Flow Behavior of Mono- and Diester Lubricants

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Several kinds of mono- and diesters were prepared by esterification of the corresponding organic acids with 2-ethylhexanol. Some of the synthesized esters were hydroxy-esters. Pressure and temperature dependences of viscosity were measured to determine the flow activation quantities based on Eyring's theory. The effects of hydrogen bonding, chain length, and branching in the molecular structure on activation quantities have been investigated and the results were used for discussion of flow behaviors of these esters.

1. Introduction

Much effort has been made to prepare lubricants of high performance, because the conditions under which they are used are becoming increasingly severe by recent developments in mechanical technology. Therefore, it is necessary to be able to design and synthesize lubricants with predictable properties based on molecular structure. It is well known that rheological properties under high pressures are very important for lubricating oils. Thus, we have investigated relationships between these properties and molecular structures of various kinds of lubricating oils by using Eyring's hole theory for viscous flow.^{1)–2)} It has been shown that flow process of lubricating oils is resolvable into independent movements of oil molecular segments. Further, a procedure has been proposed to estimate the flow activation volume from molecular structure.^{3),4),5)}

The most popular guiding principle for synthesis of good lubricants is to use compounds containing an ester linkage which is more stable to heat than a hydrocarbon C-C linkage in mineral oils. Ester lubricants are considered for various reasons to be good synthetic lubricants. Dibasic acid esters and neopentyl polyol esters are now being most widely used as synthetic lubricants, especially in the aircraft industry. We have previously reported about flow behavior of neopentyl polyol esters.¹⁾

Recently, much attention has been paid to flow behavior of compounds containing OH group because of the increasingly utilization of water based lubricants such as HWBF (high water base fluid). Some researchers have investigated flow properties of polyglycol and water mixtures to correlate these properties with lubricity.^{6),7)} However, no one has yet reported about the effect of OH group on flow behavior of such typical synthetic oils as ester lubricants.

In this work, several kinds of mono- and diesters with or without OH group were synthesized and their viscosities were measured as a function of pressure and of temperature to determine their flow activation quantities based on Eyring's theory. The effects of hydrogen bonding and molecular structure on their activation quantities were investigated and the results were used for discussion of their flow behaviors.

2. Experimental

2.1 Materials

A list of molecular structure of the ester lubricants used in this study is given in **Table 1**. All of the fluids are formed by the combination of mono or dibasic organic acids with 2-ethylhexanol. Fluid 6 was obtained from Nippon Oils & Fats Co. Fluids 7, 8, and 9 are commercially available (Tokyo Kasei Kogyo Co.), and the others were prepared by esterification of the corresponding acids with 2-ethylhexanol in the presence of *p*-toluenesulfonic acid as a catalyst. The products were identified by IR, NMR spectra, and elemental analysis. Gas chromatography analysis

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Table 1 Molecular Structures of Mono- and Diesters

Fluid No.	Structure	Fluid No.	Structure
1	CH ₃ CH ₂ COOR	7	<div>COOR (CH₂)₇ COOR</div>
2	<div>CH₃ CH₃CHCOOR</div>	8	<div>COOR (CH₂)₈ COOR</div>
3	HOCH ₂ COOR	9	<div>COOR COOR</div>
4	<div>OH CH₃CHCOOR</div>	10	<div>CH₂COOR HO-CHCOOR</div>
5	<div>COOR (CH₂)₂ COOR</div>	11	<div>HO-CHCOOR HO-CHCOOR</div>
6	<div>COOR (CH₂)₄ COOR</div>		

ROH = 2-ethylhexanol

Table 2 Pressure Dependence of Kinematic Viscosity (10⁻⁶ m² s⁻¹) at 313.2 K

Fluid No.	Pressure (MPa)				
	0.1	25	50	75	100
1	1.31	1.67	2.11	2.63	3.26
2	1.46	1.91	2.46	3.13	3.94
3	4.93	6.44	8.49	11.1	14.2
4	3.97	5.28	7.13	9.44	12.4
5	6.91	9.77	13.5	18.8	25.6
6	7.70	10.7	14.7	20.1	26.9
7	10.4	14.7	20.5	28.0	37.6
8	11.6	16.3	22.9	31.3	42.2
9	26.8	43.0	68.4	106	162
10	15.4	23.0	34.6	50.4	72.6
11	49.7	82.1	131	204	321

