

Nanorheology and Nanotribology of Two-Component Liquid Crystal

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ABSTRACT

Rheological and tribological properties of a model lubricant consisting of a two-component liquid crystal, mixtures of Sudan Black B (dye) and 4-cyano-4'-hexylbiphenyl (6CB, liquid crystal), nano-films confined between mica surfaces were studied as functions of the surface separation distance (D) and the normal load (N). The compositions of Sudan Black B/6CB binary system were determined by FECO spectroscopy. The rheological properties which reflects the structuring and packing of binary system were examined employing the resonance shear measurement with varying the separation distance at the nanometer resolution. FECO spectroscopy revealed that apparent extinction coefficient κ of Sudan Black B/6CB increased monotonically with decreasing D , especially below ca. 6 nm, at all initial dye concentrations studied, 0.06–1.03 wt%. This indicated the increase in the Sudan Black B concentration in the gap between mica surfaces with the decreasing D , due to the interaction of a large planar structure dye, Sudan Black B, with mica surface. The resonance shear measurement revealed the sudden drop of the amplitude during the shear, which was not observed for one component 6CB. This drop corresponded to the stick-slip transition, which reflected the structural change in the confined dye/liquid crystal from the solid-like to liquid-like state. The combination of FECO spectroscopy and resonance shear measurement can give insights into the properties of multi-component mixtures depending on their composition.

INTRODUCTION

Liquid materials such as lubricants and liquid crystals for display, are often used as mixtures of appropriate components for achieving necessary properties based on empirical knowledge. To elucidate the mechanism of their properties at the molecular level, it is important to develop a method to know not only the mechanical properties but also the compositions, arrangements and packing of mixtures in nano-space and/or on the surface.

Various surface forces apparatus (SFA) based shear measurements were proposed. Among them, the methods by Israelachvili^{1, 2} and Granick³ have been applied for studying the stick-slip motions. We have developed the resonance shear method that allows us to continuously measure rheological and frictional properties of liquids between two solid surfaces as a function of the surface separation distance⁴⁻⁶ based on the SFA.⁷ The resonance shear method has already been applied for studying liquid crystals,^{4-6, 8} OMCTS,⁸ water,⁹ di-n-octyl phthalate^{10, 11} etc., and provided insights into their structuring, and rheological and tribological properties in the confined geometry. An interferometric technique (Fringes of Equal Chromatic Order, FECO) has been used to accurately determine the distance and the normal force.¹²

A method to determine the composition of multi-component liquid confined between surfaces was also developed based on the SFA. C. Helm et al. have reported that it is possible to extract the absorption properties of the solutions confined between mica surfaces by analyzing the transmitted light intensities of FECO.^{13, 14} However, their discussion of the absorption properties was limited because of the anomalous behavior of the transmitted intensity of the odd order FECO. Later on, Haraszti and Kurihara gave the interpretation of this anomalous behavior by considering the deformation of surface, and established the procedure to obtain the absorption of confined dyes as a function of surface separation distance from micrometer to contact.¹⁵ We call this method "FECO spectroscopy". Its combination with the resonance shear measurement, can be a powerful tool to study the properties, composition, molecular arrangement of confined multi-component liquid systems. In this study, we extended the study to a two-component system, i.e., and a model lubricant consisting of a two-component liquid crystal (6CB/Sudan Black B mixture), confined between mica surfaces were studied. Here, we employed a liquid crystal because it is known as an excellent lubricant and additive for lubricants,^{16, 17} and for its potential application of active control of friction by the external field such as electric and magnetic fields.^{18, 19}

MAIN SECTION

EXPERIMENTAL

Materials - Liquid crystal and dye used in this study are shown in Figure 1. Sudan Black B is an azo dye, nonpolar and oil soluble, was purchased from Aldrich Inc. 4-cyano-4'-hexyl biphenyl (6CB) from Merck was used as received. 6CB is in a crystalline phase below 14.5 °C, a nematic phase at 14.5–29.4 °C, and an isotropic phase above 29.4 °C. The temperature during measurement was kept at ca. 22 °C. The homogeneous mixtures of Sudan Black B/6CB were obtained by warming up to the temperature above the nematic to isotropic transition temperature, then kept at the room temperature for 24 hours. The concentration of Sudan Black B in the mixtures was adjusted to 1.03 wt %, 0.14 wt %, and 0.06 wt %. The transition temperature from the nematic phase to isotropic phase after mixing was determined to be 24.7 ± 0.2 °C at 1.03 wt% dye. The molar absorption coefficient (ϵ) of Sudan Black B in ethanol (spectrum grade from Nacalai Tesque) was determined to be $\epsilon=20070$ at 602.2 nm using a spectrophotometer (HITACHI, U-3300).

