

Gelation of Aqueous Pectin Solutions: A Dynamic Light Scattering Study

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Received May 2, 2001; accepted October 22, 2001

We report the dynamic light scattering study of the gelation of aqueous solutions of the biopolymer, pectin, induced by the addition of calcium chloride. The time correlation function data are analyzed under the framework of the coupling model. As the solution enters the semidilute regime where gelation sets in, the relaxation process shows a stretched exponential behavior. The stretching exponent decreases and the characteristic time of the stretched exponential diverges as the system evolves to a gel. Aqueous pectin solutions in the presence of 0.1 M NaCl show similar behavior. Thus, the molecular relaxation modes of pectin solutions can be well described by the coupling model. © 2002 Elsevier Science

Key Words: pectin; dynamic light scattering; coupling model; sol-gel transition.

INTRODUCTION

Polymer species can form a variety of supramolecular structures via gelation, aggregation, phase separation, and ordering. Gels can be prepared by chemically cross-linking branched polymer chains or physical aggregation of polymer chains into three-dimensional structure (1). Hydrogen bonding, Coulomb interaction, and dipolar forces are some of the types of bonding which lead to network formation resulting in gelation. It is sometimes possible to break these types of bonds by increasing the temperature. Systems with these properties are said to form thermoreversible gels.

Dynamics and relaxation process in sol-gel systems have been the subject of continued interest (2–7). In the semidilute solutions of polymers and polymer-related systems, topological constraints on the polymer molecular motion due to polymer overlap strongly affect the dynamics. As gelation progresses through the semidilute solution, the complexity of the phenomenon increases. Dynamic light scattering (DLS) has served as a useful technique to study the dynamics of diffusion of polymers in solutions. In this paper we present a DLS study of gelation in aqueous solutions of the biopolymer, pectin. The decay rate of the time correlation function of the scattered electric field is determined as the system undergoes sol-gel transition and the

results are analyzed in the framework of the coupling model, devised by Ngai and co-workers (8–13).

Pectins are important polysaccharides, which are used in the food industry as gelling agents (14). Apple pomace and orange peels are the two major sources of commercial pectins. In native pectins, about 70% of the carboxyl groups are methyl-esterified. These “high methoxyl” (HM) pectins form gels in acidic medium in the presence of high concentrations of sucrose. Pectins of lower ester content are produced by controlled deesterification of native pectins and the resulting polysaccharide forms gels upon addition of calcium or related divalent ions (15). In these “low-methoxyl” (LM) pectins, gelation results from ionic linkages via Ca^{2+} ion bridges between two carboxyl groups belonging to two different chains (16). Gelation of LM pectins is affected by several intrinsic and extrinsic parameters such as the degree of methylation, the average molecular weight of the sample, the ionic strength, the pH, the temperature. An increase in the ionic strength, a neutral pH, and a decrease in the setting temperature and in the degree of methylation lower the amount of calcium chloride required to obtain the sol-gel transition (17). Molecular weight distribution and conformation of high methoxy citrus pectins were studied using light scattering and gel-permeation chromatography with low-speed sedimentation equilibrium (18, 19). Solution conformation of apple and citrus pectins with a large range of degree of methylation was studied by small angle neutron scattering, viscometry, and molecular modeling (20). These studies showed that pectins are relatively stiff molecules with persistence length and flexibility of the polymeric backbone dependent on the degree of methylation. In a good solvent such as 0.1 M NaCl aqueous solution at 25°C, the pectin molecules exhibit the general behavior of linear flexible polymers in good solvent (21). The sol-gel transition brought forth by increasing calcium chloride concentration was monitored by rheological measurements close to the gel point (22). The dynamic exponents for viscosity and elastic moduli were found to be consistent with the predictions of the scalar elasticity percolation model (23–25). Thus in the evolution from sol to gel, the pectin solution can be expected to exhibit molecular relaxation modes characteristic of semidilute polymer solutions.

