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Citation	電気材料技術雑誌. 2011, 20(2), p. 5-9
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/76867">https://hdl.handle.net/11094/76867</a>
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## Viscosity Measurement of Ionic Liquid Using Shear Horizontal Wave

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### Abstract

Viscosity of an ionic liquid (1-methyl-3propyl imidazolium iodide) in ethylisopropylsulfone is measured using the shear horizontal (SH) wave method in which viscosity is determined by a delay in phase propagation of the SH wave. The sample is filled into a cell structure on a SH wave device. In the cell structure, there are two indium-tin oxide electrodes on the surfaces of the cell which allow us to measure the electroviscous effect of the ionic liquid. The results of electroviscous measurements show phase shift depending on voltage. The increase of a voltage decreases the phase of the SH wave, and then the phase recovers in the absence of the applied voltage. Further we found the phase shift depends on the cell thickness. These indicate that the viscosity of the sample increases with increasing electric field.

### 1. Introduction

Viscosity plays significant role in the performance of electronic devices and electrical equipments such as dye-sensitized solar cells, liquid crystal devices, electric double layer capacitors, electrolytic capacitor, and so on. In these applications, ionic liquids have recently attracted much attention because of the possibility for a breakthrough of electrochemical devices [1-3]. Ionic liquids are liquids composed of only ions at room-temperature. They are expected to lead development of high performance of capacitors, fuel cells, Li-ion batteries, and dye-sensitized solar cells, because they have high ionic conductivity and wide voltage potential window. In particular, as the ion conductivity depends on viscosity, the viscosity measurements of electrolyte solutions and ionic liquids are important for fundamental and application researches.

Viscosity of a liquid is generally measured with a rotational viscosity meter, which requires a large amount of sample. Therefore, it is not suited for a small amount of sample or quite expensive materials. We have proposed a new method for viscosity measurement of a liquid crystal by using shear horizontal (SH) wave propagation [4-7]. The

viscosity meter using a SH wave device has a thin cell structure composed of two glass plates in which an orientation treatment can be prepared for the viscosity anisotropy measurement of a liquid crystal. Moreover, when electrodes are prepared on the glass plates, an electroviscosity effect can be measured by applying a voltage to the electrodes. Therefore, this viscosity method is especially suited for liquids having electronic properties, such as liquid crystals, electrolyte solutions and ionic liquids. Using this technique, we have measured the change in viscosity of liquid crystals which is caused by reorientation with applying electric field.

In this study, viscosity of an ionic liquid in a solvent is measured using the SH wave method. The results of electroviscous measurements show the phase propagation of the SH wave depending on voltage. To discuss the electroviscous effect, the electric field dependence of viscosity is investigated by phase propagation analysis.

### 2. Basics of viscosity measurement using SH wave

In this section, we will discuss the basics of the viscosity measurement using the SH wave. We

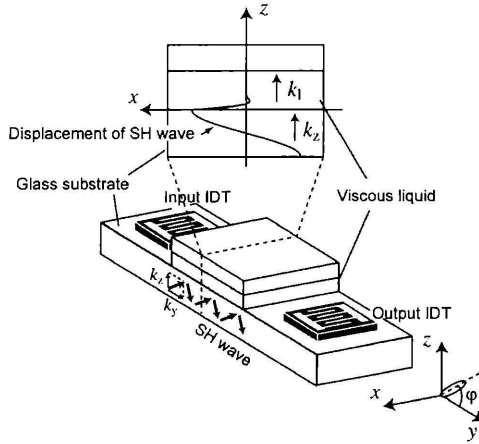


Fig. 1 Schematic of SH wave device with a cell structure for viscosity measurement.

here consider a SH wave propagating through a thin glass substrate loaded with a viscous liquid, as shown in Fig. 1. The SH wave propagates in the  $yz$ -plane, and the shear direction is parallel to the  $x$ -direction. In the glass substrate, the SH wave is confined by reflections at the top and bottom boundaries. At the boundary between the glass and the viscous liquid, the SH wave slightly penetrates into the viscous liquid layer. The cross-section view in Fig. 1 illustrates the displacement and penetration of the SH wave. The penetration depending on viscosity causes a phase shift of the SH wave propagation. The measurement of the phase shift at the output interdigital transducer (IDT) determines the viscosity of the liquid on the glass substrate.

