Viscosity prediction for perfluoropolyalkylether fluids

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Abstract

The temperature dependence of a fluid's shear viscosity is critical in determining its suitability as a liquid lubricant over an extended temperature range. We have applied van Krevelen's equations to a series of ten linear and branched perfluropolyalkylethers (PFPAEs) to predict viscosity–temperature. Calculated viscosities were a factor of ten or more greater than experiment at all temperatures, indicating that these "universal" equations are inadequate for these atypical fluids.

Therefore, new semi-empirical viscosity equations have been derived and parameterized specifically for PFPAEs utilizing recent data. The new equations predict values within a factor of two of experimental viscosities in almost all systems, and hence should be useful in the molecular design of new PFPAE fluids for high temperature lubricants. © 1997 Elsevier Science S.A.

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1. Introduction

Because of their numerous desirable properties such as thermal and oxidative stability, low volatility, non-flammability, good lubricity, compatibility with structural materials, perfluoropolyalkylether (PFPAE) fluids have found increasing use in such diverse fields as vacuum technology [1], electronic materials fabrication [2], biomedical research [3] and surface protection [4]. They have also been used effectively as lubricants in spacecraft [5] and on computer magnetic disks [6].

We have been interested in extending the application of PFPAE liquids to the lubrication of gas turbine jet engines, which require stability at temperatures well over 350 °C. None of the commercially available perfluoroether lubricants possess both the chemical stability and viscosity characteristics to be effective in this application, and there is a need to design new PFPAEs with all the requisite properties.

One of the most important physical properties required is the temperature dependence of viscosity.[1] It would be extremely useful in the molecular design of new lubricants if one could obtain good a priori predictions of a fluid's viscosity behavior prior to its synthesis.

As part of his extensive work on characterization of the structural dependence of polymer properties and development of quantitative structure–property relationships, van Krevelen [7] related the temperature dependence of shear viscosity of polymeric fluids to the structural repeat units. His "universal" equations have been applied to materials of widely differing structure and have yielded excellent semi-quantitative agreement with experimentally measured viscosities. However, on applying his equations, as adapted by Bicerano [8],[2] to various PFPAEs, the calculated viscosities differed by as much as several orders of magnitude from experiment [3] (vide infra).

This indicates that the "universal" parameters incorporated in van Krevelen's semi-empirical equations were ill-adapted to model the viscous behavior of perfluoroether fluids. Therefore, we developed a set of equations parameterized specifically for these systems, based on data recently reported by Marchionni [9,10] and co-workers on a series of linear and branched PFPAE fluids.

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[1] A wide temperature range lubricant should have a high "viscosity index," which is roughly equivalent to a low activation energy for viscous flow (E_η).

[2] In Ref. [7], one must interpolate the critical viscosity (as a function of T_g/T) from a series of master curves (Fig. 15.4 of Ref. [7]). Bicerano [8] used these curves with an empirical equation, permitting direct calculation of $\eta_{cr}(T)$.

[3] We are grateful to Ms Lois Gswender and Mr George Fultz of the Materials Directorate at Wright Laboratory for furnishing us with temperature dependent shear viscosity data on a series of linear and branched PFPAEs.

2. Predictive viscosity equations for PFPAEs

In many polymer fluids in a temperature range from the glass transition temperature, T_g to a higher reference temperature, T_R, (often taken as either $1.2T_g$ or $T_g + 100$ K), shear viscosities follow the Williams–Landel–Ferry (WLF) equation [11], based upon the free volume theory of fluid viscosity:

$$\log\left(\frac{\eta(T)}{\eta(T_g)}\right) = -\frac{C_1(T-T_g)}{C_2+(T-T_g)} \quad T_g < T < T_R \tag{1}$$

The WLF constants, C_1 and C_2, are dependent upon the free volume and thermal expansion coefficients of the liquid and solid, but are usually taken to be "universal" constants.

At temperatures far above T_g, it is generally assumed that fluid flow is an activated process well represented experimentally by an Arrhenius type equation [7,12], with an activation energy for viscous flow, E_η:

$$\log\left(\frac{\eta(T)}{\eta(T_R)}\right) = \frac{E_\eta}{2.303R}\left[\frac{1}{T}-\frac{1}{T_R}\right] \quad T > T_R \tag{2}$$

While one expects the viscosity of a polymer at its glass transition temperature, $\eta(T_g)$, to depend upon its structure and mass, it is generally observed that the viscosities of different fluids with relative molar masses (RMM), M_w, equal to their critical molar masses, M_{cr},[4] are approximately equal at T_g (i.e. $\eta_{cr}(T_g)$ is roughly constant). Hence, to establish a universal relationship, one may apply Eq. (1) or Eq. (2) to determine $\eta_{cr}(T)$,[5] which can then be related to $\eta(T)$ via the standard relation [7,8]:

$$\frac{\eta(T)}{\eta_{cr}(T)} = \left[\frac{M_w}{M_{cr}}\right]^\alpha \tag{3}$$

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[4] The critical molar mass, M_{cr}, of a polymer is the mass above which intermolecular entanglements affect the shear viscosity [7]. It is determined by the mass at which the slope of $\ln(\eta)$ vs. $\ln(M_w)$ changes discontinuously.

