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The kinetics of the acetylation of gelatinised potato starch

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The reaction rates, in the base-catalysed acetylation of gelatinised aqueous starch (4 wt%), by vinylacetate (ViAc), were investigated in a semibatch reactor at temperatures ranging from 20 to 50°C. The desired starch acetylation reaction is accompanied by an undesired parallel base-catalysed hydrolysis reaction of vinylacetate and a consecutive hydrolysis reaction of the acetylated starch. The rate equations are:

Starch acetylation:	$R_{\mathrm{ViAc}} = -k_1\, c_{\mathrm{ViAc}}\, c_{\mathrm{RO^-}}$
Starch acetate hydrolysis:	$R_{\mathrm{RAc}} = -k_2\, c_{\mathrm{RAc}}\, c_{\mathrm{OH^-}}$
Vinylacetate hydrolysis:	$R_{\mathrm{ViAc}} = -k_3\, c_{\mathrm{ViAc}}\, c_{\mathrm{OH^-}}$

where $k_{1,2,3} = k_{1,2,3'}\, c_{\mathrm{H_2O}}$, c_{ViAc} is the vinylacetate concentration, $c_{\mathrm{RO^-}}$ is the concentration of the dissociated starch hydroxyl group, c_{RAc} is the concentration of acetylated starch and $c_{\mathrm{OH^-}}$ is the sodium hydroxide concentration; k is the reaction rate constant. The temperature dependency of the rate constants was measured as:

Acetylation of starch:	$k_1 = 1.14\,10^{14}\, e\left(\frac{-93{,}200}{RT}\right)\ (\mathrm{m^3\,s^{-1}\,mol^{-1}})$
Deacetylation of the starch ester:	$k_2 = 9.28\,10^{1}\, e\left(\frac{-46{,}650}{RT}\right)\ (\mathrm{m^3\,s^{-1}\,mol^{-1}})$
Hydrolysis of vinylacetate:	$k_3 = 1.84\,10^{3}\, e\left(\frac{-31{,}975}{RT}\right)\ (\mathrm{m^3\,s^{-1}\,mol^{-1}})$

where R (gas constant) = 121.8 J/mol°C.

INTRODUCTION

The acetylation of starch is a chemical modification that has been known for more than a century (Jarowenko, 1982). In the modified starch, part of the hydroxyl groups of the glucose monomers have been converted into -*O*-(-ethanoate) groups. Highly acetylated starches with a degree of substitution (DS) of 2 to 3 were of research interest from 1950 to 1980 for their solubility in acetone and chloroform and for their thermoplasticity (Jarowenko, 1982; Wolff *et al.*, 1951). Because these could not compete with similar cellulose derivatives in terms of costs and strength, they have not been developed commercially. Low acetylated starches with a DS of 0.01–0.2 are still of commercial interest. Their use is based on properties with respect to film forming, binding, adhesivity, thickening, stabilising, and texturing.

Acetylated starch can be produced in a direct way using acetic acid. However, this equilibrium controlled reaction is not recommended (Roberts, 1965). Other possible reactions are with acetic anhydride, acetylchloride or vinylacetate (ViAc). All these esterifications are kinetically rate controlled. Production of acetylated starch using ViAc is commercially performed in an aqueous slurry in the presence of alkali. The suspension is buffered with sodium carbonate to a pH of 9–10. After 1 h of reaction at 38°C, the reaction medium is acidified with dilute sulphuric acid to a pH of 6–7. The starch is recovered by filtration, washing and drying.

Kinetic data on the acetylation of potato starch in a slurry system have been reported by Jetten *et al.* (1980). However, no data have yet been published on the rates of the acetylation reactions of dissolved starch.

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THEORY

Reactions

The acetylation of potato starch by ViAc has been carried out in aqueous suspensions of starch under alkaline conditions at temperatures between 20 and 72°C. Starch dissolved in water has as a weak polyacid nature (Doppert *et al.*, 1966; Lammers *et al.*, 1993):

$$ROH + H_2O \overset{K_{eq}}{\longleftrightarrow} RO^- + H_3O^+ \qquad (a)$$

K_{eq} is the dissociation constant of starch in water and is defined as:

$$K_{eq} = \frac{c_{H_3O^+} c_{RO^-}}{c_{ROH} c_{H_2O}} \qquad (1)$$

where c is the concentration.

This dissociation constant has been determined by several authors (Doppert *et al.*, 1966; Lammers *et al.*, 1993; Saric *et al.*, 1946). They assumed that only one hydroxyl group per anhydroglucose unit can dissociate and found that the dissociation constant (pK_{eq}) is not dependent on the degree of dissociating hydroxyl groups on starch. Theoretically, it has been shown (Katchalsky *et al.*, 1949; Manning, 1969; Cleland, 1984), that the dissociation constants of polyacids are a function of the degree of dissociation. In our experiments, this change can be neglected because the change in the dissociation constants remains smaller than 0.02% for a change in the degree of dissociation up to 20%. The amount of RO^- present in our reaction medium was calculated from Lammers *et al.* (1993):

$$pK_{eq} = 12.2 + 12\ 10^3/(T + 273.15) \qquad (2)$$

where T is the temperature.