The theoretical phase depending on viscosity can be calculated using propagation mode analysis [8-10]. Let us consider SH wave propagation in the  $yz$ -plane of the glass substrate with wave vectors  $k_y$  and  $k_z$ , as shown in Fig. 1. In the glass substrate, the acoustic velocity  $u_g$  of the SH wave, which represents the shear displacement along the  $x$ -direction, is given by

$$u_g = \{A_1 \exp(ik_z z) + A_2 \exp(-ik_z z)\} \exp(ik_y y - i\omega t), \quad (1)$$

where  $A_1$  and  $A_2$  are the amplitudes of the SH waves.  $k_z$  is written as

$$k_z = \frac{\omega}{u_p} \sqrt{\rho_g \frac{u_p^2}{\mu} - 1}, \quad (2)$$

where  $u_p$  is the phase velocity of the SH wave,  $\rho_g$  is the mass density of the glass substrate, and  $\mu$  is the modulus of elasticity in shear of the glass substrate.

The flow velocity  $u_l$  of the SH wave in the liquid layer is obtained using the Navier-Stokes equation

$$\frac{\partial u_l}{\partial t} = \frac{1}{\rho_l} \frac{\partial}{\partial z} \left( \eta \frac{\partial u_l}{\partial z} \right), \quad (3)$$

where  $\rho_l$  and  $\eta$  are the mass density and viscosity of the liquid, respectively. When  $\eta$  is spatially uniform, the solution  $u_l$  is given by

$$u_l = A_3 \exp(-k_l z) \exp(ik_l z - i\omega t), \quad (4)$$

where  $A_3$  is the amplitude of the SH wave that penetrated into the liquid layer, and  $k_l$  is the wave vector of the SH wave. Equation (4) denotes the flow velocity that exponentially decays with  $\exp(-k_l z)$  in the liquid layer, where  $k_l$  is written as

$$k_l = \sqrt{\frac{\omega \rho_l}{2\eta}}. \quad (5)$$

For propagation mode analysis, stresses in the glass substrate and liquid are also necessary. In the glass substrate, the relation between the stress  $T_g$  and the acoustic velocity  $u_g$  is given by

$$\frac{\partial T_g}{\partial t} = \mu \frac{\partial u_g}{\partial z}, \quad (6)$$

while the shear stress in the liquid layer is written as

$$T_l = \eta \frac{\partial u_l}{\partial z}. \quad (7)$$

The boundary conditions of the velocities and stresses along the  $z$ -axis are summarized as

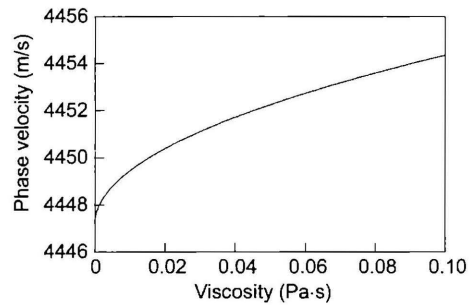


Fig. 2 Viscosity dependence of phase velocity for second-mode SH wave in glass substrate loaded with viscous liquid.

$$\begin{bmatrix} \mu k_z & -\mu k_z & -i\omega\eta k_l \\ \exp(-ik_z D) & -\exp(ik_z D) & 0 \\ 1 & 1 & -1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = 0, \quad (8)$$

where  $D$  is the thickness of the glass substrate. The wave vector  $k_z$  including  $u_p$  is determined by solving Eq. (8). Figure 2 shows the viscosity dependence of  $u_p$ . Here, we calculated it using the following experimental parameters:  $\mu$  of  $2.64 \times 10^{10}$  N/m<sup>2</sup>,  $\rho_g$  of 2760 kg/m<sup>3</sup>,  $\rho_l$  of 1019 kg/m<sup>3</sup>,  $D$  of 400  $\mu$ m,  $f$  of 10.76 MHz. Details of the experimental conditions and procedure are described in the next section. As is evident in Fig. 2, phase velocity increases with increasing viscosity and is proportional to the square root of viscosity. Note that the propagation phase of the SH wave is linked to viscosity. Using this relation, we can determine the viscosity of the viscous liquid on the glass substrate by measuring phase propagation.