Table 4 Temperature Dependence of Kinematic Viscosity (10⁻⁶ m² s⁻¹) at Atmospheric Pressure

Fluid No.	Temperature (K)		
	293.2	313.2	333.2
1	1.87	1.31	1.02
2	2.07	1.46	1.11
3	10.6	4.93	2.81
4	8.03	3.97	2.37
5	13.7	6.91	4.16
6	12.5	7.69	4.71
7	17.5	10.4	6.20
8	19.7	11.6	6.85
9	67.6	26.8	12.1
10	43.4	16.1	7.90
11	208	50.4	18.8

Table 3 Pressure Dependence of Density (10³ kg m⁻³) at 313.2 K

Fluid No.	Pressure (MPa)				
	0.1	25	50	75	100
1	0.857	0.874	0.887	0.903	0.914
2	0.844	0.862	0.888	0.890	0.901
3	0.943	0.957	0.972	0.983	0.990
4	0.926	0.942	0.957	0.968	0.978
5	0.919	0.932	0.947	0.957	0.964
6	0.910	0.925	0.938	0.949	0.959
7	0.902	0.917	0.930	0.941	0.950
8	0.901	0.916	0.928	0.939	0.948
9	0.970	0.984	0.996	1.007	1.017
10	0.954	0.968	0.982	0.996	1.004
11	0.987	1.002	1.015	1.026	1.031

indicated that purity of the synthesized esters except fluid-11 (purity 87%) was greater than 95%.

2.2 Measurements

A rolling-ball viscometer was used to measure viscosity as a function of pressure. Measurements were made at 313.2 K and pressures up to 100 MPa. Changes in density with pressure were measured

using a glass piezometer under the same conditions. Details about the measurements have been given in the previous paper.¹⁾ Atmospheric viscosity was measured at 293.2 K, 313.2 K, and 333.2 K.

3. Results

The results of pressure dependence of kinematic viscosity and density of the esters are listed in **Tables 2** and **3**. Atmospheric kinematic viscosities are listed in **Table 4**. Introduction of an OH group into the molecular structure significantly increases viscosity. Viscosities of fluids 3 and 4 are about three or four times larger than those of the other monoesters. Furthermore, as observed in fluids 5, 10, and 11, viscosity increases exponentially with the number of OH groups. A similar effect on viscosity increase is also observed by introducing a benzene ring (fluid 9).

According to Eyring's theory of flow process,

Table 5 Flow Activation Volume, Enthalpy, and Entropy at 313.2 K

Fluid No.	$\Delta V^*(10^{-6} \text{ m}^3/\text{mol})$	$\Delta H^*(\text{kJ/mol})$	$\Delta S^*(\text{J/k mol})$
1	$26.0-4.3 \times 10^{-2} \times P$	12.4	-13.7
2	$28.3-4.8 \times 10^{-2} \times P$	12.7	-14.3
3	$29.0-2.4 \times 10^{-2} \times P$	27.1	22.1
4	$31.3-3.2 \times 10^{-2} \times P$	24.8	16.0
5	$36.1-4.0 \times 10^{-2} \times P$	24.3	5.4
6	$35.3-5.4 \times 10^{-2} \times P$	19.8	-10.5
7	$36.9-7.1 \times 10^{-2} \times P$	21.0	-10.1
8	$36.8-6.6 \times 10^{-2} \times P$	21.4	-10.0
9	$50.7-7.4 \times 10^{-2} \times P$	34.9	26.9
10	$42.1-5.8 \times 10^{-2} \times P$	34.7	31.2
11	$51.8-8.8 \times 10^{-2} \times P$	48.9	66.7

P: Pressure in MPa

flow activation quantities are given by the following relations:

$$\Delta V^* = RT(\partial \ln \nu / \partial P)_T \tag{1}$$

$$\Delta H^* = R(\partial \ln \nu / \partial T^{-1})_P \tag{2}$$

$$\Delta S^* = R \ln(Nh/M\nu) + \Delta H^*/T \tag{3}$$

where *R* is the gas constant; *T* is the absolute temperature; ν is the kinematic viscosity; *P* is the pressure; *N* is Avogadro's number; *h* is Planck's constant; *M* is the molecular weight; ΔV^* , ΔH^* , and ΔS^* are the volume, enthalpy, and entropy of activation for viscous flow, respectively. Values of ΔV^* , ΔH^* , and ΔS^* were determined using the same method described in the previous paper.¹⁾ Resulting activation quantities of the esters at 313.2 K are given in Table 5. Flow behaviors of mono- and diesters will be discussed in a following section using these flow activation quantities.