When NaOH is added to a starch solution, the hydroxyl groups of the starch react according to:

$$ROH + OH^- \overset{K_s}{\longleftrightarrow} RO^- + H_2O \qquad (b)$$

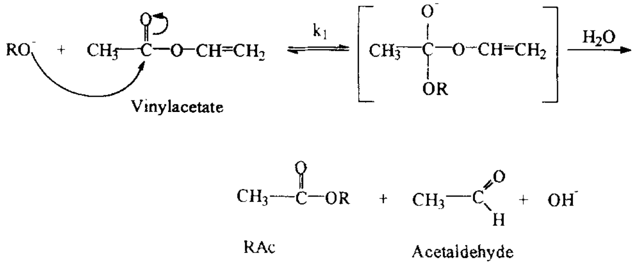
K_s is the dissociation constant of dissolved starch in an alkaline medium and can be defined as:

$$K_s = \frac{(c_{H_2O}\, c_{RO^-})}{(c_{ROH}\, c_{OH^-})} \qquad (3)$$

The dissociation constant for this reaction is equal to K_{eq} divided by K_a (the dissociation constant of water).

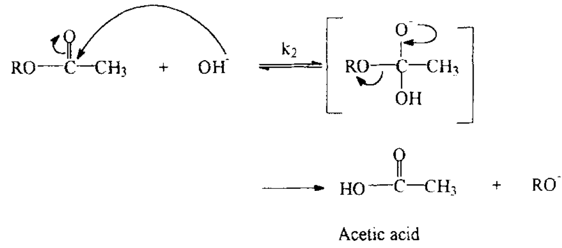
Beside these equilibria, the following chemical reactions are involved:

(i) The acetylation of the hydroxyl groups of the starch molecules (Scheme 1):
(ii) The hydrolysis of the starch acetate (RAc) (Scheme 2):
(iii) The hydrolysis of ViAc (Scheme 3):



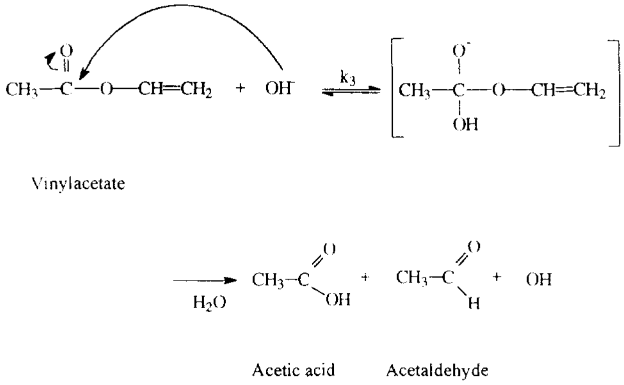
(c)

Scheme 1



(d)

Scheme 2



(e)

Scheme 3

The reactions proceed according to a nucleophilic substitution at the unsaturated carbon. Sodium hydroxide (NaOH) acts as a promotor. Both the hydrolysis reactions produce acetic acid which is neutralised by a fast reaction with a hydroxide ion. For all reactants, a first order dependency is assumed (Jetten *et al.*, 1980; Warners *et al.*, 1988) resulting in the following reaction rate equations:

Starch acetylation: $R_{RAc} = -k_1\, c_{ViAc}\, c_{RO^-}$ (4)

RAC hydrolysis: $R_{RAc} = k_2\, c_{RAc}\, c_{OH^-}$ (5)

ViAc hydrolysis: $R_{ViAc} = -k_3\, c_{ViAc}\, c_{OH^-}$ (6)

where $k_{1,2,3} = k'\, c_{H_2O}$.

MATERIALS AND METHODS

Background of the kinetic measurements

The hydrolysis rates were measured separately from the acetylation reaction. Both hydrolysis reactions use OH^- to neutralise the acetic acid formed. The pH of the reacting medium was kept constant by adding sodium hydroxide. Addition of alkali caused an increase in the reaction volume of less than 1%, which was neglected in all experiments. In the hydrolysis experiments of ViAc, this reagent was added in excess, resulting in a constant ViAc concentration in the water phase equal to the saturation concentration. The hydrolysis rate of ViAc (R_{Viac}) is constant under these conditions. During the reaction, the stirring speed was varied to test on absence of liquid–liquid mass transfer limitation. The addition rate of NaOH appeared not to be affected by the stirring rate, indicating that no mass transfer limitation occurred. Figure 1 shows a typical graph of the amount of NaOH added vs time. The rate of hydrolysis of starch acetate was measured in the same way. A slightly different approach was used for the acetylation reaction. Again the pH was kept constant but now the DS of the starch acetate was followed with time. The tangent of the slope of the DS vs time is a measure of the rate constant as long as the water phase is saturated with ViAc and the concentration of RAc is low. Figure 2 gives an example of such a graph. When all the ViAc has reacted, the DS of the RAc reaches a constant value. The saturation concentration of ViAc in water has to be known for the specific temperature range. The results are shown in Fig. 3. Also, the concentration of the starch dissolved in water is important. Starch concentration which is too high results in too high viscosity leading to poor mixing. A starch content of 4 wt% gave the best results. This way, mass transfer limitations could be eliminated so that the intrinsic kinetics were measured.

