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Dielectric analysis of food polysaccharides in aqueous solution

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Abstract

The dielectric properties of typical ionic food polysaccharides, alginate and κ-carrageenan, were investigated in the frequency range from 10^3 Hz to 10^7 Hz. For both polymers, two kinds of dielectric relaxation processes were observed; the higher-frequency relaxation being analyzed. The concentration dependence of the dielectric increment, $\Delta\varepsilon_H$, and that of the relaxation time, τ_H, agreed well with the scaling law derived from polyelectrolyte solution theory. This result indicates that the mechanism of the high-frequency relaxation is ascribed to fluctuation of the loosely bound counterions to the polyelectrolyte within the range of the correlation length, ξ. Using the dielectric relaxation data, the crossover concentration from the dilute to the semi-dilute region for polysaccharide solutions was estimated. In addition, the fluctuation length of the bound counterions, d, and the concentration of counterions bound to the polyelectrolytes, N_b, were evaluated. The dielectric relaxation measurement was an effective method for analyzing the polymer chain distribution and the counterion binding nature in the polysaccharide solutions. © 1997 Elsevier Science Ltd.

Keywords: Dielectric relaxation; Alginate; κ-Carrageenan; Counterion fluctuation; Correlation length; Scaling law

1. Introduction

Food polysaccharides are widely used for modifying such physical properties as viscosity, elasticity, and the thermal properties of food. From a practical point of view, a great number of experiments have been carried out, and a knowledge of the macroscopic properties of food polysaccharides systems has been accumulated [1]. However, the mechanism of producing the physical properties of these systems is still not clearly understood, only the correlation between composition and the properties having been repeatedly discussed so far [2–6]. This is mainly because of a lack of methods for quantitatively analyzing the interaction among molecules and the resulting structures within these systems.

In recent years, the dielectric properties of polyelectrolyte solutions have been widely investigated [7–9]. The dielectric properties of polyelectrolyte solutions are considered to be dominated by the electrostatic interactions among the fixed charges on the polyelectrolyte and its counterions. The electrostatic interaction is significantly related to the polymer conformation and the physical properties or functions

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of the system. Therefore, it is considered that a dielectric relaxation analysis gives useful information on the polymer conformation and polymer/counterion interaction. However, such an analysis of food carbohydrate polymers has rarely been reported.

The dielectric relaxation for such linear polyelectrolyte solutions as polyglutamate [10], DNA [11], and polyacrylic acid [12] shows two kinds of relaxation processes; one is the low-frequency relaxation around kHz, the other is the high-frequency one around MHz. The low-frequency relaxation is considered to reflect such phenomena as the oriental polarization of the polymer or the fluctuation of bound counterions along the polyelectrolytes, because of the strong dependence on the molecular weight [13,14]. For the mechanism of the high-frequency relaxation, the bound counterion fluctuation within the range of the correlation length along [14,15] or perpendicular [13,16,17] to the polyelectrolyte was suggested. Part of the counterions are known to be bound to the polyelectrolyte due to an electrostatic force arising from the charges on the polymer chain [13,18]. Recent computer simulations, using the Poisson–Boltzmann equation around the polymer chain, have shown that the bound counterions in the semi-dilute region are classified into two groups, the tightly bound counterions and the loosely bound ones [19,20]. The tightly bound counterions are distributed around the polyelectrolyte within a narrow range of the same order as the polyelectrolyte radius. Because they are trapped in a strong electric potential due to the polyelectrolyte and are hardly affected by the ionic atmosphere, their distribution is nearly independent of ionic concentration. The loosely bound counterions are, on the other hand, sparsely dispersed within a several times larger range than the polyelectrolyte radius, the same order as the average distance between the adjacent polymers. Because they are trapped in the potential valley formed by the polyelectrolyte, which has a depth on the order of thermal energy, the loosely bound counterions can move locally or fluctuate even in the direction perpendicular to the polymer chain axis. As a result, loosely bound counterions would cause polarizability, namely the dielectric properties, instead of losing their contribution to activities or conductivity. Ito et al. investigated the high-frequency relaxation for a linear synthetic polyelectrolyte solution, sodium polystyrene sulfonate (Na-PSS), in the dilute and the semi-dilute region [21]. Based on the results of the frequency-domain electric birefringence [22] and the dielectric relaxation spectroscopy [21], they have revealed that the dielectric parameters for linear polyelectrolyte solutions can be formulated by a scaling law [23] derived from the polyelectrolyte solution theory, and concluded that the high-frequency relaxation is ascribed to the fluctuation of the loosely bound counterion in the direction perpendicular to the polymer chain axis.

