Evaluation of Dielectric Permittivity by DC Transient Current Method

by

Ryusuke NOZAKI,

Shin YAGIHARA,

Shoji TAKEISHI

and

Satoru MASHIMO

Department of Physics, Faculty of Science, Tokai University

(Received on Oct. 19, 1982)

Refinements in the dc transient current method using a fast transient recorder are described for precision measurement of dielectric permittivity over a wide frequency range from 1 μHz to 10 Hz. For numerical Fourier transformation of the transient current observed, convenient procedure is described to obtain the complex permittivity easily and quickly over an extremely wide frequency range.

1. Introduction

Recent techniques of measuring dipolar relaxation process in time domain are remarkablly developed. Complex permittivity can be measured easily over an extremely wide frequency range from 1 μHz to several GHz.[1-7] An example is the time domain reflectometry method developed by Cole et al.[1,2] A step pulse applied to dielectric sample in a coaxial line, which is terminated by an open circuit, and a reflected wave form from the sample is measured in the time domain together with the applied pulse form. Fourier transformations of these two forms give the complex permittivity. Recent refinements have made it possible to measure the complex permittivity from 100 kHz to several GHz.

Pseudorandom noise dielectric spectroscopy method developed by Wada et al.[4,5] covers frequency range from 0.1 Hz to 1 MHz. A pseudorandom noise is applied to a sample and its response function is measured in a time domain. Fourier transformation of the function gives the complex permittivity.

Another example of dielectric measurement in time domain is the dc transient current method which is, in principle, the simplest method of measuring the dipolar relaxation process.[7-9] However it has long been thought that this method covers only mHz region, because the transient current smaller than 10^{-12} A is too small to be measured. Fourier transformation of the transient current gives the complex permittivity. Recent refinements of this method by Takeishi et al.[10] have made it possible to measure even a small current of the order 10^{-16} A during a long time period of 10^5 sec. Complex permittivity over a low frequency range from 1 μHz to 0.1 Hz can be measured with sufficient accuracy by this method. When the transient current is recorded and digitized by a fast transient recorder, the dc transient current method is expected to be useful for measurements in higher frequency region, too. In this paper, a precise description of measuring system of the dc transient current method using a transient recorder is given.

In general, relaxation processes observed in the low frequency region have a wide distribution of the relaxation times. Therefore Forier transformation of the current has to be performed over a wide frequency range. In this paper, a precise and convenient procedure for numerical Fourier transformation of the current is described in detail to obtain the complex permittivity easily and quickly over the wide frequency range. Examples of the measurments are given for poly (vinyl acetate), PVAc.

2. Principle

For a sample section with geometric capacitance C_0 subjected to a time dependent voltage $V(t)$, the corresponding charge $Q(t)$ for a linear dielectric is given by

$$Q(t)=C_0[\varepsilon_\infty V(t)+\int_{-\infty}^{t} dt'\dot{\Phi}(t-t')V(t')], \tag{1}$$

where ε_∞ is the high frequency limiting permittivity and $\Phi(t)$ is a response function.

When a step voltage $V(t)=0$ $(t<0)$, $V(t)=V_0$ $(t>0)$ is applied to the dielectric, the transient current $I(t)$ is given by

$$I(t)=dQ(t)/dt=C_0V_0[\varepsilon_\infty\delta(t)+\dot{\Phi}(t)]. \tag{2}$$

The response function $\Phi(t)$ is related to the complex permittivity by

$$\varepsilon^*=\varepsilon'-j\varepsilon''=\varepsilon_\infty+\mathscr{L}\dot{\Phi}(t), \tag{3}$$

$$\mathscr{L}\dot{\Phi}(t)=\int_0^\infty \exp(-j\omega t)\dot{\Phi}(t)dt. \tag{4}$$

Substitution of eq. (2) into eq. (3) gives

$$\varepsilon^*=(1/C_0V_0)\mathscr{L}I(t). \tag{5}$$

This equation means that the complex permittivity is obtained by Fourier transformation of the transient current.

3. Measuring System

The block diagram of measuring system of the dc transient current method employed here is shown in Fig. 1.