4. Discussion

ΔV^* is the volume change in the process of activation for viscous flow and is a measure of the size of the hole required for activated jump; therefore, the value of ΔV^* is a function of molecular size. As can be seen from Table 5, ΔV^* of diesters are larger than those of monoesters due to the difference in their molecular sizes. However, the change in ΔV^* with chemical structure cannot be explained merely by molecular size. ΔV^* of fluids 5–8 are almost independent of chain length between two ester groups in spite of the increase in their molecular weights. The effect of chain length can be interpreted by assuming a segmental movement for viscous flow, as previously described in detail.¹⁾ According to the concept of segmental flow, ΔV^* is defined as the average size of the hole volumes required for the segments to move. Therefore, in fluids 5–8, these chains in the molecules behave as if they are flowing in a segmental unit of a certain size, which itself is independent of the size of the chain. On the other hand, fluid 9 has a rigid benzene ring

which cannot be separated into segments during its flow process causing its ΔV^* to be larger than ΔV^* of fluids 5–8.

Chain branching has an important effect on increasing ΔV^* , because it decreases the flexibility of a molecular structure. As expected, mono- and diesters having a branched chain in the acid (fluids 2, 4, 10, and 11) have higher ΔV^* values than the corresponding esters with no-branching (fluids 1 and 5). However, in the case of fluids 4, 10, and 11, hydrogen bonding by their OH groups may also play an important role in increasing ΔV^* as will be described later.

The effect of OH group on ΔH^* and ΔS^* as well as on viscosity is remarkable. ΔH^* and ΔS^* of the esters containing OH groups are much larger than those of the other esters except fluid 9. A similar trend was observed in the values of ΔV^* to some extent. These findings can be explained as a result of strong intermolecular attraction due to hydrogen bonding. According to Bondi,^{8),9),10)} hydrogen bonding can basically have two different effects on liquid structure. The first effect: if the attractive force is strong and specific enough to form a stable dimer such as that formed by certain carboxylic acids, the dimer can be treated as a compound with a molecular structure of a dimer. For example, viscosities and ΔH^* of propionic acid and oleic acid are almost the same as those of propionic anhydride and oleyl oleate, respectively.^{8),9),10)} The other effect: hydrogen bond may not be sufficiently strong to form distinguishable dimers; thus, a weak but continuous chain association is formed throughout the liquid phase instead of stable dimers.

Hydrogen bonding in hydroxy-esters can be investigated by considering the results of their IR spectra. It is a well established fact that hydrogen bonding decreases the C=O stretching frequency. In the present study, esters having no OH group had a strong C=O absorption at 1,740 cm⁻¹ and this frequency remained unchanged even in the presence of OH groups in the ester molecules, implying that there is no hydrogen bond formation between C=O and OH groups in these hydroxy-esters. A broad peak was observed at 3,450–3,500 cm⁻¹ in each of the hydroxyl esters. These absorption bands can be ascribed to the OH stretching band which is shifted to lower frequency by hydrogen bond formation. It is well known that alcohol molecules which undergo self-association by hydrogen bonding do not form stable dimer but produce various kinds of unstable polymeric species.¹¹⁾ This is the reason why the observed peak was broad. Such self-association of alcohols tends to decrease with increasing degree

of steric hindrance in their structures and also with increasing molecular weights.¹²⁾ Since the hydroxy-esters in this study are of rather high molecular weights, sterically hindered alcohols, dimers and/or trimers should be predominant species. From above considerations, it is reasonable to imagine that unstable polymers (dimers and/or trimers) are formed through hydrogen bonds of the OH groups in the hydroxy-esters, and these bonds are partially broken whenever one molecule has to jump into a hole. This act of breaking is reflected in the very high values of viscosity and ΔH^* . The degree of freedom in these esters may increase at the transition state in flow process because of the cleavage of the hydrogen bonds. This leads to very high values of ΔS^* as observed in Table 5.

