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Gelling Properties of Gellan Solutions Containing Monovalent and Divalent Cations

J. TANG, M.A. TUNG and Y. ZENG

ABSTRACT

Gelling temperatures of gellan solutions with the addition of Na^+ and K^+ ranging from 15 to 450 mM or Ca^{++} and Mg^{++} from 2 to 40 mM were determined by dynamic rheological testing at four polymer concentrations between 0.4 and 2.0% (w/w). Gelling temperatures were much higher for gellan solutions containing divalent cations than for those containing the same amount of monovalent cations. Solutions containing K^+ gelled at higher temperatures than those containing Na^+. Effects of Ca^{++} and Mg^{++} on gelling temperatures were not significantly different. A general model was developed to predict the gelling temperature of gellan solutions as functions of cation and polymer concentrations.

Key Words: gellan, gels, gelling temperature, cations, rheology, biopolymer

INTRODUCTION

GELLAN POLYMER is an anionic polysaccharide produced by the bacterium *Pseudomonas elodea* in aerobic fermentation. Gellan was granted full approval in 1992 by the U.S. Food and Drug Administration for use in foods (Anon., 1992). Gellan molecules are linear chains consisting of tetrasaccharide repeating units, each with a carboxyl group. At low polymer concentrations, thermoreversible gels may be produced by cooling aqueous solutions containing cations. Divalent cations are more effective gel-formers than monovalent cations in gellan solutions; only 1/25 to 1/40 of the monovalent cation concentration is needed to form divalent cation gels with similar strength (Chandrasekaran et al., 1988a; Sanderson, 1990; Tang et al., 1996). The mechanism of gelation was hypothesized to be by formation of threefold double-helix structures followed by aggregation of double-helical sections through functions of cations to develop three-dimensional networks (Upstill et al., 1986; Chandrasekaran et al., 1988a b). In the presence of suitable cations, gellan solutions can form gels at polymer concentrations as low as 0.4% (w/w). Because of its many unique properties, gellan has been increasingly used as a gelling agent in many food applications. Improved understanding of the gelling properties would enable better selection of food formulation and processing parameters.

Gelation of gellan solutions occurs abruptly upon cooling to specific temperatures and the gels are thermo-reversible. Such sol-gel transitions are considered "phase transitions" (Snoeren and Payens, 1976). Thermodynamically, a spontaneous phase change takes place at a constant pressure when the change in Gibbs free energy is less than or equal to zero (Billmeyer, 1962; Atkins, 1990). That is:

$$\Delta H + T(-\Delta S) \le 0 \tag{1}$$

where ΔH represents the enthalpy of reaction, T is absolute temperature and ΔS is the entropy change. The gel-forming process in gellan solutions is exothermic, that is $\Delta H < 0$ (Moritaka et al., 1992; Miyoshi et al., 1994). During gelling, long polymer chains in random configurations in the sol-state are arranged to form into a more organized three-dimensional network. This results in a decrease in entropy ($\Delta S < 0$). Thus, the second term in Eq. (1) becomes positive for the sol-gel transition process, while the first term is negative. In order to satisfy Eq. (1), a gellan solution must be cooled below a specific temperature for the sol-gel transition to take place.

Eldridge and Ferry (1954) developed a mathematical model to relate gelling temperature of gelatin solutions to polymer concentration:

$$\log_{10}[X] = \frac{\Delta H}{2.303RT_{gel}} + c \tag{2}$$

where [X] is polymer concentration, R is the gas constant and c is a constant. This model was used for many other polymer gels (Gekko and Fukamizu, 1991; Moritaka et al., 1991; Gekko et al., 1992; Moritaka et al., 1992). Equation (2), however, only includes polymer concentration as an independent variable. Gelation of metal ion cross-linking polysaccharides such as kappa carrageenan, alginates and gellan are also influenced by cation concentrations. For those polymers, it is advisable to include cation concentration as a variable in models to describe gelling properties.

