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The Determination of the Kinetics of Polysaccharide Thermal Degradation using High Temperature Viscosity Measurements

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ABSTRACT

Information about the thermal degradation of the polysaccharides sodium alginate, carrageenan and carboxymethyl cellulose has been obtained from the time dependence of the viscosity at high temperatures measured using a slit viscometer. The viscosity is related to the molecular weight using previously-published relations between the zero shear specific viscosity and the coil overlap parameter in conjunction with the appropriate Mark–Houwink equation. It is found that alginate is much less stable than carboxymethyl cellulose and carrageenan. Activation energies for depolymerisation obtained from Arrhenius plots in the presence of oxygen ranged from 50 kJ/mol for alginate to 105 kJ/mol for κ-carrageenan.

INTRODUCTION

The majority of investigations into the rheology of polysaccharide solutions have been carried out at ambient temperature. There are several applications however, where high temperatures are involved. The most important of these are in the thickening of food products which are to be subjected to heat sterilisation, and in oil-well drilling applications. In the latter area in particular there is a demand for water-soluble polymers that have a high temperature stability both in terms of a weak dependence of viscosity on temperature and a small degree of thermal degradation (Lambert & Rinaudo, 1985). Generally the thermal stability has been evaluated by comparing the viscosity at ambient temperature before and after the solution has been subjected to a standard heat treatment (Foss *et al.*, 1987).

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A slit viscometer that can make viscosity measurements on aqueous solutions at temperatures above 100°C has recently been described (Berrington *et al.*, 1987). This has the potential advantage, in terms of monitoring thermal depolymerisation, that the viscosity change with time at one temperature can be determined. Hence degradation as a function of temperature can be measured without resorting to any specific assumption about the temperature dependence of the reaction rate, which would be the case when determining the molecular weight change as a result of a heating cycle, which would inevitably involve a complicated time temperature cycle.

In this paper the use of the slit viscometer to follow the thermal degradation of three polyelectrolytes, sodium alginate, carrageenan and carboxymethyl cellulose (CMC) commonly used in the food industry, is reported. The objective of the work was to evaluate the method and obtain rate constants for the degradation process. It is recognised that the degree of thermal stability can be significantly improved by the exclusion of oxygen from the system and by the inclusion of free-radical scavengers. Such systems are not relevant to practical applications and attempts to increase stability in this way have not been made in this work.

THEORY

The hydrolysis reaction which causes polysaccharide degradation has been established as a first-order reaction with a rate constant K (Masson & Caines, 1954; Masson, 1955; Smidsrød *et al.*, 1965; Rao *et al.*, 1981; Desai & Hansen, 1985; Parsons *et al.*, 1985).

A method to determine the value of the rate constant from viscosity measurements at constant temperature has been devised. If it is considered that a polymer of initially-random molecular-weight distribution is degraded by the process of random scission of the bonds, then the true initial rate constant of degradation can be expressed (Tanford, 1961) as

$$\frac{1}{\bar{x}_{wt}} = \frac{1}{\bar{x}_{w0}} + \frac{KT}{2} \tag{1}$$

where $\bar{x}_{wt}$ and $\bar{x}_{w0}$ are weight average degrees of polymerisation at times t and zero, K = true rate constant and T = time.

Molecular weight data can be substituted for x_w values to give

$$\frac{1}{\bar{M}_{wt}} = \frac{1}{\bar{M}_{w0}} + \frac{KT}{2L} \tag{2}$$

where L = weight of a monomer unit.

The molecular weight can be related to the intrinsic viscosity $[\eta]$ by the Mark–Houwink equation

$$[\eta]=K\bar{M}_{\mathrm{w}}^{a}$$

where K and a are constants. If the zero shear rate viscosity is known, then the intrinsic viscosities can be estimated from previously published relationships of the zero shear rate specific viscosity, η_0, to the coil overlap parameter $C[\eta]$. The relationship for concentrated solutions, where $C[\eta]\geqslant 4$, of most random-coil polymers is (Morris *et al.*, 1981)

$$\eta_0\approx\eta_{\mathrm{s}}\frac{C[\eta]^{3\cdot 3}}{10}$$

where η_{s} = solvent viscosity.

The more difficult step is that of relating the viscosity data obtained using the slit viscometer, which makes measurements over a wide range of wall shear rates (1000–10000 s^{-1}), where the power law equation $\tau=B\dot{\gamma}^{n}$ or $\eta=B\dot{\gamma}^{n-1}$ is applicable to the zero shear rate viscosity of the solution. B = the consistency index.