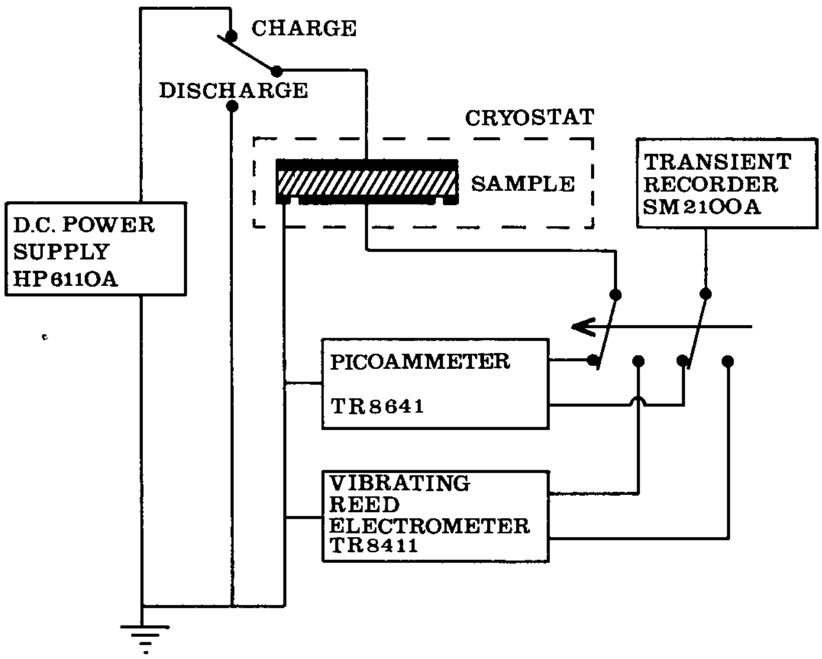

Fig. 1. Block diagram of measuring system of dc transient current.

In a short time region, the current falls quickly. After a while the current decreases slowly. The intensity of the current is small, sometimes smaller than 10^{-12} A. In order to measure such a current in the whole range of time, two different kinds of ammeters are used. For the measurement in the short time region, a picoammeter (TR8641 ; Takeda Riken) with a fast resonance of 1 msec is employed. For the measurement of the current which decreases slowly, a vibrating reed electrometer (TR8411 ; Takeda Riken) is used, resonance of which is 1 sec. A small current is measured by this electrometer.

The transient current is recorded and digitized by a transient recorder (SM 2100 A ; Iwatsu Electric) which has a A/D converter with resolution of 12 bits and 64 k bytes memories for recording. The current can be recorded for a long time of 10^5 sec using this recorder.

A step pulse of 100-300 V height with rising time of 1 m sec is generated by a regulated dc power supply (HP6110A ; Hewlett Packard) and a snap switch. In order to reduce various kinds of noises, a low noise cable (RG58/C-LN ; Showa Electric Wire and Cable) was used for every cable in the circuit. Sample section was placed in a cryostat in a vacuum of 10^{-3} Torr. Standard resistors and preamplifier in the vibrating reed electrometer were put in a dry box to keep from humidity. The dry box was put again in an electromagnetic shielding box. The whole system is kept at a constant room temperature within ± 1℃. Temperature of the sample is controlled within ± 0.02℃ by a temperature control system. In the case of solid sample, gold was usually evapolated on both sides of the sample film to form electrodes and a guard ring.

After these arrangements, the transient current could be measured down to 10^{-16} A for a long time period from 1 msec to 10^5 sec.

4. Data Aquisition

When the step pulse voltage, $V(t)=0$ $(t<0)$, $V(t)=V_0$ $(t>0)$ is applied to the sample, a charging current is observed as shown in Fig. 2. When the step pulse

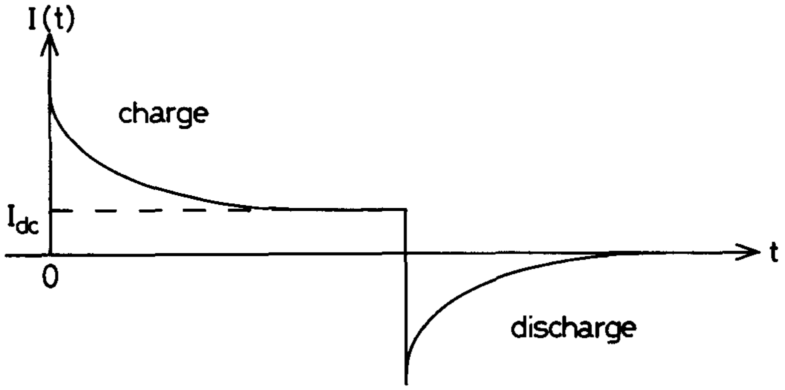

Fig. 2. Schematic charge-discharge current.

voltage, $V(t)=V_0$ $(t<0)$, $V(t)=0$ $(t>0)$ is applied, a charging current has a dc component I_{dc}, but the discharging current does not include the dc component, that is,

$$I_{charge}(t)=I(t)+I_{dc}, \tag{6}$$

$$I_{discharge}(t)=-I(t), \tag{7}$$

where $I_{charge}(t)$ and $I_{discharge}(t)$ are the charging current and the discharging current respectively. Generally it is quite difficult to determine the dc component from the charging current measurement. The transient current is usually obtained from the discharging current measurement.

