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Gelling Temperature of Gellan Solutions Containing Calcium Ions

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

ABSTRACT

Gelling temperatures were measured using a dynamic rheological testing method, a spectrophotometric method and direct visual examination combined with use of a thermocouple. Results from the dynamic testing method were most consistent. Gelling temperatures of gellan solutions increased from 30 to 72°C, as polymer concentrations increased from 0.4 to 2.0% w/v and Ca^{++} concentrations increased from 2 to 40 mM. A mathematical model was developed based on the van't Hoff equation to relate gelling temperatures to composition and polymer molecular weight. The heat of cross-linking in Ca-gellan gels was estimated to be 428.6 kJ/mole, about 1.4 to 2.1 times greater than for gelatin gels.

Key Words: gellan, gels, gelling temperature, cross-linking, rheology

INTRODUCTION

GELLAN POLYMER is a gelling and thickening agent (Anon., 1992) of great potential in food and nonfood applications (Sanderson, 1990). It is an anionic polysaccharide secreted by the bacterium *Pseudomonas elodea* during aerobic fermentation. Gellan gum polymers are linear chains consisting of tetrasaccharide repeating units -3)-β-D-Glcp-(1→4)-β-D-GlcpA-(1→4)-β-D-Glcp-(1→4)-α-L-Rhap(1→). Gellan gum produces thermoreversible gels in aqueous solutions containing cations. The cross-linking mechanism in the gel-forming process of gellan solutions has been studied. Gellan forms gels possibly through formation of threefold double-helix and then aggregation of double-helical sections to form a three-dimensional network (Upstill et al., 1986; Chandrasekaran et al., 1988a, b). This is very similar to the mechanism of cross-linking in κ-carrageenan solutions (Morris, 1986). Quantitative information on gelling properties of gellan solutions are, however, very limited (Moritaka et al., 1991, 1992). Information on gelling properties of gellan solutions can help to control the process of gelation and quality of resulting gels.

Gelation in gellan solutions, as in carrageenan solutions, occurs abruptly once the gelling temperatures are reached, and the gels are thermoreversible. Gelling properties of κ-carrageenan solutions have been studied extensively. Rees (1969) and Snoeren and Payens (1976) considered abrupt and thermoreversible gelling processes to be "phase transitions." In thermodynamic terms, spontaneous changes of state of a solution at constant pressure take place only when the change in Gibbs free energy ΔG satisfies (Billmeyer, 1962; Atkins, 1990):

$$\Delta G \le 0 \tag{1}$$

The Gibbs free energy change is defined as:

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

where, ΔH is enthalpy of reaction, T is absolute temperature, and ΔS is the entropy change.

Gel formation in gellan solutions is an exothermic process (Moritaka et al., 1992), that is $\Delta H < 0$. During gelation, long polymer chains in random configurations are arranged to form 3-dimensional networks, resulting in a decrease in entropy ($\Delta S < 0$). Therefore, according to Eq. (1) and (2), the gelling process is spontaneous when the temperature is reduced to a specific level. Assuming this gelling process is reversible ($\Delta G=0$), the gelling temperature T_{gel} can be derived from Eq. (2) as:

$$T_{gel} = \frac{\Delta H}{\Delta S} \tag{3}$$

The values of ΔH and ΔS are usually dependent upon solution composition. Thus according to Eq. (3), the gelling temperatures may also be different with different solution compositions. Moritaka et al. (1992) reported an increase in absolute value of ΔH and a rise in gelling temperature with increased gellan polymer concentration.

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

$$\log_{10} X = \frac{\Delta H}{2.303RT_{gel}} + c \tag{4}$$

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, 1992; Gekko et al., 1992). The model has two limitations. First, it includes only polymer concentration as an independent variable, whereas gelation of several polysaccharide polymers such as kappa carrageenan, alginates and gellan are influenced by polymer concentration and also by cation concentrations. Secondly, Eq. (4) is applicable to cases where only two strands of polymers are involved in forming a cross-link, while more than two strands are associated in many food polymer gel networks (Rees, 1969; Ledward, 1986; Morris, 1986; Chandrasekaran et al., 1988a, b).

Our objectives were to determine the effects of polymer and calcium ion concentrations on gelling temperatures of gellan solutions upon cooling, and to develop a general mathematical model to relate gelling temperature of gellan solutions to composition.

