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NEW METHOD FOR SIMULTANEOUS MEASUREMENT OF FREQUENCY SPECTRA OF COMPLEX DIELECTRIC CONSTANTS OF POLYELECTROLYTE SOLUTIONS

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A high-speed and high-accuracy measurement of relaxational frequency spectra of complex dielectric constants of polyelectrolyte solutions with a high conductivity was realized by a new digital signal processing technique. In this method, a sum of sinusoidal waves of geometrical series of frequencies is utilized as a multifrequency excitation signal and demodulation of the resulting response is carried out simply by addition and subtraction of digital signals in a minicomputer. This new technique is superior to the conventional cross correlation method using the fast Fourier transform in that it greatly reduces the processing time and avoids effectively the influence of a quantization error. The result for a DNA solution obtained by this method is presented to demonstrate the utility of this method.

1. Introduction

The measurement of the dielectric relaxational spectra of polyelectrolyte solutions in a wide frequency range provides us with useful informations on the motion of polyelectrolyte molecules as well as small ions around them. Owing to the highly conductive nature of polyelectrolyte solutions, however, a precise dielectric measurement was very difficult at low frequencies if the usual bridge balance methods were used. Difficulties in measuring the complex dielectric constant of polyelectrolyte solutions arise from effects of the electrode polarization and the fluctuation of solution admittance owing to the drift of the d.c. conductivity with time [1].

In order to remove these two difficulties, we previously developed a measuring apparatus in which two techniques were employed [1,2]: one was a four-electrode technique useful for avoiding the effect of electrode polarization and the other was the simultaneous measurement of specimen impedances $Z(\omega)$ and $Z(\omega_0)$ at two frequencies (variable, measuring frequency ω and fixed, reference frequency ω_0) by use of the sum of sinusoidal waves of ω and ω_0 as an excitation signal. The difference $\Delta Z = Z(\omega) - Z(\omega_0)$ thus obtained does not include the contribution of d.c. conductance, and hence the influence of conductivity drift can be perfectly eliminated by this technique. This measuring apparatus made it possible to observe low-frequency dielectric relaxations of DNA [3–5] and collagen [2].

In this paper, we describe a new method for simultaneous measurement of the relaxational frequency spectrum of the complex dielectric constant with a digital signal processing technique. In this method, we employ as an excitation signal a sum of sinusoidal waves of geometrical series of frequencies and analyze the resulting response by a digital phase sensitive detection technique using reference signals of square waveform.

This multifrequency method which is a straightforward generalization of our previous two-frequency method is also unaffected by the influence of conductivity drift because an overall frequency spectrum of specimen admittance can be simultaneously obtained in a short time during which the conductivity remains constant. In addition, this method greatly reduces the measuring time compared with our previous method which requires a repetition of measurements for each ω to obtain an overall frequency spectrum.

An outline of the new method and exemplifying data obtained by the method will be presented in this paper.

2. Outline of the measuring apparatus

Essential points of our new measuring principles which can be applied to relaxational frequency spectra of any kinds of response functions have been already reported elsewhere [6] and are briefly summarized for a special case of the dielectric relaxational spectrum measurement as follows.

A sum of sinusoidal waves

$$\sum_{n=1}^{N} \sin \omega_n t \tag{1}$$

is applied to a specimen as an excitation signal (the electric field E), where the angular frequency ω_n makes a geometrical series of common ratio of 2 as

$$\omega_n = 2^{n-1}\omega_1 , \quad n = 1,2,\ldots N. \tag{2}$$

The signal (1) which has a discrete but uniform distribution of the power spectrum on the logarithmic frequency scale is a most suitable one for measuring relaxation-type frequency spectra of response functions, because this type of spectra exhibits a broad distribution spread over 3 or 4 decades of the frequency range even for the case of a single relaxation time.

