

Chapter 3. EXPERIMENTS

In order to investigate experimentally the slow dynamics of supercooled liquid during glass transition, various techniques have been used. Here are the examples of these techniques: dielectric spectroscopy, viscosity measurement, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, Brillouin scattering, Raman scattering, far-infrared spectroscopy, inelastic neutron scattering, quasielastic neutron scattering and (modulated) differential scanning calorimetry, etc [5].

Although the problem of glass transition is an old topic, the continuous focus on this subject can be attributed to the development of modern electronics which makes possible to perform the measurements in a wide range. Dielectric relaxation has been studied by the broadband dielectric spectroscopy, which may be performed using fast Fourier transform analyzer, LCR meter, network analyzer, time domain reflectometry (TDR) and Fourier transform infrared spectroscopy in the frequency range of $10^6 - 10^{14}$ Hz [5]. More precise enthalpy relaxation measurement has been carried out using the ac calorimetric measurements including modulated differential scanning calorimetry (MDSC) [5].

We used two experimental methods to clarify the slow dynamics of supercooled intermediate liquids of alcohols: complex dielectric permittivity and complex heat capacity. The former was performed by using the impedance analyzer and the TDR system, the latter was obtained by MDSC techniques. TDR and MDSC measurements are relatively new probes [26, 34].

In this Chapter, the basic principles and real setups of experimental systems used are described in detail. The samples studied are also illustrated.

3.1 Broadband dielectric spectroscopy

To cover the broadband frequency range from 10 mHz to 10 GHz, two kinds of dielectric measurement systems were used in this present work; the Impedance/Gain-phase analyzer in low-frequency range from 10 mHz to 10 MHz and the time domain reflectometry (TDR) system in high frequency range from 1 MHz to 10 GHz.

3.1.1 Impedance analyzer

In low frequency range from 1 mHz to 10 MHz, the well-known Impedance/Gain-Phase Analyzer (IA) was used. The block diagram of this system is in Fig. 3. 1. Solartron SI 1260 was used as IA. This IA drives the sinusoidal pulse to the sample with sweeping from higher frequency to lower one, and then records the impedance Z and phase θ of the sample. This system was controlled by the NEC98 PC. The software program named MAP, which is produced by Toyo Technica Co., controls the system condition, acquires the measured data and analyzes it.

The liquid samples are contained in the sample cell described in Fig. 3. 2. The principal structure of the sample cell is the plane plate condenser. The samples were kept between two electrodes of which distance was fixed to 0.3 - 0.4 mm by the inserted spacer. In order to improve the signal/noise ratio, the length of the cable connecting the sample cell and IA system is as shorter as possible.

Frequency scans were performed at a constant temperature, which was decreased in steps. The current amplifier was used additionally below 100 Hz. The temperature was recorded by the digital voltmeter.

3.1.2 Time domain reflectometry (TDR)

The dielectric measurement by time domain reflectometry (TDR) has been developed recently. Due to this system covers VHF and microwave bands, it is a popular and important method to obtain the complex dielectric permittivity. The basic structure of TDR system is shown in Fig. 3. 3. In TDR technique, the dielectric information of material is included to the reflected response $R(t)$ to a fast rising voltage step $V_i(t)$. The incident and reflected pulses are measured in the time domain and are converted to the frequency domain by Fourier transform. An incident step-like voltage $V_i(t)$ propagates through the coaxial transmission line and is reflected from the sample mounted at the end of the line. The reflected voltage $R(t)$ also propagates through the same line. The difference between the reflected and the incident pulses recorded in the time domain contains the information of the dielectric properties of the sample.

In 1969, TDR was first introduced for the measurement of dielectric permittivity by Fellner-Feldegg [35]. Nicolson and Ross developed a method which uses a combination of both the reflected and transmitted pulses to measure the complex permittivity and permeability of a material using Fourier transform [36].

Cole and his coworkers evaluated the complex dielectric permittivity of a wide range materials from strongly polar liquids to dilute solution with suitable choice of cell lengths at the range of 1 MHz to several GHz [34]. The main idea proposed by Cole's group is the difference method. The unknown complex dielectric permittivity can be derived using the comparison with the reference liquid which its complex dielectric permittivity is well-known. This method is very popular and will be explained in detail later.