The effect of OH group on ΔV^* is somewhat complex. Fluids 1 and 3, or fluids 2 and 4 have almost the same molecular weight and have a similar molecular geometry, but ΔV^* of the hydroxy-ester is larger than that of the corresponding ester having no OH group. If hydrogen bonds were completely broken in the flow process for these esters, the value of ΔV^* should be unchanged irrespective of the presence of OH group. Therefore, the difference in ΔV^* is considered to be stemming from hydrogen bonding during the flow process. It is suggested that a certain fraction of hydroxy-esters flow as polymeric molecules, that is, without the cleavage of the hydrogen bonds. The proportion of the polymers at the transition state in flow process can be roughly estimated in the case of fluid 3. If only stable dimers present in the liquid state and then flow, the value of ΔV^* would have been nearly equal to that of fluid 6 whose molecular weight is twice that of fluid 3; but, in the absence of hydrogen bonding, the ΔV^* of fluid 3 might become equal to that of fluid 1. Since the actual flow pattern is believed to be intermediate between these two cases, ΔV^* of fluid 3 may be approximately expressed as:

$$\Delta V_{\text{fluid3}}^* = (1-p)\Delta V_{\text{fluid1}}^* + p\Delta V_{\text{fluid6}}^* \quad (4)$$

where p is the probability of the presence of a dimer in the flow process. By using the data in Table 5, p is calculated to be about 0.3. This means that about 70% of the hydrogen bonds will be broken by shear stress.

Viscosity, ΔH^* and ΔS^* of fluid 4 are smaller than those of fluid 3. This may be due to the shielding effect of OH group by chain branching in the acid of fluid 4. Such shielding effect is well known also in the case of isomeric alcohols.⁹⁾ On the other hand, ΔV^* of fluid 4 is slightly larger owing to the effect of chain branching on

Fig. 1 Plot of Activation Enthalpy (ΔH^*) and Volume (ΔV^*)

molecular flexibility.

We have reported that the relation between ΔH^* and ΔV^* is nearly linear for homologous series of various kinds of lubricating oils.^{1), 2), 13)} Fig. 1 shows that a similar linear relation holds for esters with or without OH groups. ΔH^* is considered to be consisting of two terms: ΔH_h^* , the heat of hole formation, and ΔH_j^* , the heat of activation for molecular or segmental translation. If the work required to create a hole, ΔH_h^* , is proportional to ΔV^* , then ΔH^* can be expressed as:

$$\Delta H^* = \Delta H_h^* + \Delta H_j^* = A\Delta V^* + \Delta H_j^* \quad (5)$$

where A is a constant corresponding to internal pressure. The two lines with the same slope in Fig. 1 indicate that the values of A for the two groups of esters are almost the same, and ΔH_j^* of the hydroxy-ester group is larger than that of the other. These findings mean that ΔH^* increment by OH group introduction is ascribed to the increase in ΔH_j^* . Since ΔH_j^* is a measure of the energy of a molecule required to past its neighbors to jump into the hole, the hydrogen bond cleavage occurred during the flow process may contribute mainly to the increase in ΔH_j^* .

5. Conclusion

ΔV^* of diesters are larger than those of monoesters because of the difference in their molecular weights. However, ΔV^* of diesters are independent of the chain length between the two

ester groups in spite of molecular weight increase. This is due to the segmental movement of the chain in flow process. The chain branching on molecular geometry increases $\Delta V^\ddagger$. Introduction of OH groups into the esters has remarkable effects on increasing viscosity, $\Delta H^\ddagger$, and $\Delta S^\ddagger$. Polymeric species are formed through hydrogen bonds of the OH groups in the hydroxy-esters, and these bonds are partially broken during the flow process. The cleavage of hydrogen bonds is ascribed to the increases in viscosity, $\Delta H^\ddagger$, and $\Delta S^\ddagger$. Since some fractions of hydroxy-ester molecules flow without cleavage of their hydrogen bonds, these esters have somewhat larger $\Delta V^\ddagger$. A linear relation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ was found in either of the esters with or without OH groups.

