

κ -Carrageenan Gels: Effect of Sucrose, Glucose, Urea, and Guanidine Hydrochloride on the Rheological and Thermal Properties[†]

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The effect of sucrose, glucose, urea, and guanidine hydrochloride on dynamic viscoelasticity and differential scanning calorimetry (DSC) curves of κ -carrageenan gels were studied. The dynamic Young's modulus E' and the melting point of κ -carrageenan gels increased with increasing sugar content. Urea weakened the gelling ability. Guanidine hydrochloride strengthened the gelling ability up to a certain amount, but excessive addition of guanidine hydrochloride weakened the gelling ability. The heat absorbed on forming 1 mol of junction zones showed a maximum as a function of added content of sugars or guanidine hydrochloride. It is suggested that sugars may create junction zones and stabilize the structure of junction zones, but the excessive addition of sugars immobilizes free water necessary for junction zone formation. Low concentrations of guanidine hydrochloride shield the electrostatic repulsions between sulfate groups in κ -carrageenan molecules and stabilize the structure of junction zones. However, higher concentrations of guanidine hydrochloride disrupt hydrogen bonds and weaken the gel-forming ability.

Carrageenan is frequently used as a gelling agent or stabilizer in food products, and its physicochemical properties have been studied by many investigators. It is well-known that alkali metal ions or alkaline-earth metal ions promote the gelation of κ -carrageenan (Morris et al., 1980; Paoletti et al., 1984; Rochas and Rinaudo, 1984; Rochas, 1987; Piculell et al., 1987; Day et al., 1988; Norton et al., 1983; Snoeren and Payens, 1976), although excessive addition of these cations can inhibit gelation (Watase and Nishinari, 1982). It has also been shown that urea or formamide inhibits the gelation of κ -carrageenan, while guanidine hydrochloride (Gu·HCl) enhances the gelling ability (Watase and Nishinari, 1988a). However, excessive addition of Gu·HCl has also been shown to inhibit gelation (Watase and Nishinari, 1988a). Ethylene glycol or glycerin also promotes the gelation; however, once again excessive addition of these polyhydric alcohols has been shown to inhibit gelation (Nishinari and Watase, 1987). This paper examines the effect of added sucrose and glucose on the rheological and thermal properties of κ -carrageenan, and the effect of adding guanidine hydrochloride and urea on these properties has been reexamined. Since κ -carrageenan is used to produce dessert gels, the examination of the effect of these sugars will give useful information to the food formulator.

EXPERIMENTAL SECTION

Materials. κ -Carrageenan was extracted from *Eucheuma cottonii*, produced in The Philippines in 1987 by the method described previously (Watase and Nishinari, 1987). *E. cot-*

tonii was washed with water and then pretreated with potassium hydroxide, and after being washed again in water, κ -carrageenan was extracted. Amberlite 120-B resin was washed with dilute hydrochloride and then converted to the potassium form, before being added to the κ -carrageenan solution. The solution was stirred slowly and gently at about 50 °C, then the resin was removed by filtration, and the filtrate was freeze-dried.

The molecular weight was determined as $(6.16 \pm 0.025) \times 10^6$ by gel filtration chromatography at 40 °C using dextran as a standard material. Sucrose, glucose, guanidine hydrochloride, and urea of extra reagent grade (Wako Pure Chemical, Ltd.) were used without further purification. Samples for rheological and thermal measurements were prepared by the method described previously (Watase and Nishinari, 1982). Sucrose, glucose, Gu·HCl, or urea was added to the dispersion of κ -carrageenan and then heated at 70 °C for 1 h. Then, the temperature was raised to 100 °C to attain complete dissolution, which can be recognized by its transparency. The solution was then poured into Teflon molds, the diameter and length of which were 20 and 30 mm, respectively. The temperature was gradually lowered to room temperature in a thermostated box. After the gels were taken out from the molds, the samples for rheological measurements were kept in silicone oil at 5 °C for 40 h. The samples for thermal measurements were wrapped by nylon films and kept at 5 °C for 40 h. The gels were kept at 25 °C for 1 h before the measurements were taken.