Dilute solutions of monodisperse polymers as well as some semidilute solutions of flexible polymers at good solvent

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conditions show single exponential relaxation behavior of the concentration fluctuations that can be probed by DLS experiments. However, for several associating polymer solutions (26), polymeric cluster solutions (2), and thermoreversible gelling solutions (3–7), a broad distribution of relaxation times is often recorded. For these systems, DLS showed an initial exponential decay followed by a stretched exponential with width parameter, β . The characteristic time of the stretched exponential diverged to infinity as the system set to a gel. In some cases such as gelatine sol-gel transition (5, 7), intermediate power law decay was also observed. The coupling model of Ngai and co-workers is found to be well adapted for interpreting the experimental findings in several complex systems exhibiting a stretched exponential mode of relaxation (8). In this DLS study on aqueous solutions of pectin, we find that most of the experimental findings are in accordance with the coupling model. Though several aspects of sol-gel transition in aqueous pectin solutions have been thoroughly investigated by Axelos and co-workers (17, 21, 22, 27), to the best of our knowledge, this is the first DLS study which applies coupling model to the sol-gel transition of pectin solutions. The present study strengthens the findings of Axelos and co-workers on gelation of pectin solutions.

EXPERIMENTAL DETAILS

Pectin from citrus fruit (Potassium salt) with degree of esterification 22% was obtained from Sigma Chemicals (P-9311) and was used without further purification. The manufacturer has quoted the viscosity average molecular weight of this product to be 17,000. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium chloride (NaCl) were bought from Merck and used as received. Stock solutions of calcium chloride and sodium chloride of appropriate concentrations were prepared. Pectin concentrations of 2.5 and 10.0 g L^{-1} were chosen for DLS studies. Homogeneous samples were obtained by mixing aqueous pectin solution with calcium chloride and sodium chloride solutions of appropriate volumes to get the required molarity of the salts. The solution was stirred for half an hour and then poured into 1-cm-diameter glass vial for DLS studies. The measurements were made after the sample was cured for 24 h at room temperature.

The DLS measurements on 2.5 g L^{-1} pectin solutions were made at the Indian Institute of Science, Bangalore, using a homemade photon correlation spectrometer employing Kr^+ laser ($\lambda = 647 \text{ nm}$) and Malvern digital correlator at 60, 90, and 120° scattering angles. Measurements on 10 g L^{-1} pectin solutions were made at Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Mumbai, using a standard Brook Haven light scattering instrument BI-90 with 5 mW He-Ne Laser ($\lambda = 632.8 \text{ nm}$), the angle of scattering being 90°. In DLS experiments, the normalized intensity autocorrelation function of the scattered light, $g^{(2)}(q, t) = \langle I(q, t) I(q, 0) \rangle / \langle I \rangle^2$ is measured and is used to calculate the normalized time correlation function of the scattered electric field, $g^{(1)}(q, t) = \langle E^*(q, t) E(q, 0) \rangle / \langle E \rangle^2$. The function

$g^{(1)}(q, t)$ can be identified with the dynamic structure factor $S(q, t)$ which, for a Gaussian signal, is related to $g^{(2)}(q, t)$ by the Siegert relation $g^{(2)}(q, t) = 1 + f |S(q, t)|^2$, where the coherence factor f measures the degree of coherence of the scattered light (28). Four or more different sampling times were used to obtain the scattered intensity autocorrelation function $\langle I(0) I(t) \rangle$ and then the data were spliced together. The background subtracted normalized dynamic structure factor

$$S(q, t) = \sqrt{\frac{g^{(2)}(t) - 1}{f}} \quad [1]$$

was calculated from the intensity autocorrelation function. f is determined from the value of the intercept of the plot of $g^{(2)}(q, t)$ vs t . Here, q is the scattering wave vector given by

$$q = \frac{4\pi\mu \sin(\theta/2)}{\lambda}, \quad [2]$$

μ being the refractive index of the solution and θ , the scattering angle. The data were fitted using (26)

$$S(q, t) = A_f \exp(-t/\tau_f) + A_s \exp(-(t/\tau_{sc})^\beta), \quad [3]$$

where A_f and A_s are the amplitudes of the fast and slow relaxation modes, respectively, with $A_f + A_s = 1$. τ_f and τ_s are the characteristic times of fast and slow decays with

$$\tau_s = \frac{\tau_{sc}}{\beta} \Gamma(1/\beta), \quad [4]$$

where β , the stretching exponent, is a measure of the width of the distribution of relaxation times and $\Gamma(1/\beta)$ is the gamma function.

The viscosity measurements were carried out with the use of Ubbelohde viscometer on pectin solutions in the concentration range 0.1 to 20 g L^{-1} in order to determine C^* , the crossover concentration from the dilute to the semidilute regime of the pectin solutions.