To fully understand the physical properties of food polymer systems, a quantitative investigation on polyelectrolyte/counterion interaction and the resulting structure determination in the system are necessary [24]. The dielectric relaxation measurement is expected to be a promising tool to provide information not only on the electrostatic interaction but also on the structure within the systems. In addition, the scaling relations for electric properties would be useful for systematically understanding the producing mechanism of such physical properties as viscosity, osmotic pressure, and diffusion coefficient, because the scaling theory describes the general relationship between physical properties and structures [23,25,26]. In this paper, the concentration dependence and counterion specificity of the high-frequency dielectric relaxation properties of typical ionic food polysaccharides, alginate, the copolymer of β-(1–4)-D-mannuronate and α-(1–4)-L-guluronate, and κ-carrageenan, the alternating disaccharide of β-(1–3)-D-galactose-4-sulphate and α-(1–4)-3,6-anhydro-D-galactose, were analyzed by applying the scaling law based on the loosely bound counterion fluctuation.

2. Theoretical

Scaling law [23, 25, 26].—Fig. 1 schematically shows the linear polyelectrolyte solutions in (a) the dilute and (b) the semi-dilute regions. The average distance between adjacent polyelectrolytes is known as the correlation length ξ. In the dilute region, the polyelectrolyte concentration is low enough for each polyelectrolyte to be fully extended due to electro-

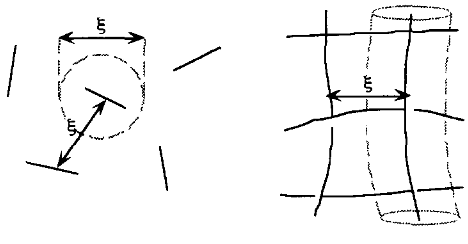

Fig. 1. Schematic diagram of the polyelectrolyte solution in the (a) dilute and (b) semi-dilute region.

static repulsion between the fixed charges on the polymer, and the interaction between polyelectrolytes is negligible. Since a spherical free volume, V, with a diameter equal to the average distance between polyelectrolytes can be assumed,

$$V \propto \xi^3. \tag{1}$$

With increasing concentration, polymer chains become entangled with each other, and the network like structure emerges. In this semi-dilute region, a cylindrical free volume with a diameter equal to the average distance between polyelectrolytes can be assumed,

$$V \propto \xi^2. \tag{2}$$

Since the polymer concentration C in the solution is inversely proportional to the free volume,

$$\xi \propto C^{-1/3} \quad \text{for dilute region}, \tag{3}$$

$$\xi \propto C^{-1/2} \quad \text{for semi-dilute region}. \tag{4}$$

The scaling equations for the dielectric properties are derived in the following section.

Dielectric relaxation [21, 27].—In general, the electric polarizability α induced by the electric dipole moment μ is given by

$$\alpha = \frac{\langle \mu^2 \rangle}{3kT} \tag{5}$$

where k is the Boltzmann constant; T, the absolute temperature; $< \mu^2 >$, the mean-square fluctuation of the dipole moment μ. The dielectric increment $\Delta\varepsilon$, which is induced by the electrical polarization, is expressed as

$$\Delta\varepsilon = \frac{N_{AV} N_b \alpha}{\varepsilon_0} \tag{6}$$

where N_{AV} is Avogadro's number; N_b, the molar concentration of the dipole moment; ε_0, the vacuum permittivity. By substituting Eq. (5) into Eq. (6), the following equation is obtained.

$$\Delta\varepsilon = \frac{N_{AV} N_b \langle \mu^2 \rangle}{3\varepsilon_0 kT}. \tag{7}$$

In the case of the dielectric relaxation due to the counterion fluctuation within the range of d, $< \mu^2 >$ is given by

$$\langle \mu^2 \rangle = q^2 d^2 \tag{8}$$

where q is the charge of the counterion; N_b is given by the molar concentration of the loosely bound counterion. By substituting Eq. (8) into Eq. (7)

$$\Delta\varepsilon = \frac{N_{AV} N_b q^2 d^2}{3\varepsilon_0 kT} \propto N_b d^2. \tag{9}$$

Since the loosely bound counterion fluctuates within the range of d, the relaxation time τ is estimated as

$$\tau = \frac{d^2}{2D} \tag{10}$$

where D is the diffusion coefficient of the counterion.