[5] $\eta_{cr}(T)$ represents the viscosity of a polymer with $M_w = M_{cr}$ at that temperature; e.g. $\eta_{cr}(T_g)$ is the viscosity of a polymer with the critical molar mass at the glass transition temperature.

where the exponent is given by $\alpha = 1.0$ for $M_w < M_{cr}$ and $\alpha = 3.4$ for $M_w > M_{cr}$.

Taking the logarithm of Eq. (3), and employing Eq. (1) to determine $\eta_{cr}(T)$, one finds that, for $T_g < T_R$:

$$\log[\eta(T)] = \log[\eta_{cr}(T_g)] + \alpha \log(M_w/M_{cr})$$
$$-\frac{C_1(T-T_g)}{C_2+(T-T_g)} \tag{4}$$

For temperatures, $T \geq T_R$, one may similarly combine Eqs. (2) and (3) to obtain:

$$\log[\eta(T)] = \log[\eta_{cr}(T_g)] + \alpha \log(M_w/M_{cr})$$
$$-\frac{C_1(T_R-T_g)}{C_2+(T_R-T_g)} + \frac{E_\eta}{2.303R}\left[\frac{1}{T}-\frac{1}{T_R}\right] \tag{5}$$

In deriving this expression, we have utilized Eq. (4) to determine $\log[\eta(T_R)]$, which ensures that viscosities calculated by the two equations will be the same at the reference temperature.

In order to apply Eqs. (4) and (5) to calculate shear viscosities, it is necessary to estimate parameters in the two equations.

3. Computational procedures

All calculations were performed utilizing a FORTRAN program. Comparison was made with experimental viscosity data on a series of PFPAEs, whose structures are given in Table 1, and experimental viscosities are given in Table 2 [η(exp)]. The experimental activation energies, E_η(exp) in Table 1, were calculated by Arrhenius fits of the viscosity data above 313 K.

3.1. The glass transition temperature

Estimates of T_g, required in Eqs. (4) and (5), can be obtained from the "molar glass transition function," Y_g,

Table 1
Activation energies for viscous flow

No.	Formula	M_w [a]	T_g(K)	E_η(exp) (kJ mol^{-1})	E_η(calc) (kJ mol^{-1})	E_η(calc) $- E_\eta$(exp) (kJ mol^{-1})
1	[CF$_2$CF$_2$O]$_n$	4980	154	21.5	[b]	–
2	[CF$_2$CF$_2$OCF$_2$O]$_n$	4360	141	19.0	[b]	–
3	[CF$_2$CF(CF$_3$)O]$_n$	2820	206	28.9	[b]	–
4	[CF$_2$CF$_2$CF$_2$O]$_n$	5970	168	22.6	24.5	1.9
5	[CF$_2$CF$_2$CF$_2$CF$_2$O]$_n$	8170	177	26.2	26.2	0.0
6	[CF$_2$CF$_2$CF$_2$CF$_2$OCF$_2$O]$_n$	5380	162	21.6	23.2	1.6
7	[{CF$_2$CF$_2$O}$_4$CF$_2$O]$_n$	4840	149	20.9	20.6	−0.3
8	[CF$_2$O]$_x$[CF$_2$CF$_2$O]$_y$	4980	138	18.4	18.4	0.0
9	[{CF$_2$CF(CF$_3$)O}2CF$_2$O]$_n$	3330	192	23.0	26.2	3.2
10	[CF$_2$CF(CF$_3$)O{CF$_2$CF$_2$O}$_3$]	4780	172	23.7	23.7	0.0
				AVG(RMS)		1.5

[a] Relative molar masses were estimated, as described in the text.
[b] The experimental activation energies for compounds 1–3 were used to determine the H_ηs used to obtain E_η(cal) for the other molecules.