Measurements. Differential scanning calorimetry (DSC) measurements were carried out with a sensitive DSC SSC 500U (Seiko Electronics Ltd.). A 45-mg portion of each κ -carrageenan gel was sealed into a silver pan of 70 μ L. 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 $\tan \delta$ were determined by observation of longitudinal vibrations of κ -carrageenan gels molded into cylinders (30-mm length and 20-mm diameter). The apparatus used was a Rheograph 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, which also prevented water evaporation from the gel surfaces.

Details of measurement procedure were described previously (Watase and Nishinari, 1982, 1987, 1988a; Nishinari and Watase, 1987).

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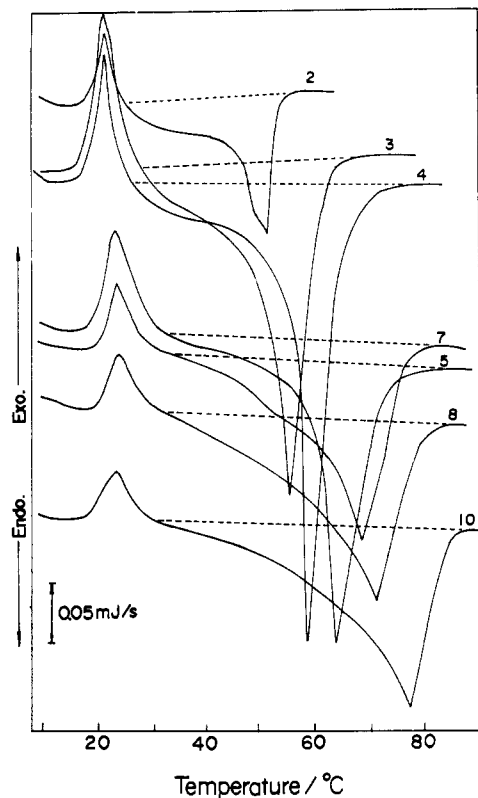


Figure 1. Heating DSC curves of κ -carrageenan gels of various concentrations. Base lines are shown by broken lines. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w. Heating rate: 2 °C/min.

RESULTS AND DISCUSSIONS

Figure 1 shows the heating DSC curves of κ -carrageenan gels (KC) of various concentrations. Sharp endothermic peaks around 50–76 °C are attributed to the transition from gel to sol. This endothermic temperature will be called the melting temperature, T_m hereafter. T_m shifted remarkably to higher temperatures with increasing polymer concentration, which is in contrast with agarose gels in the accompanying paper (Watase et al., 1990). The meaning of this will be discussed later in the discussion about Figure 11.

The endothermic peak is the sharpest at a concentration of 4% w/w. Below this concentration, the number of junction zones will increase with increasing polymer concentration, and it tends to be in a more crystalline state. However, beyond this concentration, the entanglement of molecular chains becomes important, and the amorphous region also increases. Therefore, the peak became less sharp. The conformation of molecular chains connecting junction zones and the structure of junction zones seem to change at about 4% w/w.

An endothermic shoulder below T_m may be due to polydispersity of molecular weight or to the distribution of bonding energies in junction zones. The origin of small endothermic peaks around room temperature, which have been also observed in agarose gels (Watase et al., 1990), is not clear at present. When the sample is heated to 100 °C, and after being cooled slowly, the reheating DSC curves at the same heating rate, 2 °C/min, did not show these small exothermic peaks.

Figure 2 shows the heating DSC curves of κ -carrageenan gels of various concentrations containing Gu·HCl of various concentrations.

The endothermic enthalpy of melting, ΔH , determined from the area enclosed by DSC peak and the base

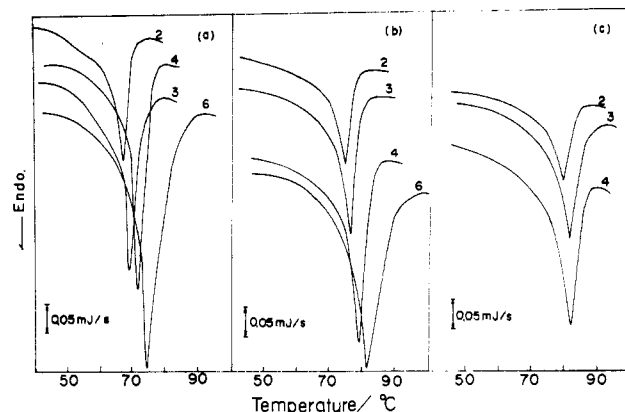


Figure 2. Heating DSC curves of κ -carrageenan gels of various concentrations containing Gu·HCl of various concentrations. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w. Concentrations of Gu·HCl: (a) 0.5 mol/L; (b) 1 mol/L; (c) 1.5 mol/L. Heating rate: 2 °C/min.

line, and the entropy of melting, $\Delta S = \Delta H/T_m$, are shown in Table Id.

