Rheological Properties of Lubricating Oil and its Relation to Molecular Structure

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Rheological properties of lubricating oils based on their molecular structures were studied based on Eyring’s theory. A brief survey of the molecular theory of viscosity was made to compare the free-volume theory with the rate-process theory. Indicating by the segment flow mechanism the usefulness of Eyring’s theory for lubricating oils, a semi-empirical formula was proposed by which estimation of activation volume was successfully conducted on Waterman’s ring analysis. The relation between viscosity functions was also discussed. As examples of viscosity function analysis of rheological problems on lubricating oils, polymer-blending and traction coefficients were correlated to the activation volume and entropy. An industrial application was tried for a lubricating oil of polymer-blended type for cold rolling of steel with tandem mills. The polymer-blended oil possessed as good lubricity as fatty oils and as good mill-clean properties as mineral oils. The possibility of molecular design of lubricating oil together with the importance of relaxation process was emphasized.

1. Introduction

In the technology of lubrication, the flow property or rheological property, in its modern sense, of a lubricating oil is very important, because the lubricated machine parts should be under hydrodynamic or elasto-hydrodynamic lubrication conditions to be operating satisfactorily. As is well known, viscosity \( \eta \) of the lubricating oil determines the oil film thickness \( h \) between two moving surfaces of the lubricated machine parts, and the film separates the loaded surfaces by so-called wedge action due to viscosity. In the case of classical hydrodynamic lubrication, \( h \) is expressed by the following equation for two rolling disks.

\[
\frac{h}{R} = 4.83 \frac{\eta u}{W} \quad \text{[Martin equation]}
\]

where \( R \) is the radius of the disk, \( u \) is the rolling speed, and \( W \) is the load per unit contact length. In the case of elasto-hydrodynamic lubrication in which the increase in the elastic deformation of the disks under high load and the increase in the viscosity at high contact pressure are both taken into account, \( h \) is expressed in the simplest form by

\[
\frac{h}{R} = 1.95 \left( \frac{\alpha \eta u}{2R} \right)^{8/11} \left( \frac{W}{ER} \right)^{-1/11} \quad \text{[Grubin equation]}
\]

where \( \alpha \) is the pressure coefficient of viscosity in

\[
\eta_p = \eta \exp(\alpha p) \quad \text{[Barus equation]}
\]

and \( p \) is the pressure, \( E \) is the effective elastic modulus of the disk material, and \( \eta_p \) is the viscosity at pressure \( p \). Thus \( \eta \) and \( \alpha \) determine \( h \).

It is readily understandable that the magnitude of \( h \) plays an essential role in lubrication. To avoid the trouble of severe wear, scuffing, or even seizure, \( h \) must be larger than the standard deviation \( \sigma \) of surface roughness from the average. The ratio of \( h/\sigma \) is called the film factor, and it is a very reliable indicator for judging whether direct metallic contact would occur. Therefore, by selection of a suitable lubricating oil which means a selection of suitable \( \eta \) and \( \alpha \), \( h \) can be expected to be larger than \( \sigma \) to guarantee safe performance.

It is most stimulating to search a relation between molecular structure and \( \eta \) or \( \alpha \). For this purpose one may accumulate viscosity data with various types of oils. However, the understanding of viscosity from the molecular standpoint should be desirable.

2. Molecular Theory of Viscous Flow

There are many theories on viscosity. From the molecular standpoint they are categorized into two groups. On of them belongs to so-called free volume or hole theory, and the other belongs to the theory of absolute rate process originated by Eyring\(^1\).