Nozaki and Bose improved TDR system using both the hardware of high speed digital sampling oscilloscope and the software of reflection method over a wide frequency range from 100 kHz to 25 GHz [37].

In recent years, the development of the electronics and computer techniques such as fast Fourier transform makes the TDR system measure the complex dielectric permittivity easily and fast.

It is possible for TDR system to measure the broadband complex permittivity in a short time owing to the recording of the response in the time domain and its analyzing of the response in the frequency domain by Fourier transforms. It covers a variety of materials including liquid, liquid crystal, solid, living body system etc. with a quite simple set up. This TDR system is less expensive than that used in frequency domain method. TDR allows measurements to be made precisely without any destruction.

3.1.2.1 Basic theory of TDR

The basic theory of TDR has been described by Felleger-Feldegg, Cole, Nozaki and others [34, 35, 37]. Fig. 3. 3 illustrates the basic diagram of TDR. A step-like voltage, $V_i(t)$, propagates along a coaxial line of characteristic conductance G and the corresponding reflected voltage, $R(t)$, also propagates along the same line but in the opposite direction. The combined voltage across the sample is $V_i(t) + R(t)$ and the combined current is $G[V_i(t) - R(t)]$. The frequency expressions of combined voltage and current are $V_i(\omega) + R(\omega)$ and $G[V_i(\omega) - R(\omega)]$, respectively, where $V_i(\omega)$ and $R(\omega)$ are the Fourier transforms of $V_i(t)$ and $R(t)$. In this case, the input admittance Y_{in} of the line is given by the ratio of current to voltage,

$$Y_{in} = G \frac{[V_i(\omega) - R_i(\omega)]}{[V_i(\omega) + R_i(\omega)]} \quad (3. 1)$$

We consider a section of uniform transmission line of length d filled with non-magnetic and dielectric of complex permittivity ϵ^* and the sample section is open-ended. This section has an input admittance Y_{in} given by,

$$Y_{in} = Y_0 \tanh(\gamma d), \quad (3. 2)$$

where Y_0 is the characteristic admittance of the line and $\gamma = i \frac{\omega(\epsilon^*)^{1/2}}{c} = i \frac{x}{d}$ is the propagation constant without sample line loss. Here, c is the speed of light and $x = (\frac{d\omega}{c}) (\epsilon^*)^{1/2}$. Eq. (3. 2) is also given by using the term of x as follow:

$$\begin{aligned} Y_{in} &= \frac{Y_0 x}{[x \coth(ix)]} \\ &= \frac{G_0 (\epsilon^*)^{1/2} x}{[x \coth(ix)]}, \quad (3. 3) \\ &= G_0 \left(i \frac{d\omega}{c} \right) \frac{\epsilon^*}{x \cot x} \end{aligned}$$

where $G_0 = \frac{Y_0}{(\epsilon^*)^{1/2}}$ is the characteristic conductance of sample section filled with air and $\coth(ix) = -i \cot(x)$.

Combining Eqs. (3. 1) and (3. 3) gives an expression for complex permittivity,

$$\begin{aligned}
\varepsilon^* &= \frac{G}{G_0} \frac{c}{d} \frac{1}{i\omega} \frac{[V_i(\omega) - R(\omega)]}{[V_i(\omega) + R(\omega)]} x \cot x \\
&= \frac{c}{gd} \frac{1}{i\omega} \frac{[V_i(\omega) - R(\omega)]}{[V_i(\omega) + R(\omega)]} x \cot x, \\
&= \rho x \cot x
\end{aligned} \tag{3.4}$$

where $g = \frac{G_0}{G}$ is the normalized characteristic conductance between the line and the sample section and $\rho = \frac{c}{gd} \frac{1}{i\omega} \frac{[V_i(\omega) - R(\omega)]}{[V_i(\omega) + R(\omega)]}$.