The van't Hoff equation is often used to describe the equilibrium constant for cross-link formation for a quasi-equilibrium condition in the sol-gel transition process (Eldridge and Ferry, 1954; Rees, 1969):

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \tag{3}$$

where T is absolute temperature, R is the gas constant, ΔH is the energy of cross-linking, and K was the equilibrium constant. From Eq. (3), Tang et al. (1997) developed an expression to relate gelling temperature (T_{gel}) to polymer and cation concentrations:

$$\frac{1}{T_{gel}} = A\log_{10}[X_p] + B\log_{10}[X_i] + C \tag{4}$$

where $[X_p]$ was polymer concentration (%), $[X_i]$ was cation concentration in mM, $A = aR/\Delta H$, $B = bR/\Delta H$; and a, b, and C were constants. Equation (4) resembled the model of Eldridge and Ferry (1954), except that Eq. (4) had an additional term to include the effects of cation concentrations. This equation has been used to relate the gelling temperature of gellan solutions to polymer and Ca^{++} concentrations (Tang et al., 1997).

Miyoshi et al. (1994) studied the gelling properties of gellan solutions using differential scanning calorimetry (DSC) with 1 and 2% gellan solutions and low cation concentrations. Tang et al. (1997) reported Ca^{++} ion effects on gelling temperatures of gellan solutions with polymer concentrations of 0.4 to 2.0% w/w and cation concentrations of 2 to 40 mM. Our objective in this study was to consider effects of monovalent Na^+ and K^+ in comparison with divalent Ca^{++} and Mg^{++} with respect to gelling temperatures of gellan solutions. We also examined the potential influence of cooling rates on gelling temperatures and Eq. (4) was extended to include effects of different cations to provide a more general model for prediction of gelling temperatures.

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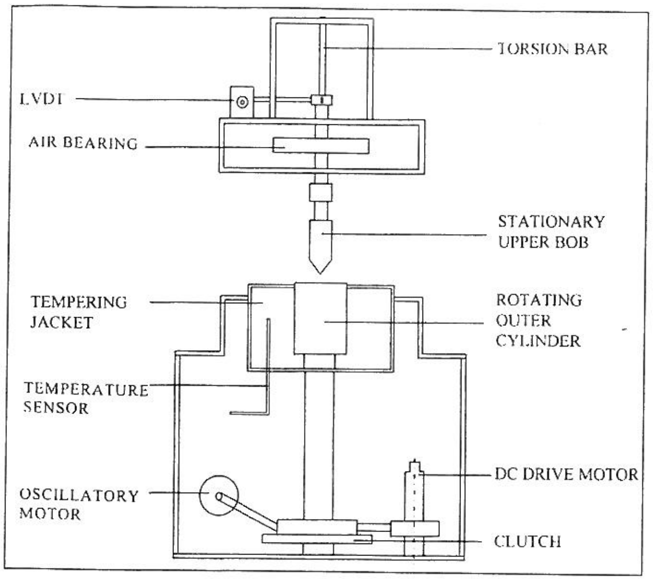

Fig. 1—Schematic of the coaxial cylinder system for measurement of gelling temperatures with a Bohlin VOR Rheometer in small-deformation oscillatory testing.

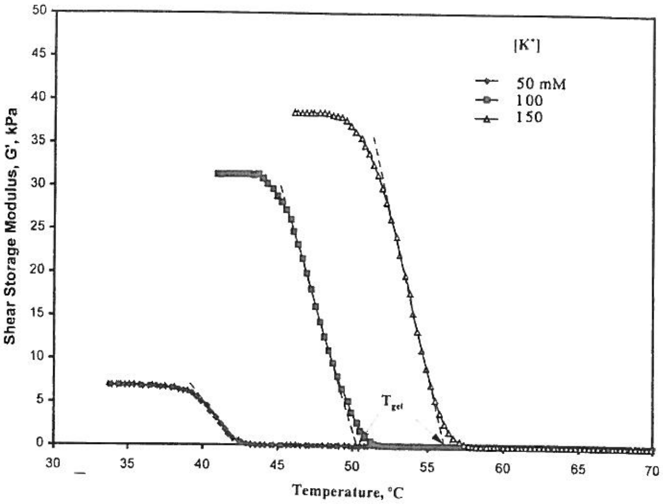

Fig. 2—Changes in shear storage moduli of 1% gellan solutions containing K⁺ during dynamic rheological testing at a cooling rate of 0.6 °C/min.