The free volume theory is based on a defect-diffusion model, in which the transport phenomena

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such as viscous flow are controlled mainly by density or free volume. The presence of holes of about molecular size is necessary for a molecule to move, for example, under shear, and the rate is determined by that of diffusion of the hole to the adjacent site of that molecule by Brownian motion. According to this theory, viscosity is expressed by

\[ \ln \eta = A + B/(V - V_0) \]

where \( V \) is the molar volume and \( V_0 \) is the molar van der Waals volume, that is, the real volume of molecule itself. This equation is readily convertible to

\[ \ln \eta = A + B/(T - T_0) \]

[Vogel equation]

where \( T \) is the absolute temperature and \( T_0 \) is a characteristic temperature corresponding to \( V_0 \). The Vogel equation agrees well with the observed temperature dependence of viscosity of the lubricating oil. Therefore, the free volume theory has been thought to be more appropriate.

However, recent rheological studies on lubricating oils such as those by Hirst\(^2\) and by Johnson\(^3\) suggest that Eyring’s energy-barrier model is more applicable for the lubricating oil especially under elasto-hydrodynamic condition. In short, Eyring’s theory postulates the followings:

1. A molecule under shear can move to the direction of shear by making a hole of suitable size, and for this process work or activation energy is required.

2. Besides making a hole, a molecule also needs activation energy to move against the intermolecular attractive forces of the surrounding neighboring molecules.

These processes are treated theoretically in the same way as a chemical reaction, and the resulting viscosity expression is

\[ \eta = \frac{N\hbar}{V} \exp \left( \frac{JE^*}{RT} \right) \exp \left( -\frac{JS^*}{R} \right) \exp \left( \frac{pJV^*}{RT} \right) \]

(1)

with the restriction that shear energy (shear force × cross sectional area of the molecule) is far smaller than the thermal energy of that molecule. In this equation \( N \) is the Avogadro number, \( \hbar \) is Planck’s constant, \( R \) is the gas constant, and \( JE^* \), \( JS^* \), and \( JV^* \) are the activation energy, entropy and volume, respectively, in accordance with the chemical process. These activation quantities are called viscosity functions and obtained experimentally from the following equations.

\[ JH^* = JE^* + pJV^* = R \frac{\partial \ln \nu}{\partial(1/T)} \]

(2)

where \( JH^* \) is the activation enthalpy and \( r \) the kinematic viscosity

\[ \nu = \eta V/M \]

and \( M \) is the molecular weight. Among these viscosity functions, the activation volume is regarded approximately as the volume of the necessary hole and it is closely related to the molecular structure. One of the aims of the present study is to find out whether any correlation exists between them.

There still remain the problems concerning the theory of viscosity, that is, to examine an energy-barrier model in comparison with a free volume or hole-diffusion model. As mentioned before, in the former theory, a necessary, and adjacent hole of molecular size must be created by the molecule of sufficient activation energy. In contrast, no activation energy is required in the latter theory, because, as a result of thermal expansion, many holes are present spontaneously. This discrepancy should be overcome. One way would be to introduce an intermediate view on the hole formation. For example, a spontaneous hole of smaller size than that of a moving molecule may be enlarged adequately through the work done by the molecule of sufficient activation energy. Further research along this line is desirable.

3. Evidence of Segment Flow

According to the modern molecular theory of viscosity, the macroscopic bulk flow involves a molecular movement to the direction of shear through the hole. However, a large molecule like a lubricating oil cannot move as a whole but only in stepwise in the form of an independently moving segment of the molecule. This fact was proved by Schiesler and others\(^6\) from the data presented in Table 1 where A, B, C, and D are the molecules shown in Fig. 1. As is readily seen, the

