Pressure and Temperature Effects on Viscosity of Synthetic Lubricants*

Ikuya FUJISHIRO**, Yuichi NAKAMURA**, Cao GUIHE*** and Yoshitaka FUJII****

Viscosity of several synthetic lubricants is measured in a diamond-anvil high-pressure cell by the falling sphere method at elevated temperature. Viscosity-pressure coefficients of bicyclohexylcyclohexylmethane, dimethylsilicone and a mixture of them, which are important in elastohydrodynamic lubrication and traction coefficient, are obtained. In order to discuss the property of the mixture, the Wright method is applied and shows agreement with the present data. Viscosity-temperature characteristics under high pressure are also discussed using Walther's equation, and this equation proves to be effective even under high pressure. Factors relating the viscosity-temperature property of the mixture are close to those of dimethylsilicone.

Key Words: Tribology, Lubrication, Synthetic Lubricants, Traction Drive, Viscosity, High Pressure,

1. Introduction

Synthetic lubricants have outstanding properties, such as low-temperature fluidity and a high viscosity index (V.I.), which natural mineral oils do not. Nowadays synthetics are used widely because of their long life and high performance, despite their high price. For traction drive, in addition to a general requirement for lubricants such as a high viscosity index, a high viscosity-pressure coefficient is necessary. However, it is difficult for natural mineral oils to satisfy both requirements. Under these circumstances, synthetic lubricants are effective, but the viscosity-pressure characteristics of synthetic lubricants are not well known. Generally, natural lubricants (especially mineral oils) are mixtures of thousands of different kinds of molecules mainly composed of hydrocarbons, and it is almost impossible to define molecular structures. Synthetic lubricants, on the other hand, are mixtures composed of polymers which have a definite chemical structure or a homologous series. The component is either a hydrocarbon such as α-olefinic oligomer, or a hydrocarbon with oxygen or silicone added, which enables the less dependence on temperature and pressure owing to its molecular flexibility without additives.

The authors previously proposed the measurement of viscosity-temperature-pressure characteristics of lubricants by a diamond-anvil falling-sphere viscometer(12). This paper shows the effects of temperature and pressure on the viscosity of synthetic oils using this method. The synthetic oils used here were bicyclohexylcyclohexylmethane (BCCM), dimethylsilicone (DMS) and a mixture of them. BCCM is assumed to be sensitive to the pressure and DMS shows favorable viscosity-temperature characteristics as a lubricant. Also, in consideration of the fact that lubricants now in use generally contain some additives, a mixture of the above two synthetic oils is examined. In this study, a diamond-anvil cell which generates high pressure over the solidified pressure of lubricants is employed. Thus, it is possible to investigate the effects of temperature and pressure on the viscosity over a wide range.

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** Faculty of Engineering, Mie University, 1515 Kamihama-cho, Tsu, 514, Japan
*** Department of Mechanical Engineering, Jilin University of Technology, Chang Chun, China
**** Toyobo Co., Ltd., 2-1-1 Katada, Otsu, Shiga, 520-02, Japan

2. Experimental Procedure

2.1 Experimental

In this study, the diamond-anvil apparatus is employed for pressure generation, the ruby fluorescence method for pressure measurement and the falling sphere method for viscometry. These apparatus are improved as follows: ① An argon ion laser (NEC GLG 3201) is used for excitation of ruby fluorescence. (In the former report, a high-pressure mercury lamp was used.) Moreover, the wooden mounting plate for optical instrumentation is replaced by a steel plate. As a result, the stability of the optical source is improved, which contributes to the accuracy of the pressure measurement. ② In elevating temperature, hot air from a heat gun is blown against the outside of the diamond-anvil apparatus. In this experiment, this apparatus is heated within a box in order to obtain a uniform temperature distribution. Temperature is measured by a digital thermometer consisting of a Chromel-Alumel thermocouple whose resolution is 0.1 °C. ③ For the viscometry, to obtain accurate estimation of the influence of the pressure chamber wall on the falling sphere speed, the falling path must be at the center of the pressure chamber. Therefore, a micrometer is attached to the viscometer for accurate measurement of the distance between the sphere and the walls of the pressure chamber.

Viscosities at atmospheric pressure are measured by Canon-Manning Semimicro Viscometer (JIS K 2283) in the temperature-controlled water bath.