MATERIALS & METHODS

Preparation of gellan solutions

Deacetylated gellan gum powder (KELCOGEL) was used (NutraSweet Kelco Company, San Diego, CA). Besides gellan polymers, the product also contained 0.3% Na, 4.9% K, 0.4% Ca and 0.1% Mg (data provided by supplier). Weighed amounts of gellan samples were dispersed in distilled deionized water at room temperature (≈22°C) to form mixtures with four polymer concentrations (0.4, 0.6, 1.0 and 2.0% w/w). The mixtures were heated to 90°C in 250 mL beakers on hot plates with constant stirring. Temperature of the hot mixtures was maintained until the polymer powders were dissolved and solutions became clear. Weights of mixtures were checked and distilled water was added at about 80°C to make up sample weight losses due to evaporation. Pre-determined amounts of NaCl or KCl were then added to the hot gellan solutions to make dispersions with 8 monovalent cations concentrations (15 to 450 mM). Anhydrous $CaCl_2$ or $MgCl_2$ salts were added to prepare dispersions containing eight divalent concentrations (2 to 40 mM). Gelling temperatures were determined during cooling of hot solutions by measuring the onset of structural rigidity development using dynamic rheological testing and by direct visual observation of gel development while monitoring sample temperature by thermocouples.

Gelling temperature by direct observation and thermocouple measurement

Gellan solutions (16 mL) were poured into 18 mL glass test tubes (13 mm dia and 125 mm deep) in support stands. Pre-calibrated 30-gauge Type T thermocouples were inserted into the upper center portion of the solutions. Temperatures of the solutions (from thermocouples) were continuously displayed on a data logger and recorded at 10-sec intervals. Samples were allowed to cool in air from about 80°C to room temperature. The cooling rates varied from about 5°C/min at high solution temperatures to about 1°C/min at about 30°C. The hot solutions were gently stirred by manually moving the thermocouple tips. Stirring ensured a uniform temperature distributions around the thermocouple junctions. The sol-gel transition was noted when solutions suddenly solidified and the corresponding gelation temperature was recorded. These measurements were made in three replicates.

Dynamic rheological testing

Dynamic rheological testing was conducted using a Bohlin Rheometer (Model VOR, Bohlin Rheology AB, Lund, Sweden) equipped with coaxial cylinder system C24.4HS. These fixtures consisted of a stationary inner cylinder and an outer rotating cylindrical cup (Fig. 1). The sample was contained in a 2 mm annular gap between the two cylinders. The rotating outer cylinder was driven in a small amplitude sinusoidal motion by an oscillatory motor. The torque transmitted through the sample to the inner cylinder was continuously monitored by means of a rotational strain transducer in combination with a torsion bar. Signals from the oscillatory drive and resulting torque were gathered by a data acquisition system and analyzed by a microcomputer. Temperature of sample was controlled by a circulating water bath (Model RTE100, Neslab Instruments, Inc., Portsmouth, NH) connected to a tempering jacket surrounding the outer fixture. A water trap was placed on top of the sample cup to reduce evaporative cooling which could otherwise result in partial gelation near the exposed sample surface. Dynamic testing was conducted at a frequency of 1 Hz and 0.5% strain amplitude in sinusoidal oscillation. The small strain amplitude and frequency were chosen to ensure that specimens were tested within a range of linear viscoelasticity and would not separate from the cylinder walls upon solidification. During testing, the solution temperature was reduced from 80 to 20°C at a controlled cooling rate, while the viscoelastic properties were recorded so they could be related to sample temperature at any times. The dynamic shear storage modulus (G') represents the ability of a gel to store energy through recoverable deformation. Gelling temperature corresponded to a point when the dynamic shear storage modulus of the solutions started to increase rapidly (Fernandes et al., 1991; Hansen et al., 1991; Moritaka et al., 1991; Hsieh et al., 1993). The gelling temperatures of gellan solutions with Na^+, K^+, Ca^{++} or Mg^{++} were determined using the dynamic rheological method at 0.6°C/min cooling rate in two replicated tests. Differences between duplicated gelling temperature readings varied from 0.2 to 1.5°C.

The effect of cooling rates, from 0.2 to 1.4°C/min, on gelling temperature was also studied with dynamic rheological testing of solutions containing 0.4 or 1% polymer concentrations and 50, 150 or 350 mM monovalent cations, or 6, 14 or 20 mM divalent cations. The thermal lags between sample temperature and tempering jacket temperature indicated by the Bohlin Rheometer software were corrected based on calibration tests. During the calibration tests, sample temperatures were monitored by inserting pre-calibrated 30-gauge Type T (copper/constantan) thermocouples, and the temperature of circulating water in the tempering jacket was read from rheometer software. Thermal lags increased slightly with more rapid cooling rates. The solution temperature was about 0.4°C higher than the Bohlin tempering jacket temperature at the cooling rate of 0.6°C/min, and 2°C higher than water temperature in the tempering jacket at cooling rate 1.4°C/min.

