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Effects of sugars and polyols on the gel–sol transition of kappa-carrageenan gels

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Abstract

The effects of various sugars and polyols, such as ethylene glycol, glycerol, ribose, glucose, fructose, mannose, galactose, sucrose, maltose and raffinose, on the gel–sol transition of kappa-carrageenan gels were studied by differential scanning calorimetry (DSC) in the present work. The melting temperature T_m and the setting temperature T_s were shifted to higher values with increasing concentration of the added polyol or sugar. This shift was linearly related with the dynamic hydration number or the number of equatorially attached hydroxyl groups in the added polyol or sugar. This suggests that the hydrogen bonding between hydroxyl groups in kappa-carrageenan and polyol or sugar is newly created, and that it stabilizes the structure of junction zones.

INTRODUCTION

Carrageenan has been studied as a model for gelling substance in the food industry and in biology. Many investigations have been aimed at clarifying the gelation mechanism and gel properties of carrageenan [1–5]. Its gelling properties are influenced strongly by the addition of alkali metal ions [6], anions [7,8], urea [9] and guanidine hydrochloride (GuHCl) [9]. κ-Carrageenan is extracted from a red seaweed. It consists of D-galactose and 3,6-anhydro-D-galactose, and contains some sulfate groups attached mainly to C_4.

The effects of sucrose and glucose on the dynamic viscoelasticity and the differential scanning calorimetry (DSC) curves of kappa-carrageenan gels were studied [10]. The dynamic Young's modulus E' and the melting point of kappa-carrageenan gels increased with increasing sugar content. The heat absorbed on forming 1 mol of junction zones showed a maximum as a function of added content of sugars. It is suggested that sugars may create

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junction zones and stabilize the structure of junction zones, but that the excessive addition of sugars immobilizes the free water necessary for junction zone formation [10].

The effects of glycerol and ethylene glycol on the elastic modulus and DSC thermograms of agarose and kappa-carrageenan gels were examined to clarify the relationship between structure and properties [11]. The elastic modulus of these gels as a function of the concentration of polyols increased up to a certain concentration, and then decreased with increasing concentration of polyols. These polyols shifted the melting temperature of the gel to higher temperatures in kappa-carrageenan gels but to lower temperatures in agarose gels. The temperature dependence of the elastic modulus was changed in opposite directions in agarose and kappa-carrageenan gels by the addition of polyols, and this is dicussed on the basis of a model consisting of junction zones which are connected by Langevin chains. It was suggested that the mean distance between junction zones became shorter in the presence of a small amount of polyols [10].

According to the zipper model approach [12], the heat capacity C of a gel consisting of $\mathcal{N}$ zippers is written as

$$C = k\mathcal{N}\left(\log \frac{G}{x}\right)^2 \left\{ \frac{2x}{(1-x)^2} + \frac{N(N+1)x^N[-x^{N+1} + (N+1)x - N]}{[1-(N+1)x^N + Nk^{N+1}]^2} \right\} \qquad (1)$$

where N is the number of parallel links in a single zipper, ε is the energy required to open a link, G is the rotational freedom of a link, $x = G\exp(-\varepsilon/kT)$, and T is the absolute temperature. In a DSC measurement, the heat flow difference $\mathrm{d}q/\mathrm{d}t$ between sample and reference is recorded as a function of temperature. Here, q and t represent the heat and time respectively. Since $\mathrm{d}q = C\mathrm{d}T$, or $\mathrm{d}q/\mathrm{d}t = C\mathrm{d}T/\mathrm{d}t$, the number $\mathcal{N}$ represents the number of zippers per total mass of the gel sample. Since eqn. (1) is based on equilibrium statistical thermodynamics, it is necessary to choose the scanning rate $\mathrm{d}T/\mathrm{d}t$ to be as slow as possible.

The effects of polyols or sugars on DSC curves for kappa-carrageenan gels were studied in the present work.