THEORETICAL CONSIDERATIONS

The coupling model (8–13) is a general approach to dynamics of the constrained or interacting systems. According to this model, there exists a temperature-insensitive crossover time, t_C such that for $t < t_C$, the relaxation process is not affected by coupling effects. The basic units relax independently with a single exponential correlation function. At long times, i.e., $t > t_C$, dynamic constraints come into play and give rise to fractional decay of the correlation function. Thus,

$$\phi(t) = \exp(-t/\tau_0) \quad \text{for } t < t_C \quad [5]$$

and

$$\phi(t) = \exp\left(-\left(\frac{t}{\tau}\right)^{1-n}\right) \quad \text{for } t > t_c. \quad [6]$$

τ_0 is the initial relaxation time in the absence of coupling, τ is the effective relaxation time, t_c is the characteristic time beyond which coupling effects influence the dynamics, and n is the coupling parameter in the range $0 \leq n \leq 1$ and depends on the intermolecular interaction. For continuity of $\phi(t)$ at $t = t_c$,

$$\tau = (t_c^{-n} \tau_0)^{1/(1-n)}. \quad [7]$$

When the condition $\tau_0/t_c \gg 1$ holds, the linear exponential, namely, $\exp(-t/\tau_0)$ decays by an insignificant amount at $t = t_c$ and the correlation function is practically given at all times by the stretched exponential.

The concentration fluctuation correlation function is given by

$$\phi(t) = \frac{\langle \delta c_q(t) \delta c_{-q}(0) \rangle}{\langle |\delta c_q|^2 \rangle}, \quad [8]$$

where $\delta c_q(t)$ is the concentration fluctuation of wave vector q . The function $\phi(t)$ is identified with $S(q, t)$. Hence τ_0 in Eq. [5] is the correlation time of free diffusion given by

$$\tau_0(q) = (D_0 q^2)^{-1}, \quad [9]$$

where D_0 is the free translational diffusion coefficient of the center of mass of the polymer. The experimentally observed width parameter β in Eq. [3] is related to the coupling parameter n through $\beta = 1 - n$. Substituting Eq. [9] in Eq. [7] gives

$$\tau \propto q^{-2/\beta}. \quad [10]$$

We recall that the theoretical approach of the coupling model is semiempirical, as it does not identify the particular mechanism or the exact nature of the interaction responsible for the coupling. However, it has been very effective in describing various relaxation processes in complex systems. It has been demonstrated (29) that general results from anomalous diffusion in disordered fractal-like systems produce the features of the time-dependent rate proposed by the coupling model.

RESULTS AND DISCUSSION

The intrinsic viscosity $[\eta]$ was determined by using Huggin's and Kraemer's extrapolation equations. Huggin's equation:

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2 C \quad [11]$$

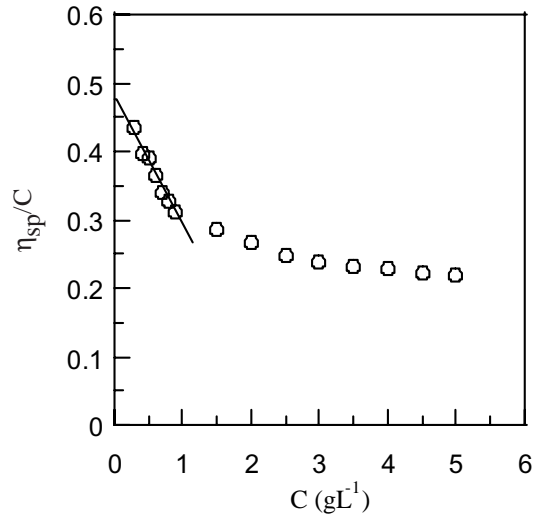


FIG. 1. Plot of η_{sp}/C against C . The intrinsic viscosity $[\eta]$ given by the intercept is 475 ml g^{-1} . The deviation from linearity occurs at $C^* \sim 1.5 \text{ g L}^{-1}$.

