Scaling Behavior of Physical Properties of Food Polysaccharide Solutions: Dielectric Properties and Viscosity of Sodium Alginate Aqueous Solutions

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The dielectric properties of a typical ionic food polysaccharide, alginates with different chemical compositions and molecular sizes, were investigated with special relevance to the solution viscosity. The dielectric relaxation around 1 MHz due to the fluctuation of bound counterions was analyzed. The polymer concentration, C, dependence of the dielectric increment, $\Delta\epsilon$, and that of the relaxation time, τ, are summarized as $\Delta\epsilon \propto C^{1/3}$ and $\tau \propto C^{-2/3}$ at the dilute region and as $\Delta\epsilon \propto C^0$ and $\tau \propto C^{-1}$ at the semidilute region for all of the samples, in good agreement with the scaling relations predicted by polyelectrolyte solution theories. The crossover concentration, C^*, from the dilute to the semidilute region was determined as the concentration at the intersection of the two regions. The concentration dependence of the relative viscosity, η_{rel}, was also expressed by two scaling equations: $(\eta_{rel} - 1) \propto C^1$ at low concentration and $\eta_{rel} \propto C^{1/2}$ at high concentration. The crossover concentration, C^*, determined by the viscosity agreed with that determined by the dielectric measurement. These results suggest that the behavior of the physical properties of the food polysaccharide solutions would be understandable on the basis of the scaling concept, the dielectric relaxation measurement being an effective method for analyzing the polyelectrolyte solution structure contributing to the physical properties of the systems.

Keywords: *Dielectric relaxation; viscosity; alginate; scaling law*

INTRODUCTION

The physical properties of food polysaccharide systems have been widely investigated not only from a scientific point of view to clarify the nature of biopolymers but also from a practical standpoint. Because macroscopic physical properties such as viscosity, elasticity, and the thermal properties of food would be essential in an industrial food process, a knowledge of the macroscopic properties of food polysaccharide systems has been accumulated (Stephen, 1995). However, in most cases, only the correlation between the composition and the properties is discussed qualitatively, the mechanism of producing the physical properties of these systems being still unclear. A quantitative method is needed for analyzing the structure within these systems and the resulting physical properties.

The physical properties of the polyelectrolyte systems are significantly related to the electrostatic interactions among the fixed charges on the polymer and its counterions (Oosawa, 1971). The dielectric properties are considered to be one of the most sensitive properties to such electrostatic interactions; those of the linear polyelectrolyte solutions have become recently clarified (Ookubo et al., 1989; Ito et al., 1990). In polyelectrolyte solutions, part of the counterions are trapped in the potential valley formed by the polyelectrolyte and considered to be bound to the polyelectrolyte (Manning, 1978). Such bound counterions would cause the dielectric properties, instead of losing their contribution to activities or conductivity. Ito et al. (1990) investigated the dielectric relaxation for a linear synthetic polyelectrolyte solution, sodium polystyrene sulfonate (Na-PSS), in the dilute and semidilute regions and revealed that

the concentration dependence of the dielectric parameters for linear polyelectrolyte solutions can be formulated using scaling theories.

The scaling theories provide a novel approach for predicting the physical properties of polymer systems (De Gennes et al., 1976; Odijk, 1979). The theory has recently become applicable to polyelectrolyte solutions (Dobrynin et al., 1995) because the static configuration of the polymer chain for calculating the electrostatic potential of the polyelectrolytes was elucidated with the aid of computer simulations. In addition, the relationship between the polymer solution structure and such physical properties as dielectricity, viscosity, osmotic pressure, and diffusion coefficient has been formulated on the basis of the theory (Ito et al., 1990; Rubinstein et al., 1994; Dobrynin et al., 1995; Bordi et al., 1996). A scaling approach, therefore, is expected to provide useful information for systematically understanding the producing mechanism of the physical properties. However, such studies for food macromolecular systems have scarcely been reported.