<table>
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<th>Oil</th>
<th>Viscosity (cSt)</th>
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<td>( \nu ) (20°C)</td>
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<tr>
<td>A</td>
<td>16.03</td>
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<tr>
<td>B</td>
<td>29.85</td>
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<tr>
<td>2A + D</td>
<td>30.74</td>
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<tr>
<td>C</td>
<td>84.39</td>
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Table 1 Segment Flow Characteristics
average composition of 2A+D or A+2D is the same as that of B or C as far as the rings and para-ffinic chains are concerned. Astonishingly, their viscosity characteristics are quite similar to each other, suggesting that the rings and chains, which are called segments, act as independent flow units. We also proved the segment flow characteristics by examining the activation volume and enthalpy of trimethylolpropane esters of different acid structures. In Table 2 the structures of four esters are shown. Two of them have almost the same carbon number in their acid chains. For these samples the kinematic viscosity was measured with a rolling ball viscometer at 40°C from 1 to 1,000 atm, and at 1 atm from 20 to 60°C. It is easy to calculate $JV^*$ and $JH^*$ from these observed viscosity data by Eqs. (4) and (2). The results are shown in Table 2. The $JH^*$ and $JV^*$ determine the viscosity-temperature and viscosity-pressure characteristics of the oil, respectively. Therefore, the good agreement observed between the same acid-carbon esters proves the reasonableness of segment flow.

4. Flow Activation Volume and Segment

It is a very stimulating exercise to express $JV^*$ as a function of molecular structure of the lubricating oil, which is a mixture of different molecules. For this purpose the complicated structure of the oil is simply analyzed by Waterman's method into the average number of carbon of the aromatic ring, naphthenic ring, and paraffinic chain. However, so far as the flow property is concerned, the oil can be regarded as a random mixture of segments, that is, each with rings and chains. Therefore, it is assumed that the observed activation volume can be expressed as the segment-average of segmental volumes.

$$JV^* = \frac{aVa + bVb + cVc}{a + b + c}$$  \hspace{1cm} (5)

where $a$, $b$, and $c$ are the average number of aromatic ring, naphthenic ring, and paraffinic unit of six carbon atoms in the average molecule, respectively. $Va$, $Vb$, and $Vc$ are the volumes of the holes necessary for the segments to move into, respectively.

Fig. 2 illustrates how to estimate the size of the necessary hole. The molecular volume of benzene at room temperature is about 100 cm$^3$/mol which has been adopted as $Va$. The estimation of $Vb$ and $Vc$ is not so simple. For common lubricating oils $b$ is more than 2 and $c$ is more than 4. This means that a molecule may contain condensed rings and branched chains. Therefore, $Vb$ and $Vc$ may not be a constant but a function of $b$ and $c$. After successive trial and error attempts, $Vb$ and $Vc$ were determined as

$$Vb = 30b + 10$$
$$Vc = 60 - \frac{40}{c}$$

so that calculated values agree better with the observed.

Twelve oils of a wide variety of molecular structures were employed to compare the calculated activation volumes with those measured. In Table 3, structures of the oils and the results are shown. The agreement between them is satisfactory, and
the activation volume can be estimated from the ring analysis data of the oil with the maximum deviation of 10%.

5. Relation between Viscosity Functions

According to Eq. (1), viscosity can be deduced from the average molecular weight $M$, density $\rho$, $DE^*$, $JS^*$, and $JV^*$. The $JV^*$ is now calculated based on the molecular structure of the oil. Therefore, any relation between $JV^*$ and other functions is important and worthwhile to investigate.

Experimental studies were conducted on twelve oils, and the results obtained at 25°C and 1 atm are listed in Table 4. The characteristics of the oils are indicated by their average molecular weights and their ratios of carbon atom number of the ring and that of the chain in the molecule. In order to find any other relevant relation, $JH^*$/$JV^*$ and $JS^*$/$JH^*$ are also given in this table. It is a very interesting finding that $JH^*$/$JV^*$ which is 0.15±0.01 kcal/cm³ is almost common to all the oils tested. The $JH^*$ is regarded as the sum of the necessary energy to create the hole and that necessary to move into the hole. For comparison, the cohesive energy density (evaporation heat (molar volume)) is 0.07 for $n$-C₁₆H₃₄, 0.07 for cyclo-C₆H₁₂, and 0.08 for decalin. However, it seems difficult at present to explain in further detail the meaning of the common ratio of 0.15.

As for the ratio of activation entropy to activation enthalpy, a general tendency may be noticed. The value is larger with naphthenic oils. In addition, a detailed examination suggests that the larger be the molecular weight the higher the ratio. Further research on this relation would also be desirable.