T_m shifted to higher temperatures with increasing concentration of Gu·HCl. Since Gu·HCl is a hydrogen bond breaking reagent, its addition shifts T_m to lower temperatures for agarose gels. However, Gu·HCl is an electrolyte, and the guanidinium ions may shield the electrostatic repulsion of sulfate groups in κ -carrageenan molecules. The electrostatic shielding promotes the formation of helical molecules and the aggregation of helices; thus, new junction zones are created, and existing junction zones are stabilized. In κ -carrageenan gels, these two opposite actions of Gu·HCl—the hydrogen bonds breaking and the electrostatic shielding of the repulsion between sulfate groups—coexist, but judging from the experimental fact that T_m shifted to higher temperatures by the addition of Gu·HCl, the latter action seems to be predominant.

Figure 3 shows the heating DSC curves of κ -carrageenan gels of various concentrations containing urea of various concentrations. T_m shifted to higher temperatures with increasing polymer concentration as observed in Figure 2 (see also Table Ic). However, T_m shifted to lower temperatures with increasing concentration of urea for 4% w/w and 5% w/w gels, but T_m did not change significantly for 6% w/w gels. Since urea is not an electrolyte, it acts only as a hydrogen bond breaker. As a result of this, the formation of helices and the aggregation of helices are inhibited, and T_m shifts to lower temperatures.

Figure 4 shows the heating DSC curves of κ -carrageenan gels of various concentrations containing sucrose of various concentrations. T_m shifted to higher temperatures with increasing concentration of polymer and added sucrose (see also Table Ia). An endothermic shoulder appeared just before the gel melting temperature for gels with concentration greater than 4% w/w. Sucrose will promote hydrogen bonding and will increase the number of junction zones, and at the same time the structure of junction zones will be stabilized.

Figure 5 shows the heating DSC curves of κ -carrageenan gels of various concentrations containing glucose of various concentrations (see also Table Ib). A similar tendency was observed for κ -carrageenan gels containing sucrose shown in Figure 4. Glucose also may strengthen the gel-forming ability of κ -carrageenan gels by forming hydrogen bonds.

Figure 6 shows the temperature dependence of the

Table I. Effects of Sucrose, Glucose, Urea, and Guanidine Hydrochloride on the Melting Temperature (T_m) and Enthalpy (ΔH) and Entropy (ΔS) of Melting of κ -Carrageenan Gels

(a) Sucrose					
		sucrose, mol L ⁻¹			
	% w/w KC	0	0.5	1	1.5
T_m	1	320.0	320.6	324.3	340.9
	2	324.7	330.1	337.2	352.5
	3	327.8	334.8		356.1
	4	332.2	337.6	343.0	360.6
	6	340.1	343.1	348.3	
	ΔH /mJ mg ⁻¹	1	0.48	0.50	0.39
2		1.15	1.06	1.02	0.88
3		2.60	1.70		0.95
4		3.08	2.49	1.89	1.12
6		3.32	3.51	2.61	
ΔS /mJ g ⁻¹ K ⁻¹		1	1.50	1.56	1.20
	2	3.54	3.21	3.02	2.50
	3	7.93	5.08		2.67
	4	9.27	7.38	5.51	3.11
	6	9.76	10.23	7.49	

(b) Glucose					
		glucose, mol L ⁻¹			
	% w/w KC	0	1	2	3
T_m /K	2	324.7	328.9	333.0	346.4
	3	327.8		338.1	351.4
	4	332.2	339.0	345.2	356.3
	6	340.1	346.3		
	ΔH /mJ mg ⁻¹	2	1.15	0.97	0.92
3		2.60		1.14	1.01
4		3.08	2.84	2.43	2.42
6		3.22	2.55		
ΔS /mJ g ⁻¹ K ⁻¹		2	3.54	2.95	2.76
	3	7.83		3.37	2.87
	4	9.27	8.38	7.04	6.79
	6	9.47	7.36		

