VISCOSITIES OF CHLOROFLUOROCARBON LUBRICANTS

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Measurements have given empirical formulas for the viscosities of chlorofluorocarbon lubricants.

An activation model often describes satisfactorily the temperature dependence of the viscosity [1]:

$$\eta = A\exp\frac{E}{RT}. \tag{1}$$

The temperature dependence of the mechanical and electrical properties of a polymer above the vitrification temperature can [2] be described by the single empirical function

$$a_T = \frac{\eta T_r \rho_r}{\eta_r T\rho}. \tag{2}$$

As the factor $T_r\rho_r/T\rho$ has a relatively weak temperature dependence, the value a_T is virtually the same as the ratio of the viscosities, so this formula gives a satisfactory method of describing the viscosity of a molten polymer as a function of temperature. The usual form given to the equation is as follows:

$$\lg\frac{\eta}{\eta_r} = \frac{-C_1(T-T_r)}{C_2+(T-T_r)}. \tag{3}$$

As T_r, Williams suggested a temperature (the reduction temperature) some 50 ± 4° above the vitrification temperature.

This activation model has been used with this reduction method to describe the temperature dependence of the viscosity for chlorofluorocarbon lubricants of various molecular weights.

We examined the materials 11F, 12F, 13FM, 4LF, and 4F having the general formula $X(CF_2-CFCl)_nX$ (where X = F or Cl) [3], whose mean molecular weights were, respectively, 340, 380, 650, 750, and 950; we also examined a mixture of 11F and 4F in equal parts having M = 570. Distinctive features of these substances are the wide temperature range for the liquid state (above 300°) and the high temperature coefficient of the viscosity.

We constructed a rolling-sphere viscometer to work over the range from −150°C to 300°C, which enabled us to measure viscosities from 10^{-4} to 10^2 N · sec/m². The thermostatic system and the electronic temperature regulator [4] maintained any set temperature to better than 0.1°; temperatures above room temperature were provided by heaters, while those below room temperature were provided by cold nitrogen.

Two specimens with molecular weights of 340 and 950 were examined with an oscillation viscometer [5] over a wide temperature range; the results from the two methods agreed within the error of measurement. The viscosities of the lubricants were measured over the wide temperature range for the liquid state. The lower temperature limit was set by the viscosity of $5 \cdot 10^2$ N · sec/m², while the upper was set by the production of gas bubbles. Figure 1 shows the results.

The temperature dependence can be represented as two straight lines, whose point of intersection separates the parts differing in slope. In all cases, the slope in the low-temperature range was higher than that in the high-temperature one, while both slopes increased with the molecular weight. This

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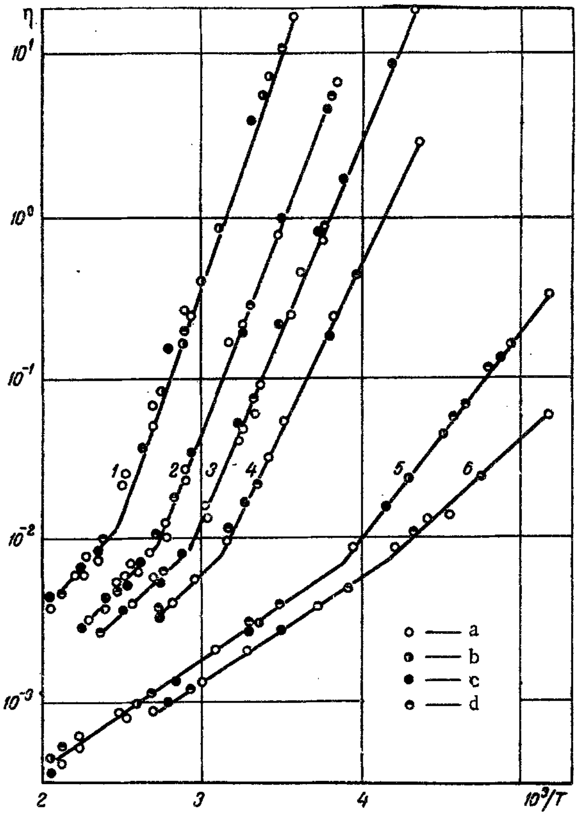