It is well known that the complex permittivity is described completely by Havriliak-Negami (H-N) equation[11]

$$\varepsilon^*-\varepsilon_\infty=\frac{\Delta\varepsilon}{[1+(j\omega\tau_0)^\beta]^\alpha}, \tag{8}$$

where α is a parameter representing asymmetric distribution of the relaxation times,

β the broadness of the distribution, τ_0 the relaxation time, and $\Delta\varepsilon$ the relaxation increment.

Recently Yagihara et al.[13] have indicated from calculation of inverse Fourier transformation that when log $I(t)$ is plotted against log t, a straight line is obtained in the region of $t/\tau_0 \ll 1$. The slope of the line gives a value of $\alpha\beta-1$. When this slope can be determined, the transient current in a short time region can be estimated sufficiently by extrapolating the observed straight line in the short time region. This short time behavior of the current is very important for the Fourier transformations at high frequencies.

As an example of the measurements, the transient current observed for PVAc is shown in Fig. 3. In this measurement, an electrode of radius 10 mm and a sample

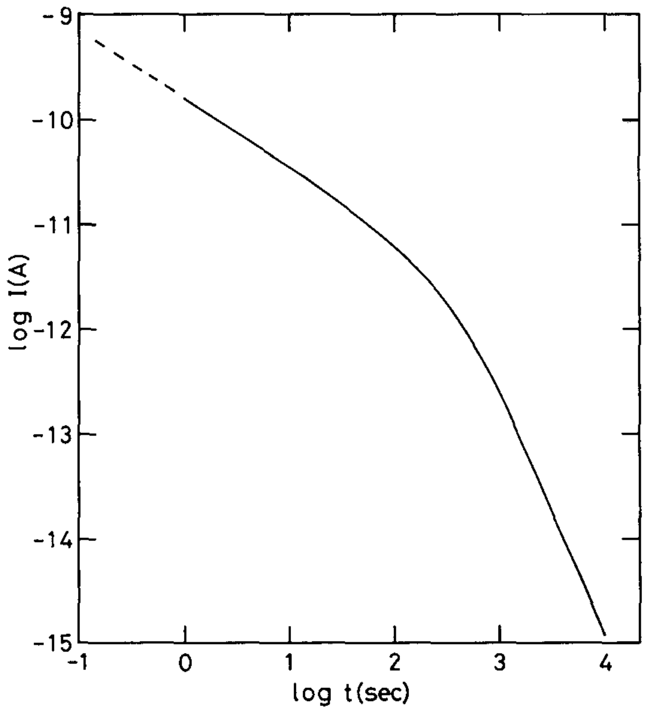

Fig. 3. Transient current $I(t)$ of PVAc at 32.61°C. The dashed line indicates short time behavior of the current estimated by the extrapolation procedure.

thickness 0.656 mm were employed. The applied voltage used was 100 V.

5. Numerical Fourier Transformation

The numerical integration is usually accomplished by a descrete Fourier sum at N equal time interval Δ as

$$C_0 V_0 \varepsilon^* = \Delta \sum_{n=0}^{N} \exp(-j\omega n\Delta) I(n\Delta). \tag{9}$$

Fundamentally this sum can be calculated easily by a computer.

In general, relaxation processes in the low frequency region have a wide distribution of the relaxation times. Therefore measurement of the transient current has to be performed over a long time period such as 10^5 sec. If the same interval Δ is chosen over the whole range of time, extremely large numbers of data have to be used to carry out the Fourier transformation of eq. (9).

Time dependence of the transient current can be seen more definitely if the logarithm of the current is plotted against the logarithm of time. Hence it seems to be more convenient to choose time intervals in logarithmic scale.

The short time limit t_0 at which the trandient current can be measured sufficiently depends largely on the resonance of the electrometer. The highest frequency for the Fourier integration is restricted by the time limit t_0. The imaginary part ε'' of the permittivity, the highest frequency f_{hi} is estimated as

$$f_{hi}=\frac{1}{10^2 t_0}. \tag{10}$$

For the real part ε', the highest frequency f_{hr} is estimated as

$$f_{hr}=\frac{1}{10^6 t_0}. \tag{11}$$

Difference between f_{hi} and f_{hr} comes from the difference between short time behavior of sin (ωt) used for calculation of the imaginary part and that of cos (ωt) in the real part. Current in the short time region is much more effective on the real part than the imaginary part.