Based on the assumptions that (I) N_b is proportional to the polymer concentration and (II) the value of d is proportional to that of ξ, the concentration dependence of $\Delta\varepsilon$ is obtained from Eqs. (3), (4) and (9):

$$\Delta\varepsilon \propto C^{1/3} \quad \text{(dilute)}, \tag{11}$$

$$\Delta\varepsilon \propto C^{0} \quad \text{(semi-dilute)}. \tag{12}$$

From Eqs. (3), (4) and (10), the concentration dependence of τ is obtained:

$$\tau \propto C^{-2/3} \quad \text{(dilute)}, \tag{13}$$

$$\tau \propto C^{-1} \quad \text{(semi-dilute)}. \tag{14}$$

If assumptions (I) and (II) are confirmed and Eqs. (11)–(14) are valid, the scaling theory based on the fluctuation of the loosely bound counterion is applicable to the system.

3. Materials and methods

Materials.—Sodium alginate (Kanto Chem., Tokyo, Japan; Lot No. 802S1707; Intrinsic viscosity in 0.1 M NaCl at 25 °C $[\eta] = 1030$ mL/g) and κ-carrageenan (Sigma Chemical, Lot No. 16H0616; $[\eta] = 671$ mL/g) were dissolved in water and then passed through a large excess of the H-form cation exchange resin (Dowex 50W-X8) and the OH-form anion exchange resin (Amberlite IRA-400). These solutions were then neutralized in a nitrogen atmosphere using NaOH, KOH, or $Ca(OH)_2$ solutions. Water used in preparation and in the experiments was Millipore-purified (resistivity 18 MΩ cm) after distillation.

Measurement.—The capacitance in the frequency range from 10^3 Hz to 10^7 Hz was measured using LCR meters (Yokogawa–Hewlett–Packard Ltd., Tokyo, Japan, 4284A, 4285A), equipped with a nickel plated parallel plate type cell. All measurements were performed at 25 ± 0.1 °C. The dielectric constant was determined as the ratio of the capacitance of the sample to that of air. Only the value of the real part of the frequency dependence for the complex dielectric constant was determined, because the imaginary part can be determined by the accurate conductivity measurement of the samples. It is well-known that, for ionic materials, part of the mobile ions accumulate at the interface between the electrode and the sample, which is the so-called electrode polarization [28,29]. The error in the dielectric constant caused by the electrode polarization effect would be considerable, especially in the lower frequency range. Therefore, to ascertain the absence of the electrode polarization effect, the comparative measurements between the polyelectrolyte solution and the NaCl one with similar conductivity were carried out for each solution.

4. Results

As typical examples of the data, Fig. 2 shows the frequency dependence of the dielectric constant of (a) alginate and (b) κ-carrageenan solutions with different species of counterion. To confirm the absence of the electrode polarization effect, data for an NaCl solution with the same order conductivity is also shown. The values of ε of the NaCl solution were almost constant irrespective of frequency. For all the polymer solutions, two kinds of relaxation processes were observed, which is the same results as those reported for other linear polyelectrolytes [10–12]. Therefore, it was assumed that the dielectric constant is given as the sum of two Cole–Cole relaxation functions:

