Effect of Chain Matching between Hydrocarbon and Fatty Acid on High Pressure Rheology

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For estimation of chain-matching phenomena between normal paraffin as a solvent and straight-chain fatty acid as an additive, the density measurement of n-dodecane, n-tetradecane and n-hexadecane were carried out at oil temperature 313K and pressure up to 1.3 GPa. Their solidification pressure were easily determined by the appearance of molecular crystal, abrupt volumetric contraction and generation of heat of solidification and showed minima under the matching condition. The bulk modulus K of molecular crystal was evaluated using phase diagram. The bulk modulus showed maxima under the each matching condition. The chain matching effect on the bulk modulus beyond the scope of the interfacial phenomena are confirmed.

Keywords: Chain Matching, Normal Paraffin, Fatty Acid, Solidification, Bulk Modulus

1. INTRODUCTION

Cameron et al. [1] pointed out the presence of the chain matching effect in boundary lubrication: When numbers of carbon atoms or chain lengths of normal paraffin as a solvent and straight chain fatty acid as an additive coincide each other, resistance to scuffing becomes highest. Afterwards, one of the present authors [2] developed a number of investigations to show further evidence in various aspects relevant to interfacial phenomena, and also under the matching condition an increase in the freezing temperature at non-matching condition was clearly confirmed. The cooperative action of adhesive and cohesive forces being developed at the chain matching condition is considered to influence the bulk modulus. The present work is investigated the chain matching effect on bulk modulus of molecular crystal under high pressure.

2. EXPERIMENTAL METHOD

2.1 Apparatus to determine bulk modulus K

Accurate measuring of the density of the oil under the high pressure should be necessary to estimate the bulk modulus K. Density measurement was done by using plunger type high pressure dilatometer of Fig.1. The outer cylinder, with a outer diameter of 80.0mm and inner diameter of 29.93mm, made of nickel-chromium-molybdenum steel. The inner cylinder, with a outer diameter of 30mm and inner diameter of 12mm, made of die steel and it is shrinkage fitted to the outer cylinder.

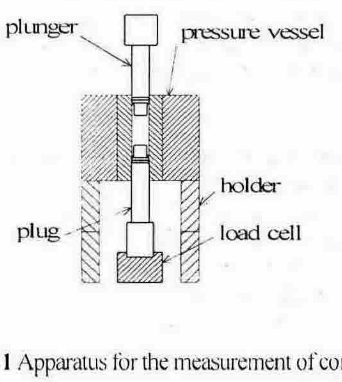

Fig. 1 Apparatus for the measurement of compressibility

The plunger and plug are made of chromium-molybdenum steel. The plunger and plug each have a high pressure seal. The high pressure seal is comprised of the O ring, back up ring and the antiextrusion ring made of beryllium copper. The volume of the tested oils at ambient pressure was V=2.0mL. The volume of lubricant in the chamber corresponding to a pressure is determined from the displacement of the plunger by using a linear gauge. Fluid volume was converted to density. The high pressure chamber was used for measurement of the density of the fluids to 1.3 GPa.

2.2 Test fluids

The physical and chemical properties used for solvents and additives are listed Tables 1 and 2. Where, M: molecular weight and T_M: melting point. The hydrocarbons and fatty acids are added to them at a concentration 0.05mol/l.

Table 1 Properties of hydrocarbons used as solvents

Base liquid	M	T_M, K
n-Dodecane $C_{12}H_{26}$	170.34	263.4
n-Tetradecane $C_{14}H_{30}$	198.39	278.9
n-Hexadecane $C_{16}H_{34}$	226.45	291.2

Table 2 Properties of fatty acids used as additives

Additive	M	T_M, K
Capric acid $C_9H_{19}COOH$	172.3	304.3
Lauric acid $C_{11}H_{23}COOH$	200.3	316.6
Myristic acid $C_{13}H_{27}COOH$	228.4	326.8
Palmitic acid $C_{15}H_{31}COOH$	256.4	335.6
Stearic acid $C_{17}H_{35}COOH$	284.4	342.3

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Density and bulk modulus of base liquids

One of the basic equations for the solidification of oils is the equation of volume change which is used in the strength of materials. The volumetric strain ε is defined as the ratio of the decrease in volume to the original volume: where V is volume, ρ is density, p is pressure, T is temperature, K is bulk modulus, and δ is coefficient of thermal expansion.

$$\varepsilon = \frac{dV}{V} = d\ln V = \left(-\frac{\partial \ln\rho}{\partial p}\right)_T dp + \left(-\frac{\partial \ln\rho}{\partial T}\right)_p dT$$
$$= \left(-\frac{1}{K}\right)dp + 3\delta dT \qquad (1)$$

Figure 2 shows the change in the density ρ against pressure at 313K of base liquids n-dodecane (C12), n-tetradecane (C14) and n-hexadecane (C16). By differentiating the pressure- density curve, the bulk moduli $K=(\partial \ln\rho / \partial p)^{-1}$ are estimated and is shown in Fig.3. The solidification pressure is easily determined by appearance of molecular crystal, abrupt volumetric contraction and generation of heat of solidification and it showed the minimum of bulk modulus K. Here, the solidification pressure of each liquids at 313K are 0.285 GPa for C12, 0.168 GPa for C14 and 0.110 GPa for C16. Beyond the solidification the bulk modulus depends on pressure. In the case of traction fluids transition to amorphous solids at high pressure the bulk modulus attained constant values from 12 to 14 GPa [3]. The effect of pressure on bulk modulus is much different between molecular crystal and amorphous solid.

