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Kinetic compensation effect in depolymerisation of food polysaccharides

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Abstract

The thermal depolymerisation kinetics of agarose and κ-carrageenan in water were investigated by measurement of intrinsic viscosity ([η]). An isokinetic relationship (IKR) revealing a kinetic compensation effect in polysaccharide depolymerisation was then discovered from the obtained kinetic data and those reported in the literature. Generally, the Arrhenius frequency factor, k_0, and activation energy, E_a, of depolymerisation of agarose, κ/λ-carrageenan, κ-carrageenan and schizophyllan, under commonly used thermal conditions (high temperature, in water or pH-7 solvents, without deaeration and in disordered conformation), were in the ranges of 1.8×10^7–7.8×10^{10} s^{-1} and 97–126 kJ mol^{-1}, respectively. These two variables showed parallel increases when using solvents of lower pH values (especially in k_0) or with deaeration, and polysaccharides in ordered conformation or at lower concentrations. The IKR for the polysaccharide depolymerisation was: $\ln k_0/s^{-1} = 0.379.E_a/kJ\ mol^{-1} - 18.5$ ($R^2 = 0.906$), giving an isokinetic temperature (T_{iso}) of 317 K. Conclusively, the depolymerisation mechanism was the same for all polysaccharide systems examined.

1. Introduction

The functionality of food polysaccharides is greatly governed by molecular weight. During thermal, hydrolytic and oxidative processes, food polysaccharides generally depolymerise to a low molecular weight level, depending on processing variables and polysaccharide variety (Bradley & Mitchell, 1988; Capron, Yvon & Muller, 1996; Hjerde, Kristiansen, Stokke, Smidsrød & Christensen, 1994; Karlsson & Singh, 1999; Masson, 1954). The importance of molecular characteristics and solvation quality are roughly noted in these works when interpreting the depolymerisation kinetics of polysaccharides. By measurements of intrinsic viscosity, molecular weight or the amount of reducing end, depolymerisation kinetics have been elucidated for several polysaccharides, including carrageenans (Bradley & Mitchell, 1988; Desai & Hansen, 1986; Hjerde, Smidsrød & Christensen, 1996; Hjerde, Smidsrød, Stokke & Christensen, 1998; Karlsson & Singh; Masson; Myslabodski, Stancioff & Heckert, 1996; Singh & Jacobsson, 1994), dextran sulphate (Karlsson & Singh, 1999), sodium alginate, carboxymethyl cellulose (Bradley & Mitchell, 1988), schizophyllan (Zentz, Verchère & Muller, 1992), and guar gum (Bradley, Ball, Harding & Mitchell, 1989). Generally, various indices for evaluating the depolymerisation process, e.g. intrinsic viscosity, molecular weight, reducing end, gel strength and low-shear viscosity, indicate distinct kinetic results (Singh & Jacobsson, 1994). Besides, the experimental conditions applied (e.g. pH, heating temperature range, solvent quality, and polysaccharide concentration) differ between these investigations. These difflerences increase the difficulty in understanding of the depolymerisation mechanism.

It is known that, for a structurally-related series of compounds undergoing a defined chemical reaction, parallel changes in enthalpy and entropy are usually found (Leffler, 1955; Petersen, 1964). This is the so-called enthalpy–entropy compensation effect and can alternatively be described by the systematic variation of frequency factor (i.e. preexponential factor, k_0) with activation energy (E_a) for the same family of reactions, where the k_0 and E_a are usually derived by Arrhenius laws (Krug, Hunter & Grieger, 1976; Labuza, 1980;

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Petersen, 1964). The increase in E_a is accompanied by a parallel increase in k_0. This relationship is also named an isokinetic relationship (IKR), because the resultant slope suggests an isokinetic temperature at which the reaction rate constant is identical for all processes concerned (Rhim, Nunes, Jones & Swartzel, 1989; Vyazovkin & Linert, 1995). The existence of an IKR implies that only one reaction mechanism is followed by all members of the reaction series, and a reliable evaluation of IKR helps to elucidate the reaction mechanisms (Vyazovkin & Linert, 1995). Some isokinetic relationships have been observed in the acid-catalyzed hydrolysis of a series of disaccharides (Rhim et al., 1989), the thermal death of microorganisms, protein denaturation, ascorbic acid degradation (Labuza, 1980; Rhim, Jones & Swartzel, 1990), and water isotherms in some food systems (Aguerre, Súarez & Viollaz, 1986). Nevertheless, the IKR for polysaccharide depolymerisation was seldom discovered.