Table 2

Temperature dependence of experimental and calcualted viscosities [a]

No.	Formula		219 K	233 K	255 K	313 K	373 K	473 K	573 K	R_{avg} [b]
1	$[CF_2CF_2O]_n$	$\eta(exp)$	–	–	–	30	7.0	1.8	0.7	–
		$\eta(calc)$	6.6E+3	1.9E+3	440	40	11	2.4	0.9	1.4
		$\eta(vK)$	4.7E+4	2.3E+4	8.9E+3	1.4E+3	360	83	32	47
2	$[CF_2CF_2ICF_2O]_n$	$\eta(exp)$	2.2E+3	670	–	19	5.7	1.6	0.7	–
		$\eta(calc)$	1.8E+3	660	190	23	7.1	1.9	0.8	1.1
		$\eta(vK)$	1.7E+4	9.1E+3	3.9E+3	740	230	63	27	30
3	$[CF_2CF_2(CF_3(O]_n$	$\eta(exp)$	–	–	1.7E+4	180	22	3.7	1.3	–
		$\eta(calc)$	2.8E+7	10.E+5	3.0E+4	350	58	8.1	2.2	2.0
		$\eta(vK)$	7.9E+9	6.7E+7	2.0E+5	4.4E+3	740	100	29	22
4	$[CF_2CF_2CF_2O]_n$	$\eta(exp)$	2.7E+4	6.0E+3	950	49	10	2.3	1.0	–
		$\eta(calc)$	3.9E+4	8.4E+3	1.3E+3	79	18	3.3	1.1	1.4
		$\eta(vK)$	1.6E+5	7.2E+4	2.4E+4	2.8E+3	630	120	40	36
5	$[CF_2CF_2CF_2CF_2O]_n$	$\eta(exp)$	–	4.7E+4	4.6E+3	95	13	2.6	0.9	–
		$\eta(calc)$	1.9E+5	3.2E+4	3.9E+3	170	34	5.7	1.8	1.7
		$\eta(vK)$	4.5E+5	1.9E+5	5.9E+4	6.0E+3	1.2E+3	200	62	53
6	$[CF_2CF_2CF_2CF_2OCF_2O]_n$	$\eta(exp)$	1.7E+4	–	–	38	8.7	2.1	0.9	
		$\eta(calc)$	1.7E+4	4.2E+3	790	57	14	2.8	1.0	1.3
		$\eta(vK)$	9.2E+4	4.3E+4	1.5E+4	2.0E+3	480	99	35	40
7	$[\{CF_2CF_2O\}_4CF_2O]_n$	$\eta(exp)$	1.9E+4	3.7E+3	–	28	6.8	1.8	0.7	–
		$\eta(calc)$	4.2E+3	1.4E+3	330	33	9.3	2.3	0.9	1.0
		$\eta(vK)$	3.3E+4	1.7E+4	6.7E+3	1.1E+3	310	77	31	30
8	$[CF_2O]_x[CF_2CF_2O]_y$	$\eta(exp)$	2.3E+3	8.9E+2	–	31	10	3.0	1.2	–
		$\eta(calc)$	1.7E+3	6.4E+2	190	25	7.9	2.3	1.0	0.8
		$\eta(vK)$	1.6E+4	8.6E+3	3.8E+3	760	240	69	31	19
9	$[\{CF_2CF(CF_3)O\}2CF_2O]_n$	$\eta(exp)$	1.1E+5	1.5E+4	–	54	11	2.5	0.9	–
		$\eta(calc)$	1.2E+6	10.E+4	690	170	33	5.6	1.7	4.6
		$\eta(vK)$	4.8E+7	8.0E+5	2.7E+4	2.7E+3	540	91	29	108
10	$[CF_2CF(CF_3)O\{CF_2CF_2O\}_3]$	$\eta(exp)$	–	–	1.8E+3	45	8.3	1.9	0.7	–
		$\eta(calc)$	5.2E+4	10.E+3	1.5E+3	80	19	3.7	1.3	1.7
		$\eta(vK)$	1.1E+5	4.8E+4	1.7E+4	2.1E+3	490	98	34	43

[a] Viscosities are in units of cP (1.0E+4 represents 1.0×10^4).

[b] R_{avg} represents the average (over temperature) of either $\eta(cal)/\eta(exp)$ or $\eta(vK)/\eta(exp)$.

introduced by van Krevelen and Hoftyzer [7,13], via the simple relation, $T_g^\infty = Y_g/M_R = \Sigma Y_{g,i}/M_R$, where M_R is the RMM of the repeat unit, and the $Y_{g,i}$ represent the contributions from the individual bivalent groups in the polymer's repeat unit; T_g^∞ is for a polymer of infinite mass. Marchionni and coworkers [10] have reported values for the group contributions, $Y_g(-CF_2-)$, $Y_g(-CF(CF_3)-)$ and $Y_g(-O-)$, in the PFPAEs. They further showed that corrections to T_g for PFPAEs of finite mass could be estimated from: $T_g = T_g^\infty - K_w/M_w$, where $K_w = 3 \times 10^4$ K (for both linear and branched polymers). In fluids with multiple repeat units, the values of M_R and Y_g were weighted by their mole fractions. The calculated viscosities are in column 4 of Table 1.