Finally we employed the following equation for the Fourier transformation

$$C_0 V_0 \varepsilon''=\frac{1}{2}\sum_{i=0}^{N-1}(t_{i+1}-t_i)[\exp(-j\omega t_i)I(t_i)+\exp(-j\omega t_{i+1})I(t_{i+1})], \tag{12}$$

$$t_{i+1}=10^l t_i,$$

where l represents the time intervals in logarithmic scale. Since the integrand vibrates with the angular frequency ω, it is not convenient to choose l as constant over the whole range of frequency. In the frequency region $f<100/t_S$, l is chosen to be 0.01 over the whole time range, where t_S is a critical time at which $d\log I(t)/d\log t$ takes a value of $\alpha\beta-2$. In the region $f>100/t_S$, l is taken to be 0.01 in the time region $t_0<t<t_S/10$, and 0.001 in $t>t_S/10$.

Usefulness of this program was examined carefully by using a test current. The inverse Fourier transformation of H-N equation with $\beta=1$ can be obtained analytically.[8] Therefore it is possible to compare the result of numerical Fourier transformation of the analytical inverse Fourier transformation and the H-N equation itself. Figure 4 confirms perfectly the adequacy of this program.

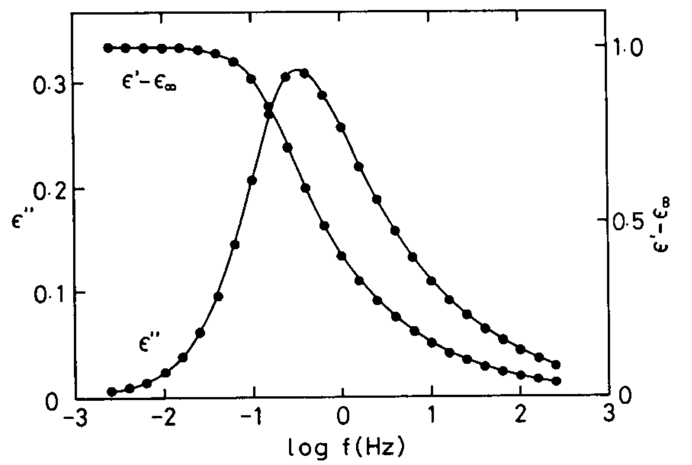

Fig. 4. Dispersion and absorption curves given by H-N equation. Solid curves are calculated directly from H-N equation with $\alpha=0.4, \beta=1.0, \Delta\varepsilon=1.0$, and $\tau_0=1.0$. Plots are calculated by numerical Fourier transformation of H-N equation for analytical solution.

6. Example of Result

As examples of the results obtained from the dc transient current method, frequency dependence of $\varepsilon'-\varepsilon_\infty$ and that of ε'' for PVAc are shown in Figs. 4 and 5. The results from the steady state measurements using a transformer bridge (TR-10A ; 10-10^6 Hz ; Ando Electric) are also shown. These figures show that the

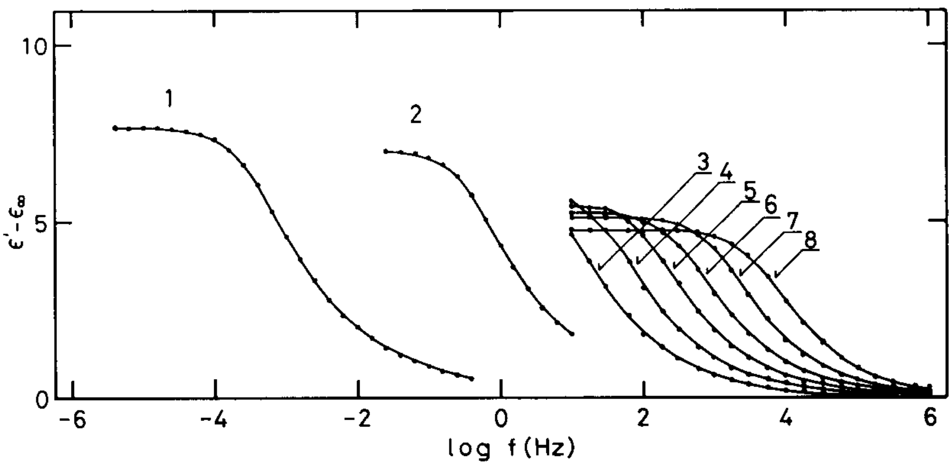

Fig. 5. Dispersion curves of PVAc at various temperatures. 1 : 32.61°C ; 2 : 43.87° ; 3 : 53.10° ; 4 : 57.32° ; 5 : 61.90° ; 6 : 66.15° ; 7 : 70.60° ; 8 : 76.65°. Data in the frequency range from 4 μHz to 10 Hz were obtained from the dc transient current method and those in the range from 10 Hz to 1 MHz were from the bridge measurements. Solid curves were calculated from H-N equation.

