Estimation of the Lubricating Oil Rheology at High Pressure Based on Phase Diagram

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For rheology investigation of lubricating oils, first phase diagrams were made from determined free volume based on density measurements and the temperature-pressure relation was estimated using the expansion coefficient of free volume and the temperature-pressure relation of the viscoelastic transition point. Next, the authors proposed the density-pressure-temperature relation and the viscosity-pressure-temperature relation of the tested oils based on the free volume and the phase diagrams. Moreover, it was shown that the Ehrenfest equation or the gradient of the phase diagram is closely related to the expansion coefficient of free volume.

Keywords: Lubricant Properties, Rheology, Expansion Coefficient, Free Volume, Density, Viscosity

1. INTRODUCTION

It is established that the oil film thickness calculation in the dynamic contact part of the elastohydrodynamic lubrication (EHL) compiled by the Hamrock-Dowson cannot describe the traction characteristics completely [1]. One of the reasons is that in the high pressure rheology of the lubricating oil is not properly defined. Thus the rheology of lubricants at very high pressure is vitally important to determine their effect in bearing life, stability of films and to understand EHL.

In this report, the authors first build the density-pressure-temperature relationship for solidified region of the test oils, and the viscosity-pressure-temperature relationship based on the free volume theory. On these relationships, the phase diagram is built based on the synthetic naphthenic oil, polybutene, the silicone oil and mineral oil. It is also reported that the Ehrenfest equation has a very close relationship with that of the slope of pressure-temperature of the phase diagram.

2. EXPERIMENTAL DETAILS

2.1 The sample oils

Ten kinds of lubricating oils are tested. They are synthetic naphthenic oil (SN-LV, SN-MV, SN-HV), polybutene (PB-LV, PB-MV, PB-HV), dimethyl silicon oil DMS, fluoro silicon oil FS, paraffinic mineral oil BS, and naphthenic mineral oil N1200. Their names and properties are listed in Table 1.

Table 1 The properties of tested oils

Oil name	Density ρ (g/mL)	Viscosity v (mm²/s)	
	288K	313K	373K
SN-LV	0.9610	213	3.89
SN-MV	0.9754	60.6	6.33
SN-HV	0.9895	311	12.1
PB-LV	0.8359	28.2	4.53
PB-MV	0.8403	95.7	8.98
PB-HV	0.8645	541	29.9
DMS	0.9787	3279	1331
FS	1.2897	1481	207
BS	0.8840	405	31.0
N1200	0.9046	228	15.7

2.2 High pressure density measurement and bulk modulus

A device to measure high pressure density is a plunger type high pressure dilatometer [2] that can measure pressure up to 1.2GPa. The testing oil of 2mL is poured into the test machine and density measurement could be carried out easily by measuring the oil volume at different oil pressures and the bulk modulus is calculated from a change in density- pressure. The experiment is made up from 303K to 353K.

2.3 High pressure viscosity measurement

A high pressure viscometer [3] having 12mm inner diameter can measure pressure up to 0.4GPa. The time when the dropping steel ball of 7.94mm diameter passed through the 3mm diameter observation window was measured, and viscosity measurement was done from simple calculations.

3. EXPERIMENT RESULTS

3.1 Phase diagram

The phase diagram of the tested oils are shown in Fig. 1.The equation related to the temperature-pressure of viscoelastic solid transition point T_{VE} is represented by,

$$T_{VE} = T_{VE0} + A_1 \ln(1 + A_2 p) \qquad (1)$$

where A_1 and A_2 are constant parameters. T_{VE0} is viscoelastic solid transition temperature at atmospheric pressure.
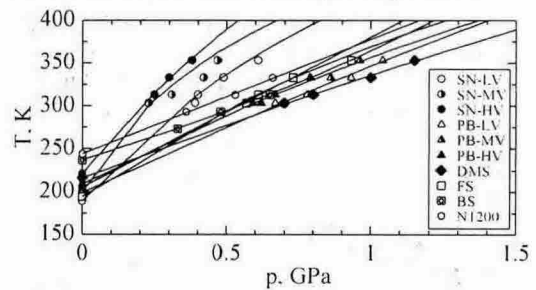

Fig. 1 The phase diagram of the tested oils

3.2 Density with temperature-pressure relationship

The relationship of the temperature-pressure with the density ρ (g/cm³) based on free volume is: In the liquid state,

$$\ln \rho = \ln \rho_L + \alpha_f \cdot T\left(1 - \frac{T_{VE0}}{T_{VE}}\right) + \frac{p}{K_{max}} \qquad (2)$$

Similarly, in the solid state,

$$\ln \rho = \ln \rho_L + \alpha_f \left(T - T_{VE0}\right) + f_{VEd} + \frac{p}{K_{max}} \qquad (3)$$

The thermal expansion coefficient of the free volume α_f, the bulk modulus at the elastic plastic solid K_{max}, the density of liquid ρ_L and the fractional free volume at viscoelastic solid transition point f_{VEd} are found from the high pressure density measurement. The high pressure density as a function of the pressure-temperature of PB-MV and Dowson-Higginson relation [4] are shown in the Fig. 2.

