

Measurement of shear viscosity of liquids up to GHz region using electrodeless quartz crystal transducer

無電極水晶振動子を用いた液体の GHz 領域に至る粘性測定

Tsuyoshi Yamaguchi and Tatsuro Matsuoka (Grad. School Eng., Nagoya Univ.)

山口 毅, 松岡辰郎 (名大院 工)

1. Introduction

Shear viscosity is a transport property of liquid important in various fields including chemistry, chemical engineering, mechanics, and so on. It is actually a complex quantity dependent on frequency, reflecting microscopic structural relaxation. The measurement of the frequency-dependent complex viscosity is thus a popular method in studying soft matters including polymer systems and surfactant solutions. However, the number of experimental studies on the viscoelastic relaxation of low molecular-weight liquids is limited at present, mainly due to the lack of experimental methods to measure the complex shear viscosity at frequency as high as their viscoelastic relaxation frequency.

We have studied the viscoelastic relaxation of viscous liquids in the MHz region including non-aqueous electrolyte solutions, ionic liquids and higher alcohols by shear impedance method using AT-cut quartz crystal.¹⁾ The application of this method is however limited up to 200 MHz because the finite thickness of the gold electrode attached to the crystal disturbs the transmission of the transverse acoustic wave into the sample liquid. In this work, we try to extend the high-frequency limit using an electrodeless quartz transducer, coupling the electric circuit and the transducer through the dielectric property of the sample itself.

2. Experimental Method

The sample cell developed in this work is schematically shown in Fig. 1. An AT-cut quartz plate without metal electrode, whose fundamental frequency is 64.5 MHz, is immersed in sample liquid, and both sides of the quartz are in contact with the sample. The electrode on the upper side is connected to a vector network analyzer (VNA, ZNL3, Rhode & Schwarz), and alternating-current (AC) electric signal is applied. The body of the sample cell is connected to the ground, and the electric field is applied to the quartz vertically. The bottom of the sample cell is attached to a Peltier element, and the temperature of the cell is controlled at 25.0 ± 0.1 °C.

The resonance of the quartz transducer is

E-mail to T. Yamaguchi:

yamaguchi.tsuyoshi@material.nagoya-u.ac.jp

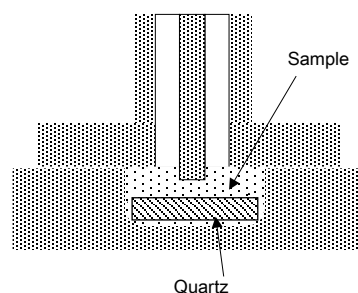


Fig. 1. Schematic picture of the sample cell.

observed by measuring S_{11} as a function of frequency. The intensity of the resonance signal increases with increasing the polarity or the electric conductivity of the sample, because the transducer is coupled to the dielectric response of the sample. The frequency range of the measurement is thus limited for nonpolar liquids such as hexane. However, the measurement up to 3GHz (45th overtone) is possible when the dielectric constant of the sample is larger than 20.

The complex viscosity is determined from the differences in the resonance frequencies and the bandwidths in a reference and a sample liquid. The measurement of various overtones enables us to obtain the frequency-dependent complex shear viscosity. We choose acetonitrile as a reference liquid because of its high polarity and low viscosity. The shear viscosity of acetonitrile is assumed to be frequency-independent within the frequency range of our measurement (below 3 GHz). The apparent resonance signal of $S_{11}(\nu)$ in the reference liquid is approximated as a sum of Lorentz functions, and $S_{11}(\nu)$ in a sample liquid is fitted by optimizing the total amplitude and shifting the complex poles of Lorentz functions, keeping the relative amplitudes and positions of the poles. The complex shift of the poles of $S_{11}(\nu)$ is then converted to that of complex admittance under the assumption that the dielectric loss of the reference liquid, acetonitrile, is negligibly small.

3. Results and Discussion

In the case of liquids whose viscosity is independent of frequency, the changes in both the acoustic resonance frequency and the bandwidth are given by

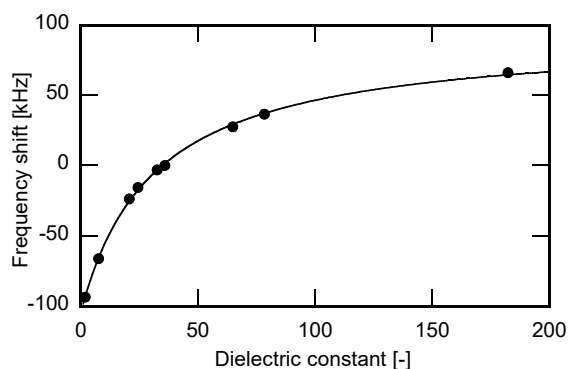


Fig. 2. Difference between the experimental and theoretical frequency shifts plotted against the dielectric constant of the sample.