3.1.2.2 Difference method in TDR

In order to make a more precise measurement, $V_i(\omega)$ can be avoided from the Eq. (3.4). We consider two materials with known permittivity ε_s^* and unknown permittivity ε_x^* . The known permittivity ε_s^* can be written as,

$$\begin{aligned}
\varepsilon_s^* &= \rho_s x_s \cot x_s \\
\rho_s &= \frac{c}{gd} \frac{1}{i\omega} \frac{[V_i(\omega) - R_s(\omega)]}{[V_i(\omega) + R_s(\omega)]},
\end{aligned} \tag{3.5}$$

and the unknown permittivity ε_x^* also,

$$\begin{aligned}
\varepsilon_x^* &= \rho_x x_x \cot x_x \\
\rho_x &= \frac{c}{gd} \frac{1}{i\omega} \frac{[V_i(\omega) - R_x(\omega)]}{[V_i(\omega) + R_x(\omega)]},
\end{aligned} \tag{3.6}$$

where $R_s(\omega)$ and $R_x(\omega)$ are the Fourier transforms of the reflected pulses of both samples, respectively.

Combining Eqs. (3.5) and (3.6) to cancel the incident term $V_i(\omega)$ makes the unknown permittivity ε_x^* be given by,

$$\begin{aligned}
\varepsilon_x^* &= \frac{[\rho_s + \frac{\varepsilon_s^*}{f_s} f_x]}{[1 - g^2 (\frac{d\omega}{c})^2 \frac{\rho_s \varepsilon_s^*}{f_s}]} \\
\rho_s &= \frac{c}{gd} \frac{1}{i\omega} \frac{[R_s(\omega) - R_x(\omega)]}{[R_s(\omega) + R_x(\omega)]}
\end{aligned} \tag{3.7}$$

where $f_s = x_s \cot x_s$ and $f_x = x_x \cot x_x$, respectively. This equation does not include the incident pulse $V_i(\omega)$. The unknown dielectric permittivity can be obtained by recording the reflected signals from a standard material and an unknown sample. Air with $\epsilon_s^* = 1$ is usually used as a standard material. Only two measurements of the time domain pulses gives us the information of the complex permittivity of material.

3.1.2.3 Real measurement by TDR

To obtain the complex permittivity of liquid in high frequency range from 1 MHz to 10 GHz, the block diagram of the TDR system which was really used is shown in Fig. 3. 4. The difference method was applied in this work.

The incident pulse $V_i(t)$ with 0.2 V voltage and 40 ps risetime is generated from the HP54754A Differential TDR module with bandwidth up to 18 GHz. This pulse propagates through the coaxial transmission line with impedance of 50 Ω . The corresponding reflected pulse $R(t)$ also propagates along the same line but in the opposite direction. This feature is monitored by the HP54750A digitizing oscilloscope. The averaging number of the signals is 16.

As the difference method was applied, only the reflected pulse $R(t)$ was saved. Air was used as the standard sample. To calculate the value of gd in Eq. (3. 4), the complex dielectric permittivity of ethanol and n-propanol were measured and then compared with the reference values reported already [38, 39] prior to measuring the dielectric permittivity of other liquids. Then, to evaluate the complex permittivity of unknown liquid, two measurements of the reflected pulses of air and sample, $R_s(t)$ and $R_x(t)$, were carried out and saved each other at a constant temperature. The temperature of a sample was monitored by an alumel-chromel thermocouple. The voltage difference from the thermocouple is monitored by the digital multimeter TR6846 made by ADVANTEST. The temperature was controlled by the flow of the dry nitrogen.

The two saved pulses, $R_s(t)$ and $R_x(t)$, were transferred to the Macintosh computer through MacSCSI488 bus controller made by IOtech. And then, to evaluate the complex permittivity of the sample, the calculation of ϵ_x^* was performed according to Eq. (3. 7) with the Fourier transforms, $R_s(\omega)$ and $R_x(\omega)$ respectively, of $R_s(t)$ and $R_x(t)$.