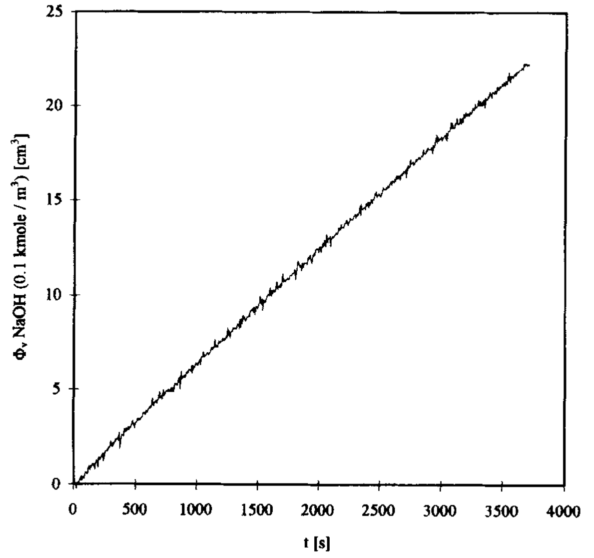


Fig. 1. NaOH (0.1 N) added as a function of time in the hydrolysis of ViAc at pH = 7.5 and $T = 26$°C.

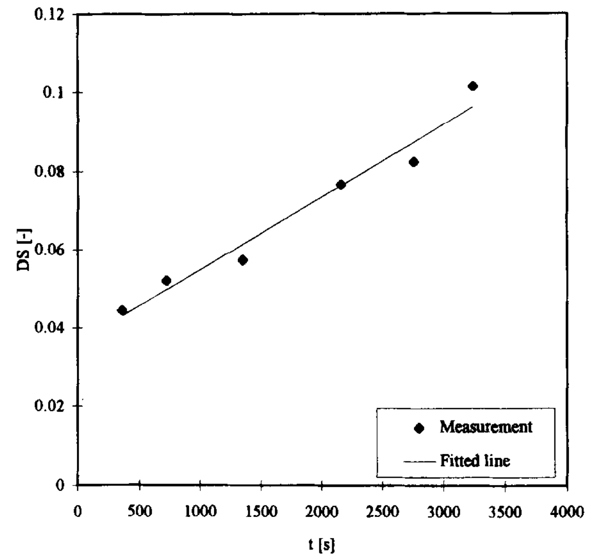


Fig. 2. Acetylation of starch: degree of substitution as a function of time. pH, 7.5; $c_{\text{ViAc,s}}$, 0.28 mol/g; c_{RO^-}, 1.27 mol/g; $T = 37$°C.

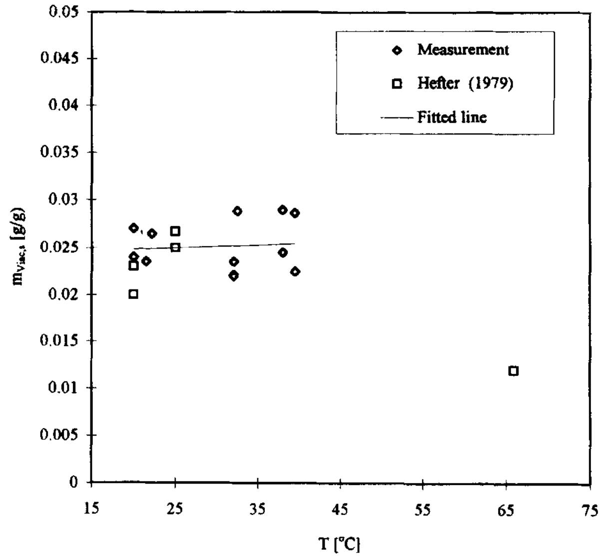


Fig. 3. Solubility of ViAc in water.