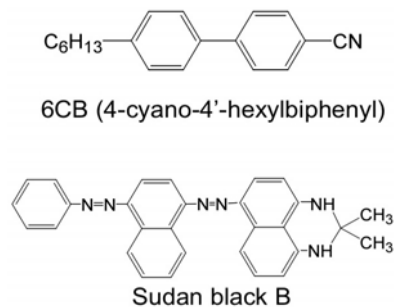


Figure 1. The chemical structures of 6CB and Sudan Black B.

Resonance Shear Measurement - Figure 2 shows a schematic illustration of the resonance shear measurement system. It is composed of an upper unit (an upper surface connected to the four-sectored piezo tube and hanged by a pair of vertical leaf springs) and lower units (a lower surface mounted on the horizontal leaf spring). The upper surface is moved laterally by applying a sinusoidal input voltage (amplitude (U_{in}) = ± 2.5 V, frequency (f): 20–100 Hz) to one sector of the piezo tube as well as an opposite phase input voltage to the opposing sector of the piezo tube. The deflection of the vertical leaf spring was detected by a capacitance probe (U_{out} , Microsense3401HR, Japan ADE). The sensitivity of the capacitance probe was 2.518 $\mu\text{m/V}$. The normalized shear amplitude measured by the capacitance probe (U_{out}/U_{in}) shows the maximum at a resonant frequency, and its amplitude and frequency sensitively reflect the physical properties of the sample liquids. Details were previously described.^{4-6, 8-10} This system was used in combination with the surface forces apparatus (SFA: Mark IV, ANUTECH Co. or NL-SF001, Nippon Laser & Electronics Lab.). The backside of the mica sheets used as substrates were coated by vacuum

deposited silver layer of 50 nm in thickness to produce interference fringes, then glued onto cylindrical quartz discs (a radius of curvature of ca. 20 mm) using epoxy resin (Shell, Epikote 1004). The distance between the mica surfaces (D) was determined using the fringes of equal chromatic order (FECO) with a resolution of 0.1 nm.¹² As a white light source of the FECO, Xenon lamp from USHIO Inc. (Optical Module X) was used. Sudan Black B/6CB ($\sim 10 \mu\text{l}$) was injected into the gap between the mica surfaces, and the resonance curves were measured as functions of the surface separation distance and the normal load. The physical properties of the sample can be obtained by fitting the obtained resonance curves using the equation 1 and 2 derived based on the physical model shown in Figure 3.^{4, 5}

$$\frac{U_{out}}{U_{in}} = \frac{C}{m} \frac{1}{\sqrt{\left(\frac{k}{m} - \omega^2\right)^2 + \left(\frac{b}{m}\right)^2 \omega^2}} \quad (1)$$

$$\begin{aligned} m &= m_0 + \Delta m \\ k &= k_0 + \Delta k \\ b &= b_0 + \Delta b \end{aligned} \quad (2)$$

Here, the C is the apparatus constant, m_0 is the effective mass of the upper unit, m is the effective mass of the sample and lower unit, k_0 is the elastic parameter of the upper unit, k is the elastic parameter of the sample and lower unit, b_0 is the viscosity (damping) parameter of the upper unit, Δb is the viscosity (damping) parameter of the sample and lower unit. When the surfaces are separated in air, the parameters of Δm , Δk , Δb become zero.

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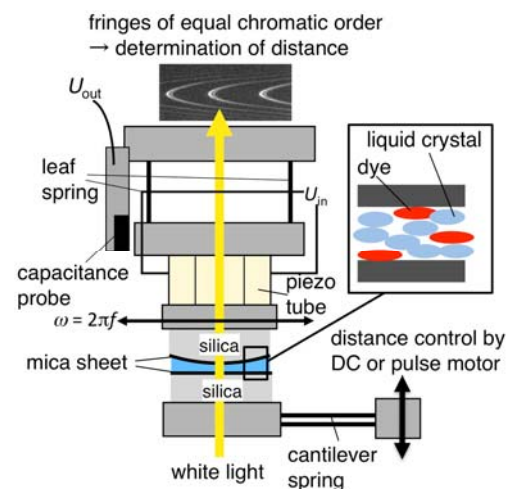


Figure 2. Schematic illustration of resonance shear apparatus. The surface separation distance was changed using a DC or pulse motor connected to the lower surface. The normal force (load) can be calculated based on the bending of the cantilever spring using Hook's law ($F=k\Delta x$).

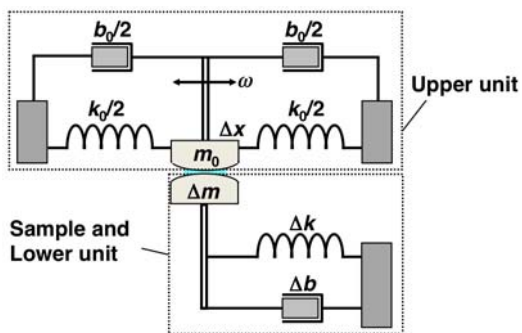


Figure 3. A physical models of oscillating unit.