3.2. Activation energy for viscous flow

Van Krevelen and Hoftyzer [14] were also able to relate the activation energy, E_η, to an additive function, H_η, which they termed the molar viscosity temperature gradient, via the relationship:

$$E_\eta = \left[\frac{H_\eta}{M_R}\right]^3 = \left[\frac{\Sigma_i H_{\eta,i}}{M_R}\right]^3 \qquad (6)$$

As there were no available data on values of $H_{\eta,i}$ for the bivalent groups in PFPAEs, we fit the experimental activation energies of two linear (Nos. 1 and 2) and one branched (No. 3) perfluoroethers to obtain the group contributions, $H_\eta(-O-)$

$= 38$ $J^{1/3}$, $H_\eta(-CF_2-) = 1594$ $J^{1/3}$ and $H_\eta(-CF(CF_3)-)$
$= 3463$ $J^{1/3}$. These results were used in Eq. (6) to predict values for E_η in the other PFPAEs in Table 1 $[E_\eta(\text{calc})]$.

3.3. Other parameters

As noted earlier, the extensive investigations by Marchionni et al. [9,10] on the experimental temperature and

mass dependence of viscosities in linear (Fomblin-Z) and branched (Fomblin-Y) perfluoroethers has permitted estimation of the parameters necessary for the application of Eqs. (4) and (5). $C_1 = 11$ and $C_2 = 60$ K are taken directly from their work, as were the critical RMMs of the linear and branched compounds, $M_{cr}(\text{lin}) = 7800$ and $M_{cr}(\text{br}) = 5500$. The value, $\eta_{cr}(T_g) = 5.5 \times 10^9$ cP was obtained by extrapolation of viscosity data given in Ref. [9]. The reference temperature, T_R, used to determine which of the two viscosity
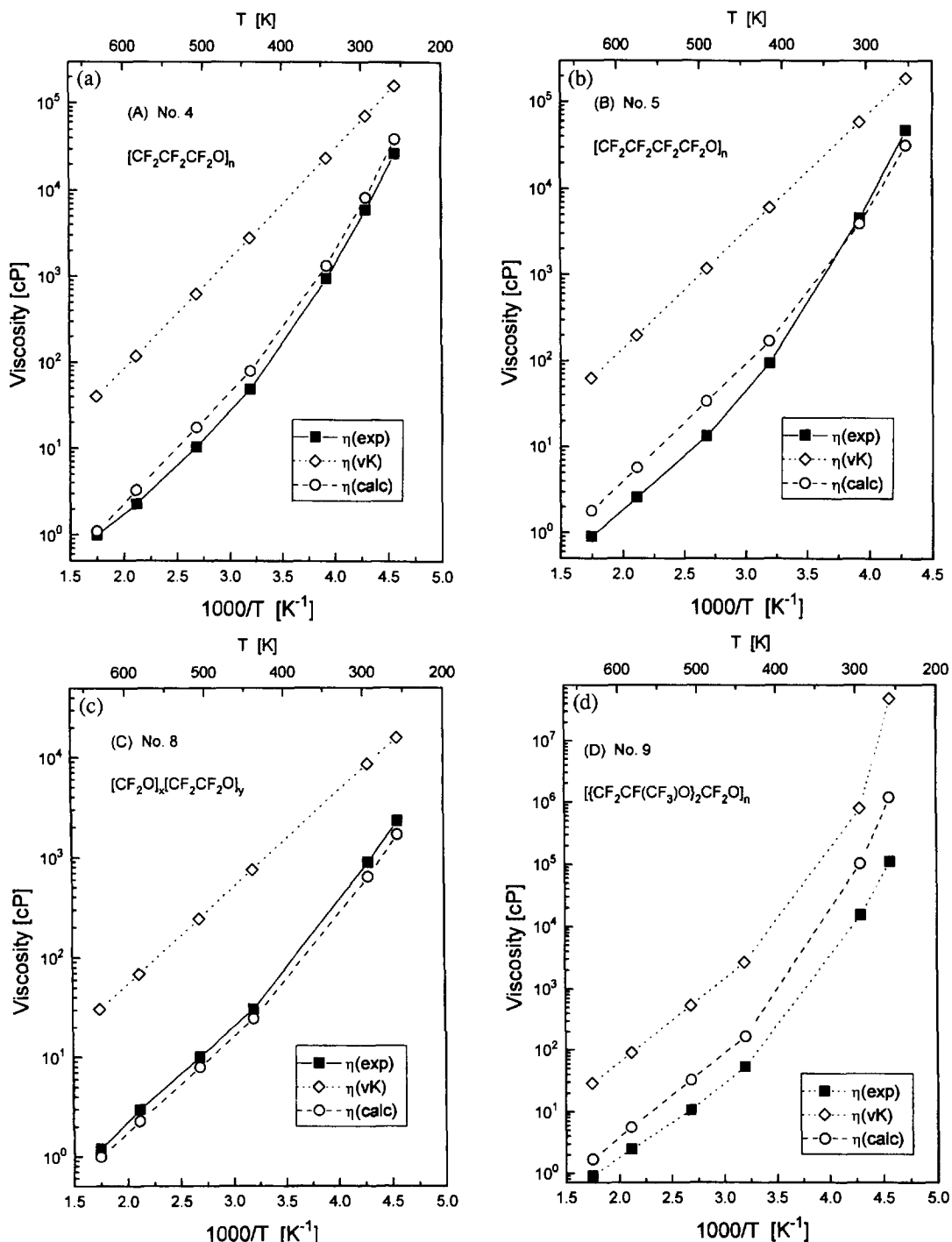