Kraemer's equation:

$$(\ln \eta_r)/C = [\eta] + k_2[\eta]^2 C. \quad [12]$$

k_1 and k_2 are the interaction parameters characteristic of the polymer-solvent system, $\eta_r = \eta/\eta_s$ is the relative viscosity of the solution with respect to the solvent and η_{sp} is the specific viscosity given by $\eta_{sp} = \eta_r - 1$. The concentration range chosen for the double extrapolation was 0.3 to 0.9 g L^{-1} corresponding to η_r in the range 1.1 to 1.3 . The intrinsic viscosity was found to be 475 ml g^{-1} . Figure 1 shows the plot of (η_{sp}/C) against the concentration of the polymer, C . The deviation from linearity as given by Huggin's equation occurs at $C^* \sim 1.5 \text{ g L}^{-1}$. For a polymer solution (30), the overlap concentration from dilute to semidilute regime is expected to be at $C^* = 0.77/[\eta]$. The value of $C^* \sim 1.5 \text{ g L}^{-1}$ is close to this expected value.

Garnier *et al.* (17) had determined the phase diagrams of citrus pectins of large range of degree of methoxylation. The different phases (sol, gel, and syneresis) observed in pectin solutions on addition of calcium chloride were presented by plotting molar concentration of calcium chloride versus the reduced polymer concentration $C[\eta]$. The sol-gel transition curves showed that the minimal polymer concentration able to promote gelation, C_0 , depended on the solvent conditions. In the presence of an excess of monovalent salt (0.1 M NaCl), gelation was possible before the overlap threshold concentration, C^* , and the amount of calcium required to obtain a gel was independent of the polymer concentration for $C > C^*$. In salt-free solutions, C_0 was very near C^* and the amount of calcium required to obtain a gel increased with polymer concentration. Guided by these results, we selected two pectin concentrations, 2.5 and 10 g L^{-1} for the DLS study of the sol-gel transition induced by calcium chloride in aqueous salt-free pectin solutions. The gelation in

10 g L⁻¹ pectin solution in the presence of 0.1 M NaCl was also studied.

A. Pectin Gelation in the Absence of NaCl

For a pectin concentration of 2.5 g L⁻¹, the sol-gel transition was investigated by increasing calcium chloride concentration from 0 to 3.5 mM. After curing for 24 h, if there was flow in the sample when the sample vial was tilted, the system was considered to be sol. If there was no deformation of the meniscus when the vial was tilted, the sample was considered as gel. The samples with 3.0 and 3.5 mM calcium chloride were gels. Above 3.5 mM, syneresis was observed with the presence of water above gel surface. For the gelled samples, the DLS data were collected at scattering angles 90° ($q = 1.826 \times 10^7 \text{ m}^{-1}$), while for other samples the data were collected for scattering angles 60, 90, and 120°.

Figure 2 depicts the dynamic structure factor $S(q, t)$ obtained for 2.5 g L⁻¹ aqueous pectin solutions in the presence of 0, 2.5, and 3.5 mM calcium chloride at scattering angle 90°. The theoretical fits to the data using Eq. [3] are also shown. As the concentration of calcium chloride increases there is a progressive slowing down of the relaxation process. This type of slowing down has been observed in a number of DLS studies (2–7, 26). Figures 3 and 4 show the variation of the amplitudes of the fast and slow relaxation modes with calcium chloride concentration. With increase in calcium chloride concentration, the coupling effects influence the relaxation process as the solution is driven from sol to gel phase. Hence the slow mode becomes more dominant at higher calcium concentrations.

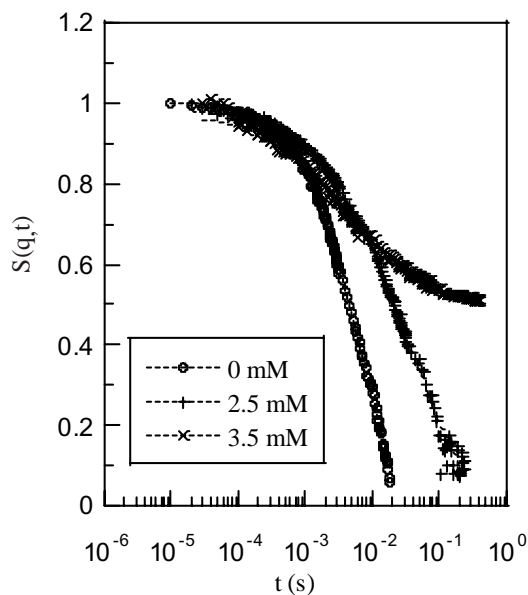


FIG. 2. The dynamic structure factor $S(q, t)$ for 2.5 g L⁻¹ aqueous pectin solution as a function of time in the presence of 0, 2.5, and 3.5 mM CaCl₂. Dotted lines are theoretical fits using Eq. [3].