2.2 Synthetic oils

Three kinds of synthetic oils, whose chemical structures are shown in Table 1, are examined. BCCM is a mixture of isomers of cyclopentaffinic synthetic hydrocarbons. This oil is expected to show a high viscosity-pressure coefficient. DMS with siloxane bonds has high-performance viscosity-temperature properties. It is difficult for natural mineral oils to offer both high-temperature and high-pressure features. These synthetic oils might overcome this difficulty, which leads to high traction performance. In Table 1, the molecular weight is from 200 to 1 250, and the number of covalent bond is about 15 on average. In consideration of the fact that practical oils are mixtures of additives, the effects of mixing on the viscosity are also examined. A mixture is composed of BCCM and DMS, whose ratio is 1:1 in volume.

The density of lubricants, which depends on both temperature and pressure, is needed for the falling sphere viscometer. The coefficient of thermal expansion at atmospheric pressure is measured by a pycnometer at an elevated temperature. Figure 1 shows the volume change vs. temperature. The data of mercury are also inserted in the figure and agree well with those from the Chronological Scientific Tables (Rika Nenpyou). Data on all of the lubricants show a linearity. Using data in Fig. 1, density under high pressure is approximated by the following equation, which is commonly given for mineral oils

\[ \rho = \rho_0 \left( 1 + \frac{0.000581P}{1 + 0.00167P} \right) \]  

where \( \rho \) and \( \rho_0 \) are densities under high pressure and atmospheric pressure, respectively, and \( P \) is the pressure (MPa). When viscosity is calculated from the equilibrium equation of a falling sphere in the pressure chamber, the density of the falling sphere is predominant compared with that of oils. The density of the metal sphere and oil is about 8 and 0.9, respectively. The error of viscosity measurement is, at most, 2%, even if we do not take the volume change of oil due to pressure into account. Thus Eq. (1) seems to ensure sufficient accuracy for density evaluation under high pressure.

3. Experimental Results and Discussion

3.1 Pressure increment induced by temperature elevation

The pressure chamber is compressed due to the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical structure</th>
<th>Density (g/cm³)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>bicyclohexyl</td>
<td>C₅H₁₀</td>
<td>0.9236</td>
<td>23°C</td>
</tr>
<tr>
<td>cyclohexylmethane</td>
<td>(BCCM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dimethylsilicone</td>
<td>CH₃(CH₂-O)nCH₃</td>
<td>0.9376</td>
<td>22°C</td>
</tr>
<tr>
<td>(DMS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCCM-DMS Mixture</td>
<td>1:1 (Volumetric ratio)</td>
<td>0.9272</td>
<td>27°C</td>
</tr>
</tbody>
</table>

Table 1  Tested lubricants

Fig. 1  Volume change vs. temperature

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temperature elevation because of the larger thermal expansion coefficient of liquids compared with that of metals of the apparatus (stainless steel), and it seems to be pressurized more than at room temperature. Measured pressure increments for each synthetic oil are shown in Fig. 2. BCCM shows the highest pressure increment at 100°C, followed by DMS, and a mixture. Pressure varies linearly with temperature for DMS, whereas the slope gradually increases with temperature (almost parabolic) for BCCM and a mixture. These data are fitted by a straight line for DMS and by quadratic curve for BCCM and a mixture. The pressure at elevated temperature is calculated by adding the pressure increment from the fitting lines or curves to the pressure at room temperature. These pressure increments might be dependent on the thermal expansion coefficient and bulk modulus of the liquids. The volume change by temperature elevation (i.e. thermal expansion coefficient) is almost linear for all oils, shown in Fig. 1. In contrast, Fig. 2 indicates that the pressure increment changes in parabolic for BCCM and mixture with temperature elevation. Quantitatively, BCCM shows the largest pressure increment at 100°C, shown in Fig. 2, which is not consistent with the data of the thermal expansion coefficient. Accordingly, the pressure increment at elevated temperature does not correlate directly with the thermal expansion coefficient. Alternately, this increment is assumed to be correlated with other factors such as the bulk modulus of liquids, thermal expansion coefficient under high pressure and the deformation of a metal gasket as a pressure chamber.

