Electric Properties of Ionic Polysaccharide *Sacran* Aqueous Solutions

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We have investigated the electric conductivity and dielectric constant of an aqueous solution of polysaccharide, *Aphanothece sacrum*, that is called *sacran*. The molar conductivity at high concentrations obeyed Kohlrausch's law. The equivalent conductivity at infinite dilution was in good agreement with that of Na^+ ion in an aqueous solution. The complex dielectric constant ε^* of the aqueous solutions was measured from 42 Hz to 5 MHz by an ac two-terminals method. The dielectric spectra of the aqueous solutions after subtracting the electrode polarization effect could be fitted by two Debye type relaxations. The low frequency relaxation and high frequency one appeared at 100 Hz and 100 kHz, respectively. The low frequency relaxation time for the aqueous solution of 2.0×10^{-3} wt.% was determined to be 2.1×10^{-3} s. The contour length of the *sacran* was estimated to be ~5.5 μm using the diffusion constant of Na^+ ion in a free medium. This value was in the same magnitude with the length evaluated from transmission electron microscopy and static light scattering experiments.
Key words: polysaccharide, polyelectrolyte, dielectric relaxation, electric conductivity

1. INTRODUCTION

Polyelectrolytes in the semidilute solution demonstrate two dielectric relaxations; the low frequency relaxation at kHz range and high frequency one at MHz range [1]. Both relaxations are based on a strong Coulombic attractive force from the potential well on the polyion. According to the various reports [1-12] the molecular mechanism of these two relaxations has been understood as follows. The low frequency relaxation strongly depends on the degree of polymerization or the molecular weight of a polyion [2-7]. Therefore, the relaxation is ascribable to the fluctuation of strongly bound counterions along the polyion [8]. On the other hand, the high frequency relaxation is nearly independent of the degree of polymerization [8-10]. Accordingly the high frequency relaxation is attributed to the fluctuation of loosely bound counterions spreading over the average distance between polyions [11, 12].

We have mainly discussed here the low frequency relaxation of a polysaccharide aqueous solution. The dielectric relaxation at low frequency regime gives us important information related to the characteristics length of polyion. In spite of this, there have been few reports describing the molecular mechanism of the low frequency relaxation. One main reason is that the large electrode polarization effect is significant particular in the low frequency regime [13]. The low frequency relaxation has to be extracted from the large capacitance of the electrode polarization. In our experiment, the relaxation component values to >6 % of the capacitance of the electrode polarization. Accurate measurement is acquired in order to detect the low frequency relaxation.

In this paper, electric properties mainly dielectric properties of an ionic polysaccharide have been reported. The ionic polysaccharide is a huge sugar chain which was extracted from *Aphanothece sacrum* (*A. sacrum*).

The radius of gyration of the *sacran* was estimated to be 400 nm by a Zimm-Berry plot in static light scattering. The molecular weight was determined to be 2×10^4 kg/mol by gel permeation chromatography [14]. We have tried to determine the fluctuation length of strongly bound counterion in order to know the contour length of the *sacran*.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of Sacran Aqueous Solutions

Sugar chains were extracted from *A. sacrum* by the following procedure. The *A. sacrum* samples were freeze-thawed and washed in pure water, followed by lyophilization. The samples were washed three times using a large amount of ethanol with shaking (120 rpm) overnight, and then collected by filtration using gauze. The ethanol-washed samples were put into 0.1 M NaOH aq. at 100 °C, and agitated at constant temperature for 4 h to yield the transparent solution. The solution was dialyzed with pure water for more than 72 h using the regenerated cellulose membrane (MWCO: 14000) until the pH value decreased to 8.0–9.0, and then filtrated. Then the filtrate was concentrated by rotary evaporator to create a highly viscous solution. The viscous solution was slowly poured into 100 % isopropanol (1000 ml) to precipitate white fibrous material. The fibers were dissolved in hot water again, concentrated, and reprecipitated, and these operations were repeated three times in total. The fibrous precipitates in isopropanol were collected and dried using vacuum oven.

2.2 Electric Measurements

The complex dielectric constant ε^* of *sacran* aqueous solutions was measured by an ac two-terminals method using an LCZ meter (HIOKI 3532-50). The frequency range was from 42 Hz to 5 MHz, and the applied voltage was 0.1 V. The sample cell used in the present study was
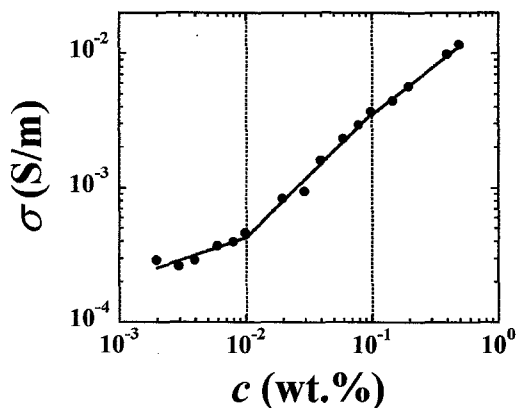
Fig. 1. Electric conductivity vs. concentration of *sacran* aqueous solutions.