RESULTS & DISCUSSION

CHANGES OF STORAGE MODULI G' with sample temperature at a cooling rate of 0.6°C/min were compared for solutions containing monovalent ions (Fig. 2) and divalent cations (Fig. 3). At high temperatures, gellan solutions demonstrated near zero shear storage modulus. As they were cooled to specific temperatures, G' started to increase rapidly, suggesting the development of more rigid gel structures. These temperatures marked the beginning of the sol-gel transition. With decreasing temperature, G' increased with further development of gel structure, until it

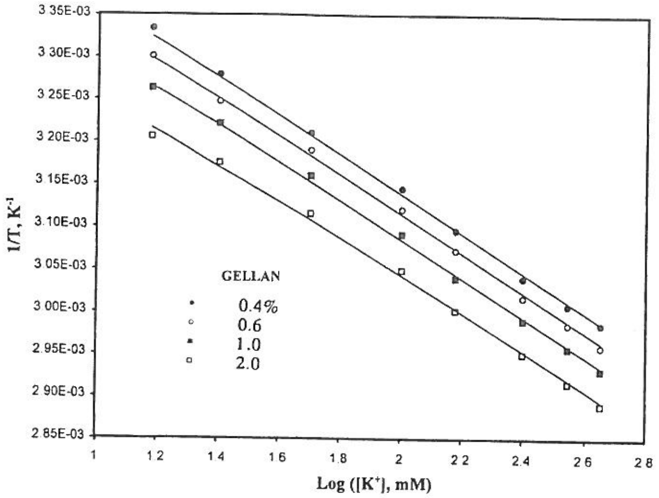

Fig. 7—Gelling temperatures of gellan solutions with added K⁺ as fitted by Eq. (4).

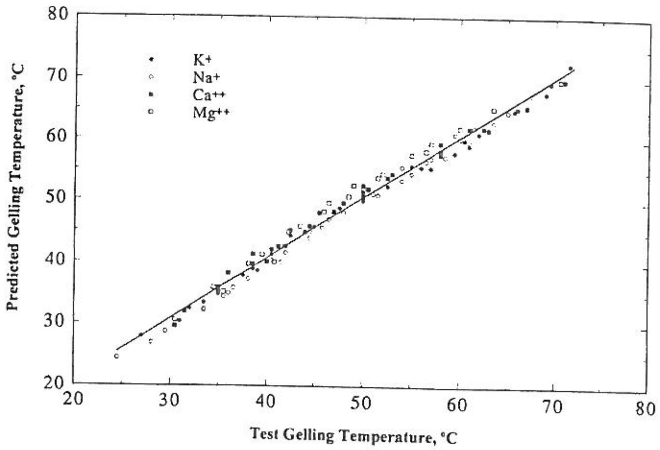

Fig. 8—Correlation between experimental and predicted gelling temperatures for gellan solutions with K⁺, Na⁺ (15 to 450 mM) and Ca⁺⁺ and Mg⁺⁺ (2 to 40 mM) using Eq. (5).

Table 1—Coefficients in Eq. (4) for gellan solutions of 0.2 to 2.0% (w/w) polymer concentrations with different cations

Cation type	Cation conc. mM	A × 10⁴ K⁻¹	B × 10⁴ K⁻¹	C × 10³ K⁻¹
Na⁺⁺	15 - 450	− 1.33 ± 0.24	2.32 ± 0.16	3.60 ± 0.07
K⁺	15 - 450	− 1.31 ± 0.25	2.32 ± 0.18	3.55 ± 0.08
Ca⁺⁺	2 - 40	− 1.34 ± 0.24	2.33 ± 0.16	3.33 ± 0.04
Mg⁺⁺	2 - 40	− 1.35 ± 0.21	2.33 ± 0.12	3.33 ± 0.03

R^2 values for the regressions were greater than 0.98.

