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# Structural Characterisation of Thermoreversible Anionic Polysaccharide Gels by Their Elastoviscous Properties

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*SUMMARY*

*Previously reported results obtained for the elastoviscous properties of some thermoreversible gels formed from anionic polysaccharides (high methoxyl pectin, furcellaran and κ-carrageenan) and also gelatin and maltodextrin are discussed and some conclusions about the structure of the gels are presented.*

*The rate at which the relaxation processes take place in the gel is independent of the polymer concentration suggesting that the gels are structurally inhomogeneous.*

*If the helical conformation of the individual macromolecule is stable the standard enthalpy change on crosslink breakdown is less than 45 kJ mol$^{-1}$. A relatively small decrease in standard enthalpy is sufficient for network stability because of the low standard entropy loss on gelation which is typical of semi-rigid chain polymers. If, however, the helical conformation is unstable the gelation process is cooperative and the standard enthalpy change on crosslink breakdown exceeds 200 kJ mol$^{-1}$.*

## INTRODUCTION

In this paper the recent work carried out in our laboratories on the elastoviscous properties of polysaccharide gels is summarised. A range of thermodynamic parameters are derived from the rheological measurements. From these results some general views on the structure of these gels are presented.

## METHODS

### Polysaccharides

Five polysaccharide solvent systems have been studied.

1. High methoxyl pectin (conc. 0·5–2·5% w/w)–70% w/w sucrose, pH 3·0 (Plashchina *et al.*, 1979).
2. Calcium furcellaran (conc. 0·5–2·0% w/w)–70% w/w sucrose (Plashchina *et al.*, 1980*a*).
3. κ-Carrageenan (conc. 1·0–2·5% w/w), 0·11 M KCl (Plashchina *et al.*, 1980*b*).
4. High methoxyl pectin (conc. 2·0–5·0% w/w)–glycerol (50% w/w), pH 2·7.
5. κ-Furcellaran (conc. 1·5–3·0% w/w)–0·15 M KCl.

As indicated, data for systems 1–3 have been published whereas the results obtained for the systems 4 and 5 will be published in more detail in the near future.

### Creep measurement

The measurements of the uniaxial compression strain (Slonimsky *et al.*, 1969; Braudo *et al.*, 1974*a*) for the system pectin–glycerol and of the simple shear strain (Braudo *et al.*, 1974*a*,*b*) for the other systems under the action of constant stress were performed. The Young's modulus $E$ was converted to the shear modulus $G$ by the equation $E = 3G$ (Ferry, 1970).

The maximum strain did not exceed 10%. It was demonstrated experimentally that all measurements were in the linear viscoelastic region, i.e. compliance was independent of applied stress.

## RESULTS

### Analysis of creep compliance response

Initially the creep compliance response was separated into an irreversible viscous flow component and a reversible component. The conventional way of doing this is to obtain the Newtonian viscosity from the

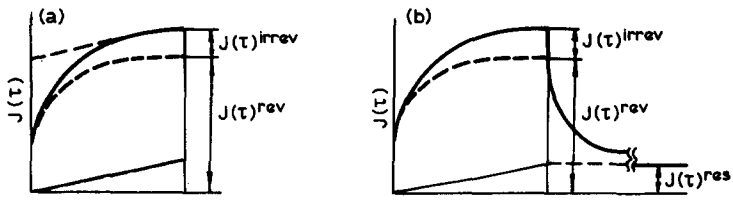


**Fig. 1.** Separation of the reversible and irreversible compliance components of the creep compliance (see Results section for explanation of (a) and (b)).

terminal slope of the creep curve at long times (see Fig. 1(a)). In view of the mechanisms with long retardation times that are present in these systems we consider that this underestimates the viscosity.

The approach we have employed has been previously described by Kargin & Sogolova (1949), and is illustrated in Fig. 1(b). The largest Newtonian viscosity was obtained from the expression

$$\eta_N = \tau_{max}/J^{res}$$

where $\tau_{max}$ is the longest loading time employed, $J^{res}$, the equilibrium compliance obtained after creep recovery. In order to obtain equilibrium during creep recovery the samples were subjected to prolonged annealing. The linear dependence of the irreversible deformation on loading time was checked experimentally. The reversible compliance was obtained by subtracting the viscous flow term from the total compliance.

Typical values for $\eta_N$ obtained for these systems were in the range $10^8$–$10^9$ Pa s. This compares with values of about $3 \times 10^7$ Pa s obtained from the terminal slope of the creep curve for similar types of polysaccharide gels (Mitchell, 1980).

## Concentration and temperature dependence of rheological parameters

### *Concentration dependence*

For all five systems the dependence of $\eta_N$ on concentration can be described by the equation $\eta_N \propto c^r$ (Fig. 2) where $r = 3{\cdot}3 \pm 0{\cdot}1$. This exponent is the same as that observed for concentrated polymer solutions (Vinogradov & Malkin, 1977) and more recently for polysaccharide solutions above the concentration threshold at which entanglement coupling commences (Morris *et al.*, 1981).

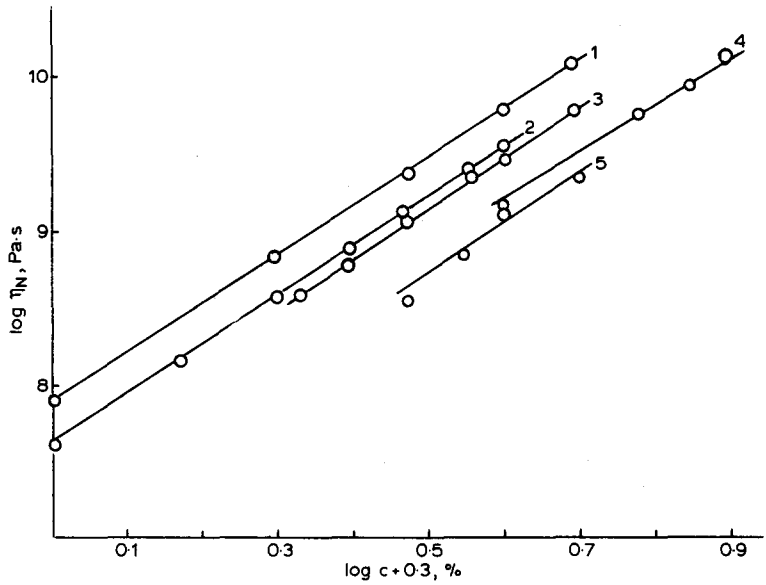


**Fig. 2.** Dependence of the largest Newtonian viscosity on the polysaccharide concentration in the gel ($T = 298{\cdot}2$ K). (1) Pectin gels in a water-sucrose mixture (70% w/w); (2) furcellaran Ca-salt gels in a water-sucrose mixture (70% w/w); (3) κ-carrageenan gels in 0·11 M KCl; (4) pectin gels in a water-glycerol mixture (50% w/w); (5) κ-furcellaran gels in 0·15 M KCl.

For the reversible component of the creep compliance it was possible to construct concentration invariant master curves by plotting $\log(J^{rev}(\tau)\, b_c)$ against $\log \tau$ where $b_c$ is a shift factor which is a function of concentration (Fig. 3). In other words, in all cases the superposition of the experimental curves can be effected by a shift along the compliance axis only. The absence of any shift along the time axis implies that the rate of the relaxation process is independent of polymer concentration.