This can be overcome by the use of a standard curve η/η_0 versus $\dot{\gamma}/\dot{\gamma}_{0\cdot 1}$ (Morris *et al.*, 1981) ($\dot{\gamma}_{0\cdot 1}$ = shear rate where viscosity is a tenth of its zero shear value) which fits all random-coil polymers. If the power law equation holds then the slope M of the curve should be equal to $n-1$ at some point. Thus the ratio η/η_0 can be found at the point $M=n-1$.Values of η_0 can then be found for each experimental value of η.

The change in molecular weight with time can be determined, and by using the slope of a plot of $1/\bar{M}_{\mathrm{w}}$ versus time, in the equation

$$\mathrm{Slope}=K/2L$$

we can determine the rate constant k for the first order degradation reaction.

The wall shear stress and the wall shear rates are calculated using the following equations

$$\text{Wall shear stress } \tau_{\mathrm{w}}=\frac{\Delta Pb}{2C}$$

where b = slit height, ΔP = differential pressure and C = distance between the centres of the pressure ports.

Wall shear rate for a Newtonian fluid is given by

$$\dot{\gamma}_{\mathrm{wN}}=\frac{6Q}{ab^{2}}$$

where Q = volumetric flow rate, b = slit height and a = slit width. The power law exponent n is related to τ_{wN} and $\dot{\gamma}_{wN}$ by

$$n = \frac{d \log \tau_{wN}}{d \log \dot{\gamma}_{wN}}$$

Plots of $\log \tau_{wN}$ versus $\log \dot{\gamma}_{wN}$ show excellent linearity. The true wall shear rate $\dot{\gamma}_w$ is related to $\dot{\gamma}_{wN}$ by

$$\dot{\gamma}_w = \dot{\gamma}_{wN} \frac{2n+1}{3n}$$

The Mark–Houwink expressions employed were

1. Sodium alginate (Smidsrød, 1970)
   $[\eta] = 3{\cdot}09 \times 10^{-5} \bar{M}_w^{0{\cdot}955}$
2. Carboxymethyl cellulose (Wirick, 1968)
   $[\eta] = 2{\cdot}85 \times 10^{-4} \bar{M}_w^{0{\cdot}78}$
3. κ-Carrageenan (Vreeman *et al.*, 1980)
   $[\eta] = 2{\cdot}09 \times 10^{-4} \bar{M}_w^{0{\cdot}78}$

$[\eta]$ is expressed in units of dlg^{-1}.

The solvent system for each of these polymers was chosen so as to give the correct total ionic strength of the solution, as specified in the literature source of the Mark–Houwink equation, whilst also imparting a measure of pH control.

EXPERIMENTAL

Materials

The materials used in this study were all of commercial origin. Samples of κ-carrageenan (80% κ–20% λ) were purchased from Sigma, Dorset, UK, sodium alginate (Manucol DM) was supplied by Kelco/AIL International Ltd, Surrey, UK, and a low-viscosity sodium carboxymethyl cellulose (DS 0·7–0·8) sample was purchased from BDH Chemicals Ltd, Dorset, UK.

Solution preparation
Solutions for viscosity measurements were made at ambient temperature by thorough dispersion of the polymer using a high speed Silverson mixer. The subsequent treatment of each type of sample varied.

Alginate samples were prepared in a mixed phosphate buffer ($KH_2PO_4.Na_2HPO_4$) of pH 7 and containing 0·2 M NaCl; CMC samples were prepared in a mixed phosphate buffer of pH 6 and containing 0·1 M NaCl. These solutions were allowed to stand for 2 h before use. The solutions of κ-carrageenan were made up in a solvent containing 0·005 M EDTA and 0·2 M NaCl, then heated to 80°C with continuous stirring. The pH was adjusted to 7 by the addition of 0·5 M NaOH, and the solutions were used immediately.

Viscosity measurements

All viscosity measurements were made using a slit viscometer as described by Berrington *et al.* (1987). This instrument continuously cycles the sample through a slit, enabling viscosity measurements to be made at regular intervals and under controlled conditions of shear stress and temperature.

Two modes of experimentation were employed in this study.

1. The solution was run through the die slit whilst the temperature and wall shear stress were maintained constant. This enabled the reduction in viscosity of the solution, due to thermal depolymerisation, to be studied as a function of time.
2. The solution was subjected to a shear stress which was incremented after the completion of each pass through the slit, whilst a constant temperature was maintained. In this way the power law exponent n was evaluated.