Table 2—Gelling temperatures predicted by Eq. (5) compared with measured gelling temperatures of gellan solutions for ten combinations of cation and polymer concentrations

Gellan	Added cations, mM				Gelling temp, °C	
%, w/w	Na⁺	K⁺	Ca⁺⁺	Mg⁺⁺	Measured	Predicted
0.2	0.0	0.0	40.0	0.0	55.0	54.6
0.4	0.0	50.0	0.0	2.0	41.5	41.4
0.8	0.0	50.0	2.0	0.0	43.6	45.4
1.0	50.0	25.0	2.0	2.0	48.8	50.2
1.0	100.0	50.0	2.5	2.5	55.7	55.8
1.0	150.0	100.0	3.0	3.0	61.5	60.8
1.2	300.0	0.0	1.0	1.0	61.6	60.3
1.5	100.0	50.0	2.5	2.5	57.5	58.5
2.0	400.0	0.0	10.0	10.0	73.7	72.1
2.5	150.0	100.0	0.0	0.0	65.0	64.2

findings for gelling temperatures corresponded closely to those by visual observation. For gelling temperatures >50°C, the visual observation/thermocouple method usually indicated lower temperatures than the dynamic rheological method. The high rate of cooling (about 4°C/min at 70°C) brought about by the combined evaporative and convection cooling might have caused delayed detection of gelling points by the visual method. Inconsistency in results by the visual method also increased for high gelling temperatures, perhaps due to non-uniform temperature distributions as a result of surface evaporative cooling.

Gelling temperatures by dynamic rheological testing were slightly higher than those reported by Miyoshi et al. (1994) with a DSC method at a cooling rate of 0.5°C/min for solutions with the same amounts of added cations. If onset temperatures instead of peak temperatures of DSC exothermic peaks had been considered to be gelling temperatures, then differences between their results and ours in most cases (over 80%) were between 0 and 2°C. Such discrepancies might have been caused in part by different compositions of the gellan polymer sources. The Ca and Mg contents of the gellan powder they used were 0.1 and 0.02%, respectively, which were lower than 0.4 and 0.1% levels we used.

The GLM procedure in SAS (SAS Institute, Inc., 1985) was used to determine constants in Eq. (4) by fitting the equation to experimental data of gellan solutions with four different cations. $[X_p]$ in Eq. (4) was taken as the gellan powder concentration (w/w) in gellan solutions, and $[X_i]$ was taken as the added ion concentrations in mM. The curve fittings were close (Fig. 7) for gellan solutions with added K⁺. Similar fittings were observed with the other cations. Coefficients for Eq. (4) were determined (Table 1) representing the gelling temperature as functions of cation concentrations for aqueous gellan solutions ranging from 0.2 to 2.0% w/w of polymer. Only minor differences occurred among all coefficients for gellan solutions containing Ca⁺⁺ or Mg⁺⁺. Values for the coefficient C for gellan solutions with monovalent cations (Na⁺ and K⁺) were larger than those for solutions with divalent cations (Ca⁺⁺ and Mg⁺⁺). From these coefficients (Table 1), a general expression was developed for gellan solutions with more than one type of cation. This expression was derived by assuming that each type of cation contributed independently to the gelling process and that the effects of the cations were additive:

$$\frac{1}{T_{gel}}=3.33\times10^{-3}-1.34\times10^{-4}\log_{10}[X_p]-2.33\times10^{-4}\log_{10}[0.0726X_{Na}+0.111X_K+X_{Ca}+X_{Mg}] \quad (5)$$

where T_{gel} is the gelling temperature in K, X_p is the concentration of gellan powder (% w/w), X_{Na}, X_K, X_{Ca} and X_{Mg} are concentrations (mM) for added Na⁺, K⁺, Ca⁺⁺ and Mg⁺⁺, respectively. Equation (5) fitted well the experimental data for gellan solutions when the 4 different cations were added separately (Fig. 8, $R^2 = 0.98$). In order to validate Eq. (5) for applications in which 2 or more types of cations were added to gellan solutions, gelling temperatures were determined with 10 combinations of polymer and cation concentrations. The measured gelling temperatures agreed very well with the prediction by Eq. (5) with a discrepancy of <2 C° (Table 2). This discrepancy would be considered acceptable in most industrial applications.

Effects of cooling rate on gelling temperatures of gellan solutions with K⁺ and Ca⁺⁺ determined by dynamic rheological testing are presented in Fig. 9 and 10, respectively. Cooling rates >0.6°C/min had no apparent effect on gelling temperatures. However, gelling temperatures increased in a linear manner with reducing cooling rates of <0.6°C/min. Precautions taken to obtain accurate sample temperatures in dynamic rheological testing (through pre-calibration and thermal lag correction) eliminated any possibility that the effect of cooling rates was a result of test method. Further study is required to understand the responsible mechanisms.

