Agarose Gels: Effect of Sucrose, Glucose, Urea, and Guanidine Hydrochloride on the Rheological and Thermal Properties†

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The effect of sucrose, glucose, guanidine hydrochloride, or urea on the dynamic elastic modulus E' and mechanical loss tangent and on the differential scanning calorimetry (DSC) curves of agarose gels were examined. E' increased with increasing concentration of sugars up to a certain amount, but the excessive addition of sugars decreased E'. The DSC endothermic peak accompanying the transition from gel to sol shifted to higher temperatures, while the heat absorbed on forming 1 mol of junction zones increased and then decreased with increasing sugar concentration. Guanidine hydrochloride or urea decreased E' and shifted the gel to sol transition temperature to lower temperatures. The mechanism by which these chemical reagents weaken or strengthen the gel-forming ability was discussed.

Agarose is a seaweed extract that gives rise to thermoreversible gels; their physicochemical properties and the mechanism of gelation have been the subject of many investigations (Indovina et al., 1979; Nishinari and Watase, 1983; Hayashi and Kanzaki, 1987; Tokita and Hikichi, 1987; Watase and Nishinari, 1987, 1988a; Watase et al., 1989; Clark et al., 1990).

Agarose is also an important food hydrocolloid that modifies or controls the functional properties of foods by its strong gel-forming ability. When it is used with sugars, the gel-forming ability is expected to be influenced, but this has not been studied quantitatively. The effects of sucrose and glucose together with hydrogen bond breaking agents, urea and guanidine hydrochloride, are examined in the present work.

EXPERIMENTAL SECTION

Materials. Agarose was extracted from *Gelidium amansii* produced in 1987 in the Izu Suzaki region (Japan). *G. amansii* was pretreated by sodium hydroxide to remove the sulfate groups and increase 3,6-anhydro-L-galactose. The extraction was then carried out at 130 °C. The molecular weight was determined as (7.8 ± 0.032) × 10^4 by gel filtration chromatography at 50 °C using dextran as a standard material. Details of the preparation of agarose were described elsewhere (Watase and Nishinari, 1987).

Urea, guanidine hydrochloride (Gu·HCl), sucrose, and glucose of pure reagent form (Wako Pure Chemical Industries, Ltd.) were used without further purification.

Measurements. Differential scanning calorimetry (DSC) measurements were carried out with a sensitive DSC SSC 500U (Seiko Electronics, Ltd.). A 45-mg portion of each agarose gel was sealed into a silver pan of 70 μL. Distilled water was used as the reference material. The heating rate was 2 °C/min.

The dynamic Young's modulus E' and the mechanical loss tan δ were determined by observation of longitudinal vibrations of agarose gels molded into cylinders (30-mm length and 20-mm diameter). The apparatus used was a Rheolograph gel (Toyo Seiki Seisakusho). The frequency was 2.5 Hz, and the temperature was controlled by a silicone oil bath at each measurement temperature ±0.2 °C.

Details of measurement procedures were described previously (Watase and Nishinari, 1987a, 1988a; Watase et al., 1989).

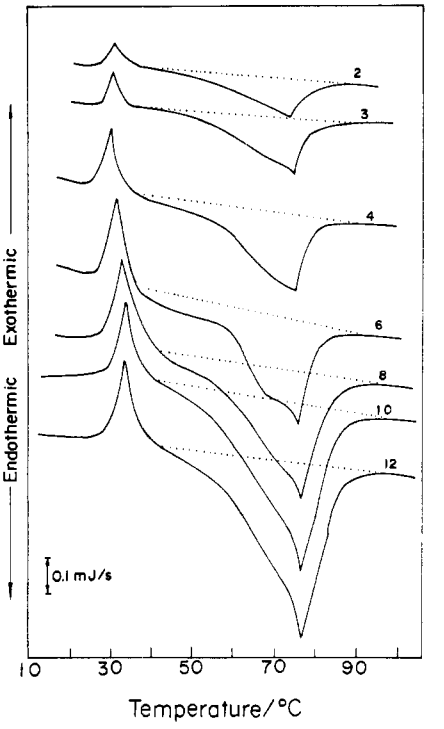

Figure 1. Heating DSC curves of agarose gels of various concentrations. Base lines are shown by dotted lines. Figures beside each curve represent the concentration of agarose in percent w/w.

