

Dielectric Analysis of Sol–Gel Transition of κ -Carrageenan with Scaling Concept

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The dielectric properties of a typical ionic food polysaccharide, κ -carrageenan, were investigated with special relevance to the sol–gel transition of its dispersed system. The dielectric relaxation around 1 MHz due to counterions bound to the polyelectrolyte was analyzed. For the disordered (coil) state of κ -carrageenan solutions, dependence of the dielectric increment, $\Delta\epsilon$, and that of the relaxation time, τ , on the polymer concentration, C , were summarized as $\Delta\epsilon \propto C^0$ and $\tau \propto C^{-1}$, respectively, in good agreement with the scaling relations for the semidilute solutions derived from the polyelectrolyte solution theories. For the ordered (helix) state of κ -carrageenan dispersed systems, the values of the dielectric parameters, $\Delta\epsilon$ and τ , were larger than the predicted values using the scaling equations for the semidilute solutions. The deviation between the measured and predicted values can be understood as a result of the association of the helical conformers in gels.

Keywords: Dielectric relaxation; κ -carrageenan; sol–gel transition; coil–helix transition; scaling law

INTRODUCTION

Gel-forming natural polysaccharides are commonly used in food industries for controlling physical properties and functionalities of food products such as texture, stability, and the water-holding or thermal properties. Knowledge of the macroscopic properties of food polysaccharide systems has been accumulated through applying various techniques such as rheological measurements, differential scanning calorimetry (DSC), light or X-ray scattering, circular dichroism (CD), and so forth (Clark and Ross-Murphy, 1987; Stephen, 1995). However, only the correlation between the composition and the properties is discussed qualitatively in many cases. Because the physical properties are considered to result from the interaction and structure within these systems, analysis of the structure contributing to the physical properties is needed for food polysaccharide dispersed systems.

Most of the important food polysaccharides, κ -carrageenan, alginate, or xanthan, etc., are polyelectrolytes consisting of saccharide repeating units with ionic groups. The physical properties of the polyelectrolyte dispersed systems are significantly related to the electrostatic interactions arising from Coulomb interactions among the fixed charges on the polymer and its counterions (Oosawa, 1971). Because the dielectric properties are one of the most sensitive properties to such electrostatic interactions, we have been investigating the dielectric properties of several food polysaccharides such as κ -carrageenan, alginate, and gellan gum (Ikeda et al., 1997a,b; Ikeda and Kumagai, 1997). Some of the counterions are electrostatically bound to the polyelectrolyte in such systems. While free counterions con-

tribute to the conductance properties of the system, the bound counterions contribute to the dielectric properties and would cause a dielectric relaxation phenomenon (Blythe, 1979; Mandel and Odijk, 1984; Ookubo et al., 1989; Ito et al., 1990). In our investigation (Ikeda et al., 1997a), the dynamic behavior of such bound counterions to the ionic polysaccharides was observed as dielectric relaxation around megahertz frequency in accordance with the previous results for a linear synthetic polyelectrolyte (Ito et al., 1990). The two dielectric parameters characterizing the relaxation, the dielectric increment $\Delta\epsilon$ and the relaxation time τ , were confirmed to reflect the amount of the bound counterions and the average distance between adjacent polymers in the solution, respectively. In addition, the concentration dependence of the two dielectric parameters, $\Delta\epsilon$ and τ , was consistent with the scaling law derived from the polyelectrolyte theories (Ito et al., 1990), namely, $\Delta\epsilon \propto C^{1/3}$, $\tau \propto C^{-2/3}$ at the dilute region where polymer chains were dispersed independently and $\Delta\epsilon \propto C^0$, $\tau \propto C^{-1}$ at the semidilute region where the polymer chains overlap.

The scaling theory adopted to the dielectric analysis of natural polysaccharides is a relatively recent approach for analyzing the physical properties of polymer dispersed systems. On the basis of the theory, formulas for describing the correlation of the polymer dispersed structure with physical properties such as dielectricity, viscosity, osmotic pressure, and diffusion have already been proposed (Ito et al., 1990; Rubinstein et al., 1994; Dobrynin et al., 1995; Bordi et al., 1996). In our preceding work (Ikeda and Kumagai, 1997), the concentration dependence of the dielectric properties and that of the viscosity for the alginate solutions agreed with the respective scaling equations. In addition, the crossover concentration from the dilute to semidilute region obtained by the dielectric analysis was almost identical to that obtained by the viscosity measurement. These results suggest that the physical properties of the

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food polysaccharide solutions are systematically understandable on the basis of the scaling concept. A scaling approach with the dielectric measurement, therefore, is expected to provide useful information for comprehensive understanding of the producing mechanism of the physical properties of ionic polysaccharide dispersed systems.