Accordingly, the purpose of this investigation was to reveal an isokinetic relationship in polysaccharide depolymerisation, based on the degradation kinetic data of two commonly-used polysaccharides, agarose and κ-carrageenan, by heat and those of food polysaccharides reported previously. Thermal conditions (75–95°C) used in this study were those ordinarily applied in the laboratory and industry. The intrinsic viscosity of polysaccharides was measured because it is a practically convenient index for evaluating the molecular mass of a polymer. The depolymerisation mechanism and the potential influences of degradation variables (e.g. polysaccharide concentration, pH, temperature range), as well as the molecular effects of polysaccharides on the depolymerisation kinetics were basically identified.

2. Materials and methods

2.1. Sample preparation

Agarose (type I-A, low EEO), and κ-carrageenan (κ-carr, type III, from *Eucheuma cottonii*) were obtained from Sigma Chemical Co. (St. Louis, MO, USA). The sample was completely dissolved in deionised water (1.0 wt%, 300 ml) in a cap-screwed flask, followed by thermal treatment at 75, 85 and 95°C in a thermostatic water bath. The partially degraded sample was periodically taken out for viscosity measurements in triplicate.

2.2. Measurement of intrinsic viscosity

Intrinsic viscosity ([η]) of agarose and κ-carrageenan in water and aqueous 0.1 M NaCl solution, respectively, was immediately determined at 45.0 ± 0.1°C after thermal degradation, using an Ubbelohde viscometer (type 531 030c and AVS control unit (Schott-Geräte, Germany). A portion of hot water or NaCl solution at a proper concentration was added to adjust polysaccharide concentrations and then equilibrated for about 3 min prior to measurement. The solvent and temperature applied were to keep polysaccharlde molecules in coil conformation remote from intermolecular aggregation (Lai, Li & Lii, 1994; Lai & Lii, 1997). The [η] value was the mean intercept of Huggins and Kraemer plots (Young & Lovell, 1991), and in 0.10 M NaCl Consequently, for agarose it was the product of the original data ([η] in water) divided by the cube of expansion coefficient ($\alpha_\eta = 1.09$) (Lai et al.).

2.3. Mathematical treatment for kinetic parameter

By using the Mark–Houwink equation [Eq. (1)] (Young & Lovell, 1991), the relative molecular mass M, of a polymer can be expressed in terms of an empirical [η] value, according to Eq. (2).

$$[\eta] = k_{MH} \cdot M^a \tag{1}$$

$$M = ([\eta]/k_{MH})^{1/a} \tag{2}$$

where k_{MH} and a are constants for a given system. In this study they were, respectively, 0.70 and 0.0788 (Rochas & Lahaye, 1989) for agarose or 0.90 and 0.00598 [means of data in the reports of Vreeman, Soneren and Paynes (1980) and Rochas, Rinaudo and Landry, (1990)] for κ-carrageenan. Since the chain scission of the glycosidic linkage of polysaccharides during thermal and acid-catalyzed degredation appears to follow a *pseudo* first-order reaction (Hjerde et al., 1994; Karlsson & Singh, 1999; Masson, 1954; Myslabodski et al., 1996; Singh & Jacobsson, 1994), the rate constant (k) of depolymerisation can be obtained from the plot of the reciprical molecular mass against time [Eq. (3)] (Myslabodski et al.; Singh & Jacobsson, 1994; Tanford, 1961).

