethers presented in Figs. 7–9 illustrate these aspects. Of special interest are the closely packed helical structures exhibited by the branched arrangements, namely $CF_3O[CF_2CF_2OCF_2CF(CF_2CF_3)OCF_2O]_6CF_3$, CF_3O-$[CF_2CF(CF_3)OCF_2CF(CF_3)OCF_2O]_6CF_3$ and CF_3O-$[CF_2CF(CF_3)O]_{14}CF_3$. Another oligomer of the last material was reported by Pacansky et al. [13]. The coiling effect is absent in the short-chain analogs [14]; this aspect illustrates the inherent danger in developing theories regarding the behavior of polymers based on low molecular weight model compounds.

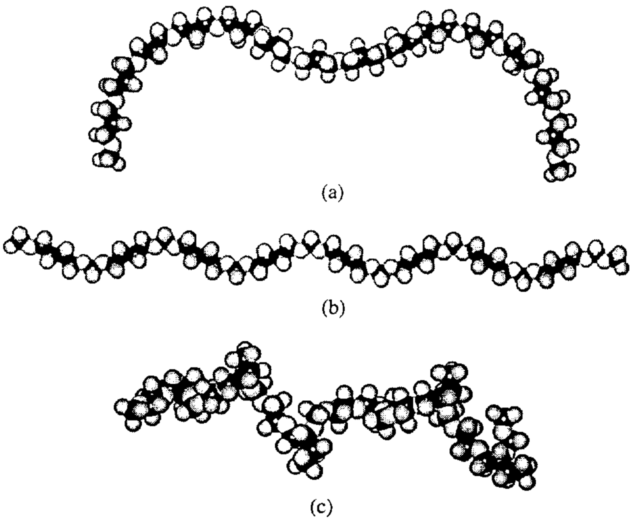


Fig. 8. The conformations obtained with molecular mechanics for perfluoropolyalkyl ethers: (a) $CF_3O(CF_2CF_2CF_2O)_{14}CF_3$, (b) $CF_3O(CF_2CF_2CF_2CF_2CF_2O)_8CF_3$, (c) $CF_3O[CF_2CF_2OCF_2CF$-$(CF_2CF_3)OCF_2O]_6CF_3$.

It is obvious that bonding energies, in particular bending energies, are the major factors contributing to the viscosity characteristics of a given material. To calculate the energy parameters, a number of assumptions and simplifications had to be made. Thus it was assumed that the behavior of a unimolecular fluid parallels that of a telomer mixture of the same number average molecular weight. Furthermore, the end-groups as such do not affect the viscosity. Using these constraints, the bending energies were calculated for the 2500 and 4000 molecular weight systems. The molecular weights of actual arrangements were selected to be as close as possible to these limits. These data are listed in Table 3.