MATERIALS & METHODS

Preparation of gellan solutions

Deacetylated gellan gum powder (KELCOGEL, Kelco Inc., San Diego, CA) was dispersed in 100 mL distilled and deionized water in a 250 mL beaker with constant stirring. The mixtures were heated to 90°C to give clear solutions. Mixtures were weighed and distilled water was added to make up any weight lost in evaporation. Calcium chloride ($CaCl_2 \cdot 2H_2O$) salt at predetermined levels was added to the hot gellan solutions so that cross-links could be formed during cooling. Gelling temperatures of the solutions were determined by three different methods.

Dynamic rheological testing

Gelling temperature in gellan solutions was measured in a dynamic testing mode on a Bohlin Rheometer (Model VOR, Bohlin Rheology AB, Lund, Sweden) using a coaxial cylinder system C24.4HS. This temperature-controlled system consisted of a fixed inner cylinder and a sin-

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usoidally oscillating outer cup. A rotational strain transducer in combination with a torsion bar measured the torque transmitted through the sample in a thin annular gap between the two cylinders. Signals from the oscillatory drive and resulting torque were gathered by a data acquisition system and analyzed by the microcomputer that controlled the rheometer. A water trap was placed on top of the cup to reduce evaporation from the aqueous solution (Fig. 1a). This reduced the possibility that gel would form near the upper layer due to evaporative cooling. Dynamic testing was conducted at 1 Hz and 0.5% strain amplitude in sinusoidal oscillation, used to ensure that the specimen would not separate from the cylinder walls upon solidification. The temperature of the solution was reduced from 80 to 20°C at a controlled cooling rate, while the viscoelastic properties were recorded via a personal computer. The gelling point corresponded to the temperature at which the dynamic shear storage modulus G' of the solution started to increase rapidly as a result of initiation of gelation (Fernandes et al., 1991; Hansen et al., 1991; Moritaka et al., 1991; Hsieh et al., 1993). Preliminary tests using dynamic rheological testing showed that gelling temperatures of gellan solutions were not affected by cooling rate above 0.6°C/min. Thus, 0.6°C/min was used as the cooling rate for all solutions. All tests were carried out in duplicate.

Visible light spectrophotometry

Gellan solutions were generally clear at elevated temperatures; however, turbidity increased during gelation. This property was used to indirectly measure gelling temperature of gellan solutions, with a spectrophotometer (Spectronic Model 501, Fisher Scientific, Pittsburgh, PA). For each test, a hot gellan solution was poured into a pre-warmed 4.5 mL square polystyrene cuvette. A precalibrated (±0.3°C) fine gage type T thermocouple (TT-T-30, Omega Engineering Inc., Stamford, CT) was inserted into the solution and secured at its center through a small hole in a plastic lid so that the junction was slightly above the light path through the cuvette (Fig. 1b). Temperatures at this location in samples were monitored via a data logger. The spectrophotometer was zeroed against a blank consisting of distilled, deionized water prior to insertion of the test sample. Preliminary scanning of gellan solutions from 400 to 800 nm indicated that maximum absorbance occurred at the low wavelength end of this spectrum. Thus, changes in light absorbance through gellan samples were measured at 490 nm at predetermined time intervals. Sample temperatures were also recorded simultaneously until gels were formed. Cooling rates in the samples ranged from 1.5 to 4°C/min. An abrupt change in light absorbance of the sample marked the beginning of gelation.

Direct visual observation

A gellan solution of 16 mL was poured into an 18 mL glass test tube (13 mm diam × 125 mm deep) in a support stand. A precalibrated fine gage type T thermocouple was inserted into the solution. Temperatures were displayed and recorded with a data logger. The sample was allowed to cool in air from about 80°C to room temperature (about 23°C) at 1 to 5°C/min. The state of the solution was monitored by gentle stirring with the thermocouple. Stirring also ensured a more uniform temperature distribution in the solution around the thermocouple junction. The sol-gel transition was noted when the thermocouple tip was difficult to move without bending the wire. This change was abrupt and the transition was obvious, thus the corresponding temperature was noted as the gelation temperature of the solution. Measurements were made in triplicate.