$$1/M_t - 1/M_0 = (k/m) \cdot t \tag{3}$$

where M_t and M_0 (Da) are the molecular mass at time t and 0, respectively; k (s^{-1}), the first-order rate constant; t (s), heating time; and m (Da), the average molecular weight of disaccharide unit [306 and 392 Da for agarose and κ-carrageenan, respectively, based on the assumption that chain breakage occurs primarily at the 3,6-anhydrogalactose linkage (Hjerde et al., 1996; Masson, 1954; Myslabodski et al.)]. Combination of Eqs. (2) and (3) leads to Eq. (4) and the k value can alternatively be obtained from the slope ($= k/(m \cdot k_{MH}^{1/a})$) of ($1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a}$) versus t plot.

$$1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a} = [k/(m \cdot {k_{MH}}^{1/a})] \cdot t \tag{4}$$

The temperature dependence of the k value can be given by the Arrhenius law [Eq. (5) or (6)] (Labuza, 1980):

$$k = k_0 \exp(-E_a/RT) \quad (5)$$

$$\ln k = \ln k_0 - E_a/RT \quad (6)$$

where k_0 (s^{-1}) is Arrhenius frequency factor; E_a (J mol^{-1}), activation energy of depolymerisation; R, gas constant ($=8.314$ J $K^{-1}mol^{-1}$); and T (K), heating temperature.

2.4. Calculation of isokinetic relationship (IKR)

Deduced from Eq. (6), the IKR for a reaction of the same family is presented as in Eq. (7).

$$\ln k_0 = aE_a + b \quad (7)$$

where $a = 1/RT_{iso}$; $b = \ln k$; and T_{iso}, the isokinetic temperature at which the rate constant is identical for all concerned reactions (Labuza, 1980; Rhim et al, 1989, 1990). True compensation occurs only when $T_{iso} \neq T_{hm}$, the harmonic measuring temperatures [Eq. (8)] (Krug et al., 1976).

$$T_{hm} = n/\Sigma(1/T) \quad (8)$$

where n is the total number of thermal treatments used; and $\Sigma(1/T)$, the sum of reciprocal temperatures.

3. Results and discussion

3.1. Kinetics of thermal depolymerisation indicated by viscosity change

Fig. 1A and B indicate, respectively, that the $[\eta]$ values of agarose and κ-carrageenan decreased linearly with increasing heating time (t), certainly with a greater slope at a higher temperature. Plots of $(1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a})$ versus t (Fig. 2A and B) clearly showed excellent linearity for agarose, and κ-carrageenan, respectively, at various temperatures (75–95°C). The slopes of $(1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a}) - t$ plots and the depolymerisation rate constants (k) of these two polysaccharides are listed in Table 1. It is clear that, for each polysaccharide, the slope increased by 2–3-fold for a temperature increment of 10°C. The slope for agarose was roughly 20–30 times that for κ-carrageenan at the same temperature. The regression equations accounted for 95.8–99.8% of data deviation ($R^2 = 0.958-0.998$). Derived from the slope $[= k/(m \cdot k_{MH}^{1/a})]$, the resultant k values, at 75–95°C were in the range of $2.3\times10^{-5}-1.6\times10^{-4}$ s^{-1} for agarose and $2.0\times10^{-7}-1.3\times10^{-6}$ s^{-1} for κ-carrageenan. At the same temperature, the k value of agarose was greater than that of κ-carrageenan by two orders. If chain scission is actually occurring at the 3,6-anhydrogalactose linkage (Hjerde et al., 1996; Masson, 1954; Myslabodski et al., 1996) the result implies that the glycosidic linkage of the anhydro sugar residue in agarose is more susceptible to breakage than that in κ-carrageenan.

Fig. 3 shows that the temperature dependence of the k closely followed Arrhenius laws: $\ln k = -1.24 \times 10^{-4} \times T^1 + 25.0 (R^2 = 0.988$ for agarose and $\ln k = -1.17 \times 10^4 \times T^1 + 18.1 (R^2 = 0.955)$ for κ-carrageenan. Deduced from the intercept and slope, the frequency factor (k_0) and activation energy (E_a) of depolymerisation appeared to be, respectively, 7.8×10^{10} s^{-1} and 103 kJ/mol for agarose and 7.0×10^7 s^{-1} and 97.2 kJ/mol for κ-carrageenan. Since a high k value can be the consequence of high k_0 or low E_a, the greater k for agarose than for κ-carrageenan (Table 1) is attributed to the contribution of k_0, not E_a.