6. Polymer Blending

Polymer blending is a very promising way to improve and control the rheological property of a lubricating oil, especially of a mineral oil. Indeed, the addition of so-called VI improver has been applied since 1930’s. The representative polymers used are polyisobutylene and polyalkylmethacrylate. These rheological characteristics were studies from the standpoint of viscosity functions.

Research was conducted on a series of mixtures of a mineral base oil ($M=362$, $v_{38}=21.3$, $v_{99}=4.0$) and a sufficient amount of polyisobutylene PIB ($M=930$) or polyalkylmethacrylate PLMA ($M=360,000$) to form additive concentrations up to 10%. The $JV^*$ was obtained at 25°C in the pressure ranges from 1 to 50 atm and from 250 to 300 atm. The $JH^*$ and $JS^*$ were determined at 25°C and 1 atm. Figs. 3, 4, and 5 illustrate $JV^*$, $JS^*$ and $JH^*$, respectively.

From these results it can be readily observed that rheological modification by polymer addition is quite different with different polymers used. In particular, the difference is noticeable in $JV^*$.
and $\Delta S^\ast$. Under atmospheric pressure $\Delta V^\ast$ changes markedly with PLMA at 2% concentration and decreases at 10%. In contrast, $\Delta V^\ast$ decreases with PIB at 2% concentration and gradually increases at higher concentrations. The bulky structure of PLMA and the linear paraffin-like structure of PIB may be responsible for these differences. At 10% concentration, each polymer molecule is surrounded with mineral oil molecules of about one-molecule layer in average, restricting the flexible movement of the polymer molecule. Under high pressures, the polymer molecule seems to behave as a frozen rigid body. In both cases the existence of a polymer affects $\Delta S^\ast$ to a rather small extent.

As for $\Delta S^\ast$, PLMA decreases it considerably. This means that the activated state of the segment is restricted, for example, in its rotational freedom. The addition of PLMA should affect the movement of the segment in this way. Further research thereon will be needed, probably at higher temperatures.

The effect on $\Delta H^\ast$ by addition of a polymer is comparably small. However, a simple relation between $\Delta H^\ast$ and $\Delta V^\ast$ is not observed and it is entirely different from the case with pure hydrocarbon mineral lubricating oils. This is also another problem to be solved later.

7. Traction and Activation Volume

Traction under sliding friction contact is very important in many industrial fields. The recent increasing interest in the traction drive element emphasizes the need for high traction, whereas in cold rolling of steel, lower traction is required. They are all in the region of elastohydrodynamic lubrication in which, for example, the friction contact of two rolling-sliding disks is shaped flat as shown in Fig. 6. In such a case traction is caused by the shear stress developed in the oil film between the parallel planes of the contact zone. The shear stress depends on the gap which is determined mainly by the inlet viscosity of the oil and on the rheological nature of the oil film which may behave as a viscoelastic material under high pressure. However, as a first approximation, $\Delta V^\ast$ should play a role as a measure of the rheological nature, because any transport process is closely related to $\Delta V^\ast$.

For the purpose of finding any correlation between traction and activation volume, measurements both of $\Delta V^\ast$ and traction coefficient $T$ were made with several different types of lubricants. The friction device used was a kind of two-disk machine. The two bearing-steel disks of the same size (dia. 4 cm, width 1.2 cm) with a curved face were rotated separately under pressurized contact caused by loading spring. Oil was adequately applied to the contact at room temperature. One disk was rotated at a constant speed of 45 cm/sec, and the sliding speed of the other disk was controlled such that it was 20 cm/sec at the contact load of 100 kg (mild condition) and 100 cm/sec.

Fig. 4 Effect of Polymer Addition on Activation Entropy

Fig. 5 Effect of Polymer Addition on Activation Enthalpy

Fig. 6 Elastohydrodynamic Contact of Two Disks
at 150 kg (severe condition). The torque was measured electronically.