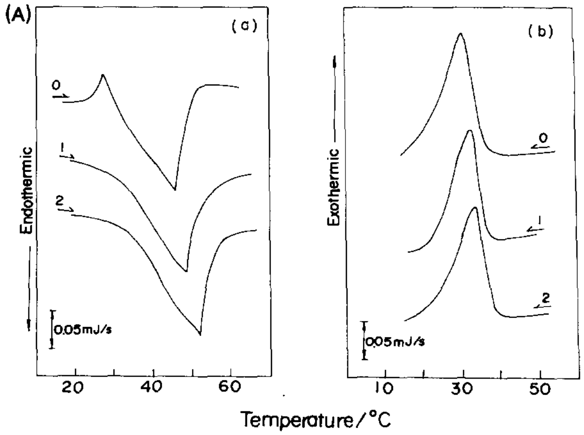
EXPERIMENTAL

Materials

κ-Carrageenan was extracted from *Eucheuma cottonii* produced in Korea in 1989 using potassium hydroxide, as described previously [9,10]. The sulfur content by elemental analysis was 6.3% and the molecular weight by gel permeation chromatography (GPC) at 40°C was about 1.8×10^6. Dextran was used as a standard material in GPC, and 4 M urea was used as a solvent. The contents of the inorganic ions K, Na, Ca and Mg were determined using an SAS-760 atomic absorption spectrum frame method as K 7.93%, Na 0.31%, Ca 0.6% and Mg 0.05%, respectively. Sugars and polyols of extra reagent grade (Wako Pure Chemical, Ltd.) were used without further purification. The preparation of gels and the method for DSC measurements were described previously [9,10].

RESULTS AND DISCUSSION

Figures 1A–1J show heating and cooling DSC curves of 2% kappa-carrageenan gels with and without polyols and sugars. A small exothermic



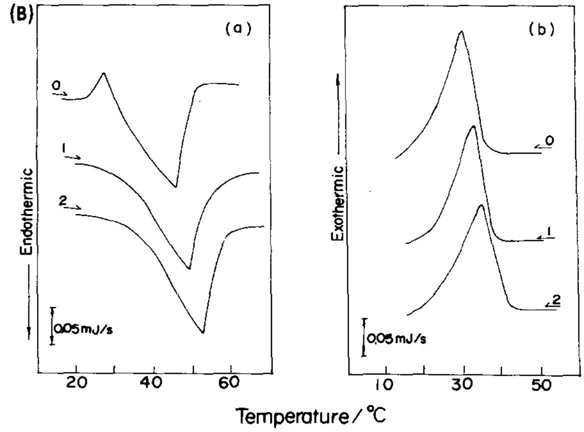
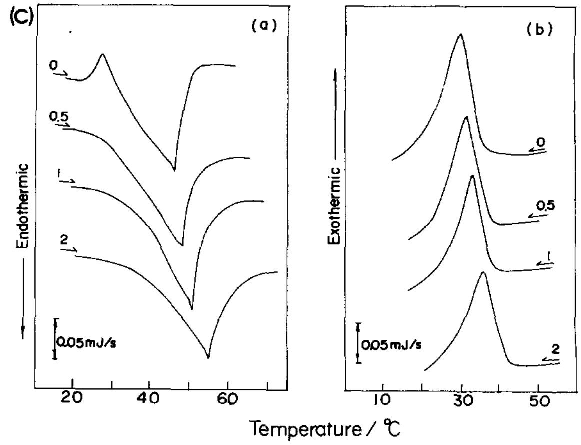


Fig. 1A. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without ethylene glycol. Figures beside each curve represent the concentration of ethylene glycol (M).

Fig. 1B. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without glycerol. Figures beside each curve represent the concentration of glycerol (M).



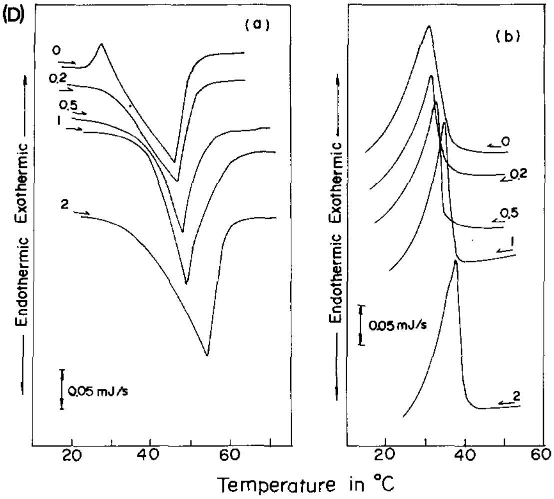
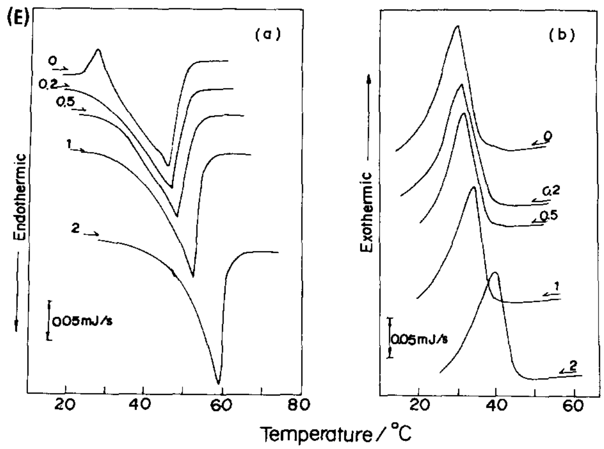