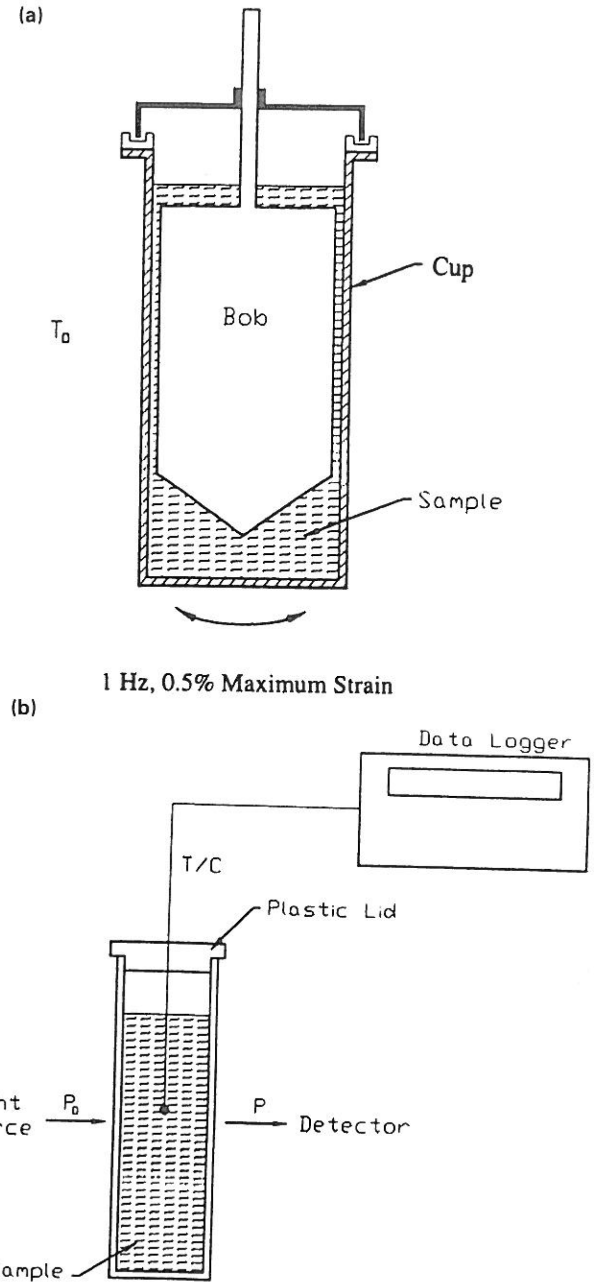

Fig. 1—(a) Coaxial cylinder measuring system for measurement of gelling temperatures with a Bohlin VOR Rheometer in small-deformation oscillatory testing. The cup was surrounded by a water jacket which controlled the desired ramping temperature; (b) Schematic drawing of the set-up for determining gelling temperature by visible spectrophotometry. The cuvette containing the gellan sample was placed in a spectrophotometer.

MODEL FOR GELLING TEMPERATURE

ASSUMING that a quasi-equilibrium condition exists in a gelling process, the van't Hoff equation can be used to describe the temperature dependence of the equilibrium constant for cross-link formation:

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \tag{5}$$

where, T is absolute temperature, R is the gas constant, ΔH is the energy of cross-linking. K is the equilibrium constant, defined as:

$$K = \frac{[J]^{l}}{[X_l]^{n}\,[X_i]^{m}} \tag{6}$$

in which, [J] represents the molar concentration of the cross-links, $[X_l]$ is the molar concentration of free cross-linking loci on the gellan polymer chains, and $[X_i]$ is the molar concentration of cations. Parameters *l*, *n*, and *m* are stoichiometric coefficients. Since more than one polymer chain is involved in making a cross-link, *n* should be $> l$.

Assuming ΔH to be constant over a wide temperature range for the same solution, Eq. (5) can be integrated to form:

$$\ln K = -\frac{\Delta H}{RT} + c \tag{7}$$

where, c is a constant.