RESULTS AND DISCUSSION

Implicit in this method is the assumption that the power law index n is temperature independent. This view has been put forward by several authors, for example Doublier & Launay (1981). The authors own power law measurements made over a wide temperature range show temperature independence. Figure 1 presents a selection of data, covering the three polymers under study, and Table 1 shows all the power law data and the conditions under which they were obtained.

For alginate and CMC, the more concentrated solutions show a greater degree of non-Newtonian behaviour, whereas the carrageenan shows anomalous behaviour, in that the concentrated solution shows a slightly higher power law index.

The theory for a first-order random degradation predicts that a plot of the reciprocal of the molecular weight against the time of reaction should

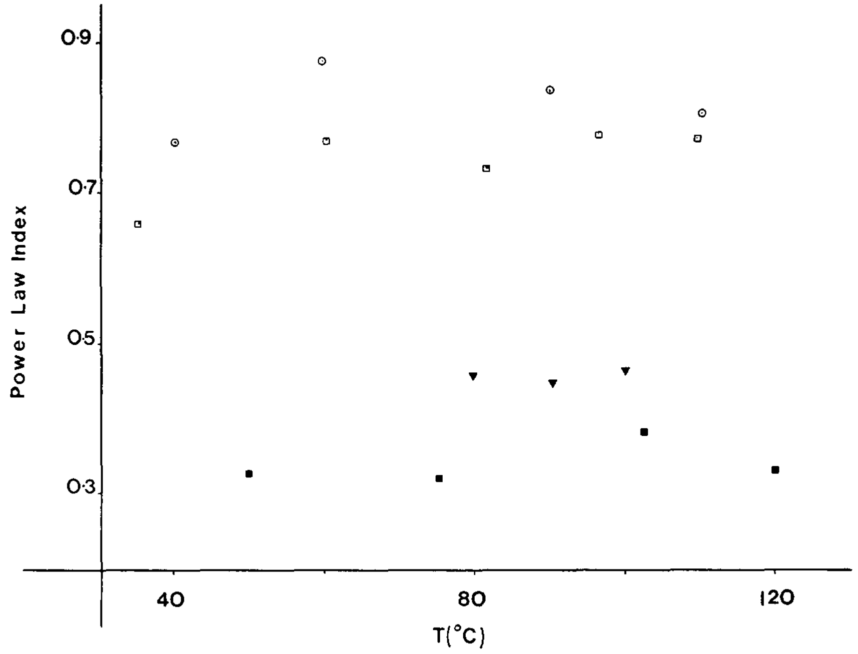

Fig. 1. Effect of temperature on the power law index *n*. Sodium alginate: ■, 1%; □, 0·5%; κ-carrageenan: ▼, 2·5%, CMC: ○, 1%.

TABLE 1
Power Law Indices for Polyelectrolyte Solutions

Polymer	*pH*	*Concentration (%, w/v)*	*Temperature range (°C)*	*n ± S.E.*
CMC	6	1	40–110	0·830 ± 0·02
		2		0·673 ± 0·03
Alginate	7	0·5	35–110	0·747 ± 0·03
		1·0		0·340 ± 0·02
κ-Carrageenan	7	1·5	80–100	0·454 ± 0·02
		2·5		0·467 ± 0·02

be linear. Figure 2 shows this to be the case. The example used is that of 1·5% κ-carrageenan at a temperature of 118°C. Also shown in Fig. 2 is the raw viscosity versus time data from which the $\bar{M}_w$ data has been extracted.