Fig. 1C. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without ribose. Figures beside each curve represent the concentration of ribose (M).

Fig. 1D. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without fructose. Figures beside each curve represent the concentration of fructose (M).

peak appeared at around 30°C in the heating DSC curve for gels without polyols or sugars. The origin of this small exothermic peak is not clear at present, but it is probably due to the reorganization of kappa-carrageenan molecules during heating.

A sharp endothermic peak was observed in the heating DSC curves around 40–60°C for 2 wt% kappa-carrageenan gels, which is attributed to the gel-to-sol transition. The endothermic peak temperature T_m in a heating DSC curve is higher than the exothermic peak temperature T_s observed in a cooling DSC curve. Both T_m and T_s shifted to higher temperatures with increasing concentration of added sugars or polyols, as shown in Figs. 1A–1J, and T_m was always higher than T_s. This is explained



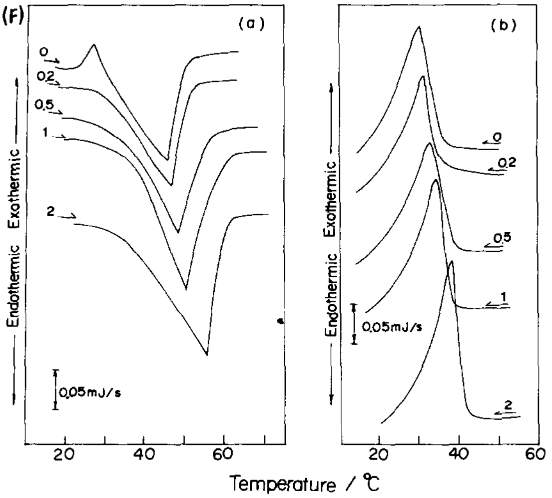
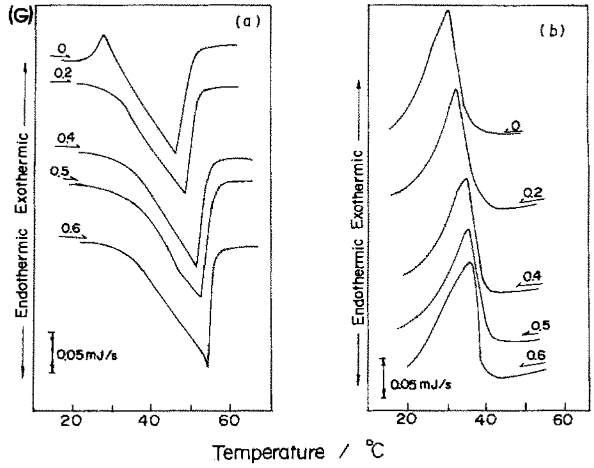


Fig. 1E. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without mannose. Figures beside each curve represent the concentration of mannose (M).