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要 旨

モノエステルおよびジエステル油の流動挙動

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潤滑油において, その粘度が重要な物性であることは周知の事実である。したがって, 潤滑油を分子設計するためには, 潤滑油の分子構造とその粘度との関係を明らかにする必要がある。前報までは鉱油系潤滑油, 合成ナフテン油, ヒンダードエステル油の粘度を Eyring の粘性理論を用いて解析し, その分子構造との関係を議論した。本報では代表的エステル系潤滑油であるモノエステルおよびジエステル油を用い, 粘性流動下におけるそれらの分子の挙動を考察した。

試料として, 一塩基酸および二塩基酸と 2-エチルヘキサノールのエステルを用いた (Table 1)。このうち試料 4, 10, 11 は水酸基のあるエステルである。これらのエステルの高圧粘度を転落球式粘度計で 313.2 K, 常圧から 100 MPa の圧力範囲で測定した。

さて Eyring の粘性理論より活性化体積 ΔV^* , 活性化エンタルピー ΔH^* , 活性化エントロピー ΔS^* の三種類のパラメーターが導出できる (Eqs. 1-3)。その値を Table 5 に示す。 ΔV^* は分子が粘性流動するさいに必要な空孔の大きさを示す量である。ジエステルの ΔV^* はモノエステルのそれより大きい。これは大きな分子になるほど必要な空孔も大きくなるからである。しかし, 試料 5-8 のジエステルではその鎖長にもかかわらず ΔV^* の値はほとんど変化しない。一方, 酸の部分の鎖が枝分かれしたモノおよびジエステルは対応する枝分かれのないエステルのそれより大きい。また, フタル酸エステル (試料 9) の ΔV^* はかなり大きい。このような挙動は分子が節片流動していると考えたと理解できる。つまり, 分子の形状が柔軟なものほど ΔV^* は小さく, 枝分かれやベンゼン環などのような剛直な構造を持つものほど ΔV^* は大きくなる。

IR などの結果から, 水酸基のあるエステルでは安定な二量

体は形成しないが, 水酸基どうしの水素結合により分子は不安定な二量体および三量体を形成していると考えられる。流動時にはこれらの水素結合の切断にエネルギーを要するので, 水酸基のあるエステルの粘度, ΔH^* が大きくなる。また, 水素結合の切断で分子の持つ自由度が増加するので ΔS^* も大きくなる。 ΔV^* についても水酸基の導入により増加する傾向がみられる。これは先に述べた枝分かれの効果とともに水素結合も大きく関与している。つまり流動過程においては, これらのエステル分子のいくらかは水素結合をしたまま, つまり二量体あるいは三量体の状態のまま流動している。そのため, ΔV^* は単量体の状態での流動に比べて大きくなる。たとえば, 試料 3 が完全な二量体のままで流動しているとする, その ΔV^* は分子量がちょうど二倍の試料 6 の ΔV^* と等しくなるだろう。また, 水素結合が完全に切断され単量体の状態で流動しているとする, ΔV^* は類似の分子形状を持つ試料 1 とほぼ同じになるだろう。したがって, 流動の遷移状態で二量体となっている確率を p とすれば, 試料 3 の ΔV^* は Eq. 4 で表せる。これより p は約 0.3 と計算でき, このような仮定が正しければ水素結合の約 70% は流動時に切断されることになる。

水酸基のあるエステルの ΔV^* と ΔH^* およびその他のエステルの ΔV^* と ΔH^* はそれぞれ直線関係にあった (Fig. 1)。 ΔH^* は空孔生成に必要なエンタルピー ΔH^*_h と空孔に移動するのに必要なエンタルピー ΔH^*_j との和として考えられている。 ΔH^*_j が ΔV^* に比例することを考慮すれば, Fig. 1 の二つの直線から水酸基のあるエステルの ΔH^*_j はその他のエステルのそれに比べて大きいことが分かる。それは ΔH^*_j が空孔に移動するさいの水素結合の切断に要するエネルギーを反映しているからである。

Keywords

Flow activation quantity, High pressure, Hydrogen bonding, Rheology, Synthetic lubricant, Viscosity