3.1.2.4 Reflection from sample cell

The sample cell composition is illustrated in Fig. 3. 5. The sample cell was connected with the transmission coaxial line. The SMA connector with a pin of length d was

basically used as the sample cell. As the sample cell and coaxial line are impedance matched with 50Ω impedance, the signal generated from the pulse generator propagate to the reference plane. The reference plane is at $d = 0$. The sample pin is fully dipped into the liquid with the permittivity ϵ^* . The reflection occurs at the reference plane by the different impedance between the sample cell with 50Ω and the liquid sample with the impedance $Z = (1/\epsilon^*)^{1/2}$. The rest transmitted pulse, of course, propagate through the liquid sample. There is also another reflection from the sample. The plane at which the propagating pulse in the liquid is reflected is related to the structure of the sample cell and the length and thickness of pin of sample cell.

The structural factor of the sample cell is represented as g in Eq. (3. 4). It is assumed that the sample cell with $d = 0$ is completely matched with coaxial line and the transmitted pulse reflect at the distance of gd . The simple and schematic correction of the sample cell is drawn in Fig. 3. 6. The incident pulse is V_i and the transmitted pulse totally into liquid through reference plane is expressed as $\rho' V_i$. The total reflected pulse from the imaginary gd plane is $\gamma' R$ and the rest transmitted pulse through gd plane is $\rho'' V_i$. Therefore, the total reflected pulse including the information of the dielectric permittivity of the sample is R and propagates along the transmission line in the opposite direction to the V_i .

The detailed multiple transmission and reflection feature is shown in Fig. 3. 7. It is assumed that a sample with impedance $Z = (1/\epsilon^*)^{1/2}$ and length gd is inserted between materials A and B with different impedance. Let the reflection coefficient as ρ from A to sample and as γ from sample to B. For the incident pulse $V_i(t)$, $\rho V_i(t)$ reflects to A at plane x and $(1-\rho)V_i(t)$ transmits into sample. The reflected pulse is denoted as R1. After time $t = t_0 = gd/c$, where c is the speed of light, the transmitted pulse $(1-\rho)V_i(t)$ again reflects at plane y with the value of $\gamma(1-\rho)V_i(t)$ and transmits into $(1-\gamma)(1-\rho)\gamma V_i(t)$. At $t = 2t_0$, the reflected pulse, $\gamma(1-\rho)V_i(t)$, from y plane again reflects into sample and transmits into A at x plane. The transmitted pulse, $-\rho\gamma(1-\rho)V_i(t)$, into A is denoted as R2. This multiple reflection and transmission scheme will be repeated. The pulses denoted as R1, R2, R3, R4 are the ones that propagate through the material A in the opposite

direction to $V_i(t)$ and their superposition with time is the pulse, $R(t)$, reflected from the sample.

3.2 Modulated differential scanning calorimetry (MDSC)

The justification for the existence of a complex heat capacity has been expressed by virtue of fluctuation-dissipation theory by Birge [40]. It is one of the subjects on the glass transition phenomena [41].

Differential Scanning Calorimetry (DSC) has been widely used as an available tool to know thermal properties of various materials. In conventional DSC, in other word heat flux DSC, the reference and sample materials are in the environment in which temperature increase linearly with time. The temperature difference, which is proportional to the heat-flux difference between both materials, is recorded. This system can be used to measure properties such as heat capacity. Recently, a method called the modulated temperature differential scanning calorimetry (MDSC) was introduced [26] and has been developed actively [42].

3.2.1 Frequency dependent heat capacity

Steady-state technique using ac heating was introduced as a method for measuring heat capacity [24]. Specific heat spectroscopy measuring the frequency dependent heat capacity from the response of a sample is of a more later [25].

Traditionally heat capacity c_p is thought to be an equilibrium or static quantity. If a thermal system is kept at constant pressure, then the heat per unit volume, q , is equal to the change in enthalpy per unit volume, h ,

$$q = h = c_p \Delta T \quad (3.8)$$

If a dynamic heat capacity $c_p(\omega)$ is considered, the heat absorbed by this system will be a function of time after the temperature step and will relax slowly to equilibrium. If the temperature is applied to the system at $t = 0$, time dependent heat $q(t)$ can be written,

$$q(t) = \begin{cases} 0 & \text{for } t < 0 \\ \{c_p(0) + [c_p(\infty) - c_p(0)][1 - \Phi(t)]\}\Delta T & \text{for } t > 0 \end{cases}, \quad (3.9)$$

where $c_p(0) = c_p(t=0)$, $c_p(\infty) = c_p(t=\infty)$ which is equal to the equilibrium heat capacity c_p .