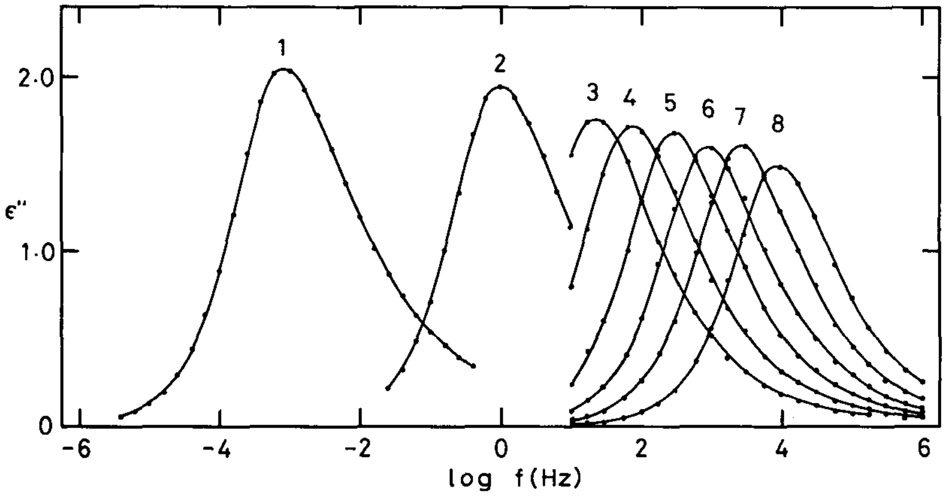

Fig. 6. Absorption curves of PVAc at various temperatures. Solid curves were calculated from H-N equation. Temperatures are indicated by the same numbers as those in Fig. 5.

complex permittivity can be described completely by H-N equation. The numerical Fourier transformation were carried out using a computer (UNIVAC 1100/80B; Computer Center, Tokai University).

In the pervious papers,[10,12] it was reported already that results of the complex permittivities of PVAc obtained from the dc transient current method are quite reasonable and accuracy is satisfactory as compared with those obtained from the bridge measurements.

7. Discussion

Complex permittivity in the frequency range from 1 μHz to 10 Hz can be measured easily with sufficient accuracy by the dc transient current method if an appropriate system and also an appropriate computer program are employed, as described above. The system presented here is fairly convenient to record and digitize the transient current. The program presented is very useful for all relaxation processes which have a wide distribution of the relaxation times such as dielectric relaxation process observed in the low frequency region.

However it should be noted that the extrapolation procedure of the current in the short time region is available only for a single relaxation process. If two or more relaxation processes are included, the short time behavior of the current is much more complicated than that of a single relaxation process. In those cases, the extrapolation procedure presented here cannot be used.

Complex permittivity at frequencies lower than 1 mHz can be measured only by the dc transient current method as far as we know. Dielectric behavior observed in this low frequency region will be important especially to interprete the glass transition phenomenon of polymers and the low frequency dielelctric properties of biopolymers such as DNA. The dc transient current method is certainly quite available for these phenomena.

References

1) R. H. Cole, J. phys. Chem. **79**, 1459, 1469 (1975).
2) R. H. Cole, S. Mashimo, and P. Winsor, J. Phys. Chem. **84** 786 (1980).
3) H. Nakamura, S. Mashimo, and A. Wada, Jpn. J. Appl. Phys. **21**, 467 (1982).
4) Y. Husimi and A. Wada, Rev. Sci. Instrum. **47**, 213 (1979).
5) H. Nakamura, Y. Husimi, and A. Wada, J. Appl. Phys. **52**, 3053 (1981).
6) R. Hayakawa and Y. Wada, IEE Conf. Publ. **177**, 396 (1979).
7) S. Uemura, R. Hayakawa, and Y. Wada, Biophys. Chem. **11**, 317 (1980).
8) N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).
9) N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies, *Dielectric properties and Molecular Behavior* (Van Nostrand Reinhold, London, 1969).
10) S. Takeishi and S. Mashimo, Rev. Sci. Instrum. **53**, 1155 (1982).
11) S. Havriliak and S. Negami, J. Polym. Sci. C **14**, 99 (1966).
12) S. Mashimo, R. Nozaki, S. Yagihara, and S. Takeishi, J. Chem. Phys. **77**, 6259 (1982).
13) S. Yagihara et al. unpublished result.