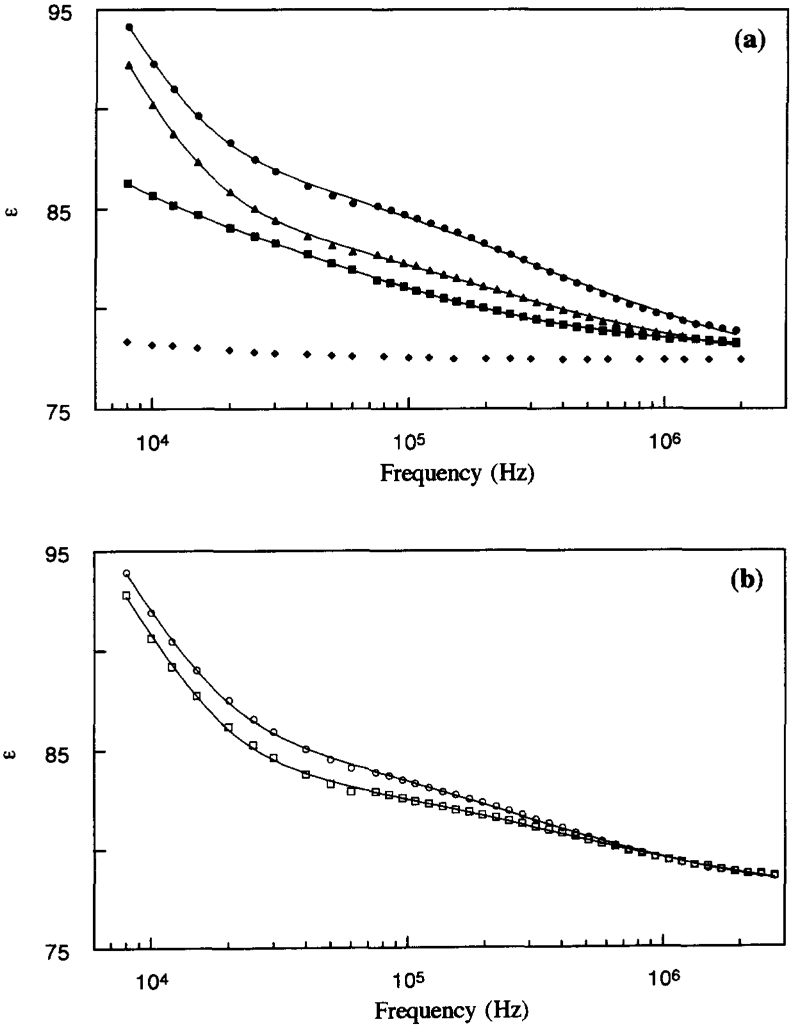

Fig. 2. Dielectric constant ε of (a) alginate and (b) κ-carrageenan with different species of counterions. Monomer concentration of polyelectrolyte is 0.1 mM. The solid curves are the best fit ones using the double Cole–Cole equation, Eq. (15). Counterion: ●, Na^+; ▲, Na^+:Ca^{2+} = 1:1 (molar ratio); ■, Ca^{2+}; ○, Na^+; □, K^+; ◆ represents ε of 0.1 mM NaCl solution.

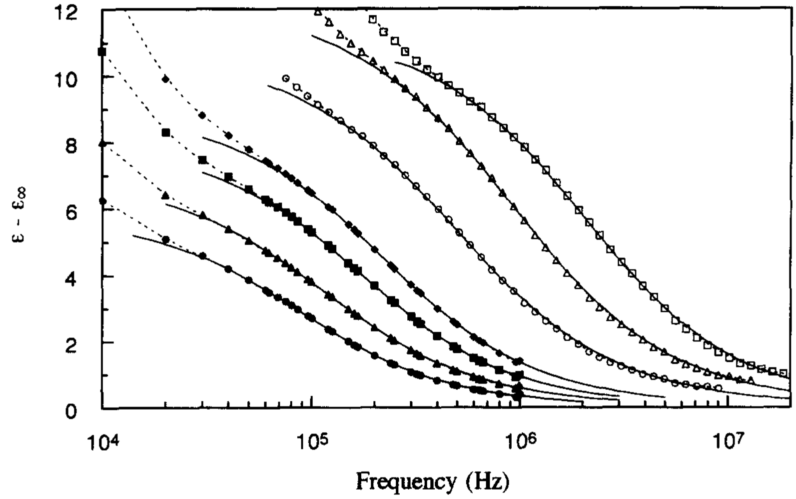

Fig. 3. Concentration dependence of the dielectric relaxation of sodium alginate solution. The solid curves are the best fit ones for the high-frequency dielectric relaxation (the third term on the right hand side of Eq. (15)). Monomer concentration: ●, 0.02 mM; ▲, 0.03 mM; ■, 0.05 mM; ◆, 0.07 mM; ○, 0.2 mM; △, 0.4 mM; □, 1 mM.