### 3. Experimental procedure

We fabricated a SH wave device shown in Fig. 1 to measure phase propagation depending on viscosity. A cell structure was prepared at the center to be filled with a measurement sample; the cell length along the  $y$ -axis was 1.0 cm. The cell length corresponds to the propagation length of the viscous liquid delay line for the SH wave. The cell consisted of two indium-tin oxide (ITO)-coated glass substrates sandwiching two poly(ethylene terephthalate) films as a spacer. The test sample was 1.5 mol/L 1-methyl-3propyl imidazolium

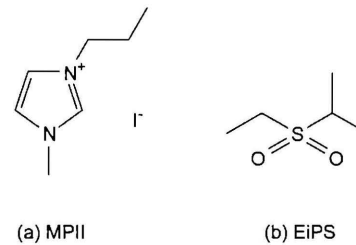


Fig. 3 Molecular structures of (a) 1-methyl-3propyl imidazolium iodide (MPII) and (b) ethylisopropylsulfone (EiPS)

iodide (MPII) in ethylisopropylsulfone (EiPS). This ionic liquid MPII has widely been investigated in the dye-sensitized solar cells because of its low viscosity (865 mPa·s) [11]. These molecular structures are shown in Fig. 3. The application of electric field to the ITO electrodes allows us to measure the electroviscous effect of the sample.

On both sides of the cell structure, two piezoelectric ceramic plates (TDK, 101A) were placed for SH wave excitation and detection, as shown in Fig. 1. The thickness of the glass substrate and piezoelectric plate were 400  $\mu$ m and 1 mm, respectively. IDTs were prepared on the piezoelectric ceramic plates by aluminum evaporation. The periodicity of the IDT was 400  $\mu$ m, and the number of the pairs of electrode fingers was 7. To excite SH wave, a sinusoidal voltage of 2 V was applied to the input IDT. Since the piezoelectric ceramic plates were polarized along the  $x$ -axis, the SH wave shear direction excited from the piezoelectric plates was parallel to the  $x$ -axis. The SH wave excited from the input IDT propagated through the lower glass plate in contact with the ionic liquid, and then the signal was detected by the output IDT. To detect the SH wave phase shift, the output IDT was connected to a lock-in amplifier (Stanford Research System, SR844).

### 4. Experimental results

Figure 4 shows the frequency dependence of the insertion loss in the SH wave device without the ionic liquid sample. Peaks in Fig. 4 correspond to mode frequencies for the SH wave propagating in

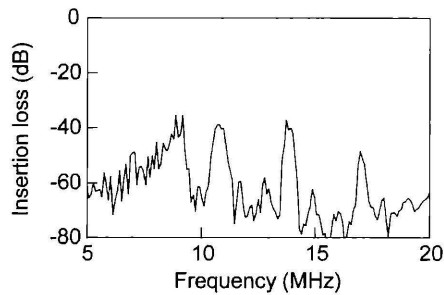


Fig. 4 Frequency dependence of insertion loss of SH wave device. Peaks correspond to propagation mode frequencies.

the glass plate. The frequencies of the 1st, 2nd, and 3rd modes are 9.1, 10.8, and 13.8 MHz, respectively. At these frequencies, we measured the phase  $\theta$  of the SH wave which is defined as

$$\theta = \omega L / u_p, \quad (9)$$

where  $L$  is the delay line length. The  $u_p$  depends on viscosity as shown in Fig. 2. Naturally,  $\theta$  also has viscosity dependence. When phase viscosity increases by  $\Delta u_p$ , the variation of phase is given by

$$\Delta\theta = \omega L / u_{p0}^2 \cdot (-\Delta u_p), \quad (10)$$

where  $u_{p0}$  is the initial phase velocity that is obtained before filling a sample into the cell structure. That is, an increase in  $u_p$  which associated with increasing viscosity brings a decrease in  $\theta$ .

Figure 5 shows the phase shift of the 2nd-mode SH wave at 10.76 MHz by filling the test sample (1.5 mol/L MPII in EiPS) into a 6- $\mu\text{m}$  thickness cell. The sample was filled at 0 min and the phase was stable within 20 min. This experiment was carried out at 27°C. The phase decreased by 5.47° after filling the sample. The phase shift is caused by the viscosity change from air to the 1.5 mol/L MPII in EiPS in the cell structure. We can determine the viscosity of the sample from  $\Delta\theta$  using the phase velocity analysis. The viscosity of the 1.5 mol/L MPII in EiPS was estimated to be 32 mPa·s. Since the viscosities of MPII and EiPS are 865 and 5.6 mPa·s, respectively, the estimated value is close to the average of the sample's viscosities.

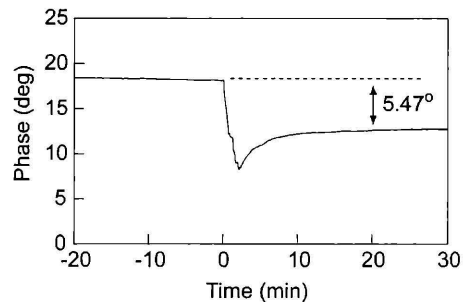


Fig. 5 Phase shift of second-mode SH wave at 10.76 MHz by filling 1.5 mol/L MPII in EiPS.