Fig. 2. Molar conductivity vs. concentration of *sacran* aqueous solutions.

a coaxial type of cylindrical condenser with stainless-steel electrodes. The dielectric measurement was carried out at the room temperature of approximately 25.0 ± 0.5 °C.

3. RESULTS AND DISCUSSIONS

The electric conductivity σ of *sacran* aqueous solutions with various concentrations c is shown in Fig. 1. The conductivity was determined by the relation of $\varepsilon''=\sigma/\omega$, using the values of ε'' at $\omega<10^4$ rad/s. The value of the electric conductivity was distributed from 10^{-4} to 10^{-2} S/m. The conductivity increased with increasing the concentration. Two kinks were seen in the conductivity at 0.01 and 0.2 wt. %. The overlap concentration of the *sacran* was calculated to be 0.012 wt.% using values of unit length (=0.65 nm) and the number of repeating unit (=8.9×10^4). The kink at 0.01 wt.% is considered to be the overlap concentration. On the other hand, it was found from birefringence experiments that the aqueous solution undergoes amorphous-liquid crystal transition at approximately 0.2 wt.%. Probably, the other kink appeared at 0.2 wt.% is originated from the amorphous-liquid crystalline transition.

The molar conductivity of *sacran* aqueous solutions Λ as a function of the square root of concentration was presented in Fig. 2. The molar conductivity at high concentrations obeyed Kohlrausch's law as $\Lambda \sim c^{0.5}$ and rapidly increased with further decreasing the concentration, which is general behavior of polyelectrolyte solutions. The solid line holding the relation of the Kohlrausch's law [19] is shown in Fig. 2. The extrapolated value of the equivalent conductivity at zero concentration gives the specific value of the *sacran* Λ_0. Λ_0 was evaluated to be 59.5 Scm²/mol. This value was in good agreement with the equivalent conductivity of Na^+ in an aqueous solution (=50.1 Scm²/mol). It was found from the electric conductivity that the counterion of *sacran* was Na^+ ion.

The relative complex dielectric constant ε^* is defined by the following equation,

$$\varepsilon^* = \varepsilon' + i\varepsilon'' \quad (1).$$

Here, ε' and ε'' stands for the real and imaginary part of the relative complex dielectric constant, respectively.
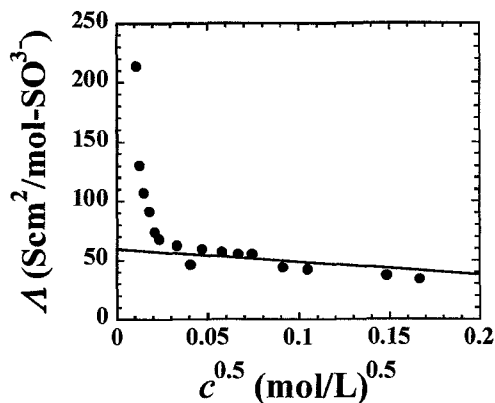
The frequency dependence of the dielectric constant of *sacran* aqueous solution with 0.02 wt.% (as-measured data) is shown in Fig. 3. The dielectric constant in lower frequencies took a huge value of $\sim 10^3$ and it largely decreased satisfying with a power law as $\varepsilon' \sim \omega^{-n}$ ($1.4<n<1.6$ in the present experiment). It is well known that ion-blocking electrodes give rise to a large frequency-dependent polarization at low frequencies, which is called the electrode polarization effect [13]. The large dielectric constant of the *sacran* aqueous solution observed here is clearly interpreted as the electrode polarization effect, not the intrinsic value of the dielectric constant. As described in the introduction, the dielectric response of the *sacran* on which we are focusing is buried under the large electrode polarization. Accordingly, we decomposed the as-measured dielectric constant ε' into the dielectric constant of *sacran* aqueous solutions ε'_s and that of the electrode polarization ε'_{EP};

$$\varepsilon' = \varepsilon'_s + \varepsilon'_{EP} \quad (2)$$

In order to extract the dielectric constant of *sacran* ε'_s, we used the dielectric constant of KCl aqueous solutions ε'_{KCl}. This is the method assuming that the component of the electrode polarization is equal to the dielectric constant of saline solutions with nearly the same electric conductivity as the sample, $\varepsilon'_{EP} \approx \varepsilon'_{KCl}$. This procedure produces an error which is far larger than the errors originating from the apparatus accuracy or the fit of relaxation curves. The concentration of the KCl aqueous solution, of course, varies at each solution. In this study, the measurement was carried out so that the difference in the capacitance of *sacran* and KCl at 42 Hz should be less than 0.5 %. The error bar in Figs. 4 and 5 stands for the variation of relaxation time made by the subtraction procedure.