The relaxation function $\Phi(t)$ should be normalized that is $\Phi(t=0) = 1$ and $\Phi(t \rightarrow \infty) = 0$.

If the temperature is a continuously changing function, $T(t)$, then $q(t)$ can be written in form of integration,

$$q(t) = \int_{-\infty}^t \{c_p(0) + [c_p(\infty) - c_p(0)][1 - \Phi(t - t')]\} \dot{T}(t') dt' \quad (3. 10)$$

where $\dot{T}(t')$ is the derivative with respect to time of $T(t')$.

The expression of the heat in the frequency domain can be obtained by the Fourier transform of its expression in the time domain, that is Eq. (3. 10),

$$q(\omega) = \{c_p(0) + [c_p(\infty) - c_p(0)] \int_0^{\infty} -\dot{\Phi}(t) \exp(-i\omega t) dt\} T(\omega) \quad (3. 11)$$

The frequency dependent heat capacity $c_p^*(\omega) = c_p'(\omega) - i c_p''(\omega)$ is,

$$c_p^*(\omega) = c_p(0) + [c_p(\infty) - c_p(0)] \int_0^{\infty} -\dot{\Phi}(t) \exp(-i\omega t) dt \quad (3. 12)$$

This means that the heat modulation has two components which are in-phase ($c_p'(\omega)$) and out-of phase ($c_p''(\omega)$) with the imposed temperature modulation.

3.2.2 Modulated DSC (MDSC)

In MDSC, a sinusoidal temperature as the external perturbation is superimposed upon an underlying linear temperature change, so that the sample temperature, $T(t)$, at time t is given by,

$$T(t) = T_0 + qt + A \sin(2\pi t/P), \quad (3. 13)$$

where T_0 is the initial temperature for the MDSC scanning, q [K/min] is the underlying heating rate, A is the amplitude of temperature modulation and P [sec] is the modulation period. The temperature changes in both MDSC and conventional DSC are shown in Fig. 3. 8.

Heat flow (HF) from MDSC can be decomposed into two parts: one is reversing heat flow (RHF) and the other is non-reversing heat flow (NHF) in the following equation:

$$dQ/dt = |C_p^*| dT/dt + f(T, t), \quad (3. 14)$$

where $C_p^* = C_p^*(\omega)$ is the complex heat capacity with the magnitude,

$|C_p^*| = \sqrt{C_p'^2 + C_p''^2}$, and $f(T, t)$ is the kinetic component. The complex heat capacity

$c_p^*(\omega) = c_p'(\omega) - i c_p''(\omega)$ can be explained as follows: The real component (c_p') is the true heat capacity of the material, which is related to molecular motion. The heat flow associated with this heat capacity is in-phase with respect to the temperature modulation. The imaginary component of the heat capacity arises from the out-of-phase response of the sample, and has been attributed to kinetic events within the sample, or from the dissipation processes relating to entropy production.

3.2.3. Experimental conditions

The MDSC (TA Instruments, DSC-2920) system was used to investigate the thermal properties of materials. MDSC has various equipment variables to affect the measuring data. These parameters are cell constant, underlying ramp rate, modulation variables (period, amplitude) and rate and quality of the purging gas. The effect of equipment parameters were tested [43]. In this study, we calibrated baseline calibration before each run and used the most suitable modulation variables as follows:

Baseline calibration measures the amount by which the heat flow curve deviates from zero, so that this deviation can be taken into account during calibration. This calibration involves heating the cell through the entire temperature range in which the measurement will be operated. The operated temperature range were from 118 K to 273 K in this study. Baseline calibration is calculated from the heat flow data gathered as an empty DSC cell is heated through the temperature range. The minimum root mean square deviation from the data is calculated to determined the best straight-line.

The modulation period P was fixed at 100 sec to compare the calorimetric glass transition temperature with the dielectric glass transition temperature where the relaxation time is 100 sec.