Equipment and procedures

All reactions were carried out in a jacketed, fully baffled, cylindrical glass vessel containing approximately 1 dm³ mixture, stirred with three pitched blade impellers, running at 25 rps. One of the impellers was near the surface to enable rapid submerging of ViAc droplets. The pH of the fluid was measured with a pH meter (Amagrus Elektroden Gmbh, Germany); the pH

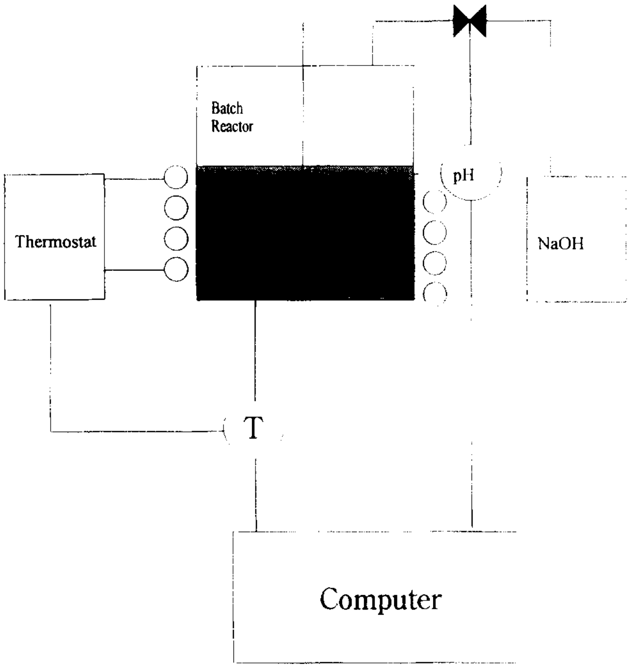


Fig. 4. Experimental set-up.

signal was amplified by means of a pH amplifier from Metrohm, Switzerland, and sent to data acquisition which consisted of an RTI-800 interface board for analogue input (Analog Devices) and a personal computer. The reaction temperature was measured with PT-100 thermocouples. All experiments were conducted at a constant pH. Figure 4 gives the experimental set-up.

The amount of NaOH consumed by the reaction was assumed to equal the amount of hydroxide fed to the vessel to maintain the pH at the set point value. Hydroxide consumption, temperature and pH data, all as a function of time, were written to disk files for subsequent processing.

To carry out kinetic experiments, the required amount of potato starch was washed with deionised water. The starch was transferred to a beaker and deionised water was added to obtain the desired starch concentration. The beaker was placed in a water bath at 95°C. The slurry was stirred with a Rushton turbine stirrer ($D = 45\,\text{mm}$) running at 4 rps. After approximately 15 min, the starch started to gelatinise, and a very viscous gel was obtained. Then, the stirring speed was increased to 13 rps resulting in a substantial increase in the viscosity due to rupture of the swollen starch granules resulting into gelatinisation. After stirring for 30 min, a carefully weighed amount of gel was transferred into the reactor. The mixture was brought to the desired temperature after which a carefully weighed amount of ViAc was added. Finally, the pH was adjusted to the desired value. The same procedure was followed to obtain gelatinised RAc.

Materials

ViAc, NaOH and all other reagents were pro analysis grade products of Merck, Germany. The potato starch and the acetylated potato starch (Farazym; $DS_O = 0.049$) were commercial products of AVEBE B.A. Cooperatieve verkoop en Productie van Aardappelmeel en Derivaten, the Netherlands.

Analysis

The DS of the RAc was determined by titration. During the reaction, samples of approximately 3 g were taken every 30 s and injected into a solution of 40 cm^3 methanol and 2 cm^3 titrisol buffer 7. The starch was precipitated, filtered, dried and weighed. An accurately known amount of this starch was then dissolved in 25 cm^3 demineralised water. The pH of this solution was determined and, subsequently, 25 cm^3 of a 0.1 kmol m^{-3} NaOH solution was added. After 12 h, the solution was titrated with 0.1 kmol m^{-3} HCl until the pH equalled the pH of the solution before NaOH was added. The DS follows from an iterative procedure:

$$m_{\text{starch}} = \frac{m_{\text{dried acetylated starch}}}{(161 + \text{DS}\, M_{\text{Acetyl}})} \tag{7}$$

$$\text{DS} = \frac{c_{\text{Acetyl groups}}}{c_{\text{AGU}}} = \frac{(m/M)_{\text{NaOH, added}} - (m/M)_{\text{HCl, added}}}{m_{\text{starch}}/M_{\text{AGU}}} \tag{7a}$$

In which M_{Acetyl} is the molecular mass of the acetylated group, (m/M) is the number of moles of a component, M_{AGU} is the molecular mass of one anhydroglucose unit and m_{starch} is the amount of starch in the final solution. The DS is initially estimated after which m_{starch} is calculated from equation (7). With the help of equation (7a) a new value for the DS is obtained which is used again as a new value in equation (7). This procedure continues until $|DS_{\text{old}} - DS_{\text{new}}| \leqslant 0.001$.