3.2 Viscosity-pressure relation
The relations between logarithmic viscosity and pressure are shown in Figs. 3, 4 and 5 for BCCM, DMS and a mixture, respectively, in terms of temperature change. In measuring, the viscosity is obtained at room temperature and 40°C, 60°C, 80°C and 100°C, respectively, under the same load; then higher load is applied and the temperature is raised again. The pressure at each temperature is determined by adding the pressure increment, as discussed in Section 3.1. The viscosity-pressure relations for every figure seem to be almost linear, somewhat concave and convex. Comparison of figures shows that the change of viscosity with the pressure is largest in BCCM and larger in the mixture than in DMS. For example, the pressure

Fig. 2 Pressure increment in pressure chamber by temperature elevation

Fig. 3 Viscosity-pressure relation on BCCM

Fig. 4 Viscosity-pressure relation on DMS

Fig. 5 Viscosity-pressure relation on a mixture
corresponding to viscosity $10^4$ mPa·s at room temperature is about 200 MPa, 500 MPa and 700 MPa for the respective oils.

The data for a mixture in Fig. 5 are located almost at the midpoint between BCCM and DMS. To enable closer observation of this feature, data of these oils are depicted in the same figure (as at 60°C, in Fig. 6). In this figure, regression curves of the 2nd- and 3 rd-order polynomials for BCCM and DMS, respectively, are drawn. The Wright method is one of the viscosity estimation methods for mixed liquids. This method approximates the viscosity of a mixture to the internal division of the equiviscosity line by the mixing ratio in the ASTM viscosity-temperature chart. This estimation is applicable to almost all mixtures. However, it is not applicable to the mixture which shows maximum viscosity at some mixing ratio, such as an alcohol-water mixture. The broken line in Fig. 6 indicates an application of the Wright method. Thus the temperature axis in the ASTM chart is replaced by a pressure axis. Data for a mixture almost agree with the broken line with some scattering. This implies that this modified Wright method is effective even under high pressure.

Next, data obtained on synthetic oils are discussed by applying the following equation of viscosity $\eta$ and pressure $P$, which is commonly used in elastohydrodynamics (EHL):

$$\eta = \eta_0 \exp(aP), \quad (2)$$

where $\eta_0$ is the viscosity at atmospheric pressure and $a$ is a viscosity-pressure coefficient. $a$ increases in proportion to the traction coefficient and, in EHL theory, the minimum film thickness between the two lubricated rollers is proportional to the 0.54th power of $a$. Figure 7 shows the variation of $a$ with temperature for each oil. In this figure, $a$ decreases with increasing temperature and the value at 100°C is about half the value at room temperature for DMS and a mixture, and one-third for BCCM. In view of the aforementioned relationship between $a$ and film thickness, the film thickness at 100°C would presumably become thinner than that at room temperature by 0.6 times and 0.55 times, respectively. Data for the mixture at 100°C are located at the midpoint between those of BCCM and DMS. The datum obtained by Muraki and Kimura shown by a solid circle, almost agrees with the present data.

3.3 Viscosity-temperature relations

The viscosity-temperature relation of lubricants under high pressure is expressed as follows by Crook in analysing temperature distributions between two lubricated rollers caused by heat conductivity of the friction heat generation.

$$\eta = \eta_0 \exp(aP - \beta DT) \quad (3)$$

where $\beta$ is the viscosity-temperature coefficient and $DT$ is the temperature increment from the reference temperature (often room temperature). Present data are fitted by Eq. (3), and the variations of $\beta$ by pressure are obtained, as shown in Fig. 8. The variation of $\beta$ for BCCM is quite large compared with that of DMS. Data for a mixture are almost consistent with that of DMS, which is not the same feature as the evaluation of the viscosity-pressure relation of a mixture (almost the midpoint between BCCM and DMS). Also, the relation between $\beta$ and pressure is almost linear for every oil. As for BCCM, the datum of Muraki and Kimura is plotted and found to agree with the present data.

Our previous report showed that Walther's equation is effective even under high pressure.

$$\log \log(\nu + 0.6) = -m \log T + b \quad (4)$$

where $\nu$ and $T$ are kinematic viscosity (cSt) and

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Fig. 6 Comparison of viscosity on 3 tested lubricants at 60°C

Fig. 7 Change of viscosity-pressure coefficient by temperature


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absolute temperature (K), $m$ and $b$ are material constants. This equation is applied to the present data shown in Fig. 9. Regression lines are inserted in the figure and data on every oil show linearity from atmospheric pressure to high pressure. Dotted lines of a mixture obtained by the Wright method are also inserted under atmospheric pressure and 400 MPa. They almost agree with the present data (which closely approach the BCCM data at elevated temperature). Figure 10 shows the variation of slope $m$ and intercept $b$ of Eq. (4) as the pressure increases. The values of $m$ and $b$ approach constant values as pressure increases (over 100 MPa for BCCM and over 200 MPa for DMS and a mixture). Data on a mixture are almost the same as those on DMS.