The most suitable modulation amplitude A is represented as the function of the underlying heating rate and period as guided in the equipment manual, i.e.,

$$A = qP / 2\pi, \quad (3.15)$$

so that the amplitude A was changed only by the underlying heating rate q because of the fixing of $P = 100$ sec. For example, the value of A for 5 K/min heating rate is 1.33 K every 100 sec.

The instrumental resolution of MDSC depends on the product of the heating rate and the modulation period, i.e., qP . The value of resolution, for example, was 8.3 K at 5 K/min heating rate.

The purge gas, which flows through the cell during the experiment, was helium with the flow rate of 25 cc/min.

The sample was encapsulated in an aluminum pan and loaded into the DSC cell at room temperature. The weight of sample was between 10 and 20 mg. And then it was first heated to 313 K to equilibrate the thermal and structural conditions and cooled through T_g to 118 K at a constant cooling rate of 5 K/min with the modulation amplitude 1.33 K every 100 sec. The sample was kept at the isothermal 118 K for 10 min and then heated to 313 K through the glass transition region with the same ramp and modulation of the cooling case.

Fig. 3. 9 shows the cross section of the DSC cell chamber. Constantan disc is used as a primary heat-transfer. A silver heating block, capped with a vented silver lid, encloses the constantan disc. The selected sample and reference are placed in pans that sit on raised positions of the disc. Heat is transferred through the constantan disc to both the sample and reference pans. Differential heat flows to the sample and reference pan and is monitored by the chromel-constantan area thermocouples formed at the junctions of the constantan disc and the chromel wafer welded to the underside of the two raised portions of the disc. Chromel and alumel wires are connected to the chromel wafers at the thermocouple junctions to measure the sample temperature. The alumel wire welded to the reference wafer is for thermal balance.

3.3 Choice of materials

To investigate the slow dynamics of the materials with -OH group, the relaxational and calorimetric features of various alcohols were measured in a wide temperature range. The chemical structures of the materials are illustrated in Fig. 3. 10. These samples are classified to intermediate glass-forming liquids according to the Angell's classification. The monomers among these chemicals were distilled and desiccated by molecular sieves 3 Å prior to use.

For the case 1, there are three monomers, n-Propanol (nPrOH), Propylene Glycol (PG) and Glycerol (Gly). These chemicals have the same backbone of -C-C-C- but different number of -OH groups which increases from one to three for nPrOH, PG and Gly. The nPrOH was purchased from Tokyo Chemical Industry Co., Ltd. The purity of nPrOH is 99.5%. The PG and Gly were purchased from Wako Pure Chemical Industries, Ltd.

The relaxational behavior varies due to the structure of the molecule. The structure of

propanol changes from the attached position of the -OH group to the -C-C-C- skeleton. For the case 2, the role of structural difference investigated by comparing the dynamical properties of nPrOH and i-Propanol (iPrOH). Two propanols have the same molecular weight ($M_w = 60.1$ g/mol) and the same backbone of -C-C-C-. However, the position of the -OH group for both propanols is different. The iPrOH was purchased from Tokyo Chemical Industry Co., Ltd. The purity of iPrOH is 99.5%.

For the case 3, the properties of nPrOH and iPrOH were compared with those of nPrOH-d1 (nPrOD) and iPrOH-d1 (iPrOD). Only the hydrogen in the -OH group is deuterated. The molecular weight of the two deuterated propanols is 61.1 g/mol. The both deuterated propanols were also purchased from Tokyo Chemical Industry Co.

For the case 4, the substitution effect between -OH and -OCH₃ groups was studied in order to investigate the role of hydrogen bond in both glass transition and slow relaxation. The samples studied are PG, its oligomers with two -OH groups, Propylene Glycol Monomethyl Ether (PGME), and its oligomers with both -OH and -OCH₃ groups as its end group.

For the case 5, we studied the structural relaxation of several alcohols with two -OH groups, i.e., PG and its five kinds of oligomers (Poly Propylene Glycol, PPG) with [OCHCH₃CH₂] repeat chain unit which has the similar chemical structure with intermolecular hydrogen bonding but different molecular weights ranging from 76 to 4000 g/mol. The tPG was purchased from Tokyo Chemical Industry Co., Ltd. and the other oligomers were purchased from Aldrich Chemical Company, Inc.