In previous works (Ikeda et al., 1997a,b), we investigated the dielectric properties of several food polyelectrolyte systems. The dielectric relaxation around megahertz for these solutions was ascribed to the fluctuation of the bound counterions to the polyelectrolytes, the concentration dependence of the dielectric parameters being formulated by the scaling law in accordance with the results of Na-PSS (Ito et al., 1990). In addition, a crossover from the dilute to the semidilute solution was definitely observed for alginate and κ-carrageenan solutions. For a comprehensive understanding of the physical properties of food polymer systems, a quantitative investigation of the molecular interaction, the structure, and the resulting physical properties is necessary. In this study, the dielectric properties of a typical food

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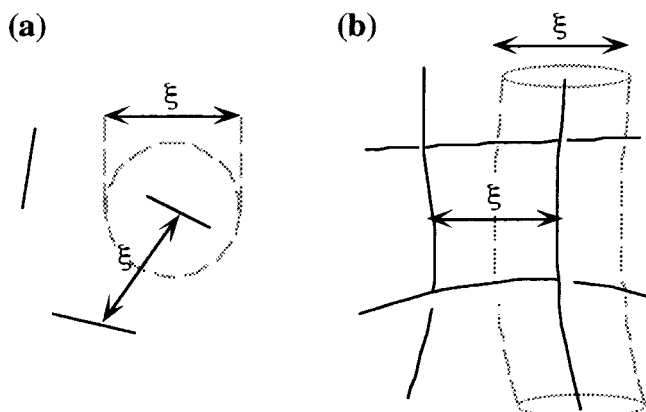
(a)   **(b)**

Figure 1. Schematic diagram of the polyelectrolyte solution in the (a) dilute and (b) semidilute region.

polysaccharide, alginates with different chemical compositions and molecular sizes, were analyzed in dilute and semidilute solutions. The solution viscosity was also analyzed on the basis of the scaling concept, because a drastic change in physical properties is anticipated at the crossover concentration.

THEORY

In this section, a brief outline of the scaling concept for linear polyelectrolyte solutions is described, and the equations for dielectric properties and viscosity are derived.

Scaling Law (De Gennes et al., 1976; Odijk, 1979; Dobrynin et al., 1995). In a dilute polyelectrolyte solution, the polyelectrolytes are considered to be fully extended due to electrostatic repulsion between the fixed charges on the polymer chain. Because the interaction between polyelectrolytes is negligible, a spherical free volume, V, with a diameter equal to the average distance between polyelectrolytes can be assumed (Figure 1)

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

where ξ is the average distance between adjacent polyelectrolytes, known as the correlation length. With increasing concentration, polymer chains become entangled with each other, and the network-like structure emerges (Figure 1). In this semidilute region, a cylindrical free volume with a diameter equal to the average distance between the polyelectrolytes can be assumed:

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

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

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

$$\xi \propto C^{-1/2} \quad \text{for the semidilute region} \tag{4}$$

Dielectric Relaxation (Blythe, 1979). The dielectric relaxation for the linear polyelectrolyte solutions is caused by the fluctuation of the bound counterion within the range of ξ (Ookubo et al., 1989; Ito et al., 1990). The dielectric increment $\Delta\epsilon$ due to the fluctuation of the bound counterions is given by (Ito et al., 1990)

$$\Delta\epsilon = \frac{N_{AV} N_b q^2 d^2}{3\epsilon_0 kT} \propto N_b d^2 \tag{5}$$

where d is the fluctuation length of the counterion, k is the Boltzmann constant, N_{AV} is Avogadro's number, N_b is the molar concentration of the counterion, q is the charge of the counterion, T, is the absolute temperature, and ϵ_0 is the vacuum permittivity. Because the loosely bound counterion fluctuates within the range of d, the relaxation time τ is estimated as follows:

$$\tau = d^2/2D \tag{6}$$

D is the diffusion coefficient of the counterion.

Investigations for several kinds of linear polyelectrolyte solutions (Ito et al., 1990; Ikeda et al., 1997a) have shown that (I) N_b is proportional to the polymer concentration C and (II) d is proportional to the correlation length ξ. Consequently, the concentration dependence of $\Delta\epsilon$ is obtained from eqs 3–5.

$$\Delta\epsilon \propto C^{1/3} \quad \text{(dilute)} \tag{7}$$

$$\Delta\epsilon \propto C^0 \quad \text{(semidilute)} \tag{8}$$

From eqs 3, 4, and 6, the concentration dependence of τ is obtained:

$$\tau \propto C^{-2/3} \quad \text{(dilute)} \tag{9}$$

$$\tau \propto C^{-1} \quad \text{(semidilute)} \tag{10}$$

Viscosity. The viscosity, η, of the polymer solution is given as the product of the modulus G and the longest relaxation time τ_l (Doi and Edwards, 1986):

$$\eta = G\tau_l \tag{11}$$

The modulus G is the thermal energy kT per polymer chain:

$$G = (kT/N)C \tag{12}$$

N is the degree of polymerization of the polymer. The longest relaxation times, τ_l, reflecting the hydrodynamic volume of the polymer chain, in the dilute and in the semidilute regions are described by the Zimm and Rouse models, respectively (Rubinstein, 1994; Dobrynin et al., 1995):