The dependence of the shear modulus $G$ and also of the shift factor $b_c$ on concentration at any particular time can be expressed by the equation $G \propto c^n$ or $b_c \propto c^n$ (Fig. 4). Values obtained for $n$ for the five systems are shown in Table 1. If the view is taken that the network crosslinks of the thermoreversible gels are formed by the binary association of macromolecules (Eldridge & Ferry, 1954) or of their associates (Haas *et al.*, 1970), then $n$ should approach 2 from greater values as

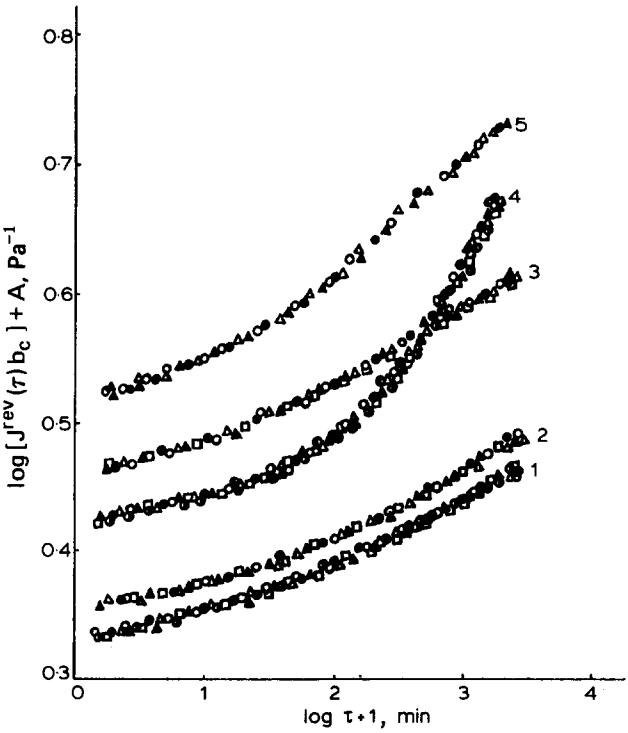


**Fig. 3.** Concentration-invariant curves for the reversible gel strain relaxation. $T = 298{\cdot}2$ K. (1) Pectin in a water-glycerol mixture (50% w/w). $A = 5$; $c_0 = 3{\cdot}0\%$. ●, 2·0%; ○, 3·0%; △, 3·5%; ▲, 3·9%; ◑, 4·4%; □, 5·0%. (2) κ-Carrageenan in 0·11 M KCl. $A = 5$; $c_0 = 1{\cdot}5\%$. ○, 1·25%; ●, 1·5%; ▲, 1·8%; △, 2·0%; □, 2·5%. (3) Pectin in a water-sucrose mixture (70% w/w). $A = 4{\cdot}5$; $c_0 = 1{\cdot}5\%$. △, 0·5%; ▲, 1·0%; ○, 1·5%; ●, 2·0%; □, 2·5%. (4) Furcellaran Ca-salt in a water-sucrose mixture (70% w/w). $A = 4{\cdot}5$; $c_0 = 1{\cdot}25\%$. ●, 0·5%; ○, 0·75%; △, 1·0%; ▲, 1·25%; ◑, 1·5%; ◐, 1·75%; □, 2·0%. (5) κ-Furcellaran in 0·15 M KCl. $A = 4{\cdot}6$; $c_0 = 2{\cdot}0\%$. ○, 1·5%; ●, 1·75%; △, 2·0%; ▲, 2·5%.

$\alpha/\alpha_0 \to \infty$ (where $\alpha$ and $\alpha_0$ are the degree of reaction completion at the measurement temperature and gel point respectively (Hermans, 1965)). If the rate of mechanical relaxation is independent of concentration this should hold for both the equilibrium and non-equilibrium moduli. Thus for thermoreversible gels it would be expected that $n = 2$ at temperatures far below the fusion temperature $T_f$, which corresponds to the gel point. Our data would support this since for pectin gels at

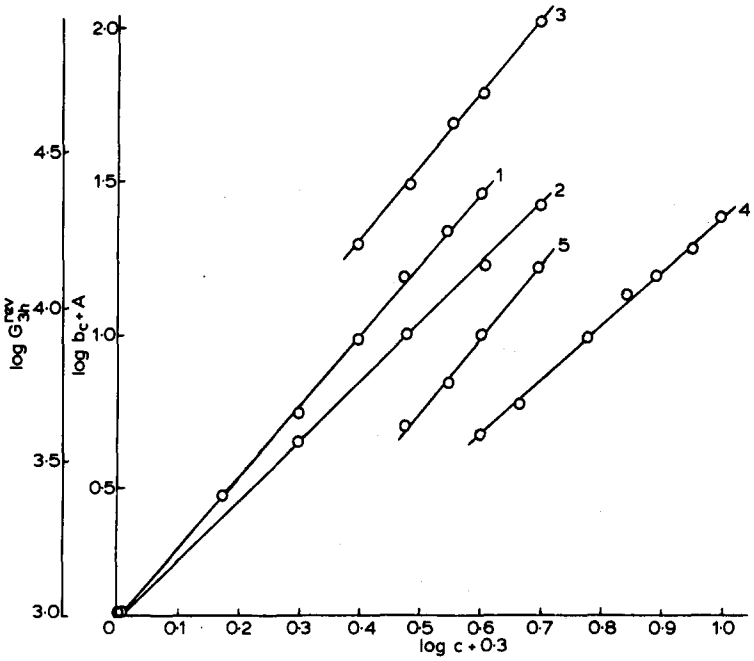


**Fig. 4.** Dependence of the gel shear modulus after a loading time of 3 h and the reduction parameter $b_c$ on polysaccharide concentration. $T = 298{\cdot}2$ K. (1) Pectin gels in a water-glycerol mixture (50% w/w), $A = 1$; (2) κ-carrageenan gels in 0·11 M KCl, $A = 1{\cdot}5$; (3) pectin gels in a water-sucrose mixture (70% w/w), $A = 1$; (4) furcellaran Ca-salt gels in a water-sucrose mixture (70% w/w), $A = 1$; (5) κ-furcellaran gels in 0·15 M KCl, $A = 1$.

298·2 K where $T_f - T \geqslant 63$ K, $n = 2$ within experimental error whereas for κ-furcellaren and κ-carrageenan gels where $T_f - T = 48 \pm 1$ K, $n > 2$.

*Temperature dependence*

The temperature dependence of $\eta_N$ can be described by the De-Guzmán-Arrhenius relationship (Figs 5 and 6)

$$\eta_N \propto \exp(-E_\eta^G/RT)$$

where $E_\eta^G$ is the activation energy for viscous flow (Table 1). For pectin-sucrose gels $E_\eta^G$ increases with polysaccharide concentration.