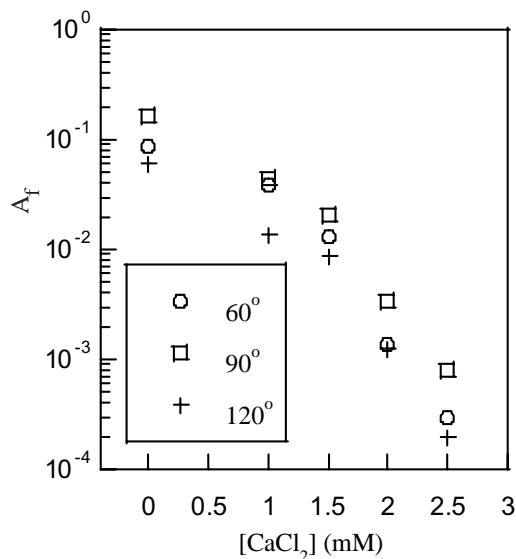


FIG. 3. Variation of the amplitude, A_f , of the fast relaxation mode of $S(q, t)$ of 2.5 g L⁻¹ aqueous pectin solution with CaCl₂ concentration for three different q values. (i) $q = 1.29 \times 10^7 \text{ m}^{-1}$ ($\theta = 60^\circ$); (ii) $q = 1.83 \times 10^7 \text{ m}^{-1}$ ($\theta = 90^\circ$); (iii) $q = 2.24 \times 10^7 \text{ m}^{-1}$ ($\theta = 120^\circ$).

The variation of the q -independent width exponent, β , with calcium chloride concentration is shown in Fig. 5. In pure pectin solution the value of β is 0.985 and it decreases to 0.22 at $[\text{CaCl}_2] = 3.5 \text{ mM}$ when the sample becomes a gel. The variations of the fast and slow relaxation times, τ_f and τ_s , respectively, at scattering angle 90° are depicted in Fig. 6. The slow relaxation time increases by orders of magnitude when sol-gel transition occurs. From Eq. [9], we find that the fast time τ_f is

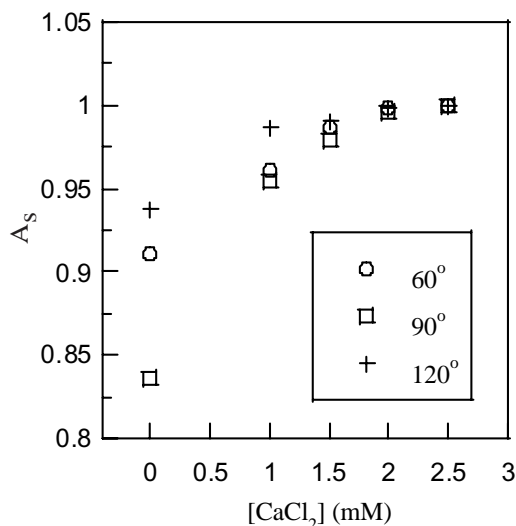


FIG. 4. Variation of the amplitude, A_s , of the slow relaxation mode of $S(q, t)$ of 2.5 g L⁻¹ aqueous pectin solution with CaCl₂ concentration for three different q values. (i) $q = 1.29 \times 10^7 \text{ m}^{-1}$ ($\theta = 60^\circ$); (ii) $q = 1.83 \times 10^7 \text{ m}^{-1}$ ($\theta = 90^\circ$); (iii) $q = 2.24 \times 10^7 \text{ m}^{-1}$ ($\theta = 120^\circ$).