$$\tau_{Zimm} \propto C^0 \quad \text{(dilute)} \tag{13}$$

$$\tau_{Rouse} \propto C^{-1/2} \quad \text{(semidilute)} \tag{14}$$

The solute contribution to the solution viscosity, namely, the specific viscosity η_{sp}, of the dilute solutions is

$$\eta_{sp} = (\eta - \eta_s)/\eta_s = G\tau_{Zimm}/\eta_s \propto C^1 \quad \text{(dilute)} \tag{15}$$

where η_s is the solvent viscosity. For the semidilute solution, the relative viscosity η_{rel} is

$$\eta_{rel} = \eta/\eta_s = G\tau_{Rouse}/\eta_s \propto C^{1/2} \quad \text{(semidilute)} \tag{16}$$

EXPERIMENTAL PROCEDURES

Materials. Five grades of alginates isolated from *Lessonia nigrescens* were supplied by Kimitsu Chemical Industries Co. (Tokyo, Japan). The sodium alginate aqueous solutions for the dielectric and viscosity measurements were prepared by neutralization of alginic acids similarly to the procedure previously described (Ikeda et al., 1997a). Water used in the preparation and in the experiments was Millipore-purified (resistivity = 18 MΩcm) after distillation.

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Table 1. Chemical Characteristics of Alginate Samples[a-c]

sample	F_M	F_G	F_{MM}	F_{GG}	F_{MG}	M/G ratio	$[\eta]$, L/mmol
M5	0.52	0.48	0.30	0.26	0.22	1.1	4.7
M3	0.56	0.44	0.36	0.26	0.19	1.2	4.5
M1	0.54	0.46	0.37	0.27	0.18	1.2	2.9
G3	0.45	0.55	0.27	0.37	0.18	0.80	4.2
G1	0.29	0.71	0.14	0.56	0.15	0.42	3.5

[a] F_M/F_G, molar fraction of mannuronate/guluronate. [b] F_{MM}/F_{GG}, frequency of mannuronate−mannuronate/guluronate−guluronate diads. [c] F_{MG}, frequency of alternating diads.

NMR Spectroscopy. The monomer composition and sequence of the alginates were determined by ^{1}H NMR spectroscopy. The partially hydrolyzed alginate samples were prepared according to the methods of Grasdalen et al. (1979) and analyzed using a JMN-A500 FT NMR system (500 MHz). The M/G ratio and the diad frequencies were calculated from the ^{1}H NMR spectra as previously described (Grasdalen et al., 1979).

Gel Permeation Chromatography (GPC). The molecular size distribution of the alginates was analyzed by GPC. Aliquots (20 μL) of the alginate samples (0.1% w/w in 0.1 M NaCl with 0.02% NaN₃) were injected into a GPC column (OHpak SB-804HQ, Showa Denko, Tokyo, Japan) and eluted with degassed 0.1 M NaCl at a flow rate of 0.5 mL/min at 30 °C using an HPLC pump (PU980, JASCO, Tokyo, Japan). The elution peaks were monitored using a refractive index (RI) detector (RI SE-61, Showa Denko, Tokyo, Japan).

Dielectric Measurements. The dielectric measurements were carried out similarly to those of the previous work (Ikeda et al., 1997a). The dielectric constants ϵ over the frequency range $10^4 - 10^7$ Hz were measured using LCR meters (4284A and 4285A, Hewlett-Packard Japan, Tokyo, Japan) equipped with a nickel-plated parallel plate-type cell. All measurements were performed at 25 °C. The two dielectric parameters, $\Delta\epsilon$ and τ, were evaluated by best-fitting the following Cole−Cole type equation (Cole and Cole, 1941) to the data as previously reported (Ikeda et al., 1997a)

$$\epsilon = \epsilon_\infty + \frac{1}{2}\Delta\epsilon\left(1 - \frac{\sinh \beta x}{\cosh \beta x + \cos(\beta/2)\pi}\right) \qquad (17)$$

where f is the frequency, $x = \ln(2\pi f\tau)$, β is the Cole−Cole parameter $(0 < \beta < 1)$, and ϵ_∞ is the high-frequency limit of the dielectric constant.