κ -Carrageenan, which is ideally composed of alternating $\beta(1-3)$ -D-galactose-4-sulfate and $\alpha(1-4)$ -3,6-anhydro-D-galactose repeating units, extracted from marine red algae, is well-known for its thermoreversible gel-forming properties and is a particularly important polysaccharide in the food industry as a gelling agent. Both the rheological behavior and the gel formation have been extensively investigated from physicochemical point of views (Piculell, 1995). When the temperature is lowered, the coil (disordered) state of κ -carrageenan transfers into a helix (ordered) state. The helices are believed to associate into rigid rods, which can align themselves into long supermolecular assemblies, in the presence of specific cation salts such as KCl (Hermansson, 1989).

coil (disordered) \rightleftharpoons

helix (ordered) \rightleftharpoons helix aggregation to gel

It is commonly accepted that a coil-to-helix transition is a necessary requirement for κ -carrageenan to initiate the gel network generation, but the nature of this conformation is still unclear and the exact mechanism of the reaction has remained largely unsolved (Morris et al., 1980a,b; Paoletti et al., 1984; Viebke et al., 1994). As a result, the prediction of the physical properties of the κ -carrageenan dispersed systems is not yet possible. Natural polymers that undergo coil-helix transition are typically polyelectrolytes (e.g., DNA, polypeptides, polysaccharides), and κ -carrageenan would therefore be a good model substance for evaluating the polymer dispersed state resulting from electrostatic interaction on such a transition.

The dielectric response of the food polysaccharides to the coil-helix transition has scarcely been investigated, much less the sol-gel transition. We have already reported on the dielectric analysis of κ -carrageenan in potassium and the sodium salt form (Ikeda et al., 1997a), but the experimental condition did not allow sol-gel transition. In this paper, we apply the dielectric method for analyzing the sol-gel transition of κ -carrageenan. First, we analyze the conformational state of κ -carrageenan dependent on temperature and concentration, thereby gaining information on the helical fraction and the association of the helices in gels. The dielectric properties for the disordered and ordered κ -carrageenan were then comparatively analyzed on the basis of the scaling concept because that method has an advantage for analyzing the polymer dispersed structure contributing to the physical properties of the system.

EXPERIMENTAL PROCEDURES

Materials. κ -Carrageenan (Sigma, Lot 16H0616) containing a few percent of metal ions (K, 7.3% (w/w); Na, 0.7% (w/w); Ca, 2.2% (w/w)) was used without further purification because the existence of the metal ions is a prerequisite for helix association to occur. The analysis on the purified sample has already been reported (Ikeda et al., 1997a). κ -Carrageenan suspended in water was stirred at 70 °C for an hour to be dissolved, and the sample temperature was then lowered to

30 °C. Water used in the preparation and in the experiments was purified (Millipore, resistivity 18 M Ω cm) after distillation.

Evaluation of κ -Carrageenan Conformation. The conformational change in κ -carrageenan in response to temperature can be monitored by several methods (Piculell, 1995). Conductivity measurement is one of the conventional techniques as well as DSC or optical rotation, having been revealed to give information identical to that from optical rotation (Rochas and Landry, 1987). The charges on the polyion are locally brought closer to each other on helix formation, the charge density of the helix conformer being higher than that of the coil conformer. Because the conductance reflects the charge density of the polyelectrolyte, the conductance of the system decreases with coil-to-helix transition on cooling or vice versa. The relative value of the helical fraction of κ -carrageenan at temperature T is therefore calculated from the conductance measurement:

$$\text{relative helical fraction} = \frac{C_{\text{coil}}(T) - C(T)}{C_{\text{coil}}(T) - C_{\text{helix}}(T)} \quad (1)$$

where $C(T)$ is the measured conductance at temperature T and $C_{\text{coil}}(T)$ and $C_{\text{helix}}(T)$ represent the conductance for the coil and helix conformer at T , respectively. $C_{\text{coil}}(T)$ and $C_{\text{helix}}(T)$ were calculated by extrapolating the respective temperature dependence data at higher or lower temperature to T . The transition temperature was also evaluated as the temperature where the value of the first derivative of the temperature dependence of the conductance, $dC(T)/dT$, is maximum.