The effects of cooling rate on gelling temperatures of gellan solutions were quantified by the following expression:

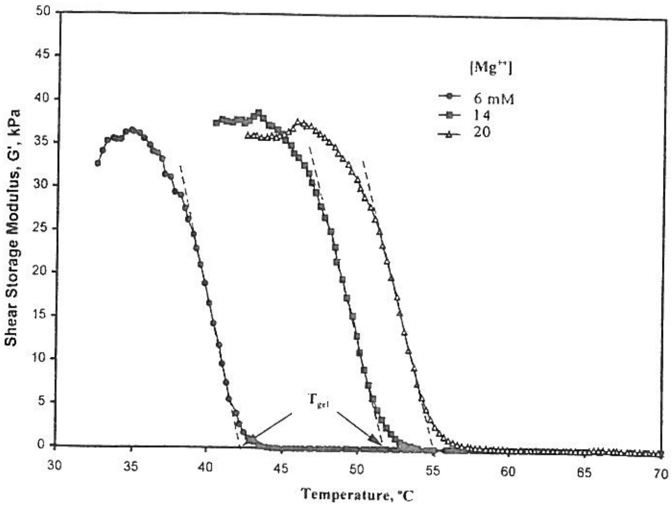

Fig. 3—Changes in shear storage moduli of 1% gellan solutions containing Mg⁺⁺ concentrations during dynamic rheological testing at a cooling rate of 0.6 °C/min.

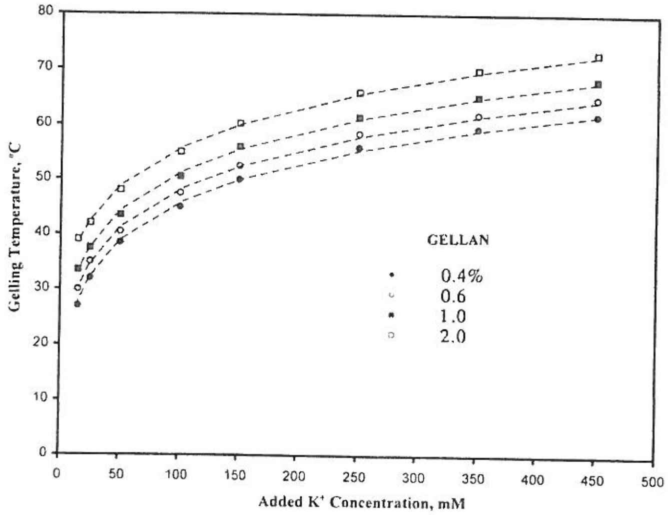

Fig. 4—Experimental data from dynamic rheological tests for the mean gelling temperatures of gellan solutions as related to gellan and added K⁺.

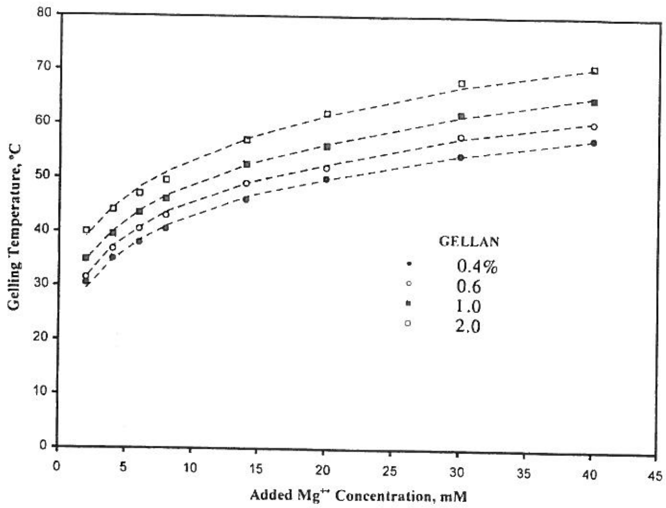

Fig. 5—Experimental data from dynamic rheological tests for the mean gelling temperatures of gellan solutions as related to gellan and added Mg⁺⁺.