Viscosity Measurements. The relative viscosity η_{rel} of the sodium alginate aqueous solutions was measured at 25 °C using an Ostwald-type viscometer (Kusano Scientific Instrument Mfg, Co., Tokyo, Japan), followed by the calculation of the specific viscosity values η_{sp} ($\eta_{sp} = \eta_{rel} - 1$). The limiting viscosity values $[\eta]$ were determined by extrapolating the concentration dependence of the reduced specific viscosity, η_{sp}/C, in the concentration range 0.05−0.3 mM back to zero concentration.

RESULTS

As shown in Table I, five kinds of alginates with different chemical compositions and molecular sizes were used in this study. The samples are classified into two types based on the M/G ratios calculated from ^{1}H NMR spectra: M5, M3, and M1 samples are the mannuronate-rich alginates, and G3 and G1 are the guluronate-rich ones. The profiles on the analytical gel permeation chromatography column are shown in Figure 2. For the M5 sample, the elution volume at the peak top was the lowest (6.2 mL), indicating that the average molecular weight of M5 is the highest in the samples. The peak area in the elution volume range above 6.6 mL, which represents the relative amount of the lower molecular weight fraction, increased in the order M1 > M3 > M5 and G1 > G3, indicating a
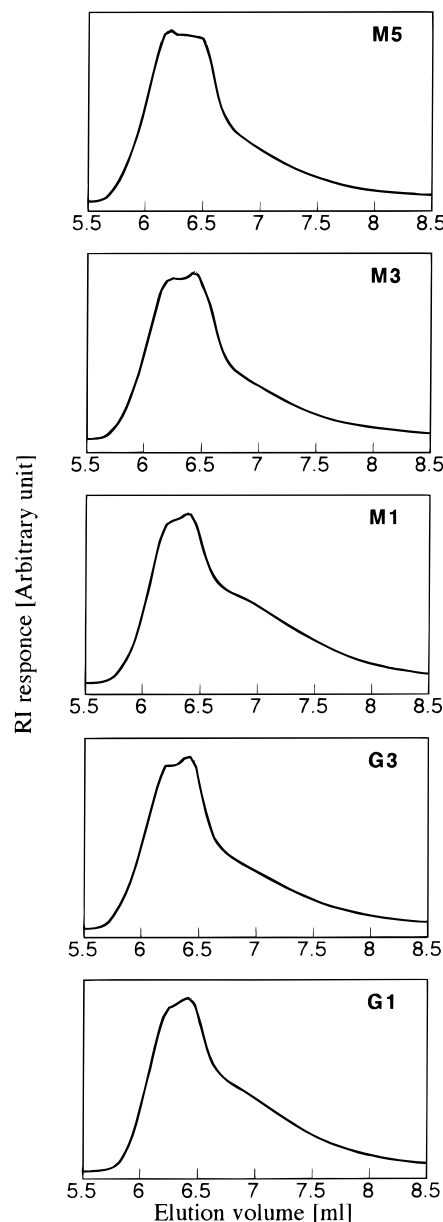

Figure 2. Elution profiles of sodium alginates on the GPC column.

progressive increase in the average molecular size in the order M1 < M3 < M5 and G1 < G3. The values of the limiting viscosity $[\eta]$ (Table 1) also indicate the same order of increase in the average molecular size.