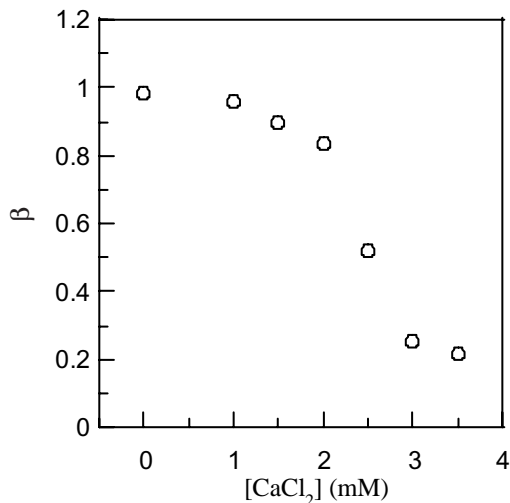


FIG. 5. Variation of the q -independent stretching exponent, β , for 2.5 g L^{-1} aqueous pectin solution with CaCl_2 concentration.

related to the diffusion coefficient, D_0 , by $D_0 = (\tau_f q^2)^{-1}$. For aqueous pectin solution in the absence of calcium chloride, for the three q values used in this study, $D_0 \sim 2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. This slow diffusion process may be due to the reasons that the solution is already in the semidilute regime ($C > C^*$) and the pectin molecules are stiffer in salt-free solution due to charge effects.

The q dependence of τ_f and τ_s are shown in Figs. 7 and 8 on log-log plots. The coupling model predicts τ_f and τ_s to scale as $\tau_f \sim q^{-\alpha_f}$ and $\tau_s \sim q^{-\alpha_s}$, where $\alpha_f = 2$ for diffusive mode and $\alpha_s = 2/\beta$. The α values obtained for the variation of τ_f and τ_s with q are listed in Table 1. The results by and large conform to the predictions of coupling model.

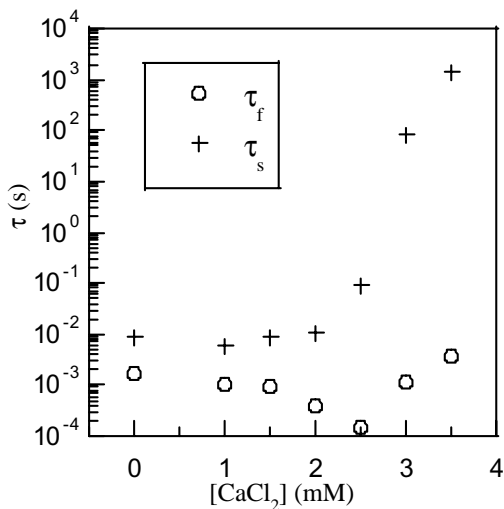


FIG. 6. Variation of the characteristic times τ_f and τ_s of the fast and slow relaxation modes of $S(q, t)$ of 2.5 g L^{-1} aqueous pectin solution with CaCl_2 concentration.

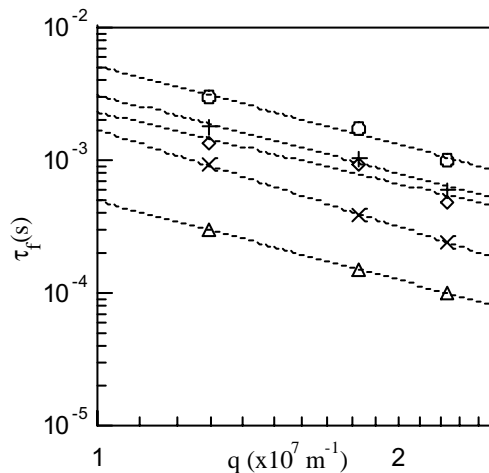


FIG. 7. Variation of τ_f with q for 2.5 g L^{-1} aqueous pectin solution for various CaCl_2 concentrations: 0 mM (\circ); 1 mM ($+$); 1.5 mM (\diamond); 2 mM (\times); 2.5 mM (\triangle).

The gelation of salt-free aqueous pectin solution of 10 g L^{-1} concentration was also studied at scattering angle 90° ($q = 1.872 \times 10^7 \text{ m}^{-1}$) using BI-90 particle sizer employing He-Ne laser. The calcium chloride concentration was varied from 0 to 4.5 mM. In this range of calcium chloride concentration, the system showed viscosification, while there was gel formation at $[\text{CaCl}_2] \geq 8 \text{ mM}$. This is in accordance with the observation of Garnier *et al.* (17), that in salt-free pectin solutions the amount of calcium for gel formation increases with the polymer concentration.