In this way, the viscosity-temperature coefficient and Walther's equation at high pressure were discussed. Viscosity-temperature characteristics at high pressure between DMS and BCCM were quite different, while that of a mixture was almost the same as that of DMS.

3.4 Discussion of measurement accuracy

In the previous report, the reproducibility of the pressure measurement was ±10 MPa. In the present study, it improved to half of that for the benefit of the stable light source of the argon ion laser for excitation of ruby fluorescence as a pressure sensor described in Section 2.1. However, the pressure measurement range for BCCM is not so wide (maximum pressure of about 250 MPa at room temperature is a quarter of that of DMS). Therefore this reproducibility causes a larger scattering of data on BCCM. Referring to the accuracy of viscosity measurement, the error was 1.5% for velocity of the falling sphere and 0.5% for wall factor, which estimate the effects of pressure chamber on the velocity. Thus the total error is 2%, a negligible value on the logarithmic scale of viscosity. At elevated temperatures, pressure increases under the same load because of the thermal expansion of oils. In estimating the pressure increment, the linear relationships of the ruby fluorescence shift factor to temperature at atmospheric pressure and to pressure at room temperature given by Barnett et al. were employed. However, it has not been confirmed that

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Fig. 8 Change of viscosity-temperature coefficient by pressure

![Graph showing change of viscosity-temperature coefficient by pressure](image)

Fig. 9 Walther's equation under high pressure

![Graph showing Walther's equation under high pressure](image)

Fig. 10 Change of coefficient in Walther's equation by pressure

![Graph showing change of coefficient in Walther's equation by pressure](image)
these factors are effective under both high-pressure and elevated-temperature conditions, and so the obtained data possibly reflect these effects to some extent. Consequently, the error in the present study is dominated by the pressure measurement in terms of ruby fluorescence. In order to improve accuracy, refinement of an optical system, the employment of a high-resolution monochromator and fundamental research of ruby fluorescence are needed.

4. Conclusions

Viscosities of synthetic lubricant oils under high pressure at elevated temperature were measured by the diamond-anvil apparatus proposed in our earlier report. Some improvements on the experimental instruments were made, such as the use of an argon ion laser for the ruby fluorescence excitation light source. This enhances accuracy and reproducibility of both pressure and viscosity measurements. Synthetic oils such as BCCM, DMS and a volumetric mixture of them at a 1:1 ratio were measured, and the obtained data were discussed by applying Walther's equation and formulation of mixed oil viscosity. The results may be summarized as follows.

(1) In heating the diamond-anvil cell, the pressure at an elevated temperature was higher than that at room temperature under the same load. The amount of pressure increment depended on each liquid and not on the load. Such a pressure increment is considered to be relevant not only to the thermal expansion coefficient of liquids but also to the bulk modulus and the deformation of the pressure chamber (metal gasket).

(2) The data obtained show less dispersion in the diagram of pressure vs. the logarithmic viscosity, which indicates that the improvements in the instruments contributed to the accuracy of the measurements. The variation of the viscosity by the pressure is linear (to some extent concave and convex) for all oils studied. Referring to the slope of the regression line which is important in EHL and traction drive, BCCM showed the largest value, and is expected to show high performance as a traction base oil. The Wright method, which is often used for the estimation of viscosity of mixed oils, was successfully applied even under high pressure.

(3) In discussing the viscosity change by temperature under high pressure, the viscosity-temperature coefficient was calculated from the obtained data and increased by pressure for both BCCM and DMS. But the coefficient of BCCM is much larger than that of DMS, and the coefficient of a mixture is almost the same as that of DMS. Walther's equation was applied to the data and the linearity in the figures for the data of every synthetic oil was confirmed, which indicates the applicability of Walther's equation even under high pressure. Examination of the variation in the parameters of Walther's equation by pressure revealed that BCCM had larger parameters than the rest and that those of a mixture approached those of DMS. Consequently, the pressure dependence of BCCM on the viscosity-temperature characteristic was large, and that of a mixture was almost the same as that of DMS. This seems to be an interesting phenomenon in considering molecular structures.

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