As typical examples of the dielectric relaxation data, Figure 3 represents the frequency dependence of the dielectric constant, ϵ, of the G3 alginate (the solvent contribution ϵ_∞ having been subtracted). In accordance with our previous results (Ikeda et al., 1997a), two kinds of relaxation processes were observed. For the higher relaxation process due to the fluctuation of the bound counterion (Ikeda et al., 1997a), the experimental data were in good agreement with the best fit curves using the Cole−Cole equation (eq 17), the values of the dielectric relaxation parameters, $\Delta\epsilon$ and τ, being obtained. The dielectric increment $\Delta\epsilon$ for the higher frequency relaxation seems to slightly increase with increasing concentration, and the relaxation curve shifts toward the higher frequency. 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 of the solutions.
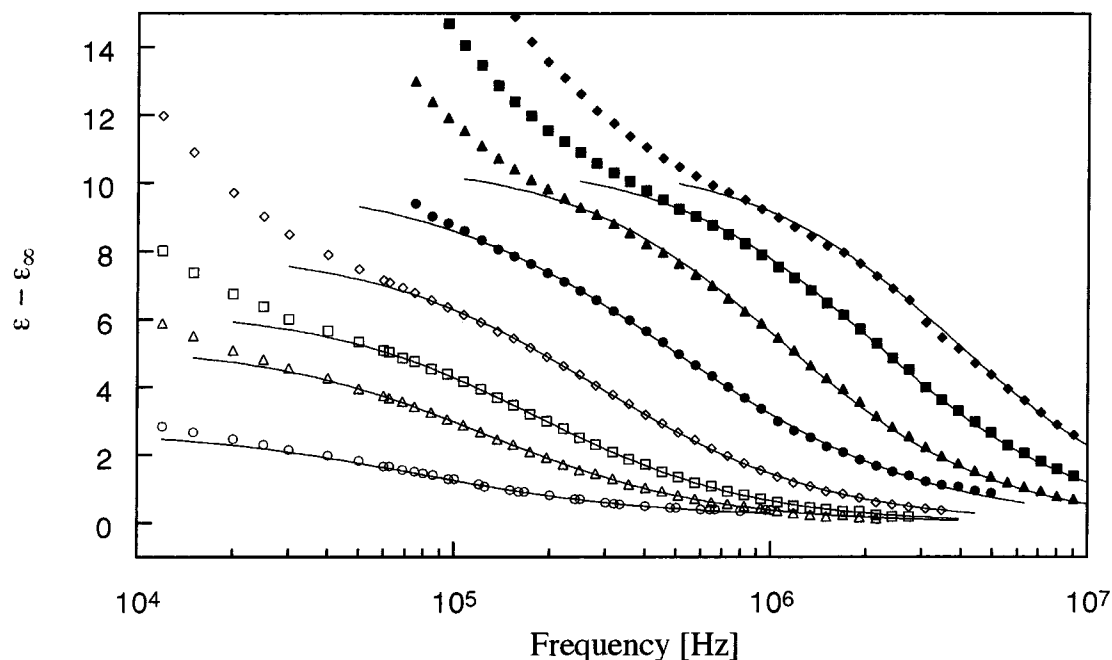
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Figure 3. Concentration dependence of the dielectric relaxation of sodium alginate solution. The solid curves are the best fit ones of the Cole–Cole equation (eq 17). Monomer concentration: (○) 0.010 mM; (△) 0.030 mM; (□) 0.050 mM; (◇) 0.096 mM; (●) 0.20 mM; (▲) 0.51 mM; (■) 1.0 mM; (◆) 2.0 mM.

Figure 4a represents the concentration dependence of the dielectric increment $\Delta\epsilon$ for the G3 alginate solutions. The solid lines have a slope of $^1/_3$ at low concentration or 0 at high concentration as predicted by eqs 7 and 8. In Figure 4b, the concentration dependence of τ for the G3 alginate solutions is shown. The solid lines have a slope of $-^2/_3$ at low concentration or -1 at high concentration, as predicted by eqs 9 and 10. Because the results can be summarized as eqs 7–10, the turning point concentration in Figure 4 is recognized as the crossover concentration from the dilute to semidilute region for the alginate solutions. These findings are in agreement with our previous results on alginate and κ-carrageenan in dilute and semidilute solutions (Ikeda et al., 1997a).

The concentration dependence of the specific viscosity for the G3 alginate solutions is shown in Figure 5a as an example of the viscosity data. The left ordinate represents the corresponding relative viscosity values. The specific viscosity values were proportional to the concentration in the low η_{sp} range below $\eta_{sp} = 1$ as predicted by eq 15. In Figure 5b, the relative viscosity values calculated from the same data as in Figure 5a are plotted against the concentration. In the high η_{rel} range above $\eta_{rel} = 2$, the concentration dependence of the relative viscosity agreed well with the solid line with the slope of $^1/_2$ as predicted by eq 16. To visualize the crossover behavior, these results are summarized as Figure 5c using two different scales above and below $\eta_{rel} = 2$: the lower part below $\eta_{rel} = 2$ is that of Figure 5a and the upper part above $\eta_{rel} = 2$ is that of Figure 5b. The solid lines have a slope of 1 at low concentration or $^1/_2$ at high concentration, the crossover concentration from the dilute to the semidilute region for the alginate solutions being expressed by the concentration at the intersection of these two lines. The value of the crossover concentration shown in Figure 5, 0.3 mM, was consistent with that determined by the dielectric measurement shown in Figure 4.