Fig. 1F. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without galactose. Figures beside each curve represent the concentration of galactose (M).

by a zipper model approach [12] as follows. When the temperature is raised, the rotational freedom G of a link will start from a smaller value G_g corresponding to the gel state. Then the gel will expand, which will increase the rotational freedom G. When the temperature is lowered, G will start from a larger value G_s corresponding to the sol state. Therefore, T_m is determined by $\overline{G}_g$, a certain average value of G_g, and T_s is determined by $\overline{G}_s$, a certain average value of G_s. Since $\overline{G}_g < \overline{G}_s$, T_m is higher than T_s. The exothermic peaks accompanying sol-to-gel transition in the cooling DSC curves are always sharper than the endothermic peaks accompanying gel-to-sol transition in the heating DSC curves. This can be interpreted as follows by a zipper model approach [12]. In the case of



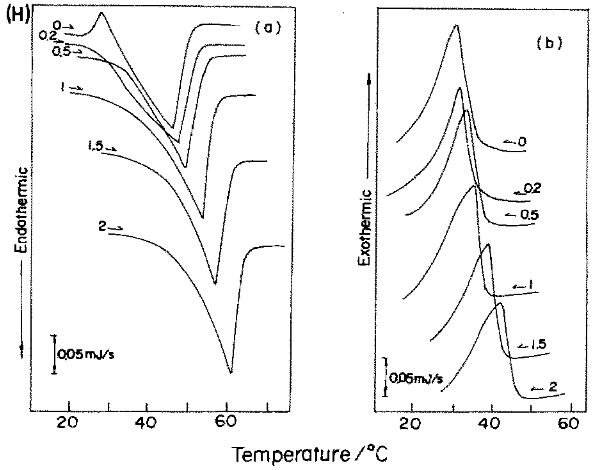
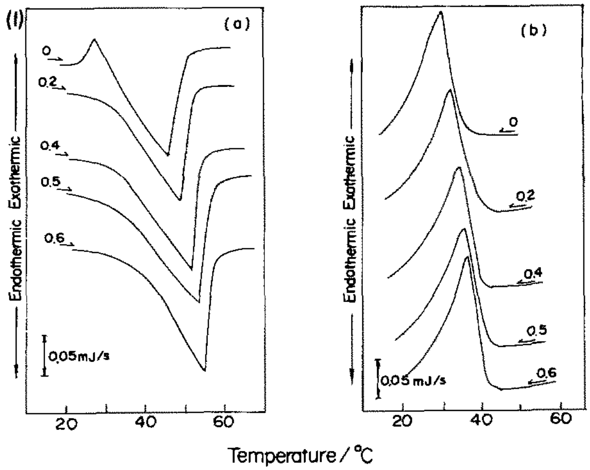


Fig. 1G. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without glucose. Figures beside each curve represent the concentration of glucose (M).

Fig. 1H. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without sucrose. Figures beside each curve represent the concentration of sucrose (M).

heating, the transition caused by the opening of the zippers will start as soon as the temperature arrives at the tail of the heat capacity–temperature curve corresponding to $G = G_g$. In cooling, the pairwise coupling cannot start so easily because of the difficulty for a long molecule to find its partner in the appropriate position for zipper construction. Hence a state like supercooling may occur in the course of cooling. It is therefore reasonable that the transition is sharper in cooling than in heating, as has been observed for agarose gels [13].

The relation between the temperature T_m and the concentration of added polyols or sugars is shown for 2% w/w kappa-carrageenan gels in Fig. 2. The value of T_m increased linearly with increasing concentration of



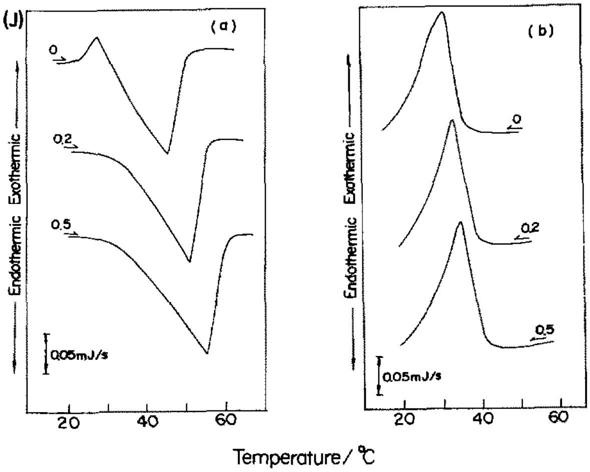


Fig. 1I. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without maltose. Figures beside each curve represent the concentration of maltose (M).

Fig. 1J. Heating (a) and cooling (b) DSC curves for 2% κ-carrageenan gels with and without raffinose. Figures beside each curve represent the concentration of raffinose (M).

all these sugars and polyols. In the case of agarose, T_m decreased linearly with increasing concentration of ethylene glycol, glycerol and ribose, whereas it increased linearly with increasing concentration of mannose, fructose, glucose, galactose, sucrose, maltose and raffinose [13]. The reason why T_m decreased in agarose gels and increased in kappa-carrageenan gel with increasing concentration of ethylene glycol, glycerol or ribose must be attributed to the difference of chemical structures of agarose and kappa-carrageenan.