Table 2 Free volume parameters of the tested oils of Equation (2), (3) and (4)

| Oil name	T_{VE0}, K	A_1, K	A_2, GPa^{-1}	α_f, K^{-1}	K_{max}, GPa	f_{VEd}	B_1	B_2
SN-LV	189	258.6	1.54	0.0011	12.8	0.0173	10.76	27.77
SN-MV	199	150.3	4.18	0.0010	11.0	0.0274	9.85	18.32
SN-HV	221	346.5	1.25	0.0011	10.6	0.0082	10.84	37.45
PB-LV	199	891.8	0.180	0.0018	11.4	0.0025	15.14	96.24
PB-MV	209	401.4	0.445	0.0019	11.9	0.0075	14.81	94.22
PB-HV	205	58616	0.00274	0.0017	11.8	0.0030	15.50	128.90
DMS	216	696.7	0.188	0.0027	13.6	0.0128	8.54	41.76
FS	194	258.1	0.972	0.0016	11.5	0.0219	10.37	67.50
BS	237	-324	-0.325	0.0022	10.6	0.0109	10.87	40.69
N1200	244	-17041	-0.00982	0.0021	11.4	0.0125	11.05	34.74
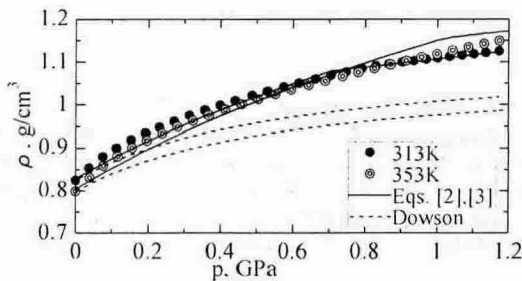
Fig. 2 Comparison of high pressure density of polybutene PB-MV: Eq. (2), (3) and the Dowson-Higginson relation

3.3 Relationship with viscosity-temperature-pressure

The relationship of absolute viscosity η (Pas) with the temperature-pressure is explored [2] and is given by.

$$\log_{10}\eta = 7 - \frac{B_1(T - T_{VE})(T_{VE0}/T_{VE})}{B_2 + (T - T_{VE0})(T_{VE0}/T_{VE})} \quad (4)$$

B_1 and B_2 are determined as $B_1 = B/2.303f_{VE}$, $B_2 = f_{VE}/\alpha_f$ respectively. The solids lines are the theoretical curves from equation (4) and Roelands relation [5] plotted in Fig. 3.
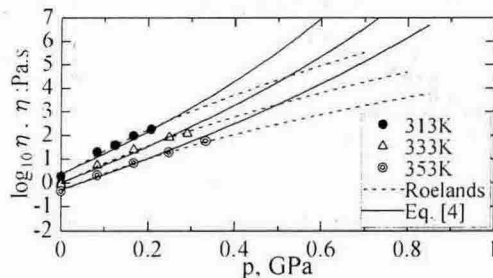

Fig. 3 Comparison of high pressure viscosity results on silicon oil FS: Eq. (4) and Roelands relation

4. DISCUSSION

From the phase diagram the lubricants rheological behavior at high pressure with pressure-temperature relationship could be easily identified. Though the formula of Clausius-Clapeyron can explain the behavior of first order phase transition of molecular crystal. Ehrenfest equation can explain behavior of second order glass transition. On the occurrence of the transition. the thermal expansion coefficient α_0 and compressibility in the isothermal condition κ_T changes at $\Delta\alpha_0$ and $\Delta\kappa_T$ respectively. The Ehrenfest equation [6] represents the pressure dependence of the transition temperature as.

$$\frac{dT}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_0} = \frac{K_S - K_L}{K_S \cdot K_L(\alpha_L - \alpha_S)} \quad (5)$$

Here. α_L and α_S are the thermal expression coefficient of the liquid and the solid. K_L and K_S are the bulk modulus of liquid and solid respectively. In the phase diagram of Fig. 1. the difference in viscoelastic solid transition pressure at temperature 313K and 353K is shown as Δp and $\Delta T/\Delta p$ was estimated. Moreover. from the Ehrenfest equation the slope of second order phase diagram dT/dp ($=\Delta T/\Delta p$) depends on α_f as $\alpha_f = (\alpha_L - \alpha_S)$ at viscoelastic solid transition point as shown in Fig. 4.
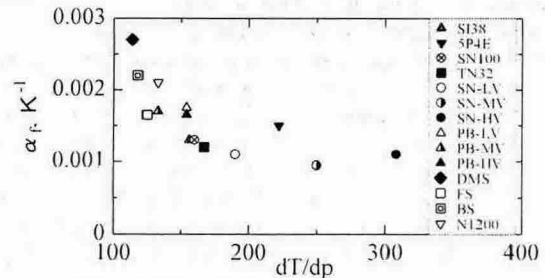

Fig. 4 The relationship of α_f and dT/dp

5. CONCLUTION

The expression related to the temperature-pressure of the viscosity and the temperature-pressure of the density was built newly based on the phase diagram of the synthetic naphthenic oil. polybutene, silicon oil and mineral oil. It was found that solidification phenomenon of the lubricating oils could be explained by the related type of Ehrenfest equation in the second order phase transition point. Traction control under the complete separated condition by an oil film influences the phase diagram closely and it makes a future subject as for traction character of the sample oils used here.

6. REFERENCES

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