Fig. 1. The temperature dependence of experimental [filled squares] and calculated [open diamonds (van Krevelen) and open circles (this work)] viscosities in four representative PFPAE fluids.

equations to employ, was arbitrarily taken to be 298 K.[6] Since masses for the model compounds in Table 1 were not available, they were estimated by comparison of 293 K (interpolated) viscosities to results for the various molar mass fractions in Ref. [9].

4. Results and discussion

The agreement of the calculated activation energies (Table 1) is within 2 kJ mol^{-1} for all compounds except No. 9, with an RMS average deviation of 1.5 kJ mol^{-1}. Even these relatively small differences may be attributed, at least in part, to the fact that Eq. (6) was developed to calculate E_η for polymers of infinite mass, whereas Marchionni et al. have shown [10] that E_η values are dependent on M_w for perfluoroethers, reaching an asymptotic limit at high masses. Hence, a more accurate calculation of the activation energy would require a correction for finite mass. There are insufficient data to establish a correction for perfluoroethers of general structure.

In Table 2 the experimental PFPAE viscosities [$\eta(\exp)$] over an extended range of temperature up to 573 K, together with values calculated from the original van Krevelen equations [7,8] [$\eta(vK)$] and from Eqs. (4) and (5) above [$\eta(\text{calc})$] are compared. The ratios, R_{avg}, representing the average over the temperatures of either $\eta(vK)/\eta(\exp)$ or $\eta(\text{calc})/\eta(\exp)$, show the quality of the calculations. The viscosities obtained from the van Krevelen equations are poor, with average ratios ranging from 20 to over 100. The predicted viscosities are one to two orders of magnitude high for the PFPAE fluids.

In contrast, viscosities calculated from the new equations [$\eta(\text{calc})$] are in good agreement within a factor of two. The exception is for the mixed linear/branched PFPAE (No. 9), where $R_{avg} \approx 5$ and low temperature calculated viscosities are a factor of ten greater than experiment.

Arrhenius plots of measured and calculated viscosities for four representative PFPAEs (Nos. 4, 5, 8, 9) are given in Fig. 1. The high temperature experimental viscosities (closed squares) are, indeed, linear on a semi-logarithmic Arrhenius plot, as assumed in determining E_η values.

The capability of the original van Krevelen equations to furnish only order of magnitude estimates of PFPAE viscosities can be attributed to the values of the parameters used in

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6 The common estimate that $T_R = T_g + 100$ K yielded viscosities that were significantly too high for the linear PFPAEs.

their development. The "universal" values of the WLF constants in these equations of $C_1 = 17.4$ and $C_2 = 51.6$ differ significantly from the PFPAE values of 11 and 60 [10]. Similarly, the "standard" value of $\eta_{cr}(T_g) = 1 \times 10^{15}$ cP is quite different from the value 5.5×10^9 cP used here. The parameters obtained from experiments on most polymeric systems are not applicable to viscosity prediction in the PFPAEs, whereas Eqs. (4) and (5) are capable of furnishing good semi-empirical estimates of in these polymeric fluids.

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