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Thermodynamic Parameters of the Junction Zones in Thermoreversible Maltodextrin Gels

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ABSTRACT

The standard breakdown entropy ΔS^0 *and Gibbs free energy* ΔG^0 *of the junction zones in thermally reversible maltodextrin gels are calculated from thermal data as a function of the alignment coefficient P. Based on a value for* $P \simeq 170$, ΔS^0 *and* ΔG^0 *are 24 J* mol^{-1} *K and 18 kJ* mol^{-1} *respectively.*

The definition range of the equation for calculating ΔS^0 *and* ΔG^0 *ends at* $P \simeq 210$. *This comes quite near the value* $P \simeq 170$ *for the magnitude of the coherent scattering units in maltodextrin gels as estimated by wide angle X-ray scattering. Maltodextrin gelation is a weakly cooperative process. Because of the low entropic effect, small changes in enthalpy result in the formation of thermodynamically stable gel structures.*

INTRODUCTION

Gelling maltodextrins are obtained by hydrolysis of potato starch with bacterial alpha-amylase. At concentrations above 10% (w/w) and temperatures below 303 K their aqueous solutions solidify to give thermally reversible gels. Melting takes place as a function of concentration between 318 and 358 K. Maldodextrins are used as gelling agents and emulsion stabilizers in foods (Richter *et al.*, 1972; Schierbaum *et al.*, 1977). Their properties are determined by a broad molecular weight

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distribution of the saccharides. These maltodextrins consist of amylopectin degradation products, low molecular weight amylose degradation products and a very small amount of high molecular weight amylose (Schierbaum *et al.*, 1984).

The sol–gel transition and gel properties have been characterized by rheological, mechanical, thermal and NMR-relaxation methods (Braudo, 1979, Bulpin *et al.*, 1984; Vorwerg, 1985). The gel structure was investigated by the use of small-angle and wide-angle X-ray scattering experiments (Reuther *et al.*, 1983, 1984), transmission electron microscopy (Schierbaum *et al.*, 1984), and electron spin resonance (Ebert *et al.*, 1985). Maltodextrin gels are two-phase systems resulting from mutual interactions between amylose molecules and sufficiently long amylopectin chains resulting in the formation of a mixed gel structure (Schierbaum *et al.*, 1986; Vorwerg *et al.*, 1988). The possibility of such structures has been anticipated by other authors too, (Miles *et al.*, 1985, Lineback, 1986; Gidley *et al.*, 1987). It was calculated, from wide angle X-ray scattering curves, that maltodextrin gels contain crystallites, 17 μm in size, showing the structure of the B-polymorph of starch which is found in retrograded starch (Gernat *et al.*, 1987). The crystallites (16% of entire carbohydrate)are embedded in a phase containing the non-crystallizing parts of the maltodextrin. Since a portion of the molecule is sufficiently long and can be involved in the formation of several crystalline domains, an aggregation network, in which the domains represent the junction zones, arises (Reuther *et al.*, 1984). Despite the high rigidity of the maltodextrin gels the heat changes associated with the melting of the gels are small (Vorwerg *et al.*, 1988). Therefore the breakdown enthalpy and entropy of the junction zones yield important data which characterize thermoreversible gels. The methods for determining them have been reported elsewhere (Braudo *et al.*, 1983). In this paper the parameters for 20% (w/w) aqueous maltodextrin gels are estimated from measurements of the Young's modulus at various temperatures and data from thermorheological and calorimetric investigations obtained previously (Braudo *et al.*, 1979). It has to be pointed out that in maltodextrin gels many macromolecules are associated into a crosslinking structural building unit, therefore it is more appropriate to describe the contacts between these units as junction zones rather than as network crosslinks.

THEORY

The breakdown enthalpy of the junction zones of thermoreversible gels ΔH is given by

$$\Delta H = E^{G} - E^{S} \tag{1}$$

where E^{G} = activation energy of viscous flow. For the 20% maltodextrin gel $E^{G} = 38$ kJ mol^{-1} (Braudo *et al.*, 1979, Vorwerg 1985). E^{S} = activation energy of viscous flow. For the solvent $E^{S} = 13$ kJ mol^{-1} (Glasstone *et al.*, 1941). For the maltodextrin gel we obtain $\Delta H^{0} = 25$ kJ mol^{-1} (Braudo *et al.*, 1979). For a number of thermoreversible gels it is shown that ΔH, calculated according to eqn (1), is close to the standard breakdown enthalpy of junction zones ΔH^{0} (Braudo *et al.*, 1984). The standard breakdown entropy of the junction zones of thermoreversible gels ΔS^{0} is calculated from (Braudo *et al.*, 1984)

$$\Delta S^{0} \approx \frac{\Delta H^{0}}{T} + R \ln c \left[\frac{1}{P^{2}(\nu/c)} - \frac{4}{P} + 4(\nu/c) \right] \tag{2}$$