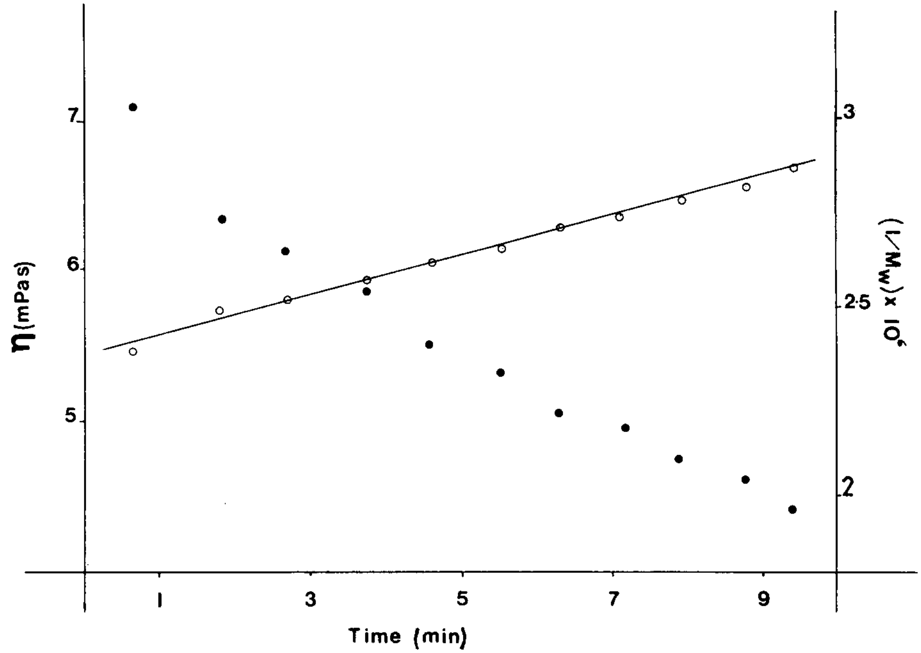

Fig. 2. Viscosity and reciprocal molecular weight of 1·5% κ-carrageenan at 118°C plotted against time. ●, Viscosity data; ○, $\bar{M}_w$ data.

The calculated rate constant data have been fitted to the Arrhenius relationship

$$k_r = Ae\frac{-E_a}{RT}$$

where k_r = rate constant, E_a = activation energy of reaction, A = pre-exponential factor, R = gas constant, T = temperature in K; these data are plotted in Fig. 3. It can be seen that the rate constants of reaction are not strongly dependent on the sample concentration and that both sets of data can be incorporated into a single Arrhenius plot. This shows reasonable linearity for sodium alginate and carrageenan but there is a suggestion that at low temperatures CMC degrades more rapidly than would be expected for Arrhenius kinetics. The data indicates that the sodium alginate is much less resistant to thermal depolymerisation than either CMC or carrageenan since the rate constant k_r is greater at any comparable temperature. The comparison between CMC and alginate is qualitatively in agreement with Pilnik & Macdonald (1968) (Table 2).

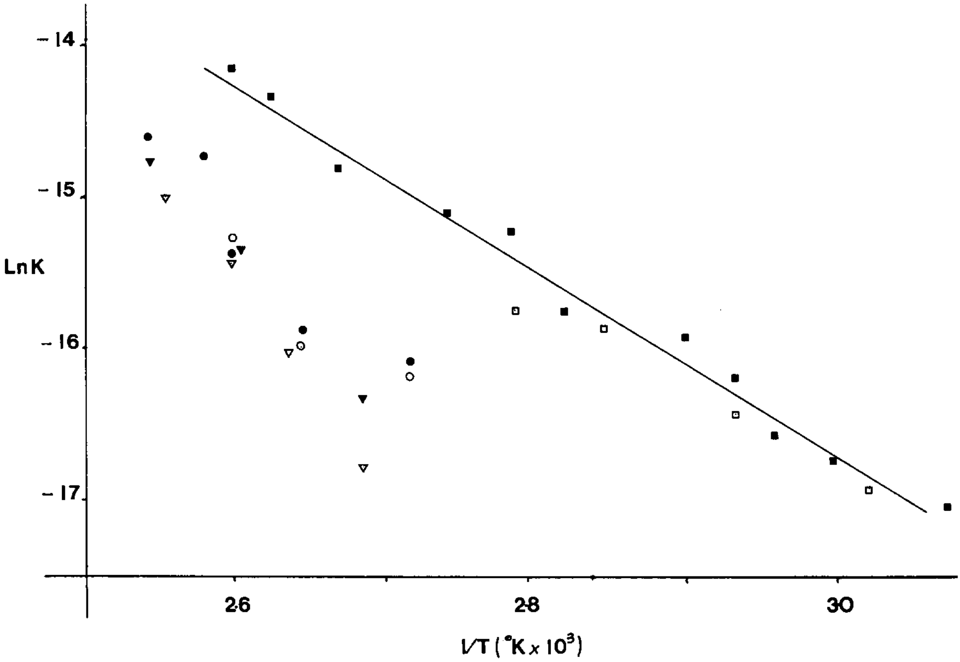

Fig. 3. Arrhenius plots for CMC: ●, 2%; ○, 1%; sodium alginate: ■, 1%; □, 0·5%; κ-carrageenan: ▽, 1·5%; ▼, 2·5%.