The electric conductance was measured at 100 kHz using an LCR meter (4285A, Hewlett-Packard Japan, Tokyo, Japan) equipped with a nickel-plated parallel plate-type cell (11.3 cm³). The conductance value in the frequency range of 1–100 kHz was almost constant, the difference between the value at 1 kHz and at 100 kHz being less than 0.05%. The specimen cell was placed in a thermocontrolled chamber (SU220, Tabai ESPEC, Japan). The cooling and heating rate was 0.1 °C/min. The temperature of the sample was measured using a thermocouple thermometer placed in the cell.

Dielectric Measurements. The electric capacitance and conductance over the frequency range of 75 kHz to 14 MHz were measured using the LCR meter equipped with the cell. The absence of stray capacitance in the measuring system was confirmed by measuring the capacitance of several organic solvents the dielectric constants of which were known. The real part ϵ' of the complex dielectric constant ϵ^* ($=\epsilon' - i\epsilon''$) was calculated as the ratio of the measured capacitance value of the sample to that of the air. The imaginary part ϵ'' was calculated using the value of the electric conductivity κ' .

$$\epsilon'' = \frac{\kappa' - \kappa'_0}{\epsilon_0 \omega} \quad (2)$$

where ϵ_0 is the vacuum permittivity; κ'_0 , the low-frequency limit value of κ' ; and ω , the angular frequency. The values of κ' were calibrated at each measured frequency with several standard simple salt solutions of known conductivity. The frequency dependence data of κ' were approximated by a trinomial expression, the constant value of which was taken as κ'_0 , the low-frequency limit value of κ' .

The κ -carrageenan solutions were fed into the specimen cell at 25 °C. After the values of the electric capacitance and conductance became constant, the first measurement was done. The cell was then kept in ice water for an hour for κ -carrageenan to become a helix conformer. The cell was placed at 25 °C once again, and the second measurement was done after constant values of the electric capacitance and conductance were observed. All of the dielectric measurements were performed at 25 \pm 0.1 °C.

Evaluation of Dielectric Parameters. The dielectric spectrum of polyelectrolyte solutions have been well-described by the so-called Cole-Cole equation (Muller et al., 1974; Ito et al., 1990; Bordi et al., 1991, 1993; Penafiel and Litoviz, 1992). The dielectric parameters, $\Delta\epsilon$ and τ , were evaluated

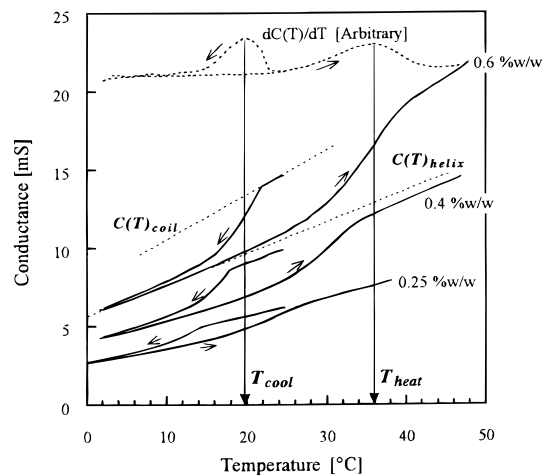


Figure 1. Temperature profiles of conductance during coil–helix transition of κ -carrageenan. Digits [% (w/w)] represent the concentration of κ -carrageenan.

by best-fitting the following Cole–Cole-type equation (Cole and Cole, 1941) to the data:

$$\epsilon' = \epsilon_{\infty} + \frac{1}{2}\Delta\epsilon \left(1 - \frac{\sinh(\alpha x)}{\cosh(\alpha x) + \cos(\alpha\pi/2)} \right) \quad (3)$$

$$\epsilon'' = \frac{1}{2}\Delta\epsilon \left(\frac{\sin(\alpha\pi/2)}{\cosh(\alpha x) + \cos(\alpha\pi/2)} \right) \quad (4)$$

where x is $\ln(2\omega\tau)$; α , the Cole–Cole parameter ($0 < \alpha < 1$); and ϵ_{∞} , the high-frequency limit of the dielectric constant.