(c) Urea					
		urea, mol L ⁻¹			
	% w/w KC	0	4	6	
T_m /K	3	327.8	310.7		
	4	332.2	317.2	314.7	
	5		323.0	320.8	
	6	340.1	327.6	327.2	
	ΔH /mJ mg ⁻¹	3	2.60	0.75	
4		3.08	1.16	1.68	
5			1.52	1.30	
6		3.22	1.92	1.17	
ΔS /mJ g ⁻¹ K ⁻¹		3	7.93	2.41	
	4	9.27	3.66	5.34	
	5		4.71	4.05	
	6	9.41	5.86	3.58	

(d) Guanidine Hydrochloride					
		Gu·HCl, mol L ⁻¹			
	% w/w KC	0	0.5	1	1.5
T_m /K	2	324.7	340.3	347.2	351.7
	3	327.8	342.1	349.4	353.9
	4	332.2	344.6	352.3	354.9
	6	340.1	347.4	354.6	
	ΔH /mJ mg ⁻¹	2	1.15	1.12	0.93
3		2.60	1.55	1.33	1.23
4		3.08	1.85	1.71	1.42
6		3.22	3.00	2.52	
ΔS /mJ g ⁻¹ K ⁻¹		2	3.54	3.29	2.68
	3	7.93	4.53	3.81	3.48
	4	9.27	5.37	4.85	4.00
	6	9.47	8.64	7.11	

dynamic Young's modulus E' and mechanical loss $\tan \delta$ of κ -carrageenan gels of various concentrations. E' decreased monotonically with increasing temperature. E' decreased gradually, and beyond a certain temperature,

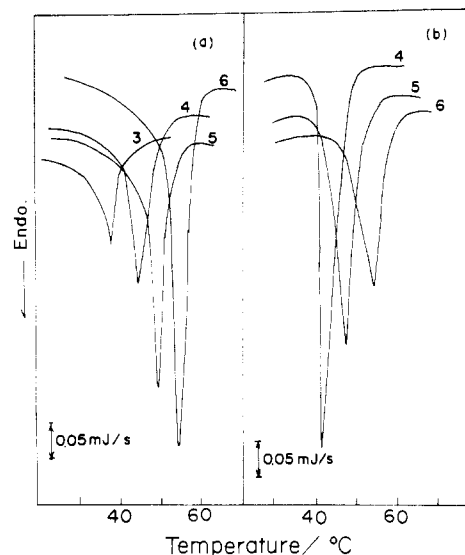


Figure 3. Heating DSC curves of κ -carrageenan gels of various concentrations containing urea of various concentrations. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w. Concentrations of urea: (a) 4 mol/L; (b) 6 mol/L. Heating rate: 2 °C/min.

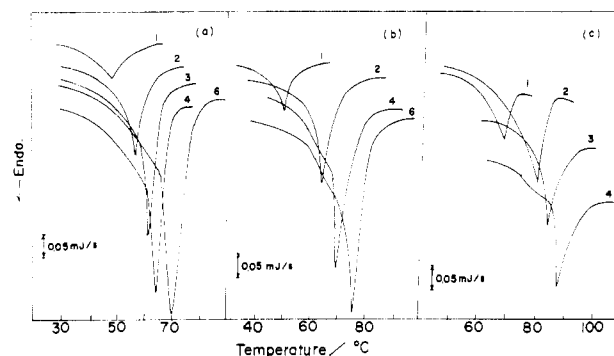


Figure 4. Heating DSC curves of κ -carrageenan gels of various concentrations containing sucrose of various concentrations. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w. Concentrations of sucrose: (a) 0.5 mol/L; (b) 1 mol/L; (c) 1.5 mol/L. Heating rate: 2 °C/min.