RESULTS AND DISCUSSION

Figure 1 shows the heating DSC curves of agarose (AG) gels of various concentrations. Sharp endothermic peaks around 75 °C are attributed to the transition from gel to sol, i.e., the melting of the gel. This endothermic peak

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Table I. Melting Temperature (T_m) and Enthalpy (ΔH) and Entropy (ΔS) of Melting of Concentrated Agarose Gels

	% w/w AG						
	2	3	4	6	8	10	12
T_m/K	347.9	348.1	348.3	348.6	348.8	349.1	349.3
ΔH/mJ mg^{-1}	1.2	1.8	2.3	3.2	4.3	5.2	6.0
ΔS/mJ g^{-1} K^{-1}	3.4	5.2	6.6	9.2	12.3	14.9	17.2

temperature will be called the melting temperature T_m hereafter. This melting temperature is shifted slightly to higher temperatures and the endothermic enthalpy ΔH determined from the area enclosed by the DSC endothermic peak, and the base line and the entropy of melting $\Delta S = \Delta H/T_m$ increased remarkably with increasing concentration of agarose as shown in Table I. The origin of small exothermic peaks around 35 °C is not clear at present, but it is supposed that rearrangement of molecular chains occurs during heating. When the gel is once heated to 100 °C, and then cooled slowly, the second heating run at the same heating rate does not show this small exothermic peak. Once gels are melted, and when they were cooled slowly, the most ordered molecular arrangement would have been already realized; then, the second heating run does not show the small exothermic peak. As far as we are aware, this small exothermic peak is observed only for very "strong" gels such as agarose (Watase and Nishinari, 1987a; Watase et al., 1989), some κ-carrageenans (Watase and Nishinari, 1987b; Nishinari et al., 1990), and poly(vinyl alcohol) gels prepared by repeated freeze–thaw cycles (Watase and Nishinari, 1988a). Gelatins and other thermoreversible gels with low gel-forming ability do not show this exothermic peak.

Parts a–d of Figure 2 show the heating DSC curves of agarose gels of various concentrations containing guanidine hydrochloride (Gu·HCl). T_m shifted to lower temperatures, and ΔH and ΔS decreased by addition of Gu·HCl (Table II). An endothermic shoulder appeared around 50 °C in the presence of 2 mol/L (Figure 2c) and 3 mol/L (Figure 2d) Gu·HCl. This may be a consequence of the fact that the structure of the junction zones is not homogeneous. For instance, some links at the end of the junction zones may be able to rotate more easily than others. Gu·HCl could make this inhomogeneity more prominent, causing the endothermic peak associated with the gel–sol transition to split into multiple peaks and appear as a shoulder.

Since Gu·HCl breaks hydrogen bonds, it inhibits helix formation and the aggregation of helices, thus preventing the formation of junction zones. The endothermic shoulder around 50 °C may be due to the weakening action of Gu·HCl against structural stabilization. This is particularly so in dilute gels where junction zones are not so dense and where the network structure may be very sensitive to heating.

Urea showed similar action to agarose gels as indicated in parts a–c of Figure 3: T_m shifted to lower temperatures with increasing concentrations of urea added. This is also understood by the hydrogen bond breaking action of urea. An endothermic shoulder appeared in a and c and as discussed above may be due to inhomogeneity in the structure of the junction zones.

T_m of agarose gels containing sucrose shifted to higher temperatures with increasing concentration of sucrose (Figure 4). It was difficult to remove air bubbles completely for concentrated agarose gels (>10%). The origin of shoulders observed just below T_m in 6% and 8% agarose gels containing 1.0 mol/L sucrose (Figure 4b) is not clear at present. Similar shoulders have been observed in κ-carrageenan gels containing sucrose (Nishinari et al., 1990).

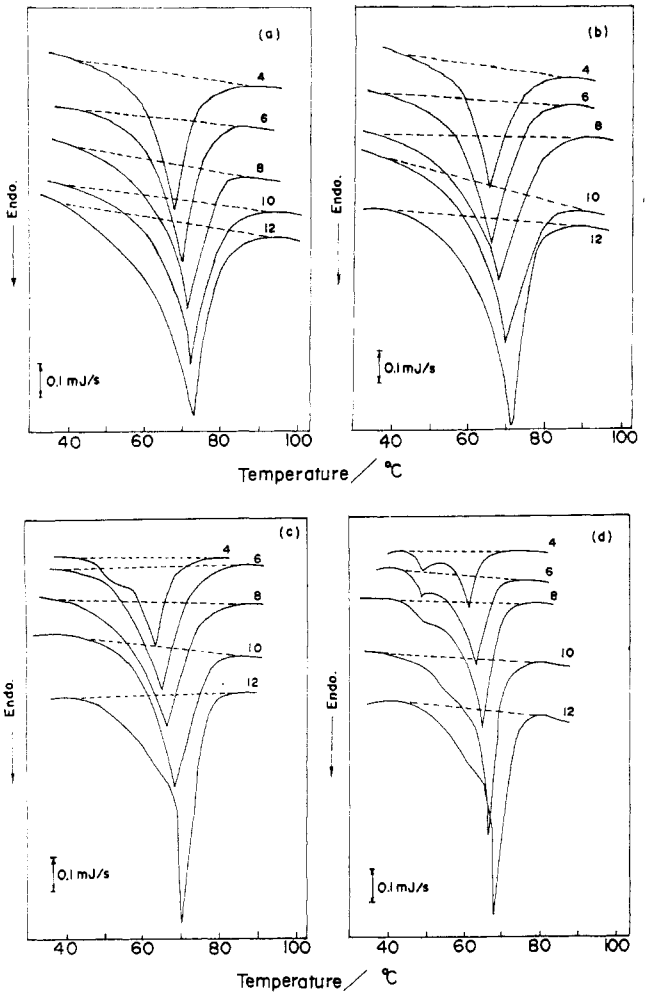

Figure 2. Heating DSC curves of agarose gels of various concentrations containing Gu·HCl of various concentrations. Base lines are shown by broken lines. Figures beside each curve represent the concentration of agarose in percent w/w concentrations of Gu·HCl: (a) 0.5 mol/L; (b) 1 mol/L; (c) 2 mol/L; (d) 3 mol/L.