When measuring the dielectric properties of ionic materials, substantially large values of the real part of the dielectric constant ϵ' are usually observed, especially at a lower frequency. The accumulation of charges in the material on electrode surfaces results in electrode polarization that leads to the formation of electrode double layers (Schwan, 1968; Grant et al., 1978; Takashima, 1989; Davey et al., 1990). The associated capacitance and complex impedance due to this polarization is so large that the correction for it is one of the major requisites in obtaining meaningful measurements on conductive samples (Davidson and Cole, 1951; Scheider, 1975; Blythe, 1979). In this study, the dielectric constants for NaCl or KCl solutions with the same conductivities as κ -carrageenan solutions were measured as references. The measured values for κ -carrageenan solutions only in the frequency range where the electrode polarization effect was not observed were used for analysis. To evaluate the dielectric parameters, the real part ϵ' and the imaginary part ϵ'' were fitted simultaneously to minimize the square sum of the residuals between the measured and calculated values according to the method of Bordi et al. (1993).

RESULTS

Figure 1 represents the temperature dependence of conductance of κ -carrageenan dispersed systems. The conformational transition was observed as a change in the temperature dependence of the measured conductance. The broken curves are the first derivative values of the conductance for the 0.6% (w/w) sample. The two transition temperatures in the course of the cooling process, T_{cool} , and in the course of the heating process, T_{heat} , were determined as the temperature where the derivative value was maximum. At any concentration, the coil-to-helix transition occurred at a lower temperature than the helix-to-coil transition ($T_{heat} > T_{cool}$). The difference between the two transition temperatures became larger with increasing concentration.

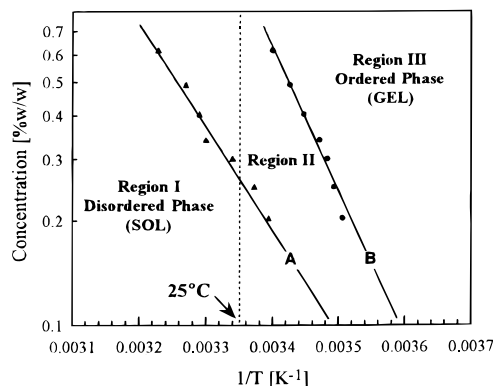


Figure 2. Phase diagram of κ -carrageenan. Transition temperature in the course of the following: \blacktriangle , heating process (T_{heat}); \bullet , cooling process (T_{cool}).

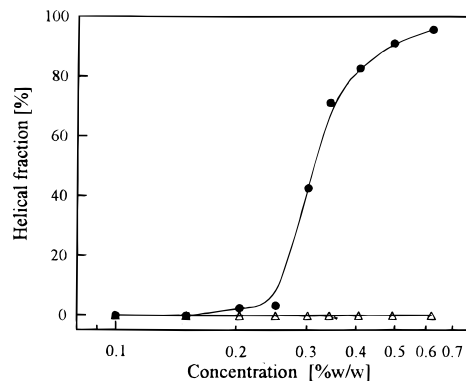


Figure 3. Concentration dependence of the relative helical fraction of κ -carrageenan at 25 °C. In the course of the following: \triangle , cooling; \bullet , heating process.

The concentration values were plotted against the reciprocal of the transition temperature in Figure 2, this being the so-called phase diagram of κ -carrageenan. Region I delimited by line A representing the conformational change during the heating process corresponds to the sol (disordered) phase, while region III delimited by line B representing the conformational change during the cooling process corresponds to the gel (ordered) phase. Region II indicates the overlap of the two regions corresponding to the hysteresis. At 25 °C where we investigated the dielectric properties, all the samples were in a disordered state in the course of cooling, while part of the samples at a higher concentration formed helices to gel in the course of heating after the cooling process.

Figure 3 shows the concentration dependence of the relative helical fraction at 25 °C calculated using eq 1. All of the κ -carrageenan was in a disordered state before cooling. For the samples after the cooling process, the helical fraction increased with increasing concentration in the region above 0.2% (w/w), about 97% of the κ -carrageenan forming a helix at 0.6% (w/w). The result suggests that at 25 °C after cooling with ice water, sol-to-gel transition will occur above 0.2% (w/w) with increasing concentration.