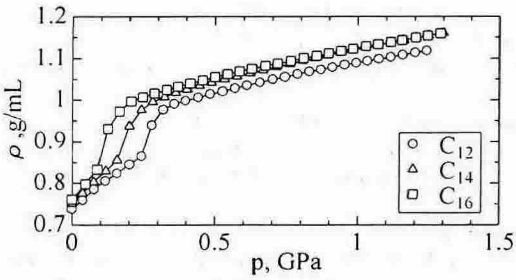

Fig. 2 Density – pressure curves of base oils at 313K

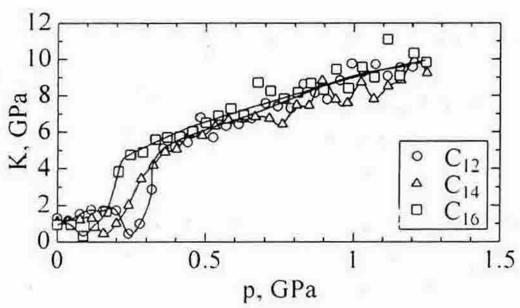

Fig.3 Relation between bulk modulus K and pressure p of base oils at 313K

3.2 Effects of chain matching on bulk modulus K

Figure 4 shows the relation between bulk modulus K and pressure p under the matching condition C14-acid/C14 and non-matching conditions C12-acid/C14 and C16-acid/C14. Here, Capric acid is designated C10-acid, Lauric acid is C12-acid, Myristic acid is C14-acid, Palmitic acid is C16-acid, and also Stearic acid is C18-acid.

The solidification pressure of each liquids at 313K were 0.168 GPa for C12-acid/C14, 0.16 GPa for C14-acid/C14 and 0.176 GPa for C16-acid/C14. The lowest solidification pressure was found under the chain matching condition in our previous report [2]. The bulk

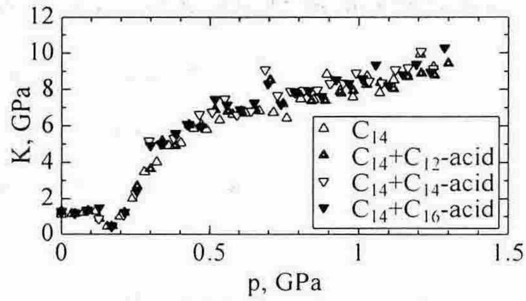

Fig. 4 Bulk modulus K of series Cn-acid/C14 (Base: Tetradecane)

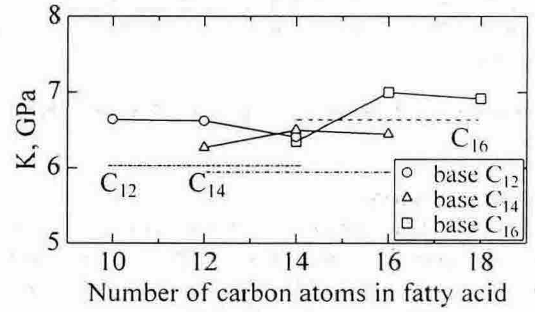

Fig. 5 Effects of chain matching on bulk modulus K of three series at pressure p = 0.5 GPa and temperature 313K

modulus K at pressure p = 0.5 GPa are K = 6.45 GPa for C12-acid/C14, K = 6.50 GPa for C14-acid/C14 and 6.27 GPa for C16-acid/C14.

Figure 5 shows the results of three series of hydrocarbons C12, C14 and C16 as solvents. The highest bulk modulus is found under the chain matching conditions. The direct observation of crystallization at high pressure under the matching and non-matching conditions was already shown by one of the authors [2]. Under the matching condition numerous minute nuclei appeared simultaneously. On the other hand, the non-matching condition was characterized by lengthwise growth of larger fibrous crystallines from small number of nuclei. Therefore, these features of the nucleation and the crystal growth are considered to influence the bulk modulus at high pressure.

4. CONCLUSIONS

(1) Beyond the solidification bulk modulus K of hydrocarbons molecular crystal increases linearly with pressure.
(2) The highest bulk modulus is found under the each matching conditions of three series of hydrocarbons as solvents.
(3) The effect of chain matching on bulk modulus is closely related to the feature of the nucleation and the crystal growth.

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