Over the time scale of the experiment the shear moduli of the gels lie in the range $10^3$–$10^5$ Pa and show a decrease with increasing

**TABLE 1**
Rheological Characteristics of Anionic Polysaccharide Gels

| *Gel composition* | | | *Activation energy of viscous flow, kJ mol$^{-1}$* | | $r = \frac{\partial(\lg \eta_N)}{\partial(\lg c)}$ | $n = \frac{\partial(\lg G)}{\partial(\lg c)}$ |
|---|---|---|---|---|---|---|
| *polymer* | *solvent* | *polymer conc. %, w/w* | *gel* ($E_\eta^G$) | *solvent* ($E_\eta^S$) | (298·2 K) | (298·2 K) |
| Pectin | Sucrose (70% w/w)–water (pH 3·0) | 0·5 | 51 ± 5 | 44 | 3·3 ± 0·1 | 1·9 ± 0·1 |
| | | 1·0 | 63 ± 5 | | | |
| | | 1·5 | 67 ± 3 | | | |
| | | 2·0 | 72 ± 3 | | | |
| | | 2·5 | 74 ± 3 | | | |
| Pectin | Glycerol (50% w/w)–water (pH 2·7) | 2·0 | 64 ± 2 | 25 | 3·3 ± 0·1 | 1·8 ± 0·1 |
| Ca-salt of furcellaran | Sucrose (70% w/w)–water (pH 7·6) | 1·25 | 63 ± 5 | 44 | 3·3 ± 0·1 | 2·3 ± 0·1 |
| κ-Furcellaran | Water–0·15 M KCl (pH 7·6) | 2·0 | 57 ± 0·1 | 15 | 3·4 ± 0·1 | 2·4 ± 0·1 |
| κ-Carrageenan | Water–0·11 M KCl (pH 7·6) | 1·5 | 51 ± 2 (< 314·2 K)<br>250 ± 2 (⩾ 314·2 K) | 15 | 3·3 ± 0·1 | 2·4 ± 0·1 |

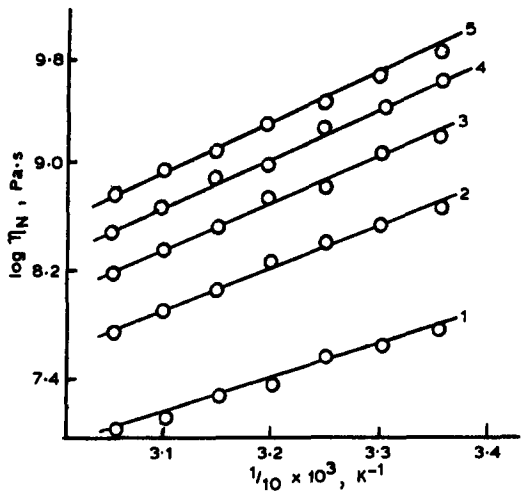


**Fig. 5.** Temperature dependence of the largest Newtonian viscosity for pectin gels in a water-sucrose mixture (70% w/w). 1, 0·5%; 2, 1·0%; 3, 1·5%; 4, 2·0%; 5, 2·5%.

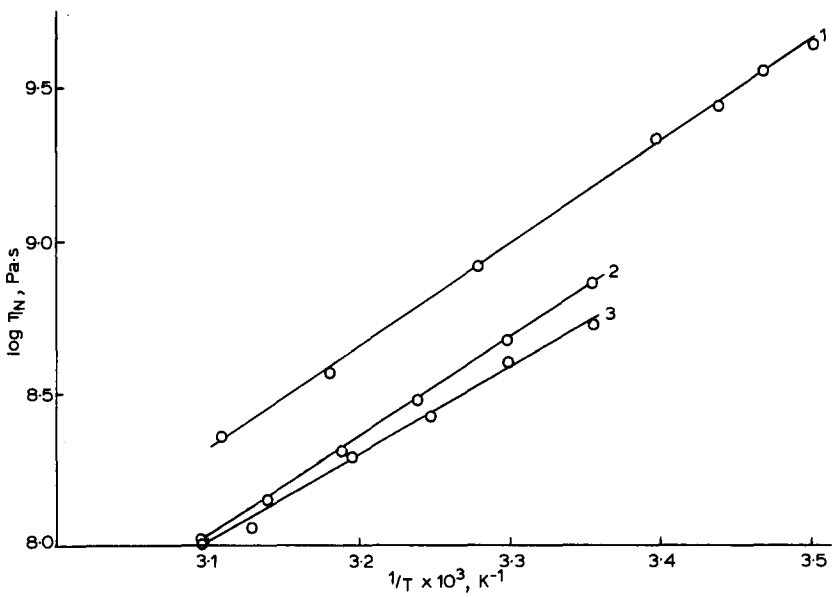


**Fig. 6.** Temperature dependence of the largest Newtonian viscosity for (1) 2·0% pectin gel in a water-glycerol mixture (50% w/w), (2) 1·25% gel of furcellaran Ca-salt in a water-sucrose mixture (70% w/w) and (3) 2·0% κ-furcellaran gel in 0·15 M KCl.

temperature. This type of temperature dependence is characteristic of thermoreversible gels at temperatures which are not far removed from the fusion temperature of the gel ($T_f$) (Hirai, 1955). As a rule the rate of the modulus drop decreases on approaching $T_f$. For the pectin–sucrose gels there is a linear decrease in the shear modulus with temperature in the interval 298·2–328·2 K, the slope increasing with concentration.

For the reversible component of the creep compliance the temperature invariant master curves can be constructed by plotting $\log(J^{rev}(\tau)(T/T_0)b_T)$ against $\log(\tau/a_T)$ where $J^{rev}(\tau)$ is the reversible component of the compliance, $T_0$ is the reduction temperature and $\tau$ is the loading time (Figs 7 and 8). The shift factor $a_T$ characterises the temperature dependence of the gel relaxation processes and $((T/T_0)b_T)$ is a measure of the variation of the equilibrium compliance with temperature. Where the equilibrium compliance is of a purely entropic nature, $b_T$ is a measure of the change in the number of gel crosslinks with temperature.

The temperature dependence of the shift factors obeys the following relationships (see Fig. 9):

$$a_T \propto \exp(-E_{a_T}/RT)$$

$$b_T \propto \exp(-\Delta H_{b_T}/RT)$$

Values for the activation energy of mechanical relaxation ($E_{a_T}$) and the standard breakdown enthalpy of the gel network crosslinks ($\Delta H_{b_T}$) (Schultz & Myers, 1969) are listed in Table 2.

An unusual temperature dependence was observed for the Ca-furcellaran gel (conc. 1·25%). For this system $a_T = 1$ over the entire temperature range studied. That is to say the rate of the relaxation processes in the gel was temperature independent.

The shape of the master curves obtained using time–temperature superposition are generally typical of the initial region of the transition zone. Similar behaviour has been observed for other thermoreversible gels (Miller *et al.*, 1951; Arakawa, 1958, 1959, 1960, 1961, 1962; Arakawa & Takenaka, 1962; Watase & Arakawa, 1967, 1969; Braudo *et al.*, 1974*b*, 1979; Mitchell & Blanshard, 1976; Kawabata & Sawayama, 1976; Sawayama *et al.*, 1978). For the κ-carrageenan and κ-furcellaran gels however the shape of the master curves corresponds to the terminal region of the transition zone. In no case did the reversible compliance reach an equilibrium value, confirming that the use of the terminal