As typical examples of the dielectric measurement data, Figure 4 represents the frequency dependence of the real part of the dielectric constant, ϵ' , and that of the electric conductance, κ' , of a 0.2% (w/w) κ -carrageenan solution. The real part of the dielectric constant ϵ' decreased with increasing frequency, a two relaxation process below and above 200 kHz being indicated in

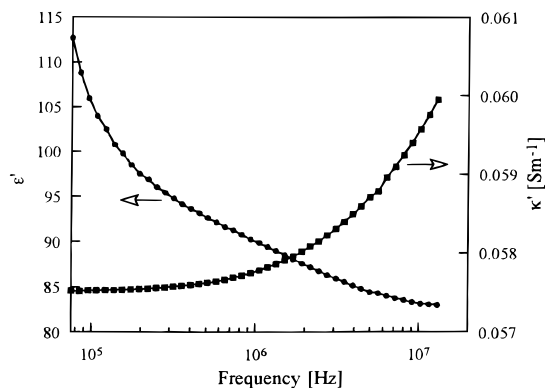


Figure 4. Dielectric relaxation spectrum of 0.2% (w/w) κ -carrageenan: \bullet , ϵ'' ; \blacksquare , κ' .

accordance with our previous results (Ikeda et al., 1997a). Because the higher frequency relaxation has been ascribed to the fluctuation of bound counterions (Ikeda et al., 1997a) and scaling relations for higher frequency relaxation has been derived (Ito et al., 1990), only the higher frequency relaxation was analyzed in the subsequent part. The values of κ' increased with increasing frequency, being satisfactorily constant at lower frequency to calculate accurate values of ϵ'' using eq 2.

As can be seen in Figures 2 and 3, the κ -carrageenan at 25 °C was disordered at any concentration in the course of the cooling process, while in the course of the heating process, part of the polymers at 25 °C was in a helical state at a higher concentration. Figure 5 shows the dielectric spectrum for (a) the disordered (in cooling) and (b) partly ordered (in heating) κ -carrageenan systems. The experimental data were fitted well to the Cole–Cole-type eqs 3 and 4 in the higher frequency region in accordance with our previous results for purified κ -carrageenan (Ikeda et al., 1997a), the values of the higher frequency relaxation parameters, $\Delta\epsilon$ and τ , being obtained. The values for the α parameters representing the broadness in the distribution of relaxation times were about 0.6–0.7 for all systems.

Figure 6a represents the concentration dependence of the dielectric increment $\Delta\epsilon$ and that of the relaxation time τ for the disordered κ -carrageenan solutions. Each of the parameters' behavior was well-described by the solid lines with a slope of 0 for $\Delta\epsilon$ or -1 for τ representing the scaling relations for the semidilute solutions (Ito et al., 1990). This result was in agreement with our preceding results on κ -carrageenan with no salt added in the semidilute region (Ikeda et al., 1997a). In Figure 6b, the concentration dependence of the dielectric increment $\Delta\epsilon$ and the relaxation time τ for the partly ordered κ -carrageenan systems are shown. At a lower concentration than about 0.2% (w/w), the experimental results agreed with the same scaling equations as those for disordered κ -carrageenan solutions. In the concentration region above 0.2% (w/w), the deviation between the measured values and the scaling equations increased with increasing concentration for both $\Delta\epsilon$ and τ . With increasing values of the dielectric parameters, the system transferred to a gel as shown in Figure 2, the helical fraction shown in Figure 3 also increasing in this concentration region.

DISCUSSION

The gelation phenomenon of κ -carrageenan is the most extensively studied in the food polysaccharides

because it is one of the most widely used as a gelling agent in food industries. Not only the analysis of the polymer network using optical rotation (Rees et al., 1970; Rochas and Rinaudo, 1980; Rinaudo and Rochas, 1981), light scattering (Morris et al., 1980b), electron microscopy (Hermansson, 1989; Hermansson et al., 1991), or rheological measurement (Oakenful and Scott, 1986), but also polyion/cation interaction analysis using NMR (Belton et al., 1986; Piculell et al., 1989; Nilsson and Piculell, 1991) or ESR (Day et al., 1988) has been done. However, even the gelation mechanism is still controversial (Viebeck et al., 1994). We applied the dielectric relaxation method with scaling analysis as an effective method for analyzing the dispersed structure of the polymer, which is strongly related to the producing mechanism of the physical properties of the system.