$$\delta\nu_{\text{theo}} = \frac{2\nu_0}{Z_q} \sqrt{\frac{\rho\eta\nu}{\pi}}, \quad (1)$$

where ν_0 , ν , Z_q , ρ and η stand for the fundamental frequency, resonance frequency, shear impedance of quartz, density and viscosity of the liquid, respectively. The frequency shift and the broadening from reference to sample liquids is thus given by the difference in their values of $\delta\nu_{\text{theo}}$. The resonance signal of eight molecular liquids, hexane, tetrahydrofurane, acetone, methanol, ethanol, acetonitrile, propylene carbonate (PC), water and N-methylformamide are measured at $n = 1$, where n stands for the order of overtones. However, the frequency shift does not follow the theoretical prediction.

The difference in the theoretical and experimental frequency shifts is ascribed to the effect of electric coupling of the sample. Approximating the coupling as an equivalent circuit in which the transducer is in series connection with a capacitor whose capacitance is proportional to the dielectric constant of the sample, ϵ , the correction of the frequency shift, $\delta\nu_{\text{cor}}$, is given by

$$n\delta\nu_{\text{cor}} = A - \frac{B}{\epsilon + C}, \quad (2)$$

where A , B and C are constants determined by the geometry of the sample cell and the transducer. The difference in the theoretical and the experimental frequency shifts is plotted against ϵ in Fig. 2, and fitted into Eq. (2) regarding A , B and C as fitting parameters. The difference is described well by Eq. (2), demonstrating that the equivalent circuit works to correct the frequency shift.

The resonance signals in water were then measured up to 45th mode of overtone. The frequency shift and the broadening of the apparent resonance signal in $S_{11}(\nu)$ were converted into those of the complex admittance of the transducer using Eq. (2), and the frequency-dependent shear viscosity, $\eta(\nu) = \eta'(\nu) - \eta''(\nu)$ was determined up to 3 GHz. The result is plotted as the function of frequency in Fig. 3. The low-frequency limiting value of the shear

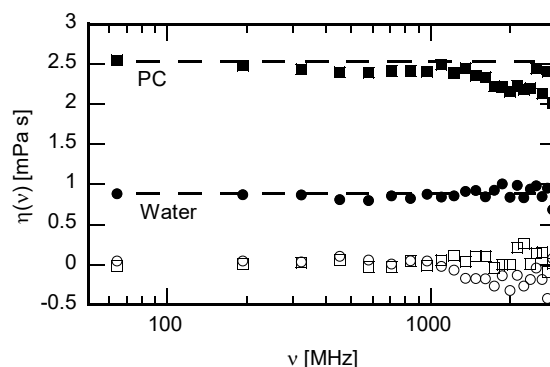


Fig. 3. Frequency-dependent complex shear viscosity of water (circles) and PC (squares). The real and imaginary parts are shown with filled and open symbols, respectively. The horizontal dashed line indicate the low-frequency limiting value of shear viscosity.

viscosity, η_0 , was also shown with the horizontal dashed line for comparison. At all the frequency, the real and the imaginary parts of the viscosity is close to η_0 and 0, respectively. It has been shown by ultrasonic spectroscopy that both the longitudinal and the shear viscosities do not depend on frequency up to 3 GHz, and our experimental result is consistent with these experimental studies. It is thus demonstrated that we succeeded in measuring the complex shear viscosity of liquid water up to 3 GHz. The scattering of both the real and the imaginary parts from the ideal values is larger at higher frequency, which can be ascribed to the weaker intensity of the resonance signal at the higher frequency.

The experimental results of PC are also shown in Fig. 3. The complex shear viscosity of PC is independent of frequency below 1 GHz, and its value is equal to the low-frequency limiting value. The real part slightly decreases with frequency at higher frequency, which might be ascribed to the edge of the relaxation at frequency higher than 3 GHz.

4. Summary

An experimental method to measure the frequency-dependent complex viscosity of liquid is proposed using an electrodeless quartz transducer, and the validity of the method is demonstrated by applying it to liquid water.

Acknowledgment

This work was supported by Grant-in-Aid (KAKENHI) from the Japan Society for the Promotion of Science (JSPS) (No 19K03768).

References

1. T. Yamaguchi, M. Hayakawa, T. Matsuoka and S. Koda, J. Phys. Chem. B **113** (2009) 11988.