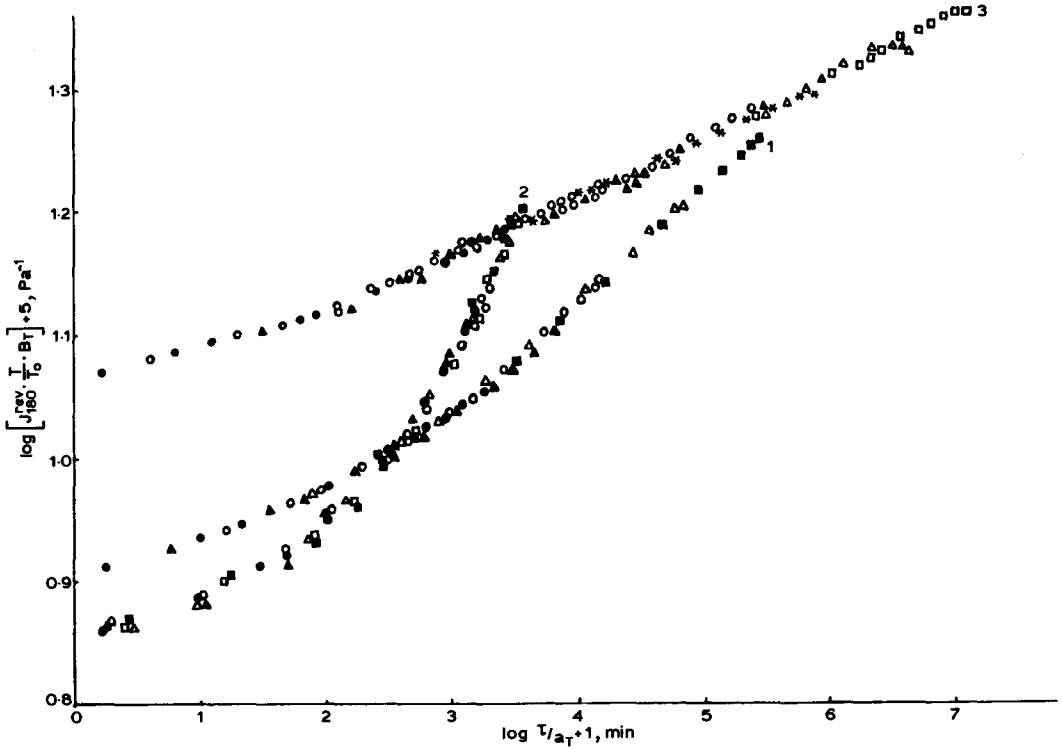


**Fig. 7.** Temperature-invariant curves for the reversible strain relaxation. (1) 2·0% Pectin gel in a water-glycerol mixture (50% w/w); $T_0 = 284{\cdot}7$ K; ●, 284·7 K; ○, 288·2 K; ▲, 290·7 K; ◑, 294·2 K; ★, 305·2 K; △, 314·2 K; □, 321·7 K. (2) 1·5% Pectin gel in a water-sucrose mixture (70% w/w); $T_0 = 298{\cdot}2$ K; ●, 298·2 K; ▲, 303·2 K; ○, 308·2 K; △, 313·2 K; ■, 323·2 K. (3) 1·25% gel of furcellaran Ca-salt in a water-sucrose mixture (70% w/w). $T_0 = 298{\cdot}2$ K; ●, 298·2 K; ○, 303·2 K; ▲, 308·2 K; △, 313·2 K; □, 318·2 K; ■, 323·2 K.

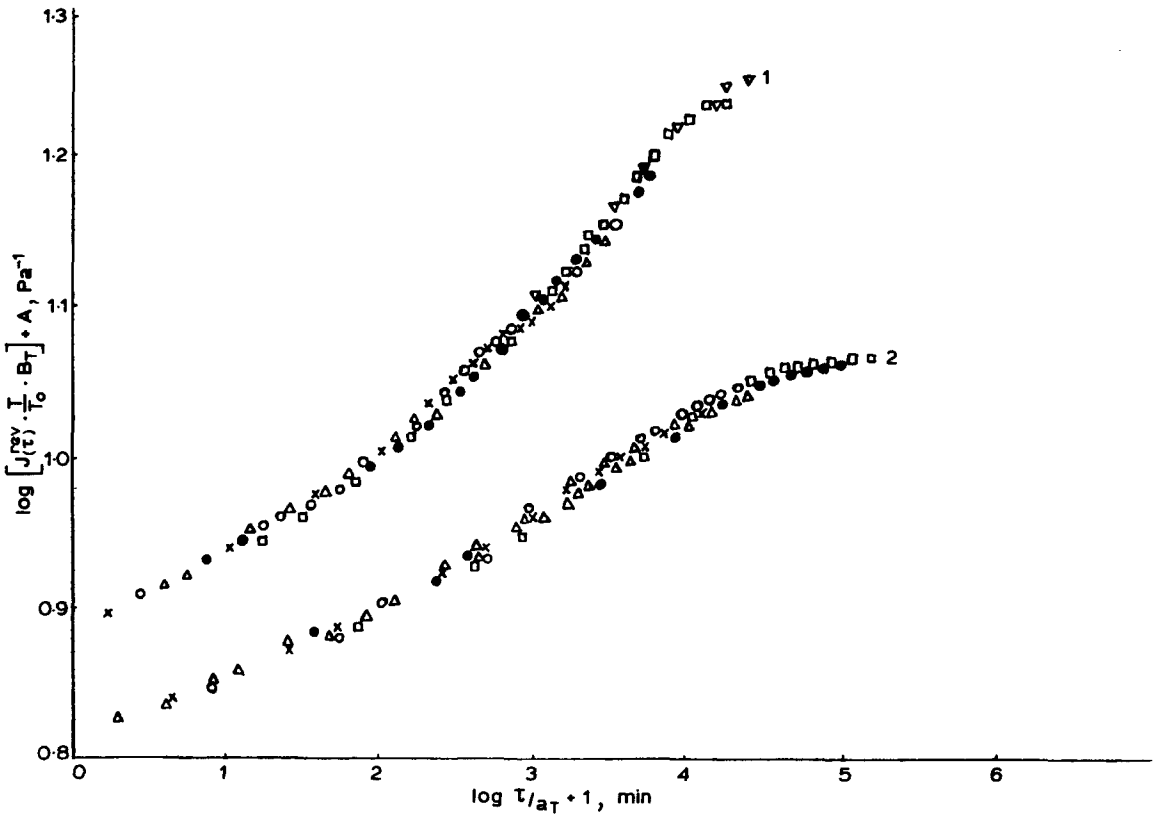


**Fig. 8.** Temperature-invariant curves for the reversible strain relaxation. $T_0 = 293{\cdot}2$ K. (1) 2·0% κ-Furcellaran gel in 0·15 M KCl. $A = 5$. x, 293·2 K; ○, 298·2 K; △, 303·2 K; ●, 308·2 K; □, 313·2 K; ▽, 316·2 K. (2) 1·5% κ-carrageenan gel in 0·11 M KCl. △, 282·2 K; x, 287·9 K; ○, 293·2 K; ▲, 297·7 K; ●, 303·7 K; □, 313·7 K.