Figure 3 shows the relationship between the setting temperature T_s and the concentration of added polyols or sugars. The relationship is again

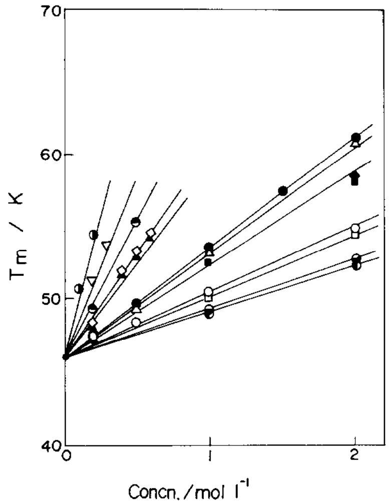


Fig. 2. Relationship between T_m of the gel and the concentration of added sugars or polyols: ◐, ethylene glycol; ⊖, glycerol; ○, ribose; △, sorbitol; □, fructose; ◆, galactose; ■, mannose; ●, glucose; ▲, sucrose; ◇, maltose; ◒, raffinose; ▽, maltotetraose; ◑, α-cyclodextrin.

almost linear, as in the case of T_m (Fig. 2), but the slope is far smaller for T_s than for T_m.

The differences $\Delta T_m = T_m - T_{m0}$ and $\Delta T_s = T_s - T_{s0}$, where T_{m0} and T_{s0} are the melting temperature T_m and the setting temperature T_s respectively of kappa-carrageenan gels without sugars, as functions of the dynamic hydration number n_{DHN} of added sugars, are shown in Figs. 4 and 5 respectively. Both ΔT_m and ΔT_s increased linearly with increasing n_{DHN} of added sugars for kappa-carrageenan gels with the addition of 0.5 or 1.0 M sugars.

Relationships between ΔT_m or ΔT_s and the mean value of the number n(e-OH) of equatorial OH groups existing in the various conformers of

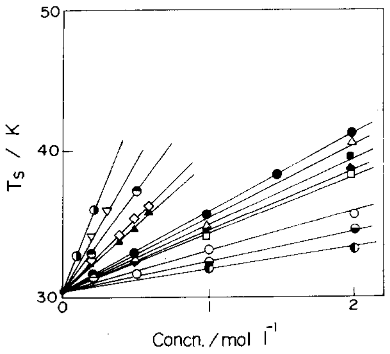


Fig. 3. Relationship between T_s of the gel and the concentration of added sugars or polyols. The symbols have the same meaning as in Fig. 2.

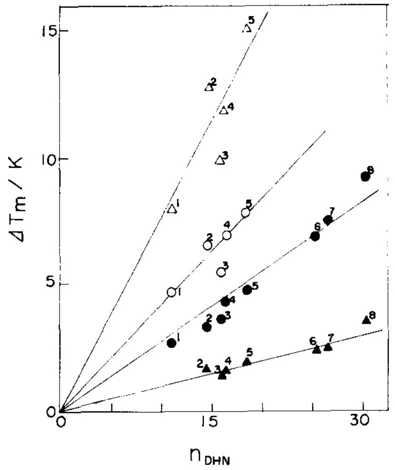


Fig. 4. The relation between ΔT_m and the dynamic hydration number n_{DHN} of added sugars or polyols. Concentration of added sugars: ▲, 0.2 M; ●, 0.5 M; ○, 1 M; △, 2 M. 1, ribose; 2, mannose; 3, fructose; 4, galactose; 5, glucose; 6, sucrose; 7, maltose; 8, raffinose.

sugar usually found in solutions are shown in Figs. 6 and 7. The increase in ΔT_m or ΔT_s was in the following order: raffinose > maltose > sucrose > glucose > galactose > mannose > fructose > ribose. The increase in ΔT_m with increasing concentration of added sugars or polyols has been attributed to the stabilization of junction zones in kappa-carrageenan gels by newly created hydrogen bonds between hydroxyl groups in the sugar or polyol molecules and in the kappa-carrageenan molecules.