R	univeral gas constant, $R = 8{\cdot}3143$ kJ mol^{-1} K^{-1}
T	absolute temperature (K)
c	polymer concentration (moles of the repeating unit per l). For the maltodextrins the weight of the repeating unit is $M_0 = 162$ g mol^{-1}
P	alignment coefficient; number of molecules or molecular segments being associated to an assumed acceptor chain
ν	concentration of the junction zones of the gel network

ν/c is obtained from

$$\nu/c \approx \frac{\Delta \bar{h}_{f}}{\Delta H^{0} \exp\left[\dfrac{\Delta H^{0}}{R} \left(\dfrac{1}{T^{0}} - \dfrac{1}{T} \right) \right]} \tag{3}$$

$\Delta \bar{h}_{f}$	fusion heat of the gel, related to 1 repeating unit of the polymer (kJ mol^{-1})
T_0	temperature of the initial breakdown of the gel junction zones (K).

The value for the heat of fusion of a maltodextrin gel has been found, $\Delta \bar{h}_{f} = 0{\cdot}10$ kJ mol^{-1} glucose units (Braudo *et al.*, 1979). The existence of a temperature T_0 can be derived according to Hirai (1955) from the temperature dependence of the Young's modulus E of a thermoreversible gel. Far below the melting point of the gel, the Young's modulus increases with increasing temperature. At higher temperatures it shows a decrease up to the melting of the gel. The increase can be explained by means of the kinetic rubber elasticity theory, according to which the equilibrium Young's modulus of the system is directly proportional to the absolute temperature, when the number of the junction zones remains constant (Treloar *et al.*, 1975). On approaching the melting point of the gel, the number of the junction zones quickly diminished. Consequently the Young's modulus decreases too. The temperature at which $E/T = 0$, is defined as T_0. We obtained T_0 for a maltodextrin gel from measurements of the temperature dependence of the Young's modulus.

EXPERIMENTAL

Materials

Technical maltodextrin 'SHP', produced by VEB Stärkefabrik, Kyritz, GDR, according to Standard TGL 32 479 was used in this work. The molecular data of the technical maltodextrin under investigation are listed in Table 1. Gels were prepared by boiling maltodextrin–water suspensions until complete dissolution and replacing the loss of water. The solutions were poured into stainless steel moulds each with a cylindrical bore, 13 mm in diameter, 18 mm in height, hermetically sealed and stored for 24 h 277 K.

Methods

Measurements of uniaxial compression were performed on gels using a dynamometric balance as described by Braudo *et al.* (1974). The deformation did not exceed 3% at a constant stress of 515 Pa so that the measurements were within the linear viscoelastic region. To prevent evaporation from the cylindrical gel pieces during the measurements, the

TABLE 1

Molecular Parameters and Sugar Composition of Maltodextrin

Dextrose equivalent	6·2%
$\bar{P}_n$, calculated from reducing power	27
$\bar{P}_w$, by light scattering in 0·01 M NaOH	1100
$\bar{P}_w/\bar{P}_n$	41
Iodine complexing values:	λ_{max} 548 nm, E_{450} 0·110
Oligosaccharides (soluble in 80 vol % ethanol) 18 ± 3% $\bar{P}_n \approx 7$	
Polysaccharides (insoluble in 80 vol % ethanol) 82 ± 3% $\bar{P}_n \approx 70$	
Linear polysaccharides (cyclohexanol precipitation) 8 – 11%	
	$\bar{P}_n \approx 50-150$

samples were covered with silicon oil. After thermostating the gel for 30 min at the initial temperature of 274 K the sample was loaded at this temperature for 10 min, the temperature was then raised to the next measurement temperature at a rate of 0·17 K min^{-1}, and loaded at this temperature again for 10 min, heated to the next temperature etc. The Young's modulus was determined at 3 to 5 K intervals up to nearly 310 K. At each temperature the gel deformation was measured between 5 and 600 s. The difference between the initial height of the gel and that height after a 600 s loading deformation was used to calculate the Young's modulus. The time dependence of the Young's modulus at three different temperatures is shown in Fig. 1.