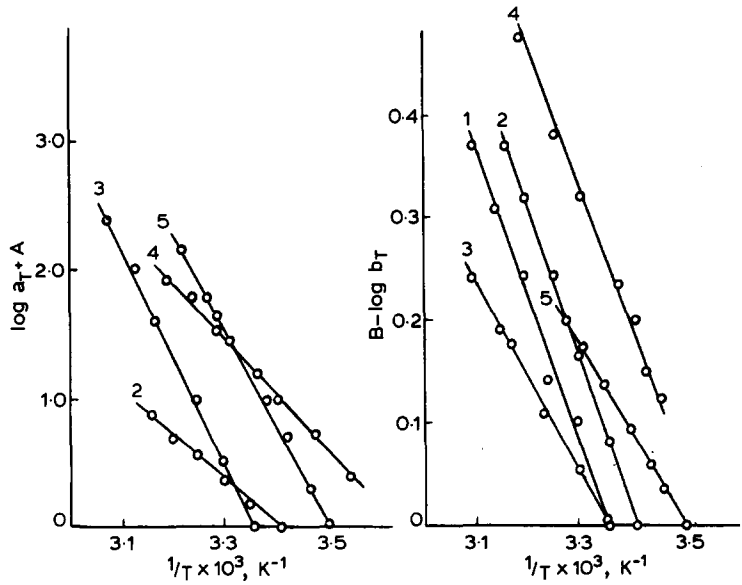


**Fig. 9.** Temperature dependence of reduction parameters $a_T$ and $b_T$. (1) 2·0% gel of pectin in a water-glycerol mixture (50% w/w); (2) 1·5% gel of pectin in a water-sucrose mixture (70% w/w); (3) 1·25% gel of furcellaran Ca-salt in a water-sucrose mixture (70% w/w); (4) 2·0% gel of κ-furcellaran in 0·15 M KCl; (5) 1·5% gel of κ-carrageenan in 0·11 M KCl. $A = 1$; $B = 0·2$.

slope of the creep curve to obtain $\eta_N$ is not possible. The inapplicability of the rubber elasticity theory to polysaccharide gels on account of the high rigidity of the network chains has also been discussed by Mitchell (1980).

*Structural inhomogeneity of gels*

The independence of the rate of the relaxation processes on concentration suggests that the gels are structurally inhomogeneous (but not necessarily heterophasic), the gel networks being composed of associations. An increase in the overall polymer concentration would increase the number of associations of macromolecules but the polymer concentration inside these associations would remain unchanged. The local viscosity inside the associations would not change with overall concentration and hence the relaxation rates would also be concentration-independent. A similar interpretation has been suggested for soy bean globulin gels (Bikbov *et al.*, 1981).

**TABLE 2**
Some Thermorheological Parameters of Thermoreversible Gels

| *Gel composition* | | | *Activation energy of mechanical relaxation* ($E_{a_T}$), *kJ mol*$^{-1}$ | *Standard breakdown enthalpy of the network crosslinks, kJ mol*$^{-1}$ | | |
|---|---|---|---|---|---|---|
| *polymer* | *solvent* | *polymer conc., %* | | $\Delta H_f$ | $\Delta H_{b_T}$ | $\Delta H_1^{\ddagger}$ |
| Pectin | Sucrose (70%, w/w)-water (pH 3·0) | 0·5 | – | – | – | 7 ± 1 |
| | | 1·0 | – | – | – | 19 ± 1 |
| | | 1·5 | 155 ± 6 | – | 15 ± 1 | 24 ± 1 |
| | | 2·0 | 160 ± 6 | – | 20 ± 1 | 28 ± 1 |
| | | 2·5 | 160 ± 5 | | 26 ± 1 | 30 ± 1 |
| Pectin | Glycerol (50%, w/w)-water (pH 2·7) | 2·0 | 144 ± 5 | 126 ± 4 | 17 ± 1 | 39 ± 2 |
| Ca-salt of furcellaran | Sucrose (70%, w/w)-water (pH 7·6) | 2·0 | – | 121 ± 3 | 19 ± 2 | 19 ± 2 |
| κ-Furcellaran | Water-0·15 M KCl (pH 7·6) | 2·0 | 88 ± 2 | 54 ± 0·5 | 40 ± 5 | 42 ± 1 |
| κ-Carrageenan | Water-0·11 M KCl (pH 7·6) | 1·5 | 87 ± 2 (< 314·2 K) | 38 ± 0·5 | 27 ± 4 (< 314·2 K) | 36 ± 2 (< 314·2 K)<br>235 ± 2 (⩾ 314·2 K) |
| Gelatin | Water (pH 4·7) | 5·0 | – | 426 ± 0·3 | – | 295 ± 13 |
| Maltodextrin | Water (pH 7·0) | 20·0 | – | 27 ± 1 | – | 25 ± 2 |

Other intensive properties would also be expected to be independent of the overall concentration, and it has been shown that the relative activity of counter-ions is independent of concentration for alginate, pectin and κ-carrageenan above a minimum concentration of 0·04–1·4% (Yuryev *et al.*, 1981). We would suggest that this structural inhomogeneity is a common feature of polysaccharides as semi-rigid chain polymers having a low affinity for the solvent (Whistler, 1973).

The inhomogeneous structure of the κ-carrageenan gels is consistent with the domain model proposed by Morris *et al.* (1980*a*, *b*) and was taken as the basis for calculating the entropy change on crosslink breakdown (see below).

*Thermodynamic parameters associated with crosslink breakdown*

The standard breakdown enthalpy of network crosslinks can be obtained by two methods.

(i) The concentration dependence of the gel melting temperature ($T_f$) (Fig. 10) using the equation employed by Ferry & Eldridge (1954)

$$\Delta H_f = -R\,\delta(\ln c)/\delta(T_f^{-1})$$

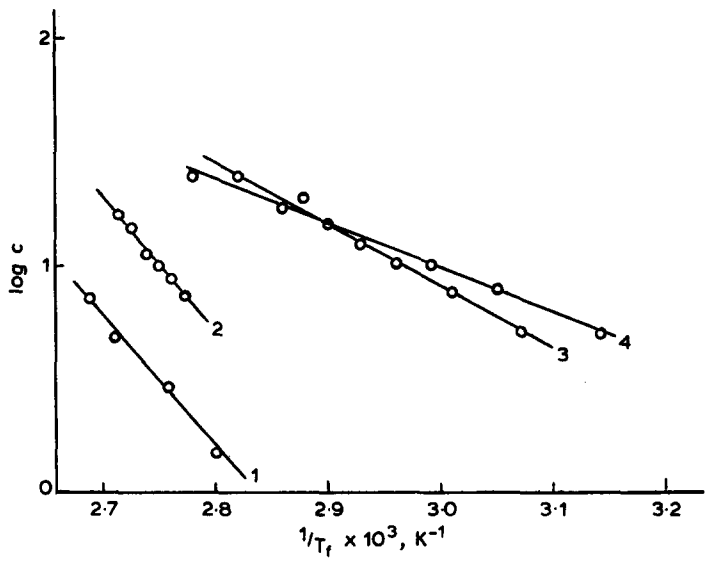


**Fig. 10.** Dependence of the gel fusion temperature on polysaccharide concentration. (1) Furcellaran Ca-salt gels in a water–sucrose mixture (70% w/w); (2) pectin gels in a water–glycerol mixture (50% w/w); (3) κ-furcellaran gels in 0·15 M KCl; (4) κ-carrageenan gels in 0·11 M KCl.

Values of $\Delta H_f$ obtained using this equation are shown in Table 2. The gel fusion temperature was obtained by the method described elsewhere (Braudo *et al.*, 1973, 1974*c*). $\Delta H_f$ obtained in this way characterises the enthalpy of the strongest network crosslinks averaged over the concentration range; i.e. the crosslinks that remain stable until the fusion temperature is reached.