Typical dielectric spectrum for the KCl aqueous solution is also shown in Fig. 3. Similar electrode polarization effect was observed in the dielectric spectrum of HCl aqueous solution as well as *sacran*. However, note that the dielectric constant of KCl aqueous solution was clearly lower than that of *sacran* in the frequency range of 10^2-10^5 Hz. This strongly suggests that the *sacran* aqueous solution shows a
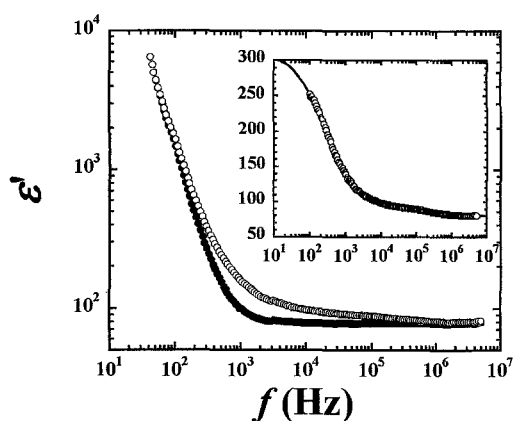
Fig. 3. Frequency dependences of the real part of dielectric constant for *sacran* and KCl aqueous solutions. Inset: Dielectric spectrum of *sacran* aqueous solution after subtracting the electrode polarization effect.

Fig. 4. Low-frequency relaxation time vs. concentration of sacran aqueous solutions.

low-frequency dielectric relaxation in the frequency range. The dielectric constant of the *sacran* at 10^6 Hz was 85, which was equal to the dielectric constant of the KCl aqueous solution (=85) or pure water (=84). This means no dielectric relaxation due to the counterions which were dissociated from *sacran* occurs above 10^6 Hz. Experimental errors were indicated by the arrows, which were estimated by two measurements with different solutions.

The inset in Fig. 3 shows the dielectric spectrum of *sacran* aqueous solutions ε'_s after subtracting the dielectric constant of KCl aqueous solutions ε'_{KCl} from the as-measured data ε'. Large low-frequency relaxation and high-frequency one were observed around at 100 Hz and 100 kHz, respectively.

The dielectric spectra of *sacran* aqueous solutions can be fitted by the following two Debye type relaxations

$$\varepsilon'_s = \varepsilon'_w + \frac{\Delta\varepsilon_L}{2}\left\{1 - \frac{\sinh x_L}{\cosh x_L + \cos(\pi/2)}\right\} + $$
$$\frac{\Delta\varepsilon_H}{2}\left\{1 - \frac{\sinh x_H}{\cosh x_H + \cos(\pi/2)}\right\} \quad (3)$$

, where $x_{L,H}$=$\ln\omega\tau_{L,H}$; ω is the angular frequency of the electric field, $\tau_{L,H}$ is the mean relaxation time of low- or high frequency relaxations. ε'_w is the dielectric constant of pure water, which is equal to 84. $\Delta\varepsilon_{L,H}$ is the dielectric increment of low- or high relaxations. The least mean squares fitting by eq. (3) was carried out and the fitting line is presented in the inset of Fig. 3. Both low- and high- frequency relaxations were well fitted by eq (3) as seen in the figure.

According to the fitting by eq. (3), the relaxation times were obtained. Fig. 4 shows the concentration dependence of the low-frequency relaxation time τ_L. Two kinks corresponding to the kinks seen in the electric conductivity were observed in the relaxation time. When the *sacran* concentration was lower than 0.01 wt.%, the low frequency relaxation time lied in the order of $\sim10^{-3}$ s and it was nearly independent of the *sacran* concentration. Such long relaxation time has
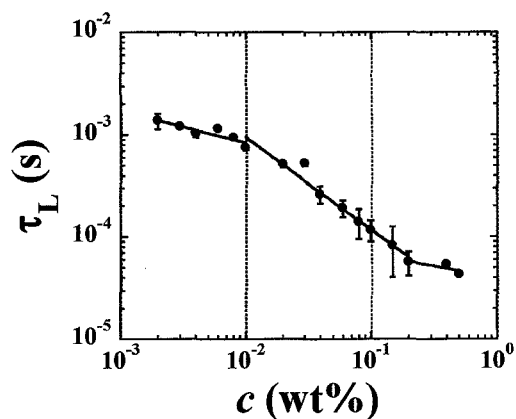
been observed in a polyelectrolyte gel ($0.7<\tau<2.1$ ms) [15] or Na-DNA (τ=6.8×10^{-2} s: degree of polymerization 12000) [16, 17]. As increasing the *sacran* concentration, the relaxation time decreased showing a power dependency. In the liquid crystalline regime at $c\geq0.2$ wt.%, the relaxation time took a value of 10^{-5} s and it was nearly independent of the *sacran* concentration. The first kink at 0.01 wt.% can be considered as the dilute-semidilute transition, and second kink at 0.2 wt.% is probably due to the amorphous-liquid crystalline transition.