3.2. Depolymerisation kinetics of food polysaccharides

The above kinetic parameters were compared with the results of various polysaccharides in the literature and

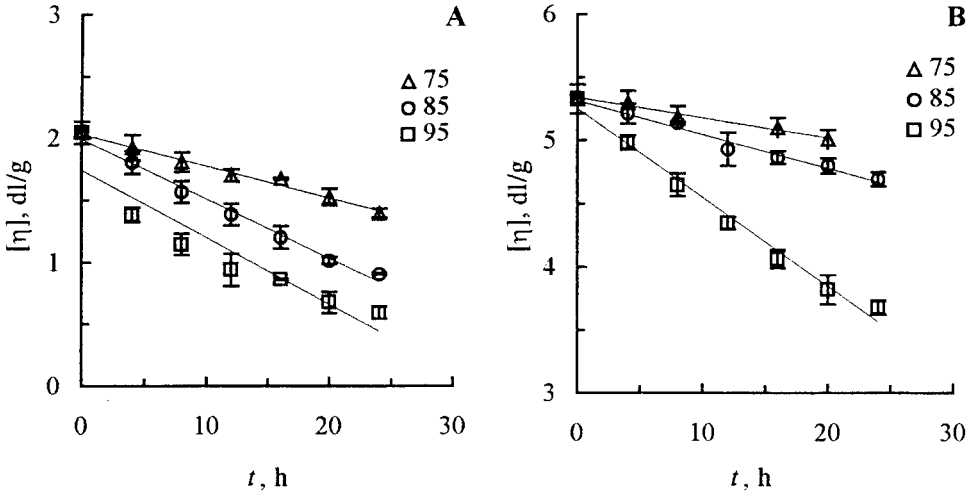

Fig. 1. Plots of intrinsic viscosity, $[\eta]$, against heating time, t, for agarose (A) and κ-carrageenan (B) depolymerised at 75–95°C.

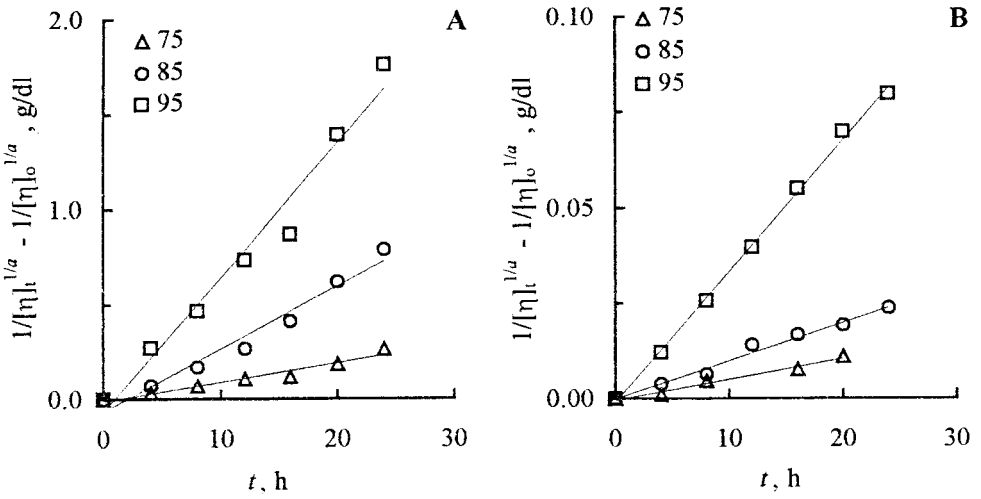

Fig. 2. Time-dependencies of $[1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/Va}]$ value for agarose (A) κ-carrageenan (B) depolymerised at 75–95°C.