Agarose gels containing glucose (Figure 5) showed a tendency similar to that observed in agarose gels containing sucrose (Figure 4): T_m shifted to higher temperatures with increasing concentration of glucose.

Figure 6 shows the temperature dependence of dynamic Young's modulus E' and mechanical loss tan δ for agarose gels of various concentrations. E' increased up to 35 °C, then began to decrease slowly, and began to decrease rapidly around 55 °C. tan δ did not change very much around room temperature, and then it began to increase rapidly and then decreased over the temperature range where E' began to decrease rapidly. This means that agarose gels changed from solidlike behavior to liquidlike behavior over the temperature range from 45 to 65 °C. Such a fact that tan δ showed a maximum at the temperature range where E' decreased rapidly with increasing temperature has been widely observed in polymeric systems: in glass transitions (Ferry, 1971) and in small-scale molecular motion in solid polymers at lower temperatures (Nishinari and Fukada, 1980). The temperature dependence of E' will be discussed later.

Parts a–d of Figure 7 show the temperature dependence of dynamic Young's modulus E' and mechanical loss tan δ of agarose gels containing Gu·HCl of various concentrations. E' decreased slowly around room temperature and then began to decrease rapidly at higher temperatures between 45 and 65 °C. The temperature range at which E' begins to decrease rapidly and tan δ

Table II. Effect of Sucrose, Urea, and Guanidine Hydrochloride on the Melting Temperature (T_m) and Enthalpy (ΔH) and Entropy (ΔS) of Melting of Concentrated Agarose Gels

(a) Sucrose

		% w/w AG						
	sucrose, mol^{-1}	2	3	4	6	8	10	12
T_m/K	0.5	348.0	348.4	348.8	349.4	350.6	354.2	360.0
	1	351.8	352.0	352.1	353.8	354.5		
ΔH/mJ mg^{-1}	0.5	1.4	2.2	2.7	3.4	4.0	4.5	5.1
	1	1.6	2.3	2.8	3.7	4.2		
ΔS/mg g^{-1} K^{-1}	0.5	4.0	6.3	7.8	9.7	11.4	12.7	14.2
	1	4.5	6.3	7.9	10.4	11.7		

(b) Glucose

		% w/w AG				
	glucose, mol^{-1}	2	3	4	6	8
T_m/K	1	348.5	348.8	349.2	349.7	351.4
	2	351.3	351.6	352.0	353.0	354.7
ΔH/mg mg^{-1}	1	1.6	2.4	2.8	3.5	4.1
	2	1.7	2.4	2.9	3.8	4.2
ΔS/mJ g^{-1} K^{-1}	1	4.6	6.9	8.0	10.0	11.7
	2	4.8	6.8	8.2	10.8	11.8

(c) Urea

		% w/w AG				
	urea, mol L^{-1}	4	6	8	10	12
T_m/K	2		335.8	336.6	337.5	338.1
	4	331.0	332.2	333.5	334.2	335.2
	6		324.6	325.5	326.3	327.0
ΔH/mJ mg^{-1}	2		1.9	2.3	2.8	3.4
	4	1.7	2.2	2.4	2.8	3.4
	6		1.9	2.1	2.5	2.9
ΔS/mJ g^{-1} K^{-1}	2		5.7	7.0	8.2	10.1
	4	5.2	7.1	8.5	8.5	10.2
	6		6.6	7.2	7.6	8.8

(d) Guanidine Hydrochloride

		% w/w AG				
	Gu·HCl, mol L^{-1}	4	6	8	10	12
T_m/K	0.5	340.8	342.5	343.8	345.0	346.2
	1	337.5	339.0	340.8	342.5	344.0
	2	336.5	337.9	339.6	341.5	343.0
	3	334.0	336.2	337.4	339.0	340.5
ΔH/mJ mg^{-1}	0.5	2.8	3.7	4.6	5.3	5.9
	1	2.9	4.1	5.0	5.2	5.3
	2	2.3	3.5	4.4	4.2	3.8
	3	1.2	2.0	2.6	3.2	3.3
ΔS/mJ g^{-1} k^{-1}	0.5	8.2	10.8	13.4	15.4	16.9
	1	8.5	12.0	14.8	15.3	15.5
	2	6.9	10.4	12.9	12.3	11.0
	3	3.5	6.0	7.6	9.3	9.7