(ii) The temperature dependence of the viscoelastic behaviour of the gel. As previously described the parameter $\Delta H_{b_T}$ can be obtained from the temperature dependence of the shift factor $b_T$. The apparent viscous flow activation energy $E_\eta^G$ has also been identified with the enthalpy of the gel network crosslinks (Rogovina *et al.*, 1971).

Using the theory of rate processes (Glasstone *et al.*, 1941)

$$E_\eta^G = \Delta H^\ddagger + RT$$

where $\Delta H^\ddagger$, the activation enthalpy of viscous flow, can be regarded as the sum of three terms

$$\Delta H^\ddagger = \Delta H_1^\ddagger + \Delta H_2^\ddagger + \Delta H_3^\ddagger$$

$\Delta H_1^\ddagger$ is the enthalpy required to break the linkages between the displaced segment and its neighbours when the former passes to the activated state. $\Delta H_1^\ddagger$ is assumed to be equal to the standard enthalpy of the gel network crosslinks. $\Delta H_2^\ddagger$ is the enthalpy of the processes associated with the changing state of the medium surrounding the displaced segment. $\Delta H_3^\ddagger$ is the enthalpy of the processes relating to the segment displacement. $\Delta H_3^\ddagger$ for the liquids studied is as small as $2\,\mathrm{kJ\,mol^{-1}}$ (Glasstone *et al.*, 1941) and hence was ignored.

$\Delta H_2^\ddagger$ will include the contribution from the polymer–solvent interaction (Frenkel, 1945). It has been shown (Brown & Chitumbo, 1975) that in a tightly crosslinked cellulose gel, this interaction enhances the apparent activation energy of water self-diffusion by $11{\cdot}5\,\mathrm{kJ\,mol^{-1}}$, i.e. by 56%. For the gels considered in this paper this interaction is unknown and has therefore been ignored. Thus:

$$\Delta H_2^\ddagger = E_\eta^S - RT$$

where $E_\eta^S$ is the activation energy of the viscous flow of solvent. Hence:

$$\Delta H_1^\ddagger = E_\eta^G - E_\eta^S$$

Table 2 compares the values of $\Delta H_1^\ddagger$, $\Delta H_{b_T}$ and $\Delta H_f$ for the gels discussed in this paper. Also included in Table 2 are results for malto-

dextrin and gelatin gels taken from previously reported work (Braudo *et al.*, 1974*a*,*c*; 1979). From Table 2 it can be seen that $\Delta H_{b_T}$ and $\Delta H_1^{\ddagger}$ are of the same order of magnitude, though generally $\Delta H_{b_T} < \Delta H_1^{\ddagger}$. It is possible that $\Delta H_1^{\ddagger}$ is too high because the polymer–solvent interaction has been ignored in evaluating $\Delta H_2^{\ddagger}$. As distinct from $\Delta H_f$, the enthalpies $\Delta H_{b_T}$ and $\Delta H_1^{\ddagger}$ characterise gels of a certain concentration and relate to the temperature interval for which the elastoviscous properties were measured. The ratio $\Delta H_f/\Delta H_1^{\ddagger}$ (or $\Delta H_{b_T}$) can be regarded as a measure of the variation in the crosslink strength within the gel. The limited amount of data shown in Table 2 suggests that this variation is greatest when a low water activity is necessary for gel formation.

*Co-operative and non-cooperative mechanisms for gel formation*

It is apparent from Table 2 that the gels can be divided into groups depending upon the value of $\Delta H_1^{\ddagger}$. For gelatin and for κ-carrageenan gels at $T \geqslant 314{\cdot}2$ K, $\Delta H_1^{\ddagger}$ is 200–300 kJ mol$^{-1}$ whereas for the other gels $\Delta H_1^{\ddagger}$ is an order of magnitude lower. We consider that gels of the former type are formed by a cooperative mechanism. In these cases the isolated macromolecules exist in an essentially random coil conformation. On helix formation, gel network crosslinks or junction zones are formed. This results in a large entropy decrease for which there must be a concomitant large enthalpy decrease. The non-cooperative gelation behaviour shown by pectin, furcellaran and maltodextrin is characteristic of semi-rigid chain polymers. The entropy decrease on crosslink formation is small so that only a small enthalpy decrease is required for the process to be thermodynamically favourable.

The 1·5% κ-carrageenan gel is of interest because at temperatures below 314·2 K the gelation mechanism is non-cooperative whereas at temperatures above 314·2 K it gels by a cooperative mechanism. This is because below this temperature κ-carrageenan exists in a stable helical form and thus behaves as a semi-rigid chain polymer whereas above this temperature the helix–coil conformational transition occurs (Fig. 11) and the helical form is only stable when it is a constituent of the junction zone.

Note that the temperature for complete helix-unwinding of κ-carrageenan lies below the fusion temperature of the gel (Fig. 11). Therefore the coincidence of $\Delta H_f$ and of $\Delta H_1^{\ddagger}$ in the low-temperature region is accidental.

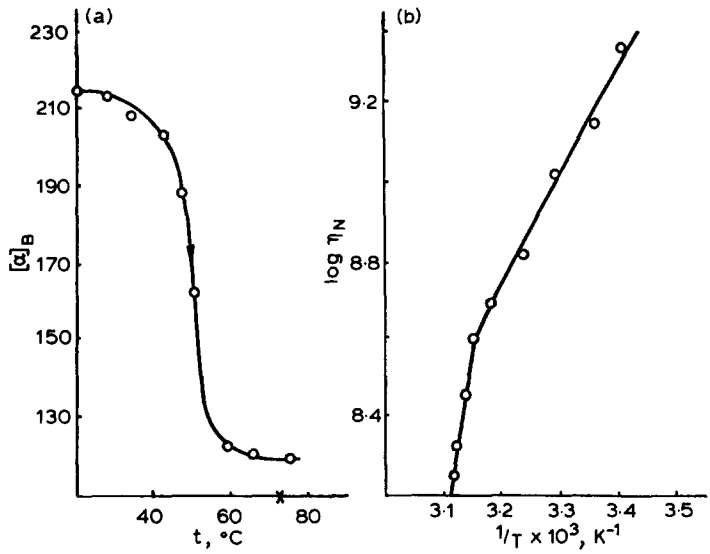


**Fig. 11.** Temperature dependences of some properties of the 1·5% gel of κ-carrageenan in 0·11 M KCl. (a) Specific optical rotation at 436 nm; (b) the largest Newtonian viscosity. x, Gel fusion temperature (344·7 K).

**TABLE 3**
Some Network Characteristics of a 1·5% Gel of κ-Carrageenan

| *Temperature, K* | *Thermodynamic parameters of the breakdown process of the network crosslinks* | | | | *Number of disaccharide residues in the chain,* $\bar{l}_N$ |
|---|---|---|---|---|---|
| | $\Delta S^\circ$, *J (mol K)*$^{-1}$ | | $-\Delta G^\circ$, *kJ mol*$^{-1}$ | | |
| | $P = 1$ | $P = 5$ | $P = 1$ | $P = 5$ | |
| 283·2 | 170 | 120 | 12 | −2 | 4·3 |
| 298·2 | 175 | 135 | 16 | 4 | 9·2 |
| 314·2 | 810 | 775 | 18 | 9 | 19·2 |

The change in the cooperativity of the gelation process with increasing temperature for κ-carrageenan is confirmed by the values for the standard breakdown entropy of the network crosslinks shown in Table 3. Details of the calculation are given in the Appendix (see eqns (7) and

(16)). In contrast to the standard entropy, the change in standard Gibbs free energy of the network crosslinks varies little with temperature. Also shown in Table 3 is the number-average of the disaccharide residues in the network chain of the κ-carrageenan on gelation, calculated from the equation:

$$\bar{l}_N = c/2\nu$$

where $\nu$ is the concentration of the crosslinks (calculated according to eqn (16) given in the Appendix). It can be seen from Table 3 that in the κ-carrageenan gel the minimum value of $\bar{l}_N$ is 4·3 disaccharide residues. Hence it follows that the value $P = 5$ (see Appendix) used in the calculation of the standard entropy change on crosslink breakdown is close to the maximum admissible one on geometric considerations.