Table 1
Time-dependencies of $[1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a}]$ and the rate constant (k) of depolymerisation of agarose and κ-carrageenan at various temperatures

Polysaccharide	Temperature (°C)	Plots of $(1/[\eta]_t^{1/a} - 1/[\eta]_0^{1/a})$ versus t		Rate constant k (s^{-1})
		Slope×10^3	R^2	
Agarose	75	10.2	0.958	2.3×10^{-5}
	85	33.1	0.968	7.5×10^{-5}
	95	70.7	0.971	1.6×10^{-4}
κ-carrageenan	75	0.55	0.977	2.0×10^{-7}
	85	1.00	0.983	3.7×10^{-7}
	95	3.43	0.998	1.3×10^{-6}

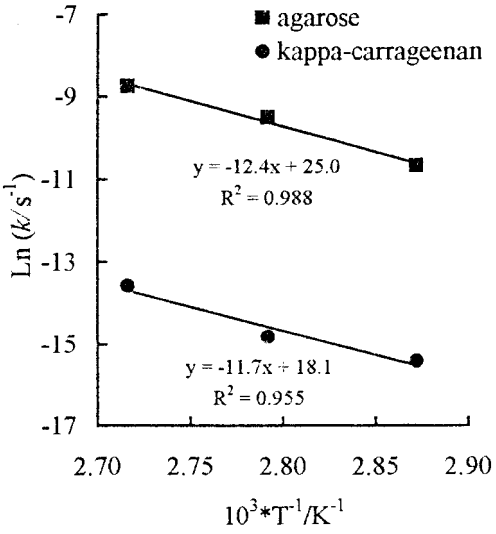

Fig. 3. Plots of logarithmic rate constant against reciprocal temperature for thermal depolymerisation of agarose and κ-carrageenan.

are listed in Table 2. The influences of degradation variables (e.g. polysaccharide concentration, pH, deaeration), the molecular properties of polysaccharides applied and experimental method, on the kinetic parameters are sequentially introduced. Firstly, the k_0 and E_a values of agarose (#1), κ/λ-carrageenan mixture (#2,3), κ-carrageenan (#5,6) and schizophyllan (#16) depolymerised in disordered conformation, and in pH-7 media without deaeration, were in the ranges of 1.8×10^7–7.8×10^{10} s^{-1} and 97–126 kJ mol^{-1}, respectively. The depolymerisation of κ-carrageenan in disordered conformation at pH 2 (# 7–10) showed a higher k_0 (8.8×10^{10}–1.4×10^{14} s^{-1}), but with a comparable E_a (105–126 kJ mol^{-1}), than those at pH 7 (#5,6) (7.0×10^7–1.3×10^{10} s^{-1} and 97–126 kJ mol^{-1}). The values for the disordered conformer of κ-carrageenan were markedly lower than those for its ordered conformer (#11) (3.0×10^{24} s^{-1} and 190 kJ mol^{-1}). This phenomenon was also true for the case of ι-carrageenan (#12,13). Depolymerisation, of κ/λ-carrageenan in a deaeration condition (#4) also showed a notably higher k_0 and E_a (1.2×10^{14} s^{-1} and 161 kJ mol^{-1}) than those without deaeration (#2,3). The acceleration of polysaccharide depolymerisation in the presence of dissolved oxygen was also found by Masson, Santry and Caines (1954) and Desai and Hansen (1986). Again, the data for κ/λ-carrageenans in pH-7 buffers (#2,3), and κ-carrageenan in media of pH 7 or 2 (#5–10), generally suggested that both parameters tended to increase with decreased polysaccharide concentrations, in agreement with the results on guar gums (Bradley et al., 1989). Besides, using the condition of 1.0% polysaccharide concentration, LiCl–HCl buffers of pH-2, and 35–55°C, Karlsson and Singh (1999) found that these kinetic variables of depolymerisation were generally in the order of dextran sulphate (# 15) < κ-carrageenan (#7) < λ-carrageenans (#14) < ι-carrageenan (#12). As compared with the above polysaccharides, remarkably low k_0 and E_a values were found for sodium alginate in a

Table 2
Applied conditions and kinetic parameters of polysaccharides depolymerisation