The concentration of ViAc dissolved in water was determined by gas chromatography (GC). A sample from the reacting system was injected into a mixture of methanol, isopropyl alcohol (IPA) and titrisol buffer 7 (see above). As an internal standard, IPA was used. The details can be found in Table 1. The same technique was used to determine the saturation concentration of ViAc in water, at various temperatures, though the preparation of the samples was different. In a 4 cm^3 autosampler vial, commonly used in gas chromatography, 1 cm^3 of water was injected into 0.89 cm^3 of ViAc. The vial was closed with a cap containing a self-sealing Teflon coated septum liner and placed in a water bath at the desired temperature. At regular intervals, this was shaken vigorously. After 1 h, the concentration of dissolved ViAc was measured by sampling part of the water phase with a syringe. The saturation concentration of ViAc in water and in a starch mixture appeared to be the same.

Table 1. Data on gas chromatographic analysis

GC type	HP, model 5890
Integrator type	HP, model 3393a
Injection temperature	220°C
Detection temperature	200°C
Start temperature	50°C
Temperature rise	0.83°C/s
End temperature	100°C
Column packing	Tenax GC (60–80 mesh)
Carrier gas	Helium
Retention time (ViAc)	570 s
Retention time (IPA)	426 s
Injection volume	10 nm^3
Detector	Flame ionisation detector
Peak width	0.1
Column length	100 cm
Internal column diameter	2.1 mm

Table 2. Reaction rate constants of the acetylation of starch as a function of T

T (°C)	k_1' 10^6 (m^6/mol^2 s)
23.4	0.19
25.0	0.22
26.2	0.22
31.4	0.42
34.6	0.45
37.6	0.87
37.7	0.85
37.8	0.86
46.6	1.63
48.6	1.67

RESULTS AND DISCUSSION

The acetylation of potato starch

Figure 2 shows a graph of the DS vs time. The slope of this graph is equal to the production rate of acetylated starch. The concentration of RO$^-$ in the reacting solution was taken from Lammers *et al.* (1993). Table 2 gives the measured rate constants as a function of the temperature. Figure 5 shows ln(k_1) vs $1/T$. The activation energy of the reaction follows from the slope of this graph. The result is (26°C < T < 43°C; 7.5 < pH < 8.5; and 0 < DS < 0.3):

$$\begin{aligned} k_1 &= k_{1,\infty} e^{\left(\frac{-E_a}{RT}\right)} \\ k_{1,\infty} &= 1.14\,10^{14}\,\mathrm{m^3\,mol^{-1}\,s^{-1}} \\ E_a &= 93.2\,10^3\,\mathrm{J\,mol^{-1}} \\ r^2 &= 0.99 \end{aligned} \tag{8}$$

where the gas constant $R = 121.8\,\mathrm{J\,mol^{-1}\,°C^{-1}}$, k_∞ is the frequency factor, E_a is the activation energy and r^2 is the regression coefficient. The kinetic reaction order of the acetylation in $c_{\mathrm{RO^-}}$ follows from a plot of the values of $R_{\mathrm{RAc}}/c_{\mathrm{ViAc}}$ as a function of $c_{\mathrm{RO^-}}$. For reaction temperatures of 37.3, 26.2, 42.5 and 31.8°C this is shown in Fig. 6. It proves that the kinetics of the starch acetylation are indeed, first order in $c_{\mathrm{RO^-}}$. The reaction order in c_{ViAc} was determined indirectly. Because the c_{ViAc} always equalled $c_{\mathrm{ViAc,s}}$, independently of temperature, the reaction order could not be measured directly. Figure 7 shows a graph of the DS vs the reaction time. As can be seen, the DS levels off with increasing time. Then, the $c_{\mathrm{ViAc,s}}$ decreases with time in c. Assuming a first order kinetic starch acetylation rate dependency in c_{ViAc} and taking the reaction kinetics of the deacetylation and the ViAc hydrolysis into account, the DS vs time could be calculated (simulated line in Fig. 7). The calculated line fits the measured DS curve neatly. Indirectly, it proves that the kinetics of the starch acetylation is also first order in $c_{\mathrm{ViAc,s}}$.

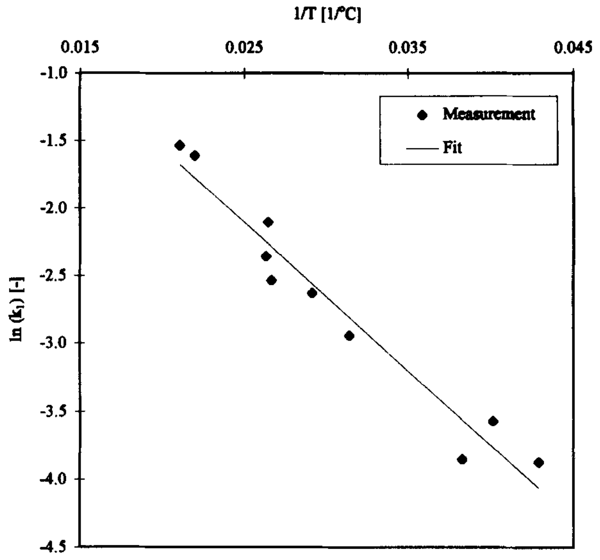


Fig. 5. The acetylation of starch: ln(k_1) vs $1/T$.