Parts a, b, and c of Figure 6 summarize all of the results about the concentration dependence of ϵ, τ, and
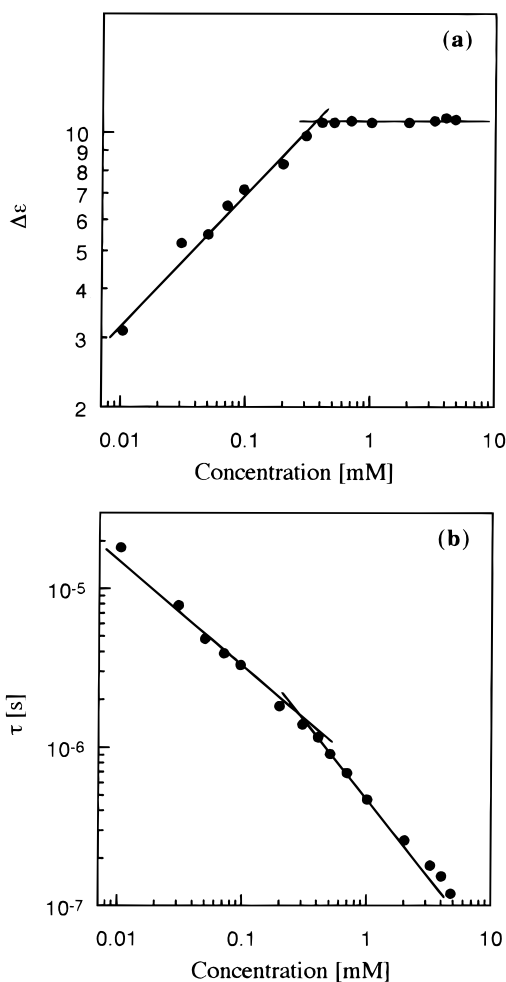

Figure 4. (a) Concentration dependence of $\Delta\epsilon$ of M3 alginate solutions; the solid lines have a slope of $^1/_3$ or 0. (b) Concentration dependence of τ of M3 alginate solutions; the solid lines have a slope of $-^2/_3$ or -1. The concentration is expressed by the monomer concentration.
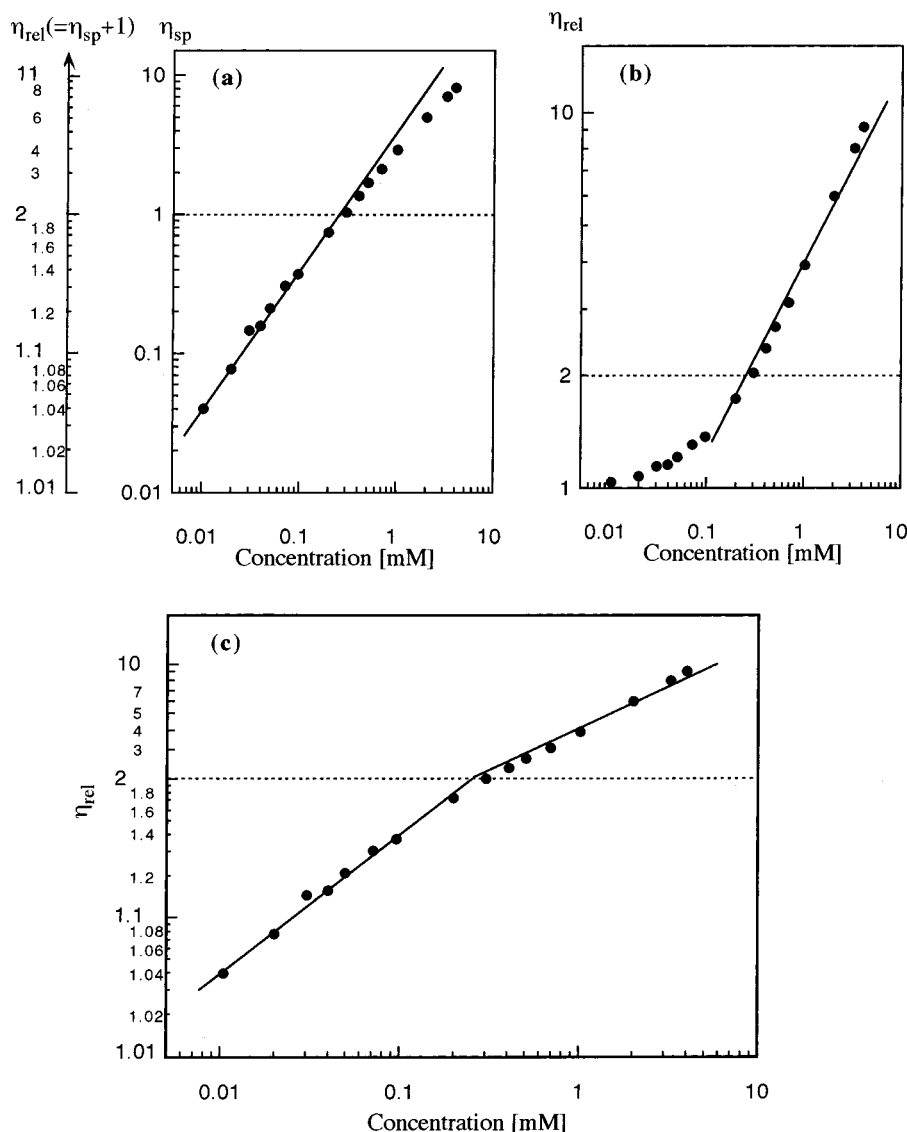
Figure 5. (a) Concentration dependence of η_{sp} of M3 alginate solutions; the solid line has a slope of 1. (b) Concentration dependence of η_{rel} of M3 alginate solutions; the solid line has a slope of $^1/_2$. (c) Concentration dependence of η_{rel} of M3 alginate solutions; the solid lines have a slope of 1 or $^1/_2$. The concentration is expressed by the monomer concentration.