The carrageenan gelation has been studied with respect to the helix–coil transition (Piculell, 1995). It is well-established that the associated helix conformers form the cross-linking region in a gel. The evidence of interhelical association is usually observed as thermal hysteresis in the transition between cooling and heating curves; the coil-to-helix transition occurs at a temperature lower than the helix-to-coil one. The cooling transition is considered to reflect the equilibrium between coil and helix, while the heating transition reflects the increased thermal stability of associated helices (Nilsson et al., 1989; Nilsson and Piculell, 1989, 1990, 1991). As shown in Figures 1 and 2, thermal hysteresis was observed for all samples, indicating the existence of helical association in region III. In addition, a sample with higher concentration showed wider hysteresis, indicating that a larger amount of associated helices existed in the higher concentration system.

In our preceding studies (Ikeda et al., 1997a; Ikeda and Kumagai, 1997), we applied the dielectric scaling analysis to typical food polysaccharides, alginate and κ -carrageenan, as solutions with no added salts and revealed that the method is effective for analyzing these polymer solution structures in the dilute and semidilute regions. For the disordered state κ -carrageenan with potassium salt, the concentration dependence of the two dielectric parameters, $\Delta\epsilon$ and τ , were satisfactorily described by the scaling equations for the semidilute solutions, as can be seen in Figure 6a. These solutions were considered in the vicinity of the sol–gel transition point because all of these solutions gelled on cooling (Figure 2). Additionally, as shown in Figure 6b, the κ -carrageenan dispersed systems in the course of the heating process were in the semidilute region at a concentration lower than ca. 0.2% (w/w). These systems transformed into gels with increasing concentration, and the dielectric parameters were no longer described by the scaling equations for the semidilute solutions. Therefore, it turned out that the disordered κ -carrageenan dispersed system formed a structure typified as a semidilute solution, in which the extended polymer chains overlap, even in the vicinity of the sol–gel transition point. Gelation of a semidilute polymer solution is also a controversial subject in polymer science (Allain and Salomé, 1990). It is generally considered that polymer dispersed structure in linear polyelectrolyte solutions is categorized as to concentration, that is, dilute, semidilute, and then a blob region with increasing concentration (De Gennes, 1976; Odijk, 1979). In the blob region, the polymer chain looks like a folded sphere because the charges on the polyelectro-

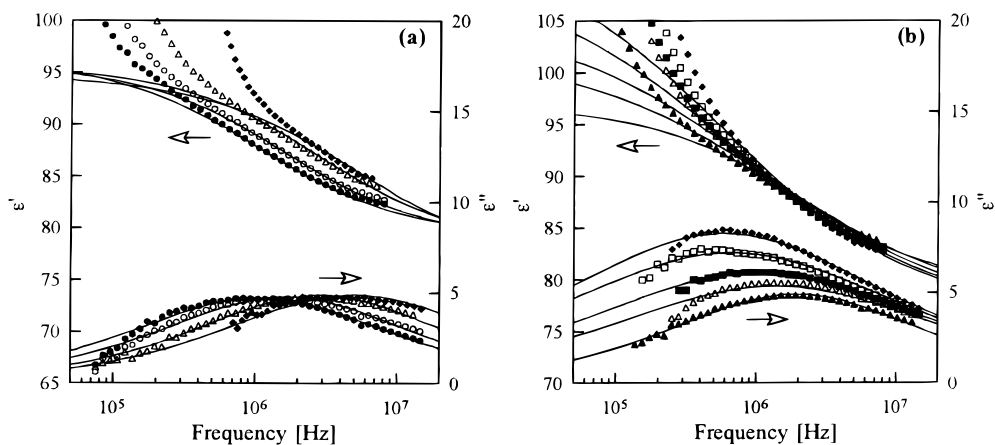


Figure 5. Dielectric relaxation of κ -carrageenan at 25 °C in the course of the (a) cooling and (b) heating process. The solid curves are the best fit ones for the Cole–Cole equations, eqs 3 for the real part ϵ' and 4 for the imaginary part ϵ'' . Concentration [% (w/w)]: ●, 0.10; ○, 0.15; ▲, 0.21; △, 0.30; ■, 0.34; □, 0.40; ◆, 0.49.