Fig. 1. Viscosity as a function of temperature for chlorofluorocarbon lubricants of molecular weights: 1) M = 950; 2) 750; 3) 650; 4) 570; 5) 380; 6) 340; experimental results: a) ball viscometer; b) oscillation viscometer. Calculations: c) from (16); d) (18).

indicates that the kink corresponds to a kinetic transition, which corresponds to the parameters η_r and T_r. Parts a and b of Fig. 2 show the dependence of these parameters on the molecular weight, which can be represented as

$$\lg \eta_r = 3.23\cdot 10^{-4}M + 0.7243, \tag{4}$$

$$T_r = 370 \lg M - 697. \tag{5}$$

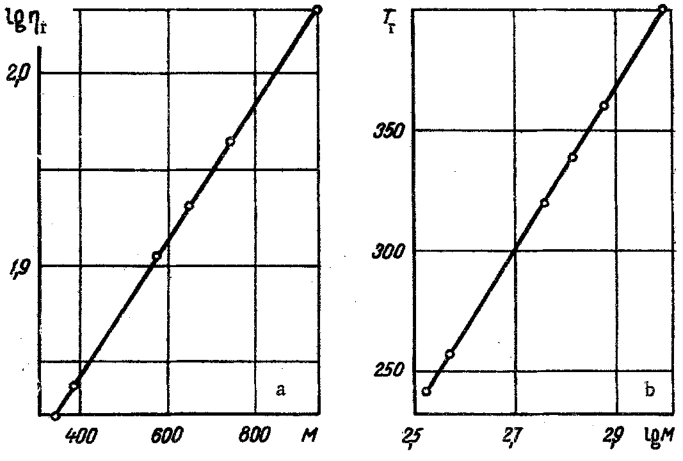

Fig. 2. Molecular-weight dependence of : a) η_r; b) T_r.

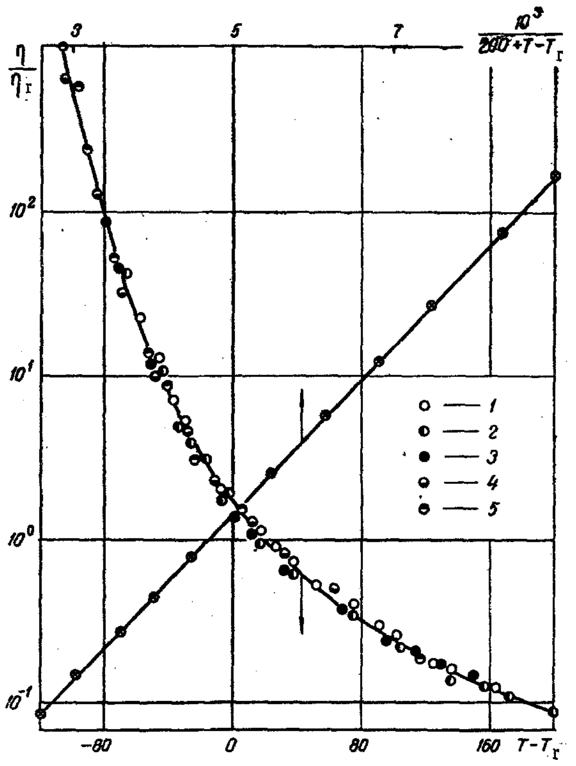

Fig. 3. Dependence of η/η_r on $T - T_r$ for: 1) M=340; 2) 380; 3) 650; 4) 950; 5) calculated from (18). η, N • sec/m²; T, °K.

A similar transition has been observed in molten macromolecular compounds and has been classified as a T_u transition [6]; it has been found [7-9] after suitable processing [10] that T_u transitions occur when the molecular weight of the polymer exceeds several thousand and is due to replacement of segmental displacements by motion of the chain as a whole.

These chlorofluorocarbon polymers are of relatively low molecular weight, and Boyer's kinetic-transition mechanism is not really applicable. It would seem that this trend in the viscosity is governed in the main by the structure of the liquid and by the intramolecular and intermolecular interactions.