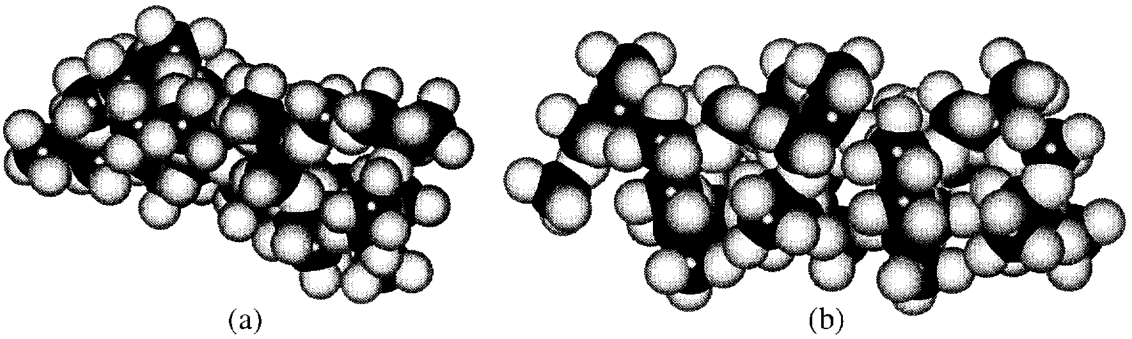
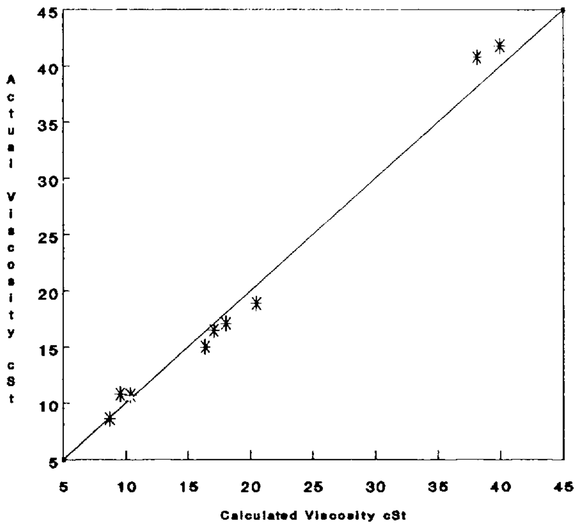


Fig. 9. The conformations obtained with molecular mechanics for perfluoropolyalkyl ethers: (a) $CF_3O[CF_2CF(CF_3)OCF_2CF(CF_3)OCF_2O]_6CF_3$, (b) $CF_3O[CF_2CF(CF_3)O]_{14}CF_3$.

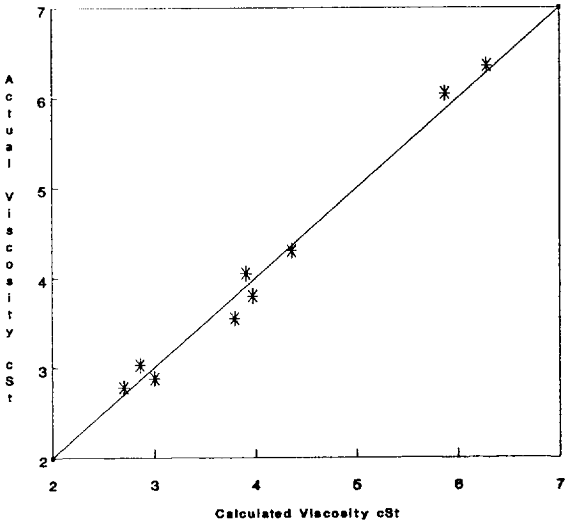
Table 3
Perfluoropolyalkyl ether bending energy data

Structure	MW ~2500			MW ~4000		
	n	MW	BEND (kcal mol^{-1})	n	MW	BEND (kcal mol^{-1})
$CF_3O(CF_2CF_2OCF_2O)_nCF_3$	13	2520	13.4	21	3977	21.1
$CF_3O(CF_2CF_2O)_nCF_3$	20	2474	11.3	33	3983	18.1
$CF_3O[(CF_2CF_2O)_4CF_2O]_nCF_3$	4	2274	11.9	7	3865	20.5
$CF_3O[CF_2CF_2OCF_2CF(CF_2CF_3)OCF_2O]_nCF_3$	6	2542	17.0	10	4135	28.3
$CF_3O(CF_2CF_2CF_2CF_2OCF_2O)_nCF_3$	8	2410	15.6	14	4103	26.9
$CF_3O[CF_2CF(CF_3)OCF_2CF(CF_3)OCF_2O]_nCF_3$	6	2542	18.9	10	4135	30.3
$CF_3O(CF_2CF_2CF_2O)_nCF_3$	14	2478	13.6	23	3973	22.4
$CF_3O[CF_2CF(CF_3)O]_nCF_3$	14	2478	25.9	23	3973	48.3
$CF_3O(CF_2CF_2CF_2CF_2O)_nCF_3$	11	2530	15.7	18	4043	25.1



Log 40°C Viscosity 2500 MW = 0.244(C/O) + 0.022(BEND) + 0.279

Fig. 10. Calculated versus actual viscosity at 40 °C of ~2500 MW perfluoropolyalkyl ethers as a function of the carbon to oxygen ratio and the bending energy.



