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CONSTRUCTION OF A HEAT CAPACITY SPECTROMETER AND APPLICATION TO SOME MOLECULAR GLASS FORMING SUBSTANCES

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SUMMARY

A heat capacity spectrometer which works in the frequency region between 10 Hz and 10 kHz has been constructed. Measurements have been made for molecular glass forming substances such as glycerol, propylene glycol and their mixtures. The frequency-dependent heat capacities are clearly observed near the glass transition temperatures.

INTRODUCTION

The heat capacity of a substance is defined as amount of heat required to increase a unit of temperature, and usually considered as static value of a thermodynamic quantity. However, near the glass transition temperature, the heat capacity depends strongly on the time that is relaxation phenomenon, and a kind of dispersion in heat capacity is expected to be observed as a function of the measuring frequency. So-called AC calorimetry may be applicable to such measurements in the lower frequency region less than c.a. 1 Hz. At higher frequencies, thermal uniformity can not be held throughout the specimen because of finite value of thermal diffusivity. Recently, Birge and Nagel have developed a new technique which is suitable for measuring the dynamical heat capacity in the wide frequency range from 0.035 Hz to 3.5 kHz (refs. 1-3). An important characteristic of the technique is that the electric heater resistor is used as the thermometer at the same time.

The relaxation phenomenon which is essential to the glass transition has been widely studied by measuring the frequency dependence of the dielectric constants, viscoelasticity and so on. It must be very fruitful to extend such studies of relaxation mechanism to the field of calorimetry by using the new heat capacity spectroscopy (refs. 1-3).

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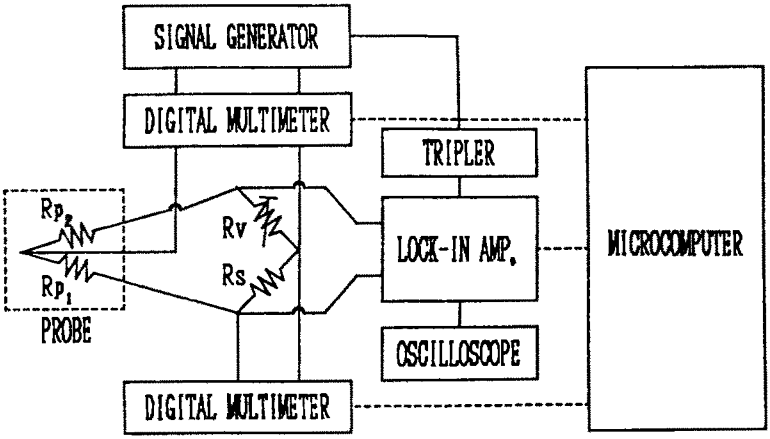

Fig. 1. Block diagram of the system of heat capacity spectroscopy.

EXPERIMENTAL

The block diagram of the heat capacity spectrometer is shown in Fig. 1. The probe resistor works as both heater and resistance thermometer. Sinusoidal current $I(t)=I_0\cos(\omega t/2)$ generated by the low distortion signal generator (E1202, NF Electronic Instruments) is supplied to the heater/thermometer. Thus, a heat flux $J(t)=(I_0{}^2R_0/2S)(1+\cos(\omega t))$ is introduced into the sample. Here S is the surface area of the heater. The temperature of the heater/thermometer oscillates at the frequency ω as $T(t)=T_{dc}+T_0\cos(\omega t-\phi)$. T_{dc} is the average temperature of the heater/thermometer and T_0 is the amplitude of the temperature oscillation. Since the resistance of the heater/thermometer depends on temperature, the resistance also oscillates at the frequency ω as $R(t)=R_0(T)+\alpha R_0(T)T_0\cos(\omega t-\phi)$, where α is the temperature coefficient of resistance of the heater/thermometer. The voltage across the heater/thermometer is represented approximately as

$$
\begin{aligned}
V(t)&=I(t)R(t)\\
&\simeq I_0R_0(T)\cos(\omega t/2)+(1/2)\alpha I_0R_0(T)T_0\cos(3\omega t/2-\phi). \qquad (1)
\end{aligned}
$$