Figure 9 shows the variations of the amplitudes and characteristic times of fast and slow relaxation modes and the stretching exponent with calcium chloride concentration for 10 g L^{-1}

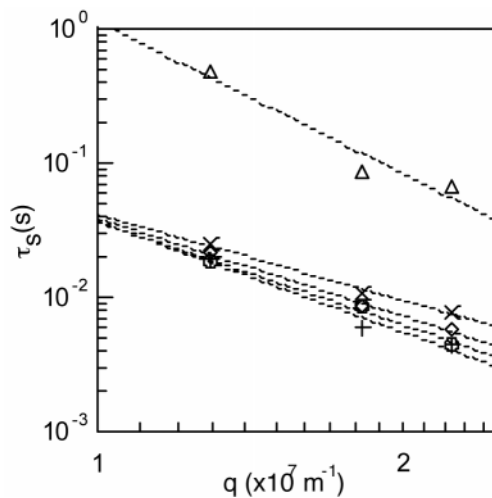


FIG. 8. Variation of τ_s with q for 2.5 g L^{-1} aqueous pectin solution for various CaCl_2 concentrations: 0 mM (\circ); 1 mM ($+$); 1.5 mM (\diamond); 2 mM (\times); 2.5 mM (\triangle).

TABLE 1

Values of Exponents α_f and α_s Obtained for the Variation of the Characteristic Times τ_f and τ_s , Respectively, with the Wave Vector q and the Values of the Stretching Exponent β for 2.5 g L^{-1} Aqueous Pectin Solution in the Presence of Different CaCl_2 Concentrations

| $[\text{CaCl}_2]$ in mM | α_f | α_s | β |
|-------------------------|------------|------------|---------|
| 0 | 1.96 | 2.55 | 0.985 |
| 1.0 | 1.95 | 2.74 | 0.956 |
| 1.5 | 1.78 | 2.42 | 0.9 |
| 2.0 | 2.43 | 2.11 | 0.835 |
| 2.5 | 2.00 | 3.77 | 0.52 |

aqueous pectin solution. The general behavior of these parameters is similar to that found in 2.5 g L^{-1} aqueous pectin solution. However, since the samples are in a pregel state, the parameters do not show the drastic variation observed in samples under-

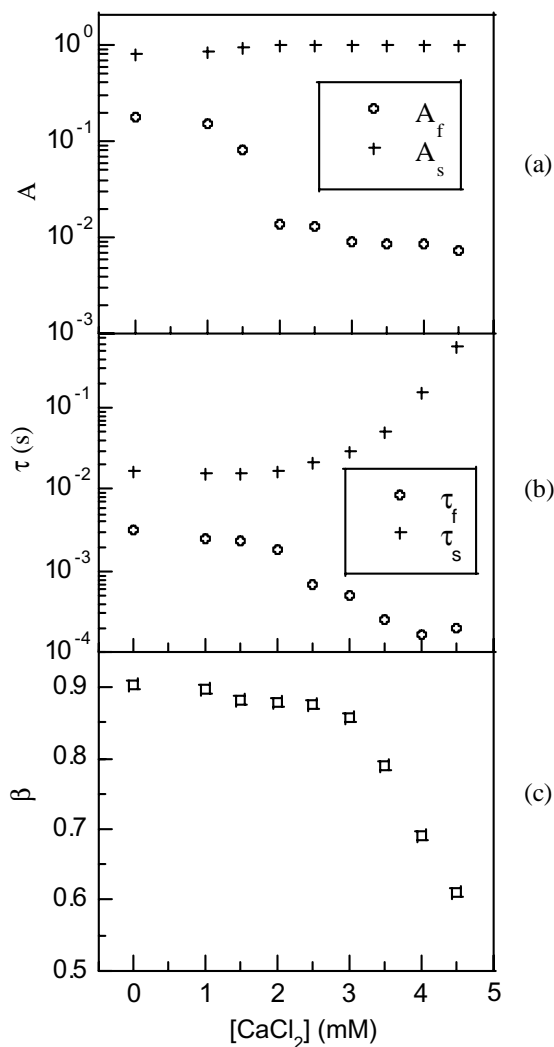


FIG. 9. Variation of amplitudes, characteristic times, and stretching exponent of the relaxation modes of $S(q, t)$ for 10 g L^{-1} pectin solution with CaCl_2 concentration.