η_{rel}, respectively. The concentration was expressed by the reduced concentration (i.e. dimensionless), $C[\eta]$, according to conventional methods (Izydorczyk and Biliaderis, 1992) for taking into account the differences between the hydrodynamic dimensions among samples. For the same reason, the dielectric relaxation time was also expressed by the reduced relaxation time, $D\tau/[\eta]^{2/3}$ (Ito et al., 1990). The relative viscosity data are plotted in the same manner as in Figure 5c. For all samples, the concentration dependence of each parameter was expressed by a single master curve with a slope changing at the same crossover concentration C^* from the dilute to the semidilute region, as predicted by eqs 7−10, 15, and 16.

DISCUSSION

Quite recently, the scaling theory has become applicable to such synthetic linear polymers as Na-PSS (Rubinstein et al., 1994; Dobrynin et al., 1995). Because the scaling theory can combine structural information obtained from the dielectric measurement with other physical properties (Odijk, 1979; Ito et al., 1990), the relevance of the dielectric properties with other physical properties is the subsequent important subject. In this

study, the concentration dependence of the dielectric parameters was compared to that of viscosity in view of the scaling concept.

The mechanism of the dielectric relaxation around megahertz for linear polyelectrolyte solutions had been a controversial issue (Minakata, 1972; Mandel and Odijk, 1984). Ito et al. (1990) have shown that the relaxation is ascribed to the fluctuation of the bound counterion within the range of the average distance between adjacent polymers within the solution. In our preceding work (Ikeda et al., 1997a,b), we applied the procedure to typical food polysaccharides and revealed the effectiveness of the method for analyzing these polymer solution structures. As can be seen in Figures 4, 6a, and 6b, the concentration dependence of the two dielectric parameters, $\Delta\epsilon$ and τ, was well described by the scaling equations, eqs 7−10, the crossover behavior from the dilute to the semidilute solution being clearly observed. Therefore, in terms of dielectric properties, the scaling concept explained under Theory was applicable to the food polyelectrolyte solutions.