Log 100°C Viscosity 2500 MW = 0.137(C/O) + 0.011(BEND) + 0.084

Fig. 11. Calculated versus actual viscosity at 100 °C of ~2500 MW perfluoroalkyl ethers as a function of the carbon to oxygen ratio and the bending energy.

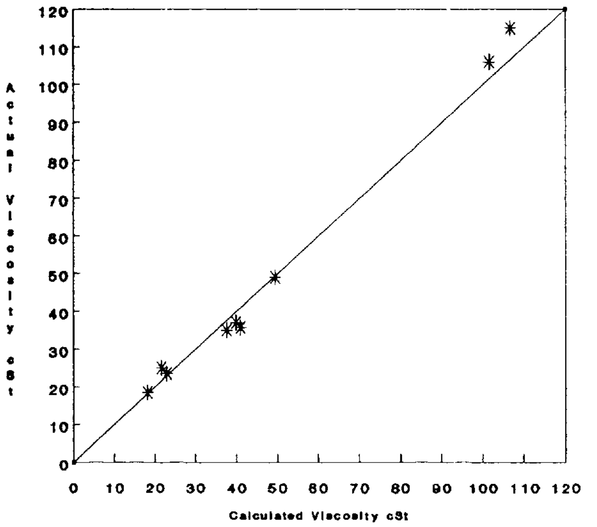
Using C/O ratios and bending energies, the expressions given below were developed for the viscosities of the 2500 and 4000 molecular weight series at 40 °C and 100 °C.

$$\log 40\ ^{\circ}\mathrm{C\ viscosity\ (MW,\ 2500)} = 0.244(\mathrm{C/O}) + 0.022(\mathrm{BEND}) + 0.279$$

$$(r = 0.992,\ s = 0.04,\ n = 9)$$

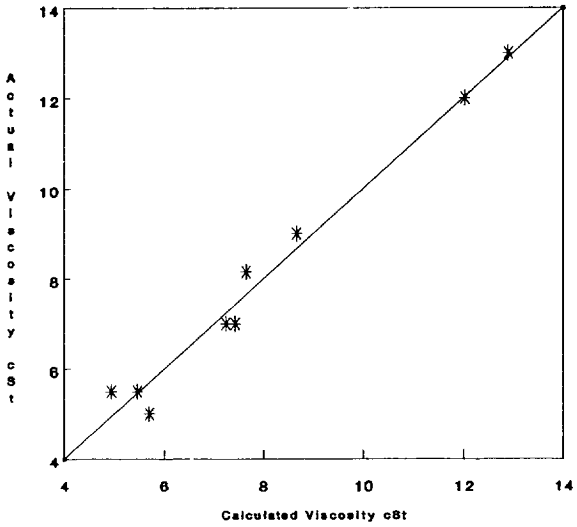
Table 4
Viscosities calculated from equations derived from data excluding the fluid of interest