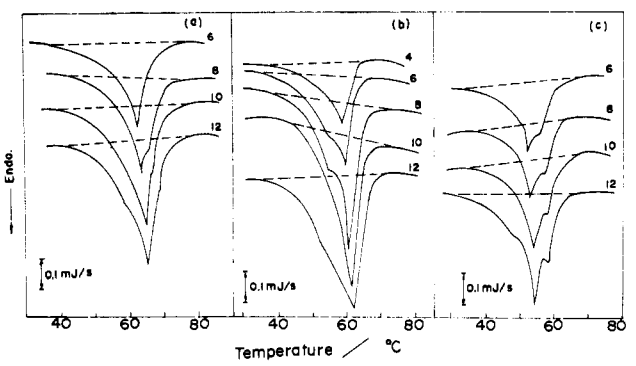

Figure 3. Heating DSC curves of agarose gels of various concentrations containing urea of various concentrations. Base lines are shown by broken lines. Figures beside each curve represent the concentration of agarose in percent w/w. Concentrations of urea: (a) 2 mol/L; (b) 4 mol/L; (c) 6 mol/L.

increases rapidly shifted to higher temperatures with increasing agarose concentration. E' increased and tan δ decreased with increasing concentration of agarose. This means agarose gels show solidlike behavior at higher polymer concentration and liquidlike behavior at lower polymer concentration. The number of junction zones will increase with increasing polymer concentration, resulting in more solidlike behavior. At room temperature, E' was proportional to approximately the square power of concentration of agarose, as has been shown previously (Hirai, 1955). tan δ did not change very much around room temperature and then it began to increase rapidly over the temperature range where E' began to decrease rapidly. E' decreased and tan δ increased with increasing Gu·HCl concentration. The temperature range at which E' begins to decrease rapidly shifted to lower temperatures with increasing Gu·HCl concentration.

The temperature range at which E' begins to decrease and tan δ begins to increase rapidly was lower than T_m as shown in Figure 2. It is well-known that T_m observed in DSC curves shifts to higher temperatures with increasing heating rate (Wunderlich, 1981). In the present work,

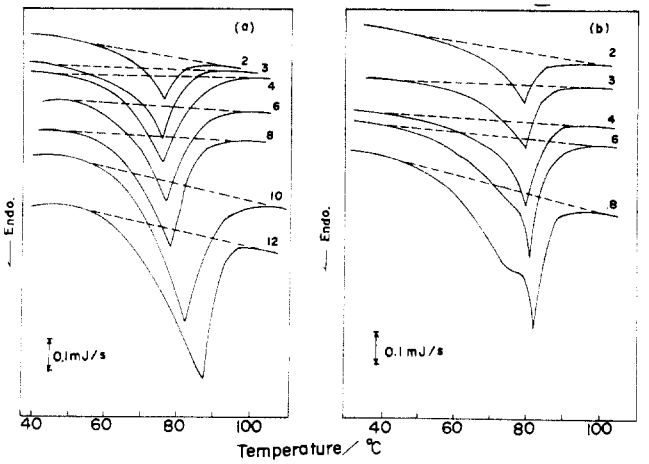

Figure 4. Heating DSC curves of agarose gels of various concentrations containing sucrose of various concentrations. Base lines are shown by broken lines. Figures beside each curve represent the concentration of agarose in percent w/w. Concentrations of sucrose: (a) 0.5 mol/L; (b) 1 mol/L.

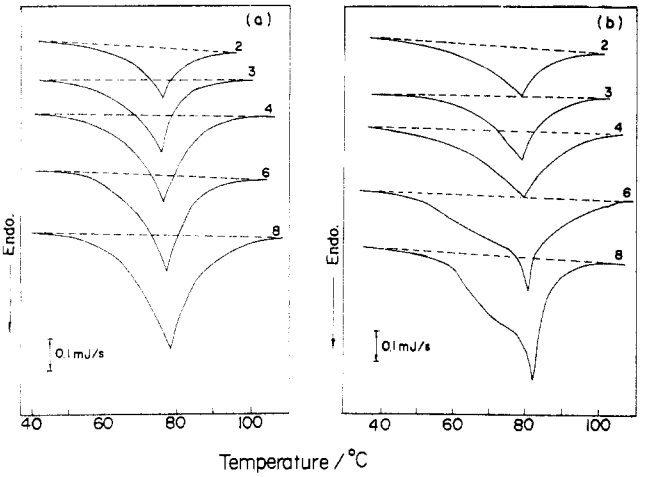

Figure 5. Heating DSC curves of agarose gels of various concentrations containing glucose of various concentrations. Base lines are shown by broken lines. Figures beside each curve represent the concentration of agarose in percent w/w. Concentrations of glucose: (a) 1 mol/L; (b) 2 mol/L.

the temperature is raised at 2 °C/min in DSC measurements, while it was kept at the measurement temperature for 20 min in the viscoelastic measurements. The viscoelastic data suggest that, even at temperatures far lower than T_m observed in DSC, some structural change occurs: probably the decrease of the number of junction zones or a conformational change from stiffer helical molecules to more flexible molecules.