Assuming a strict cooperativity for the helix–coil transition of κ-carrageenan, the standard enthalpy and entropy changes per mg-equiv. of disaccharide residues associated with this transition (calculated according to eqns (12), (17) and (18) given in the Appendix) were obtained:

$$\Delta\bar{h}^{\circ}_{h-c} = 5{\cdot}2 \text{ kJ mol}^{-1}$$

$$\Delta\bar{s}^{\circ}_{h-c} = 16{\cdot}5 \text{ kJ (mol K)}^{-1}$$

These quantities include breakdown parameters for one hydrogen bond stabilising the double helix of κ-carrageenan (Rees, 1969) and also a contribution from the interaction between the helices within the association representing a structural element of the gel network.

## On the nature of the relaxation processes in gels

We believe that the slow-rate relaxation processes observed in creep experiments occur chiefly in macromolecule associations forming the gel network rather than in the crosslinks. If the latter is the case then $E^G_\eta \approx E_{a_T}$ (Bartenev, 1977, 1979) which does not hold for the gels under study.

The very long retardation times observed in the gels may be explained by the high local viscosity existing within the associations. However, the nature of the temperature dependence of the relaxation processes allows one to conclude that the polymer concentration in the associations is substantially below that at which they undergo glass transition at the temperature of the experiment. Otherwise the rate of these

processes would be limited by the free volume in the associations, and the temperature dependence of the parameter $a_T$ would be described by the Williams–Landel–Ferry equation rather than the Arrhenius equation (Vinogradov & Malkin, 1977). In practice, however, the former equation is not applicable to the systems under study.

The values of $E_{a_T}$ (90–160 kJ mol$^{-1}$) suggest that the elementary relaxation processes are cooperative in character involving the rupture of several non-covalent bonds.

## CONCLUSIONS

1. The rate of the relaxation processes in gels under study is independent of polymer concentration. This suggests that the gels are structurally inhomogeneous, the gel network being formed by the associations of macromolecules.

2. When crosslink breakdown does not involve the unwinding of individual helices (non-cooperative mechanism of gelation) the standard breakdown enthalpy of the crosslinks does not exceed 45 kJ mol$^{-1}$. The reason why this small enthalpy decrease is sufficient to stabilise the network is probably due to the low entropy decrease on gelation which is typical of semi-rigid chain polymers. When the gelation mechanism is cooperative the large decrease in entropy during gelation is compensated by a decrease in enthalpy exceeding 200 kJ mol$^{-1}$ due to the formation of hydrogen bonds stabilising the helical conformation.

3. The slow relaxation processes seen in the creep compliance response are likely to be associated with the breaking of several intermolecular bonds within the macromolecular associations which form the gel network.

4. The reasonable agreement between the values of standard breakdown enthalpy of the crosslinks obtained by two independent methods ($\Delta H_1^{\ddagger}$ and $\Delta H_{b_T}$) and also the consistency of the values of $\Delta H_1^{\ddagger}$, with what is known about the stability of the helical conformation of the macromolecules, give support to the following considerations regarding the mechanisms of the gel flow process in the region to which the largest Newtonian viscosity is applicable.

The elementary act of the flow involves the breakdown of the network crosslink and its re-establishment in a new equilibrium state (Miller *et al.*, 1951). Under conditions where the helical conformation is unstable, in the absence of intermolecular linkages (cooperative

mechanism of gelation) the viscous flow process involves a cooperative breakdown of the bonds stabilising the helical conformation as the displaced segment passes to the activated state with a subsequent re-establishment of these bonds as the segment passes to a new equilibrium state. (Such fluctuations in structure were found in polynucleotides using the hydrogen-deuterium exchange method (Nakanishi *et al.*, 1980).)

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## APPENDIX: CALCULATION OF THE CROSSLINK CONCENTRATION AND STANDARD BREAKDOWN ENTROPY OF THE THERMOREVERSIBLE GEL NETWORK CROSSLINKS

### Nomenclature and values for 1·5% gel of κ-carrageenan in 0·11 M KCl

$\Delta H^\circ$ = standard breakdown enthalpy of the network crosslinks at the temperature $T$;
$T_0$ = temperature of the initial breakdown of the gel network crosslinks ($T_0 = 283{\cdot}2$ K (see Plaschina *et al.*, 1980*b* in earlier ref. list));
$T_{h\text{-}c}$ = temperature of the helix–coil transition ($T_{h\text{-}c} = 314{\cdot}2$ K);
$\Delta H_1^\circ$ = standard breakdown enthalpy of the gel network crosslinks at $T < T_{h\text{-}c}$ ($\Delta H_1^\circ = (\Delta H_1^\ddagger)_{T<314{\cdot}2\,K} = 36$ kJ mol$^{-1}$);
$\Delta H_2^\circ$ = the same, at $T \geqslant T_{h\text{-}c}$ ($\Delta H_2^\circ = (\Delta H_1^\ddagger)_{T\geqslant 314{\cdot}2\,K} = 235$ kJ mol$^{-1}$);
$\nu$ = concentration of the gel network crosslinks;
$c$ = concentration of the polymer ($c = 36{\cdot}8$ g-equiv. m$^{-3}$ of disaccharide residues);
$P$ = alignment coefficient (calculations are performed for $P = 1$ and $P = 5$);
$\Delta\bar{h}_f$ = fusion heat of the gel, related to 1 g-equiv. of disaccharide residues ($\Delta\bar{h}_f = 9{\cdot}4$ kJ mol$^{-1}$) for fusion heat of a 1·84% κ-carrageenan gel containing 0·1 M KCl (Morris *et al.*, 1980*c*).

### Method

The relation between the equilibrium constant, $K_d$, for the breakdown of gel network crosslinks and the thermodynamic parameters for this process is given by the equation

$$-RT \ln K_d = \Delta H^\circ - T\Delta S^\circ \qquad (1)$$

The equilibrium constant (for the point contacts) is given by

$$K_d = \frac{(\gamma c - 2\nu)^2}{\nu} \tag{2}$$

where $c$ is the equivalent concentration of the polymer, $\gamma$ is the activity coefficient of the polyion and $\nu$ is the concentration of the gel network crosslinks.

For the microinhomogeneous systems the activity coefficient of the polyion is probably determined essentially by the degree of its association. Therefore it is assumed that

$$\gamma = P^{-1}$$

where $P$ is the alignment coefficient, i.e. the number of macromolecules in an association.