The elastic modulus of kappa-carrageenan gels was increased by the addition of ethylene glycol and glycerol. The elastic modulus of thermore-

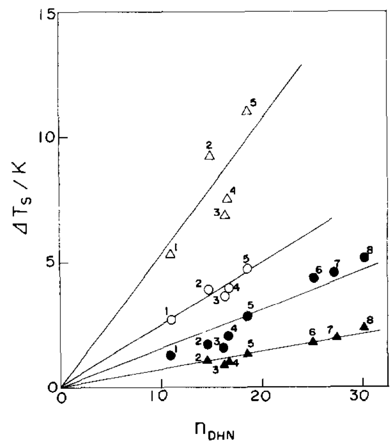


Fig. 5. Relationship between ΔT_s of the gel and the dynamic hydration number n_{DHN} of added sugars or polyols. The symbols and figures have the same meaning as in Fig. 4.

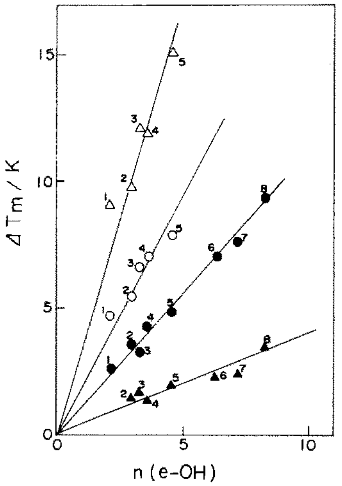


Fig. 6. Relationship between ΔT_m and the number of equatorially attached OH groups in an added sugar. The symbols and figures have the same meaning as in Fig. 4.

versible gels was proposed to be a function of the number $\mathcal{N}$ of junction zones, the bonding energy ε, the number n of segments liberated from the junction zone, and the ceiling number ν, which is the upper limit number of segments which can be liberated from the junction zone before the gel-to-sol transition occurs. The addition of polyols seems to increase the number of junction zones, which is equivalent to the number of zippers in a zipper model approach. The endothermic peak accompanying gel-to-sol transition became larger with increasing concentration of these polyols. Since the DSC peak height is mainly determined by the number of zippers

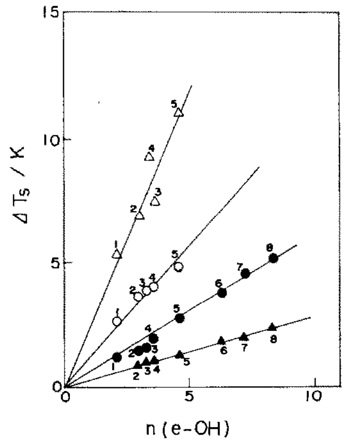


Fig. 7. Relationship between ΔT_s and the number of equatorially attached OH groups in an added sugar. The symbols and figures have the same meaning as in Fig. 4.

$\mathcal{N}$, this experimental result is explained by the increase of $\mathcal{N}$ by the addition of polyols. The shift of T_m or T_s to higher temperatures suggests that the structure of kappa-carrageenan gels has become thermally stable. This may be due mainly to the decrease of the rotational freedom of parallel links constituting a zipper by the addition of polyols.

The elastic modulus of kappa-carrageenan gels increased and T_m and T_s shifted to higher temperatures with increasing concentration of added sugars or polyols. As was discussed recently, the number of zippers $\mathcal{N}$ increases, the rotational freedom of parallel links G decreases and the number N of parallel links decreases with the addition of sucrose to agarose gels [14]. Other sugars may have a similar influence also on kappa-carrageenan gels. The rotational freedom of parallel links G in kappa-carrageenan gels will decrease with increasing n_{DHN} or n(e-OH) of added sugars; sugars with large n_{DHN} or n(e-OH) stabilize the structure of water more effectively than sugars with small n_{DHN} or n(e-OH) [15] and, as a result, the rotational motion of parallel links in a zipper is inhibited. Therefore, T_m is shifted to higher temperatures with increasing n_{DHN} or n(e-OH) of added sugars as is seen in Figs. 4 and 5 and Figs. 6 and 7.