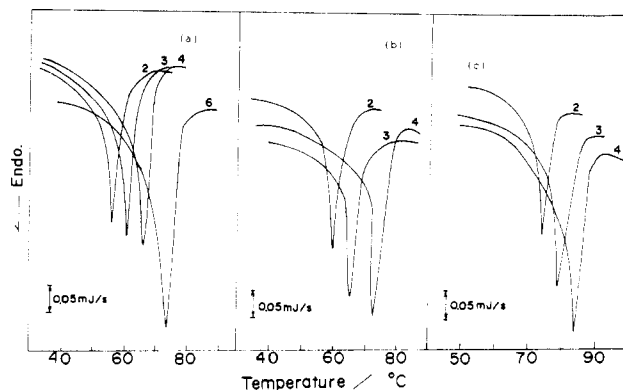


Figure 5. Heating DSC curves of κ -carrageenan gels of various concentrations containing glucose of various concentrations. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w. Concentrations of glucose: (a) 1 mol/L; (b) 2 mol/L; (c) 3 mol/L. Heating rate: 2 °C/min.

it began to decrease rapidly. Although E' of agarose gels showed a maximum as a function of temperature, E' of κ -carrageenan gels decreased monotonically. E' increased while $\tan \delta$ decreased with increasing polymer concentration; i.e., gels become more solidlike with increasing

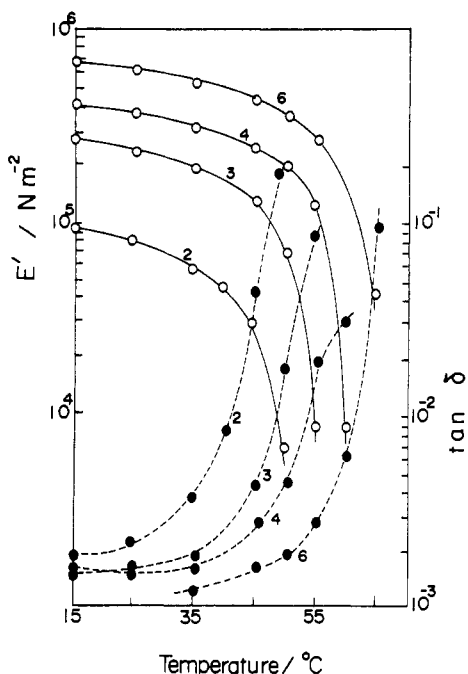


Figure 6. Temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations. Figures beside each curve represent the concentration of κ -carrageenan in percent w/w.

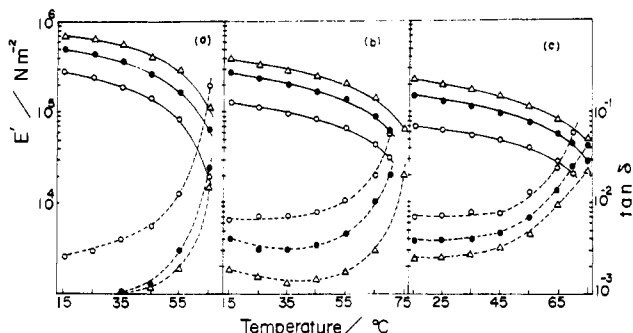


Figure 7. Temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing Gu-HCl of various concentrations. Concentrations of κ -carrageenan: \circ , 2% w/w; \bullet , 3% w/w; Δ , 4% w/w. Concentrations of Gu-HCl: (a) 2 mol/L; (b) 3 mol/L; (c) 4 mol/L.

polymer concentration as in the case of agarose gels (Watase et al., 1990). Since κ -carrageenan molecules contain sulfate groups, the junction zones consisting of aggregated double or single helices are not so stable because of the electrostatic repulsion of bulky sulfate groups that do not exist in agarose. The bonding energy ϵ and the ceiling number ν as discussed elsewhere may be smaller than those of agarose.

Figure 7 shows the temperature dependence of the dynamic Young's modulus E' and the mechanical loss $\tan \delta$ for κ -carrageenan gels of various concentrations containing Gu-HCl of various concentrations.

E' decreased gradually, and beyond a certain temperature, it began to decrease rapidly. The temperature at which E' begins to decrease rapidly and $\tan \delta$ begins to increase rapidly shifted to higher temperatures with increasing Gu-HCl concentration (about 55 °C in Figure 7a and 60–65 °C in parts b and c of Figure 7). This corresponds well to the fact that T_m shifted to higher temperatures with increasing concentration of Gu-HCl shown in Figure 2. E' increased while $\tan \delta$ decreased with increasing polymer concentration as in the κ -carrageenan gels without Gu-HCl (Figure 6). E' decreased with