Accordingly,

$$K_d = \frac{[(c/P) - 2\nu]^2}{\nu} \tag{3}$$

If the standard breakdown enthalpy of the network crosslinks is temperature independent, then the concentration of network crosslinks at temperature $T$ is

$$\nu \approx \nu_{max} \exp\left\{-\frac{\Delta H^\circ_{(T_0 - T)}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\} \tag{4}$$

where $\nu_{max}$ is the maximum concentration of network crosslinks, corresponding to the temperature $T_0$ which marks the onset of the breakdown of the gel network crosslinks; $\Delta H^\circ_{(T_0 - T)}$ is the standard breakdown enthalpy of the network crosslinks in the temperature interval $(T_0 - T)$.

The method of calculating the maximum number of crosslinks is discussed for two cases.

(a) A thermorheologically simple system, i.e. a system characterised by one value for the standard breakdown enthalpy of the network crosslinks ($\Delta H^\circ$).

(b) A thermorheologically complex system with two substates:
   (1) A low-temperature state (at $T < T_{h\text{-}c}$, where $T_{h\text{-}c}$ is the temperature of the onset of the helix–coil transition), in which the macromolecular helix conformation is stable; in

this region the standard breakdown enthalpy of the network crosslinks is $\Delta H_1^\circ$.

(2) A high-temperature state ($T \geqslant T_{h\text{-}c}$) in which the breakdown of the crosslinks is accompanied by a complete helix unwinding; in this case the standard breakdown enthalpy of the network crosslinks is $\Delta H_2^\circ$.

It is assumed that in the latter state the standard breakdown enthalpy of the network crosslinks represents the sum of the standard breakdown enthalpies of the bonds between the structural network elements (equal to $\Delta H_1$), and of the enthalpy of the helix–coil transition for the equivalent network fragment. According to this last assumption, the helix–coil transition is considered to be a strictly cooperative one.

A thermorheologically complex system of this type can be exemplified by a κ-carrageenan gel. For this gel:

$$\Delta H_1^\circ = (\Delta H_1^\ddagger)_{T < 314{\cdot}2\ \mathrm{K}}$$

and

$$\Delta H_2^\circ = (\Delta H_1^\ddagger)_{T \geqslant 314{\cdot}2\ \mathrm{K}}$$

(a) *The thermorheologically simple system*
For this system

$$\Delta H^\circ_{(T_0 - T)} = \Delta H^\circ \tag{5}$$

The maximum concentration of the network crosslinks is given by

$$\nu_{\max} = \frac{\Delta \bar{h}_f c}{\Delta H^\circ} \tag{6}$$

where $\Delta \bar{h}_f$ is the heat of fusion of the gel per 1 g-equiv. of the monomeric residues.

From eqns (1)–(6) we obtain the equation for calculating the breakdown entropy of the gel network crosslinks:

$$\Delta S^\circ = \frac{\Delta H}{T} + R \ln c \left[ P^{-2} \left(\frac{\nu}{c}\right)^{-1} - 4P^{-1} + 4\left(\frac{\nu}{c}\right)\right] \tag{7}$$

where

$$\frac{\nu}{c} = \frac{\Delta \bar{h}_f}{\Delta H^\circ \exp\left\{\frac{\Delta H^\circ}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\}} \tag{8}$$

(b) *The thermorheologically complex system*

For simplicity we shall restrict ourselves to calculations for the temperature interval $T_0 < T \leqslant T_{h\text{-}c}$. In this case

$$\Delta H^{\circ}_{(T_0 - T)} = \Delta H^{\circ}_1 \tag{9}$$

The maximum concentration of the network crosslinks is

$$\nu_{max} = \frac{\Delta \bar{h}_f c}{\Delta H^{max}_{(T_0)}} \tag{10}$$

where $\Delta H^{max}_{(T_0)}$ is the hypothetical standard breakdown enthalpy of the gel network crosslinks at the temperature $T_0$ and includes contributions from the breakdown of all the levels of structure pattern up to the gel fusion temperature.

In particular, if gel fusion is accompanied by helix unwinding of macromolecules, then $\Delta H^{max}_{(T_0)}$ includes, along with the breakdown enthalpy of the bonds between the structural elements of the gel network, the helix–coil transition enthalpy for the equivalent network fragment. In the latter case

$$\Delta H^{max}_{(T_0)} = \Delta H^{\circ}_1 + \frac{\Delta \bar{h}^{\circ}_{h\text{-}c} c}{\nu_{max}} \tag{11}$$

where $\Delta \bar{h}^{\circ}_{h\text{-}c}$ is the helix–coil transition enthalpy per 1 g-equiv. of the monomeric residues.

If we assume that the contributions of the breakdown enthalpy of the bonds between the structural elements of the gel network and those of the equivalent network fragment to the breakdown enthalpy of the network crosslinks are additive, then

$$\Delta \bar{h}^{\circ}_{h\text{-}c} = \frac{(\Delta H^{\circ}_2 - \Delta H^{\circ}_1)\, \nu_{(T_{h\text{-}c})}}{c} \tag{12}$$

where $\nu_{(T_{h\text{-}c})}$ is the concentration of the gel network crosslinks at the temperature marking the onset of the helix–coil transition. By combining eqns (11) and (12) we obtain

$$\Delta H^{max}_{(T_0)} = \Delta H^{\circ}_1 + (\Delta H^{\circ}_2 - \Delta H^{\circ}_1) \frac{\nu_{(T_{h\text{-}c})}}{\nu_{max}} \tag{13}$$

The ratio of concentrations of the crosslinks at the two temperatures is given by

$$\frac{\nu_{(T_{h\text{-}c})}}{\nu_{max}} \approx \exp\left\{-\frac{\Delta H_1^\circ}{R}\left(\frac{1}{T_0}-\frac{1}{T_{h\text{-}c}}\right)\right\} \tag{14}$$

Finally, from eqns (9)–(14) we have

$$\nu_{max} \approx \frac{\Delta\bar{h}_f c}{\Delta H_2^\circ + \Delta H_1^\circ\left[1-\exp\left\{-\frac{\Delta H_1^\circ}{R}\left(\frac{1}{T_0}-\frac{1}{T_{h\text{-}c}}\right)\right\}\right]} \tag{15}$$

Thus eqn (7) follows, where (taking into account eqn (4))

$$\frac{\nu}{c} \approx \frac{\Delta\bar{h}_f}{\Delta H_2^\circ - \Delta H_1^\circ\left[1-\exp\left\{\frac{\Delta H_1^\circ}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right\}\right]} \tag{16}$$

For the exact calculation of the crosslink concentration and breakdown entropy of the κ-carrageenan gel crosslinks from eqns (7) and (16) it is necessary to use a heat of fusion which may be obtained by subtracting the heat change due to the breakdown of the crosslinks formed by potassium ions at temperatures above the helix–coil transition from the experimentally determined heat of fusion of the gel. Since the former is not known, it was ignored in the calculations.

For the calculation of standard enthalpy and entropy changes per 1 g-equiv. of monomeric residues associated with the helix–coil transition, eqn (12) and the following equations are used:

$$\nu_{(T_{h\text{-}c})} = \frac{\Delta\bar{h}_f c}{\Delta H_2^\circ - \Delta H_1^\circ\left[1-\exp\left\{\frac{\Delta H_1^\circ}{R}\left(\frac{1}{T_0}-\frac{1}{T_{h\text{-}c}}\right)\right\}\right]} \tag{17}$$

$$\Delta\bar{s}_{(T_{h\text{-}c})} = \frac{\Delta\bar{h}^\circ_{(T_{h\text{-}c})}}{T_{h\text{-}c}} \tag{18}$$