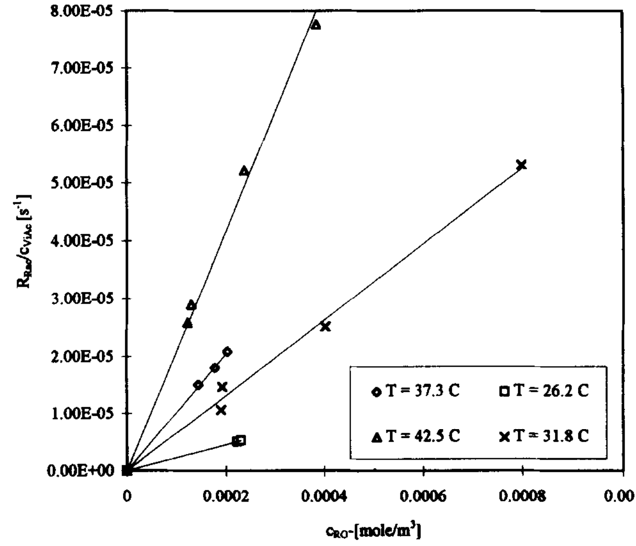


Fig. 6. $R_{\mathrm{RAc}}/c_{\mathrm{ViAc}}$ as a function of $c_{\mathrm{RO^-}}$ in the aqueous phase.

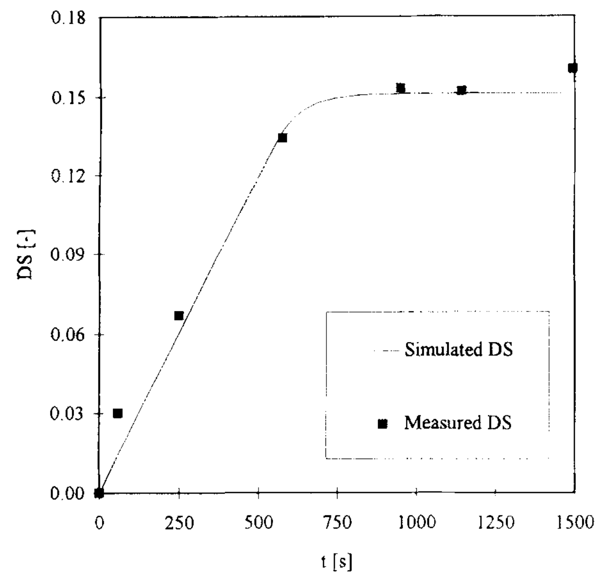


Fig. 7. Simulated and measured DS vs reaction time (pH = 7.5, $c_{ViAc,0}$, 1783.72 mol m^{-3}; c_{RO}, 384.14 mol m^{-3}; c_{H_2O}, 44 762 mol m^{-3}, T = 35.4 C).

Table 3. Reaction rate constants of the hydrolysis of RAc as a function of *T*

T (°C)	k_2' 10^6 (m^6/mol^2 s)
52.5	3.03
56.15	3.81
63.25	5.12
63.55	5.51
67.65	6.32
67.65	5.84
76.55	10.11
77.84	11.22

The hydrolysis of acetylated potato starch

As explained earlier, the reaction rate of the deacetylation of starch can be determined by measuring the amount of NaOH (0.1 N) added to neutralise the amount of acetic acid formed during the deacetylation of starch. Table 3 shows the rate constants observed. A plot of $\ln(k_2)$ vs $1/T$ is shown in Fig. 8. The frequency factor and energy of activation were measured as $k_{2,\infty} = 9.28 \times 10^1\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$ and $E_{a,2} = 46\,650 \times 10^3\,\mathrm{J\,mol^{-1}}$, respectively, with $r^2 = 0.98$ (50°C < T < 78°C; 7.5 < pH < 8.5; $DS_O = 0.049$).

The kinetic reaction order of the deacetylation in c_{OH} follows from a plot of the values of R_{RAc}/c_{RAc} as a function of the hydroxide concentration in the reaction mixture. This is shown in Fig. 9. A straight line through the origin is obtained, proving that the reaction is indeed first order in c_{OH^-}. In a similar way the reaction order of the deacetylation in c_{RAc} can be determined. The values of R_{RAc}/c_{OH^-} are plotted as a function of c_{RAc} in Fig. 10. This proves that the acetylation is also first order in c_{RAc}.