RESULTS AND DISCUSSION

As shown in Fig. 2, in the temperature range observed, the sign of the temperature dependence of the Young's modulus, $\mathrm{d}E/\mathrm{d}T$, changes. The maximum of the function $E = f(T)$ is found at $T_0 = 283$ K. The position of the maximum does not change with the loading time (Fig. 2). It has been shown elsewhere that in thermoreversible gels, very slow mechanical relaxation processes take place (Braudo *et al.*, 1984) so that the values of the Young's moduli determined will differ slightly from the equilibrium moduli. Since, however, only the relative change of the Young's modulus with the temperature is required for determining T_0, this inaccuracy may be neglected.

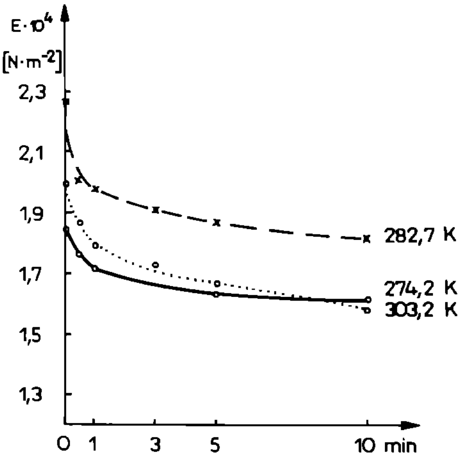

Fig. 1. Time dependence of the Young's modulus E of a 20% maltodextrin gel at different temperatures.

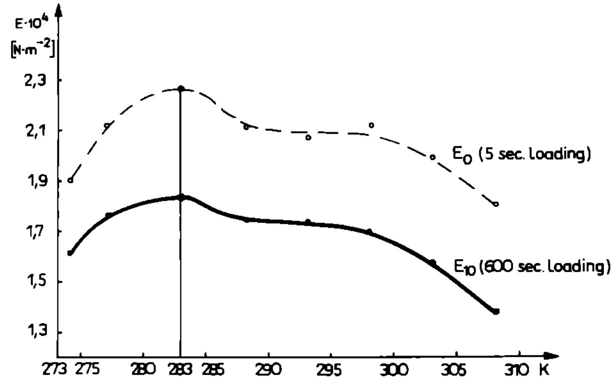

Fig. 2. Temperature dependence of the Young's modulus E of a 20% maltodextrin gel.

A further parameter needed to calculate the standard breakdown entropy of the junction zones ΔS^0 in the gel is the association coefficient, P. The estimation of its magnitude is based on the gel structure of the maltodextrin. Small-angle X-ray scattering investigations have demonstrated the presence of regions with a higher density in the gel. These regions are the shape of flat discs with diameters of 280 nm and heights of 30 nm (Reuther *et al.*, 1983). As proved by wide-angle X-ray scattering of the gels, the regions have the same crystalline structure as B-amylose (Reuther *et al.*, 1984). The anhydroglucose units in this structure form double helices arranged in a hexagonal unit cell ($a = b = 1{\cdot}85$ nm, c (fibre repeat) $= 1{\cdot}04$ nm, $\gamma = 120$°C) (Sarko & Wu, 1978). From the wide-angle X-ray scattering experiments a diameter of the coherent scattering regions of 16–17 nm has been calculated (Gernat *et al.*, 1987). Hence, it is almost certain that the discs found by the small-angle X-ray scattering are not ideal crystals, but are composed of many of these crystallites.

1. The association of two chains is considered as the primary gelation process (binary association of the macromolecules): $P = 1$.
2. The smallest structural unit is the unit-cell. Each unit-cell contains 4 chains (helices): $P = 3$.
3. The significant association step is the formation of the coherent regions by crystallization of the double helices. Since the regions are of approximately isometric dimensions, a cubic body can be taken as a basis for estimating P which is obtained as the number of the double helices 'running from top to bottom'. When the square surface of the cube is related to the plane defined by the

lattice vectors a and $b_{(n)}$ the number of unit-cells corresponding to the square surface is calculated as 85. So $1 + P \simeq 170$.

4. The essential structural units are the regions of higher density. Analogous to the treatment of the coherent scattering regions, in this case a value of $P \sim 40\,000$ is obtained for the number of double helices running through a disc.