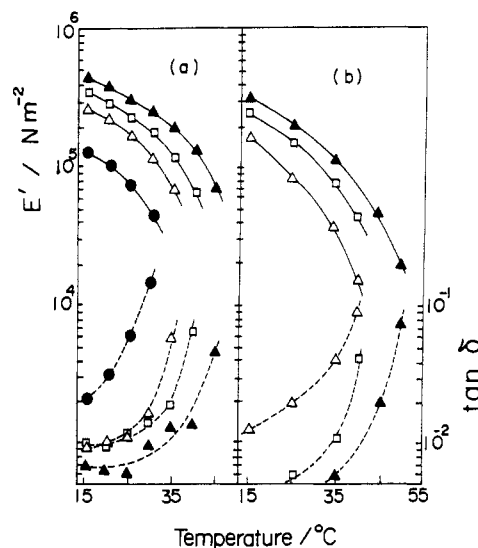


Figure 8. Temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing urea of various concentrations. Concentrations of κ -carrageenan: shown by the same symbols as in Figure 7; \square , 5% w/w; \blacktriangle , 6% w/w. Concentrations of urea: (a) 4 mol/L; (b) 6 mol/L.

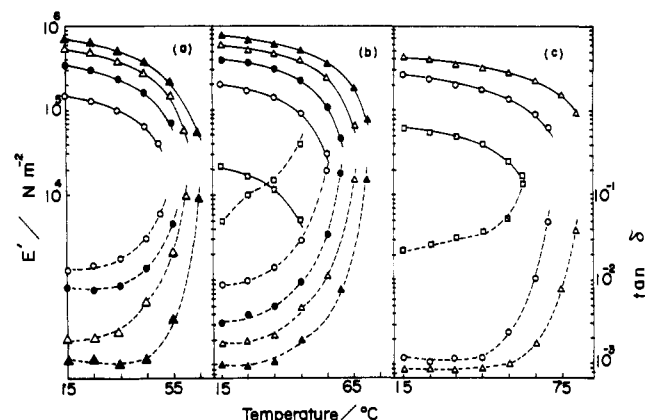


Figure 9. Temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing sucrose of various concentrations. Concentrations of κ -carrageenan shown by the same symbols as in Figures 7 and 8 except \square , 1% w/w. Concentrations of sucrose: (a) 0.5 mol/L; (b) 1 mol/L; (c) 1.5 mol/L.

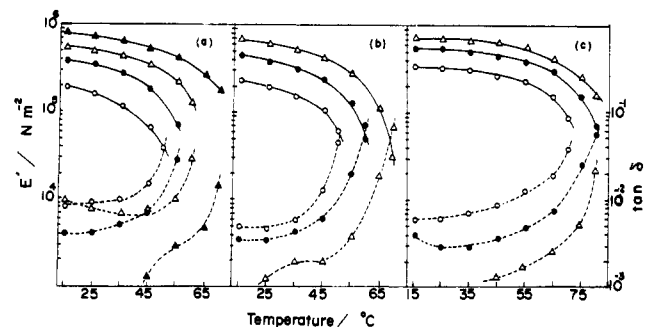


Figure 10. Temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing glucose of various concentrations. Concentrations of κ -carrageenan shown by the same symbols as in Figures 7 and 8. Concentrations of glucose: (a) 1 mol/L; (b) 2 mol/L; (c) 3 mol/L.

increasing Gu-HCl concentration; however, the decrease of E' with increasing temperature was restrained by the addition of Gu-HCl.