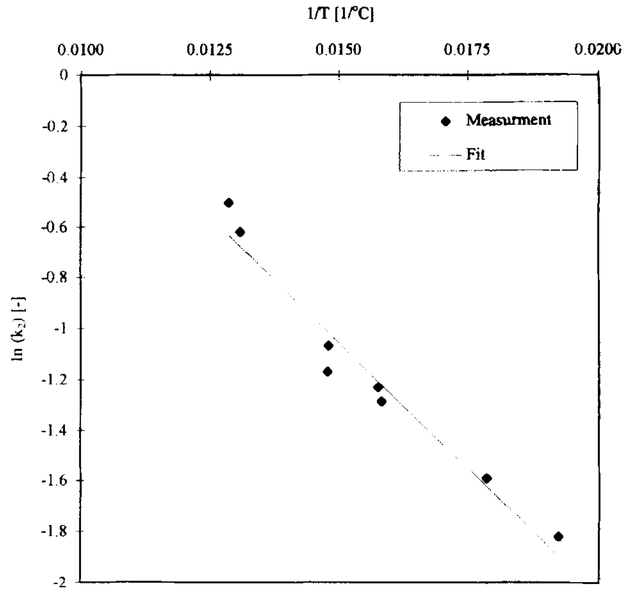


Fig. 8. The deacetylation of starch: $\ln(k_2)$ vs $1/T$.

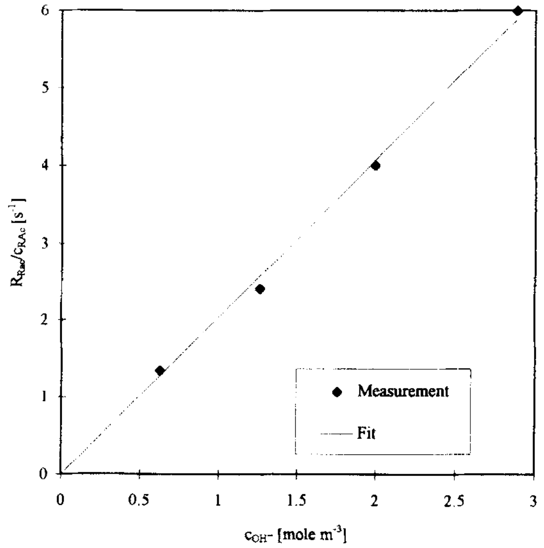


Fig. 9. Deacetylation of acetylated starch: R_{RAc}/c_{RAc} as a function of the NaOH concentration.

Jetten *et al.* (1980) measured the kinetics of the deacetylation of granular starch. Comparing their reaction rate constants at 30°C; $k_2 c_{H_2O} = 5 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$) with our data ($k_2' c_{H_2O} = 4.38 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$) shows that the reaction rate in solution is 88 times faster. In the case of Jetten *et al.* (1980), reactant has to diffuse in the starch granules resulting in mass transfer limitations. In solution, no such mass transfer limitations occur.

The hydrolysis of ViAc

The rate of hydrolysis of ViAc was measured in aqueous solutions. The acetic acid formed was immediately neutralised by 0.1 N NaOH. The reaction rate followed

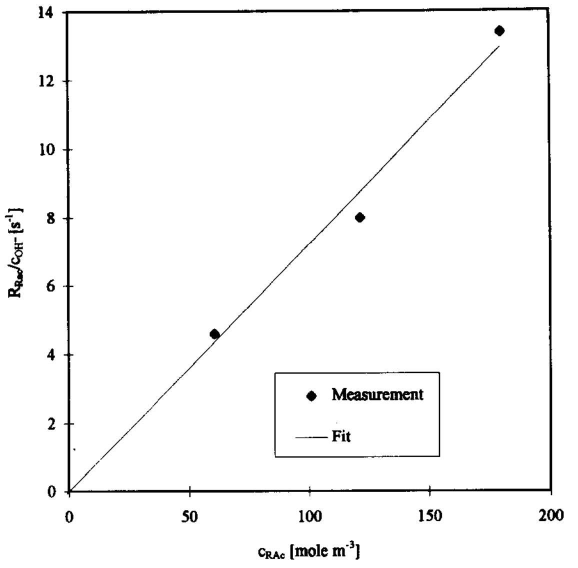


Fig. 10. Deacetylation of acetylated starch: $R_{\mathrm{RAc}}/c_{\mathrm{OH^-}}$ as a function of the NaOH concentration.

directly from the rate of alkali added to the solution. Solubility values of ViAc were taken from Fig. 3. The kinetic results are given in Table 4 and in Fig. 11 in form of an Arrhenius plot. The kinetic orders in both reactants were determined by Jetten *et al.* (1980) and de Puy *et al.* (1969). The frequency factor and the energy of activation were measured as $k_{3,\infty} = 1.84 \times 10^3\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$ and $E_{a,3} = 31.6975 \times 10^3\,\mathrm{J\,mol^{-1}}$, respectively. $r^2 = 0.99$, ($24°\mathrm{C} < T < 43°\mathrm{C}$; $7.5 < \mathrm{pH}\,8.5$). In the literature (Wolff *et al.*, 1951; Sharma *et al.*, 1970) several reaction constants can be found at 20°C. The values vary from 1.6×10^{-3} to $4.9 \times 10^{-3}\,\mathrm{m^3 mol^{-1} s^{-1}}$. Extrapolation of the fitted line in Fig. 11 to 20°C gives a value of $3.68 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$. Indeed, this value is of the same order of magnitude as found by de Puy *et al.* (1969).