Substituting Eq. (6) into Eq. (7) yields:

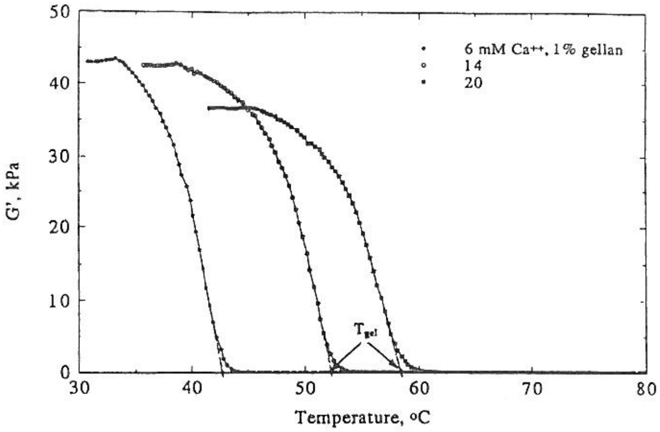

Fig. 2—Changes in storage moduli of three gellan solutions as temperatures were reduced at 0.6°C/min during dynamic testing.

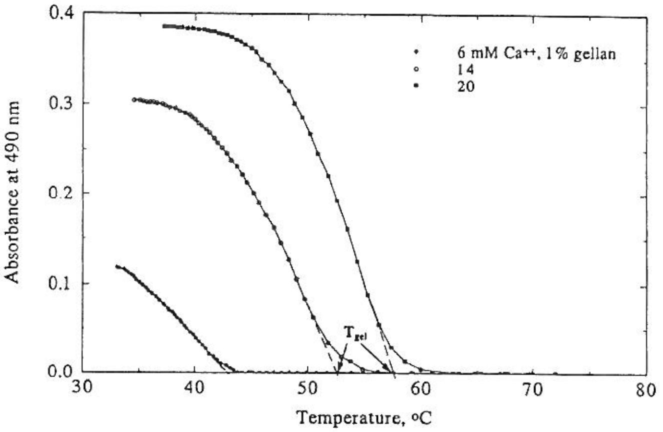

Fig. 3—Changes in light absorbance at 490 nm in three gellan solutions as temperatures were reduced.

$$l\ln[J] - n\ln[X_\ell] - m\ln[X_i] = -\frac{\Delta H}{RT} + c \qquad (8)$$

Gelation of gellan solutions would take place upon cooling to the gelling temperature T_{gel} at which the concentration of cross-links [J] had increased to a level $[J]_{gel}$ to form a three-dimensional network. At that point, Eq. (8) becomes:

$$l\ln[J]_{gel} - n\ln[X_\ell] - m\ln[X_i] = -\frac{\Delta H}{RT_{gel}} + c \qquad (9)$$

An average gellan polymer consists of about 800 tetrasaccharide repeating units. Only a few of these units are required to form a three-dimensional network. Therefore, it was assumed that the number of cross-linking loci combined at the gelling temperature was relatively very small (Eldridge and Ferry, 1954), compared to the total available cross-linking loci on a polymer chain. Thus, $[X_\ell]$ and $[X_i]$ in the above equation could be taken as the original molar concentrations in the gellan solution before gelling. The minimum number of cross-links to form a three-dimensional network is proportional to the number of polymer chains (Ferry, 1948; Eldridge and Ferry, 1954), then:

$$[J]_{gel} = a\frac{[X_p]}{M_w} \qquad (10)$$

where $[X_p]$ is polymer concentration (g/mL), M_w is the average molecular weight of gellan polymers (about 500,000 Daltons) before gelling, *a* is a proportionality factor. For linear molecules, such as gelatin, and for gels with no cyclic cross-links, $a = 0.5$ (Ferry, 1948).

In addition, the molar concentration of free loci for cross-links on gellan polymers is proportional to the polymer concentration. That is,

$$[X_\ell] = b[X_p] \qquad (11)$$

where, *b* is a proportionality factor.

Substituting Eq. (10) and (11) into Eq. (9) and re-arranging the resulting equation yields:

$$l\{\ln(a) + \ln[X_p] - \ln M_w\} - n\{\ln(b) + \ln[X_p]\} - m\ln[X_i] = -\frac{\Delta H}{RT_{gel}} + c \qquad (12)$$

or

$$\frac{1}{T_{gel}} = \frac{(n-l)R}{\Delta H}\ln[X_p] + \frac{mR}{\Delta H}\ln[X_i] + \frac{lR}{\Delta H}\ln[M_w] + c' \qquad (13)$$

In our study, M_w is a constant, thus Eq. (13) could be further simplified into:

$$\frac{1}{T_{gel}} = A\ln[X_p] + B\ln[X_i] + C \qquad (14)$$

where,

$$A = \frac{(n-l)R}{\Delta H},\ B = \frac{mR}{\Delta H},\ C = \frac{lR}{\Delta H}\ln[M_w] + c' \qquad (15)$$

Equation (14) resembles the model (Eq. 4) developed by Eldridge and Ferry (1954) for gelatin gels, except that it has additional terms to include the effects of cation concentration and molecular weight. Parameter *n* is > *l*, and the value of ΔH is negative (Moritaka et al., 1992). Thus, constants A and B should be negative.