Structure	MW 2500 Viscosity, (cSt)				MW 4000 Viscosity, (cSt)			
	40 °C		100 °C		40 °C		100 °C	
	Actual	Calc.	Actual	Calc.	Actual	Calc.	Actual	Calc.
$-(CF_2CF_2OCF_2O)_n-$	8.61	8.75	2.78	2.66	18.5	18.1	5.5	4.7
$-(CF_2CF_2O)_n-$	10.7	10.3	2.88	3.05	23.5	22.8	5.0	5.9
$-[(CF_2CF_2O)_4CF_2O]_n-$	10.8	9.15	3.03	2.80	25.0	20.8	5.5	5.4
$-[CF_2CF_2OCF_2CF(CF_2CF_3)OCF_2O]_n-$	15.0	16.6	3.55	3.83	35.0	38.0	7.0	7.3
$-(CF_2CF_2CF_2CF_2OCF_2O)_n-$	16.5	17.2	4.05	3.89	35.5	41.8	8.0	7.6
$-[CF_2CF(CF_3)OCF_2CF(CF_3)OCF_2O]_n-$	17.1	18.3	3.80	4.02	37.0	40.5	7.0	7.5
$-(CF_2CF_2CF_2O)_n-$	18.9	21.0	4.30	4.37	49.0	49.6	9.0	8.6
$-[CF_2CF(CF_3)O]_n-$	40.8	31.4	6.05	5.39	115.0	73.6	12.0	12.3
$-(CF_2CF_2CF_2CF_2O)_n-$	41.8	35.8	6.36	6.10	106.0	90.7	13.0	12.6



Log 40°C Viscosity 4000 MW = 0.278(C/O) + 0.013(BEND) + 0.572

Fig. 12. Calculated versus actual viscosity at 40 °C of ~4000 MW perfluoropolyalkyl ethers as a function of the carbon to oxygen ratio and the bending energy.



Log 100°C Viscosity 4000 MW = 0.158(C/O) + 0.006(BEND) + 0.340

Fig. 13. Calculated versus actual viscosity at 100 °C of ~4000 MW perfluoropolyalkyl ethers as a function of the carbon to oxygen ratio and the bending energy.

$$\log 100\ ^\circ\mathrm{C}\ \text{viscosity}\ (\mathrm{MW},\ 2500) = 0.137(\mathrm{C/O}) + 0.011(\mathrm{BEND}) + 0.084$$

$(r = 0.990, s = 0.02, n = 9)$

$$\log 40\ ^\circ\mathrm{C}\ \text{viscosity}\ (\mathrm{MW},\ 4000) = 0.278(\mathrm{C/O}) + 0.013(\mathrm{BEND}) + 0.572$$

$(r = 0.991, s = 0.04, n = 9)$

$$\log 100\ ^\circ\mathrm{C}\ \text{viscosity}\ (\mathrm{MW},\ 4000) = 0.158(\mathrm{C/O}) + 0.006(\mathrm{BEND}) + 0.340$$

$(r = 0.979, s = 0.04, n = 9)$

The corresponding graphical presentations are depicted in Figs. 10–13. As is evident from the high r values, using just the two parameters gives an unexpectedly good correlation when the assumptions made in developing these expressions are taken into consideration. The actual graphs also show relatively low scatter.

To test the validity of the above relationships, analogous expressions were developed using eight of the materials. The viscosity of the excluded perfluoropolyalkyl ether was then calculated from these equations. This was undertaken for each member of the series. The comparisons between the actual (obtained from the experimental plots given in Figs. 1 and 2) and calculated viscosities are compiled in Table 4. With the exception of $-(CF_2CF(CF_3)O)_n-$, the agreements are reasonably close. On the basis of the conformation presented in Fig. 9, it is believed that this perfluoropolyalkyl ether deviates strongly from the other arrangements because of its tightly coiled structure. Consequently, an equation derived without an input from a related conformation would not be expected to provide valid results. Allowing for this inconsistency, the relationships thus developed, using the carbon to oxygen ratios and the bending energies as the sole parameters, provide surprisingly reliable expressions for predicting the viscosity/temperature and viscosity/molecular weight profiles. This capability is of great value in assessing the behavior of potential lubricants without a need to synthesize the actual materials. These techniques also permit accurate predictions for the increase in viscosity with an increase in molecular weight for known compositions. It is apparent from the molecular conformations and related considerations that any predictions derived by extrapolation from low molecular weight arrangements, i.e. model compounds, are unreliable if not meaningless.

Acknowledgment

We wish to acknowledge the support of US Air Force, Wright Laboratory/Materials Directorate for this work under Contract No. F33615-89-C-5646 and we wish to thank Dr. W.M. Warner for helpful discussions.

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