Agarose gels containing urea (Figure 8) showed a tendency similar to that observed in agarose gels containing Gu·HCl (Figure 7): E' decreased and tan δ increased with increasing temperature. The temperature range at whith E' begins to decrease and tan δ begins to increase rapidly shifted to higher temperatures with increasing agarose concentration and shifted to lower temperatures with increasing urea concentration.

Figure 9 shows the temperature dependence of E' and tan δ of agarose gels containing sucrose. E' decreased and tan δ increased with increasing temperature. The temperature range at which E' begins to decrease rapidly and tan δ begins to increase rapidly shifted to higher temperatures with increasing concentration of sucrose. This is more pronounced in dilute gels than in concentrated gels.

Agarose gels containing glucose (Figure 10) showed a

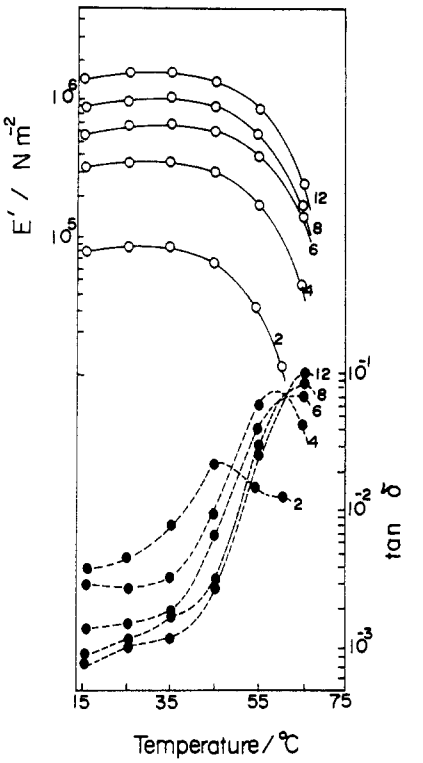

Figure 6. Temperature dependence of E' (solid line) and tan δ (broken line) for agarose gels of various concentrations. Figures beside each curve represent the concentration of agarose in percent w/w.

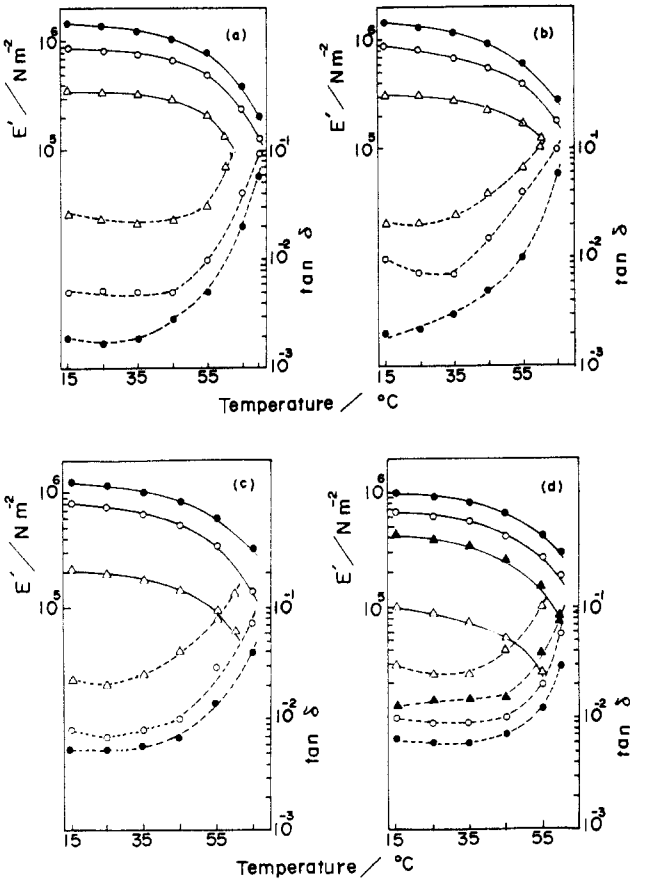

Figure 7. Temperature dependence of E' (solid line) and tan δ (broken line) for agarose gels of various concentrations containing Gu·HCl of various concentrations. Concentrations of agarose gels in percent w/w: △, 4; ○, 8; ● 12. Concentrations of Gu·HCl: (a) 0.5 mol/L; (b) 1 mol/L; (c) 2 mol/L; (d) 3 mol/L.

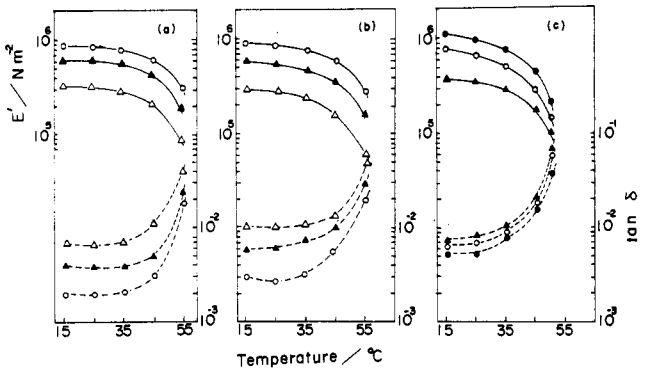

Figure 8. Temperature dependence of E' (solid line) and tan δ (broken line) for agarose gels of various concentrations containing urea of various concentrations. Concentrations of agarose gels: shown by the same symbols as in Figure 7; ▲, 6% w/w. Concentrations of urea: (a) 2 mol/L; (b) 4 mol/L; (c) 6 mol/L.