Figure 8 shows the temperature dependence of E' and

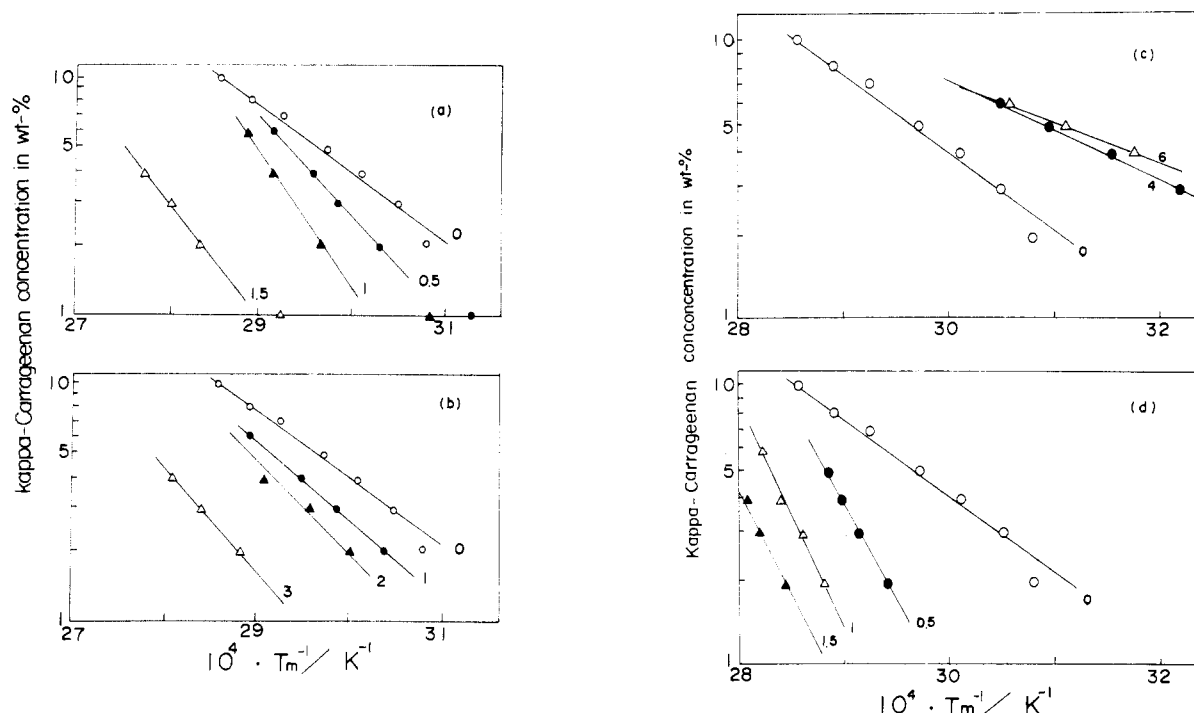


Figure 11. Eldridge-Ferry plot for κ -carrageenan gels containing various chemical reagents: (a) sucrose; (b) glucose; (c) urea; (d) Gu-HCl. Figures beside each curve represent the concentration of these chemical reagents in moles per liter.

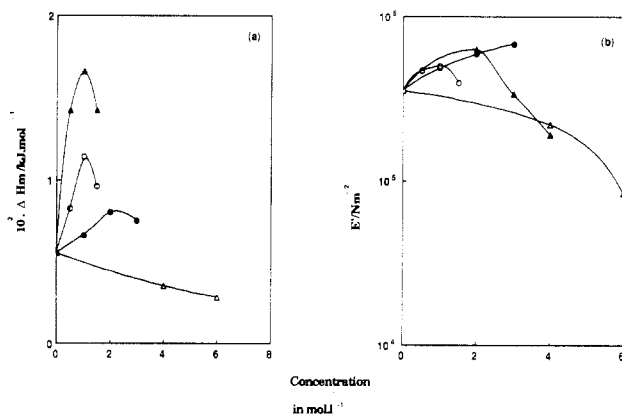


Figure 12. (a) Heat absorbed on forming 1 mol of junction zones, ΔH_m , as a function of the concentration of added chemical reagents: \blacktriangle , Gu-HCl; \triangle , urea; \circ , sucrose; \bullet , glucose. (b) E' of 4% w/w κ -carrageenan gels at 25 °C as a function of added chemical reagents. Symbols have the same meaning as in Figure 12a.

$\tan \delta$ for κ -carrageenan gels of various concentrations containing urea of various concentrations. General tendencies are similar as in case of the addition of Gu-HCl, but urea accelerates the decrease in E' with increasing temperature. This corresponds well with the findings that T_m shifted to lower temperatures with increasing urea concentration (Figure 3) as a result of the breaking of hydrogen bonds.

Figure 9 shows the temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing sucrose of various concentrations. The decrease of E' with increasing temperature was less, and the temperature at which E' begins to decrease rapidly and $\tan \delta$ begins to increase rapidly shifted to higher temperatures with increasing concentration of sucrose. E' increased with increasing sucrose concentration for dilute gels (<3% w/w); however, E' showed a maximum at 1.0 mol/L sucrose concentration for concentrated gels (>4% w/w). Sucrose may promote the formation of hydrogen bonds and the structure of junction zones will be stabilized, but the exces-

sive addition of sucrose will reduce the amount of free water necessary to form junction zones. This interpretation will be explored further in future work.