Polysaccharide	No.	Depolymerisation condition (concentration, pH-solvent, temperature)	Experimental method	k_0 (s^{-1})	E_a (kJ mol^{-1})	Literature cited
Agarose	1	1.0%, ~7-water, 75–95°C	[η] measurement	7.8×10^{10}	103	This work
κ+λ-Carrageenan	2	1.5–2.5%, 7-EDTA buffer, 80–100°C	[η] measurement	1.8×10^{7}	105	Bradley and Mitchell, 1988
	3	0.9%, 7-phosphate buffer, 60–101°C	reducing-end titration	7.7×10^{9}	122	Masson, 1954
	4	0.4%, 7-cacodylate buffer, 100–130°C[a]	ultracentrifugation	1.2×10^{14}	161	Desai and Hansen, 1986
κ-Carrageenan	5	1.0%, ~7-water, 75–95°C	[η] measurement	7.0×10^{7}	97	This work
	6	0.06%, 7-citrate buffer, 75–85°C	HPGPC-triple detector	1.3×10^{10}	126	Myslabodski et al., 1996
	7	1.0%, 2-LiCl–HCl buffer, 35–55°C	HPSEC-RI	8.8×10^{10}	105	Karlsson and Singh, 1999
	8	0.5%, 2-LiCl–HCl buffer, 33–55°C	HPSEC-MALLS-RI	4.2×10^{11}	113	Singh and Jacobsson, 1994
	9	0.2%, 2-LiI–HCl buffer, 55–75°C	reducing-end titration	1.4×10^{14}	120	Hjerde et al., 1996
	10	0.06%, 2-citrate buffer, 54–85°C	HPGPC-triple detector	7.7×10^{13}	126	Myslabodski et al., 1996
	11	0.2%, 2-LiI–HCl buffer, 25–44°C[b]	reducing-end titration	3.0×10^{24}	190	Hjerde et al., 1996
ι-Carrageenan	12	1.0%, 2-LiCl–HCl buffer, 35–55°C[b]	HPSEC-RI	2.2×10^{19}	162	Karlsson and Singh, 1999
	13	0.2%, 2-LiCl–HCl buffer, 30–80°C[c]	reducing-end titration	2.3×10^{16}	140	Hjerde et al., 1996
λ-Carrageenan	14	1.0%, 2-LiCl–HCl buffer, 35–55°C	HPSEC-RI	3.2×10^{11}	116	Karlsson and Singh, 1999
Dextran sulphate	15	1.0%, 2-LiCl–HCl buffer, 35–55°C	HPSEC-RI	1.6×10^{9}	103	Karlsson and Singh, 1999
Schizophyllan	16	0.01–0.03%, 7–2.0%NaCl, 102–161°C	HPSEC-LALL	9.0×10^{9}	104	Zentz et al., 1992
Sodium-alginate	17	0.5–1.0%, 7-phosphate buffer, 35–110°C	[η] measurement	4.9×10^{0}	51	Bradley and Mitchell, 1988
Carboxymethyl cellulose	18	1.0–2.0%, 6-phosphate buffer, 40–110°C	[η] measurement	1.8×10^{4}	80	Bradey and Mitchell, 1988
Guar gum	19	0.5%, 6-phosphate buffer, 100–120°C	[η] measurement	5.1×10^{-1}	56	Bradley et al., 1989

[a] In deaerated conditions.
[b] Polysaccharides in ordered conformation.
[c] Polysaccharides in disordered or ordered conformation over the temperature range used.

buffer of pH 7 (# 17, 4.9 s^{-1} and 51 kJ mol^{-1}), carboxymethyl cellulose in a buffer of pH 6 (#18, 1.8×10^4 s^{-1} and 80 kJ mol^{-1}) (Bradley & Mitchell, 1988), and guar gum in a buffer of pH 6 (# 19, 5.1×10^{-1} s^{-1} and 56 kJ mol^{-1}) (Bradley et al.). As to experimental indices, low k_0 and E_a values frequently appeared in the results investigated by $[\eta]$ measurement, rather than reducing end and molecular weight measurements. This agrees with the results based on low-shear viscosity measurement (Singh & Jacobsson, 1994). It should be noted that the above results did not exclude the complicated influences arising from the differences in buffering capacity of solutions and in microconformation of polysaccharides in various solvent conditions or due to potential desulphation on degradation (Karlsson & Singh, 1999).