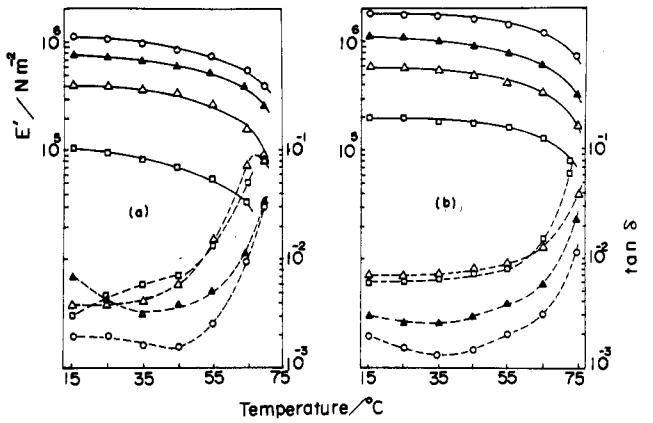

Figure 9. Temperature dependence of E' (solid line) and tan δ (broken line) for agarose gels of various concentrations containing sucrose of various concentrations. Concentrations of agarose gels: shown by the same symbols as in Figure 6 and 7; □, 2% w/w. Concentrations of sucrose: (a) 0.5 mol/L; (b) 1 mol/L.

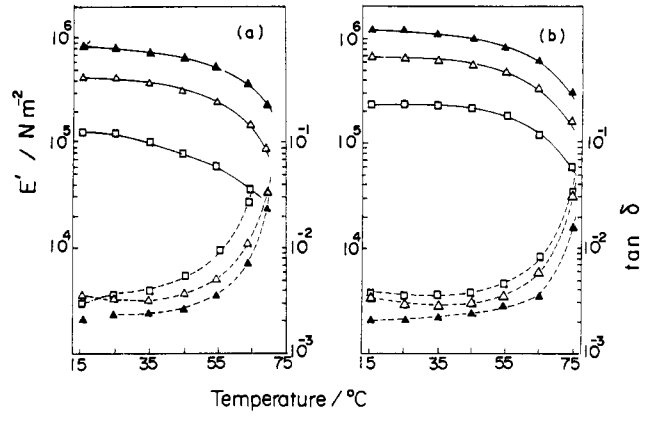

Figure 10. Temperature dependence of E' (solid line) and tan δ (broken line) for agarose gels of various concentrations containing glucose of various concentrations. Concentrations of agarose gels shown by the same symbols as in Figures 7–9. Concentrations of glucose: (a) 1 mol/L; (b) 2 mol/L.

tendency similar to that observed in agarose gels containing sucrose (Figure 9). The temperature dependence of the elastic modulus of thermoreversible gels has been explained on the basis of a model consisting of junction zones and flexible chains connecting the junction zones (Nishinari et al., 1985) at the temperature range lower than the gel–sol transition. The flexible chains were assumed to be Langevin chains; i.e., the ratio of the end-to-end distance of the chain to the extended chain length is given by the Langevin function, so that the case of highly extended molecular chains can be taken into account (Treloar, 1975). Both ends of each chain are bound to two of the junction zones by weak secondary interactions such as hydrogen bonds, entanglement, and van der Waals interactions. The number of segments incorporated into the junction zone may change with temperature: the segments are released from the junction zone with increasing temperature and become incorporated with decreasing temperature.

The gel consists of Langevin chains having N segments of length a. A partition function is given by

$$Z = \sum_n f_n \qquad f_n = \left(\frac{\sinh \beta}{\beta}\right)^n e^{-\beta r}\, e^{(N-n)\epsilon/kT} \tag{1}$$

where n is the number of segments released into the amorphous region between two junction zones distant from each other by na and β is related to r by

$$r/n = \mathcal{L}(\beta) = \coth \beta - \frac{1}{\beta} \tag{2}$$

Here, $\mathcal{L}(\beta)$ is the Langevin function and ϵ is the bonding energy. Some calculation based on this model led to an expression for the elastic modulus

$$E = \frac{\mathcal{N}kT}{10}\left\langle \phi(\eta)\left[1 + \frac{MPr^2}{2(2\pi)^{1/2}}\left(\frac{1}{r} + \eta\alpha^{1/2}M + \frac{MP}{(2\pi)^{1/2}}\right)\right]\right\rangle_r \tag{3}$$

where

$$M = \frac{\nu}{r} - \frac{1}{\mathcal{L}(\beta_0)} \qquad P = \alpha^{1/2}\, e^{-\eta^2/2}/\phi(\eta) \tag{4}$$

and

$$\langle \ldots \rangle_r = 4\pi \int_0^\infty \ldots f(r)\, r^2\, dr/\mathcal{N}$$

represents the average over the distance r. $f(r)$ is a distribution function of the end-to-end distance r, and $\phi(\eta)$ is an error function

$$\phi(\eta) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\eta} e^{-x^2/2}\, dx \qquad \eta = (\nu - n_0)\alpha^{1/2} \tag{5}$$

$$\alpha = \frac{r^2}{n_0^3} \frac{\beta_0^2 e^{2\epsilon/kT}}{e^{2\epsilon/kT} - 1} \tag{6}$$

n_0 is the value of n at which the summand f_n of the partition function becomes maximum.