Figure 10 shows the temperature dependence of E' and $\tan \delta$ for κ -carrageenan gels of various concentrations containing glucose of various concentrations. Similar tendencies were observed as shown for gels containing sucrose (Figure 9): the temperature at which E' begins to decrease rapidly and $\tan \delta$ begins to increase rapidly shifted to higher temperatures with increasing glucose concentration. E' increased with increasing concentration of glucose at a fixed temperature for gels of all the concentrations examined. This is different from the observation for gels containing sucrose shown in Figure 9. Both sucrose and glucose may promote hydrogen bonding and the formation of junction zones, and both of them immobilize free water, thus changing the water structure.

The mechanism of promoting junction zone formation by hydrogen bonds newly created by the addition of these sugars and the mechanism of hydration for these sugars are unfortunately not as clear at present. However, the difference lies in the fact that the change of the structure of water seems to be the dominant factor causing the difference in E' of gels with sucrose or with glucose. The quantity of nonfreezing water determined by DSC is 0.56 (gram/gram of solid) for sucrose and 0.41 (gram/gram of solid) for glucose (Levine and Slade, 1988). Therefore, it is considered that sucrose immobilizes much more free water than glucose.

Figure 11 shows the Eldridge-Ferry plot for κ -carrageenan gels containing sucrose (Figure 11a), glucose (Figure 11b), urea (Figure 11c), or Gu-HCl (Figure 11d). The plot gave a straight line in each case, and the slope of the line is proportional to the heat absorbed on forming 1 mol of junction zones. The slope increased up to a certain concentration of sugars, 1 mol/L for sucrose and 2 mol/L for glucose, beyond which it decreased with increasing sugar concentration. T_m shifted to higher temperatures with increasing sugar concentration for all the cases examined in the present work.

Urea shifted T_m to lower temperatures, while Gu-HCl shifted T_m to higher temperatures. The slope of the straight line in the Eldridge-Ferry plot decreased by the addition of urea, while it increased by the addition of Gu-HCl up to 1 mol/L Gu-HCl and then decreased by the excessive addition of Gu-HCl.

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

The experimental fact that ΔH_m showed a maximum at a certain concentration of sucrose, glucose, or Gu-HCl suggests that some structural change occurred at that concentration of added chemical reagent, as mentioned above. It is well-known that in many cases when T_m shifts to higher temperatures, the heat absorbed on forming 1 mol of junction zones, ΔH_m , also increases. When κ -carrageenan is pretreated with alkali, T_m shifts to higher temperatures and ΔH_m increases concurrently (Watase and Nishinari, 1987). The gel of the polysaccharide extracted from *Gracilariopsis chorda* showed a similar phenomenon when it is pretreated by alkali (Watase and Nishinari, 1988b). Atactic polystyrene-carbon disulfide gels also showed a concurrent increase of ΔH_m and a shift of T_m to higher temperatures (Tan et al., 1983).

In the present case of κ -carrageenan gels containing sucrose or glucose, the heat absorbed on forming 1 mol of junction zones showed a maximum at a certain sugar concentration, while T_m increased with increasing sugar concentration (Figure 11a,b). The excess sugar immobilizes free water, which is necessary for junction zone formation, but the structures of the junction zones themselves are strengthened by the presence of sugar. Therefore, the melting temperature shifts to higher temperatures. When ethylene glycol or glycerin is added to κ -carrageenan gels, a similar phenomenon has been observed (Nishinari and Watase, 1987): Although T_m shifted to higher temperatures with increasing concentration of added polyhydric alcohols, ΔH_m showed a maximum at a certain concentration. In these cases, the structure of the junction zones is stabilized by the presence of polyhydric alcohols mainly by newly created hydrogen bonds. Therefore, T_m shifted to higher temperatures with increasing concentration of polyhydric alcohols. However, the excessive addition of polyhydric alcohols immobilizes free water, which is necessary to form junction zones, and so ΔH_m begins to decrease above a certain concentration.

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