FECO spectroscopy - FECO spectroscopy was used for absorbance measurements of Sudan Black B/6CB confined between mica surfaces as a function of the surface separation distance. The FECO images on a spectrograph (Nippon Jarrell Co.) were recorded with a digital CCD camera (Y.O. Systems Inc. SpectraVideo™ system) attached to the spectrograph. The images were 1100×330 pixels, with a horizontal resolution of 12.7 pixel/nm (ca. 0.08 nm/pixel); the intensity was converted by a 16 bit A/D converter. Each image was taken with the 100 ms exposure time. A set of neighboring even and odd fringes were chosen from a wavelength range of the absorption of Sudan Black B, and their intensities I_{even} and I_{odd} were digitized of which background intensity was subtracted.

As shown in Figure 4, at the centre of the symmetric interferometer (five layers which is consisted of two silver coated mica sheets confining the sample), odd order fringes have a nodal plane and their intensities are minimum, whereas even fringes have antinodal plane and their intensities take maximum. According to these properties of FECO, the transmittance T was defined as the ratio of I_{odd} and I_{even} ,^{15, 20}

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$$T = \frac{I_{\text{even}}/I_{0,\text{even}}}{I_{\text{odd}}/I_{0,\text{odd}}} \quad (3)$$

here, I_0 is the intensity of the fringe when the mica surfaces are in contact in air without sample. By defining the T according to equation 3, the influence of the change in light intensity caused by the change in the surface morphology from cylinder to flat can be eliminated. By using this transmittance T , the extinction coefficient κ can be obtained using the following equation 4.^{14, 15, 20}

$$\kappa \approx \frac{\lambda_0 n_{\text{mica}} (1-r)}{2\pi n_{\text{sample}} D(1+r)} \left(\sqrt{\frac{1}{T}} - 1 \right) \quad (4)$$

where r is the reflectance from the silver layer deposited on the backside of each mica sheet, n_{mica} and n_{sample} are

the refractive indices of mica and sample respectively, λ_0 is the wavelength for mica contact, and D is the surface separation distance determined from the odd order fringe using the following equation 5.^{15, 20}

$$D \approx N \frac{\Delta\lambda_N}{2n_{\text{mica}}} \quad \text{for } N \text{ odd} \quad (5)$$

where N is the order of the fringe, $\Delta\lambda$ is the shift in the wavelength of the N th order fringe from that measured at mica contact in air ($D=0$). By using the relation between the extinction coefficient κ and the molar absorption coefficient ε , the concentration of the absorbing species c can be written as follows.

$$c = \frac{4\pi\kappa}{\varepsilon\lambda} \quad (6)$$

where λ is the wavelength of the even fringe. When the change in the absorption coefficient ε is negligible, the concentration of absorbing species can be obtained from κ determined FECO spectroscopy.

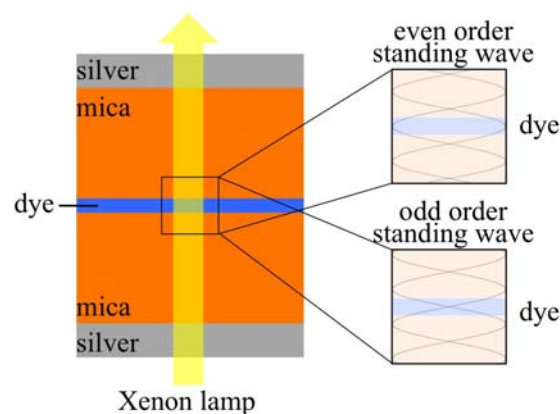


Figure 4. Schematic illustration of optical interferometer of the sample, and the intensities of odd and even order standing waves.

RESULTS AND DISCUSSIONS

FECO spectroscopy on Sudan Black B/6CB - Figure 5 shows the examples of the FECO images in the spectrograph obtained (a) at mica contact in air, and (b) at $D = 3.9$ nm in the presence of Sudan Black B / 6CB (1.03 wt% Sudan Black B). The odd and even fringes could be distinguished from the shape of the fringe, i.e., the fringes of narrower shape are odd order and the fringes of wider shape are even order. Figure 6 shows the light intensity profiles along the center of the fringes. The obtained light intensity profile at mica contact shown in Figure 6a reflect the intensity profile of Xenon lamp. After injection of the sample, only even order fringes showed the decrease in the intensity due to the absorption of Sudan Black B molecules (Figure 6b). We calculated the extinction coefficient κ using these fringe intensities based on equation 4.