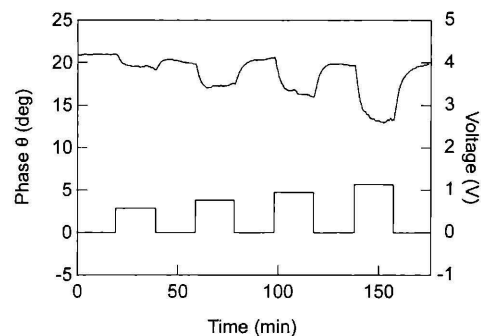


Fig. 6 Phase shift of SH wave in a 6- $\mu\text{m}$  cell by applying DC voltage to 1.5 mol/L MPII in EiPS.

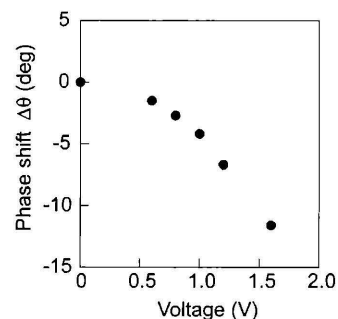


Fig. 7 Voltage dependence of phase shift of SH wave in a 6- $\mu\text{m}$  cell.

After filling the sample into the cell structure, we investigated the electroviscous effect of the 1.5 mol/L MPII in EiPS. Figure 6 shows the phase shift with applying DC voltages. The phase decreased with the applied voltage, and then the phase recovered in the absence of the applied voltage. The responses of the phase shifts are not so fast, but it is clear that the phase of the SH wave decreases with increasing voltage. The variations of these phase shifts are plotted in Fig. 7. The decrease in the phase follows a parabolic curve.

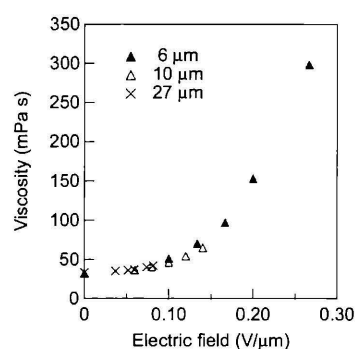


Fig. 8 Electric field dependence of viscosity of 1.5 mol/L MPII in EiPS.

This indicates that the viscosity of the 1.5 mol/L MPII in EiPS largely increased with increasing voltage.

The thickness dependence of the electroviscous effect has also been investigated. We here measured phase shifts in 6, 10, 27- $\mu\text{m}$  cells with voltages from 0 V to 1.6 V. Although the 6- $\mu\text{m}$  cell shows large phase shifts, the phase hardly shifted in the 27- $\mu\text{m}$  cell when the voltage was applied. Figure 8 shows the electric field dependence of the viscosity of the sample. It is clear that the viscosity of the 0.15 mol/L MPII in EiPS depends on electric field. The viscosity increased approximately 10 times from 0 to 0.25 V/ $\mu\text{m}$ . The mechanism of this effect is now under study. The density of the ion may have influence on viscosity.

Further we have also measured the electroviscous effect using 0.2, 0.7, and 1.5 mol/L MPII in EiPS. Figure 9 shows the MPII concentration dependence of the electroviscous effect. As the sample of 1.5 mol/L has a large electroviscous effect, we found the electroviscous effect depends on MPII concentration.

## 5. Conclusions

We measured the viscosity of MPII in EiPS using the SH wave method. The measured viscosity was close to the average viscosity of MPII in EiPS. The electroviscous effect of the sample was also investigated. The increase of a DC voltage to the sample decreased the phase of the SH wave, and then the phase recovered in the absence of the applied voltage. The viscosity of the

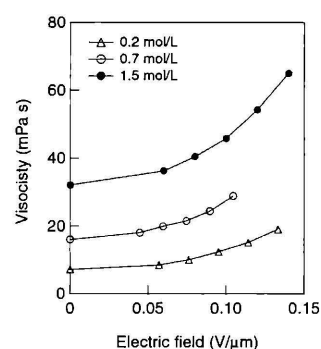


Fig. 9 Electroviscous effects in 0.2, 0.7 and 1.5 mol/L MPII in EiPS.

MPII in EiPS increased with increasing electric field. We found that the electroviscous effect depends on MPII concentration. The mechanism of this effect is now under study. However, we consider that the large electroviscous effect becomes important role in development of electric devices using ionic liquids and electrolyte solutions.

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