Recently, a cross correlation method (fast Fourier transform method) using a pseudorandom noise as a multifrequency excitation signal was applied to the dielectric spectrometry by Husimi and Wada [7]. In this kind of multifrequency method, the power spectral density of the excitation signal is uniform on the linear frequency scale and therefore rapidly decreases at the lower frequency side on the logarithmic frequency scale. The measuring accuracy in this case is greatly reduced at lower frequencies due to a quantization error arising in the A/D conversion process which precedes the fast Fourier transform of digitized data. For avoiding this disadvantage, Nakamura et al. [8] adopted the $1/f$ noise as an excitation signal instead of the random noise, but the quantization error in the A/D conversion is still serious.

On the other hand, our present method using the frequency series (2) is free from this influence of the quantization error.

The multifrequency response (the electric displacement D) which results from the excitation signal (1) is expressed as

$$\sum_{n=1}^{N} (A_n \sin \omega_n t + B_n \cos \omega_n t) . \tag{3}$$

The coefficients (A_n, B_n) in (3) are related with the complex dielectric constant $\epsilon^*(\omega_n) = \epsilon'(\omega_n) - j\epsilon''(\omega_n)$ for the angular frequency ω_n as

$$A_n = \epsilon'(\omega_n) , \quad B_n = -\epsilon''(\omega_n) . \tag{4}$$

In order to detect (A_n, B_n) for each ω_n and obtain the frequency spectrum of complex dielectric constant, the multifrequency response (3) should be demodulated by sinusoidal waves $\sin \omega_n t$ and $\cos \omega_n t$, respectively. For our frequency series (2), however, the sinusoidal waves can be replaced by square waves, because the square waves include odd harmonics alone while the frequency series (2) include only even harmonics. In demodulation by the square waves, only addition and subtraction are necessary in place of multiplication, since the square waves take merely two values, +1 and −1. The demodulation of this kind is performed most efficiently for all ω_n's simultaneously by a digital signal processing in which addition and subtraction are much easier operations than multiplication.

By this digital phase sensitive detection technique, we can obtain the frequency spectrum of the complex dielectric constant in a wide frequency range in a very short time and with a high accuracy. This high-speed data processing is another advantage to the conventional cross correlation method where the fast Fourier transform involves time-consuming multiplication processes.

The frequency range of the present apparatus covers 0.5 mHz to 1 MHz and is divided into three subranges:

(a) Low frequency (LF) range: 0.5 mHz–30 Hz.

(b) Medium-frequency (MF) range: 30 kHz–1 MHz.

(c) High-frequency (HF) range: 30 kHz–1 MHz.

Simultaneous measurement of the dielectric spectrum is performed separately for each subrange on account of the requirements of system hardware and software.

The outline of the apparatus is as follows. A sum of sinusoidal waves of the frequency series (2) is synthesized by signal generators external to a minicomputer for MF and HF ranges, or by a minicomputer software for the LF range, and is fed to the specimen as an excitation voltage V. The resulting current output I from the specimen is detected by a charge amplifier after a rough cancellation of its conductive component by a conductance compensator. These V and I signals are then converted to digital quantities by a high-speed

A/D converter for LF and MF ranges or by a waveform recorder (ultrahigh-speed A/D converter with a buffer memory) for the HF range. Digital V and I signals are fed to the minicomputer and are demodulated by the digital phase sensitive detection technique using a minicomputer firmware (microprogramming). From the ratio of complex amplitudes of I and V obtained in this way, we get the apparent complex dielectric constant ϵ^* for all frequencies in each subrange simultaneously.

In the present high-speed dielectric measurement, a two-electrode cell with variable electrode separation can be used in place of a four-electrode cell in order to eliminate the effect of electrode polarization impedance Z_p, because we can neglect the drift of Z_p for a short time during which two runs of measurements are made for two electrode separations.

After obtaining the data of the apparent complex dielectric constant, we carry out a best fitting of the semi-empirical formula for the observed spectrum:

$$\epsilon^*(j\omega) = \sum_{k=1}^{3} \frac{\Delta\epsilon_k}{[1+(j\omega\tau_k)^{\beta_k}]^{\alpha_k}} + \epsilon_\infty + \frac{\sigma}{j\omega\epsilon_0} + \frac{A}{(j\omega)^\gamma}. \quad (5)$$

Here, the first terms on the rhs of eq. (5) correspond to the dielectric relaxation of the Havriliak-Negami type which is a general expression of the relaxational spectra [9]. The second term is the high-frequency limit of the dielectric constant, and the third term the contribution of d.c. conductivity σ where ϵ_0 is the vacuum permittivity. The fourth term which is the correction for the electrode polarization impedance may be added when necessary.