The relative viscosity of linear polyelectrolyte solutions without added salt had been thought to decrease with lowering concentration, conforming to a phenom-
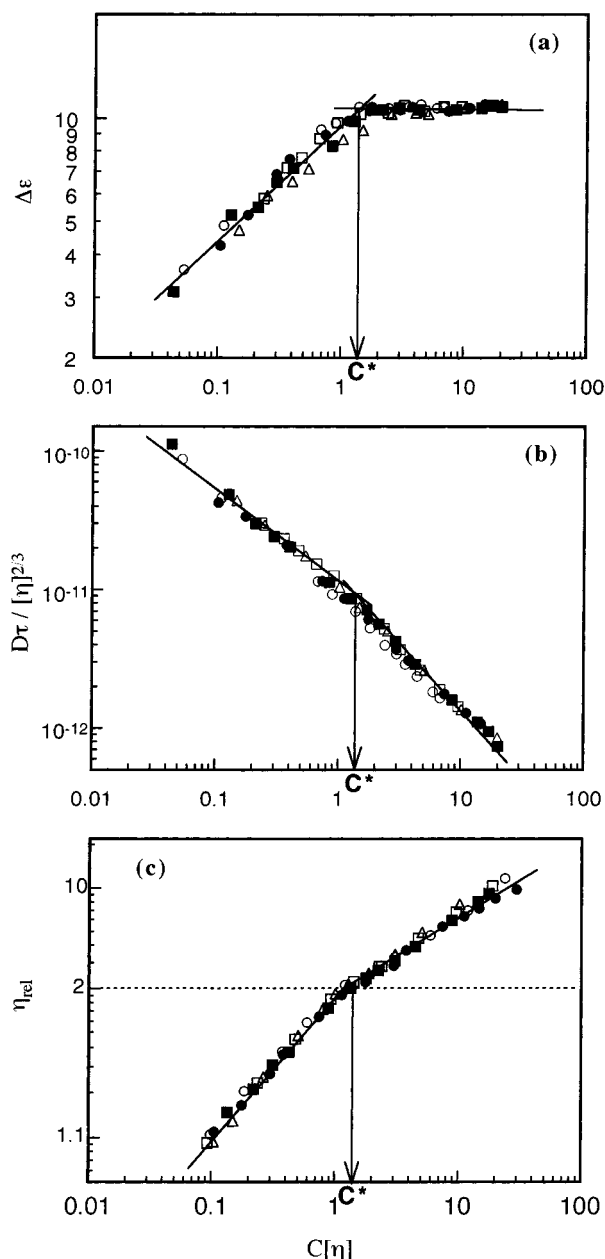
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Figure 6. Summary of the concentration dependence of (a) $\Delta\epsilon$ (the solid lines have a slope of $^1/_3$ or 0), (b) τ (the solid lines have a slope of $-^2/_3$ or -1), and (c) η_{rel} (the solid lines have a slope of 1 or $^1/_2$). The concentration is expressed by the reduced concentration $C[\eta]$. Samples: (O) M1; (□) M3; (△) M5; (●) G1; (■) G3.

enological law proposed by Fuoss (1951), namely, $\eta_{rel} \propto C^{1/2}$. As can be seen in Figures 5b, 5c, and 6c, the relative viscosity was proportional to the square root of the concentration in the semidilute region, in agreement with the empirical Fuoss law. In the dilute region, on the other hand, the specific viscosity values were proportional to the concentration as shown in Figures 5a, 5c, and 6c. A stronger concentration dependence of viscosity values than according to Fuoss law was also observed in a recent work for Na-PSS (Cohen et al., 1988) at a lower concentration than the Fuoss region. For ideally dilute solutions, the concentration dependence of the solution viscosity is known to be expressed by Einstein's viscosity equation, namely, the specific viscosity is proportional to the volume fraction of the material ($\eta_{sp} \propto C^1$). The results of the specific viscosity in the dilute region shown in Figure 5a were consistent with Einstein's equation. Consequently, the scaling

relations for viscosity, eqs 15 and 16, derived from recent polyelectrolyte theory were totally in agreement with the conventional theories and experimental results.

Dobrynin et al. (1995) derived the scaling equations for solution viscosity and applied them to Na-PSS solutions with no added salt. They defined the crossover concentration from the dilute to the semidilute region as the concentration at which the viscosity is twice the solvent viscosity and determined the concentration by extrapolating the viscosity data far from the crossover point. As shown in Figures 5 and 6c, the crossover behavior was observed at about $\eta_{rel} = 2$ for all of the samples. These results support the validity of the assumption of Dobrynin et al. In addition, this crossover concentration C^* of the viscosity values was in agreement with that obtained from the dielectric parameters as shown in Figure 6, indicating these two physical properties reflect the identical scaling aspect of the alginate solutions.

Some of the studies on polysaccharide solution viscosity were carried out in higher concentration solutions with added salt (Castelain et al., 1987; Cuvelier and Launay, 1986). In the solutions of higher concentration or those with added salt in which the charges on the polyelectrolyte are shielded, the polymer chains are considered to behave like an uncharged random coil (Oosawa, 1971). In such a case, the scaling formulas for uncharged polymers (Khokhlov, 1980) would be applicable.

As shown in Figure 6, all of the results for the alginate samples with chemical diversity were summarized as respective single master curves showing crossover behavior from the dilute to the semidilute region, while it is well-known that the physical properties of alginate systems are strongly dependent on their chemical composition like the M/G ratio (Moe et al., 1995). These results suggest that the alginate solution properties were dependent mostly on the molecular size of the alginates, which could be explained if the alginates behave like ideally flexible chains in the low concentration solutions without added salt.

The findings of the present work clearly indicate that the scaling concept will benefit the comprehensive understanding of the physical properties of food polymer solutions, the dielectric measurement providing a useful method for such analysis. Further investigation on the system with added salts, in higher concentration, or the relevance to other physical properties will give us novel information on the physicochemical aspects of the natural polymers.

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