RESULTS & DISCUSSION

TYPICAL RESULTS from dynamic rheological testing are shown in Fig. 2. Near zero storage modulus G' at high temperatures indicated a liquid state. A rapid increase in G' marked the beginning of the gel-forming process as solution temperatures were reduced. The plateaus corresponded to rigidity of final gels. Gelling temperature T_{gel} was taken as the intersection of the steepest slope for the portion of the rapid increase in G' and the horizontal axis representing G' = 0 for each gel. As indicated in Fig. 2, gelling temperatures for these 1% gellan solutions with 6, 14 and 20 mM Ca^{++} were 43.0, 52.5, and 58.5°C, respectively.

The trends for changes in absorbance at 490 nm with decreasing temperature (Fig. 3) were very similar to changes in storage modulus G' during dynamic testing. Near zero light absorbance at elevated temperatures indicated that the solutions were transparent. The transparency decreased when the solutions started to gel, as the temperatures were reduced. The plateaus indicated the turbidity of final gels, which increased sharply with increasing Ca^{++} concentrations. The gelling temperature for a solution was taken as the intersection of the straight line tangent to the steepest slope of the light absorbance vs. temperature curve and the abscissa (absorbance = 0). Gelling temperatures for these 1% gellan solutions with 6, 14 and 20 mM Ca^{++} were determined to be 43.0, 52.6, and 58.0°C. In general, there was no significant difference ($p > 0.05$) between gelling temperatures measured by the two methods.

Gelling temperatures determined by direct visual observation (Table 1) were compared with those obtained by dynamic testing. Gelling temperatures by direct observation were generally lower than those by dynamic rheological testing, especially at

Table 1—Average gelling temperatures (°C) of gellan solutions by dynamic rheological testing (*n* = 2) and direct visual observation (*n* = 3)(in parentheses)

Gellan polymer (%)	Added Ca^{++} (mM)							
	2	4	6	8	14	20	30	40
0.4	30.0* (31.0)**	35.0 (35.0)	38.5 (38.5)	41.0 (41.5)	47.5 (47.0)	51.0 (49.5)	55.5 (52.5)	58.0 (54.5)
0.6	31.5 (32.0)	36.5 (36.0)	42.0 (41.0)	43.5 (43.0)	50.0 (50.0)	53.5 (53.0)	59.0 (58.0)	61.0 (59.0)
1.0	35.0 (35.0)	40.0 (39.5)	44.0 (43.0)	46.5 (46.0)	53.5 (52.0)	58.0 (56.0)	64.0 (62.0)	65.5 (63.0)
2.0	40.5 (40.0)	44.5 (45.0)	48.0 (48.0)	50.5 (50.0)	58.5 (56.0)	64.0 (61.0)	67.5 (66.0)	71.5 (68.5)

* S.D. values for gelling temperatures measured by the dynamic testing method were between 0.2 to 1.4°C.

** S.D. values for gelling temperatures measured by direct visual observation were between 0.2 to 2°C.

higher Ca^{++} concentrations. Below 50°C, differences were < 0.5°C, but the deviation was up to 3.5°C at higher gelling temperatures. With the direct visual method, detection of gelling points for high gelling temperature solutions may have been delayed due to high cooling rates in those samples (about 5°C/min at 70°C). Evaporative cooling at the top layer of these samples also caused some difficulty in detecting sample gelling points, and standard deviations among replicates were about 2°C. The cooling rates were reduced to 1 to 2°C/min as sample temperatures fell below 50°C, and readings were more consistent (S.D. < 1°C).