The purpose of the best fitting is to pick up the first, relaxational terms separately from the other terms which are overwhelmingly large at low frequencies for highly conductive specimens such as polyelectrolyte solutions. The best-fitted parameters $\Delta\epsilon_k$, τ_k, α_k, β_k, ϵ_∞, σ, A and γ are determined by the least-square method with minicomputer software. Eq. (5) is a nonlinear function of the parameters, and the least-square method is applied iteratively to a linearized form of eq. (5).

3. Exemplifying data

To exemplify the effectiveness of the present apparatus, we measured the dielectric spectrum of an aqueous solution of sodium salt of salmon testes DNA at 10°C in the MF range of this apparatus. The DNA used was a sonicated one whose average molecular weight was 5×10^5, and the DNA concentration in solution was 0.2% in weight. The concentration of added salt (NaCl) was 1 mM. The specimen cell was a two-electrode cylindrical cell of variable electrode separation type with a diameter of 1.1 cm. The diameter of the electrodes made of platinum-black was 1.0 cm. The electrode separations of the cell were varied as 8.0 and 3.0 cm.

By applying the best fitting procedure above described to the frequency spectrum of the difference between the specimen impedances for the two electrode separations, we obtained the frequency spectrum of the complex dielectric constant as shown in fig. 1, where

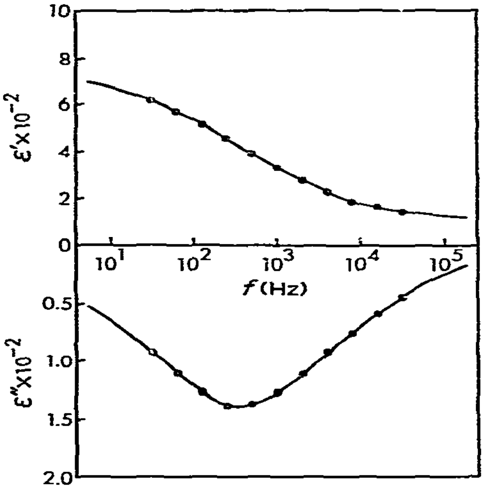

Fig. 1. Complex dielectric constant of DNA in aqueous solution. Points and curves represent experimental values and best-fitted curves, respectively.

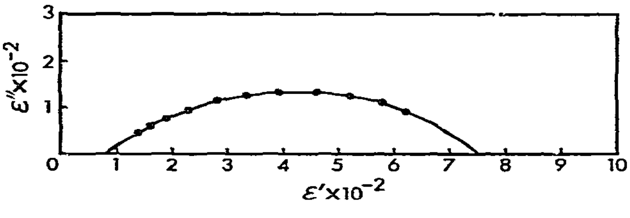

Fig. 2. Cole-Cole plot of the data in fig. 1.

the points and the curves represent experimental values and best-fitted curves, respectively. In fig. 1, the d.c. conductivity component has been perfectly eliminated and the curve fitting is found to be quite satisfactory. Fig. 2 illustrates a Cole-Cole plot of the data in fig. 1 and clearly shows the existence of a broad and nearly symmetrical distribution of relaxation times.

From the curve fitting, the values of dielectric relaxation parameters were determined as

$$\Delta\epsilon = 6.7 \times 10^2, \quad \tau = 0.53 \text{ ms}, \quad \alpha = 0.91, \quad \beta = 0.50. \tag{6}$$

In this case, the d.c. conductivity σ of the solution was 8.3×10^{-4} mho cm^{-1}, and hence the ratio of admittance component due to the dielectric loss to the d.c. conductance was as low as 2×10^{-6} at the lower limit of MF range. The complex dielectric constant in fig. 1 was obtained by eliminating such an overwhelmingly large d.c. conductance from the original data by use of the best fitting procedure.

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