SELECTIVITY OF THE ACETYLATION OF STARCH

The selectivity of ViAc towards the formation of RAc can be determined as a function of the reaction conditions.

$$\sigma_{\mathrm{AS}} = \frac{k_1\, c_{\mathrm{ViAc}}\, c_{\mathrm{RO^-}} - k_2\, c_{\mathrm{RAc}}\, c_{\mathrm{OH^-}}}{k_1\, c_{\mathrm{ViAc}}\, c_{\mathrm{RO^-}} - k_2\, c_{\mathrm{RAc}}\, c_{\mathrm{OH^-}} + k_3\, c_{\mathrm{ViAc}}\, c_{\mathrm{OH^-}}} \qquad (9)$$

in which σ_{AS} is the selectivity towards RAc.

Values of the rate constants were calculated from the Arrhenius equations. The concentrations of $c_{\mathrm{RO^-}}$ in the reaction mixture were calculated from the pK_a of the starch, taking into account the actual water concentration in the starch solution. Figure 12 shows a plot of the initial selectivity as a function of the temperature at several starch water ratios. Owing to the higher E_a of the acetylation reaction, the selectivity increases at higher temperatures and starch concentrations.

Table 4. Reaction rate constants of the hydrolysis of ViAc as a function of *T*

T (°C)	k_3' 10^6 ($\mathrm{m^6/mol^2\,s}$)
23.5	1.02
23.7	0.98
28.3	1.22
31.6	1.48
38.1	1.80
38.1	1.81
39.6	1.97
43.1	2.22
47.2	2.68

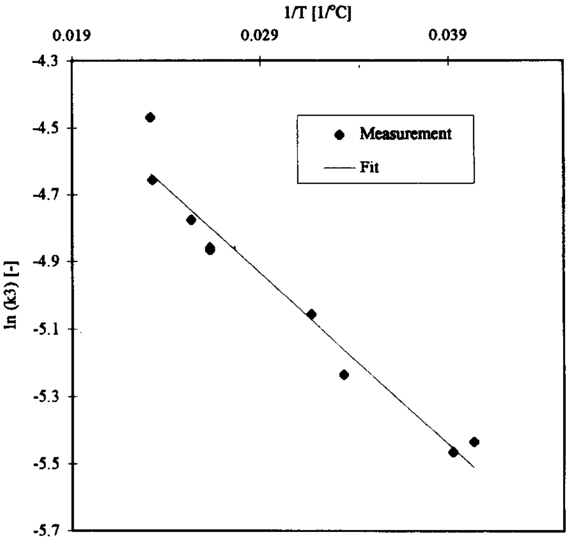


Fig. 11. The hydrolysis of ViAc: $\ln(k_3)$ vs $1/T$.

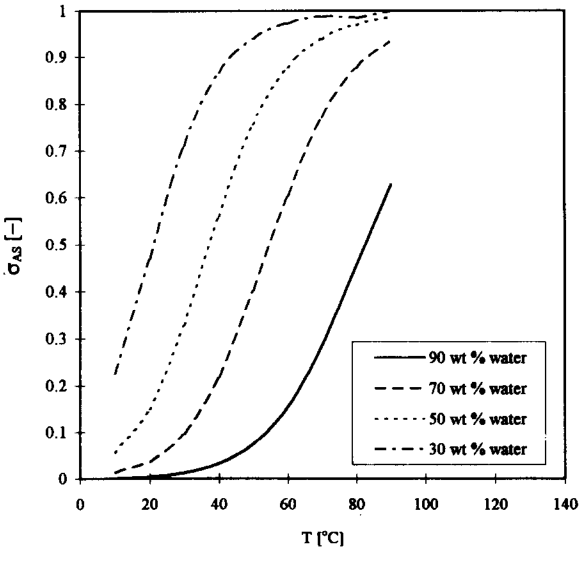


Fig. 12. Selectivity of the reaction towards acetylated starch as a function of the water concentration and temperature in the reaction mixture.

CONCLUSIONS

The reaction kinetics of the acetylation of starch in aqueous solution were studied using NaOH as a catalyst. Three parallel reactions were involved, the catalysed acetylation of starch, the hydrolysis of RAc and the hydrolysis of ViAc. The deacetylation reaction appeared to be first order in both RAc and NaOH. The acetylation reaction was first order in $c_{\mathrm{RO^-}}$ and $c_{\mathrm{ViAc,s}}$. The temperature dependency of the rate constants and reaction selectivities could be determined as a function of starch concentration and temperature. These data showed that due to the relatively low E_a of both undesired reactions, a high selectivity towards the desired product, RAc, at increasing temperatures, starch and NaOH concentrations could be achieved.

ACKNOWLEDGEMENT

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