TABLE 2
Kinetic Equations for Depolymerisation Reactions

Polymer	*Kinetic equation*	*Correlation coefficient*
CMC	$1{\cdot}90 \times 10^4 \, e^{-79\,900/RT}$	0·938
Alginate	$4{\cdot}94 \, e^{-50\,700/RT}$	0·984
κ-Carrageenan	$1{\cdot}85 \times 10^7 \, e^{-104\,700/RT}$	0·977

The activation energies of reaction, E_a, indicate that the temperature dependence of the rate constants decreases in the order

Alginate > CMC = carrageenan

The value of E_a for carrageenan recorded in this study, of 104 kJ mol^{-1}, compares favourably with the value obtained by Masson (1955) of 122 kJ mol^{-1}. The value of the pre-exponential factor A of $1{\cdot}85 \times 10^7$ does not however compare well wtih that of Masson (1955) of

$7{\cdot}64 \times 10^9$, but the overall kinetic equations produce rate constants in reasonable agreement, such that at 100°C, $k'/k'' = 1{\cdot}45$ and at 90°C, $k'/k'' = 1{\cdot}33$ (k' = Masson rate constant, k'' = rate constant from the present study).

Recently Desai & Hansen (1985) reported an E_a value of 161·0 kJ mol^{-1} for carrageenan, with correspondingly low rate constants, and attributed this fact to the removal of oxygen from the system under study. The effect of oxygen, dissolved in the polymer solution, on the rate constants for the degradation of carrageenan has been investigated by Masson *et al.* (1955).

A basic assumption in the method of calculating the rate constants reaction is that the Morris relationship is valid at the temperature employed in this study, i.e.

$$\eta_0 \approx \eta_s \frac{C[\eta]^{3{\cdot}3}}{10}$$

The zero shear specific viscosity has been found to increase as a function of $([\eta]C)^a$, where $[\eta]$ is the intrinsic viscosity, C is the concentration and a is the characteristic constant of the particular polymer solvent system. The constant a has been found to be temperature independent (Patel *et al.*, 1987).

The temperature dependence of $[\eta]$ can be investigated by the method of Hunt *et al.* (1956) and the application of this method has shown that for flexible polymers in good solvents the temperature coefficient is generally quite small. Cowie (1962) and Brown *et al.* (1963) have found some exceptions to this statement with cellulose nitrate, amylose (Cowie) and hydroxethyl cellulose (Brown).

The temperature dependence of the $[\eta]$ of xanthan (Hacche *et al.*, 1987; Wei Lui & Takashi Norisuye, 1988) has been determined and shows that $[\eta]$ is essentially temperature independent between 20 and 80°C for xanthan polymers of $\bar{M}_w$ 200 000..Bo *et al.*, 1987 obtained a similar conclusion from studies on scleroglucan over the temperature range 30–75°C.

The $[\eta]$ calculated from the viscosity data, assuming the Morris relationship, can be used to make a comparison with $[\eta]$ data determined at 25°C using a U-tube viscometer. Both methods were found to give similar results. The intrinsic viscosity calculated from the slit viscosity data for a 1% sodium alginate solution at 102°C and $t = 0$ was found to be 10·1 $\mathrm{dl\,g}^{-1}$, whereas $[\eta]^{25°\mathrm{C}}$ U-tube $= 8{\cdot}83$ $\mathrm{dl\,g}^{-1}$ at a comparable solution ionic strength. Thus it seems reasonable to say that the function $(C[\eta]^a)$ is essentially temperature independent.

The temperature dependence of the zero shear rate specific viscosity has been considered in terms of the activation energy of flow E_f for the polymer solutions in comparison to that of the solvent. E_f for the solvent has been determined as 13·9 kJ mol^{-1}, and the values of E_f for all the polymer solutions were found to be within ± 2 kJ mol^{-1} of that value. Thus any change in η_{SP} with temperature will be small and the error in the $[\eta]$ associated with that change will be a function of

$$3{\cdot}3\sqrt{\frac{\eta_{SP}}{C}}$$

Thus for a 10% change in η_{SP} where η_{SP} lies between 10 and 100 and $C > 1\%$, the error in the value of the $[\eta]$ will be less than 3%. Thus it can be assumed that the Morris relationship holds true over the range of temperatures used.

The data in this paper would suggest that useful information can be obtained about biopolymer degradation from continuous viscosity measurements at high temperature. A necessary condition is that the viscosity change is due only to a molecular weight decrease and not to reversible thixotropic effects. If the latter were important then the rate constants would be concentration dependent.

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