Since we know very little about the distribution function $f(r)$, we replace it by a δ function having the peak at certain average value r_m of the end-to-end distance r. The elastic modulus can be calculated from eq 3 for the fixed values of $\mu = \nu/r_m$ as a function of temperature and for various mean end-to-end distances.

If the number of segments liberated from junction zones n becomes larger than an upper limit ν, the transition from gel to sol occurs. For a smaller value of the bonding energy ϵ, the ceiling number ν, or the mean distance r_m, the elastic modulus decreases monotonically with increasing temperature. For intermediate values of ϵ, ν, and r_m, the elastic modulus increases up to a certain temperature T_0 and then decreases with increasing temperature. For large values of ϵ, ν, and r_m, the elastic modulus increases monotonically with increasing temperature

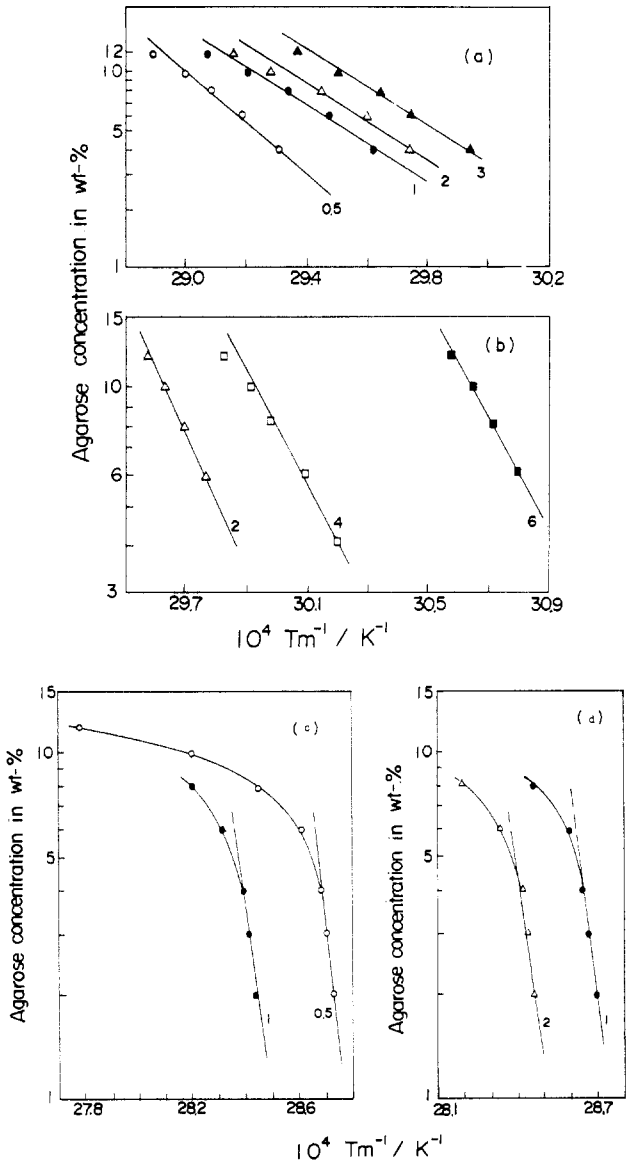

Figure 11. Eldridge–Ferry plot for agarose gels containing various chemical reagents: (a) Gu·HCl; (b) urea; (c) sucrose; (d) glucose. Figures beside each curve represent the concentration of the chemical reagent in moles per liter.

as in the case of rubber (Treloar, 1975).

According to this treatment, the elastic modulus as a function of temperature may depend on the bonding energy ϵ, the mean end-to-end distance r_m of the chains connecting the junction zones, and the ceiling number ν, i.e., the upper limit of the number of segments that can be liberated from junction zones just before the transition from gel to sol occurs. According to the model, the elastic modulus E increases monotonically for large values of the bonding energy ϵ, the mean end-to-end distance r_m, or the ceiling number ν, while E decreases monotonically for small values of these three parameters. Rubber, which has large ϵ, shows a monotonical increase, while carrageenan and gelatin, which have small ϵ, show a monotonical decrease (Nishinari et al., 1985; Nishinari and Watase, 1987; Watase et al., 1989). The experimental findings that the temperature range at which E' begins to decrease rapidly shifted to lower temperatures by the addition of Gu·HCl or urea and shifted to higher temperatures by the addition of sucrose or glucose may be explained as follows: The addition of Gu·HCl or urea decreases ϵ, consistent with the results shown in parts a and b of Figure 11, and ν also may decrease. As for r_m, it is not possible