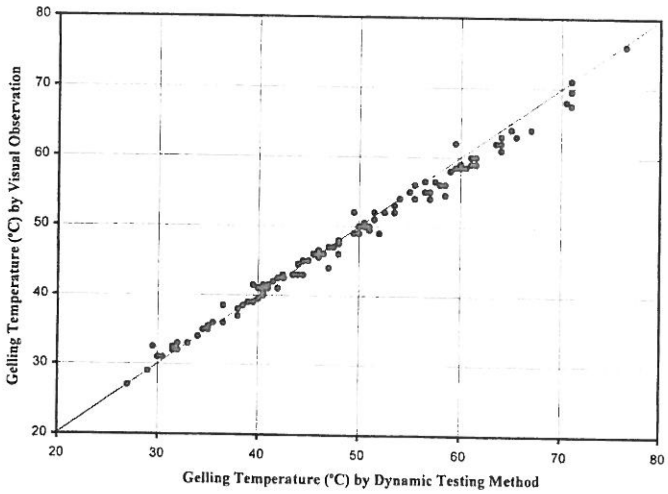

Fig. 6—Correlation between gelling temperatures by visual observation with thermocouple measurement and those determined by dynamic rheological testing.

leveled. Gelling temperature (T_{gel}) was determined by drawing a tangent line at the point where the slope of the rapid increasing G' curve was steepest and extending this line to intersect the horizontal axis. As indicated (Fig. 2), gelling temperatures for 1% gellan solutions with 50, 100 and 150 mM K^+ were 42.5, 50.3 and 56.0°C, respectively, and with 6, 14, and 20 mM Mg^{++} were 42.5, 52.0 and 55.2°C, respectively (Fig. 3).

With added K^+ cations, gelling temperatures increased with increasing cation and polymer concentrations (Fig. 4). Similar patterns were observed with gellan solutions containing Na^+. In general, gelling temperatures of solutions containing K^+ were 2 to 6°C higher than those containing Na^+, and differences increased with gelling temperatures. Possibly K^+ was more effective than Na^+ for inducing gelation in anionic polysaccharide solutions (Morris, 1986). The larger effective size of K^+ might provide for better shielding of electrostatic repulsion between carboxyl groups in adjacent polymer chains during gel. Tang et al. (1996) reported that between 10 and 22 K^+ ions were needed for each repeated gellan polymer unit to make gels with maximal strength. However, 15 to 30 Na^+ ions per polymer repeating unit were needed for maximal strength gels. At maximal strength, gels formed with K^+ were also stronger than those with Na^+ (Tang et al., 1996).

Increased polymer and divalent Mg^{++} concentrations also resulted in higher gelling temperatures (Fig. 5) which were not greatly different from those for solutions with Ca^{++}. Using divalent cations, only about 1/14 to 1/9 of the amount was needed as for monovalent cations to form gellan solutions with the same gelling temperatures. Divalent cations might act differently when inducing cross-linking between polymers. Divalent cations are more highly charged and are more effective in shielding electrostatic repulsive forces between adjacent carboxyl groups in junction zones (Miyoshi et al., 1994). Divalent cations may also form direct polyanion-cation-polyanion linkages between polymer chains (Chandrasekaran, 1988b; Miyoshi et al., 1994; Tang et al., 1995). Such mechanism was supported by observations reported by Tang et al., (1996) that the maximal strength gellan gels were formed at each polymer concentration when the divalent cations to polymer repeated unit ratio in gellan solutions was ≈ 0.5.

Mean gelling temperatures determined by the visual observation/thermocouple method were compared (Fig. 6) with the mean gelling temperatures determined by the dynamic testing method. Except for a few points, the gelling temperatures by the two methods agreed well up to 50°C, with discrepancies of <1.5°C. This confirmed that the dynamic rheological method