Figure 3 shows that the standard breakdown entropy ΔS^0 of the junction zones calculated at $T_0 = 283$ K and $T = 298$ K as a function of the association coefficient, P. ΔS^0 decreases rapidly with increasing P at small and large P-values. It only slightly decreases in the region of medium P-values and the rapid decrease at high P values starts towards the end of the definition range of eqn (2). The standard Gibbs free energy ΔG^0 shows the corresponding inverse behaviour. The alignment coefficient $P \simeq 170$, which was derived from the size of the coherently scattering crystalline regions, is situated near to the limit of $P \simeq 210$. Thus the dimensions of 16–17 nm should be the upper limit for the size of the junction zones which is consistent with the thermodynamic model. The stability of the aggregates diminishes the nearer the number of

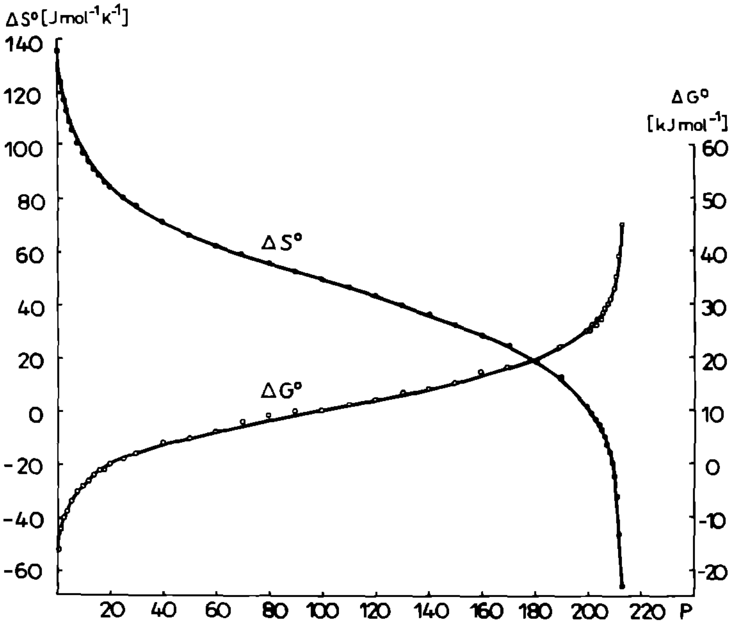

Fig. 3. Standard entropy ΔS^0 and standard Gibbs free energy ΔG^0 for the breakdown of the junction zones in a 20% maltodextrin gel as a function of the alignment coefficient P.

the segments involved in this process comes to the limit. The result of this thermodynamical approximation coincides closely with the conclusion drawn from wide angle X-ray scattering i.e., the crystallites in maltodextrin gels, independent of the concentration, have a characteristic dimension of 16–17 nm (Gernat *et al.*, 1987). The value of $P \simeq 40\,000$, obtained from the total size of the scattering inhomogenities, is found to be out of the range of validity of eqn (2). In this case the number of glucose units interacting within the junction zones would exceed the number of the units at the surface of the associates.

The results of the calculation are summarized in Table 2. In this table the thermodynamic parameters of a kappa-carrageenan gel at two temperatures reported previously (Braudo *et al.*, 1984), are given for comparison. At 298 K the macromolecules of kappa-carrageenan are in a stable helical conformation, but at 314 K the network crosslink break down accompanied by helix-unwinding begins. Based on the standard breakdown entropy of the network crosslinks, gelations at lower and higher temperatures were characterized as weakly and highly cooperative processes, respectively.

CONCLUSION

Since the formation of maltodextrin gels is associated with rather small changes both in the enthalpy and entropy, this process has a low level of cooperativity. Due to the low entropic effect a small change in enthalpy is

TABLE 2

Thermodynamic Parameters for the Breakdown of the Junction Zones in Thermally Reversible Maltodextrin Gels (Data for Kappa Carrageenan from Braudo *et al.* (1984) Included for Comparison)

Gel concentration	*Breakdown temperature T_0 (exp) K*	*ΔH^0 kJ mol^{-1}*	*Assumed alignment coefficient P*	*ΔS^0 J mol K^{-1}*	*ΔG^0 kJ mol^{-1}*
Maltodextrin			1	136	−16
20 wt/wt	283·2	25	3	118	−10
in water			170	24	18
			P_{limit} 210	−67	45
Kappa-carrageenan					
1·5 wt/wt	298·2	36	5	135	−4
in 0·15 M *KCl*					
solution	314·2	235	5	775	−10

sufficient for the formation of a thermodynamically stable gel network. The standard Gibbs free energy of gelation is not strongly influenced by the degree of cooperativity of this process. These results are related to the thermal reversibility of maltodextrin gels.

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