$$\varepsilon = \varepsilon_\infty + \tfrac{1}{2}\Delta\varepsilon_{\mathrm{L}}\left(1 - \frac{\sinh \beta_{\mathrm{L}} x_{\mathrm{L}}}{\cosh \beta_{\mathrm{L}} x_{\mathrm{L}} + \cos \frac{1}{2}\beta_{\mathrm{L}}\pi}\right) + \tfrac{1}{2}\Delta\varepsilon_{\mathrm{H}}\left(1 - \frac{\sinh \beta_{\mathrm{H}} x_{\mathrm{H}}}{\cosh \beta_{\mathrm{H}} x_{\mathrm{H}} + \cos \frac{1}{2}\beta_{\mathrm{H}}\pi}\right) \qquad (15)$$

where ε_∞ is the high-frequency limit of ε; β, the Cole–Cole parameter ($0 < \beta < 1$); $x = \ln(2\pi f\tau)$; f, the frequency; τ, the relaxation time. The second and third terms on the right hand side of Eq. (15) correspond to the low-frequency and the high-frequency relaxation, respectively; the suffix L and H in Eq. (15) represent the low-frequency and the high-frequency relaxation, respectively. The solid curves in Fig. 2 represent the Cole–Cole type equation, Eq. (15), fitted to the data. All the experimental data on the dielectric relaxation were in good agreement with the best fit curves using the equation, the values of the dielectric relaxation parameters, $\Delta\varepsilon$ and τ, being obtained. The values for the β parameters representing the asymmetry and broadness in the distribution of relaxation times were varied from 0.8 to unity for all the solutions.

The high-frequency relaxation data of the sodium alginate solutions with the best fit curves (the third term on the right hand of Eq. (15)) are shown in Fig. 3. The high-frequency limit of ε, ε_∞, has been subtracted from the dielectric constants. With increasing concentration, the dielectric increment, $\Delta\varepsilon_{\mathrm{H}}$, seems to slightly increase and the relaxation curve shifts toward the higher frequency.

Fig. 4(a) represents the concentration dependence of the high-frequency dielectric increment $\Delta\varepsilon_{\mathrm{H}}$ for

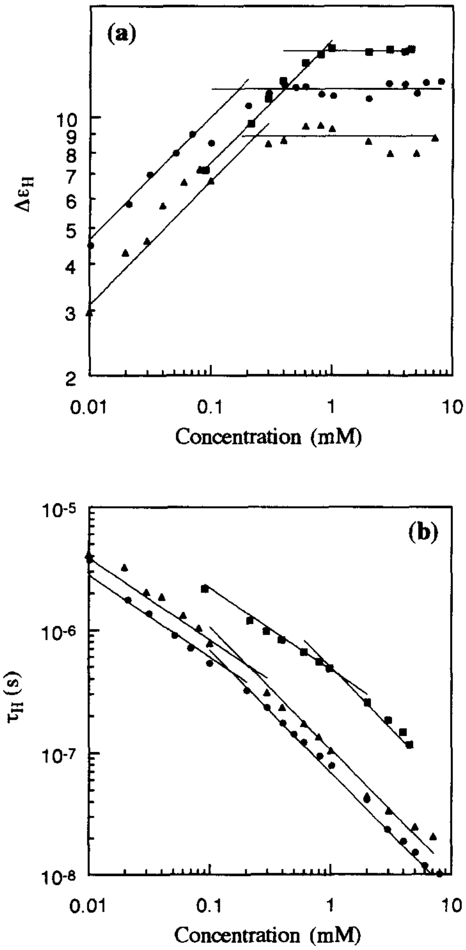

Fig. 4. (a) Concentration dependence of $\Delta\varepsilon_{\mathrm{H}}$ of alginate solutions; the solid lines have a slope of 1/3 or 0. (b) Concentration dependence of τ_{H} of alginate solutions; the solid lines have a slope of $-2/3$ or -1. Each symbol represents the counterion difference as in Fig. 2(a). The concentration is expressed by the monomer concentration.