Studies were made under the mild condition on six oils, which are listed in Table 5. The results are shown in Table 5 together with the viscosities of the oils at 40°C and their $J^*V$ at 2,000 atm. The naphthenic oils could be good traction fluids. So far as these oils are concerned the traction coefficient is larger as $J^*V$ is larger at the same level of viscosity.

Under the severe condition, eight oils were examined of their suitability as so-called mill-clean cold-rolling oils for steel. Five oils were polymer-blended oils of a light paraffinic mineral base oil (5.4 cSt 25°C, 3.1 cSt 50°C). The polymers were polymethacrylates of stearyl S, tridecanoyl T, and lauryl L. Some of them were a mixed ester. The other three were mixtures of a light mineral oil containing paraffinic bright stock, a mixture of castor oil 3 and olive oil 7, and pentaerythritol tetraoleate, respectively. Their viscosities were adjusted to be about 120 cSt 25°C. In Table 6 the results are shown with the values of their kinematic viscosity at 25°C and $J^*V$ at 1 atm. The relation between $J^*V$ and T is plotted in Fig. 7.

From the observed results, it is seemed that, at least, among similar materials, traction is larger for the oil of larger activation volume, if compared at the same viscosity level. At the present stage of investigation, however, any detailed discussion is difficult and further research on this problem is expected.

8. Cold Rolling Fluid for Steel

It is well known that fatty oil is one of the best lubricants for cold rolling of steel to produce thin plates. This superior performance is generally believed to be due to the oiliness of the fatty acid liberated from the oil during rolling. However, the effectiveness of the fatty acid is not so clear-cut. For example, the addition of 1% stearic acid to a mineral oil reduces drastically the friction coefficient measured with a friction pendulum from 0.18 to 0.10. In contrast, tested with a laboratory mill, the effect of stearic acid addition is very small and it reduced the friction coefficient from 0.080 to 0.075 under the condition of single pass of the steel sheet with a reduction of 16.5%5). This fact suggests the existence of a thin oil film probably under conditions of elastohydrodynamic lubrication. With this expectation we conducted a series of experiments with a high speed laboratory mill constructed by Nippon Steel Corporation.

As lubricating oils palm oil, as reference, and the PSTMA(21%)-blended mineral base oil were employed. The reason of this selection is first that the oil is almost comparable to vegetable oils in both $J^*V$ and T. The second reason is rather industrial. In the cold rolling of thin
gauge strips of steel a vegetable oil is commonly used because of its good lubricity but the worked steel surface is sometimes contaminated with oil burns or with foreign materials. Mineral-oil-based lubricants can be used without any contamination trouble, that is, mill-clean not for thin gauge strips but for thicker ones because of their poor lubricity. The polymer-blended oil may satisfy the needs for both good lubricity and mill-clean performance.

One test was on roll load. A sheet of low carbon steel was cold rolled at a reduction of 20% at the rolling speed of 1,000 m/min. The oil was applied as a precoated thin film on the test steel specimen in various thicknesses. The necessary load was measured and shown in Fig. 8. It was proved that the polymer-blended oil is comparable in lubricity to palm oil when the oil film is thick. Next test was done on oil film thickness. The polymer-blended oil was compared with a commercial oil. A low carbon steel sheet was rolled at various speeds at a reduction of 20%. A measured amount of test oil was coated on a fixed square area. After rolling, the square shape was deformed and it was spread to a bullet-shaped area which was measured, and the mean thickness of the oil film was calculated by dividing the amount of the oil by the spread bullet-shaped area. The results are shown in Fig. 9.

The behavior of the two tested oils was quite different. According to a simple hydrodynamic theory, the oil thickness should be proportional to the rolling speed, provided that viscosity and the shape of the solid element are unchanged. However, the observed behavior of the commercial oil is in common with the rolling practice, and it is explained by such factor as temperature rise on viscosity decrease at higher speeds. The behavior of the polymer-blended oil is rather strange. The reason may rheological, but at present no adequate explanation can be given.