Each of the three methods had advantages and served to corroborate results by the other methods. The direct visual observation method was simple and straightforward. However, the gelling point was somewhat subjective. The visible light spectrophotometry method was reliable at high cation levels, but less sensitive at low gellan and Ca^{++} concentrations. The dynamic rheological method gave more consistent results, perhaps due to improved temperature control in the sample. Moreover, the measurement resulted from the response of a relatively large volume of sample within the annular gap of the coaxial cylinder fixture. Therefore, gelling temperature by this method was used in the remainder of the study for further analysis.

The mean gelling temperatures determined by dynamic rheological testing were compared (Table 1) for four gellan concentrations and seven Ca^{++} concentrations. The gel-forming temperatures of gellan solutions increased from 30 to 71.5°C as gellan concentrations increased from 0.4 to 2.0% (w/v) and cation concentrations from 2 to 40 mM.

The GLM procedure in SAS (SAS Institute, Inc., 1985) was used to obtain constants in Eq. (14) by fitting the equation to experimental data (Fig. 4). $[X_i]$ in Eq. (14) was taken as the total equivalent calcium ions in the solution. It included calcium ions added to the solutions during sample preparation and the amount of calcium and magnesium ions originally in the polymer power. Gellan polymers as supplied contained 0.4% w/v calcium and 0.1% magnesium ions. Preliminary tests showed the effects of two types of divalent ions on gelling temperature of gellan solutions were identical. The constants in Eq. (14) were determined as:

$$\begin{aligned} A &= -5.82 \times 10^{-5} \quad 1/°K \\ B &= -1.01 \times 10^{-4} \quad 1/°K \\ C &= 3.33 \times 10^{-3} \quad 1/°K \end{aligned} \tag{16}$$

Thus, the following model was obtained which related gelling temperatures of gellan solutions to gellan and Ca^{++} concentrations:

$$\frac{1}{T_{gel}} = -5.82 \times 10^{-5} \ln[X_p] - 1.01 \times 10^{-4} \ln[X_i] + 3.33 \times 10^{-3} \tag{17}$$

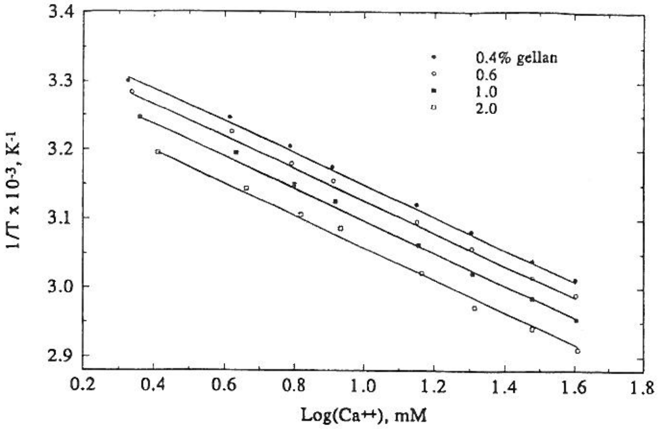

Fig. 4—Experimental data (scattered points) for gelling temperatures of gellan solutions containing Ca^{++} shown along with fitted functions according to Eq. (17) (continuous curves).

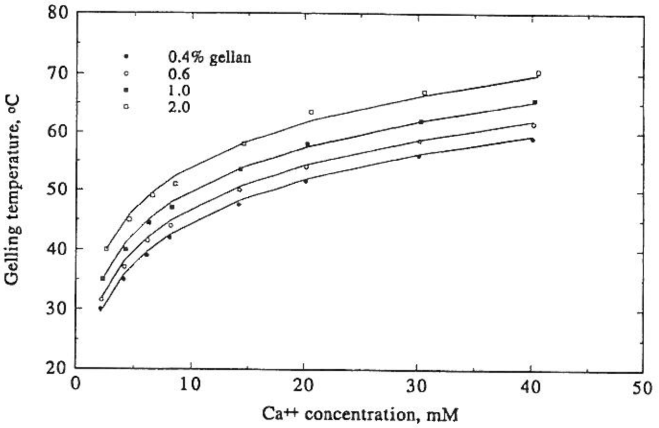

Fig. 5—Effects of polymer and Ca^{++} concentrations on gelling temperatures of gellan solutions as described by Eq. (17) (continuous curves).

The R^2 for this equation was 0.99. This model described the dependence of gelling temperature on gellan polymer and Ca^{++} concentrations with a discrepancy of < 1°C from experimental data (Fig. 5).