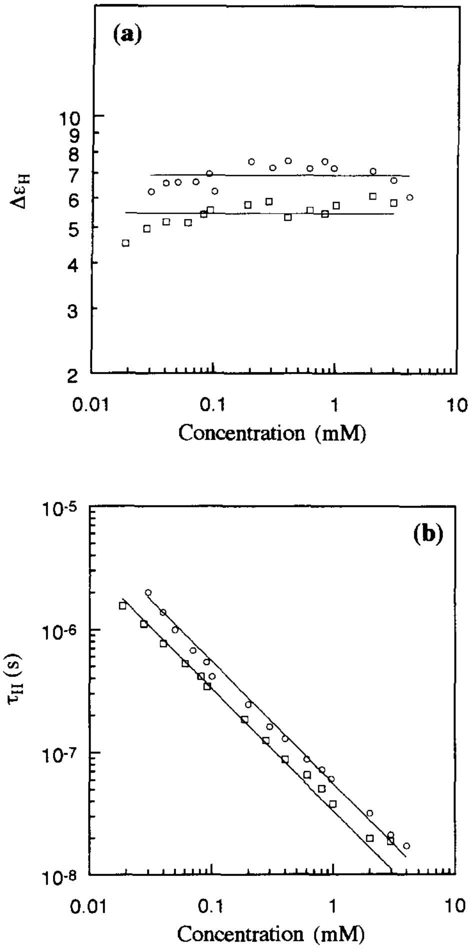

Fig. 5. (a) Concentration dependence of $\Delta\varepsilon_{\mathrm{H}}$ of κ-carrageenan solutions; the solid line has a slope of 0. (b) Concentration dependence of τ_{H} of κ-carrageenan solutions; the solid line has a slope of -1. Each symbol represents the counterion difference as in Fig. 2(b). The concentration is expressed by the monomer concentration.

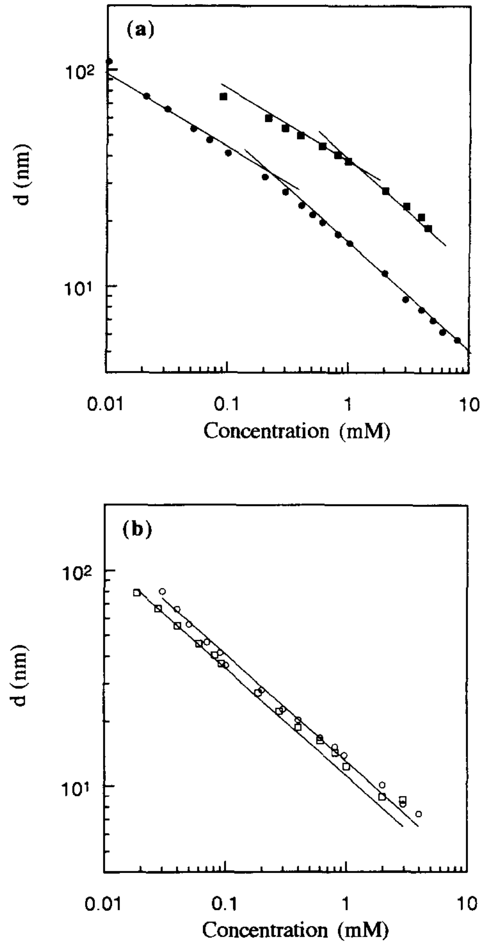

Fig. 6. Concentration dependence of the fluctuation length of the loosely bound counterion d of (a) alginate and (b) κ-carrageenan. Each symbol represents the sample difference as in Fig. 2. The concentration is expressed by the monomer concentration.

alginate solutions with different species of counterion. The solid lines have a slope of 1/3 at low concentration or 0 at high concentration, as predicted by Eqs. (11) and (12). The turning point concentration increased in the order $\mathrm{Ca}^{2+} > \mathrm{Na}^{+}\text{–}\mathrm{Ca}^{2+} > \mathrm{Na}^{+}$. In Fig. 5(a), the concentration dependence of the high-frequency dielectric increment, $\Delta\varepsilon_{\mathrm{H}}$, for κ-carrageenan solutions with different species of counterion are also shown. For all the solutions, $\Delta\varepsilon_{\mathrm{H}}$ was almost constant. The values of $\Delta\varepsilon_{\mathrm{H}}$ for sodium κ-carrageenan solutions were slightly larger than those for potassium κ-carrageenan. As shown in Fig. 4(b), the concentration dependence of τ_{H} for alginate solutions has a slope change at some concentration. The solid lines have a slope of $-2/3$ at low concentration or -1 at high concentration, as predicted by Eqs. (13) and (14). The turning point concentration increased in the order $\mathrm{Ca}^{2+} > \mathrm{Na}^{+}\text{–}\mathrm{Ca}^{2+} > \mathrm{Na}^{+}$. Fig. 5(b) represents the concentration dependence of τ_{H} for the κ-carrageenan solutions. For all the samples, τ_{H} was inversely proportional to the concentration.