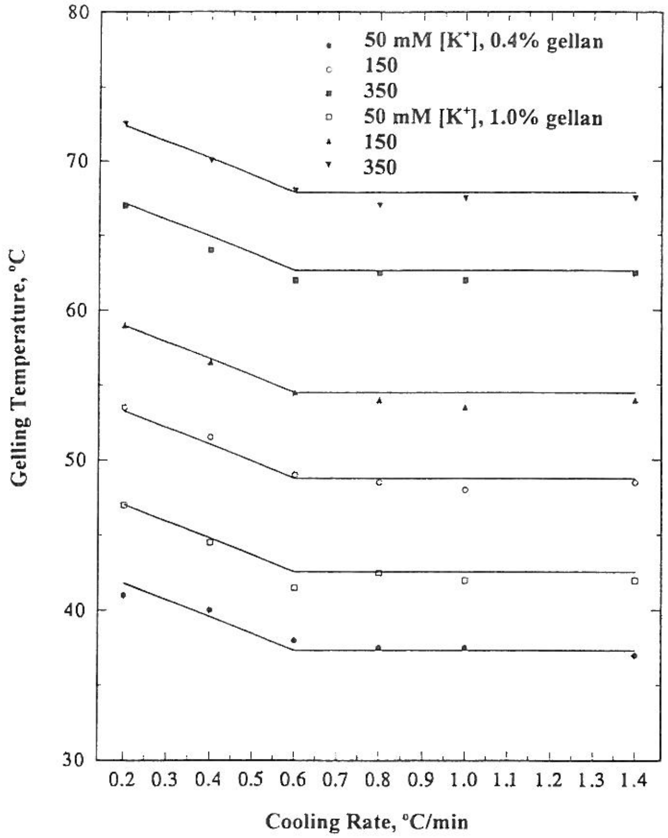

Fig. 9—Effect of cooling rates on gelling temperature of gellan solutions with added K^+. (means of two repeated tests).

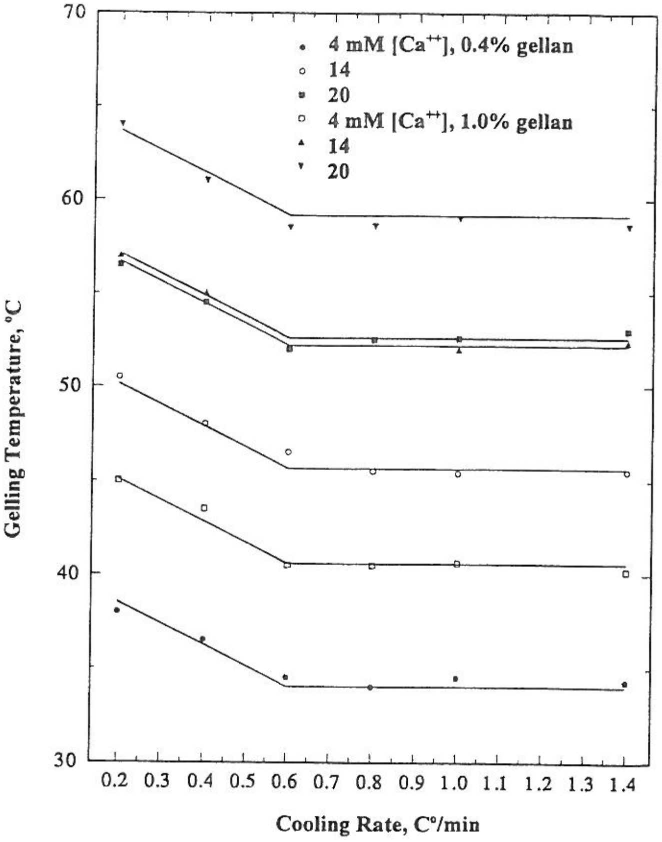

Fig. 10—Effect of cooling rates on gelling temperature of gellan solutions with added Ca^{++}. (means of two repeated tests).

$$T_{gel}^* = T_{gel} + 10.5\,(0.6 - \alpha) \qquad R^2=0.95 \qquad (6)$$

where, T_{gel}^* indicates gelling temperatures measured at a cooling rate $\alpha < 0.6$°C/min, and T_{gel} is the gelling temperature of gellan solution determined at any cooling rates >0.6°C/min. For cooling rates >0.6°C/min, only Eq. (5) is required to predict gelling temperature, but Eq. (6) should also be used to correct for effects of very slow cooling rates.

Applications of these findings for estimating gelling temperatures of food systems stabilized by gellan polymers and metal ions would require caution. Complex formulations of food dispersions may include ingredients with associated metal ions which could augment or influence the intended gelling mechanism. The presence of other components in manufactured food systems may also have strong influences on development of gellan gel structures. For instance, each 10% (w/w) sucrose added to gellan solutions would increase gelling temperatures by about 3°C, regardless of type and concentration of cations (unpublished data). Fructose up to 25% (w/w) and pH levels of 4 to 10 had, however, little effect on gelling temperatures of gellan solutions.

CONCLUSIONS

GELLING TEMPERATURES of gellan solutions increased with polymer and cation concentration and the effects of cations were additive. A general model was developed to predict gelling temperatures of gellan solutions with combinations of four different cations at various concentrations. In order to provide a given gelling temperature, about 9 to 14 times more monovalent cations were needed as compared to the requirements for divalent cations. Gelling temperatures of gellan solutions containing K^+ were 2 to 6°C higher than those of gellan solutions containing the same amounts of Na^+. However, gellan solutions with Ca^{++} formed gels at temperatures that were essentially the same as those with Mg^{++}.

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