The second term is of the third harmonic of the driving frequency and can be measured separately from the total signal $V(t)$ by using two-phase lock-in amplifier (5610A, NF Electronic Instruments). The reference signal of the frequency $3\omega/2$ is generated by the frequency tripler (ref. 3). In order to measure the small voltage at the frequency $3\omega/2$ superimposed on the much larger voltage at $\omega/2$, the heater/thermometer is put into an arm of Wheatstone's bridge. When the bridge is balanced at the supplied frequency $\omega/2$, only the $3\omega/2$ signal is taken into the lock-in amplifier. The amplitude of the temperature oscillation is determined from the equation (1). The balance condition of the bridge varies depending on the resistance change of the heater/thermometer, and the adjustment is required during the experiments. To avoid this procedure, two heaters/thermometers which have the same α and different resistance have been introduced into the arms of Wheatstone's bridge. Thus, the balance condition $R_{p1}/R_{p2}=R_s/R_v$ is always satisfied. The balance condition is monitored with an oscilloscope (model 552JS, Kikusui Electronics Corp.). The current through the heater/thermometer and the values of resistance of R_{p1} and R_{p2} are obtained by measuring the voltages across the bridge and R_s with digital multimeters (TR-6851, Advantest Corp.). The temperature dependences of R_{p1} and R_{p2} were measured prior to the experiments. The average temperature of the sample (T_{dc}) is determined from the resistance of R_{p1}. All the measurements are made automatically by the microcomputer (PC-9801vm2, NEC Corp.) connected with IEEE-488 bus lines.

Two types of probes were tested. One is thin nickel film vapor-deposited onto a glass substrate. The probe is shown schematically in Fig. 2. The thick copper films deposited onto the glass are used as electrical leads. The copper lead wires are connected to the thick copper films by pressing with indium metal.

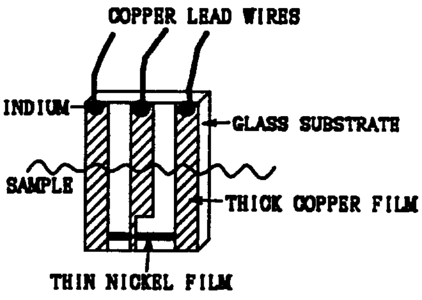

Fig. 2. Probe of the thin film method.

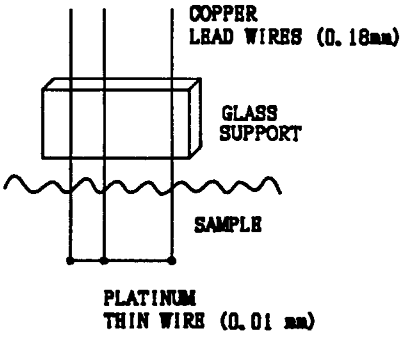

Fig. 3. Probe of the fine wire method.

The amplitude of temperature oscillation is given as

$$T_\theta = (I_0{}^2 R_0/2S)\exp(i\pi/4)/(\sqrt{\omega C_p \kappa}+\sqrt{\omega C_{p\,\mathrm{sub}}\kappa_{\mathrm{sub}}}). \qquad (2)$$

where $C_{p\,\mathrm{sub}}$ and κ_{sub} are the heat capacity and thermal conductivity of the substrate, respectively. The value of $C_p\kappa$ (thermal effusivity of the sample) is estimated by subtracting the value of $C_{p\,\mathrm{sub}}\kappa_{\mathrm{sub}}$ which is obtained by measuring the empty cell. As the thermal conductivity (κ) is less temperature-dependent near glass transition temperature, the change in the $C_p\kappa$ can be considered to be due to the heat capacity (C_p). The other type of probe is a platinum wire (0.01 mm in diameter, about 10 and 5 mm in length) (Fig. 3). Although the amplitude of the temperature oscillation T_0 represents rather complicated function of C_p and κ, this probe is rather easy to handle compared with the thin film probe.

A simple conventional cryostat was constructed for the heat capacity spectrometer working in the temperature range from 100 to 400 K. The major portion of the cryostat is shown in Fig. 4. The sample is put into a glass tube (30 cm^3 in volume) together with the probe and thermocouple (type E). They are in the copper mantle (50 mm in diameter, 5 mm in wall-thickness, 100 mm in length). The assembly is placed in a Dewar vessel which is used as empty or filled with liquid nitrogen depending on the operation temperature.

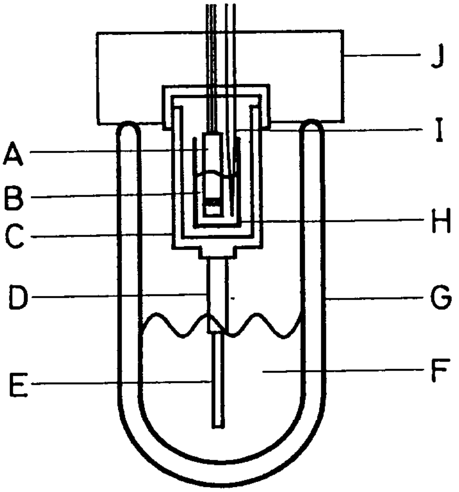

Fig. 4. Cryostat of the heat capacity spectrometer.
A, heater/thermometer; B, sample;
C, copper mantle; D, brass rod;
E, copper rod; F, liquid nitrogen;
G, Dewar vessel; H, sample vessel;
I, thermocouple; J, foaming polystyrene.