Fig. 4 shows that there was a linear isokinetic relationship (IKR) between $\ln k_0$ and E_a data shown in Table 2: $\ln k_0/s^{-1} = 0.379 \cdot E_a/\text{kJ mol}^{-1} - 18.5 (R^2 = 0.906)$. From the slope ($0.379 = 1/RT_{iso}$) of this plot, a T_{iso} of 317 K, i.e. 44°C, was found for the series reaction of polysaccharide depolymerisation. The existence of true compensation effects was further examined by comparing the T_{iso} with the harmonic mean of experimental temperatures used (T_{hm}). For clear illustration, only a few thermal conditions shown in Table 2 are discussed here. The T_{hm} appeared to be 358 K for the experimental sets of 75–95°C (this work), 317 K for the 35–55°C (Karlsson & Singh, 1999), 327 K for the 30–80°C and 305 K for the 25–44°C (Hjerde et al., 1996). Evidently, a true compensation effect exists in most of the depolymerisation processes except for those at 35–55°C that $T_{hm} = T_{iso}$. Theoretically, the reaction is entropy-controlled at a temperature above T_{iso} and enthalpy-controlled at below T_{iso} (Labuza, 1980). The polysaccharide degradation at higher temperatures (#1–6, 9–10, 13, 16–19) is thus dependent on the entropy state of polysaccharide system. This is in agreement with the findings in Table 1 since the k_0 is proportional to the entropy of formation of the activated complex, e.g. activation entropy (Hjerde et al.; Labuza, 1980). The depolymerisation of κ-carrageenan in pH-2 buffer at 25–44°C (#11) can be expected to be enthalpy-controlled. The T_{iso} for polysaccharide depolymerisation is much lower than those for oxidative degradation of several synthetic polymers (543–841 K; Gupta & Viswanath 1996), the acid-catalyzed hydrolysis of some disaccharides (405.6 K, Rhim et al., 1989), the isotherms of polysaccharides (380.5 K, Aguerre et al., 1986), protein denaturation and the thermal death of microorganisms (325–331 K; Labuza, 1980).

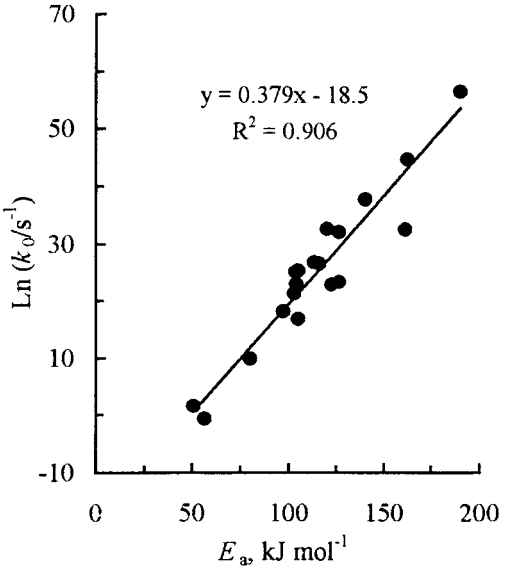

Fig. 4. Relationship between frequency factor k_0 and activation energy E_a of polysaccharide depolymerisation.

The individual influence of degradation variables and the molecular effects of polysaccharide on the depolymerisation kinetic parameters are primarily identified in this investigation. Water structure interactions would play an important role in determining the depolymerisation rate (Labuza, 1980). But, the presence of an IKR suggests that the reaction mechanism, or the nature of the transition state, is independent of the solvent variety or solvent structural change (Leffler, 1955). Accordingly, the depolymerisation mechanisms of the above polysaccharide systems can be regarded as similar and is probaby not influenced by the changes in solvent conditions listed in Table 2. The IKR holds for guar gum, a branched polysaccharide, and other linear polysaccharides, in accord with the reports of Leffler (1955) that moderate changes in the degree of steric hindrance often do not remove a reaction from its isokinetic line but merely move it to a new location on the same line. More investigations are needed to prove the suitability of using $[\eta]$ in calculating depolymerisation kinetics, since many degradation variables were involved, but not clarified, in the investigations. The obtained isokinetic relationship would be of great physiological and practical importance in the stability of polysaccharides.

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