However, the excessive addition of sugars or polyols decreases the elastic modulus of kappa-carrageenan gels [11]. The excessive sugar still decreases G, hence T_m or T_s is shifted to higher temperatures. On the other hand, the excessive sugar cannot increase $\mathcal{N}$ probably because this could reorganize the structure of the kappa-carrageenan gels; it might promote the aggregation of zippers. This explains why the endothermic peak in the

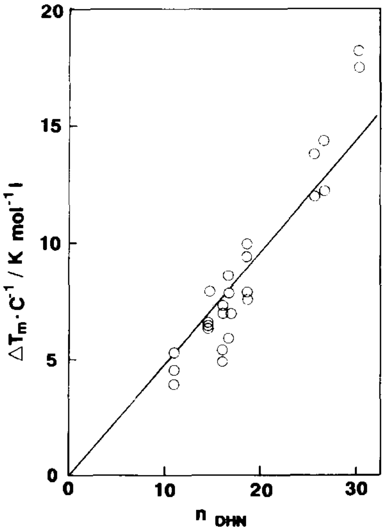


Fig. 8. $\Delta T_m / C$ as a function of n_{DHN}.

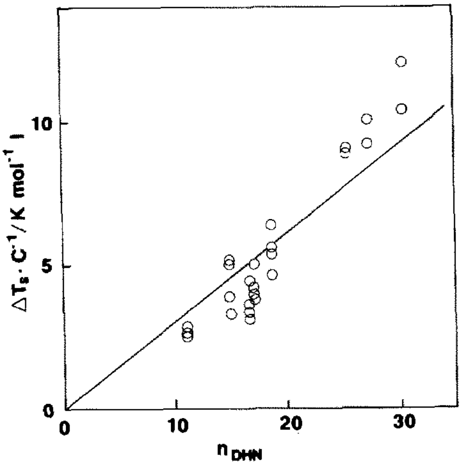


Fig. 9. $\Delta T_s/C$ as a function of n_{DHN}.

heating DSC curves for kappa-carrageenan gels became smaller with the excessive addition of sucrose.

The shifts ΔT_m and ΔT_s per unit concentration of added sugars as a function of n_{DHN} or n(e-OH) are shown in Figs. 8 and 9 and Figs. 10 and 11. These relationships seem to be linear within the experimental errors.

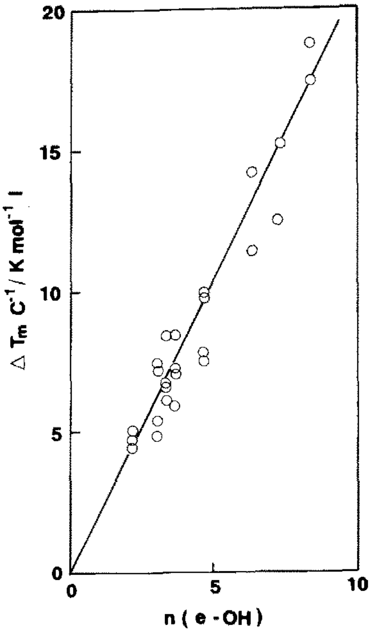


Fig. 10. $\Delta T_m/C$ as a function of n(e-OH).

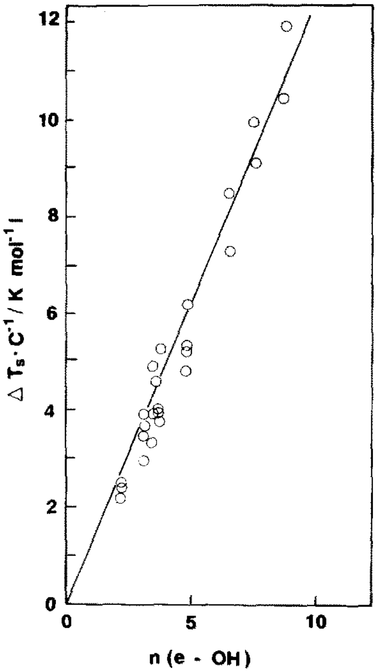


Fig. 11. $\Delta T_s / C$ as a function of n(e-OH).

It is not possible to conclude which factor is more decisive for the conformational change of kappa-carrageenan molecules; the structure of water as a solvent is changed by the addition of sugars or polyols, and this may then change the conformation of kappa-carrageenan. The other possibility is direct interaction between the hydroxyl groups of sugars or polyols and those of kappa-carrageenan molecules. Structural studies which may shed light upon this point are urgently required.

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