The apparatus was tested by measuring the frequency-dependent heat capacities of the typical glass forming substances of commercially available glycerol and propylene glycol (Special Grade, Wako Pure Chem. Ind., Inc.) near the glass transition temperature. The measurements for mixtures of glycerol and propylene glycol were also carried out with the fine wire method to investigate the composition dependence of glass transition temperature.

RESULTS AND DISCUSSION

The results of the measurements carried out for glycerol at a frequency of 4.4 kHz in the cooling direction by using the thin film method are shown in Fig. 5, where the temperature dependences of the real part (upper) and the imaginary part (lower) of the thermal effusivities $C_p\kappa$ are given. On the cooling the real part of $C_p\kappa$ decreases at about 225 K, where the imaginary part has a peak.

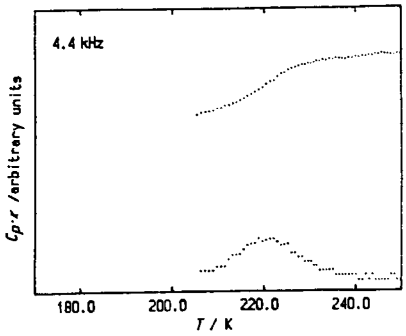

Fig. 5. Complex thermal effusivity of glycerol measured at 4.4 kHz.

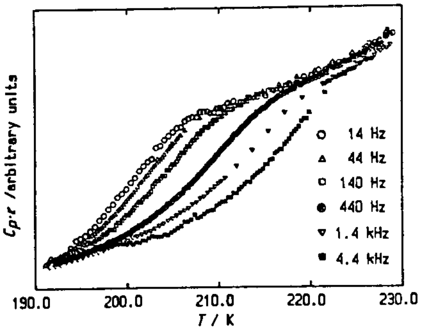

Fig. 6. Real part of thermal effusivity of glycerol near the glass transition temperature.

At the peak temperature, the frequency of the relaxation process is considered to be the same as the measurement frequency, and the temperature is regarded as the glass transition temperature T_g at the frequency. The Kramers-Kronig relation seems to be satisfied between the real part and imaginary part of the thermal effusivity. The real parts of the thermal effusivities $C_p\kappa$ measured at various frequencies are shown in Fig. 6. The temperature where the real part changes decreases with decreasing the frequency of measurements. Thus, the relaxation time in the sample increases as the temperature decreases. The glass transition temperature measured by a static experiment (adiabatic calorimetry) (ref. 4) is about 190 K which is much lower than the present results. Figure 7 shows the frequency dependence of the T_g measured by the fine wire method for glycerol and propylene glycol.

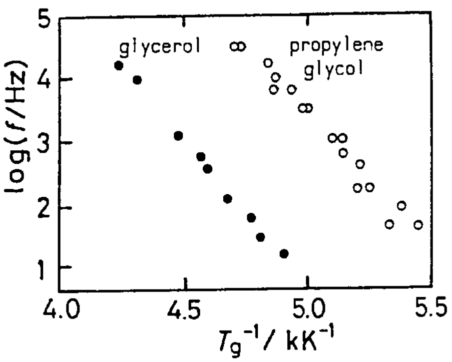

Fig. 7. Frequency dependences of glass transition temperatures of glycerol and propylene glycol.

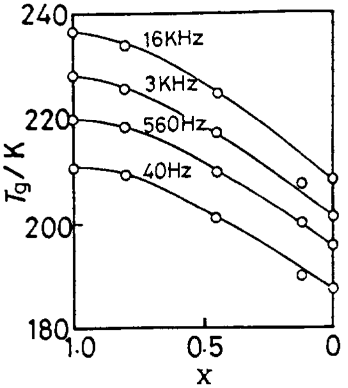

Fig. 8. Glass transition temperature versus mole fraction for (glycerol)$_x$(propylene glycol)$_{1-x}$.

The measurements were made also for binary mixtures of glycerol and propylene glycol. The results are given in Fig. 8, which shows positive deviation from simple linear relation between T_g and composition x. There have been some reports of such studies by differential thermal analysis (DTA) (refs. 5,6), and in most cases, simple linear composition dependence is observed for the T_g. There are some cases of positive or negative deviations from the linear relation. For the deviations, a semiquantitative analysis has been made by Gordon et al. (ref. 7) on the basis of configurational entropy theory. The heat capacity spectroscopy developed by present investigation must be useful also to clarify such problems. The detailed analysis of this result will be discussed elsewhere.

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