Information from Eq. (17) also helps to provide an improved understanding of cross-links in gellan gel networks. As explicitly expressed in Eq. (15), negative values for A and B in Eq. (16) suggested that cross-linking processes were exothermic as also indicated by a DSC study (Moritaka et al., 1992). From Eq. (15) and (16), we have:

$$\Delta H = -\frac{(n - l)\, R}{5.82 \times 10^{-5}} \tag{18}$$

According to Chandrasekaran et al. (1988b), cross-links in gellan gels were formed as associations of two pairs of double stranded polymer chains. Thus, the stoichiometric coefficients *l* and *n* in Eq. (18) are 1 and 4, respectively, and ΔH for calcium cross-linking in gellan gels was calculated to be −428.6 kJ/mole. This was 1.4 to 2.1 times the heat of cross-linking reported by Eldridge and Ferry (1954) and Gekko et al. (1992) for gelatin gels. Gelatin gels are formed mainly through hydrogen bonding (Eldridge and Ferry, 1954; Ledward, 1986; Johnston-Banks, 1990), whereas direct ion-ion interactions may be responsible for calcium ion cross-linking in gellan gels (Chandrasekaran et al., 1988b; Moritaka et al., 1991; Tang et al., 1995). Thus, cross-links in gellan gels would be expected to be stronger than those in gelatin gels. This, in part, explains the report by Sanderson (1990) that gellan gels were stronger than gelatin gels and melted at higher temperatures.

Based on Eq. (15), the stoichiometric coefficient m can be obtained from:

$$m = \frac{B(n - l)}{A} \tag{19}$$

Substituting values for A and B obtained from Eq. (16), and setting $n = 4$ and $l = 1$, m was calculated to be 5.2. That is, about five Ca^{++} ions were used to form a cross-link with four gellan polymer chains; however, this value seems too high. According to Sanderson (1990), the repeat unit in gellan polymers contains one carboxyl group(COO^-). The ratio of divalent cations to the number of repeat polymer units in gellan solutions to produce gels of maximal strength was found to be 0.5 (Tang et al., 1996). Thus, presumably, only two divalent cations, instead of five, were needed to make a cross-link with four strands of gellan polymers. This discrepancy needs further investigation.

CONCLUSIONS

GELLING TEMPERATURES for gellan solutions of various polymer and calcium ion concentrations measured by dynamic rheological testing agreed well with those measured by visible light spectrophotometry. Gelling temperatures by direct visual observation in conjunction with readings taken using a thermocouple agreed with the other methods at temperatures below 50°C, but deviated as much as 3.5°C at higher temperatures. In general, the dynamic testing method was most consistent. Gelling temperatures of gellan solutions increased from 30.0 to 71.5°C, as polymer concentrations increased from 0.4 to 2.0% w/v and Ca^{++} concentrations increased from 2 to 40 mM. A mathematical model based on the van't Hoff equation was used to relate gelling temperatures to compositions and polymer molecular weights. The model predicted gelling temperatures ± 1°C within experimental values. Using this model, the heat of calcium ion cross-linking in gellan gels was estimated to be 428.6 kJ/mole, about 1.4 to 2.1 times the heat for hydrogen bonding gelation of gelatin gels.

NOMENCLATURE

A, B, C	constants
G'	dynamic shear storage modulus (kPa)
K	equilibrium constant for formation of cross-links
M_w	weight average molecular weight
R	the gas constant (0.008314 kJ/mole K)
S.D.	standard deviation
T	absolute temperature (K)
T_{gel}	gelling temperature (K)
ΔG	change in Gibbs free energy (kJ/mole)
ΔH	energy of cross-linking (kJ/mole)
ΔS	enthalpy change during gelation (kJ/mole K)
[J]	molar concentration of cross-links
$[J]_{gel}$	molar concentration of cross-links at gelling point
$[X_i]$	molar concentration of cations
$[X_l]$	molar concentration of free loci for cross-links on gellan polymers
$[X_p]$	concentration of gellan polymer in solutions (g/mL)
a, b, c, c'	constants
l, m, n	stoichiometric coefficients
ln(X)	Natural logarithm of variable X

REFERENCES

Anon. 1992. 21 CFR 172-Food additives permitted for direct addition to food for human consumption: Gellan gum. Federal Register 57(228): 55444–55445.