As mentioned in the introduction, it has been widely accepted that the low-frequency relaxation arising at kHz is ascribable to the fluctuation of strongly bound counterions along polymer chains [6]. The fluctuation length of the bound counterions can be estimated from the mean relaxation time as follows [7],

$$\tau \cong \frac{L_f^2}{D} \quad (4).$$

Here, L_f and D appear the fluctuation length and the diffusion constant of the bound counterions. We assumed that the diffusion constant is equal to that of Na^+ ion in a free medium (=1.2×10^{-9} m^2/s).

The fluctuation length at $c\leq0.01$ wt.% was determined to be ~1.6 μm using 2.1×10^{-3} s of the mean relaxation time. At $0.01<c<0.2$ wt.%, the fluctuation length decreased satisfying with the relation of $L_{f,L}\sim c^{-0.47}$ and then it was constant to be 100 nm when $c\geq0.2$ wt.%. Assuming a square type potential well along the polymer chain [18], the contour length of the polymer chain L_c can be explained as

$$L_c = \sqrt{12}L_f \quad (5)$$

instead of the fluctuation length L_f in eq.(4). At $c<0.08$ wt.%, the contour length of *sacran* was estimated to be 5.5 μm using a constant value of 1.6 μm of the mean fluctuation length.

The relaxation time, fluctuation length, and contour length for the high frequency relaxation were also
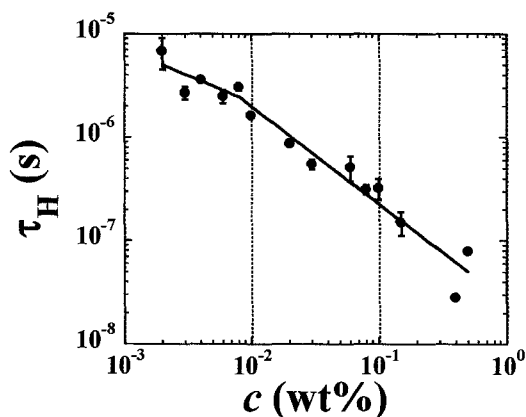
Fig. 5. High-frequency relaxation time vs. concentration of *sacran* aqueous solutions.

determined by means of the same procedure. Fig. 5 shows the *sacran* concentration dependence of the high-frequency relaxation time τ_H. The relaxation time was distributed from 10^{-8} to 10^{-5}, and decreased as increasing the concentration. In the dilute region ($c \leq 0.01$ wt.%), the relaxation time decreased as $\tau_H \sim c^{-0.52}$. This means that the fluctuation length of loosely bound counterions behaves as $\xi_H \sim c^{-0.33}$. This strongly suggests that the loosely bound counterions fluctuate between the polyions. In the semidilute regime below the amorphous-liquid crystalline transition ($0.01 < c < 0.2$ wt.%), the relaxation time decreased as $\tau_H \sim c^{-0.91}$; that is, the fluctuation length of loosely bound counterions varies as $\xi_H \sim c^{-0.5}$. Similar concentration dependency was observed in sodium poly(styrene sulfonate) (NaPSS) aqueous solutions [8]. The high frequency relaxation of *sacran* aqueous solution can be understood by the cell model as well as the NaPSS solution.

4. CONCLUSION

The electric conductivity and dielectric constant of the polysaccharide aqueous solution (*sacran*), which was extracted from *Aphanothece sacrum*, have been investigated. The equivalent conductivity at infinite dilution was in good agreement with that of Na^+ ion in an aqueous solution. This revealed the counterion of the *sacran* is Na^+ ion. The dielectric spectrum of the aqueous solution demonstrated a large value of the dielectric constant at low frequencies, indicating electrode polarization effect. The dielectric spectra after subtracting the electrode polarization suggested that the low frequency relaxation and high frequency one appeared at 100 Hz and 100 kHz, respectively. Both relaxations could be fitted by Debye type relaxation. The low frequency relaxation time for the aqueous solution of 2.0×10^{-3} wt.% was determined to be 2.1×10^{-3} s. The contour length of the *sacran* was estimated to be ~1.6 μm using the diffusion constant of Na^+ ion in a free medium. This value was in the same magnitude with the length evaluated from the length of *sacran* chain observed in transmission electron microscopy and a Zimm-Berry plot in static light scattering experiments [14].

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