The results shown in Figs. 4 and 5 can be summarized as Eqs. (11)–(14). It indicates that the turning point concentration in Fig. 4(a) and (b) is recognized as the crossover concentration from the dilute to semi-dilute region for the alginate solutions, while the κ-carrageenan solutions shown in Fig. 5 were in the semi-dilute region in the measured concentration range. These findings are in agreement with the results obtained by Ito et al. on Na-PSS in dilute and semi-dilute solutions [21].

Using Eq. (10), Fig. 6 shows the concentration dependence of the fluctuation length d of counterions loosely bound to the polyelectrolyte. For the alginate solutions, the concentration dependence was expressed by $d \propto C^{-1/3}$ at low concentration and $d \propto C^{-1/2}$ at high concentration. For the κ-carrageenan solution, the concentration dependence of d was expressed by $d \propto C^{-1/2}$ in all the measured concentration region. These results in comparison with the concentration dependence of ξ, Eqs. (3) and (4), indicate that d is proportional to ξ, namely assumption (II) in the Theoretical section was confirmed. Therefore, parameter d is considered to reflect the distance between polymers distributed in the solution.

5. Discussion

Because dielectric relaxation is a method for analyzing the electrical response to electrical stimulation, it is expected to serve as a method for obtaining information on the internal ionic environment of a polymer system. Ito et al. investigated the high-frequency relaxation for Na-PSS solutions, concluding that the relaxation was caused by the fluctuation of counterions loosely bound to the polyelectrolyte [21]. However, the effect of the counterion species on the high-frequency relaxation has scarcely been analyzed in terms of the counterion fluctuation, especially, for carbohydrate polymers. In this study, the high-frequency relaxation for two food polysaccharides, alginate and κ-carrageenan, with different species of counterion was investigated.

Dielectric relaxation.—To ascertain the validity of assumption (I) mentioned in the Theoretical section, we derived the following equation from Eqs. (9) and (10):

$$\frac{\varepsilon_0 \Delta\varepsilon}{\tau} \propto N_b. \qquad (16)$$

Fig. 7 shows the concentration dependence of $\varepsilon_0 \Delta\varepsilon_H / \tau_H$ for alginate and κ-carrageenan with different species of counterion. For all the samples, the value of $\varepsilon_0 \Delta\varepsilon_H / \tau_H$ is proportional to concentration. From the comparison with Eq. (16), it was confirmed that N_b was proportional to the polymer concentration C.

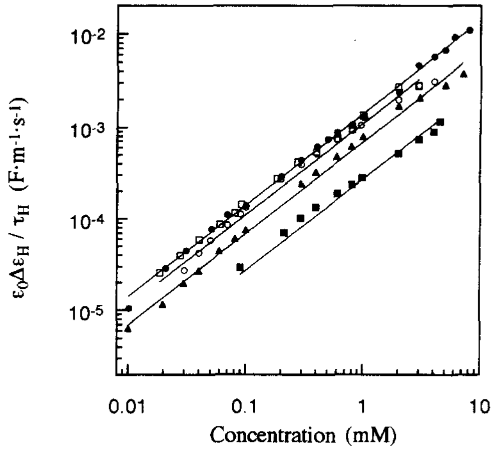

Fig. 7. Double logarithmic plot of $\varepsilon_0 \Delta\varepsilon_H / \tau_H$ versus concentration; the solid line has a slope of unity. Each symbol represents the sample difference as in Fig. 2. The concentration is expressed by the monomer concentration.

The validity of assumptions (I) and (II) in the theoretical section having been confirmed, the scaling relations, Eqs. (11)–(14), were valid for these experiments. As can be seen in Figs. 4 and 5, the concentration dependence of $\Delta\varepsilon_H$ and τ_H were well described by the scaling equations based on the fluctuation of the loosely bound counterions. Consequently, the high-frequency dielectric relaxation for the ionic polysaccharide solutions is ascribed to the fluctuation of the loosely bound counterion.