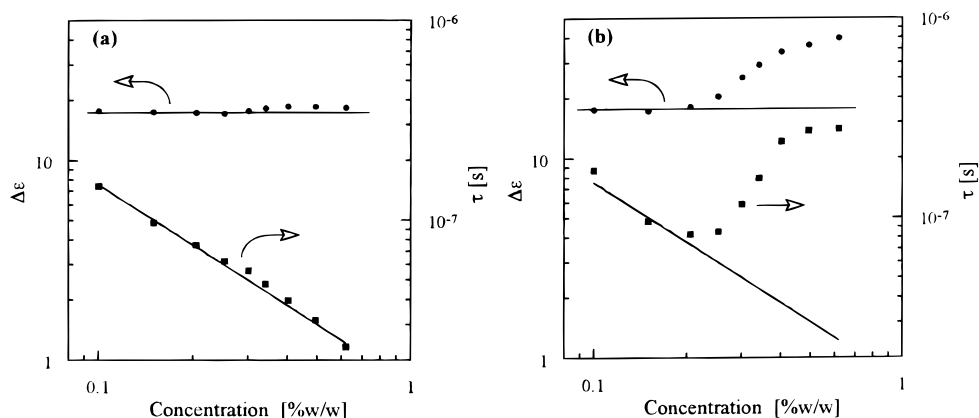


Figure 6. Concentration dependence of $\Delta\epsilon$ and τ of κ -carrageenan at 25 °C in the course of the (a) cooling and (b) heating process. The solid lines have a slope of (●) 0 or (■) -1 .

lyte chain are shielded due to high ionic concentration. However, for κ -carrageenan at least, it is suggested that the semidilute solution gels before forming a blob structure with increasing concentration.

For the helical state κ -carrageenan, the values of dielectric parameters, $\Delta\epsilon$ and τ , became larger than those predicted by the scaling equations for the semidilute solutions, as can be seen in Figure 6b. Moreover, the deviation between the measured and predicted values increased with increasing concentration, the helix formation shown in Figures 3 and the association of helices shown in Figure 2 also proceeding. The formation of the helical association would influence the dielectric parameters as follows:

(I) The dielectric increment $\Delta\epsilon$ increases with increasing bound counterion concentration due to the high charge density of the helical association.

(II) The relaxation time τ increases with increasing distance between the adjacent polymers due to the apparent decreasing polymer concentration.

An apparent decrease in polymer concentration due to association of the polymer chains has been observed in calcium alginate solutions (Ikeda et al., 1997a). One can estimate the apparent concentration of the polymer C_{app} using the measured value of the relaxation time τ and the scaling equation for semidilute solutions. The apparent degree of association N would then be estimated as $N = C/C_{app}$. In Figure 7, the dielectric parameters were plotted against the calculated apparent degree of association N . Although the details of the

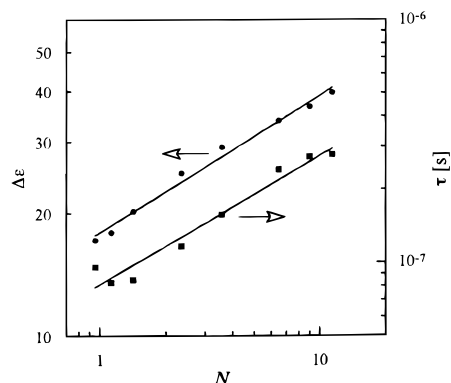


Figure 7. Comparison of $\Delta\epsilon$ and τ with the apparent degree of helical association N .

mechanism must be investigated more accurately, the results in Figure 7 represent a good indication that the dielectric parameters reflect the association phenomenon of the helical κ -carrageenan.

Consequently, the dielectric relaxation was an effective method for analyzing the change in the dispersed structure of the food polysaccharide accompanied by the sol–gel transition of the system. Many natural polymers with the ability to form a gel, e.g., agarose, gellan gum, or gelatin, have one essential feature in common, namely, following a scheme very similar to that of κ -carrageenan. To gain further insight into the gelation mechanism of these polysaccharides, a separate inves-

tigation on the dielectric response to helix formation and its association would be necessary.

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