Atkins, P.W. 1990. *Physical Chemistry*. W. H. Freeman and Company, New York.

Billmeyer, F.W. 1962. *Textbook of Polymer Science*. Interscience Publishers, New York.

Chandrasekaran, R., Millane, R.P., and Arnott, S. 1988a. The crystal structure of gellan. Carbohydrate Res. 175: 1–15.

Chandrasekaran, R., Puigjaner, L.C., Joyce, K.L., and Arnott, S. 1988b. Cation interactions in gellan: an X-ray study of the potassium salt. Carbohydrate Res. 181: 23–40.

Eldridge, J. and Ferry, J.D. 1954. Studies of the cross-linking process in gelatin gels. III. Dependence of melting point on concentration and molecular weight. J. Phys. Chem. 58: 992–995.

Fernandes, P.B., Goncalves, M.P. and Doublier, S.L. 1991. Phase diagrams in Kappa-carrageenan/locust bean gum systems. Food Hydrocolloids 5: 71–73.

Ferry, J.D. 1948. Protein gels. Adv. in Protein Chem. 4: 1–78.

Gekko, K. and Fukamizu, M. 1991. Effect of pressure on the sol-gel transition of agarose. Agric. Biol. Chem. 55(9): 2427–2428.

Gekko, K., X. Li, and Makino, S. 1992. Effects of polyols and sugars on the sol-gel transition of gelatin. Biosci., Biotech. Biochem. 56(8): 1279–1284.

Hansen, L.M., Hoseney, R.C., and Faubion, J.M.. 1991. Oscillatory probe rheometry as a tool for determining the rheological properties of starch-water systems. J. Texture Stud. 21: 213–224.

Hsieh, Y.L., Regenstein, S.M., and Rao, M.A. 1993. Gel point of whey and egg protein using dynamic rheological data. J. Food Sci. 58(1): 116–119.

Johnston-Banks, F.A. 1990. Gelatin. In *Food Gels*, P. Harris (Ed.), p. 233–289. Elsevier Science Publishers Ltd., New York.

Ledward, D.A. 1986. Gelation of gelatin. In *Functional Properties of Food Macromolecules*, J.R. Mitchell and D.A. Ledward (Ed.), p. 171–201. Elsevier Applied Science Publishers Ltd., New York.

Moritaka, H., Fukuba, H., Kumeno, K., Nakahama, N., and Nishinari, K. 1991. Effect of monovalent and divalent cations on the rheological properties of gellan gels. Food Hydrocolloids, 4(6): 495–507.

Moritaka, H., Nishinari, K., Nakahama, N., and Fukuba, H. 1992. Effect of potassium chloride and sodium chloride on the thermal properties of gellan gum gels. Biosci., Biotechnol., and Biochem. 56(4): 595–599.

Morris, V.J. 1986. Gelation of polysaccharides. In *Functional Properties of Food Macromolecules*, J.R. Mitchell and D.A. Ledward (Ed.), p. 121–170. Elsevier Applied Science Publishers Ltd., New York.

Rees, D.A. 1969. Structure, conformation, and mechanism in the formation of polysaccharide gels and networks. In *Advances in Carbohydrate Chemistry and Biochemistry*, M.L. Wolfrom, R.S. Tipson, and D. Horton (Ed.), Vol. 24: 267–332. Academic Press, New York.

Sanderson, G.R. 1990. Gellan gum. In *Food Gels*, P. Harris (Ed.), p. 201–232. Elsevier Science Publishers Ltd., New York.

SAS Institute, Inc. 1985. *SAS Users Guide: Statistics, Version 5*. SAS Institute Inc., Cary, NC.

Snoeren, T.H.M. and Payens, T.A.J. 1976. On the sol-gel transition in solutions of kappa-carrageenan. Biochim. Biophys. Acta 437: 264–272.

Tang, J., Tung, M.A., and Zeng, Y. 1995. Mechanical properties of gellan gels in relation to divalent cations. J. Food Sci. 60(4): 748–759.

Tang, J., Tung, M.A., and Y. Zeng, Y. 1996. Compression strength and deformation of gellan gels formed with mono and divalent cations. Carbohydrate Polymers 29(1): 11–16.

Upstill, C., Atkins, E.D.T., and Attwool, P.T. 1986. Helical conformation of gellan gum. Int. J. Biol. Macromol. 8: 275–88.

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