Counterion specificity.—The correlation between the counterion species of ionic polysaccharides and the macroscopic properties of their solutions has been widely investigated. By adding a multivalent ion like a calcium ion to an alginate solution, a heat stable gel can be obtained. The calcium ions are considered to fit into the guluronate structures like an egg in an egg-box, forming rod-like junction zones of polymer chains leading to gelation [30,31]. For κ-carrageenan, the secondary structure in aqueous solution can change from a flexible coil to a helical conformation induced by such conditions as metal salts and temperature, potassium ion being one of the most effective ion species to promote coil-helix transition and gelation [32,33]. Although such qualitative models are generally accepted, the nature of the cation binding site and the gelation mechanism of such natural polymers are still unclear. The dielectric analysis would give unique information on the polymer distribution and the interaction of the polymer with counterions in the polymer solutions.

Ito et al. have concluded that the fluctuation length of the loosely bound counterions, d, is identical with the correlation length, ξ, the average distance between the adjacent polymers in the solution [21]. As can be seen in Fig. 4, the turning point concentration from the dilute to the semi-dilute region is about 0.1 mM and 1 mM for the sodium and calcium alginate solutions, respectively. Because carboxyl groups on alginate chains are chelated in the presence of calcium [30], the calcium alginate chain would be poly-

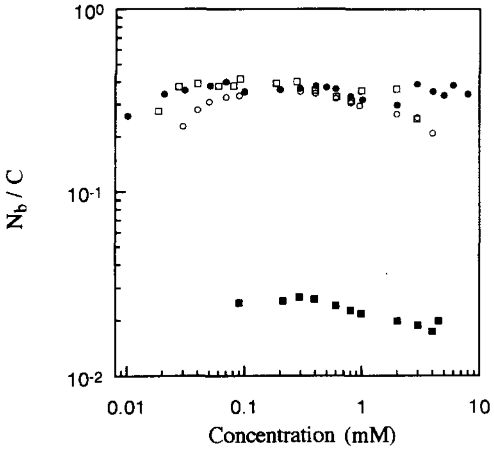

Fig. 8. The ratio of the amount of the loosely bound counterion to that of all the counterions. Each symbol represents the sample difference as in Fig. 2. The concentration is expressed by the monomer concentration.

merized. As a result, the polymer concentration would apparently decrease, and the average distance between the adjacent polymer chain would apparently increase. The result in Fig. 4 indicates that the polymer concentration of calcium alginate solutions was about 10 times smaller than that of sodium alginate at the same monomer concentration apparently in terms of the dielectric relaxation.

In such general methods as activity measurements or d.c. conductivity, osmotic pressure, and so forth, both tightly and loosely bound counterions are observed as a single kind of bound counterion. By substituting Eq. (10) into Eq. (9), however, the molar concentration of the loosely bound counterions, N_b, is obtained,

$$N_b = \frac{\varepsilon_0 \Delta \varepsilon_H}{\tau_H} \times \frac{3kT}{2 N_{AV} D q^2} \tag{17}$$

Fig. 8 shows the concentration dependence of the ratio of the amount of loosely bound counterion to that of all the counterions. The concentration dependence of N_b/C for sodium κ-carrageenan and that for the potassium salt are almost equal, which suggests that there is no specific difference in the binding nature of the sodium and potassium ions. Under these experimental conditions, i.e., at low concentration without adding any excess amount of metal salts, κ-carrageenan is a coil conformer [34]. In the studies so far [32–35], there is no evidence of specific binding of any cations to the random coil κ-carrageenan conformer, while specific cations like potassium bind to the helix κ-carrageenan conformer and stabilize the helix structure [36,37]. Therefore, the result in Fig. 8 supports further confidence in the absence of a specific binding site to the κ-carrageenan coil conformer. For alginate solutions, the calcium alginate shows a much smaller amount of loosely bound counterions in comparison with the sodium alginate. If the negative charges of guluronate residues are shielded due to calcium ion chelation, the potential formed by the polymer becomes smaller, and as a result, the amount of loosely bound counterions decreases for the calcium alginate. The result in Fig. 8, therefore, suggests that in the calcium alginate solution, more calcium ions are binding tightly to the alginate rather than atmospherically trapped.

The high-frequency dielectric relaxation of the polysaccharide solutions were explicable based on the scaling concept. Because the scaling relations for such physical properties of the polyelectrolyte solutions as viscosity, osmotic pressure, and diffusion coefficient are theoretically predicted [23,25,26], further comparative study will contribute to a comprehensive understanding of polysaccharide solution properties.

Acknowledgements

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