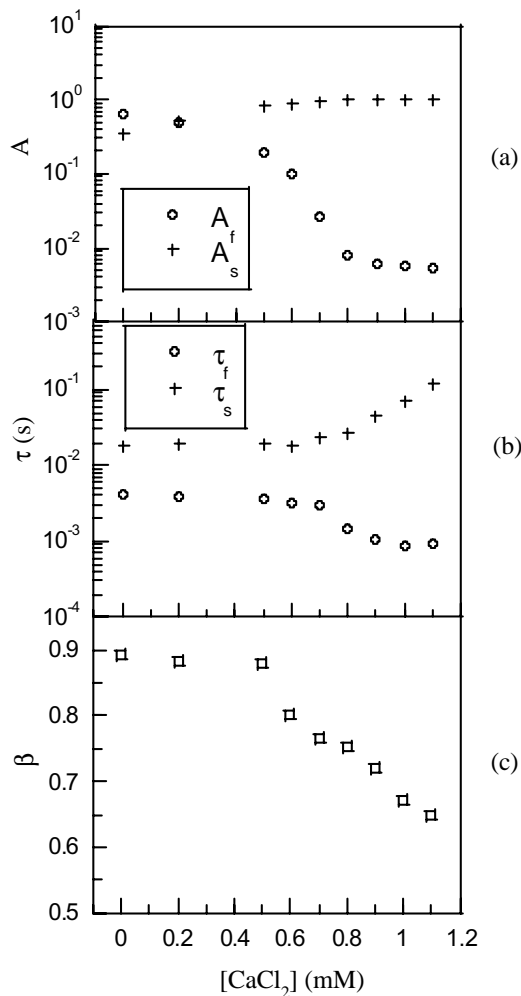


FIG. 10. Variation of amplitudes, characteristic times, and stretching exponent of the relaxation modes of $S(q, t)$ for 10 g L^{-1} pectin solution in the presence of 0.1 M NaCl with CaCl_2 concentration.

going sol-gel transition. The width parameter, β , for salt-free 10 g L^{-1} pectin solution is 0.9 which shows that the coupling effects are quite strong since the solution is close to the concentrated regime.

B. Pectin Gelation in the Presence of NaCl

Figure 10 shows the variations of the amplitudes and characteristic times of fast and slow relaxation modes and the stretching exponent with calcium chloride concentration for 10 g L^{-1} aqueous pectin solution in the presence of 0.1 M NaCl . Comparison with Fig. 9 shows that the amount of CaCl_2 required to produce coupling effects similar to that observed in the absence of NaCl is about four times less. As observed by Axelos and co-workers (17, 27), the amount of calcium chloride required to obtain the sol-gel transition is larger in the absence of NaCl . When a large amount of salt (0.1 M NaCl) is added, the ionic strength of the solution, I , increases. The range of the repulsive

Coulomb interaction between the pectin molecules is decided by the Debye screening length κ^{-1} . At room temperature, $\kappa^{-1} \sim 3 \text{ \AA}/\sqrt{I}$. Increasing the ionic strength of the solution decreases the repulsive part of the interaction energy between the pectin molecules, which would help the gelation process. Hence in the presence of 0.1 M NaCl, smaller amount of CaCl_2 would be sufficient to bring forth the sol-gel transition.

CONCLUSIONS

The dynamic light scattering measurements were carried out on aqueous pectin solutions, which undergo a sol-gel transition upon addition of calcium chloride. As the solution enters the gelation threshold the relaxation behavior of the correlation function is described by a stretched exponential. The stretching exponent, β , decreases rapidly as gelation progresses and the characteristic time of decay, τ_s , tends to diverge. These experimental findings are in accordance with the predictions of coupling model of Ngai and co-workers (8). The DLS measurements on pectin solutions in the presence of 0.1 M NaCl also gave similar results but the amount of calcium chloride required to induce sol-gel transition was found to be much smaller.

ACKNOWLEDGMENTS

The authors are thankful to Drs. C. Manohar and P. A. Hassan for discussions. Suggestions by Dr. Ramesh Chander on the preparation of the pectin samples are gratefully acknowledged. J.N. and V.W.D. express their gratitude to Dr. P. A. Hassan of Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai, for help in DLS measurements using a BI-90 particle sizer. This work was supported by the Board of Research in Nuclear Sciences under Project No. 37/9/96-R&D-II of the Department of Atomic Energy, Government of India.

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