Based on the fundamental results obtained an industrial scale test was conducted with the six tandem mills at Kimitsu Works of Nippon Steel Corporation. The polymer-blended oil was compared with a commercial mill-clean oil and with a commercial fatty oil. In this test, all oils were applied in the form of a water emulsion of about 3%. The highest roll speed at which the performance continued satisfactorily was determined. It was, of course, dependent on the ultimate thickness of the rolled strip, and the results are listed in Table 7. The mill-clean properties were reported comparable to those of the commercial mill-clean oil.

9. Conclusions

One of the most important and interesting problems in lubricant technology is to design the oil on a molecular basis. Recent synthetic lubricants, for example, traction fluids, are now products of planned and of predictable nature, and are chemically designed to have certain shaped molecular structures. For this purpose it is not sufficient merely to correlate viscosity with molecular knowledge of the oil. If viscosity is analyzed into three viscosity functions the amount of information available should be tripled and it would be easier to
correlate the information with molecular understanding. This is indeed so with the activation volume, as we find in mineral oils and in polymer-blended oils. The activation volume is a powerful tool for designing an ideal oil.

Another important problem is the viscoelasticity or the relaxation property of the lubricating oil. As an unsolved problem, we leave the relation between activation volume and traction coefficient. Lastly, the effect of higher rolling speeds on the oil film thickness is difficult to explain. However, one speculation is that a relation may exist between activation volume and relaxation time, as shown schematically in Fig. 10. In the near future extensive work should be undertaken to clarify and solve these problems, because elasohydrodynamic lubrication cannot be understood without viscoelastic consideration of the oil.

Fig. 10 Schematic Model Viscoelastic Change

References

General References
要旨

潤滑油のレオロジーと分子構造

玉井 康雄

潤滑油の流動学的性質は流体潤滑、弾性流体潤滑の条件で事故のない運転を行うために重要な因子である。摩擦接点での油膜厚さは流体潤滑ではマーチンの式、弾性流体潤滑ではグリッピの式で表されるが、いずれも粘度 \( \eta \)、粘度圧力係数 \( \alpha \) で支配される。そして摩擦面の変形を防ぐには、表面粗さの標準偏差 \( \sigma \) と \( \eta \) の比で決まり、\( h/\sigma \approx 1 \) ならよい。そこでこの条件を満たす油、そのような \( \eta \) と \( \alpha \) をもつ油が求められ、それには \( \eta, \alpha \) の分子構造による理解がある。

油の粘度の分子論は2大別され、自由体積論と速度過程論（アイニング理論）がある。かつて実験式としてフォーギル式が用いられたため前者がよいとされたが、弾性流体潤滑が重要されてからアイニング式が見直された。これによる粘度は化学反応速度と同様にあつかわれ、

\[ \eta = (N_h/V) \exp(-JE*/RT) \exp(-JS*/R) \exp(pJV*/RT) \]

となる。 \( N_h \) ポアサルド数、 \( J \) プランク定数、 \( V \) ポアス球体、 \( R \) ガス定数、 \( T \) 絶対温度で、 \( JE* \), \( JS* \), \( JV* \) は流動の活性化エネルギー、エンタルピー、体積、 \( p \) は圧力である。 \( JE* \), \( JV* \) は粘度測定から実験的求められる。

アイニングの理論は粘性流動が分子的には流動方向への個々の分子の空孔を仲立ちとする移動の和と考えることが事実に基づいており、潤滑油のような大きな分子でもこの考が成立つことが経験による移動の証明によって示された。ついて \( JV* \) は節が移動するのに必要な空孔とみとめられることから、潤滑油の分子構造と \( JV* \) の間に密接な関係があることがわかれ、環分析による分子の平均の芳香環、ナフテン環、炭素 6 を単位とするバリアンス推算から \( JV* \) が計算できる半実験式が提案され

Keywords

Eyring theory, Flow activation volume, Lubricating oil, Molecular structure, Polymer blended oil, Rheological property

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