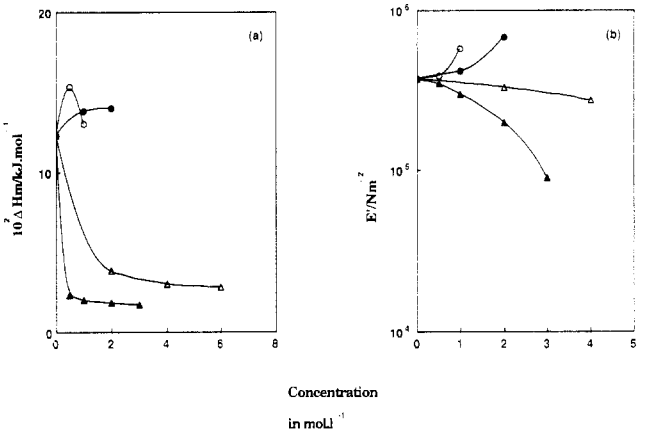

Figure 12. (a) Heat absorbed on forming 1 mol of junction zones ΔH_m as a function of added chemical reagents: ▲, Gu·HCl; Δ, urea; O, sucrose; ●, glucose. (b) E' of 4% w/w agarose gels at 25 °C as a function of added chemical reagents. Symbols represent the same meaning as in Figure 12a.

to determine whether it increases or decreases; probably some will increase and other will decrease. On average, r_m may be assumed to be constant. Then, the decreasing tendency of E is promoted by the addition of Gu·HCl or urea. On the contrary, the addition of sucrose or glucose increases E, consistent with the results shown in parts c and d of Figure 11. In this case, ϵ and ν may increase while r_m may be assumed unchanged. Thus, the decreasing tendency of E' is weakened, and the temperature range at which E' begins to decrease rapidly shifted to higher temperatures.

Figure 11 shows the Eldridge–Ferry plot for agarose gels containing Gu·HCl (Figure 11a) and urea (Figure 11b). In the case of agarose gels containing Gu·HCl or urea, the plot gave straight lines; however, in the case of agarose gels containing sucrose or glucose, the plot gave a straight line only for agarose concentrations lower than 4% (w/w). Although the Eldridge–Ferry plot was proposed only for dilute gels, it is reported that the plot gave straight lines even for very concentrated gels of agarose (Watase and Nishinari, 1987a), κ-carrageenan (Watase and Nishinari, 1987b) and poly(vinyl alcohol) (Watase and Nishinari, 1989). The slope of the straight line is proportional to the heat absorbed on forming 1 mol of junction zones ΔH_m. The value of ΔH_m decreased with increasing concentration of Gu·HCl or urea (Figure 12a). The fact that the plot deviates from the straight line in agarose gels containing sucrose or glucose at about 4% suggests that different types of gel structure are formed around this concentration.

ΔH_m determined from the Eldridge–Ferry plots shown in parts a–d of Figure 11 is shown as a function of the concentration of added chemical reagents in Figure 12a together with the Young's modulus E' of 4% w/w agarose gels at 25 °C as a function of the concentration of added chemical reagents (Figure 12b). Sucrose and glucose increase both ΔH_m and E' of agarose gels, while urea and Gu·HCl decrease both ΔH_m and E'.

Sucrose and glucose may promote the formation of helical molecules and the aggregation of these helical molecules. Then, the structure of the junction zones is stabilized, and the number of junction zones will increase. Therefore, the elastic modulus increased in the presence of sucrose and glucose. A similar phenomenon has been observed for gelatin gels containing sucrose (Oakenfull and Scott, 1986). However, the excessive addition of sucrose or glucose weakens the gel-forming ability of agarose. A similar phenomenon has been observed for aga-

rose gels containing polyhydric alcohols (Nishinari and Watase, 1987) or dimethyl sulfoxide (Watase and Nishinari, 1988b). The mechanism of promotion of the gel-forming ability of these chemical reagents is not completely clear at present; probably, they increase hydrogen bonding and promote the formation of helices and the aggregation of helices. At the same time, they change the water structure. E' and ΔH_m of agarose gels containing glycerin (Nishinari and Watase, 1987), ethylene glycol (Nishinari and Watase, 1987), and dimethyl sulfoxide (Watase and Nishinari, 1988b) exhibited a maximum at certain concentrations of these chemical reagents. By excessive addition of these chemical reagents, free water, which is necessary to form junction zones, is made insufficient by these chemical reagents. These chemical reagents induce the agarose molecules to change conformation and to change the structure of the junction zones, in addition to immobilizing free water. Both of these phenomena will occur simultaneously; however, it is not yet clear which is the most predominant.

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Registry No. Agarose, 9012-36-6; sucrose, 57-50-1; glucose, 50-99-7.