Activation Study

The activation model indicates that each observed trend consists of two exponential parts, each having its own activation energy and preexponential factor:

$$\eta_1 = \eta_{01} \exp \frac{E_1}{RT}, \tag{6}$$

$$\eta_2 = \eta_{02} \exp \frac{E_2}{RT}. \tag{7}$$

The subscripts 1 and 2 relate, respectively, to the low-temperature and high-temperature parts; Figure 1 shows that E_1 is greater than E_2.

The activation energy is determined by the intermolecular interaction and by the degree of order; the intermolecular distances increase with temperature, and so the interactions fall. The attractive forces vary in inverse proportion to the sixth power of the intermolecular distance, so an estimate may be made of the variation between the extreme points for the liquid state on the basis of the density. This indicates a 20% change in the intermolecular forces, whereas the activation energy changes on average by a factor 2.11 at the kink. Also, the molecular interactions vary monotonically, whereas the activation energy alters stepwise. It would appear that the ordering in the system is responsible for this effect. Molecular aggregation should also produce the same result.

The activation energy also increases with the molecular weight, and the relationship can be represented as a straight line described by the empirical relations

$$E_1 = R(9.1M - 10^3), \tag{8}$$

$$E_2 = R(2.22M + 910). \tag{9}$$

The preexponential factor for the low-temperature part is also dependent on the molecular weight:

$$\eta_{01} = \exp(-8.3 - 1.6 \cdot 10^{-2}M), \tag{10}$$

whereas η_{02} is constant at

$$\eta_{02} = 8.2 \cdot 10^{-6}. \tag{11}$$

Here E is in kcal/mol, while η is in $N \cdot sec/m^2 \cdot 10^{-3}$.

The full formula for the viscosity may be derived by combining (6) and (7) together with a unit Heaviside function [11], which satisfies the following conditions:

$$H(t) = \begin{cases} 0 & \text{for } t < 0, \\ 1/2 & \text{for } t = 0, \\ 1 & \text{for } t > 0. \end{cases} \tag{12}$$

Then

$$\eta = H(t_1)\eta_1 + H(t_2)\eta_2, \tag{13}$$

where

$$t_1 = T - 370 \lg M + 697, \tag{14}$$

$$t_2 = 370 \lg M - 697 - T. \tag{15}$$

We substitute (6)-(11) into (13) and get

$$\eta = H(t_1)\exp(-8.3 - 1.6 \cdot 10^{-2}M)\exp\left(\frac{9{,}1M - 10^3}{T}\right) + H(t_2)\,8.2 \cdot 10^{-6}\exp\left(\frac{910 + 2.22M}{T}\right). \tag{16}$$

Williams – Landel – Ferry (WLF) Calculation of the Viscosity

The Williams–Landel–Ferry method is valuable in that it allows one to combine various experimental data in reduced coordinates; the choice of reduction parameters is here very important. We use the coordinates of the kink (Fig. 1) as η_r and T_r. The curves for five homologs in this series shows good agreement between the temperature dependence of the viscosity in each case in reduced coordinates (Fig. 3). The logarithm of the reduced viscosity as a function of the reciprocal of the reduced temperature is a straight line that can be described by

$$\lg \frac{\eta}{\eta_r} = \frac{520}{200 + T - T_r} - 2.47. \tag{17}$$

Substitution for η_r and T_r from (4) and (5) gives a reasonably simple relationship for the viscosities of these chlorofluorocarbon lubricants in terms of the molecular weight throughout the liquid range;

$$\lg \eta = 3.23 \cdot 10^{-4}M + \frac{520}{897 - 370 \lg M + T} - 1.7457. \tag{18}$$

NOTATION

η, dynamic viscosity; A, preexponential factor; E, E_1, and E_2, activation energies; R, gas constant; T, temperature; a_T, Williams–Landel–Ferry reduction factor; ρ, density; η_r, ρ_r, and Tr, reduction viscosity, density, and temperature; M, molecular weight; T_u, transition temperature; η_{01} and η_{02}, preexponential factors; H(t), Heaviside function.

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